

**Synthesis of isoindigo-derived conjugated polymers via ball-milling metal-free polymerization**

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## 1. Materials and characterization

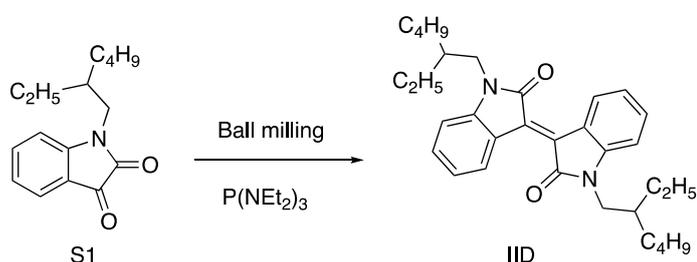
Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Methanol, toluene, *N,N*-dimethylformamide are pre-dried over potassium hydroxide pellets and then dried by heating under reflux over calcium hydride. 6-Bromooxindole was purchased from Shanghai Darui Finechemical Co.Ltd. 6-Bromo-1*H*-pyrrolo[2,3-*b*]pyridine was purchased from Accela ChemBio Co. Ltd .

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-600 spectrometer. Gel permeation chromatography (GPC) was tested with a Waters 1515 liquid chromatography instrument using tetrahydrofuran as eluent with polystyrene as standards. Thermal gravimetric analysis (TGA) was performed under a nitrogen flow at a heating rate of 20 °C/min with a STA449C system. UV-Vis spectra were measured by Perkinelmer LAMBDA 950. Cyclic voltammetry (CV) was tested on the Ingsens IGS1200 electrochemical analyzer with a three-electrode cell and experiments were carried out in the deoxidation anhydrous acetonitrile solution of tetra-*n*-butylammonium-hexafluorophosphate (0.1 M) under a nitrogen environment. Platinum disk electrode, platinum wire electrode and Ag/AgNO<sub>3</sub> electrode were used as a working electrode, a counter electrode and a reference electrode, respectively. The sample films for electrochemical measurements were coated on the surface of platinum electrode. The CV curves were calibrated using the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as an external standard, which was measured under same condition before and after the measurement of samples. The energy level of Fc/Fc<sup>+</sup> was assumed at -4.8 eV to vacuum. The half-wave potential of Fc/Fc<sup>+</sup> was found to 0.09 V, related to the Ag/Ag<sup>+</sup> reference electrode. The HOMO energy levels of the polymer were calculated using the equation:  $E_{\text{HOMO}} = -e(4.71 + E_{\text{ox}})$  (eV), where  $E_{\text{ox}}$  is the onset oxidation potential relative to the Ag/Ag<sup>+</sup> reference electrode. The LUMO energy levels of the polymer were calculated using the equation:  $E_{\text{LUMO}} = -e(4.71 + E_{\text{red}})$  (eV), where  $E_{\text{red}}$  is the onset reduction potential relative to the Ag/Ag<sup>+</sup> reference electrode.

## 2. Synthetic procedure

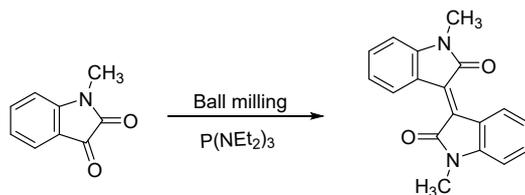
### 2.1. Synthetic procedures of model small molecules

Mechanochemical experiments were carried out in a planetary ball mill FOCUCY F-P400E that was equipped with steel jars (28 mL, 38 mm inner diameter, 60 mm outer diameter) with stainless steel spheres inside (see Figure S1). To equilibrate the system, another parallel jar was used. The reactions were performed at ambient condition. Each reaction progress was monitored by the thin layer chromatography (TLC).



**(E)-1,1'-Bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (IID):** The parameters setting for the operation of planetary ball mill were as follows: ball milling speed was 720 rpm, the size of balls was 6 mm, and the number of balls was 50. The 1-(2-ethylhexyl)indoline-2,3-dione (S1) (1 mmol, 0.2594 g) and P(NEt<sub>2</sub>)<sub>3</sub> (1 mmol, 0.2550 g, 97%) were milled for 30 min. The resulting crude product was dissolved in dichloromethane. The organic phase was washed with water and dried with anhydrous magnesium sulphate. After removing the solvent, silica gel column chromatography was used to purify the product with the mixture of petroleum ether and dichloromethane (2:1, v/v) as the eluent to afford a red solid (0.1327 g, 55%). TLC (petroleum ether: dichloromethane, 2:1, v/v):  $R_f = 0.38$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  9.16 (d,  $J = 8.7$  Hz, 2H), 7.36-7.31 (dd,  $J=7.4, 1.1$  Hz, 2H), 7.04 (dd,  $J_1=7.4, 1.2$  Hz, 2H), 6.78 (d,  $J = 7.9$  Hz, 2H), 3.60-3.48 (m, 4H), 1.90-1.72 (m, 2H), 1.43-1.20 (m, 16H), 0.95-0.82 (m, 12H).

Comparison experiment: In a glass bottle, directly mixing the oil S1 (1 mmol, 0.2594 g) with P(NEt<sub>2</sub>)<sub>3</sub> (1 mmol, 0.2550 g, 97%) and then aging the mixture for 30 min. After similar workup process as above, the red solid IID was obtained (0.0936 g, 37%).

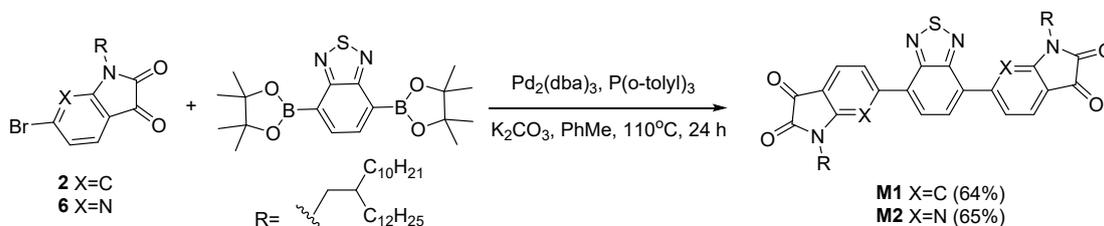


**(E)-1,1'-dimethyl-[3,3'-biindolinylidene]-2,2'-dione (IID-Me):** 1-methylindoline -2,3-dione (1 mmol, 0.1616) and  $P(NEt_2)_3$  (1 mmol, 0.2550 g, 97%) were conducted at ambient condition for 30 min. The ball milling speed and size of milling balls were employed to optimize this procedure. The ball milling speed (180, 450 and 720 rpm) was evaluated (Table 1, entries 1–3). The resulting crude product mixture was dissolved in dichloromethane. The organic phase was washed with water and dried with anhydrous  $MgSO_4$ . After removing the solvent, silica gel column chromatography was used to purify the product with dichloromethane as the eluent to afford a red solid. The optimized parameters and corresponding results were listed in Table 1. TLC (dichloromethane):  $R_f = 0.30$ .  $^1H$  NMR (600 MHz,  $CDCl_3$ , ppm):  $\delta$  9.22 (dd,  $J = 8.0, 1.2$  Hz, 2H), 7.38 (td,  $J = 7.7, 1.2$  Hz, 2H), 7.07 (td,  $J = 7.8, 1.1$  Hz, 2H), 6.79 (dd,  $J = 7.5$  Hz, 2H), 3.29 (s, 6H).

