Supporting Information

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Efficient Electron Transport Layer Free Small-Molecule Organic Solar Cells with Superior Device Stability

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Supporting Information

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Experimental Section

Materials. Acceptor Y6, 5''-bromo-3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (1), and ((2,6-bis(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(thiophene-5,2-diyl))bis(tripropylsilane) (4) were obtained from (Solarmer Materials Inc. Beijing, China). 2-Ethylhexyl 2-cyanoacetate (2), pyridine, and Pd(PPh3)4 were purchased from Sigma Aldrich Chemical Co. 2-Ethylhexyl (E)-3-(5''-bromo-3',3''-dihexyl-[2,2':5',2''-terthiophene]-5-yl)-2-cyanoacrylate (3) was synthesized according following a published procedure.[S1] H31 was synthesized according to Scheme S1.

Scheme S1. Synthetic route to H31.

Synthesis of bis(2-ethylhexyl) 3,3'-(4,8-bis(5-(tripropylsilyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3',3''-dihexyl-[2,2':5',2''-terthiophene]-5'',5-diyl)(2E,2'E)-bis(2-cyanoacrylate) (H31). Compound 3 (0.50 mmol, 350 mg), compound 4
(0.20 mmol, 198 mg), and dry toluene (15 mL) were added to a 50 mL Schlenk tube. The Schlenk tube was purged with N$_2$ for 20 min, and then the catalyst Pd(PPh$_3$)$_4$ (12 mg, 5% equivalent) was added. After another flushing with N$_2$ for 20 min, the reactant was heated to reflux for over 48 h in the sealed tube. The reaction mixture was cooled down to room temperature and poured into MeOH (200 mL) and filtered. The crude product was purified using silica gel column chromatograph (eluent: heptane/dichloromethane = 1:2) to give H31 as a dark solid. The solid was dried under vacuum and characterized by $^1$H NMR, $^{13}$C NMR and MALDI-TOF MS: (351 mg, 92% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 8.25 (s, 2H), 7.77-7.76 (d, 2H, $J = 4.0$ Hz), 7.64 (s, 2H), 7.59-7.58 (d, 2H, $J = 4.0$ Hz), 7.41-7.40 (d, 2H, $J = 4.0$ Hz), 7.25-7.24 (d, 2H, $J = 4.0$ Hz), 7.12 (s, 2H), 7.02 (s, 2H), 4.24-4.18 (m, 4H), 2.85-2.76 (m, 8H), 1.72-1.65 (m, 10H), 1.55-1.31 (m, 52H), 1.08-1.04 (t, 18 H, $J = 8.0$ Hz), 0.96-0.88 (m, 36H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 163.25, 146.33, 145.81, 144.39, 142.97, 141.34, 139.59, 138.60, 137.92, 137.51, 137.36, 136.38, 135.65, 134.98, 134.84, 130.43, 129.47, 129.24, 122.13, 128.50, 126.18, 123.35, 119.38, 116.00, 97.70, 68.78, 38.80, 31.65, 30.33, 30.21, 29.97, 29.68, 29.24, 29.21, 28.93, 23.77, 22.95, 22.59, 18.54, 17.53, 16.33, 14.09, 14.05, 11.03. MALDI-TOF MS: Calcd. for C$_{108}$H$_{144}$N$_2$O$_4$Si$_2$ m/z = 1908.79 (1$^{st}$ peak) and 1909.79 (100% peak). Found m/z = 1908.82 (1$^{st}$ peak) and 1910.82 (100% peak) (Figure S17-S19).

**Molecular characterization.** $^1$H NMR spectra were measured on a Bruker DMX–400 spectrometer with $d$–chloroform as the solvent and tetramethylsilane as the internal reference. UV-visible spectroscopy was recorded on a PekinElmer Lambda 1050 UV–vis–NIR spectrophotometer at room temperature. Films were prepared by spin coating chloroform solutions on glass substrates. Square wave voltammetry (SWV) studies were performed with a scan rate of 0.1 V s$^{-1}$ under an inert atmosphere with 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte. A platinum wire coated with the a thin films of the material, a silver wire, and a silver/silver chloride (Ag/AgCl) electrode served as
working electrode, counter electrode, and quasi-reference electrode, respectively. All potentials are reported versus Ag/AgCl. Ferrocene/ferrocenium (Fc/Fc\(^+\)) was used as an internal reference. The redox potential of Fc/Fc\(^+\) was measured to be 0.37 V. The morphologies of films were characterized by a Dimension 3100 AFM with tapping mode.

