Electronic Supplementary Information

Side-chain effect of perylene diimide tetramer-based non-fullerene acceptors for improving the performance of organic solar cells

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General Information.

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker ARX 400 MHz spectrometer. High-resolution mass spectrometry (HRMS) were recorded on a GCT Premier CAB 048 mass spectrometer operating in MALDI-TOF mode. Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. The steady-state absorption measurements were recorded on a Rarian 50 Conc UV-vis spectrophotometer. Photoluminescence (PL) spectra and absolute fluorescence quantum yields were measured on Fluorolog®-3 spectrofluorometer with an integrating sphere. TGA measurements were carried out on a SHIMADZU DTG-60 instruments under a dry nitrogen flow, heating from room temperature to 650 °C, with a heating rate of 10 K/min. Cyclic voltammetry was carried out on a CHI610E electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt as the counter electrode, and a glassy carbon as the working electrode. 0.1 mol·L^{-1} tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane was used as the supporting electrolyte. The LUMO energy levels were determined by $E_{\mathrm{LUMO}} = -[q(E_{\mathrm{re}} - E_{\mathrm{ferrocene}}) + 4.8]$. AFM measurements were performed by using a Scanning Probe Microscope Dimension 3100 in tapping mode. All film samples were spin-cast on ITO/ZnO substrates. The GIXD data were obtained at beamline of BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) for 2D diffraction profiles.

Materials.

P3TEA was synthesized according to a previous report.[S1] PDI-Br was purchased from Derthon Optoelectronic Materials Science Technology Co LTD. All other reagents and chemicals were purchased from commercial sources and used without further purification.

Solar cell fabrication and testing.

Pre-patterned ITO-coated glass substrates were cleaned by successive sonication in detergent, deionized water, acetone, and isopropanol for 30 min of each step. After UV-ozone treatment for 30 min, a ZnO layer (~23 nm) was prepared by spin coating a ZnO precursor solution (diethyl zinc, diluted with tetrahydrofuran) at 5000 rpm in the air, then baked at 185 °C for 20 min. Active layer solutions (D/A ratio 1:1.5, polymer concentration 8 mg/ml) were prepared in 1,2,4-trimethylbenzene with 2.5% 1,8-diiodooctane. To completely dissolve the polymer, the active layer solution should be stirred on the hotplate at 90 °C for at least 1 hour. Before spin coating, both the active layer solution and ITO substrate are preheated on a hotplate at about 90 °C. Then the warm active layer solution was spin-coated onto the glass/ITO/ZnO substrates at 90 °C in the N_2 glovebox at 1200-1400 rpm. The active layers were then treated with vacuum to remove the solvent. The blend films were thermally annealed at 90 °C for 5 min before being transferred to the vacuum chamber of a thermal evaporator inside the same glovebox. The thin layer of V_2O_5 (10 nm) was deposited as the anode interlayer, followed by the deposition of 100 nm of Al as the top electrode at a vacuum level below 1.0×10^{-4} Pa. All devices were encapsulated using epoxy inside the same N_2 glovebox. Device J-V characteristics were measured under AM 1.5G ($100\ \mathrm{mW \cdot cm^{-2}}$) using a Newport solar simulator in ambient atmosphere. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. J-V characteristics were recorded using a Keithley 2400 source meter unit. Typical cells have devices area of 5.9 mm^2, defined by a metal mask with an aperture aligned with the device area.

EQE measurements.

EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

Theoretical calculations.

Calculations were done on Gaussian09, input files and results were visualized using GausView5.08. All alkyl chains were replaced with a methyl group. The optimized geometry of the ground state and energy levels were carried out using B3LYP/6-31g(d,p) method.

Synthesis of materials.

Synthesis of compound 1

A mixture of 4,4'-dibromobenzil (3.68 g, 10 mmol) and 1,2,4,5-benzenetetramine tetrahydrochloride (1.42 g, 5 mmol) in acetic acid (50 mL) was stirred at 130 °C overnight. After cooling to room temperature, a yellow solid emerged. The solid was filtered and washed by acetic acid and ethyl ether for next step without further purification. Yield: 75 %.

