

Electronic Supplementary Information for:

**Significantly Enhancement of Photovoltaic Performances
Through Introducing S···N Conformational Locks**

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Materials.

The PTB7-Th, PBDB-T and other chemical reagents used were gained commercially and without further purification. 1,1-dicyanomethylene-3-indanone, compound **2** and the small molecule IDT-T were synthesized following the previous literatures.^{1,2} Toluene was distilled from sodium under nitrogen before use. Chloroform was purified by drying with CaCl₂, refluxing with CaCl₂ and distilling. The distilled CHCl₃ was stored in the dark to avoid photochemical formation of phosgene.

Synthesis of IDT-Tz.

To a Schlenk flask were added compound **2** (60 mg, 0.05 mmol), 1,1-dicyanomethylene-3-indanone (62 mg, 0.3 mmol) and dry CHCl₃ (15 mL). The mixture was deoxygenated with nitrogen for 30 min. Then three drops of pyridine were added and the mixture was heated at 65 °C for 15 h under the protection of nitrogen atmosphere. After being cooled to room temperature, the solvent was removed by evaporation, and the crude product was purified by silica gel column chromatography using petroleum ether/dichloromethane (1:2) as an eluent, yielding a black-colored solid (44.5 mg, 60.1%). ¹H-NMR (300 MHz, CDCl₃): δ 8.86 (s, 2H), 8.71 (d, 2H), 8.32 (s, 2H), 7.92 (d, 2H), 7.77 (d, 4H), 7.72 (s, 2H), 7.55 (s, 2H), 7.18 (d, 8H), 7.11 (d, 8H), 2.57 (t, 8H), 1.58 (m, 8H), 1.26 (m, 24H), 0.86 (s, 12H). ¹³C-NMR (400 MHz, CDCl₃): δ 188.66, 172.90, 160.59, 159.61, 158.41, 154.89, 147.92, 142.26, 140.82, 140.15, 139.44, 136.77, 136.02, 135.81, 135.05, 134.93, 131.50, 128.79, 127.86, 125.82,

125.62, 124.15, 123.36, 118.70, 114.27, 114.24, 71.00, 63.18, 35.67, 31.82, 31.45, 29.21, 22.70, 14.23. MS (MALDI-TOF): m/z 1481.6. Anal. Calc. for $C_{96}H_{84}N_6O_2S_4$: C, 77.80; H, 5.71; N, 5.67. Found: C, 76.79; H, 5.63; N, 5.71%.

Characterization.

The UV-vis absorption spectra of solution (chloroform) and thin film were measured on a Gary 60 UV-vis Spectrophotometer and the thin film was spin casted on a quartz substrate. The electrochemical cyclic voltammetry (CV) measurements were carried out under nitrogen in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at a potential scan speed at 0.1 V/s. The ferrocene/ferrocenium (Fc/Fc^+) was used as external standard in the measurement. A glassy-carbon disc coated with IDT-Tz or IDT-T film was used as the working electrode, a Pt wire was used as the counter electrode and an Ag/AgCl electrode was used as a reference electrode. AFM images were obtained by NTEGRA Prima in the tapping mode. All the samples were spin casted on silicon substrates. And TEM images were performed by HT7700Ex instrument at 110 kV accelerating voltage. Density functional theory calculations were performed with the B3LYP/6-31G(d, p) level.^{3, 4} Vibration frequency calculation was carried out to check the stable structures without imaginary frequency. Charge distribution of the molecules was calculated by Mulliken population analysis. All torsional potentials between central core and π -bridge units were computed at 10° intervals. For each data point, we fixed the dihedral angle and performed geometry optimization on all remaining degrees of freedom.⁵ And all small molecules were performed for the structures with simplified side chains.

Device fabrication and characterization.

Organic solar cells were fabricated with an inverted structure of ITO/ZnO/active layer/MoO₃/Ag, where the active layer is consisted of PTB7-Th and IDT-Tz or IDT-T. Patterned indium tin oxide (ITO) glass was cleaned in an ultrasonic bath with detergent, deionized water, acetone and isopropanol, dried in an oven at 80 °C overnight and treated in an ultraviolet ozone for 30 min. 25 μL ZnO precursor solution was then spin-coated onto the precleaned ITO glass (4500 rpm, 40 s), and baked at 200 °C for 30 min. Blends of PTB7-Th:IDT-T or PTB7-Th:IDT-Tz at a D/A ratio of 1:1.3 with 1.5% 1-chloronaphthalene (CN) as additive or blends of PBDB-T:IDT-T or PBDB-T:IDT-Tz at different D/A ratios with/without solvent additive (CN) were fully dissolved in chlorobenzene solution (CB) at concentration of 10 mg/mL. Then, the solution was spin-coated on the substrate to achieve the active layer, and the thin films were transferred into a vacuum evaporator connected to the glove box. Finally, about 10 nm MoO₃ and 100 nm Ag were deposited onto the active layer sequentially by thermal evaporation at a pressure under 10⁻⁵ Pa. The current density-voltage (*J-V*) characterizations were recorded under air mass (AM) 1.5G using a Newport solar simulator. Besides, the incident photon to converted current efficiency (IPCE) spectrum was measured using Newport IPCE system.

