

Supplementary Information

An Alternating D-A₁-D-A₂ Copolymer Containing Two Acceptors for Efficient Polymer Solar Cells

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Experimental Section

Characterization

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were acquired using a Varian Inova 400 MHz NMR spectrometer. Tetramethylsilane was used as an internal reference with deuterated chloroform as solvent. TGA was performed on Perkin Elmer TGA7. Size exclusion chromatography (SEC) was performed on Waters Alliance GPCV2000 with a refractive index detector. Columns: Waters Styvigel HT GE \times 1, Waters Styvigel HMW GE \times 2. The eluent was 1,2,4-trichlorobenzene. The working temperature was 135 °C, and the resolution time was 2 h. The concentration of the samples was 0.5 mg mL $^{-1}$, which were filtered (filter: 0.45 μm) prior to the analysis. The molecular weights were calculated according to relative calibration with polystyrene standards. UV-vis absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer. The electroluminescence (EL) spectra were recorded using an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector). The surface morphologies of active layers of PSCs were characterized by using Atomic Force Microscopy (AFM) with a Dimension 3100 system (Digital Instruments/Veeco) operating in tapping mode.

Device fabrication and characterization

The structure of the solar cells was Glass/ITO/PEDOT:PSS/Active Layer/LiF/Al. As a buffer layer, the conductive polymer, PEDOT:PSS (Baytron P VP Al 4083), was spin-coated onto ITO-coated glass substrates, followed by annealing at 120 °C for 10 minutes to remove water. The thickness of the PEDOT:PSS layer was about 45 nm, as determined by a Dektak 6M surface profilometer. The active layer consisting of polymers and PC $_{61}$ BM was spin-coated from *o*-dichlorobenzene (*o*DCB) solution (or

with DIO additive) onto the PEDOT:PSS layer. The spin-coating was done in a glove box and the material was directly transferred to a vapor deposition system mounted inside of the glove box. LiF (0.6 nm) and Al (80 nm) were used as top electrodes and were deposited via a mask in vacuum onto the active layer. The accurate area of every device (4-6 mm²), defined by the overlap of the ITO and metal electrode, was measured carefully by microscope image. EQEs were calculated from the photocurrents at short-circuit conditions. The currents were recorded by a Keithley 485 picoammeter under illumination of monochromatic light (MS257) through the ITO side of the devices. PCE was calculated from $J-V$ characteristics recorded by a Keithley 2400 source meter under illumination of an AM1.5G solar simulator with an intensity of 100 mW cm⁻² (Model SS-50A, Photo Emission Tech., Inc.). The light intensity was determined by a standard silicon photodiode. Device characterization was conducted in ambient environment.

Electrochemical studies

Square-wave voltammetry (SWV) measurements were carried out on a CH-Instruments 650A Electrochemical Workstation. A three-electrode setup was used with platinum wires both as working electrode and counter electrode, and Ag/Ag⁺ was used as reference electrode calibrated with ferrocene/ferrocenyl couple (Fc/Fc⁺). A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in anhydrous acetonitrile was used as supporting electrolyte. The polymer was deposited onto the working electrode from chloroform solution. In order to remove oxygen from the electrolyte, the system was bubbled with nitrogen prior to each experiment. The nitrogen inlet was then moved to above the liquid surface and left there during the

scans. HOMO and LUMO levels were estimated from peak potentials of the third scan by setting the oxidative peak potential of Fc/Fc⁺ vs. the normal hydrogen electrode (NHE) to 0.63 V,¹ and the NHE vs. the vacuum level to 4.5 V.² The HOMO and LUMO levels were calculated according to the formula HOMO = $-(E^{\text{ox}} + 5.13)$ eV and LUMO = $-(E^{\text{red}} + 5.13)$ eV, where E^{ox} and E^{red} were determined from oxidation and reduction peaks, respectively.³

