

Supporting Information

New Aspect of Cyclopentadithiophene Based Polymers: Narrow Band Gap Polymer upon Protonation

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Experimental Details

Materials

Compound 4H-cyclopenta[2,1-b:3,4-b']dithiophene (**CPDT**) was purchased from BOC Sciences while 9,9-dihexyl-2,7-dibromofluorene, N-Bromosuccinimide(97%), trifluoroacetic acid (99%) and biphenyl-4,4'-diboronic acid bis(pinacol) ester (95%) were purchased from Sigma-Aldrich. Compound 9,9-Di-n-hexylfluorene-2,7-diboronic acid bis(pinacol) ester and 2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-di(2-ethylhexyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene were prepared by literature methods.^{1, 2} Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl solution. Other commercially available solvents and reagents were used as received.

Instrumentation

¹H-NMR (400.13 MHz) and ¹³C-NMR (100.61 MHz) spectra were recorded on Bruker DRX 400-MHZ NMR spectrometer in the solvent of CDCl₃ at room temperature. Tetramethylsilane (TMS) was used as an internal standard to express chemical shift. Elemental analyses were conducted on a Flash EA 1112 series elemental analyzer for C, H and S determination. Gel permeation chromatography (GPC) was carried out on a Waters 2690 system with polystyrene as standards and THF (HPLC) as eluent. Thermogravimetry was conducted on TGA Q500 of TA system in air. A heating rate of 20 °C min⁻¹ and airflow of 50 cm³ min⁻¹ were performed to test runs from room temperature to 900 °C. FT-IR spectra were recorded on PEKIN ELMER FT-IR Spectrometer Spectrum 2000. UV-vis-NIR spectra were conducted on Shimadzu UV-3600. Fluorescence Spectroscopy was conducted on RF-5301PC of Shimadzu.

Simulation

All calculations were performed with the Gaussian 09 program employing the Becke Three Parameter Hybrid Functionals Lee–Yang–Parr (B3LYP) in conjunction with the 6-31+G(d,p) basis set.³ Full geometry optimizations without symmetry constraints were carried out in the gas phase for the singlet ground states (S₀). The energies of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and other frontier orbitals were calculated at the optimized structure. The zero-point vibrational energies (ZPE) were scaled according to Wong (0.9804).⁴ In all cases, the normal modes revealed no imaginary frequencies indicating that they represent minima on the potential energy surface.

Synthesis of Compounds and Polymers

5,5'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(2-bromo-3-methylthiophene) (1). To a two necked 100 ml RBF was added 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.984 g, 2 mmol) and 4,4,5,5-tetramethyl-2-(4-methylthiophen-2-yl)-1,3,2-dioxaborolane (0.941 g, 4.2 mmol), 16 ml of THF, 8 ml of Na₂CO₃ solution (2 M), and four drops of Aliquat 336 under argon protection. The mixture was then degassed for half hour under argon. Catalytic amount of Pd(PPh₃)₄ (9.7 mg, 0.0084 mmol) was added and another 20 mins degas was applied. The mixture was then transferred to an oil bath and stirred and refluxed at 80 °C for 18 hours. After cooling, the reaction mixture was extracted with CH₂Cl₂ and the organic layers were collected, washed with water (three times) and dried over magnesium sulfate. After filtration, the volatile CH₂Cl₂ and THF were removed through rotary evaporator. The crude product was chromatographed on silica using ethyl acetate : hexane (1:30, v:v) as eluent, followed by recrystallization in hexane. This was obtained as yellow crystals (75%). The above product (1.24 g, 2.36 mmol) was dissolved in 40 ml THF under argon atmosphere at 0 °C with the absence of light. NBS (0.88 g, 4.9 mmol) was added to the solution as one portion. The mixture was reacted under argon at 0 °C for 1 hour and then stirred at room temperature for 7 hours. Then the reaction was stopped by addition of water and extracted with CH₂Cl₂ (15 ml x 3). The organic layers were combined and washed with 30 ml water (three times) and dried over magnesium sulfate. After filtration, the volatile THF and CH₂Cl₂ were removed through rotary evaporator. The crude product was chromatographed on silica using ethyl acetate : hexane (1:60, v:v) as eluant. This was obtained as light yellow solid (99%). ¹H-NMR (δ, CDCl₃): 7.69 (d, 2 H), 7.48 (m, 4 H), 7.06 (s, 2 H), 2.23 (s, 6 H), 1.98 (m, 4 H), 1.04 (m, 12 H), 1.75 (m, 10H).

