Electronic Supplementary Information for:

Combination of Noncovalent Conformational Locks and Side Chain Engineering to Tune Crystallinity of Nonfullerene Acceptors for P3HT based Organic Solar Cells

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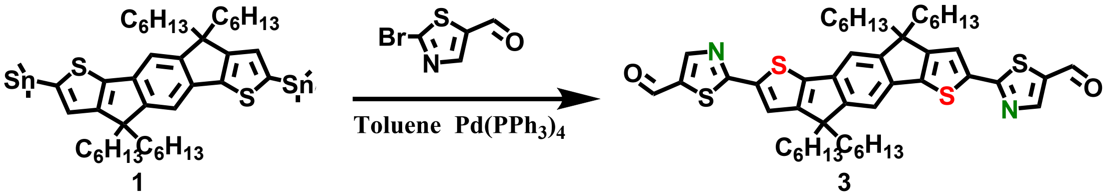
1. Materials.

All chemicals were purchased from commercial sources and employed without further purification unless indicated otherwise. All reactions were carried out under nitrogen atmosphere. Compound **1** and **2** were prepared according to literature procedure.[1, 2] Toluene was freshly distilled from sodium, and chloroform was freshly distilled from $CaCl_2$.

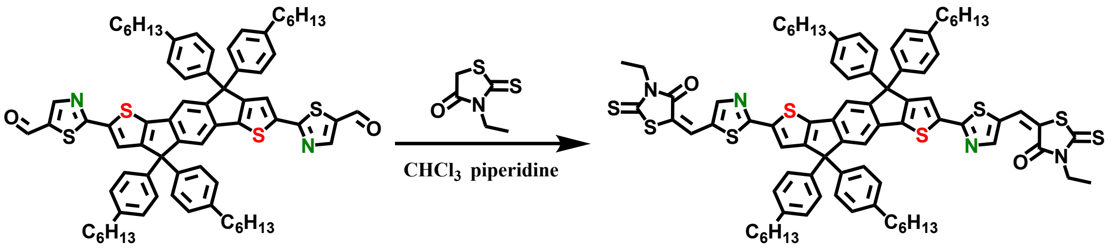
2. Experimental Section.

Materials synthesis

All the synthetic routes were shown as follow:

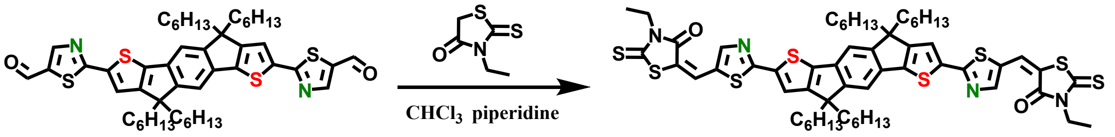


Synthesis of compound 3: Compound **1** (300.0 mg, 0.320 mmol) and 2-bromothiazole-5-carbaldehyde (186.0 mg, 0.97 mmol), and $Pd(PPh_3)_4$ (20.0 mg, 0.017 mmol) were dissolved in dry toluene (30 mL) under nitrogen. The mixed system was heated at 110 °C for 24 h. Then the mixed system was poured into CH_3OH (100 mL) to afford a red solid. Afterwards, the solid was collected and dried in air. Then, the solid was purified by column chromatography on silica gel using petroleum ether/CH_2Cl_2 (1:1,v/v) as an eluent, affording a red solid (~100 mg, 40%). ^1H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 2H), 8.33 (s, 2H), 7.56 (s, 2H), 7.37 (s, 2H), 2.03 (m, 4H), 1.91 (m, 4H), 1.2 (m, 32H), 0.75 (m, 12H). MS (MALDI-TOF): calculated for $C_{48}H_{60}N_2O_2S_4$, 824.3; found: 824.4.



