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Aggregation of a Polyphilic Janus Polythiophene in Solution

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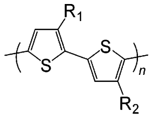
ABSTRACT: Solutions of poly(4′-perfluorooctyl-3-octyl-2,2′-bithiophene) display strong thermochromism and solvatochromism that are consistent with formation of solid-state-like aggregates. The polyphilicity of the structure (having alkyl, fluoroalkyl, and arene segments) provides a Janus structure in which the two edges of a ribbonlike polymer chain have distinctly different surface energies. In addition, the placement of electron-donating and electron-withdrawing substituents provides an alternation of charge density along the polymer backbone. The chromic effects are not observed for analogous polymers that only have one type of side chain or for an analogue with alternating alkyl and semifluoroalkyl side chains that is polyphilic but does not have the alternation of charge density along the polymer chain.

Introduction

The π-conjugation of polythiophenes[1] and other conjugated polymers[2] facilitates the delocalization of the charge carriers which are formed upon oxidation or reduction ("doping") and imparts high charge mobility in both the neutral and charged polymers. This delocalization leads to characteristic absorptions and emissions in the visible region of the electromagnetic spectrum that may be exploited in the development of OLEDs and sensors. Attachment of flexible side chains to the rigid or semirigid conjugated backbones provides materials with improved processibility (solubility, fusibility) and allows for control of the conformation of the backbone and formation of supermolecular structures.

Modification of the molecular structure of polythiophenes and changes in the environment of the polymer chains (e.g., temperature,[3] solvent quality, pressure, ions and small molecules[4]) often lead to dramatic chromic effects that might be ascribed to intramolecular and intermolecular effects. Steric interactions between side chains on adjacent repeat units (i.e., an intramolecular effect) lead to twisting around the backbone and a decrease in the effective conjugation length.[1] Other changes to the electronic structure of the conjugated backbone may be ascribed to intermolecular effects associated with aggregation of the polymer chains which often gives rise to a red shift in the absorption and quenching of emission. Thus, the effects of structure, solvent, and temperature on the chromism of polymer solutions are a delicate balance between repulsive intrachain steric interactions and attractive interchain interactions that lead to assemblies of planar segments of the polymer. The presence of an isosbestic point in UV−vis spectra of solutions of regioregular poly(3-alkylthiophene)s in response to changes in solvent quality or temperature has been explained by a transition between a planar conformation and a "twiston" conformation without any intermediate states.[5,6] On the other hand, a continuous blue shift of the absorption maximum takes place upon heating solutions or films of regiorandom poly(3-alkylthiophene)s by virtue of a continuously increasing density of twisted conformations in these less ordered polymers.[7]

The organization of conjugated polymer chains into supermolecular structures plays an important role in determining their optical properties. Aggregates of conjugated polymer chains in solution are often formed upon cooling or on addition of poor solvents. The red shift associated with this process is consistent with the planarization and close-packing of the conjugated chains,[8] although few models for packing of the polymer chains in these aggregates have been proposed. Most recently, studies of a regioregular poly(3-alkylthiophene) by TEM,[9] SPM,[10] and TEM[11] studies of assemblies formed by amphiphilic oligo(ethylene glycol)-substituted polythiophenes in water have revealed some structural details related to these supermolecular aggregates.



$R_1 = C_8F_{17}$, $R_2 = C_8H_{17}$ **PT-H8-*alt*-F8**
$R_1 = (CH_2)_3C_6F_{13}$, $R_2 = C_9H_{19}$ **PT-H3/F6-*alt*-H9**
$R_1 = R_2 = C_8F_{17}$ **PT-F8**
$R_1 = R_2 = C_8H_{17}$ **PT-H8**

Figure 1. Structures of **PT-H8-*alt*-F8**, **PT-H3/F6-*alt*-H9**, **PT-F8**, and **PT-H8**.

