Supporting Information

Thiophene-Fused 1,10-Phenanthroline and Its Conjugated Polymers

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Materials and Methods

General. Unless otherwise noted, all chemicals were purchased from Aldrich, Acros or Adamas and used without further purification. Dichloromethane (CH_2Cl_2) was distilled over CaH_2. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. Other solvents were dried with standard procedures. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254. Column chromatography was carried out on silica gel (200-300 mesh).

The catalyst precursor Pd(PPh_3)$_4$ was prepared according to the literature (*S1*), and stored in a Schlenk tube under nitrogen. 9,9-Dioctyl-2,7-diboronic ester-fluorene, 9,9-bis(6-bromohexyl)-2,7-diboronic ester-fluorene were prepared according to the literature procedures (*S2, S3*). Britton-Robinson buffers with different pH values were prepared according to the literature procedure (*S4*).

Measurements. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a 400 MHz Bruker AV400 spectrometer in $CDCl_3$ or *d*-DMSO. Matrix assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF) was performed on a Perseptive DE PRO Voyager MALDI-TOF mass spectrometer using α-cyano-4-hydroxycinnamic acid as the matrix. The gel permeation chromatography (GPC) measurements were performed on PL-GPC 50 system against polystyrene standards with THF as an eluent. UV-vis absorption spectra were obtained on Shimadzu UV-vis model UV-1601 PC and PerkinElmer Lamda 750 spectrophotometers. Fluorescence spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. TGA (PerkinElmer Pyris 1 TGA) and DSC (PerkinElmer DSC-8000) measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C/min to record the differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively. Cyclic voltammetric experiments were carried out using a CHI 660E electrochemical workstation (CH Instruments, ChenHua, Shanghai, China). All voltammograms were acquired at room temperature. A standard three electrode electrochemical cell arrangement was employed using a glassy carbon (GC) as working electrode, a Pt wire as counter electrode, and Ag/AgCl as reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at the scan rate of 100 mV/s. The potentials are reported *vs* the Fc^+/Fc redox couple as a standard.

pH Sensing Experiment: 2 mL of Britton-Robinson buffer (pH = 4-8) was taken into the cuvette, then 10 μL of **P3** solution (2×10^{-3} mol/L in methanol) was added to the buffer solution by a microinjector. As a very small amount of **P3** solution was added, the final volume of the solution was nearly unchanged (2 mL). The mixed solutions were excited at 408 nm and the corresponding emission spectra were recorded.

Metal-ion Sensing Experiment: 2 mL of chloroform (for **P1**) or acetonitrile (for **P3**) was taken into the cuvette, then 10 μL of polymer solution (2×10^{-3} mol/L, **P1** in chloroform or **P3** methanol) and 40 μL of different metal chloride solutions (0.05 mol/L in methanol) were added to the polymer solution by a microinjector. As a very small amount of polymer and metal ion solutions were added, the final volume of the solution was nearly unchanged (2 mL). The mixed solution was excited at 406 nm (for **P1**) or 408 nm (for **P3**), and the corresponding emission spectra were recorded.

Experimental Details.

3,6-Dibromobenzene-1,2-diamine (2). 2 was synthesized according the literature procedure (*S5*): to a stirred solution of 4,7-dibromo-2,1,3-benzothiadiazole (5.0 g, 17.0 mmol) in ethyl alcohol (300 mL) at 0 °C under N_2 was added portion-wise sodium borohydride (6.4 g, 170.1 mmol). After being stirred at 0 °C for 10 min, the reaction mixture was stirred at room temperature for 3 h. After being cooled to 0 ^{o}C, the reaction mixture was treated with distilled water (100 mL). After removing the solvent under reduced pressure, the residue was diluted with ether (200 mL), washed with brine (2 × 200 mL), dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel column eluting with petroleum ether/CH_2Cl_2 (v:v, 3:2) to afford **2** as a colorless solid (4.0 g, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.85 (2H, s, ArH), 3.89 (4H, s, NH_2).

N,N'-(3,6-Dibromo-1,2-phenylene)bis(2,2-dimethylpropanamide) (3). To a dry THF solution of **2** (5.0 g, 18.9 mmol**)** and triethylamine (3 mL) was added dropwise a dry THF solution (100 mL) of pivaloyl chloride (4.7 g, 38.8 mmol) at 0 ^{o}C. After stirring at room temperature for 24 h, the solution was poured into water (100 mL) and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel column eluting with petroleum ether/CH_2Cl_2 (v:v, 1:2) to afford **3** as a colorless solid (7.1 g, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (2H, s, NH), 7.41 (2H, s, ArH), 1.33 (18H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.13, 133.21, 131.54, 121.09, 39.67, 27.60. MALDI-TOF, m/z: cacld, 434.0; found, 457.0 ($[M + Na]^+$).

N,N'-(3,6-Di(thiophen-2-yl)-1,2-phenylene)bis(2,2-dimethylpropanamide) (4). A mixture of **3** (1.0 g, 2.3 mmol), thiophene-2-bronic ester (1.0 g, 4.7 mmol), $NaHCO_3$ (9.8 g, 117 mmol), THF (50 mL) and H_2O (20 mL) was degassed before and after $Pd(PPh_3)_4$ (0.1 g, 0.09 mmol) was added. The mixture was heated to reflux and stirred under nitrogen for 24 h. The reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel column eluting with petroleum ether/CH_2Cl_2 (v:v, 2:3) to afford **4** as an ivory solid (0.7 g, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (2H, s, NH), 7.41 (2H, s, ArH), 7.38 (2H, dd, ArH), 7.15 (2H, dd, ArH), 7.09 (2H, m, ArH), 1.15 (18H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.12, 139.50, 132.04, 131.13, 128.83, 127.24, 126.98, 126.33, 39.41, 27.50. MALDI-TOF, m/z: cacld, 440.1; found, 463.1 ($[M + Na]^+$).