Comparison experiment: In a mortar, directly mixing the solid 1-methylindoline-2,3-dione (1 mmol, 0.1616 g) with  $P(NEt_2)_3$  (1 mmol, 0.2550 g, 97%) well by stirring gently with grinding rod and then aging the mixture for 30 min. After similar workup process as above, the red solid IID-Me was obtained (0.0413 g, 28%).

## 2.2. Synthetic procedures of monomers

Compounds **2**<sup>1</sup> and **6**<sup>2</sup> were synthesized according to the published procedures.

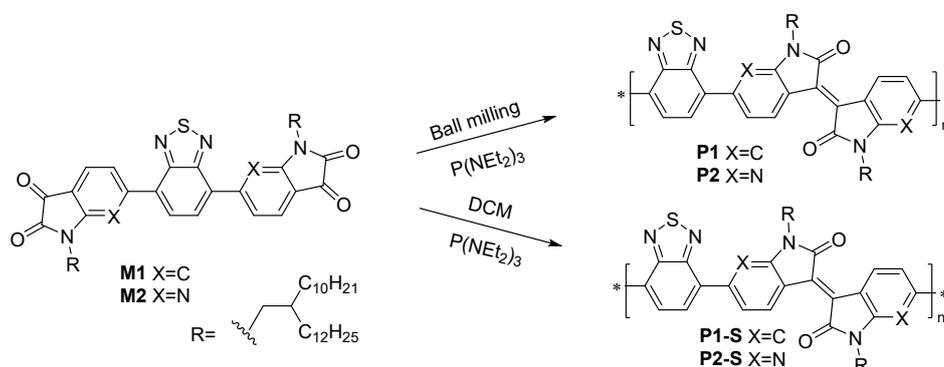


**6,6'-(Benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(1-(2-decyltetradecyl)indoline-2,3-dione (M1):** under the atmosphere, compound **2** (9.35 mmol, 5.2693 g), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (4.25

mmol, 1.4369 g), potassium phosphate (11.05 mmol, 2.3455 g), methyltrioctyl ammonium chloride (1 drop), toluene (20 mL), and deoxygenated water (2.5 mL) were added to a Schlenk tube. Then, Pd<sub>2</sub>(dba)<sub>3</sub> (0.04 mmol, 0.0389 g) and P(*o*-tolyl)<sub>3</sub> (0.27 mmol, 0.0828 g) were added. After 20 min of deoxygenation, the mixture was heated at 110 °C for 24 h. After cooling to ambient temperature, the mixture was poured into ice water to quench the reaction. It was extracted with ethyl acetate, dried with anhydrous sodium sulfate. After removing the solvent, silica gel column chromatography was used to purify the product with the mixture of petroleum ether and dichloromethane (1:3, v/v), and the crude product was then recrystallized with methanol to afford an orange solid M1 (2.86 g, 64%). TLC (petroleum ether: dichloromethane, 1:3, v/v): *R*<sub>f</sub> = 0.30. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm) δ 7.98 (s, 2H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 1.3 Hz, 2H), 7.67 (dd, *J* = 7.8, 1.3 Hz, 2H), 3.73 (d, *J* = 7.4 Hz, 4H), 1.98 (m, 2H), 1.41-1.20 (m, 80H), 0.87-0.84 (m, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, ppm) δ 182.66, 168.24, 153.22, 146.05, 143.19, 137.13, 136.47, 132.65, 130.64, 125.02, 122.61, 120.08, 105.53, 77.24, 77.03, 76.82, 44.69, 36.35, 31.94, 31.93, 31.69, 30.03, 29.72, 29.69, 29.68, 29.64, 29.38, 29.37, 26.55, 22.70, 14.14.

**6,6'-(Benzo[*c*][1,2,5]thiadiazole-4,7-diyl)bis(1-(2-decyltetradecyl)-1H-pyrrolo[2,3-*b*]pyridine-2,3-dione (M2):** M2 was synthesized via the same experimental method used for M1, The starting monomers were compound **6** (3.02 mmol, 1.7000 g). 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole (1.37 mmol, 0.5318 g), M2 was also obtained as an orange solid (0.99 g, 65%). TLC (petroleum ether : ethyl acetate, 6:1, v/v): *R*<sub>f</sub> = 0.3. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm) δ 8.91-8.89 (d, *J* = 7.9 Hz, 2H), 8.88 (s, 2H), 8.07 (d, *J* = 7.8 Hz, 2H), 3.91 (d, *J* = 7.2 Hz, 4H), 2.12 (m, 2H), 1.38-1.21 (m, 80H), 0.84 (m, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>, ppm) δ 181.63, 163.92, 159.08, 158.53, 153.46, 133.55, 131.91, 130.93, 121.05, 111.58, 43.56, 36.46, 31.92, 31.90, 31.65, 30.03, 29.72, 29.66, 29.36, 26.46, 22.68, 22.66, 14.12, 14.11.

### 2.3. Synthetic procedures of polymers via ball milling method



These polymerization reactions were carried out at ambient condition. The optimized ball mill parameters of model small molecules were used. The ball milling reactions were interrupted 30 min each time and the reactants adhered to the inner wall of the ball mill jar were scraped off with a spoon. The optimal results were obtained via adjusting the molar ratios of M1 to  $\text{P}(\text{NEt}_2)_3$  and the total ball milling time.

P1: The reaction was carried out with M1 (0.09 mmol, 0.10 g, 1.0 equivalent), and different equivalents of  $\text{P}(\text{NEt}_2)_3$ , then the jar was sealed. The mixture was then milled. After the ball milling reactions were carried out for a certain time, the resulting mixtures were dissolved in chloroform, and the chloroform solution was concentrated and poured into methanol to precipitate the crude product. The precipitate was collected by filtration and purified by Soxhlet extractions with methanol, petroleum ether and chloroform in sequence. The petroleum ether or chloroform extraction part was re-precipitated with methanol. The solid was collected and then dried to obtain the target products. Table 1 showed the detailed information and results.

P1 (Table 1, entry 5):  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  9.33(br, 2H), 7.95-6.67(br, 6H), 3.84(br, 4H), 2.20(br, 2H), 1.41-1.12(br, 92H).  $M_n=13.45$  kDa,  $M_w=34.31$  kDa,  $D=2.55$ . TGA (5% weight loss): 374 °C

P2: The reaction was carried out with M2 (0.09 mmol, 0.10 g) and  $\text{P}(\text{NEt}_2)_3$  (1.09 mmol, 0.27 g, 97%). The mixture was milled under the optimized condition. After the

ball milling reactions were carried out for total 6 hours, the resulting mixtures were dissolved in chloroform, and the chloroform solution was concentrated and poured into methanol to precipitate the crude product. The precipitate was collected by filtration and purified by Soxhlet extractions with methanol, petroleum ether and chloroform in sequence. The chloroform extraction part was re-precipitated with methanol. The solid was collected and then dried to obtain the target polymer P2 as a deep blue solid (0.0686 g, 69%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  9.59 (br, 2H), 9.03-8.48 (br, 4H), 4.20-3.62 (br, 4H), 2.13 (br, 2H), 1.43-1.02 (br, 80H), 0.83 (br, 12H).  $M_n = 13.48$  kDa,  $M_w = 39.03$  kDa,  $D = 2.90$ . TGA (5% weight loss): 409 °C.

