Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers

An Isomerized Alkyl Side Chain Enables Efficient Nonfullerene Organic Photovoltaics with Good Tolerance to Pre/Post-Treatments

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Experimental Procedures

Materials and Characterization Techniques

Donor material PM6 were purchased from Solarmer Materials Inc. The starting material IDT was purchased from Derthon Co. All solvents and reagents were purchased from Alfa Aesar, Sigma-Aldrich, et al., which were utilized directly unless stated otherwise.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE III 600 MHz or Bruker AVANCE III 400 MHz spectrometer at 298 K. The absorption spectra were recorded using a Hitachi U-4100 UV-Vis scanning spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation, equipped with a three-electrode cell consisting of a platinum working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire counter electrode. CV measurements were carried out in anhydrous acetonitrile containing 0.1 M n-Bu_4NPF_6 as a supporting electrolyte under an argon atmosphere at a scan rate of 100 mV s^{-1} assuming that the absolute energy level of Fc/Fc^+ was -4.80 eV. Thin films were deposited from $CHCl_3$ solution onto the working electrodes. Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were acquired by detector Pilatus3R 1M, Dectris (X-ray Source: MetalJet-D2, Excillum). Transmission electron microscopy (TEM) images were obtained by using a HITACHI H-7650 electron microscope with an acceleration voltage of 100kV. Atomic force microscopy (AFM) images were obtained using Agilent 5400 scanning probe microscope in tapping mode with MikroMasch NSC-15 AFM tips.

Device Fabrication and Evaluations

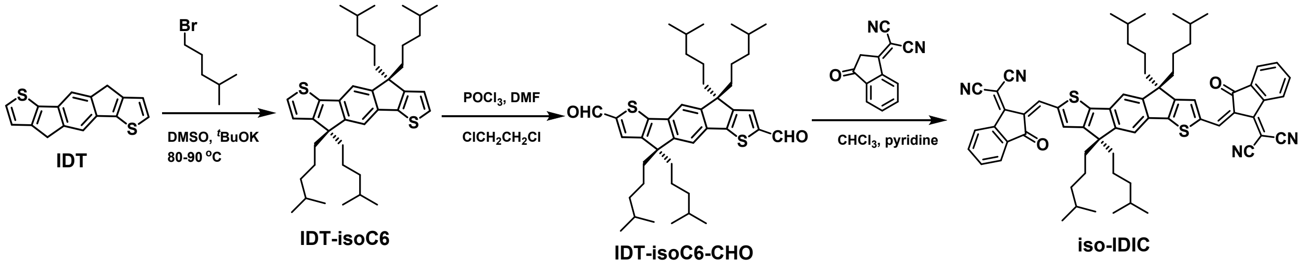
All the organic photovoltaic devices were fabricated with a conventional device structure of ITO/PEDOT:PSS/PM6: IDIC or *iso*-IDIC/PDINO/Al. The patterned ITO glass (sheet resistance = 15 Ω/ square) was pre-cleaned in an ultrasonic bath of acetone and isopropyl alcohol and treated in an ultraviolet-ozone chamber (PREEN II-862) for 6 min. Then a thin layer (about 30 nm) of PEDOT:PSS was spin-coated onto the ITO glass at 4000 rpm and baked at 150 ^{o}C for 15 min. Solutions of PM6:acceptor in chlorobenzene (18 mg/mL, the total concentration) were stirred overnight and warmed to 50 ^{o}C for 30 mins before spin-coating on the PEDOT:PSS layer to form the active layer about 100±30 nm. The thickness of the active layer was measured using a Veeco Dektak 150 profilometer. Then PDINO solution (in CH_3OH, 1mg/mL) was spin-coating at 3000 rpm to form the electron transfer layer. Finally, Al (60 nm) metal electrode was thermal evaporated under about 4×10^{-4} Pa and the device area was 0.1 cm^2 defined by shadow mask.

The current density–voltage (*J–V*) characteristics were recorded with a Keithley 2400 source measurement unit under simulated 100 mW cm^{-2} irradiation from a Newport solar simulator. The external quantum efficiencies (EQEs) were analysed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. The hole mobility and electron mobility were measured by space-charge-limited current (SCLC) method with a device configuration of ITO/PEDOT:PSS/active layer/MoO_3/Al and ITO/ZnO/active layer/PDINO/Al structure, respectively. The SCLC is described by the Mott–Gurney law:

$$J = 9\varepsilon\mu V^2/(8L^3)$$

where ε represents the dielectric constant of the metal, and μ is the carrier mobility, V is the voltage drop across the device and L is the thickness of the active layer.

The synthetic details of *iso*-IDIC



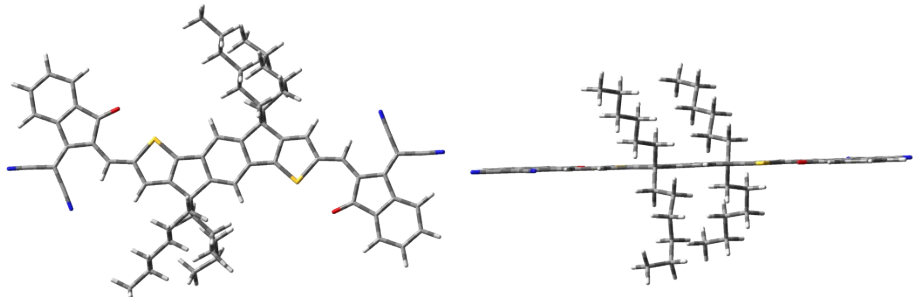
Scheme S1. The synthetic routes of *iso*-IDIC

