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Supporting Information

Pseudo Two-dimensional Conjugated Polysquaraine: An Efficient P-type Polymer Semiconductor for Organic Photovoltaics and Perovskite Solar Cells

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Materials

For synthesis, most materials were purchased from commercial sources (Adamas, Titan Scientific, Shanghai, China) except IDT-Sn (Derthon Optoelectronic Materials Science Technology Co LTD, Shenzhen, China)，and used without further purification except for additional statement. Toluene was redistilled from sodium and benzophenone for the remove of water, and n-butanol was purchased as absolute solvent. Dichloromethane was redistilled under $CaCl_2$ at room temperature. Semi-squaraine (**3**) was synthesized following the methods reported by previous literature[1].

For device fabrication, most materials were purchased from commercial sources and used without further purification, including PbI_2 (Xi'an p-OLED Corp., >99.99 %), MAI (Xi'an p-OLED Corp., ≥99.5 %), C60 (Xi'an p-OLED Corp.), BCP (Xi'an p-OLED Corp.), $PC_{71}BM$ (American Dye Source, Inc.), DMF (Sigma-Aldrich, 99.8 %), DMSO (Sigma-Aldrich, 99.8 %) and CB (Sigma-Aldrich, 99.8 %).

Instruments and characterization methods

All the ^{1}H NMR and ^{13}C NMR spectra were recorded by Bruker Avance III 400 MHz and high resolution mass spectra (HRMS) were collected by electron spray ionic(ESI) method. Thermogravimetric analysis(TGA) and Differential Scanning Calorimetry (DSC) were carried out on Netzsch STA449F3 at nitrogen atmosphere with a heating rate of 10 °C/min. UV-Vis-NIR absorption of the polymer sample in organic solvents were carried out in chloroform with a concentration of 0.01 mg/mL while the film samples were spin-coated on quartz glass base at a rate of 1100 rpm for 30s. All the absorption spectra were obtained by SHIMADZU 3600 spectrophotometer and the band gap of **PASQ-IDT** was calculated according to the λ_{onset} of the film absorption curve. The information of the energy level of HOMO was gathered by investigating the cyclic voltammetry(CV) curve of the polymer and the value of LUMO was calculated according to the gap between HOMO and E_g^{opt}. A three-electrode system was employed in cyclic voltammetry test in which Pt disk, Pt wire and Ag/AgCl were used as working electrode, counter electrode and reference electrode, respectively. A solution of $Bu_4N^+PF_6^-$ (0.1 mol/L in acetonitrile) was used as electrolyte and the characterization was carried out by CH 2000 test system with a scan rate of 0.1 V/s. Gel Permeation Chromatography (GPC) was used to investigate the molecular weight of the **PASQ-IDT** which was operated on Agilent PL-GPC 50 instrument. Steady-state PL spectra were recorded on FS5 fluorescence spectrometer. Time-resolved PL decay curves were measured by a single photon counting spectrometer from Edinburgh Instruments (FS5) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation source. Atomic Force Microscope (AFM) was completed on SHIMADZU SPM-9700 for the morphology of the film samples. The morphology of perovskite films were characterized by FE-SEM images (JSM-7800F). Water contact angles were measured on contact angle measurement apparatus JC2000D, Shanghai Zhongchen Digital Technology Co., Ltd., China. XRD measurement was performed by PANalytical PW3040-60 MRD. UPS (ESCALAB 250Xi) measurements were performed in an ultrahigh vacuum system at base pressures 10−7 Pa. He-UPS measurements with an excitation energy of 21.22 eV were conducted to determine the ionization potentials, and the energy resolution is ∼50 meV. The work function was determined by fitting a Boltzmann sigmoid function to the secondary electron cutoff.

Device Fabrication

Bulk-junction Polymer solar cells

Patterned ITO glass was cleaned in an ultrasonic bath in detergent, deionized water, acetone, isopropanol sequentially, following a treatment with a plasma for 3 mi. The substrates then were transferred into a high vacuum chamber for deposition of 8 nm MoO_3 at a pressure of less than 10^{-5} Pa with a rate of 5 Å/min. Subsequently, photoactive layers (thickness:~90 nm) were fabricated by spin-coating a chlorobenzene blend solution of **PASQ-IDT** and $PC_{71}BM$ (25 mg mL^{-1}) in a N_2-filling glovebox. Afterwards, the substrates were transferred back to the high vacuum chamber, wherein BCP (4 nm) and Al (100 nm) were deposited as the top electrode at pressures of less than 10^{-5} Pa with a rate of 4 Å/min, and 10^{-5} Pa with a rate of 5 nm/min, respectively. The final PSCs exhibits a structure of ITO/MoO_3(8 nm)/**PASQ-IDT**:$PC_{71}BM$/BCP(4 nm)/Al(100 nm), and the active area of cell is 0.06 cm^2.

To fabricate the semitransparent polymer solar cells, the same fabrication conditions were used except the thickness of top Ag electrode was controlled at 13 nm, resulting in the final devices with the structure of ITO/MoO_3 (8 nm)/**PASQ-IDT**:$PC_{71}BM$/BCP (4 nm)/Ag (13 nm).

Hole Mobility Measurements

Hole-only and electron-only devices are fabricated with the structure ITO/MoO_3(8 nm)/**PASQ-IDT** or **PASQ-IDT**:$PC_{71}BM$(1/5)/MoO_3(8 nm)/Al(100 nm) and FTO/TiO_2/ **PASQ-IDT**:$PC_{71}BM$(1/5)/BCP(4 nm)/Al(100 nm), respectively. Mobility is extracted by fitting the current density-voltage curves using space charge limited current (SCLC).

Perovskite Solar cells

Patterned ITO glass was cleaned in an ultrasonic bath in detergent, deionized water, acetone, isopropanol sequentially, following with a plasma for 3 min. Then the samples were transferred into a N_2-filled glovebox. The hole transporting layer of **PASQ-IDT** (1.0 mg/mL in Chlorobenzene) was depoisted on ITO substrates by spin coating speed at 6000 rpm for 60 s. The reference PEDOT:PSS device was fabricated according to literature method[2]. The PEDOT:PSS solution (Clevios PVP Al 4083) was spin-coated at 5000 rpm and then annealed on a hot plate at 120 °C for 30 min in air. Various spin-coating speeds have been tried (2000-8000 rpm) to optimize the film thickness, however, no significant difference has been made on device performance. A $CH_3NH_3PbI_3$ precursor solution (1.4 M in DMF/DMSO mixed solution with a V/V of 4/1) was spin-coated in a two-step program at 400 and 5000 rpm for 3 and 30 s, respectively. During the second step, 200 μL of chlorobenzene was poured on the spinning substrate at 10 s after the start-up. Next, the as-spun perovskite layer was annealed on a hot plate at 60 °C for 1 min and at 80 °C for 2 min to drive off solvent and form the perovskite phase. Then, C_{60} (40 nm) and BCP (6 nm) were evaporated under high vacuum on top of the perovskite layer. Finally, a 100 nm thick Ag electrode was deposited through a shadow mask. The active area of our cells is 0.06 cm^2.

