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UNIVERSITY OF CALIFORNIA,
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Adaptive Materials and Systems Inspired by Cephalopod Skin

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Materials Science and Engineering

by

Chengyi Xu

Dissertation Committee:
Professor Alon A. Gorodetsky, Chair
Professor Albert F. Yee
Professor Plamen Atanassov

2020

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DEDICATION

To Mom and Dad

&

Yachen

Thank you for always being there for me!

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Figure 2.1. Reflectin protein found in *Euprymna scolopes* squid. From left to right: a digital camera image of an *Euprymna scolopes* squid (left), a transmission electron microscope (TEM) image of light-reflecting proteinaceous platelets found inside the *E. scolopes* squid’s skin (middle), and the entire amino acid sequence of a full-length reflectin 1b protein that was found in the light-reflectin platelets.^[19] Note that the blue-circled region denoted a singly represented 2C domain in the sequence.

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Figure S2.4. 2D ^{13}C - ^{13}C correlation spectra in the aromatic and carbonyl region of self-assembled (ref2C)₄ protein with the Arg-selectively labeled (ref2C)₄ protein spectrum (blue contours) overlaid onto the uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein spectrum (red contours). The spectra were from the same measurement as those in Figure 2.5B. The sample preparation was described in the Supporting Information Section 2.7.6.

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Figure S2.6. A representative 2D ^{13}C - ^{13}C correlation spectrum for a second-batch sample made from uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein. The sample preparation was described in the Supporting Information Section 2.7.6.

Figure S2.7. A representative 2D ^{13}C - ^{13}C correlation spectrum for a third-batch sample made from uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein. The sample preparation was described in the Supporting Information Section 2.7.6.

Figure 3.1. Cephalopod-inspired design of the multimodal camouflage systems. (A) Pictures of representative *Japetella heathi* octopuses with their bodies in opaque and transparent states.^[28] (B) Pictures of representative *Taonius borealis* glass squids with their bodies in opaque and transparent states.^[29,30] (C) Cross-sectional illustration of cephalopod skin and its embedded pigment granule-packed chromatophore organs, proteinaceous microstructure-containing iridophore cells, and intracellular nanoparticle-filled leucophore cells. Note that the image shows generalized depictions of the interactions of visible light with these organs and cells. (D) Cross-sectional (left) and top-view (right) schematics of the designed adaptive multimodal camouflage system before and after actuation. Upon mechanical or electrical actuation, the active area is reversibly switched from a contracted state (large thickness and small area) with a wrinkled surface to an expanded state (small thickness and large area) with a smooth surface. The schematics illustrate the absorption (A%) and transmission (T%) of light before and after actuation within both the visible and infrared regions of the electromagnetic spectrum.

Figure 3.2. Electrical and physical characterization of sulfonated pentablock copolymer membranes. (A) A general schematic of the two-terminal devices used for electrochemical impedance spectroscopy (EIS) measurements in the absence of strain, wherein a freestanding pentablock copolymer membrane bridges two gold electrodes. (B) Nyquist plots for a representative freestanding membrane-based device at relative humidities of 50% (red), 60% (orange), 70% (green), 80% (blue), and 90% (black). (C) A plot of the protonic conductivity as a function of the relative humidity for freestanding membrane-based devices. (D) Nyquist plots for a representative freestanding membrane-based device in the presence of water (H₂O) (black squares) and deuterium oxide (D₂O) (red circles)

vapor at a relative humidity of 90%. **(E)** A general schematic of the two-terminal devices used for EIS measurements in the presence of strain, wherein an elastomeric acrylate substrate-bound pentablock copolymer membrane bridges two gold electrodes. **(F)** Nyquist plots for a representative substrate-bound pentablock copolymer membrane at applied uniaxial strains of 0% (black squares), 200% (green circles), and 500% (red triangles). **(G)** The protonic conductivity of elastic acrylic substrate-bound pentablock copolymer membranes at applied uniaxial strains of 0%, 100%, 200%, 300%, 400%, and 500%. Note that the conductivity increased with strain. **(H)** A direct comparison of the change in conductivity with strain for our membranes and representative state-of-the-art stretchable conductors, including silver nanoparticles/fluorinated rubber,^[44] silver nanowires/polyurethane acrylate,^[45] silver flakes/fluorinated rubber,^[46] gold nanoparticles/polyurethane,^[47] single-walled carbon nanotubes/fluorinated rubber,^[48] a poly(3,4-ethylenedioxythiophene):polystyrene sulfonate/ionic liquid blend on an elastic styrene ethylene butylene styrene substrate,^[53] and an ionic hydrogel.^[56]

Figure 3.3. Mechanical actuation of changes in the microscale surface morphology and spectral functionality for tri-layer systems within the visible and infrared. **(A)** A side-view schematic of the change in spectral functionality and microscale morphology for a tri-layer system upon mechanical actuation with equiaxial strain. Representative scanning electron microscopy (SEM) and atomic force microscopy (AFM) images, which show the surface microstructure of the system before (left) and after (right) actuation, are inset. **(B)** (Top) Representative digital camera images of a tri-layer system above a cartoon anteater logo both before (left) and after (right) mechanical actuation. (Bottom) Representative transmittance spectra within the visible to short-wavelength infrared regions (400 nm – 2 μ m) for a tri-layer system both before (left) and after (right) mechanical actuation. The total transmittances (solid black lines) are shown, along with their diffuse (dashed blue lines) and specular (dashed green lines) components. **(C)** (Top) Representative infrared camera images of a tri-layer system above a warm hand both before (left) and after (right)

mechanical actuation. (Bottom) Representative transmittance spectra within the mid-wavelength to long-wavelength infrared regions ($2.5\text{ }\mu\text{m} - 16.6\text{ }\mu\text{m}$) for a tri-layer device both before (left) and after (right) mechanical actuation. The total transmittances (solid black lines) are shown, along with their diffuse (dashed orange lines) and specular (dashed red lines) components.

Figure 3.4. Electrical characterization and demonstration of multispectral camouflage functionality for dielectric elastomer actuators within the visible and infrared. (A) A top-view schematic of the change in the size of the active area for a tri-layer device upon electrical actuation. (B) A plot of the areal strain as a function of the applied voltage for the tri-layer devices. (C) A representative plot of the areal strain as a function of time for five consecutive cycles of a square waveform with a 0.5 Hz frequency (minima at 0 kV and maxima at ~ 3.5 kV). (D) (Top) Schematic of the digital camera visualization of a tri-layer device positioned above a reproduction of Vincent van Gogh’s *Starry Night* both before (left) and after (right) electrical actuation. (Bottom) Representative digital camera images of a tri-layer device above a reproduction of Vincent van Gogh’s *Starry Night* both before (left) and after (right) electrical actuation. (E) (Top) Schematic of the infrared camera visualization of a tri-layer device positioned above a silhouette of Vincent van Gogh’s *Starry Night* and an underlying thermal source, both before (left) and after (right) electrical actuation. (Bottom) Representative infrared camera images of a tri-layer device positioned above a silhouette of Vincent van Gogh’s *Starry Night* and an underlying thermal source, both before (left) and after (right) electrical actuation.

Figure S3.1. (A) Digital camera images of a thin freestanding sulfonated pentablock copolymer membrane (square window) within a flexible frame. Note the optical transparency of the membrane, which affords clear visualization of the background. (B) Digital camera image of a representative two-terminal device wherein a thin freestanding

membrane bridges two gold electrodes. Note that the blue tint of the freestanding membrane is due to thin film interference, as observed at a specific viewing angle.

Figure S3.2. Digital camera images of a substrate-bound sulfonated pentablock copolymer membrane in an adjustable holder at uniaxial strains of 0% (left), 200% (middle), and 500% (right). Note that the membrane has been marked with a dotted orange outline for clarity.

Figure S3.3. Nyquist plots for a representative acrylate substrate-bound pentablock copolymer membrane before the application of strain (black squares) and after the application of 1,000 consecutive load/unload cycles at a strain of 200% (red circles).

Figure S3.4. (A) Representative topographical AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 45\%$. (B) Representative phase contrast AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 45\%$. (C) Representative topographical AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 90\%$. (D) Representative phase contrast AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 90\%$.

Figure S3.5. (A) A schematic of the change in geometry of an elastic acrylate substrate-bound pentablock copolymer membrane upon the application of uniaxial strain. Representative optical microscopy images, which show the membranes' surface microstructure, at uniaxial strains of 0% (left), 200% (middle), and 500% (right), are inset. (B) Representative topographical atomic force microscopy (AFM) images, which show the membranes' nanoscale surface morphology, at uniaxial strains of 0% (left), 200% (middle), and 500% (right). (C) Representative phase AFM images, which show the membranes' nanoscale phase contrast, at uniaxial strains of 0% (left), 200% (middle), and 500% (right), are inset.

Figure S3.6. Scheme for the fabrication of a mechanically-actuated tri-layer system within a size-adjustable holder.

Figure S3.7. (A) Representative scanning electron microscopy (SEM) images of the surface morphology of the tri-layer systems before (left) and after (right) the 500th mechanical actuation cycle. The scale bar is 10 μm for the SEM images. (B) Representative atomic force microscopy (AFM) images of the surface morphology of the tri-layer systems before (left) and after (right) the 500th mechanical actuation cycle.

Figure S3.8. (A) Representative reflectance spectra within the visible to short-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation. The total reflectances (solid black lines) are shown, along with their diffuse (dashed blue lines) and specular (dashed green lines) components. (B) Representative absorbance spectra within the visible to short-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation.

Figure S3.9. (A) Optical camera images of a representative tri-layer system at different relative humidities before mechanical actuation. (B) Optical camera images of a representative tri-layer system at different relative humidities after mechanical actuation. Note that the active areas have been marked with dotted yellow outlines for clarity.

Figure S3.10. (A) Representative reflectance spectra within the mid-wavelength to long-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation. The total reflectances (solid black lines) are shown, along with their diffuse (dashed orange lines) and specular (dashed red lines) components. (B) Representative absorbance spectra within the mid-wavelength to long-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation.

Figure S3.11. (A) Schematic of the infrared camera visualization of a tri-layer device positioned above a warm surface, both before (left) and after (right) mechanical actuation. (B) Plot of the apparent temperatures measured for the central region of a device, both before (black squares) and after (red dots) mechanical actuation, as a function of the device's distance from a warm surface. The dashed orange line indicates the constant temperature of the surface, i.e. 26.5 °C. Note that the distance was varied between 1 cm and 25 cm.

Figure S3.12. Scheme for the fabrication of an electrically-actuated tri-layer device within a size-adjustable holder.

Figure S3.13. (A) Plot of the apparent temperatures for the central region of a device in the unactuated (black squares) and actuated (red dots) states as a function of the total number of actuation cycles. The devices were actuated by means of 0.5 Hz-frequency square waveform, for which the minima at 0 kV and the maxima at 3.5 kV correlated with the devices' unactuated (off) and actuated (on) states, respectively. The device was positioned above a warm surface, and the apparent temperature was measured in the same spot for each off/on actuation cycle. (B) The difference in apparent temperature between the unactuated and actuated devices as a function of the total number of off/on actuation cycles.

Figure 4.1. Biological inspiration and system design. (A) Camera images of a squid changing its appearance in front of a rocky background. (B) An image of squid skin. The yellow, red, and brown circular regions are chromatophore organs, and the underlying bright iridescent regions are iridocytes. (C) A schematic of a cephalopod chromatophore organ, in which a central chromatophore pigment cell is ringed by muscle cells. The adaptive chromatophore pigment cells contain internal sacculi packed with pigment granule (inset), and they are expanded and contracted through the mechanical action of the muscle cells. The chromatophore pigment cells function like size-variable biological

spectral filters that absorb and reflect visible light of specific wavelengths. **(D)** A schematic of a squid iridocyte. The adaptive iridocytes contain alternating arrangements of membrane-enclosed protein layers and extracellular space (inset), for which the geometries and refractive index differences are altered via a biochemical signaling cascade. The iridocytes function like reconfigurable biological Bragg reflectors that reflect visible light of variable wavelengths. **(E)** A generic schematic of the top view of our infrared-reflecting platform before (left) and after (right) actuation. Described is the areal change for the active region upon actuation. **(F)** A generic schematic of the side-view of our infrared-reflecting platform before (left) and after (right) actuation. Described is the surface morphology change for the active region upon actuation. [The images in (A) are reproduced from a video by H. Steinfeldt under the YouTube Creative Commons Attribution license, and the images in (B) were obtained by G. Hanlon and reproduced with permission of R. Hanlon.]

Figure 4.2. Mechanical modulation of the broadband and narrowband reflectance. **(A)** (Top) Schematics of an aluminum-modified device before (left) and after (right) mechanical actuation in an adjustable holder, illustrating the change in the surface morphology and the reflection of infrared light. (Bottom) The infrared reflectance spectra of an aluminum-modified device before (left) and after (right) mechanical actuation. The total reflectances (solid orange traces) are shown along with their specular (dotted yellow traces) and diffuse (dotted blue traces) components. **(B)** Digital camera images of an aluminum-modified device's active area before (left) and after (right) mechanical actuation. The yellow dashed lines indicate the active area. **(C)** Optical microscope images of the surface morphology of an aluminum-modified device's active region before (left) and after (right) mechanical actuation. **(D)** Scanning electron microscopy images of the surface morphology of an aluminum-modified device's active region before (left) and after (right) mechanical actuation. **(E)** (Top) Schematics of a $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified device before (left) and after (right) mechanical actuation in an adjustable holder,

illustrating the change in the surface morphology and the reflection of infrared light. (Bottom) The infrared reflectance spectra of a $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified device, with a peak reflectance intensity at $3\text{ }\mu\text{m}$, before (left) and after (right) mechanical actuation. The total reflectances (solid orange traces) are shown along with their specular (dotted yellow traces) and diffuse (dotted blue traces) components. (F) The infrared spectra of three unactuated devices that have been designed to feature peak reflectance wavelengths of $3\text{ }\mu\text{m}$ (red trace), $4\text{ }\mu\text{m}$ (green trace), and $5\text{ }\mu\text{m}$ (blue trace). (G) Plots of the total (orange squares), specular (yellow triangles), and diffuse (blue circles) peak reflectances of the $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified devices as functions of the applied length strain. The lines represent linear fits of the data.

Figure 4.3. Electrical characteristics of single devices. (A) (Top) Schematics of an aluminum-modified device before (left) and after (right) electrical actuation, illustrating the areal change for the active region. (Bottom) Digital camera images of an aluminum-modified device's active region before (left) and after (right) electrical actuation. (B) A plot of the areal strain as a function of the applied voltage for aluminum-modified devices. (C) A plot of the areal strain as a function of the frequency for square waveforms with identical minima of 0 kV and maxima of 3.2 kV. (D) A plot of the areal strain as a function of time for three consecutive cycles of a square waveform with a frequency of 0.5 Hz, as well as minima of 0 kV and maxima of 3.2 kV.

Figure 4.4. Electrical modulation of the infrared appearance for single and multiplexed devices. (A) (Top) Schematics of an aluminum-modified device under a constant thermal flux before (left) and after (right) electrical actuation, illustrating the change in surface morphology and the reflection of infrared light. (Bottom) Infrared camera images of a representative aluminum-modified device's active region before (left) and after (right) electrical actuation. The change in apparent temperature and thermal appearance is represented by a change in color. (B) (Top) Schematics of a three-by-three array of

multiplexed devices before electrical actuation (left) and after (right) selective electrical actuation of different device (pixel) combinations as the letters “U,” “C,” and “I.” (Bottom) Infrared camera images of representative three-by-three arrays of multiplexed devices before electrical actuation (left) and after (right) selective electrical actuation of different device (pixel) combinations as the letters “U,” “C,” and “I.” The changes in apparent temperature and thermal appearance are represented by changes in color.

Figure 4.5. Autonomous operation and reversible concealment of devices in the infrared.

(A) (Top) Schematics of a sensor-connected, aluminum-modified device. The remote sensor is positioned in a different local thermal environment, with increasing temperatures of $\sim 26\text{ }^{\circ}\text{C}$, $\sim 34\text{ }^{\circ}\text{C}$, $\sim 42\text{ }^{\circ}\text{C}$ and $\sim 48\text{ }^{\circ}\text{C}$ (from left to right). (Middle) Digital camera images of a representative device’s active region at the different sensor temperatures. (Bottom) Infrared camera images of the same device’s active region at the different sensor temperatures. Shown are the expansion and change in thermal appearance for the autonomous device’s active region, with increasing local temperature for the sensor. (B) (Top) Schematics of a squid silhouette-shaped, aluminum-modified device maintained under a constant thermal flux and positioned above a warm surface before (left) and after (right) electrical actuation. (Middle) Digital camera images of a representative squid silhouette-shaped, aluminum-modified device’s active region before (left) and after (right) electrical actuation. (Bottom) Infrared camera images of the same squid silhouette-shaped, aluminum-modified device’s active region before (left) and after (right) electrical actuation. The device alters its thermal appearance and becomes distinguishable from the background only after actuation.

Figure S4.1. Fabrication of the devices. (A) Scheme for the fabrication of the aluminum-modified infrared-reflecting devices within a holder. (B) Scheme for the fabrication of the Bragg stack-modified infrared-reflecting devices within a holder.

Figure S4.2. Mechanical modulation of the broadband transmittance and absorptance.

(A) The infrared transmittance spectra of an aluminum-modified device before (left) and after (right) mechanical actuation. (B) The infrared absorptance spectra of an aluminum-modified device before (left) and after (right) mechanical actuation.

Figure S4.3. Angular dependence of the mechanical modulation of the broadband reflectance.

(A) The specular component of the reflectance for an aluminum-modified device as a function of the incident light angle before (left) and after (right) mechanical actuation. (B) The average specular reflectance for an aluminum-modified device as a function of the incident light angle before (black triangles) and after (red dots) mechanical actuation. The error bars represent the standard deviation for measurements from four independent devices.

Figure S4.4. Stability of the aluminum-modified devices' functionality after repeated mechanical actuation.

(A) The infrared reflectance spectra of an aluminum-modified device before (left) and after (right) 75 mechanical actuation cycles. The total reflectance (solid orange traces) is shown along with its specular (dotted yellow traces) and diffuse components (dotted blue traces). (B) The infrared transmittance spectra of an aluminum-modified device before (left) and after (right) 75 mechanical actuation cycles. (C) The infrared absorptance spectra of an aluminum-modified device before (left) and after (right) 75 mechanical actuation cycles. (D) The infrared reflectance spectra of an aluminum-modified device before (left) and after (right) 750 mechanical actuation cycles. The total reflectance (solid orange traces) is shown along with its specular (dotted yellow traces) and diffuse components (dotted blue traces). (E) The infrared transmittance spectra of an aluminum-modified device before (left) and after (right) 750 mechanical actuation cycles.

(F) The infrared absorptance spectra of an aluminum-modified device before (left) and after (right) 750 mechanical actuation cycles.

Figure S4.5. Stability of the Bragg stack-modified devices' functionality after repeated mechanical actuation. The infrared reflectance spectra of a $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified device, with a peak reflectance intensity at 3 μm , before (left) and after (right) 100 mechanical actuation cycles. The total reflectances (solid orange traces) are shown along with their specular (dotted yellow traces) and diffuse components (dotted blue traces) both before and after mechanical actuation.

Figure S4.6. Images of multiplexed devices and electrical modulation of their appearance in the thermal infrared. (A) A digital camera image of a three by three array of multiplexed devices. (B) Schematics of a three by three array of multiplexed devices before electrical actuation (left) and after (right) selective electrical actuation of a single device. (C) Infrared camera images of a three by three array of multiplexed devices before electrical actuation (left) and after selective electrical actuation of different single devices in the array (right). Note the change in apparent temperature and thermal appearance upon actuation for specific devices, as indicated by the color scheme and the red arrows. The temperature range and scale bar of the actuated devices on the right are identical to those of the unactuated device on the left.

Figure S4.7. Autonomous modulation of a device's active area. Plot of the areal strain (relative to the value at 26 °C) as a function of the sensor temperature for a sensor-connected aluminum-modified device. The data were obtained for temperatures between 26 °C and 48 °C. The error bars represent the standard deviation for measurements from four independent devices.

Figure 5.1. Biological Inspiration from the Blue-ringed Octopus for the Device Design. (A) Pictures of a blue-ringed octopus (*H. lunulata*) reversibly changing the global

appearance of its body.^[26] (B) Close-up pictures of an individual blue ring on the skin of the *H. lunulata* octopus reversibly changing its appearance in response to neural stimuli.^[26] (C) A side-view schematic of a typical blue ring from the *H. lunulata* octopus. Each natural blue ring represents a dynamic bio-optical system that consists of a blue-ring containing iridophore cells and a surrounding dark brown area containing chromatophore organs. The iridophores in the blue ring are arranged to provide vibrant blue-green iridescence, and the chromatophores are arranged to enhance the ring's color contrast. (D) A localized cross-sectional schematic of a typical blue ring from the *H. lunulata* octopus. The muscular system covers the blue-green iridescence from the iridophores by contracting (top muscles) and relaxing (peripheral muscles) in tandem or exposes the blue-green iridescence by relaxing (top muscles) and contracting (peripheral muscles) in tandem. (E) A side-view schematic of an octopus-inspired nonacene-based device before (left) and after (right) actuation. The optically active regions of the device consist of a blue outer annulus and a brown inner circle, with the appearance of these colored regions determined by the different chemical states of the constituent nonacene dye. Upon actuation, the optically active regions can be reversibly altered from a contracted state with a small areal coverage to an expanded state with a large areal coverage, with a concomitant change in the appearance for the colored regions. (F) A cross-sectional schematic of the octopus-inspired nonacene-based device before (left) and after (right) actuation. Upon actuation, the optically active regions of the device can be reversibly altered from a textured surface morphology with a large overall thickness to a flattened surface morphology with a small overall thickness.

Figure 5.2. Molecular Design and Theoretical Calculations for the Tetrabenzononacene.

(A) The molecular design of a soluble, stable, and stimuli-responsive tetrabenzononacene, which alters its electronic structure upon protonation. (B) The calculated HOMOs and LUMOs for unprotonated tetrabenzononacene (TBN, **4**) (left) and protonated tetrabenzononacene (PTBN, **4**+2H⁺) (right). (C) The simulated UV/Vis-NIR absorbance

spectra for unprotonated tetrabenzononacene (TBN, **4**) (left) and protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) (right). Note that all the simulated absorbance spectra were normalized to unity.

Figure 5.3. Characterization of the Tetrabenzononacene. (A) The SEC-RI chromatogram for tetrabenzononacene (**4**). (B) The MALDI spectra for tetrabenzononacene (**4**). The experimental spectrum (blue) was overlaid on the simulated spectrum (black). (C) The 1D ¹H NMR spectrum for tetrabenzononacene (**4**). (D) The 2D ¹H-¹H COSY spectrum for tetrabenzononacene (**4**). (E) The definitive molecular structure of tetrabenzononacene (**4**). The arrows indicated specific through-space interactions between different protons observed in the ROESY spectrum. Note that the assignment of protons in the structure was performed analyzing the combined 1D ¹H NMR, COSY, and ROESY spectra. (F) The UV/Vis-NIR absorbance spectrum for unprotonated tetrabenzononacene (**4**). The inset is a picture of unprotonated tetrabenzononacene (TBN, **4**) in solution. (G) The UV/Vis-NIR absorbance spectrum for protonated tetrabenzononacene (PTBN, **4**+**2H**⁺). The inset is a picture of protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) in solution. Note that all the simulated absorbance spectra were normalized to unity. (H) Plots of the normalized absorbance as a function of time for solutions of unprotonated tetrabenzononacene (TBN, **4**) (blue, circles), protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) (brown, squares), and a TMS-pentacene reference (green, hexagons).

Figure 5.4. Mechanical Modulation of the Tri-layer Tetrabenzononacene-based Devices. (A) A cross-sectional schematic of the change in the surface morphology, geometry, and color for an unprotonated tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. (B) Representative 3D topographic AFM images for a unprotonated tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. (C) Representative UV/Vis-NIR spectra for the total absorption (Total A%, blue line) and total transmission (Total T%, green line) for an unprotonated

tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. (D) A cross-sectional schematic of the change in the surface morphology, geometry, and color for a protonated tetrabenzononacene (PTBN, **4**+**2H**⁺)-based device before (left) and after (right) mechanical actuation. (E) Representative 3D topographic AFM images for a protonated tetrabenzononacene (PTBN, **4**+**2H**⁺)-based device before (left) and after (right) mechanical actuation. (F) Representative UV/Vis-NIR spectra for the total absorption (Total A%, blue line) and total transmission (Total T%, green line) for a protonated tetrabenzononacene (PTBN, **4**+**2H**⁺)-based device before (left) and after (right) mechanical actuation.

Figure 5.5. Electromechanical Modulation and Optical Functionality of the Blue Ring-like Quad-layer Devices. (A) A side-view schematic of a blue ring-like device before (left) and after (right) electrical actuation, illustrating the change in the areal coverage and color brightness for the device’s optically-active regions (i.e., the blue outer annulus from TBN (**4**) and the brown inner circle from PTBN (**4**+**2H**⁺)). (B) Digital camera images of a representative blue ring-like device’s optically active regions before (left) and after (right) electrical actuation. (C) (Top) Plots of the areal strain as a function of the applied voltage for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device. (Bottom) Plots of the simultaneous relative color brightness as a function of the applied voltage for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of the same device. (D) (Top) Plots of the areal strain as a function of time over three consecutive on/off electrical actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device. (Bottom) Plots of the simultaneous relative color brightness as a function of time over three consecutive electrical actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of the same device. (E) Plots of the relative color brightness as a function of cycle number for the blue

outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device for over 500 repeated electrical actuation cycles.

Figure 5.6. Fluorescence and Near-IR Functionality of the Blue Ring-like Quad-layer Tetrabenzononacene-based Devices. (A) Schematics of the fluorescence imaging of a blue ring-like device before (left) and after (right) electrical actuation. (B) Representative fluorescence images of a blue ring-like device before (left) and after (right) electrical actuation. (C) Plots of the relative fluorescence intensity as a function of time over three consecutive electrical actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device after 200 continuous on/off cycles. (D) Schematics of the near-IR imaging of a blue ring-like device before (left) and after (right) electrical actuation. (E) Representative near-IR camera images of a blue ring-like device before (left) and after (right) electrical actuation. (F) Plots of the relative near-IR intensity as a function of time over three consecutive actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device after 200 continuous on/off cycles.

Figure S5.1. Energy minimized geometry for tetrabenzononacene (TBN, **4**).

Figure S5.2. Energy minimized geometry for protonated tetrabenzononacene (PTBN, **4**+2H⁺).

Figure S5.3. The ¹H NMR spectrum for intermediate (**2**). Note that a trace amount of didodecylbenzaldehyde was observed and labeled with red crosses (**X**).

Figure S5.4. The ¹³C NMR spectrum for intermediate (**2**).

Figure S5.5. The ¹H NMR spectrum for intermediate (**3-isomer 1**).

Figure S5.6. The ¹³C NMR spectrum for intermediate (**3-isomer 1**).

Figure S5.7. The ^1H NMR spectrum for intermediate (**3-isomer 2**).

Figure S5.8. The ^{13}C NMR spectrum for intermediate (**3-isomer 2**).

Figure S5.9. The ^1H NMR spectrum for tetrabenzononacene (TBN, **4**).

Figure S5.10. The ^{13}C NMR spectrum for tetrabenzononacene (TBN, **4**). Note that the signal obtained for the carbon disulfide (CS_2) solvent was labeled with a red cross (**X**).

Figure S5.11. The ROESY spectrum for tetrabenzononacene (TBN, **4**). The through-space interactions between different protons are labeled with black circles in the spectrum.

Figure S5.12. (A) The fluorescence emission spectrum (dashed blue line) for tetrabenzononacene (TBN, **4**) in solution, which was overlaid with its UV/Vis-NIR absorbance spectrum (solid blue line). (B) The fluorescence emission spectrum (dashed brown line) for protonated tetrabenzononacene (PTBN, **4**+ 2H^+) in solution, which was overlaid with its UV/Vis-NIR absorbance spectrum (solid brown line). Note that all the fluorescence emission spectra were plotted by using absolute intensity values from experimental measurements, while all the UV/Vis-NIR absorbance spectra were normalized to unity.

Figure S5.13. (A) Representative UV/Vis-NIR transmittance spectra for a tri-layer unprotonated tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. The total transmittances (solid green lines) were shown, along with their specular (dashed grey lines) and diffuse (solid grey lines) components. (B) Representative UV/Vis-NIR reflectance spectra for a tri-layer unprotonated tetrabenzononacene (TBN, **4**) device before (left) and after (right) mechanical actuation. The total transmittances (solid blue lines) were shown, along with their specular (dashed grey lines) and diffuse (solid grey lines) components.

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1. **C. Xu**, A. A. Gorodetsky, “Cephalopod-Inspired Adaptive Multispectral Camouflage from a Stretchable Polymeric Conductor”, SPIE Conference: Bioinspiration, Biomimetics, and Bioreplication X, Anaheim, CA, USA, 2020. (Platform, Abstract Accepted)
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ABSTRACT OF THE DISSERTATION

Adaptive Materials and Systems Inspired by Cephalopod Skin

by

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Doctor of Philosophy in Materials Science and Engineering

University of California, Irvine, 2020

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Cephalopods (e.g., squid, octopuses, and cuttlefishes) are a class of marine invertebrates known for their marvelous color-changing and camouflage capabilities. Such stunning visual feats are physically enabled by cephalopods' sophisticated skin architectures that consist of various types of optically active organs and cells, including pigmentary chromatophores, reflective iridophores, and diffusive leucophores. Because of the unmatched optical functionalities, these soft-bodied animals (and their bio-optical skin components) have recently emerged as numerous inspiration sources for a variety of bio-derived and bio-inspired technologies. Within this context, we concentrate on adaptive optical and protonic materials and systems inspired by cephalopod skin. First, we study the long-range proton conduction in a designer cephalopod protein and explore the possible correlations between the protein's self-assembled structures and electrical functions. Next, we draw inspiration from cephalopod skin and develop a stretchable multimodal camouflage platform from a high-performance synthetic proton conductor. Then, we

develop and validate a new class of squid-inspired adaptive infrared-reflecting materials and systems that allow on-demand modulation of infrared radiation. Subsequently, we develop blue-ringed octopus-inspired multifunctional camouflage and signaling platforms from an exceptionally stable nonacene with adaptive visible and near-infrared optical and fluorescent functionalities. Last, we draw inspiration from cephalopods' size-variable chromatophores and engineer a series of large-area camouflage applications with an unprecedented combination of characteristics. Overall, our findings may open opportunities for stealth technologies, bioinspired photonics, flexible optoelectronics, bioelectronics, energy conservation, and soft robotics.

CHAPTER 1

Cephalopod Skin as Biological Inspiration Sources

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1.1. Abstract

Cephalopods are a large class of marine invertebrates that are well known for their color-changing and camouflage abilities. These soft-bodied animals showcase a vast repertoire of camouflage tactics by dynamically modulating the color, pattern, transparency, light emission, texture, and even behavior. The dazzling visual feats performed by cephalopods are physically enabled by their highly evolved skin architectures that mainly consist of three types of optically active organs and cells, including pigmentary chromatophores, reflective iridophores, and diffusive leucophores. The synergistic function of these bio-optical components readily allows cephalopod skin to dynamically interact with light and function like bioelectronic displays with unprecedented optical functionalities. As such, cephalopods (particularly their skin) have garnered much research attention for the development of dynamic optical materials and systems. Biological materials, such as reflectin proteins and xanthommatin pigments, have been derived from cephalopod skin and readily enabled various color-changing and camouflage device applications. Besides, artificial materials and systems that featured unprecedented optical functionalities have also been developed by drawing inspiration from biological designs of natural cephalopod skin. Overall, this chapter constitutes an expanded introduction to cephalopod camouflage and represents a detailed overview of the state-of-the-art progress in cephalopod-derived/inspired materials and technologies.

1.2. Cephalopod and Human History

Cephalopods are a class of marine invertebrates in the molluscan phylum. The evolution of cephalopods can be traced back to ~ 530 million years ago in the late Cambrian, which is widely agreed upon paleontologists to be earlier than the first appearance of vertebrates.^[1] After millions of years' evolution, there are over 750 cephalopod species nowadays that have been discovered and distributed in most parts of the ocean around the world, from shallow-water coastal regions to dark water columns at abyssal depths.^[2,3] Indeed, modern cephalopods are strikingly different from species to species when evaluated with various metrics, such as size, weight, appearance, body structure, and behavior, but in general, these animals can be categorized into two major divisions that include nautiloids and coleoids.^[2,3] Nautiloids have only a handful of existing species, for example, *Nautilus* and *Allonautilus*, which feature rigid external shells with gas-filled chambers that are mainly used for buoyancy and protection.^[4,5] These very few remaining species of nautiloids are known as 'living fossils', because their primitive shelled body structures highly resemble those of ancient cephalopods that went extinct quite a long time ago.^[4,5] Coleoids constitute the majority of modern cephalopods and encompass subdivisions that include decapodiformes (eight arms and two tentacles) and octopodiformes (only eight arms), as represented by common examples such as squid, cuttlefishes, and octopuses.^[2,3] Unlike nautiloids, coleoid cephalopods usually feature soft bodies, with rigid shells being internalized, reduced, or even completely lost during

evolution.^[2,3] Overall, cephalopods, including nautiloids and coleoids, have a high level of species diversity and play a crucial role in global marine ecosystems.

Cephalopods share close ties with our human beings from historical, cultural, and scientific perspectives. Early around 4,000 years ago, ancient Chinese people described the discovery of an unusual ‘ten-body’ fish in a classic geographical and cultural account called “*The Classic of Mountains and Seas* (山海经).”^[6] This mysterious ‘ten-body’ fish was later believed to be shallow-water squid that was known to have eight arms and two tentacles.^[6] Around 350 BCE, the Greek philosopher Aristotle described in his book “*History of Animals*” about color-changing cephalopods (Figure 1.1A).^[7,8] Aristotle observed that octopuses and sepia cuttlefishes could render their body colors to match adjacent stones in the surrounding environments for hunting purposes, and they could perform similar color-changing tricks when alarmed.^[7,8] These two examples represented early written reports of cephalopods in human history and confirmed our ancestors’ direct observation and interaction with these animals. Indeed, cephalopods have been served as inspiration sources for countless fictional mythologies and novels, such as the famous sea monster named *Kraken* in Scandinavian folklore (Figure 1.1B)^[9,10] and the giant squid in Jules Verne’s “*Twenty Thousand Leagues under the Sea*” (Figure 1.1C)^[11,12]. In addition, cephalopods are aesthetically appealing for their marvelous body forms and appearances, and they have been continuously stimulating the creation of numerous artworks, from ancient ceramic wares, as exemplified by a delicate octopus-patterned vase that was

unearthed in Palaikastro (Figure 1.1D)^[13], to more recent oil paintings, as exemplified by Omar Rayyan’s “*Contessa with Squid*” (Figure 1.1E)^[14]. Since around a century ago, cephalopods have also started to garner growing interest within the scientific community, with an extensive amount of research performed to explore and elucidate the evolutionary^[15,16], physiological^[17], structural^[18], and ethological^[3] properties of these marine animals, which in turn have facilitated progress in other emerging areas such as neuroscience^[19], bioelectronics^[20], and robotics^[21]. Taken together, cephalopods have demonstrated enormous impacts on our culture and science along with the human history.

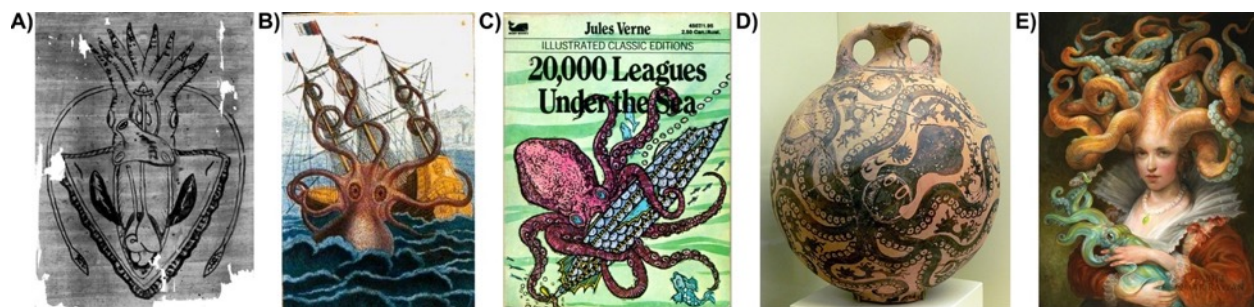


Figure 1.1. Cephalopods in Human History. (A) A lost diagram of a cuttlefish in Aristotle’s book “*History of Animals*” (c. 350 BCE).^[7] The diagram was reconstructed by Armand Marie Leroi (2015 CE).^[8] (B) A drawing of an imaginary colossal octopus called the *Kraken* devouring a ship by Pierre Dénys de Montfort (1801 CE).^[10] (C) A front-cover illustration of Jules Verne’s “*Twenty Thousand Leagues Under the Sea*” by Al Leiner (1977 CE), showing a giant squid attacking the *Nautilus* submarine in the novel.^[12] (D) A picture of an ancient octopus-patterned vase unearthed at Palaikastro, Greece (c. 1500 BCE).^[13] The picture was taken by Wolfgang Sauber (2009 CE). (E) A contemporary oil painting “*Contessa with Squid*” by Omar Rayyan (2011 CE).^[14] Part B is in the Public Domain and was reproduced via Wikimedia Commons. Part D was reproduced under the terms of the GNU Free Documentation License via Wikimedia Commons.

1.3. Cephalopod Color-Changing and Camouflage Abilities

Cephalopods are considered as the most intelligent invertebrates with a high level of intelligence that is comparable to or even exceeds many vertebrate rivals.^[22,23] During evolution, cephalopods have developed highly complex central and peripheral nervous systems, which are served as physical foundations for their intelligence, thus enabling a variety of advanced functions, such as episodic-like memory (i.e., remember what occurred during an episode, where it took place, and when it happened), ability to learn from experience, ability to perform certain activities (e.g., opening jars and using tools), and rapid decision-making in ever-changing marine environments.^[22,23] Among all, the most iconic feature of cephalopods, particularly for coleoid species that include squid, octopuses, and cuttlefishes, is their fascinating abilities to change colors and perform active camouflage, which is an unparalleled feat among all living animals on this planet.^[2,3] Indeed, active camouflage, as an evolutionary result after millions of years, is adopted by these soft-bodied animals as a primary defense mechanism to avoid themselves being detected by predators and thus increase chances of survival (note that some species are also confirmed to use camouflage for hunting or mating purposes).^[2,3] Cephalopods showcase a large repertoire of visual tactics to blend into surrounding environments by altering their appearances, in a much faster and more dynamic fashion when compared to other famous camouflage examples of terrestrial animals, such as chameleons^[24], stick insects^[25], and moths^[26]. To achieve effective camouflage, cephalopods are capable of manipulating their body color, pattern, transparency, contrast, and even texture.^[2,3] Many

cephalopods can also adapt to surrounding lighting conditions by modulating the emission of light from their bodies through symbiotic relationships with bioluminescent bacteria.^[2,3] Besides, some cephalopods are known to mimic appearances, postures, and behaviors of other extra-specific marine animals such as flatfishes and sea snakes.^[2,3] Because there are ~ 750 cephalopod species and they may vary significantly from species to species, it is nearly impossible to enumerate what is possible for each single species. Instead, in this part, we will emphasize a more general discussion on various types of camouflage mechanisms, along with detailed examples of a few representative (and truly exciting) species.

1.3.1. Coloration and Patterning Modulation

The most common (and probably the most fascinating) feature of cephalopods is their unmatched abilities to change skin coloration and patterning.^[2,3] As an essential tactic for camouflage and communication, adaptive color modulation in the skin has been observed and confirmed for almost all coleoid cephalopods (with only very few exceptions of deep-sea species that live at light-impenetrable depths), as exemplified by a swimming pencil squid (*Loliginidae*) reversibly changing color in front of rocks above the seafloor (Figure 1.2A)^[27]. Such dazzling visual feats performed by cephalopods are physically enabled by sophisticated skin architectures that are mainly composed of three different types of light-interacting organs and cells beneath outer transparent epidermises, including pigmentary chromatophore organs, reflective iridophore cells, and diffusive leucophore

cells, as illustrated in Figure 1.2B.^[3,28,29] Chromatophore organs feature highly elastic sacculi filled with color pigments, and they can change their size and shape to modulate the overall pigmentary coloration, functioning like biological color filters (Figure 1.2B).^[3,28,30] Iridophore cells feature highly periodic surface structures that are alternated with proteinaceous platelets and extracellular space, and they can reflect light at specific wavelengths due to constructive interference and display bright structural colors, functioning like biological Bragg reflectors (Figure 1.2B).^[3,28,31] Leucophore cells feature proteinaceous micro-/nano- particles that are randomly distributed near the surface, and they can scatter light into all random directions, functioning like biological optical diffusers (Figure 1.2B).^[3,28,32] Here, we note that the presence, distribution, and functionality of these three types of organs and cells may vary among cephalopod species, and we will have a more detailed discussion about these bio-optical components at the cellular level in Section 1.4. In combination, the unique skin architecture and the synergistic function of these skin components contribute to cephalopods' unparalleled color-changing abilities.

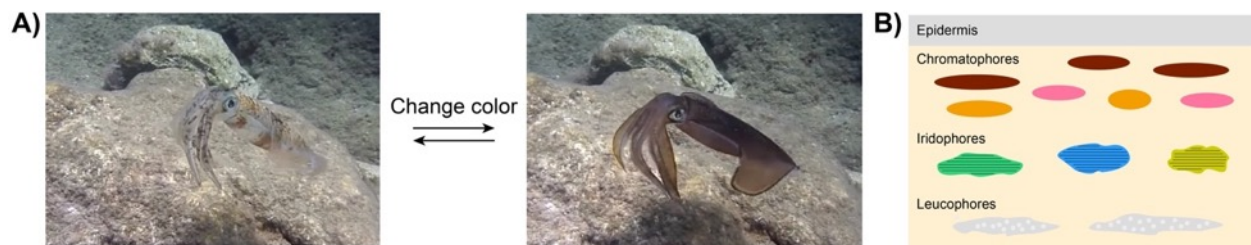


Figure 1.2. Color-Changing Cephalopod Skin. (A) Digital camera images of a swimming pencil squid (*Loliginidae*) reversibly changing its body color in front of rocks above the seafloor.^[27] The images were adapted from a video by Henrik Steinfeldt. (B) A generic

illustration of the cross-sectional architecture of cephalopod skin, which consists of pigmentary chromatophore organs, reflective iridophore cells, and diffusive leucophore cells. Part **A** was reproduced under the YouTube Creative Commons (CC BY) license.

Cephalopods are known to exhibit complex color-changing behaviors for camouflage that are often associated with dynamic patterning, particularly for those species that inhabit diverse nearshore shallow-water environments.^[3,33,34] These animals are capable of generating a variety of global body patterns, which are built upon the synchronous functions of thousands of (or millions of) tiny individual light-interacting organs and cells in the skin (mainly related to pigmentary chromatophores) (Figure 1.3A).^[3,33–36] Based on previous observational studies, cephalopods' camouflage patterns can be generalized into three main categories, i.e., uniform, mottled, and disruptive (Figure 1.3B).^[3,36–39] Uniform patterning features the dominant use of single colors throughout the body to resemble similar single-colored (usually bland) backgrounds, as shown by a beige-colored European common cuttlefish (*Sepia officinalis*) matching its appearance to the sandy floor (Figure 1.3B, left).^[39] Mottled patterning features the use of relatively small-sized patches in light and dark colors that are randomly distributed across the skin to match speckled backgrounds, as shown by the same cuttlefish changing its appearance to match a different background with gravels and small pebbles (Figure 1.3B, middle).^[39] Disruptive patterning features the display of sharply contrasting colors in relatively large-sized regions in the skin to make the body outline less conspicuous, as shown by the same cuttlefish adapting its appearance above a new background with large

pebbles (Figure 1.3B, right).^[39] These three basic patterns (plus many variants) can be dynamically switched under direct neural control, which allows cephalopods to quickly match almost any background within a second and thus effectively hide in complex environments.^[3]

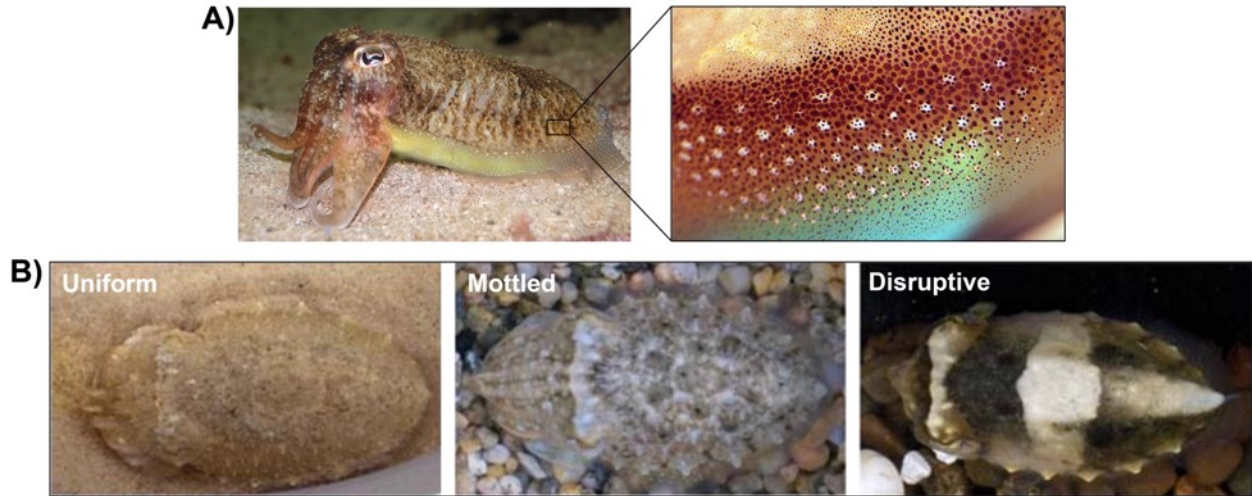


Figure 1.3. Patterning Modulation of Cephalopod Skin. (A) A digital camera image of a European common cuttlefish (*Sepia officinalis*) above a sandy background.^[33] The image was taken by Jarek Tuszyński. Inset is a close-up view of the skin of an *S. officinalis* cuttlefish, featuring a dense distribution of thousands of tiny light-interacting organs and cells.^[34] The image was taken by Roger Hanlon. (B) An *S. officinalis* cuttlefish adapting its body appearance to match different backgrounds, with the skin pattern changing from uniform (left) to mottled (middle) to disruptive (right).^[39] Part A was reproduced under the terms of the GNU Free Documentation License via Wikimedia Commons. Part B was reproduced with permission of Springer Nature (Copyright © 2009).

Besides camouflage, many cephalopods also use dynamic body patterning for a variety of other purposes, such as secondary defense mechanism, communication, and signaling.^[3,35] As one example, in cases where the primary defense mechanism (i.e.,

camouflage) fails, an Atlantic white-spotted octopus (*Callistoctopus macropus*) can suddenly change its body appearance into a high-contrast reddish pattern with sparsely distributed white spots, as shown in Figure 1.4A.^[40] This dramatic deimatic display is often effective to startle the predators and thus gain the octopus more time to expel ink and escape. As another example, a male Caribbean reef squid (*Sepioteuthis sepioides*) can split its body pattern into two strikingly different halves, with the right half appearing dark brown to attract a female squid and the left half appearing silvery-white to repel rival males, as shown in Figure 1.4B.^[41] Note that the half-bodied pattern can be rapidly flipped in seconds. As a third example, flamboyant cuttlefishes (*Metasepia pfefferi*) are famous for their vivid coloration with a series of pigmentary black stripes constantly moving across the body, which are known as ‘passing clouds’, as shown in Figure 1.4C.^[42] These eye-catching flashing patterns can send out warning (poisonous) signals to confuse or dismay potential predators, although, interestingly, the *M. pfefferi* cuttlefishes only produce neurotoxins at trace amounts. Altogether, these examples readily showcase cephalopods’ versatile abilities to change color and patterning under various circumstances.

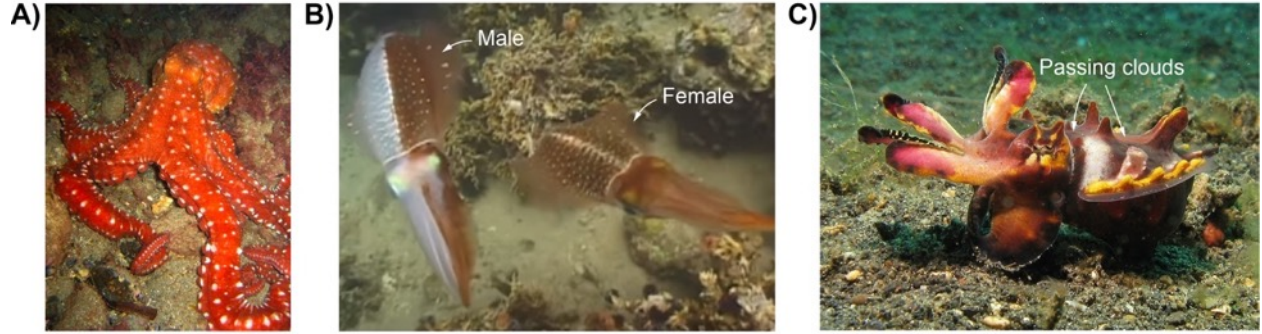


Figure 1.4. Dynamic Skin Patterning for Various Purposes. (A) An Atlantic white-spotted octopus (*Callistoctopus macropus*) displaying a deimatic reddish pattern with sparsely distributed white spots.^[40] The image was taken by the SUBnormali Team. (B) A male Caribbean reef squid (*Sepioteuthis sepioides*) splitting its body pattern into two different halves to attract a female squid during mating activities.^[41] The image was taken by Roger Hanlon. (C) A flamboyant cuttlefish (*Metasepia pfefferi*) showing vivid skin coloration with constantly moving pigmentary stripes (known as passing clouds) on the dorsal side of the mantle.^[42] The image was taken by Silke Baron. Part **A** was reproduced under the Creative Commons Attribution-Share Alike 3.0 Unported license via Wikimedia Commons. Part **C** was reproduced under the Creative Commons Attribution 2.0 Generic license via Wikimedia Commons.

1.3.2. Transparency Modulation

Transparency modulation is another common tactic that is frequently performed by many cephalopods to hide from the detection of predators. Such transparency-modulating cephalopod species, as exemplified by mesopelagic octopuses (*Japetella heathi*) (Figure 1.5A)^[43] and glass squid (*Taonius borealis*) (Figure 1.5B)^[44,45], are usually found in the deep ocean (600 m – 1,000 m), where only two sources of light are available: 1) extremely weak downwelling light from the ocean’s surface, and 2) bioluminescence. As one example, a *J. heathi* octopus can achieve active camouflage in somewhat featureless

water columns by dynamically adjusting the transmission of light and switching between a highly transparent state and a highly opaque (pigmentary) state (Figure 1.5A).^[43] In the transparent state, the *J. heathi* octopus allows the very weak downwelling light to directly pass through its nearly transparent body, which largely minimizes the overall silhouette when viewed from below in the same water column, thus making the octopus invisible to many deep-sea predators that rely on the variation of downwelling light and silhouette to forage (Figure 1.5A, left).^[43] However, it is noted that being transparent does not protect the *J. heathi* octopus from a specific group of predators that have evolved with bioluminescence headlights (usually in blue color), because the non-ideally transparent body of the *J. heathi* octopus inevitably scatters a fraction of light upon bioluminescence illumination, making it appear bright in the dark and visually distinguishable from the surrounding environment. Therefore, the highly opaque (pigmentary) state comes into play, where the skin of the *J. heathi* octopus becomes predominantly covered with much expanded pigment-containing chromatophore organs that could not be seen in the transparent state (Figure 1.5A, right).^[43] These expanded skin-bound chromatophores are in red or black, with very strong absorption and weak scattering of the blue-colored bioluminescence, thus making the *J. heathi* octopus appear much less conspicuous to those predators that rely on bioluminescence to forage. Notably, the *J. heathi* octopus can dynamically, reversibly, and rapidly modulate its body appearance under direct neural control and take on different transparency states in response to various lighting conditions in the environment.^[43] Overall, transparency

modulation represents an effective approach for dynamic camouflage among deep-sea cephalopods.

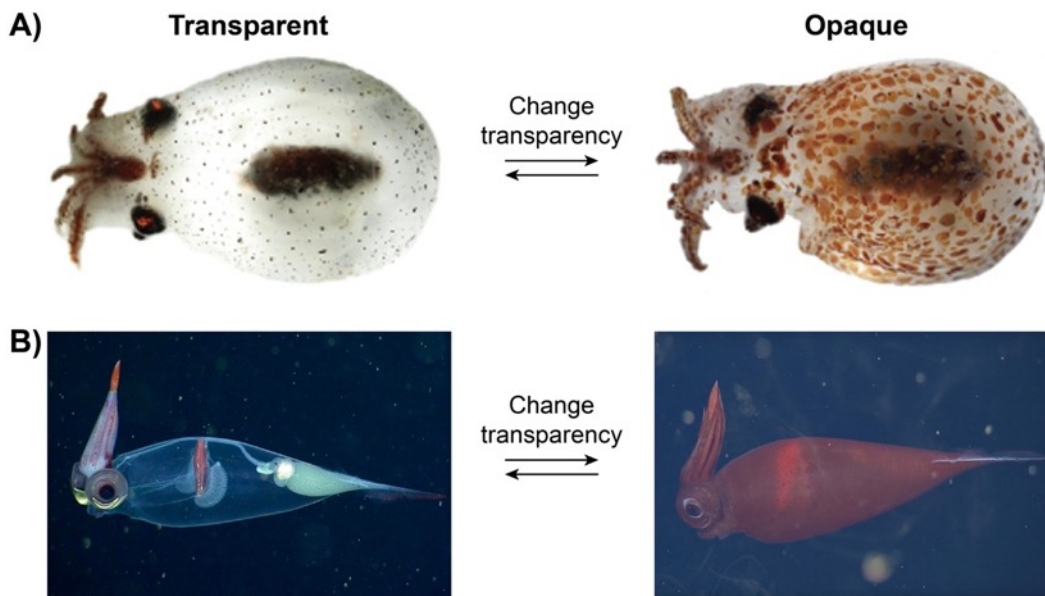


Figure 1.5. Transparency Modulation of Cephalopod Skin. (A) Pictures of a representative mesopelagic octopus (*Japetella heathi*) reversibly switching its body appearance between transparent and opaque states.^[43] (B) Pictures of a representative glass squid (*Taonius borealis*) reversibly switching its body appearance between transparent and opaque states.^[44,45] The images were obtained from the Monterey Bay Aquarium Research Institute. Part A was reproduced with permission of Elsevier Ltd. (Copyright © 2011).

1.3.3. Contrast Modulation

Another fascinating tactic for cephalopods to perform camouflage feats is through contrast modulation. Many coastal cephalopods are capable of manipulating their skin color contrast to match the color intensity and brightness of often complex marine environments.^[2,3] However, in terms of contrast modulation, there may not be any examples as amazing as octopuses in the genus of *Hapalochlaena* that include blue-ringed

octopuses (*Hapalochlaena lunulata*) and blue-lined octopuses (*Hapalochlaena fasciata*). As one example, an *H. lunulata* octopus can dramatically alter the color contrast of its body by flashing blue rings in the skin (Figure 1.6A).^[46] When at rest, the octopus adopts a relatively low-contrast appearance with hardly noticeable ring-like patterns and thus blends perfectly into the background (Figure 1.6A, left), but when disturbed, the same octopus can instantaneously switch to a highly conspicuous appearance with a drastically increased color contrast that now features vibrant blue rings and dark brown surrounding regions (Figure 1.6A, right).^[46] Indeed, the *H. lunulata* octopuses have evolved a unique actuation mechanism, along with distinct skin architectures known as blue rings (Figure 1.6B), specifically for color contrast modulation, which are different from almost all other known cephalopod species.^[47] Each individual blue ring is a miniaturized bio-optical system comprised of highly reflective iridophore cells, pigment-containing chromatophore organs, and proximal muscles (Figure 1.6C).^[47] The iridophores, which make up the interior of the rings, function as biological Bragg stacks that reflect narrowband blue-green light and are arranged to ensure visibility of their bright iridescence over a broad range of viewing angles (Figure 1.6C).^[47] The chromatophores, which are located beneath and around the rings, provide a pigmented dark brown background and are arranged to enhance the overall color contrast (Figure 1.6C).^[47] The muscles, which are found on top of and around the periphery of the rings, cover the blue-green iridescence by contracting (top muscles) and relaxing (peripheral muscles) in tandem or expose the blue-green iridescence by relaxing (top muscles) and contracting (peripheral muscles) in tandem (Figure 1.6C).^[47]

Notably, hundreds of blue rings can be simultaneously activated by this neuromuscularly-controlled process within only hundreds of milliseconds, which enables the *H. lunulata* octopus' skin to rapidly flash between different contrast states (Figure 1.6A).^[46] Overall, contrast modulation constitutes an integral part of cephalopods' large repertoire of camouflage mechanisms.

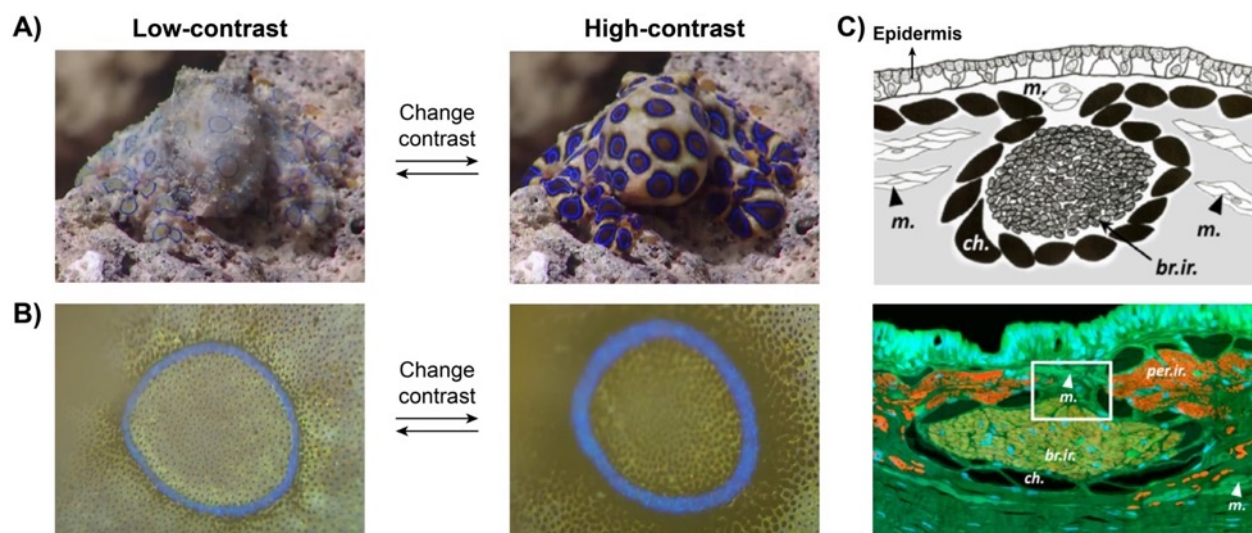


Figure 1.6. Contrast Modulation of Cephalopod Skin. (A) Images of a blue-ringed octopus (*Hapalochlaena lunulata*) flashing blue rings and switching the body appearance from a low-contrast state (left) to a high-contrast state (right).^[46] (B) Close-up images of an individual blue ring in the same octopus' skin switching from a low-contrast state (left) to a high-contrast state (right).^[46] (C) Top: A schematic of the cross-sectional architecture of a blue ring, showing the arrangement of bright iridophores in the blue ring (*br.ir.*), surrounding chromatophore organs (*ch.*), and proximal muscles (*m.*). Bottom: A confocal microscope image of the cross-sectional architecture of a blue ring.^[47] Part C was reproduced with permission of The Company of Biologists Ltd. (Copyright © 2012).

1.3.4. Symbiotic Bioluminescence

Symbiotic bioluminescence is a distinct approach adopted by some cephalopod species for adaptive camouflage. Unlike other skin-enabled visual camouflage mechanisms, the function of symbiotic bioluminescence necessitates the involvement of a third party that can produce light, usually bioluminescent bacteria that are abundant in the ocean, to match complex lighting conditions in the marine environment. This camouflage mechanism is also known as counter-illumination, as exemplified by firefly squid (*Watasenia scintillans*, Hawaiian bobtail squid (*Euprymna scolopes*), and hummingbird bobtail squid (*Euprymna berryi*) (Figure 1.7A).^[48] As one example, the *E. scolopes* squid cannot produce light by itself, instead, it shares a symbiosis relationship with bioluminescent bacteria (*Vibrio fischeri*), which colonize and live inside specialized light organs that are located in the squid skin (Figure 1.7B).^[49-51] When the sky turns dark at night, the *V. fischeri* bacteria automatically start to glow with blue-/green-colored bioluminescence through a luciferin/luciferase-mediated biochemical reaction.^[3,50,51] Then, the emitted light is reflected by a collection of well-arranged reflective tissues inside the light organs that are mainly made of high-refractive-index protein platelets.^[3,50,51] Subsequently, the reflected light travels out of the ventral surface of the *E. scolopes* squid in a downward direction, which essentially emulates the downwelling moonlight and starlight that you would expect from a clear night sky.^[3,50,51] In this way, the *E. scolopes* squid can effectively soften and minimize the shadow of its body and thus deceive potential predators that are located at greater depths of the same water column. Moreover, the *E.*

scolopes squid demonstrates the ability to sense the environmental lighting condition and then autonomously adjust the intensity and frequency of the bioluminescence emitted from the bacteria to achieve better camouflage.^[3,50,51] In addition, it is also notable that this symbiotic mechanism between the *E. scolopes* squid and the *V. fischeri* bacteria has been extensively explored and served as a simple model system for the study of natural mutualistic symbiosis.^[52] Overall, cephalopods showcase a delicate and beautiful camouflage mechanism through symbiotic relationships with bioluminescent bacteria.

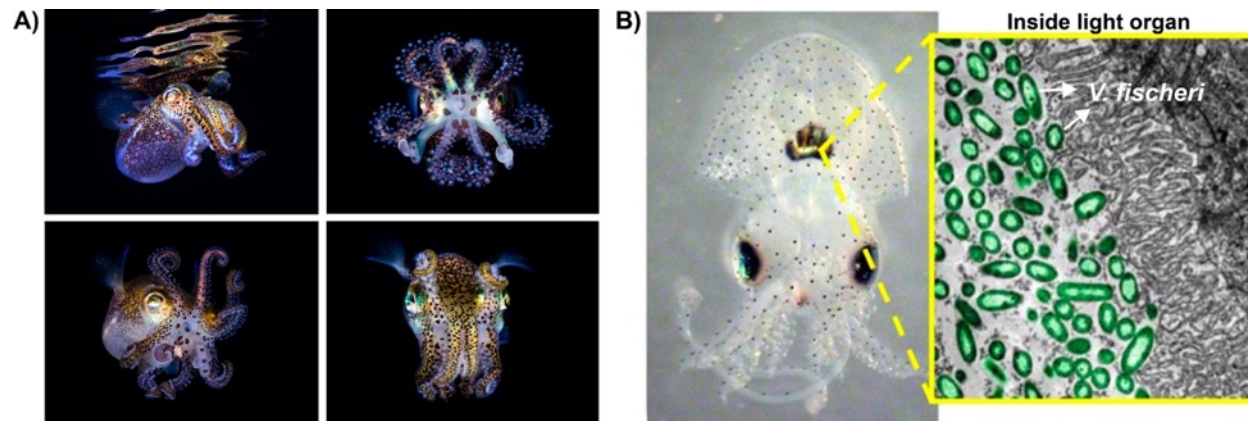


Figure 1.7. Symbiotic Bioluminescence of Cephalopod Skin. (A) Digital camera images of a Hawaiian bobtail squid (*Euprymna scolopes*) glowing in the dark through symbiotic bioluminescence.^[48] The images were taken from different angles by Todd Bretl. (B) A digital camera image of another *Euprymna scolopes* squid. The inset shows that bioluminescent bacteria (*Vibrio fischeri*) occupy and live inside a light organ that is located in the squid mantle.^[49] Note that the bioluminescent bacteria were colored in green for visualization. The images were taken by Eric Stabb.

1.3.5. Texture Manipulation

While all the aforementioned camouflage mechanisms are enabled by dynamic optical interaction between the incident light and bio-optical components in the skin, the ability of cephalopods to manipulate skin textures allows them to accomplish precise and realistic three-dimensional (3D) camouflage via a mechanical approach, as exemplified by many shallow-water species such as Australian giant cuttlefishes (*Sepia apama*) and common octopuses (*Octopus vulgaris*) (Figure 1.8).^[36,53] These shallow-water cephalopods are adept at mimicking the shapes and textures of a variety of objects in their surrounding environments (e.g., rocks, coral reefs, seaweeds, and seafloors). In general, the elaborate shape-shifting behaviors of cephalopods are enabled by neurally controlled mechanical actuation of their skin musculatures (usually muscular hydrostats) to form different types of dermal protuberances called papillae.^[54-57] As one example, an *S. apama* cuttlefish can express individual papillae through surface buckling within a second in response to external stimuli, featuring a drastic change from smooth skin before activation (Figure 1.8A, left) to rather rough skin after activation (Figure 1.8A, right).^[53] These papillae can be maintained in the extended position for over one hour via a unique ‘catch-like’ mechanism, without the necessity of continuous neural input, which represents a sophisticated biomechanical strategy to reduce energy cost that is usually associated with long-term camouflage!^[57] As another example, an *O. vulgaris* octopus is able to transform its body into an algae-like form, with the bumpy papillae to resemble the algae texture and the pigmentary dark skin to match the algae coloration, perfectly blending itself into

these natural algae undulating above the seafloor (Figure 1.8B, right).^[36] After being disturbed by the scuba diver, it reconfigures its body, now with much smoother skin and more conspicuous bright color, and immediately jets away (Figure 1.8B, left).^[36] Indeed, rapid texture modulation, along with color change, is routinely performed by these bottom-dwelling octopuses (over 150 times per hour observed for a day octopus (*Octopus cyanea*)) when out for foraging on a daily basis.^[2] Taken together, cephalopods demonstrate unparalleled abilities of texture manipulation through mechanical actuation of skin musculatures to enable background resemblance and achieve advanced 3D camouflage.

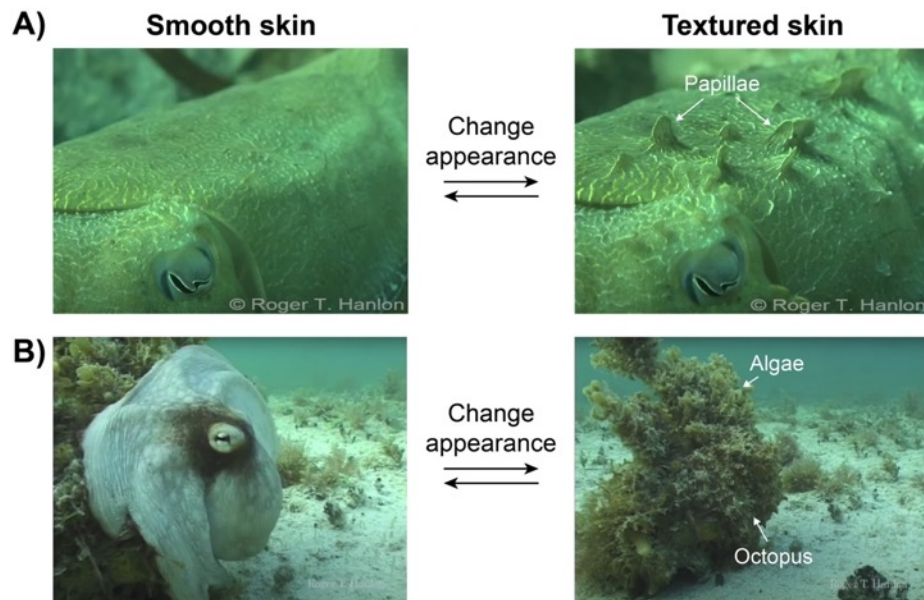


Figure 1.8. Texture Manipulation of Cephalopod Skin. (A) Images of an Australian giant cuttlefish (*Sepia apama*) reversibly changing its skin texture.^[53] Note that papillae can be expressed to form a highly textured skin surface. The images were taken by Roger Hanlon. (B) Images of a common octopus (*Octopus Vulgaris*) reversibly changing its skin texture and appearance.^[36] Note that the octopus can perform realistic 3D camouflage and

perfectly blend itself into the undulating algae above the seafloor. The images were taken by Roger Hanlon. Part **B** was reproduced with permission of Elsevier Ltd. (Copyright © 2007).

1.3.6. Behavioral Mimicry

Some cephalopod species have evolved an advanced camouflage mechanism that is known as behavioral mimicry. These masters of masquerade can not only imitate inanimate objects (described in 2.5) but also mimic appearances and characteristic behaviors of other extra-specific animals. Such cephalopod species are usually found on featureless sandy sea floors, as exemplified by wunderpus octopuses (*Wunderpus photogenicus*) and mimic octopuses (*Thaumoctopus mimicus*) (Figure 1.9A).^[58] As one example, a *T. mimicus* octopus is capable of mimicking the behaviors of up to 13 different types of marine animals (mobile and sessile) or organisms that are locally present in its natural habitat, including flatfishes, sea snakes, lionfishes, stingrays, eels, and jellyfishes (Figure 1.9B–1.9E).^[59,60] When moving fast across the open sand plain, the *T. mimicus* octopus can swim like flatfishes by matching its motion, speed, and duration, as well as displaying a flatfish-like mottled body appearance (Figure 1.9B).^[59,60] When sitting still on the sand plain, the *T. mimicus* octopus can impersonate sessile invertebrates, such as sponges, tunicates, and tube worms, by reshaping its malleable body to hold a relative static posture for a long time (Figure 1.9C).^[59,60] When disturbed by small damselfishes, the *T. mimicus* octopus can bury its body into a sand burrow and leave only two long black-and-white banded arms undulating outside the burrow, which highly resembles the

shape, pattern, and movement of typical sea snakes (known to prey on small damselfishes) (Figure 1.9D).^[59,60] In addition, more observational studies have reported that *T. mimicus* octopuses can take on different mimicry forms during different activities in different environments, allowing the octopuses to remain camouflaged or unrecognized by potential predators.^[59,60] However, to date, there is still no clear experimental or quantitative evidence to determine whether this behavioral intelligence of the *T. mimicus* octopuses is intrinsic or learned from experience over time, although it has been widely speculated to be a result of both.^[61] Overall, versatile behavioral mimicry, together with other visual camouflage mechanisms, readily makes cephalopods the best example of camouflage in nature.

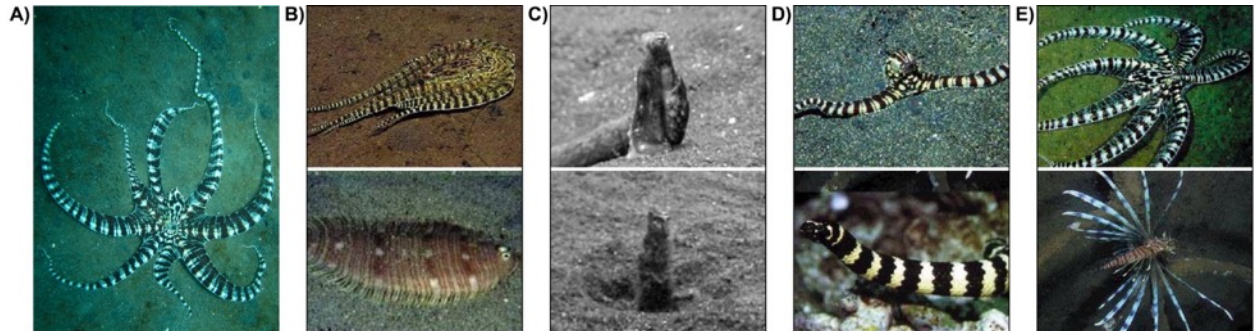


Figure 1.9. Behavioral Mimicry. (A) A picture of a mimic octopus (*Thaumoctopus mimicus*) by Steven Childs.^[58] (B) A mimic octopus swimming across the seafloor (top), mimicking the typical appearance and motion of a flatfish (bottom).^[59] The pictures were taken by Mark Norman and Roger Steene. (C) A mimic octopus sitting still on the seafloor, resembling the typical posture of a sessile tube worm.^[60] The pictures were taken by Roger Hanlon. (D) A mimic octopus buried itself in a sand burrow with two long black-and-white banded arms undulating outside (top), mimicking the shape, pattern, and movement of a typical sea snake (bottom).^[59] The pictures were taken by Mark Norman

and Roger Steene. **(E)** A mimic octopus moving above the seafloor with all eight arms extended (top), resembling the typical body form of a lionfish (bottom).^[59] The pictures were taken by Mark Norman and Roger Steene. Part **A** was reproduced under the terms of the Creative Commons Attribution 2.0 Generic license via Wikimedia Commons. Part **B**, **D**, and **E** was reproduced with permission of the Royal Society (Copyright © 2001). Part **C** was reproduced with permissions of John Wiley and Sons (Copyright © 2007).

