Supporting Information

6*H*-[1,2,5]Thiadiazolo[3,4-*e*]thieno[3,2-*b*]indole-flanked *para*-azaquinodimethane based aromatic-quinoidal polymer semiconductors with high molecular weights synthesized via direct arylation polycondensation

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Contents

1. Materials and characterization

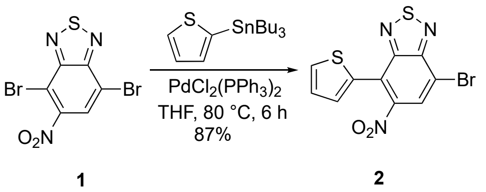
Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Dry methanol, toluene, N, N-dimethylformamide were distilled by calcium hydride prior to use. Tributyl(thiophen-2-yl)stannane, N,N'-diacetylglycine anhydride and 2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophene were purchased from Shanghai Bide Pharmatech Co., Ltd. Thieno[3,2-*b*]thiophene was purchased from Shanghai Darui Fine Chemicals Co., Ltd. 11-(Bromomethyl)tricosane[1], 4,7-dibromo-5-nitrobenzo[*c*][1,2,5]thiadiazole[2], and (2*Z*,5*Z*)-2,5-bis((5- bromothiophen-2-yl)methylene)-3,6-bis((2-decyltetradecyl)oxy)-2,5-dihydropyrazine (**M-ref**)[3] were synthesized according to the published procedures.

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance-600 spectrometer. High temperature gel permeation chromatography (HT-GPC) was tested with a ShimadzuSIL-20A liquid chromatography instrument using 1,2,4-trichlorobenzene (TCB) as eluent at 150 ^{o}C with polystyrenes as standards. Thermal gravimetric analysis (TGA) was performed under a nitrogen flow at a heating rate of 20 ^{o}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 $Ag/AgNO_3$ 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^+) 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^+ was assumed at -4.8 eV to vacuum. The half-wave potential of Fc/Fc^+ was found to 0.09 V, related to the Ag/Ag^+ reference electrode. The HOMO energy levels of the polymer were calculated using the equation: $E_{\mathrm{HOMO}} = -e(4.71+E_{\mathrm{ox}})$ (eV), where E_{ox} is the onset oxidation potential relative to the Ag/Ag$^+$ reference electrode. The LUMO energy levels of the polymer were calculated using the equation: E_{LUMO} = -e(4.71+E_{red}) (eV), where E_{red} is the onset reduction potential relative to the Ag/Ag$^+$ reference electrode. Mass spectrum (MS) was recorded on an Applied Bruker Solarix XR Fourier transform ion cyclotron resonance mass spectrometry. X-ray diffraction (XRD) measurement was recorded in the range of $2\theta = 3\sim32°$ on a desktop X-ray diffractometer (Rigaku MiniFlex 600) with Cu K_α radiation (λ = 1.5406 Å). The density functional theory (DFT) calculations were performed with the Gaussian 09 Rev. D.01 employing the B3LYP/6-31g(d) level. The long-branched alkyl chains were all replaced by methyl groups to simplify the calculation.

2. Synthetic procedure

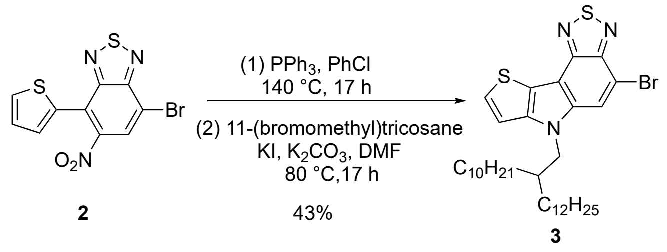
2.1. Synthetic procedures of the monomer M

Synthesis of 7-bromo-5-nitro-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2)



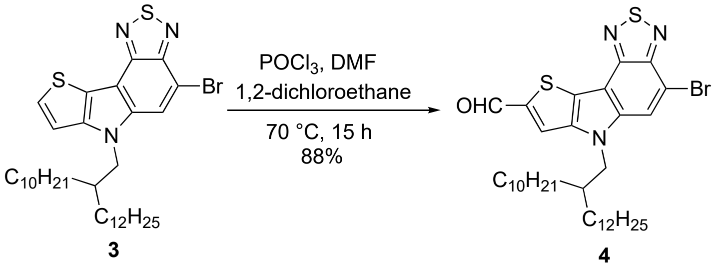
To a dry 100 mL Schlenk tube, compound **1** (3.39 g, 10 mmol), 2-(tributylstannyl)thiophene (3.73 g, 10 mmol), $PdCl_2(PPh_3)_2$ (0.14 g, 0.2 mmol), and anhydrous tetrahydrofuran (THF) (50 mL) was added under argon protection. Then, the mixture was refluxed at 80 °C for 6 h. After cooling to room temperature, the solvent was evaporated and the crude product was then recrystallized with methanol to get the compound **2** as an orange solid (2.97 g, 87%). R_f = 0.45 (petroleum ether /dichloromethane, 3:2, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.67 (dd, J = 5.1, 1.1 Hz, 1H), 7.42 (dd, J = 3.7, 1.1 Hz, 1H), 7.21 (dd, J = 5.1, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 152.9, 130.7, 130.5, 130.3, 127.9, 126.9, 121.5, 114.6.

Synthesis of 4-bromo-6-(2-decyltetradecyl)-6H-[1,2,5]thiadiazolo[3,4-e]thieno- [3,2-b]indole (3)



To a dry 100 mL Schlenk tube, compound **2** (3.42 g, 10 mmol), triphenylphosphine (8.39 g, 31.98 mmol) and anhydrous chlorobenzene was added under argon protection. Then, the mixture was heated to 140 °C and kept stirring for 17 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The solvent was removed under reduced pressure to give the corresponding residue, which was purified by silicon chromatography using petroleum ether/ethyl acetate (1:4, v/v) as eluent to get an orange solid (2.0 g). This crude product was also directly added to an anhydrous N,N-dimethylformamide (40 mL) solution of the 11-(bromomethyl)tricosane (6.73 g, 16.12 mmol), potassium iodide (0.57 mg, 3.44 mmol), and potassium carbonate (2.67 g, 19.34 mmol). Then, the mixture was kept stirring at 80 °C for 17 h. After cooling to room temperature, the mixture was extracted with dichloromethane and washed with water. The collected organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by silicon chromatography using petroleum ether/dichloromethane (3:2, v/v) as eluent to get the compound **3** as an orange oil (2.81 g, 43%). R_f = 0.61 (petroleum ether/dichloromethane, 1:1, v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.50 (s, 1H), 7.10 (s, 1H), 4.22 (s, 2H), 2.05 (t, J = 6.9 Hz, 1H), 1.21 (m, 40H), 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 148.3, 144.8, 138.8, 128.8, 119.9, 118.0, 110.7, 110.4, 106.9, 50.6, 39.3, 32.1, 32.0, 31.7, 30.0, 29.8, 29.7, 29.7, 29.5, 29.4, 26.5, 22.8, 14.3.

