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BODIPY-Containing Polymers with Ultralow Band Gaps and Ambipolar Charge Mobilities

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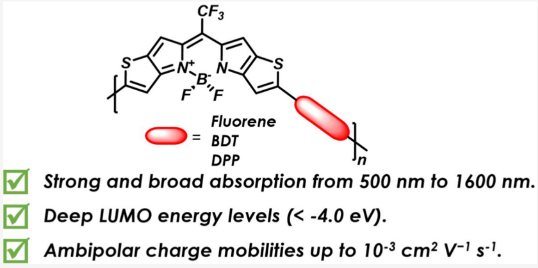
ABSTRACT: A series of BODIPY-containing donor−acceptor conjugated polymers was designed and synthesized through Pd-catalyzed cross-coupling reactions. The obtained polymers were characterized with NMR, UV−vis, and fluorescence spectroscopies, as well as cyclic voltammetry and thermal gravimetric analysis. These polymers were found to possess a strong and broad NIR absorption approaching 1600 nm, deep LUMO energy levels (<−4.0 eV), and good thermal stability. In-plane charge transport properties were studied in an organic thin-film transistor (OTFT) structure with the polymers exhibiting ambipolar charge mobilities up to 10^{-3} cm^2 V^{-1} s^{-1}, which is one of the highest values for BODIPY-containing polymers. Due to the outstanding optoelectronic properties and good stability, our work demonstrates that BODIPY-containing polymers could be promising candidates for applications in NIR devices and bioimaging technologies.



☑ *Strong and broad absorption from 500 nm to 1600 nm.*

☑ *Deep LUMO energy levels (< -4.0 eV).*

☑ *Ambipolar charge mobilities up to 10^{-3} cm^2 V^{-1} s^{-1}.*

INTRODUCTION

Boron−dipyrromethene (BODIPY)-based compounds have attracted enormous interest due to their large absorption coefficients, high photoluminescence quantum yields, and good photostability.[1−10] Therefore, this class of materials, especially BODIPY-based small molecules, has been intensively investigated. Due to the outstanding optical and electronic properties, a wide range of promising applications have been demonstrated, such as in organic electronics/photovoltaics,[11−16] fluorescent probes,[17−22] and photodynamic therapy.[23−28] At the same time, there is a growing effort to develop BODIPY-containing conjugated polymers that absorb and emit within the deep-red region and also possess desirable electronic properties.[29−34] Compared to small molecules, conjugated polymers exhibit several advantages, including excellent processability,[35−37] high charge carrier mobility,[38−40] and film flexibility while retaining most of the merits of the corresponding small molecules, such as a large molar absorption coefficient and good thermal stability. Thus, polymers containing BODIPY motifs have the potential to become promising candidates for applications in electronics and biorelated fields.

To be responsive to NIR light, a series of BODIPY-based polymers exhibiting deep-red or NIR absorption and emission has been developed.[30,41−44] For example, Chujo et al. synthesized a class of aromatic ring-fused BODIPY-based conjugated polymers which were shown to exhibit NIR emission approaching 800 nm.[45] Burgess et al. investigated several BODIPY−fluorene copolymers with dispersed absorption and emission maxima at ca. 750 nm.[46] Thus far, most of the reported BODIPY-containing polymers absorb and emit at relatively short wavelengths. Furthermore, this class of materials usually displays low charge carrier mobilities,[47,48] significantly limiting their further applications.

We report here a series of BODIPY-containing conjugated copolymers that exhibit strong absorption and emission in the NIR region approaching 1600 nm as well as sizable ambipolar charge mobilities up to 10^{-3} cm^2 V^{-1} s^{-1}. We take advantage of the donor−acceptor interactions between various electron-rich units and the electron-deficient BODIPY unit to achieve ultralow band gaps. The resulting polymers are fully conjugated through the polymer chains, differing from most BODIPY polymers with cross-conjugation.[29,30,47,49,50] The highly fused BODIPY moieties endow the polymer backbones with good planarity, leading to the improved charge mobilities and rendering these polymers as promising candidates for device applications.

