Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Organic photovoltaic electron acceptors showing aggregation-induced emission for reduced nonradiative recombination

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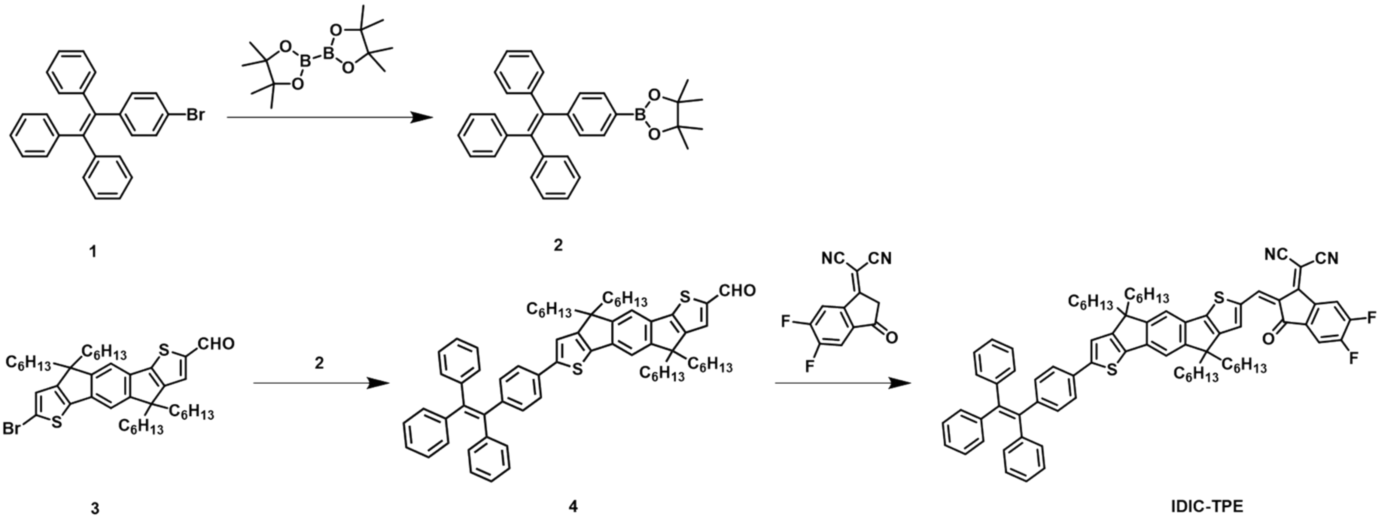
Materials and Synthesis

Y6 were purchased from eFlexPV Ltd. PM6 was purchased from Solarmer Materials Inc. Other reagents and solvents were purchased from Innochem Co. and SunaTech Co. without further purification. All chemical reactions were carried out under nitrogen atmosphere.



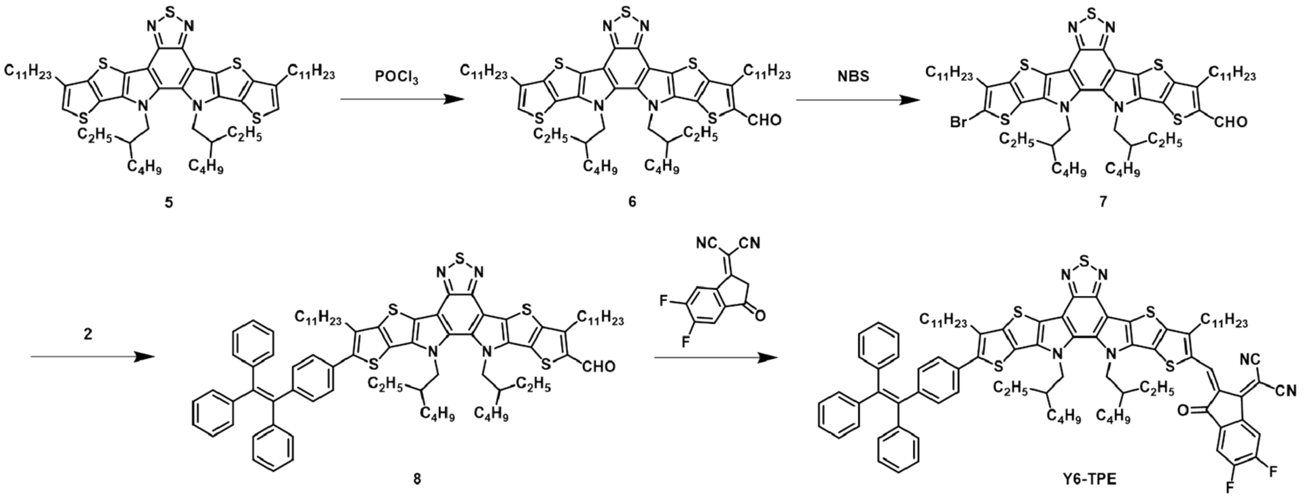
Scheme S1 The synthetic route for IDIC-TPE.