Synthesis of IDT-isoC6: IDT (533 mg, 2.0 mmol) was dispersed in 20 mL extra-dry DMSO and stirred under argon atmosphere. Then ^{t}BuOK (1.35 g, 12.0 mmol) was added in small portions. After then, the solution was heated at 80 °C for 1.0 hr. Subsequently, the isomerized alkyl chain1-bromo-4-methylpentane (2.64 g, 16.0 mmol) was dropwise added into the solution and heated at 85-90 °C for another 5.0 hrs. When the solution cooled into room temperature, it was poured into ice water and extracted with dichloromethane (50 mL×3), dried with anhydrous Na_2SO_4, and removed the solvent by rotary evaporator. The crude product was subjected into silica gel column chromatography with petroleum ether: dichloromethane (4:1, v:v) as eluent to afford IDT-isoC6 as pale solids (400 mg, yield: 33%). δ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (s, 2H), 7.25 (d, J = 4.6 Hz, 2H), 6.96 (d, J = 4.8 Hz, 2H), 1.96 (td, J = 13.0, 5.0 Hz, 4H), 1.88 – 1.77 (m, 4H), 1.33 (dd, J = 13.3, 6.6 Hz, 4H), 0.98 (dd, J = 14.8, 7.4 Hz, 8H), 0.87 – 0.75 (m, 9H), 0.68 (d, J = 6.7 Hz, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.15, 153.35, 141.86, 135.78, 126.27, 121.82, 113.19, 53.86, 39.40, 39.38, 27.63, 22.68, 22.59, 22.00.

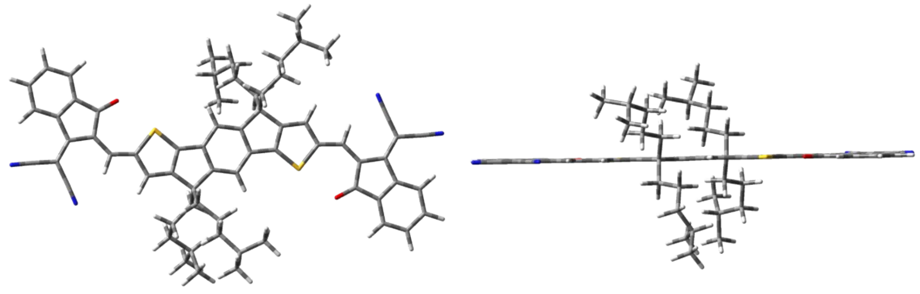
Synthesis of IDT-isoC6-CHO: Dry DMF (1.0 mL) dissolved into 10 mL 1, 2-dichloroethane was stirred at 0 °C under argon atmosphere. After dry $POCl_3$ (1.5 mL) was added dropwise, the solution was stirred at 0 °C for another 1.0 hr. Then IDT-isoC6 (185 mg, 0.31 mmol) dissolved into 10 mL dry 1,2-dichloroethane was added dropwise.

Then the solution was refluxed for 48 hrs under argon protection. When the solution cooled into room temperature, it was poured into ice water and stirred for 4.0 hrs and extracted with dichloromethane (30 mL×3), dried with anhydrous Na_2SO_4, and removed the solvent by rotary evaporator. The crude product was subjected into silica gel column chromatography with petroleum ether: dichloromethane (1:1, v:v) as eluent to afford IDT-isoC6-CHO as yellow solids (142 mg, yield: 70%). ^1H NMR (600 MHz, $CDCl_3$) δ 9.92 (s, 2H), 7.65 (s, 2H), 7.47 (s, 2H), 2.04 (td, J = 13.0, 4.6 Hz, 4H), 1.90 (td, J = 13.0, 4.5 Hz, 4H), 1.33 (dd, J = 13.3, 6.7 Hz, 4H), 1.00 (dd, J = 14.7, 7.4 Hz, 8H), 0.89 – 0.81 (m, 5H), 0.80 – 0.73 (m, 4H), 0.68 (d, J = 6.7 Hz, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.18, 156.16, 155.28, 151.58, 145.80, 136.69, 130.50, 115.11, 54.50, 39.20, 39.18, 27.62, 22.57, 22.54, 22.08.

Synthesis of iso-IDIC: IDT-isoC6-CHO (142 mg, 0.21 mmol) and 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (335 mg, 1.72 mmol) were dissolved into 30 mL $CHCl_3$ and stirred under argon atmosphere. Then pyridine (1.0 mL) was added dropwise. Then the solution was refluxed for 8 hrs. When the solution cooled into room temperature, most of the solvent was removed. The remaining solution was precipitated into CH_3OH, filtered and the residue was washed by 100 mL CH_3OH to remove most of the end-cap compound. Then the crude product was subjected into silica gel column chromatography with dichloromethane as eluent to afford IDIC-C5Ph as deep blue solids (150 mg, yield: 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 2H), 8.71 (dd, J = 6.5, 1.6 Hz, 2H), 7.99 – 7.91 (m, 2H), 7.83 – 7.69 (m, 6H), 7.61 (s, 2H), 2.07 (td, J = 13.4, 4.8 Hz, 4H), 1.94 (td, J = 13.4, 4.5 Hz, 4H), 1.34 (dt, J = 13.2, 6.6 Hz, 4H), 1.02 (ddd, J = 10.4, 9.6, 6.6 Hz, 8H), 0.93 – 0.81 (m, 4H), 0.81 – 0.72 (m, 4H), 0.68 (d, J = 6.6 Hz, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.53, 160.82, 160.35, 157.56, 156.70, 141.31, 140.11, 138.66, 138.16, 137.86, 137.09, 135.28, 134.62, 125.46, 123.89, 122.24, 116.06, 114.94, 114.87, 69.14, 54.59, 39.39, 39.15, 27.62, 22.59, 22.57, 22.14.

