Electronic Supplementary information (ESI)

An Extraordinary Cyclohexylmethyl Side Chain Dominating the Polymeric Donor's Packing Patterns and Energy Levels for Efficient Non-fullerene Polymer Solar Cells

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Materials and Methods

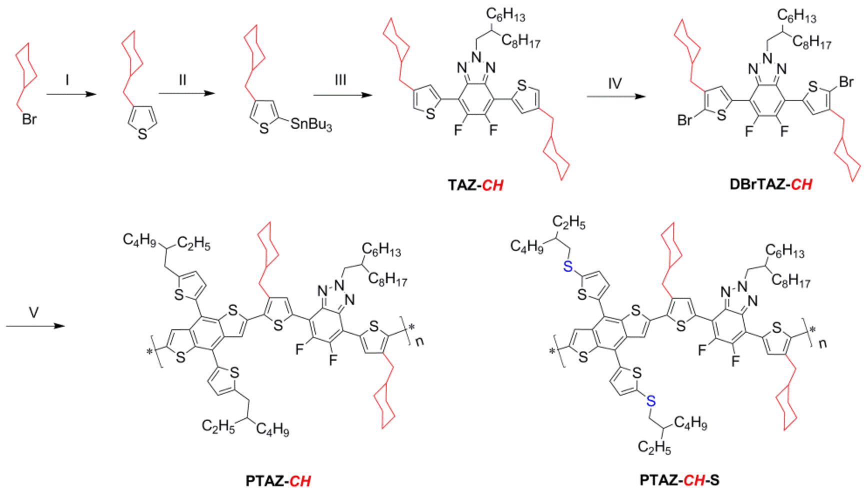
Common solvents were obtained as reagent grade, deuterated chloroform ($CDCl_3$), anhydrous chlorobenzene (CB, 99.8%) and *o*-dichlorobenzene (*o*-DCB) were purchased from Sigma-Aldrich without further treatment. Dry tetrahydrofuran (THF) and toluene were carefully dried and distilled from appropriate drying agents prior to use. 4,7-Dibromo-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole, 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexylthio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene were purchased from SunaTech Inc. Commercially available reagents 3-bromothiophene, (bromomethyl)cyclohexane, *n*-butyllithium (1.6 M in hexane), tributyltin chloride, tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu_4NPF_6), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) and tri(*o*-tolyl)phosphine (P(*o*-tol)$_3$) were purchased from Aladdin or Sigma-Aldrich and used without further purification unless otherwise stated. Indium tin oxide (ITO) coated glass substrates with sheet resistance of $10\ \Omega\ \square^{-1}$ were obtained from Shenzhen Display Inc. (China). PFN–Br, ITIC and IT–M were purchased from Derthon Optoelectronic Materials and PEDOT:PSS (CleviosTM PVP. Al 4083) was obtained from Heraeus Materials Technology Ltd. Nuclear magnetic resonance (NMR) spectra were measured in $CDCl_3$ on a Bruker AVANCE 600 MHz Fourier transform NMR spectrometer, chemical shifts were quoted relative to the internal standard tetramethylsilane (TMS). The molecular weights of the polymers were measured by the gel permeation chromatography (GPC) performed on PL–GPC 220 (Agilent), and polystyrene was used as the standard (150 °C, TCB as the eluent). Absorption spectra were recorded with a Hitachi U–4100 UV–vis–NIR scanning spectrophotometer. Photoluminescence (PL) spectra of thin films on a quartz substrate were measured using a Hitachi F4500 spectrofluorometer. Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation. It is equipped with a three-electrode cell consisting of a glassy carbon working electrode, a saturated calomel electrode (SCE) reference electrode and a platinum wire counter electrode. The measurements were carried out in anhydrous acetonitrile containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte under argon atmosphere at a scan rate of 100 mV/s. Thin films were deposited from chloroform solution onto the working electrodes and dried under nitrogen prior to measurement. The redox potential of the Fc/Fc^+ internal reference is 0.40 V vs. SCE. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels, were determined by calculating the empirical formula of $E_{\mathrm{HOMO}} = -\mathrm{e}(E_{\mathrm{ox}} + 4.8 - \mathrm{E}_{(\mathrm{Fc/Fc+})}{}^{1/2})$, $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{g}}$, where E_{ox} and E_{g} were the onset oxidation potential and the optical band gap, respectively. Atomic force microscope (AFM) images were acquired with Agilent–5400 scanning probe microscope with a Nanodrive controller in tapping mode with MikroMasch NSC–15 AFM tips with resonant frequencies ~300 kHz. Bright field transmission electron microscopy (TEM) data were acquired using a HITACHI H–7650 electron microscope operating at an acceleration voltage of 100 kV. Grazing incidence wide–angle X–ray scattering (GIWAXS) patterns were acquired by beamline BL16B1 (Shanghai Synchrotron Radiation Facility). The X–ray wavelength was 0.124 nm (E = 10 keV), and the incidence angle was set to 0.2 degree. The ground-state geometries of BDT–ffTAZ repeating units were fully optimized with DFT method under ωB97XD[1]/6-31g(d) level using Gaussian 09 package.[2] Mass spectrometry experiments were performed on a 15 T SolariX XR Fourier transform ion cyclotron resonance (FTICR) spectrometer (Bruker Daltonics, Bremen, Germany) coupled with a standard APPI source.

Device Fabrication and Testing

The devices were fabricated with a configuration of ITO/PEDOT:PSS/polymer:SMA/PFN–Br/Al.[3] ITO coated substrates were cleaned with detergent, deionized water, acetone and isopropyl alcohol in an ultrasonic bath sequentially for 15 minutes, and dried by ultra-pure N_2 and then treated with O_2 plasma for 6 min. Then, a 30 nm PEDOT:PSS was spin-cast on ITO coated glass at 4000 rpm and baked at 150 °C for 20 min in an oven, the substrates were transferred to a glove box filled with N_2. CB solutions consisting of polymers and SMA in different blend ratios were stirred overnight at room temperature (the optimized polymer concentrations for PTAZ–*CH* and PTAZ–*CH*–S are 7.5 and 10 mg mL^{-1}, respectively). The solution was spin-coated to form the active layer on the ITO/PEDOT:PSS substrate, the optimized thicknesses of PTAZ–*CH*/ITIC and PTAZ–*CH*–S/ITIC film are ~110 and ~114 nm respectively, estimated using Veeco Dektak 150 surface profiler. Subsequently, an ultrathin layer of PFN–Br (0.2 mg mL^{-1} in methanol) was cast on the active layer under 2600 rpm for 20 s. Finally, Al (100 nm) metal electrode was thermal evaporated under about 4×10^{-4} Pa and the device area was 0.1 cm^2 defined by shadow mask.

