

Electronic Supplementary Information

Twisted-Graphene-like Perylene Diimide with Dangling Functional Chromophores as Tunable Small-Molecule Acceptors in Binary-Blend Active Layers of Organic Photovoltaics

Yu-Che Lin^a, Chung-Hao Chen^a, Nian-Zu She^b, Chien-Yao Juan^a, Bin Chang^a, Meng-Hua Li^a, Hao-Cheng Wang^a, Hao-Wen Cheng^a, Atsushi Yabushita^b, Yang Yang^c and Kung-Hwa Wei^{a,d}*

- a. Address here. Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan.
- b. Address here. Department of Material Science and Engineering, University of California, Los Angeles, CA 90095 USA
- c. Department of Electrophysics, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan
- d. Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan

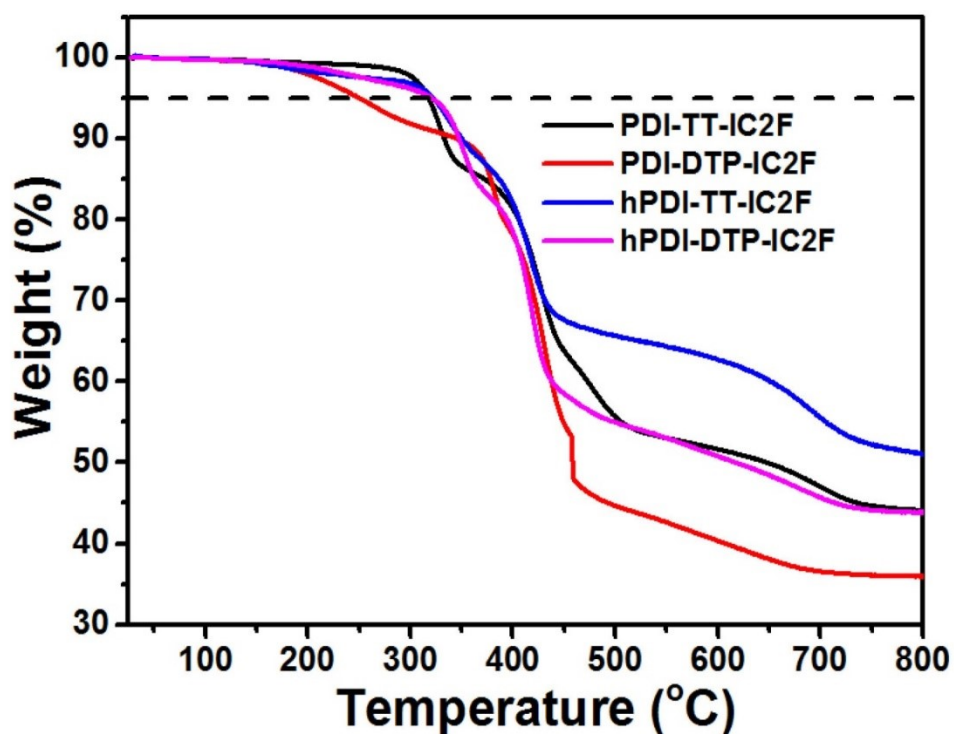


Fig. S1 TGA thermograms of four small molecules, recorded at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere.

Table S1. Thermal properties of PDI-TT-IC2F, PDI-DTP-IC2F, hPDI-TT-IC2F, and hPDI-DTP-IC2F.

| Material | T_d^b |
|---------------|---------|
| PDI-TT-IC2F | 317 |
| PDI-DTP-IC2F | 250 |
| hPDI-TT-IC2F | 322 |
| hPDI-DTP-IC2F | 321 |

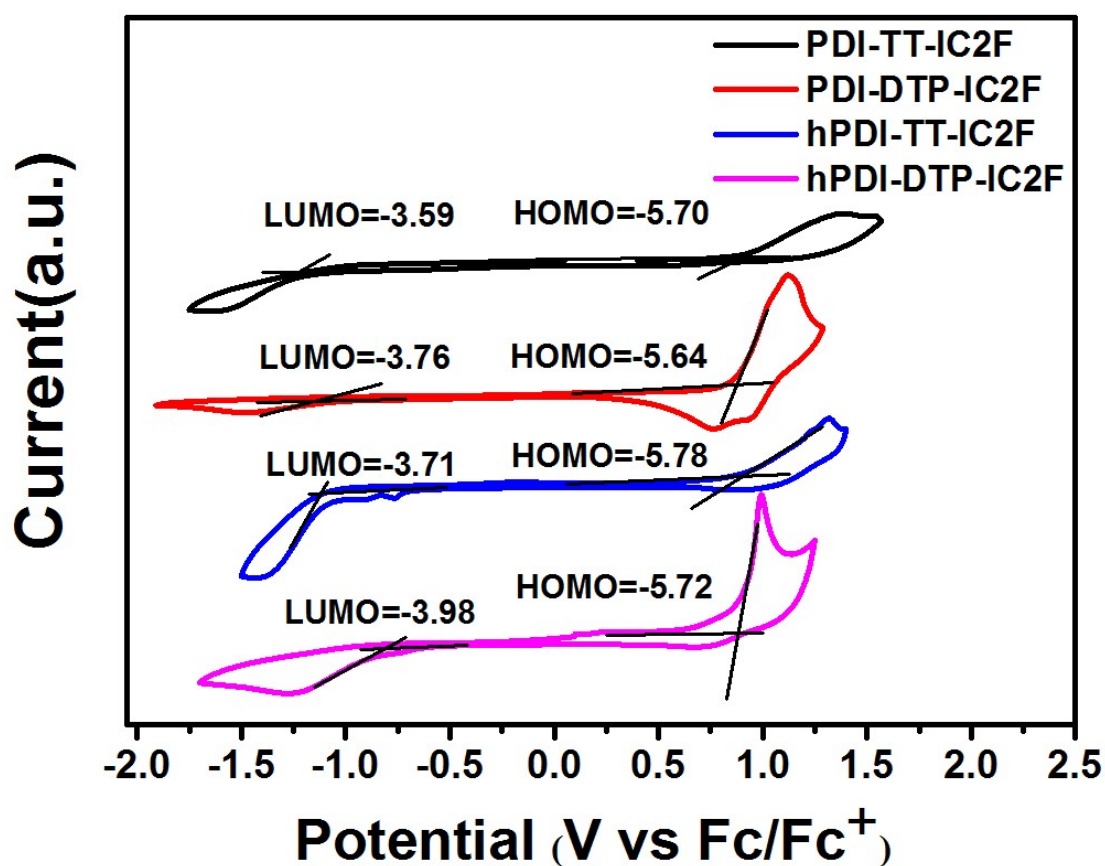


Fig. S2 Cyclic voltammograms of the synthesized small molecules as solid films.

