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Supporting Information for

Influence of Backbone Modification of Difluoroquinoxaline-based Copolymers on the Interchain Packing, Blend Morphology and Photovoltaic Properties in Nonfullerene Organic Solar Cells

Yuxiang Li[†,¶,#], *Minseok Kim*[‡,#], *Ziang Wu*[†], *Changyeon Lee*[‡], *Young Woong Lee*[†], *Jin-woo Lee*[‡], *Young Jun Lee*[‡], *Ergang Wang*[§], *Bumjoon J. Kim*[‡,*] *and Han Young Woo*[†,*]

[†]Department of Chemistry, Korea University, Seoul 136-701, Republic of Korea

[‡]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

[§]Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

[¶]School of Materials Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, China

*Electronic mail: bumjoonkim@kaist.ac.kr (B. J. Kim), hywoo@korea.ac.kr (H. Y. Woo)

1. Experimental.

General

All the chemical reagents were purchased from Aldrich, Tokyo Chemical Industry, Junsei and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Advance III HD system operating at 500 and 125 MHz, respectively. UV-vis spectra were obtained using a JASCO V-630 spectrophotometer. CV data were measured using a Versa STAT3 (Princeton Applied Research) with a three-electrode cell in 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in CH_3CN at a scan rate of 50 mV s^{-1}. TGA (2050 TGA V5.4A) and DSC (DSC Q200 V24.4) measurements were performed at a heating and cooling rate of 10 °C min^{-1} under nitrogen (purity, 99.999%). The RSoXS measurement was executed at BL 11.0.1.2 in the Advanced Light Source (USA). The samples were prepared on a 1.0 mm × 1.0 mm, 100 nm-thick Si_3N_4 membrane, which was supported by a 5 mm × 5 mm, 200 μm-thick Si frame (Norcada Inc.). 2D-GIXS measurements were carried out at a beamline 3C at the Pohang Accelerator Laboratory in South Korea. Pristine PDFQx polymer films and PDFQx:ITIC blend films were prepared by spin coating on the PEDOT:PSS/Si substrate. The wavelength of X-ray was 1.1198 Å, and the incidence angles were 0.12˚. The space-charge-limited current (SCLC) mobilities were measured by fabricating electron-only and hole-only devices with device architectures of ITO/ZnO/active layer/LiF/Al and ITO/PEDOT:PSS/active layer/Au, respectively. The active layer was deposited by spin coating at the optimized condition for the photovoltaic devices.

Fabrication and Characterization of Nonfullerene Solar Cells

The PSC devices were fabricated with a configuration of ITO/PEDOT:PSS/PDFQx:ITIC/LiF/Al. ITO-patterned glass with a sheet resistance of ~15

Ω/sq was cleaned with acetone, de-ionized water, and isopropyl alcohol in the ultrasonicator for 20 min in each step. After, the cleaned ITO substrates were dried at 80 °C for 1 h, and treated with UV-ozone plasma for 10 min prior to the deposition of PEDOT:PSS. A filtered PEDOT:PSS solution in water (PH 500) was spin-coated at 3000 rpm for 40 s and baked at 150 °C for 20 min in ambient condition. The optimized PDFQx:ITIC OSCs were prepared using chlorobenzene as a solvent with 0.5 vol% 1,8-diiodooctane (DIO). The optimized D:A ratio was 1.3:1 (w/w) for PDFQx-2T:ITIC, 1:1.5 (w/w) for PDFQx-2T2F, 1:1 (w/w) for PDFQx-3T, and 1.3:1 (w/w) for PDFQx-2TB, respectively. The optimal concentration of (D+A) was 16 mg mL^{-1} for all blends. Each blend solution was stirred for ~2 hr at 85 °C. After the solution was filtered by a 0.45 μm polytetrafluoroethylene syringe filter, the active layer was spin-coated onto the ITO/PEDOT:PSS substrate at 1000 rpm for 60 s. The thickness of each active layer was 90-105 nm. Finally, the substrates were transferred to a vacuum evaporation chamber under high vacuum condition (< 10^{-6} Torr), 0.8 nm of LiF and 100 nm of Al were sequentially deposited. The resulting active area was 0.09 cm^2. The current density-voltage (*J*-*V*) characteristics were measured under AM 1.5G solar irradiation (100 mW cm^{-2}, Peccell: PEC-L01, the Class AAB, ASTM Standards) under ambient condition using a Keithley 2400 SMU after calibrating the intensity of the solar simulator by using a standard silicon reference cell with a KG-5 visible color filter. The EQE spectra were measured by a spectral measurement system (K3100 IQX, MacScience Inc.) with monochromatic light from a xenon arc lamp at 300 W filtered by a monochromator (Newport) and an optical chopper (MC 2000 Thorlabs).

