Supporting Information

Achieving Record-Efficiency Organic Solar Cells upon Tuning the Conformation of Solid Additives

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1 Experimental Section

1.1 Materials and instruments

All reagents were purchased from Innochem, J&K, or Energy Chemical unless specified and used as received. PM6, Y6, L8-BO, BTP-eC9, and PDIN were purchased from Solarmer Materials Inc. PEDOT:PSS (CLEVIOS PVP AI 4083) was provided by Heraeus. $^1$H, $^{13}$C NMR and $^1$H-$^1$H NOESY NMR spectra were recorded on a JEOL JNM-ECZ500R (500 MHz) spectrometer with CDCl$_3$ as a solvent and tetramethylsilane as an internal reference. Thermogravimetric analysis (TGA) was measured on a Q50 instrument under a nitrogen flow. Absorption spectra and photoluminescence spectra were measured on an Agilent Cary 60 UV−vis spectrophotometer and Edinburgh steady state/transient fluorescence spectrometer (FLS1000), respectively. Transient absorption (TA) measurement was conducted on a femtosecond pump–probe system (Transient Absorption Spectrometer, Newport Corporation). To avoid exciton annihilation, an 800 nm excitation wavelength with $\sim$23 $\mu$J cm$^{-2}$ excitation fluence was selected. The probe beam was a white continuum beam spanning the 500-900 nm spectral region. FT-IR tests were performed on NICOLETiS50 of Thermo Scientific Company at ATR mode. X-ray crystallographic data were collected at 113K on Rigaku mm007 with a rotating anode and Saturn70 detector. Exposure time of 3 s and scan width of 1° were set per frames for SAD1. Exposure time of 10 s and scan width of 1° were set per frames for SAD2. The structure was solved by intrinsic phasing method (SHELXT) and refined by least squares method (SHELXL) integrated in Olex2. 2D-GIWAXS data were measured on the XEUSS SAXS/WAXS equipment at National Center for Nanoscience and Technology (NCNST) of China.

1.2 Sample preparations and characterizations

For steady-state and transient UV-vis, and PL measurement, the neat or blend films were all prepared on quartz substrate. For GIWAXS measurements, the neat and blend films were prepared on the silicon substrate.

1.3 Solar cell device fabrications and measurements

The solar cells were fabricated and characterized with a conventional device structure of ITO/PEDOT:PSS/active layer/PDIN/Ag. The ITO-coated glasses were ultrasonic precleaned with detergent, deionized water, acetone and 2-propanol for 30 min each and dried by a nitrogen blow. The ITO glasses were treated by UV-ozone for 20 min before used. PEDOT:PSS was spin-coated onto the ITO substrate (20 nm) and then annealed in an oven for 15 min at 150 °C. The mixed PM6:Y6, PM6:BTP-eC9, and PM6:L8-BO with the same D:A ratio of 1:1.2 were dissolved in chloroform (CF) solvent at a total weight concentration of 15.4 mg mL$^{-1}$ and stirred at least 4 h. SAD1 and SAD2 (7% by the weight to the acceptors) were added into the blend solutions, and the solutions were kept stirring for 30 min.
After the active layer solutions were spin coated, thermal annealing was utilized to remove the additives. Next, the electron transport layer PDIN were spin coated on the films. Finally, about 110 nm Ag were deposited onto the active layer by evaporating at a pressure under $10^{-5}$ Pa.

The cells were characterized under a temperature of 25–30 °C in a glove box filled with nitrogen. The current density–voltage ($J–V$) characteristics of photovoltaic devices were obtained along the forward scan direction from −0.5 to 1 V, with a scan step of 20 mV and a dwell time of 1 ms using a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated 100 mW cm$^{-2}$ AM1.5G irradiation using a Newport solar simulator in an argon filled glove box. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using a certified silicon diode (SRC-2020, Enlitech). External quantum efficiency (EQE) values of the devices were measured using a QE-R3011 instrument (Enli Technology Co. Ltd., Taiwan) with a scan increment of 5 nm per point.

### 1.4 Measurements of the hole and electron mobility by the SCLC method

The hole and electron mobility were obtained using the space charge limited current (SCLC) method. The mobility was measured with the device structure of ITO/PEDOT:PSS/active layer/Ag for hole and ITO/ZnO/active layer/PDIN/Ag for electron. The hole and electron mobility was extracted by fitting the current density–voltage curves using the Mott–Gurney law,\(^1\)

$$J_{SCL} = \frac{9\varepsilon\varepsilon_0\mu V^2}{(8L^3)}$$  \hspace{1cm} (1)

Where $J$ is the current density, $\varepsilon_0$ is the permittivity of free space, $\varepsilon$ is the relative permittivity of the active layer, $\mu$ is the zero-field mobility, $V$ is the voltage, and $L$ is the film thickness.

