

# A Semiconducting Conjugated Radical Polymer: Ambipolar Redox Activity and Faraday Effect

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## 1. General Experimental Information

Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen using the standard Schlenk technique. All solvents and reagents were obtained from commercial sources and were purified following standard procedures before use.

<sup>1</sup>H NMR spectra were recorded on a 400 MHz or 500 MHz Bruker Avance spectrometer. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or that of CHCl<sub>3</sub> at 7.26 ppm as the standard. <sup>13</sup>C NMR spectra were recorded on a 101 MHz or 126 MHz Bruker Avance spectrometer. All signals are reported in ppm with the internal CDCl<sub>3</sub> signal at 77.0 ppm as the standard. <sup>31</sup>P NMR spectra were recorded using a 162 MHz spectrometer. Data for <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>31</sup>P NMR are presented in the order of chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved), coupling constant (Hz), and integration.

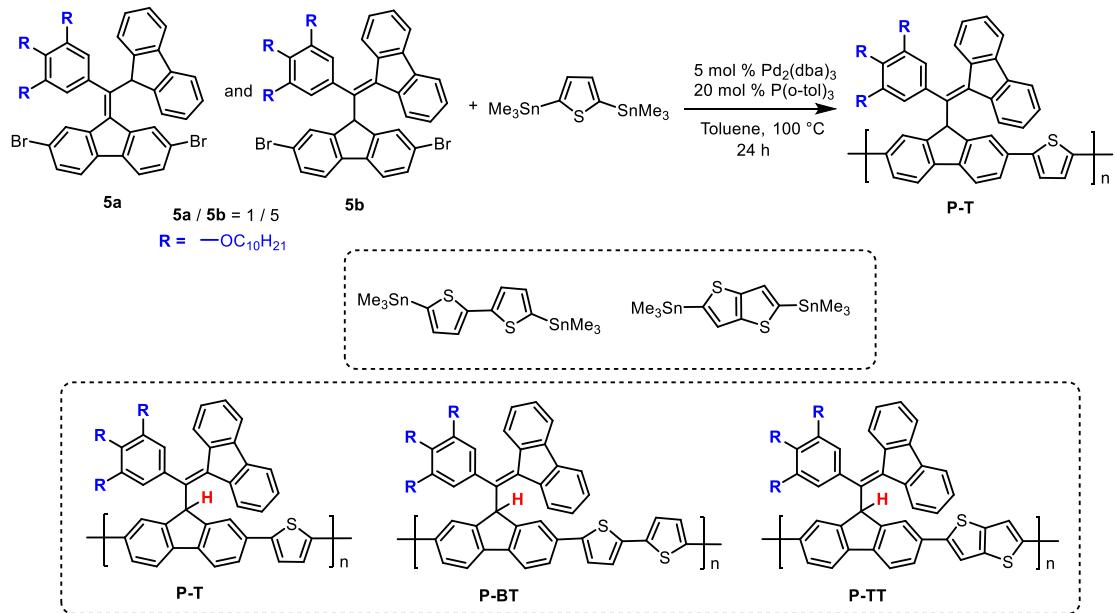
Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 Fourier Transform Infrared Spectrometer (FT-IR) using the attenuated total reflectance (ATR) technique on a Ge crystal. Frequencies are given in reciprocal centimeters (cm<sup>-1</sup>), and only those of selected absorptions are reported. High resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) at the MIT DCIF (Department of Chemistry Instrumentation Facility).

UV-vis spectra were recorded on an Agilent Cary 4000 spectrometer at room temperature. Fluorescence measurements were performed at room temperature on a Horiba Jobin Yvon SPEX Fluorolog-t3 fluorimeter (model FL-321, 450 W Xenon lamp) using the right-angle mode for solution samples and the front-face mode for thin-film samples.

EPR measurements were performed on a Bruker EMX spectrometer. Experimental parameters for solution-based EPR measurements are provided as follows: modulation amplitude = 1.0 G, receiver gain = 30 dB, receiver harmonic = 1, microwave power = 2 mW, and frequency = 9.81 GHz. Experimental parameters for EPR spectroelectrochemical measurements are provided as follows: modulation amplitude = 1.0 G; field = 3453.5 to 3553.4 G, width = 99.90 G, center = 3503.5 G, receiver gain = 30 dB, receiver harmonic = 1, microwave power = 2 mW, and frequency = 9.81 GHz.

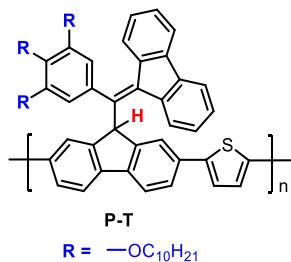
THF gel permeation chromatography (GPC) was performed with the sample at a concentration of 0.5 mg/mL on an Agilent 1260 Infinity system equipped with three PL gel columns (103 Å, 104 Å, 105 Å) in series, calibrated using the monodisperse polystyrene standards.

## 2. General Polymerization Procedure for Polymers P-T, P-BT, and P-TT.

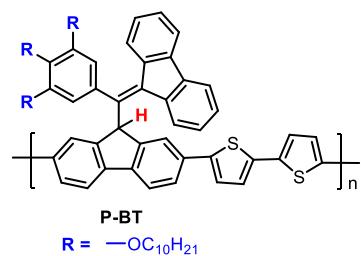


**Scheme S1.** General polymerization pathways for **P-T**, **P-BT**, and **P-TT**

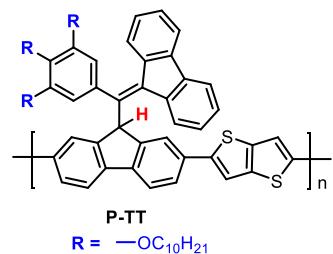
To an oven-dried Schlenk flask,  $\text{Pd}_2(\text{dba})_3$  (97%) (5 mol%, 0.015 mmol, 14.2 mg),  $\text{P}(o\text{-tol})_3$  (97%) (20 mol%, 0.06 mmol, 18.8 mg), 2,5-bis(trimethylstannyl)thiophene (97%) (1.0 equiv., 0.3 mmol, 126.7 mg) and 7 mL of toluene were added. Monomer **5** (1.0 equiv., 0.3 mmol) was dissolved with 5 mL of toluene and was added to the Schlenk flask. The mixture was treated with 3 freeze-pump-thaw cycles and was then heated to  $100^\circ\text{C}$  with a cold finger condenser. After the reaction was stirred at  $100^\circ\text{C}$  for 24 h, the mixture was cooled down to room temperature and diluted with  $\text{CH}_2\text{Cl}_2$ , and a small amount of  $\text{CsF}$  (100 mg) was added. The mixture was washed with  $\text{H}_2\text{O}$  and extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL×3). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , after which the solvent was removed under reduced pressure. The material was then dissolved with 3 mL of  $\text{CH}_2\text{Cl}_2$ , added dropwise to 100 mL of MeOH and stirred vigorously to form precipitates. The mixture was filtered, and the residue was washed with MeOH repeatedly. The resulting solid material was Soxhlet extracted with MeOH and then with  $\text{CHCl}_3$ . The  $\text{CHCl}_3$  phase was collected, after which the solvent was removed under reduced pressure. The obtained dark red solid was dried under reduced pressure to afford polymer **P-T**. **P-BT** and **P-TT** were polymerized following similar procedures. The structural and spectral information of **P-T**, **P-BT**, and **P-TT** is provided as follows.



**P-T:** Dark red solid (0.3 mmol scale, 278 mg, 96% yield). GPC (THF):  $M_n = 35.0$  kDa,  $D = 2.70$ . IR (KBr): 3060, 2920, 2850, 1570, 1500, 1460, 1420, 1340, 1240, 1110, 796, 730, 646 cm<sup>-1</sup>.

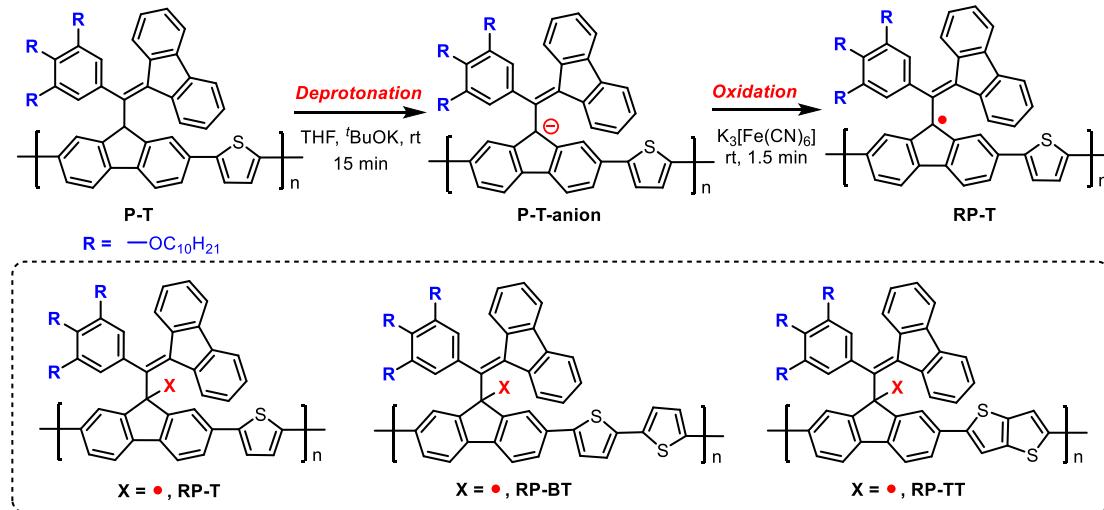


**P-BT:** Dark red solid (0.08 mmol scale, 80 mg, 95% yield). GPC (THF):  $M_n = 55.3$  kDa,  $D = 3.96$ . IR (KBr): 2924, 2854, 1574, 1467, 1447, 1417, 1338, 1241, 1111, 794, 730 cm<sup>-1</sup>.



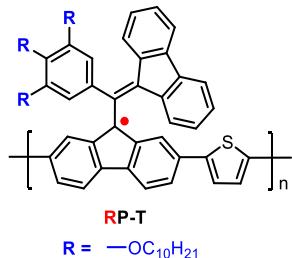
**P-TT:** Dark red solid (0.10 mmol scale, 103 mg, 99% yield). GPC (THF):  $M_n = 21.1$  kDa,  $D = 2.41$ . IR (KBr): 2925, 2854, 1576, 1499, 1466, 1448, 1420, 1335, 1234, 1112, 809, 729, 666 cm<sup>-1</sup>.

### 3. General Synthetic Procedures for Radical Polymers RP-T, RP-BT, and RP-TT

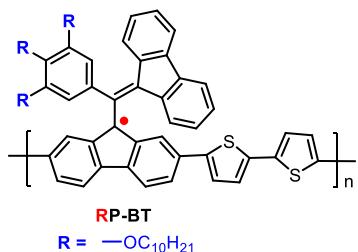


**Scheme S2.** General synthetic pathways for **RP-T**, **RP-BT**, and **RP-TT**

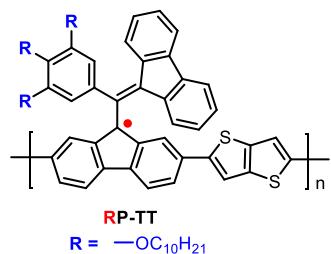
To an oven-dried Schlenk flask, polymer **P-T** (827  $\mu$ mol, 80 mg) and 30 mL of THF were added. *t*-BuOK (4.0 equiv., 331  $\mu$ mol, 37.0 mg) was added slowly in small portions, and the mixture was stirred at room temperature for 15 min. The reaction mixture turned from dark red to dark green.  $K_3[Fe(CN)_6]$  (6.0 equiv., 496  $\mu$ mol, 163.4 mg) was dissolved with 4 mL of saturated  $NaHCO_3$  aqueous solution and was added to the mixture within 30 seconds. The reaction mixture turned from dark green to red and then to dark brown. The reaction was quenched by adding 10 mL of  $H_2O$  after 1.5 min and was extracted with  $CH_2Cl_2$  (50 mL $\times$ 3). The combined organic phase was washed with brine and then dried over anhydrous  $Na_2SO_4$ . The solvent was removed under reduced pressure, washed with MeOH repeatedly, and dried in vacuum at room temperature for 12 h, affording a dark red solid of **RP-T**. Dark red solids **RP-BT** and **RP-TT** were synthesized following similar procedures starting from **P-BT** and **P-TT** respectively. The structural and spectral information of **RP-T**, **RP-BT**, and **RP-TT** is provided as follows.



**RP-T:** Dark red solid (827  $\mu$ mol scale, 75 mg, 94% yield). GPC (THF):  $M_n = 25.7$  kDa,  $D = 4.78$ . IR (KBr): 2930, 2850, 1580, 1450, 1420, 1320, 1111, 799, 778, 728, 644  $cm^{-1}$ .



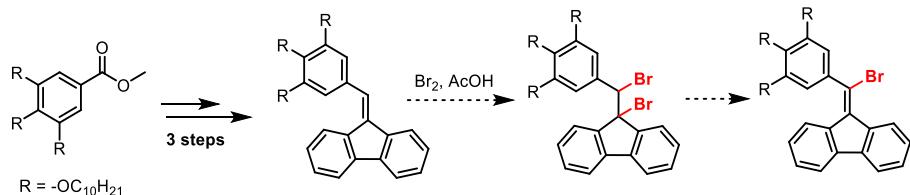
**RP-BT:** Dark red solid (28.6  $\mu\text{mol}$  scale, 30 mg, 60% yield). GPC (THF):  $M_n = 39.0$  kDa,  $D = 4.36$ . IR (KBr): 2954, 2926, 2855, 1589, 1505, 1467, 1441, 1334, 1259, 1114, 1028, 973  $\text{cm}^{-1}$ .



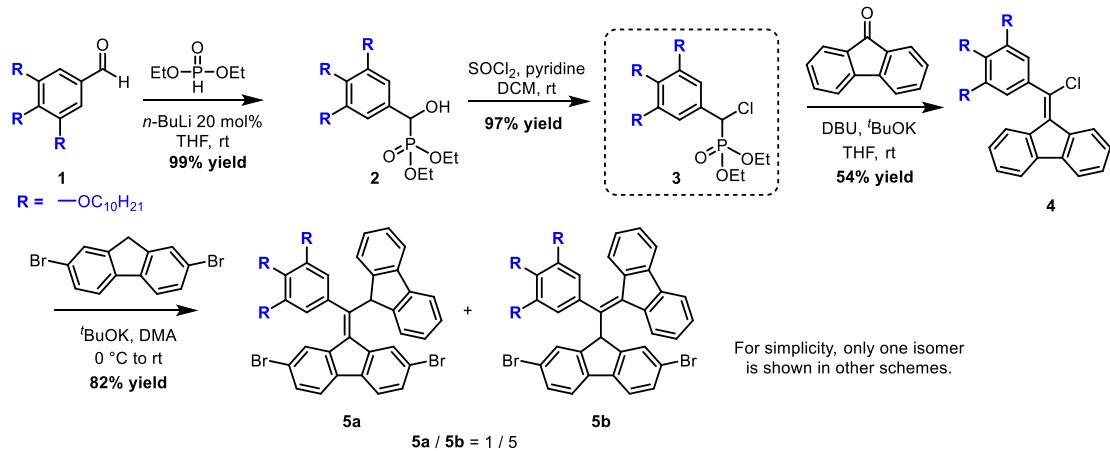
**RP-TT:** Dark red solid (24.4  $\mu\text{mol}$  scale, 25 mg, 72% yield). GPC (THF):  $M_n = 18.7$  kDa,  $D = 5.40$ . IR (KBr): 2954, 2924, 2853, 1576, 1499, 1465, 1452, 1419, 1334, 1235, 1113, 809, 737  $\text{cm}^{-1}$ .

## 4. Synthesis of Monomers

Previous synthetic method:



**Scheme S3.** Synthetic pathway for monomers reported in an earlier study.<sup>1</sup>



**Scheme S4.** General synthetic pathway for monomers developed in the present study.

#### Synthetic Procedure for 2:

To an oven-dried Schlenk flask, anhydrous THF (40 mL), compound **1** (20.9 mmol, 12 g) and diethyl phosphite (2.0 equiv., 41.8 mmol, 5.4 mL) were added. *n*-BuLi (1 M in THF) (0.2 equiv., 4.18 mmol, 4.2 mL) was added dropwise, and the reaction mixture was stirred at room temperature. The reaction was monitored by TLC. As soon as the starting material disappeared, 10 mL of H<sub>2</sub>O was added slowly to quench the reaction, and most of the solvent was removed using a rotary evaporator. The mixture was diluted with H<sub>2</sub>O and was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL×3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, after which the solvent was removed under reduced pressure. The residue was isolated by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/EtOAc = 20/1) to give product **2** in 99% yield (14.7 g).