Synthesis of N,N-bis(4-bromophenyl)-3,5-dimethoxyaniline (1)

To a 200 mL Schlenk flask was added 2 g (13 mmol) of 3,5-Dimethoxyaniline, 11 g (39 mmol) of 1-bromo-4-iodobenzene, 0.3 g (1.3 mmol) of CuI, 3.6 g (65 mmol) of KOH and 0.2 g (1.3 mmol) of 1,10-phenanthroline hydrate under nitrogen, then 40 mL of toluene was injected to the mixture and the reaction was heated to 120°C for 12 h. Then, the reaction was cooled to room temperature and quenched with water. After extracted with CH_2Cl_2 and washed with brine, the organic layer was removed under rotary evaporator and the mixture was then purified by column chromatography (SiO_2, n-hexanes/CH_2Cl_2, 85/15, V/V). The pure product was gathered as a pale yellow oil (3.4 g, 56%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 4H, ArH), 6.95 (d, *J* = 8.8 Hz, 4H, ArH), 6.17 (s, 3H, ArH), 3.70 (s, 6H, -OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.49, 148.72, 146.30, 132.31, 125.80, 115.75, 102.77, 95.80, 55.38. HRMS(ESI) *m/z*: calculated for $[M+H]^+$: 463.9684; Found: 463.9717.

Synthesis of 5-(bis(4-bromophenyl)amino)benzene-1,3-diol (2)

To a Schlenk flask, 0.9 g (1.9 mmol) of compound **1** and 10 mL anhydrous CH_2Cl_2 was added under nitrogen. After cooled to -78 °C, the BBr_3 solution (1.4 g diluted in 5 mL anhydrous CH_2Cl_2) was slowly added dropwise by a syringe. The mixture was then warmed to room temperature and stirred for 48 h. An extraction with ethyl acetate was needed following the carefully quench with ice water, the organic layer was collected and washed with brine. After dried with anhydrous sodium sulfate and condensed by a rotary evaporator, the crude product was purified through a column chromatography (SiO_2, CH_2Cl_2/ethyl acetate, 95/5, V/V). The pure product was obtained as a grey solid (0.7 g, 80%). Mp. 143-144 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 9.27 (s, 2H, -OH), 7.45 (d, *J* = 8.8 Hz, 4H, ArH), 6.94 (d, *J* = 8.4 Hz, 4H, ArH), 5.95 (s, 1H, ArH), 5.86 (s, 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.68, 148.36, 146.67, 132.67, 126.13, 115.07, 102.97, 99.19. HRMS(ESI) *m/z*: calculated for $[M+H]^+$: 435.9371; found: 435.9405.

Synthesis of asymmetrical squaraine (4)

0.5 g (1.2 mmol) of compound **2** and 0.4 g (1.2 mmol) of semi-squaraine (**3**) were dissolved in 30 mL of toluene and n-butanol (1/1, V/V) and heated to reflux with a Dean-Stark apparatus under nitrogen. The mixture was refluxed for 24 h and then the solvent was removed under rotary evaporator. The crude product was purified by a column chromatography (SiO_2, CH_2Cl_2) to afford the pure product as a green solid (0.4 g, 47%). Mp. 275-276 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.21 (s, 2H, -OH), 8.20 (d, *J* = 8.8 Hz, 1H, ArH), 7.98 (m, 2H, ArH), 7.65 (t, *J* = 7.6 Hz, 1H, ArH), 7.54 (t, *J* = 7.6 Hz, 1H, ArH), 7.45 (d,

J = 8.4 Hz, 4H, ArH), 7.04 (d, J = 8.8 Hz, 4H, ArH), 6.00 (s, 1H, -C=CH), 5.91 (s, 2H, ArH), 3.86 (s, 3H, $-NCH_3$), 2.01 (s, 6H, $-(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.15, 176.63, 171.41, 169.18, 168.99, 155.72, 144.24, 139.11, 135.88, 132.75, 132.62, 132.31, 130.51, 129.93, 129.68, 128.48, 128.17, 128.02, 127.30, 125.81, 122.75, 118.83, 110.33, 105.14, 99.93, 88.24, 52.45, 32.41, 26.25. HRMS (ESI) *m/z*: calculated for $[M+H]^+$: 737.0468; found: 737.0505.

Synthesis of PASQ-IDT

90 mg (0.1 mmol) of squaraine **4**, 151 mg (0.1 mmol) of **IDT-Sn** were dissolved in 8 mL of dried toluene and degassed with argon for 6 times. Afterwards, 3.4 mg (0.004 mmol) of $Pd_2(dba)_3$ and 4.5 mg (0.015 mmol) of tri(*o*-tolyl)phosphine (P-(*o*-Tol)$_3$) were added to the solution under argon, and after degassed once more, the mixture was heated to reflux and stirred for 2 d. After that, 2-bromo-thiophene and 2-tri(n-butylstannyl)-thiophene were added, respectively, to end-cap the polymer. The reaction mixture was cooled to room temperature and then precipitated into methanol and filtered. Finally, the collected solid were Soxhlet extracted with methanol, acetone, hexanes and chloroform. The chloroform extracts were concentrated and precipitated into methanol again. The resulting products were filtered and washed with methanol, acetone and dried under vacuum to afford product as a dark green solid (150 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 12.21 (-OH), 8.19 (ArH), 7.96 (ArH), 7.64 (ArH), 7.57-7.47 (ArH), 7.46-7.37 (ArH), 7.24-7.20 (ArH), 7.20-7.12 (ArH), 7.12-7.03 (ArH), 6.04-5.90 (ArH, -C=CH), 3.82 ($-NCH_3$), 2.61-2.48 ($-CH_2-$), 2.00 ($-(CH_3)_2$), 1.39-1.19 ($-CH_2-$), 0.95-0.78 ($-CH_3$). M_w: 38600; PDI: 2.68.

Table S1. Photovoltaic performances based on forward and reverse scans of inverted PVSCs using **PASQ-IDT** as the dopant-free HTM

	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE (%)
Forward	1.30	22.18	0.80	18.29
Reverse	1025	22.07	0.80	18.13

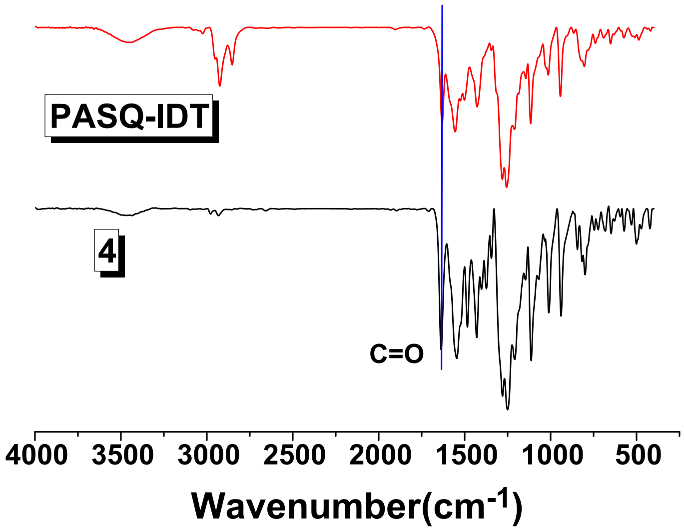


Figure S1. IR spectra of monomer **4** and polymer **PASQ-IDT**.

