Electronic Supplementary Information

Synthesis and properties of a series of quinoxaline-based copolymers: An example to see the effect of the structure of the mainchain and sidechain on charge transport ability of the polymers

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General Information

^{1}H NMR and ^{13}C NMR spectra were measured on a MERCURY-VX300 spectrometer. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a Vario EL III microanalyzer. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Gel permeation chromatography (GPC) analysis was perfomed on an Agilent 1100 series HPLC system equipped with a G1326A refractive index detector, in which polystyrene standards were used as calibration standards and THF was used as an eluent, and the flow rate was 1.0 mL/min. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min^{-1}. Cyclic voltammetry (CV) was carried out in nitrogen purged anhydrous CH_3CN solution at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s^{-1}. Formal potentials were calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Atomic force microscopy (AFM) images were obtained on an Asylum Research Cypher ES AFM in tapping mode. X-ray diffraction (XRD) was performed using a Empyrean (PANalytical B. V.) X-ray diffractometer.

Device Fabrication and Characterization

OTFT devices were fabricated with a bottom-gate, bottom-contact configuration. A heavily doped n-type Si wafer with a SiO_2 layer of 300 nm and a capacitance of 11 nF/cm^2 was used as the gate dielectric. Octadecyltrichlorosilane (OTS) was used as a self-assembled surface modifier for SiO_2. The Au source/drain electrodes were prepared by photolithography. For spin-coated thin film device, a 50 nm-thick (± 10 nm) semiconductor film was spin-coated on top of the OTS-treated SiO_2 from 10 mg/mL $CHCl_3$ solution of the compound. The channel length was 50 μm, and the channel width was 1400 μm. Device annealing was carried out at 120 °C for 1 h in a vacuum oven under a pressure of 0.1 Pa. The current-voltage (I-V) characteristics were measured with the Micromanipulator 6150 probe station in a clean and metallic shielded box at room temperature in air, and recorded with a Keithley 4200 SCS. The field-effect mobility was calculated in the saturation regime by using the equation $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_T is the threshold voltage.

Synthesis of intermediates

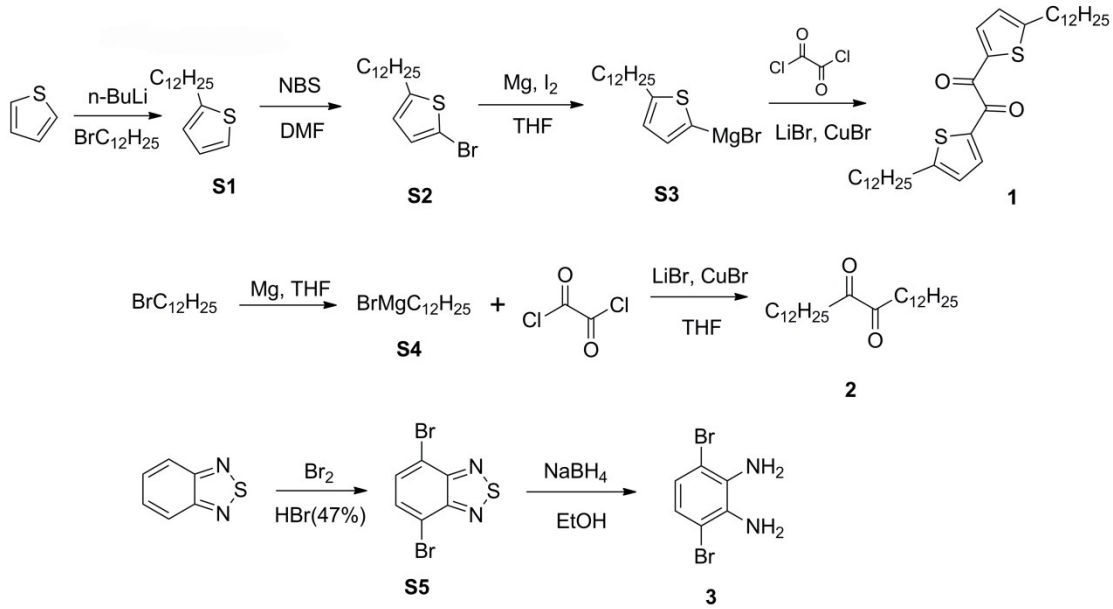

Figure S1 Synthetic routes of intermediates for acceptors.

