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

Dugang Chen,\textsuperscript{ab,*} Cheng Zhong,\textsuperscript{b} Yan Zhao,\textsuperscript{c} Yunqi Liu\textsuperscript{c} and Jingui Qin\textsuperscript{b,*}

\textsuperscript{a} School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, Wuhan 430205, China
\textsuperscript{b} College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China
\textsuperscript{c} Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

*Correspondence to:
J. Qin (E-mail: jgqin@whu.edu.cn) or D. Chen (dg.chen@163.com)
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 performed 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$_3$CN 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 ($\text{Fc}^+/\text{Fc}$) 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 $I_{DS} = (\mu WC/2L)(V_G - V_T)^2$, where $I_{DS}$ is the drain-source current, $\mu$ 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)*: 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 Na₂SO₄. 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 (CDCl₃, 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)*: 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 Na₂SO₄. 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 (CDCl₃, 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 $-78^\circ$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$_2$SO$_4$. 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, $J = 3$ Hz, 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 $-78^\circ$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$_2$SO$_4$. 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 Br₂ (17.6 g, 110.16 mmol) in HBr solution (50 mL). Then the solution was refluxed for 6 h. 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%). ¹H NMR (CDCl₃, 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. NaBH₄ (10 g, 26 mmol) was slowly added to the solution. Then the mixture was stirred at room temperature for 2 h. 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%). ¹H NMR (CDCl₃, 300 MHz) δ [ppm]: 6.85 (s, 2H), 3.71 (s, 4H).
4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (S8): S8 was prepared with similar procedure as S7. 1H NMR (CDCl$_3$, 300 MHz) $\delta$ [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): 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 $-78^\circ$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 $-78^\circ$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$_2$SO$_4$. The crude product was recrystallized from ethanol for twice. M1 was obtained as white solid (1.12 g, 85%). 1H NMR (CDCl$_3$, 300 MHz) $\delta$ [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): M2 was prepared with similar procedure as M1. 1H NMR (CDCl$_3$, 300 MHz) $\delta$ [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): 2-bromothiophene (4.89 g, 30 mmol), Ni(PPh$_3$)$_2$Cl$_2$ (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$_2$SO$_4$. 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 %). 1H NMR (CDCl$_3$, 300 MHz) $\delta$ [ppm]: 7.22-7.18 (m, 4H), 7.03-7.00 (m, 2H).
5,5′-bis(trimethylstannyl)-2,2′-bithiophene (M5): 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 1 h. 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 Na₂SO₄. The solvent was concentrated and the crude product was recrystallized from ethanol to give M5 as white solid (2.1 g, 84%). ¹H 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 ¹H NMR spectra of M1.
Figure S5 $^1$H NMR spectra of M2.

Figure S6 $^1$H NMR spectra M3.
Figure S7 ¹³C NMR spectra of M3.

Figure S8 ¹H 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.

Reference: