Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

# Supporting Information

## Wide Bandgap Small Molecular Acceptor with Noncovalent Conformational Locks for Low Energy Loss Organic Solar Cell

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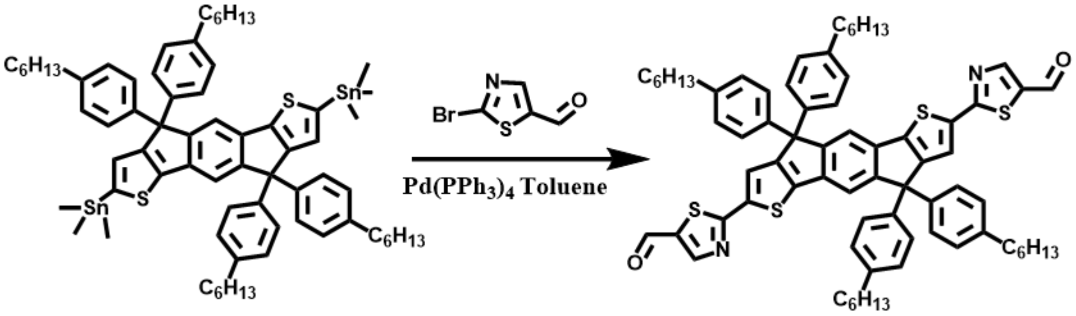
## 1. Materials.

All the reagents and chemicals were purchased from commercial sources and employed without further purification unless indicated otherwise. All reactions were carried out under nitrogen atmosphere. Compound rhodanine-$(CN)_2$ and compound **1** were prepared according to literature procedure.[1, 2] Toluene was freshly distilled before use from sodium, and chloroform was freshly distilled before use from $CaCl_2$.

## 2. Experimental Section.

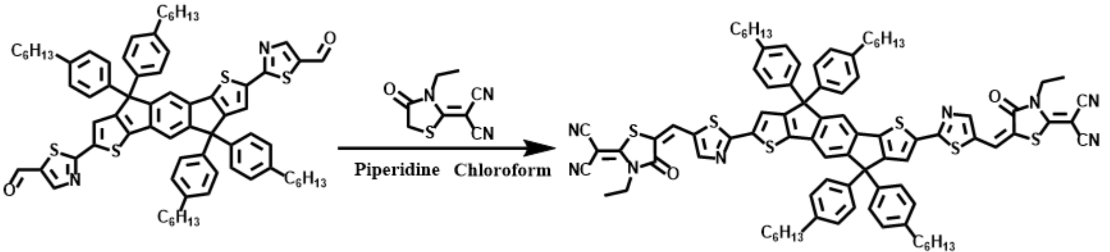
### Materials synthesis.

All the synthetic routes were shown as follow:



1 2

**Synthesis of compound 2:** Compound **1** (400 mg, 0.32 mmol) and 2-bromothiazole-5-carbaldehyde (184 mg, 0.96 mmol) were dissolved in a dry toluene (30 mL) solution under nitrogen, and the $Pd(PPh_3)_4$ (18 mg, 0.016mmol) was added to the mixed system under nitrogen. The mixed system was heated to 110 °C for 24 h and cooled to room temperature. Then the mixed system was poured into $CH_3OH$ (100 mL). After the solvent was removed, the solid was purified by column chromatography on silica gel using petroleum ether/$CH_2Cl_2$ (2:1,v/v) as an eluent, affording an orange-red solid (240 mg, 66.5%). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 9.97 (s, 2H), 8.28 (s, 2H), 7.55 (s, 2H), 7.50 (s, 2H), 7.17-7.14 (m, 8H), 7.10-7.07 (m, 8H), 2.56 (m, 8H), 1.32-1.23 (m, 32H), 0.86 (m, 12H). MS (MALDI-TOF): calculated for $C_{72}H_{76}N_2O_2S_4$, 1128.5; found: 1129.4. Elemental analysis Calc. C, 76.55%; H, 6.78%; N, 2.48%. Found: C, 74.66%; H, 6.71%; N, 2.49%.