2-dodecylthiophene (**S1**)[1]: Thiophene (6 mL, 75 mmol) and 100 mL of THF was added to a Schlenk tube filled full with argon by syringe. Then the solution was cooled to –78 °C, and n-BuLi (2.2 M in hexane, 32 mL, 70.4 mmol) was added dropwise at this temperature. After addition, the mixture was stirred at room temperature for another 1h, and cooled to –78 °C again. 1-bromododecane (15 g, 60.2 mmol) was added to the solution at once. 30 min later, the solution was warmed up to room temperature and stirred overnight. 5 mL of water was added to the mixture to quench the reaction and the organic solvent was evaporated. Then 100 mL of water was added and the mixture was extracted with chloroform. The organics were collected and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was purified by column chromatography on silica gel with petroleum ether as eluent to give **S1** (12 g, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.09 (d, J = 5.2 Hz, 1H), 6.91 (dd, *J* = 3.6 Hz, 1H), 6.77 (d, *J* = 2.8 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.72-1.62 (m, 2H), 1.41-1.30 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H).

2-bromo-5-dodecylthiophene (**S2**)[1]: 2-dodecylthiophene (6 g, 23.8 mmol) and 100 mL DMF were mixed in a round bottom flask, then NBS (4.25 g, 23.9 mmol) was slowly added to the solution at room temperature. The solution was stirred overnight. 300 mL of water was added, and the mixture was extracted with hexane. The organics were washed with water by three times and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was purified by column chromatography on silica gel with petroleum ether as eluent to give **S2** (5.1 g, 65%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 6.82 (d, *J* = 3.7 Hz, 1H), 6.51 (d, *J* = 3.7 Hz, 1H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.61 (m, 2H), 1.30 (m, 18H), 0.87 (t, *J* = 6.7 Hz, 3H).

(5-dodecylthiophen-2-yl)magnesium bromide (**S3**)[2]: 2-bromo-5-dodecylthiophene 4.8 g, 14.5 mmol) and magnesium chips (0.42 g, 17.5 mmol) were added to 10 mL of anhydrous THF under argon. Then a small amount of iodine was added as initiator, and the mixture was warmed up to reflux for 1 h. The solution of **S3** in THF was obtained as light red liquid and used in the next step without further purification.

1,2-bis(5-dodecylthiophen-2-yl)ethane-1,2-dione (**1**)[2]: A Schlenk tube containing LiBr (2.5 g, 28.7 mmol) and CuBr (2 g, 13.9 mmol) was connected to vacuum line and filled with argon. 20 mL of THF was injected to the tube and the mixture was cooled to –78 ^{o}C. Then the solution of **S3** was slowly added to the mixture, followed by the addition of oxalyl chloride (0.55 mL, 5.8 mmol). 40 min later, the solution was warmed up to room temperature and stirred overnight. The reaction was quenched by saturated ammonium chloride solution, and extracted with diethyl ether. The organics were collected and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was purified by column chromatography on silica gel with chloroform/petroleum ether (v/v, 1:3) as eluent to give compound **1** as yellow solid (2.5 g, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.86 (t, J = 3Hz, 2H), 6.88 (d, J = 2.7 Hz, 2H), 2.88 (t, J =7.5 Hz, 4H), 1.74-1.68 (m, 4H), 1.33-1.26 (m, 36H), 0.88 (t, J = 6 Hz, 6H).

dodecylmagnesium bromide (**S4**)[3]: 1-bromododecane (6 g, 24.1 mmol) and Mg (0.64 g, 26.6 mmol) were added to 10 mL of THF under argon. Then a small amount of iodine was added as initiator, and the mixture was warmed up to reflux for 1 h. The solution of **S4** in THF was obtained and used in the next step without further purification.

hexacosane-13,14-dione (**2**)[3]: A Schlenk tube containing LiBr (4.4 g, 50.6 mmol) and CuBr (3.5 g, 24.3 mmol) was connected to vacuum line and filled with argon. 30 mL of THF was injected to the tube and the mixture was cooled to –78 ^{o}C. Then the solution of **S4** was slowly added to the mixture, followed by the addition of oxalyl chloride (0.92 mL, 9.7 mmol). 40 min later, the solution was warmed up to room temperature and stirred overnight. The reaction was quenched by saturated ammonium chloride solution, and extracted with diethyl ether. The organics were collected and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was purified by column chromatography on silica gel with chloroform/petroleum ether (v/v, 1:3) as eluent to give compound **2** as colorless oil (2 g, 42%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 2.72 (t, J = 7.2 Hz, 4H), 1.56 (m, 4H), 1.25 (m, 36H), 0.87 (t, J = 7.2 Hz, 6H).