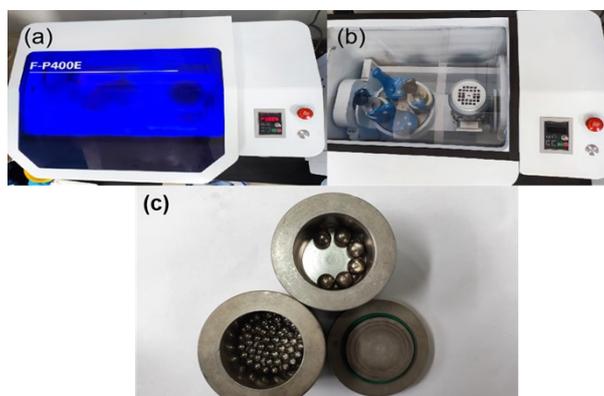
#### *2.4. Synthetic procedures of polymers via solution method.*

**P1-S:** M1 (0.09 mmol, 0.1000 g) and dichloromethane (1 mL) were added to a flask, and  $\text{P}(\text{NEt}_2)_3$  (1.44 mmol, 0.0360 g) was dropped at 0 °C, which was then stirred for 4 hours at ambient condition. After polymerization, the reaction mixture was poured into stirring methanol to precipitate the crude product. The precipitate was collected by filtration and purified by sequential Soxhlet extractions with dried methanol, petroleum ether and chloroform. The chloroform extraction part was re-precipitated with methanol. The solid was collected and then dried to obtain the target polymer P1-S as a black solid (0.0501 g, 52%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  9.43 (br, 2H), 7.64-6.89 (br, 6H), 3.92 (br, 4H), 2.10 (br, 2H), 1.43-1.09 (br, 80H), 0.89-0.80 (br, 12H).  $M_n = 17.73$  kDa,  $M_w = 50.94$  kDa,  $D = 2.87$ .

**P2-S:** P2-S was synthesized via the parallel experimental method used for P1-S, the starting monomers were M2 (0.09 mmol, 0.1000 g), dichloromethane (1 ml),  $\text{P}(\text{NEt}_2)_3$  (1.44 mmol, 0.0360 g). The final polymer was also collected from chloroform extracted fraction as a deep blue solid (0.0913 g, 93%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  9.59 (br, 2H), 8.84 (br, 2H), 8.02 (br, 2H), 4.04-3.78 (br, 4H), 2.19 (br, 2H), 1.43-1.12 (br, 80H), 0.83 (br, 12H).  $M_n = 14.4$  kDa,  $M_w = 38.5$  kDa,  $D = 2.67$ .  $M_n = 14.43$  kDa,  $M_w = 38.50$  kDa,  $D = 2.87$ .

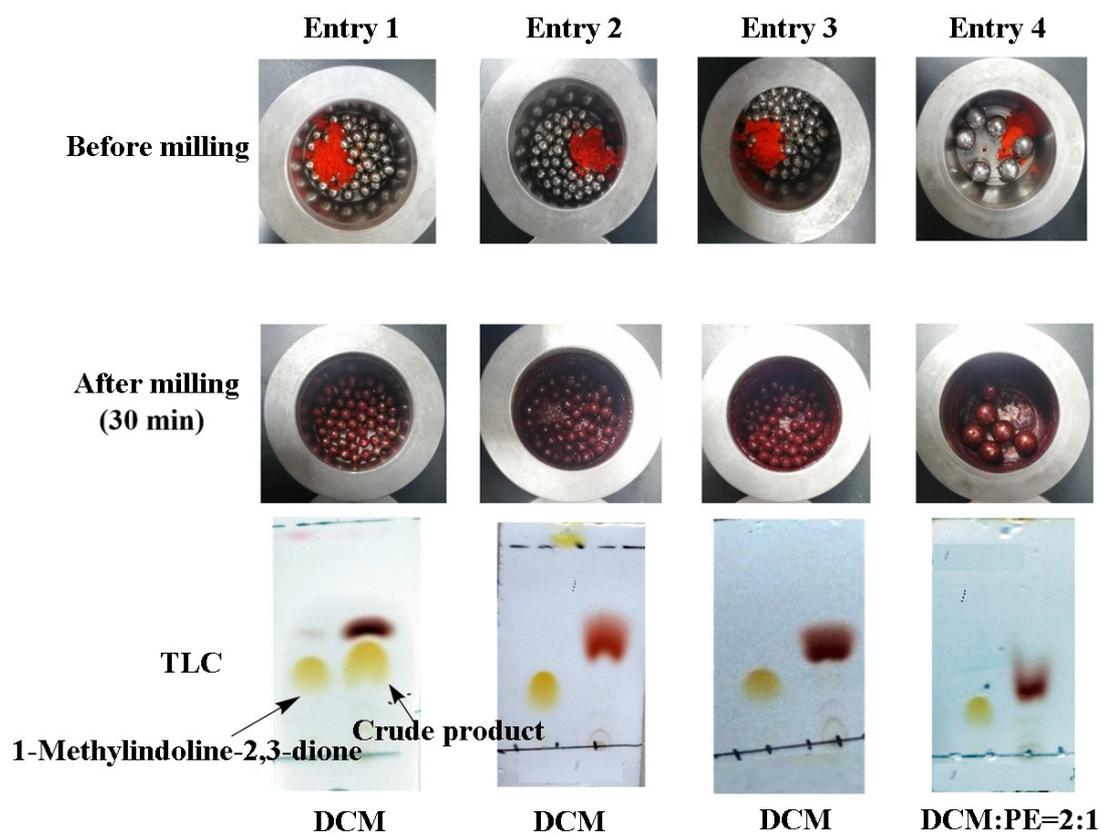
### 3. Supporting data

#### 3.1. The photos of planetary ball mill, stainless balls and jars.



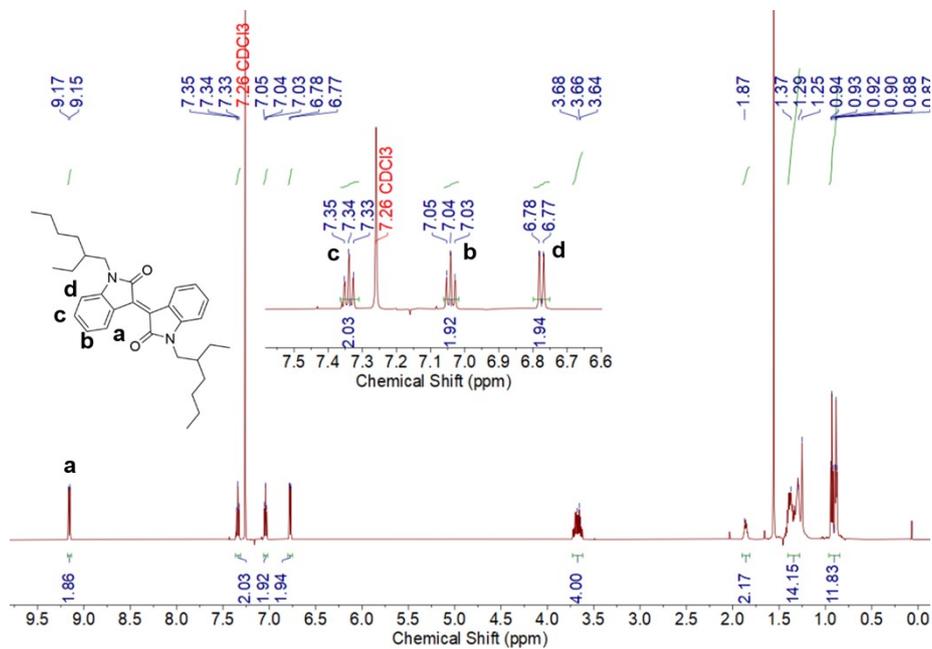
**Figure S1.** (a) and (b) Planetary ball mill (FOCUCY F-P400E); (c) stainless balls and jars.