Synthesis of compound 2.

Compound 1 (400 mg, 0.97 mmol), potassium acetate (336 mg, 3.42 mmol), bis(pinacolato)diboron (372 mg, 1.46 mmol) and Pd(dppf)Cl$_2$ (35.2 mg, 0.048 mmol) were added to anhydrous 1,4-dioxane (20 mL) then reacted at 85°C for 15 h. After cooling to room temperature, the mixture was extracted with dichloromethane (CH$_2$Cl$_2$), dried with anhydrous MgSO$_4$. The filtrates were concentrated under reduced pressure and the crude product was purified by silica-gel column chromatograph using a mixture of ethyl acetate/petroleum ether (1:2, v/v) as eluent to give compound 2 (337 mg, 76 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm*)* 7.16 – 6.84 (m, 19H), 1.56 – 1.24 (m, 12H).

Synthesis of compound 4. Compound 2 (74 mg, 0.16 mmol), Compound 3 (58 mg, 0.08 mmol), potassium carbonate water solution (1.66 g, 12 mmol, 2 mol/L), and Pd(dppf)Cl$_2$ (5.9 mg, 0.008 mmol) were added into a 50 mL flask in toluene/water (21 mL, 5:2, v/v) and then stirred at 110°C for 12 h under nitrogen. Then the solution was extracted with CH_2Cl_2. The precipitate was purified by column chromatograph on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:2, v/v) as eluent to give compound 4 (38 mg, 49 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.81 (s, 1H), 7.33 – 6.99 (m, 19H), 1.96 – 1.78 (m, 8H), 1.20 (d, J = 11.6 Hz, 10H), 1.04 (dt, J = 12.3, 3.9 Hz, 20H), 0.82 – 0.76 (m, 6H), 0.70 (dt, J = 7.1, 3.4 Hz, 12H). MS (MALDI-TOF) m/z calcd. for ($C_{67}H_{76}OS_2$): 961.5. Found: 960.9.

Synthesis of compound IDIC-TPE. Compound 4 (38 mg, 0.04mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (46 mg, 0.20mmol) in $CHCl_3$ (20 mL) were added to a three-necked round-bottomed flask followed by adding pyridine (0.3 ml). The reaction mixture was stirred and refluxed for 16h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2, dried with anhydrous Na_2SO_4. The filtrates were concentrated under reduced pressure and the crude product was purified by column chromatograph on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:1, v/v) as eluent to give IDIC-TPE (18 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.87 (s, 1H), 8.46 (dd, J = 10.1, 6.5 Hz, 1H), 7.61 (d, J = 8.9 Hz, 1H), 7.36 – 6.97 (m, 19H), 4.70 (s, 2H), 2.26 – 2.04 (m, 2H), 1.95 – 1.79 (m, 6H), 1.18 (s, 6H), 1.05 (dd, J = 10.5, 5.1 Hz, 20H), 0.83 – 0.66 (m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 206.91, 158.87, 157.11, 154.09, 148.94, 143.68, 141.43, 141.12, 140.25, 140.10, 139.76, 138.64, 133.69, 132.74, 132.04, 131.42, 131.38, 131.33, 127.89, 127.77, 127.67, 126.63, 124.68, 117.58, 115.94, 114.79, 113.21, 54.25, 54.20, 39.18, 39.05, 31.56, 31.53, 30.93, 29.71, 29.65, 29.56, 24.32, 24.19, 22.57, 22.54, 14.00, 13.98. MS (MALDI-TOF) m/z calcd. for ($C_{79}H_{78}F_2N_2OS_2$): 1173.6. Found: 1172.9.