Mobility measurements.

The bulk charge transport mobility was investigated by the space charge limit current (SCLC) method. The hole mobility were measured with a device structure of ITO/PEDOT:PSS/active layer/MoO₃/Ag, while electron mobility were characterized

with a device structure of ITO/ZnO/active layer/Al.

Figures.

Table S1 Photovoltaic parameters of PBDB-T:IDT-Tz OSC devices with a D/A ratio of 1:1 and different quantity of solvent additive 1-chloronaphthalene.

| Additive | PCE (%) | V_{oc} (V) | J_{sc} (mA·cm⁻²) | FF (%) | R_{sh} (kΩ cm²) | R_s (Ω cm²) |
|-----------------|----------------|--------------------------------|---|---------------|--|--|
| 0.5% CN | 8.07 | 0.89 | 13.14 | 69.0 | 0.868 | 9.36 |
| 1.5% CN | 8.21 | 0.89 | 13.31 | 69.3 | 1.068 | 8.32 |
| 3% CN | 6.70 | 0.89 | 11.09 | 67.8 | 0.884 | 9.40 |

Table S2 Photovoltaic parameters of PBDB-T:IDT-Tz OSC devices with 1.5% 1-chloronaphthalene and different D/A ratios.

| D:A | PCE (%) | V_{oc} (V) | J_{sc} (mA·cm⁻²) | FF (%) | R_{sh} (kΩ cm²) | R_s (Ω cm²) |
|--------------|----------------|--------------------------------|---|---------------|--|--|
| 1:1 | 8.21 | 0.89 | 13.31 | 69.3 | 1.068 | 8.32 |
| 1:1.3 | 8.52 | 0.88 | 13.67 | 70.8 | 1.072 | 9.04 |
| 1:1.5 | 7.56 | 0.87 | 14.18 | 61.3 | 1.132 | 10.20 |

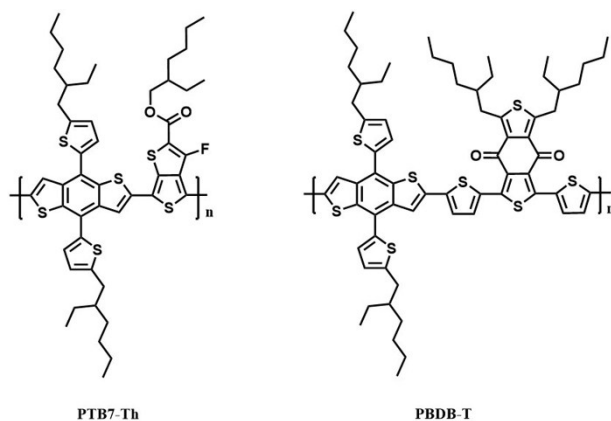


Fig. S3 Chemical structure of PTB7-Th and PBDB-T.

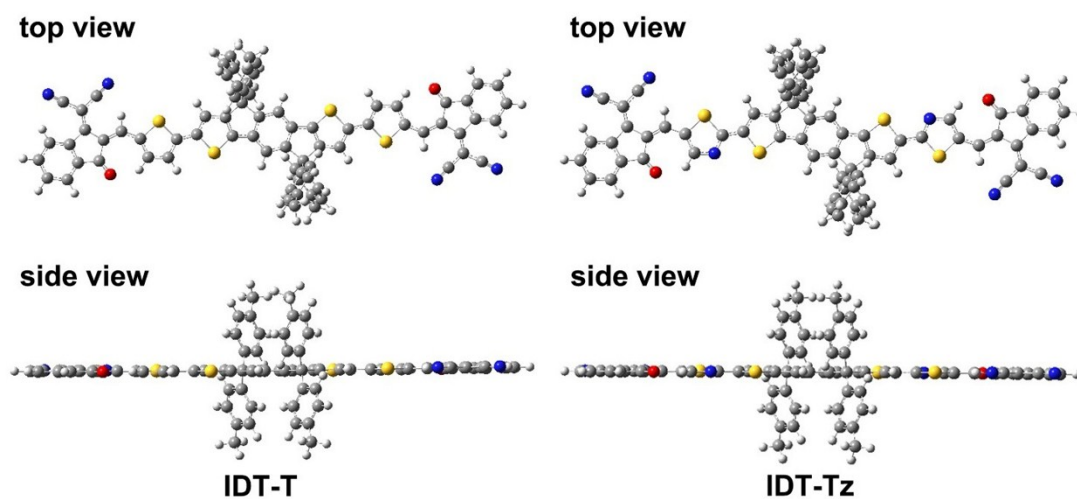


Fig. S4 Simulated molecular geometries obtained by DFT calculations for simplified molecules of IDT-T and IDT-Tz.

