Supplementary Information (SI) for Materials Chemistry Frontiers.

Polymeric mixed ionic-electronic conductors based on quinoid–azaisoindigo for n-type organic electrochemical transistors

Juntao Tan [+a], Yiming Wang [+ab], Xiuyuan Zhu [ab], Jiayao Duan [ab], Riping Liu [ab], Chaoyue Chen [ab], Chong Ran [a], Zhengke Li* [a], Bin Ai* [a], Wan Yue* [ab]

School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, People's Republic of China

State Key Laboratory of Optoelectronic Materials and Technologies, Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, People's Republic of China

Supplementary Information

Table of Contents

1. **UV-vis-NIR absorption of Compounds**
2. **CV of Compounds**
3. **DFT calculations of compounds**
4. **TGA of Compounds**
5. **DSC of Compounds**
6. **AFM images of polymers**
7. **Electrochemical transistors characterization**
8. **The Details of the GIWAXs Study**
9. **Material synthesis and characterization**
10. **References**

Materials and Methods

All of the starting materials were purchased from commercial suppliers and used as received, unless otherwise specified. The intermediates and monomers were purified by column chromatography using silica gel (General-Regent, 300-400 mesh). ^{1}H NMR and ^{13}C NMR was conducted in chloroform-d or 1, 1, 2, 2-tetrachloroethane-d2 (TCE-D2) with a 400 HMZ Bruker Avance III spectrometer. The molecular weight was calculated by Matrix-assisted Laser Desorption/ionization time-of-flight (MALDI-TOF) mass spectra (matrix is trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)), using a Bruker Daltonik (solariX) mass spectrometer. The number-average molecular weights (Mn) were determined using a PL-GPC 220 in hexafluoroisopropanol at 40 °C using a calibration curve with standard linear polystyrene as a reference.

UV-vis absorption spectra were measured by an Agilent Technologies Cary 5000/6000i spectrophotometer. Thin films were prepared by spin-coating on ITO glass substrates from a hexafluoroisopropanol solution (6 mg mL^{-1}) under ambient conditions.

Cyclic voltammetry was performed employing a CHI760E electrochemical workstation (Shanghai Chenhua Instrument co., Ltd.) with a standard three-electrode configuration, including polymers coated ITO as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The potential of the Ag/AgCl reference electrode was internally calibrated against ferrocene. The supporting electrolyte was either a deoxygenated dichloromethane containing 0.1 M n-Bu_4NPF_6 or 0.1 M NaCl aqueous solution.

Spectroelectrochemical measurements were conducted by fitting the CV setup inside a quartz cuvette in the UV-vis absorption spectrophotometer. The polymers were spin-casted ITO-coated glass from a solution (6 mg mL^{-1}) of hexafluoroisopropanol. Then potentials were applied for 30 s before recording the UV-vis absorption spectrum at each voltage to ensure stabilization of the optical trace. UV-vis spectra were continuously recorded within a potential range from 0.0 V to -0.7 V with potential interval of 0.1 V. All spectroelectrochemical measurements were performed using a 0.1 M NaCl solution as the supporting electrolyte.

Thermogravimetric analysis (TGA) was conducted on a Netzsch STA 449F3 apparatus. Samples placed into small ceramic crucibles were heated under nitrogen atmosphere from 25 to 800°C at a heating rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) was conducted on a TA Instruments Discovery 250 equipped with a RCS40 refrigerated cooling system. DSC traces of each material were recorded across a temperature range of 28 to 280°C while heating at 10 °C min^{-1}.

Electrochemical impedance spectroscopy (EIS) was performed using a three-terminal set-up same as CV measurement, employing polymers coated gold electrodes (the area of 0.2 cm^2) as the working electrode, a Pt foil as the counter electrode and an Ag/AgCl electrode as the reference electrode. A sinusoidal AC amplitude of 10 mV and a frequency range between 10 kHz to 0.1 Hz was chosen. Fitting the EIS spectrums by using the Randles circuit Rs(Rp//C) in ZSimDemo software were to extract capacitance.

The gold patterned electrodes were immersed in a 5 mM ethanolic solution of 4-methoxythiophenol molecules overnight for functionalization, followed by gently rinsing several times with ethanol and dried with nitrogen. Solutions of the polymers (concentration = 6 mg mL^{-1}) in hexafluoroisopropanol were spin-coated on the cleaned substrates (500 rpm for 5 s and 1000 rpm for 30 s). Film thicknesses were measured by atomic force microscopy. OECTs were gated with 0.1 M NaCl aqueous solution using an Ag/AgCl pellet as the gate electrode. Electrical characterization of the OECTs was performed at room temperature using a semiconductor parameter analyzer (Keysight B1500A) and an electrical probe station.

GIWAXS characterization. Samples for X-ray scattering were prepared using the same procedures for the preparation of active channel layer in device fabrication except using pure silicon wafers as the substrates. An incidence angle of 0.18° and a photon energy of 8 keV were used to record the scattering patterns. The 2D GIWAXS patterns were collected from films with resistivity of 0.001-30 Ohm cm^{-1}.

AFM measurements. Atomic force microscopy measurements were performed in tapping mode, using Bruker dimension icon AFM with a silicon tip. The polymer films were spin-coated on ITO substrates from hexafluoroisopropanol solution (6 mg ml^{-1}) under ambient conditions.

1. UV-vis-NIR absorption of Compounds

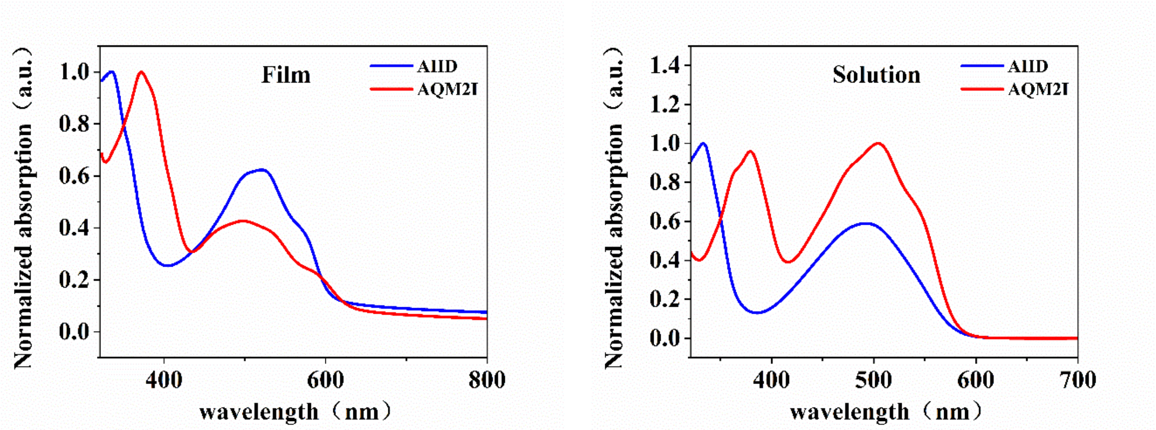


Figure S1. UV-vis-NIR absorption spectra of AIID and AQM2I in dichloromethane solution (~10^{-5} M) and thin film spin-cast from dichloromethane solution (10 mg ml^{-1}).

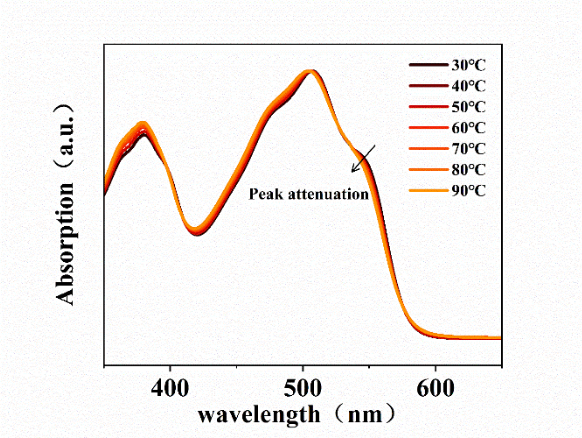


Figure S2. UV-vis-NIR absorption spectra of AQM2I at different temperature gradients in chlorobenzene solution (~10^{-5} M)