4,7-Di-*tert*-butyldithieno[3,2-c:2',3'-*i*][1,10]phenanthroline (5). A solution of **4** (0.5 g, 1.1 mmol), P_2O_5 (3.2 g, 22.7 mmol) and $POCl_3$ (15 mL) was stirred at reflux for 30 h under N_2. The mixture was concentrated under vacuum, the residue was diluted with dichloromethane (50 mL), and water (50 mL) was added slowly. The aqueous layer was adjusted to pH = 10 with KOH solution (5 M) and extracted with dichloromethane (2 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to dryness. The product was purified by chromatography on alkaline Al_2O_3 column eluting with CH_2Cl_2 and the residue was recrystallized in CH_2Cl_2/petroleum ether to afford **5** as a slightly brown solid (0.18 g, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (s, 2H, ArH), 7.99 (2H, d, ArH), 7.62 (2H, d, ArH), 1.79 (18H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.38, 147.23, 139.87, 131.59, 125.60, 125.30, 123.04, 122.12, 40.58, 30.10. MALDI-TOF, m/z: cacld, 404.1; found, 405.1 ($[M +H]^+$).

2,9-Dibromo-4,7-di-*tert*-butyldithieno[3,2-c:2',3'-*i*][1,10]phenanthroline (6). To a solution of diisopropylamine (1.4 g, 14.2 mmol) in THF (50 mL) cooled to -50 ^{o}C was added *n*-butyllithium (10.9 mmol, 2.5 M in hexane) and the resulting solution was stirred at -50 ^{o}C for 0.5 h. The mixture was added into the THF solution of **5** (1 g, 2.5 mmol) at -50 ^{o}C and stirred for 45 min, then added the THF solution of CBr_4 (4.7 g, 14.2 mmol) at -50 ^{o}C and stirred for 24 h. The reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to dryness. The product was purified by chromatography on alkaline Al_2O_3 column eluting with CH_2Cl_2 and the residue was recrystallized in CH_2Cl_2/ petroleum ether to afford a slight brown solid (0.84 g, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (2H, s, ArH), 7.95 (2H, s, ArH), 1.75 (18H, s, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.38, 148.26, 139.74, 131.78, 128.27, 121.99, 121.93, 114.57, 40.54, 30.02. MALDI-TOF, m/z: cacld, 561.9; found, 562.9 ($[M +H]^{+}$).

Polymer **P1**. A mixture of **6** (50.0 mg, 88.9 μmol), 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (58.7 mg, 94.2 μmol), $NaHCO_3$ (284.5 mg, 3.4 mmol), THF (5 mL), toluene (1 mL) and H_2O (1 mL) was carefully degassed before and after $Pd(PPh_3)_4$ (2 mg, 1.7 μmol) was added. The mixture was heated to reflux and stirred under nitrogen for 96 h. The reaction mixture was extracted with $CHCl_3$ (3 × 30mL), and combined organic layers were dried over anhydrous $MgSO_4$. After the removal of most of solvent, the residue was precipitated into methanol. The resulted precipitate was collected by filtration and dried under vacuum to give **P1** as a green-yellow solid (60 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (4H, broad), 7.86-7.75 (6H, broad), 2.22-1.88 (22H, m), 1.14 (24H, broad), 0.79 (6H, broad). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.21, 152.51, 151.20, 150.27, 146.61, 144.35, 141.18, 139.90, 133.04, 132.81, 129.93, 128.88, 125.86, 125.53, 122.85, 122.18, 120.95, 120.65, 55.69, 55.44, 49.90, 40.66, 31.88, 30.26, 30.12, 29.96, 29.76, 29.36, 29.22, 27.23, 24.98, 23.86, 22.61, 14.11.

Polymer **P2**. A mixture of **6** (50.0 mg, 88.9 μmol), 2,2'-(9,9-bis(6-bromohexyl)-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxabo-rolane) (67.2 mg, 91.4 μmol), $NaHCO_3$ (284.5 mg, 3.4 mmol), THF (5 mL), toluene (1 mL) and H_2O (1 mL) was carefully degassed before and after $Pd(PPh_3)_4$ (2 mg, 1.7 μmol) was added. The mixture was heated to reflux and stirred under nitrogen for 96 h. The reaction mixture was extracted with $CHCl_3$ (3 × 30 mL), and combined organic layers were dried over anhydrous $MgSO_4$. After the removal of most of solvent, the residue was precipitated into methanol. The resulted precipitate was collected by filtration and dried under vacuum to give **P2** (66 mg, 88%) as a dark green solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23-8.20 (4H, broad), 7.88-7.79 (6H, broad), 3.29 (4H, m), 2.22-1.71 (26H, m), 1.25-1.13 (12H, broad). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.24, 151.82, 146.60, 144.19, 141.10, 139.88, 132.79, 125.99, 122.82, 122.18, 120.76, 55.57, 40.66, 33.98, 32.60, 30.26, 29.71, 29.04, 27.80, 24.99, 23.68.

Polymer **P3**. Trimethylamine (1 mL, 20% wt) was added dropwise to a solution of the neutral precursor polymer **2** (25 mg, 0.028 μmol) in THF (5 mL) at -78 ^{o}C under N_2. The mixture was allowed to warm up to room temperature and the precipitate was redissolved by addition of water (10 mL). After the mixture was cooled down to -78 ^{o}C, extra trimethylamine (1 mL, 20% wt) was added and the mixture was stirred for

24 h at room temperature. The green product was collected after removing the solvent (25 mg, 90%). ^{1}H NMR (*d*-DMSO, 353K, 400 MHz): δ 8.49-8.37 (4H, m), 8.24-7.98 (6H, m), 2.98-2.94 (22H, m), 1.84-1.68 (22H, m), 1.52-1.15 (16H, m).