4,7-dibromobenzo[c][1,2,5]thiadiazole (**S5**)[4]: benzo[c][1,2,5]thiadiazole (5 g, 36.72 mmol) and 70 mL of HBr (47%) were mixed in a flask. To the mixture was

added Br_2 (17.6 g, 110.16 mmol) in HBr solution (50 mL). Then the solution was refluxed for 6h. Some orange solid was precipitated during reaction. After cooling to room temperature, saturated sodium hydrogen sulfite was added to the mixture and stirred for 2 min. The mixture was filtered, and the residue was washed by water for three times and cold ethanol for two times. **S5** was obtained after dried over vacuum (10 g, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.73 (s, 2H).

3,6-dibromobenzene-1,2-diamine (**3**)[5]: 4,7-dibromobenzo[c][1,2,5]thiadiazole (3.8 g, 13 mmol) was dissolved in 100 mL of ethanol and cooled in an ice-water bath. $NaBH_4$ (10 g, 26 mmol) was slowly added to the solution. Then the mixture was stirred at room temperature for 2h. 20 mL of water was added to quench the reaction, and the ethanol was removed by evaporation. The organics was then extracted with ethyl ether. The crude product was purified by column chromatography on neutral alumina with chloroform as eluent to give compound **3** as grey solid (3 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 6.85 (s, 2H), 3.71 (s, 4H).

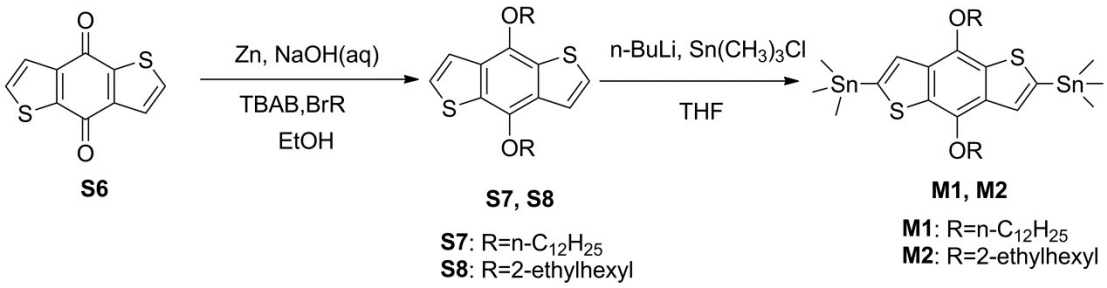

Figure S2 Synthetic route of **M1** and **M2**.

4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene (**S7**)[6]: benzo[1,2-b:4,5-b']dithiophene-4,8-dione (**S6**), Zn powder (0.65 g, 10 mmol), 15 mL of NaOH solution (20%) and 4ml of ethanol were mixed together and warmed to 85 ^{o}C for 1 h. 1-bromododecane (3 g, 12 mmol) and tetrabutylammonium bromide (20 mg) was added and the solution turned to pink after 2 h. Another more Zn powder (0.5g) was added and the solution became yellow. The mixture was refluxed for 6 h. After cooling to room temperature, the solution was diluted by 50 mL of water and 50 mL of chloroform, and then filtered. The organics in the filtrate were collected and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was purified by column chromatography on silica gel with chloroform/petroleum ether (v/v, 1:20) as eluent to give **S7** as white solid (1.9 g, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.48 (d, 2H), 7.36 (d, 2H), 4.27 (t, 4H), 1.92-1.86 (m, 4H), 1.54 (m, 4H), 1.37-1.23 (m, 32H), 0.88 (t, 6H).

4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (**S8**)[7]: **S8** was prepared with similar procedure as **S7**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.48 (d, 2H), 7.36 (d, 2H), 4.18 (t, 4H), 1.78 (m, 2H), 1.53-1.17 (m, 16H), 0.88 (t, 12H).