P1. To a two necked RBF of 50 ml was added 2,2'-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.3 g, 0.46 mmol), 2,7-dibromo-9,9-dihexyl-9H-fluorene (0.224 g, 0.46 mmol), 8 ml of toluene, 4 ml of Na₂CO₃ solution (2 M), and one drop of Aliquat 336 under argon protection. The mixture was then vacuum degassed through several freeze-pump-thaw cycles. Catalytic amount of Pd(PPh₃)₄ (2.1 mg, 0.0018mmol) was added and one more freeze-pump-thaw degas cycle was applied. The mixture was then transferred to an oil bath and stirred and refluxed at 110 °C for 3 days. After the polymerization completed, the reaction mixture was poured into excess amount of methanol with stirring. The collected green precipitates were re-dissolved into toluene and precipitated from methanol. The process was repeated several times until purify of polymer is satisfied. Finally the polymers were dried in a vacuum oven and then directed used for the following characterization. Yield: 71%, Mn= 7029, PDI= 1.31. ¹H-NMR (δ, CDCl₃): 7.72 (m, 4 H), 7.56 (m, 4 H), 1.98 (m, 8 H), 1.66 (m, 4 H), 1.09-0.70 (m, 48 H). ¹³C NMR: δ 158.1, 152.1, 142.1, 140.6, 137.3, 136.7, 134.7, 133.9, 133.3, 132.3, 132.2, 132.1, 129.0, 128.9, 127.8, 125.7, 125.2, 124.9, 121.0, 120.5, 120.3, 120.0, 55.7, 54.5, 43.7, 40.9, 36.2, 35.6, 34.8, 31.9, 30.1, 29.2, 27.9, 24.2, 23.3, 23.0, 16.2, 14.5, 14.4. FTIR (KBr): 3420.5, 3063.9, 2953.4, 2922.9, 2851.1, 2316.9, 1601.8, 1507.9, 1462.8, 1434.9, 1376.2, 1254.8, 1179.2, 1117.0, 874.0, 814.7, 744.6, 719.6, 692.6, 551.7, 438.8, 425.2. Anal Calcd for C₅₀H₇₀S₂: C, 81.68; H, 9.60; S, 8.72. Found: C, 80.69; H, 8.84; S, 8.28%.

P2. To a two necked RBF of 50 ml was added 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene (0.34 g, 0.61 mmol), biphenyl-4,4''-diboronic acid bis(pinacol) ester (0.25 g, 0.61 mmol), 8 ml of toluene, 4 ml of Na₂CO₃ solution (2 M), and one drop of Aliquat 336 under argon protection. The mixture was then vacuum degassed through several freeze-pump-thaw cycles. Catalytic amount of Pd(PPh₃)₄ (2.8 mg, 0.0024mmol) was added and one more freeze-pump-thaw degas cycle was applied. The mixture was then transferred to an oil bath and stirred and refluxed at 110 °C for 3 days. After the polymerization completed, the reaction mixture was poured into excess amount of methanol with stirring. The collected green precipitates were re-dissolved into toluene and precipitated from methanol. The process was repeated several times until purify of polymer is satisfied. Finally the polymers were dried in a vacuum oven and then directed used for the following characterization. Yield: 75%, Mn=

15465, PDI= 2. $^1\text{H-NMR}$ (δ , CDCl_3): 7.35 (m, 10 H), 1.95 (m, 4 H), 0.99-0.57 (m, 30 H). $^{13}\text{C NMR}$: δ 158.6, 144.5, 139.1, 138.2, 135.1, 132.3, 129.0, 127.7, 126.3, 118.9, 54.1, 43.6, 35.4, 34.7, 28.8, 27.8, 23.4, 14.6, 10.8. FTIR (KBr): 3429.7, 3028.8, 2953.3, 2919.1, 2869.2, 2329.0, 1603.3, 1508.1, 1485.8, 1456.9, 1413.6, 1376.6, 1178.2, 1110.5, 1001.0, 815.9, 726.5, 667.7, 494.9. Anal Calcd for $\text{C}_{37}\text{H}_{46}\text{S}_2$: C, 80.09; H, 8.36; S, 11.56. Found: C, 78.26; H, 7.52; S, 10.74%.

P3. To a two necked RBF of 50 ml was added 2,2'-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.37 g, 0.56 mmol), 5,5'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(2-bromo-3-methylthiophene) (**1**, 0.385 g, 0.56 mmol), 8 ml of toluene, 4 ml of Na_2CO_3 solution (2 M), and one drop of Aliquat 336 under argon protection. The mixture was then vacuum degassed through several freeze-pump-thaw cycles. Catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ (2.6 mg, 0.0022mmol) was added and one more freeze-pump-thaw degas cycle was applied. The mixture was then transferred to an oil bath and stirred and refluxed at 110 °C for 3 days. After the polymerization completed, the reaction mixture was poured into excess amount of methanol with stirring. The collected yellow precipitates were re-dissolved into toluene and precipitated from methanol. The process was repeated several times until purify of polymer is satisfied. Finally the polymers were dried in a vacuum oven and then directed used for the following characterization. Yield: 66%, M_n = 11265, PDI= 1.35. $^1\text{H-NMR}$ (δ , CDCl_3): 7.68 (m, 6 H), 7.21 (s, 2H), 7.07 (s, 2H), 2.46 (m, 6H), 2.02 (m, 8 H), 1.65 (m, 4H), 1.06-0.66 (m, 48 H). $^{13}\text{C NMR}$: δ 158.6, 144.5, 139.1, 138.2, 135.1, 132.3, 129.0, 127.7, 126.3, 118.9, 54.1, 43.6, 35.4, 34.7, 28.8, 27.8, 23.4, 14.6, 10.8. FTIR (KBr): 3429.2, 3056.1, 2951.7, 2918.2, 2849.3, 2318.1, 1636.9, 1576.9, 1455.9, 1417.9, 1375.0, 1257.2, 1176.4, 1131.1, 879.5, 832.0, 812.5, 719.7, 667.1, 617.6, 589.4, 522.8. Anal Calcd for $\text{C}_{60}\text{H}_{78}\text{S}_4$: C, 77.70; H, 8.48; S, 13.83. Found: C, 75.39; H, 8.12; S, 13.88%.