2. CV of Compounds

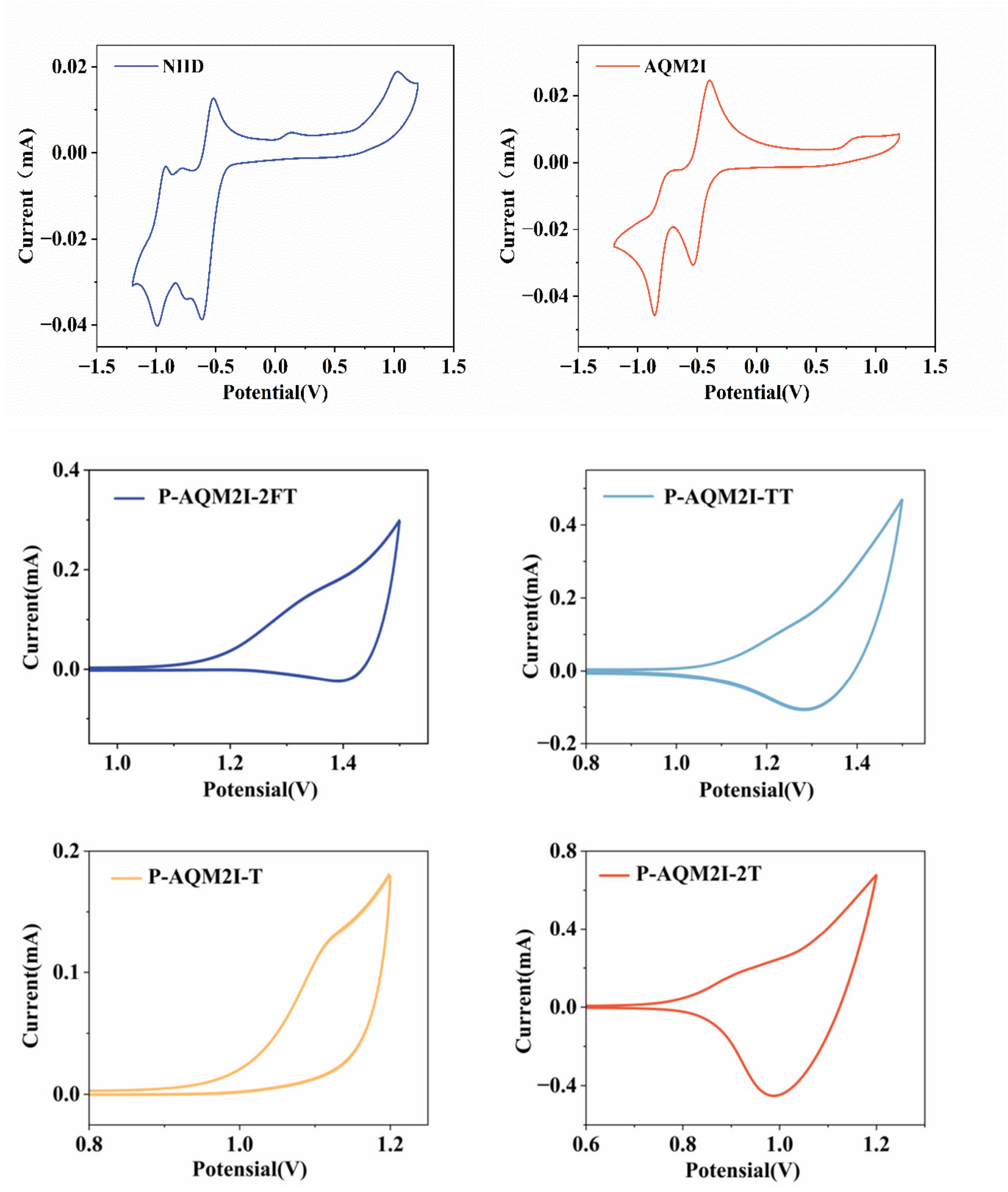


Figure S3. Cyclic voltammetry curves of **AIID** and **AQM2I** in dichloromethane solution (approximately 1 mg ml^{-1}) with 0.1 M n-Bu$_4$NPF$_6$ and P-AQM2I-2FT, P-AQM2I-TT, P-AQM2I-T, P-AQM2I-2T in chloroform solution with 0.1 M n-Bu$_4$NPF$_6$ as supporting electrolyte at a scan rate of 0.1 V s^{-1}. The potential of Ag/AgCl reference electrode was internally calibrated against the ferrocene/ferrocenium redox couple.

3. DFT calculations of compounds

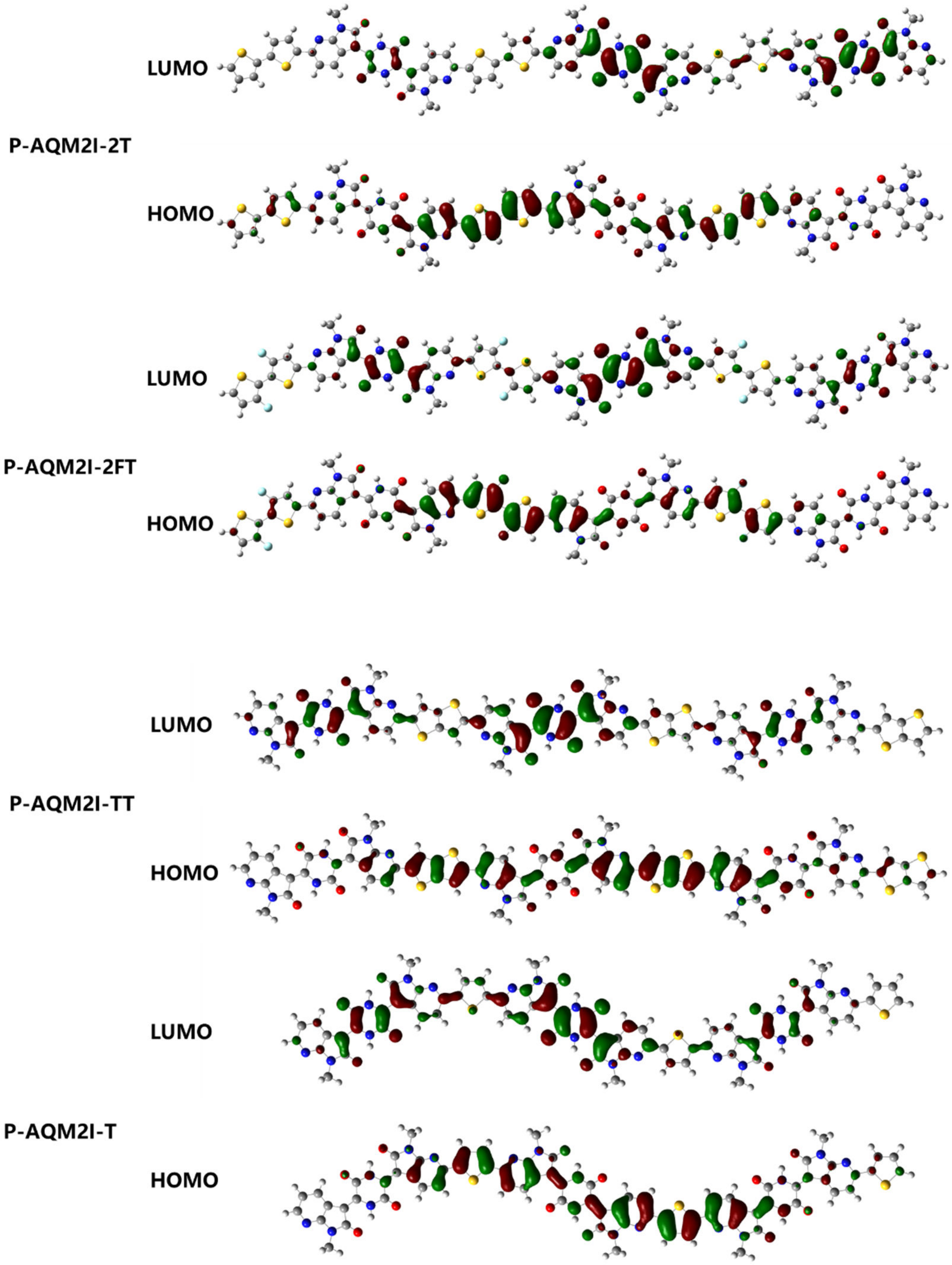


Figure S4. Molecular frontier orbitals (HOMO and LUMO) of **P-AQM2I-2FT, P-AQM2I-TT, P-AQM2I-T** and **P-AQM2I-2T**, obtained from TD-rb3lyp/6-31G* calculation (side chains are replaced by methyl groups) .