Current density–voltage (J–V) characteristics of the devices were recorded using Keithley 2420 source measurement unit under the illumination of AM 1.5G (100 mW cm^{-2}, Newport solar simulator). Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. The hole only device employed a device architecture of ITO/PEDOT:PSS/active layer/MoO_3/Al and the electron-only device employed a device architecture of ITO/ZnO/active layer/ PFN–Br/Al, and related thicknesses of the active layers determined by Dektak 150 surface profiler. The mobility was measured using the space-charge-limited current (SCLC) method,[4] which fits J–V curve with a space charge limited form, where the SCLC is described by $J = 9\varepsilon_0\varepsilon_r\mu_{h(e)}V^2/8d^3$, where ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative permittivity of the material (assumed to be 3), μ_h is the hole mobility and μ_e is the electron mobility. $V = V_{appl} - V_{bi} - V_s$ (V_{appl} is the applied voltage, V_{bi} is the built-in voltage, V_s is the voltage drop from the substrates series resistance) and d is the thickness of the related films.

Synthesis and Characterization



Scheme S1. Synthetic routes of the monomers and polymers. I, (1) Mg, I_2, ether, reflux; (2) 3-bromothiophene, Ni(dppp)Cl_2, reflux, overnight; II, (3) *n*-BuLi, THF, −78 °C to rt, 2 hours; (4)

tributyltin chloride, rt, overnight; III, 4,7-dibromo-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole, $Pd_2(dba)_3$, P(*o*-tol)$_3$, toluene, reflux, overnight; IV, NBS, $CHCl_3$/AcOH, 30 minutes; V, 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene or 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexylthio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene, $Pd_2(dba)_3$, P(*o*-tol)$_3$, toluene, reflux, overnight.

3-(cyclohexylmethyl)thiophene was synthesized using the Ni (II) catalyzed cross-coupling method between 3-bromothiophene and Grignard reagents.[5] ^{1}HNMR (600 MHz, $CDCl_3$): δ (ppm) 7.224–7.211 (dd, J_1 = 4.86 Hz, J_2 = 3 Hz, 1H), 6.898 (d, J = 4.86 Hz, 1H), 6.882 (d, J = 2.16 Hz, 1H), 2.501 (d, J = 7.08 Hz, 2H), 1.695–1.654 (m, 5H), 1.234–1.141 (m, 4H), 0.946–0.891 (m, 2H).

4,7-bis(4-(cyclohexylmethyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole. To a stirred solution of 3-(cyclohexylmethyl)thiophene (9.0 g, 50 mmol) in dry THF (100 mL) was added dropwise *n*-BuLi (34.4 mL, 55 mmol, 1.6 M in hexane) at −78 °C, the reaction mixture was kept at −78 °C for 1h, then warmed up to room temperature and stirred for 2h. After cooling the mixture to −78 °C, tributyltin chloride (17.9 g, 55 mmol) was added dropwise. The acetone-liquid nitrogen bath was moved away and the mixture was stirred for another 2h. The solvents were removed under reduced pressure and then 50 mL hexane was added, the white precipitate was filtered off and washed with hexane for three times. The filtrate was combined and hexane was removed under reduced pressure, tributyl(4-(cyclohexylmethyl)thiophen-2-yl)stannane was obtained as brown liquid and used for next step without further purification. Under an argon atmosphere, 4,7-dibromo-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole (0.54 g, 1 mmol), tributyl(4-(cyclohexylmethyl)thiophen-2-yl)stannane (1.41 g, 3 mmol), $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol) and P(*o*-tol)$_3$ (36.5 mg, 0.12 mmol) were mixed into a 50 mL flask, then 20 mL dry toluene was added. The mixture was heated reflux overnight, then cooled to room temperature and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: petroleum ether/CH_2Cl_2=10:1, v/v) and dried under vacuum to provide 4,7-bis(4-(cyclohexylmethyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole as a light yellow liquid (yield = 80.2%, 0.59 g). ^{1}HNMR (600 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 2.1 Hz, 2H), 7.10 (d, J = 2.04 Hz, 2H), 4.73 (d, J = 9.48 Hz, 2H), 2.59 (d, J = 10.44 Hz, 4H), 2.31–2.23 (m, 1H), 1.79–1.57 (m, 12H), 1.44–1.18 (m, 30H), 1.03–0.96 (m, 4H), 0.88–0.84 (m, 6H). ^{13}CNMR (150 MHz, $CDCl_3$): δ (ppm) 148.53, 148.33, 146.02, 145.82, 141.99, 137.61, 131.87, 131.77, 123.76, 110.02, 109.93, 59.84, 39.16, 39.05, 38.47, 33.22, 31.92, 31.86, 31.53, 29.88, 29.62, 29.55, 29.34, 26.94, 26.57, 26.40, 26.35, 26.33, 22.68, 22.67, 14.12, 14.10.