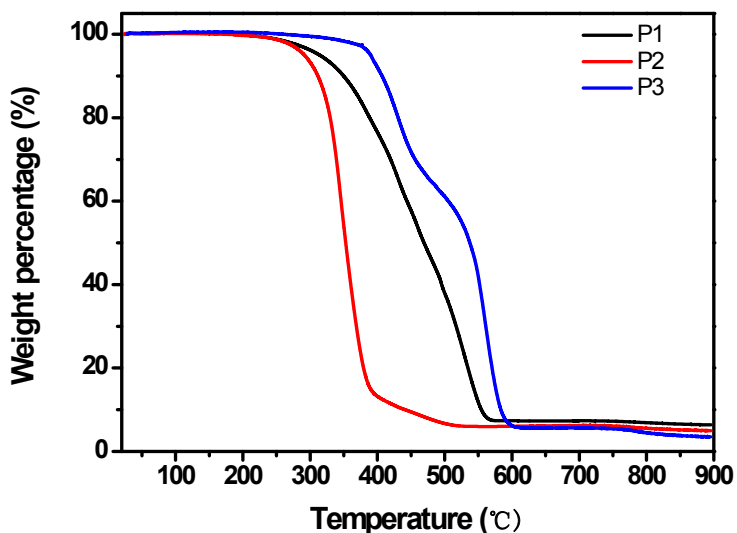


Fig. S1 TGA plots of polymers in air.

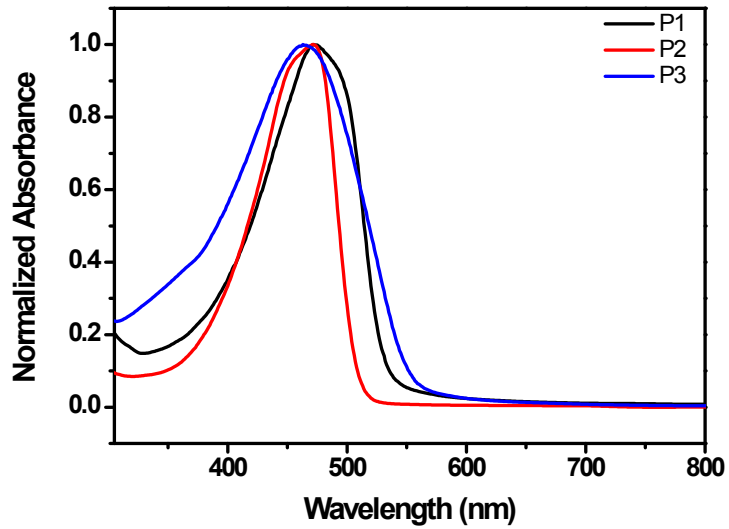
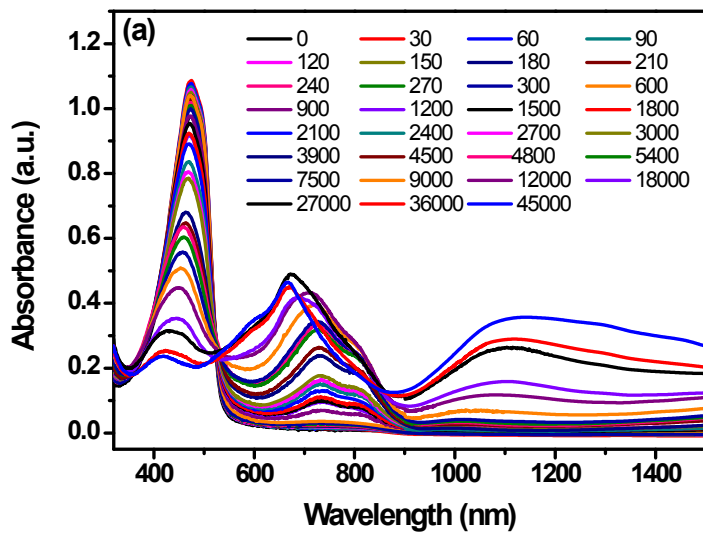