### 1.5 Quantum chemical calculations

Density functional theory (DFT) calculations were performed using the Gaussian 09 program with the B3LYP exchange-correlation functional.\(^2\) All-electron triple-$\xi$ valence basis sets with polarization functions (6-31G) are used for all atoms. Geometry optimizations were performed with full relaxation of all atoms. Calculations were performed in gas phase without solvent effects. Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency. The ESP analysis was carried out after the geometry optimizations by a wavefunction analysis tool Multiwfn.\(^3\) Reorganization energy analysis was performed using Molecular Materials Property Prediction Package (MOMAP).\(^4\)

### 1.6 Single-crystal growth

Diffraction quality crystals were grown by gas-liquid diffusion. SADs (10 mg) was dissolved in CHCl$_3$.
(0.5 mL) and placed in a 4 mL vial, which was then placed in a 20 mL vial containing 10 mL methanol. The 20 mL vial was then sealed tightly, and left undisturbed for 7 days.
2 Synthetic Section

Scheme S1. Synthetic routes of SAD1 and SAD2.

Synthesis of SAD1

A mixture of 1,4-dibromo-2,5-dimethylbenzene (132.0 mg, 0.50 mmol), thiophen-2-ylboronic acid (140.8 mg, 1.10 mmol), potassium carbonate (207.3 mg, 1.50 mmol) and Pd(PPh₃)₄ (57.8 mg, 0.05 mmol) in THF/H₂O (20 mL, 4:1, v/v) was stirred under protection of argon at 60 °C for 12 h. The reaction mixture was extracted with dichloromethane, washed with water, and dried with anhydrous Na₂SO₄. After removal of the solvent, the product was purified via column chromatography on silica gel (petroleum ether) to afford the product as a white solid (129.6 mg, 0.48 mmol, 95.9%). ¹H NMR (500 MHz, CDCl₃, δ): 7.35 (dd, J = 4.1, 2.2 Hz, 2H), 7.33 (s, 2H), 7.12–7.10 (m, 4H), 2.43 (s, 6H).

Synthesis of SAD2

A mixture of 1,4-dibromo-2,5-dimethoxybenzene (146.9 mg, 0.50 mmol), thiophen-2-ylboronic acid (140.8 mg, 1.10 mmol), potassium carbonate (207.3 mg, 1.50 mmol) and Pd(PPh₃)₄ (57.8 mg, 0.050 mmol) in THF/H₂O (20 mL, 4:1, v/v) was stirred under protection of argon at 60 °C for 12 h. The reaction mixture was extracted with dichloromethane, washed with water, and dried with anhydrous Na₂SO₄. After removal of the solvent, the product was purified via column chromatography on silica gel (petroleum ether/CH₂Cl₂, 8:1) to afford the product as a white solid (143.3 mg, 0.47 mmol, 94.8%). ¹H NMR (500 MHz, CDCl₃, δ): 7.54 (dd, J = 3.7, 1.1 Hz, 2H), 7.36 (dd, J = 5.2, 1.1 Hz, 2H), 7.26 (s, 2H), 7.11 (dd, J = 5.2, 3.7 Hz, 2H), 3.95 (s, 6H).
3 Supporting Figures

Figure S1. Electrostatic potential (ESP) distribution of SAD1, SAD2, and Y6.

Figure S2. Normalized absorption (solid line) and emission spectra (dash line) of SAD1 and SAD2 (a) in chloroform solution and (b) in thin film.

Figure S3. TGA plots of SAD1- and SAD2-added PM6:Y6 blends (PM6:Y6-1 and PM6:Y6-2) at a scan rate of 2 °C min\(^{-1}\). During the heating process, the temperature was held constant for 2 h at 100 °C for SAD1, and 140 °C for SAD2, respectively.
**Figure S4.** UV–vis absorption spectra of (a) SAD1-added and (b) SAD2-added PM6:Y6 blend films during the TA process (tested every 30 s).

**Figure S5.** UV–vis absorption spectra (solid line) and emission spectra (dash line) of Y6-T0, Y6-T1, and Y6-T2.

**Figure S6.** 2D-GIWAXS of Y6 films under various treatments.
Figure S7. FTIR spectra of (a-b) SAD1, Y6, Y6-1, and (c-d) SAD2, Y6, Y6-2.

