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UNIVERSITY OF CALIFORNIA
SANTA CRUZ

**Charge Generation and Energy Transfer Through Extended Electronic
States in Conjugated Polyelectrolyte Complexes**

A dissertation submitted in partial satisfaction
of the requirement for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

By

Rachael L. Richards

June 2026

The Dissertation of Rachael L. Richards
is approved:

Professor Alexander Ayzner, Chair

Professor Rebecca Braslau

Assistant Professor Xiao Wang

Peter Biehl
Vice Provost and Dean of Graduate Studies

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ABSTRACT

Charge Generation and Energy Transfer Through Extended Electronic States in Conjugated Polyelectrolyte Complexes

Rachael L. Richards

Natural photosynthetic systems achieve remarkable light-harvesting efficiency through the precise supramolecular organization of chromophores, where non-covalent interactions govern excitonic energy capture and directional transport. Conjugated polyelectrolytes (CPEs), semiconducting polymers bearing pendant ionic side chains, offer a synthetic platform capable of replicating these design principles in aqueous environments. Their tunable electronic structure, combined with electrostatic and hydrophobic driving forces for self-assembly, enables the formation of conjugated polyelectrolyte complexes (CPECs) that support long-range exciton migration on timescales comparable to biological antenna systems. Despite this promise, the fundamental exciton dynamics governing energy transfer and charge generation in these materials remain insufficiently understood, limiting the rational design of CPE-based light-harvesting architectures.

This dissertation pursues a two-pronged investigation addressing both the mechanistic photophysics of CPECs and their application in aqueous-processed organic photovoltaic (aOPV) devices. The first thrust examines how the molecular architecture of CPEs governs electronic energy transfer (EET) in CPECs. Because

excitonic wavefunctions in these systems are spatially delocalized over length scales commensurate with donor-acceptor separations, the point-dipole approximation underlying conventional Förster theory becomes physically inadequate. This work therefore investigates how the real-space distribution of π -electron density along conjugated backbones modulates interchain excitonic coupling and EET rate constants, with complementary studies exploring the relationships between morphological organization, electronic structure, and excited-state dynamics in complex fluid phases.

The second thrust demonstrates a novel fabrication methodology for organic photovoltaic devices processed entirely in aqueous media. Conventional device fabrication relies on halogenated or toxic organic solvents, fundamentally undermining the environmental promise of organic solar technologies. By exploiting the directed self-assembly of oppositely charged CPEs in water, this work establishes the proof-of-concept viability of constructing functional photovoltaic devices using water as the exclusive processing solvent. Together, these investigations advance a mechanistic foundation for the rational design of CPE-based light-harvesting systems and delineate a pathway toward environmentally responsible manufacturing of thin-film solar technologies.

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To my husband Marcel: the things you have done for me, to help me, support me, love me, and make me happy, go above and beyond what any person deserves. I dedicate this work to you.

Chapter I: Introduction

1.1 General Overview

Natural photosynthesis offers an instructive precedent for the engineering of efficient artificial light-harvesting antennae, most strikingly exemplified by the Fenna–Matthews–Olson complex, wherein the precise spatial arrangement and electronic structure of chlorophyll chromophores within a protein scaffold together govern highly efficient excitonic energy capture and directional transport to reaction centers. Critically, this performance arises not from covalent linkage of the pigments, but from their non-covalent supramolecular organization. This demonstrates that simultaneously controlling chromophore geometry and the degree of electronic coupling between them are the key determinants of exciton dynamics in any viable artificial light-harvesting system. This insight suggests that synthetic light-harvesting materials capable of similar hierarchical, non-covalently directed self-assembly from tunable organic chromophores represent a compelling design target for the replication and potential surpassing of natural photosynthetic efficiency.

Conjugated polyelectrolytes (CPEs) represent a particularly compelling materials class satisfying many of these criteria simultaneously. CPEs are π -conjugated semiconducting macromolecules bearing pendant ionizable side chains that have pronounced aqueous solubility while remaining electronically orthogonal to the delocalized backbone, giving rise to numerous benefits. Consequently, the frontier

orbital energetics and optical absorption profiles of CPEs can be systematically modulated through backbone substitution, heteroatom incorporation, or controlled copolymerization strategies. This offers precise, independent handles on both chromophore electronic structure and spatial organization.

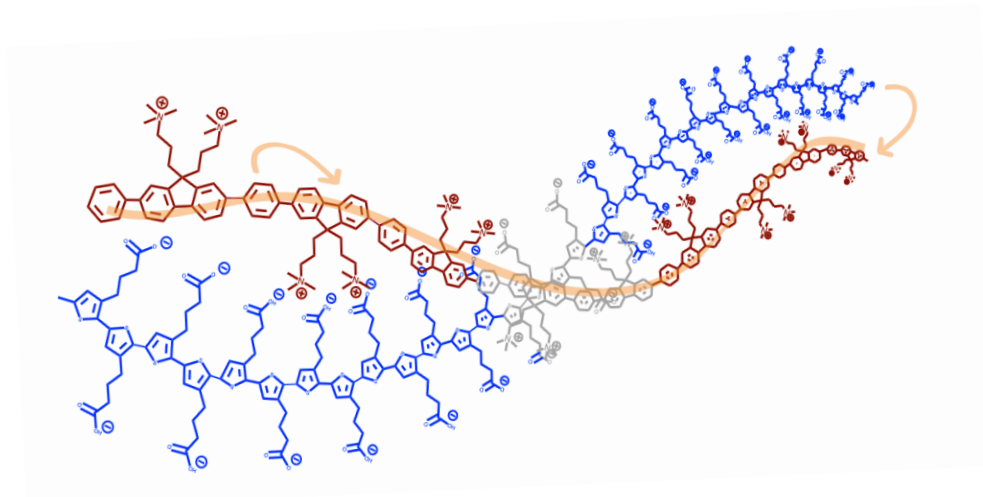


Figure 1.1: Schematic depiction of electronic energy transfer within and between conjugated polyelectrolytes (CPEs). Arrows indicate one possible direction of exciton migration and the extent of exciton delocalization along the polymer backbone.

Furthermore, the charged peripheral groups facilitate electrostatic co-assembly between polyanionic and polycationic species, while intermolecular π - π stacking and hydrophobic interactions provide additional driving forces for supramolecular organization. The resulting hierarchical assemblies between oppositely charged polyelectrolytes, termed conjugated polyelectrolyte complexes (CPECs), support long-range exciton migration along and between conjugated backbone segments, illustrated in Figure 1.1 Within these complexes, the spatially delocalized π -electronic

structure of the conjugated backbone mediates ultrafast exciton migration on timescales quantitatively comparable to those operative in biological antenna systems.

Yet the primary transformations of CPE excitons remain poorly understood, limiting their light-harvesting potential. The influence of backbone chemical structure on exciton binding energy in high-dielectric aqueous media remains an open question of central importance, as this binding energy governs the thermodynamic competition between tightly bound Frenkel-type excitons and weakly correlated charge-transfer states amenable to dissociation into free polarons. Compounding this, electronic energy transfer (EET) in CPECs frequently proceeds over donor–acceptor separations commensurate with the spatial extent of the excitonic wavefunction itself, rendering the point-dipole approximation underlying conventional Förster theory physically untenable. Under these conditions, the real-space distribution of excitonic electron density along the conjugated backbone emerges as a primary determinant of inter-chain electronic coupling and EET kinetics. A rigorous mechanistic understanding of these processes is therefore prerequisite to the rational design of CPE-based light harvesting architectures with deterministic photon-to-charge conversion efficiencies and constitutes one of the two central thrusts of this thesis.

This dissertation adopts a two-pronged strategy, addressing both the fundamental exciton dynamics intrinsic to CPECs and their application as active layer components in aqueous-processed organic photovoltaic (aOPV) devices, where the mechanistic insights gained from the former directly inform the interpretation of device photophysics in the latter. Both research directions are conducted exclusively

in the aqueous phase, exploiting the inherent hydrophilicity of CPEs to enable environmentally benign processing conditions.

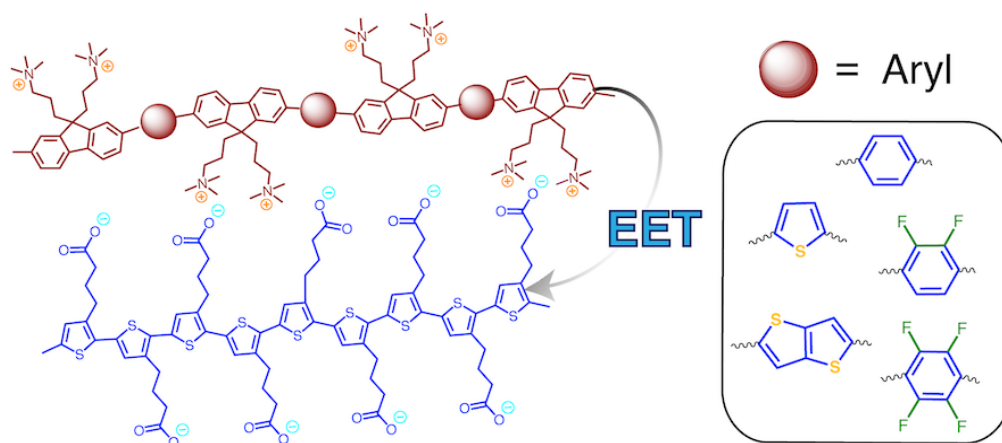


Figure 1.2: Cartoon of conjugated polyelectrolyte complexes (CPECs) formed by electrostatic assembly of oppositely charged CPEs, which act as donor–acceptor pairs for excitonic energy transfer (EET). Polymerization of electron-donating and electron-withdrawing monomers tunes the spatial distribution of the π -electronic wavefunction, modulating excitonic coupling and EET efficiency.

The first research direction examines how the molecular architecture of conjugated polyelectrolytes governs electronic energy transfer (EET) in conjugated polyelectrolyte complexes (CPECs). Although EET is conventionally described within the Förster resonance energy transfer (FRET) framework, which models the interchromophoric interaction as a classical point-dipole coupling with a characteristic inverse sixth-power distance dependence, this approximation is expected to fail in CPECs wherein the excitonic wavefunction is spatially delocalized

over dimensions comparable to the physical donor–acceptor separation. In this intermediate coupling regime, the real-space distribution of π -electron density along the conjugated backbone is anticipated to exert a significant influence over excitonic coupling matrix elements and the resulting EET rate constants.

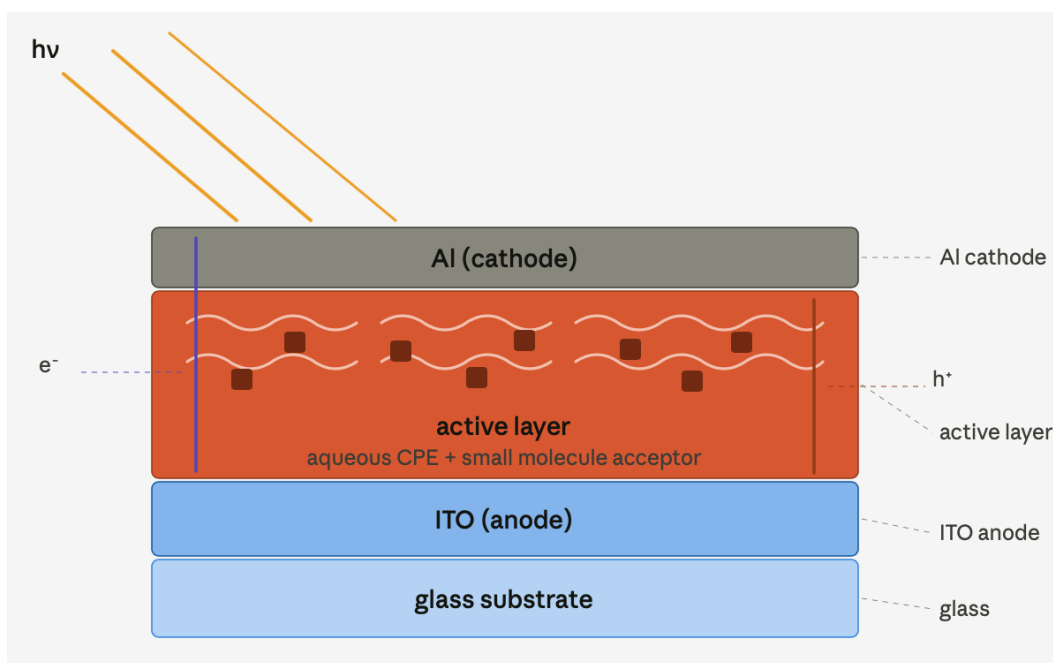


Figure 1.3: Cross-section schematic of an aOPV device fabricated using water as the sole processing solvent, comprising an aqueous CPE donor and small molecule acceptor active layer sandwiched between an ITO anode and Al cathode.

This portion of the dissertation therefore interrogates the central mechanistic question of how the characteristics of the π -electronic wavefunction modulate the efficiency of interchain energy transfer between donor and acceptor CPE components within a CPEC (Figure 1.2). Complementary investigations further examine the

relationships between morphological organization, electronic structure, and excited-state dynamics of CPECs in complex fluid phases, with implications for their utilization as functional soft matter, including the formulation of aqueous complex fluids as rheological precursors for 3D-printable semi-conductive inks.

The second research direction describes the development of a novel fabrication methodology for aqueous organic photovoltaic (aOPV) devices employing exclusively aqueous, environmentally benign processing media. These aOPVs constitute a technologically promising class of renewable energy devices by virtue of their mechanical flexibility and compatibility with high-throughput roll-to-roll manufacturing; however, conventional device fabrication protocols rely extensively on halogenated or otherwise toxic organic solvents, fundamentally compromising their environmental sustainability profile. To overcome this limitation, this work employs water-soluble semiconducting polymers—specifically CPEs—that undergo directed self-assembly in aqueous environments to yield optically active, excitonic heterojunction morphologies. By exploiting the distinctive photophysical and charge-transport properties of these materials, this dissertation demonstrates the proof-of-concept viability of constructing functional photovoltaic devices using water as the exclusive processing solvent (Figure 1.3). This approach delineates a credible pathway toward environmentally responsible manufacturing of thin-film solar technologies and underscores the broader transformative potential of aqueous organic electronics within the emerging landscape of sustainable energy solutions.

1.1.1 Electronic States in Conjugated Polymers

Idealized Isolated Conjugated Polymers

Before examining the complexity introduced by interchain interactions, morphological disorder, and the solid-state environment, it is important to consider the optical properties of a single, perfectly ordered conjugated polymer chain in the absence of any external perturbation. This idealized limit, an isolated chain in vacuum provides the conceptual and mathematical foundation upon which more realistic models are built. The key features that emerge, the nature of the lowest-energy optical transition, the factors governing its rate, and the large oscillator strengths observed experimentally, form a recurring reference point throughout this thesis.

In molecular systems as well as CPEs and other semiconducting polymers, the rate of light-induced HOMO-LUMO transition is well-described by Fermi's Golden Rule¹⁰:

$$\lambda_{if} = \frac{2\pi}{\hbar} |M_{if}|^2 \rho_f \quad (1.1)$$

where ρ_f is the density of final states, and M_{if} is the matrix element joining the initial and final states, given as

$$M_{if} = \int \Psi_f^* V \Psi_i dv \quad (1.2)$$

where V is the perturbation describing the light-matter interaction that connects the initial and final states. Conjugated polymers are characterized by an alternating pattern of single and double bonds along their backbone, giving rise to a delocalized π -electron system extending over many repeat units.^{1,2} In a molecular orbital framework, the filled

bonding π orbitals constitute the valence band while the empty antibonding π^* orbitals form the conduction band.³ For a finite chain of N repeat units, the relevant frontier orbitals are the HOMO and LUMO, and the energy difference between them defines the onset of optical absorption and is the central parameter governing the photophysics of the material. In the idealized limit of a perfectly planar, defect-free chain, this gap converges toward a finite asymptotic value as N approaches infinity, a consequence of bond-length alternation stabilized by a Peierls distortion.^{4,5,9}

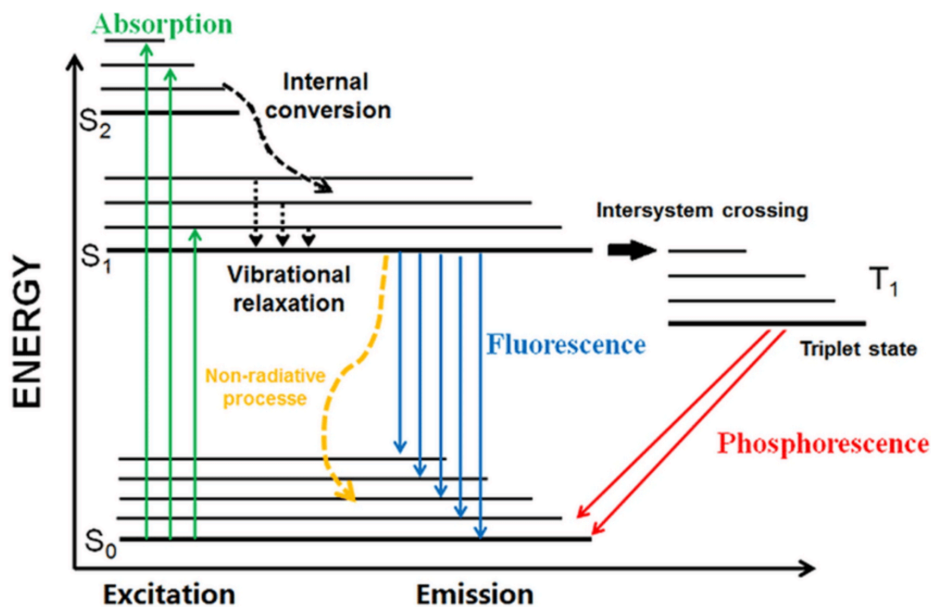


Figure 1.4: Jablonski diagram illustrating the primary photophysical pathways of an electronically excited conjugated polymer.

The Golden Rule states that the rate of an electronic transition between two eigenstates of the unperturbed Hamiltonian are proportional to both the strength of the

squared coupling between the states and their energy density. In semiconducting CPEs, the HOMO-LUMO transition rate tends to be quite high, which correspondingly leads to large molar extinction coefficients and hence strong light absorption. Although the semiconductor band picture is often thought of as an analogy, the molecular description is likely more appropriate for conjugated polymer chains because the exciton binding energy, the Coulombic attraction between the photogenerated electron and hole, is substantial (typically 0.1-1.0 eV). In fact, it far exceeds the thermal energy $k_B T$ at room temperature.^{7,8} Consequently, optical excitation does not directly produce free charge carriers but instead generates a bound electron-hole pair called a Frenkel exciton.^{6,8} The lowest optically allowed transition is therefore the $S_0 \rightarrow S_1$ (HOMO $\rightarrow$ LUMO) excitation, which dominates the linear absorption spectrum of an isolated chain.^{9,10} This excited state does not remain localized on a single repeat unit but rapidly delocalizes across the conjugated system. This tendency is in part responsible for exciton diffusion in conjugated polymeric systems.^{6,8}

For an optical transition, the oscillator strength is a dimensionless quantity that describes the strength of coupling between two states, and is proportional to the square of the transition dipole moment. For the $S_0 \rightarrow S_1$ transition in conjugated polymers, the oscillator strength is largely due to the substantial spatial overlap of the HOMO and LUMO wavefunctions across the delocalized π system. Because these frontier orbitals are delocalized over many repeat units in an extended π -conjugated system, this overlap is inherently large, giving rise to the characteristically high molar extinction

coefficients observed in these materials. For an optical transition from state $|i\rangle$ to state $|j\rangle$, the transition dipole moment is defined as¹²

$$\mu_{ij} = e\langle j|\hat{r}|i\rangle \quad (1.3)$$

where $\hat{r}$ is the position operator and e is the electronic charge.¹² The oscillator strength grows with conjugation length as the spatial extent of the frontier orbital wavefunctions increases; and high-molecular-weight CPEs can therefore reach molar extinction coefficients of 10^5 to 10^6 L mol⁻¹ cm⁻¹ per chain, in most cases far exceeding small-molecule chromophores.^{12,11}

Once absorbed, the photon energy drives the system into an excited state that may undergo a number of competing photophysical pathways, summarized in Figure 1.4, including radiative decay via fluorescence, non-radiative internal conversion, or intersystem crossing to the triplet manifold. The structure of the absorption spectrum encodes information about the backbone conformation responsible for the light absorption. Isolated conjugated chains exhibit a vibronic progression whose peak intensity ratios are governed by the Huang-Rhys factor S , which defines the degree of relaxation upon excitation.¹⁹ For well-ordered, planar chains, the 0-0 (the vibronic transition between the ground vibrational levels of the excited and ground electronic states) peak dominates, providing a direct spectroscopic handle on chain planarity and delocalization.¹² This makes analyzing the line shape a powerful tool in understanding CPE systems, where backbone conformation is strongly coupled to both the assembly state and solvent environment.^{13,17} Regardless of chain conformation, optical excitation

does not produce free charge carriers but instead generates a tightly bound electron-hole pair whose binding energy is governed by Coulombic confinement of the wavefunction along the one-dimensional conjugated backbone. It is the fate of this bound exciton that lies at the heart of both light-harvesting and photovoltaic function.¹⁷

Exciton Formation in Conjugated Polymers

As introduced in the section above, when a conjugated polymer absorbs a photon, an electron is promoted from the HOMO to the LUMO, leaving a positively charged hole behind. Because organic semiconductors have low dielectric constants, Coulombic screening is weak and the electron and hole remain bound as a neutral quasiparticle, an exciton.^{15,9} Unlike inorganic semiconductors, where large dielectric screening produces weakly bound Mott–Wannier excitons with binding energies of only a few meV, the binding energies of excitons in conjugated polymers are substantial, typically 0.1–1.0 eV, and these tightly bound states are more accurately described as Frenkel excitons.^{15,21}

Barford has shown that the properties of an exciton in a conjugated polymer are most clearly understood by deconvolving it into two quasi-independent effective particles.¹⁵ The total exciton wavefunction separates as

$$\Phi_{nj}(r, R) = \psi_n(r)\Psi_j(R) \quad (1.4)$$

where r is the electron–hole separation and R is the center-of-mass coordinate.²¹ The relative wavefunction, described by $\psi_n(r)$, determines the average size and thus the

binding energy of the electron–hole pair. For the primary photoexcited state in phenyl-based conjugated polymers, the electron and hole are tightly bound within a single monomer unit, a Frenkel exciton. The center-of-mass particle, described by $\Psi_j(R)$, describes how this bound pair delocalizes along the chain. On a uniform, disorder-free chain, the center-of-mass wavefunction takes the particle-in-a-box form¹⁵

$$\Psi_j(R) = \left(\frac{2}{N+1}\right)^{1/2} \sin(\beta_j R) \quad (1.5)$$

where $\beta_j = j\pi/(N+1)d$ is the center-of-mass pseudo-wavevector, j is the quantum number satisfying $1 \leq j \leq N$, and N is the number of monomers.²¹

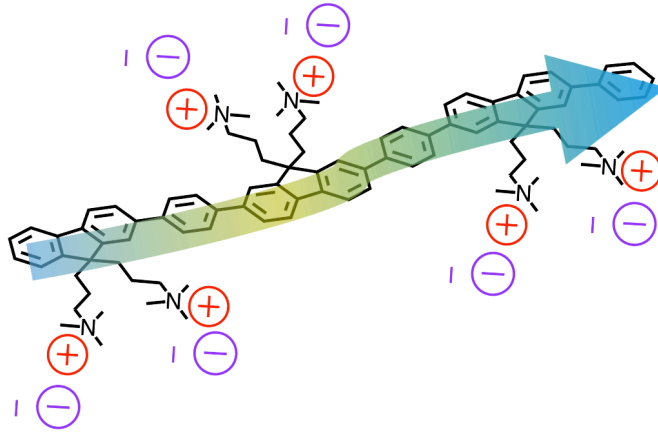


Figure 1.5: Illustration of exciton delocalization along a conjugated polymer backbone.

In practice, conjugated polymers are subject to conformational and environmental disorder, which localizes the center-of-mass particle onto segments of

the chain shorter than the full contour length.¹⁵ These localized states, termed local exciton ground states, define the quasi-independent light-absorbing units called chromophores. Immediately following excitation, coupling to the nuclear degrees of freedom drives ultrafast vibrational relaxation on the timescale of a few C–C bond vibrations (~40 fs), producing vibrationally relaxed states that define the emissive chromophores, which are generally smaller and lower in energy than their absorbing counterparts.^{15,9}

Following formation, excitons can migrate between chromophores via electronic energy transfer before recombining radiatively or non-radiatively. For singlet excitons, this process is driven by a Coulomb-induced dipole–dipole mechanism that is approximately described by the Förster transfer integral^{15,21}

$$J_{DD} = -\frac{1\mu_0^2}{2\pi\epsilon_0\epsilon_r d^3} \quad (1.6)$$

where μ_0 is the transition dipole moment of a single moiety and d is the inter-moiety distance.^{15,9} Exciton migration largely proceeds via hopping between progressively lower-energy chromophores, resulting in spectral diffusion, and is ultimately limited by the finite exciton diffusion length, which in typical conjugated polymers is on the order of 10 nm.¹⁵ This finite diffusion length has direct consequences for photovoltaic device performance, as excitons must reach a donor–acceptor interface before recombination occurs.^{15,9,21}

Isolated Conjugated Polymers with Translational Invariance

As a starting point, it is helpful to consider an idealized, translationally invariant conjugated chain: a perfectly periodic backbone in which every repeat unit is structurally and electronically equivalent. No real polymer achieves this limit, but it provides a nice analytical framework from which the consequences of finite

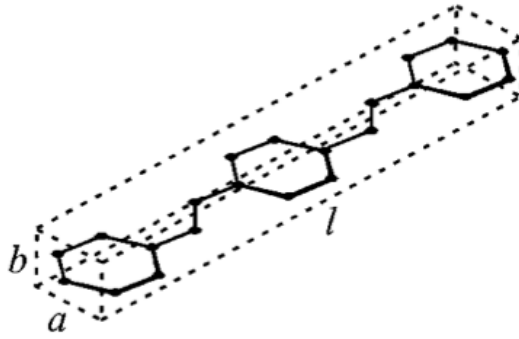


Figure 1.6: Representation of a one-dimensional particle-in-a-box model for an exciton confined to an idealized conjugated polymer chain of length l , with lattice parameter a and chain width b . Adapted from Pedersen et al., *Phys. Rev. B* **2000**, *61*, 10504

conjugation length, confinement, and electron–hole interaction can be understood before the complexity of real systems is introduced.^{15,17} In this idealized picture, the exciton can be treated as an electron–hole pair interacting via a screened Coulomb potential and spatially confined to the polymer backbone. This maps onto

a particle-in-a-box problem in one dimension, shown in Figure 1.6.¹⁷ In the limit of long conjugation length, the two-particle wavefunction separates into relative and center-of-mass coordinates, and the relative motion satisfies¹⁷

$$\left\{ -\frac{\hbar^2}{m^*} \frac{d^2}{dz^2} - \frac{e^2}{4\pi\epsilon\epsilon_0} C(z) - \tilde{E} \right\} \tilde{\varphi}(z) = 0 \quad (1.13)$$

where z is the electron–hole separation, m^* is the reduced effective mass, ϵ is the dielectric constant, and $C(z)$ is a regularized one-dimensional Coulomb function that removes the unphysical divergence of the bare $1/|z|$ potential and $\tilde{E}$ is the exciton

energy eigenvalue (binding energy measured relative to the free electron-hole continuum).¹⁷ The structure of this equation captures the essential physics of the idealized chain: the exciton binding energy, optical transition energy, and oscillator strength are all determined by the nexus between quantum confinement and Coulombic attraction; and all three scale with conjugation length. Longer, more ordered chains absorb at lower energies with greater oscillator strength. This is a direct consequence of the box becoming larger and the Coulomb interaction becoming relatively weaker.¹⁷

Following absorption, rapid vibrational relaxation brings the system to the lowest vibrational level of S_1 , from which radiative decay produces photoluminescence red-shifted relative to absorption, known as the Stokes shift, arising from reorganization of the backbone upon excitation.¹⁵ In this idealized limit, with no quenching sites or conformational defects, the fluorescence quantum yield can approach one (numerically).¹⁵ The introduction of conformational disorder, interchain interactions, and π -stacking, which are all the hallmarks of real conjugated polymer systems, breaks this translational symmetry and gives rise to the complex photophysics discussed in the sections that follow.

Conformational Disorder in Conjugated Polymers

The idealized translationally invariant chain described in the previous section represents a theoretical upper bound on optical performance. In reality, conjugated polymer backbones are subject to pervasive conformational disorder arising from the

interplay of backbone geometry, torsional flexibility, and side chain interactions — all of which determine the persistence length l_p , the characteristic length scale over which monomer-to-monomer orientational correlations decay.²⁹ As shown in Figure 1.7, the ratio of l_p to the contour length L_c determines the overall chain statistics: chains with $l_p \ll L_c$ behave as flexible coils, those with $l_p \gg L_c$ as rigid rods, and the intermediate semiflexible regime, where $l_p \approx L_c$ is where most conjugated polymers reside in solution.²⁹ This semi-flexibility is governed by the interplay of unit lengths, unit angles, dihedral distributions, and side chain orientation, size, and branching molecular parameters.²⁹

The dominant contribution to chain rigidity is the torsional potential governing the average dihedral angle between adjacent monomer units. Because the effective π -orbital overlap across a given inter-ring bond scales as $\cos(\varphi)$, where φ is the inter-ring dihedral angle, coplanar backbones maximize both conjugation length

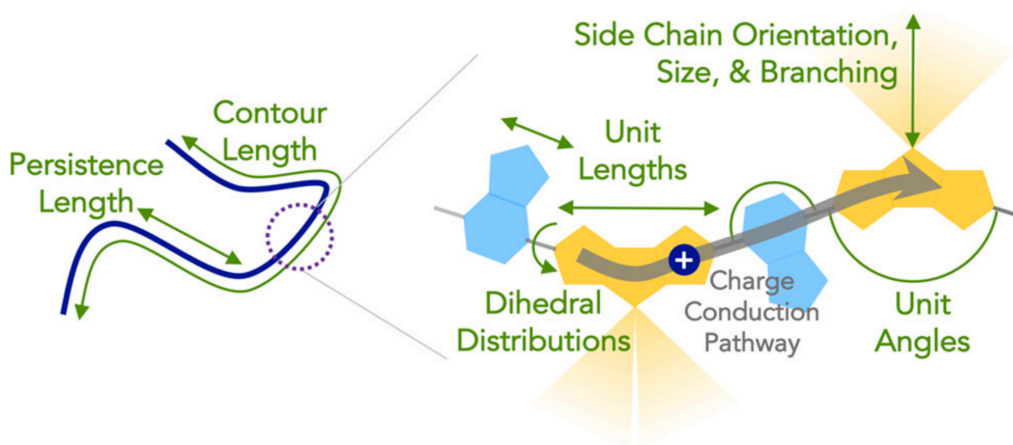


Figure 1.7: Key structural parameters governing conjugated polymer chain conformation and charge transport. Adapted from Danielsen et al., *Macromolecules* **2022**, 55, 437.

and intrachain exciton transport, while torsional disorder breaks the chain into a distribution of shorter, electronically quasi-independent chromophores.²⁹ Intramolecular noncovalent interactions between adjacent units can lock the backbone near coplanarity and dramatically increase l_p , while side chain architecture, particularly the size and branch point location of pendant alkyl chains exerts an equally significant influence through steric effects on backbone torsion.²⁹ Larger persistence lengths correlate directly with increased charge-carrier mobility, establishing backbone planarity and chain stiffness as primary design targets.²⁹

For CPEs specifically, these conformational effects are further modulated by the ionic side chains, and the electrostatic and solvation interactions introduce additional conformational degrees of freedom. Electrostatic repulsion between like-charged side chains in a good solvent favors backbone extension and planarity, while charge screening by added salt or a change of solvent permits more disordered, compact conformations.¹³ These structural changes are directly reflected in the optical spectra: a blue shift and loss of vibronic resolution upon increasing disorder, and a red shift with recovery of vibronic fine structure upon increasing planarity making CPE absorption and emission spectra sensitive reporters of backbone conformation.^{13,17} When chromophore segments come into spatial proximity, their transition dipole moments interact via Coulombic coupling, mixing the excited states of individual chromophores into collective excitonic eigenstates, which fundamentally alters the absorption spectrum, emission spectrum, and resulting excited-state dynamics.^{15,9} The nature of this coupling (and whether it produces a blue or red-shifted state) depends

critically on the physical arrangement of the interacting chromophores, giving rise to the two distinct and well-known aggregate types, H and J, whose spectroscopic signatures and photophysical consequences are the subject of the following section.

H- and J-Aggregates in Conjugated Polymers

The nature of these collective excitonic eigenstates, and the resulting spectroscopic consequences, depends critically on the geometric arrangement of the interacting chromophores. The theoretical framework for understanding these effects was established by Kasha, who classified molecular aggregates according to the relative orientation of the interacting transition dipoles.¹⁸ For a pair of identical molecules with parallel transition dipoles, the intermolecular coupling is¹⁸

$$J_c = \frac{\mu^2(1-3\cos^2\theta)}{(4\pi\epsilon R^3)} \quad (1.14)$$

where μ is the transition dipole moment, R is the intermolecular separation, ϵ is the dielectric constant of the medium, and θ is the angle between the transition dipole and the displacement vector connecting the two chromophores.¹⁸ The sign of J_c is the fundamental discriminator between aggregate types. When $\theta > 54.7^\circ$ the coupling is positive and the aggregate is of H-type; when $\theta < 54.7^\circ$ the coupling is negative and the aggregate is of J-type.¹⁸

In an H-aggregate, the optically bright state lies at the top of the excitonic band, blue-shifted from the monomer. Following absorption, rapid intra-band

relaxation populates the lowest-energy (optically dark state) resulting in suppressed emission and reduced fluorescence quantum yield.¹⁸ On the other hand, in a J-aggregate the energetic ordering is reversed. This means that the bright state lies at the bottom of the band, red-shifted from the monomer, producing narrow and intense absorption and emission.¹⁸

A key advancement beyond the Kasha picture came with the incorporation of vibronic coupling into the aggregate Hamiltonian by Spano and coworkers, who showed that the relative intensities of the 0-0 and 0-1 vibronic peaks provide a direct and quantitative window into the nature and strength of the excitonic coupling.^{8,20}

The ratio

$$S_R = I_{(0-0)}/I_{(0-1)} \quad (1.15)$$

serves as a sensitive experimental diagnostic: $S_R < 1$ indicates H-like behavior in which interchain coupling reduces the 0-0 peak, while $S_R \geq 1$ indicates J-like behavior in which the 0-0 peak is enhanced.^{8,20} For aggregated conjugated polymers, the situation is more complex than for small-molecule aggregates because isolated polymer chains already possess significant intrachain excitonic coupling along the backbone. Aggregated conjugated polymers therefore exhibit both through-bond intrachain coupling J_{intra} and through-space interchain coupling J_{inter} simultaneously, and their photophysical response reflects the competition between these two contributions: and an HJ-aggregate is born.³⁰ When interchain coupling dominates, H-

like behavior prevails; when intrachain coupling dominates, J-like character emerges, and the ratio S_R shifts accordingly.³⁰

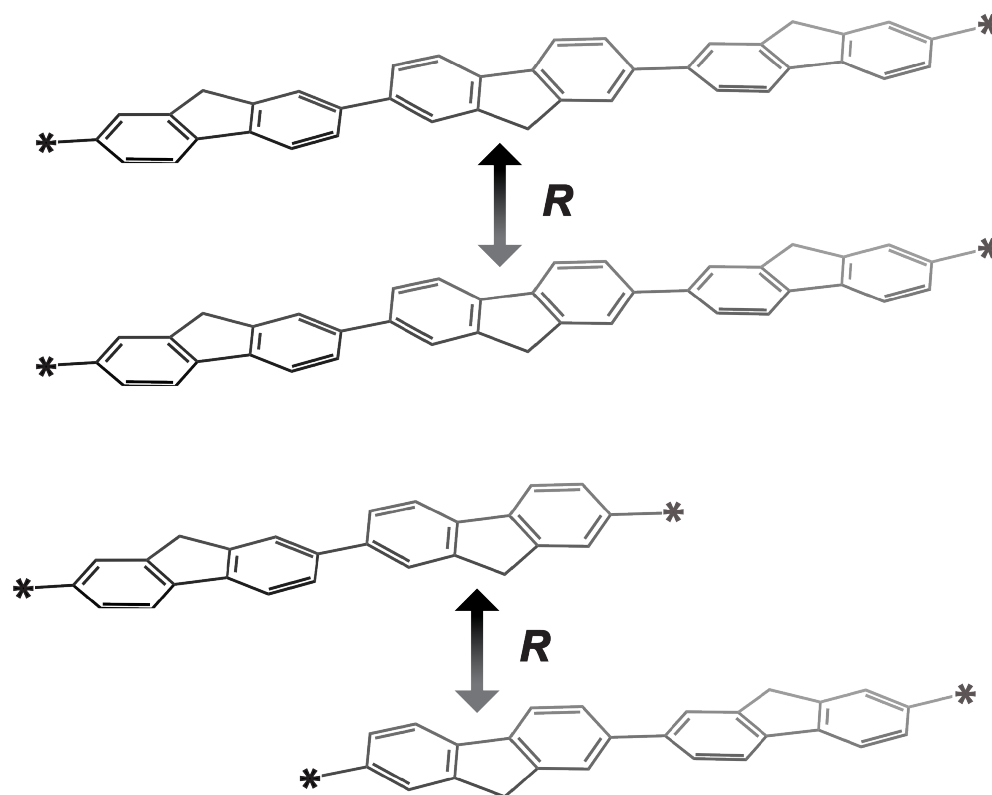


Figure 1.8: Schematic illustration of H- and J-aggregate geometries (top and bottom, respectively) in conjugated polymer chains, distinguished by the interchain displacement R relative to the molecular backbone.

For CPEs, ionic side chains introduce an additional layer of control: electrostatic, hydrophobic, and hydrogen-bonding interactions can template specific stacking geometries that favor either H- or J-type coupling, and these are highly sensitive to ionic strength, solvent environment, and the presence of complementary

polyelectrolytes.⁸ Understanding how CPE aggregation state and excitonic coupling respond to solution conditions is a theme that will be discussed in more detail throughout the remainder of this thesis.

1.1.2 Electronic Energy Transfer in CPEs

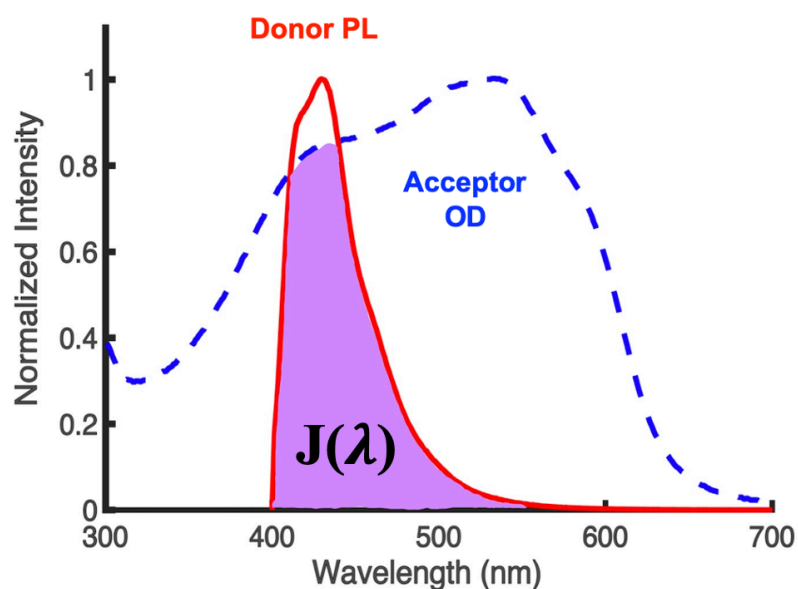


Figure 1.9. Representative donor photoluminescence (PL) spectrum and acceptor absorbance (OD) spectrum illustrating the spectral overlap integral $J(\lambda)$.

Electronic energy transfer (EET) is the nonradiative transfer of an excited state from a donor chromophore to an acceptor chromophore.³¹ It is a photophysical process of central importance to all high-performance light-harvesting systems: both natural and artificial alike: in natural photosynthesis, EET funnels absorbed photon energy from antenna complexes to the reaction center with near-unit efficiency on

femtosecond to picosecond timescales.³² Achieving analogous performance in synthetic materials requires understanding how EET depends on the electronic structure of the donor and acceptor, the geometry of their assembly, and critically, the spatial extent of their excitonic wavefunctions.^{31,33}

Conjugated polyelectrolyte complexes (CPECs), formed by the electrostatic co-assembly of oppositely charged CPEs in aqueous solution, are the regime in which EET will be discussed for the entirety of this work: their ionic side chains permit aqueous hierarchical assembly while their delocalized conjugated backbones support the extended electronic states essential to rapid EET.^{33,34} This section develops the framework for EET in CPECs, beginning with the celebrated Förster model, proceeding through its breakdown in proximal extended systems, and arriving at the more complete excitonic coupling picture that governs EET between extended conjugated polymer chains.

The Förster Resonance Energy Transfer Model

The most widely used model for EET was formulated by Theodor Förster in 1959.³⁵ In the Förster model, EET arises from the Coulombic interaction between the transition dipole moments of a donor and an acceptor. Both the donor and acceptor are treated as point dipoles, and the coupling between them is given by^{31,35}

$$V = \frac{\mu_A \cdot \mu_D}{4\pi\epsilon_0 n^2 R_{AD}^3} - \frac{3(\mu_A \cdot R_{AD})(\mu_D \cdot R_{AD})}{4\pi\epsilon_0 n^2 R_{AD}^5} \quad (1.17)$$

where μ_A and μ_D are the transition dipole moment vectors of the acceptor and donor, $\mathbf{R}_{AD}$ is the vector connecting the centers of the dipoles, ϵ_0 is the permittivity of free space, and n is the refractive index of the medium.³¹ In the weak coupling limit, the EET rate from this interaction can be evaluated using Fermi's Golden Rule. A natural length scale emerges, the Förster radius R_0 , defined as the donor-acceptor separation at which the EET rate equals the radiative decay rate of the isolated donor. R_0 is a central parameter to this body of work and is determined by^{33,35}

$$R_0^6 = 0.02108 \kappa^2 \Phi_D n^{-4} J \quad (1.18)$$

where R_0 is in nm, κ^2 is the transition dipole orientation factor, Φ_D is the photoluminescence quantum yield of the isolated donor, n is the refractive index of the medium, and J (shown in Figure 1.9) is the spectral overlap integral:^{33,35}

$$J = \int I_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad (1.19)$$

where I_D is the photoluminescence spectrum of the isolated donor normalized to unit area, and ϵ_A is the molar extinction coefficient spectrum of the isolated acceptor.³³

From R_0 , the Förster EET efficiency and rate take the familiar forms, key to this thesis^{33,35}

$$E = \frac{1}{1 + (r/R_0)^6} \quad (1.20)$$

$$k_F = \left(\frac{1}{\tau_D}\right) \left(\frac{R_0}{R}\right)^6 \quad (1.21)$$

where τ_D is the radiative lifetime of the isolated donor.³³ The power of the Förster model lies in its connection between EET and easily obtained experimental observables: the donor emission spectrum, the acceptor absorption spectrum, the donor quantum yield, and the donor lifetime. The spectral overlap integral J encodes the degree of resonance between donor emission and acceptor absorption, making it a natural first-order design parameter. The characteristic R^{-6} distance dependence further makes Förster theory a powerful ruler for measuring nanoscale distances in biological systems, where it has found widespread application, illustrated in Figure 1.10.^{31,35}

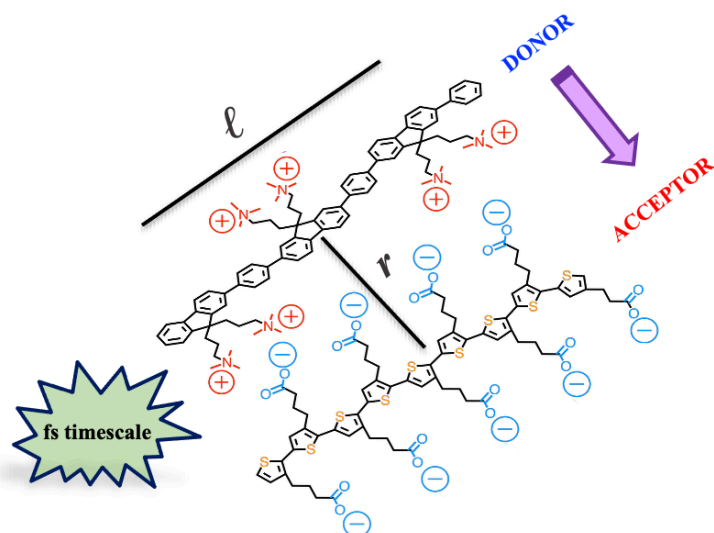


Figure 1.10: Schematic of Förster excitation energy transfer (EET) between a cationic CPE donor and anionic CPE acceptor separated by distance r along a chain of contour length l , occurring on the femtosecond timescale via dipole-dipole coupling.

Breakdown of the Förster Model in Proximal Extended Systems

The Förster model rests on four key assumptions: (1) both donor and acceptor can be treated as point dipoles, meaning their separation is significantly larger than the spatial extent of their excitonic wavefunctions; (2) neither donor nor acceptor are significantly self-interacting; (3) the donor and acceptor are free from inhomogeneous broadening; and (4) EET is incoherent.^{31,36} While these assumptions are well satisfied for dilute small-molecule dye solutions or for dyes tethered to isolated protein residues, they are not valid, to varying degrees, in many scenarios relevant to CPECs.

