Tuning the Electronic Structure of Conjugated Polymers with Fluoroalkyl Substitution: Alternating Alkyl/Perfluoroalkyl-Substituted Polythiophene

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ABSTRACT: The electronic properties of the conjugated backbone of polythiophene can be tailored by the incorporation of alkyl and perfluoroalkyl substituents. A regioregular copolymer with alternating alkyl and perfluoroalkyl substituents displays absorption and emission maxima between those of the homopolymers composed of the individual structural units. However, the combination of the alternating electron-rich and electron-poor units, together with a small twisting influence of the perfluoroalkyl groups, provides a material which displays enhanced solution-phase fluorescence and strong solid-state fluorescence which is absent for the wholly alkyl analogue.

Introduction

Semifluoroalkyl side chains have been attached to a wide variety of polymers to provide materials with unusual properties which arise as a consequence of the hydrophobicity, rigidity, thermal stability, chemical and oxidative resistance, and self-organization of fluoroalkyl chains.[1] Following a number of reports on the synthesis and polymerization of 3-(semifluoroalkyl)thiophenes (3-Th$(CH_2)_m(CF_2)_nF$, where $m = 1, 2,$ or 3),[2] we developed approaches to control the supermolecular organization of polythiophenes based on the immiscibility of hydrocarbon ($m > 3$) and fluorocarbon segments in the side chains.[3−5] Control of supermolecular packing of conjugated chains is expected to have profound effects on their properties and the efficiency of devices incorporating these materials (e.g., LEDs and FETs).[6−8] With certain lengths of alkyl and perfluoroalkyl segments in the side chain, poly(3-(semifluoroalkyl)thiophene)s display liquid crystallinity[3,5] and form highly ordered, and oriented, solid-state structures.[4] These studies made use of side chains in which an alkyl spacer, $(CH_2)_m$, insulates the electron-withdrawing influence of the fluoroalkyl segment from the conjugated backbone. The effects of attachment of perfluoroalkyl side chains on thiophene (i.e., 3-Th$(CF_2)_nF$), oligothiophenes,[9,10] and polythiophenes[11,12] have only been reported recently. The direct attachment of fluoroalkyl substituents raises the oxidation potential of monomers, oligomers, and polymers relative to the alkyl-substituted analogues. In addition, the electron-withdrawing nature of the side chains renders oligothiophenes and polythiophenes n-dopable. The perfluoroalkyl substituents also have a significant effect on the absorption and emission spectra and provide materials that are soluble in supercritical CO_2.[12]

Copolymerization is a general approach to expand the range of properties of polythiophenes and to create self-assembling supermolecular structures. In addition to the variation of the comonomers used, the properties of copolymers depend on their microstructural sequence (e.g., random, alternating, block, and graft). Random copolymers containing thiophene have been prepared which incorporate a variety of other arenes (e.g., pyrrole,[13] fluorene,[14,15] quinoxaline,[16] thiazole[17]) to provide materials with tunable electronic properties. Extensive studies have also led to the preparation of copolymers of 3-alkylthiophenes and other 3-substituted thiophenes such as those with alkyl,[18] alkoxyl,[19] oligo(ethylene glycol),[20] and ionic[21] substituents.

Block[22] and alternating[23−25] copolythiophene microstructures have attracted less attention. These approaches both offer opportunities to prepare well-defined materials with electron-rich and electron-poor segments in the backbone and thereby provide new materials for use in electronic and optoelectronic applications. The high electron density of the π-conjugated polymers backbones makes hole injection (and transport) more favorable than electron injection in most cases. A balance in the energies for injection of holes and electrons might be achieved by incorporation of other hetereocycles[16] or by placing substituents along a wholly polythiophene backbone (e.g., poly(3-cyano-3′-methoxy-2,2′-bithiophene)[24]).

Here we report the preparation and characterization of a regioregular alternating copolymer consisting of 3-octylthiophene and 3-(perfluorooctyl)thiophene units (PT-H8-*alt*-F8). The properties are compared to those of the regioregular homopolymers: poly(3-octylthiophene), PT-H8, and poly(3-(perfluorooctyl)thiophene), PT-F8. This illustrates the use of perfluorinated substituents to tune the electronic structure of polythiophenes and provides a material with enhanced fluorescence.

Results and Discussion

Synthesis and Polymerization. 4′-Perfluoroctyl-3-octyl-[2,2′]-bithiophene, **5**, was prepared by Suzuki coupling of 2-bromo-4-perfluorooctylthiophene, **4**,[11] and [1′,3′-(2′,2′-dimethylpropylene)]-3-octyl-2-thienylboronate, **3**,[26] which were both prepared according to literature procedures. Bromination of **5** with *N*-bromosuccinimide in DMF at room temperature resulted in regioselective bromination of the α-thienyl position of the electron-rich alkyl-substituted thiophene ring to give **6** (Scheme 1).