Polyphilic molecules, those containing more than two mutually incompatible segments (e.g., rigid cores and flexible tails, hydrophilic and hydrophobic, or fluorophilic and fluorophobic), provide the possibility of forming a diverse array of interesting self-assembled structures.[12] We have previously shown that introduction of semifluoroalkyl side chains on the polythiophene backbone leads to the formation of a highly ordered solid-state structure[13] and thermotropic mesophases[14] by virtue of segregation of hydrocarbon, fluorocarbon, and polyarylene segments. In addition, direct attachment of perfluoroalkyl chains to the polythiophene backbone affords homopolymers that are soluble in supercritical CO_2[15] and copolymers with a 3-alkylthiophene that retain their fluorescence in the solid state.[16]

To explore the potential role of polyphilicity on the assembly of polymers in solution, we set out to investigate the spectroscopic properties of solutions of poly(4′-perfluorooctyl-3-octyl-2,2′-bithiophene) (**PT-H8-*alt*-F8**),[16] Figure 1, a polyphilic alternating copolymer consisting of alkyl- and perfluoroalkyl-substituted thiophene rings. If the polymer backbone of **PT-H8-*alt*-F8** adopts an all-anti conformation (as our semifluoroalkyl polythiophenes do in the solid state), the alternating substitution pattern provides a ribbonlike Janus structure which possesses edges with distinct surface energies (i.e., fluoroalkyl

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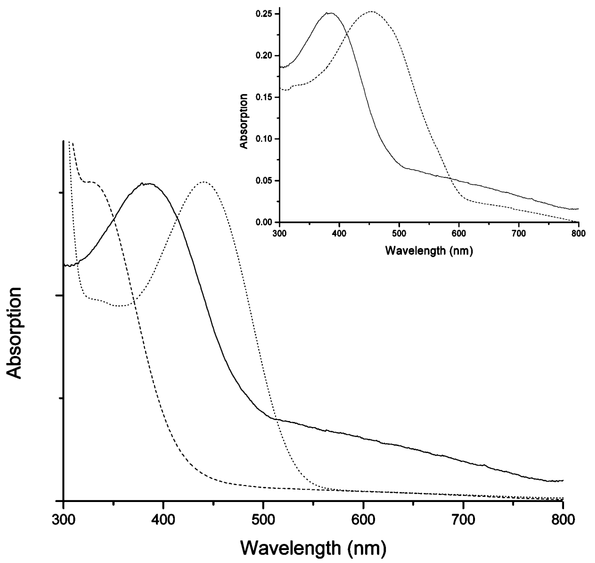

Figure 2. UV−vis absorption spectra (normalized) of **PT-F8** (- - -), **PT-H8-*alt*-F8** (—), and **PT-H8** (···) in 10^{-5} M solution in chloroform. Inset: absorption of solution (—) and film (···) of **PT-H8-*alt*-F8**.

vs alkyl). In addition, the conjugated backbone itself consists of an alternating sequence of electron-rich and electron-poor thiophene units by virtue of the different substitutents. The thermochromism and solvatochromism of solutions of this polymer are compared to those of other polythiophenes by both absorption and emission spectroscopies. The morphology of aggregates formed by **PT-H8-*alt*-F8** was explored by TEM.

Results

Absorbance and Fluorescence Spectra. PT-H8-*alt*-F8 (1.4×10^4 g/mol) and two head-to-tail regioregular homopolymers, poly(3-octylthiophene) (**PT-H8**) and poly(3-perfluorooctylthiophene) (**PT-F8**) (Figure 1), were examined to explore the potential aggregation of polyphilic conjugated polymers in solution. The previously published mode of synthesis of **PT-H8-*alt*-F8** by GRIM polymerization[17] of 2-bromo-4′-perfluoroctyl-3-octyl-2,2′-bithiophene[16] provides an alternating sequence of alkyl and perfluoroalkyl groups along the backbone with a head-to-tail regioregularity that is analogous to that of the regioregular homopolymers. Comparison of the UV−vis absorption spectra (10^{-5} M in $CHCl_3$) of **PT-H8** ($\lambda_{max} = 441$ nm), the alternating copolymer **PT-H8-*alt*-F8** ($\lambda_{max} = 384$ nm), and **PT-F8** ($\lambda_{max} = 326$ nm) indicates a blue shift in the absorption peak upon increasing the density of perfluoroalkyl substitutents (Figure 2). This shift arises primarily due to twisting of the backbone by steric interactions between the perfluoroalkyl substituents.[15] However, whereas the wholly alkyl and perfluoroalkyl-substituted polymers display sharp onsets to the absorption peak (ca. 550 and 430 nm, respectively), the absorption of the copolymer has a distinct tail out to higher wavelengths (Figure 2). For comparison, a spin-coated thin film of the copolymer gives a broad absorption with a peak at 456 nm (Figure 2 inset). Thus, we reasoned that the tail to long wavelengths in the absorption spectrum of a dilute solution of **PT-H8-*alt*-F8** might arise from the presence of aggregates.