Scheme S2 The synthetic route for Y6-TPE.

Synthesis of compound 6. Compound 5 (309 mg, 0.32 mmol), N,N-dimethylformide (0.05 mL, 0.62 mmol) and phosphorus chloride oxide (0.05 mL, 0.52 mmol) were added into a 50 mL flask with 1,2-dichloroethane (20 mL) at 0°C. The reaction solution was stirred at 0°C for 12 h and then was added saturated sodium acetate aqueous solution (40 mL). Then the mixture was extracted with CH_2Cl_2, dried with anhydrous Na_2SO_4. The filtrates were concentrated under reduced pressure and the crude product was purified by column chromatograph on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:1, v/v) as eluent to give compound 6 (137 mg, 43%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 10.05 (s, 1H), 6.97 (d, J = 1.0 Hz, 1H), 4.60-4.46 (m, 4H), 3.11 (t, J = 7.7 Hz, 2H), 2.75 (t, J = 7.7 Hz, 2H), 1.95 (q, J = 6.4 Hz, 2H), 1.83-1.74 (m, 4H), 1.41 (s, 4H), 1.24- 1.19 (m, 22H), 0.87 (s, 8H), 0.80 (d, J = 2.2 Hz, 22H), 0.59-0.51 (m, 10H).

Synthesis of compound 7. Compound 6 (137 mg, 0.14 mmol) and N-bromosuccinimide (38 mg, 0.21 mmol) were added tetrahydrofuran (30 mL) at 0°C under nitrogen. The mixture was warmed up to room temperature and stirred overnight. The crude product was extracted into dichloromethane, and the organic layer was washed with water. The filtrates were concentrated under reduced pressure and the crude product was purified by column chromatograph on silica gel using a mixture of

CH_2Cl_2/petroleum ether (1:1, v/v) as eluent to give compound 7 (133 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.04 (s, 1H), 4.60 – 4.38 (m, 4H), 3.10 (t, J = 7.6 Hz, 2H), 2.78 – 2.67 (m, 2H), 1.83 (tdd, J = 26.5, 24.2, 10.3, 5.1 Hz, 6H), 1.17 (s, 34H), 1.02 – 0.94 (m, 4H), 0.81 (dt, J = 22.6, 6.9 Hz, 18H), 0.60 – 0.49 (m, 10H).

Synthesis of compound 8. Compound 2 (111 mg, 0.24 mmol), compound 7 (133 mg, 0.12 mmol), potassium carbonate (1.66 g, 12 mmol, 2 mol/L), and Pd(dppf)Cl_2 (8.9 mg, 0.012 mmol) were added into a 50 mL flask in toluene/water (21 mL, 5:2, v/v) and then stirred at 110 °C for 12 h under nitrogen. Then the solution was extracted with CH_2Cl_2. The precipitate was purified by column chromatograph on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:2, v/v) as eluent to give compound 8 (93 mg, 56 %). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.05 (s, 1H), 7.03 (ddt, J = 17.7, 7.0, 2.8 Hz, 19H), 4.60-4.45 (m, 4H), 3.12 (t, J = 7.7 Hz, 2H), 2.77 (t, J = 8.1 Hz, 2H), 1.49 (s, 2H), 1.43 (s, 4H), 1.24 (s, 18H), 0.90 (s, 4H), 0.88 (d, J = 7.6 Hz, 10H), 0.82 (d, J = 2.3 Hz, 16H), 0.59-0.52 (m, 10H).

