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Abstract: We present the relationship between the spatial arrangement and the photophysical properties of fluorescent polymers in thin films with controlled structures. Eight surfactant poly(\(p\)-phenyleneethynylene)s were designed and studied. These detailed studies of the behavior of the polymers at the air–water interface, and of the photophysical properties of their transferred LB films, revealed key structure–property relationships. Some of the polymers displayed \(\pi\)-aggregates that are characteristic of an edge-on structure at the air–water interface. Monolayer LB films of these polymers showed greatly reduced quantum yields relative to solution values. Other polymers exhibited a highly emissive face-on structure at the air–water interface, and did not form \(\pi\)-aggregates. The combination of pressure–area isotherms and the surface pressure dependent in situ UV–vis spectra of the polymers at the air–water interface revealed different behavioral details. In addition, the UV–vis spectra, fluorescence spectra, and quantum yields of the LB films provide design principles for making highly emissive films.

Introduction

A comprehensive understanding of the electronic states of conjugated polymers is pivotal to the continued development of these materials. In general, the electronic structure of isolated chains is well understood and is readily approximated by oligomeric compounds due to the limited effective chromophore dimensions in these materials. However, there is invariably electronic coupling between polymer chains, and these secondary interactions often dominate a material’s redox potential, band gap, fluorescence efficiency, and electrical energy transport. The transport properties of conjugated polymers, their most interesting feature, are extremely sensitive to interpolymer electronic coupling between polymer chains, and these second-order interactions often dominate a material’s redox potential, band gap, fluorescence efficiency, and electrical energy transport. The transport properties of conjugated polymers, their most interesting feature, are extremely sensitive to interpolymer interactions. This fact follows from the necessity of transfer of charge or excitations between polymer chains.

Much of the technological promise of conjugated polymers rests on their emissive properties. Applications include electroluminescent displays, organic lasers, and sensors. Our group’s interest in conjugated polymers for the amplification of sensory signals requires optimization of their transport properties. Within this framework, many factors need be considered. Among these are the polymer’s absorption and emission spectra, degree of organization, bandwidth, band gap, emission quantum yield and lifetimes, and energy transport dynamics. The evolution of electronic structure from the constituent chromophores of a polymer is reasonably well understood; however, interchain interactions have less predictable consequences. Nevertheless, strong electronic coupling between polymer chains has the prospect to increase intermolecular energy transfer. Most often strong interpolymer interactions give rise to distinct red shifts in the absorption spectra and generally produce less emissive (quenched) materials. It is generally assumed that polymers prefer to organize with cofacial \(\pi\) interactions, and structural studies support this fact. However, the detailed role of interpolymer interactions on luminescent polymers’ absorption and emission properties has not been systematically studied due to the difficulty in controlling interpolymer arrangement. Greater understanding of chain–chain interactions in conjugated polymers is clearly necessary.

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to reveal which circumstances these interactions will lead to emissive\textsuperscript{10} or quenched $\pi$-aggregated materials. Added fidelity is required to understand the circumstances, wherein proximal chain--chain interactions can lead to excited-state aggregation and produce strong exciplex emissions.

Investigations are best performed when organized assemblies of polymers can be prepared with predictable or manipulatable conformations and intermolecular interactions. In this regard, combination of surfactant polymer design and the Langmuir--Blodgett (LB) technique\textsuperscript{11} is very useful. We have recently synthesized surfactant poly($p$-phenyleneethynylene)s (PPEs) and used a LB trough to create spatially well-defined Langmuir films.\textsuperscript{12} In these previous studies, we identified three specific geometries. The first involves cofacial organization of the $\pi$-plane with the air--water interface, referred to as the face-on structure. The second geometry wherein the plane of the conjugated $\pi$-system lies normal to the air--water interface is referred to as the edge-on structure. The third one is the zipper structure, alternating face-on and edge-on structures. In our earlier systems,\textsuperscript{13} we determined that the face-on structure, alternating face-on and edge-on structures. The second geometry wherein the plane of the conjugated $\pi$-plane with the air--water interface, referred to as the face-on structure. The second geometry wherein the plane of the conjugated $\pi$-system lies normal to the air--water interface was readily transferred to a support to give highly aligned materials. Chain alignment plays an important role in Förster energy transfer since those processes are highly dependent upon the coincidence of transition dipoles between donors and acceptor chromophores.\textsuperscript{14,15} The edge-on structure gives crystalline aggregates on the LB trough that are not amendable to organization by flow fields or anisotropic compression. Nevertheless, these edge-on structures represent an ideal situation for the organization of materials into well-defined cofacial $\pi$-aggregated structures. In both cases, the structures can be manipulated by applying pressure with the LB trough. This exquisite structural control, as well as the ability to transfer materials monolayer by monolayer, provides the most controlled preparation of conjugated polymer assemblies to date. The LB method also creates an extraordinary venue for investigations at interfacing conjugated polymers with water-soluble elements, and thereby establishes a firm foundation from which to construct novel biosensorial materials.