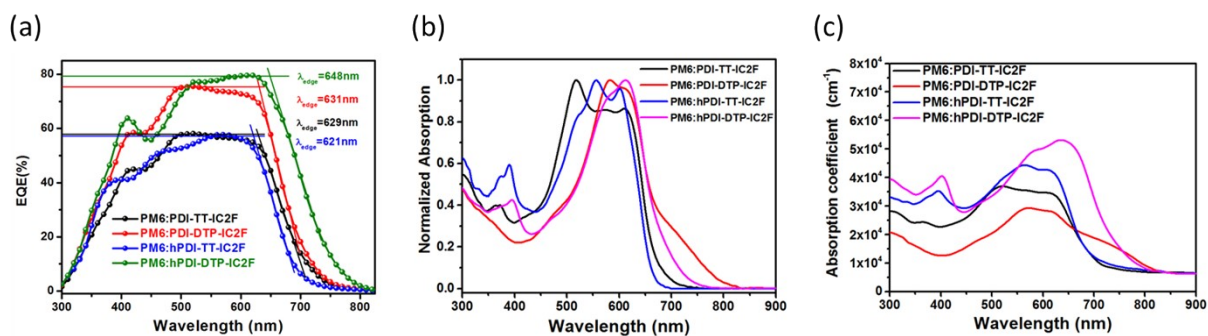


Fig. S3 (a) Graphical determination of Edge. (b) UV-vis absorption spectra the four kinds of binary blend films solutions (1×10^{-5} M) in CF and (c) solid films [D/A blend ratio, 1:1 (w/w)].

Table S2. The maximum absorption peak position and absorption coefficient with calculated error bar for the four acceptors.

| | PDI-TT-IC2F | PDI-DTP-IC2F | hPDI-TT-IC2F | hPDI-DTP-IC2F |
|--|--|--|--|---|
| λ_{max} (nm) | 524 ± 2.1 | 588 ± 1.8 | 564 ± 1.5 | 656 ± 1.8 |
| absorption coefficient (ϵ) (cm^{-1}) | $3.96 \times 10^4 \pm 1.1 \times 10^3$ | $4.25 \times 10^4 \pm 1.5 \times 10^3$ | $4.69 \times 10^4 \pm 1.3 \times 10^3$ | $6.46 \times 10^4 \pm 1.05 \times 10^3$ |

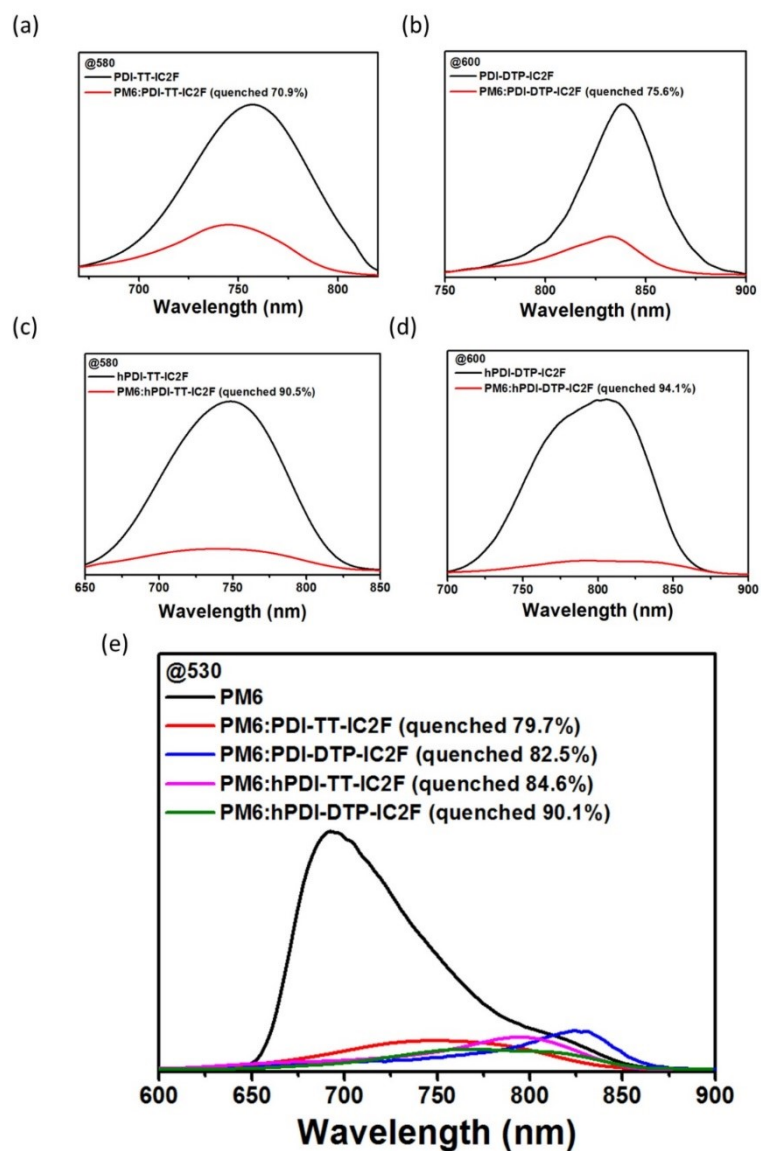


Fig. S4 PL spectra of solid films of (a-c) small molecule acceptors, as well as the PM6/small molecule binary blends and (d) PM6, recorded using various excitation wavelengths [D/A blend ratio, 1:1(w/w)].