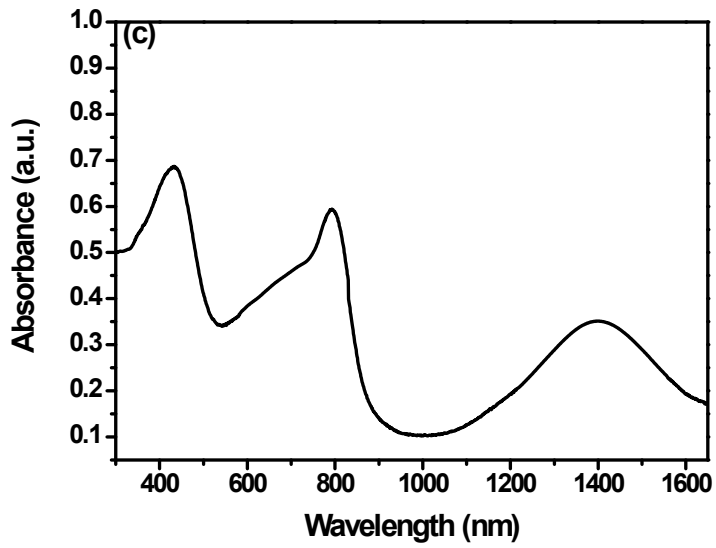
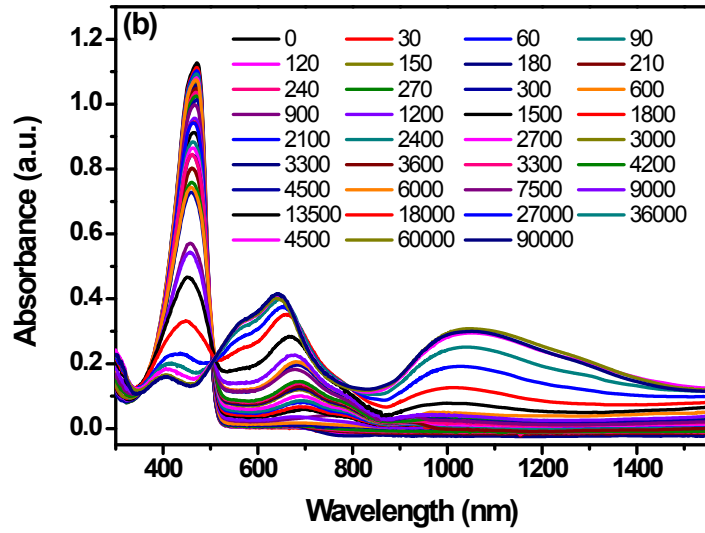
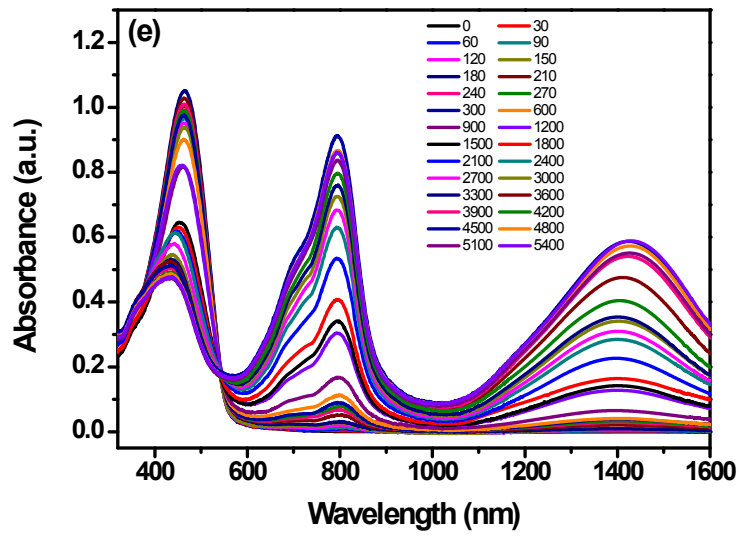
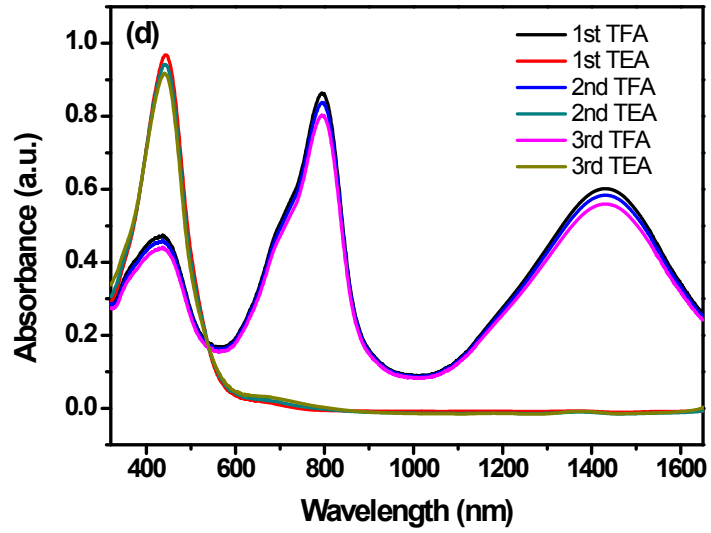