2

Synthesis of P-IDTzR: Compound **2** (140.0 mg, 0.12 mmol) and 3-ethylrhodanine (116.0 mg, 0.72 mmol) were dissolved in dry $CHCl_3$ (20 mL) under nitrogen. And the piperidine (0.1 mL) was added to the mixed system dropwise. The mixed system was heated at 65 °C for 15 h and was cooled to room temperature. Afterwards, the mixed system was poured into CH_3OH (100 mL). After filtration, 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 (~60 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 2H), 7.85 (s, 2H), 7.52 (s, 2H), 7.50 (s, 2H), 7.19-7.16 (m, 8H), 7.11-7.08 (m, 8H), 4.17 (m, 4H), 2.56 (m, 6H), 1.29-1.24 (m, 40H), 0.85 (m, 12H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 191.23, 167.00, 166.91, 157.64, 154.53, 149.10, 145.94, 142.15, 140.93, 138.99, 135.68, 132.45, 128.71, 127.85, 124.31, 123.56, 121.97, 118.37, 63.18, 40.17, 35.65, 31.79, 31.42, 29.22, 22.67, 14.18, 12.35. MS (MALDI-TOF): calculated for $C_{82}H_{86}N_4O_2S_8$, 1416.1; found: 1416.0. Elemental analysis Calc. C, 69.55%; H, 6.12%; N, 3.96%. Found: C, 68.74%; H, 6.19%; N, 3.81%.



3

Synthesis of H-IDTzR: The synthetic route of H-IDTzR is the same as that of P-IDTzR. Compound **3** (140.0 mg, 0.170 mmol), 3-ethylrhodanine (161.0 mg, 1 mmol) and color of H-IDTzR is a dark solid (~60 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 2H), 7.90 (s, 2H), 7.53 (s, 2H), 7.36 (s, 2H), 4.19 (d, 4H), 2.10-1.99 (m, 4H), 1.97-1.87(m, 4H), 1.29 (m, 6H), 1.17-1.05 (m, 24H), 0.95-0.78(m, 8H), 0.76(m, 12H). ^{13}C NMR(100 MHz, $CDCl_3$): δ191.29, 165.51, 166.95, 156.90, 154.45, 149.62, 146.93, 138.01, 136.27, 132.17, 123.27, 122.94, 122.15, 114.25, 54.48, 40.19, 39.17, 31.66, 29.71, 24.31, 22.66, 14.13, 12.38. MS (MALDI-TOF): calculated for $C_{58}H_{70}N_4O_2S_8$, 1111.7; found: 1111.5. Elemental analysis Calc. C, 62.66%; H, 6.35%; N, 5.04%. Found: C, 62.37%; H, 6.42%; N, 4.96%.

Measurements and Instruments

The ^{1}H and ^{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·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·s^{-1} under nitrogen in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The geometrical conformation of H-IDTzR and P-IDTzR molecules were optimized by density functional theory (DFT) calculation. 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 an inverstedstructure of Glass/ITO/ZnO/P3HT:aceeptor/MoO_3/Ag. 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. The active layer of P3HT:aceeptor were processed in different conditions at concentration of 12 mg/mL. The optimized active layer thickness was ca.100 nm. After thermal annealing under different temperature, 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·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 extracted by fitting the current density–voltage curves using space charge limited current (SCLC). The devices structure of ITO/PEDOT:PSS/active layer/MoO_3/Ag for holes mobility and ITO/Al/active layer/Al for electrons mobility. 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, μ_e is electron mobility, μ_h is hole mobility, ε_r is relative dielectric constant of the transport medium, and ε_0 is permittivity of free space. $V = V_{appl}–V_{bi}$, V is the applied voltage, V_{bi} is the offset voltage (for hole-only diodes and electron-only diodes, V_{bi} are all 0.4 V).

3. Tables.

Table S1. Photovoltaic performance of P3HT:P-IDTzR based OSCs with a ratio of 1:0.8 under illumination of AM 1.5 G, 100 mW·cm^{-2}.

Solvent	PCE (%)	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF
CF	4.15	1.00	7.81	53.1
CB	3.80	0.99	6.47	59.3

Table S2. Photovoltaic performance of P3HT:P-IDTzR based OSCs 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
1:1.3	4.21	1.00	8.05	52.3
1:1	4.49	1.01	8.42	52.8
1:0.8	4.15	1.00	7.81	53.1

Table S3. Photovoltaic performance of P3HT:P-IDTzR based OSCs with different thermal annealing (TA) temperature under illumination of AM 1.5 G, 100 mW cm^{-2}.