Figure S8. $J^{1/2}$--$V$ plots for (a) hole-only and (b) electron-only devices based on PM6:Y6-T0, PM6:Y6-T1, PM6:Y6-T2, respectively.

Figure S9. Normalized reduced PL and absorption spectra of (a) Y6-T0, (b) Y6-T1, and (c) Y6-T2 films.
Figure S10. $J-V$ curves and EQE responses of the (a-b) PM6:BTP-eC9- and PM6:L8-BO-based devices (c-d), respectively.

Figure S11. Certification report for the PM6:L8-BO-T2-based device from National Institute of Metrology (NIM), China.
4 Supporting Tables

Table S1. Crystallographic data and structural refinement for SAD1 and SAD2.

| Identification code   | 2152137    | 2152138    |
|-----------------------|------------|------------|
| Empirical formula     | C₁₆H₁₄S₂   | C₈H₂OS     |
| Formula weight        | 270.39     | 151.20     |
| Temperature/K         | 113.15     | 113.15     |
| Crystal system        | triclinic  | triclinic  |
| Space group           | P-1        | P-1        |
| a/Å                   | 8.2388(7)  | 7.4512(4)  |
| b/Å                   | 8.9763(7)  | 11.1493(9) |
| c/Å                   | 9.7250(6)  | 16.9714(14)|
| α/°                   | 87.025(6)  | 79.825(7)  |
| β/°                   | 78.472(7)  | 88.423(6)  |
| γ/°                   | 70.028(8)  | 87.305(6)  |
| Volume/Å³             | 662.21(9)  | 1385.94(18)|
| Z                     | 2          | 8          |
| ρcalc/(g/cm³)         | 1.356      | 1.449      |
| μ/mm⁻¹                | 0.380      | 0.381      |
| F(000)                | 284.0      | 632.0      |
| Crystal size/mm³      | 0.16 × 0.13 × 0.1 | 0.19 × 0.16 × 0.14 |
| Radiation             | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| 2θ range for data collection/° | 4.276 to 65.76 | 3.714 to 52.746 |
| Index ranges          | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14 | -9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21 |
| Reflections collected | 10016     | 13403      |
| Independent reflections | 4461 [Rint = 0.0491, Rsigma = 0.0682] | 5646 [Rint = 0.0715, Rsigma = 0.0904] |
| Data/restraints/parameters | 4461/446/258 | 5646/0/365 |
| Goodness-of-fit on F²  | 1.018      | 1.042      |
Final R indexes \([I=2\sigma(I)]\)

\[
R_1 = 0.0483, \quad wR_2 = 0.1063
\]

Final R indexes [all data]

\[
R_1 = 0.0801, \quad wR_2 = 0.1226
\]

Largest diff. peak/hole / e Å\(^3\)

\[
0.36/-0.24, \quad 1.02/-0.50
\]

**Table S2.** Absorption and emission properties of SAD1 and SAD2 in chloroform solution and film.

|       | \(\lambda_{\text{abs},\text{max}}\)\(_{\text{sol.}}\) [nm] | \(\lambda_{\text{em},\text{max}}\)\(_{\text{sol.}}\) [nm] | \(\lambda_{\text{abs},\text{max}}\)\(_{\text{film}}\) [nm] | \(\lambda_{\text{em},\text{max}}\)\(_{\text{film}}\) [nm] | \(\Delta\nu_{\text{sol.}}\) [cm\(^{-1}\)] | \(\Delta\nu_{\text{film}}\) [cm\(^{-1}\)] |
|-------|---------------------------------|-----------------|-----------------|-----------------|----------------------------|-----------------|
| SAD1  | 294                             | 368             | 304             | 378             | 6840                       | 6440            |
| SAD2  | 358                             | 397             | 370             | 432             | 2744                       | 3879            |

**Table S3.** Absorption and emission properties of Y6-T0, Y6-T1, and Y6-T2 films.

|       | \(\lambda_{\text{abs},\text{max}}\)\(_{\text{film}}\) [nm] | \(\lambda_{\text{em},\text{max}}\)\(_{\text{film}}\) [nm] | \(I_{0-0}/I_{0-1}\) |
|-------|---------------------------------|-----------------|-----------------|
| Y6-0  | 834                             | -               | -               |
| Y6-1  | 822                             | -               | -               |
| Y6-2  | 813                             | -               | -               |
| Y6-T0 | 838                             | 955             | 1.58            |
| Y6-T1 | 843                             | 950             | 1.62            |
| Y6-T2 | 841                             | 945             | 1.68            |