Supporting Figures.

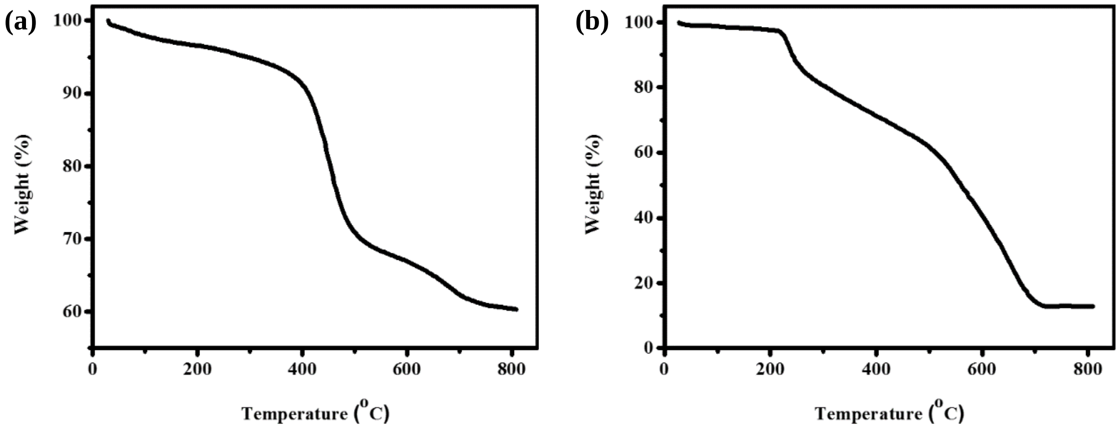


Figure S1. TGA traces of (a) **P1** and (b) **P2**.

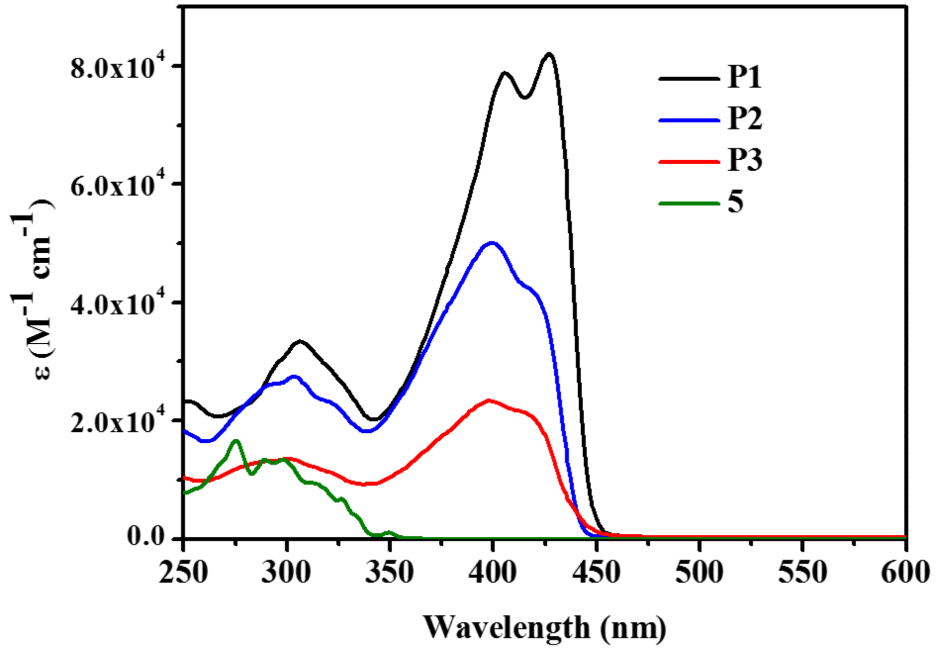


Figure S2. UV-vis absorption spectra of **5**, **P1** and **P2** in chloroform, and **P3** in methanol.

