

Supporting Information for

Indacenodithieno[3,2-b]thiophene-Based Broad Bandgap Polymers for High Efficiency Polymer Solar Cells

Yun-Xiang Xu,^a Chu-Chen Chueh,^a Hin-Lap Yip,^a Chih-Yu Chang,^a Po-Wei Liang,^a Jeremy J. Intemann,^a Wen-Chang Chen,^b and Alex K.-Y. Jen^{*a}

^aDepartment of Materials Science and Engineering, University of Washington, Seattle, WA 98195 (USA) E-mail: ajen@u.washington.edu

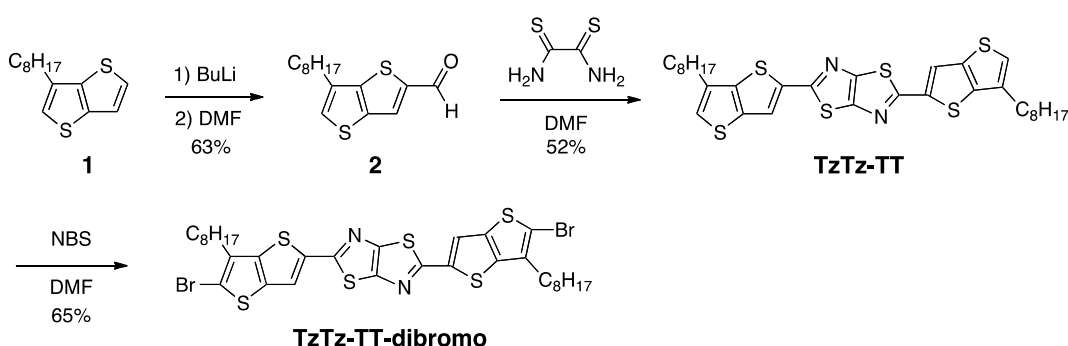
^bDepartment of Chemical Engineering and Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan

Experimental details

Materials: All chemicals, unless otherwise specified, were purchased from Aldrich and used as received. Compound IDTT-di-Tin, 2,5-bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole (TzTz-dibromo) and 3-octylthieno[3,2-b]thiophene were synthesized according to the reported procedures.¹⁻³

General characterization methods: UV-Vis spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. The ¹H and ¹³C NMR spectra were collected on a Bruker AV 300 and 500 spectrometer operating at 300 and 125 MHz in deuterated chloroform solution with TMS as reference, respectively. High-resolution mass spectroscopy (HRMS) measurements were performed on a Bruker Apex-Qe FT/ICR and MALDI-TOF experiment was performed using a Bruker Autoflex II from UW Department of Medicinal Chemistry. Elemental analysis was determined at QTI (Whitehouse, NJ). Gel permeation chromatography (GPC) measurements were performed on GPC Model 120 (DRI, PLBV400HT viscometer) against polystyrene standards in chlorobenzene at 60 °C. Thermal transitions were measured on a TA Instruments Q20-

1066 Differential Scanning Calorimeter with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Cyclic voltammetry of polymer films was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate using a scan rate of 100 mV s^{-1} . ITO, Ag/AgCl and Pt mesh were used as working electrode, reference electrode and counter electrode, respectively. AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller.



Synthesis of compound 2: n-BuLi (2.5 M in hexane, 1.74 mL, 4.36 mmol) was added to a solution of 3-octylthieno[3,2-b]thiophene (1.00 g, 3.96 mmol) in dry THF (25 mL) at $0\text{ }^{\circ}\text{C}$ under Argon. After 1 h, DMF (0.61 mL, 7.92 mmol) was added dropwise at $0\text{ }^{\circ}\text{C}$ and stirred overnight at room temperature. The solution was washed with 5% hydrogen chloride solution and dried with sodium sulfate and the solvent was evaporated. The residue was purified by silica gel chromatography (hexane/DCM = 1:1) to afford an oil (698 mg, 63%). $^1\text{H NMR}$ (300 MHz, CDCl_3 , δ): 9.91 (s, 1 H), 7.86 (s, 1 H), 7.26 (s, 1 H), 2.69 (t, $J = 7.5\text{ Hz}$, 2 H), 1.76-1.66 (m, 2 H), 1.29-1.22 (m, 10 H), 0.84 (t, $J = 7.5\text{ Hz}$, 3 H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3 , δ): 183.4, 146.2, 144.6, 138.5, 135.5, 129.6, 128.4, 31.8,

29.6, 29.2, 29.2, 29.1, 28.3, 22.6, 14.0. HRMS (ESI) m/z : $[M + Na]^+$ calcd for $C_{15}H_{20}OS_2Na$, 303.0848; found, 303.0848.

Synthesis of compound TzTz-TT: In a 25 mL three-neck flask was added compound 2 (600 mg, 2.14 mmol), dithioamide (122 mg, 1.02 mmol) and DMF (20 mL) under argon. The mixture was heated to reflux and stirred overnight. Then the solution was cooled down, poured into water (50 ml) and extracted with dichloromethane (3×30 mL). The organic layer was combined and washed with water (3×30 mL) and dried over sodium sulfate. The solvent was evaporated and the residue was purified by silica gel chromatography (hexane/DCM = 2:1) to afford a solid (339 mg, 52%). mp 148-151 °C. 1H NMR (300 MHz, $CDCl_3$, δ): 7.74 (s, 1 H), 7.11 (s, 1 H), 2.75 (t, $J = 7.5$ Hz, 2 H), 1.78-1.75 (m, 2 H), 1.35-1.28 (m, 10 H), 0.88 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 162.7, 149.8, 141.5, 139.0, 138.1, 135.3, 124.5, 119.5, 31.9, 29.8, 29.4, 29.2, 28.5, 22.7, 14.1. HRMS (ESI) m/z : $[M]^+$ calcd for $C_{32}H_{38}N_2S_6$, 642.1354; found, 642.1364.

Synthesis of compound TzTz-TT-dibromo: N-bromosuccinimide (201 mg, 1.13 mmol) was slowly added into a stirred solution of compound TzTz-TT (316 mg, 0.49 mmol) in DMF (20 mL). the mixture was heated at 80 °C for an hour and then cool down to room temperature. The reaction was quenched with water. The precipitate was filtered and washed with water and methanol. After drying, the residue was purified by recrystallization from dichloromethane to provide a solid (255 mg, 65%). mp 225-228 °C. 1H NMR (300 MHz, $CDCl_3$, δ): 7.65 (s, 1 H), 2.76 (t, $J = 7.5$ Hz, 2 H), 1.78-1.69 (m, 2 H), 1.35-1.26 (m, 10 H), 0.88 (t, $J = 7.5$ Hz, 3 H). MS (MALDI) m/z : $[M]^+$ calcd for

$C_{32}H_{36}Br_2N_2S_6$, 797.957; found, 798.279. Anal. Calcd for $C_{32}H_{36}Br_2N_2S_6$: C, 47.99; H, 4.53; N, 3.50. Found: C, 47.82; H, 4.35; N, 3.34.