Synthesis of 4-bromo-6-(2-decyltetradecyl)-6H-[1,2,5]thiadiazolo[3,4-e]thieno- [3,2-b]indole-8-carbaldehyde (4)

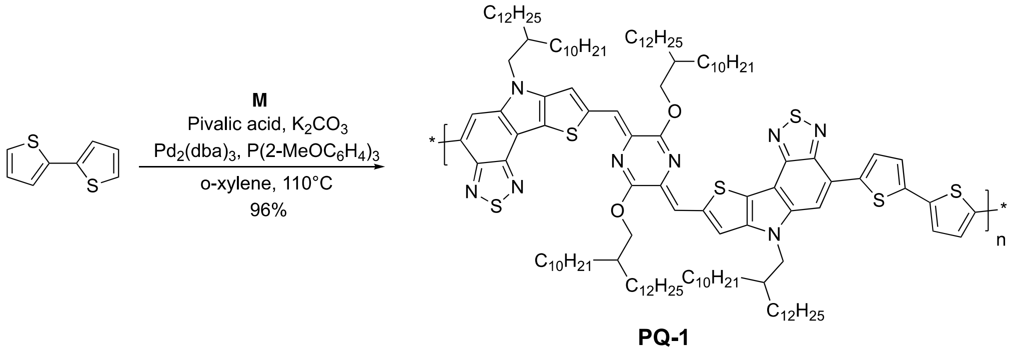


To a dry 250 mL round-bottom flask, compound **3** (3.11 g, 4.80 mmol), anhydrous *N*, *N*-dimethylformamide (2.5 mL) and 1,2-dichloroethane (70 mL) was added under argon protection. The mixture was stirred at 0 °C for 0.5 hour, followed by adding phosphorus oxychloride (3.7 mL) dropwise and was heated to 70 °C for 15 h. After cooling to room temperature, 70 mL 0.1 M aqueous K_2CO_3 solution was added and the mixture was extracted three times with dichloromethane. The combined organic layers were washed three times with brine, and then dried with magnesium sulphate. After removal of the solvent under reduced pressure, the residue was purified by silicon chromatography using petroleum ether/dichloromethane (1:5, v/v) as eluent to get the compound **4** as a yellow solid (3.15 g, 97%). R_f = 0.33 (petroleum ether/dichloromethane, 1:5, v/v). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.99 (s, 1H), 7.91 (s, 1H), 7.72 (s, 1H), 4.23 (s, 2H), 2.05 (s, 1H), 1.21 (m, 40H), 0.87 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 183.4, 150.4, 148.3, 145.2, 143.3, 141.6, 124.8, 119.5, 118.5, 111.3, 110.0, 50.8, 39.3, 32.1, 32.0, 31.7, 30.0, 29.8, 29.7, 29.6, 29.5, 29.4, 26.5, 22.8, 14.3.

Synthesis of 8,8'-((1Z,1'Z)-(3,6-bis((2-decyltetradecyl)oxy)pyrazine-2,5-diylidene)bis(methaneylylidene))bis(4-bromo-6-(2-decyltetradecyl)-6H-[1,2,5]thiadiazolo[3,4-e]thieno[3,2-b]indole) (M)

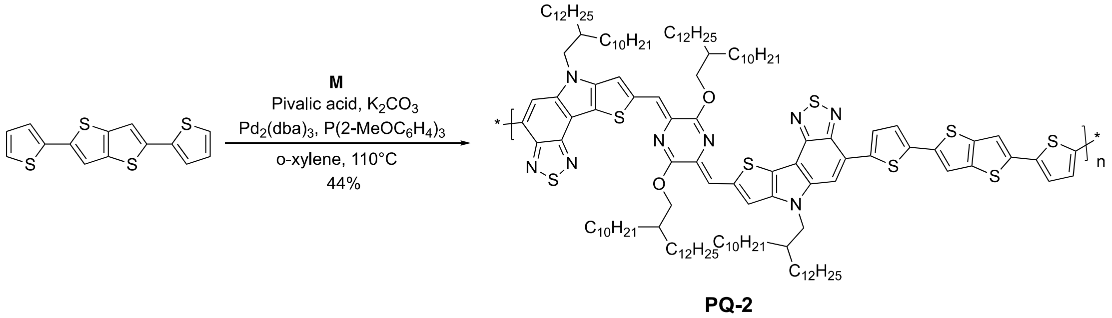
To a dry 48 mL Schlenk tube, compound **4** (1.52 g, 2.25 mmol), N,N'-diacetylglycine anhydride (0.18 g, 0.9 mmol), triethylamine (3.5 mL, 25.2 mmol) and anhydrous N,N-dimethylformamide (5.0 mL) was added under argon protection. Then, the mixture was heated to 120 °C and kept stirring for 20 h. After cooling to room temperature, 100 mL methanol was added and the precipitate was collected by filtration. The residue was purified by silicon chromatography using petroleum ether/ dichloromethane (1:14, v/v) as eluent to get the diarylidene piperazinedione as a red solid (0.75 g). This crude intermediate product was also directly added to an anhydrous N,N-dimethylformamide (15 mL) solution of the potassium carbonate (0.36 g, 2.63 mmol) and 11-(bromomethyl)tricosane (0.88 g, 2.12 mmol). Then, the mixture was heated to 100 °C for 20 h under argon. After cooling to room temperature, 100 mL methanol was added and the precipitate was collected by filtration. The residue was purified by silicon chromatography using petroleum ether/dichloromethane (5:2, v/v) as eluent and the residue was then recrystallized with ethyl acetate to get the **M** as a black solid (0.91 g, 82.4%). R_f = 0.45 (petroleum ether/dichloromethane, 2:5, v/v). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.78 (d, J = 34.7 Hz, 2H), 7.21 (s, 2H), 7.15 (d, J = 27.6 Hz, 2H), 4.61 (m, 4H), 4.06 (d, J = 36.1 Hz, 4H), 2.10 (s, 2H), 2.01 (s, 2H), 1.69-1.60 (m, 10H), 1.44 (s, 8H), 1.34-1.21 (m, 132H), 0.85 (m, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 150.3, 148.4, 144.1, 143.6, 139.2, 129.3, 124.4, 119.5, 117.6, 111.9, 110.7, 107.0, 71.8, 50.4, 39.0, 37.5, 32.0, 31.7, 30.4, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 27.0, 26.5, 22.8, 14.2. HRMS (MALDI FT-ICR) (m/z): $[M+H]^+$ calcd for: Calcd. for $C_{122}H_{203}Br_2N_8O_2S_4$: 2098.3273, found: 2098.3295.