Fig. S2 UV-vis spectra of the obtained polymers in chloroform solution.







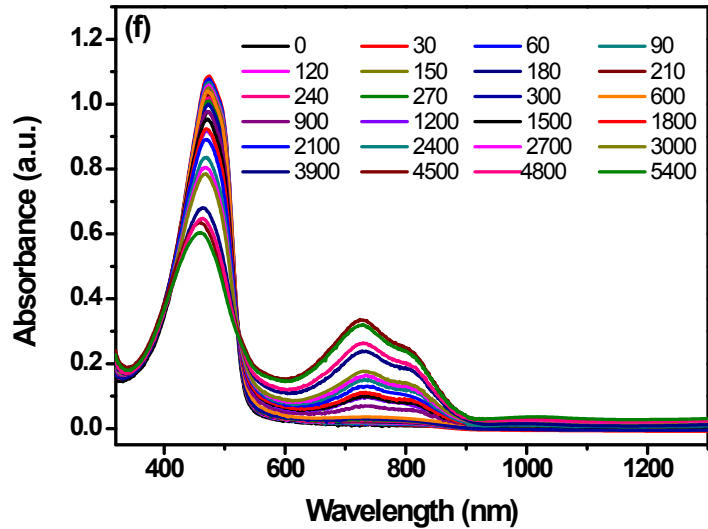
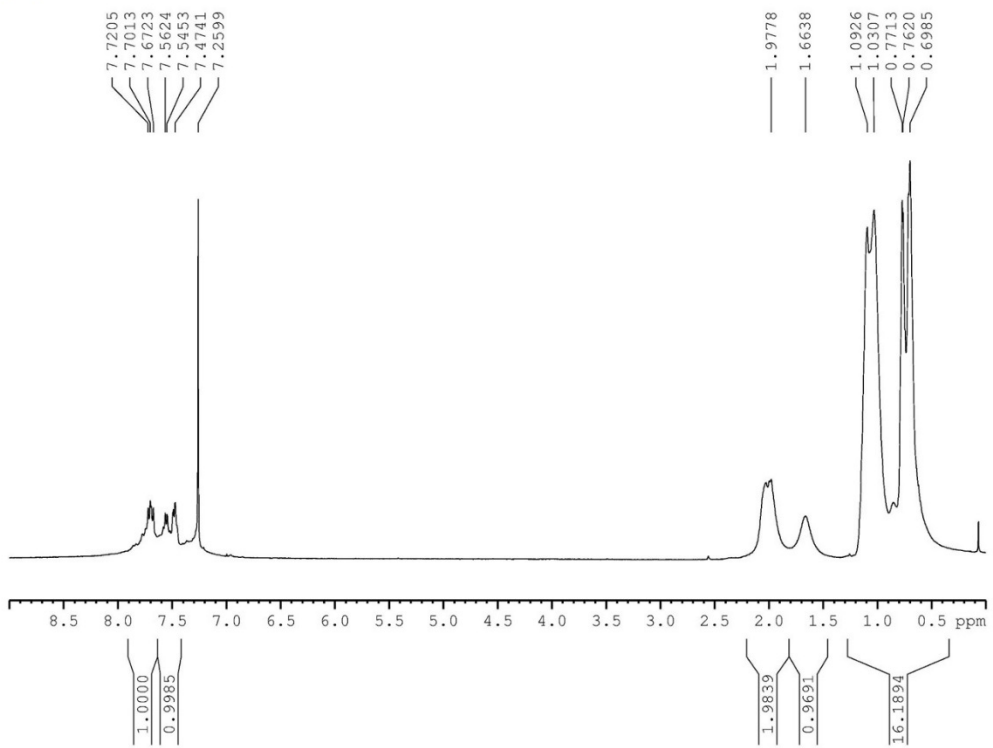
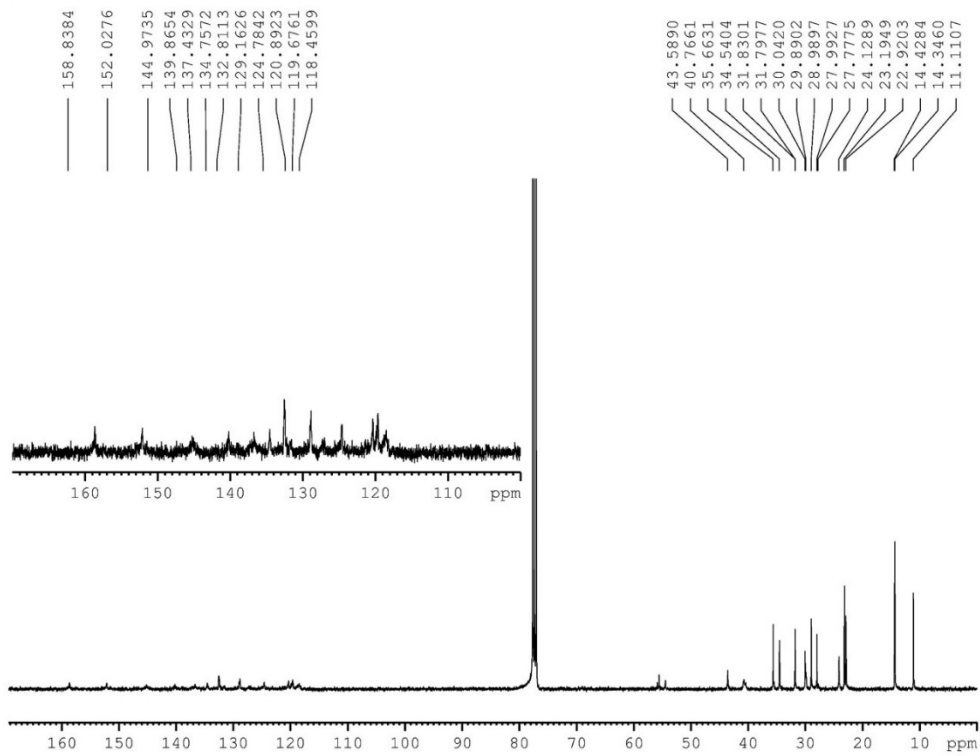


Fig. S3 (a) UV-vis-NIR spectra of the polymer **P1** as a function of TFA concentration (ppm) in chloroform solution at room temperature; (b) UV-vis-NIR spectra of the polymer **P2** as a function of TFA concentration (ppm) in chloroform solution at room temperature; (c) UV-vis-NIR spectra of the polymer **P3** in chloroform/ methanesulfonic acid (v/v: 99/1) solution at room temperature; (d) Reversible UV-vis-NIR spectra of the polymer **P3** in chloroform upon the treatment of TFA and then TEA for three cycles; (e) UV-vis-NIR spectra of the polymer **P3** as a function of TFA concentration (up to 5400 ppm) in chloroform solution at room temperature and (f) UV-vis-NIR spectra of the polymer **P1** as a function of TFA concentration (up to ppm) in chloroform solution at room temperature.