#### Synthetic Procedure for 3:

To an oven-dried Schlenk flask, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (30 mL), compound **1** (16.8 mmol, 12 g), and pyridine (2.0 equiv., 33.6 mmol, 2.4 mL) were added. SOCl<sub>2</sub> (2.0 equiv., 33.6 mmol, 2.7 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 14 h. 10 mL of H<sub>2</sub>O was added slowly to quench the reaction. The resulting mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL×3), washed with brine (50 mL×3) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to give product **3** (11.9 g, 97% yield), which was used for the next step without further purification.

#### Synthetic Procedure for 4:

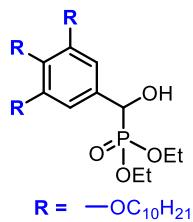
To an oven-dried Schlenk flask, anhydrous THF (30 mL), compound **3** (6.8 mmol, 5 g) and fluorenone (1.2 equiv., 8.2 mmol, 1.5 g) were added. DBU (1.2 equiv., 8.2 mmol, 1.2 mL) was added slowly, and the reaction mixture was stirred at room temperature for 45 min. *t*-BuOK (1 M in THF) (1.5 equiv., 10.2 mmol, 10.2 mL) was added slowly, and the reaction mixture was stirred at room temperature for additional 5 h. 10 mL of

$\text{H}_2\text{O}$  was added slowly to quench the reaction, and most of the solvent was removed using a rotary evaporator. The resulting mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL $\times$ 3), washed with brine (50 mL $\times$ 3), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , after which the solvent was removed under reduced pressure. The residue was isolated by flash chromatography ( $\text{CH}_2\text{Cl}_2/\text{EtOAc} = 20/1$ ) to give product **4** in 54% yield (2.8 g).

### Synthetic Procedure for **5**:

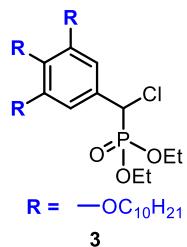
To an oven-dried Schlenk flask, was added anhydrous dimethylacetamide (DMA) (12 mL), 2,7-dibromofluorene (1.5 equiv., 1.98 mmol, 1.5 g) and *t*-BuOK (3.5 equiv., 6.93 mmol, 0.78 g) were added. The mixture was cooled to 0 °C for 30 min. Compound **4** (1.98 mmol, 1.5 g) was dissolved with 8 mL of DMA and was added to the mixture dropwise. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 1 hour while being monitored using TLC. After TLC showed that the starting material **4** had disappeared, the reaction was quenched by adding 10 mL of 0.5 M HCl at 0 °C and was extracted with EtOAc (50 mL $\times$ 3). The combined organic phase was washed with brine (50 mL $\times$ 3), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , after which the solvent was removed under reduced pressure. The residue was isolated by flash chromatography (Hexane/ $\text{CH}_2\text{Cl}_2 = 2/1$ ) to give product **5** (**5a**/**5b** = 1/5) (isomers **5a** and **5b** have very similar  $R_f$  values and are difficult to separate using chromatography) in 82% yield (1.7 g).

The structural and spectral information of **2**, **3**, **4**, and **5** is provided as follows.

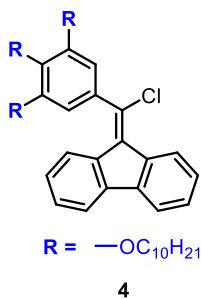


2

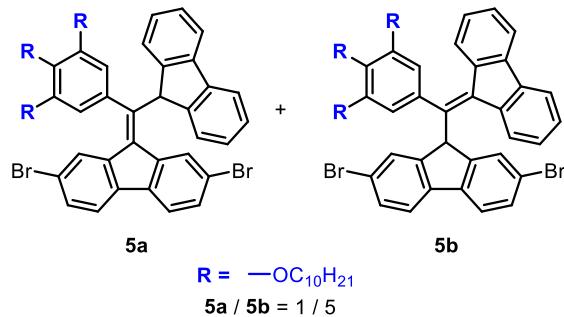
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.687 (s, 1H), 6.681 (s, 1H), 4.90 (dd,  $J = 10.4, 4.9$  Hz, 1H), 4.19–4.11 (m, 2H), 4.08–4.02 (m, 2H), 3.98–3.91 (m, 6H), 2.93 (dd,  $J = 11.5, 4.9$  Hz, 1H), 1.80–1.70 (m, 6H), 1.46–1.35 (m, 6H), 1.30–1.24 (m, 42H), 0.89–0.86 (m, 9H).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.48–21.26 (m, 1P).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.96, 137.86, 131.22, 105.52, 73.31, 71.46, 70.20, 69.03, 63.26 (dd,  $J = 31.9, 7.1$  Hz), 31.90, 31.88, 30.29, 29.71, 29.65, 29.62, 29.58, 29.56, 29.40, 29.36, 29.32, 26.09, 26.07, 22.66, 22.65, 16.41, 16.37, 16.33, 14.07. IR (KBr): 2923, 2850, 1590, 1466, 1437, 1333, 1232, 1115, 1052, 1022, 960, 753, 721, 637  $\text{cm}^{-1}$ . HRMS-ESI: Exact mass calcd. for  $\text{C}_{41}\text{H}_{77}\text{O}_7\text{PNa}^+$  [ $\text{M}+\text{Na}$ ] $^+$ : 735.5305; Found: 735.5323.



Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.72 (m, 2H), 4.76 (d,  $J = 13.8\text{Hz}$ , 1H), 4.29–4.17 (m, 4H), 4.00–3.91 (m, 6H), 1.81–1.69 (m, 6H), 1.47–1.44 (m, 6H), 1.32–1.26 (m, 42H), 0.88–0.85 (m, 9H).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  17.52–17.30 (m, 1P).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.96, 138.74, 128.72, 107.51, 73.35, 69.14, 65.80, 65.73, 63.91 (dd,  $J = 11.1, 6.9\text{ Hz}$ ), 54.79, 53.19, 31.88, 31.86, 30.27, 29.68, 29.62, 29.58, 29.53, 29.36, 29.34, 29.29, 26.05, 26.02, 22.63, 16.42 (d,  $J = 5.7\text{ Hz}$ ), 16.21 (d,  $J = 5.8\text{ Hz}$ ), 14.04. IR (KBr): 2956, 2925, 2855, 1587, 466, 1441, 1335, 1259, 115, 1030, 974  $\text{cm}^{-1}$ . HRMS-ESI: Exact mass calcd. for  $\text{C}_{41}\text{H}_{76}\text{O}_6\text{P}^+ [\text{M}-\text{Cl}]^+$ : 695.5374; Found: 695.5365.



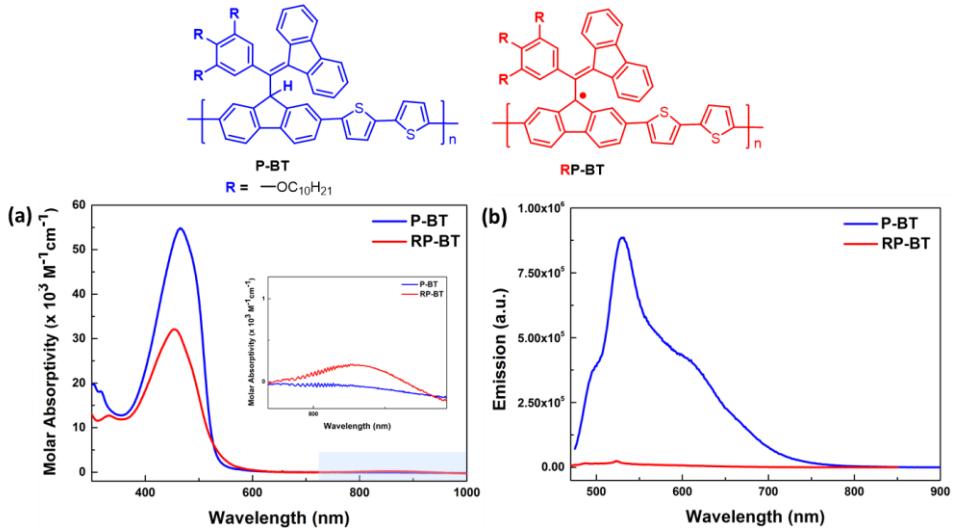
Yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.56 (d,  $J = 7.5\text{ Hz}$ , 1H), 7.65 (d,  $J = 7.0\text{ Hz}$ , 1H), 7.57 (d,  $J = 7.5\text{ Hz}$ , 1H), 7.36–7.27 (m, 2H), 7.17–7.13 (m, 1H), 6.84 (t,  $J = 7.6\text{ Hz}$ , 1H), 6.61 (s, 2H), 6.39 (d,  $J = 8.0\text{ Hz}$ , 1H), 3.99 (t,  $J = 6.5\text{ Hz}$ , 2H), 3.89–3.84 (m, 4H), 1.75–1.67 (m, 6H), 1.47–1.44 (m, 2H), 1.36–1.18 (m, 40H), 0.82–0.78 (m, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.69, 140.74, 139.76, 139.04, 137.52, 137.45, 135.06, 134.21, 133.40, 128.77, 127.98, 127.32, 126.88, 126.39, 124.80, 119.44, 119.22, 106.99, 73.55, 69.14, 31.95, 31.90, 30.39, 29.77, 29.70, 29.63, 29.60, 29.56, 29.41, 29.38, 29.33, 29.27, 26.15, 26.03, 22.71, 22.67, 14.12, 14.10. IR (KBr): 2925, 2852, 1577, 1496, 1457, 1421, 1328, 1232, 1112, 799, 728, 644  $\text{cm}^{-1}$ . HRMS-ESI: Exact mass calcd. for  $\text{C}_{50}\text{H}_{74}\text{O}_3\text{Cl}^+ [\text{M}+\text{H}]^+$ : 757.5326; Found: 757.5331.



Red oil. **5a/5b = 1/5.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) for major **5b**: δ 8.24 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.66–7.64 (m, 3H), 7.41–7.36 (m, 4H), 7.31–7.28 (m, 1H), 7.19–7.16 (m, 2H), 6.81 (t, *J* = 7.7 Hz, 1H), 6.37 (s, 1H), 6.14–6.13 (m, 1H), 5.72 (s, 2H), 3.78–3.76 (m, 2H), 3.57–3.52 (m, 2H), 3.32–3.27 (m, 2H), 1.57–1.46 (m, 6H), 1.33–1.18 (m, 42H), 0.82–2.79 (m, 9H). <sup>13</sup>C NMR for **5a** and **5b** (126 MHz, CDCl<sub>3</sub>) δ 152.54, 152.48, 148.76, 146.40, 143.79, 142.58, 142.21, 141.52, 140.28, 140.12, 140.05, 139.66, 139.09, 138.45, 138.12, 138.07, 137.24, 136.98, 136.30, 133.78, 132.31, 132.13, 131.05, 130.75, 130.29, 129.23, 128.98, 128.49, 127.87, 127.81, 127.71, 127.39, 126.98, 125.78, 125.66, 124.61, 121.39, 121.34, 121.08, 120.96, 120.14, 120.11, 119.05, 107.43, 107.19, 73.52, 73.14, 69.00, 68.83, 52.51, 31.92, 30.12, 30.03, 29.73, 29.63, 29.60, 29.39, 29.36, 29.33, 29.28, 29.06, 28.97, 26.03, 25.90, 25.87, 22.69, 14.12. IR (KBr): 2954, 2851, 1577, 1502, 1448, 1416, 1337, 1239, 1113, 809, 730 cm<sup>-1</sup>. HRMS-ESI: Exact mass calcd. for C<sub>63</sub>H<sub>81</sub>O<sub>3</sub>Br<sub>2</sub><sup>+</sup>[M+H]<sup>+</sup>: 1045.4532; Found: 1045.4551.

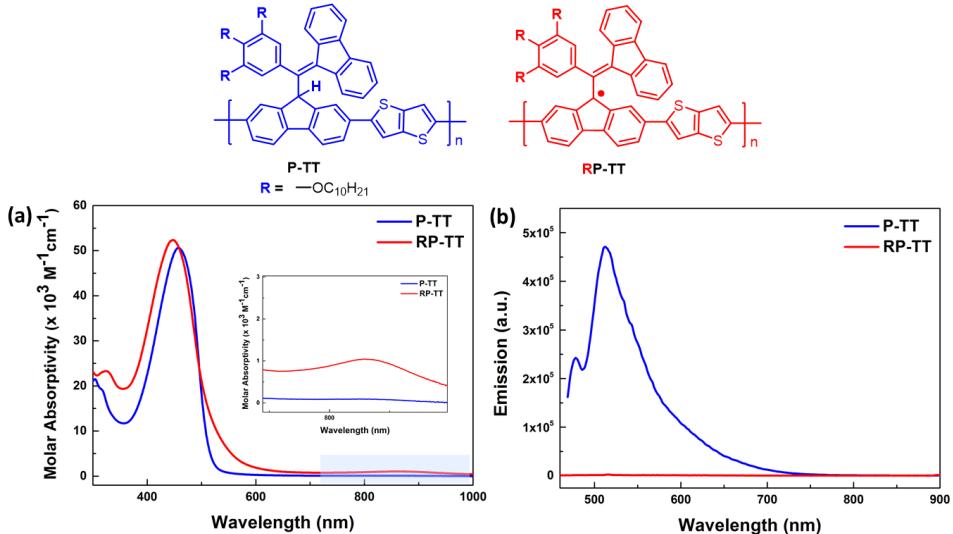
## 5. UV-vis Absorption and Emission Spectra

### Polymers P-BT and RP-BT:



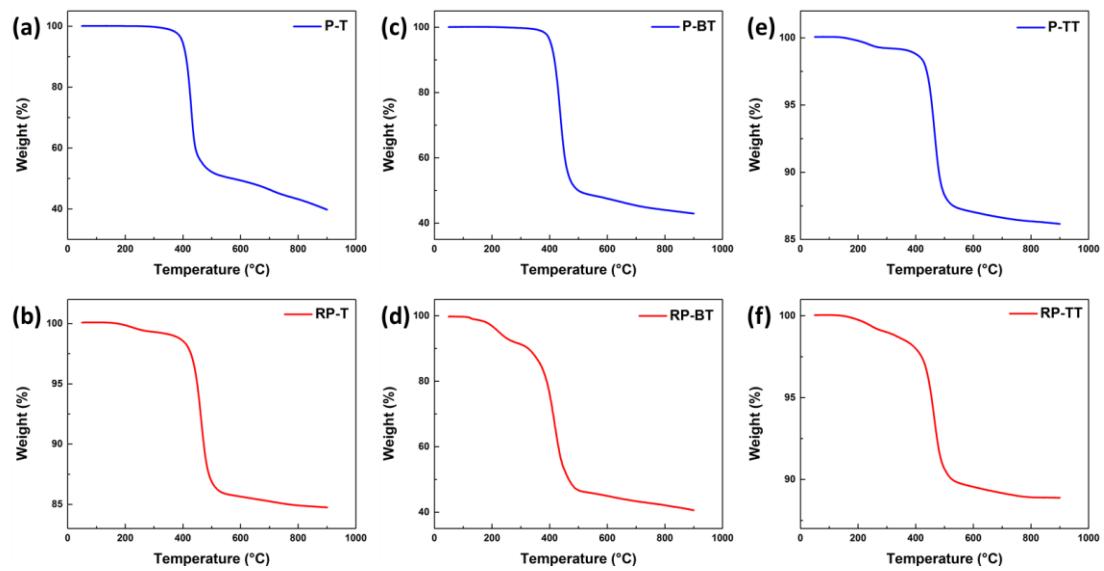
**Figure S1.** UV-vis absorption and emission spectra of polymers **P-BT** and **RP-BT** measured in the THF solution. (a) Absorption spectra, with the inset showing the enlarged spectra between 750~1000 nm; (b) Emission spectra, with the excitation wavelength at 453 nm.