2.2. Synthetic procedures of polymers PQ-1 and PQ-2



PQ-1

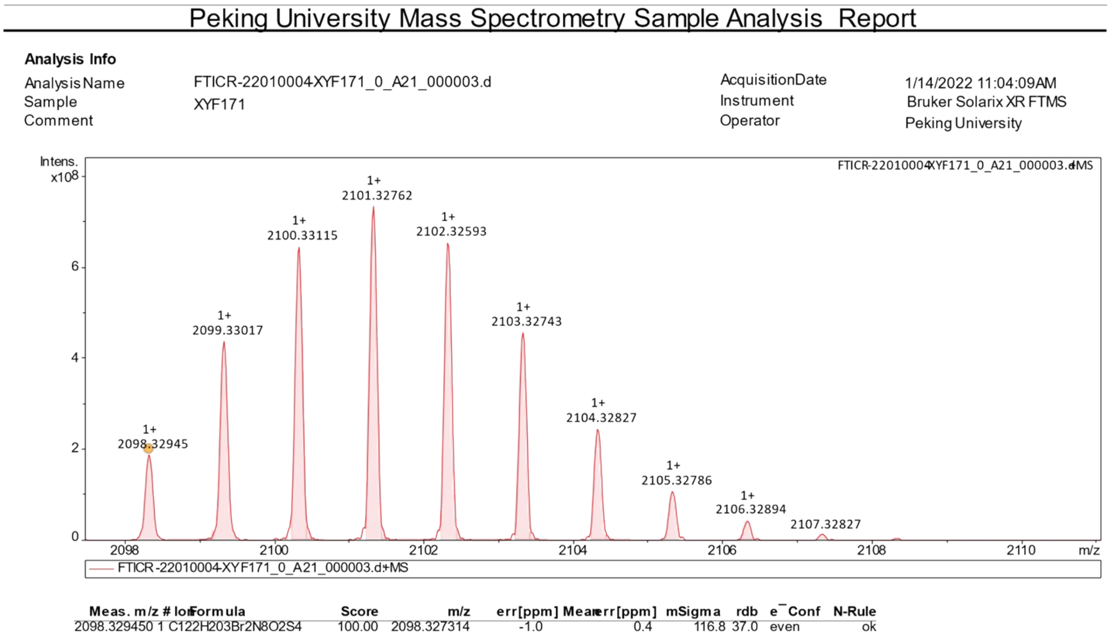
The monomer **M** (210.1 mg, 0.1 mmol), 2,2'-bithiophene (16.9 mg, 0.1 mmol), K_2CO_3 (41.4 mg, 0.3 mmol), and pivalic acid (12.2 mg, 0.12 mmol) were carefully weighed into a dry Schlenk tube containing a stirr bar. The degassed dry 1,2-dichlorobenzene (0.7 mL) was then added under argon and the whole was stirred for 5 min at room temperature in order to fully dissolve the monomers. Then $Pd_2(dba)_3$ (2.75 mg, 0.003 mmol) and tris(o-methoxyphenyl)phosphine (3.5 mg, 0.01mmol) was added under argon. The Schlenk tube was sealed and placed into a preheated oil bath and stirred for 48 h at 130 °C. After cooling to room temperature and additional K_2CO_3 (41.4 mg, 0.3 mmol), pivalic acid (12.2 mg, 0.12 mmol), Pd_2dba_3 (2.75 mg, 0.003 mmol), and tris(o-methoxyphenyl)phosphine (3.5 mg, 0.01mmol) were added. The solution was heated at 130 °C for additional 24 h. After cooling to room temperature, the mixture was precipitated into methanol. Then the crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, and petroleum ether. The petroleum ether solution was then concentrated by evaporation, and it was precipitated from stirring methanol and dried in vacuum at 60 °C to give the black polymer **PQ-1** (202 mg, 96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (br, 1H), 8.10 (br, 1H), 8.05 (br, 1H), 8.01 (br, 1H), 7.71 (br, 1H), 7.43 (br, 1H), 7.22 (br, 1H), 7.13 (br, 1H), 7.08 (br, 1H), 6.91 (br, 1H), 4.66 (br, 4H), 3.98 (br, 4H), 2.19 (br, 2H), 2.11 (br, 2H), 1.70 - 1.23 (m, 150H), 0.86 (m, 24H). HT-GPC (150 °C, TCB): M_n = 155.7 kDa, M_w = 426.5 kDa, $Đ$ = 2.74.



The **M** (210.1 mg, 0.1 mmol), 2,5-dithiophen-2-ylthieno[3,2-*b*]thiophene (31.1 mg, 0.1 mmol), K_2CO_3 (41.4 mg, 0.3 mmol), and pivalic acid (12.2 mg, 0.12 mmol) were carefully weighed into a dry vial containing a stirr bar. The degassed dry 1,2-dichlorobenzene (0.7 mL) was then added under argon and the whole was stirred for 5 min at room temperature in order to fully dissolve the monomers. Then $Pd_2(dba)_3$ (4.5 mg, 0.005 mmol) and tris(o-methoxyphenyl)phosphine (3.5 mg, 0.01mmol) was added under argon. The vial was sealed and placed into a preheated oil bath and stirred for 3.5 h at 110 °C. After cooling to room temperature, the mixture was precipitated into methanol. Then the crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, petroleum ether, and then chloroform. The chloroform solution was then concentrated by evaporation, and it was precipitated from stirring methanol and dried in vacuum at 60 °C to give the black polymer **PQ-2** (101 mg, 44%). ^{1}H NMR (600 MHz, CDCl3) δ 8.22 (br, 1H), 8.10 (br, 1H), 8.08 (br, 1H), 7.97 (br, 1H, 7.74 (br, 1H), 7.68 (br, 1H), 7.43 (br, 1H), 7.31 (br, 1H), 7.21 (br, 1H), 7.15 (br, 1H), 7.08 (br, 1H), 7.00 (br, 1H), 4.63 (br, 4H), 3.95 (br, 4H), 2.12 (br, 2H), 2.05 (br, 2H), 1.68-1.22 (m, 150H), 0.85 (m, 24H). HT-GPC (150 °C, TCB): M_n = 128.7 kDa, M_w = 311.7 kDa, $Đ$ = 2.43.

3. Supporting data

3.1. Fourier transform mass spectrometry (FT-MS) data of the monomer M



Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	FTICR-22010004-XYF171_0_A21_000003.d	AcquisitionDate	1/14/2022 11:04:09AM
Sample	XYF171	Instrument	Bruker Solarix XR FTMS
Comment		Operator	Peking University

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
2098.329450	1	C122H203Br2N8O2S4	100.00	2098.327314	-1.0	0.4	116.8	37.0	even	ok

Figure S1. Fourier transform mass spectrometry (FT-MS) data of the monomer **M**.

