

Supporting Information

Tunable green electrochromic polymers via direct arylation polymerization

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Experimental Section

Materials and characterizations

All reagents were purchased from Sigma Aldrich, Acros or Alfa Aesar and used without further purification unless otherwise noted. Anhydrous N,N-dimethylformamide is prepared from MB-SPS solvent purifying system. ITO slides (CG-501N-CUV) were purchased from delta technologies, LTD. Anhydrous propylene carbonate (PC), Tetrabutylammonium hexafluorophosphate (TBAPF₆) (≥ 99.0%, for electrochemical analysis), silver wire (≥ 99.0%) with 1.5 mm diameter, platinum wire (99.0%) with 0.5 mm in diameter were purchased from Sigma-Aldrich. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX 400 or Mercury 300 at 293 K with deuterized chloroform as solvent. Size exclusive chromatography (SEC) was performed in tetrahydrofuran under room temperature with calibration curve based on polystyrene standards. UV-vis-NIR spectra were measured with an Agilent Technologies Cary 6000i UV-Vis-NIR spectrophotometer or Agilent Cary 5000 UV-Vis-NIR spectrophotometer. All solution spectra were collected in chloroform and thin film spectra from drop-casted samples on glass substrate. All the electrochemistry related experiments were performed using BioLogic SP-150. CV experiments were carried out by using a conventional three-electrode system. The working electrode is ITO coated by polymer thin film; the pseudoreference electrode is an Ag wire coated by AgCl; the counter electrode is the platinum wire; the electrolyte is 0.2 M TBAPF₆ in PC.

Fabrication of devices.

The working electrode was prepared by spin-coating of the 40mg/ml P4 solution onto the

ITO substrate with an area of 2.5 x 2.5 cm. The counter electrode was prepared by drop-casting of PEDOT/PSS solution onto the ITO substrate where the center area was covered by a 0.05 mm thick tape with an area of 1.6 x 1.6 cm and dried at 100 °C oven. The electrolytes were 0.2 M TBAPF₆ dissolved in propylene carbonate. The tape on the counter-electrode was removed, and the two as-prepared electrodes were laminated and sealed by the epoxy with leaving two holes for the filling of liquid electrolytes and removing the bubbles. After adding the electrolyte, the holes were sealed by epoxy.

Device characterization

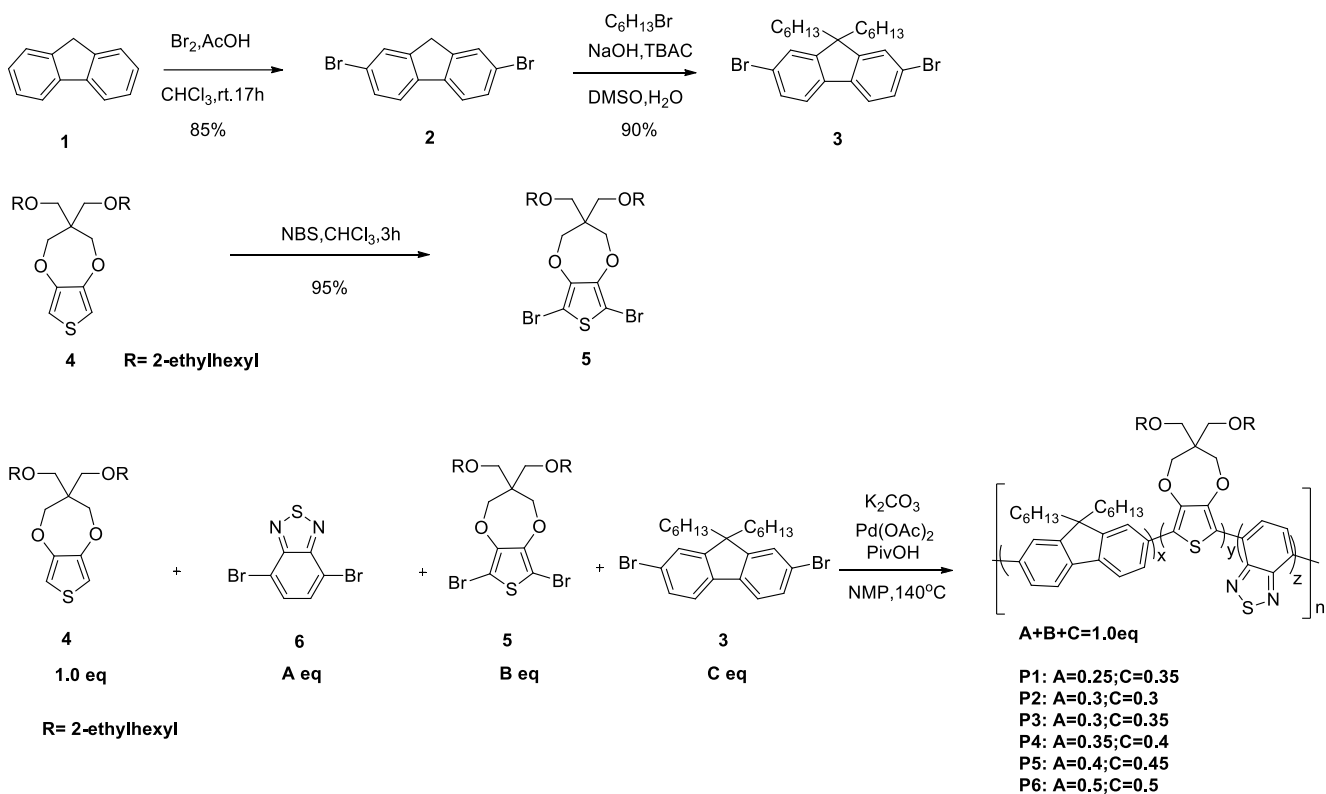
CV cycles were performed to condition the device prior to the spectro-electrochemical and double-potential chronoamperometric experiments. In the spectro-electrochemical measurement, a - 0.6 V was applied for 2 mins to reset the device, and thereafter the colored state spectrum was taken. The bleached state spectrum was measured after a 1.2 V was applied for 2 mins to bleach the device. In the double-potential chronoamperometric experiment, 1.2 V and -0.6 V were applied for 60 s alternatively. In the meanwhile, the transmittance was measured at 430 nm to record the color switching of the device.