#### 3.2. The photos in terms of synthesizing model molecule IID-Me by ball milling

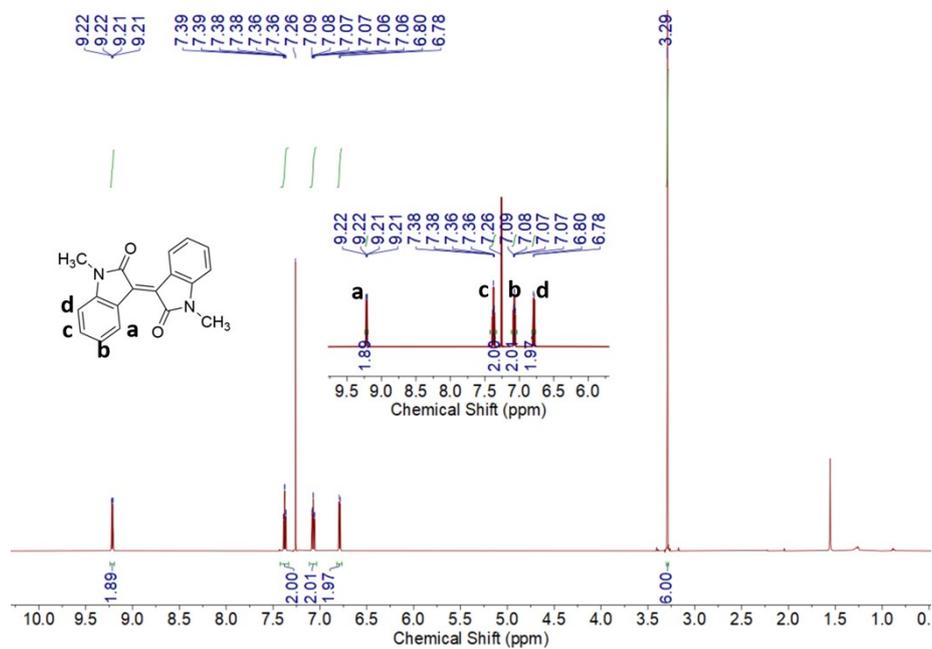


**Figure S2.** The photos in terms of synthesizing model molecule IID-Me by ball milling.

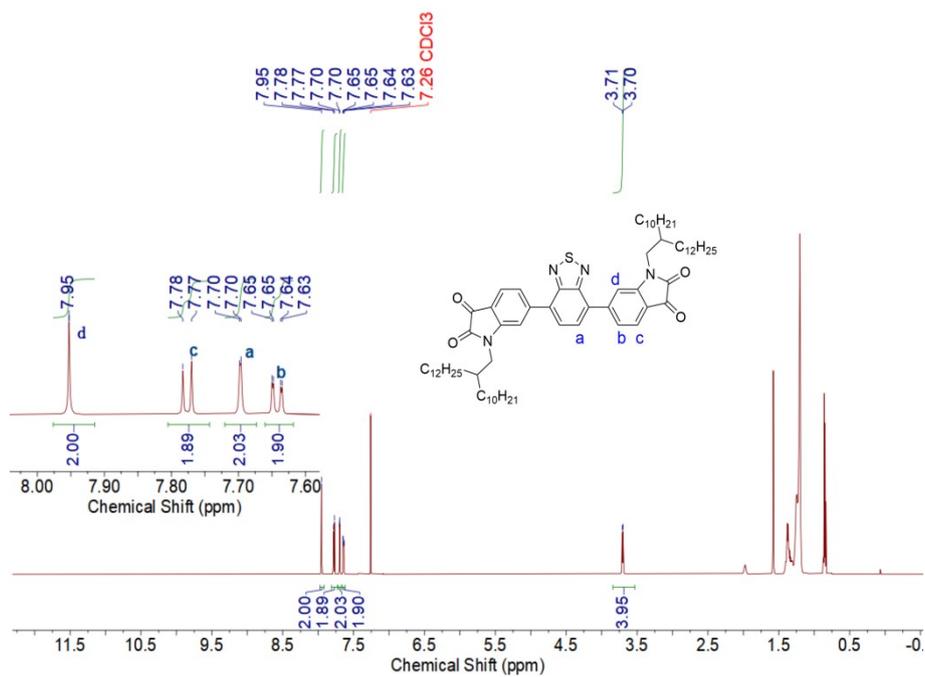
### 3.3. NMR spectra



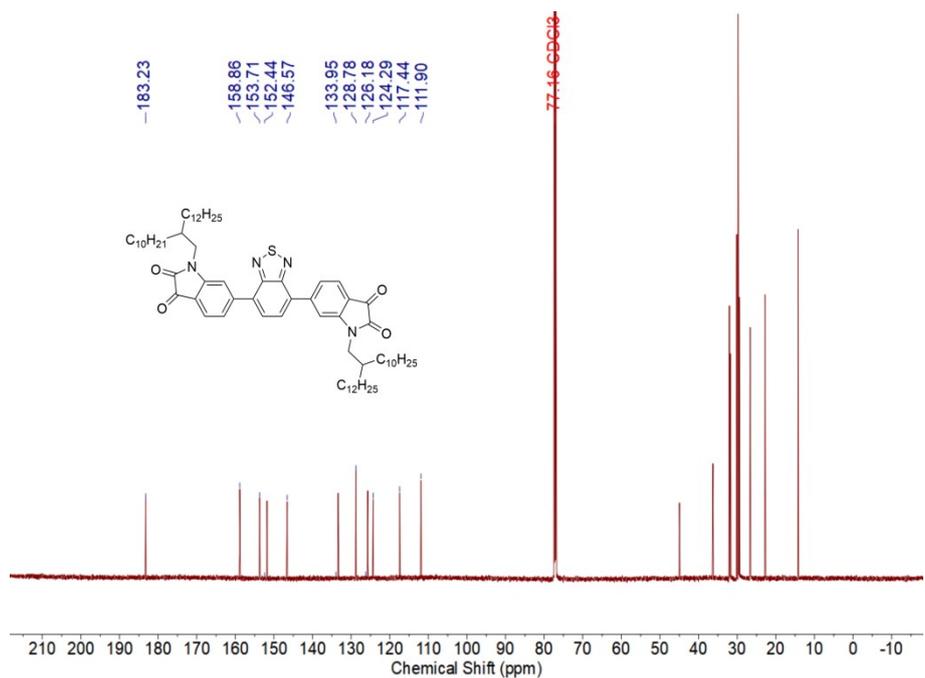
**Figure S3.**  $^1\text{H}$  NMR spectrum of IID in  $\text{CDCl}_3$ .