In a CPEC, the electrostatic co-assembly of oppositely charged chains brings the conjugated backbones into proximity, with center-to-center separations typically on the order of the repeat unit length.³³ At the same time, the conjugated backbone supports excitonic wavefunctions that can delocalize over many repeat units, producing exciton delocalization radii that are comparable to or larger than the interchain separation.^{37,38} This directly violates the point-dipole approximation: when the chromophore length L is comparable to or larger than the interchain separation R , collapsing the extended transition density of each chain to a single point dipole at its center of mass averages away precisely the spatial information that determines the coupling. In this way, the EET rate and efficiency depend not only on the spectral overlap but critically on the detailed real-space distribution of electron density along

the polymer backbone. This is information that is encoded in the chemical structure of the conjugated backbone but invisible from the spectral overlap integral.^{33,38,39}

CPEs further violate the self-interaction assumption: their photophysical properties are sensitive to backbone conformation, aggregation state, and ionic environment, all of which are perturbed upon the complexation of one CPE with another oppositely charged CPE.^{31,34} The high conformational disorder along CPE backbones also produces substantial inhomogeneous broadening, meaning that the spectral overlap computed from isolated CPE spectra does not accurately represent the degree of spectral overlap between the donor emission and acceptor absorption as they exist within the electrostatically assembled complex. Variations in backbone conformation and ionic environment shift and broaden the relevant spectra relative to their isolated-chain forms, a concept central to Chapter 2.³¹ Finally, EET in CPECs has been observed to proceed on sub-picosecond timescales commensurate with natural photosynthetic antenna, a regime where the incoherent hopping assumption of the Förster model is at best an approximation.^{33,34}

In this work, these considerations have been confronted directly in the context of polyfluorene-phenylene derivative CPEs, ionically assembled complexes of polyfluorene-based donor CPEs with a common thiophene-based acceptor CPE, shown as the red polymer in Figure 1.2.³³ In this system, subtle modifications to the backbone chemical structure of the donor CPE, which alter the excitonic wavefunction without substantially changing the electrostatic assembly thermodynamics, were found to produce large changes in EET efficiency and rate for

which the Förster model cannot account. Specifically, the Förster model predicts EET rates two orders of magnitude slower than those measured, and the ordering of EET efficiencies across the donor series does not follow the ordering of the spectral overlap integral. This failure motivates the need to move beyond the current theoretical framework and is discussed in detail in the coming chapter.³³

The Excitonic Coupling and the Exciton Transfer Integral

For incoherent EET within the Fermi Golden Rule, the EET rate is proportional to the product of two independent factors: the square of the excitonic coupling V_{EX} between donor and acceptor, and a factor ensuring energy conservation that is related to the spectral overlap integral J . The excitonic coupling is defined as³³

$$V_{EX} = \langle \Psi_D \Psi_A^* | \hat{V} | \Psi_D^* \Psi_A \rangle \quad (1.22)$$

where Ψ_D and Ψ_A are the ground-state wavefunctions of the donor and acceptor, $*$ denotes an excited state, and $\hat{V}$ is the operator describing the electronic coupling between them.³³ It is V_{EX} that encodes the dependence of EET on the precise excitonic wavefunctions of the donor and acceptor, and thus on the spatial distribution of electronic density along the conjugated backbone. The Förster model approximates V_{EX} as a point dipole-dipole interaction. Moreover, its failure in CPECs is that this approximation discards the spatial structure of Ψ that governs the coupling at short range, discussed in detail in Chapter 2.^{33,38} Isolating the coupling contribution experimentally, by dividing the measured EET efficiency by the spectral overlap integral, provides the square of V_{EX} . This, in turn reveals how the excitonic coupling

changes with backbone chemical structure, independent of spectral resonance effects.³³

The Line-Dipole Approximation

A natural first step beyond the point-dipole approximation for conjugated polymer chains is the line-dipole approximation, in which the coupling between two parallel chains is evaluated as a sum of pairwise dipole-dipole interactions between individual monomer units on the donor chain and individual monomer units on the acceptor chain.^{31,38} Rather than averaging away the spatial electron density distribution, this approach preserves the spatial extent of the transition density along the backbone, while still using the dipole term in the multipole expansion for each monomer-monomer interaction. In the line-dipole approximation, the exciton transfer integral J_{ld} is related to the corresponding point-dipole result J_{pd} by^{31,38}

$$J_{ld} = f J_{pd} \quad (1.23)$$

where the correction factor f is given by^{31,38}

$$f = \frac{2R^2}{L^2} \left(1 - \frac{R}{\sqrt{R^2 + L^2}}\right) \quad (1.24)$$

where R is the interchain separation and L is the chromophore length, the spatial extent over which the excitonic wavefunction is coherently delocalized.^{31,38} In the limit $L \gg R$, the EET rate in the line-dipole approximation falls off as R^{-2} rather than the R^{-6} dependence of the Förster model, making interchain EET competitive with intrachain exciton migration.³¹ The rate in this approximation then becomes³¹

$$k_{ld} = \frac{1}{\tau_D} \left(\frac{R_0^{ld}}{R} \right)^2 \quad (1.25)$$

Perhaps the most significant and counterintuitive result of the line-dipole framework established by Barford is the dependence of the excitonic coupling on chromophore length.^{33,38} For parallel conjugated polymer chains, the excitonic coupling V_{EX} is a decreasing function of chromophore length L : for identical chains,^{33,38}

$$V_{EX} \sim L^{-p} \quad (1.26)$$

where p ranges from 1 to approximately 2 depending on the assumed functional form of the center-of-mass excitonic wavefunction.^{33,38} This result is supported by quantum-chemical calculations, which show that the coupling increases as either the donor or acceptor chromophore length decreases beyond a few repeat units.^{33,40} The physical origin is as follows: a longer, more delocalized excitonic wavefunction spreads the transition density over more space, reducing the peak transition dipole moment per unit length and thus the coupling to a neighboring chain. Conversely, a shorter, more localized exciton concentrates the transition density, producing stronger coupling. This has direct and important implications for CPEC design: backbone chemical modifications that increase torsional disorder and reduce the exciton delocalization radius, even at the cost of reducing conjugation length, may surprisingly enhance EET by increasing the excitonic coupling, a concept discussed in detail in Chapter 2 of this work.³³

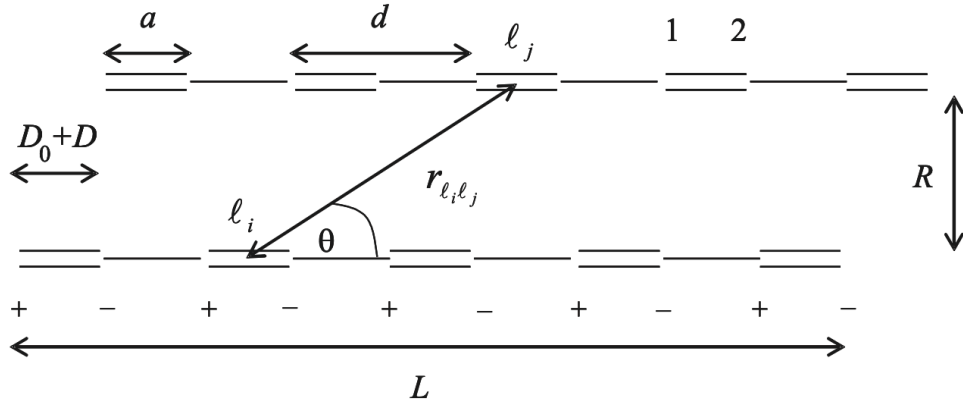


Figure 1.11: Geometric parameters defining interchain EET between two parallel conjugated polymer chains of length L separated by distance R , where chromophore segments l_i and l_j are separated by center-to-center distance $r_{l_i l_j}$ at angle θ , with repeat unit length a , segment length d , and chain offset $D_0 + D$. Adapted from Barford et al., arXiv:physics/0703233

EET in CPECs: How Backbone Chemical Structure Governs Excitonic Coupling

The line-dipole scaling $V_{\text{EX}} \sim L^{-p}$ establishes that the exciton delocalization radius is a primary determinant of EET in proximal conjugated polymer assemblies, one that is entirely invisible to the spectral overlap integral. As previously mentioned, in the conjugated polymer two-particle model, the excitonic wavefunction separates into a center-of-mass component that governs the spatial extent of the exciton and a relative component describing the electron-hole separation.^{37,38} Backbone chemical structure controls both of these. The torsional potential between adjacent monomers sets the degree of dynamic localization of the center-of-mass wavefunction, while the electronic character of the monomers determines the spatial distribution of the transition density along each chromophore.^{33,38} A larger average torsion angle

produces more dynamic localization and thus a smaller mean exciton delocalization radius, leading to larger excitonic coupling.³³ The spatial distribution of the transition density across the two monomers of an alternating copolymer introduces an additional position-dependent modulation of the coupling that is likewise absent from the point-dipole description.³³

These considerations establish that for CPECs in the proximal regime, where donor and acceptor backbone separations are comparable to the exciton delocalization radius, rational design of EET requires simultaneous control over both the spectral overlap and the excitonic coupling. The spectral overlap integral J remains a necessary condition for EET and provides a useful first-order estimate, but it is not sufficient. The precise chemical structure of the conjugated backbone must be considered because it determines V_{EX} through its influence on the exciton delocalization radius and transition density distribution. These two quantities can be independently varied through the choice of comonomer in an alternating copolymer architecture, making CPEs with well-defined alternating copolymer backbones, such as the PFPI-derivative series shown in Figure 1.2, a judiciously selected platform for systematically interrogating the relationship between backbone electronic structure and EET, as is the central theme of Chapter 2.³³

Ultimately, the ability of CPECs to support ultrafast EET on timescales commensurate with naturally occurring light-harvesting antennae arises from precisely this regime: the proximity of the donor and acceptor chains within the electrostatically assembled complex produces strong short-range excitonic coupling

between their extended electronic states, coupling that the Förster model cannot describe but that can be understood within both the line-dipole and the excitonic coupling framework developed in this work.^{33,34} A rigorous understanding of these processes is one of two central objectives of this thesis.³³

1.1.3 Charge Transfer in CPEs and CPE Complexes

The preceding sections treated excitation energy as a quantity that migrates between chromophores while remaining confined to the neutral singlet manifold. Another functional objective of a light-harvesting material, however, is the conversion of that bound electron-hole pair into spatially separated charge carriers that can perform useful electrical work. In organic semiconductors, including CPEs and CPECs, this conversion is thermodynamically non-trivial. The low dielectric environments of organic π -systems sustain exciton binding energies must be overcome before free polarons can be generated.^{6,7} Understanding the pathways by which singlet excitons evolve into charge-transfer (CT) states, and how those CT states subsequently dissociate or recombine, is central to the design of any CPE-based photoconversion application.

The Marcus Framework for Charge Transfer

The standard framework for describing non-adiabatic electron transfer in molecular donor-acceptor systems is the Marcus rate expression.^{16,24} In this picture, charge transfer occurs as a discrete hop between localized electronic states when the donor and acceptor potential energy surfaces intersect. The rate is governed by two

independent quantities: the electronic coupling between donor and acceptor, V_{DA} , and the free energy balance between the thermodynamic driving force and the energetic cost of nuclear reorganization. The Marcus rate is^{16,24,41}

$$k_{ET} = \frac{2\pi|J|^2}{\hbar} \frac{1}{\sqrt{4\pi\lambda kT}} \exp\left[-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda kT}\right] \quad (1.27)$$

where ΔG° is the thermodynamic driving force for the electron transfer, λ is the total reorganization energy, k_B is Boltzmann's constant, and T is temperature.⁴¹ The reorganization energy λ has two contributions: an inner-sphere component arising from geometric relaxation of the donor and acceptor backbones upon charge transfer, and an outer-sphere component arising from reorientation of the surrounding medium. For CPEs assembled in water, the high dielectric constant of the aqueous environment ($\epsilon_r \approx 80$) substantially reduces the outer-sphere reorganization energy relative to low-polarity organic solvents. This environmental dielectric screening is among the most distinctive features of aqueous CPE photophysics and places CPE electron-transfer kinetics in a regime qualitatively distinct from solid-state conjugated polymer devices.²⁵

Charge-Transfer States and Polaron Formation in CPECs

The initial product of interfacial electron transfer in a donor-acceptor pair is not a fully separated polaron pair but a charge-transfer (CT) exciton: a geminate electron-hole pair that is Coulombically bound but partially spatially delocalized across the donor-acceptor interface. CT states occupy an intermediate position in the photophysical hierarchy, between the locally excited (LE) singlet exciton and the fully

charge-separated polaron pair. They are characterized by partial (or complete) transfer of electron density from donor to acceptor, reduced oscillator strength relative to the parent LE state, and a characteristic red-shifted (and broad) emission band that serves as a spectroscopic signature of heterojunction formation.^{22,25}

In conjugated polymer systems, including CPECs, the spatial extent of the CT state is distributed over many repeat units on each chain rather than localized to a single molecular site. This delocalization has important consequences, one of which being that a CT state whose electron and hole wavefunctions each span several nanometers has a larger effective volume and experiences a smaller average Coulombic binding energy than a point-localized (otherwise identical) pair at the same separation.^{15,26} The driving force for charge separation is set by the frontier orbital offset between donor and acceptor. That is, when the LUMO offset ΔE exceeds the CT state binding energy, the ultrafast electron transfer can then generate a CT state with persistent quantum efficiency before any other kind of recombination can compete.^{22,23} Within a CPEC, this heterojunction is not a solid-state blend interface but a surface of electrostatic interactions between the donor and acceptor chains. Here, the inter-backbone separation is governed by the balance of electrostatic attraction, ionic sidechain steric repulsion, and aqueous solvation forces. The intimate, extended contact between donor and acceptor backbones in a CPEC means that every segment of the complexed CPEs creates a potential dissociation site, potentially enabling efficient charge generation without the requirement for long-range exciton diffusion.^{25,28}

Once charge separation has occurred, the resulting carriers are polarons. Polarons can be thought of in this case as charges dressed by local backbone geometric distortion.^{4,25} In conjugated polymers, the introduction of a charge onto the π -backbone induces an aromatic distortion (depending on the backbone architecture), and the resulting polaronic quasiparticle moves through the material by hopping between adjacent sites.^{1,4} In CPEs, the charged pendant groups and the environment created by their counterions introduce an additional reorganization energy contribution to each hopping event. This can be thought of as a counterion rearrangement in response to polaron motion that enters λ and reduces carrier mobility relative to what we might predict from the specific backbone electronic structure. The same π -orbital overlap that governs excitonic coupling between chains also mediates interchain charge hopping, but the relevant matrix element is now the direct HOMO or LUMO overlap rather than the transition dipole coupling discussed in the next section.^{3,26}

1.1.3.1 Charge Transfer with CPEs and Small-Molecule Acceptors: Aqueous Organic Photovoltaics

The charge-transfer framework described above applies directly to the design of aqueous organic photovoltaic (aOPV) devices in which CPEs serve as light absorbers and a small-molecule acceptor (SMA) drives charge separation. Canonical SMAs in organic photovoltaics include fullerene derivatives, whose deep-lying LUMOs and favorable electron affinity have made them the workhorse acceptors in conventional bulk heterojunction devices.^{14,28} Extending this architecture to the aqueous phase requires processing a CPE or CPEC active layer with an infiltrated

SMA, using the LUMO offset between the CPE donor backbone and the SMA as the thermodynamic driving force for interfacial electron transfer.

The aqueous environment modifies the energetics of this process in ways not encountered in conventional solid-state devices: solvation of the ionic sidechains shifts the effective ionization potential and electron affinity of the CPE backbone relative to the isolated neutral polymer, and the high dielectric constant of water reduces the CT state binding energy, making free carrier generation more thermodynamically accessible.²⁵

The architectural strategy pursued here centers on forming a phase-separated CPEC fluid as the primary light-absorbing layer, subsequently infiltrated with a fullerene acceptor to create mesoscale charge-transporting pathways. The key photophysical requirement is that electron transfer from the excited CPE to the fullerene be competitive with exciton decay, placing demands on the frontier orbital offset, CPE-fullerene interfacial contact geometry, and reorganization energy in the aqueous environment. Establishing a mechanistic understanding of charge generation and transport in this system is a central objective of the experimental work described in the chapters that follow.^{14,25,27,28}

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1.3 Overview of Experimental and Analytical Methodology

1.3.1 Time-Resolved Photoluminescence & Anisotropy

Time-resolved photoluminescence (TRPL) measurements occupy an important position among spectroscopic tools for investigating conjugated polyelectrolytes and related fluorescent macromolecules. While steady-state absorption and emission spectra encode the averaged response of an excited-state population, time-resolved measurements resolve the kinetics of that population's decay, yielding direct access to fluorescence lifetimes, non-radiative rate constants, and, most importantly, the rates of excited-state processes such as electronic energy transfer (EET) that compete with spontaneous emission. In CPE systems where absorption and photoluminescence spectra of structurally distinct species overlap substantially, differences in excited-state lifetimes frequently provide the only unambiguous means of resolving contributions from conformationally distinct chromophores or donor-acceptor complexes. More broadly, time-resolved measurements are integral to confirming the presence of EET and testing the mechanistic predictions of Forster and generalized energy transfer theories, and for extracting exciton diffusion lengths, as described in Chapter 2. These characteristics are also directly relevant to the photovoltaic applications described in Chapter 3.^{1,2}

Excited-State Decay Kinetics and Fluorescence Lifetimes

The total excited-state decay rate k_{total} is determined by the sum of the radiative rate k_r and all non-radiative rates. In the framework given by Lakowicz,⁵ this relationship is written:

$$k_{total} = k_r + k_{nr} + k_s^{Ic} \quad (1.28)$$

where k_{nr} encompasses all non-radiative processes, including vibrational relaxation, collisional quenching, singlet-singlet annihilation, and charge recombination, and k_s^{Ic} is the rate of intersystem crossing to the triplet manifold. Equation 1.28 reflects the excited-state depopulation: each pathway competes in parallel, and the total rate is then additive. The fluorescence lifetime τ is the reciprocal of the total decay rate,⁵

$$\tau = 1/k_{total} \quad (1.29)$$

and the fluorescence quantum yield Φ^f represents the fraction of excited-state decay events that result in photon emission:⁵

$$\Phi^f = k_r/k_{total} \quad (1.30)$$

For CPEs, which predominantly decay via fluorescence rather than phosphorescence, τ corresponds to the fluorescence lifetime. Equations 1.28 through 1.30 together reveal a central physical principle: any process that opens a new non-radiative decay channel will simultaneously shorten the lifetime and reduce the quantum yield. The radiative rate k_r , ultimately depends on the square of the transition dipole moment and is therefore sensitive to the spatial extent of the excitonic

wavefunction, the degree of backbone planarity, and the aggregate state of the polymer. H-aggregate formation, for instance, creates low-energy exciton traps to which population is rapidly funneled and from which non-radiative decay dominates, reducing both Φ^f and often τ relative to the isolated chain.^{3,4} Monitoring changes in τ as a function of variables such as CPE concentration, ionic strength, or complexation ratio with a complementary CPE provides a sensitive reporter of structural and electronic reorganization in the system. This reporter is often resolvable in cases where steady-state spectra show only modest changes.

For systems characterized by a single fluorescence decay pathway, an idealized limit applicable to dilute solutions of conformationally homogeneous chromophores, the time-dependent intensity follows a single exponential:⁵

$$I(t) = I_0 \exp(-t/\tau) \quad (1.31)$$

In practice, CPEs (in solution) exhibit multiexponential decays reflecting the statistical distribution of chromophore lengths along the polymer backbone, each chromophore having its own distinct conjugation length and therefore a distinct excited-state energy and decay rate. Each component is characterized by a lifetime τ_i and a pre-exponential amplitude α_i :⁵

$$I(t) = \sum \alpha_i \exp(-t/\tau_i) \quad (1.32)$$

where the amplitudes α_i represent the fractional contribution of each decay component to the total initial intensity. The physical interpretation of the pre-exponential amplitudes depends on the excitation and detection conditions: for delta-function

excitation, α_i corresponds to the fraction of excited-state population in the i th decay channel at time zero. Two distinct average lifetimes are commonly employed. The intensity-weighted mean lifetime, defined as $\langle\tau\rangle = \sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i$, weights each component by its fractional contribution to the total emitted intensity and is the most physically meaningful average for comparing systems with different degrees of heterogeneity.⁵ The amplitude-weighted mean $\langle\tau\rangle = \sum \alpha_i \tau_i$, instead, reflects the relative populations of each species and is more appropriate when estimating quenching efficiencies.⁵ The distinction between these two averages becomes especially important in CPE complexes (CPECs), where short-lived (quenched) donor components may coexist with longer-lived unquenched donors in the same ensemble, for example.

Time-Correlated Single Photon Counting

The standard experimental method for accessing fluorescence lifetimes in the nanosecond-to-microsecond regime is time-correlated single photon counting (TCSPC), a technique that has numerous and substantial technical advantages with the development of compact pulsed laser sources, high-repetition-rate electronics, and hybrid photomultiplier detectors.⁵ The operating principle exploits the probabilistic and statistical nature of single-photon emission from a continuous wave lasing source where: a sample is repetitively excited by a short laser pulse, and for each excitation cycle, the delay time between the excitation pulse and the first detected emitted photon is recorded in a histogram. Given that the detection probability per excitation cycle is kept sufficiently low, conventionally below one photon per hundred laser pulses, the resulting histogram accurately reconstructs the temporal probability distribution of

photon emission: this is proportional to the true fluorescence decay function $I(t)$.^{6,7} This “low-count” rate condition is essential because at higher count rates (where detection of multiple photons per excitation cycle biases the histogram toward shorter apparent delay times), a systematic artifact known as pile-up emerges.⁵

In a standard configuration, a signal from the photodetector triggers the start of a time-to-amplitude converter (TAC), which initiates a linear voltage ramp that is then stopped by the subsequent laser synchronization pulse. The resulting voltage, proportional to the photon arrival delay, is digitized and binned in the memory. The reverse configuration is often employed to avoid the high dead-time fraction that would arise from the TAC being perpetually reset by a high-repetition-rate laser in the conventional “start-stop” arrangement.⁵ The collected decay histogram is inherently Poisson-distributed, as the uncertainty in the count of the i th channel, σ_i , equals $\sqrt{N_i}$; precision improves only as the square root of accumulated counts. Furthermore, achieving reliable multiexponential analysis requires accumulation of at minimum 10^4 counts in the peak channel, ensuring a relative uncertainty of no greater than 1% at the point where the decay has fallen to 1% of its maximum value.⁵

In practice, the measured decay $I_0(t)$ is not the true sample response $I(t)$ but rather its convolution with the instrument response function (IRF), $P_0(t)$, shown in equation 1.33. This term encodes the temporal profile of the excitation pulse together with all electronic broadening contributions from the detector and timing electronics:⁵

$$I_0(t) = \int P_0(t')I(t - t')dt' \quad (1.33)$$

Because there is no closed-form expression available for deconvolution of Equation 1.33 in the general case, fluorescence lifetimes are extracted by iterative forward convolution. This re-convolution is a (trial) decay function of Equation 1.32 and is numerically convolved with the measured IRF and compared to the experimental data via weighted least-squares minimization. The goodness-of-fit is assessed using the reduced chi-square statistic, as formulated by O'Connor and Phillips⁵ for Poisson-distributed TCSPC data:

$$\chi^2 = \left[\frac{1}{(n_2 - n_1 + 1 - p)} \right] \frac{\sum [I_0(t_i) - I(t_i)]^2}{I_0(t_i)} \quad (1.34)$$

where n_1 and n_2 define the fitting range in channel space and p is the number of free parameters. The denominator, $(n_2 - n_1 + 1 - p)$, represents the number of degrees of freedom for the fit. For Poisson-distributed data, the variance in each channel equals the expected count. Thus, the weighting factor $1/I_0(t_i)$ is the appropriate inverse-variance weight. An ideal fit of an adequate model to noise-free Poisson data yields $\chi^2 = 1.0$, so values in the range 0.8-1.3 are generally considered acceptable.⁵ Convergence to an acceptable χ^2 is necessary but not sufficient to validate a fit. The weighted residuals $r(t_i) = [I_0(t_i) - I(t_i)] / \sqrt{I(t_i)}$ must also be randomly distributed about zero without systematic structure, and the recovered lifetimes must also be physically plausible to support desired measurements. Parameter minimization in this work is carried out using the Levenberg-Marquardt algorithm as implemented in the DecayFit MATLAB-based software package.⁵

Time-Resolved Fluorescence Anisotropy

The informational content of TCSPC measurements can be substantially extended through the measurement of time-resolved fluorescence anisotropy (TRPLA). TRPLA encodes both rotational dynamics and excitation energy migration within a chromophore assembly. When a population of randomly oriented chromophores is excited by linearly polarized light, photo-selection preferentially excites those molecules whose transition dipole moments are aligned with the excitation polarization. This is due to the fact that the transition probability scales as $\cos^2\theta$, where θ is the angle between the transition dipole and the electric field vector.⁵ The resulting anisotropic excited-state population gradually depolarizes over time through two primary mechanisms: (1) rotational diffusion of the chromophore and (2) EET to acceptors with differently oriented transition dipoles. The time-dependent anisotropy $r(t)$ is defined as:⁵

$$r(t) = \frac{I_{\parallel}(t) - GI_{\perp}(t)}{I_{\parallel}(t) + 2GI_{\perp}(t)} \quad (1.35)$$

where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the time-dependent fluorescence intensities collected with emission polarization parallel and perpendicular to the excitation polarization, respectively. G is an instrumental correction factor that largely accounts for the polarization-dependent detection efficiency associated with the optical elements such as the diffraction grating of the emission monochromator. The denominator $I_{\parallel}(t) + 2G \cdot I_{\perp}(t)$ is proportional to the total fluorescence intensity and serves as a normalization.

The G factor is determined experimentally from horizontally polarized excitation measurements:⁵

$$G = \frac{\int I^{HV}(t)dt}{\int I^{HH}(t)dt} \quad (1.36)$$

where $I^{HV}(t)$ and $I^{HH}(t)$ are the vertically and horizontally polarized emission intensities under horizontal excitation. This measurement isolates the instrumental polarization bias because horizontal excitation, in the absence of any preferential orientation in the sample, should in principle produce equal intensities in both polarization channels. For a randomly oriented solution of chromophores, the anisotropy at time zero is bounded from above by the fundamental anisotropy r_0 , which is determined by the angle β between the absorption and emission transition dipole moments. This relationship, derived from the photoselection probability distribution for one-photon excitation of a randomly oriented ensemble, is given by⁵

$$r_0 = \left(\frac{2}{5}\right) \left[\frac{3\cos^2\beta - 1}{2} \right] \quad (1.37)$$

For a collinear absorption-emission dipole pair ($\beta = 0$), Equation 1.37 gives $r_0 = 0.4$, the theoretical maximum for a randomly oriented ensemble under one-photon excitation. This upper bound arises from the averaging according to the $\cos^2\theta$ distribution, because even in the limit of perfectly collinear dipoles a significant fraction of excited molecules has its transition moment offset from the excitation polarization axis. The emission from these molecules contribute to depolarization.⁵ Deviation of r_0 from 0.4 in practice may signal the presence of energetically close electronic transitions whose transition dipoles are not collinear, rapid local motion on

timescales faster than the experimental time resolution, or other ultrafast depolarization mechanisms.

For a dilute solution of small spherical chromophores, $r(t)$ decays as a single exponential with a rotational correlation time, θ_{rot} , governed by the Stokes-Einstein-Debye relationship. In this limit the anisotropy decay takes the form:⁵

$$r(t) = r_0 \exp\left(-\frac{t}{\theta_{rot}}\right) \quad (1.38)$$

where $\theta_{rot} = \eta V/k_B T$, with η the solvent viscosity, V the hydrodynamic volume of the rotating species, k_B Boltzmann's constant, and T the absolute temperature. For macromolecular systems such as CPEs, the large hydrodynamic volume substantially increases θ_{rot} , placing rotational diffusion on timescales of tens to hundreds of nanoseconds, which is far slower than the nanosecond-scale fluorescence lifetime.⁵ In this limit, $r(t)$ does not decay appreciably via molecular tumbling over the observation window, and depolarization may instead be dominated by EET between chromophores with differently oriented transition dipoles. This property makes time-resolved anisotropy a sensitive probe of EET dynamics in CPE systems: the rate of anisotropy decay reports on the rate of interchromophore energy transfer, independently of changes in fluorescence intensity that might arise from competing photophysical processes, discussed in Chapter 2.^{1,5}

Ayzner Laboratory TCSPC Apparatus

The instrument is configured in right-angle geometry, wherein excitation and emission optical paths are orthogonal. This research used two excitation sources: (1) a

supercontinuum pulsed white-light laser, from which specific excitation wavelengths are selected by a radio-frequency-driven acousto-optic tunable filter (AOTF), and (2) a 375-nm pulsed blue laser-diode. In regard to the white-light laser, the modulation of the applied radio frequency tunes the refractive index of the acousto-optic crystal and directs the desired wavelength component through the excitation aperture.

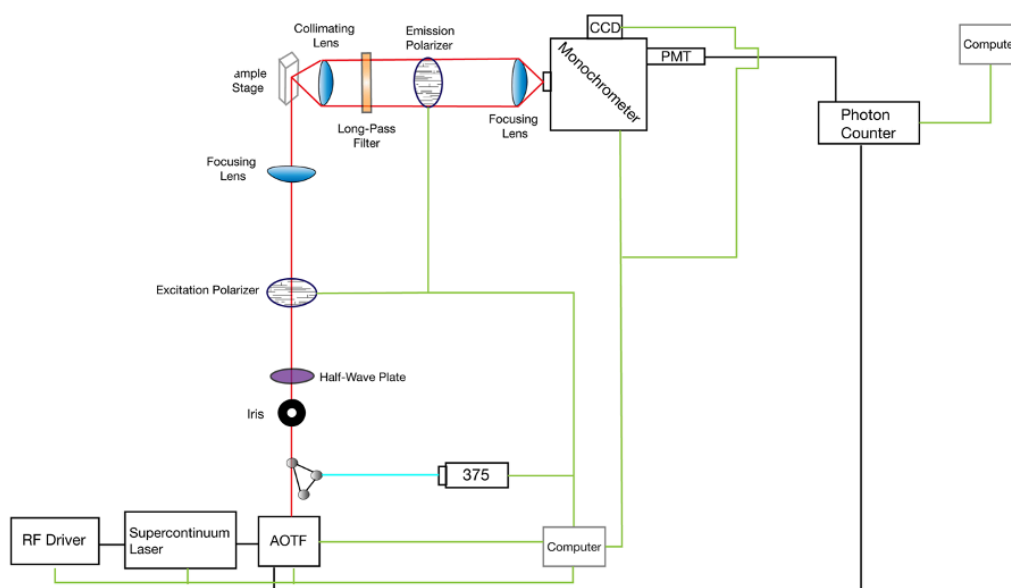


Figure 1.12: Schematic of the Ayzner lab TCSPC.

This architecture provides excitation wavelength selection across a broad range (397-1400 nm) at multiple repetition rates (approximately 5-80 MHz), enabling interrogation of multiple electronic transitions without optical realignment. The principal limitation of this approach is a broader excitation pulse bandwidth relative to single-frequency

laser sources, yielding an instrument response function with a full-width at half-maximum of approximately 120 ps.

The native elliptical polarization of the supercontinuum source is converted to linear vertical polarization by passing the beam sequentially through an achromatic half-wave plate, with its fast axis oriented at 45° from vertical to rotate the polarization by 90° , and a vertically oriented Glan-Thompson polarizer. The linearly polarized excitation beam is focused onto the sample via an achromatic doublet lens. The sample stage accommodates either a standard 1 cm cuvette with right-angle (90°) emission collection, or a 1 mm cuvette or thin film oriented at 45° for front-face collection from concentrated solutions or solid samples, the latter has severe limitations and will be discussed in the next section. Emitted light is collimated by an achromatic doublet, passed through a long-pass filter to suppress scattered excitation light, and directed through a second Glan-Thompson polarizer mounted on a motorized rotation stage. For standard TCSPC lifetime measurements, the emission polarizer is set at the magic angle (54.75°) to eliminate polarization bias in the recovered decay.⁵ For anisotropy measurements, the emission polarizer is swapped between vertical (0°) and horizontal (90°) orientations, while the excitation polarizer is similarly motorized to facilitate G-factor determination under horizontal excitation.

The emission beam is focused onto the entrance slit of a grating monochromator equipped with both an air-cooled CCD, used for steady-state fluorescence spectral acquisition, and a hybrid photomultiplier tube (hybrid-PMT) for time-resolved detection. The hybrid-PMT output is directed to an integrated TCSPC electronics

module operating in reverse start-stop configuration, with the start pulse derived from the hybrid-PMT and the stop pulse from the NIM synchronization output of the laser. Photon arrival delay is adjusted by varying the cable length between the stop pulse source and the TCSPC electronics, with approximately 10 cm of coaxial cable corresponding to a 3 ns delay. Data acquisition, laser wavelength and repetition rate, monochromator position, and polarizer orientation are all controlled through a unified software interface, and lifetime fitting is performed using the DecayFit package with Levenberg-Marquardt least-squares minimization.⁵

Adaptation of the TCSPC Apparatus for Thin Film Front-Face Measurements

The right-angle TCSPC geometry described above is optimized for dilute solutions in standard square cuvettes, where the excitation and emission paths are orthogonal and the sample is optically dilute enough that re-absorption and inner filter effects are negligible. Effectively extending the apparatus to thin films deposited on glass substrates required a targeted modification to the experimental setup, motivated by a fundamental incompatibility between standard right-angle geometry and solid, reflecting samples.

In the standard right-angle geometry, when a thin film on a glass substrate is placed into the beam path at the $\sim 45^\circ$ orientation natural to that configuration, the specular reflection from the glass-air interface is directed precisely along the emission collection axis. Because specular reflection from a smooth glass surface is governed by the Fresnel equations, which at near-normal incidence return several percent of the incident intensity,¹ this reflected excitation scatter overwhelms the comparatively weak

photoluminescence signal from the thin film. Even with long-pass filters in the emission path, the wings of an intense specular reflection can contribute a non-negligible background within the fluorescence band.

Critical to anisotropy measurements, the polarization state of the specularly reflected beam is not identical to that of the incident beam. At non-normal incidence, the Fresnel reflection coefficients for s- and p-polarized components differ, causing a differential reflectivity that selectively attenuates the horizontally polarized component relative to the vertically polarized one. This polarization-dependent intensity imbalance introduces a "pseudo-like" artifact into the detected signal that is indistinguishable from the intrinsic emission anisotropy of the film, corrupting the measured $r(t)$ in a way that cannot be corrected by even the G-factor. The Fresnel reflection coefficients for s- and p-polarized components differ at non-normal angles of incidence; a polarization-dependent reflectivity that becomes increasingly severe as the incidence angle departs from normal.¹ This differential reflectivity introduces a change in the polarization, changing the apparent magnitude of the horizontal component into the detected signal that is indistinguishable from the intrinsic emission anisotropy of the film which corrupts the measured $r(t)$ in a way that cannot be corrected by even the G-factor. The G-factor (Equation 1.36) corrects only for the polarization-dependent transmission efficiency of the emission optics train and is unable to subtract from a co-propagating, partially polarized reflected beam.⁵

Both the geometric origin of this artifact, and the target configuration that was developed to eliminate it, are illustrated schematically in Figure 1.13. As shown,

adapting the existing square geometry to approximate front-faced (FF) conditions by tilting the film within the right-angle excitation-emission plane does not resolve the problem. The specular reflection from the film surface remains directed into or near the emission collection axis, and the polarization imbalance introduced by the angle-dependent Fresnel reflectivities persist. The traditional FF geometry shown in the right panel, in which the excitation beam is brought in at a sufficiently oblique angle that the specular reflection exits well outside the emission collection cone, represents the only geometry that fully eliminates these artifacts.

The appropriate solution, well established for measurements on optically dense or scattering samples such as membranes, gels, and solid films, is FF geometry, in which the excitation beam is directed at an oblique angle to the sample surface and emission is collected from the same face of the sample.⁵ Here, where to be front-faced, means for the film plane to be normal to the detector direction, the specular reflection exits at an angle well away from the emission collection axis. The critical requirement is that the specular reflection exits well outside the collection cone, of the emission optics. In practice a larger angular offset than the strict minimum is preferred as it provides comfortable separation between the reflected beam and the collection cone. Thus reducing the contribution of scattered excitation light at its edges.⁵

A further design constraint requiring explicit calculation was the avoidance of Brewster's angle for the glass substrate. At Brewster's angle, the p-polarized component of the excitation beam undergoes zero reflection, while the s-polarized component retains finite reflectivity governed by the Fresnel equations.¹ This complete

suppression of p-polarized reflection maximizes the differential reflectivity between the two polarization components, producing the most severe possible polarization imbalance in any residual scattered excitation reaching the detector. For the glass cuvettes and substrates used in this work ($n \approx 1.52$), Brewster's angle is given by:

$$\theta_B = \arctan(n_2/n_1) = \arctan(1.52/1.00) \approx 56.7^\circ \quad (1.39)$$

measured from the surface normal. The excitation angle was therefore chosen to be well away from Brewster's angle, so that both polarization components of the excitation beam reflect off the glass surface with similarly low and nearly equal intensity. This minimizes both the total amount of stray excitation light reaching the detector and any polarization imbalance it might introduce.¹

The practical challenge in achieving FF geometry was that the existing optical table is configured in right-angle format, with the excitation beam propagating along one axis and the emission collection path propagating along the orthogonal axis. Neither of these axes is naturally oriented at a small oblique angle to a thin film sample. To achieve the traditional FF geometry without a complete rebuild of the optical table, a two-mirror assembly was introduced into the excitation beam path upstream of the sample position. The mirrors redirect the excitation beam sequentially to produce the desired angular offset between the excitation and emission axes at the sample plane. A focusing achromatic doublet lens was incorporated into this redirected excitation arm to refocus the beam onto the film surface, compensating for the additional path length introduced by the mirror assembly and maintaining a tight excitation spot at the sample. In this configuration, emission from the film surface is collected along an axis close to

the sample normal and directed into the existing collimating optics, long-pass filter, emission polarizer, and monochromator assembly without modification to the detection path.

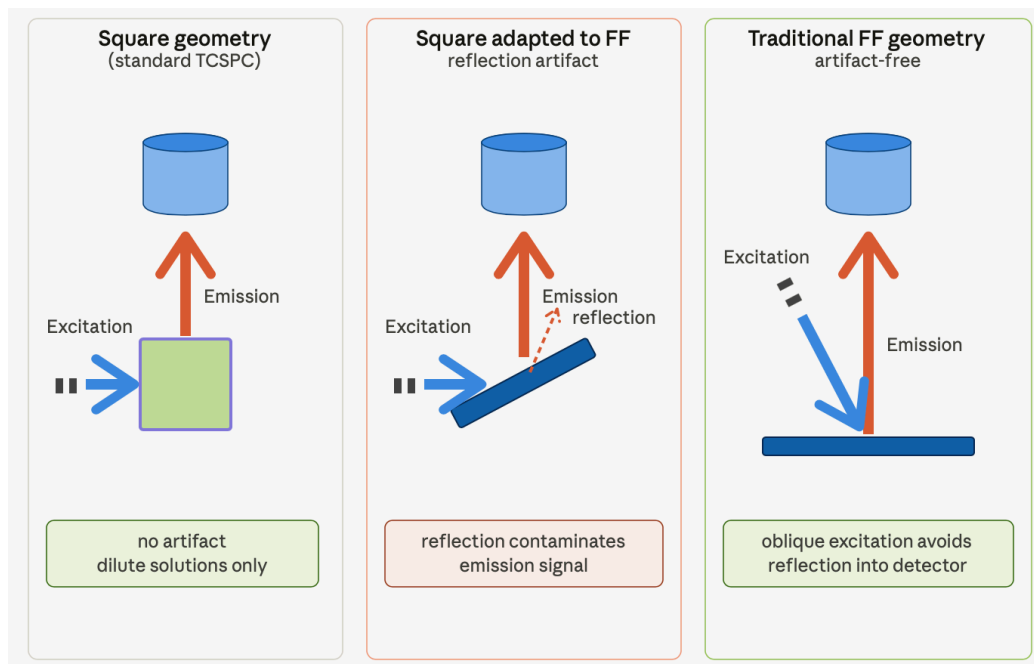


Figure 1.13. Comparison of TCSPC geometries for anisotropy measurements. The standard square geometry (left) works for dilute solutions but adapting it to thin films by tilting the substrate (center) directs specular reflection into the emission axis. Traditional front-face geometry (right) sends the reflection away from the collection cone, enabling artifact-free measurements on films.

The successful achievement of this geometry was validated by recording the TCSPC anisotropy decay of a well-characterized small-molecule fluorophore deposited on a quartz substrate, confirming that the parallel (VV) and perpendicular (VH) polarized decay components behave as expected. Specifically, the initial amplitude of $r(t)$ approaches the theoretical fundamental anisotropy r_0 and no polarized artifact is

present at time zero that would indicate residual specular contamination of the emission.

1.3.2 Ultrafast Pump-Probe Spectroscopy

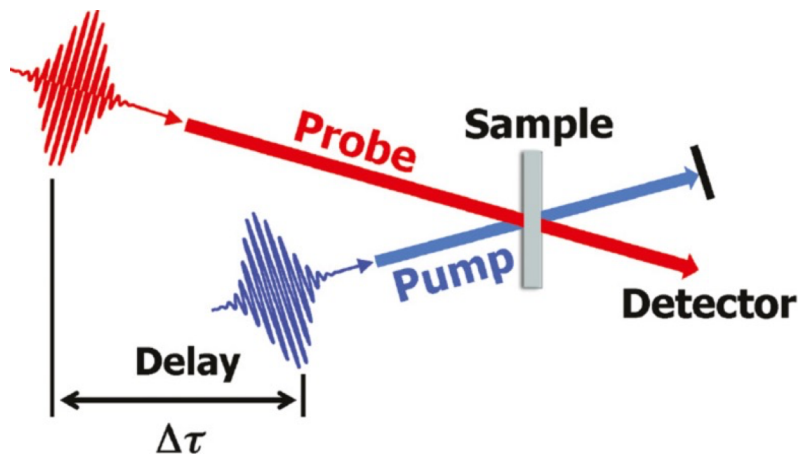


Figure 1.14. Schematic of a transient absorption measurement, in which a pump pulse photoexcites the sample and a time-delayed probe pulse ($\Delta\tau$) monitors the resulting changes in optical transmission.

Whereas TCSPC provides access to excited-state dynamics on the ~100 picoseconds to nanosecond timescale, many of the most physically important processes in CPEs and CPECs, including intrachain exciton relaxation, interchain electronic energy transfer, and charge separation at donor-acceptor interfaces, occur on femtosecond to few-picosecond timescales that lie well beyond the temporal resolution of time-correlated single-photon-counting techniques. Ultrafast transient absorption (TA) spectroscopy bridges this gap by using two synchronized laser pulses to directly time-resolve changes in the optical properties of a photoexcited sample with sub-100

femtosecond precision.⁵ It is the primary technique used in this thesis to characterize ultrafast exciton and EET dynamics in CPEC systems. The ultrafast TA measurements presented in this dissertation were performed in collaboration with the Bragg laboratory at Johns Hopkins University and the Zhang laboratory at the University of California, Santa Cruz.

In a pump-probe TA experiment, a femtosecond pump pulse photoexcites the sample, promoting a fraction of the ground-state population to an excited electronic state. A second, time-delayed broadband probe pulse then interrogates the sample, and the wavelength-resolved change in optical density relative to the unexcited sample is recorded as a function of pump-probe delay time τ . The transient signal ΔOD is defined as¹

$$\Delta OD_t = OD_t - OD_0 \quad (1.40)$$

where OD_t is the optical density of the photoexcited sample measured by the probe at delay time τ after the pump pulse, and OD_0 is the optical density of the probe pulse in the absence of the pump pulse. This is illustrated in Figure 1.14.¹ By recording absorption across a range of pump-probe delay times, a two-dimensional dataset is constructed that encodes the full spectral and temporal evolution of the photoexcited sample. The sign and spectral shape of ΔOD at each wavelength and delay time reflect the superposition of several distinct photophysical contributions, each carrying specific information about the excited-state or ground-state populations.¹³

There are three distinct contributions to ΔOD commonly encountered in conjugated polymer systems, all illustrated in Figure 1.15.¹³ Ground-state bleach (GSB) appears as a negative ΔOD signal at wavelengths corresponding to the ground-state absorption band of the photoexcited species. It arises because the pump pulse depopulates the ground state, reducing the number of molecules available to absorb the probe at the wavelengths specifically corresponding to the ground-state absorption spectrum. Its spectral profile mirrors the steady-state absorption spectrum of the excited chromophore and persists as long as the excited-state population has not returned to the ground state. Stimulated emission (SE) also appears as a negative ΔOD signal, at wavelengths corresponding to the emission spectrum of the excited state. It arises from stimulated de-excitation of excited-state molecules by the probe pulse, adding photons to the transmitted probe beam. The spectral profile of SE therefore mirrors the steady-state photoluminescence spectrum of the excited chromophore. Excited-state absorption (ESA), by contrast, appears as a positive ΔOD signal at wavelengths where the excited state absorbs the probe. It arises from transitions from the populated excited state S_1 to higher-lying states S_n and is absent from the steady-state ground-state spectrum. The spectral position and temporal evolution of ESA features encode information about the electronic structure of higher excited states and the dynamics of excited-state relaxation and population transfer.

In CPE and CPEC systems, the spectral evolution of ΔOD with pump-probe delay is particularly rich because multiple species contribute simultaneously: photoexcited donor and acceptor chromophores, charge-transfer states, and polaronic

species can each produce overlapping GSB, SE, and ESA features in the same spectral window. Disentangling these

contributions requires careful comparison of CPEC TA spectra with those of the isolated component CPEs under identical excitation conditions.¹³

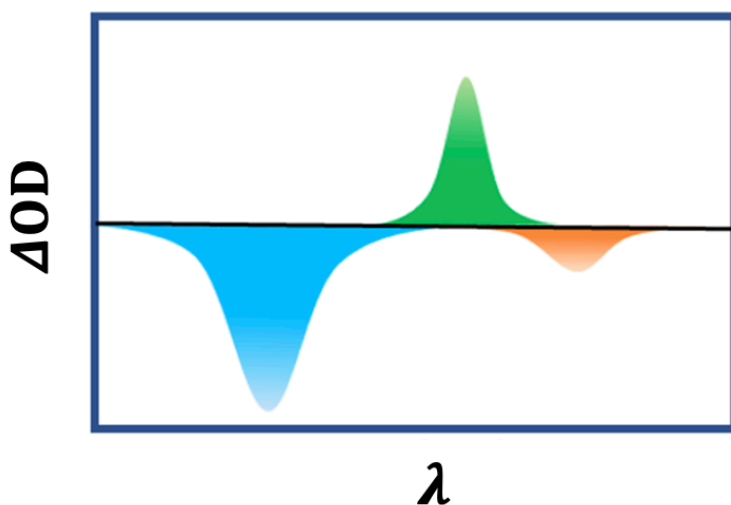
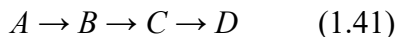


Figure 1.15. Representative transient absorption spectrum illustrating the GSB (blue), SE (red), and ESA (green) contributions to the ΔOD signal.

Two complementary analytical approaches are used in this thesis to extract quantitative excited-state dynamics from TA datasets. The first is single-wavelength kinetic analysis, in which the time dependence of ΔOD at a selected probe wavelength is fit to a sum of exponential decay and rise components. Probe wavelengths are chosen to correspond to spectral regions dominated by a single contributor, so that the extracted time constants can be assigned to specific photophysical processes. In CPEC systems,

the appearance of acceptor GSB or SE at early pump-probe delays following donor excitation is direct spectroscopic evidence of EET, and the time constant of its rise directly reports the EET rate.¹³

The second approach is global spectral analysis, in which the aforementioned two-dimensional $\Delta OD(\lambda, \tau)$ dataset is fit simultaneously across all probe wavelengths subject to a kinetic model. In this work, global analysis is carried out using a sequential kinetic interconversion model,⁵



where each arrow represents an irreversible first-order interconversion with an associated lifetime τ_i . This model produces species-associated difference spectra (SADS), each representing the spectral signature of the transient excited-state population present during the corresponding kinetic window. SADS analysis is particularly powerful in CPEC systems because the sequential model naturally captures the temporal evolution from initially photoexcited donor states, through EET to the acceptor, to the subsequent dynamics of the acceptor excited state. Lifetimes extracted from global analysis provide EET rates and excited-state lifetimes that are free from the spectral crosstalk that can bias single-wavelength fits in spectrally congested systems, as discussed in Chapter 2.⁵

A practical advantage of ultrafast TA spectroscopy in studies pertaining to CPEs and CPECs is the ability to selectively excite donor or acceptor chromophores by tuning

the pump wavelength. In the CPECs studied in this thesis, the donor and acceptor CPEs absorb in complementary spectral windows, allowing UV-visible pump pulses (360-400 nm) to preferentially excite the donor CPE and visible pump pulses (600 nm) to selectively excite the acceptor CPE. Selective acceptor excitation is particularly informative as a control experiment: TA spectra collected under these conditions capture the intrinsic excited-state dynamics of the acceptor within the complex in the complete absence of EET, providing a reference against which CPEC spectra collected under donor excitation can be compared to isolate the EET contribution.¹³ The combination of donor- and acceptor-selective excitation, broadband probe detection, and both single-wavelength and global kinetic analysis constitutes the core TA methodology employed throughout the experimental chapters of this thesis.

1.3.3 Small-Angle and Grazing-Incidence Small-Angle X-Ray Scattering

Small-angle X-ray scattering (SAXS) is a powerful, non-destructive technique for probing the structural organization of materials at the nanometer to mesoscale length scale, typically spanning 1 to 100 nm.^{1,5} In a SAXS experiment, a collimated X-ray beam is directed through or onto a sample, and the intensity of the scattered radiation is recorded as a function of the scattering angle. The relevant experimental quantity is the length of the (photon) momentum transfer vector q , defined as:

$$q = \frac{4\pi \sin\theta}{\lambda} \quad (1.42)$$

where 2θ is the scattering angle and λ is the X-ray wavelength. Structural information is encoded in the q -dependence of the scattered intensity through the reciprocal relationship between q and the real-space length scale d :

$$d = \frac{2\pi}{q} \quad (1.43)$$

such that features at small q probe to large-scale structural organization, while features at high q report on shorter-range correlations. Sharp peaks in the scattering profile indicate well-defined periodicities such as lamellar spacings or domain repeat distances.^{1,5}

The physical basis of SAXS is the elastic scattering of X-rays by spatial variations in electron density within the sample.^{1,5} Because X-rays interact with the electron clouds of atoms, any interface between regions of differing electron density gives rise to scattering contrast. In soft matter systems such as polymer blends, block copolymers, colloidal suspensions, and self-assembled materials, the relevant contrast arises from the electron density difference between chemically or structurally distinct phases or domains. The resulting scattering profile is essentially the Fourier transform of the electron density autocorrelation function. This interpretation requires modeling the expected scattering from candidate structural models. A key practical advantage of SAXS is that it probes a statistically representative, macroscopic sample volume simultaneously, providing ensemble-averaged structural information that complements the local, real-space images obtainable by electron or scanning probe microscopy.¹

SAXS can be performed in transmission geometry on bulk materials, solutions, or gels, in which case the beam passes through the sample and the scattering pattern reflects the three-dimensional structural correlations averaged over the illuminated volume. For isotropic samples, azimuthal averaging of the two-dimensional detector image yields a one-dimensional $I(q)$ profile that encodes structural information about domain size, shape, and spatial arrangement. In the work described in Chapter 2, SAXS in transmission geometry was employed to characterize the structural organization of the CPECs in dilute solution.

Grazing-Incidence Small-Angle X-Ray Scattering (GI-SAXS)

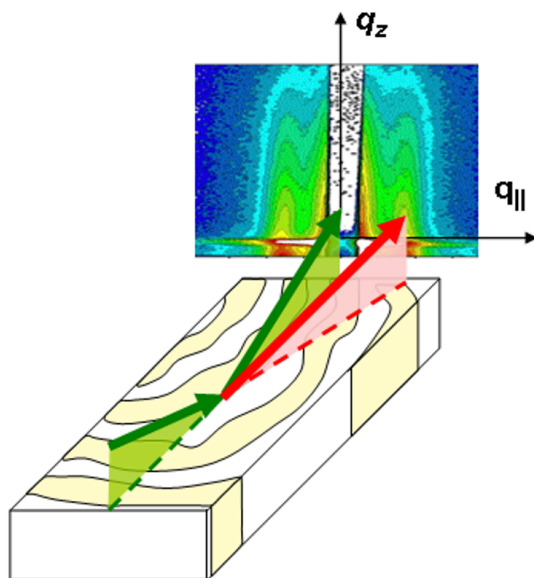


Figure 1.16. GISAXS experimental geometry.⁵

When the sample of interest is a thin film rather than a solution or bulk material, transmission SAXS becomes impractical because the scattering volume is too small to

generate adequate signal. Grazing-incidence small-angle X-ray scattering (GI-SAXS) circumvents these limitations by directing the X-ray beam at the sample at a very shallow incidence angle, α_i .^{16,17} At this angle, the footprint of the beam on the sample surface is elongated, dramatically increasing the scattering volume relative to the film thickness and enabling the detection of nanoscale structural features within films as thin as tens of nanometers. GI-SAXS provides statistically representative structural information averaged over a macroscopic sample area, making it an ideal complement to local real-space probes such as electron microscopy, shown in Figure 1.16.⁵

A key feature of the grazing-incidence geometry is the critical angle of total external reflection, α_c . For X-rays, the refractive index of a material is slightly less than 1: $n = 1 - \delta + i\beta$, where δ is the refractive index decrement and β accounts for absorption. The critical angle is related to δ by¹:

$$\alpha_c = \sqrt{2\delta} \quad (1.44)$$

Below α_c , X-rays undergo total external reflection from the film surface and penetrate only as an evanescent wave extending a few nanometers into the material, making the measurement surface-sensitive. When the incident angle is set above α_c of the film, the X-ray beam fully penetrates the film and the resulting scattering pattern reflects the bulk morphology of the entire film thickness.¹ This tunability of the probed depth is a significant practical advantage of GI-SAXS. In the thin film measurements described in Chapter 3, GI-SAXS data were collected with the incident angle set both above and below the critical angle of the active layer film. Measurements above the critical angle

probe the bulk morphology of the CPEC active layer, while those below are sensitive to the near-surface region.