(4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M1**)[8]: **S7** (0.83 g, 1.49 mmol) was added to a Schlenk tube filled with argon, then 40 mL of THF was injected to the solution by syringe. The tube was cooled to – 78°C, and n-BuLi in hexane (2.73 mL, 3.67 mmol) was added slowly to the solution. After stirring for 30 min, the solution was moved to room temperature and reacted for 1h. Then it was cooled to –78°C again, and trimethyltin chloride (1M in hexane, 4 mL) was added at one time. 30min later, the solution was allowed to warm to room temperature and stirred overnight. 100 mL of water was added to the solution, and it was extracted with hexane. The organics were collected and dried over anhydrous Na_2SO_4. The crude product was recrystallized from ethanol for twice. **M1** was obtained as white solid (1.12 g, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.51 (s, 2H), 4.29 (t, 4H), 1.86 (m, 4H), 1.57 (m, 4H), 1.37-1.23 (m, 32H), 0.88 (t, 6H), 0.45 (s, 18H).

(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M2**)[9]: **M2** was prepared with similar procedure as **M1**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.51 (s, 2H), 4.19 (d, 4H), 1.84-1.78 (m, 2H), 1.74-1.52 (m, 8H), 1.44-1.37 (m, 8H), 1.03 (t, 6H), 0.94 (t, 6H), 0.43 (s, 18H).

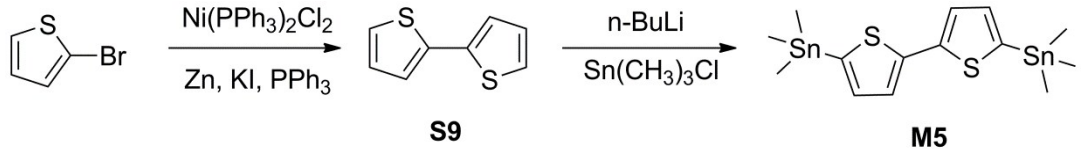

Figure S3 Synthetic route of **M5**.

2,2'-bithiophene (**S9**)[10]: 2-bromothiophene (4.89 g, 30 mmol), $Ni(PPh_3)_2Cl_2$ (1.96 g, 3 mmol), zinc powder (1.95 g, 30 mmol), PPh_3(1.57 g, 6 mmol) and KI (0.2 g, 1.2 mmol) were added to a Schlenk tube which was then filled full with argon. 80 mL of THF was injected to the tube by syringe. Then the mixture was heated to reflux for 24h. After cooled to room temperature, the mixture was filtered, and filtrate was evaporated to remove the solvent. The crude product was dissolved in 100 mL of chloroform and 100 mL of water was added to wash the organic phase. Then the organics were collected and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was purified by column chromatography on silica gel with petroleum ether as eluent to give **S9** as oil (4.0 g, 80 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.22-7.18 (m, 4H), 7.03-7.00 (m, 2H).

5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**M5**)[10]: 2,2'-bithiophene (1 g, 6.02 mmol) was added to a Schlenk tube filled with argon. 80 mL of THF was then injected to the tube by syringe. The solution was cooled to – 78°C and n-BuLi in hexane (2.18 M, 6.9 mL, 15 mmol) was slowly added. 30 min later, the mixture was moved to room temperature and stirred for 1h. Then it was cooled to – 78°C again, and trimethyltin chloride (1 M, 15 mL) was added to the solution at one time. 30 min later, the solution was moved to room temperature and stirred overnight. 50 mL of saturated NaCl was added, and the mixture was extracted with ethyl ether. The organics were collected and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was recrystallized from ethanol to give **M5** as white solid (2.1 g, 84 %). ^{1}H NMR (*d*-DMSO, 300 MHz) δ [ppm]: 7.33 (d, 2H), 7.14-7.12(m, 2H), 0.35 (s, 18 H).

