Supporting Information

Reversible color modulation of luminescent conjugated polymer based on chemical redox mechanism and applications in rewritable paper and multiple information encryption

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Materials and Instruments

Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and used without further purification. All other chemical reagents were of analytical grade and used as received without further purification.

^{1}H NMR (600 MHz) spectra was recorded on a Bruker AVANCE IIITM 600-MHz spectrometer at room temperature using deuterated solvents. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS) (0.00 ppm) or residual protonated solvents (7.26 ppm for $CDCl_3$ or 2.50 ppm for DMSO-d_6). Gel-Permeation Chromatography (GPC) acquired at Georgia Tech was utilized to estimate molecular weights were determined at 35 °C in THF. The UV–vis absorption spectra were obtained with a Shimadzu UV-1800 spectrophotometer. PL spectra were measured with Horiba F-3000 fluorescence spectrophotometer. Graphics printing was done by a HP Desk Jet 2132 printer. Photoirradiation was performed using a typical laboratory 365 nm UV lamp. Electrochemical measurements were carried out in a 3-electrode cell configuration, using ITO working electrodes, Ag/Ag+ (used for non-aqueous solutions) reference electrodes, and Pt wire counter electrodes, in which an electrolyte system of 0.1 M $LiPF_6$ was also used.

Preparation of Rewritable Paper

Rewritable paper with adsorbed oxidized luminescent conjugated polymers (P1, P2 and P3) were prepared on the filter paper. Firstly, the filter paper was cut into a suitable size (A6), afterwards it was immersed into the solution of luminescent polymer (1 mg/mL) in DCM for 3 minutes to allow good adsorption on paper. Then it was taken out and dried in the environment, showing the initial color and fluorescence of the polymer itself. Next, the dried paper was immersed into the acetonitrile solution of $FeCl_3$ (0.02 M) for 5 minutes to complete oxidation, i.e., the color of polymer faded out. Finally, it was taken out and dried in the environment to obtain the rewritable paper with the color of dark-blue.

Preparation of Encryption paper

Firstly, P1, P4, P5 and P6 were dissolved in DCM and the concentrations were adjusted to 0.028, 0.021, 0.027 and 0.041 mg/mL respectively to get an indistinguishable color state. Next, different information was recorded by P1, P4 and P6 respectively on a piece of clean filter paper by using capillary tubes, and then P5 was used to fill in the remaining part to complete the encryption of information.

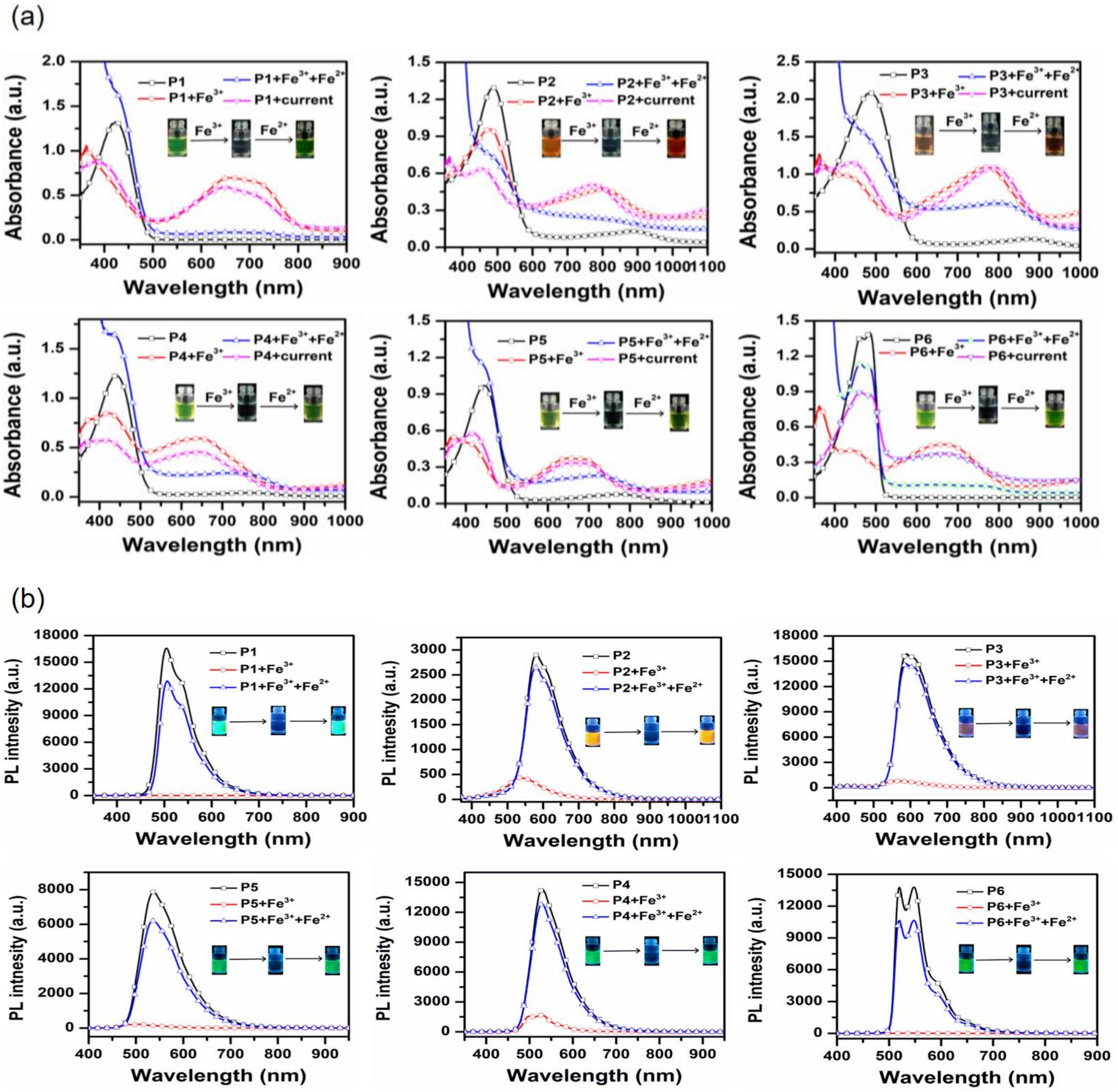


Fig. S1 (a) UV-vis spectra of DCM solution of polymer upon addition of Fe^{3+}, Fe^{2+} (10^{-3}M, 20μl) in turn and oxidized by current; (b) PL spectra of dichloromethane solution of polymer upon addition of Fe^{3+}and Fe^{2+} (10^{-3}M, 20μl) in turn.

