Supporting Information

Synthesis and Application of a Thienoisoindigo-Based Acceptor Small Molecule for Organic Photodetectors

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1. Characterization

Nuclear magnetic data ^{1}H NMR spectrum was collected by BRUKER 500 MHz AVANCE-NEO nuclear magnetic resonance instrument produced by Bruker Instrument Company in Germany. Tetramethylchlorosilane (TMS) was used as the internal standard, and the single peak, double peak, triple peak, quadruple peak, multiple peak and wide peak were expressed by s, d, t, q, m and br, respectively. The deuterium reagent used is deuterium chloroform ($CDCl_3$). HRMS was determined by Bruker Esquire 6000 mass spectrometer. UV-visible absorption spectra were measured on a UV-2550 spectrophotometer (Shimadzu). The cyclic voltammetry (CV) was measured on CHI 600D electrochemical workstations (Shanghai Chen hua Co) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN) with glass carbon and $Ag/AgNO_3$ electrode as the working and reference electrode, respectively.

The photo-stabilities of the small molecule TIIG-T-EM in solid state were investigated as the following process, the small molecule TIIG-T-EM thin films on glass substrates were irradiated with UV-radiation ex-situ for varying amounts of time with a Jinaopu UV lamp (UV-1800 Spectro photometer shimadzu co), then the absorption spectra of the irradiated thin films were monitored on the UV-2500 spectrophotometer. The photo-degradation of the small molecule TIIG-T-EM were carried on as following approaches: the dilute CB solution of copolymers were put into a silica glass tube, degassed and kept under argon, then irradiated with UV-radiation ex-situ for varying amounts of time with a Jinaopu UV lamp (UV-1800 Spectro photometer shimadzu co). The vial was placed within 15 cm of the UV lamp, and circumrotated of 400 cyclic per minute, ensuring that the entire solution volume being uniformly irradiated. After that, the UV absorption spectra of the small molecule TIIG-T-EM in solution were monitored. Thermal gravimetric analysis (TGA) was conducted on a TGA 2050 (TA instruments) thermal analyses system under a heating rate of 10°C/min and a nitrogen flow rate of 20 mL/min. The Atomic force microscope (AFM) uses MFP-3D-SA produced by Oxford Instruments, Santa Barbara, California, USA, to

test the atomic force height diagram and phase diagram (tap mode) of the film sample. The X-ray diffraction (XRD) was carried out on a PAN alytical X'Pert PRO diffractometer equipped with a rotating anode (Cu Kα radiation, λ = 1.54Å).

2. Fabrication and characterization of the organic Photodetectors

Indium tin oxide (ITO) patterned glass substrates were cleaned by scrubbing with soap water, followed by sonication in soapy water, deionized water, acetone, and isopropanol. Then the treated ITO was put into a drying oven for 2 h at 80 ℃. The drying ITO substrates were treated with UV-ozone for 8 min and a layer of Poly(3,4-ethylenedioxythiophene)- poly(styrenesulfonate) (PEDOT:PSS) was spin-coated at 3000 rpm for 30 s on the ITO substrates and follow by annealing at 150 ℃ for 15 min. Then, the active layer blend solutions were prepared with the PBDB-T and TIIG-T-EM weight ratios of 1:1 in chloroform. Then 1mg/mL of PDINN in methyl alcohol solutions were used to prepare the electrode modification layer. Finally, the substrates were placed into vacuum coating equipment. A 100 nm thick silver electrode was deposited on top of the substrate by thermal evaporation.

The current density-voltage (*J-V*) characteristics of the devices were measured in a glovebox with a Keithley 2400 measuring unit under dark conditions, The dark current density (J_d) was measured at 0 V bias after allowing the current to stabilize for 15 min, and the reported value represents the average obtained from 5 independent devices fabricated under identical conditions. The EQE was measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Beijing 7-star Opt. In. Co.), in which an integrated standard single-crystal Si photovoltaic cell (S1337-101BQ, SOFN instruments co., Ltd. calibrated by National Institute of Metrology of China) was employed to calibrate the light intensity at each wavelength.

3. Synthesis of the small molecule TIIG-T-EM

3.1 Synthesis of the compound **TIIG-T**

Under an argon atmosphere, compound TIIG-Br (1.5 g, 1.7 mmol) and bis(triphenylphosphine)palladium (II) dichloride (12 mg, 0.017 mmol) were added to a

dried three-neck flask. Toluene (40 mL) and DMF (5 mL) were then introduced, and the mixture was degassed by bubbling argon for 20 minutes to remove dissolved oxygen. Subsequently, compound Th12-Sn (3.75 g, 6.9 mmol) was injected into the reaction mixture via syringe. The reaction was heated to reflux and maintained for 4–5 hours. Upon completion, the mixture was extracted with dichloromethane (DCM), and the combined organic layers were concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a mixed eluent of petroleum ether and DCM (v:v = 2:1), affording the desired product as a green solid (1.67 g, 1.36 mmol, 80.3% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.4 Hz, 2H), 6.88 (d, *J* = 1.2 Hz, 2H), 6.80 (s, 2H), 3.68 (d, *J* = 7.5 Hz, 4H), 2.59 (t, *J* = 7.7 Hz, 4H), 1.94 – 1.85 (m, 2H), 1.68 – 1.58 (m, 4H), 1.40 – 1.17 (m, 84H), 0.92 – 0.80 (m, 18H).

3.2 Synthesis of the compound **TIIG-T-CHO**

Under an argon atmosphere, TIIG-T (1.53 g, 1.25 mmol) was placed in a dried two-neck flask and dissolved in 1,2-dichloroethane (15 mL). At 0 °C, a mixture of phosphorus oxychloride (2.88 g, 18.75 mmol) and anhydrous DMF (2.9 g, 18.8 mmol) was added dropwise to the solution. The reaction was allowed to warm to room temperature, then heated to 50 °C for 2 h, and finally to 75 °C overnight. After cooling, the mixture was poured into ice-water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel column chromatography (petroleum ether / DCM, 1 : 3 v/v) afforded the title compound as a green solid (1.10 g, 0.86 mmol, 68.8 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 2H), 7.28 (s, 2H), 6.96 (s, 2H), 3.71 (d, *J* = 7.5 Hz, 4H), 2.93 (t, *J* = 7.7 Hz, 4H), 1.91 (m, 2H), 1.71 (m, 4H), 1.35 – 1.25 (m, 84H), 0.92 – 0.76 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.42, 170.78, 153.89, 152.09, 145.49, 144.24, 136.87, 127.37, 120.09, 116.26, 109.21, 46.28, 37.19, 31.93, 31.88, 31.81, 31.42, 31.26, 30.00, 29.67, 29.65, 29.53, 29.41, 29.36, 29.32, 28.59, 26.37, 26.34, 22.70, 22.67, 14.13, 14.10.

3.3 Synthesis of the compound **TIIG-T-EM**

Under a nitrogen atmosphere, TIIG-T-CHO (200 mg, 0.157 mmol) and 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile (300 mg, 1.57 mmol) were charged into a dried 25 mL three-neck flask. Anhydrous chloroform (15 mL, freshly distilled) was added,

and triethylamine (0.6 mL) was introduced dropwise. The mixture was degassed by bubbling nitrogen through a long needle for 10 min, then heated to reflux while monitoring by TLC. After completion, the reaction was quenched with water. The mixture was extracted with DCM, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica-gel column chromatography (petroleum ether / DCM, 1 : 1 v/v) gave the product as a dark-green solid (152 mg, 0.093 mmol, 59 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.35 (s, 2H), 6.95 (s, 2H), 4.34 (q, J = 7.2 Hz, 4H), 3.76 (d, J = 7.6 Hz, 4H), 2.79 (t, J = 7.7 Hz, 4H), 2.00 (m, 2H), 1.67 (m, 4H), 1.43 (m, 8H), 1.40 – 1.22 (m, 82H), 0.89 – 0.80 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.63, 165.93, 165.34, 153.18, 152.67, 144.80, 143.63, 131.42, 127.56, 126.11, 119.63, 116.96, 113.42, 112.64, 112.32, 108.90, 55.52, 46.83, 40.77, 37.16, 31.94, 31.89, 31.81, 31.38, 30.99, 30.09, 29.75, 29.69, 29.67, 29.56, 29.47, 29.44, 29.38, 29.35, 29.22, 26.42, 26.37, 22.71, 22.67, 14.23, 14.13, 14.11. the HRMS spectra showed ion peak *m/z* at 1629.87356 for $[M + H]^+$.

4. ^{1}H NMR and ^{13}C NMR spectra of the monomers.