Synthesis of compound Y6-TPE. Compound 8 (93 mg, 0.07 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (81 mg, 0.35 mmol) in $CHCl_3$ (30 mL) was added to a three-necked round-bottomed flask followed by adding pyridine (0.5 ml). The reaction mixture was stirred and refluxed for 16h. After cooling to room temperature, the mixture was poured into methanol and filtered. The filtrates were concentrated under reduced pressure and the crude product was purified by column chromatograph on silica gel using a mixture of CH_2Cl_2/petroleum ether (1:1, v/v) as eluent to give Y6-TPE (54 mg, 51%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.05 (s, 1H), 8.47 (dd, J = 10.0, 6.4 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.30 – 6.90 (m, 19H), 4.77 – 4.44 (m, 4H), 3.15 (t, J = 7.9 Hz, 2H), 2.77 (t, J = 8.0 Hz, 2H), 2.01 (p, J = 6.7 Hz, 2H), 1.88 – 1.67 (m, 4H), 1.53 – 1.37 (m, 6H), 1.36 – 1.12 (m, 32H), 0.97 – 0.84 (m, 10H), 0.80 (q, J = 6.6 Hz, 8H), 0.58 (ddd, J = 19.2, 11.9, 6.7 Hz, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 206.91, 159.05, 148.44, 147.85, 145.00, 144.46, 143.60, 141.75, 138.90, 138.90, 136.61, 135.23, 132.76, 131.74, 131.74, 131.42, 131.33, 131.33, 128.37, 127.81, 127.77, 127.71, 126.65, 118.87, 114.30, 40.25, 31.94, 31.92, 31.26, 30.93, 29.84, 29.77, 29.68, 29.64, 29.62, 29.52, 29.46, 29.38, 29.34, 29.15, 28.34, 27.87, 22.77, 22.71, 22.69, 14.14, 14.12, 13.74, 10.19. MS (MALDI-TOF) m/z calcd. for ($C_{95}H_{102}F_2N_6OS_5$): 1542.2. Found: 1541.7.

Measurements and Instruments

^{1}H NMR spectra were recorded on Bruker AVANCE (300 MHz and 400 MHz) in $CDCl_3$. ^{13}C NMR spectra were recorded on Bruker AVANCE III (500 MHz) in $CDCl_3$. The MALDI-TOF mass spectrometry experiments were performed on an autoflex III instrument (Bruker Daltonics, Inc.).

The UV-vis absorption spectra were obtained on a UH4150 Spectrophotometer. Cyclic voltammogram measurements were obtained on a CHI660C electrochemical workstation under a nitrogen atmosphere in acetonitrile, with sample film coated Platinum disk electrode as the working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode, and tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte. Ferrocenium/Ferrocene (Fc/Fc^+) couple was chosen as the inner reference.

Photoluminescence (PL) measurements were obtained on a F-4500 fluorescence spectrophotometer. For AIE measurements, the solution of IDIC-4F, IDIC-TPE, Y6 and Y6-TPE were dissolved in tetrahydrofuran (THF) (10^{-6} mol L^{-1}), respectively. Then the THF solution (200 μL) was added into 1.8 mL THF/water mixture (with proportions of H_2O from 0% to 90%) and the final mixture was mixed well before measuring PL.

Electroluminescence quantum efficiency (EQE_{EL}) and electroluminescence (EL) measurements were performed by an integrated system (REPS, Enli Technology Co., Ltd.).