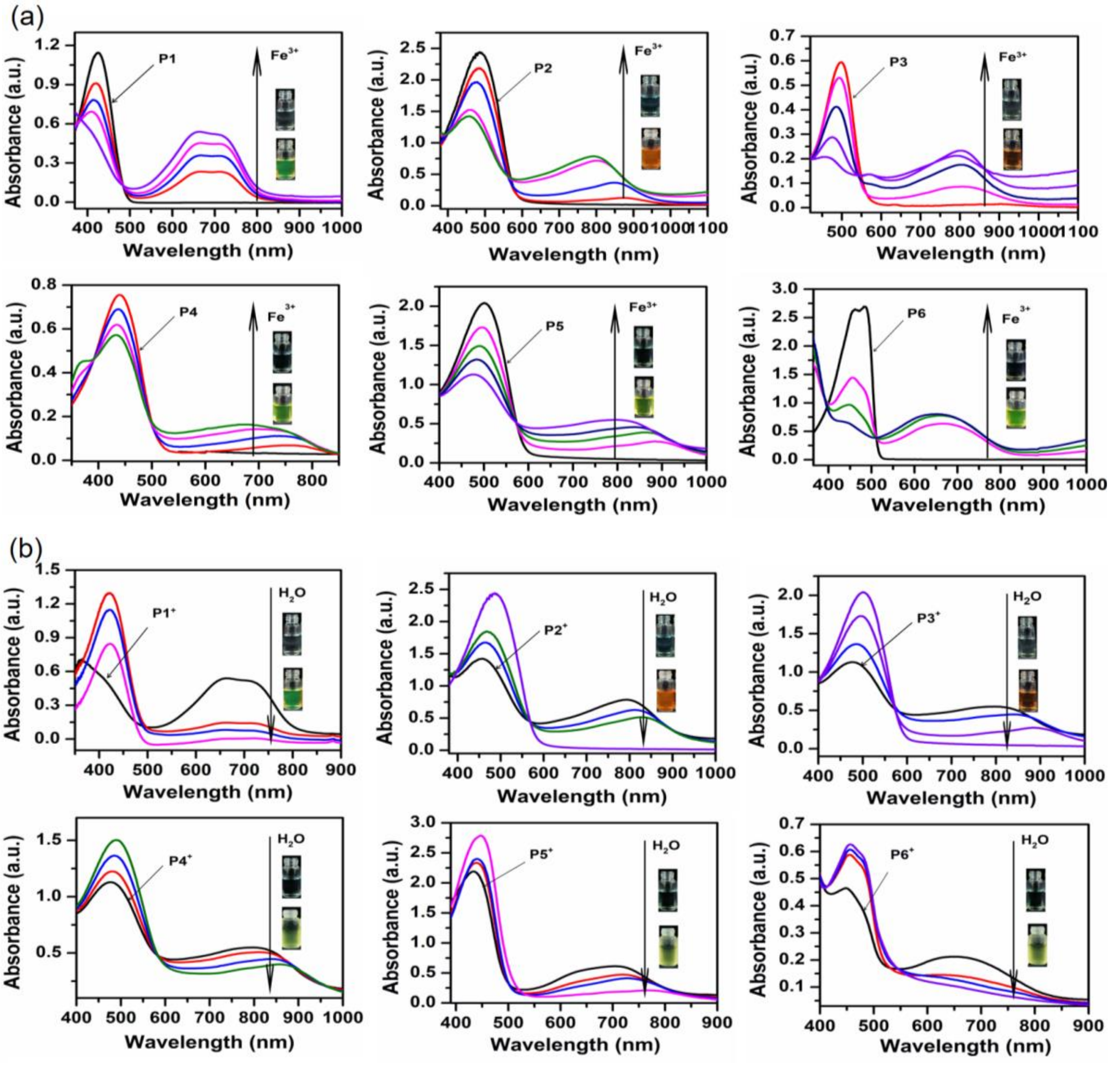


Fig. S2 UV-vis spectra of DCM solution of polymers upon addition of Fe^{3+} (a, 10^{-3}M, 30μl) and H_2O (b, 25μl) in turn.

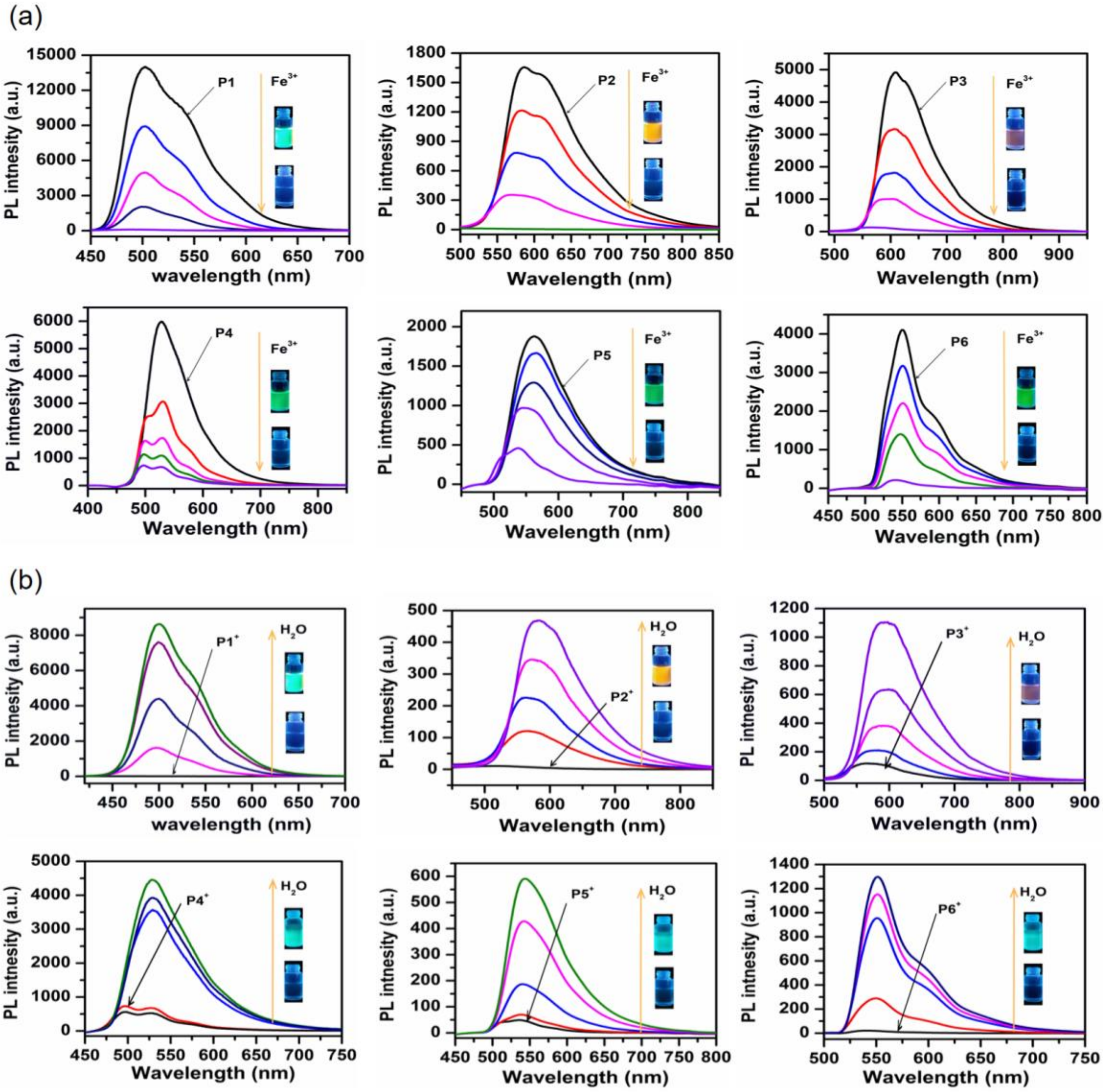


Fig. S3 PL spectra of DCM solution of polymers upon addition of Fe^{3+} in turn.

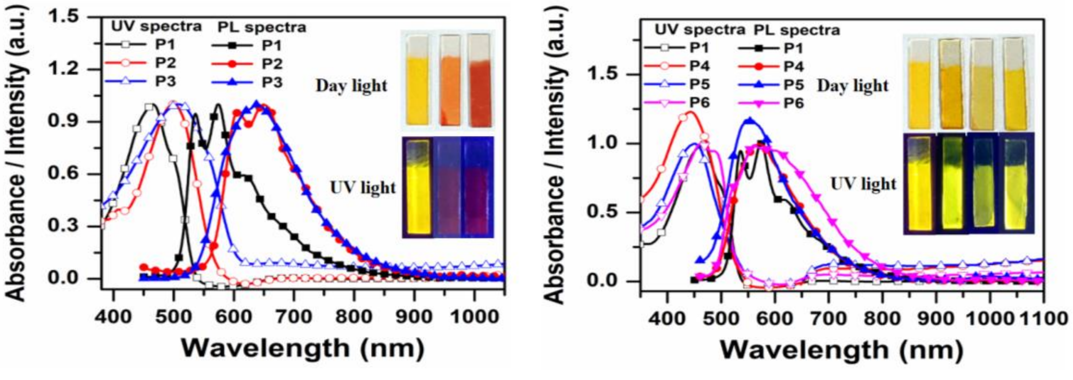


Fig. S4 UV-vis spectra and PL spectra of P1, P2, P3 and P1, P4, P5, P6 films.

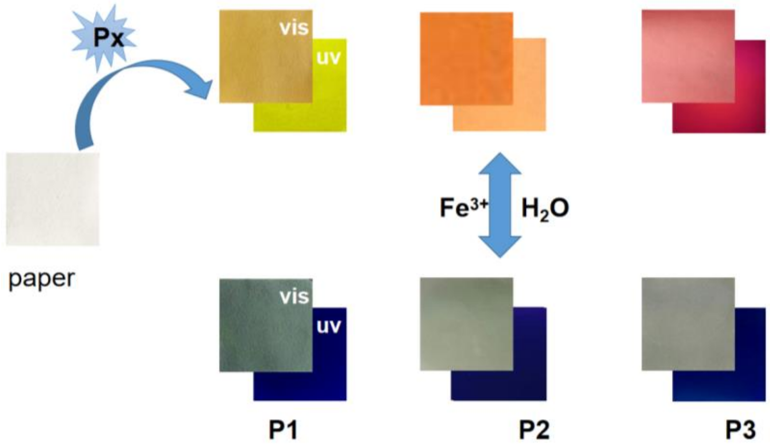


Fig. S5 Photographs of rewritable papers (made of polymers**),** printed by water and erased by immersing it into ACN solution of $FeCl_3$.

Fig. S6 Handwriting on rewritable paper (**P1**) by using water as ink.