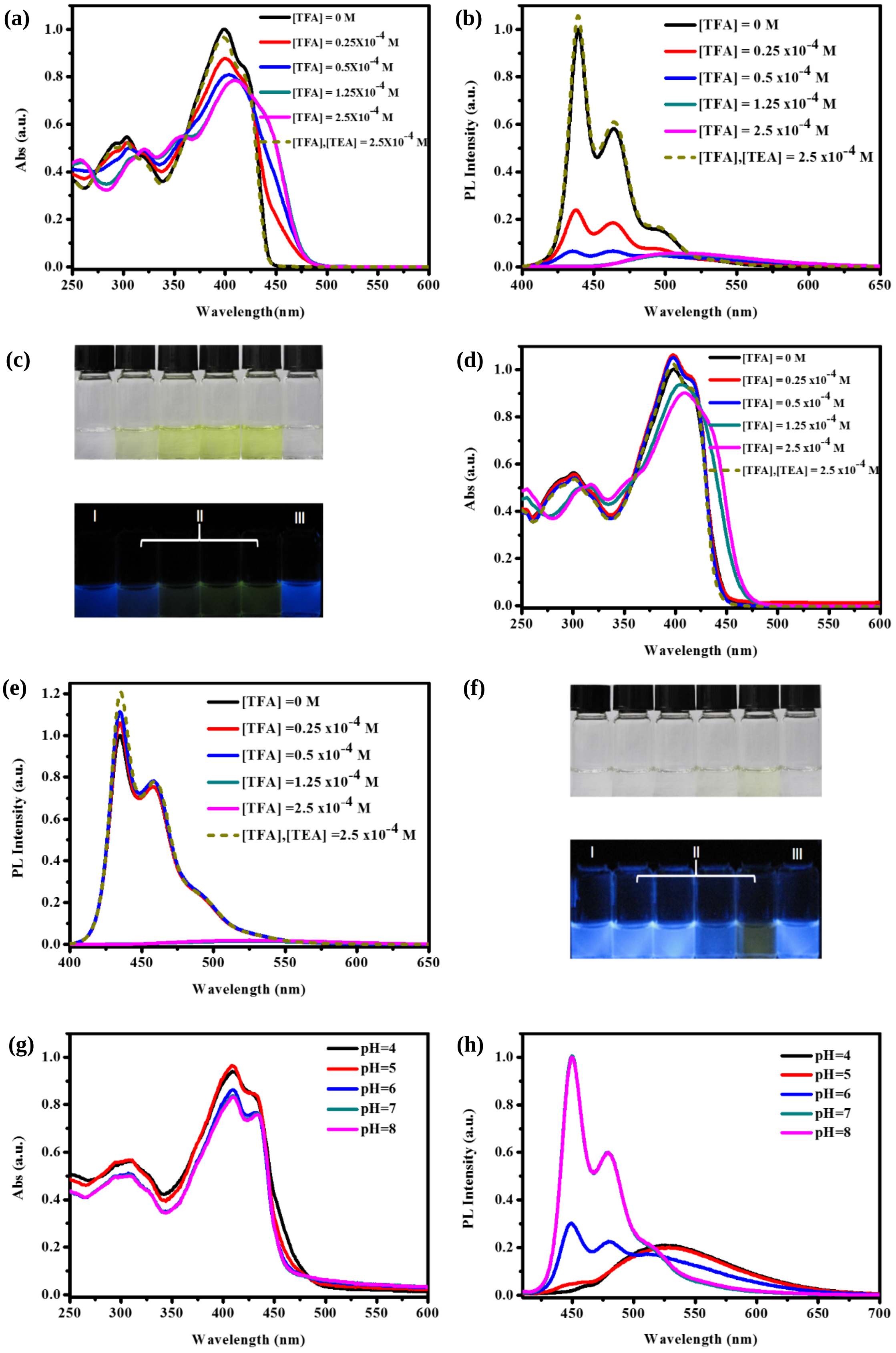


Figure S3. (a), (d), (g) UV-vis absorption and (b), (e), (h) PL spectra of **P2** (a, b) in chloroform, **P3** (d, e) in methanol at various concentrations of TFA, and **P3** (g, h) in Britton-Robinson buffer with different pH (10^{-5} M for repeating unit). Dash lines represent the recovery of the optical properties when the protonated polymer solution was treated with TEA; Pictures of (c) **P2** in chloroform, (f) **P3** in methanol (I) before and (II) after the titration of TFA, and (III) the recovery of optical property after treated with TEA (taken under nature light and under the illumination with 365 nm UV light).

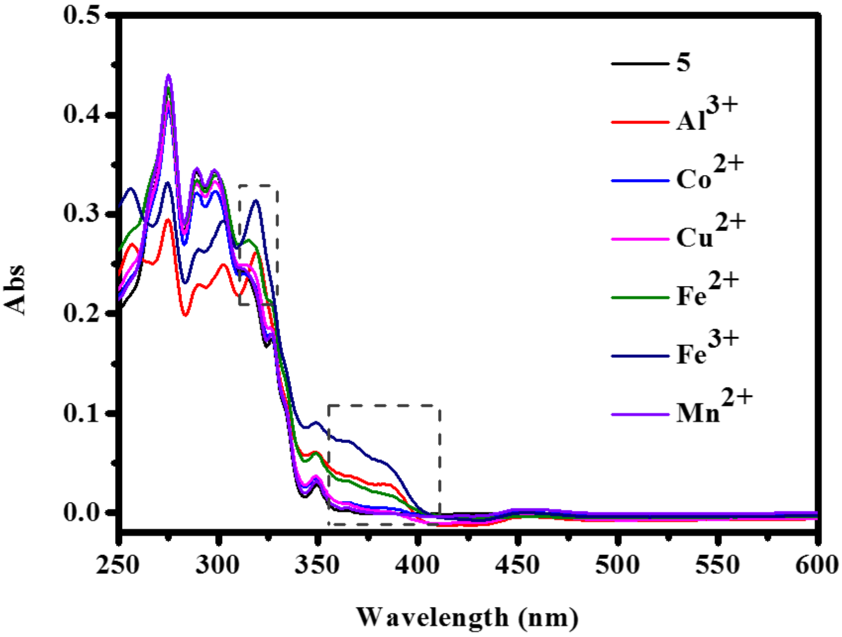


Figure S4. UV-vis absorption spectra of **5** in chloroform after the addition of methanol solutions of metal chlorides ([5], $[M^{n+}] = 10^{-5}$ M).

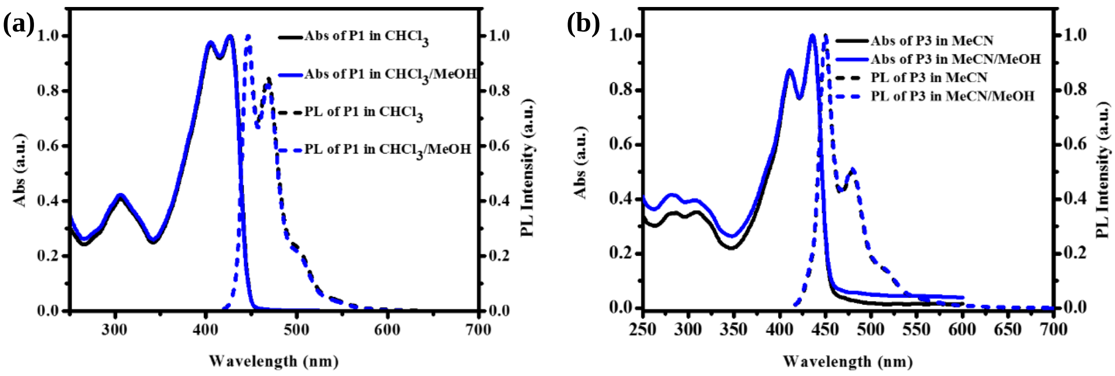


Figure S5. Control experiments with the addition of methanol to the polymer solutions showed no changes of their optical properties: UV-vis absorption and PL spectra of (a) **P1** in chloroform, and (b) **P3** in acetonitrile with and without methanol (3 vol%) (10^{-5} M for repeating unit).