Polymerization of PIDTT-TzTz. IDT-di-Tin (150 mg, 0.11 mmol) and TzTz-dibromo (49 mg, 0.11 mmol) were charged in a 25 mL three-neck flask under argon. After adding toluene (5 mL), the mixture was degassed by three freeze/pump/thaw cycles to remove O_2 . Then $Pd_2(dba)_3$ (5.1 mg, 5mol%) and $P(o-tol)_3$ (13.8 mg, 0.045 mmol) were added. The mixture was degassed once more. Then the mixture was heated at 120 °C for 3 d. After cooling to RT, the mixture was poured into methanol. The precipitate was collected and washed by Soxhlet extraction sequentially with acetone, hexane, and chloroform. The remaining solid in the filter was collected and dried (85 mg, 61%). 1H NMR (500 MHz, $CDCl_3$, δ): 7.52-7.45 (m, 6 H), 7.34 (m, 2 H), 7.21-7.10 (m, 16 H), 2.60-2.54 (m, 8 H), 1.62-1.55 (m, 8 H), 1.30 (m, 24 H), 0.88-0.84 (m, 12 H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 128.6, 128.5, 128.0, 127.9, 35.6, 31.7, 31.3, 29.2, 22.6, 14.1. Molecular weight: $M_n = 26$ kDa, PDI = 4.18. Anal. Calcd for $C_{80}H_{78}N_2S_8$: C, 72.57; H, 5.94; N, 2.12. Found: C, 72.10; H, 5.34; N 1.84.

Polymerization of PIDTT-TzTz-TT. IDT-di-Tin (114 mg, 0.085 mmol) and TzTz-TT-dibromo (64.5 mg, 0.081 mmol) were charged in a 25 mL three-neck flask under argon. After adding toluene (3 mL), the mixture was degassed by three freeze/pump/thaw cycles to remove O_2 . Then $Pd_2(dba)_3$ (3.9 mg, 5mol%) and $P(o-tol)_3$ (10.3 mg, 0.034 mmol) were added. The mixture was degassed once more. Then the mixture was heated at 120 °C for 3 d. After cooling to RT, the mixture was poured into methanol. The precipitate was collected and washed by Soxhlet extraction sequentially with acetone, hexane, and chloroform. The remaining solid in the filter was collected and dried (80 mg, 59%). 1H

NMR (500 MHz, CDCl_3 , δ): 7.70 (s, 2 H), 7.54 (s, 2 H), 7.39 (s, 2 H), 7.23-7.11 (m, 16 H), 2.91 (m, 4 H), 2.60-2.55 (m, 8 H), 1.77 (m, 4 H), 1.60-1.55 (m, 8 H), 1.30-1.28 (m, 44 H), 0.88-0.84 (m, 18 H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 128.5, 128.0, 35.6, 31.9, 31.7, 31.3, 29.4, 29.2, 22.7, 22.6, 14.0. Molecular weight: $M_n = 34$ kDa, PDI = 3.91. Anal. Calcd for $\text{C}_{100}\text{H}_{110}\text{N}_2\text{S}_{10}$: C, 72.33; H, 6.68; N, 1.69. Found: C, 70.78; H, 6.13; N, 1.51.

Device Fabrication and Characterization of FET: Field-effect transistors were fabricated through the top-contact and bottom-gate geometry. Heavily doped p-type silicon <100> substrates with a 300 nm thermal oxide layer were purchased from Montco Silicon Technologies INC. After cleaning the substrate by sequential ultrasonication in acetone and isopropyl alcohol for 15 min followed by air plasma treatment, the oxide layer was passivated with a thin divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) buffer layer. Polymer thin films were spin-coated from a 0.5 wt % DCB solution. Interdigitated source and drain electrodes ($W=1000$ μm , $L= 20/30$ μm) were defined by evaporating a Au (40 nm) through a shadow mask from the resistively heated Mo boat below 2×10^{-6} Torr. OFET characterization was carried out in a N_2 -filled glovebox using an Agilent 4155B semiconductor parameter S6 analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of $(I_{\text{ds}})_{1/2}$ vs V_{gs} . The threshold voltage (V_t) was estimated as the x intercept of the linear section of the plot of $(I_{\text{ds}})_{1/2}$ vs V_{gs} . The sub threshold swing was calculated by taking the inverse of the slope of I_{ds} vs V_{gs} in the region of exponential current increase.

Device Fabrication and Characterization of PSCs: To fabricate the conventional solar cells, ITO-coated glass substrates (15 Ω /sq.) were cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol. A thin layer (ca. 40 nm) of PEDOT:PSS (Baytron® P VP AI 4083, filtered at 0.45 μ m) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 5,000 rpm and baked at 140 $^{\circ}$ C for 10 minutes under ambient conditions. The substrates were then transferred into an N_2 -filled glove-box. Subsequently, the polymer:PC₇₁BM active layer (1:3 wt, 80~90 nm, prepared by dissolving the polymer in o-dichlorobenzene and filtered with a 0.2 μ m PTFE filter) was spin-coated on the PEDOT:PSS layer from a homogeneously blended solution. The substrates were annealed at 110 $^{\circ}$ C for 10 minutes. After the fullerene surfactant was spin-coated onto the BHJ layer, the substrates were annealed at 110 $^{\circ}$ C for 5 minutes prior to electrode deposition. At the final stage, the substrates were pumped down to high vacuum ($< 2 \times 10^{-6}$ Torr), and silver (100 nm) was thermally evaporated onto the active layer through shadow masks to define the active area (10.08×10^{-2} cm²) of the devices. The current-voltage (I-V) characteristics of unencapsulated photovoltaic devices were measured into an N_2 -filled glove-box using a Keithley 2400 source- measurement unit. An Oriel xenon lamp (450 Watt) with an AM1.5 G filter was used as the solar simulator. A Hamamatsu silicon solar cell with a KG5 color filter, which is traced to the National Renewable Energy Laboratory (NREL), was used as the reference cell. To calibrate the light intensity of the solar simulator, the power of the xenon lamp was adjusted to make the short-circuit current (I_{SC}) of the reference cell under simulated sun light as high as it was under the calibration condition. The spectral mismatches resulting from the test cells,