NMR spectra of monomers

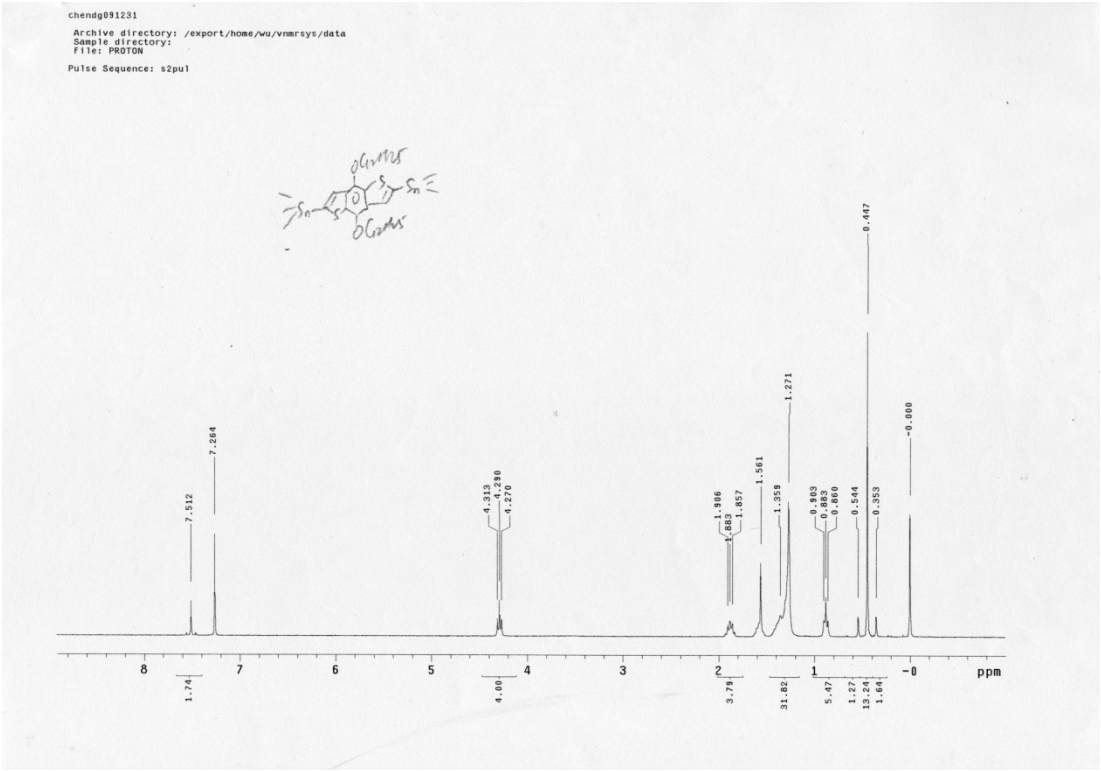

Figure S4 ^{1}H NMR spectra of **M1**.

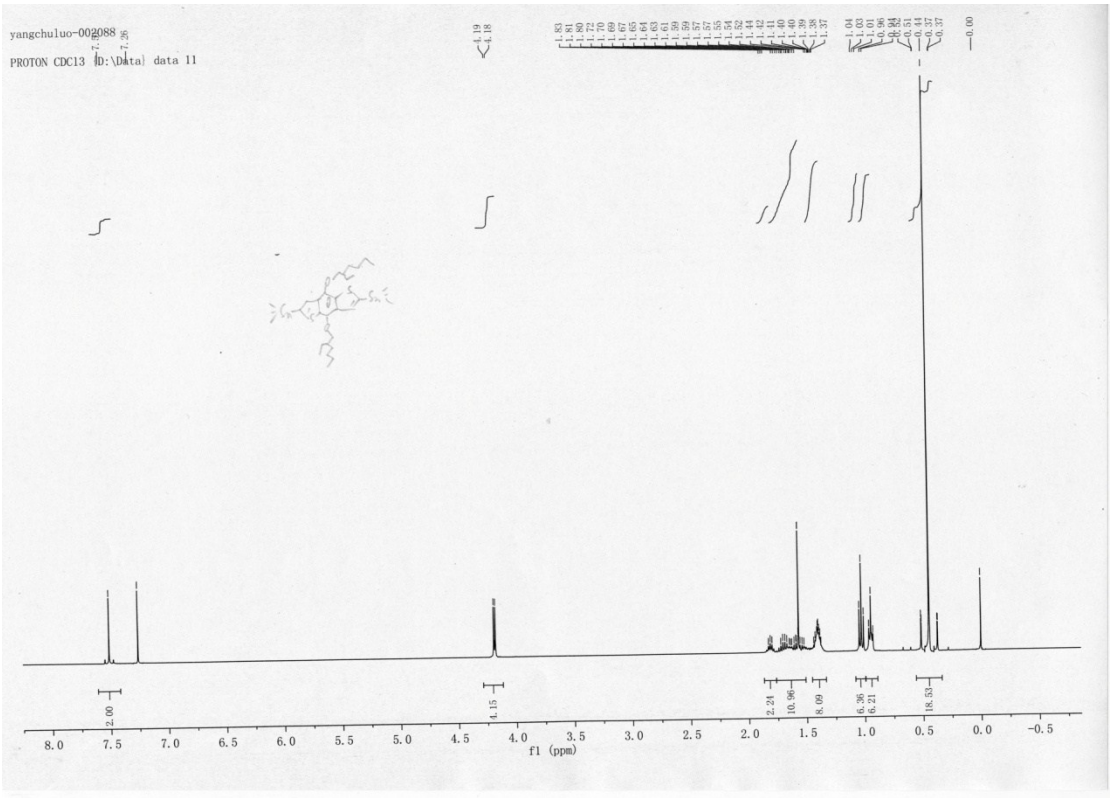

Figure S5 ^{1}H NMR spectra of **M2**.