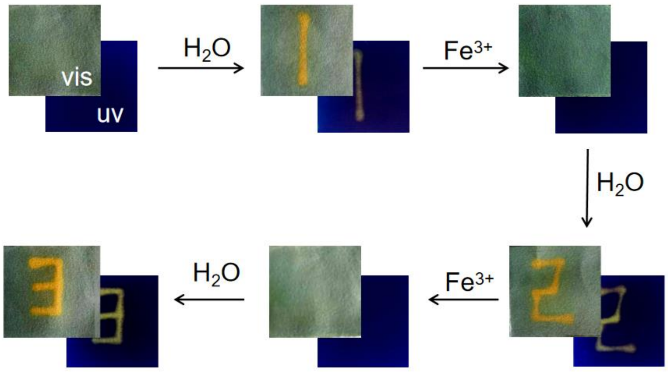


Fig. S7 Repeatedly recording Arabic numbers on the rewritable paper (made of P1).

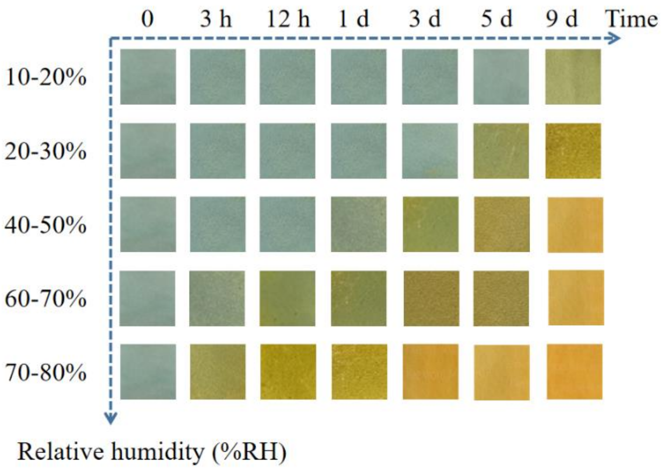


Fig. S8 The results about humidity-dependent long-term stability.

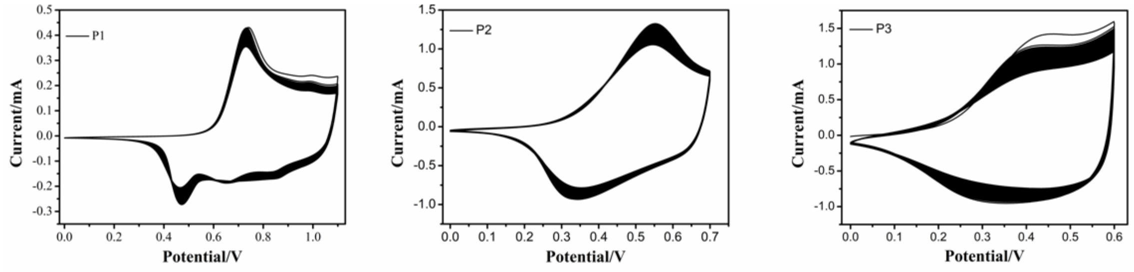


Fig. S9 Cyclic voltammograms of P1, P2 and P3 films for one hundred times.

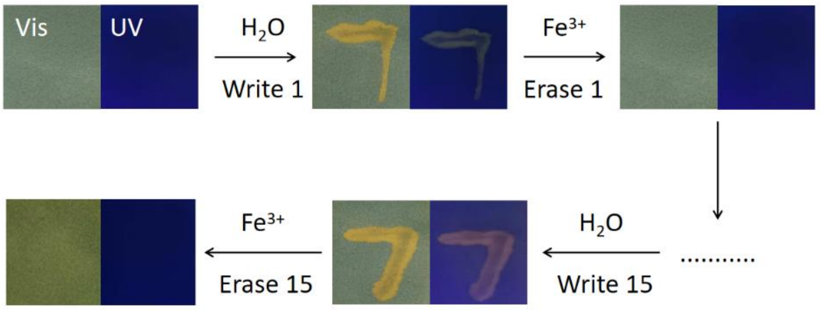


Fig. S10 Repeatedly recording Arabic number “7”on the rewritable paper for15 times (made of P1).

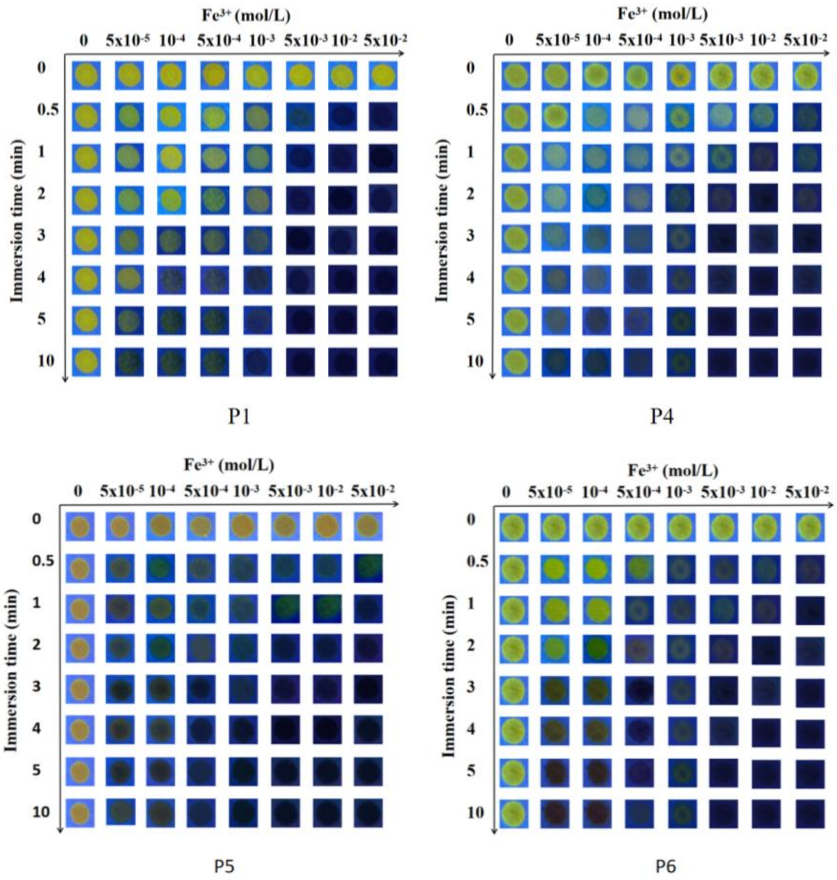
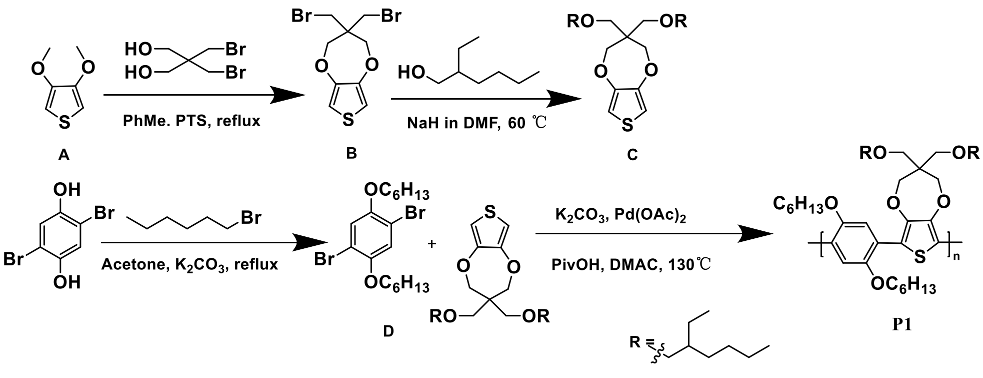


Fig. S11 Fe^{3+}-concentration dependent and time-dependent redox transition behaviors of P1, P4, P5 and P6.

Synthesis:

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted.



Scheme S1: Synthesis route of P1.

Synthesis of **B**

B was synthesized according to reported literature[1]: **A** (2.163 g, 15 mmol), 2,2-bis(bromomethyl)propane-1,3-diol (3.9 g, 15 mmol) and *p*-toluenesulfonic acid (0.6 g, 3.4 mmol) were dissolved in toluene (30 mL) in a 100 mL 3-neck round bottom flask. The solution was heated to 130 °C and kept reacting for 1 day. Then the solution was cooled to room temperature and poured into deionized water (100 mL). The mixture was extracted with DCM, the organic layer was washed with brine and dried with magnesium sulfate. After filtration through a Büchner funnel, the solvent was evaporated and a white liquid was collected. This raw product was purified by column chromatography (DCM: PE = 1: 5) to afford a colorless liquid(3.67 g, yield: 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.50 (s, 2H), 4.10 (s, 4H), 3.61 (s, 4H).