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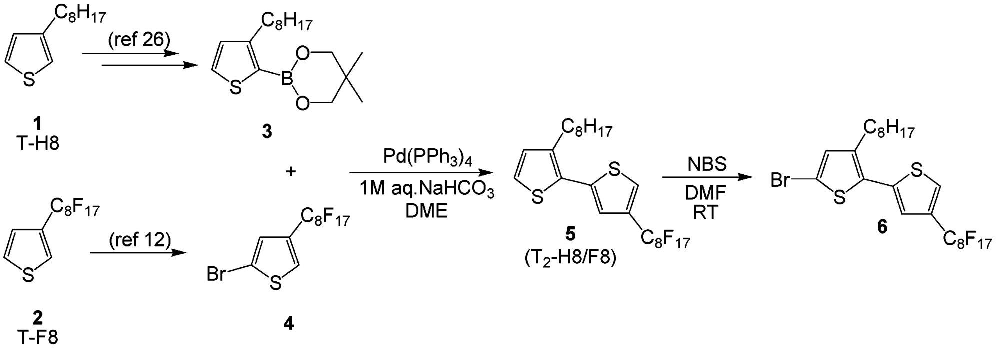
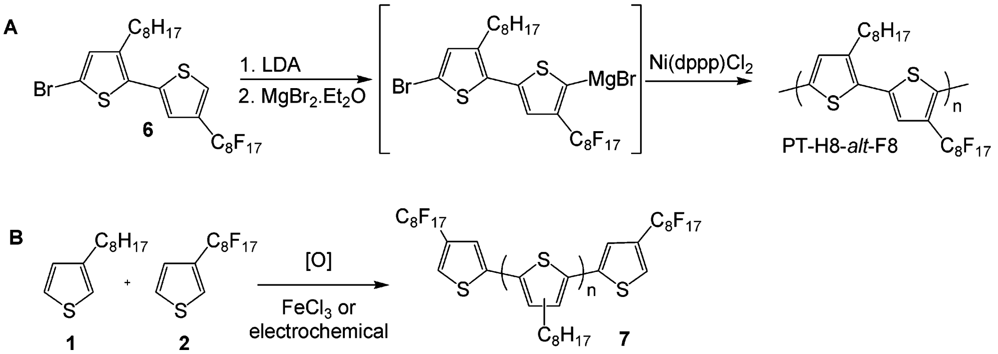
Scheme 1. Synthesis of Monomers 4 and 6



Scheme 2. Polymerizations



Polymerization of **6** to form the regioregular alternating copolymer PT-H8-*alt*-F8 was performed using McCullough's method for the preparation regioregular poly(3-alkylthiophene)s[27] (Scheme 2A). Lithiation of **6** with LDA, transmetalation with $MgBr_2$, and treatment with a catalytic amount of Ni(II) resulted in a bright red solution. Addition of methanol to the reaction mixture resulted in precipitation of polymer which was fractionated by successive extraction in a Soxhlet extractor with MeOH, acetone, hexane, and $CHCl_3$. The $CHCl_3$ fraction was characterized further.

^1H NMR was used to characterize the structure of PT-H8-*alt*-F8 prepared in this manner. A singlet at δ7.21 ppm is assigned to β-proton on the fluoroalkyl-substituted thiophene ring, and a singlet at δ7.08 ppm corresponds to the β-proton on the alkyl-substituted ring (Figure 1, top). The sharpness of these peaks and lack of other peaks in this region indicates formation of a highly regioregular (i.e., head-to-tail) and therefore alternating, copolymer structure. Small signals appear in this spectrum for the end groups. Peaks at δ 7.69 and 7.01 ppm arise from the α and β protons on terminal perfluoroalkyl-substituted thiophene rings; the corresponding protons in bithiophene **5** appear at δ 7.66 and 7.18 ppm (Figure 1, middle). A peak at δ 6.91 ppm corresponds to the β proton on terminal alkyl-substituted thiophene rings (for comparison, the proton on C4 of **6** appears at δ 6.91 ppm). Comparison of the integrals of these peaks indicates that the polymer has a number-average molecular weight greater than 1.4×10^4 g/mol, corresponding to a degree of polymerization ≥ 20 (i.e., ≥ 40 thiophene rings per chain). A triplet at 2.78 ppm is assigned to α-methylene group of alkyl side chain. The absence of additional peaks in this region further indicates that the polymer is highly regioregular.[28]

Oxidative Polymerizations. To explore a wider variety of copolymer microstructures, we also attempted to prepare the random copolymer by oxidative polymerization of a 1:1 mixture of 3-octylthiophene, **1**, and 3-(perfluorooctyl)thiophene, **2**, by treatment with $FeCl_3$ in $CHCl_3$ (Scheme 2B). The resulting polymer was precipitated from methanol. Fractionation afforded a deep red $CHCl_3$-soluble polymer. The ^1H NMR spectrum of the polymer prepared in this manner shows a singlet at δ 6.90 ppm, which is typical of the β-proton on the poly(3-alkylthiophene) backbone. Several peaks slightly shifted from this peak indicate the polymer has a regiorandom linkage of 3-alkylthiophenes, which is expected for the oxidative polymerization. Small peaks

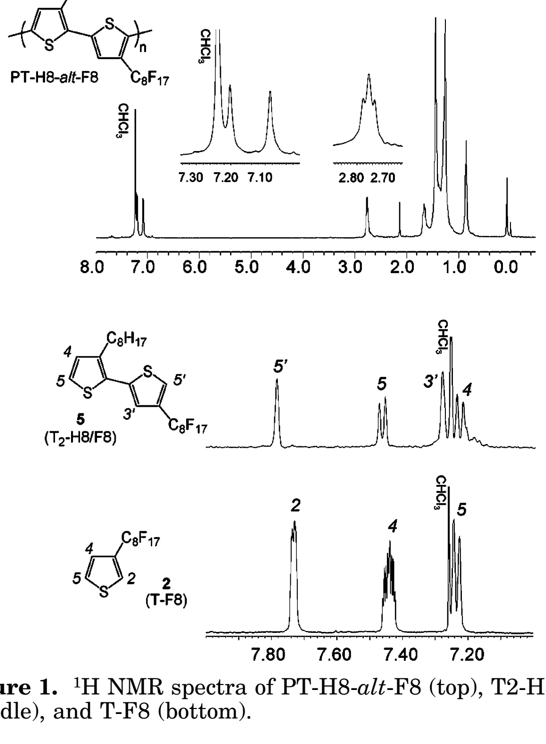
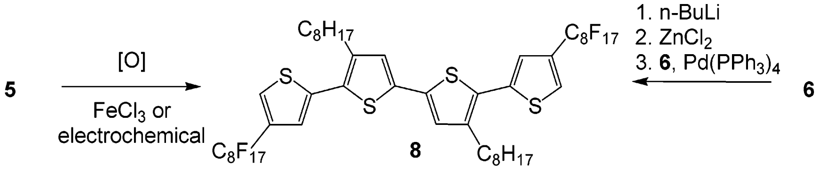


Figure 1. ^1H NMR spectra of PT-H8-*alt*-F8 (top), T2-H8/F8 (middle), and T-F8 (bottom).