**Device fabrication and characterization.** The SM-OSCs devices were fabricated and characterized in a N\(_2\)-filled glovebox. Pre-structured ITO coated glass substrates were cleaned in acetone and isopropyl alcohol for 10 min each. After drying, the substrates were coated via doctor blading with 40 nm PEDOT:PSS (Heraeus, Clevios P VP.Al 4083). The active layer was spin coated in a N\(_2\)-filled glovebox from a solution of H\(_3\):Y6 with total concentration of 20 mg mL\(^{-1}\). After spin-coating, the active layers were annealed at 140 °C for 1 min. Then a solution of PDINO in methanol at a concentration of 1.0 mg mL\(^{-1}\) was deposited atop the active layer for the PDINO-based device. Finally, top Al electrode was deposited in vacuum onto the cathode buffer layer at a pressure of \(\approx 5.0 \times 10^{-7}\) Pa.

The \(J–V\) and EQE characteristics were performed in the N\(_2\) glovebox at room temperature. A tungsten-halogen lamp combined with a UV-filter (Schott GG385) and a daylight filter (Hoya LB120) was used to simulate the solar spectrum, the light intensity was calibrated by Si photodiode to be \(~100\) mW cm\(^{-2}\). In the EQE measurements, a modulated (Oriel, Cornerstone 130) tungsten-halogen lamp (Philips focusline, 50 W) was used as the light source. The signal of solar cells was amplified by a current preamplifier (Stanford Research, SR 570) and measured by a lock-in amplifier (Stanford Research, SR 830). The spectral response was then transformed into EQE using a calibrated silicon reference cell.

The light intensity-dependent measurement was using a light of a 730 nm LED (Thorlabs) illuminating the cell through a aperture, and recoding \(I_{sc}\) the \(V_{oc}\) at different light intensities with a Keithley 2400 source meter. The light intensity was calibrated using a So photodiode and converted to photon flux.
GIWAXS. Grazing incidence wide angle X-ray scattering (GIWAXS) experiments were carried out on a GANESHA 300 XL+ system from JJ X-ray equipped with a Pilatus 300K detector (pixel size 172 µm × 172 µm). The X-ray source is a Genix 3D Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (multilayer optic “3D version” optimized for SAXS) (30 W) and the wavelength used was $\lambda = 1.5408$ Å. The sample was placed vertically on the goniometer and tilted to a glancing angle of 0.2° with respect to the incoming beam. A small beam was used to get a better resolution. The primary slits have a size of 0.3 × 0.5 mm², and the guard slits have a size of 0.1 × 0.9 mm². The accumulation time was 2 h for each measurement.

X-ray photoelectron spectroscopy. A Thermo Scientific K-Alpha was used to measure the surface XPS with a 180° double-focusing hemispherical analyzer and a 128-channel detector. Monochromatic Al Kα (1486.6 eV) radiation was used with a spot size of 400 µm. The measurements were performed under a dark condition, with a base pressure below $8 \times 10^{-8}$ mbar. A survey spectrum (15 scans) was first measured with a pass energy of 200 eV, followed by a high-resolution scan (30 scans) of each element with a pass energy of 50 eV.
**Figure S1.** AFM images of H31 (left) and Y6 (right) films with scan areas of 3 μm × 3 μm and 1 μm × 1 μm.

**Figure S2.** 2D GIWAXS patterns and in-plane and out-of-plane line cuts of H31 and Y6. The tables lists the $q$ values and corresponding distances.
**Figure S3.** DSC thermograms of H31 and Y6 at a rate of 10 °C min⁻¹, the lower traces represent the heating and the upper traces the cooling runs.

**Figure S4.** (a) Light intensity dependence of short circuit current ($I_{sc}$). (b) Light intensity dependence of $V_{oc}$. In these experiments the cell were illuminated with light from a 730 nm LED. The small difference in $V_{oc}$ between cells with and without PDINO compared to the identical values in Table 1 (main text) is due to batch-to-batch variations.