General method for polymerization

To a Schlenk flask was added 3,4-propylenedioxythiophene (1.0 eq.), 4,7-Dibromo-2,1,3-benzothiadiazole (A eq.), dibromo-3,4-propylenedioxythiophene (B eq.), 2,7-dibromo-9,9-dihexyl-9H-fluorene (C eq.), K₂CO₃ (2.6 eq.), PivOH (0.3 eq.) and Pd(OAc)₂ (0.02 eq.) into the tube. The flask was kept under vacuum for about 15 min and

purged with N₂, and this process was repeated three times. Then, nitrogen degassed solvent NMP (1.0 g 3,4-propylenedioxythiophene use 30 ml of solvent) was added to the flask and the flask was heated in an oil bath at 120°C for 6h under nitrogen. Transfer the hot reaction mixture to a 1:1 mixture solvent of CH₃OH and 1M HCl with stir. Filter to get the solid. The solid was dissolved in chloroform and washed with 1M HCl solution. The organic phase was concentrated and precipitate with CH₃OH. Filter and dry to get the polymer.

Synthesis



Compound 3 and compound 5 was prepared by the reported method.^{1,2}

2,7-dibromofluorene (Compound 2). Fluorene (1 g, 6 mmol) was added into 10ml of

CHCl₃ and bubble with N₂ for 15min. 1.2ml of Br₂ (24mmol) was dissolved in 10ml of acetic acid and added into the fluorene CHCl₃ solution in 10min at 0°C. After 2h the reaction mixture was quenched with 20ml of 10% sodium thiosulfate. The white solid was filtered and dried. The filtrate was extracted with 20ml CHCl₃ and distilled with rotovape. Combine the solid and slurry with methanol to get 1.7g white solid. 85%. ¹H NMR (300MHz, CDCl₃), δ (ppm): 7.67 (d, 2H, $J = 0.9$ Hz), 7.61 (d, 2H, $J = 8.1$ Hz), 7.51 (dd, 2H, $J_1 = 8.1$ Hz, $J_2 = 1.2$ Hz), 3.87 (s, 2H).

2,7-dibromo-9,9-dihexyl-9H-fluorene (Compound 3). To a 100ml schlenk tube was added 2,7-dibromofluorene (1g, 3.1 mmol), tetrabutylammonium chloride (0.1g, 0.36mmol). Vacuum and purged with N₂ for three times. 8ml of DMSO was added and heat to 60°C to dissolve the solid. 1-bromohexane (1.3 g, 8 mmol) was added and cool to room temperature. 5ml of 50% aqueous NaOH was added to the mixture. After 12h, 50ml of hexane and 100ml water was added, the hexane phase was washed with 50ml 1N HCl solution and water. The crude material was submitted to silica gel chromatography(100%hexane) to get 1.3g white solid. (90%). ¹H NMR (300MHz, CDCl₃), δ (ppm): 7.53-7.50 (m, 2H), 7.46-7.43 (m, 4H), 1.94-1.88 (m, 4H), 1.13-1.03 (m, 12H), 0.8-0.75 (m, 6H), 0.59-0.55 (m, 4H).

Dibromo-3,4-propylenedioxythiophene (Compound 5). To 250ml flask was added compound 4 (5g, 11.4mmol), DCM 100ml and degas with N₂ for 10min. N-bromosuccinimide (NBS, 5.05g, 28.4mmol) was dissolved in acetonitrile and drop into the flask at 0 °C. After 2h quench the reaction with 10% Na₂CO₃ and wash the organic phase with water. The crude oil was submitted to silica gel chromatography(hexane/DCM=4/1) get colorless oil 6.5g (95%). ¹H NMR (300MHz,

CDCl₃), δ (ppm): 4.07 (s, 4H), 3.48 (s, 4H), 3.28 (d, 4H, $J = 5.7$ Hz), 1.47-1.45 (m, 2H), 1.35-1.25 (m, 16H), 0.91-0.84 (m, 12H).

For P1. Follow the general method for polymerization. Use 3,4-propylenedioxythiophene (0.22 g, 1.0 eq.), 4,7-Dibromo-2,1,3-benzothiadiazole (0.037 g, 0.25 eq.), dibromo-3,4-propylenedioxythiophene (0.12 g, 0.4 eq.), 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.086 g, 0.35 eq.) for polymerization. 0.23g polymer P1 was got. Yield=60%. ($M_n=14.6$ kDa, PDI=1.9)

For P2. Follow the general method for polymerization. Use 3,4-propylenedioxythiophene (0.22 g, 1.0 eq.), 4,7-Dibromo-2,1,3-benzothiadiazole (0.044 g, 0.3 eq.), dibromo-3,4-propylenedioxythiophene (0.12 g, 0.4 eq.), 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.074 g, 0.3 eq.) for polymerization. 0.24g polymer P2 was got. Yield=64%. ($M_n=7.9$ kDa, PDI=1.5)

For P3. Follow the general method for polymerization. Use 3,4-propylenedioxythiophene (0.22 g, 1.0 eq.), 4,7-Dibromo-2,1,3-benzothiadiazole (0.044 g, 0.3 eq.), dibromo-3,4-propylenedioxythiophene (0.105 g, 0.35 eq.), 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.086 g, 0.35 eq.) for polymerization. 0.24g polymer P3 was got. Yield=64%. ($M_n=18.4$ kDa, PDI=2.5)

For P4. Follow the general method for polymerization. Use 3,4-propylenedioxythiophene (0.3 g, 1.0 eq.), 4,7-Dibromo-2,1,3-benzothiadiazole (0.07 g, 0.35 eq.), dibromo-3,4-propylenedioxythiophene (0.102 g, 0.25 eq.), 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.134 g, 0.4 eq.) for polymerization. 0.41g polymer P4 was got. Yield=83%. ($M_n=17.3$ kDa, PDI=2.4)

For P5. Follow the general method for polymerization. Use 3,4-propylenedioxythiophene

(0.3 g, 1.0 eq.), 4,7-Dibromo-2,1,3-benzothiadiazole (0.08 g, 0.4 eq.), dibromo-3,4-propylenedioxythiophene (0.061 g, 0.15 eq.), 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.151 g, 0.45 eq.) for polymerization. 0.39g polymer P5 was got. Yield=81%. ($M_n=18.5\text{kDa}$, PDI=2.9)

For P6. Follow the general method for polymerization. Use 3,4-propylenedioxythiophene (0.25 g, 1.0 eq.), 4,7-Dibromo-2,1,3-benzothiadiazole (0.083 g, 0.5 eq.), 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.14 g, 0.5 eq.) for polymerization. 0.29g polymer P6 was got. Yield=76%. ($M_n=13.4\text{kDa}$, PDI=2.5)