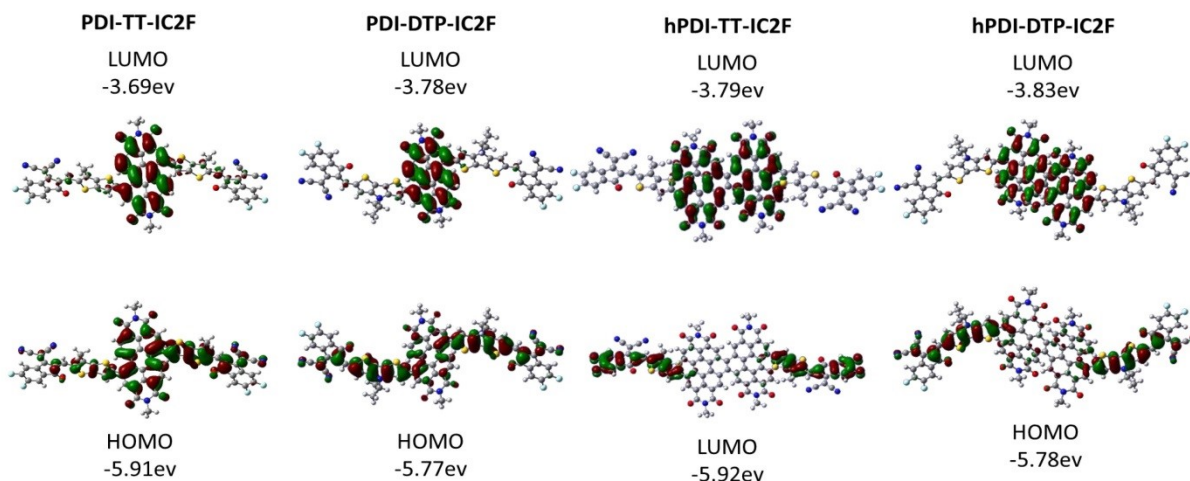


Fig. S5 HOMO and LUMO distributions for the minimum-energy conformations of three small molecules calculated by Gaussian 09 at B3LYP/6-31G level.

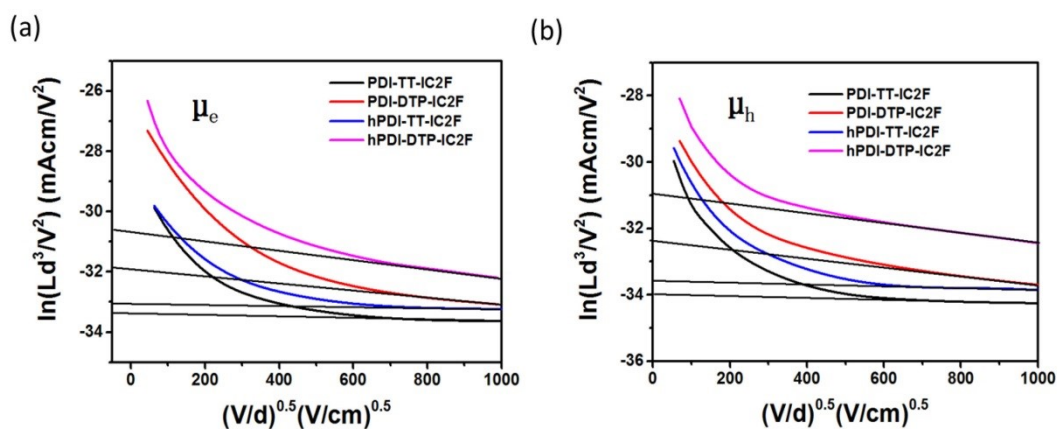


Fig. S6 (a) Hole-only and (b) electron-only devices based on the three binary blend films.

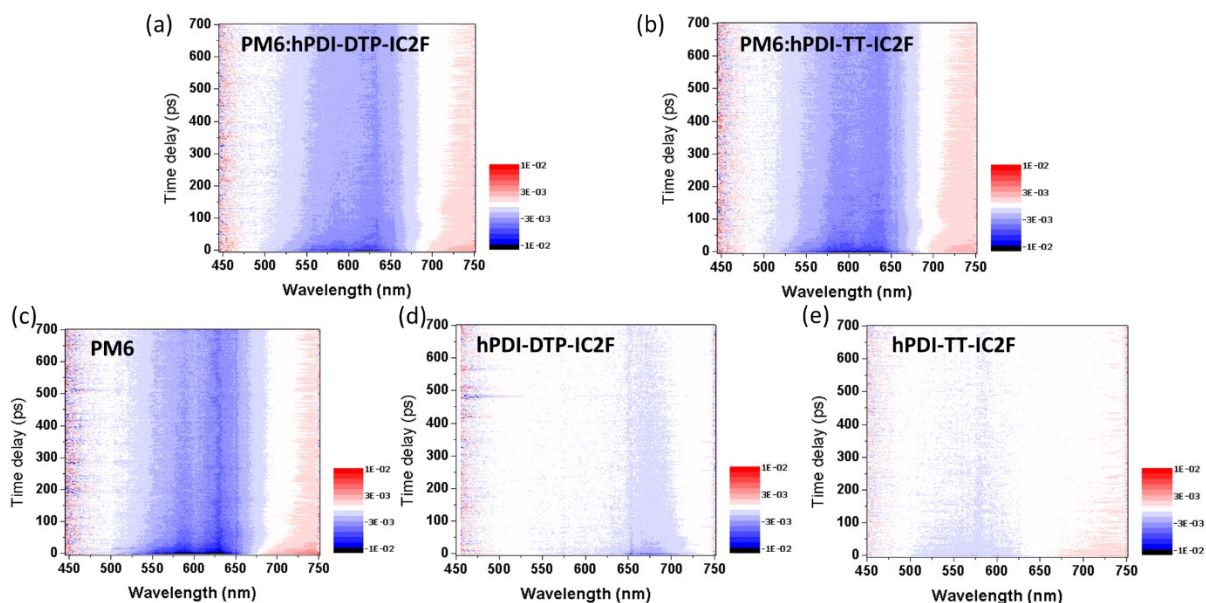


Fig. S7 (a)-(e) 2D plots of time evolution of transient absorption spectra (ΔA) in PM6: hPDI-DTP-IC2F, PM6: hPDI-TT-IC2F, PM6, hPDI-DTP-IC2F and hPDI-TT-IC2F, respectively.