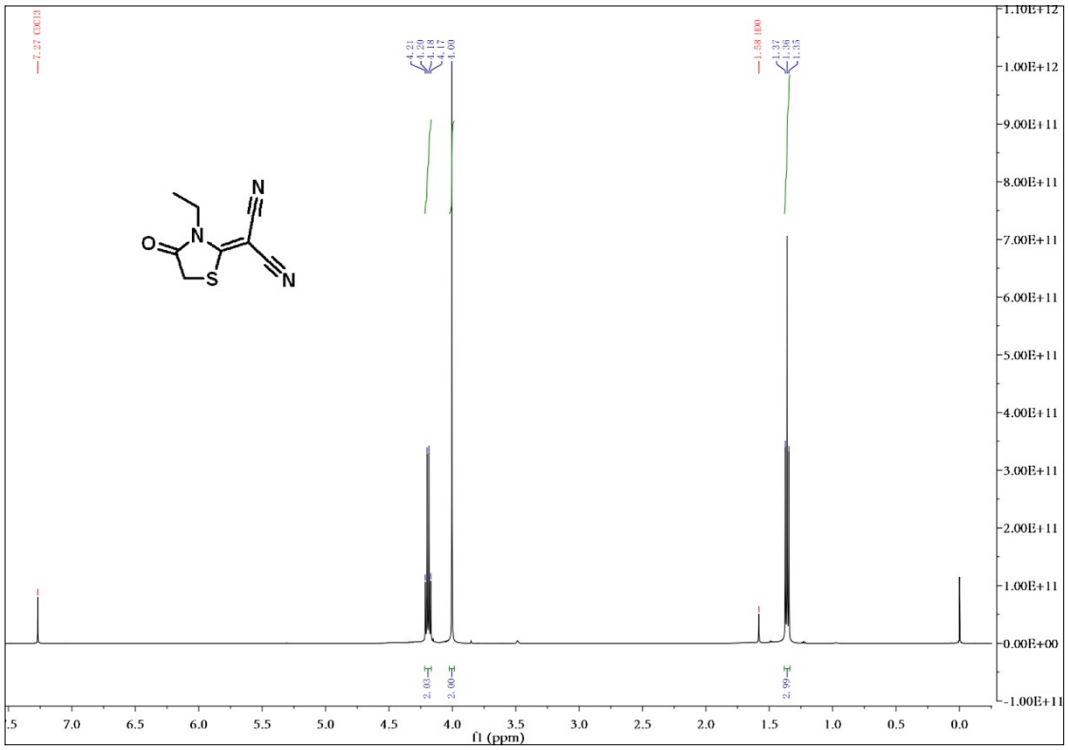

Fig. S1 ^{1}H NMR spectrum of 2-(3-ethyl-4-oxo-thiazolidin-2-ylidene)-malononitrile in $CDCl_3$

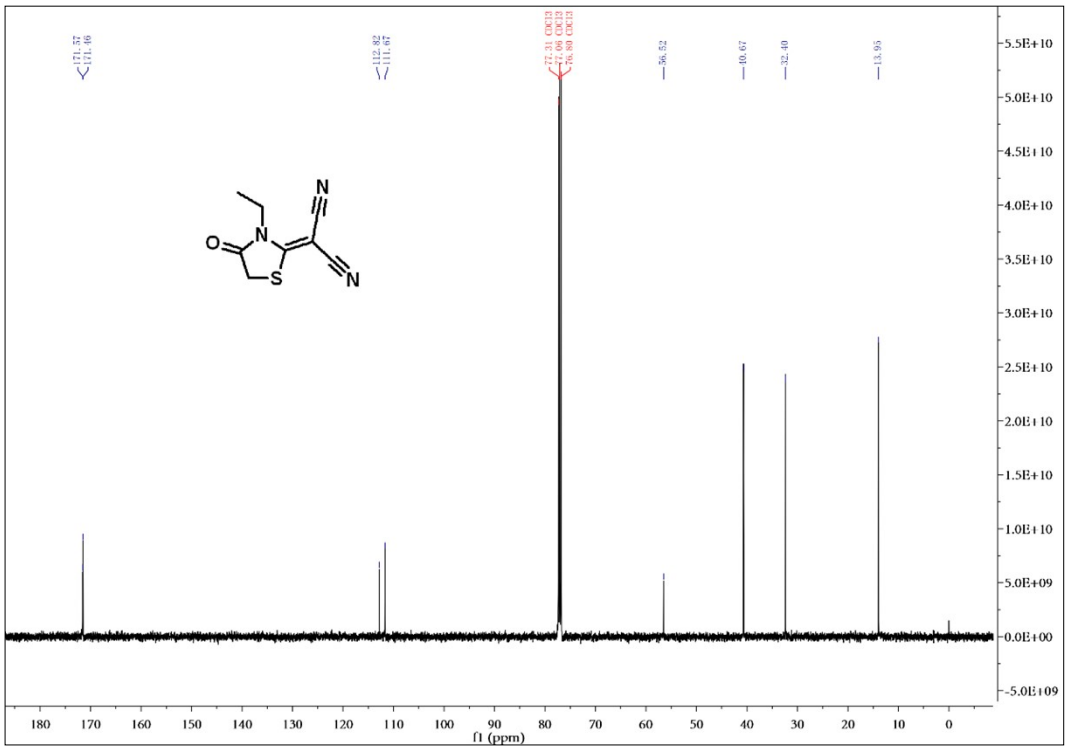

Fig. S2 ^{13}C NMR spectrum of 2-(3-ethyl-4-oxo-thiazolidin-2-ylidene)-malononitrile in $CDCl_3$