the reference cell, the solar simulator, and the AM1.5 were calibrated with mismatch factors (M). According to Shrotriya et al. The mismatch factor is defined as

$$M = \frac{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_R(\lambda) d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_T(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_T(\lambda) d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_R(\lambda) d\lambda}$$

where $E_{Ref}(\lambda)$ is the reference spectral irradiance (AM1.5), $E_S(\lambda)$ is the source spectral irradiance, $S_R(\lambda)$ is the spectral responsivity of the reference cell, and $S_T(\lambda)$ is the spectral responsivity of the test cell, each as a function of wavelength (λ). The spectral responsivities of the test cells and the reference cell were calculated from the corresponding external quantum efficiencies (EQE) by the relationship

$$S(\lambda) = \frac{q\lambda}{hc} EQE(\lambda)$$

where the constant term q/hc equals 8.0655×10^5 for wavelength in units of meters and $S(\lambda)$ in units of AW^{-1} . The Hamamatsu solar cell was also used as the detector for determining the spectral irradiance of the solar simulator. To minimize the spectral transformation, the irradiance spectrum has been calibrated with the spectral responsivity of the Hamamatsu cell and the grating efficiency curve of the monochromator (Oriel Cornerstone 130). It should be noted that the spectral irradiance of the solar simulator and the EQE were only recorded between 350 nm to 800 nm because of the limitation of the calibrated region of the Hamamatsu cell. The slight extend in the EQE response compared to the absorption of polymer film is a common phenomenon in the polymer photovoltaic cells. The reason is coming from either the charge-transfer absorption between polymer and acceptor (PCBM) or the absorption of PCBM at the interface or in the polymer rich phase. This phenomenon has been reported and discussed in literature.

For the inverted architecture, a ZnO precursor solution, consisting of 20 mg/mL zinc acetylacetonate hydrate in ethanol, was spin coated onto ITO-coated glass, followed by thermal annealing at 130 °C for 10 min (thickness=20 nm) in air. Subsequently, C₆₀-SAM layer was deposited on ZnO using a spin-coating process as previously reported.⁴ The substrates were washed with THF twice to remove unbound C₆₀-SAM molecules. The same process for the active layer in the conventional architecture was used for the inverted devices. Subsequently, the PEDOT:PSS solution diluted with equal volume of isopropyl alcohol and 0.2 wt.% of Zonyl FSO fluorosurfactant, was then spin coated on top of the active layer. A silver top electrode (thickness=150 nm) was then thermally evaporated through shadow masks to define the active area ($10.08 \times 10^{-2} \text{ cm}^2$) of the inverted device. Finally, the complete device was thermally annealed at 130 °C for 5 min.

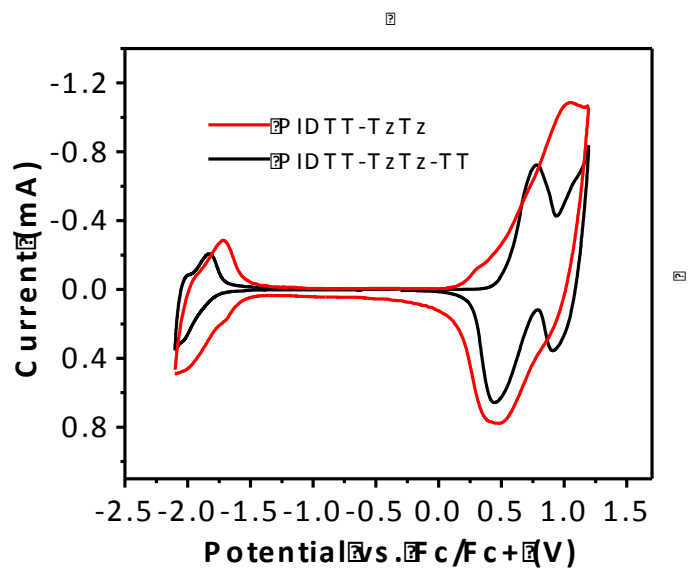


Fig. S1 CV curves of polymers PIDTT-TzTz and PIDTT-TzTz-TT.

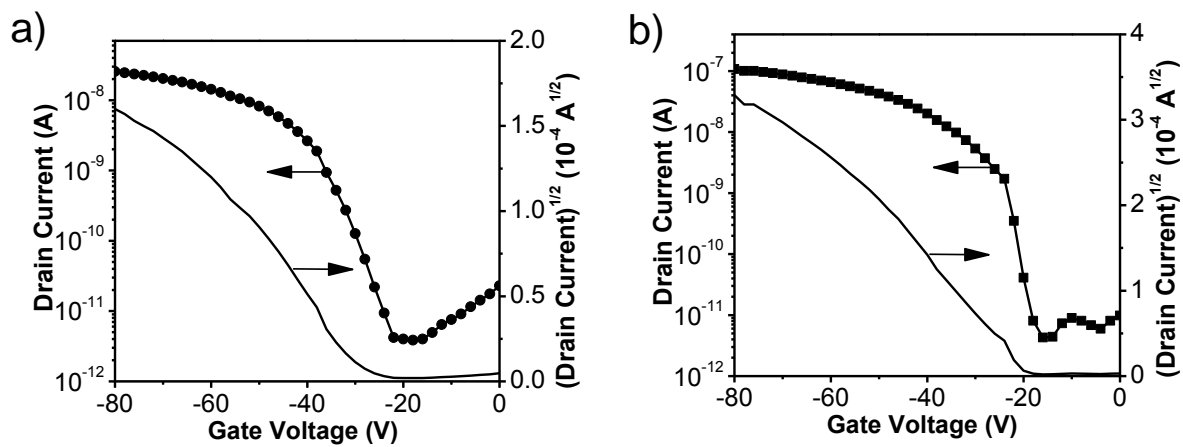


Fig. S2 Typical transfer curves of (a) PIDTT-TzTz and (b) PIDTT-TzTz-TT based hole-only devices, where $V_{ds} = \pm 60$ V.

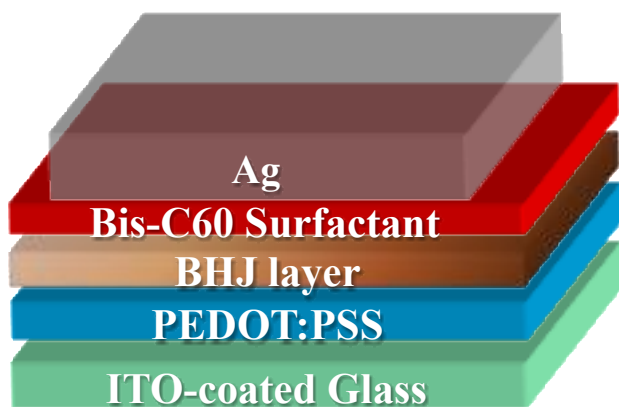


Fig. S3 Regular device configuration used in this study.

