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Stabilizing Liquids Using Interfacial Supramolecular Polymerization

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Abstract: The strong electrostatic interactions at the oil-water interface between a small molecule, 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, H₆TPPS, dissolved in water, and an amine terminated hydrophobic polymer dissolved in oil are shown to produce a supramolecular polymer surfactant (SPS) of H₆TPPS at the interface with a binding energy that is sufficiently strong to allow an intermolecular aggregation of the supramolecular polymers. SPSs at the oil-water interface are confirmed by *in situ* real-space atomic force microscopy imaging. The assemblies of these aggregates can jam at the interface, opening a novel route to kinetically trap the liquids in non-equilibrium shapes. The elastic film, comprised of SPSs, wrinkles upon compression, providing a strategy to stabilize liquids in non-equilibrium shapes.

The assembly of nanostructures (NSs) at liquid-liquid interfaces has attracted much theoretical and experimental attention, owing to the potential use of these assemblies as encapsulants and the collective magnetic, optical, and electronic properties arising from the dense packing of the NSs in a two-dimensional array.^[1-12] These assemblies are dynamic in that the energy holding the NSs at the interface is only several kT and the NSs are forced from the interface with an in-plane compressive force.^[13-24] With typical organic molecular systems, such as surfactants, block copolymers, and Janus-type dendrimers, a significant lowering of the interfacial tension can be achieved but the binding energy holding these to the interface is not sufficient to withstand the compressive force when the interfacial area decreases to reduce the free energy of the system and they are ejected from the interface, preventing the liquids from being held in non-equilibrium shapes. Here we show small molecule-based supramolecular systems where the interfacial binding energy can be increased

sufficiently to allow liquids to be structured and that can be used to impart specific functionality to the interfacial assemblies, leading to tailorable interfaces.

As a model system, three different small molecules (Scheme 1 a) are used to demonstrate the importance of supramolecular polymer formation in structuring liquids. Specifically, 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin, H₆TPPS, 5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphine manganese(III) chloride, MnH₄TPPS, and mellitic acid, MA, show decreasing abilities to structure liquids.^[25,26]

As shown in Scheme 1, small molecules in the aqueous phase provide free protons to amine terminated hydrophobic polymers (ligands) in the oil phase at the interface between the two fluids, enabling the formation of two different types of surfactants by electrostatic interactions owing to the different intermolecular interaction. One surfactant is a supramolecular polymer surfactant (SPS) with a NS (Scheme 1 b) and another surfactant is a typical surfactant (Scheme 1 c). Both of two types of surfactants can lower the interfacial tension of the oil-water interface but they show different stabilities at the oil-water interface. H₆TPPS can form SPSs by an intermolecular p-p stacking, while MnH₄TPPS, even though the structure is similar, one of the porphyrin surfaces is shielded by chloride, decreasing or impeding the SPS formation of MnH₄TPPS because of decreasing intermolecular interactions. Furthermore, MA in the absence of porphyrins has only a benzene ring, which is too small to produce enough intermolecular interaction to form SPSs.

The electrostatic interactions of H₆TPPS have been investigated in the water solution^[27-38] but have not been investigated at the oil-water interface. Herein, we show that all three small molecules can form surfactants at the oil-water

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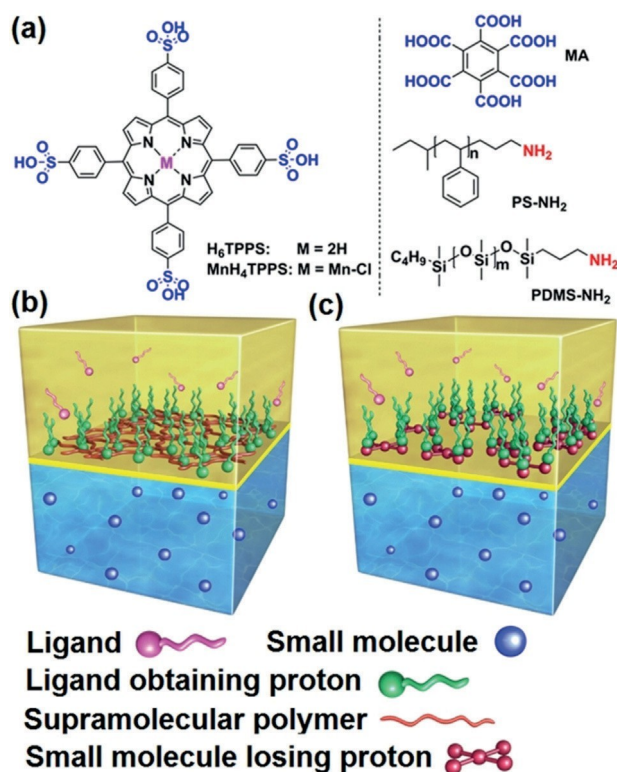
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Scheme 1. Chemical structures and illustration of the interface.