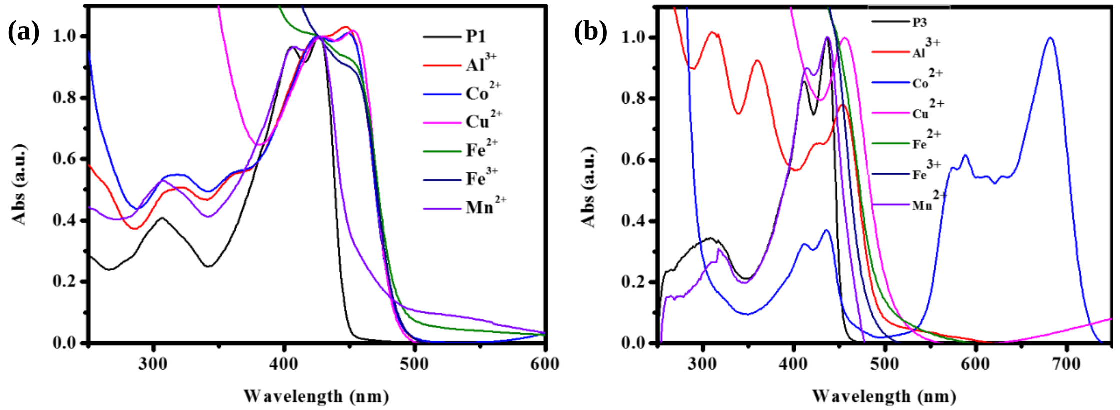


Figure S6. UV-vis absorption spectra of (a) **P1** in chloroform and (b) **P3** in acetonitrile (10^{-5} M for repeating unit) to metal chlorides (10^{-3} M).

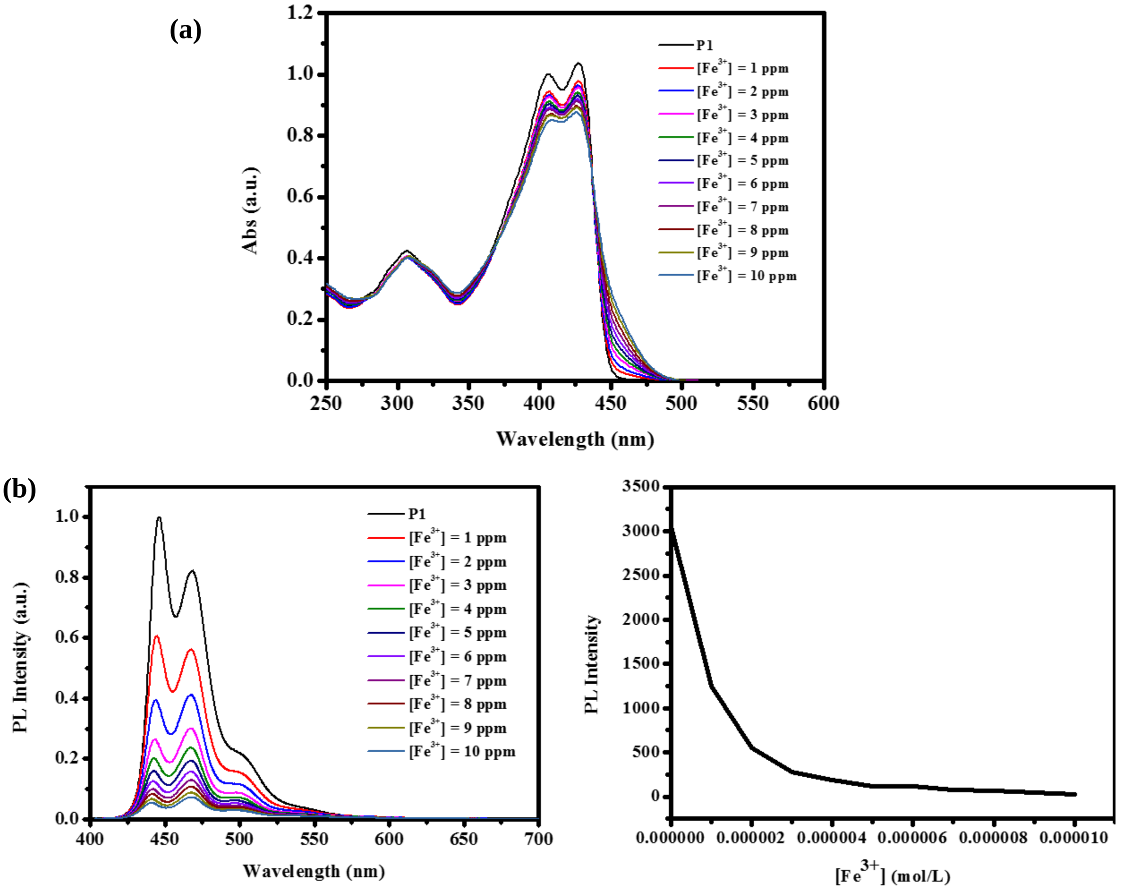
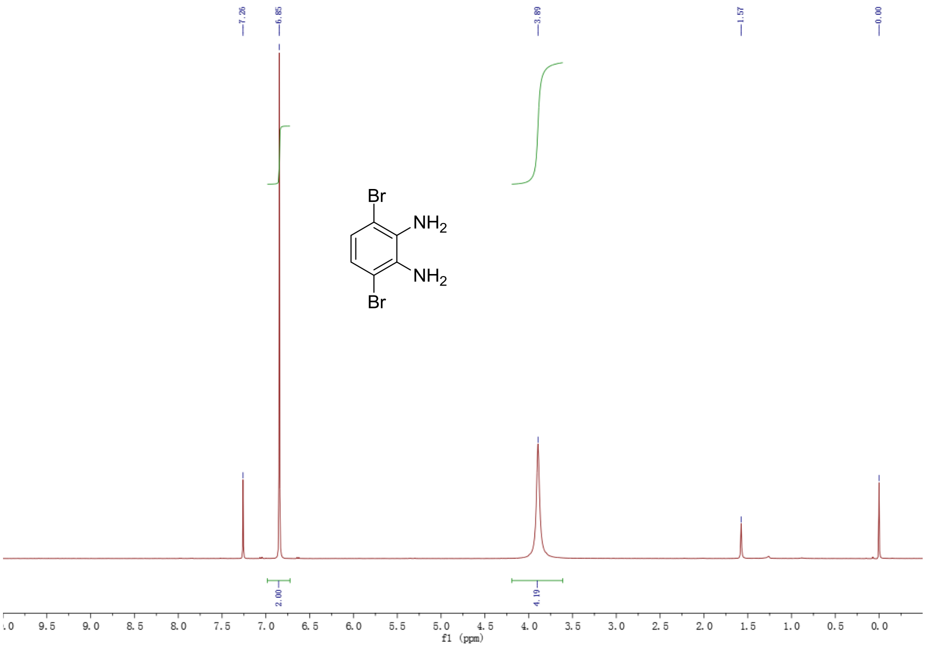