GI-SAXS produces a two-dimensional scattering pattern on the area detector, with the in-plane (q_y) and out-of-plane (q_z) components of the scattering vector encoding structural information about lateral and vertical correlations in the film, respectively. For solution-processed thin films, which are typically uniaxial systems with random in-plane orientation of structural domains, the in-plane scattering reflects the lateral organization of domains parallel to the substrate surface.^{17,18} The slope of the power-law decay in $I(q)$ carries information about the nature of the structural correlations: steeper slopes reflect more compact, well-defined interfaces, while shallower slopes indicate broader, more diffuse density fluctuations over a wider range of length scales. These power-law characteristics are particularly informative for disordered systems such as the CPEC active layers studied in Chapter 3, where sharp diffraction peaks are absent but systematic variation in slope and intensity between conditions encodes genuine information about the mesoscale organization of the film.⁵

GI-SAXS has become an important characterization tool in organic semiconductor thin films for photovoltaic applications, where the nanoscale phase separation between donor and acceptor domains is a critical determinant of device performance.⁵ By probing the mesoscale density correlations in the active layer, GI-SAXS provides information about domain size, phase separation length scale, and the degree of structural reorganization induced by processing conditions. In Chapter 3, GI-SAXS is employed to characterize the morphological consequences of a CPEC

containing active layer for an aOPV device, providing a multiscale picture of the CPE network in a thin film.^{16,18}

1.3.4 Organic Photovoltaic Device Fabrication

Demonstrating photovoltaic function requires more than a well-characterized active layer. An OPV device is a complete multilayer system in which the active layer is sandwiched between two electrodes with carefully matched work functions, one of which must be semitransparent to allow illumination, and the other of which must be deposited on top of the organic material without destroying it. Each interface in this stack presents its own set of materials compatibility and charge extraction requirements, and the overall device performance reflects the combined efficiency of light absorption, exciton dissociation, charge transport, and charge collection at the electrodes.¹⁹ In the context of an aqueous active layer, these requirements introduce challenges that are not encountered in conventional OPV fabrication, and that make the translation from a well-characterized photophysical system to a functional device a non-trivial step.

The anode in OPV devices is typically indium tin oxide (ITO)-coated glass, the standard transparent electrode in organic optoelectronics. ITO is chosen for its combination of optical transparency across the visible spectrum and sufficient electrical conductivity to collect photogenerated holes from the active layer. The specific demands that the CPEC active layer places on the anode interface are discussed in Chapter 3.

The most demanding step in OPV fabrication is the deposition of the metal cathode. Aluminum is the standard cathode material: its work function of approximately 4.1 eV is well-matched to the electron affinity of common acceptors including C60 and non-fullerene acceptors such as ITIC, and it is routinely deposited by physical vapor deposition (PVD) under high vacuum. However, depositing a metal cathode onto an organic active layer by thermal evaporation carries an inherent risk: hot metal atoms impinging on the soft organic film can penetrate into the material rather than simply accumulating on its surface, potentially forming metallic filaments that bridge the anode and cathode and create electrical shorts. This risk is particularly acute for the viscoelastic, gel-like CPEC active layer, whose mechanical properties differ substantially from conventional dried polymer films. This is a challenge taken up in detail in Chapter 3.

Cathode deposition and device characterization were performed at the Molecular Foundry, a U.S. Department of Energy nanoscience user facility at Lawrence Berkeley National Laboratory. Access to the Molecular Foundry was essential for two reasons. First, it provides thermal evaporation systems integrated with nitrogen glovebox environments, allowing samples to be transferred from active layer deposition into the evaporator without exposure to ambient oxygen and moisture, which would degrade both the organic film and the freshly deposited cathode.^{19,20} Second, it provides a calibrated photovoltaic characterization station with an AM 1.5G solar simulator and a quantum efficiency measurement system, which are necessary to extract the standard device figures of merit. These include the short-circuit current

density, open-circuit voltage, fill factor, and power conversion efficiency, all in a manner that is directly comparable to the broader OPV literature.

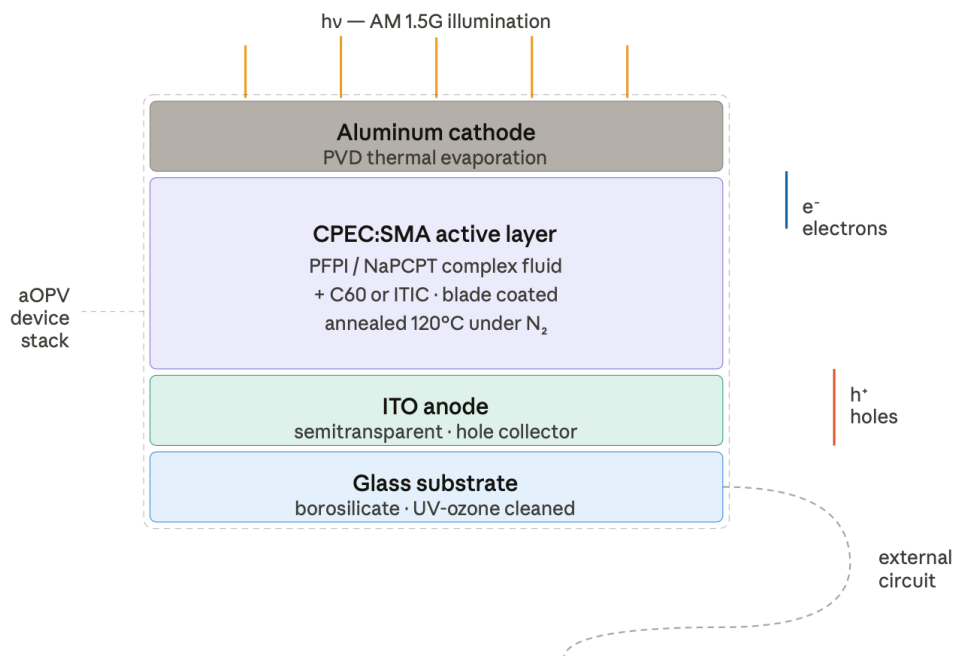


Figure 1.17. Schematic of the aOPV device stack and charge collection geometry under AM 1.5G illumination.

Taken together, the fabrication of a working aOPV device from an entirely aqueous active layer represents the translation of a photophysical proof of concept into a functional device architecture, illustrated in Figure 1.17. The photovoltaic metrics that result from this effort, and their relationship to the morphological and charge-transfer properties of the CPEC active layer characterized by GI-SAXS, Cryo-EM, TRPL, and transient absorption spectroscopy, are the subject of Chapter 3. The goal of the present introduction is simply to establish the conceptual context: that the same

material properties that make the CPEC complex fluid an attractive photophysical system, its aqueous processability, its remarkable charge generation efficiency, and its ability to incorporate small-molecule acceptors via micellar delivery, also define the fabrication constraints and challenges that must be navigated to realize it as a working solar cell.

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1.5 Description of Chapters to Follow

The following chapters progress from the fundamental excitonic behavior of CPECs in dilute solution through their application as the active layer of a fully aqueous-processed organic photovoltaic device, and finally to the CPEC complex fluid as a designable soft material in its own right.

Chapter 2 asks how the chemical structure of the donor CPE backbone governs the rate and efficiency of EET to the acceptor CPE within the complex. It is found that relatively subtle changes in backbone chemistry can produce large changes in EET rate, and that this sensitivity arises primarily through the effect of backbone structure on the exciton delocalization radius. A more delocalized excitonic wave function transfers energy more rapidly, because the larger spatial extent of the exciton increases the excitonic coupling to the acceptor in a manner that the classical Förster framework does not capture. This establishes backbone engineering of the donor CPE as a viable lever for rationally tuning EET rates in CPEC-based light-harvesting materials.

Chapter 3 extends the CPEC system to a functional aqueous organic photovoltaic (aOPV) device. The central question is whether the excited-state population arriving at the NaPCPT acceptor CPE can be converted into separated charge carriers by introducing a small-molecule electron acceptor into the active layer. C60 and ITIC are incorporated via a nonionic surfactant micelle delivery strategy, and their structural consequences are characterized by GI-SAXS and cryo-EM, which reveal that both acceptors nucleate nanoscale crystalline order within the CPEC network, with ITIC inducing substantially greater mesoscale reorganization. Charge transfer is confirmed by magic angle TRPL and ultrafast transient absorption spectroscopy: the NaPCPT excited state is quenched on an instrument-response-limited timescale, and the resulting hole-polaron population outlives the exciton that produced it. The

chapter concludes with photovoltaic characterization of the first aOPV devices fabricated from this system at the Molecular Foundry, LBNL.

Chapter 4 investigates the CPEC complex fluid phase as a functional soft material whose properties can be actively tuned by the temperature at which complexation occurs. It is found that complexation temperature is a powerful handle for modulating the viscoelastic properties of the CPEC phase across a range spanning from a freely flowing liquid to a self-supporting gel, with corresponding changes in the mesoscale microstructure revealed by SAXS. This rheological tunability is shown to be compatible with 3D-printing, opening a pathway to spatially structured, photoactive polyelectrolyte gels fabricated entirely from water. The chapter establishes that the CPEC complex fluid is not simply a passive scaffold for light harvesting, but a soft material whose form is itself designable.

CHAPTER II:

Exciton Transfer Between Extended Electronic States in Conjugated Inter-Polyelectrolyte Complexes

Credit Line:

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Abstract: Artificial light harvesting, a process that involves converting sunlight into chemical potential energy, is considered to be a promising part of the overall solution to address urgent global energy challenges. Conjugated polyelectrolyte complexes (CPECs) are particularly attractive for this purpose due to their extended electronic states, tunable assembly thermodynamics, and sensitivity to their local environment. Importantly, ionically assembled complexes of conjugated polyelectrolytes can act as efficient donor–acceptor pairs for electronic energy transfer (EET). However, to be of

use in material applications, we must understand how modifying the chemical structure of the CPE backbone alters the EET rate beyond spectral overlap considerations. In this report we investigate the dependence of the EET efficiency and rate on the electronic structure and excitonic wave function of the CPE backbone. To do so, we synthesized a series of alternating copolymers where the electronic states are systematically altered by introducing comonomers with electron withdrawing and electron-rich character while keeping the linear ionic charge density nearly fixed. We find evidence that the excitonic coupling may be significantly affected by the exciton delocalization radius, in accordance with analytical models based on the line-dipole approximation and quantum chemistry calculations. Our results imply that care should be taken when selecting CPE components for optimal CPEC EET. These results have implications for using CPECs as key components in water-based light-harvesting materials, either as standalone assemblies or as adsorbates on nanoparticles and thin films.

2.1 Introduction

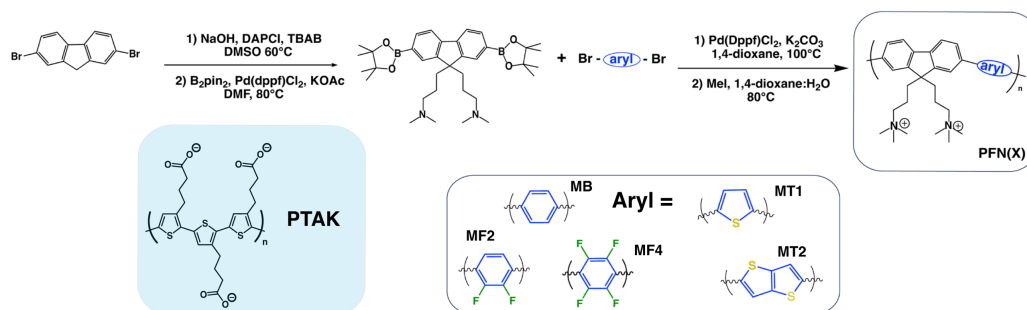
Light-harvesting materials based on polymeric semiconductors have been the subject of research for multiple decades. The overwhelming focus has been on solution-processed organic photovoltaics cast from volatile organic solvents and deposited as thin films.¹⁻³ Yet there is a complementary need to form self-assembled systems capable of eventually converting photon energy into chemical potential energy,⁴⁻⁸ and it would be desirable to do so using environmentally benign aqueous processing. Conjugated polyelectrolytes (CPEs) are attractive for such an application

because, in addition to their highly delocalized electronic states, they can be made to be water-soluble and to have the potential for hierarchical self-assembly given the diversity of their noncovalent interactions.⁹⁻¹⁶

We previously showed that oppositely charged inter-CPE complexes (CPECs) can be electrostatically assembled in water over a broad range of ionic strengths.^{17,18} If the two CPEs comprising the CPEC are judiciously chosen to act as an exciton donor/acceptor pair, they may undergo extremely rapid electronic energy transfer (EET) from the donor to the acceptor. The EET timescale can be commensurate with natural photosynthetic pigments.¹⁸ Since EET is critical to all high-performance light-harvesting systems,¹⁹⁻²¹ CPECs can be attractive artificial light-harvesting antennae in overarching, aqueous light-harvesting systems.

Although we previously demonstrated that EET between a model donor and acceptor CPE within a CPEC could be ultrafast,¹⁸ it remains unclear how the EET timescale responds to changes in the chemical structures of the complexed CPEs. In particular, depending on the desired material, it may be necessary to tune the electronic bandgap or the emission spectrum to harvest a particular wavelength range. Doing so requires modifying the backbone chemical structure, which may significantly affect the CPEC excitonic coupling. That is, tuning the backbone chemistry inevitably modifies the excitonic wavefunction and thus the excitonic coupling that determines the EET rate.

To evaluate how the EET rate responds to changes in chemical structure, one often uses the celebrated Förster model.^{22,23} Within this model, changes in chemical structure are encoded in the emission spectrum of the isolated exciton donor and the absorption spectrum of the isolated exciton acceptor. The key assumption implicit to this model is that the separation between the donor and the acceptor is significantly larger than the spatial extent of their excitonic wavefunctions. But within a CPEC, it is often the case that the separation between donor and acceptor chains is comparable to or smaller than the exciton delocalization radius, or mean chromophore length.^{24,25} In such a case, the Förster model may break down, making it challenging to determine how changes in backbone chemical structure will influence the EET rate. This knowledge gap limits the application of these materials as energy transfer antennae.



Scheme 1. Synthetic scheme for the PFNX polymer series. Once synthesized, monomer FNB is then coupled to one of the aryl co-monomers shown via Suzuki cross-coupling to produce the neutral precursor polymers. The final CPE series is obtained by reacting all neutral polymers with methyl iodide.

In this report, we interrogate the dependence of EET within a CPEC on the chemical structure of the CPEs. To do so, we fixed the anionic acceptor CPE and synthesized a series of cationic, alternating co-polymer donor CPEs with identical ionic monomers but differing in subtle modifications of the second co-monomer. Variation of the second monomer while keeping the linear charge density nearly fixed allows us to manipulate the excitonic wavefunction on the donor without significantly changing the thermodynamics of electrostatic self-assembly. We then used a combination of steady-state and ultrafast optical probes to characterize the relative EET efficiencies and rates. We find that relatively subtle changes in the chemical structure of one monomer can lead to large differences in EET. We argue that the primary influence of the second nonionic monomer on the donor CPE is to alter the exciton delocalization radius, in turn influencing the exciton transfer integral. This work provides a clear demonstration that manipulating EET between proximal conjugated polymer chains requires considerations that go well beyond the spectral overlap. Our results have direct implications for the choice of CPEC constituents in water-based light-harvesting materials.

2.2 Results

In this work, we focus on oppositely charged CPECs composed of variable cationic CPEs, which act as exciton donors, and a common anionic exciton-acceptor CPE. The synthesized exciton-donor CPE set is composed of a series of alternating copolymers, abbreviated PFNX, containing chemically identical charged fluorene

monomers but differing in the chemical structure of the co-monomer. Here X refers to the variable monomer in the alternating copolymer series. The chemical structures of all CPEs are shown in Scheme 1.

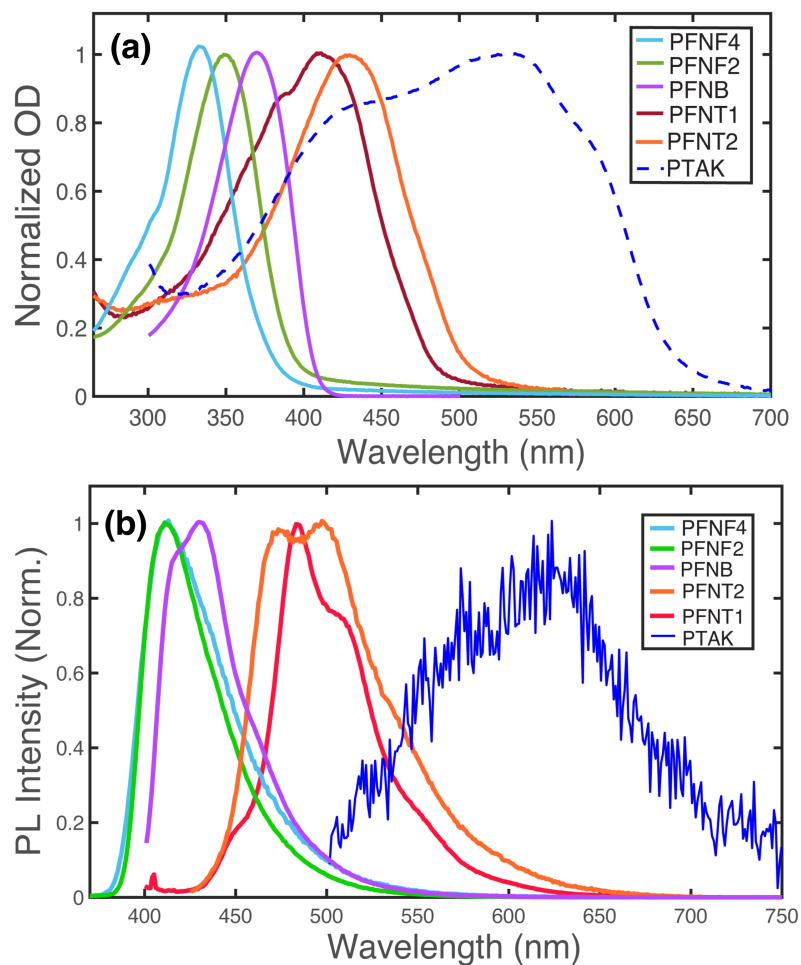


Figure 1. Optical properties of isolated donor and acceptor CPEs. a) Normalized absorption (OD) spectra. b) Normalized PL spectra. The progression in peak OD wavelength illustrates the systematic variation in the bandgap and thus the electronic states comprising the low-lying exciton transition.

The specific variable monomer choice was motivated by the following. (1) We desired to systematically vary the electronic wavefunction along the donor backbone in a tractable manner while ensuring that there would be spectral overlap with the fixed exciton acceptor. (2) We aimed to keep the donor counterion identity and linear ionic charge density along the donor contour very similar across the series. Doing so helps ensure that the electrostatic free energy of inter-polyelectrolyte complexation, which includes both the inter-polyelectrolyte binding energy and the change in entropy upon counterion release, are similar across the series. The linear charge densities of the donor CPEs are (in units of $e/\text{\AA}$) 0.34, 0.34, 0.34, 0.36, and 0.28 for PFNF4, PFNF2, PFNB, PFNT1, and PFNT2, respectively.

The common acceptor CPE, PTAK, is a regioregular polythiophene derivative with butylcarboxylate sidechains. The choice of PTAK as the anionic acceptor CPE was partially motivated by the fact that its homo-polythiophene backbone is relatively simple compared to other reasonable anionic CPEs that could function as exciton acceptors. Additionally, the PTAK PL quantum yield (PLQY), while low in isolation due to its collapsed coil structure, becomes substantially higher upon complexation to the donor due to the extension of the PTAK backbone.^{18,34}

We believe that at relatively early times after being formed (of order few days), the complexes are to a good approximation largely composed of at most a few oppositely charged chains. This is consistent with the lack of significant light scattering from CPEC solutions shortly after complexation. The scattered light intensity from fresh CPEC solutions was evaluated by measuring the sample turbidity.

Here turbidity is defined as the negative logarithm of the ratio of the transmitted to the incident light intensity at a nonabsorptive wavelength, which was 800 nm in this work. We find that turbidity in fresh CPEC solutions is negligible: The scattered light intensity increases monotonically with decreasing wavelength, and the CPEC absorption spectrum is effectively seen to decay to zero by 650 nm (*vide infra*). Furthermore, we expect the thermodynamic driving force for CPEC formation across the CPE series to be dominated by electrostatic sidechain interactions and the increase in solution entropy due to counterion release upon complexation. Because of these factors, we believe that the average number of chains per complex is similar and likely near two. Thus, care was taken to ensure that all measurements were performed relatively shortly after preparing CPEC solutions.

Below we first interrogate the relative EET efficiencies by analyzing photoluminescence (PL) excitation spectra of the complexes. We then measure the ultrafast EET dynamics using pump/probe spectroscopy. Finally, we characterize potential differences in CPEC structure using both structural and optical probes.

Steady-State Photophysics.

Figure 1a shows the peak-normalized ground-state absorption spectra (or optical density, OD) of both the native anionic acceptor CPE, PTAK, and the isolated cationic donor CPE series, PFNX, in dilute, salt-free aqueous solution. By keeping the ionic fluorene monomer fixed and varying the other monomer, we aimed to systematically alter the electronic states and thus the bandgap along the polymer

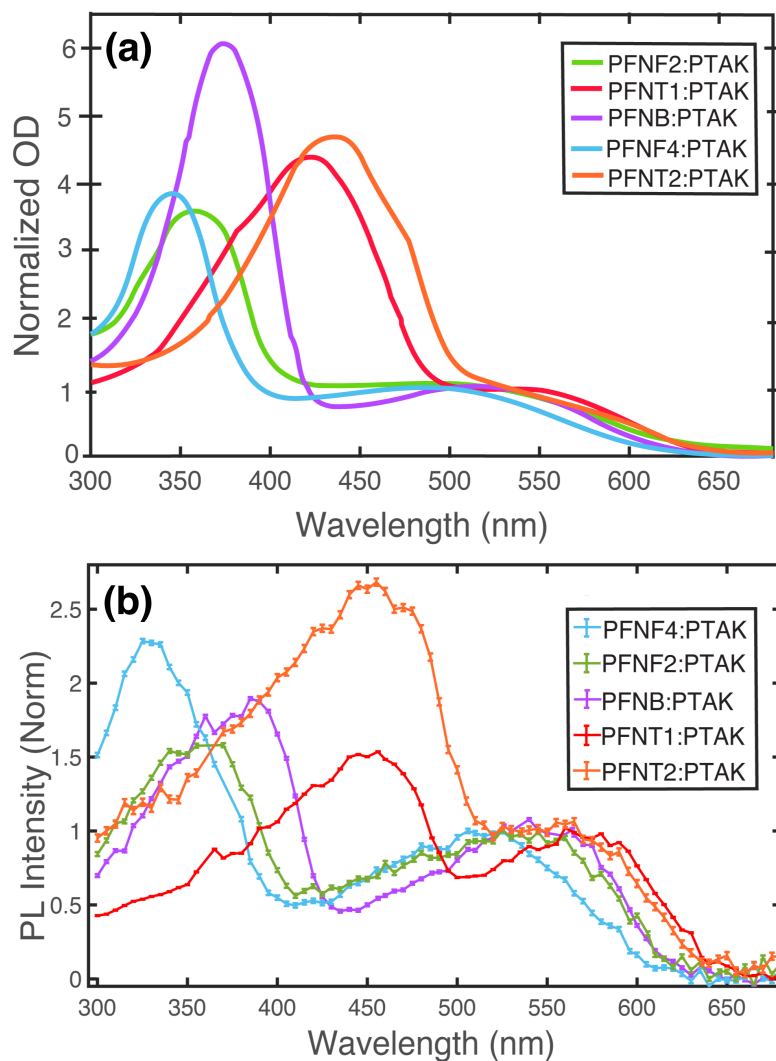


Figure 2. Optical spectroscopy of CPECs. a) OD spectra normalized to the PTAK absorption band on the red side. b) PLE spectra collected at a fixed emission wavelength on the red side of the PTAK PL spectrum. Spectra have been normalized on the red side, exclusively corresponding to direct PTAK excitation. The specific choice of the fixed wavelength was made to ensure a vanishing probability that donor PL would be detected. The shape of the PLE spectra provide unambiguous evidence of EET. The contribution on the blue side due to EET from the donor can be isolated and used to quantify a relative EET efficiency.

series without inducing significant changes in the ionic linear charge density of the CPEs. The progression in bandgap is clearly demonstrated in the shift in λ_{max} among the donor CPEs. It is convenient to partition the PFNX donor series into two sub-families: (i) the poly(fluorene-*alt*-phenylene) family, with increasing fluorine content on the phenyl monomer (PFNB, PFNF2, PFNF4), and (ii) the thiophene family containing poly(fluorene-*alt*-thiophene) (PFNT1) and poly(fluorene-*alt*-thienothiophene) (PFNT2). In what follows, we will refer to the polymers by their shorthand X monomer abbreviation.

The phenyl sub-family CPEs exhibit absorption spectra that are quite similar, only differing in a slight blueshift of approximately 20 nm between the polymers: λ_{max} for B, F2, and F4 was 375, 348, and 332 nm, respectively. This corresponds to a slight increase in bandgap as a function of increasing fluorine substitution. The λ_{max} for the two CPEs in the thiophene sub-family are shifted by ~30 nm corresponding to 405 nm and 435 nm for T1 and T2, respectively. The change in bandgap reflects both a change in the electronic structure of the variable monomer and any differences in the torsional potential. The latter can influence the delocalization radius of the exciton and thus the splitting between frontier orbital energy levels.³⁵ Figure 1b shows normalized PL spectra of the exciton donor series and the common exciton acceptor in isolated aqueous solution. Interestingly, although the OD peaks for fluorinated polymers are blueshifted with respect to B, the F2 and F4 peaks are effectively on top of each other. The T1 and T2 emission bands also encompass a comparable wavelength range albeit with substantially different apparent vibronic structure. All

donor emission bands have spectral overlap with the PTAK absorption spectrum, which we quantify below. The native PTAK PL spectrum lies to the red of the donor polymers as expected. The large noise level given the comparable solution concentration reflects the fact that the native conformation of regioregular PTAK chains is highly coiled, leading to a very low PLQY.³⁴

Having characterized the OD and PL spectra of isolated CPE solutions, we went on to form CPECs. This was done by combining the polymers at the fixed molar polycation: polyanion charge ratios of 70:30, respectively, as described in more detail in the Experimental section. Thus, in all cases the donor polymer was in molar excess. This choice was made for the following reasons: (i) In our previous work, we showed that this CPEC ratio produced extended PTAK chains within the complex with a PLQY that increased substantially compared to isolated PTAK solution. (ii) Having the acceptor CPE be the limiting component minimizes the probability that any PTAK chains remain uncomplexed. This in turn allowed us to use PL excitation spectroscopy to compare relative EET efficiencies (*vide infra*) by monitoring PTAK PL signal. Figure 2a shows OD spectra of CPECs prepared with all the donor CPEs and the common acceptor CPE. The spectra show the characteristic peak for each of the donor and acceptor components of the CPEC. The absorption bands spanning the 300 nm to 550 nm range correspond to the PFNX donors, while the broader peak centered about 525 nm corresponds to PTAK.

We then went on to characterize the steady-state EET efficiency, E , within the CPEC across the donor CPE series. The common way of calculating E from steady-

state measurements is to calculate the ratio of the difference in PL intensity of the donor when it is isolated vs. in the presence of acceptor relative to the donor PL signal in isolation.³⁶ We believe this method may lead to inaccuracies for CPECs because it relies on assuming that the PLQY of the donor is unchanged when it is electrostatically bound to the acceptor. In the CPEC this is likely a severe assumption, as complex formation may lead to differences in the ensemble of thermally accessible conformations of the donor polymer and thus its PLQY. Our previous measurements support this concern.¹⁸ Instead, it is desirable to extract E directly from spectra of the complex without the need to compare these to control donor-only measurements.

To bypass the need to rely on such an assumption, we turned to PL excitation (PLE) spectroscopy. In this measurement, we fixed the emission wavelength on the red side (715 nm) of the PTAK PL spectrum to ensure that this wavelength was significantly redshifted relative to the tail of all the donor PL spectra. The acceptor PL intensity was then measured as a function of excitation wavelength λ_{ex} across the CPEC OD spectrum from 300 nm to 700 nm, encompassing both the donor and acceptor absorption windows. The choice to limit the lower integration bound to 300 nm was made largely to avoid the region where the $S_0 \rightarrow S_2$ absorption band of PTAK, T1, and T2 begins to acquire substantial amplitude.

PLE spectra for all PFNX:PTAK CPECs are shown in Figure 2b. It is clear that the PLE spectrum qualitatively resembles the corresponding OD spectrum of the CPEC for all donor CPEs. Since only PTAK emission is monitored in this experiment, it is expected that the PLE spectrum on the red side will reflect the OD

spectrum of PTAK. The fact that the PLE spectrum clearly traces out the donor OD spectrum on the blue side is unambiguous evidence of EET from the exciton donor to the exciton acceptor. To compare E across the donor series, we first normalized the PLE spectra to the intensity in the acceptor-only region, *i.e.* in the region to the red of ~ 525 nm, and then attempted to isolate the donor contribution to the PLE, I_D^{PLE} . This procedure provides not an absolute but a relative EET efficiency, E^{rel} , which can be defined as

$$E^{rel} \equiv \int I_D^{PLE}(\lambda_{ex}) d\lambda_{ex} \quad (1.45)$$

where the limits of integration encompass the 300 – 700 nm range. Nevertheless, this approach would allow us to elucidate how varying monomer X while keeping the rest of the donor CPE chemical structure fixed influences E .

Estimating E^{rel} from PLE spectra requires some care. This is because calculating I_D^{PLE} necessitates subtracting the contribution to the PLE that comes from native PTAK PL within the complex. That is, there is nonzero PTAK absorption at excitation wavelengths where the donors primarily absorb, giving rise to a PTAK PLE background due to direct excitation of PTAK. The PLE signal due to direct PTAK excitation must then be subtracted off, but this presents a complication: On the blue side of the PLE spectrum we do not know the precise functional form of the acceptor PL signal due to direct acceptor excitation, $I_A^{PLE}(\lambda_{ex})$. Our approach was to estimate the wavelength dependence of I_A^{PLE} in the blue by using the Gaussian fit parameters of an isolated PTAK OD spectrum as an initial guess for a constrained fit of the red

side of the PLE spectra. The PLE fitting range was bounded from below by the excitation wavelength above which the donor contribution went to zero. The detailed procedure used to estimate I_A^{PLE} is provided in Section S2 of the Supporting Information.

The PLE fits together with the isolated PTAK OD spectrum are shown in 16-S15 of the Supporting Information. It is clear that the red side of the PLE spectrum is fit very well for all CPECs. Subtracting the PLE fit from the measured PLE spectrum gives us the contribution to PTAK PL that comes from exciting the donor CPEs, $I_D^{PLE}(\lambda_{ex})$, *i.e.* the contribution due to EET. Despite the fact that the fits on the red side of the spectrum are of a good quality, there is intrinsically an error associated with inferring $I_A^{PLE}(\lambda_{ex})$ in the donor region, which will give rise to an error associated with estimating the donor contribution and thus an error in E^{rel} . To get a rough estimate for this error, we subtracted the $I_A^{PLE}(\lambda_{ex})$ fit from the PTAK OD spectrum (both normalized to the PTAK peak on the red side) to form a difference curve, the magnitude of which at every wavelength we associate with the standard deviation of $I_D^{PLE}(\lambda_{ex})$. Section S2 of the Supporting Information describes our rationale and justification for this means of estimating the error and the background intensity on top of which $I_D^{PLE}(\lambda_{ex})$ sits. We note that setting the lower limit on the integral in $I_D^{PLE}(\lambda_{ex})$ to 300 nm will almost certainly preferentially *underestimate* this quantity for F4 and F2. Nevertheless, we believe this is the appropriate conservative choice if one wants to systematically avoid having to account for potential EET between higher-energy excitonic states.

To obtain insight into the ordering of E^{rel} across the donor series, it is desirable to compare it to the ordering predicted by the celebrated Förster EET model. The model assumes that the average distance between the donor and the acceptor is large compared to the spatial extent of the excitonic wavefunctions. The excitonic coupling is then assumed to be described by a dipole-dipole interaction between the point transition dipole moments of the donor and the acceptor. A natural length scale characterizing E called the Förster radius R_0 emerges; at this distance the Förster EET rate and the radiative relaxation rate are equal.³⁷ R_0 is determined by

$$R_0^6 = 0.02108 \kappa^2 \Phi_D n^{-4} J \quad (1.46)$$

Here, R_0 is in nm, κ^2 is the transition dipole orientation factor, Φ_D is the PLQY of the donor, n is the refractive index of the medium taken to be that of pure water, and J is the spectral overall integral given by

$$J = \int I_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (1.47)$$

where I_D is the PL spectrum of the isolated exciton donor normalized to unit area, ε_A is the extinction coefficient spectrum of the isolated acceptor in units of $M^{-1}cm^{-1}$, and λ is in nm.

The transition dipole orientation factor κ^2 ranges from 0 to 4, where a value of 1 corresponds to parallel transition dipoles, $2/3$ represents a random orientation, and 4 is a consequence of dipoles that are both parallel and collinear.³⁸ In this work we set

κ^2 to 1 for all Förster model calculations. We believe this is the least biased choice as it is expected that the donor and acceptor CPEs assemble in approximately parallel. Such local complex structures are consistent with structures obtained to calculate mean separations between donor and acceptor CPE backbones (Figure I18).

The Förster EET efficiency E^F is related to the Förster radius via

$$E^F = \frac{1}{1 + \left(\frac{R}{R_0}\right)^6} \quad (1.48)$$

where R is separation between the donor and the acceptor. To estimate R , we found the center-to-center distance between the backbones by using semiempirical quantum mechanical calculations. Results from these calculations are shown in Table S2 of the Supporting Information. The calculated values of E^F and the estimated values of E^{rel} are shown in Table 1. We see that the ordering of E^{rel} does not follow that of E^F .

For incoherent exciton transfer described by the Fermi Golden Rule, the EET rate scales as the product of the square of the excitonic coupling, V_{EX} , and a factor that ensures energy conservation between initial and final states participating in the EET process. To a first approximation, the latter is proportional to J , which tracks the position of the donor emission spectrum relative to that of the acceptor OD. Arguably the more interesting quantity is $V_{EX} = \langle \Psi_D \Psi_A^* | \hat{V} | \Psi_D^* \Psi_A \rangle$. Here Ψ_D is the wavefunction of the donor, Ψ_A is that of the acceptor, $\hat{V}$ is the operator that describes the electronic coupling between the donor and the acceptor, and $*$ indicates an excited state. It is V_{EX} that will reflect the precise excitonic wavefunctions of the donor and the acceptor

and thus will encode the dependence of the delocalized electronic states on monomer X. It is instructive to divide out J to form a normalized (relative) EET efficiency $E^{norm} = E^{rel}/J$, the quantity most directly related to (the square of) V_{EX} . Doing so implicitly assumes that the donor exciton population undergoes rapid relaxation within its density of states before EET takes place, since J is based on the steady-state PL spectrum of the donor. Interestingly, although E^{rel} is largest for T2, we find that E^{norm} (Table 1) is largest for F4.

Table 1. Measured and calculated quantities used to compute relative EET efficiencies and predictions from the Förster model.

CPE	PLQY (%)	Spectral Overlap Integral (J) ($\times 10^{12}$)	Förster Radius (R_0) (Å)	Donor-Acceptor Distance (R) (Å)	FRET Efficiency (E) (%)	E^{rel}	E^{norm} ($\times 10^{-11}$)
PFNF4	43	2.29	17.3	13.0	84.7	142 ± 7	6.18
PFNF2	44	2.53	17.7	12.7	87.9	99 ± 11	3.91
PFNB	41	2.93	17.9	13.2	86.1	139 ± 14	4.27
PFNT1	69	4.81	21.2	13.7	93.2	132 ± 19	2.74
PFNT2	67	5.60	21.6	13.1	94.7	218 ± 22	3.89

2.2.2 Ultrafast Energy Transfer Dynamics

Having characterized the relative EET efficiency via steady-state measurements, we directly investigated the timescale over which EET occurred

across the donor series. In our previous work, we showed that excitons were transferred from the donor PFNB to the acceptor PTAK in approximately 240 fs.⁴ Since we previously characterized EET dynamics in the PFNB:PTAK CPEC, below we focus on complexes involving the remaining members of the donor CPE set.

Figures 3a-d present transient absorption spectra measured at various pump-probe delays with the dilute aqueous solutions of the donor CPEs (isolated/no acceptors present). The color gradient scale to the right of each panel maps to the pump-probe time delay in ps. (A corresponding false-color contour representation of these data are presented in Figure I20.) The uncomplexed polymers were excited near their absorption maxima: 360 nm for the phenyl sub-family (F2 and F4), and 400 nm for the thiophene sub-family (T1 and T2). All pump-probe spectra are comprised of primarily two features in the wavelength range probed (450-750 nm): (1) negative signal arising from stimulated emission of the excited donor, which has a spectral profile that approximately matches the steady-state PL spectrum of each donor; and (2) positive signal due to excited-state transient absorption (TA) from the low-lying exciton state S_1 to higher-lying states S_n . For T1 and T2, the stimulated emission signal is likely to be overlapped partially with ground-state bleach (GSB), which lies to the blue of the emission signal. For F2 and F4, only the very red tail of the stimulated emission is observed in the spectral range probed. The time-dependent spectral evolution for the donor CPEs following photoexcitation appears to be qualitatively similar, involving a decay of excited donor absorption and stimulated emission over 10s-100s of picoseconds.

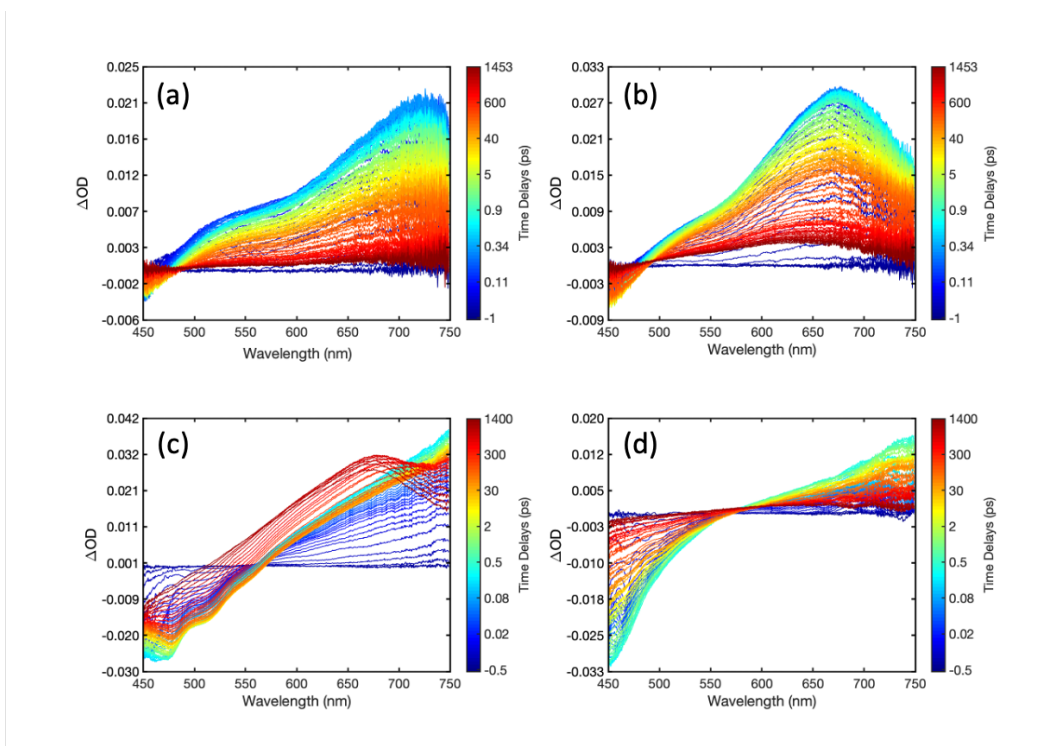


Figure 3. Transient absorption spectra obtained with uncomplexed (isolated) donor CPEs: (a) F4, (b) F2, (c) T1, (d) T2. Spectra were collected following excitation near the peak of the steady-state absorption spectrum of each donor (360 nm for F4 and F2; 400 nm for T1 and T2). Spectral dynamics are explained in the text. The same data is presented as false-color contour plots in Figure I19.

However, the spectral evolution of PFNT1 appears to be qualitatively different from the rest of the polymers, with a rise in excited-state absorption signal in the region of ~650-700 nm and a distinct blueshift of the absorption maximum with a corresponding reduction in the stimulated emission (450-650 nm). This spectral evolution is characteristic of intersystem crossing (ISC) from singlet to triplet excitons. We expect that the yield for ISC will be greater for thiophene-containing conjugated polymers compared to the phenyl sub-family because of an increased

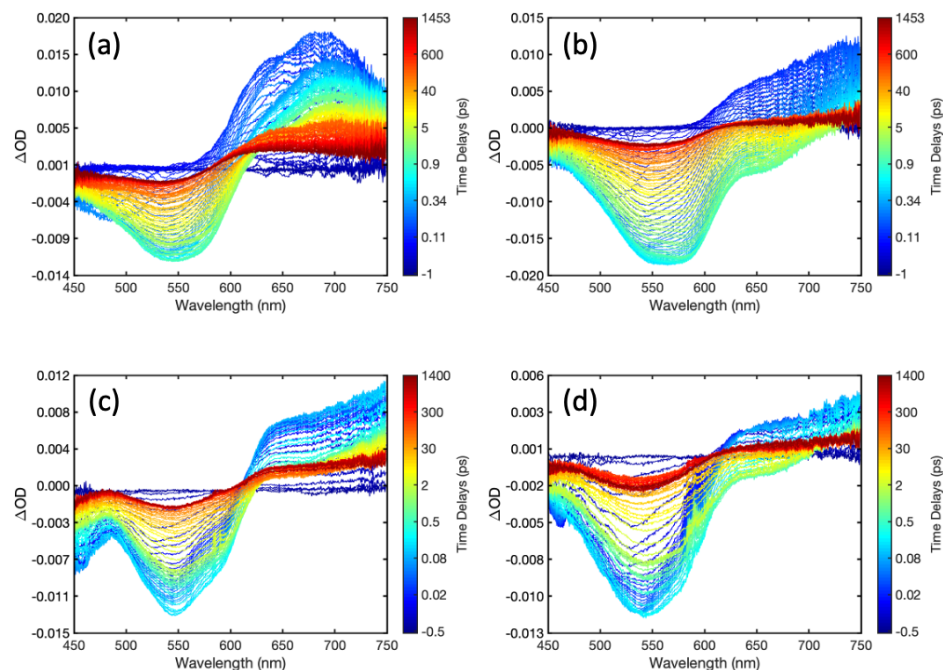


Figure 4. Transient absorption spectra obtained with PFNX:PTAK CPECs (70:30 ratio): (a) F4, (b) F2, (c) T1, (d) T2. Spectra were collected following excitation near the peak of the steady-state absorption spectrum of each donor (360 nm for F4 and F2; 400 nm for T1 and T2). Spectral dynamics are explained in the text. The same data is presented as false-color contour plots in Figure I21.

spin-orbit coupling due to the presence of relatively heavy sulfur atoms. Coupling to the triplet manifold is likely promoted by intra-ring nuclear motions of the thiophene monomer. Close inspection of transient spectra for the other donor CPEs 1 ns after excitation, which reveals a weak and somewhat blue-shifted absorption relative to that of the initially populated singlet excited state, suggests that ISC may take place in all donor CPEs, but with ISC quantum yields that are less significant than excited T1.

We hypothesize that the rigidity of the fused bithiophene ring in T2 reduces vibrationally enhanced coupling, thereby lowering the ISC rate relative to T1.

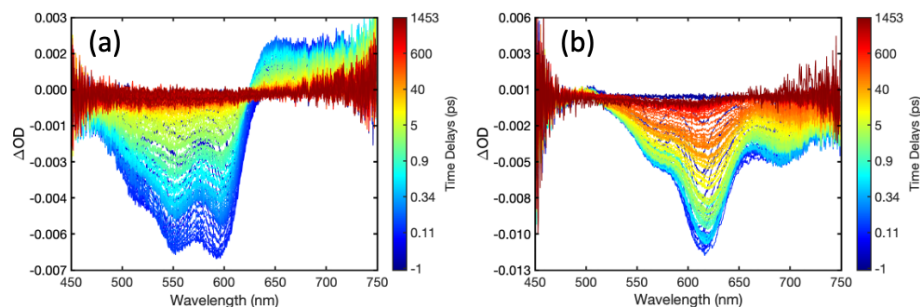


Figure 5. Transient absorption spectra obtained for isolated PTAK (a) and a representative CPEC (PFNT1:PTAK) (b) excited at 600 nm, which exclusively excited PTAK. Spectral dynamics are explained in the text. Data for all CPECs excited at 600 nm are presented in Figure I22.

Figures 4a-d presents pump-probe spectra obtained with the PFNX:PTAK CPECs, which were collected under identical conditions as those used with solutions of uncomplexed donor CPE. (A false-color contour representation of this data is presented in Figures S20 and S21.) In addition to the donor features seen in Figures 3a-d, there are additional contributions from PTAK GSB and stimulated emission spanning from below 500 nm to above 650 nm that appear rapidly after photoexcitation (*vide infra*).⁹ We cannot discount the possibility that the appearance of PTAK features in transient spectra may arise from both EET from the donor CPE

and direct excitation of PTAK chromophores within complexes given that the ground-state absorption of the uncomplexed acceptor extends down to 360 nm.

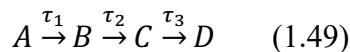
However, the donor absorption dominates the absorption spectrum of CPECs with F2/F4 and T1/T2 at 360 nm or 400 nm, respectively, such that we expect that the rapid appearance of these significant features arises predominantly from EET. To assess whether the observed spectral dynamics reflect EET, we examined the signal time dependence at wavelengths that correspond to TA features associated with the donor CPEs. When compared to the TA spectra of uncomplexed donors, we find a pronounced, rapid decrease in transient signals attributable to the excited donor in multiple spectral regions immediately following excitation. The clearest differences are observed in the blue at ~450 nm, a region that contains contributions from stimulated emission from donor CPEs, as well as in the 600-750 nm range, the region of donor TA (Figure 3) and where signal due to directly excited PTAK is minimal (c.f. Figure 5 below).⁹ Most notably, for T1 and T2 CPECs, there are rises at 450 nm which correspond to a rapid (sub-ps) reduction in the donor stimulated emission. The spectral dynamics that occur at 650-700 nm likewise reflect a sub-ps drop in the donor TA. The dynamics in this spectral region are particularly notable for F2 and T2: For these complexes, we observe an ultrafast flip from positive to negative signals, consistent with an interconversion from excited donor CPEs (absorption) to excited PTAK (stimulated emission). Given that all four complexes were prepared at exactly the same donor:acceptor ratios, the fact that such an ultrafast flip from positive to negative signal is not observed for F4 and T1 complexes likely indicates

that there are chain regions for these donors that are not fully complexed to the acceptor. Charged donor sidechains in such regions likely have partially condensed counterions as described by the Manning-Oosawa model.³⁹ The acceptor's stimulated emission subsequently disappears as a result of PTAK exciton dynamics – we speculate that there may be some PTAK to-PFNB electron transfer, similar to what has been observed for PFNB previously, based on the relative energies of donor and acceptor frontier orbitals.^{40,41}

In order to examine spectral contributions from directly excited PTAK, we also studied the photophysics of CPECs excited directly at 600 nm, which selectively excites the PTAK component, and compared these to the photophysics of uncomplexed PTAK. Transient absorption data for PTAK and the PFNT1:PTAK complex are presented in Figure 5. (TA data for all complexes excited at 600 nm are presented in Figure I22.) As described previously, the spectrum of uncomplexed PTAK exhibits signatures of both H-like excitons and “free coil” states; excitation at 600 nm is selective for the former and gives rise to the characteristic polaron-pair absorption feature at 650 nm that is associated with charge separation in π -stacked polymer regions.¹⁸ In contrast, polaron-pair absorption is not observed for PTAK in a CPEC when excited at 600 nm; rather, the region of 650-700 nm is dominated by stimulated emission. This difference and the change in the vibronic structure of the PTAK bleach with complexation reflect an isolation of PTAK chain segments, as discussed in more detail below. The stimulated emission observed with 600-nm excitation matches the feature observed within a few hundred femtoseconds following

donor excitation (F2 and T2). Notably, the polaron-pair absorption feature observed for uncomplexed PTAK (650-700 nm) has a much slower spectral evolution (decay) than the ultrafast spectral evolution observed in this region for all CPECs, supporting assignment of the latter to PFNX-to-PTAK EET.

We used global spectral analysis subject to sequential kinetic interconversion models to determine timescales on which spectral dynamics occur for all donor CPEs and PFNX:PTAK CPECs. We found the best fitting agreement was obtained using a four-state sequential kinetic model, as expressed in Equation 5, producing sensible species associated difference spectra (SADS) that reflect the composition of excited species that give rise to TA signals for both donor CPEs and CPECs.



SADS obtained from analysis of CPEC TA spectra are presented in Figure 6, with fitted transients at selected wavelengths presented in Figure I24. SADS obtained from global analysis of TA data obtained with uncomplexed donors and corresponding fitted transients at select wavelengths are presented in Figures S24 and S25. Lifetimes corresponding with each SADS are presented in Table S3 and S4 for complexes and donor CPEs, respectively.