Synthesis of compound 2

A mixture of compound **1** (200 mg, 0.25 mmol), bis(pinacolato)diboron (285 mg, 1.12 mmol), KOAc (220 mg, 2.47 mmol), Pd(dppf)Cl_2·DCM (41 mg, 0.05 mmol) in 1,4-dioxane (30 mL) was stirred at 85 °C under nitrogen atmosphere for 48 h. After cooling to room temperature, the mixture was extracted by chloroform and washed with brine. The organic layer was combined and dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was subjected to column chromatography with chloroform/ethyl acetate (8/1, v/v) as eluent. Compound **2** was obtained as a yellow solid. Yield: 70 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 2H), 7.83 (d, J = 7.6 Hz, 8H), 7.64 (d, J = 7.6 Hz, 8H), 1.40 (s, 48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.11, 141.26, 140.39, 134.67, 129.17, 128.93, 84.00, 24.93.

Synthesis of PDIPQ-C5

A mixture of compound **2** (30 mg, 0.03 mmol), 1-bromo-N,N'-di(undecan-6-yl)-3,4,9,10-perylene dicarboximide (112 mg, 0.144 mmol), K_2CO_3 (21 mg, 0.15 mmol), Pd(dppf)Cl_2·DCM (9.8 mg, 0.012 mmol), *t*-Bu_3P (30 mg, 0.15 mmol) in THF/H_2O (30 mL, 5/1, v/v) was stirred at 80 °C under nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was extracted by chloroform and washed with brine. The organic layer was combined and dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was subjected to column chromatography with chloroform/petroleum ether (1/1, v/v) as eluent. The product was recrystallized from methanol/dichloromethane three times. PDIPQ-C5 was obtained as a deep-red solid. Yield: 65 %. ^1H NMR (400 MHz, $Cl_2CDCDCl_2$, 353 K) δ 9.33 (s, 2H), 8.72 – 8.65 (m, 20H), 8.22 – 8.05 (m, 16H), 7.77 (d, J = 7.8 Hz, 8H), 5.17 (br, 4H), 5.03 (br, 4H), 2.23 (br, 8H), 2.11 (br, 8H), 1.92 (br, 8H), 1.80 (br, 8H), 1.52 – 1.25 (m, 96H), 0.89 – 0.82 (m, 48H). MS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{218}H_{230}N_{12}O_{16}$, 3274.3060, found: 3274.3430. Elemental analysis for $C_{218}H_{230}N_{12}O_{16}$: C, 79.97; H, 7.08; N, 5.13; O, 7.82; Found: C, 79.88; H, 7.05; N, 5.08; O, 7.74.

Synthesis of PDIPQ-C6

A mixture of compound **2** (30 mg, 0.03 mmol), 1-bromo-N, N'-di(tridecan-7-yl)-3,4,9,10-perylene dicarboximide (120 mg, 0.144 mmol), K_2CO_3 (21 mg, 0.15 mmol), Pd(dppf)Cl_2·DCM (9.8 mg, 0.012 mmol), *t*-Bu_3P (30 mg, 0.15 mmol) in THF/H_2O (30 mL, 5/1, v/v) was stirred at 80 ^oC under nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was extracted by chloroform and washed with brine. The organic layer was combined and dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was subjected to column chromatography with chloroform/petroleum ether (1/1, v/v) as eluent. The product was recrystallized from methanol/dichloromethane three times. PDIPQ-C6 was obtained as a deep-red solid. Yield: 73 %. ^1H NMR (400 MHz, $Cl_2CDCDCl_2$, 353 K) δ 9.33 (s, 2H), 8.74 – 8.63 (m, 20H), 8.22 – 8.03 (m, 16H), 7.77 (d, J = 7.7 Hz, 8H), 5.17 (br, 4H), 5.04 (br, 4H), 2.24 (br, 8H), 2.09 (br, 8H), 1.93 (br, 8H), 1.81 (br, 8H), 1.53 – 1.23 (m, 119H), 0.92 – 0.82 (m, 48H). MS (MALDI-TOF) m/z: $[M+H]^+$ calcd for $C_{234}H_{263}N_{12}O_{16}$, 3497.0, found: 3497.9. Elemental analysis for $C_{234}H_{262}N_{12}O_{16}$: C, 80.33; H, 7.55; N, 4.80; O, 7.32; Found: C, 80.14; H, 7.58; N, 4.74; O, 7.23.

