

Supporting Information

**Synthesis of fused conjugated polymers containing imidazo[2,1-
b]thiazole units by multicomponent one-pot polymerization**

Ru Dong,^a Qi Chen,^a Xuediao Cai,^{*,a} Qi Zhang,^{a,*} Zhike Liu^b

a Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, No. 620, West Chang'an Avenue, 710119 Xi'an, P. R. China

b Key Laboratory of Applied Surface and Colloid Chemistry Ministry of Education, Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, No. 620, West Chang'an Avenue, 710119 Xi'an, P. R. China

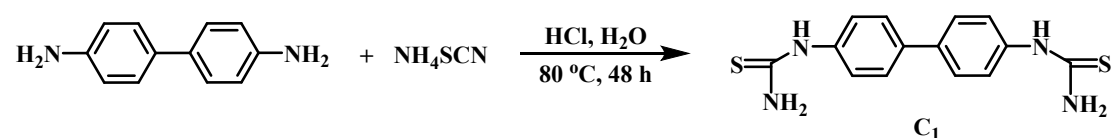
Table of contents

1. Materials and Methods.....	3
2. Synthesis of monomer M₁.....	3
3. Synthesis and Optical Properties of polymers.....	8
4. TGA curve of polymers.....	21
5. Cyclic voltammogram of polymers.....	21

1. Materials and Methods

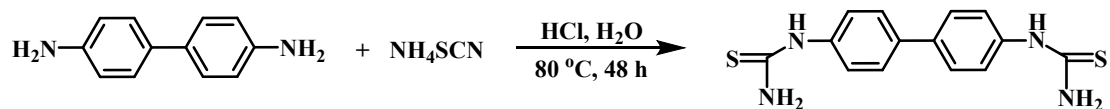
Benzidine (Energy Chemical, 98%); Ammonium thiocyanate (Energy Chemical, 99%); 1,4-Phthalaldehyde (Energy Chemical, 98%); 2,5-Thiophenedicarboxaldehyde (Aladdin, 95%); 1-Ethynyl-4-hexylbenzene (TCI, >95%); Phenylpropionic acid (Energy Chemical, 97%), Ethyl propiolate (Energy Chemical, 98%) and Copper(I) iodide were used without further purification. All reagents and solvents were obtained commercially and used as received without further purification. Column chromatography was performed on silica gel (Qingdao Haiyang Chemical Co., LTD, 200-300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AVANCE-400 spectrometer using CDCl_3 or DMSO-d_6 as solvent. High-resolution mass spectra were recorded on a Bruker Impact mass spectrometer. FT-IR spectra were measured on a Tensor 27 spectrophotometer. Thermogravimetric analysis (TGA) measurements were performed under nitrogen flow using a Q1000DSC+LNCS+FACSQ600SDT Instruments with a heating rate of $20^\circ\text{C}/\text{min}$ from ambient temperature to 600°C . UV-Vis spectra of the copolymers were obtained on U-3900/3900H spectrometer. Photoluminescence (PL) spectra of the polymers were obtained on F-7000 luminescence spectrometer. Cyclic voltammetry (CV) was conducted on an electrochemistry workstation (CHI 660A, Chenhua Shanghai). The average molecular weight and polydispersity index (PDI) of the polymers were determined using Viscotek gel permeation chromatography (GPC) analysis with THF as the eluent and polystyrene as the standard.

2. Synthesis of monomer M_1



Synthesis of compound:

Compound (C_1)



Benzidine (1.0 g, 0.005 mol) and HCl (3 mL) were added to a 50 mL flask and stirred at 50 °C until they were completely dissolved. Then, saturated NH₄SCN (2.0 g, 0.025 mol) aqueous solution was added. Then, the mixture was refluxed at 80 °C for 4 h till a light yellow, and continued to reflux for 48 h. After the reaction is finished, cooling to room temperature, dropwise adding NaOH solution to adjust the pH = 7-8, then filtering, washing (hot water washing for three times) and drying to obtain light yellow solid (5.6 g, 91.1%). ¹H NMR (400MHz, DMSO-d₆) δ(ppm) 9.73(s, 2H), 7.57(d, J=8.0HZ, 4H), 7.44(d, J=8.0HZ, 4H). ¹³C NMR (100MHz) δ(ppm) 181.40, 138.87, 135.90, 127.04, 123.71. FT-IR (KBr) 3384, 3260, 3028, 1620, 1500, 1406, 1244, 1178, 811.

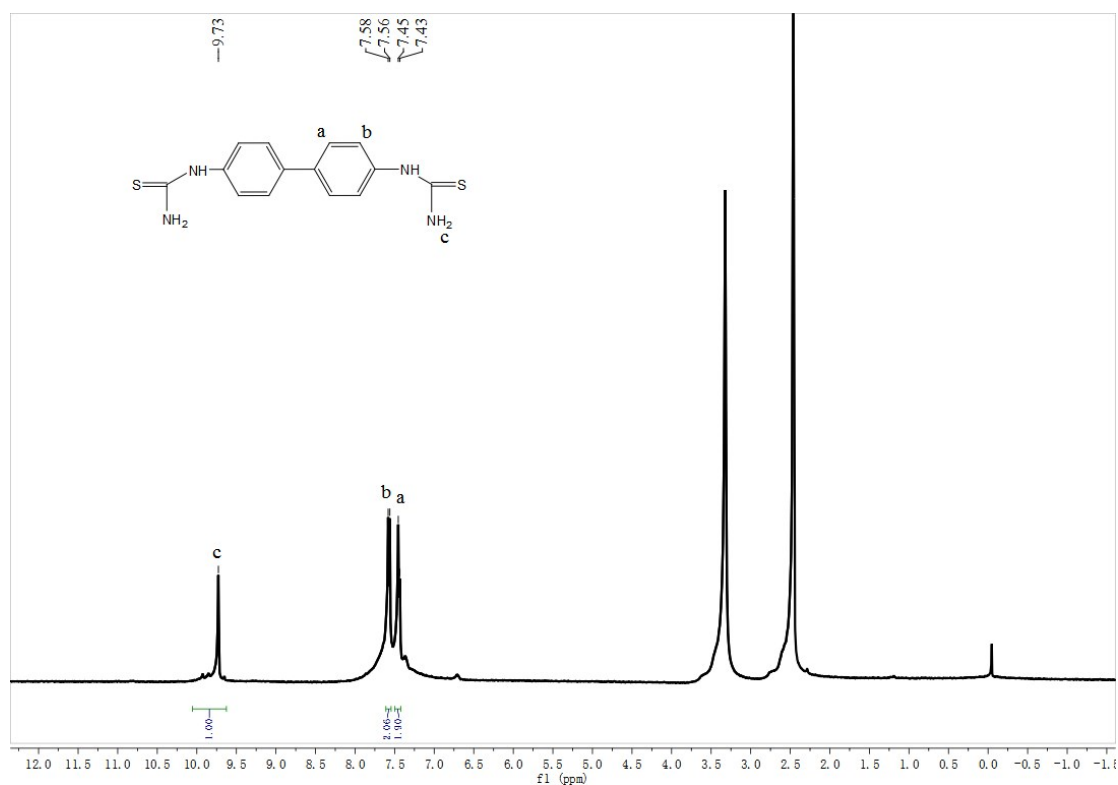


Fig. S1. ¹H NMR spectrum of C₁ measured in DMSO-d₆.

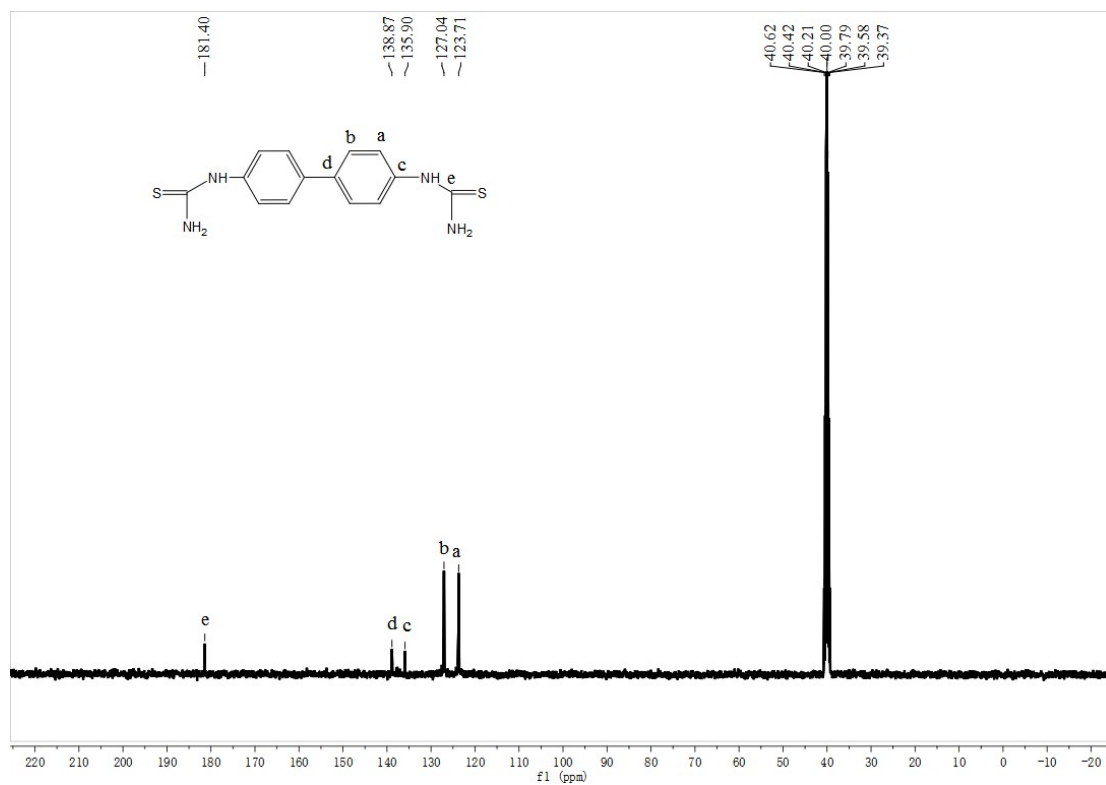


Fig. S2. ^{13}C NMR spectrum of C_1 measured in DMSO-d_6 .

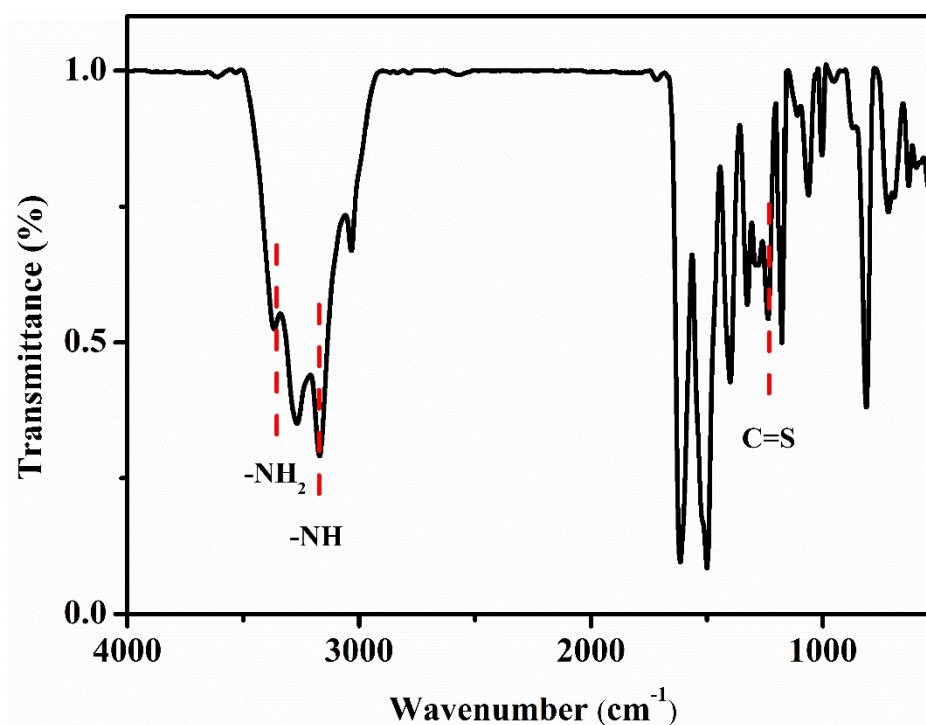
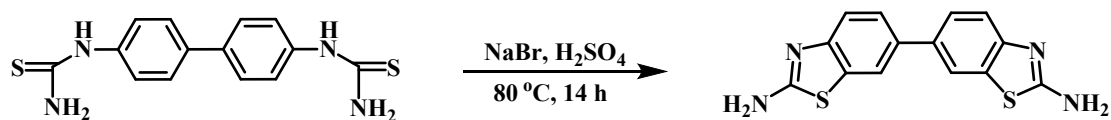


Fig. S3. FT-IR spectrum of C_1 .