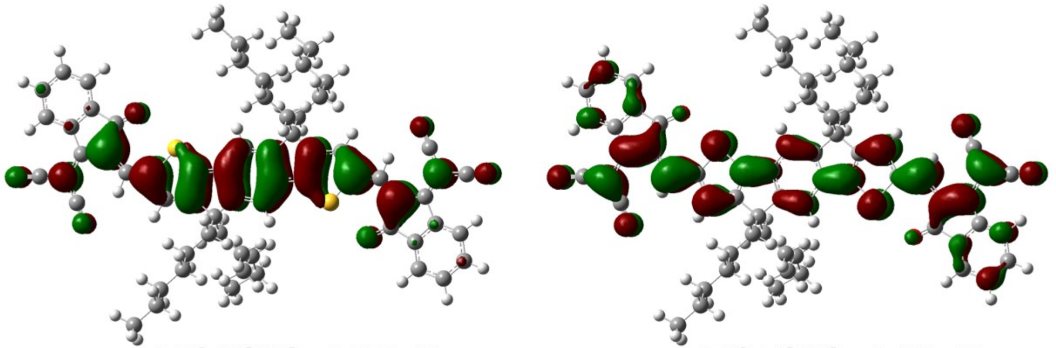


IDIC-front view **IDIC-side view**

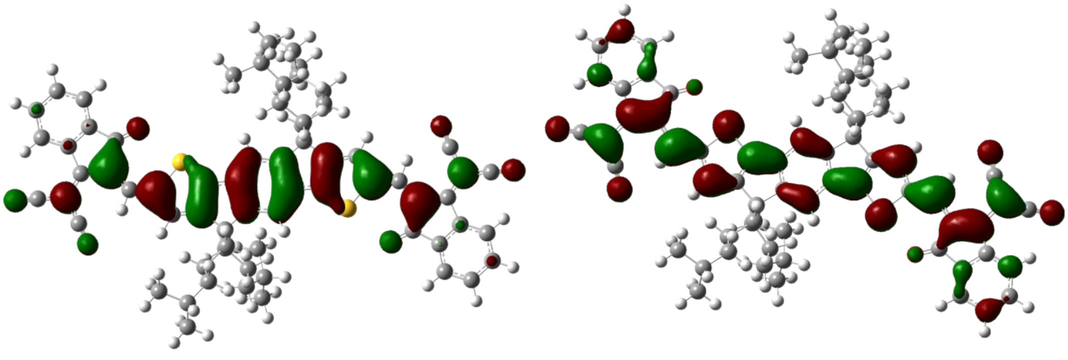


***iso*-IDIC-front view** ***iso*-IDIC-side view**

Fig. S1 The DFT calculated molecular conformations of IDIC and iso-IDIC at the B3LYP/6-31G level.



IDIC HOMO=-5.653 eV **IDIC HOMO=-3.423 eV**



iso-IDIC HOMO=-5.647 eV **iso-IDIC HOMO=-3.418 eV**

Fig. S2 The DFT calculated electron cloud density distributions and frontier energy levels of IDIC and iso-IDIC at the B3LYP/6-31G level.

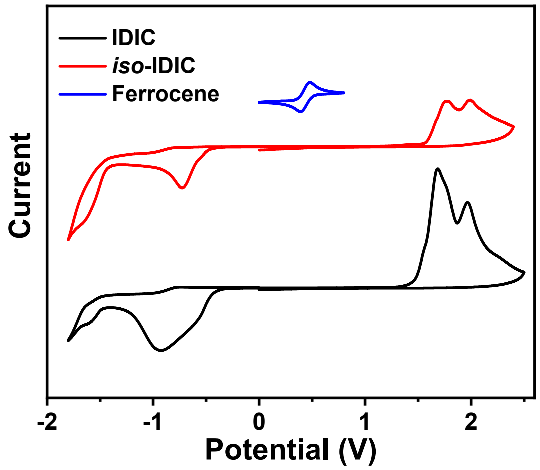


Fig. S3 The CV curves of IDIC and iso-IDIC deposited films at a scan rate of 100 mV s^{-1}.

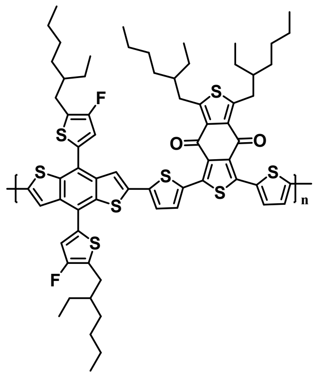


Fig. S4 The chemical structure of polymeric donor PM6.

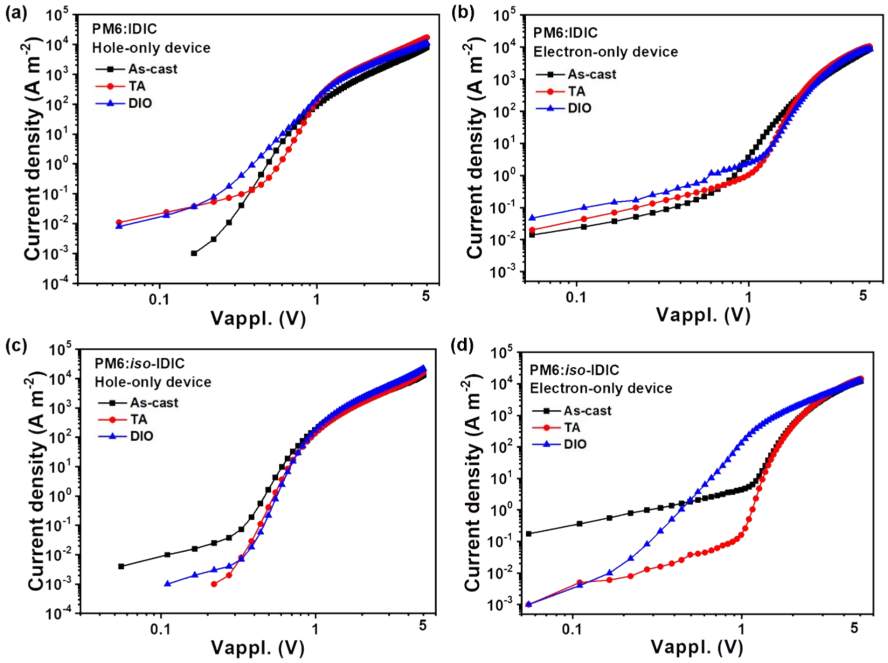


Fig. S5 *J-V* plots of (a and c) hole-only and (b and d) electron-only devices of PM6:IDIC and PM6:iso-IDIC.