Scheme 3. Dimerization of Bithiophene 5



appear in the spectrum from 3-(perfluorooctyl)thiophene end groups: at δ 7.53 ppm corresponding to the proton in the 4-position of a 3-(perfluoroalkyl)thiophene unit (which appears as a singlet at δ 7.47 ppm for PT-F8) and at δ 7.70 ppm (typical for the proton in the 5-position of a 3-perfluoroalkyl-substituted thiophene ring). The integrations of these peaks relative to those for the alkylthiophene units (i.e., in the chain) indicate that the material prepared in this manner is a relatively low molecular weight poly(3-octylthiophene) (DP ~ 44) bearing 3-(perfluorooctyl)thiophene rings at each end. The occurrence of 3-(perfluorooctyl)thiophene units at the termini arises from the electron-poor nature of these thiophene rings. While **1** is subject to oxidation by $FeCl_3$, once the fluoroalkylated ring is incorporated onto the end of the growing conjugated backbone, the radical cation generated by further oxidation localizes on electron-rich alkylthiophene rings rather than at the termini. Thus, the (perfluoroalkyl)thiophene chain end is unreactive to chain extension, and the polymerization is thereby halted.

We also attempted to oxidatively polymerize bithiophene **5** (Scheme 3). This bithiophene has a lower oxidation potential than either of the substituted monothiophenes by virtue of its more extended conjugation. Bulk electrolysis (+1.60 V vs SCE) resulted in the formation of a violet species which diffused from the electrode surface. No film was deposited, even after a long electrolysis time. Chemical oxidation of the bithiophene **5** with $FeCl_3$ also failed to afford polymer. The major product obtained by this procedure was the tetrathiophene **8**. (This tail-to-tail dimer was prepared separately by halogen−lithium exchange of **6** with butyllithium, transmetalation with $ZnCl_2$, and palladium(0)-catalyzed coupling to another equivalent of **6** (Scheme 3)). This product is formed upon oxidation of **5** as a consequence of the localization of the radical cation on the electron-rich ring of the bithiophene (i.e., the alkyl-substituted ring) and coupling of two bithiophene radical cations via the 5-positions. While the tetrathiophene **8** is subject to further oxidation under the oxidative conditions, the resulting radical cation is localized on the central thiophene rings. The localization of the unpaired electron density on the interior of the radical cation and the presence of perfluoroalkyl substituents ortho to unsubstituted α-thienyl positions on the terminal rings hinders further coupling reactions.

Electrochemistry. The redox properties of substituted thiophenes, bithiophenes, and polymers were characterized by cyclic voltammetry. In the case of both thiophenes and bithiophenes, fluoroalkyl substitution increases the oxidation potential by over 200 mV relative to the alkyl analogues, consistent with the electron-withdrawing nature of the perfluoroalkyl substituent (Table 1). Cyclic voltammetry of bithiophene **5** shows an irreversible oxidation at +1510 mV (vs SCE). However, multiple potential cycles between 0 and +1600 mV did not result in growth of a film on the electrode surface. Bulk electrolysis (+1600 mV vs SCE) also did not result in film deposition.

Table 1. Redox Behavior of Alkyl and Perfluoroalkylthiophenes, Bithiophenes, and Polythiophenes

	monomer[a]	polymer[b]		
	oxidation E (V)		oxidation E (V)	reduction E (V)
1, T-H8	+1.84	PT-H8[c]	+0.94	NA
2, T-F8	+2.05	PT-F8[d]	+1.19	−1.18
6, T_2-H8/F8	+1.51	PT-H8-*alt*-F8	+1.07	−2.30
T_2-F8/F8[e]	+1.75			

[a] 10^{-5} M, gold electrode, 100 mV/s, 0.1 M Bu_4NPF_6 in CH_2Cl_2. [b] Regioregular polymer films dip-coated on a carbon electrode, 100 mV/s, 0.1 M Bu_4NPF_6 in CH_2Cl_2. [c] Poly(3-octylthiophene). [d] Poly(3-perfluorooctyl)thiophene. [e] From ref 12.

Cyclic voltammetry of a dip-coated film of PT-H8-*alt*-F8 shows a reversible oxidation peak at +1070 mV. For comparison, poly(3-octylthiophene) undergoes oxidation at +940 mV, and the perfluoroalkyl homopolymer has a peak potential of +1190 mV. Thus, the oxidation potential of the alternating polymer falls between those of the two homopolymers. Increasing the density of fluoroalkyl substituents on the polythiophene backbone leads to a higher oxidation potential. In addition to the inductive electron-withdrawing nature of the perfluoroalkyl substituents, steric interactions between the α-fluorine atoms of the side chain and the sulfur atom of the adjacent thiophene ring cause twisting of the backbone. While fluorine and hydrogen have similar van der Waals radii, fluorine is approximately 15% larger and causes twisting of the backbone, as shown by absorbance and fluorescence data (see below). The decrease in conjugation arising from this twisting effect may also contribute to the higher oxidation potential of the fluoroalkyl analogues.