3.2. Fourier transform infrared (FT-IR) spectra of the intermediate and the monomer M

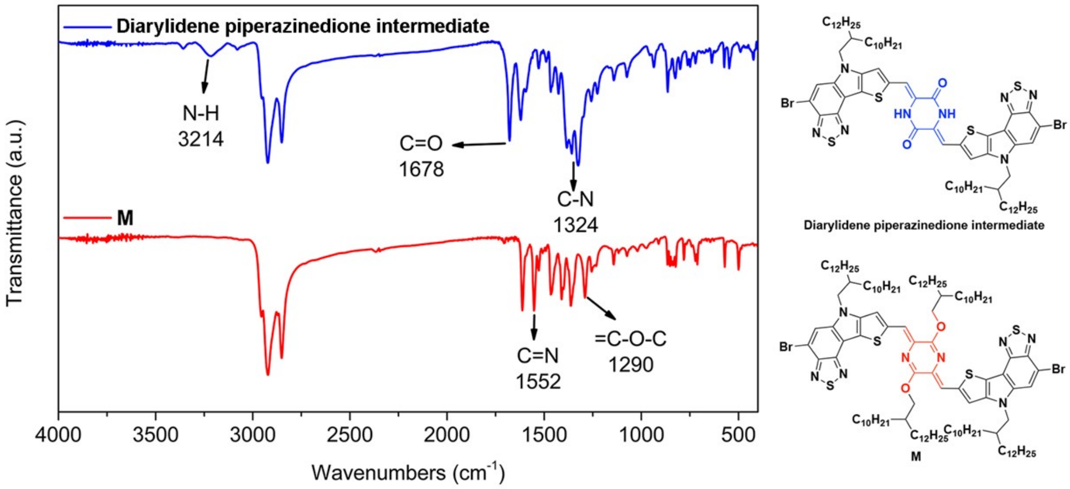


Figure S2. FT-IR spectra of the diarylidene piperazinedione intermediate and the monomer **M**.