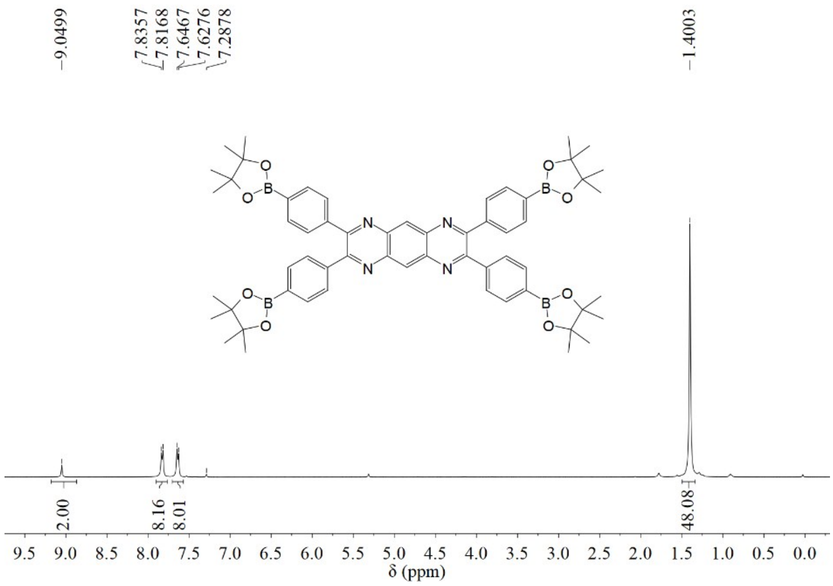

Figure S1. ^{1}H NMR of **2** in $CDCl_3$.

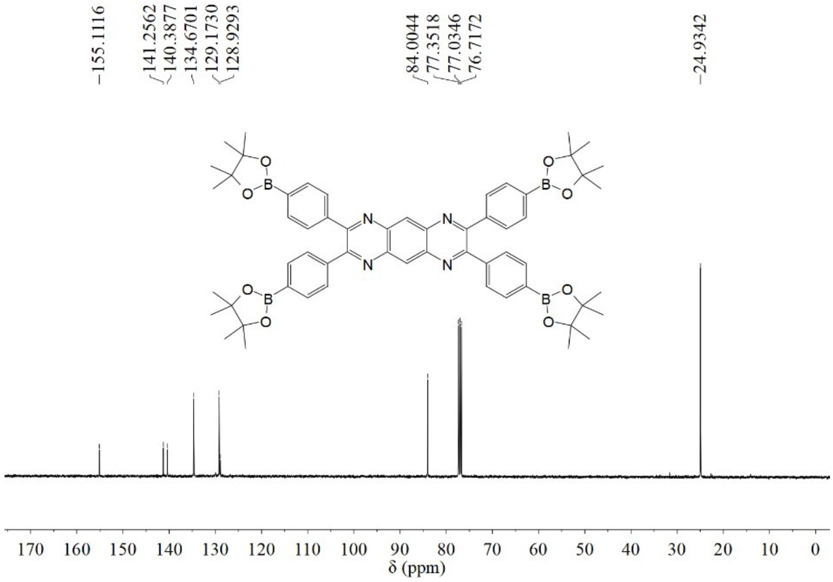

Figure S2. ^{13}C NMR of **2** in $CDCl_3$.