Herein we describe studies of PPEs designed to have specific surfactant characteristics. We have broadened the scope of structures that display edge-on or face-on structures and have discovered conditions wherein the applied pressure can manipulate the polymer chromophores at the air--water interface. We have also systematically studied how interpolymer interactions affect the fluorescent polymers’ ground and excited states in structurally defined monolayer films and solid solutions of the polymers in PMMA. The approaches described herein have broad applicability to a range of conjugated polymer structures and illustrate the utility of LB techniques for the elucidation of the structure–property relationships in conjugated polymers.

**Results and Discussion**

Building upon our designs of PPEs that adopt face-on or edge-on geometries at the air--water interface,\textsuperscript{12,13} eight polymers were investigated (Chart 1). Palladium-catalyzed cross-coupling methods figure prominently into the synthesis of these polymers.\textsuperscript{16,17} The preparation of polymers 1, 3, 4, and 6 was reported elsewhere.\textsuperscript{5d,12,13,23} Polymers 2 and 8 were synthesized as described in eq 1. The preparation of 9 was reported elsewhere.\textsuperscript{12} Monomer 9 was further reacted with 1-((triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-diodobenzene or 1,4-bis($N$,N-diocylcarbamoyl)-2,5-diodobenzene to produce polymers 2 and 8, respectively.

Polymers 5 was synthesized from the palladium coupling reaction of 10 with 1,4-bis($N$,N-diocylcarbamoyl)-2,5-diodobenzene (eq 2). Pentaethylene glycol ditosylate was reacted with 1,4-bis($N$,N-diocylcarbamoyl)-2,5-diodobenzene under standard Williamson ether conditions, followed by palladium-catalyzed coupling (trimethylsilyl)acetylene and deprotection to give 2,5-diethynyl-$p$-phenylene-20-crown-6 (10).

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As shown in eq 3, polymer 7 was synthesized from the coupling reaction of 11 with 1,4-bis(N,N-dioctylcarbamoyl)-2,5-diiodobenzene. 1,4-Bis[2-(2-hydroxyethoxy)ethoxy]-2,5-diiodobenzene was subjected to palladium-catalyzed coupling (tri-methylsilylacetylene followed by deprotection to give 1,4-bis-[2-(2-hydroxyethoxy)ethoxy]-2,5-diethynylbenzene (11).

Figure 1. Pressure–area isotherms of polymers.

Our designs allowed us to control the interpolymer arrangement and intrapolymer conformations at the air–water interface. Polymers 1, 2, and 3 have the edge-on structure at the air–water interface due to the presence of hydrophilic groups on only one side of each phenyl ring. Polymers 4–8 comprise a second group that have a face-on structure with a symmetric para disposition of side groups. The edge-on polymers have π-aggregation between polymer chains, but the face-on polymers do not.

The pressure–area (PA) isotherms of polymers 1–8 at the air–water interface confirm our assertions of the polymers’ orientational preferences (Figure 1). The extrapolated areas per phenyleneethynylene group for polymers 1, 2, and 3 range from 32 to 37 Å².18 Combining this area with one phenyleneethynylene unit length of 7 Å provides the average distance between polymer main chains of 4.6 to 4.9 Å for an edge-on structure. In contrast, polymers 4–8 exhibit areas of 175–230 Å² per each repeating unit that has two phenyleneethynylene units. Considering a face-on structure, we calculated a distance between adjacent main chain acetylene carbons of 12.1–16.4 Å. The sustainable maximum pressure above which monolayers fold into multilayers was approximately 40 mN/m for the edge-on polymers, a value 10 mN/m higher than those for the face-on polymers. It is intuitive that the edge-on structure, which likely are positioned next to a macrocycle containing units of adjacent chains to give an interdigitated structure.