3.3. NMR spectra

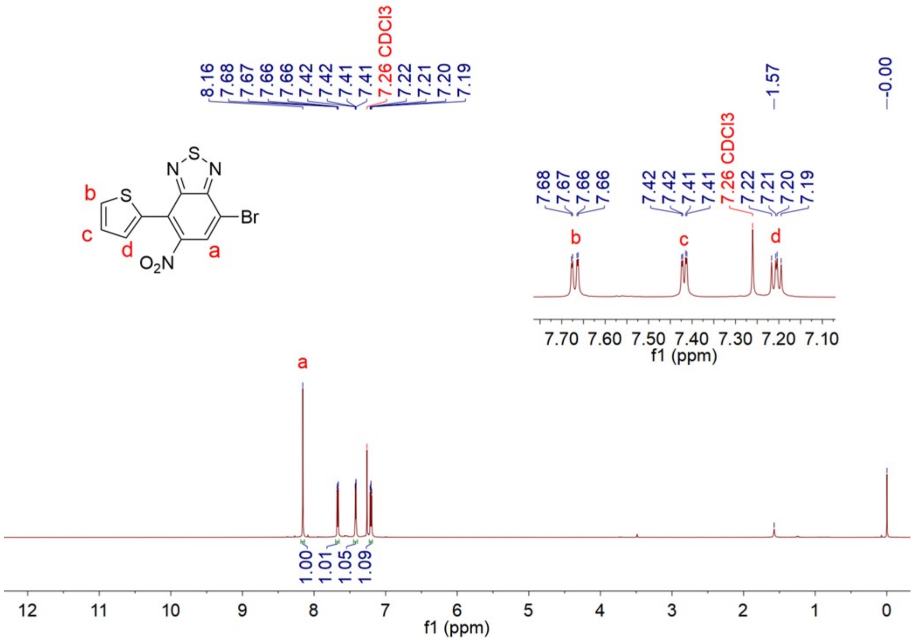


Figure S3. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

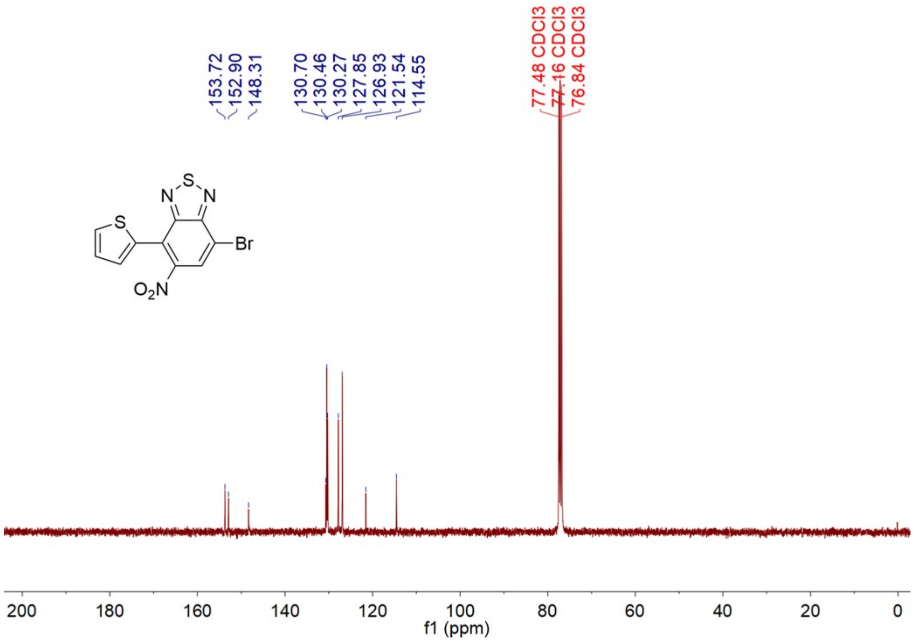


Figure S4. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

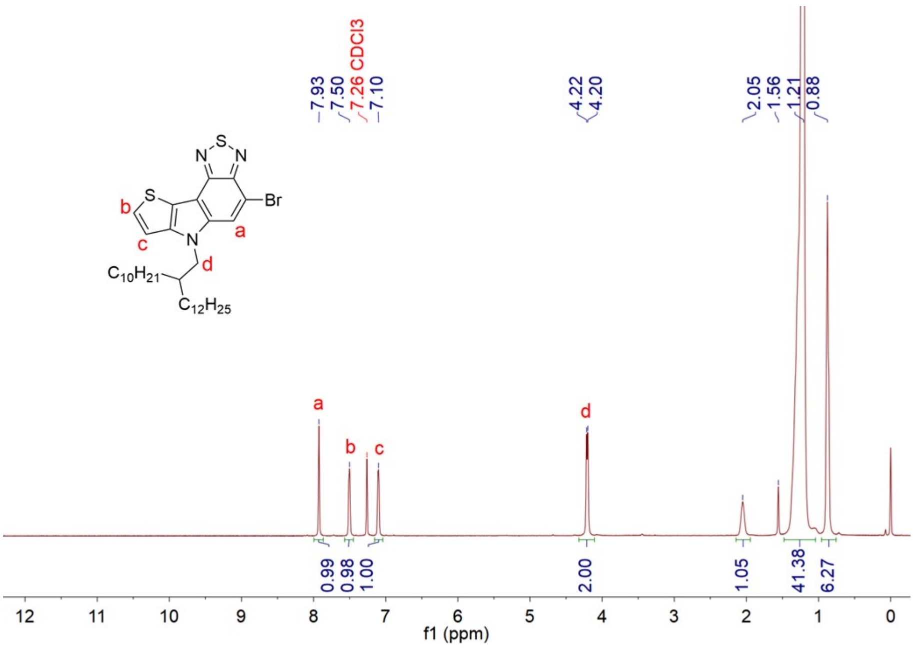


Figure S5. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

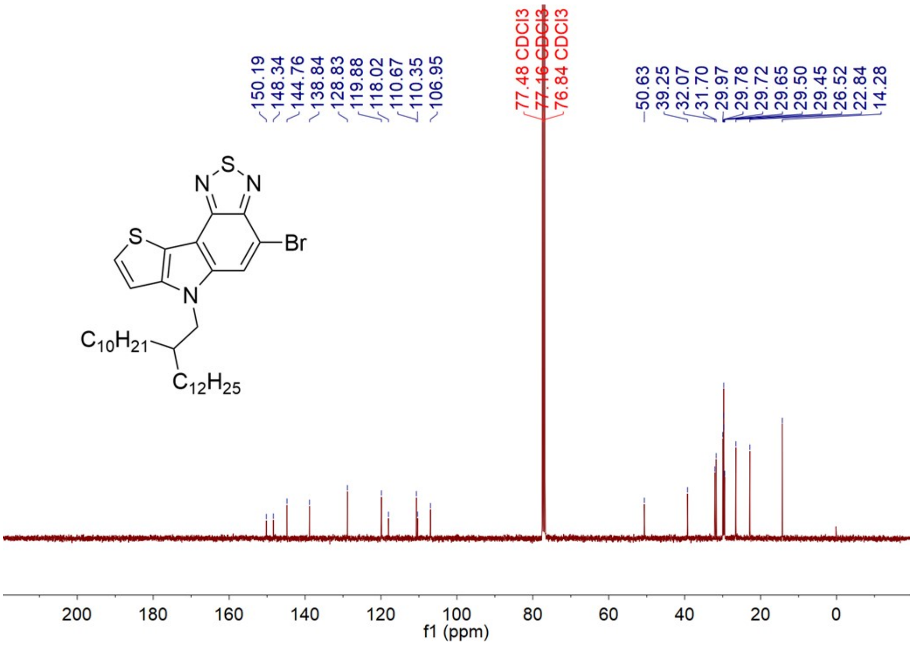


Figure S6. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

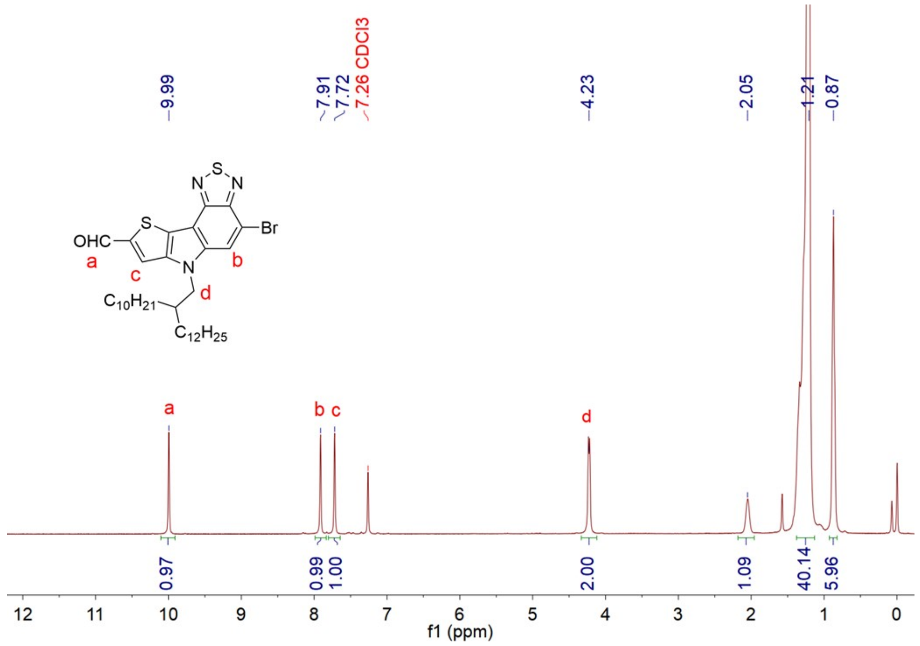