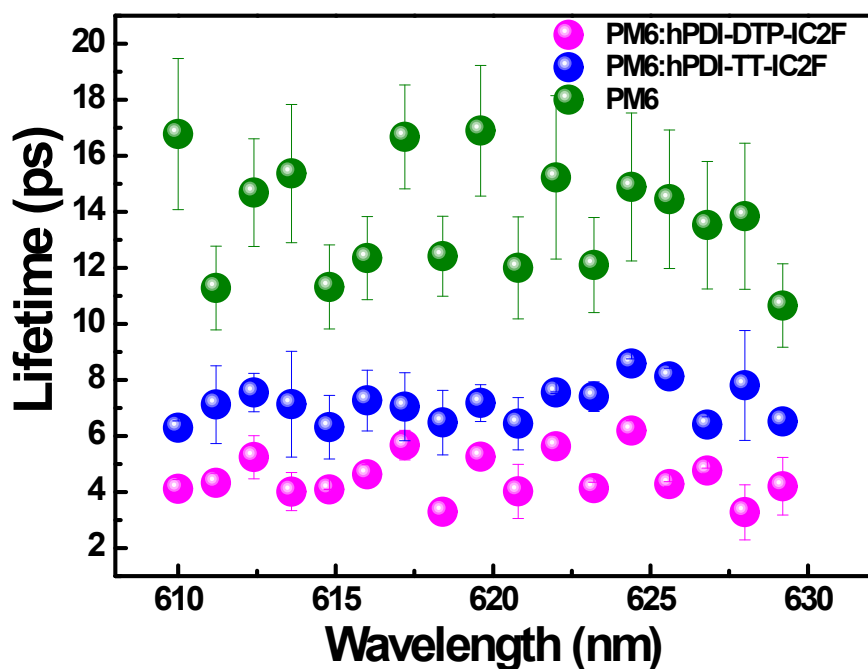


Fig. S8 Lifetimes of PM6: hPDI-DTP-IC2F, PM6: hPDI-TT-IC2F and PM6 were estimated by single exponential fitting.

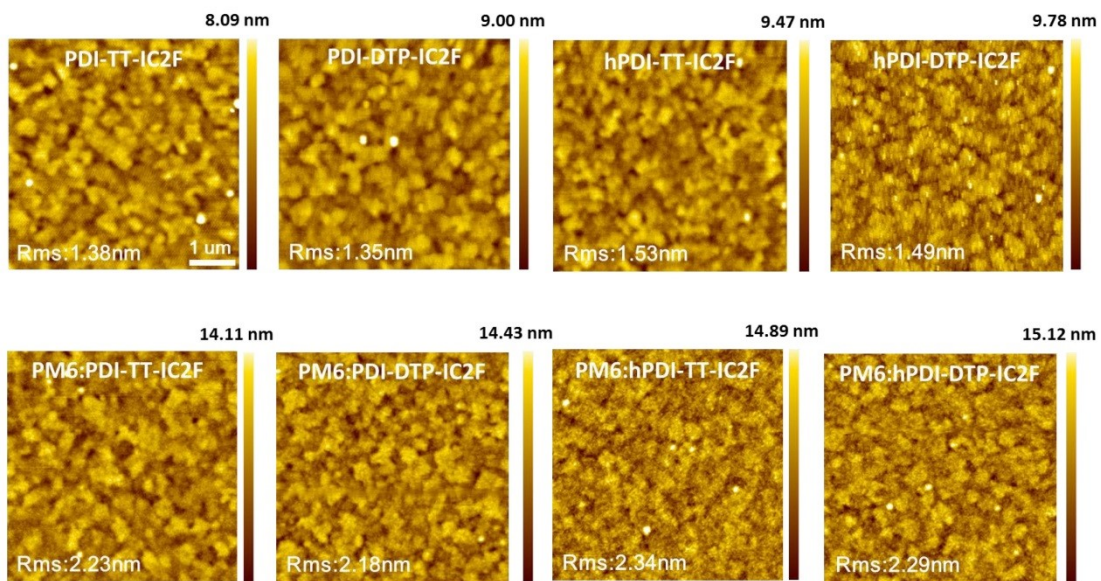


Fig. S9 AFM height images ($5 \times 5 \mu\text{m}$) of the four kinds of pure and binary blend films.

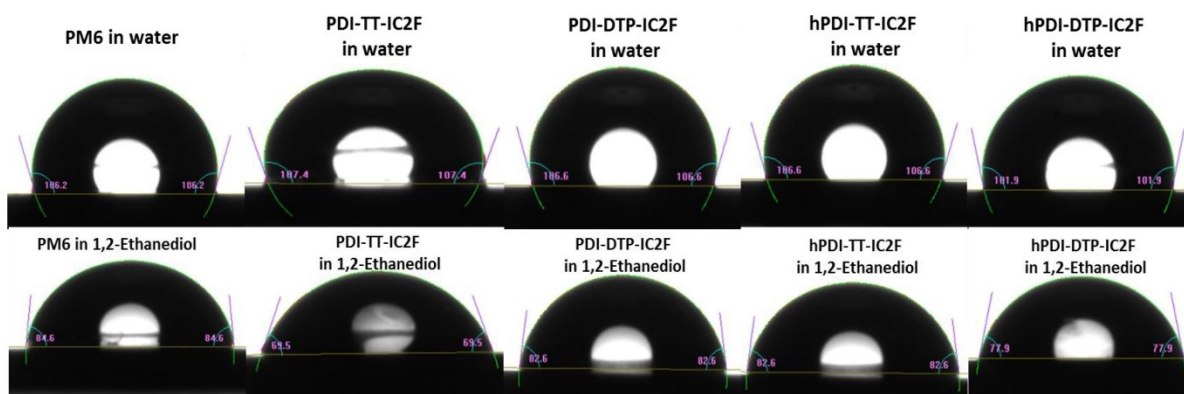


Fig. S10 The contact angle of the three synthesized small molecular and PM6.