4,7-bis(5-bromo-4-(cyclohexylmethyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole. To a dry two necked 20 mL round bottom flask, 4,7-bis(4-(cyclohexylmethyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole (0.37 g, 0.5 mmol) was added, the flask was charged with nitrogen and 5 mL chloroform and 1 mL acetic acid were added in sequence. The reaction mixture was stirred with exclusion of light, and then *N*-bromosuccinimide (NBS) (0.18 g, 1 mmol) was added in 5 minutes. Afterward, the reaction mixture was detected by TLC until the start material was consumed, 10 mL deionized water was added and the product was extracted by dichloromethane for three times, the organic phase was combined and washed with water then dried using anhydrous sodium sulfate. After removing the solvent the crude product was purified by silica gel column chromatography (eluent: petroleum ether/CH_2Cl_2=15:1, v/v) and dried under vacuum to provide 4,7-bis(5-bromo-4-(cyclohexylmethyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*][1,2,3]triazole as a light yellow solid, which was recrystallized from the mixture of ethanol and tetrahydrofuran as needle-like crystal (yield = 96%, 0.4 g). ^{1}HNMR (600 MHz, $CDCl_3$): δ (ppm) 7.87 (s, 2H), 4.71 (d, *J* = 6.3 Hz, 2H), 2.54 (d, *J* = 7.2 Hz, 4H), 2.26–2.20 (m, 1H), 1.76–1.71 (m, 8H), 1.67–1.62 (m, 4H), 1.46–1.38 (m, 4H), 1.36–1.13 (m, 26H), 1.09–0.99 (m, 4H), 0.90–0.82 (m 6H). ^{13}CNMR (150 MHz, $CDCl_3$): δ (ppm) 147.99, 147.86, 146.31, 146.18, 141.18, 137.18, 131.66, 131.47, 113.74, 109.42, 109.35, 59.85, 39.09, 38.77, 37.20, 33.12, 31.93, 31.88, 31.54, 29.90, 29.64, 29.58, 29.35, 26.49, 26.41, 26.36, 26.28, 22.70, 14.14, 14.12. HRMS (APPI): *m/z* calcd for $C_{44}H_{61}Br_2F_2N_3S_2$: 891.26417; found: 891.26370 (spectrum shown in Figure S14).

Synthesis of Polymers. Polymers were synthesized according to a previous report. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene or 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexylthio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene (0.2 mmol), 4,7-bis(5-bromo-4-(cyclohexylmethyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[*d*][1,2,3]triazole (0.2 mmol), $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol) and $P(o\text{-}tol)_3$ (3.6 mg, 0.012 mmol) were dissolved into 6 mL toluene in a 25 mL round bottom flask protected by argon. The flask was purged three times with successive vacuum and argon filling cycles. The oil bath was heated to 110 °C gradually, and the reaction mixture was stirred for 18 h at 110 °C under argon atmosphere. After cooling, the mixture was cooled to room temperature and precipitated in 200 mL methanol. The precipitate was filtered and washed with methanol and hexane successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight.

PTAZ–*CH*, black solid, GPC: M_n = 68.61 kDa, PDI = 2.55. ^{1}HNMR (600 MHz, $CDCl_3$): δ (ppm) 8.10–8.03 (br, ArH), 7.71–7.67 (br, ArH), 7.34–7.30 (br, ArH), 6.90–6.86 (br, ArH), 4.71–4.65 (br, N-CH_2), 2.87–2.79 (br, CH_2), 2.77–2.71 (br, CH_2), 2.54–2.49 (br, CH), 2.25–2.16 (br, CH), 1.99–0.85 (br).

PTAZ–*CH*–S, GPC: M_n = 56.07 kDa, PDI = 2.58. ^{1}HNMR (600 M Hz, $CDCl_3$): δ (ppm) 8.10–8.04 (br, ArH), 7.68–7.61 (br, ArH), 7.39–7.34 (br, ArH), 7.08–7.03 (br, ArH), 4.72–4.71 (br, N-CH_2), 3.31–2.62 (br), 2.16–0.54 (br).

DFT Calculation

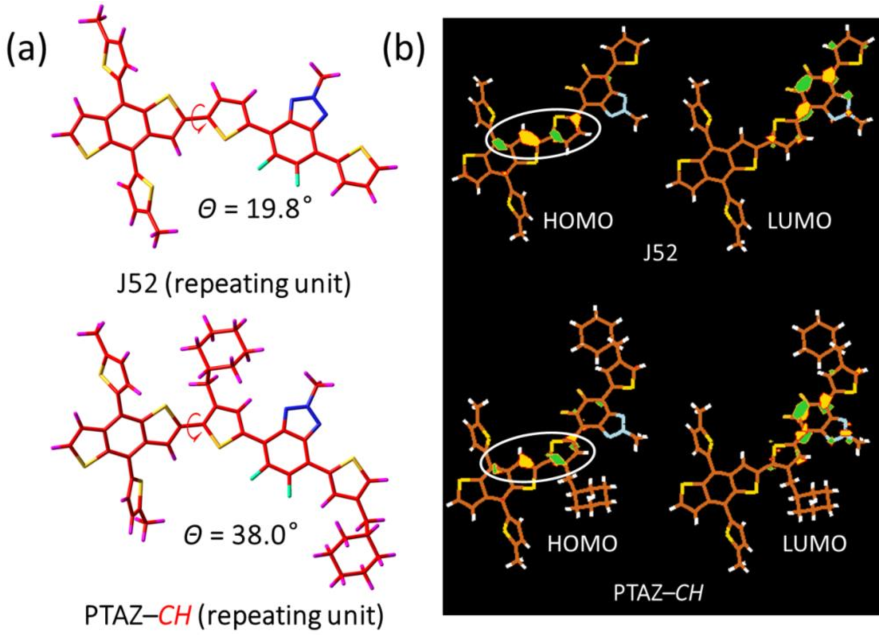


Figure S1. The ground-state geometries of J52 and PTAZ–*CH* repeating units (a, carbon atom: red, nitrogen atom: blue, sulfur atom: yellow, fluorine atom: green, hydrogen atom: purple), and the HOMO (left) and LUMO (right) distribution for polymer J52 and PTAZ–*CH* (b). To simplify the calculation, only one repeating unit of each polymer was subjected to the calculation, and 2-ethylhexyl and 2-hexyldecyl were replaced by CH_3 groups.