For F2 and F4, the SADS capture the spectral evolution expected for donor-acceptor EET: In both cases, SADS A is dominated by the singlet excited-state absorption of the donor in the red (> 550 nm) and stimulated emission below 500 nm; in both cases SADS A crosses ‘0’ at a wavelength similar to that observed in the

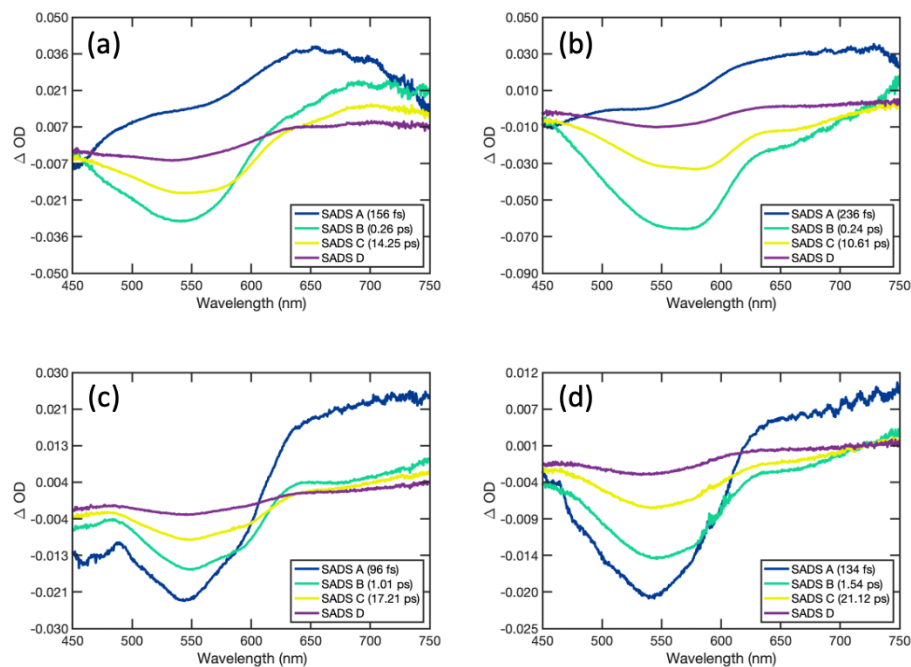


Figure 6. Species Associated Difference Spectra (SADS) obtained from global analysis of transient absorption spectra collected with PFNX:PTAK CPECs using the four-state kinetic interconversion model expressed by Equation 5. (a) F4, (b) F2, (c) T1, (d) T2. Lifetimes corresponding with each SADS are listed in Table S4.

donor CPE TA data. In contrast, SADS B is dominated by the PTAK bleach (475-625 nm). SADS B for F2 exhibits the PTAK stimulated emission (625-700 nm) observed via direct excitation of PTAK in CPECs (Figure 5). In contrast, the absorption that remains in this region for F4 most likely reflects uncomplexed regions of the donor in the corresponding solution. The transition from SADS B to C reflects spectral dynamics of PTAK excited by EET and, for F4, contributions from spectral dynamics of uncomplexed regions of the donor. The differences in the PTAK bleach intensities

in SADS B, C and D reflects fractions of PTAK excitons that deactivate on associated kinetic lifetimes summarized in Table S3. We previously demonstrated that charge separation is a viable quenching mechanism in PFNB:PTAK complexes probed in ultrafast experiments and is a likely origin of the long-lived bleach observed in these measurements.^{7,10}

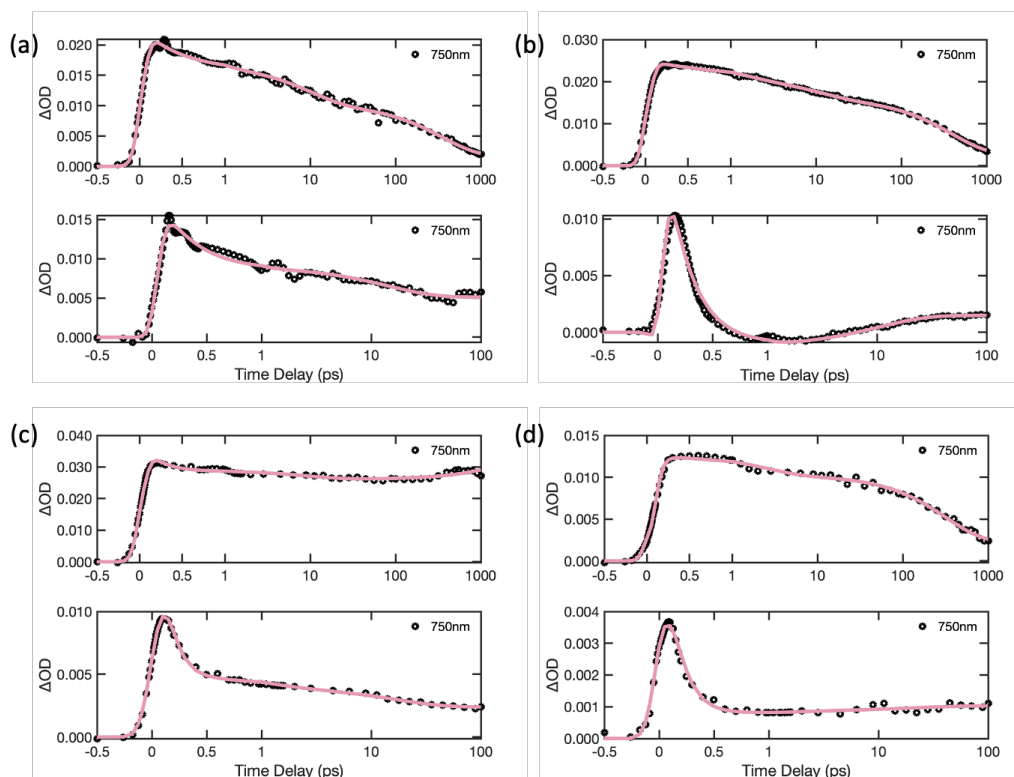


Figure 7. Comparison of transients obtained with donor CPEs and PFNB:PTAK CPECs by probing at 740 nm, within the region of photoinduced (transient) absorption of the donor: (a) F4, (b) F2, (c) T1 and (d) T2. Transients at more wavelengths for both donors and CPECs can be found in Figures S24 and S26.

The SADS obtained for T1 and T2 are somewhat different. In both cases, the PTAK bleach features dominantly in SADS A; this is consistent with either some direct excitation of the acceptor or very rapid (faster than our time resolution) EET from the donor. The former is plausible, given that the excitation wavelength used for these complexes, although close to the peak of the donor absorption feature, is also closer to that of PTAK. The latter is feasible, given the predicted rate of energy transfer (*e.g.*, Table 2 below). Nonetheless, a rapid decay of TA (> 600 nm) and stimulated emission (< 500 nm) signatures associated with the donor occurs on a timescale of less than 200 fs. The evolution of SADS B, C and D are largely similar across all complexes regardless of the donor, indicating that the associated spectral dynamics are largely attributed to excited PTAK.

Figure 7 compares the measured time-dependence for donor CPEs and PFNX:PTAK complexes at a probe wavelength of 740 nm together with fits generated from global spectral analysis. These comparisons highlight the dramatic differences in excited donor CPE lifetimes upon complexation with PTAK that is consistent with rapid inter-CPE EET. Overall, the fits are of excellent quality, which allows us to extract quantitatively the EET time scales across the donor series. The EET rates (inverse EET times) from global analysis (t_1 from Equation 5, values listed in Table S5) are shown in Table 2 along with EET rates calculated from the Förster model according to

$$k_F = \frac{1}{\tau_D} \left(\frac{R_0}{R} \right)^6 \quad (1.50)$$

where τ_D is the average radiative lifetime of the isolated donor. We note that the PL lifetime at room temperature was used for τ_D , which is a lower bound given the presence of nonradiative relaxation pathways, and κ^2 was taken to be unity for all CPECs. From global analysis we find that the shortest times (largest rates) are associated with T1 and T2 CPECs, followed by F4, F2 and B CPECs. We see that, although the overall trend predicted by the Forster model is observed experimentally for F2, T1, and T2, it is clear that F4 stands out: its rate is comparable to T2 despite the large difference in spectral overlap. Despite some trend agreement between the model and experiment, there is also an apparent disparity between the ratios of the rates. For example, under the assumption of a similar κ^2 , the ratio of k_F for T2 relative to F4 is ~ 3.0 , while the measured k_{EET} ratio is ~ 1.2 . Similarly, the predicted F2 to F4 k_F rate ratio is ~ 1.3 , while the measured k_{EET} ratio is ~ 0.7 .

Table 2. Measured EET rates from global analysis along with estimations using the Förster model.

	PFNF4	PFNF2	PFNT1	PFNT2
EET rate (ps ⁻¹)				
(1/ τ_{EET})	6.41	4.24	10.4	7.46
Förster ET Rate				
(ps ⁻¹)	0.03	0.05	0.06	0.10

2.2.3 Role of CPEC Conformation

Since all donor CPE have similar ionic charge densities, it is tempting to assume that the CPEC conformation would be similar across the donor series. To determine whether this assumption is safe, we interrogated the CPEC conformation across the series using both structural and spectroscopic probes. Since CPECs are not expected to display long-range order, one of the more direct means of comparing the CPEC structure is to do so in reciprocal space by performing small-angle X-ray scattering (SAXS) measurements. We collected SAXS scattering images using a synchrotron X-ray source, and the isotropic SAXS intensity was then azimuthally averaged to produce reduced 1-D scattering intensity curves as a function of scattering vector length Q . These results for all CPECs are shown in Figure 8.

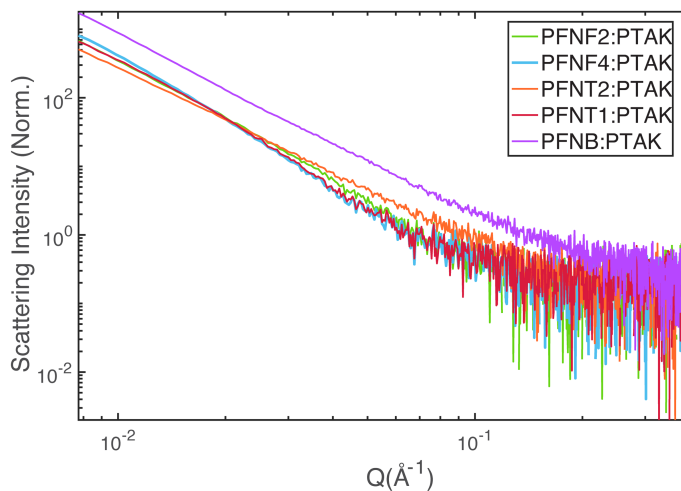


Figure 8. Azimuthally averaged small-angle X-ray scattering intensities as a function of the scattering vector length Q for all CPECs. All samples show monotonically decreasing intensities with no visible Guinier plateau regions.

The scattering intensity for all CPECs is monotonically decreasing, rather featureless, and reasonably similar in appearance. This suggests that, coarsely, the complexes have similar microstructure. At low Q , the approximately linear slopes on a log-log plot suggest a Q scaling with a comparable negative power-law exponent. However, closer inspection makes apparent the subtle differences between the curves. In particular, there appears to be an intermediate Q value ($\sim 0.02 \text{ \AA}^{-1}$) at which the slope of the scattering intensity for the F2, F4, and T1 complexes undergoes a small decrease, which is not observed for B and T2 CPECs. This observation gives the first indication that the CPEC structures are similar but not identical across the donor series.

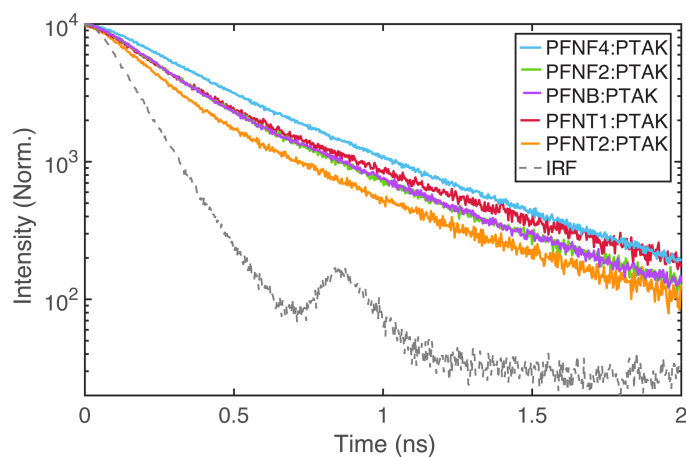


Figure 9. TRPL decays of selectively excited PTAK (600 nm) within each CPEC. The instrument response function is shown in grey.

With this indication in hand, we went on to interrogate the spectral characteristics of PTAK within the CPEC, since it is common to each complex and may thus act as a reporter for differences in complex conformation. Using time-correlated single-photon counting, we first collected time-resolved PL (TRPL) decays for each CPEC while exciting at 600 nm where only PTAK absorbs. These results are shown in Figure 9. Each decay curve is well-described by a convolution of the instrument response function (IRF) with a sum of two exponential decays, with the relatively short component being dominant. Fitting parameters following deconvolution of the IRF are shown in Table S5 of the Supporting Information. We

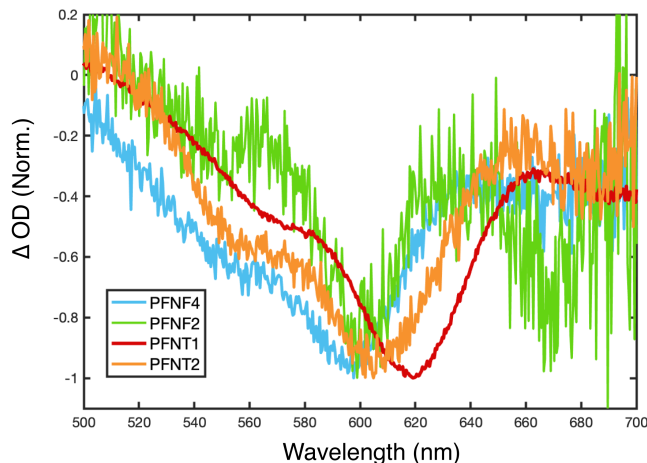


Figure 10. Normalized GSB spectra of CPECs at a 1-ps pump/probe delay excited at 600 nm. This wavelength corresponds to exclusive PTAK excitation. Small shifts in the absolute value of the peak are apparent across the donor series.

find that PTAK in the T2 CPEC gives the shortest average PL lifetime (119 ps), while F4 gives the largest (150 ps). F2, B, and T1 show remarkably similar fast components, only showing subtle differences in the low-amplitude long component.

We then compared ultrafast GSB spectra of CPECs when PTAK is directly and exclusively excited within the complex at 600 nm. None of the donor CPEs absorb at this wavelength; thus, there is no possibility of EET. GSB spectra following 600-nm excitation at a pump-probe delay of 1 ps for all CPECs are shown in Figure 10. All the PTAK GSB spectra within the CPEC across the donor CPE series are qualitatively similar to each and qualitatively distinct from that of isolated PTAK (Figure 5). The similarity in PTAK GSB across different CPECs is consistent with PTAK vibronic 0-0/0-1 peak ratios in steady-state PL spectra of the complexes (Figure I19 of the Supporting Information), showing a J-aggregate-like vibronic ratio (0-0 intensity > 0-1 intensity). However, it is clear that the wavelength onsets of GSB signals on the red side exhibit minor shifts and some differences in the ratio of the 0-0 and 0-1 peak intensities, consistent with small differences in the onset of PLE and OD spectra of the CPECs. Taken together, the SAXS, TRPL, and GSB following selective PTAK excitation all paint a similar picture: that the CPEC microstructure is qualitatively similar across the donor CPE series but exhibits quantitative differences as a function of monomer X.

2.3 Neutral Polymer Molecular Weight Calculations

SEC measurements were performed on nPFNF2, the neutral dimethylamine precursor to the PFNF2 CPE, by collaborators at the Molecular Foundry, Lawrence Berkeley National Laboratory. The weight-average molecular weight of ~140,000 g/mol and dispersity of ~1.7 correspond to a degree of polymerization of ~311.

Although the remaining neutral precursor polymers were insufficiently soluble in standard SEC solvents to yield data of comparable quality, the identical synthetic procedures used across all donor CPEs suggest their molecular weights are comparable to that of nPFNF2.

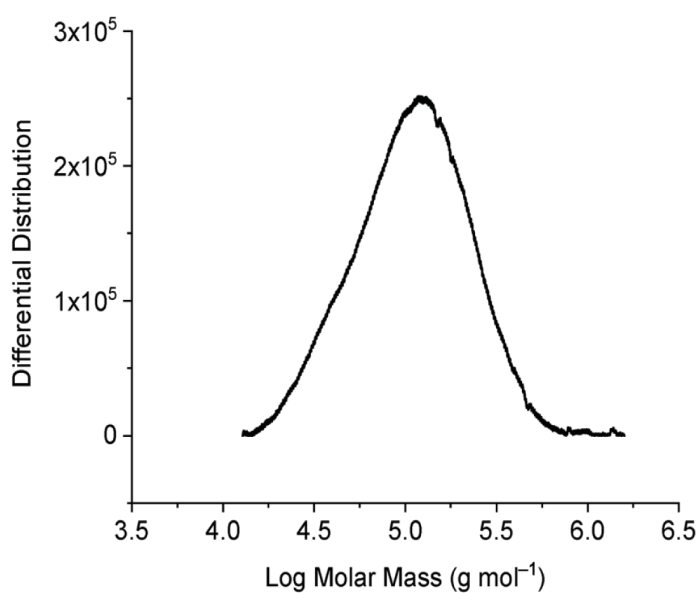


Figure 11. nPFNF2 (a) distribution plot for extraction of neutral conjugated polymer molecular weight, shown in Table S1.

Table 3. Polymer Molecular Weight

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n	DP
nPFNF2	84133	139535	1.69	311.05

2.4 Synthesis of the PFNX Series

Materials: The reagents and materials utilized in this study were obtained directly from the specified distributors without any further modifications: 2,7-dibromofluorene and 4-toluenesulfonyl chloride obtained from Oakwood Chemical. Poly[3-(potassium-4-butanoate)thiophene-2,5-diyl] regioregular was obtained from Rieke Metals. Monomers 3,6-Dibromothieno[3,2-b]thiophene (98.0%) and 1,4-Dibromo-2,3-difluorobenzene, (98.0%) were purchased from TCI America. Monomer 1,4-Dibromotetrafluorobenzene (99%) was purchased from Sigma Aldrich. Monomer 1,4-Dibromobenzene (97.0%) was purchased from Spectrum Laboratory Products Inc. SlideALyzer Dialysis Flasks, 10K MWCO, 250mL obtained from Fisher Scientific Company LLC. Bis(pinacolato)diboron (98%) and 1,4-dioxane (anhydrous, 99.8%) were obtained from Alfa Aesar. Tetraethylammonium bromide (100%) was obtained from Chem-Impex International Inc. Palladium catalyst [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium (II), dimethyl aminopropyl chloride hydrochloride (96%), were obtained from Sigma-Aldrich. Methyl iodide (99.5%), tetrahydrofuran (HPLC grade), and dichloromethane (99.5%) were obtained from Spectrum Laboratory Products. Sodium hydroxide, sodium hydroxide solution (50% w/w), potassium carbonate (anhydrous, 99.7%), triethylamine (99%), diethyl ether (99%), methanol (99.9%), acetone (HPLC grade), chloroform (99.9%), ethyl acetate (99.5%), hexanes (98.5%), and potassium acetate (>99%) were obtained from Fisher Scientific Company LLC. Deuterated solvents CDCl₃ (D 99.8%) and D₂O (D 99.9%) were both purchased from Cambridge Isotope Laboratories. Nuclear magnetic

resonance (NMR) spectra of the polymers were collected on a Bruker Avance III HD 4 channel 800 MHz NMR with a cryoprobe. **Due to solubility restrictions of the conjugated polymers, ^{13}C NMR was not obtained. Below are the ^1H NMR spectra of all materials synthesized.**

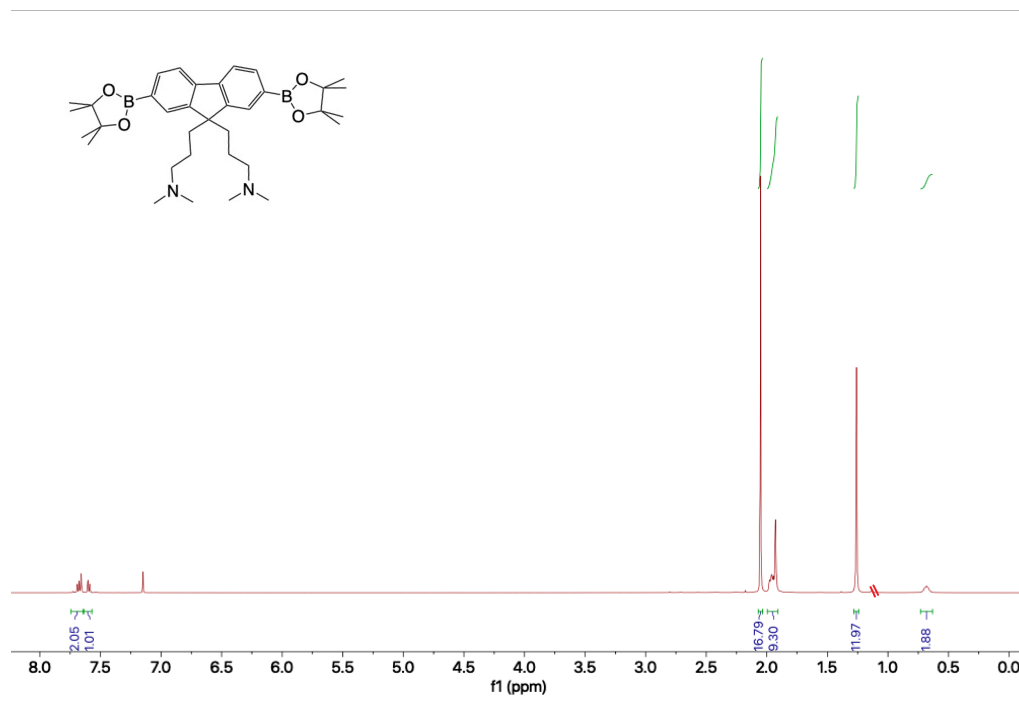


Figure 12. FNB ^1H 500 MHz NMR in CDCl_3

Synthesis of monomer FN: Synthesis of (2,7-dibromo-9,9-bis(3'-(*N,N*-dimethyl-amino)-propyl)-fluorene) To a clean, dried, 100 mL two neck round bottom flask, a Teflon coated stir bar, dimethyl sulfoxide (*DMSO*, 30.9 mL, 434.6 mmol), 2,7-dibromofluorene (*F*, 2 g, 6.2 mmol), tetrabutylammonium bromide (*TBAB*, 39.8 mg, 0.12 mmol), and 4 mL of a 50 wt. % aqueous sodium hydroxide solution (50 wt. % *aq. NaOH*, 4 mL, 154.3 mmol) was added under an atmosphere of $\text{N}_2(\text{g})$. An

additional aliquot of DMSO (10.5 mL, 145.1 mmol) was added to the reaction flask, followed by dimethyl aminopropyl chloride hydrochloride salt (DAPCl, 2.6 g, 16.4 mmol). The reaction was stirred and heated at 60 °C for 12 hours. Reaction progress was monitored by thin-layer chromatography (TLC). DI H₂O (40 mL, 2.216 mmol) was added to the reaction flask to dissolve precipitated salts as well as to solvate DMSO. The product (FN) was extracted from the wet DMSO layer with diethyl ether (*Et*₂O, 8 x 25 mL), washed with a 10 wt. % aqueous NaOH (2 x 50 mL). The organic layer was washed with DI H₂O (3 x 50 mL), followed by a brine wash (1 x 50 mL), and then dried over Na₂SO₄. Concentration of the anhydrous organic layer under reduced pressure lead to crude solid which was purified with a silica gel column (Hexanes: Ethyl Acetate: Triethylamine, 49:49:2) to obtain FN (59% yield, 1.81 g).

Synthesis of monomer FNB: Synthesis of (2,7-diboryl pinacol ester-9,9-bis(3'-(*N,N*-dimethyl- amino)-propyl)-fluorene) To a clean, dried, 100 mL two neck round bottom flask, a Teflon coated stir bar, dimethylformamide (*DMF*, 39 mL, 505.8 mmol), FN (1 g, 2.0 mmol), bis(pinacolato)diboron (*B*₂*Pin*₂, 2.26 g, 8.9 mmol), potassium acetate (KOAc, 3.53 g, 17.8 mmol), [1,1'-Bis(diphenyl-phosphino)ferrocene]dichloro-palladium(II) (*Pd(dppf)Cl*₂, 0.296 g, 0.40 mmol) were added under an atmosphere of N₂(g). The contents of the reaction were stirred and heated at 80 °C for 24 hours. Reaction progress was monitored by TLC. Upon completion, the reaction was concentrated to dryness, and the crude solid was extracted with hot HPLC-grade hexanes (7 x 100 mL). The combined hexanes layer

was filtered, concentrated to dryness, reextracted with hot hexanes, and re-concentrated to dryness. Acetone was used to extract the product from the re-dried hexanes layer and was allowed to crystallize out of the solution as an off-white solid. The crystals of FNB were collected via filtration and washed with a minimal amount of cold acetone to obtain FNB (55% yield, 0.6647 mg).

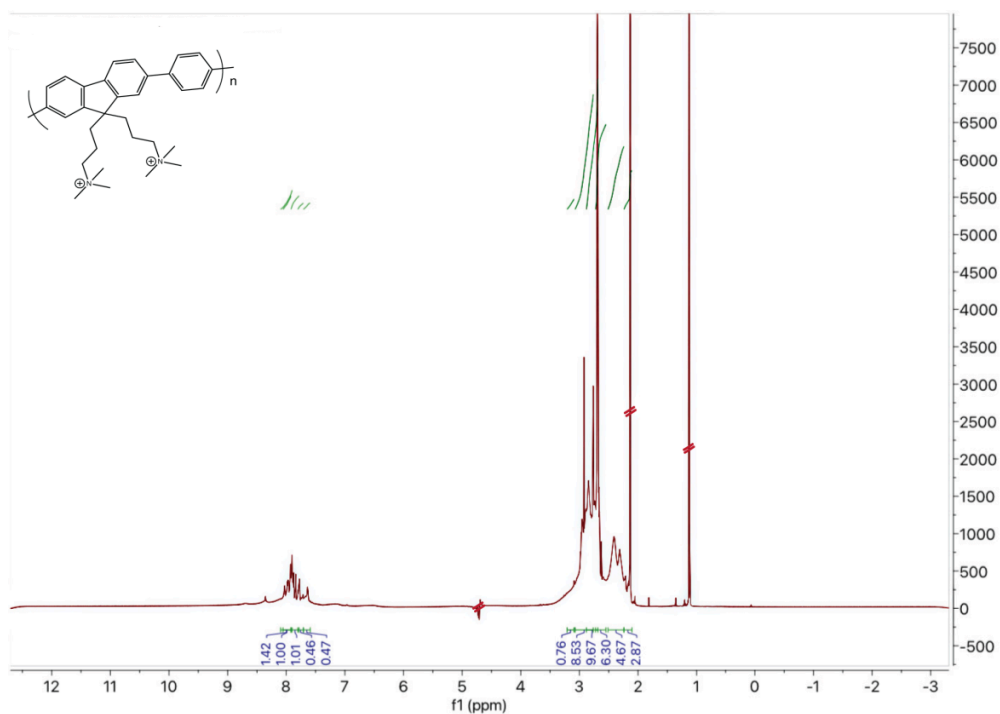


Figure 13. PFNB ^1H 800 MHz NMR in D_2O with a small water suppression peak $\sim 4.7\text{ppm}$ and trace amounts of acetone and hexanes. Broadening of baseline observed around 6.5-7.3ppm due to low solubility.

Synthesis of Neutral Polymer nPFNB: Polymerization of 3,3'-(2-methyl-7-(*p*-tolyl)-9*H*-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine). To a clean pressured vial 1,4-dibromobenzene (300 mg, 0.74 mmol), FNB (500 mg, 0.84 mmol), potassium carbonate (K_2CO_3 , 1.25 g, 9.6 mmol), 1,4- dioxane (*Dioxane*, 8 mL, 90.4 mmol), DI

H₂O (7.0 mL, 277.0 mmol), and Pd(dppf)Cl₂ (4 mg, 0.005 mmol) were added. The entire reaction vessel, including the solution was flushed with N₂(g). The pressured vial was placed into a silicon oil bath, stirred, and heated at 100 °C for 48 hours. To stop the reaction, the stirring function was turned off and the polymer in the dioxane layer was pipetted into DI H₂O to induce precipitation of nPFNB, decanted and vacuum filtrated to dry.

Synthesis Conjugated Polyelectrolyte PFNB: Conjugated polyelectrolyte 3,3'-(2-methyl-7-(*p*-tolyl)-9H-fluorene-9,9-diyl)bis(*N,N,N*-trimethylpropan-1-aminium). In-situ quaternization of nPFNB was done with the addition of iodomethane (MeI, 4 mL, 62 mmol) directly to the remaining dioxane layer containing nPFNF2 and was left to react for 2 hours before the addition of DI H₂O, to assist in the dissolution of the polymer. The reaction was then heated to 50 °C for 5 days and aliquots of DI H₂O were systematically added until there was no more headspace in the 250mL. pressured vial and the polymer was well dissolved. The solution was then dialyzed via the Thermo Scientific™ Slide-A-Lyzer Dialysis Cassette (10,000 MWCO) submerged in a vat of DI H₂O. The DI H₂O was exchanged with fresh DI H₂O every day for 3 days. After 3 days, the dialyzed solution of PFNB was concentrated under reduced pressure, filtered, transferred into multiple 25 mL Falcon tubes, and lyophilized to yield PFNB as a light yellow solid (61.41% yield).

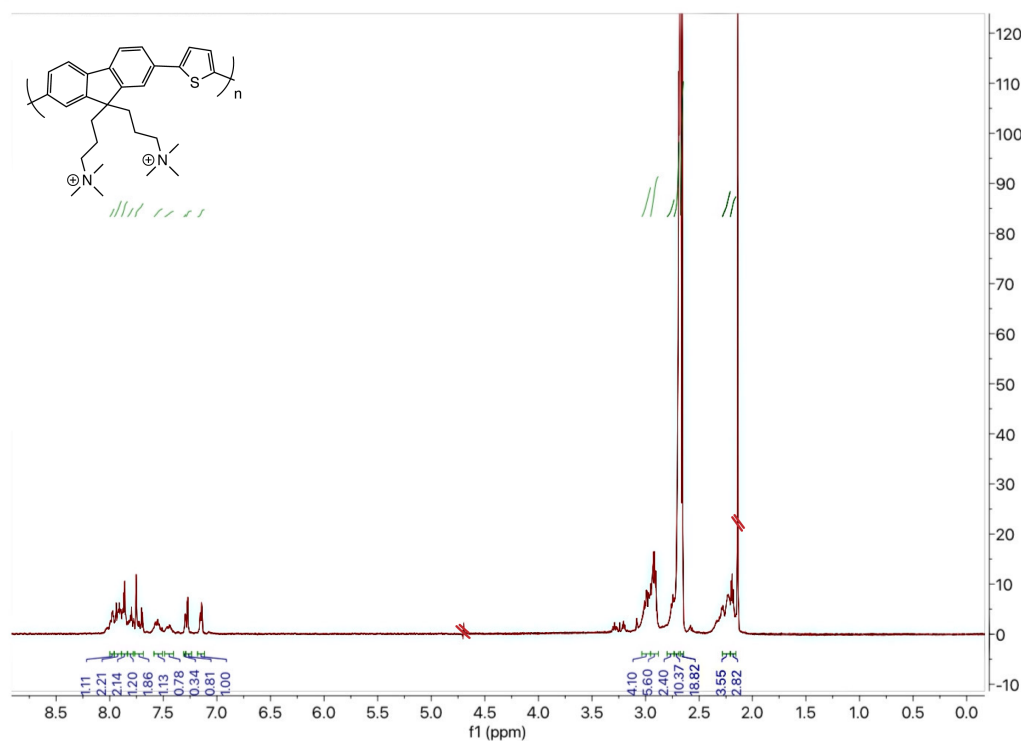


Figure 14. PFNT1 ^1H 800 MHz NMR in D_2O with a small water suppression peak ~ 4.7 ppm and trace amounts of acetone

Synthesis of Neutral Polymer nPFNT1: Polymerization of 3,3'-(2-methyl-7-(5-methylthiophen-2-yl)-9H-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine) clean pressured vial, 2,5-Dibromothiophene (350 mg, 1 mmol), FNB (500 mg, 0.84 mmol), potassium carbonate (K_2CO_3 , 1.25 g, 9.6 mmol), 1,4- dioxane (*Dioxane*, 8 mL, 90.4 mmol), DI H_2O (7.0 mL, 277.0 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (4 mg, 0.005 mmol) were added. The entire reaction vessel, including the solution was flushed with $\text{N}_2(\text{g})$. The pressured vial was placed into a silicon oil bath, stirred, and heated at $100\text{ }^\circ\text{C}$ for 48 hours. To stop the reaction, the stirring function was turned off and the polymer in the

dioxane layer was pipetted into DI H₂O to induce precipitation of nPFNT1, decanted and vacuum filtrated.

Synthesis Conjugated Polyelectrolyte PFNT1: Conjugated polyelectrolyte 3,3'-(2-methyl-7-(5-methylthiophen-2-yl)-9*H*-fluorene-9,9-diyl) bis(*N,N,N*-trimethylpropan-1-aminium). In-situ quaternization of nPFNT1 was done with the addition of iodomethane (MeI, 4 mL, 62 mmol) directly to the remaining dioxane layer containing nPFNT1 and was left to react for 2 hours before the addition of DI H₂O, to assist in the dissolution of the polymer. The reaction was then heated to 50 °C for 5 days and aliquots of DI H₂O were systematically added until there was no more headspace in the 250mL pressured vial and the polymer was well dissolved. The solution was then dialyzed via the Thermo Scientific™ Slide-A-Lyzer Dialysis Cassette (10,000 MWCO) submerged in a vat of DI H₂O. The DI H₂O was exchanged with fresh DI H₂O every day for 3 days. After 3 days, the dialyzed solution of PFNT1 was concentrated under reduced pressure, filtered, transferred into multiple 25 mL Falcon tubes, and lyophilized to yield PFNT1 as a rusty-brown solid (71.2% yield).

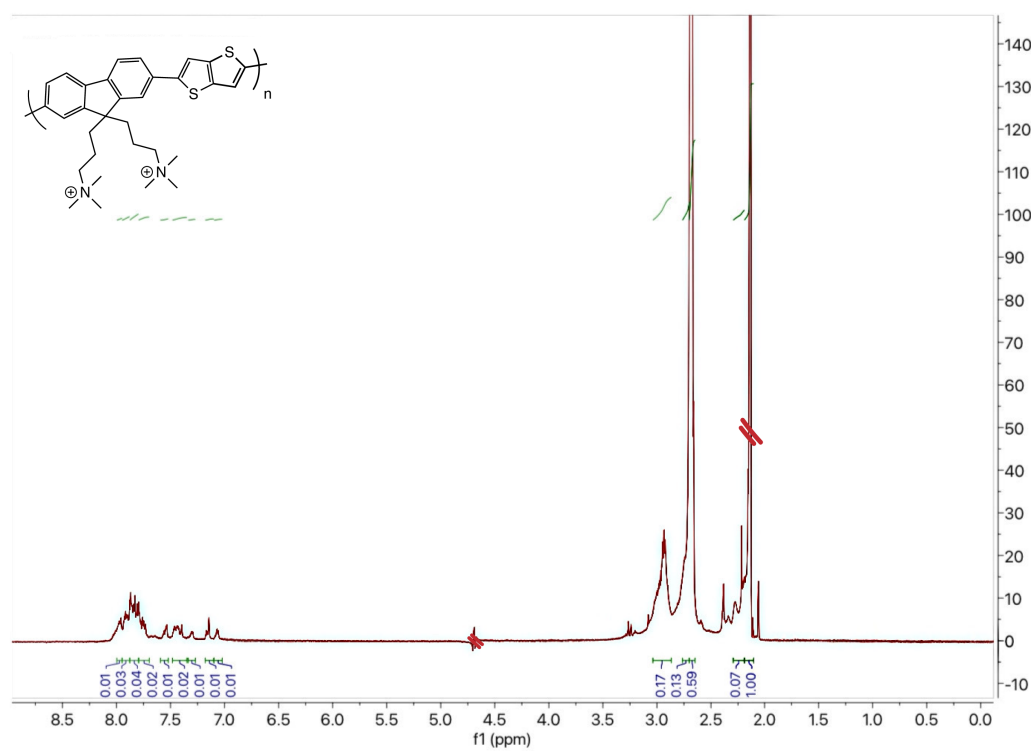


Figure 15. PFNT2 ^1H 800 MHz NMR in D_2O with a small water suppression peak $\sim 4.7\text{ppm}$ and trace amounts of acetone

Synthesis of Neutral Polymer nPFNT2: Polymerization of 3,3'-(2-methyl-7-(5-methylthieno[3,2-b]thiophen-2-yl)-9H-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine). To a clean pressured vial, 2,5-dibromothieno[3,2-b]thiophene (300 mg, 1 mmol), FNB (500 mg, 0.84 mmol), potassium carbonate (K_2CO_3 , 1.25 g, 9.6 mmol), 1,4- dioxane (*Dioxane*, 8 mL, 90.4 mmol), DI H_2O (7.0 mL, 277.0 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (4 mg, 0.005 mmol) were added. The entire reaction vessel, including the solution was flushed with $\text{N}_2(\text{g})$. The pressured vial was placed into a silicon oil bath, stirred, and heated at $100\text{ }^\circ\text{C}$ for 48 hours. To stop the reaction, the stirring

function was turned off and the polymer in the dioxane layer was pipetted into DI H₂O to induce precipitation of nPFNT2, decanted and vacuum filtrated to dry.

Synthesis Conjugated Polyelectrolyte PFNT2: Conjugated polyelectrolyte 3-(2-methyl-7-(5-methylthieno[3,2-b]thiophen-2-yl)-9-(3-(trimethylammonio)propyl)-9H-fluoren-9-yl)propyl)-14-azaneyl)methylum. In-situ quaternization of nPFNT2 was done with the addition of iodomethane (MeI, 4 mL, 62 mmol) directly to the remaining dioxane layer containing nPFNT2 and was left to react for 2 hours before the addition of DI H₂O, to assist in the dissolution of the polymer. The reaction was then heated to 50 °C for 5 days and aliquots of DI H₂O were systematically added until there was no more headspace in the 250mL pressured vial and the polymer was well dissolved. The solution was then dialyzed via the Thermo Scientific™ Slide-A-Lyzer Dialysis Cassette (10,000 MWCO) submerged in a vat of DI H₂O. The DI H₂O was exchanged with fresh DI H₂O every day for 3 days. After 3 days, the dialyzed solution of PFNT2 was concentrated under reduced pressure, filtered, transferred into multiple 25 mL Falcon tubes, and lyophilized to yield PFNT2 as a rusty-brown solid (65.03% yield).

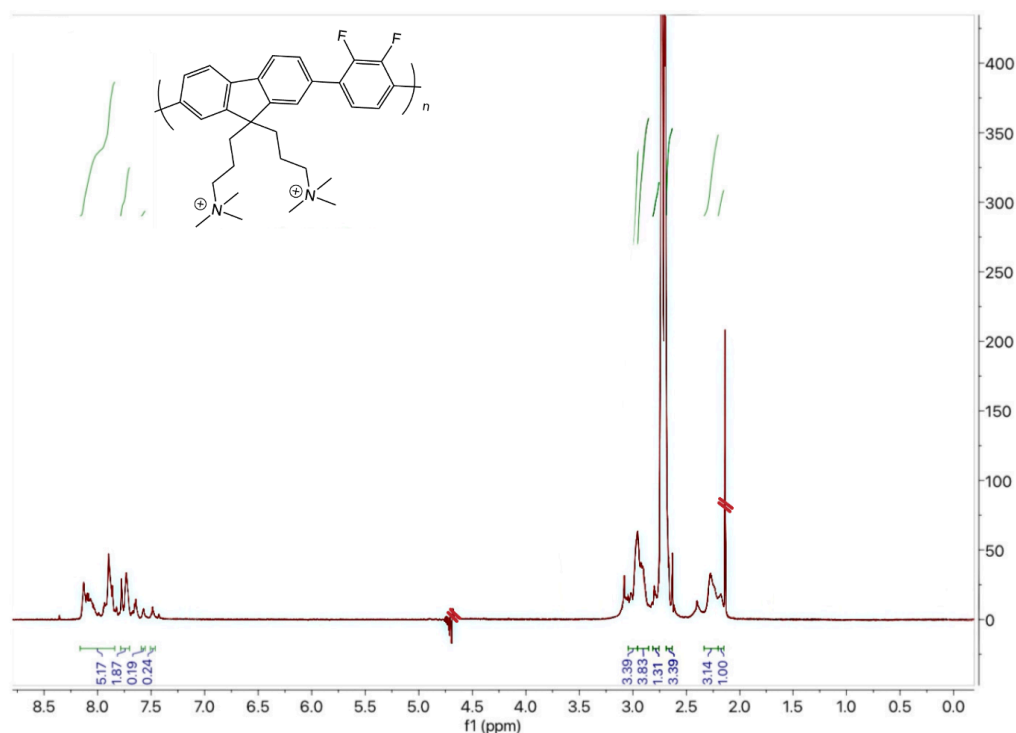


Figure 16. PFNF2 ^1H 800 MHz NMR in D_2O with a small water suppression peak ~ 4.7 ppm and trace amounts of acetone

Synthesis of Neutral Polymer nPFNF2: Polymerization of 3,3'-(2-(2,3-difluoro-4-methylphenyl)-7-methyl-9H-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine). To a clean pressured vial 1,4-dibromo-2,3-difluorobenzene (300 mg, 0.98 mmol), FNB (500 mg, 0.84 mmol), potassium carbonate (K_2CO_3 , 1.25 g, 9.6 mmol), 1,4-dioxane (*Dioxane*, 8 mL, 90.4 mmol), DI H_2O (7.0 mL, 277.0 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (4 mg, 0.005 mmol) were added. The entire reaction vessel, including the solution was flushed with $\text{N}_2(\text{g})$. The pressured vial was placed into a silicon oil bath, stirred, and heated at 100°C for 48 hours. To stop the reaction, the stirring function was turned

off and the polymer in the dioxane layer was pipetted into DI H₂O to induce precipitation of nPFNF2, decanted and vacuum filtrated to dry.

Synthesis Conjugated Polyelectrolyte PFNF2: Conjugated polyelectrolyte 3,3'-(2-(2,3-difluoro-4-methylphenyl)-7-methyl-9H-fluorene-9,9-diyl)bis(*N,N,N*-trimethylpropan-1-aminium). In-situ quaternization of nPFNF2 was done with the addition of iodomethane (MeI, 4 mL, 62 mmol) directly to the remaining dioxane layer containing nPFNF2 and was left to react for 2 hours before the addition of DI H₂O, to assist in the dissolution of the polymer. The reaction was then heated to 50 °C for 5 days and aliquots of DI H₂O were systematically added until there was no more headspace in the 250mL pressured vial and the polymer was well dissolved. The solution was then dialyzed via the Thermo Scientific™ Slide-A-Lyzer Dialysis Cassette (10,000 MWCO) submerged in a vat of DI H₂O. The DI H₂O was exchanged with fresh DI H₂O every day for 3 days. After 3 days, the dialyzed solution of PFNF2 was concentrated under reduced pressure, filtered, transferred into multiple 25 mL Falcon tubes, and lyophilized to yield PFNF2 as a light grey solid (79.08% yield).

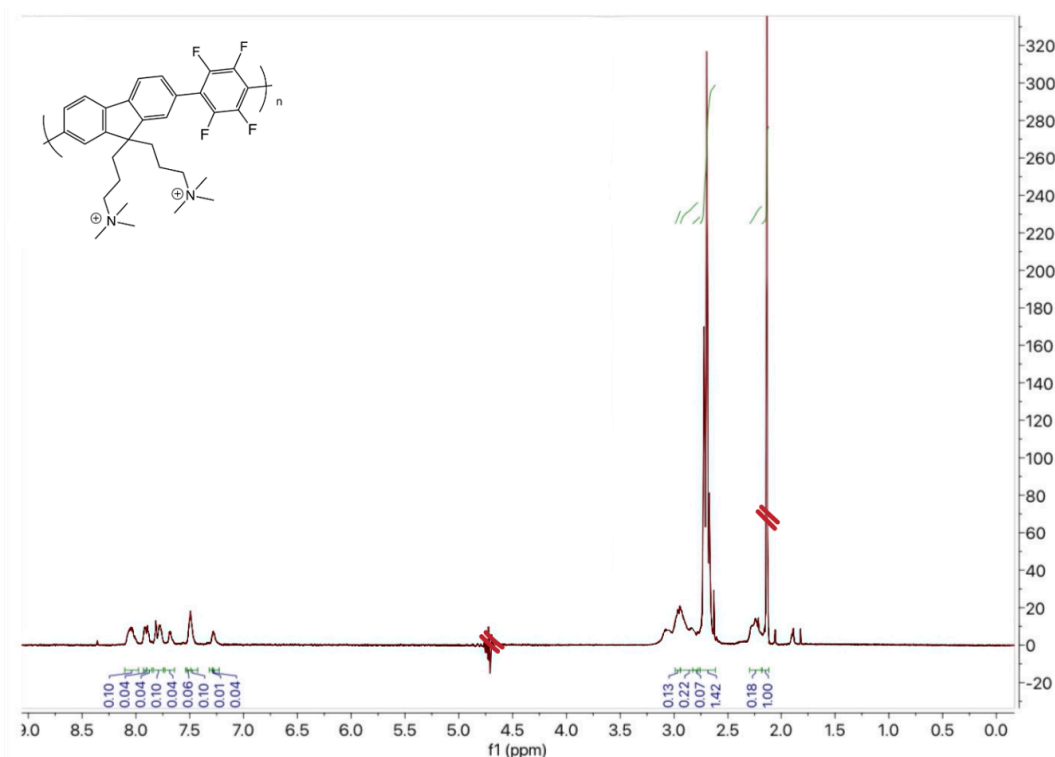


Figure 17. PFNF4 ^1H 800 MHz NMR in D_2O with a small water suppression peak $\sim 4.7\text{ppm}$ and trace amounts of acetone.

Synthesis of Neutral Polymer nPFNF4: Polymerization of 3,3'-(2-methyl-7-(5-methylthieno[3,2-b]thiophen-2-yl)-9H-fluorene-9,9-diyl)bis(*N,N*-dimethylpropan-1-amine). To a clean pressured vial, 1,4-dibromo-2,3,5,6-tetrafluorobenzene (300 mg, 1.05 mmol), FNB (500 mg, 0.84 mmol), potassium carbonate (K_2CO_3 , 1.25 g, 9.6 mmol), 1,4- dioxane (*Dioxane*, 8 mL, 90.4 mmol), DI H_2O (7.0 mL, 277.0 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2$ (4 mg, 0.005 mmol) were added. The entire reaction vessel, including the solution was flushed with $\text{N}_2(\text{g})$. The pressured vial was placed into a silicon oil bath, stirred, and heated at $100\text{ }^\circ\text{C}$ for 48 hours. To stop the reaction, the

stirring function was turned off and the polymer in the dioxane layer was pipetted into DI H₂O to induce precipitation of nPFNF4, decanted and vacuum filtrated to dry.

Synthesis Conjugated Polyelectrolyte PFNF4: Conjugated polyelectrolyte 3-(2-methyl-7-(5-methylthieno[3,2-b]thiophen-2-yl)-9-(3-(trimethylammonio)propyl)-9H-fluoren-9-yl)propyl)-14-azaneyl)methylum. In-situ quaternization of nPFNF4 was done with the addition of iodomethane (MeI, 4 mL, 62 mmol) directly to the remaining dioxane layer containing nPFNF4 and was left to react for 2 hours before the addition of DI H₂O, to assist in the dissolution of the polymer. The reaction was then heated to 50 °C for 5 days and aliquots of DI H₂O were systematically added until there was no more headspace in the 250mL pressured vial and the polymer was well dissolved. The solution was then dialyzed via the Thermo Scientific™ Slide-A-Lyzer Dialysis Cassette (10,000 MWCO) submerged in a vat of DI H₂O. The DI H₂O was exchanged with fresh DI H₂O every day for 3 days. After 3 days, the dialyzed solution of PFNF4 was concentrated under reduced pressure, filtered, transferred into multiple 25 mL Falcon tubes, and lyophilized to yield PFNF4 as a grey solid (74.6% yield).

2.5 Discussion

The steady-state PLE and ultrafast pump/probe data show that, although we observe some qualitative agreement with the Förster model, it fails to account for the relative magnitude of E^{rel} and the EET rate for F4 as well as some of the rate ratios that we observe. This is not entirely surprising given the core assumption of the model,

namely that the Coulombic coupling between the exciton donor and acceptor could be described as a dipole-dipole interaction between *point* transition dipole moments. This assumption averages away all the details of the spatially extended transition densities of the two EET partners. As such, this model may become a progressively poorer approximation as the separation between the centers of mass of the two species becomes comparable to the lengths of their respective chromophores, *i.e.* the spatial extent of the excitonic wavefunctions.

Table 5. Repeat unit calculations using DFT and TDDFT at the ω B97X-D3 / def2-TZVPD level of theory. Torsional angles along the linkage bonds of copolymer units for PFNX are calculated for the ground-state equilibrium geometries; transition dipole moments along the linkage axis and oscillator strengths are calculated for the lowest excited states.