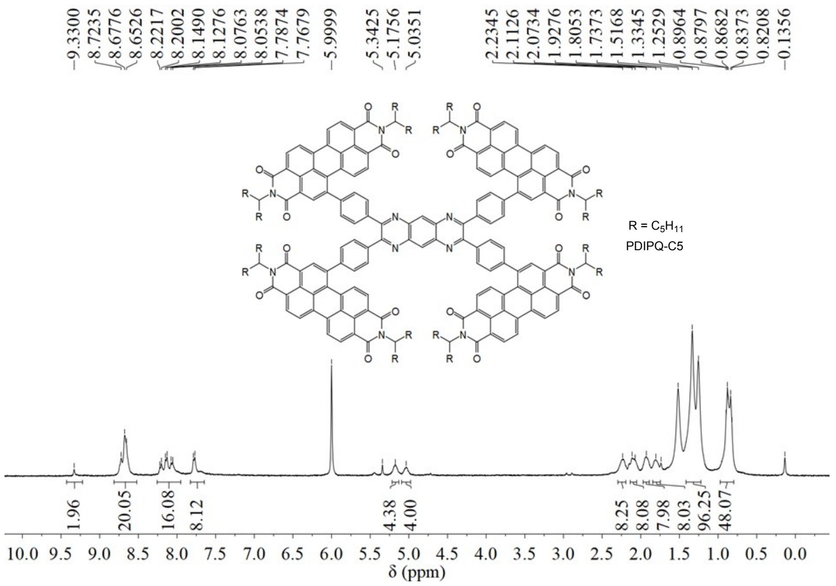

Figure S3. ^{1}H NMR of PDIPQ-C5 in $(CDCl_2)_2$ at 80 ^{o}C.

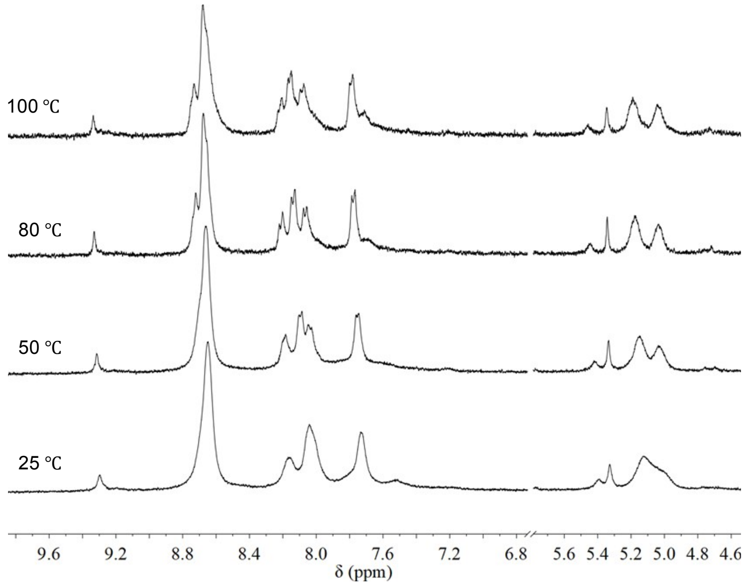

Figure S4. ^{1}H NMR of PDIPQ-C5 in $(CDCl_2)_2$ at different temperature.

