

Supporting Information

Hydrogen bonded azine as building block for π -conjugated polymers and their semiconducting properties

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Materials and Characterization

Materials

The reagents were purchased from Adamas, Sigma-Aldrich, J&K Scientific, Bide Pharmatech, SunaTech and Derthon. All chemicals were reagent grade and used as received. Tetrahydrofuran (THF) was freshly distilled over sodium wires and benzophenone prior to use. The (*IE,2E*)-1,2-bis(thiophen-2-ylmethylene)hydrazine (**Az**) and (*IE,2E*)-1,2-bis((5-bromothiophen-2-yl)methylene)hydrazine (**Az-Br**) were synthesized according to the literature.¹ (2,2'-((2*Z*,2'*Z*)-((12,13-Bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]-thiadiazolo-[3,4-*e*]thieno[2,"3":4'5']thieno[2',3':4,5]-pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))-bis(5,6-di-fluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalono-nitrile (**Y6**) was purchased from Solarmer Materials Inc.

Characterization

¹H NMR and ¹³C NMR spectra were measured on a Bruker 400 MHz spectrometer with tetramethylsilane (TMS) as an internal reference at room temperature. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was carried on a Bruker Daltonics. Elemental analyses were carried on an Elementar Vario EL Cube system. The single Crystal X-ray diffraction analysis was performed on a Bruker D8 VENTURE X-ray diffractometer. UV-vis spectra were obtained with a Perkin Elmer Lambda 20 UV-vis spectrophotometer. Cyclic voltammetry (CV) was carried on a CHI600 electrochemical workstation in a deoxygenated anhydrous acetonitrile solution of *tetra*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆) (0.10 M) at the scan rate of 100 mV s⁻¹ under nitrogen. A platinum, an Ag/Ag⁺ (AgNO₃, 0.01 M in acetonitrile) electrode, and a platinum disk electrode were used as the counter electrode, reference electrode and working electrode, respectively. Before and after measuring the samples, the cell was calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below vacuum level) as an external standard which was measured under the same conditions. Polymer films were coated on the surface of the platinum disk. Gel permeation chromatography (GPC) analyses of polymers were carried out on

a Waters HPLC with a polystyrene gel column (Agilent PL gel 5 μm , MIXEDC) at room temperature. A PerkinElmer Pyris 1 was used for thermogravimetric analyses (TGAs) at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen. Differential scanning calorimetry (DSC) analysis was carried out on a Netzsch Instruments DSC 204 F1 at a scan rate of $10^\circ\text{C min}^{-1}$ under nitrogen. The sample of **P1** and **P2** was heated to 200°C and was held for 2 min to remove thermal history, followed by cooling to 20°C and then by heating to 200°C . The sample of **P3** was heated to 350°C and was held for 2 min to remove thermal history, followed by cooling to 20°C and then by heating to 350°C . The atomic force microscopy (AFM) images of thin films were taken on a Bruker JPK atomic force microscope. Grazing-incidence wide-angle X-ray scattering (GIWAXS) study were carried out at the beamline 14B1 of Shanghai Synchrotron Radiation Facility (SSRF).

Organic photovoltaic (OPV) device fabrication and measurement

The structure of solar cell devices was ITO/PEDOT:PSS/**P1:Y6**/PFN-Br/Ag. After cleaning and sonicating the ITO substrates, PEDOT:PSS (A14083 from Hareus) was spin-cast onto the substrates at 5000 rpm for 30 s, and then dried at 150°C for 15 min in N_2 atmosphere. The **P1:Y6** (1:1.2 w/w) was dissolved in chloroform (the total concentration of blends was 14 mg mL^{-1}) with 1-chloronaphthalene (0.5 wt.%) as additive. The **P1:Y6** solution was spin-cast at 3500 rpm for 30 s onto PEDOT:PSS film followed by a temperature annealing of 100°C for 10 min. A thin PFN-Br layer (0.5 mg/mL in methanol and 0.5% vol% glacial acetic acid, 3000 rpm) was coated on the active layer, followed by the deposition of Ag (evaporated under $6 \times 10^{-6} \text{ Pa}$ through a shadow mask). The effective device area was 4.0 mm^2 defined by shallow masks. The current density-voltage (J - V) curves of devices were measured using a Keithley 2400 system in the N_2 -filled glovebox under AM 1.5G (100 mW cm^{-2}) using an Enlitech solar simulator. The EQE spectra were measured using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated using a standard monocrystalline Si photovoltaic cell.

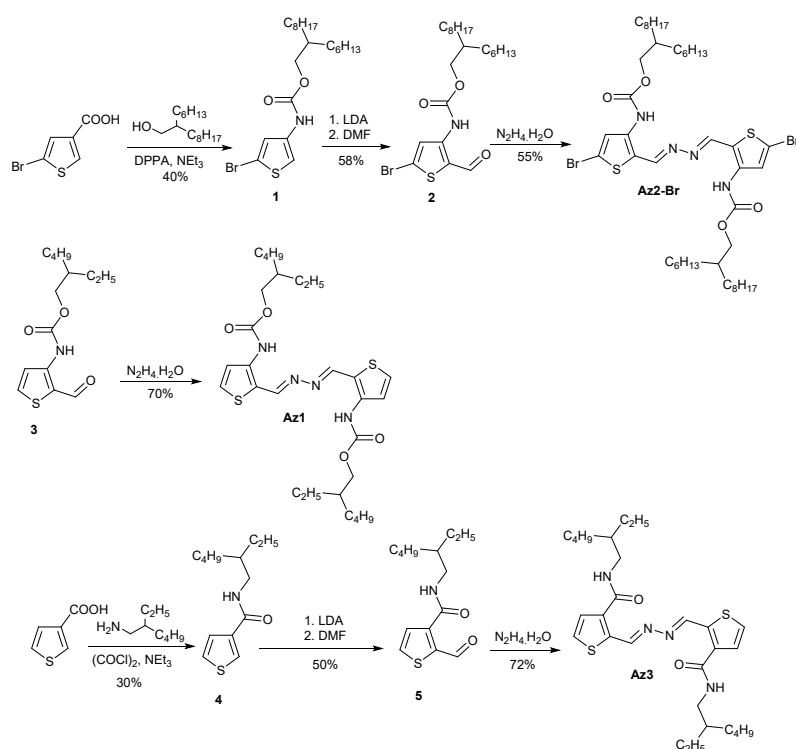
Organic field-effect transistor (OFET) device fabrication

An n-type heavily doped Si wafer with a 300-nm SiO₂ layer (capacitance =10 nF cm⁻²) was used as a bottom-gate electrode and dielectric layer. To fabricate BGBC structured OTFTs, 5/50-nm-thick Cr/Ag layers were thermally evaporated on the pristine SiO₂/Si substrates through the photolithography process as bottom S/D electrodes (W/L = 3753/82 μm). During the photolithography, the S1813 photoresist was liftoff by the stripper Remove PG and the substrate with S/D electrodes was ultrasonic cleaned with heptane, ethanol, acetone, and chloroform. The cleaned substrate with electrodes was treated with OTS in a vacuum oven at a temperature of 120°C, forming an OTS self-assembled monolayer, and then sonicated in heptane, ethanol, and chloroform to remove extra OTS molecules. The π-conjugated polymer was deposited on the OTS treated Si/SiO₂ substrates by spin-coating from its chloroform solution (5 mg mL⁻¹). The electrical characteristics of the OFET devices were measured by a Keithley 4200 semiconductor analyzer in ambient condition. The field-effect mobility is calculated in the saturation regime by the following equation:

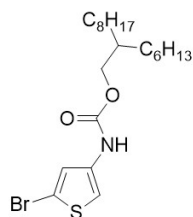
$$\mu = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_D}}{\partial V_G} \right)^2$$

where I_D 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.

Scheme S1. The synthesis of intermediates and monomers.

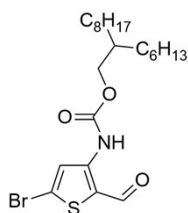


Synthesis of monomers and polymers



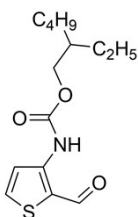
Synthesis of 2-hexyldecyl (5-bromothiophen-3-yl)carbamate (1). It was synthesized according to literature.² 5-bromothiophene-3-carboxylic acid (5.00 g, 24.15 mmol), diphenyl phosphorazidate (DPPA) (8.64 g, 31.39 mmol), 2-hexyldecan-1-ol (5.86 g, 24.15 mmol) and triethylamine (4.89 g, 48.30 mmol) were dissolved in anhydrous tetrahydrofuran (50.0 mL). The mixture was refluxed overnight under nitrogen. After cooling down to room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (35:1) as the eluent to give compound **1** (4.31 g, 40%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 4.06 (d, *J* = 4.4 Hz, 2H), 1.64 (s, 1H), 1.29 (m, 24H), 0.89 (m, 6H). ¹³C NMR (101 MHz,

CDCl₃) δ 153.85, 135.61, 123.73, 111.99, 109.17, 68.45, 37.67, 32.02, 31.94, 31.26, 30.10, 29.76, 29.69, 29.45, 26.82, 26.79, 22.80, 22.78, 14.24, 14.23.



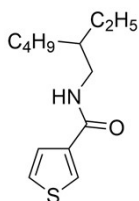
Synthesis of 2-hexyldecyl (5-bromo-2-formylthiophen-3-yl)carbamate (2).

Diisopropylamine (1.81 g, 17.92 mmol) and *n*-butyllithium (7.2 mL, 2.5 M, 17.92 mmol) were added to anhydrous tetrahydrofuran (30.0 mL) at -78°C under nitrogen to prepare lithium diisopropyl amide (LDA). After stirring for 1 h, a solution of compound **1** (4.00 g, 8.96 mmol) in anhydrous tetrahydrofuran (20.0 mL) was added dropwise at -78°C. After stirring for another 1 h, piperidine-1-carbaldehyde (2.03 g, 17.92 mmol) was added to the mixture, and the reaction was stirred for 1 h at -78°C. Then, the reaction was warmed to room temperature and stirred for 2 h. Subsequently, the mixture was poured into water (50 mL), and acidified with aqueous hydrochloric acid solution (1.0 M), then the mixture was extracted with dichloromethane for three times. The organic phase was dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (35:1) as the eluent to give compound **2** (2.47 g, 58%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 9.96 (s, 1H), 9.51 (s, 1H), 8.01 (s, 1H), 4.09 (d, *J* = 5.6 Hz, 2H), 1.67 (s, 1H), 1.32 (m, 24H), 0.89 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 182.27, 153.29, 145.00, 125.59, 120.87, 69.12, 37.61, 32.00, 31.92, 31.15, 31.13, 30.03, 29.70, 29.67, 29.42, 26.80, 26.77, 22.79, 22.77, 14.23, 14.21.