	PFNF4	PFNF2	PFNB	PFNT1	PFNT2
Torsional					
Angle	61.0°	53.3 °	43.8 °	34.5 °	33.5°
Transition Dipole					
Magnitude	2.31	2.47	2.63	3.01	3.58
Oscillator Strength					
	0.640	0.728	0.817	1.021	1.378

Indeed, it was shown previously that even for pigment molecules in natural light-harvesting antenna complexes, such as chlorophyll and carotenoid derivatives, the Förster approximation cannot always be justified.⁴² Division of E^{rel} by the

spectral overlap integral further suggests that the excitonic coupling V_{EX} may differ substantially across the CPEC series. Specifically, it appears to be largest for F4 and comparable for F2 and T2. It is important to underscore once again that in calculating E^{rel} we implicitly assumed that relaxation rate of donor excitons immediately following photoexcitation is faster than the EET rate. Given the relatively large EET rates that we measured, this assumption can be reasonably questioned. In the extreme case, the EET rate may be comparable or faster than the relaxation rate of the donor exciton. In such a case, division by J may no longer be justified to isolate V_{EX} . However, even in this case, the EET rate should scale like V_{EX} multiplied by the density of final states at the exciton energy. We expect the latter to still be related to the magnitude of the PTAK absorption spectrum at that energy. The fact that the PTAK OD ratio for 400 nm relative to 360 nm (the wavelengths used to pump T2 and F4, respectively) is ~ 2 while the ratio of E^{rel} and EET rates for T2 relative to F4 are ~ 1.5 and ~ 1.2 , respectively, suggests that the same conclusion about the difference in V_{EX} for T2 vs. F4 holds qualitatively as when J is divided out. As mentioned above, E^{rel} is likely preferentially underestimated for F4 compared to T2 given the deliberately limited PLE integration window.

The question that we aim to answer is, how can we understand the fact that E^{rel} and the EET rate for F4 are as large as they are given the fact that it has the smallest spectral overlap integral (or expectedly smallest density of final states at the pump wavelength)? To help answer this question, we began by calculating several useful parameters of isolated donor CPE repeat units at the level of (time-dependent)

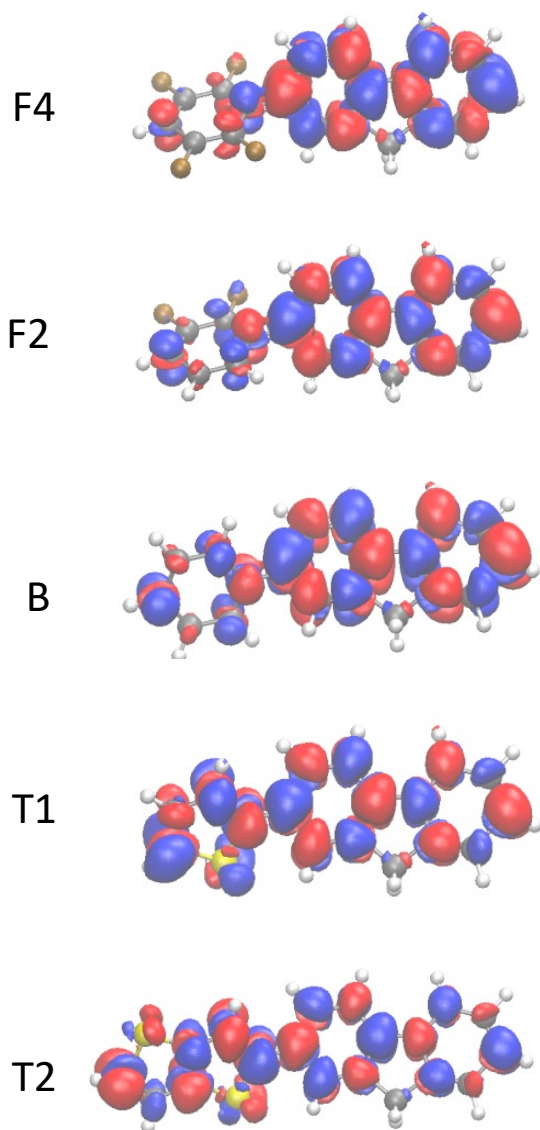


Figure 18. Transition density for each donor repeat unit on the electronic transition from the ground state to the lowest excited state. The blue and red colors correspond to negative and positive isosurfaces, respectively. The isovalue is 8×10^{-4} in a.u.

DFT. Although the calculations are performed on a single repeat unit, we believe that this still provides a valuable comparison across the donor series treated on an equal footing. The fact that the calculation is carried out in vacuum means that the role of the environment on the repeat unit conformation is not taken into account. However, we expect that, to a good approximation, the intrinsic monomer-monomer interactions will dominate the electronic structure of the repeat unit. The results of these calculations are shown in Table 3. Two primary takeaways stand out. We find that the equilibrium torsion (dihedral) angle between the fluorene monomer and monomer X varies significantly (see Figure I28 of the Supporting Information for the explicit definition of the torsional angle). F4 has by far the largest angle (most twisted monomers), followed by F2 and B, while the thiophene-containing repeat units have the smallest angles. We find the opposite ordering of the transition dipole moments, with T2 having the largest value and F4 the smallest.

It is instructive to also visualize the transition densities of the repeat units, which are plotted in Figure 11. The transition density on the fluorene monomer is similar for all. However, it is clear that the thiophene and thienothiophene monomers contain a significantly larger share of the transition density than the F2 and F4 repeat units, leading to a correspondingly larger degree of charge transfer across the two monomers (see Figure I29 of the Supporting Information for charge difference densities between the ground states and the lowest excited states of PFNF4, PFNF2, PFNT1, and PFNT2). This suggests that over the length of a donor polymer chromophore the transition density for F2 and F4 will display significant position-

dependent variations in magnitude, whereas for T1 and T2 the transition density will depend significantly more weakly on position along the chromophore.

What are the implications of these calculations for EET within CPECs? We first consider the influence of the torsion angle. In conjugated polymers, the excitonic wavefunction can be described as a product of (i) a center-of-mass (envelope) wavefunction that dictates the spatial extent of the exciton and (ii) a relative wavefunction that describes the probability to observe the electron and the hole at a given separation.^{43,44} It is reasonable to expect that as the torsion angle increases, the center-of-mass excitonic wavefunction will become dynamically more localized, leading to a smaller mean exciton extent. Thus, we expect that F4 will have the smallest exciton radius. To appreciate the significance of this expectation for EET, it is instructive to consider the line-dipole approximation, which is a substantial improvement on the Förster model for conjugated polymers. Within this approximation, the electronic coupling between two proximal conjugated polymer chains is given by a sum of pairwise interactions between transition dipole moments of each monomer on the first chain with that of each monomer on the second chain.

The specific monomer-monomer interaction is still described by the dipole term in the multipole expansion of the full Coulomb interaction. We doubt that even this approximation is an excellent one given the relatively small separation between the donor and the acceptor within the CPEC. The approximate condition for its validity is that the length of the repeat unit be significantly smaller than the center-to-center separation between the two parallel conjugated-polymer chains, which is not

expected to be completely fulfilled in our CPECs. A more accurate way of describing the excitonic coupling is the transition-density cube method, but it is computationally taxing and does not readily yield qualitative insight.⁴⁵ In contrast, the line-dipole approximation provides significant qualitative insight that can aid the interpretation of our results.

Barford has shown analytically that for parallel conjugated polymer chains within the line-dipole approximation, the excitonic coupling is a decreasing function of chromophore length, *i.e.* the length over which the excitonic wavefunction is coherently delocalized.⁴⁶ For identical chains, $V_{EX} \sim L^{-p}$, where L is the chromophore length, and p ranges from 1 to ~ 2 depending on the assumptions made about the functional form of the center-of-mass excitonic wavefunction. In other words, perhaps somewhat counterintuitively, as the exciton radius *decreases*, the excitonic coupling is expected to *increase*. Barford's analytical results are supported by quantum-chemical calculations, which show that the coupling increases as either the donor or the acceptor chromophore length decreases as soon as the chromophore length extends beyond a couple of repeat units.^{47,48}

These analytical and computational results allow us to propose an explanation for why F4 stands out in the magnitude of its E^{rel} and its relatively large EET rate given its relatively large bandgap and thus poor spectral overlap with PTAK. Its largest torsion angle likely leads to the smallest extent of the center-of-mass excitonic wavefunction. Moreover, the red edge of the OD and the PLE spectra for the F4 CPEC (blue curves in Figures 2A and 2B, respectively) shows that the PTAK region

is most blue-shifted compared to the rest of the CPECs. Within the particle-in-a-box approximation, this suggests that the spatial extent of the PTAK exciton is also smallest for the F4 CPEC. Taken together, we believe these observations are largely responsible for the apparently disproportionately large excitonic coupling in the F4 CPEC. The fact that E^{norm} is comparable for F2 and T2 can be rationalized by the fact that, although the torsion angle for F2 is larger than that of T2, the transition dipole moment of the T2 repeat unit is larger than that of the F2 repeat unit. We note that at the moment it is not entirely clear what the source of the disagreement is between the relative position of E^{norm} for T1 within the donor series compared to its measured EET rate.

Although we believe that the above considerations are largely responsible for our EET observations, there are two additional considerations that are worth mentioning. First, it is possible that the larger spatial variation in the transition density magnitude along the chromophore for F2 and F4 compared to T1 and T2 may lead to further differences. We may anticipate two potential effects: (i) The lateral shifts between monomers in parallel chains may lead to variations in the inter-chain excitonic coupling.^{14,49} The somewhat smaller linear charge density of T2 could be one source of an average lateral shift between donor and acceptor excitonic wavefunctions compared to other donor CPEs. (ii) As the degree of charge transfer between the fluorene monomer and the variable monomer increases, the relative wavefunction of the exciton may become a mixture of neutral Frenkel-type and charge-transfer-type states.^{15,50}

Second, our results show that, although the average CPEC structures appear similar, they are not identical. Differences in structure could lead to subtle variations in the relative orientation between the donor and acceptor chromophores, which would modify the EET rate.

In addition to electrostatic interactions between the polyanion and the polycation, the fluorinated benzene monomer in F4 may participate in anion- π interactions with the carboxylate group at the terminus of the PTAK sidechain. Moreover, it is conceivable that there may be some degree of π -stacking between the donor and acceptor backbones, although we believe the extent of such interactions would likely be limited due to the geometry of the electrostatic binding. Nevertheless, π -stacking would lead to a modification of the exciton transfer integral.¹⁵

In closing, we note that we observe a steady increase in EET efficiency of the CPEC for all donor CPEs as measured by PLE spectroscopy on the days to weeks timescale, as shown in Figure I27 of the Supporting Information. We attribute this increase primarily to the condensation of multiple chains onto the complex, leading to an increase in the local concentration of donor and acceptor chromophores.⁵¹ This is consistent with the onset of a measurable sample turbidity after approximately 1 week, in contrast to fresh CPEC solutions. In the very long-time limit, we expect to observe the onset of macroscopic phase separation. Although EET efficiencies increase for all donor CPEs, the increase for F4 and F2 is much more dramatic relative to the rest of the donor polymers. Future work will focus on elucidating the details of this slow evolution in the CPEC assembly.

2.6 Conclusion

In this report, we synthesized two subfamilies of exciton-donor alternating copolymers consisting of ionic fluorene monomers and alternating thiophene-based and fluorine-substituted phenyl-based monomers while keeping the linear ionic charge density fixed within a narrow range. We then interrogated their EET characteristics and found that, although the Förster model is qualitatively consistent with *some* of the EET trends that we observe, it fails to qualitatively account for the ordering of the entire donor CPE series and to apparently quantitatively account for the ratios of relative EET efficiencies and EET rates. Specifically, we find that the donor CPE containing a tetrafluoro-substituted phenyl co-monomer displays a disproportionately large EET rate and relative EET efficiency. We largely rationalize this finding by considering how the excitonic coupling is expected to scale with the mean exciton delocalization length.

Our results indicate that, although the positions of steady-state donor PL and acceptor OD spectra provide a reasonable starting point for a rough expectation of EET efficiency within a CPEC, given the relatively small donor/acceptor separations involved, the influence of precise chemical structure of the CPE backbone on the excitonic coupling cannot be overlooked. This has implications for the choice of a particular donor/acceptor CPE pair if the goal is to maximize the EET rate in a particular spectral window.

We envision CPECs functioning as key exciton-transferring antenna components in an overarching soft-matter-based, water-based light-harvesting material. In such materials, different rate processes must often be carefully balanced to ensure optimal energy conversion efficiencies. Knowing how subtle modifications to the chemical structure of a CPE backbone alter EET is a key first step towards engineering CPECs to serve as rapid relays for exciton energy transport.

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Appendix I

I.1 Energy Transfer Efficiency and the PLE Spectra

To extract relative energy transfer efficiencies from PTAK PLE spectra, we first fit the OD spectrum of a dilute isolated PTAK solution to a sum of 4 Gaussian functions with *unconstrained* fitting parameters over the 300 nm to 700 nm range. These fitting parameters were then used as starting inputs for a *constrained* fit of CPEC PLE spectra. First, for each CPEC, we identified the longest wavelength above which the donor EET contribution to the PTAK PL was approximately zero such that the PLE in this region was due to directly excited PTAK alone. Then we fit the PLE spectrum above this wavelength cutoff to a sum of 4 Gaussian functions where each fitting parameter (amplitude, center, and width) was allowed to vary by ~10-15% of the values found in the PTAK OD fit. An additional common multiplicative scaling factor was applied identically to each Gaussian fitting function. The need to allow each OD fitting parameter to vary by ~10-15% relative to the OD fit arose because the PTAK spectrum underwent a qualitative change upon binding to a cationic donor CPE. Although a fully constrained fit was also attempted, it was clear that such a functional form was qualitatively inappropriate given the change in PLE peak position and spectrum shape on the red side compared to the isolated PTAK OD spectrum. Fits to the red side of the PLE are shown below as dashed red curves. Above the lower wavelength cutoff the PLE fit is clearly of excellent quality.

We proceeded to subtract the red-side PLE fit from the measured PLE spectrum, obtaining the raw contribution to the PTAK PLE due to EET from the donor CPE (teal dashed curves below). As described in the main text, the integral under the resulting curve is related to the relative EET efficiency. The complication that accompanies this estimation stems from the fact that the behavior of the PLE spectrum in the donor EET region is not known. The fitted PLE on the red side, which forms the background intensity on top of which the donor EET contribution sits, is effectively a reasonable guess.

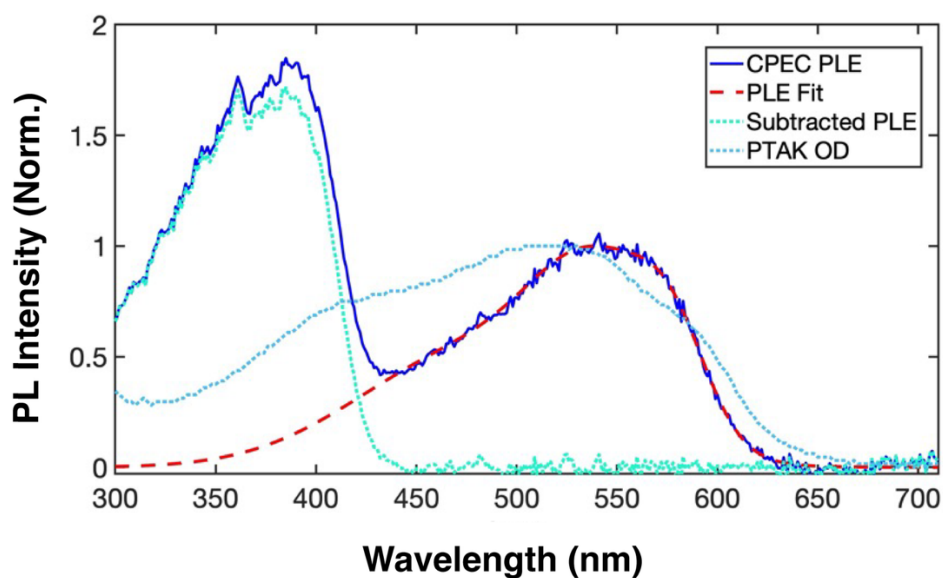


Figure II: CPEC PLE Fit for PFNB:PTAK and native PTAK OD.

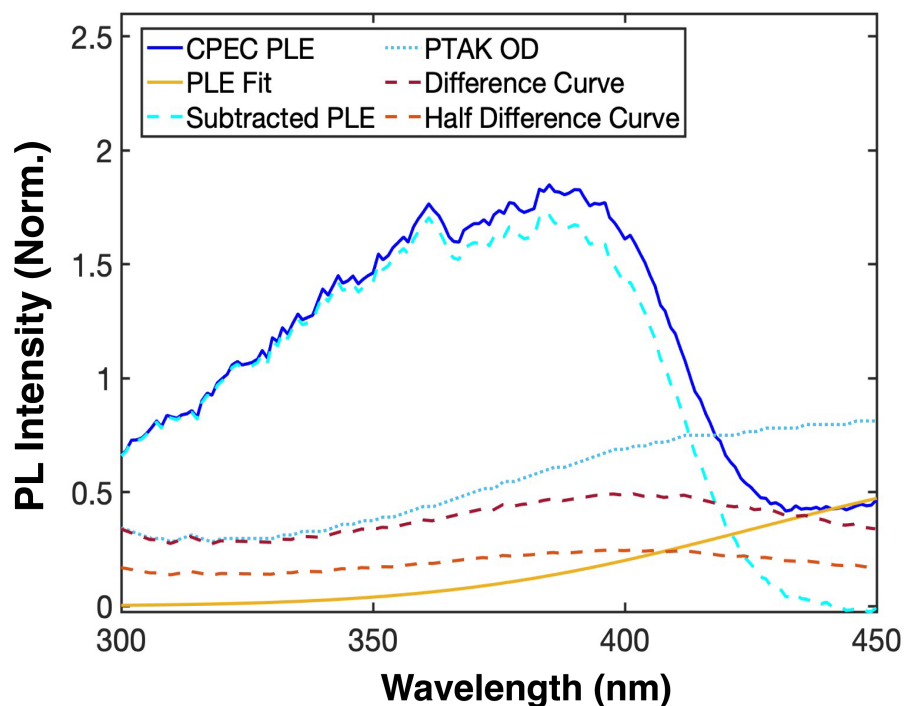


Figure I2: Shown as the blue dashed curve is the calculated PFNB donor contribution to the PLE curve. The difference curve (red dashed curve) is the product of the experimental PTAK OD and the calculated PTAK contribution. The half of this difference curve was produced (orange dashed curve) to calculate the error in E^{rel} .

We aimed to obtain a conservative estimate of the donor EET contribution that would at least partially and systematically account for the fact that the fitted background intensity corresponded to an estimate. To do so, we note that the normalized PTAK OD spectrum (dashed light blue curve below) lies well above the

fitted PLE spectrum. Thus, we reasoned that the true PLE background intensity on top of which the donor EET contribution sits would lay somewhere between the fitted spectrum and the measured OD spectrum. To obtain a minimally biased estimate of the relative EET efficiency, we subtracted the (peak-normalized) PLE fit from the (peak-normalized) OD spectrum to form a difference curve which, point by point, represented the effective uncertainty in the true background intensity of the EET contribution. We thus believed that the least biased estimate was to take the background intensity as equal to half the difference curve. That is, the estimated background intensity at every wavelength was taken to lie exactly halfway between the fitted PLE spectrum and the measured OD spectrum. This contribution was further subtracted from the extracted donor EET peak (teal curve), and the remaining curve was integrated to form E^{rel} as described in the main text.

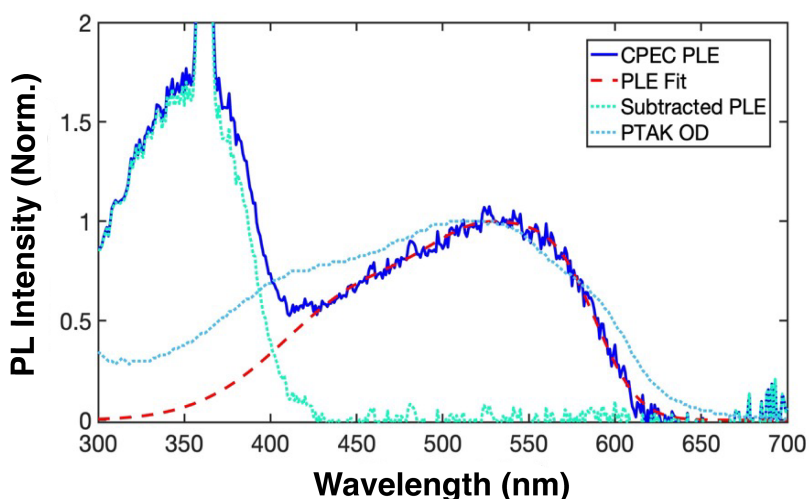


Figure I3. CPEC PLE fir for PFNF2:PTAK and native PTAK OD

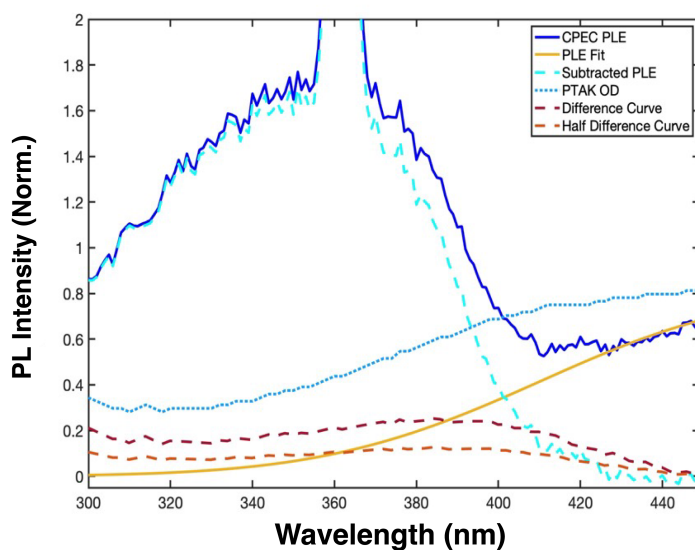


Figure I4: Shown as the blue dashed curve is the calculated PFNF2 donor contribution to the PLE curve. The difference curve (red dashed curve) is the product of the experimental PTAK OD and the calculated PTAK contribution. The half of this difference curve was produced (orange dashed curve) to calculate the error in E^{rel} .

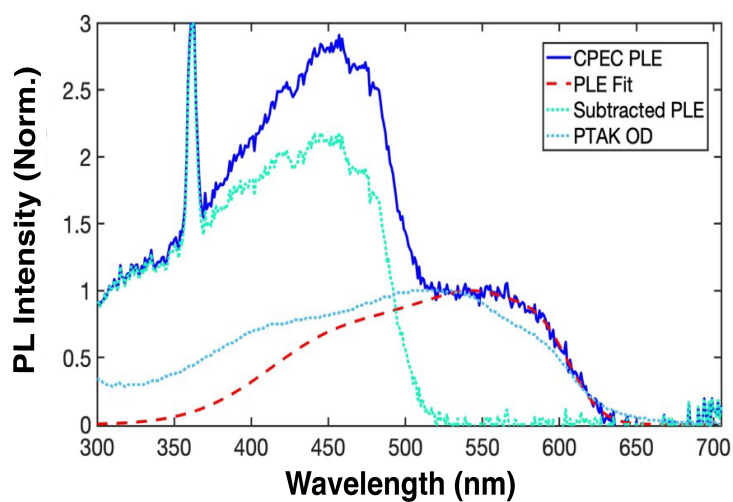


Figure I5: CPEC PLE Fit for PFNT2:PTAK and native PTAK OD

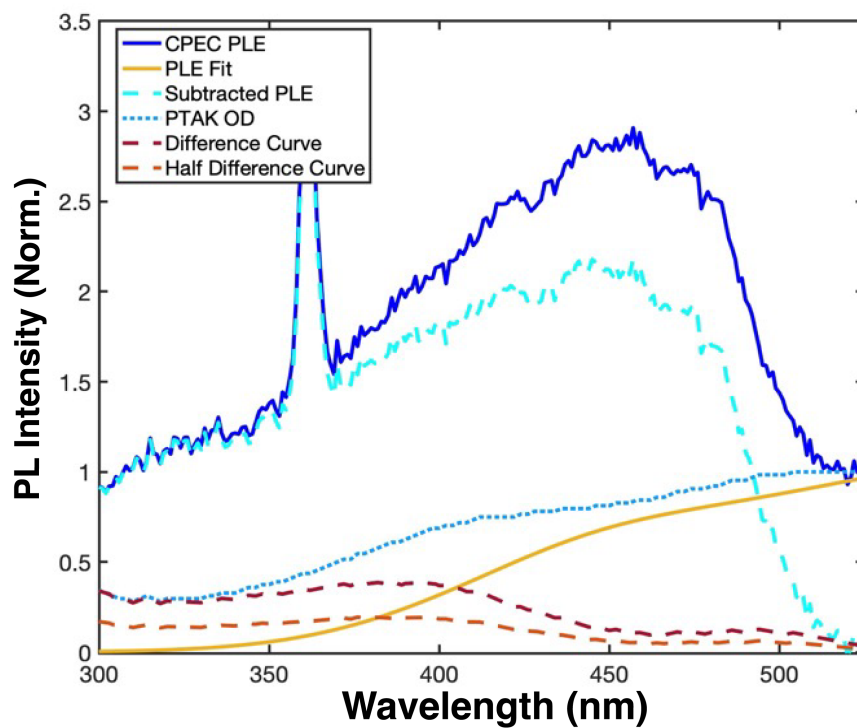


Figure I6. Shown as the blue dashed curve is the calculated PFNT2 donor contribution to the PLE curve. The difference curve (red dashed curve) is the product of the experimental PTAK OD and the calculated PTAK contribution. The half of this difference curve was produced (orange dashed curve) to calculate the error in E^{rel} .

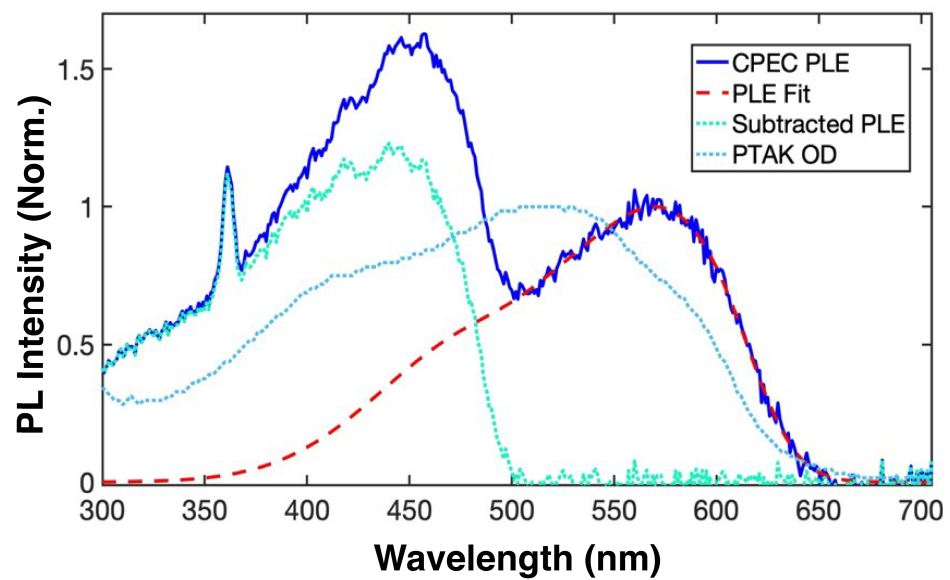


Figure I7. CPEC PLE Fit for PFNT1:PTAK and native PTAK OD

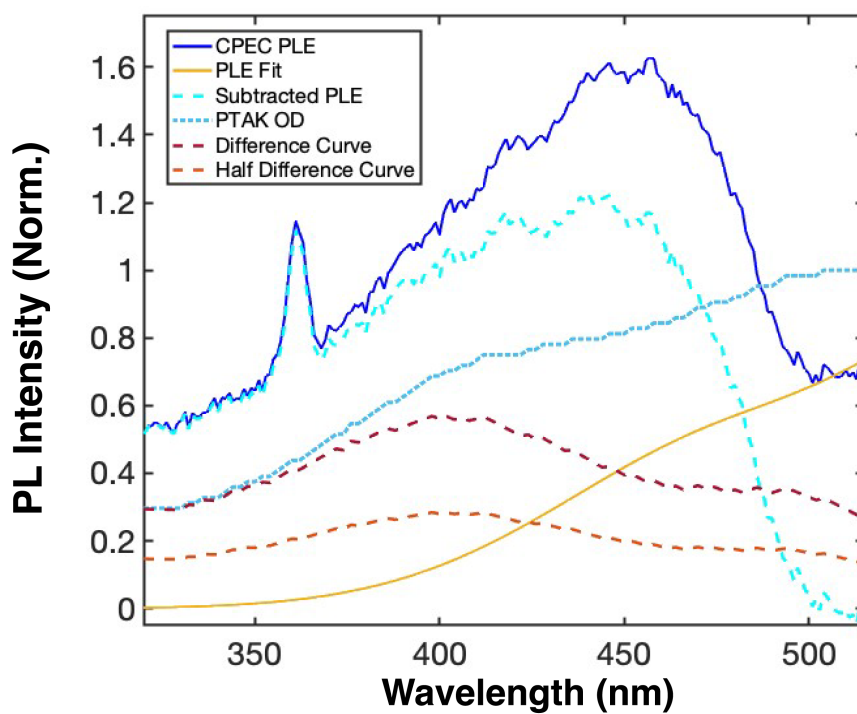


Figure I8. Shown as the blue dashed curve is the calculated PFNT2 donor contribution to the PLE curve. The difference curve (red dashed curve) is the product of the experimental PTAK OD and the calculated PTAK

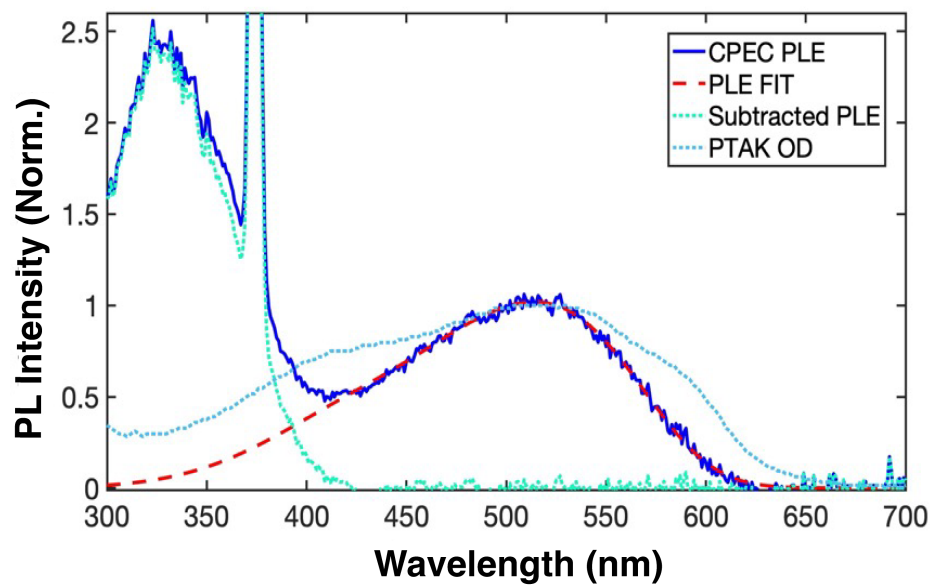


Figure I9: CPEC PLE Fit for PFNF4:PTAK and native PTAK OD

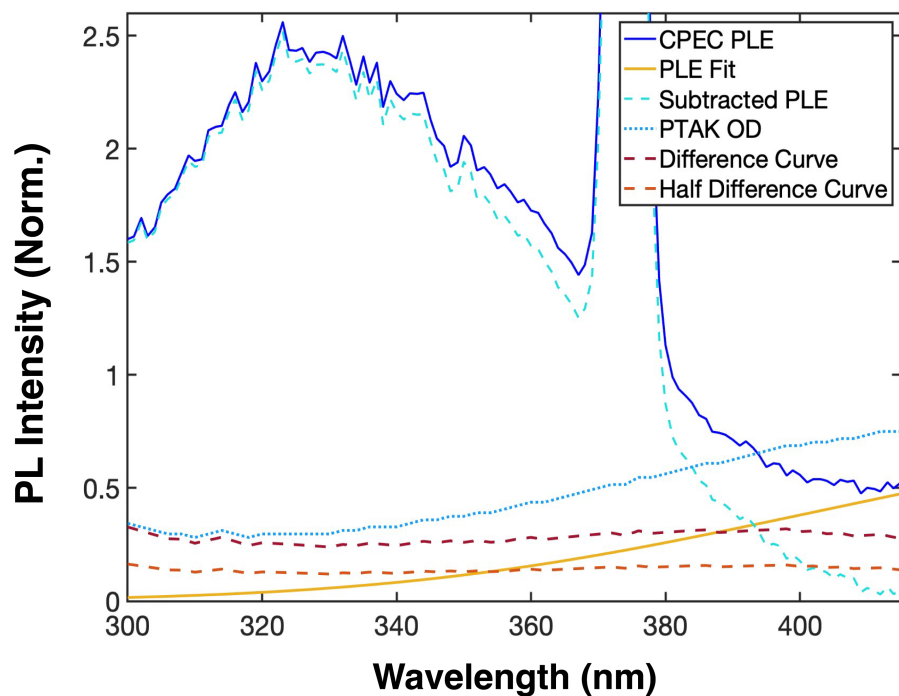


Figure I10 Shown as the blue dashed curve is the calculated PFNT2 donor contribution to the PLE curve. The difference curve (red dashed curve) is the product of the experimental PTAK OD and the calculated PTAK contribution. The half of this difference curve was produced (orange dashed curve) to calculate the error in E^{rel} .

I.2 Transient Absorption of PFNX:PTAK CPECs

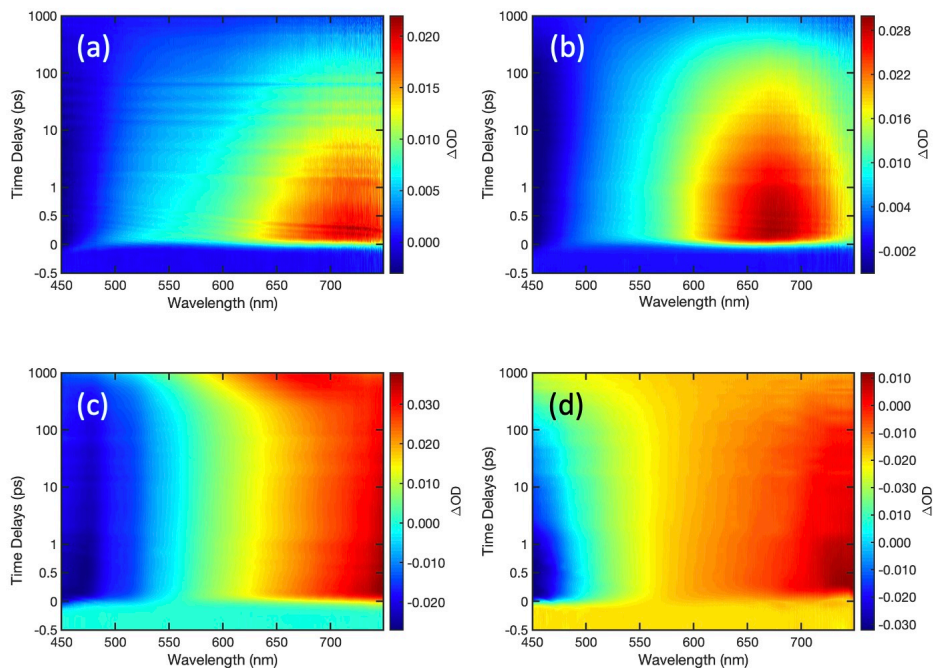


Figure I11. Transient absorption spectra obtained with uncomplexed (isolated) donor CPEs presented in a false-color contour representation: (a) F4, (b) F2, (c) T1, (d) T2. Spectra were collected following excitation near the peak of the steady-state absorption spectrum of each donor (excitation wavelength is indicated in each subpanel). Spectral dynamics are explained in the text. The same data is presented as a spectral waterfall plot in Figure 3 of the main text.

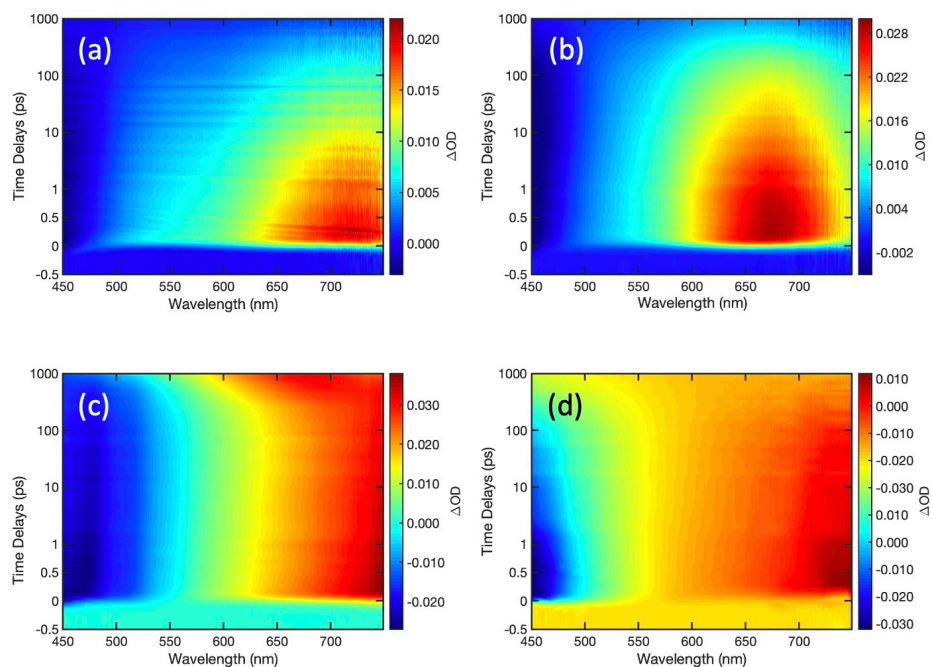


Figure I12. Transient absorption spectra obtained with PFNX:PTAK CPECs presented in a false-color contour representation: (a) F4, (b) F2, (c) T1, (d) T2. Spectra were collected following excitation near the peak of the steady-state absorption spectrum of each donor (excitation wavelength is indicated in each subpanel). Spectral dynamics are explained in the text. The same data is presented as a spectral waterfall plot in Figure 4 of the main text.

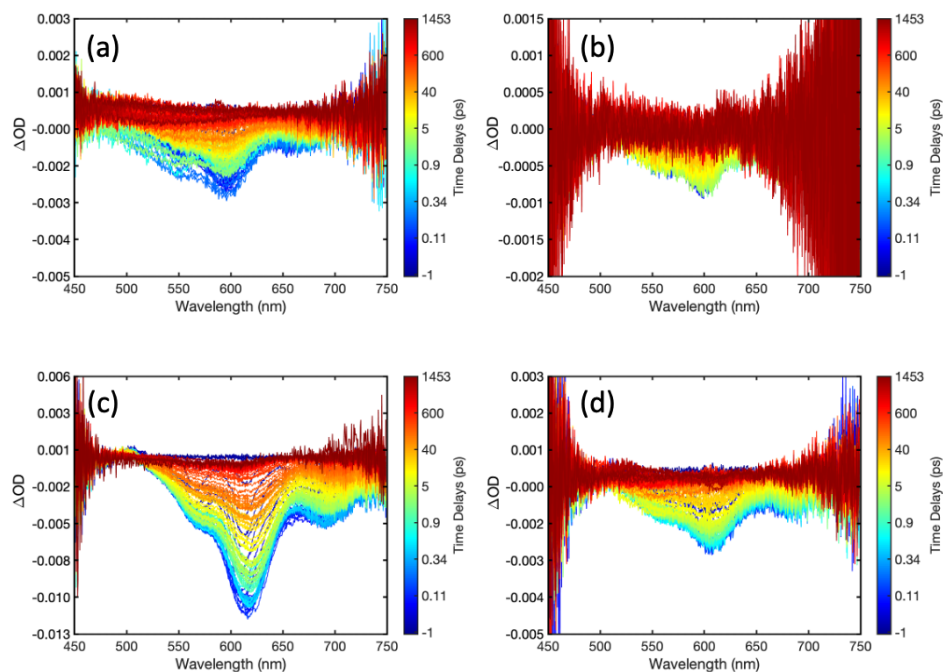


Figure I13. Transient absorption spectra obtained through selective excitation of PTAK in PFNX:PTAK CPECs at 600 nm: (a) F4, (b) F2, (c) T1, (d) T2.

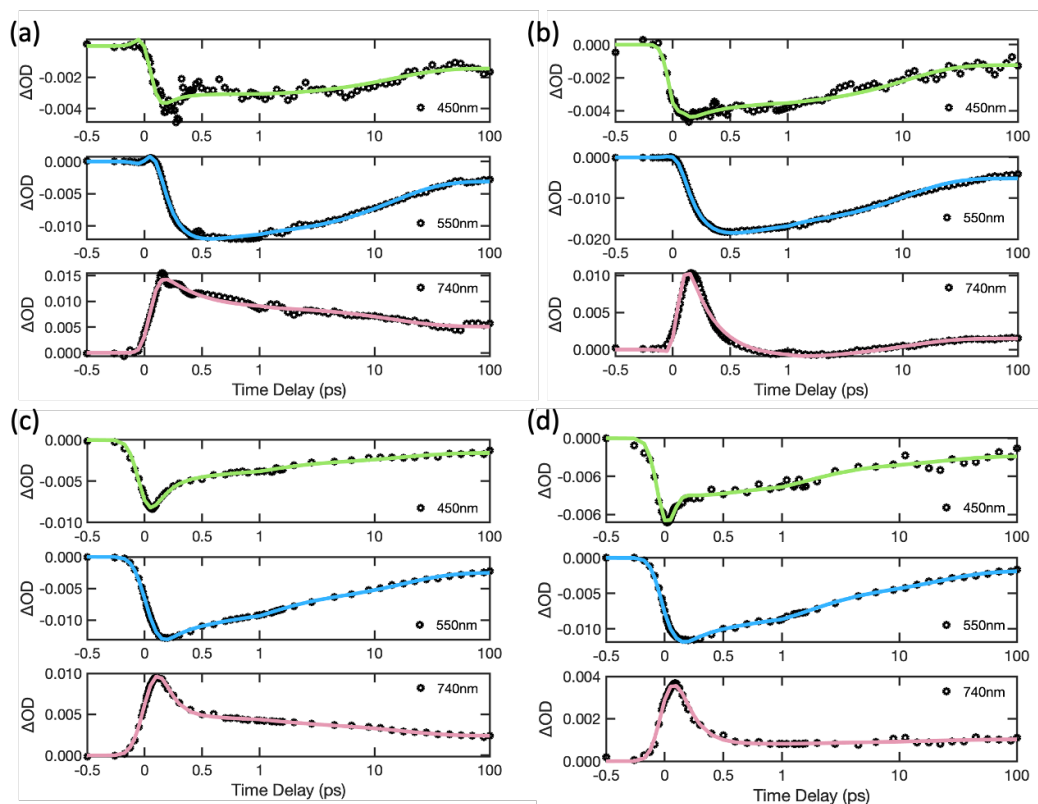


Figure I14. Time-dependence at selected probe wavelengths with excitation of PFNX:PTAK CPECs. (a) F4, (b) F2, (c) T1, (d) T2. Data are shown with symbols, fits determined by global analysis as lines. Lifetimes corresponding with fitted kinetic models are summarized in Table S3.1.

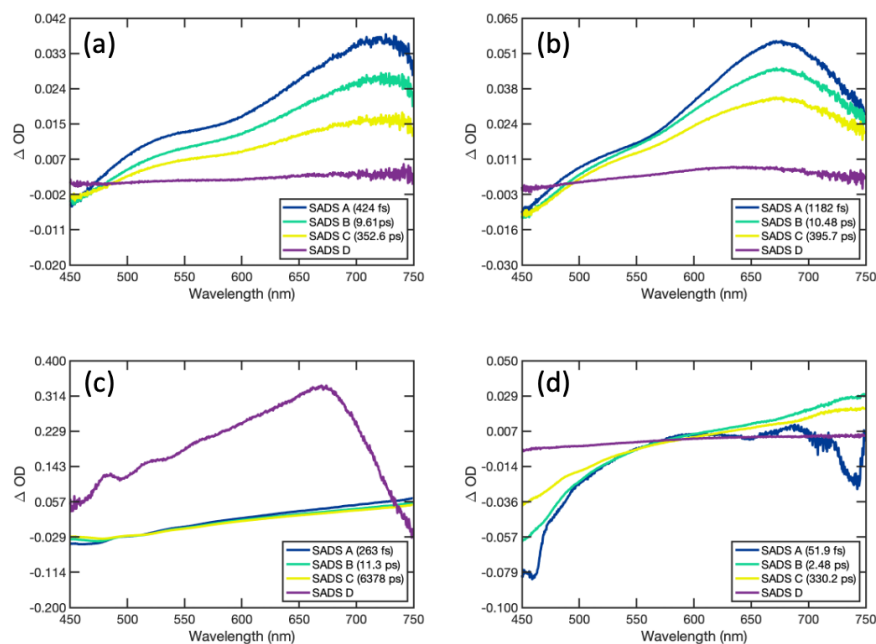


Figure I15. Species Associated Difference Spectra (SADS) obtained from global analysis of transient absorption spectra collected with donor CPEs using the four-state kinetic interconversion model expressed by Equation 5. (a) F4, (b) F2, (c) T1, (d) T2. Lifetimes corresponding with each SADS are listed in Table S3.2.

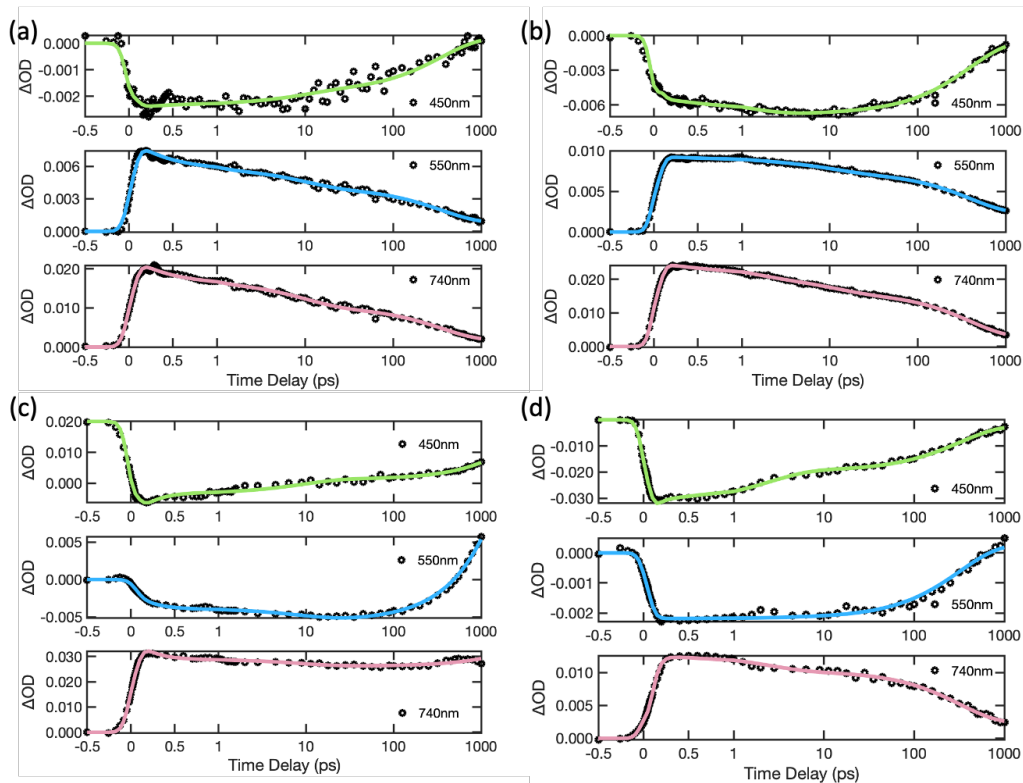


Figure I16. Time-dependence at selected probe wavelengths with excitation of donor CPEs. (a) F4, (b) F2, (c) T1, (d) T2. Data are shown with symbols, fits determined by global analysis as lines. Lifetimes corresponding with fitted kinetic models are summarized in Table S3.2.

Table I1. Best-fit lifetimes determined from global analysis of TA data collected with PFNX:PTAK CPECs subject to a four-state sequential kinetic interconversion model (Equation 5 of the main text).

	F4	F2	T1	T2
τ_1 (fs)	156	236	95.6	134
τ_2 (ps)	0.259	0.241	1.0	1.54
τ_3 (ps)	14.2	10.6	17.2	21.1

Table I2. Best-fit lifetimes determined from global analysis of TA data collected with donor CPEs subject to a four-state sequential kinetic interconversion model (Equation 5 of the main text).