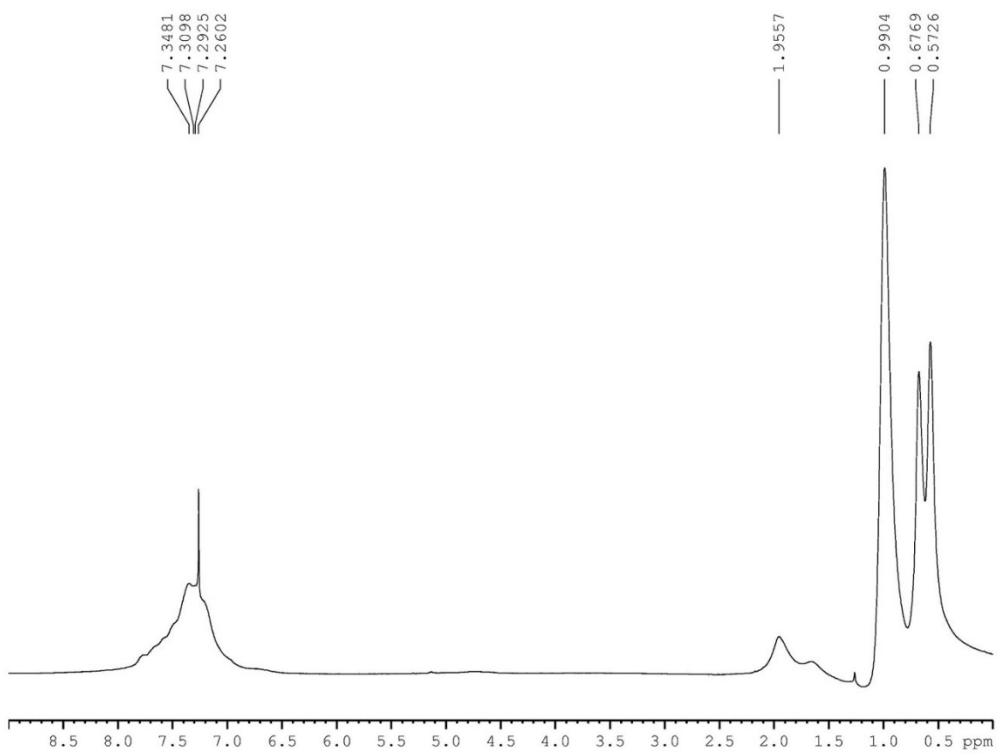
(a)



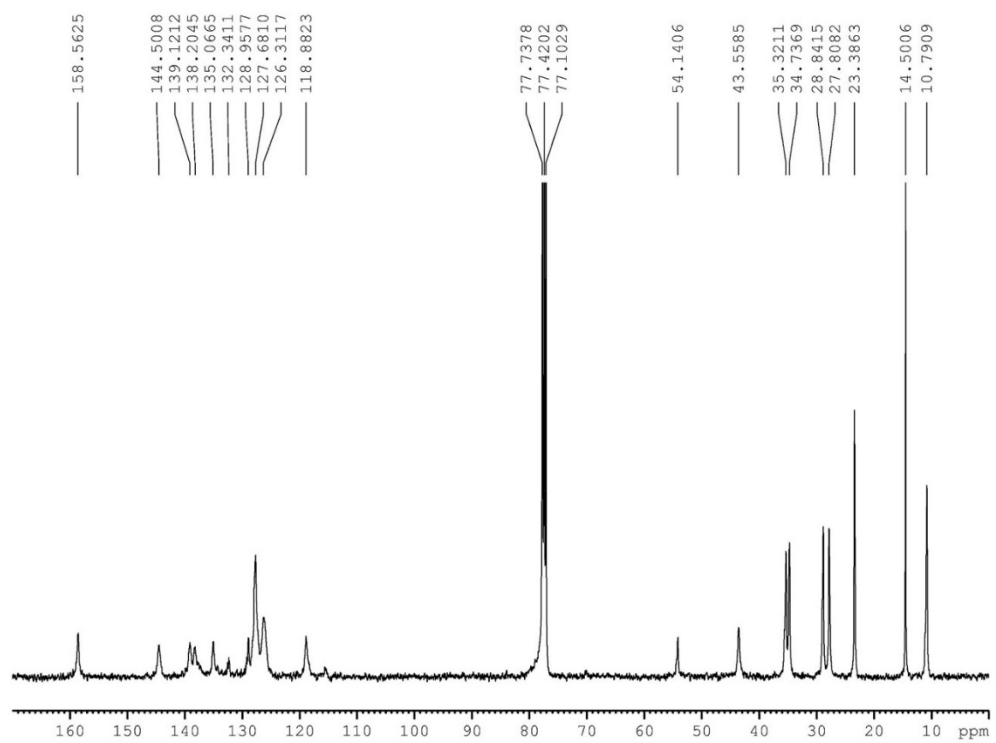
(b)



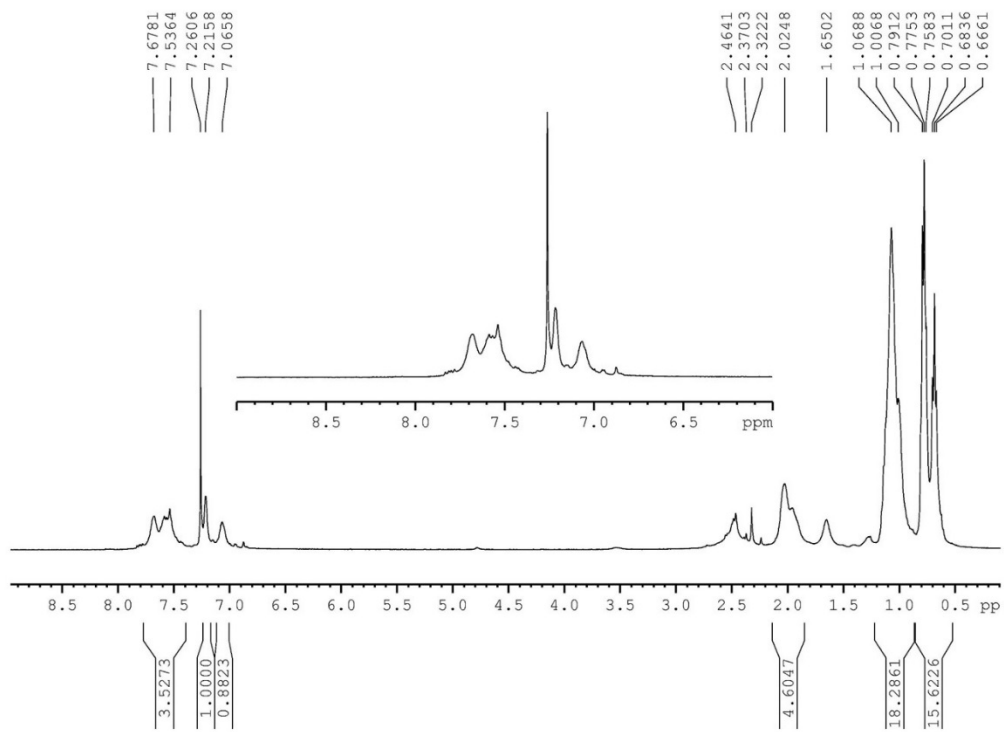
(c)