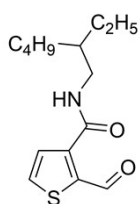
Synthesis of 2-ethylhexyl (2-formylthiophen-3-yl)carbamate (3). Compound **3** was prepared by a similar synthetic procedure to **2**. 2-Ethylhexyl thiophen-3-ylcarbamate

(1.70 g, 6.66 mmol) and anhydrous THF (20.0 mL) were added into a dry Schlenk bottle at -78°C under nitrogen. After stirring a few minutes, *n*-butyllithium (5.3 mL, 2.5 M, 13.31 mmol) was slowly added, and the reaction was stirred at -78°C for 1 h under nitrogen. Subsequently, anhydrous *N,N*-dimethylformamide (0.97 g, 13.31 mmol) was quickly added into the reaction. After stirring for 1 h, the mixture was warmed to room temperature and was further stirred for 2 h. The mixture was poured into water (50 mL), and acidified with aqueous hydrochloric acid solution (1.0 M), then extracted with dichloromethane for three times. The organic phase was dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (30:1) as the eluent to give compound **3** (1.53 g, 81%) as a pale-yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 9.93 (s, 1H), 9.65 (s, 1H), 7.93 (d, $J = 5.2$ Hz, 1H), 7.65 (d, $J = 5.2$ Hz, 1H), 4.12 (m, 2H), 1.63 (m, 1H), 1.40 (m, 8H), 0.91 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.79, 153.45, 145.30, 136.10, 122.09, 119.79, 68.42, 38.97, 30.27, 28.98, 23.64, 23.03, 14.12, 11.01.

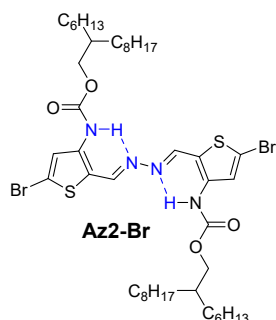


Synthesis of *N*-(2-ethylhexyl)thiophene-3-carboxamide (4). It was synthesized according to literature.³ In an oven-dried 2-neck round bottom flask, thiophene-3-carboxylic acid (5.00 g, 39.02 mmol) was dissolved in anhydrous dichloromethane (50 mL) and anhydrous dimethylformamide (2.5 mL) under nitrogen atmosphere. After cooling to 0°C , oxalyl chloride (9.90 g, 78.04 mmol) was dropwise via syringe. Then, ice bath was removed and the mixture was stirred overnight. The mixture was concentrated under reduced pressure to remove oxalyl chloride and dichloromethane. The resulting yellow solid was re-dissolved in anhydrous dichloromethane (50 mL), a solution of 2-ethyl-1-hexylamine (12.61 g, 97.55 mmol) and triethylamine (9.87 g, 97.55 mmol) were added dropwise under ice-bath. The mixture was allowed to stir overnight, and then it was poured in water and extracted with dichloromethane three

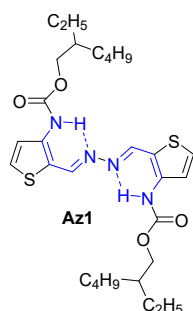
times. The combined organic layer was washed with water, dried with MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was further purified via column chromatography on silica gel using hexanes/ethyl acetate (8:2) to give compound **4** as a pale-yellow solid (2.82 g, 30%). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (m, 1H), 7.38 (m, 1H), 7.32 (m, 1H), 6.11 (s, 1H), 3.37 (m, 2H), 1.55 (m, 1H), 1.39 (m, 8H), 0.92 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.34, 137.97, 127.94, 126.51, 126.11, 42.81, 39.60, 31.18, 29.01, 24.41, 23.13, 14.19, 11.01.



Synthesis of N-(2-ethylhexyl)-2-formylthiophene-3-carboxamide (5). An anhydrous THF (30.0 mL) solution of compound **4** (1.50 g, 6.27 mmol) was added to a dry flask under nitrogen atmosphere. The solution was cooled to -78°C and *n*-butyl lithium (5.0 mL, 2.5 M, 12.53 mmol) was added dropwise. After stirring for 2 h, anhydrous dimethylformamide (0.92 g, 12.53 mmol) was added. After stirring at -78°C for another 1 h, the mixture was warmed to room temperature and stirred for 2 h. The mixture was poured into water (50 mL), and acidified with aqueous hydrochloric acid solution (1.0 M), then extracted with dichloromethane. The organic phase was dried over anhydrous NaSO_4 . After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1) as the eluent to give compound **5** (0.84 g, 50%) as a pale-yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 10.08 (s, 1H), 8.12 (s, 1H), 7.76 (d, $J = 5.2$ Hz, 1H), 7.68 (d, $J = 4.8$ Hz, 1H), 3.42 (m, 2H), 1.60 (m, 1H), 1.44 (m, 8H), 0.95 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.90, 161.66, 142.08, 141.62, 134.44, 132.24, 42.95, 39.38, 31.22, 29.01, 24.49, 23.13, 14.21, 11.06.

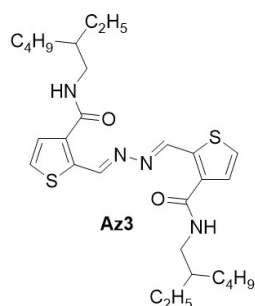


Synthesis of bis(2-hexyldecyl) (((1E,1'E)-hydrazine-1,2-diylidenebis(methaneylidene))bis(5-bromothiophene-2,3-diyl))dicarbamate (Az2-Br). Monomer **Az2-Br** was synthesized according to literature.⁴⁻⁶ Compound **2** (1.90 g, 4.00 mmol) was dissolved in absolute ethanol (10.0 mL). Hydrazine hydrate (0.10 g, 80%, 2.01 mmol) in ethanol solution (5.0 mL) was added dropwise, and then 2 drops of acetic acid were added to the solution. After stirring for a few minutes, the solution turned yellow and solid precipitated. The reaction was stirred at room temperature for 4 h. The precipitate was filtrated, and washed with ethanol for several times. The product was purified by recrystallization in mixed solvent of ethanol and chloroform to give the titled compound (1.04 g, 55%) as a yellow powder. ¹H NMR (400 MHz, CDCl₃) δ 10.29 (s, 2H), 8.40 (s, 2H), 7.96 (s, 2H), 4.12 (d, *J* = 6.0 Hz, 4H), 1.72 (s, 2H), 1.33 (m, 48H), 0.88 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.16, 153.51, 140.82, 125.67, 119.15, 116.07, 69.04, 37.67, 32.05, 31.96, 31.48, 30.19, 29.83, 29.74, 29.50, 26.91, 26.86, 22.84, 22.82, 14.27, 14.26. HRMS MALDI-TOF: *m/z* calcd for C₄₄H₇₂Br₂N₄O₄S₂, 945.3375; found, 945.3427.

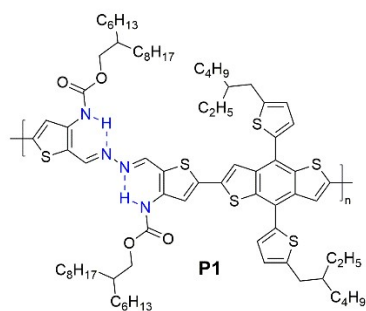


Synthesis of bis(2-ethylhexyl) (((1E,1'E)-hydrazine-1,2-diylidenebis(methaneylidene))bis(thiophene-2,3-diyl))dicarbamate (Az1). The same procedure described for the synthesis of **Az2-Br** was followed. 2-Ethylhexyl(5-bromo-2-formylthiophen-3-yl) carbamate² (**3**) (1.14 g, 4.02 mmol), hydrazine hydrate (80%, 0.10 g, 2.01 mmol)

and ethanol (10.0 mL) were used. The product was purified by recrystallization in mixed solvent of ethanol and chloroform to give the titled compound (0.79 g, 70%) as a bright yellow powder. ^1H NMR (400 MHz, CDCl_3) δ 10.35 (s, 2H), 8.57 (s, 2H), 7.92 (s, 2H), 7.49 (d, $J = 5.6$ Hz, 2H), 4.14 (d, $J = 6.0$ Hz, 4H), 1.72 (m, 2H), 1.46 (m, 16H), 0.97 (m, 12 H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.28, 153.76, 141.12, 130.74, 122.41, 115.01, 68.43, 39.09, 30.61, 29.06, 24.03, 23.15, 14.24, 11.24. HRMS MALDI-TOF: m/z calcd for $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}_4\text{S}_2$, 563.2681; found, 563.2740.

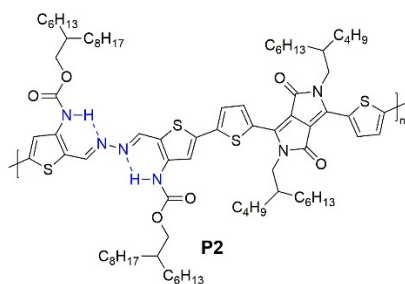


Synthesis of 2,2'-((1E,1'E)-hydrazine-1,2-diylidenebis(methaneylylidene))bis(N-(2-ethylhexyl)thiophene-3-carboxamide) (Az3). The same procedure described for the synthesis of Az1. *N*-(2-ethylhexyl)-2-formylthiophene-3-carboxamide (**5**) (0.50 g, 1.87 mmol), hydrazine hydrate (80%, 0.10 g, 2.01 mmol) and ethanol (10 mL) were used. The product was purified by recrystallization in mixed solvent of ethanol and chloroform to give the titled compound (0.36 g, 72%) as bright yellow needle-like solid. ^1H NMR (400 MHz, CDCl_3) δ 9.22 (s, 2H), 7.46 (d, $J = 5.2$ Hz, 2H), 7.35f (d, $J = 5.2$ Hz, 2H), 6.81 (s, 2H), 3.41 (m, 4H), 1.59 (s, 2H), 1.41 (m, 16H), 0.95 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.16, 156.05, 139.89, 138.86, 129.71, 128.60, 43.07, 39.53, 31.28, 29.02, 24.50, 23.19, 14.23, 11.03. HRMS MALDI-TOF: m/z calcd for $\text{C}_{28}\text{H}_{42}\text{N}_4\text{O}_2\text{S}_2$, 531.2783; found, 531.2815.



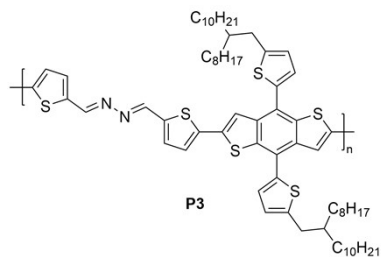
Synthesis of polymer **P1**.

Az2-Br (0.095 g, 0.10 mmol), (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**BDT**) (0.097 g, 0.10 mmol), Pd₂(dba)₃ (0.002 g, 0.002 mmol) and P(*o*-tol)₃ (0.003 g, 0.084 mmol) and degassed anhydrous toluene (6.0 mL) were added to a Schlenk flask. The mixture was stirred at 120°C for 2 h. After cooling to room temperature, the mixture was precipitated in methanol and was filtered. The residue was washed with methanol, *n*-hexane, dichloromethane under nitrogen in a Soxhlet extractor. The polymer was dissolved and concentrated in the chloroform, and was precipitated with methanol and filtered to give **P1** (0.127 g, 87%) as a dark purple solid. $M_n = 160.1$ kDa; $M_w = 488.6$ kDa; PDI = 3.1. Anal. Calcd for C₈₀H₁₁₈N₄O₄S₆: C 69.10, H 8.73, N 3.54; Found: C 69.02, H 8.54, N 3.54.