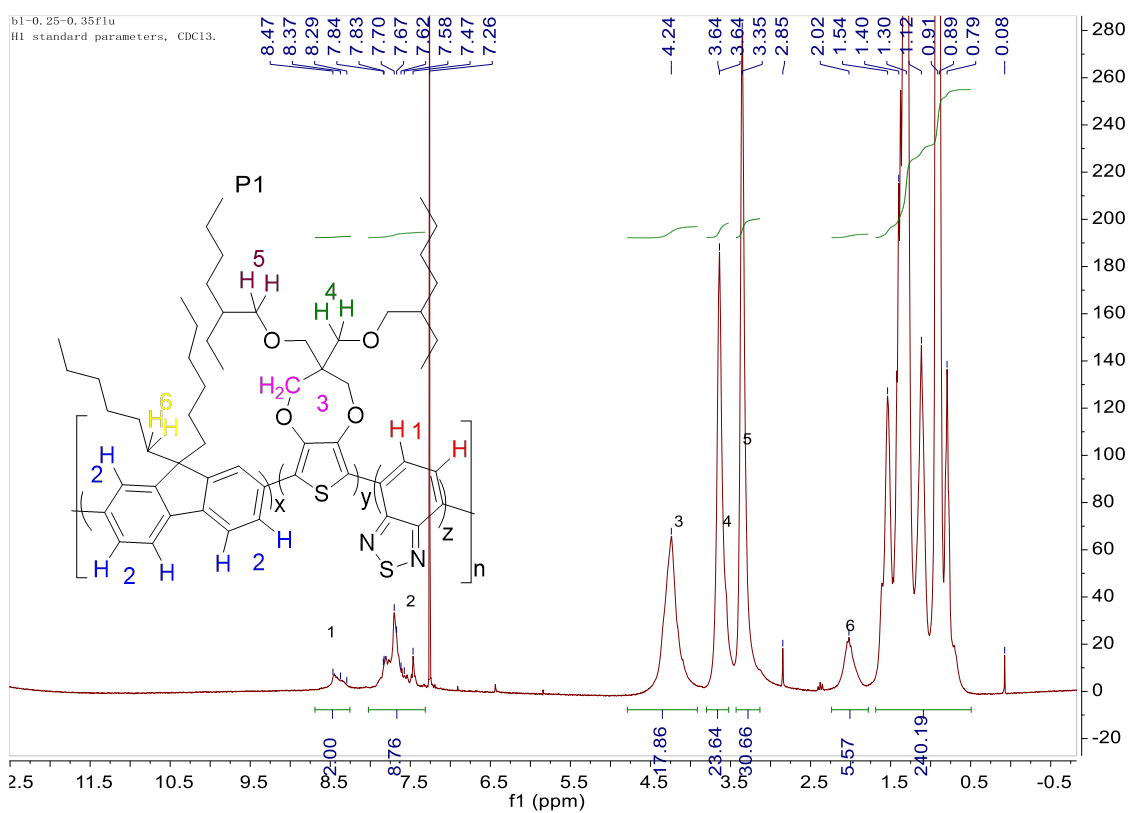


Figure S1. ^1H NMR spectrum of polymer P1.

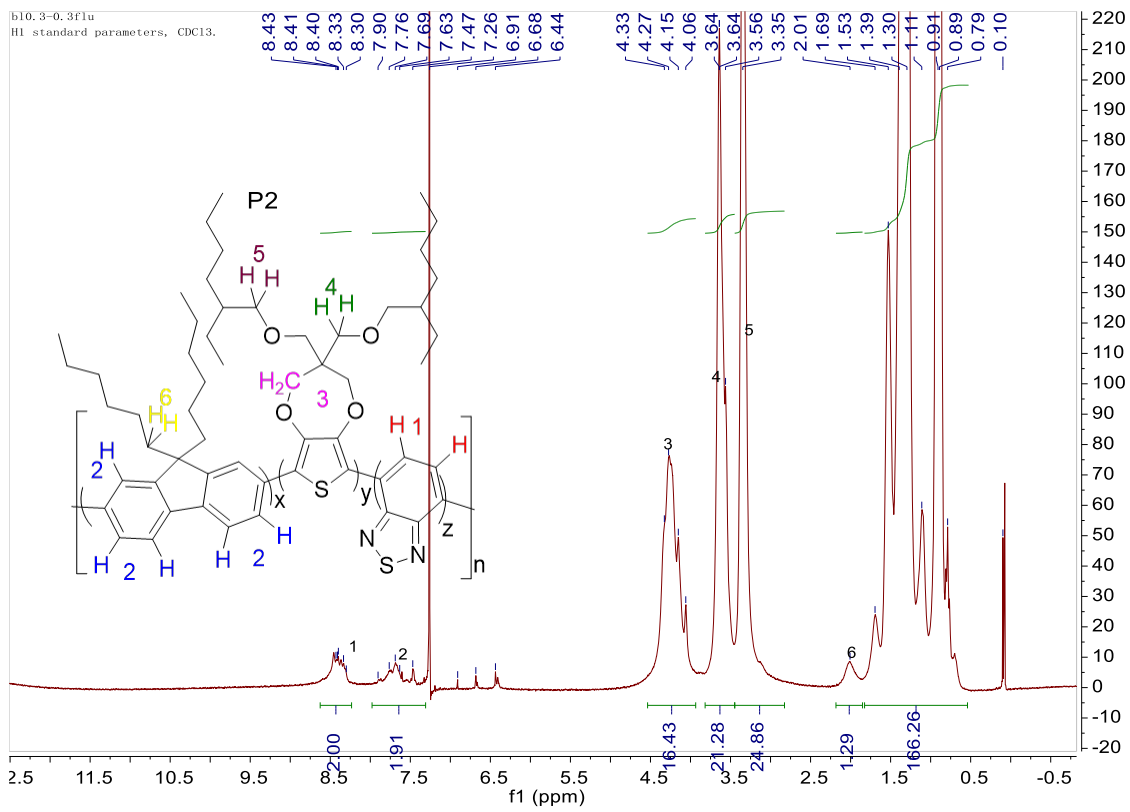


Figure S2. ^1H NMR spectrum of polymer P2.