The area per repeating units at which the polymers fold into multilayers is similar for polymers 4–7 (125–140 Å²) but is much smaller for polymer 8 (90 Å²), indicating more compressible nature of polymer 8. An explanation is that the main chain phenyl rings of polymers 4–7 maintain a face-on structure until the monolayers fold into multilayers at 30 mN/m. However, polymer 8 undergoes a two-stage transformation. It begins in a face-on structure, but as it is compressed, the orientation of the 1-(triethylene glycol monomethyl ether)oxy)-4-decyloxyphenylene groups, which have surfactant characteristics, rotates to an edge-on structure.12 The reluctance of the hydrophobic repeating group to adapt an edge-on structure produces an intermediate structure with alternating edge-on and face-on residues, which we refer to as a zipper structure as shown in Scheme 1.12 Therefore, the first slope of 8’s PA isotherm is smaller than those of the other face-on polymers. After an intermediate (ca. 16 mN/m) transition point, the polymers become less compressible with a steep slope until the monolayers fold into multilayers at 30 mN/m. We synthesized two different molecular weights of polymer 8. One is the polymer with a lower molecular weight (Mn = 16 700) that is used for this contribution, and the other one we used in previous studies12 has a higher molecular weight (Mn = 293 000). The lower molecular polymer shows less featured PA isotherm and lower

(18) The extrapolated area per repeating unit for polymer 3 was divided by 2 because there are two phenyleneethynylene groups on the repeating unit.
maximum surface pressure (30 vs 37 mN/m) as compared to the higher molecular weight one because chain ends would disrupt the interlocking zipper structure. Likewise, we previously reported that diacetylene defects in this structure destroy long-range registry between neighboring polymer chains and the presence of these groups prevents well-defined phase transitions.

The in situ UV–vis spectra versus surface pressure of the Langmuir polymer films strongly support the above PA isotherm-based explanation of the arrangements and conformations of the polymers. At the air–water interface, the face-on polymers have a flat geometry with a maximum conjugation length. The in situ UV–vis spectra of the face-on polymers at the air–water interface are red-shifted about 30 nm from these in solution, showing surface-induced conjugation length increases (compare Figures 2 and 3). The absorption $\lambda_{\text{max}}$ of polymers 4–7 is blue-shifted, and the shape of the spectra becomes less structured during the compression (Figure 2). This disturbance of the $\pi-\pi$ conjugation system is likely due to interpolymer steric interactions that create a more heterogeneous distribution of conjugation lengths. The case of polymer 8 is again different and is characteristic of a zipper organization where the absorption $\lambda_{\text{max}}$ blue shifts by 37 nm relative to its initial uncompressed face-on structure. The in situ absorption $\lambda_{\text{max}}$ of the edge-on polymers at the air–water interface is essentially constant during compression because there is no perturbation of the $\pi-\pi$ conjugation system due to a highly packed crystalline monolayer structure (Figure 2). As described above, we have demonstrated control of intramolecular conformation and interpolymer arrangement of the fluorescent polymers by rational surfactant designs and the types of interactions that occur with increased surface pressure. In the following section, the nature of each peak of the in situ UV–vis spectra, the red-shifted absorption peaks of transferred LB films, and corresponding fluorescent spectra are elaborated.

Interpolymer Effects on the Ground and Excited States. Both the edge-on and the face-on Langmuir films were transferred onto hydrophobic and hydrophilic substrates. The transfer ratios at a surface pressure of 20 mN/m for polymers 1–3, displaying an edge-on structure, were quantitative (>95%) for both upstrokes and downstrokes. However, the transfer ratios of the downstrokes for polymers 4–8 depended on the area per repeating unit rather than on the surface pressure. For example, the second downstroke transfer ratios of polymer 4 at 18 mN/m were negligible (<10%). In contrast, the second downstroke for polymer 5 at the same surface pressure gave an 80% transfer ratio. The area/repeating unit of polymer 4 at 18 mN/m is 175 Å$^2$, while that of polymer 5 is 145 Å$^2$. Therefore, at 18 mN/m the hydrophobic octyl side chains of polymer 5 are more compressed than those of polymer 4, which leads to greater extension of the chains from the surface and a more hydrophobic surface with better transfer ratios. This effect is confirmed by transferring polymer 4 at an area per repeating unit of 145 Å$^2$, and the second downstroke transfer ratio was greater than 80%.