4. TGA of Compounds

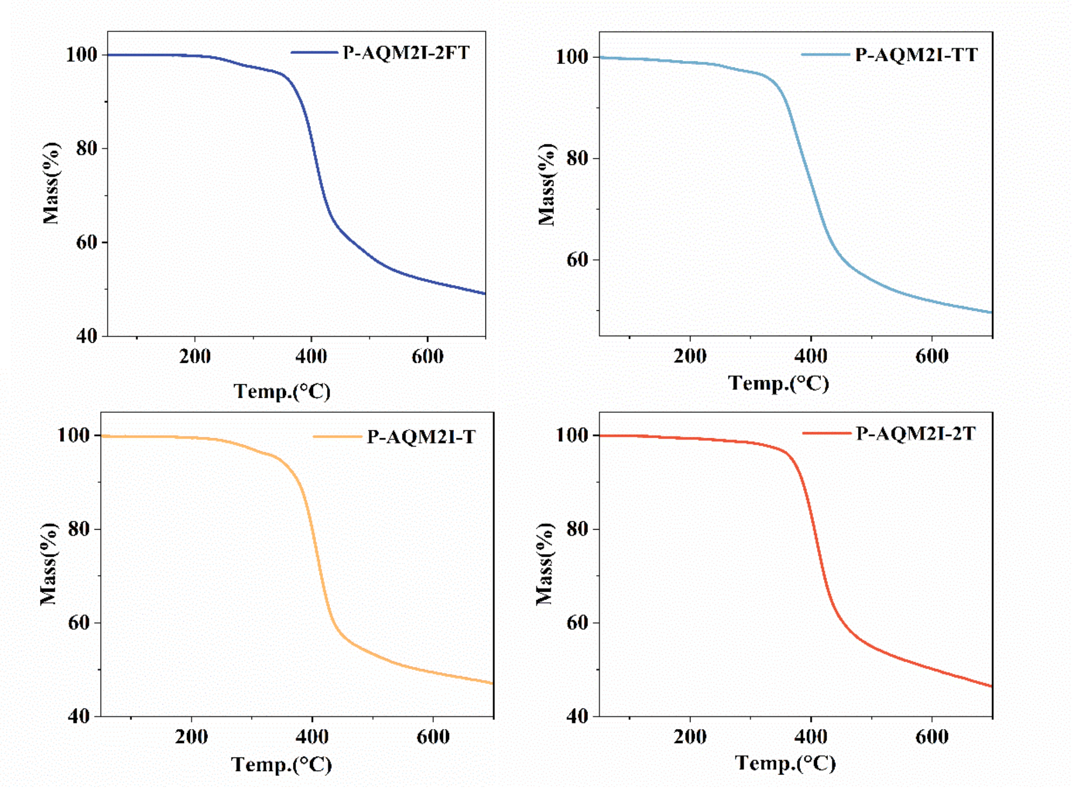


Figure S5. TGA of **P-AQM2I-2FT, P-AQM2I-TT, P-AQM2I-T** and **P-AQM2I-2T** measured at a rate of 10 °C min^{-1} in nitrogen.

5. DSC of Compounds

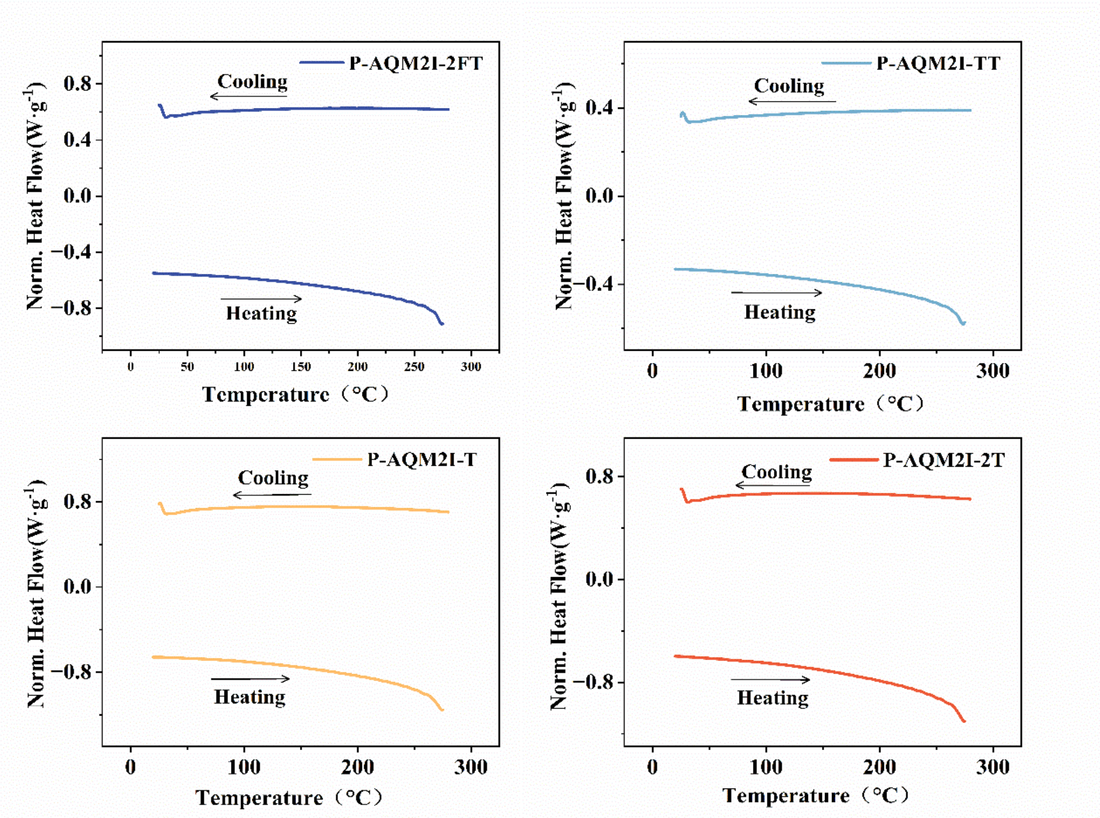


Figure S6. The second heating and cooling cycle of **P-AQM2I-2FT, P-AQM2I-TT, P-AQM2I-T** and **P-AQM2I-2T** in DSC measurement at a heating rate of 10 °C min^{-1} under nitrogen.

6. AFM Images of polymers

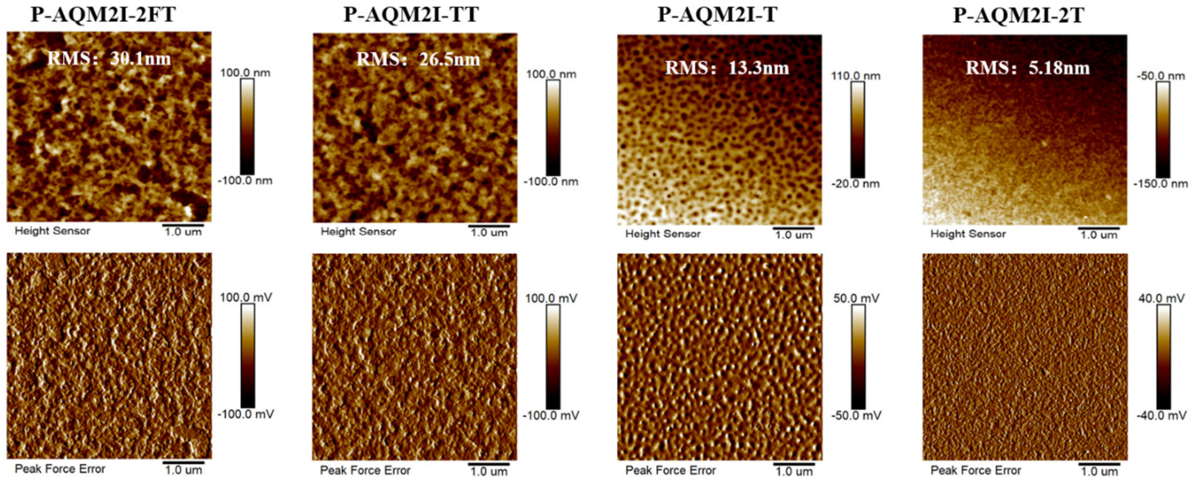


Figure S7. AFM images (5 × 5 μm) of **P-AQM2I-2FT, P-AQM2I-TT, P-AQM2I-T** and **P-AQM2I-2T**.