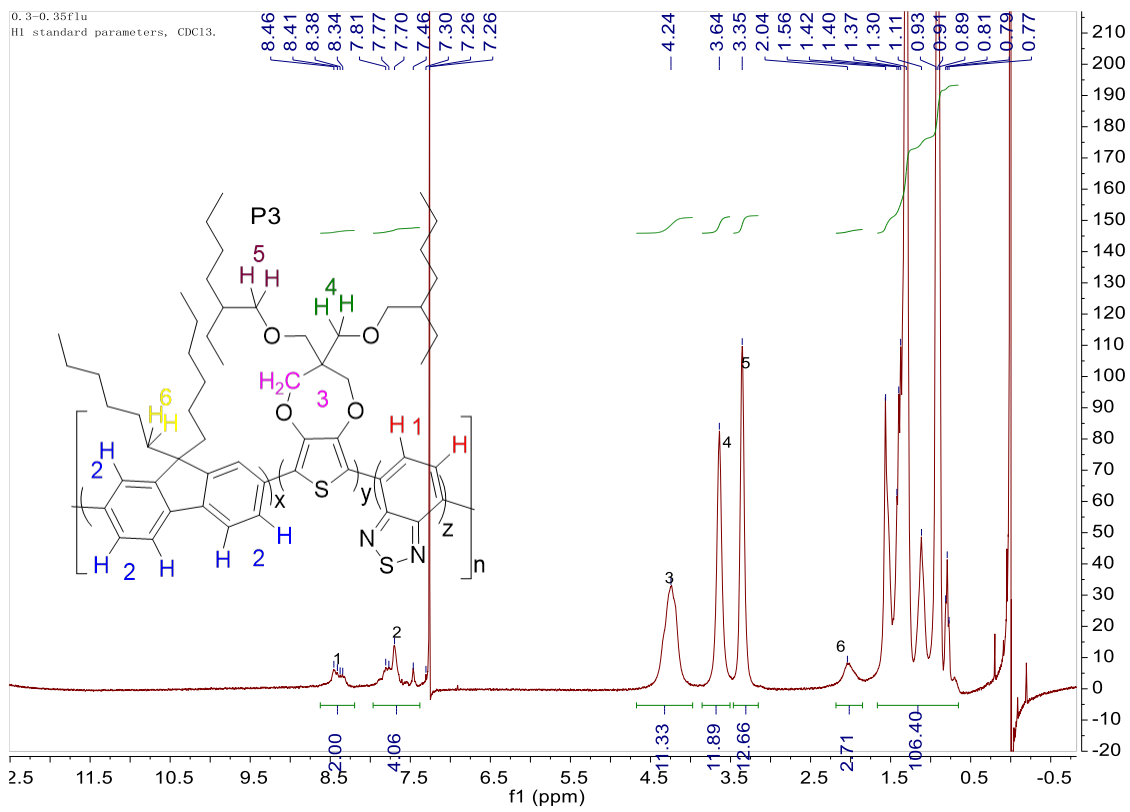


Figure S3. ^1H NMR spectrum of polymer P3.

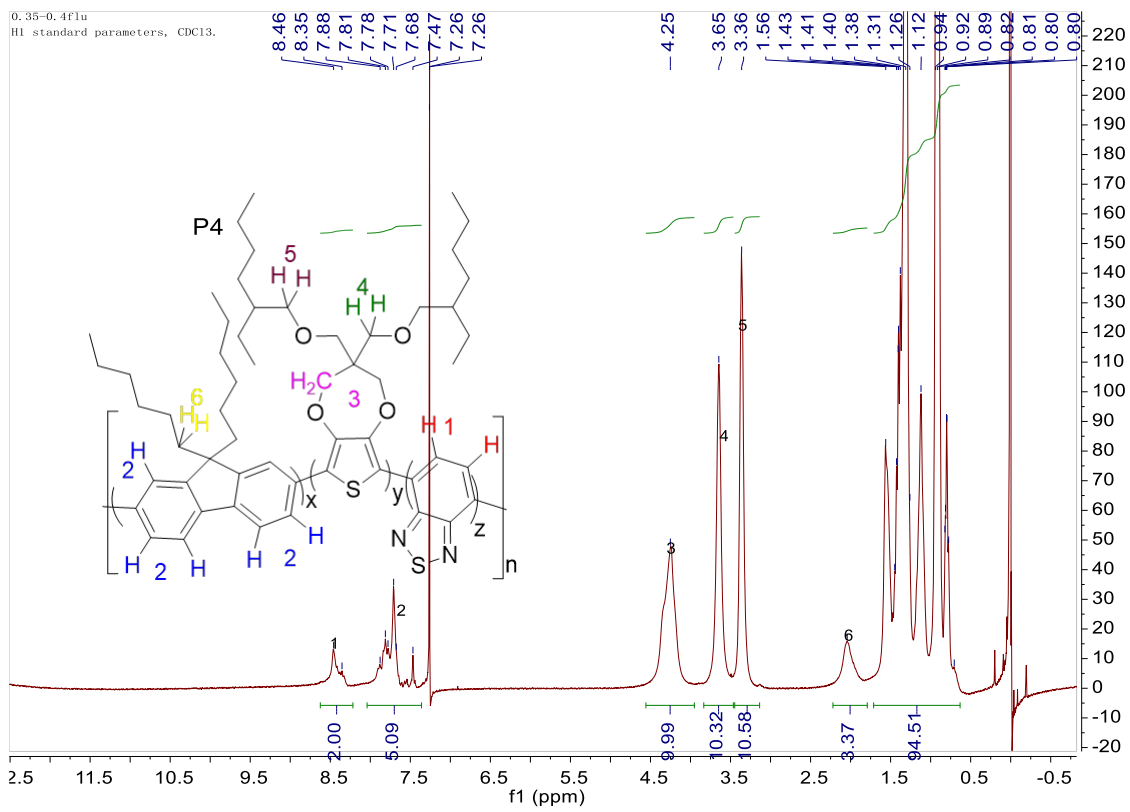


Figure S4. ^1H NMR spectrum of polymer P4.