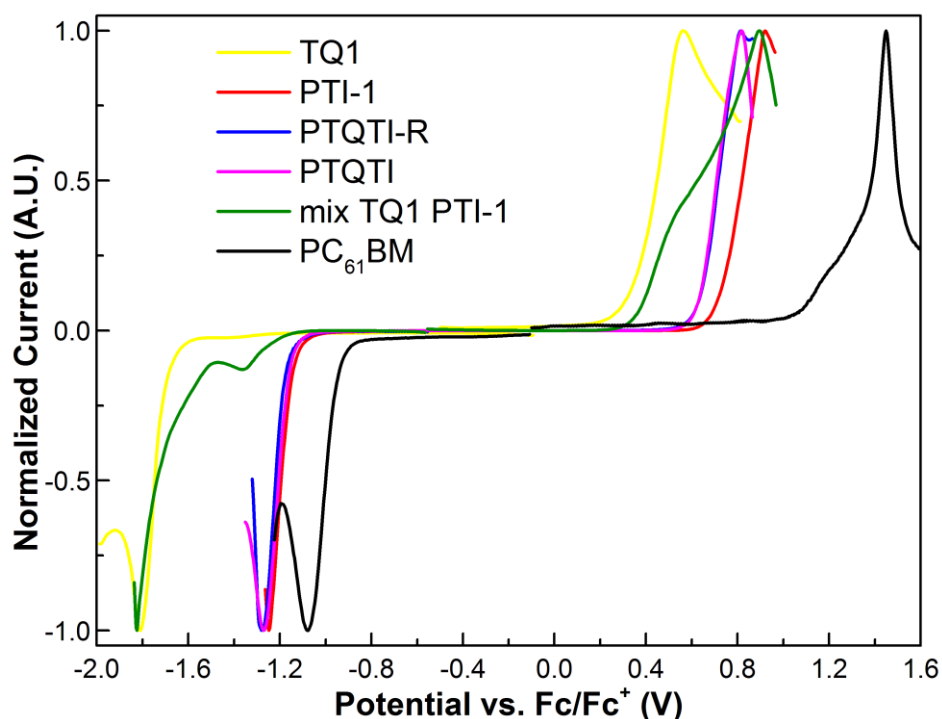


Figure S1. SWV of polymers, mixed polymers TQ1:PTI-1 (1:1, wt.) and PC₆₁BM.

Theoretical Calculations

The density functional theory (DFT) calculations were performed by using Gaussian 09 with hybrid B3LYP correlation functional^{4,5} and a split valence 6-31G* basis set.⁶ Oligomers containing three repeat units were taken as a model for calculations and methyl or ethyl was used instead of long side chains. The optimized molecular

geometries of the models and their calculated LUMO and HOMO frontier orbitals are depicted in Figure S2 and side views of the optimized molecular geometries are shown in Figure S3.

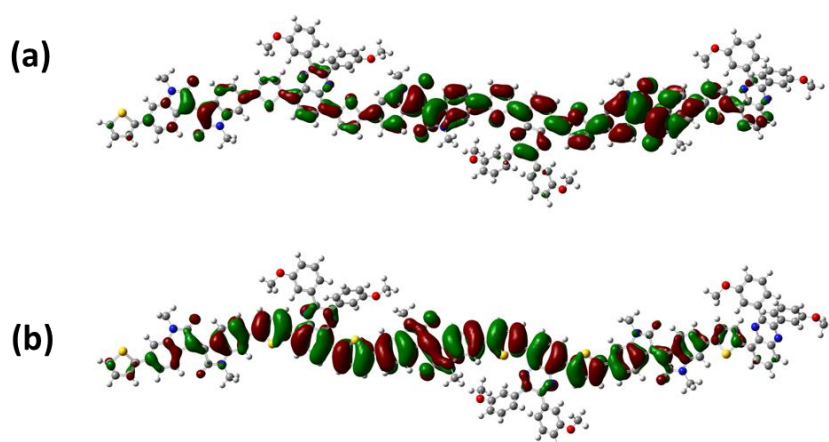


Figure S2. The (a) LUMO and (b) HOMO orbital distributions of PTQTI.

