Supplementary Information

Fluorine Substitution Enhanced Photovoltaic Performance of a D-A_1-D-A_2 Copolymer

Dongfeng Dang,[a,b] Weichao Chen,[c] Renqiang Yang,*[c] Weiguo Zhu,*[a] Wendimagegn Mammo[d] and Ergang Wang*[b]

[a]*Key Lab of Environment-Friendly Chemistry and Application of the Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China; E-mail: zhuwg18@126.com*
[b]*Department of Chemical and Biological Engineering/Polymer Technology, Chalmers University of Technology, SE-412 96 Göteborg, Sweden; E-mail: ergang@chalmers.se*
[c]*Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China; E-mail: yangrq@qibebt.ac.cn*
[d]*Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia.*

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Experimental Section

Characterization

^{1}H 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. Size exclusion chromatography (SEC) was performed on Waters Alliance GPCV2000 with a refractive index detector. Columns: Waters Styvagel HT GE×1, Waters Styvagel HMW GE×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. AFM images were acquired with Agilent-5400 scanning probe microscope with a Nanodrive controller in tapping mode with MikroMasch NSC-15 AFM tips with resonant frequencies ~300 kHz.

Device fabrication and characterization

The structure of the solar cells was Glass/ITO/PEDOT:PSS/Active Layer/Ca/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 160 °C for 30 minutes to remove water. The thickness of the PEDOT:PSS layer was about 40 nm, as determined by a Dektak 150 surface profilometer. The active layer consisting of polymers and PC$_{61}$BM was spin-coated from *o*-dichlorobenzene (*o*DCB) solution (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. Ca (10 nm) and Al (100 nm) were used as top electrodes and were deposited via a mask in vacuum onto the active layer. The accurate area of every device (10 mm^2), defined by the overlap of the ITO and metal electrode, was measured carefully by microscope image. PCE was calculated from *J-V* characteristics recorded by a Keithley 2420 source meter under illumination of an AM1.5G solar simulator with an intensity of 100 mW cm^{-2} (Newport Orial 1000W). The light intensity was determined by a standard silicon photodiode. EQEs were measured using a Newport 2931-C coupled with 300 W Xenon lamp.

Electrochemical studies

Cyclic voltammetry (CV) 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 tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) 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 = $-(E^{ox} + 5.13)$ eV and LUMO = $-(E^{red} + 5.13)$ eV, where E^{ox} and E^{red} were determined from oxidation and reduction peaks, respectively.[3]

Theoretical Calculations

The density functional theory (DFT) calculations were performed by using Gaussian 09 with hybrid B3LYP correlation functional[4] and a split valence 6-31G* basis set.[5] 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 **S1** and side views of the optimized molecular geometries are shown in Figure **S2**.

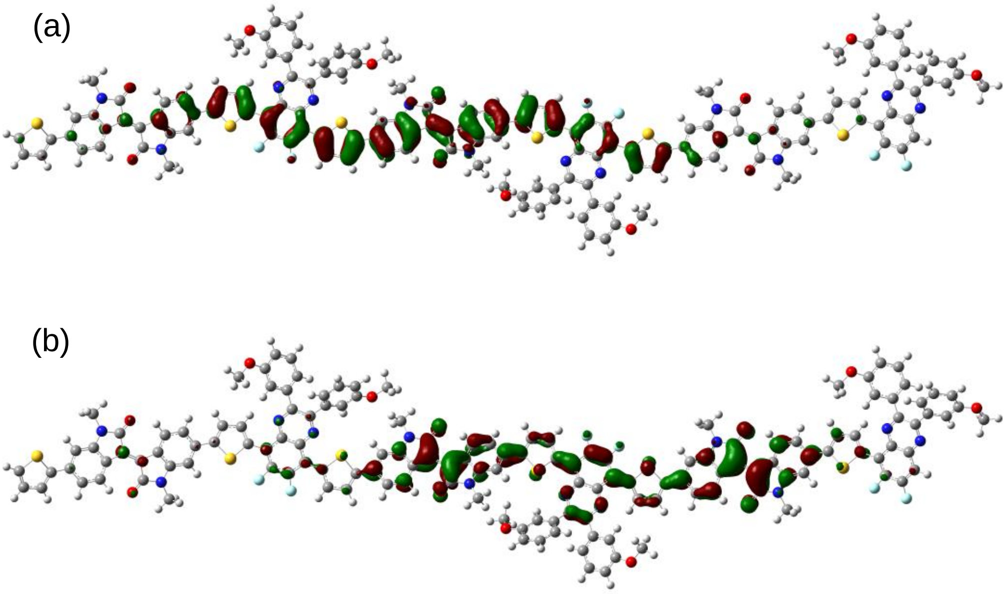


Figure S1. The (a) HOMO and (b) LUMO orbital distributions of **PTQTI-F**.