Figure S7. (a) UV-vis absorption spectra and (b) fluorescence quenching of **P1** in chloroform (10^{-5} M for repeating unit) in the presence of Fe^{3+}.

Crystal Data of 6 (CCDC 1450922).

Empirical formula	$C24H22Br2N2S2$
Space group	P 21/c
Cell lengths	a/Å 6.25656(20) b/Å 20.1295(8) c/Å 17.8928(6)
Cell angels	α/° 90.00 β/° 96.663(3) γ/°90.00
Cell volume	2238.22/$Å^3$
Z, Z'	Z: 4 Z': 0
R-Factor(%)	3.44

^{1}H NMR spectra.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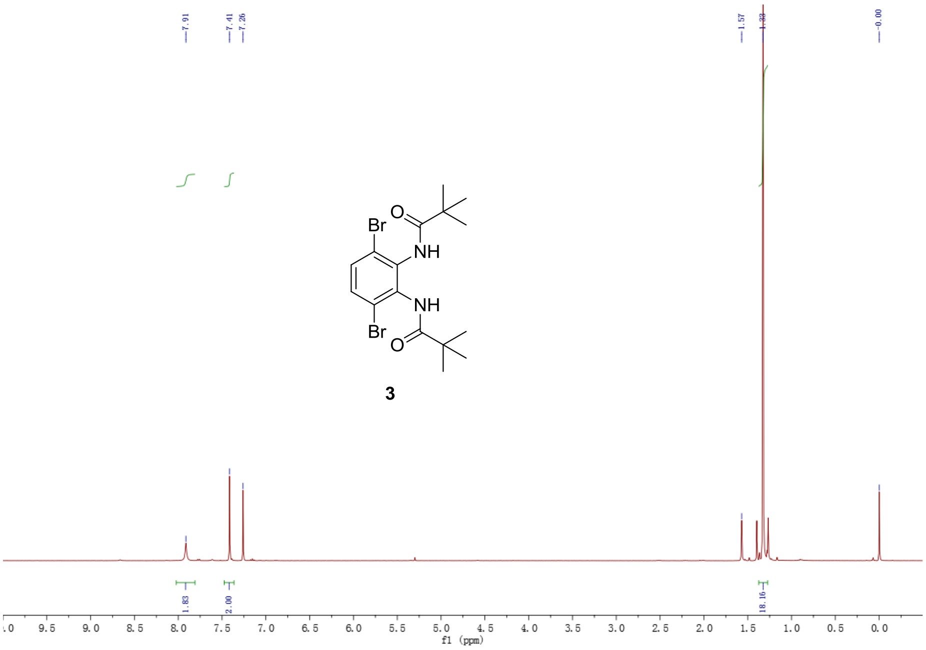