TA	PCE (%)	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF
100°C	4.57	1.01	9.10	49.8
130°C	4.88	1.02	8.89	53.8
160°C	4.49	1.01	8.42	52.8

4. Figures.

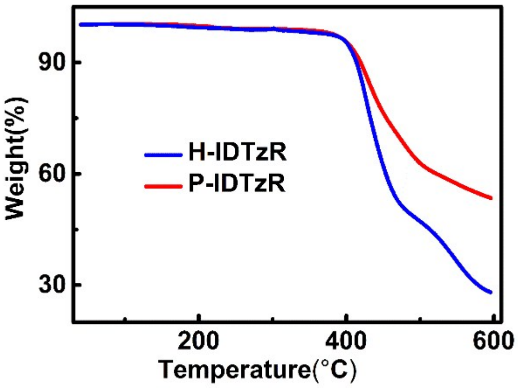


Fig. S1. TGA curves for H-IDTzR and P-IDTzR.

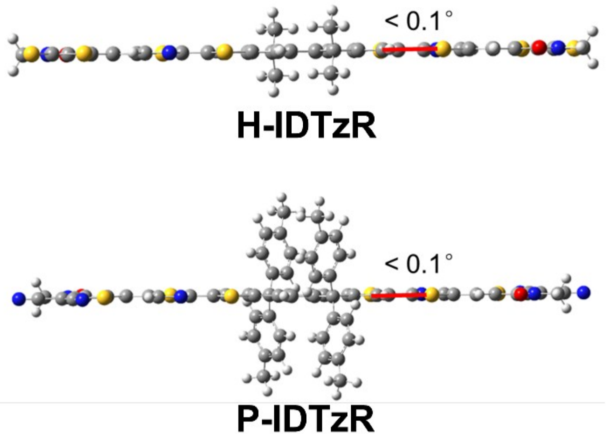


Fig. S2. Side view of optimized molecular geometries for H-IDTzR and P-IDTzR.

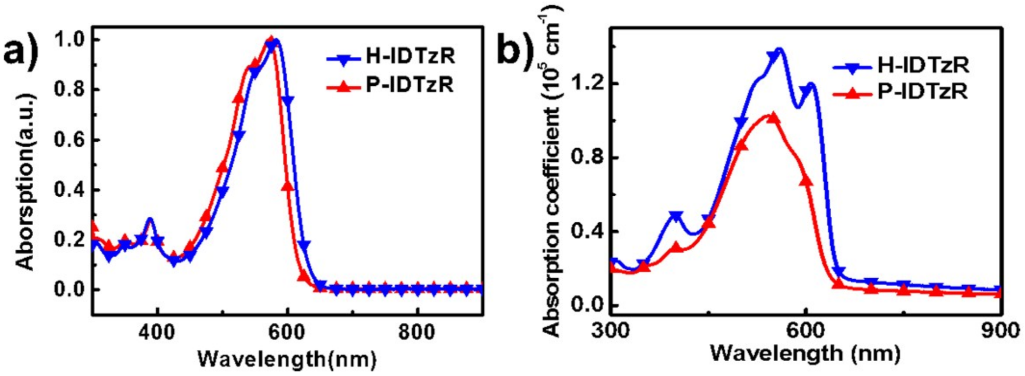


Fig. S3. a) UV-Vis absorption spectra of the solution for H-IDTzR and P-IDTzR. b) UV-Vis absorption spectra of blend film for H-IDTzR and P-IDTzR.

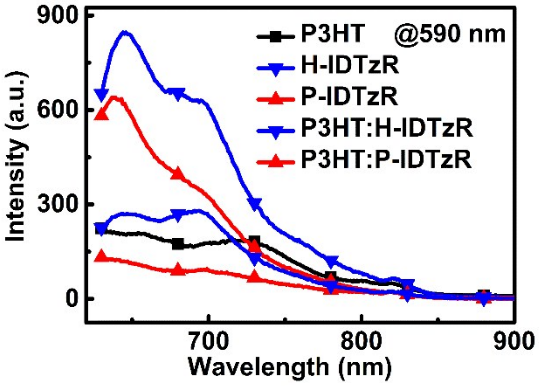


Fig. S4. Photoluminescence spectra of P3HT, H-IDTzR and P-IDTzR pristine films and corresponding blended films excited at 590 nm, respectively.