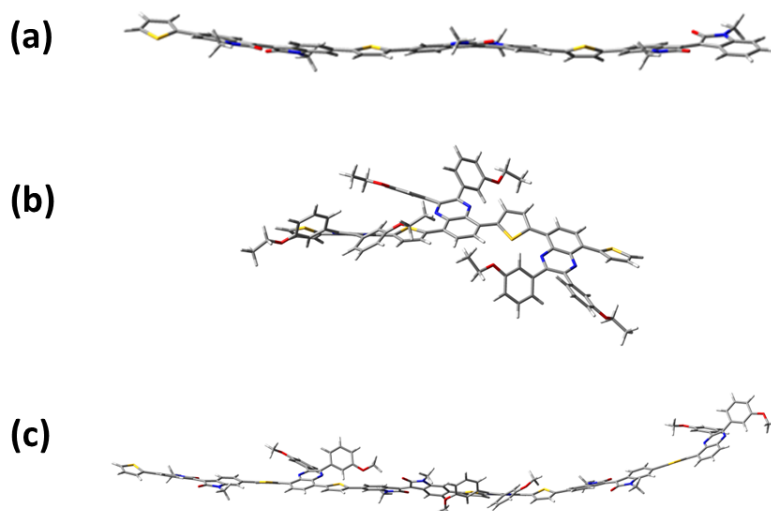
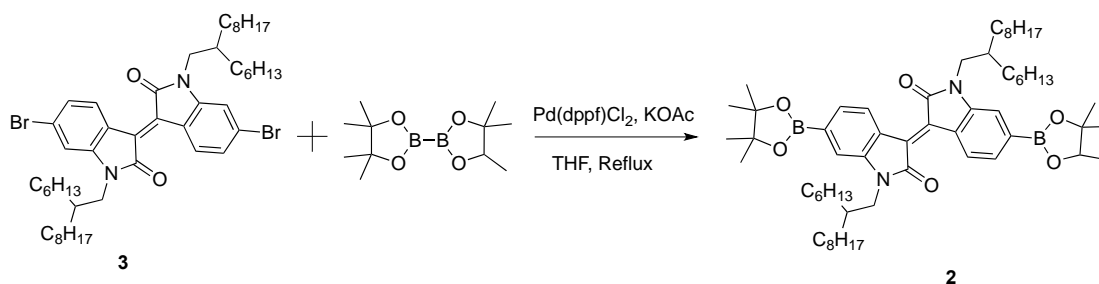


Figure S3. Side views of the simulated molecular geometries of (a) PTI-1, (b) TQ1 and (c) PTQTI.

Synthetic Procedures

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. The monomers 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxaline (**1**), (*E*)-6,6'-dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (**3**), 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline (**4**), and 2,5-bis(trimethylstannyl)thiophene (**5**) were prepared according to the literature methods.⁷⁻⁹

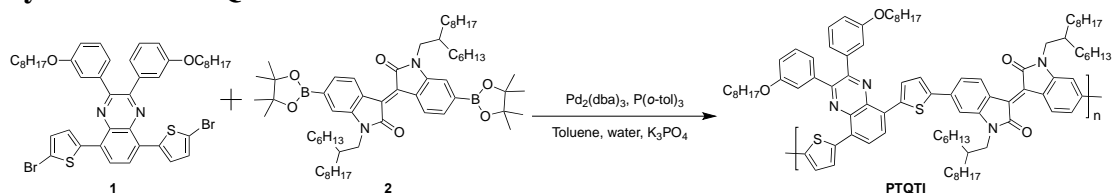
(*E*)-1,1'-bis(2-hexyldecyl)-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (2**)¹⁰**



