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Interfacial Pressure/Area Sensing: Dual-Fluorescence of Amphiphilic Conjugated Polymers at Water Interfaces

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ABSTRACT: Exciton migration to emissive defects in π -conjugated polymers is a robust signal amplification strategy for optoelectronic sensors. Herein we report endcapped conjugated polymers that show two distinct emissions as a function of interpolymer distances at the air-water and hydrocarbon-water interfaces. Amphiphilic poly(phenylene ethynylene)s (PPEs) endcapped with perylene monoimides display two distinct emission colors (cyan from PPE and red from perylene), the relative intensity of which depends on the surface pressure applied on the Langmuir monolayers. This behavior produces a ratiometric interfacial pressure indicator. Relative quantum yields are maintained at the different surface pressures and hence display no sign of self-quenching of the excitons in an aggregated state. These polymers can be organized at the micelle-water interface in lyotropic liquid crystals, thereby paving the way for potential applications of endcapped amphiphilic conjugated polymers in biosensors and bioimaging.

Understanding the optoelectronic properties of semiconductive polymers underpins technological advances in organic photovoltaics, organic light-emitting diodes, and many chemical sensors.^{1–6} π -Conjugated polymers feature direct optical band gaps that produce large extinction coefficients and high fluorescence quantum yields,⁷ and the delocalization of the π -orbitals facilitates efficient transport of charged carriers and excitons. In particular, exciton migration to low-energy sites in the solid-state of π -conjugated polymers has been recognized as a key mechanism for signal amplification of the sensory systems.^{8,9} The higher dimensionality associated with interchain electronic couplings in solids is understood to enhance energy transfer. Specifically, the ability of excitons to undergo a 3D random walk (interchain) in films provides a statistical improvement, in contrast to 1D random walk (intrachain), wherein excitons revisit the same segments of the polymer backbone many times.¹⁰

The transport properties of exciton migration can be probed by using the Langmuir-Blodgett (LB) technique to create precise organizations. LB molecular processing can create highly aligned polymer films on substrates after sequential monolayer depositions. The thickness of multilayers can be precisely controlled, and in previous studies efficient intralayer and interlayer exciton migration in LB films were analyzed to determine the exciton diffusion length.¹¹ Additionally, vectorial energy transfer has been demonstrated in structured polymer films that create energy gradient.¹² In our present studies, we are exploiting the dynamic nature of the air-water and liquid-liquid interfaces. Given that energy transfer is enhanced by reducing interpolymer distances, we envision that compression and expansion of surfactant polymer monolayers with

varying interfacial surface tension will modulate exciton migration to minority emitters and display two distinct fluorescence. To achieve these properties, we have produced specially designed conjugated polymers with low-energy emissive traps. Changes in interfacial tension can then be translated to ratiometric fluorescent signals.

There are two general types of sensitive fluorescent sensors that make use of exciton migration. On-off sensors are systems wherein analytes trigger aggregations or electron transfer of π -conjugated polymers that cause fluorescence quenching.^{13,14} In the case where less-emissive aggregates are formed, excitons migrate through an efficient random walk and are trapped at weakly emissive lower energy trapping sites. Such response can be produced, for example, by potassium ion sandwich complexation with crown-ether functionalized PPEs.¹⁵ A second type of sensor makes use of exciton transfer to efficient low-energy emitters that are either proximate or covalently integrated in the polymer backbone. For example, polyanionic PPEs with a few percent of low bandgap emitters undergo blue-to-green fluorescence changes when aggregated by electrostatic assembly with multicationic amines.¹⁶ These dual-fluorescence systems potentially have broader appeal owing to the ability to tune emission colors by incorporating a variety of dyes (green, red, and even near-infrared) to meet specific applications. Building upon this methodology, we herein report surfactant poly(phenylene ethynylene)s with low bandgap emissive endgroups that display enhanced energy transfer at the air-water interface upon compression (Figure 1). The quantum yields remain relatively constant over this process and we achieve a dual-fluorescence interfacial pressure indicator with high color contrast. We

Figure 1. Schematic illustration of enhanced energy transfer to red endcaps in conjugated polymers upon applied surface pressure (top). The structure of the PPE **P1** (bottom).

further demonstrate this energy transfer scheme at micelle-water interfaces, suggesting potential applications in bioimaging and biosensors.

The choice of the amphiphilic PPE is critical to promote the proper organizations. Although energy transfer is efficient in the solid state, aggregation-induced quenching of singlet excitons is notoriously common and can lower the exciton diffusion lengths, giving diminished fluorescence quantum yields.^{13,16} We previously showed that PPEs having amphiphilic side chains displayed novel behavior wherein the compressed monolayers at the air-water interface formed highly emissive excimers with the increase in relative quantum yields compared to non-compressed states.¹⁷ Therefore, we have targeted this system for further applications by functionalization with low-energy emissive perylene dye endgroups (Figure 1). The perylene has emission bands (~575 nm) that do not overlap the

Figure 2. (a) Synthesis of **P1** using **M1** and **M2** (5% excess) with sequential *in situ* endgroup functionalization. Yield 71%, M_n = 27 kDa, and $\bar{D}$ 1.38. (b) Absorption and emission spectra of **P1** in solution (top) and spin-coated films (bottom).