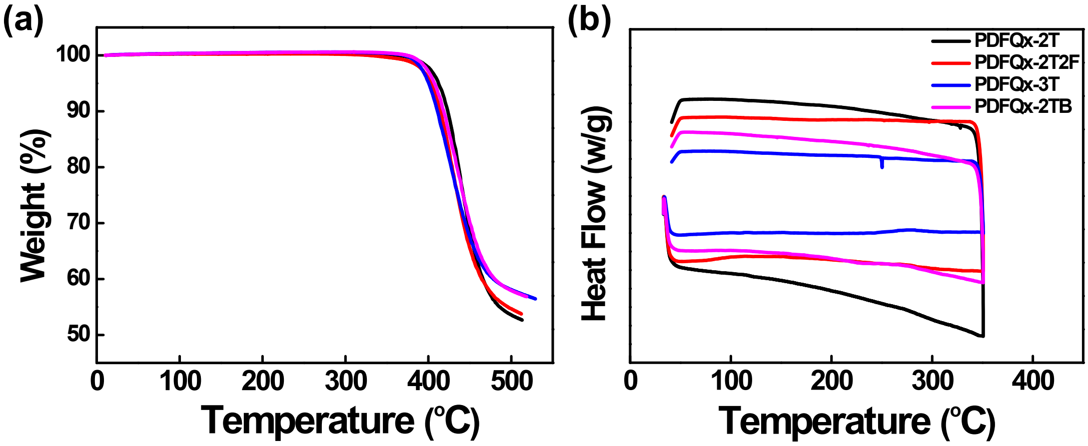

Figure S1. (a) TGA and (b) DSC thermograms of PDFQx polymers.