- a) Chemical structures of H_6TPPS , MnH_4TPPS , MA, PS-NH₂, and PDMS-NH₂. b) Formation of supramolecular polymer surfactants at the interface (upper solution is oil and lower solution is water). c) Formation of typical surfactants at the interface.

interface, lowering the interfacial tension (γ). γ was measured using a pendant drop of H_6TPPS -water solution in the PS-NH₂-toluene solution. The γ value between the pure water and pure toluene is 35 mNm⁻¹ (Supporting Information, Figure S2). With only H_6TPPS (0.4 g L⁻¹, pH 3.4) present in the water solution, γ is 34 mNm⁻¹, indicating that H_6TPPS is not interfacially active. By adding PS-NH₂ (800 gmol⁻¹ (0.8 k), 0.01 g L⁻¹) into the toluene solution, γ decreases to 30 mNm⁻¹, showing that PS-NH₂ behaves like a surfactant. Figure 1a shows the time evolution of γ between water and toluene with H_6TPPS in the water solution and PS-NH₂ in the toluene solution, where the concentration of PS-NH₂ was varied. The equilibrium value of γ decreases with increasing PS-NH₂ concentration. At the lowest concentration, that is, 0.001 g L⁻¹, the equilibrium value of γ is about 22 mNm⁻¹.

While at the highest concentration, that is, 0.04 g L⁻¹, γ is about 5 mNm⁻¹. Similarly, both MnH_4TPPS and MA show a large decrease in γ as the concentration of PS-NH₂ in toluene increases, showing that all three small molecules can form surfactants with oppositely charged ligands at the toluene-water interface. If the volumes of the aqueous droplets are decreased, wrinkles should be observed, if the surfactants are not ejected from the interface. The ratio of the volume at which wrinkling is observed to the initial volume, V_w/V_i , serves as an approximate measure of the initial coverage of the interface. Figure 1d to Figure 1f show V_w/V_i is about 0.93 for H_6TPPS but only 0.05 for MnH_4TPPS and

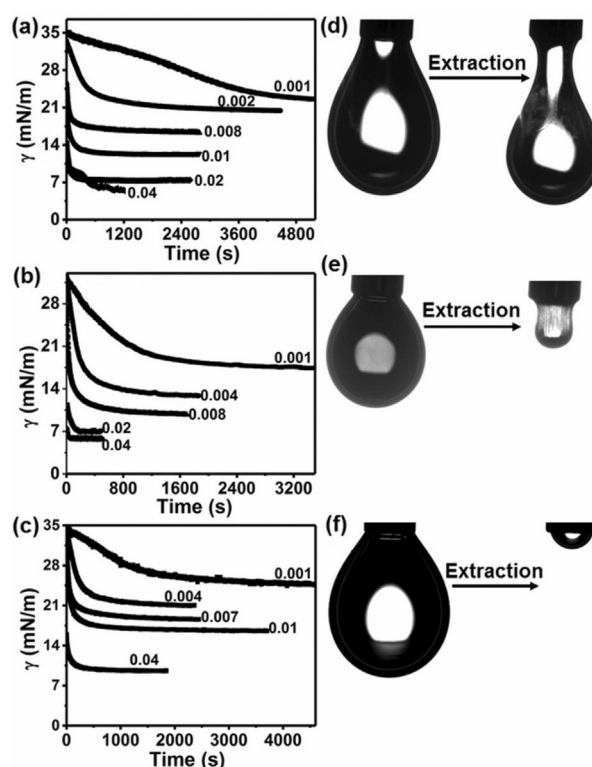


Figure 1. Interfacial tension and behavior of the droplet surface at water-toluene interface. Interfacial tension of a) H_6TPPS (0.4 g L⁻¹, pH 3.4), b) MnH_4TPPS (0.4 g L⁻¹, pH 3.16), and c) MA (1.0 g L⁻¹, pH 2.27) in water against PS-NH₂ (0.8 K) in toluene solution at different concentration [g L⁻¹]. Behavior of the droplet surface after the system has reached an equilibrium state. The concentrations of d) H_6TPPS (pH 3.4), e) MnH_4TPPS (pH 3.16), and f) MA (pH 2.27) in water and PS-NH₂ in toluene are 0.4 g L⁻¹, 0.4 g L⁻¹, 1.0 g L⁻¹, and 0.04 g L⁻¹, respectively.