GPC Measurement

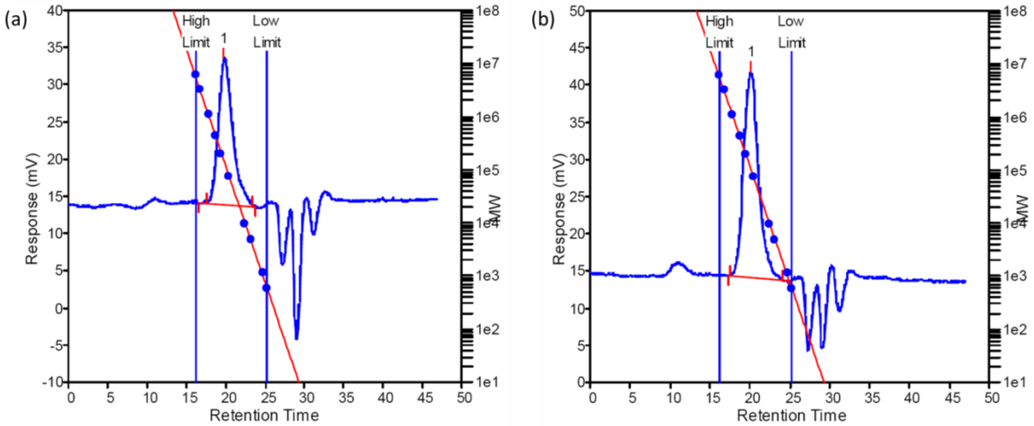


Figure S2. GPC chromatograms of polymer PTAZ−*CH* (a) and PTAZ−*CH*−S (b), 1,2,4-trichlorobenzene as an eluent at a column temperature of 150 °C.

UV-vis and Absorption Coefficient

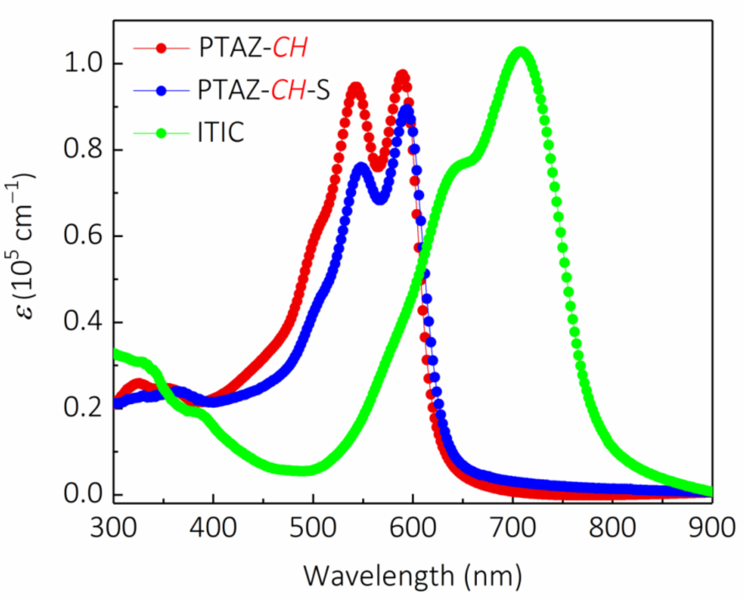


Figure S3. UV–vis absorption spectra for pristine PTAZ–*CH*, PTAZ–*CH*–S and ITIC films.

AFM of the Pristine Films

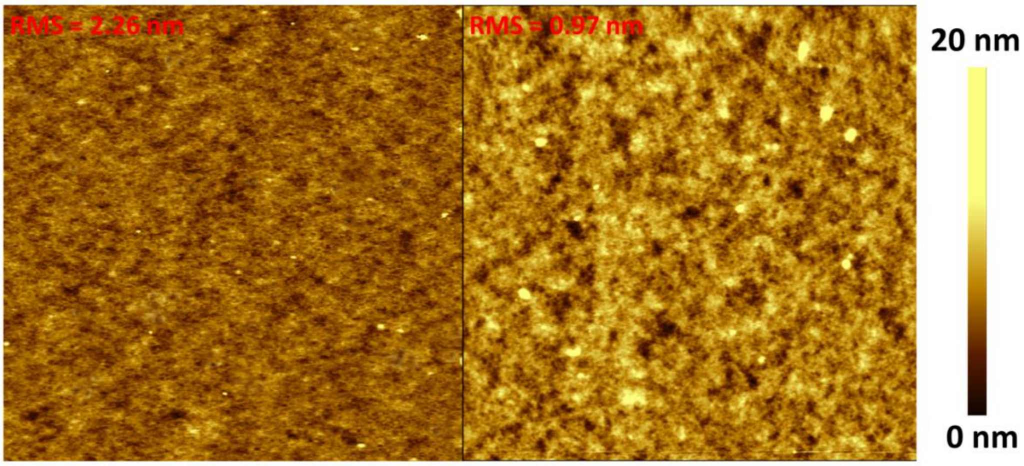


Figure S4. AFM height images (5×5 μm) for PTAZ–*CH* (left) and TAZ–*CH*–S (right) pristine films.

Photoluminescence (PL) Measurement

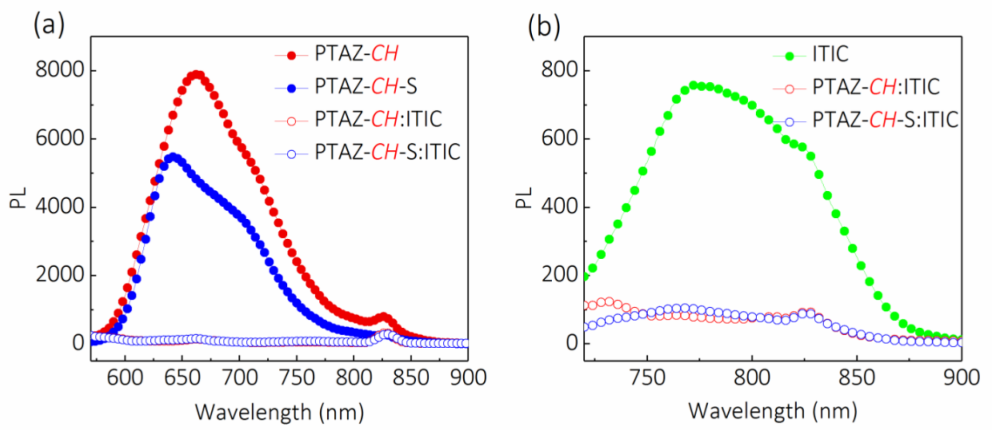


Figure S5. PL spectra of PTAZ–*CH*, PTAZ–*CH*–S, PTAZ–*CH*:ITIC and PTAZ–*CH*–S:ITIC films excited at 550 nm (a), and ITIC, PTAZ–*CH*:ITIC and PTAZ–*CH*–S:ITIC films excited at 700 nm (b).