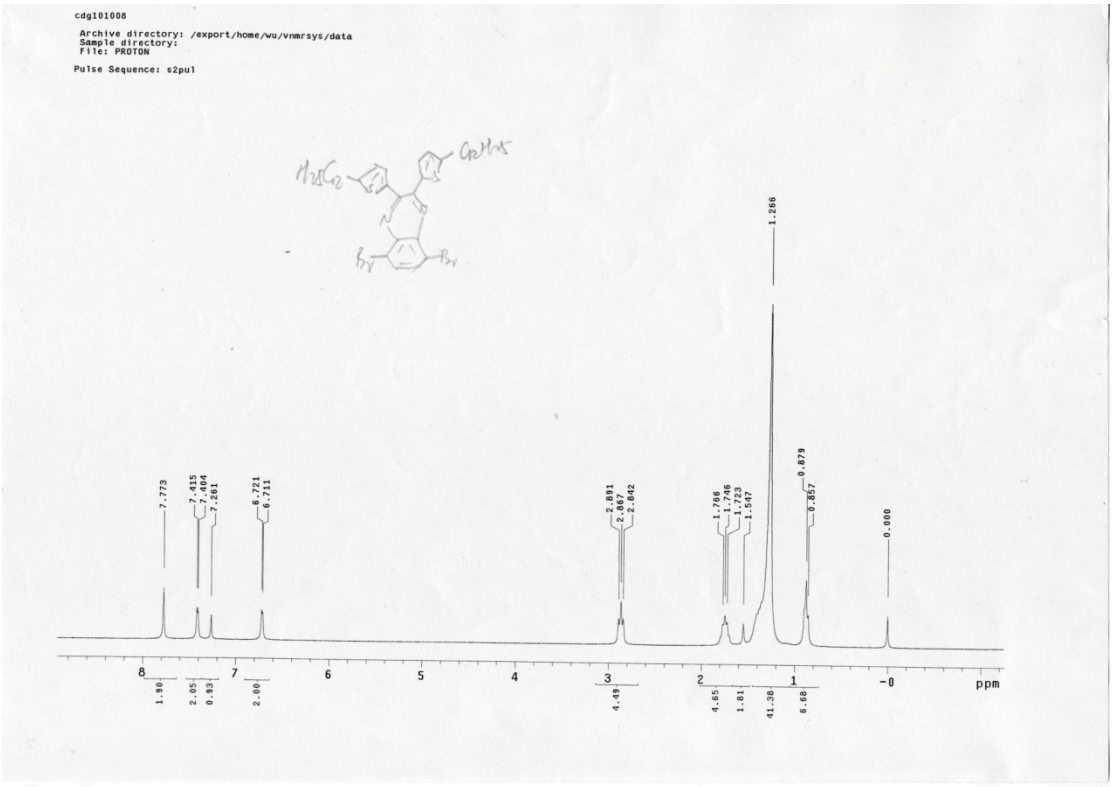

Figure S6 ^{1}H NMR spectra **M3**.