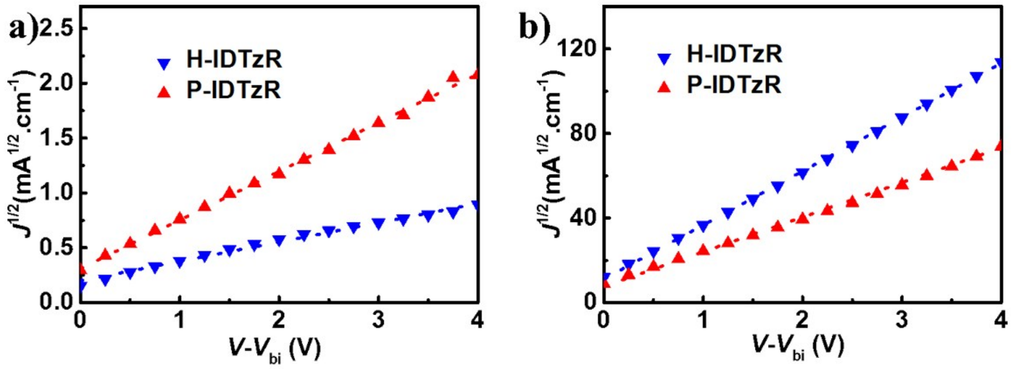


Fig. S5. a) Typical current density-applied voltage lines for electron-only diodes. b) Typical current density-applied voltage lines for hole-only diodes.

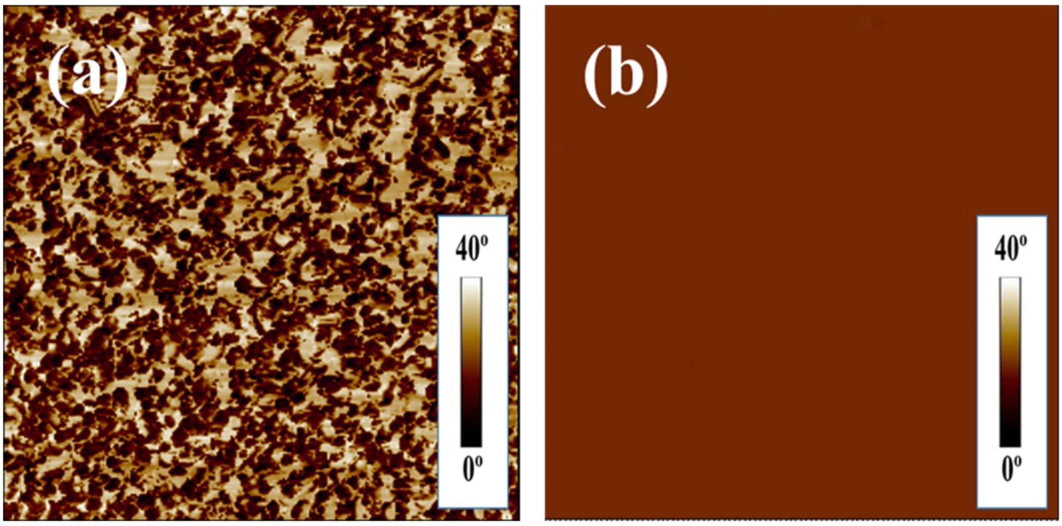


Fig. S6. AFM phase images of blended films of P3HT:H-IDTzR (a) and P3HT:P-IDTzR (b).