Figure S7. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

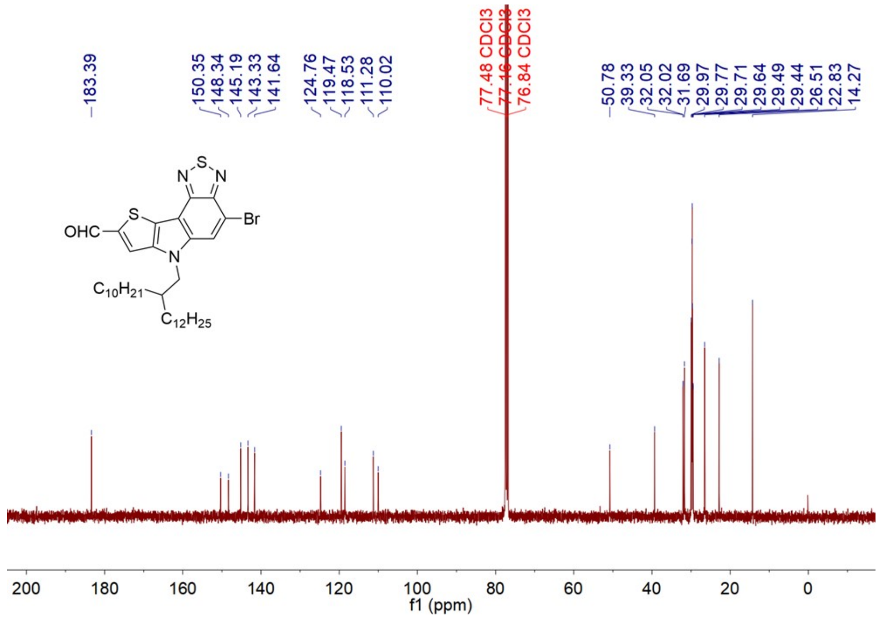


Figure S8. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

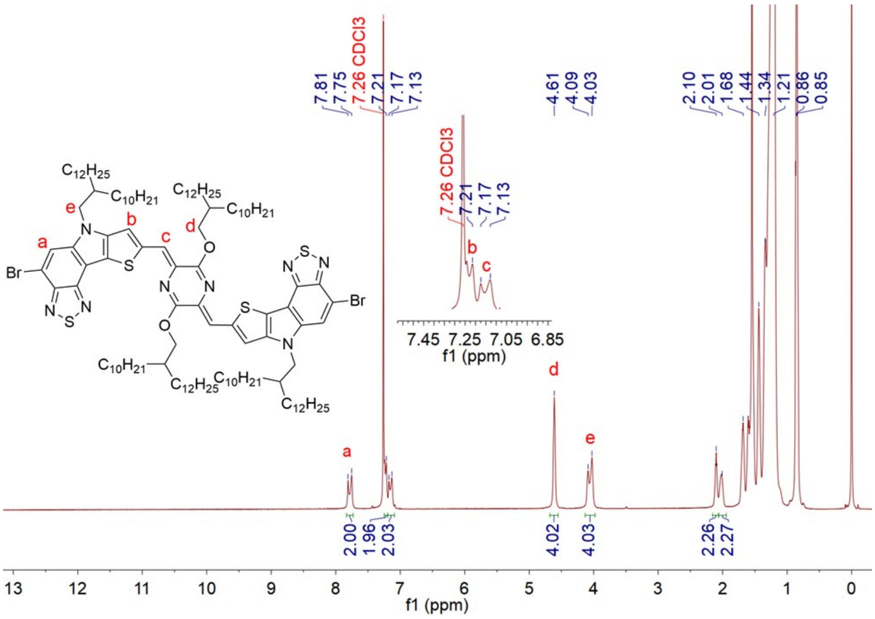


Figure S9. ^{1}H NMR spectrum of the monomer **M** in $\mathrm{CDCl_3}$.

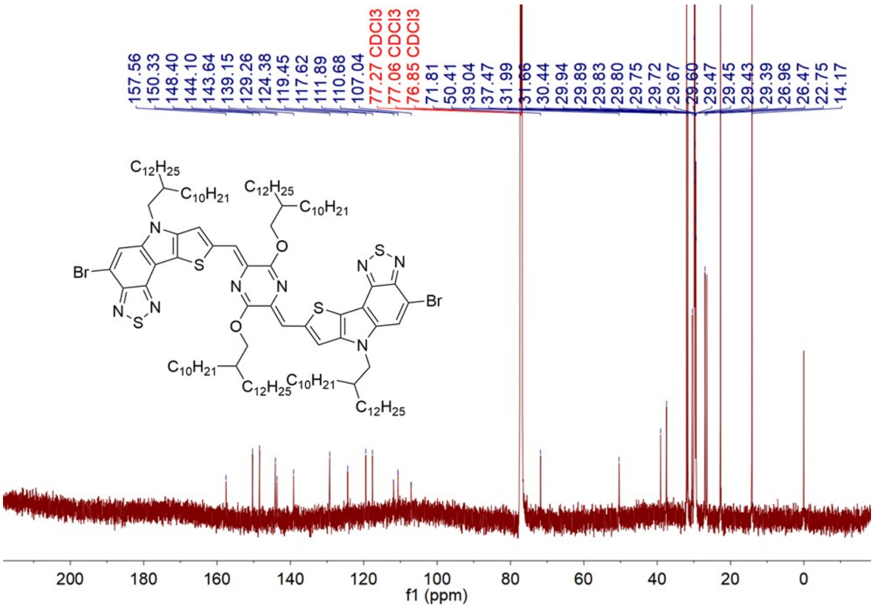


Figure S10. ^{1}H NMR spectrum of the monomer **M** in $\mathrm{CDCl_3}$.

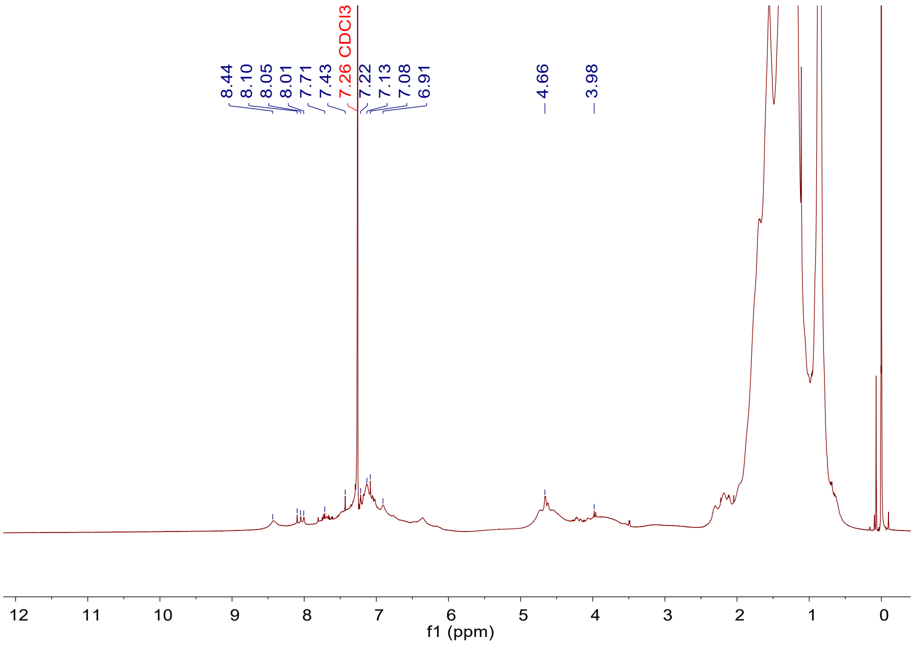


Figure S11. ^{1}H NMR spectrum of **PQ-1** in $CDCl_3$.