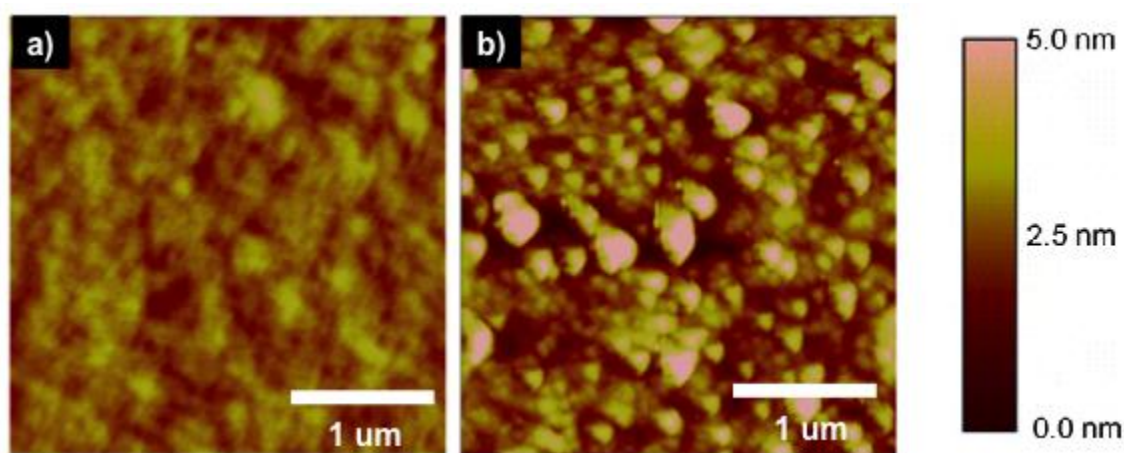


Fig. S4 AFM topography images of polymer:PC₇₁BM blend films: (a) PIDTT-TzTz (the root mean square roughness = 0.29 nm) and (b) PIDTT-TzTz-TT (the root mean square roughness = 1.25 nm). The scan size was 3 μm × 3 μm.

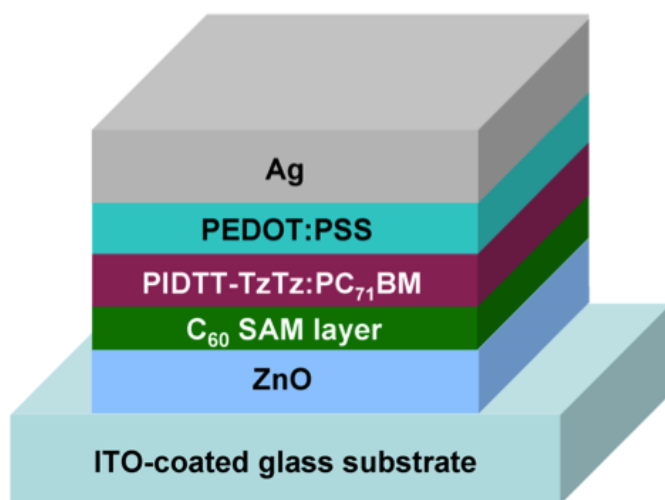


Fig. S5 Inverted device configuration used in this study.

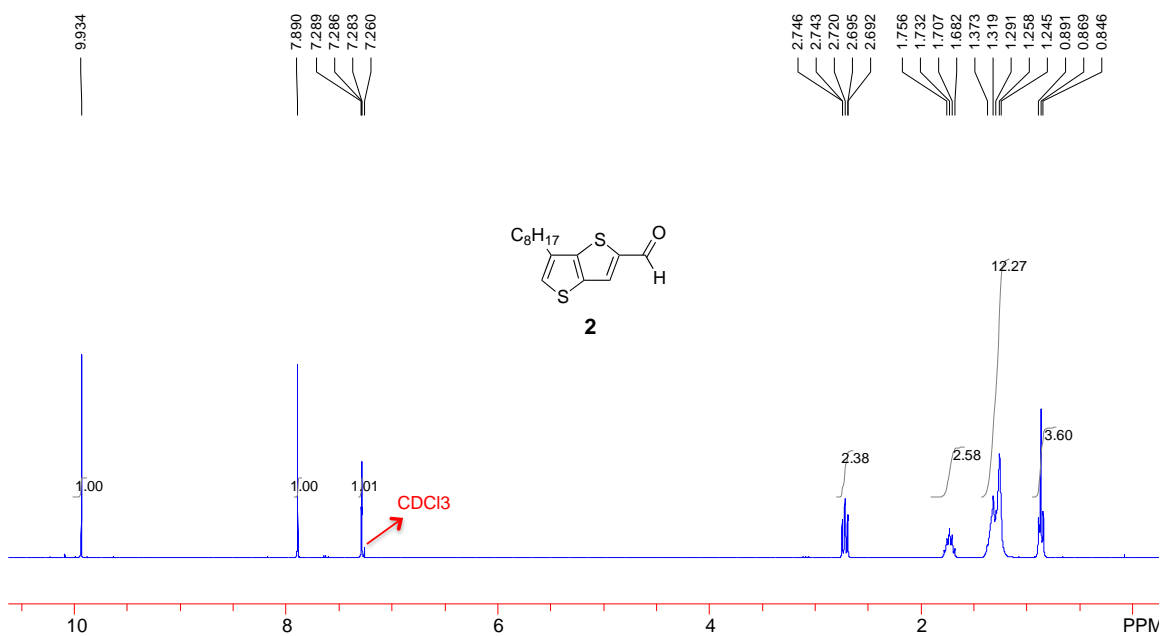


Fig. S6 ^1H NMR spectrum of compound **2** in CDCl_3 .

