Electronic Supplementary Information for:

Polymer donors with phenylacetate pendants for efficient organic photovoltaics

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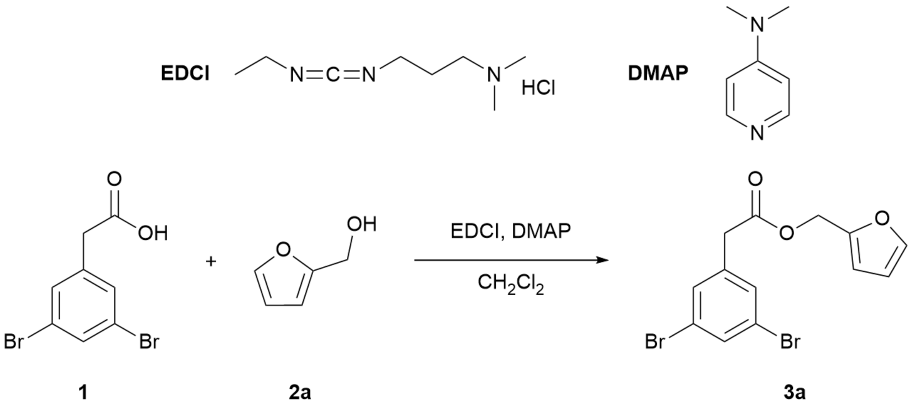
Materials

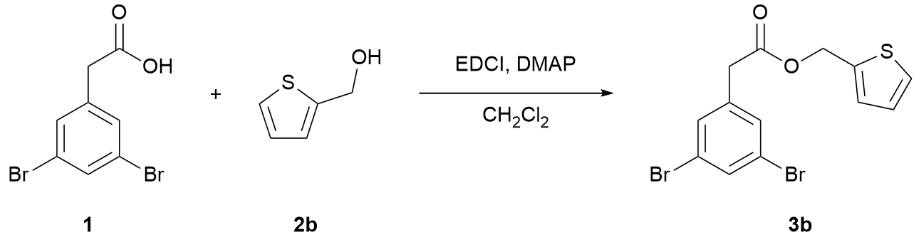
Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Toluene was purified by MBraun MB-SPS-5 Solvent Purifiers system. Intermediates 4 and 5 were purchased from Suna Tech Inc. PEDOT: PSS (P VP Al 4083) was purchased from Heraeus Clevis. BTP-eC9 and PDINN were purchased from Solarmer Materials (Beijing) Inc. Chlorobenzene was purchased from J&K Scientific, Inc. Other chemicals were purchased from Titan Technology (Shanghai) Inc.

Synthesis

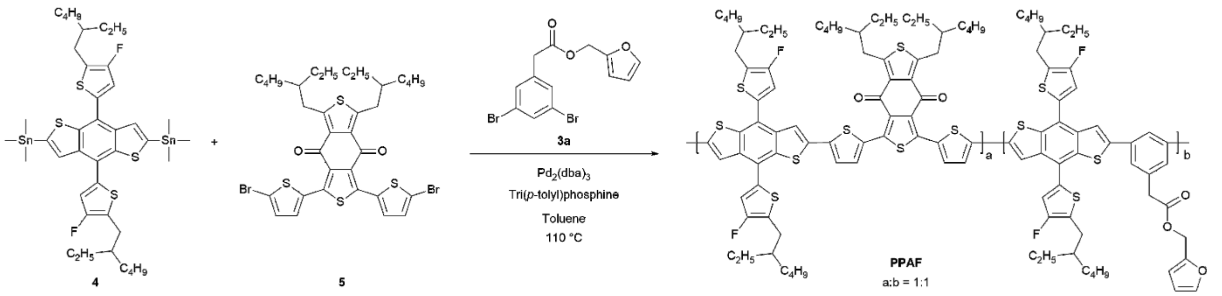


Furan-2-ylmethyl 2-(3,5-dibromophenyl)acetate (3a). 2-(3,5-dibromophenyl)acetic acid (**1**, 326.6 mg, 1.12 mmol), EDCI (234.2 mg, 1.23 mmol), DMAP (13.6 mg, 0.11 mmol) and furan-2-ylmethanol (**2a**, 137.8 mg, 1.41 mmol) were consecutively added into a 10 mL Schlenk tube with 3 mL dichloromethane. The mixture was stirred at room temperature overnight. After removing the solvent, the crude product was purified with column chromatography on silica gel using hexanes/ethyl acetate (2:1) as the eluent to obtain the target product as yellow oil (282.8 mg, 67.9%). ^{1}H NMR (400 MHz, DMSO): δ 7.74 (t, 1H, J = 1.0 Hz), 7.69 (dd, 1H, J_1 = 1.2 Hz, J_2 = 0.4 Hz), 7.54 (d, 2H, J = 1.6 Hz), 6.53 (d, 1H, J =

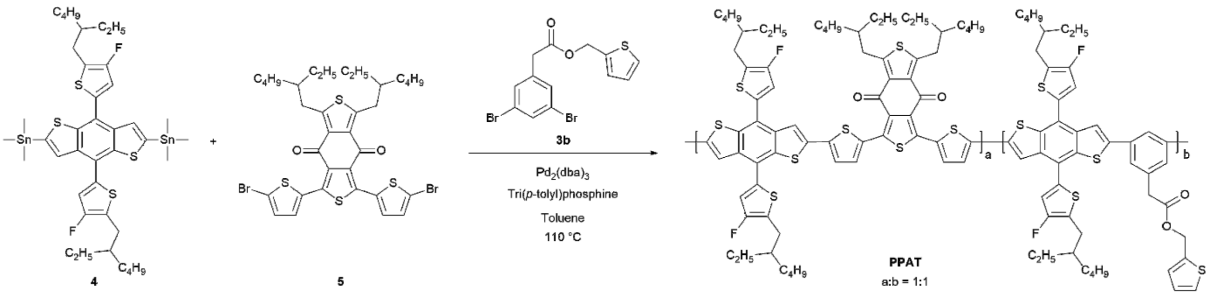
3.2 Hz), 6.47 (dd, 1H, J_1 = 1.9 Hz, J_2 =1.3 Hz), 5.10 (s, 2H), 3.79 (s, 2H). ^{13}C NMR (100 MHz, DMSO): δ 170.58, 149.52, 144.29, 139.35, 132.33, 132.14, 122.60, 111.51, 111.22, 58.57, 39.07.