1.4. Cephalopod Color-Changing Skin at Cellular Levels

Cephalopods are known as masters of disguise that have evolved with a large repertoire of visual tactics to dynamically alter coloration, appearance, and behavior for camouflage and signaling purposes. These stunning visual feats are performed across an extended surface area that covers the whole body, which are directly enabled by the synergistic function of thousands of (or millions of) tiny constituent bio-optical and bio-mechanical components in the skin. In general, the architecture of cephalopod skin is highly evolved and quite sophisticated at the cellular level, which is often composed of several well-arranged organs and cells, including pigmentary organs like chromatophores, reflective cells like iridophores and leucophores, light-emitting photophores (also known as light organs), and muscles.^[3,62] Because of our scope and interest in this thesis, we will give an expanded discussion exclusively on the structure, function, and mechanism of chromatophores, iridophores, and leucophores, which represent three major types of organs and cells that have been well studied about their dynamic interaction with light (Figure 1.10).^[3,62] For additional information on photophores and muscles, readers may find a handful of useful references in the literature.

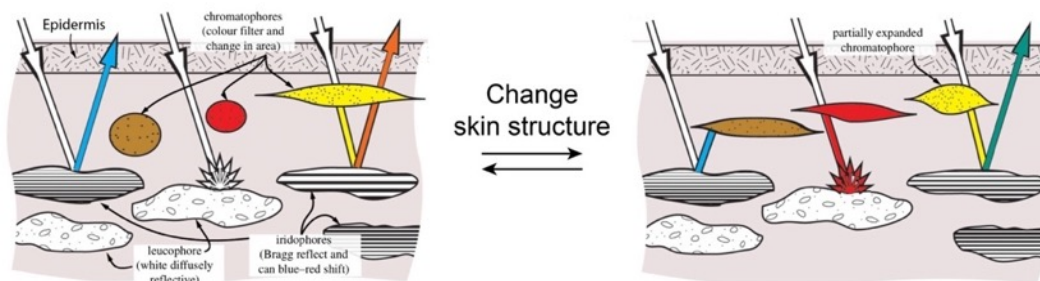


Figure 1.10. Cephalopod Skin Architecture. A generic illustration of the cross-sectional architecture of color-changing cephalopod skin, featuring the dynamic interaction between light and three types of skin-embedded bio-optical components that include pigmentary chromatophore organs, reflective iridophore cells, and diffusive leucophore cells.^[62] The figure was reproduced with permission of the Royal Society (Copyright © 2013).

1.4.1. Pigmentary Chromatophores

Chromatophore organs are the major optically active components in cephalopod skin that are responsible for the dominant pigmentary coloration of the whole body. These color-changing organs can be found in most parts of the body, such as mantles, fins, arms, tentacles (for squid and cuttlefishes), and near eyes (Figure 1.11A).^[3,30,63,64] They constitute the topmost chromatic layer under the epidermis and situate above the underlying light-reflecting cells (i.e., iridophores and leucophores) (Figure 1.10).^[62] Chromatophores can display multiple dark and light colors dictated by constituent pigments, including yellow, orange, pink, red, brown, and black, which are mostly located in the long-wavelength visible region of the electromagnetic spectrum.^[3,28-30] Many coastal cephalopod species have no fewer than three types of color pigments in their chromatophores, due to their adaption to complex shallow-water habitats, while some

deep-sea species only have one type, due to extreme dim lighting conditions at depths.^[3] The size of chromatophores varies significantly among different species, as evaluated by the diameter in their fully expanded states, from a few hundred microns ($\sim 300\ \mu\text{m}$ for *Sepia officinalis* cuttlefishes) to several millimeters ($> 1.5\ \text{mm}$ for *Loligo plei* squid).^[3,30] Dark-colored chromatophores (e.g., black and brown) usually have relatively larger sizes, and light-colored ones (e.g., yellow and red) have relatively smaller sizes.^[3] In addition, the population of chromatophores in cephalopods differs from species to species, for example, a few hundred for some pelagic squid species and millions for many coastal cephalopod species such as *S. officinalis* and *O. vulgaris*.^[3]

The optically active component of a chromatophore organ is the central cytoelastic sacculus that encompasses packed pigment granules with diameters of hundreds of nanometers (Figure 1.11A).^[65-67] A set of wedge-shaped radial muscles (15–25) are attached and anchored onto the highly deformable pigment-containing sacculus (Figure 1.11A).^[3,30,65,68] Because cephalopod skin is highly innervated with nerve bundles, these radial muscles are subject to direct neural control from the central nervous system without the involvement of any synapse (Figure 1.11A).^[3,30,65,68] At the resting state, the radial muscles are relaxed, and the sacculus is retracted into a tiny dot with the internal pigmentary granules closely packed in a small volume (Figure 1.11B, left and Figure 1.11C, left).^[68] Therefore, more light is allowed to transmit through the skin, and less is absorbed. At the activated state, the radial muscles are contracted, and the sacculus is

radially pulled and expanded into a much larger area with the internal pigment granules spread out in a relatively sparse distribution (Figure 1.11B, right and Figure 1.11C, right).^[68] Therefore, less light is allowed to transmit through the skin, and more is absorbed. The size of the elastic pigment-containing sacculus can dramatically change upon activation, up to over 100 times, thus enabling a remarkable visible change in the overall pigmentary coloration.^[30] Note that this neuromuscular control of chromatophore organs in cephalopod skin is quite different from the function mechanism of common chromatophore cells found in fishes and reptiles, where pigmentary coloration is modulated by forming pigment aggregation/dispersion upon hormonal stimuli.^[69] In comparison, one obvious advantage of direct neuromuscular control is the rapid response of chromatophores, which can be instantly activated/deactivated within only hundreds of milliseconds.^[3,30,68] As a result, cephalopods are capable of changing color multiple times within only a few seconds, and thousands of chromatophores can be synchronously switched on and off in multiplexed formats to generate a variety of complex global patterns for dynamic camouflage in real time.

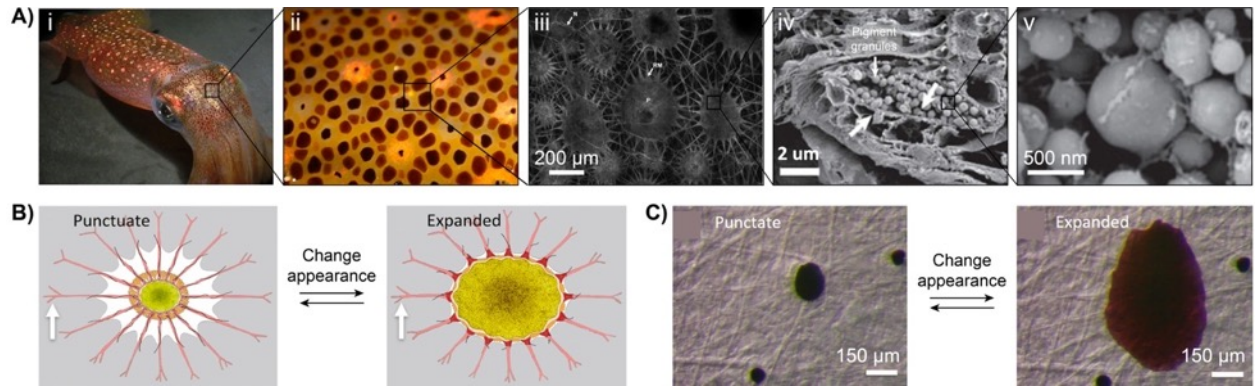


Figure 1.11. Pigmentary Chromatophore Organs in Cephalopod Skin. (A) Chromatophore organs at different length scales (from left to right): (i) a digital camera image of a longfin inshore squid (*Doryteuthis pealeii*).^[63] The image was taken by Paloma T. Gonzalez-Bellido; (ii) a close-up image of the skin of a *D. pealeii* squid, showing a dense distribution of pigmentary chromatophores (dark colored spots).^[64] The image was taken by Minette Layne; (iii) a confocal microscope image of chromatophore organs, showing radial muscles (RM) and nerve bundles (N) connected to the central elastic pigment-containing sacculus (P) of each individual chromatophore;^[68] (iv) a scanning electron microscope (SEM) image of the cross section of a chromatophore;^[66] (v) a close-up SEM image of closely packed pigment granules inside the same chromatophore.^[66] (B) A schematic of the reversible actuation of a chromatophore under direct neural control, showing a clear change in the areal coverage upon activation.^[68] (C) Optical microscope images of the reversible actuation of a chromatophore in the skin of a *D. pealeii* squid, showing visible changes in both the areal coverage and pigmentary coloration upon activation.^[68] Part A (i) was reproduced with permission of the Company of Biologists Ltd. (Copyright © 2014). Part A (ii) was reproduced under the Creative Commons Attribution 2.0 Generic license via Wikimedia Commons. Part A (iii) was reproduced with permission of John Wiley and Sons (Copyright © 2013). Part A (iv) and (v) were reproduced with permission of the Royal Society (Copyright © 2014). Part B and C were reproduced with permission of John Wiley and Sons (Copyright © 2013).

1.4.2. Light-Reflecting Iridophores

Iridophores are a type of light-reflecting cells that accounts for the bright iridescence observed in cephalopod skin. These reflective cells are found in different regions on the body surface that include mantles, fins, heads, and arms (Figure 1.12A).^[3,31,70] They are usually situated below the top layer of chromatophore organs and above the bottom layer of leucophore cells (Figure 1.10).^[62] The size of iridophores varies from species to species and is usually below 1 mm.^[3,28] Unlike pigmentary colors produced by chromatophores, most iridophores are known to display vibrant structural colors that are mostly located in the short-wavelength visible region of the electromagnetic spectrum, including blue, green, and violet, although a few exceptions of red and orange were observed in some cephalopod species.^[3,28,31,71,72] Iridophores do not contain any color pigments, instead, they possess highly invaginated (or folded) surface morphologies that are composed of alternating micro-/nano- structures (Figure 1.12A).^[73] These multilayered structures feature periodic arrangements of membrane-enclosed proteinaceous platelets with a relatively high refractive index (mostly made of reflectin proteins) and extracellular space with a relatively low refractive index (mostly made of cytoplasm), which essentially resembles the typical stacked configuration of a distributed Bragg reflector (Figure 1.12A).^[73] Therefore, iridophores can reflect narrowband light at specific wavelengths due to constructive interference, thus producing angle-dependent bright iridescence on the surface.

In most cephalopod species, iridophores are found to be physiologically static, i.e., their optical functionality is not responsive to external stimuli. However, there are exceptions in a few species, such as longfin inshore squid (*Doryteuthis pealeii*), where iridophores have been confirmed to exhibit tunable coloration.^[74] Experiments have demonstrated that these dynamic iridophores are often connected or terminated with nerve fibers, which indicates that the observed tunable iridescences are related to neurally mediated processes (Figure 1.12B).^[74] The application of a neurotransmitter acetylcholine (ACh) triggers a biochemical signaling cascade process within the iridophore cells, which initiates the phosphorylation/dephosphorylation of the constituent reflectin proteins in the alternating proteinaceous platelets, accompanied with fluxes of ions and water across cell membranes (Figure 1.12C).^[73] The subsequent condensation of the proteinaceous platelets leads to a change in the overall geometry and arrangement of the Bragg-reflector-like structures on the iridophore surface (Figure 1.12C).^[73] As a result, the iridophores can shift their reflectance peaks (i.e., colors) across a broad wavelength range within the visible region of the electromagnetic spectrum (Figure 1.12D).^[74] The response time of these tunable iridophores is usually between a few seconds and a few minutes^[3,74], much slower compared to that of chromatophores.

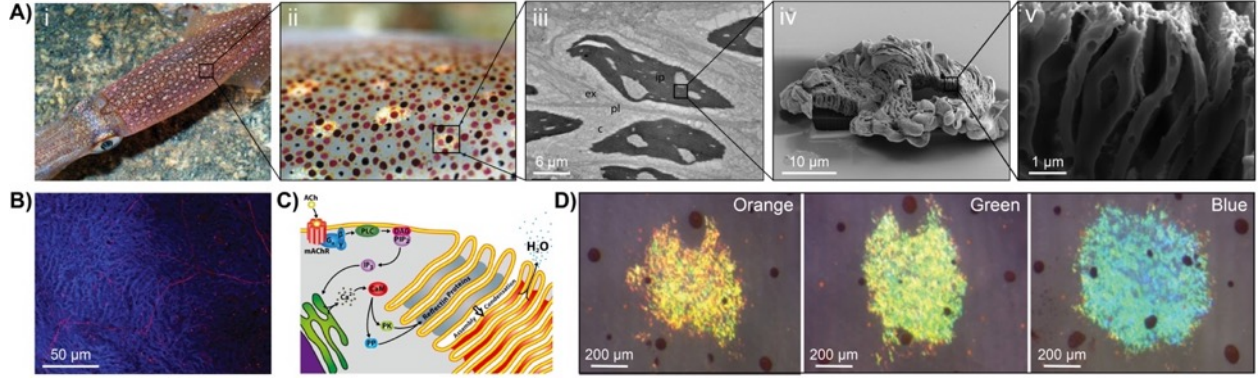


Figure 1.12. Light-Reflecting Iridophore Cells in Cephalopod Skin. (A) Iridophore cells at different length scales (from left to right): (i) a digital camera image of a longfin inshore squid (*Doryteuthis pealeii*).^[70] The image was taken by Grayson Hanlon. (ii) a close-up image of the skin of a *D. pealeii* squid, showing sparsely distributed light-reflecting iridophore cells (bright spots).^[70] The image was taken by Grayson Hanlon. (iii) A cross-sectional transmission electron microscope (TEM) image of several iridophore cells from a different inshore squid (*Doryteuthis opalescens*);^[73] (iv) an SEM image of a portion of an iridophore from a *D. opalescens* squid;^[73] (v) a close-up SEM image of the surface of the same iridophore, showing a periodic arrangement of highly invaginated structures.^[73] (B) A confocal maximum-intensity projection image of fine neural structures (in red color) within an iridophore, confirming that iridophores are innervated.^[74] (C) An illustration of a proposed biochemical signaling cascade process that may contribute to iridophores' tunable iridescence in response to acetylcholine (ACh).^[73] (D) Optical microscope images of single iridophores in the skin of a *D. pealeii* squid displaying neurally tunable structure coloration from orange (left) to green (middle) to blue (right) in response to stimuli.^[74] Part A (iii)–(v) and Part C were reproduced with permission of National Academy of Sciences (Copyright © 2013). Part B and D were reproduced with permission of the Royal Society (Copyright © 2012).

1.4.3. Light-Scattering Leucophores

Leucophores are a type of light-scattering cells that mainly contribute to bright white patterns observed in cephalopod skin. These cells can be found in many octopuses and cuttlefishes, in the forms of white spots, white stripes, white head bars, and white zebra-like bands (Figure 1.13A), while their presence in squid is only identified for a few species.^[3,28,32] Leucophores are usually situated beneath the aforementioned optically active layers (i.e., chromatophore organs and iridophore cells) and serve as the bottom layer in the general cephalopod skin architecture.^[62] Each leucophore is an elongated and fattened cell that contains thousands of membrane-enclosed spherical particles (named leucosomes) near the surface (Figure 1.13A).^[3,28,32] These randomly distributed leucosomes consist of high-refractive-index reflectin proteins and sulfated mucoproteins as the major structural components, and they possess variable sizes with diameters from hundreds of nanometers to a few microns (Figure 1.13A).^[32] Note that the size distribution of spherical leucosomes perfectly overlaps with the wavelength range of the visible light. Therefore, leucophores can diffusively reflect incident visible light into all random directions, due to the presence of high-refractive-index disordered structures on the surface, which can be explained and modeled using the Mie scattering mechanism.^[32] As a result, leucophores can function like nearly perfect optical diffusers on the background to complement the pigmentary and structural colors produced by the overlying layers made of chromatophores and iridophores. In addition, such broadband-reflecting properties of leucophores span across a wide spectral range from the ultraviolet to the visible and even

to the near-infrared region of the electromagnetic spectrum (e.g., $\sim 70\%$ in reflectance from 300 nm to 1,000 nm measured for a *Sepia officinalis* cuttlefish^[75]), which allows these cells to reflect light at different wavelengths that match well with incident illuminations^[32], i.e., they appear white under white light, green under green light, or red under red light (Figure 1.13B).

For a long time, leucophores were thought to be physiologically static, because no clear evidence of nerve or muscle connections was found in these cells.^[3] More recently, it was demonstrated that leucophores found in the dorsal mantle of female *Doryteuthis opalescens* squid are optically active upon the stimuli of a neurotransmitter (ACh) (Figure 1.13C).^[76] The leucophore-based white stripes in these animals can dynamically switch their appearances from a highly transparent state to a diffusive white-colored state upon activation (Figure 1.13C), as quantified by an over 15% increase in the broadband reflectance, and the whole process takes around three minutes.^[76] This finding constitutes the only reported example of tunable leucophores in any cephalopod species, and a comprehensive understanding of possible structural and molecular mechanisms behind such optical modulation remains unexplored.

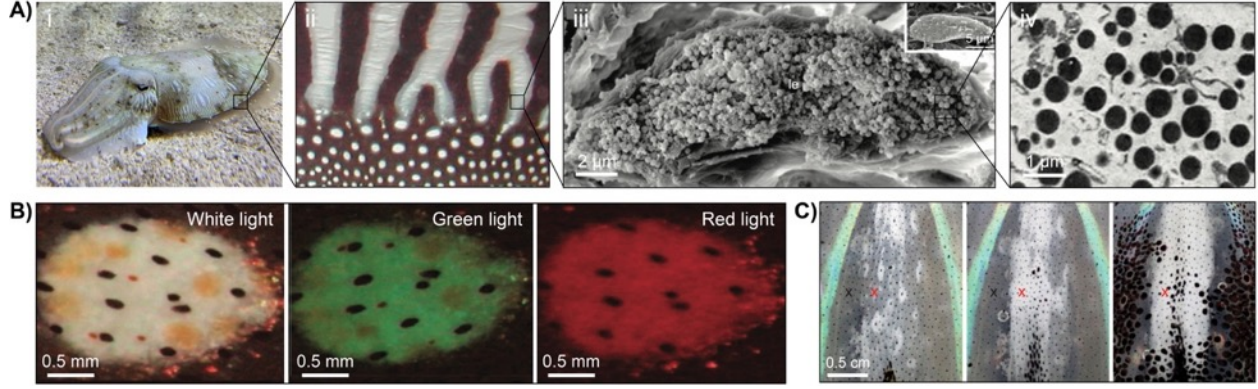


Figure 1.13. Light-Scattering Leucophore Cells. (A) Leucophore cells at different length scales (from left to right): (i) a digital camera image of a European common cuttlefish (*Sepia officinalis*) on the sandy floor. The image was taken by Chengyi Xu. (ii) a close-up image of the skin of an *S. officinalis* cuttlefish, featuring zebra-like bands with white regions that are mainly composed of leucophores;^[32] (iii) a cross-sectional SEM image of a fractured leucophore cell from an *S. officinalis* cuttlefish, featuring densely packed spherical leucosome particles within the cell;^[32] (iv) a close-up TEM image of spherical leucosome particles.^[32] (B) Optical microscope images of a single leucophore from an *S. officinalis* cuttlefish displaying different colors when illuminated with lights at different wavelengths.^[32] (C) Digital camera images of tunable white stripe in the skin of a female *Doryteuthis opalescens* squid upon the stimuli of a neurotransmitter (ACh), featuring a gradual change in the appearance as indicated by the red cross.^[76] Part A (ii)–(iv) and B were reproduced with permission of the IOP Publishing (Copyright © 2018). Part C was reproduced with permission of the Company of Biologists Ltd. (Copyright © 2013).

1.5. Dynamic Optical Materials Derived from Cephalopod Skin

Cephalopods are known for their fascinating color-changing and camouflage capabilities. These unique visual feats are enabled by their distinct bio-optical components in the skin that include chromatophores, iridophores, and leucophores.^[3,62] As such,

biological materials that are directly derived from these skin-embedded optically active organs (or cells) have received much research interest. These biological materials not only serve as important structural foundations for cephalopod skin but also exhibit dynamic optical and electrical functionalities at the molecular level.^[20,77] Two representative types of cephalopod skin-derived materials include (1) reflectin proteins that are abundant in various light-reflecting photonic structures, such as multilayered platelets in iridophore cells,^[73] spherical leucosome particles in leucophore cells,^[32] and assemblies in chromatophore organs;^[66] and (2) xanthommatin-based color pigments that are predominantly found in pigment granules inside chromatophore organs.^[66,67,78] Recently, these cephalopod-derived materials have demonstrated their enormous potential of being integrated as optically active components into artificial devices and systems that are designed and engineered by drawing inspiration from natural color-changing cephalopods to achieve analogous (or even unprecedented) optical functionalities.^[20,77,79] Here, we will review recent progress in the development of dynamic optical devices and systems that are built upon cephalopod-derived biomaterials (i.e., reflectin proteins and xanthommatin pigments).

1.5.1. Reflectin Protein-Based Materials and Applications

Reflectin proteins are a family of cephalopod structural proteins that were first discovered in the light-reflecting platelets inside the light organs of Hawaiian bobtail squid (*Euprymna scolopes*) and later confirmed as one of the major compositions in other

optically active skin components such as chromatophores, iridophores, and leucophores.^[32,66,73,80] These unusual proteins are composed of highly conserved amino acid sequences and contain a large proportion of hydrophilic charged aliphatic and polar aromatic residues.^[80] Reflectins are known to self-assemble into a variety of responsive photonic structures that underpin cephalopods' dynamic camouflage, and they have the highest refractive index among all reported naturally occurring proteins.^[81-83] Given these favorable characteristics, reflectin proteins are suitable for the development of artificial color-changing devices with tunable optical properties.

Reflectins have been integrated into device applications for their excellent *in vitro* self-assembly properties and dynamic optical functionalities in the visible region of the electromagnetic spectrum. Kramer and coworkers prepared a recombinant reflectin isoform (reflectin 1a, from *Euprymna scolopes* squid) and processed the reflectin protein into thin planar films on rigid silicon substrates through a controlled flowing coating process (Figure 1.14A).^[84] These reflectin 1a-based films displayed vibrant colors that were determined by a simple thin-film interference mechanism, and the films were shown to dynamically shift their coloration across the entire visible region upon exposure to various chemical vapors (i.e., water, methanol, and ethanol) (Figure 1.14B).^[84] In addition, the same reflectin protein was compatible with multiple processing approaches (e.g., dip-coating and extrusion) and could be fabricated into a variety of advanced photonic structures, such as diffraction gratings with tunable spacing and highly amorphous fibers

(Figure 1.14C).^[84] These reflectin 1a-based photonic structures were demonstrated to maintain excellent uniformity over millimeter-scale ranges. In a follow-up study, Qin and coworkers reported similar self-assembly properties and optical characteristics for a variant of reflectin 1a protein (named refCBA).^[85] Their refCBA-based thin-film devices could dynamically change color in response to the variation of the relative humidity in the environment.

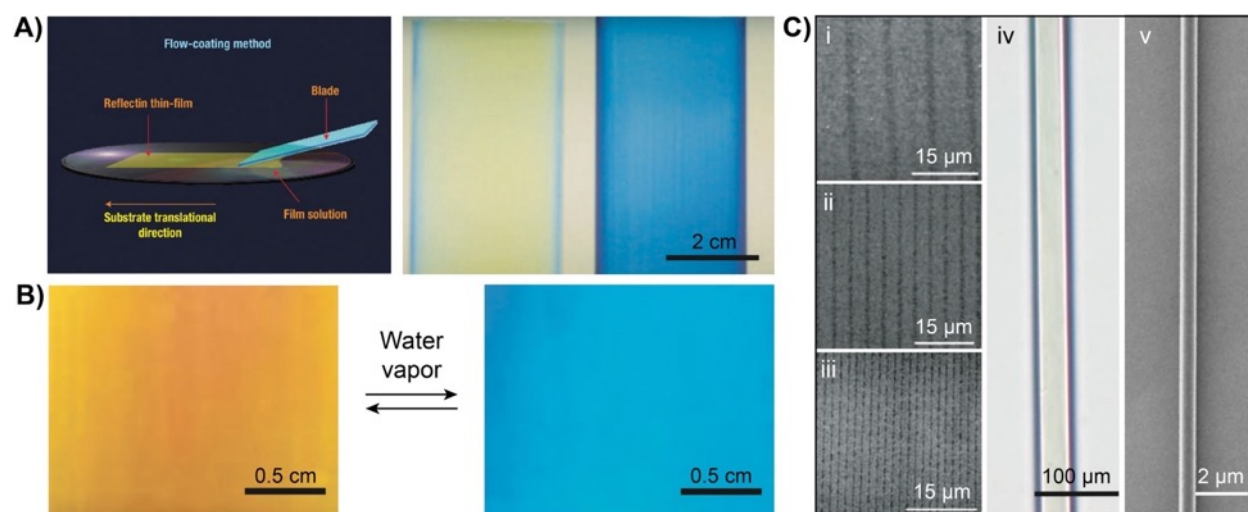


Figure 1.14. Cephalopod Reflectin Protein-Based Devices with Dynamic Optical Properties in the Visible. (A) An illustration of the fabrication of a reflectin 1a-based thin film on a rigid substrate by flow coating.^[84] (B) Images of a reflectin 1a-based thin film reversibly changing the color from orange (left) to blue (right) upon the application of water vapor.^[84] (C) (i-iii) SEM images of diffraction grating made from reflectin 1a, featuring tunable grating spacing; (iv) an optical microscope image of a highly amorphous fiber made from reflectin 1a; (v) an SEM image of another amorphous fiber made from reflectin 1a with a much smaller diameter.^[84] Part A–C were reproduced with permission of Springer Nature (Copyright © 2007).

Reflectins have been further explored to extend their optical functionalities into the near-infrared region of the electromagnetic spectrum for adaptive camouflage applications. Phan and coworkers expressed and purified a recombinant histidine-tagged reflectin isoform (RfA1, from *Doryteuthis pealeii* squid) that featured good water solubility.^[86] The RfA1 protein could be readily fabricated into thin films on graphene oxide-modified silica/glass substrates through a doctor-blading process (Figure 1.15A). These RfA1-based films displayed tunable coloration that was dependent on the film thickness due to a simple thin-film interference mechanism (Figure 1.15B). The application of acetic acid vapor to the RfA1-based films was shown to dynamically shift their reflectance peaks over a broad spectral range of > 600 nm from the visible to the near-IR region of the electromagnetic spectrum (Figure 1.15C). Such chemically induced actuation was highly reversible and could be maintained for over 140 cycles before performance degradation. Furthermore, RfA1-coated devices were showcased for active near-IR camouflage applications and could dynamically alter their near-IR signatures in response to acetic acid vapor. In a subsequent study, Phan and coworkers introduced a new actuation mechanism to achieve near-IR camouflage by mechanical stretch.^[87] RfA1 protein films were fabricated through a modified doctor-blading approach onto adhesive fluorinated ethylene propylene (FEP) tape-based substrates that were highly conformable and stretchable. These RfA1-coated tapes could be easily adhered to a camouflage fabric and endow the integrated fabric with the ability to match the near-IR intensity and appearance to that of a natural leaf, indicating excellent camouflage in the near-IR (Figure

1.15D). Upon mechanical actuation (i.e., uniaxial stretch), these RfA1-coated tapes could dynamically alter their visible and near-IR appearances, with a > 275 nm shift in the reflectance peak from the near-IR to the visible (Figure 1.15E).

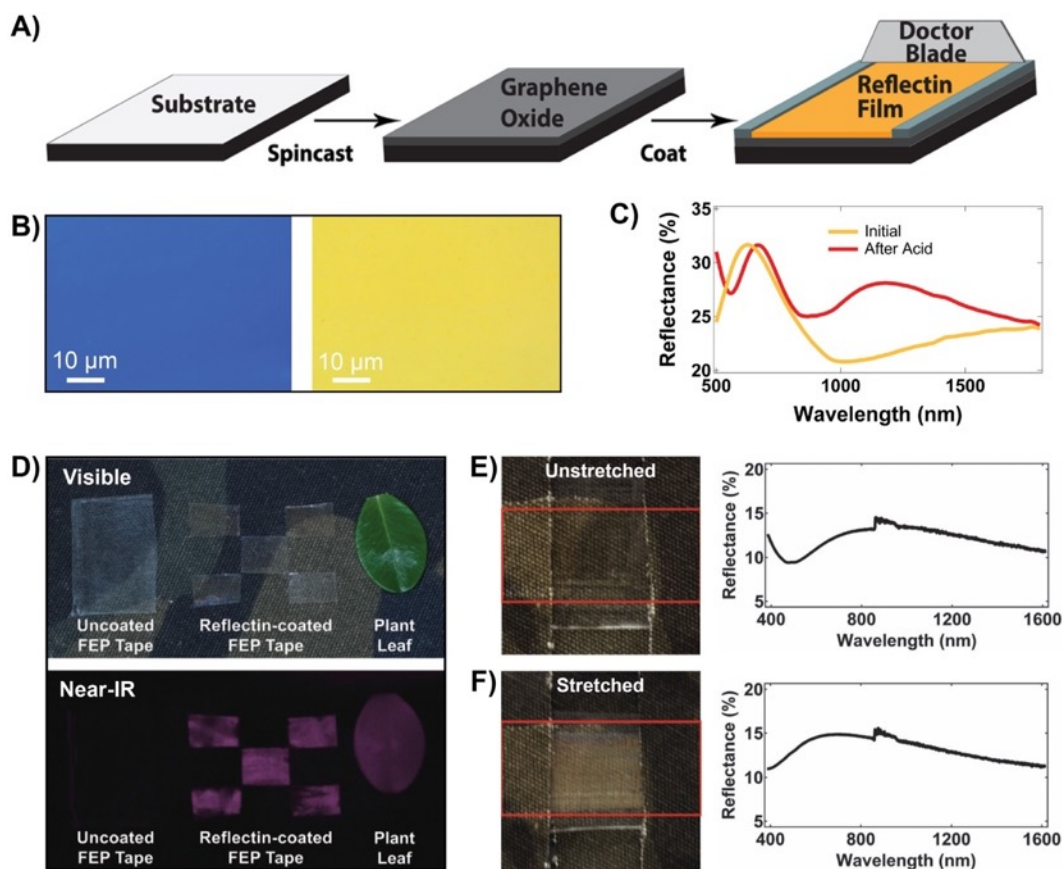


Figure 1.15. Cephalopod Reflectin Protein-Based Devices with Dynamic Optical Properties in the Near-Infrared. (A) A scheme of the fabrication of a reflectin A1 (RfA1)-based thin film on a graphene-modified substrate by doctor-blading.^[86] (B) Optical microscope images of two RfA1-based thin films with colors dependent on the film thickness. The thicknesses of the blue (left) and yellow (right) films were 125 nm and 207 nm, respectively.^[86] (C) Reflectance spectra of an RfA1 film before (orange curve) and after (red curve) the application of acetic acid vapor, featuring a significant peak shift from the visible to the near-IR.^[86] (D) A demonstration of near-IR camouflage of fabric-bound, RfA1-based FEP tapes. Note that the near-IR intensity of the fabric-bound, RfA1-

based FEP tapes matched that of a natural leaf.^[87] **(E)** A digital camera image (left) and a reflectance spectrum (right) of a RfA1-based FEP tape before uniaxial stretch, featuring a reflectance maxima in the near-IR.^[87] **(F)** A digital camera image (left) and a reflectance spectrum (right) of the same RfA1-based FEP tape after uniaxial stretch, featured a shifted reflectance maxima in the visible.^[87] Part **A–C** were reproduced with permission of John Wiley and Sons (Copyright © 2013). Part **D–F** were reproduced with permission of the Royal Society of Chemistry (Copyright © 2015).

Besides, reflectins have been examined for their unique combination of optical and electrical properties to enable advanced photo-sensitive and photochromic devices. Ordinario and coworkers designed a new type of photochemically active devices from a proton-conducting reflectin isoform (RfA1, from *Doryteuthis pealeii* squid).^[88] Such photo-sensitive devices were fabricated with a typical protonic transistor-type architecture that featured a photoacid-doped RfA1-based film bridging over two proton-conducting palladium hydride (PdH_x) electrodes on silicon dioxide/silicon (SiO_2/Si) substrates (Figure 1.16A). Upon exposure to blue light, these devices experienced a maximum of $\sim 31\%$ increase in the protonic current density in a two-terminal configuration (Figure 16B), which was directly resulted from the ability of the photoacid dopant to release mobile protons from its hydroxyl groups upon photoexcitation. Similarly, when operated in a three-terminal configuration, these photoacid-doped RfA1-based devices showed a clear increase in the protonic current (I_{DS}) between the source and the drain (at a certain gate voltage) upon the illumination of blue light. In a later study, Ordinario and coworkers developed a new type of photochromic devices from the same proton-conducting reflectin

isoform (RfA1).^[89] These photochromic devices were constructed on SiO₂/Si substrates with a sandwiched structure that consisted of a top electron-conducting gold electrode, a middle layer of RfA1 thin film, and a bottom proton-conducting PdH_x electrode (Figure 1.16C). The application of a small bias on the PdH_x electrodes could readily modulate the color of these RfA1-based devices, e.g., a positive bias (+ 1.5 V) induced a red shift in the reflectance peak by ~ 21 nm (Figure 1.16D), and a negative bias (− 1.5 V) induced an opposite blue shift by ~ 19 nm (Figure 1.16E). This electrically induced color change of the RfA1-based devices was experimentally confirmed to be dictated by a dynamic thin-film interference mechanism, i.e., protons could be injected (extracted) into (out of) the constituent RfA1 layers upon electrical stimuli, thus allowing the constituent RfA1 layers to dynamically change their thicknesses, as well as their light-reflecting properties (Figure 1.16C).

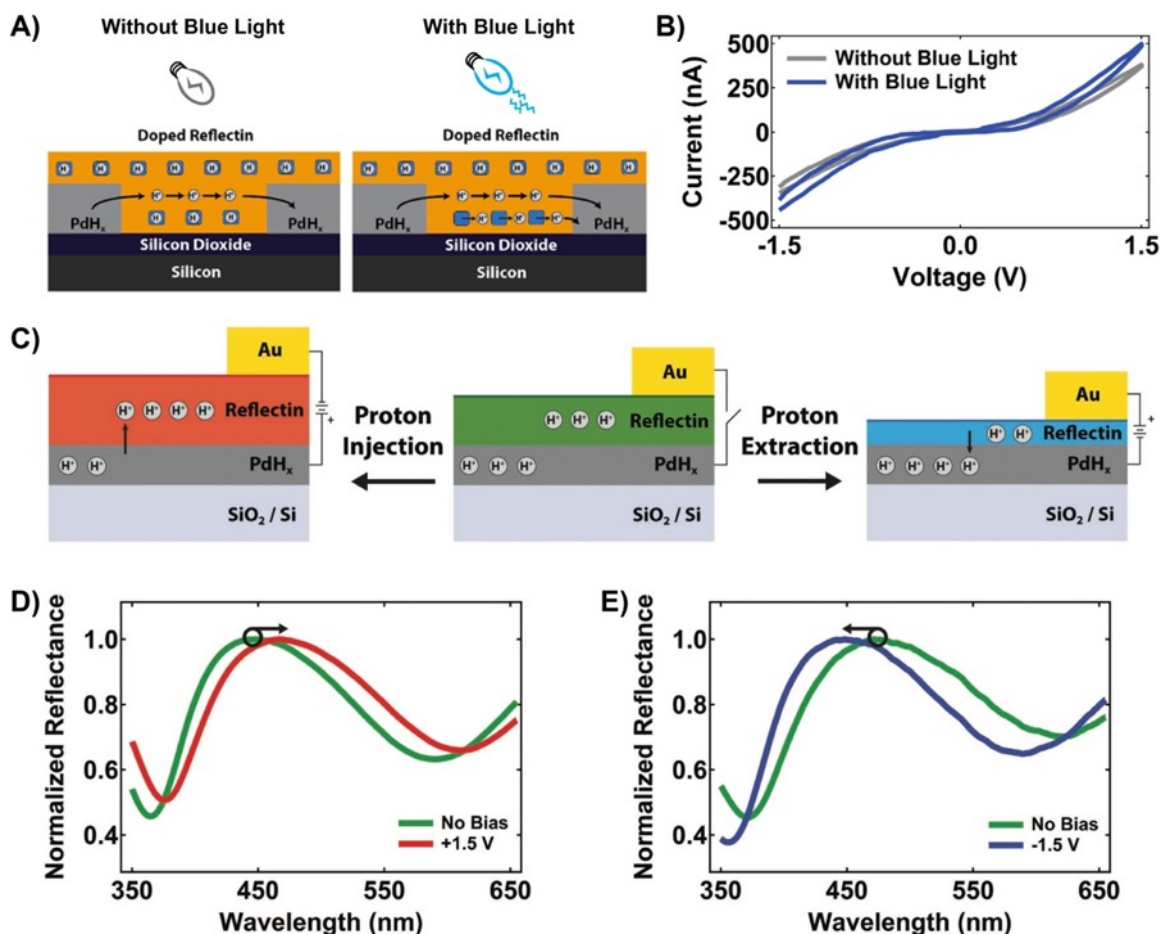


Figure 1.16. Cephalopod Reflectin Protein-Based Photo-Sensitive and Protochromic Devices. (A) Schematics of a RfA1-based photo-sensitive device without (left) and with (right) exposure to blue light illumination.^[88] (B) Plots of current as a function of applied voltage for a representative photo-sensitive RfA1-based device without (gray curve) and with (blue curve) exposure to blue light illumination.^[88] (C) Schematics of a RfA1-based protochromic device with the application of no bias (middle), a positive bias (left), and a negative bias (right) on the palladium hydride (PdH_x) electrode, featuring a thickness change in the constituent RfA1 layer upon proton injection or extraction.^[89] (D) Normalized reflectance spectra for a representative RfA1-based protochromic device before (green curve) and after (red curve) the application of a positive bias of + 1.5 V on the PdH_x electrode.^[89] (E) Normalized reflectance spectra for a representative RfA1-based protochromic device before (green curve) and after (blue curve) the application of a

negative bias of -1.5 V on the PdH_x electrode.^[89] Part **A–B** were reproduced with permission of the American Chemical Society (Copyright © 2016). Part **C–E** were reproduced with permission of John Wiley and Sons (Copyright © 2017).

1.5.2. Xanthommatin-Pigment Based Materials and Applications

Naturally occurring pigments are found in the pigment granules of color-changing chromatophore organs, and they are mainly responsible for the predominant pigmentary coloration exhibited by cephalopod skin.^[66,67,78] These pigments extracted from chromatophores have been confirmed as ommochromes, including xanthommatin and decarboxylated xanthommatin, which are aromatic metabolites of tryptophan formed through biological processes.^[66,67,78] The combination of xanthommatin and decarboxylated xanthommatin enables chromatophores to display a broad range of colors across the visible region of the electromagnetic spectrum. As such, xanthommatin-based pigments are technologically valuable and promising for artificial color-changing applications.

Given that cephalopod-derived xanthommatin-based pigments were only isolated and identified a few years ago, it is not surprising that there is only one example of integrating these pigments into device applications. Kumar and coworkers drew inspiration from the dynamic pigmentary coloration of chromatophores and developed a new type of electrochromic devices from xanthommatin.^[90] The authors first studied the electrochemical properties of xanthommatin molecule and found that the pigment could reversibly change its molecular structure at different redox states (Figure 1.17A). Then,

chemically synthesized xanthommatin was electrodeposited onto indium-doped tin oxide (ITO)-coated substrates that were pre-modified with poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Figure 1.17B). The substrate-bound xanthommatin films were shown to change color at different redox states, which could switch from yellow under an oxidizing potential (+ 1.5 V) to red under a reducing potential (− 1.5 V), along with a red shift in the absorption peak by ~ 70 nm within several seconds (Figure 17B). Standard electrochromic devices were fabricated from xanthommatin and assembled with a multilayered device structure (Figure 1.17C). The colors of these devices were determined by the compositional ratio of xanthommatin and could be reversibly modulated upon the application of a small voltage (Figure 1.17D). These xanthommatin-based electrochromic devices featured excellent optical functionalities, with a transparency modulation window of $\sim 21.5\%$ at a wavelength of 555 nm, a response time of > 15 seconds, and good cyclability with only a small performance decay after being operated for five hours.

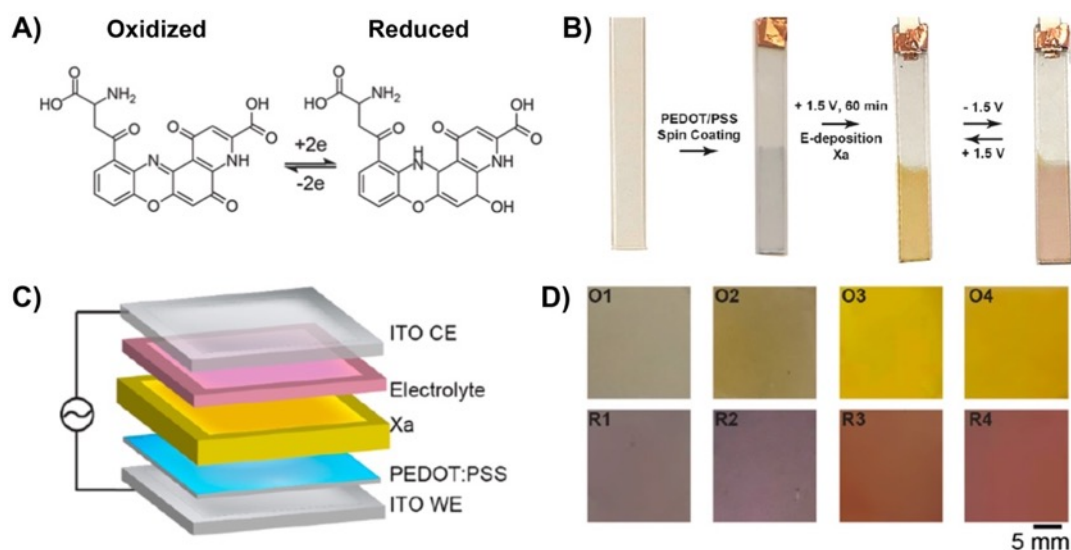


Figure 1.17. Cephalopod Xanthommatin Pigment-Based Electrochromic Devices. (A) Proposed chemical structures of xanthommatin at oxidized (left) and reduced (right) states.^[90] (B) Optical images of the electrodeposited xanthommatin film switching the color from yellow (oxidized) to light red (reduced) upon electrical stimuli.^[90] (C) A schematic of a xanthommatin-based electrochromic device with a multilayered structure.^[90] (D) (Top) Optical images of the colors of four independent xanthommatin-based electrochromic devices at oxidized states. Note that O1-O4 denoted four devices fabricated with different xanthommatin-to-PEDOT:PSS ratios). (Bottom) Optical images of the colors of the same four independent devices at reduced states. Note that the devices in R1-R4 corresponded to those devices in O1-O4.^[90] Part A–D were reproduced with permission of the American Chemical Society (Copyright © 2018).

1.6. Dynamic Optical Materials and Systems Inspired by Cephalopod Skin

Cephalopods are perfect living examples of dynamic bioelectronic displays in the animal kingdom. Their unparalleled camouflage and color-changing capabilities are achieved by the unique skin architecture and the synergistic function of thousands (or millions) of optically active skin components. Within this context, these marvelous marine

animals have been served as numerous inspiration sources for the design and development of artificial technologies with analogous optical functionalities. Here, we will review recent progress in the development of dynamic optical materials and systems inspired by cephalopods.

Morin and coworkers drew inspiration from color-changing cephalopod skin and developed a class of soft machines for display and camouflage applications.^[91] The cephalopod-inspired soft machines were constructed by embedding an intricate network of microfluidic channels into a mechanically deformable matrix made from silicone rubber (Figure 1.18A), featuring excellent stretchability and optical transparency. These soft machines could be actuated by pneumatic pressurization and perform simple movements through tethered cables. Besides, these soft machines were demonstrated suitable for display applications (Figure 1.18B). The appearances of the soft machines could be readily modulated by the injection of different liquids into the internal microfluidic channels. Depending on the optical properties of the injected liquids, these soft machines showcased the ability to dynamically change the pigmentary, fluorescent, and chemiluminescent appearances, as shown in Figure 1.18B, although we note that the switching speed between different appearances was dependent on the rate of liquid injection. In addition, these cephalopod-inspired soft machines demonstrated their potential for active camouflage applications (Figure 1.18C). By altering the color and temperature of pigmented liquids, the soft machines were able to manage their signatures to resemble different backgrounds

and perform on-demand camouflage in both the visible and thermal-infrared regions (Figure 1.18C).

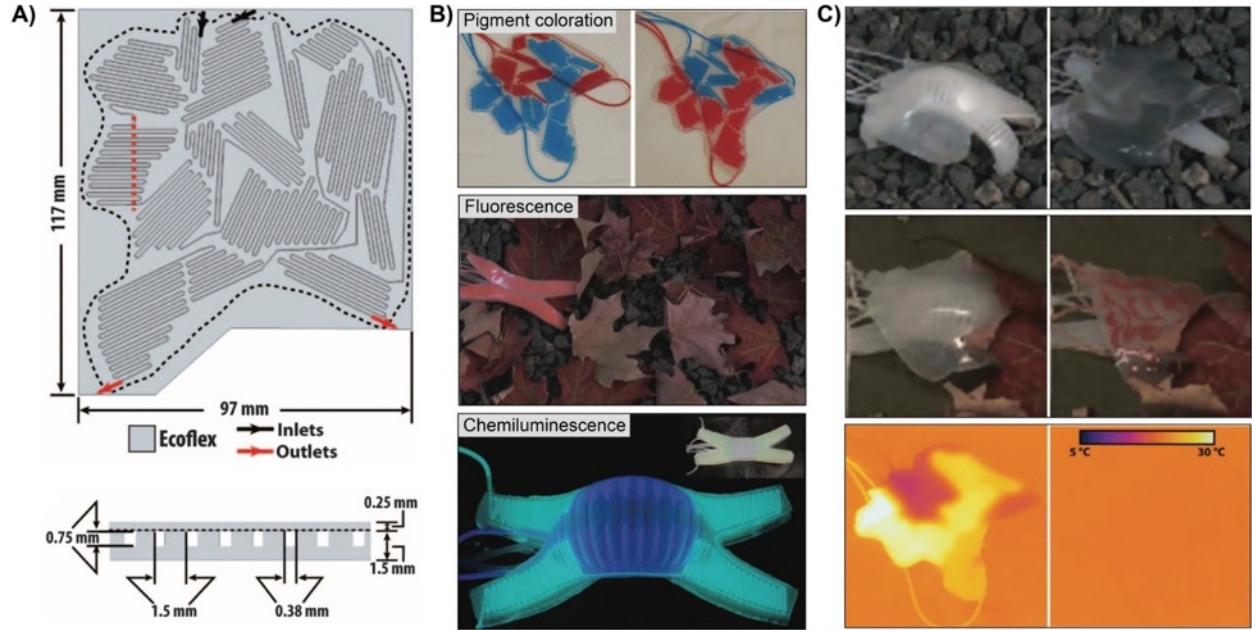


Figure 1.18. Soft Machines Inspired by Cephalopods. (A) Top view (top) and cross-sectional view (bottom) of the design of cephalopod-inspired soft machines, featuring microfluidic channels embedded in a silicone (Ecoflex) matrix.^[91] (B) Optical images of cephalopod-inspired soft machines for display applications, showing pigmentary (top), fluorescent (middle), and chemiluminescent (bottom) patterns.^[91] (C) Optical and infrared images of cephalopod-inspired soft machines for camouflage applications, showing dynamic alternation of their appearances to resemble gravels (top), leaves (middle), and the thermal infrared background (bottom).^[91] Part A–C were reproduced with permission of The American Association for the Advancement of Science (Copyright © 2012).

Yu and coworkers drew inspiration from the general cephalopod skin architecture and developed a new class of multiplexed color-changing platforms with autonomous operation capability.^[92] To this end, the authors leveraged technical foundations

established for silicon-based electronics and constructed a highly integrated system with distributed sensing and actuating capabilities, which could adaptively change its coloration and patterning. Each pixel unit in the system featured a cephalopod skin-inspired multilayered architecture, as illustrated in an expanded layout in Figure 1.19A, which contained (from top to bottom) a thermochromic leucodye layer that could change color from black to transparent when heated (analogous to biological color-changing chromatophores), a reflective silver layer (analogous to biological light-reflecting leucophores), a silicon diode layer that could activate the overlying leucodye layer by Joule heating (analogous to biological muscles that control the actuation of chromatophores), a transparent polydimethylsiloxane (PDMS) elastomer substrate, and a back-sided silicon photodetector layer for light sensing (analogous to biological light-sensitive opsins in cephalopod skin). The integration of these single pixels readily afforded a dynamic color-changing display in a multiplexed format, as demonstrated by a 16×16 array with 256 active pixels (Figure 1.19B). Each individual pixel within the multiplexed display could be independently addressed, thus enabling the display to generate different patterns on demand, as shown by an example of spelling out ‘U o I’ in Figure 1.19C. Due to the intrinsic mechanical flexibility of the PDMS substrate, the multiplexed display could maintain the optical functionality even under bent conditions (Figure 1.19C). Moreover, this cephalopod-inspired color-changing display was able to sense the environment directly and adapt its pattern autonomously to match a continuously changing background without any user input (Figure 1.19D).

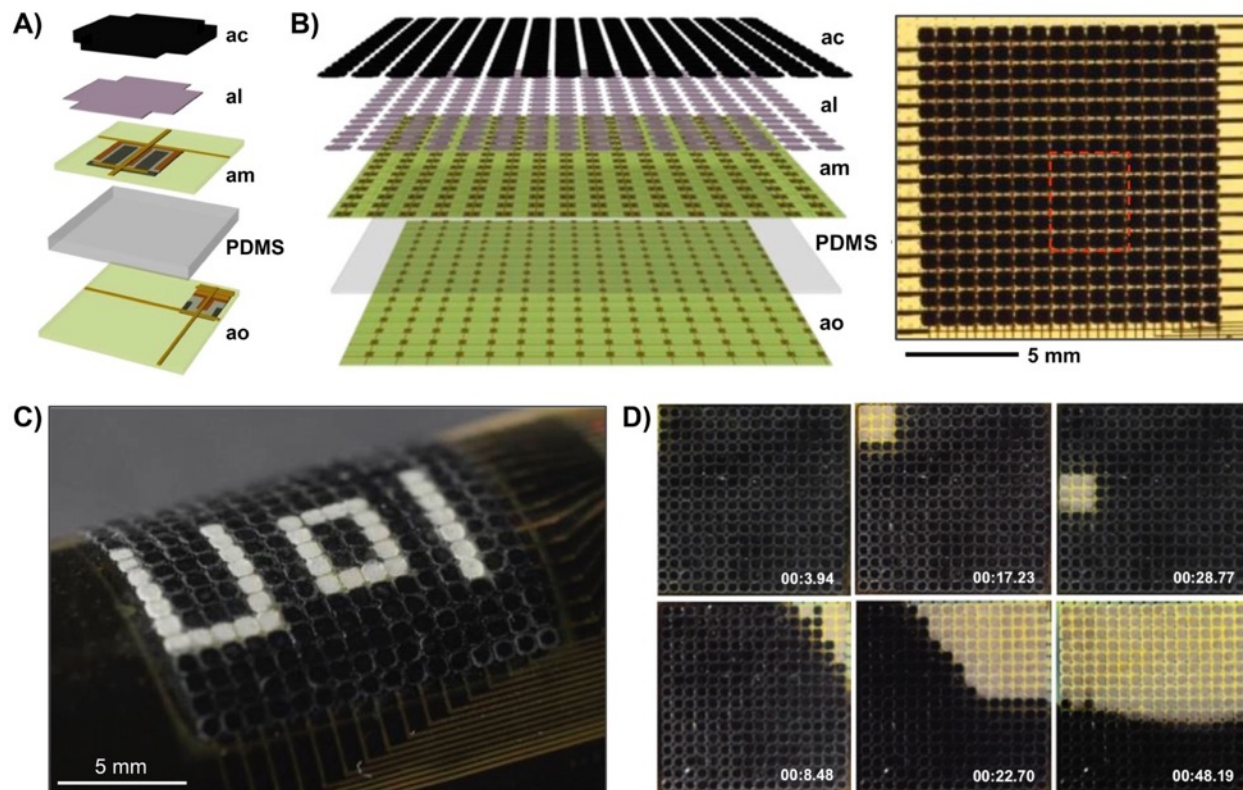


Figure 1.19. Autonomous Color-Changing Display Inspired by Cephalopod Skin. (A) An illustration of a single pixel unit for the cephalopod-inspired display, featuring a five-layer device structure that consisted of artificial chromatophore (ac), an artificial leucophore (al), artificial muscle (am), a PDMS substrate, and an artificial opsin unit (ao).^[92] (B) An illustration (left) and an optical image (right) of a multiplexed cephalopod-inspired display with 256 active pixel units.^[92] (C) An optical camera image of the multiplexed display showing letters of ‘U o I’ when bent.^[92] (D) Sequential optical images showing the autonomous operation of the multiplexed display by matching its pattern to a continuously changing background.^[92] Part A–D were reproduced with permission of National Academy of Sciences (Copyright © 2014).

Wang and coworkers drew inspiration from cephalopod chromatophores and developed a new type of electro-mechano-chemical systems for active optical and fluorescent modulation.^[93] For this purpose, mechanochromic composite elastomers were

prepared by incorporating spiropyran (a known mechanophore) into a crosslinked elastomeric matrix made from PDMS. The application of a 200% uniaxial strain on the composite elastomers readily induced a significant color change from light yellow to blue, accompanied with a strong increase in the intensity (brightness) of the fluorescence emission (Figure 1.20A), due to a ring-opening reaction of the constituent spiropyran to form merocyanine upon the stretch. These mechanochromic composite elastomers showed excellent processability and could be easily integrated into multilayered devices that were responsive to electrical actuation (Figure 1.20B, top). The application of a high voltage across a composite elastomer-integrated device induced electromechanical deformation of the constituent composite elastomer and led to the formation of irregularly shaped craters on the surface (Figure 1.20B, middle). Such electrically induced deformation readily initiated the ring-opening reaction of spiropyran near the contours of those crater-like structures, thus allowing the generation of bright fluorescent patterns on the surface (Figure 1.20B, bottom). The intensity of the fluorescent patterns could be tuned by adjusting the strength of the applied electric field. In addition, it was also demonstrated that the fluorescent patterns could be further tailored into various shapes and geometries, such as well-aligned circles, lines, and letters, by surface strain engineering.

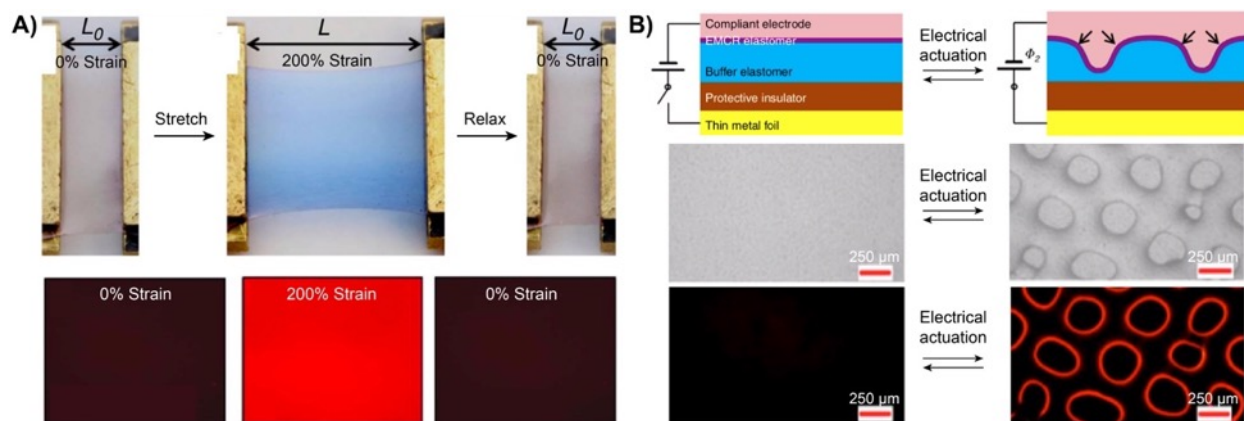


Figure 1.20. Electro-Mechano-Chemical Systems Inspired by Cephalopod Chromatophores. (A) (Top) Digital camera images of a typical spiropyran-blended mechanochromic composite elastomer (EMCR) upon uniaxial strain, with a clear change in the color. (Bottom) Fluorescent microscope images of the same composite elastomer upon uniaxial strain, with a clear change in the fluorescence intensity.^[93] (B) (Top) A schematic of an EMCR elastomer-integrated device before (left) and after (right) electrical actuation, featuring an electrically induced deformation of the EMCR elastomer; (Middle) Optical microscope images of an EMCR elastomer-integrated device before (left) and after (right) electrical actuation, featuring dynamic modulation of surface structures; (Bottom) Fluorescent microscope images of the same EMCR elastomer-integrated device before (left) and after (right) electrical actuation, featuring dynamic modulation of fluorescent patterning.^[93] Part **A** and **B** were reproduced with permission of Springer Nature (Copyright © 2014).

Rossiter and coworkers drew inspiration from cephalopod chromatophores and developed a series of dielectric elastomer actuator (DEA)-based devices for dynamic modulation of pigmentary coloration.^[94,95] In general, their cephalopod-inspired DEA devices featured a capacitor-like configuration with a soft dielectric elastomer sandwiched by two compliant electrodes, which could expand (or contract) the electrode area upon

the application (or withdrawal) of an electric field. Single-pixel and multiplexed DEA devices with black carbon grease electrodes were shown to change the areal coverage of the black-pigmented regions upon electrical actuation (Figure 1.21A).^[94] This electrically induced areal change allowed the devices to dynamically modulate the overall light absorption and transmission through the whole devices, although the optically active regions were monochromatic (Figure 1.21A). Likewise, a modified DEA device with a central blue-pigmented coating was observed to shrink the size of the pigmented region upon electrical actuation, presumably due to the squeezing effect of the annular-shaped carbon black electrodes (Figure 1.21B).^[94] The decrease in the size of the central blue-pigmented region directly led to a simultaneous increase in the color concentration of the same region (Figure 1.21B). In a follow-up study, Rossiter and coworkers proposed a new type of tri-layer polychromatic DEA-based devices with three vertically stacked chromatic layers (Figure 1.21C).^[95] The authors envisioned that each layer in the structure would have a pigmented region with a different color (for example, red, green, or blue) (Figure 1.21C). These pigmented regions would be independently addressed by selective electrical actuation, and different pigmented regions would be able to overlay on one another, thus enabling a variety of color combinations within a single device platform. However, no solid experimental results on such polychromatic devices were presented in their work.

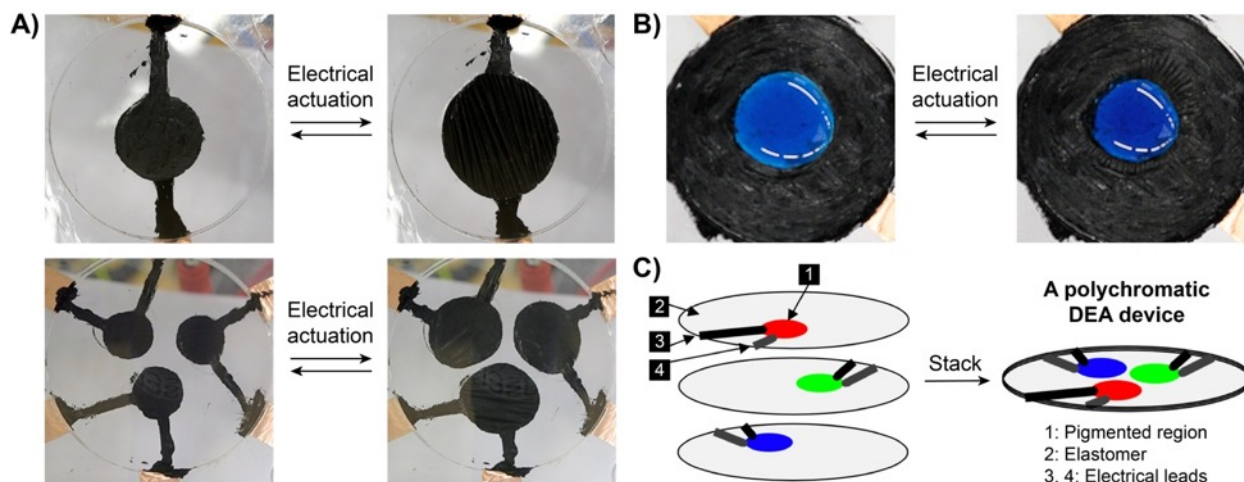


Figure 1.21. Dielectric Elastomer Actuator (DEA)-Based Systems Inspired by Cephalopod Chromatophores. (A) (Top) Digital camera images of a single-pixel DEA device with black carbon grease electrodes before (left) and after (right) electrical actuation. (Bottom) Digital camera images of a multiplexed DEA device with black carbon grease electrodes before (left) and after (right) electrical actuation.^[94] (B) Digital camera images of a modified DEA device with a central blue-pigmented coating before (left) and after (right) electrical actuation.^[94] (C) An illustration of the design of a proposed polychromatic device with a multilayered structure. Each layer has a pigmented region with a different color, for example, red, green, or blue.^[95] Part A and B were reproduced with permission of the IOP Publishing (Copyright © 2012). Part C was reproduced with permission of the Society of Photo-Optical Instrumentation Engineers (SPIE) (Copyright © 2014).

Larson and coworkers drew inspiration from malleable color-changing cephalopod skin and developed a highly stretchable electroluminescent skin for display and pressure-sensing applications.^[96] Their cephalopod-inspired skin featured a five-layer structure that was composed of an electroluminescent layer sandwiched by two ion-conducting hydrogel electrodes and then encapsulated by a pair of silicone-based shells, as illustrated in Figure

1.22A. As the optically active component in the artificial skin, the electroluminescent layer was fabricated from a modified silicone elastomer that was blended with doped zinc sulfide (ZnS) phosphors and could emit luminescence upon the application of an AC electric field, with the color of the emitted light adjustable by the addition of different metal dopants into the ZnS (Figure 1.22B and 1.22C). As one example, single-pixel electroluminescent skins demonstrated excellent stretchability and could maintain the light-emitting property even under an extreme elongation of $\sim 400\%$ without any structural failure (Figure 1.22B). As another example, multiplexed electroluminescence skins exhibited nearly unchanged performance under a variety of deformation modes that included stretching, rolling, folding, and wrapping, and they could display different patterns upon selective actuation of multiple pixels at one time (Figure 1.22C). Besides, the cephalopod-inspired electroluminescent skin could be easily attached onto the surface of a pneumatically actuated soft robot and demonstrated its capability of not only sensing externally applied pressure but also displaying different brightnesses under different pneumatic actuation states.

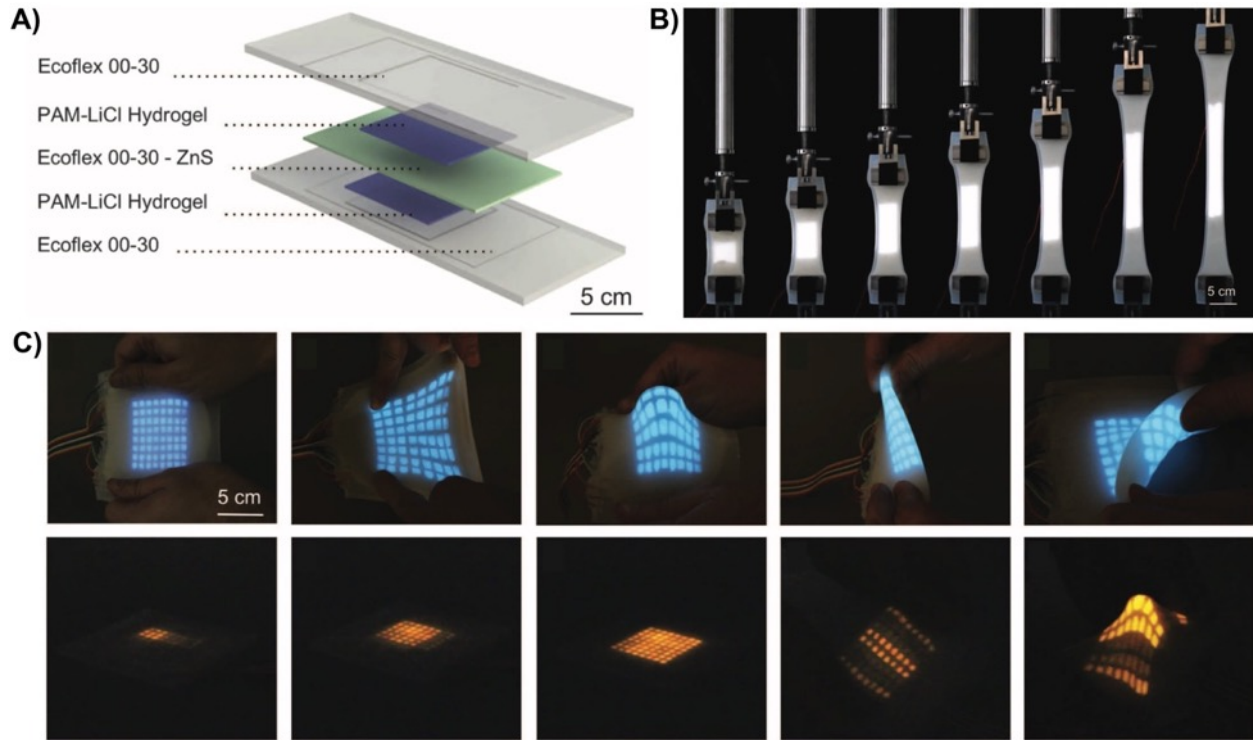


Figure 1.22. Stretchable Electroluminescence Skin Inspired by Cephalopods. (A) An illustration of the design of the cephalopod-inspired electroluminescence skin with a five-layer device structure.^[96] (B) Stitched digital camera images of an electroluminescence skin under various uniaxial strains (up to $\sim 400\%$), featuring nearly unchanged optical functionality.^[96] (C) (Top) Digital camera images of a multiplexed electroluminescent skin (with blue-light emission) under various deformation modes, including stretching, rolling, folding, and wrapping. (Bottom) Digital camera images of another multiplexed electroluminescent skin (with orange-light emission) displaying various patterns.^[96] Part A–C were reproduced with permission of The American Association for the Advancement of Science (Copyright © 2016).

1.7. Summary

To summarize, cephalopods, as a class of marine invertebrates, are known for their fascinating color-changing and camouflage abilities. These soft-bodied animals showcase a

vast repertoire of camouflage tactics by dynamically modulating the color, pattern, transparency, contrast, bioluminescence, texture, and even behavior. These dazzling visual feats are physically enabled by sophisticated skin architectures at cellular levels that are generally composed of three types of optically active organs and cells, including pigmentary chromatophores, reflective iridophores, and diffusive leucophores. The synergistic function of these tiny bio-optical components allows cephalopod skin to dynamically interact with light, functioning like bioelectronic displays. As such, cephalopods and their adaptive skin have garnered much research attention for the development of dynamic optical materials and systems. For example, biological materials, such as reflectin proteins and xanthommatin pigments, have been derived from cephalopod skin and readily enabled various color-changing and camouflage device applications. Besides, artificial materials and systems that featured unprecedented optical functionalities have also been developed by drawing inspiration from biological designs of natural cephalopod skin. Overall, this chapter constitutes an expanded introduction to cephalopod camouflage and represents a detailed overview of the state-of-the-art progress in cephalopod-derived/inspired materials and technologies, which in turn serves as an essential background for the remaining chapters of the dissertation.

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CHAPTER 2

Long-Range Proton Transport in a Designer Cephalopod

Reflectin Protein

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2.1. Abstract

Protein-based biological proton conductors with excellent electrical functionalities have received much attention for their critical roles in a variety of biological processes and artificial applications. Reflectins, as a class of unusual cephalopod structural proteins, are of particular interest due to their remarkable self-assembly and micrometer-scale proton-transfer properties; however, long-range proton conduction within reflectins has never been explored across longer distances (i.e., at least millimeter scales), and the possible correlations between the self-assembled structures and electrical functions of reflectins remain unknown. Herein, we address these challenges by studying a designer reflectin protein of (ref2C)₄ from *Euprymna scolopes* squid. The self-assembled (ref2C)₄ films not only exhibit exceptional bulk proton conductivities of > 0.4 mS/cm, over four times greater than the best-reported value for other full-length reflectin isoforms under analogous conditions, but also maintain excellent electrical functionalities across a distance of 1 mm, at least one order of magnitude longer than that of all other reflectin-based devices. Besides, the self-assembled structures of the (ref2C)₄ protein are systematically investigated and identified across multiple length scales both in solution and in the solid state using a suite of microscopy and spectroscopy techniques. These multifaceted studies provide insight into a hierarchical structure–electrical function correlation of the (ref2C)₄ protein from the molecular to the macroscopic scale. Overall, our work may hold relevance for the understanding of analogous reflectin-based

biomolecules and the rational engineering of other biomimetic protein-based proton conductors.

2.2. Introduction

Materials that have the ability to transport protons across a distance have garnered much research interest for their critical roles underpinning the structural foundations and versatile functionalities in a variety of biological systems^[1,2] and artificial applications.^[3,4] Particularly, naturally occurring proton-conducting biomolecules, such as polysaccharides,^[5,6] melanins,^[7] and proteins,^[8–10] have received special attention because of their unique electrical properties that are intricately related to metabolism, respiration, and signaling processes at cellular or subcellular levels. Within this context, protein-based biological proton conductors have been subjected to extensive investigation as one of the most exciting research targets due to their desirable characteristics, such as modular molecular structures, tunable physical properties, programmable functionalities, *in vivo* and *in vitro* self-assembly abilities, amenity for manufacturing and scaling, and excellent biocompatibility.^[8–10] However, despite these promising features, the development of protein-based biological proton conductors that feature long-range proton conduction remains relatively rare, with only a handful of examples reported to date.^[11–18] For example, Silberbush and coworkers explored the proton conduction in a series of self-assembled films made from octa-D,L- α -peptide and amyloid β peptide across distances of < 0.02 mm.^[11,12] Amdursky and coworkers studied the directional proton transfer in electrospun-fabricated mats made from both non-modified and chemically modified bovine serum albumin proteins across a distance of 2.5 mm.^[13,14] Pena-Francesch and coworkers investigated the proton conduction in casted films made from modified squid ring teeth

proteins across a distance of 7 mm.^[15] Altogether, these limited examples constituted the state-of-the-art progress in exploring long-range proton conduction in biological proteins.

Within our group, we have exclusively focused on exploring the electrical properties of a class of unusual cephalopod structural proteins called reflectins.^[17,18] These naturally occurring proteins were first isolated from the reflective platelets within the light organs of Hawaiian bobtail squid (*Euprymna scolopes*), and they are composed of highly conserved amino acid sequences with a large proportion of charged and polar residues, as exemplified by a typical reflectin 1b isoform in Figure 2.1.^[19] Reflectins have demonstrated exceptional compatibility with multiple processing methods that include flow coating,^[20–24] drop-casting,^[17,18,25–27] dip-coating,^[20,27] and extrusion,²⁰ and can maintain their functionalities under standard lithographic fabrication conditions at elevated temperatures.^[17] They also exhibit remarkable self-assembly properties by forming a variety of structures both *in vivo* and *in vitro*, such as particles,^[28,29] platelets,^[19] fibers,^[20] gratings,^[20,21] and films.^[20–27] Besides, reflectins represent one of the best biological proton conductors and feature high proton conductivities of ~ 0.1 mS/cm at room temperature and ~ 2.6 mS/cm at 65 °C across a distance of 0.05 mm for a reflectin A1 (RfA1) isoform from *Doryteuthis pealeii* squid^[17] and ~ 0.074 mS/cm at room temperature across a slightly longer distance of 0.1 mm for a different reflectin A2 (RfA2) isoform from the same squid.^[18] Such excellent electrical properties of reflectins readily enabled the integration of these proteins for the development of a variety of bioelectronic applications, such as

protonic transistors,^[17,25] photochemically active systems,^[26] and protochromic devices.^[27] Despite these exciting technological advances in the recent years, several questions about reflectins remain unanswered: (1) electrical functionalities of reflectin isoforms from cephalopod species other than *D. pealeii* have never been explored; (2) long-range proton conduction over millimeter length scales has never been reported for reflectin assemblies; and (3) possible correlations between the molecular structure and electrical function within reflectin assemblies remain incomplete.^[28] Thus, there exists an impetus for continued study of these cephalopod proteins.