### Polymers P-TT and RP-TT:



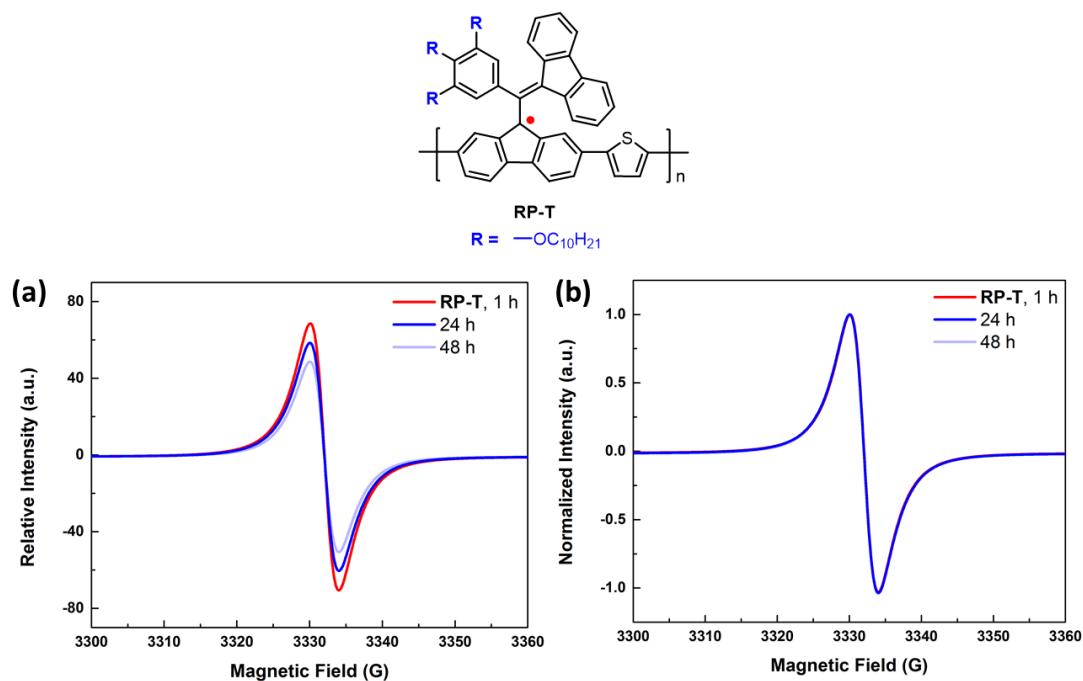
**Figure S2.** UV-vis absorption and emission spectra of polymers **P-TT** and **RP-TT** measured in THF solution. (a) Absorption spectra, with the inset showing the enlarged spectra between 750~1000 nm; (b) Emission spectra, with the excitation wavelength at 460 nm.

## 6. TGA Traces of Polymers



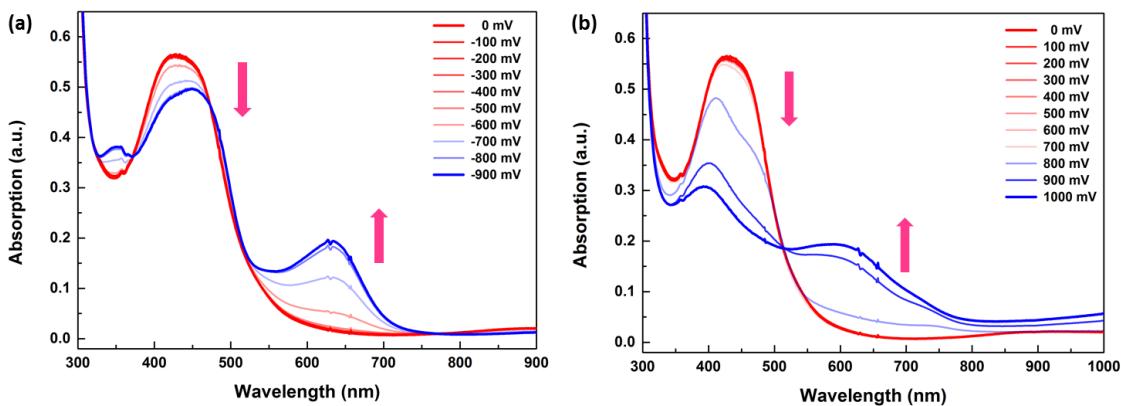
**Figure S3.** TGA traces of polymers (a) **P-T**, (b) **RP-T**, (c) **P-BT**, (d) **RP-BT**, (e) **P-TT**, and (f) **RP-TT**. TGA analysis was conducted with a ramping rate of 20 °C/min to 900 °C.

## 7. Stability Test of Radical Polymer RP-T



**Figure S4.** Stability test of **RP-T** in the toluene solution at room temperature. (a) Relative EPR intensity; (b) Normalized EPR intensity. **RP-T** was dissolved with degassed toluene with a concentration of 1 mM, protected from light in a capped EPR tube. Experimental parameters are provided as follows: modulation amplitude = 1 G, receiver gain = 30 dB, attenuation = 20 dB, microwave power = 2 mW, frequency = 9.35 GHz.

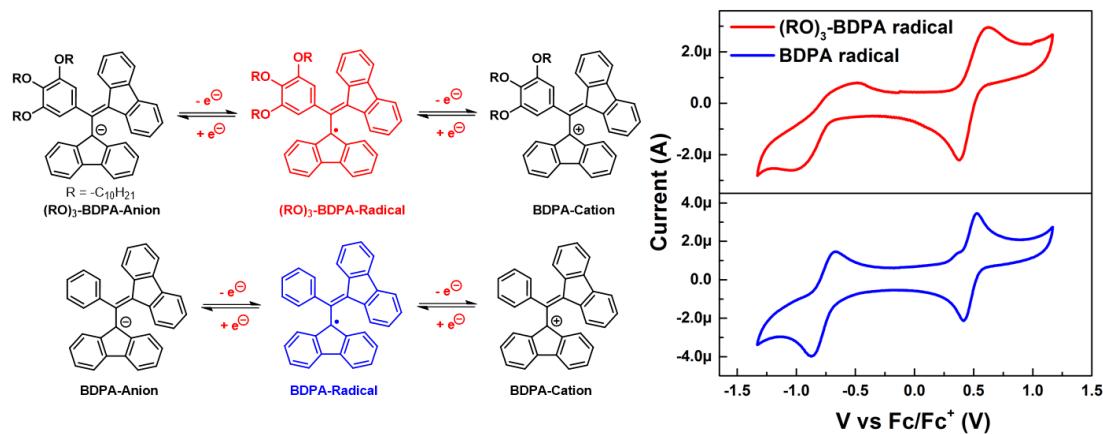
## 8. Spectroelectrochemical Studies of Radical Polymer RP-T



**Figure S5.** Spectroelectrochemistry of radical polymer **RP-T** was studied by measuring the UV-vis absorption on an ITO-coated glass at various applied potentials in the CH<sub>3</sub>CN electrolyte solution. (a) Applied potential ranging from −0.9 to 0.0 V vs Ag/Ag<sup>+</sup>; (b) Applied potential ranging from 0.0 to 1.0 V vs Ag/Ag<sup>+</sup>. 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN was used as the electrolyte, Pt wire as the counter electrode, and Ag/AgNO<sub>3</sub> as the reference electrode.

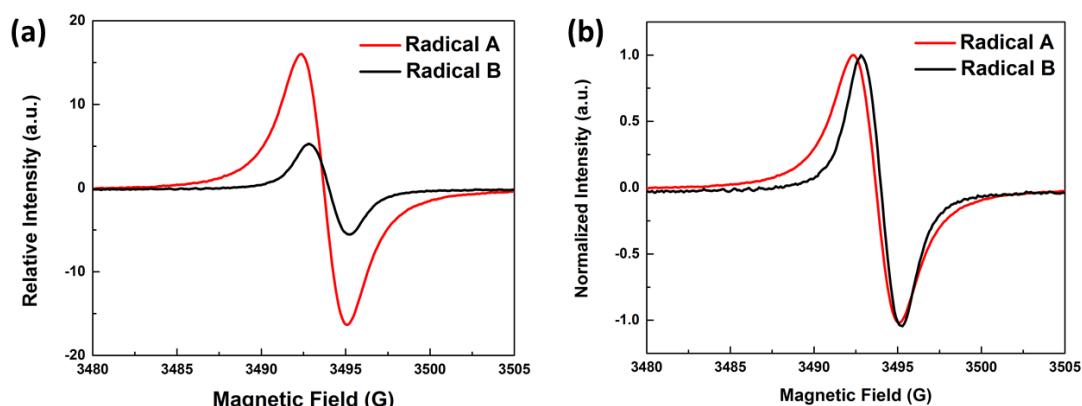
## 9. Cyclic Voltammetry of and *in situ* EPR Spectroelectrochemistry

Cyclic voltammetry of BDPA and  $(RO)_3$ -BDPA radicals:

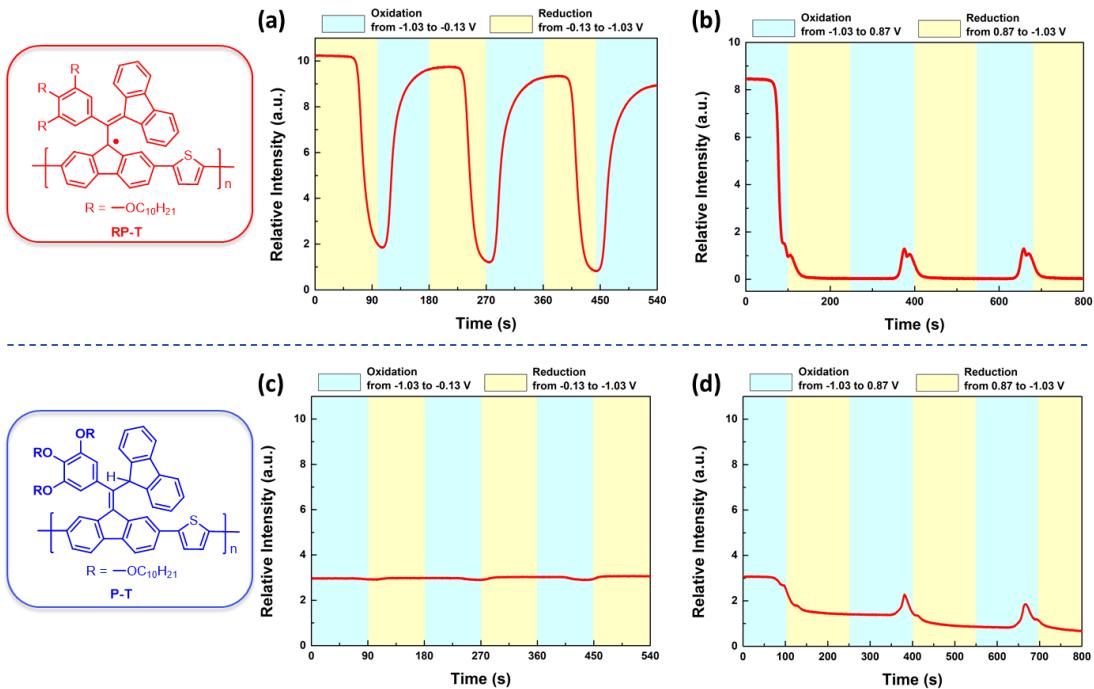


**Figure S6.** Cyclic voltammetry of for BDPA and  $(RO)_3$ -BDPA radicals in the anhydrous  $\text{CH}_2\text{Cl}_2$  solution at scan rates of 50 mV/s. 0.1 M  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$  was used as the electrolyte, Pt button as the working electrode, Pt wire as the counter electrode, and  $\text{Ag}/\text{AgNO}_3$  as the reference electrode. Ferrocene was used as the external standard.

*In situ* EPR spectroscopy of RP-T and P-T:

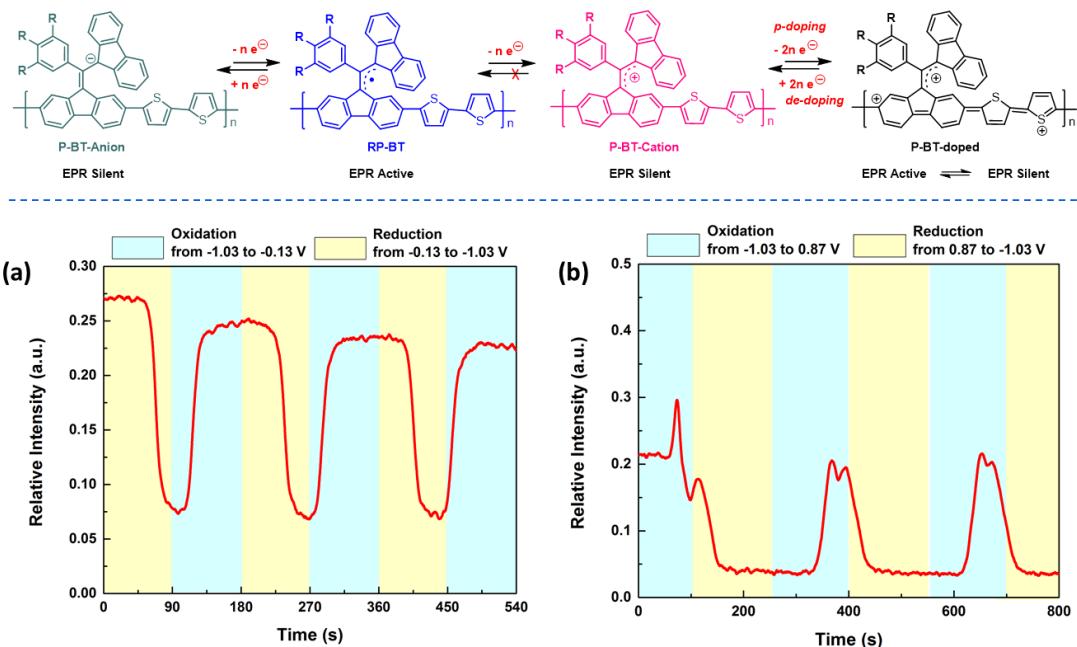


**Figure S7.** EPR spectra of two radical species **Radicals A** and **B**. (a) Relative EPR intensity; (b) Normalized EPR spectra.



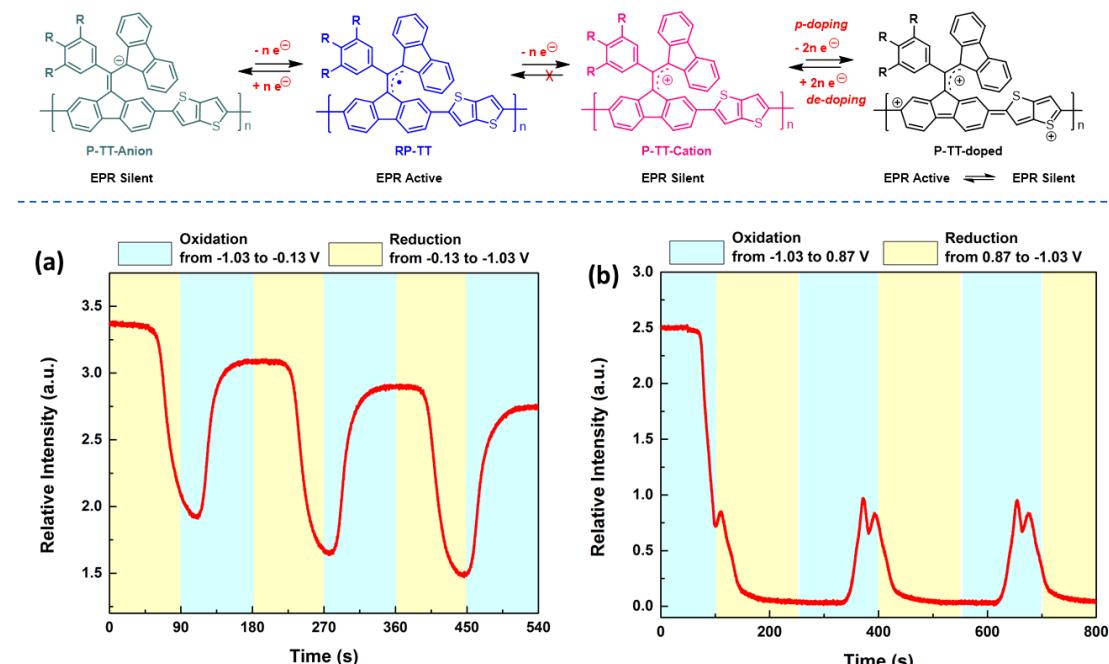
**Figure S8.** A summary of the electrochemical process occurring during EPR spectroelectrochemical study of **RP-T** (top panel) and **P-T** (bottom panel). EPR intensity change in the process (with scan rates of 10 mV/s) of (a) negative scans between  $-1.03$  and  $-0.13$  V for **RP-T**, (b) positive scans between  $-1.03$  and  $0.87$  V for **RP-T**, (c) negative scans between  $-1.03$  and  $-0.13$  V for **P-T**, and (d) positive scans between  $-1.03$  and  $0.87$  V for **P-T**. Polymers were coated on Pt wire as the working electrode.  $0.1\text{ M}$   $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$  was used as the electrolyte, Pt wire as the counter electrode, and  $\text{Ag}/\text{AgNO}_3$  as the reference electrode. Ferrocene was used as the external standard. CV and EPR were taken in a flat cell quartz EPR tube.