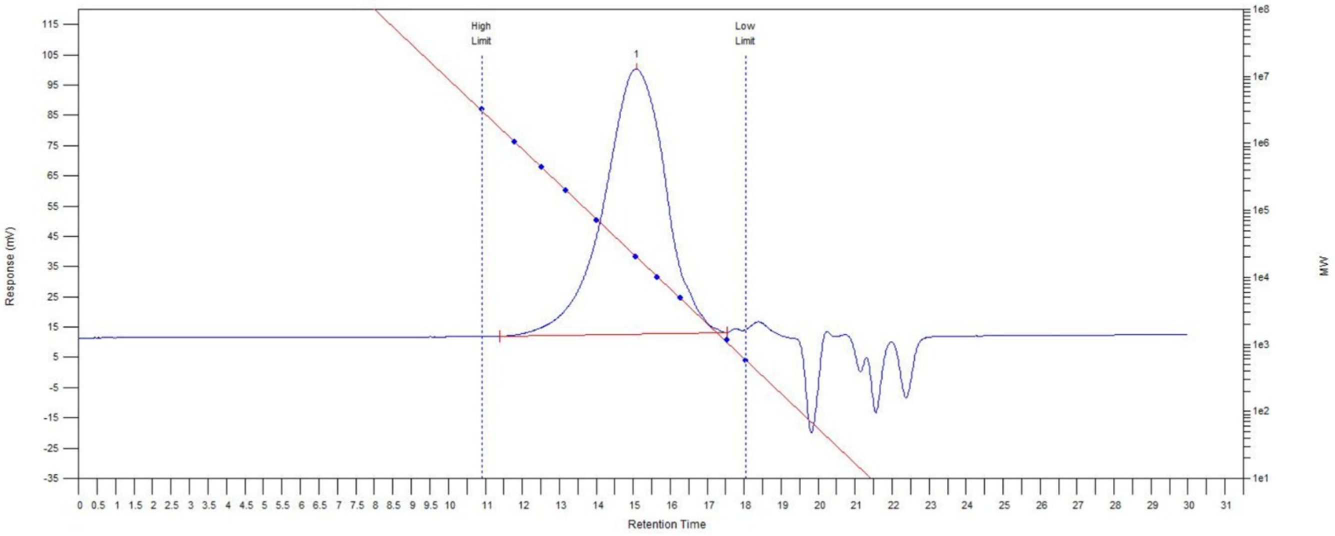


Figure S2. GPC trace of polymer **PASQ-IDT**.

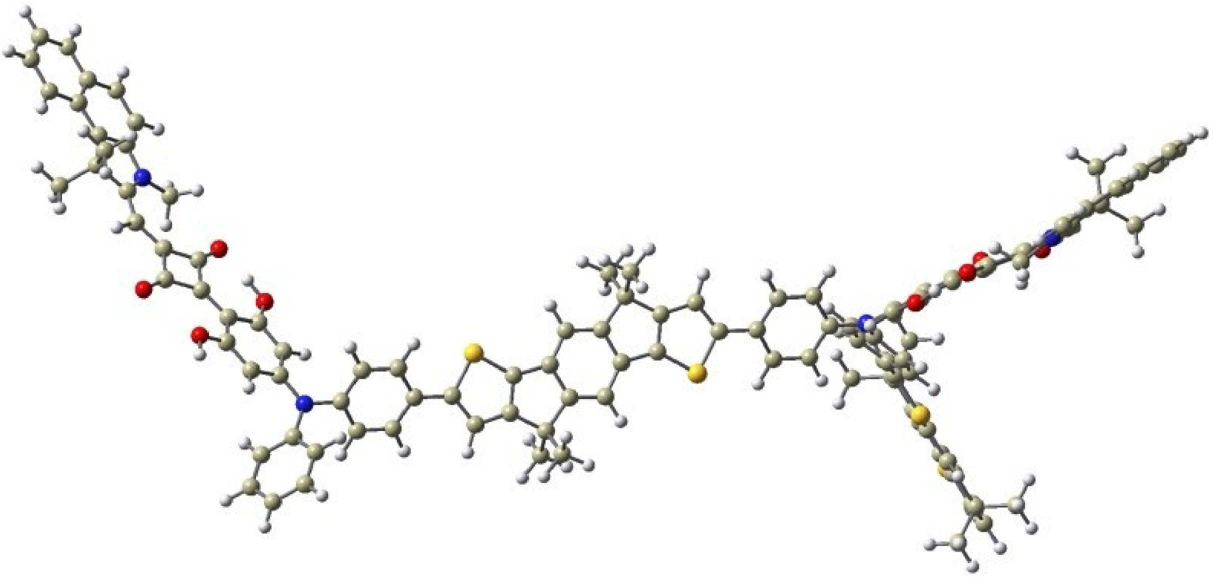


Figure S3. The geometry simulation of the analogous dimer model through employing the density functional theory (DFT) at B3LYP/6-31G level.

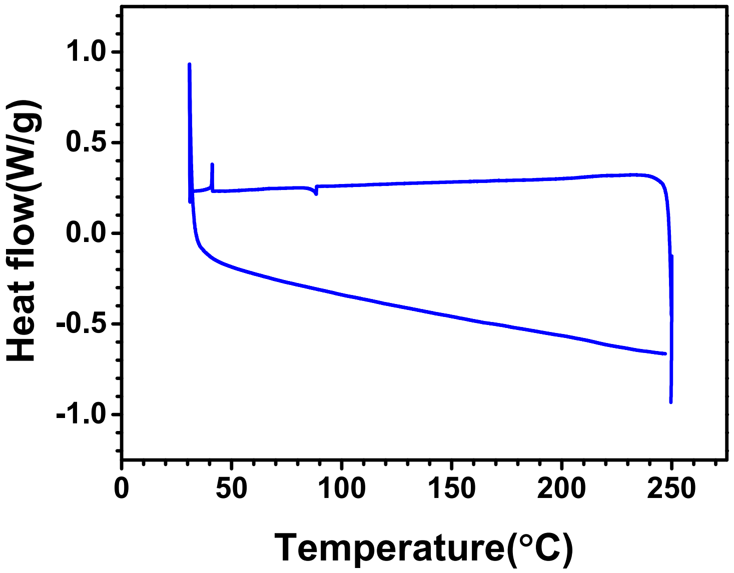


Figure S4. DSC curve of **PASQ-IDT** measured at a heating rate of 10 °C/min under nitrogen.