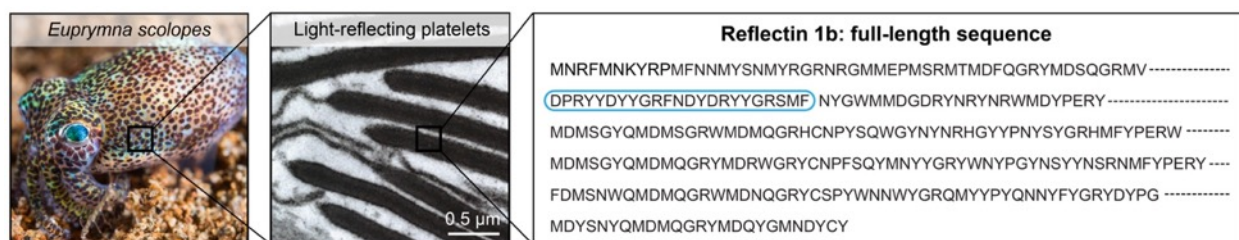


Figure 2.1. Reflectin protein found in *Euprymna scolopes* squid. From left to right: a digital camera image of an *Euprymna scolopes* squid (left), a transmission electron microscope (TEM) image of light-reflecting proteinaceous platelets found inside the *E. scolopes* squid's skin (middle), and the entire amino acid sequence of a full-length reflectin 1b protein that was found in the light-reflectin platelets.^[19] Note that the blue-circled region denoted a singly represented 2C domain in the sequence.

2.3. Sequence Design and Solution Characterization

We began our experiment by selecting a distinct singly represented 2C domain from the full-length reflectin 1b isoform with a linear sequence of DPRYYDYYGRFNDYDRYYGRSMF (see the blue-colored region of the full-length

sequence in Figure 2.1).^[19] From this motif, a recombinant concatemer protein, named (ref2C)₄, was previously designed with an extended sequence that featured a histidine tag and four identical 2C repeats with short linkers in between (Figure 2.2A).^[24] The (ref2C)₄ protein was demonstrated to recapitulate some of the key characteristics of the full-length reflectin 1b, such as water stability, self-assembled structures, and light scattering properties, representing an excellent model system for the study of reflectin proteins.^[24] Excitingly, the primary structure of the (ref2C)₄ protein consisted of a large proportion of hydrophilic residues (17 out of the total 23 residues within each 2C repeat) with highly charged side chains (i.e., Asp and Arg) and uncharged but highly polar side chains (i.e., Tyr, Asn, and Ser). As such, the (ref2C)₄ protein served as an ideal target for electrical measurements.

We started by producing the (ref2C)₄ protein and investigating its physical characteristics in solution with spectroscopy techniques. First, we expressed and purified the (ref2C)₄ protein from bacteria *Escherichia coli* according to previously established procedures and confirmed its structural identity with tryptic digestion and mass spectrometry.^[24] Next, we prepared (ref2C)₄ protein solution in hexafluoro-2-propanol (HFIP) and determined the size distribution profiles via dynamic light scattering (DLS). The DLS results revealed that the (ref2C)₄ protein formed nanoparticles in solution and possessed two dominant sizes with hydrodynamic radii of ~ 80 nm and ~ 350 nm, as confirmed in the intensity and volume plots (Figure 2.2B). Subsequently, we characterized

the optical properties of the (ref2C)₄ protein solution with UV/Vis spectroscopy. The UV/Vis absorption spectrum featured a strong absorption peak at a wavelength of ~ 272 nm, which was in good agreement with other full-length reflectin isoforms reported in the literature (Figure 2.2C).^[22] In turn, we studied the secondary structure of the (ref2C)₄ protein in solution with circular dichroism (CD) spectroscopy. The CD spectrum demonstrated the existence of a local maximum at ~ 196 nm and two local minima at ~ 208 nm and ~ 220 nm, which indicated the formation of dominant α -helical secondary structures with slight β -sheet characters in the (ref2C)₄ nanoparticles (Figure 2.2D). Overall, our measurements indicated that the (ref2C)₄ protein formed nanoparticles and provided insight into its secondary structures in solution.

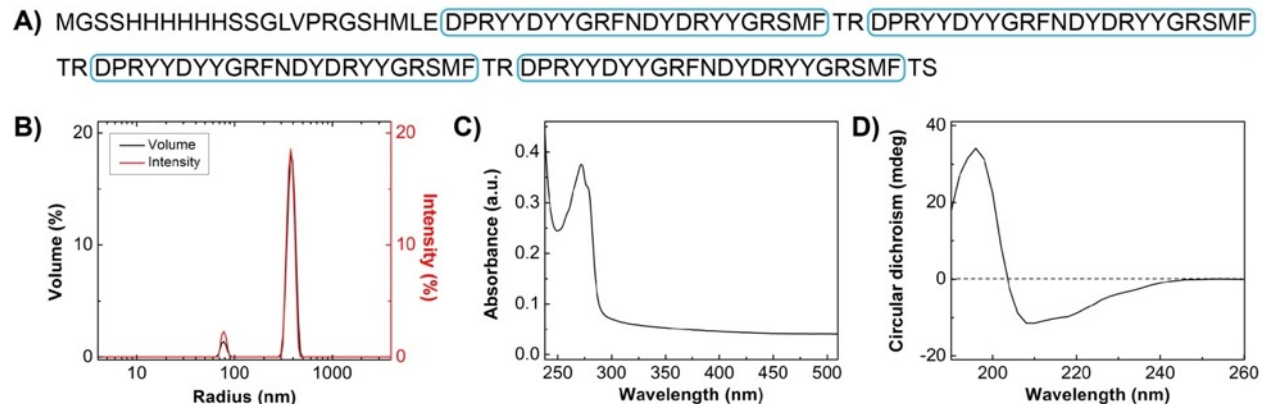


Figure 2.2. Physical characterization of the (ref2C)₄ protein in solution. (A) The amino acid sequence of the (ref2C)₄ protein, which featured a histidine tag and four identical 2C repeats (blue circled regions) intercalated with short linkers. (B) The size distribution profile obtained for the (ref2C)₄ protein in solution, which consisted of volume (black) and intensity (red) plots from dynamic light scattering (DLS) measurements. (C) The UV/Vis

absorption spectrum obtained for the (ref2C)₄ protein in solution. (D) The circular dichroism (CD) spectrum obtained for the (ref2C)₄ protein in solution.

2.4. Device Fabrication and Electrical Characterization

For the electrical measurements, we fabricated (ref2C)₄ protein-based devices as illustrated by the scheme in Figure 2.3A. Towards this end, we first spincoated the (ref2C)₄ protein solution onto glass substrates and obtained centimeter-scale, solid-state films after complete removal of the solvent. Next, we directly electron-beam deposited two gold electrodes on top of the as-spincoated (ref2C)₄ protein films as ion-blocking but electron-conducting top contacts with a gap distance of 1 mm, enabling a standard two-point-probe configuration for in-plane electrical measurements, as clearly shown by the optical microscope image in Figure 2.3B. Altogether, our fabrication procedure furnished substrate-bound, solid-state (ref2C)₄ devices ready for long-range electrical interrogation with electrochemical impedance spectroscopy (EIS).

We proceeded to characterize the long-range electrical properties of (ref2C)₄ protein-based devices. First, we recorded Nyquist plots for a representative (ref2C)₄ protein-based device in the presence of water (H₂O) and deuterium oxide (D₂O) vapor at a relative humidity of 92% (Figure 2.3C). Under both vapor environments, the Nyquist plots showed semicircles in the high-frequency region, which indicated the bulk proton transfer impedance of the (ref2C)₄ protein film with a mixture of resistive and capacitive behaviors, and inclined spurs in the low-frequency region, which indicated the

accumulation and diffusion of charges (i.e., protons) at the interfaces between the (ref2C)₄ protein film and the ion-blocking gold electrodes (Figure 2.3D) (see a detailed equivalent circuit in Figure S2.1). Interestingly, we observed an increase in the diameter of the semicircle upon moving from H₂O to D₂O *in situ*, resulting in a $\sim 30\%$ drop in the extracted proton conductivity from a value of 0.41 ± 0.06 mS/cm to a value of 0.29 ± 0.06 mS/cm (Figure 2.3D). This observed change in conductivity under different moist environments demonstrated a distinct kinetic isotope effect and was served as a fingerprint of the proton-conducting nature of our (ref2C)₄ protein films, which could be explained by the Grotthuss mechanism.^[30,31] Then, we recorded the Nyquist plots for our (ref2C)₄ protein-based devices under water (H₂O) vapor environments with different relative humidities. For a representative device, the Nyquist plots showed a clear increase in the diameters of high-frequency semicircles as the relative humidity was dropped from 92% to 70%, indicating a corresponding decrease in the proton conductivity from a value of ~ 0.31 mS/cm at a relative humidity of 92% to a value of ~ 0.09 mS/cm at a relative humidity of 80%, and then to a value of ~ 0.04 mS/cm at a relative humidity of 70% (Figure 2.3E and Figure S2.2). This observed logarithmic dependence of conductivity on the relative humidity further confirmed the proton-conducting nature of our (ref2C)₄ protein films, which could be explained by enhanced water activities under high relative humidity environments (Figure S2.2).^[32] Notably, the proton conductivity of (ref2C)₄ exceeded the values of other previously reported reflectin isoforms (i.e., reflectin A1 and A2) by ~ 4 times under analogous testing conditions at room temperature. Taken together,

our measurements validated the (ref2C)₄ protein as a biological proton conductor with excellent electrical characteristics over remarkably large distances.

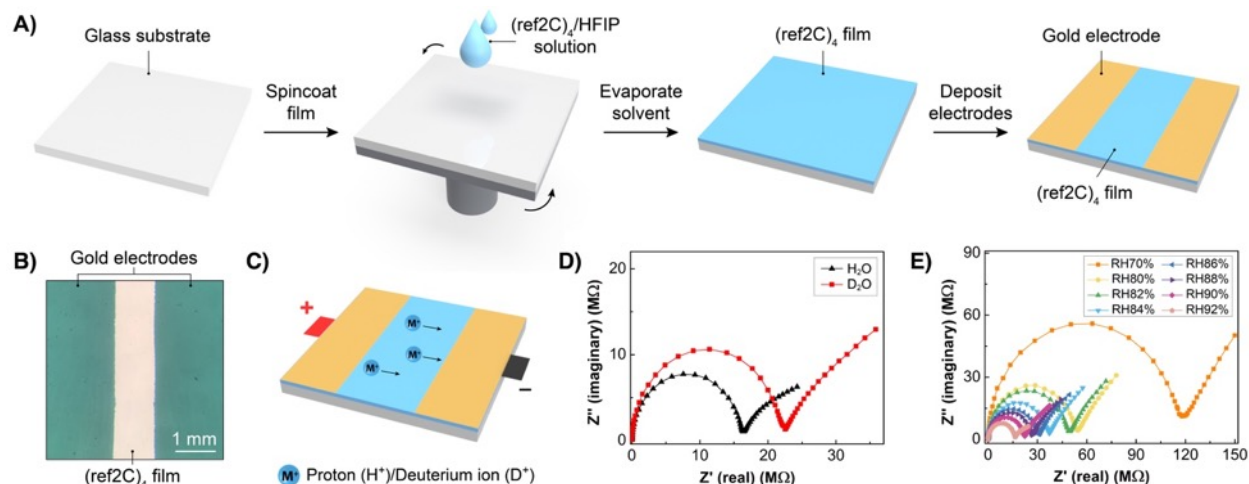


Figure 2.3. Fabrication and electrical characterization of solid-state (ref2C)₄ protein-based devices. (A) A general fabrication scheme of (ref2C)₄ protein-based devices for in-plane electrochemical impedance spectroscopy (EIS) characterization. (B) An optical microscope image of a representative (ref2C)₄ protein-based device, which featured two gold electrodes bridging over a solid-state (ref2C)₄ protein film. (C) A schematic of a (ref2C)₄ protein-based device during electrical characterization in either water (H₂O) or deuterium oxide (D₂O) vapor environments. (D) Nyquist plots for a representative (ref2C)₄ protein-based device in the presence of H₂O (black triangles) and D₂O (red squares) vapors at a relative humidity of 92%. (E) Nyquist plots for a representative (ref2C)₄ protein-based device in the presence of H₂O vapor with varied relative humidities of 70 % (orange), 80 % (yellow), 82% (green), 84% (light blue), 86% (dark blue), 88% (purple), 90% (magenta), and 92% (pink).

2.5. Solid-State Characterization

To understand the self-assembled structures in the solid state, we investigated the (ref2C)₄ protein films on glass substrates with microscopy techniques. First, we fabricated

glass substrate-bound (ref2C)₄ protein films using the previously described processing procedure. Next, we studied the morphological properties of the self-assembled (ref2C)₄ protein films. The scanning electron microscope (SEM) images demonstrated the formation of dense nanostructures on the surface, featuring randomly distributed spherical domains with radii between 50 nm and 400 nm (Figure 2.4A), which were in good agreement with the size values obtained from our previous DLS results that were measured in solution. The three-dimensional topographical atomic force microscope (AFM) images further confirmed the existence of spherical nanostructures on the surface of the (ref2C)₄ protein films, with similar size distribution to the SEM images and an average root-mean-square (RMS) surface roughness of ~ 43 nm (Figure 2.4B). Altogether, these microscopy measurements readily confirmed that the (ref2C)₄ protein formed nanoscale spherical assemblies in the solid state.

We further studied the structural properties of the self-assembled (ref2C)₄ protein films with spectroscopy techniques. The Fourier-transform infrared spectroscopy (FTIR) absorbance spectrum featured a prominent peak at a wavenumber of ~ 1654 cm⁻¹, corresponding to the existence of amide-I from the stretching vibrations of C=O and C-N groups, and a secondary peak at ~ 1536 cm⁻¹ with a small shoulder peak at ~ 1520 cm⁻¹, corresponding to the existence of amide-II from the in-plane bending of N-H groups and the stretching vibrations of C-N and C-C groups (Figure 2.4C). These absorption bands in the FTIR spectrum indicated the presence of α -helical structures with slight β -sheet

characters in the (ref2C)₄ protein films. The solid-state circular dichroism (ssCD) spectrum demonstrated the existence of a local maximum at ~ 194 nm and broadening local minima convoluted between ~ 210 nm and ~ 220 nm, which also indicated the formation of α -helical secondary structures with slight β -sheet characters within the (ref2C)₄ protein films (Figure 2.4D). Combined, our experiments revealed that the substrate-bound (ref2C)₄ protein films formed a mixed secondary structure in the solid state, again, in excellent agreement with our previous results obtained in solution.

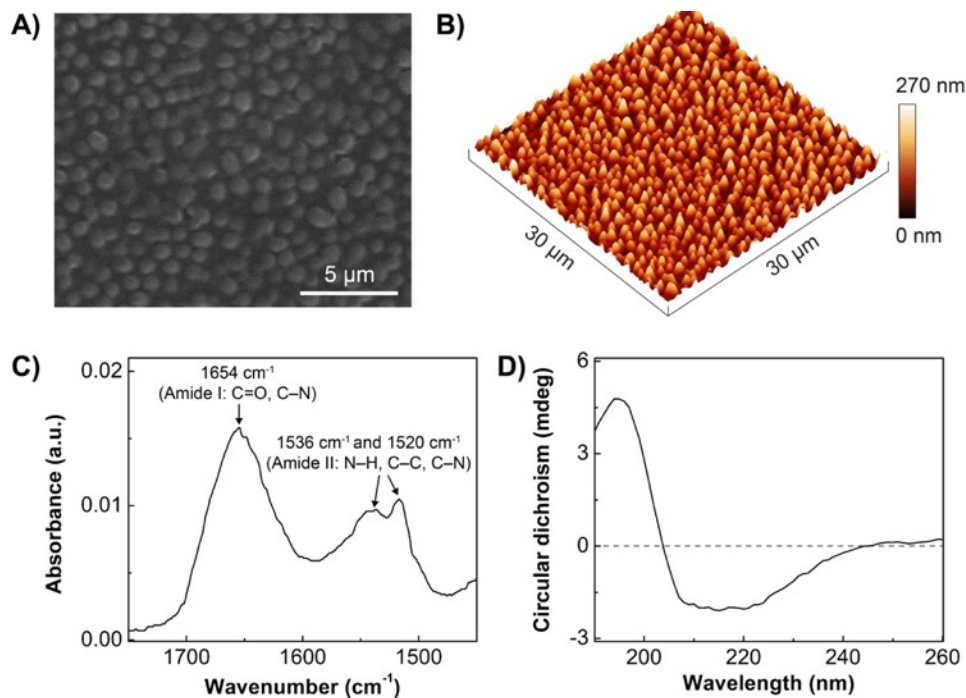


Figure 2.4. Solid-state characterization of the (ref2C)₄ protein assemblies. (A) A representative scanning electron microscope (SEM) image of the self-assembled structures of the (ref2C)₄ protein on a glass substrate. (B) A representative topographical atomic force microscope (AFM) image of the self-assembled structures of the (ref2C)₄ protein on a glass substrate. (C) A representative Fourier-transform infrared spectroscopy (FTIR) absorbance spectrum obtained for a self-assembled (ref2C)₄ protein film on a glass

substrate. (D) A representative solid-state circular dichroism (ssCD) spectrum obtained for a self-assembled (ref2C)₄ protein film.

To better understand the molecular conformation and structural arrangement of the (ref2C)₄ protein, we investigated its nanoscale assemblies with solid-state nuclear magnetic resonance (ssNMR) spectroscopy. For this purpose, we prepared solid-state samples of uniformly ¹³C and ¹⁵N labeled, selectively Tyr-labeled, and selectively Arg-labeled (ref2C)₄, processed them into films analogous to those used for electrical measurements, transferred the films to an ssNMR rotor, and recorded the 2D ¹³C–¹³C correlation spectra. In such spectra, resonance positions (aka. chemical shifts) reveal residues’ secondary structures by referring upshifts/downshifts to random coil ¹³C chemical shifts, resonance linewidths reveal global structural uniformity, resonance intensities reveal molecular mobility, and cross-peaks generated by polarization transfer between sites reveal intra- or inter-residue contacts.^[33] Overall, our ssNMR measurements allowed the assignment of amino acid residue types with invaluable insight into the structural ordering of the (ref2C)₄ assemblies at the molecular level.

Initially, we identified the Gly, Pro, Thr, and Ser residues from the aliphatic regions of 2D ¹³C–¹³C correlation spectra for uniformly ¹³C- and ¹⁵N-labeled (ref2C)₄ protein samples. First, we found that the Gly residues exhibited a single set of resonances centered at C_α ~ 45.02 ppm, for which the upshifts of C_α indicated an α-helical structure (Figure 2.5A and 2.5B, red contours). The Gly residues’ signals featured a relatively narrow

linewidth of ~ 1.2 to ~ 2 ppm, suggesting that they all adopted a similar relatively ordered backbone conformation (Figure 2.5A and 2.5B, red contours). Second, we found that the Pro residues exhibited two sets of resonances centered at $C_a \sim 62.87$ ppm and $C_b \sim 29.87$ ppm, for which the upshifts of C_a and downshifts of C_b also indicated an α -helical structure (Figure 2.5A and 2.5B, red contours). The Pro residues' signals both featured narrow linewidths of ~ 1 ppm, confirming that they adopted an ordered backbone conformation (Figure 2.5A and 2.5B, red contours). Third, we found that the Thr residues displayed multiple sets of overlapping resonances with a dominant signal centered at $C_a \sim 60.7$ ppm and $C_b \sim 67.8$ ppm, for which the upshifts of C_a and downshifts of C_b yet again indicated an α -helical structure (Figure 2.5A and 2.5B, red contours). The Thr residues' clustered signals together featured narrow linewidths of ~ 1.2 to ~ 2 ppm, suggesting that they adopted ordered but clearly distinguishable backbone conformations (Figure 2.5A and 2.5B, red contours). Fourth, we observed that the Ser residues displayed multiple sets of strong resonances with signals centered at $C_a \sim 55.38$ ppm and $C_b \sim 59.35$ ppm and at $C_a \sim 55.67$ ppm and $C_b \sim 59.06$ ppm, for which the downshifts of C_b were consistent with multiple different α -helical structures (Figure 2.5A and 2.5B, red contours). The Ser residues' signals featured broad linewidths of > 2 ppm, suggesting that they adopted disordered backbone conformations (Figure 2.5A and 2.5B, red contours). Altogether, our analysis demonstrated that the Gly, Pro, Thr, and Ser residues were associated with α -helical secondary structures, in agreement with the previous CD and FTIR measurements.

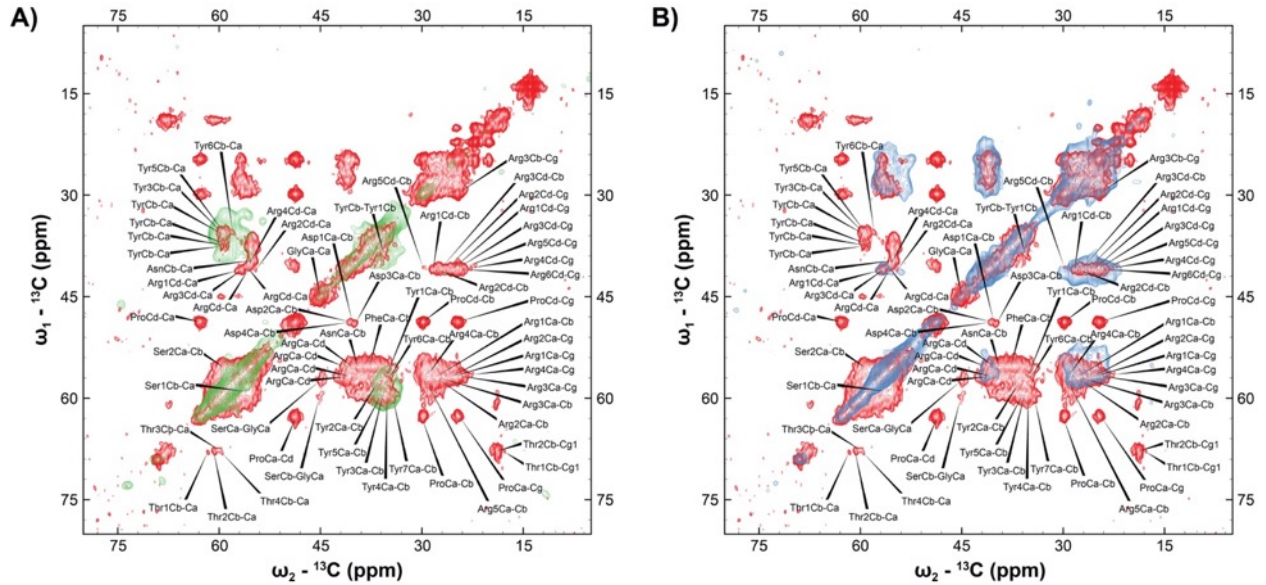


Figure 2.5. Solid-state nuclear magnetic resonance (ssNMR) spectroscopy characterization of the (ref2C)₄ protein assemblies. (A) A 2D ^{13}C - ^{13}C correlation spectra of self-assembled (ref2C)₄ protein with the Tyr-selectively labeled (ref2C)₄ protein spectrum (green contours) overlaid onto the uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein spectrum (red contours). (B) A 2D ^{13}C - ^{13}C correlation spectra of self-assembled (ref2C)₄ protein with the Arg-selectively labeled (ref2C)₄ protein spectrum (blue contours) overlaid onto the uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein spectrum (red contours).

Next, we identified the Asp and Asn residues from the aliphatic and carbonyl regions of the 2D ^{13}C - ^{13}C correlation spectra for uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein samples. First, we found that the Asp residues displayed multiple closely-spaced resonances centered at $C_a \sim 48.83$ ppm and $C_b \sim 40.25$ ppm, for which the downshifts of C_a indicated β character (Figure 2.5A and 2.5B, red contours). For these residues, the assignment was further corroborated by their four distinguishable C_g signals between ~ 177.7 and ~ 179.5 ppm, i.e., within the typical carbonyl region of aspartic acid (Figure

S2.3 and S2.4, red contours). The Asp residues' pronounced C_a and C_b signals featured a narrow linewidth of ~ 1.3 ppm, which was consistent with ordered backbone conformations, and reduced intensities when compared to other amino acids less common in the sequence, e.g., proline, suggesting a high degree of local mobility (Figure S2.5). Second, we found that the Asn residues displayed resonances within a congested region centered at $C_a \sim 55.28$ ppm and $C_b \sim 40.31$ ppm, for which the upshifts of C_a indicated some α -helical structure (Figure 2.5A and 2.5B, red contours). For these residues, the assignment was further corroborated by their strong overlapping C_g signals at ~ 176.8 ppm, i.e., the typical carbonyl region of asparagine (Figure S2.3 and S2.4, red contours). The Asn residues' C_g signals featured a narrow linewidth of ~ 1.5 ppm, suggesting that they adopted ordered backbone conformations (Figure S2.3 and S2.4, red contours). Overall, our analysis demonstrated that the Asp residues were mobile and associated with β -character secondary structure, while the Asn residues were likely static and associated with α -helical secondary structures, in agreement with the previous CD and FTIR measurements.

In turn, we proceeded to identify the Tyr and Phe residues using the aliphatic and aromatic regions of 2D ^{13}C - ^{13}C correlation spectra for uniformly ^{13}C - and ^{15}N -labeled and Tyr-selectively labeled (ref2C)₄ protein samples. First, we found that Tyr residues exhibited multiple sets of resonances at $C_a \sim 57.20$ to 57.70 ppm and $C_b \sim 35.17$ to 35.62 ppm for which the upshifts of C_a and downshifts of C_b indicated an α -helical structure.

For these residues, the assignment was further verified by their aromatic resonance patterns at ~ 155.3 to 156.1 ppm in 2D ^{13}C - ^{13}C correlation spectra for both uniformly labeled (Figure 2.5A, red contours) and Tyr-selectively labeled samples (Figure 2.5A, green contours). Moreover, the C_α and C_β signals of these residues featured a narrow linewidth of ~ 1.5 ppm, suggesting that they adopted ordered backbone conformations (Figure 2.5A). Interestingly, the observed cross-peaks between C_β sites of different Tyr residues revealed close contacts between Tyr residues (Figure 2.5A). Second, we observed that the Phe residues displayed resonance patterns at $\text{C}_\alpha \sim 55.31$ ppm and $\text{C}_\beta \sim 37.88$ ppm, for which the downshifts of C_β indicated an α -helical structure. These resonances featured broad linewidths of ~ 3 ppm, suggesting that they adopted disordered structures spanning from α -helical to random coil conformations (Figure 2.5A and 2.5B, red contours). Taken together, our analysis demonstrated that the Tyr residues were associated with α -helical secondary structure, while the Phe residues were associated with secondary structures spanning from α -helix to random coil conformations, in agreement with the previous CD and FTIR measurements.

Similarly, we completed the assignments by identifying the Arg residues using the aliphatic regions of the 2D ^{13}C - ^{13}C correlation spectra for both uniformly ^{13}C - and ^{15}N -labeled and Arg-selectively labeled (ref2C)₄ protein samples. We found that the Arg residues displayed multiple sets of closely-spaced resonances between $\text{C}_\alpha \sim 53.58$ to ~ 56.69 ppm and $\text{C}_\beta \sim 27.39$ to ~ 28.23 ppm, for which the upshifts of C_α and downshifts of C_β

indicated α -helical structures (Figure 2.5B, blue contours). These closely-spaced signals featured relatively narrow linewidths of < 2 ppm, suggesting that the residues possessed ordered backbone conformations (Figure 2.5B, blue contours). Furthermore, the residues' assignment was confirmed by their C_d signals centered at ~ 41.03 ppm and C_g signals located between ~ 23.91 ppm and ~ 25.76 ppm (Figure 2.5B, blue contours). Notably, the Arg residues in both uniformly-labeled and Arg-selectively labeled samples featured C_d and C_g signals that were in excellent agreement, but their C_a demonstrated some differences, presumably due to reflectins' known propensity for conformational disorder (Figure 2.5B, red and blue contours).^[21] Altogether, our analysis constituted a highly specific assessment of the Arg residues' conformations and confirmed that they were associated with α -helical secondary structure, again, in agreement with the previous CD and FTIR measurements.

Because the self-assembly and structure of reflectins have been proven difficult to control and are prone to change under a variety of processing parameters, including (but not limited to) temperatures, solubilization approach, type of solvent, ionic strength, residual salt, solution storage time, redox environment, casting strategy, and film storage condition,^[19–21,24,28,29] we explored the effects of different processing conditions on the self-assembled structures of our (ref2C)₄ protein. For this purpose, we performed ssNMR spectroscopy measurements to investigate the molecular structures of two additional sets of solid-state (ref2C)₄ samples that were independently prepared from (1) a second batch

of uniformly ^{13}C - and ^{15}N -labeled (ref2C) $_4$ protein under the same protocols as those used in Figure 2.5A and 2.5B and (2) a third batch of uniformly ^{13}C - and ^{15}N -labeled (ref2C) $_4$ protein under slightly modified sample loading conditions (see the Supporting Information for details). The corresponding ssNMR spectra of these two sets of (ref2C) $_4$ samples (Figure S2.6 and S2.7) exhibited some differences in chemical shifts with generally similar structural information at the molecular level, compared to our previous results shown in Figure 2.5A and 2.5B. These variabilities demonstrated by the ssNMR spectra were presumably due to the extreme sensitivity of our (ref2C) $_4$ protein to different sample preparation conditions, consistent with other reported reflectin proteins, which in turn may open up potential paths for establishing strategies to precisely control the self-assembled reflectin structures, although a lot of extra experimental efforts are expected.

2.6. Discussion and Conclusion

To summarize, we prepared a designer protein of (ref2C) $_4$ modified from the full-length reflectin 1b isoform from *E. scolopes* squid and validated its exceptional electrical characteristics in the solid state. The (ref2C) $_4$ protein-based films featured high room-temperature proton conductivities of 0.41 ± 0.06 mS/cm at a relative humidity of 92% across millimeter-scale distances, nearly four times greater than the best reported conductivity values for other full-length reflectin isoforms under analogous testing conditions across at least one-order-of-magnitude shorter micron-scale distances. We observed a distinct kinetic isotope effect for the (ref2C) $_4$ -based films with a $\sim 30\%$ decrease

in their proton conductivity upon changing the moist environment from H₂O to D₂O. Moreover, we found that the proton conductivity in the (ref2C)₄-based films was logarithmically dependent on the relative humidity with an observed > 7-fold increase in the proton conductivity upon changing the relative humidity from 70% to 92%. These findings confirmed and underscored our (ref2C)₄ protein as an exceptional solid-state long-range biological proton conductor.

Based on our findings obtained from a suite of physical characterization techniques, we can propose a hierarchical model across multiple length scales for our (ref2C)₄ protein (Figure 2.6). At the macro-scale, we found that the bulk films formed from the (ref2C)₄ protein displayed excellent proton conduction characteristics. At the micro-scale, we found the surfaces of the (ref2C)₄ protein films were covered with a dense and homogeneous distribution of structured assemblies. At the nanoscale, we found that the (ref2C)₄ protein was self-assembled into sphere-like particles with diameters of hundreds of nanometers that were in close contact with one another. At the molecular scale, we identified that the assemblies of the (ref2C)₄ protein possessed relatively fixed molecular conformations with the majority of the constituent amino acid residues (including those hydrophilic residues with highly charged or polar side chains) in α -helical secondary structures and thus good global structural ordering (as summarized in Table S2.1). The unique molecular conformations and structural arrangements likely facilitated the formation of intra- and inter-molecular proton transfer pathways across multiple length scales for highly efficient

proton conduction, which enabled excellent electrical functionalities that were maintained over a long distance. Overall, our hierarchical model provided insight into the structure–electrical function correlation of our (ref2C)₄ protein from the molecular to the macroscopic scale.

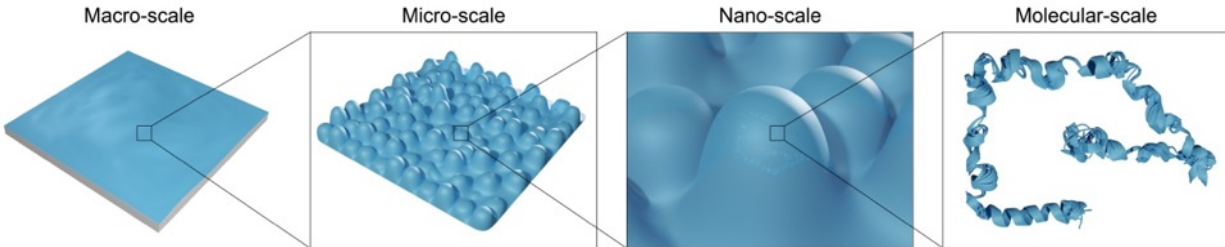


Figure 2.6. A hierarchical self-assembly model for the (ref2C)₄ protein from the molecular scale to the macroscale scale.

In conclusion, our findings hold significance for multiple reasons. First, we extend our work to explore electrical functionalities in reflectin isoforms from a new cephalopod species (i.e., *E. scolopes*). Second, the (ref2C)₄ protein is validated to possess excellent proton conductivities, which indicates the possible role of the constituent 2C domains and thus correlates very well with the previously finding that the 2C domain might be the minimal region to recapitulate the full length reflectin 1b isoform’s water stability and light scattering properties.^[24] Third, our (ref2C)₄ protein films feature exceptional proton conductivities over a quite long distance at the millimeter scale, which are at least one order of magnitude longer than that for other full-length reflectin isoforms previously studied at the micrometer scale. Fourth, our work adds to the growing body of studies attempting to understand the molecular structure of reflectins, although the sequential

assignment of our (ref2C)₄ protein at the atomic resolution requires additional experimental efforts. Fifth, our proposed hierarchical model provides additional insight into the correlation between the (ref2C)₄ protein's self-assembled structures and its excellent proton transport properties across multiple length scales. Taken together, our work may open up many opportunities for the understanding of analogous reflectin-based biomolecules and the rational engineering of other biomimetic proton conductors with programmable characteristics.

2.7. Supporting Information

2.7.1. Expression and Purification of Unlabeled and Isotope-Labeled (ref2C)₄

The plasmid of (ref2C)₄ on pET15b vector was obtained from Dr. Patrick Dennis at the Air Force Research Laboratory (USA), and transformed to BL21 *E. Coli* competent cells. Unlabeled (ref2C)₄ protein was expressed and purified following the standard protocols described in previous works.^[24,34] Uniformly-labeled, selectively Tyr-labeled, and selectively Arg-labeled (ref2C)₄ proteins were expressed and purified following different standard protocols described in previous work.^[24] First, an overnight culture was started by inoculating a 50 ml 2x YT medium with 50 μ L ampicillin (100 mg/L). The solution was grown overnight at 37 °C and at 250 rpm in a shaking incubator. Then, a 1-liter minimal medium was inoculated by addition of the overnight culture to an initial OD₆₀₀ of 0.05. The inoculated medium was grown to an OD₆₀₀ of 1.0 at 37 °C and at 250 rpm. For the expression of the uniformly-labeled protein, the cells were spun down and resuspended in another 1-liter minimum medium with ¹³C-labeled glucose and ¹⁵N-labeled NH₄Cl supplied as carbon and nitrogen sources. For the expression of selectively Tyr-labeled and selectively Arg-labeled proteins, uniformly ¹³C- and ¹⁵N-labeled amino acids of those selectively labeled residues were supplied, together with unlabeled glucose, unlabeled NH₄Cl, and other unlabeled amino acids. Subsequently, the protein expression was initiated by adding isopropyl β -D-1-thiogalactopyranoside (IPTG) at a concentration of 1 mM. After a 10-hour expression at 37 °C and at 250 rpm, the cells were harvested by centrifugation. The proteins were extracted and purified with fast protein liquid

chromatography (FPLC) following the method described in previous work and the structural identity was further confirmed with tryptic digestion and mass spectrometry.^[24]

2.7.2. Physical and Spectroscopic Characterization of ref(2C)₄ in Solution

The ref(2C)₄ protein was dissolved in hexafluoro-2-propanol (HFIP) under mechanical shaking for physical characterization in solution. The particle size distribution profiles were characterized with a Malvern Zetasizer μ V analyzer at a ref(2C)₄ concentration of 2.5 mg/mL. The UV/Vis absorbance spectra were obtained with an Agilent Cary 60 UV-Vis Absorption Spectrometer at a ref(2C)₄ concentration of 0.5 mg/mL. The circular dichroism (CD) spectra were obtained with a Jasco J-810 Spectropolarimeter at a ref(2C)₄ concentration of 0.125 mg/mL. Prior to all characterizations, the solutions were allowed to fully stabilize at a temperature of 20 °C.

2.7.3. Preparation of Solid-State, Self-Assembled ref(2C)₄ Films for Electrical Characterization

The solid-state, self-assembled ref(2C)₄ films were prepared according to standard procedures. First, a ref(2C)₄ solution with a concentration of 5 mg/mL (30 μ L) was spincoated onto a square-shaped glass substrate (dimension of 1 inch by 1 inch). Next, the as-spincoated ref(2C)₄ film was kept at room temperature for five minutes to completely remove the remaining solvent. Then, the resulting substrate-bound ref(2C)₄ films were used for relevant microscopy and spectroscopy characterization experiments. For electrical

characterization, a pair of rectangular-shaped gold electrodes (40 nm in thickness) were directly electron-beam deposited through a shadow mask onto the ref(2C)₄ film with a gap distance of 1 mm by using an Angstrom Engineering EvoVac Glovebox Evaporator. Note that unlabeled ref(2C)₄ proteins were used for electrical measurements.

2.7.4. Electrical Characterization of Solid-State, Self-Assembled ref(2C)₄ Films

The two-terminal devices from self-assembled ref(2C)₄ films were characterized with electrochemical impedance spectroscopy (EIS) by using a Gamry Reference 600 potentiostat. The responses of the devices to a small sinusoidal perturbation with an amplitude of 500 mV were recorded over a wide frequency range of 1 MHz to 0.5 Hz. The measurements were performed within an enclosed chamber with controlled moisture levels of water or deuterium oxide vapors at room temperature (~ 21 °C). The relative humidity was allowed to stabilize at desired levels and continuously monitored with a hygrometer during all measurements. The resulting data was analyzed with the Gamry Echem AnalystTM software package.

2.7.5. Microscopic and Spectroscopic Characterization of Solid-State, Self-Assembled ref(2C)₄ Films

The microscale and nanoscale surface morphologies of the self-assembled ref(2C)₄ films were characterized with optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). The optical microscopy images were obtained with an Olympus optical microscope. The surface microstructure images were obtained with an

FEI Quanta 3D FEG scanning electron microscope. The 3D topography images and the values of film thickness and surface roughness were obtained with an Asylum Cypher ES AFM equipped with an environmental chamber. The FTIR absorbance spectra were obtained with a Perkin Elmer Frontier Fourier Transform Infrared Spectrometer equipped with a Perkin Elmer Universal ATR module.

2.7.6. Preparation of Solid-State, Self-Assembled ref(2C)₄ Samples for Solid-State NMR Characterization

The solid-state, self-assembled ref(2C)₄ samples for the solid-state NMR experiments were prepared according to standard procedures. The isotope-labeled ref(2C)₄ protein solutions were prepared by separately dissolving different batches of ref(2C)₄ protein in HFIP at a concentration of 5 mg/mL with an intermittent shaking procedure, where the ref(2C)₄/HFIP mixture was kept at 27 °C and intermittently shaken with a 2-minute brief vortexing followed by a 4-minute sonication in water bath for a total of 4 repeats during a 3-week period. The first-batch ref(2C)₄ samples for the ssNMR experiments (corresponding to Figures 2.5A, Figure 2.5B, Figure S2.4, and Figure S2.5) were prepared by dropcasting the first-batch ref(2C)₄ solution (500 μ L) onto a glass substrate. The dropcasted ref(2C)₄ films were scratched and lifted by a razor blade and then packed into a ssNMR rotor for characterization. The second-batch ref(2C)₄ samples for the ssNMR experiments (corresponding to Figure S2.6) was prepared by dropcasting the second-batch ref(2C)₄ solution (500 μ L) onto a glass substrate. The dropcasted

ref(2C)₄ films were scratched and lifted by a razor blade and then packed into a ssNMR rotor for characterization. The third-batch ref(2C)₄ samples for the ssNMR experiments (corresponding to Figure S2.7) was prepared by directly loading the third-batch ref(2C)₄ solution (30 μ L) into a ssNMR rotor, where the solution was formed into solid-state films after complete solvent evaporation. The process was repeated until the rotor was filled with dry ref(2C)₄ films. The dry-film-filled rotor was then used for ssNMR characterization.

2.7.7. Solid-State NMR Characterization of Self-Assembled ref(2C)₄ Films

The solid-state NMR (ssNMR) experiments were performed on an Agilent spectrometer operating at ¹H NMR frequency of 600 MHz (14.1 Tesla) with a 3.2 mm BioMAS probe at University of Central Florida. All spectra were recorded with samples spun at 13.5 kHz Magic Angle Spinning (MAS). The temperature of samples was maintained at ~ 4 °C by a VT controller. The ¹H-¹³C cross polarization (CP) was recorded with 60 kHz and 46.5 kHz field on ¹H and ¹³C channel, respectively.^[35] Dipolar assisted rotational resonance (DARR) mixing of 100 ms was used for all homonuclear ¹³C-¹³C recoupling.^[35] Two-pulse phase-modulated (TPPM) ¹H decoupling at ~ 100 kHz was applied during the indirect and direct acquisition dimension.^[36,37] The resulting spectra were processed and analyzed with the NMRPipe software.^[38] Each dimension was zero-filled to twice the acquisition number. A Gaussian broadening function of 50 and 50 Hz was applied to the direct and indirect dimension. Forward linear prediction was applied

with twice the number of data points in indirect dimensions. The processed spectra were plotted with the NMR-FAM SPARKY software.^[39]

2.7.8. Supporting Information Figures and Tables

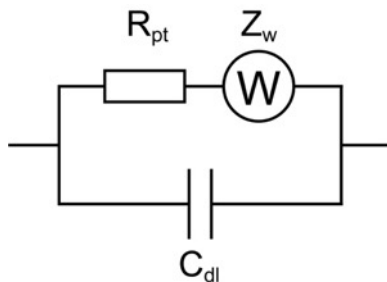


Figure S2.1. The equivalent circuit for the proposed proton conduction mechanism within the (ref2C)₄ protein-based devices during the EIS measurements. R_{pt} denotes the proton transfer resistance in the (ref2C)₄ film, Z_w denotes the complex Warburg impedance that is related to diffusion-related processes in the low-frequency region, and C_{dl} denotes the double-layer capacitance between the (ref2C)₄ film and gold electrodes.

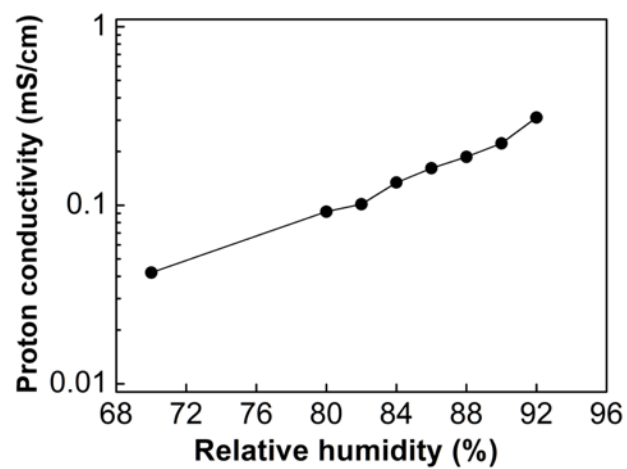


Figure S2.2. A plot of proton conductivity as a function of relative humidity for the same (ref2C)₄ protein-based device shown in Figure 2.3E.

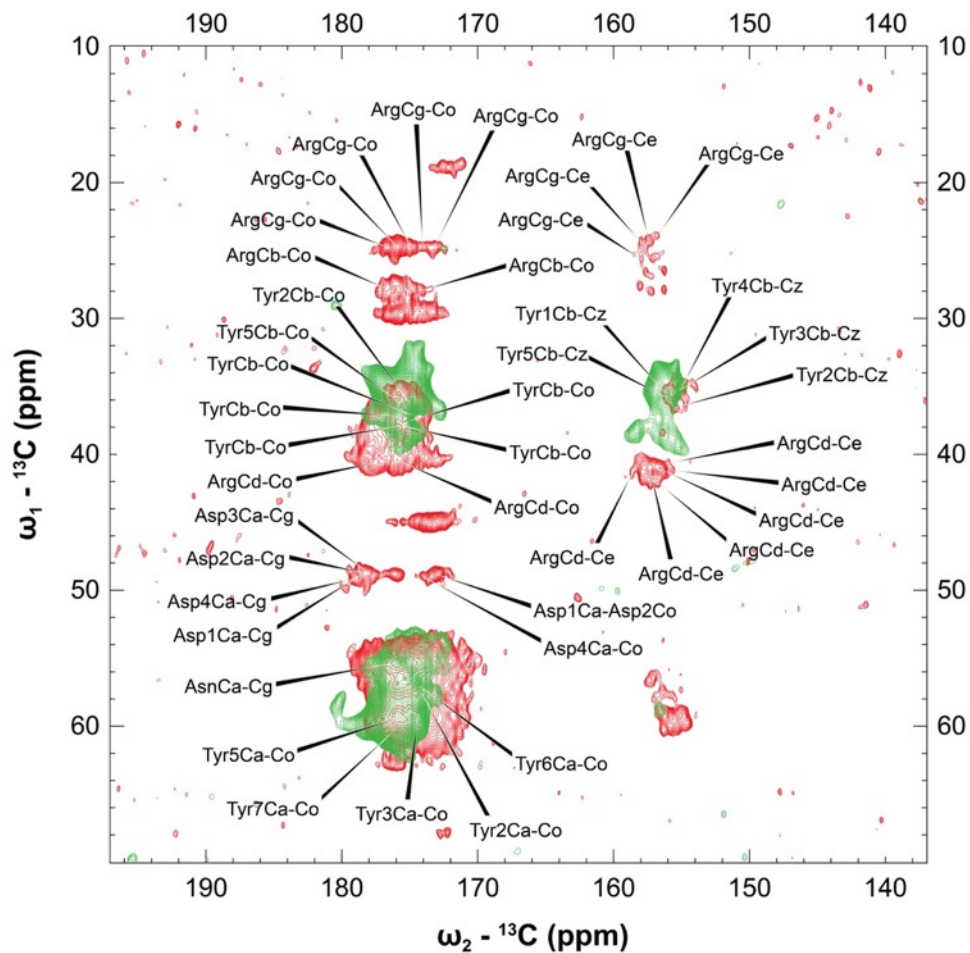


Figure S2.3. 2D ^{13}C - ^{13}C correlation spectra in the aromatic and carbonyl region of self-assembled (ref2C)₄ protein with the Tyr-selectively labeled (ref2C)₄ protein spectrum (green contours) overlaid onto the uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein spectrum (red contours). The spectra were from the same measurement as those in Figure 2.5A. The sample preparation was described in the Supporting Information Section 2.7.6.

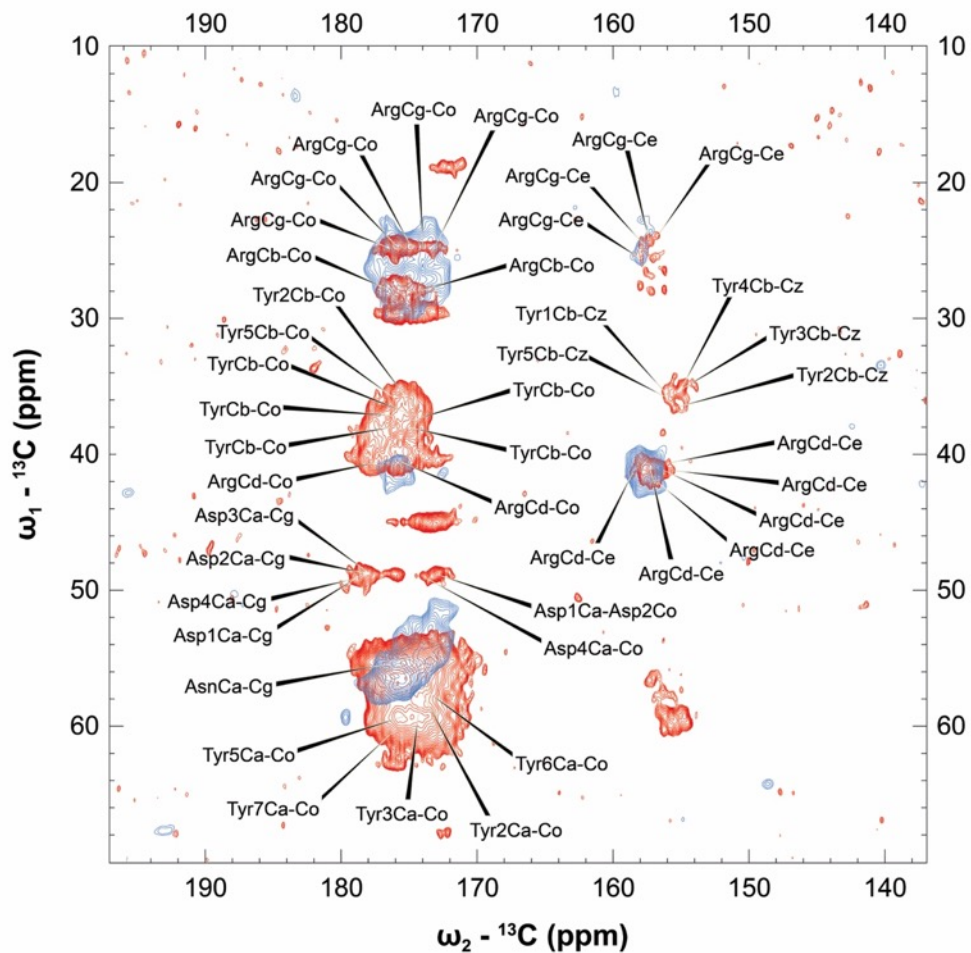


Figure S2.4. 2D ^{13}C - ^{13}C correlation spectra in the aromatic and carbonyl region of self-assembled (ref2C)₄ protein with the Arg-selectively labeled (ref2C)₄ protein spectrum (blue contours) overlaid onto the uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein spectrum (red contours). The spectra were from the same measurement as those in Figure 2.5B. The sample preparation was described in the Supporting Information Section 2.7.6.

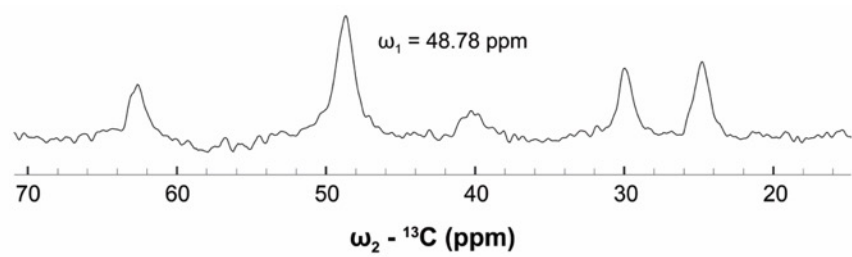


Figure S2.5. A 1D-sliced spectrum extracted from the vertical position at 48.78 ppm in the 2D ^{13}C - ^{13}C correlation spectra (Figure 2.5A and 2.5B) obtained for the uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein.

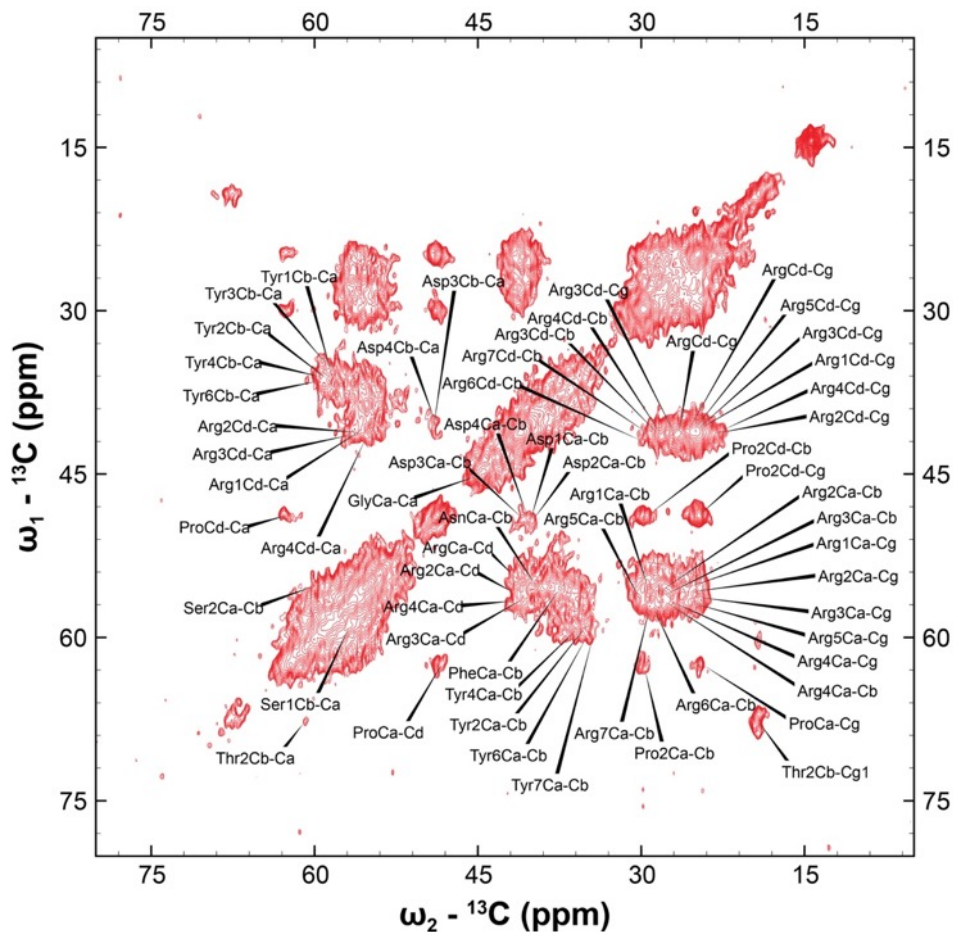


Figure S2.6. A representative 2D ^{13}C - ^{13}C correlation spectrum for a second-batch sample made from uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein. The sample preparation was described in the Supporting Information Section 2.7.6.

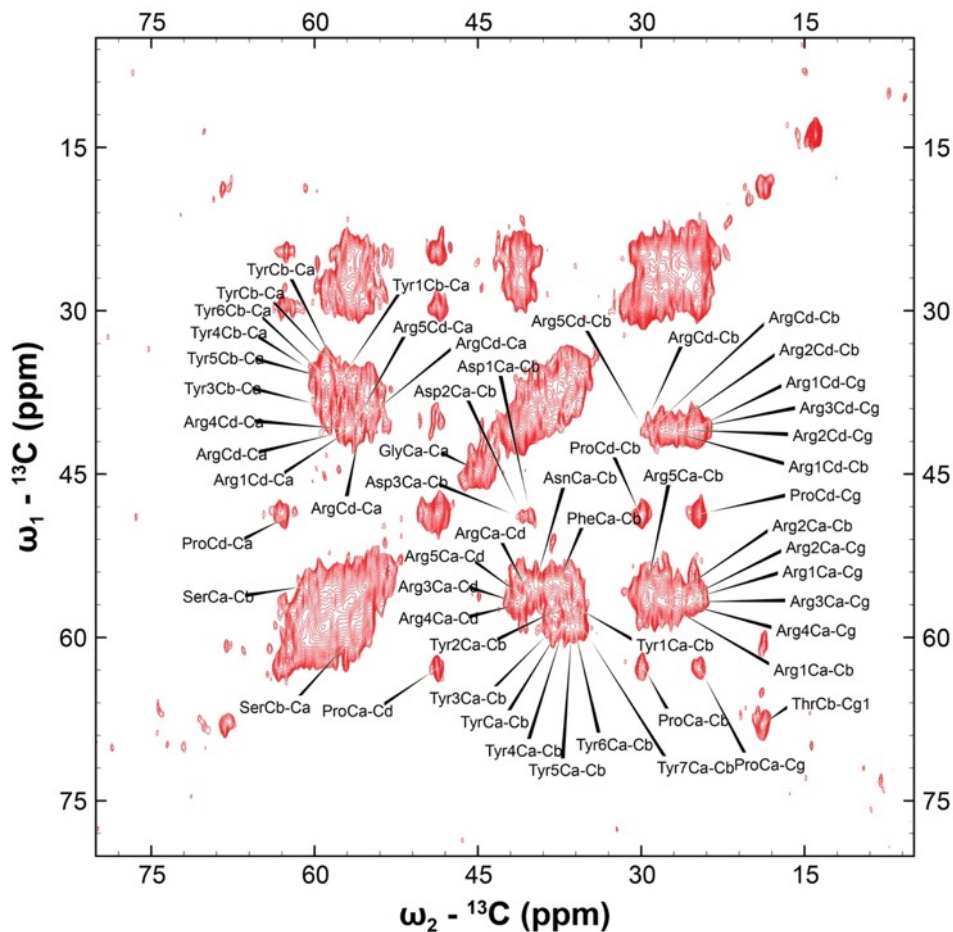


Figure S2.7. A representative 2D ^{13}C - ^{13}C correlation spectrum for a third-batch sample made from uniformly ^{13}C - and ^{15}N -labeled (ref2C)₄ protein. The sample preparation was described in the Supporting Information Section 2.7.6.

Table S2.1. A summary of residue type assignments for self-assembled (ref2C)₄ structures from the ssNMR measurements (corresponding to the ssNMR spectra shown in Figure 2.5A, Figure 2.5B, Figure S2.3, and Figure S2.4).

Residue Type	Arg (R)	Asp (D)	Tyr (Y)	Ser (S)	Asn (N)	Thr (T)	Gly (G)	Phe (F)	Pro (P)
Charge Status	Charged	Charged	Polar	Polar	Polar	Polar	Hydrophobic	Hydrophobic	Hydrophobic
Compositional Ratio	16%	13%	23%	8%	4%	4%	9%	7%	4%
Secondary Structure	α -helix	β -character	α -helix	α -helix	α -helix	α -helix	α -helix	α -helix to random coil	α -helix
Global Structural Uniformity	O (M)*	O (M)	O (M)	D***	O (S)**	O (M)	O (S)	D	O (S)

* O (M) stands for Ordered (multiple conformations).

** O (S) stands for Ordered (single conformation).

*** D stands for Disordered.

2.8. Acknowledgements

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CHAPTER 3

Stretchable Cephalopod-Inspired Multimodal Camouflage Systems

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3.1. Abstract

Soft, mechanically-deformable materials and systems that can, on demand, manipulate light propagation within both the visible and infrared regions of the electromagnetic spectrum are desirable for applications that include sensing, optoelectronics, robotics, energy conservation, and thermal management. However, the development of such technologies remains exceptionally difficult, with relatively few examples reported to date. Herein, we address this challenge by engineering cephalopod-inspired adaptive camouflage platforms with multispectral functionality. First, we describe stretchable copolymer membranes that feature outstanding unstrained protonic conductivities of up to ~ 90 mS/cm, demonstrate increases of $\sim 80\%$ in their conductivities at strains of 200%, and uniquely exhibit no loss in electrical performance even under extreme elongations of 500%. Next, we use these membranes for the fabrication of mechanically- and electrically-actuated camouflage devices that function over an unprecedented spectral window; can simultaneously modulate their visible and infrared specular-to-diffuse transmittance ratios by $> \sim 3000$ -fold and $> \sim 4$ -fold, respectively; feature rapid ~ 0.6 second response times; and exhibit good performance after repeated actuation. Our findings may afford new scientific and technological opportunities not only for adaptive optics and photonics but also for any platform that would benefit from simultaneously controlling visible light and heat.

3.2. Introduction

Soft, mechanically-deformable systems that can reversibly change their appearance (e.g., coloration, opacity, or luminescence) within the visible range of the electromagnetic spectrum have attracted much research interest for applications that include smart windows,^[1,2] colorimetric sensors,^[3,4] optoelectronic displays,^[5,6] artificial skin,^[7,8] and bioinspired robotics.^[9,10] More recently, the emergence of analogous platforms that dynamically modulate the propagation of infrared radiation (i.e., heat) has facilitated exciting proof-of-principle demonstrations in areas such as energy conservation,^[11,12] thermal management,^[13,14] and infrared camouflage.^[15,16] Within this context, devices or systems that can potentially manipulate light across both the visible (400–740 nm) and infrared (740 nm to 15 μm) spectral regions remain quite rare. To date, relatively few classes of these technologies have been reported, such as thermochromic phase-change materials,^[17–20] electrochromic devices,^[21–23] infrared-reflecting platforms,^[24,25] and reconfigurable soft machines^[9] (see Table S3.1), and they have featured drawbacks that include a limited degree of spectral modulation, impractical actuation requirements, poor stability to repeated actuation, slow response times, and/or complicated fabrication.^[9,17–25] Indeed, the engineering of devices and systems with tandem adaptive functionality across a broad spectral window (i.e., encompassing the visible, near-infrared, short-wavelength infrared, mid-wavelength infrared, and long-wavelength infrared) has proven challenging, in large part because of the order of magnitude difference in the length scales associated with the propagation of visible and long-wavelength infrared light.

Consequently, there exists an impetus for the development of advanced multimodal camouflage platforms, which can present new scientific and technological opportunities across multiple fields.

Some of the most prominent and impressive examples of soft, deformable systems that can reversibly and precisely change their appearance are found in nature – they are animals called coleoid cephalopods,^[26–32] such as the *Japetella heathi* pelagic octopus (Figure 3.1A)^[28] and the *Taonius borealis* glass squid (Figure 3.1B).^[29,30] These animals are capable of stunning feats of concealment, which include changing the transparency of their bodies by means of a sophisticated skin architecture that controls the transmission, absorption, and reflection of light (Figure 3.1C).^[26–32] In its most general form, the skin consists of multiple layers containing pigmented size-changing organs called chromatophores,^[33–35] typically narrowband-reflecting cells called iridophores,^[36–38] and broadband-reflecting cells called leucophores^[39–41] (Figure 3.1C). Although their precise arrangement and optical functionalities tend to vary among different cephalopod species, these organs and cells operate in tandem as natural optical components, thus allowing cephalopod skin to adaptively manipulate different wavelengths of light in unique ways.^[26–32]

Because cephalopods undergo appearance changes in part by stretching or deforming their skin, some optoelectronic devices and systems have drawn inspiration from these animals and incorporated pliable electronic/ionic conductors as electrodes,

sensors, actuators, or active components.^[4,26,27,31,32] More generally, stretchable conductors have received substantial attention for various applications,^[42,43] leading to the development of multiple materials classes that include heterogeneous nanocomposites,^[43–48] liquid metals,^[49,50] substrates pre-patterned with metallic structures,^[42,51,52] conjugated polymers blended with ionic additives,^[42,53] and ionic hydrogels.^[54–56] However, none of the stretchable conductors reported to date have proven themselves to be ideally suited for the development of mechanically-deformable adaptive camouflage platforms with multispectral functionality. Indeed, for this demanding application, a conductive material would need to meet a variety of competing criteria, including straightforward processability into freestanding transparent membranes, excellent adhesion to other surfaces, outstanding stretchability and conformability, high electrical conductivity even under significant deformation, stability to repeated mechanical and electrical cycling, tolerance for different environmental conditions, and spectral tunability within both the visible and the infrared.

3.3. Conceptualization of Adaptive Multimodal Camouflage Platforms

For the design of our adaptive multimodal camouflage platforms, we drew inspiration from the established technology of dielectric elastomer actuators^[57,58] and from the properties of different optical components found within cephalopod skin.^[26,27,33–41] Thus, we conceived tri-layer devices, wherein an elastomer layer was sandwiched between two highly-conductive membranes (Figure 3.1D). As the material for the central elastomer

layer, we chose an acrylate elastomer due to its excellent elasticity, transparency in the visible spectral range, and ability to absorb infrared radiation. As the material for the membranes, we chose a sulfonated pentablock copolymer not only due to its proton-conducting properties but also due to its transparency in both the visible and the infrared spectral ranges. Before actuation, we envisioned that the devices would feature relatively small active areas and large effective thicknesses, as well as irregular wrinkled surface morphologies (Figure 3.1D). Within the infrared, the devices' larger thicknesses would increase the absorptance and decrease the transmittance, analogously to contracted chromatophore organs,^[33–35] and within the visible, the laterally-disordered surface morphology would lead to substantial opacity (e.g., enhanced diffuse transmission), analogously to some leucophores and iridophores^[36–41] (Figure 3.1D). After actuation, we envisioned that the devices would feature enlarged active areas but reduced effective thicknesses, as well as more flattened smooth surface morphologies (Figure 3.1D). Within the infrared, the devices' smaller thicknesses would decrease the absorptance and increase the transmittance, analogously to expanded chromatophore organs,^[33–35] and within the visible, the more-ordered surface morphology would lead to substantial transparency (e.g., enhanced specular transmission), analogously to some leucophores and iridophores^[36–41] (Figure 3.1D). Accordingly, the described design strategy would enable our systems to simultaneously reconfigure their optical properties across the entirety of the visible and infrared regions of the electromagnetic spectrum.

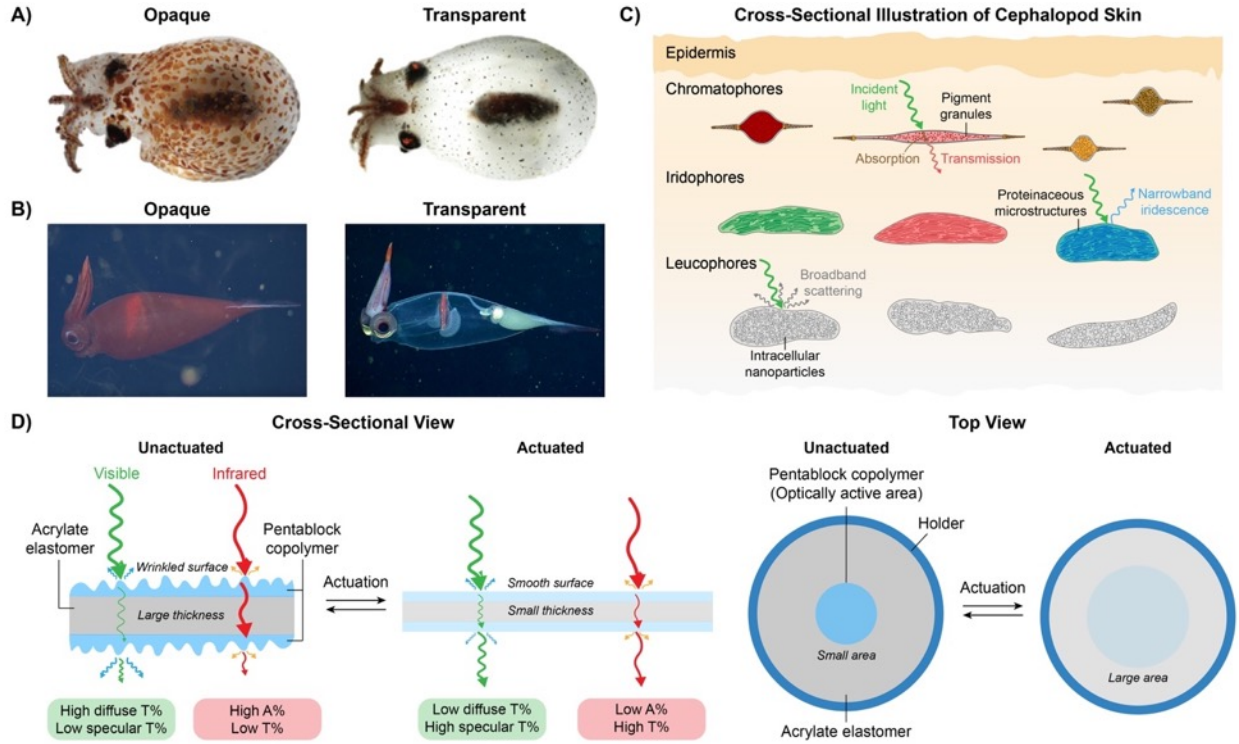


Figure 3.1. Cephalopod-inspired design of the multimodal camouflage systems. (A) Pictures of representative *Japetella heathi* octopuses with their bodies in opaque and transparent states.^[28] (B) Pictures of representative *Taonius borealis* glass squids with their bodies in opaque and transparent states.^[29,30] (C) Cross-sectional illustration of cephalopod skin and its embedded pigment granule-packed chromatophore organs, proteinaceous microstructure-containing iridophore cells, and intracellular nanoparticle-filled leucophore cells. Note that the image shows generalized depictions of the interactions of visible light with these organs and cells. (D) Cross-sectional (left) and top-view (right) schematics of the designed adaptive multimodal camouflage system before and after actuation. Upon mechanical or electrical actuation, the active area is reversibly switched from a contracted state (large thickness and small area) with a wrinkled surface to an expanded state (small thickness and large area) with a smooth surface. The schematics illustrate the absorption (A%) and transmission (T%) of light before and after actuation within both the visible and infrared regions of the electromagnetic spectrum.

3.4. Evaluation of Stretchable Proton Conductor Membranes as Materials for Adaptive Camouflage Platforms

We began our experiments by characterizing the electrical properties of the freestanding pentablock copolymer membranes necessary for our adaptive camouflage systems with electrochemical impedance spectroscopy (EIS). Toward this end, we fabricated two-terminal devices wherein thin optically-transparent membranes (thicknesses of < 300 nm) bridged two gold electrodes (Figure 3.2A, Figure S3.1, and see the Supporting Information for details). First, we recorded Nyquist plots (the imaginary versus the real parts of the impedance) for our devices at different relative humidities, which revealed semicircles in the high-frequency region, due to the resistance and capacitance of the bulk membranes, and inclined spurs in the low-frequency region, due to the accumulation of protons at the membrane/electrode interfaces (Figure 3.2B).^[59,60] By fitting the curves with a simple equivalent circuit, we calculated the bulk protonic conductivity for our freestanding films, which increased from a value of 6.3 ± 0.1 mS/cm at a low relative humidity of $\sim 50\%$ to a value of 87.0 ± 6.1 mS/cm at a high relative humidity of $\sim 90\%$ (Figure 3.2B and 3.2C). The conductivity featured a logarithmic dependence on the relative humidity, as reported for typical proton-conducting materials (Figure 3.2B and 3.2C).^[61,62] Next, we recorded Nyquist plots for our devices in the presence of water (H_2O) and deuterium oxide (D_2O) vapor at a relative humidity of 90%, finding an increase in the diameter of the semicircle upon moving from H_2O to D_2O *in situ* (Figure 3.2D). From these curves, we extracted the bulk protonic conductivity for

our freestanding films, which decreased from ~ 84 mS/cm in the presence of H_2O to ~ 52 mS/cm in the presence of D_2O (Figure 3.2D). The observed change of ~ 38 % in the conductivity revealed a distinct kinetic isotope effect and was consistent with the transport of protons in our membranes *via* the Grotthuss mechanism.^[63,64] Excitingly, our membranes featured protonic conductivities that matched or even exceeded those reported for the best known solid-state proton conductors, including solid polymer electrolytes such as Nafion 117, crystalline porous solids, graphene oxide derivatives, and biomolecules (see the detailed comparison in Table S3.2), as well as maintained their structural and mechanical integrities at different relative humidities. Altogether, these measurements demonstrated that our thin freestanding copolymer membranes possessed outstanding electrical functionalities.