PT-H8-*alt*-F8 also undergoes reduction at −2300 mV vs SCE compared to −1180 mV for the perfluoroalkyl homopolymer (Table 1). The alkyl-substituted homopolymer cannot be reduced under normal conditions.[29] Thus, the electron-withdrawing nature of perfluoroalkyl chain stabilizes negative charge on the polythiophene backbone. A higher density of perfluoroalkyl substitution makes the reduced state more accessible, resulting in a lower reduction potential.

Electronic Spectra of Polymer Solutions. UV−vis and fluorescence spectroscopy were used to further characterize the electronic structure of PT-H8-*alt*-F8, with comparisons to spectra of the two homopolymers PT-H8 and PT-F8. A solution of PT-H8-*alt*-F8 in $CHCl_3$ gives an absorption maximum at 384 nm and yellow emission with a maximum intensity at 547 nm (Figure 2). These values for the alternating copolymer are between those of the two homopolymers (Table 2). As the density of fluoroalkyl substitution on the polythiophene backbone increases, there is a blue shift in the absorption maximum from 441 nm for the PT-H8 to 384 nm for the PT-H8-*alt*-F8 copolymer and 326 nm for the fully fluoroalkylated polymer PT-F8. There is a corresponding blue shift of the emission maximum: 570 nm for PT-H8, 547 nm for PT-H8-*alt*-F8, and 504 nm

Table 2. UV−vis Absorption and Emission Spectra

	solution[a]			film[b]				
	abs λ_{max} (nm)	fluor λ_{max} (nm)	Stokes shift (nm)	abs λ_{max} (nm)	fluor λ_{max} (nm)	Stokes shift (nm)	band gap[c] (eV)	abs $\Delta\lambda_{max}$[d] (nm)
PT-H8[e]	441	570	129	515			1.83	74
PT-H8-*alt*-F8	384	547	163	456	612	156	2.07	72
PT-F8[f]	326	504	178	338	505	167	2.52	12

[a] $CHCl_3$ solution. [b] Spin-coated solid film. [c] Calculated from onset of UV−vis spectra of solid films. [d] $\Delta\lambda_{max} = \lambda_{max}(\text{film}) - \lambda_{max}(\text{solution})$. [e] Poly(3-octylthiophene). [f] Poly(3-(perfluorooctyl)thiophene).

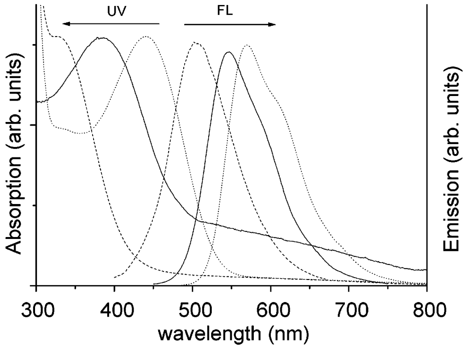


Figure 2. UV−vis and fluorescence spectra (in 10^{-5} M solution in chloroform, normalized) of poly(3-perfluorooctyl)-thiophene), PT-F8 (- - -); alternating copolymer PT-H8-*alt*-F8 (—); and poly(3-ocylthiophene), PT-H8 (· · ·).

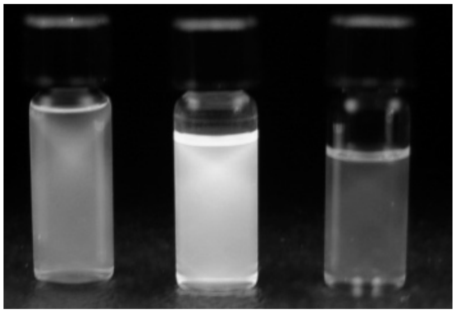


Figure 3. Fluorescence of solution of polymers upon irradiation at 365 nm (10^{-4} M solution in chloroform). Left-to-right: poly(3-(perfluorooctyl)thiophene), PT-F8; alternating copolymer, PT-H8-*alt*-F8; and poly(3-ocylthiophene), PT-H8.

for PT-F8. There is also a trend in the Stokes shift, which increases with greater perfluoroalkyl substitution: PT-H8 129 nm, PT-H8-*alt*-F8 163 nm, and PT-F8 178 nm. We ascribe the systematic changes in absorption, emission, and Stokes shift to the steric influence of perfluoroalkyl groups. Steric interactions between the perfluoroalkyl substituents and the adjacent repeat units lead to a twisting of the backbone and a decrease in the conjugation length. Such interactions have recently been observed in the crystal structure of perfluoroalkyl-substituted oligothiophenes and are in accord with results of ^{1}H NMR spectra of solutions of oligomer and with DFT calculations.[30] The decrease in conjugation in the ground states becomes more apparent with more perfluoroalkyl substituents. This explains the dramatic decrease in the wavelength of the absorption band with a higher density of perfluoroalkyl substituents. In the excited states, although the polythiophene backbone adopts a more planar quinoid form, substituents still have an influence on the conformation and electronic structure. The Stokes shift arises from the difference in the conformation of the polymer backbone between the ground state and the excited state. The increase of the Stokes shift with the increase in density of perfluoroalkyl substituents can be explained by the argument that the twisting effect has a larger influence on absorption than emission and that this twisting effect can be partly overcome in the excited state by formation of the quinoid form.