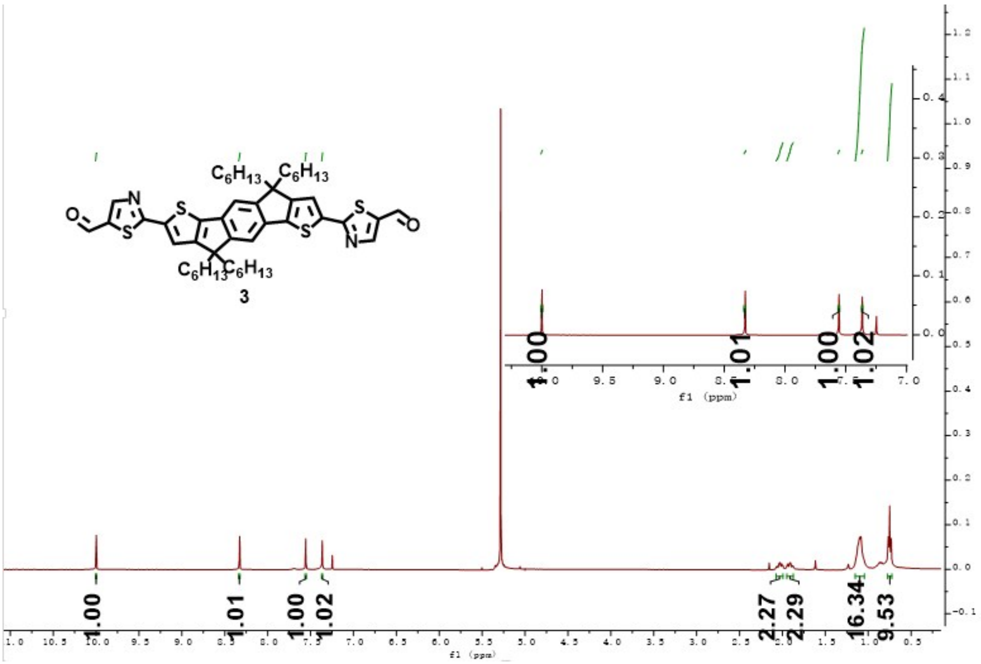


Fig. S7. ^{1}H NMR (400 MHz, CDCl$_3$) spectra of compound **3**$_3$.

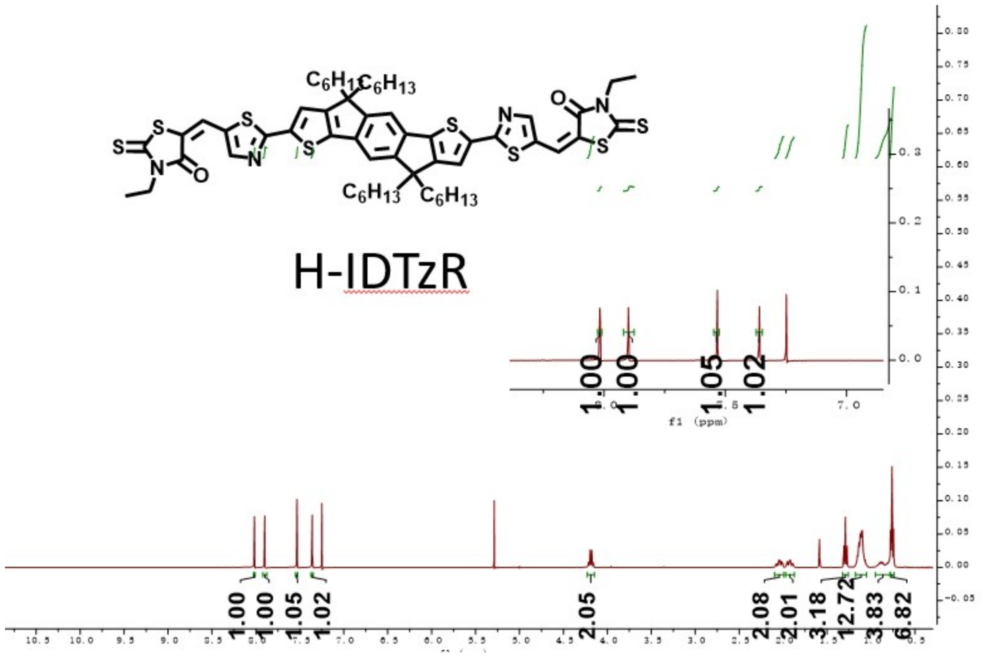


Fig. S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of H-IDTzR.