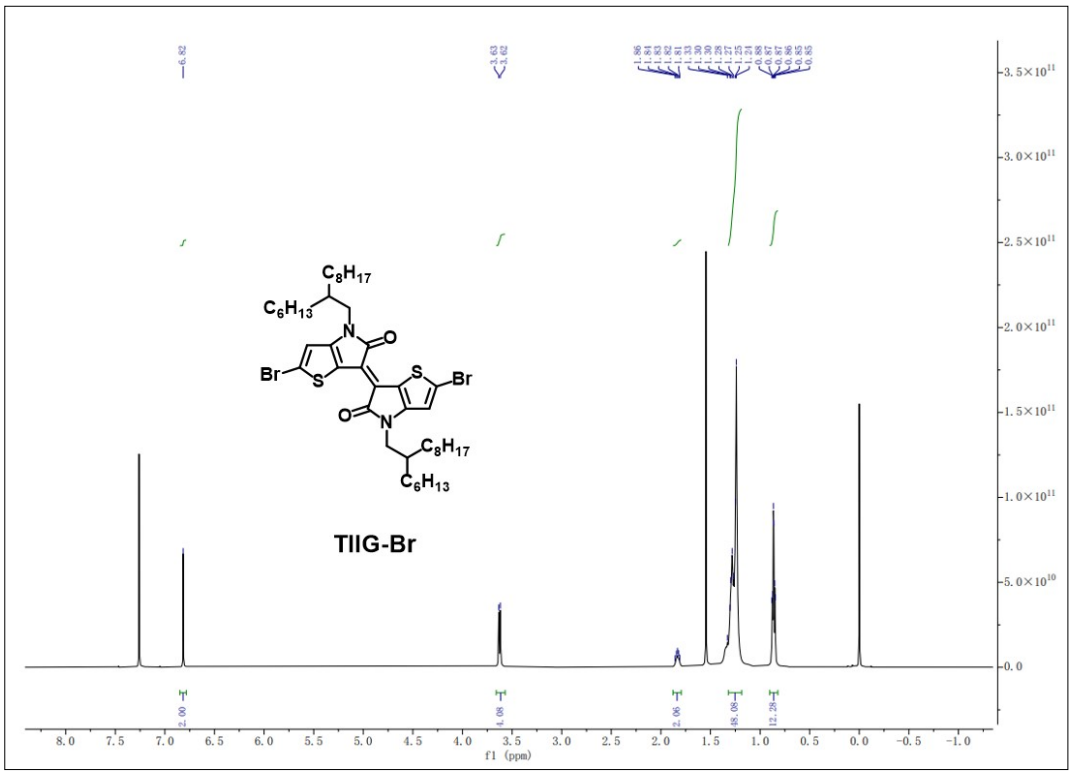

Fig. S3 ^{1}H NMR spectrum of TIIG-Br in $CDCl_3$

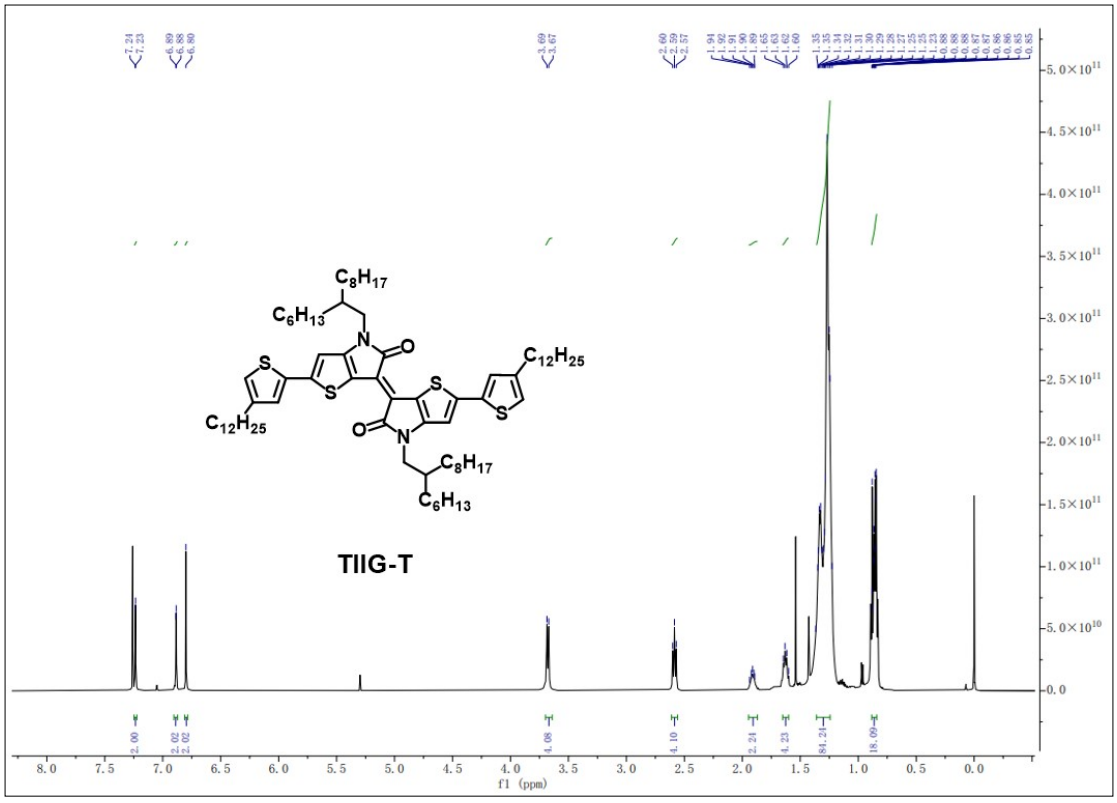

Fig. S4 ^{1}H NMR spectrum of TIIG-T in $CDCl_3$