Space-charge limited current was employed to measure electron mobility of the device based on PM6: IDIC-TPE. The electron-only diodes were fabricated using the architectures: ITO/ ZnO/ PM6: IDIC-TPE (1:1.2, w/w)/ Ca/ Al. The result was plotted as Current density (J)~ Voltage (V) curve with double logarithm coordinates and electron mobility (μ_e) was calculated by MOTT-Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu_e V^2/8L^3$, where L stands for the film thickness of the active layer (*ca*. 120 nm), ε_r is the relative permittivity of free space (The regular value in orgainc films is *ca*. 3), J is current density and V is the applied voltage. The thickness of the film was measured *via* the Bruker Dektak-XT.

Photovoltaic device fabrication and characterization.

Devices were fabricated with the conventional structure of indium-tin-oxide (ITO)/Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/ active layer/ N,N'-bis[7-(dimethylamino)-4-azaheptyl]-3,4,9,10-perylenetetracarboxylic diimide (PDINN)/ Ag. ITO substrates were cleaned in deionized water, acetone, and isopropyl alcohol by sonication subsequently, and finally dried. The PEDOT:PSS layer was spin-coated onto precleaned ITO glass substrates at 4000 rpm for 30 s, and subsequently dried at 150 °C for 15 min in air. The active layer of PM6:IDIC-TPE:IDIC-4F (totally 12.5 mg mL^{-1}) blends were dissolved in chloroform with 0.2 vol.% DIO then deposited onto PEDOT:PSS layer through spin-coating at 2000 rpm for 40 s in nitrogen glove box. The active layer of PM6:Y6-TPE:Y6 (totally 16 mg mL^{-1}) blends were dissolved in with 0.5 vol.% 1-chloronaphthalene (CN) then deposited onto PEDOT:PSS layer through spin-coating at 4000 rpm for 40 s in nitrogen glove box followed by a thermal annealing at 110 °C for 5 min. The PDINN solution was dissolved in methanol (1 mg mL^{-1}) and then spin-coated on the active layer at 4000 rpm for 30 s.

Ag electrode (*ca.* 120 nm) was slowly deposited onto the surface of the PDINN layer by the thermal evaporation method under vacuum (*ca.* 10^{-5} Pa). The active area of the cells was 0.040 cm^2.

The *J–V* curves of all devices were employed using an AAA solar simulator (XES-70S1, SAN-EI Electric Co., Ltd) under illumination (AM1.5G, 100 mW cm^{-2}) and calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology) and a Keithley 2450 source-measure unit.

The molecular conformation of IDIC-4F and IDIC-TPE were investigated by density functional theory (DFT) approaches, using Gaussian 16 package[1] at the B3LYP/6-31+G(d,p) level.