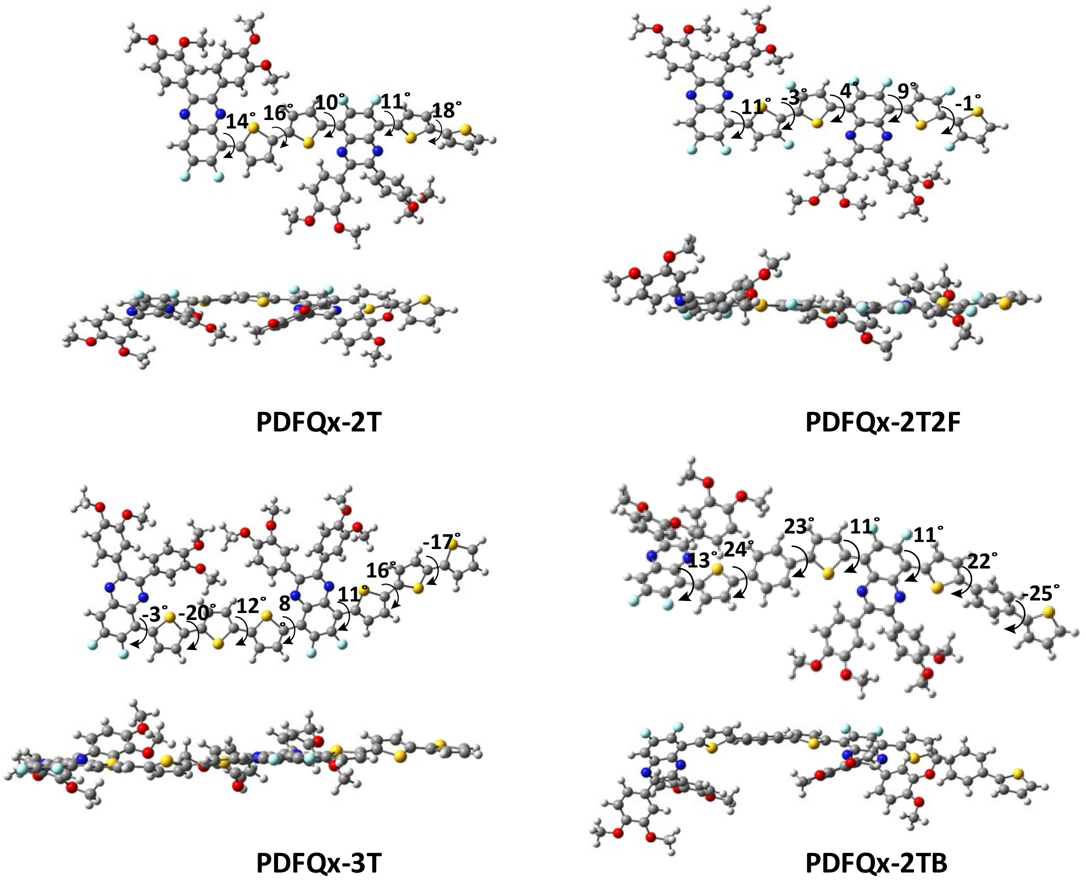

Figure S2. Energy minimized molecular geometries based on dimers of PDFQx polymers.

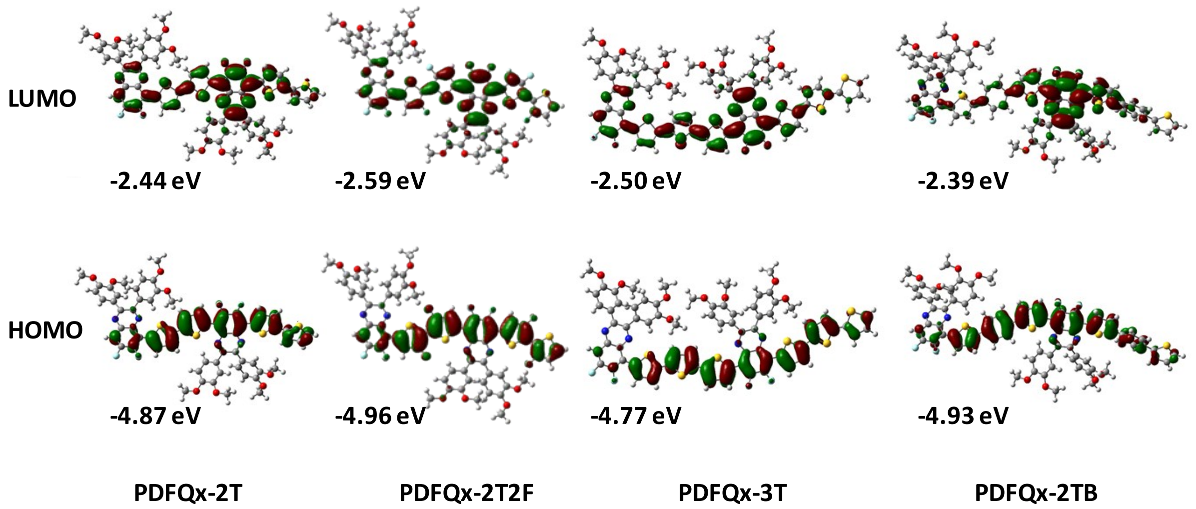

Figure S3. Frontier molecular orbital structures of PDFQx-based polymers.