Solutions of the alternating copolymer (PT-H8-*alt*-F8) show much brighter fluorescence than the two homopolymers (PT-F8 and PT-H8) (Figure 3). The quantum yields of the polymers were calibrated against Coumarin 500. The quantum yield of the alternating copolymer PT-H8-*alt*-F8, $\phi = 0.31$, is 3 times that of the two homopolymers (PT-F8, $\phi = 0.10$; PT-H8, $\phi = 0.11$). This is in contrast to the other electronic properties of the polythiophenes (e.g., oxidation potential, absorption energy, emission energy, and Stokes shift) which all increase with the density of perfluoroalkyl substituents along the backbone. The enhancement of the quantum yield arises from the electronic structure of the copolymer PT-H8-*alt*-F8, which has an alternating sequence of electron-rich and electron-poor thiophene rings. This alternation imparts an intrinsic dipole to the diads in the backbone. The quantum yield for fluorescence is proportional to the square of the change in dipole moment between the ground and excited states. In the case of the two homopolymers the diads have only a small intrinsic dipole moment, and there is only a small change in dipole upon excitation. In the case of the alternating copolymer, the planarization upon photoexcitation (i.e., bringing more repeat units into conjugation) results in a larger change in dipole moment between the ground state and the excited state, resulting in the enhanced quantum yield relative to the homopolymers.

Electronic Spectra of Polymer Films. UV−vis and fluorescence spectroscopies were also used to investigate the photophysics of solid films of the polymers. Spin-coated films of PT-H8-*alt*-F8 absorb at $\lambda_{max} = 456$ nm. PF8T absorbs at $\lambda_{max} = 338$ nm, and PH8T absorbs at $\lambda_{max} = 515$ nm. Again, the absorption of the solid-state polythiophenes can be tuned by varying the density of fluoroalkyl substituents. The absorbance maximum of the solid-state alternating copolymer fits between that of the two homopolymers.

The difference between the wavelength of the absorption maximum of conjugated polymers in solutions and that of solid films is often ascribed to the assembly of conjugated backbones in an ordered solid-state structure. In particular, the enhanced planarity of the backbone of regioregular poly(3-alkylthiophene)s in the solid-state accounts for a large observed red shift relative to the solution spectra. A large shift (72−74 nm) is observed for the alkyl-substituted regioregular homopolymer (PT-H8) and alternating copolymer (PT-H8-*alt*-F8), but only a small shift (12 nm) is observed for the fluoroalkyl homopolymer (PT-F8) (Table 2). The small shift for the perfluoroalkyl-substituted homopolymer suggests that the steric influence of the fluoroalkyl

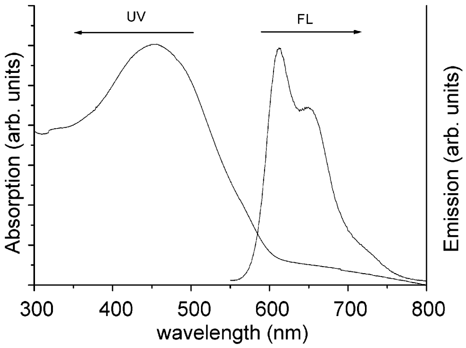


Figure 4. UV−vis and fluorescence spectra of spin-coated film of alternating copolymer, PT-H8-*alt*-F8.

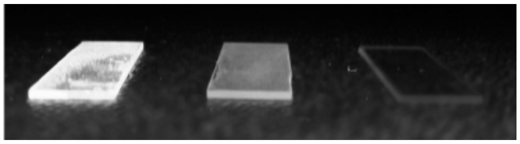


Figure 5. Fluorescence of polymer films upon irradiation at 365 nm. Left-to-right: poly(3-(perfluorooctyl)thiophene), PT-F8; alternating copolymer, PT-H8-*alt*-F8; and poly(3-ocylthiophene), PT-H8.

groups causes twisting of the polymer backbone even in the solid state and that the films are largely disordered, resulting in a low conjugation length The larger value of $\Delta\lambda_{max}$ for the alkyl-substituted polymer and alternating copolymer indicate formation of an ordered solid-state structure which leads to planarization of the backbone and a longer conjugation length.

Given the planarization of the copolymer in the solid state, it is perhaps surprising to note that films of PT-H8-*alt*-F8 fluoresce strongly ($\lambda_{max} = 612$ nm) (Figure 4) compared to PT-F8 which emits green fluorescence at $\lambda_{max} = 505$ nm and PT-H8 which does not fluoresce (Figure 5). In the case of the alkyl homopolymer, a lamellar crystalline structure in the solid state results in self-quenching of the excited state through nonradiative relaxation. The strong red fluorescence displayed by films of the alternating copolymer suggests that while this polymer crystallizes, this organization does not lead to self-quenching of the excited state. The fluorescence from films of PT-H8-*alt*-F8 is stable under ambient conditions; the bright fluorescence is retained after more than 6 months.

The band gap of polythiophene increases with more fluoroalkyl substitution, as determined from the edge of the visible absorption. For PT-H8 the badgap is 1.83 eV. With 50% replacement of the alkyl substituents with fluoroalkyl chains (PT-H8-*alt*-F8) the alternating copolymer has a band gap of 2.07 eV, and for the wholly fluoroalkyl substituted polymer (PT-F8) it increases further to 2.52 eV (Figure 6). Incorportation of the 3-perfluoroalkyl groups has the effect of lowering both the HOMO and LUMO energies of the polythiophene backbone relative to poly(3-alkylthiophene)s. The effect on the LUMO is smaller than on the HOMO, thereby increasing the band gap. A similar trend has been observed for perfluoroalkyl-substituted oligothiophenes.[31] However, there is a poor correlation between the band gap determined from the electronic spectra with the difference between the potentials for oxidation and reduction. While in principle these should be the same, the electrochemical potentials are sensitive to the electrolyte and solvent, possibly accounting for the discrepancy noted here.