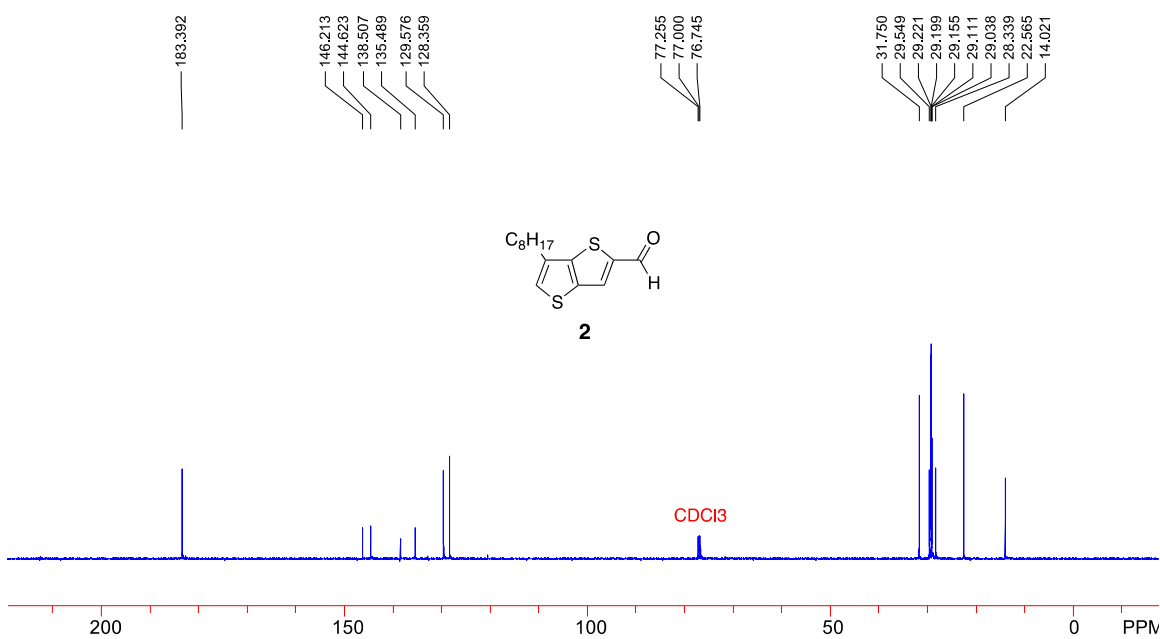


Fig. S7 ^{13}C NMR spectrum of compound **2** in CDCl_3 .

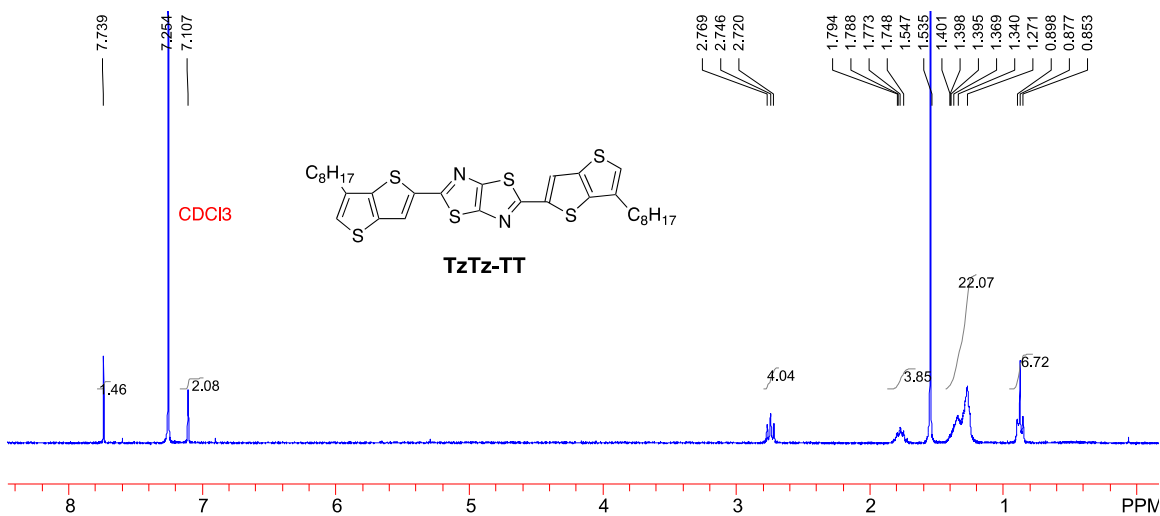


Fig. S8 1H NMR spectrum of compound **TzTz-TT** in $CDCl_3$.

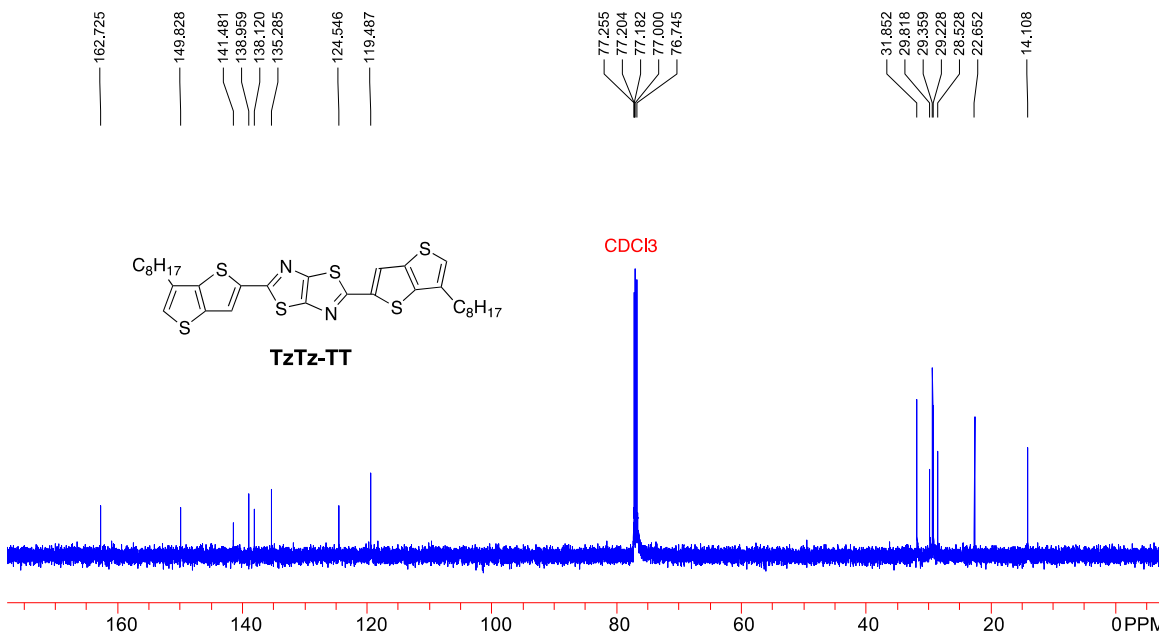


Fig. S9 ^{13}C NMR spectrum of compound **TzTz-TT** in $CDCl_3$.