MA does not wrinkle. These results show that the binding energy holding H_6TPPS at the interface is much stronger than that for either MnH_4TPPS or MA. The origin of this difference must arise from intermolecular interactions of the H_6TPPS surfactants at the interface that is absent with MnH_4TPPS and MA.

Figure 2 a,b shows the UV/Vis absorption results of the aqueous H_6TPPS and MnH_4TPPS solutions in contact with a PS-NH₂ solution in toluene. As shown in the Supporting Information, Figure S4, the top of the toluene phase was used for the UV/Vis absorption measurement. For H_6TPPS , the absorption intensity is very weak and remains weak after 5 h, indicating the near absence of the H_6TPPS surfactant in the toluene phase, suggesting that the H_6TPPS surfactants can stabilize at the toluene-water interface. However, the absorption intensity of MnH_4TPPS is about 65 times more intense after 1 h and increases with increasing time. Additionally, diffusion at the interface could be directly visualized by laser scanning fluorescence confocal microscopy (LSFCM). As shown in Figure 2 c, when a water droplet containing H_6TPPS (0.4 g L⁻¹, pH 3.4) is placed in a solution of PS-NH₂ (0.8 K, 0.05 g L⁻¹) in toluene, no obvious color appears in the toluene phase. However, for MnH_4TPPS , a red

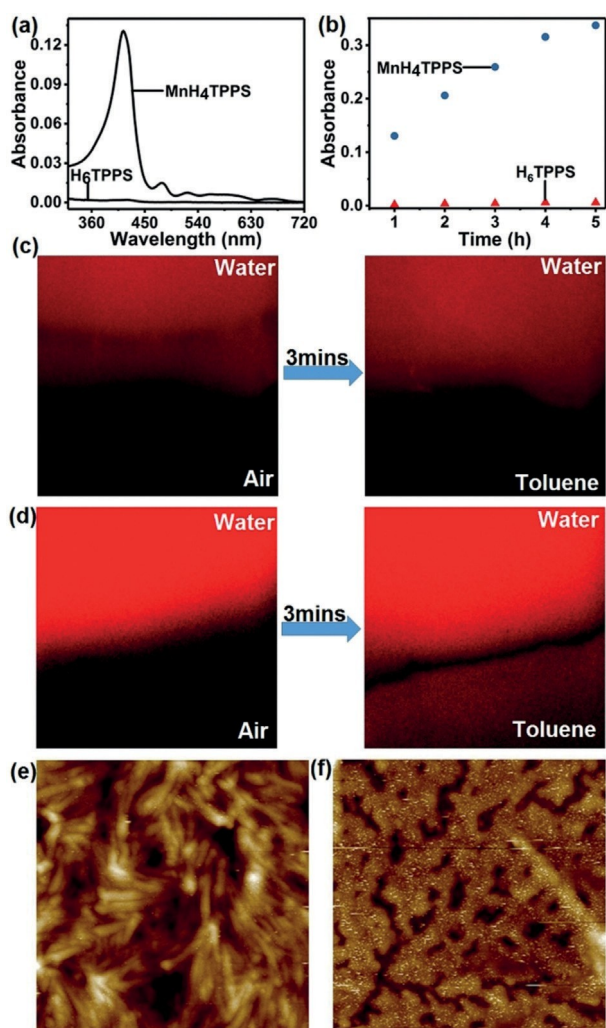


Figure 2. Characteristics at the toluene-water interface. a) The UV/Vis absorption spectra of H₆TPPS surfactant and MnH₄TPPS surfactant in toluene solution. b) The evolution of UV/Vis absorption intensity dependent on the aging time. c) Confocal fluorescence microscopy images of a water droplet containing H₆TPPS (0.4 g L⁻¹, pH 3.4) and d) MnH₄TPPS (0.4 g L⁻¹, pH 3.16) surrounded by toluene solution containing PS-NH₂ (0.8 K, 0.05 gL⁻¹) over time. e) The AFM image of H₆TPPS-water and PS-NH₂-toluene interface. The x, y, and z scales are 1000, 1000, and 30 nm, respectively. f) The AFM image of the MnH₄TPPS-water and PS-NH₂-toluene interface. The x, y, and z scales are 1000, 1000, and 30 nm, respectively.