**In situ EPR spectroelectrochemistry of RP-BT:**

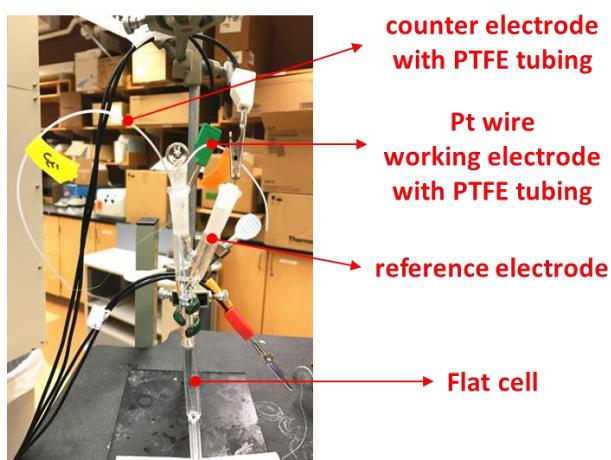


**Figure S9.** A summary of the electrochemical process occurring during EPR spectroelectrochemical study of **RP-BT**. EPR intensity change in the process (with scan rates of 10 mV/s) of (a) negative scans between  $-1.03$  and  $-0.13$  V and (b) positive scans between  $-1.03$  and  $0.87$  V. **RP-BT** was coated on Pt wire as the working electrode.  $0.1$  M  $Bu_4NPF_6$  in  $CH_3CN$  was used as the electrolyte, Pt wire as the counter electrode, and  $Ag/AgNO_3$  as the reference electrode. Ferrocene was used as external standard. CV and EPR were taken in a flat cell quartz EPR tube.

### In situ EPR spectroelectrochemistry of RP-TT:



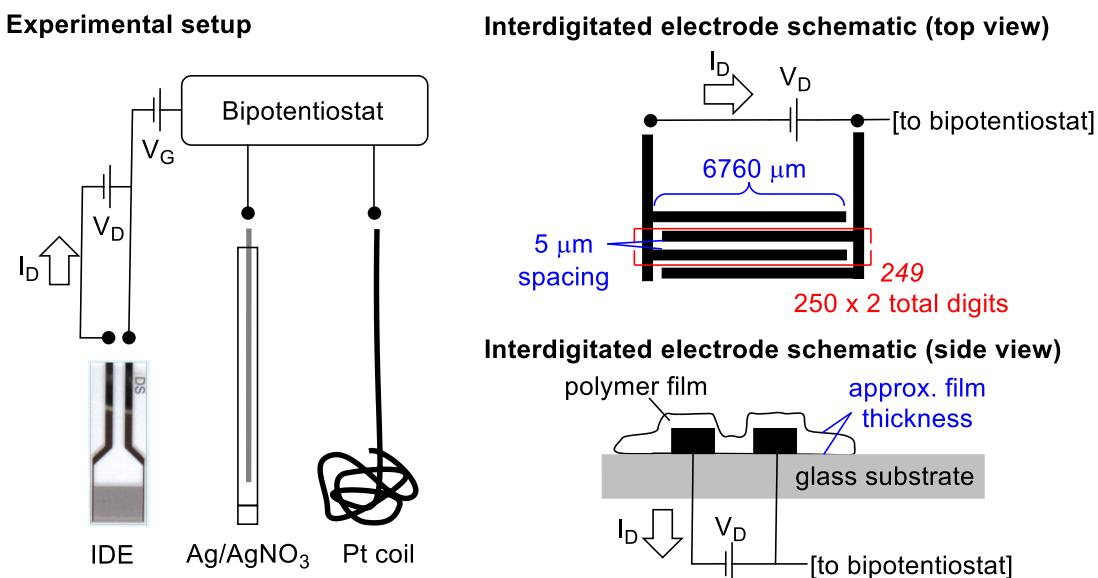
**Figure S10.** A summary of the electrochemical process occurring during EPR spectroelectrochemical study of **RP-TT**. EPR intensity change in the process (with scan rates of 10 mV/s) of (a) negative scans between  $-1.03$  and  $-0.13$  V and (b) positive scans between  $-1.03$  and  $0.87$  V. **RP-TT** was coated on Pt wire as the working electrode.  $0.1$  M  $\text{Bu}_4\text{NPF}_6$  dissolved with  $\text{CH}_3\text{CN}$  was used as the electrolyte, Pt wire as the counter electrode, and  $\text{Ag}/\text{AgNO}_3$  as the reference electrode. Ferrocene was used as the external standard. CV and EPR were taken in a flat cell quartz EPR tube.



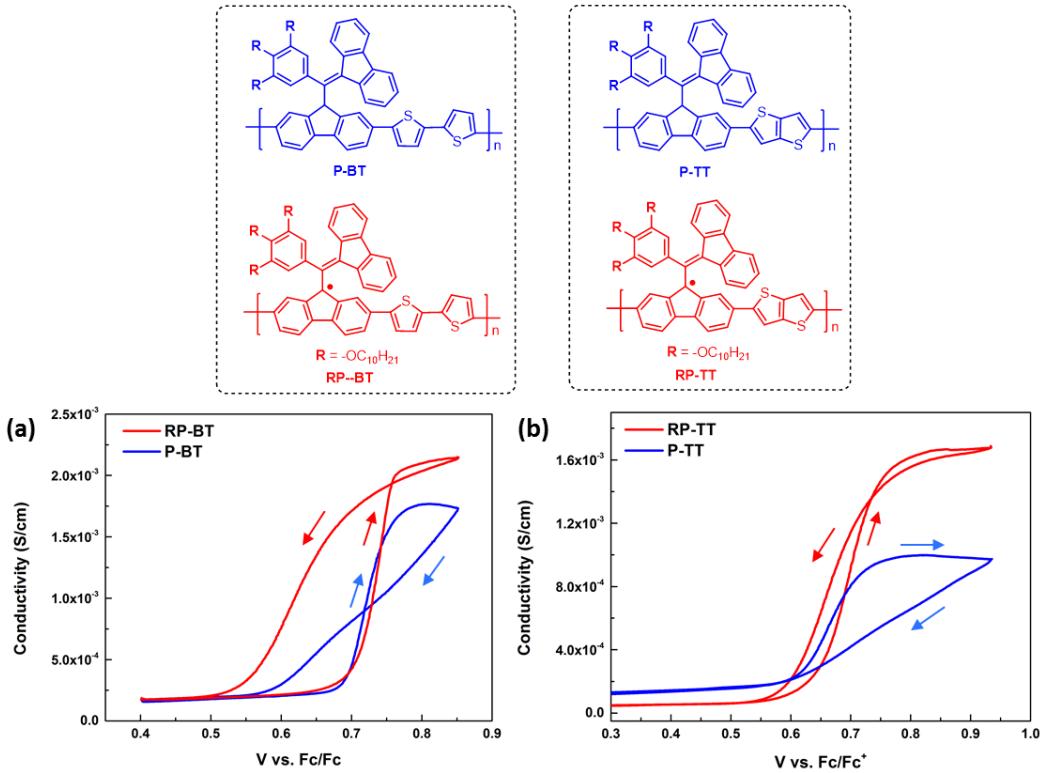
**Figure S10-2.** Experimental apparatus of the *in situ* flat cell for EPR spectroelectrochemistry.

## 10. Conductivity Mapping with Microelectrochemical Transistors

*In situ* conductivity was measured with  $5\text{ }\mu\text{m}$  spacing Pt interdigitated electrodes (IDEs) (Dropsens, #G-IDEPT5). Polymers were dissolved with  $\text{CHCl}_3$  to reach a concentration of  $15\text{ mg/mL}$  and were applied to the IDE using spin-coating at  $1500\text{ rpm}$ . The two sets of fingers were used as working electrodes 1 and 2. A flame-cleaned Pt-wire and  $\text{Ag}/\text{AgNO}_3$  pseudo-reference electrode were used with a Bio-logic VSP Bipotentiostat in the "CE-to-ground" bipotentiostat mode.  $100\text{ mM}$  of  $\text{Bu}_4\text{NPF}_6$  (in  $\text{CH}_3\text{CN}$ ) was used as the electrolyte. The two working electrodes were used to perform synchronized cyclic voltammograms with an offset of  $50\text{ mV}$  at a scan rate of  $2\text{ mV/s}$ . The observed current minus the background current from single-channel mode (to account for Faradaic charging) was then used to calculate the conductivity.<sup>2</sup>



**Figure S11.** Schematic of a microelectrochemical transistor utilized in the present study.

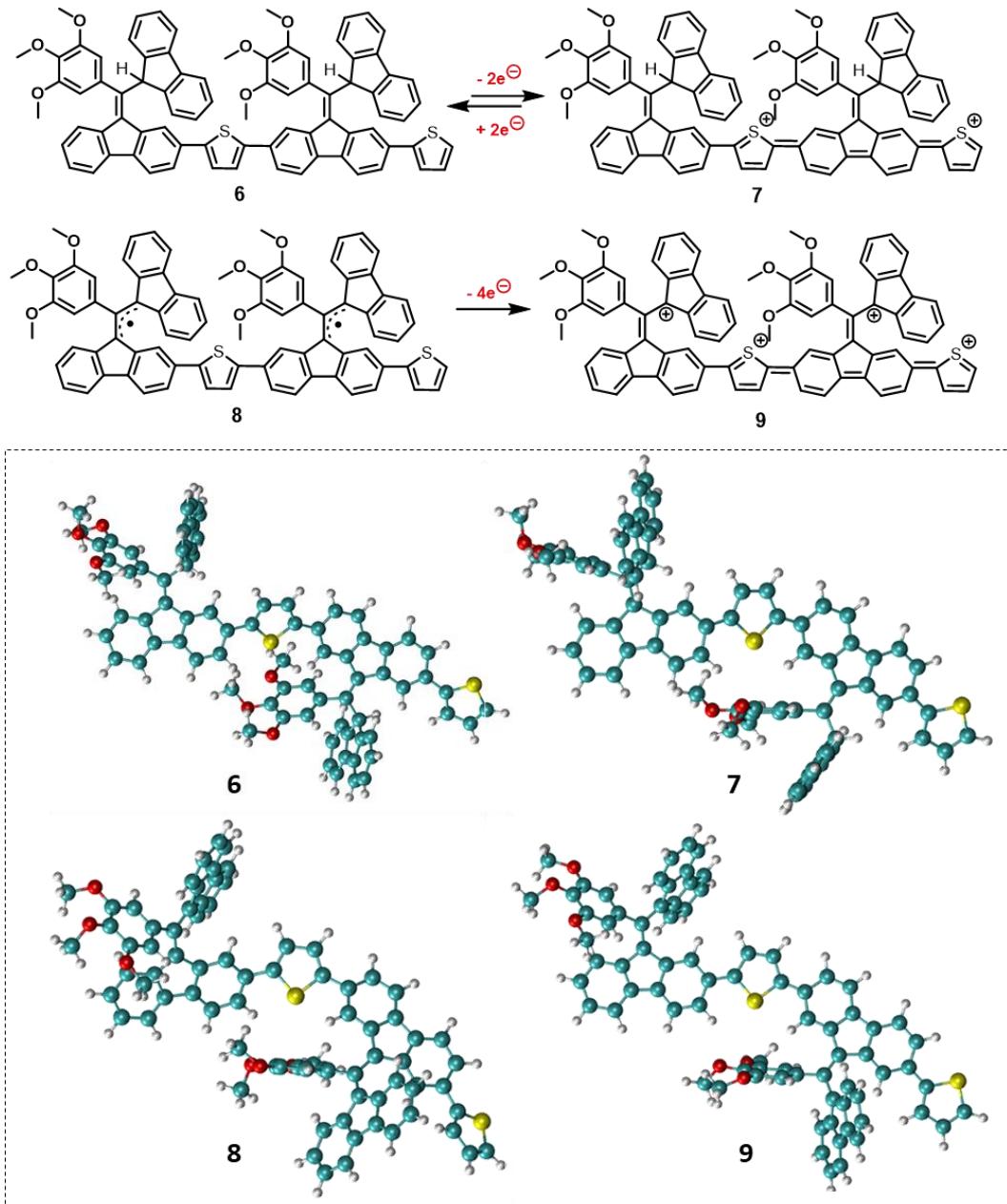


**Figure S12.** Conductivity mapping of polymer films of (a) **P-BT** and **RP-BT**; (b) **P-TT** and **RP-TT** using an interdigitated array electrode with a  $5 \mu\text{m}$  spacing, 499 gaps, and a  $6760 \mu\text{m}$  length (Figure S11). Film thickness was measured on a Dektak 3 surface profilometer. Conductivity profiles were recorded with an applied offset potential of 50 mV and a scan rate of 2 mV/s in acetonitrile electrolyte solution.

## 11. Density Functional Theory (DFT) Calculations

### DFT-optimized geometries of dimers **6**, **7**, **8** and **9**:

Ground-state geometries of dimers **6**, **7**, **8** and **9** were optimized using the restricted ground-state DFT method with the  $\omega$ B97X-D3<sup>3</sup> exchange-correlation (XC) functional and the 6-31G\* basis set. All calculations were performed in the Q-Chem 5.0 package.<sup>4</sup>



**Figure S13.** DFT-optimized geometries of dimers **6**, **7**, **8**, and **9**.

To evaluate the planarity of these dimers, the root-mean-square deviation (RMSD) of the non-H main-chain atoms from their regressed plane was calculated based on DFT-

optimized geometries. For dimers **6**, **7**, **8**, and **9**, we obtained RMSD = 0.579 Å, 0.310 Å, 0.451 Å and 0.164 Å respectively. When the original dimers **6** and **8** were oxidized to **7** and **9**, their single bonds that play key roles in torsions acquire the character of double bonds or quinoids, reducing the bond lengths from 1.471 Å and 1.472 Å to 1.389 Å and 1.385 Å respectively, blocking the torsions, and promoting the electron/hole conductivity. Also, the RMSDs of **8** and **9** are significantly smaller than **6** and **7**, in agreement with the larger conductivity corresponding to the original and *p*-doped **RP-T** (Table S1).