PPE peaks at 475 nm (o-o) and 510 nm (o-i), thereby allowing for straightforward analysis of the ratiometric responses.

We produced perylene monoimide-endcapped PPEs (**P1**, Figure 1) with amphiphilic side chains by Pd-catalyzed Sonogashira-type couplings (Figure 2a and see SI for detailed synthetic procedures). In this process we added a 5% excess of diiodide monomer (**M2**) with the expectation that after monomer consumption there are Ar-Pd-I endgroups, which will react with a sequentially added perylene monoimide bearing a terminal acetylene (**Perylene-1**). The resulting polymers have a M_n of 27 kDa (degree of polymerization (n) = 18) and $\bar{D}$ of 1.38. The theoretical degree of polymerization on this composition of monomers is 41. The lower n may be related to incomplete polycondensation and/or also attributed to Glaser-type acetylene-acetylene linkages that are often present in PPEs, which effectively change the stoichiometry by depleting the alkynes. The degree of **Perylene-1** incorporation was analyzed by ^1H NMR spectrum (see **P1** NMR spectrum in SI). The perylene-associated signal at 8.27 ppm (2H per **Perylene-1**) is compared with the 4.85 ppm peak of the monomers (8H per repeat unit). With a degree of polymerization of 18, one polymer chain has 144 protons at 4.85 ppm. With this number, the integration at 8.27 ppm shows 1.38 protons and thus assuming 18 repeating units each polymer chain has an average of 0.69 **Perylene-1** or about one for every 26 repeating units. The lowered incorporation of **Perylene-1** can be attributed to homocouplings between **Perylene-1** (confirmed by preparative GPC), or the fact that the Ar-PdX endgroups decompose prior to coupling with **Perylene-1**. Assuming that the decomposition was problematic, we shortened the polymerization time before adding **Perylene-1**. However, the lowered polymerization times did not show increased endgroup incorporation (Table S1). Combining the monomers and endgroups at the same time (condition 3 in Table S1) was also ineffective and oligomers with endcaps were removed during the work-up. As a consequence this latter one-step strategy produced polymers with fewer endgroups. It is also important to note that the small integrations of the NMR introduce errors and the n is perhaps overestimated in rigid-rod polymers¹⁸ (the GPC calibrated with polystyrene). Although the endcapping reaction is not perfect, as will become apparent (*vide infra*) the concentration of the perylene endgroups is sufficient for our applications.

The absorption and emission spectra of **P1** in solution and thin films are shown in Figure 2b. The absorption spectrum in spin-coated films is red-shifted relative to that of solution, reflecting increased planarization of the backbone in the solid state. We observe larger differences in emission between solution and thin films. In solution, the emission primarily originates from the backbone at 469 nm ($I_{\text{backbone}} : I_{\text{endcap}} = 1 : 0.24$), whereas in thin films the red endgroup emission at 615 nm is dominant ($I_{\text{backbone}} : I_{\text{endcap}} = 1 : 7.1$). The 30-fold increase in the relative endgroup emission intensity is not necessarily the result of higher exciton diffusion lengths in the solid state for this case. The analysis is complicated by the fact that the quantum yield of the thin films is 2.7%, which is substantially decreased from its solution quantum yield, 72%.¹⁹

Figure 3. (a) Pressure-area isotherm of **P1**. The extrapolated area per one Ph-CC unit is ca. 150 $\text{\AA}^2$, indicative of face-on conformation below 25 mN/m. The inflection point at 25 mN/m (the arrow in inset) indicates the transition from face-on to incline-stack conformation. (b) *In situ* absorption spectra of **P1**. A new peak (planarization) at 477 nm is observed above 25 mN/m. (c) *In situ* emission spectra (raw data) of **P1** and (d) its normalized spectra. The varying relative intensity of backbone to perylene depending on the surface pressure suggests **P1** as an interfacial pressure indicator.

Figure 4. (a) Schemes of energy transfer in aqueous solution. More polymers are localized at the micelle-water interface with the increased **P1** concentration, resulting in enhanced energy transfer to perylene. (b) Absorption and (c) emission spectra of LLCs with different concentrations of **P1**. Planarization of the polymers at the micelle-water interface results in the red-shifted sharp absorption shapes with clear vibronic transitions. Owing to energy transfer, the relative perylene emission is enhanced. (d) The LLC solutions are transparent (left) and their fluorescence is highly emissive with varying colors (right).

This decrease is likely the result of the lack of organiza-

tion and thus inevitable cofacial contacts between polymer backbones or endgroup-polymer contacts, resulting in aggregation-induced quenching. The perylene endgroups are known to have near unity quantum yields in solution, so the reduced quantum yield is not the result of intrinsic photophysical properties.