Monomer (M_1)



C₁ (1.0 g, 0.003 mol) was placed in a 50 mL flask, then H₂SO₄ (1.76 mL, 0.03 mol) was added and stirred at 50 °C. NaBr (0.136 g, 0.0012mol) were added in batches and reacted at 80 °C for 14 h. The reaction solution was poured into cold water, NaOH is added to adjust the pH = 7-8, the reaction solution is cooled to room temperature, filtering and drying to obtain grayish yellow solid (2.92 g, 98.1%). ¹H NMR (400MHz, DMSO-d₆) δ(ppm) 8.01(d, J=18.4HZ, 2H), 7.57(d, J=10.8HZ, 2H), 7.43(d, J=11.2HZ, 2H), 4.31(s, 4H). ¹³C NMR (100MHz) δ(ppm) 167.78, 149.51, 134.28, 130.96, 125.09, 119.68, 117.68. FT-IR (KBr) 3373, 3097, 1645, 1448, 1099, 813. ESI calcd for C₁₄H₁₀N₄S₂ [M+H]⁺ 299.0425, found 299.0423.

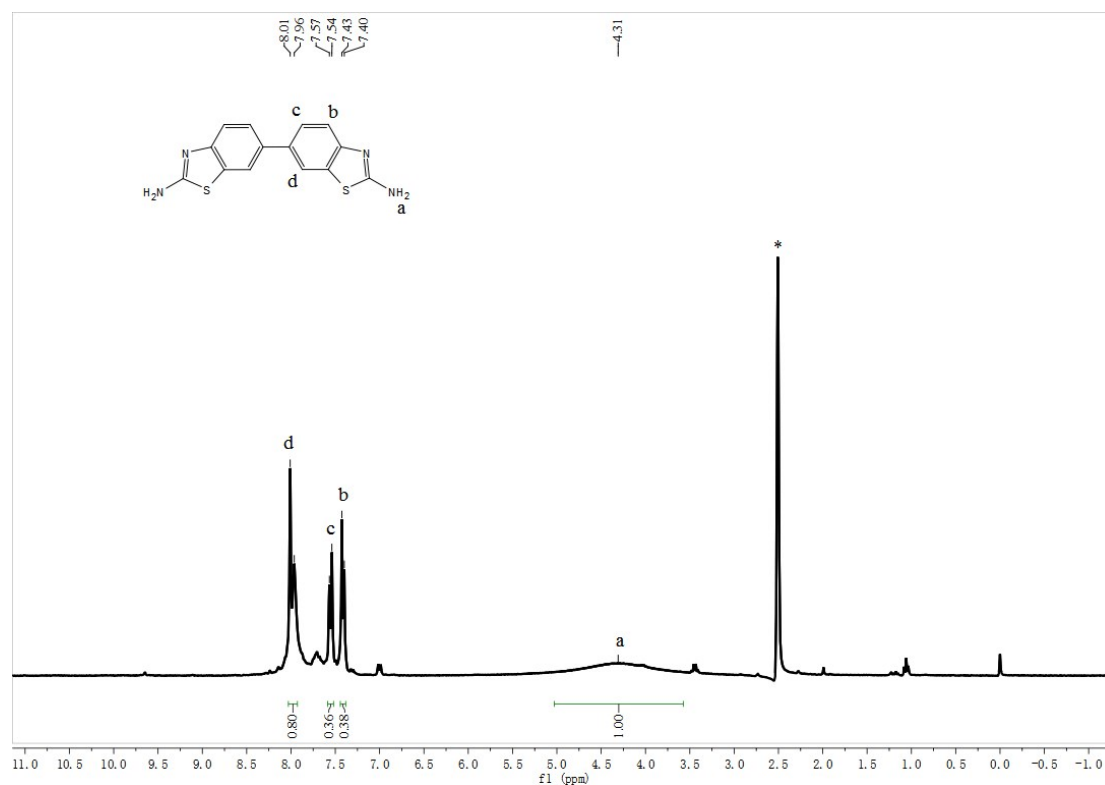


Fig. S4. ¹H NMR spectrum of **M₁** measured in DMSO-d₆.

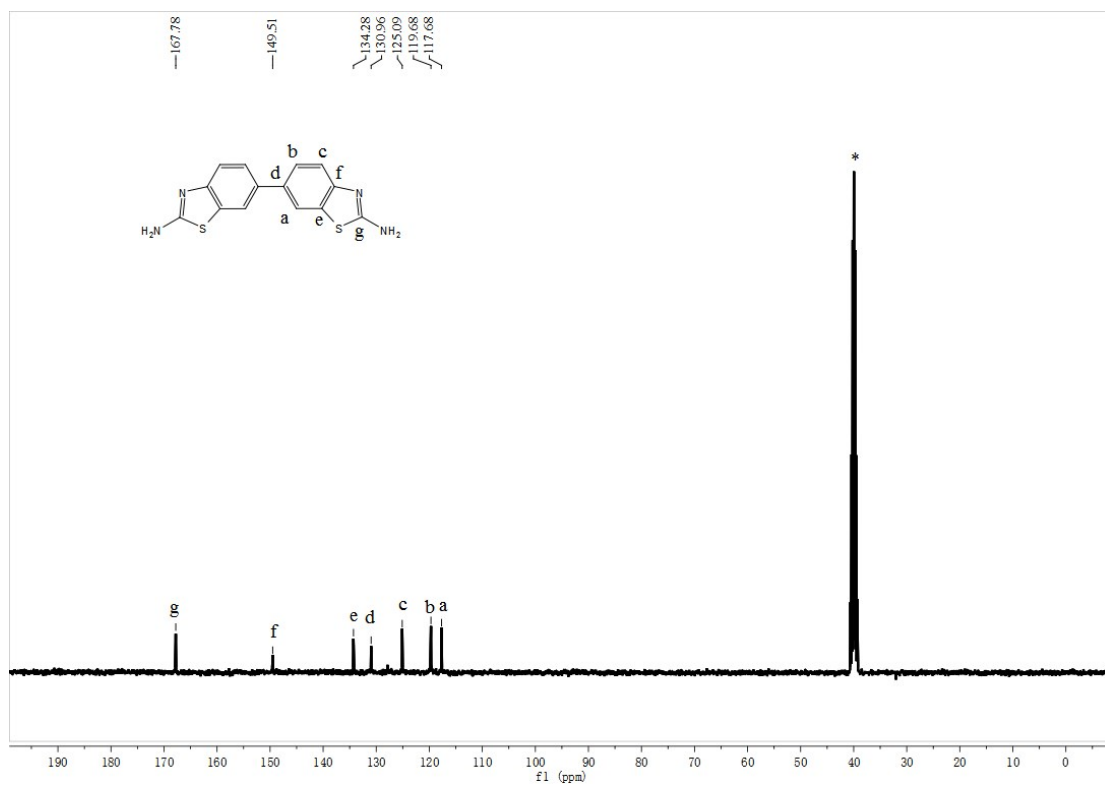


Fig. S5. ^{13}C NMR spectrum of M_1 measured in DMSO-d_6 .

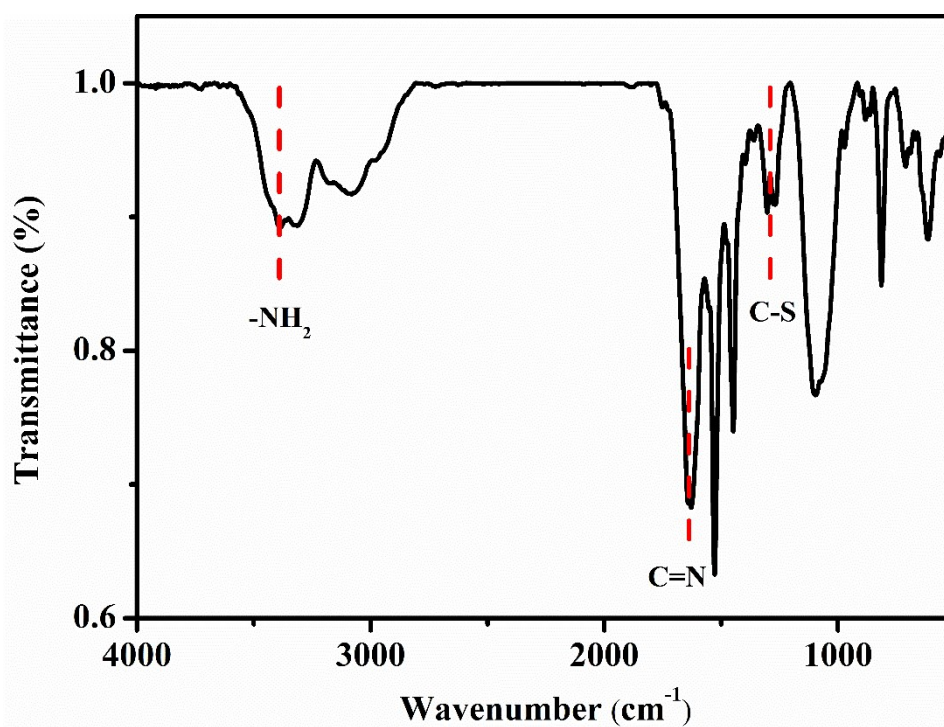


Fig. S6. IR spectrum of M_1 .

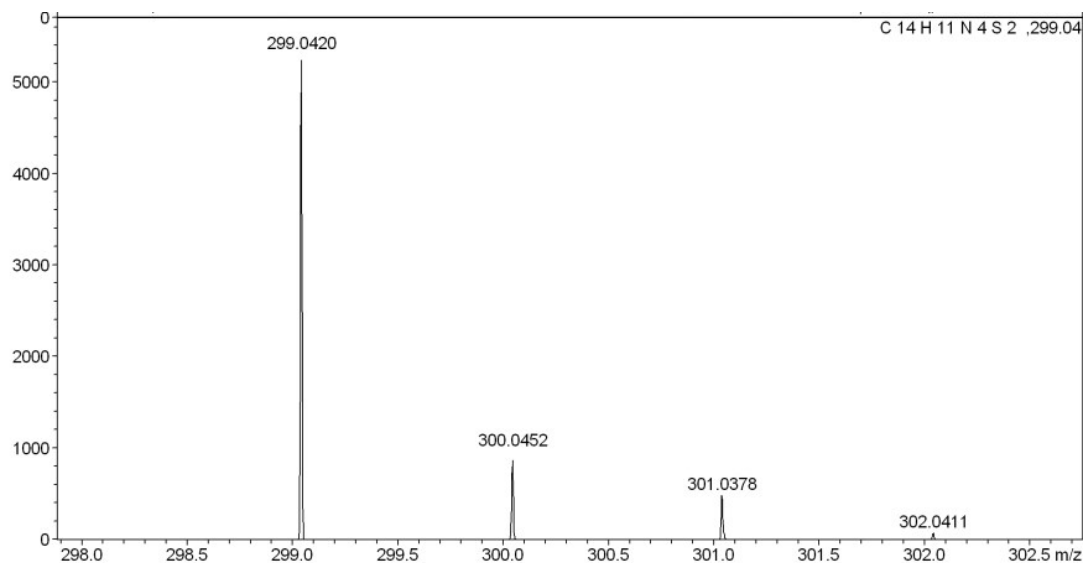


Fig. S7. High-resolution mass spectra of **M₁**.

3. Synthesis and Optical Properties of polymers

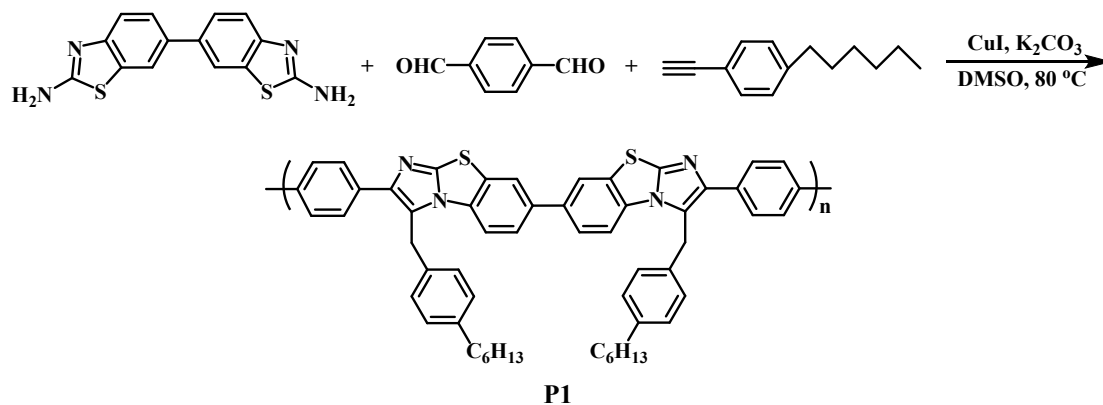
General polymerization:

All the polymerizations were conducted under argon and anhydrous conditions. To a flask charged with monomer in anhydrous DMSO solution, CuI and K₂CO₃ were added to the solution. The reaction mixture was tightly sealed and heated at 80 °C for 72 h.