**Table S1.** RMSD for **6**, **7**, **8** and **9**

	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>
RMSD (Å)	0.579	0.310	0.451	0.164

### Spin density of **8**:

Spin density of dimer **8** was evaluated using the single-point restricted open-shell DFT approach based on the  $\omega$ B97X-D3<sup>3</sup> XC functional and the 6-31G\* basis set, and the results were presented in Figure 5b in the main text. The calculation was performed in the Q-Chem 5.0 package.<sup>4</sup>

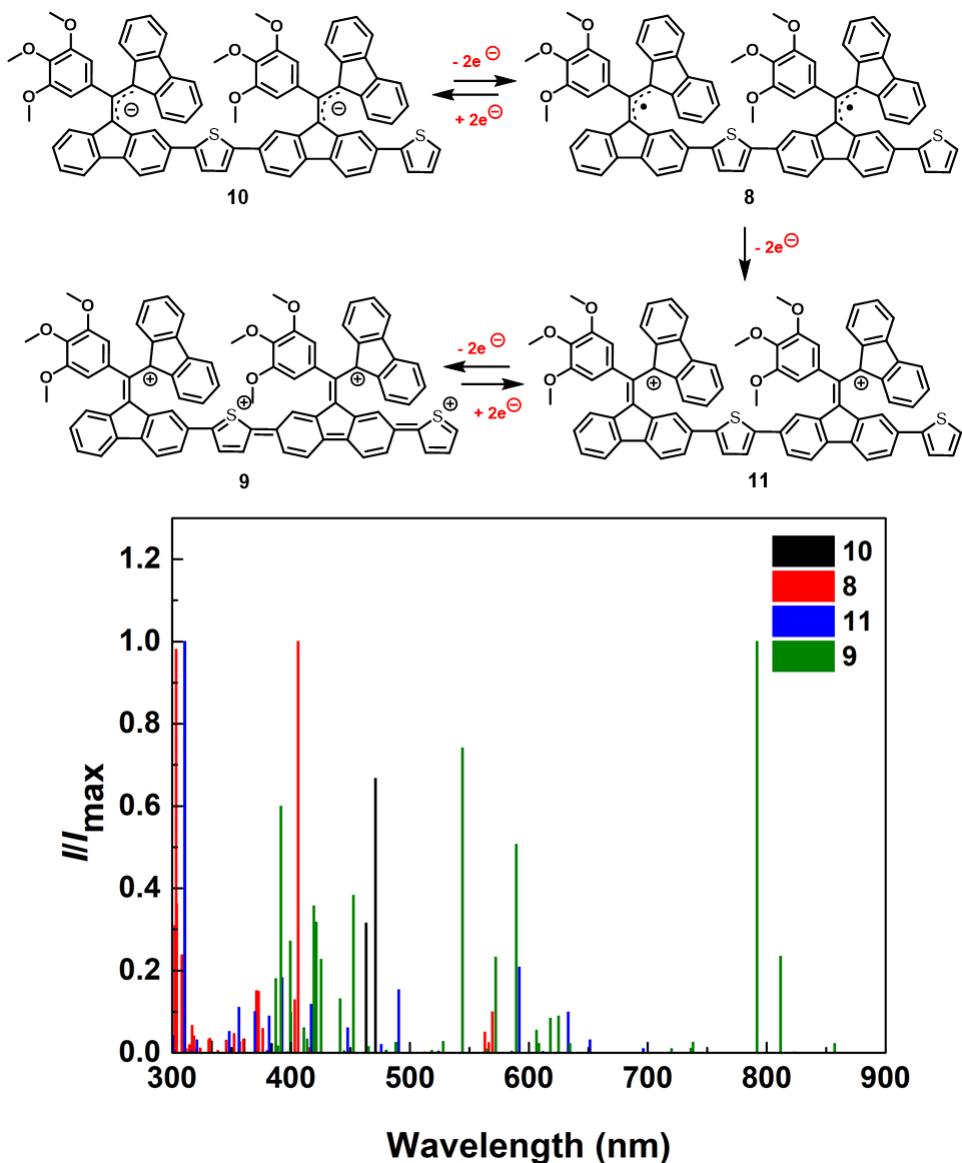
### TDDFT-based simulation of UV-vis spectroelectrochemistry for dimers **8**, **9**, **10**, and **11**:

In order to rationalize the difference between **RP-T** and its different oxidation states, we also evaluated the wavelengths and intensities for the ground-state UV-vis absorptions of dimers **10** (anion), **8**, **11** (cation), and **9** using the time-dependent DFT (TDDFT) approach with the Tamm–Dancoff approximation (TDA).<sup>5</sup> The wavelengths ( $\lambda$ , in nm) and relative intensities ( $I/I_{\max}$ ) associated with the 40 lowest excited states are illustrated in Error! Reference source not found., and the wavelengths, relative intensities and largest orbital contributions of transitions associated with the 5 strongest absorptions are summarized in **Table S2**. All calculations were performed in the Q-Chem 5.0 package.<sup>4</sup>

**Table S2.** Five strongest UV-vis absorptions for dimers **10**, **8**, **11**, and **9**.

10			8		
$\lambda$ (nm)	$I/I_{\max}$	transition	$\lambda$ (nm)	$I/I_{\max}$	transition
319.9	1.00	HOMO-3→LUMO+1 HOMO-2→LUMO HOMO-2→LUMO+2 HOMO-2→LUMO+3	407.3	1.00	SOMO→LUMO SOMO→LUMO+1 HOMO-3→SOMO HOMO-1→LUMO
463.5	0.82	HOMO-1→LUMO HOMO-1→LUMO+1 HOMO→LUMO HOMO→LUMO+1	304.4	0.98	SOMO→LUMO+4 HOMO→SOMO HOMO→LUMO HOMO→LUMO+2
265.0	0.47	HOMO-1→LUMO+3 HOMO-1→LUMO+11 HOMO-1→LUMO+13 HOMO→LUMO+15	304.9	0.36	SOMO→LUMO+4 HOMO-19→SOMO HOMO→LUMO HOMO→LUMO+2
252.6	0.45	HOMO-3→LUMO+2 HOMO-2→LUMO+3 HOMO-1→LUMO+11 HOMO→LUMO+15	303.4	0.31	SOMO→LUMO+4 SOMO→LUMO+5 HOMO-11→SOMO HOMO→LUMO
275.2	0.33	HOMO-6→LUMO HOMO-6→LUMO+1 HOMO-2→LUMO+2 HOMO-1→LUMO+9	287.3	0.27	HOMO→LUMO+2 HOMO-1→LUMO+1 HOMO→LUMO HOMO→LUMO+1
11			9		
$\lambda$ (nm)	$I/I_{\max}$	transition	$\lambda$ (nm)	$I/I_{\max}$	transition
310.4	1.00	HOMO-2→LUMO+4 HOMO→LUMO+2 HOMO→LUMO+4	790.9	1.00	HOMO-3→SOMO HOMO→SOMO SOMO→LUMO+1 HOMO-5→LUMO+1
278.5	0.33	HOMO-4→LUMO+2 HOMO-4→LUMO+3	543.2	0.74	HOMO-5→SOMO HOMO-8→LUMO HOMO-2→LUMO HOMO-5→LUMO+1
592.0	0.21	HOMO-9→LUMO HOMO-4→LUMO	390.4	0.60	HOMO-13→LUMO HOMO-12→LUMO HOMO-11→LUMO HOMO-10→LUMO+1
392.4	0.18	HOMO-14→LUMO	588.3	0.51	SOMO→LUMO+1

		HOMO-12→LUMO HOMO-11→LUMO			HOMO-2→LUMO HOMO-1→LUMO+1 HOMO→LUMO+1
490.6	0.15	HOMO-13→LUMO+1 HOMO-9→LUMO+1 HOMO-1→LUMO+1	451.4	0.38	SOMO→LUMO+5 HOMO-8→LUMO HOMO-7→LUMO HOMO-5→LUMO+1



**Figure S14.** TDDFT-based simulation of UV-vis absorptions for dimers **10**, **8**, **11**, and **9**.

From Error! Reference source not found. we can clearly observe the disappearance of the SOMO $\rightarrow$ LUMO peak (407 nm) from **8** upon its oxidation into **11** or reduction into **10**. Instead, **10** presents two shoulder peaks at 463.5 nm and 458.8 nm, and **11** shows a few shoulder peaks between 447.6 nm and 696.2 nm. These redshifts qualitatively agree with the observations shown in **Figure S5**. It is also worth noting that the lowest excited states involving the HOMO $\rightarrow$ SOMO transition of **8** appear at 567.4 nm and 538.8 nm. Overall these absorptions are blueshifted from experiments because the extension of conjugation in the dimer is smaller than that in the polymer. When the oxidation continues and produces **9**, strong superposition of HOMO $\rightarrow$ SOMO and SOMO $\rightarrow$ LUMO+1 peaks appear at 790.8 nm and 588.3 nm, indicating further redshifts. This trend agrees with our observation of ground-state DFT calculations. Upon oxidation of dimers, SOMOs are more and more delocalized over the conjugated backbones and less energetic.

## **XYZ coordinates (in Å) and energies of dimers 6, 7, 8, 9, 10 and 11.**

The energies and the XYZ coordinates for the optimized geometries of dimers 6, 7, 8, 9, 10, and 11 are provided in the present section.

**6** ( $E = -4330.1518795923$  Hartree)

C -5.571812 1.292635 5.061537  
C -5.003632 1.239682 6.350350  
C -3.554394 1.450894 6.228966  
C -3.261008 1.721606 4.880042  
C -4.518045 1.682602 4.085789  
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C -1.210308 1.293606 6.722538  
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C -6.947556 1.128306 4.906332  
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C -5.791497 0.993934 7.469115  
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C -4.277294 4.031586 1.332204  
C -4.355697 5.083050 -0.850119  
C -5.209649 6.049881 -0.322804  
C -5.581821 6.014953 1.022330  
C -5.109483 5.005913 1.862632  
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C 5.680060 -2.057012 -0.446382  
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C 3.395628 -1.822860 -1.022209  
C 7.001419 -2.463755 -0.592327  
C 7.402543 -3.064427 -1.779392  
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C 5.150646 -2.901127 -2.641251  
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H 4.440763 -3.179328 -3.412006  
H 1.710658 -0.562471 1.018708  
H 4.961470 -0.162267 3.803738  
H 6.519024 -1.165659 2.167551  
H 0.135839 0.638019 -6.554270  
H 0.133239 2.823935 -5.377004  
H 1.185950 3.050805 -3.151782  
H 2.282122 1.096858 -2.068913  
H 2.512240 -4.438300 -3.633491  
H 1.624113 -5.603572 -5.634827  
H 0.542134 -4.327317 -7.453692  
H 0.304761 -1.863940 -7.293080  
H 1.427201 -2.889240 0.632886  
H -0.054462 -1.586294 -3.197455  
H 5.492989 -3.164218 -5.504147  
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H -2.179754 -2.134000 2.114459  
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H -4.830701 -2.946490 0.307417  
H -3.767952 -1.548142 -0.004418  
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H -3.185940 -2.340078 -4.632454  
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H -1.485793 -2.879299 -4.506665

**7** ( $E = -4329.5952262587$  Hartree)

C -6.602417 0.725574 1.472645  
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C -4.525722 -0.277752 1.394771

C -4.285290 1.134057 1.543478  
C -5.606362 1.800490 1.696834  
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C -2.211453 -0.736570 1.059673  
C -1.950444 0.683001 1.036105  
C -3.019669 1.605370 1.325676  
C -8.002247 0.712107 1.436935  
C -8.659220 -0.503780 1.307077  
C -7.975391 -1.731116 1.209983  
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C -7.267186 3.589835 1.939723  
C -4.892004 3.951607 2.824279  
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C -5.248427 6.289400 3.232521  
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C -5.997022 6.009011 5.718750  
C -6.227894 5.071500 6.724420  
C -6.002776 3.711080 6.504460  
C -5.545020 3.263198 5.265445  
C -4.568762 5.755223 0.963552  
C -4.646531 7.110111 0.645438  
C -5.018847 8.041738 1.615056  
C -5.324493 7.640870 2.914028  
C -7.673155 3.834330 0.633841  
C -8.968840 4.289031 0.362872  
C -9.864809 4.486100 1.417966  
C -9.448339 4.220839 2.739604  
C -8.154540 3.781400 3.004658  
C -0.696363 1.114605 0.617847  
C -0.149677 2.450929 0.511467  
C 1.118078 2.484544 0.027482  
C 1.641709 1.181805 -0.319240  
S 0.469018 -0.048352 0.067210  
O -9.243937 4.529069 -0.939031  
O -11.142660 4.900326 1.187743  
O -10.386804 4.432211 3.685116  
C -10.549834 4.280395 -1.455909

C -11.360122 6.287753 1.434371  
C -10.030247 4.201208 5.035385  
H -3.901129 3.488331 2.823694  
C 4.260603 -1.059118 -1.556012  
C 5.368678 -0.149818 -1.681215  
C 6.507083 -0.885889 -2.079454  
C 6.153699 -2.269323 -2.188646  
C 4.733888 -2.441419 -1.803069  
C 7.804212 -0.450674 -2.425027  
C 8.706196 -1.360113 -2.913983  
C 8.350575 -2.726528 -3.096284  
C 7.067072 -3.162045 -2.711987  
C 3.046383 -0.581135 -1.190335  
C 2.860292 0.806826 -0.869239  
C 3.967716 1.711479 -1.051051  
C 5.187569 1.244054 -1.443498  
C 4.008606 -3.574139 -1.626971  
C 2.515032 -3.543245 -1.495484  
C 4.593187 -4.976310 -1.617217  
C 4.000801 -5.824458 -0.499733  
C 3.242908 -6.872862 -1.034844  
C 3.331455 -6.815261 -2.502071  
C 4.147807 -5.734366 -2.861099  
C 2.756119 -7.616694 -3.483216  
C 3.005786 -7.324181 -4.822746  
C 3.814839 -6.243822 -5.178741  
C 4.387962 -5.435745 -4.195681  
C 4.125979 -5.665524 0.871470  
C 3.456995 -6.556441 1.710857  
C 2.683176 -7.589288 1.178470  
C 2.574568 -7.760431 -0.199414  
C 1.865222 -3.491471 -0.265923  
C 0.473893 -3.465605 -0.223120  
C -0.296758 -3.536200 -1.387553  
C 0.364918 -3.674513 -2.623258  
C 1.758761 -3.628525 -2.668985  
C 9.272143 -3.671271 -3.695305  
C 8.986428 -4.933468 -4.184125  
C 10.112099 -5.589868 -4.726986

C 11.246147 -4.825643 -4.644729  
S 10.957195 -3.308192 -3.917821  
O -0.146140 -3.321019 0.991369  
O -1.648947 -3.539123 -1.238869  
O -0.418833 -3.847323 -3.709937  
C -0.736462 -4.529074 1.479958  
C -2.426735 -2.715302 -2.103855  
C 0.202812 -4.164447 -4.946192  
H 5.679246 -4.942113 -1.512454  
H -3.671833 -2.272708 1.196054  
H -1.409359 -1.461316 0.925244  
H -2.820106 2.670875 1.294459  
H -8.586966 1.618788 1.496556  
H -9.745317 -0.505618 1.277803  
H -8.536301 -2.654814 1.111023  
H -6.053558 -2.681096 1.170306  
H -6.177422 7.064529 5.901071  
H -6.585672 5.404070 7.694357  
H -6.186700 2.997988 7.302613  
H -5.388464 2.202005 5.082673  
H -4.308023 5.023806 0.200020  
H -4.428535 7.442241 -0.365382  
H -5.080521 9.093012 1.350221  
H -5.625871 8.374308 3.656342  
H -7.007176 3.669514 -0.206739  
H -7.847734 3.553310 4.016001  
H -0.706639 3.334013 0.802087  
H 1.683358 3.398308 -0.113890  
H -10.409822 4.122117 -2.526792  
H -10.990667 3.386631 -1.004701  
H -11.217584 5.128705 -1.294493  
H -12.410441 6.475249 1.207588  
H -11.163201 6.533503 2.482327  
H -10.726583 6.901041 0.781851  
H -10.909376 4.464576 5.623025  
H -9.782841 3.146010 5.204696  
H -9.181972 4.827217 5.338113  
H 8.080712 0.595111 -2.332927  
H 9.694645 -1.022254 -3.208495

H 6.809143 -4.201269 -2.863432  
 H 2.202191 -1.254179 -1.134798  
 H 3.838472 2.768410 -0.842109  
 H 6.021397 1.928477 -1.558397  
 H 2.123500 -8.459089 -3.217401  
 H 2.569558 -7.946446 -5.599017  
 H 4.000523 -6.032850 -6.228064  
 H 4.995126 -4.579166 -4.481926  
 H 4.730655 -4.863540 1.288665  
 H 3.546956 -6.453034 2.787988  
 H 2.175366 -8.279068 1.846269  
 H 1.986823 -8.578056 -0.608035  
 H 2.410528 -3.448725 0.670015  
 H 2.267877 -3.708923 -3.621898  
 H 7.994707 -5.373303 -4.181772  
 H 10.088707 -6.581645 -5.161889  
 H 12.244573 -5.085376 -4.972383  
 H -1.136929 -4.296584 2.467908  
 H -1.540351 -4.863711 0.817242  
 H 0.025232 -5.312092 1.566379  
 H -3.400877 -2.614931 -1.620984  
 H -1.970738 -1.722987 -2.209462  
 H -2.546290 -3.167226 -3.088919  
 H -0.611599 -4.364234 -5.642199  
 H 0.798965 -3.323820 -5.320342  
 H 0.835589 -5.054978 -4.853060