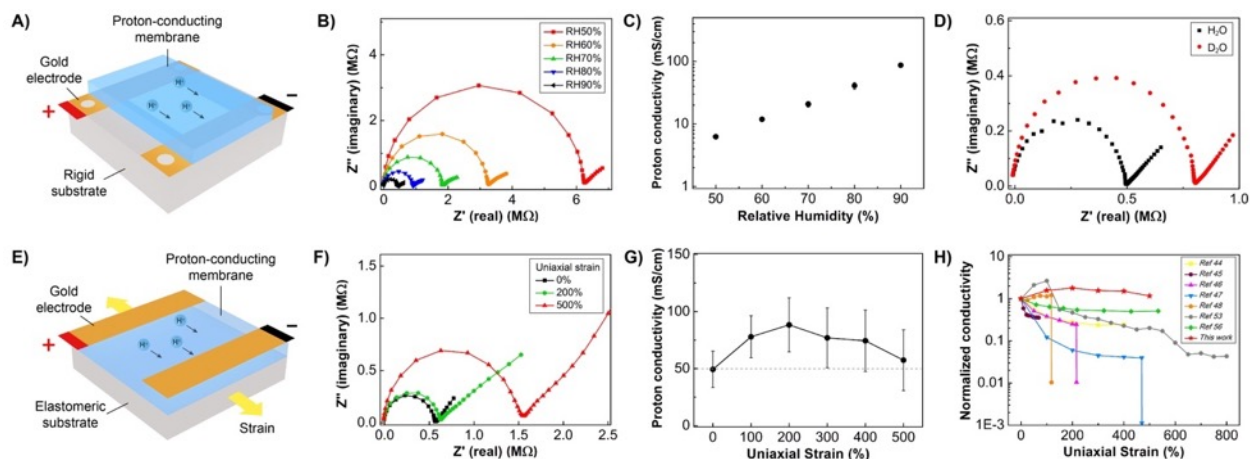


Figure 3.2. Electrical and physical characterization of sulfonated pentablock copolymer membranes. (A) A general schematic of the two-terminal devices used for electrochemical impedance spectroscopy (EIS) measurements in the absence of strain, wherein a freestanding pentablock copolymer membrane bridges two gold electrodes. (B) Nyquist plots for a representative freestanding membrane-based device at relative humidities of

50% (red), 60% (orange), 70% (green), 80% (blue), and 90% (black). **(C)** A plot of the protonic conductivity as a function of the relative humidity for freestanding membrane-based devices. **(D)** Nyquist plots for a representative freestanding membrane-based device in the presence of water (H_2O) (black squares) and deuterium oxide (D_2O) (red circles) vapor at a relative humidity of 90%. **(E)** A general schematic of the two-terminal devices used for EIS measurements in the presence of strain, wherein an elastomeric acrylate substrate-bound pentablock copolymer membrane bridges two gold electrodes. **(F)** Nyquist plots for a representative substrate-bound pentablock copolymer membrane at applied uniaxial strains of 0% (black squares), 200% (green circles), and 500% (red triangles). **(G)** The protonic conductivity of elastic acrylic substrate-bound pentablock copolymer membranes at applied uniaxial strains of 0%, 100%, 200%, 300%, 400%, and 500%. Note that the conductivity increased with strain. **(H)** A direct comparison of the change in conductivity with strain for our membranes and representative state-of-the-art stretchable conductors, including silver nanoparticles/fluorinated rubber,^[44] silver nanowires/polyurethane acrylate,^[45] silver flakes/fluorinated rubber,^[46] gold nanoparticles/polyurethane,^[47] single-walled carbon nanotubes/fluorinated rubber,^[48] a poly(3,4-ethylenedioxythiophene):polystyrene sulfonate/ionic liquid blend on an elastic styrene ethylene butylene styrene substrate,^[53] and an ionic hydrogel.^[56]

We continued our experiments by exploring the electrical properties of our optically-transparent proton-conducting copolymer membranes when bound to elastomeric substrates (a configuration necessary for the designed dielectric elastomer actuator-type camouflage platforms) as a function of applied strain. Toward this end, we laminated our freestanding copolymer membranes onto one side of elastic acrylate substrates, mounted such substrate-bound membranes in a custom-designed holder, and then contacted the membranes with gold electrodes *in situ* (Figure 3.2E, Figure S3.2, and

see the Supporting Information for details). Importantly, this approach allowed for electrical interrogation under large uniaxial strains without fracturing or tearing the thin transparent membranes. First, we recorded Nyquist plots for our devices in the absence and presence of strain, which revealed semicircles with variable diameters in the high-frequency region and inclined spurs in the low-frequency region, in analogy to the measurements for the freestanding membranes (Figure 3.2F). From curves obtained at a relative humidity of $\sim 90\%$, we calculated the bulk conductivity of our substrate-bound membranes, which was 49.4 ± 15.9 mS/cm in the absence of strain, 88.4 ± 23.7 mS/cm under a strain of $\sim 200\%$, and 57.4 ± 26.6 mS/cm under a strain of $\sim 500\%$ (Figure 3.2F and 3.2G) (note that lamination onto the acrylate substrates appeared to decrease the unstrained membranes' protonic conductivity by approximately two-fold). The observed protonic conductivity featured a non-linear strain dependence, with an initial maximum increase of $\sim 80\%$ at a strain of $\sim 200\%$ followed by a smaller increase of $\sim 16\%$ at a strain of $\sim 500\%$ (Figure 3.2G). The membranes' strain-dependent electrical properties improved on those of typical state-of-the-art stretchable conductors, with our membranes even demonstrating an enhancement in performance upon extreme elongation (Figure 3.2H).^[44–48,53,56] Next, we recorded Nyquist plots for the substrate-bound membranes before and after repeated mechanical actuation, finding an increase in the diameter of the semicircles upon the repeated application of strain (Figure S3.3). From the obtained curves, we extracted a bulk protonic conductivity of 46.0 ± 2.4 mS/cm prior to cycling and 22.0 ± 4.4 mS/cm after 10^3 load/unload cycles at a strain of 200% (Figure S3.3). The

conductivity decrease of only $\sim 50\%$ compared favorably to the more substantial conductivity losses reported for other state-of-the-art stretchable conductors that were cycled a similar number of times at lower strains.^[44,45] Overall, these measurements revealed an excellent combination of electrical and mechanical characteristics for our transparent substrate-bound membranes, highlighting their suitability for the envisioned dielectric elastomer actuator-type multimodal camouflage systems.

To better understand why our unstrained membranes exhibited such exceptional protonic conductivities, we visualized their elastomeric substrate-bound variants' nanoscale morphologies with atomic force microscopy (AFM) at low ($\leq 50\%$) and high relative humidities (90%). At a low relative humidity of 45%, representative topographic AFM images revealed that the membrane's surface consisted of protruding, relatively-dehydrated nanoscale spherical domains, which had average diameters of ~ 16 nm and were embedded within an interconnected matrix (Figure S3.4A). The simultaneously-obtained representative phase contrast AFM images demonstrated a clear phase difference between the domains, which presumably consisted of the copolymer's stiffer hydrophilic poly(styrene-*co*-styrene sulfonate) blocks (dark areas in Figure S3.4B), and the surrounding phase-segregated matrix, which presumably consisted of the copolymer's softer hydrophobic poly(hydrogenated isoprene) and poly(*tert*-butyl styrene) blocks (light areas in Figure S3.4B). At a high relative humidity of 90%, representative topographic AFM images revealed that the membrane's surface still consisted of protruding, water-

swollen nanoscale spherical domains, which now had larger average diameters of ~ 27 nm and remained embedded within the surrounding phase-segregated matrix (Figure S3.4C). The simultaneously-obtained representative phase contrast AFM images now demonstrated a clear but inverted phase difference between the hydrophilic domains (light areas in Figure S3.4D), which had become softer presumably due to water uptake, and the hydrophobic surrounding matrix (dark areas in Figure S3.4D), which had become compressed presumably due to the domains' swelling. Importantly, these observations were fully consistent with literature precedent for analogous block copolymers,^[65–70] suggesting the formation of a continuous, extended water percolation network within the interiors of our membranes and providing a rationale for their outstanding electrical properties.

To gain insight into the unexpected discovery that stretching dramatically enhanced our copolymer membranes' conductivities, we further visualized their morphologies with optical microscopy and atomic force microscopy (AFM) at a low relative humidity (≤ 50 %), both before and after uniaxial strain. For this purpose, we, again, used our elastomeric substrate-bound copolymer membranes and applied uniaxial strain *in situ* during AFM measurements by means of a custom-designed holder (Figure S3.2, Figure S3.5, and see the Supporting Information for details). First, representative optical microscopy images indicated that, without uniaxial strain, a visibly transparent substrate-bound membrane had a smooth surface with few obvious micron-sized features

at low relative humidity (Figure S3.2 and Figure S3.5A, left). The corresponding topographic and phase contrast AFM images, again, revealed that our membranes possessed a nanostructure consisting of stiff, spherical, hydrophilic domains with an average diameter of ~ 16 nm, which were encompassed by a soft, uniform hydrophobic matrix (Figure S3.5B, left and Figure S3.5C, left). The unstrained membrane’s nanoscale morphology, together with the electrical measurements above, suggested that the membrane copolymer’s hydrophilic regions formed an interconnected network, which facilitated highly effective long-range proton transport in the absence of strain. Next, representative optical microscopy images indicated that, under an intermediate applied uniaxial strain of 200%, the substrate-bound membrane remained transparent, with its surface adopting a slightly corrugated micron-scale morphology consisting of “valleys” and “hills” aligned along the direction of stretching (Figure S3.2 and Figure S3.5A, middle). The corresponding topographic and phase contrast AFM images revealed that the membrane’s nanostructure now consisted of stiff, oblong, hydrophilic domains with average lengths of ~ 43 nm and widths of ~ 15 nm, which were still encompassed by the soft, somewhat distended, hydrophobic matrix (Figure S3.5B, middle and Figure S3.5C, middle). The moderately-strained membrane’s nanoscale morphology suggested that strain induced elongation, alignment, and/or merger of the polymer’s hydrophilic regions, with this structural rearrangement presumably improving the regions’ overall connectivity and thus leading to a significant enhancement in long-range proton transport relative to the unstrained state. Last, representative optical microscopy images indicated that, after

application of an extreme uniaxial strain of 500%, the substrate-bound membrane was still transparent but that its surface’s corrugated morphology had changed, with the stretching direction-aligned “valleys” and “hills” becoming deeper and taller, respectively (Figure S3.2 and Figure S3.5A, right). The corresponding topographic and phase contrast AFM images revealed that the membrane’s nanostructure had also evolved further into a combination of spherical domains with an average diameter of ~ 17 nm and oblong domains with average lengths of ~ 80 nm and widths of ~ 8 nm, wherein both domain types remained encompassed by the further-distended hydrophobic matrix (Figure S3.5B, right and Figure S3.5C, right). The highly-strained membrane’s nanoscale morphology suggested that moving from intermediate to extreme elongation likely caused a reduction in the strain-induced connectivity of the polymer’s hydrophilic regions, resulting in long-range proton transport properties that were between those of the unstrained and moderately-strained membranes. Overall, our findings provided a compelling rationale for the evolution of our material’s protonic conductivity under extreme deformation, positioning it for integration as a high-performance electrode in dielectric elastomer actuator platforms.

3.5. Development of Mechanically- and Electrically-Actuated Adaptive Camouflage Platforms with Multispectral Functionality

After gaining an understanding of our membranes’ proton-conducting properties, we investigated the morphologies of the membrane-based tri-layer architectures necessary

for our camouflage platforms with scanning electron microscopy (SEM) and AFM (under the conditions anticipated during actuation of such systems). For these experiments, we laminated square-shaped copolymer membranes onto both sides of elastic acrylate substrates, mounted the resulting tri-layer laminate structures in an adjustable holder under tension, and then released some of the tension to introduce wrinkling to the laminate structures' surfaces (Figure 3.3A, Figure S3.6, and see the Supporting Information for details). Initially, the SEM images of the tri-layer laminates revealed that, in the absence of equiaxial strain, their surfaces consisted of a three-dimensional network of randomly-oriented wrinkles with variable micron-scale lengths (Figure 3.3A, left inset). The corresponding AFM images indicated that the surfaces possessed a root-mean-square (RMS) roughness of 564 ± 16 nm and that the wrinkles featured heights and widths on the order of ~ 1 to ~ 2 microns (Figure 3.3A, left inset). Next, the SEM images of the tri-layer laminates revealed that, in the presence of equiaxial strain, their surfaces were flattened and consisted of a two-dimensional network of irregularly-shaped micron-scale domains (Figure 3.3A, right inset). The corresponding AFM images indicated that the surfaces possessed an RMS roughness of 15 ± 1 nm and that the domains featured areas on the order of tens of microns (Figure 3.3A, right inset). Notably, the morphological changes for our systems were stable and fully reversible even after hundreds of strain cycles (Figure S3.7). These observations confirmed that the surface microstructure of the designed platforms could be controllably reconfigured with equiaxial strain, as desired for multispectral camouflage applications.

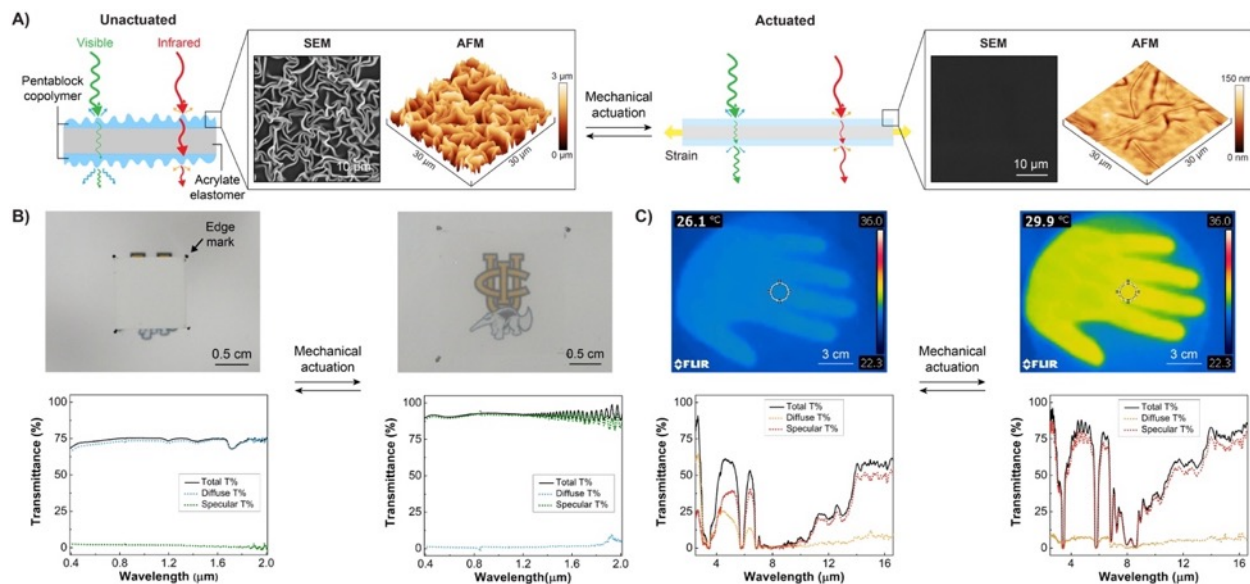


Figure 3.3. Mechanical actuation of changes in the microscale surface morphology and spectral functionality for tri-layer systems within the visible and infrared. (A) A side-view schematic of the change in spectral functionality and microscale morphology for a tri-layer system upon mechanical actuation with equiaxial strain. Representative scanning electron microscopy (SEM) and atomic force microscopy (AFM) images, which show the surface microstructure of the system before (left) and after (right) actuation, are inset. (B) (Top) Representative digital camera images of a tri-layer system above a cartoon anteater logo both before (left) and after (right) mechanical actuation. (Bottom) Representative transmittance spectra within the visible to short-wavelength infrared regions (400 nm – 2 μm) for a tri-layer system both before (left) and after (right) mechanical actuation. The total transmittances (solid black lines) are shown, along with their diffuse (dashed blue lines) and specular (dashed green lines) components. (C) (Top) Representative infrared camera images of a tri-layer system above a warm hand both before (left) and after (right) mechanical actuation. (Bottom) Representative transmittance spectra within the mid-wavelength to long-wavelength infrared regions (2.5 μm – 16.6 μm) for a tri-layer device both before (left) and after (right) mechanical actuation. The total transmittances (solid

black lines) are shown, along with their diffuse (dashed orange lines) and specular (dashed red lines) components.

We next assessed how the application of a mechanical stimulus, i.e. equiaxial strain, affected the optical appearance and spectroscopic properties of our tri-layer systems within the visible, near-infrared, and short-wavelength infrared regions of the electromagnetic spectrum. First, before mechanical actuation, the wrinkled systems possessed relatively small areas and were optically opaque, as gauged from visualization of an underlying cartoon anteater logo with a digital camera (Figure 3.3B, top left). The corresponding spectra revealed a high average total transmittance of $73.9 \pm 0.1\%$ (Figure 3B, bottom left), a moderate average total reflectance of $19.3 \pm 0.3\%$ (Figure S3.8), and a low average total absorptance of $6.8 \pm 0.4\%$ (Figure S3.8). The total transmittance consisted of a small specular (direct transmission) component of $1.2 \pm 0.3\%$ and a dominant diffuse (indirect transmission) component of $72.7 \pm 0.4\%$, in a specular-to-diffuse transmittance ratio of ~ 0.02 (Figure 3.3B, bottom left). Next, after mechanical actuation, the flattened systems possessed relatively larger areas and were far more optically transparent, as gauged from visualization of the underlying cartoon anteater logo (Figure 3.3B, top right). The corresponding spectra revealed a higher average total transmittance of $91.7 \pm 0.2\%$ (Figure 3.3B, bottom right), a lower average total reflectance of $9.3 \pm 0.2\%$ (Figure S3.8), and an almost negligible total absorptance (Figure S3.8). The total transmittance now consisted of a dominant specular component of $90.2 \pm 0.2\%$ and a small diffuse component of $1.5 \pm$

0.1%, in a specular-to-diffuse transmittance ratio of ~ 60 (Figure 3.3B, bottom right). Therefore, mechanical actuation reduced the total absorptance by over an order of magnitude and reversibly altered the specular-to-diffuse transmittance ratio by more than three orders of magnitude, presumably due to the dramatic change in the laminates' surface morphologies between the wrinkled and flattened states (Figure 3.3A). Notably, the optical appearance of our systems was insensitive to changes in the relative humidity both in the absence and presence of mechanical actuation (Figure S3.9). These findings showcased dynamic modulation of our systems' visible, near-infrared, and short-wavelength infrared transparency via mechanical means, while also highlighting their potential as multimodal adaptive camouflage platforms.

We in turn studied how the application of a mechanical stimulus, i.e. equiaxial strain, influenced the infrared appearance and spectroscopic properties of our tri-layer systems in the mid-wavelength and long-wavelength infrared regions of the electromagnetic spectrum. First, before mechanical actuation, the wrinkled systems largely blocked the infrared radiation (heat) emitted by an underlying warm hand, which featured an apparent temperature of ~ 26 °C at its center and resembled the thermal surroundings, as confirmed by visualization with an infrared camera (Figure 3.3C, top left). The corresponding infrared spectra revealed a moderate average total transmittance of $27.6 \pm 1.1\%$ (Figure 3.3C, bottom left), a low average total reflectance of $10.4 \pm 0.1\%$ (Figure S3.10), and a high average total absorptance of $61.9 \pm 1.2\%$ (Figure S3.10). The total

transmittance consisted of a large specular component of $19.9 \pm 1.0\%$ and a smaller diffuse component of $7.7 \pm 0.1\%$, in a specular-to-diffuse transmittance ratio of ~ 2.5 (Figure 3.3C, bottom left). Next, after mechanical actuation, the flattened systems blocked less of the infrared radiation emitted by the underlying warm hand, which featured an apparent temperature of $\sim 30\text{ }^{\circ}\text{C}$ at its center and stood out from the thermal surroundings, as confirmed by visualization with an infrared camera (Figure 3.3C, top right). The corresponding infrared spectra revealed a high average total transmittance of $53.5 \pm 0.6\%$ (Figure 3.3C, bottom right), a low average total reflectance of $13.4 \pm 0.2\%$ (Figure S3.10), and a moderate average total absorptance of $33.1 \pm 0.4\%$ (Figure S3.10). The total transmittance consisted of a large specular component of $48.8 \pm 0.5\%$ and a smaller diffuse component of $4.7 \pm 0.5\%$, in a specular-to-diffuse transmittance ratio of ~ 10.4 (Figure 3.3C, bottom right). Thus, mechanical actuation reversibly decreased the total absorptance by approximately two-fold, presumably due to a reduction in the laminates' effective thicknesses, and reversibly increased the specular-to-diffuse transmittance ratio by approximately four-fold, presumably due to the change in the laminates' surface morphologies from wrinkled to flattened (Figure 3.3A). Notably, the camouflage performance of our systems remained consistent even at variable distances from an underlying warm surface (Figure S3.11). These findings demonstrated dynamic modulation of our systems' mid-wavelength and long-wavelength infrared transparency

via mechanical means, further underscoring and confirming their potential as multimodal adaptive camouflage platforms.

We subsequently proceeded to leverage our proton-conducting membranes outstanding combination of electrical and mechanical properties by employing them as electrodes for electromechanical actuation of the tri-layer systems in a dielectric elastomer actuator architecture. For this purpose, we fabricated prototypical capacitor-like devices featuring circular active areas wherein the top and bottom membranes were interfaced with an external circuit (Figure 3.4A, Figure S3.12, and see the Supporting Information for details).^[57,58] For such devices, electrical actuation, i.e. the application of a voltage between the highly-conductive membranes, induced electrostatic pressure on the central elastomer layers, thereby causing their circular active areas to decrease in thickness and increase in size (Figure 3.4A).^[57,58] Here, the devices' areal strain featured an exponential dependence on the voltage and reached a maximum value of $214 \pm 11\%$ at 3.8 kV, corresponding to significant in-plane deformation (Figure 3.4B). Additionally, the devices' response time (defined as the time needed to go from 10% to 90% of the areal strain change during each cycle) remained consistent across multiple cycles of a 0.5 Hz-frequency square waveform (minima at 0 kV and maxima at ~ 3.5 kV) and was relatively fast with a value of 570 ± 80 ms (Figure 3.4C). The observed figures of merit likely resulted from the membranes' ability to maintain their conductivities at large strains. Overall, our

devices' excellent performance was comparable to that of analogous dielectric elastomer actuators.^[24,56–58]

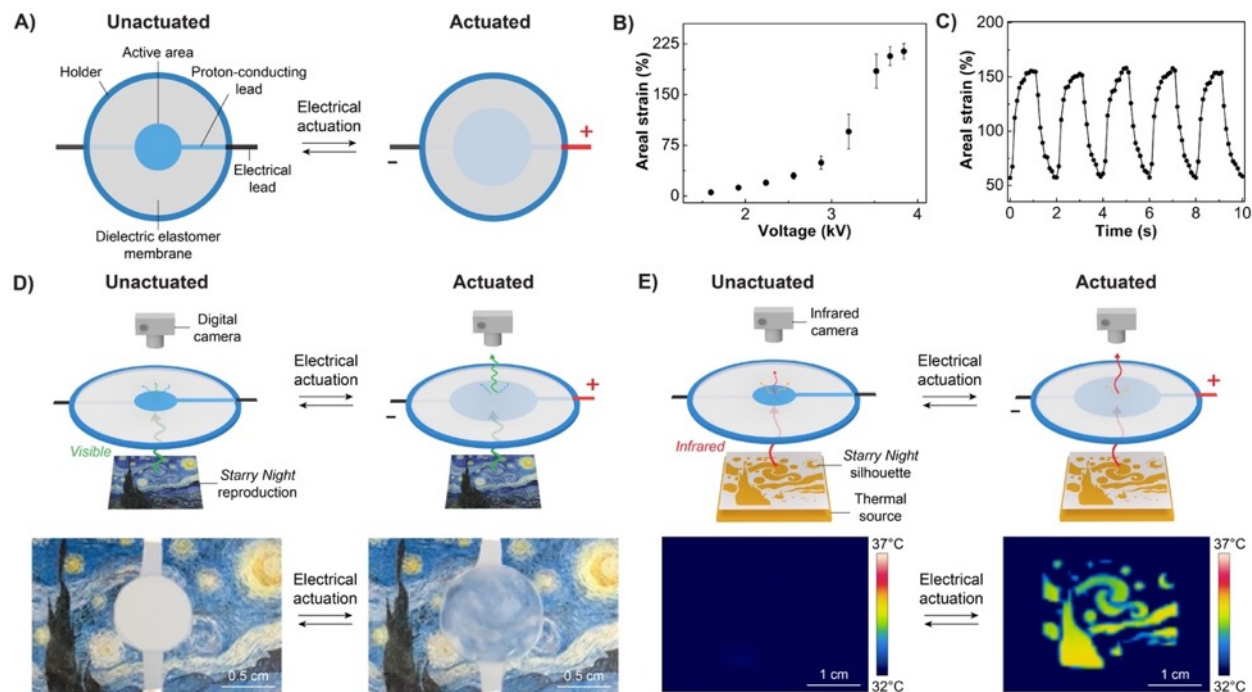


Figure 3.4. Electrical characterization and demonstration of multispectral camouflage functionality for dielectric elastomer actuators within the visible and infrared. (A) A top-view schematic of the change in the size of the active area for a tri-layer device upon electrical actuation. (B) A plot of the areal strain as a function of the applied voltage for the tri-layer devices. (C) A representative plot of the areal strain as a function of time for five consecutive cycles of a square waveform with a 0.5 Hz frequency (minima at 0 kV and maxima at ~ 3.5 kV). (D) (Top) Schematic of the digital camera visualization of a tri-layer device positioned above a reproduction of Vincent van Gogh's *Starry Night* both before (left) and after (right) electrical actuation. (Bottom) Representative digital camera images of a tri-layer device above a reproduction of Vincent van Gogh's *Starry Night* both before (left) and after (right) electrical actuation. (E) (Top) Schematic of the infrared camera visualization of a tri-layer device positioned above a silhouette of Vincent van Gogh's *Starry Night* and an underlying thermal source, both before (left) and after (right)

electrical actuation. (Bottom) Representative infrared camera images of a tri-layer device positioned above a silhouette of Vincent van Gogh’s *Starry Night* and an underlying thermal source, both before (left) and after (right) electrical actuation.

Having validated the functionality of our devices, we sought to confirm that they could manipulate the propagation of light within both the visible and infrared regions of the electromagnetic spectrum upon electromechanical actuation. Towards this end, we again applied a 0.5 Hz-frequency square waveform (minima at 0 kV and maxima at ~ 3.5 kV), with the devices’ unactuated (off) and actuated (on) states each having a duration of one second during a typical cycle. First, for experiments in the visible spectral region, we positioned the devices directly above a reproduction of Vincent van Gogh’s *Starry Night* and visualized the picture’s appearance with a standard digital camera (Figure 3.4D). Before actuation (i.e. at 0 kV), the devices possessed relatively small circular active areas and were opaque, presumably due to their minimal visible specular transmittances in the wrinkled state (Figure 3.4D, top left). The devices thus completely obscured a portion of the underlying picture (Figure 3.4D, bottom left). After actuation (i.e. at ~ 3.5 kV), the same devices possessed larger active areas and increased transparencies, presumably due to their substantially increased visible specular transmittances in the flattened state (Figure 3.4D, top right). The devices now revealed the underlying picture (Figure 3.4D, bottom right). Notably, the observed optical appearance changes could be maintained for extended durations under an applied voltage and also remained fully reversible even after repeated actuation cycles (Video S3.1). Next, for experiments in the

infrared region, we positioned the devices directly above a thermal source and an intervening silhouette of Vincent van Gogh’s *Starry Night* and then captured the silhouette’s thermal appearance with an infrared camera (Figure 3.4E). Before electrical actuation (i.e. at 0 kV), the devices possessed relatively small circular active areas and relatively increased thicknesses, blocking the infrared radiation (i.e. heat) emitted by the thermal source through the intervening silhouette, likely due to the devices’ relatively lower infrared transmittances and higher infrared absorptances in the wrinkled state (Figure 3.4E, top left). The silhouette thus effectively disappeared into its surrounding environment (Figure 3.4E, bottom left). After electrical actuation (i.e. at ~ 3.5 kV), the same devices possessed larger active areas and reduced thicknesses, transmitting some of the infrared radiation emitted by the thermal source through the intervening silhouette, likely due to the devices’ increased infrared transmittances and decreased infrared absorptances in the flattened state (Figure 3.4E, top right). The silhouette was now quite distinct and stood out from its thermal surroundings (Figure 3.4E, bottom right). The observed thermal appearance changes remained reversible after hundreds of actuation cycles, further demonstrating the stability of our devices and their constituent materials (Video S3.2 and Figure S3.13). Together with the other findings, these experiments unambiguously validated our systems as electrically-controlled adaptive camouflage platforms with functionalities that encompass an unprecedented spectral range.

3.6. Discussion and Conclusion

In summary, we have developed and characterized high-performance proton-conducting polymer membranes, and the reported findings hold significance from the perspective of deformable electrically-conductive materials. Specifically, we have fabricated optically-transparent, freestanding sulfonated pentablock copolymer membranes via straightforward processing techniques and discovered that they feature high protonic conductivities of ~ 90 mS/cm, which compare favorably to the values reported for “gold-standard” proton conductors like Nafion. These exceptional electrical characteristics originate from the membranes’ phase-segregated nanostructured morphologies, which constitute a continuous water percolation network and promote effective long-range proton transport. Excitingly, when compared to other stretchable conductors, our substrate-bound membranes not only withstand extreme strains of > 500 % while maintaining (and even improving) their bulk proton conductivities but also exhibit good electrical stabilities upon repeated mechanical cycling. Such properties result from reorganization of the membranes’ nanostructured morphologies with applied strain, which seemingly increases the efficacy of proton transport (relative to the unstrained state). Altogether, our proton-conducting polymer membranes’ feature a unique combination of optical transparency, electrical conductivity, and mechanical stability that makes them well suited for applications in adaptive camouflage devices.

By drawing inspiration from cephalopod skin and leveraging the functionality of our proton-conducting membranes, we have furthermore developed adaptive multimodal camouflage platforms, and our observations represent a substantial advance with regard to the state-of-the-art for concealment technologies. Indeed, we have prepared tri-layer systems via robust benchtop fabrication methods and demonstrated that they can alter their specular-to-diffuse transmittance ratios by more than > 3000 -fold in the visible and approximately four-fold in the infrared, affording dynamic spectral signature modulation across an unprecedented wavelength range (400 nm to 2 μm and 2.5–16.6 μm). These unique capabilities result from our cephalopod-inspired design, in which the sizes, thicknesses, and surface microstructures of our systems' active areas are reconfigured across multiple length scales by mechanical stimuli. Moreover, when actuated electromechanically, the reported camouflage devices feature exceptional figures of merit, including rapid sub-second response times and good stabilities upon repeated cycling. Such metrics are a direct consequence of our proton-conducting membranes' combined optical, electrical, and mechanical properties, which enable and underpin the devices' functionality. Altogether, our findings may facilitate the development of technologies that rely upon tandem manipulation of visible light and heat.

Moving forward, there exist multiple exciting opportunities for further improving and advancing the described adaptive multimodal camouflage systems. First, because surface wrinkling can be implemented at different length scales, we anticipate extending

the capabilities of our systems to other technologically valuable regions of the electromagnetic spectrum, e.g. the ultra-violet and terahertz bands. The added functionality could be achieved by controlling the relative sizes and spacing of the wrinkles covering the devices' active areas. Second, although our systems' exhibit similar capabilities in different environmental conditions, we expect to potentially refine their performance via implementation of protective packaging solutions. However, any packaging design would need to simultaneously meet multiple challenging criteria, including moisture impermeability, transparency within multiple spectral regions, and mechanical pliability and stretchability. Third, given our demonstration of two complementary actuation strategies, we envision optimizing our systems' configurations for different specific target applications. For instance, electrically-actuated large-area variants of our devices would be appropriate for situations requiring minimal steady state power consumption, e.g. buildings and vehicles, whereas mechanically-actuated non-planar variants of our devices would be appropriate for situations where large voltages are not desirable, e.g. clothing or skin-interfaced iontronics. Last, to broaden the applications scope for our systems, we will certainly need to reduce the high operating voltages associated with their electromechanical actuation, which remain a notorious problem for dielectric elastomer actuator-type platforms. Such voltage reduction can be achieved by modifying the central dielectric elastomer layer's properties, e.g. thickness, dielectric constant, or Young's modulus, as well as by selecting an entirely different dielectric elastomer material, e.g. polysiloxane or polyurethane. In general, through continued

development, our systems may facilitate and enable a variety of other emerging technologies, such as electronic/ionic circuits, soft robotics, human-machine interfaces, conformable bioelectronics, flexible optoelectronics, and energy-conserving building installations.

3.7. Supporting Information

3.7.1. Fabrication of freestanding sulfonated pentablock copolymer membranes

The freestanding membranes were prepared according to reported procedures. First, a dilute solution ($\sim 5\%$ by weight in a mixed solvent of cyclohexane, heptane, A150, and VM&P Naphtha) of a commercially available sulfonated pentablock copolymer (NEXARTM, Kraton Polymers LLC) was spincoated onto a silicon substrate. Next, the coated substrate was annealed at a temperature of ~ 60 °C to remove any residual solvent. In turn, the copolymer was delaminated from the silicon substrate as a freestanding membrane. The membranes prepared in this fashion were used for all electrical, optical, and physical characterization experiments, as well as for the fabrication of multi-layer devices.

3.7.2. Preparation of two-terminal devices from free-standing sulfonated pentablock copolymer membranes

The devices from the freestanding copolymer membranes (Figure 3.2A) were prepared according to standard lithographic protocols. First, a rigid, insulating support frame featuring a central square opening (dimensions of $1\text{ cm} \times 1\text{ cm}$) was fabricated from a plexiglass acrylic sheet by using an Epilog Fusion laser cutter. Next, two electrodes consisting of a $\sim 4\text{ nm}$ chromium (Cr) layer overlaid with a $\sim 40\text{ nm}$ gold (Au) layer were deposited through a shadow mask onto opposite sides of the rigid substrate by using an Angstrom Engineering EvoVac Glovebox Evaporator. In turn, the as-prepared sulfonated

pentablock copolymer membrane was laminated onto the support housing, in which it bridged the two opposing Au/Cr electrodes and was suspended in air. Subsequently, the electrodes were connected to external copper leads as electrical contacts. The resulting devices were used for all relevant electrical characterization experiments.

3.7.3. Preparation of two-terminal devices from substrate-bound sulfonated pentablock copolymer membranes

The devices from the substrate-bound copolymer membranes (Figure 3.2E) were prepared according to standard lithographic protocols. Initially, an as-prepared sulfonated pentablock copolymer membrane was laminated onto an acrylate elastomer (VHB 4905, 3M) as the elastic substrate. The substrate-bound copolymer membrane was then transferred to a customized holder designed for the application of uniaxial strain, wherein the membrane was suspended in air between the holder's opposite sides. In tandem, two separate acrylic blocks were fabricated from a plexiglass acrylic sheet by using an Epilog Fusion laser cutter. An electrode consisting of a ~ 4 nm Cr layer overlaid with a ~ 40 nm Au layer was deposited through a shadow mask onto both of the blocks by using an Angstrom Engineering EvoVac Glovebox Evaporator. Subsequently, the electrode-modified blocks were mounted onto the substrate-bound copolymer membrane and modified with external copper leads as electrical contacts. Note that the electrode blocks were designed for easy attachment/detachment, making it possible to measure the dimensions of the membranes' central rectangular regions under different strains and to

maintain a constant electrode separation during the measurements. The resulting devices facilitated reliable electrical characterization at various strains.

3.7.4. Preparation of tri-layer device architectures from the sulfonated pentablock copolymer and acrylate elastomer

The tri-layer structures were fabricated according to established procedures (Figure S3.6 and Figure S3.11). First, as the central device layer, an acrylate elastomer (VHB 4905, 3M) was mounted and equiaxially stretched by $\sim 1,600\%$ (relative to its initial area) on a home-built size-adjustable holder. Next, as the top and bottom layers, either two square (dimensions of ~ 3.6 cm by ~ 3.6 cm for mechanical actuation) or two circular (radius of ~ 1 cm for electrical actuation) sections of the as-prepared sulfonated pentablock copolymer membrane were laminated onto both sides of the acrylate elastomer central layer. For the mechanical actuation experiments, the partially-completed device was mechanically contracted by $\sim 40\%$ with respect to the initial length of the optically-active square region. For the electrical actuation experiments, the partially-completed device was modified with additional stripe-shaped copolymer membranes as electrical leads, prior to mechanical contraction by $\sim 40\%$ with respect to the diameter of the optically active circular region. To enable electrical actuation, the proton-conducting electrical leads were interfaced with an external electronic circuit and power supply via lamination of thin strips of an electron-conducting aluminum foil directly onto the polymer membrane (note that the leads and foil were kept as smooth as possible during integration). Note that

contraction of the devices by the aforementioned value of 40 % was found to generally afford optimal multispectral modulation, electromechanical performance, and camouflage functionality. The resulting completed devices were used for the relevant physical, mechanical, electrical, optical, and/or infrared characterization experiments as required.

3.7.5. Electrical characterization of two-terminal devices from free-standing and substrate-bound sulfonated pentablock copolymer membranes

The two-terminal devices from either the free-standing or substrate-bound copolymer membranes were characterized with electrochemical impedance spectroscopy (EIS) by using a Gamry Reference 600+ potentiostat. The response of the devices to a sinusoidal perturbation with an amplitude of 500 mV was recorded over a frequency range of 3 MHz to 0.5 Hz. The measurements were performed within an enclosed chamber in the presence of water or deuterium oxide vapor at room temperature ($\sim 22\text{ }^{\circ}\text{C}$). The relative humidity was stabilized at the desired level between 50 % and 90%, as noted, and was continuously monitored with a hygrometer during all measurements. The experiments corresponding to Figure 3.2B and 3.2C were performed for at least 5 independent devices, the experiments corresponding to Figure 3.2D were performed for at least 3 independent devices, the experiments corresponding to Figure 3.2F and 3.2G were performed for at least 9 independent devices, and the experiments corresponding to Figure S3.3 were performed for at least 3 independent devices. The resulting data was analyzed and plotted with the Gamry Echem Analyst and Origin Pro software packages.

3.7.6. Calculation of the protonic conductivity

The obtained Nyquist plots from the EIS measurements were simplified to an equivalent circuit, in which a resistor and a capacitor were connected in parallel with a diffusion-controlled element. The in-plane protonic conductivity of the pentablock copolymer membranes was calculated according to the equation:

$$\text{Proton conductivity (mS/cm)} = \frac{l}{R_b \cdot (wt)}$$

where l is the distance between the electrodes, w is the width of the copolymer membrane, t is the thickness of the copolymer membrane, and R_b is the measured bulk resistance extracted from the simplified equivalent circuit.

3.7.7. Mechanical actuation of tri-layer structures from the sulfonated pentablock copolymer and acrylate elastomer

The tri-layer structures were mechanically actuated in a home-built size-adjustable holder, which was used to apply/release equiaxial mechanical strain to/from the devices. During mechanical actuation of the devices, the lengths of their optically-active square regions were increased by $\sim 67\%$ for actuation and then contracted by $\sim 40\%$ to return to the initial position. The mechanical actuation was performed at a relative humidity of $\sim 50\%$ under ambient conditions, unless otherwise noted. The relevant experiments shown in Figure 3.3B and 3.3C were all repeated for at least 3 independent systems.

3.7.8. Physical characterization of the substrate-bound copolymer membranes and tri-layer structures both without and with mechanical actuation

The nanoscale and microscale morphologies of the membranes and devices were characterized with atomic force microscopy (AFM), optical microscopy, and scanning electron microscopy (SEM). The height, and phase images were obtained with an Asylum Cypher ES atomic force microscope that was equipped with an environmental chamber. When necessary, the relative humidity was controlled with saturated salt solutions, e.g. sodium chloride (NaCl) and magnesium sulfate (MgSO_4) and continuously monitored with a built-in sensor inside the environmental chamber. The optical microscopy images were obtained with the Asylum Cypher ES system's integrated optical microscope. The surface microstructure images were obtained with an FEI Quanta 3D FEG scanning electron microscope. The AFM data was analyzed with the Gwyddion software package.

3.7.9. Electrical actuation of tri-layer devices from the sulfonated pentablock copolymer and acrylate elastomer

The tri-layer structures were electrically actuated in a size-adjustable support frame. For all experiments, the devices were connected to a home-built high-voltage power supply consisting of a Stanford Research DS345 function generator, a Texas Instruments OPA 548 operational amplifier, and an EMCO E80 high-voltage amplifier. The areal strain obtained during electrical actuation with different voltages was recorded and calculated according to the equation:

$$Areal\ strain\ (\%) = [(A_1 - A_0)/A_0] \times 100\%$$

where A_0 is the area before actuation and A_1 is the area after actuation. The device response time (t_{res}) observed during electrical actuation was calculated according to the equation:

$$t_{res} = t_{90\%} - t_{10\%}$$

where $t_{90\%}$ is the rise time to reach 90% of the maximum change in area during one typical actuation cycle and $t_{10\%}$ is the rise time to reach 10% of the maximum change in area during one typical actuation cycle. The electrical actuation was performed at a relative humidity of $\sim 50\%$ under ambient conditions, unless otherwise noted. The relevant experiments shown in Figure 3.4B and 3.4C were all repeated for at least 3 independent systems.

3.7.10. Digital and infrared camera imaging of the tri-layer structures under mechanical or electrical actuation

The tri-layer structures were imaged during both mechanical and electrical actuation experiments. For digital imaging, the devices were positioned above specific visible objects, such as a cartoon anteater logo or a reproduction of Vincent van Gogh's *Starry Night*. The pictures and videos of the devices were then recorded both without and with actuation by using a Canon PowerShot SX520 HS digital camera. For infrared imaging, the devices were positioned at distances between 1 cm and 25 cm above objects with specific temperatures, such as a human hand, a bare warm surface, or a warm surface

partially obscured by an intervening piece of paper patterned with a silhouette. The devices were not in direct contact with the hand or warm surfaces, in order to minimize thermal crosstalk/interference, and were visualized under conditions relevant for camouflage applications. The pictures and videos of the devices were then recorded with a FLIR C2 infrared camera featuring a built-in rainbow color palette for the temperature and an effective spectral range between wavelengths of 7.5 μm to 14 μm . The infrared videos were captured through live streaming to a computer with the FLIR Plus software package. The obtained images and videos were processed and analyzed with the QuickTime Player, MATLAB, and FLIR Tool Plus software packages. The imaging was performed at a relative humidity of $\sim 50\%$ under ambient conditions, unless otherwise noted. The relevant experiments shown in Figure 3.3B and 3.3C; Figure 3.4D and 3.4E; Figure S3.11; Video S3.1; and Video S3.2 were all repeated for at least 3 independent systems.

3.7.11. Visible and infrared spectroscopic characterization of the tri-layer structures both without and with mechanical actuation

The tri-layer structures were spectroscopically characterized both without and with mechanical actuation. To obtain the total transmittance, diffuse transmittance, total reflectance, and diffuse reflectance in the infrared region of the electromagnetic spectrum, the devices were characterized with a Perkin Elmer Frontier Fourier Transform Infrared Spectrometer that was equipped with a PIKE Technologies Mid-Infrared integrating

sphere, which features a circular sample port with a ~ 2.1 cm diameter. The devices' optically active regions in both their unactuated and actuated states were sufficiently large to cover the sample port. The measurements were performed at an incidence angle of 12° and were referenced to a Pike Technologies diffuse gold standard as appropriate. To obtain the total transmittance, diffuse transmittance, total reflectance, and diffuse reflectance in the visible region of the electromagnetic spectrum, the devices were characterized with a Jasco V670 UV-Vis-NIR Spectrometer that was equipped with a Jasco ILN-925 150 mm integrating sphere, which features a rectangular-shaped sample port with a ~ 0.9 cm length and a ~ 1.3 cm width in transmission mode and a square-shaped sample port with a ~ 1.6 cm length in reflection mode. The devices' optically active regions in both their unactuated and actuated states were sufficiently large to cover the sample ports. The measurements were performed at normal incidence in transmission mode or at an incidence angle of 5° in reflection mode and were referenced to Jasco Spectralon standards as appropriate. The specular transmittance was calculated according to the equation:

$$\text{Specular Transmittance (\%)} + \text{Diffuse Transmittance (\%)} = \text{Total Transmittance (\%)}$$

The specular reflectance was calculated according to the equation

$$\text{Specular Reflectance (\%)} + \text{Diffuse Reflectance (\%)} = \text{Total Reflectance (\%)}$$

The absorptance was calculated according to the equation:

$$\text{Total Transmittance (\%)} + \text{Total Reflectance (\%)} + \text{Total Absorptance (\%)} = 100\%$$

The emissivity (ε) can be calculated according to Kirchhoff's Law:

$$\varepsilon = a = 1 - \varrho - \tau$$

where ϱ is the reflectivity, τ is the transmissivity, and a is the absorptivity.^[25] Thus, for our systems, the emissivity can be approximated from the absorptance spectra shown in Figure S3.8 and Figure S3.10. The spectroscopic characterization was performed at a relative humidity of ~ 50 % under ambient conditions, unless otherwise noted. The relevant experiments shown in Figure 3.3B and 3.3C; Figure S3.8; and Figure S3.10 were all repeated for at least 3 independent systems. The obtained spectra were processed and analyzed with the Perkin Elmer Spectrum, Jasco Spectra ManagerTM Suite, and Origin Pro software packages.

3.7.12. Supporting Information Figures and Tables

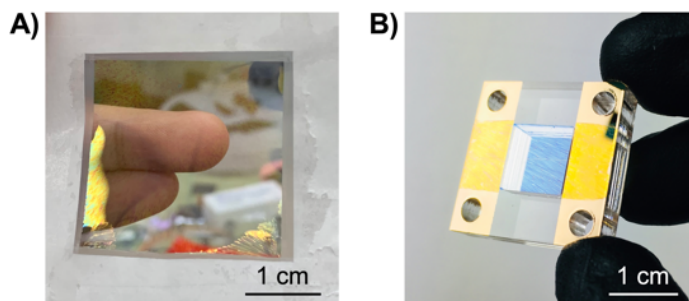


Figure S3.1. (A) Digital camera images of a thin freestanding sulfonated pentablock copolymer membrane (square window) within a flexible frame. Note the optical transparency of the membrane, which affords clear visualization of the background. (B) Digital camera image of a representative two-terminal device wherein a thin freestanding membrane bridges two gold electrodes. Note that the blue tint of the freestanding membrane is due to thin film interference, as observed at a specific viewing angle.

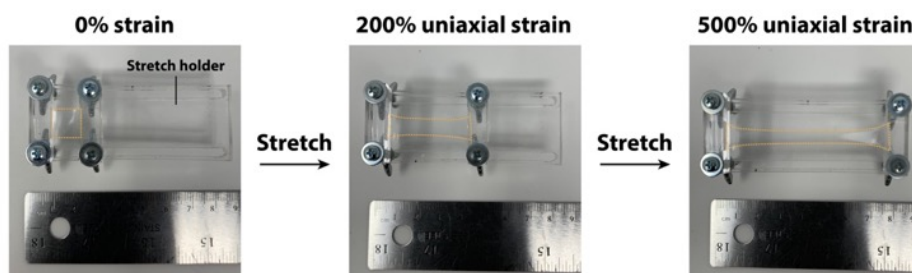


Figure S3.2. Digital camera images of a substrate-bound sulfonated pentablock copolymer membrane in an adjustable holder at uniaxial strains of 0% (left), 200% (middle), and 500% (right). Note that the membrane has been marked with a dotted orange outline for clarity.

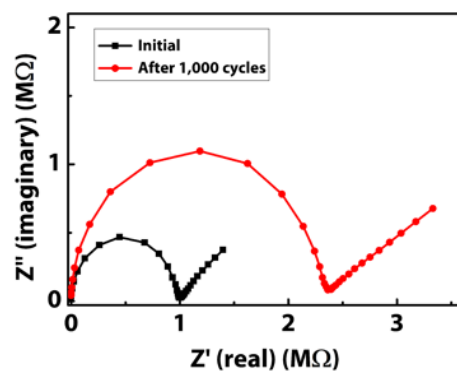


Figure S3.3. Nyquist plots for a representative acrylate substrate-bound pentablock copolymer membrane before the application of strain (black squares) and after the application of 1,000 consecutive load/unload cycles at a strain of 200% (red circles).

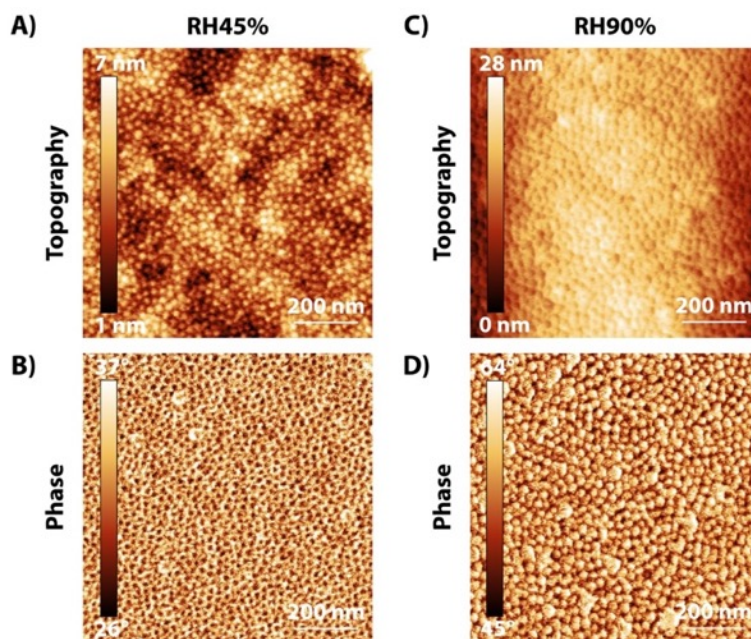


Figure S3.4. (A) Representative topographical AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 45\%$. (B) Representative phase contrast AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 45\%$. (C) Representative topographical AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 90\%$. (D) Representative phase contrast AFM image, which shows the membranes' nanoscale surface morphology, at a low relative humidity of $\sim 90\%$.

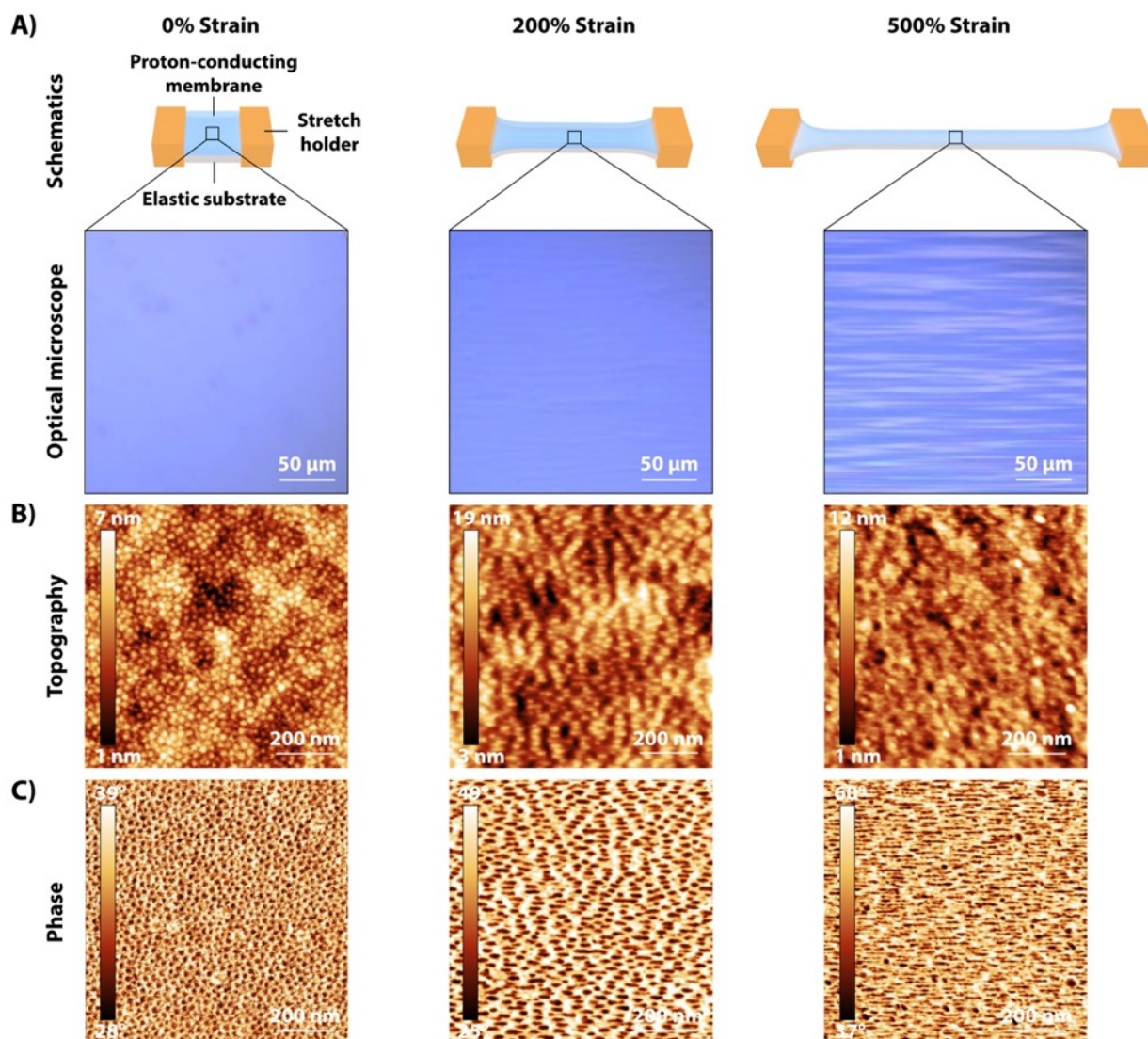


Figure S3.5. (A) A schematic of the change in geometry of an elastic acrylate substrate-bound pentablock copolymer membrane upon the application of uniaxial strain. Representative optical microscopy images, which show the membranes' surface microstructure, at uniaxial strains of 0% (left), 200% (middle), and 500% (right), are inset. (B) Representative topographical atomic force microscopy (AFM) images, which show the membranes' nanoscale surface morphology, at uniaxial strains of 0% (left), 200% (middle), and 500% (right). (C) Representative phase AFM images, which show the membranes' nanoscale phase contrast, at uniaxial strains of 0% (left), 200% (middle), and 500% (right), are inset.

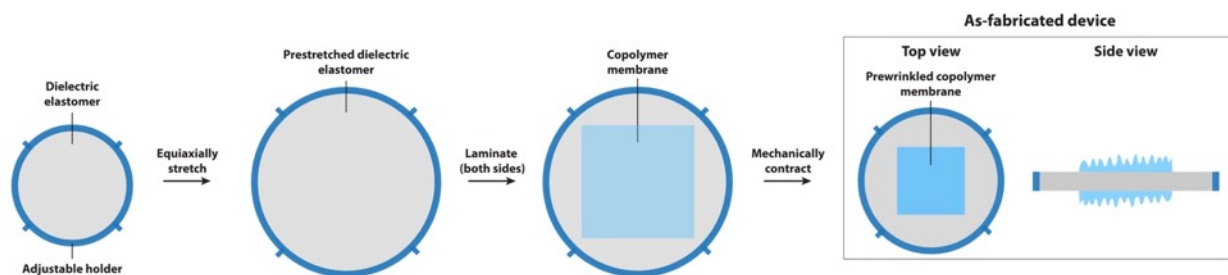


Figure S3.6. Scheme for the fabrication of a mechanically-actuated tri-layer system within a size-adjustable holder.

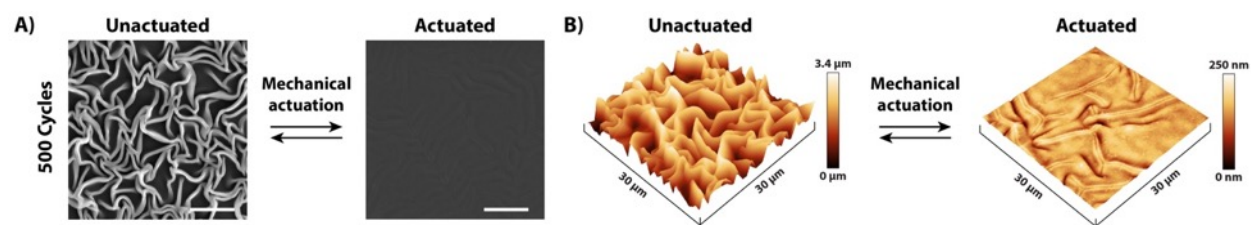


Figure S3.7. (A) Representative scanning electron microscopy (SEM) images of the surface morphology of the tri-layer systems before (left) and after (right) the 500th mechanical actuation cycle. The scale bar is 10 μm for the SEM images. (B) Representative atomic force microscopy (AFM) images of the surface morphology of the tri-layer systems before (left) and after (right) the 500th mechanical actuation cycle.

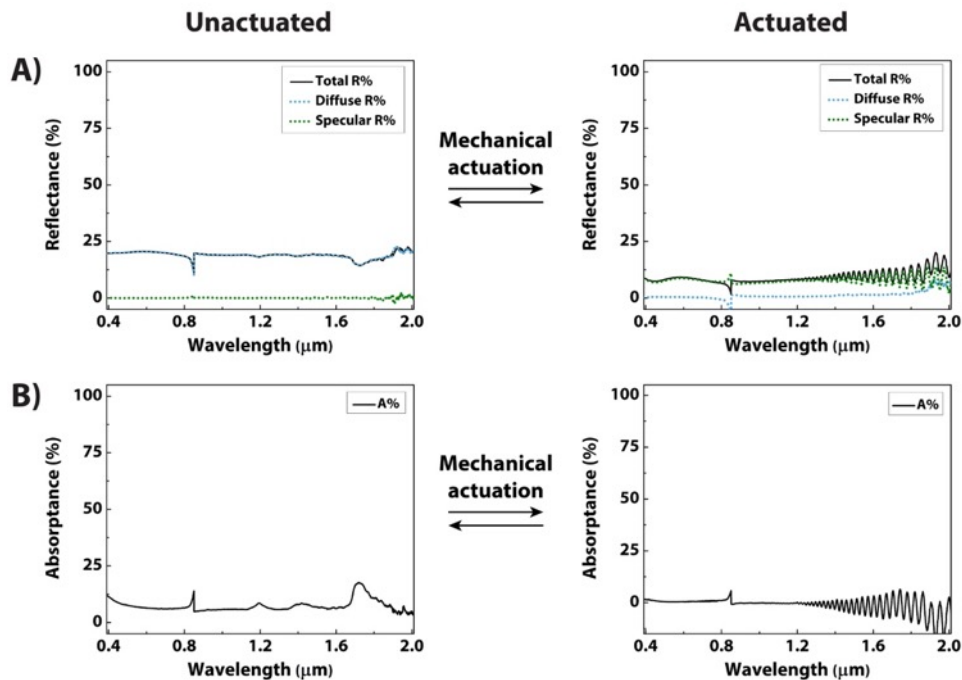


Figure S3.8. (A) Representative reflectance spectra within the visible to short-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation. The total reflectances (solid black lines) are shown, along with their diffuse (dashed blue lines) and specular (dashed green lines) components. (B) Representative absorbance spectra within the visible to short-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation.

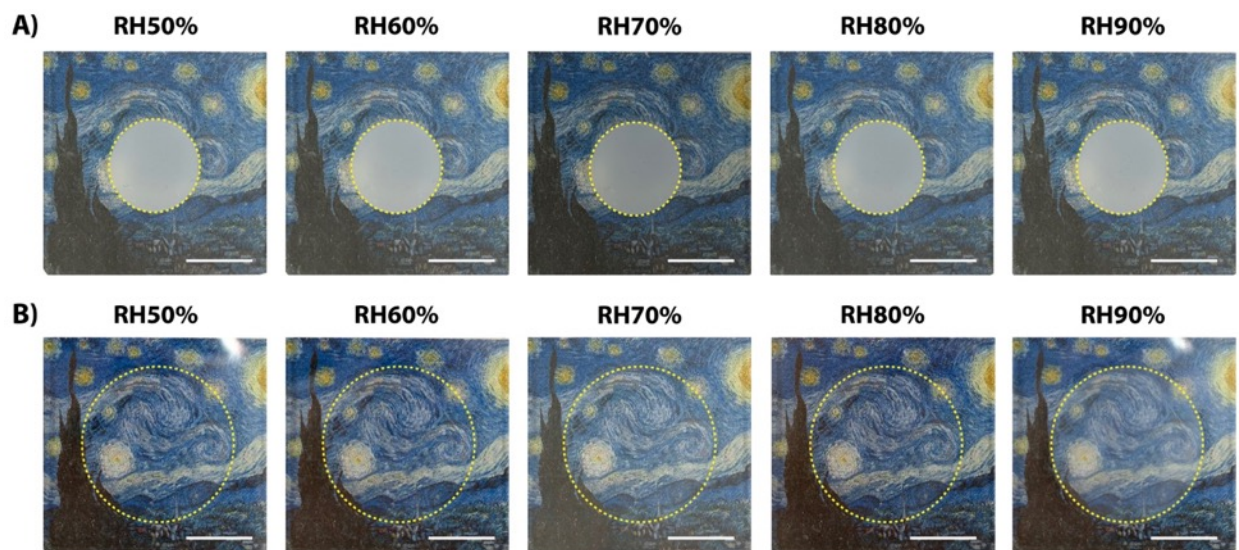


Figure S3.9. (A) Optical camera images of a representative tri-layer system at different relative humidities before mechanical actuation. (B) Optical camera images of a representative tri-layer system at different relative humidities after mechanical actuation. Note that the active areas have been marked with dotted yellow outlines for clarity.

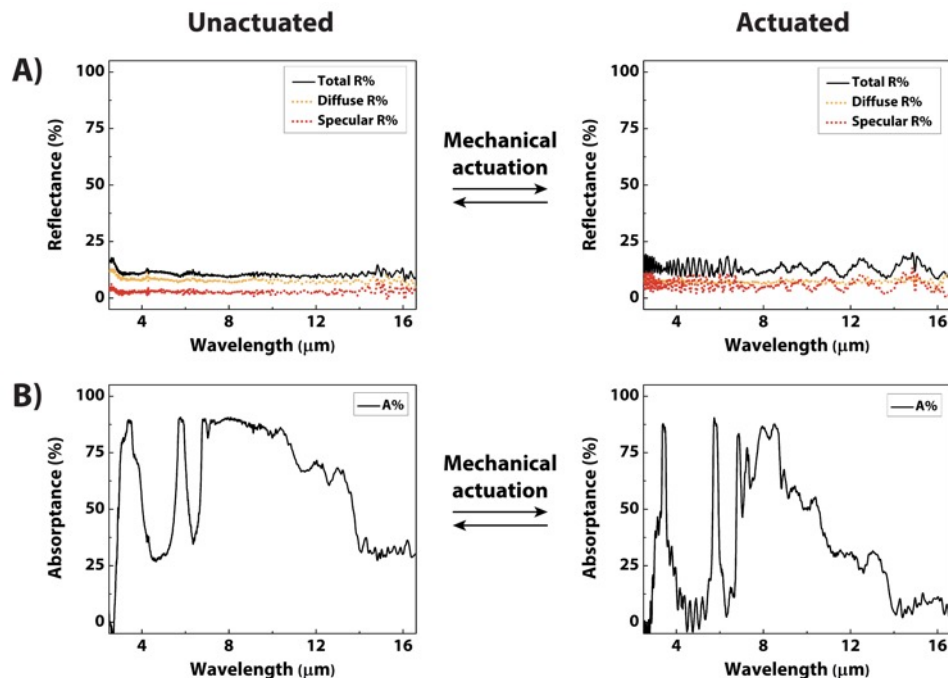


Figure S3.10. (A) Representative reflectance spectra within the mid-wavelength to long-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation. The total reflectances (solid black lines) are shown, along with their diffuse (dashed orange lines) and specular (dashed red lines) components. (B) Representative absorbance spectra within the mid-wavelength to long-wavelength infrared regions for a tri-layer system both before (left) and after (right) mechanical actuation.

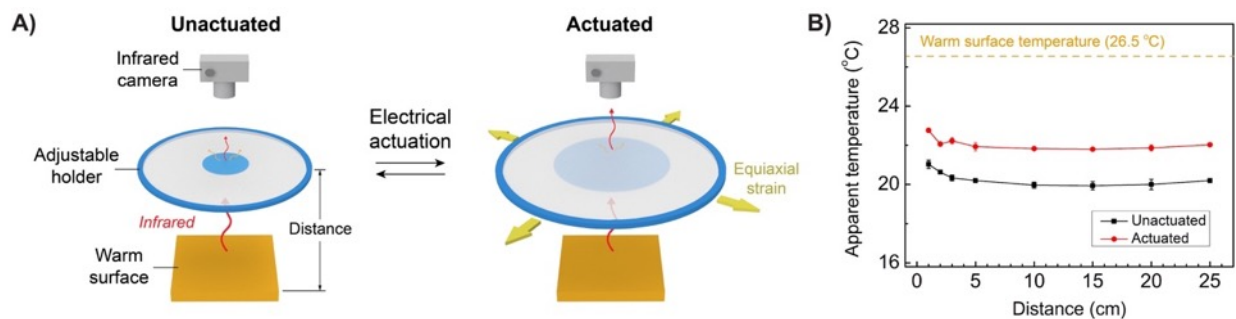


Figure S3.11. (A) Schematic of the infrared camera visualization of a tri-layer device positioned above a warm surface, both before (left) and after (right) mechanical actuation. (B) Plot of the apparent temperatures measured for the central region of a device, both before (black squares) and after (red dots) mechanical actuation, as a function of the device's distance from a warm surface. The dashed orange line indicates the constant temperature of the surface, i.e. 26.5 °C. Note that the distance was varied between 1 cm and 25 cm.

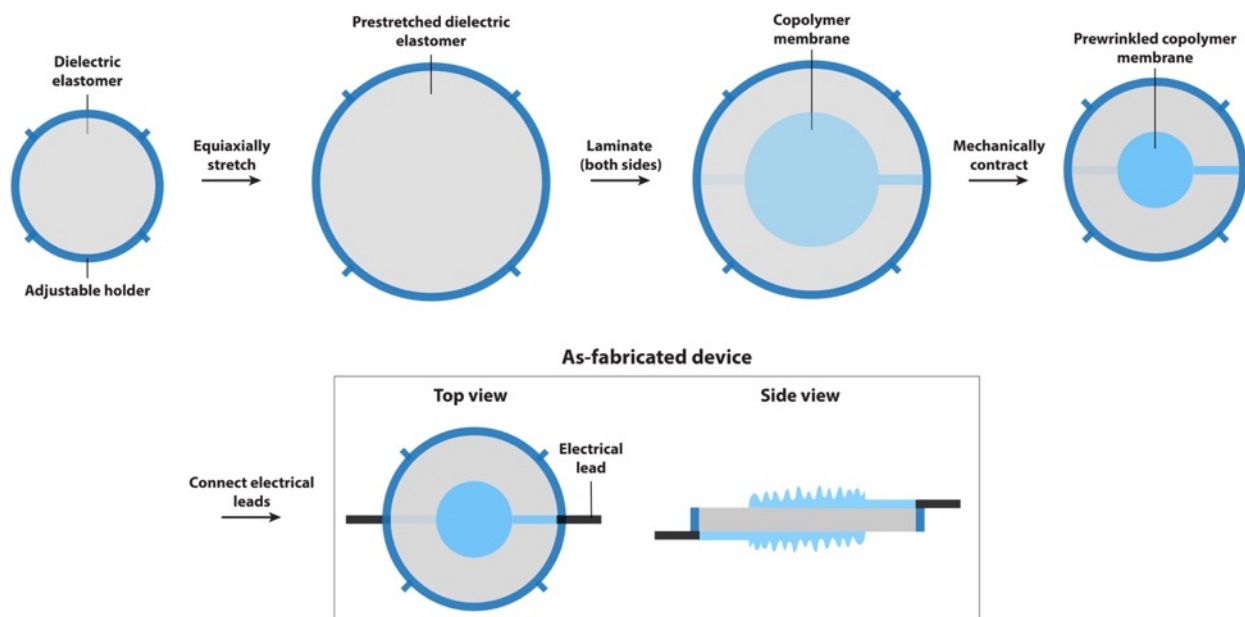


Figure S3.12. Scheme for the fabrication of an electrically-actuated tri-layer device within a size-adjustable holder.

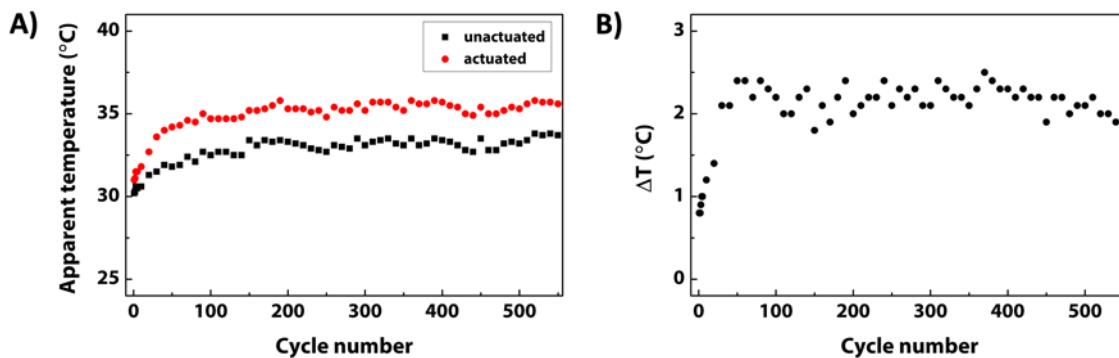


Figure S3.13. (A) Plot of the apparent temperatures for the central region of a device in the unactuated (black squares) and actuated (red dots) states as a function of the total number of actuation cycles. The devices were actuated by means of 0.5 Hz-frequency square waveform, for which the minima at 0 kV and the maxima at 3.5 kV correlated with the devices' unactuated (off) and actuated (on) states, respectively. The device was positioned above a warm surface, and the apparent temperature was measured in the same spot for each off/on actuation cycle. (B) The difference in apparent temperature between the unactuated and actuated devices as a function of the total number of off/on actuation cycles.

Table S3.1. A summary of the representative state-of-the-art materials and systems with multispectral adaptive functionality.

Major category	Representative material system	Actuation strategy	Type of spectral modulation	Spectral range	Reference
Phase-change materials	Gold triangle arrays embedded in vanadium dioxide thin films on gold substrates	Change in temperature	Absorption	400 nm – 1.6 μm	17
	Vanadium dioxide films on fused silica substrates	Change in temperature	Transmission	240 nm – 2.6 μm	18
	Vanadium dioxide films on sapphire substrates	Change in temperature	Emissivity	7 μm – 16.7 μm	19
	PANIPAm hydrogels on silver nanowire-based electrical heaters	Change in temperature	Transmission	250 nm – 2.5 μm	20
Electrochromic devices	Dimethyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-ME2)/poly[3,6-bis(2-(3,4-ethyl-enedioxy)thienyl)-N-methylcarbazole (PBEDOT-NMeCz)-based devices	Electrochemical	Reflection	400 nm – 5 μm	21
	Polyaniline (PANI)/poly(diphenyl amine) (PDPA)-based devices	Electrochemical	Reflection	330 nm – 20 μm	22
	Tin-doped indium oxide (ITO)/niobium oxide (NbO_x) nanocomposite-based devices	Electrochemical	Transmission	400 nm – 2.2 μm	23
Infrared-reflecting materials	Reconfigurable aluminum films on elastomer substrates	Mechanical and electrical	Reflection/absorption	3 μm – 15 μm (visible range not specified)	24
	Nanostructured copper films on elastomer substrates	Mechanical	Transmission/reflection	4 μm – 16.5 μm (visible range not specified)	25
Robotic systems	Microfluidic channel-embedded soft machines	Fluidic and pneumatic	Appearance	Visible/thermal infrared (ranges not specified)	9
<i>Our soft and stretchable platforms</i>	<i>Dielectric elastomer-based devices with reconfigurable surface morphologies</i>	<i>Mechanical and electrical</i>	<i>Transmission/absorption</i>	<i>400 nm – 16.5 μm</i>	<i>This work</i>

Table S3.2. A comparison of the proton conductivity of our freestanding pentablock copolymer membrane with representative state-of-the-art proton-conducting materials that were characterized under similar conditions.