P1-P2: After cooling, the mixture was poured into CH₂Cl₂ (30 mL), washed with water (2×10 mL), saturated aqueous NH₄Cl (3×10 mL) and brine (2×10 mL), subsequently, the organic solvent was dried with Mg₂SO₄. The solvent was removed under reduced pressure to obtain the crude product. Finally, the crude product is dissolved in THF and dialyzed to obtain the target polymer.

P3-P6: After cooling, the mixture was poured into cold water (100 mL) and solids precipitated. The solid crude product was dissolved in THF, and the pure product was obtained after dialysis treatment.

Polymer (**P1**)



Polymer **P1** was obtained as tan powder in 54.3% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm) 8.10-7.25(22H, ArH), 4.29(s, 4H, CH_2), 2.69-2.65(m, 8H, CH_2), 1.58-1.55(m, 8H, CH_2), 1.32-1.24(m, 8H, CH_2), 0.96-0.87(t, 6H, CH_3). ^{13}C NMR (100MHz) δ (ppm) 144.4, 140.5, 136.2, 133.7, 129.6, 128.0, 126.0, 124.9, 121.1, 115.0, 103.5, 41.7, 39.5, 34.02, 28.9, 27.5, 21.7. FT-IR (KBr) 3031, 2923, 2852, 2729, 1604, 1465, 1207, 1122, 1014, 817.

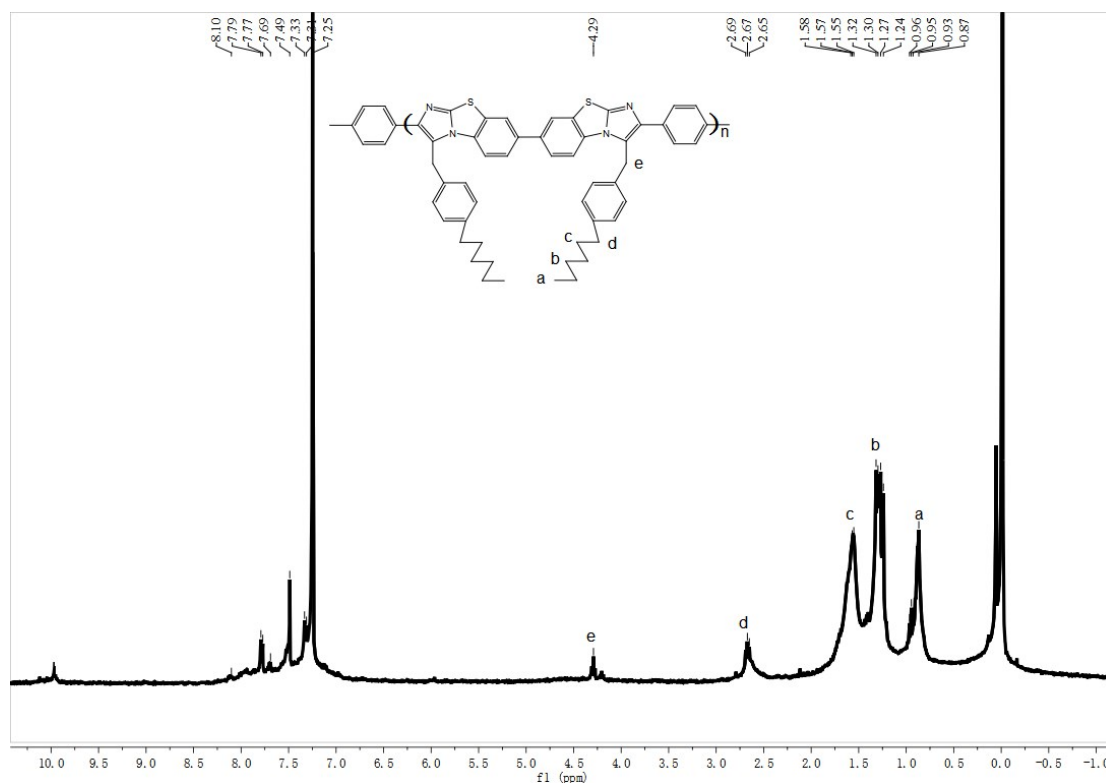


Fig. S8. ^1H NMR spectrum of **P1** measured in CDCl_3 .

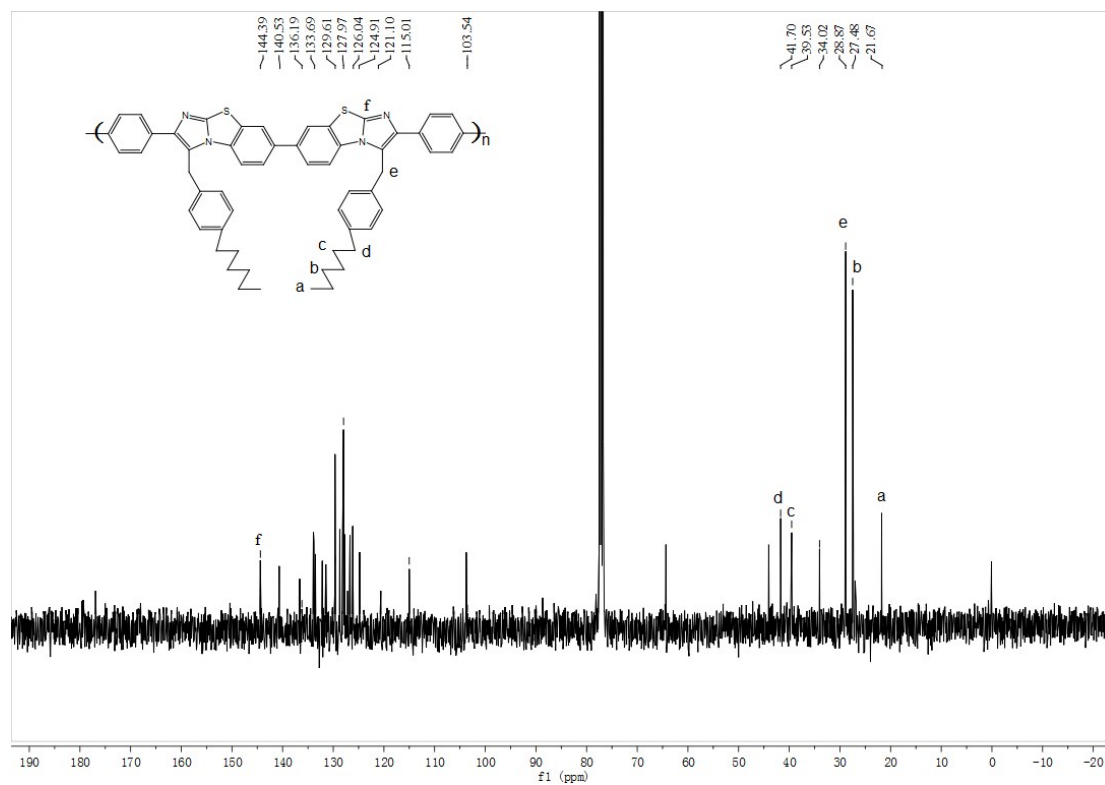


Fig. S9. ¹³C NMR spectrum of P1 measured in CDCl₃.

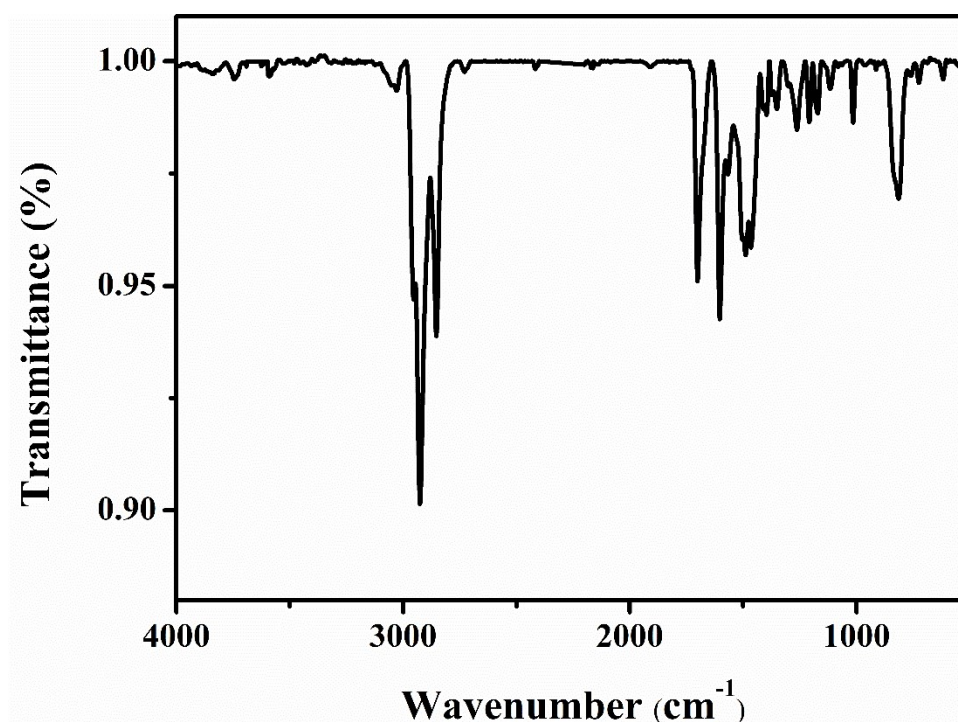


Fig. S10. IR spectrum of P1.

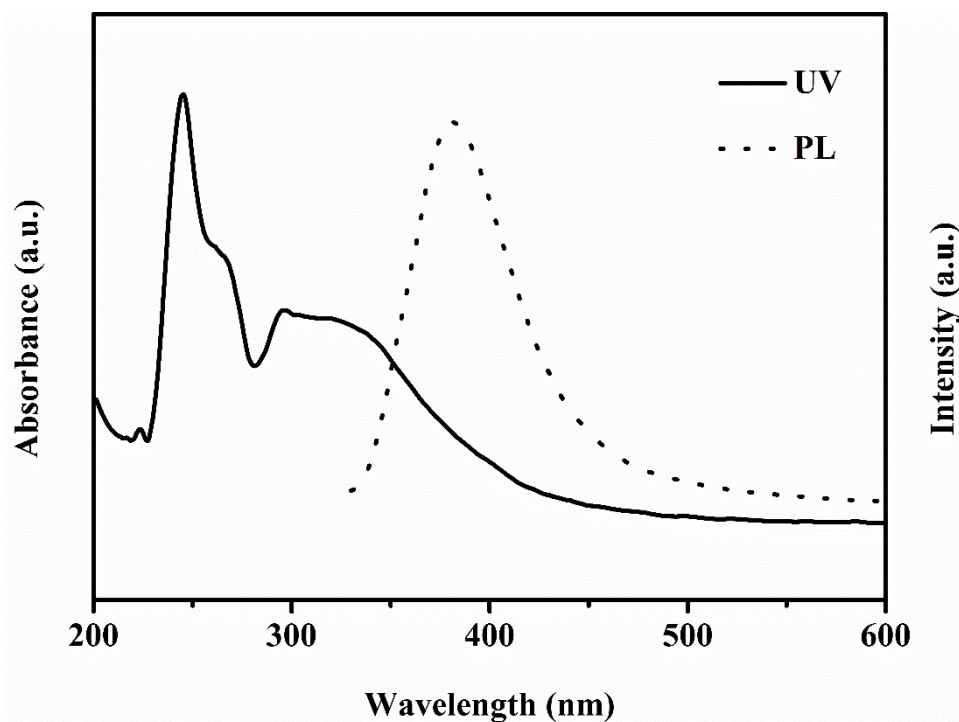
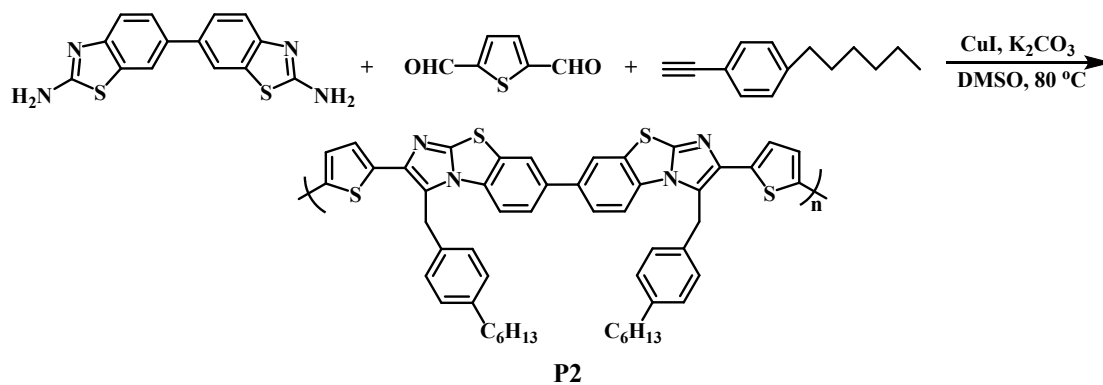


Fig. S11. UV-Vis absorption and Photoluminescence spectra of **P1** in THF solution.