Table S1. Summary of the device parameters with variety of spinning rates

Blends	rotation rate (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTAZ−*CH*:ITIC	1500	0.89	17.70	67.10	10.51
	1700	0.89	18.15	69.47	11.19
	1800	0.89	18.20	70.04	11.28
	2000	0.90	17.69	70.67	11.22
	2100	0.90	16.91	71.13	10.81
PTAZ−*CH*-S:ITIC	1800	0.95	17.479	71.87	11.87
	2000	0.95	17.22	72.36	11.82
	2200	0.95	17.14	70.98	11.56
	2500	0.94	17.61	73.19	12.15
	2700	0.95	16.45	73.73	11.52

TA Treated PSCs

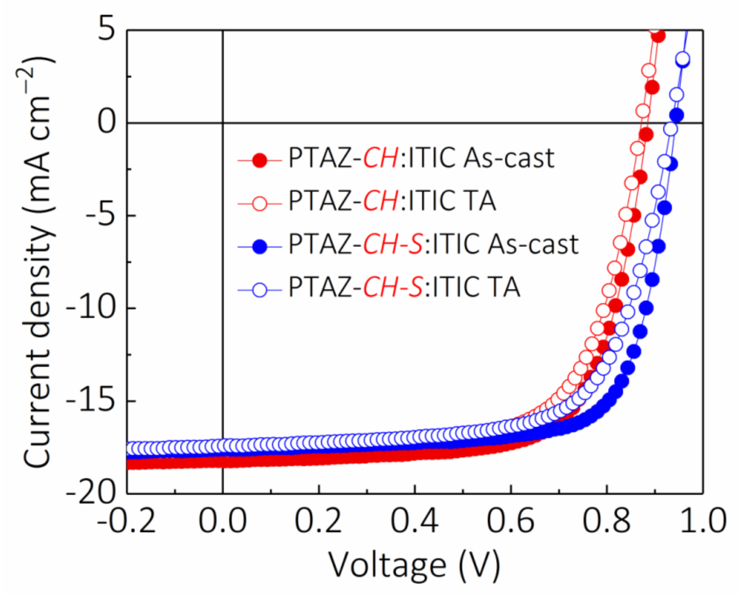


Figure S6. *J–V* curves of the as-cast and thermal annealed devices.

Table S2. Summary of the device characteristics for the as-cast and thermal annealed PSCs

Active layer	TA	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTAZ−*CH*: ITIC	None	0.89	18.20	70.037	11.28
	130 °C for10 min	0.87	17.63	67.90	10.49
PTAZ−*CH* −S:ITIC	None	0.94	17.61	73.19	12.15
	130 °C for10 min	0.93	17.42	67.71	11.03

Charge Carrier Mobility

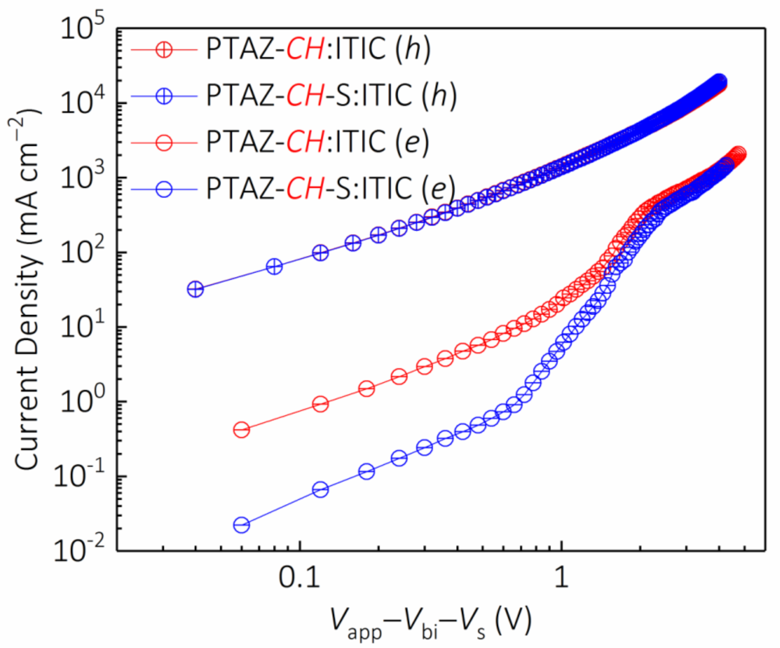


Figure S7. J–(V_{app}–V_{bi}–V_s) characteristics for PTAZ–*CH*:ITIC and PTAZ–*CH*–S:ITIC based devices. The film thickness:

PTAZ–*CH*:ITIC (*h*), 115 nm.

PTAZ–*CH*–S:ITIC (*h*), 121 nm.

PTAZ–*CH*:ITIC (*e*), 152 nm.

PTAZ–*CH*–S:ITIC (*e*), 152 nm.