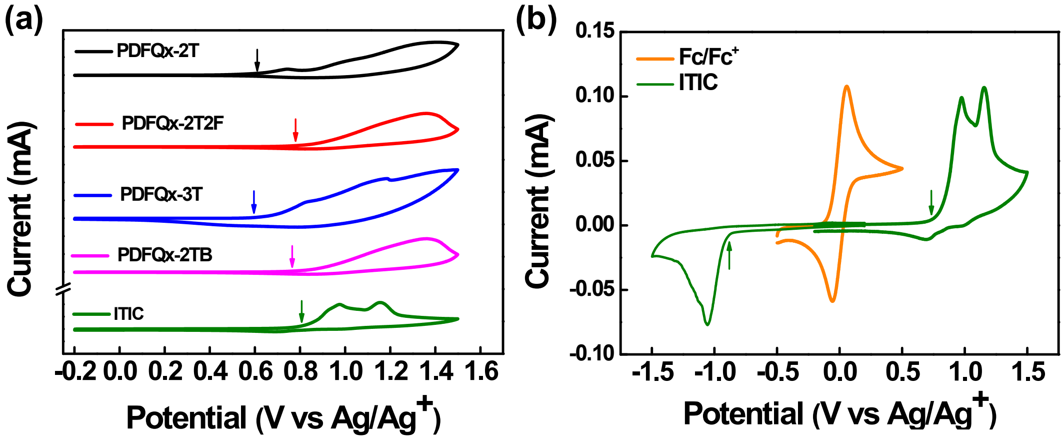

Figure S4. Cyclic voltammograms of (a) PDFQx polymers and (b) ITIC.