Synthesis of **C**

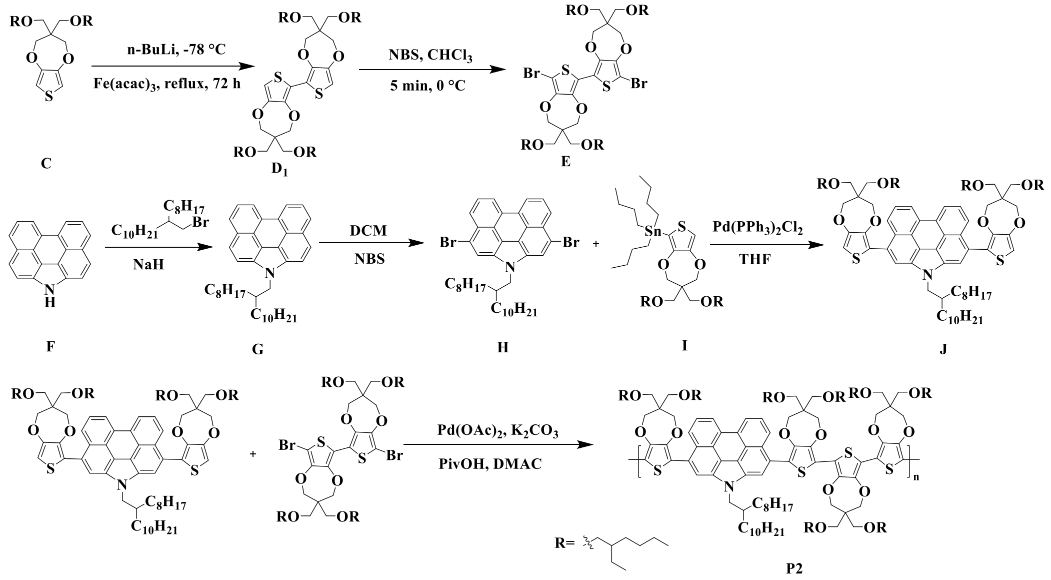
B (1.368 g, 4 mmol) and NaH (0.144 g, 12 mmol) were dissolved in anhydrous DMF (50 mL) in a 100 mL 3-neck flask under nitrogen. 2-Ethyl hexanol (1.04 g, 8 mmol) was added after 0.5 h and the mixed solution was heated to 60 °C for 10 h. Then the reaction was stopped by addition of a salt solution and the mixture was stirred for 0.5 h to cool to room temperature. The mixture was extracted with hexane and the organic layer was dried with magnesium sulfate. After filtration through a Büchner funnel the solvent was evaporated and a white oil was collected (1.32 g, yield: 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.45 (s, 2H), 4.02 (s, 4H), 3.48 (s, 4H), 3.29 (d, *J* = 5.7 Hz, 4H), 1.51-1.47 (m, 2H), 1.26-1.28 (m, 16H), 0.85-0.90 (m, 12H).

Synthesis of **D**

2,5-Dibromobenzene-1,4-diol (1.33 g, 5 mmol), 1-bromohexane (1.65 g, 10 mmol) and K_2CO_3 (2.07 g, 15 mmol) were dissolved in acetone (40 mL) in a 100 mL 3-neck round bottom flask. The solution was heated to reflux and kept reacting for 10 h. Then the solution was cooled to room temperature and poured into deionized water (300 mL). The mixture was extracted with DCM and water, and the organic layer was dried with magnesium sulfate. After filtration through a Büchner funnel, the solvent was evaporated and a yellow solid was collected. This solid was purified by column chromatography (PE: DCM = 3: 1) to give a light-yellow solid (1.43 g, yield: 66%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (s, 2H), 3.95 (t, *J* = 6.5 Hz, 4H), 1.85-1.74 (m, 4H), 1.53-1.44 (m, 4H), 1.40-1.29 (m, 8H), 0.97-0.86 (m, 6H).

Synthesis of **P1**

P1 was synthesized according to reported literature[2]: The mixture of **C** (0.88 g, 2 mmol), **D** (0.686 g, 2 mmol), $Pd(OAc)_2$ (0.0225 g, 1 mmol), K_2CO_3 (0.69 g, 5 mmol), PivOH (0.204 g, 2mmoL) and DMAC (30 mL) were refluxed under a nitrogen atmosphere at 130 ºC for 72 h. After cooling to room temperature, methanol (30 mL) was added to the mixture, then the resulting orange precipitate was collected by filtration and washed with methanol. The crude products were extracted with methanol, acetone and PE in turn to get a yellow solid (1.39 g, Yield: 81%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.54-7.48 (m, 2H), 4.20-4.10 (m, 4H), 4.08-4.00 (m, 4H), 3.60-3.51 (m, 4H), 3.35-3.26 (m, 4H), 1.90-1.81 (m, 4H), 1.51-1.44 (m, 6H), 1.40-1.21 (m, 24H), 0.91-0.83 (m, 18H). GPC: Mn: 26.4 kDa, Mw: 59.9 kDa, PDI: 2.3, in THF vs PS.



Scheme S2: Synthesis route of P2.

Synthesis of **D_1**

D_1 was synthesized according to reported literature[2]: To a dry 250 mL 3-neck round bottom flask with **C** (3.96 g, 10 mmol) was dissolved in 80 mL of dry THF and bubbled with nitrogen for 0.5 h then cooled to -78 °C where *n*-butyl lithium (2.5 M, 10 mmol) in hexane was added drop-wise. After Stirring for 45 mins at -78 °C and the solution was transferred into a dry-degassed THF solution (80 mL) of $Fe(acac)_3$ (3.5317 g, 10 mmol) under nitrogen at r.t *via* cannula. The reaction mixture was refluxed for 72 h. Volatiles were evaporated, and the residue was purified by column chromatography through silica using PE: DCM (6: 1) to obtain a pale yellow-green oil (5.86 g, yield: 67%). ^1H NMR (500 MHz, $CDCl_3$): δ 6.36 (s, 2H), 4.10 (s, 4H), 4.02 (s, 4H), 3.50 (s, 8H), 3.28 (d, *J* = 5.8 Hz, 8H), 1.51-1.45 (m, 4H), 1.35-1.21 (m, 32H), 0.92-0.83 (m, 24H).

Synthesis of **E**

To a dry 100 mL single neck round bottom flask **D$_1$** (3.95 g, 5 mmol) was added and dissolved in CHCl$_3$ (40 mL). The flask containing the solution was lowered to 0 °C and **NBS** (1.79 g, 10 mmol) was added into the solution. After all NBS was added, the reaction was stirred for 2 h at 0 °C. The mixture was extracted with DCM and the organic layer was dried with magnesium sulfate. After filtration through a Büchner funnel the solvent was evaporated and a brown oil was collected. The crude product was purified by column chromatography on silica gel with PE/DCM (9/1) to afford a purple oil (4.55 g, yield: 88%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 4.10 (s, 4H), 4.01 (s, 4H), 3.51 (s, 8H), 3.33 (d, *J* = 6.0 Hz, 8H), 1.53-1.44 (m, 4H), 1.40-1.18 (m, 32H), 0.94-0.81 (m, 24H).

Synthesis of **G**

F (1.3365 g, 5 mmol) was dissolved in toluene (30 mL) in a 100 mL 3-neck round bottom flask equipped with a condenser under nitrogen. 9- (Bromomethyl)nonadecane (1.801 g, 5 mmol) was added after adding NaH (0.48 g, 20 mmol) to the solution and stirring for 0.5 h. The solution was heated to 106 ºC for 10 h. The mixture was cooled to room temperature and diluted with water (100 mL), and then extracted with DCM. The product was isolated by silica gel chromatography using PE and DCM (4/1, v/v) (1.42 g, yield: 52%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.66 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.84 – 7.76 (m, 4H), 4.58 (d, *J* = 7.4 Hz, 2H), 2.03-2.00 (m, 1H), 1.35-1.23 (m, 32H), 0.92-0.81 (m, 6H).

Synthesis of **H**

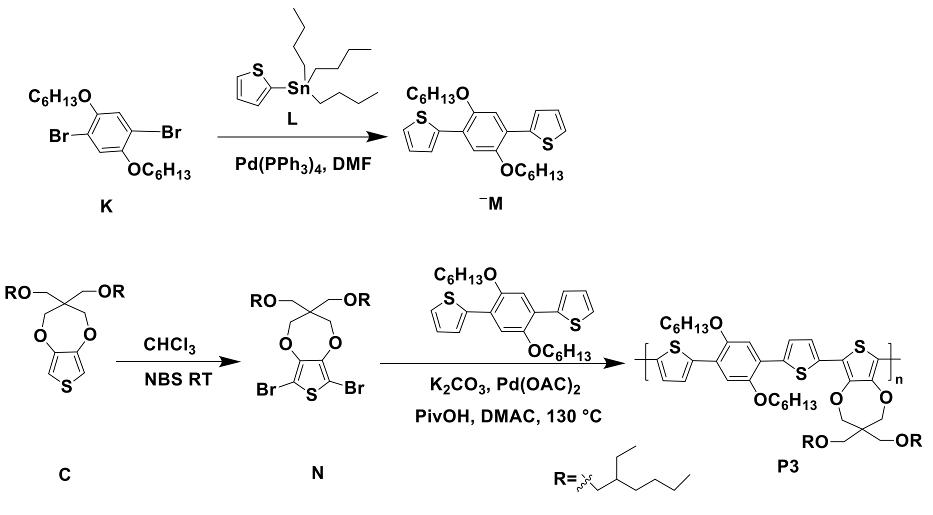
G (1.091 g, 2 mmol) was dissolved in CHCl$_3$ (30 mL) in a single flask. N-Bromosuccinimide (0.356 g, 2 mmol) was added in three times with an interval of 30 min each time. After stirring and reacting at room temperature for 6 h, the mixture was extracted with DCM and water. The product can be obtained by rotary evaporation of organic phase (0.953 g, yield: 68%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.73 (d, *J* = 7.6 Hz, 2H), 8.38 (d, *J* = 8.2 Hz, 2H), 8.10 (s, 2H), 7.96-7.91 (m, 2H), 4.50 (d, *J* = 7.4 Hz, 2H), 2.04-1.99 (m, 1H), 1.34-1.23 (m, 32H), 0.91-0.80 (m, 6H).