In a dry 100 mL flask, monomer **3** (4.35 g, 5.0 mmol), bis(pinacolato)diboron (3.05 g, 12 mmol), 1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) [PdCl₂(dppf)] (220 mg), and potassium acetate (2.95 g, 30 mmol) were mixed under nitrogen atmosphere. Anhydrous THF (25 mL) was injected with a syringe. The mixture was refluxed for 24 h and then cooled to room temperature. THF was removed and the residue was purified by passing through a short silica gel column with dichloromethane:hexane (1:1) as eluent. After concentration, the solution was poured into methanol to afford **2** as a precipitate, which was collected by filtration (3.98 g, 82.5%). ¹H NMR (400 MHz, CDCl₃, δ): 9.14 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.16 (s, 2H), 3.69 (d, *J* = 7.9 Hz, 4H), 1.95 (bs, 2H), 1.44-1.16 (m, 72H), 0.86 (t, *J* = 6.5 Hz, 12H). ¹³C NMR (400 MHz, CDCl₃, δ): 168.12, 144.52, 134.07, 128.82, 128.67, 124.13, 112.79, 83.71, 44.24, 36.14, 31.87, 31.81, 31.57, 29.99,

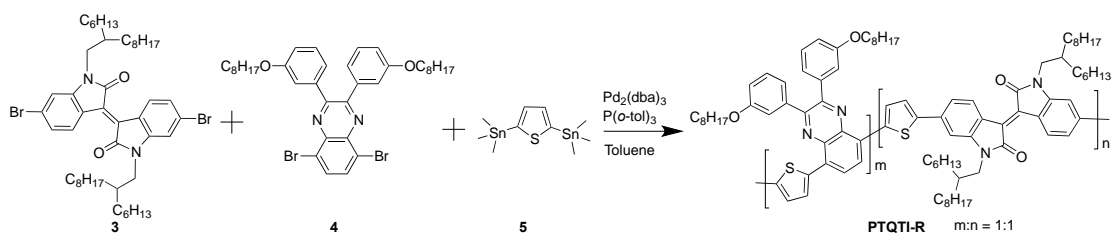
29.78, 29.62, 29.56, 29.28, 26.37, 24.85, 22.65, 22.58, 14.09, 14.07.

Synthesis of PTQTI



In a dry 25 mL flask, monomer **1** (252 mg, 0.25 mmol), monomer **2** (240 mg, 0.25 mmol), Aliquat 336 (50 mg), tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] (3.5 mg), tri(*o*-tolyl)phosphine [P(*o*-Tol)₃] (6 mg) and K₃PO₄ (424 mg) were dissolved in a mixture of degassed toluene (6 mL) and deionized water (2 mL). The mixture was vigorously stirred at 100 °C for 4 h under nitrogen. After that, it was cooled down and poured into acetone. The polymer was collected by filtration through 0.45 μm Teflon filter and Soxhlet-extracted first with diethyl ether, and then with chloroform. The chloroform solution was concentrated to a small volume and precipitated by pouring this solution into acetone. Finally, the polymer was collected by filtration using a 0.45 μm Teflon filter and dried under vacuum at 40 °C overnight (240 mg, 68%).

Synthesis of PTQTI-R



In a 25 mL dry flask, **3** (174 mg, 0.2 mmol), **4** (139 mg, 0.2 mmol), **5** (164 mg, 0.4 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (3 mg) and tri(*o*-

tolyl)phosphine ($P(o\text{-Tol})_3$) (6 mg) were dissolved in degassed toluene (9 mL). The mixture was vigorously stirred at 100 °C for 24 h under nitrogen. After cooling to room temperature, the solution was poured into acetone. The polymer was collected by filtration through 0.45 μm Teflon filter. And then the polymer was washed in a Soxhlet extractor with acetone and diethyl ether for 24 h each. After that, the polymer was Soxhlet-extracted with chloroform. The chloroform fraction was purified by passing it through a short silica gel column and then precipitated into acetone. Finally, the polymer was collected by filtration through 0.45 μm Teflon filter and dried under vacuum at 40 °C overnight (220 mg, 78%).