The effects of the spatial arrangement on the electronic ground states of the polymers are revealed in the absorption spectra of the polymers’ LB films (Figure 3) as well as in the in situ absorption spectra of polymers’ Langmuir films at the air–water interface (Figure 2). As mentioned earlier, the edge-on structure gives crystalline aggregants at the onset. Therefore, Langmuir and LB films of the edge-on polymers show a new red-shifted absorption $\lambda_{\text{max}}$ that is 30–40 nm to the red of the solution values. The spectra are unchanged when the monolayers fold into multilayers indicating that the aggregates are formed in a monolayer state. To further investigate the origin of the red-shifted absorption spectra of the edge-on polymers, three spin-cast films of polymer 1 in poly(methyl methacrylate) (PMMA) with different weight ratios from 10$^{-3}$/1 to 10$^{-1}$/1 (polymer 1/PMMA) were prepared. As the concentration of polymer 1

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increases in these films, the intensity of the higher wavelength absorption increases and is further red-shifted (Figure 4). These results are consistent with strong intermolecular π-stacking interactions promoted by the edge-on geometry. The broad peak at ca. 440 nm is similar to the solution spectra and represents a distribution of conjugation lengths. Therefore, the presence of these two peaks in absorption spectra indicates the coexistence of monomer-like and aggregated regions in the film.22

Fluorescence spectra provide additional information about the relationship between the different polymer’s excitation characteristics and film structures. The fluorescence spectra of monolayer LB films of the edge-on polymers 1–3 clearly demonstrate that all emission emanates from π-aggregated excited states. Figure 5a shows the fluorescence spectra of polymer 1 in solution, in spin-cast films with PMMA, and in monolayer LB films. As the concentration of polymer 1 in PMMA matrix increases and the aggregation band in absorption spectra increases (Figure 4), the short wavelength (solution-like) peak disappears, and a long wavelength peak grows in, thereby indicating the formation of π-aggregates. Excitation at different wavelengths resulted in the intensity redistribution between these two peaks (Figure 5b), proving that these two peaks belong to different excited and ground states. Therefore, we can exclude excimer species. In the case of polymer 1, the fluorescence peak of π-aggregated PMMA films perfectly matched those of the LB film, and similar trends for polymers 2 and 3 were observed. Therefore, we conclude that the polymers 1–3 have both solution-like and π-aggregated regions in PMMA solid solutions, LB films, and Langmuir films, but all the fluorescence is emitted only from the aggregated states. This latter result is due to a fast energy migration from solution-like regions to the aggregated regions that have lower energy.

Figure 3. UV–vis spectra of polymers 1–8 in solution (solid line) and in LB films (dashed line). All LB films are monolayers on hydrophobic substrates unless otherwise noted.

Figure 4. UV–vis spectra of polymer 1/PMMA (weight ratio) spin-cast films.

Figure 5. Fluorescence spectra of polymer 1 (a) normalized spectra in various environments, (b) in B at different excitation wavelength. The mass ratio of polymer 1/PMMA in the spin-cast films is A = 10^{-1}/1, B = 10^{-2}/1, C = 10^{-3}/1, respectively.

of the reversible nature of the PA isotherm, the muir monolayers are folded into multilayers (Figure 2). Because the absorption spectra showed LB films of aromatic rings. It follows that the folded Langmuir or multilayer prevent direct interpolymer interactions between the conjugated hydrophobic substrates also show the additional values about 50 nm red to their solution peaks at longer wavelengths, 464 and 467 nm, respectively, does not persist upon removal of the surface pressure. The macrocycles in the polymer. In contrast, monolayers of the face-on polymers on a weak anchoring hydrophobic substrate reconstruct into “nanofibrils” to relieve the high surface energy of the polar macrocycles as described in Scheme 2 and shown in Figure 6.13 Because these monolayers cannot have π-aggregation when they are tightly bound (anchored) to hydrophilic substrates, no aggregation peaks are observed in their UV−vis spectra. However, for nanofibril monolayer films on hydrophobic substrates, the formation of an aggregation peak depends on the structure of the hydrophilic repeating group. Macrocycles containing polymers 4 and 5 display solution-like absorption spectra without any aggregation peak after assembly into nanofibrils. The spectra of 4 and 5 are slightly red-shifted from those in solution due to an increase in conjugation length imposed by the surface. The lack of π-aggregation is due to the macrocycles in 4 and 5 that by virtue of their structure prevent direct interpolymer interactions between the conjugated aromatic rings. It follows that the folded Langmuir or multilayer LB films of 4 and 5 did not show the π-aggregation peak.