Category	Name	Proton conductivity (mS/cm)	Relative humidity (%)	Temperature (°C)	Reference
<i>Freestanding pentablock copolymer membranes</i>	<i>Sulfonated Kraton (SK) (~ 250 nm in thickness)</i>	<i>87.0 ± 6.1</i>	<i>90</i>	<i>22</i>	<i>This work</i>
Hydrogen-bonded organic frameworks (HOFs)	HOF-GS10	7.5	95	30	71
	HOF-GS11	18	95	30	71
	HOF-6A	0.0034	97	27	72
Crystalline porous organic salts (CPOS)	CPOS-1	10	98	30	73
	CPOS-2	22	98	30	73
Metal-organic frameworks (MOFs)	PCMOF21/2(Tz)	117	90	85	74
	UiO-66(SO ₃ H) ₂	84	90	80	75
	PCMOF10	35.5	95	70	76
Covalent organic frameworks (COFs)	H ₃ PO ₄ -doped Tp-Azo	0.99	98	60	77
	EBCOF:PW ₁₂	3.32	97	25	78
	1S	77.2	90	80	79
Graphene oxide (GO)	GO nanosheet	15	95	87	80
	Multilayered GO sheet (200 nm)	0.4	60	25	81
	GO papers (18 µm)	2	60	25	82
Inorganic Phosphates	Zirconium phosphate gel	~ 10	50	40	83
	Calcium phosphate gel	~ 20	70	30	84
	P ₂ O ₅ /SiO ₂ glass	22	70	50	85
Solid polymer electrolytes	Nafion 117	90	100	20	61
	Nafion 117	1.4	40	31	62
	SPEKK	60	98	25	86
	PSU-sb	10	98	70	87
	SK (50 wt% n-propanol) (casted thick film)	0.02	52 ± 3%	25	65
Biomolecules	Reflectin A1(squid protein)	0.1	90	25	88
	Eumelanin (natural pigment)	0.71	90	RT	89
	AoL jelly (shark biopolymers)	1.8	90	RT	90

3.7.13. Supporting Information Videos

Video S3.1. A real-time digital camera video of a tri-layer system subjected to a square waveform (minima at 0 kV and maxima at 3.5 kV) with a 0.5 Hz frequency. During the course of the video, the system undergoes multiple sequential off/on cycles, with each cycle having a total duration of 2 seconds. The video was obtained after the system had already undergone ~ 200 actuation cycles.

Video S3.2. A real-time infrared camera video of a tri-layer system subjected to a square waveform (minima at 0 kV and maxima at 3.5 kV) with a 0.5 Hz frequency. During the course of the video, the system undergoes multiple sequential off/on cycles, with each cycle having a total duration of 2 seconds. The video was obtained after the system had already undergone ~ 200 actuation cycles.

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CHAPTER 4

Adaptive Infrared-Reflecting Systems Inspired by Cephalopods

Contents

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4.1. Abstract

Materials and systems that statically reflect radiation in the infrared region of the electromagnetic spectrum underpin the performance of many entrenched technologies, including building insulation, energy-conserving windows, spacecraft components, electronics shielding, container packaging, protective clothing, and camouflage platforms. The development of their adaptive variants, where the infrared-reflecting properties dynamically change in response to external stimuli, has emerged as an important unmet scientific challenge. By drawing inspiration from cephalopod skin, we develop adaptive infrared-reflecting platforms that feature a simple actuation mechanism, low working temperature, tunable spectral range, weak angular dependence, fast response, stability to repeated cycling, amenability to patterning and multiplexing, autonomous operation, robust mechanical properties, and straightforward manufacturability. Our findings may open opportunities for infrared camouflage and other technologies that regulate infrared radiation.

4.2. Introduction

Materials and systems that statically reflect radiation in the short- to long-wavelength infrared region of the electromagnetic spectrum have been studied for decades and critically underpin the performance of many entrenched technologies, including building insulation,^[1] energy-conserving windows,^[2] spacecraft components,^[3] electronics shielding,^[4] container packaging,^[5] protective clothing,^[6] and camouflage platforms.^[7] One highly desirable but not easily attainable property for infrared-reflecting materials (and related technologies) is on-demand adaptability, i.e. precise and sensitive real-time dynamic responsiveness to changes in the surrounding environment. To date, only a limited number of adaptive infrared systems, e.g. infrared camouflage platforms, have been reported because they must satisfy stringent and demanding technical performance criteria, making the development of these technologies extremely challenging (a comparative overview for adaptive camouflage is provided in Table S4.1). For example, thermochromic materials can display substantial infrared emissivity changes due to thermally-induced phase transitions but feature high operating temperatures, hysteresis during cycling, and structural characteristics that are difficult to control.^[8–12] In addition, infrared electrochromic devices have optical properties that can be altered with electrochemical redox reactions but struggle with precise spectral tunability and necessitate the use of inert noble metals in order to achieve functionality and stability.^{[13–}
^{16]} Moreover, certain metamaterial-based systems can spatiotemporally modulate their emissivity through photogenerated carrier doping but use ultraviolet light for actuation,

need elevated working temperatures for adequate contrast, and display long recovery times.^[17] Furthermore, thermal cloaking platforms modify the infrared signatures of other objects by manipulating the heat flow in the surroundings but require large temperature gradients and demand complete object immersion, restricting implementation.^[18,19] Last, soft robots with integrated microfluidics can alter their thermal appearance and infrared patterning via the pneumatic injection of heated or cooled liquids but rely on the continuous flow of multiple liquids maintained at different temperatures and have slow response times dictated by their thermal conductivities.^[20] Consequently, in order to enable a broad range of practical applications (such as camouflage), the “ideal” adaptive infrared-reflecting system would simultaneously possess a simple actuation mechanism, low working temperature, tunable spectral range, weak angular dependence, fast response, stability to repeated cycling, amenability to patterning and multiplexing, autonomous operation, robust mechanical properties, and straightforward manufacturability (see Table S4.1).

4.3. Biomimetic system design

As an active color-changing system, the skin of coleoid cephalopods (e.g. squid, octopuses, and cuttlefishes) represents an exciting source of inspiration.^[21–23] The patterning and coloration of cephalopod skin can be altered autonomously and repeatedly for the purposes of concealment or signaling, as illustrated for the squid in Figure 4.1A. Such remarkable feats of camouflage are enabled by the sophisticated architecture of the

squid’s soft and flexible skin, in which innervated dermal layers contain chromatophore pigment cells (as part of larger chromatophore organs) and reflective cells called iridocytes (Figure 4.1B).^[21,24,25] These two cell types operate in tandem but perform distinct optical functions (adaptive chromatophores are present in many cephalopods, but adaptive iridocytes have only been identified in a few squid species to date).^[21,24–27] The adaptive chromatophore pigment cells contain pigment granule-packed internal sacculi, which are expanded and contracted through the mechanical action of radial muscle cells (Figure 4.1C). These yellow, red, and brown cells feature response times of hundreds of milliseconds and function like size-variable biological spectral filters that absorb and reflect visible light of specific wavelengths.^[21,26] The adaptive iridocytes contain alternating arrangements of membrane-enclosed nanostructured protein layers and extracellular space, for which the geometries and refractive index differences are altered via a biochemical signaling cascade (Figure 4.1D). These iridescent cells feature response times of tens of seconds and function like reconfigurable biological Bragg stacks that reflect visible light of variable wavelengths.^[21,27] In part because of the properties of these cells, the skin of squid (and by extension, other cephalopods) behaves as a dynamic bioelectronic display, with the functionality summarized in Table S4.1.

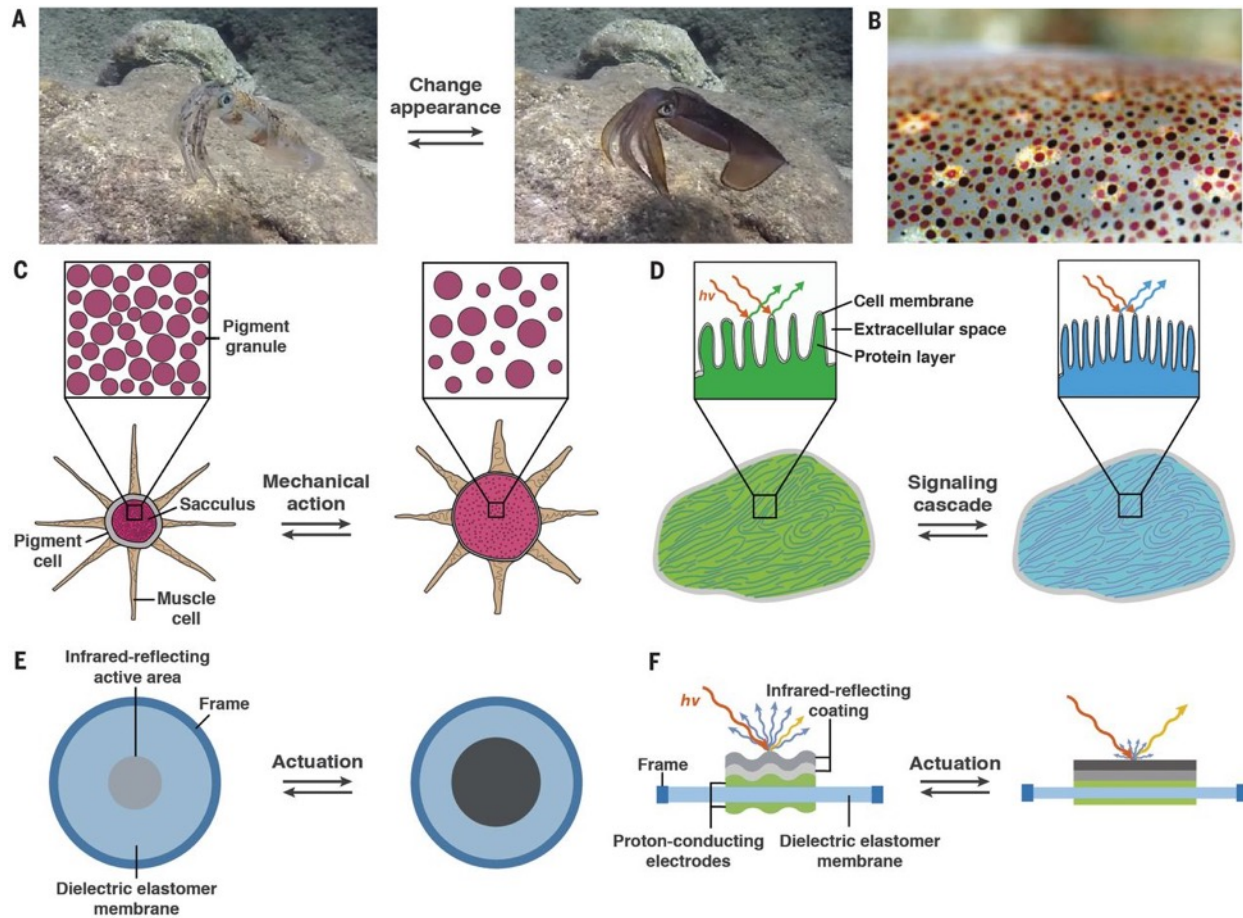


Figure 4.1. Biological inspiration and system design. (A) Camera images of a squid changing its appearance in front of a rocky background. (B) An image of squid skin. The yellow, red, and brown circular regions are chromatophore organs, and the underlying bright iridescent regions are iridocytes. (C) A schematic of a cephalopod chromatophore organ, in which a central chromatophore pigment cell is ringed by muscle cells. The adaptive chromatophore pigment cells contain internal sacculi packed with pigment granule (inset), and they are expanded and contracted through the mechanical action of the muscle cells. The chromatophore pigment cells function like size-variable biological spectral filters that absorb and reflect visible light of specific wavelengths. (D) A schematic of a squid iridocyte. The adaptive iridocytes contain alternating arrangements of membrane-enclosed protein layers and extracellular space (inset), for which the geometries and refractive index differences are altered via a biochemical signaling cascade. The

iridocytes function like reconfigurable biological Bragg reflectors that reflect visible light of variable wavelengths. (E) A generic schematic of the top view of our infrared-reflecting platform before (left) and after (right) actuation. Described is the areal change for the active region upon actuation. (F) A generic schematic of the side-view of our infrared-reflecting platform before (left) and after (right) actuation. Described is the surface morphology change for the active region upon actuation. [The images in (A) are reproduced from a video by H. Steinfeldt under the YouTube Creative Commons Attribution license, and the images in (B) were obtained by G. Hanlon and reproduced with permission of R. Hanlon.]

The remarkable capabilities of cephalopod skin and its components have inspired the engineering of various adaptive artificial optoelectronic devices.^[28–32] For example, dielectric elastomer actuators have been leveraged for cephalopod-inspired color-changing systems that function within the visible region of the electromagnetic spectrum.^[30–32] In the most basic incarnation, such devices consist of an elastomer membrane sandwiched between two electrodes, where the application of a voltage between the electrodes induces electrostatic pressure, leading to a decrease in the membrane’s thickness and an increase in the overall electrodes’ areas.^[33–35] More generally, such actuators, which essentially translate electrical stimuli into mechanical outputs, have been explored for a variety of applications, including artificial muscles, pneumatic automation, energy generation, tactile displays, and adaptive optics.^[33–35] However, the technological viability of dielectric elastomer actuators has been limited by challenges associated with a requirement for both high operating voltages and electrodes with a demanding combination of properties.^[33–37]

For infrared camouflage applications, the latter requirement is particularly daunting, as the electrode materials must simultaneously demonstrate straightforward processability into thin freestanding membranes, amenability to surface modification/patterning, excellent flexibility and compliance, high conductivity that does not drop upon deformation, transparency over a broad spectral range, lack of degradation under variable humidity, and stability to repeated cycling.

We design a platform inspired by squid skin’s highly evolved bio-optical components while leveraging the technical foundations established for dielectric elastomer actuators. We conceptualize a device in a parallel plate capacitor–type configuration, which consists of a proton-conducting bottom electrode, a dielectric elastomer membrane, a proton-conducting top electrode, and an infrared-reflecting coating (Figure 4.1E and 4.1F). Before actuation, the devices feature relatively small but size-variable active areas (Figure 4.1E, left), analogous to cephalopod chromatophores (Figure 4.1C, left),^[26] with the surfaces covered by a dense but geometrically reconfigurable arrangement of reflective microstructures (Figure 4.1F, left), analogous to squid iridocytes (Figure 4.1D, left).^[27] After actuation, the devices expand their active areas to modulate the amount of absorbed incident infrared light (Figure 4.1E, right) – again analogous to cephalopod chromatophores (Figure 4.1C, right),^[26] as well as alter the geometry of their active areas’ microstructured surfaces to modulate the relative intensity of the reflected incident

infrared light (Figure 4.1F, right) – again analogous to squid iridocytes (Figure 4.1D, right).^[27]

4.4. System fabrication, characterization, and testing

We fabricated the cephalopod-inspired adaptive infrared-reflecting systems as detailed in the supporting information. We adapted protocols used for the lithographic fabrication of various dielectric elastomer actuators^[33–35] and chose to manufacture devices with centimeter-scale active areas, allowing for benchtop assembly and simplifying spectroscopic characterization. For the compliant electrodes, we prepared films from a sulfonated pentablock copolymer that features exceptional protonic conductivity, with the size and shape of the films defining the device’s active area.^[38,39] For the electroactive layer, we mounted an acrylate dielectric elastomer membrane within a size-adjustable holder and equiaxially stretched the membrane. Subsequently, to facilitate experiments within different infrared wavelength regimes, we produced two types of devices featuring chemically and structurally distinct infrared-reflecting coatings. In order to fabricate broadband infrared-reflecting devices, we used electron-beam evaporation to deposit a thin film of aluminum (Al) metal onto a proton-conducting top electrode, which was then laminated onto a mounted acrylate membrane already outfitted with an unmodified bottom electrode (Figure S4.1A). In order to fabricate narrowband infrared-reflecting devices, we used electron-beam evaporation to deposit alternating layers of titanium dioxide (TiO₂) and silicon dioxide (SiO₂) directly onto the top electrode of a mounted

acrylate membrane, which was already outfitted with both the top and bottom electrodes (Figure S4.1B). For both device types, we mechanically contracted the holder to release some of the tension introduced during the initial mounting of the membrane and thus introduced microstructuring (wrinkles) to the surfaces of the devices' active areas. Last, when necessary for characterization, we transferred electrical lead- modified devices to rigid support frames. The overall scalable procedure furnished infrared-reflecting systems with the general architecture depicted in Figure 4.1E and 4.1F.

We investigated the effect of mechanical actuation (equiaxial strain) on the properties of devices with a broadband infrared reflectance (Figure 4.2A). Before mechanical actuation, our devices possessed relatively small active areas (Figure 4.2B) and relatively large thicknesses, with their surfaces covered by a dense three-dimensional network of micrometer-sized wrinkles, as revealed by optical microscopy (Figure 4.2C) and scanning electron microscopy (Figure 4.2D). The corresponding infrared spectra showed that the unactuated devices featured a high average total reflectance of $71 \pm 3\%$ (Figure 4.2A, bottom left), a low average total transmittance of $< 1\%$ (Figure S4.2), and a moderate average total absorptance of $28 \pm 2\%$ (Figure S4.2). For the wrinkled surfaces, the total reflectance featured a weak average specular component of $23 \pm 1\%$ and a dominant average diffuse component of $48 \pm 2\%$, in a ratio of ~ 0.5 (Figure 4.2A, bottom left). By contrast, upon mechanical actuation, our devices possessed larger active areas (Figure 4.2B) and smaller thicknesses, with the wrinkles flattened into a quasi two-

dimensional network of irregular domains, as revealed by optical microscopy (Figure 4.2C) and scanning electron microscopy (Figure 4.2D). The corresponding infrared spectra showed that the actuated devices featured an increased average total reflectance of $96 \pm 1\%$ (Figure 4.2A, bottom right), a low average total transmittance of $< 1\%$ (Figure S4.2), and a low average total absorptance of $3 \pm 1\%$ (Figure S4.2). For the flattened surfaces, the total reflectance featured a much larger average specular component of $88 \pm 3\%$ and a smaller average diffuse component of $8 \pm 2\%$, in a ratio of ~ 11 (Figure 4.2A, bottom right). For our devices, mechanical actuation dynamically modulated both the specular to diffuse reflectance ratios (owing to the change in the morphology) and the total absorptance (owing to the change in the thickness) by approximately an order of magnitude. Moreover, the specular component of the reflectance exhibited a weak angular dependence in the devices' unactuated and actuated states (Figure S4.3). The changes in the devices' infrared-reflecting properties were consistent and fully reversible upon repeated actuation, with no physical delamination and only minor performance degradation observed after 75 and 750 cycles (Figure S4.4). Thus, actuation of our devices induced a change in the microstructure of their active areas and enabled concomitant reversible, angle-independent, and stable modulation of the broadband reflectance (and absorptance) within the short- to long-wavelength infrared region.

We investigated the effect of mechanical actuation (equiaxial strain) on the properties of devices with a narrowband infrared reflectance (Figure 4.2E). To obtain

reflectances that featured peak wavelengths (λ_{peak}) in the mid-wavelength infrared region of the electromagnetic spectrum, we used infrared-reflecting coatings comprised of Bragg stacks, i.e. alternating TiO_2 and SiO_2 layers with thicknesses of $\lambda_{\text{peak}}/(4*n_{\text{TiO}_2})$ and $\lambda_{\text{peak}}/(4*n_{\text{SiO}_2})$ (where n_{TiO_2} and n_{SiO_2} are the refractive indices). This straightforward approach furnished devices with peak reflectance intensities at wavelengths of 3, 4, and 5 microns (Figure 4.2F). For such narrowband-reflecting devices, the optical properties were responsive to the applied strain, analogous to their broadband-reflecting counterparts. As a specific example, before mechanical actuation, the infrared spectra obtained for representative microstructured (wrinkled) and relatively thicker devices featured peak total reflectance intensities of $34 \pm 3\%$ at a wavelength of 3 microns, with a weak specular component of $8 \pm 1\%$ and a dominant diffuse component of $26 \pm 2\%$ in a ratio of ~ 0.3 (Figure 4.2E, bottom left). However, after mechanical actuation, the infrared spectra of the now flattened and relatively thinner devices featured increased peak total reflectance intensities of $55 \pm 7\%$ at a wavelength of 3 microns, with a much larger specular component of $29 \pm 5\%$ and a nearly unchanged diffuse component of $26 \pm 2\%$ in a ratio of ~ 1.1 (Figure 4.2E, bottom right). In general, the devices' total reflectances at this specific wavelength increased as a function of the strain (whereas the corresponding total absorptances presumably decreased) (Figure 4.2G). The reflectances' specular components likewise increased with the strain, but the diffuse components remained relatively unaffected (Figure 4.2G). Moreover, the changes in the devices' infrared-reflecting

properties were fully reversible, with only minor performance degradation observed after 100 actuation cycles (Figure S4.5). Therefore, mechanical actuation of our devices directly induced dynamic modulation of their reflectance within a specific narrow wavelength range of the infrared region.

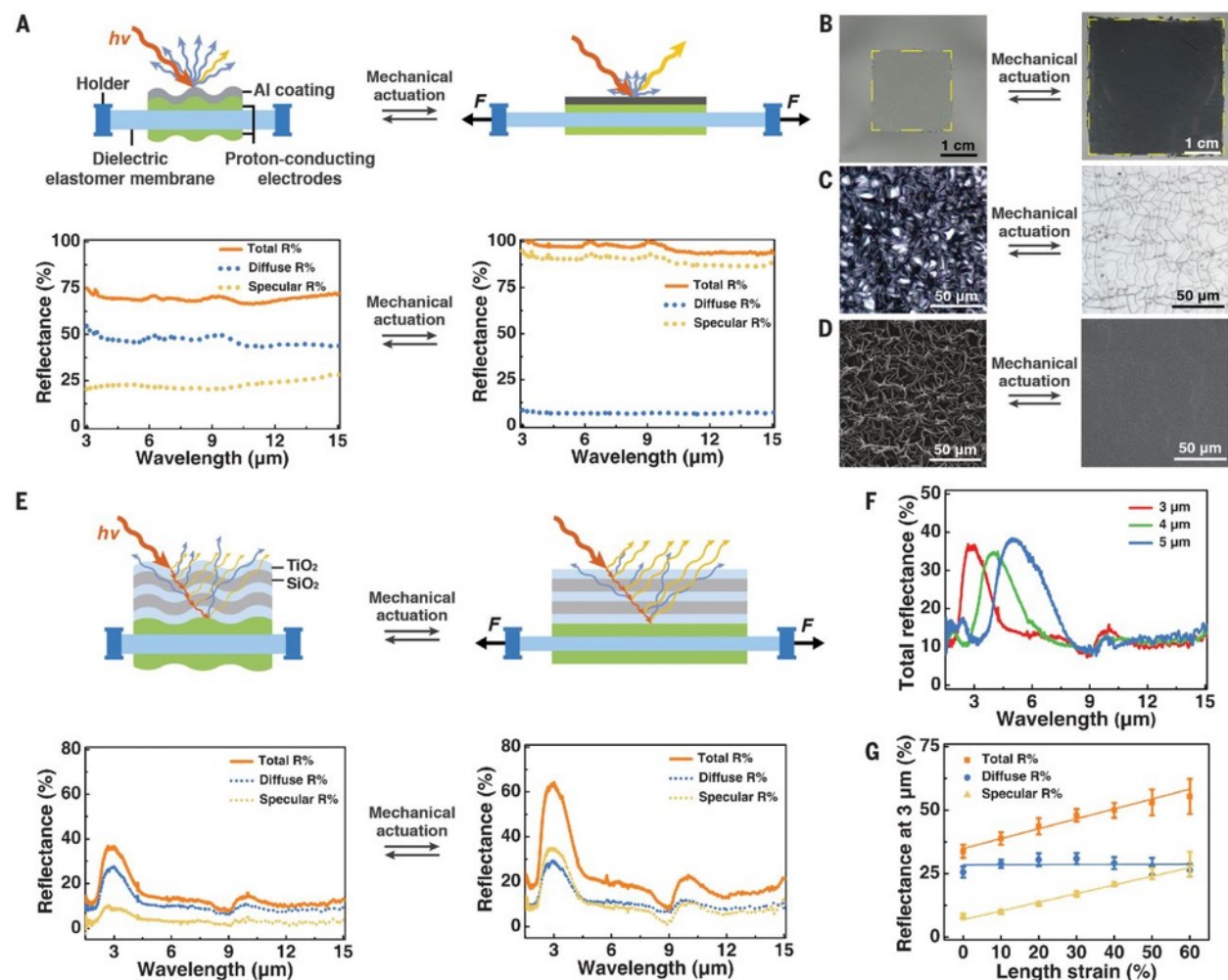


Figure 4.2. Mechanical modulation of the broadband and narrowband reflectance. (A) (Top) Schematics of an aluminum-modified device before (left) and after (right) mechanical actuation in an adjustable holder, illustrating the change in the surface morphology and the reflection of infrared light. (Bottom) The infrared reflectance spectra of an aluminum-modified device before (left) and after (right) mechanical actuation. The

total reflectances (solid orange traces) are shown along with their specular (dotted yellow traces) and diffuse (dotted blue traces) components. **(B)** Digital camera images of an aluminum-modified device's active area before (left) and after (right) mechanical actuation. The yellow dashed lines indicate the active area. **(C)** Optical microscope images of the surface morphology of an aluminum-modified device's active region before (left) and after (right) mechanical actuation. **(D)** Scanning electron microscopy images of the surface morphology of an aluminum-modified device's active region before (left) and after (right) mechanical actuation. **(E)** (Top) Schematics of a $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified device before (left) and after (right) mechanical actuation in an adjustable holder, illustrating the change in the surface morphology and the reflection of infrared light. (Bottom) The infrared reflectance spectra of a $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified device, with a peak reflectance intensity at $3\text{ }\mu\text{m}$, before (left) and after (right) mechanical actuation. The total reflectances (solid orange traces) are shown along with their specular (dotted yellow traces) and diffuse (dotted blue traces) components. **(F)** The infrared spectra of three unactuated devices that have been designed to feature peak reflectance wavelengths of $3\text{ }\mu\text{m}$ (red trace), $4\text{ }\mu\text{m}$ (green trace), and $5\text{ }\mu\text{m}$ (blue trace). **(G)** Plots of the total (orange squares), specular (yellow triangles), and diffuse (blue circles) peak reflectances of the $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified devices as functions of the applied length strain. The lines represent linear fits of the data.

We studied electrical actuation of our devices in a standard dielectric elastomer actuator configuration (Figure 4.3A). In agreement with the mechanical actuation experiments, the devices possessed a relatively small active area with a wrinkled surface prior to electrical actuation, but a larger active area with a flattened surface after electrical actuation (Figure 4.3A and Video S4.1). We found that the areal strain demonstrated an exponential dependence on the applied voltage, with an applied voltage of $\sim 3.5\text{ kV}$

resulting in a maximum strain of $\sim 230\%$ (Figure 4.3B). In addition, the areal strain exhibited a distinct dependence on the frequency of the applied voltage; for example, a variable-frequency square waveform (minima of 0 kV and maxima of 3.2 kV) induced a drop in the maximum strain from $181 \pm 11\%$ to $85 \pm 5\%$ between the frequencies of 0.05 Hz and 2 Hz, followed by an increase in the maximum areal strain to $110 \pm 5\%$ at 16 Hz (Figure 4.3C). Moreover, for the aforementioned square waveform at a frequency of 0.5 Hz, the devices' response time (defined as the rise time from 10 % to 90 % of the strain change) was 720 ± 50 ms, because of the rapid areal expansion and shrinkage rates of $55.8 \pm 1.6\%$ and $56.8 \pm 0.8\%$ per second, respectively (Figure 4.3D), and the energy associated with device actuation during one typical cycle was estimated to be > 8 J/m² (see the Supporting Information). These systems' figures of merit were comparable with or even exceeded those reported for analogous acrylate dielectric elastomer-based devices with conventional ionic hydrogel, carbon grease, or conductive nanowire composite electrodes.^[36,37]

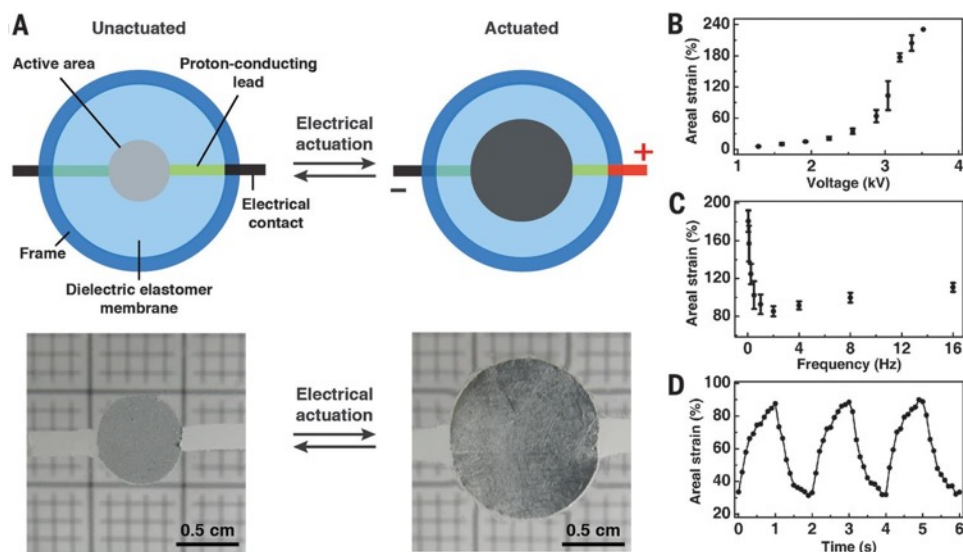


Figure 4.3. Electrical characteristics of single devices. (A) (Top) Schematics of an aluminum-modified device before (left) and after (right) electrical actuation, illustrating the areal change for the active region. (Bottom) Digital camera images of an aluminum-modified device’s active region before (left) and after (right) electrical actuation. (B) A plot of the areal strain as a function of the applied voltage for aluminum-modified devices. (C) A plot of the areal strain as a function of the frequency for square waveforms with identical minima of 0 kV and maxima of 3.2 kV. (D) A plot of the areal strain as a function of time for three consecutive cycles of a square waveform with a frequency of 0.5 Hz, as well as minima of 0 kV and maxima of 3.2 kV.

We showed electrical modulation of our systems’ infrared-reflecting properties in multiple configurations (Figure 4.4). To this end, we prepared not only single devices but also three-by-three arrays in which such devices served as independently addressable “pixels” and then visualized both platforms with a thermal infrared camera under an incident heat flux (see Supporting Information). We focused our experiments on aluminum-coated devices because of most commercial infrared cameras’ spectral range of

7.5 to 14 microns. As an example, a representative single device featured an apparent temperature difference of ~ 3.6 °C between its aluminum-coated active area and the surrounding membrane before electrical actuation (Figure 4.4A), presumably because of the dominance of the reflectance’s diffuse component in the unactuated state. In contrast, the same device featured an increased apparent temperature difference of ~ 6.8 °C between its aluminum-coated active area and the surrounding membrane after electrical actuation (Figure 4.4A), presumably because of the dominance of the reflectance’s specular component in the actuated state. The observed change in apparent temperature was rapid, stable, and fully reversible over numerous distinct on/off cycles for such devices (Video S4.2). As another example, the devices in a representative array featured analogous modulation of the apparent temperature differences between their active areas and the surrounding membranes upon device-specific, independent electrical actuation (Figure S4.6). Multiple devices in the arrays also readily exhibited tandem changes in their active areas’ local apparent temperatures (Figure 4.4B). Indeed, electrical actuation of different combinations of seven multiplexed devices enabled distinct representative arrays to “spell out” the letters “U,” “C,” and “T” (Figure 4.4B). In principle, the general fabrication approach is amenable to the fabrication of advanced displays with higher pixel densities and/or submillimeter pixel sizes.^[35,40]

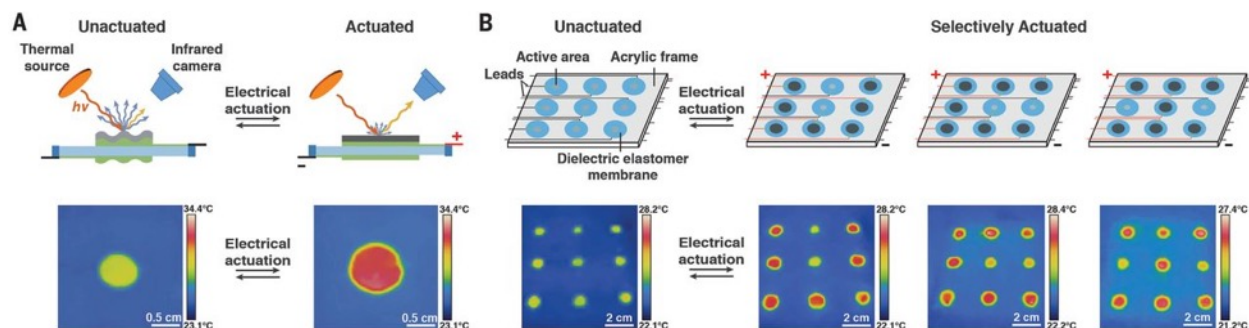


Figure 4.4. Electrical modulation of the infrared appearance for single and multiplexed devices. (A) (Top) Schematics of an aluminum-modified device under a constant thermal flux before (left) and after (right) electrical actuation, illustrating the change in surface morphology and the reflection of infrared light. (Bottom) Infrared camera images of a representative aluminum-modified device’s active region before (left) and after (right) electrical actuation. The change in apparent temperature and thermal appearance is represented by a change in color. (B) (Top) Schematics of a three-by-three array of multiplexed devices before electrical actuation (left) and after (right) selective electrical actuation of different device (pixel) combinations as the letters “U,” “C,” and “I.” (Bottom) Infrared camera images of representative three-by-three arrays of multiplexed devices before electrical actuation (left) and after (right) selective electrical actuation of different device (pixel) combinations as the letters “U,” “C,” and “I.” The changes in apparent temperature and thermal appearance are represented by changes in color.

We demonstrated that our systems could operate without input from an external operator (Figure 4.5A). We connected electrically controlled devices (with aluminum-coated active areas) to a remotely positioned, independently-heated temperature sensor, which transduced thermal information from a distal environment while avoiding undesired cross-talk. At a sensor temperature of ~ 26 °C, the autonomous system possessed a wrinkled active area and an apparent temperature difference between the active area and

surrounding unmodified membrane of ~ 3.4 °C, as revealed by digital and infrared camera imaging, respectively (Figure 4.5A). Upon a change in the temperature of the sensor to ~ 34 °C, the system’s active area flattened and expanded by $18 \pm 5\%$ (relative to the initial value), and its apparent temperature difference increased to ~ 3.7 °C with respect to the unmodified membrane (Figure 4.5A). After a further rise in the sensor’s temperature to ~ 42 °C, the active area flattened and expanded further by $35 \pm 6\%$ (relative to the initial value), and its apparent temperature difference increased to ~ 4.0 °C with respect to the unmodified membrane (Figure 4.5A). With an additional rise in the sensor’s temperature to ~ 48 °C, the active area flattened and expanded even more by $74 \pm 3\%$ (relative to the initial value), and its temperature difference increased to ~ 4.4 °C with respect to the unmodified membrane (Figure 4.5A). Over a temperature window of > 20 °C for the sensor, our autonomous system exhibited reproducible and stable changes in the size of its active area (and apparent temperature), albeit in non-linear fashion (Figure S4.7).

Last, we evaluated the ability of our infrared camouflage systems to conceal themselves under infrared visualization (Figure 4.5B). We prepared devices with aluminum-coated active areas in the shape of a swimming squid’s silhouette and then imaged them with a thermal infrared camera under an incident heat flux above a surface with a locally elevated temperature (see Figure 4.5B and the Supporting Information). Before electrical actuation, a representative squid silhouette-shaped device featured a relatively small microstructured (wrinkled) active area (Figure 4.5B) and a negligible

apparent temperature difference with the immediate surroundings that effectively made it invisible above a warm surface with a temperature of $\sim 35\text{ }^{\circ}\text{C}$, as revealed with infrared camera imaging (Figure 4.5B). By contrast, after electrical actuation, the squid silhouette-shaped device featured a larger flattened active area (Figure 4.5B) and an apparent temperature difference of $\sim 2\text{ }^{\circ}\text{C}$ with the immediate surroundings that made it stand out as a specific shape, as revealed with infrared camera imaging (Figure 4.5B). In general, the observed changes in appearance under infrared visualization were again rapid, stable, and fully reversible over numerous distinct on/off cycles (Video S4.3).

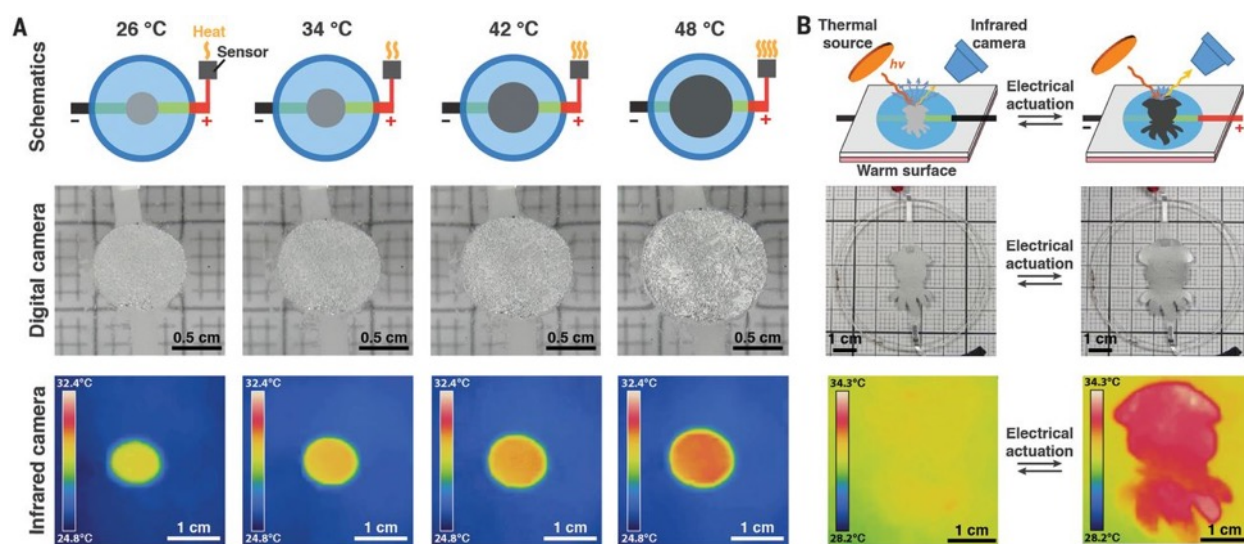


Figure 4.5. Autonomous operation and reversible concealment of devices in the infrared.

(A) (Top) Schematics of a sensor-connected, aluminum-modified device. The remote sensor is positioned in a different local thermal environment, with increasing temperatures of $\sim 26\text{ }^{\circ}\text{C}$, $\sim 34\text{ }^{\circ}\text{C}$, $\sim 42\text{ }^{\circ}\text{C}$ and $\sim 48\text{ }^{\circ}\text{C}$ (from left to right). (Middle) Digital camera images of a representative device's active region at the different sensor temperatures. (Bottom) Infrared camera images of the same device's active region at the different sensor temperatures. Shown are the expansion and change in thermal appearance for the

autonomous device’s active region, with increasing local temperature for the sensor. **(B)** (Top) Schematics of a squid silhouette-shaped, aluminum-modified device maintained under a constant thermal flux and positioned above a warm surface before (left) and after (right) electrical actuation. (Middle) Digital camera images of a representative squid silhouette-shaped, aluminum-modified device’s active region before (left) and after (right) electrical actuation. (Bottom) Infrared camera images of the same squid silhouette-shaped, aluminum-modified device’s active region before (left) and after (right) electrical actuation. The device alters its thermal appearance and becomes distinguishable from the background only after actuation.

4.5. Conclusion

By drawing inspiration from cephalopods, we have developed and validated a new class of adaptive infrared-reflecting materials and devices with an unprecedented combination of properties. First, our artificial platforms translate many of the key natural capabilities of cephalopods from the visible to the infrared regions of the electromagnetic spectrum (although in principle they could be adapted for functionality within the visible). Second, our presented systems feature capabilities and figures-of-merit that exceed or match the state-of-the-art for adaptive infrared camouflage technologies (see Table S4.1). Third, the systems have been intrinsically designed for ready manufacturability and straightforward integration, potentially facilitating applications in dielectric elastomer-based artificial muscles, pneumatic automation, energy generation, and adaptive optics (as well as in other areas). Last, the systems may enable new autonomous portable or wearable thermoregulatory technologies, although such applications will likely require

optimization of mechanical actuation strategies or the reduction of the associated operating voltages. Ultimately, the described materials and devices may afford new possibilities for the many modern technologies that rely on controlling the transfer of thermal radiation, and thus may help transform many aspects of daily life.

4.6. Supporting Information

4.6.1 Fabrication of independent infrared-reflecting, aluminum-modified devices

The devices were prepared according to standard lithographic protocols. First, to fabricate the electrodes, a commercially available sulfonated pentablock co-polymer (NEXARTM, Kraton Polymers LLC) was spincoated onto a 6-inch diameter silicon wafer (University Wafer) and cured via heating at 60 °C. For the unmodified bottom electrode, the co-polymer film was directly delaminated from the support substrate, and for the aluminum-modified top electrode, 20 nm of aluminum was electron-beam evaporated onto the co-polymer film with an Angstrom Engineering EvoVac system prior to delamination from the support substrate. Next, to prepare the central device layer, an acrylate elastomer (VHB 4905, 3M) was mounted and equiaxially stretched by 1,600 % (relative to its initial area) on a home-built size-adjustable holder (with the exception of the sensor-integrated devices where the equiaxial stretching was 1,100 %). In turn, either a circular or a square section of the unmodified co-polymer film was laminated onto the acrylate elastomer as the bottom electrode, and either a circular or a square section of an aluminum-modified co-polymer film was laminated onto the acrylate elastomer as the top electrode. For mechanical actuation experiments, the partially completed device was mechanically contracted by ~ 40 % with respect to the length of the square electrodes. For electrical actuation experiments, the partially completed device was modified with stripe-shaped co-polymer films as the electrical leads, prior to mechanical contraction by ~ 40 % with respect to the diameter of the electrodes, and was then transferred to an

appropriate support frame as required. The resulting completed devices were used for the physical, mechanical, electrical, optical, and/or infrared characterization experiments as needed.

4.6.2 Fabrication of independent infrared-reflecting, $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified devices

The devices were prepared according to standard lithographic protocols. First, to fabricate the electrodes, a sulfonated pentablock co-polymer (NEXARTM Polymers, Kraton Polymers LLC) was spincoated onto a 6-inch diameter silicon wafer (University Wafer) and cured via heating at 60 °C. Next, to prepare the central device layer, an acrylate elastomer (VHB 4905, 3M) was mounted and equiaxially stretched by 1,600 % (relative to its initial area) on a home-built size-adjustable holder. In turn, square sections of the unmodified co-polymer film were laminated onto the acrylate elastomer as the top and bottom electrodes. Subsequently, alternating layers of titanium dioxide (TiO_2) and silicon dioxide (SiO_2) were electron-beam evaporated onto the top co-polymer electrode in the sequence $\text{TiO}_2/\text{SiO}_2/\text{TiO}_2/\text{SiO}_2/\text{TiO}_2$ with an Angstrom Engineering EvoVac system (to produce a 3 μm peak reflectance, the SiO_2 thickness was 0.560 μm and the TiO_2 thickness was 0.326 μm ; to produce a 4 μm peak reflectance, the SiO_2 thickness was 0.747 μm and the TiO_2 thickness was 0.435 μm ; and to produce a 5 μm peak reflectance, the SiO_2 thickness was 0.933 μm and the TiO_2 thickness was 0.543 μm). Finally, for mechanical actuation experiments, the partially-completed device was mechanically

contracted by $\sim 37.5\%$ with respect to the length of the square electrodes. The resulting completed devices were used for the physical, mechanical, optical, and infrared characterization experiments as needed.

4.6.3 Fabrication of multiplexed infrared-reflecting, aluminum-modified devices in an array configuration

The devices were prepared in similar fashion to their aluminum-modified analogues. First, we designed three by three arrays consisting of individual devices with center-to-center distances of ~ 2.7 cm and edge-to-edge distances of ~ 2.0 cm (note that the device spacing was selected to facilitate benchtop fabrication and to minimize inter-device electrical crosstalk at kilovolt operating voltages). Next, nine regularly arranged circular openings were introduced into a flexible acrylic substrate with an Epilog Fusion laser cutter. In turn, nine independent devices that each consisted of an unmodified sulfonated pentablock co-polymer bottom electrode, an acrylate elastomer central layer, and an aluminum-modified sulfonated pentablock co-polymer top electrode were fabricated within the circular openings of the acrylic frame according to the procedures described above. Finally, electrical leads consisting of scotch-tape covered aluminum foil were connected to each of the independent multiplexed devices. The process furnished the device architecture shown in Figure S4.6A, which was used for all physical, electrical, optical, and infrared characterization experiments.

4.6.4 Fabrication of squid silhouette-shaped infrared-reflecting, aluminum-modified devices

The devices were prepared in similar fashion to their aluminum-modified analogues. First, squid silhouette-shaped masks were cut from plastic-modified freezer paper (Reynolds) with an Epilog Fusion laser cutter. Next, the masks were used to excise appropriately shaped electrodes from unmodified and aluminum-modified sulfonated pentablock co-polymer films. In turn, these electrodes were used to fabricate the devices shown in Figure 4.5B according to the procedures described above. The resulting completed devices were used for the physical, electrical, optical, and infrared characterization experiments as needed.

4.6.5 Mechanical actuation of the aluminum-modified and TiO₂/SiO₂ Bragg stack-modified devices

The devices were mechanically actuated in a home-built size-adjustable holder, which was used to apply/release equiaxial mechanical strain to/from the devices. During standard mechanical actuation of the aluminum-modified devices, the lengths of their square-shaped active areas were increased by $\sim 66.7\%$ for actuation and then contracted by $\sim 40\%$ to return to the initial position, unless otherwise noted. During standard mechanical actuation of the TiO₂/SiO₂ Bragg Stack-modified devices, the lengths of their square-shaped active areas were increased by $\sim 60\%$ for actuation and then contracted by

$\sim 37.5\%$ to return to the initial position, unless otherwise noted. These protocols maintained stringent consistency between experiments.

4.6.6 Infrared spectroscopy of the aluminum-modified and TiO₂/SiO₂ Bragg stack-modified devices

The infrared-reflecting devices were spectroscopically characterized in custom-built holders both before and after mechanical actuation. To obtain the diffuse reflectance, total reflectance, and total transmittance, the devices were characterized with a Frontier Fourier Transform Infrared Spectrometer (FTIR, Perkin Elmer) that was equipped with an upward-looking Mid-Infrared integrating sphere (Pike Technologies), which featured a sample port with a ~ 2.1 cm diameter. The active areas of the devices used for all experiments were large enough to completely cover the sample port both before and after mechanical actuation. The measurements were performed at an illumination angle of 12 degrees over a wavelength range of 1.5 to 15 μm and referenced to a diffuse gold standard (Pike Technologies). From these measurements, the specular reflectance was calculated according to the equation (41):

$$\text{Specular reflectance (\%)} + \text{Diffuse reflectance (\%)} = \text{Total reflectance (\%)}$$

and the absorptance was calculated according to the equation^[41]:

$$\text{Total reflectance (\%)} + \text{Total transmittance (\%)} + \text{Total absorptance (\%)} = 100\%$$

To obtain the angle-dependent specular reflectance, the devices were characterized with a Frontier Optica Fourier Transform Infrared Spectrometer (FTIR, Perkin Elmer)

that was equipped either with a 10-degree specular reflectance accessory (10Spec, Pike Technologies) or a Variable Angle specular reflectance accessory (VeeMAX III, Pike Technologies), both of which featured sample ports with a ~ 1 cm diameter. The active areas of the devices used for all experiments were large enough to completely cover the sample ports both before and after mechanical actuation. The measurements were performed at various angles over a wavelength range of 1.5 to 15 μm and referenced to a reflective gold standard (Pike Technologies). In all cases, the measurements were performed for at least three devices and independently verified at least three times for each device with the room temperature maintained at ~ 21 $^{\circ}\text{C}$ and the relative humidity maintained at ~ 49 %, unless otherwise noted. During analysis, the obtained spectra were processed and evaluated with the Spectrum (Perkin Elmer) and Origin Pro software packages.

4.6.7 Physical characterization of the aluminum-modified and $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified Devices

The infrared-reflecting devices were physically characterized both before and after mechanical actuation. The global device surface morphologies were characterized in reflection mode with an Axio Imager A1M optical microscope (Zeiss) equipped with an AxioCam MRc5 Digital Camera (Zeiss). The local surface morphologies were characterized with an XL-30 FEG scanning electron microscope (Philips). The measurements were

performed for at least three devices and independently verified a minimum of five times for each device.

4.6.8 Digital and infrared camera imaging of the aluminum-modified devices

The infrared-reflecting devices were directly imaged throughout all of the electrical actuation experiments below. For the digital imaging, the pictures and videos were obtained with a PowerShot SX520 HS digital camera (Canon). For the infrared imaging, the pictures and videos were obtained with a C2 infrared camera (FLIR) featuring a built-in rainbow color palette for the temperature and an effective spectral range from wavelengths of 7.5 μm to 14 μm . The videos were captured through live streaming to a computer with the FLIR software package and recording with the Icecream Screen Recorder software package. The areal strain was calculated from the images/videos according to the equation:

$$\text{Areal strain (\%)} = [(A_1 - A_0)/A_0] \times 100\%$$

where A_0 is the area prior to actuation and A_1 is the area after actuation. For analysis, the obtained digital camera and infrared camera images/videos were processed with the QuickTime Player and MATLAB software packages. In all cases, the measurements were performed for at least three devices and independently verified multiple times for each device. During all measurements, the devices were exposed to an incident thermal flux from a warm surface with a temperature of $\sim 37^\circ\text{C}$ and an orientation of 45° , while the

room temperature was maintained at ~ 23 °C and the relative humidity was maintained at ~ 49 %, unless otherwise noted.

4.6.9 Electrical actuation of the aluminum-modified devices

The infrared-reflecting devices were electrically actuated with custom-modified electronics in both stand-alone and multiplexed configurations. For all measurements, the devices were connected to a home-built high-voltage power supply consisting of a DS345 function generator (Stanford Research), an OPA 548 operational amplifier (Texas Instruments), and an E80 high-voltage amplifier (EMCO). For multiplexed measurements, the device arrays were also connected to a home-built switching/control system featuring nine switches (McMaster-Carr), which allowed for independent control of each device in the multiplexed array. The obtained electrical characteristics were analyzed with the QuickTime Player and MATLAB software packages. In all cases, the measurements were performed for at least three devices and independently verified multiple times for each device. During all measurements, the devices were exposed to an incident thermal flux from a warm surface with a temperature of ~ 37 °C and an orientation of 45° , while the room temperature was maintained at ~ 23 °C and the relative humidity was maintained at $\sim 49\%$, unless otherwise noted.

4.6.10 Autonomous electrical actuation of the sensor-integrated aluminum-modified devices

The infrared-reflecting devices were actuated autonomously without any user input with signals from an integrated sensor. For all measurements, the devices were connected to a home-built autonomous operation system consisting of a TMP36 integrated circuit temperature sensor (Analog) powered by two AA batteries, an OPA 548 operational amplifier (Texas Instruments), and an E80 high-voltage amplifier (EMCO). In this configuration, the sensor's voltage output V_{sens} was dependent on the local temperature according to the equation:

$$Temp (^{\circ}C) = [V_{sens} (mV) - 500]/10$$

To generate the appropriate voltage, the sensor's output was connected in series with another AA battery of voltage V_b , and the overall output $V_{overall}$ (i.e., $V_{sens} + V_b$) of the system was increased 1,600-fold by the amplifier. To systematically alter its local thermal environment, the sensor was positioned remotely from the devices and independently heated over a temperature range of 26 °C to 48 °C, with the resulting device areal strain allowed to equilibrate and stabilize after heating to each temperature point. Note that the sensor was remote (not local) relative to the devices to mitigate the possibility of undesired thermal cross-talk (interference). The obtained electrical characteristics were analyzed with the MATLAB software package. In all cases, the experiments were performed for at least four devices and independently verified multiple times for each device. During all

measurements, the devices were exposed to an incident thermal flux from a warm surface with a temperature of $\sim 37\text{ }^{\circ}\text{C}$ and an orientation of 45° , while the room temperature was maintained at $\sim 26\text{ }^{\circ}\text{C}$ and the relative humidity was maintained at $\sim 47\%$, unless otherwise noted.

4.6.11 Electrical actuation of squid silhouette-shaped Aluminum-modified Devices

The infrared-reflecting devices were electrically actuated in variable local thermal environments to demonstrate their camouflage capabilities. For all measurements, the devices were connected to a home-built high-voltage power supply consisting of a DS345 function generator (Stanford Research), an OPA 548 operational amplifier (Texas Instruments), and an E80 high-voltage amplifier (EMCO). To maintain a specific local temperature, the devices were positioned above a surface maintained at a constant temperature of $\sim 35\text{ }^{\circ}\text{C}$. The obtained electrical characteristics were analyzed with the QuickTime Player and MATLAB software packages. In all cases, the experiments were performed for at least three devices and independently verified multiple times for each device. During all measurements, the devices were exposed to an incident thermal flux from a warm surface with a temperature of $\sim 37\text{ }^{\circ}\text{C}$ oriented at a 45° angle with respect to the devices, while the room temperature was maintained at $\sim 23\text{ }^{\circ}\text{C}$ and the relative humidity was maintained at $\sim 45\%$, unless otherwise noted.

4.6.12 Representative calculation of the energy associated with device electrical actuation

We used established literature protocols to estimate the energy associated with the electrical actuation of our devices.^[33,35] To simplify our calculation, we assumed that the dielectric elastomer actuators behaved as ideal dynamic parallel plate capacitors, where the elastomer was a perfect electrical insulator with no leakage current, and we did not account for the contribution from electrode resistance. As an example, we performed the calculation for the representative device in Figure 4.3D, which was actuated with a square waveform voltage at a frequency of 0.5 Hz (minima of 0 kV and maxima of 3.2 kV).

After the application of the voltage ($t \sim 1$ s), the capacitance (C) of the device was described by the equation:

$$C = \epsilon_r \epsilon_0 \frac{A}{d}$$

where ϵ_r is the relative permittivity of the 3M VHB 4905 dielectric elastomer (~ 4.7), ϵ_0 is the permittivity of free space ($\sim 8.854 \times 10^{-12}$ F/m), A is the device active area after actuation ($\sim 6.5 \times 10^{-5}$ m²), and d is the estimated dielectric elastomer thickness after actuation ($\sim 2.6 \times 10^{-5}$ m). This calculation yielded a capacitance of ~ 104 pF for the device.

Moreover, the energy (E) stored in the device was described by the equation:

$$E = \frac{1}{2} C U^2$$

where C is the capacitance (~ 104 pF) and U is the applied voltage (3.2 kV). This calculation yielded a stored energy (E) of $\sim 5.3 \times 10^{-4}$ J and a corresponding stored energy per active area (E_A) of ~ 8.1 J/m² for the device.

4.6.13 Supporting Information Figures and Tables

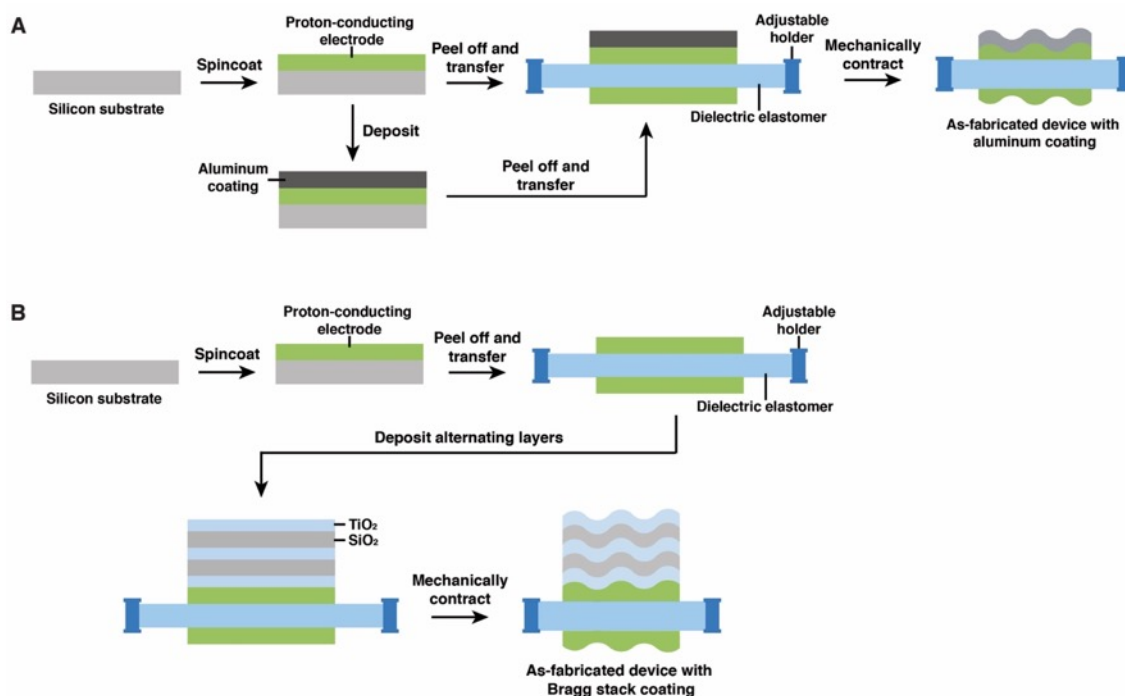


Figure S4.1. Fabrication of the devices. (A) Scheme for the fabrication of the aluminum-modified infrared-reflecting devices within a holder. (B) Scheme for the fabrication of the Bragg stack-modified infrared-reflecting devices within a holder.

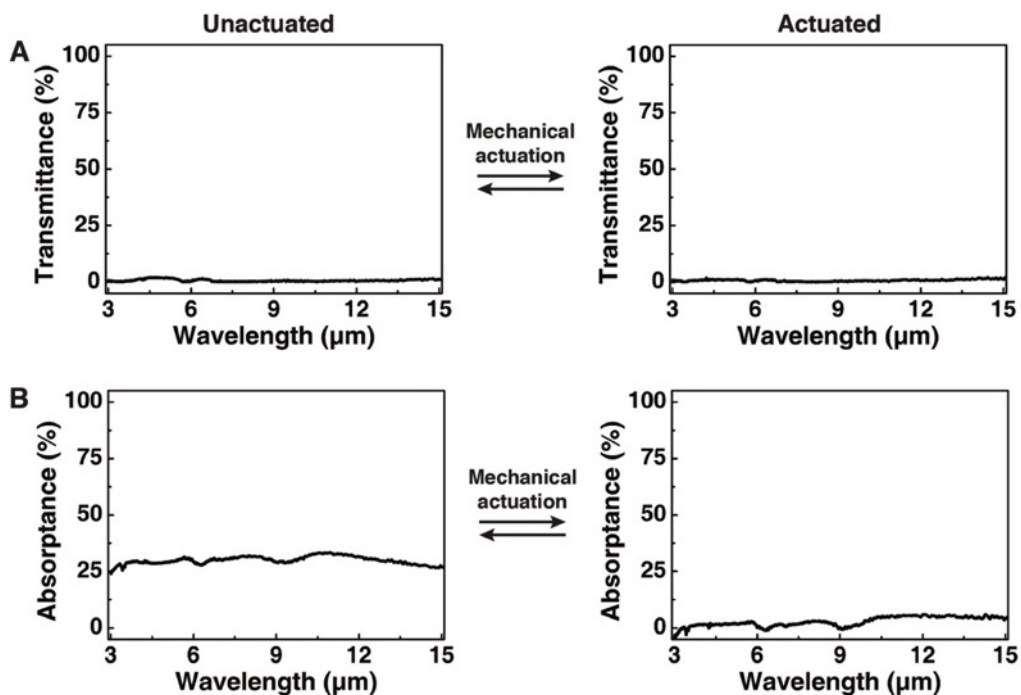


Figure S4.2. Mechanical modulation of the broadband transmittance and absorbance.

(**A**) The infrared transmittance spectra of an aluminum-modified device before (left) and after (right) mechanical actuation. (**B**) The infrared absorbance spectra of an aluminum-modified device before (left) and after (right) mechanical actuation.

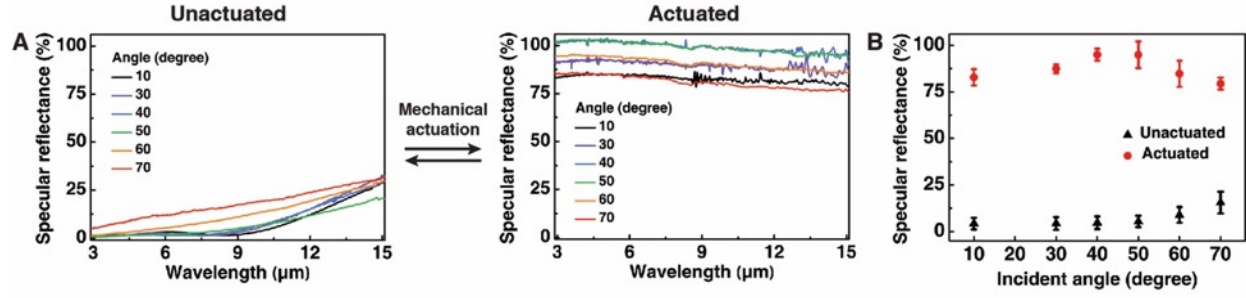


Figure S4.3. Angular dependence of the mechanical modulation of the broadband reflectance. (A) The specular component of the reflectance for an aluminum-modified device as a function of the incident light angle before (left) and after (right) mechanical actuation. (B) The average specular reflectance for an aluminum-modified device as a function of the incident light angle before (black triangles) and after (red dots) mechanical actuation. The error bars represent the standard deviation for measurements from four independent devices.

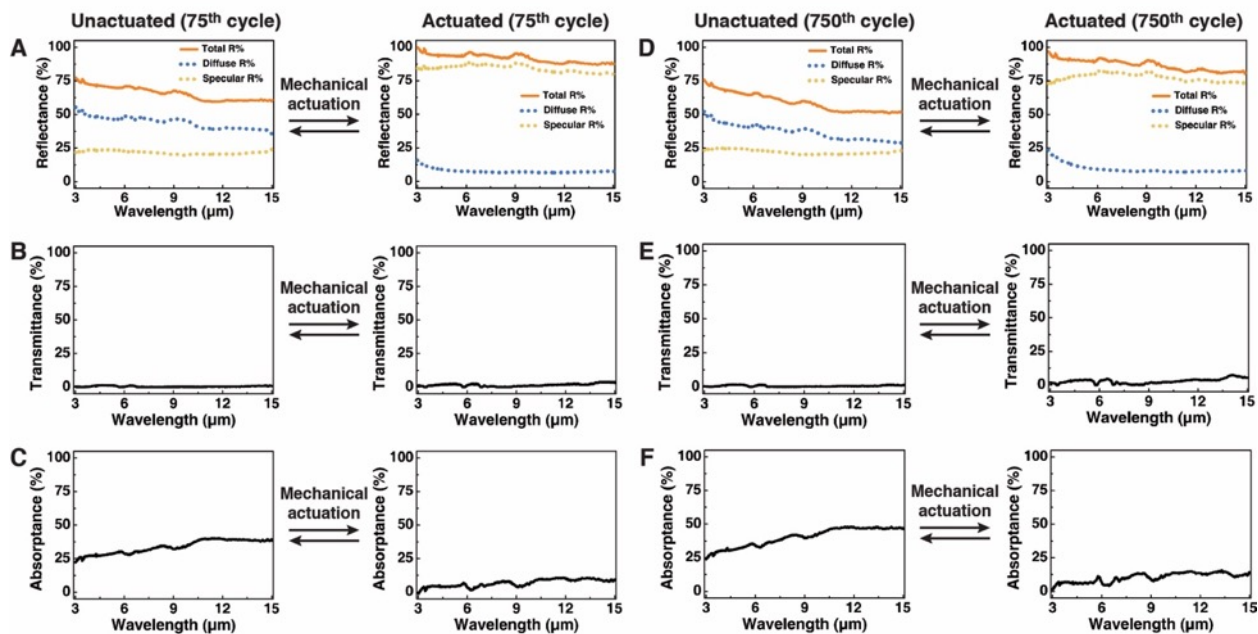


Figure S4.4. Stability of the aluminum-modified devices' functionality after repeated mechanical actuation. (A) The infrared reflectance spectra of an aluminum-modified device before (left) and after (right) 75 mechanical actuation cycles. The total reflectance (solid orange traces) is shown along with its specular (dotted yellow traces) and diffuse components (dotted blue traces). (B) The infrared transmittance spectra of an aluminum-modified device before (left) and after (right) 75 mechanical actuation cycles. (C) The infrared absorptance spectra of an aluminum-modified device before (left) and after (right) 75 mechanical actuation cycles. (D) The infrared reflectance spectra of an aluminum-modified device before (left) and after (right) 750 mechanical actuation cycles. The total reflectance (solid orange traces) is shown along with its specular (dotted yellow traces) and diffuse components (dotted blue traces). (E) The infrared transmittance spectra of an aluminum-modified device before (left) and after (right) 750 mechanical actuation cycles. (F) The infrared absorptance spectra of an aluminum-modified device before (left) and after (right) 750 mechanical actuation cycles.

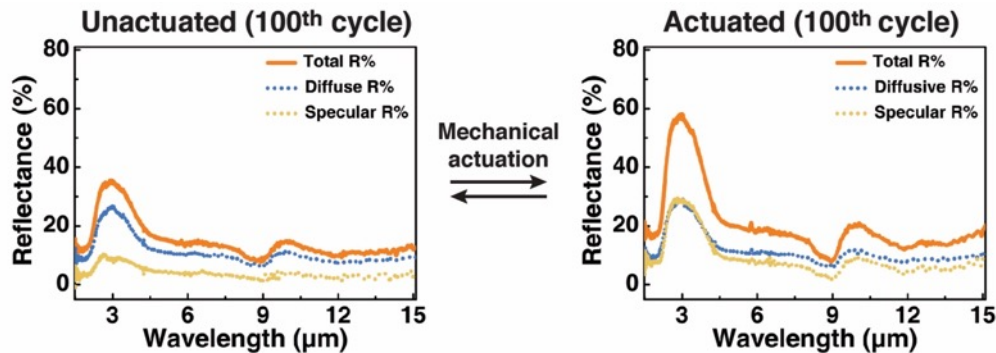


Figure S4.5. Stability of the Bragg stack-modified devices' functionality after repeated **mechanical actuation**. The infrared reflectance spectra of a $\text{TiO}_2/\text{SiO}_2$ Bragg stack-modified device, with a peak reflectance intensity at 3 μm , before (left) and after (right) 100 mechanical actuation cycles. The total reflectances (solid orange traces) are shown along with their specular (dotted yellow traces) and diffuse components (dotted blue traces) both before and after mechanical actuation.

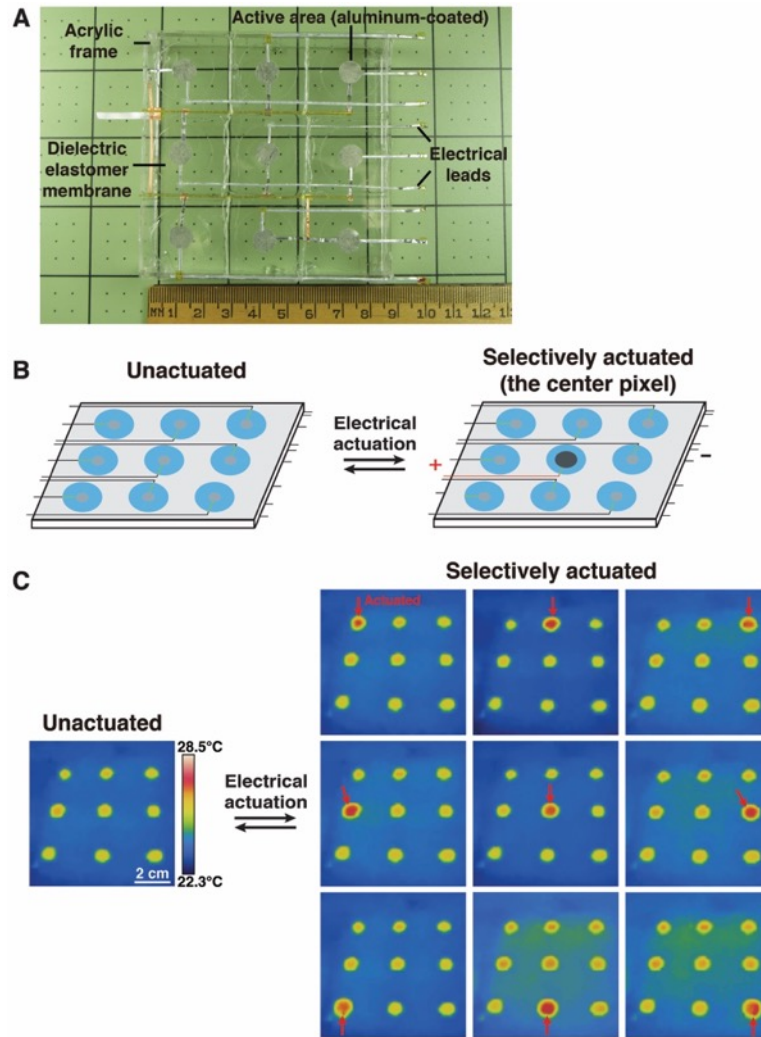


Figure S4.6. Images of multiplexed devices and electrical modulation of their appearance in the thermal infrared. (A) A digital camera image of a three by three array of multiplexed devices. (B) Schematics of a three by three array of multiplexed devices before electrical actuation (left) and after (right) selective electrical actuation of a single device. (C) Infrared camera images of a three by three array of multiplexed devices before electrical actuation (left) and after selective electrical actuation of different single devices in the array (right). Note the change in apparent temperature and thermal appearance upon actuation for specific devices, as indicated by the color scheme and the red arrows. The temperature range and scale bar of the actuated devices on the right are identical to those of the unactuated device on the left.

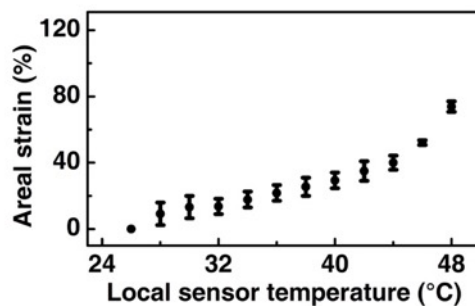


Figure S4.7. Autonomous modulation of a device’s active area. Plot of the areal strain (relative to the value at 26 °C) as a function of the sensor temperature for a sensor-connected aluminum-modified device. The data were obtained for temperatures between 26 °C and 48 °C. The error bars represent the standard deviation for measurements from four independent devices.

Table S4.1. Compilation of the key capabilities and figures-of-merit for various adaptive infrared camouflage systems. The list includes representative examples of the major classes of adaptive infrared camouflage. Note that the top row summarizes the capabilities of cephalopods as the natural inspiration source, even though these animals adaptively change their appearance within the visible region of the electromagnetic spectrum.

	Working material/device	Working mechanism	Actuation approach	Actuation voltage	Working temperature	Tunable spectral range		Angular dependence	Response time	Cyclability	Patterning/multiplexing	Autonomous operation	Mechanical properties	Power consumption	Ref.
						Broadband	Narrowband								
Natural inspiration	Cephalopods (e.g. squid, octopuses, and cuttlefish)	Morphological and areal changes	Bioelectrical/biochemical	N/A	Typically 4 °C – 30 °C	Yes	Yes	Weak (chromatophore); strong (iridophore)	Seconds (a whole animal); hundreds of milliseconds (chromatophore); tens of seconds (iridophore)	Lifetime of the animal (typically < 5 years)	Yes	Yes	Soft and flexible	Variable among different species	21-27, 42-49
Adaptive infrared camouflage systems	VO ₂ nanopowders	Thermochromic	Thermal	N/A	> 75 °C	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Rigid	Not reported	8
	Tungsten (W)-doped VO ₂ on quartz	Thermochromic	Thermal	N/A	> 55 °C (1 wt.% W) > 38 °C (2 wt.% W) > 30 °C (4 wt.% W)	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Not reported	Rigid	Not reported	9
	VO ₂ /Graphene/CNT	Thermochromic	Thermal	Not reported	> 54 °C	Not reported	Not reported	Not reported	0.04 s	100,000 (with hysteresis)	Not reported	Not reported	Flexible	4,200 W/m ²	10
	Tungsten-doped VO ₂ on cotton fabric	Thermochromic	Thermal	N/A	> 48.2 °C (1 wt.% W)	Not reported	Not reported	Not reported	Not reported	10 (with hysteresis)	Not reported	Not reported	Flexible	Not reported	11
	VO ₂ on sapphire	Thermochromic	Thermal	N/A	> 74.5 °C	Yes	No	Not reported	Not reported	Not reported	Not reported	Not reported	Rigid	Not reported	12
	Dodecylbenzene sulfonate acid-doped polyaniline-integrated device	Infrared electrochromic	Electrical	1.5 V	55.6 °C	Yes	No	Not reported	Not reported	Not reported	Not reported	Not reported	Flexible	Not reported	13
	Poly(3,4-ethylenedioxythiophene)-integrated device	Infrared electrochromic	Electrical	2.5 V	Room temperature	Yes	No	Not reported	23 s (bleaching) 1.4 s (darkening)	20	Not reported	Not reported	Rigid	Not reported	14
	Polyaniline/poly(diphenylamine)-integrated device	Infrared electrochromic	Electrical	1.2 V	Room temperature	Not reported	Not reported	Not reported	0.3-1.5 s	100,000-300,000	Yes	Not reported	Flexible	0.4 W/m ²	15,16
	N-doped zinc oxide (ZnO) with gold resonators	Photocurrent doping	Optical (ultraviolet light)	N/A	80 °C	Yes	No	Not reported	100 s	Not reported	Yes	Not reported	Rigid	Not reported	17
	Thermal cloaking system	Heat flow manipulation	Thermal	N/A	Gradient between 80 °C and room temperature	Not reported	Not reported	Not reported	A few minutes	Not reported	Not reported	Not reported	N/A	Not reported	18,19
	Soft machine with microfluidic networks	Direct temperature control	Pneumatic	N/A	Flowing solutions at 70 °C and 2 °C	Not reported	Not reported	Not reported	> 80 s	Not reported	Yes	Not reported	Soft and flexible	Not reported	20
	Dielectric elastomer actuator with photonic coating	Morphological and areal changes	Mechanical/electrical	N/A (mechanical); < 3.5 kV (electrical)	Room temperature	Yes	Yes	Weak (aluminum-coated devices)	< 1 s	750	Yes	Yes	Soft and flexible	~ 4.1 W/m ²	Our work

4.6.14 Supporting Information Videos

Video S4.1. A real-time digital camera video of the electrical actuation of a stand-alone, aluminum-modified device due to the application of a square waveform (minima of 0 kV and maxima of 3.2 kV) at a frequency of 0.25 Hz.