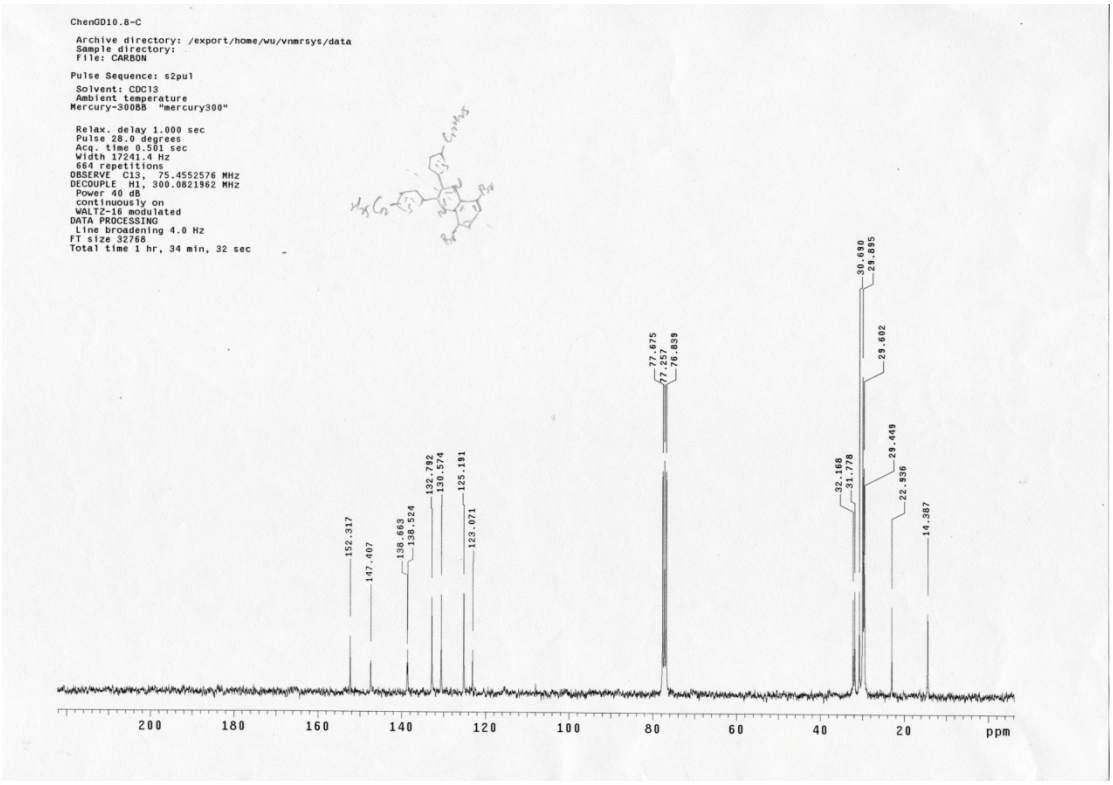

Figure S7 ^{13}C NMR spectra of **M3**.

Figure S8 ^{1}H NMR spectra of **M4**.

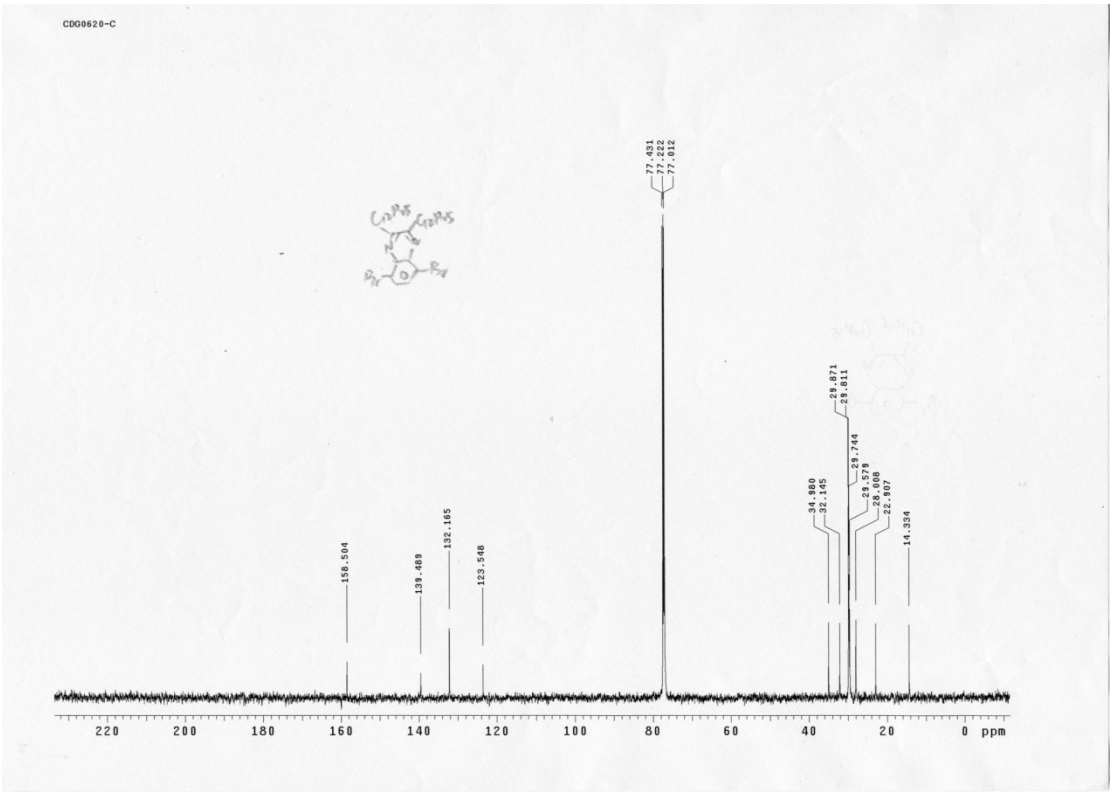

Figure S9 ^{13}C NMR spectra of **M4**.