Thiophen-2-ylmethyl 2-(3,5-dibromophenyl)acetate (3b). 2-(3,5-dibromophenyl)acetic acid (**1**, 293.9 mg, 1.0 mmol), EDCI (210.9 mg, 1.1 mmol), DMAP (12.2 mg, 0.1 mmol) and thiophen-2-ylmethanol (**2b**, 137.0 mg, 1.2 mmol) were consecutively added into a 10 mL Schlenk tube with 3 mL dichloromethane. The mixture was stirred at room temperature overnight. After removing the solvent, the product was purified with column chromatography on silica gel using hexanes/ethyl acetate (2:1) as the eluent to obtain the target product as faint yellow oil (122.1 mg, 31.5%). ^{1}H NMR (400 MHz, DMSO): δ 7.74 (t, 1H, J = 1.6 Hz), 7.57 (dd, 1H, J_1 = 4.0 Hz, J_2 = 0.8 Hz), 7.54 (d, 2H, J = 1.6 Hz), 7.17 (d, 1H, J = 3.2 Hz), 7.02 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz), 5.30 (s, 2H), 3.79 (s, 2H). ^{13}C NMR (100 MHz, DMSO): δ 170.64, 139.34, 138.13, 132.32, 132.14, 129.10, 128.06, 127.33, 122.60, 61.09, 39.19.



PPAF. Intermediate **4** (0.1 mmol, 94.1 mg), intermediate **5** (0.05 mmol, 37.5 mg) and **3a** (0.05mmol, 18.7 mg) were dissolved in toluene (5 mL) at 10 mL Schlenk tube. Then, $Pd_2(dba)_3$ (0.003 mmol, 3.0 mg) and tri(*p*-tolyl)phosphine (0.03 mmol, 9.0 mg) were added into the mixtures after being flushed with argon for five minutes. After that, the mixtures were purged with argon for another 10 min. The reactions were stirred at 110 °C for 24 h. The production was precipitated in methanol (150 mL) and filtrated. The dried precipitates were purified via Soxhlet extraction using hexane, dichloromethane, chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. Then, the product was filtrated, dried under vacuum overnight and obtained as a purple solid (67.2 mg, 66.2%).



PPAT. Intermediate **4** (0.1 mmol, 94.1 mg), intermediate **5** (0.05 mmol, 37.5 mg) and **3b** (0.05 mmol, 19.5 mg) were dissolved in toluene (5 mL) at 10 mL Schlenk tube. Then, $Pd_2(dba)_3$ (0.003 mmol, 3 mg) and tri(*p*-tolyl)phosphine (0.03 mmol, 9 mg) were added into the mixtures after being flushed with argon for five minutes. After that, the mixtures were purged with argon for another 10 min. The reactions were stirred at 110 °C for 24 h. The production was precipitated in methanol (150 mL) and filtrated. The dried precipitates were purified via Soxhlet extraction using hexane, dichloromethane, chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. Then, the product was filtrated, dried under vacuum overnight and obtained as a purple solid (79.8 mg, 78.0%).

Characterization

The ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV III HD 400 MHz spectrometer. Molecular weights were measured using gel permeation chromatography (GPC), which was performed with Agilent PL-GPC220 using 1,2,4-trichlorobenzene as the eluent at 150 °C. Flow rate was 1.00 mL min^{-1} and column set length was 650 mm. Polystyrene was used as the standard sample used for calibration. Solution (chloroform) and film (on quartz substrate) absorption spectra were recorded on a Shimadzu UV-2600i spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate ($[^{n}Bu_4N]^{+}[PF_6]^{-}$, 0.1 M) in CH_3CN using a computer-controlled CHI660E electrochemical workstation, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl reference electrode. The potential scan rate is 100 mV s^{-1}. Potentials were referenced to ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an external standard. The thickness of active layer was measured on a Bruker DektakXT profilometer. Contact angle measurements were performed on a KRÜSS DSA25 optical contact angle measuring system. Atomic force microscopy was conducted on a Bruker Innova atomic force microscope.

Molecular modeling

Density functional theory (DFT) calculations were performed with the ORCA 5.0.4[S1, S2] program using the B3LYP functional[S3, S4] and visualized by VMD.[S5] All-electron split valence basis set with polarization functions def2-SVP was used for all atoms.[S6] The molecules were neutral species with charges set as zero and spin multiplicity set as singlet. Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. The vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency.

Fabrication and characterization of OPVs

OPVs were fabricated with the device structure of ITO/PEDOT:PSS/active layers/PDINN/Ag. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried in an oven. The ITO substrates were treated by ultraviolet-ozone cleaner for 20 min before use. Then, PEDOT:PSS was spin-cast onto the ITO substrates at 4000 rpm for 40 s, and dried at 150 °C for 20 min in air. The donor:BTP-eC9 blend (w:w = 1:1, the donor concentration was 15 mg mL^{-1}) was dissolved in chlorobenzene with 0.6% (by volume) of 1,8-diiodooctane as the additive and stirred on a hotplate at 60°C in a nitrogen-filled glove box overnight. The donor:BTP-eC9 solution was spin-cast at 3000 rpm for 40 s on PEDOT:PSS to form the active layer. The thickness of the active layer was ~120 nm. A methanol solution of PDINN (1 mg mL^{-1}) was spin-cast on the active layer to from the cathode interlayer. Ag electrode (120 nm) was evaporated on PDINN under vacuum (5×10^{-5} Pa). The current density-voltage (*J-V*) curves of the devices were measured using a Keysight B2901B Precision Source/Measure Unit in glove box. An SS-X50 (Enlitech Co., Ltd.) solar simulator (AAA grade) coupled with AM 1.5G solar spectrum filters was used as the light source, and the optical power at the device was calibrated as 100 mW cm^{-2} using a polycrystalline silicon reference cell (SRC2020). The device area was 3.90 mm^2.