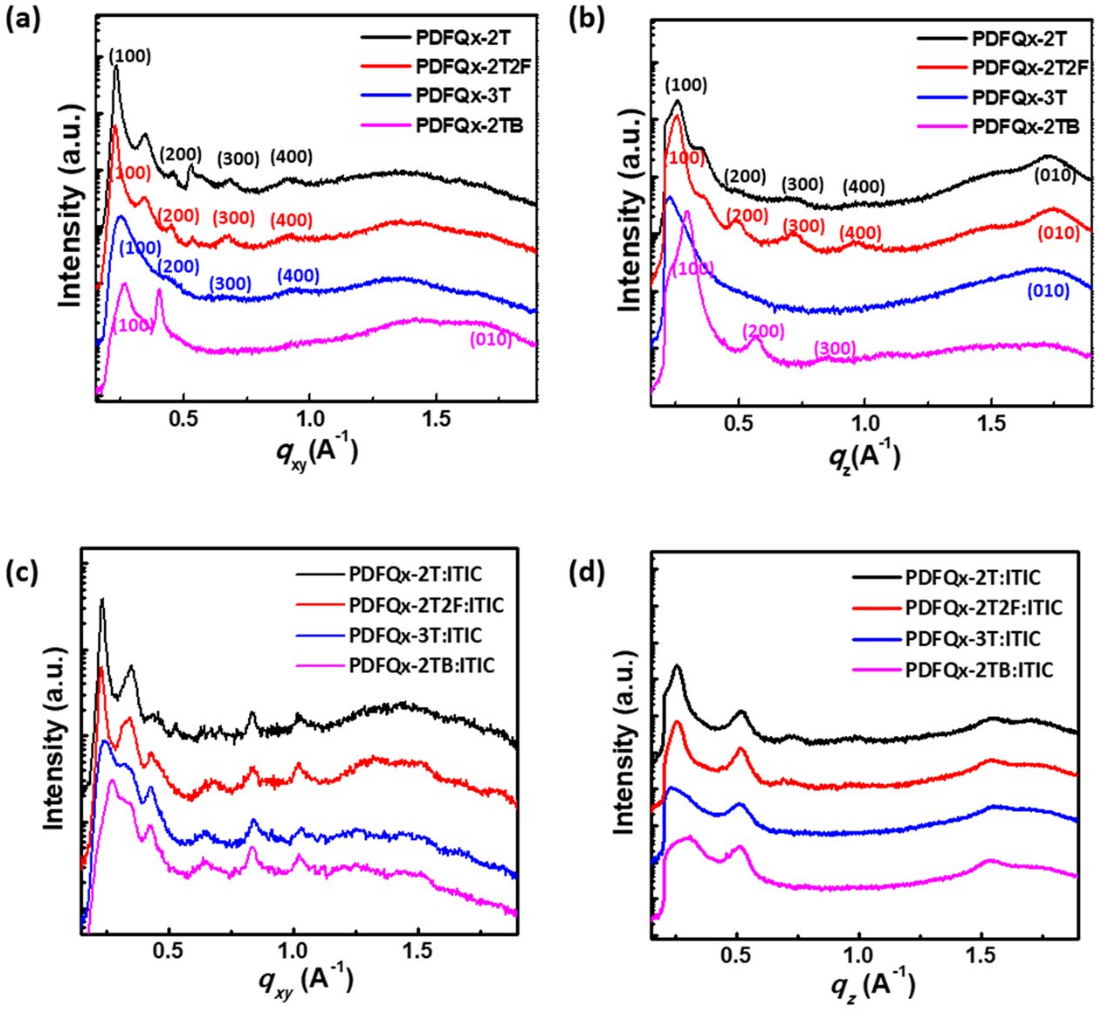

Figure S5. In-plane and out-of-plane line-cuts of the 2D-GIXS images of (a, b) PDFQx pristine films and (c, d) PDFQx:ITIC blend films.

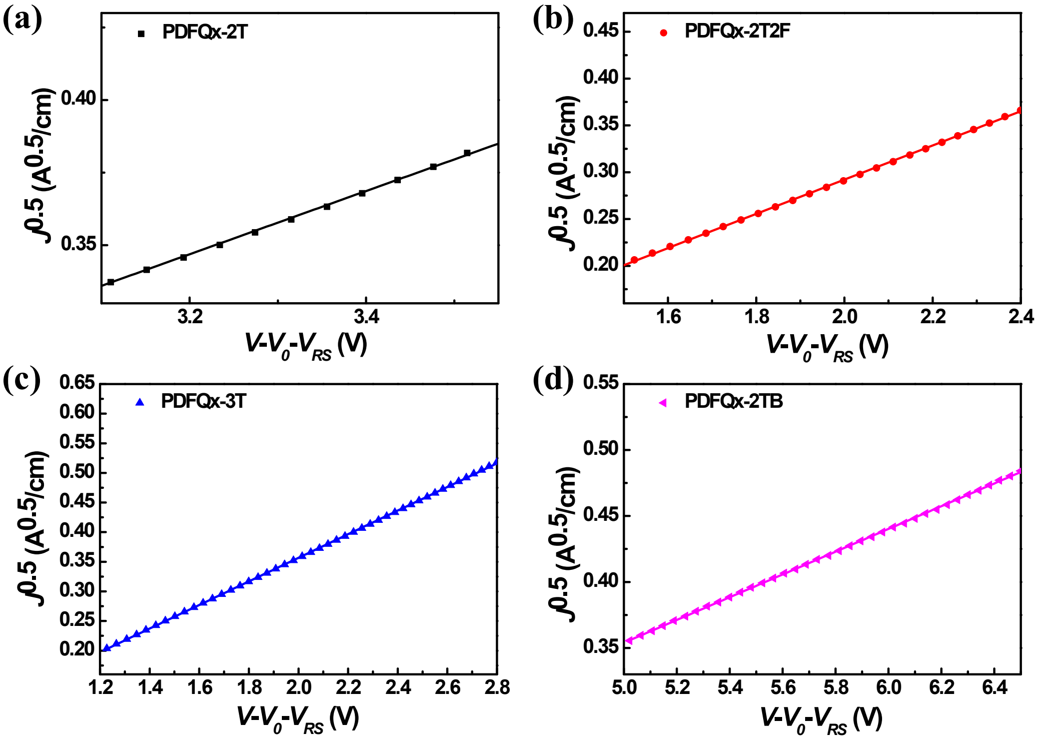

Figure S6. J-V characteristics of hole-only devices for (a) PDFQx-2T:ITIC, (b) PDFQx-2T2F:ITIC, (c) PDFQx-3T:ITIC and (d) PDFQx-2TB:ITIC blend films.