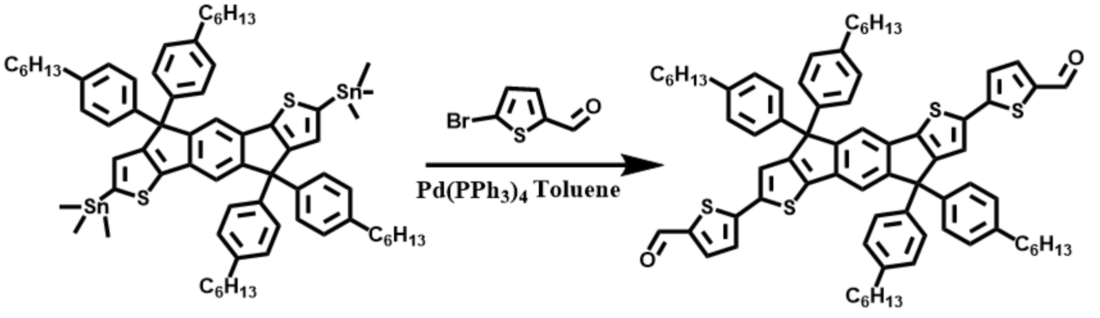


2

IDTzCR

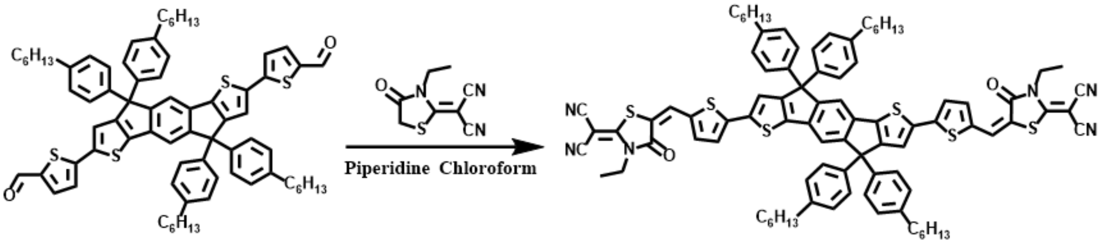
**Synthesis of IDTzCR:** Compound **2** (120 mg, 0.1 mmol) and rhodanine-$(CN)_2$ (115 mg, 0.6 mmol) were dissolved in a dry $CHCl_3$ (20 mL) solution under nitrogen. And the piperidine (0.1 mL) was added to the mixed system dropwise. The mixed system was heated to 65 °C for 15 h and was cooled to room temperature. Afterwards, the mixed system was poured into $CH_3OH$ (100 mL). After the solvent was removed, the solid was purified by column chromatography on silica gel using petroleum ether/$CH_2Cl_2$ (1:2, v/v) as an eluent, affording a purplish red solid (65 mg, 44%). $^1H$-NMR (400 MHz, $CDCl_3$): $\delta$ 8.08 (s, 2H), 8.03 (s, 2H), 7.60 (s, 2H), 7.53 (s, 2H), 7.20-7.17 (m, 8H), 7.12-7.09 (m, 8H), 4.31 (m, 4H), 2.56 (m, 8H), 1.40 (m, 6H), 1.34-1.23 (m, 32H), 0.85 (m, 12H). $^{13}C$-NMR(100 MHz, $CDCl_3$): $\delta$ 167.64, 165.41, 165.00, 157.98, 154.74, 151.00, 146.74, 142.82, 140.82, 138.70, 135.78, 131.36, 131.00, 128.75, 127.88, 125.87, 125.09, 118.53, 116.55, 113.13, 112.04, 63.30, 56.45, 40.95, 35.65, 31.79, 31.42, 29.22, 22.68, 14.27, 14.18. MS (MALDI-TOF): calculated for $C_{88}H_{86}N_8O_2S_6$, 1478.5; found: 1479.3. Elemental analysis Calc. C, 71.41%; H, 5.86%;

N, 7.57%. Found: C, 70.13%; H, 5.82%; N, 7.27%.



1 3

**Synthesis of compound 3:** Compound **1** (200 mg, 0.16 mmol), 5-bromothiophene-2-carbaldehyde (93 mg, 0.48 mmol), and Pd $(PPh_3)_4$ (10 mg, 0.09 mmol) were dissolved in a dry toluene (30 mL) solution under nitrogen. The mixed system was heated to 110 °C for 24 h and was cooled to room temperature. Afterwards, the mixed system was poured into $CH_3OH$ (100 mL). The solvent was removed to afford a solid, which was purified by column chromatography on silica gel using petroleum ether/$CH_2Cl_2$ (2:1, v/v) as an eluent, affording an orange-red solid (131 mg, 73%). $^1$H-NMR (400 MHz, CDCl3): *δ* 9.81 (s, 2H), 7.26 (s, 2H), 7.42 (d, 2H), 7.20 (d, 2H), 7.17-7.13 (m, 8H), 7.10-7.06 (m, 8H), 2.55 (m, 8H), 1.38-1.21 (m, 32H), 0.85 (m, 12H). MS (MALDI-TOF): calculated for $C_{74}H_{78}O_2S_4$, 1126.5; found: 1126.4. Elemental analysis Calc. C, 78.82%; H, 6.97%. Found: C, 78.31%; H, 7.05%.