7. Electrochemical Transistors Characterization

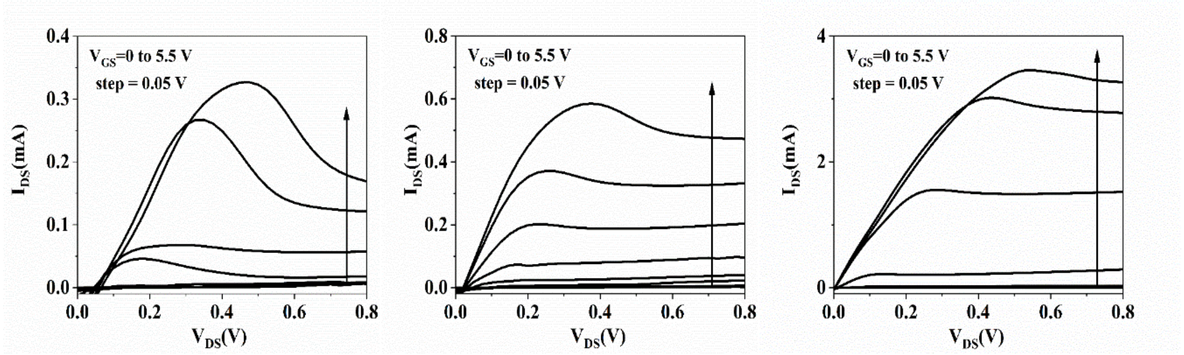


Figure S8. Output curves of OECTs based on **P-AQM2I-2T, P-AQM2I-TT** and **P-AQM2I-2T**.

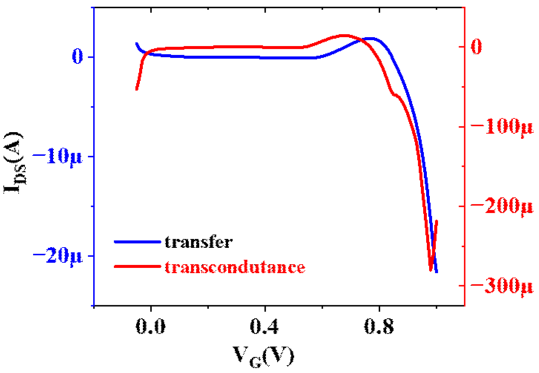


Figure S9. Transfer and normalized transconductance curves of OECTs based on P-AQM2I-2T with a V_{DS} of 0.3 V after annealing at 100 ° C for 10 min.

8. The Details of the GIWAXs Study

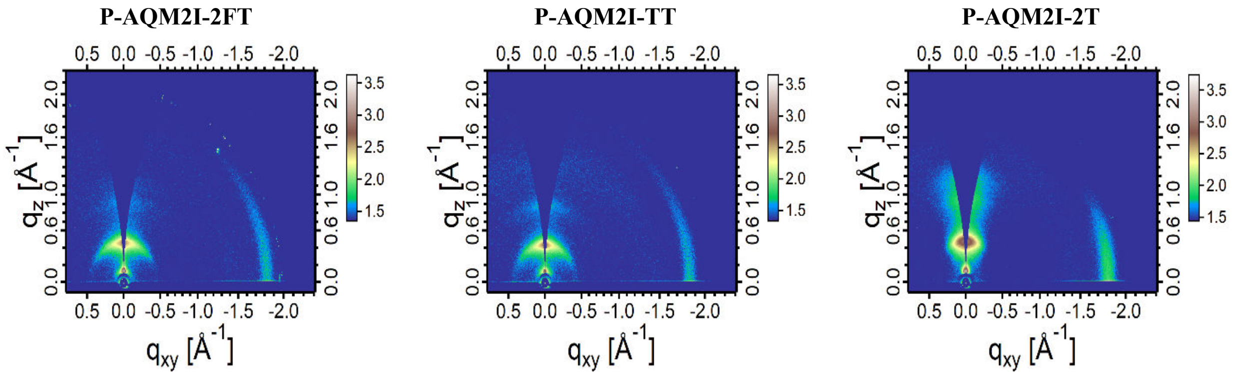


Figure S10. 2D GIWAXs images of **P-AQM2I-2FT**, **P-AQM2I-TT** and **P-AQM2I-2T** thin film

Table S1. Solid states packing parameters of **P-AQM2I-2FT**, **P-AQM2I-TT** and **P-AQM2I-2T** in the out-of-plane (OOP) direction.

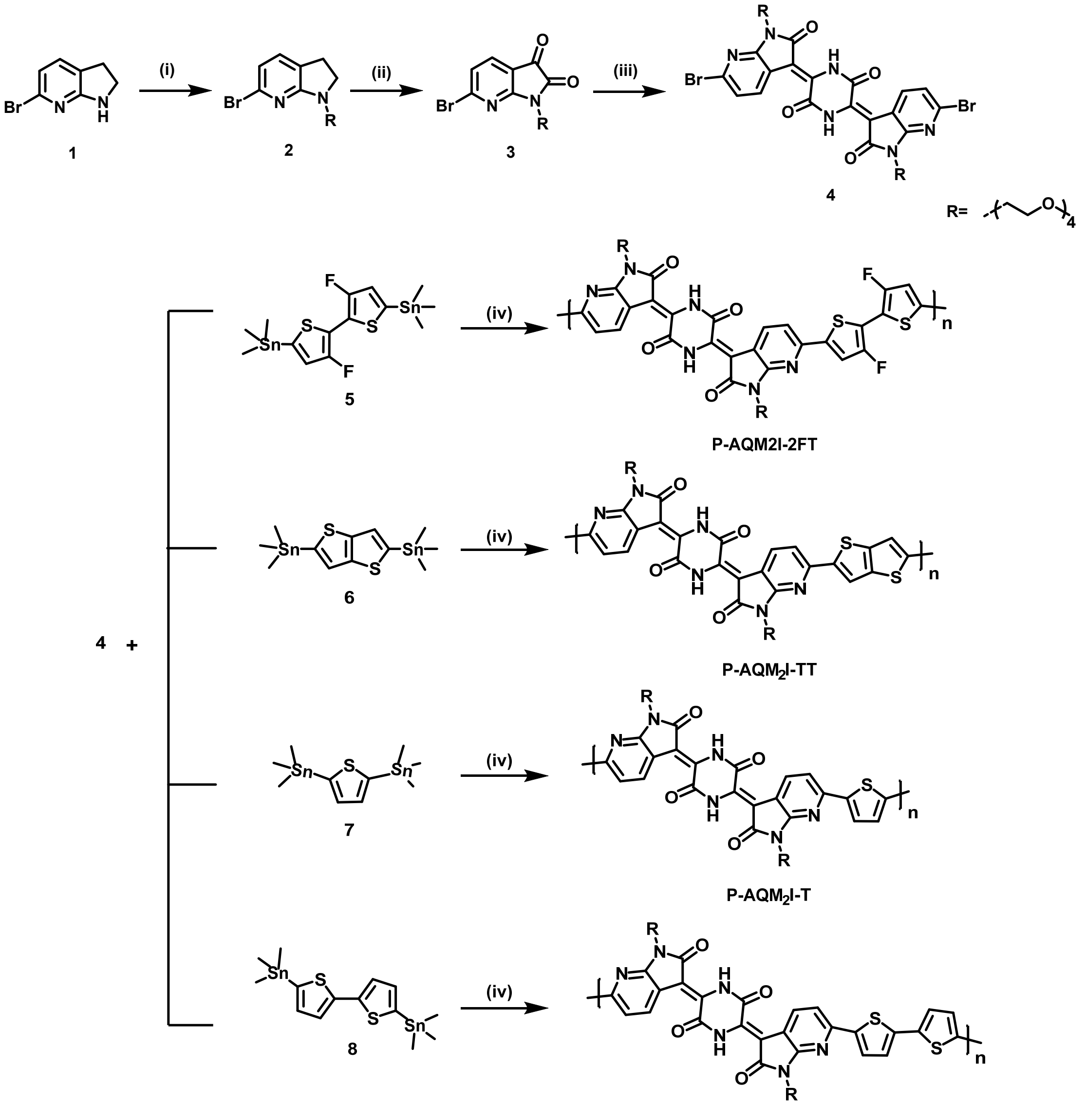
	Material	**P-AQM2I-2FT**	**P-AQM2I-TT**	**P-AQM2I-2T**
Lamellar packing (100)	q ($Å^{-1}$)	0.457	0.432	0.473
	d-spacing (Å)	13.748	14.544	13.284
	FWHM ($Å^{-1}$)	0.1015	0.0931	0.1259
	Correlation length (Å)	55.7	60.7	44.9
Lamellar packing (200)	q ($Å^{-1}$)	0.906	0.873	0.935
	d-spacing (Å)	6.9	7.2	6.7

Table S2. Solid states packing parameters of **P-AQM2I-2FT, P-AQM2I-TT and P-AQM2I-2T** in the in-plane (IP) direction.