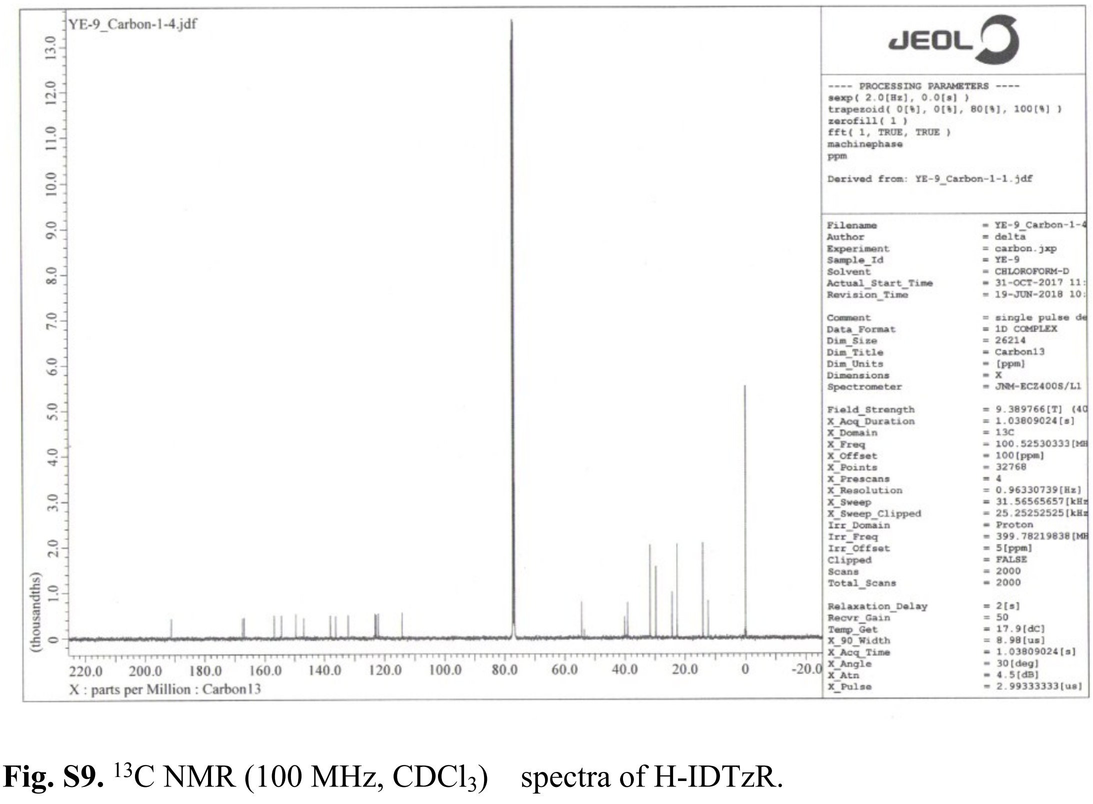


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Fig. S9. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of H-IDTzR.