RESULTS AND DISCUSSION

Synthesis and Characterization of the BODIPY-Containing Polymers. Thienopyrrole-fused dibromo BODIPY compound **1** was selected as the electron-deficient unit, which exhibits absorption and emission within the NIR region.

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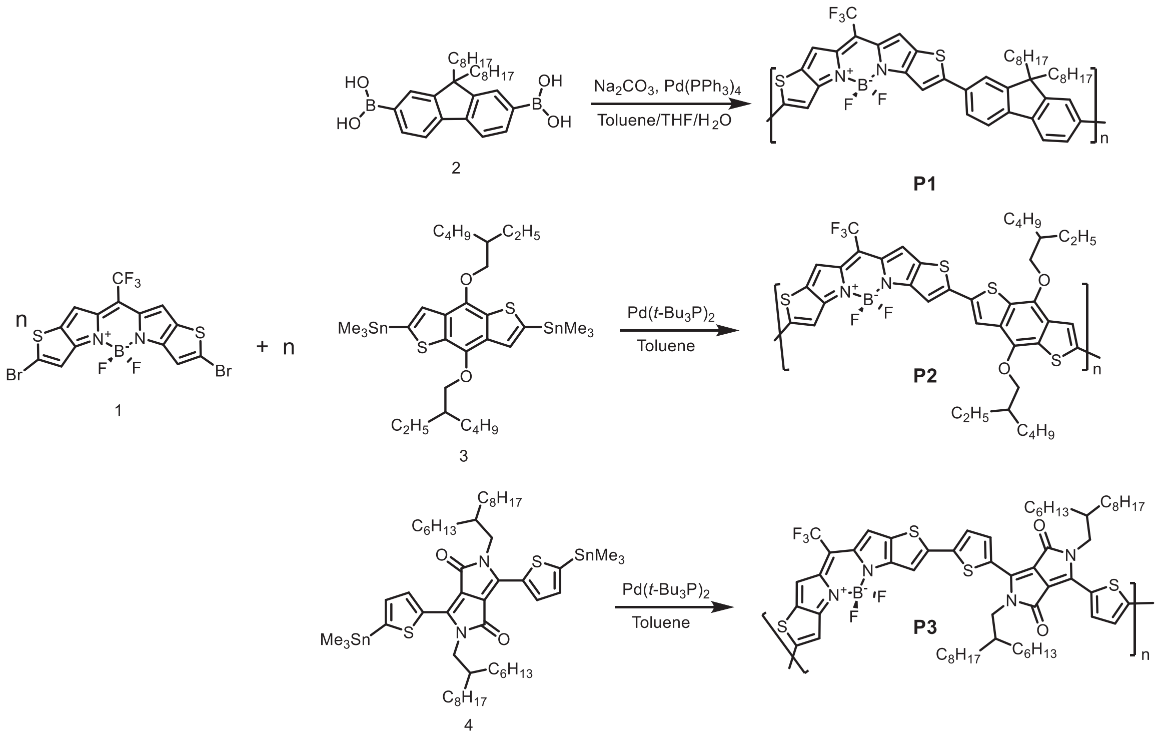
Scheme 1. Synthetic Route of BODIPY-Containing Polymers