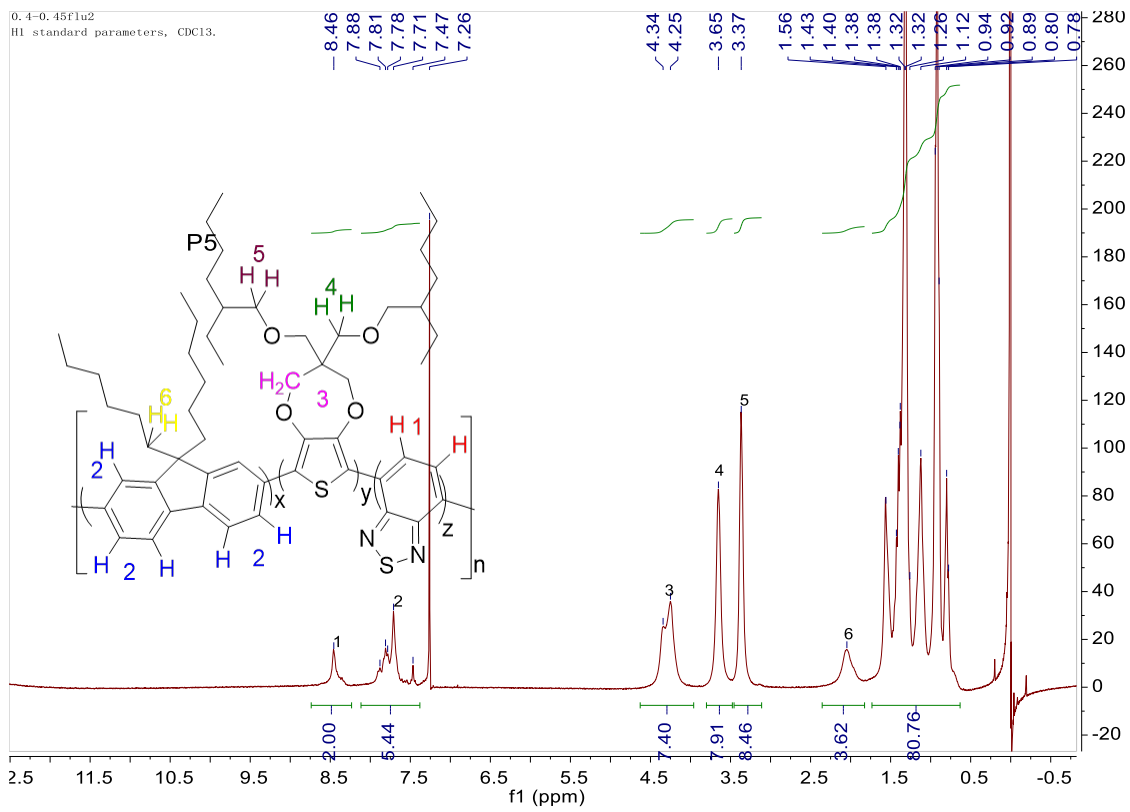


Figure S5. ^1H NMR spectrum of polymer P5.

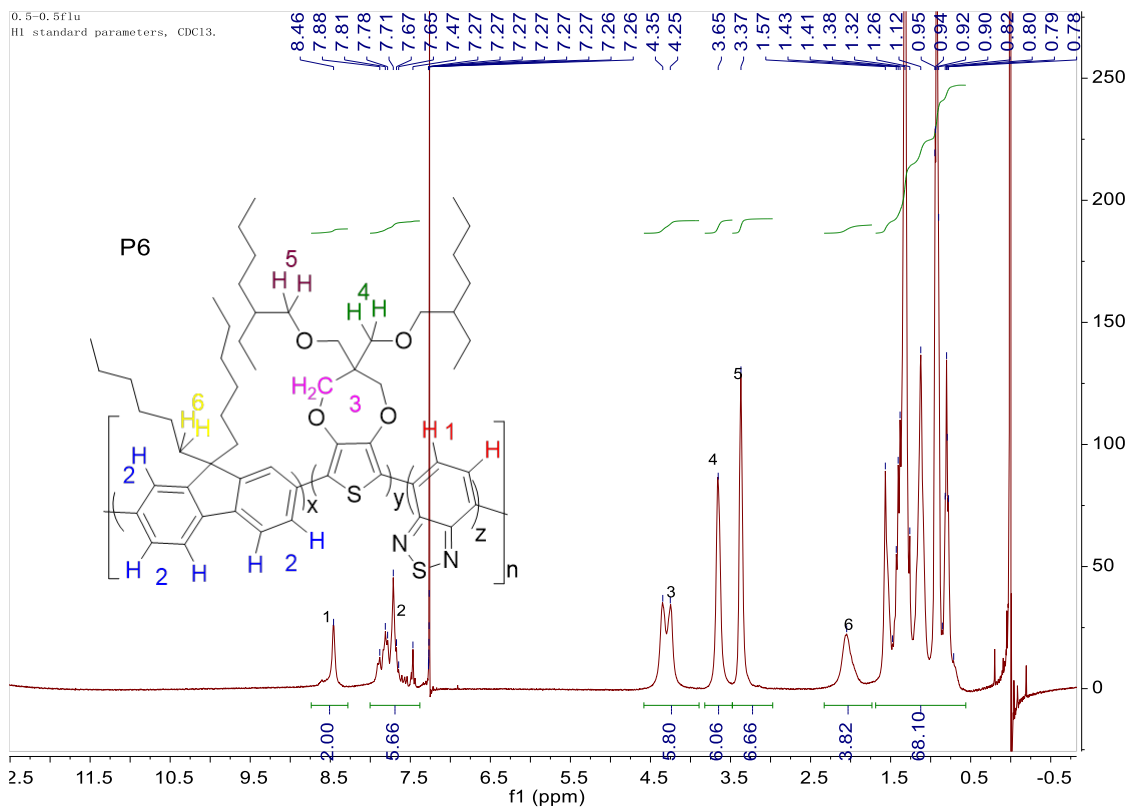


Figure S6. ^1H NMR spectrum of polymer P6.

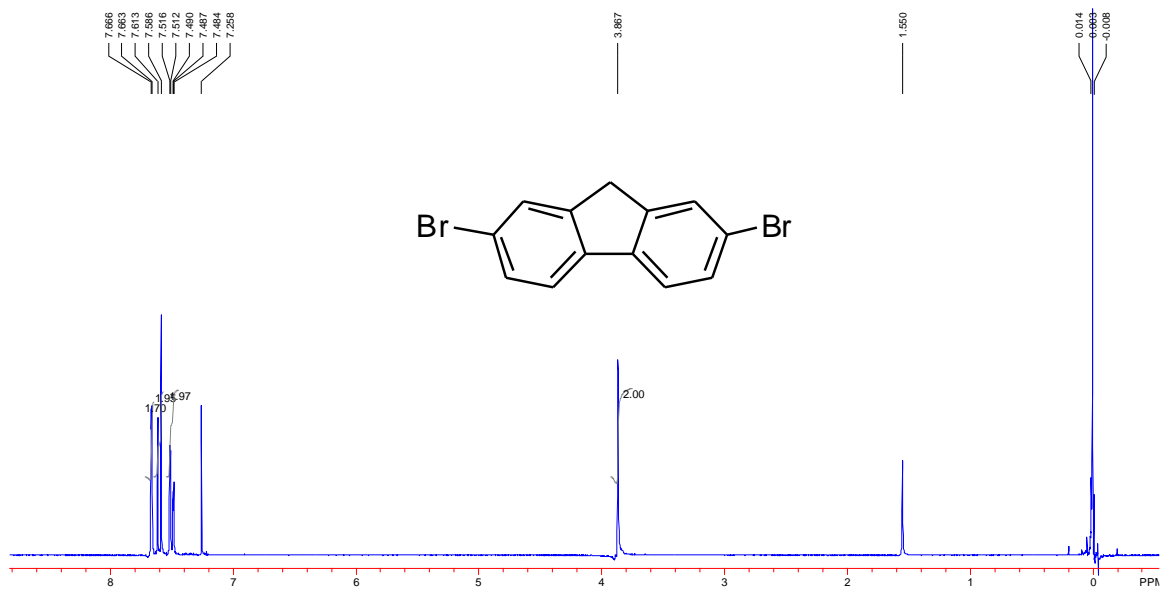


Figure S7. ^1H NMR spectrum of compound 2.