Synthesis of polymer **P2**.

Polymer **P2** was synthesized by a similar experimental procedure as **P1**. **Az2-Br** (0.095 g, 0.10 mmol), 2,5-bis(2-butyloctyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**DPP**) (0.091 g, 0.10 mmol), Pd₂(dba)₃ (0.002 g, 0.002 mmol) and P(*o*-tol)₃ (0.003 g, 0.084 mmol) and anhydrous toluene (6.0 mL) were used. The polymer **P2** (0.126 g, 90%) was a dark green solid. $M_n = 66.0$ kDa; $M_w = 226.9$ kDa; PDI = 3.4. Anal. Calcd for C₈₄H₁₃₂N₆O₆S₄: C 69.25, H 9.23, N 5.67; Found: C 69.57, H 9.17, N 5.79.



Synthesis of polymer **P3**.

Polymer **P3** was synthesized by a similar experimental procedure as **P1**. **Az-Br**¹ (0.049 g, 0.13 mmol), (4,8-bis(5-(2-octyldodecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (0.162 g, 0.13 mmol), Pd₂(dba)₃ (0.002 g, 0.002 mmol) and P(*o*-tol)₃ (0.003 g, 0.084 mmol) were added in degassed anhydrous toluene (6 mL) under nitrogen. The mixture was stirred at 120°C for 72 h. The polymer **P3** (0.127 g, 84%) was a dark purple solid. $M_n = 36.2$ kDa; $M_w = 110.6$ kDa; PDI = 3.1. Anal. Calcd for C₇₀H₁₀₀N₂S₆: C 72.28, H 8.65, N 2.32; Found: C 72.36, H 8.68, N 2.41.

Crystallographic data

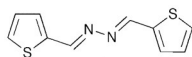
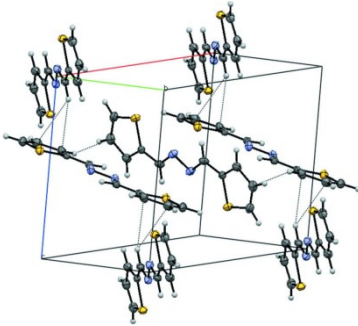
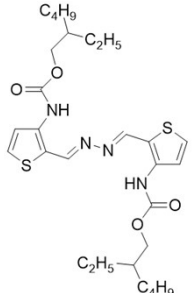
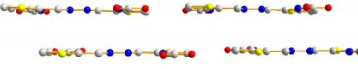
Table S1. Crystal data and structure refinement for **Az2**.

Empirical formula	$C_{28}H_{42}N_4O_4S_2$
Formula weight	562.77
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.0119(4) Å alpha = 101.744(5) deg. b = 10.5046(8) Å beta = 99.652(5) deg. c = 14.7245(13) Å gamma = 96.654(4) deg.
Volume	739.15(11) Å ³
Z, Calculated density	1, 1.264 Mg/m ³
Absorption coefficient	1.947 mm ⁻¹
F(000)	302
Crystal size	0.160 x 0.140 x 0.120 mm
Theta range for data collection	3.126 to 66.642 deg.
Limiting indices	-5 ≤ h ≤ 5, -12 ≤ k ≤ 11, -17 ≤ l ≤ 17
Reflections collected / unique	6767 / 2509 [R(int) = 0.0725]
Completeness to theta	66.642 96.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.5301
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2509 / 0 / 177
Goodness-of-fit on F ²	1.102
Final R indices [I > 2σ(I)]	R1 = 0.1326, wR2 = 0.3773
R indices (all data)	R1 = 0.1703, wR2 = 0.4003
Extinction coefficient	n/a
Largest diff. peak and hole	1.233 and -0.490 e.Å ⁻³

Table S2. Selected bond distances and torsion angles for compound **Az2**.

Bond type	Bond length (Å)	Torsion angles (°)
N(1)=C(5)	1.281(11)	
N(1)—N(1A)	1.378(12)	
N(1)···H	2.2230(889)	
N(1)···N(2)	2.8701(85)	
N(2)—H	0.7930(998)	
N(1A)—C(5A)	1.281(11)	
N(1A)···H	2.2230(889)	
N(1A)—N(2A)	2.8701(85)	
N(2A)—H	0.7930(998)	
S(1)-C(4)-C(5)-N(1)		179.097(669)
S(1A)-C(4A)-C(5A)-N(1A)		-179.097(669)
C(5)=N(1)-N(1A)=C(5A)		180.000(745)

Table S3. Summary of X-ray crystallographic results of two single crystals.

	Structure	Packing motif	Packing motif picture	Bond length (Å)	
				C=N	N-N
Previous reports	<p>Az 1, 7</p> 	Slipped herringbone packing		1.280, 1.281	1.402, 1.412
This work	<p>Az1</p> 	Lamellar packing		1.281	1.378

Theoretical calculation of P1 and P2

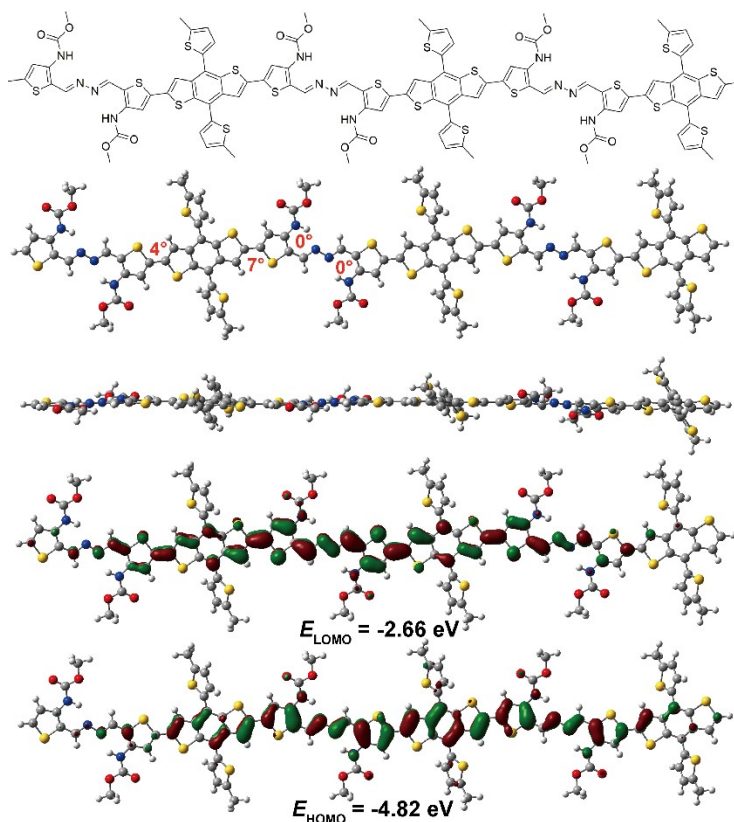


Figure S1. Calculated molecular geometries and frontier molecular orbitals of P1 trimers at B3LYP-D3/6-31G(d) level.

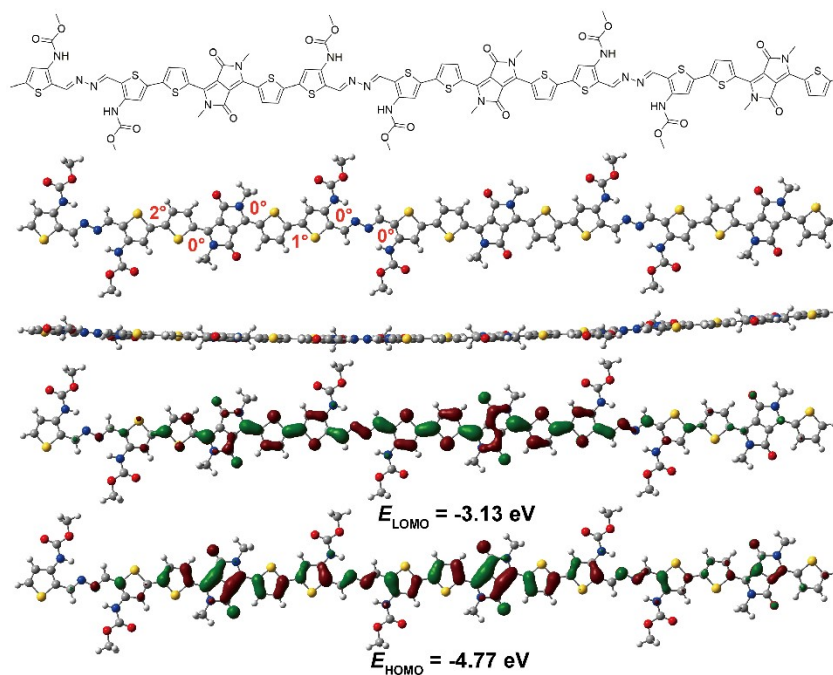


Figure S2. Calculated molecular geometries and frontier molecular orbitals of P2 trimers at B3LYP-D3/6-31G(d) level.

Thermal properties of polymers

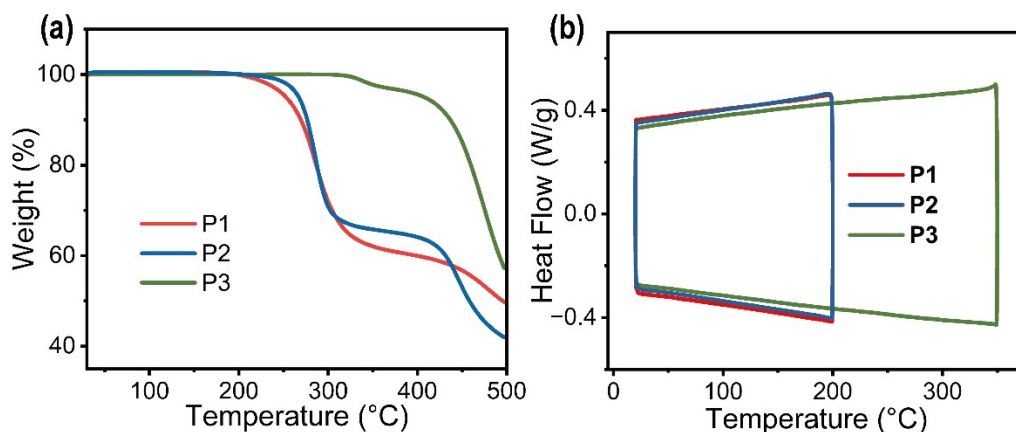


Figure S3. The (a) TGA and (b) DSC curves of **P1**, **P2** and **P3**.