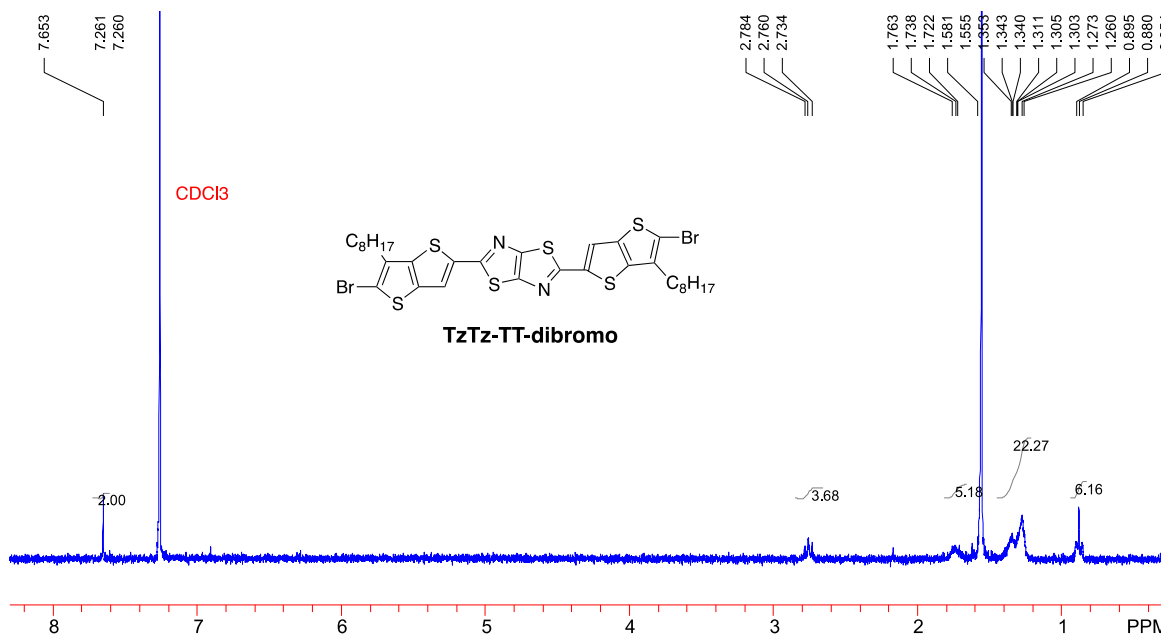


Fig. S10 ^1H NMR spectrum of compound **TzTz-TT-dibromo** in CDCl_3 .

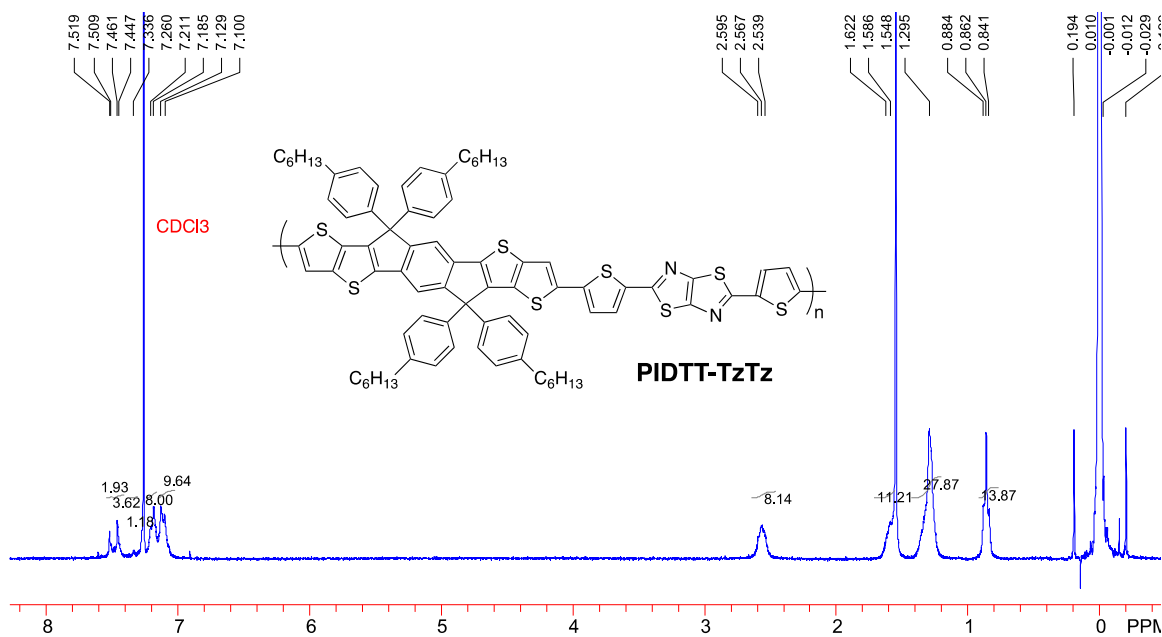


Fig. S11 ^1H NMR spectrum of polymer **PIDTT-TzTz** in CDCl_3 .

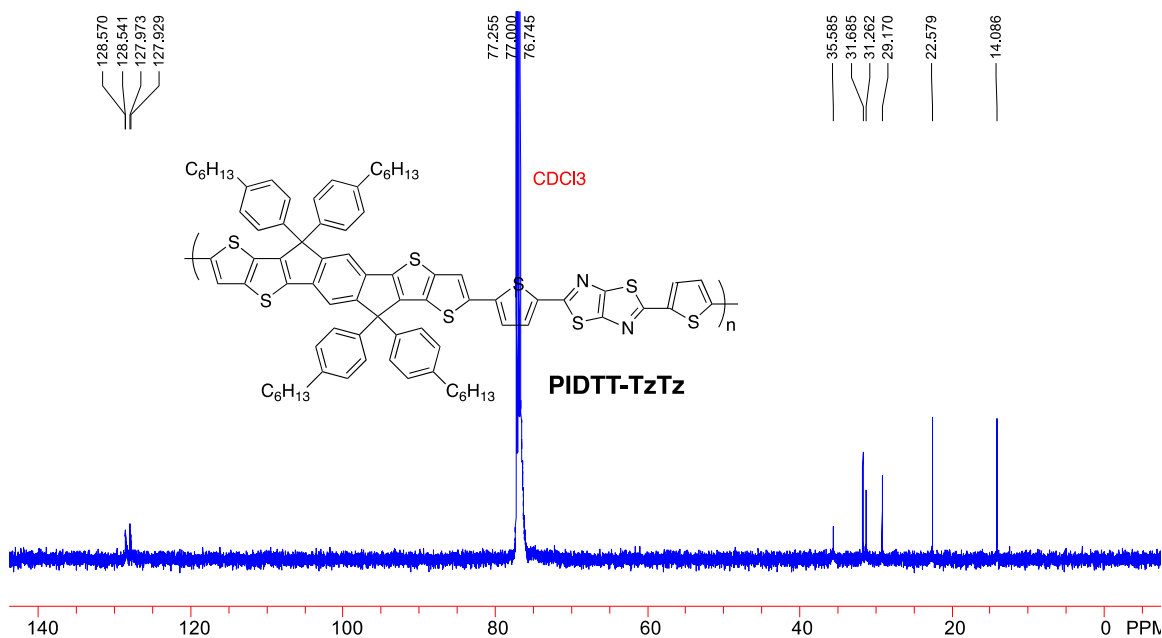


Fig. S12 ¹³C NMR spectrum of polymer **PIDTT-TzTz** in CDCl₃.