The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard monocrystalline Si photovoltaic cell. For stability test, a white LED sunlight simulator with an intensity equivalent to 1 sun was used as the light source (spectral region: 420-940 nm, Shenzhen Lancheng Technology Co., Ltd., LED-80).

3. GIWAXS and GISAXS measurements

GIWAXS data were obtained at beamline BL02U2 of Shanghai Synchrotron Radiation Facility (SSRF). The monochromatic of the light source was 1.24 Å. The data were recorded by using the two-dimensional image plate detector of Pilatus 2 M from Dectris, Switzerland. GISAXS data of films were obtained at beamline BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF). The monochromatic of the light source was 1.24 Å. The incidence angle was 0.2°, and the sample-to-detector distance was 2200 mm by calibration for GISAXS. The GISAXS 1D profiles were fitted with a universal model (Equation S1). Data fitting was done using SasView (version 5.01) software.

$$I(q) = \frac{A_1}{[1+(q\xi)^2]^2} + A_2 P(q,R) S(q,R,\eta,D) + B \tag{S1}$$

$$S(q) = 1 + \frac{\sin((D-1)tan^{-1}(q\eta))}{(qR)^D} \frac{D\Gamma(D-1)}{[1+\frac{1}{(q\eta)^2}]^{\frac{(D-1)}{2}}} \tag{S2}$$

where A_1, A_2, and B are independent fitting parameters and q is the scattering wave vector. The average correlation length ξ of the donor domain and the Debye–Anderson–Brumberger (DAB) term make up the first term $I(q)$. The contribution from acceptor fractal-like aggregations is seen in the second term $S(q)$ (Equation S2). Here, R is the mean spherical radius of the primary acceptor particles, $P(q, R)$ is the form factor of the acceptor, $S(q, R, \eta, D)$

is the fractal structure factor to explain the primary particles interaction in this fractal-like aggregation system, η is the correlation length of the fractal-like structure, and D is the fractal dimension of the network. Equation S3 was used to calculate the average domain size by the Guinier radius of the fractal-like network R_g.