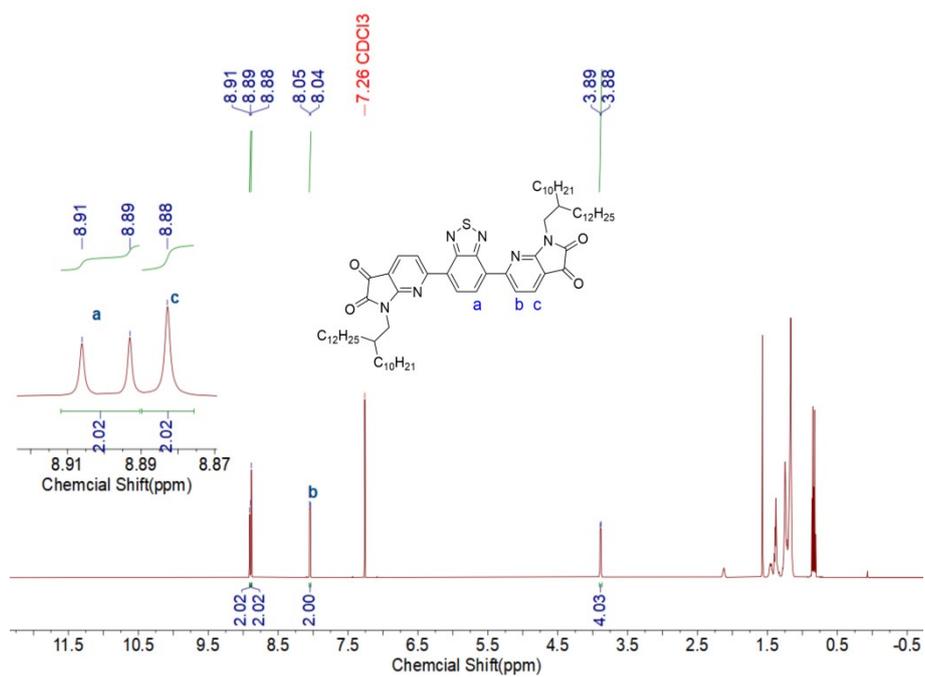
**Figure S4.**  $^1\text{H}$  NMR spectrum of IID-Me in  $\text{CDCl}_3$ .



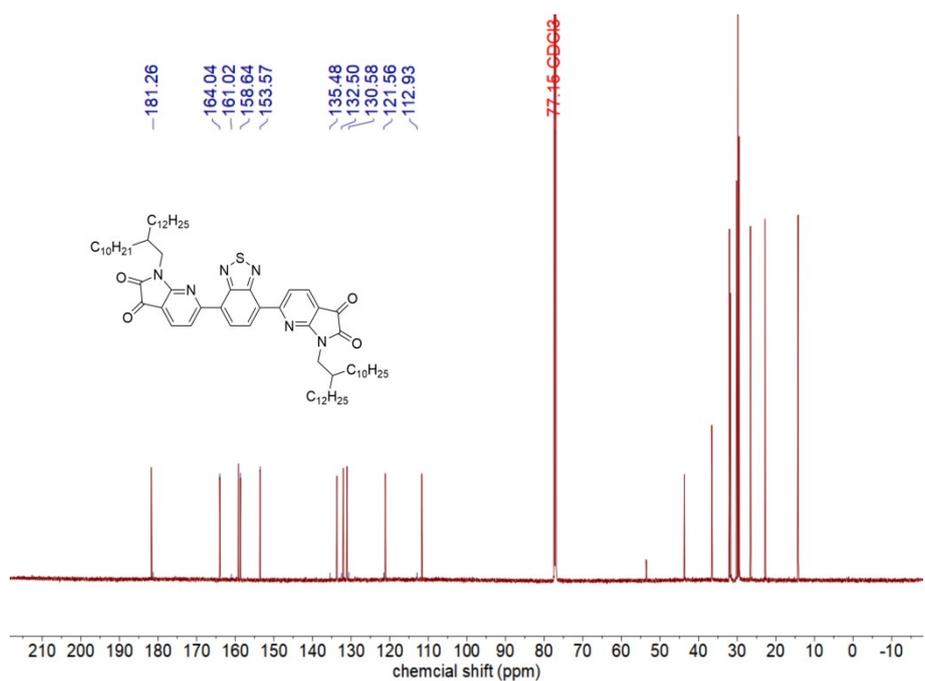
**Figure S5.**  $^1\text{H}$  NMR spectrum of M1 in  $\text{CDCl}_3$ .



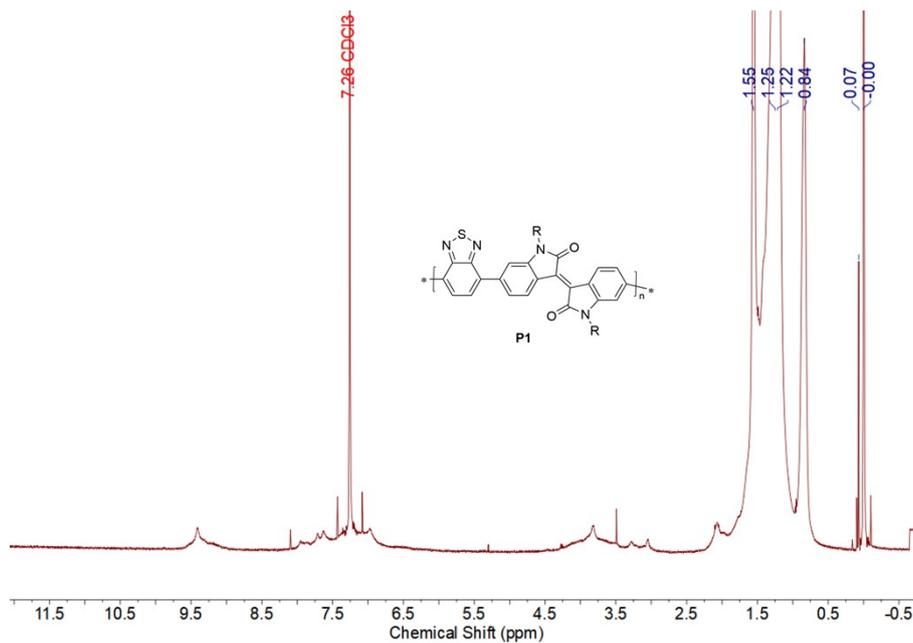
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of M1 in  $\text{CDCl}_3$ .



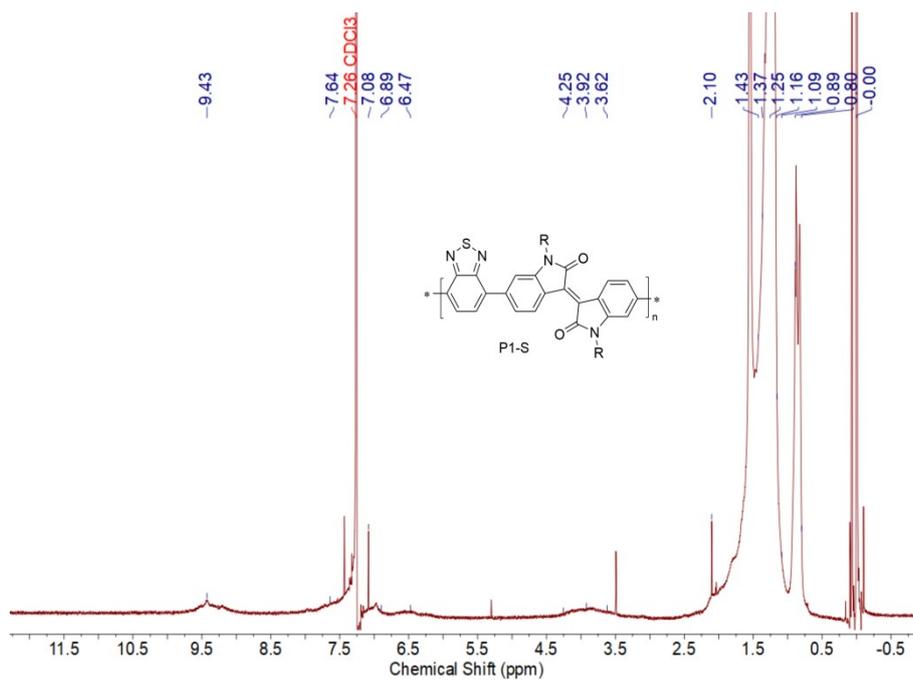
**Figure S7.** <sup>1</sup>H NMR spectrum of M2 in CDCl<sub>3</sub>.