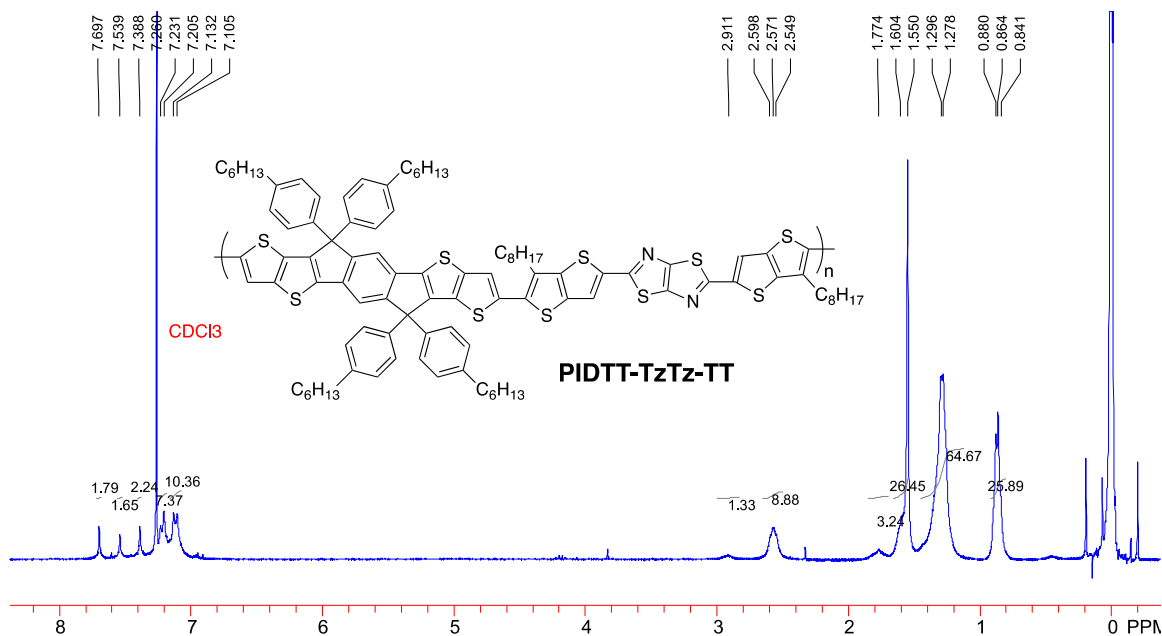


Fig. S13 ¹H NMR spectrum of polymer **PIDTT-TzTz-TT** in CDCl₃.

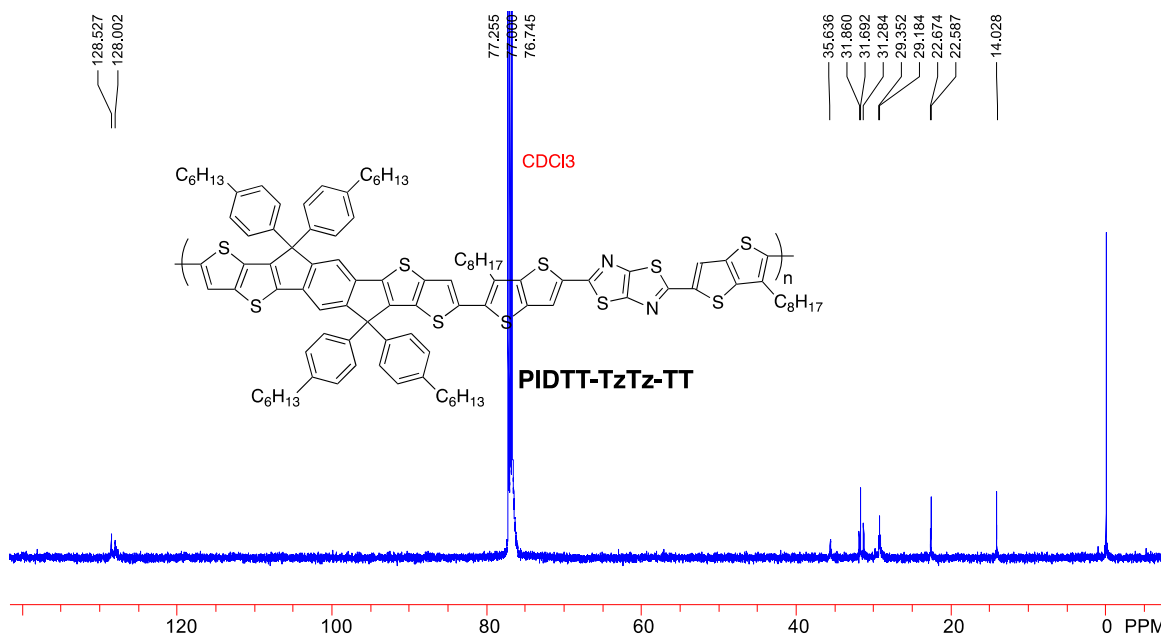


Fig. S14 ^{13}C NMR spectrum of polymer **PIDTT-TzTz-TT** in CDCl₃.

