

Electronic Supplementary Information

Molecular Orbital Energy Level Modulation through Incorporation of Selenium and Fluorine into Conjugated Polymers for Organic Photovoltaic Cells

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Experimental section

Materials. All reagents, unless otherwise specified, were purchased from Sigma-Aldrich, TCI, Alfa Aesar, Acros or Puyang Huicheng Chemical Co. Ltd. and used as received. Anhydrous THF was dried over and distilled from sodium benzophenone ketyl under an atmosphere of dry nitrogen. Monomers 5,8-dibromo-2,3-bis(3-octylphenyl)quinoxaline (**M1**), 5,8-dibromo-6,7-difluoro-2,3-bis(3-(octyloxy)phenyl) quinoxaline (**M2**) and 2,5-bis(trimethylstannanyl)thiophene (**M3**) were prepared according to the published literature.¹ The synthesis of polymers poly[2,3-bis(3-(octyloxy)phenyl)quinoxaline-*alt*-thiophene] (**PTQ**, **TQ1**) and poly[6,7-difluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline-*alt*-thiophene] (**PTQF2**, **TQ-F**) was previously reported.^{1c} Polymers poly[2,3-bis(3-(octyloxy)phenyl)quinoxaline-*alt*-selenophene] (**PSeQ**) and poly[6,7-difluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline-*alt*-selenophene] (**PSeQF2**) were synthesized in the same manner.

Characterization. All manipulations involving air-sensitive reagents were carried out in an atmosphere of high purity nitrogen. ¹H and ¹³C NMR spectra were recorded at ambient temperature on a Varian Inova 400 MHz NMR spectrometer operating at 400 and 100 MHz, respectively, with tetramethylsilane ($\delta_{\text{H}} = 0$ ppm) as the reference and J values given in Hz. Size-exclusion chromatography (SEC) was performed on a Waters Alliance GPCV2000 System with a refractive index detector. Columns: Waters Styragel[®] HT 6E \times 1, Waters Styragel[®] HMW 6E \times 2. The working temperature was 135 °C, the eluent used was 1,2,4-trichlorobenzene, and the resolution time was 2 hr with a flow rate of 1 mL/min. The concentration of the samples was 0.5 mg/mL, which were filtered (filter: 0.45 μm) prior to analysis. The molar masses and molar-mass dispersities were obtained by calibration relative to polystyrene standards. Ultraviolet-visible (UV-Vis) absorption spectra were measured with a PerkinElmer Lambda 900 UV-Vis-NIR absorption spectrometer. All square wave voltammetry (SWV) measurements were performed on a CH Instruments Model 650A Potentiostat/Galvanostat Electrochemical Workstation. In the voltammetry experiments, a three electrode setup was used, with two platinum electrodes as the working and counter electrodes, respectively, together with a Ag/Ag⁺ quasi-reference electrode. A nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in anhydrous acetonitrile was used as a supporting electrolyte. Thin polymer films were cast from *o*-dichlorobenzene (ODCB) solution onto the working electrode. A small amount of Bu₄NPF₆ was added to the sample solution prior to deposition to improve charge transport in the polymer matrix during the scans. In order to remove oxygen, the electrolyte was purged with nitrogen gas prior to each experiment. During the scans the nitrogen inlet was moved above the electrolyte surface. The third scan of the anodic and cathodic electrochemical waves was recorded and calibrated against the ferrocene/ferrocenyl (Fc/Fc⁺) redox couple. HOMO and LUMO levels were deduced from their respective ionization potentials and electron affinities, estimated from the first oxidation and reduction peak potentials according to the formulae HOMO = $-(E^{\text{ox}} + 5.13)$ eV and LUMO = $-(E^{\text{red}} + 5.13)$ eV, by setting the oxidative peak potential of Fc/Fc⁺ vs. the normal hydrogen electrode (NHE) to 0.63 V,² and the NHE vs. the vacuum level to 4.50 V.³

Device Fabrication and Characterization. The PSCs were fabricated using a device structure of glass/ITO/PEDOT:PSS (40 nm)/active layer/LiF (0.6 nm)/Al (100 nm). The device architecture of the PSCs is schematically illustrated in Figure S1.⁴ The ITO covered glass substrates were cleaned by detergent and acetone prior to TL-1 (a mixture of water, ammonia (25%), and hydrogen peroxide (28%), 5:1:1 by volume) treatment. PEDOT:PSS (40 nm) was spin-cast onto the cleaned substrate and heated at 120 °C for 30 min. Then, the substrates were transferred into a glove box filled with N₂. The active layers were spin-coated from ODCB solutions on top of the PEDOT:PSS coated ITO glass substrates. The substrates were moved into a vacuum chamber where 0.6 nm LiF and 80 nm Al were thermally evaporated at a pressure less than 4×10^{-4} Pa. The active areas of all PSCs are roughly 4.5 mm² defined by the overlap between two electrodes, which were measured by optical microscopy. All the un-encapsulated devices were tested in the atmosphere. Current density-voltage (J - V) curves were measured by using Keithley 2400 Source Meter under illumination of AM 1.5 filtered light, with intensity of 100 mW cm⁻² (solar simulator Model SS-50A, Photo Emission Tech., Inc.). External quantum efficiency (EQE) spectra were obtained using a Newport Merlin lock-in with the solar cells illuminated with chopped monochromatic light through the ITO side. Atomic force microscopy (AFM) was performed

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directly on these films, with a Dimension 3100 system (Digital Instruments/Veeco) by using Antimony (n) doped Silicon cantilevers (SCM-PIT, Veeco) in tapping mode.