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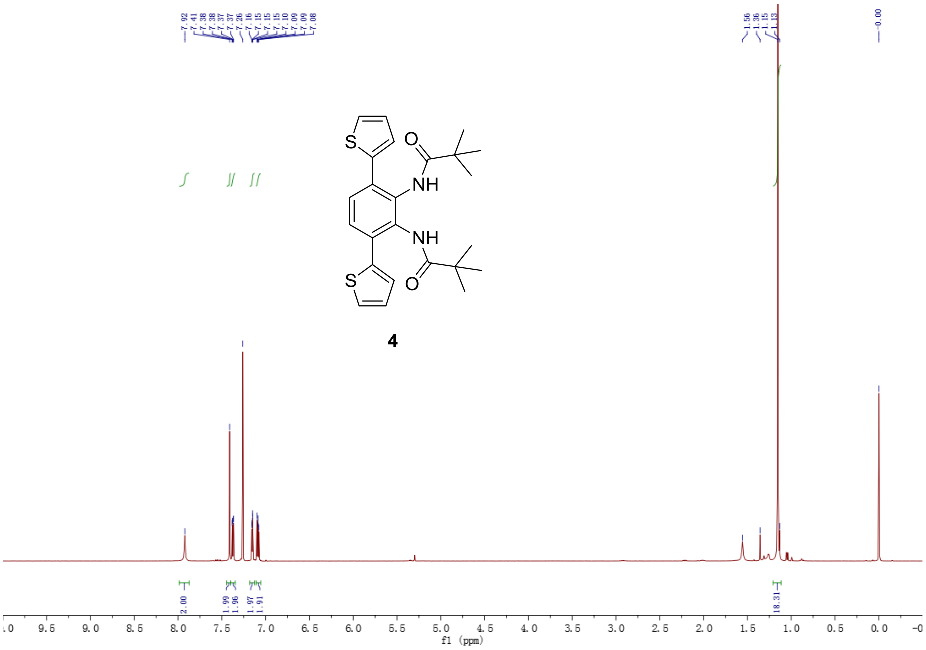
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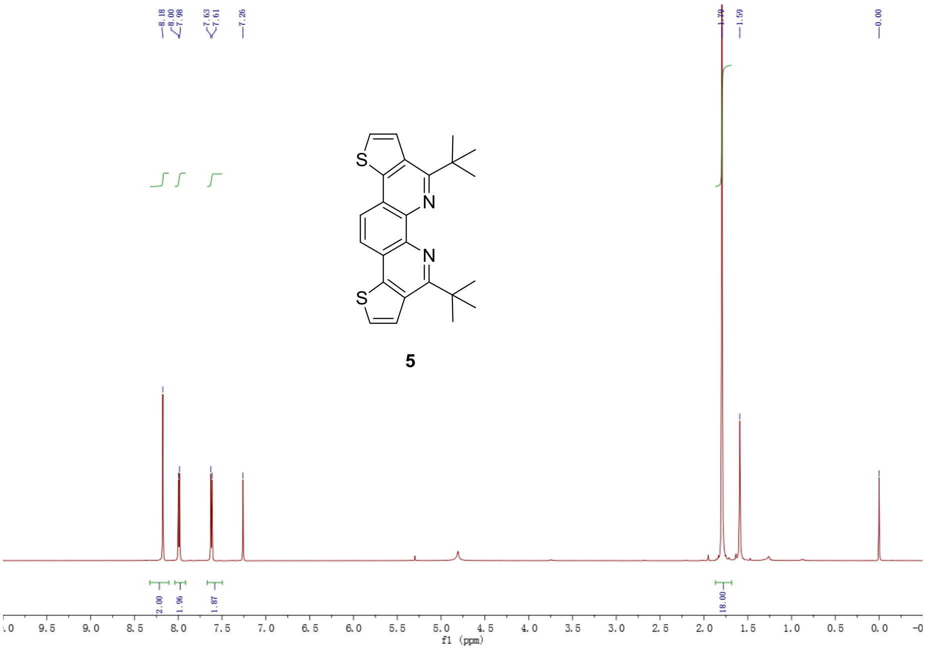
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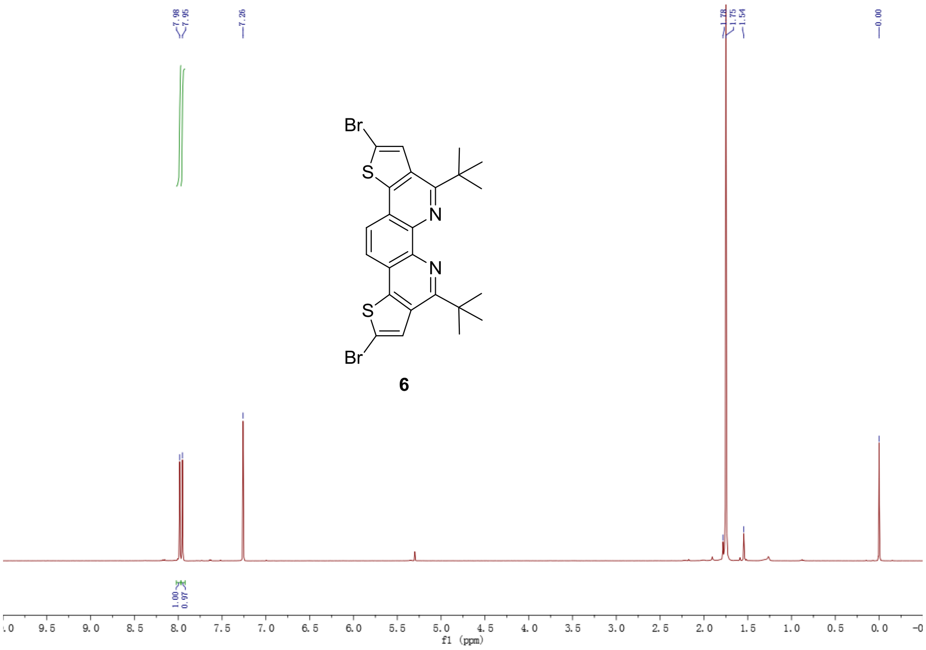
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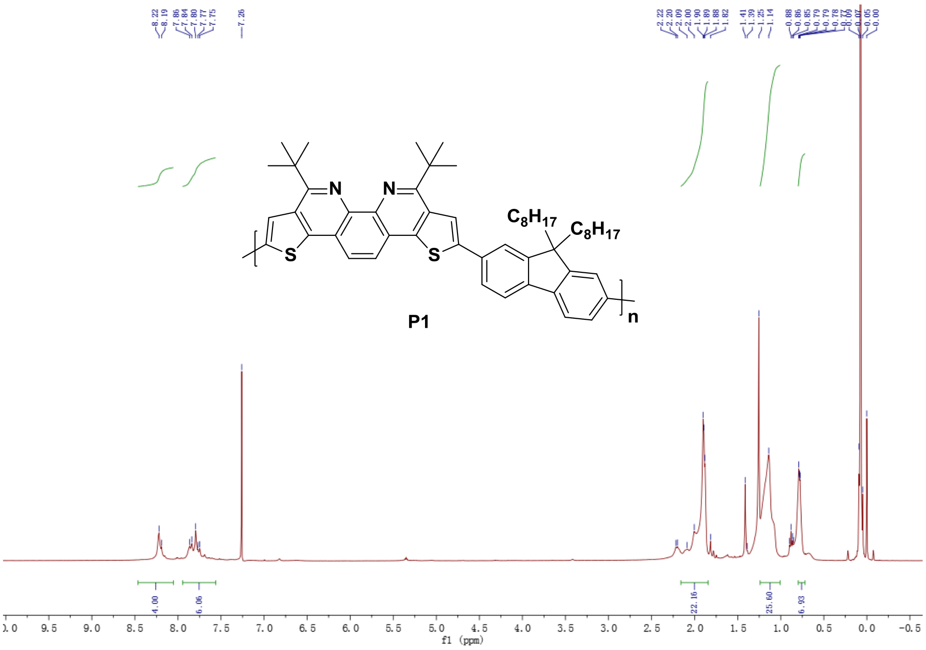
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C_8H_{17}