XRD for ITIC

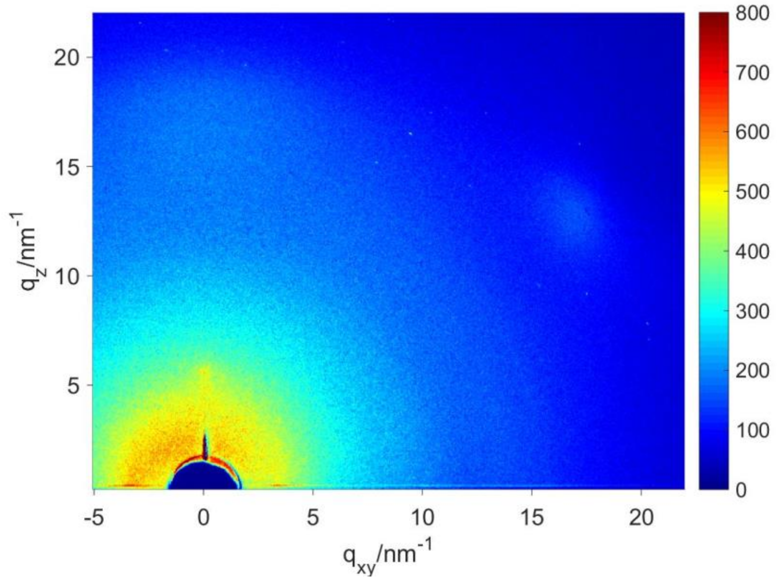


Figure S8. 2D–GIWAXS patterns for as-cast pristine ITIC film.

Device Performance for Polymer:IT−M

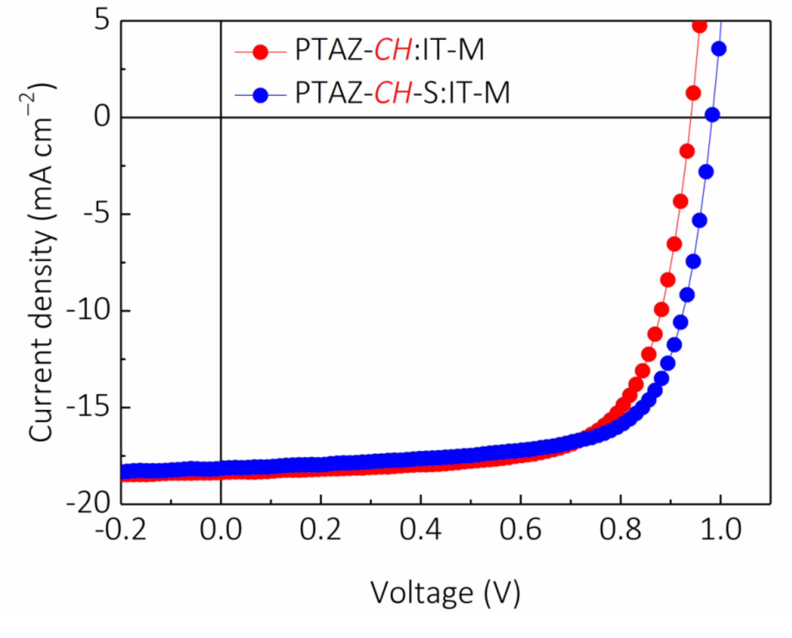


Figure S9. *J*–*V* curves for the optimized PTAZ−*CH*:IT−M and PTAZ−*CH*−S:IT−M based PSCs.

Table S3. Summary of the device performances for polymer:IT−M based PSCs

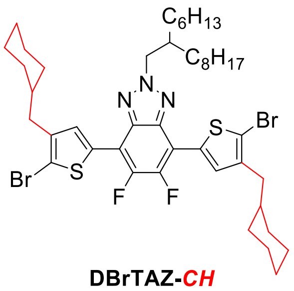
Active layer	Rotation rate (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTAZ−*CH*:IT−M	1300	0.94	17.48	71.16	11.66
	1500	0.94	18.35	70.85	12.22
	1600	0.94	16.79	72.27	11.46
	1700	0.94	16.66	72.24	11.28
	1800	0.94	17.41	71.87	11.81
	2000	0.94	16.86	72.25	11.44
PTAZ−*CH*−S:IT−M	1400	0.98	16.48	71.27	11.47
	1600	0.99	18.01	71.47	12.70
	1700	0.98	17.93	70.99	12.46
	1800	0.99	17.84	71.55	12.59
	1900	0.98	18.14	71.62	12.76
	2000	0.98	17.76	71.41	12.41
	2300	0.98	16.75	71.71	11.80

Device architecture: ITO/PEDOT:PSS/polymer:IT−M/PFN–Br/Al.

Solution concentration: 7.5 mg mL^{-1} for PTAZ–*CH* and 10 mg mL^{-1} for PTAZ–*CH*–S in CB solution.

Donor:acceptor ratio = 1:1 wt%.

NMR spectra



DBrTAZ-*CH*

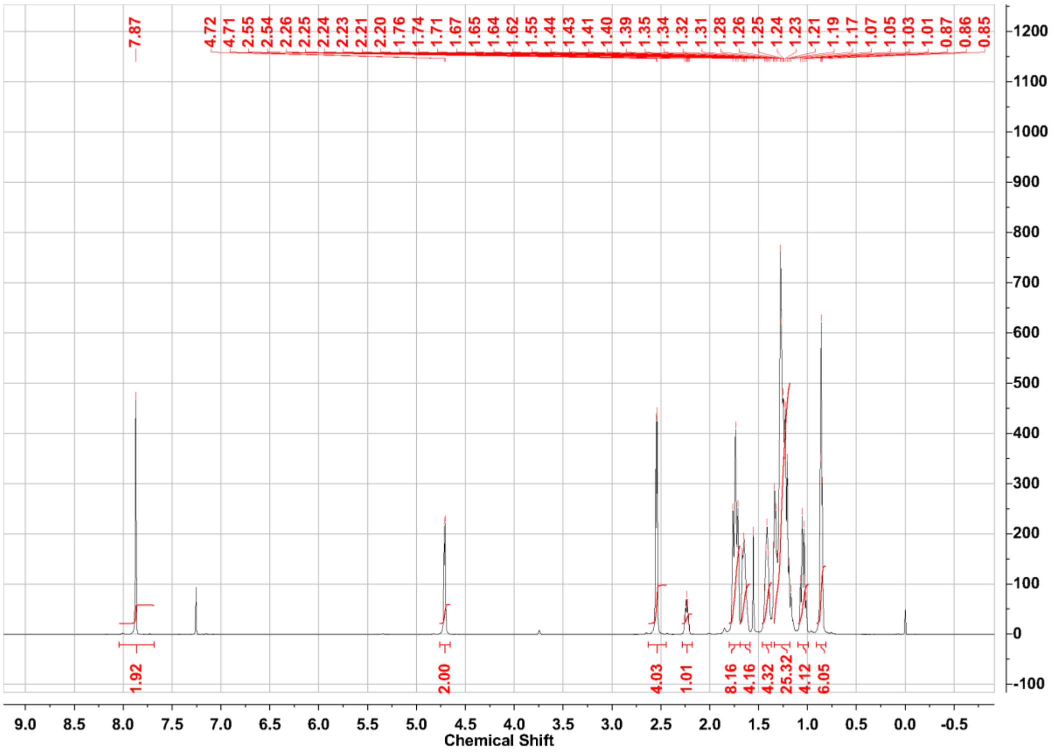
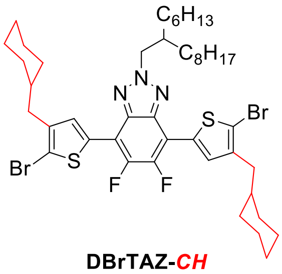