Synthesis of **J**

The mixture of **H** (0.7012 g, 1 mmol), **I** (1.4608 g, 2 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.0702 g, 0.01 mmol) and THF (30 mL) was refluxed under a nitrogen atmosphere at 72 ºC for 12 h. The solution was quenched with water and extracted with DCM. Finally, the product was isolated by silica gel chromatography using PE and DCM (3/2, v/v) (1.12 g, yield: 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (d, *J* = 7.6 Hz, 2H), 8.18 (d, *J* = 8.2 Hz, 2H), 7.86-7.80 (m, 4H), 6.63 (s, 2H), 4.56 (d, *J* = 7.3 Hz, 2H), 4.18 (s, 4H), 4.11 (s, 4H), 3.55-3.47 (m, 8H), 3.28 (d, *J* = 5.7 Hz, 8H), 2.03-1.99 (m, 1H), 1.49-1.44 (m, 4H), 1.36-1.22 (m, 64H), 0.91-0.79 (m, 30H).

Synthesis of **P2**

The mixture of **J** (0.79 g, 0.5 mmol), **E** (0.517 g, 0.5 mmol), $Pd(OAc)_2$ (0.0112 g, 0.5 mmol), K_2CO_3 (0.3474 g, 2.5 mmol), PivOH (0.0204 g, 0.2 mmol) and DMAC (30 mL) was refluxed under a nitrogen atmosphere (100 mL) at 130 ºC for 72 h. After cooling to room temperature, methanol (30 mL) was added to the mixture, then the resulting brown precipitate was collected by filtration and washed with methanol. The crude products were extracted with methanol, acetone and PE in turn to produce a purple-black solid (1.08 g, yield: 88%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.86-8.68 (m, 2H), 8.38-8.22 (m, 2H), 8.01-7.82 (m, 4H), 4.65-4.55 (m, 2H), 4.46-4.07 (m, 16H), 3.74-3.48 (m, 16H), 3.44-3.18 (m, 16H), 2.07-2.01 (m, 1H), 1.49-1.45 (m, 8H), 1.42-1.16 (m, 96H), 0.98-0.77 (m, 96H). GPC: Mn: 23.6 kDa, Mw: 88.4 kDa, PDI: 3.7, in THF vs PS.



Scheme S3: Synthesis route of P3.

Synthesis of **M**

M was synthesized according to reported literature[3]: **K** (1.744 g, 4mmoL), **L** (2.624 g, 8 mmol) and $Pd(PPh_3)_4$ (0.1828 g, 0.2 mmol) were added in a 100 mL 3-neck round bottom flask. Under a nitrogen atmosphere, DMF (40 mL) was added to the flask and the mixture was heated to reflux for 12 h. The solution was cooled to room temperature and poured into deionized water (300 mL). The mixture was extracted with DCM, the organic layer was dried with magnesium sulfate.

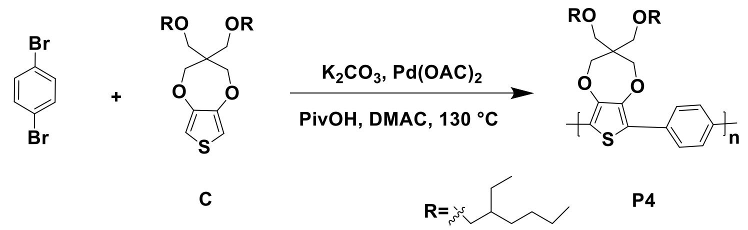
After filtration through a Büchner funnel, the solvent was evaporated and a brown solid was collected. This solid was purified by column chromatography (PE: DCM = 2: 1) to get a white solid (1.27 g, yield: 72%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 3.7, 1.1 Hz, 2H), 7.34 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.25 (s, 2H), 7.10 (dd, *J* = 5.1, 3.7 Hz, 2H), 4.08 (t, *J* = 6.6 Hz, 4H), 1.93-1.87 (m, 4H), 1.56-1.48 (m, 4H), 1.40-1.32 (m, 8H), 0.95-0.88 (m, 6H).

Synthesis of **N**

C (0.792 g, 2 mmol) was dissolved in $CHCl_3$ (30 mL) in a 100 mL single neck flask and NBS (0.7113 g, 4 mmol) was added to the solution in three times. After reacting in dark for 5 h, the reaction was stopped by addition of deionized water (100 mL). The mixture was extracted with DCM and the organic layer was dried with magnesium sulfate. After filtration through a Büchner funnel the solvent was evaporated and a light white oil was collected. The crude product was purified by column chromatography on silica gel with PE/DCM (5: 1) to give a white solid (0.79 g, yield: 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.09 (s, 4H), 3.49 (s, 4H), 3.29 (d, *J* = 5.6 Hz, 4H), 1.51-1.45 (m, 2H), 1.34-1.25 (m, 16H), 0.94-0.84 (m, 12H).

Synthesis of **P3**

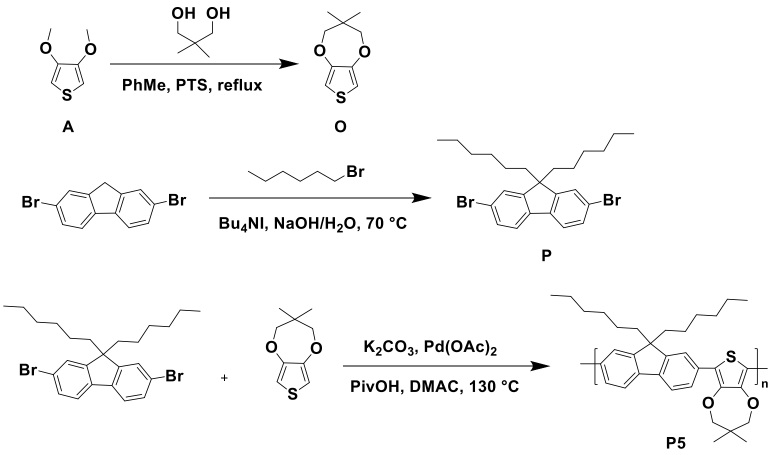
The mixture of **M** (0.3 g, 0.5 mmol), **N** (0.277 g, 0.5 mmol), $Pd(OAc)_2$ (0.0056 g, 0.25 mmol), K_2CO_3 (0.1737 g, 1.25 mmol), PivOH (0.0102 g, 0.1 mmol) and DMAC (10 mL) was refluxed under a nitrogen atmosphere (100 mL) at 130 ºC for 12 h. After cooling to room temperature, methanol (25 mL) was added to the mixture, then the resulting brown precipitate was collected by filtration and washed with methanol. The crude products were extracted with methanol, acetone and PE in turn to afford a dark red solid (0.28 g, yield: 65%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57-7.53 (m, 1H), 7.52-7.47 (m, 2H), 7.36-7.32 (m, 1H), 7.23-7.19 (m, 1H), 7.11-7.09 (m, 1H), 4.36-3.93 (m, 8H), 3.68-3.52 (m, 4H), 3.39-3.24 (m, 4H), 2.04-1.86 (m, 4H), 1.66-1.48 (m, 6H), 1.42-1.22 (m, 24H), 0.96-0.77 (m, 18H). GPC: Mn: 6.1 kDa, Mw:12.0 kDa, PDI: 2.0, in THF vs PS.



Scheme S4: Synthesis route of P4.