The fluorescence spectra of a $CHCl_3$ solution and a thin film of **PT-H8-*alt*-F8** are shown in Figure 3. When excited at the solution absorption maximum of 390 nm, the alternating copolymer solution emits yellow fluorescence with the maximum intensity at 547 nm (i.e., a Stokes shift of 157 nm). The polymer film, when excited at the 456 nm (the film absorption maximum), emits red fluorescence with a maximum at 612 nm and a shoulder at 649 nm (Stokes shift = 156 nm).

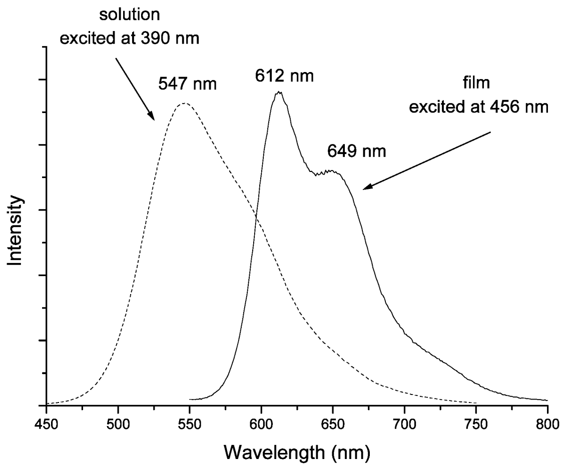

Figure 3. Emission spectra (normalized) of **PT-H8-*alt*-F8**: 10^{-5} M solution in chloroform (- - -); excited at 390 nm and spin-coated film (—).

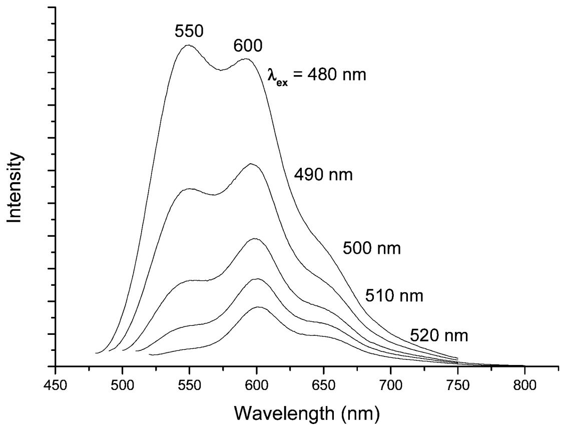

Figure 4. Emission spectra of **PT-H8-*alt*-F8** (10^{-5} M solution in chloroform) excited at various wavelengths.

The fluorescence spectrum of a 10^{-5} M solution of the copolymer in $CHCl_3$ displays significant changes upon varying the excitation wavelength, thereby allowing us to further investigate the assembly process (Figure 4). Upon increasing the excitation wavelength from the absorption maximum (384 nm, Figure 2) into the tail (>500 nm), the solution-like emission peak at 550 nm decreases in intensity, and there is an increase in the intensity of a peak at 600 nm with a shoulder at 650 nm, reminiscent of the solid-state emission. Excitation at 520 nm (i.e., well into the absorption tail) results solely in solid-state-like emission with no contribution from the band at 550 nm. Similar effects were also observed on even more dilute solutions (10^{-6} M).