	Material	**P-AQM2I-2FT**	**P-AQM2I-TT**	**P-AQM2I-2T**
π-π stack (010)	q ($Å^{-1}$)	1.825	1.836	1.812
	d-spacing (Å)	3.44	3.42	3.47
	FWHM ($Å^{-1}$)	0.1603	0.1269	0.1567
	Correlation length (Å)	35.3	44.6	36.1

9. Materials Synthesis and Characterization

Compound 1, 5, 6, 7 and **8** is commercially available. **compound 2-4** were synthesized according to the literature. [1,2]



Scheme S1. Synthetic route for copolymers. (i) R-OTs, NaH, DMF, r.t.; (ii) CrO_3, HAc, H_2O, r.t.; (iii) 1,4-diacetylpiperazine-2,5-dione, $CHCl_3$, DMF, TEA, 45 ℃ ; (iv) $Pd_2(dba)_3$, $P(o\text{-}Meph)_3$, toluene, 110℃.

Compound 2

6-bromo-1H-pyrrolo[2,3-b]pyridine **1** (552 mg, 2.8 mmol, 1.0 equiv.), 3,6,9,12-Tetraoxatridecan-1-ol, 1-(4-methylbenzenesulfonate）(1.0 g, 2.8 mmol，1.0 equiv.) and sodium hydride (60% dispersion in mineral oil, 145 mg, 6 mmol, 2.1 equiv.) were mixed under N_2 atmosphere in a two-necked round bottom flask under magnetic stirring. DMF (15.0 mL) was added and left to react at room temperature overnight. DMF was removed under vacuum. The crude product was purified by silica gel column chromatography using dichloromethane as the eluent to give compound **2** as a colorless liquid（683 mg, 63 % yield). ^{1}H NMR (500 MHz, TCE-D_2, 393 K), δ (ppm): 7.70 (d, J = 8.1Hz 1H), 7.33 (d, J = 3.5 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 6.38 (d, J = 3.5 Hz, 1H), 4.14 (t, 2H), 3.79 (t, 2H), 3.55-3.62 (m, 10H), 3.49-3.52 (m, 2H), 3.38 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 146.90, 134.23, 130.70, 129.49, 119.25, 119.12, 99.62, 77.48, 77.27, 77.05, 71.88, 70.55, 70.44, 70.12, 58.93, 44.28. Calculated for $C_{16}H_{23}BrN_2O_4$: 386.0841, $[M+H]^+$, found: 387.0914.

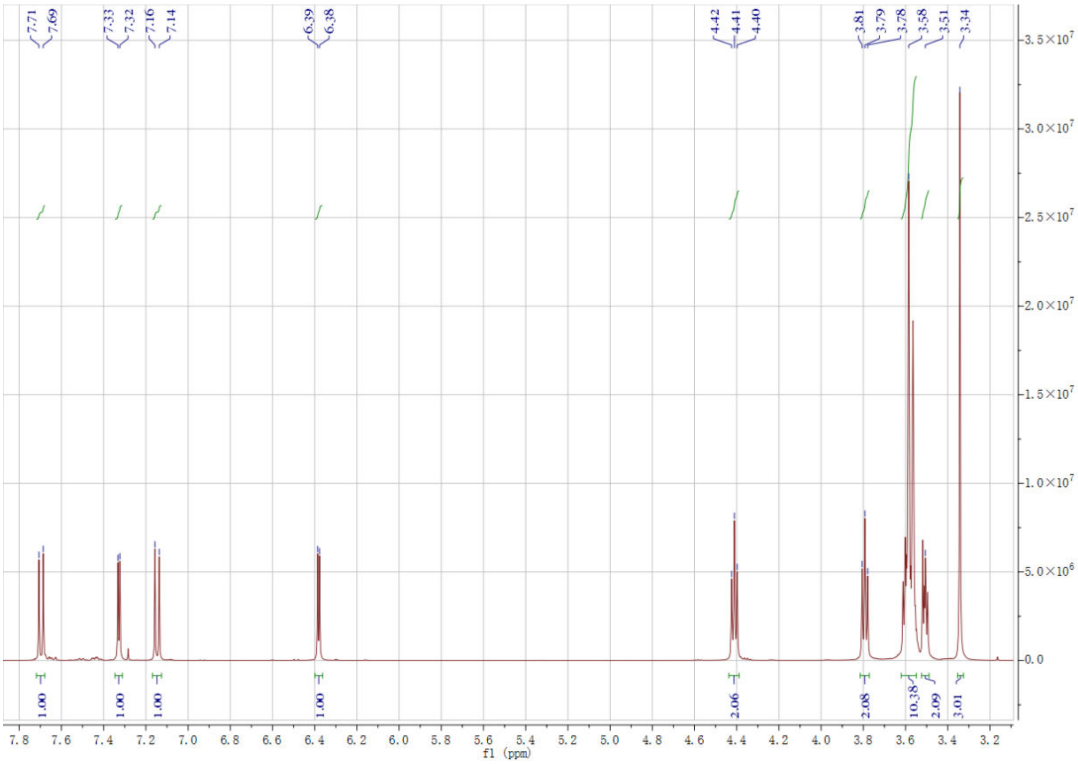


Figure S11. ^{1}H NMR of compound **2**.

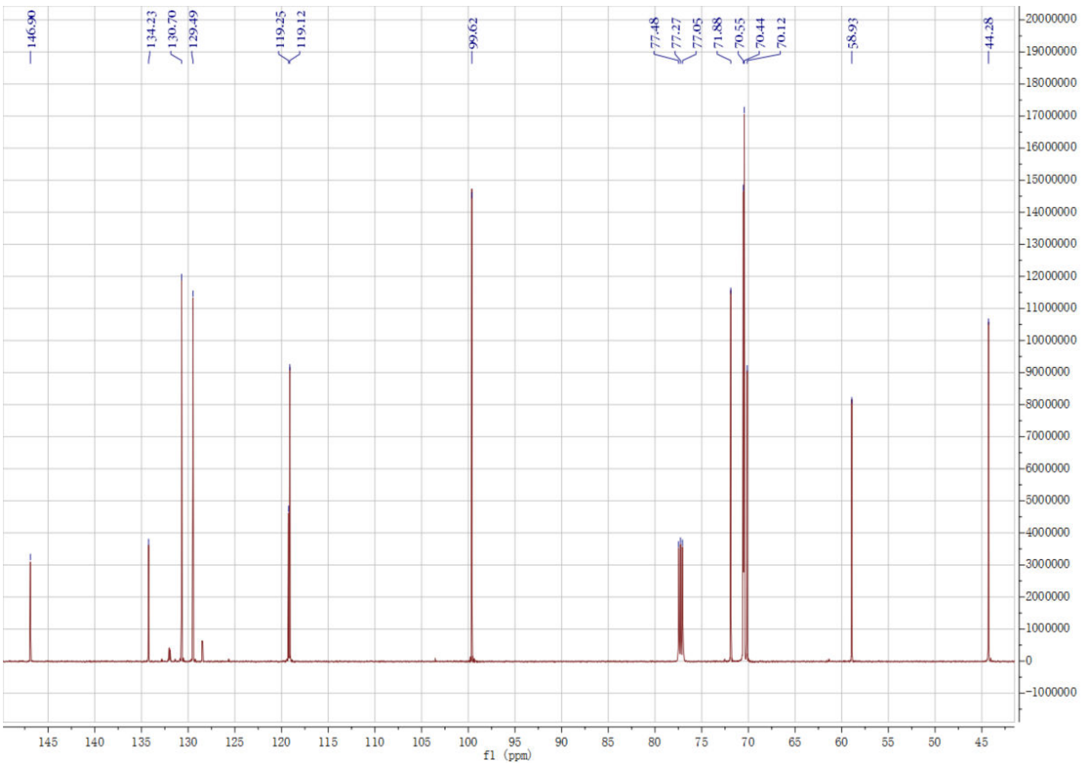


Figure S12. ^{13}C NMR of compound **2**.

Compoud 3

Chromium trioxide (0.9 g, 9.1 mmol, 2.5 equiv.) was dissolved in 3.0 mL water and was added to a two-necked round bottom flask containing a solution of compound **2** (1.51 g, 0.39 mmol, 1.0 equiv.) in 40 mL of glacial acetic acid at room temperature for 4 h. The product was extracted with dichloromethane, and the organic phase was collected and dried with magnesium sulphate for 5 min. Then, the solvent was removed by reduced pressure and the crude product was purified by column chromatography eluting with dichloromethane: ethyl acetate (2:1) to afford a bright yellow solid **3** (1.22 g, 75 % yield). ^{1}H NMR (500 MHz, TCE-D_2, 393 K), δ (ppm): 7.65 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 4.06 (t, 2H), 3.84 (t, 2H), 3.52-3.70 (m, 12H), 3.38 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 180.55, 163.89, 158.21, 149.77, 134.09, 123.35, 110.46, 77.38, 77.17, 76.95, 71.83, 70.45, 69.98, 66.85, 58.90, 38.65. Calculated for $C_{16}H_{21}BrN_2O_6$: 416.0583, $[M+H]^+$, found: 417.0656.