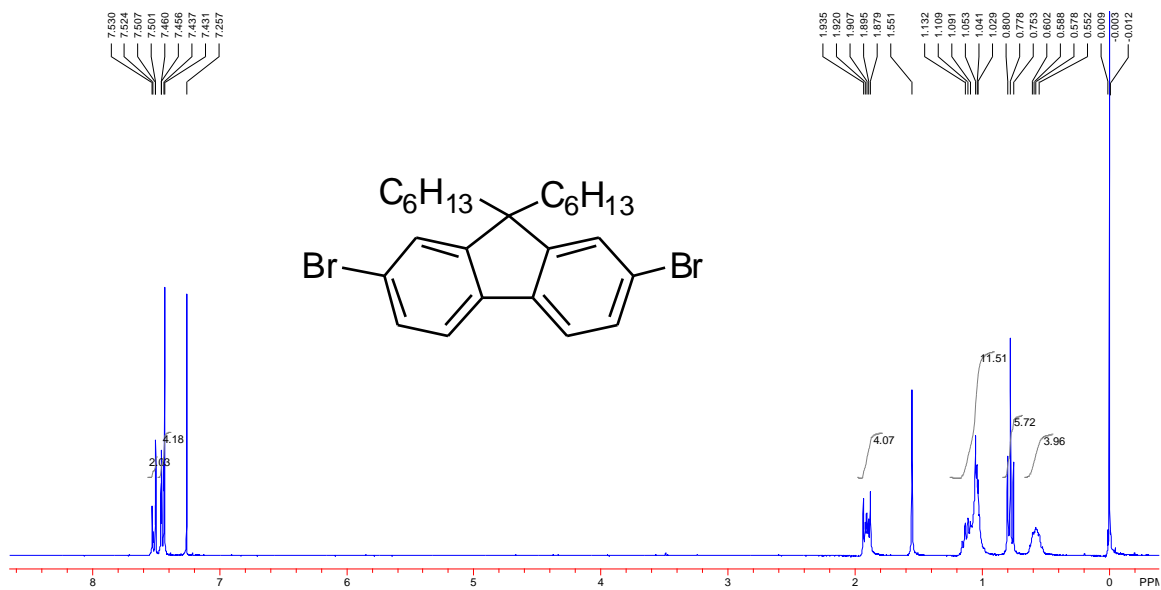


Figure S8. ^1H NMR spectrum of compound 3.

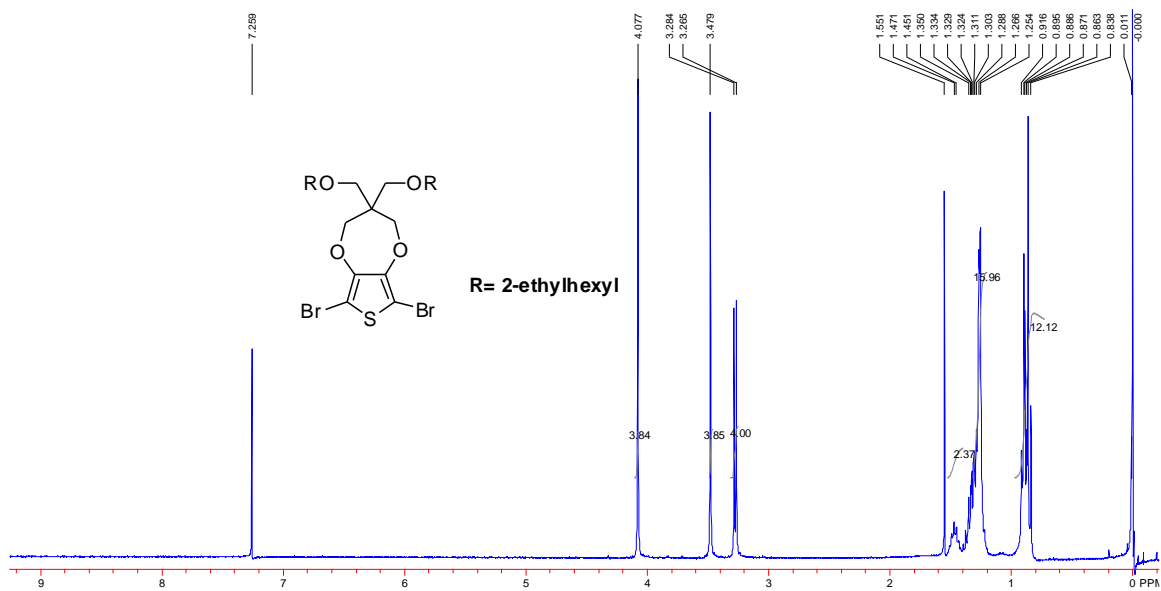


Figure S9. ^1H NMR spectrum of compound 5.

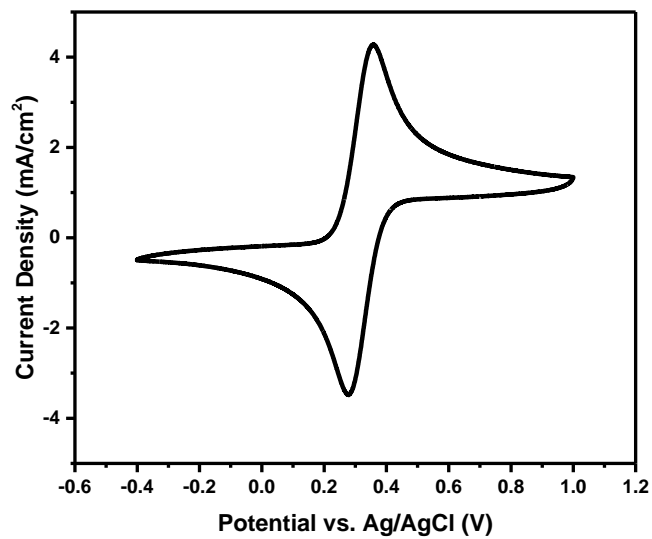
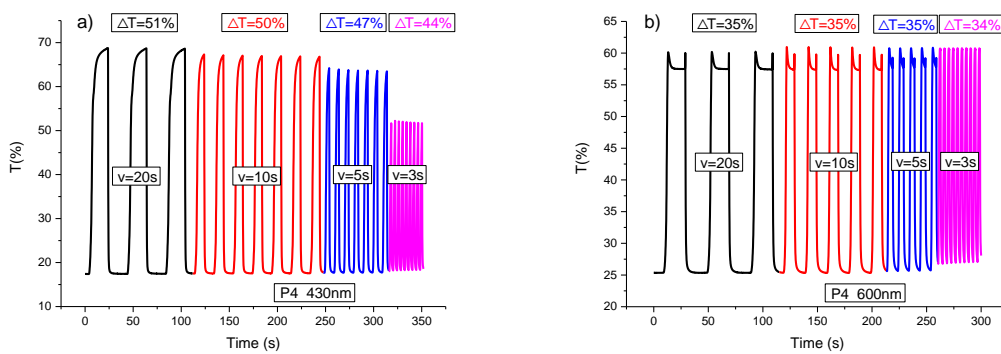


Figure S10. Cyclic voltammograms of ferrocene.