$$R_g = \eta\sqrt{\frac{D(D+1)}{2}} \qquad \text{(S3)}$$

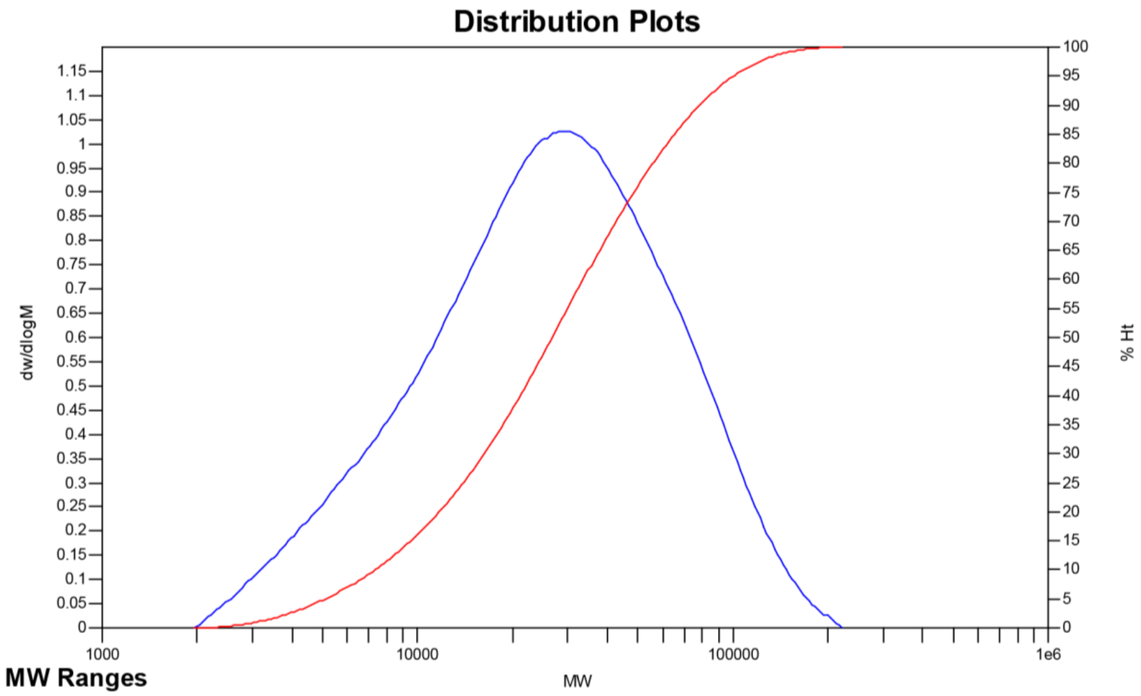


Fig. S1 GPC traces of PPAF

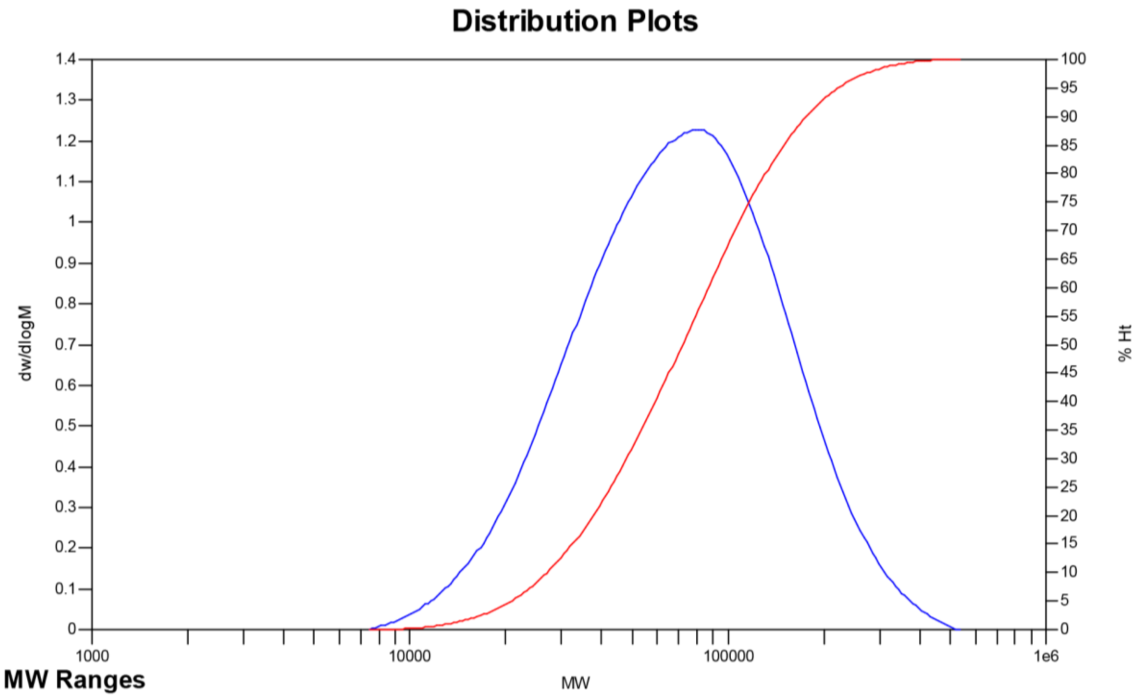


Fig. S2 GPC traces of PPAT

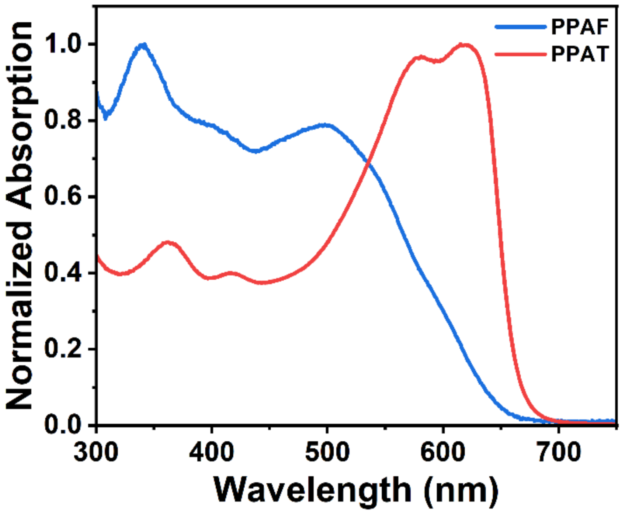


Fig. S3 The normalized absorption spectra of PPAF and PPAT chloroform solutions.

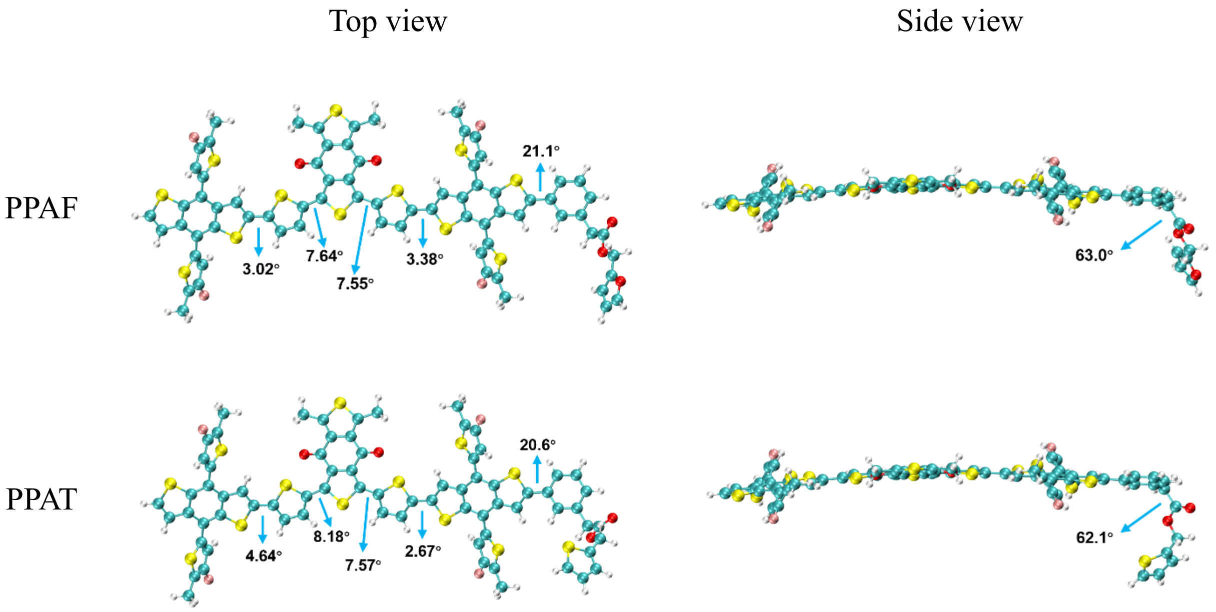


Fig. S4 The geometries of PPAF and PPAT segments (alkyl chains are simplified to methyl). The dihedral angles between adjacent moieties are presented.