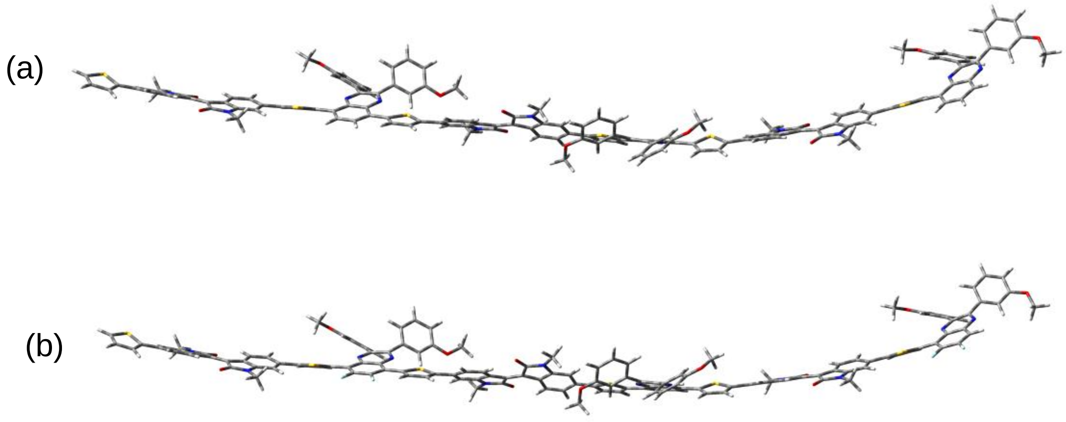


Figure S2. Side views of the simulated molecular geometries of (a) **PTQTI** and (b) **PTQTI-F**.

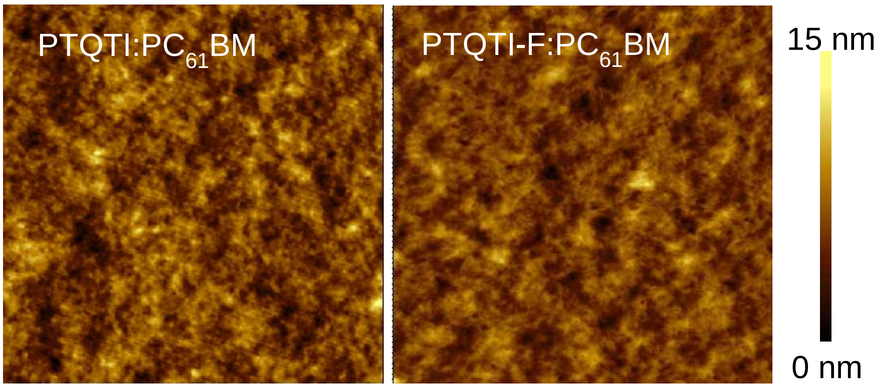


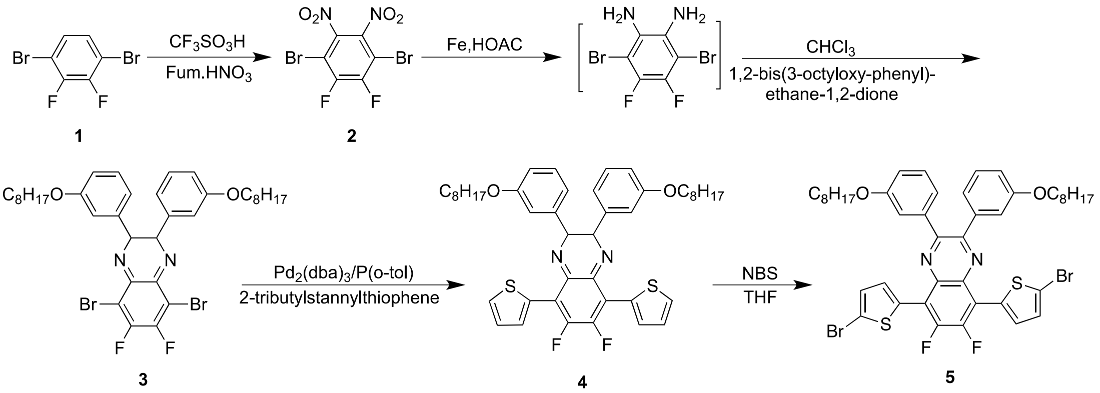
Figure S3. AFM images for the active layers of **PTQTI**:$PC_{61}BM$ and **PTQTI-F**:$PC_{61}BM$.

Synthetic Procedures

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. 1,4-Dibromo-2,3-difluorobenzene was purchased from Simple Pharms Co. The monomers, 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (**5**)[6] and

(*E*)-6,6′-dibromo-1,1′-bis(2-hexyldecyl)-[3,3′-biindolinylidene]-2,2′-dione (**6**)[7] were prepared according to the literature methods.

Synthesis of the fluorinated monomer 5



Synthesis of 1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene (2)

Fuming nitric acid (5 mL) was slowly added dropwise to trifluoromethanesulfonic acid (100 mL) in ice bath and stirred for 0.5 h. Then1,4-dibromo-2,3-difluorobenzene (**1**) (10.0g, 37.7 mmol) was added in portions over 30 minutes. After stirring at room temperature for two hours, the mixture was cooled down to 0 °C. Another 5 mL of fuming nitric acid was added slowly and then stirred overnight at 70 °C. After that the reaction mixture was poured into cold water. After filtration and recrystallization from ethanol, the desired product was obtained as a yellow solid (10.02g, 75.2%).