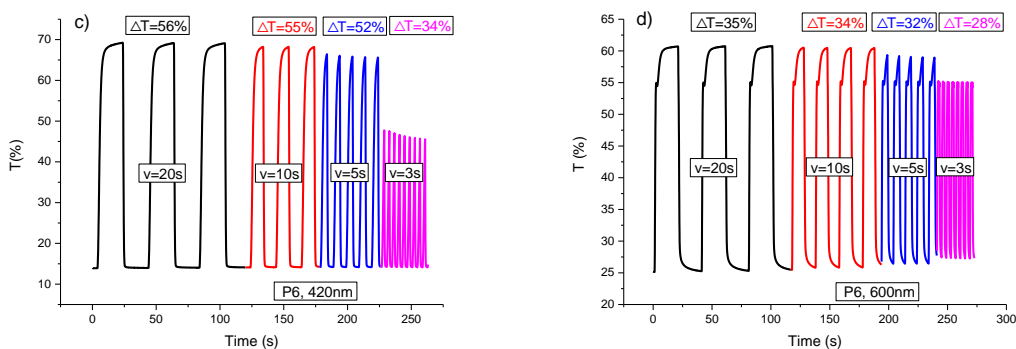


Figure S11. Square-wave potential step absorptiometry of spin-coating films of (a) P4 (monitored at 430nm), (b) P4 (monitored at 600nm), (c) P6 (monitored at 420nm), (d) P6 (monitored at 600nm) in 0.2M TBAP/PC electrolyte solution.

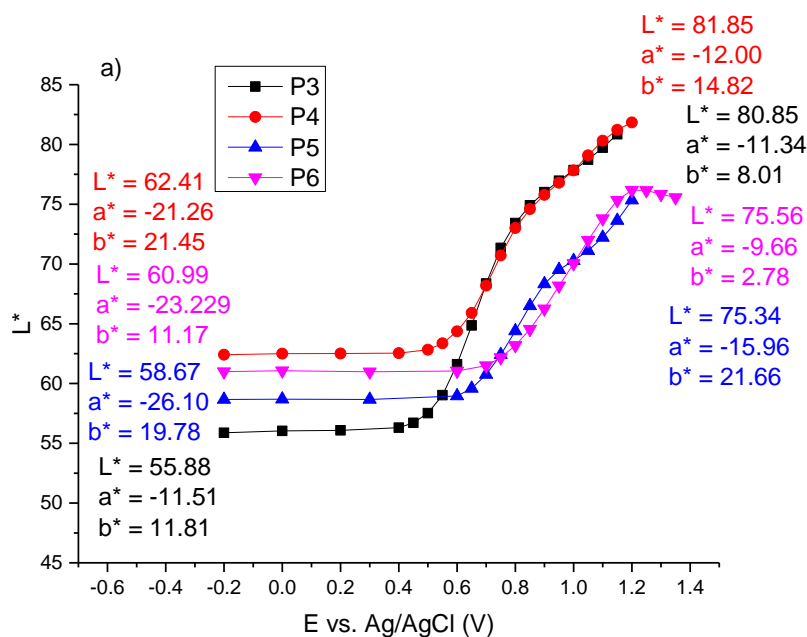


Figure S12. Lightness (L^*) as a function of applied potential for spin-coating green polymer films, $L^*a^*b^*$ values of fully neutral and oxidized states are reported for the films.

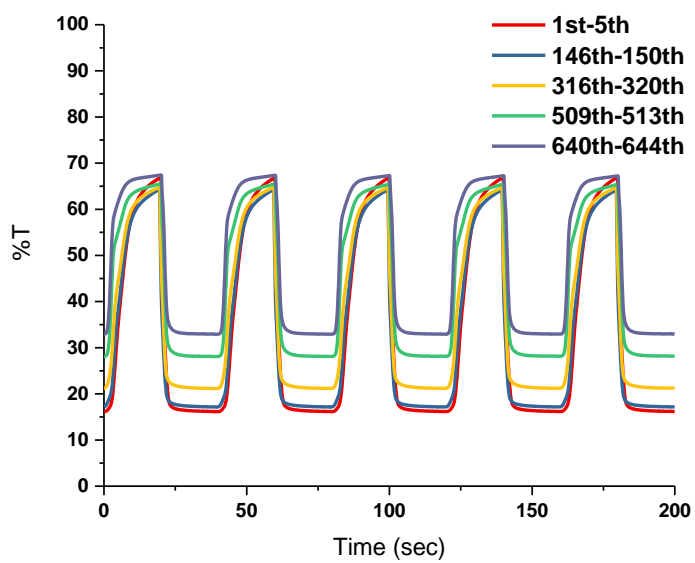


Figure S13. The transmittance at 430 nm of P4 thin films under double potential step chronoamperometric experiments switching between 1.2 V and -0.2 V VS. Ag/AgCl.

DI

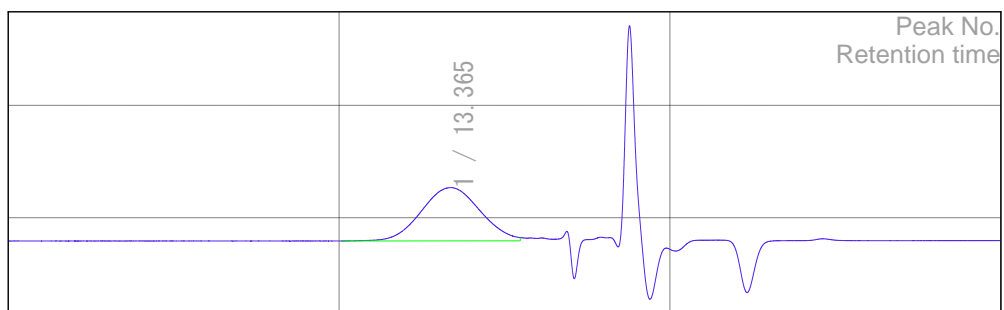


Figure S14. GPC trace of polymer P1.