3 IDTCR

**Synthesis of IDTCR:** Compound **3** (100 mg, 0.09 mmol) and rhodanine-$(CN)_2$ (103 mg, 0.6 mmol) were dissolved in a dry $CHCl_3$ (20 mL) solution under nitrogen, followed by addition of piperidine (0.1 mL). The mixed system was heated to 65 °C for 15 h and was cooled to room temperature. The mixed system was poured into $CH_3OH$ (100 mL). After the solvent was removed, the solid was purified by column chromatography on silica gel using petroleum ether/$CH_2Cl_2$ (1:2, v/v) as an eluent, affording a dark-red solid (54 mg, 41%). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.01 (s, 2H), 7.43 (s, 2H), 7.36 (d, 2H), 7.30 (d, 2H), 7.22 (s, 2H), 7.20-7.16 (m, 8H), 7.12-7.08 (m, 8H), 4.31 (d, 4H), 2.56 (m, 8H), 1.39 (m, 6H), 1.37-1.22 (m, 32H), 0.85 (m, 12H). $^{13}$C-NMR(100 MHz, $CDCl_3$): $\delta$165.93, 165.54, 157.72, 154.12, 147.54, 143.26, 142.02, 141.13, 138.44, 136.97, 135.37, 134.85, 128.75, 128.66, 127.92, 124.63, 122.09, 117.87, 113.42, 113.12, 112.39, 76.79, 63.29, 55.62, 40.77, 35.67, 31.80, 31.44 ,29.24 ,22.67 ,14.29 ,14.20. MS (MALDI-TOF): calculated for $C_{90}H_{88}N_6O_2S_6$, 1476.5; found: 1477.3. Elemental analysis Calc. C, 73.13%; H, 6.00%; N, 5.69%. Found: C, 72.31%; H, 5.97%; N, 5.49%.

## Measurements and Instruments

The $^1$H/$^{13}$C-NMR spectra were tested on a JEOL-ECZ400S. Mass spectra were performed on a Bruker Daltonics Biflex III MALDI-TOF Analyzer. Element analysis was recorded on a Flash EA 1112 elemental analyzer. Ultraviolet-vis spectrophotometer spectra were carried out on a Perkin Elmer Lambda 20 UV/Vis Spectrophotometer. Thermogravimetric analyzer were measured on a Q50 at a heating rate of 10 $°C\cdot min^{-1}$ under a nitrogen atmosphere. Photoluminescience spectra were conducted on an excitation of a laser beam using a Renishaw RM 3000 Micro-Raman/Photoluminescence system, all films samples were spin-casted on quartz glass substrates. Cyclic voltammetry measurements were proceeded on a CHI600E electrochemical workstation with a potential scan rate of 0.05 $mV\cdot s^{-1}$ under nitrogen in 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$) acetonitrile solution. The ferrocene/ferrocenium ($Fc/Fc^+$) was used as external standard in the measurement. A glassy-carbon disc coated with IDTCR or IDTzCR film were 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. The HOMO/LUMO levels was calculated based on the formula $E_{HOMO}/E_{LUMO} = -e\ (\varphi_{oxd}/\varphi_{red} + 4.80 - \varphi_{Fc/Fc+})$ (eV). The geometrical conformation of IDTzCR and IDTCR molecules were optimized by density functional theory (DFT) calculation, and torsional potentials between central core and π-bridge units were calculated at 10 ° intervals.[3] All film samples of AFM were spin-casted on ITO glass substrates, and AFM images were obtained by NTEGRA Prima in the tapping mode. TEM images were performed by HT7700Ex instrument at 110 kV accelerating voltage.

## Device fabrication and characterization

The OPV devices were fabricated with a reversed structure of Glass/ITO/ZnO/PEIE/active layer/$MoO_3$/Ag, where the active layer is consisted of PTB7-Th and IDTCR/IDTzCR. Patterned indium tin oxide (ITO) glass substrates were cleaned in an ultrasonic bath with detergent, deionized water, acetone and isopropanol, dried in an oven at 80 ºC overnight and treated in an ultraviolet ozone for 30 min. ZnO (25 μL) precursor solution was then spin-coated onto the pre-cleaned ITO glass (4500 rpm, 40 s), and baked at 200 ºC for 30 min. Active layer solution of PTB7-Th:IDTzCR or PTB7-Th:IDTCR with a D/A ratio of 1:1 and with 1.5% 1-chloronaphthalene (CN) were prepared in chlorobenzene solution (CB) at concentration of 10 mg/mL. Then, the solution was spin-coated on the substrate to achieve the active layer, the optimized active layer thickness was ca.100 nm. After solvent annealed under chloroform vapour, thin films were transferred into a vacuum evaporator connected to the glove box. Finally, about 10 nm $MoO_3$ and 100 nm Ag were deposited onto the active layer sequentially by thermal evaporation at a vacuum level of $10^{-5}$ Pa. The current density-voltage ($J$-$V$) characterizations were recorded under air mass 1.5G (100 $Mw\cdot cm^{-2}$) using a Newport solar simulator. Besides, the incident photon to converted current efficiency (IPCE) spectrum was measured using Newport IPCE system.