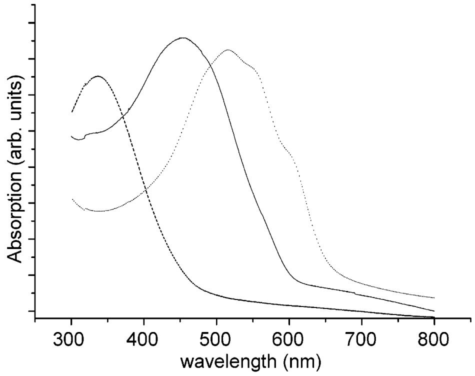


Figure 6. UV−vis spectra of the spin-coated film of poly(3-perfluorooctyl)thiophene), PT-F8 (- - -); alternating copolymer PT-H8-*alt*-F8 (—); and poly(3-ocylthiophene), PT-H8 (· · ·).

In conclusion, the photophysics and electrochemistry of polythiophenes bearing inductively electron-donating alkyl and electron-withdrawing perfluoroalkyl groups allow us to tune the electronic structure of the conjugated backbone. The alternating copolymer displays absorption and emission maxima between those of homopolymers composed of the individual structural units. While the van der Waals radius of fluorine is only slightly larger than that of hydrogen, the steric differences between an alkyl and perfluoroalkyl substituents have important consequences on the conformation of the polymer backbone. The combination of alternating electron-rich and electron-poor thiophene units along the backbone of PT-H8-*alt*-F8, together with a small twisting influence of the perfluoroalkyl group, provides a material which displays enhanced solution-phase fluorescence and strong solid-state fluorescence which is absent for the wholly alkyl analogue.

Experimental Section

General Methods. All reagents were obtained from commercial sources and used without further purification unless stated otherwise. Tetrahydrofuran (THF) and diethyl ether were dried over sodium benzophenone ketyl prior to distillation under nitrogen. Column chromatography was performed on silica gel (40 mesh, 60 Å, Baker). Thin-layer chromatography was performed on 3×5 cm plates of silica gel (0.2 mm thick, 60 F254) on an aluminum support (EM Separations). All ^{1}H NMR spectra were collected on a Varian Gemini 300 MHz instrument using CDCl$_3$ as the solvent unless otherwise specified. Chemical shifts are reported relative to internal tetramethylsilane. ^{13}C NMR spectra were obtained at 75.5 MHz. IR analysis was performed on a Nicolet 520 FTIR spectrometer. UV−vis analysis was performed with a Perkin-Elmer Lambda 19 spectrometer. Fluorescence spectra were collected with a Spex Fluorolog Fluometer 1681 0.22 m spectrometer. Electron ionization or chemical ionization mass spectra were obtained using a VG Analytical 70-SE instrument with a L-250J data system analyzer.

Polymer films were spin-coated onto glass slides or ITO glass slides using a Specialty Coating System P-6000 spin-coater. Electrochemical experiments were performed using a BAS 100B electrochemical analyzer in three-electrode cell equipped with a 2.0 mm^2 gold, platinum, or graphite disk working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE). 3-(Perfluorooctyl)thiophene, **2**, and 2-bromo-4-(perfluorooctyl)thiophene, **4**, were synthesized following the methods we reported previously.[12]

[1′,3′-(2′,2′-Dimethylpropylene)]-3-octyl-2-thienyl Boronate, 3. A mixture of magnesium (50.0 mmol, 1.22 g) in dry THF (45 mL) was heated to maintain a gentle reflux. 2-Bromo-3-octylthiophene (9.08 g, 33.0 mmol) was added, and the mixture was kept at reflux for 3 h. The resulting solution was cooled and transferred via a cannula to a solution of trimethyl boronate (130 mmol, 14.6 mL) in dry THF (45 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into 10% HCl (45 mL) and extracted with Et_2O (3 × 100 mL) The combined extracts were dried over Na_2SO_4 and molecular sieves (4 Å) in the presence of 2,2-dimethyl-1,3-propanediol (3.45 g, 33.0 mmol). The solvent was removed using a rotary evaporator to provide 9.65 g of a yellow liquid contaminated by white crystals. This crude product was dissolved in hexanes and filtered. The solvent was removed, and the crude product was heated under vacuum for 1 day at 140 °C to remove 3-octylthiophene to give **3** (8.33 g, 82%) as a viscous yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, $J = 4.7$, 1 H), 6.99 (d, $J = 4.7$, 1 H), 3.75 (s, 4 H), 2.86 (m, 2 H), 1.55 (m, 2 H), 1.27 (m, 10 H), 1.02 (s, 6 H), 0.88 (m, 3 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 153.3, 130.7, 130.2, 72.5, 32.3, 32.1, 30.6, 30.4, 30.0, 29.8, 29.6, 23.1, 22.3, 14.5; IR (NaCl): 3118, 2961, 2933, 1530, 1488, 1298, 1123, 751, 646 cm^{-1}. MS (EI): $M^+ = 276$.

4′-Perfluorooctyl-3-octyl-[2,2′]-bithiophene, 5. N_2 was bubbled through a solution of 2-bromo-4-(perfluorooctyl)-thiophene (**4**)[12] (4.64 mmol, 2.70 g) in DME (60 mL) for 10 min. $Pd(PPh_3)_4$ (0.139 mmol, 0.161 g) was added, and the mixture was stirred for 10 min at room temperature. [1′,3′-(2′,2′-Dimethylpropylene)]-3-octyl-2-thienylboronate, **3** (5.10 mmol, 1.86 g), and 13 mL of 1 M $NaHCO_3$ were added, and the mixture was heated to reflux overnight with vigorous stirring. The reaction mixture was poured into water (100 mL) and extracted with Et_2O (3 × 100 mL).The combined organic extracts were dried over Na_2SO_4, the solvent was removed on a rotary evaporator, and the residue was heated under vacuum for 1 day at 140 °C to remove 3-octylthiophene. The crude product was purified by column chromatography (silica gel/hexane) to give **5** (2.91 g, 90%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (s, 1 H), 7.23 (d, $J = 5.8$, 1 H), 7.18 (s, 1 H), 6.95 (d, $J = 5.8$, 1 H), 2.72 (t, $J = 8.1$, 2 H), 1.60 (m, 2 H), 1.27 (m, 10H), 0.86 (m, 3 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 141.3, 139.5, 130.3, 128.0, 125.2, 124.0, 32.0, 30.8, 29.7, 29.6, 29.5, 29.3, 23.7, 14.2. IR (NaCl): 3118 (C−H, sp^3), 2973, 2855 (C−H, sp^2), 1467, 1237, 1209 (C−F), 707 cm^{-1}. MS (EI): $M^+ = 696$.