**8** ( $E_S = -4328.8262223161$  Hartree,  $E_T = -4328.8946616264$  Hartree)

C -6.591083 2.095806 -0.929163  
 C -6.077928 0.954337 -1.588717  
 C -4.649200 1.163501 -1.811534  
 C -4.302558 2.439004 -1.308179  
 C -5.506513 3.067589 -0.759982  
 C -3.696195 0.328696 -2.364778  
 C -2.374575 0.755022 -2.405128  
 C -1.994064 1.992576 -1.855119  
 C -2.963970 2.833713 -1.300245  
 C -7.965002 2.159718 -0.653564  
 C -8.778268 1.085100 -0.996090

C -8.252321 -0.048719 -1.620444  
C -6.895304 -0.114001 -1.929658  
C -5.605847 4.323101 -0.127865  
C -6.664589 4.465783 0.914655  
C -4.813997 5.426702 -0.461084  
C -4.439184 6.547654 0.403962  
C -3.618174 7.433352 -0.334350  
C -3.520259 6.927047 -1.710225  
C -4.253220 5.722401 -1.782571  
C -2.912637 7.457246 -2.839237  
C -3.058948 6.793492 -4.058207  
C -3.830812 5.633157 -4.146603  
C -4.440612 5.097151 -3.018086  
C -4.672672 6.788096 1.759964  
C -4.112317 7.917387 2.349674  
C -3.316504 8.793779 1.610146  
C -3.058345 8.551371 0.260250  
C -7.628770 5.456397 0.788564  
C -8.716741 5.502911 1.664351  
C -8.832413 4.556629 2.689511  
C -7.834014 3.569803 2.827974  
C -6.762337 3.524735 1.945981  
C -0.565348 2.327078 -1.769012  
C 0.097886 3.525633 -1.714654  
C 1.507964 3.376679 -1.541717  
C 1.905580 2.067445 -1.455816  
S 0.541673 1.014956 -1.621919  
O -9.598603 6.517799 1.468433  
O -9.866913 4.643471 3.577789  
O -8.006897 2.706876 3.861450  
C -10.988834 6.241030 1.530803  
C -10.776256 3.549447 3.582783  
C -7.126883 1.604399 3.947535  
C 4.355656 -0.629813 -0.663758  
C 5.580620 -0.082677 -1.116420  
C 6.599147 -1.129154 -0.979661  
C 5.965781 -2.282093 -0.449683  
C 4.550496 -2.001532 -0.219530  
C 7.937110 -1.179618 -1.348686

C 8.642920 -2.371302 -1.199044  
 C 8.012266 -3.533333 -0.723648  
 C 6.663310 -3.484688 -0.373161  
 C 3.201853 0.139211 -0.687449  
 C 3.210108 1.411810 -1.268509  
 C 4.424315 1.941323 -1.727642  
 C 5.610516 1.207466 -1.627570  
 C 3.539781 -2.917276 0.161828  
 C 2.156454 -2.736528 -0.394727  
 C 3.742763 -4.027496 0.988956  
 C 2.983138 -5.288029 0.972126  
 C 3.530803 -6.160488 1.942036  
 C 4.612771 -5.454559 2.635255  
 C 4.734237 -4.169627 2.062864  
 C 5.426139 -5.852676 3.685865  
 C 6.362377 -4.949821 4.188211  
 C 6.456659 -3.660748 3.658242  
 C 5.641056 -3.258450 2.605435  
 C 1.965951 -5.760528 0.133195  
 C 1.494830 -7.059641 0.296539  
 C 2.026908 -7.901932 1.273263  
 C 3.058427 -7.455158 2.097946  
 C 1.061300 -2.660235 0.457472  
 C -0.236492 -2.554521 -0.056958  
 C -0.432895 -2.540887 -1.437823  
 C 0.678905 -2.580037 -2.299693  
 C 1.965693 -2.681112 -1.782952  
 C 8.721917 -4.815633 -0.581100  
 C 8.510155 -5.779752 0.368441  
 C 9.344261 -6.923487 0.200538  
 C 10.177445 -6.812186 -0.871656  
 S 9.952317 -5.317885 -1.696189  
 O -1.254988 -2.521302 0.840298  
 O -1.693463 -2.456924 -1.973436  
 O 0.372334 -2.530432 -3.619544  
 C -2.333784 -1.618203 0.616993  
 C -2.215271 -3.714452 -2.378691  
 C 1.444490 -2.453024 -4.536189  
 H -3.957484 -0.653283 -2.750041

H -1.630788 0.093704 -2.840910  
H -2.662931 3.768835 -0.840312  
H -8.406509 3.029781 -0.180823  
H -9.841415 1.131220 -0.775582  
H -8.906845 -0.877556 -1.876735  
H -6.488933 -0.985792 -2.436449  
H -2.345907 8.383157 -2.785937  
H -2.588268 7.195618 -4.951159  
H -3.962408 5.144446 -5.107927  
H -5.054004 4.206133 -3.106907  
H -5.286150 6.114387 2.348688  
H -4.299705 8.117962 3.400507  
H -2.889722 9.669655 2.090530  
H -2.426687 9.227181 -0.310626  
H -7.585257 6.181745 -0.017232  
H -6.009867 2.748339 2.019738  
H -0.405295 4.483927 -1.800045  
H 2.193519 4.213254 -1.457028  
H -11.476361 7.031141 0.955576  
H -11.217159 5.272294 1.068046  
H -11.357575 6.251272 2.558668  
H -11.611257 3.853439 4.217028  
H -11.146651 3.344925 2.569465  
H -10.312451 2.647629 3.988722  
H -7.475645 1.009434 4.792379  
H -7.158183 0.998004 3.033509  
H -6.095990 1.927259 4.136237  
H 8.433229 -0.304830 -1.760534  
H 9.696983 -2.406531 -1.462047  
H 6.160341 -4.397251 -0.072176  
H 2.278864 -0.261788 -0.285272  
H 4.435367 2.920047 -2.199014  
H 6.539623 1.639028 -1.990592  
H 5.330791 -6.846109 4.117262  
H 7.011813 -5.245166 5.007549  
H 7.175619 -2.960303 4.072938  
H 5.717788 -2.251418 2.209713  
H 1.536855 -5.136075 -0.641985  
H 0.699597 -7.421298 -0.349890

H 1.643224 -8.912497 1.384844  
 H 3.489184 -8.117938 2.844345  
 H 1.185736 -2.698724 1.534450  
 H 2.829583 -2.730707 -2.435635  
 H 7.792223 -5.663998 1.174887  
 H 9.325642 -7.786977 0.856176  
 H 10.909473 -7.524889 -1.227770  
 H -2.736990 -1.389311 1.605997  
 H -1.988815 -0.695768 0.138804  
 H -3.114504 -2.063629 -0.004852  
 H -3.222583 -3.525094 -2.756612  
 H -1.605066 -4.152956 -3.175893  
 H -2.268332 -4.406511 -1.528927  
 H 0.987679 -2.352865 -5.521497  
 H 2.074124 -1.578207 -4.334520  
 H 2.060569 -3.360765 -4.513182  
**9** ( $E = -4327.5727052132$  Hartree)  
 C -6.827395 2.450067 -0.458666  
 C -6.349863 1.133012 -0.635540  
 C -4.911888 1.164132 -0.648918  
 C -4.458390 2.512527 -0.527716  
 C -5.676138 3.375361 -0.357471  
 C -4.022575 0.088692 -0.757770  
 C -2.677942 0.341625 -0.745480  
 C -2.182231 1.675123 -0.627961  
 C -3.106847 2.761899 -0.505053  
 C -8.202050 2.685521 -0.529874  
 C -9.057513 1.602094 -0.722936  
 C -8.576206 0.294199 -0.848873  
 C -7.210811 0.049808 -0.818079  
 C -5.773797 4.705342 -0.054745  
 C -7.030802 5.273505 0.506131  
 C -4.735908 5.683091 -0.305754  
 C -4.334685 6.768917 0.540371  
 C -3.345472 7.530410 -0.142689  
 C -3.167000 6.926754 -1.490178  
 C -4.034044 5.808074 -1.564908  
 C -2.434785 7.304944 -2.589819

C -2.587883 6.562394 -3.780910  
C -3.463717 5.485009 -3.868492  
C -4.217819 5.105758 -2.756194  
C -4.757694 7.120658 1.827154  
C -4.181224 8.239897 2.426271  
C -3.217617 8.980006 1.747793  
C -2.783096 8.630612 0.448968  
C -7.686411 6.277598 -0.187913  
C -8.912238 6.786897 0.275441  
C -9.455274 6.286612 1.469957  
C -8.759672 5.274894 2.180067  
C -7.557614 4.761722 1.702271  
C -0.783823 1.883095 -0.627651  
C -0.054367 3.118508 -0.696291  
C 1.297437 2.954736 -0.716176  
C 1.718138 1.580204 -0.645966  
S 0.304558 0.543454 -0.562367  
O -9.427212 7.754603 -0.493054  
O -10.574529 6.839839 1.989058  
O -9.348305 4.886249 3.324387  
C -10.808887 8.127049 -0.450343  
C -11.738280 6.012313 2.093623  
C -8.751297 3.849022 4.081672  
C 4.382321 -0.951131 -0.552558  
C 5.566412 -0.122159 -0.663784  
C 6.699544 -0.937552 -0.655714  
C 6.292429 -2.314817 -0.530079  
C 4.818546 -2.361354 -0.395830  
C 8.077874 -0.628044 -0.809749  
C 8.982955 -1.645708 -0.890988  
C 8.582665 -3.024968 -0.845364  
C 7.199169 -3.327738 -0.647521  
C 3.151766 -0.390392 -0.521547  
C 2.994347 1.040921 -0.637707  
C 4.187995 1.854954 -0.753246  
C 5.427329 1.298342 -0.767732  
C 4.027336 -3.432963 -0.157435  
C 2.535957 -3.405980 -0.276844  
C 4.513575 -4.736873 0.314878

C 4.390298 -5.993054 -0.365049  
 C 4.881070 -7.016465 0.492752  
 C 5.295867 -6.366009 1.764370  
 C 5.061064 -4.970790 1.617368  
 C 5.792967 -6.865495 2.938246  
 C 6.054504 -5.952213 3.986943  
 C 5.816773 -4.586008 3.856617  
 C 5.307230 -4.076256 2.663023  
 C 3.914910 -6.289329 -1.647130  
 C 3.929009 -7.619699 -2.066542  
 C 4.407683 -8.614009 -1.218218  
 C 4.894049 -8.322970 0.078056  
 C 1.756777 -3.576409 0.855599  
 C 0.355583 -3.474746 0.780547  
 C -0.246261 -3.204662 -0.454582  
 C 0.557201 -3.089407 -1.613995  
 C 1.943277 -3.196687 -1.532640  
 C 9.527066 -4.073425 -1.019119  
 C 9.281462 -5.453127 -1.073348  
 C 10.432383 -6.212759 -1.286241  
 C 11.562245 -5.420516 -1.393003  
 S 11.232651 -3.767405 -1.240241  
 O -0.285066 -3.593383 1.952175  
 O -1.583893 -2.950862 -0.522900  
 O -0.123161 -2.813228 -2.742117  
 C -1.607633 -4.134706 2.024032  
 C -2.384374 -3.867432 -1.286946  
 C 0.582066 -2.777621 -3.975153  
 H -4.391039 -0.927698 -0.848372  
 H -1.999999 -0.504329 -0.841002  
 H -2.729139 3.770362 -0.381069  
 H -8.619964 3.680176 -0.445407  
 H -10.127215 1.779898 -0.778556  
 H -9.274224 -0.524914 -0.990054  
 H -6.831349 -0.959036 -0.950656  
 H -1.781250 8.171682 -2.573717  
 H -2.031999 6.865917 -4.663486  
 H -3.590566 4.966660 -4.813307  
 H -4.951200 4.307362 -2.831437

H -5.537946 6.558045 2.330931  
H -4.500424 8.548261 3.415821  
H -2.793475 9.859693 2.222872  
H -2.039205 9.238255 -0.056915  
H -7.309812 6.668229 -1.128810  
H -7.039086 3.970212 2.231223  
H -0.545539 4.082202 -0.759554  
H 1.996506 3.780354 -0.782283  
H -10.949087 8.763980 -1.323311  
H -11.452384 7.246075 -0.538082  
H -11.045601 8.677009 0.459715  
H -12.554599 6.684370 2.357163  
H -11.955056 5.533462 1.131084  
H -11.615968 5.255100 2.869678  
H -9.400458 3.700371 4.943460  
H -8.694559 2.919433 3.501758  
H -7.751143 4.136302 4.427004  
H 8.410730 0.402365 -0.882764  
H 10.032161 -1.403288 -1.025212  
H 6.882060 -4.364323 -0.629598  
H 2.272609 -1.013020 -0.414680  
H 4.090234 2.931644 -0.838076  
H 6.306356 1.927885 -0.856059  
H 5.976279 -7.925791 3.083014  
H 6.444269 -6.334093 4.926163  
H 6.020440 -3.923158 4.690304  
H 5.097796 -3.016176 2.551501  
H 3.530160 -5.510776 -2.298768  
H 3.563603 -7.884472 -3.053074  
H 4.407294 -9.645985 -1.558003  
H 5.256058 -9.126930 0.711464  
H 2.190298 -3.769877 1.831657  
H 2.563304 -3.063672 -2.412359  
H 8.296828 -5.896405 -0.973455  
H 10.456504 -7.292642 -1.364984  
H 12.580531 -5.754347 -1.556773  
H -1.730719 -4.447686 3.060496  
H -2.356644 -3.384255 1.768716  
H -1.707130 -5.006014 1.368983

H -3.396755 -3.793015 -0.886008  
H -2.374774 -3.601279 -2.345134  
H -2.023110 -4.892510 -1.160306  
H -0.171561 -2.613986 -4.744283  
H 1.304928 -1.953721 -3.993263  
H 1.091720 -3.728698 -4.164365