color appears after the PS-NH₂ toluene solution is placed on the water droplet surface (Figure 2 d). Figure 2e shows the AFM image of H₆TPPS-water and PS-NH₂-toluene interface is the formation of nanofibers. Figure 2f shows that the morphology at MnH₄TPPS-water and PS-NH₂-toluene interface is amorphous. Consequently, the MnH₄TPPS surfactant is not stable at the toluene-water interface and is being drawn away from the interface and into the toluene phase, that is, MnH₄TPPS is transferred from the aqueous phase into the toluene phase, owing to interaction with PS-NH₂. Thus, even a small change in the molecular structure can lead to large changes in the interfacial activity.

The competition between the interfacial binding and solvation in the toluene phase can be altered by decreasing

the solubility of the ligand in the toluene phase. Using amine terminated poly(dimethylsiloxane) (PDMS-NH₂, 2000 gmol⁻¹ (2k)) as the ligand and poly(dimethylsiloxane) (PDMS) as the oil phase, the oil phase is changed from a good solvent to a theta solvent for the ligands. Figure 3a shows dynamic interfacial tension between water containing H₆TPPS, MnH₄TPPS or MA and PDMS-NH₂ in PDMS. It is

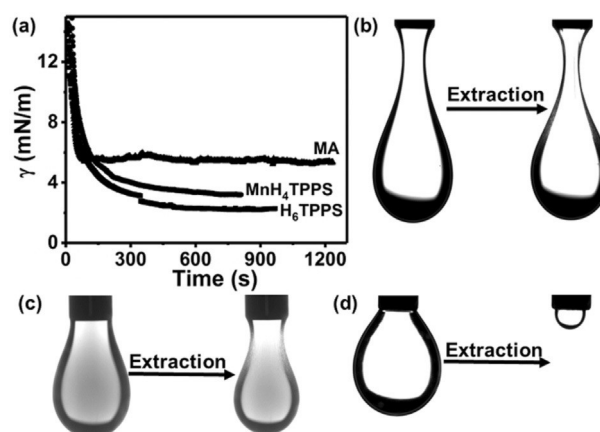


Figure 3. Interfacial tension and behavior of the droplet surface at PDMS-water interface. a) Interfacial tension of H₆TPPS (0.4 g L⁻¹, pH 3.4), MnH₄TPPS (0.4 gL⁻¹, pH 3.16), and MA (1.0 g L⁻¹, pH 2.27) in water against PDMS-NH₂ (2.0 K, 0.05 gL⁻¹) in PDMS solution. b)- d) Behavior of the droplet surface after the system has reached an equilibrium state: b) H₆TPPS, c) MnH₄TPPS, and d) MA.

evident that the interfacial tension decreases for the three small molecules, indicating that all of them form surfactants at the PDMS-water interface. However, V_w/V_i is now 0.99 for H₆TPPS, and 0.50 for MnH₄TPPS, respectively, while MA still does not wrinkle. This clearly shows that the initial coverage of the interface for MnH₄TPPS has increased and that the binding energy has increased due to the decrease of the solubility of the ligands in PDMS. The UV/Vis absorption of the aqueous MnH₄TPPS solution in contact with a PDMS-NH₂ solution in PDMS is given in the Supporting Information, Figure S5. The absorption intensity at 413 nm is only 0.075, which is about 17 times less intense than that of the aqueous MnH₄TPPS solution in toluene, indicating that the stability of MnH₄TPPS surfactants dramatically increases at the PDMS-water interface. Additionally, as shown in the Supporting Information, Figure S6, when a water droplet containing MnH₄TPPS (0.4 g L⁻¹, pH 3.16) is placed in a solution of PDMS-NH₂ (2 K, 0.05 g L⁻¹) in PDMS, no obvious color appears in the PDMS phase. The binding energy of the H₆TPPS surfactant has, also, increased slightly, while that for the MA has remained unchanged.