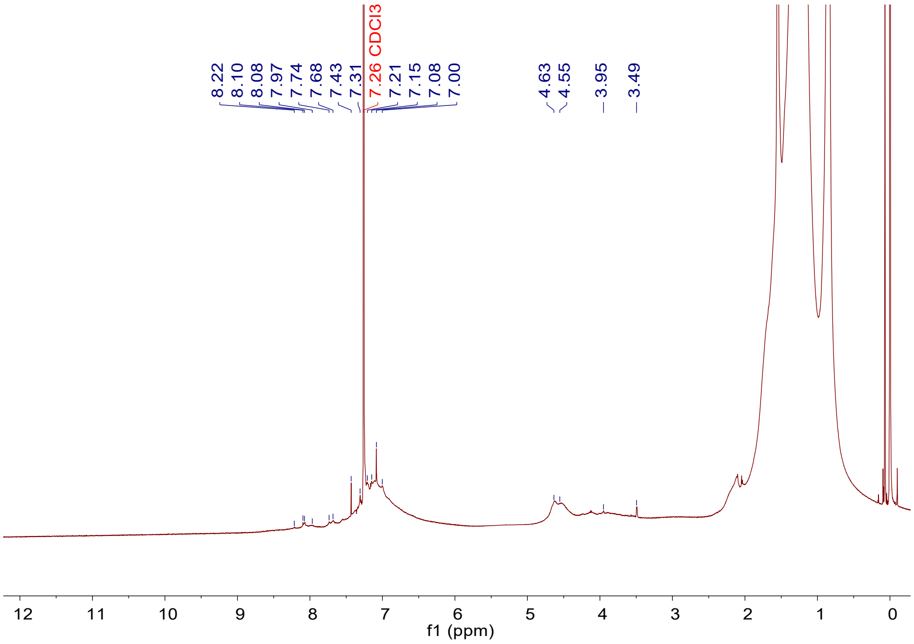


Figure S12. ^{1}H NMR spectrum of **PQ-2** in $CDCl_3$.

3.4. GPC test results of the polymers

Workbook Details

Eluent: TCB stabilised with 0.0125% BHT

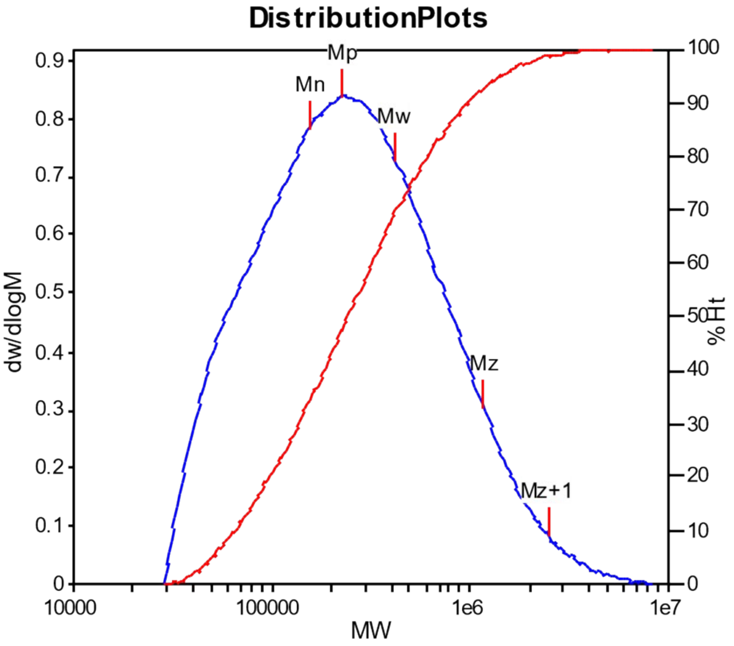
Column Set: PLgel MIXED-B LS 300x7.5mm X 2

Detector:

Flow Rate: 1.00 ml/min

Temperature: 150

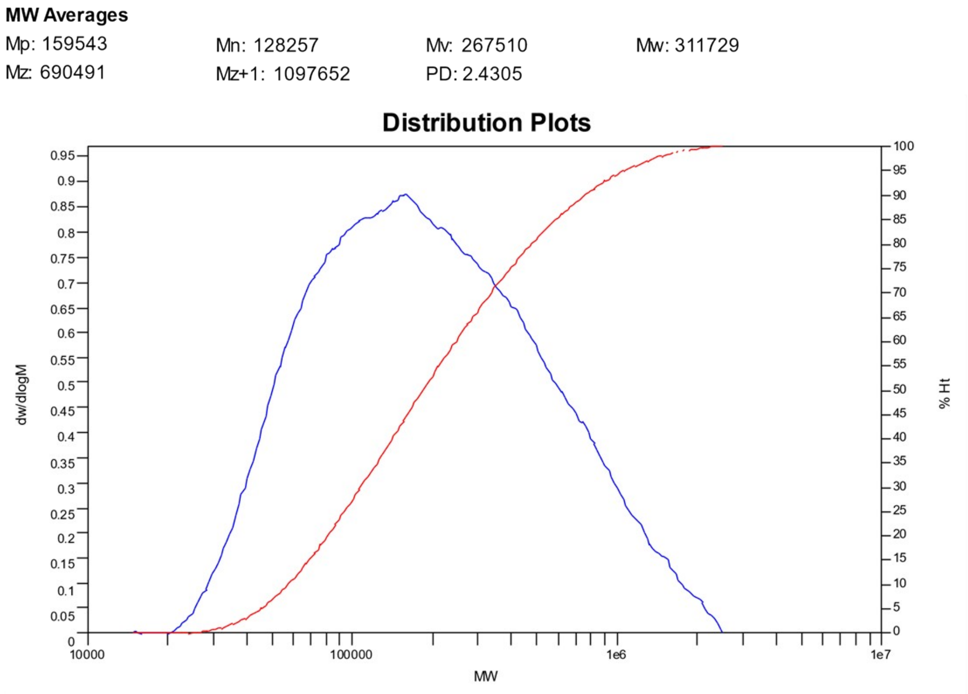
Injection Volume: 200.0 ul



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	226379	155740	426466	1182620	2469905	356025	2.73832

Figure S13. GPC test result of the polymer **PQ-1** (TCB as eluent, 150 ^{o}C).



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MW Averages
Mp: 159543          Mn: 128257          Mv: 267510          Mw: 311729
Mz: 690491          Mz+1: 1097652       PD: 2.4305
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Figure S14. GPC test result of the polymer **PQ-2** (TCB as eluent, 150 °C).

3.5. TGA and DSC plots of the polymers

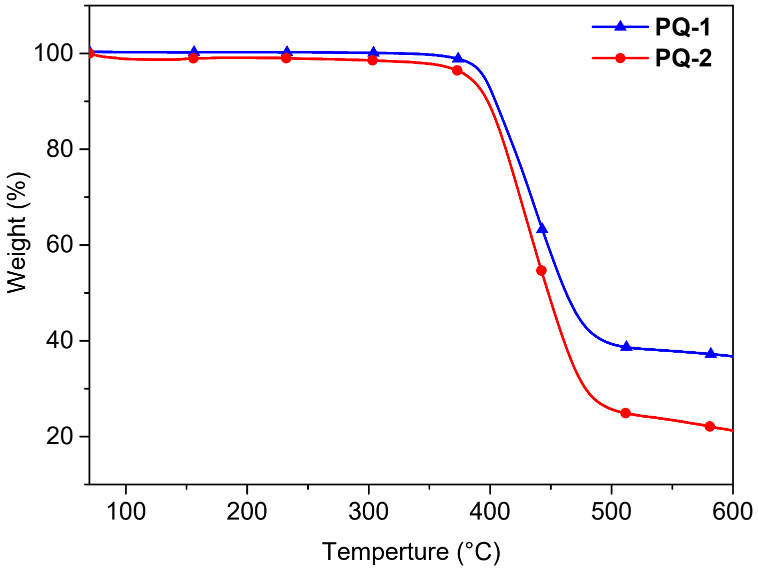


Figure S15. TGA plots of the polymers **PQ-1** and **PQ-2**.