**10** ( $E = -4329.0236013593$  Hartree)

C -6.785663 2.401373 -0.892539  
C -6.308169 1.177356 -1.428752  
C -4.867651 1.273687 -1.537663  
C -4.466984 2.558823 -1.086586  
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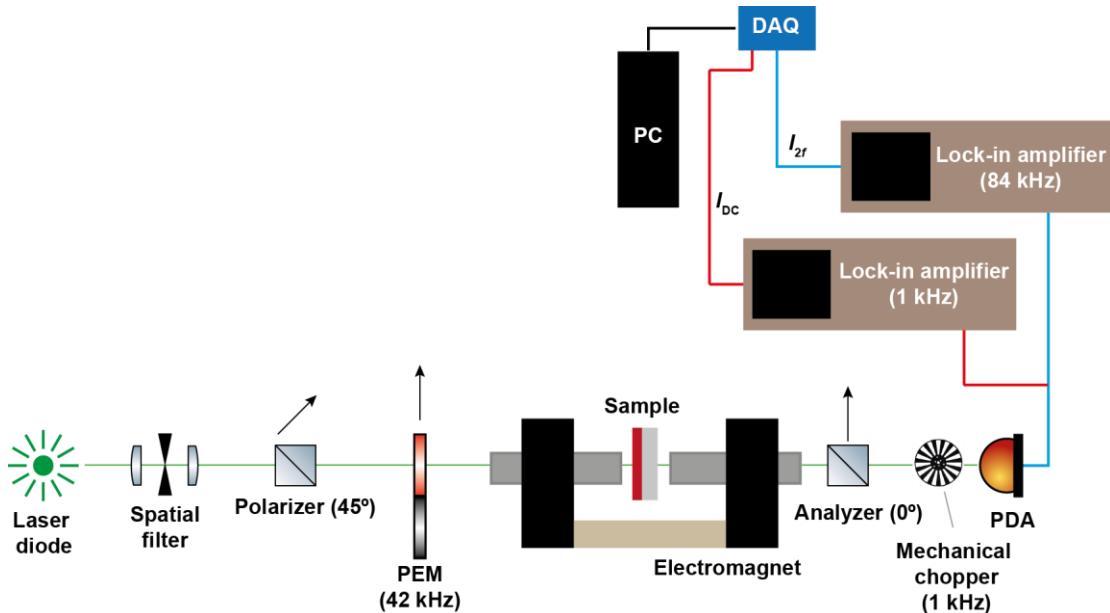
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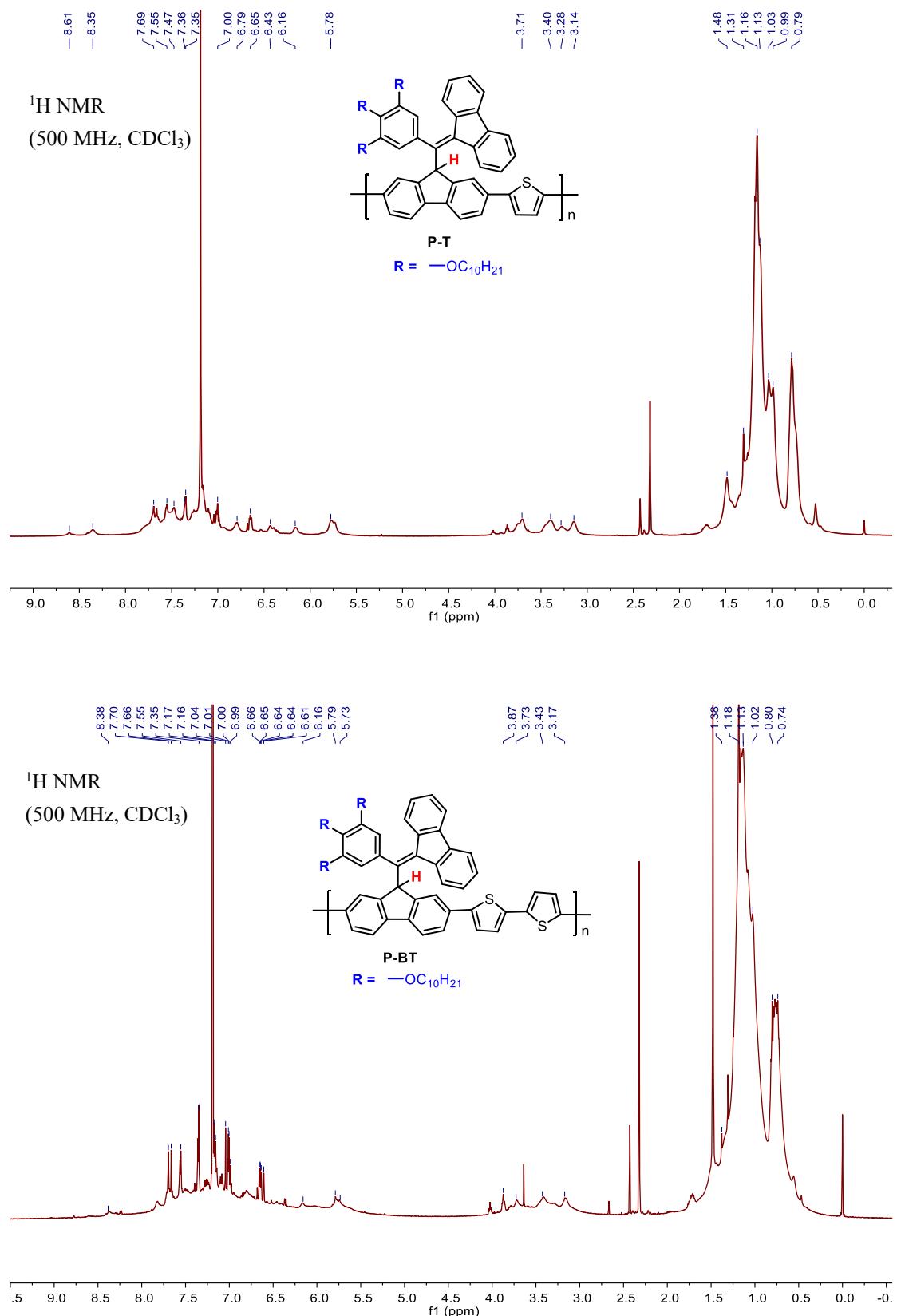
## 12. Instrumental Setup for Faraday Rotation Measurement

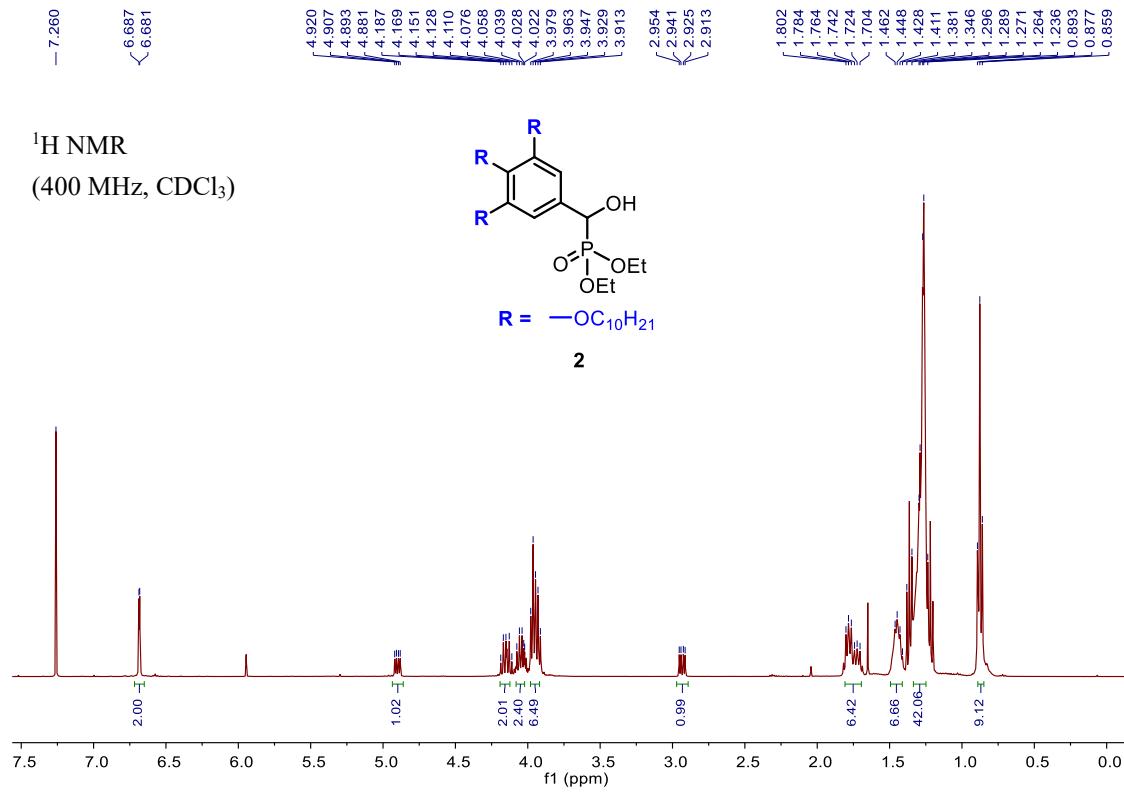
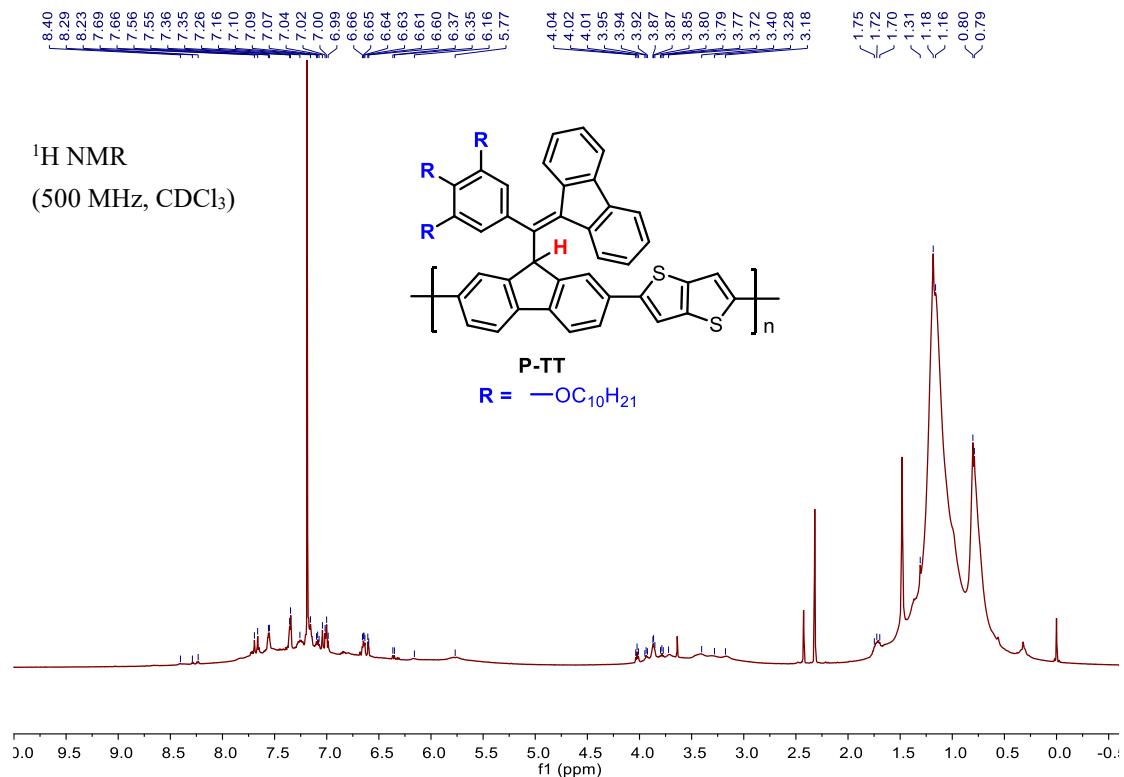
The construction and operation of the instrument for Faraday rotation measurement follow the description in our earlier study,<sup>6</sup> with the addition of a spatial filter ( $10\times$  objective,  $25\ \mu\text{m}$  pinhole) between the laser diode module and the polarizer (**Figure S15**). This addition improves the homogeneity of the laser beam profile.



**Figure S15.** Schematic of the instrument for Faraday rotation measurement. The arrows above the PEM, the polarizer, and the analyzer show the relative orientations of their optical axes. The laser diode is slightly polarized and is oriented as close to  $45^\circ$  as possible to ensure maximum transmission through the polarizer. Green lines show light propagation; red lines show the collection and conditioning of the DC part of the signal; blue lines show the collection and conditioning of the AC part of the signal. The abbreviations PEM = photoelastic modulator, PDA = photodiode array (detector), DAQ = digital acquisition controller, and PC = personal computer.

### 13. NMR Spectra





— 152.96

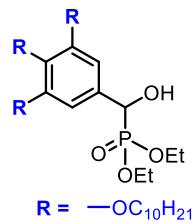
— 137.86

— 131.22

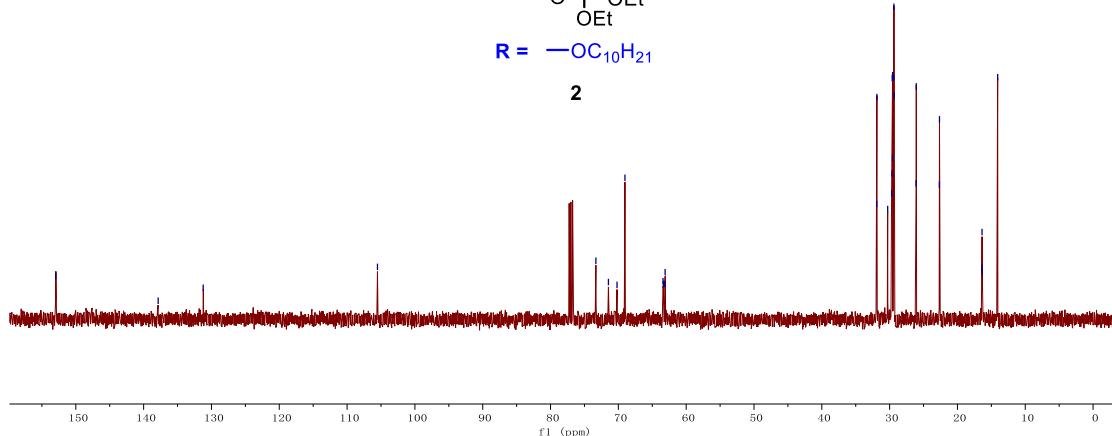
— 105.52

$^{13}\text{C}$  NMR

(126 MHz,  $\text{CDCl}_3$ )