2-Bromo-4′-perfluorooctyl-3-octyl-[2,2′]-bithiophene, 6. A mixture of 4′-perfluorooctyl-3-octyl-[2,2′]-bithiophene (1.10 g, 1.58 mmol) and NBS (0.338 g, 1.90 mmol) in DMF (5 mL) was stirred at room temperature overnight. The reaction mixture was poured into water (10 mL) and extracted with petroleum ether (3 × 20 mL). The combined extracts were dried over Na_2SO_4, and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography (silica gel/petroleum ether) to give **6** (0.88 g, 72%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 1 H), 7.12 (s, 1 H), 6.91 (s, 1 H), 2.64 (t, $J = 8.1$, 2 H), 1.60 (m, 2 H), 1.27 (m, 10H), 0.86 (m, 3 H). IR (NaCl): 3118, 2973, 2933, 2861, 1466, 1262, 1209, 1163, 908, 715, 657 cm^{-1}. HRMS (EI): 773.991 53 (observed), 773.991 83 (calculated); $\Delta = 0.4$ ppm.

Poly(4′-Perfluorooctyl-3-octyl-[2,2′]-bithiophene) (PT-H8-*alt*-F8). Into a dry Shlenk flask was placed a solution of dry diisopropylamine (0.86 mL, 6.1 mmol) in freshly distilled THF (35 mL). A solution of *n*-butyllithium (2.5 M in hexane, 2.55 mL, 6.13 mmol) was added at room temperature. The mixture was cooled to −40 °C and stirred for 40 min. The fresh LDA was then cooled to −78 °C, and 2-bromo-4′-perfluoroctyl-3-octyl-[2,2′]-bithiophene (4.32 g, 5.57 mmol) was added. The mixture was stirred for 40 min at −40 °C and then cooled to −60 °C, $MgBr_2.Et_2O$ (1.58 g, 6.13 mmol) was added, and the reaction was stirred at − 60 °C. After 20 min, the reaction was then warmed to − 40 °C and stirred for another 15 min. The reaction mixture was allowed to slowly warm to −5 °C. At −5 °C, 0.5 mol % $Ni(dppp)Cl_2$ (16.6 mg, 0.0310 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight. The solution was poured into MeOH (300 mL), and the resulting precipitate was filtered and washed with MeOH (100 mL), H_2O (100 mL), and MeOH (100 mL) again. The solid was dried under vacuum to give a deep red solid (1.20 g, 31%). Removal of oligomers and impurities was achieved by subjecting the solid to extractions in a Soxhlet extractor with MeOH and acetone, followed by hexane, chloroform, THF, and chlorobenzene. The chloroform fraction was characterized in detail.

3,3′-Di(perfluorooctyl)-3′′,3′′′-dioctyl-[2′,5]-[5′,5′′]-[2′′-5′′′]-tetrathiophene (8). *Organometallic Coupling. n*-BuLi (2.5 M in hexane, 0.13 mL, 0.32 mmol) was added to a solution of **6** (0.18 g, 0.23 mmol) in dry Et_2O (10 mL) under argon at −78 °C. The mixture was stirred at −78 °C for 1 h, $ZnCl_2$ (65 mg, 0.48 mmol) was added, and the mixture was warmed to room temperature and stirred for 1 h. A solution of $Pd(PPh_3)_4$ (19 mg, 16 μmol) and another portion of **6** (0.18 g, 0.23 mmol) in 10 mL dry Et_2O was added, and the mixture was heated to reflux overnight. The mixture was poured into H_2O (100 mL) and extracted with Et_2O (3 × 100 mL). The extract was washed with brine (100 mL) and dried over anhydrous $MgSO_4$. The crude product was purified by column chromatography (silica/hexane) to give **8** (0.27 g, 84%) as a red solid; mp 73−75 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (s, 1 H), 7.23 (s, 1 H), 7.08 (s, 1 H), 2.75 (t, $J = 8.1$, 2 H), 1.60 (m, 2 H), 1.27 (m, 10H), 0.86 (m, 3 H).^{13}C NMR (300 MHz, $CDCl_3$): δ 141.3, 139.5, 130.3, 128.0, 125.2, 124.0, 32.1, 30.7, 29.5, 29.3, 29.0, 28.6, 23.0, 14.4. IR (NaCl): 2926, 2856, 1249, 1214, 1151, 674. MS (FAB): $M^+ = 1390$.

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References and Notes

(1) Recent examples include: (a) Poly(methyl methacrylate)s: Johansson, G.; Percec, V.; Ungar, G.; Zhou, J. P. *Macromolecules* **1996**, *29*, 646. Hwang, H. S.; Heo, J. Y.; Jin, S. H.; Cho, D.; Chang, T.; Lim, K. T. *Polymer* **2003**, *44*, 5153. (b) Ionenes: Wang, J.; Ober, C. K. *Macromolecules* **1997**, *30*, 7560. (c) Norbornenes: Tran, H. V.; Hung, R. J.; Chiba, T.; Yamada, S.; Mrozek, T.; Hsieh, Y. T.; Chambers, C. R.; Osborn, B. P.; Trinque, B. C.; Pinnow, M. J.; MacDonald, S. A.; Willson, C. G.; Sanders, D. P.; Connor, E. F.; Grubbs, R. H.; Conley, W. *Macromolecules* **2002**, *35*, 6539. (d) Styrene−butadiene: Ren, Y.; Lodge, T. P.; Hillmyer, M. A. *Macromolecules* **2001**, *34*, 4780. (e) Styrene−isoprene block copolymers: Hayakawa, T.; Wang, J.; Xiang, M.; Li, X.; Ueda, M.; Ober, C. K.; Genzer, J.; Sivaniah, E.; Kramer, E. J.; Fisher, D. A. *Macromolecules* **2000**, *33*, 8012.