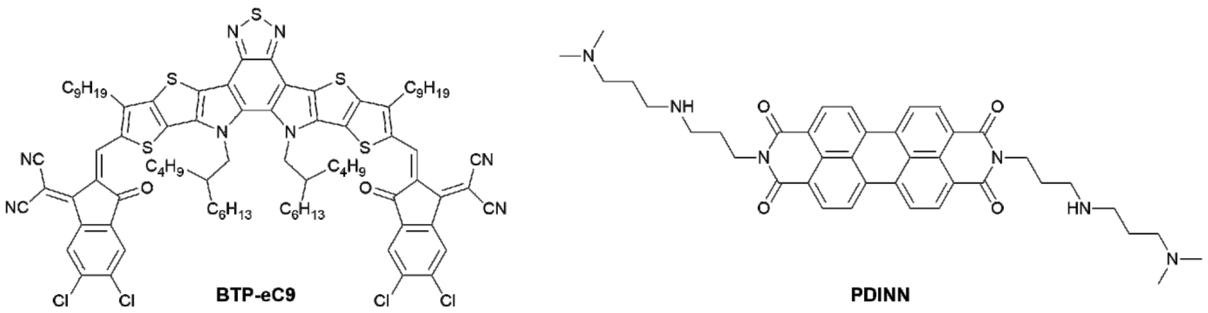


Fig. S5 The molecular structures of BTP-eC9 and PDINN.

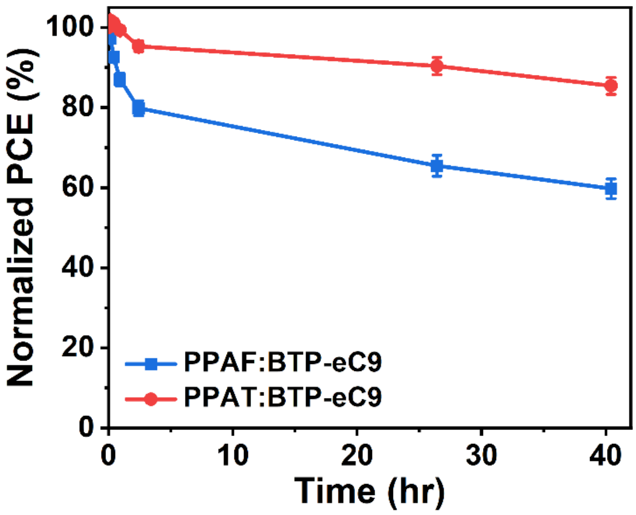
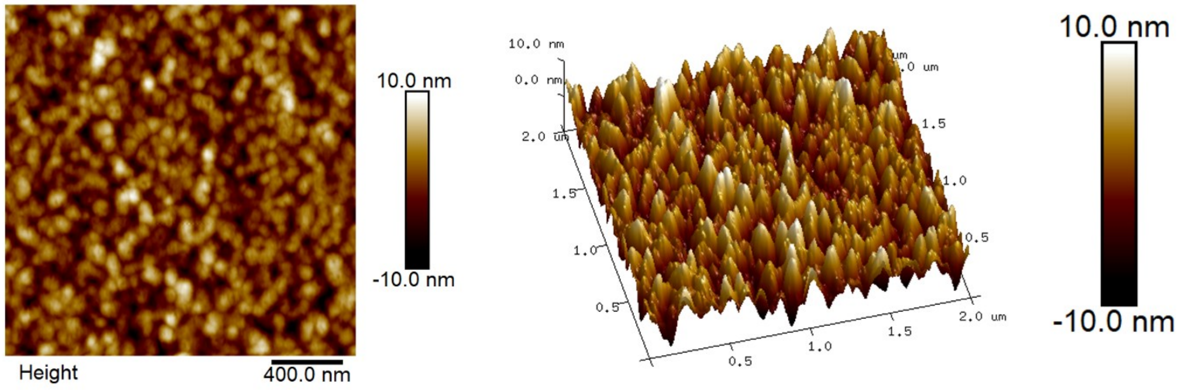


Fig. S6 Normalized PCEs of the devices under continuous 1 sun illumination of an array of white LED. Average PCEs and error bars are calculated from eight devices.

(a) PPAF:BTP-eC9



(b) PPAT:BTP-eC9

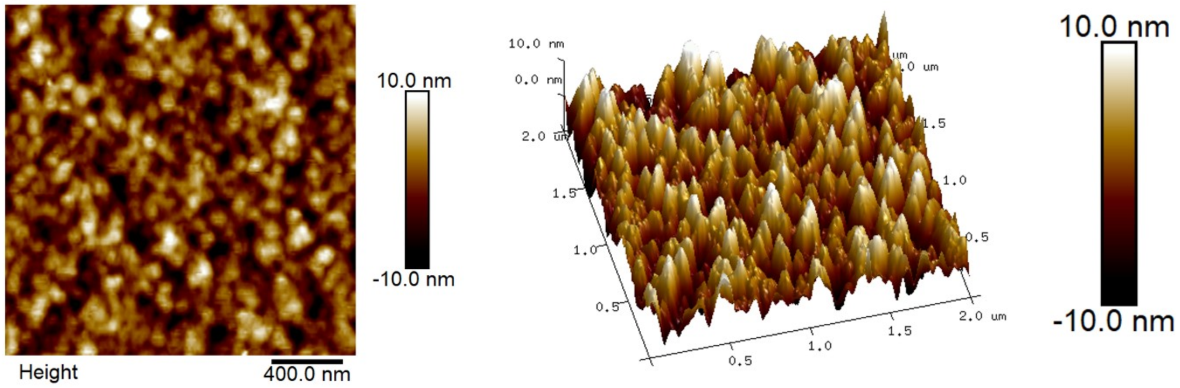


Fig. S7 AFM height images of PPAF:BTP-eC9 and PPAT:BTP-eC9 films.