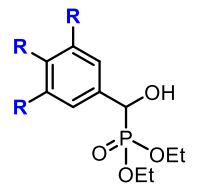
**2**



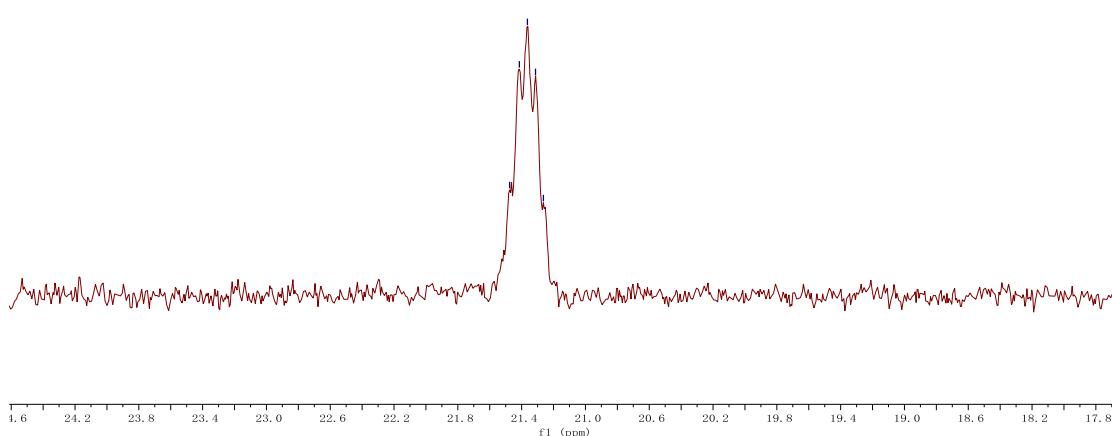
$^{31}\text{P}$  NMR

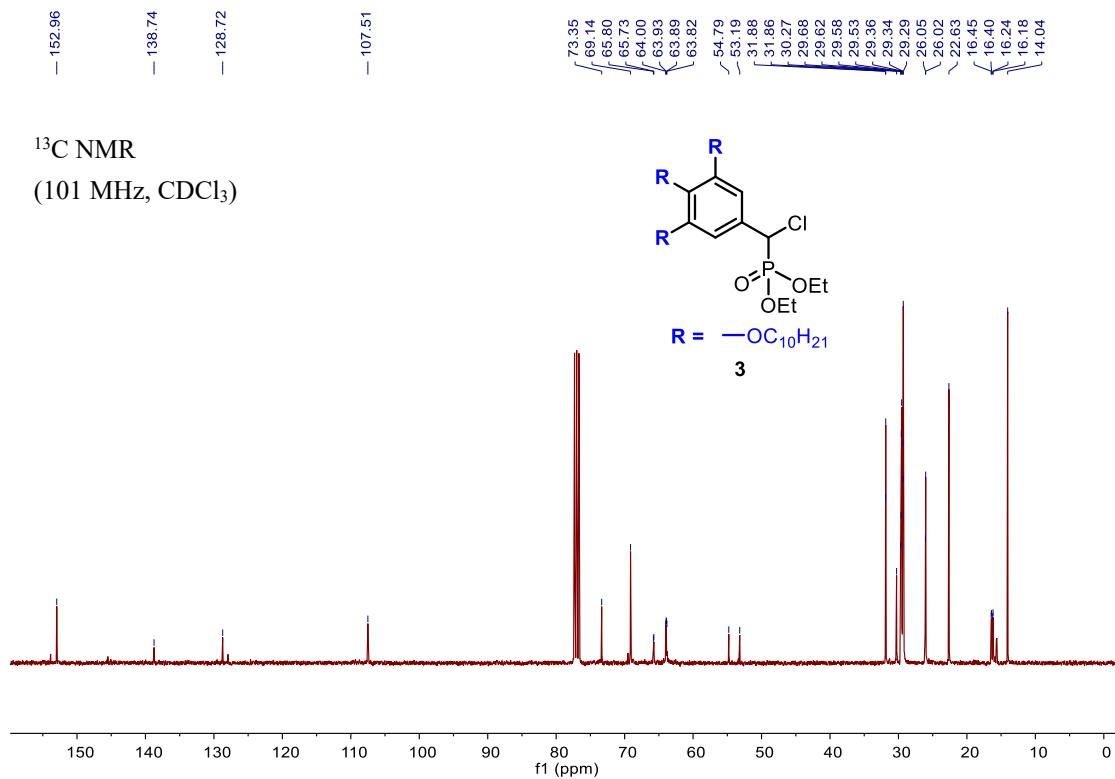
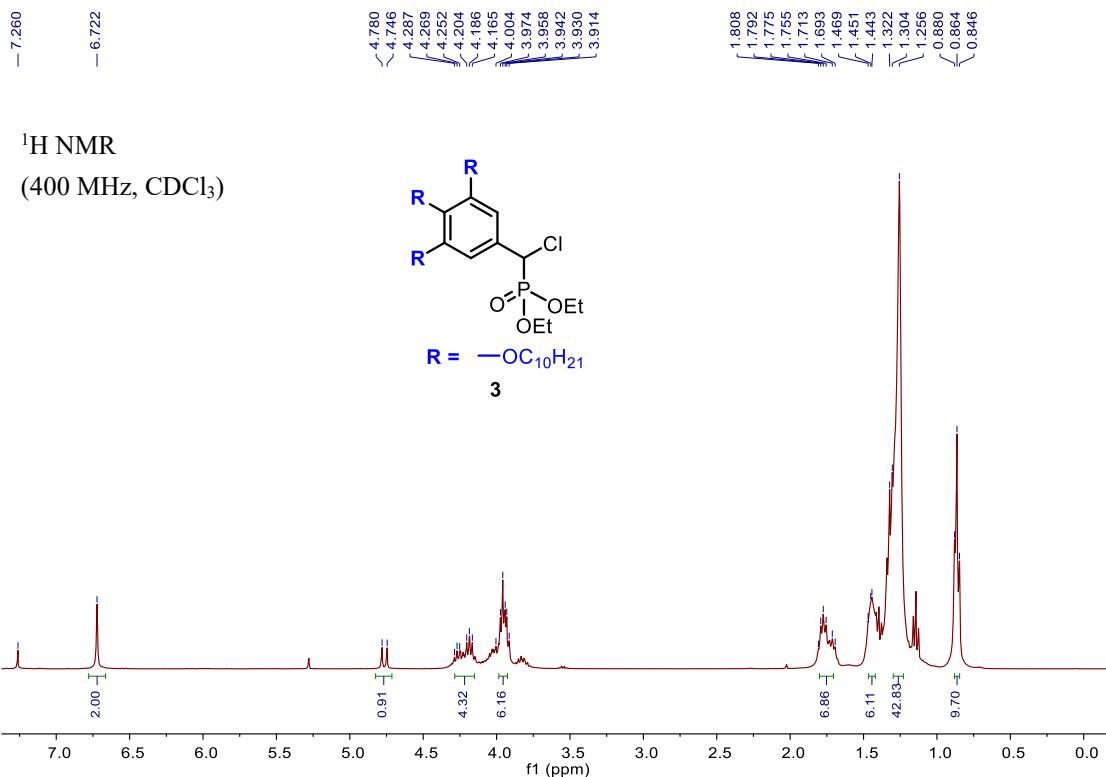
(162 MHz,  $\text{CDCl}_3$ )

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211.41  
211.36  
211.31  
211.26

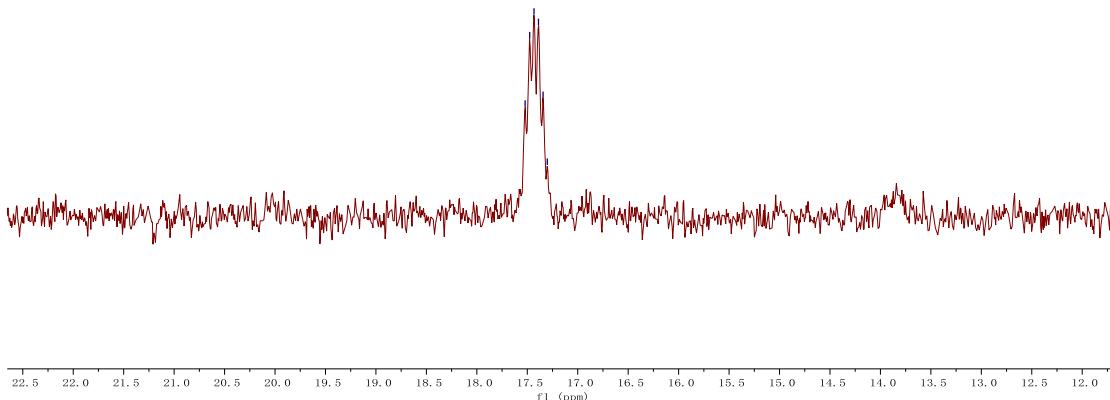
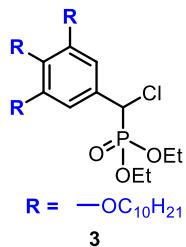


**2**





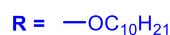
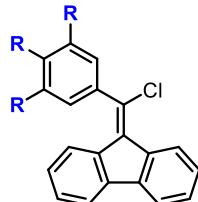
<sup>31</sup>P NMR  
(162 MHz, CDCl<sub>3</sub>)



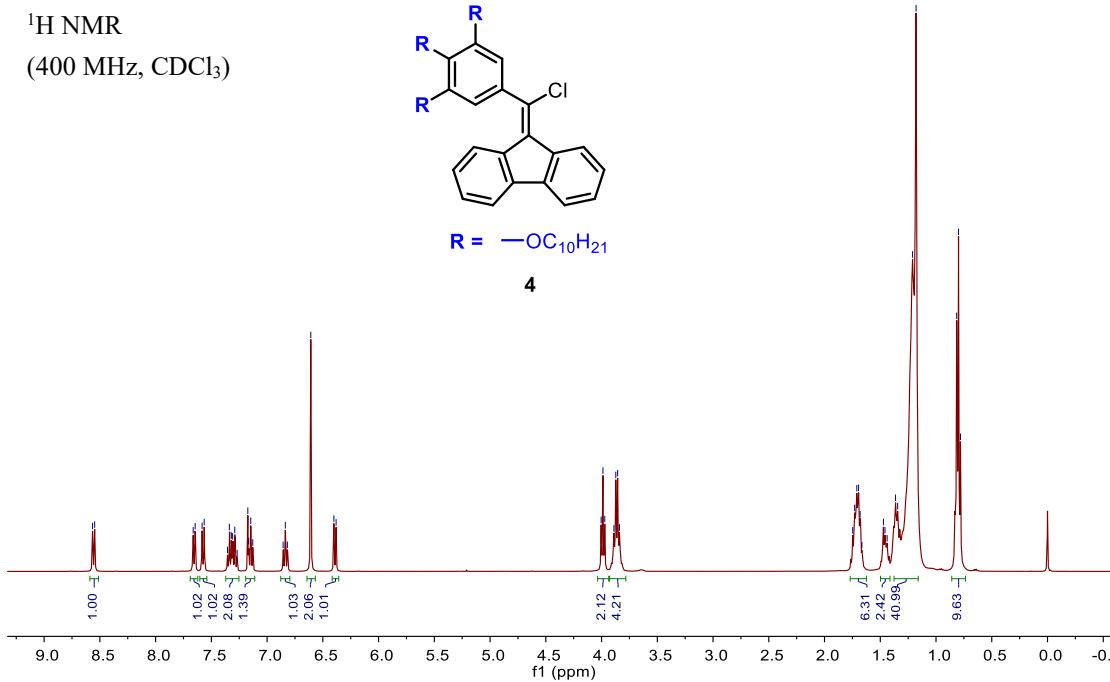
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7.555  
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7.268  
7.173  
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7.147  
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6.818  
6.808  
6.401  
6.381

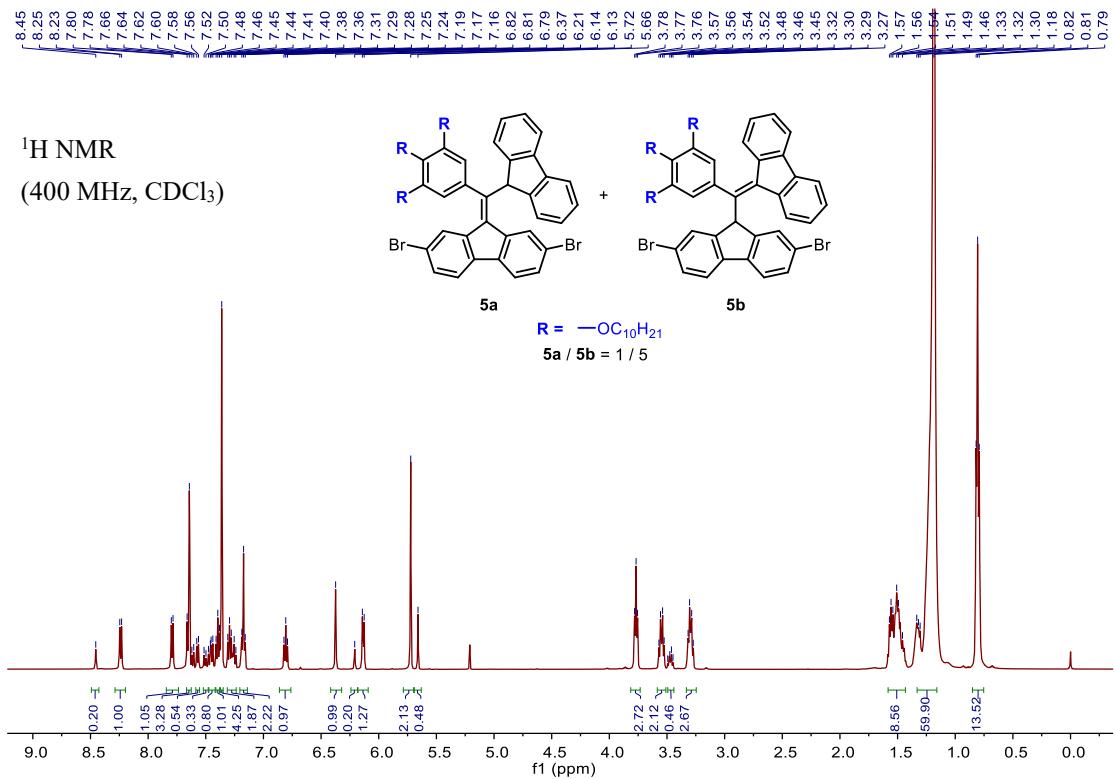
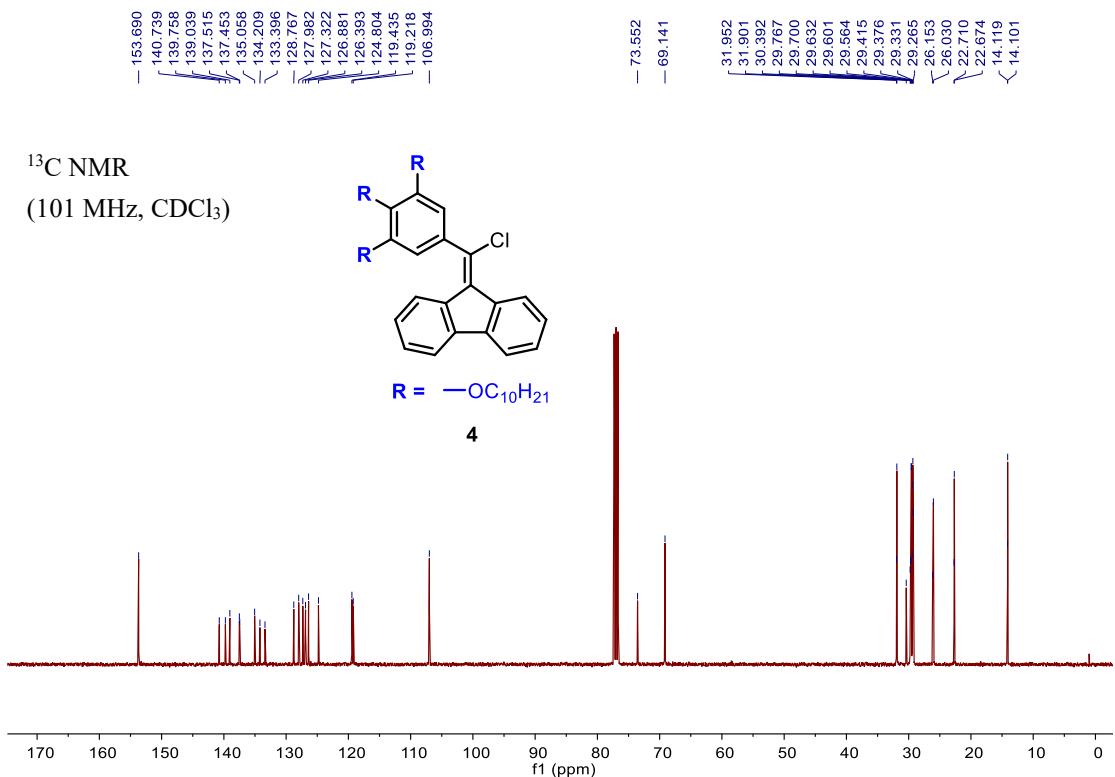
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3.971  
3.889  
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3.839

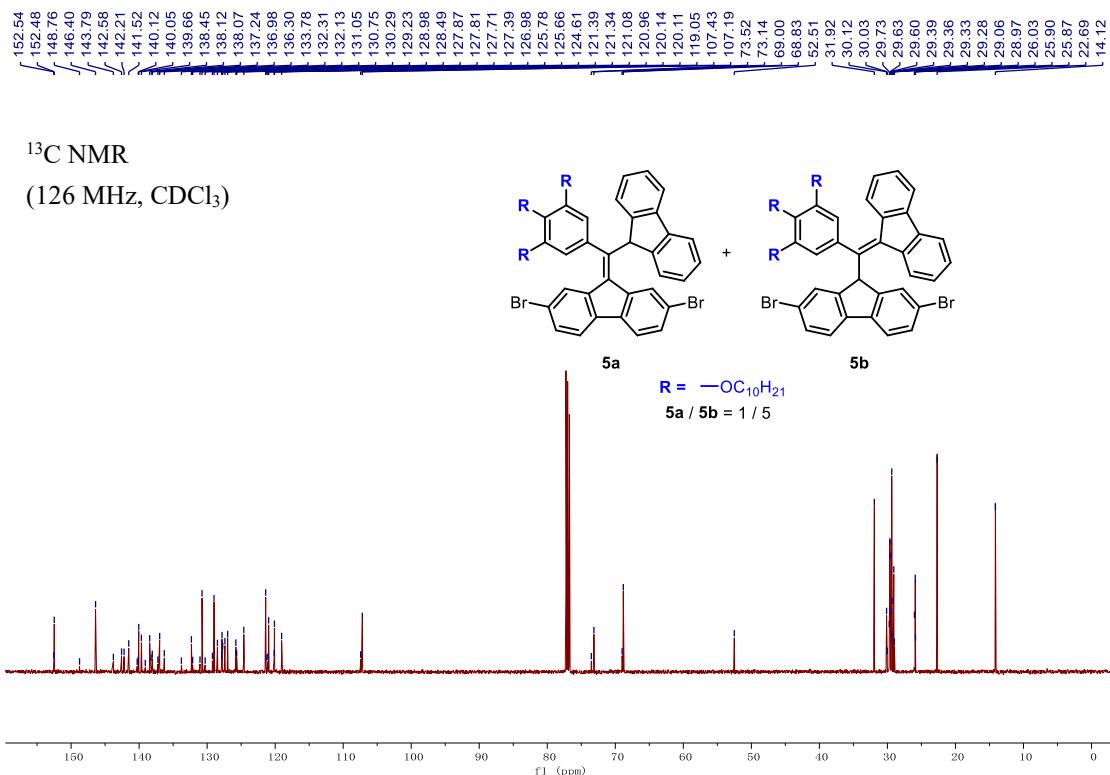
<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)



**4**







## 14. References

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