Absorption spectra of polymers

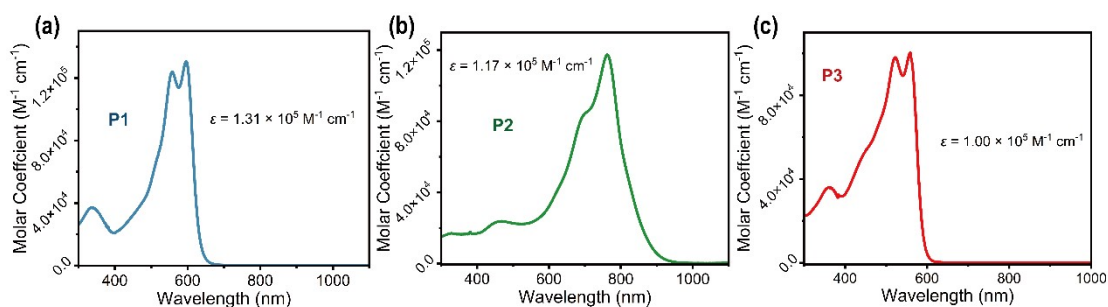


Figure S4. Absorption spectra of polymer solutions at room temperature (a) **P1**, (b) **P2** and (c) **P3**.

Performances of OPV and OFET devices

Table S4. Device performances of the **P1:Y6** based solar cells fabricated with different D/A ratios (with 0.5% of CN).

Solvent	D: A	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
CF	1:1	0.82 (0.80 ± 0.03)	19.4 (19.1 ± 0.4)	42.3 (41.2 ± 1.1)	6.5 (6.3 ± 0.3)
	1:1.2	0.87 (0.84 ± 0.04)	20.0 (19.5 ± 0.6)	53.0 (50.8 ± 2.2)	8.2 (8.1 ± 0.2)
	1:1.5	0.85 (0.82 ± 0.04)	19.0 (18.8 ± 0.5)	47.4 (46.6 ± 0.8)	7.6 (7.5 ± 0.2)

Average values were obtained from 10 OPV devices.

Table S5. The Field-Effect Performances of **P2** based devices.

Annealing temperature (°C)	$\mu_{h,max}/\mu_{h,avg}$ ^a (cm ² V ⁻¹ s ⁻¹)	V_T (V)	I_{on}/I_{off}
as-spun	0.013/0.011	-18 to -21	10 ⁴ -10 ⁵
60	0.017/0.015	-13 to -21	10 ⁵ -10 ⁶
120	0.022/0.022	-9 to -12	10 ⁴ -10 ⁵
180	0.034/0.033	-11 to -16	10 ⁵ -10 ⁶

^a Average values were obtained from 10 OFET devices.

2D Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) data

Table S6. The parameters of 2D GIWAXS.

Films	π-π stacking			Lamella stacking		
	q (nm ⁻¹)	d-Spacing ^a (nm)	CCL ^b (nm)	q (nm ⁻¹)	d-Spacing ^a (nm)	CCL ^b (nm)
P1	17.0272	0.3690	2.1436	2.7444	2.2895	8.7433
P1:Y6	17.5970	0.3571	2.2597	2.6362	2.3834	9.7817
P2 As-spun	17.1985	0.3650	1.9244	3.0415	2.0658	8.2020
P2 Annealed at 180°C	17.2458	0.3643	2.1772	3.0514	2.0591	11.2920

^a Computed using the relationship $d = 2\pi/q$, where q is the diffraction peak in the x-coordinate. ^b CCL = $2\pi/\text{FWHM}$, where FWHM indicates full width at half maximum.

^1H NMR, ^{13}C NMR and MALDI-MS Spectrum

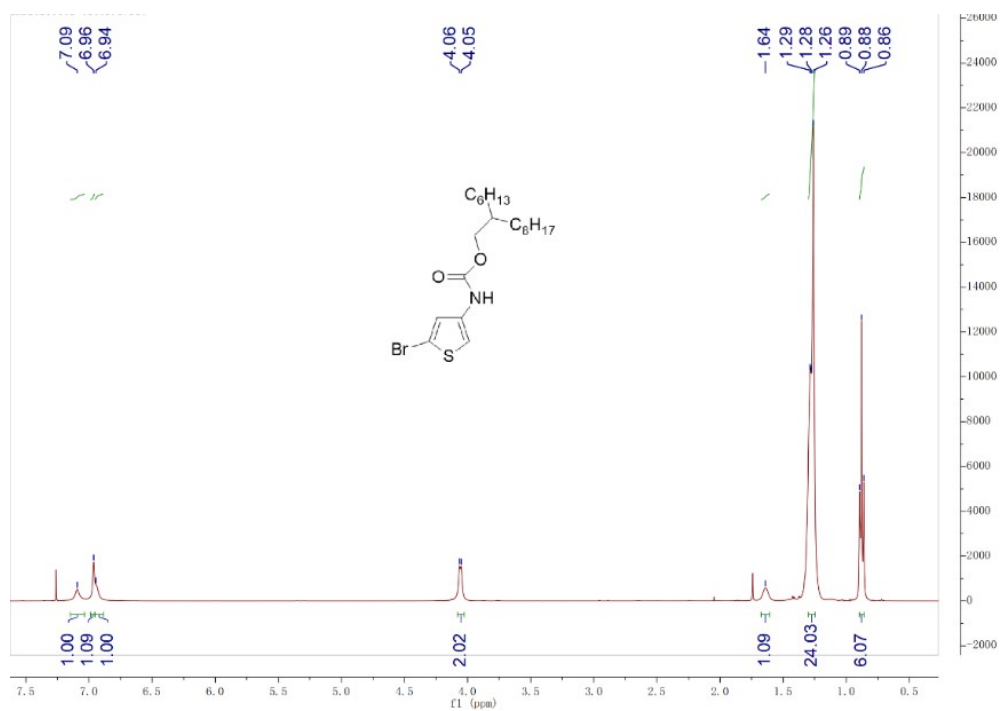


Figure S5. The ^1H NMR spectrum of compound **1** in CDCl_3 .

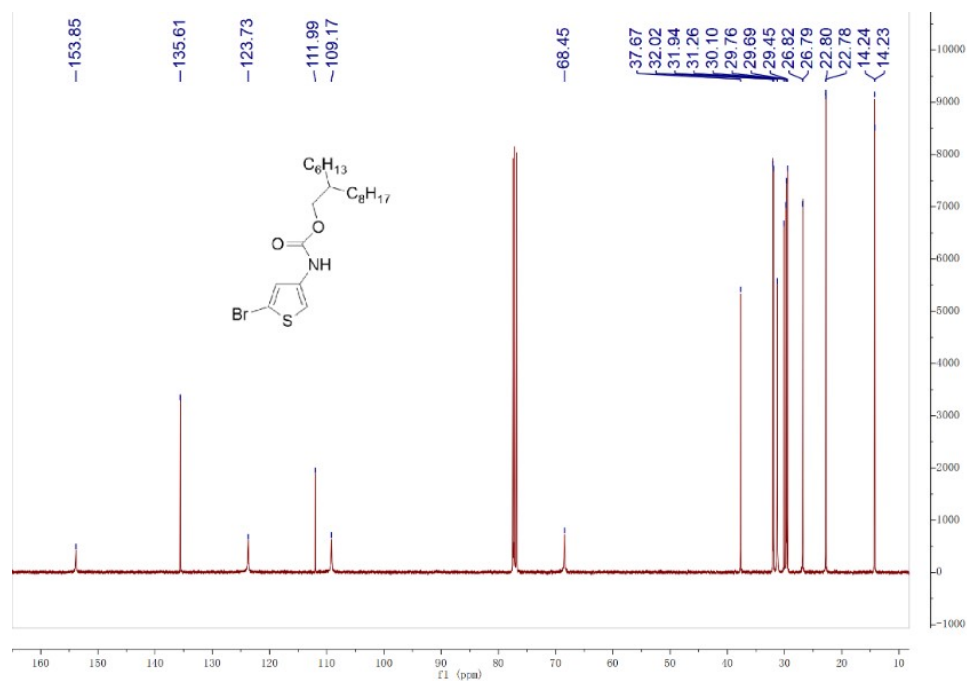


Figure S6. The ^{13}C NMR spectrum of compound **1** in CDCl_3 .

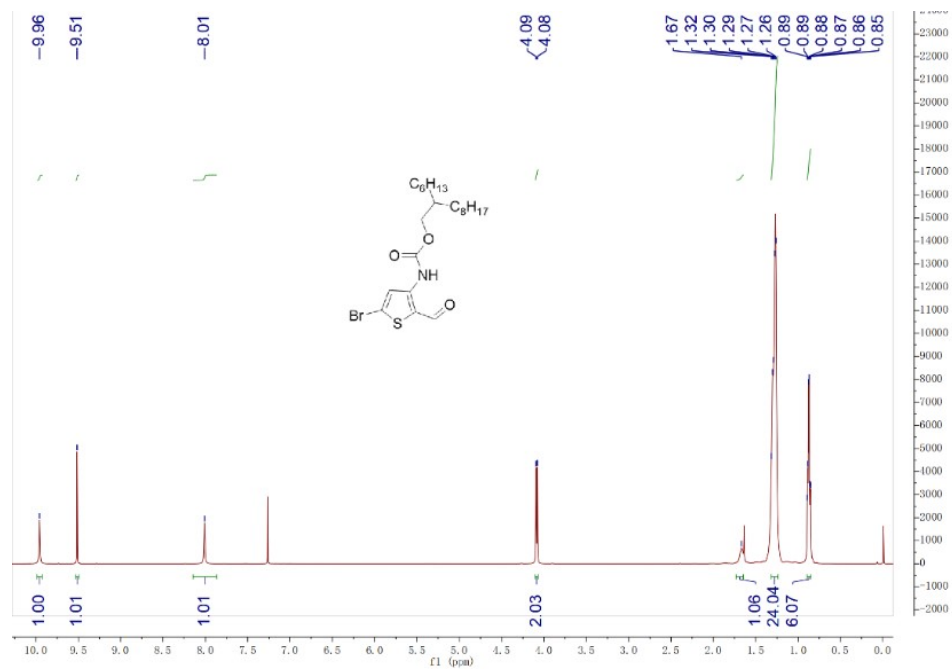


Figure S7. The ^1H NMR spectrum of compound **2** in CDCl_3 .