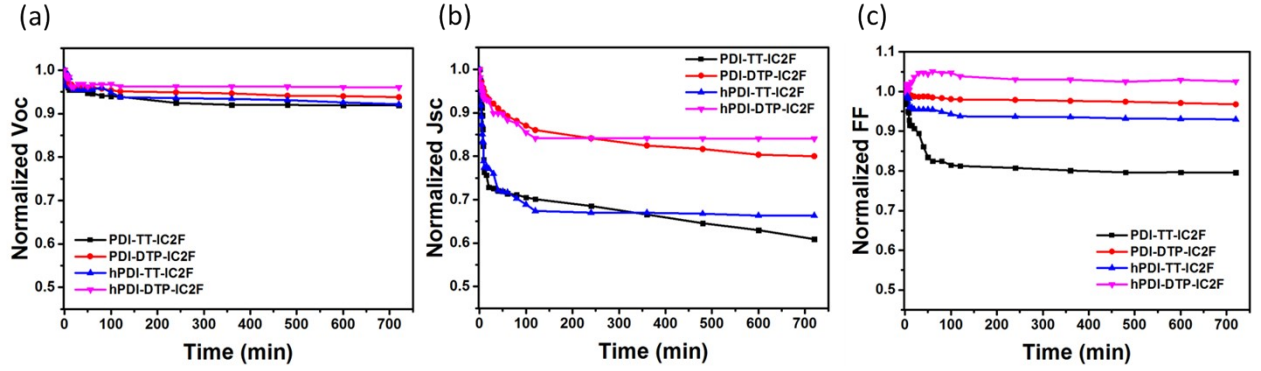
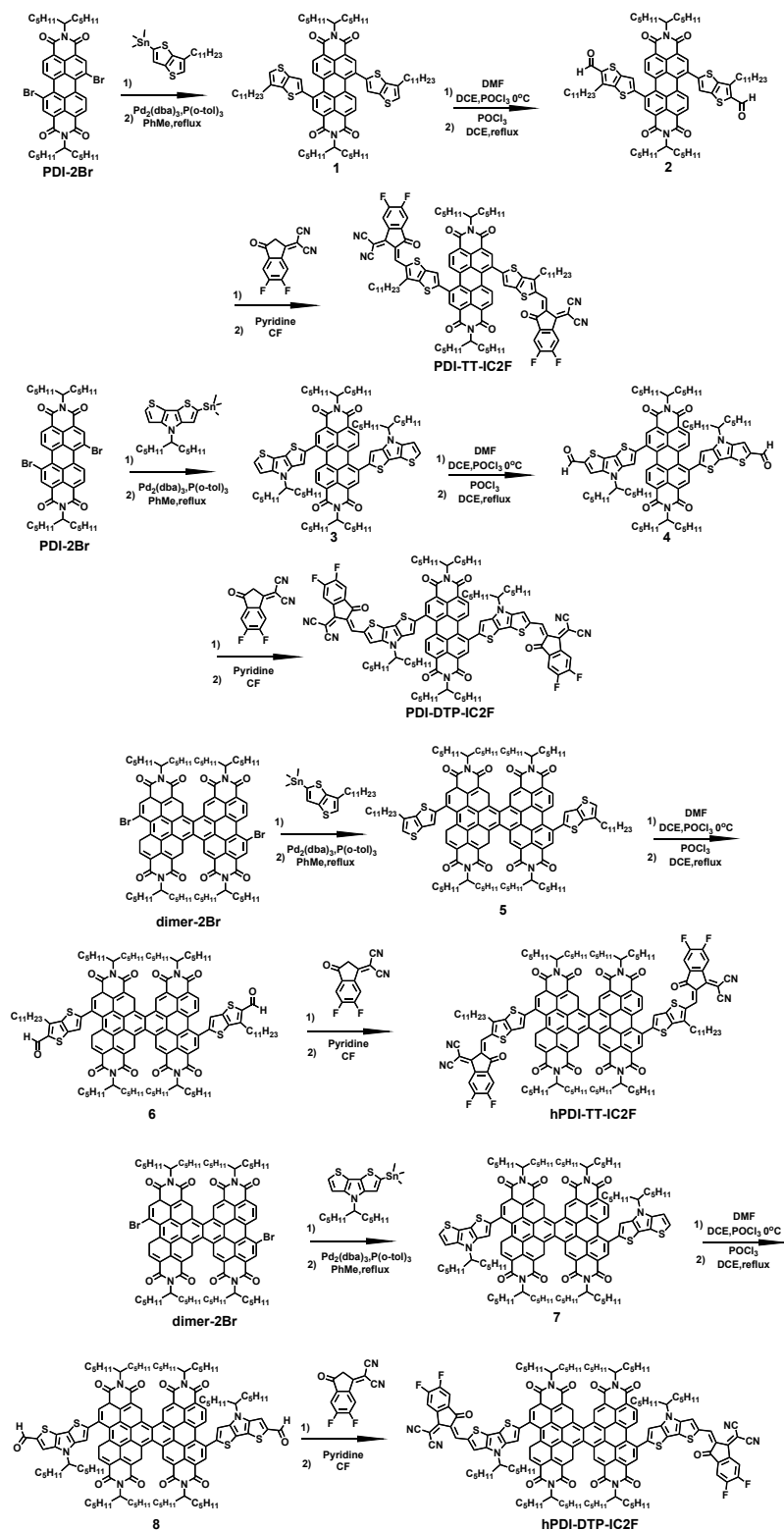


Fig. S11 The thermal stability of PDI-TT-IC2F, PDI-DTP-IC2F, hPDI-TT-IC2F, and hPDI-DTP-IC2F devices at 85 °C in nitrogen environment (a) V_{OC} , (b) J_{SC} and (c) FF of the devices.

Table S3. Summarized of molecular structure and photovoltaic parameters of PM6 with small molecules devices.

| | PDI-TT-IC2F | PDI-DTP-IC2F | hPDI-TT-IC2F | hPDI-DTP-IC2F |
|---|--------------------------------|---------------------------------|--------------------------------|---------------------------------|
| Molecular structure | 1. One PDI unit 2. TT donor | 1. One PDI unit 2. DTP donor | 1. Two PDI unit 2. TT donor | 1. Two PDI unit 2. DTP donor |
| J_{SC} (mA cm^{-2}) | 10.8 | 13.6 | 9.46 | 16.5 |
| V_{OC} (V) | 0.74 | 0.77 | 0.90 | 0.91 |
| Fill factors (FF) | 58.0 | 44.1 | 59.1 | 74.0 |
| Dihedral angle | 66.83 ° | 68.07 ° | 10.3 ° 30.1 ° | 43.13 ° 75.06 ° |
| Optical band gaps (eV) | 1.80 | 1.67 | 1.78 | 1.67 |
| Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) | Hole | 1.03×10^{-5} | 5.93×10^{-5} | 2.14×10^{-4} |
| | Electron | 1.92×10^{-5} | 8.78×10^{-5} | 3.02×10^{-4} |
| μ_h/μ_e ratio | 0.54 | 0.68 | 0.60 | 0.71 |
| RMS (nm) | 2.23 | 2.18 | 2.34 | 2.29 |
| Relative crystallinity of PM6 | lowest | lowest | Medium | Highest |
| Best efficiency (%) | 4.8 | 4.8 | 5.2 | 11.6 |



Scheme S1 The synthetic procedure of the four small molecules.