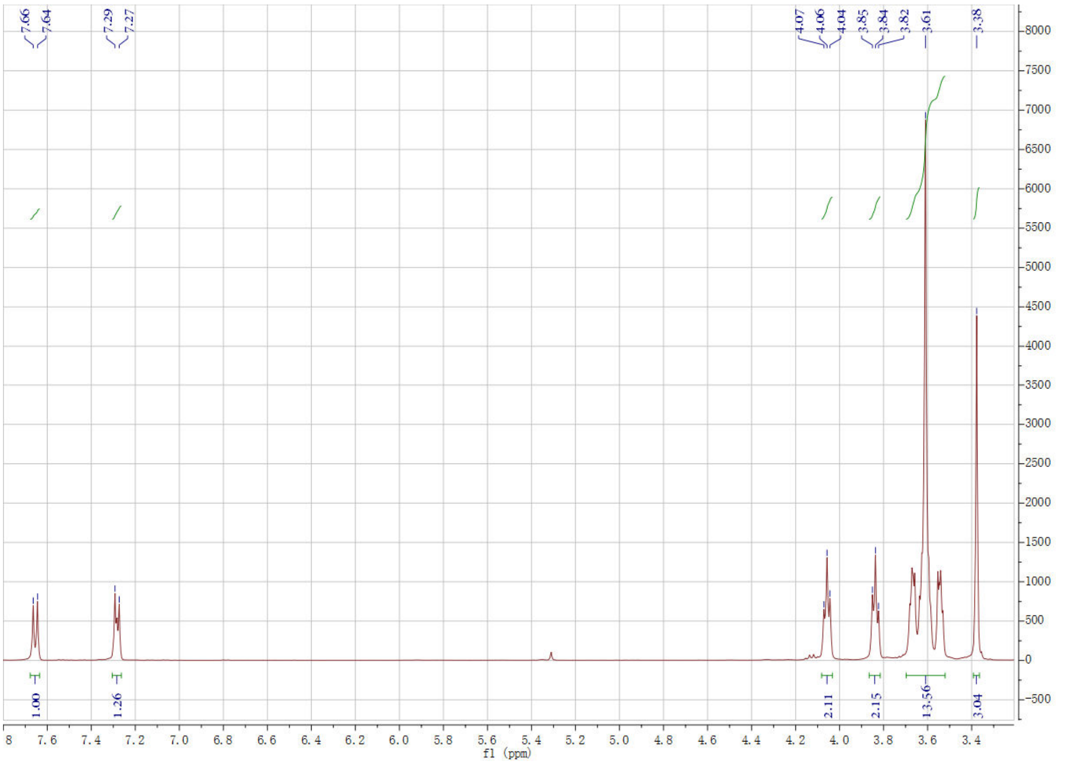


Figure S13. ^{1}H NMR of compound **3**.

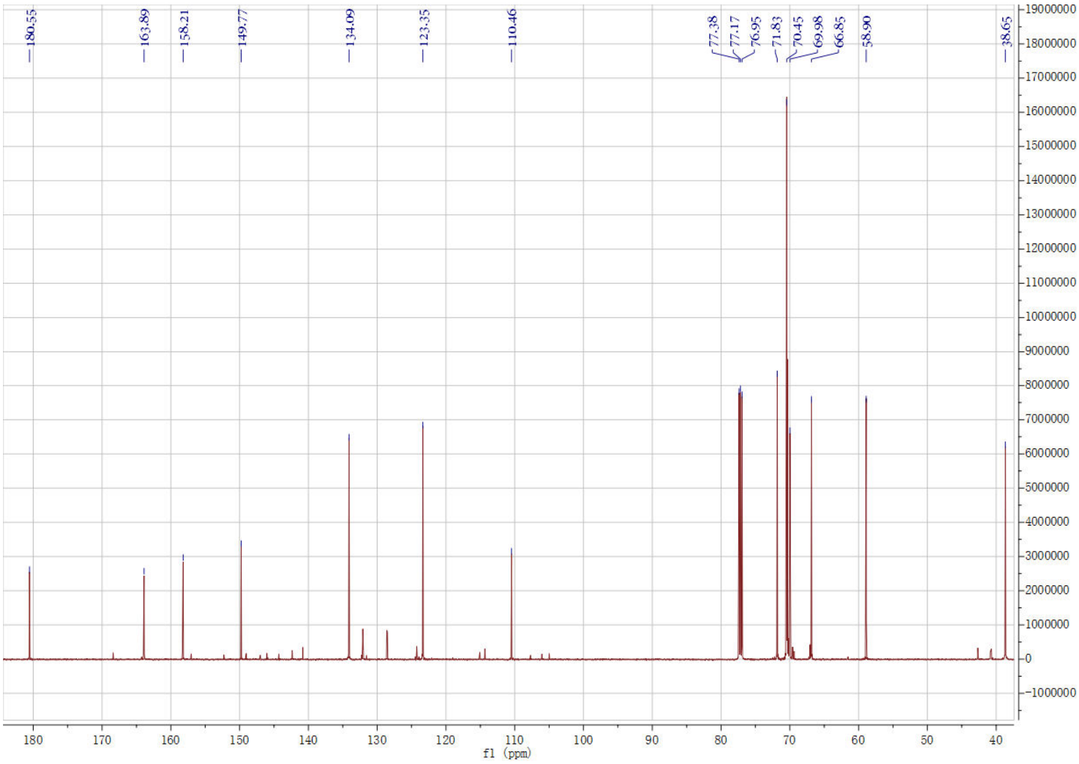


Figure S14. ^{13}C NMR of compound **3**.

Compound 4

Into a mixture of 1,4-diacetylpiperazine-2,5-dione (198 mg, 1.0 mmol, 1.0 equiv.) and compound **3** (1.04 g, 2.5 mmol, 2.5 equiv.) in DMF (20 mL) and chloroform (10 mL) was syringe injected triethylamine (4 mmol, 4 equiv.) at 45°C under N_2 sphere for 3h. Upon addition, the original colorless solution turned red immediately. After cooling to room temperature, the solvent was removed by reduced pressure and the crude product was purified by column chromatography eluting with dichloromethane: ethyl acetate (1:1) to afford a deep red solid **4** (546 mg, 60 % yield). ^{1}H NMR (500 MHz, TCE-D_2, 393 K), δ (ppm): 13.12 (s, 1H), 8.90 (d, J = 8.2Hz, 1H), 7.25 (d, J = 8.2Hz, 1H), 4.16 (t, 2H), 3.87 (t, 2H), 3.52-3.72 (m, 12H), 3.38 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 169.46, 155.71, 155.12, 141.29, 137.62, 133.65, 122.43, 113.39, 108.38, 77.26, 77.05, 76.84, 71.91, 70.58, 70.47, 70.06, 67.27, 59.03. MALDI-TOF:Calculated for $C_{36}H_{44}Br_2N_6O_{12}$: 910.1384, found $[M+H]^+$: 911.1465.