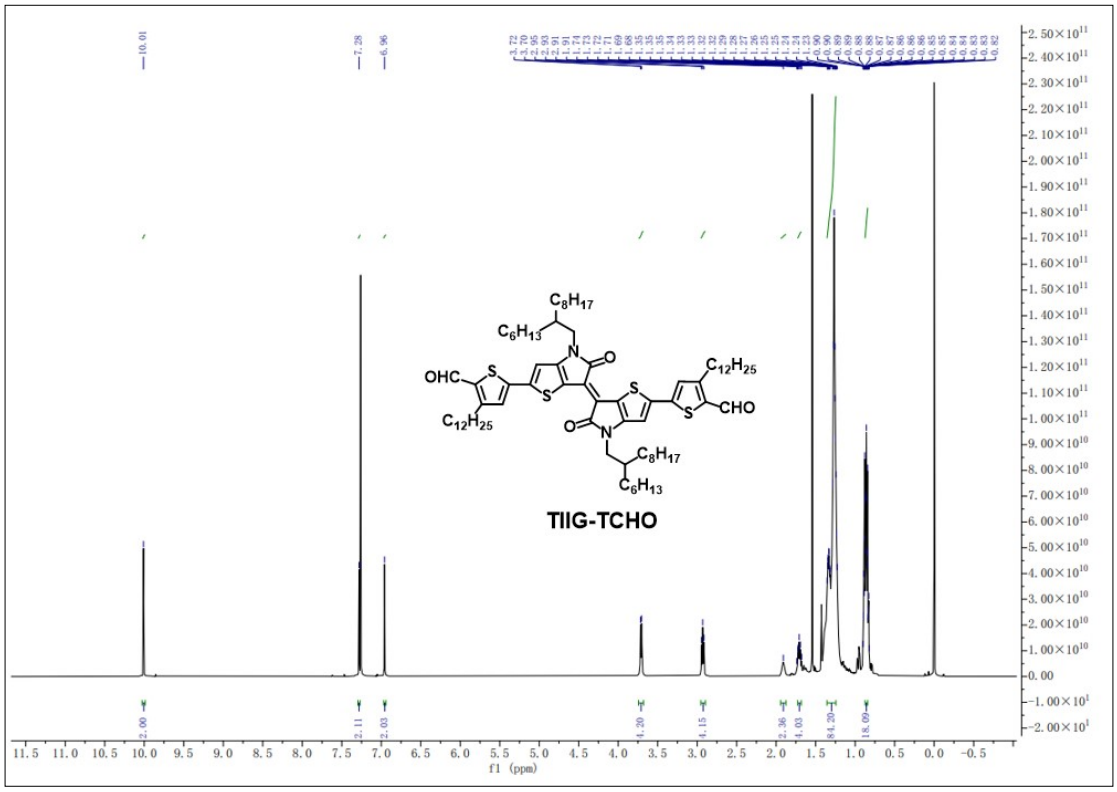

Fig. S5 ^{1}H NMR spectrum of TIIG-TCHO in $CDCl_3$

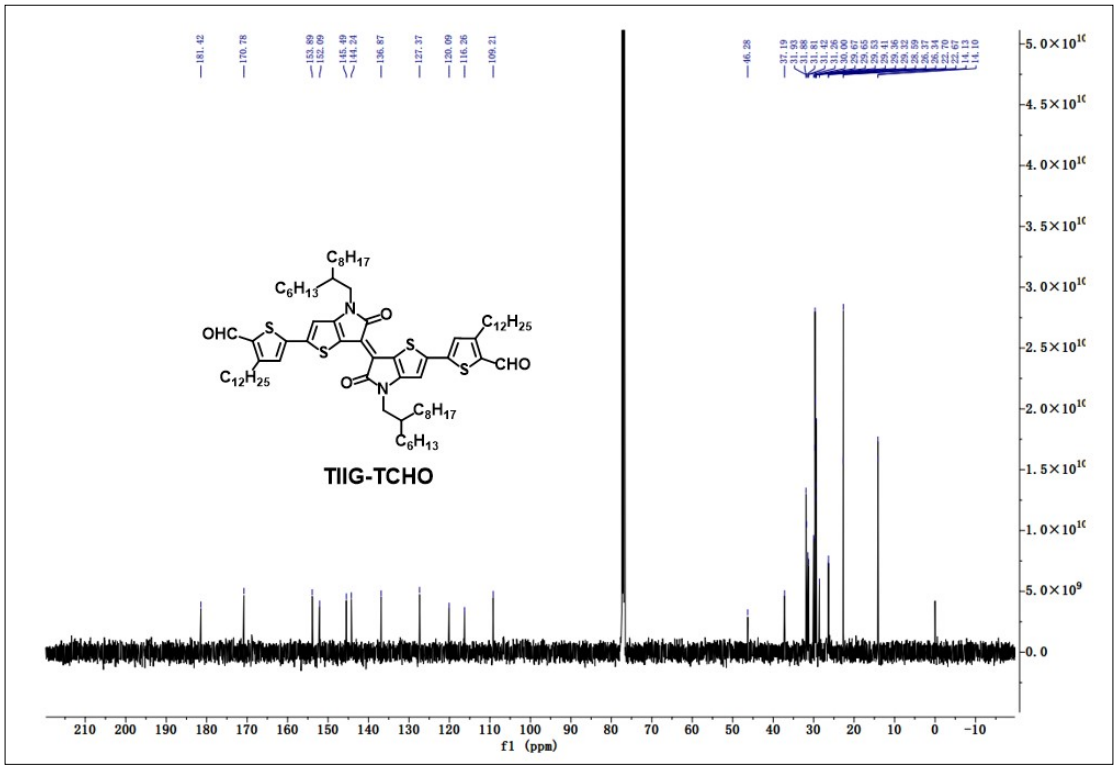