Polymers 6 and 8 have acyclic polar residues, and the in situ absorption spectra showed π-aggregation peaks after the Langmuir monolayers are folded into multilayers (Figure 2). Because of the reversible nature of the PA isotherm, the π-aggregation does not persist upon removal of the surface pressure. The absorption spectra of these polymer nanofibril monolayers on hydrophobic substrates also show the additional π-aggregation peaks at longer wavelengths, 464 and 467 nm, respectively, values about 50 nm red to their solution λmax (Figure 3). Interestingly, the extent of π-aggregation in their nanofibril LB films is responsive to its environment. Dipping a nanofibril monolayer of 6 with a π-aggregation peak in water produces a solution-like UV−vis spectra. The π-aggregation peak is then reestablished with drying. Because the cores of the nanofibrils are hydrophilic (Scheme 2), water dilates the nanofibrils, thereby diminishing intermolecular interactions between polymers. Consistently, hydrophobic solvents are not absorbed into the fibrils, and the same film retains the aggregation peak upon dipping in hexane.

The polarized UV−vis spectra of nanofibril monolayer films of polymers 6 and 7 in Figure 7 provide additional information about the aggregate regions. For polymer 6, the aggregation peak at 464 nm in the parallel polarized UV−vis spectrum along the polymer alignment direction is of greater intensity than the solution-like peak at 438 nm. In contrast, the intensity of the aggregation peak in perpendicularly polarized spectra is less intense relative to the solution-like peak, indicating that the aggregate regions are better aligned along the dipping direction than are the nonaggregated regions. This result is intuitive because coincident alignment of polymer chains promotes aggregation. Even though it lacks macrocycles, nanofibrils of polymer 7 do not form π-aggregation peaks in absorption spectrum. It appears that the hydroxyl groups play an important role in reducing intermolecular interaction in the nanofibrils by strongly holding water molecules in the cores of the nanofibrils. This explanation is also supported by the behavior of 6 and 8 that form π-aggregates in dry nanofibrils, but then deaggregate when immersed in water. Folded Langmuir films of polymer 7 did not show additional π-aggregation peaks either (Figure 2). However, multilayer LB films of polymer 7 display a π-aggregation peak that increased with dehydration in a vacuum.
As shown in Figure 7b, these multilayer films show π-aggregate absorptions that are polarized along the direction of the polymer alignment.

Structural differences in monolayer LB films of the face-on polymers also affect emission spectra. The nanofibril monolayers of polymers 6 and 8 on hydrophobic substrates, with an aggregation peak in their absorption spectra, have structured fluorescence spectra with three peaks. On the other hand, the UV–vis spectra of the nanofibriled monolayers of polymers 4, 5, and 7 on hydrophobic substrates do not show aggregation, and their fluorescence spectra are less structured. In the case of polymer 7, we observed that the aggregation peak increased when the number of layers in the LB films increased, indicating a gradual increase of intermolecular interactions. We observed the same effect of intermolecular interactions on the fluorescence spectra of multilayer films of polymer 7. From a relatively featureless solution-like shape for a monolayer film, the spectra developed structure as the number of layers increased. Aggregation and highly ordered segments are mutually reinforcing and produce narrowed and structured fluorescence spectra. Energy migration to the aggregates also facilitates the band narrowing by reducing the contribution of solution-like fluorescence.

Fluorescence studies of spin-cast films of these polymers in PMMA solid solutions are consistent with the UV–vis analysis, that polymers 4, 5, and 7 do not form aggregates, whereas polymers 6 and 8 do. Figure 8 shows fluorescence spectra of polymers 4 and 8 in solution, in spin-cast films with PMMA, and in LB films on both hydrophobic and hydrophilic substrates. As the concentration of polymer 4 in a spin-cast film with PMMA increased, the emission \( \lambda_{\text{max}} \) undergoes slight red shifts (Figure 8a). However, polymers with a tendency to aggregate showed significant spectral changes. In Figure 8b, increasing concentrations of polymer 8 in spin-cast films with PMMA induced the evolution of fluorescence spectra from solution-like behavior to those characteristics of π-aggregation. The fluorescence spectrum of a spin-cast film at a low concentration (10^{-2}/1, polymer 8/PMMA) clearly showed a solution-like shoulder that decreases at higher concentrations of polymer 8.