Thermochromism. The process of self-assembly in solution should be an equilibrium process which can be controlled by external stimuli. Thermochromism of the polymer solution in both UV−vis and fluorescence spectra suggests the existence of such an equilibrium. At high temperatures (e.g., 60 °C) the tail to higher wavelengths of the main adsorption almost completely disappears, and the spectrum has a sharp cutoff, consistent with the absorption of a single (solution) species (Figure 5A). An isosbestic point at 420 nm indicates there are two absorbing states of the polymer that are in equilibrium, the solution state and the aggregate state. The presence of an isosbestic point and absence of a continuous shift of the absorption peak indicates that there is no intermediate confor-

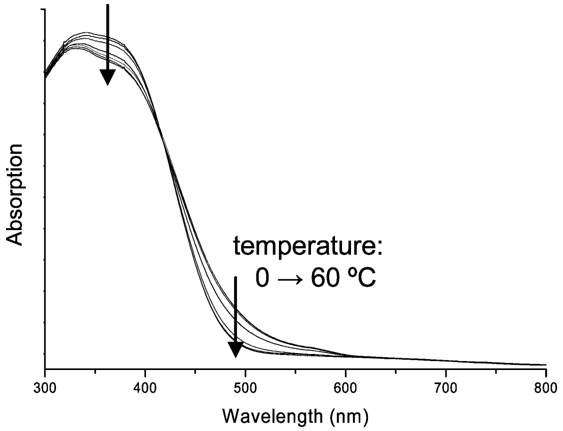

Figure 5. Effect of temperature on UV−vis absorption spectra of **PT-H8-*alt*-F8** (10^{-5} M solution in chloroform; spectra recorded every 10 °C from 0 to 60 °C).

mational change between the random coil twisted conformation in solution and a self-assembled planar (more conjugated) conformation in the aggregate state.

The thermally induced changes occurring in solutions of the copolymer are much more evident in fluorescence spectra recorded at various excitation wavelengths. Variation of the excitation wavelength allows for selective excitation of the two chromophores present (the putative solution and aggregated states), giving rise to distinct emission peaks. Whereas excitation of the polymer solution at 390 nm (i.e., near λ_{max} of the solution state) at room temperature results in an emission maximum at 547 nm, decreasing the temperature results in the appearance of a distinct shoulder at 600 nm (Figure 6A), consistent with formation of aggregates with emission similar to that of the solid state.

The polymer solution was also examined as a function of temperature upon excitation at 500 nm, in the tail of the absorption where only the aggregate state has a contribution to the absorption. At 0 °C the solution exhibits strong fluorescence with peaks at 600 and 650 nm. The intensity of this emission decreases as the temperature is raised (Figure 6B), especially upon proceeding from 30 to 50 °C. At 60 °C there is no emission at 600 nm, evidence for the complete dissolution of the aggregates formed at lower temperature. Thus, these emission experiments provide much greater insight into the aggregation process as a function of temperature than the absorption experiments alone.

Solvatochromism. Addition of methanol to a 10^{-5} M solution of **PT-H8-*alt*-F8** in $CHCl_3$ results in the emergence of a distinct tail in the absorbance spectrum, with a decrease in the absorption at 390 nm. An isosbestic point at 451 nm, as was observed in the thermochromic transition, indicates that two states of the polymer are in equilibrium with one another. However, once again, stronger solvatochromic effects were observed in emission spectra (Figure 7A). Excitation of a solution of **PT-H8-*alt*-F8** in $CHCl_3$ at the absorption maximum (390 nm) results in strong fluorescence with $\lambda_{max} = 547$ nm. Addition of up to 17% v/v methanol gives rise to a new peak at 600 nm in the emission spectrum with a distinct shoulder at 650 nm, consistent with the emission noted in experiments to investigate the effect of temperature (Figure 6) and with emission from solid films (Figure 3). Once again, excitation at 500 nm shows more distinct changes, with the enhancement of the aggregate emissions at 600 and 650 nm upon addition of more methanol.