Table S1. The photovoltaic parameters of *iso*-IDIC based as-cast OSCs with different weight ratios

Donor/acceptor *w/w*	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)[a]
1:0.75	0.952	17.44	72.75	12.08 (11.90)
1:1	0.963	18.55	73.26	13.10 (12.96)
1:1.25	0.961	18.14	73.84	12.87 (12.55)
1:1.5	0.958	17.87	72.38	12.39 (12.14)

[a] The PCEs in brackets represent the average values based on at least 10 devices.

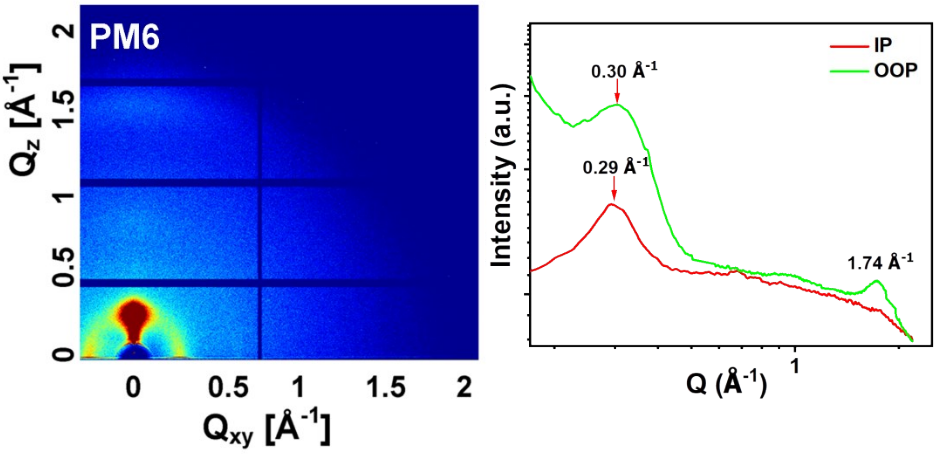


Fig. S6 The 2D-GIWAXS pattern and line-cut profiles of as-cast PM6 film.

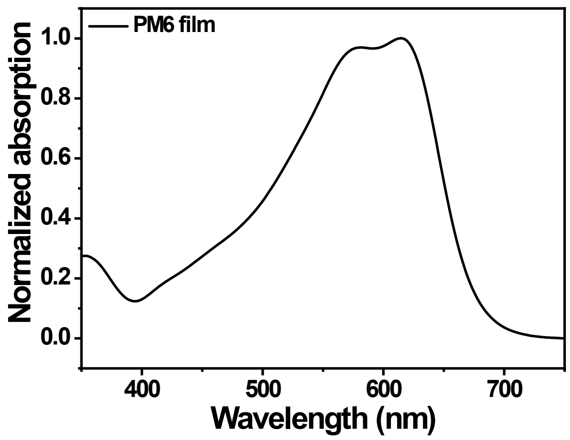


Fig. S7 The normalized absorption spectrum of PM6 film spin-coating from its choloroform solution (10 mg ml^{-1}).

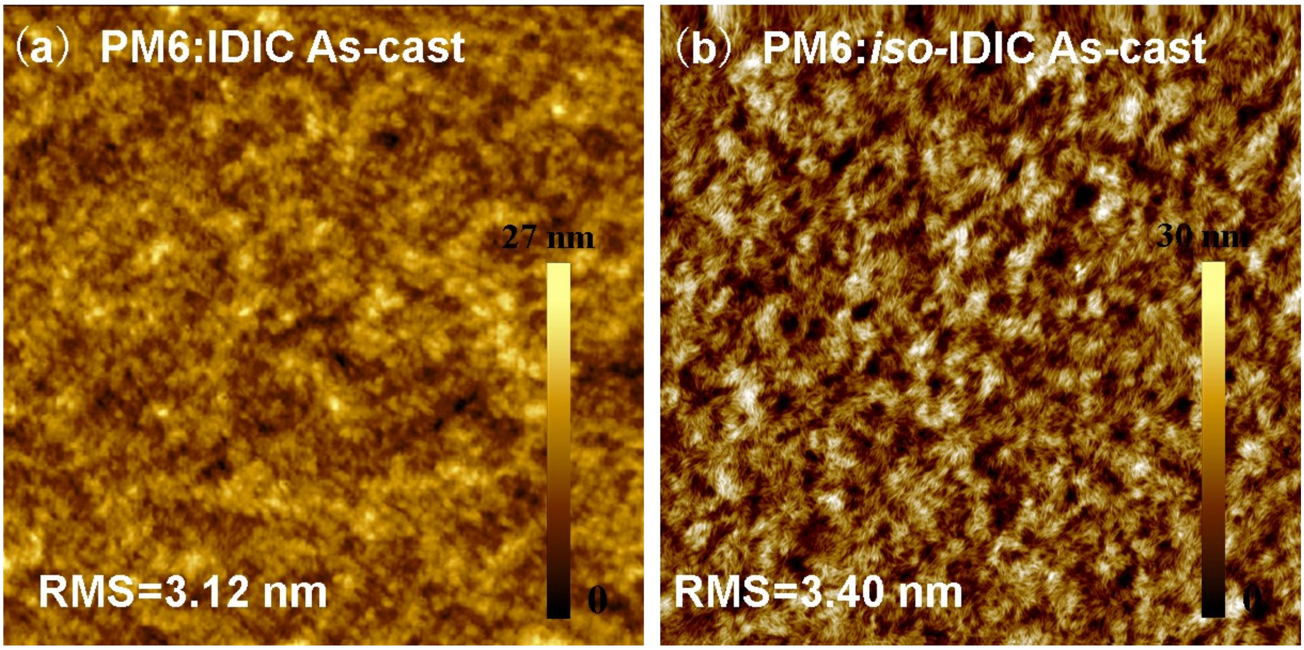


Fig. S8 The AFM images (5 μm×5 μm) of (a) PM6:IDIC and (b) PM6:*iso*-IDIC films without treatments.