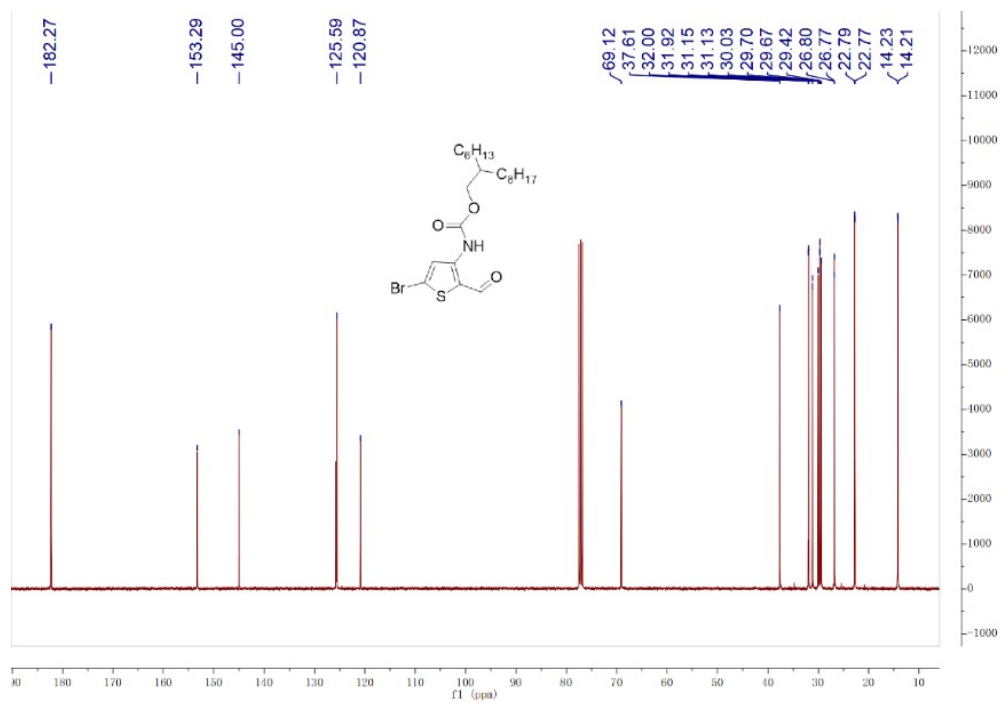


Figure S8. The ^{13}C NMR spectrum of compound **2** in CDCl_3 .

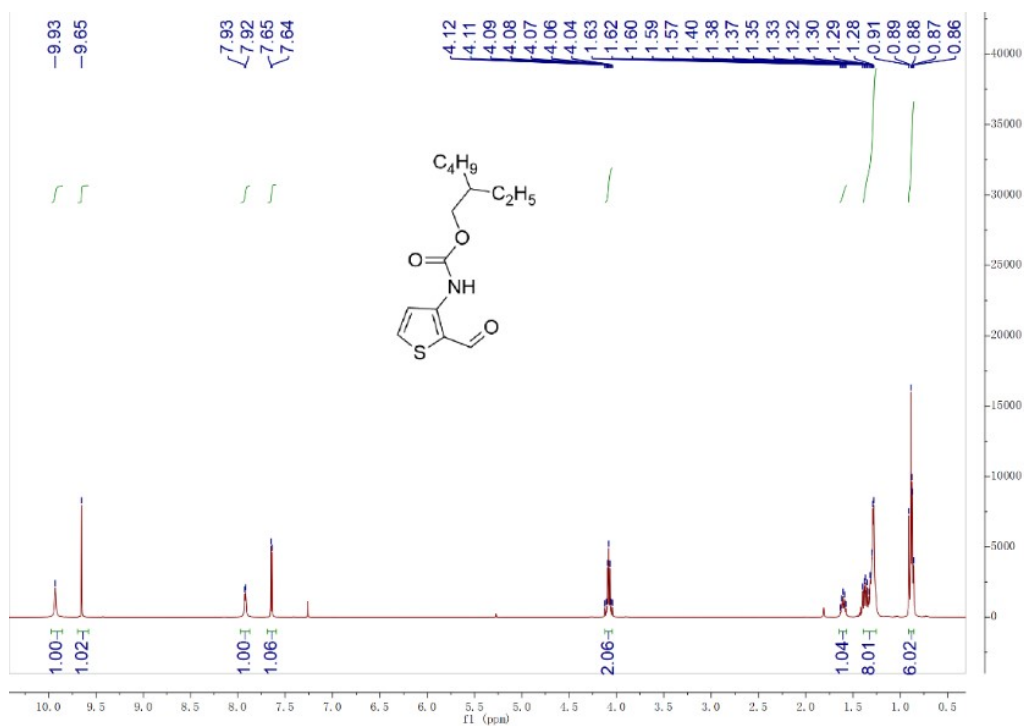


Figure S9. The ^1H NMR spectrum of compound 3 in CDCl_3 .

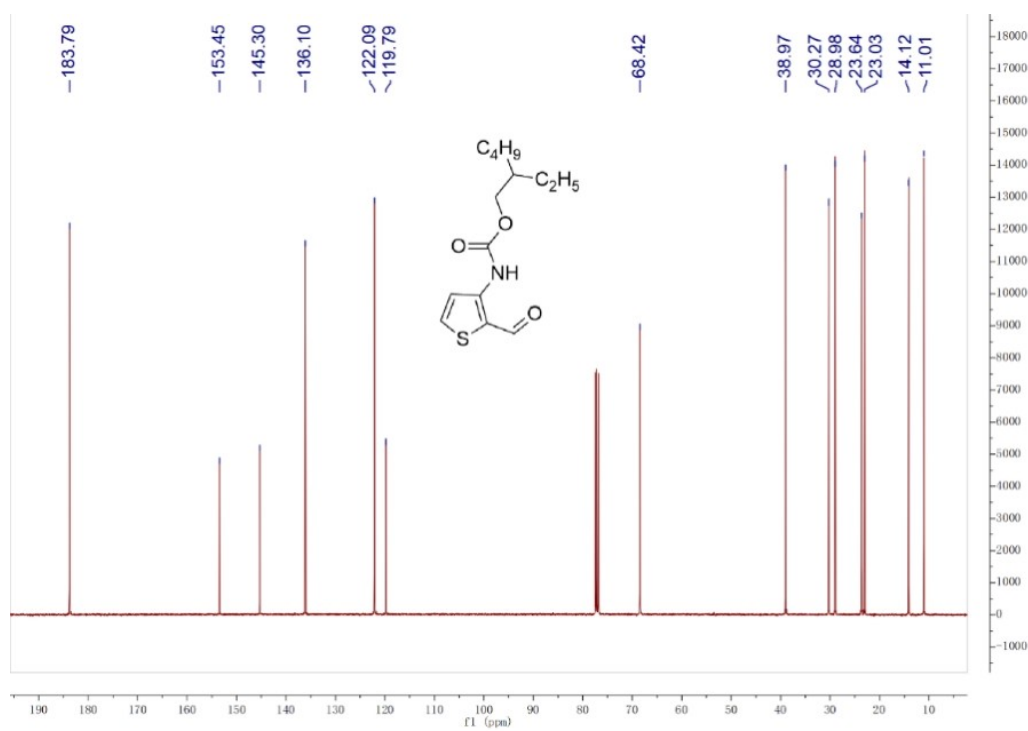


Figure S10. The ^{13}C NMR spectrum of compound 3 in CDCl_3 .

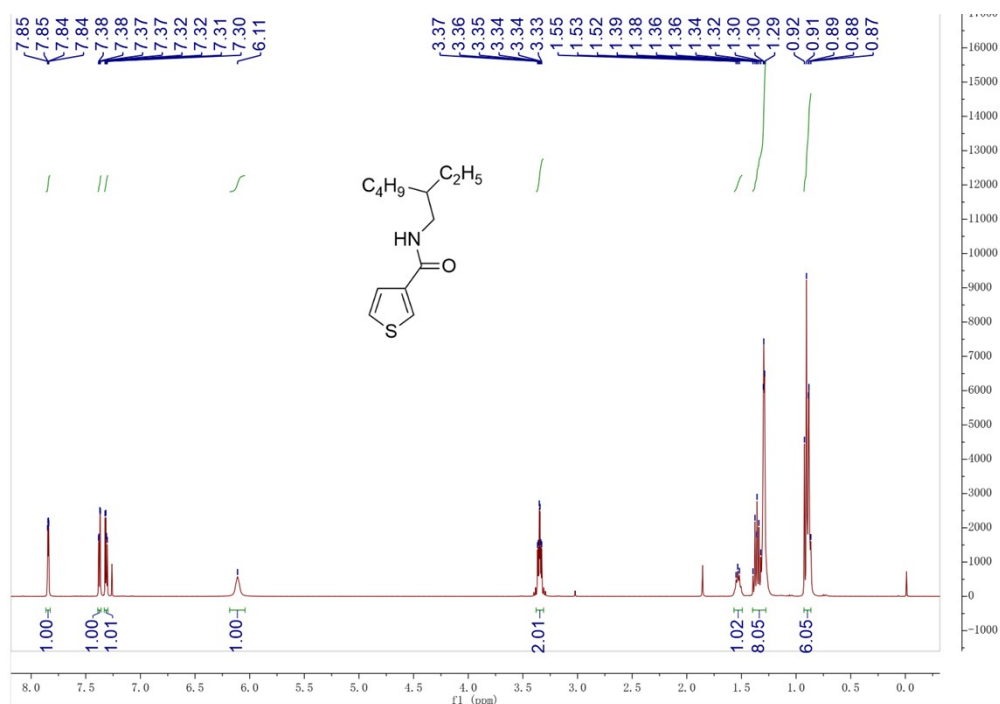


Figure S11. The ^1H NMR spectrum of compound 4 in CDCl_3 .

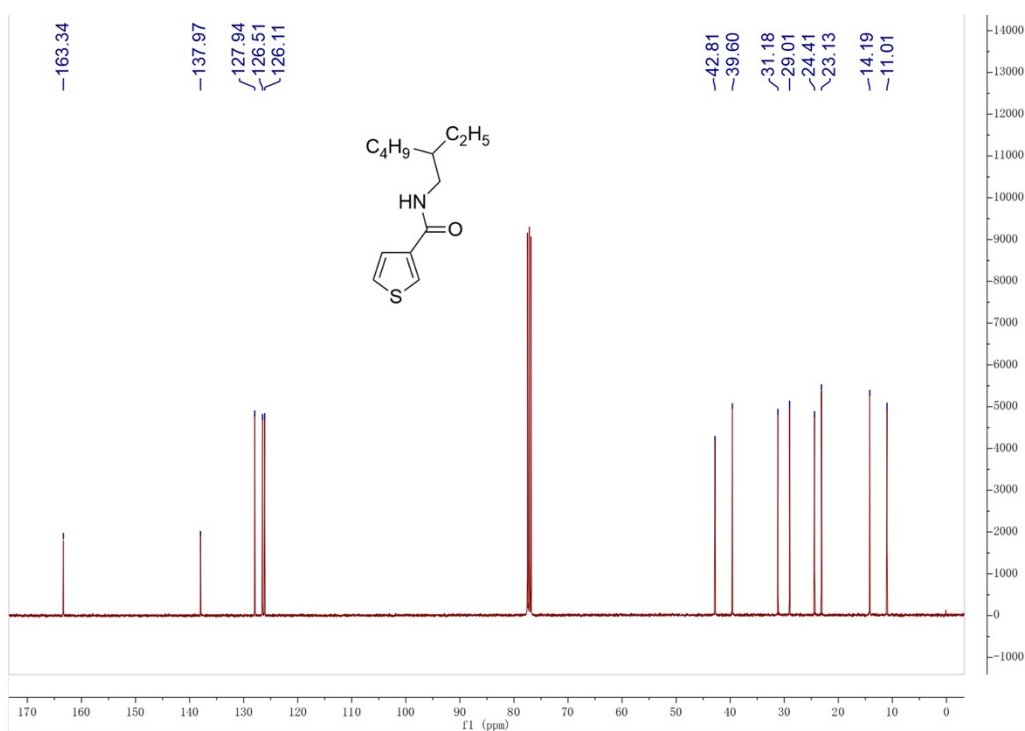


Figure S12. The ^{13}C NMR spectrum of compound 4 in CDCl_3 .