(2) Büchner, W.; Garreau, R.; Lemaire, M.; Roncali, J.; Garnier, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *277*, 355. Büchner, W.; Garreau, R.; Roncali, J.; Lemaire, M. *J. Fluorine Chem.* **1992**, *59*, 301. Robitaille, L.; Leclerc, M. *Macromolecules* **1994**, *27*, 1847. Leclerc, M.; Robitaille, L.; Bergeron, J. Y.; Callender, C. L. *Polym. Prepr.* **1994**, *35*, 305.

(3) Hong, X.; Tyson, J. C.; Middlecoff, J. S.; Collard, D. M. *Macromolecules* **1999**, *32*, 4232.

(4) Hong, X.; Collard, D. M. *Macromolecules* **2000**, *33*, 3502.

(5) Hong, X.; Tyson, J. C.; Collard, D. M. *Macromolecules* **2000**, *33*, 6916.

(6) Cornil, J.; Beljonne, D.; Calbert, J.; Brédas, J. L. *Adv. Mater.* **2001**, *13*, 1053.

(7) Hajlaoui, R.; Fichou, D.; Horowitz, G.; Nessakh, B.; Constant, M.; Garnier, F. *Adv. Mater.* **1997**, *9*, 557.

(8) Garnier, F.; Horowitz, G.; Fichou, D.; Yassar, A. *Synth. Met.* **1996**, *81*, 163.

(9) Facchetti, A.; Deng, Y.; Wang, A.; Koide, Y.; Sirringhaus, H.; Marks, T. J.; Friend, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4547.

(10) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33.

(11) Endo, T.; Takeoka, Y.; Rikukawa, M.; Sanui, K. *Synth. Met.* **2003**, *135*, 333.

(12) Li, L.; Counts, K. E.; Kurosawa, S.; Teja, A. S.; Collard, D. M. *Adv. Mater.* **2004**, *16*, 180.

(13) Czerwinski, W.; Wrzeszcz, G.; Kania, K. Rabek, J. F.; Linden, L. A. *J. Mater. Sci.* **2000**, *35*, 2305.

(14) Beaupre, S.; Leclerc, M. *Adv. Funct. Mater.* **2002**, *12*, 192.

(15) Charas, A.; Morgado, J.; Martinbo, J. M. G.; Alcacer, L.; Cacilli. F. *Synth. Met.* **2002**, *127*, 251.

(16) Yamamoto, T.; Zhou, Z.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389.
(17) Yamamoto, T.; Arai, M.; Kokubo, H.; Sasaki, S. *Macromolecules* **2003**, *36*, 7986.
(18) McCullough, R. D.; Jayaraman, M. *J. Chem. Soc., Chem. Commun.* **1995**, 135.
(19) Iraqi, A.; Clark, D.; Jones, R.; Krier, A. *Synth. Met.* **1999**, *102*, 1220.
(20) Bjornholm, T.; Hassenkam, T.; Greve, D. R.; McCullough, R. D.; Jayaraman, M.; Savoy, S. M.; Jones, C. E.; McDevitt, J. T. *Adv. Mater.* **1999**, *11*, 1218. Reitzel, N.; Greve, D. R.; Kjaer, K. P.; Howes, B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDevitt, J. T.; Bjornholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788.
(21) Stokes, K. K.; Heuze, K.; McCullough, R. D. *Macromolecules* **2003**, *36*, 7114.
(22) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329. Henze, O.; Feast, W. J. *J. Mater. Chem.* **2003**, *13*, 1274. Francois, B.; Olinga, T. *Synth. Met.* **1993**, *57*, 3489.
(23) Kowalik, J.; Tolbert, L. M.; Narayan, S.; Abhiraman, A. S. *Macromolecules* **2001**, *34*, 5471. Demadrille, R.; Divisia-Blohorn, B.; Zagorska, M.; Quillard, S.; Rannou, P.; Travers, J. P.; Pron, A. *New J. Chem.* **2003**, *27*, 1479. Era, M.; Yoneda, S.; Sano, T.; Noto, M. *Thin Solid Films* **2003**, *438−439*, 322.
(24) Demanze, F.; Yassar, A.; Garnier, F. *Macromolecules* **1996**, *29*, 4267. Demanze, F.; Yassar, A.; Garnier, F. *Synth. Met.* **1996**, *78*, 143. Demanze, F.; Yassar, A.; Garnier, F. *Adv. Mater.* **1995**, *7*, 907.
(25) Greve, D. R.; Apperloo, J. J.; Janssen, R. A. J. *Eur. J. Org. Chem.* **2001**, 3437.
(26) Bidan, G.; De Nicola, A.; Enee, V.; Guillerez, S. *Chem. Mater.* **1998**, *10*, 1052.
(27) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.
(28) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
(29) Crooks, R. M.; Chyan, O M. R.; Wrighton, M. S. *Chem. Mater.* **1989**, *1*, 2.
(30) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480.
(31) Facchetti, A.; Marks, T. J. *Polym. Prepr. (Div. Polym. Chem., Am. Chem. Soc.)* **2002**, *43* (1), 734.

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