	F4	F2	T1	T2
τ_1 (fs)	424	1180	263	52
τ_2 (ps)	9.6	10.5	11.3	2.5
τ_3 (ps)	353	396	6380	330

I.3 Slow Dynamics and Energy Transfer of PFNX:PTAK Complexes

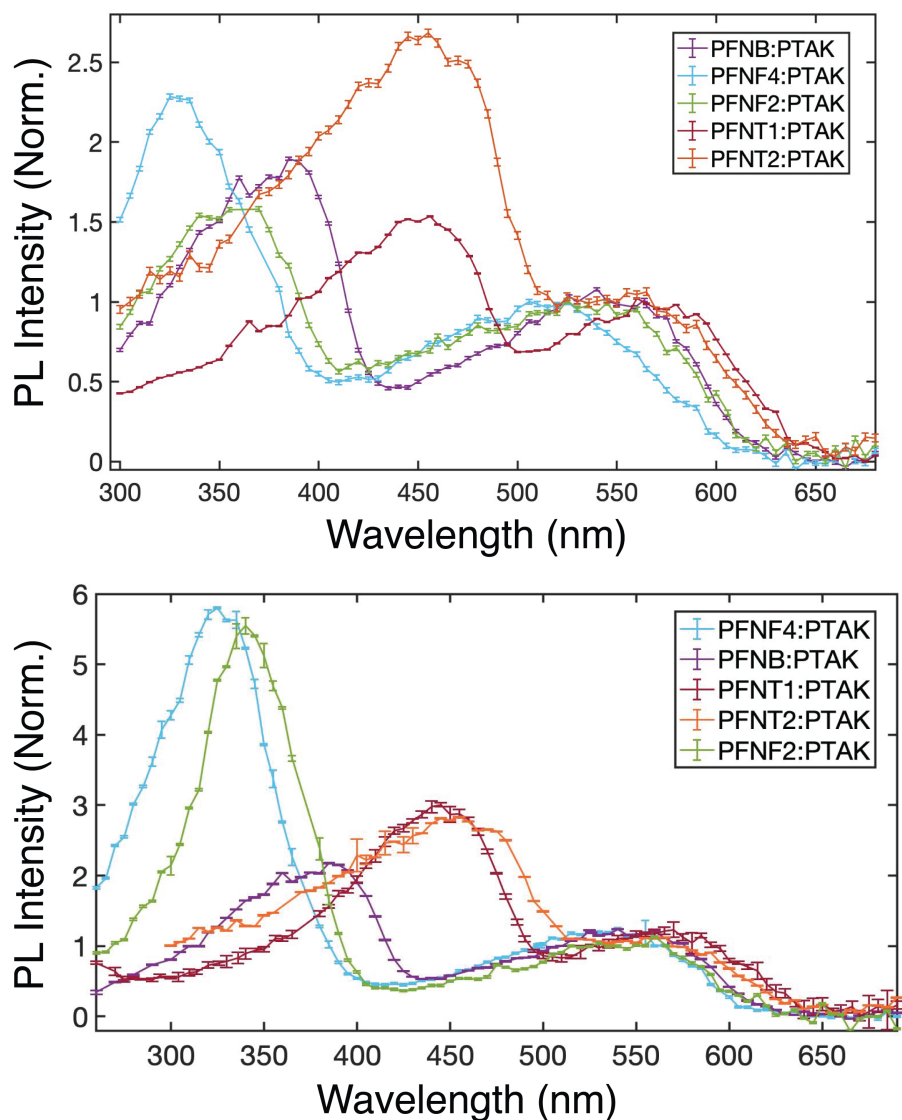


Figure I17: Photoluminescence excitation (PLE) spectra of the PFNX: PTAK series when complexes were (a) freshly made and (b) after 2 weeks.

I.4 DFT Calculations

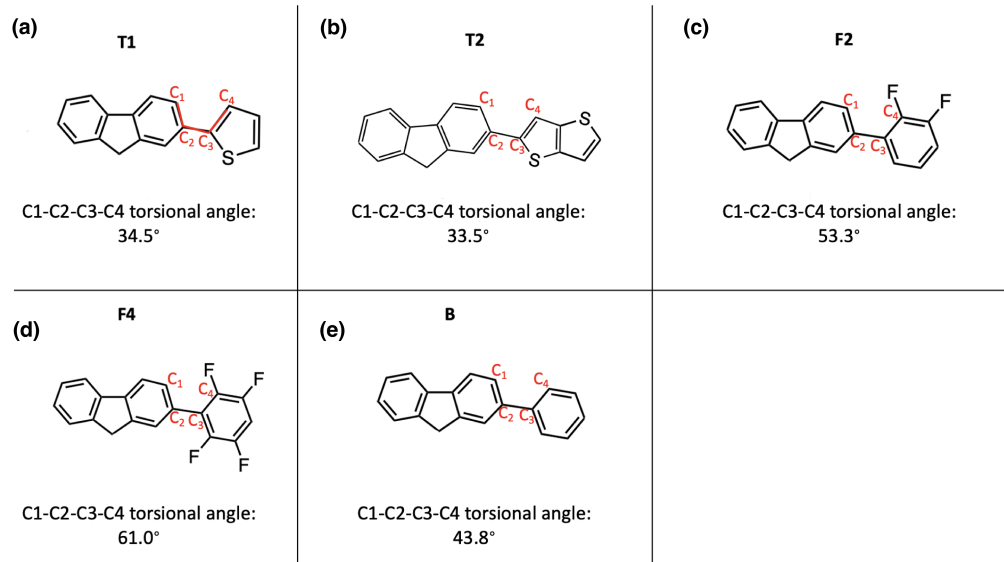


Figure I18: Torsional angles along linkage bonds of the ground-state equilibrium geometries of co-monomer units for PFNF2 (a), PFNF4 (b), PFNT1 (c), PFNT2 (d), and PFNB (e).

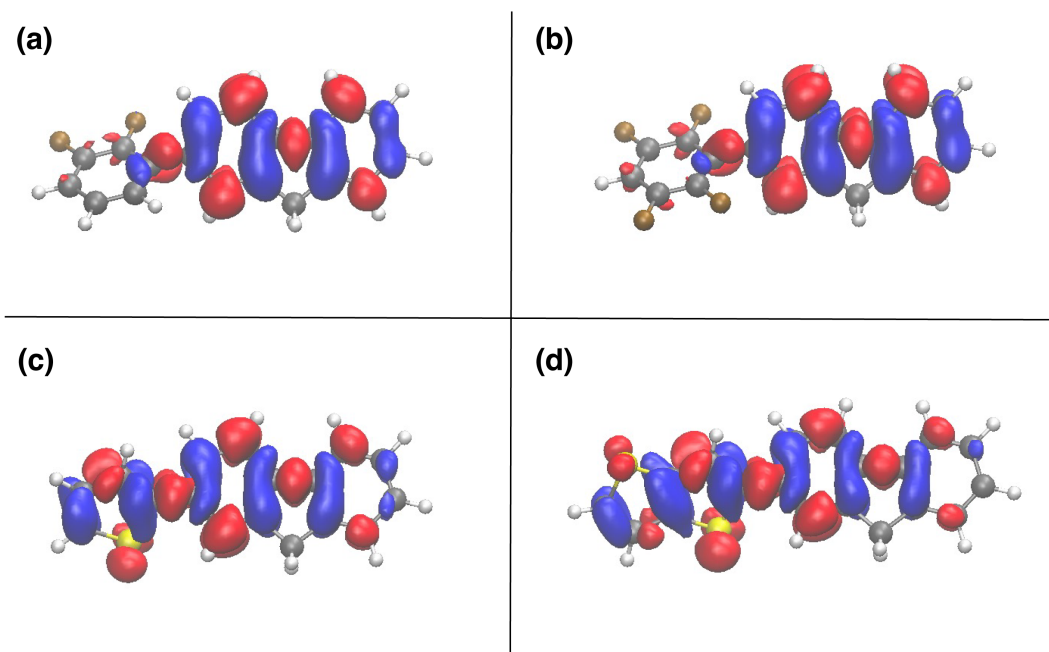


Figure I19 Charge difference density for donor repeat unit of PFNF2 (a), PFNF4 (b), PFNT1 (c), and PFNT2 (d) on the electronic transition from the ground state to the lowest excited state. The blue and red colors correspond to negative and positive isosurfaces, respectively. The isovalue is 8×10^{-4} in a.u.

Chapter III:

A New Pathway Towards Aqueous Organic Photovoltaics via Associative Phase Separation of Conjugated Polyelectrolytes

Acknowledgements: This chapter includes ultra-fast pump-probe transient absorption spectroscopy that was done in collaboration with Dr. Jin Zhang's group at UCSC. Atomic Force Microscopy measurements were conducted in collaboration with Dr. David Lederman's group at UCSC. Cryo-EM images and subsequent analysis were completed in collaboration with Dr. Vitor Hugo Balasco Serrão, in the Biomolecular Cryoelectron Microscopy Facility at UCSC. Grazing-Incidence X-Ray Scattering measurements performed at the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. Thin-film deposition and photovoltaic characterization were carried out at the Molecular Foundry at Lawrence Berkeley National Laboratory with the help of Dr. Steven Shelton.

Abstract: We report a fully aqueous-processable organic active layer based on electrostatically assembled conjugated polyelectrolyte complexes (CPECs) formed by associative phase separation of the cationic poly(fluorene-*alt*-phenylene) CPE (PFNB) and anionic poly(cyclopentadithiophene-*alt*-phenylene) CPE (PCPT). Upon complexation, the CPEC forms a concentrated complex fluid with viscoelastic

rheological properties that render it directly coatable as an active layer material. Small-molecule electron acceptors, both a fullerene and a non-fullerene acceptor, are incorporated into the CPEC via a nonionic surfactant micelle delivery strategy, with quantitative surfactant removal confirmed by dynamic light scattering and systematic acceptor retention confirmed by UV-Vis spectroscopy. Grazing-incidence small-angle X-ray scattering and cryogenic electron microscopy reveal that both acceptors create long-range order within the amorphous CPEC network, with NFA inducing substantially greater long-range domain coherence. Magic angle time-resolved photoluminescence demonstrates instrument-response-limited quenching of the PCPT excited state by both acceptors. Ultrafast transient absorption spectroscopy provides definitive mechanistic confirmation of charge transfer at the CPEC-acceptor interface: in acceptor-loaded films, the polaron band persists significantly longer than the exciton band (172 ps versus 92.4 ps for NFA; 175 ps versus 54.3 ps for FA), while in the bare CPEC reference all probe wavelengths yield identical lifetimes of 270–291 ps with no such differential, establishing the longer-lived polaron band as a direct consequence of hole-polaron accumulation following interfacial charge transfer to the small molecule acceptor.

3.1 INTRODUCTION

The global need to replace fossil fuels with renewable energy has driven sustained interest in solar cell technologies that are not only efficient but genuinely sustainable in their manufacturing. Organic photovoltaics (OPVs) are compelling in this regard: they can be fabricated on lightweight, flexible substrates using solution

casting methods, and their active-layer chemistry and the subsequent spectral response give bandgap tunability across a wide range of the visible and near-IR spectrum.¹⁹ Power conversion efficiencies in the OPV field have become quite impressive with the emergence of non-fullerene acceptors (NFAs), enabling devices that now routinely exceed 19% in single-junction architectures.¹⁹ Yet a stubborn contradiction sits at the heart of OPV technology: the organic semiconductors at the core of these devices are almost universally processed from aromatic solvents such as chlorobenzene, chloroform, 1,2-dichlorobenzene, and other benzene derivatives. These solvents are acutely toxic, require costly containment and disposal infrastructure, and impose a substantial environmental burden that is largely incompatible with the sustainability narrative OPVs are meant to embody.^{11,19} The field's push toward "green" processing has largely substituted one class of organic solvents for another: non-halogenated alternatives such as tetrahydrofuran, 2-methyltetrahydrofuran, and *o*-xylene reduce some toxicity concerns but remain volatile organic compounds subject to handling, emissions, and regulatory constraints.¹⁹ Truly eliminating organic solvents from OPV fabrication altogether has remained a grand challenge in this field.

By far the most attractive route to overcome these issues is to use water as the medium from which the solar cell active layer is deposited. To date, the most promising strategy for achieving aqueous processing of nonpolar organic semiconductors has been the use of semiconducting nanoparticle (NP) dispersions. There are two primary approaches: mini-emulsion and nanoprecipitation. In the mini-

emulsion method, NPs are created starting with an organic solution containing either the isolated donor and acceptor separately or a blend of the two. Amphiphiles such as surfactants or block co-polymers are added, and the organic solution is brought in contact with water. Evaporation of the organic solvent leads to an aqueous solution containing surfactant-coated organic-semiconductor NPs. In nanoprecipitation, organic semiconductors are first dissolved in an organic solvent that is miscible with water, such as THF. Water is then added, which changes the dielectric constant and induces precipitation of the photoactive components, forming NPs free of surfactants. These methods have received substantial attention, and recent results clearly demonstrate that these approaches hold significant promise.

As successful as mini-emulsion and nanoprecipitation strategies have been, NP approaches to aqueous organic photovoltaics (aOPV) are nevertheless characterized by certain limitations. First, an organic solvents is still needed for the formation of the solar-cell active layer. Fully aqueous processing would be significantly more attractive for industrial mass production. Second, exquisite control over NP characteristics is required, and the formation of the thin film itself may be challenging or lead to metastable morphologies. Finally, the rheological properties of NP solutions may lead to challenges with forming flexible and stretchable devices. The preferred fabrication method largely remains spin-coating. For mass production, solution-shearing or related approaches would likely take the place of spin-coating. Such methods are still likely to lead to challenges with fabrication of large-area panels, particularly those requiring coating of surfaces with complicated form factors.

A qualitatively different route to aOPVs becomes possible when the semiconductors are water-soluble π -conjugated polyelectrolytes (CPEs). In the context of organic solar cells, CPEs have been extensively studied as ultrathin *interlayers* to modify electrode work functions and to promote charge extraction.²¹ In contrast, the rich phase behavior of aqueous CPE solutions may make them particularly intriguing as potential aOPV *active layers* that utilize entirely aqueous processing in their formation. Our lab has shown that when a cationic and an anionic CPE are electrostatically complexed in water at near-stoichiometric charge ratios, the system undergoes associative phase separation to form a concentrated complex fluid enriched with CPE complexes that coexists with the dilute aqueous solution.¹ The rheological properties of the CPE complex fluid (CPEC fluid) are such that it can be directly coated as a paste onto substrates of varying form factors; the resulting dried films are stable against delamination in water or in humid environments.¹ The thermodynamics of CPEC fluid formation depends on the CPEC charge density and the presence of excess salt, allowing one to use the ionic environment to manipulate both the mechanical and optoelectronic properties of the fluid.

We previously demonstrated that if the two CPEs form an exciton donor/acceptor pair, highly efficient, ultrafast electronic energy transfer takes place between the two polymers in the CPEC fluid. This is advantageous for increasing the spectral range of light harvesting. In this report, two primary questions are addressed: (i) can an *exciton* donor/acceptor CPEC fluid be constructed to convert excitons into photoinduced *electron/hole* pairs? (ii) If so, are the electron/hole pairs sufficiently

mobile to give rise to a photocurrent? To answer these questions, we used nonionic micelles were impregnated with two quintessential fullerene- and nonfullerene-based electron acceptors to infiltrate the CPEC fluid. The photoinduced generation of electron/hole pairs was demonstrated. Proof-of-principle devices were constructed showing the generation of a photocurrent upon illumination. After considering the advantages and shortcomings of the current approach, a viable, purely water-based pathway towards aOPV devices based on CPEC fluids has been demonstrated.

3.2 EXPERIMENTAL

Sample Preparation. The aOPV devices were prepared using the same strategy. The CPEC active layer was formed from a complex fluid at a 1:1 charge-matched electrostatic assembly. The anionic CPE (PCPT) with a MW = 40,000 Da (PDI = 3), obtained from 1-Material, and used as received. The cationic CPE (PFNB) with a MW = 21,000 Da (PDI = 1.2), obtained from Solaris Chem, and used as received. The resulting CPEC rich complex fluid was then infiltrated with photoinduced electron acceptors: fullerene (FA) was obtained from  and was used as received and non-fullerene acceptor NFA was obtained from  and was used as received. Infiltration of acceptor into CPEC complex fluid was achieved via a micelle delivery method, where the micelle was impregnated with a small-molecule acceptor of a desired concentration, the details of which can be found in “II-1.2. Acceptor Incorporation via Micelle Delivery” in Appendix II. The acceptor-containing micelles were then added to a solution containing each of the CPEs before the thermally driven complexation process began. The complex fluid was then blade-coated uniformly

onto the substrate. After deposition and subsequent drying of the film, the micelles were thermally burst and forced to release the acceptor into the active layer interface. This release procedure includes a two pronged approach: (1) soaking the film in HPLC water at 80°C for 3 hours and (2) heated complex fluid before deposition onto substrate. More information regarding surfactant extraction from active layer can be found in “**II-1.4. Surfactant Extraction Procedure**”. The active layer was then annealed onto the substrate at 150°C in an inert environment. The resulting aqueous solution containing only surfactant was retained for further analysis and the film was then prepared for cathode deposition. Aluminum devices were deposited via physical vapor deposition onto the chips, which resulted in fully realized devices.

Steady-State Spectroscopic Measurements. Optical density (absorption) measurements were collected from the above solutions using a Shimadzu UV-2700 spectrometer. Spectra were collected over the 300–800 nm wavelength range in 1.0-nm increments, with a thin film adaptation to the sample holder.

Time-Resolved Photoluminescence. Time-correlated single photon counting (TCSPC) measurements were carried out on a home-built setup, described in **Chapter I**. Briefly, the excitation source was a pulsed picosecond SuperK EXTREME (NKT Photonics) supercontinuum laser coupled to a SuperK SELECT (NKT Photonics) acousto-optic filter and an external RF driver (NKT Photonics) to select the wavelength of the excitation pulse. With the supercontinuum laser, all samples were excited at 480 nm, resonant with PCPT absorption, which serves as a spectroscopic handle for the CPEC excited state. Emission was measured on a hybrid

photomultiplier tube (Becker and Hickl, GmbH). The signals were then sent to a Simple Tau SPC-130 (Becker and Hickl, GmbH) for initial data visualization and analysis. Long-pass filters were used on the detection arm with a 580 nm onset. Subsequently, the monochromator was set to collect emission intensity at 625 nm. All measurements were taken in a front-faced sample configuration while the excitation and detection Glan-Thompson polarizers were offset from each other by the magic-angle (54.7°) to minimize polarization effects.

Dynamic Light Scattering. Dynamic light scattering (DLS) measurements were performed on salt-free solutions of the charged polymer series using a BI-200SM goniometer (Brookhaven Instruments Corporation) equipped with a 637 nm CW diode laser (Mini L-30, Brookhaven Instruments Corporation). Scattered light was collected at 90° by an avalanche photodiode (BI-APDX, Brookhaven Instruments Corporation). Prior to measurement, samples were passed through a $0.45\ \mu\text{m}$ nylon fiber filter and transferred into 12 mm borosilicate glass tubes, which were immersed in a decahydronaphthalene index-matching bath to suppress stray scattering from the tube walls. Intensity signals were routed to a TurboCorr correlator (Brookhaven Instruments Corporation) to generate the autocorrelation function, from which diffusion coefficients were extracted via CONTIN analysis implemented in MATLAB. The regularization parameter α was set to 0.1; varying both α and point density produced negligibly different relaxation times, confirming that this value does not over-smooth the relaxation time distribution.

Small Angle X-ray Scattering. SAXS measurements were conducted at Stanford Synchrotron Radiation Laboratory, specifically using beamline 4-2. This beamline is equipped with a Pilatus 3X detector and a robotic autosampler that feeds samples from a 96-well plate to a thin-walled quartz capillary cell. In order to avoid degradation, each sample was oscillated during the duration of exposure to radiation. The samples were irradiated with 10 consecutive 1s exposures at 11 keV at a sample distance of 1.7 m, this setup yielded an effective q -range of 0.0068–0.67 Å⁻¹. With the aid of the SASools software suite, averaged, totaled, and background-subtracted datasets were used in analysis and plotting of SAXS data.

Grazing Incidence Small-Angle X-ray Scattering (GI-SAXS).

GI-SAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 1-5. The beamline is equipped with a Pilatus area detector configured for grazing-incidence geometry. Polymer thin films were mounted on silicon substrates and aligned at an incident angle slightly above the critical angle to enhance surface sensitivity and minimize substrate scattering. Measurements were conducted at an X-ray energy of 12 keV with a sample-to-detector distance of approximately 2 m, yielding an effective q -range of 0.006–0.7 Å⁻¹. Scattering patterns were averaged over multiple 1s exposures to minimize radiation damage. Data were corrected for background, detector geometry, and polarization effects, then azimuthally integrated using the Nika software package implemented in Igor Pro.

Grazing Incidence Wide-Angle X-ray Scattering (GI-WAXS). GI-WAXS

measurements were conducted at SSRL on beamline 11-3, equipped with a Pilatus detector optimized for high- q measurements in grazing-incidence geometry. Samples were measured at an X-ray energy of 12 keV with a sample-to-detector distance of approximately 0.25 m, providing access to crystalline and molecular-scale ordering. Data were collected as a series of 1 s exposures to reduce radiation-induced effects. Two-dimensional scattering images were corrected for detector response and background, then processed and azimuthally integrated using the WAXStools suite in Igor Pro to obtain one-dimensional intensity profiles for structural analysis.

Atomic Force Microscopy. Sample topography was measured at room temperature using tapping-mode atomic force microscopy (AFM) on an Oxford Cypher AFM. Measurements were performed using a NanoWorld POINTPROBE FMR-50 silicon SPM sensor with an aluminum coating on the detector side. During imaging, the drive frequency and drive amplitude were 81.071 kHz and 2.64 V, respectively. For the $30 \times 30 \mu\text{m}^2$ scan windows, a scan rate of 0.10 Hz was used, while the $10 \times 10 \mu\text{m}^2$ scan window was acquired at 0.25 Hz. A scan rate of 0.10 Hz was also used for the $30 \times 30 \mu\text{m}^2$ scan window used to measure the step height. These relatively low scan rates were selected to improve tip tracking and image quality due to the rough nature of the sample surface.

Electrode Evaporation. Thin-film deposition was carried out at the Molecular Foundry (Lawrence Berkeley National Laboratory) using two thermal evaporation systems integrated with nitrogen glove boxes for controlled atmosphere processing

and precise rate and thickness monitoring. The MBRAUN thermal evaporator was used for depositing thin layers of organic and metallic materials under high vacuum conditions ($\sim 10^{-6}$ mbar). The system accommodates up to four independent sources for sequential multilayer deposition (without co-deposition) and includes an optional quartz lamp heater for substrate treatment. The MBRAUN thermal evaporator was employed for the deposition of organic, metallic, and lead halide precursor layers, dedicated to the processing of perovskite-containing samples. This system supports up to two independent sources for sequential multilayer deposition (without co-deposition).

Photovoltaic Characterization. Photovoltaic characterization was conducted at the Molecular Foundry (Lawrence Berkeley National Laboratory). Current–voltage characteristics of the devices were measured using a 150 W Thermal-Oriel solar simulator equipped with an AM 1.5G filter and a Keithley 2400 source meter. Custom-designed test cells were employed to hermetically seal devices under nitrogen for measurements performed outside of the glove box.

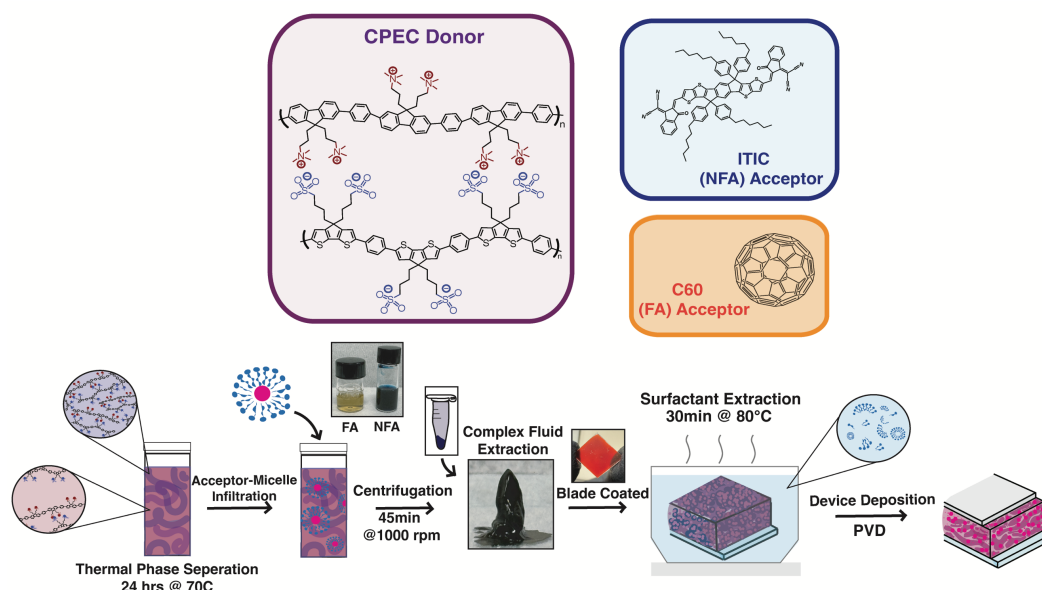
Ultra-Fast Pump-Probe Transient Absorption. Femtosecond TA measurements were taken using a Light Conversion laser system in a previously reported configuration.^{1,2} The fundamental beam with an output fundamental wavelength of 1030 nm, 10 W power, a repetition rate of 20 kHz, and pulse width of 160 fs was generated by PHAROS (Light Conversion). PHAROS is equipped with a ytterbium-doped potassium gadolinium tungstate (Yb:KGW) lasing medium. Tunable pump wavelengths were produced by feeding 80% of the fundamental beam into an optical

parametric amplifier (OPA), ORPHEUS (Light Conversion). A white light continuum probe beam was generated by passing the remaining 20% of the fundamental through a nonlinear sapphire crystal. The generated pump and probe beams were aligned in an ultrafast TA system, HARPIA (Light Conversion). Spatial alignment was controlled by mirrors, while temporal overlap was controlled by a translating delay stage. For measurements, the time delay between pump and probe pulses was varied from -10 to 5000 ps. Data were collected using the Light Conversion HARPIA data acquisition software and using an Oxford Instruments Andor spectrometer.

3.3 RESULTS

Active Layer Formation

The chemical structures of the cationic poly(fluorene-*alt*-phenylene) CPE (PFNB) and anionic poly(cyclopentadithiophene-*alt*-phenylene) CPE (PCPT) are shown in Figure 3.1. To prepare the CPEC fluid, associative phase separation was induced by complexing the oppositely charged CPEs at 70°C at a nominal polyion molar charge ratio of 1:1. The temperature at which the associative phase separation is induced is a critical parameter that can significantly modulate the viscoelastic properties of the resulting CPEC fluid.²⁷ This is consistent with the complexation of oppositely charged CPEs being a thermally activated process.²⁴ The specific choice of CPEs is rooted in the fact that they form an exciton donor/acceptor pair, with PFNB acting as the exciton donor and PCPT as the exciton acceptor.^{1,18}



Scheme 3.1. Chemical structures of the CPEC donor, ITIC (NFA) acceptor, and C60 (FA) acceptor (top), and schematic of the aqueous device fabrication process (bottom): thermal phase separation of the CPEC, acceptor-micelle infiltration, centrifugation to extract the complex fluid, blade coating onto ITO, surfactant extraction, and device completion by PVD of the cathode.

Associative phase separation leads to a highly polymer-enriched complex fluid phase composed of hydrated inter-CPEC complexes (CPEC fluid) in coexistence with an extremely dilute aqueous solution. Although previous studies have demonstrated that excess salt could significantly alter the photophysical and rheological properties of the CPEC fluid, for simplicity no excess salt was added in this study.¹ When separated from the dilute solution, the rheological properties of the viscoelastic, paste-like CPEC fluid render it amenable to facile deposition via blade-coating techniques.

A critical requirement for a functioning OPV device is a photoinduced electron acceptor. Photogenerated excitons must be able to diffuse to an *electron* donor-acceptor interface where the energetic difference between the donor and acceptor frontier orbitals helps convert excitons into electron-hole pairs: the charge carrier precursors to a photocurrent.² This may occur either via the conduction-band or LUMO states if the electron donor is excited or through the valence-band or HOMO states if the electron acceptor is excited. Excited-state electron transfer is expected between the two CPEs used in this work to only a very small extent. Thus, a proper electron acceptor must be incorporated onto the CPEC fluid.

Given that the interplay between electronic and rheological properties of CPEC fluids is not well-understood, one can minimize complicating the thermodynamics and kinetics of assembly and phase separation by avoiding the use of ionic electron acceptors. However, neutral organic semiconductors are effectively insoluble in water, which precludes their direct introduction into the aqueous CPEC system. To overcome this, the nonionic oligo(ethylene glycol)-based surfactant C₁₂E₅ was utilized. Above the critical micelle concentration, the hydrophobic micelle cores can solubilize and encapsulate water-insoluble organic semiconductors, effectively rendering them water-dispersible without chemical modification.^{3,4} Quintessential fullerene (C₆₀) and non-fullerene (ITIC) small-molecule acceptors were chosen to probe the generality of our approach. In what follows, the fullerene acceptor and non-fullerene acceptor will be referred to as FA and NFA, respectively.

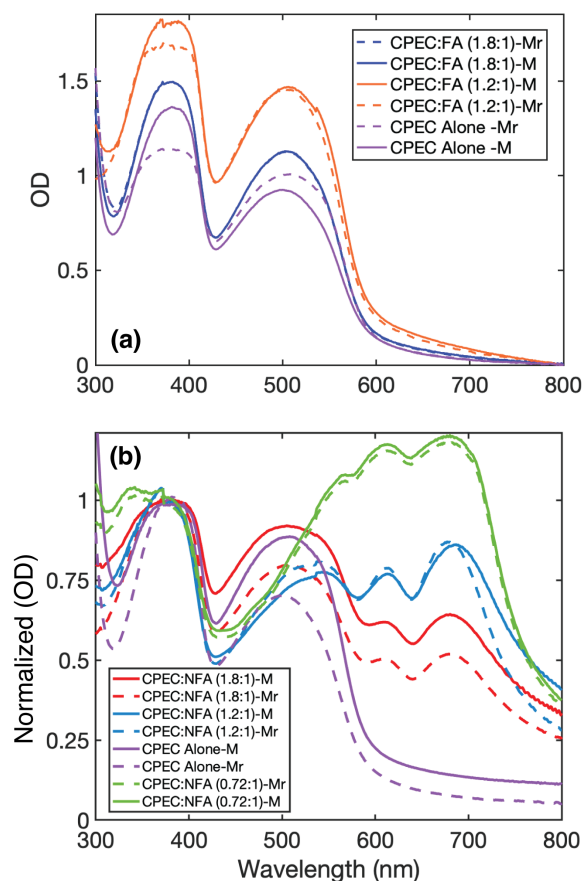


Figure 3.1. OD spectra of CPEC films as a function of acceptor loading for (A) FA and (B) NFA. Solid curves correspond to as-coated films; dashed curves correspond to films after the surfactant extraction procedure. The bare CPEC film after surfactant extraction serves as the reference in both panels.

The concentration of micelles available to solubilize electron acceptors can be calculated from the total surfactant concentration, c_s , the critical micelle concentration, c_m , and the aggregation number, N_{agg} , according to Equation 1. The encapsulated

acceptor concentration, c_{en} , is then obtained by subtracting the free (unencapsulated) acceptor concentration, c_f , from the initial acceptor concentration, c_i , as shown in Equation 2. Using this approach, the encapsulation efficiency was found to be approximately 85% for FA and approximately 91% for NFA, confirming that the micelle delivery platform is highly effective with both acceptor classes.

$$c_{en} = \frac{c_s - c_m}{N_{agg}} \quad (1)$$

$$c_{en} = c_i - c_f \quad (2)$$

Acceptor-loaded micelles were added to a vessel containing biphasic solutions containing the CPEC fluid in coexistence with its dilute phase. The sample was then stirred and centrifuged, and the hydrated acceptor-loaded CPEC fluid was isolated. The CPEC fluid was coated by hand onto either glass or ITO substrates and subsequently dried to form films.

Figure 3.1 shows UV-Vis absorption spectra of the CPEC films as a function of acceptor loading for both the FA and NFA (solid curves in panels A and B, respectively). The films exhibit the characteristic absorption bands of PFNB ($\lambda_{max} = 375$ nm) and PCPT ($\lambda_{max} = 510$ nm). The spectra show that both CPEs are present in similar concentrations when accounting for the difference in their extinction coefficients. Due to its high symmetry, FA has a very low extinction coefficient in the visible, and thus no distinct absorption band becomes clearly visible upon FA addition. However, the overall absorption magnitude increases in the UV relative to the pure CPEC film, as

expected. Figure 3.1b shows that ITIC loading in the CPEC film monotonically increases as the ITIC-containing micelle concentration increases.

Surfactant Extraction

The trapping of surfactant molecules in the film upon drying is likely to be detrimental for both the generation of polaron pairs at the polymer/acceptor interface and for long-range charge carrier transport through the resulting device.^{4,5} To remove the surfactant, we took advantage of the fact that coated and dried CPEC films are resistant to dissolution in aqueous solution. Thus, the dried films were soaked in water at 80°C for 45 minutes. For nonionic PEG-type surfactants such as C₁₂E₅, increasing the temperature causes progressive dehydration of the ethylene oxide head groups, which reduces the effective head-group area and destabilizes the micellar packing geometry. This ultimately disrupts the micelle integrity and releases the encapsulated contents.⁶ Given the hydrophobic nature of the acceptors, we hypothesize that the hot water soak would burst the micelles, releasing the surfactants into the soaking solution while leaving the acceptors in the CPEC film.

UV-Vis spectra of films after the solvent extraction procedure described above are shown in Figure 3.1 as dashed curves. In both panels the bare CPEC film measured after empty surfactant-extraction, serves as the relevant reference. This confirms that the hot water soak effectively leaves the CPEC unaffected. Critically, acceptor absorption features are retained after the surfactant-extraction step in all cases, and no acceptor absorption signal is found in the soaking solution, demonstrating that the

acceptor remains trapped within the film rather than extracted back into the soaking solution.

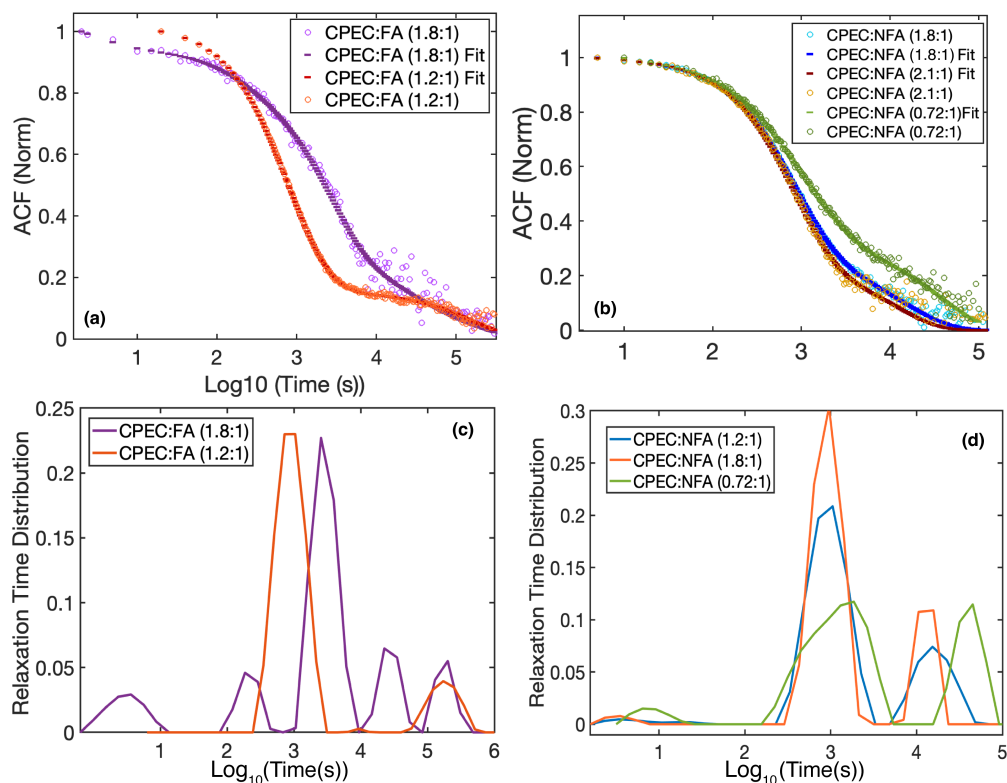


Figure 3.2. Dynamic light scattering measurements of the aqueous soaking solutions collected after the 80°C surfactant-extraction procedure. (A, B) Normalized scattered electric field autocorrelation functions for FA and NFA, respectively. (C, D) Corresponding relaxation time distributions for FA and NFA, respectively.

To determine whether the soaking procedure was able to extract surfactant molecules from the films, we performed dynamic light scattering (DLS) measurements on aqueous solutions following the surfactant extraction procedure. The normalized scattered electric-field autocorrelation functions are shown in Figure 3.2a and b for

CPECs with FA and NFA, respectively. It is immediately clear that scattering particles are present in soaking solutions for both acceptors and for different acceptor loadings. To extract decay time distributions from the autocorrelation functions, we applied the regularized inverse Laplace transform method via the CONTIN algorithm, as done previously.¹ The resulting distribution functions are shown for FA and NFA in Figure 3.2c and d, respectively.

Across all samples and both acceptor types, the relaxation time distributions exhibit a dominant population with a peak position that varies little with acceptor concentration. This shared peak position identifies the primary scattering species in the soaking solution as free E5 micelles in all cases, confirming that the extraction procedure successfully expels the surfactant from the active layer into the surrounding solution. As the acceptor loading the films increases, the ACFs of the surfactant-extracting solutions acquire features at relatively long decay times, consistent with aggregation of micelles into larger-sized clusters due to a higher extracted surfactant concentration. This is reasonable, as the surfactant concentration needed to encapsulate the acceptor scales with acceptor loading. DLS results suggest that the 80°C soak is effective at bursting micelles and removing the surfactant across the range of acceptor concentrations. In what follows, a CPEC:Acceptor ratio of 1.8:1 was selected for all subsequent structural and spectroscopic characterization. This ratio provides clear signatures of charge transfer (*vide infra*) while avoiding excessive acceptor loading.

Structural Characterization of CPEC Films

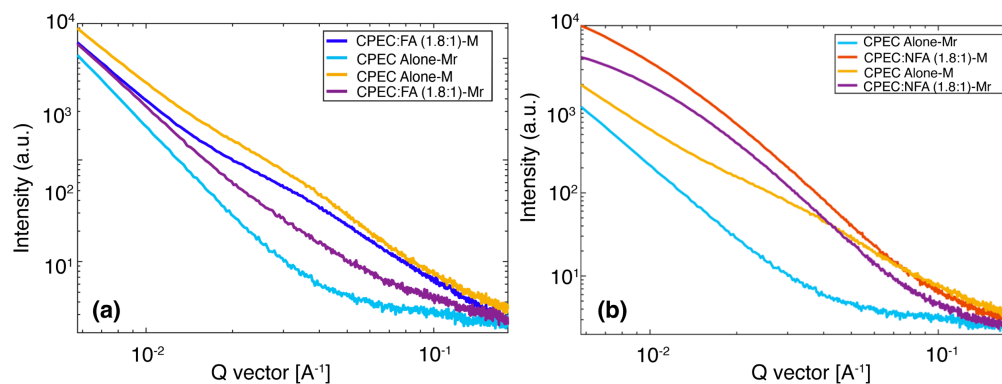


Figure 3.3. Grazing-incidence small-angle X-ray scattering (GI-SAXS) intensity profiles as a function of Q_{xy} for CPEC films at CPEC:A(1.8:1) loading. (A) FA-loaded films and (B) NFA-loaded films, shown pre- and post-surfactant extraction, along with bare CPEC and CPEC with empty micelles for comparison.

To probe how acceptor incorporation and subsequent surfactant extraction affects the nanoscale morphology of the CPEC active layer, grazing-incidence small-angle X-ray scattering (GI-SAXS) measurements were performed on CPEC:films before and after surfactant extraction, along with bare CPEC films with and without empty micelles. The reduced 1D scattered intensity profiles as a function of the in-plane scattering vector component Q_{xy} are shown in Figure 3.3 for FA (panel a) and NFA (panel b). At low to intermediate Q_{xy} the scattered intensity of a bare CPEC film is well-approximated by a power-law decay representative of a fractal-like morphology. This is reasonable for an electrostatically cross-linked CPEC network. Incorporation of empty micelles into the CPEC film leads to the appearance of a shoulder at $Q_{xy} \approx 0.03 \text{ Å}^{-1}$, corresponding to a correlation distance of $\sim(\pi/Q)$. Figure 3.3a shows that

incorporation of FA micelles leads to the appearance of a nearly identical feature which largely disappears after surfactant extraction.

Films with NFA present a different picture. For both the as-cast film and the film after surfactant extraction, the scattered intensity exhibits a Guinier-type plateau at low Q_{xy} , indicating the formation of large particles with a characteristic length scale on the order of 100 nm. Upon extracting surfactants, the overall intensity decreases, and the Guinier plateau becomes slightly clarified. This behavior points to a genuine reorganization of the CPEC mesoscale morphology driven by NFA incorporation. It is important to note that this reorganization persists after the surfactant is removed, which confirms that it reflects the true bulk structure of the acceptor-loaded active layer rather than an artifact of the micellar carrier. The concentration dependence of this structural evolution further suggests that above a threshold NFA loading, cooperative interactions between NFA molecules and the CPE network drive a mesoscale morphological transition.

The GI-SAXS findings are corroborated by cryogenic transmission electron microscopy (cryo-TEM) of the acceptor-loaded CPEC fluid, providing a direct real-space visualization of the structural reorganization induced by each acceptor at the molecular scale. Cryo-EM images of the vitrified CPEC fluids containing acceptor and minimal remaining surfactant, are shown in Figure 3.4 for the CPEC fluid with NFA post surfactant-extraction (panels e, f), CPEC with FA post surfactant-extraction (panels c, d), and bare CPEC containing no acceptor (panels a, b), at two magnifications each. The bare CPEC fluid is devoid of pronounced features at both magnifications,

displaying an amorphous, fractal-like network morphology, consistent with GI-SAXS results.

CPEC films containing NFA and FA exhibit long-range order, but the character of the ordering differs between the two acceptors in a manner that is consistent with the GI-SAXS data. In the NFA-loaded films (Figure 3.1e and f), one observes ordered lamellar structures with d-spacings of approximately 1.5 nm and relatively large crystalline coherence lengths. These spacings are significantly larger than the typical π -stacking distance of 0.35-0.4 nm, suggesting that the lamellar periodicity reflects the packing of NFA molecules. In FA-loaded films (panels c and d), lattice fringes are also clearly visible, with a d-spacing of approximately 0.8 nm. This spacing is consistent with the known face-centered cubic (FCC) crystal lattice of solid C₆₀, which has a room-temperature lattice parameter of approximately 1.415 nm.^{12,13} This corresponds to a nearest-neighbor intermolecular spacing of $a/\sqrt{2} \approx 1.00$ nm, in close agreement with observed structural spacing and confirming that the d-spacing in the FA-loaded films reflect the nucleation of FA crystallites within the CPEC active layer. However, in contrast to the NFA, the ordered regions in the FA films are characterized by significantly smaller crystalline coherence lengths.

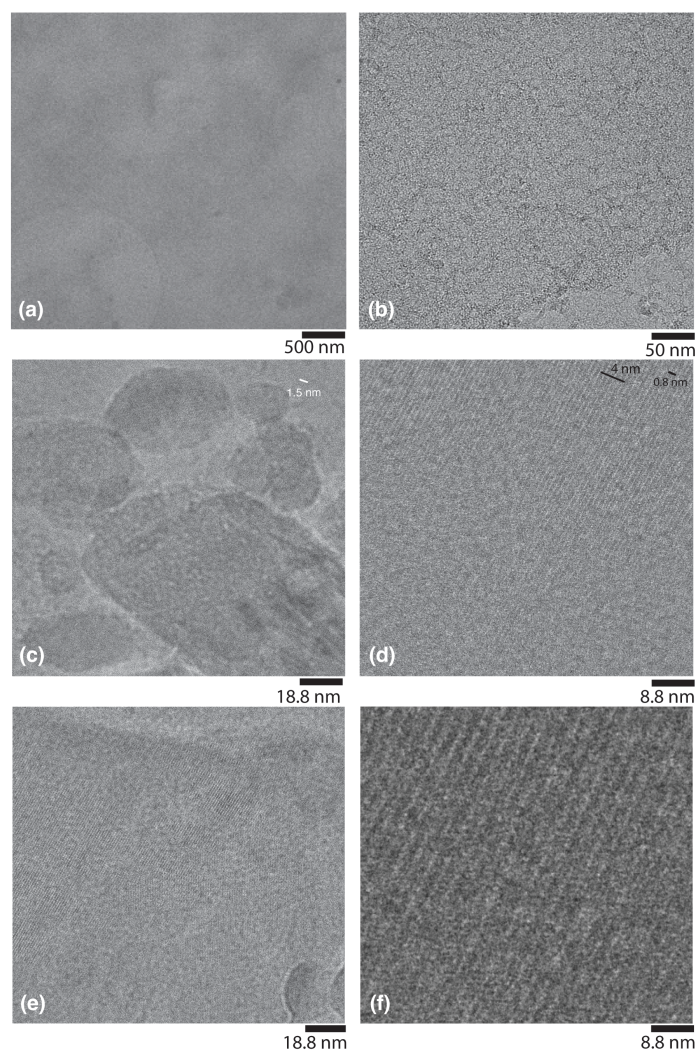


Figure 3.4. Cryogenic transmission electron microscopy (cryo-TEM) images of vitrified CPEC complex fluids after surfactant extraction. (A, C) CPEC with NFA at two magnifications, showing ordered lamellar structures with d-spacings of approximately 1.5 nm. (B, D) CPEC with FA at two magnifications, showing lattice fringes with a d-spacing of approximately 0.8 nm, and (E, F) are bare CPEC at two magnifications.

Probing Photoinduced Charge Transfer

If the micelles burst inside the CPEC film thereby forming a CPE/acceptor heterojunction, one expects to observe spectroscopic signatures of exciton dissociation via polaron pair formation. To assess whether the incorporated small-molecule acceptors engage in charge transfer with the photoexcited CPEC, time-resolved photoluminescence (TRPL) measurements were performed. Films were excited at 500 nm, and emission was collected at 630 nm, which corresponds to the absorption and emission maxima of PCPT, respectively. Excitation of PCPT instead of PFNB was chosen to avoid the complicating influence of ultrafast electronic energy transfer from PFNB to PCPT. If charge transfer from the CPEC to the small-molecule acceptor was occurring, the PCPT excited state would be depopulated more rapidly than in the bare CPEC, manifesting as accelerated PL quenching relative to the acceptor-free reference.

The time-resolved photoluminescence lifetime (TRPL) decays for all samples following surfactant extraction are shown in Figure 3.5. The bare CPEC film exhibits a PL decay with $\langle\tau\rangle = 0.15$ ns, which is a significantly slower timescale than that of the PCPT TRPL signal in all acceptor-loaded films. This indicates that a significant fraction of PCPT excitons undergo a transition to a nonemissive state in the presence of either acceptor on a timescale that is shorter than the instrument response function. These results are consistent with photoinduced charge transfer and support that acceptor infiltration of the CPEC network occurred.

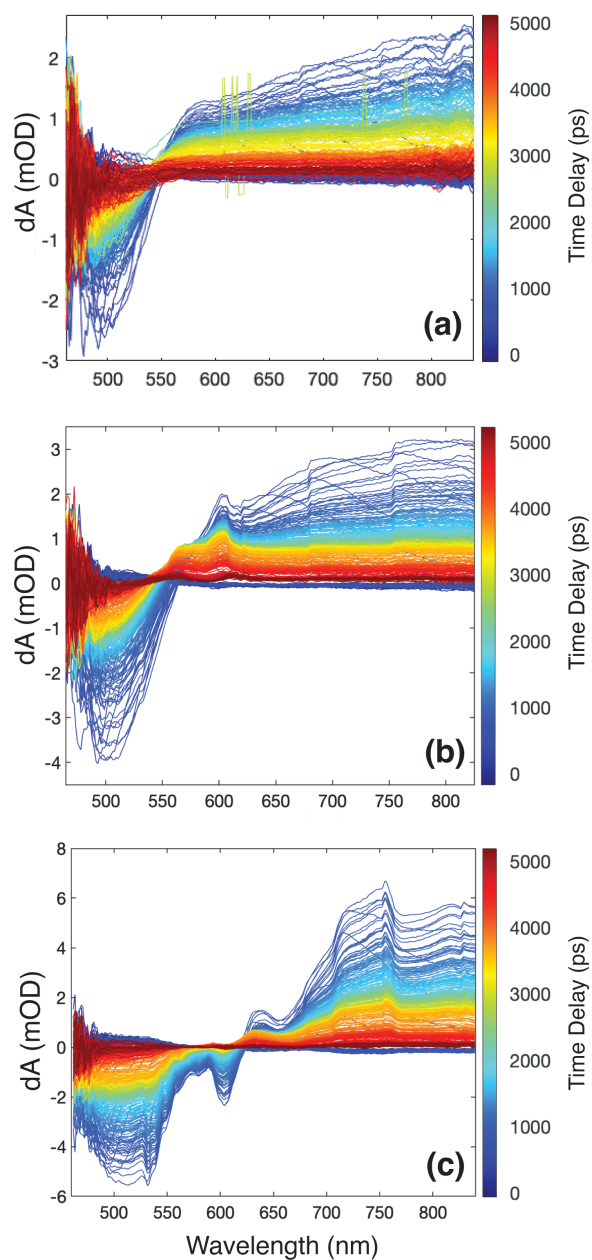


Figure 3.6. Ultrafast transient absorption spectra of CPEC films after surfactant extraction, pumped at 480 nm. (A) Bare CPEC, (B) CPEC:FA, and (C) CPEC:NFA.

Although consistent with charge transfer, a large drop in the PL lifetime alone cannot distinguish between charge transfer and other quenching mechanisms such as electronic energy transfer from PCPT to the acceptor or concentration-type quenching due to an increase in the density of PCPT H-aggregate exciton states.²⁸ We thus turned to ultrafast transient absorption (TA) spectroscopy primarily due to two factors. First, in the pump/probe spectrum polaron absorption, dominated by the hole polaron on the polymer backbone, usually leads to the formation of a new, sub-gap excited-state absorption (ESA) band that is spectroscopically distinct from the ESA of the neutral exciton.