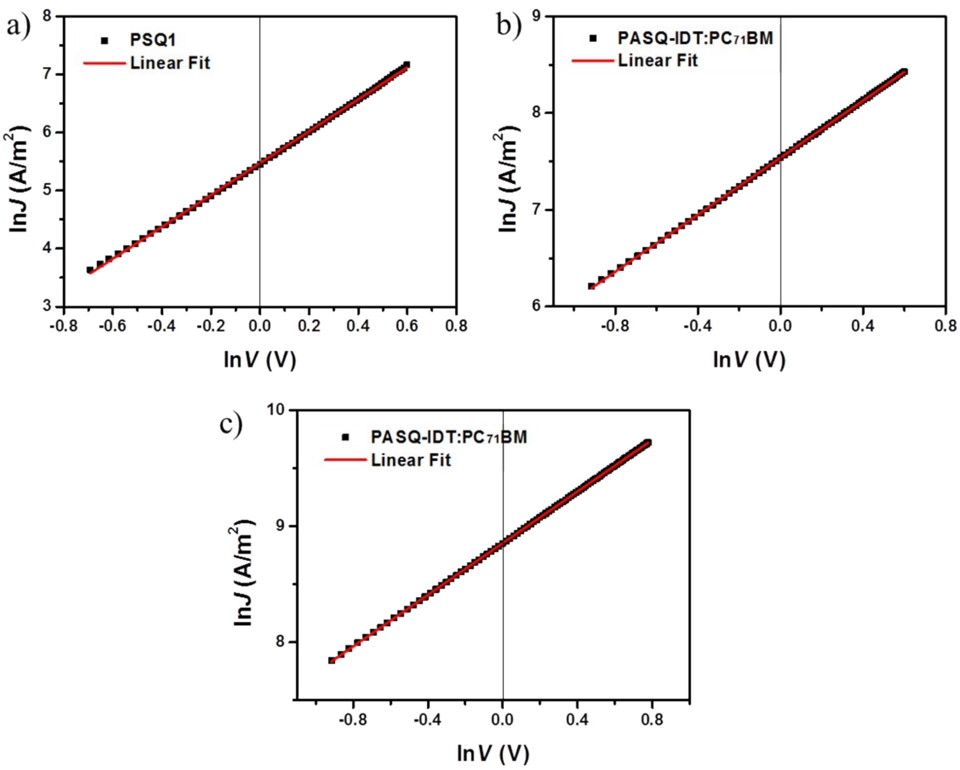


Figure S5. Hole injection characteristics of hole-only devices based on the structure of (a) ITO/MoO_3/**PASQ-IDT** or **PASQ-IDT**:$PC_{71}BM$(1/5)/MoO_3/Al and (b) ITO/MoO_3/**PASQ-IDT**:$PC_{71}BM$(1/5)/MoO_3/Al; (c) Electron injection characteristic of electron-only device based on the structure of FTO/TiO_2/**PASQ-IDT**:$PC_{71}BM$(1/5)/BCP/Al. Mobility is extracted by fitting the current density-voltage curves using space charge limited current (SCLC).

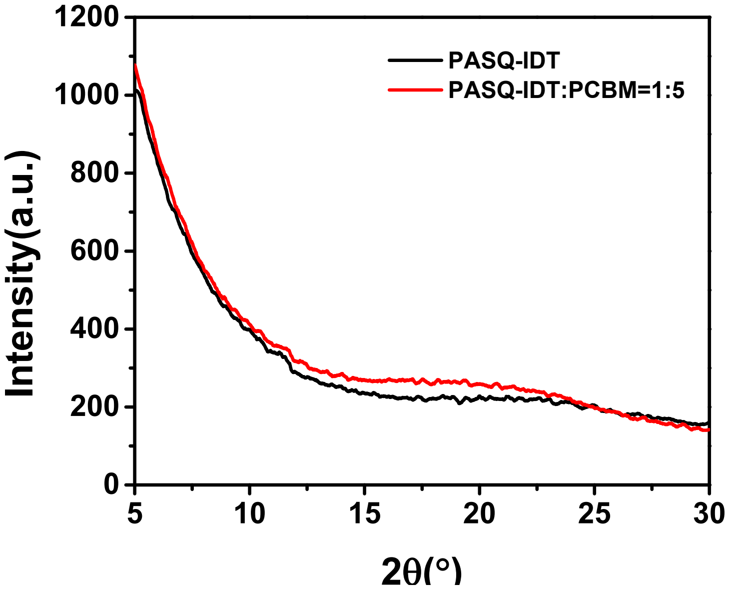


Figure S6. XRD patterns of pristine PASQ-IDT film and PASQ-IDT:PCBM blend film.

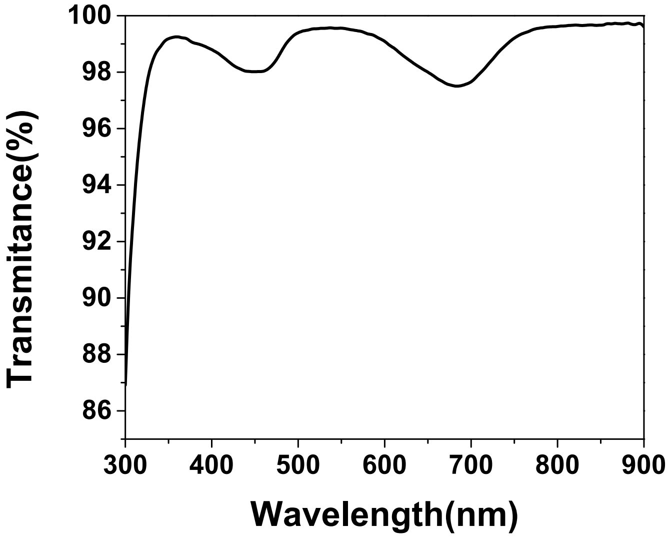


Figure S7. The transparent spectrum of **PASQ-IDT** thin film. Note: The film was processing through spin-coating **PASQ-IDT** solution (1.0 mg/mL in chlorobenzene) on glass substrate by a speed at 6000 rpm for 60 s.

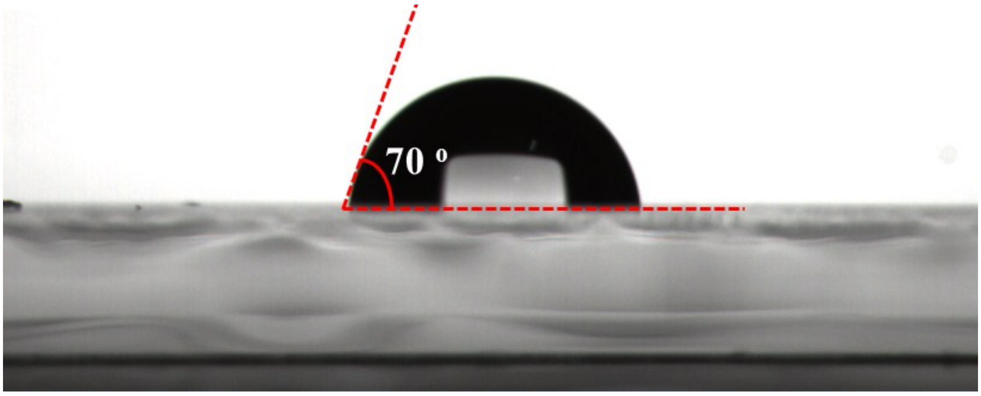


Figure S8. Water contact angle of **PASQ-IDT** film.