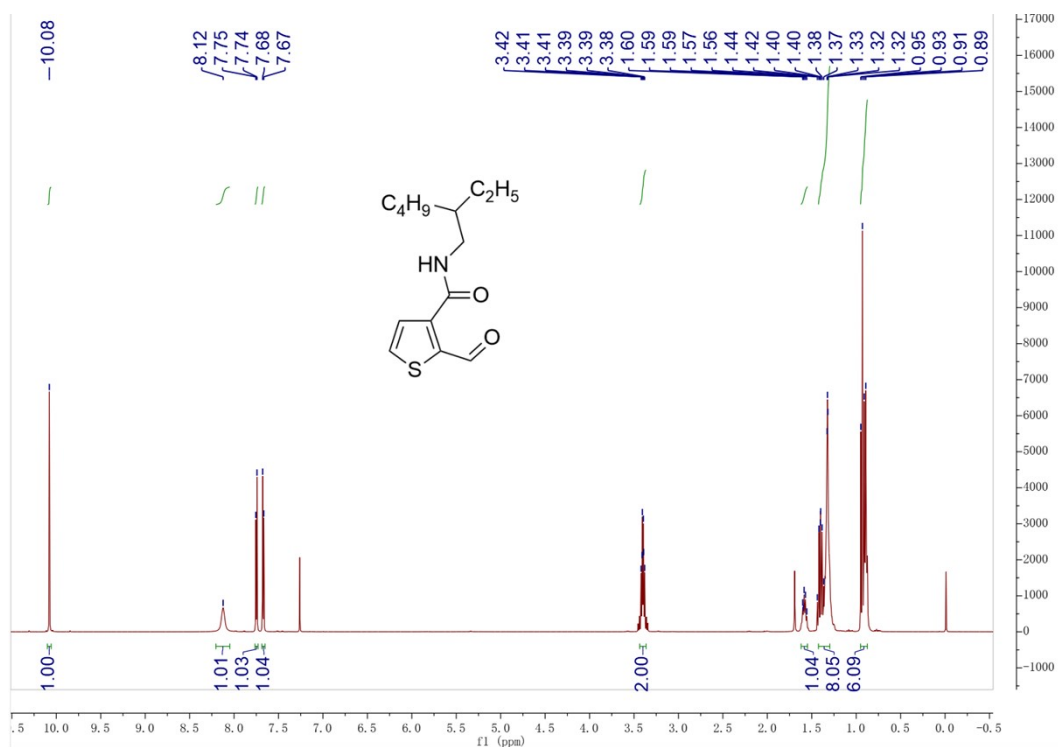


Figure S13. The ¹H NMR spectrum of compound 5 in CDCl₃.

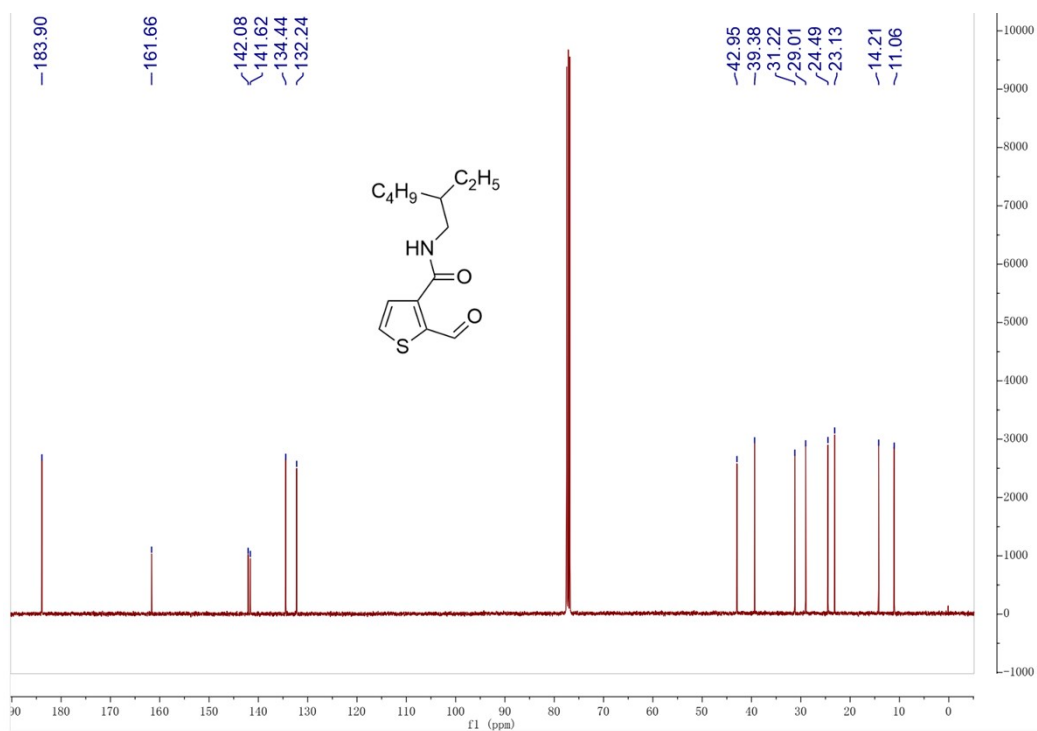


Figure S14. The ¹³C NMR spectrum of compound 5 in CDCl₃.

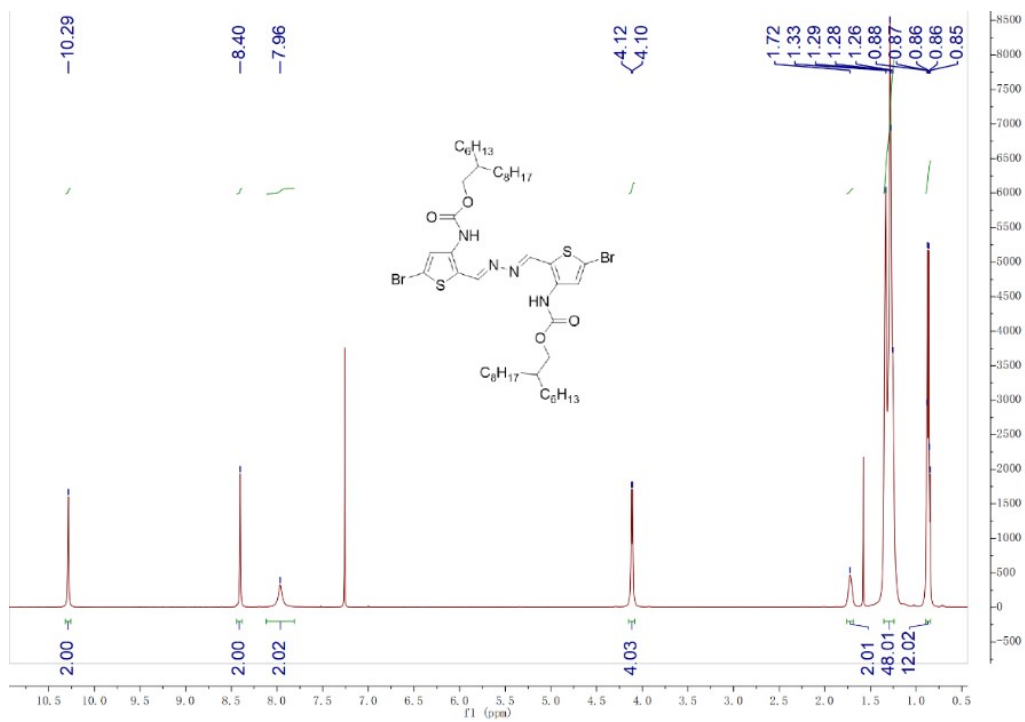


Figure S15. The 1H NMR spectrum of monomer Az2-Br in $CDCl_3$.

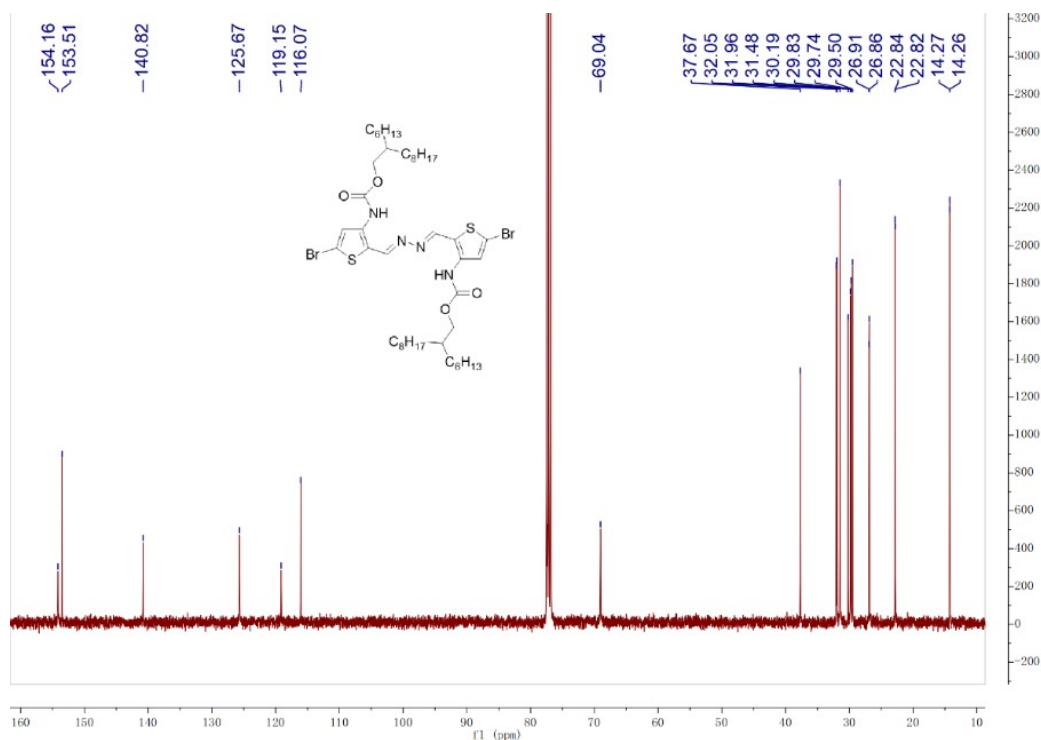


Figure S16. The ^{13}C NMR spectrum of monomer Az2-Br in $CDCl_3$.