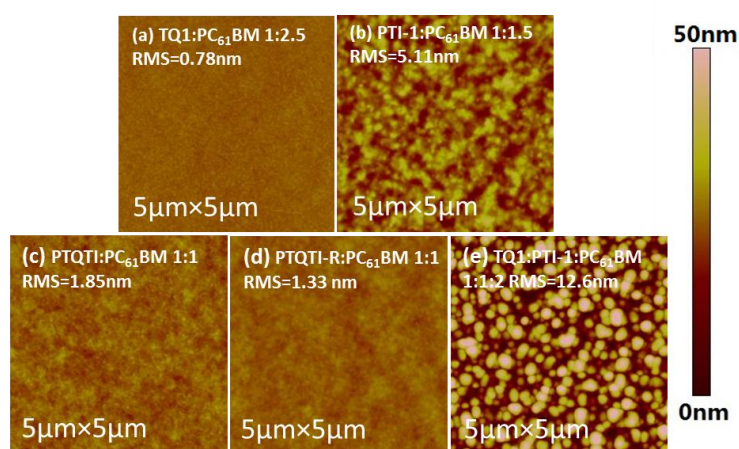


Figure S4. AFM images for the active layers of (a) TQ1:PC₆₁BM, (b) PTI-1:PC₆₁BM, (c) PTQTI:PC₆₁BM, (d) PTQTI-R:PC₆₁BM and (e) TQ1:PTI-1:PC₆₁BM. The films of (a) and (e) were prepared from *o*DCB solution and the films of (b), (c), and (d) were spin-coated from DIO in *o*DCB (2.5% by volume) solution.

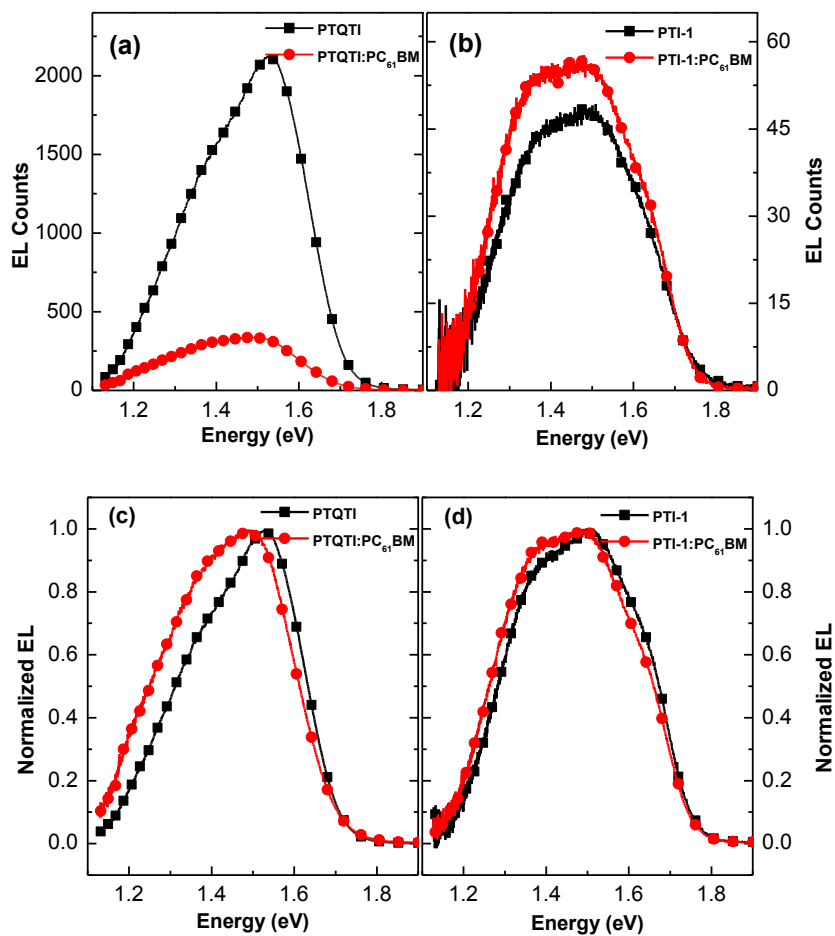


Figure S5. EL spectra obtained from PSCs of (a) PTQTI (black), PTQTI:PC₆₁BM (red) and (b) PTI-1 (black), PTI-1:PC₆₁BM (red). And the normalized EL spectra obtained from PSCs of (c) PTQTI (black), PTQTI:PC₆₁BM (red) and (d) PTI-1 (black), PTI-1:PC₆₁BM (red).