Video S4.2. A real-time infrared camera video of the electrical actuation of a stand-alone, aluminum-modified device with a voltage of 3.2 kV. The device undergoes multiple sequential on/off cycles during the course of the video.

Video S4.3. A real-time infrared camera video of the electrical actuation of a squid silhouette-shaped, aluminum-modified device with a voltage of 3.2 kV. The device, which is positioned above a warm surface at a constant temperature and maintained under a constant thermal flux, undergoes multiple sequential on/off cycles during the course of the video.

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CHAPTER 5

Octopus-Inspired Camouflage and Signaling Systems from an Exceptionally Stable Nonacene

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5.1. Abstract

Multifunctional platforms that can adaptively modulate their color and appearance have attracted significant attention for applications as varied as signaling, displays, sensors, camouflage, biomedical imaging, and energy harvesting. However, the development of technologically-valuable camouflage and signaling platforms with adaptive visible and near-IR optical and fluorescent functionality has proven challenging because they must meet multiple demanding and frequently competing technical requirements. Herein, by drawing inspiration from the natural highly-evolved architecture and dynamic color-changing functionality of the blue-ringed octopus, we address this challenge by developing such platforms from a nonacene derivative with exceptional properties and then demonstrate that our systems feature an unprecedented combination of capabilities. Notably, the reported nonacene derivative is accessible via common synthetic procedures, readily solubilized and processed into films, color-tunable over a broad wavelength range, and over two orders of magnitude more stable than comparable acenes. The devices that incorporate this nonacene are straightforward to fabricate over large areas, compatible with dual-mode mechanical and electromechanical actuation, have rapid response times of < 460 ms, demonstrate little performance loss after > 500 on/off cycles, and autonomously self-repair upon catastrophic failure. Such multifunctional devices also exhibit peak absorptance and transmittance changes of $> 50\%$ and $> 40\%$, respectively, and can controllably modulate their visible coloration, near-infrared appearance, and fluorescence signature in tandem. Together, our findings represent a landmark and appear

poised to afford exciting fundamental and applications-oriented opportunities for not only organic chemistry and materials science but also for multiple other scientific disciplines.

5.2. Introduction

Multifunctional platforms that can adaptively modulate their color and appearance have attracted significant attention for applications in signaling,^[1,2] displays,^[3,4] sensors,^[5,6] camouflage,^[7–9] biomedical imaging,^[10,11] and energy harvesting.^[12,13] Such ubiquitous and technologically-valuable systems typically exhibit dynamic optical or spectroscopic properties that are enabled by constituent materials engineered for responsiveness to an external stimulus, e.g., a mechanical, electrical, magnetic, chemical, or thermal input.^[1,2,6] Within this context, the development of platforms that possess adaptive optical and fluorescent properties within both the visible and near-infrared (near-IR) regions of the electromagnetic spectrum has proven quite challenging, particularly for camouflage and signaling applications. Indeed, relatively few general classes of applicable systems have been explored to date, including dual-band electrochromic devices,^[14,15] photonic gels,^[16,17] metamaterials/metasurfaces,^[18,19] electroactive polymer-based systems,^[9,20,21] and biological protein films^[22,23] (Table S5.1). However, the known technologies have consistently struggled with multiple technical issues/limitations, such as complicated constituent material preparation procedures, challenging fabrication schemes over large areas, inadequate control over surface structure, the requirement for a single type of actuation strategy, limited functionality within multiple spectral windows, difficult incorporation of multiple optical capabilities, slow switching times, poor or inconsistent performance upon repeated actuation, and/or susceptibility to irreversible global failure (see the detailed comparison in Table S5.1).^[9,14–23] As such, there exists an

exciting opportunity and powerful incentive for the development of unique camouflage and signaling technologies that meet and exceed the requisite technical criteria, i.e., easily accessible constituent materials, straightforward fabrication and manufacturing procedures, controllable surface morphologies, responsiveness to multiple well-defined actuation mechanisms, tunable multispectral functionality in the visible and near-IR, additional optical capabilities such as fluorescence modulation, rapid response times, outstanding stability upon repeated actuation, and autonomous self-repair during extended operation.

For multifunctional color- and appearance-changing platforms, coleoid cephalopods, e.g., squid, octopuses, and cuttlefishes, represent exciting sources of inspiration because these animals are renowned for their unmatched camouflage and signaling abilities.^[24,25] For example, the blue-ringed octopus *Hapalochlaena lunulata* (*H. lunulata*) can adaptively modulate the coloration, contrast, brightness, and texture of its skin, as demonstrated by its ability to dramatically change appearance (Figure 5.1A).^[26] Such camouflage and signaling feats are enabled by a distribution of skin-embedded dynamic bio-optical systems, i.e., blue rings (Figure 5.1B), which consist of cells called iridophores, organs known as chromatophores, and proximal muscles.^[26] The iridophores, which are located within the interior of the blue rings, feature blue-green iridescence, i.e., narrowband reflectance, and are arranged to endow the rings with a vibrant color visible from multiple angles (Figure 5.1C and 5.1D). The chromatophores, which are located

beneath and around the blue rings, provide a pigmented dark brown background and are arranged to enhance the rings' color contrast with the surrounding skin (Figure 5.1C and 5.1D). The muscles, which partially cover (top muscles) and surround (peripheral muscles) the blue rings, tandemly contract and relax in order to change the local morphology/texture of the skin and thus modulate the individual rings' visibility and brightness (Figure 5.1C and Figure 5.1D). Notably, this entire sophisticated neuromuscularly-controlled process usually occurs within a second, and the rings can maintain their ability to repeatedly and stably change color and morphology throughout the octopus' lifetime. Given their remarkable functionality, the blue rings of the *H. lunulata* octopus represent unique and untapped paradigms for the development of multifunctional reconfigurable camouflage and signaling platforms with unprecedented combinations of capabilities.

Within the realm of camouflage and signaling technologies, one well-known class of organic materials that has received little-to-no attention is acenes, which are organic polycyclic aromatic hydrocarbons made up of linearly fused benzene rings.^[27,28] This lack of attention is surprising because acenes exhibit a variety of favorable characteristics, which include straightforward synthetic accessibilities, chemically-modular conjugated core structures, amenability to peripheral substitution and functionalization, compatibility with standard fabrication and processing procedures, well-understood tunable electronic and electrical properties, and stimuli-responsive optical and spectroscopic properties.^[27-31]

Historically, the shorter acenes (especially pentacene) have played pivotal roles not only in the evolution of materials chemistry by serving as synthetically- and theoretically-tractable model polycyclic aromatic hydrocarbons^[27–31] but also in the emergence of organic optoelectronics by serving as prototypical active materials in light-emitting diodes,^[32–34] photovoltaics,^[35,36] and field-effect transistors.^[37–39] More recently, significant research effort has been expended on the development of longer acenes (particularly nonacenes) because of their significance from a fundamental organic chemistry perspective and their theoretically-predicted superior properties for device applications (e.g., smaller band gaps, higher charge carrier mobilities, and tunable near-IR spectral features).^[40–44] However, the unambiguous synthesis and characterization of nonacene derivatives have only been reported in a handful of studies (7 total) to date, and the known compounds were produced in uncertain or moderate yields via complex procedures, featured poor stabilities of hours or (at most) days under impractical conditions, and often could not be easily solubilized or processed into thin films (see Table S5.2).^[45–51] Due to such key limitations, the device applications of nonacene derivatives have not been reported,^[45–51] and consequently, the true technological potential of these molecules remains unknown and unfulfilled.

Herein, we realize an artificial multifunctional camouflage and signaling platform with adaptive visible and near-IR optical and fluorescent capabilities by drawing inspiration from the natural highly-evolved architecture and dynamic functionality of the

blue rings of the *H. lunulata* octopus.^[26] For this purpose, we leverage the technical foundation established by predictions of favorable chemical, physical, and optical properties for judiciously-designed expanded acenes (specifically nonacene)^[40–51] and by our previous reports of infrared-reflecting and infrared-transmitting dielectric elastomer actuators.^[8,9] As such, we conceptualize a quad-layer device architecture consisting of a top transparent proton-conducting membrane (an electrode), an underlying patterned and variable-colored nonacene dye film, an intermediate soft and pliable acrylate elastomer layer, and a bottom transparent proton-conducting membrane (an electrode), with variants of this overall arrangement facilitating dual-mode mechanical and electromechanical artificial muscle-like actuation (Figure 5.1E and Figure 5.1F).^[8,9] Consequently, before actuation, we envision that our devices will possess relatively small, textured optically-active regions consisting of a brown inner circle surrounded by a blue outer annulus, with the appearance of these colored regions determined by the different chemical states of the nonacene dye within the film (Figure 5.1E, left and Figure 5.1F, left). This unactuated device configuration will thus mimic the closed form of *H. lunulata*’s blue rings (Figure 5.1C, left and Figure 5.1D, left).^[26] After actuation, we envision that our devices will simultaneously expand and flatten their optically-active regions (the brown inner circle and blue outer annulus), with the appearance of the colored regions dictated by the altered brightness and contrast of the nonacene dye-based film relative to the surroundings (Figure 5.1E, right and Figure 5.1F, right). This actuated device configuration will thus mimic the open form of *H. lunulata*’s blue rings (Figure 5.1C, right

and Figure 5.1D, right).^[26] In our platform, we theorize that the blue outer annular film with the nonacene in one chemical state will function like *H. lunulata*'s iridophores by furnishing bright coloration, the brown inner circular film with the nonacene in a different chemical state will function like *H. lunulata*'s chromatophores by augmenting background contrast, and the top and bottom proton-conducting membranes together with the acrylate elastomer layer will function like *H. lunulata*'s neurally-responsive musculature by allowing electromechanical actuation.^[26] Moreover, we anticipate that the predicted favorable electronic and spectroscopic properties of designer expanded nonacene dyes will endow our platform with unique near-IR optical and fluorescent capabilities. Altogether, we propose that this powerful design strategy will yield a color- and appearance-changing platform with unprecedented metrics and capabilities that meet or exceed those reported not only for the biological system but also for analogous artificial technologies.

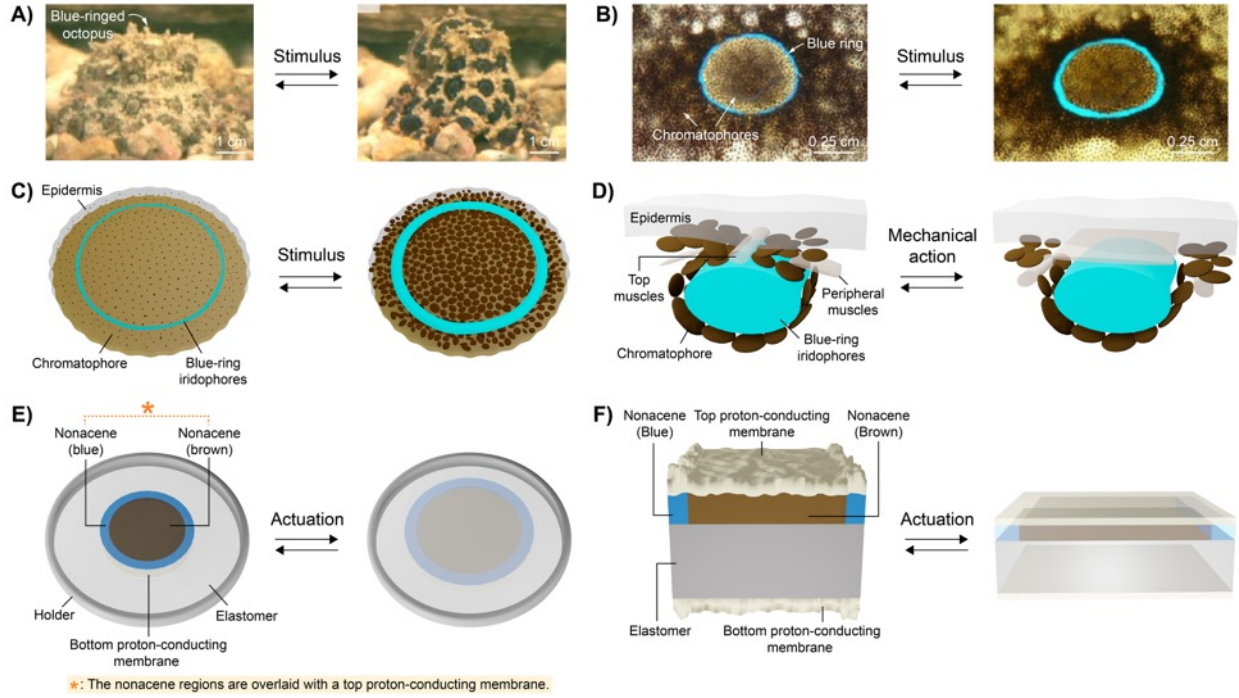


Figure 5.1. Biological Inspiration from the Blue-ringed Octopus for the Device Design.

(A) Pictures of a blue-ringed octopus (*H. lunulata*) reversibly changing the global appearance of its body.^[26] (B) Close-up pictures of an individual blue ring on the skin of the *H. lunulata* octopus reversibly changing its appearance in response to neural stimuli.^[26] (C) A side-view schematic of a typical blue ring from the *H. lunulata* octopus. Each natural blue ring represents a dynamic bio-optical system that consists of a blue-ring containing iridophore cells and a surrounding dark brown area containing chromatophore organs. The iridophores in the blue ring are arranged to provide vibrant blue-green iridescence, and the chromatophores are arranged to enhance the ring's color contrast. (D) A localized cross-sectional schematic of a typical blue ring from the *H. lunulata* octopus. The muscular system covers the blue-green iridescence from the iridophores by contracting (top muscles) and relaxing (peripheral muscles) in tandem or exposes the blue-green iridescence by relaxing (top muscles) and contracting (peripheral muscles) in tandem. (E) A side-view schematic of an octopus-inspired nonacene-based device before (left) and after (right) actuation. The optically active regions of the device consist of a blue outer annulus and a brown inner circle, with the appearance of these colored regions

determined by the different chemical states of the constituent nonacene dye. Upon actuation, the optically active regions can be reversibly altered from a contracted state with a small areal coverage to an expanded state with a large areal coverage, with a concomitant change in the appearance for the colored regions. (F) A cross-sectional schematic of the octopus-inspired nonacene-based device before (left) and after (right) actuation. Upon actuation, the optically active regions of the device can be reversibly altered from a textured surface morphology with a large overall thickness to a flattened surface morphology with a small overall thickness.

5.3. Molecular Design and Simulation

We began our efforts by introducing a strategic molecular design for a unique nonacene derivative. Towards this end, we drew inspiration upon the previous theoretical and experimental literature precedents for derivatized nonacenes (and expanded acenes in general),^[40–51] classical formalisms for derivatized and functionalized all-carbon tetrabenzopentacenes,^[52–54] and our previous report of the synthesis of nitrogen-containing tetrabenzopentacene analogues.^[55] In our design, we first started with the classic nonacene motif, which consists of nine ortho-fused benzene rings in a linear arrangement, and visualized incorporating two fused benzene rings, two fused pyridine rings, and two pendant alkyl-functionalized phenyl rings at peripheral locations on this motif (Figure 5.2A, left, tetrabenzononacene (TBN, **4**)). Here, the benzene rings (and pyridine rings) would enhance stability by allowing for cross-conjugation within the linear nonacene core, the nitrogen atoms in the pyridine rings would serve as specific sites that introduce responsiveness to a chemical stimulus (protonation), and the pendant alkyl-functionalized

phenyl rings would enhance solubility in common organic solvents (Figure 5.2A, left, (TBN, **4**)). For this neutral molecular framework, we postulated that protonation of the nitrogen atoms would lead to a rearrangement of the charge on the central nonacene core and thus would modify the molecule’s overall electronic structure (Figure 5.2A, center, square brackets). As such, the protonated (now positively charged) molecular framework would feature a dominant resonance structure consistent with a core all-carbon nonacene motif (Figure 5.2A, right, protonated tetrabenzononacene (PTBN, **4**+**2H**⁺)). Overall, the hypothesized tetrabenzononacene would be expected to possess stability, solubility, and stimulus-responsiveness and would thus represent an enticing synthetic target.

To justify our rational design strategy, we performed theoretical calculations for our tetrabenzononacene, with the goal of understanding its electronic structure and optical properties. For this purpose, we used density functional theory (DFT) to calculate the molecular orbitals for unprotonated tetrabenzononacene (TBN, **4**) and protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) and time-dependent DFT (TDDFT) that accounted for vibronic effects within the Franck-Condon approximation to simulate the visible and near-IR spectra for unprotonated tetrabenzononacene (TBN, **4**) and protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) (see the Supporting Information). For TBN (**4**), we found that the HOMO and LUMO orbitals were primarily localized on the central molecular core and possessed a relatively lower density at the termini, with corresponding energies of −5.01 eV and −3.11 eV, respectively (Figure 5.2B, left and Figure S5.1). For

PTBN (**4**+**2H**⁺), we found that the HOMO and LUMO orbitals were more distributed throughout the entire molecule and possessed a relatively higher density at the periphery, with corresponding energies of -9.59 eV and -8.07 eV, respectively (Figure 5.2B, right and Figure S5.2). Notably, protonation significantly altered the theoretically-predicted energies of the molecular orbitals for PTBN (**4**+**2H**⁺) with respect to TBN (**4**), suggesting improved solution-phase photophysical stability upon protonation.^[56,57] Additionally, for TBN (**4**), the simulated UV/Vis-NIR absorbance spectrum revealed two major peaks with the maxima located at ~ 616 nm and ~ 670 nm, as well as smaller side peaks (Figure 5.2C, left). For PTBN (**4**+**2H**⁺), the simulated UV/Vis-NIR absorbance spectrum likewise revealed two major peaks with the maxima located at ~ 796 nm and ~ 896 nm, as well as smaller side peaks (Figure 5.2C, right). Notably, protonation shifted the theoretically-predicted absorbance peaks by ~ 200 nm for PTBN (**4**+**2H**⁺) with respect to TBN (**4**), suggesting that solutions of the molecule would undergo a drastic color change upon protonation (Figure 5.2C). Together, the calculations validated our molecular design approach and indicated that our tetrabenzononacenes would display enhanced stability upon protonation and would exhibit readily-tunable, stimuli-responsive electronic and optical properties.

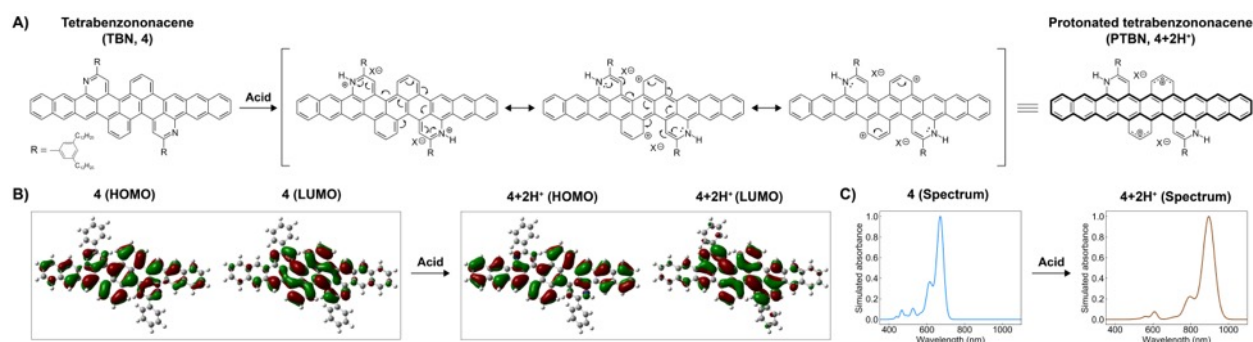


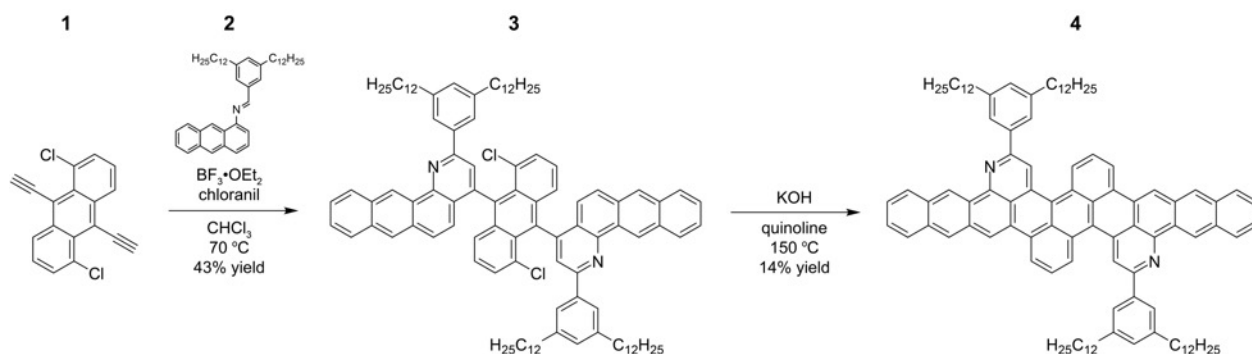
Figure 5.2. Molecular Design and Theoretical Calculations for the Tetrabenzononacene.

(A) The molecular design of a soluble, stable, and stimuli-responsive tetrabenzononacene, which alters its electronic structure upon protonation. (B) The calculated HOMOs and LUMOs for unprotonated tetrabenzononacene (TBN, **4**) (left) and protonated tetrabenzononacene (PTBN, **4+2H⁺**) (right). (C) The simulated UV/Vis-NIR absorbance spectra for unprotonated tetrabenzononacene (TBN, **4**) (left) and protonated tetrabenzononacene (PTBN, **4+2H⁺**) (right). Note that all the simulated absorbance spectra were normalized to unity.

5.4. Materials Synthesis and Characterization

We next proceeded to develop a strategy for the facile synthesis of tetrabenzononacene (**4**) (Scheme 1). For this purpose, we adopted our demonstrated literature protocols and employed the Lewis acid promoted aza-Diels–Alder (Povarov) reaction for the key synthetic steps.^[55,58-64] First, we synthesized the 1,5-dichloro-9,10-diethynylantracene (**1**) and didodecyl-substituted phenylmethanimine anthracene (**2**) starting materials according to known procedures.^[55,63] Second, we reacted (**1**) and (**2**) in the presence of boron trifluoride diethyl etherate (BF₃•OEt₂) as a Lewis acid mediator and chloranil as a sacrificial oxidant to obtain key intermediate

dinaphthoquinolineanthracene (**3**) with a yield of $\sim 43\%$ (note that (**3**) was isolated as two atropisomers). Last, we used a base-mediated cyclodehydrohalogenation reaction to form intramolecular C–C bonds between anthracene cores and pendant naphthylquinolines and to therefore convert intermediate (**3**) into target tetrabenzononacene (**4**) with a yield of $\sim 14\%$. Here, we note that the identities and purities of all intermediates, as well as the final product, were rigorously characterized with a combination of 1D ^1H NMR, ^{13}C NMR spectroscopy, and high-resolution mass spectrometry, as appropriate (see the Supporting Information and Figure S5.3–S5.10). Overall, our synthetic approach furnished tetrabenzononacene (**4**) in reasonable yield and good solubility under straightforward reaction conditions.



Scheme 5.1. Synthetic scheme for the preparation of tetrabenzononacene (**4**).

Given the size and complexity of our targeted molecule, we proceeded to definitively confirm the purity, chemical composition, and three-dimensional structure of tetrabenzononacene (**4**). For this purpose, we used a synergistic combination of size-exclusion chromatography with a refractive index detector (SEC-RI), matrix-assisted laser

desorption/ionization (MALDI) mass spectrometry, 1D ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, 2D ^1H – ^1H correlation spectroscopy (COSY), and 2D rotating frame nuclear Overhauser effect spectroscopy (ROESY) (see the Supporting Information). First, we assessed the purity of the tetrabenzononacene (**4**) via SEC-RI and found a single sharp peak in the corresponding chromatogram, confirming the pristine purity of our material and the absence of any contaminants (Figure 5.3A). Next, we determined the molecular weight of the tetrabenzononacene (**4**) via MALDI mass spectrometry and found an experimentally-measured $[\text{M}]^+$ ion mass of 1452.8 g/mol, which was in excellent agreement with the theoretically-predicted $[\text{M}]^+$ ion mass of 1453.0 g/mol (Figure 5.3B). In turn, we confirmed the chemical composition of tetrabenzononacene (**4**) via 1D ^1H and ^{13}C NMR spectroscopy (Figure 5.3C, Figure S5.9, and Figure S5.10). We found that the aromatic region of the 1D ^1H NMR spectrum featured 13 distinct aromatic proton resonances, with eleven of them integrating to independent protons and two of them integrating to overlapping protons, i.e., $\text{H}_\text{E}/\text{H}_\text{K}$ and $\text{H}_\text{F}/\text{H}_\text{G}$ (Figure 5.3C and Figure S5.9), and we found that the aromatic region of the 1D ^{13}C NMR spectrum featured the expected 28 distinct carbon resonances (Figure S5.10). These observations were fully consistent with the symmetric molecular structure of tetrabenzononacene (**4**), which contains exactly 13 aromatic protons and 28 aromatic carbon atoms in distinct chemical environments (Figure 5.3E). Subsequently, we assessed the relative spatial arrangement of the protons of tetrabenzononacene (**4**) by evaluating their spin-spin coupling via 2D ^1H – ^1H correlation spectroscopy (COSY). The corresponding COSY spectrum revealed three different multi-

nuclear spin systems, corresponding to protons located on the pendant phenyl rings (H_A and H_B , blue labels), the terminal naphthyl moieties (H_E , H_F , H_G , and H_H , green labels), and the central anthracene core (H_K , H_L , and H_M , red labels) (Figure 5.3D and Figure 5.3E). Furthermore, to complement the COSY analysis, we again probed the relative spatial arrangement of the protons of tetrabenzononacene (**4**) and identified the remaining unassigned singlet proton resonances via 2D rotating frame Overhauser enhancement spectroscopy (ROESY). The corresponding ROESY spectrum revealed detailed through-space interactions between the already assigned multi-nuclear spin systems (H_B , H_E , H_H , H_K , and H_M) (Figure 5.3D) and the unassigned singlet proton resonances (H_C , H_D , H_I , and H_J , black labels) (Figure 5.3E, black arrows, and Figure S5.11). When considered together, these experiments confirmed the structure and identity of tetrabenzononacene (**4**) with no ambiguity.

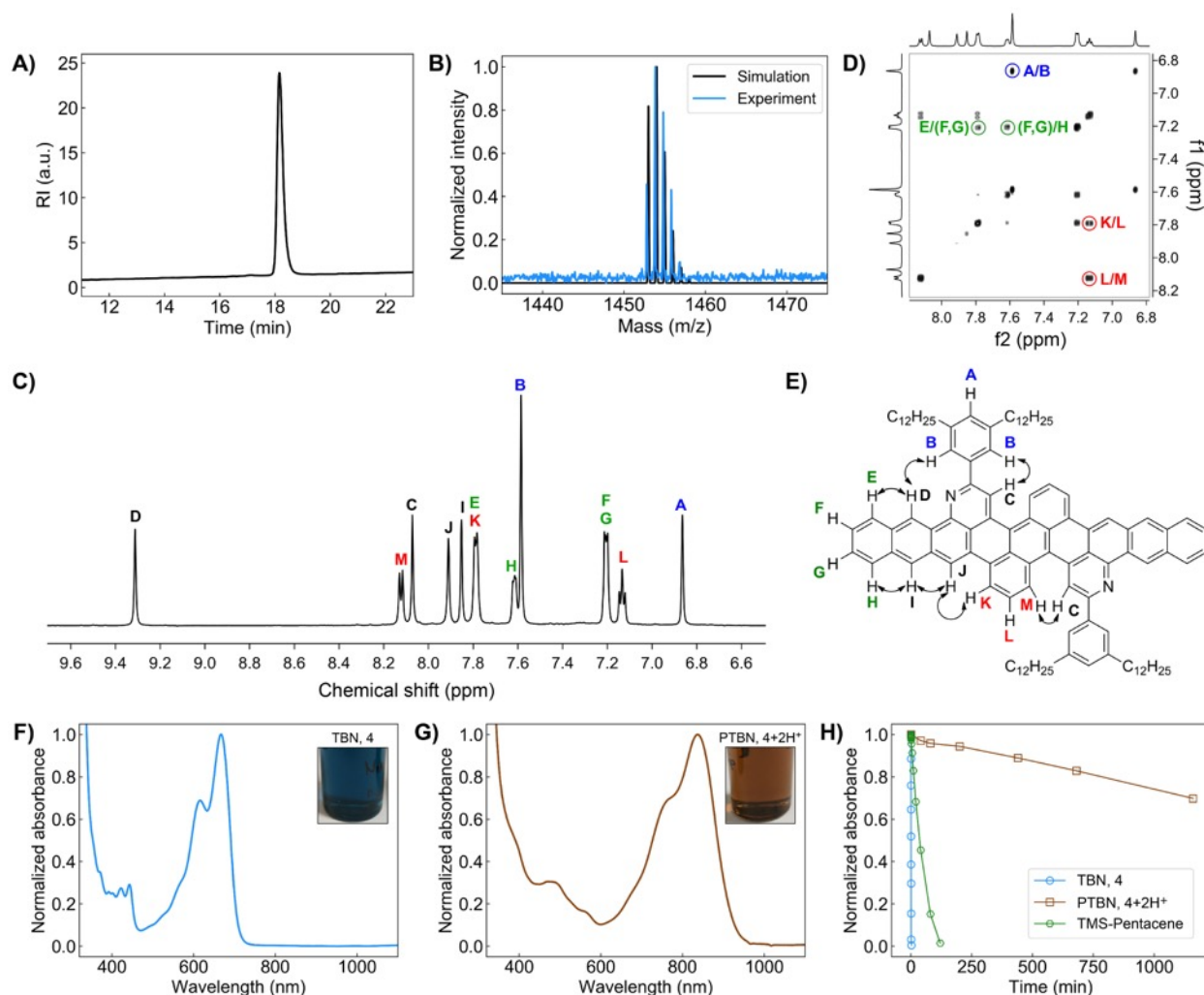


Figure 5.3. Characterization of the Tetrabenzononacene. (A) The SEC-RI chromatogram for tetrabenzononacene (4). (B) The MALDI spectra for tetrabenzononacene (4). The experimental spectrum (blue) was overlaid on the simulated spectrum (black). (C) The 1D ¹H NMR spectrum for tetrabenzononacene (4). (D) The 2D ¹H-¹H COSY spectrum for tetrabenzononacene (4). (E) The definitive molecular structure of tetrabenzononacene (4). The arrows indicated specific through-space interactions between different protons observed in the ROESY spectrum. Note that the assignment of protons in the structure was performed analyzing the combined 1D ¹H NMR, COSY, and ROESY spectra. (F) The UV/Vis-NIR absorbance spectrum for unprotonated tetrabenzononacene (4). The inset is a picture of unprotonated tetrabenzononacene (TBN, 4) in solution. (G) The

UV/Vis-NIR absorbance spectrum for protonated tetrabenzononacene (PTBN, **4**+**2H**⁺). The inset is a picture of protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) in solution. Note that all the simulated absorbance spectra were normalized to unity. (**H**) Plots of the normalized absorbance as a function of time for solutions of unprotonated tetrabenzononacene (TBN, **4**) (blue, circles), protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) (brown, squares), and a TMS-pentacene reference (green, hexagons).

Having obtained our target molecule, we systematically investigated its electronic and optical properties solution. For this purpose, we solubilized tetrabenzononacene (**4**) in a standard organic solvent (chloroform) and interrogated such solutions in the presence and absence of trifluoroacetic acid (TFA) with both UV/Vis-NIR spectroscopy and fluorescence spectroscopy (see the Supporting Information). First, we prepared solutions of unprotonated tetrabenzononacene (TBN, **4**), which featured a vibrant blue color (Figure 5.3F). The corresponding UV/Vis-NIR absorbance spectrum revealed a cluster of peaks at ~ 422 nm and ~ 443 nm, a major peak with the maxima located at ~ 616 nm and ~ 668 nm, and an absorption onset of ~ 707 nm that indicated a band gap of ~ 1.75 eV (Figure 5.3F), in good qualitative agreement with the TDDFT simulations (Figure 5.2C, left). The fluorescence emission spectrum revealed a high intensity and a clear Stokes shift, with the major peak featuring a maximum at ~ 702 nm and a shoulder at ~ 764 nm (Figure S5.12). Next, we prepared solutions of protonated tetrabenzononacene (PTBN, **4**+**2H**⁺), which featured a dark brown color (Figure 5.3G). The corresponding UV/Vis-NIR absorbance spectrum revealed a cluster of peaks at ~ 475 nm and ~ 560 nm, a major peak with the maxima located at ~ 837 nm and ~ 755 nm (Figure 5.3G), and an absorption

onset of ~ 921 nm that indicated a smaller band gap of ~ 1.35 eV, in good qualitative agreement with the TDDFT simulations (Figure 5.2C, right). The fluorescence emission spectrum revealed very weak (negligible) intensity, presumably due to the quenching of the fluorescence upon protonation (Figure S5.12). These measurements were remarkably consistent with expectations from our rational molecular design approach and demonstrated that a chemical stimulus (protonation) could dramatically shift both the solution-phase absorbance and the visual appearance of our tetrabenzononacene material.

We proceeded to investigate the photophysical stability of our tetrabenzononacenes both before and after protonation in solution under ambient conditions. For this purpose, we initially prepared solutions of TBN (**4**), PTBN (**4**+**2H**⁺), and a reference functionalized pentacene with well-known improved stability (6,13-bis((trimethylsilyl)ethynyl)pentacene, abbreviated as TMS-pentacene).^[57] We then recorded the evolution of these three solutions' absorptances as a function of time with UV/Vis-NIR spectroscopy and calculated the constituent molecules' half-lives (defined as the time needed to decrease the initial maximum peak intensity by 2-fold) under illumination with high-intensity broadband light at an effective power of ~ 460 mW/cm² (see the Supporting Information). For TBN (**4**), the measured solution-phase half-life was 0.22 ± 0.01 minutes at a peak wavelength of ~ 668 nm (Figure 5.3H, blue). For PTBN (**4**+**2H**⁺), the measured solution-phase half-life was 3241 ± 328 minutes at a peak wavelength of ~ 837 nm (Figure 5.3H, brown). For the reference TMS-pentacene, the

measured solution-phase half-life was 21.6 ± 1.10 minutes at a peak wavelength of ~ 642 nm (Figure 5.3H, green). Excitingly, TBN (**4**) and PTBN (**4**+**2H**⁺) were both far more stable than all previously reported nonacene derivatives in solution,^[45-51] and PTBN (**4**+**2H**⁺) was over 150 times more stable than the TMS-pentacene reference in solution. Moreover, both the TBN (**4**) and the PTBN (**4**+**2H**⁺) could be stored in standard organic solvents for extended periods of time (> 6 months) in the dark, with their coloration and appearance remaining virtually unchanged. The observations were in agreement with the DFT predictions of improved photophysical stability for our molecules. These experiments were again consistent with expectations from our rational molecular design approach, and conclusively demonstrated that our protonated and unprotonated tetrabenzononacenes featured remarkable stabilities.

5.5. Device Integration and Testing

Having confirmed the solubility and solution-phase stability of unprotonated tetrabenzononacene (TBN, **4**), we proceeded to evaluate the suitability of films processed from this molecule for applications in mechanically-actuated appearance-changing devices. Thus, we used our established techniques^[8,9] to fabricate tri-layer devices that featured microstructured morphologies and consisted of a top transparent proton-conducting membrane, a central square-shaped large-area film from TBN (**4**), and a bottom acrylate elastomer layer (see Figure 5.4A and the Supporting Information). We then interrogated the reconfigurable morphological characteristics and tunable optical properties of these

devices with atomic force microscopy (AFM) and UV/Vis-NIR spectroscopy, respectively, before and after actuation with equiaxial strain (Figure 5.4A and see the Supporting Information). Prior to mechanical actuation, the tri-layer devices' surfaces primarily consisted of large sparse microstructures with widths on the order of ten microns, peak-to-valley heights of a couple of microns, and surface protrusions with sizes of a few hundred nanometers, as confirmed by representative 3D topographic AFM images (Figure 5.4B, left). The tri-layer devices from TBN (4) films were relatively small in area with a vivid dark blue color, and their corresponding UV/Vis-NIR spectra indicated high total absorptances of 49 ± 4 % at ~ 612 nm and 31 ± 3 % at ~ 676 nm; low total transmittances of 46 ± 4 % at ~ 612 nm and 63 ± 2 % at ~ 676 nm (for which the specular components were dominant due to the low density and large size of the surface microstructures); and negligible total reflectances of 5.3 ± 0.1 % at ~ 612 nm and 6.0 ± 0.1 % at ~ 676 nm (Figure 5.4C, left and Figure S5.13). After mechanical actuation, the tri-layer devices' surfaces primarily consisted of relatively smaller sparse microstructures with widths on the order of a couple of microns, peak-to-valley heights of approximately hundreds of nanometers, and surface protrusions with sizes of a hundred nanometers, as confirmed by representative 3D topographic AFM images (Figure 5.4B, right). The tri-layer devices from TBN (4) films were now larger in area with a light blue color, and their corresponding UV/Vis-NIR spectra indicated decreased absorptances of 21 ± 3 % at ~ 612 nm and 12 ± 2 % at ~ 676 nm; increased total transmittances of 73 ± 2 % at ~ 612 nm and 81 ± 1 % at ~ 676 nm (for which the specular components dominated to a lesser extent because

of the reduced size of the surface microstructures); and negligible total reflectances of $6.2 \pm 0.6 \%$ at $\sim 612 \text{ nm}$ and $7.2 \pm 0.6 \%$ at $\sim 676 \text{ nm}$ (Figure 5.4C, right and Figure S5.13). Consequently, the application of a mechanical stimulus (equiaxial strain) directly modulated our TBN (**4**)-based devices' surface morphologies (i.e., by > 3 -fold) and substantially changed their appearance and optical characteristics (i.e., decreased their peak absorptances by $\sim 60\%$ and increased their peak transmittances by $\sim 60\%$).

We furthermore proceeded to evaluate the suitability of films processed from the even more stable protonated tetrabenzononacene (PTBN, **4+2H⁺**) for applications in mechanically-actuated appearance-changing devices. Thus, we again used our established techniques^[8,9] to fabricate tri-layer devices that featured microstructured morphologies and consisted of a top transparent proton-conducting membrane, a central square-shaped large-area film from PTBN (**4+2H⁺**), and a bottom acrylate elastomer layer (Figure 5.4D and see the Supporting Information). We then similarly interrogated the reconfigurable morphological characteristics and tunable optical properties of these devices with AFM and UV/Vis-NIR, respectively, before and after actuation with equiaxial strain (see Figure 5.4D and the Supporting Information). Prior to mechanical actuation, the tri-layer devices' surfaces primarily consisted of large sparse microstructures with widths of several microns and peak-to-valley heights of hundreds of nanometers (note that the structures differed in distribution and size when compared to those measured in films from TBN (**4**)), as confirmed by representative 3D topographic AFM images (Figure 5.4E, left). The

tri-layer devices from PTBN (**4+2H⁺**) films were relatively small in area with a dark brown color, and their corresponding broadened UV/Vis-NIR spectra indicated high total absorptances of $44 \pm 1 \%$ at ~ 792 nm; low total transmittances of $51 \pm 1 \%$ at ~ 792 nm (for which the specular components were the only significant contribution due to the low density and smaller sizes of the microstructures); and negligible total reflectances of $5.0 \pm 0.1\%$ at ~ 792 nm (Figure 5.4F, left and Figure S5.14). After mechanical actuation, the tri-layer devices' surfaces were flattened and primarily consisted of smaller and even sparser microstructures with widths of a micron and peak-to-valley heights of tens of nanometers, as confirmed by representative 3D topographic AFM images (Figure 5.4E, right). The tri-layer devices from PTBN (**4+2H⁺**) films were now larger in area with a light brown color, and their corresponding broadened UV/Vis-NIR indicated decreased total absorptances of $21 \pm 2 \%$ at ~ 792 nm; increased total transmittances of $72 \pm 2 \%$ at ~ 792 nm (for which the specular components were the only significant contribution due to the flattened surface morphologies); and negligible total reflectances of $6.1 \pm 0.2 \%$ at ~ 792 nm (Figure 5.4F, right and Figure S5.14). Consequently, the application of a mechanical stimulus (equiaxial strain) directly modulated our PTBN (**4+2H⁺**)-based devices' surface morphologies (i.e., by > 3 -fold) and again substantially changed their appearance and optical characteristics (i.e., decreased their peak absorptances by $\sim 50\%$ and increased their peak transmittances by $\sim 40\%$).

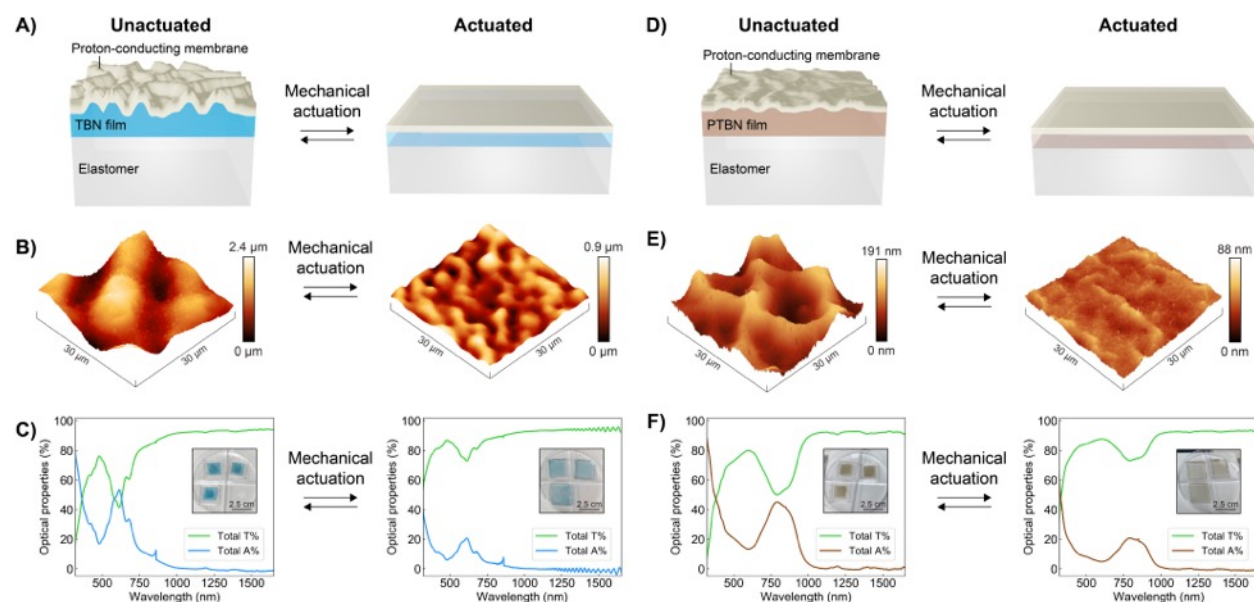


Figure 5.4. Mechanical Modulation of the Tri-layer Tetrabenzononacene-based Devices.

(A) A cross-sectional schematic of the change in the surface morphology, geometry, and color for an unprotonated tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. (B) Representative 3D topographic AFM images for a unprotonated tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. (C) Representative UV/Vis-NIR spectra for the total absorption (Total A%, blue line) and total transmission (Total T%, green line) for an unprotonated tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. (D) A cross-sectional schematic of the change in the surface morphology, geometry, and color for a protonated tetrabenzononacene (PTBN, **4**+**2H**⁺)-based device before (left) and after (right) mechanical actuation. (E) Representative 3D topographic AFM images for a protonated tetrabenzononacene (PTBN, **4**+**2H**⁺)-based device before (left) and after (right) mechanical actuation. (F) Representative UV/Vis-NIR spectra for the total absorption (Total A%, blue line) and total transmission (Total T%, green line) for a protonated tetrabenzononacene (PTBN, **4**+**2H**⁺)-based device before (left) and after (right) mechanical actuation.

After demonstrating modulation of our rudimentary devices' color intensity via mechanical actuation, we subsequently sought to demonstrate that analogous appearance changes could be achieved within the context of our targeted octopus blue ring-like platform via electromechanical actuation. For this purpose, we fabricated a quad-layer device architecture consisting of a top proton-conducting membrane electrode; an intermediate pre-patterned film (consisting of a brown inner circular area from PTBN ($4+2\text{H}^+$) and an outer annular area from TBN (**4**); an underlying intermediate acrylate elastomer layer, and a bottom proton-conducting membrane electrode (Figure 5.5A, Figure S5.15, and see the Supporting Information). We then simultaneously investigated these platforms' electromechanical characteristics, e.g., voltage-dependent strain and response time, and visible optical properties, e.g., changes in color brightness, according to established methodologies under ambient conditions (i.e., in air and without any encapsulation) (see the Supporting Information).^[8,9] For such devices, we observed that the application of a bias (an electrostatic voltage) between the top and bottom proton-conducting electrodes resulted in the simultaneous compression and lateral expansion of the optically active region, which consisted of a circular pre-patterned film/acrylate elastomer bilayer arrangement (Figures 5.5A and 5.5B; Video S5.1). The systems' areal strain featured a nearly exponential dependence on the applied bias, with a voltage of ~ 3.2 kV resulting in maximum strains of $\sim 41\%$ for the brown inner circle and $\sim 86\%$ for the blue outer annulus, as demonstrated by a representative device (Figure 5.5C, top; Video S5.1). The systems' relative color brightness exhibited the same dependence on the

applied bias, with a voltage of ~ 3.2 kV resulting in a maximum brightness of $\sim 106\%$ for the brown inner circle and $\sim 116\%$ the blue outer annulus, as demonstrated by a representative device (Figure 5.5C, bottom; Video S5.1). Such changes presumably resulted from decreased peak absorptances and increased peak transmittances during electromechanical modulation of the quad-layer platforms, in agreement with the spectral changes observed during mechanical modulation of analogous tri-layer devices (Figure 5.4C and 5.4F). Moreover, for our devices, we found that the application of a square waveform at a frequency of 0.5 Hz (minima of 0 kV and maxima of ~ 2.9 kV) enabled us to directly evaluate their response times (defined as the rise time from 10% to 90% of the maximum areal strain change) (Figure 5.5D). The systems' areal strain recorded over multiple on/off cycles furnished response times of ~ 460 ms for the brown inner circle and ~ 350 ms for the blue outer annulus, as demonstrated for a representative device's three consecutive on/off cycles (Figure 5.5D, top). The systems' relative color brightness recorded over multiple on/off cycles furnished nearly identical response times and also revealed that the brightness modulation was fully reversible and almost perfectly tracked the changes in areal strain (Figure 5.5D, bottom). Taken together, these experiments indicated that the dynamic appearance-changing optical functionality of our electromechanically-actuated artificial systems was quite similar to that reported for the natural blue rings of the *H. lunulata* octopus.

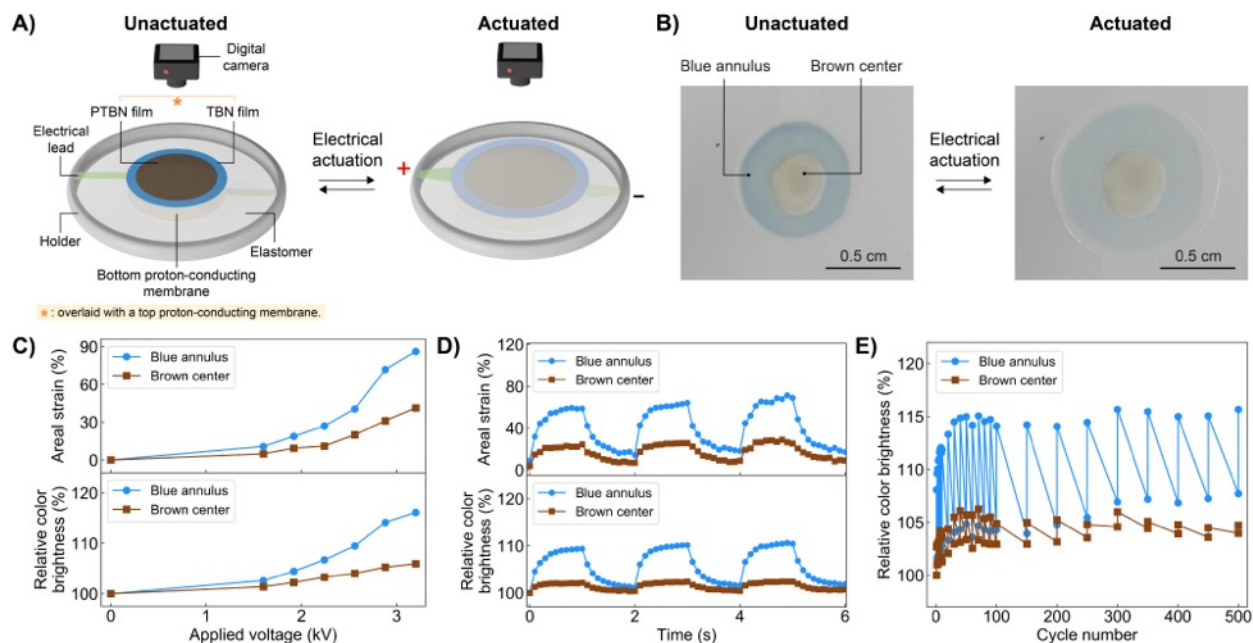


Figure 5.5. Electromechanical Modulation and Optical Functionality of the Blue Ring-like Quad-layer Devices. (A) A side-view schematic of a blue ring-like device before (left) and after (right) electrical actuation, illustrating the change in the areal coverage and color brightness for the device's optically-active regions (i.e., the blue outer annulus from TBN (4) and the brown inner circle from PTBN ($4+2\text{H}^+$)). (B) Digital camera images of a representative blue ring-like device's optically active regions before (left) and after (right) electrical actuation. (C) (Top) Plots of the areal strain as a function of the applied voltage for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device. (Bottom) Plots of the simultaneous relative color brightness as a function of the applied voltage for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of the same device. (D) (Top) Plots of the areal strain as a function of time over three consecutive on/off electrical actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device. (Bottom) Plots of the simultaneous relative color brightness as a function of time over three consecutive electrical actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of the same device. (E) Plots of the relative color brightness as a function of cycle number for the blue

outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device for over 500 repeated electrical actuation cycles.

Having validated the optical functionality of our octopus blue ring-like devices, we sought to further challenge the devices by evaluating their stabilities during repeated and extended electromechanical actuation. To achieve this goal, we fabricated multiple (10) quad-layer devices and actuated them via the application of a square waveform with a frequency of 0.5 Hz (minima of 0 kV and maxima of ~ 2.9 kV) for hundreds of on/off cycles under ambient conditions (i.e., in air and without any encapsulation) (see the Supporting Information). For ~ 70 % of our devices, we observed that they exhibited rapid and reversible changes in area and color brightness during long-term operation. For example, a representative device fully maintained its optical functionality over > 500 continuous on/off cycles (Figure 5.5E). Here, we generally observed no visible evidence of electrode delamination or local color changes indicative of materials degradation during the tests (see, for instance, Video S5.1). For the other ~ 30 % of the devices, we likewise observed that they first exhibited rapid and reversible changes in area and color brightness, unexpectedly experienced transient local electrical breakdown and malfunctioned (i.e., catastrophically failed analogously to classic dielectric elastomer actuators),^[66] and quite surprisingly resumed operation merely several seconds later. For example, a representative device stopped functioning at ~ 385 independent on/off cycles due to electrical breakdown but then spontaneously self-repaired and again started functioning (albeit with slightly degraded performance) for a net total of > 550 cycles

(Figure S5.16). Here, we initially observed a noticeable change in color at the breakdown site upon device failure and then subsequently observed a further change in color at the same site upon spontaneous device self-repair (Figure S5.17). These color changes suggested that the current discharged via the localized conductive pathway formed in our capacitor-like device (a typical electrical breakdown mechanism for dielectric elastomer actuators) converted the tetrabenzononacene material into an electrical insulator at the breakdown site, thus preventing further current leakage/spikes and affording a resumption of normal operation.^[67] Altogether, the combined wholly unexpected and surprising findings not only further underscored the exceptional stability of our tetrabenzononacene materials in the solid state but also revealed that our appearance-changing devices featured an absolutely unprecedented combination of long-term stability and propensity for self-repair in ambient conditions.

We furthermore proceeded to show that our octopus-inspired platforms were not only effective, rapid, and stable camouflage systems but moreover featured additional signaling capabilities. For this purpose, we actuated our devices with a square waveform (frequency of 0.5 Hz, as well as minima of 0 kV and maxima of ~ 3.2 kV) and visualized their fluorescence signatures with a digital camera under constant ultraviolet (UV) irradiation (Figure 5.6A and see the Supporting Information). Before electrical actuation, we observed that the devices' outer annular regions appeared quite bright and featured high fluorescence intensities, presumably due to strong visible fluorescence emission from

the TBN (**4**)-based films, and that the same devices' inner circular regions appeared dark, presumably due to negligible (quenched) fluorescence emission from the constituent PTBN (**4**+**2H**⁺)-based films (Figure 5.6A, left; Figure 5.6B, left; Video S5.2). After electrical actuation, we observed that the devices' outer annular regions had expanded in area and appeared relatively less bright, with substantially reduced fluorescence intensities, and that the same devices' inner circular regions had expanded in area but still remained quite dark, with slightly reduced fluorescence intensities (Figure 5.6A, right; Figure 5.6B, right; Video S5.2). These findings were consistent with the fluorescence spectra collected for our TBN (**4**) and PTBN (**4**+**2H**⁺) molecules in solution (Figure S5.12). Furthermore, we observed that the relative fluorescence intensity of the devices' outer annular regions and inner circular regions could be reversibly, rapidly, and repeatedly modulated, as demonstrated by three consecutive actuation cycles for a representative device after 200 previous on/off cycles (Figure 5.6C). As such, our devices generally maintained their outstanding electromechanical performance and figures of merit even under UV irradiation. These experiments further underscored the unprecedented stability of our devices and their constituent tetrabenzononacene films even under extreme conditions, while also demonstrating that the devices possessed visible camouflage and signaling characteristics analogous to those of the natural blue rings of the *H. lunulata* octopus.

Last, we demonstrated that our octopus-inspired platforms could not only alter their appearance within the visible but could also display analogous camouflage

functionality in the near-IR. For this purpose, we actuated our devices with a square waveform (frequency of 0.5 Hz, as well as minima of 0 kV and maxima of ~ 3.2 kV) and visualized their near-IR appearances with an infrared camera under near-IR irradiation (Figure 5.6D and see the Supporting Information). Before electrical actuation, we observed that the devices' outer annular regions featured a high contrast with the surrounding background, presumably due to the TBN (**4**)-based films' relatively weak absorption of incident near-IR light, and that the same devices' inner circular regions appeared similar to the surrounding background, presumably due to the PTBN (**4**+**2H**⁺)-based films' strong absorption of incident near-IR light (Figure 5.6D, left; Figure 5.6E, left; Video S5.3). After electrical actuation, we observed that the devices' outer annular regions had expanded in area and featured a relatively reduced contrast with the surrounding background and that the same devices' inner circular regions had expanded in area but still appeared similar to the surrounding background (Figure 5.6D, right; Figure 5.6E, right; Video S5.3). These findings were consistent with the absorptance and transmittance spectra collected for our protonated and unprotonated tetrabenzononacene in the solid state (Figure 5.4). Furthermore, we observed that the near-IR signatures and appearances of the devices' outer annular regions and inner circular regions could be reversibly, rapidly, and repeatedly modulated, as demonstrated by three consecutive actuation cycles for a representative device after 200 previous on/off cycles (Figure 5.6F). As such, our devices maintained their outstanding electromechanical performance and figures of merit even within a different technologically-valuable spectral window. These experiments

demonstrated that our platforms possessed multifunctionality beyond that achieved by the natural blue rings of the *H. lunulata* octopus and thus underscored their tremendous promise for advanced active camouflage and signature management applications.

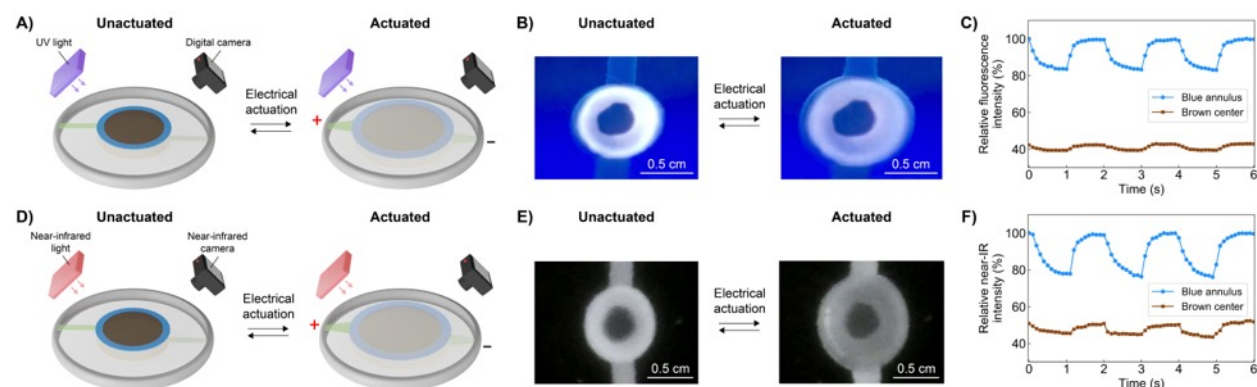


Figure 5.6. Fluorescence and Near-IR Functionality of the Blue Ring-like Quad-layer Tetrabenzononacene-based Devices. (A) Schematics of the fluorescence imaging of a blue ring-like device before (left) and after (right) electrical actuation. (B) Representative fluorescence images of a blue ring-like device before (left) and after (right) electrical actuation. (C) Plots of the relative fluorescence intensity as a function of time over three consecutive electrical actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device after 200 continuous on/off cycles. (D) Schematics of the near-IR imaging of a blue ring-like device before (left) and after (right) electrical actuation. (E) Representative near-IR camera images of a blue ring-like device before (left) and after (right) electrical actuation. (F) Plots of the relative near-IR intensity as a function of time over three consecutive actuation cycles for the blue outer annulus (blue circles) and the brown inner circle (brown squares) of a representative blue ring-like device after 200 continuous on/off cycles.

5.6. Discussion and Conclusion

In conclusion, we have reported the facile synthesis and unambiguous characterization of a processable, stimuli-responsive, and remarkably stable nonacene derivative, and our findings are significant from a materials chemistry perspective for several reasons. First, our generalizable synthetic approach furnished the desired nonacene derivative in reasonable yield and outstanding purity under straightforward reaction conditions, thus adding to the few rare examples of nonacenes reported in the literature to date. Second, our molecular-level design strategy affords expanded aromatic compounds that are not only readily soluble in standard organic solvents but can be easily processed into films with areas of multiple square centimeters on common substrates. Third, the nonacene derivative features stimuli-responsive optical, spectroscopic, and fluorescent properties within the visible and near-IR, including the ability to shift its main absorbance peak by nearly 170 nm and to simultaneously change its color from blue to brown. Last, the nonacene derivative features excellent stability in solution and in the solid state, which far exceeds that reported for any other nonacene variant under comparable conditions, and even more impressive photostability under direct high-intensity irradiation, which exceeds that found for a representative 6,13-substituted pentacene designed for stability by > 150 -fold. Overall, the reported nonacene derivative features properties and characteristics that dramatically improve upon those of the known analogous molecules (Table S5.2).

Correspondingly, we have leveraged our nonacene derivative’s outstanding properties for the design, fabrication, and testing of *H. lunulata* octopus-inspired multifunctional camouflage and signaling platforms, and our findings are significant from a materials engineering perspective for multiple reasons. First, our bioinspired platforms are fabricated via straightforward procedures and constitute the only reported utilization of any nonacene in a dielectric elastomer actuator (or any device in general), thus highlighting the processability of our new nonacene derivative. Second, the platforms are compatible with both mechanical and electromechanical actuation strategies and demonstrate outstanding corresponding figures of merit, which include > 10-fold surface micro- and nano-structure size modulation, a > 50% change in peak absorptance, a > 40% change in peak transmittance, a maximum areal strain of $\sim 90\%$, and a rapid response time of < 460 ms. Third, the systems not only exhibit almost little loss in performance after > 500 on/off cycles at an applied voltage of 3.2 kV but also exhibit the ability to autonomously self-repair upon catastrophic failure during repeated actuation, thus further underscoring the outstanding stability of our nonacene under harsh conditions. Last, our systems feature fully reversible adaptive optical and spectroscopic properties within both the visible and near-infrared, including controllable modulation of their color brightness in the visible, appearance contrast with the surroundings in the near-IR, and global fluorescence signature intensity (all in a single device configuration). Altogether, the reported platforms feature a unique combination of capabilities that are unrivaled among comparable technologies (Table S5.1).

Moving forward, the significant breakthroughs inherent to our findings appear poised to afford a range of exciting future scientific and technological opportunities. First, our molecular-level design strategy and generalizable synthetic methodology could be modified for the preparation of even longer acenes, allowing for the fundamental study of the size- and functionalization-dependent evolution of their electronic structures and chemical reactivities. Second, the demonstrated solubility, processability, and stability of our nonacene derivatives may facilitate the further exploration of their intrinsic properties within the context of established organic optoelectronic devices, such as light-emitting diodes, photovoltaics, and field-effect transistors. Third, our robust bioinspired platforms might be further enhanced via the judicious incorporation of additional optically-active materials or advanced photonic structures, further extending their capabilities into other spectral ranges or adding additional light-manipulating functionalities. Fourth, the further study of our platforms' unexpected autonomous self-repairing abilities could enable the development of general strategies for mitigating failure mechanisms (and thus enabling long-term operation) among dielectric elastomer actuators and other high-voltage capacitor-type devices. Last, our demonstrated straightforward device design and fabrication approach should allow for the engineering and development of platforms with more sophisticated layouts, including large-area camouflage systems that incorporate multiple distinct pixel types for signature management applications and small-area displays with high pixel densities for signaling applications. Given such possibilities, our discoveries may afford fundamental and applications-focused advances in numerous

research areas, including organic optoelectronic displays, bioinspired and biomimetic photonics, visible and infrared stealth technologies, biomedical imaging devices, energy harvesting systems, and soft actuators and robots.

5.7. Supporting Information

5.7.1. Theoretical Calculations

The initial structure of tetrabenzononacene were obtained from the JSME molecule editor.^[68] The ground state geometry and vibrational properties of the unprotonated and protonated tetrabenzononacene molecules were calculated based on first-principles density-functional theory (DFT) utilizing the B3LYP functional with a 6-311G (d,p) basis set, as implemented in the Gaussian 16 software package.^[69–71] This functional was shown to be accurate for calculations of optical properties of small molecules.^[72,73] Optimized geometries were verified by ensuring no imaginary frequencies in normal mode calculations. Because larger polyacene chains tend to form an open-shell singlet ground state,^[42,47,74] the unprotonated and protonated tetrabenzononacene molecules were checked for an open-shell nature using unrestricted broken symmetry DFT⁴². The ground-state energy predicted using this approach was within 10^{-6} eV of the restricted DFT, and no spin contamination was observed for all cases ($\langle S^2 \rangle = 0$). Additionally, all occupied molecular orbitals were doubly occupied and closed-shell.

Tamm-Dancoff time-dependent DFT (TDDFT) was utilized to describe the optical absorption of the compounds including vibronic effects via the vertical gradient (VG) Franck-Condon method. The optical absorption was computed as an excitation from the vibrational ground state of the electronic ground state to the electronic and vibrational excited states of the compounds. Within the VG approach, the excited-state normal modes were assumed to be the same as those of the ground state and the excited state geometry

is extrapolated by excited-state energy gradient.^[75,76] This method was shown to reproduce the full Adiabatic Hessian optical spectra of large molecules at a lower computational cost.^[76,77] The contribution of five low-energy excited states was considered in absorption spectra for both molecules in order to describe all states contained within the measured energy window. The vibronic spectra of these low-energy excited states were averaged in order to obtain a final absorption spectrum.

Natural transition orbital analysis was used to understand the nature of the lowest vertical excitation via TDDFT. The electron and hole orbitals represent the change in electron density during the excitation.

5.7.2. Chemical Synthesis, Purification, and Characterization

5.7.2.1. Materials

All chemicals and solvents were purchased from Sigma Aldrich, Acros Organics, Aurum Pharmatech Inc., or Combi-Blocks. The toluene and chloroform were dried with 3Å molecular sieves and stored under argon. The glassware was oven dried at 150–200 °C. The reactions were performed under dry argon, unless otherwise noted. 3,5-didodecylbenzaldehyde and 1,5-dichloro-9,10-diethynylanthracene (**1**) were prepared according to previously established routes.^[53,61]

5.7.2.2. Detailed Synthetic Protocols

5.7.2.2.1. *N*-(3,5-didodecylbenzylidene)anthracene-1-amine (**2**)

First, a mixture of 1-anthrylamine (2.88 g, 14.9 mmol), 3,5-didodecylbenzaldehyde (6.00g, 13.6 mmol), glacial acetic acid ($\sim$ 0.1 mL), molecular sieves (10.0 g), in toluene (200 mL) was sealed in a pressure vessel and stirred at 150 °C for 5 days. Next, the reaction mixture was cooled to room temperature and filtered through Celite. Subsequently, the solvent was removed *in vacuo*. Last, the crude product of (**2**) was purified by dissolution into chloroform and precipitation from methanol to yield a brown oil (6.80 g, 81% yield): ^1H NMR (500 MHz, CDCl_3) δ 8.88 (s, 1H), 8.58 (s, 1H), 8.43 (s, 1H), 8.08 – 7.98 (m, 2H), 7.88 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 1.6 Hz, 2H), 7.53 – 7.41 (m, 3H), 7.20 (t, J = 1.7 Hz, 1H), 6.98 (d, J = 6.9 Hz, 1H), 2.71 (t, J = 7.6 Hz, 4H), 1.71 (quint, J = 7.4 Hz, 4H), 1.43 – 1.22 (m, 36H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.2, 150.2, 143.7, 135.1, 132.2, 132.1, 131.6, 128.9, 128.0, 127.7, 127.2, 126.6, 126.0, 125.9, 125.64, 125.57, 125.3, 123.0, 111.3, 35.9, 32.0, 31.7, 29.8, 29.72, 29.70, 29.6, 29.5, 29.4, 22.8, 14.2; HRMS (ESI) m/z calculated for $\text{C}_{45}\text{H}_{63}\text{NNa}$ $[\text{M} + \text{Na}]^+$ 640.4858, found 640.4840.

5.7.2.2.2. 4,4'-(1,5-dichloroanthracene-9,10-diyl)bis(2-(3,5-didodecylphenyl)naphtho[2,3-*h*]quinoline) (**3**)

First, a solution of compound (**2**) (6.80 g, 11.0 mmol), 1,5-dichloro-9,10-diethynylantracene (**1**) (1.08 g, 3.66 mmol), chloranil (1.99 g, 8.09 mmol), boron

trifluoride diethyl etherate ($\text{BF}_3 \bullet \text{OEt}_2$) (1.34 mL, 10.9 mmol), and chloroform (184 mL) under dry argon was heated to 70 °C. After 48 hours, the reaction mixture was cooled and sequentially washed with a saturated aqueous sodium bicarbonate solution (200 mL $\times$ 3) and water (200 mL $\times$ 3). Next, the organics were poured through a cotton plug, and the solvent was removed *in vacuo*. Subsequently, the reaction mixture was dissolved in chloroform and precipitated from methanol. Last, the crude product of (**3**) was purified by flash chromatography (100/0 to 70/30 hexanes/chloroform) to yield two atropisomers followed by trituration of each isomer with hot ethanol to yield a pale yellow solids (2.43 g (*isomer 1* + *isomer 2*), 43% yield): (*isomer 1*): ^1H NMR (500 MHz, CDCl_3) δ 10.22 (s, 2H), 8.44 – 8.36 (m, 4H), 8.18 (s, 2H), 8.14 – 8.08 (m, 6H), 7.72 (d, J = 9.2 Hz, 2H), 7.68 – 7.59 (m, 6H), 7.53 (d, J = 7.0 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.12 (d, J = 9.1 Hz, 2H), 2.81 (t, J = 7.9 Hz, 8H), 1.79 (quint, J = 7.5 Hz, 8H), 1.51 – 1.21 (m, 74H), 0.89 (t, J = 6.8 Hz, 12H); (*isomer 2*): ^1H NMR (500 MHz, CDCl_3) δ 10.21 (s, 2H), 8.43 (s, 2H), 8.42 – 8.36 (m, 2H), 8.14 – 8.10 (m, 2H), 8.07 (br s, 6H), 7.77 (d, J = 9.2 Hz, 2H), 7.68 – 7.61 (m, 4H), 7.58 (d, J = 9.2 Hz, 2H), 7.52 (d, J = 7.0 Hz, 2H), 7.22 (d, J = 9.2 Hz, 2H), 7.20 – 7.14 (m, 4H), 2.77 (t, J = 7.8 Hz, 8H), 1.76 (quint, J = 7.5 Hz, 8H), 1.48 – 1.21 (m, 75H), 0.87 (t, J = 6.9 Hz, 12H); (*isomer 1*): ^{13}C NMR (126 MHz, CDCl_3) δ 155.3, 148.3, 147.2, 143.8, 139.7, 134.5, 133.4, 133.2, 132.5, 132.0, 131.4, 130.5, 130.4, 130.0, 129.5, 128.4, 128.1, 127.8, 127.4, 126.59, 126.55, 126.0, 125.3, 125.0, 123.3, 122.8, 36.4, 32.1, 32.0, 29.90, 29.88, 29.86, 29.83, 29.80, 29.7, 29.5, 22.9, 14.3; (*isomer 2*): ^{13}C NMR (126 MHz, CDCl_3) δ 155.4, 148.3, 147.1, 143.8, 139.7, 134.4, 133.5, 133.3, 132.5, 132.0,

131.5, 130.5, 130.4, 130.0, 129.5, 128.5, 128.1, 127.7, 127.5, 126.64, 126.59, 126.1, 126.0, 125.3, 125.0, 123.6, 122.5, 36.4, 32.1, 31.9, 29.88, 29.87, 29.84, 29.82, 29.78, 29.72, 29.68, 29.5, 29.4, 22.8, 14.3; MALDI (dithranol) m/z calculated for $C_{108}H_{131}Cl_2N_2$ $[M+H]^+$ 1526.0, found 1525.2.