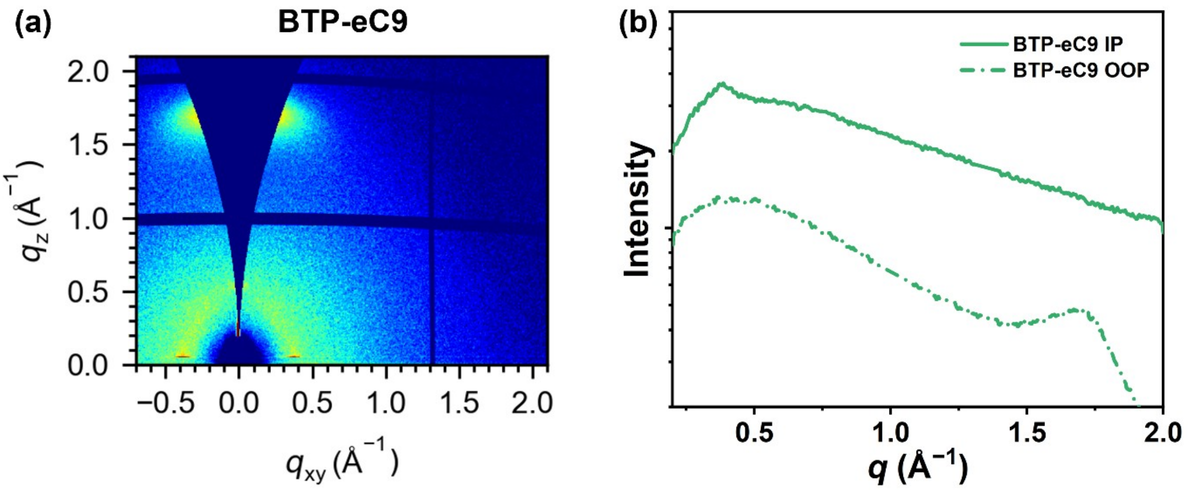


Fig. S8 (a) 2D GIWAXS pattern and (b) the corresponding line cut profiles of neat BTP-eC9 film.