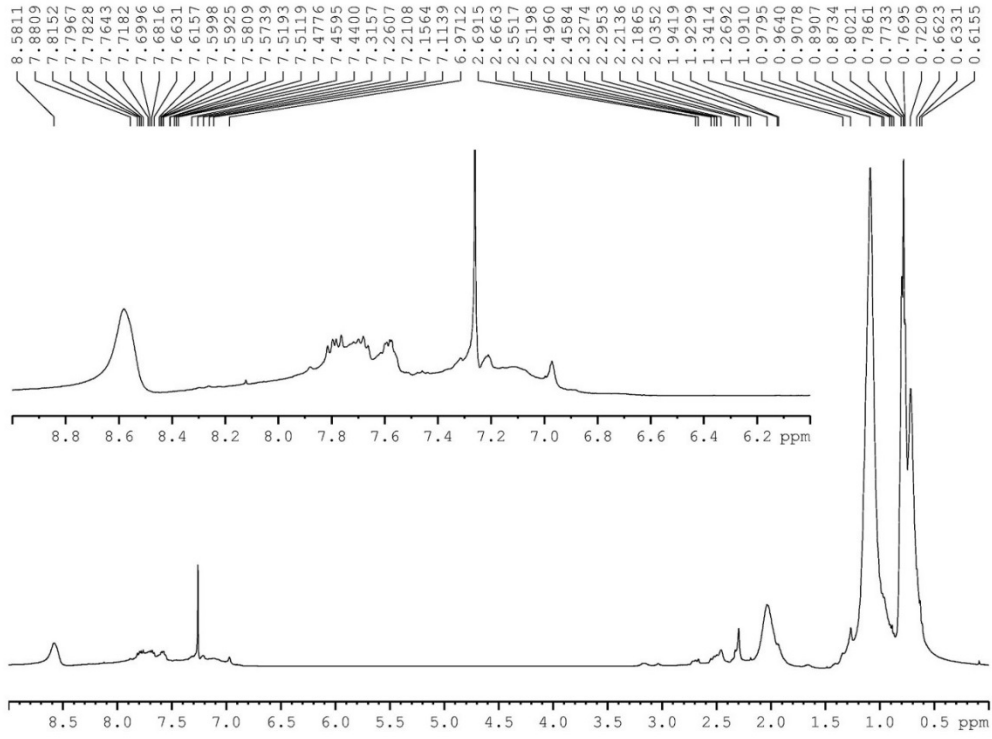
(d)



(e)



(f)



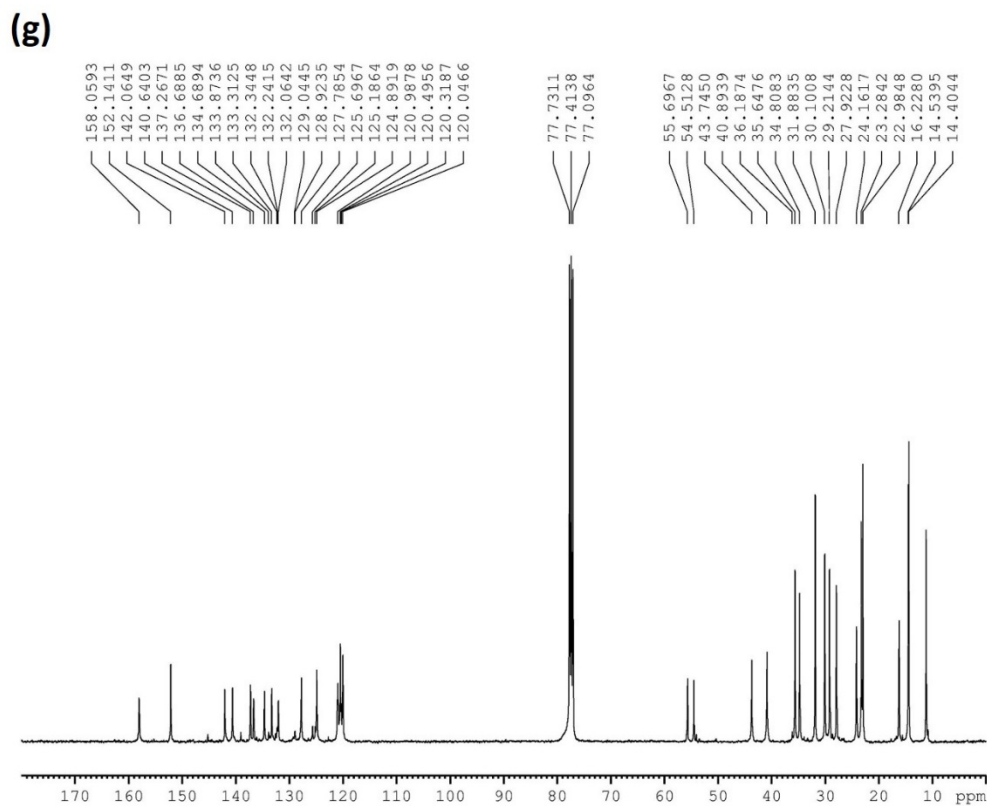


Fig. S4 NMR spectra of polymers. (a) and (b), ^1H -NMR and ^{13}C -NMR spectra of polymer **P1** in CDCl_3 ; (c) and (d), ^1H -NMR and ^{13}C -NMR spectra of polymer **P2** in CDCl_3 ; (e) and (g), ^1H -NMR and ^{13}C -NMR spectra of polymer **P3** in CDCl_3 ; (f) ^1H -NMR spectra of polymer **P3** in CDCl_3 with 5% trifluoroacetic acid-d.