The fused structure is expected to induce improved charge carrier mobility of the final conjugated polymers. Compound **1** was synthesized according to reported procedure.[51] Compounds **2**, **3**, and **4** are widely studied conjugated blocks and exhibit excellent optoelectronic properties in the system of conjugated polymers.[52−56] The Pd-catalyzed cross-coupling reactions between compound **1** and compounds **2**, **3**, or **4** lead to formation of the conjugated BODIPY-containing donor−acceptor copolymers P1, P2, and P3, as illustrated in Scheme 1. Detailed synthetic procedures are provided in the Experimental Section. It was observed that the solution mixture containing BODIPY molecules turned purple at elevated temperatures when DMF was used as a cosolvent for the Stille coupling reaction, indicating decomposition of the BODIPY monomers. After optimization of the reaction conditions, it was found that the reaction proceeded well in toluene at 50 °C. The chemical structures of the obtained polymers were characterized using nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. The obtained polymers show good solubility in common organic solvents, such as chloroform and chlorobenzene. Thermogravimetric analysis (TGA) revealed that the new BODIPY-containing polymers exhibit good thermal stability with no significant mass loss detected up to 265 °C for P1, 274.5 °C for P2, and 274.7 °C for P3. DSC studies showed T_g values of 104.7, 97.0, and 97.3 °C for polymers P1, P2, and P3, respectively. Their molecular weights (M_w) and M_w distributions were determined with gel permeation chromatography (GPC) using polystyrene as the standard. The results are summarized in Table 1.

Table 1. Molecular Weight of the BODIPY-Containing Polymers

polymer	M_n[a] (KDa)	M_w[a] (KDa)	PDI[a]	T_d[b] (°C)
P1	6.5	7.8	1.2	265.0
P2	6.9	11.1	1.6	274.5
P3	10.3	19.6	1.9	274.7

[a] Molar mass (M_n, M_w) and polydispersity (PDI) were determined by GPC in chloroform against polystyrene standards with UV detection set at absorption maxima. [b] TGA data shows the temperature for 5% mass loss onset.

Optical and Electrochemical Properties. The optical properties of the polymers were studied with UV−vis−NIR spectroscopy and are illustrated in Figure 1. Compared to the dibromo BODIPY compound **1**, the absorption peaks of the polymers are significantly red shifted from 635 nm for compound **1** gradually to 1005 nm for P3, caused by the intermolecular donor−acceptor interactions and extended conjugated system. Moreover, the absorption peaks of the polymers are broadened with the full width at half-maximum (fwhm) changing from 23.4 to 186.2 nm for P1, to 384.7 nm for P2, and eventually to 746.0 nm for P3. Furthermore, sharp differences in the shapes of the absorption profiles between the polymers and the monomers are clearly observed. For example, the 0−0 transition in P1 is significantly depressed compared to the 0−1 transition, which seems to indicate the P1 formed H aggregations (Figure 1a). The absorption spectra showed no change with respect to concentration and overlapped after normalization. The photoluminescent spectrum of P1 is in the NIR region with the main peak (0−0 transition) at 897 nm and a shoulder peak (0−1transition) at 1043 nm in diluted solutions. With increasing concentration, these two peaks are slightly red shifted and the ratio of 0−1/0−0 intensity increases. Polymers P2 and P3 are nonemissive. GIWAX studies indicated that the polymers are largely amorphous in the solid state. (Figure S7)

The broadened absorption peak also reflects the effect of polymer dispersity (PDI) values, orbital delocalization, and conformational diversity along the conjugation pathway. It is important to point out that the absorption peak of P3 ranging from 500 nm all the way to 1600 nm is impressively wide,