Polymer (**P2**)



Polymer **P2** was obtained as tan powder in 58.9% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm) 8.03-7.06(18H, ArH), 4.62(s, 4H, CH_2), 2.63-2.55(m, 8H, CH_2), 1.55-1.51(m, 8H, CH_2), 1.23-1.19(m, 8H, CH_2), 0.81-0.77(t, 6H, CH_3). ^{13}C NMR (100MHz) δ (ppm) 141.0, 136.0, 135.5, 134.5, 132.5, 126.7, 122.9, 122.6, 39.6, 33.2, 25.3, 25.0. FT-IR (KBr) 2930, 2862, 2725, 1701, 1606, 1465, 1261, 1099, 1018, 833.

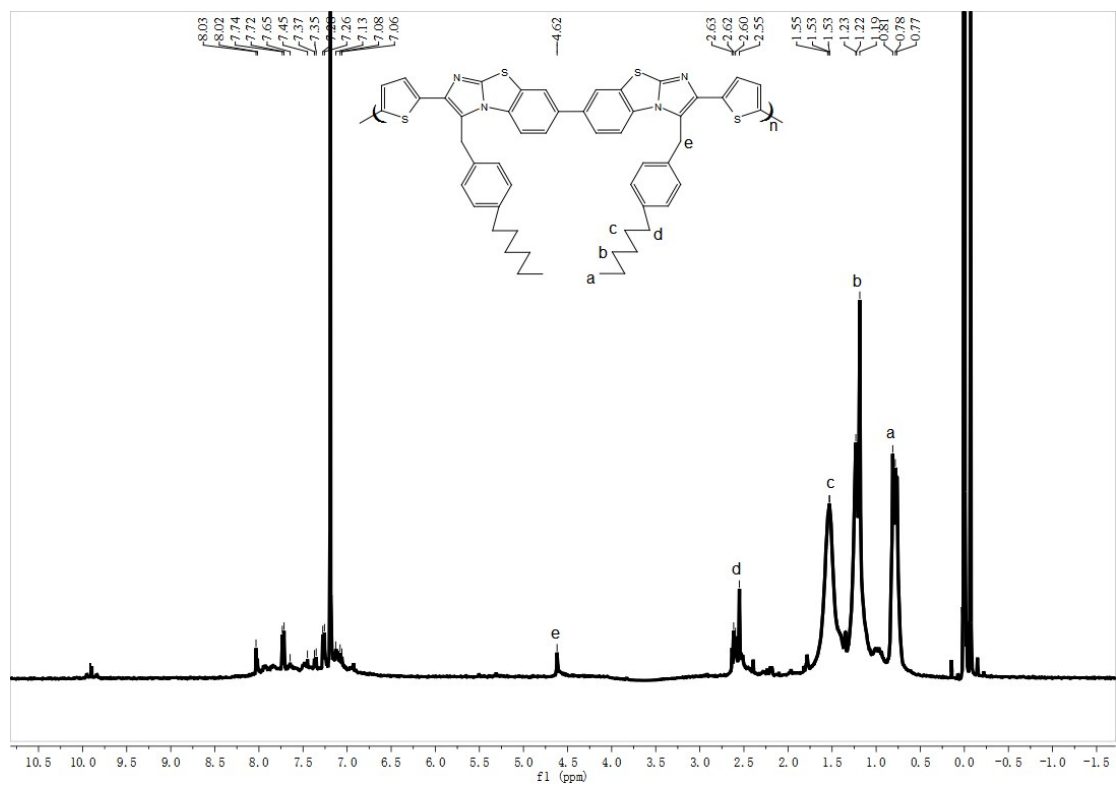


Fig. S12. ^1H NMR spectrum of **P2** measured in CDCl_3 .

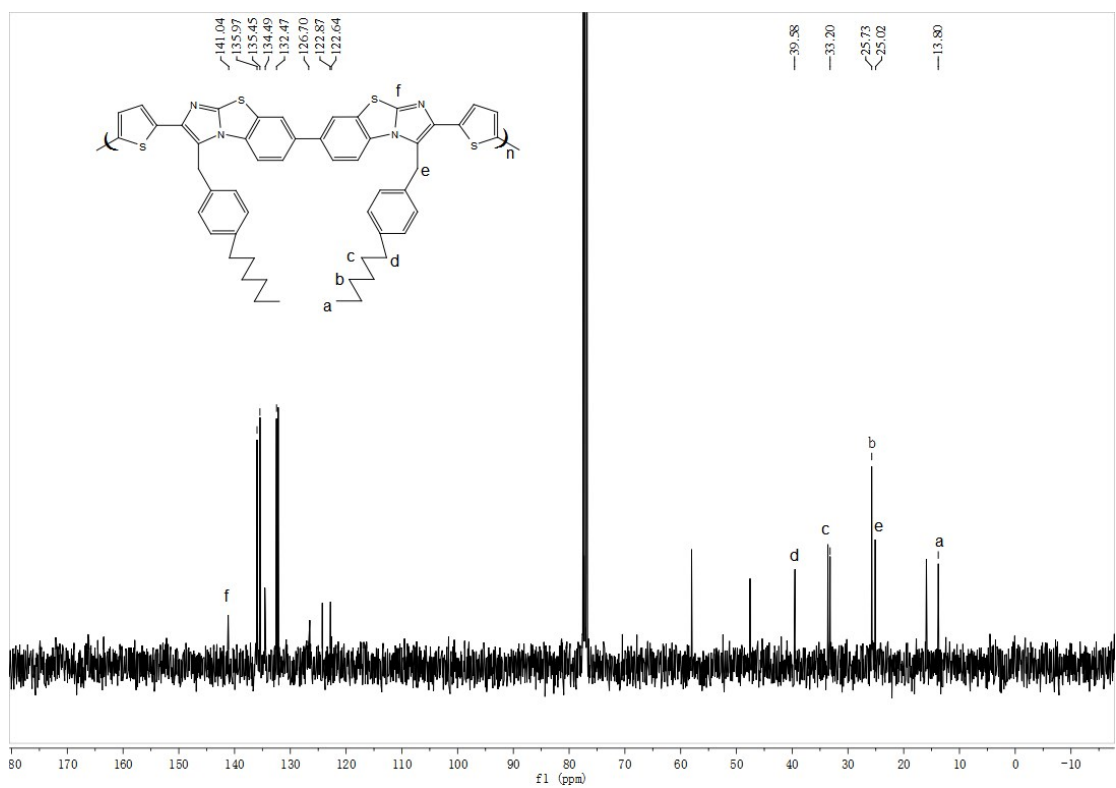


Fig. S13. ^{13}C NMR spectrum of **P2** measured in CDCl_3 .

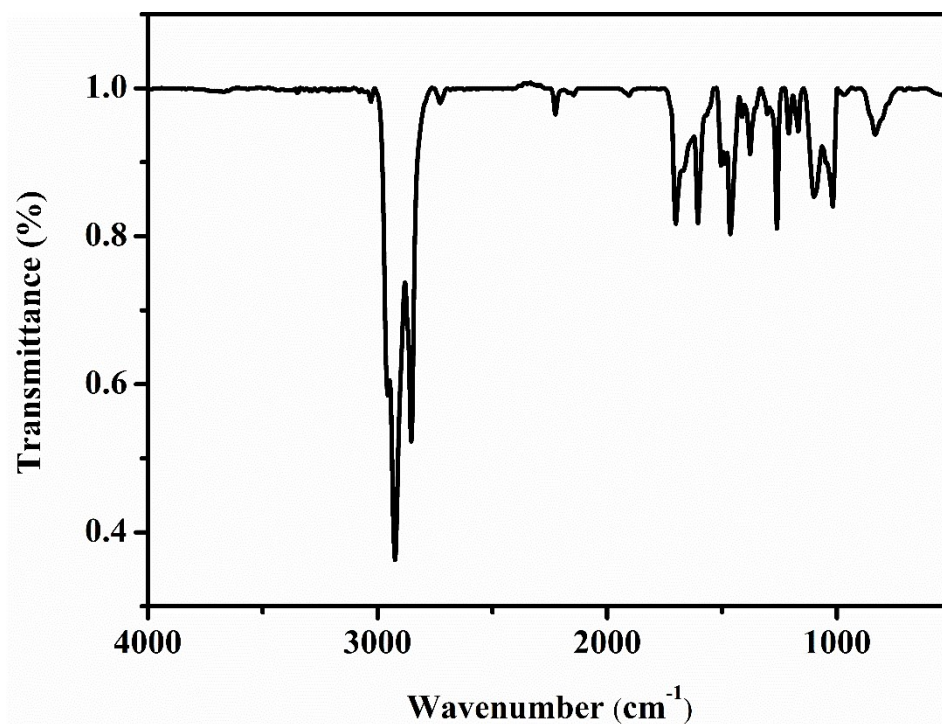


Fig. S14. IR spectrum of P2.

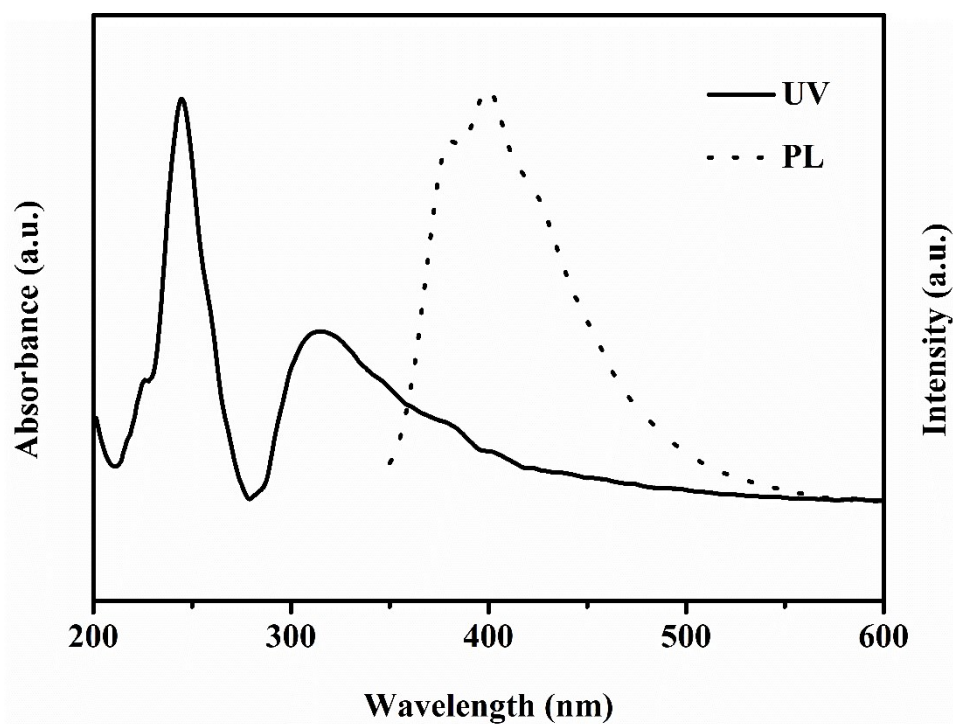
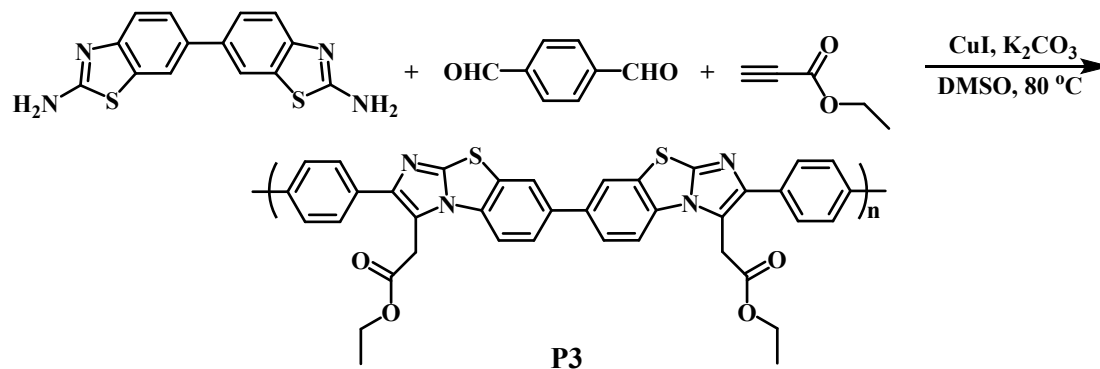


Fig. S15. UV-Vis absorption and Photoluminescence spectra of P2 in THF solution.

Polymer (P3)



Polymer **P3** was obtained as yellow powder in 45.4% yield. $^1\text{H NMR}$ (400MHz, CDCl_3) δ (ppm) 8.13-7.29(14H, ArH), 4.32(s, 4H, CH_2), 4.13-4.09(m, 4H, CH_2), 1.22-1.18(t, 6H, CH_3). $^{13}\text{C NMR}$ (100MHz) δ (ppm) 166.2, 162.8, 154.8, 150.2, 133.2, 133.0, 130.0, 127.8, 127.4, 124.3. FT-IR (KBr) 2985, 2902, 2827, 2735, 1720, 1607, 1271, 1219, 1166, 1039, 985, 825.