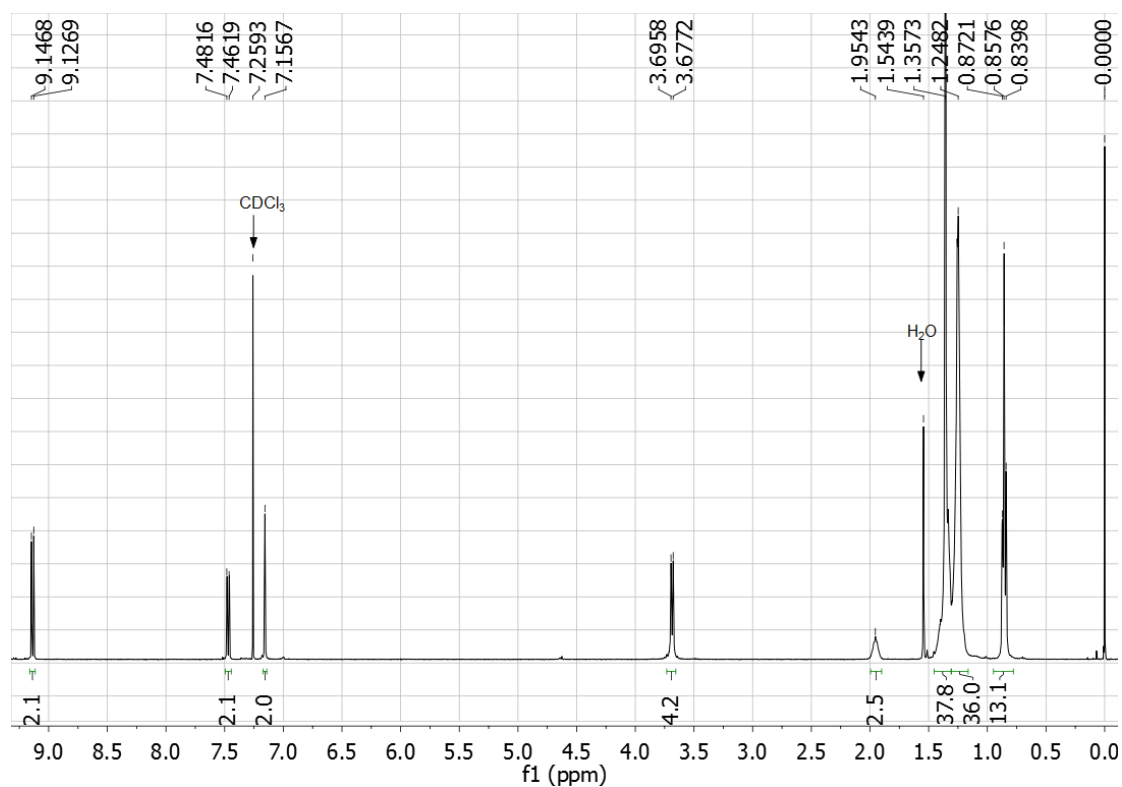


Figure S6. ^1H NMR spectrum of the monomer **2**.