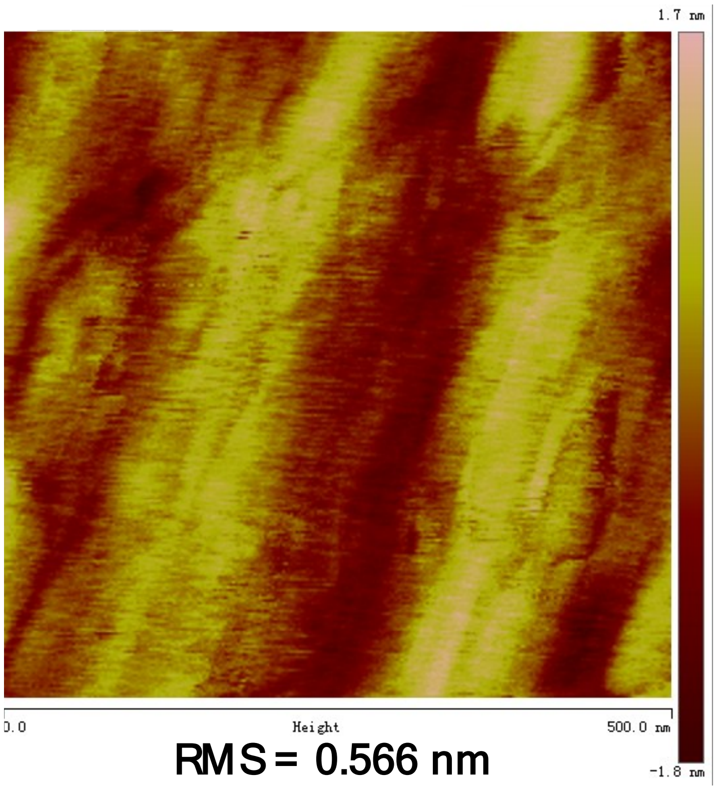


Figure S9. AFM image of pristine **PASQ-IDT** film.

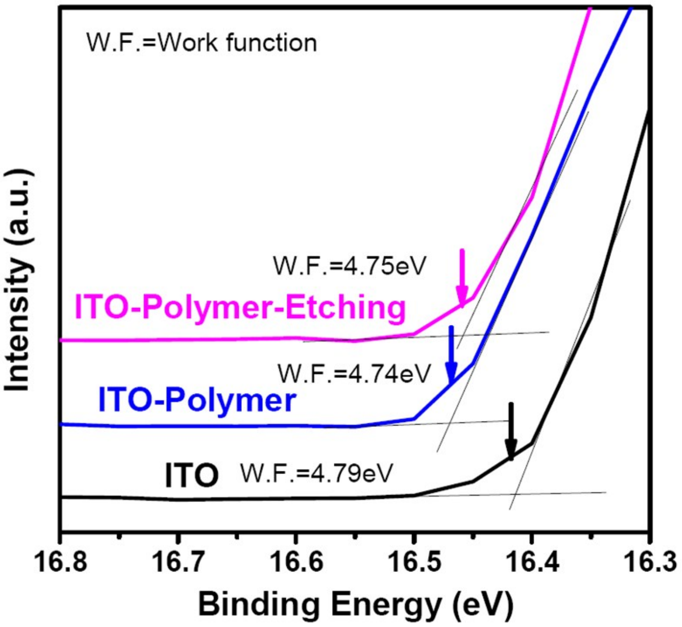


Figure S10. Photoemission cutoff obtained via UPS for ITO with and without **PASQ-IDT**.

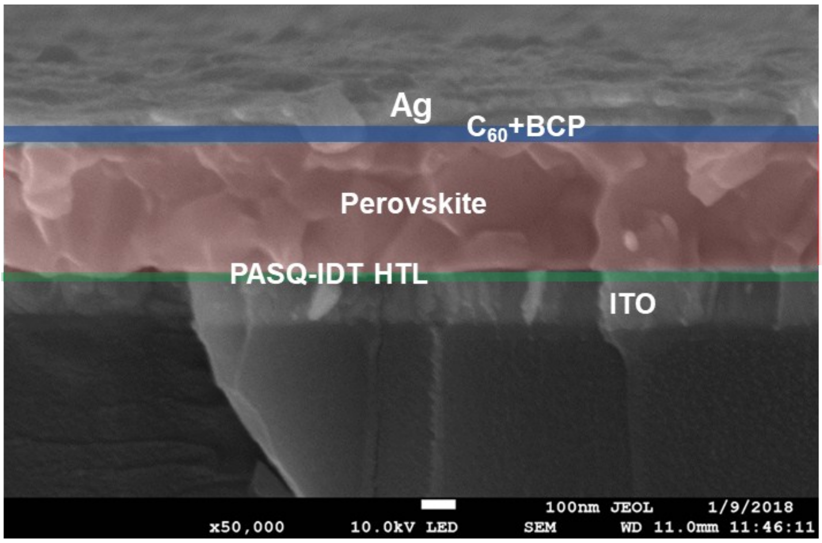
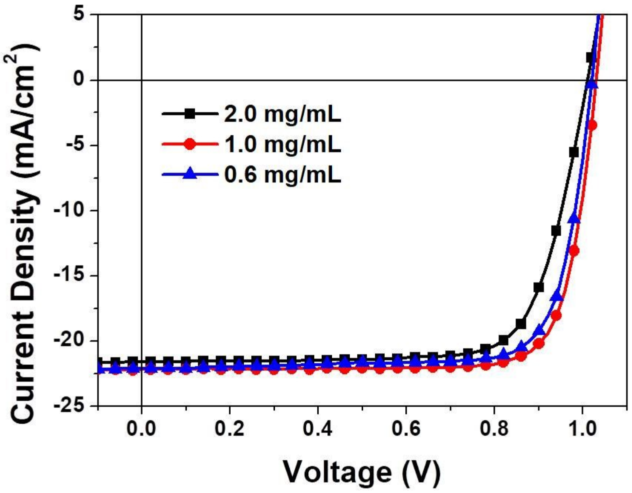
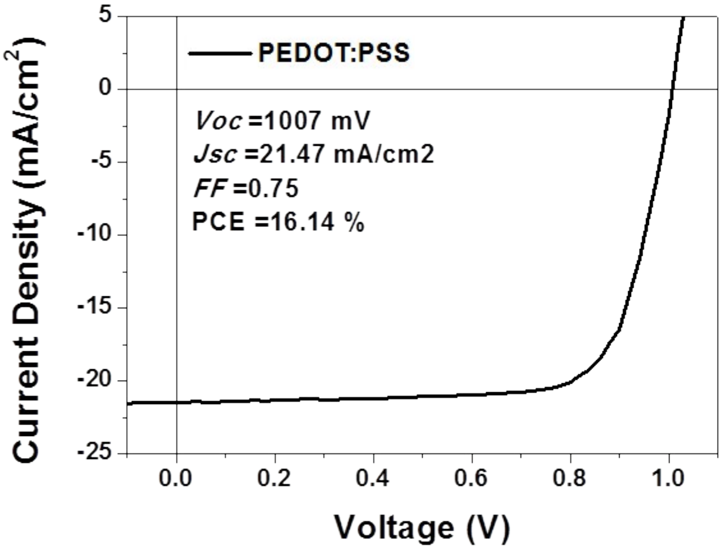


Figure S11. The cross-section of SEM image of inverted PVSC with a structure of ITO/**PASQ-IDT**/Perovskite/C_{60}/BCP/Ag.