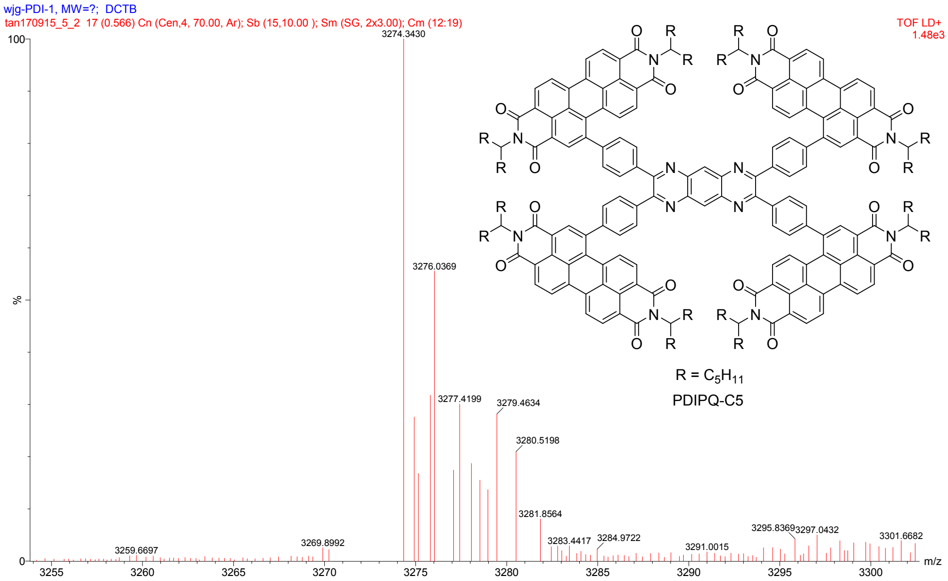

Figure S5. MS of PDIPQ-C5.

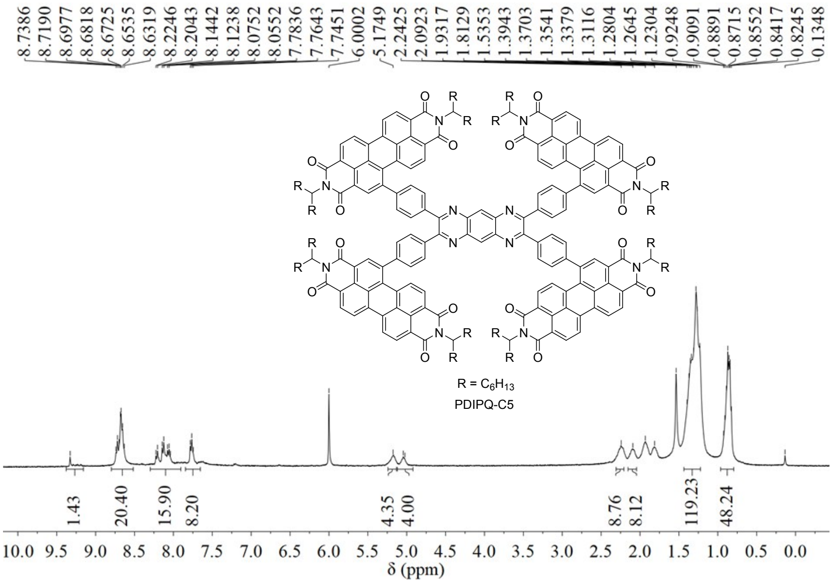

Figure S6. ^{1}H NMR of PDIPQ-C6 in $(CDCl_2)_2$ at 80 ^{o}C.

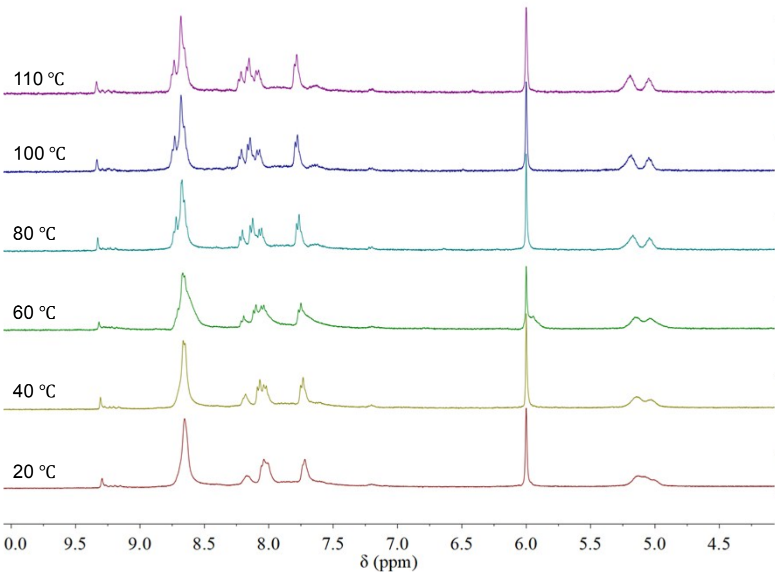

Figure S7. ^{1}H NMR of PDIPQ-C6 in $(CDCl_2)_2$ at different temperature.