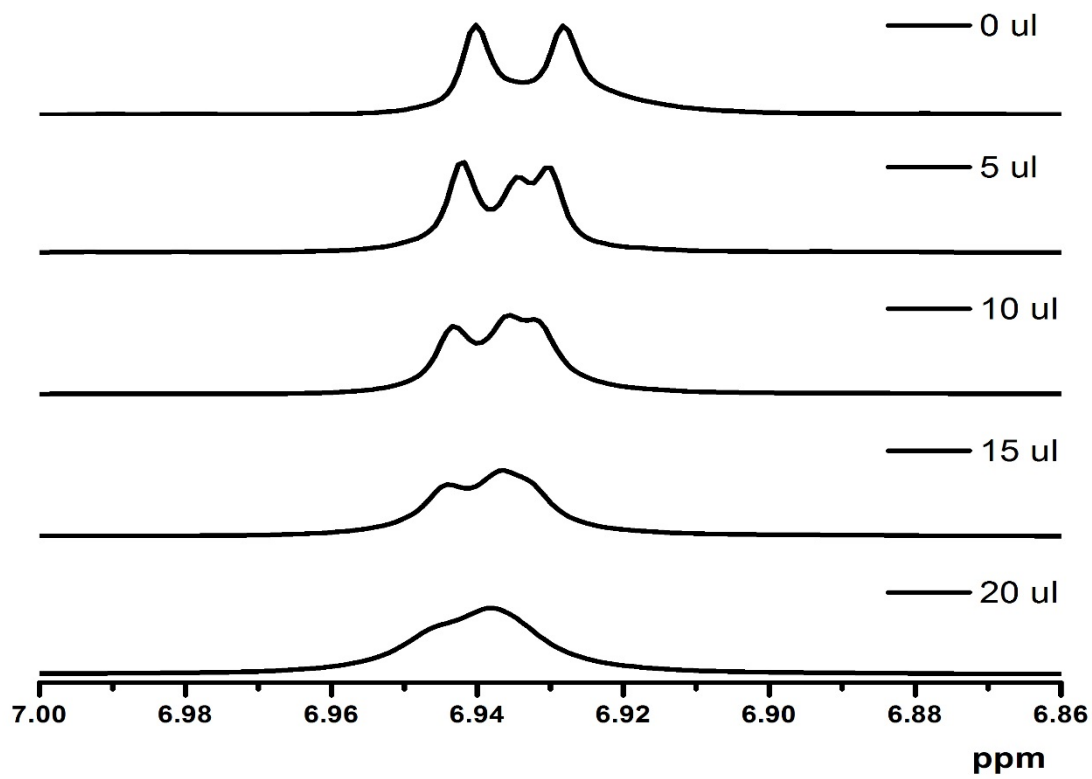
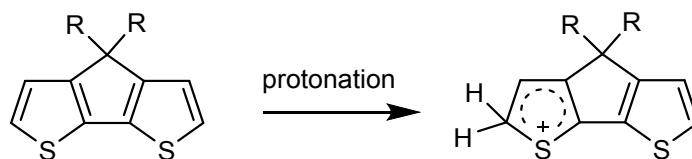


Fig. S5 Aromatic regions (6.86 – 7 ppm) of the ^1H NMR spectra of **CPDT** as a function of trifluoroacetic acid-d concentration from 0 to 20 μl at 300 K. All spectra were recorded in CDCl_3



Scheme S1 The process of protonation of **CPDT** with TFA.

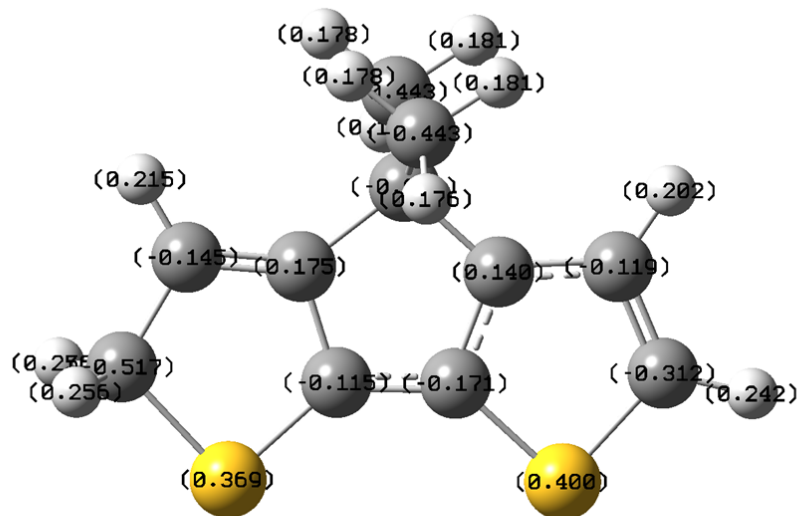


Fig. S6 Computer simulation results of the protonated CPDT.

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