DI

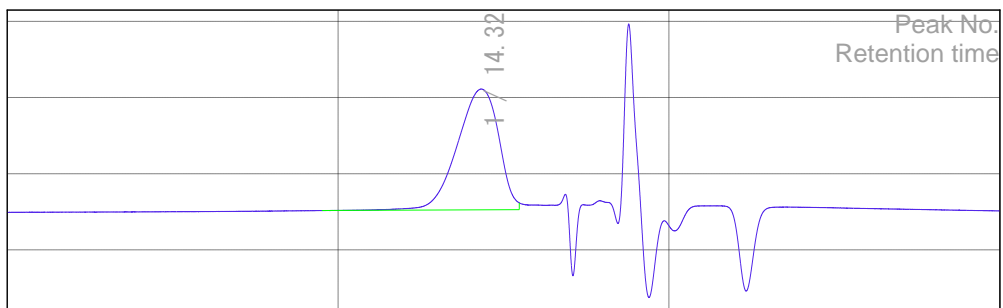


Figure S15. GPC trace of polymer P2.

DI

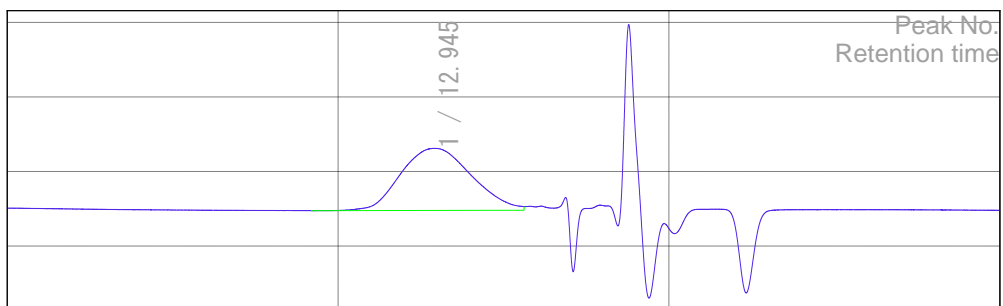


Figure S16. GPC trace of polymer P3.

DI

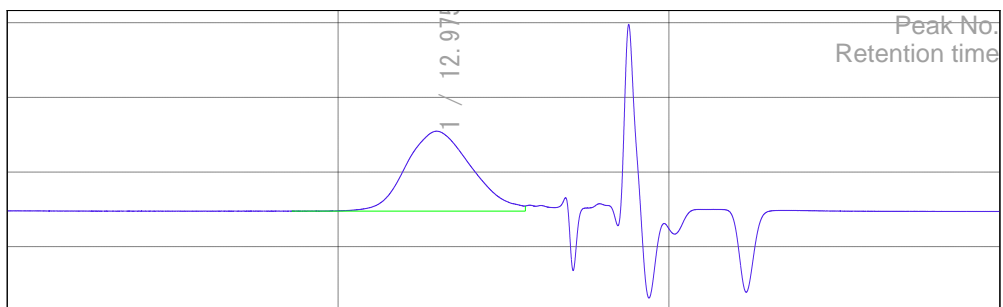


Figure S17. GPC trace of polymer P4.

RI

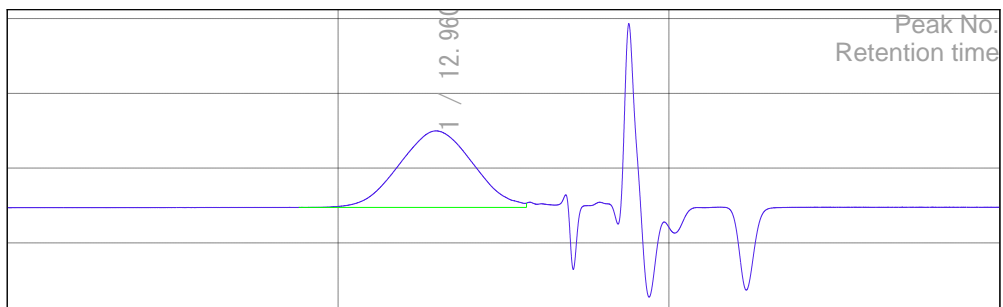


Figure S18. GPC trace of polymer P5.

RI

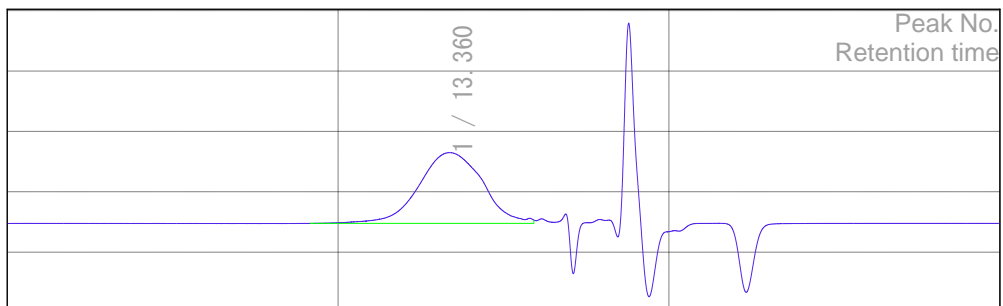


Figure S19. GPC trace of polymer P6.

Table S1. The x/y/z composition of each polymer based on the value of ¹H NMR integration and ratio of starting material.

Polymers	Fluorene-%	ProDOT-%	2,1,3-benzothiadiazole-%	Note
	x	y	z	
P1	18%	70%	12%	Based on NMR
	17.5%	70%	12.5%	Based on ratio of SM
P2	5%	80%	15%	Based on NMR
	15%	70%	15%	Based on ratio of SM
P3	15%	64%	21%	Based on NMR
	17.5%	67.5%	15%	Based on ratio of SM
P4	19%	58%	23%	Based on NMR
	20%	62.5%	17.5%	Based on ratio of SM
P5	23%	51%	26%	Based on NMR
	22.5%	57.5%	20%	Based on ratio of SM
P6	27%	44%	29%	Based on NMR
	25%	50%	25%	Based on ratio of SM

Reference

1. S. Song, Y. Jin, S. H. Kim, J. Y. Shim, S. Son, I. Kim, K. Lee and H. Suh, *J Polym Sci Pol Chem*, 2009, **47**, 6540-6551.
2. L. A. Estrada, J. J. Deininger, G. D. Kamenov and J. R. Reynolds, *Acs Macro Lett*, 2013, **2**, 869-873.