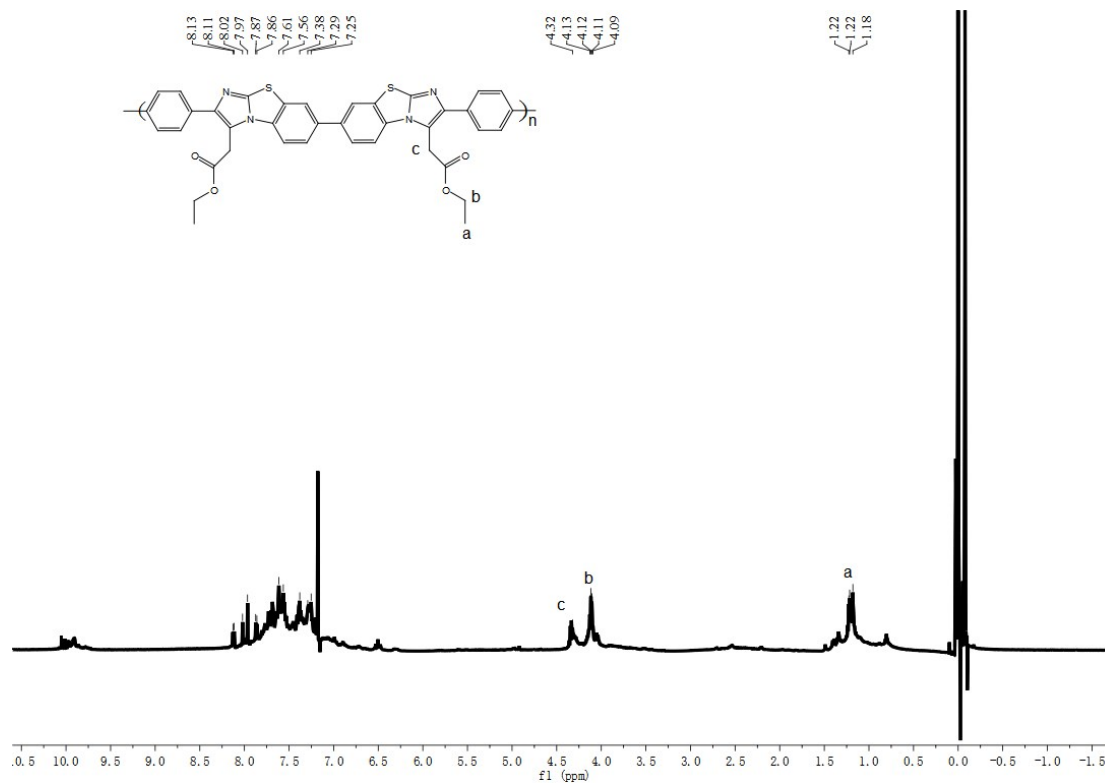


Fig. S16. $^1\text{H NMR}$ spectrum of **P3** measured in CDCl_3 .

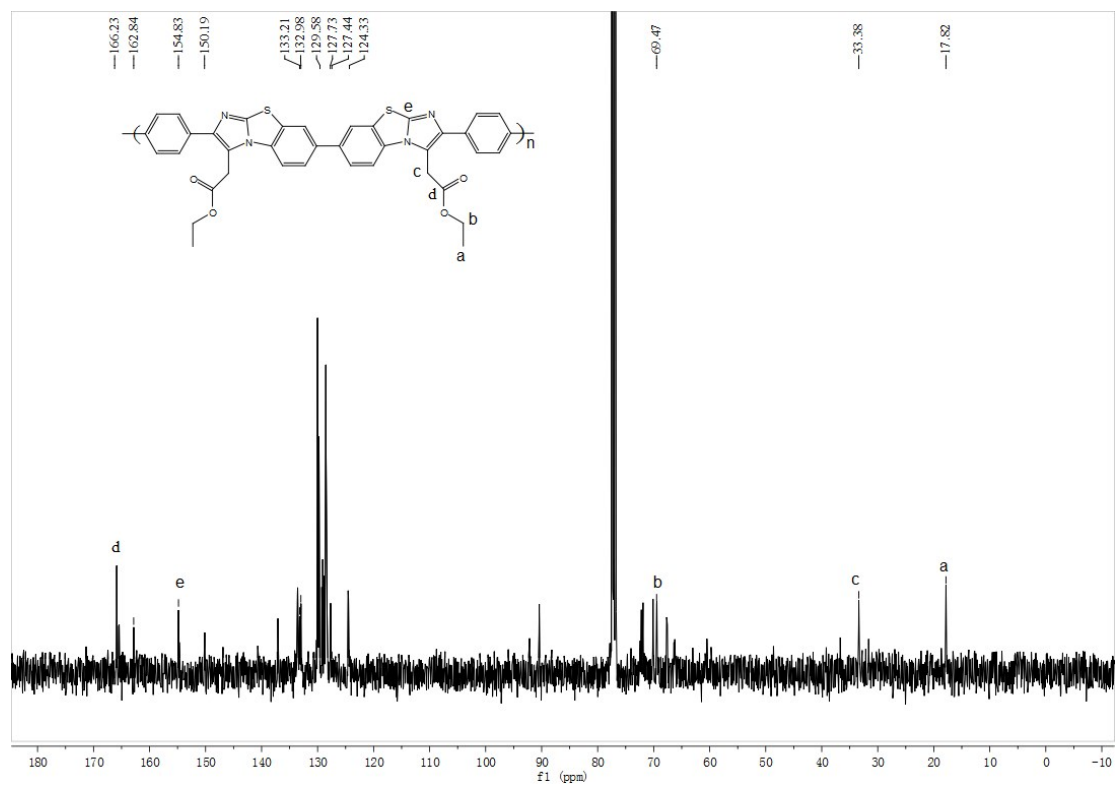


Fig. S17. ¹³C NMR spectrum of **P3** measured in CDCl₃.

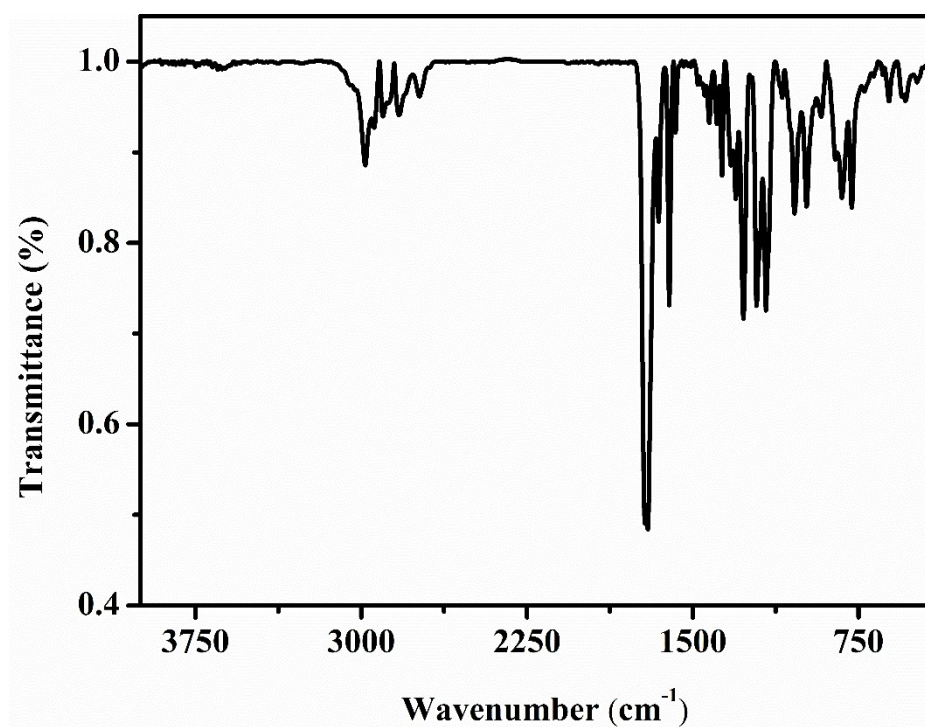


Fig. S18. IR spectrum of **P3**.

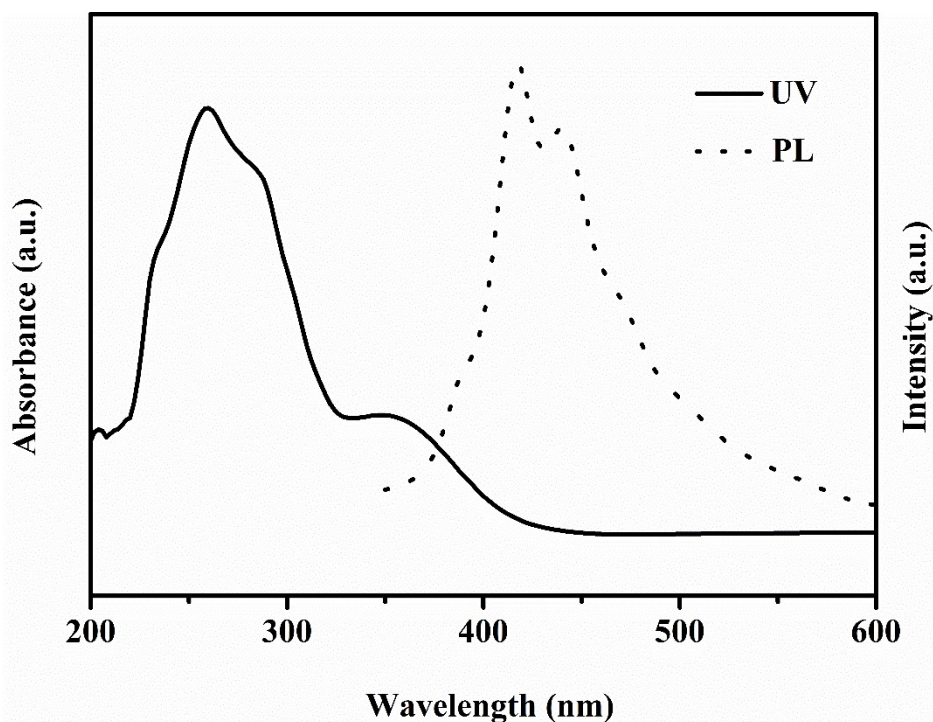
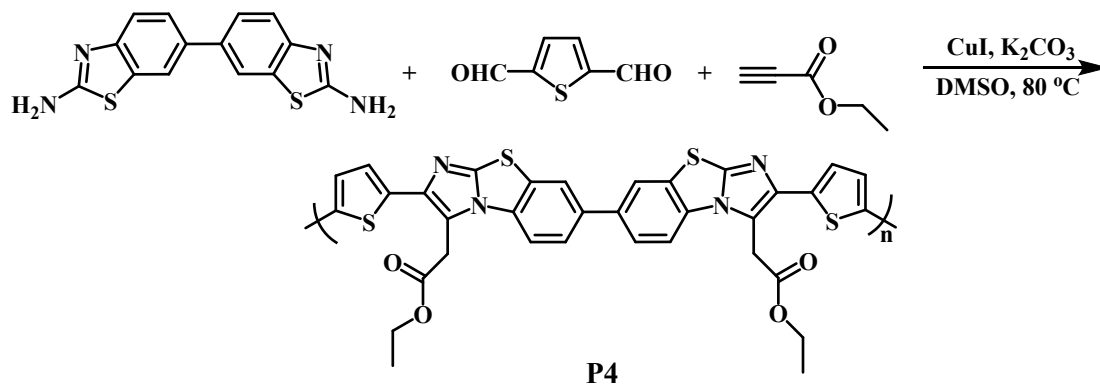


Fig. S19. UV-Vis absorption and Photoluminescence spectra of **P3** in THF solution.

Polymer (**P4**)



Polymer **P4** was obtained as yellow powder in 47.3% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm) 8.41-7.30(10H, ArH), 4.32(s, 4H, CH_2), 4.23-4.18(m, 4H, CH_2), 1.22-1.88(t, 6H, CH_3). ^{13}C NMR (100MHz) δ (ppm) 170.7, 152.9, 144.9, 137.5, 137.0, 134.00, 132.8, 128.5, 126.0, 125.3, 121.6, 120.4, 119.3, 119.0, 70.3, 59.8, 46.0, 37.6, 26.3, 13.2. FT-IR (KBr) 2979, 2933, 2862, 1722, 1637, 1537, 1444, 1373, 1205, 1026, 810.