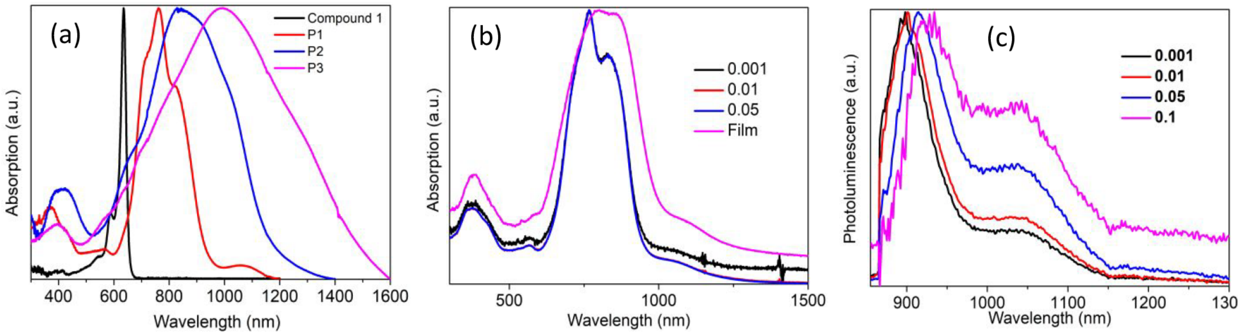


Figure 1. (a) Absorption spectra of compound 1 and P1−P3. (b) Concentration dependence of absorption spectra of P1 (mg mL^{-1}). (c) Photoluminescence spectra of P1 as a function of concentration (mg mL^{-1}).

which has the potential to harvest most of the photons from solar emission.

Cyclic voltammetry (CV) was performed on the BODIPY-containing polymers to estimate their HOMO and LUMO energy levels as displayed in Figure S8, and the results are summarized in Table 2. All of the polymers exhibit deep HOMO energy levels below −5.2 eV, leading to good oxidation stability under ambient conditions. The electron-deficient BODIPY units effectively lowered the LUMO energy levels (<−4.0 eV), which in turn significantly benefited electron injection and transport as demonstrated in the performance measurements of the field-effect transistor (FET) devices. Two reduction peaks were observed from the CV curves: the peaks at ca. −0.75 eV are largely reversible, and those at ca. −1.25 eV are mostly quasi-reversible, indicating formation of the respective radical anion and dianion species as well as their relatively good stability.

Table 2. Optical and Electrochemical Properties of Polymers P1−P3

polymer	λ_{max}^{Sol} (nm)	λ_{max}^{film} (nm)	fwhm (nm)	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
P1	760	774	186.2	1.24	−5.43	−4.03	1.40
P2	836	868	384.7	1.01	−5.25	−4.10	1.15
P3	1005	1063	746.0	0.80	−5.24	−4.18	1.06

DFT Calculation. To better understand the properties of the newly synthesized polymers, DFT calculations (B3LYP, 6-31G**) were performed on oligomers composed of 2.5 repeating units of the corresponding polymers, and the results are summarized in Figure 2. From the optimized molecular structures and orbital distributions, it was found that both the HOMO and the LUMO orbitals overlapped well and were distributed evenly across the calculated backbones, indicating extensive delocalization. From P1 to P3, band gaps are gradually decreased due to the stabilized LUMO and increased HOMO energy levels, consistent with the experimental results from UV−vis and CV measurements. The dihedral angles between the two building blocks for P1, P2, and P3 are 20.2°, 16.9°, and 4.3°, respectively. The more planar polymeric backbones of P2 and P3 are beneficial to the charge mobilities, which was confirmed by FET measurements.

FET Performance. The deep LUMO energy levels of these BODIPY-containing polymers should enable desirable electron injection and transport, making them good candidates for organic thin-film field-effect transistors (OFET). The combination of the solution-process property and NIR luminescence makes these polymers worth being explored for advanced electronic devices. To test the FET performance, n-doped Si was used as the gate electrode and SiO_2 with a thickness of 300 nm as the dielectric layer. In order to reduce the charge traps on SiO_2, a *n*-octadecyltrichlorosilane (OTS) single layer was immobilized on the surface of SiO_2. The polymers were dissolved in chloroform at a concentration of 8 mg/mL and spin coated on the OTS-modified substrates. The films were then transferred onto a hot plate at 120 °C and thermal annealed for 30 min under a nitrogen atmosphere. Gold electrodes were subsequently deposited on the top of the prepared films through a mask as the drain and source electrodes. The OFET property measurements were conducted by Keithly semiconductor devices in a N_2-filled glovebox.