## Mobility measurements

The blend films charge transport mobility was measured by the space charge limit current (SCLC) method. The hole mobility were measured with a device structure of ITO/PEDOT:PSS/active layer/$MoO_3$/Ag. Electron mobility were characterized with a device structure of ITO/ZnO/PEIE/active layer/Al. Mobility was extracted by fitting the current density–voltage curves using space charge limited current (SCLC). The $J$–$V$ curves of the devices were plotted as $J^{0.5}$ versus $V$ using Eq. $J = 9\varepsilon_0\varepsilon_r\mu_h(\mu_e)V^2/8L^3$ for holes and electrons, where $J$ is current density, $L$ is film thickness of active layer, $\mu_e$ is electron mobility, $\mu_{\mathrm{h}}$ is hole mobility, $\varepsilon_r$ is relative dielectric constant of the transport medium, and $\varepsilon_0$ is permittivity of free space. $V = V_{appl}–V_{\mathrm{bi}}$, $V$ is the applied voltage, $V_{\mathrm{bi}}$ is the offset voltage (for hole-only diodes and electron-only diodes, $V_{\mathrm{bi}}$ are all 0.4 V).

## 3. Figures.

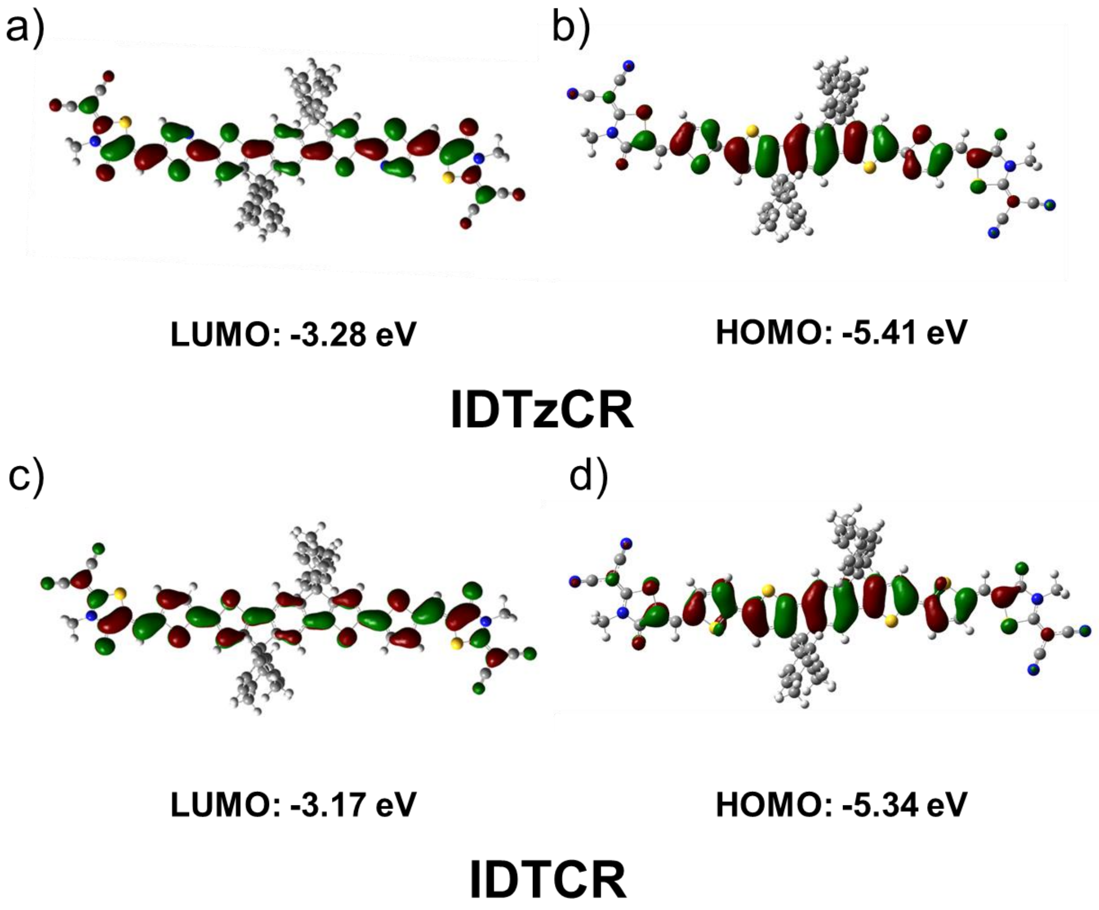


**Figure S1.** a), b) DFT calculation of frontier molecule orbitals for IDTzCR. c), d) DFT calculation of frontier molecule orbitals for IDTCR.

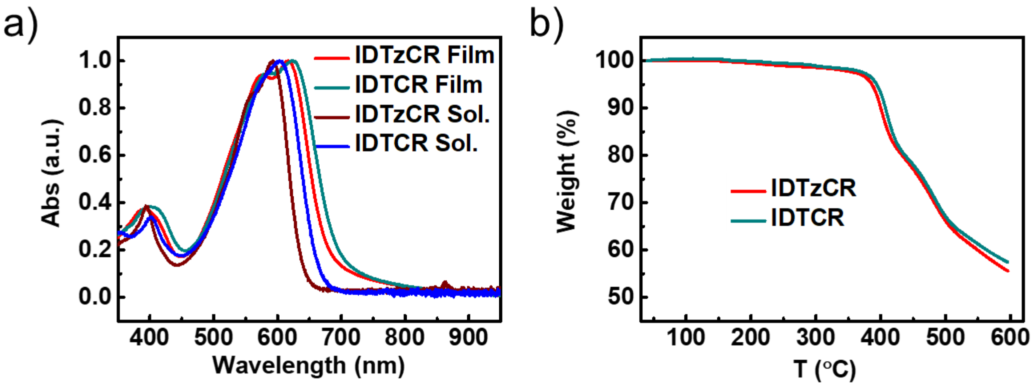


**Figure S2.** a) UV-Vis absorption spectra of solution and film for IDTzCR and IDTCR. b) TGA curves for IDTzCR and IDTCR.

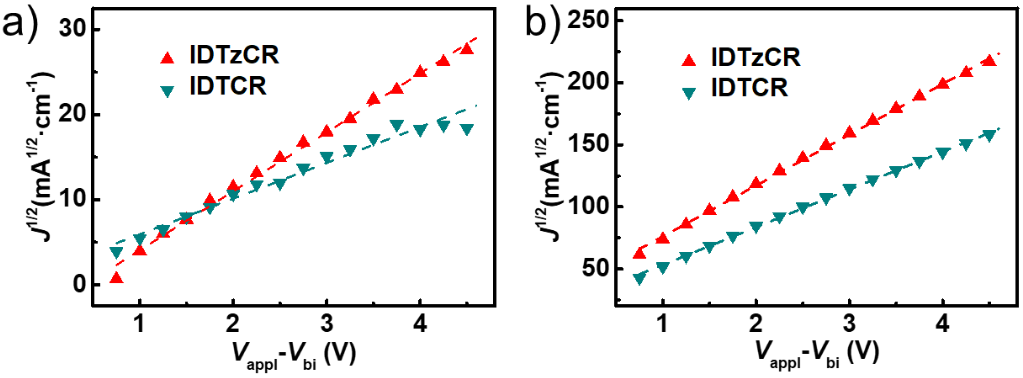


**Figure S3.** a) Typical current density-applied voltage lines for electron-only diodes. b) Typical current density-applied voltage lines for hole-only diodes.