Fig. S6 ^{13}C NMR spectrum of TIIG-TCHO in $CDCl_3$

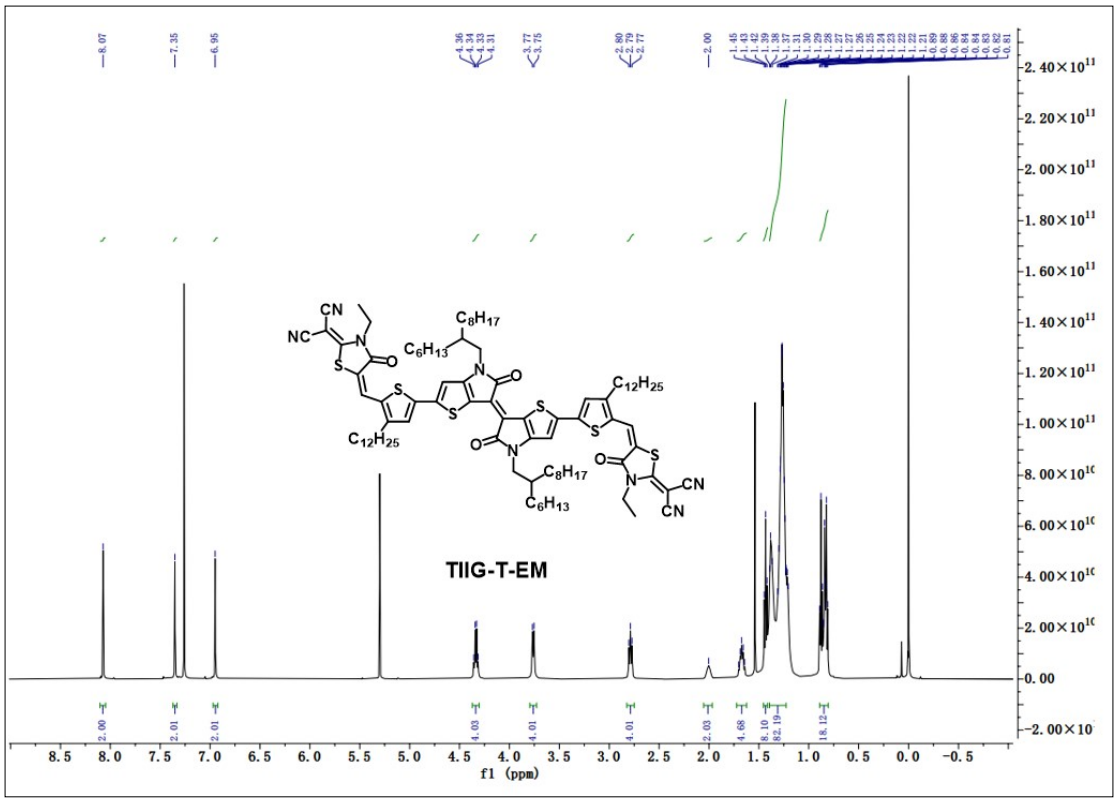

Fig. S7 ^{1}H NMR spectrum of TIIG-T-EM in $CDCl_3$