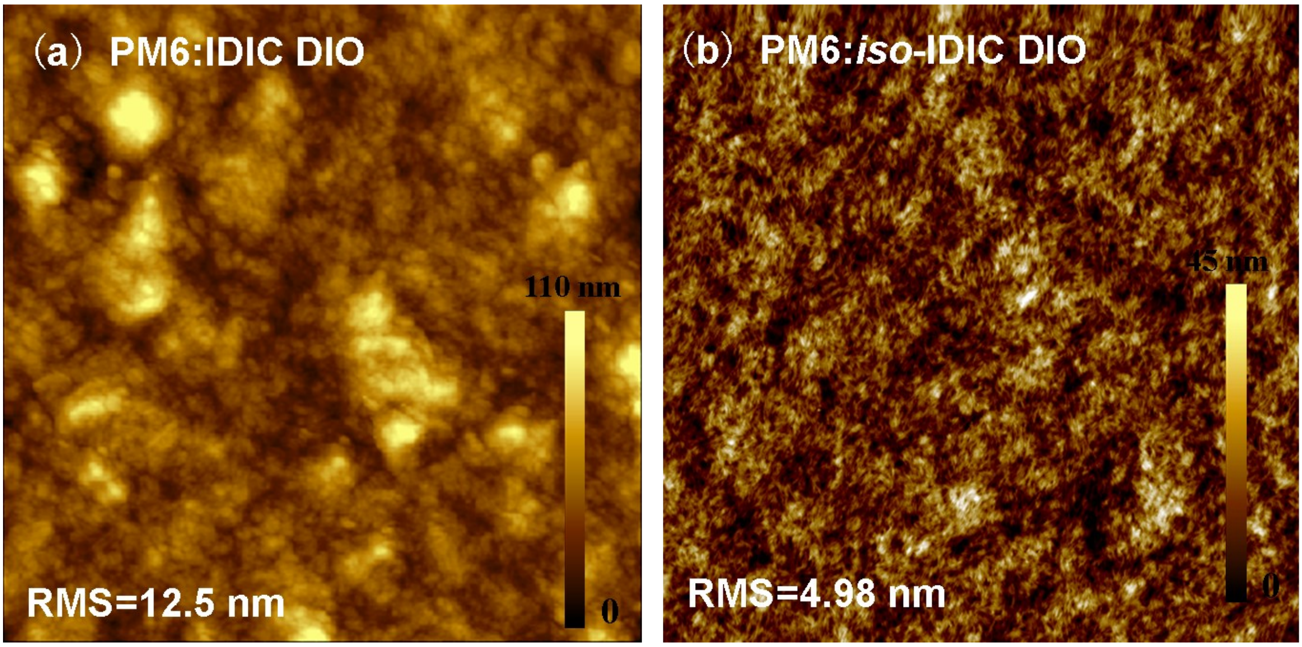


Fig. S9 The AFM images (5 μm×5 μm) of (a) PM6:IDIC and (b) PM6:*iso*-IDIC films without DIO treatments.

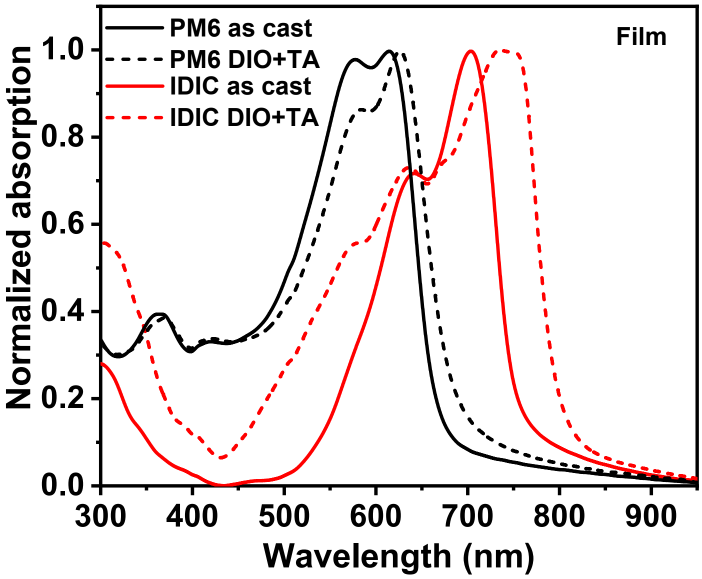


Fig. S10 The normalized absorption spectra of PM6 and IDIC with or without DIO treatments.

NMR spectra (Fig. S10-S15)