Additional Figures

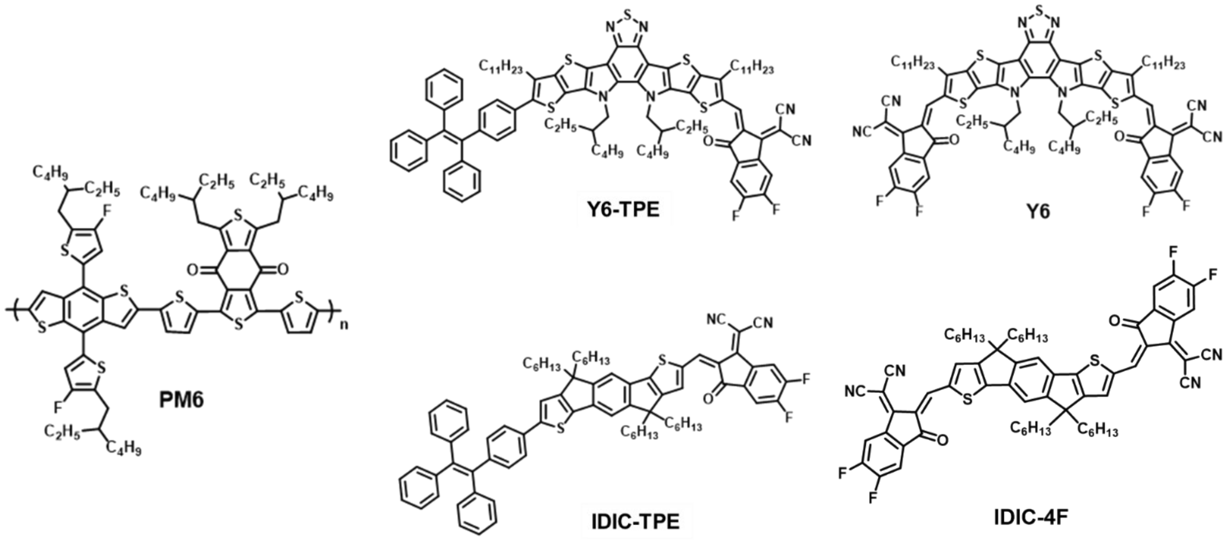
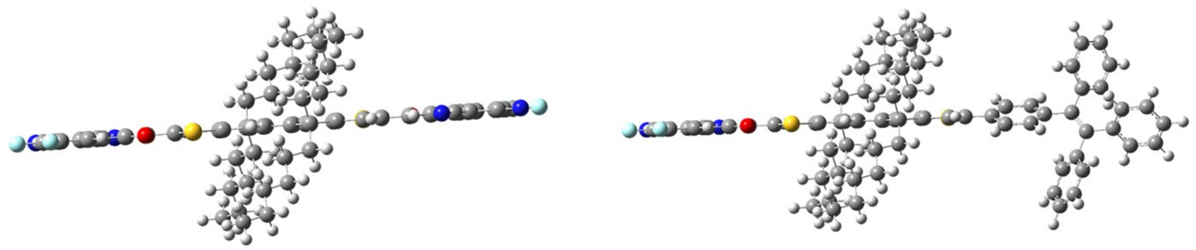


Figure S1. Chemical structures of PM6, IDIC-4F, IDIC-TPE, Y6, Y6-TPE.



IDIC-4F IDIC-TPE

Figure S2. The molecular conformation of IDIC-4F and IDIC-TPE.