Figure S10. ^{1}HNMR spectra for monomer DBrTAZ–*CH*.



DBrTAZ-*CH*

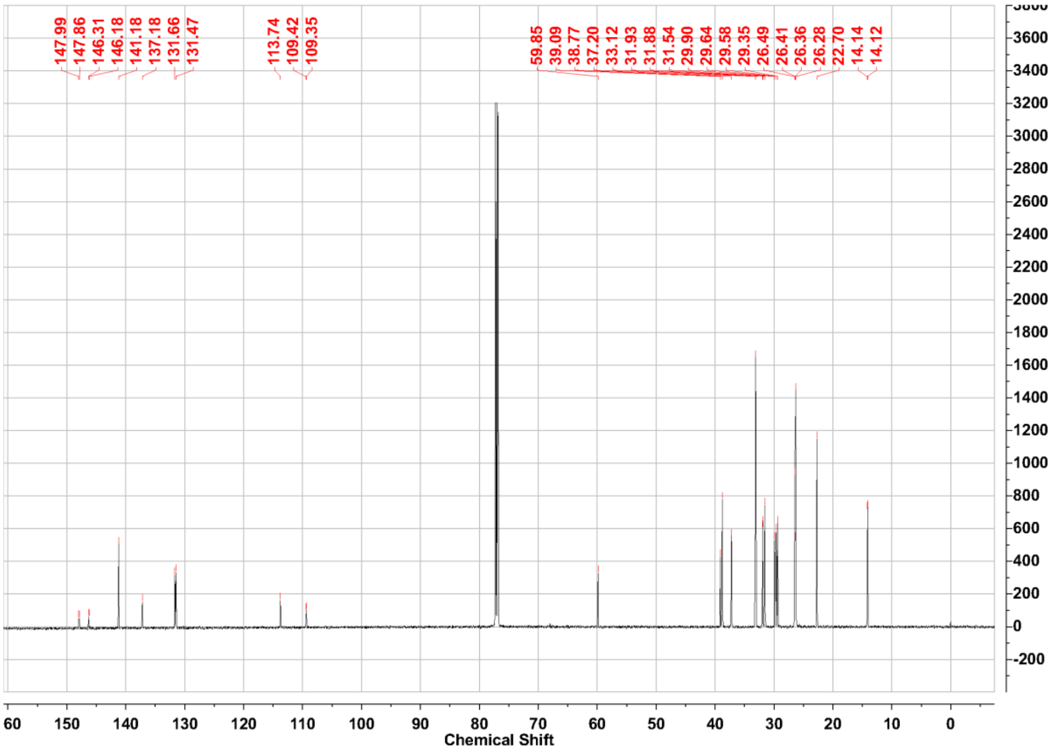
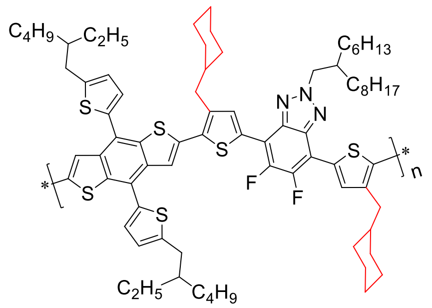


Figure S11. ^{13}CNMR spectra for monomer DBrTAZ–*CH*.



PTAZ-*CH*

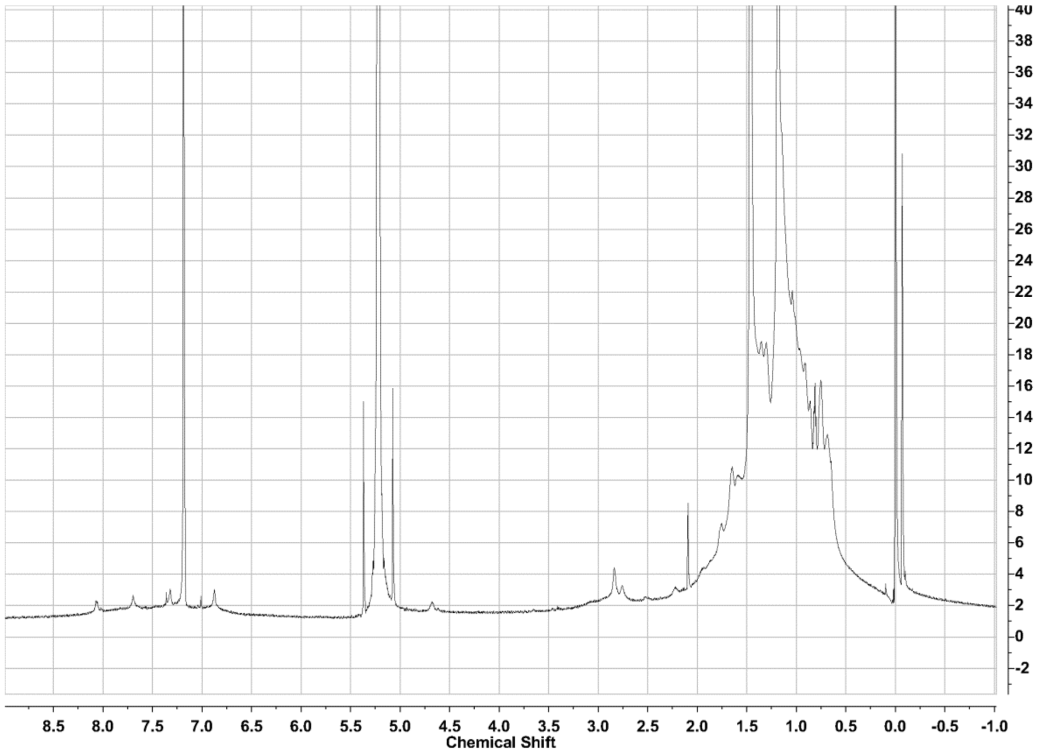
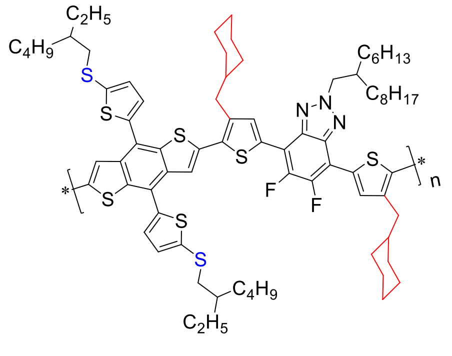