Conc.	V_{oc} (mV)	J_{sc} (mA/cm2)	*FF*	PCE (%)
2.0 mg/mL	1011 (1005±9)	21.57 (21.31±0.33)	0.75 (0.71±0.04)	16.36 (15.24±0.94)
1.0 mg/mL	1030 (1028±6)	22.18 (21.99±0.19)	0.80 (0.78±0.02)	18.29 (17.69±0.54)
0.6 mg/mL	1021 (1018±9)	22.10 (21.87±0.30)	0.78 (0.75±0.04)	17.61 (16.69±1.03)

Figure S12. Best-performing *J-V* curves of inverted PVSCs with a structure of ITO/**PASQ-IDT**/Perovskite/C_{60}/BCP/Ag, in which the **PASQ-IDT** HTL was processed based on different concentrations. The photovoltaic parameters were obtained based on 20 individual devices.



V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE (%)
1007 (1003±9)	21.47 (21.33±0.21)	0.75 (0.73±0.03)	16.14 (15.52±0.65)

Figure S13. Best-performing *J-V* curve of the PEDOT:PSS reference inverted PVSCs with a structure of ITO/PEDOT:PSS/Perovskite/C_{60}/BCP/Ag. The photovoltaic parameters were obtained based on 20 individual devices.

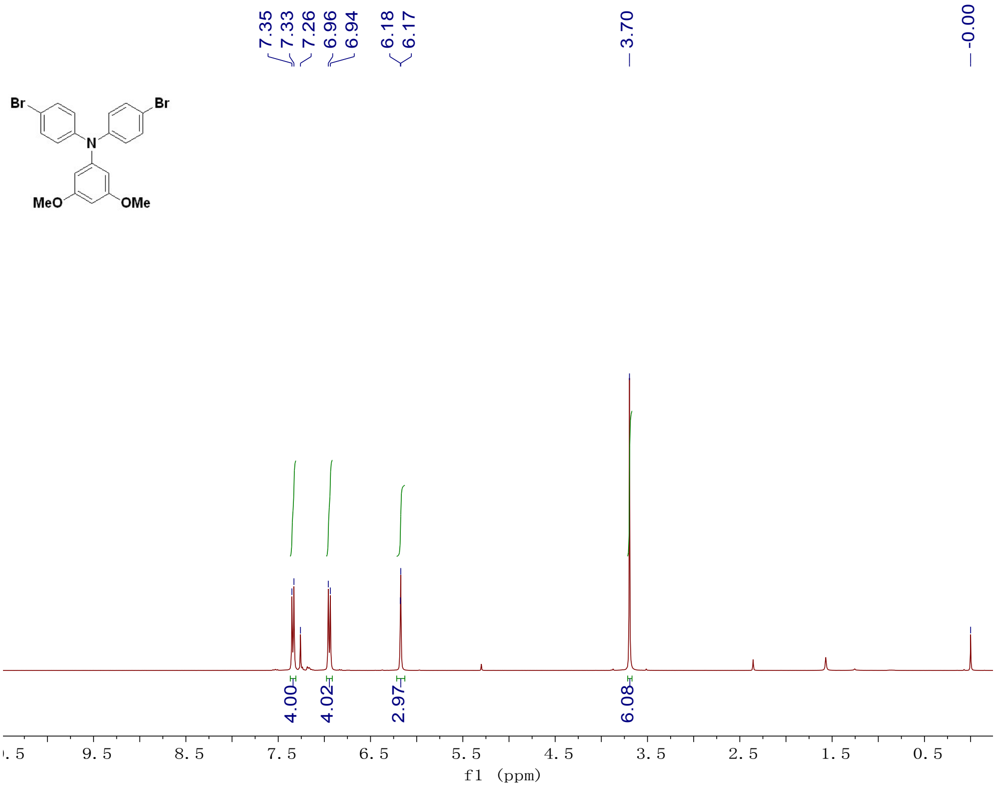


Figure S14. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

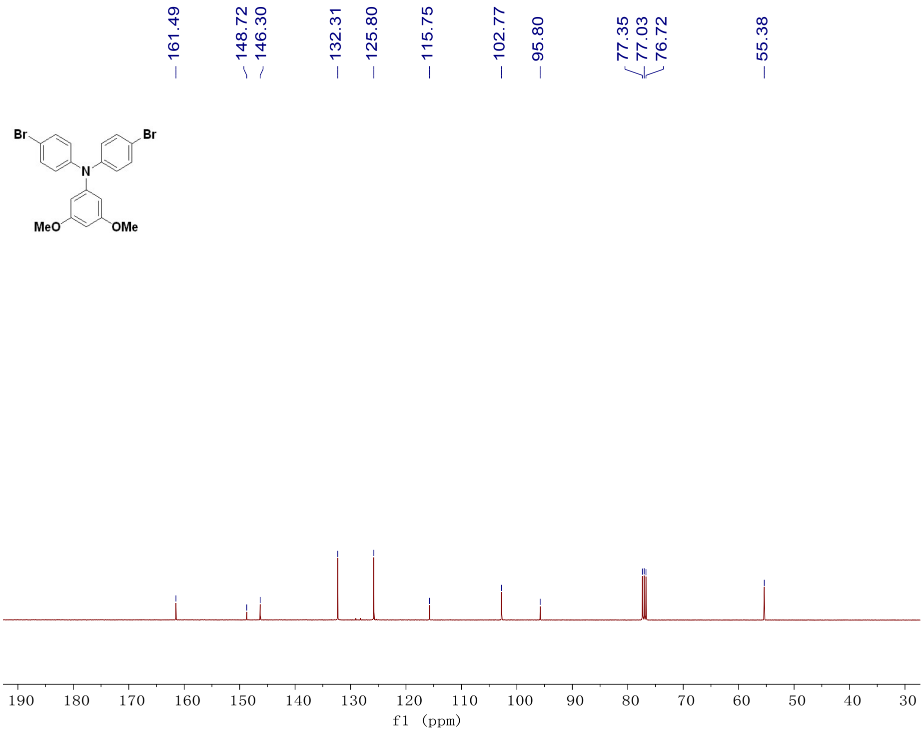


Figure S15. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

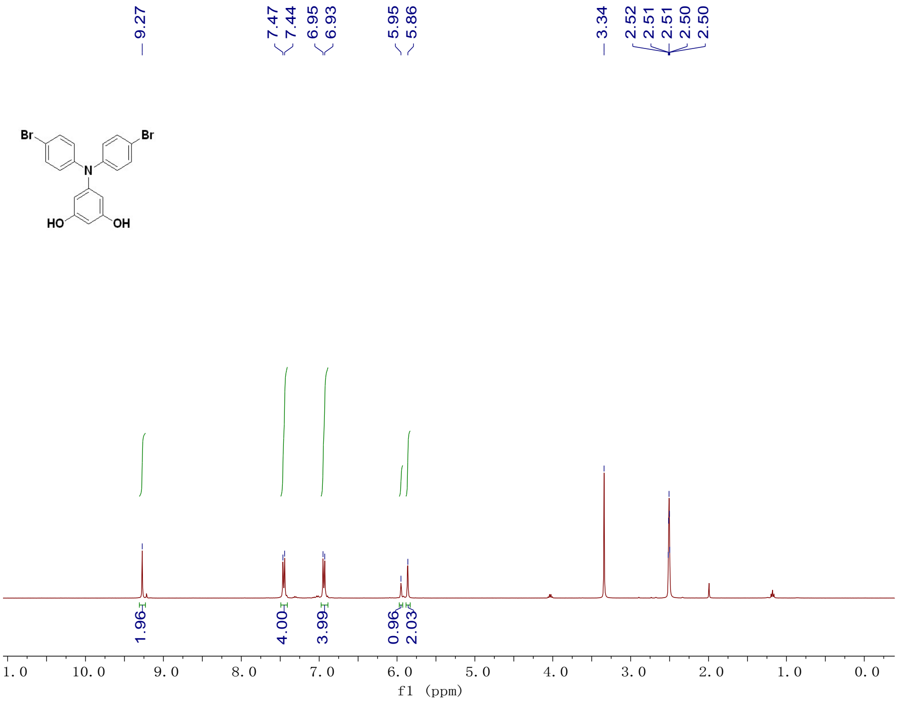


Figure S16. ^{1}H NMR spectrum of compound **2** in DMSO-d_6.

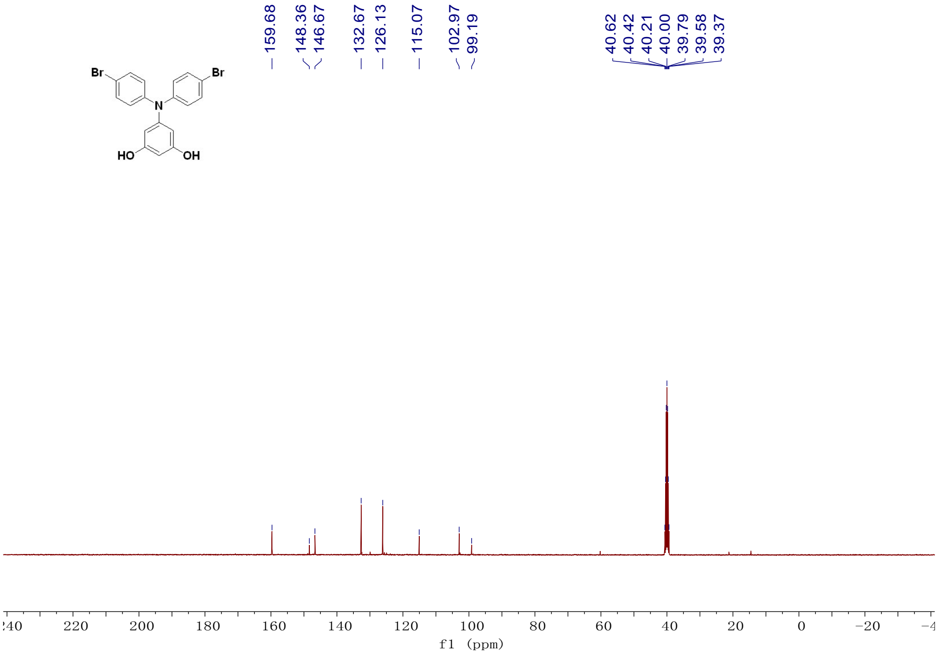


Figure S17. ^{13}C NMR spectrum of compound **2** in DMSO-d_6.

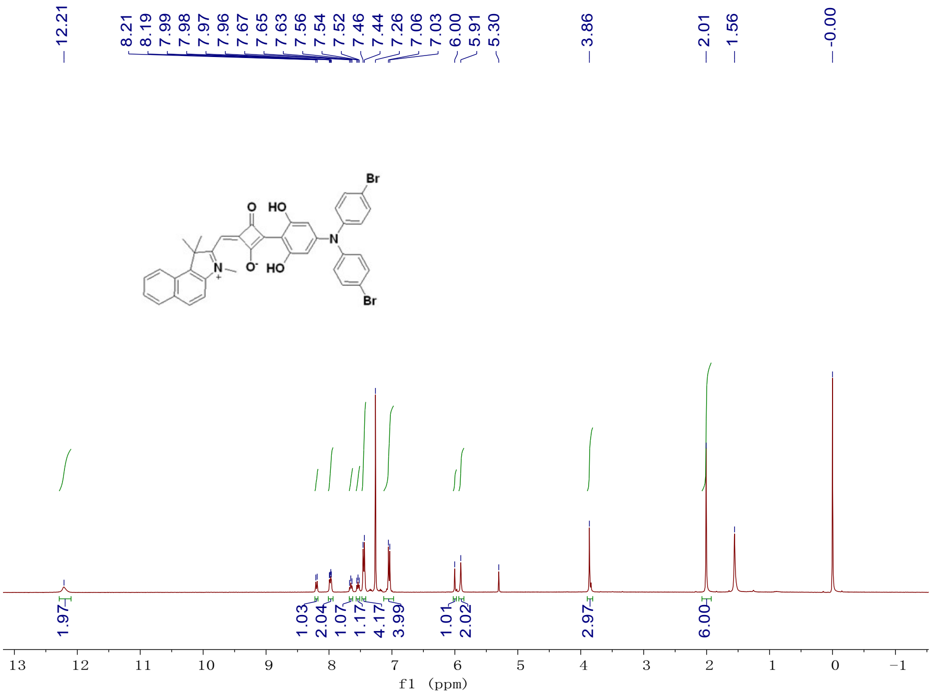


Figure S18. ^{1}H NMR spectrum of **4** in CDCl$_3$.