Synthesis of **P4**

The mixture of **C** (0.596 g, 1 mmol), 1,4-dibromobenzene (0.2339 g, 1 mmol), $Pd(OAc)_2$ (0.0113 g, 0.5 mmol), K_2CO_3 (0.345 g, 2.5 mmol), PivOH (0.102 g, 1 mmol) and DMAC (20 mL) was refluxed under a nitrogen atmosphere at 130 ºC for 72 h. After cooling to room temperature, methanol (30 mL) was added to the mixture, then the resulting orange precipitate was collected by filtration and washed with methanol. The crude products were extracted with methanol, acetone and PE in turn to get a tan solid (0.43 g, yield: 85%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.62 (m, 4H), 4.28-4.13 (m, 4H), 3.65-3.53 (m, 4H), 3.39-3.27 (m, 4H), 1.53-1.47 (m, 2H), 1.45-1.19 (m, 16H), 0.99-0.82 (m, 12H). GPC: Mn: 7.9 kDa, Mw: 18.4 kDa, PDI: 2.3, in THF vs PS.



Scheme S5: Synthesis route of P5.

Synthesis of **O**

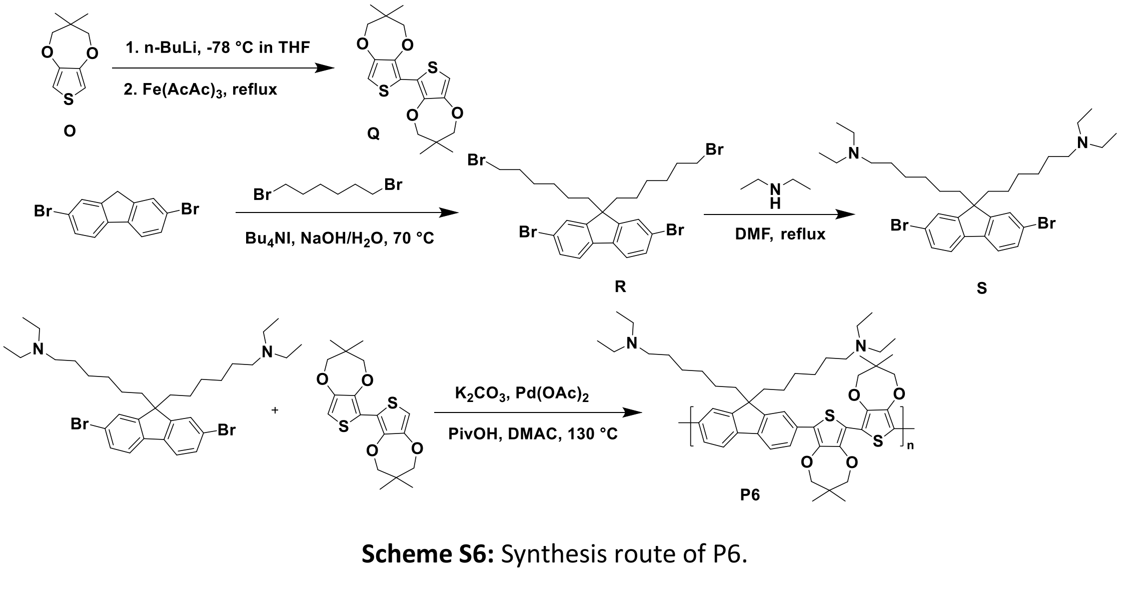
A (1.442 g, 10 mmol), 2,2-bis(bromomethyl)propane-1,3-diol (2.6 g, 10 mmol) and *p*-toluenesulfonic acid (0.6 g, 3.4 mmol) were dissolved in toluene (35 mL) in a 100 mL 3-neck round bottom flask. The solution was heated to 110 °C and kept reacting for 1 day. Then the solution was cooled to room temperature and poured into deionized water (120 mL). The mixture was extracted with DCM, the DCM layer was washed with brine and dried with magnesium sulfate.. After filtration through a Büchner funnel, the solvent was evaporated and a white liquid was collected. This raw product was purified by column chromatography (DCM: PE = 1: 5) to get a colorless liquid (1.53 g, yield: 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.47 (s, 2H), 3.73 (s, 4H), 1.03 (s, 6H).

Synthesis of **P**

2,7-Dibromo-9*H*-fluorene (1.62 g, 5 mmol), Bu$_4$NI (0.1847 g, 0.5 mmol), 1-bromohexane (1.98 g, 12 mmol) and NaOH (7.5g, 0.1875 moL) were dissolved in H$_2$O (15 mL) at 0 °C under nitrogen. Then the mixture was heated to 70 °C and kept reacting for 6 h. After cooling to room temperature, the mixture was extracted with DCM, the organic layer was washed with brine and dried with magnesium sulfate. After filtration through a Büchner funnel, the solvent was evaporated and pale brown solid collected. This raw product was purified by column chromatography (PE) to give a white solid (2.01 g, yield: 82%). ^{1}H NMR (600 MHz, CDCl$_3$): 7.52 (d, *J* = 7.9 Hz, 2H), 7.48-7.44 (m, 4H), 1.96-1.90 (m, 4H), 1.15-1.11 (m, 4H), 1.08-1.02 (m, 8H), 0.79 (t, *J* = 7.3 Hz, 6H), 0.64-0.56 (m, 4H).

Synthesis of **P5**

P5 was synthesized according to reported literature[4]: the mixture of **P** (1.47 g, 3 mmol), **O** (0.5529 g, 3 mmol), Pd(OAc)$_2$ (0.0113 g, 0.5 mmol), K$_2$CO$_3$ (1.065 g, 7.5 mmol), PivOH (0.306g, 3 mmol) and DMAC (25 mL) were stirred at 130 °C for 24 h under nitrogen. Then the solution was cooled to room temperature and poured into methyl alcohol (50 mL). The resulting precipitate was collected by filtration and washed with methanol. The crude products were extracted with methanol, acetone and PE in turn to obtain a brown solid (1.52g, Yield: 76%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.85-7.80 (m, 2H), 7.76-7.69 (m, 4H), 4.02-3.96 (m, 4H), 2.11-2.02 (m, 4H), 1.36-1.07 (m, 18H), 0.93-0.78 (m, 10H). GPC: Mn: 14.8 kDa, Mw: 35.8 kDa, PDI: 2.4, in THF vs PS.



Scheme S6: Synthesis route of P6.

Synthesis of **Q**

To a dry 100 mL 3-neck round bottom flask with **O** (1.843 g, 10 mmol) was dissolved in 40 mL of dry THF and bubbled with nitrogen for 0.5 h and then cooled to -78 °C where *n*-butyl lithium (2.5 M, 10 mmol) in hexane was added drop-wise. After Stirring for 45 min at -78 °C and the solution was transferred into a dry-degassed THF solution (80 mL) of Fe(acac)$_3$ (3.5317 g, 10 mmol) under nitrogen at r.t *via* cannula. The reaction mixture was refluxed for 72 h. Volatiles were evaporated, and the residue was purified by column chromatography through silica using PE: DCM (6:1) to gain a white solid (2.71 g, yield: 74%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.40 (s, 2H), 3.81 (s, 4H), 3.73 (s, 4H), 1.06 (s, 12H).

Synthesis of **R**

2,7-Dibromo-9*H*-fluorene (1.62 g, 5 mmol), Bu$_4$NI (0.1847 g, 0.5 mmol), 1,6-dibromohexane (2.904 g, 12 mmol) and NaOH (7.5 g, 0.1875 moL) were dissolved in H$_2$O (15 mL) at 0 °C under nitrogen. Then the mixture was heated to 70 °C and kept reacting for 7 h. After cooling to room temperature, the mixture was extracted with DCM, the organic layer was washed with brine and dried with magnesium sulfate. After filtration through a Büchner funnel, the solvent was evaporated and a pale brown solid was collected. This raw product was purified by column chromatography (PE) to get a white solid (1.55 g, yield: 48%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.43 (d, *J* = 1.6 Hz, 2H), 3.29 (t, *J* = 6.8 Hz, 4H), 1.97-1.89 (m, 4H), 1.72-1.63 (m, 4H), 1.24-1.16 (m, 4H), 1.14-1.06 (m, 4H), 0.64-0.54 (m, 4H).

Synthesis of **S**

S was synthesized according to reported literature[5]: **R** (0.9719 g, 1.5 mmol) and dimethylamine（0.3285 g, 4.5 mmol）were dissolved in DMF (30 mL) in a 100 mL 2-neck round bottom flask. Then the mixture was heated to reflux for 10 h. After cooling to room temperature, the solution was extracted with water and DCM. The organic layer was concentrated and then purified by silica gel chromatography using PE to give the white sold (0.73 g, yield: 77%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.46-7.40 (m, 4H), 2.44 (q, *J* = 7.1 Hz, 8H), 2.30-2.23 (m, 4H), 1.95-1.90 (m, 4H), 1.30-1.21 (m, 4H), 1.11-1.00 (m, 8H), 0.95 (t, *J* = 7.2 Hz, 12H), 0.62-0.54 (m, 4H).