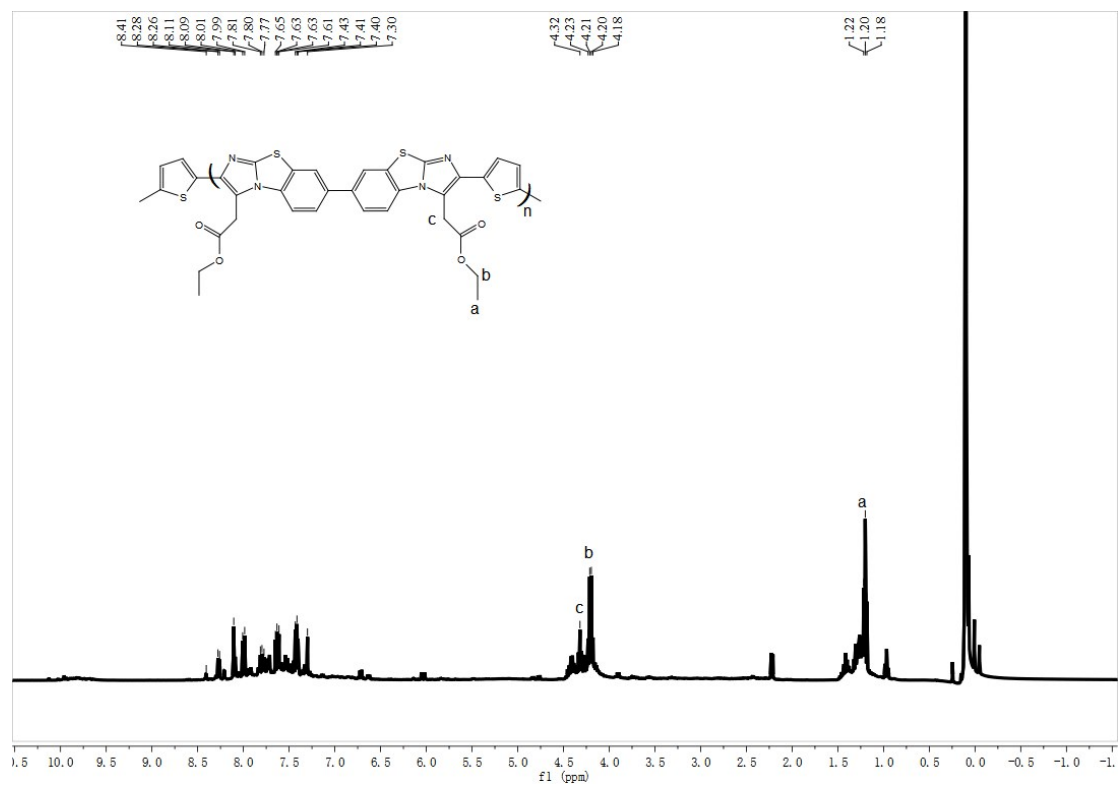


Fig. S20. ¹H NMR spectrum of **P4** measured in CDCl₃.

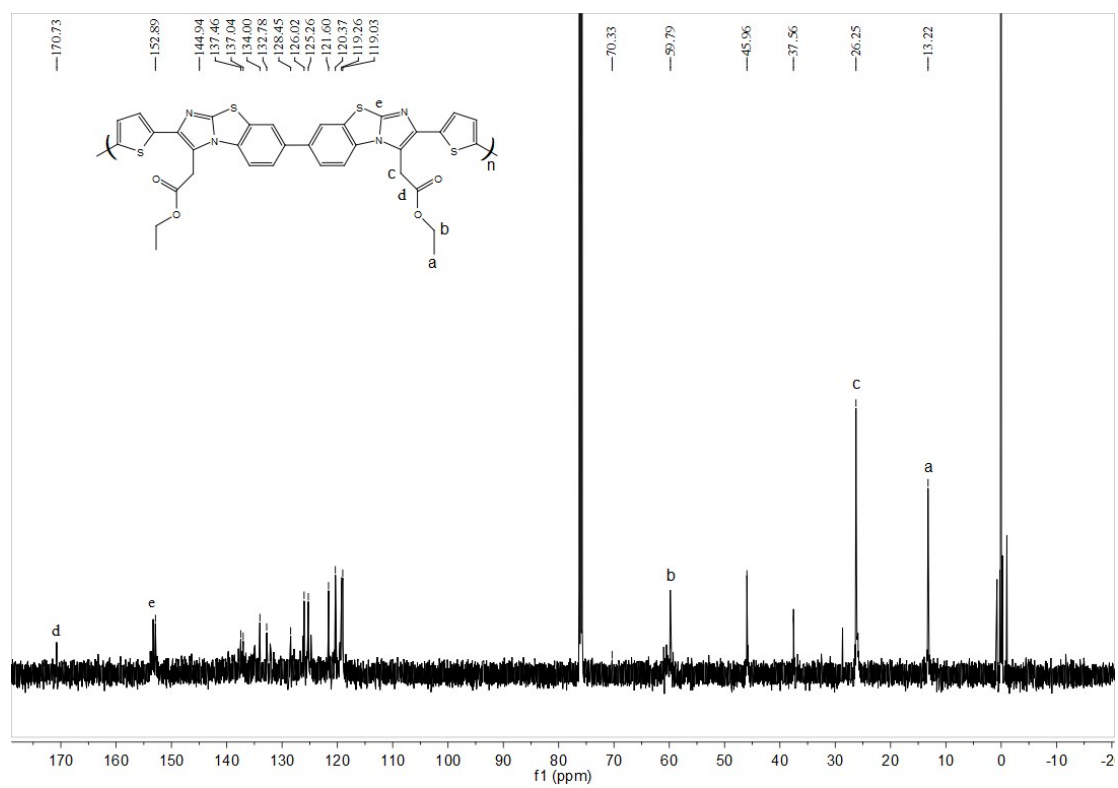


Fig. S21 ¹³C NMR spectrum of **P4** measured in CDCl₃.

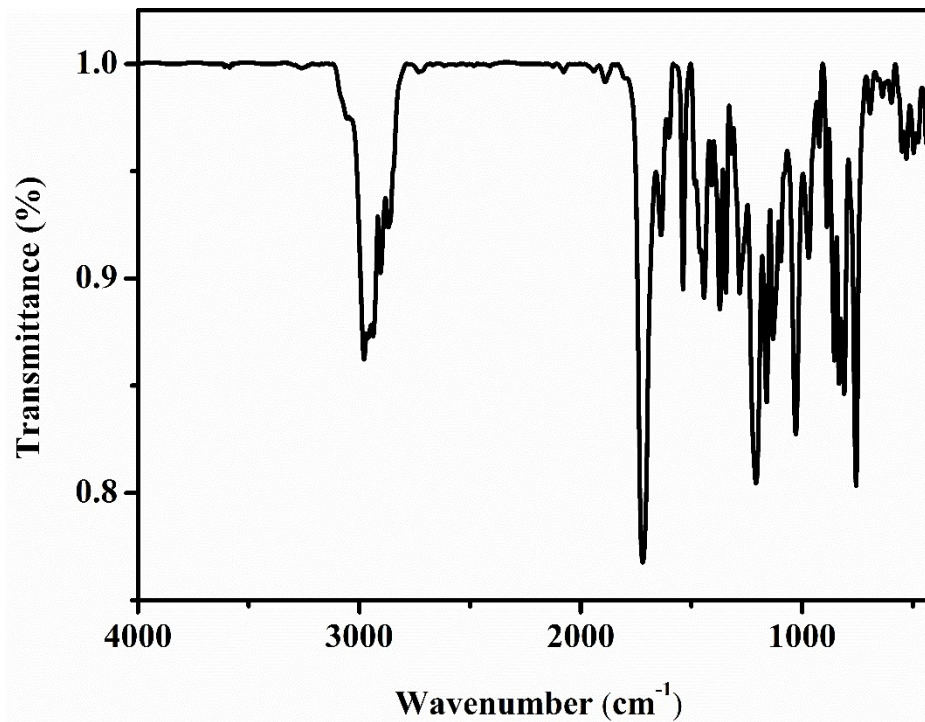


Fig. S22. IR spectrum of P4.

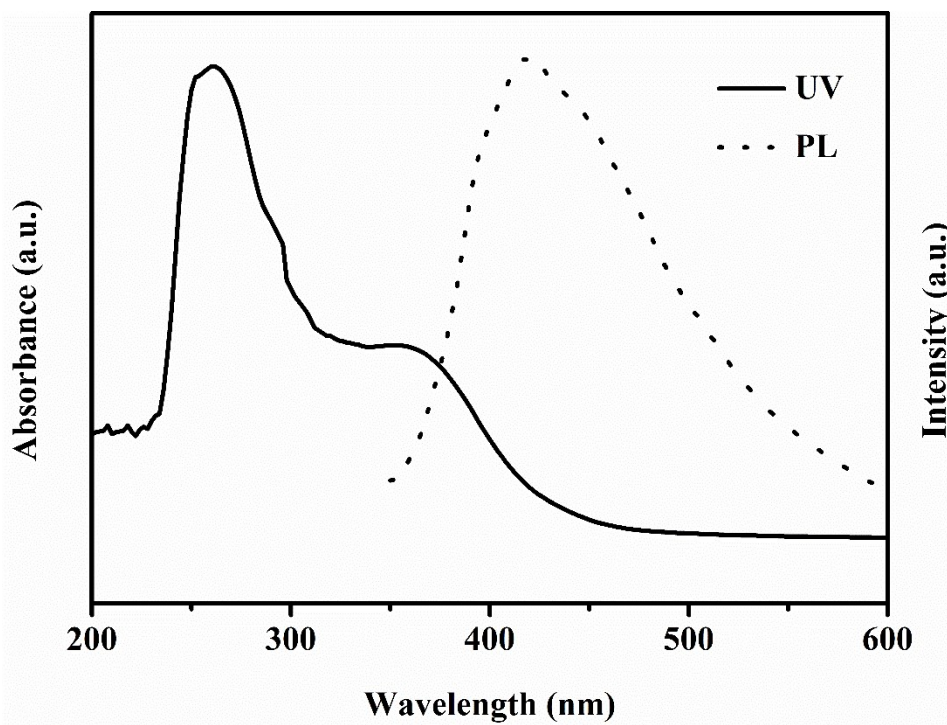
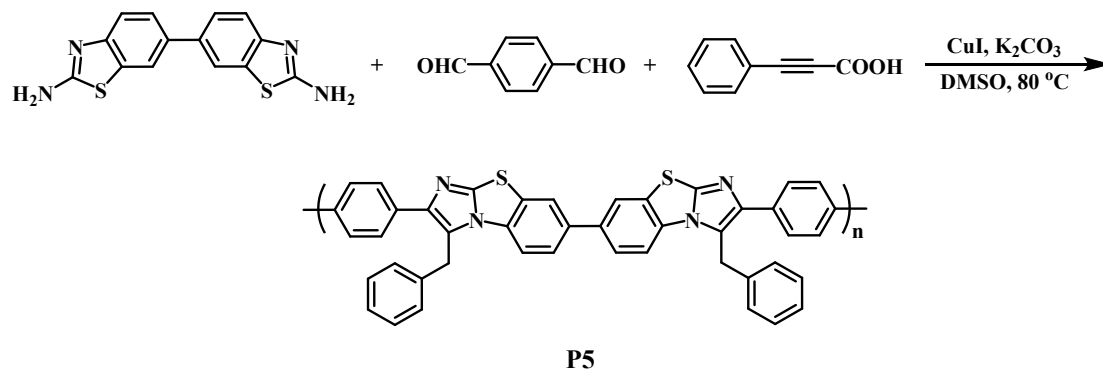


Fig. S23. UV-Vis absorption and Photoluminescence spectra of P4 in THF solution.

Polymer (P5)



Polymer **P5** was obtained as yellow powder in 44.9% yield. $^1\text{H NMR}$ (400MHz, CDCl_3) δ (ppm) 7.91-7.22(24H, ArH), 4.02(s, 4H, CH_2). $^{13}\text{C NMR}$ (100MHz) δ (ppm) 151.6, 137.6, 135.3, 131.0, 128.9, 124.1, 124.1, 119.2, 118.9, 117.1, 117.0. FT-IR (KBr) 3080, 2920, 1701, 1625, 1446, 1299, 1186, 1107, 1107, 817.