Compound 1. A mixture of compound PDI-2Br (600 mg, 0.70 mmol), trimethyl(6-undecylthieno[3,2-b]thiophen-2-yl)stannane (688 mg, 1.5 mmol), Tris(dibenzylideneacetone) dipalladium(0) (12.8 mg, 0.014 mmol), and Tri(o-

tolyl)phosphine (17.1 mg, 0.056 mmol) was heated under reflux in toluene (20 mL) for 24 h. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:1) as the eluent to give compound 1 (0.727 g, 81%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.71-8.71 (d, 2H), 8.32-8.20 (m, 4H), 7.52 (s, 2H), 7.11 (s, 2H), 5.15 (s, 2H), 2.76-2.73 (t, 4H), 2.24-2.18 (m, 4H), 1.81-1.71 (m, 12H), 1.37-1.24 (m, 52H), 0.87-0.82 (m, 18H).

Compound 2. A mixture of dimethylformamide (2.4g, 9.4 mmol) and phosphoryl chloride (720 mg, 4.7 mmol) in DCE (20 mL) at 0°C for 1 h. Subsequently, compound 1 (600 mg, 0.47 mmol) was added to the reaction mixture, which was then stirred for another 24 h under reflux in DCE. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was passed through a plug of silica gel using DCM as the eluent to give compound 2 (377 mg, 59%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.17 (s, 2H), 8.75-8.71 (d, 2H), 8.28-8.23 (m, 4H), 7.58 (s, 2H), 5.51 (s, 2H), 3.16-3.13 (m, 4H), 2.22-2.19 (m, 4H), 1.98-1.78 (m, 12H), 1.38-1.20 (m, 52H), 0.86-0.82 (m, 18H).

Compound PDI-TT-IC2F. The compound 2 (100 mg, 0.074 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (140 mg, 0.74 mmol) in dry CHCl₃ (50 mL) was added 3 drop pyridine under argon. The mixture was refluxed for 12 h and then allowed to cool to room temperature. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:3) as eluent to give the product compound **PDI-TT-IC2F** (81 mg, 62%) ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.14 (s, 2H), 8.77-8.73 (m, 2H), 8.58-8.55 (m, 4H), 8.26-8.23 (m, 4H), 7.71-7.69 (m, 2H), 7.62 (s, 2H), 5.13 (s, 2H), 3.15-3.13 (t, 4H), 2.20-2.17 (m, 4H), 1.78-1.77 (m, 8H), 1.31-1.91 (m, 16H), 1.58-1.21 (m, 56H), 0.82-0.80 (m, 18H). ¹³C NMR (100 MHz, CDCl₃, δ): 186.53, 164.75, 163.69, 153.58, 159.55, 156.28, 154.51, 154.33, 152.86, 151.67, 143.46, 137.24, 136.49, 136.33, 135.69, 135.29, 134.53, 133.97, 132.93, 131.54, 131.12, 130.75, 129.74, 129.28, 124.18, 123.39, 122.64, 121.51, 115.82, 115.64, 115.16, 114.83, 113.61, 113.45, 71.11, 55.66, 32.94, 32.56, 32.40, 31.56, 30.89, 30.32, 30.26, 30.15, 30.04, 30.01, 27.27, 23.34, 23.24, 14.77, 14.73.

Compound 3. A mixture of compound PDI-2Br (600 mg, 0.70 mmol), 2-(trimethylstannyl)-4-(undecan-6-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (746 mg, 1.5 mmol), Tris(dibenzylideneacetone) dipalladium(0) (12.8 mg, 0.014 mmol), and Tri(o-tolyl)phosphine (17.1 mg, 0.056 mmol) was heated under reflux in toluene (20 mL) for 24 h. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:1) as the eluent to give compound 3 (0.753 g, 79%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.87-8.75 (d, 2H), 8.28-8.26 (d, 2H), 8.14-8.10 (m, 2H), 7.32-7.29 (m, 2H), 7.23-7.22 (d, 2H), 7.06-7.05 (d, 2H), 5.15 (s, 2H), 4.23-4.19 (m, 2H), 2.22-2.17 (m, 4H), 2.03-2.00 (m, 4H), 1.84-1.81 (m, 8H), 1.37-1.24 (m, 48H), 0.86-0.81 (m, 24H).

Compound 4. A mixture of dimethylformamide (2.3g, 9 mmol) and phosphoryl chloride (674 mg, 4.4 mmol) in DCE (20 mL) at 0°C for 1 h. Subsequently, compound 1 (600 mg, 0.44 mmol) was added to the reaction mixture, which was then stirred for another 24 h under reflux in DCE. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was passed through a plug of silica gel using DCM as the eluent to give compound 4 (374 mg, 60%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.94 (s, 2H), 8.78-8.75 (m, 2H), 8.24-8.16 (m, 4H), 7.72 (s, 2H), 7.34-7.26 (d, 2H), 5.15 (s, 2H), 4.28-4.23 (m, 2H), 2.22-2.19 (m, 4H), 2.03-2.00 (m, 4H), 1.91-1.83 (m, 8H), 1.37-1.24 (m, 48H), 0.86-0.82 (m, 24H).

Compound PDI-DTP-IC2F. The compound 4 (100 mg, 0.071 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (135 mg, 0.71 mmol) in dry CHCl₃ (50 mL) was added 3 drop pyridine under argon. The mixture was refluxed for 12 h and then allowed to cool to room temperature. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:3) as eluent to give the product compound **PDI-DTP-IC2F** (81 mg, 62%) ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.94 (s, 2H), 8.81-8.78 (m, 2H), 8.52-8.49 (m, 2H), 8.29-8.23 (m, 4H), 7.89 (s, 2H), 7.68-7.65 (m, 2H), 7.37 (s, 2H), 5.16 (s, 2H), 4.30-4.28 (m, 2H) 2.22-2.20 (m, 4H), 2.08-

2.02 (m, 4H), 1.93-1.83 (m, 8H), 1.29-1.16(m, 48H), 0.85-0.84 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, δ): 186.44, 165.05, 164.67, 163.90, 163.54, 159.28, 156.02, 155.91, 153.95, 153.84, 152.35, 151.13, 150.69, 146.33, 139.70, 137.40, 137.23, 136.40, 135.68, 135.16, 134.90, 134.62, 133.89, 133.72, 131.20, 130.74, 130.45, 130.30, 130.16, 129.92, 129.28, 129.16, 127.12, 123.89, 123.18, 121.03, 118.14, 117.84, 115.52, 115.36, 115.23, 113.24, 113.10, 112.50, 112.22, 68.86, 61.62, 55.58, 35.58, 32.94, 32.40, 32.28, 32.01, 30.86, 30.34, 27.28, 27.04, 23.24, 23.09, 22.96, 14.72, 14.64.