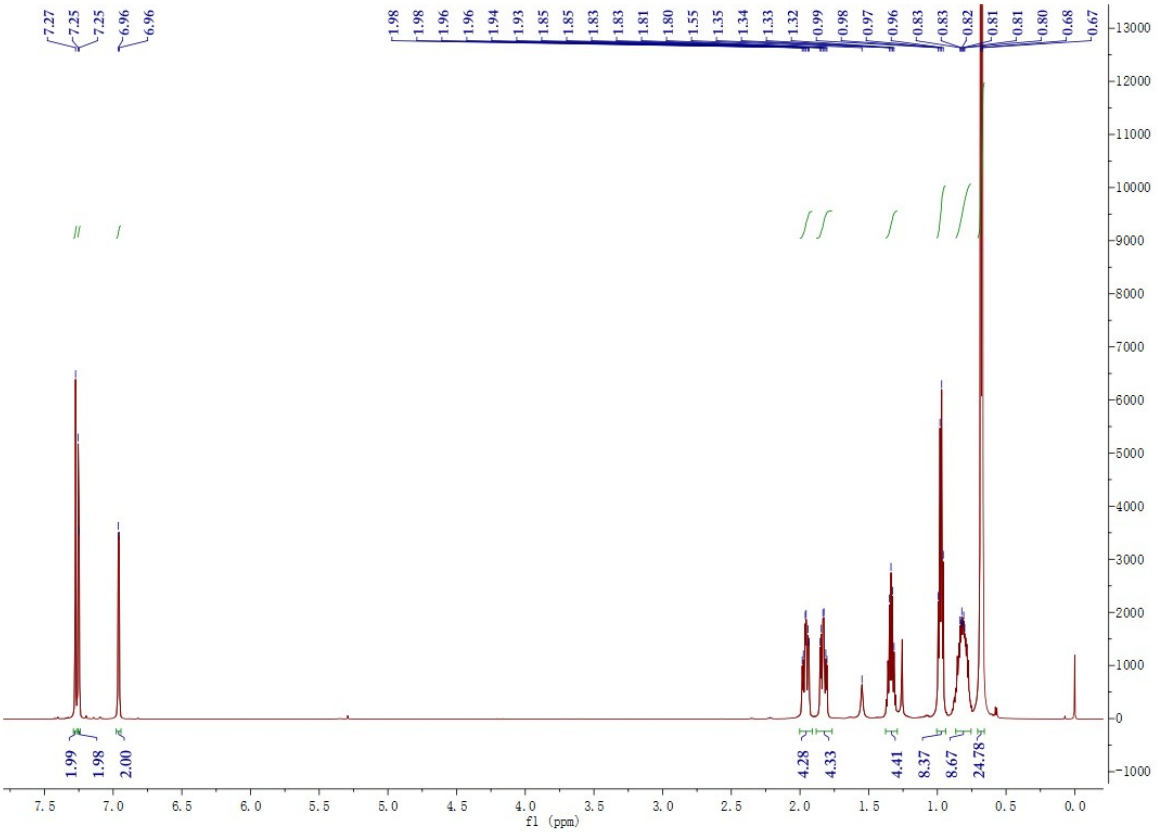


Fig. S10 The ^{1}H NMR spectrum of IDT-isoC6.

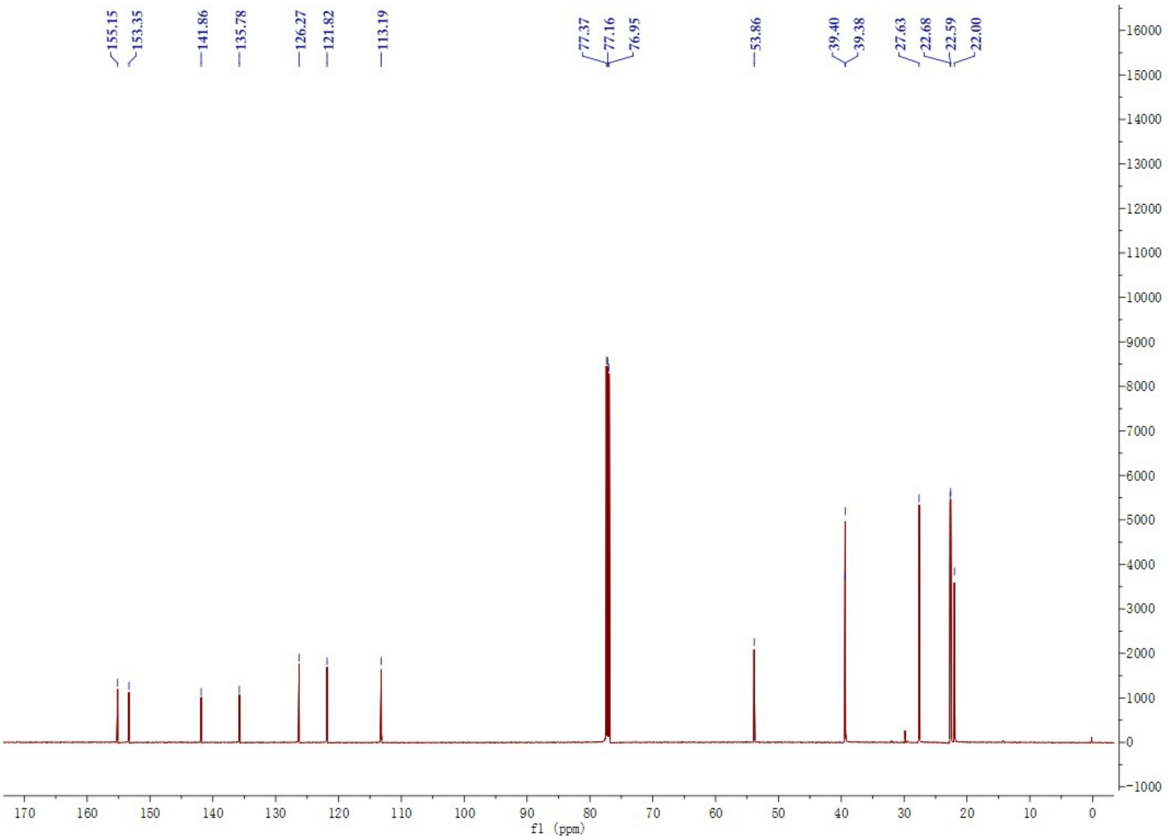


Fig. S11 The ^{13}C NMR spectrum of IDT-isoC6.