FET performances of the polymers are summarized in Table 3 and shown in Figure 3. As expected, the low-lying LUMO

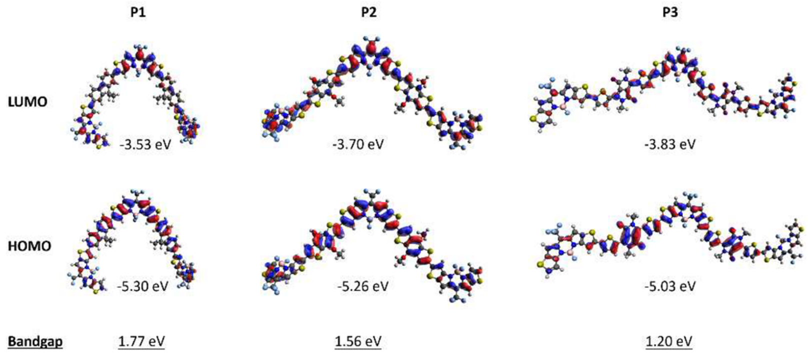


Figure 2. DFT calculations for oligomers containing 2.5 repeating units of the corresponding BODIPY-containing polymers.

Table 3. Electron and Hole Mobilities of BODIPY-Containing Polymers

polymer	μ_e (cm^2 V^{-1} s^{-1})	μ_h (cm^2 V^{-1} s^{-1})
P1	4.0×10^{-5}	[a]
P2	7.8×10^{-4}	1.0×10^{-3}
P3	5.4×10^{-4}	7.2×10^{-4}

[a] Hole transport property was not detected.

energy level of −4.03 eV of P1 benefits electron injection and transport, and thus, an electron mobility of 4×10^{-5} cm^2 V^{-1} s^{-1} was observed. Due to the deep HOMO energy level of −5.43 eV, hole transport of P1 became much less efficient and was unable to be observed in OFET devices. Substitution of the fluorene moiety with the BDT unit not only enhanced its planarity as indicated by DFT calculations but also tuned the energy levels with the LUMO being downshifted and the HOMO being upshifted, leading to improved charge transport. The deeper LUMO energy level of P2 could stabilize the injected electrons within the polymer backbone, and thus, an electron mobility of 7.8×10^{-4} cm^2 V^{-1} s^{-1} was obtained. A hole mobility of 1×10^{-3} cm^2 V^{-1} s^{-1} was observed from the same devices. P3 also exhibited an ambipolar charge transport property with an electron mobility of 5.4×10^{-4} cm^2 V^{-1} s^{-1} and a hole mobility of 7.2×10^{-4} cm^2 V^{-1} s^{-1}, which is slightly lower than that of P2. Although the dihedral angles between the two building blocks of P3 are smaller than those of P2, the twisted molecular planes between diketopyrrolopyrrole (DPP) and the two flanking thiophenes of P3 likely impede the charge carrier transport. The present results are encouraging for further research in improving the conductive properties through molecular engineering.

■ CONCLUSION

We synthesized a series of fully conjugated BODIPY-containing donor−acceptor copolymers through Pd-catalyzed cross-coupling reactions. The obtained polymers display broad UV−vis−NIR absorption from 500 to 1600 nm and sharp photoluminescence. The low-lying LUMO energy levels afford the polymers fast electron injection transport in FET devices. The fused BODIPY units endow the polymers with high molecular planarity, as suggested by DFT calculations, leading to sizable ambipolar charge mobilities of up to 10^{-3} cm^2 V^{-1} s^{-1}, which is one of the highest reported values for BODIPY-containing conjugated polymers.