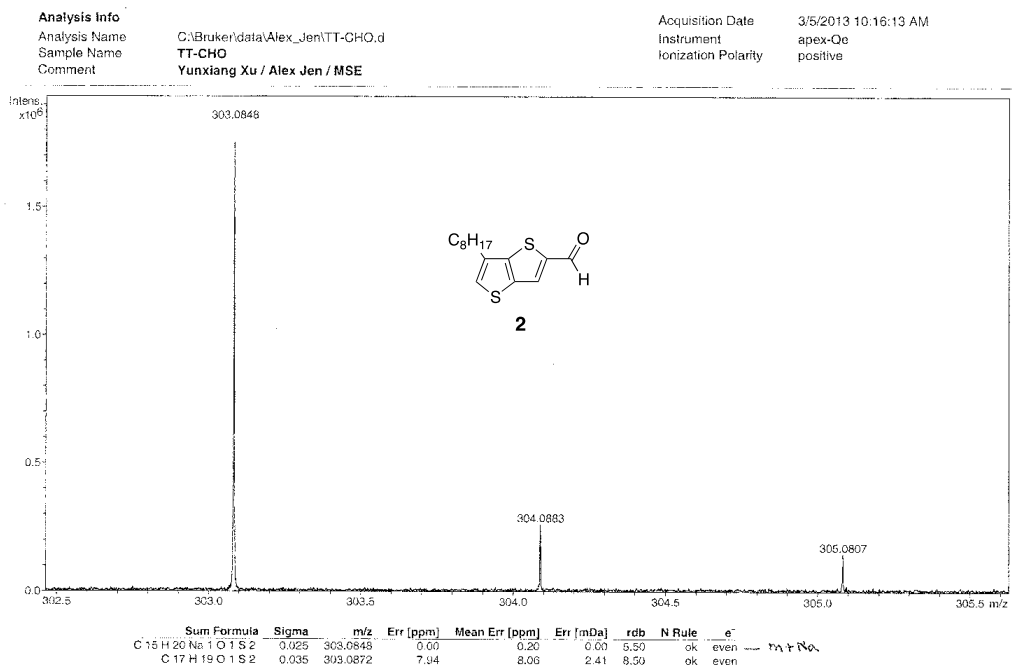


Fig. S15 High-resolution mass spectrum (ESI) of compound **2**.

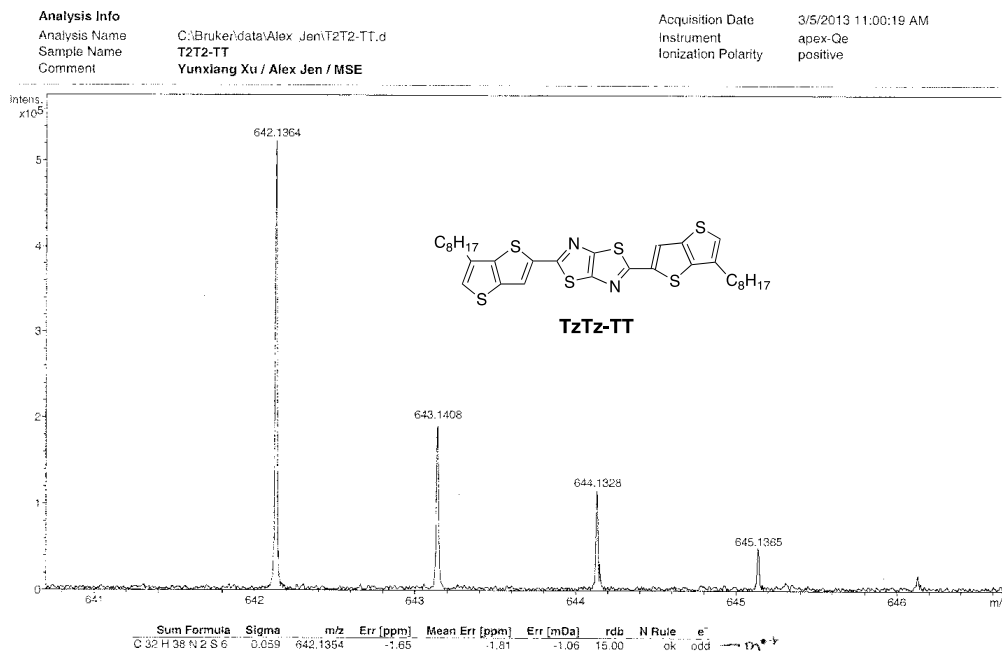


Fig. S16 High-resolution mass spectrum (ESI) of compound **TzTz-TT**.

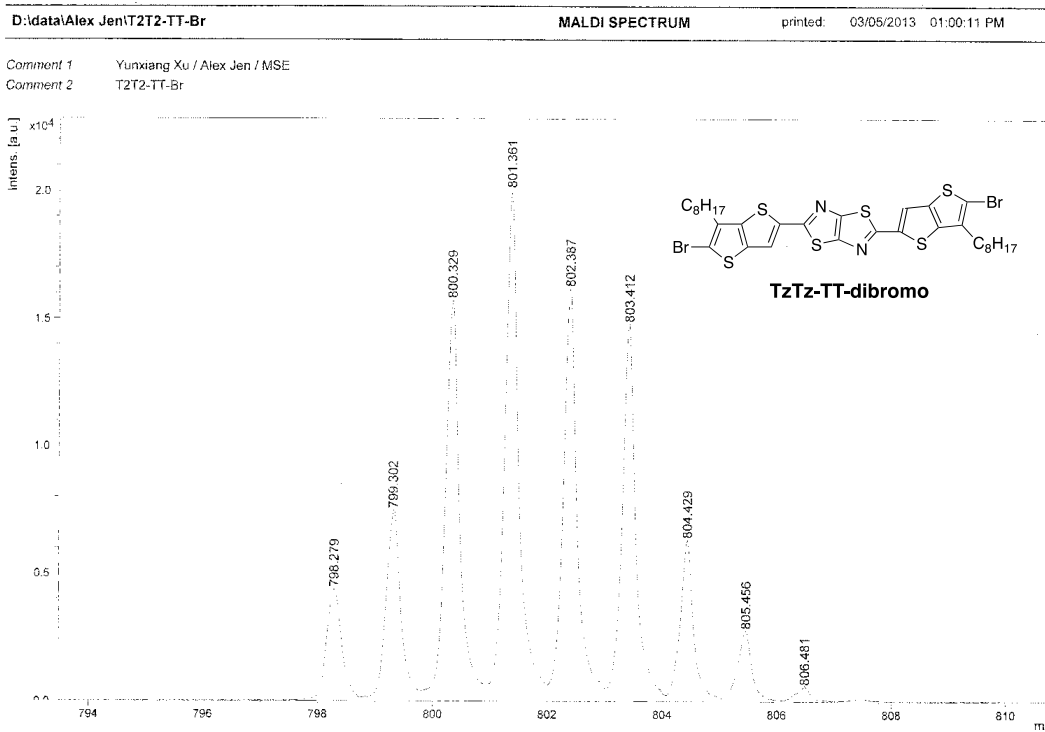


Fig. S17 MALDI mass spectrum of compound **TzTz-TT-dibromo**.

References

1. Y.-X. Xu, C.-C. Chueh, H.-L. Yip, F.-Z. Ding, Y.-X. Li, C.-Z. Li, X. Li, W.-C. Chen and A. K. Y. Jen, *Adv. Mater.*, 2012, **24**, 6356-6361.
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