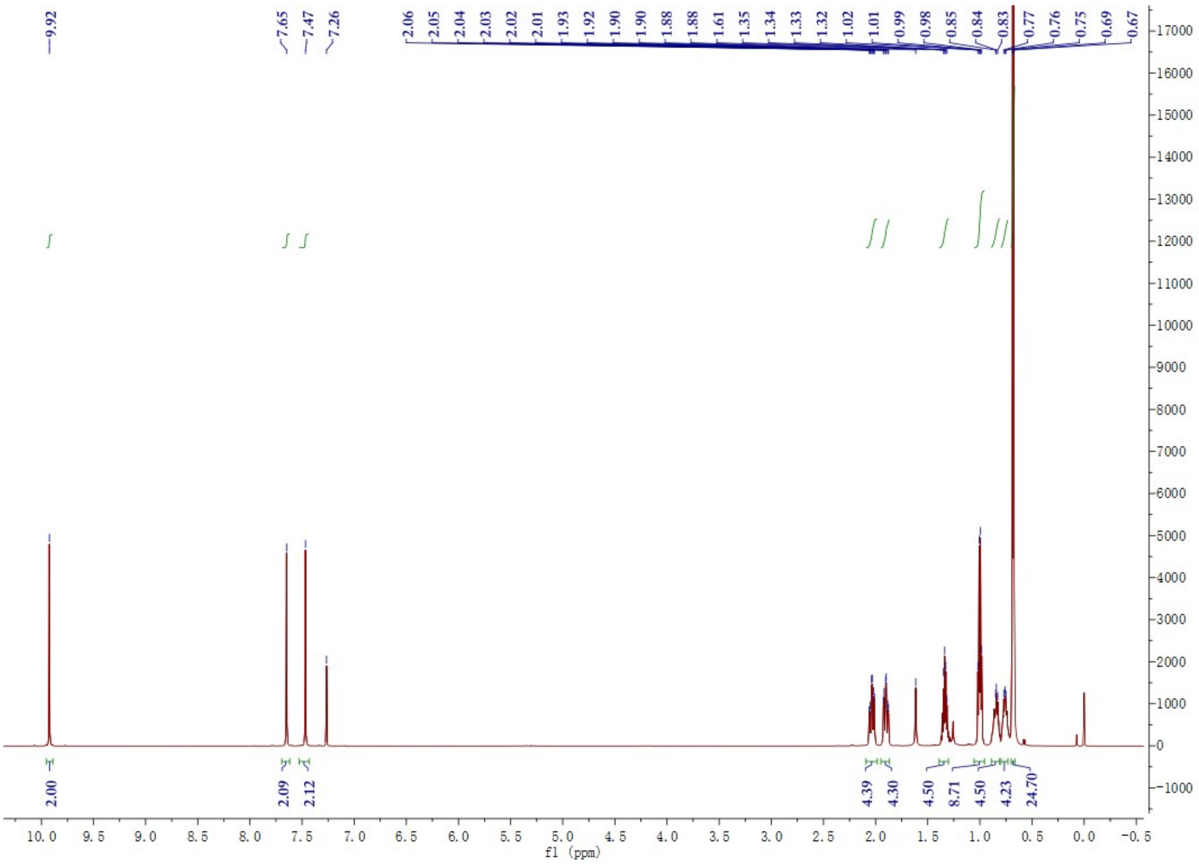


Fig. S12 The ^{1}H NMR spectrum of IDT-isoC6-CHO.

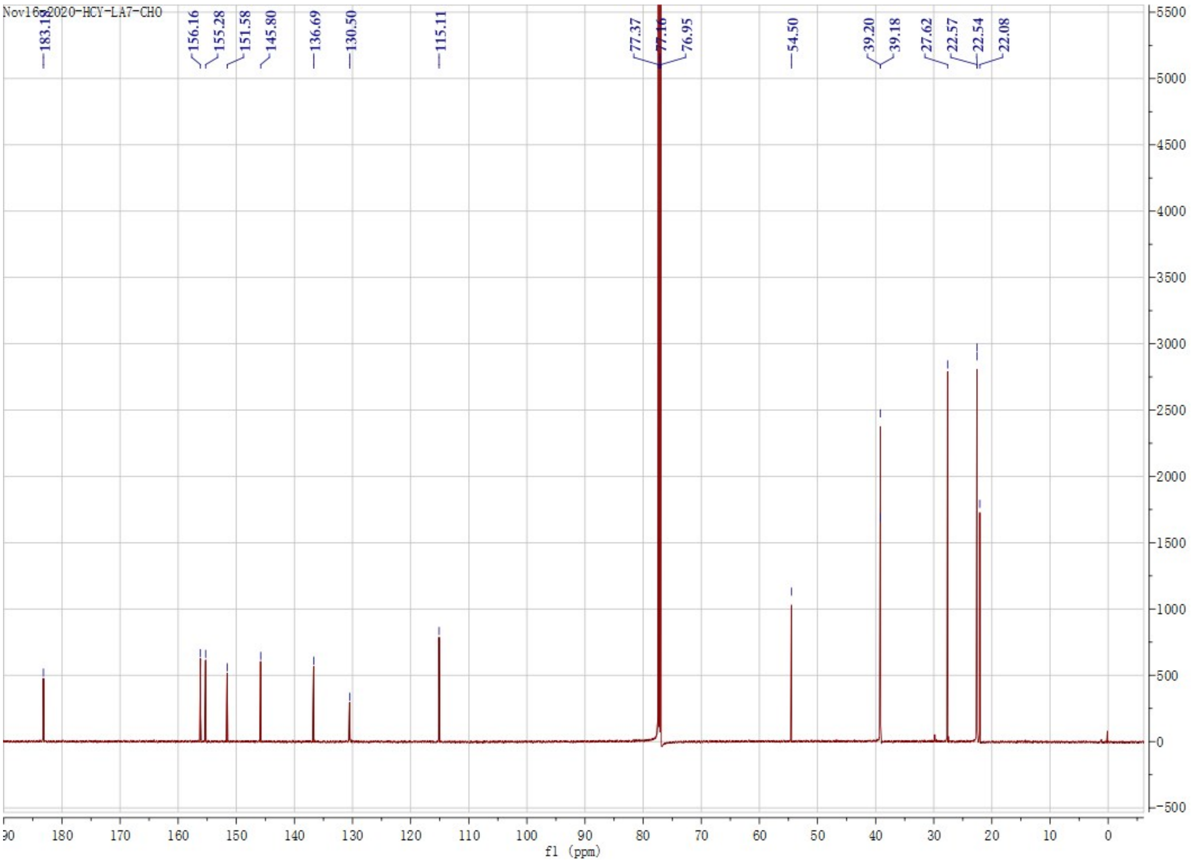


Fig. S13 The ^{13}C NMR spectrum of IDT-isoC6-CHO.