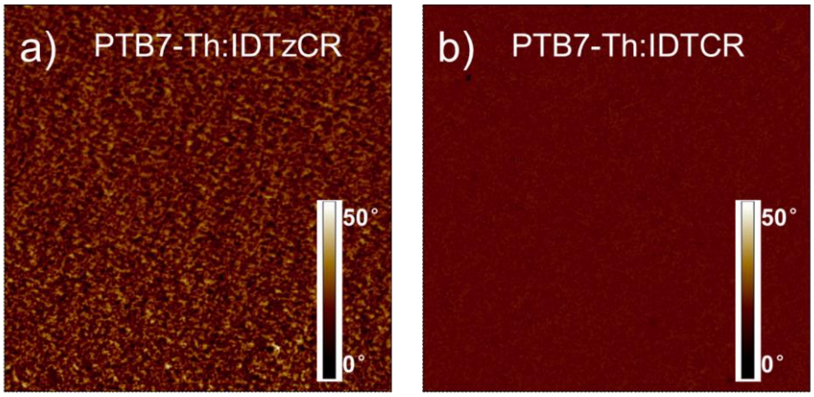


**Figure S4.** AFM phase images of PTB7-Th:IDTzCR (a) and PTB7-Th:IDTCR (b) based blend films.

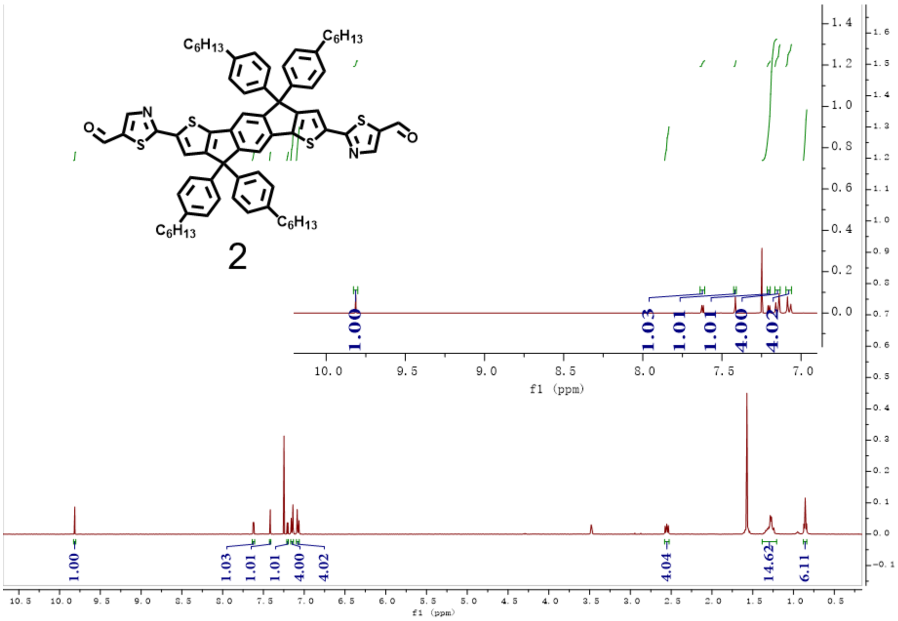


**Figure S5.** $^1$H-NMR spectra of compound 2 at 400 MHz in $CDCl_3$.

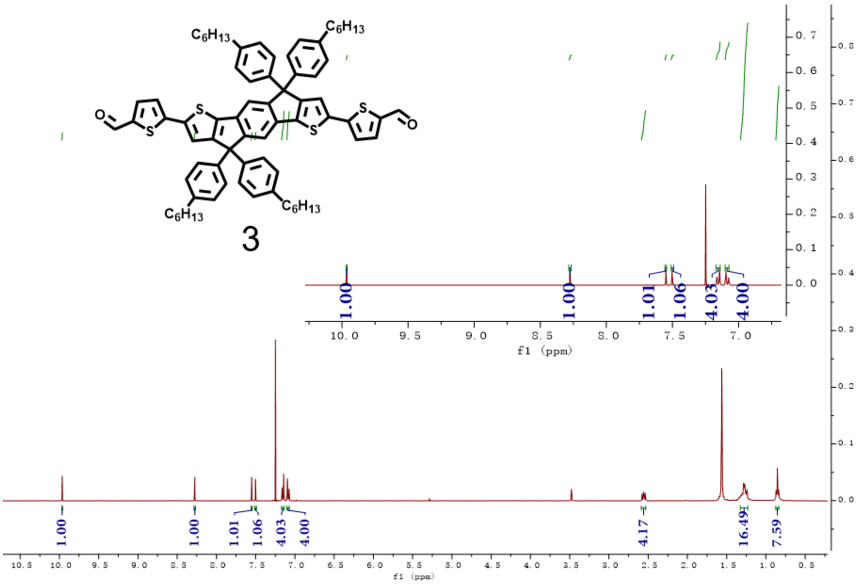


**Figure S6.** $^1$H-NMR spectra of compound 3 at 400 MHz in $CDCl_3$.

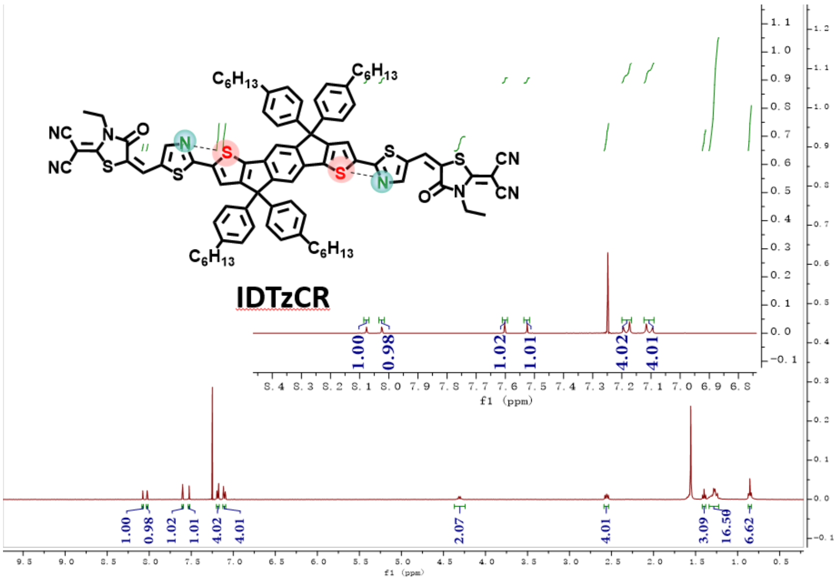


**Figure S7.** $^1$H-NMR spectra of compound IDTzCR at 400 MHz in $CDCl_3$.

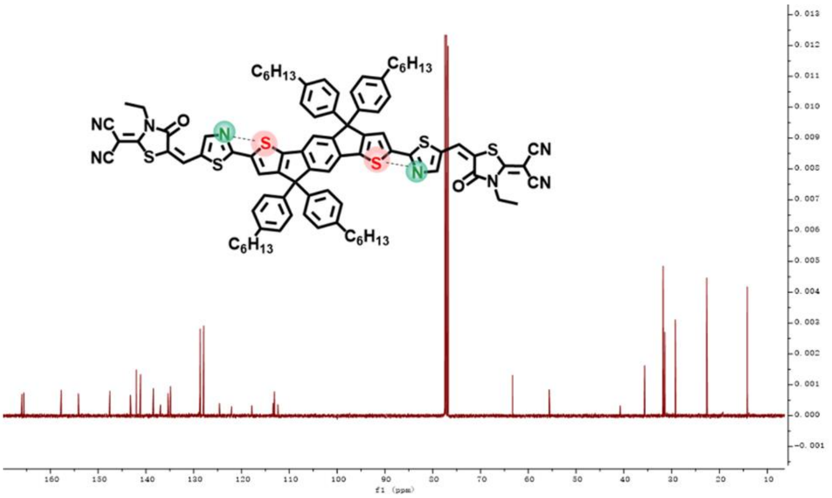


**Figure S8.** $^{13}$C-NMR spectra of compound IDTzCR at 100 MHz in $CDCl_3$.

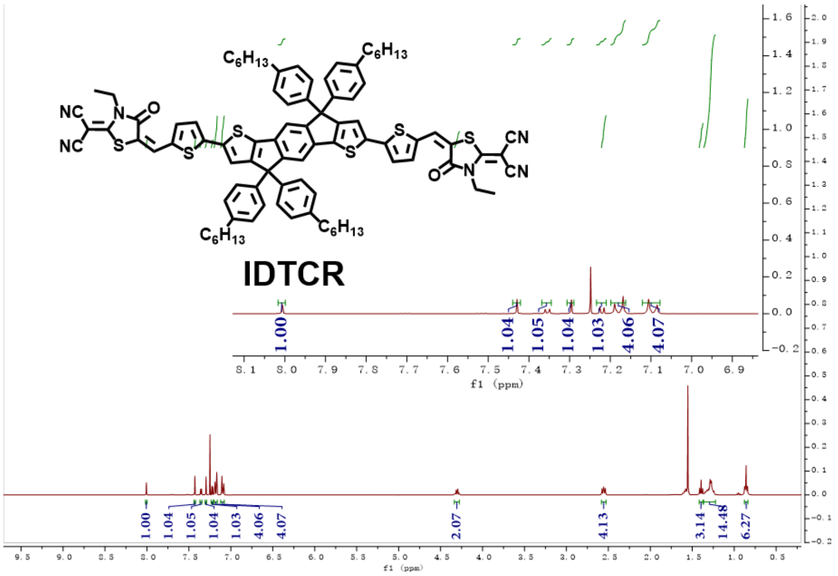


**Figure S9.** $^1$H-NMR spectra of compound IDTCR at 400 MHz in $CDCl_3$.

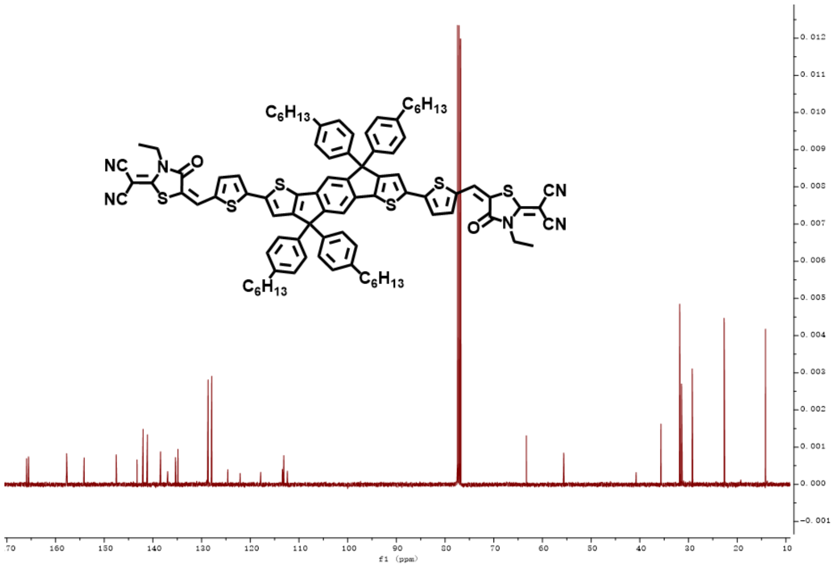


**Figure S10.** $^{13}$C-NMR spectra of compound IDTCR at 100 MHz in $CDCl_3$.

## 4. Tables.

**Table S1.** Calculated reorganization energy for IDTzCR and IDTCR.

| Compound | Hole reorganization energy (eV) | Electron reorganization energy (eV) |