In situ atomic force microscopy (AFM) was used to image the SPS formation and assembly at the interface (Supporting Information, Figure S8 a). For H₆TPPS, at a PDMS-NH₂ concentration of 0.5 g L⁻¹, the AFM image (Figure 4) shows the formation of nanofibers with height/width/length sizes of 3-4:20-30:200-1000 nm³. Although the areal density of nanofibers increases with increasing PDMS-NH₂ concentration

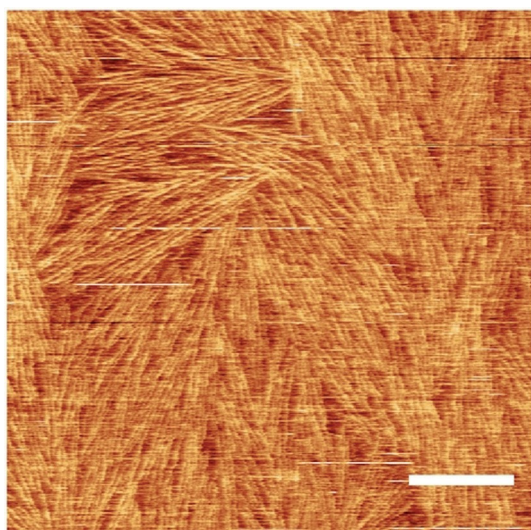


Figure 4. In situ AFM images. PDMS-NH₂ (2 K, 5.0 gL⁻¹) surrounded by water solution containing H₆TPPS (0.4 g L⁻¹, pH 3.4) after 30 min. Scale bars: 400 nm.

(Supporting Information, Figure S8), the thickness and width show no obvious change. The length of the nanofiber is shown to depend on the PDMS-NH₂ concentration which suggests that the fibril growth rate increases with increasing PDMS-NH₂ at the interface. Similar structures were also found for MnH₄TPPS (Supporting Information, Figure S9).

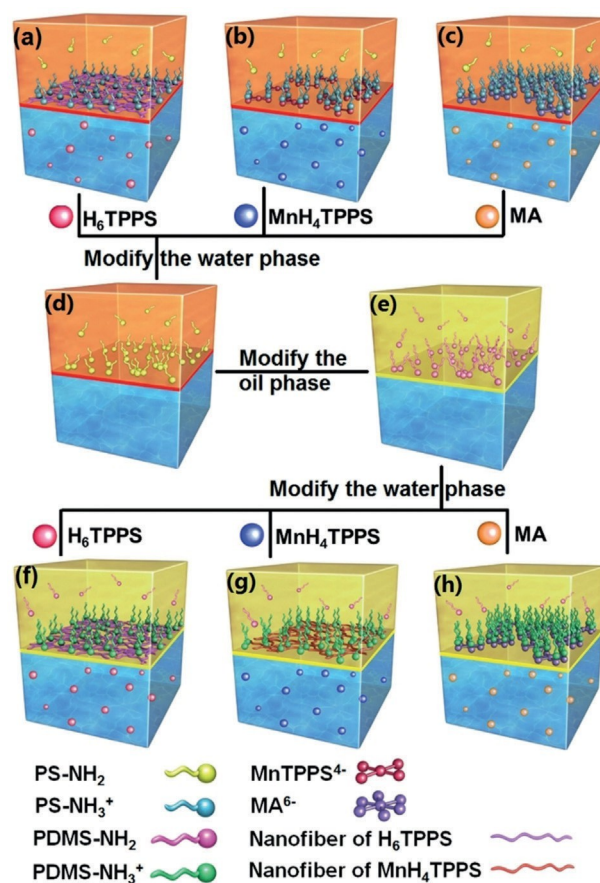
Scheme 2 provides a description of the different self-assembly behavior of H₆TPPS, MnH₄TPPS, and MA at the water-oil interface. In the case of H₆TPPS, the formation of surfactants are stabilized at the toluene-water or PDMS-water interface due to the formation of nanofibers arising from the formation of supramolecular polymers that are not easy to charge neutral, leading to essentially particulate-surfactants, like cellulose nanocrystal surfactants investigated previously,^[18,39] that are very stable against compressive forces. Intermolecular interactions between MnH_xTPPS^p⊙(PS-NH⁺)_p (x = 4 p and p = 1, 2, 3, 4), specifically p-p stacking, at the interface are decreased or impeded

by the presence of the chloride. Fibrils are not formed and the interaction of MnH₄TPPS with four PS-NH₂ chains are sufficient to transfer the individual MnH_xTPPS^p⊙ surfactants across the interface. While MnH_xTPPS^p⊙(PDMS-NH₃⁺)_p (x = 4⊙p and p = 1, 2, 3, 4) can stabilize at the PDMS-water

interface to some extent because the diffusion rate of surfactants MnH_xTPPS^p⊙(PDMS-NH₃⁺)_p (x = 4 p and p = 1, 2, 3, 4) is slow (Supporting Information, Figures S5, S6), meaning that the driving force of surfactants to PDMS phase

is low, leading that surfactants have enough time to self-assemble to some extent. For MA, the benzene ring is hydrophobic and interactions of the MA with multiple PS-NH₂ make the MA-ligand complex hydrophobic, preventing assembly at the interface. Consequently, the intermolecular p-p interactions at the interface are key to the interfacial activity.