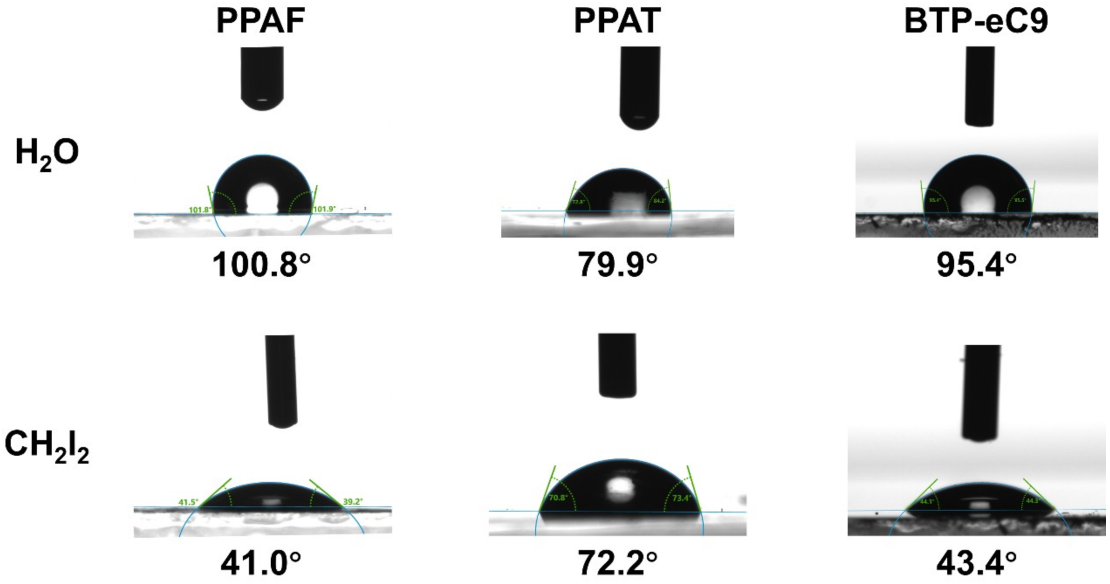


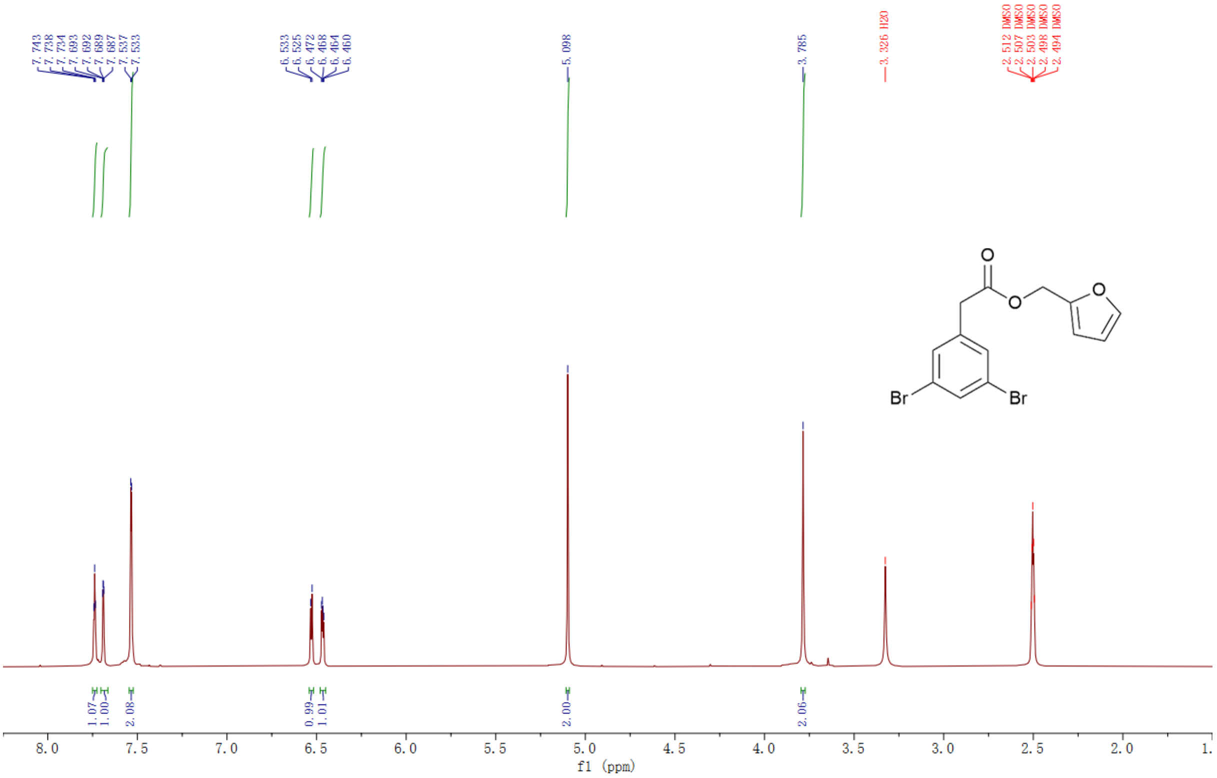
Fig. S9 Contact angle images of PPAF, PPAT and FNIC3 films using water and diiodomethane as the testing liquids.

Table S1. Basic properties of PPAF and PPAT.

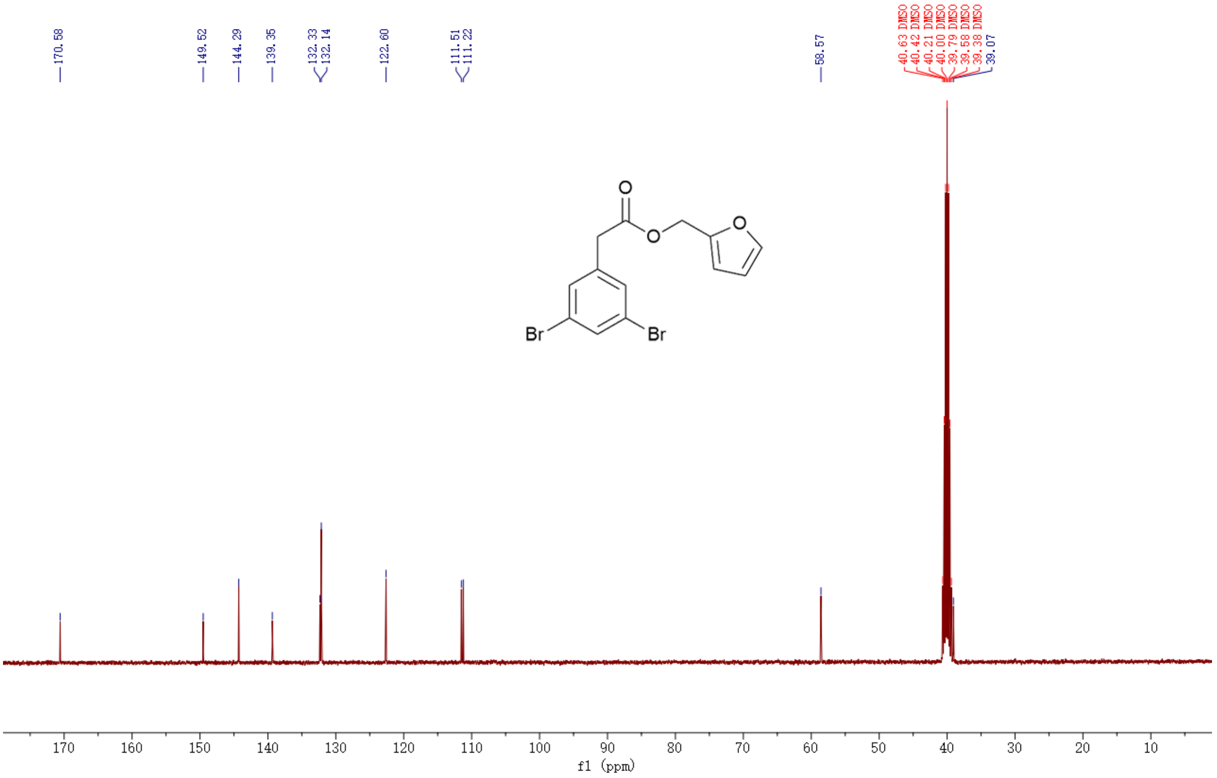
	λ_{abs} (nm)		E_g (eV)	HOMO (eV)	LUMO (eV)	M_n	M_w	PDI
	solution	film						
PPAF	498	555	1.88	–5.63	–3.50	16600	35800	2.16
PPAT	615	623	1.83	–5.57	–3.42	53600	89000	1.66

λ_{abs}: absorption maxima at longer wavelengths. E_g: optical bandgap estimated from the absorption edge in film. M_n: number-average molecular weight. M_w: weight-average molecular weight. PDI: polydispersity index.