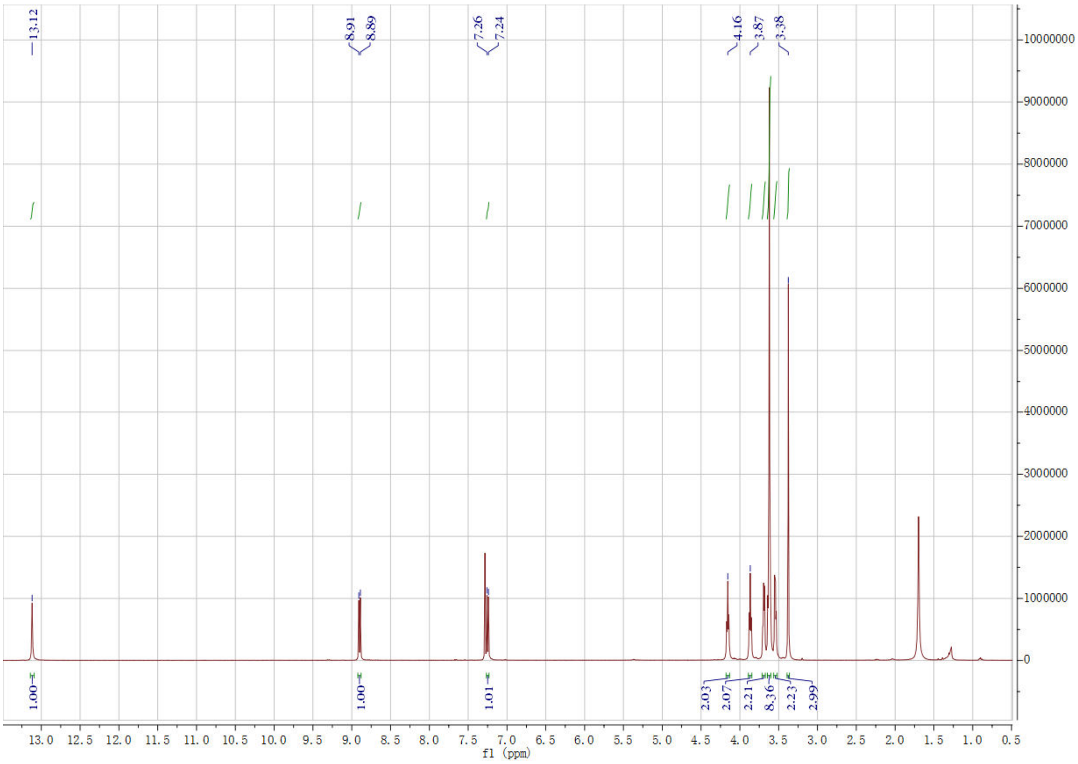


Figure S15. ^{1}H NMR of compound **4**.

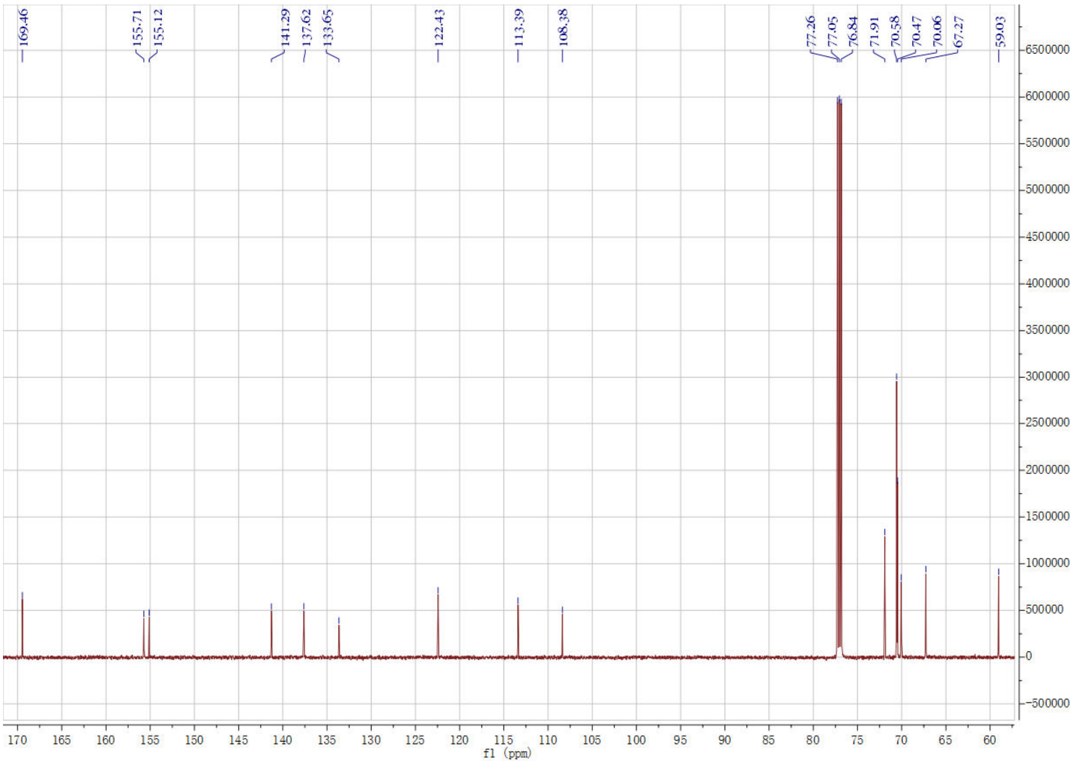


Figure S16. ^{13}C NMR of compound **4**.

General procedure for polymerization:

To a 25 mL Schlenk tube, tin reagent (1.0 equiv.), compound **4** (1.0 equiv.), $Pd_2(dba)_3$ (0.02 equiv.), P-(*o*-tol)$_3$ (0.04 equiv.), and anhydrous toluene were added under nitrogen atmosphere. The tube was charged with nitrogen through a freeze-pump-thaw cycle for three times. The sealed tube was heated to 110°C and stirred for 24 h. After cooling the reaction mixture to room temperature, the polymer was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, and chloroform. The chloroform solution was concentrated and re-precipitated into methanol. The precipitate was filtered and dried under vacuum to afford the target polymer.

P-AQM2I-2FT: Black solid (yield: 82%); GPC (HFIP, 40℃) Mn = 77.6 kDa, Mw = 85.6 Kda, PDI=1.10.

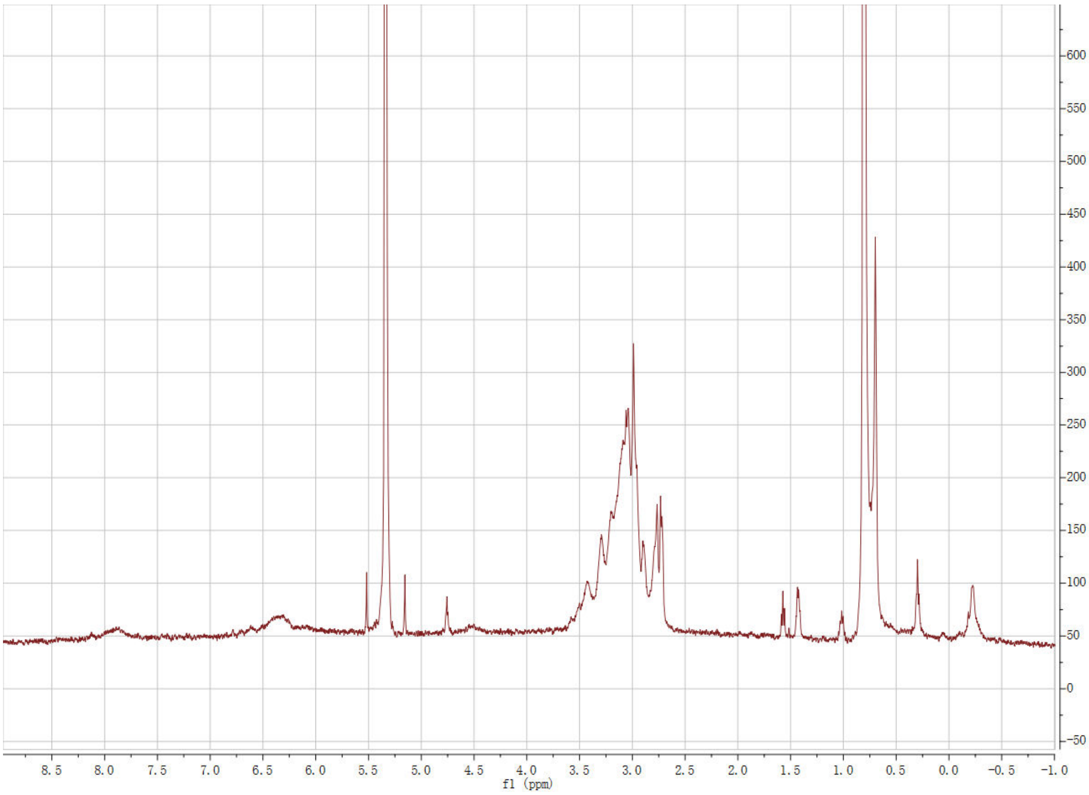


Figure S17. ^{1}H NMR of **P-AQM2I-2FT**.

P-AQM2I-TT: Black solid (yield: 76%); GPC (HFIP, 40°C) Mn = 63.2 kDa, Mw = 69.5 KDa, PDI=1.10.