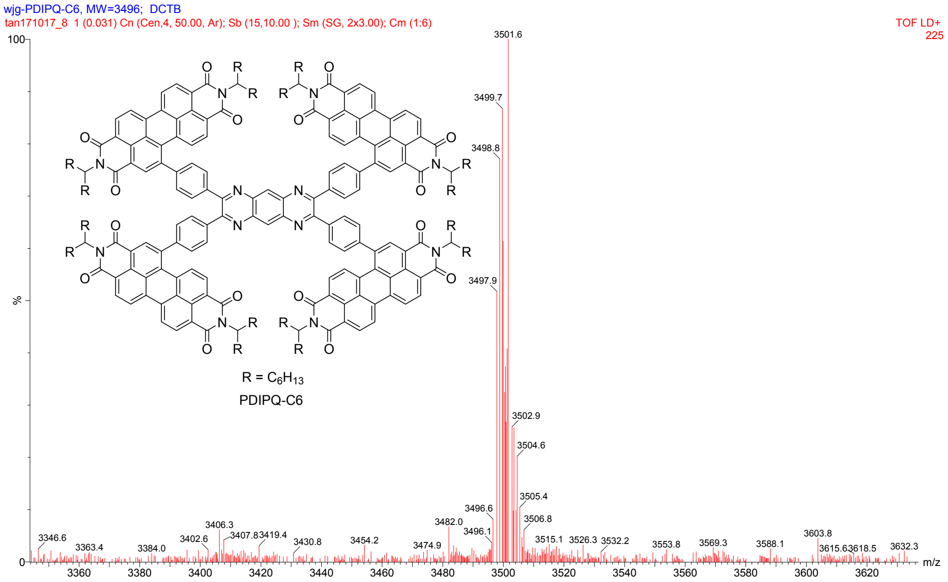

Figure S8. MS of PDIPQ-C6.

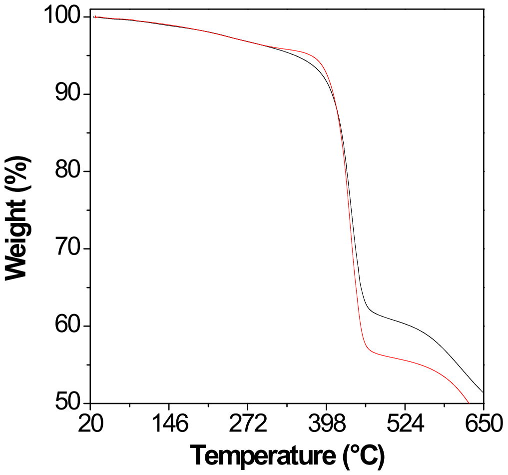

Figure S9. TGA of PDIPQ-C5 (black line) and PDIPQ-C6 (red line).

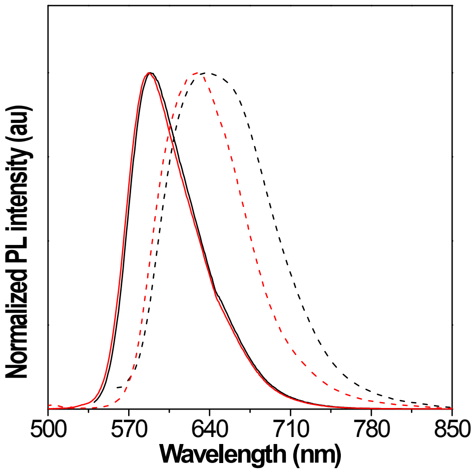

Figure S10. Photoluminescence (PL) spectra of PDIPQ-C5 (black line) and PDIPQ-C6 (red line) in CH_2Cl_2 solution (solid line) and thin film (dash line).