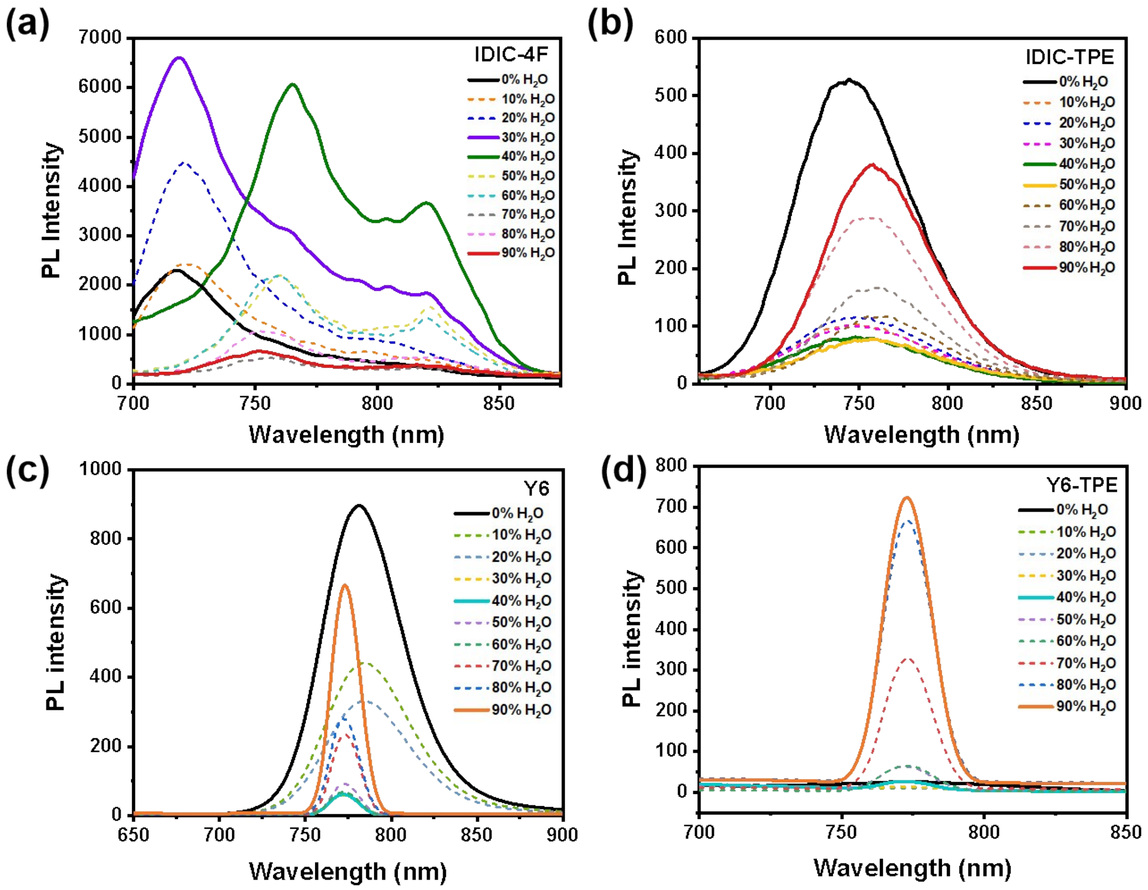


Figure S3. The PL spectra of IDIC-4F, IDIC-TPE, Y6, and Y6-TPE in THF/water mixture with different water fractions.

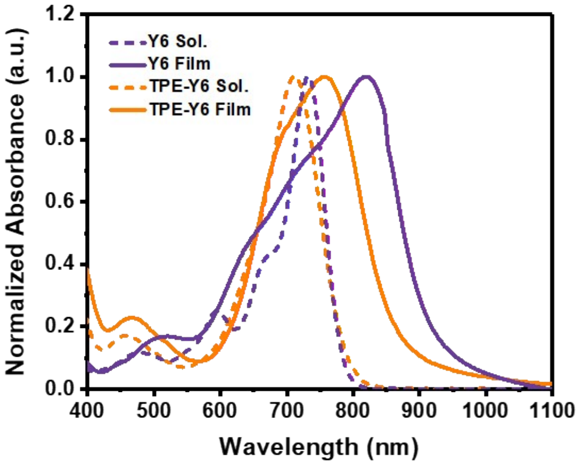


Figure S4. The absorption spectra of Y6 and Y6-TPE in chloroform solution and spin-coated film.