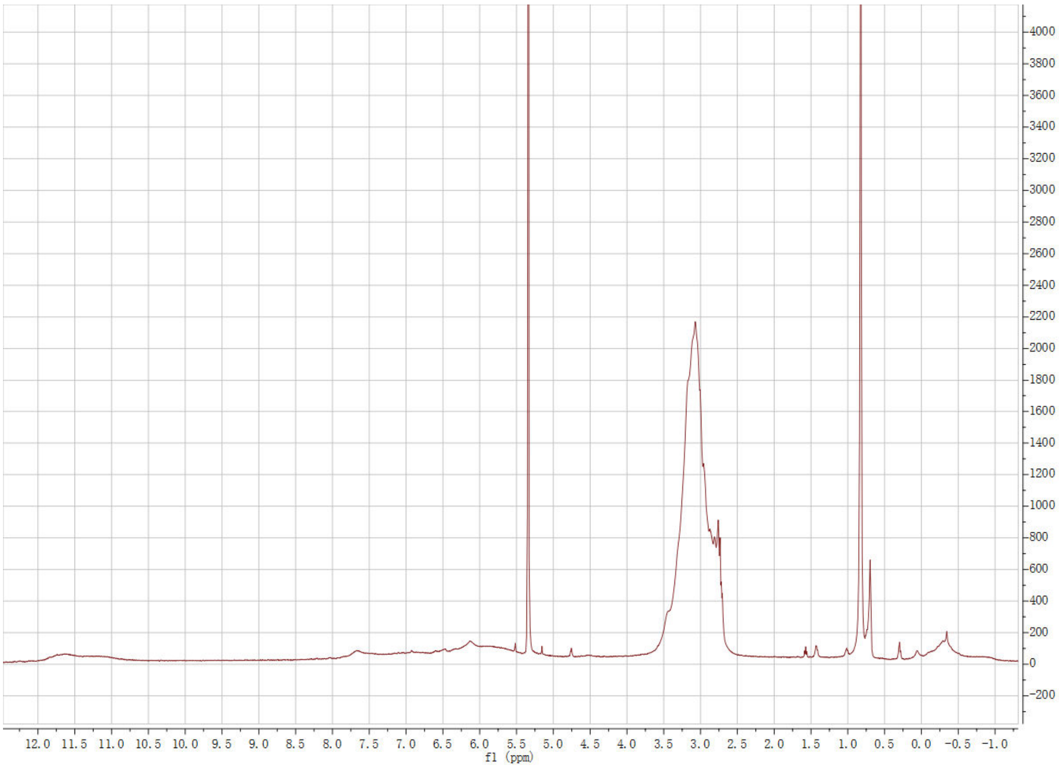


Figure S18. ^{1}H NMR of **P-AQM2I-TT**.

P-AQM2I-T: Black solid (yield: 83%); GPC (HFIP, 40°C) Mn = 60.6 kDa, Mw = 83.2 KDa, PDI=1.37.

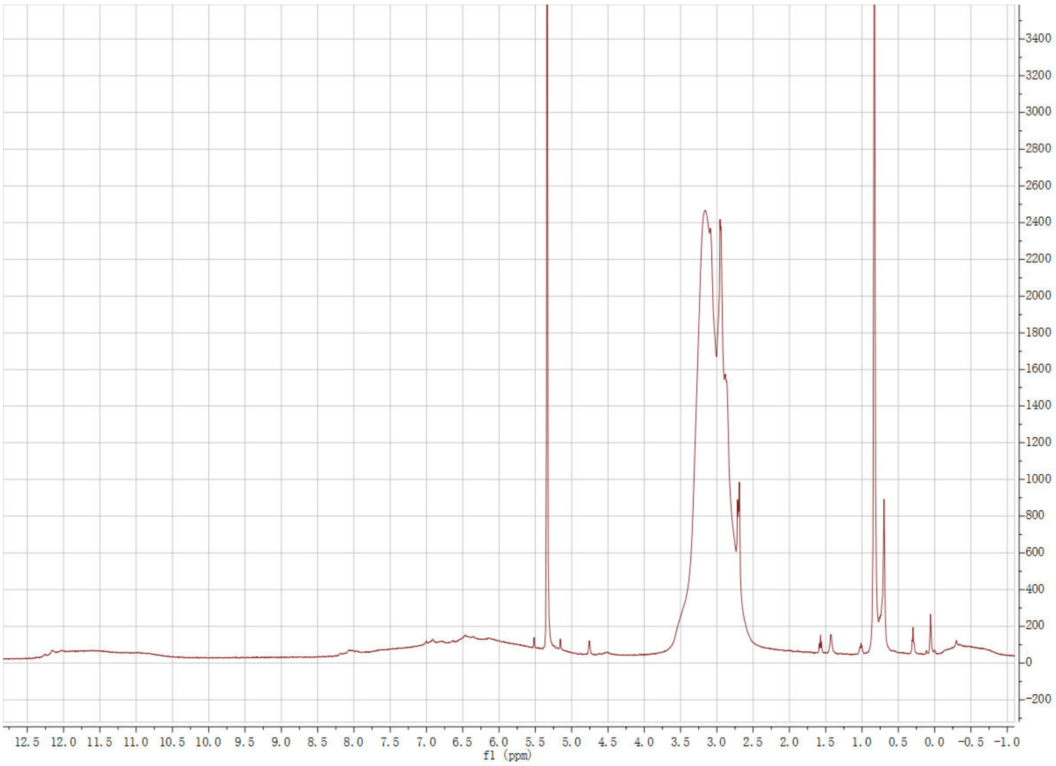


Figure S19. ^{1}H NMR of **P-AQM2I-2T**.

P-AQM2I-2T: Black solid (yield: 80%); GPC (HFIP, 40°C) Mn = 83.9 kDa, Mw = 114.3 KDa, PDI=1.36.

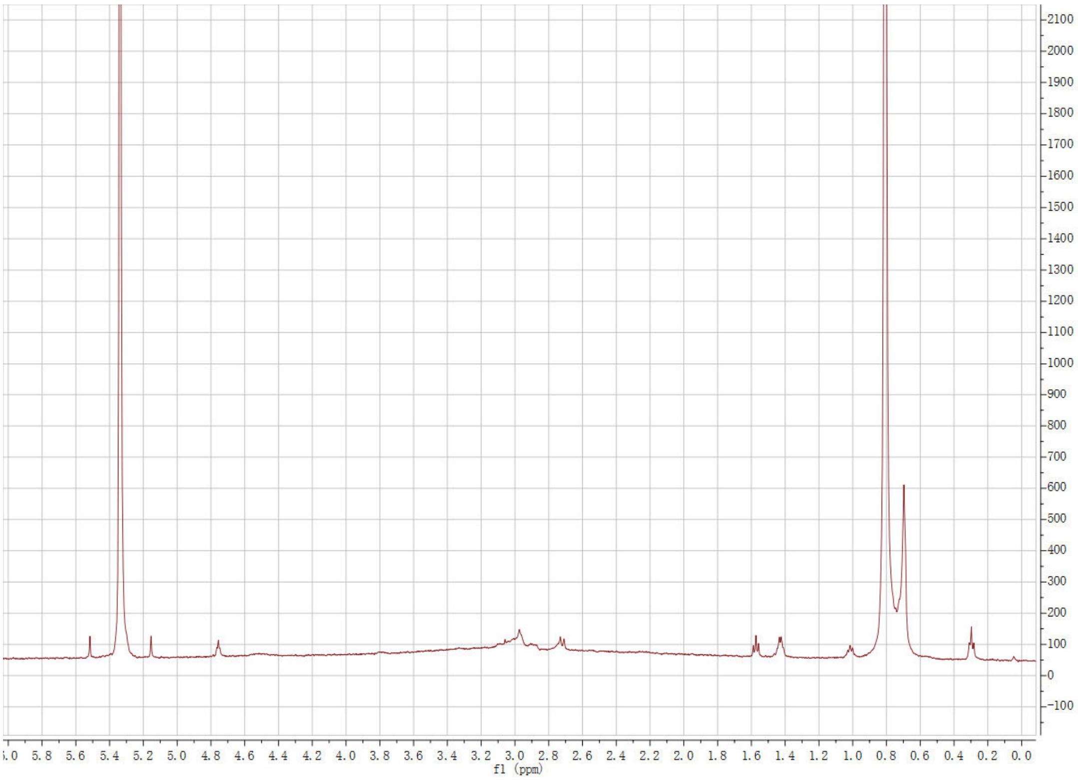


Figure S20. ^{1}H NMR of **P-AQM2I-2T**.

10. References

1 Y. Wang, G. Zhu, E. Zeglio, S. Inal and W. Yue, n-Type Organic Electrochemical Transistors with High Transconductance and Stability, Chem. Mater., 2023, 35, 2, 405-415.

2 X. Liu, B. He, C.L. Anderson, J. Chen, Y. Liu, para-Azaquinodimethane: A Compact Quinodimethane Variant as an Ambient Stable Building Block for High-Performance Low Band Gap Polymers, J. Am. Chem. Soc., 2017, 139, 24, 8355-8363.