Effect of Molecular Weight. The dependence of the thermochromism and solvatochromism on the molecular weight of

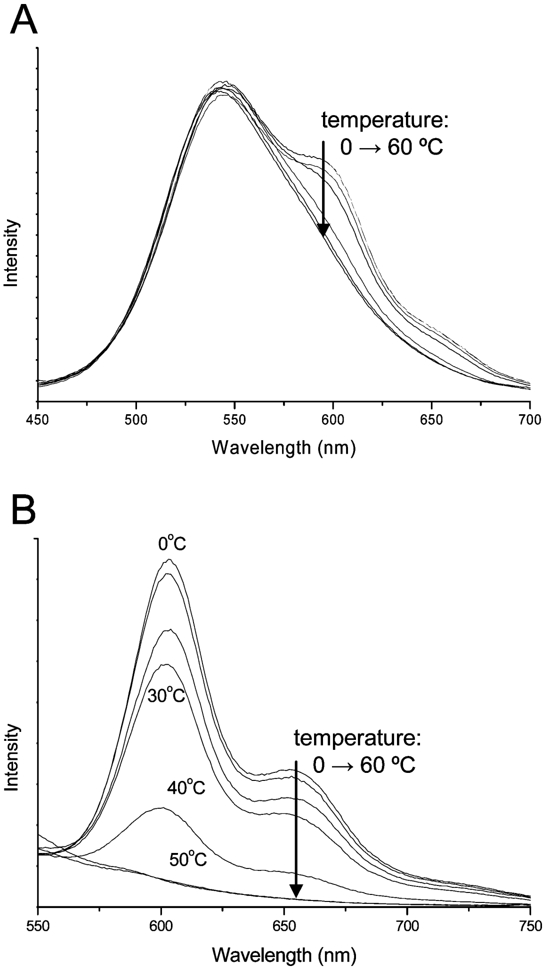

Figure 6. Effect of temperature on fluorescence emission spectra of **PT-H8-*alt*-F8**: (A) excitation at 390 nm; (B) excitation at 500 nm (10^{-5} M solution in chloroform; spectra recorded every 10 °C from 0 to 60 °C).

the polymer was also examined. Crude **PT-H8-*alt*-F8** was fractionated in a Soxhlet extractor with methanol, acetone, hexane, and chloroform. The hexane fraction consists of lower molecular weight oligomers than the $CHCl_3$ extract (with an average of ∼10 thiophene rings per chain). Solutions of the hexane extract, **oligoT-H8-*alt*-F8**, show similar thermochromism and solvatochromism as the higher molecular weight material, albeit with a lower propensity to aggregate.

Whereas the polymeric sample is partially aggregated in $CHCl_3$ at room temperature with solid-state-like contributions in the emission and absorption spectra (Figure 7), **oligoT-H8-*alt*-F8** requires addition of 8% methanol before aggregation is observed (Figure 8A). Similarly, in the thermochromism study, the solid-state-like emission of the oligomeric sample turns on between 20 and 30 °C (Figure 8B), which is lower than that of the higher molecular weight polymer **PT-H8-*alt*-F8** (40−50 °C, Figure 6).

Microscopy. Transmission electron microscopy (TEM) was performed on solid samples prepared by evaporation of solutions of **PT-H8-*alt*-F8**. Addition of 17% (v/v) methanol to a yellow fluorescing 10^{-5} M solution of copolymer in $CHCl_3$ switched the emission to the characteristic yellow of the aggregated state. A drop of this solution was evaporated to provide a thin film that was examined by TEM. Images reveal the formation of particles with an average dimension of 200 nm (Figure 9A). The micrograph shows two particles. Each of these appears to consist of a layered structure with distinct layer edges.