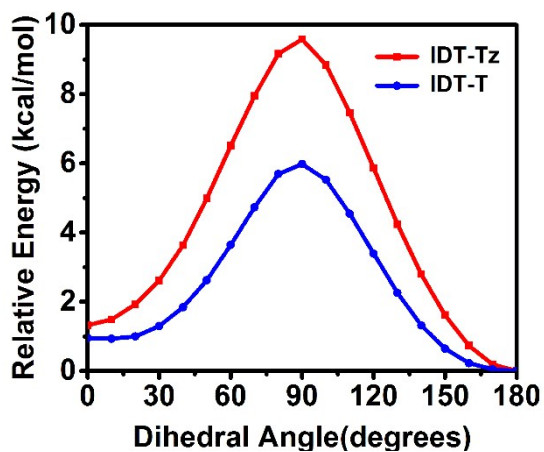


Fig. S5 Torsional potentials for small molecules IDT-T and IDT-Tz.

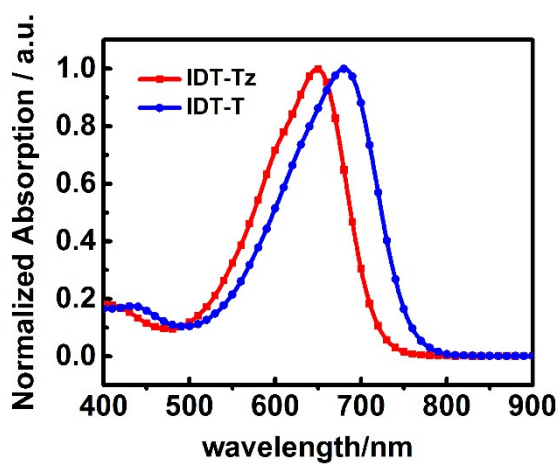


Fig. S6 Absorption spectra of IDT-T and IDT-Tz in solution.

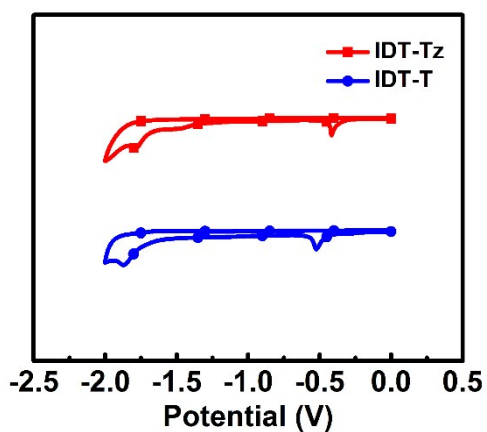


Fig. S7 Cyclic voltammograms of IDT-T and IDT-Tz.

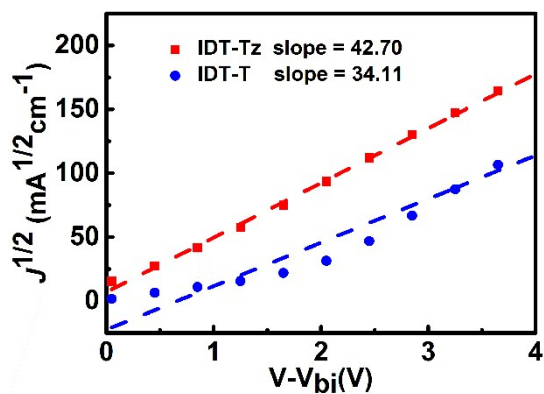


Fig. S8 Electron mobility of IDT-T and IDT-Tz neat films.

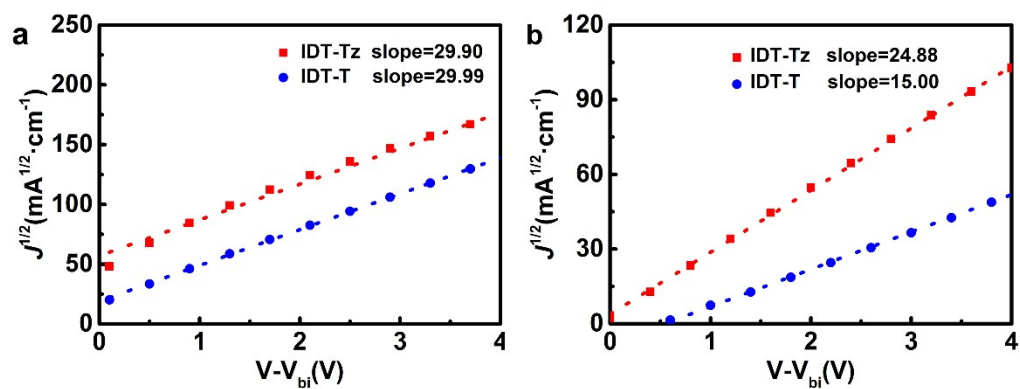


Fig. S9 a) Hole and b) electron mobility of IDT-T and IDT-Tz blend films.

References

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