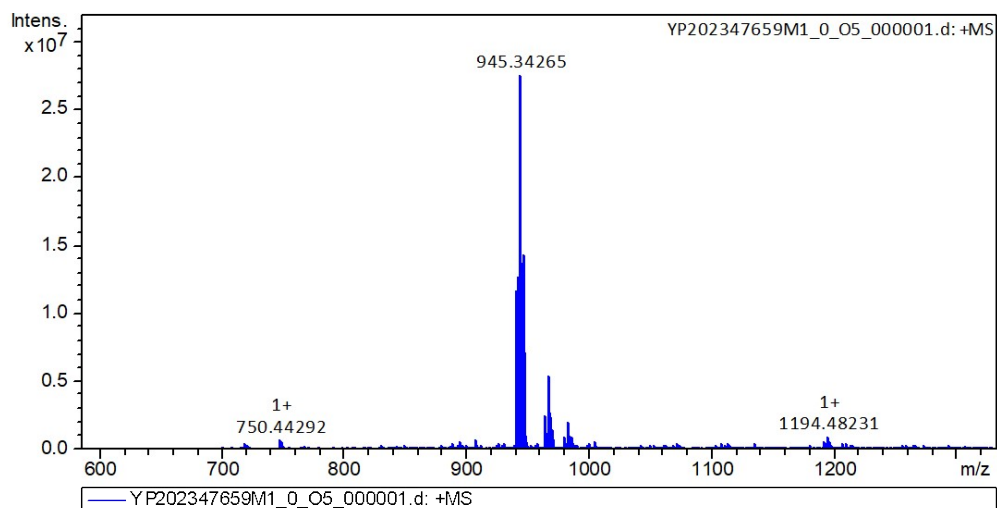


Figure S17. The MALDI-MS spectrum of Az2-Br.

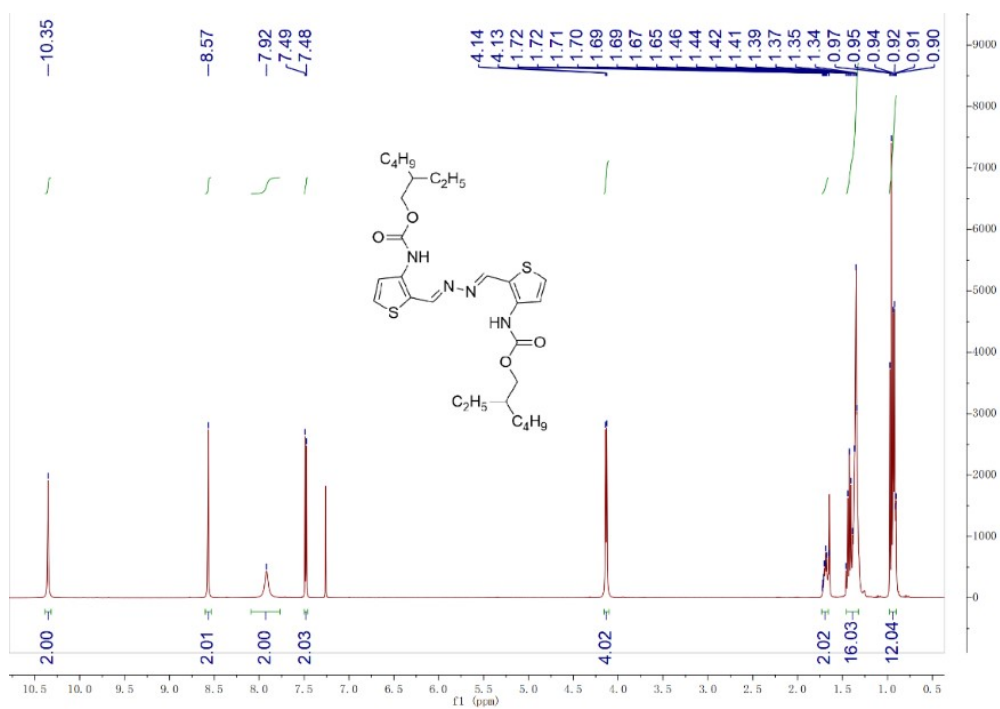


Figure S18. The ¹H NMR spectrum of monomer Az1 in CDCl₃.

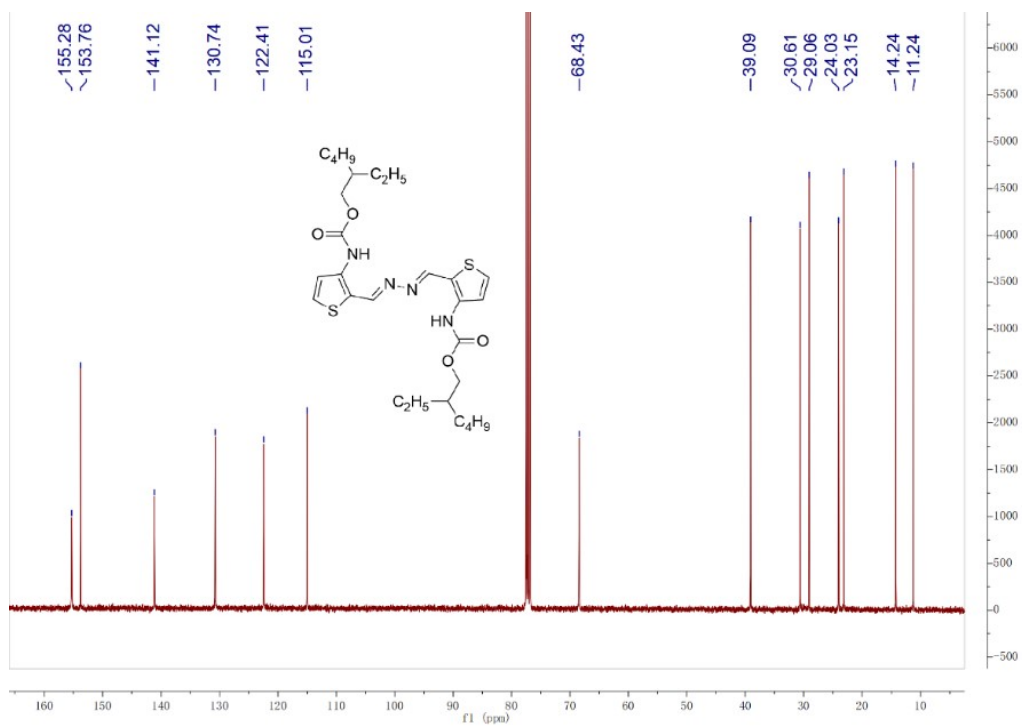


Figure S19. The ¹³C NMR spectrum of monomer **Az1** in CDCl₃.

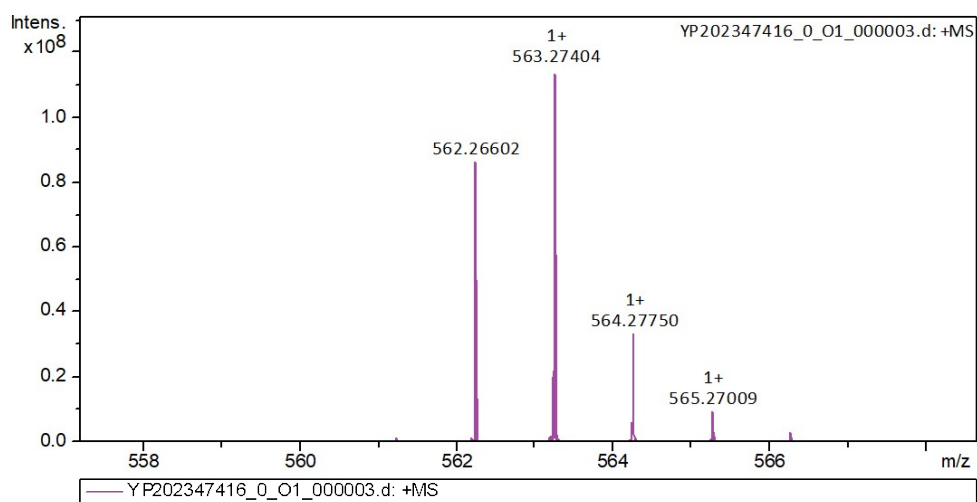


Figure S20. The MALDI-MS spectrum of **Az1**.

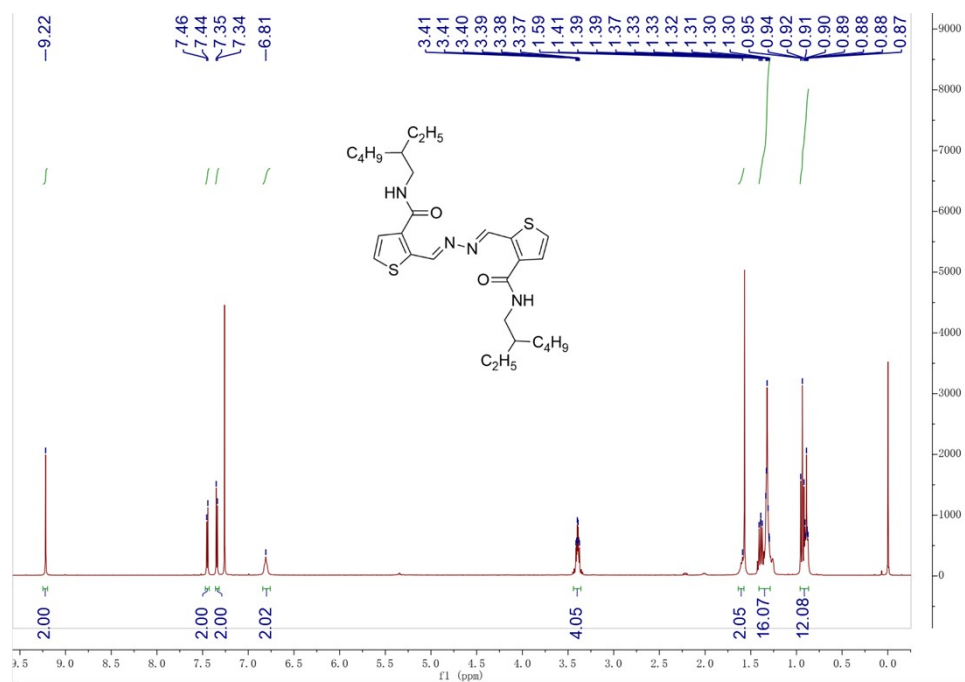


Figure S21. The 1H NMR spectrum of monomer **Az3** in $CDCl_3$.