**Figure S5.** $J$-$V$ curves of H31:Y6-based SM-OSCs with Ag as the metal electrode.
Table S1. Photovoltaic parameters of the SM-OSCs based on H31:Y6 with Ag as the metal electrode.

| Device   | J_sc (mA cm\(^{-2}\)) | V_oc (V) | FF   | PCE (%) |
|----------|------------------------|----------|------|---------|
| H31:Y6\(^a\) | 23.1                  | 0.84     | 0.64 | 12.4    |
| H31:Y6\(^b\) | 22.1                  | 0.84     | 0.68 | 12.6    |

\(^a\) with PDINO. \(^b\) without PDINO.

Figure S6. \(J−V\) characteristics of a regular H31:Y6 solar cell with PFNBr/Al as top contact.

Figure S7. (a–f) 2D GIWAXS patterns and (g, h) in-plane and out-of-plane scattering profiles of the fresh and aged H31:Y6 blend films with/without PDINO on the top surface.
**Figure S8.** AFM image of a fresh PDINO film

**Figure S9.** High-resolution XPS scans of the N 1s (top) and O 1s (bottom) core levels for neat H31 (left) and Y6 (right) films without and with PDINO on top.
Table S2. Atomic concentration determined by XPS for in different layers.

| Sample          | F 1s (%At conc.) | N 1s (%At Conc.) | O 1s (%At Conc.) | Si 2p (%At Conc.) |
|-----------------|------------------|------------------|------------------|-------------------|
| H31             | -                | 1.61             | 3.52             | 1.93              |
| H31+PDINO       | -                | 5.29             | 8.64             | 0.99              |
| Y6              | 4.58             | 7.65             | 2.44             | -                 |
| Y6+PDINO        | 1.46             | 8.68             | 9.23             | -                 |
| H31:Y6 fresh    | 0.59             | 2.28             | 3.04             | 1.51              |
| H31:Y6 aged     | 0.65             | 2.60             | 3.40             | 1.50              |
| H31:Y6+PDINO fresh | 0.80           | 5.74             | 8.78             | 0.93              |
| H31:Y6+PDINO aged | 0.64        | 5.61             | 9.34             | 0.82              |

Figure S10. The fresh and aged PDINO solutions in methanol.
Figure S11. Mass spectra of fresh and aged PDINO samples.

Figure S12. The ambient condition processed device (left) and larger area device (right) performance of PDINO-based SM-OSCs and ETLs-free SM-OSCs.
Figure S13. The molecule structures of H11 and H22.

Figure S14. The device performance and stability of H11:IDIC-4F-based and H22:Y6-based SM-OSCs with and without PDINO.
Table S3. Photovoltaic parameters of the SM-OSCs based on H11:IDIC-4F and H22:Y6.

| Blend     | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF  | PCE (%) |
|-----------|-------------------------|--------------|-----|---------|
| H11:IDIC-4F $^a$ | 19.0                    | 0.85         | 0.61| 9.9     |
| H11:IDIC-4F $^b$ | 19.1                    | 0.87         | 0.61| 10.2    |
| H22:Y6 $^a$    | 22.6                    | 0.81         | 0.59| 10.8    |
| H22:Y6 $^b$    | 22.6                    | 0.82         | 0.61| 11.1    |

$^a$ with PDINO. $^b$ without PDINO.

Figure S15. The molecule structures of J71-Cl and J101.

Figure S16. The device performance of J71-Cl:IT4F-based and J101:IT4F-based PSCs with and without PDINO.
Table S4. Photovoltaic parameters of the PSCs based on J71-Cl:IT4F and J101:IT4F.

| Blend         | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF  | PCE (%) |
|---------------|--------------------------|--------------|-----|---------|
| J71-Cl:IT4F$^a$ | 20.0                     | 0.88         | 0.61| 10.7    |
| J71-Cl:IT4F$^b$ | 12.1                     | 0.56         | 0.43| 2.92    |
| J101:IT4F$^a$  | 19.6                     | 0.91         | 0.60| 10.8    |
| J101:IT4F$^b$  | 13.5                     | 0.71         | 0.43| 4.14    |

$^a$ with PDINO. $^b$ without PDINO.

Figure S17. The MALDI mass spectrum of H31.
Figure S18. $^1$H NMR of H31.

Figure S19. $^{13}$C NMR of H31.

[S1] H. Bin, J. Yao, Y. Yang, I. Angunawela, C. Sun, L. Gao, L. Ye, B. Qiu, L. Xue, C. Zhu, C. Yang, Z. G. Zhang, H. Ade, Y. Li, *Adv. Mater.* **2018**, *30*, 1706361.