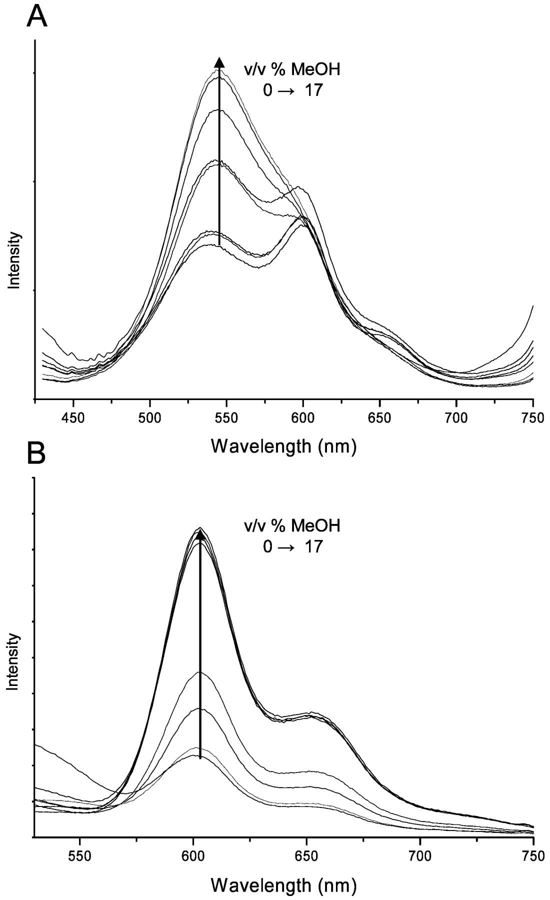

Figure 7. Effect of addition of methanol on fluorescence emission spectra of **PT-H8-*alt*-F8**: (A) excitation at 390 nm; (B) excitation at 500 nm (10^{-5} M solution in chloroform; spectra recorded every 2.4% (v/v) of MeOH from 0 to 17%).

Selected area electron diffraction of regions of the nanoscale particles that appears to consist of a single platelet (e.g., Figure 9B) shows a diffraction pattern typical for a single crystal (Figure 9C). The electron diffraction pattern is similar to that obtained for columnar assemblies of alkyl-substituted helicenes.[18] In this case the pattern was assigned to a rectangular lattice resulting from packing of the alkyl side chains in a fashion similar to the packing of linear polyethylene chains: The presence of only *hk*0 reflections was taken to indicate that the chains are oriented nearly perpendicular to the lamellae of the material. Whereas the alkyl-substituted helicenes give rise to reflections at 0.249 nm (for the (020) reflection), 0.379 nm (200), and 0.418 nm (110), the lattice spacings observed for **PT-H8-*alt*-F8** correspond to 0.24 and 0.39 nm. These small differences might arise from a tilt of the alkyl chains away from the normal to the lamellae or from contributions of perfluoroalkyl segments. Diffraction data collected on regions of a particle that appear to consist of multiple layers (e.g., the center of the particle shown in Figure 8A) provide a superposition of patterns. This suggests that the side chains are oriented perpendicular to the lamellae of the nanoscale particles. This is reasonable on the basis of known lamellar packing of regioregular poly(3-alkylthiophene)s. We have also previously shown that analogous semifluoroalkyl-substituted polymers also show a high preference to order and orient at a substrate−polymer interface, a propensity that might be supported by the amphilicity of these materials. While the amphiphilic structure of the polymer could potentially lead to cylindrical morphologies that might be expected to give rise to hexagonal lattices, the relatively small lattice spacings in the diffractogram do not support this suggestion. Neither the background area of the TEM image shown in Figure 8 nor large areas of thin polymer film formed by evaporation of the dilute polymer solution in $CHCl_3$ (without MeOH) result in diffraction, indicating that the nanometer-scale aggregates observed are formed in solution (i.e., upon addition of MeOH to the $CHCl_3$ solution of copolymer) and are not caused by the evaporation process itself.