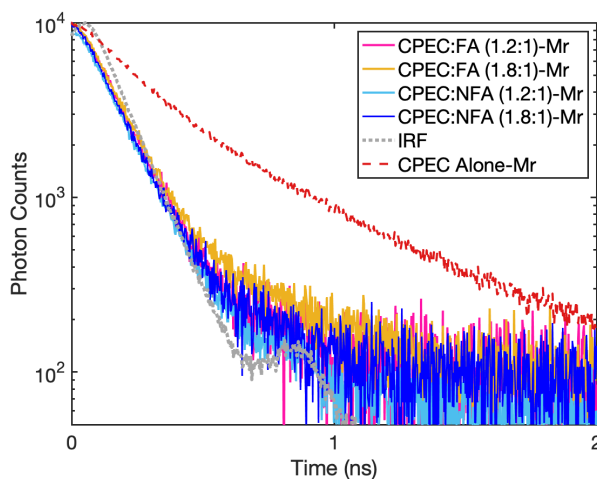


Figure 3.5. Time-resolved photoluminescence (TRPL) decays collected at magic angle for CPEC films with and without acceptor loading at two CPEC:SMA ratios (1.2:1 and 1.8:1) for both FA and NFA, after surfactant extraction. The bare CPEC film (CPEC Alone-Mr) serves as the reference. Films were excited at 500 nm and emission was collected at 630 nm

This relatively narrow band arises from optical transitions between the polaron-induced mid-gap electronic states and the valence and conduction bands of the polymer.^{14,15,17} Second, unlike in TRPL, dynamics of non- or poorly emissive states such as triplet excitons can still be observed via TA spectroscopy. Films were pumped at 480 nm, primarily resonant with PCPT, and probed across the visible to near-IR. The resulting TA spectra are shown in Figure 3.6 for bare CPEC (panel a), CPEC:FA (panel b), and CPEC:NFA (panel c). All spectra are for samples following surfactant extraction.

Pump/probe spectra for the bare CPEC film shown in Figure 3.6a display (i) a negative signal due to ground-state bleach (GSB) corresponding to PCPT absorption centered about ~480 nm at early times, and (ii) excited-state absorption (ESA) from ~550 nm to beyond 800 nm. To a good approximation, the signal decays uniformly as a function of probe wavelength, with only relatively minor differences in dynamics between 620 nm, 635 nm, and 750 nm (Table 1).

Figure 3.6b shows pump/probe spectra for CPEC:FA films. No additional GSB or stimulated emission signal due to direct excitation of FA appears in the visible region, consistent with the symmetry-forbidden nature of the $S_0 \rightarrow S_1$ transition in C_{60} .²⁷ However, a new and relatively narrow absorption band does appear on top of the broad CPEC ESA background around 620 nm. This feature appears extremely quickly: essentially within the temporal resolution of the setup.

Table 3.1. Biexponential fit parameters for single-wavelength transient absorption kinetics of bare CPEC, CPEC:FA, and CPEC:NFA films.

CPEC:NFA	τ_{fast} (ps)	τ_{slow} (ps)
Exciton Band	4.4	2.29
Polaron Band (635nm)	14.2	2.53
CPEC:FA	τ_{fast} (ps)	τ_{slow} (ps)
Exciton Band	1.9	54.3
Polaron Band (620nm)	13.2	175
CPEC alone	τ_{fast} (ps)	τ_{slow} (ps)
750nm	12.4	270
620nm	21.9	291
635nm	19.4	284

Figure 3.6c shows pump/probe spectra for CPEC:NFA films. Compared to bare CPEC films, CPEC:NFA spectra display an additional negative feature at longer wavelengths (~600-700 nm) which is attributed to the GSB of NFA, consistent with

ground-state NFA absorption (Figure II.2). Additionally, a new ESA band appears in a region similar to CPEC:FA films.

All signal decays are well-described by a biexponential model. For the CPEC control (Figure 3.7a), the ultrafast decay component with lifetime τ_{fast} (between ~ 10 -20 ps) is likely due to exciton-exciton annihilation that accompanies the diffusion of excitons spatially and spectrally within their density of states.²⁵ The rigid decay of the ESA characterized by the slow component lifetime $\tau_{slow} \sim 300$ ps reflects the intrinsic excited-state dynamics of the CPEC network in the absence of significant charge-transfer pathways and establishes the baseline against which the acceptor-loaded films will be compared.

It is instructive to compare the decay dynamics near the central wavelength of the new narrow band in acceptor-loaded films (620 nm) and dynamics at a probe wavelength relatively far from this feature but still within the CPEC ESA region (750 nm). In what follows, this region is referred to as the exciton band. For the CPEC:FA sample τ_{slow} for the decay at 620 nm is 175 ps, compared to 54 ps for the exciton band. That is, the signal at 620 nm is significantly more long-lived. Such a drastic lifetime difference at these probe wavelengths is absent in bare CPEC films. Taken together with the TRPL results, it can be concluded that the new spectral feature observed in the presence of C₆₀ is due to polaron absorption (polaron band), most likely the hole polaron delocalized over the CPE backbone.^{14,15,16} Notably, the polaron band sits on top of a much broader CPEC exciton signal. Thus, the decay of what we termed as the

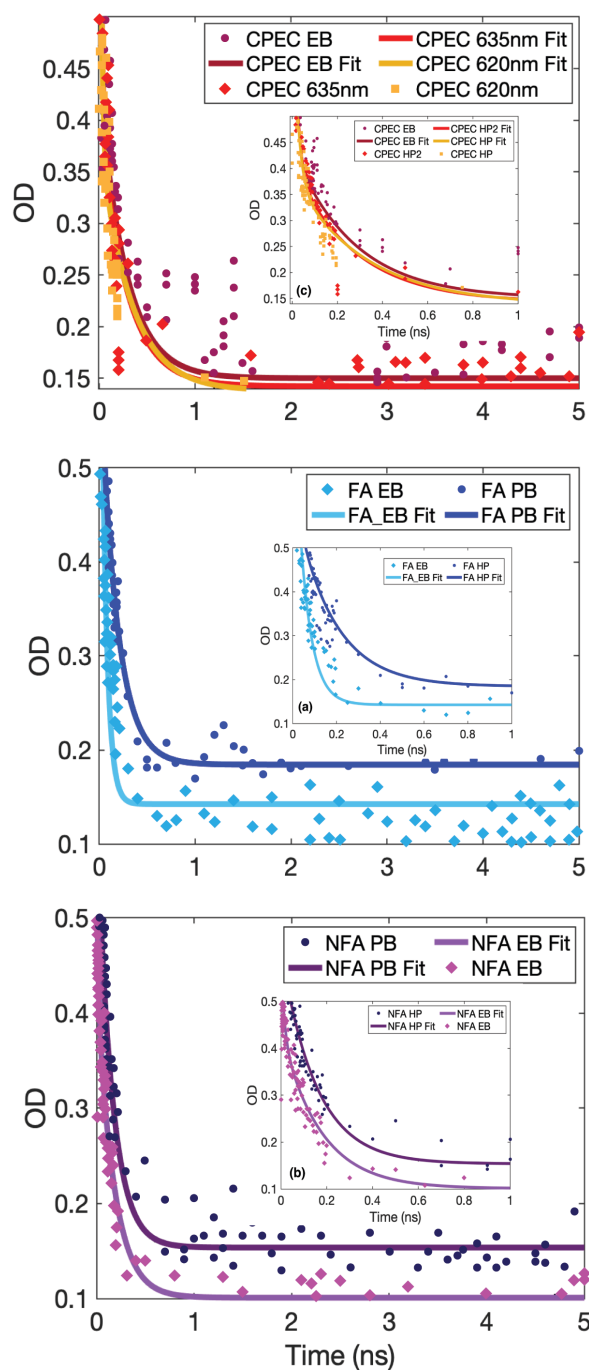


Figure 3.7. Single-wavelength transient absorption kinetics and biexponential fits for (A) bare CPEC, (B) CPEC:FA, and (C) CPEC:NFA films after surfactant extraction. Kinetics are compared at the polaron band and exciton band probe wavelengths.

polaron band reflects a weighted sum of both exciton and polaron decay channels if one assumes minimal coupling between polaronic and excitonic states.

Comparing the dynamics of the exciton (750 nm) and polaron (635 nm) bands for CPEC:NFA samples as before, the exciton band has $\tau_{slow} \sim 92$ ps, whereas for the polaron band has $\tau_{slow} \sim 172$ ps. The appearance of a polaron signal in the presence of both acceptors is consistent with interfacial charge transfer in conjugated polymer-small/molecule systems,^{14,15} showing that the micelle delivery and thermal micelle burst strategy shows promise as a means to deliver nonpolar electron acceptors into hydrated CPEC films and thereby form photoinduced charge carriers.

Probing Long-Range Charge Transport under Illumination

Although we have demonstrated the formation of photoinduced charge carriers, observing a photocurrent in a CPEC film requires that the charge carriers are able to traverse the bulk of the film to ultimately be collected by the metal electrodes. To form aOPV devices, CPEC:NFA fluids were spread by hand onto ITO substrates, after which films were subjected to the surfactant extraction procedure, thermally annealed, and capped with Al cathodes. Films formed using this process yielded very large thicknesses in excess of 1 μm with large peak-to-value variations as seen in the AFM images in Figure 3.8. No charge-transport layers were used to simplify the complexity of the device architecture

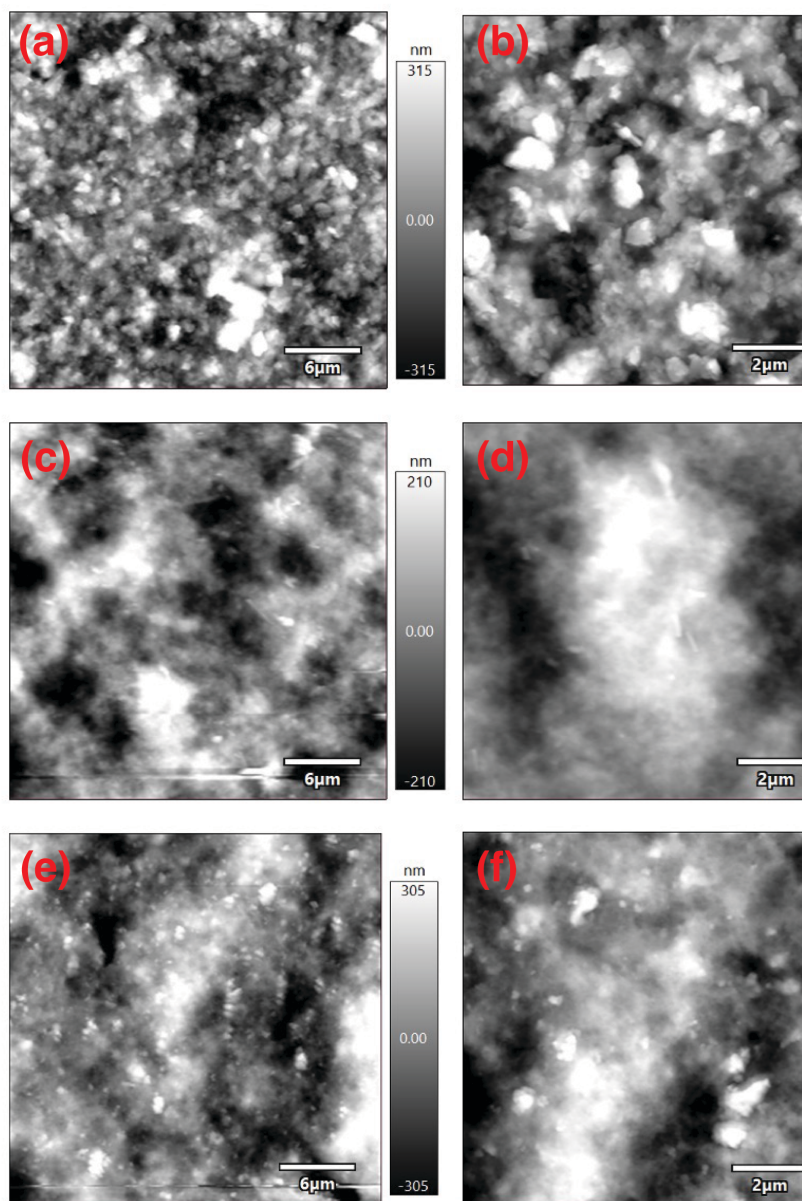


Figure 3.8. AFM topography images of active layer films at $30 \times 30 \mu\text{m}$ (left) and $10 \times 10 \mu\text{m}$ (right) scan sizes: bare CPEC control (a, b), CPEC:NFA (c, d), and CPEC:FA (e, f).

The current/voltage response was first examined in the dark (black line in Figure 3.9a), which is notable in that there is small current under zero external bias. Although it is tempting to assign this to the presence of stray light, a light-tight cover was used during electrical testing, and standard P3HT:PCBM OPV devices did not show such a dark-current response under identical testing conditions. The same curve plotted as a semi-log plot (Figure 3.9b) shows that the dark current vanishes at $V \sim -0.3$ V, suggesting that there exists a built-in potential of $\sim +0.3$ V inside the device.

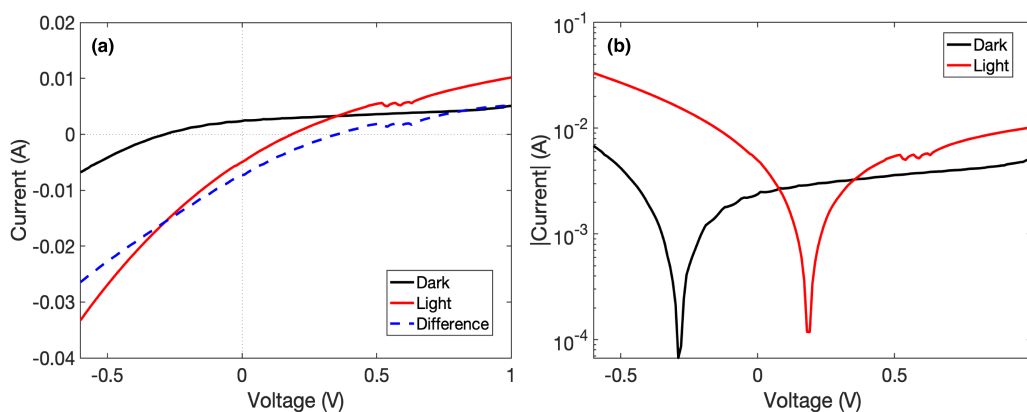


Figure 3.9. Photovoltaic characterization of an aOPV device fabricated with the CPEC:NFA active layer. (A) Current density-voltage (J-V) characteristics measured in the dark (black) and under illumination (red), with the photocurrent (difference) shown as a dashed curve. (B) The same data plotted on a semi-logarithmic scale.

The total drift current in the dark is composed of (i) an electronic contribution due to injected charge carriers and (ii) an ionic contribution due to CPE sidechains that did not participate in electrostatic cross-links with their oppositely charged partners and thus retained their small counterions. The built-in potential that drives

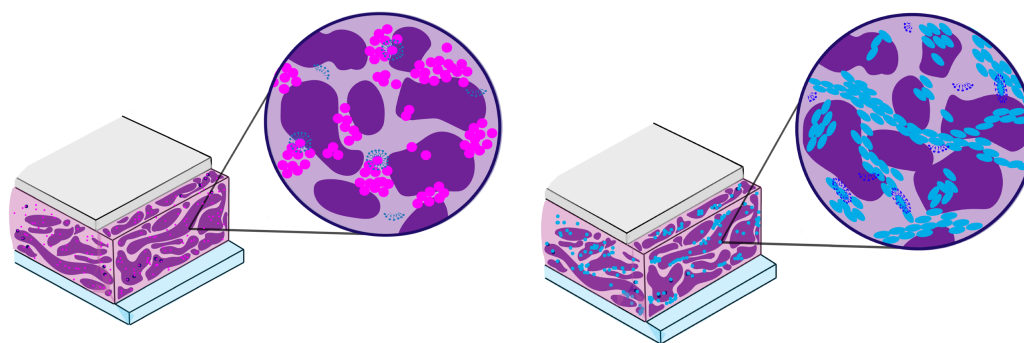
this dark current likely reflects primarily the formation of interfacial dipoles determined by the arrangement of ionic sidechains at metal/organic interfaces.

Under illumination, the current at zero bias reverses direction, and the current is enhanced at forward and reverse bias compared to the dark current. The photocurrent can be defined as the difference between the light-on and dark currents, which is shown as a dashed blue curve in Figure 3.9a on a linear scale and in Figure 3.9b on a semi-log scale. Observation of a photocurrent is unambiguous evidence of the formation of mobile charge carriers. However, the photocurrent magnitude and the fill factor in these proof-of-principle devices are quite low. The possible reasons for these observation are addressed in the Discussion section below.

3.4 DISCUSSION

This work demonstrates that CPEC fluids can be infiltrated with electron acceptors using micelle carriers as the delivery vehicle, and the corresponding surfactants can be largely removed by soaking the resulting film in water while avoiding delamination. Ultrafast photoinduced electron transfer was observed with representatives of both fullerene and non-fullerene electron-acceptor classes, suggesting that the micelle delivery route is fairly general. Interestingly, the mesoscale structure of the resulting thin films differs significantly between C_{60} and ITIC, indicating that although the ability to deliver small-molecule electron acceptors into the CPEC fluid via the micelle route is likely general, the resulting film

microstructure may depend strongly on the chemical structure and thus the molecular packing of the acceptor.



Scheme 3.2. Proposed morphological models for FA (left) and NFA (right) integration into the CPEC active layer.

The ability to imbue CPEC fluids with mobile charge carriers upon illumination is significant. The rheological properties of CPEC fluids are highly attractive for large-scale manufacturing of flexible and stretchable aOPV devices. The viscoelastic nature of CPEC fluids is particularly well-suited for forming large-area devices. Traditionally, methods related to spin-coating undergo a large drop in performance when scaling from lab-scale devices to what is needed to broadly deploy the technology. Furthermore, the potential to tune the microstructure and the optoelectronics through the ionic atmosphere gives rise to intriguing physical-chemical possibilities to modulate charge transport. Finally, the CPEC fluid approach fulfils an important desideratum that the formation of the active layer be entirely

water-based. We believe that this potentially promising pathway to aOPV devices stands apart from current approaches and deserves to be interrogated further in follow-on work.

Nevertheless, the photocurrents generated by these preliminary CPEC:NFA devices were very low. It is worth considering the reason for this result in some detail. First, the deposition method yielded extremely thick films: thicknesses well more than 1 μm . Even most conventional OPV devices with fantastic device performance metrics at thicknesses of order 100 nm dramatically decrease their performance when the thickness exceeds 1 μm . At these thicknesses, photogenerated charge carriers must traverse distances far exceeding the expected carrier diffusion lengths in the CPEC, leading to extensive bimolecular and trap-assisted recombination before collection.⁴⁰ In the future, much more control needs to be exerted over the substrate coating process to achieve significantly smaller thicknesses than these proof-of-principle devices. Additionally, for the sake of architectural simplicity our devices contained no charge transport layers, the presence of which is expected to further increase device performance.

However, the biggest issue that plagued these first devices is most likely a low interfacial area between CPE chains and the small-molecule acceptors. The addition of acceptor-containing micelles to the already formed electrostatically cross-linked CPEC network is unlikely to yield mean separations between electron donors and acceptors that are comparable to the diffusion length of CPE excitons, a requirement that must be fulfilled to maximize device performance.

Interestingly, no measurable photocurrent was observed with C_{60} , as shown in the Supporting Information. This suggests that although the electron donor/acceptor interfacial area was likely quite limited in ITIC devices, ITIC molecules nevertheless formed a percolated charge-transport network through the (extremely thick) thin film. The cryo-EM and GI-SAXS data suggest that NFAs may have a greater propensity to form extended, directional molecular pathways within the CPEC matrix where contiguous NFA stacks bridge the gap between CPE chains and provide a connected pathway toward the electrode. In contrast, the FA appears to nucleate as isolated, small crystallites that may sit outside the colloidal polymer domains rather than intercalating into the CPEC network. The spherical symmetry of C_{60} , while advantageous for isotropic electron transport within a crystallite, does not appear to promote the long-range connectivity needed to form percolating pathways through the CPEC film. This is depicted in the cartoon in Scheme 3.2. One can speculate that this disparity is rooted in the geometry of the acceptor small molecules, implying that molecular geometry should be a significant consideration when selecting the electron acceptor.^{29,30}

How can the yield of charge carrier generation and the effectiveness of long-range charge transport be improved in CPEC fluid-based aOPVs? Several future directions are proposed to answer these questions. The initial trivial answer is that the film thickness must be significantly reduced. Doing so will require modulating the blade-coating speed, substrate temperature, and humidity of the casting environment. Another approach is to avoid initially separating the concentrated complex fluid

phase from the dilute phase, instead depositing a desired volume of the biphasic mixture along with the micelle-encapsulated electron acceptors via drop-casting. Initial experiments following this approach do seem to yield significantly thinner films, but issues such as uniformity arise. We describe our attempt at this deposition method in the Supporting Information.

The physical chemistry of donor/acceptor heterojunction formation in CPEC fluids is drastically different from that of common OPVs or NP-based aOPVs. The latter largely inherit the same underlying principles used to form bulk heterojunctions. Therefore, new ideas are needed to elucidate the design principles that give rise to large donor/acceptor interfacial areas and well-defined, percolated charge-transport networks in CPEC fluid-based aOPVs. To increase the electron donor/acceptor interfacial area, the incorporation of the small-molecule acceptors should occur at the electrostatic assembly stage: an approach we are currently interrogating. Furthermore, the two CPEs themselves may comprise an electron as opposed to an exciton donor/acceptor pair, leading to extremely high interfacial areas, possibly at the cost of some light absorption and increased electron/hole recombination. There is clearly much room for further exploration and innovation.

A potential criticism of this approach to aOPVs is that the presence of ionic charges on the CPE sidechains may act as traps for mobile electrons and holes. Although this is possible in principle, it is unlikely to be a significant concern. A modest concentration of ionic charges in an OPV active layer may indeed lead to trapping of electronic charge carriers. However, a large concentration of proximal,

randomly oriented dipoles formed between complexed CPE sidechains will likely screen the kinds of long-range electrostatic interactions that tend to trap electrons and holes. Evidence for this comes from devices based on small-molecule electrolytes as electron donors. Such devices, referred to as “salt photovoltaics”, show good short-circuit currents and substantial fill factors, demonstrating that the presence of ionic charges is not a fundamental limitation for photovoltaic power generation. In fact, when the density of ionic dipoles is substantial, electrostatic interactions at short range may assist in separating the initial electron/hole pair that straddles the donor/acceptor heterojunction.

3.5 CONCLUSION

To summarize, the formation of a light-harvesting complex fluid simultaneously capable of rapid exciton and charge transfer has been demonstrated. Novel aOPV devices were prepared using the complex fluid to form the active layer. Although the device performance is rather limited for these first prototypes, this work stands as a proof of principle that associative phase separation of CPEs is an intriguing new pathway to aOPVs. The rheological properties of the complex fluid make this approach particularly promising for large-area, flexible, and stretchable devices. Although significant issues remain, there are clear and substantial opportunities to take advantage of the nontraditional driving forces that characterize the aqueous associative phase separation process.

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Appendix II

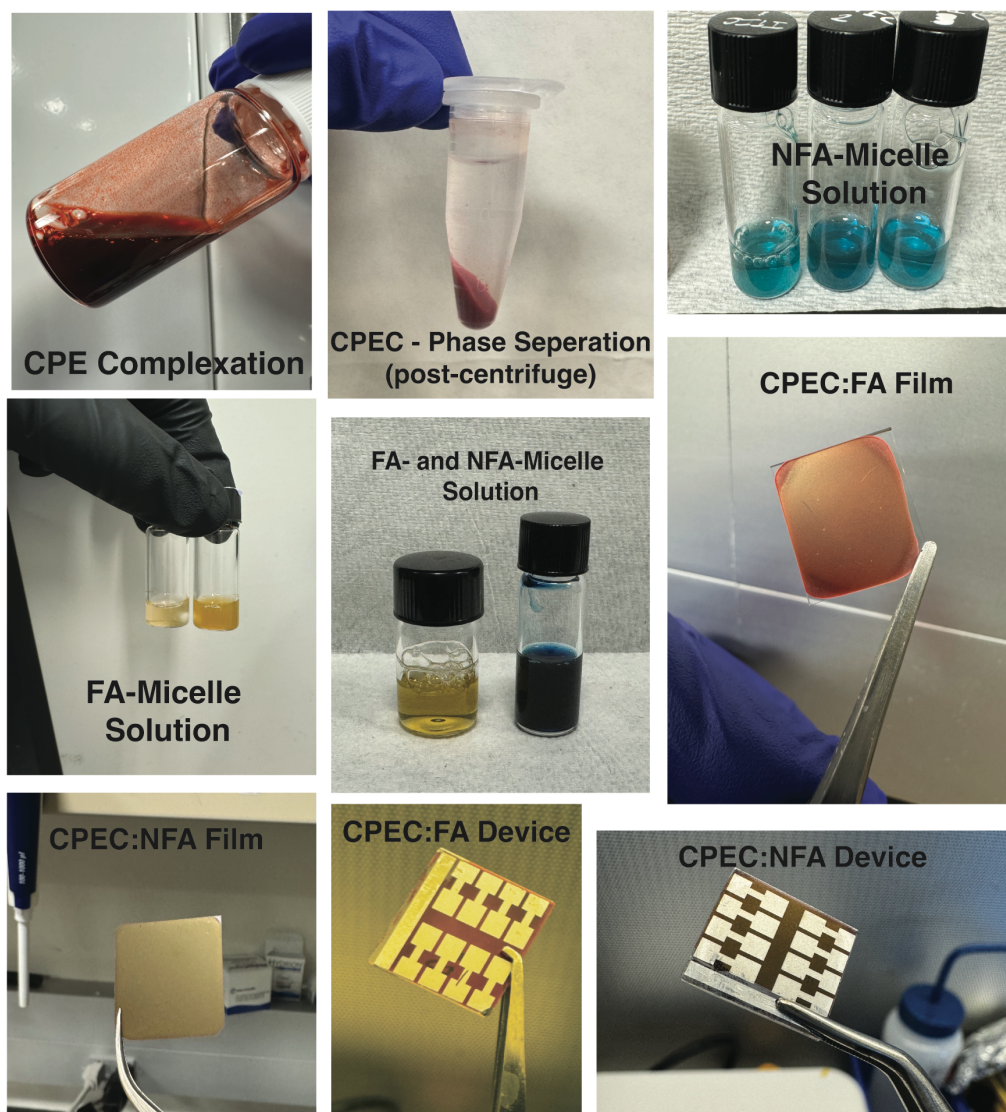
II.1 Active Layer Preparation

II.1.1 CPE Complex Fluid Preparation

Samples of complex fluid were prepared from PFNB and PCPT at a 1:1 charge-matched electrostatic assembly. The two components were added simultaneously in a dropwise fashion, and the resulting solution was degassed with argon, then heated and stirred at 70 °C for 24 hours. SMA-micelles, prepared as described in Section S1-2, were then incorporated into the complex fluid. The mixture was subsequently centrifuged at 10,000 rpm for 45 minutes to induce phase separation. Following centrifugation, the dilute supernatant was carefully removed, and the complex fluid was collected for blade coating, as described in Section S1-3. Photographs illustrating each step of this procedure are presented in Scheme S1.

II.1.2 Acceptor Incorporation via Micelle Delivery

The desired amount of SMA, calculated according to the target CPEC:SMA ratio, was placed into 500 μ L of HPLC-grade water, and the solutions were degassed prior to heating. The mixture was then heated and stirred at 80 °C for 2 hours, followed by sonication at 60 °C for 30 minutes. Next, 2 μ L of C12E5 (0.011 M), a concentration well above the critical micelle concentration (CMC), was added, and the solution was heated and stirred for an additional 1 hour. The mixture was then sonicated for 10 minutes and centrifuged gently at 1,000 rpm for 10 minutes. Finally, the supernatant was collected, and any remaining dispersed particles were noted.



Scheme II.1. Photographic overview of the fabrication process for CPEC-based organic photovoltaic devices. Top row (left to right): CPE complexation solution showing the initial conjugated polyelectrolyte complex; CPEC after phase separation via centrifugation, revealing distinct layered phases; and NFA-micelle solution in vials displaying a characteristic blue color. Middle row: FA-micelle solution in amber-toned vials; side-by-side comparison of FA- and NFA-micelle solutions; and a CPEC:FA thin film deposited on a glass substrate. Bottom row: CPEC:NFA thin film on a glass substrate; completed CPEC:FA device with patterned electrode architecture; and completed CPEC:NFA device showing the final device layout with Al contact pads.

II.1.3 Procedure for Blade-Coating Active Layer onto Substrate: ITO substrates were first washed and sonicated at 80 °C sequentially with isopropyl alcohol, soapy water, fresh HPLC-grade water, and acetone. The cleaned substrates were then ozone-treated for 60 minutes. The complex fluid containing SMAs was subsequently blade-coated manually onto the prepared substrates. The coated films were then annealed at 120 °C prior to the micelle release procedure described in Section S1-4.

II.1.4. Surfactant-Extraction Procedure: This release procedure includes soaking the film in filtered HPLC water at 80°C for 3 hours. Resulting HPLC water reservoir was kept for DLS measurements on micelle extraction efficacy.

II.2 Ultrafast Pump-probe Spectroscopy

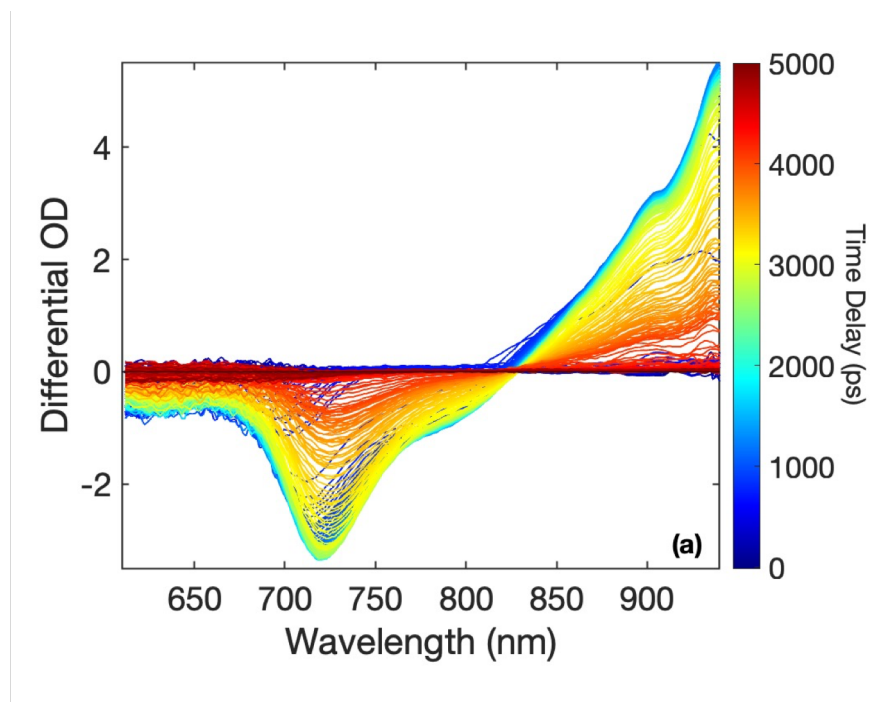


Figure II.2. Ultrafast Pump-probe Spectra of ITIC (NFA Small-Molecule Acceptor) excited at 480nm (consistent with active layer excitation).

II.3. Cryo-EM Analysis

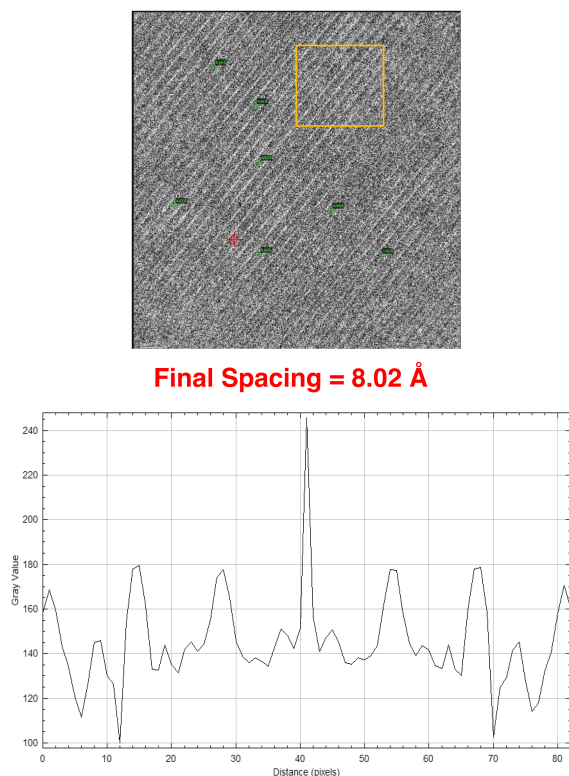
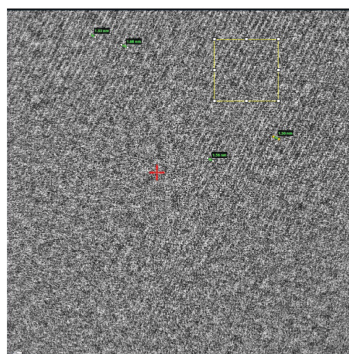


Figure II.3. FFT analysis of lattice spacing. (Left) HAADF-STEM image with the selected region outlined in yellow. (Right) Corresponding FFT pattern. The line profile extracted from the FFT spot yields a peak spacing of 13.4 pixels, corresponding to a real-space lattice spacing of 8.02 Å.

Lattice Spacing Measurement from FFT Analysis

The lattice spacing was determined from an FFT of a 4096 x 4096 pixel image at a pixel size of 0.21 Å/pix. The FFT was computed at 512 x 512 pixels, giving an FFT pixel scale of $1/(512 \times 0.21) = 0.0093 \text{ Å}^{-1}/\text{pix}$. A line profile across the FFT spot (shown in the accompanying plot of gray value vs. distance) spanned 80.6 pixels over 6 periodic sections, yielding a peak distance of 13.4 pixels. The real-space lattice spacing was then calculated as $1/(0.0093 \times 13.4) = 1/0.12462 = \mathbf{8.02 \text{ Å}}$.



Final Spacing = 7.96 Å

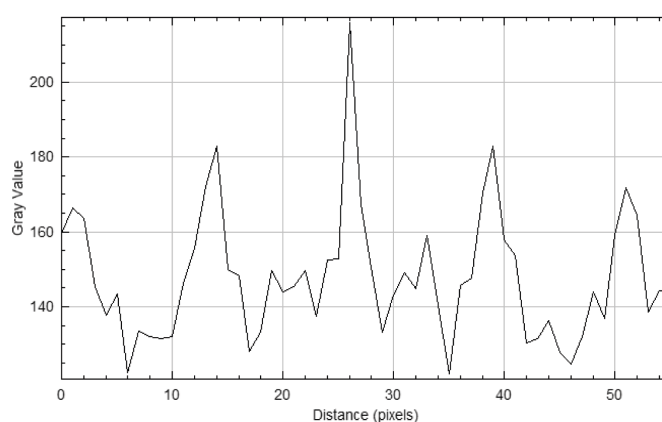


Figure II.4. FFT analysis of a second region. (Left) HAADF-STEM image showing the area of interest. (Right) Corresponding FFT pattern. The line profile yields a peak spacing of 13.5 pixels, corresponding to a real-space lattice spacing of 7.96 Å.

Lattice Spacing Measurement from FFT Analysis

The lattice spacing was determined from an FFT of a 4096 x 4096 pixel image at a pixel size of 0.21 Å/pix. The FFT was computed at 512 x 512 pixels, giving an FFT pixel scale of $1/(512 \times 0.21) = 0.0093 \text{ Å}^{-1}/\text{pix}$. A line profile across the FFT spot spanned 54 pixels over 4 periodic sections, yielding a peak distance of 13.5 pixels. The real-space lattice spacing was then calculated as $1/(0.0093 \times 13.5) = 1/0.12555 = 7.96 \text{ Å}$.

II.4. Atomic Force Microscopy

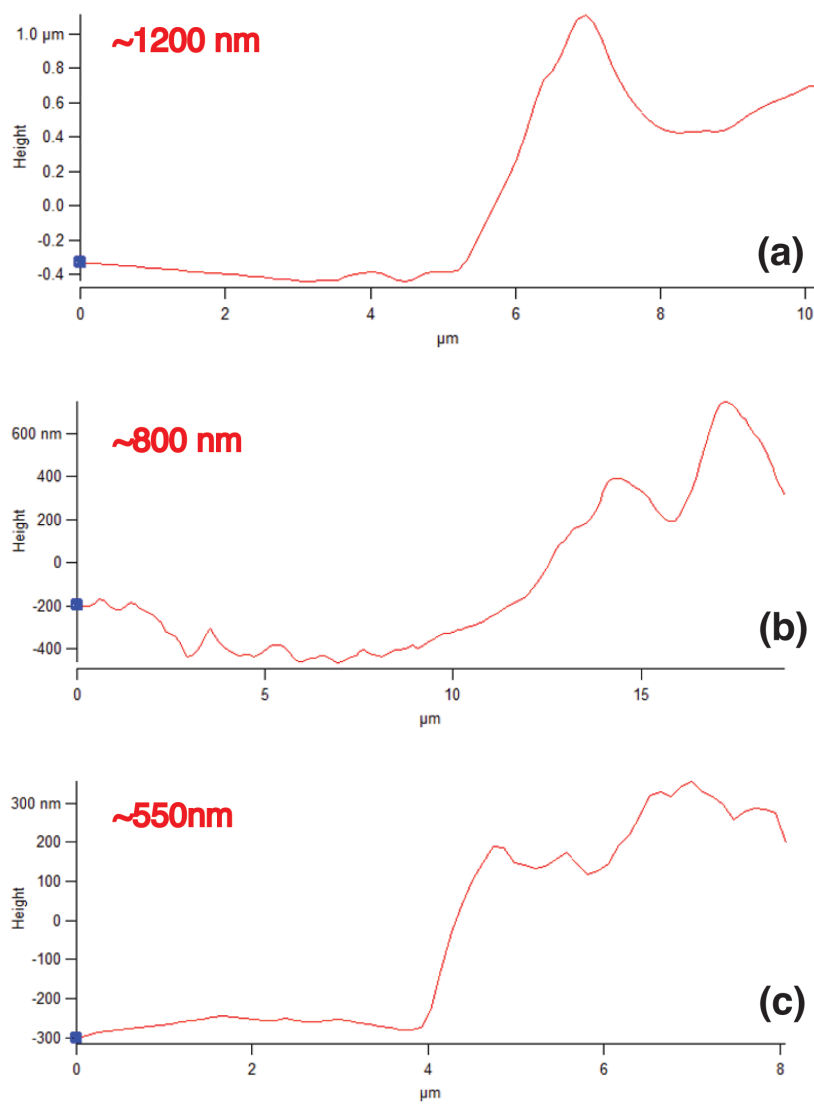


Figure II.4. AFM height profiles of (a) CPEC:FA, (b) CPEC:NFA, and (c) CPEC alone, showing film thicknesses of ~1200 nm, ~800 nm, and ~550 nm, respectively.

II.5. Device Testing: Photovoltaic Characterization

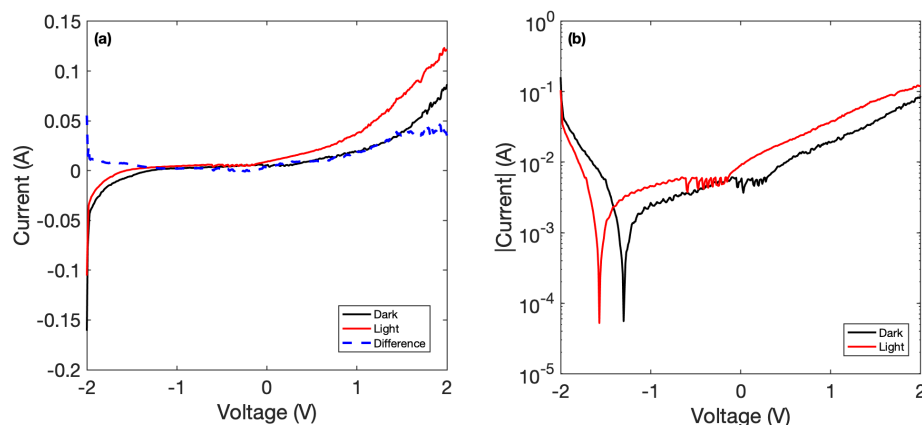


Figure II.5. Photovoltaic characterization of a CPEC:FA (1.8:1) active layer device. (A) Current-voltage (I-V) characteristics measured in the dark (black) and under illumination (red), with the photocurrent (difference) shown as a dashed blue curve. (B) The same data plotted on a semi-logarithmic scale.

II.6. Solvent-Annealed Drop Casting as an Alternative Deposition Pathway

In parallel with the blade-coating deposition strategy described above, a second, exploratory deposition pathway was investigated with the aim of achieving greater control over the film-formation process through solvent-annealing principles. This approach, solvent-annealed drop casting, represents a meaningful departure from conventional drop casting in its use of a water-vapor chamber to modulate the drying kinetics of the deposited fluid. The procedure follows the same preparative sequence as the blade-coating pathway: the small-molecule acceptors (FA or NFA) are first encapsulated in C12E5 micelles, which are then introduced into the PFNB solution. The anionic CPE (PCPT) is subsequently added, and the mixture is subjected to the thermally driven complexation protocol that induces associative phase separation. At this stage, the system exists as a biphasic mixture in which the dense, acceptor-loaded CPEC complex fluid coexists with the dilute aqueous supernatant within the

same vessel. Rather than separating the complex phase prior to deposition, the entire biphasic mixture is drop cast directly onto the substrate, while the substrate is enclosed within a water-vapor-saturated solvent chamber.

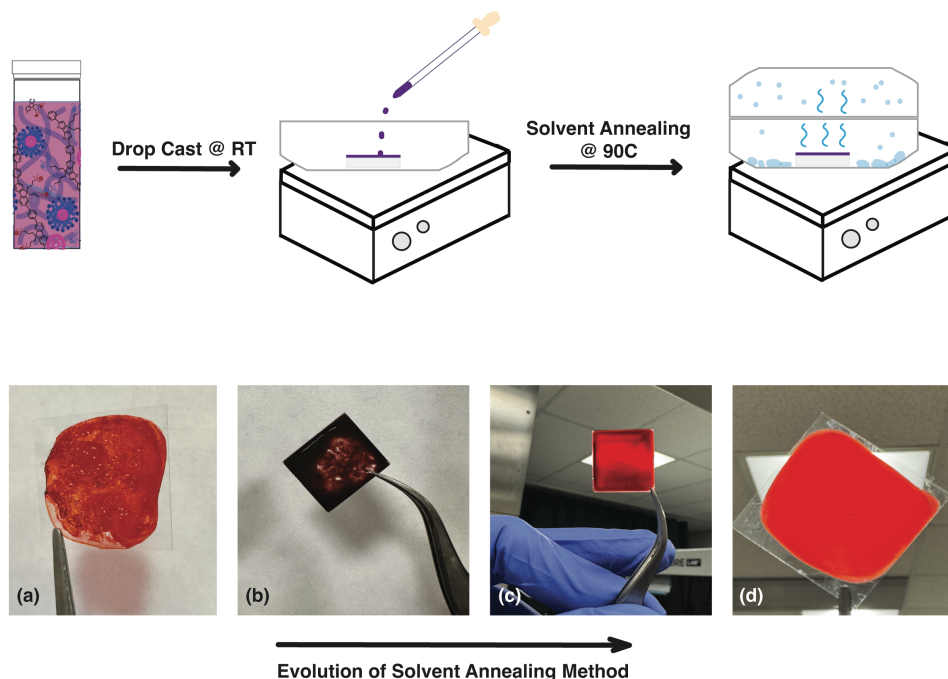


Figure II.6 Solvent-annealed drop casting procedure and film evolution. (Top) Schematic of the deposition process: the biphasic CPEC mixture is drop cast from the vial onto a substrate at room temperature, after which the substrate is enclosed in a water-vapor-saturated chamber at 90 °C to slow evaporation and promote controlled drying. (Bottom) Photographs showing the progression of film quality over successive iterations of the solvent-annealing method: (a) initial attempt showing significant non-uniformity and coffee-ring effects, (b) intermediate result with improved but still uneven coverage, (c) further optimization yielding more uniform films, and (d) best result achieved, demonstrating substantially improved film homogeneity across the substrate, although not reproducible to a reliable degree.

The conceptual motivation for this approach draws on the well-established practice of solvent annealing in organic thin-film processing, wherein films are exposed to solvent vapor during or after deposition to extend the time available for molecular reorganization and morphological equilibration before the film solidifies.²⁴ In the present aqueous context, the saturated water-vapor environment of the chamber slows the evaporation of the dilute supernatant phase, creating a controlled drying front that preferentially drives off the water-rich dilute phase while leaving the viscous, polymer-rich complex fluid behind on the substrate surface. The underlying hypothesis is that this gradual phase enrichment, in which the material retains some chain mobility in the presence of residual solvent vapor, might promote a more favorable and homogeneous distribution of the CPEC complex phase and its encapsulated acceptor across the substrate compared to the rapid drying inherent in conventional drop casting. This concept is analogous to the role of solvent additives play, and vapor annealing plays in optimizing bulk heterojunction morphology in conventional OPVs,²⁵ adapted here to the entirely aqueous processing environment of the CPEC active layer.

In practice, however, the solvent-annealed drop casting method did not match the performance of blade coating as a deposition strategy for this system. The primary limitation identified was film non-uniformity. As shown in **Figure II.6**, the deposited films exhibited significant spatial variation in thickness and coverage across the substrate area. This non-uniformity is a well-recognized challenge in drop casting of viscoelastic fluids, where the interplay between evaporation-driven Marangoni flows, contact-line pinning, and the rheological properties of the complex fluid can produce coffee-ring-like deposition patterns and other uneven film morphologies.²⁶ The elevated viscosity and gel-like character of the CPEC complex fluid, which are advantageous for blade coating, appear to exacerbate these non-uniformity effects in drop-casting. The film non-uniformity in turn compromised the

subsequent micelle release procedure: the elevated-temperature water soak required to burst the C12E5 micelles and extract the surfactant caused localized delamination of the thicker regions of the film, preventing uniform surfactant removal across the device area and precluding reliable photovoltaic characterization. These results establish blade coating as the preferred deposition method for the CPEC active layer under the processing conditions explored herein. Nevertheless, the solvent-annealed drop casting approach represents a conceptually distinct strategy whose optimization may prove valuable for future routes to CPEC-based device fabrication, particularly if the rheological properties of the complex fluid can be tuned to promote more uniform spreading within the solvent-vapor chamber geometry.

CHAPTER IV:

Temperature-Directed Complexation Enabled 3D-Printable Photoactive Polyelectrolyte Gels

Acknowledgements: This chapter includes ultra-fast pump-probe transient absorption spectroscopy that was done in collaboration with Dr. Jin Zhnag's group at UCSC with graduate student David Zeitz. Atomic Force Microscopy measurements were conducted in collaboration with Dr. David Lederman's group at UCSC. Cryo-EM images and subsequent analysis were completed in collaboration with Dr. Vitor Hugo Balasco Serrão, in the Biomolecular Cryoelectron Microscopy Facility at UCSC. Grazing-Incidence X-ray Scattering measurements performed at the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.

Abstract: Conjugated polyelectrolytes (CPEs) combine semiconducting polymer photophysics with aqueous polyelectrolyte processability, yet producing mechanically robust, printable CPE-based soft materials has remained elusive. The work in this chapter demonstrates that complexation temperature alone simultaneously controls the rheology, nanostructure, and exciton dynamics of conjugated polyelectrolyte complex (CPEC) gels formed from the cationic CPE PFNB and the anionic CPE PCPT at 1:1 charge stoichiometry. Increasing the complexation temperature from 60

to 80 °C raises the storage modulus from 530 to 790 Pa, driving a morphological transition from loosely organized networks to dense colloidal domains with sharper interfaces (GI-SAXS power-law exponent steepening from $n = -3.23$ to -3.74), and accelerates both fast ($\tau_{\text{fast}} = 8.5$ to 5.77 ps) and slow ($\tau_{\text{slow}} = 243$ to 128 ps) exciton decay components. Leveraging the rheological properties of the 80 °C gel, the first 3D-printing of a fully conjugated polyelectrolyte complex ink via direct-write extrusion is demonstrated. These results establish complexation temperature as a single processing-level handle for co-modulating the mechanical and photophysical response of CPE-based complex fluids and open a route to additive manufacturing of photoactive soft materials from aqueous semiconducting polymer inks.

4.1 Introduction

Conjugated polyelectrolytes (CPEs) occupy a unique position at the intersection of semiconducting materials science and polyelectrolyte physics.^{1,4} Their π -conjugated backbones support delocalized excitons and enable light absorption, emission, and charge transport, while their pendant ionic groups confer solubility in aqueous and polar media.^{14,18} This dual character makes CPEs attractive building blocks for optoelectronic devices, biological sensors, and light-harvesting systems that operate in aqueous and even biological environments.^{1,2,12} Despite these favorable attributes, translating their optoelectronic properties into processable soft materials suitable for advanced manufacturing remains a challenge.^{2,5,12}

Inter-polyelectrolyte complexation offers a compelling strategy for bridging this gap. When oppositely charged polyelectrolytes are mixed in solution in near

stoichiometric molar charge ratios, associative phase separation may occur, producing a concentrated, highly polymer-enriched complex phase that coexists with a dilute supernatant.^{3,6} The thermodynamics and kinetics of this process have been investigated in considerable detail for nonconjugated polyelectrolyte systems. A continuum of complex states ranging from liquid coacervates to solid-like precipitates has been established, demonstrating that the rheological character of the complex phase can be tuned through salt concentration and mixing conditions.³ At the processing end, polyelectrolyte complexes can be fabricated into dense, glassy materials with tunable mechanical properties, highlighting the versatility of these assemblies as functional soft materials.⁷ The rheological tunability of polyelectrolyte complexes has recently been exploited for 3D-printing, with demonstrations of pH-sensitive polyelectrolyte hydrogels possessing self-healing properties suitable for extrusion-based fabrication¹⁰ and 3D-printable interpenetrating network hydrogels based on polyelectrolyte complexes with customizable mechanical strength.¹¹ These advances collectively show that polyelectrolyte complexation is a powerful platform for generating soft materials with programmable mechanics.