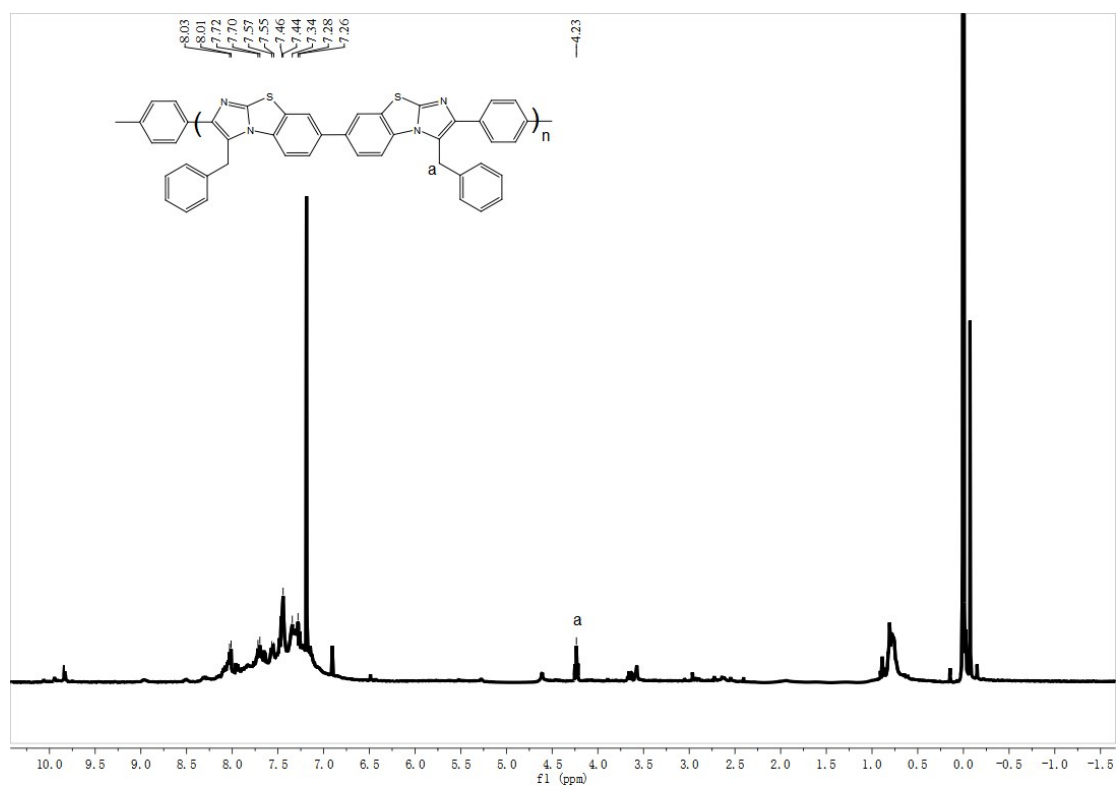


Fig. S24. $^1\text{H NMR}$ spectrum of **P5** measured in CDCl_3 .

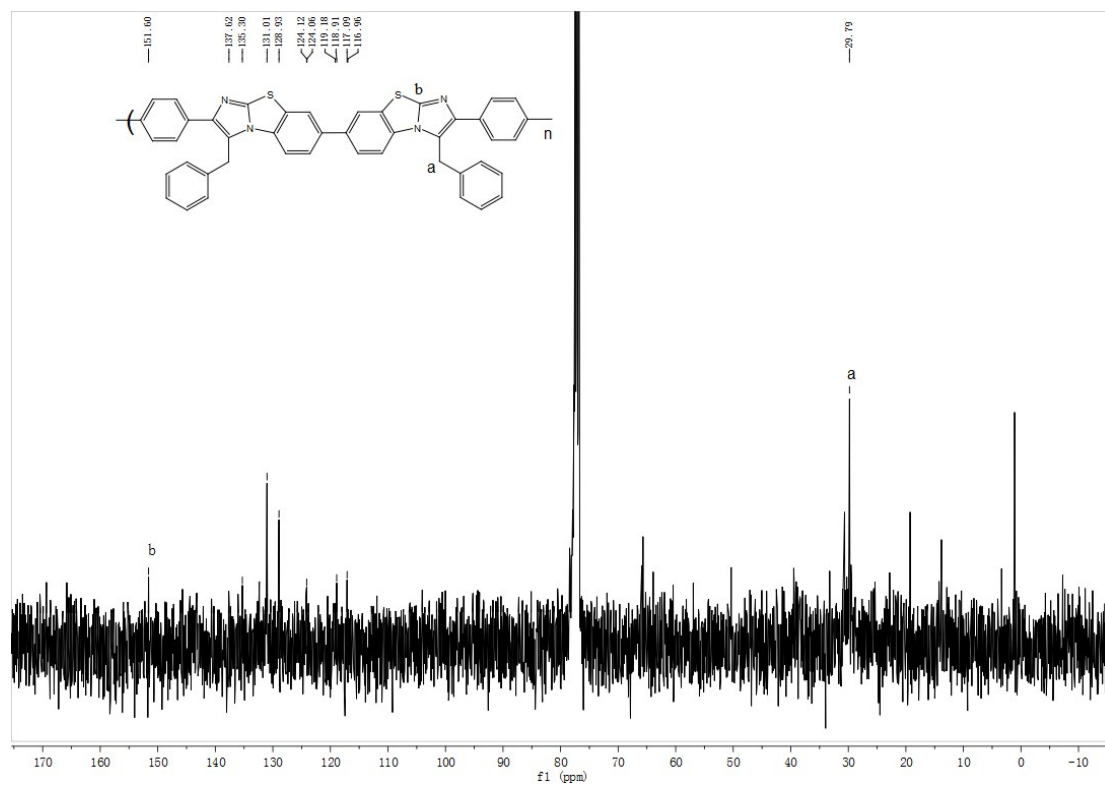


Fig. S25. ^{13}C NMR spectrum of **P5** measured in CDCl_3 .

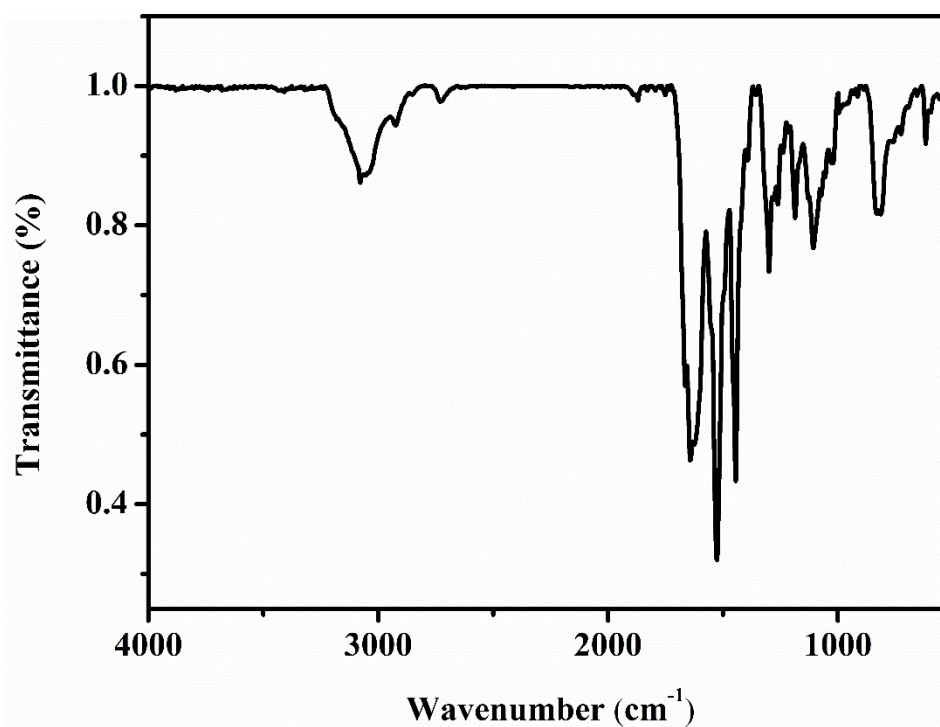


Fig. S26. IR spectrum of **P5**.

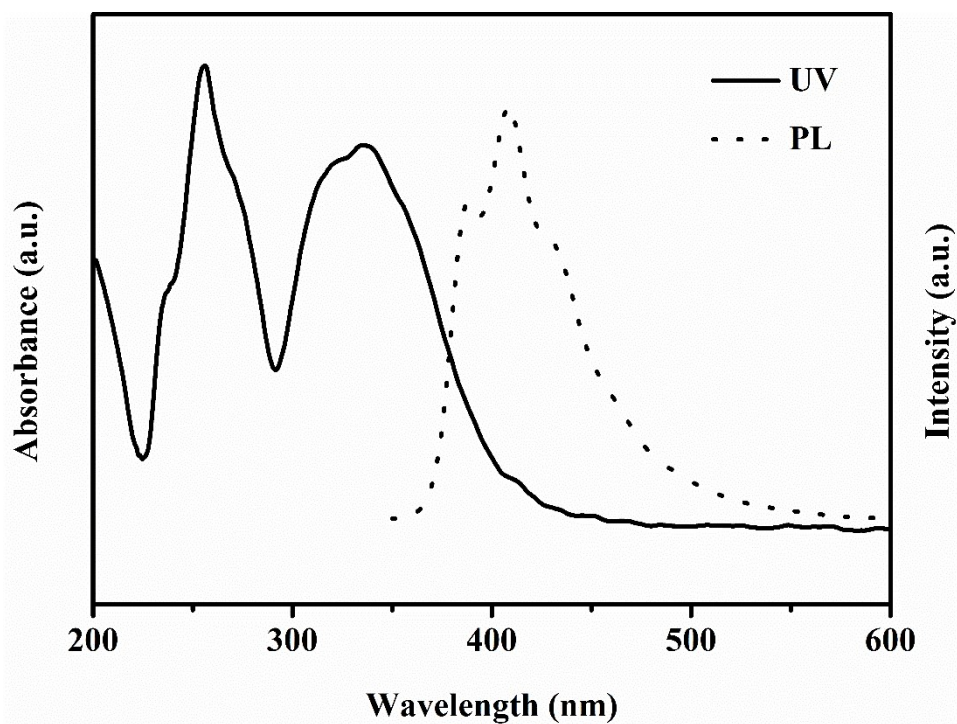
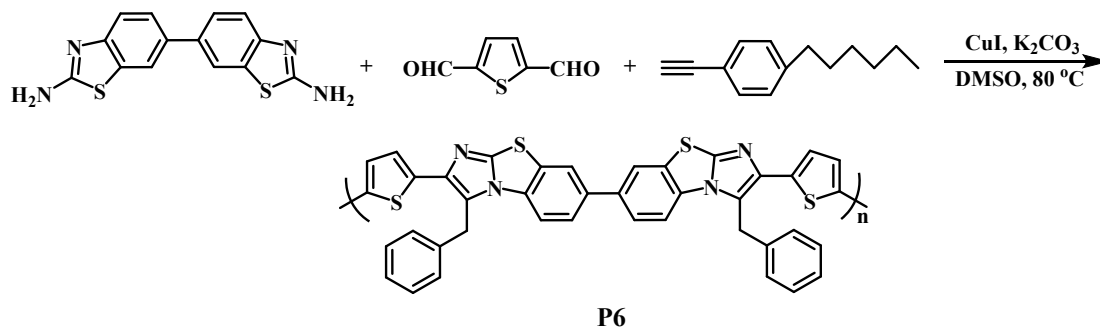


Fig. S27. UV-Vis absorption and Photoluminescence spectra of **P5** in THF solution.

Polymer (**P6**)



Polymer **P6** was obtained as yellow powder in 47.7% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm) 8.02-7.18(20H, ArH), 4.12(s, 4H, CH_2). ^{13}C NMR (100MHz) δ (ppm) 155.0, 140.4, 137.6, 135.1, 130.4, 129.4, 128.8, 128.6, 128.0, 126.3, 121.8, 119.2, 110.4, 63.6, 28.3. FT-IR (KBr) 2962, 2921, 2852, 1718, 1604, 1244, 1174, 1107, 1020, 833.

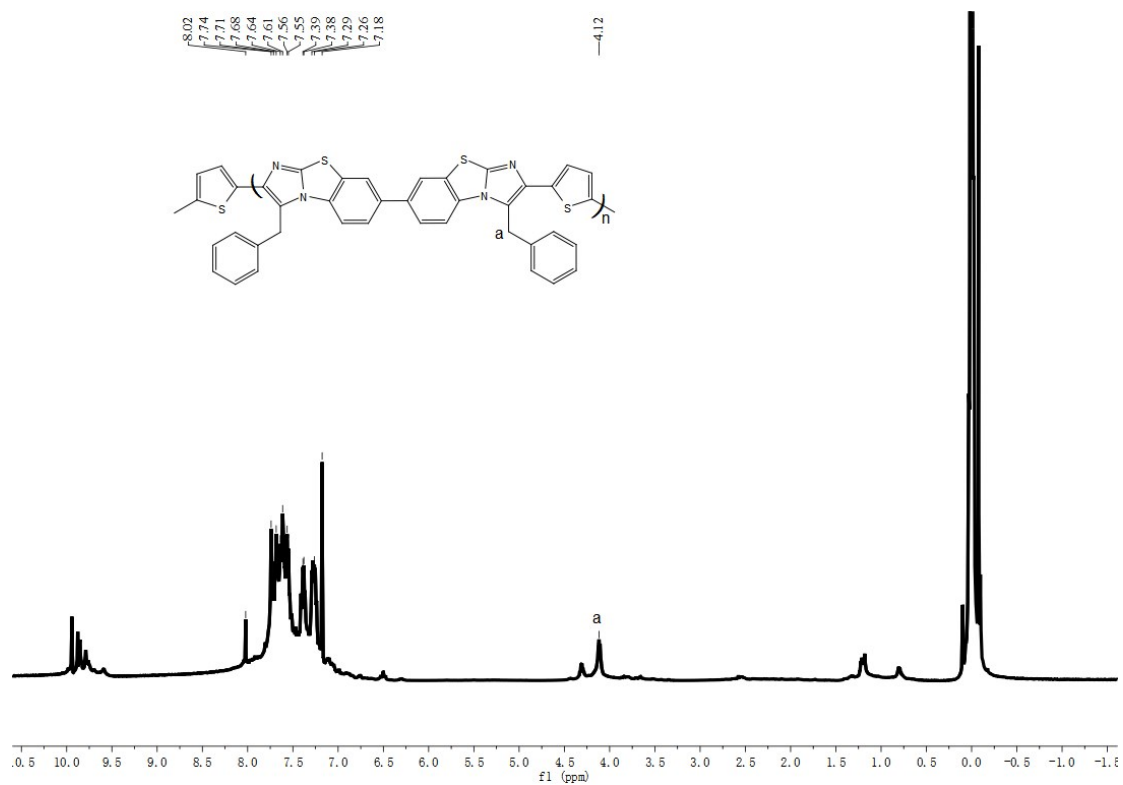


Fig. S28. ¹H NMR spectrum of P6 measured in CDCl₃.