Figure S12. ^{1}HNMR spectra for polymer PTAZ–*CH*.



PTAZ-*CH*-S

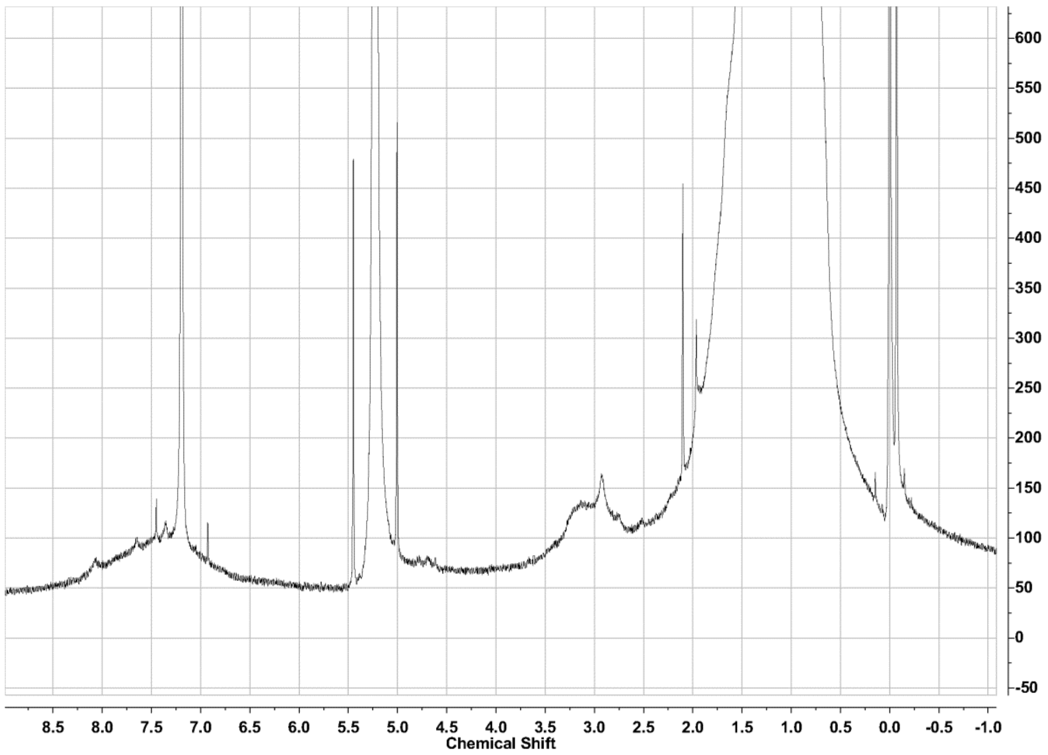


Figure S13. ^{1}HNMR spectra for polymer PTAZ–*CH*–S.

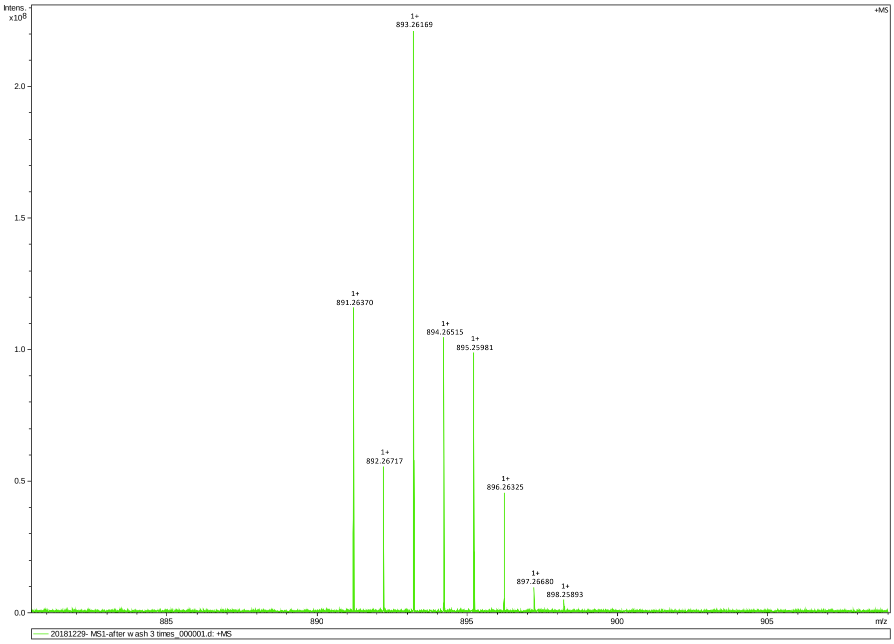


Figure S14. HRMS of the monomer DBrTAZ–*CH*.

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