■ EXPERIMENTAL SECTION

Materials and General Methods. All reagents and solvents were used as received from Sigma-Aldrich unless otherwise noted. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker DRX-500 spectrometer. The molecular weights of the polymers were determined using GPC with Waters Associates liquid chromatography equipped with a Waters 510 HPLC pump, a Waters 410 differential refractometer, and a Waters 460 tunable absorbance detector. $CHCl_3$ was used as the eluent and polystyrene as the standard. TGA measurement of the polymers was performed using a TA Q600 instrument over the temperature range from 50 to 400 °C under nitrogen with a heating rate of 10 °C/min. Solution absorption spectra were measured with a Shimadzu UV−vis−NIR spectrophotometer. Solution fluorescence spectra were measured with a Photon Technology International (PTI) device. Cyclic voltammetry was performed at 25 °C using a platinum wire working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode calibrated using the ferrocene redox couple (4.8 eV below vacuum). The DFT calculations were performed with the B3LYP/6-31G** model using Gaussian 09 in vacuum. To simplify the calculations, all alkyl chains were replaced with a single methyl group.

Synthetic Details. *P1.* To a solution of compound **1** (100 mg, 0.19 mmol) in toluene/THF/H_2O (30 mL, 1:1:1) were added compound **2** (90.26 mg, 0.19 mmol) and Na_2CO_3 (60 mg 0.57

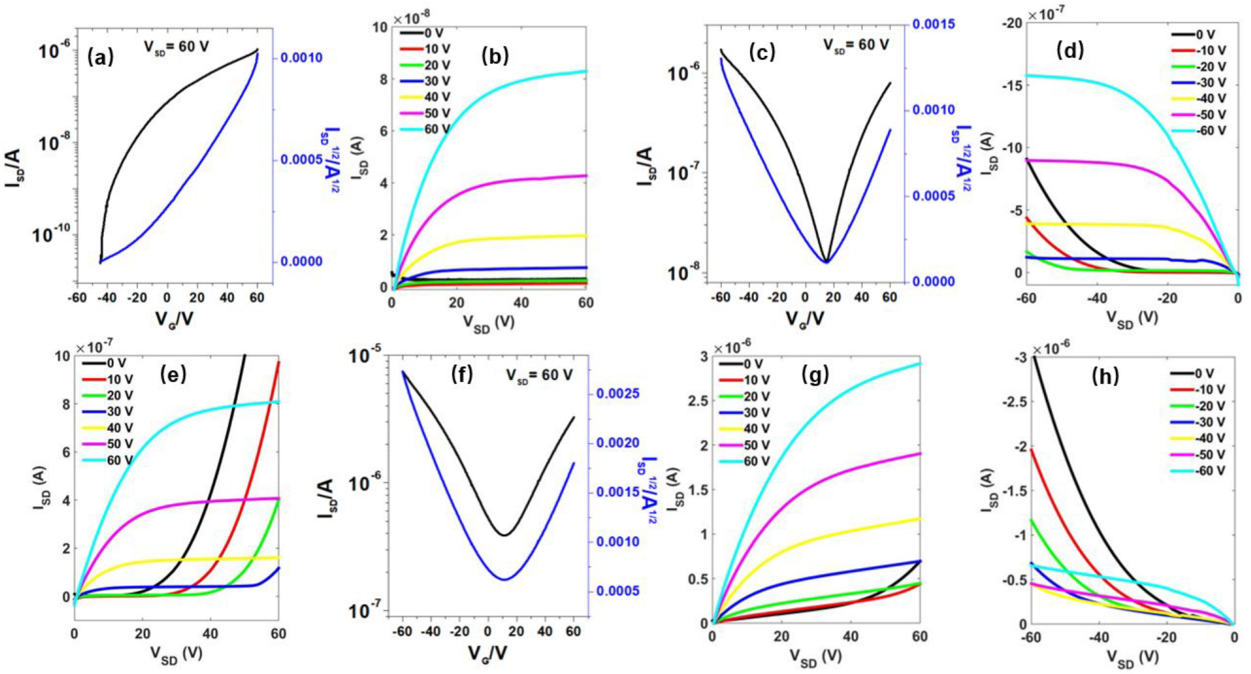


Figure 3. Characteristic transfer and output curves of P1 (a, b), P2 (c−e), and P3 (f−h) in bottom gate top contact (BGTC) FET. Channel length, L = 50 μm. Channel width, W = 18 mm.