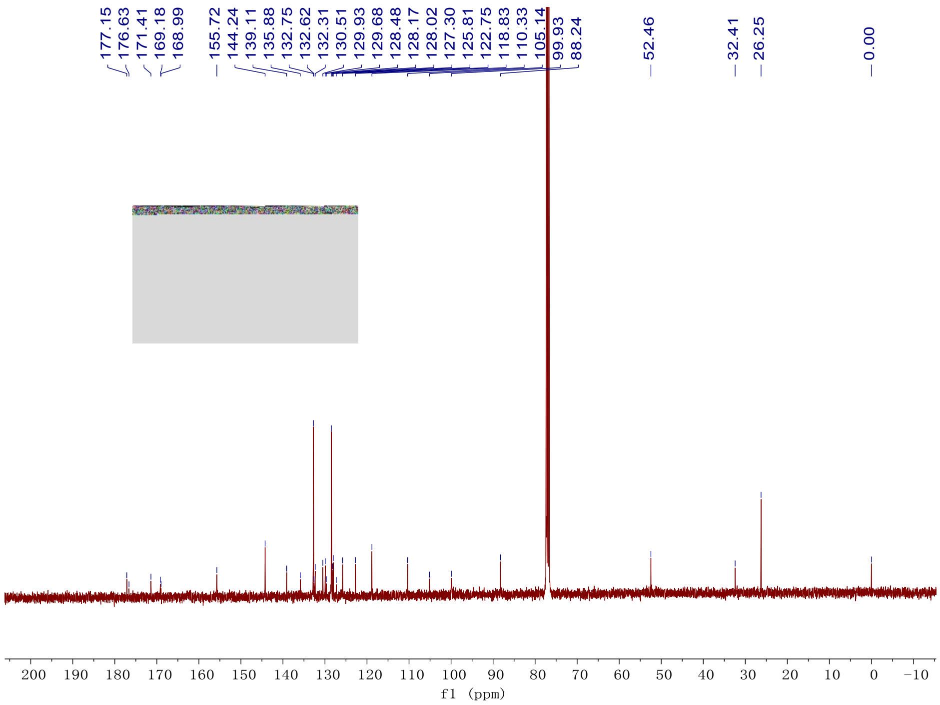


Figure S19. ^{13}C NMR spectrum of **4** in CDCl$_3$.

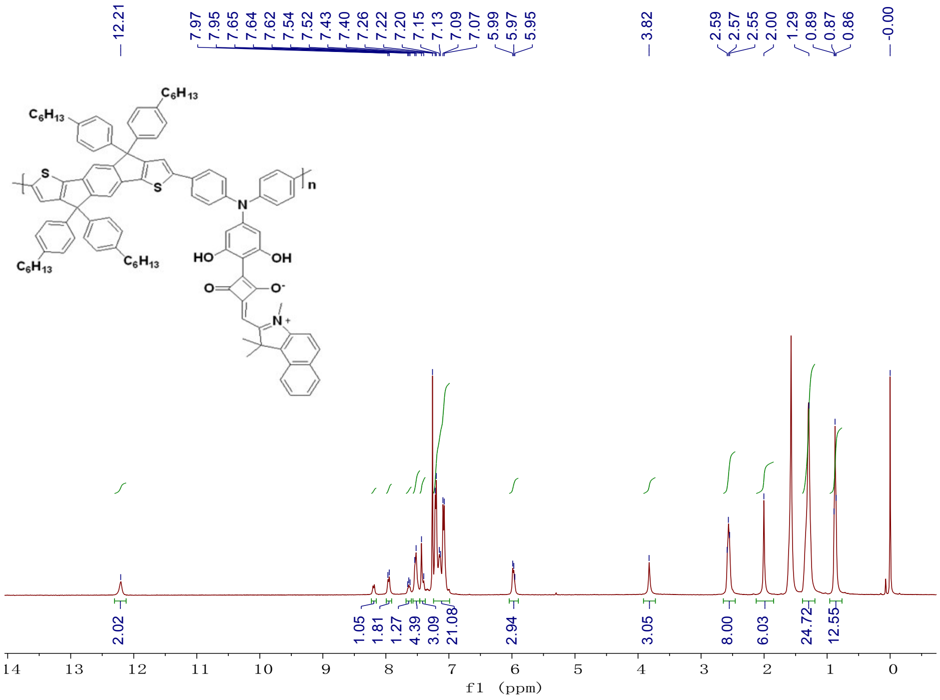


Figure S20. ^{1}H NMR spectrum of **PASQ-IDT** in CDCl$_3$.

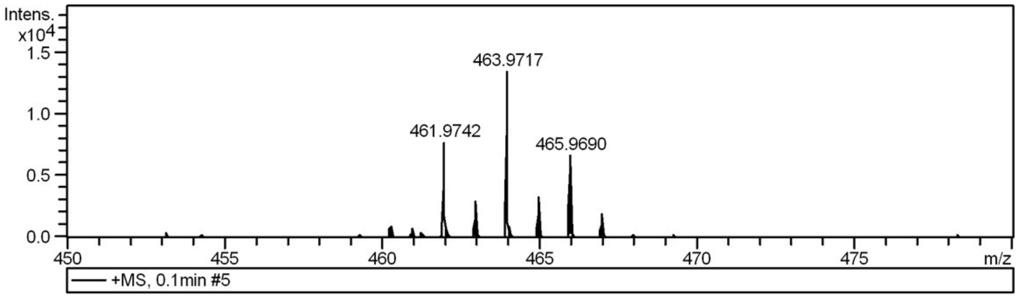


Figure S21. HRMS spectrum of compound **1**.

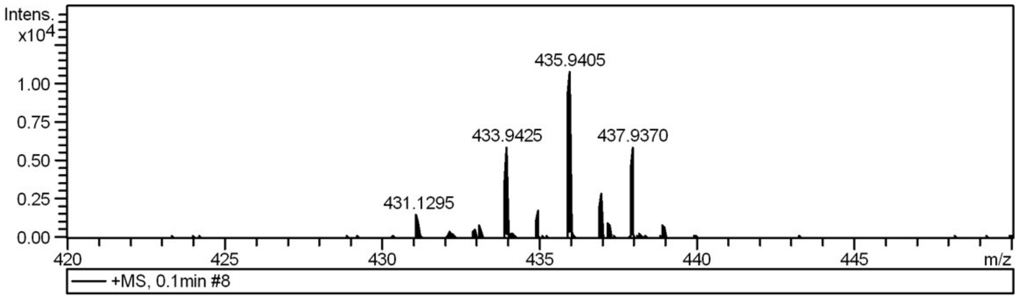


Figure S22. HRMS spectrum of compound **2**.

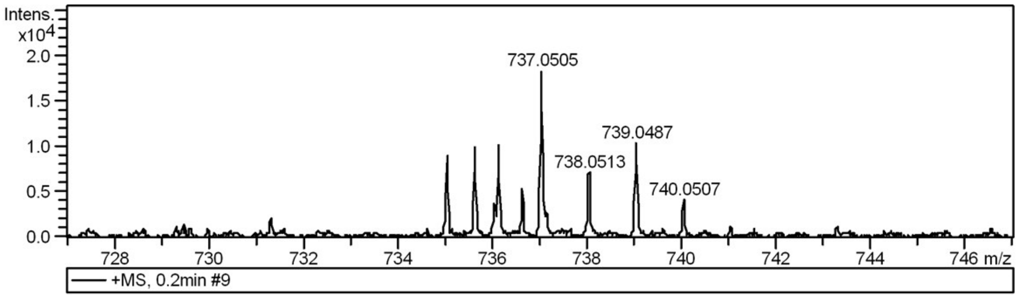


Figure S23. HRMS spectrum of **4**.

References:

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2. L. Hu, K. Sun, M. Wang, W. Chen, B. Yang, J. Fu, Z. Xiong, X. Li, X. Tang, Z. Zang, S. Zhang, L. Sun and M. Li, *ACS Appl. Mater. Interfaces*, 2017, **9**, 43902-43909.