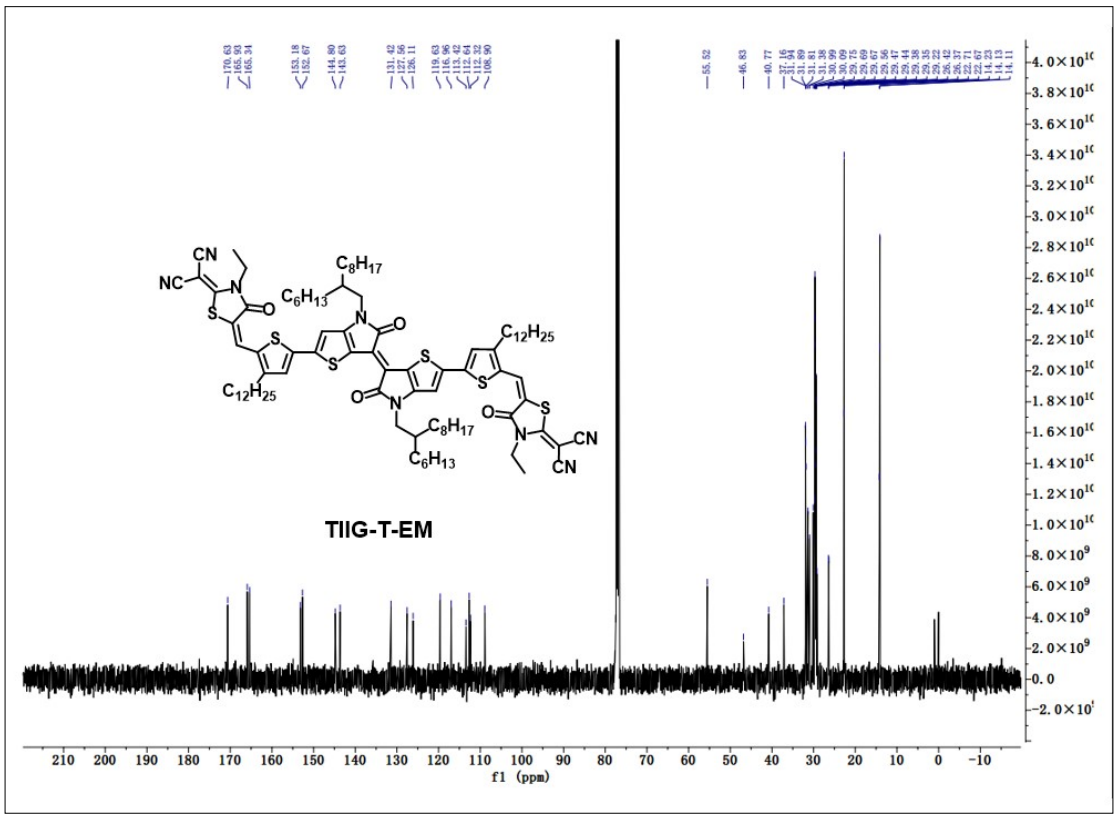

Fig. S8 ^{13}C NMR spectrum of TIIG-T-EM in $CDCl_3$

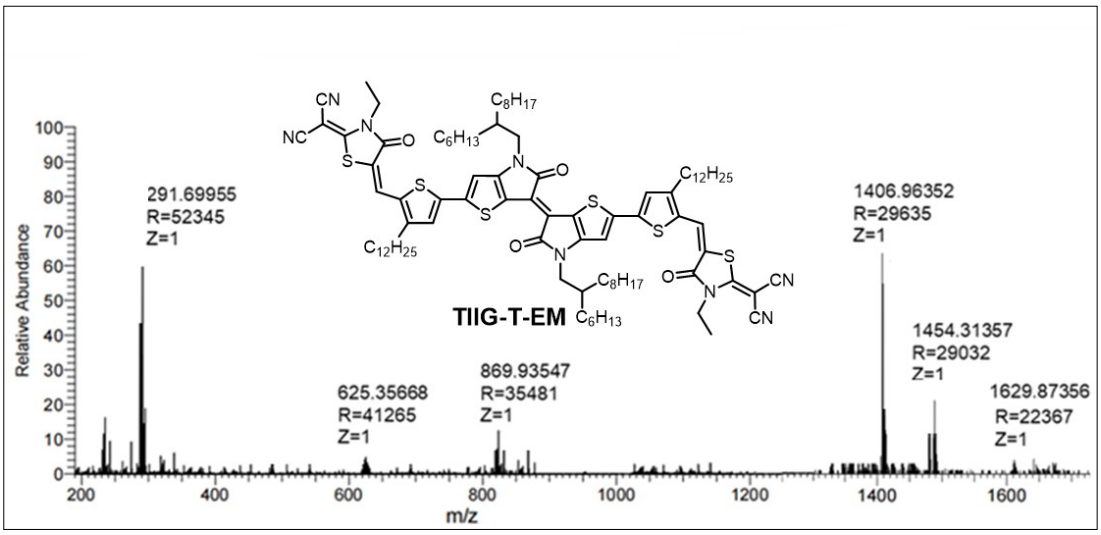

Fig. S9. HRMS spectrum of TIIG-T-M.