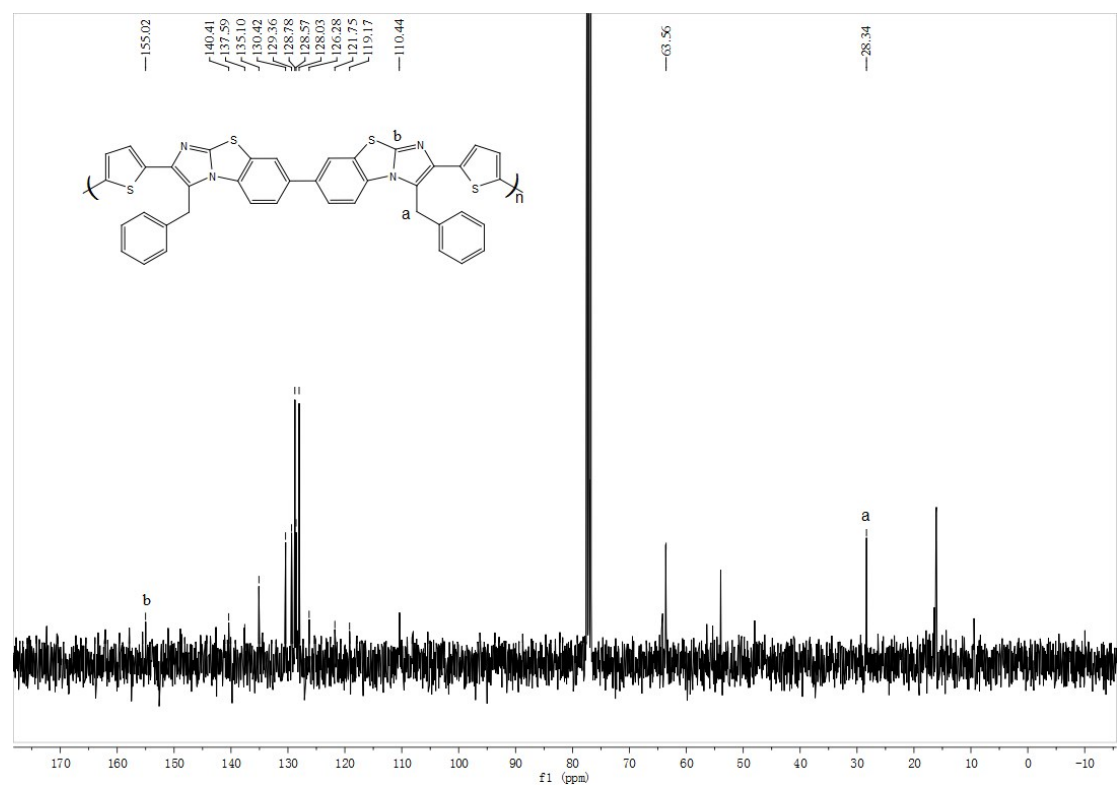


Fig. S29. ¹³C NMR spectrum of P6 measured in CDCl₃.

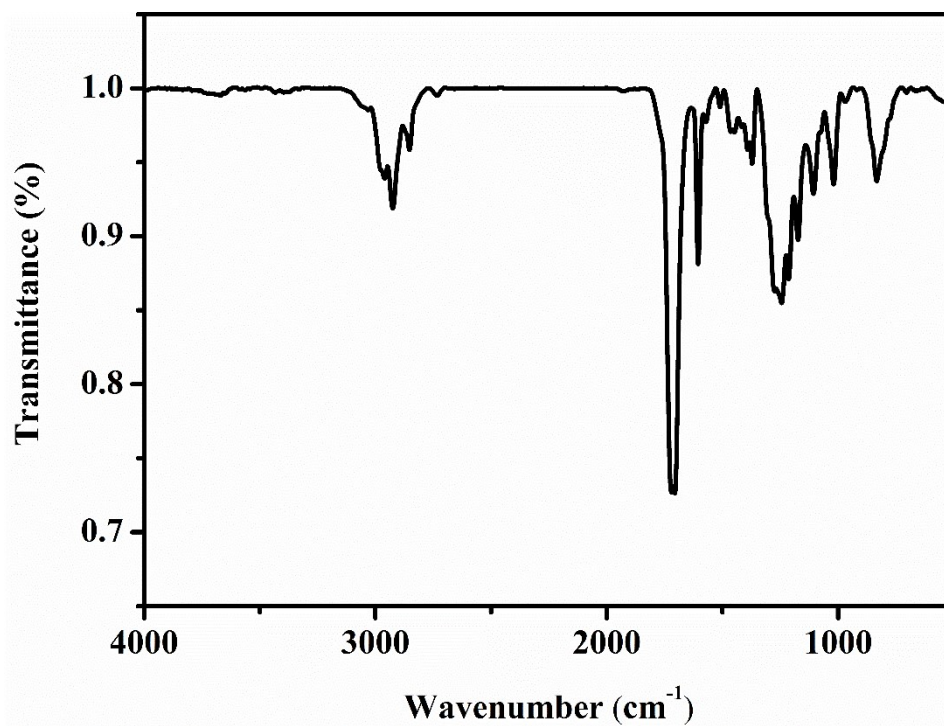


Fig. S30. IR spectrum of P6.

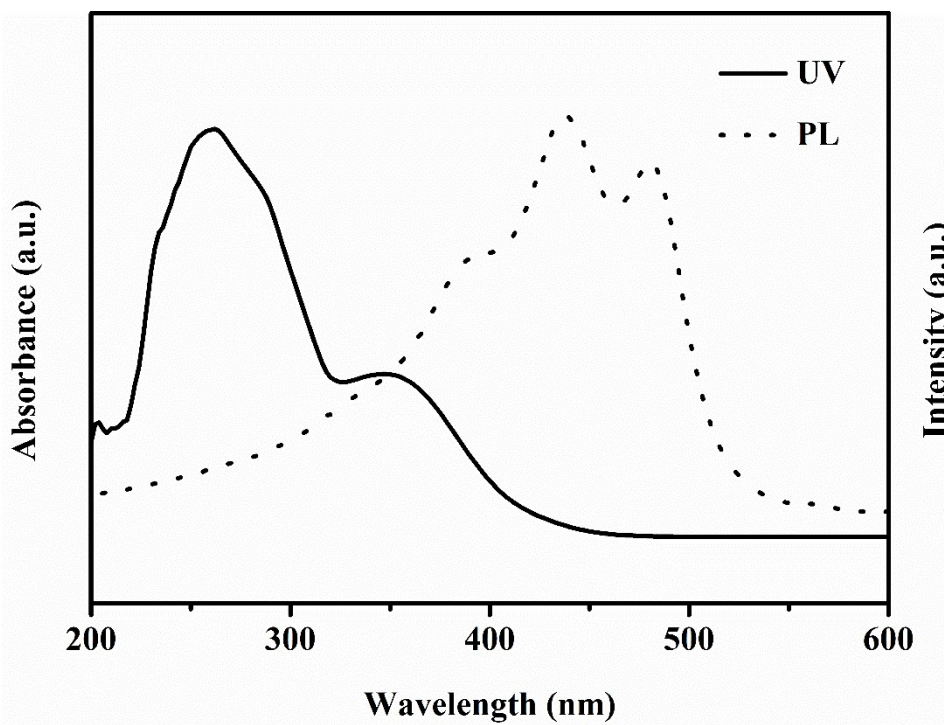


Fig. S31. UV-Vis absorption and Photoluminescence spectra of P6 in THF solution.

4. TGA curve of polymers

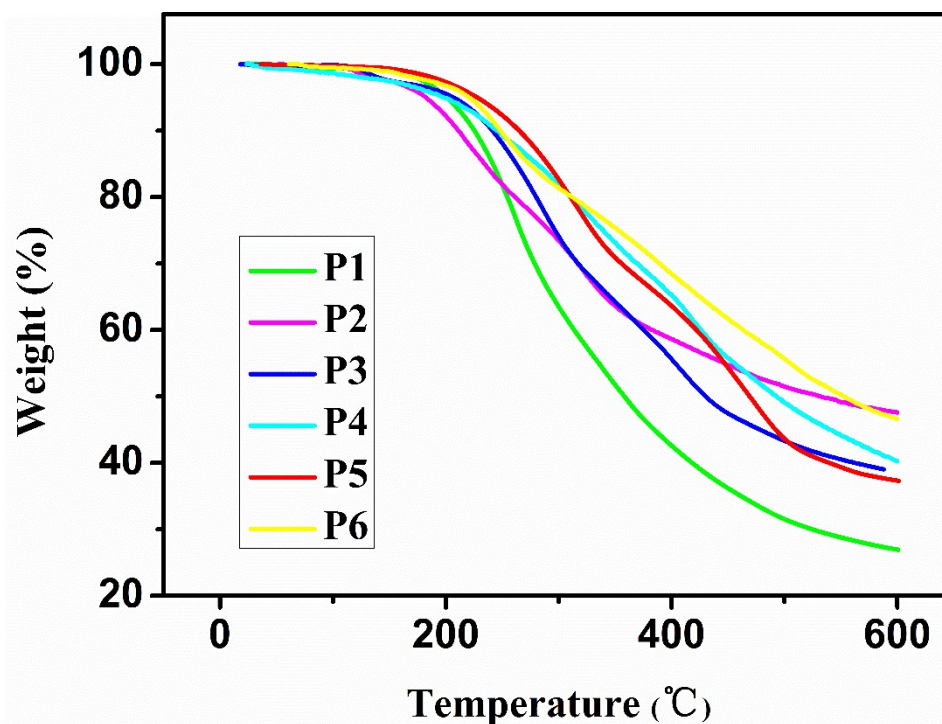


Fig. S32. TGA curve of polymers **P1-P6** with a scan rate of 20°C /min under nitrogen atmosphere.

5. Cyclic voltammogram of polymers

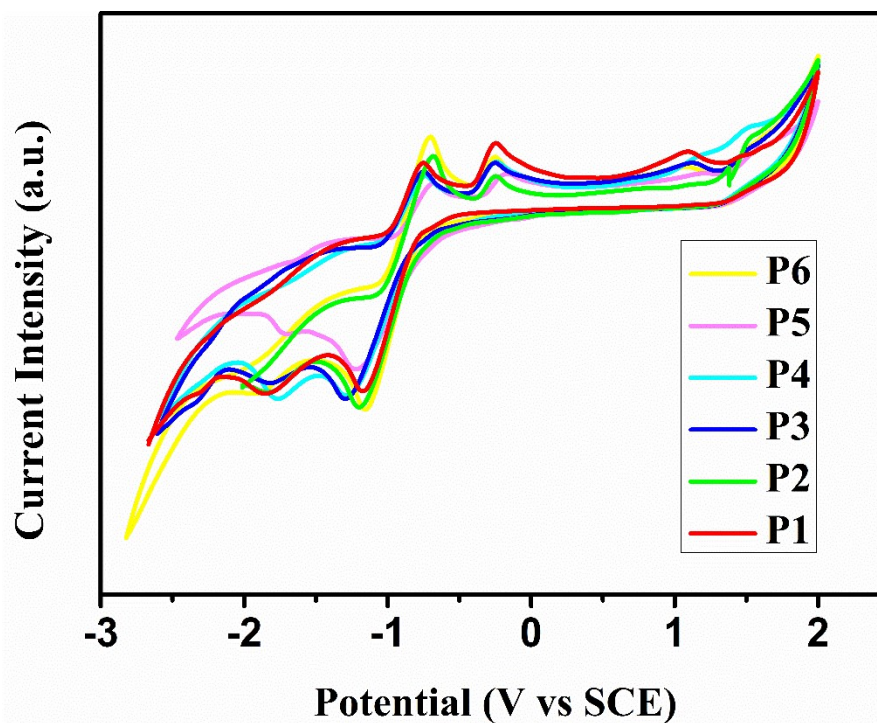


Fig. S33. Cyclic voltammogram of the **P1-P6** on glassy carbon electrode in 0.1 mol/L Bu_4NPF_6 THF solution.