Interpolymer Effects on Fluorescence Quantum Yield of Polymer Films. Table 1 shows the fluorescence quantum yields of the polymers in chloroform solution and in monolayer LB films on a hydrophobic substrate, and the ratio thereof (i.e., quantum yield in LB films/quantum yield in solution). The fluorescence quantum yields of the polymers in solution are similar and range from 0.34 to 0.54. The organizations have a larger effect, and monolayer LB films of face-on polymers have at least an order of magnitude higher quantum yield as compared to those of edge-on polymers.

Generally, monolayers on hydrophilic substrates have much smaller fluorescence quantum yields than monolayers on hydrophobic substrates. For example, the quantum yields of monolayers of polymers 1, 4, and 6 on a hydrophilic substrate are ~0.0015, 0.05, and 0.05, respectively. The lower quantum yields of the monolayers on hydrophilic substrates may arise from stronger interactions between the polymers’ hydrophilic groups and the substrates.

By comparing the ratio of quantum yield in LB films/quantum yield in solution, we can see the influence of intermolecular interactions on the quantum yield. First, the strong π-aggregating edge-on polymers display self-quenching and extremely low quantum yields. Second, the face-on polymers, which are devoid of strong π-aggregates, experience varying degrees of interpolymer interactions in nanofibrils. The ratio of quantum yield in LB films/quantum yield in solution has a tendency to increase as intermolecular interactions in nanofibrils decrease. Macromolecules of polymers 4 and 5 reduce intermolecular interactions in the nanofibrils significantly, resulting in the best ratio of quantum yield in LB films/quantum yield in solution.

Conclusions

We have demonstrated control of the spatial arrangement of PPEs by designed chemical structures and the LB method. This precise control of the spatial arrangement of conjugated polymers allowed us to elucidate aggregation mechanisms and the effect of π-aggregation on the spectroscopic properties of conjugated polymers. Through extensive structure–property correlations, we have firmly established spectroscopic features associated with nonaggregated polymers with various conjuga-
tion lengths. In well-defined LB films and various solid solutions, we demonstrated that strong π-aggregates present in fluorescent polymer thin films result in quenching due to efficient energy migration from nonaggregated regions to the aggregated ones. Intermolecular interactions in nanofibrils also affect the photophysical properties of the polymers. Macrocycles attached to the polymer backbone significantly reduce intermolecular interactions in the solid state, thereby increasing quantum yield relative to polymers without macrocycles. In well-defined monolayer LB films, orders of magnitude different quantum yields were obtained depending on spatial arrangement of polymers even though the solution quantum yields are similar to each other. These comprehensive results provide important design principles for fabricating highly luminescent polymer films. Because chemical modification can give surfactant character to other conjugated polymers, this method is potentially applicable to general conjugated polymers.

Experimental Section

General. Air- and moisture-sensitive reactions were carried out in flame-dried glassware using standard Schlenk-line or drybox techniques under an inert atmosphere of dry argon. All chemicals used were of reagent grade and were purchased from Aldrich unless otherwise noted. Anhydrous toluene was used from Aldrich Sure-seal bottles. Anhydrous CH2 Cl2 and THF were used directly from Aldrich Kilo-lab metal cylinders. Purified water (18 MΩ cm) was used as received. 1H and 13C NMR spectra were taken in CDCl3 with TMS as the internal standard. Vis spectra were obtained on a Hewlett-Packard diode array spectrophotometer. Fluorescence spectra were measured at room temperature through a window was placed in a vertically rotated UV spectrofluorometer. Gel permeation chromatography (GPC) measurements were made relative to thin-layer chromatography using standard Schlenk-line or drybox techniques.

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obtained as a brown solid. 1 H NMR (300 MHz, CDCl3): δ 7.48 (s, 2H), 7.04 (s, 2H), 4.30 (br m, 4H), 3.84 (m, 4H), 3.70–3.40 (br m, 10H), 3.37 (m, 4H), 3.20 (br m, 6H), 1.70–1.03 (m, 48H), 0.86 (m, 12H). GPC: Mw = 56 000; PDI = 2.5.