5.7.2.2.3. 2,15-bis(3,5-didodecylphenyl)dibenzo[*lm:e₁f₁*]dipyrido[2,3,4-*hi*:2,3,4-*a₁b₁*]-nonacene (4)

First, anhydrous quinoline (30 mL) was added to a mixture of compound (**3**) (0.500 g, 0.33 mmol) and powdered KOH (2.21 g, 39.3 mmol) under argon, and the mixture was degassed for 15 minutes. Next, the mixture was heated to 150° C for 2 hours. Subsequently, the mixture was cooled, poured into chloroform (50 mL), and sequentially washed with water (50 mL), an aqueous solution of HCl (2.4 M, 50 mL $\times$ 3), water (50 mL $\times$ 3), and a saturated solution of aqueous sodium bicarbonate (50 mL). Then, the resulting mixture was poured through a cotton plug, and the solvent was removed *in vacuo*. In turn, the obtained solids were rinsed with methanol. Last, the crude product of (**4**) was purified by flash chromatography using deactivated silica gel (100/0 to 90/10 hexanes/ethyl acetate) to yield a dark blue/green solid (0.068 g, 14% yield): ^1H NMR (500 MHz, CS_2) δ 9.68 (s, 2H), 8.55 (d, $J = 8.5$ Hz, 2H), 8.47 (s, 2H), 8.40 (s, 2H), 8.27 (d, $J = 7.4$ Hz, 2H), 8.25 (s, 2H), 8.11 – 8.06 (m, 2H), 7.94 – 7.89 (m, 2H), 7.83 (s, 4H), 7.54 (t, $J = 8.0$ Hz, 2H), 7.48 – 7.42 (m, 4H), 7.02 (s, 2H), 2.72 (t, $J = 7.7$ Hz, 8H), 1.72 (quint, $J = 7.5$ Hz, 8H), 1.46 – 1.13 (m, 79H), 0.82 (t, $J = 6.8$ Hz, 12H); ^{13}C NMR (126 MHz, CS_2) δ 155.1, 147.6,

142.5, 139.3, 137.6, 133.0, 132.0, 131.5, 129.7, 129.3, 129.2, 129.1, 129.0, 128.6, 127.7, 127.6, 127.1, 126.9, 126.7, 126.2, 125.8, 125.7, 124.83, 124.75, 121.3, 121.0, 120.7, 118.1, 36.3, 32.1, 31.7, 30.0, 29.93, 29.89, 29.87, 29.7, 29.6, 23.0, 14.4; MALDI (TCNQ) m/z calculated for $C_{108}H_{128}N_2 [M]^+$ 1453.0, found 1452.8.

5.7.2.3. Product Purification

Flash chromatography was performed using a CombiFlash R_f200 purification system (Teledyne Isco, Inc.) according to the manufacturer's recommended protocols. When required, the silica gel columns/cartridges were flushed with 1/9 triethylamine/hexanes to deactivate the silica gel, followed by hexanes to remove excess triethylamine.

5.7.2.4. Spectroscopic and Chromatographic Characterization of Intermediates and Products

The intermediates and products were characterized with a combination of ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and chromatography. For the NMR characterization, the ^1H NMR and ^{13}C NMR spectra were obtained with either a Bruker DRX500 spectrometer that was outfitted with a CryoProbe (Bruker TCI 500 MHz, 5 mm diameter tubes) or an Avance 600 spectrometer that was outfitted with a CryoProbe (Bruker CBBFO 600 MHz, 5 mm diameter tubes) at the University of California, Irvine's Nuclear Magnetic Resonance Spectroscopy Facility. The

chemical shifts were reported in ppm for both ^1H and ^{13}C NMR spectra and referenced as follows: for samples in CDCl_3 , the ^1H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 or the residual CHCl_3 peak at 7.26 ppm, and the ^{13}C NMR spectra were referenced to the residual CHCl_3 peak at 77.16 ppm; for samples in CS_2 , the ^1H NMR spectra were referenced to TMS at 0.00, and the ^{13}C NMR spectra were referenced to TMS at 0.00. Both ^1H and ^{13}C NMR data were labeled with the chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br s = broad singlet), coupling constants in Hertz, and integration values. For the mass spectrometry characterization, accurate mass measurements were obtained via electrospray ionization (ESI) high-resolution mass spectrometry (HRMS) with a Waters LCT Premier TOF spectrometer at the University of California, Irvine's Mass Spectrometry Facility. The matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra were recorded with an AB SCIEX TOF/TOFTM 5800 mass spectrometer using a 349 nm Nd:YAG laser and dithranol as the matrix. For the chromatographic characterization, the purified product of tetrabenzononacene (**4**) was analyzed via size exclusion chromatography with a refractive index detector (SEC-RI). The SEC-RI measurements were performed in tetrahydrofuran at 40 $^{\circ}\text{C}$ with an Agilent Technologies 1260 Infinity Series separations module that was equipped with two Agilent ResiPore columns connected in series (7.5 mm $\times$ 300 mm, 3 μm particle size). The separations module was connected to Agilent 1260 infinity dual angle light scattering,

refractive index, and viscosity detectors in series. The flow rate was ~ 1.0 mL/min with an injection volume of ~ 25 – 100 μ L and a sample concentration of ~ 1.0 – 2.5 mg/mL.

5.7.2.5. UV/Vis-NIR and Fluorescence Spectroscopic Characterization of Tetrabenzononacene Solutions

The tetrabenzononacene solutions were spectroscopically characterized both without and with protonation using the UV/Vis-NIR and fluorescence spectrometers. The solution of unprotonated tetrabenzononacene (TBN, **4**) were prepared by dissolving unprotonated tetrabenzononacene (TBN, **4**) in HPLC-grade chloroform at a concentration of $40 \mu\text{M}$, and the solution of protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) was prepared by adding trifluoroacetic acid (TFA) to previously prepared unprotonated tetrabenzononacene (TBN, **4**) solution to reach an overall TFA concentration of 1.0 M. In our experiments, all the UV/Vis-NIR absorbance spectra were obtained under ambient conditions with a Shimadzu UV-1700 spectrometer, and all the fluorescence spectra were obtained under ambient conditions with a Cary Eclipse fluorescence spectrometer at the University of California, Irvine’s Laser Spectroscopy Laboratories.

5.7.2.6. Photostability Characterization of Tetrabenzononacene Solutions

The photostability of the tetrabenzononacene solutions were characterized both without and with protonation according to standard procedures. The solutions of the unprotonated tetrabenzononacene (TBN, **4**), the protonated tetrabenzononacene (PTBN, **4**+**2H**⁺), and a pentacene-variant reference (6,13-bis((trimethylsilyl)ethynyl)pentacene,

abbreviated as TMS-pentacene) were prepared at a concentration of 40 μ M in HPLC-grade chloroform, while the protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) solution also contained trifluoroacetic acid at a concentration of 1.0 M for protonation purpose. Each solution sample was placed in a separate cuvette (1 cm in path length) under ambient conditions and sealed with a screw cap. For the photostability characterization, the solution samples were exposed to the illumination of a high-intensity xenon lamp light source that was outfitted with a neutral-density filter. The power of light that illuminated at each solution sample was measured to be constantly at 460 mW with a detector area of 1 cm². Each solution sample was sequentially exposed to the aforementioned light source for a set period of time and then instantaneously transferred to the UV/Vis-NIR spectrometer for absorbance measurements (note that the solution-containing cuvettes were completely covered to block any unwanted environmental light during sample transfer for UV/Vis-NIR measurements). The exposure-measurement process was repeated for each solution sample until either completely degraded in the case of the unprotonated tetrabenzononacene (TBN, **4**) solution and the referenced TMS-pentacene solution or for over 27 hours of total exposure time in the case of protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) solution. The photostability of each compound was evaluated and quantified by the half-life of the corresponding sample solution, which was defined as the time needed for the initial peak intensity in the UV/Vis-NIR absorbance spectra to reduce by half. All of the photostability experiments were repeated three times for each compound.

5.7.3. Device Fabrication and Characterization

5.7.3.1. Fabrication of Tri-Layer Tetrabenzononacene-Based Devices for Mechanical Actuation

The tri-layer tetrabenzononacene-based devices were fabricated according to standard procedures. For the fabrication of devices modified with unprotonated tetrabenzononacene (TBN, **4**), a piece of acrylate elastomer membrane (VHB 4905, 3M) was mounted and equiaxially stretched by $\sim 1,600$ % in area (relative to its initial area) on a size-adjustable holder. Next, a solution of unprotonated tetrabenzononacene (TBN, **4**) was dropcasted onto the top surface of the pre-stretched acrylate elastomer to form a square-shaped, blue-colored optically active layer (~ 3.5 cm in length), with the solvent allowed to completely evaporate for ~ 10 minutes. Then, a sulfonated pentablock copolymer solution (NEXARTM, Kraton Polymers LLC) was spincoated onto a silicon substrate, cured via heating at a temperature of 60 °C, and then delaminated from the substrate as optically transparent proton-conducting membranes, according to previously established procedures. Subsequently, a piece of square-shaped transparent proton-conducting membrane (~ 3.5 cm in length) was directly laminated on top of the unprotonated tetrabenzononacene-based optically active layer. Last, the partially completed device was mechanically contracted by $\sim 40\%$ in length, with respect to the initial length of the unprotonated tetrabenzononacene-based optically active layer. For the fabrication of devices modified with protonated tetrabenzononacene (PTBN, **4**+**2H**⁺), a similar general procedure was applied by replacing the unprotonated tetrabenzononacene

solution (TBN, **4**) with a protonated tetrabenzononacene solution (PTBN, **4**+**2H**⁺). The resulting tri-layer devices, which were modified with either unprotonated or protonated tetrabenzononacene, were used for physical, mechanical, morphological, and spectroscopic characterization.

5.7.3.2. Mechanical Actuation of Tri-Layer Tetrabenzononacene-Based Devices

The tri-layer tetrabenzononacene-based devices were mechanically actuated in a size-adjustable holder, which was used to apply/release equiaxial mechanical strain to/from the devices. During mechanical actuation of the tetrabenzononacene-based devices, the lengths of their square-shaped optically active regions (i.e., regions made of either unprotonated or protonated tetrabenzononacene) were increased by $\sim 67\%$ for actuation and then contracted by $\sim 40\%$ to return to the initial position. The mechanical actuation was performed under ambient conditions with bright laboratory lighting, unless otherwise noted. All the experiments were repeated for at least three independent devices.

5.7.3.3. Morphological Characterization of Tri-Layer Tetrabenzononacene-Based Devices upon Mechanical Actuation

The microscale and nanoscale morphologies of the tri-layer devices, which were modified with either unprotonated or protonated tetrabenzononacene, were characterized with an Asylum Cypher ES atomic force microscope (AFM) both with and without mechanical actuation. All the experiments were performed under ambient conditions and repeated for at least three independent devices. The obtained 3D-topographic images from

the AFM measurements were processed and analyzed with the Gwyddion software package.

5.7.3.4. Visible and Near-Infrared Spectroscopic Characterization of Tri-Layer Tetrabenzononacene-Based Devices

The tri-layer tetrabenzononacene-based devices, which were modified with either unprotonated or protonated tetrabenzononacene, were spectroscopically characterized both without and with mechanical actuation. To obtain the total transmittance, diffuse transmittance, total reflectance, and diffuse reflectance in the visible and near-infrared regions (i.e. 400 nm – 2000 nm) of the electromagnetic spectrum, the devices were characterized with a Jasco V670 UV-Vis-NIR Spectrometer that was equipped with a Jasco ILN-925 150 mm integrating sphere, which features a rectangular-shaped sample port with a length of ~ 0.9 cm and a width of ~ 1.3 cm in transmission mode and a square-shaped sample port with a length of ~ 1.6 cm length in reflection mode. The devices' optically active regions (i.e., regions made of either unprotonated or protonated tetrabenzononacene) in both their unactuated and actuated states were sufficiently large to cover the sample ports. The measurements were performed at normal incidence in transmission mode or at an incidence angle of 5° in reflection mode and were referenced to Jasco Spectralon standards as appropriate. The specular transmittance was calculated according to the equation:

$$\textit{Specular Transmittance (\%)} + \textit{Diffuse Transmittance (\%)} = \textit{Total Transmittance (\%)}$$

The specular reflectance was calculated according to the equation:

$$\text{Specular Reflectance (\%)} + \text{Diffuse Reflectance (\%)} = \text{Total Reflectance (\%)}$$

The absorption was calculated according to the equation:

$$\text{Total Transmittance (\%)} + \text{Total Reflectance (\%)} + \text{Total Absorption (\%)} = 100\%$$

The spectroscopic characterization was performed under ambient conditions. All the experiments were repeated for at least three independent devices. The obtained spectra were processed and analyzed with the Jasco Spectra Manager™ Suite and Python software packages.

5.7.3.5. Fabrication of Octopus Blue Ring-Like Quad-Layer Tetrabenzononacene-Based Devices for Electrical Actuation

The octopus blue ring-like quad-layer tetrabenzononacene-based devices were fabricated according to standard procedures, as illustrated in Figure S5.15. First, to fabricate the middle electroactive artificial muscle layer, a piece of acrylate elastomer membrane (VHB 4905, 3M) was mounted and equiaxially stretched by $\sim 1,600$ % in area (relative to its initial area) on a size-adjustable holder. Next, to fabricate the brown center of the optically active layer, a solution of protonated tetrabenzononacene (PTBN, **4**+**2H**⁺) was dropcasted onto the top surface of the pre-stretched acrylate elastomer to form a brown-colored circular shape (~ 0.5 cm in diameter), with the solvent allowed to completely evaporate. Then, to prepare the blue annulus of the optically active layer, a solution of unprotonated tetrabenzononacene (TBN, **4**) was dropcasted around the brown

inner circle to form a blue-colored annular shape (~ 1.1 cm in outer diameter and ~ 0.5 cm in inner diameter), again, with the solvent allowed to completely evaporate. Subsequently, optically transparent proton-conducting electrode membranes were prepared according to previously described procedures (see Section 5.7.3.1. for details). In turn, two identical circular-shaped proton-conducting electrode membranes (~ 1.2 cm in diameter) were separately laminated onto both sides of the pre-stretched acrylate elastomer, with the top proton-conducting electrode membrane fully covering the optically active regions (i.e., the brown inner circle and the blue outer annulus). Furthermore, the partially completed device was mechanically contracted by $\sim 40\%$ in length, with respect to the initial diameter of the circular-shaped proton-conducting electrode membranes. Last, both the top and bottom proton-conducting electrode membranes were attached with stripe-shaped electrical leads and connected to an external high-voltage power supply for electrical actuation. The resulting octopus blue ring-like devices were used for electromechanical, optical, near-infrared, fluorescence, and self-repairing characterization.

5.7.3.6. Electrical Actuation of Octopus Blue Ring-Like Quad-Layer Tetrabenzononacene-Based Devices

The octopus blue ring-like quad-layer tetrabenzononacene-based devices were electrically characterized according to standard procedures. For all measurements, the devices were connected to a high-voltage power supply that was consisted of a function generator (DS345, Stanford Research), an operational amplifier (OPA 548, Texas

Instruments), and a high-voltage converter (E80, EMCO). The areal strain (%) was calculated according to the equation:

$$\text{Areal strain (\%)} = (A_1 - A_0) / A_0 \times 100\%$$

where A_0 was the measured area of the optically active region prior to any electrical actuation and A_1 was the measured area of the optically active region after electrical actuation. The obtained images and videos were processed and analyzed with the Apple QuickTime Player and MATLAB software packages. All the measurements were performed for at least three devices and independently verified multiple times for each device.

5.7.3.7. Visible, Fluorescence, and Near-Infrared Imaging for Octopus Blue Ring-Like Quad-Layer Tetrabenzononacene-Based Devices

The visible, fluorescence, and near-infrared imaging experiments for the octopus blue ring-like quad-layer tetrabenzononacene-based devices were performed according to standard procedures. For the visible imaging, the images and videos were directly obtained under ambient conditions and bright laboratory lighting with a digital camera (PowerShot SX520 HS, Canon) that was placed right above the devices, as illustrated in Figure 5.5A. For the fluorescence imaging, the devices were exposed to an ultra-violet (UV) illumination for excitation, which was generated by a standard UV lamp (UVP EL Series). The images and videos were directly obtained under ambient conditions in darkness with a digital camera (PowerShot SX520 HS, Canon), as illustrated in Figure 5.6A. For the

near-infrared imaging, the devices were exposed to a near-infrared illumination, which was generated by a home-built near-infrared light source that was consisted of an array of 26 near-infrared LEDs (XtraLED). The images and videos were directly obtained under ambient conditions in darkness with a near-infrared camera system (Pi NoIR Camera Module v2, Raspberry Pi), which was outfitted with an infrared filter (RM-72, Hoya) that only allowed the passage of near-infrared light with wavelengths of > 720 nm, as illustrated in Figure 5.6D. All the experiments were repeated for at least three independent devices.

5.7.3.8. Quantitative Analysis of the Visible, Fluorescence, and Near-Infrared Modulation

The color brightness, near-infrared intensity, and fluorescence intensity of the blue ring-like devices were processed and quantitatively analyzed using the Apple QuickTime Player and Adobe Photoshop CC software packages according to standard protocols. In Figure 5.5C, the relative color brightness of the representative device was quantified by normalizing the color brightness of each optically active region (either blue outer annulus or brown inner circle) at different applied voltages (> 0 kV) to that of the same region at 0 kV. In Figure 5.5D, the relative color brightness of the representative device was quantified by normalizing the color brightness of each optically active region (either blue outer annulus or brown inner circle) to that of the same region at 0 second. In Figure 5.5E, the relative color brightness of the representative device was quantified by

normalizing the color brightness of each optically active region (either blue outer annulus or brown inner circle) during the cycling test (i.e., cycle number > 0) to that of the same region before the cycling test (i.e., cycle number $= 0$). In Figure 5.6C, the relative fluorescence intensity of the representative device was quantified by normalizing the fluorescence brightness of both blue outer annulus and brown inner circle to that of the blue annulus at 0 second (note again that blue outer annulus was used as a reference for the direct comparison of the fluorescence brightness between blue outer annulus and brown inner circle). Similarly, in Figure 5.6F, the relative near-IR intensity of the representative device was quantified by normalizing the near-IR brightness of both blue outer annulus and brown inner circle to that of the blue annulus at 0 second (note that blue outer annulus was used as a reference for the direct comparison of the near-IR brightness between blue outer annulus and brown inner circle).

5.7.4. Supporting Figures and Tables

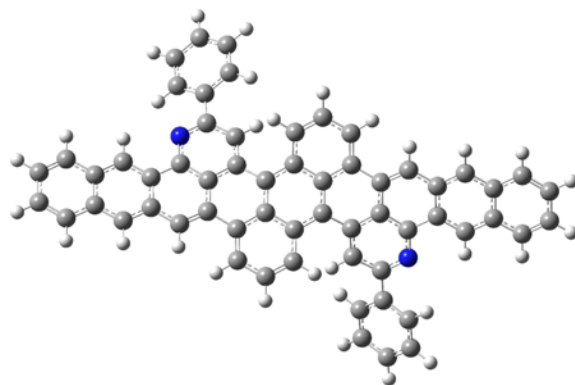


Figure S5.1. Energy minimized geometry for tetrabenzononacene (TBN, **4**).

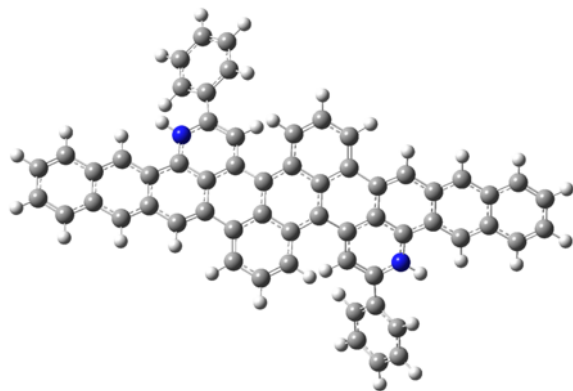


Figure S5.2. Energy minimized geometry for protonated tetrabenzononacene (PTBN, $4+2\text{H}^+$).

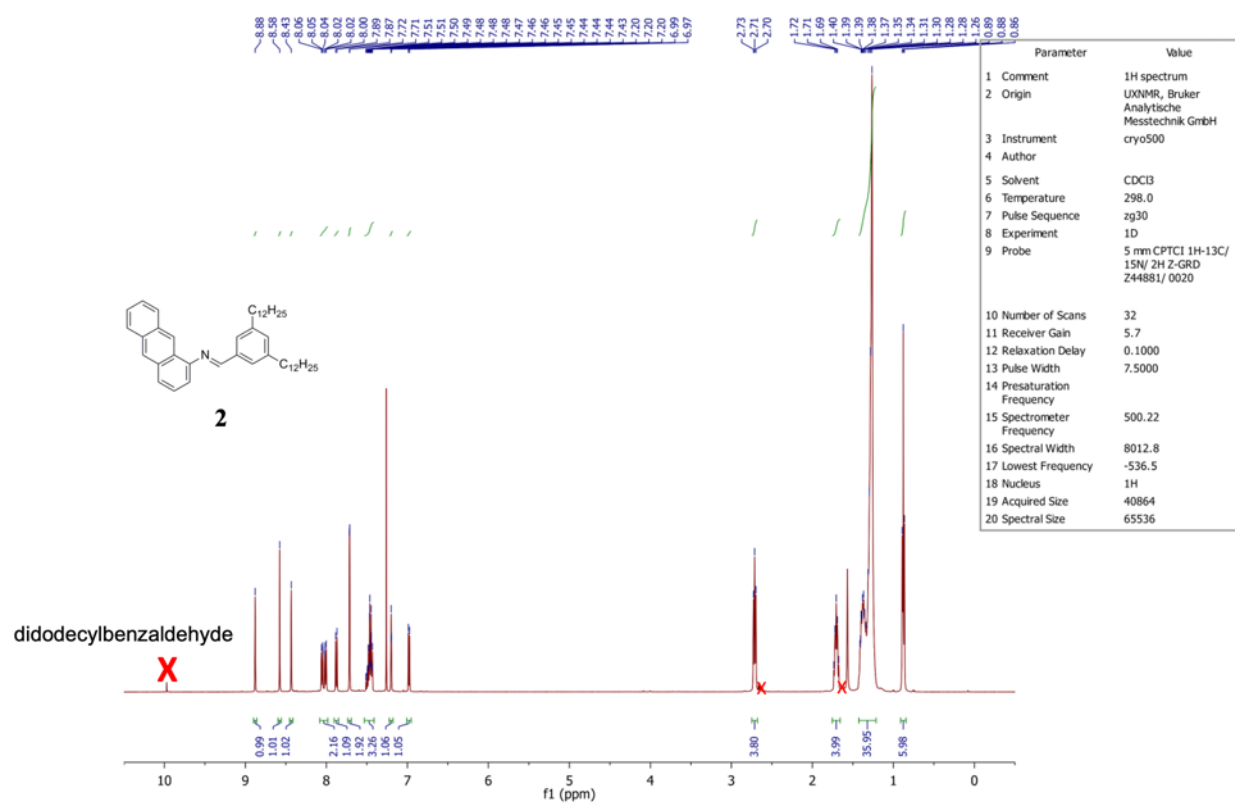


Figure S5.3. The ^1H NMR spectrum for intermediate (**2**). Note that a trace amount of didodecylbenzaldehyde was observed and labeled with red crosses (X).

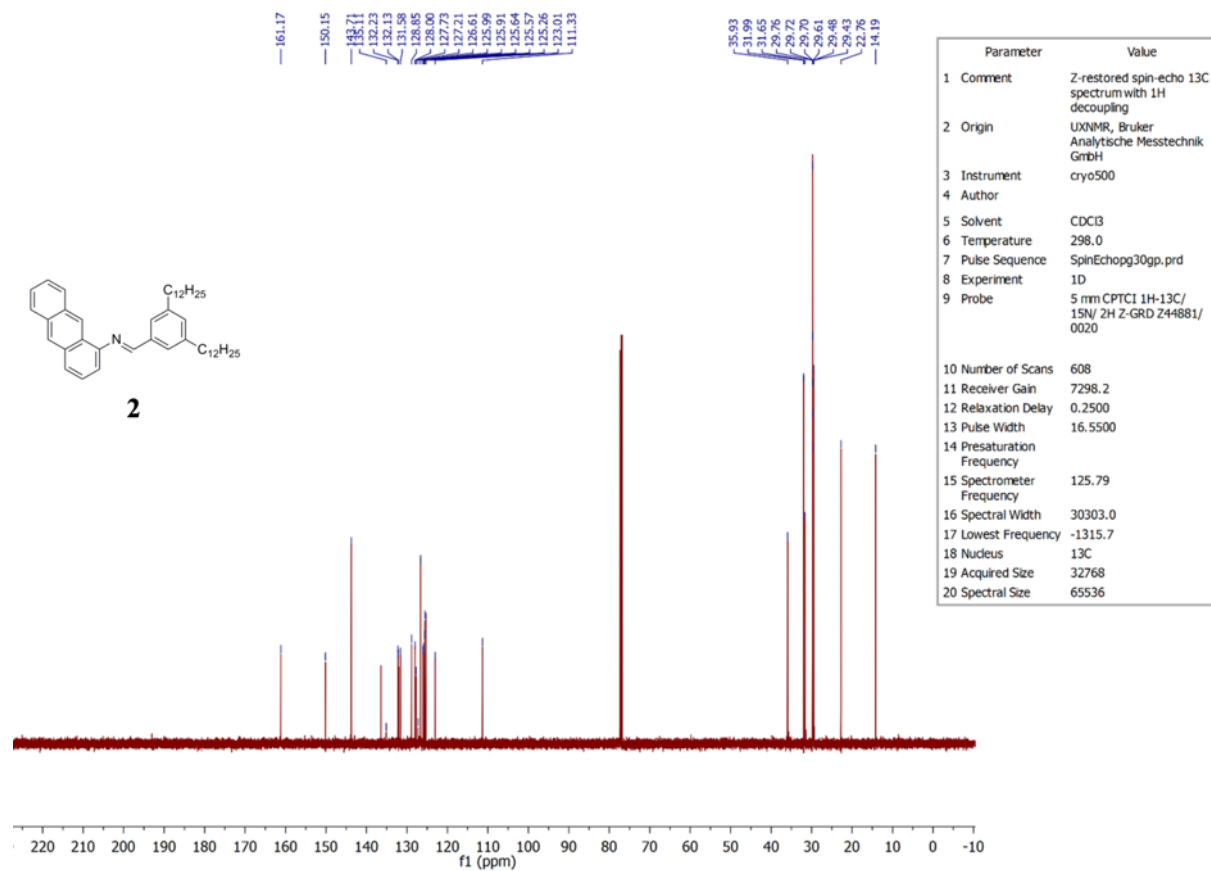


Figure S5.4. The ¹³C NMR spectrum for intermediate (2).

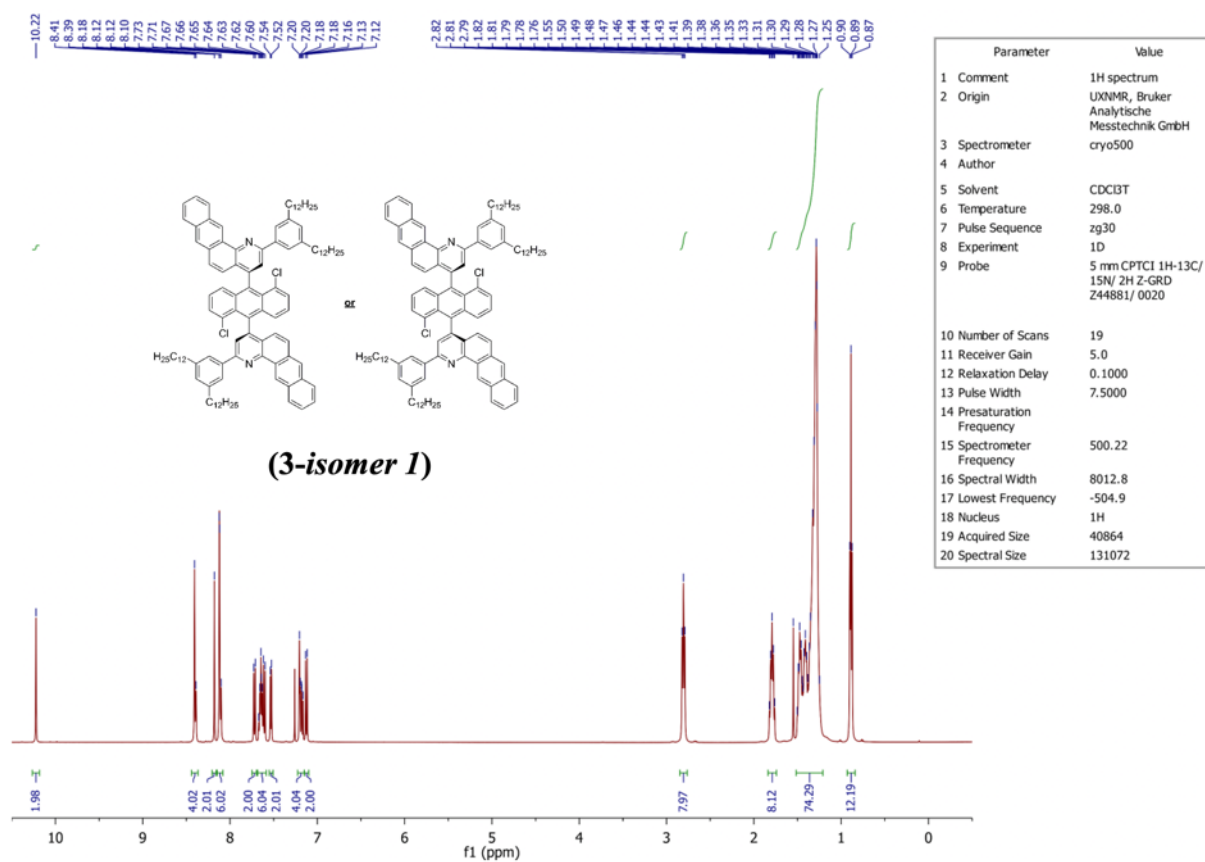


Figure S5.5. The ¹H NMR spectrum for intermediate (**3-isomer 1**).

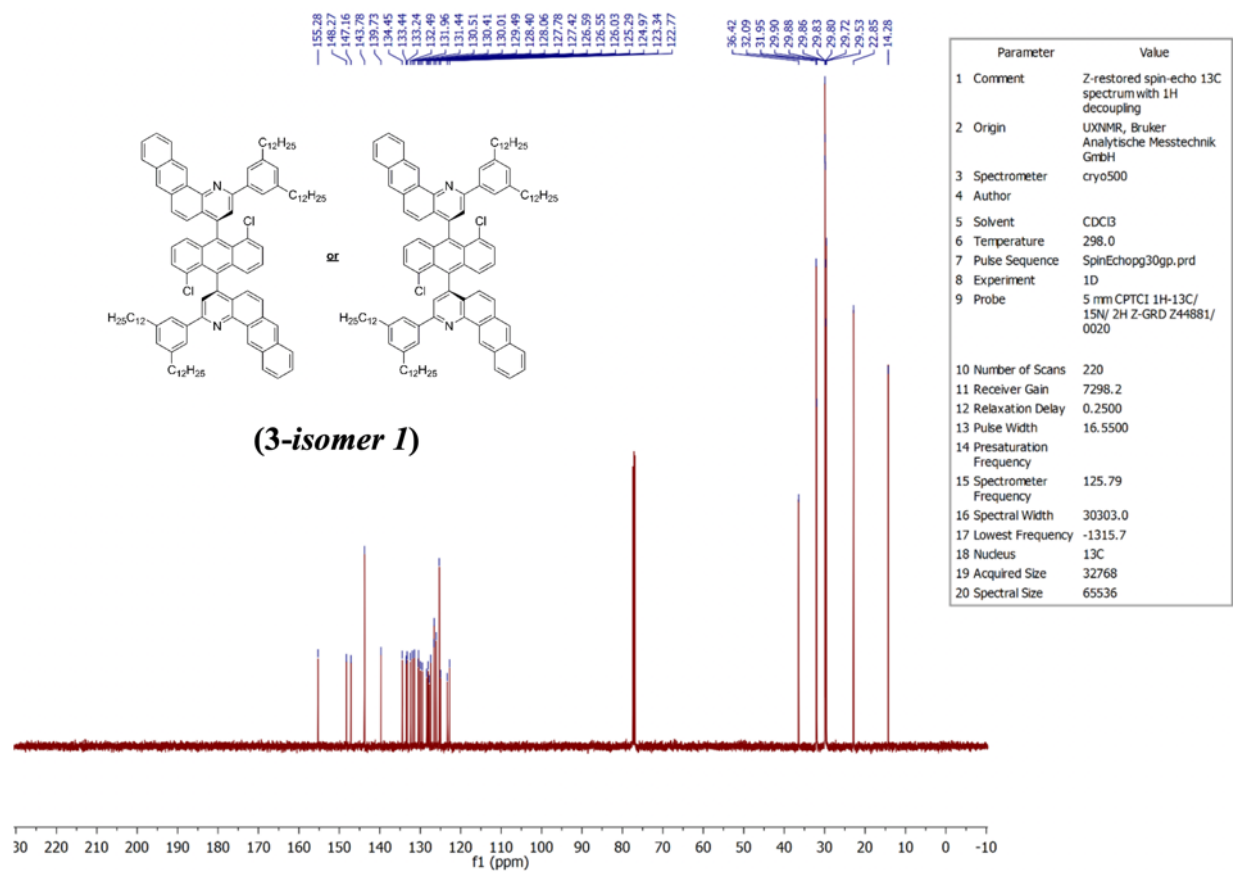


Figure S5.6. The ¹³C NMR spectrum for intermediate (**3-isomer 1**).

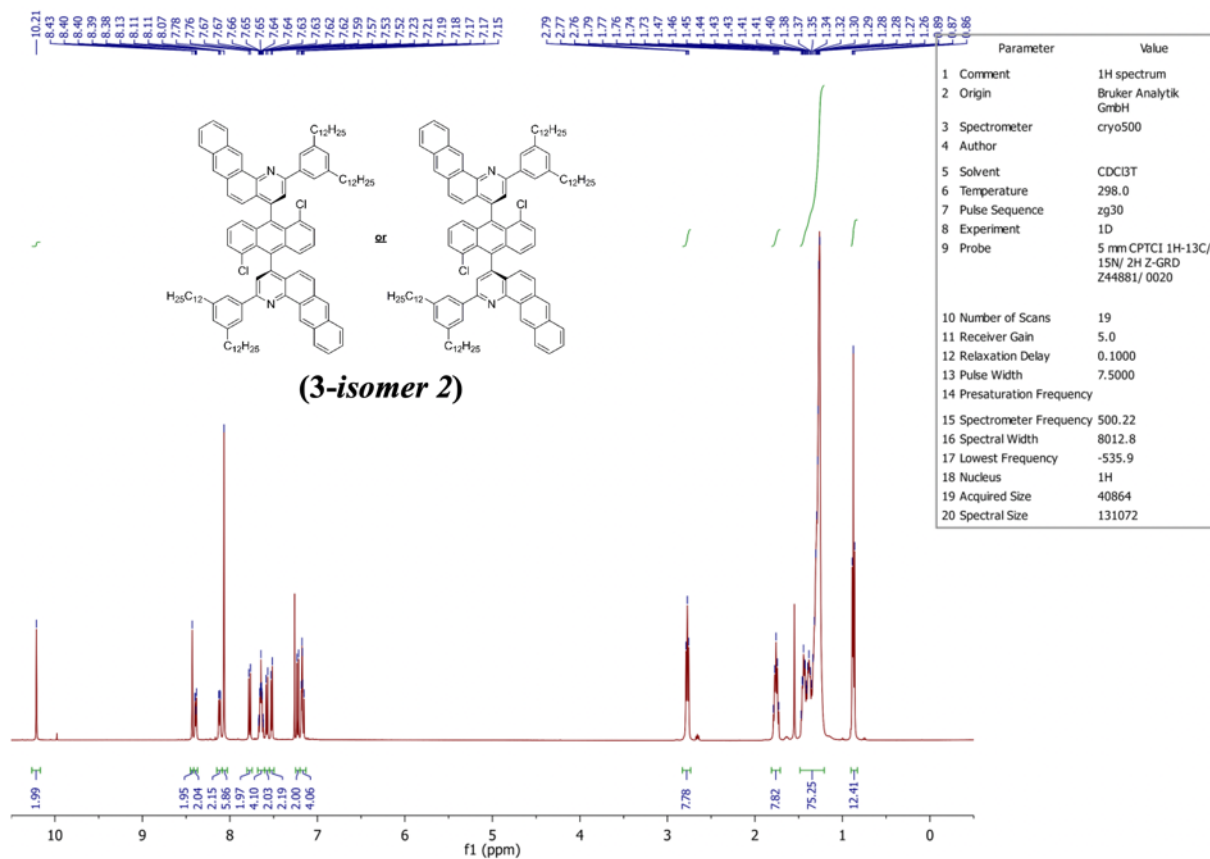


Figure S5.7. The ^1H NMR spectrum for intermediate (**3-isomer 2**).

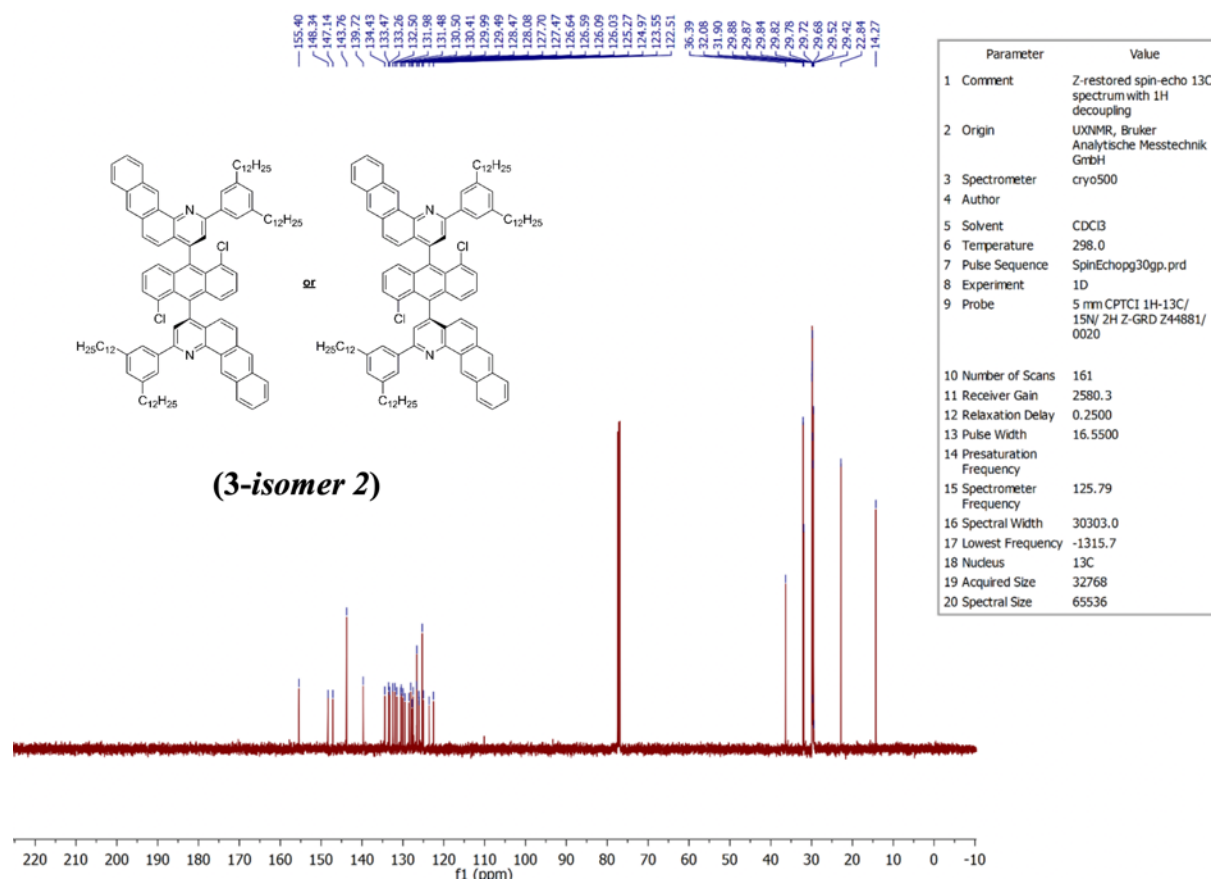


Figure S5.8. The ¹³C NMR spectrum for intermediate (**3-isomer 2**).

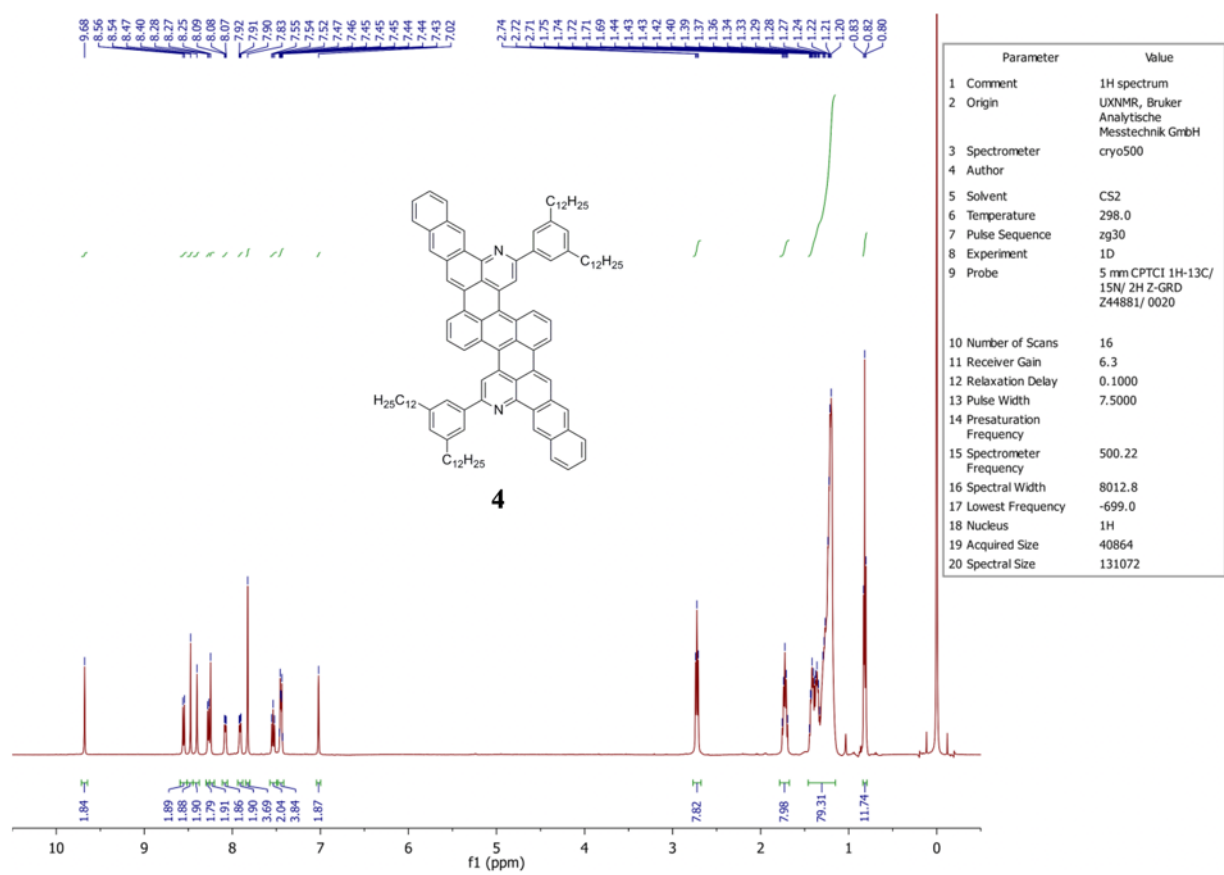


Figure S5.9. The ^1H NMR spectrum for tetrabenzononacene (TBN, 4).

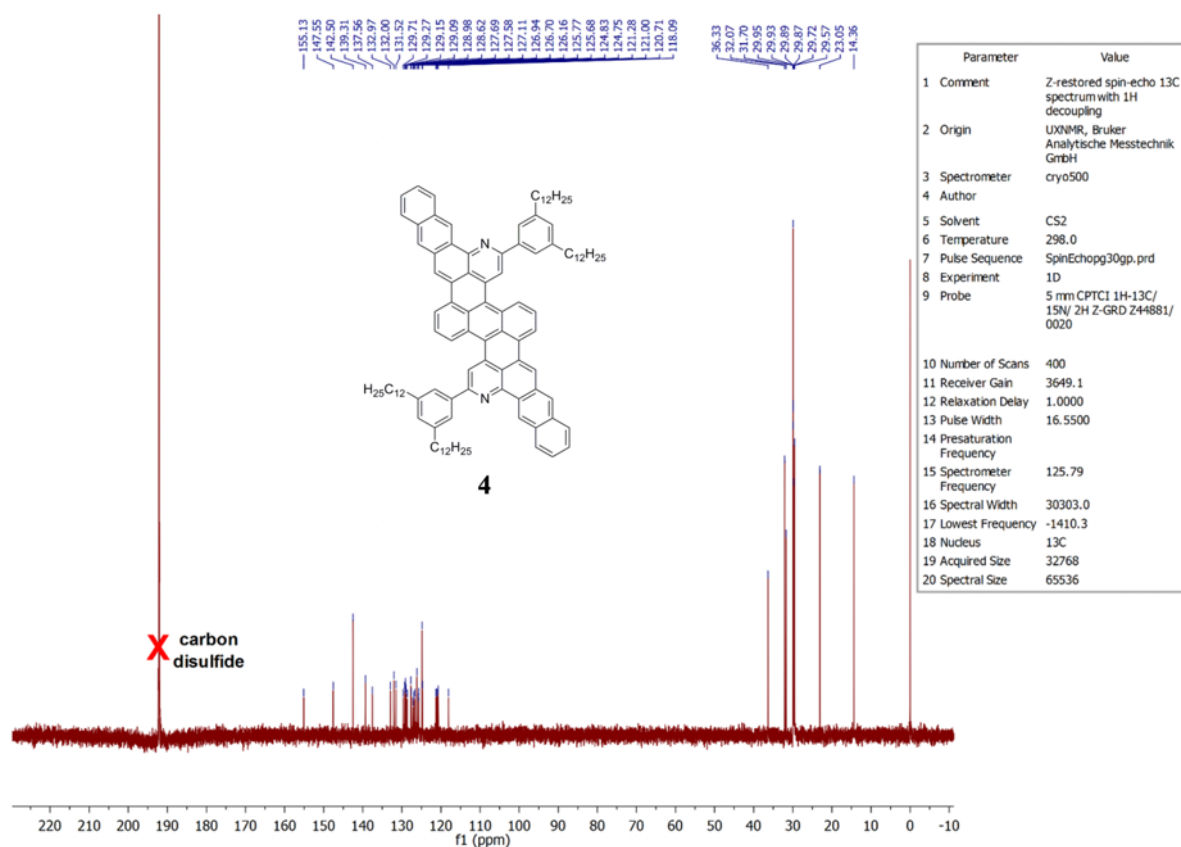


Figure S5.10. The ^{13}C NMR spectrum for tetrabenzononacene (TBN, **4**). Note that the signal obtained for the carbon disulfide (CS_2) solvent was labeled with a red cross (X).

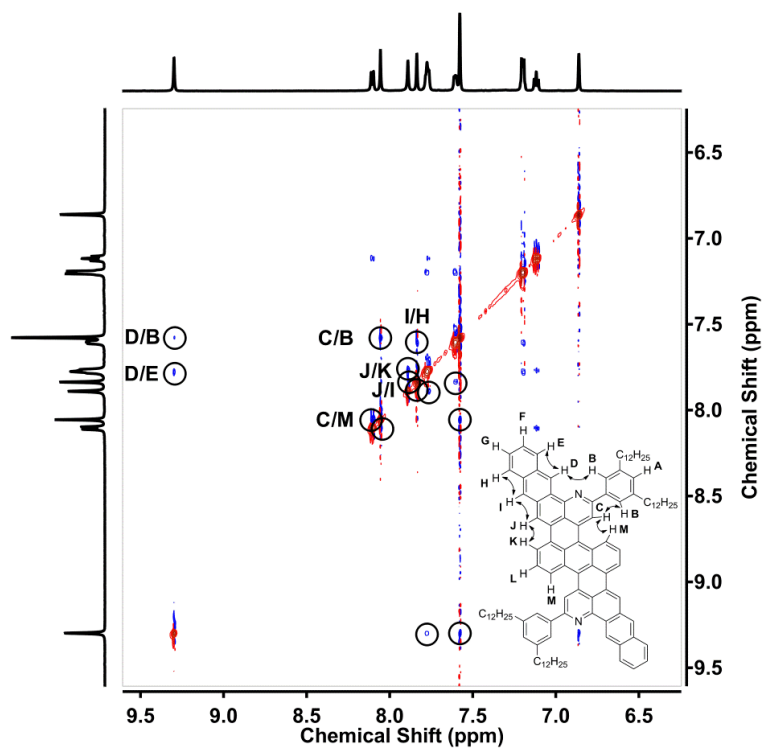


Figure S5.11. The ROESY spectrum for tetrabenzononacene (TBN, **4**). The through-space interactions between different protons are labeled with black circles in the spectrum.

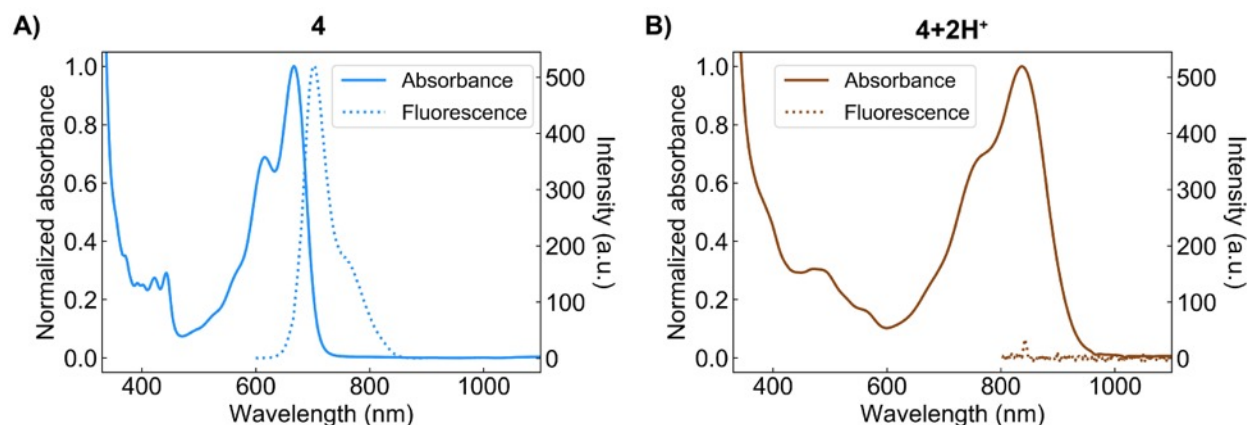


Figure S5.12. (A) The fluorescence emission spectrum (dashed blue line) for tetrabenzononacene (TBN, **4**) in solution, which was overlaid with its UV/Vis-NIR absorbance spectrum (solid blue line). (B) The fluorescence emission spectrum (dashed brown line) for protonated tetrabenzononacene (PTBN, **4**+2H⁺) in solution, which was overlaid with its UV/Vis-NIR absorbance spectrum (solid brown line). Note that all the fluorescence emission spectra were plotted by using absolute intensity values from experimental measurements, while all the UV/Vis-NIR absorbance spectra were normalized to unity.

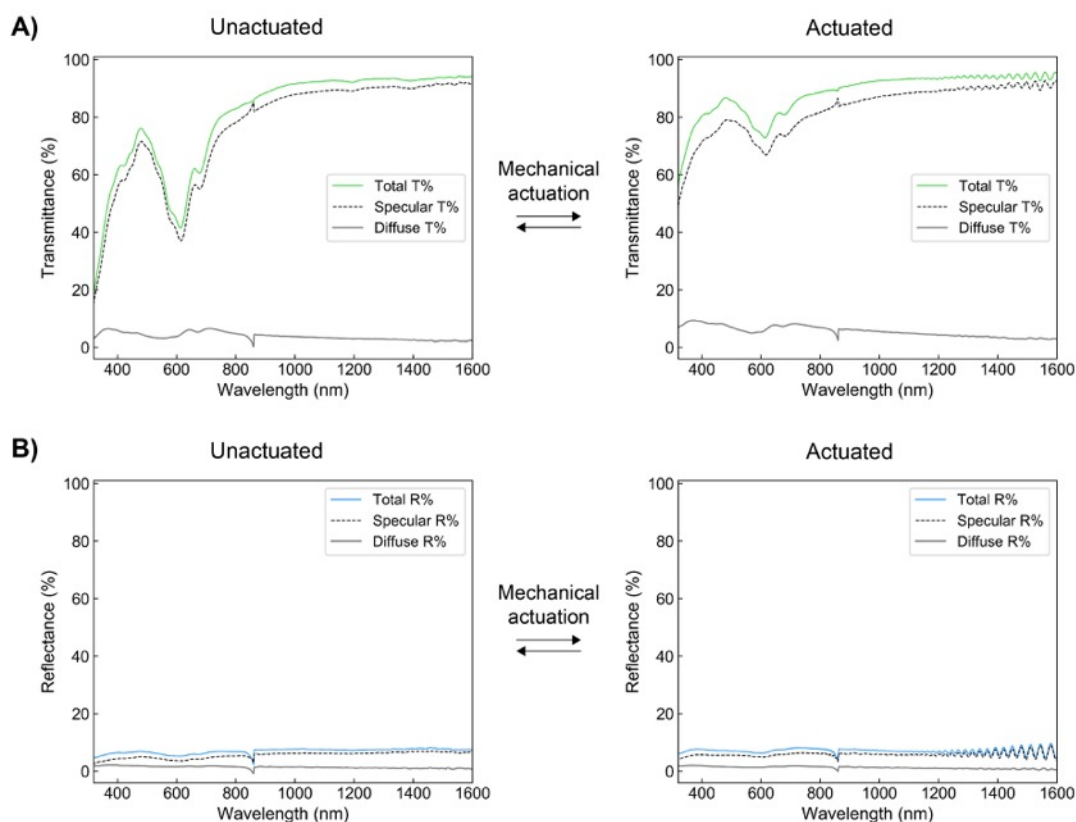


Figure S5.13. (A) Representative UV/Vis-NIR transmittance spectra for a tri-layer unprotonated tetrabenzononacene (TBN, **4**)-based device before (left) and after (right) mechanical actuation. The total transmittances (solid green lines) were shown, along with their specular (dashed grey lines) and diffuse (solid grey lines) components. (B) Representative UV/Vis-NIR reflectance spectra for a tri-layer unprotonated tetrabenzononacene (TBN, **4**) device before (left) and after (right) mechanical actuation. The total transmittances (solid blue lines) were shown, along with their specular (dashed grey lines) and diffuse (solid grey lines) components.

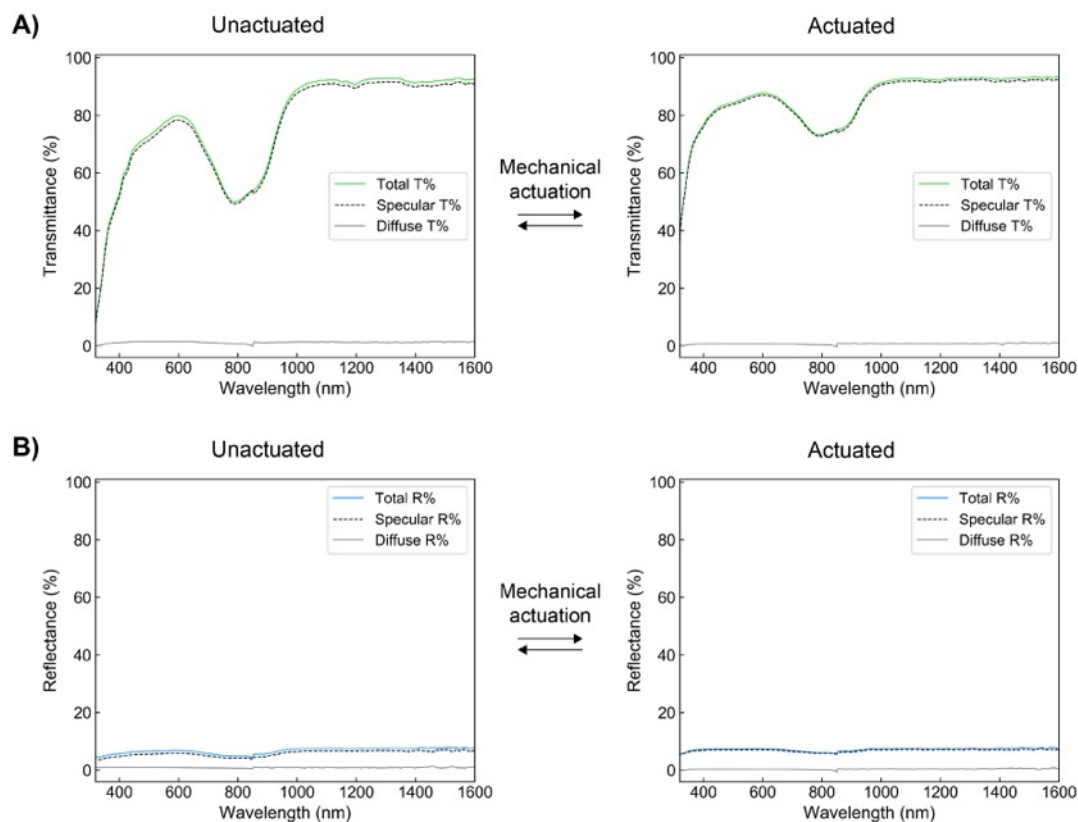


Figure S5.14. (A) Representative UV/Vis-NIR transmittance spectra for a tri-layer protonated tetrabenzononacene (PTBN, $4+2\text{H}^+$)-based device before (left) and after (right) mechanical actuation. The total transmittances (solid green lines) were shown, along with their specular (dashed grey lines) and diffuse (solid grey lines) components. (B) Representative UV/Vis-NIR reflectance spectra for a tri-layer protonated tetrabenzononacene (PTBN, $4+2\text{H}^+$)-based device before (left) and after (right) mechanical actuation. The total transmittances (solid blue lines) were shown, along with their specular (dashed grey lines) and diffuse (solid grey lines) components.

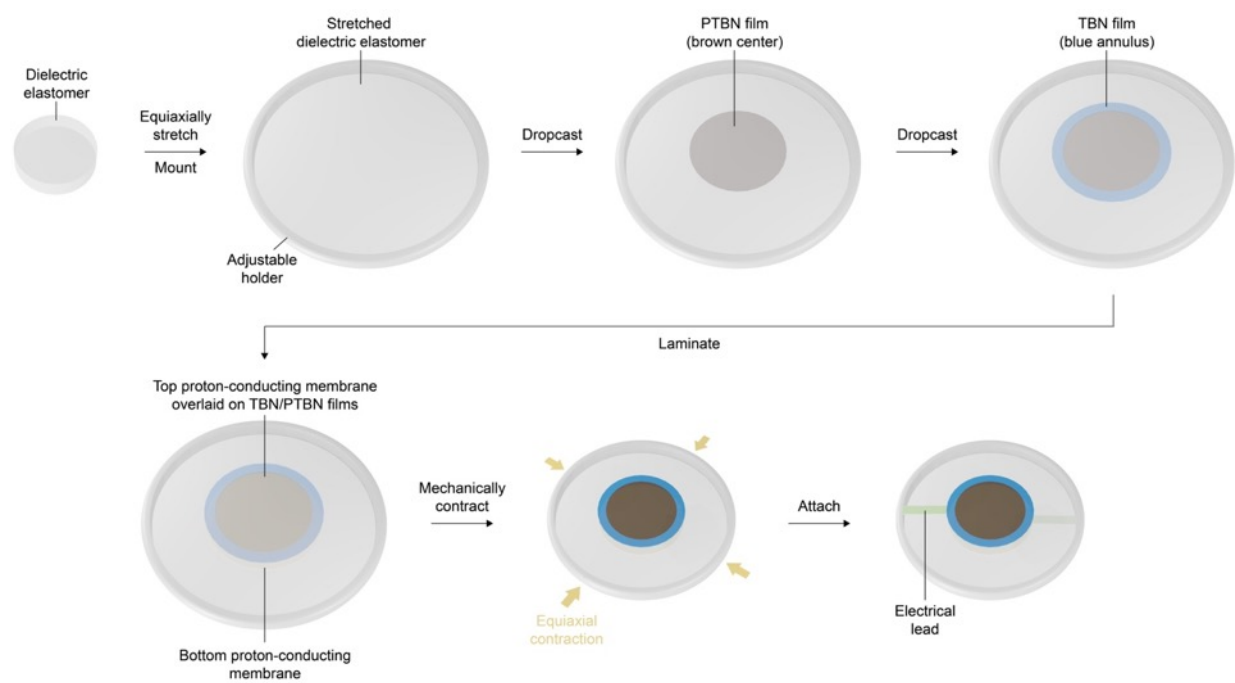


Figure S5.15. Scheme of the fabrication of an octopus blue ring-like quad-layer tetrabenzononacene-based devices used for electromechanical actuation.

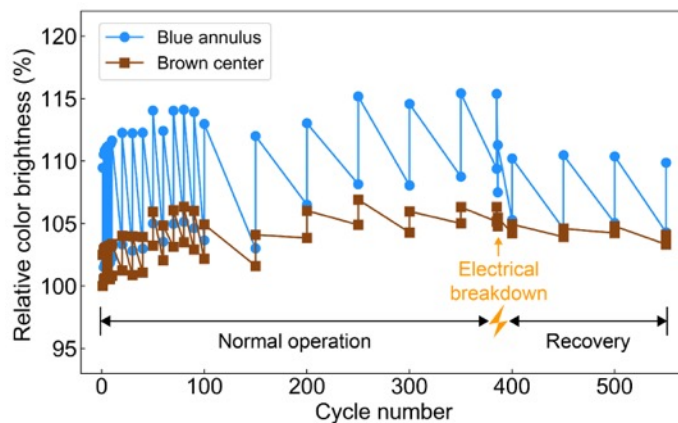


Figure S5.16. Plots of the relative color brightness (per area) as a function of cycle number for the blue outer annulus (blue circles) and the brown inner circle (brown squares) in the optically active regions of a representative blue ring-like quad-layer tetrabenzononacene-based device. Note that the device underwent a sudden electrical breakdown at the 385th cycle but recovered its electrical actuation and optical modulation abilities in the next cycle, demonstrating the device’s self-repairing characteristics.

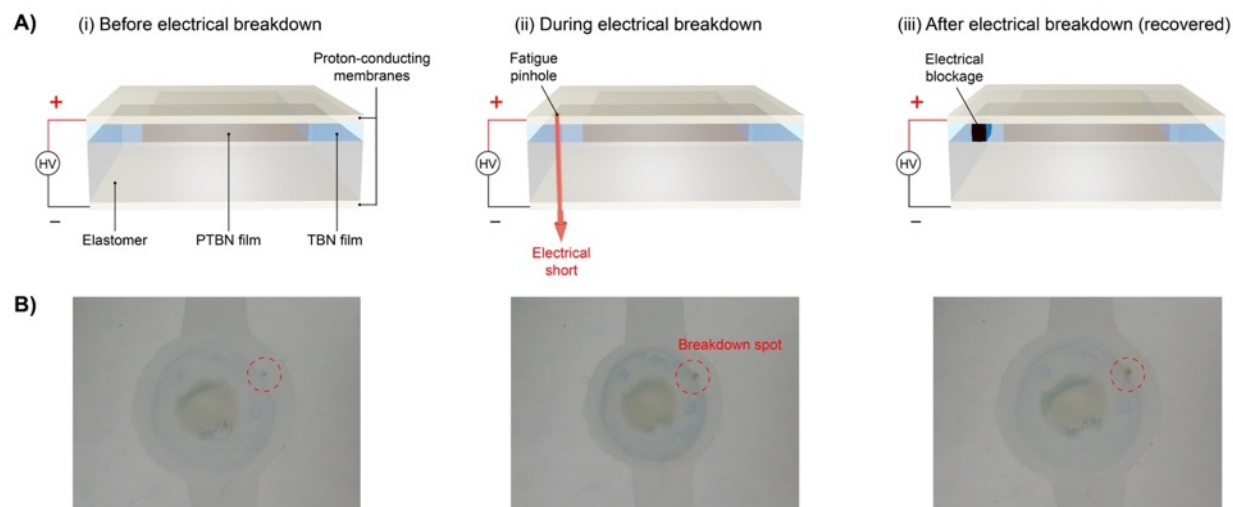
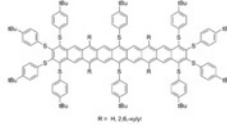
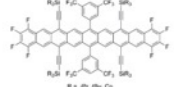
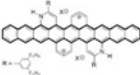


Figure S5.17. (A) Schematics of a proposed three-step mechanism for the self-repairing characteristic of blue ring-like quad-layer tetrabenzononacene-based devices, which included: (i) normal operation before electrical breakdown; (ii) occurrence of electrical breakdown at localized sites; and (iii) formation of electrically insulating blockages and recovery to normal operation. (B) Representative digital camera images of a representative device that underwent the self-repairing process with the aforementioned three steps. The localized spot where a sudden electrical breakdown took place was highlighted in red circles.

Table S5.1. A comparison of the representative device types used for camouflage and signaling.

Device Type	Mechanism	Types of Stimuli	Spectral Range	Optical Modulation	Fluorescence Functionality	Morphological Modulation	Response Time	Cyclic Stability	Self-Repairing	Device Size	Benchtop Fabrication	Reference
Dual-band electrochromic devices	Electrochemical redox reaction	Electrical	400 – 2200 nm (Visible and near-IR)	A% and T%	No	No	A few seconds to tens of seconds	A few hundreds to a few thousands	No	Centimeters (or above)	Yes	Cai, 2016 ¹⁴ Wu, 2018 ¹⁵
Photonic gels	Thin-film interference	Chemical	300 – 1800 nm (Visible and near-IR)	A% and R%	No	No	< 1 s	100	No	Centimeters	No	Kang, 2007 ¹⁶
Metamaterials/ metasurfaces	Carrier doping/ phase transition	Optical/electrical/ magnetical/ mechanical	Variable (Visible and near-IR)	A%, T%, and R%	No	Yes	Microseconds to seconds	Not shown	No	Nanometers to microns	No	He, 2019 ¹⁹
Electroactive polymer-based systems	Morphological change	Mechanical/ electrical	400 nm – 16.5 μ m (Visible and IR)	T% (specular-to-diffuse ratio)	No	Yes	570 ms	> 500	No	Centimeters	No	Xu, 2020 ⁹
Biological protein films	Thin-film interference	Chemical/ mechanical	400 nm – 1.6 μ m (Visible and near-IR)	R%	No	No	Not shown	> 140	No	Centimeters	No	Phan, 2013 ²² Phan, 2015 ²³
Octopus-inspired systems	Molecular transition and device geometry change	Chemical/ mechanical/ electrical	400 nm – 1.6 μ m (Visible and near-IR)	A% and T%	Yes	Yes	< 460 ms	> 500	Yes	Centimeters	Yes	This work

Table S5.2. A comparison of reported nonacene derivatives.

Materials	Structure	Overall Yield (%)	Synthesis Conditions	Stability	Solubility	Thin-film Fabrication	Device Integration	Reference
Nonacene		Not reported	Extreme temperature (30K), solid argon matrix	Not reported	N/A	No	No	Tönshoff, 2010 ⁴⁵
Nonacene		Not reported	STM/AFM manipulation, ultra-high vacuum, Au(111) surface	Not reported	N/A	No	No	Zuzak, 2017 ⁴⁶ Urgel, 2019 ⁴⁷
Functionalized nonacene	 R = H, Si(CH ₃) ₃	~ 17	Normal chemical reaction	~ 2 hours in solution (exposed to air and light)	CH ₂ Cl ₂ CDCl ₃	No	No	Kaur, 2010 ⁴⁸
Functionalized nonacene	 R = -H, -tBu, -Cp	Not reported	Normal chemical reaction	< 6 hours in solution (exposed to air and bright laboratory light)	Toluene	No	No	Purushothaman, 2011 ⁴⁹
Nonatwistacene		Not reported	Normal chemical reaction	5 days in solid (exposed to air)	CH ₂ Cl ₂	No	No	Xiao, 2012 ⁵⁰
Oxygen-embeded quinoidal nonacene		~ 37	Normal chemical reaction	Not specified	Poor solubility (strong aggregation)	No	No	Wang, 2019 ⁵¹
Tetrabenzononacene	 R = -H, -C(CH ₃) ₃ , -C(CH ₃) ₂ -C(CH ₃) ₃ , -C(CH ₃) ₂ -C(CH ₃) ₂ -C(CH ₃) ₃	~ 4	Normal chemical reaction	> 54 hours of half-life in solution (exposed to air and high-intensity light) > 6 months in solution in the dark	CHCl ₃ CS ₂ Cyclohexane	Yes	Yes	This work

5.7.5. Supporting Information Videos

Video S5.1. Reversible visible modulation of a blue ring-like device under a square waveform (with a frequency of 0.5 Hz, as well as minima of 0 kV and maxima of ~ 3.2 kV).

Video S5.2. Reversible fluorescence modulation of a blue ring-like device under a square waveform (with a frequency of 0.5 Hz, as well as minima of 0 kV and maxima of ~ 3.2 kV).

Video S5.3. Reversible near-IR modulation of a blue ring-like device under a square waveform (with a frequency of 0.5 Hz, as well as minima of 0 kV and maxima of ~ 3.2 kV).

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platforms. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supporting Information.

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CHAPTER 6

Large-Area Camouflage Systems Inspired by Cephalopod Skin

Contents

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6.1. Abstract

Materials and systems that can adaptively modulate their optical properties in response to external stimuli have garnered much research interest for enabling display, signaling, sensing, camouflage and energy conversion applications. However, the development of soft and stretchable large-area systems with dynamic optical functionalities have been proven technologically challenging. By drawing inspiration from cephalopods' size-variable color-changing chromatophore organs, we develop a new class of soft and stretchable large-area tri-layer platforms based on dielectric elastomer actuators for active camouflage and signaling. First, we fabricate and test prototypical small-scale tri-layer systems that exhibit excellent electromechanical performance with large areal strains of $\sim 60\%$ and extremely rapid responses of ~ 180 ms, dynamic surface morphologies upon electrical actuation with a > 17 -fold change in surface roughness, tunable optical properties across the visible and near-infrared regions with a 32-fold change in the specular-to-diffuse transmittance ratio, and exceptional compatibility for advanced device architectures such as multiplexing and stacking. Then, we fabricate and demonstrate a series of large-area tri-layer camouflage and signaling systems that are directly scaled up from those prototypical small-scale systems by an over 150-time size increase, featuring an unprecedented combination of characteristics, such as dynamic appearance and optical modulation, arbitrary patterning, angular independence, rapid response, and excellent cyclic stability. Altogether, our work holds relevance to a variety of research areas that include large-area camouflage and signaling systems, bioinspired

photonics, surface engineering, energy-conserving technologies, smart windows, and soft robotics.

6.2. Introduction

Adaptive optical materials that possess tunable transparency upon external stimuli have garnered much research interest for enabling display,^[1,2] signaling,^[3,4] sensing,^[5,6] camouflage,^[7,8] and energy conversion applications.^[9,10] Traditional stimuli-responsive, optically active systems have been extensively explored from small-scale devices to practical large-area applications, as exemplified by smart windows based on either electrochromic materials^[11,12] or polymer-dispersed liquid crystals;^[13,14] however, such large-area systems usually rely on rigid supporting substrates to function and suffer from performance degradation or even failure upon deformation.^[11–14] More recently, mechanically deformable large-area display systems have been reported, such as microfluidic channel-embedded soft machines^[15] and electroluminescent skins,^[16] but they usually suffer from limited spectral control, slow response, complicated device fabrication procedures, necessity for the injection of different liquids, poor long-term stability, rigorous requirement for device packaging, susceptibility to structural failure due to mechanical mismatch between soft and rigid components, and/or expensive constituent materials.^[15,16] Within the context, we have developed a series of soft and stretchable dielectric elastomer-based platforms for adaptive camouflage applications, featuring tunable optical functionalities in both the visible and infrared regions, excellent stretchability, cyclic stability, easily accessible actuation mechanism, and straightforward manufacture procedures.^[17,18] Despite all the advantages, there are still several challenges associated with our systems that remain unaddressed from practical applications

perspective: (1) scalability of these systems has not been explored in large-area device configurations, (2) in-situ optical characterization has not been achieved; (3) response time can be further shortened; and (4) arbitrary patterning has not been demonstrated. As such, there exist an impetus to further advance our dielectric elastomer-based systems.