|---|---|---|
| IDTzCR | 0.1670 | 0.1985 |
| IDTCR | 0.1802 | 0.2034 |

**Table S2.** Photovoltaic performance of the OPVs based on PTB7-Th:IDTzCR blend films without/with PEIE under illumination of AM 1.5 G, 100 mW·cm$^{-2}$.

| Interlayer | PCE (%) | $V_{OC}$ (V) | $J_{SC}$ (mA·cm$^{-2}$) | FF |
|---|---|---|---|---|
| Without PEIE | 5.86 | 1.06 | 11.17 | 49.5 |
| With PEIE | 7.08 | 1.08 | 13.45 | 49.3 |

**Table S3.** Photovoltaic performance of the OPVs based on PTB7-Th:IDTzCR blend films with a different D:A ratio under illumination of AM 1.5 G, 100 mW·cm$^{-2}$.

| D:A | PCE (%) | $V_{OC}$ (V) | $J_{SC}$ (mA·cm$^{-2}$) | FF |
|---|---|---|---|---|
| 1:0.8 | 6.25 | 1.08 | 11.70 | 49.5 |
| 1:1 | 7.18 | 1.08 | 13.64 | 48.8 |
| 1:1.2 | 7.08 | 1.08 | 13.45 | 49.3 |

**Table S4.** Photovoltaic performance of the OPVs based on PTB7-Th:IDTzCR blend films with different SVA time under illumination of AM 1.5 G, 100 mW cm$^{-2}$.

| Solution annealing | PCE (%) | $V_{OC}$ (V) | $J_{SC}$ (mA·cm$^{-2}$) | FF |
|---|---|---|---|---|
| 0 s | 7.18 | 1.08 | 13.64 | 48.8 |
| 30 s | 8.36 | 1.04 | 12.79 | 62.8 |
| 60 s | 8.71 | 1.04 | 13.80 | 60.7 |
| 90 s | 8.55 | 1.04 | 13.83 | 59.5 |
| 120 s | 6.40 | 1.02 | 12.77 | 49.2 |

# Reference.

1. Q. Zhang, B. Kan, F. Liu, G. Long, X. Wan, X. Chen, Y. Zuo, W. Ni, H. Zhang, M. Li, Z. Hu, F. Huang, Y. Cao, Z. Liang, M. Zhang, T. P. Russell and Y. Chen, *Nat. Photonics*, 2015, **9**, 35.
2. Y. Lin, J. Wang, Z. G. Zhang, H. Bai, Y. Li, D. Zhu and X. Zhan, *Adv. Mater.*, 2015, **27**, 1170.
3. N. E. Jackson, B. M. Savoie, K. L. Kohlstedt, M. Olvera de la Cruz, G. C. Schatz, L. X. Chen and M. A. Ratner, *J. Am. Chem. Soc.*, 2013, **135**, 10475.