Compound 5. A mixture of compound dimer-2Br (600 mg, 0.38 mmol), trimethyl(6-undecylthieno[3,2-b]thiophen-2-yl)stannane (367 mg, 0.8 mmol), Tris(dibenzylideneacetone) dipalladium(0) (7 mg, 0.0076 mmol), and Tri(*o*-tolyl)phosphine (9.2 mg, 0.034 mmol) was heated under reflux in toluene (20 mL) for 24 h. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:1) as the eluent to give compound 5 (0.601 g, 79%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.76-8.53 (m, 10H), 8.40-8.34 (m, 2H), 7.43 (s, 2H), 5.23- 5.12 (m, 4H), 2.30-2.16 (m, 12H), 1.90-1.79 (m, 14H), 1.32-1.21 (m, 78H), 0.87-0.79 (m, 30H).

Compound 6. A mixture of dimethylformamide (1.28g, 5 mmol) and phosphoryl chloride (383 mg, 2.5 mmol) in DCE (20 mL) at 0°C for 1 h. Subsequently, compound 5 (500 mg, 0.25 mmol) was added to the reaction mixture, which was then stirred for another 24 h under reflux in DCE. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was passed through a plug of silica gel using DCM as the eluent to give compound 5 (258 mg, 50%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.33-10.26 (m, 6H), 9.20 (s, 2H), 9.04-9.02 (d, 2H), 8.75 (s, 2H), 7.73 (s, 2H), 5.35-5.29 (m, 4H), 3.27-3.24 (m, 4H), 1.95-1.90 (m, 8H), 1.49-1.39 (m, 12H), 1.34-1.24 (m, 80H), 0.89-0.83 (m, 30H).

Compound hPDI-TT-IC2F. The compound 6 (100 mg, 0.048 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (110 mg, 0.48 mmol) in dry CHCl₃ (50 mL) was added 3 drop pyridine under argon. The mixture was refluxed for 12 h and then allowed to cool to room temperature. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was

extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:3) as eluent to give the product compound **hPDI-TT-IC2F** (74 mg, 62%) ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.35-10.27 (m, 4H), 9.25-9.00 (m, 4H), 8.74-8.60 (m, 4H), 8.09 (s, 2H), 7.79-7.75 (m, 4H), 5.35-5.28 (m, 4H), 3.29-3.26 (m, 4H), 2.37-2.34 (m, 6H), 1.95-1.72 (m, 10H), 1.51-1.21 (m, 84H), 0.97-0.80 (m, 30H). ¹³C NMR (100 MHz, CDCl₃, δ): 186.55, 166.64, 165.26, 164.16, 159.64, 156.40, 155.24, 154.21, 153.11, 151.91, 143.52, 137.28, 136.70, 135.59, 135.38, 134.91, 134.63, 133.61, 130.66, 130.16, 129.51, 127.83, 127.48, 127.35, 126.73, 126.57, 126.43, 126.06, 125.14, 124.46, 122.64, 121.28, 115.83, 115.65, 115.22, 114.88, 113.64, 71.08, 68.45, 56.00, 39.59, 33.05, 32.56, 32.43, 31.66, 31.25, 30.98, 30.87, 30.38, 30.31, 30.26, 30.17, 30.07, 30.01, 29.67, 27.38, 24.67, 23.33, 23.25, 14.75.

Compound 7. A mixture of compound dimer-2Br (600 mg, 0.38 mmol), 2-(trimethylstannyl)-4-(undecan-6-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (397 mg, 0.8 mmol), Tris(dibenzylideneacetone)dipalladium(0) (7 mg, 0.0076 mmol), and Tri(*o*-tolyl)phosphine (9.25 mg, 0.0304 mmol) was heated under reflux in toluene (20 mL) for 24 h. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:1) as the eluent to give compound 7 (0.634 g, 80%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.30 (s, 4H), 9.27 (s, 2H), 9.08-9.06 (d, 2H), 8.63 (s, 2H), 7.46 (s, 2H), 7.30-7.29 (d, 2H), 7.16-7.15 (d, 2H), 5.36-5.29 (m, 4H), 4.35-4.31 (m, 2H), 2.40-2.29 (m, 8H), 2.10-1.74 (m, 12H), 1.48-1.22 (m, 72H), 0.89-0.83 (m, 36H).

Compound 8. A mixture of dimethylformamide (170 mg, 2.32 mmol) and phosphoryl chloride (222 mg, 1.45 mmol) in DCE (20 mL) at 0°C for 1 h. Subsequently, compound 2 (600 mg, 0.29 mmol) was added to the reaction mixture, which was then stirred for another 24 h under reflux in DCE. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO₄) and concentrated using a rotary evaporator. The residue was passed through a plug of silica gel using DCM as the eluent to give compound 8 (446 mg, 72%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 10.30 (s, 4H), 10.0 (s, 2H), 9.27 (s, 2H), 9.03-9.01 (d, 2H), 8.67 (s, 2H), 7.83 (d, 2H), 7.50-7.49 (s, 2H), 5.38-5.29 (m, 4H), 4.42-4.36 (m, 2H), 2.41-2.32 (m, 8H), 2.18-1.92 (m, 16H), 1.41-1.26 (m, 72H), 0.89-0.84 (m, 36H).