1,4-Bis[2-(2-hydroxyethoxy)ethoxy]-2,5-diiodobenzene (11). 1,4-Bis[2-(2-hydroxyethoxy)ethoxy]-2,5-diiodobenzene (11) (39 mg, 56 μmol, 0.03 equiv) and copper(I)iodine (21 mg, 110 μmol, 0.06 equiv) in a flame-dried flask equipped with a stir bar. The flask was evacuated and back filled with argon three times. The solids were dissolved/suspended in toluene (25 mL) and diisopropylamine (652 μL). The (trimethylsilyl)actylene (0.580 mL, 4.1 mmol, 2.2 equiv) was then added, and the reaction was stirred and heated to 60 °C for 20 h. Once the reaction was cooled to room temperature, saturated ammonium chloride solution was added, and the biphasic mixture was stirred for 30 min. The layers were then separated after dilution with ether. The organic layer was washed four times with saturated ammonium chloride solution, dried with magnesium sulfate, filtered, and concentrated to give a dark brown oil that was chromatographed on silica gel (50% hexane/50% ethyl acetate).

The bistrimethylsilylactylene (850 mg, 1.8 mmol, 1 equiv) was deprotected by reaction with aqueous potassium hydroxide (200 mg, 3.6 mmol, 2 equiv; dissolved in 1 mL of DDI water) in degassed THF (17 mL) and methanol (13.3 mL). The solution was stirred for 48 h. The reaction was then poured into 50 mL of ether. The organic layer was separated and washed with water three times (40 mL). The organic layer was dried with magnesium sulfate and concentrated to provide an off-white solid that was recrystallized from ethanol to provide 11. 1 H NMR (300 MHz, CDCl3): δ 7.00 (s, 2H), 4.16 (m, 4H), 3.88 (m, 4H), 3.74 (m, 4H), 3.69 (m, 4H), 3.36 (s, 2H), 2.21 (br s, 2H). 13C NMR (75 MHz, CDCl3): δ 153.76, 118.03, 113.44, 82.99, 79.38, 72.53, 69.39, 69.22, 61.79 ppm. HR-MS: calcd for C16H25O6 (M+), 334.1416; found, 334.1424.

Polymer 7. A 10 mL Schlenk flask equipped with a stir bar was charged with 1.4-bis[2-(2-hydroxyethoxy)ethoxy]-2,5-diiodobenzene (11) (30 mg, 91.3 μmol, 1.05 equiv) and 1.4-bis(N,N-dioctylcarbamoyl)-2,5-diodobenzene (75 mg, 87 μmol, 1 equiv). Tetraakis-(triphenylphosphine)palladium (0) (3.1 mg, 4.35 μmol, 0.05 equiv) and copper(I) iodide were added to the flask under a nitrogen atmosphere. The flask was then evacuated and back filled with argon three times before adding toluene (1.5 μL) and diisopropylamine (500 μL) via cannula. The reaction was stirred while maintaining the temperature at 60 °C for 48 h. The reaction was cooled before diluting with methylene chloride and subsequent washing with ammonium hydroxide. The organic layer was concentrated to a yellow film that was redissolved in methanol and precipitated with water. After drying, polymer 7 was obtained as a fluorescent green-yellow solid. 1 H NMR (300 MHz, CDCl3): δ 7.51 (s, 2H), 6.95 (s, 2H), 4.14 (br s, 4H), 3.90 (br s, 6H), 3.82–3.52 (br m, 8H), 3.16 (br s, 6H), 2.19 (br), 1.82–1.02 (m, 48H), 0.86 (m, 12H). GPC: Mw = 51 600; PDI = 3.8.

Polymer 8. A 10 mL flame-dried Schlenk flask equipped with a stir bar was charged with 1,4-bis(N,N-dioctylcarbamoyl)-2,5-diodobenzene (86.5 mg, 100 μmol, 1 equiv), 1-((triethylene glycol monoethyl ether)oxy)-4-decyloxy-2,5-diiodobenzene (9) (45.8 mg, 103 μmol, 1.03 equiv), and copper(I)iodide (2.3 mg, 12 μmol, 0.12 equiv) in methanol and precipitated with water. After drying, polymer 8 was obtained as a brown solid. 1 H NMR (300 MHz, CDCl3): δ 7.46 (s, 2H), 6.92 (s, 1H), 6.84 (s, 1H), 4.16 (br s, 2H), 4.00–3.80 (m, 4H), 3.78 (m, 2H), 3.68 (m, 6H), 3.56 (m, 2H), 3.38 (s, 3H), 3.18 (br s, 6H), 1.80–1.03 (m, 64H), 0.89 (m, 15H) ppm. GPC: Mw = 16 700; PDI = 2.4.

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