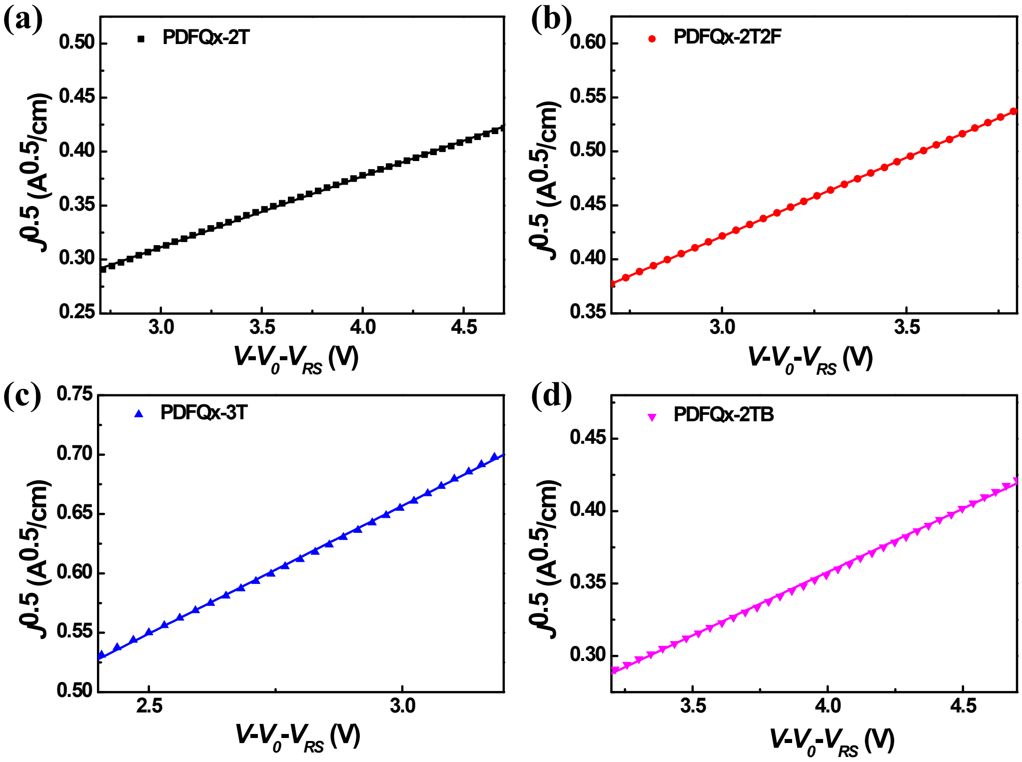

Figure S7. *J-V* characteristics of electron-only devices for (a) PDFQx-2T:ITIC, (b) PDFQx-2T2F:ITIC, (c) PDFQx-3T:ITIC and (d) PDFQx-2TB:ITIC blend films.

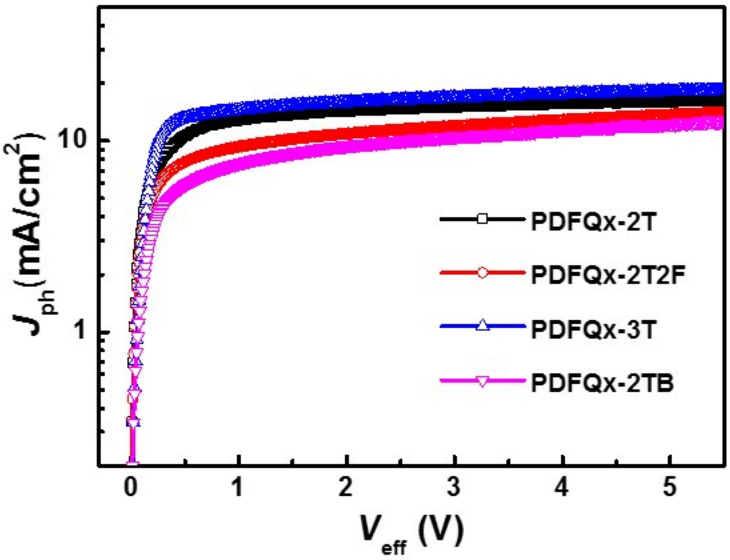

Figure S8. Photocurrent density (J_{ph}) versus effective voltage (V_{eff}) characteristics.