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mmol). The reaction solution was purged by bubbling nitrogen gas through for 10 min. A catalytic amount of [Pd(PPh$_3$)$_4$] (17.4 mg, 5 mol %) was added, and the reaction was heated to 80 °C for 2 h. The mixture was poured into 100 mL of methanol to precipitate the polymer, which was purified by Soxhlet extraction with methanol, acetone, hexanes, and chloroform to give the title compound as a black solid (45 mg, 31.3% yield). ^{1}H NMR (CDCl$_3$ ppm): δ 7.58−7.32 (m, 10H), 2.13 (t, 4H), 1.56 (m, 4H), 1.21 (m, 20H), 0.81 (t, 6H). ^{19}F NMR (CDCl$_3$, ppm): δ −53.87, −148.17. Anal. Calcd for [$C_{43}H_{44}BF_5N_2S_2$]$_n$: C, 68.06; H, 5.86; N, 3.06; S, 8.45; F, 12.52. Found: C, 68.79; H, 6.83; N, 3.06.

P2. Compounds **1** (53 mg, 0.1 mmol) and **3** (77.23 mg, 0.1 mmol) were charged into a one-neck flask. Bis(tri-*tert*-butylphosphine) palladium (5.1 mg, 0.01 mmol) and toluene (4 mL) were added into the flask in a nitrogen-filled glovebox. The mixture was stirred at 50 °C for 2 days. The reaction mixture was poured into methanol to precipitate the polymer, which was purified by Soxhlet extraction with methanol, acetone, hexanes, and chloroform to give the title compound as a black solid (40 mg, 49% yield). ^{1}H NMR (CDCl$_3$ ppm): δ 7.05 (m, 6H), 4.15 (d, 4H), 1.58−1.10 (m, 30H). ^{19}F NMR (CDCl$_3$, ppm): δ −53.89, −140.82, −154.26. Anal. Calcd For [$C_{40}H_{40}BF_5N_2O_2S_4$]$_n$: C, 58.96; H, 4.96; N, 3.44; S, 15.74; F, 11.66. Found: C, 61.13; H, 6.00; N, 2.83.

P3. Compounds **1** (106 mg, 0.2 mmol) and **4** (215 mg, 0.2 mmol) were charged into a one-neck flask. Bis(tri-*tert*-butylphosphine) palladium (10.2 mg, 0.02 mmol) and toluene (8 mL) were added into the flask in a nitrogen-filled glovebox. The mixture was stirred at 50 °C for 2 days. The reaction mixture was poured into methanol to precipitate the polymer, which was purified by Soxhlet extraction with methanol, acetone, hexanes, and chloroform to give the title compound as a black solid (59 mg, 26.4% yield). ^{1}H NMR (CDCl$_3$ ppm): δ 9.14 (d, 4H), 7.21 (s, 4H), 4.09 (d, 4H), 2.00 (m, 2H), 1.58 (m, 8H), 1.25 (m, 40H), 0.84 (t, 12H). ^{19}F NMR (CDCl$_3$, ppm): δ −53.91, −140.54, −153.98. Anal. Calcd for [$C_{60}H_{74}BF_5N_4O_2S_4$]$_n$: C, 64.49; H, 6.69; N, 5.02; S, 11.48; F, 8.50. Found: C, 63.42; H, 6.98; N, 4.80.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02653.

^{1}H NMR spectra of P1−P3; ^{19}F NMR spectra of P1−P3; GIWAXS patterns of the polymer films; cyclic voltammograms of P1−P3 (PDF)

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Notes

The authors declare no competing financial interest.

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