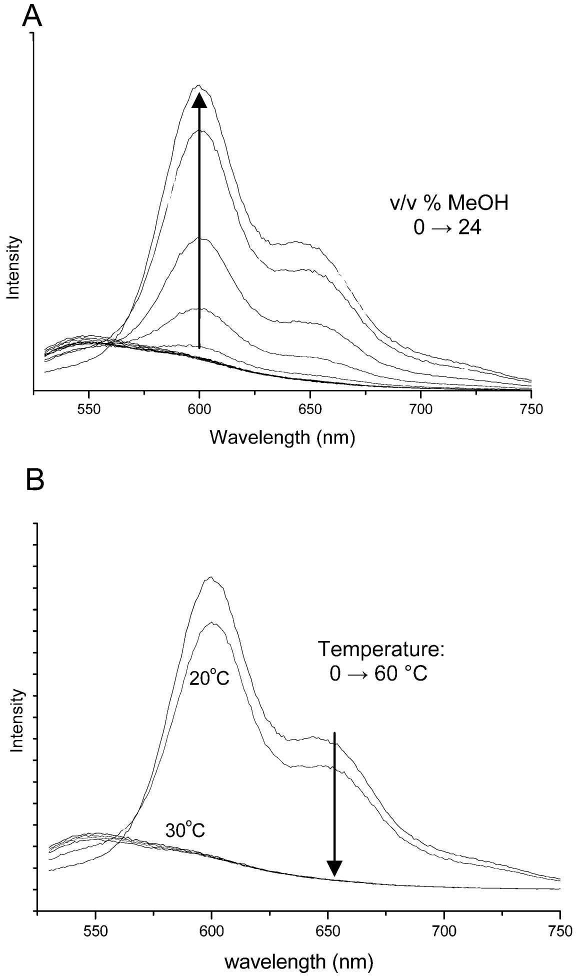

Figure 8. Solvatochromism and thermochromism in fluorescence spectra of **oligoT-H8-*alt*-F8** (10^{-5} M solution in chloroform, excited at 500 nm): (A) effect of addition of methanol on fluorescence spectra, spectra recorded every 2.4% (v/v) of MeOH from 0 to 24%; (B) thermochromism (spectra recorded every 10 °C from 0 to 60 °C).

The Origin of Assemblies. Three structural characteristics of **PT-H8-*alt*-F8** could give rise to the aggregation of nanometer-scale crystalline nuclei: (i) the incompatibility of the rigid backbone and flexible side chains; (ii) the polyphilicity of the polymer by virtue of the aromatic backbone, fluoroalkyl, and alkyl substituents; and (iii) the electronic interactions between electron-rich alkyl-substituted thiophene rings and electron-poor perfluoroalkyl-substituted rings. Control experiments were performed to identify which factor may induce this aggregation.

UV−vis and fluorescence spectra of a10^{-6} M solution of regioregular poly(3-octylthiophene), **PT-H8**, in $CHCl_3$ were collected at various temperatures (0−60 °C) and upon addition of MeOH (up to 17% v/v). **PT-H8** showed neither thermochromism nor solvatochromism under these conditions, and no solid-state-like emission was observed. This suggests that aggregation of the copolymer does not arise solely from the incompatibility of the backbone and side chains. The same experiments were performed on a copolymer with alternating alkylthiophene and sem*i*fluoroalkylthiophene units, **PT-H3/F6-**

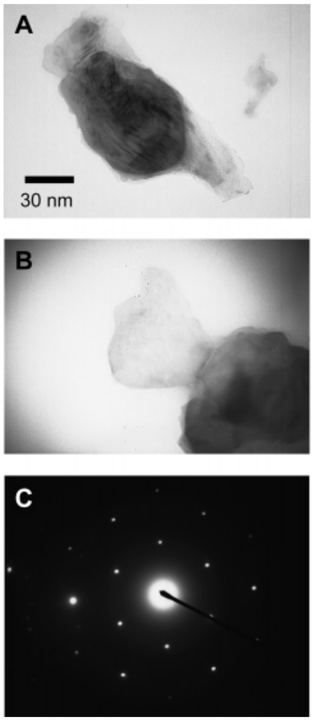

Figure 9. (A) TEM image of the nanoscale particle of **PT-H8-*alt*-F8** showing aggregate of platelets. (B) Protrusion of a single platelet from a particle. (C) Selected area electron diffraction from a single platelet.