We investigated **P1** monolayers over multiple compression-expansion cycles at the air-water interface on Langmuir trough. Previous studies revealed that conformations of surfactant-type PPEs deposited at the air-water interface include face-on, incline-stack, zipper, and edge-on organizations.^{17,20} Additionally, the recently identified incline-stack assembly shows emissive aggregates with weak π - π overlap that can form bright excimers,¹⁷ facilitating energy transfer studies in the aggregated state. The pressure-area isotherm and *in situ* absorption and emission spectra of **P1** monolayers are displayed in Figure 3. From the pressure-area isotherm, the extrapolated area to 0 mN/m is estimated to be ca. 150 Å² per one Ph-CC unit (half of repeat unit), corresponding to the typical face-on conformation in the uncompressed state.²⁰ We observed an inflection point at 25 mN/m, which indicates the transformation from face-on to incline-stack assembly. The *in situ* absorption spectra show the emergence of the red-shifted peak (~477 nm at > 25 mN/m) associated with a more ordered polymer backbone, which was also observed in the polymer lacking endgroups.¹⁷ At 1 mN/m, the emission intensity from the perylene is minor (Figure 3c and 3d, black curve), and this feature increases dramatically upon compression (8–22 mN/m). The relative quantum yields increased by ca. 20–35% upon increasing the pressure, which could be attributed to facile intra- and inter-chain energy transfer. Above 25 mN/m, the polymer has incline-stack conformation and broad excimer bands at 500–650 nm, which potentially are a radiative decay pathway in competition with energy transfer to the perylene endgroups. The relative quantum yields in highly compressed states are maintained as compared to films at 1 mN/m (parentheses in Figure 3c) as a result of the absence of cofacial π - π stacking.¹⁷ Overall, the fluorescence spectra varying from 1 mN/m to 33 mN/m are similar to the that obtained solution and thin films, respectively (Figure 2b). However, the relative quantum yields are largely constant at the air-water interface due to the organization. Figure 3d shows the varying red emissions as a function of surface pressure, relative to the polymer backbone emissions at 475 nm. This behavior constitutes a fluorescence-based ratiometric interfacial pressure indicator.

This energy transfer scheme with dual-color photoluminescence at the air-water interface can also be applied to micelle(hydrophobic)-water interface in aqueous solution. Localization of surfactant fluorescent polymers/molecules at cell-like environments (lipid bilayers) is central to many biological imaging applications with visible^{21,22} and near-infrared emission.²³ As a proof-of-concept, we fabricated nonspherical anisotropic micelles (lyotropic liquid crystals, or LLCs) composed of water/potassium dodecanate/1-decanol according to the

literature procedure.²⁴ We have previously found that structurally similar surfactant polymers without endgroups showed the localization and planarization at the micelle-water interface in LLCs.²⁵ Based upon our results at the air-water interface, we expect that changes in the interfacial density of **P1** chains in the micelle will modulate the interpolymer distance (Figure 4a) and produce changes in the polymer-to-endgroup fluorescence signals. The absorption spectra in Figure 4b display largely red-shifted sharp peak at 468 nm, indicative of highly planar and rigid conformation at the micelle-water interface. This red-shifted absorption is comparable to the LB experiments (464 nm). The emission spectra shown in Figure 4c exhibit the backbone emission maximum at 480–490 nm, which is similarly red-shifted from those obtained in solution (469 nm) and thin film (477 nm), and are even slightly lower energy than that obtained in the LB monolayers (475 nm). With increasing **P1** concentrations, we observe a concurrent increase in the red emission, demonstrating enhanced energy transfer to the perylene endgroup. Observation of the LLCs with an optical microscope equipped with cross-polarizers (Figure S2) gives optical textures characteristic of a nematic phase. The aqueous solutions of all concentrations are relatively transparent (Figure 4d, left) and their fluorescence is highly emissive with varying colors from cyan to red (Figure 4d, right). We also note that the **P1** appears to have some aggregation-induced quenching in these experiments with 12 mg/mL having a relative quantum yield 32% of the 1 mg/mL LLC compositions.

In summary, we synthesize surfactant PPEs endcapped with perylene monoimide which show dual emission colors (cyan/red) depending on the applied surface pressure in Langmuir monolayers, creating an interfacial pressure indicator. The enhanced energy transfer may originate from both intrachain (planarization) and interchain (3D) exciton migration, where both Förster and Dexter mechanism take effect. Application of the energy transfer scheme at the micelle-water interface in aqueous solution is demonstrated, significantly expanding the potential applications of the dual-fluorescent surfactant polymer probes in biosensors and bioimaging.

ASSOCIATED CONTENT

Supporting Information. Detailed synthetic procedures for **P1** and **Perylene-1** are described. Additional characterization data and NMR spectra are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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