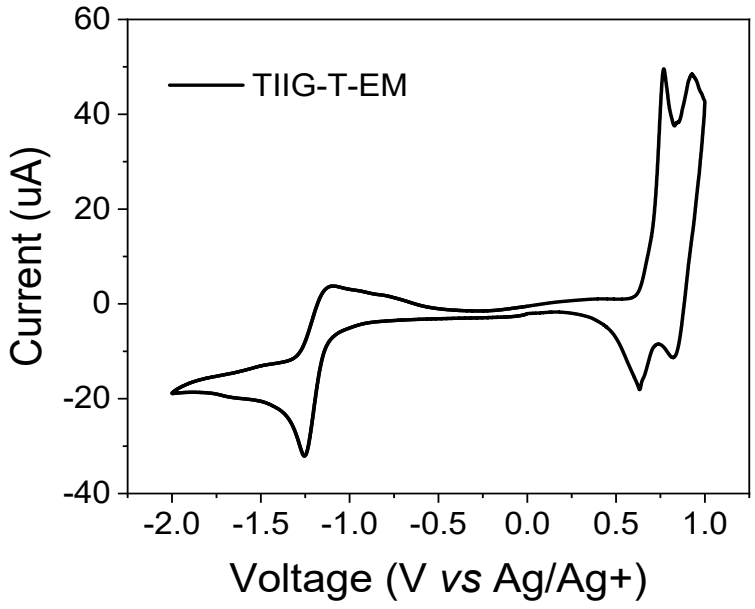

Fig. S10 CV curve of TIIG-T-EM.

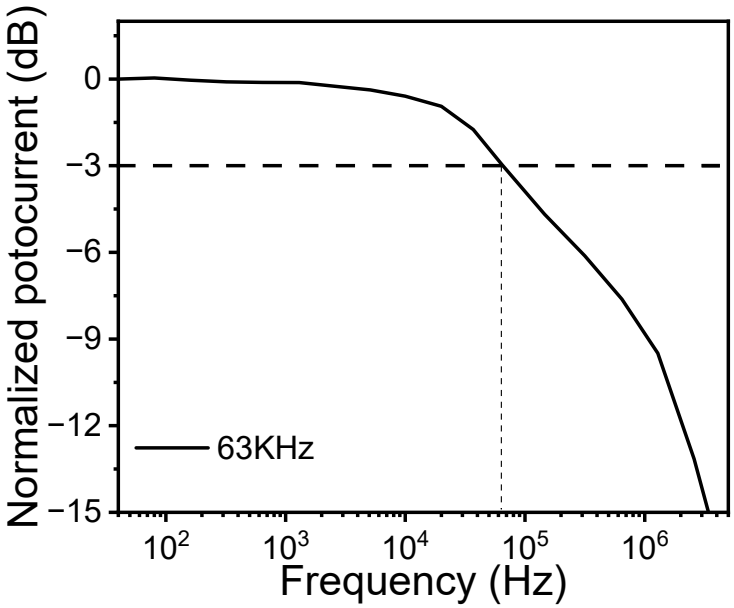

Fig. S11 −3dB cut-off frequency for the devices.