In conclusion, we demonstrated that small molecules can be used to structure liquids by intermolecular interactions.



Scheme 2. Illustration of the proposed model. Upper solution for (a-d) is PS-NH₂ toluene solution and lower solution is a) H₆TPPS water solution; b) MnH₄TPPS water solution; c) MA water solution; d) pure water. Upper solution for (e-h) is PDMS-NH₂ PDMS solution and lower solution is e) pure water; f) H₆TPPS water solution; g) MnH₄TPPS water solution; h) MA water solution.

Three different small molecules, H₆TPPS, MnH₄TPPS, and MA, were investigated. We demonstrated the influence of ligand solubility on interfacial activity by changing the oil phase from a good solvent to a theta solvent, providing a simple means to fine tune the energy binding the surfactant species to the interface. In situ AFM was used to directly image the formation of fiber-like supramolecular structures at the interface, demonstrating the importance of intermolecular interactions on stabilizing the surfactants at the water-oil interface for the first time.

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- [1] L. Hu, M. Chen, X. Fang, L. Wu, *Chem. Soc. Rev.* 2012, 41, 1350 – 1362.
- [2] H. Duan, D. Wang, D. G. Kurth, H. Mohwald, *Angew. Chem. Int. Ed.* 2004, 43, 5639 – 5642; *Angew. Chem.* 2004, 116, 5757 – 5760.
- [3] K. Piradashvili, E. M. Alexandrino, F. R. Wurm, K. Landfester, *Chem. Rev.* 2016, 116, 2141 – 2169.
- [4] Z. Yang, J. Wei, Y. I. Sobolev, B. A. Grzybowski, *Nature* 2018, 553, 313 – 318.
- [5] H. Gu, Z. Yang, J. Gao, C. Chang, B. Xu, *J. Am. Chem. Soc.* 2005, 127, 34– 35.
- [6] J. J. Armao IV, I. Nyrkova, G. Fuks, A. Osypenko, M. Maaloum, E. Moulin, R. Arenal, O. Gavati, A. Semenov, N. Giuseppone, *J. Am. Chem. Soc.* 2017, 139, 2345 – 2350.
- [7] W. H. Binder, *Angew. Chem. Int. Ed.* 2005, 44, 5172 – 5175; *Angew. Chem.* 2005, 117, 5300 – 5304.
- [8] L. Costa, G. Li-Destri, N. H. Thomson, O. Kononov, D. Pontoni, *Nano Lett.* 2016, 16, 5463 – 5468.
- [9] L. L. Dai, R. Sharma, C.-y. Wu, *Langmuir* 2005, 21, 2641 – 2643.
- [10] Y. J. Li, W. J. Huang, S. G. Sun, *Angew. Chem. Int. Ed.* 2006, 45, 2537 – 2539; *Angew. Chem.* 2006, 118, 2599 – 2601.
- [11] J. Forth, D. J. French, A. V. Gromov, S. King, S. Titmuss, K. M. Lord, M. J. Ridout, P. J. Wilde, P. S. Clegg, *Langmuir* 2015, 31, 9312 – 9324.
- [12] A.-L. Fameau, F. Cousin, L. Navailles, F. Nallet, F. Bou8, J.-P. Douliez, *J. Phys. Chem. B* 2011, 115, 9033 – 9039.
- [13] B. Su, J.-P. Abid, D. J. Fermán, H. H. Girault, H. Hoffmannov#, P. Krtíl, Z. Samec, *J. Am. Chem. Soc.* 2004, 126, 915 – 919.
- [14] M. Nagel, T. A. Tervoort, J. Vermant, *Adv. Colloid Interface Sci.* 2017, 247, 33– 51.
- [15] M. Cui, T. Emrick, T. P. Russell, *Science* 2013, 342, 460 – 463.