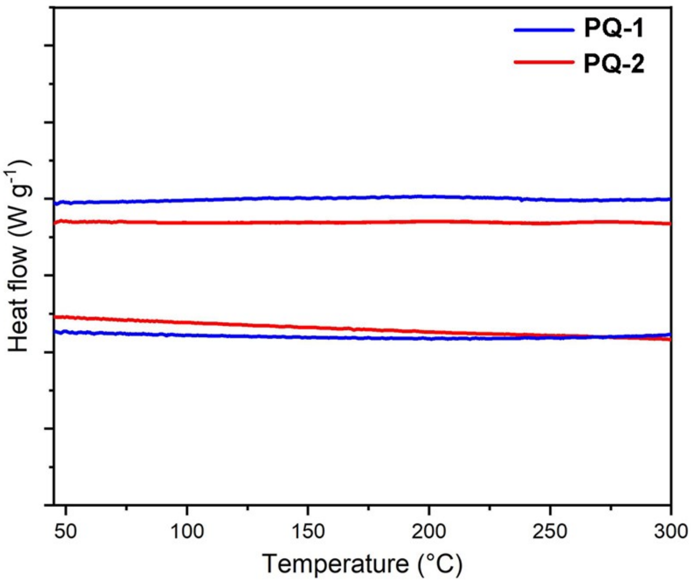
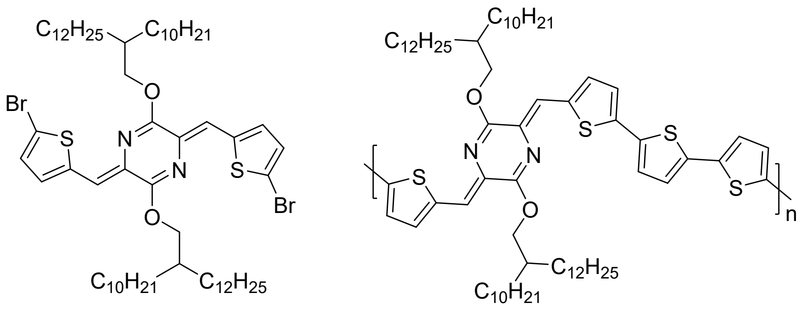


Figure S16. DSC plots of the polymers **PQ-1** and **PQ-2**.

3.6. Molecular structures of reference materials



M-ref **PQ-ref**

Figure S17. Molecular structures of the **M-ref** and **PQ-ref**.

3.7. UV-vis absorption spectra of the reference molecule M-ref

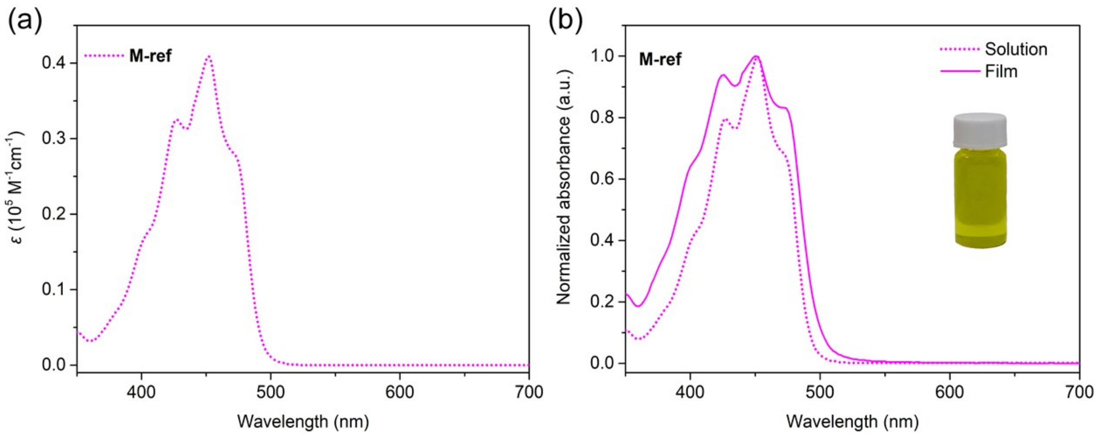


Figure S18. (a) UV-vis absorption spectra of **M-ref** in chlorobenzene solution; (b) Normalized UV-vis absorption spectra of **M-ref** in chlorobenzene solution and as thin film.

3.8. DFT calculations of model molecules

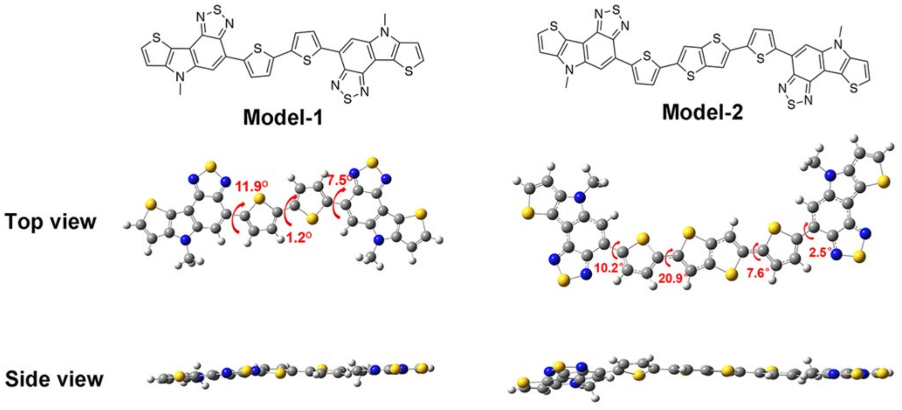


Figure S19. Optimized molecular structures of model molecules Model-1 and Model-2.

4. Device fabrication and characterization

OFET devices were fabricated in a staggered bottom-gate, top-contact configuration. The polymer samples were dissolved in chloroform or chlorobenzene at the concentration of 5 mg/mL. The channel semiconductor layers were deposited by spin coating. Thermally deposited (~40 nm) gold with fixed channel length of 80 μm and channel width of 1500 μm was used as source/drain electrode. The field-effect characterizations were conducted at room temperature in ambient conditions using a Keithley 2636B two channel Source/Meter. The field-effect mobility in the saturation regime was extracted from the $|I_{DS}|^{1/2}$ vs V_G plot.

5. References

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