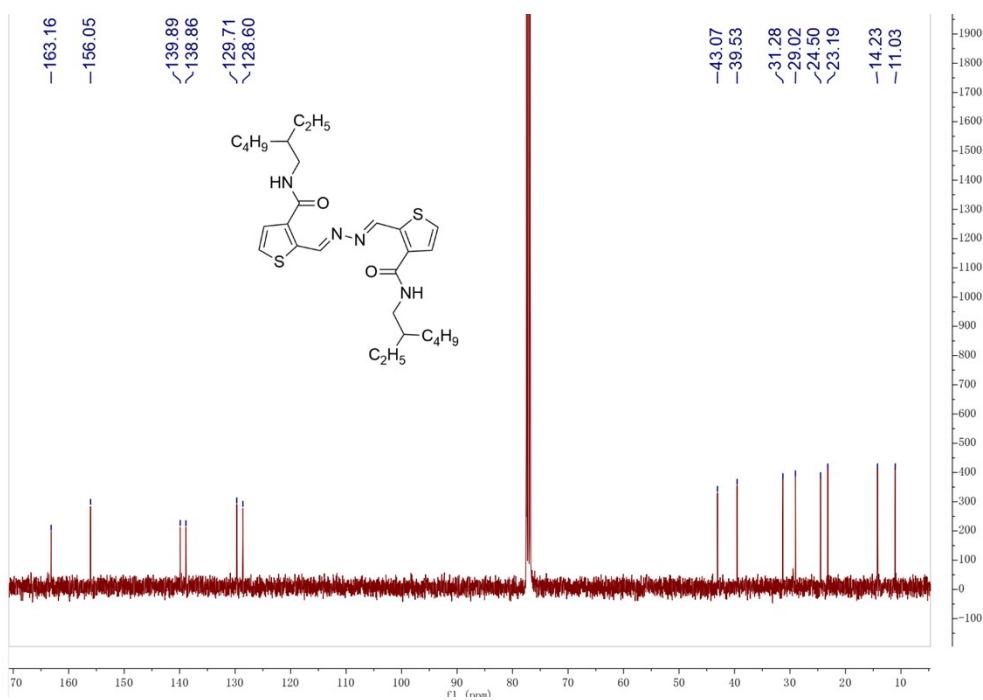


Figure S22. The ^{13}C NMR spectrum of monomer **Az3** in $CDCl_3$.

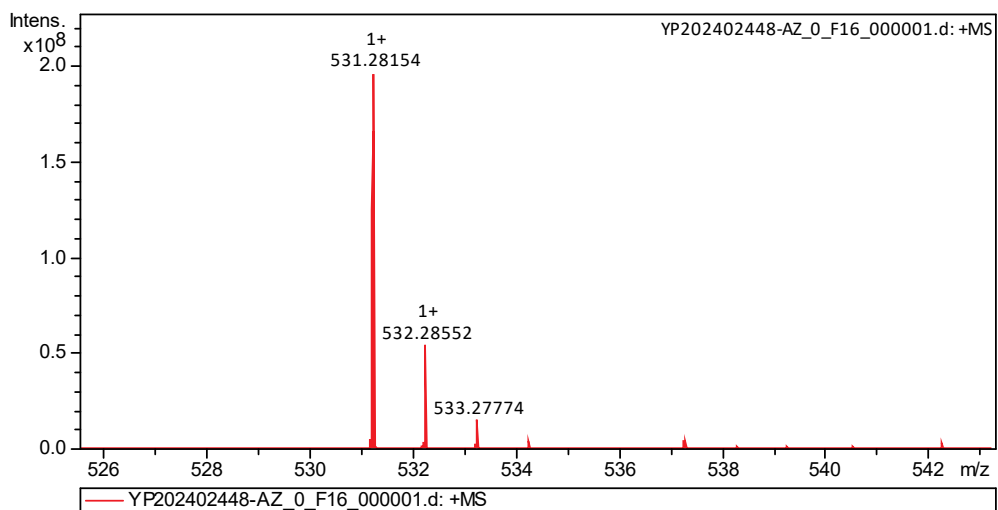


Figure S23. The MALDI-MS spectrum of **Az3**.

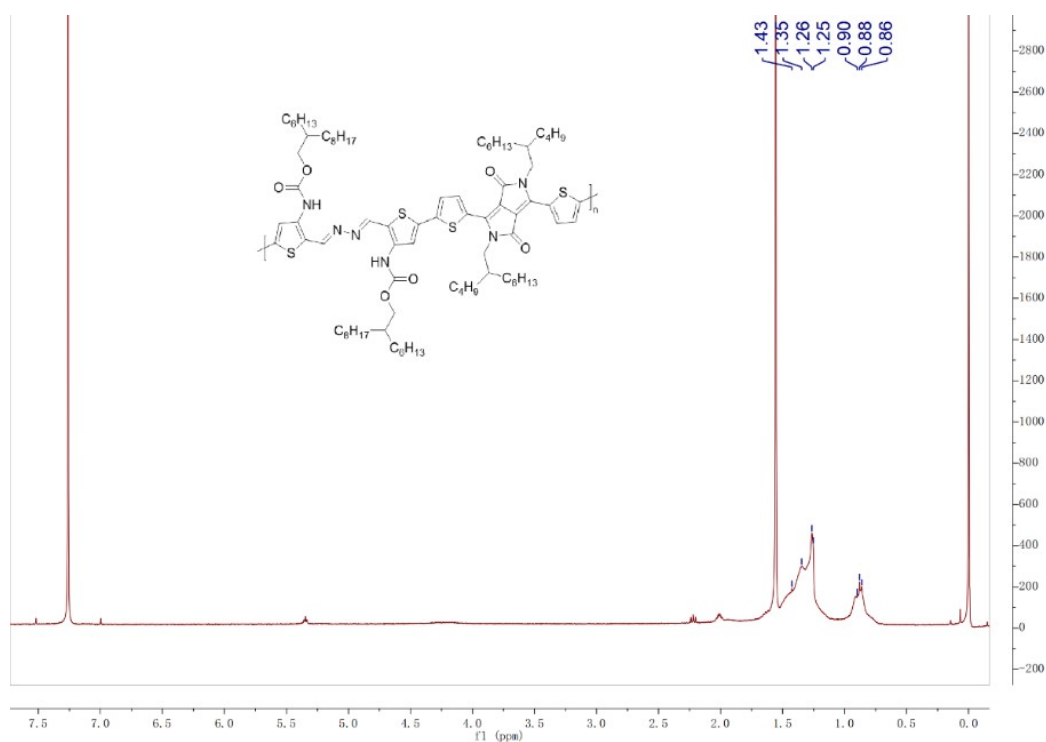


Figure S24. The 1H NMR spectrum of polymer **P1** in $CDCl_3$.

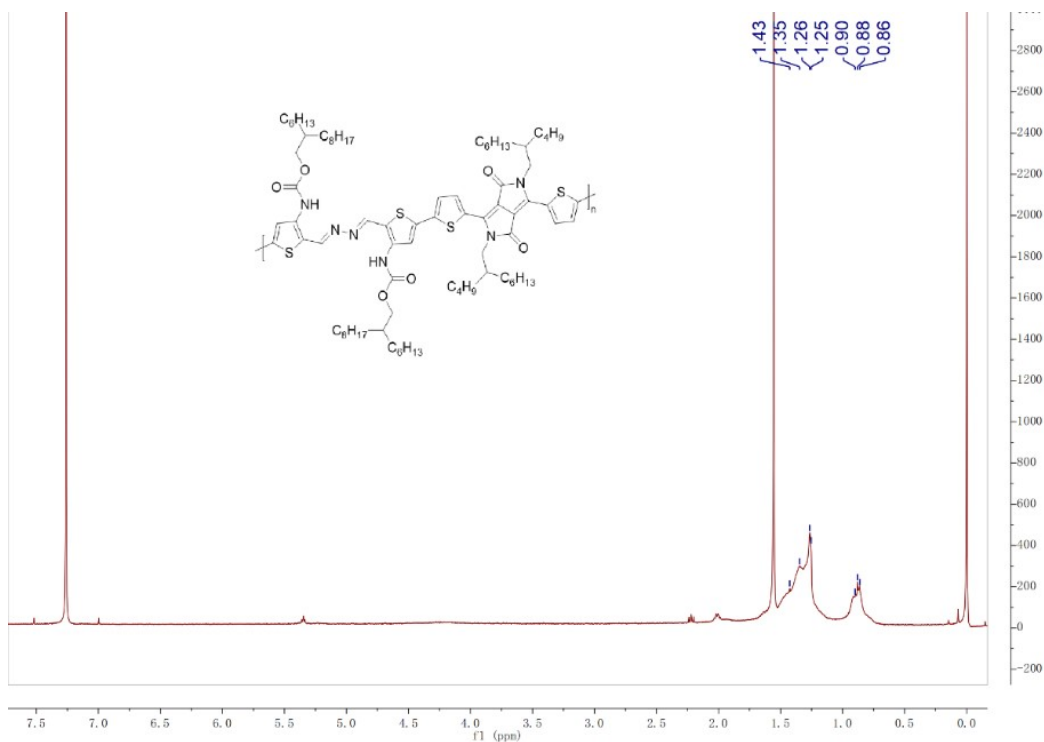


Figure S25. The ^1H NMR spectrum of polymer **P2** in CDCl_3 .

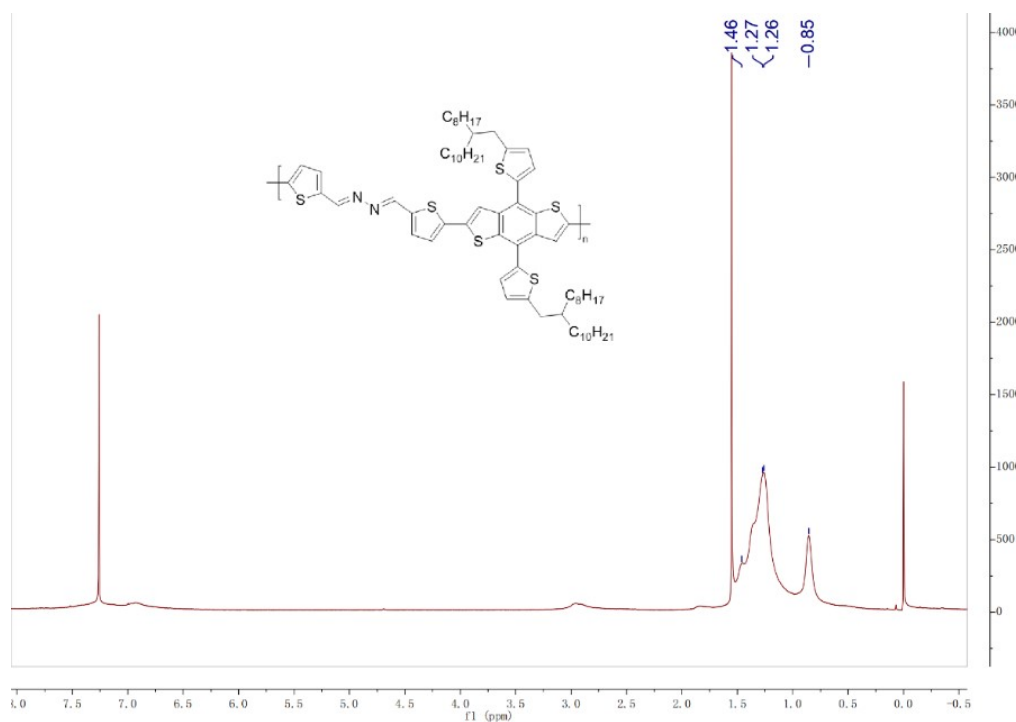


Figure S26. The ^1H NMR spectrum of polymer **P3** in CDCl_3 .

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