Synthesis of **P6**

A mixture of **Q** (0.366 g, 1 mmol), **S** (0.632 g, 1 mmol), Pd(OAc)$_2$ (0.0113 g, 0.5 mmol), K$_2$CO$_3$ (0.345 g, 2.5 mmol), PivOH (0.102g, 1 mmol) and DMAC (20 mL) were stirred at 130 °C for 24 h under nitrogen. Then the solution was cooled to room temperature and poured into methyl alcohol (50 mL). The resulting yellow precipitate was collected by filtration and washed with methanol. The crude products were extracted with methanol, acetone and PE in turn to furnish a bright yellow solid (0.83 g, yield: 83%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.83-7.77 (m, 2H), 7.73-7.65 (m, 4H), 4.04-3.96 (m, 4H), 3.96-3.90 (m, 4H), 2.51-2.41 (m, 8H), 2.33-2.27 (m, 4H), 2.11-2.01 (m, 4H), 1.35-1.25 (m, 4H), 1.22-1.17 (m, 8H), 1.17-1.08 (m, 12H), 1.00-0.94 (m, 12H), 0.83-0.73 (m, 4H).GPC: Mn: 5.8 kDa, Mw: 13.2 kDa, PDI: 2.3, in THF vs PS.

^{1}H NMR spectra of polymers:

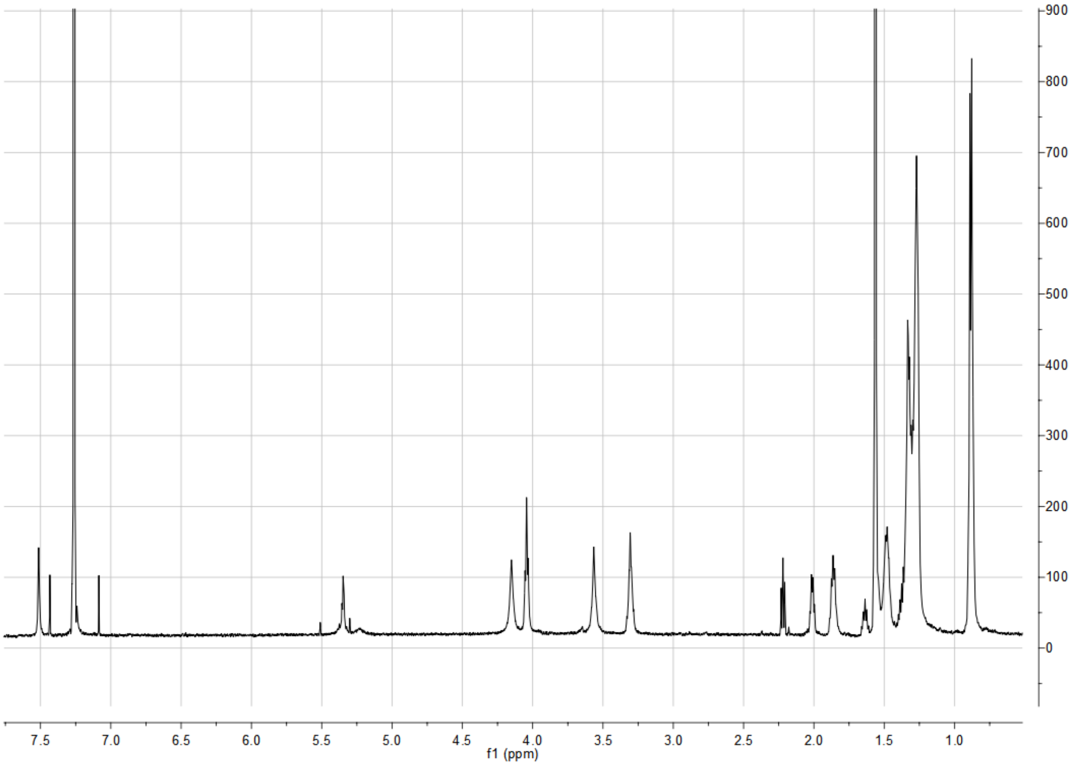


Fig. S12 ^{1}H NMR spectra of P1

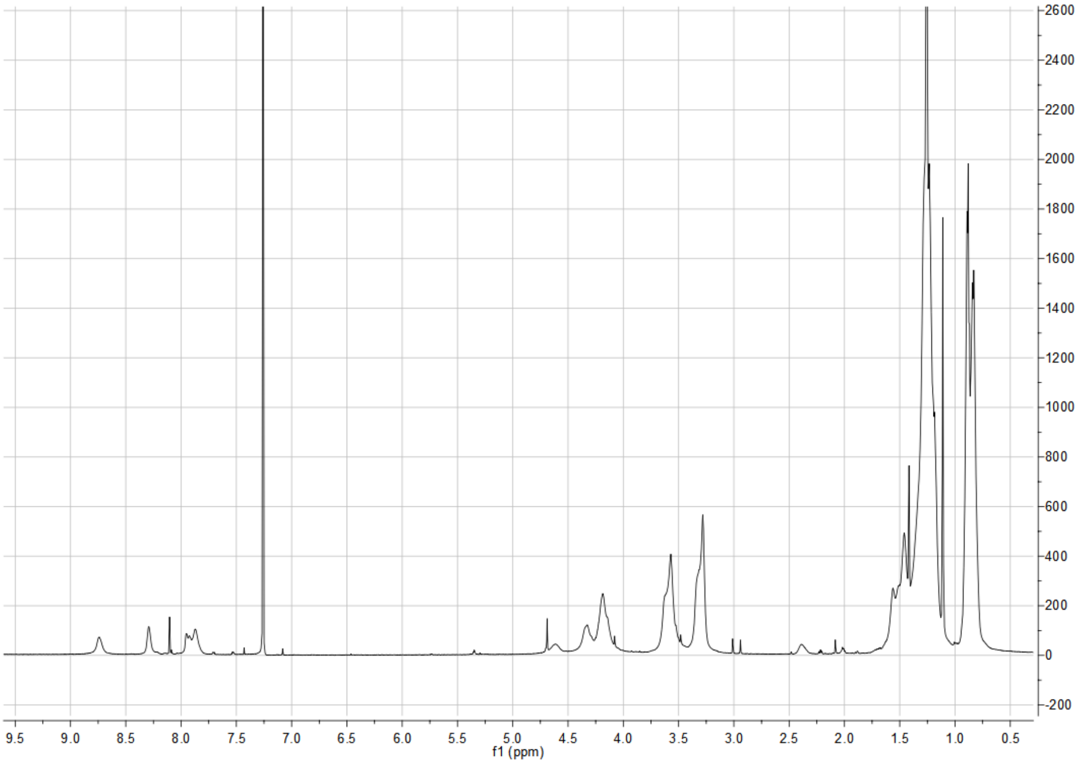


Fig. S13 ^{1}H NMR spectra of P2

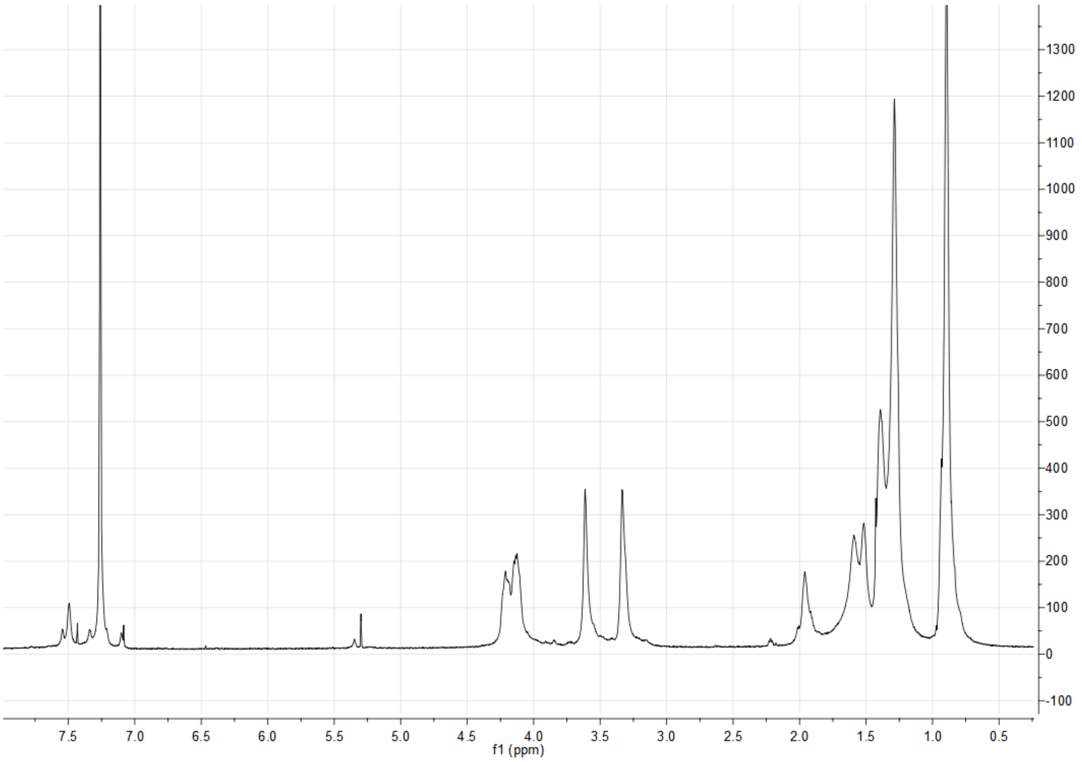


Fig. S14 ^{1}H NMR spectra of P3

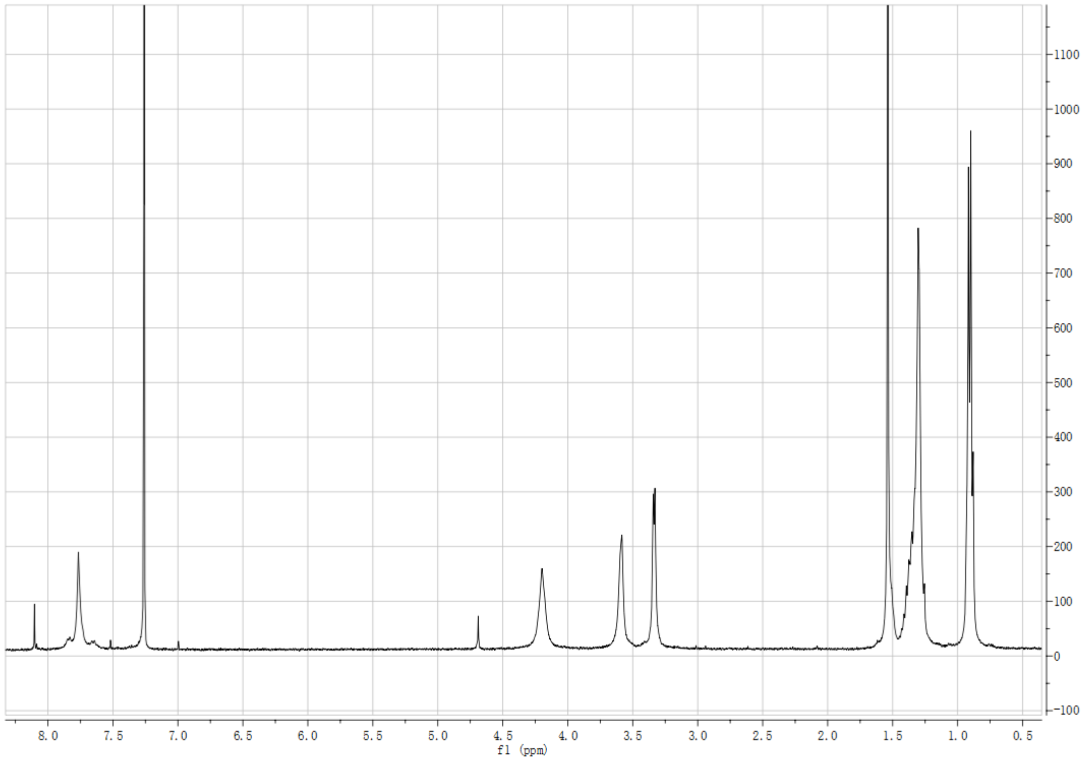


Fig. S15 ^{1}H NMR spectra of P4

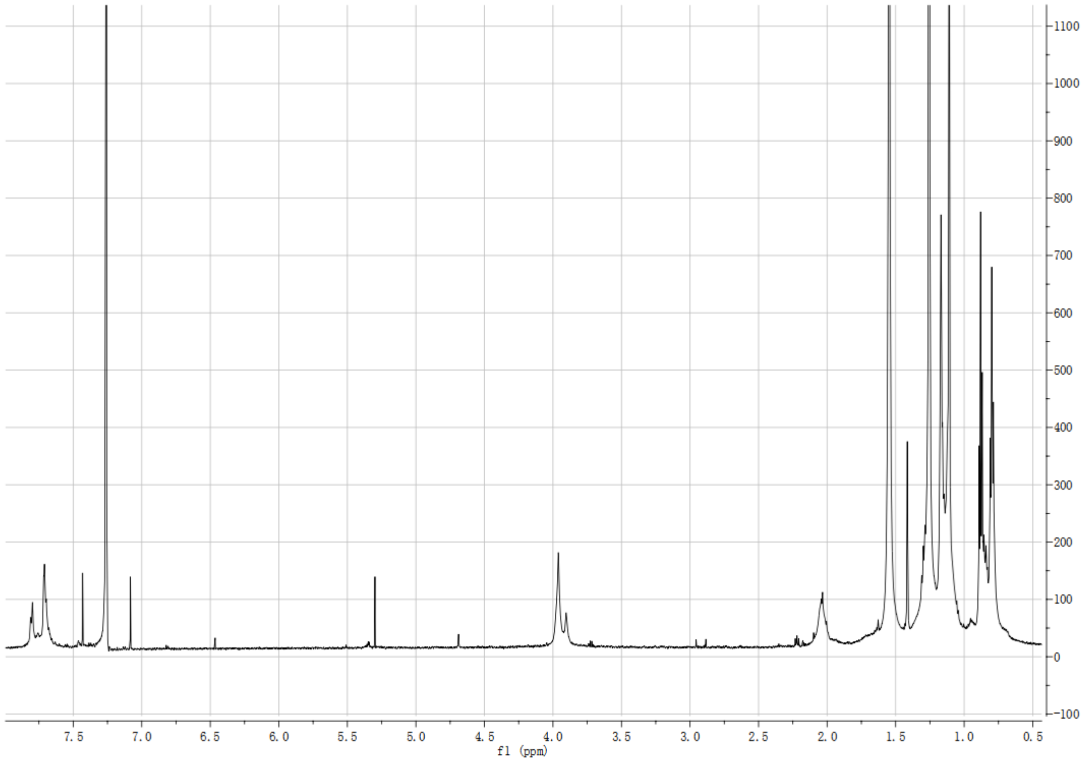


Fig. S16 ^{1}H NMR spectra of P5

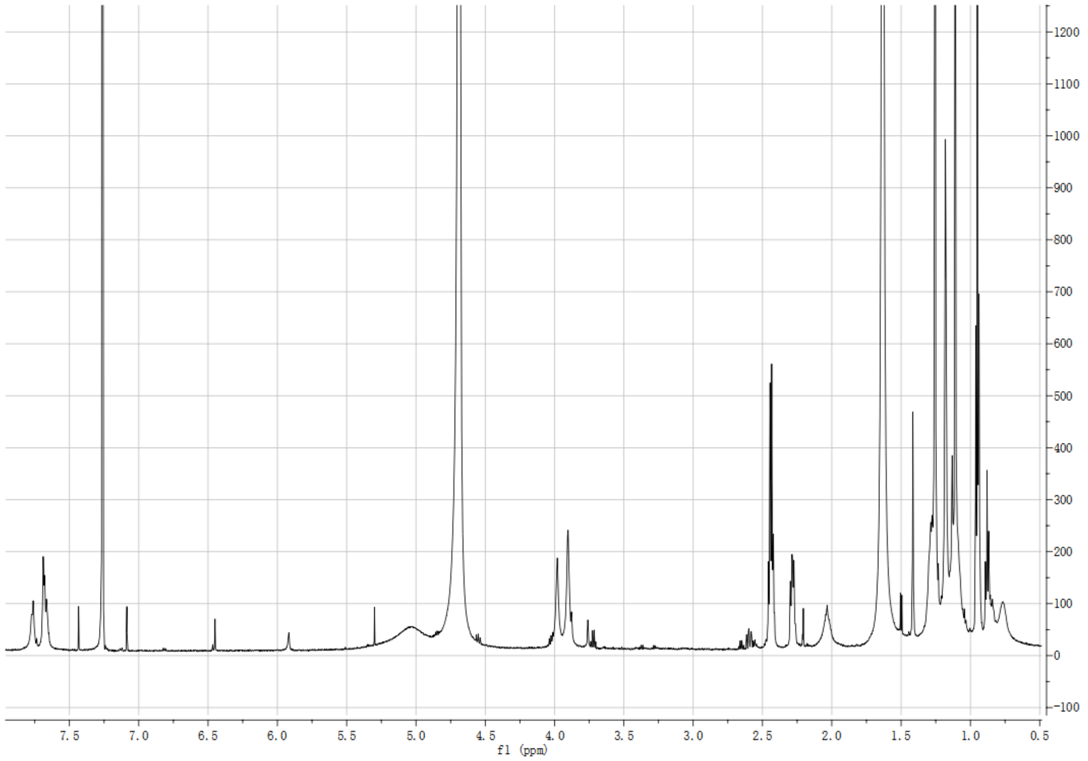


Fig. S17 ^{1}H NMR spectra of P6

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