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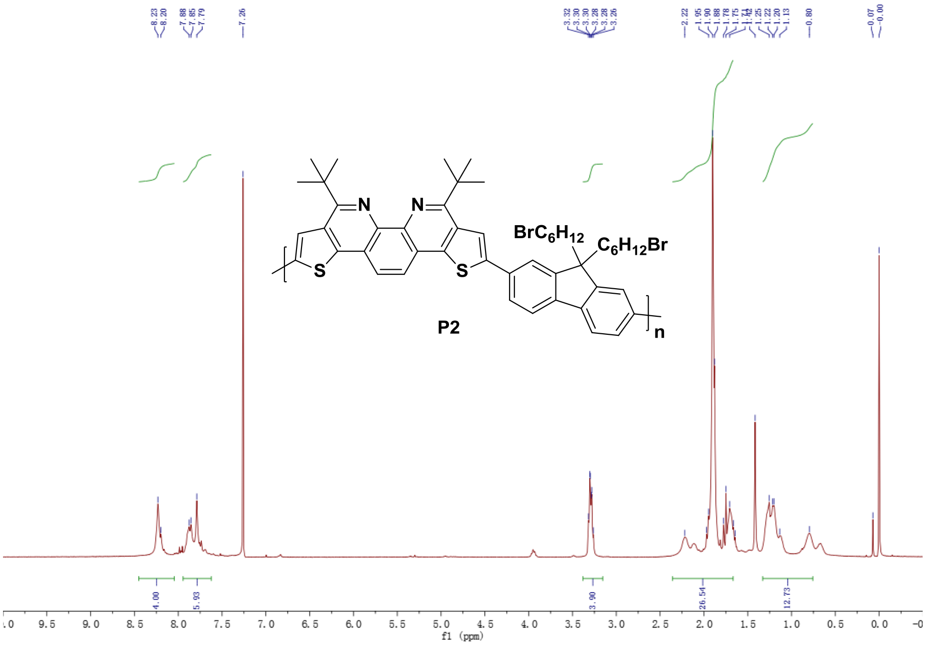
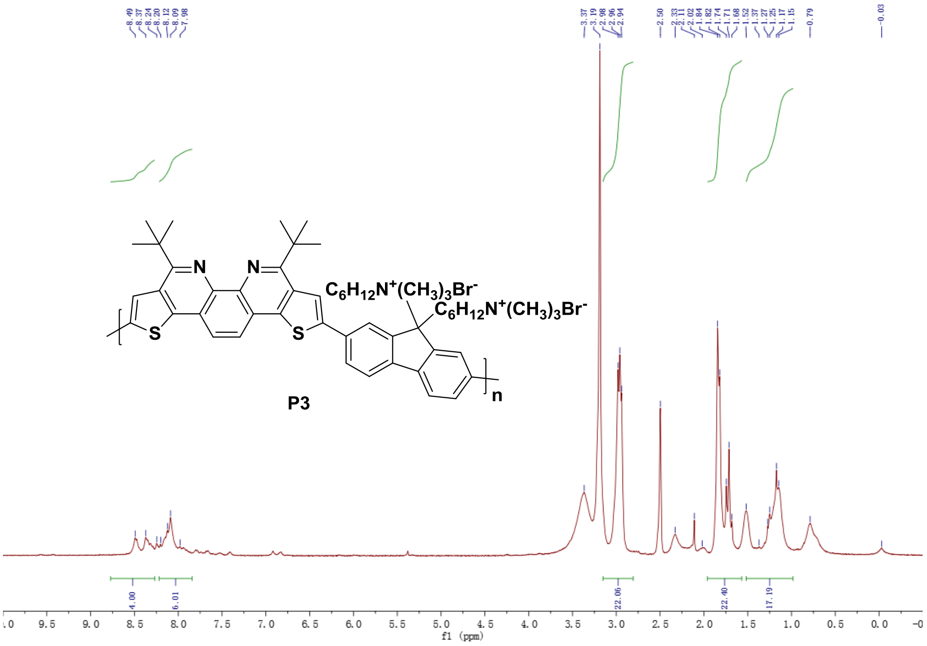
f1 (ppm)

P1





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S1. Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

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S3. Lee, W.-H.; Mohanty, A. D.; Bae, C. *ACS Macro Lett.* **2015**, *4*, 453.

S4. Britton, H. T. S.; Robinson, R. A. *J. Chem. Soc.* **1931**, 1456.

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