- [16] C. Huang, Z. Sun, M. Cui, F. Liu, B. A. Helms, T. P. Russell, *Adv. Mater.* 2016, 28, 6612 – 6618.
- [17] C. Huang, J. Forth, W. Wang, K. Hong, G. S. Smith, B. A. Helms, T. P. Russell, *Nat. Nanotechnol.* 2017, 12, 1060 – 1063.
- [18] X. Liu, S. Shi, Y. Li, J. Forth, D. Wang, T. P. Russell, *Angew. Chem. Int. Ed.* 2017, 56, 12594 – 12598; *Angew. Chem.* 2017, 129, 12768 – 12772.
- [19] F. Reincke, S. G. Hickey, W. K. Kegel, D. Vanmaekelbergh, *Angew. Chem. Int. Ed.* 2004, 43, 458 – 462; *Angew. Chem.* 2004, 116, 464 – 468.
- [20] F. Reincke, W. K. Kegel, H. Zhang, M. Nolte, D. Wang, D. Vanmaekelbergh, H. Mchwald, *Phys. Chem. Chem. Phys.* 2006, 8, 3828 – 3835.
- [21] M. E. Leunissen, A. Van Blaaderen, A. D. Hollingsworth, M. T. Sullivan, P. M. Chaikin, *Proc. Natl. Acad. Sci. USA* 2007, 104, 2585 – 2590.
- [22] B. J. Park, J. P. Pantina, E. M. Furst, M. Oettel, S. Reynaert, J. Vermant, *Langmuir* 2008, 24, 1686 – 1694.
- [23] K. Masschaele, B. J. Park, E. M. Furst, J. Fransaer, J. Vermant, *Phys. Rev. Lett.* 2010, 105, 048303.
- [24] M. E. Leunissen, J. Zwanikken, R. Van Roij, P. M. Chaikin, A. Van Blaaderen, *Phys. Chem. Chem. Phys.* 2007, 9, 6405 – 6414.
- [25] S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu, M. Takeuchi, *Nat. Chem.* 2014, 6, 188 – 195.
- [26] K. V. Rao, D. Miyajima, A. Nihonyanagi, T. Aida, *Nat. Chem.* 2017, 9, 1133 – 1139.
- [27] M. Y. Choi, J. A. Pollard, M. A. Webb, J. L. McHale, *J. Am. Chem. Soc.* 2003, 125, 810 – 820.
- [28] K. Kano, K. Fukuda, H. Wakami, R. Nishiyabu, R. F. Paster-nack, *J. Am. Chem. Soc.* 2000, 122, 7494 – 7502.
- [29] N. C. Maiti, S. Mazumdar, N. Periasamy, *J. Phys. Chem. B* 1998, 102, 1528 – 1538.
- [30] N. C. Maiti, M. Ravikanth, S. Mazumdar, N. Periasamy, *J. Phys. Chem.* 1995, 99, 17192 – 17197.
- [31] J. M. Ribl, J. Crusats, J.-A. Farrera, M. L. Valero, *Chem. Commun.* 1994, 681 – 682.
- [32] M. A. Castriciano, A. Romeo, R. Zagami, N. Micali, L. M. Scolaro, *Chem. Commun.* 2012, 48, 4872 – 4874.
- [33] S. Ishihara, J. Labuta, W. Van Rossom, D. Ishikawa, K. Minami, J. P. Hill, K. Ariga, *Phys. Chem. Chem. Phys.* 2014, 16, 9713 – 9746.
- [34] Y. Egawa, R. Hayashida, J.-i. Anzai, *Langmuir* 2007, 23, 13146 – 13150.
- [35] S. Jiang, L. Zhang, M. Liu, *Chem. Commun.* 2009, 6252 – 6254.
- [36] M. A. Castriciano, A. Carbone, A. Sacca, M. G. Donato, N. Micali, A. Romeo, G. De Luca, L. M. Scolaro, *J. Mater. Chem.* 2010, 20, 2882.
- [37] J. Crusats, J. Claret, I. Díez-P8rez, Z. El-Hachemi, H. García- Ortega, R. Rubires, F. Sagu8s, J. M. Ribl, *Chem. Commun.* 2003, 1588 – 1589.
- [38] K. Kalyanasundaram in *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 1992, p. 428.
- [39] X. Wu, Q. Yuan, S. Liu, S. Shi, T. P. Russell, D. Wang, *ACS Macro Lett.* 2019, 8, 512 – 518.