**Table S4.** Detailed photovoltaic parameters of the PM6:Y6-T1 devices processed by varied conditions.

| SAD1 | Annealing temperature [wt. %] | \(V_{\text{oc}}\) [V] | \(J_{\text{sc}}\) [mA cm\(^{-2}\)] | FF [%] | PCE [%] |
|------|--------------------------------|------------------------|-------------------------------------|--------|---------|
| 5    | 100                            | 0.821                  | 26.59                               | 71.41  | 15.59   |
| 10   | w/o                            | 0.860                  | 25.91                               | 72.99  | 16.26   |
| 10   | 100                            | 0.842                  | 27.38                               | 74.19  | 17.10   |
| 10   | 120                            | 0.833                  | 27.42                               | 71.50  | 16.33   |
| 15   | 100                            | 0.840                  | 27.16                               | 74.10  | 16.91   |
**Table S5.** Detailed photovoltaic parameters of the PM6:Y6-T2 devices processed by varied conditions.

| SAD1 [wt. %] | Annealing temperature [°C] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | PCE [%] |
|--------------|-----------------------------|--------------|--------------------------|--------|---------|
| 5            | 140                         | 0.840        | 26.53                    | 73.46  | 16.37   |
| 10           | w/o                         | 0.887        | 26.38                    | 70.09  | 16.40   |
| 10           | 140                         | 0.853        | 27.56                    | 75.46  | 17.74   |
| 10           | 160                         | 0.842        | 27.45                    | 71.66  | 16.56   |
| 15           | 140                         | 0.854        | 26.25                    | 73.37  | 16.45   |

**Table S6.** Detailed parameters of voltage loss of the photovoltaic devices.

|             | $\Delta V_{nr}$ [V] | $\Delta V_r$ [V] | $E_{CT}$ [eV] | $E_g$ [eV] | $\Delta E_{CT}$ [eV] | $V_{loss}$ [V] |
|-------------|---------------------|------------------|---------------|---------|----------------------|----------------|
| PM6:Y6-T0   | 0.212               | 0.280            | 1.338         | 1.386   | 0.048                | 0.540          |
| PM6:Y6-T1   | 0.206               | 0.280            | 1.328         | 1.380   | 0.052                | 0.538          |
| PM6:Y6-T2   | 0.198               | 0.280            | 1.331         | 1.385   | 0.054                | 0.532          |

**Table S7.** Detailed hole transfer rate and quantum efficiency of the different treated devices.

|             | $k_0$ [$\times 10^{12}$ s$^{-1}$] | $k_r$ [$\times 10^{12}$ s$^{-1}$] | $k_{HT}$ [$\times 10^{12}$ s$^{-1}$] | QE [%] |
|-------------|----------------------------------|----------------------------------|-------------------------------------|--------|
| PM6:Y6-T0   | 0.16                             | 1.86                             | 1.70                                | 91.4   |
| PM6:Y6-T1   | 0.14                             | 2.99                             | 2.85                                | 95.3   |
| PM6:Y6-T2   | 0.12                             | 3.59                             | 3.47                                | 96.7   |
$^1$H, $^{13}$C, and 2D $^1$H-$^1$H NMR Spectra

Figure S11. $^1$H NMR (500 MHz) spectrum of SAD1.

Figure S12. $^{13}$C NMR (126 MHz) spectrum of SAD1.
Figure S13. $^1$H NMR (500 MHz) spectrum of SAD2.

Figure S14. $^{13}$C NMR (126 MHz) spectrum of SAD2.
Figure S15. $^1$H NMR (500 MHz) spectrum of Y6.

Figure S16. $^1$H NMR (500 MHz) spectrum of Y6-1 solution.
Figure S17. $^1$H NMR (500 MHz) spectrum of Y6-2 solution.

Figure S18. $^1$H-$^1$H NOESY NMR spectrum of SAD1.
Figure S19. $^1$H-$^1$H NOESY NMR spectrum of SAD2.

Figure S20. $^1$H-$^1$H NOESY NMR spectrum of Y6.
Figure S21. $^1$H-$^1$H NOESY NMR spectrum of Y6-1 solution.

Figure S22. $^1$H-$^1$H NOESY NMR spectrum of Y6-2 solution.
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