**Figure S8.** <sup>13</sup>C NMR spectrum of M2 in CDCl<sub>3</sub>.



**Figure S9.** <sup>1</sup>H NMR spectrum of P1 (Table 1, entry 5) in CDCl<sub>3</sub>.



**Figure S10.** <sup>1</sup>H NMR spectrum of P1 in CDCl<sub>3</sub>.

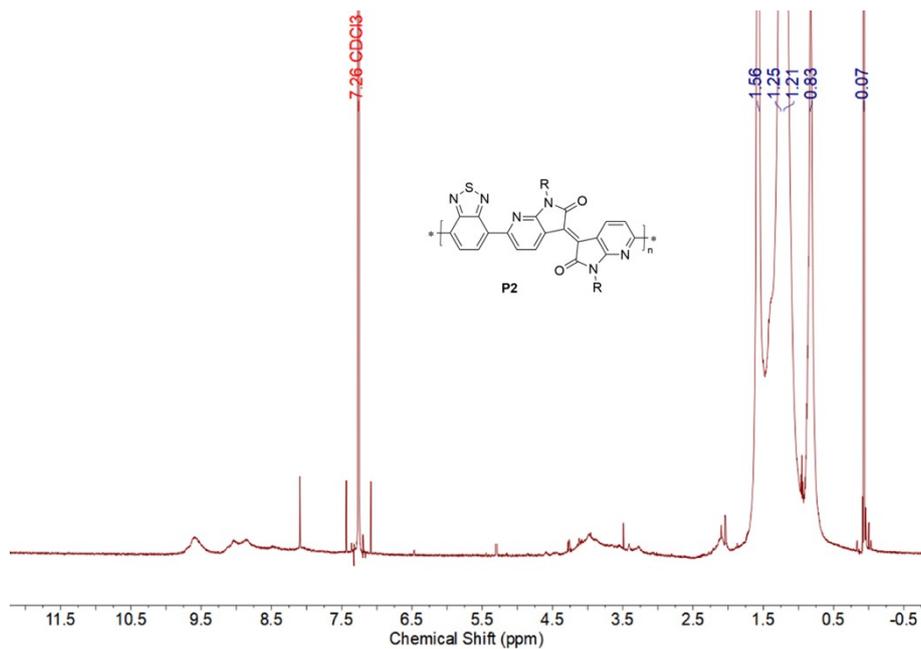


Figure S11. <sup>1</sup>H NMR spectrum of P2 in CDCl<sub>3</sub>.

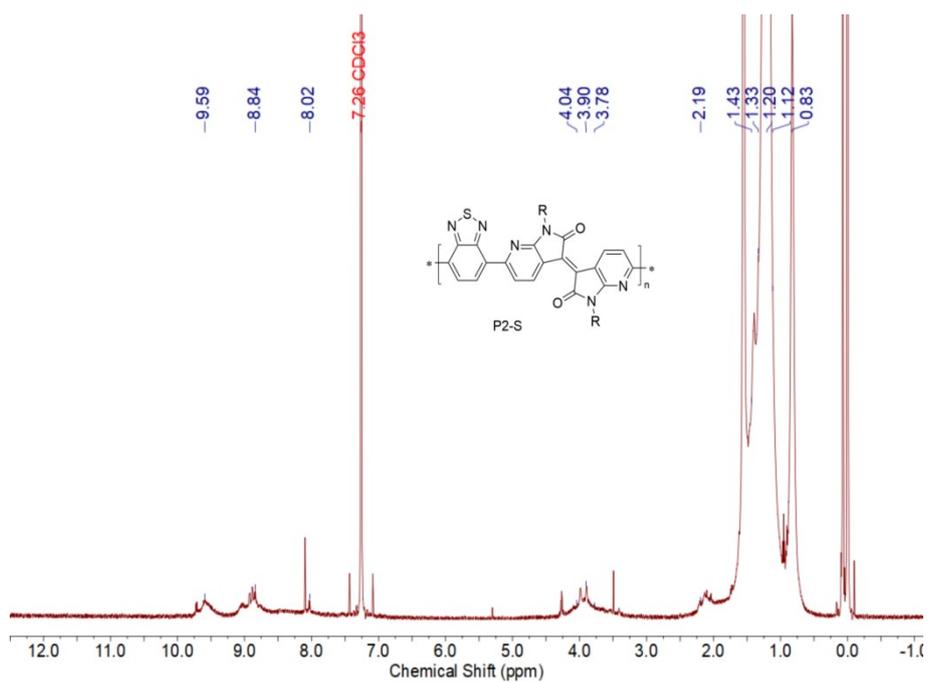
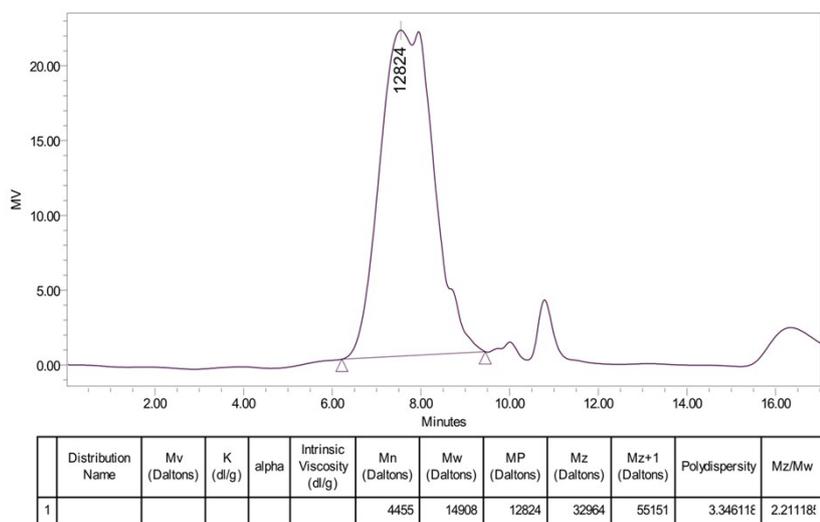


Figure S12. <sup>1</sup>H NMR spectrum of P2-S in CDCl<sub>3</sub>.