Table S1. Photophysical properties of PDIPQ-C5 and PDIPQ-C6.

Comp.	λ_{abs}/nm		λ_{em}/nm		Φ (%) [b]		HOMO /eV	LUMO /eV	Bandgap/eV
	Soln.	Solid	Soln.	Solid	Soln.	Solid			
PDIPQ-C5	532 (157261)[a]	544	588	638	19.5	2.3	-5.97	-3.82	2.15
PDIPQ-C6	535 (109146)[a]	544	587	629	18.7	5.4	-5.98	-3.83	2.15

[a] Numbers shown in parentheses are molar extinction coefficient. [b] Φ = fluorescence or phosphorescence quantum yield measured by using an integrating sphere.

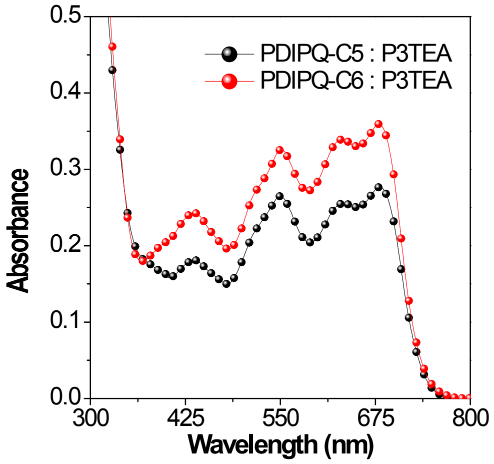

Figure S11. UV-vis spectra of the blend films. Acceptor : Donor (m/m, 1.5/1).

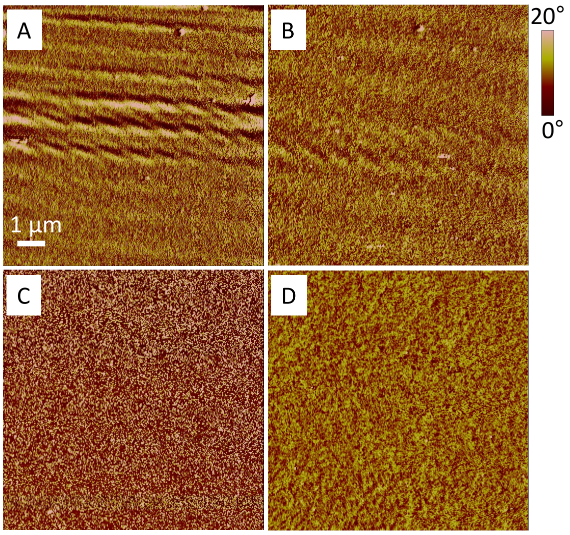

Figure S12. AFM phase images of the blend films. PDIPQ-C5:P3TEA (A) without and (B) with DIO; PDIPQ-C6:P3TEA (C) without and (D) with DIO.

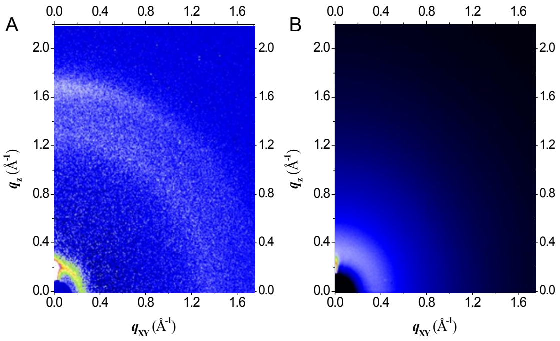

Figure S13. 2D GIXD patterns of the blend films without DIO. (A) PDIPQ-C5:P3TEA and (B) PDIPQ-C6:P3TEA.

References:

S1. J. Liu, S. Chen, D. Qian, B. Gautam, G. Yang, J. Zhao, J. Bergqvist, F. Zhang, W. Ma, H. Ade, O. Inganäs, K. Gundogdu, F. Gao and H. Yan, *Nat. Energy*, 2016, **1**, 16089.