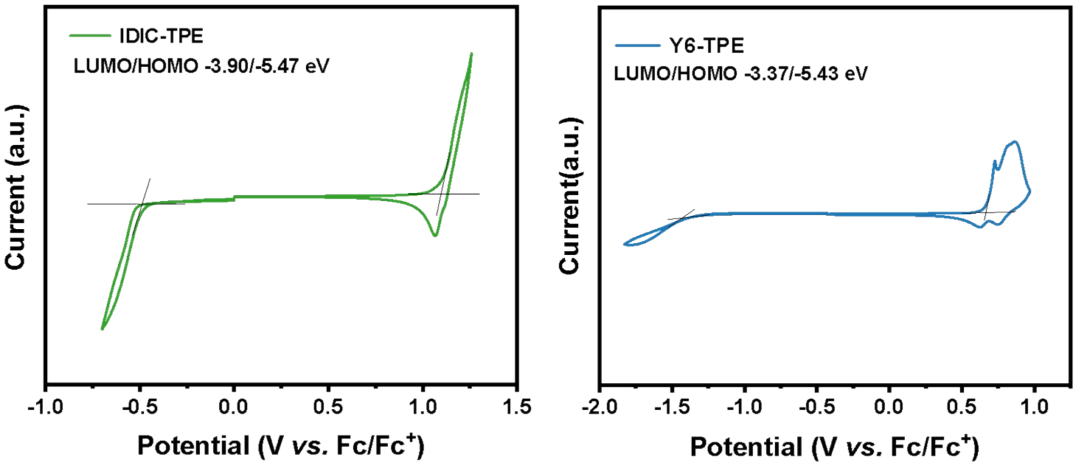


Figure S5. Cyclic voltammogram of IDIC-TPE and Y6-TPE. Potential vs. Fc/Fc$^+$.

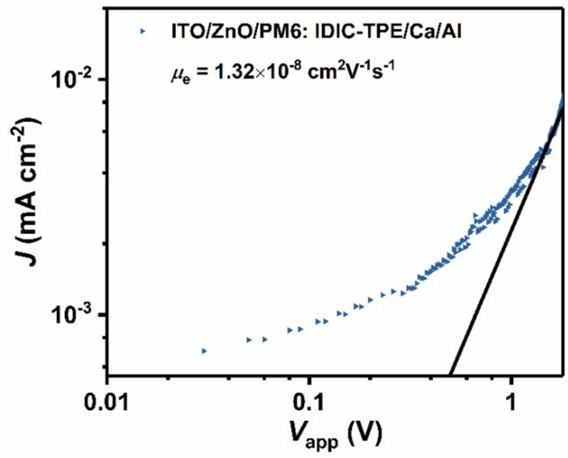


Figure S6. The J-V curve of PM6: IDIC-TPE blend film based electron-only device in the dark.

Table S1. Best photovoltaic performance of the OSCs based on ITO/ PEDOT: PSS/ PM6: IDIC-TPE: IDIC-4F/ PDINN/ Ag under the illumination of AM 1.5 G, 100 mW cm^{-2}. The average and standard deviations of 5 devices are in the brackets.

PM6: IDIC-TPE: IDIC-4F (w/w)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1:1.2:0	0.979 (0.974±0.006)	8.19 (7.73±0.30)	36.4 (34.7±1.1)	2.92 (2.62±0.20)
1: 0: 1.2	0.777 (0.783±0.009)	16.15 (16.10±0.10)	67.9 (66.8±1.4)	8.51 (8.41±0.15)
1: 0.05: 1.2	0.800 (0.805±0.011)	16.23 (15.30±0.54)	65.4 (66.2±0.8)	8.48 (8.14±0.22)
1: 0.1: 1.2	0.826 (0.825±0.003)	15.91 (15.63±0.24)	68.1 (68.6±1.0)	8.94 (8.83±0.08)
1: 0.2: 1.2	0.828 (0.821±0.007)	15.44 (14.97±0.54)	53.0 (53.7±1.3)	6.78 (6.59±0.15)

Table S2. Best photovoltaic performance of the OSCs based on ITO/ PEDOT: PSS/ PM6: Y6-TPE: Y6/ PDINN/ Ag under the illumination of AM 1.5 G, 100 mW cm^{-2}. The average and standard deviations of 4 devices are in the brackets.

PM6: Y6-TPE: Y6 (w/w)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1:1.2:0	0.872 (0.859±0.035)	0.20 (0.17±0.03)	64.7 (63.5±1.5)	0.11 (0.09±0.02)
1:0:1.2	0.843 (0.842±0.001)	26.51 (26.36±0.38)	74.0 (73.2±1.3)	16.53 (16.25±0.16)
1:0.05:1.2	0.847 (0.847±0.002)	26.35 (26.51±0.27)	74.5 (73.2±0.7)	16.63 (16.43±0.15)
1:0.2:1.2	0.844 (0.849±0.008)	25.75 (26.02±0.34)	72.7 (70.9±1.5)	15.81 (15.66±0.13)

Supplementary References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.