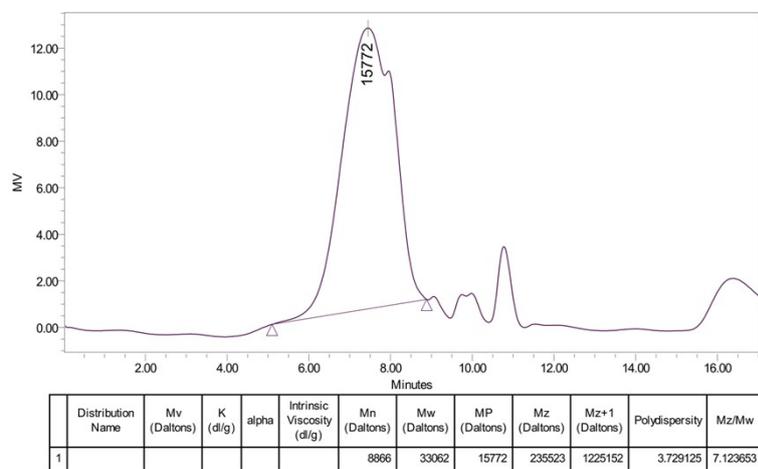
### 3.4. GPC test results of the polymers.



$$M_n \text{ (kDa)} \qquad M_w \text{ (kDa)} \qquad \mathcal{D}$$

$$4.46 \qquad 14.91 \qquad 3.35$$

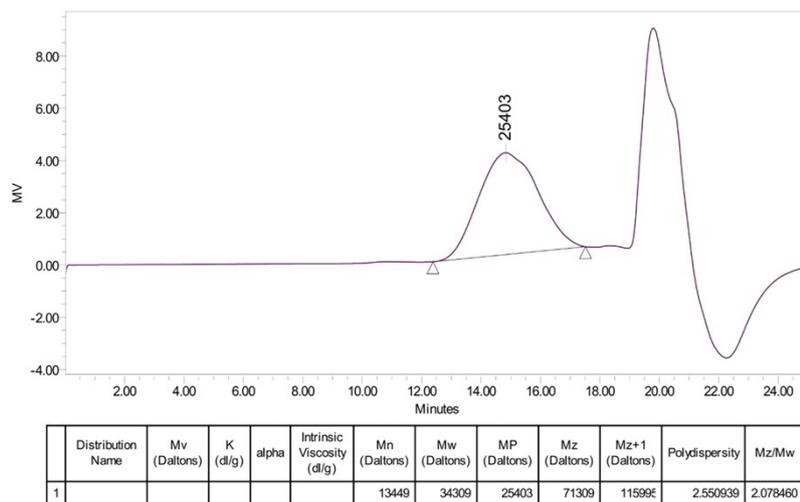
**Figure S13.** GPC test result of the polymer P1 (Table 1, entry 3) (THF as eluent, 40 °C).



$$M_n \text{ (kDa)} \qquad M_w \text{ (kDa)} \qquad \mathcal{D}$$

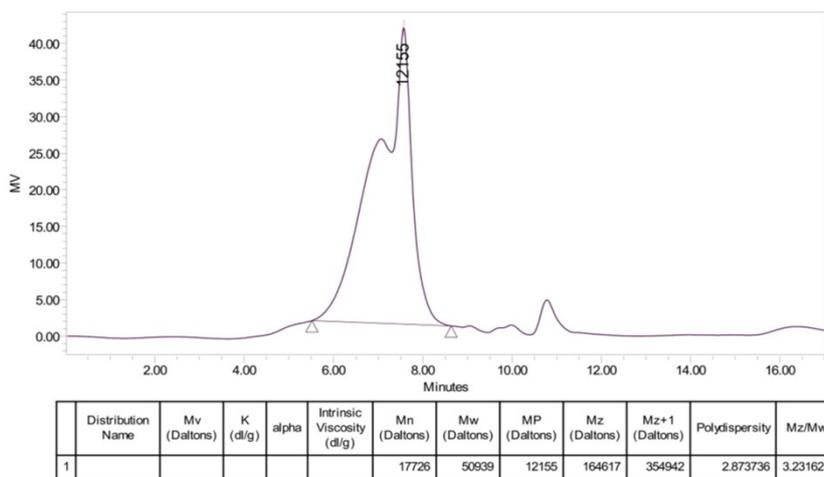
$$8.87 \qquad 33.06 \qquad 3.73$$

**Figure S14.** GPC test result of the polymer P1 (Table 1, entry 4) (THF as eluent, 40 °C).



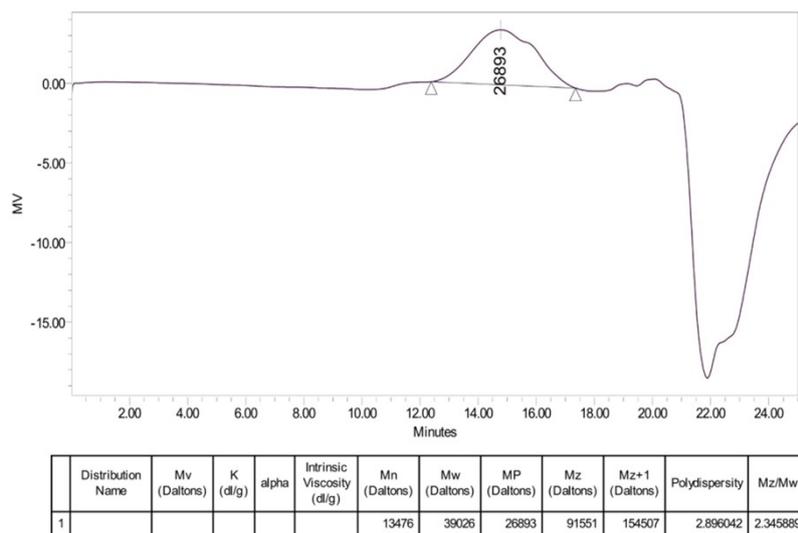
$M_n$  (kDa)                       $M_w$  (kDa)                       $\bar{D}$   
 13.45                                      34.31                                      2.55

**Figure S15.** GPC test result of the polymer P1 (Table 1, entry 5) (THF as eluent, 40 °C).



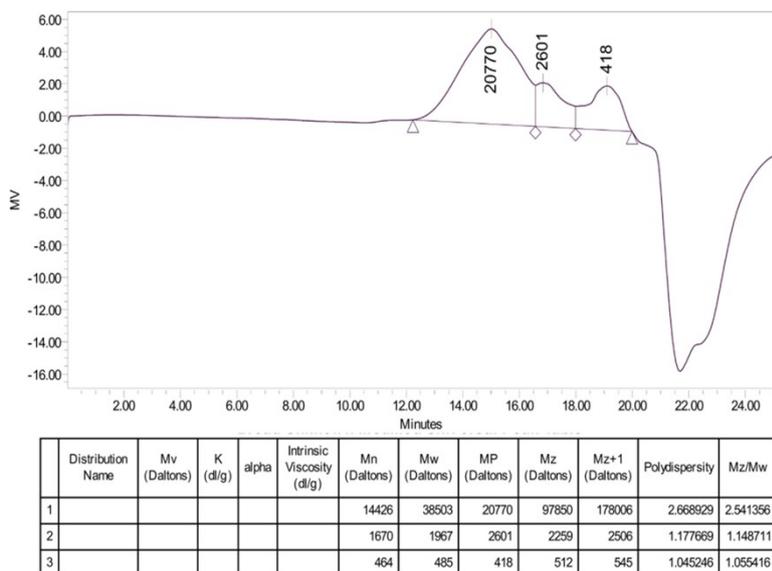
$M_n$  (kDa)                       $M_w$  (kDa)                       $\bar{D}$   
 17.73                                      50.94                                      2.87

**Figure S16.** GPC test result of the polymer P1-S (THF as eluent, 40 °C).



$M_n$  (kDa)                       $M_w$  (kDa)                       $\bar{D}$   
 13.48                                  39.03                                  2.90