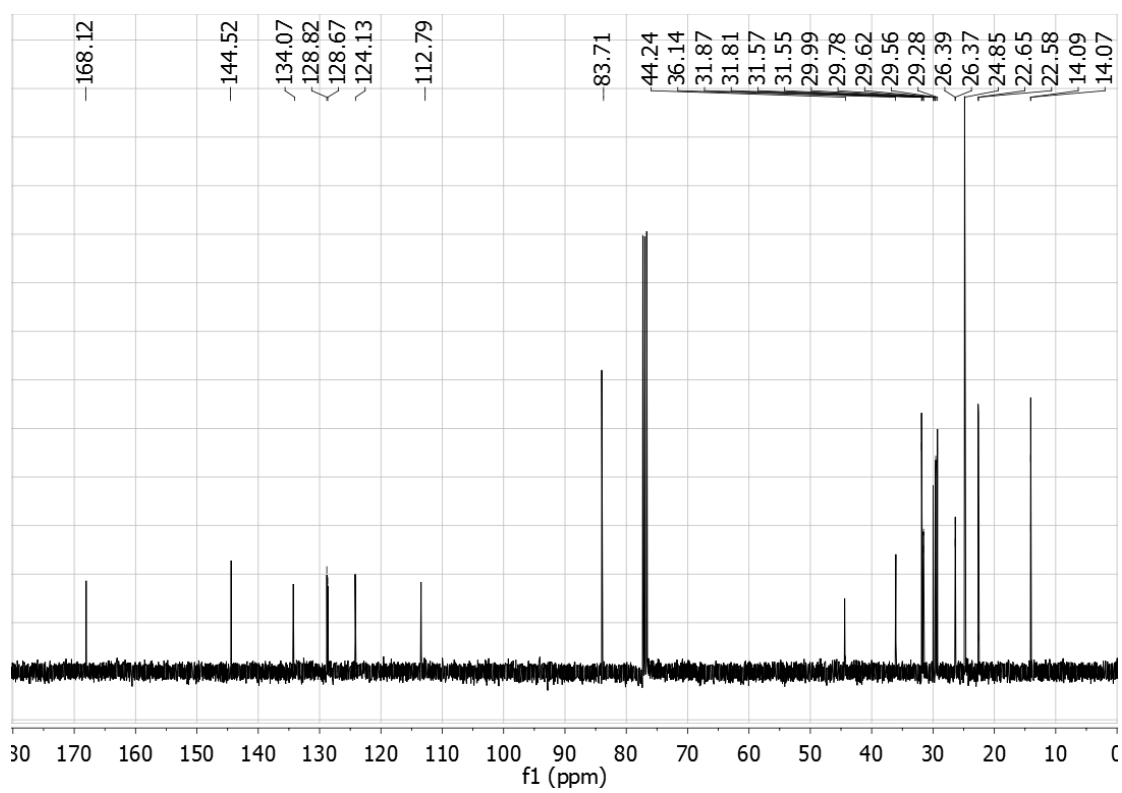


Figure S7. ^{13}C NMR spectrum of the monomer **2**.

Table S1. PV parameters of PSCs based on PTQTI:PC₆₁BM with different ratios

Ratio	J_{sc} (mA/cm ²)	FF	V_{oc} (V)	PCE (%)	Thickness (nm)
1:0.8	10.39	0.48	0.83	4.09	105nm
1:1	11.56	0.54	0.81	5.03	100nm
1:2	8.64	0.62	0.79	4.23	95nm
1:3	3.66	0.63	0.80	1.83	100nm

Table S2. Statistical data of PSCs from 10 devices

Active layer	Ratio	J_{sc} (mA/cm ²)	FF	V_{oc} (V)	PCE (%)
PTQTI:PC ₆₁ BM	1:1	11.36±0.2	0.53±0.01	0.80±0.01	4.93±0.1
PTQTI-R:PC ₆₁ BM	1:1	9.90±0.1	0.55±0.01	0.78±0.01	4.30±0.1
PTI-1:PC ₆₁ BM	1:1.5	7.00±0.2	0.66±0.01	0.90±0.01	4.20±0.1
TQ1:PC ₆₁ BM	1:2.5	7.30±0.3	0.68±0.01	0.88±0.01	4.50±0.2
TQ1:PTI-1:PC ₆₁ BM	1:1:2	5.00±0.1	0.58±0.01	0.80±0.01	2.35±0.05

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