Synthesis of 5,8-dibromo-6,7-difluoro-2,3-bis(3-octyloxyphenyl)quinoxaline (3)

A mixture of 1,4-dibromo-2,3-difluoro-5,6-dinitrobenzene (4.0 g, 11.0 mmol), iron powder (7.40 g, 132.0 mmol), and acetic acid (150 ml) was stirred at 80 °C monitoring the progress of reaction by TLC. After about 4 h, the residual iron was removed by filtration and 1,2-bis(3-octyloxyphenyl)ethane-1,2-dione (5.18 g, 11.0 mmol) was added to the filtrate, followed by heating under reflux for 8 h. The mixture was then cooled to room temperature and was poured into water. The precipitate was collected by filtration and was successively washed with water, methanol and isopropanol gradually to afford compound **3** as a white solid (5.36 g, 66.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, 2H), 7.21 (t, 2H), 7.17 (dt, *J* = 7.6, 1.2 Hz, 2H), 6.94 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 2H), 3.86 (t, *J* = 6.6 Hz, 4H), 1.90–1.61 (m, 4H), 1.47–1.13 (m, 20H), 0.89 (t, *J* = 6.9 Hz, 6H).

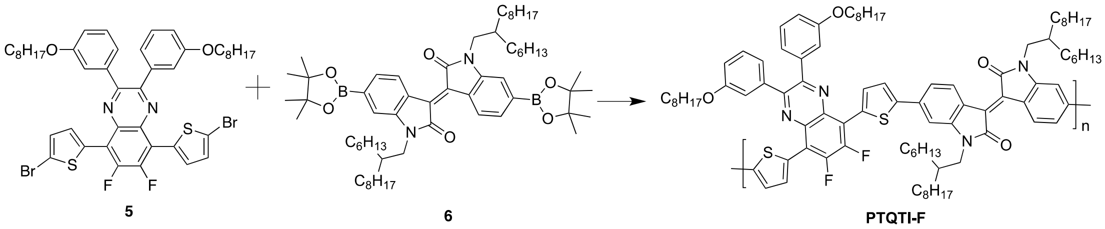
Synthesis of 6,7-difluoro-2,3-bis(3-octyloxyphenyl)-5,8-dithiophen-2-yl-quinoxaline (4)

To a solution of **3** (12.0 g, 16.3 mmol) and 2-tributylstannylthiophene (15.9 g, 42.6 mmol) in 150 mL tetrahydrofuran (THF) was added tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (160 mg, 0.18 mmol) and tri(*o*-tolyl)phosphine (P(*o*-Tol)$_3$) (320 mg, 1.0 mmol) under nitrogen and heated at reflux for 24 h. Water was then added, and then the mixture was extracted with dichloromethane (CH_2Cl_2). The organic phase was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the residue was recrystallized from ethanol to give compound **4** as a yellow solid (10.7 g, 89.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 3.8 Hz, 2H), 7.62 (dd, *J* = 5.2, 1.0 Hz, 2H), 7.36 (m, 2H), 7.29–7.20 (m, 6H), 6.94 (dt, *J* = 7.2, 2.3 Hz, 2H), 3.90 (t, *J* = 6.6 Hz, 4H), 1.82–1.66 (m, 4H), 1.50–1.40 (m, 4H), 1.32 (b, 16H), 0.93– 0.86 (m, 6H).

Synthesis of 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-bis(3-octyloxyphenyl)quinoxaline (5)

Compound **4** (2.0 g, 2.7 mmol) was dissolved in THF (60 mL) under nitrogen atmosphere, and NBS (1.1 g, 6.0 mmol) was added in several portions. The mixture was stirred at room temperature for 12 h. After that water (100 mL) was added to quench the reaction, and then extracted with CH_2Cl_2, washed with brine, and dried with anhydrous $MgSO_4$. The solvent was removed via rotary evaporation and subsequently purified by recrystallization to afford **5** as an orange solid (1.96 g, 80.3 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 4.2 Hz, 2H), 7.52 (m, 2H), 7.21 (t, 2H), 7.18 (d, J = 4.2 Hz, 2H), 7.08 (d, J = 5.6 Hz, 2H), 6.98(d, J = 10.7 Hz, 2H), 4.04 (t, J = 6.4 Hz, 4H), 1.80 (m, 4H), 1.47 (m, 4H), 1.30 (b, 16H), 0.92–0.85 (m, 6H).

Synthesis of PTQTI-F



In a dry 25 mL flask, monomer **5** (269 mg, 0.3 mmol), monomer **6** (289 mg, 0.3 mmol), Aliquat 336 (50 mg), tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] (4.2 mg), tri(*o*-tolyl)phosphine [P(*o*-Tol)$_3$] (8.1 mg) and K_3PO_4 (500 mg) were dissolved in a mixture of degassed toluene (10 mL) and deionized water (2 mL). The mixture was vigorously stirred at 100 °C for 0.5 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 (387 mg, 89%).

References

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