hPDI-DTP-IC2F. The compound 8 (100 mg, 0.047 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (108 mg, 0.47 mmol) in dry CHCl_3 (50 mL) was added 3 drop pyridine under argon. The mixture was refluxed for 12 h and then allowed to cool to room temperature. The solution was cooled and the reaction quenched by pouring into water. The aqueous phase was extracted three times with DCM. The organic phase was dried (MgSO_4) and concentrated using a rotary evaporator. The residue was purified by silica gel chromatography using hexanes to DCM/hexanes (1:3) as eluent to give the product compound **hPDI-DTP-IC2F** (73 mg, 60%) ^1H NMR (500 MHz, CDCl_3) δ (ppm): 10.36-10.28 (d, 4H), 9.24 (s, 2H), 9.03-9.01 (d, 4H), 8.68-8.55 (m, 4H), 7.98 (s, 2H), 7.73-7.70 (m, 2H), 7.47-7.46 (d, 2H), 5.34-5.27 (m, 4H), 4.39-4.35 (m, 2H), 2.37-2.29 (m, 8H), 2.13-1.94 (m, 16H), 1.58-1.21 (m, 72H), 0.88-0.82 (m, 36H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 186.48, 165.38, 164.26, 159.50, 156.04, 153.89, 152.43, 151.42, 146.32, 142.97, 139.93, 137.34, 135.24, 134.59, 133.95, 133.70, 130.34, 129.23, 127.80, 127.65, 127.49, 127.26, 126.77, 126.63, 126.48, 126.17, 121.10, 118.02, 115.64, 115.45, 115.35, 113.33, 113.18, 112.25, 68.93, 61.70, 55.98, 55.77, 37.79, 35.67, 33.06, 32.61, 32.44, 32.08, 30.72, 30.39, 30.04, 27.78, 27.39, 27.11, 23.25, 23.15, 20.41, 14.75, 14.70

Measurements and Characterization

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 apparatus; the thermal stabilities of the samples were controlled under a N_2 atmosphere by measuring their weight losses while heating at a rate of $10\text{ }^\circ\text{C min}^{-1}$. UV-Vis spectra of solid films, spin-coated from polymer solutions onto a quartz substrate, were recorded using a Hitachi U-4100 spectrophotometer. PL spectra were recorded using a HITACHI F-4500. Samples were prepared by spin-casting CB solutions onto silicon substrates; the thickness was maintained at approximately 100 nm. Cyclic voltammetry (CV) of the polymer films was performed using a BAS 100 electrochemical analyzer operated at a scan rate of 50 mV s^{-1} ; the solvent was anhydrous MeCN, containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) as the supporting electrolyte. The potentials were measured against a Ag/Ag^+ (0.01 M AgNO_3) reference electrode, using the ferrocene/ferrocenium ion (Fc/Fc^+) pair as the internal standard (0.09 V). The onset potentials were determined from the crossing of two tangents drawn at the increasing and background currents of the cyclic voltammograms. HOMO energy levels were estimated relative to the energy level of the ferrocene reference (4.8 eV below vacuum level). The geometry structures of repeating units in the synthesized polymers were optimized by using DFT calculations (B3LYP/6-31G**), and the frequency analysis

was followed to assure that the optimized structures were stable states. All calculations were carried out using Gaussian 09. Water contact angle measurements were performed using a water contact angle measurement system, and the surface energy was calculated using the equation of state. Topographic and phase images of the small molecule acceptors:PM6 films (surface area: $5 \times 5 \mu\text{m}^2$) were recorded using a Digital Nanoscope III atomic force microscope operated in tapping mode under ambient conditions. The thickness of the active layer of the device was measured using a VeecoDektak 150 surface profiler. GIWAXS/GISAXS was performed at the 23A beamline (10 keV) of the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, using an incident angle of 0.2° . Samples were prepared by spin-casting CB solutions of the synthesized small molecule acceptors:PM6 blends onto silicon substrates. GIWAXS/GISAXS experiments were conducted after the solvent had evaporated entirely.

Fabrication and Characterization of Photovoltaic Devices

Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] (1.0 g) and ethanolamine (0.28 g) were dissolved in 2-methoxyethanol (10 mL) under dynamic stirring for 12 h. Mixture solutions of the active layers were set by dissolving the small molecules (6 mg mL^{-1}) and PM6 (7.2 mg mL^{-1}) in CB, resulting in a total concentration of 1.5 wt%. The mixture solutions were stirred uninterruptedly in a glove box for 12 h at 90°C to ensure complete dissolution of the synthesized small molecule acceptors and PM6. Indium tin oxide (ITO)-coated glass substrates ($5 \Omega \text{ cm}^{-2}$, Merck) were rinsed through sequential ultrasonication with detergent, acetone, DI water, and isopropanol (20 min each) and then dried under a flow of N_2 . ZnO was spin-coated onto the UV ozone-treated ITO for 15 min and then annealed at 200°C for 1 h. The substrates were transferred to a dry N_2 -filled glove box. The ZnO layers were placed at a thickness of nearly 40 nm, followed by accumulation of the active layers. The active layers, formed from synthesized small molecule acceptors and PM6 blend solutions in CB, were prepared in a glove box and then spin-cast on top of the ZnO films. After the CB in the films had evaporated, the films were heated at 100°C for 10 min. The synthesized small molecule acceptors and PM6 blend films were then covered with Petri dishes for 20 min prior to deposition of the anode. The active layers of synthesized small molecule acceptors and PM6 blends had thicknesses of approximately 100 nm. The BHJ devices were fabricated with structures incorporating ITO/ZnO. Device fabrication was complete after thermal evaporation of the P-type material (MoO_3 , 10 nm) and the anode (Ag, 100 nm) under high vacuum (ca. 10^{-7} torr). A shadow mask was used during the thermal evaporation procedure to define a device area of 0.1 cm^2 .

The current density–voltage (J – V) characteristics were measured using a Keithley 2400 source meter. The photocurrent was measured under simulated AM 1.5 G illumination at 100 mW cm^{-2} using a Xe lamp–based Newport 150-W solar simulator. EQEs were measured using an SRF50 system (Optosolar, Germany). For measurements of hole and electron mobilities, devices were fabricated having the structure ITO/PEDOT:PSS/binary blend/Au and ITO/ZnO/binary blend/Ca/Al, respectively. Hole- and electron-only diodes were fabricated with the architectures ITO/PEDOT:PSS/active layer/gold (Au) for holes and aluminum (Al)/active layer/Al for electrons. The J – V characteristics of these diodes were recorded in the dark in a glove box under a N_2 atmosphere. Mobilities were extracted by fitting the J – V curves using the Mott–Gurney relationship (space charge-limited current).