Coleoid cephalopods are a class of soft-bodied marine invertebrates, including squid, octopuses, and cuttlefishes, known for their highly dynamic color-changing capabilities for camouflage and communication purposes.^[19,20] These marvelous visual feats are directly enabled by cephalopods' sophisticated skin architectures that are generally composed of three different types of light-interacting organs and cells, including pigmentary chromatophore organs, structurally colored iridophore cells, and diffusively reflective leucophore cells.^[20–22] Among these bio-optical organs and cells, chromatophores are of particular interest, because they are responsible for the dominant global pigmentary coloration of cephalopod skin, as shown by a *Doryteuthis pealeii* squid^[22] in Figure 6.1A and a *Sepia officinalis* cuttlefish^[23] in Figure 6.1B. The optically active component of a typical chromatophore organ is the central cytoelastic sacculus that encompasses packed pigment granules with diameters of hundreds of nanometers (note that the color of the pigment granules varies in different chromatophores, which can be yellow, red, brown, black, or pink) (Figure 6.1C and 6.1D).^[20–22,24–27] A set of radial muscles are attached and anchored into the highly deformable pigment granule-containing sacculus (Figure 6.1C and 6.1D).^[25–27] Before activation, the radial muscles are relaxed, and the sacculus is

retracted into a tiny dot with the internal pigmentary granules closely packed (Figure 6.1C, left and Figure 6.1D, left). After activation, the radial muscles are contracted, and the sacculus is radially pulled and expanded into a much thinner disc-like shape with a much larger areal coverage, as well as a much sparser distribution of the internal pigment granules (Figure 6.1C, right and Figure 6.1D, right). Thus, chromatophores are capable of dynamically and rapidly modulating the transmission and absorption of light through this neuromuscularly controlled mechanism.^[22,24–27] Excitingly, such optical functionalities of chromatophores exhibit nearly no dependence on their sizes, which usually can vary by a few orders of magnitude among different cephalopod species,^[25] as quantized by the diameter in the fully expanded state, from tens of microns ($< 50\text{ }\mu\text{m}$ for *S. officinalis* cuttlefishes)^[23] (Figure 6.1B, inset) to several millimeters ($> 1.5\text{ mm}$ for *D. pealeii* squid)^[22] (Figure 6.1A, inset). Overall, cephalopod skin, along with its constituent size-variable chromatophores, represents a perfect natural example of soft and stretchable bioelectronic displays with unmatched performance.

Within this context, we developed a new class of large-area camouflage systems by drawing inspiration from biological chromatophore organs in cephalopod skin and by leveraging our previously established technical foundations for artificial dielectric elastomer actuator-based devices.^[17,18] For this purpose, we initially conceptualize a relatively small-scale sandwich-type device architecture that consists of a top layer of a proton-conducting copolymer membrane as the top electrode and the top optically active

region, a middle layer of a dielectric elastomer membrane as the artificial muscle, and a bottom layer of another proton-conducting copolymer membrane as the bottom electrode and the bottom optically active region (Figure 6.1E and 6.1F). Before electrical actuation, our devices will possess relatively small optically active regions and relatively large overall thicknesses (Figure 6.1E, left and Figure 6.1F, left), analogous to the un-activated state of a typical chromatophore organ (Figure 6.1C, left and Figure 6.1D, left),^[24–27] with the devices’ visible appearances determined by the light-scattering effects arising from the nano-/micro-textured surface morphologies. After electrical actuation, our devices will expand the areal coverage of the optically active regions and reduce the overall thicknesses (Figure 6.1E, right and Figure 6.1F, right), analogous to the activated state of a typical chromatophore organ (Figure 6.1C, right and Figure 6.1D, right),^[24–27] with the devices’ visible appearances now determined by the altered light-scattering effects arising from the much-flattened surface morphologies. Moreover, we envision that our proposed small-scale tri-layer devices can be readily scaled up into large-area platforms with an at least a-few-orders-of-magnitude’s increase in device size while maintaining their abilities to modulate the areal coverage, overall thickness, surface morphology, and visible appearance of the optically active regions upon electrical actuation, analogous to those size-variable chromatophore organs found in different cephalopod species.^[25] Overall, our bioinspired design strategy will afford unprecedented large-area platforms with dynamic optical functionalities in the visible region for camouflage applications.

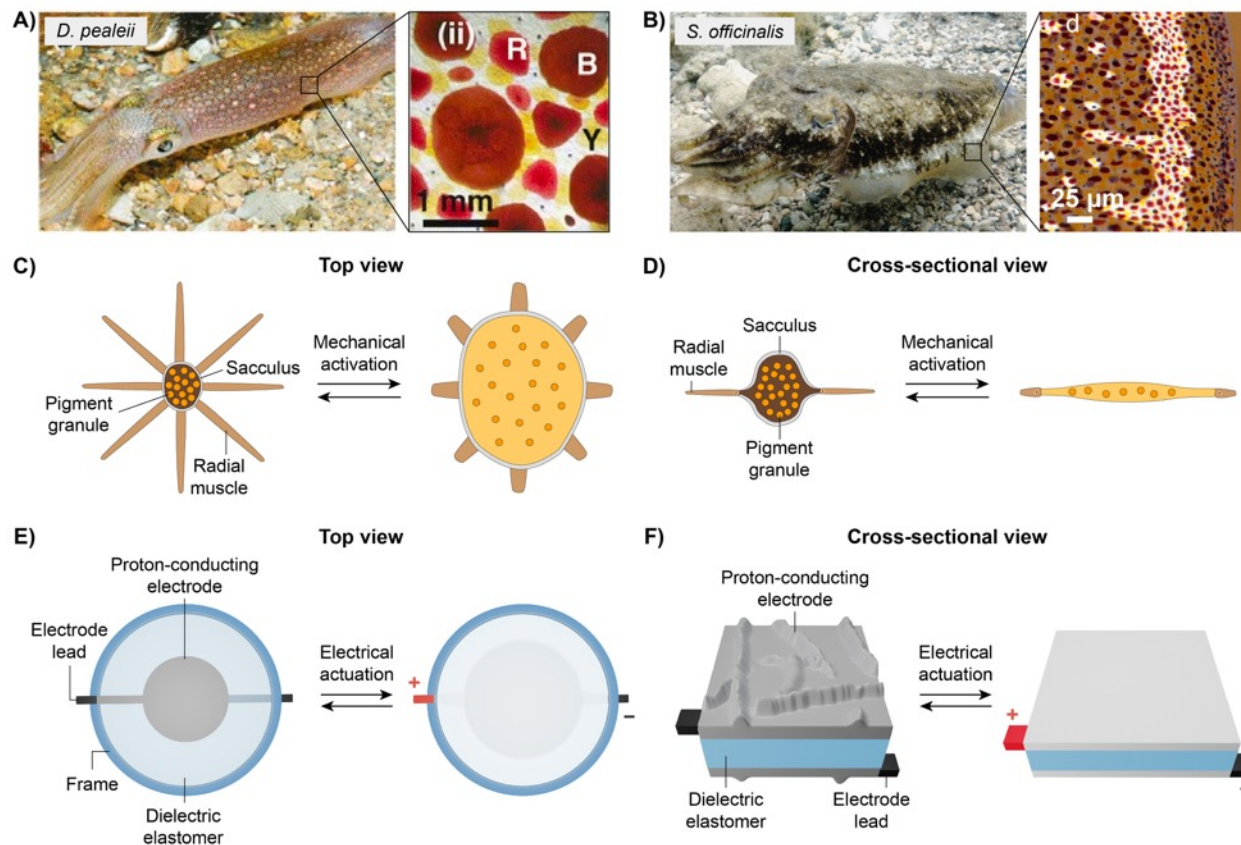


Figure 6.1. Biological Inspiration from Cephalopod Chromatophores. (A) A digital camera image of a *Doryteuthis pealeii* squid.^[22] The inset is an optical microscope image of the squid's skin, which features a dense distribution of chromatophore organs in red, brown, and yellow colors.^[22] Note that the size of the chromatophore organs varies from hundreds of microns to a few millimeters in diameter. (B) A digital camera of a *Sepia officinalis* cuttlefish.^[23] The inset is an optical microscope image of the cuttlefish's skin, which features a dense distribution of chromatophore organs in red, brown, and yellow colors.^[23] Note that the size of the chromatophore organs is estimated to be tens of microns. (C) A top-view schematic of a typical chromatophore organ before (left) and after (right) mechanical activation. Note that the radial muscles can be reversibly actuated through a neuromuscular mechanism to alter the areal coverage of the pigment granule-containing sacculus, as well the distribution of the pigment granules in the sacculus. (D) A cross-sectional schematic of a typical chromatophore organ before (left) and after (right)

mechanical activation. Note that the radial muscles can be reversibly actuated through a neuromuscular mechanism to alter the size and thickness of the pigment granule-containing sacculus, as well the distribution of the pigment granules in the sacculus. **(E)** A top-view schematic of our proposed tri-layer system before (left) and after (right) electrical actuation. Note that the size of the system’s optically active region can be reversibly altered. **(F)** A cross-sectional schematic of our proposed tri-layer system before (left) and after (right) electrical actuation. Note that the thickness and surface morphology of the system’s optically active region can be reversibly altered.

6.3. Results and Discussion

We started with the preparation of small-scale tri-layer devices according to standard procedures, which consisted of two tandem processes that were related to device fabrication (Figure 6.2A) and device activation (Figure 6.2B). In the device fabrication process, we first equiaxially stretched an optically transparent acrylate-based dielectric elastomer by $\sim 1,600\%$ in area with a home-built stretchable holder and then fixed the pre-stretched elastomer onto a rigid acrylic-based frame (Figure 6.2A, i). Second, we laminated two identical circularly shaped proton-conducting copolymer membranes that featured high optical transparency onto the top and bottom sides of the pre-stretched elastomer, forming a sandwich-type structure (Figure 6.2A, ii). Third, we attached two identical thin stripes of aluminum foil-based electrical leads to interface with the top and bottom proton-conducting electrodes (Figure 6.2A, iii). This three-step fabrication process afforded partially completed devices that were ready for electrical activation. In the following device activation process, we first connected the two electrical leads of the

partially completed device to an external power supply in the absence of voltage (Figure 6.2B, i). Second, we applied a voltage of ~ 3.5 kV to electrically actuate the device for a duration of one second (Figure 6.2B, ii). Third, we withdrew the applied voltage and allowed the device to recover (Figure 6.2B, iii). This three-step activation process resulted in a fully completed device. Combined, our straightforward device fabrication and activation procedures readily furnished small-scale tri-layer devices that were used for further electromechanical, optical, and morphological characterizations.

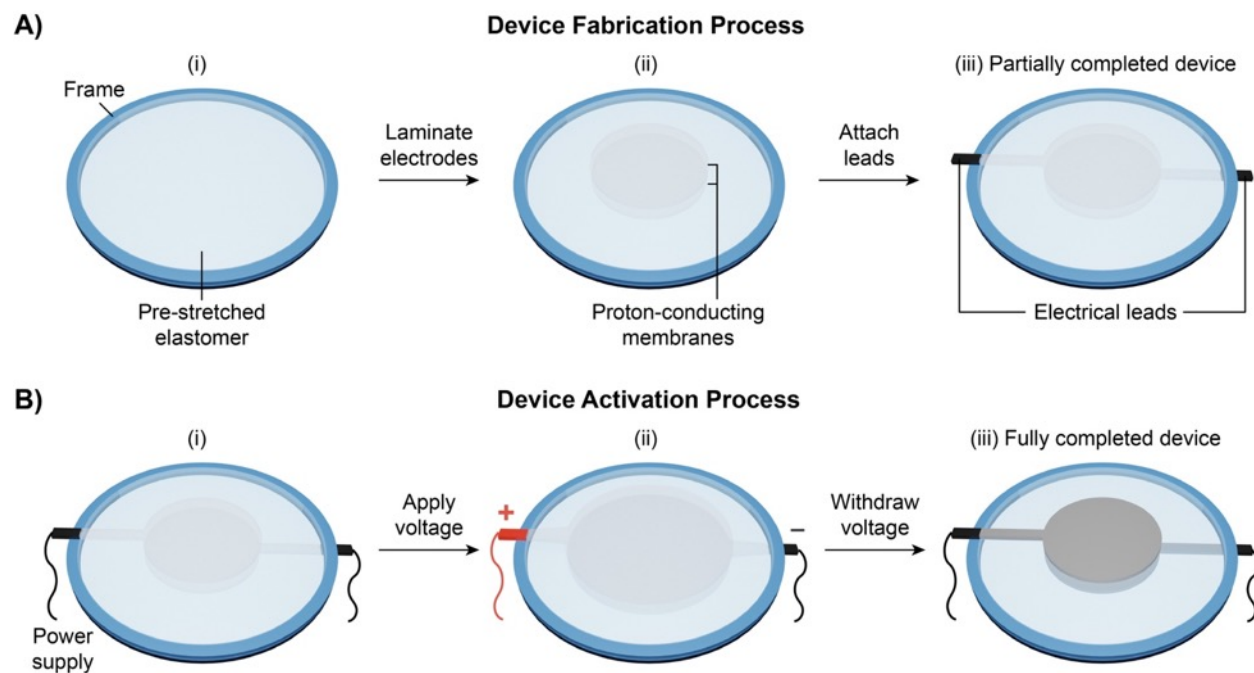


Figure 6.2. Device Fabrication and Activation. (A) A scheme of the three-step device fabrication process for partially completed small-scale tri-layer devices, which includes (i) the preparation of a pre-stretched dielectric elastomer on a rigid frame; (ii) the lamination of a pair of proton-conducting copolymer membranes; and (iii) the attachment of a pair of electrical leads. (B) A scheme of the three-step device activation process for fully completed small-scale tri-layer devices, which includes (i) the connection of a partially

completed device (from **A**, (iii)) to an external power supply; (ii) the application of a high voltage to the partially completed device for electrical activation (note the areal expansion in the optically active region); and (iii) the withdrawal of the applied voltage to obtain the fully completed device (note the appearance change in the optically active region).

We evaluated the electromechanical characteristics of our small-scale tri-layer devices in response to electrical stimuli. The application of a voltage on the top and bottom proton-conducting electrodes readily induced the generation of an electrostatic force across the middle acrylate-based dielectric elastomer, thus leading to a decrease in the thickness of the elastomer and an expansion in the area of the electrodes (i.e., the optically active regions) (Figure 6.3A). For our devices, we found that the areal strain in the optically active regions initially exhibited a nearly exponential dependence on the applied voltage with a strain of $50 \pm 5\%$ at a voltage of ~ 2.6 kV, and then followed up with a slightly slower quasi-linear increase with a maximum strain of $57 \pm 7\%$ at a voltage of ~ 3.5 kV (Figure 6.3B). Next, we studied the response time of our devices, which was defined as the rise time needed to go from 10% to 90% of the maximum areal strain change attainable in each cycle, upon the application of a square-waveform voltage at a frequency of 0.5 Hz (minima at 0 kV and maxima at ~ 3.5 kV). The devices featured rapid responses of 180 ± 10 ms upon electrical activation, with a corresponding areal expansion rate of $42 \pm 1\%$ (when the voltage was switched on) and a nearly identical areal shrinkage rate of $42 \pm 1\%$ (when the voltage was switch off), as demonstrated by three continuous electrical actuation cycles of a typical device in Figure 6.3C, which was at least two times faster

than that of analogous acrylate-based dielectric elastomer actuators in the literature.^[17,18] Overall, these experiments demonstrated the excellent electromechanical performance of our small-scale tri-layer devices that featured large areal strains and rapid responses under electrical actuation.

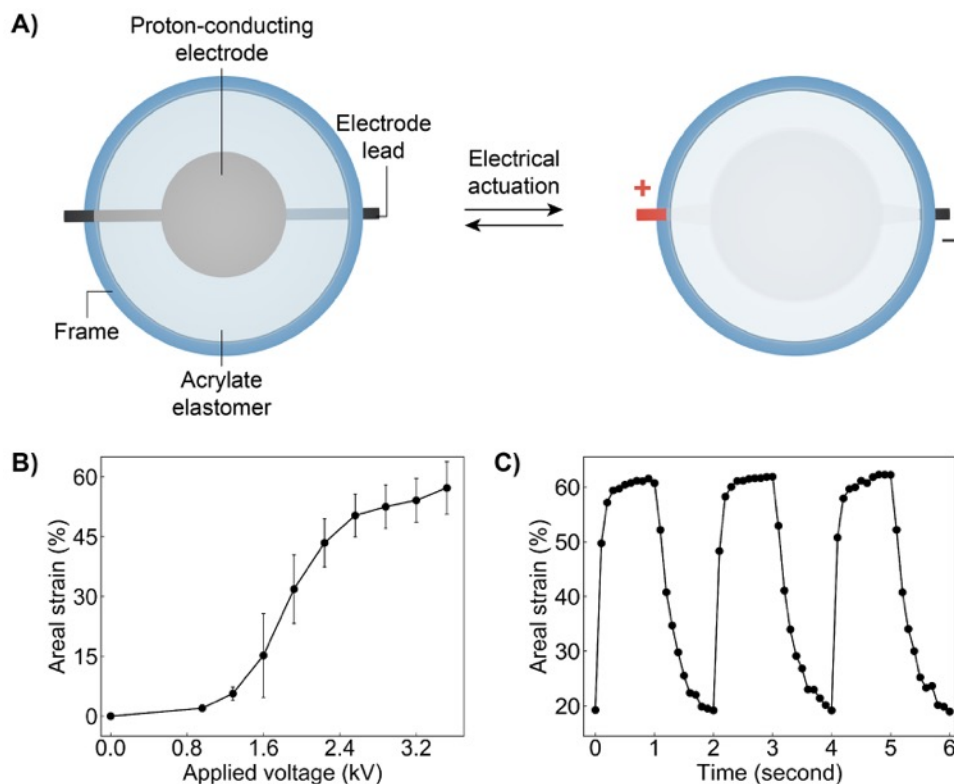


Figure 6.3. Electromechanical Characterization. (A) A schematic of a small-scale tri-layer device before (left) and after (right) electrical actuation. (B) A plot of the areal strain as a function of the applied voltage for small-scale tri-layer devices. (C) A representative plot of the areal strain as a function of time for a typical small-scale tri-layer device under a square-waveform voltage at a frequency of 0.5 Hz (minima at 0 kV and maxima at ~ 3.5 kV) over three consecutive cycles.

Having demonstrated the devices' excellent electromechanical characteristics, we proceeded to study the effects of electrical actuation on the surface morphology of our small-scale tri-layer devices with a combination of microscopy techniques (Figure 6.4A). First, we monitored the real-time (*in-situ*) change of the surface morphology within our devices upon electrical actuation using an optical microscope. Before electrical actuation, the devices were covered with a sparse distribution of micron-sized wrinkles on the surface (Figure 6.4B, left). After electrical actuation, the same devices flattened out and now possessed much smoother surfaces with no apparent wrinkles (Figure 6.4B, right). Such dynamic modulation of surface structures was rapid and fully reversible after numerous actuation cycles during the electrical tests (Video S6.1). Next, we further characterized the morphological modulation of our devices upon electrical actuation using an atomic force microscope (AFM) and a scanning electron microscope (SEM). For *ex-situ* imaging purposes, our devices were fabricated into instrument-compatible samples that were fixed onto customized substrates and were able to maintain the exact surface features at different electrical actuation states (see the Supporting Information for details). Before electrical actuation, the samples exhibited a sparsely distributed three-dimensional network of interconnected wrinkled surface microstructures with lengths of tens of microns and widths between 500 and 700 nm, as confirmed by both the AFM and SEM images (Figure 6.4C, left and Figure S6.1, left), featuring an overall root-mean-square (RMS) roughness of 246 ± 13 nm. After electrical actuation, the samples flattened out and possessed a much smoother two-dimensional surface with no apparent wrinkles, again, as

confirmed by both the AFM and SEM images (Figure 6.4C, right and Figure S6.1, right), now featuring an overall RMS roughness of 14 ± 3 nm. Note that the *ex-situ* AFM and SEM measurements were highly consistent with the direct *in-situ* observations using optical microscopy. Combined, these experiments demonstrated that electrical actuation readily modulated the surface morphology of our devices and altered the overall RMS roughness by over one order of magnitude (> 17 -fold).

After confirming the reversible surface morphological modulation of our devices, we next investigated the effects of electrical actuation on the optical and spectroscopic properties of our small-scale tri-layer devices in the visible and near-IR regions of the electromagnetic spectrum. For this purpose, we fabricated slightly modified devices that were compatible with the UV/Vis-NIR spectrometer and then applied a frequency-variable square-wave voltage (minima at 0 kV and maxima at ~ 3.5 kV) to the devices, which readily allowed direct spectral measurements through the optically active regions of our devices in real time (see Figure 6.4D and the Supporting Information for details). Before electrical actuation, our devices appeared opaque with a diffusively white color in the optically active regions, which largely obscured the underlying background picture (Figure 6.4E, left). The corresponding UV/Vis-NIR spectra revealed high broadband total transmittances of $89 \pm 1\%$ with specular components of $66 \pm 5\%$ and diffuse components of $23 \pm 5\%$, as averaged from 400 nm to 2 μm in wavelength, featuring a relatively low specular-to-diffuse ratio of ~ 2.9 (Figure 6.4F, left). After electrical actuation, the same

devices turned completely transparent in the same optically active regions, along with a noticeable expansion in the areal coverage, and now exposed the underlying background picture with a high level of optical clarity (Figure 6.4E, right). The corresponding UV/Vis-NIR spectra revealed slightly increased broadband total transmittances of $93 \pm 1\%$ with increased specular components of $92 \pm 1\%$ and decreased diffuse components of $1 \pm 1\%$, again, as averaged from 400 nm to 2 μm in wavelength, featuring a relatively high specular-to-diffuse ratio of ~ 92 (Figure 6.4F, right). Thus, electrical actuation not only reversibly switched the visual appearances but also dynamically altered the light-transmitting properties of our devices with a nearly 32-fold change in the specular-to-diffuse transmittance ratio in the visible and near-IR regions, in large parts due to their tunable surface morphologies upon electrical actuation. This dynamic modulation of optical and spectroscopic properties of our devices were rapid, stable, and fully reversible, which exhibited almost no degradation in performance after 30 and 50 repeated electrical actuation cycles that were tracked and measured *in situ* (Figure S6.2). Overall, these experiments demonstrated the dynamic optical functionality of our devices in the visible and near-IR regions upon electrical actuation.

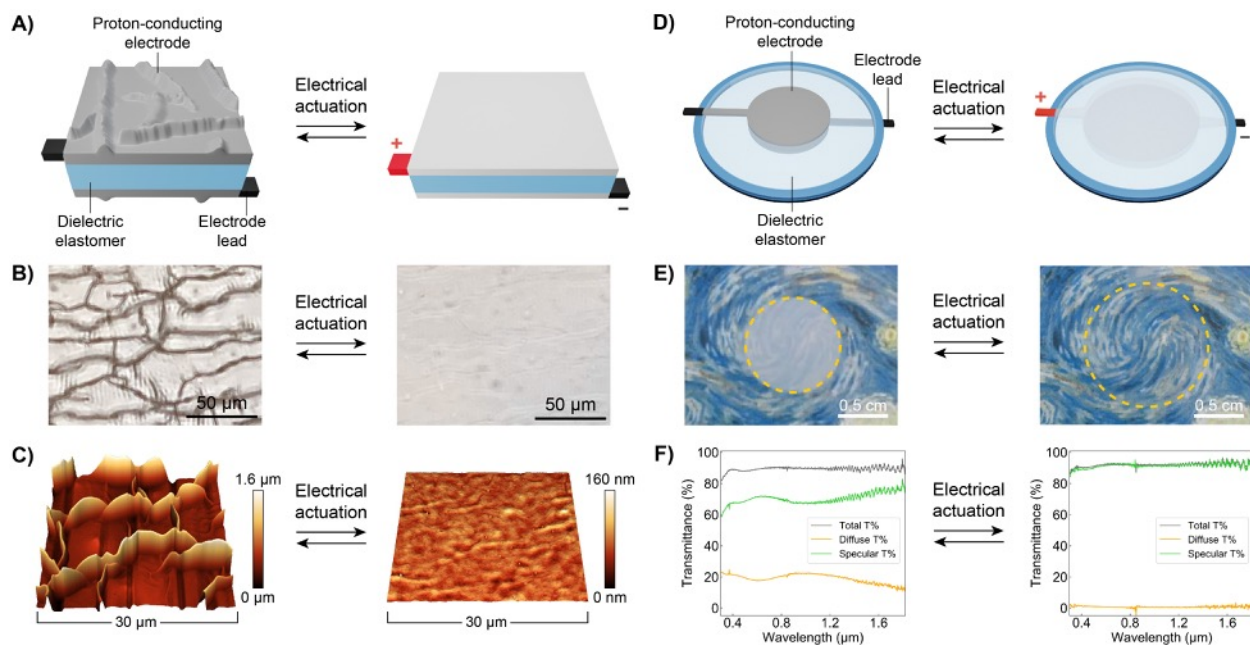


Figure 6.4. Morphological, Optical, and Spectroscopic Characterization. (A) A cross-sectional schematic of the surface morphology of a small-scale tri-layer device before (left) and after (right) electrical actuation. (B) Representative *in-situ* optical microscope images of the surface morphology of a small-scale tri-layer device before (left) and after (right) electrical actuation. (C) Representative *ex-situ* atomic force microscope (AFM) images of the surface morphology of small-scale tri-layer devices before (left) and after (right) electrical actuation. (D) A top-view schematic of a small-scale tri-layer device before (left) and after (right) electrical actuation. (E) Representative *in-situ* digital camera images of the visual appearance of a small-scale tri-layer device before (left) and after (right) electrical actuation. The optically active area of the device was highlighted with yellow-colored contours. (F) Representative *in-situ* UV/Vis-NIR transmittance spectra for a small-scale tri-layer device before (left) and after (right) electrical actuation. The total transmittances (gray curves) were shown along with the specular (green curves) and diffuse (orange curves) components.

We then investigated the effects of electrical actuation on the spectroscopic properties of our small-scale tri-layer devices in the short-wavelength, mid-wavelength, and long-wavelength regions of the electromagnetic spectrum. Similarly to previous experiments, we fabricated slightly modified devices that were compatible with the Fourier-transform infrared (FTIR) spectrometer and then applied a square-wave voltage at a frequency of 0.02 Hz (minima at 0 kV and maxima at ~ 3.5 kV) to the devices, which readily allowed direct spectral measurements of the optically active regions of our devices in real time (see the Supporting Information for details). Before electrical actuation, the *in-situ* infrared spectra revealed moderate total transmittances of $55 \pm 1\%$ with specular components of $45 \pm 1\%$ and diffuse components of $10 \pm 1\%$, as averaged from $2\text{ }\mu\text{m}$ to $16.5\text{ }\mu\text{m}$ in wavelength, featuring a relatively low specular-to-diffuse ratio of ~ 4.5 (Figure S6.3, left). After electrical actuation, the *in-situ* infrared spectra for the same devices' optically active regions revealed slightly increased total transmittances of $60 \pm 1\%$ with increased specular components of $50 \pm 1\%$ and nearly unchanged diffuse components of $10 \pm 1\%$, featuring a relatively high specular-to-diffuse ratio of ~ 5 (Figure S6.3, right). Thus, electrical actuation dynamically modulated the infrared-transmitting properties of our devices, with an $\sim 5\%$ increase in the total transmittance and an ~ 1.1 -fold change in the specular-to-diffuse transmittance ratio, in large parts due to their altered thicknesses and surface morphologies upon electrical actuation. This dynamic modulation of infrared spectroscopic properties of our devices were rapid, stable, and fully reversible, with almost no degradation in performance after 30 and 50 repeated electrical actuation cycles that

were tracked and measured *in situ* (Figure S6.4). Taken together, these experiments demonstrated the dynamic optical functionality of our devices in the short-wavelength, mid-wavelength, and long-wavelength infrared regions upon electrical actuation.

Having verified the dynamic optical functionalities of our devices, we then explored the compatibility of the small-scale tri-layer devices in advanced device architectures with a multiplexed configuration for camouflage applications. To this end, we fabricated a 1×3 multiplexed device with three identical small-scale flat-type devices arranged in a horizontal row as three independent pixels, which were in turn connected with separate electrical leads for actuation (see Figure S6.5 and the Supporting Information for fabrication details). Prior to any electrical actuation, all three pixels in the multiplexed array appeared opaque in the optically active region with a relatively small areal coverage, which obscured the underlying dark background (Figure 6.5, i). In one demonstration, only one single pixel in the multiplexed array was independently addressed. The actuated single pixel became highly transparent in its optically active region with a relatively larger areal coverage, which readily revealed the underlying dark background and drew a significant contrast to the other two standby unactuated pixels (Figure 6.5, ii and iii). In another demonstration, multiple pixels in the same array were simultaneously actuated and readily exhibited tandem changes in their appearances upon selective electrical actuation (Figure 6.5, iv, v, and vi). Such dynamic modulation of our multiplexed devices were rapid, robust, and highly reversible after repeated actuation cycles, thus enabling

the devices to display and switch between a variety of patterns through a user-specific control process (Video S6.2). Overall, our experiments showcased prototypical multiplexed devices with dynamic optical functionality for on-demand camouflage applications.

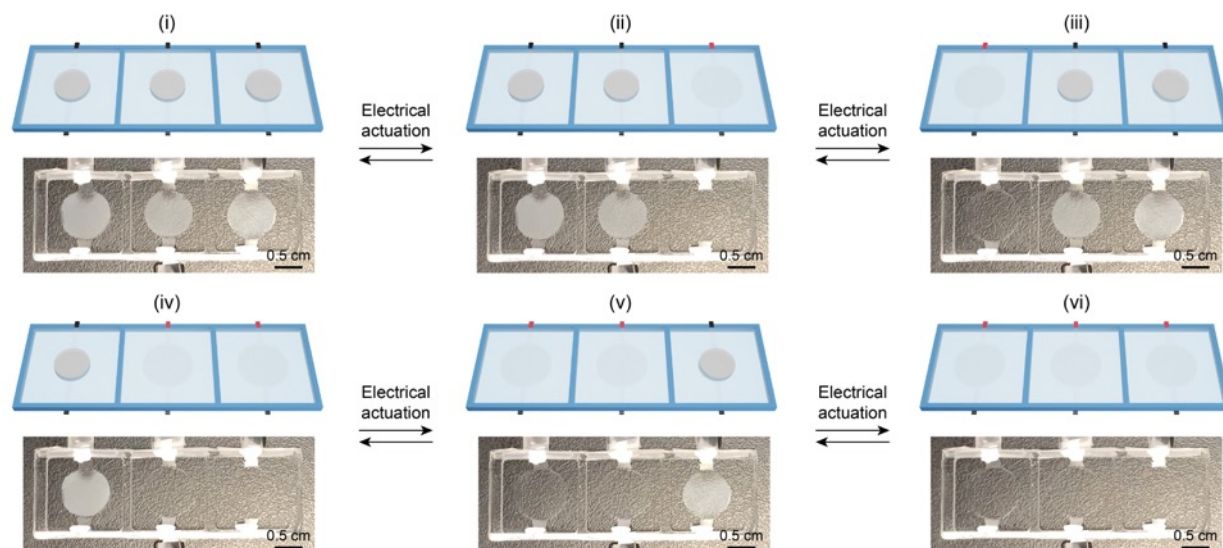


Figure 6.5. Advanced Device Architecture in Multiplexed Formats. A series of digital camera images of selective electrical actuation of a representative 1×3 multiplexed device that was fabricated with three individual small-scale tri-layer pixel units, showing that (i) all three pixels were unactuated; (ii, iii) only one pixel was electrically actuated, while the other two remained unactuated; (vi, v) two pixels were electrically actuated, while the other one remained unactuated; and (vi) all three pixels were electrically actuated at the same time.

We proceeded to explore a different type of advanced device architecture by translating the small-scale tri-layer devices in the vertical direction to enable graded transparency modulation for camouflage applications. For this purpose, we fabricated a 3×1 multilayered device by vertically stacking three identical small-scale tri-layer devices as three independent constituent layers, which were in turn connected with separate

electrical leads for actuation (see Figure S6.6 and the Supporting Information for fabrication details). In the standby mode, all three constituent layers were unactuated, and their optically active regions stayed small in area with opaque appearances. This combination allowed the multilayered device to block the view of the underlying background picture with the lowest overall transparency (defined as Grade 1 in Figure 6.6). In one operation mode, the top layer in the multilayered structure was actuated upon a selective electrical stimulus, while the other two layers remained unactuated. The corresponding optically active region of the actuated top layer turned transparent with an expansion in area, contributing to enhanced visibility of the background picture with slightly improved overall transparency (defined as Grade 2 in Figure 6.6). In a second operation mode, the top and middle layers in the multilayered structure were simultaneously actuated upon selective electrical stimuli, while the bottom layer remained unactuated. The corresponding optically active regions of the actuated top and middle layers turned transparent with clear expansions in the area, resulting in even better visibility of the background picture with much-improved overall transparency (defined as Grade 3 in Figure 6.6). In a third operation mode, all three constituent layers were electrically actuated at the same time. The corresponding optically active regions of these three layers turned transparent with nearly identical areal expansions, giving rise to a clear view of the background picture with the highest overall transparency (defined as Grade 4 in Figure 6.6). Such dynamic modulation of our vertically stacked devices was rapid, robust, and highly reversible after repeated actuation cycles (Video S6.3). Overall,

our experiments highlighted multilayered devices with exceptional graded control over their optical appearances from opaque to transparent states for active camouflage applications.

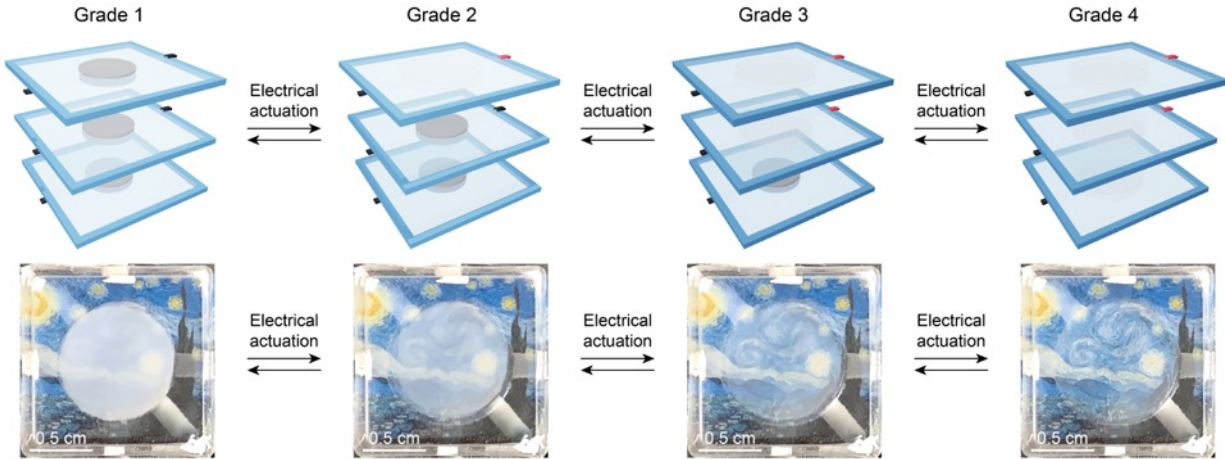


Figure 6.6. Advanced Device Architecture in Vertically Stacked Formats. A series of digital camera images of selective electrical actuation of a representative 3×1 stacked device that was fabricated with three vertically stacked small-scale tri-layer pixel units, demonstrating four different operation modes for graded transparency modulation.

After demonstrating the versatile applications enabled by our small-scale tri-layer devices, we proceeded to validate the scalability of these devices for large-area camouflage applications in the visible region of the electromagnetic spectrum. For this purpose, we fabricated large-area devices with enlarged components in an analogous sandwich-type structure according to modified fabrication procedures (see Figure 6.7A and the Supporting Information for fabrication details). These large-area devices contained circularly shaped optically active regions with diameters of ~ 12.5 cm, and the overall areas of the devices' optically active regions were over 150 times greater than those of

previously described small-scale devices. Before electrical actuation, the large-area devices exhibited relatively small optically active regions with diffusively white opaque appearances, presumably due to the presence of wrinkled surface microstructures, as demonstrated by a person completely invisible behind a typical large-area device (Figure 6.7B, left) and by an obscured background picture of *Mona Lisa* that was imaged through the central portion of the optically active region of the same device (Figure 6.7C, left). After electrical actuation, the large-area devices readily expanded the optically active regions and switched to highly transparent states, presumably due to the absence of surface microstructures, as demonstrated by the same person now fully exposed (Figure 6.7B, right) and by the same background picture of *Mona Lisa* now clearly revealing her smile (Figure 6.7C, right). Our devices' abilities to dynamically camouflage and expose arbitrary background objects were rapid, stable, and highly reversible under repeated actuation cycles (Video S6.4). Excitingly, electrical actuation readily modulated the optical functionalities of our large-area devices, which was in a highly analogous fashion to that of small-scale devices, although the overall areas of the large-area devices' optically active regions were significantly increased by over two orders of magnitude. Altogether, our experiments underscored the scalability of our devices for large-area camouflage applications with excellent performance.

Last, we explored the patterning compatibility of our large-area tri-layer devices for silhouette camouflage applications. For this purpose, we fabricated a series of large-

area devices with pre-defined surface patterns in a sandwich-type structure according to modified fabrication procedures (see Figure 6.7D and the Supporting Information for fabrication details). These large-area devices contained circularly shaped optically active regions with diameters of ~ 7.5 cm, which encompassed silhouetted regions in the center, and the areas of the devices' optically active regions were over 50 times greater than those of previously described small-scale devices. Before electrical actuation, the devices exhibited relatively small active regions with distinguishable patterns, which were consisted of two distinct sub-regions that included optically transparent silhouettes in the center and optically opaque regions in the surrounding, presumably due to the absence of surface microstructures in the transparent regions and the presence of surface microstructures in the opaque regions, as shown by representative devices with an octopus-like pattern (Figure 6.7E, left) and a soldier-like pattern (Figure 6.7F, left). After electrical actuation, the same devices expanded the optically active regions and now became highly optically transparent as a whole with no observable patterns, presumably due to the absence of surface microstructures in both sub-regions, as shown by the octopus (Figure 6.7E, right) and the soldier (Figure 6.7F, right) vanishing into the backgrounds. Notably, such electrically controlled silhouette camouflage not only exhibited the compatibility to be extended for a variety of complex patterns including (but not limited to) butterflies, birds, fighter jets, unicorns, and arbitrary combinations of letters but also displayed nearly unaffected camouflage performance at different viewing angles (Video S6.5). Combined,

these experiments showcased our large-area devices' unprecedented patterning capabilities for active silhouette camouflage applications.

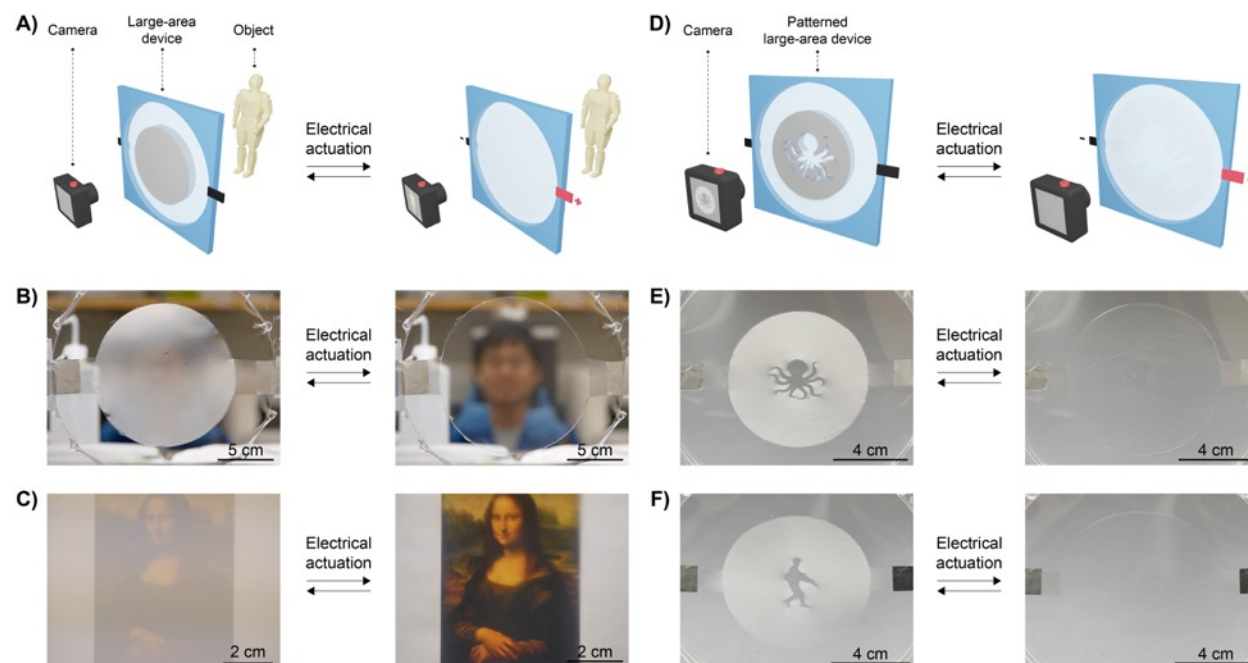


Figure 6.7. Large-Area Devices for Dynamic Camouflage in the Visible. (A) A schematic of a large-area tri-layer device before (left) and after (right) electrical actuation under the digital camera imaging mode. Note that the object located behind the large-area device (such as a human model) can be reversibly camouflaged (left) or revealed (right) by the device's optically active region upon electrical actuation. (B) Digital camera images of a real person standing behind a representative large-area device being reversibly hidden (left) or exposed (right) by the device's optically active region before (left) and after (right) electrical actuation. (C) Digital camera images of a background picture of 'Mona Lisa' placed behind the same large-area device being reversibly camouflaged (left) or revealed (right) by the device's optically active region before (left) and after (right) electrical actuation. The images were taken through the central portion of the optically active region of the large-area device. (D) A schematic of a pre-patterned large-area tri-layer device before (left) and after (right) electrical actuation under the digital camera

imaging mode. Note that the pre-defined pattern (such as an octopus) in the large-area device' optically active region can be reversibly revealed (left) or camouflaged (right) upon electrical actuation. **(E)** Digital camera images of a representative large-area device reversibly revealing (left) or camouflaging (right) the octopus-like pattern in the device's optically active region before (left) and after (right) electrical actuation. **(F)** Digital camera images of a representative large-area device reversibly revealing (left) or camouflaging (right) the solid-like pattern in the device's optically active region before (left) and after (right) electrical actuation.

6.4. Conclusion

To summarize, we have reported the design, fabrication, and characterization of a series of small-area and large-area tri-layer dielectric elastomer actuator-based systems for active camouflage applications by drawing inspiration from cephalopods' size-variable color-changing chromatophore organs, and our systems hold significance from both technological and engineering perspectives for several reasons. First, our small-scale tri-layer devices exhibit excellent electromechanical performance with large areal strains of $\sim 60\%$ and extremely rapid responses of ~ 180 ms, which are over two times faster than those of analogous dielectric elastomer actuators in the literature.^[17,18] Second, our devices demonstrate dynamic surface morphologies upon electrical actuation, with their RMS roughnesses adjustable by over one order of magnitude (> 17 -fold). Third, these electrically actuated devices highlight dynamic optical and spectroscopic functionalities not only by changing their visual appearances but also by altering their light-transmitting properties, featuring a nearly 32-fold change in the specular-to-diffuse transmittance ratio

across the visible and near-IR regions. Fourth, our devices are compatible with a variety of advanced architectures in multiplexed and stacked formats, which directly allow user-specific control for on-demand optical modulation. Fifth, our devices can be readily scaled up by over 150 times in size for large-area camouflage platforms that feature dynamic appearance modulation, arbitrary patterning, angular independence, rapid response, and excellent cyclic stability. Altogether, our cephalopod-inspired systems showcase an unprecedented combination of capabilities that makes them valuable for large-area camouflage applications.

Moving forward, our findings enable numerous opportunities for advancing the described large-area camouflage systems. First, our large-area platforms can be further optimized and modified by incorporating advanced photonic structures or coatings to improve the devices' optical properties in other technologically valuable regions (e.g., the infrared and ultra-violet regions) of the electromagnetic spectrum. Second, higher pixel densities are also possible for our large-area devices in both multiplexed and stacked configurations, which will afford more precise control of the devices' overall optical appearances and functionalities. Third, individual components that make up our prototypical large-area devices can be prepared with standard high-throughput manufacturing approaches, such as inkjet printing and spraying coating, which will allow the manufacture of such large-area devices through customized roll-to-roll processes. Fourth, our large-area platforms are readily compatible to be integrated into specific

targeted applications that include windows, building exteriors, and privacy-protecting enclosures. Fifth, high operating voltages that are associated with our large-area platforms need to be reduced, which can be achieved by optimizing the physical properties of the constituent dielectric elastomers (e.g., dielectric constants and Young's moduli). Overall, our work holds relevance to a variety of research areas that include adaptive camouflage and signaling, bioinspired photonics, dynamic surface engineering, energy-conserving technologies, smart windows, and soft robotics.

6.5. Supporting Information

6.5.1. Fabrication and Activation of Small-Scale Tri-Layer Devices

The small-scale tri-layer devices were fabricated and activated according to standard procedures as illustrated in Figure 6.2. In the device fabrication process (Figure 6.2A), first, an acrylate-based dielectric elastomer (VHB 4905, 3M) was equiaxially stretched by $\sim 1,600\%$ (relative to its initial area) and then fixed onto a rigid acrylic frame. Next, a pair of identical circularly shaped proton-conducting membranes (e.g., ~ 1 cm in diameter for the devices shown in Figure 6.3 and Figure 6.4) were prepared from a sulfonated pentablock copolymer (NEXARTM, Kraton Polymers LLC) using previously reported procedures^[17,18] and separately laminated onto the top and bottom sides of the elastomer. Last, a pair of identical stripe-shaped aluminum foil-based electrical leads were separately attached to the top and bottom proton-conducting copolymer membranes. In the following device activation process (Figure 6.2B), first, the electrical leads of the partially completed devices were connected to an external high-voltage power source. Then, a voltage of ~ 3.5 kV was applied to electrically activate the devices for a duration of one second. Last, the applied voltage was withdrawn, and the devices were allowed to recover. Combined, these six steps furnished fully completed small-scale tri-layer devices (shown in Figure 6.2B, iii) that were ready for electromechanical, optical, microscopic, and spectroscopic measurements, without any special packaging or encapsulation.

6.5.2. Electromechanical Characterization of Small-Scale Tri-Layer Devices

The small-scale tri-layer devices prepared in Section 6.5.1. were electromechanically characterized according to standard procedures. The devices were connected to an external home-built high-voltage power source that was consisted of a function generator (DS345, Stanford Research), an operational amplifier (OPA 548, Texas Instruments), and a high-voltage amplifier (E80, EMCO). The areal strain of the devices upon electrical actuation was defined according to the equation:

$$Areal\ strain\ (\%) = [(A_1 - A_0)/A_0] \times 100\%$$

where A_0 is the area before electrical actuation and A_1 is the area after electrical actuation. The devices' response time (t_{res}) during a typical actuation cycle was defined according to the equation:

$$t_{res} = t_{90\%} - t_{10\%}$$

where $t_{90\%}$ is the rise time to reach 90% of the maximum change in area during one typical actuation cycle and $t_{10\%}$ is the rise time to reach 10% of the maximum change in area during the same actuation cycle. The electrical actuation was performed at a relative humidity of $\sim 50\%$ under ambient conditions. The relevant experiments shown in Figure 6.3B were all repeated for at least 5 independent devices.

6.5.3. In-Situ Optical Microscopic Characterization of Small-Scale Tri-Layer Devices

The small-scale tri-layer devices were characterized *in situ* with optical microscopy upon electrical actuation according to standard procedures. The surface morphologies of

the devices were imaged in real time upon electrical actuation using an optical microscope imaging system (EVOS™ M5000, Thermo Fisher Scientific) with a 20X objective in the transmission mode. The experiments were repeated for at least three independent devices at a relative humidity of $\sim 50\%$ under ambient conditions.

6.5.4. Microscopic Characterization of Small-Scale Tri-Layer Devices

The small-scale tri-layer devices were characterized with ex-situ microscopy techniques that included atomic force microscopy (AFM) and scanning electron microscopy (SEM). For these purposes, the devices were fabricated into instrument-compatible samples that were tightly fixed onto customized supporting substrates and were able to maintain the exact surface features at unactuated and electrically actuated states. For the AFM imaging, the surface morphologies of the samples were imaged with a Cypher ES AFM (Asylum) using the tapping mode. The topological information of the samples, such as height distributions and root-mean-square (RMS) roughnesses, was extracted from the AFM data with the Gwyddion software package. For the SEM imaging, the surface morphologies of the samples were imaged with a Quanta 3D FEG SEM (FEI). All the AFM and SEM measurements were repeated for at least three independent devices.

6.5.5. In-Situ UV/Vis-NIR Spectroscopic Characterization of Small-Scale Tri-Layer Devices

The small-scale tri-layer devices were characterized *in situ* with UV/Vis-NIR spectroscopy upon electrical actuation according to standard procedures. To obtain the

total transmittance and diffuse transmittance in the visible and near-infrared region of the electromagnetic spectrum, the devices were characterized with a Jasco V670 UV-Vis-NIR Spectrometer that was equipped with a Jasco ILN-925 150 mm integrating sphere, which features a rectangular-shaped sample port with a length of ~ 0.9 cm and a width of ~ 1.3 cm in the transmission mode. The UV/Vis-NIR measurements were performed at normal incidence in the transmission mode and were referenced to Jasco Spectralon standards as appropriate. Both total transmittance and diffuse transmittance spectra were collected within a spectral range from wavelengths of 400 nm to 2 μ m. The specular transmittance was calculated according to the equation:

$$\text{Specular Transmittance (\%)} + \text{Diffuse Transmittance (\%)} = \text{Total Transmittance (\%)}$$

For the in-situ spectroscopic measurements for cyclic stability testing, frequency-variable square waveforms were applied. A square waveform at a frequency of 0.5 Hz (minima at 0 kV and maxima at ~ 3.5 kV) was applied to cycle the devices in between the spectroscopic measurements, and the square waveform was switched to a different frequency of 0.0025 Hz (minima at 0 kV and maxima at ~ 3.5 kV) during the *in-situ* spectroscopic measurements (corresponding to Figure 6.4F and Figure S6.2). Note that the devices' optically active regions before and after electrical actuation were always sufficiently large to cover the sample ports. The experiments were repeated for at least three independent devices at a relative humidity of ~ 50 % under ambient conditions. The obtained spectra were processed and analyzed with the Jasco Spectra ManagerTM Suite software package and Python.

6.5.6. In-Situ Infrared Spectroscopic Characterization of Small-Scale Tri-Layer Devices

The small-scale tri-layer devices were characterized *in situ* with infrared spectroscopy upon electrical actuation according to standard procedures. To obtain the total transmittance and diffuse transmittance in the short-wavelength, mid-wavelength, and long-wavelength regions of the electromagnetic spectrum, the devices were characterized with a Perkin Elmer Frontier Fourier Transform Infrared (FTIR) Spectrometer that was equipped with a PIKE Technologies Mid-Infrared integrating sphere, which features a circular sample port with a diameter of ~ 2.1 cm in the transmission mode. The FTIR measurements were performed at normal incidence in the transmission mode and were referenced to a Pike Technologies diffuse gold standard as appropriate. Both total transmittance and diffuse transmittance spectra were collected within a spectral range from wavelengths of $2\text{ }\mu\text{m}$ to $16.5\text{ }\mu\text{m}$. The specular transmittance was calculated according to the equation:

$$\textit{Specular Transmittance} (\%) + \textit{Diffuse Transmittance} (\%) = \textit{Total Transmittance} (\%)$$

For the in-situ spectroscopic measurements for cyclic stability under repeated electrical actuation, a constant square waveform was applied at a frequency of 0.02 Hz (minima at 0 kV and maxima at ~ 3.5 kV) both during and in between the spectroscopic measurements (corresponding to Figure S6.3 and Figure S6.4). Note that the devices' optically active regions before and after electrical actuation were always sufficiently large to cover the sample ports. The experiments were repeated for at least three independent devices at a relative humidity of $\sim 50\%$ under ambient conditions. The obtained spectra

were processed and analyzed with the Perkin Elmer Spectrum software package and Python.

6.5.7. Fabrication and Activation of Multiplexed Small-Scale Tri-Layer Devices

The 1×3 multiplexed devices were fabricated according to standard procedures, as illustrated in Figure S6.5. First, a rigid acrylic frame with three identical square-shaped openings in a row was prepared with a laser cutter (Fusion M2, Epilog) (Figure S6.5, i). Next, three single small-scale tri-layer devices (defined as individual pixel units) were fabricated into the openings of the acrylic frame with separate electrical leads (Figure S6.5, ii-iv). Last, all the pixel units in the partially completed multiplexed device were electrically activated using the same approach as described in Section 6.5.1. (Figure S6.5, v). These steps furnished fully completed small-scale multiplexed devices for dynamic camouflage demonstrations.

6.5.8. Fabrication and Activation of Vertically Stacked Small-Scale Tri-Layer Devices

The 3×1 vertically stacked devices were fabricated according to standard procedures, as illustrated in Figure S6.6. First, a rigid square-shaped acrylic frame was prepared with a laser cutter (Fusion M2, Epilog) (Figure S6.6, i). Next, a small-scale tri-layer device (defined as an individual pixel) was fabricated into the opening of the acrylic frame with electrical leads (Figure S6.6, ii). Then, another identical pixel was fabricated and stacked beneath the first pixel (Figure S6.6, iii). Furthermore, a third identical pixel was fabricated and stacked beneath the first two pixels, resulting in a partially completed

device (Figure S6.6, iv). Last, all the pixels in the partially completed stacked device were electrically activated using the same approach as described in Section 6.5.1. (Figure S6.6, v). Note that the optically active regions of the three pixels were perfectly aligned and overlapped in the vertical direction to ensure the best optical modulation performance. These steps furnished small-scale vertically stacked devices for camouflage demonstrations with graded transparency modulation capabilities.

6.5.9. Fabrication and Activation of Large-Area Tri-Layer Devices Without Patterns

The large-area tri-layer devices were fabricated according to slightly modified procedures from Section 6.5.1. First, an acrylate-based dielectric elastomer (VHB 4905, 3M) was equiaxially stretched by $\sim 1,300\%$ (relative to its initial area) and then fixed onto a large rigid acrylic frame that featured a central circularly-shaped opening with a diameter of ~ 20 cm. Next, a pair of identical circularly shaped large-area proton-conducting copolymer membranes (i.e., ~ 12.5 cm in diameter for the devices shown in Figure 6.7A–6.7C and Video S6.4) were prepared from a sulfonated pentablock copolymer (NEXARTM, Kraton Polymers LLC) and separately laminated onto the top and bottom sides of the elastomer. Then, a pair of identical stripe-shaped aluminum foil-based electrical leads were separately attached to the top and bottom proton-conducting copolymer membranes. Last, the partially completed large-area devices were electrically activated using a similar approach to that described in Section 6.5.1. Overall, these

fabrication and activation processes furnished fully completed large-area tri-layer devices for camouflage demonstrations, without any special packaging or encapsulation.

6.5.10. Fabrication and Activation of Large-Area Tri-Layer Devices with Various Patterns

The large-area tri-layer devices with various patterns were fabricated according to slightly modified procedures from Section 6.5.9. First, an acrylate-based dielectric elastomer (VHB 4905, 3M) was equiaxially stretched by $\sim 1,300\%$ (relative to its initial area) and then fixed onto a large rigid acrylic frame that featured a central circularly-shaped opening with a diameter of ~ 20 cm. Next, a pair of identical circularly shaped large-area proton-conducting copolymer membranes (i.e., ~ 7.5 cm in diameter for the devices shown in Figure 6.7D–6.7F and Video S6.5) were prepared from a sulfonated pentablock copolymer (NEXARTM, Kraton Polymers LLC) and separately laminated onto the top and bottom sides of the elastomer with shadow masks that enabled various pre-defined patterns, such as octopus, soldier, butterfly, bird, fighter jet, unicorn, and arbitrary combinations of letters. Then, a pair of identical stripe-shaped aluminum foil-based electrical leads were separately attached to the identically patterned top and bottom proton-conducting copolymer membranes. Last, the partially completed patterned large-area devices were electrically activated using a similar approach to that described in Section 6.5.1 and Section 6.5.9. Overall, these fabrication and activation processes furnished fully completed large-area tri-layer devices with various patterns for camouflage demonstrations, without any special packaging or encapsulation.

6.5.11. Supporting Information Figures

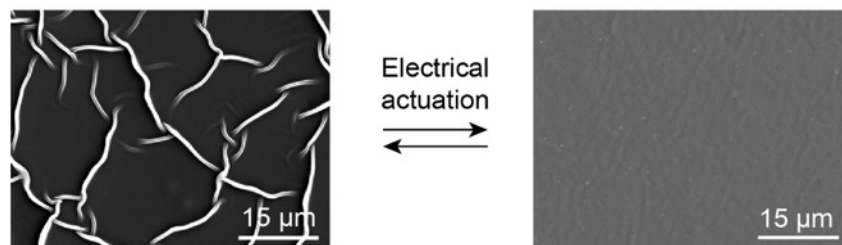


Figure S6.1. Representative *ex-situ* scanning electron microscope (SEM) images of the surface morphology of small-scale tri-layer devices before (left) and after (right) electrical actuation.

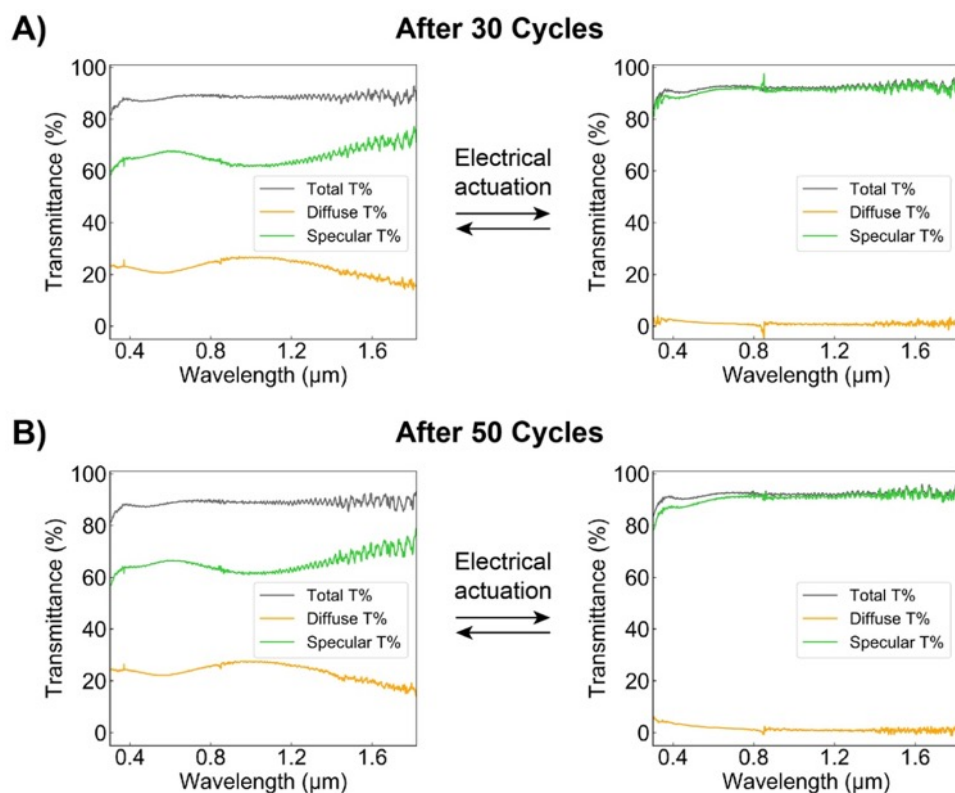


Figure S6.2. Cyclability of UV/Vis-NIR Modulation. (A) Representative *in-situ* UV/Vis-NIR transmittance spectra for a small-scale tri-layer device before (left) and after (right) the 30th electrical actuation cycle. (B) Representative *in-situ* UV/Vis-NIR transmittance spectra for the same small-scale tri-layer device before (left) and after (right) the 50th electrical actuation cycle. In both (A) and (B), the total transmittances (gray curves) were shown along with the specular (green curves) and diffuse (orange curves) components.

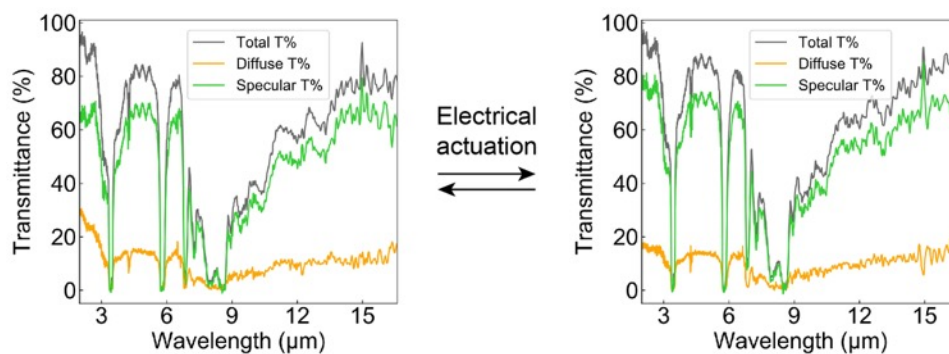


Figure S6.3. Dynamic Infrared Modulation. Representative *in-situ* infrared transmittance spectra for a small-scale tri-layer device before (left) and after (right) the 1st electrical actuation. The total transmittances (gray curves) were shown along with the specular (green curves) and diffuse (orange curves) components.

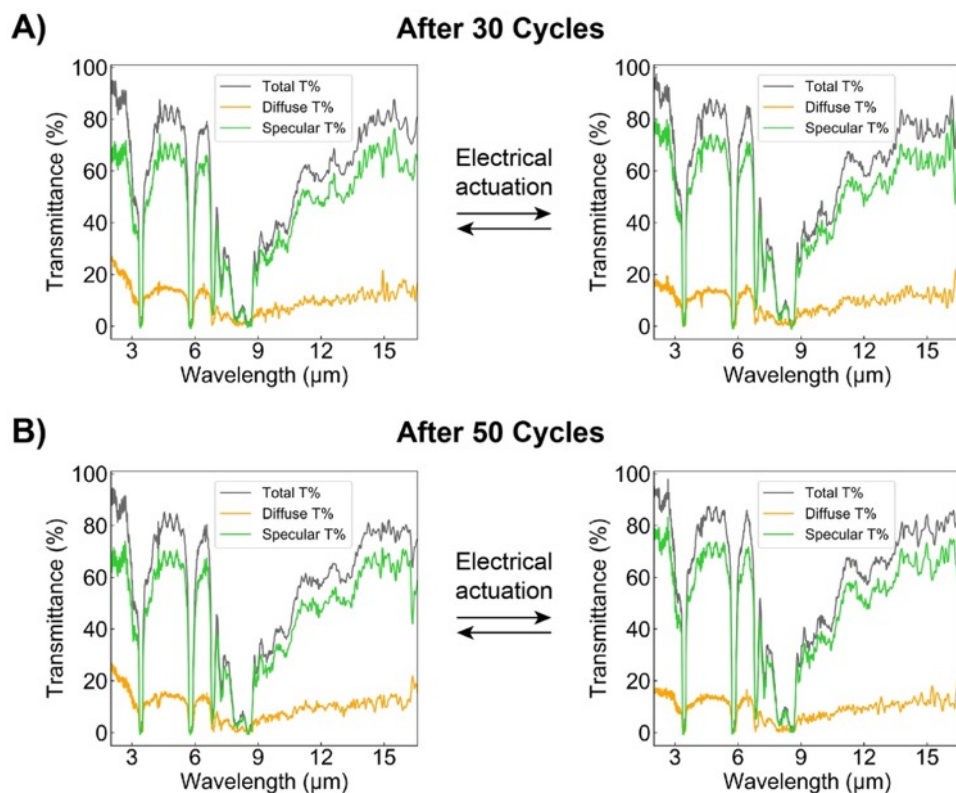


Figure S6.4. Cyclability of Infrared Modulation. (A) Representative *in-situ* infrared transmittance spectra for a small-scale tri-layer device before (left) and after (right) the 30th electrical actuation cycle. (B) Representative *in-situ* infrared transmittance spectra for the same small-scale tri-layer device before (left) and after (right) the 50th electrical actuation cycle. In both (A) and (B), the total transmittances (gray curves) were shown along with the specular (green curves) and diffuse (orange curves) components.

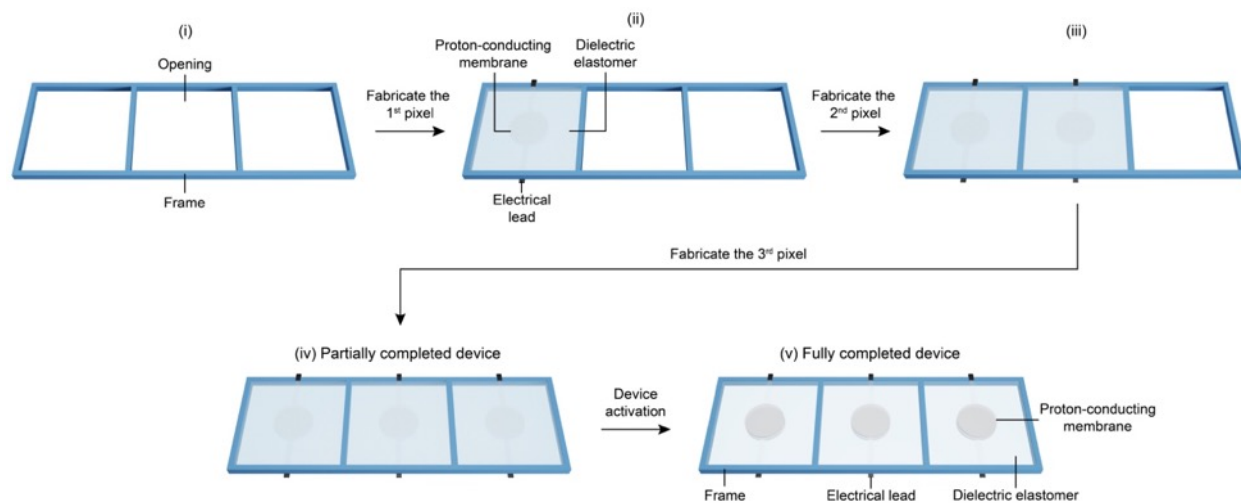


Figure S6.5. A scheme of the fabrication and activation processes for 1×3 multiplexed devices.

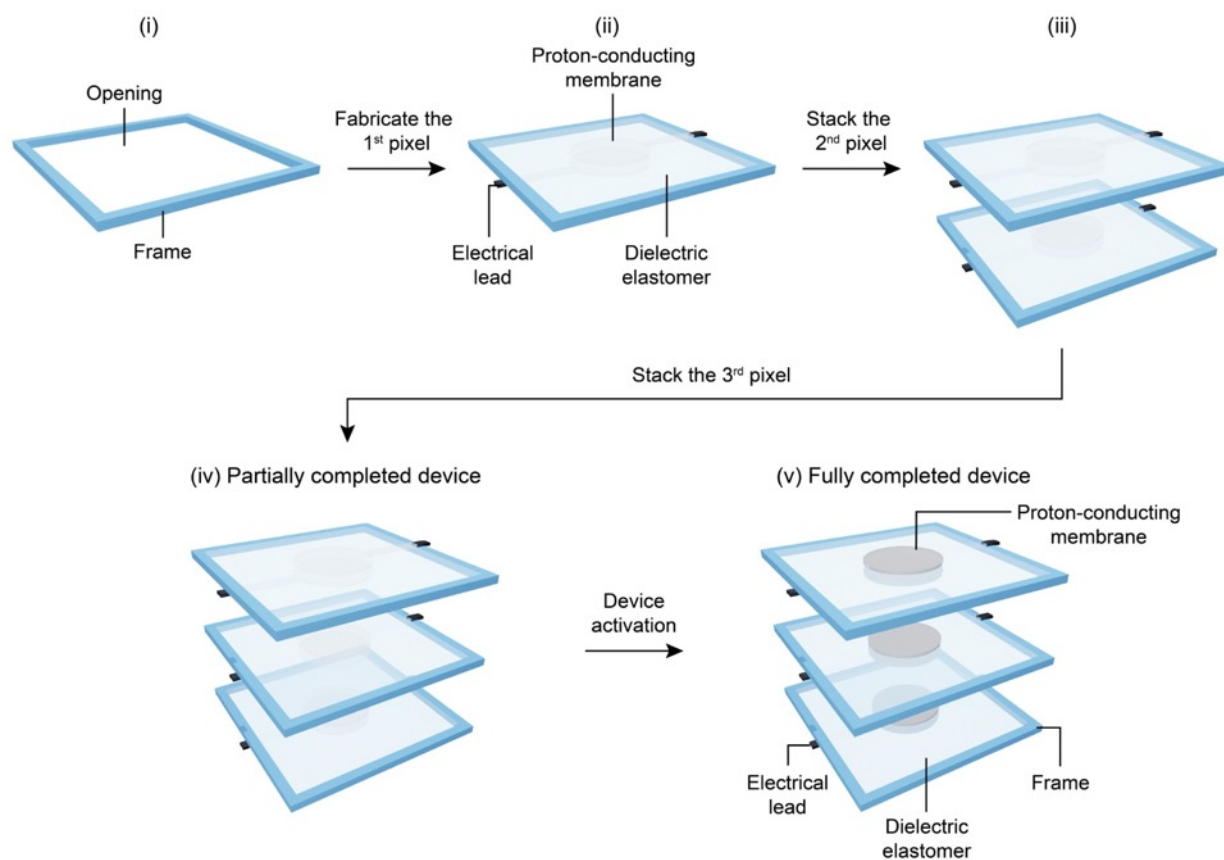


Figure S6.6. A scheme of the fabrication and activation processes for 3×1 vertically stacked devices.

6.5.12. Supporting Information Videos

Video S6.1. Dynamic modulation of the surface morphology of a representative small-scale tri-layer device upon electrical actuation under *in-situ* optical microscopy imaging.

Video S6.2. Dynamic optical modulation in a representative 1×3 multiplexed device.

Video S6.3. Graded transparency modulation in a representative 3×1 vertically stacked device.

Video S6.4. Demonstrations of large-area tri-layer devices for active camouflage.

Video S6.5. Demonstrations of large-area tri-layer devices with various pre-defined patterns for active silhouette camouflage.

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CHAPTER 7

Summary

7. Summary

To summarize, our work, as presented in this thesis, covers from biological cephalopods to adaptive materials and systems inspired by these fascinating animals. In Chapter 1, we start with a brief introduction of cephalopods and their camouflage capabilities, as well as a brief overview of the state-of-the-art materials and technologies that are either derived from or inspired by cephalopod skin. In Chapter 2, we investigate the long-range proton conduction in a designer cephalopod structural protein and explore the possible correlations between the protein's self-assembled structures and electrical functions. In Chapter 3, we draw inspiration from dynamic transparency-modulating cephalopod skin and develop a stretchable multimodal camouflage platform from a high-performance synthetic proton conductor. In Chapter 4, we translate some of the key natural capabilities of cephalopod skin from the visible to the infrared and develop a new class of adaptive infrared-reflecting materials and systems that allow on-demand modulation of infrared radiation. In Chapter 5, we draw inspiration from the unique skin architecture of blue-ringed octopuses and develop multifunctional camouflage and signaling platforms from an exceptionally stable nonacene with adaptive visible and near-infrared optical and fluorescent functionalities. In Chapter 6, we draw inspiration from size-variable chromatophores in cephalopod skin and engineer a series of large-area camouflage applications with an unprecedented combination of electromechanical and optical characteristics. Altogether, our work provides a foundation for the development of cephalopod-inspired adaptive materials and systems.

Besides, our findings also open up numerous opportunities for future research directions. First, our preliminary understanding of the possible correlations between the cephalopod-derived (ref2C)₄ protein's self-assembled structures and electrical functions remains at the molecular level. Additional experimental efforts with advanced NMR techniques are required in order to obtain a more definitive picture of the protein at the atomic resolution. Second, our cephalopod-inspired platforms might be further enhanced via the judicious incorporation of additional optically active materials or advanced photonic structures, further extending their capabilities into other technologically valuable spectral ranges (e.g., ultraviolet and terahertz) or adding additional light-manipulating functionalities. Third, our prototypical systems' configurations can be further optimized for different specific target applications. For instance, electrically-actuated large-area variants of our devices would be appropriate for situations requiring minimal steady state power consumption, e.g., buildings and vehicles, whereas mechanically-actuated non-planar variants of our devices would be appropriate for situations where large voltages are not desirable, e.g., clothing or skin-interfaced iontronics. Last, kilo-volt operating voltages associated with our electrically-actuated systems need to be reduced by at least an order of magnitude, which can be achieved by modifying the dielectric elastomer layer's physical properties (e.g., thickness, dielectric constant, or Young's modulus), as well as by selecting an entirely different dielectric elastomer material (e.g., polysiloxane or polyurethane). Overall, our findings may hold relevance to a number of research areas, such as stealth

technologies, bioinspired photonics, flexible optoelectronics, bioelectronics, energy conservation, and soft robotics.