***alt*-H9**.[13] While this copolymer is still polyphilic, the hydrocarbon linker ($-(CH_2)_3-$) of the semifluoroalkyl chains insulates polythiophene backbone from the electron-withdrawing effect of the fluoroalkyl chains. In contrast to **PT-H8-*alt*-F8**, the polymer with the three-methylene spacer does not have the alternating sequence of electron-rich and electron-poor thiophene rings. **PT-H3/F6-*alt*-H9** does not show thermochromism or solvatochromism in solution, and no solid-state-like emission in solution was observed. Combining these two control experiments, we reason that the alternation of electron-rich and -poor units along the alkyl/perfluoroalkyl copolythiophene **PT-H8-*alt*-F8** is a key factor to induce aggregation and to turn on the solid-state-like emission. Previous reports on tuning the electronic properties of polythiophenes include the incorporation of alternating resonance electron acceptors (e.g., $-CN$, $-NO_2$, $-CH{=}C(CN)_2$) and donors ($-OMe$, $-NH_2$)[19] (as well as preparation of polymers consisting of alternating thiophenes and other heteroarenes[20]). While these studies report red-shifted absorption upon cooling solutions, they do not address the potential for enhanced aggregation by virtue of the alternating charge distribution.

In conclusion, the alternating fluoroalkyl/alkyl-substituted polythiophene copolymer **PT-H8-*alt*-F8** has a chemical structure which combines alternating electron-rich and -poor units, polyphilicity arising from the placement of the fluoroalkyl and alkyl substituents on alternating units along the polyarylene backbone, and the incompatibility of rigid backbone and flexible side chains. This unusual structure leads to the aggregation behavior of this alternating copolymer in solution with a hexagonal diffraction lattice similar to that determined for assembly of an amphiphilic oligo(ethylene glycol)-substituted polythiophene in aqueous solution.[11] For most other (but not all[10]) polythiophenes, the formation of aggregates in solution usually quenches the fluorescence due to the interchain energy relaxation. In contrast to the aggregation of most other polythiophenes, this copolymer forms aggregates and solid films which display strong emission, which may have potential application in electrooptical devices and sensors.

Experimental Section

The regioregular copolymer consisting of alternating 3-(perfluoroalkyl)thiophene and 3-alkylthiophene units (**PT-H8-*alt*-F8**) was prepared by Ni(II)-catalyzed GRIM polymerization[17] of 5-bromo-5′-lithio-3-octyl-4′-perfluorooctyl-2,2′-bithiophene.[16] **PT-H8**,[21] **PT-F8**,[15] and **PT-H3F6-*alt*-H9**[16] were prepared according to literature methods. At the end of the polymerization procedure the reaction mixture was poured into a large excess of methanol. The precipitate was collected and subjected to extraction in a Soxhlet extractor with methanol, followed by acetone, then hexane, and finally chloroform. The $CHCl_3$-soluble fraction of **PT-H8-*alt*-F8** studied here has a number-average molecular weight, M_n, greater than 1.4×10^4 g/mol, corresponding to a degree of polymerization ≥ 20 (i.e., ≥ 40 thiophene rings per chain). ^1H NMR (300 MHz, $CHCl_3$); δ 7.18 (s, 1H), 7.06 (s, 1H), 2.74 (t, 2H), 1.1−1.8 (m, 12H), 0.92 (m, 3H). The earlier hexane extract consisted of oligomers with discernible end groups in the NMR spectrum.

UV−vis analysis was performed with a Perkin-Elmer Lambda 19 spectrometer. Fluorescence spectra were collected with a Spex Fluorolog Fluometer 1681 0.22m spectrometer. TEM images and diffraction patterns were collected in JEOL 100C TEM (100 keV) equipment. Samples were prepared by placing a drop of polymer solution on carbon-coated Cu grids which were then allowed to dry in air.

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Supporting Information Available: Control thermochromism and solvatochromism experiments (UV−vis and fluorescence spectra) of **PT-H8** and **PT-H3F6-*alt*-H9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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