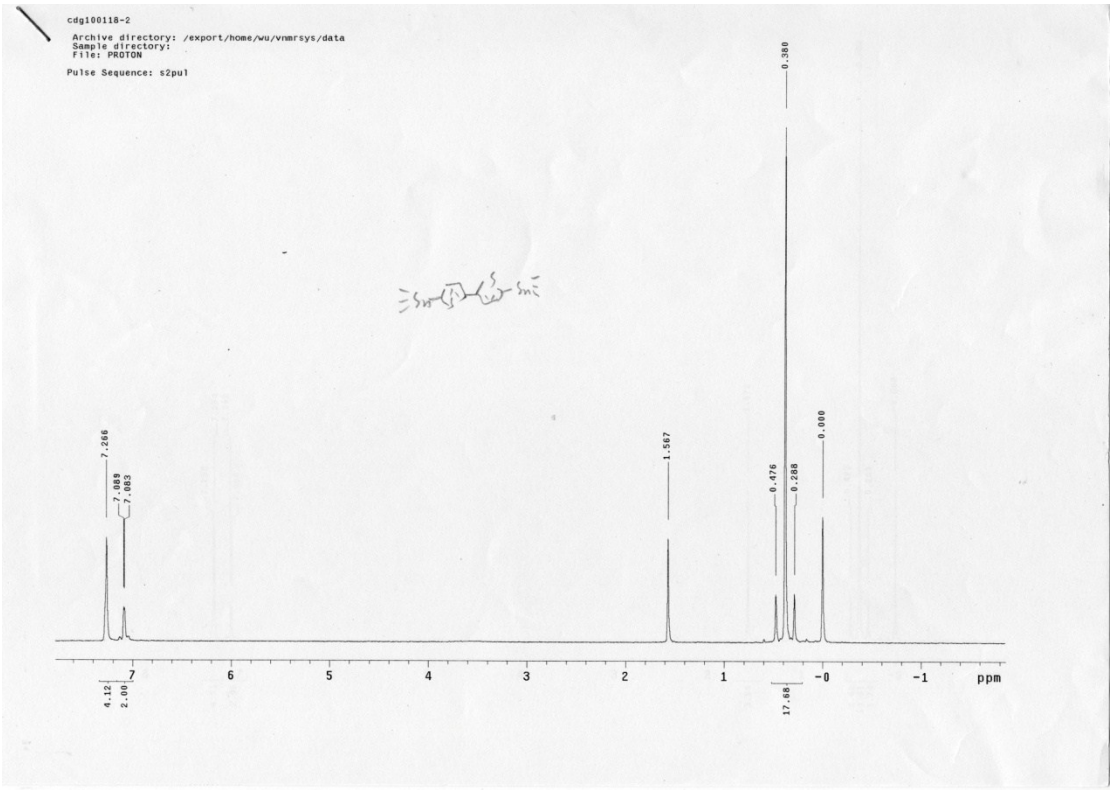

Figure S10 ^{1}H NMR spectra of **M5**.

XRD spectra

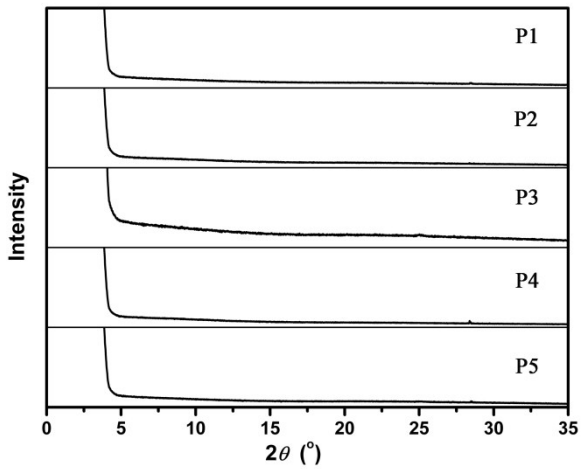

Figure S11 XRD spectra of spin-coated polymer films on silicon wafer after annealing at 120 °C for 1 hour.

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