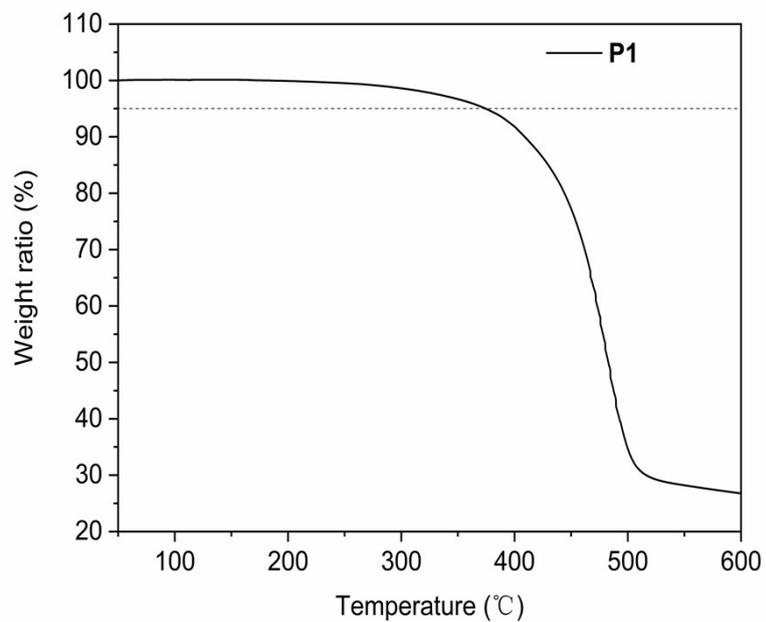
**Figure S17.** GPC test result of the polymer P2 (THF as eluent, 40 °C).



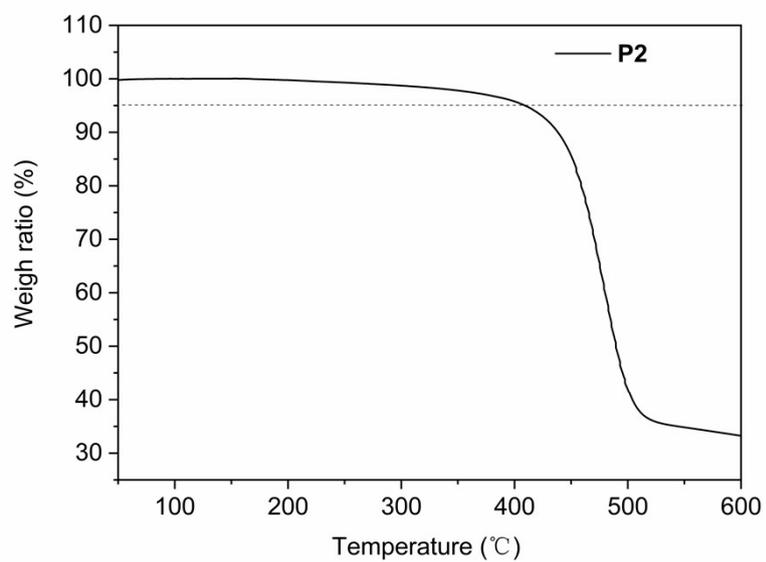
$M_n$  (kDa)                       $M_w$  (kDa)                       $\bar{D}$   
 14.43                                  38.50                                  2.67

**Figure S18.** GPC test result of the polymer P2-S (THF as eluent, 40 °C).

### 3.5. TGA plots of polymers

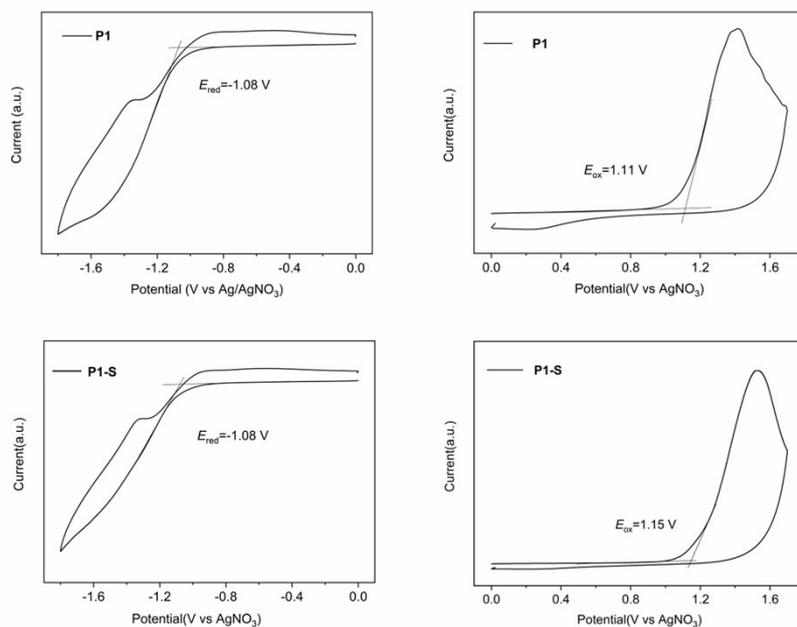


**Figure S19.** TGA plot of P1 (Table 1, entry 5).

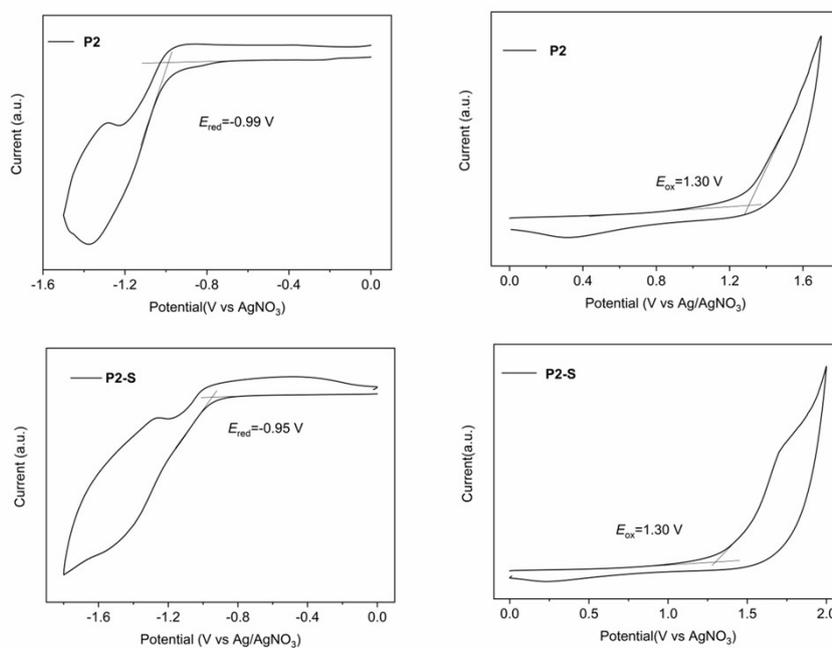


**Figure S20.** TGA plot of P2.

### 3.6. Cyclic voltammogram curves of polymers.



**Figure S21.** Cyclic voltammogram curves of P1 and P1-S (Table 1, entry 5) as thin films.



**Figure S22.** Cyclic voltammogram curves of P2 and P2-S as thin films.

#### **4. References**

- 1) H. Liao, C. Xiao, M. K. Ravva, Y. Wang, M. Little, M. V. C. Jenart, A. Onwubiko, Z. Li, Z. Wang, J.-L. Brédas, I. McCulloch and W. Yue, *Chemical Communications*, 2018, **54**, 11152-11155.
- 2) J. Huang, Z. Mao, Z. Chen, D. Gao, C. Wei, W. Zhang and G. Yu, *Chemistry of Materials*, 2016, **28**, 2209-2218.