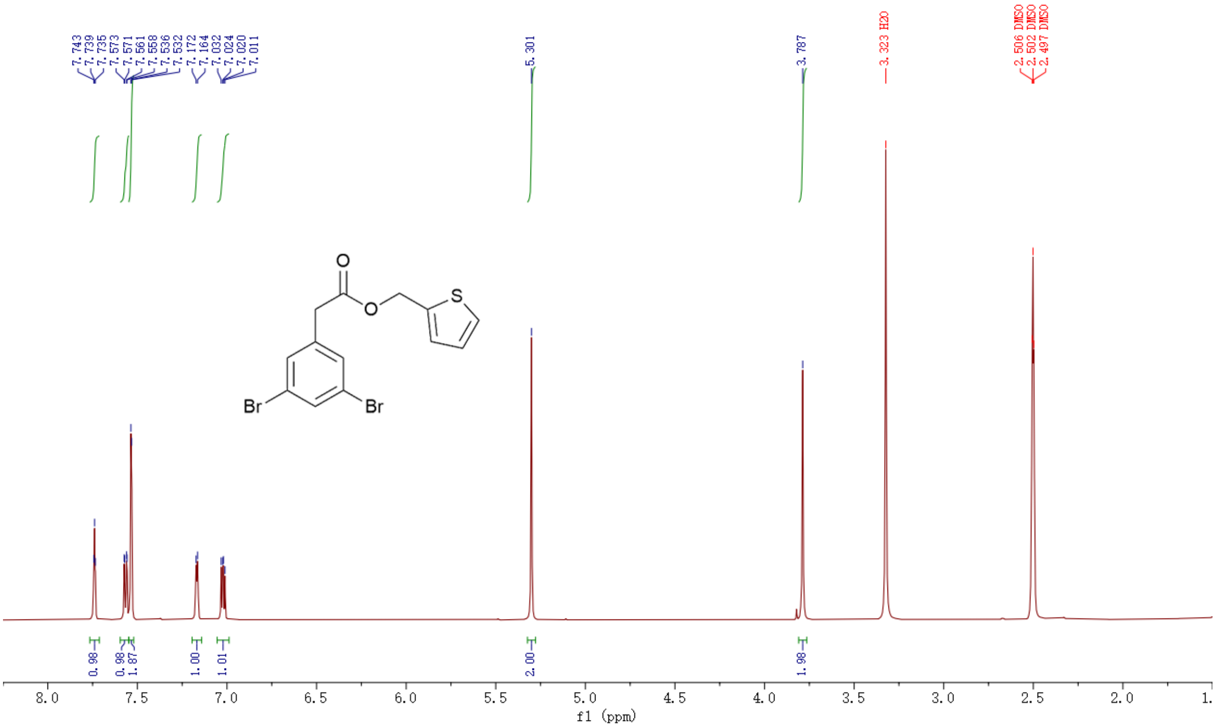
^{1}H NMR spectrum of furan-2-ylmethyl 2-(3,5-dibromophenyl)acetate (**3a**)



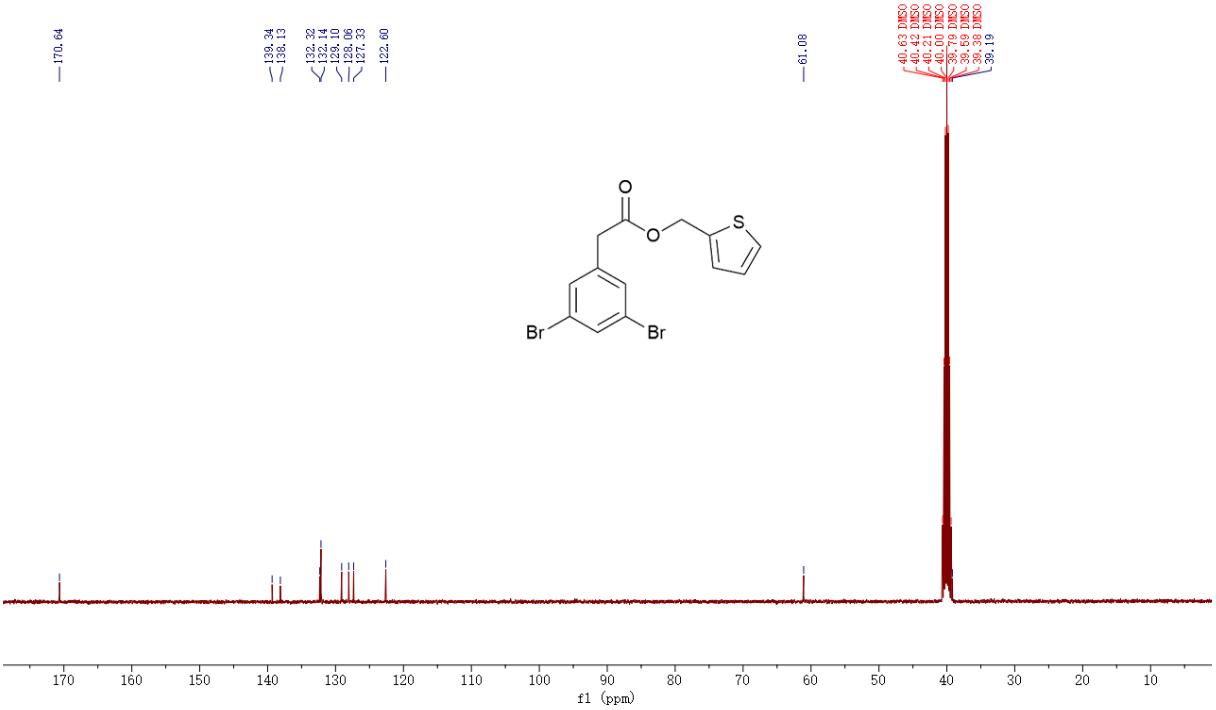
^{13}C NMR spectrum of furan-2-ylmethyl 2-(3,5-dibromophenyl)acetate (**3a**)



^{1}H NMR spectrum of thiophen-2-ylmethyl 2-(3,5-dibromophenyl)acetate (**3b**)



^{13}C NMR spectrum of thiophen-2-ylmethyl 2-(3,5-dibromophenyl)acetate (**3b**)



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