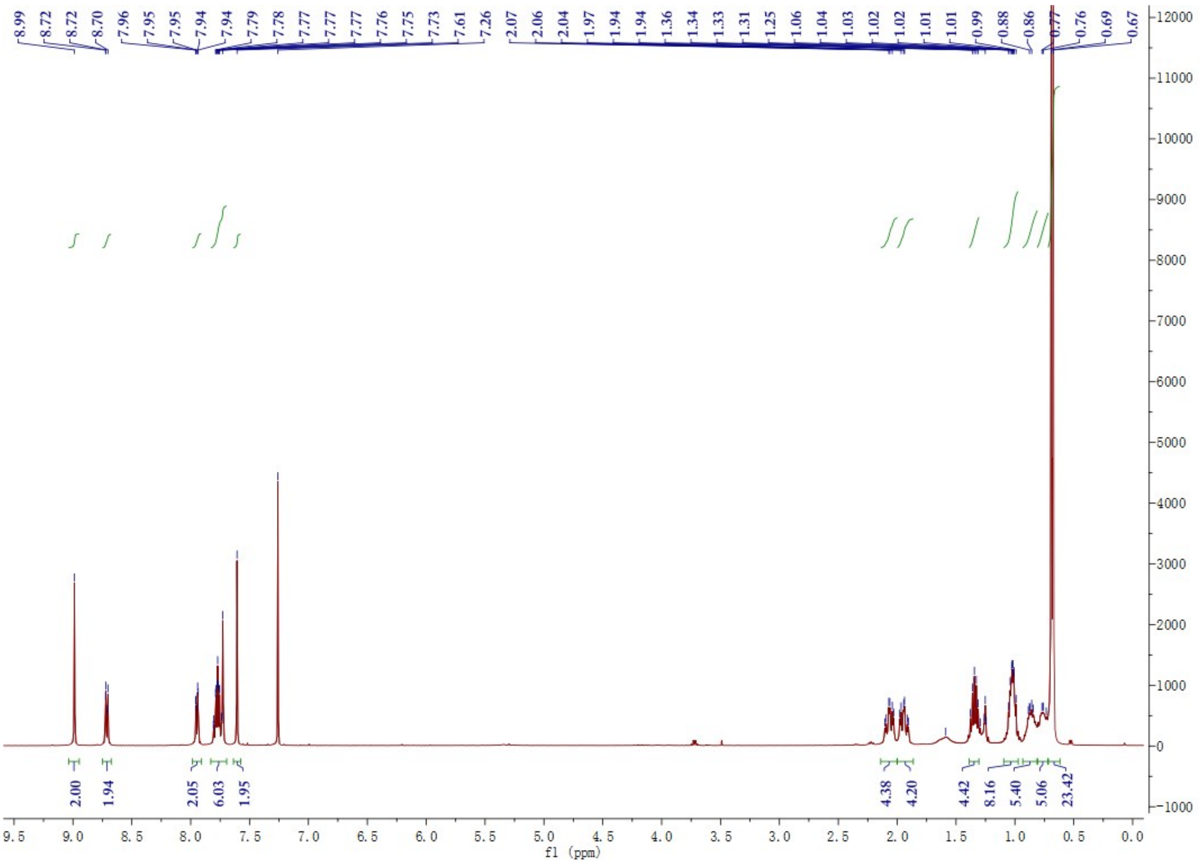


Fig. S14 The ^{1}H NMR spectrum of iso-IDIC.

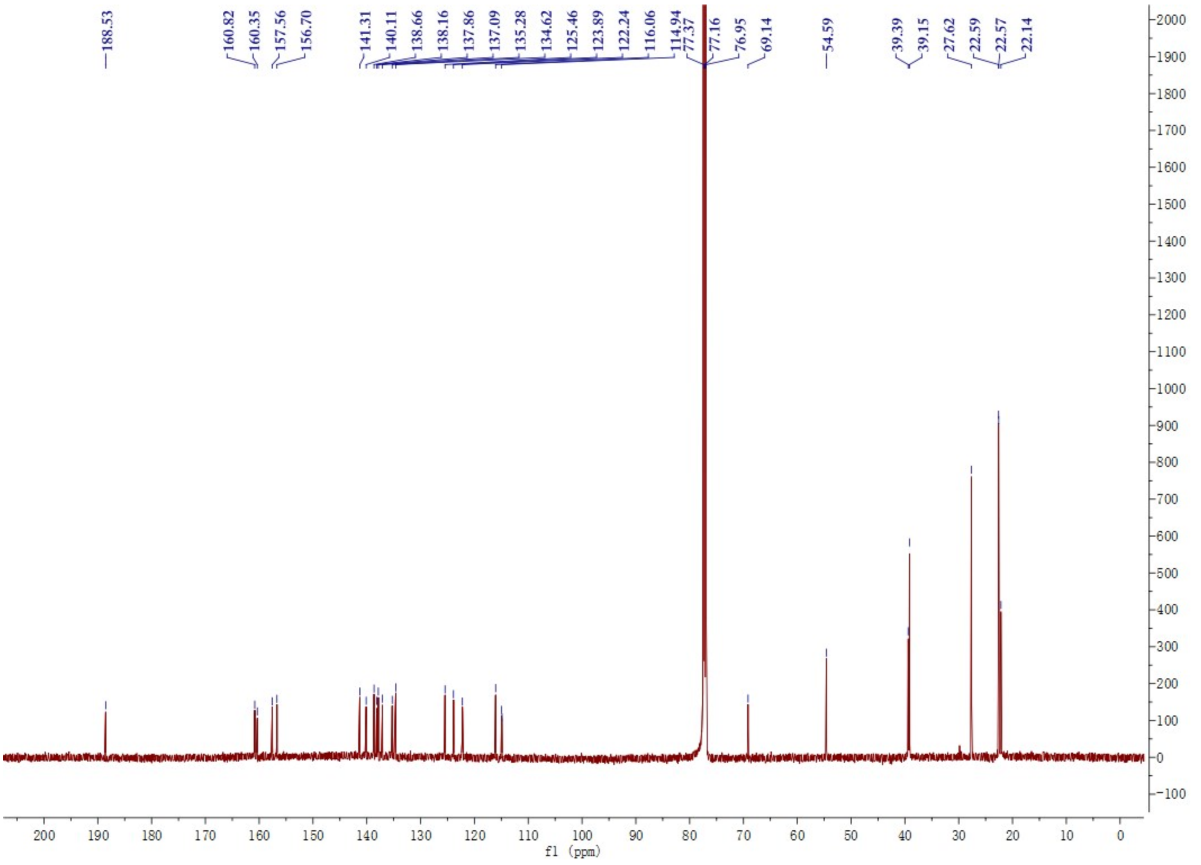


Fig. S15 The ^{13}C NMR spectrum of iso-IDIC.