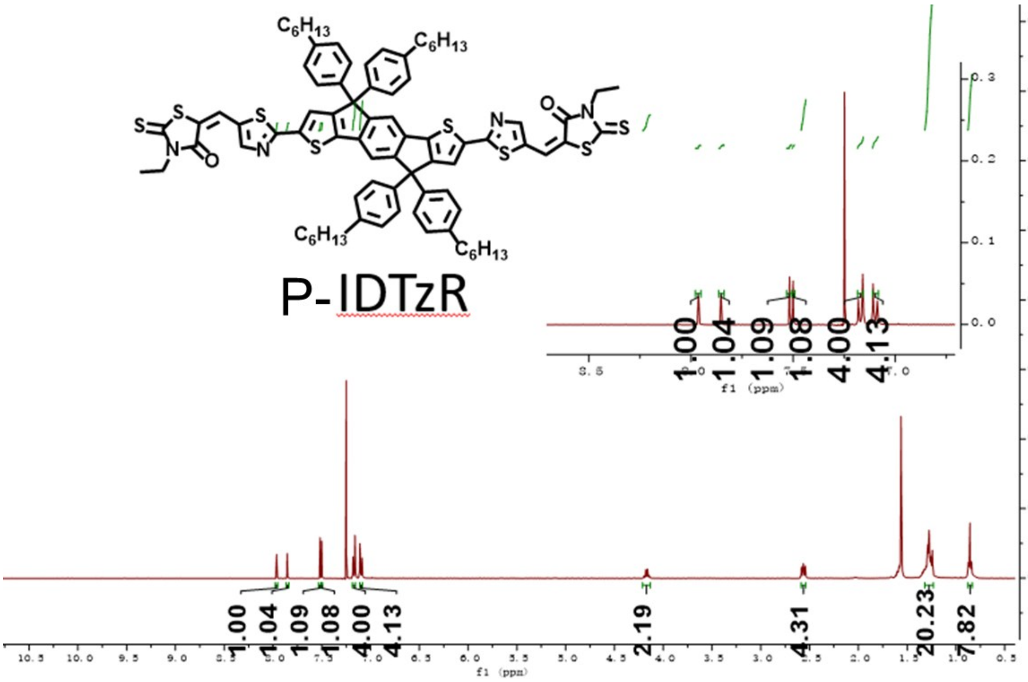

Fig. S10. ^1H NMR (400 MHz, $CDCl_3$) spectra of compound P-IDTzR.

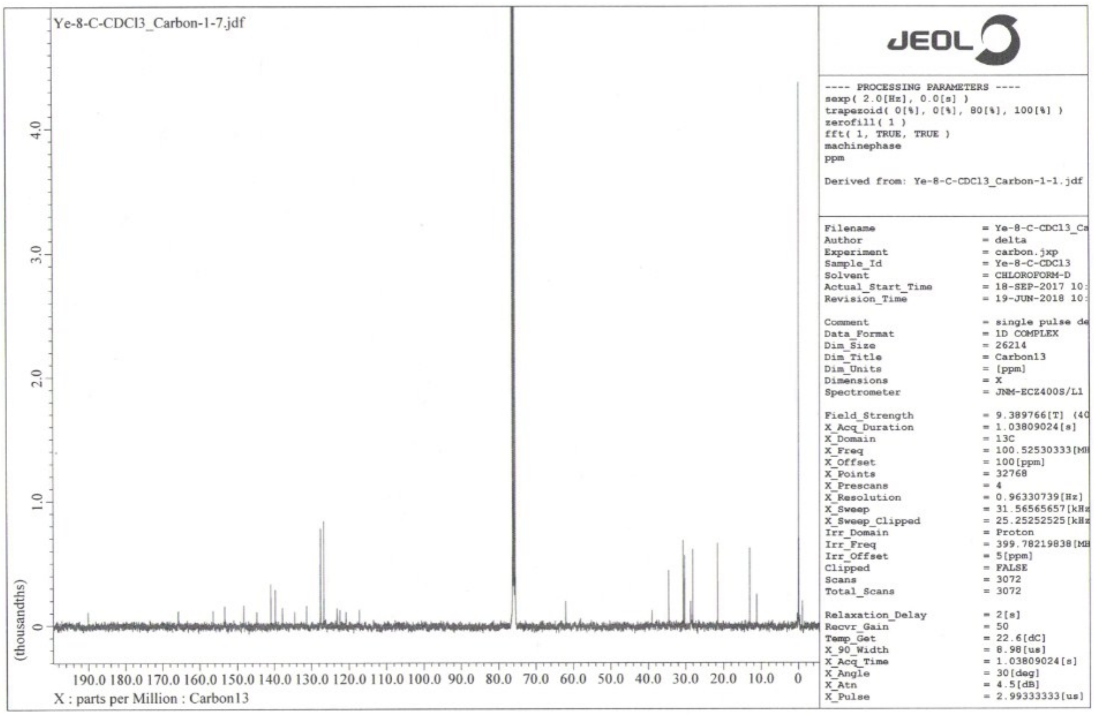

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Fig. S11. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound P-IDTzR.

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**, 35-41.
2. P. Ye, Y. Chen, J. Wu, X. Wu, S. Yu, W. Xing, Q. Liu, X. Jia, A. Peng and H. Huang, *J. Mater. Chem. C*, 2017, **5**, 12591-12596.