However, most work on associative phase separation focuses on electronically inactive, nonconjugated polyelectrolytes. Extending this framework to conjugated polyelectrolytes (CPEs) introduces an additional, important dimension: the coupling between network microstructure and electron/ion interactions.^{1,2,4} Indeed, the Chabinyc and Segalman groups have demonstrated the utility of this approach by forming

conducting and 3D-printable soft matter based on complexed polyelectrolytes between a conducting and an insulating polyelectrolyte.

For light-harvesting applications, an inter-CPE complex giving rise to the possibility of exciton and charge transfer between the two polymers in the complex is desired. It has been previously shown that associative phase separation of oppositely charged CPEs produces materials in which the photophysical and mechanical properties are intrinsically coupled through their shared dependence on the network microstructure.¹ In doing so, it is demonstrated that the complex fluids comprised of inter-CPE complexes could function as aqueous exciton transport networks, supporting long-range energy migration through the electrostatically assembled chromophore scaffold.² Facile exciton migration is often a necessary characteristic in high-efficiency light-harvesting systems.

At the same time, when studying dilute inter-CPE complexes, it was found that the complexation of exciton donor and acceptor CPEs is thermally activated, leading to an exciton transfer efficiency that was highly sensitive to the complexation temperature. This stood in stark contrast to complexation of nonconjugated polyelectrolytes, which readily proceeds at room temperature. In addition to the kinetics, it was determined that the *sign* of the complexation enthalpy changed with increasing complexation temperature. This raised the question: could the complexation temperature potentially serve as a simple yet powerful knob to modulate the optoelectronic properties of complex fluids formed via associative phase separation of oppositely charged CPEs? Similar to ionic strength, a processing parameter that could

potentially modulate the network structure without altering the chemical identity of the components could offer a practical and scalable route to on-demand property control.

To answer the above question, the influence of complexation temperature on the structural, rheological, and photophysical properties of inter-CPE complex fluids was investigated. The network quasi-continuously was found to evolve from a loose and filamentous network into a more well-defined colloidal microstructure. This is accompanied by an increase in the storage modulus and a decrease in the exciton lifetime. Based on the kinetics of exciton-exciton annihilation, one can argue that as the complexation temperature increases, the number density of ionic crosslinks in the resulting inter-CPE complex fluid phase also increases. This is further accompanied by an enhancement in the average number of local inter-chromophore interactions, which is expected to exert a strong influence on the rate of exciton and electronic charge migration.

The practical consequence of this temperature-directed tunability is the realization of 3D-printable exciton-transport network. This work demonstrates that when complexed at 80 °C, the inter-CPE complex fluid can be extruded via direct-ink writing to produce self-supporting, multilayer structures with robust shape fidelity, representing the first report of additive manufacturing using a fully π -conjugated inter-polyelectrolyte complex.^{6,20} This opens the door to patterned optoelectronic architectures and spatially heterogeneous light-harvesting structures that would be difficult to achieve through conventional thin-film deposition, particularly when using water as the medium.

4.2 Experimental

Sample Preparation. Conjugated polyelectrolyte complex gels were prepared by associative phase separation of the cationic CPE PFNB and the anionic CPE PCPT in aqueous solution. Stock solutions of each polyelectrolyte were filtered. To initiate complexation, the PFNB and PCPT stock solutions were combined at a 1:1 molar charge ratio. Three complexation temperatures were investigated: 60, 70, and 80 °C. At each temperature, the mixed solutions were degassed and held for approximately 12 h to allow associative phase separation to proceed. Following complexation, the samples were centrifuged at 10,000 rpm for 45 min to mechanically separate the polymer-rich complex phase from the dilute supernatant. The supernatant was then removed, and the concentrated complex fluid was collected for all subsequent measurements.

Steady-State Spectroscopic Measurements. Optical density (absorption) measurements were collected from the thin-films using a Shimadzu UV-2700 spectrometer. Spectra were collected over the 300–800 nm wavelength range in 1.0-nm increments, with a thin film adaptation to the sample holder.

Grazing Incidence Small-Angle X-ray Scattering (GI-SAXS).

GI-SAXS measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 1-5. The beamline is equipped with a Pilatus area detector configured for grazing-incidence geometry. Polymer thin films were mounted on silicon substrates and aligned at an incident angle slightly above the critical angle to enhance surface sensitivity and minimize substrate scattering.

Measurements were conducted at an X-ray energy of 12 keV with a sample-to-detector distance of approximately 2 m, yielding an effective q -range of 0.006–0.7 Å⁻¹. Scattering patterns were averaged over multiple 1 s exposures to minimize radiation damage. Data were corrected for background, detector geometry, and polarization effects, then azimuthally integrated using the Nika software package implemented in Igor Pro.

Grazing Incidence Wide-Angle X-ray Scattering (GI-WAXS). GI-WAXS measurements were conducted at SSRL on beamline 11-3, equipped with a Pilatus detector optimized for high- q measurements in grazing-incidence geometry. Samples were measured at an X-ray energy of 12 keV with a sample-to-detector distance of approximately 0.25 m, providing access to crystalline and molecular-scale ordering. Data were collected as a series of 1 s exposures to reduce radiation-induced effects. Two-dimensional scattering images were corrected for detector response and background, then processed and azimuthally integrated using the WAXStools suite in Igor Pro to obtain one-dimensional intensity profiles for structural analysis.

Rheology. The linear viscoelasticity of the coacervates was determined using small-amplitude oscillatory shear (SAOS) measurements on a Malvern Kinexus Pro stress-controlled rheometer at 25°C and ambient humidity (35-50% RH). A 20 mm diameter stainless steel parallel plate fixture was used for all SAOS measurements. Strain amplitude sweeps were conducted to first determine the appropriate strain amplitude to use within the linear viscoelastic region of the coacervates. Next, frequency sweeps were conducted over the range of 10-0.1 s⁻¹ on coacervates prepared at different

temperatures. Data was plotted and analyzed using OriginPro 2025 software (OriginLab Corporation, Northampton, MA).

Ultra-Fast Pump-Probe Transient Absorption. Femtosecond TA measurements were taken using a Light Conversion laser system in a previously reported configuration.^{1,2} The fundamental beam with an output fundamental wavelength of 1030 nm, 10 W power, a repetition rate of 20 kHz, and pulse width of 160 fs was generated by PHAROS (Light Conversion). PHAROS is equipped with a ytterbium-doped potassium gadolinium tungstate (Yb:KGW) lasing medium. Tunable pump wavelengths were produced by feeding 80% of the fundamental beam into an optical parametric amplifier (OPA), ORPHEUS (Light Conversion). A white light continuum probe beam was generated by passing the remaining 20% of the fundamental through a nonlinear sapphire crystal. The generated pump and probe beams were aligned in an ultrafast TA system, HARPIA (Light Conversion). Spatial alignment was controlled by mirrors, while temporal overlap was controlled by a translating delay stage. For measurements, the time delay between pump and probe pulses was varied from -10 to 5000 ps. Data were collected using the Light Conversion HARPIA data acquisition software and using an Oxford Instruments Andor spectrometer.

3D-printing All printing was done with the Hyrel 30M Printer. The polymer was first loaded into a 1mL syringe barrel and centrifuged at 1550 rpm for 2 minutes to remove air bubbles. The polymer was then extruded onto a silicon wafer through a micro nozzle (1600 μm) to form the desired shapes. The writing speed was set around 1.5-2.0 mm/s and the diameter of the cylinders was equal to the diameter of the

nozzle. The extruded polymer was gently heated using a heat gun during the printing to thicken the polymer. Printed samples were then heated at 80°C to finish the cross-linking process.

4.3 Results and Discussion

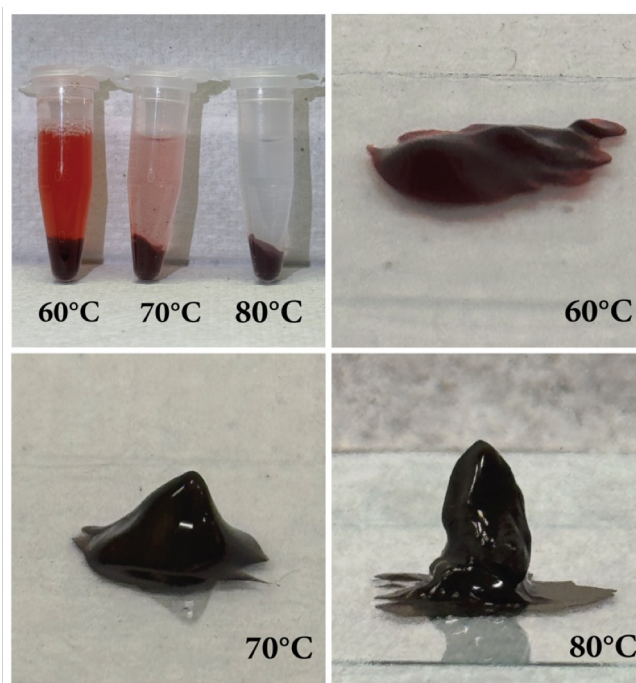


Figure 4.1. PFNB:PCPT CPEC fluids prepared at 60, 70, and 80 °C. (Top left) Centrifuge tubes after phase separation. (Top right, bottom left, bottom right) Isolated gels at each temperature, showing increasing mechanical robustness with complexation temperature.

The CPEC active layer was formed from the anionic CPE, PCPT, and the cationic CPE, PFNB. To induce associative phase separation, the total polymer concentration was fixed, and the nominal stoichiometric polyion charge ratio was

held at 1:1.^{1,2} The cationic and anionic CPEs, possessing similar charge densities and repeat unit structures, align efficiently at charge equivalence to form complexes. These complexes self-assemble and undergo associative phase separation, producing a polymer-enriched complex fluid phase composed of conjugated inter-polyelectrolyte complexes (CPEC fluid) coexisting with a dilute solution.^{3,4} Associative phase separation was induced at different complexation temperatures (T_{CPEC}), after which samples were cooled down to room temperature prior to performing measurements. When each of the CPEC fluid were isolated, the visual appearance (Figure 4.1) strongly suggests that its viscoelastic properties are directly influenced by T_{CPEC} . The photographs in Figure 4.1 show that the red color intensity in the dilute solution due to PCPT light absorption decreases monotonically with increasing T_{CPEC} , as evidenced by UV-Vis spectroscopy (SI Figure II1) and the characteristic red color of PCPT in the photograph.

Figure 4.2 shows normalized ground-state absorption spectra of CPEC fluids at $T_{CPEC} = 60, 70, \text{ and } 80\text{ }^{\circ}\text{C}$, which displays two principal features: the PFNB absorption centered near 375 nm and the PCPT absorption centered near 510 nm. The relative ratios between the PFNB and PCPT bands is consistent with a near 1:1 polyion charge ratio. Absolute absorption spectra of all three complexation temperatures are provided in the Supporting Information (Figure II1). Spectra normalized to the PCPT band (Figure II2), reveal that the line shape is largely preserved across all three temperatures, with only a slight increase in the relative

intensity of the PFNB peak at higher complexation temperatures. The near-invariance of the spectral shape indicates that complexation temperature controls the effective chromophore packing density without substantially altering the intrinsic electronic structure of the constituent CPEs.

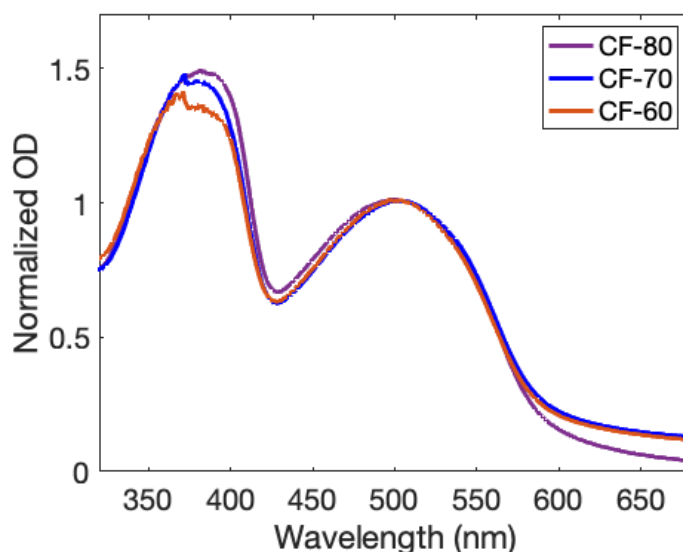


Figure 4.2. Normalized UV-Vis absorption spectra of CPEC fluids prepared at 60, 70, and 80 °C. The spectral line shape is largely preserved across all three temperatures.

To directly visualize the morphology of the CPEC fluids as a function of T_{CPEC} , cryogenic transmission electron microscopy (cryo-TEM) was performed. The aim being to take advantage of the enhancement in electron density contrast provided by π -stacking interactions and the accumulation of sulfur atoms belonging to PCPT in regions with close polyion association. Figure 4.3 presents cryo-EM images of the

CPEC networks at 60 and 80 °C at two magnifications. At 60 °C (Figure 4.3a,b) under low magnification, the morphology is largely featureless, showing only relatively mild electron density fluctuations. At higher magnification, the image reveals a loosely organized polymer network with extended, web-like chain arrangements distributed throughout the vitrified film. The polymer strands appear relatively diffuse, with large open regions separating the network filaments. Our prior work showed that in dilute solution complexation between oppositely charged CPEs may be thermally activated. Thus, this open and interconnected morphology is likely characteristic of a comparatively lightly crosslinked network in which the electrostatic junctions are spaced some distance apart, and the chains adopt extended conformations between crosslink points.

At 80 °C (Figure 4.3c,d), even the low-magnification cryo-EM image reveals a markedly different morphology, as significantly larger-scale, well-defined structures become visible. The high-magnification image shows that the network coalesces into discrete colloidal domains with substantially higher electron-density contrast in coexistence with a network that shows lower contrast than the domains but higher contrast than the network at 60 °C. The domains appear as dark, spheroidal aggregates with lateral dimensions on the order of tens of nanometers. The formation of these dense colloidal structures is consistent with more extensive electrostatic complexation at elevated temperatures, which drives the polymer chains into tightly associated clusters with a higher density of ionic crosslinks. Thus, despite little change to the UV-

Vis spectra, one observes a transition from an open, filamentous network at 60 °C to a denser, domain-structured morphology at 80 °C.

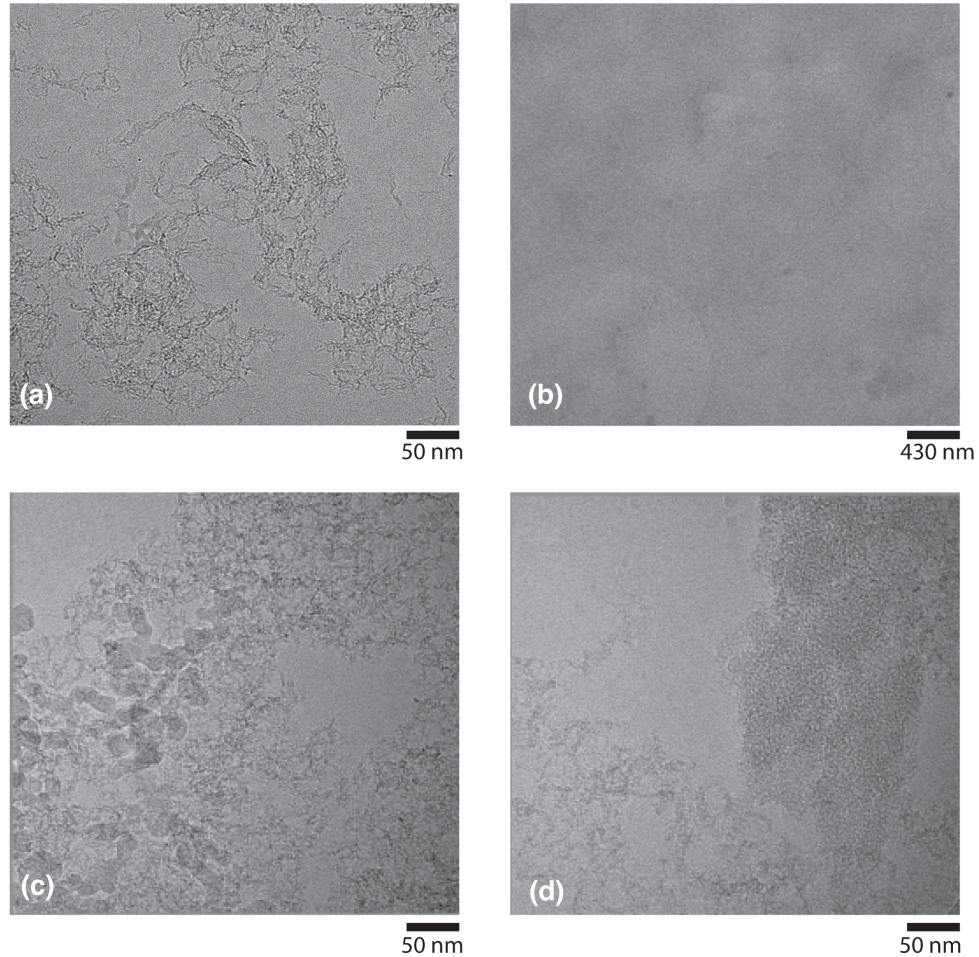


Figure 4.3. Cryo-EM images of CPEC networks at two magnifications. (a, b) At 60 °C, a loosely organized, filamentous network is observed. (c, d) At 80 °C, the network coalesces into dense colloidal domains with higher electron-density contrast.

Complementary to the small-scale, real-space cryo-EM observations are larger-scale, reciprocal-space characterization via grazing-incidence small-angle X-ray

scattering (GI-SAXS). Figure 4.4 presents the reduced GI-SAXS intensity curves as a function of the in-plane component of the scattering vector Q_{xy} for CF-60, CF-70, and CF-80 on a log-log scale. None of the scattering profiles exhibit distinct Bragg peaks, confirming that the CPEC networks adopt a disordered, amorphous morphology at all three T_{CPEC} rather than an ordered or crystalline nanostructure. This absence of long-range order is consistent with the cryo-EM observations and with general expectations for electrostatically assembled polyelectrolyte complexes.³ The so-called polyelectrolyte peak in the scattering intensity profile was not observed.

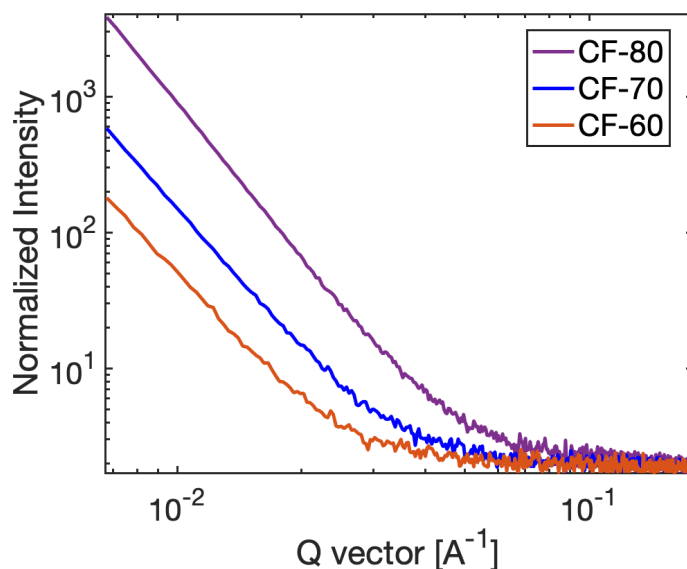


Figure 4.4. GI-SAXS intensity profiles for CPEC fluids prepared at 60, 70, and 80 °C. Increasing low- Q intensity and a steepening power-law exponent with temperature indicate sharper domain interfaces.

The overall scattering intensity increases systematically with temperature across the accessible Q range. CF-80 exhibits the highest normalized intensity at low

Q , followed by CF-70 and then CF-60. Although care was taken to minimize differences in sample volume, given the nature of the samples it was effectively impossible to eliminate the influence of slight changes in the scattering volume on the scattering intensity. However, changes in the scattering volume cannot explain such large difference in intensity. In the zero- Q limit, the intensity scales like the square of the average electron density fluctuation. Thus, the increase in the limiting scattering intensity as a function of T_{CPEC} indicates a monotonic increase in the electron density contrast of the scattering inhomogeneities is observed. This observation is consistent with the cryo-EM data.

The low- Q region for all samples appears locally linear on a log-log plot, suggesting that

$$I(Q) \sim Q^{-\alpha} \quad (1.51)$$

The exponent α can be interpreted as reporting on the fractal dimension D_s of the surface between the scattering inhomogeneities as

$$\alpha = 6 - D_s \quad (1.52)$$

The D_s values were 2.77, 2.47, and 2.26 for samples with $T_{CPEC} = 60, 70$, and 80°C , respectively. The systematic decrease in D_s as a function of T_{CPEC} reveals that the CPEC domains became progressively better defined and more sharply bounded as the network compacts at higher temperatures. This finding aligns with the cryo-EM observations which show more well-defined particles form as T_{CPEC} is increased.

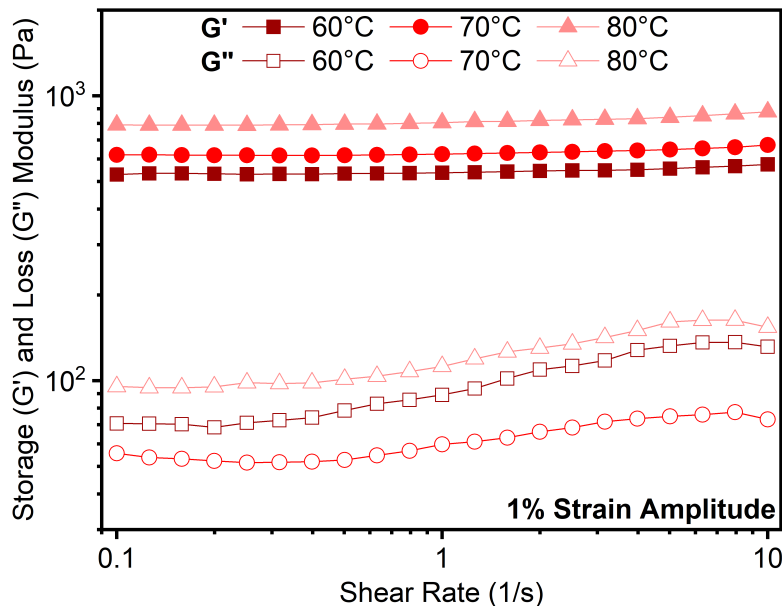


Figure 4.5. Storage modulus (G' , filled symbols) and loss modulus (G'' , open symbols) as a function of shear rate for PFNB:PCPT complex fluids prepared at 60 °C (squares), 70 °C (circles), and 80 °C (triangles). Measurements were performed at a fixed strain amplitude of 1%.

Having demonstrated the evolution of the CPEC fluid structure with increasing T_{CPEC} , the structure was shown to be correlated to the mechanical properties of the CPEC fluid, and oscillatory shear measurements were performed. Frequency sweep measurements were conducted at a fixed strain amplitude of 1%, well within the linear viscoelastic regime, over a shear rate range of 0.1 to 10 s^{-1} . Figure 4.5 presents the storage modulus (G') and loss modulus (G'') as a function of the shear rate for all T_{CPEC} . Across all temperatures, G' exceeds G'' over the entire measured frequency range. This response is characteristic of physically crosslinked polyelectrolyte networks at low

ionic strength.^{3,6-7} G' is weakly frequency-dependent, a hallmark of gel-like network materials in which the crosslink density and relaxation timescales are sufficiently long that the network does not relax appreciably over the probed timescales.⁸

T_{CPEC} exerts a pronounced effect on the magnitude of both moduli. The 80 °C complex fluid exhibits the highest G' , reaching 791 Pa at 0.1 s⁻¹, compared to 621 Pa for the 70 °C sample and 530 Pa for the 60 °C sample. This systematic increase in G' with T_{CPEC} indicates a progression to stiffer networks, presumably due to a greater number density of ionic crosslinks. The mechanistic origin of this temperature-dependent stiffening lies in the thermally activated nature of the complexation process. At elevated temperatures, increased chain mobility allows CPE chains to more effectively overcome the complexation activation barrier and thereby explore a greater conformational space, leading to more extensive ion pairing.

The loss modulus G'' follows a similar temperature-dependent hierarchy but exhibits a more pronounced frequency dependence than G' , particularly at higher shear rates. For the 80 °C sample, G'' rises from 95 Pa at 0.1 s⁻¹ to 154 Pa at 10 s⁻¹, while the 60 and 70 °C samples show G'' values of 56 to 71 Pa at low frequency that increase to 73 to 132 Pa at the highest rates. The increase of G'' with frequency reflects energy dissipation through internal friction within the polymer network, likely arising from

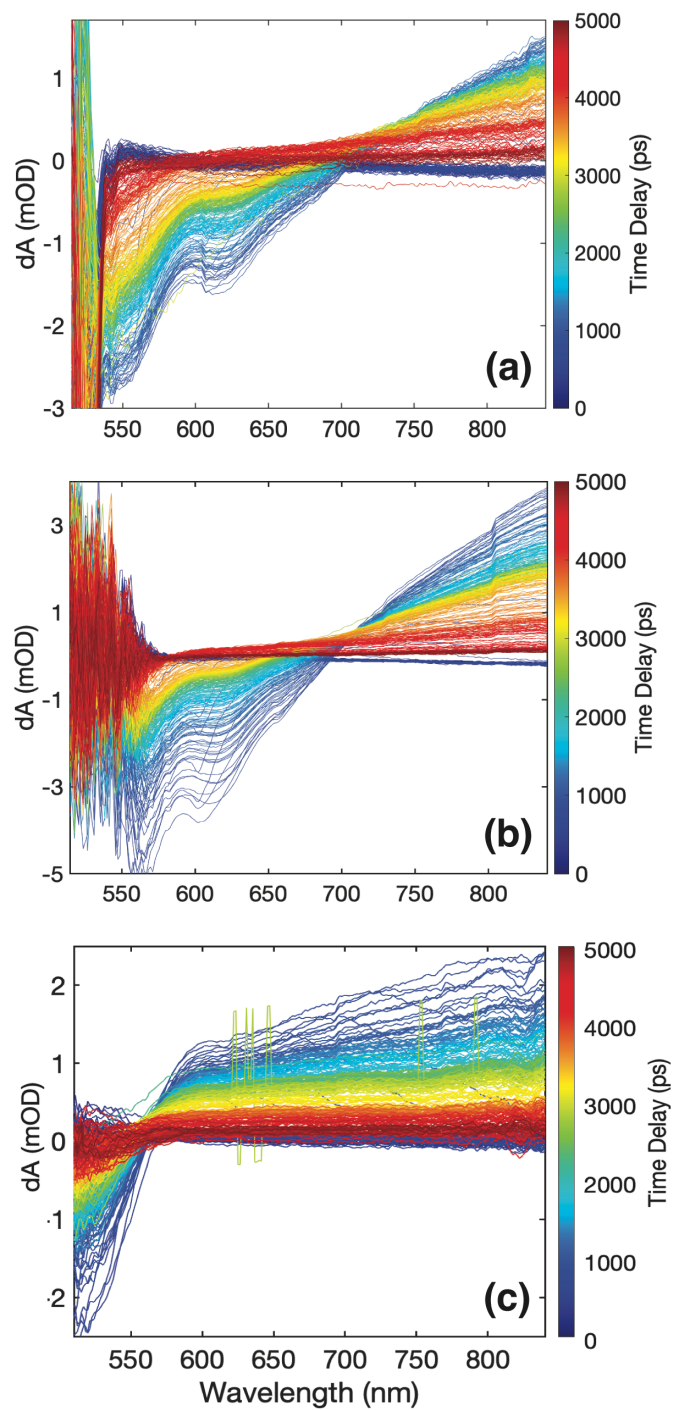


Figure 4.6. Femtosecond transient absorption spectra of CPEC fluids excited at 520 nm for (a) CF-60, (b) CF-70, and (c) CF-80. Stimulated emission diminishes at higher complexation temperatures, consistent with increased H-aggregate formation.

transient rearrangements of chain segments and ionic crosslinks under deformation.^{8,9} The larger absolute values of G'' for the 80 °C complex are consistent with a denser network in which more energy is dissipated per deformation cycle due to the greater number of interchain contacts.

The relatively modest frequency dependence of the moduli overall indicates that the CPEC networks are robust and do not undergo significant structural breakdown within the probed deformation range, a property favorable for extrusion-based processing.^{10,11} The change in structure and rheological properties as a function of T_{CPEC} leads to the hypothesis that T_{CPEC} would influence the dynamics of photogenerated excitons. To test this, ultrafast pump-probe spectroscopy on the different CPEC fluid samples were performed. Samples were excited at 520 nm, selectively pumping the PCPT chromophore within the complex to avoid the complicating influence of ultrafast exciton transfer from PFNB to PCPT. Samples were probed across the visible to near-infrared spectral window.^{2,12}

Figure 4.6 shows differential absorption spectra (dA) of the probe pulse following excitation by the pump pulse at varying pump-probe delay times. The spectra reveal several distinct photophysical features. A negative dA signal spanning the 500 to 550 nm region corresponds to ground-state bleach of the PCPT absorption band, while the negative signal between 550 and ~725 nm corresponds to stimulated emission from PCPT. A broad, positive excited-state absorption (ESA) signal extends upwards from approximately 600, corresponding to transitions from low-lying to higher-energy

exciton states.^{13,14} The ESA signal is intense at early times and decays over the course of hundreds of picoseconds, tracking the relaxation of the photoexcited exciton population back to the ground state. The data show that CPEC fluids with $T_{CPEC} < 80$ °C give rise to substantial amounts of stimulated emission, whereas the 80 °C sample shows no apparent stimulated emission. This is consistent with the structural characterization: at lower T_{CPEC} , incomplete electrostatic crosslinking leaves a fraction of PTPC chromophores relatively isolated, leading to light emission via J-aggregate-type excitonic states. In contrast, the 80 °C sample forms a large number density of electrostatic crosslinks; this leads to a local enrichment in CPE chains and a concomitant increase in the number density of π -stacking chromophores. This in turn leads to the formation of poorly emissive H-aggregate-type excitonic states, significantly diminishing the stimulated emission signal.

To quantitatively compare the exciton dynamics across T_{CPEC} , single-wavelength kinetic traces were extracted from the ESA band and fit to a biexponential decay model. Figure 4.7 shows the temporal slices through the pump/probe spectra for the three samples, along with the corresponding biexponential fits. The extracted time constants are summarized in Table 4.1. The biexponential decay reveals two distinct relaxation channels operating on markedly different timescales. The fast component (τ_{fast}), on the order of 6 to 10 ps, is assigned to ultrafast nonradiative relaxation processes including vibrational cooling, torsional relaxation of the conjugated backbone, and, at the high chromophore densities present in the concentrated CPEC fluids, exciton-exciton annihilation (EEA).^{13,15} In the EEA process, two proximal

excitons on two adjacent chromophores transform into one higher-lying exciton along one chromophore and one chromophore returning to the ground state. The result is usually a rapid decrease in the transient excited-state absorption signal by the initial excitons created upon absorption of the pump pulse.

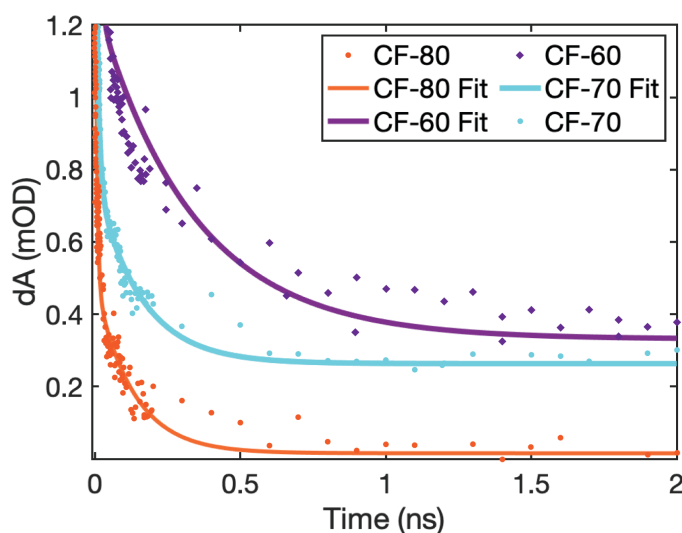


Figure 4.7. Transient absorption kinetic traces and biexponential fits for CF-60, CF-70, and CF-80. Decay accelerates with increasing complexation temperature.

The acceleration of the fast component at 80 °C is consistent with enhanced exciton-exciton annihilation in a more densely aggregated network. At higher chromophore densities, the average inter-exciton distance decreases, increasing the probability of bimolecular exciton encounters that lead to nonradiative quenching.^{15,16} In conjugated polymer systems, EEA rates have been shown to scale with the local

chromophore packing density and the extent of interchain electronic coupling,¹³ both of which are expected to increase in the more compact CPEC networks formed at higher temperatures.

Table 4.1. Biexponential decay time constants extracted from femtosecond transient absorption kinetic traces of CPEC fluids.

Sample	τ_{fast} (ps)	τ_{slow} (ps)
CF60	8.5	243
CF70	9.5	164
CF80	5.77	128

The slow component (τ_{slow}) reflects the longer-lived population decay of the vibrationally relaxed exciton through a combination of radiative and nonradiative recombination pathways.¹⁴ The shortening of τ_{slow} from 243 ps at 60 °C to 128 ps at 80 °C, representing a nearly two-fold acceleration, points to increased nonradiative relaxation channels in the densely packed network. As the density of ionic crosslinks and interchain contacts increases, excitons encounter a greater number of defect sites and regions of strong interchain coupling that serve as nonradiative quenching centers.^{5,17} This interpretation is consistent with the broader observation that more

tightly aggregated conjugated polymer networks generally exhibit shorter exciton lifetimes due to enhanced coupling to non-emissive trap states and charge-transfer states at interchain interfaces.^{18,19} The nearly two-fold reduction in τ_{slow} is particularly noteworthy, as it indicates that the mesoscale morphological differences established during complexation manifest directly in the electronic dynamics of the material at picosecond timescales.

The gel-like rheological properties of the 80 °C complex fluid, with G' values on the order of several hundred Pa, place these materials in a mechanical regime well-suited for direct-write 3D-printing, where the ink must be sufficiently elastic to maintain shape fidelity after extrusion yet compliant enough to flow under applied shear.^{10,11} Previous studies on polyelectrolyte-based 3D-printable hydrogels have demonstrated that G' values in the range of 10^2 to 10^4 Pa are typically necessary for self-supporting extrusion, and the values observed here fall squarely within this window.^{10,11}

The 3D-printing of the CPEC fluids could indeed be 3D-printed was investigated, as being able to do so would open up new applications for such optoelectronic soft matter. The CPEC ink was loaded into a 1 mL syringe and centrifuged at 1550 rpm for 2 minutes to remove air bubbles before extrusion onto a silicon wafer at a linear speed of 1.5 to 2.0 mm/s. Gentle heating with a heat gun was applied between layers to facilitate drying and improve stickability. Figure 4.8 illustrates a representative 3D-printing of the 80 °C CPEC fluid was successful,

resulting in a semiconducting, printable, and stackable gel. The resulting printed structures demonstrate robust shape retention and the ability to support multiple stacked layers, confirming that the rheological properties of the 80 °C complex fluid are well-matched to the requirements of direct-write extrusion printing.^{10,11} The printed structures maintain their shape without visible slumping or spreading, consistent with the rheological response measured for the 80 °C complex fluid. To our knowledge, this represents the first demonstration of 3D-printing a complex fluid composed of two oppositely charged CPEs, extending the materials for printable optoelectronic inks to systems that can readily undergo exciton and charge transfer between two π -conjugated polyelectrolytes.^{6,20}



Figure 4.8. Photograph of a 3D-printed conjugated polyelectrolyte complex structure fabricated by direct-ink-write extrusion of the 80 °C CPEC fluid onto a silicon wafer. The printed serpentine pattern demonstrates robust shape retention and self-supporting line definition, confirming the suitability of the CPEC gel rheology for additive manufacturing of photoactive soft materials.

4.4 Conclusion

In conclusion, it has been demonstrated that complexation temperature serves as a powerful parameter for rational manipulation of rheological, structural, and photophysical properties of CPEC fluids. By varying only the temperature at which the oppositely charged CPEs undergo associative phase separation, the resulting CPEC networks evolve from loosely organized, filamentous architectures at low complexation temperatures into dense colloidal domains with more sharply defined interfaces at elevated complexation temperatures, as confirmed by both cryo-EM and GI-SAXS. This structural compaction drives a monotonic increase in storage modulus from 530 to 790 Pa across the temperature series while preserving the elastic-dominant, gel-like character ($G' > G''$) required for extrusion-based processing. Femtosecond transient absorption spectroscopy reveals that the same morphological transition forms new excitonic states that modulate exciton and very likely electron/hole pair migration. Importantly, the intrinsic electronic structure of the constituent CPEs remains unchanged across all three temperatures, as evidenced by the near-invariant absorption lineshape, confirming that temperature modulates network architecture and chromophore packing density without altering the underlying photophysics of the individual polymers.

The practical significance of this tunability is illustrated by the first demonstration of 3D-printing a fully π -conjugated inter-polyelectrolyte complex fluid. The 80 °C CPEC ink can be extruded via direct-ink writing to produce self-supporting,

multilayer semiconducting structures with robust shape fidelity, extending the scope of printable polyelectrolyte materials into the domain of π -conjugated systems. The ability to adjust the mechanical and excitonic properties of these inks through a single processing variable, without reformulation, is particularly attractive for manufacturing workflows in which ink composition must remain fixed while target properties vary.

The framework established here provides a particularly simple design rule for tailoring CPEC fluid properties to specific applications: higher complexation temperatures favor mechanical robustness and printability at the expense of exciton lifetime, while lower temperatures preserve longer-lived excited states within softer, more open networks. Future work extending this approach to other processing variables, broadening the accessible CPE chemistry, and integrating spatial control of complexation temperature during printing could enable the fabrication of graded or patterned optoelectronic architectures from aqueous semiconducting polymer inks.

4.5 References

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APPENDIX III:

III.1. Steady State Photophysics

Steady-state absorption spectra of the CPEC fluids are presented as absolute optical density rather than the normalized spectra shown in Figure 4.2 of the main text. The absolute OD increases systematically with complexation temperature, consistent with the conclusion that higher complexation temperatures drive more extensive associative phase separation and produce CPEC networks with greater effective chromophore density. The CPEC fluid films lack a precisely defined thickness, the absolute OD values should be regarded as approximate.

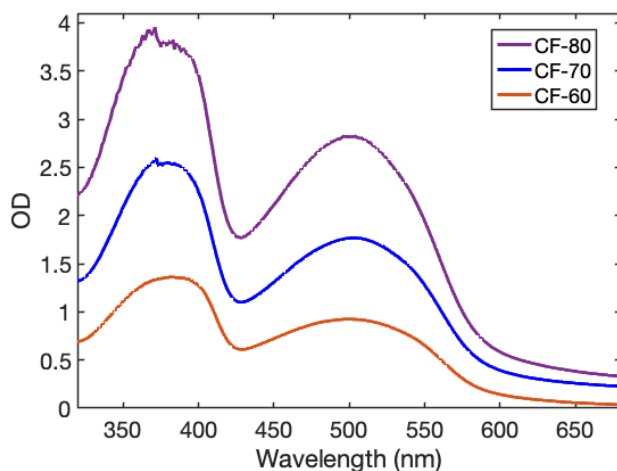


Figure III.1. UV-Vis absorption spectra of PFNB:PCPT conjugated polyelectrolyte complex (CPEC) fluids prepared at complexation temperatures of 60, 70, and 80 °C. Optical density is plotted as a function of wavelength over the 300 to 800 nm range.

Nevertheless, the clear trend across the temperature series supports the interpretation that complexation temperature controls the amount of polymer incorporated into the complex phase without substantially altering the intrinsic electronic structure of the constituent CPEs, as evidenced by the preserved spectral line shape.

III.2. GISAXS: Power-Law Fits

Figures II.2.1 through II.2.3 present the individual power-law fits to the GI-SAXS intensity profiles for CF-60, CF-70, and CF-80, respectively. In each case, the low- Q scattering data were fit to $I(Q) \sim Q^{(-\alpha)}$ on a log-log scale to extract the power-law exponent used to determine the surface fractal dimension D_s reported in the main text. The fits confirm that the power-law model provides a good description of the scattering behavior across the accessible Q range for all three complexation temperatures.

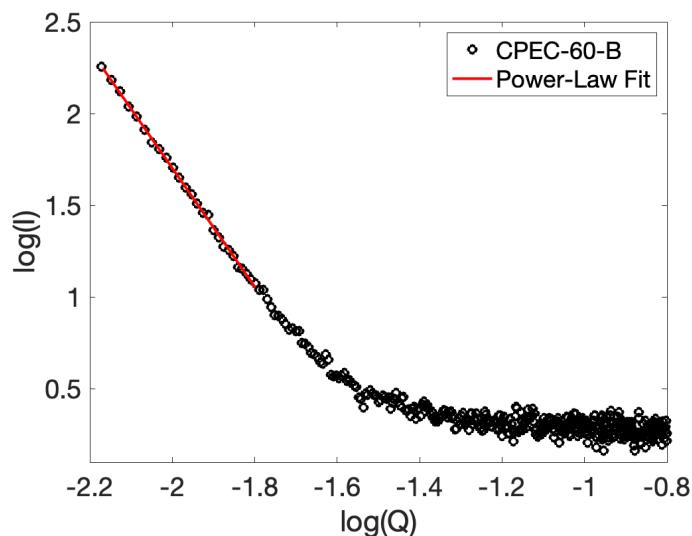


Figure III.2.1. Power-law fit of GI-SAXS intensity data for the CPEC fluid prepared at 60 °C (CF-60). Log-transformed scattering intensity is plotted against the log-transformed scattering vector, with the solid line representing the best-fit power-law model.

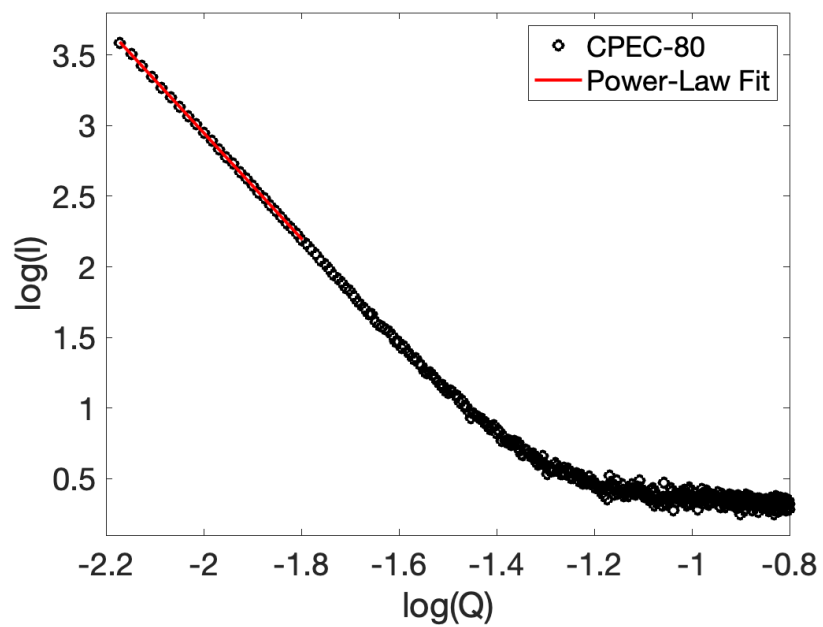


Figure III2.3. Power-law fit of GI-SAXS intensity data for the CPEC fluid prepared at 80 °C (CF-80). Experimental log(I) vs. log(Q) data are shown with the corresponding power-law fit.

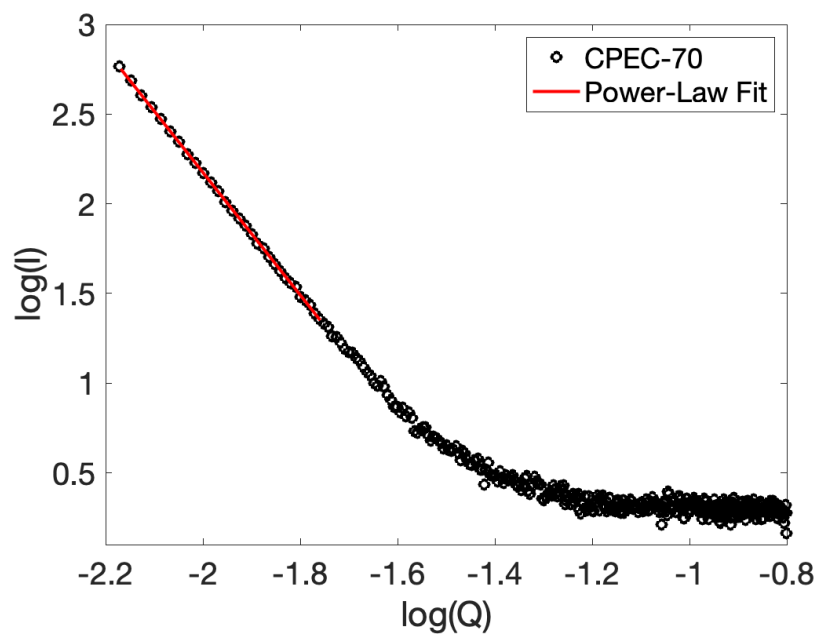


Figure III.2.2. Power-law fit of GI-SAXS intensity data for the CPEC fluid prepared at 70 °C (CF-70). $\log(I)$ is plotted versus $\log(Q)$, with the power-law fit overlaid.

CHAPTER V

Conclusion

This dissertation has developed conjugated polyelectrolyte complexes (CPECs) as a versatile, water-based materials platform for light harvesting and photovoltaic energy conversion. Across three studies, the fundamental understanding of exciton and charge-carrier processes within electrostatically assembled CPE networks was advanced. Moreover, the associative phase separation of oppositely charged CPEs offers a qualitatively new pathway toward aqueous organic photovoltaics (aOPVs) was demonstrated.

In Chapter 2, it was established that the backbone chemical structure governs exciton transfer within CPECs. By synthesizing a series of cationic donor CPEs with systematically varied comonomers while holding the linear ionic charge density nearly fixed, showing that relatively subtle modifications to the nonionic comonomer can produce large differences in electronic energy transfer (EET) efficiency and rate. Crucially, these differences could not be rationalized by spectral overlap considerations alone. Instead, evidence showed that the exciton delocalization radius plays a determining role in the excitonic coupling, consistent with analytical models based on the line-dipole approximation and quantum-chemical calculations. These findings highlight that the standard Förster framework, which assumes point-dipole interactions, can break down in CPECs where donor-acceptor separations are

comparable to or smaller than the spatial extent of the excitonic wave function. This work provided essential design principles for selecting CPE components that maximize EET in aqueous light-harvesting assemblies.

Chapter 3 translated these light-harvesting capabilities toward photovoltaic function by asking whether a CPEC fluid could be engineered to convert excitons into mobile charge carriers. A nonionic micelle delivery strategy was introduced to incorporate both fullerene (C60) and non-fullerene (ITIC) small-molecule electron acceptors into the CPEC matrix without disrupting the aqueous assembly process. Dynamic light scattering confirmed quantitative surfactant removal following a thermal extraction procedure, while UV-Vis spectroscopy verified systematic acceptor retention in the dried films. GI-SAXS and cryogenic electron microscopy revealed that acceptor incorporation induced long-range structural order within the otherwise amorphous CPEC network, with the NFA driving substantially greater domain coherence than the fullerene acceptor. Time-resolved photoluminescence showed instrument-response-limited quenching of the PCPT excited state, and ultrafast transient absorption spectroscopy provided definitive mechanistic evidence for photoinduced charge transfer at the CPEC-acceptor interface, as evidenced by a polaron absorption band whose lifetime significantly exceeded that of the excitonic signal. Proof-of-principle aOPV devices produced a measurable photocurrent under illumination, confirming that the photogenerated charge carriers possess sufficient mobility for long-range transport through the CPEC film.

Chapter 4 explored alternative deposition strategies and identified the key factors currently limiting device performance. The extremely thick films produced by manual blade coating, often exceeding 1 μm , led to extensive recombination losses. Additionally, the limited interfacial area between the CPE donor network and the small-molecule acceptors, a consequence of introducing acceptors after the electrostatically cross-linked CPEC network had already formed, constrained exciton dissociation efficiency. A solvent-annealed drop-casting approach was investigated as an alternative but was hampered by film non-uniformity and delamination during surfactant extraction. These observations underscore that future progress will require refined control over film thickness, improved strategies for maximizing the donor-acceptor interfacial area (such as incorporating acceptors at the electrostatic assembly stage), and optimization of device architecture including the addition of charge-transport interlayers.

Taken together, this body of work establishes that CPECs formed by associative phase separation represent a fundamentally distinct approach to aOPVs, one that is complementary to existing nanoparticle-based strategies. The rheological properties of CPEC fluids make them inherently suited for coating substrates of complex form factors and for the fabrication of flexible and stretchable devices, capabilities that are difficult to achieve with conventional spin-coating methods. The ability to tune both the optoelectronic and mechanical properties of the active layer through the ionic atmosphere offers a rich design space that has only begun to be explored. While substantial challenges remain in optimizing film morphology, donor-

acceptor mixing, and charge collection, the results presented here demonstrate that the core photophysical requirements for a functioning aOPV, namely efficient light absorption, ultrafast energy transfer, photoinduced charge separation, and long-range charge transport, can all be achieved within a fully aqueous processing framework. The continued investigation of this platform, guided by the structure-property relationships elucidated in this dissertation, will yield significant advances toward sustainable, water-processed organic solar cells.