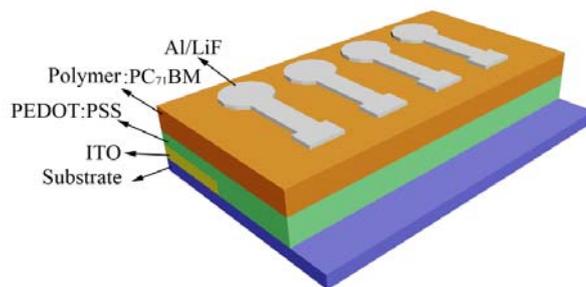


Figure S1. Schematic device structure of the PSCs

Synthesis of 2,5-Bis(trimethylstannyl)selenophene (M4). To a solution of selenophene (5.00 g, 37 mmol) in anhydrous tetrahydrofuran (THF, 190 mL) which was cooled down to -78°C under nitrogen was added a solution of *n*-butyllithium (2.5M solution in hexanes, 31 mL, 77.7 mmol) drop-wise within 40 min. The reaction mixture was stirred at this temperature for 90 min and then allowed to warm up to 37°C over 1 h. After being stirred at this temperature for another 1 h, the reaction solution was then cooled down to room temperature and trimethyltin chloride (1 M in THF, 81 mL, 81.4 mmol) was added. The reaction mixture was allowed to stir at room temperature overnight. The reaction solvent was then removed under reduced pressure and dissolved in ether (400 mL), washed with 5% NaHCO_3 solution (100 mL \times 2) and water (100 mL \times 2), dried over magnesium sulfate, filtered and concentrated under reduced pressure, giving a grey solid (11.0 g), which was further purified by Kugelrohr distillation to remove the lower boiling components (affording a 4.6 g of brownish solid residue) and further purified by recrystallization from methanol once and from hexane twice, affording a white solid (1.04 g). δ_{H} (400 MHz, acetone- d_6 , Me_4Si) 7.66 (2 H, s, ArH), 0.35 (18 H, s, $\text{Sn}(\text{CH}_3)_3$); δ_{C} (100 MHz, acetone- d_6 , Me_4Si) 150.5, 139.5, -8.0 .

Synthesis of poly[2,3-bis(3-(octyloxy)phenyl)quinoxaline-*alt*-selenophene] (PSeQ). In a 25 mL dry flask, ditin monomer **M4** (228.5 mg, 0.501 mmol), dibromide monomer **M1** (348.8 mg, 0.501 mmol), $\text{Pd}_2(\text{dba})_3$ (6.1 mg) and $\text{P}(\text{o-tol})_3$ (10.1 mg) were dissolved in degassed toluene (6 mL) under nitrogen. The mixture was bubbled with nitrogen for 30 min and then slowly heated to 105°C . After stirring for 64 hr at this temperature, the reaction mixture was cooled down and precipitated into acetone (250 mL). The polymer was collected by filtration, dissolved in ODCB (100 mL), mixed with sodium dithiocarbamate trihydrate (5 g) in distilled water (100 mL), and heated at 80°C for overnight. The organic phase was separated, washed with distilled water several times and slowly precipitated into methanol (400 mL). The solid product was isolated and subjected to Soxhlet extraction successively with ether and chloroform. The chloroform fraction was concentrated and precipitated in acetone, collected by filtration through $0.45\ \mu\text{m}$ Teflon filter and dried under vacuum at 40°C overnight to give a dark solid (306 mg, 91.8% yield). δ_{H} (400 MHz, chloroform- d_6 , Me_4Si) 8.5–6.0 (br, 12H, ArH), 4.0–3.0 (br, 4H, OCH_2), 2.0–1.0 (br, 24H, CH_2), 1.0–0.5 (br, 6H, CH_3). $M_n = 36.6\ \text{kDa}$, $M_w = 356\ \text{kDa}$.

Synthesis of poly[6,7-difluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline-*alt*-selenophene] (PSeQF2). In a 25 mL dry flask, ditin monomer **M4** (148.0 mg, 0.324 mmol), dibromide monomer **M2** (237.6 mg, 0.324 mmol), $\text{Pd}_2(\text{dba})_3$ (6.1 mg) and $\text{P}(\text{o-tol})_3$ (10.2 mg) were dissolved in degassed toluene (8 mL) under nitrogen. The mixture was bubbled with nitrogen for 30 min and then slowly heated to 90°C . After stirring for 49 hr at this temperature, the reaction mixture was cooled down and precipitated into methanol (250 mL). The polymer was collected by filtration, dissolved in ODCB (100 mL), mixed with sodium dithiocarbamate trihydrate (5 g) in distilled water (100 mL), and heated at 80°C for overnight. The organic phase was separated, washed with distilled water several times and slowly precipitated into methanol (400 mL). The solid product was isolated and subjected to Soxhlet extraction successively with methanol, acetone, ether, hexanes and finally chloroform. The chloroform fraction was concentrated and precipitated in methanol, collected by filtration through $0.45\ \mu\text{m}$ Teflon filter and dried under vacuum at 40°C overnight to give a dark solid (222 mg, 95.5% yield). δ_{H} (400 MHz, chloroform- d_6 , Me_4Si) 8.7–6.3 (br, 10H, ArH), 4.0–3.2 (br, 4H, OCH_2), 2.0–1.0 (br, 24H, CH_2), 1.0–0.5 (br, 6H, CH_3). $M_n = 51.0\ \text{kDa}$, $M_w = 122\ \text{kDa}$.

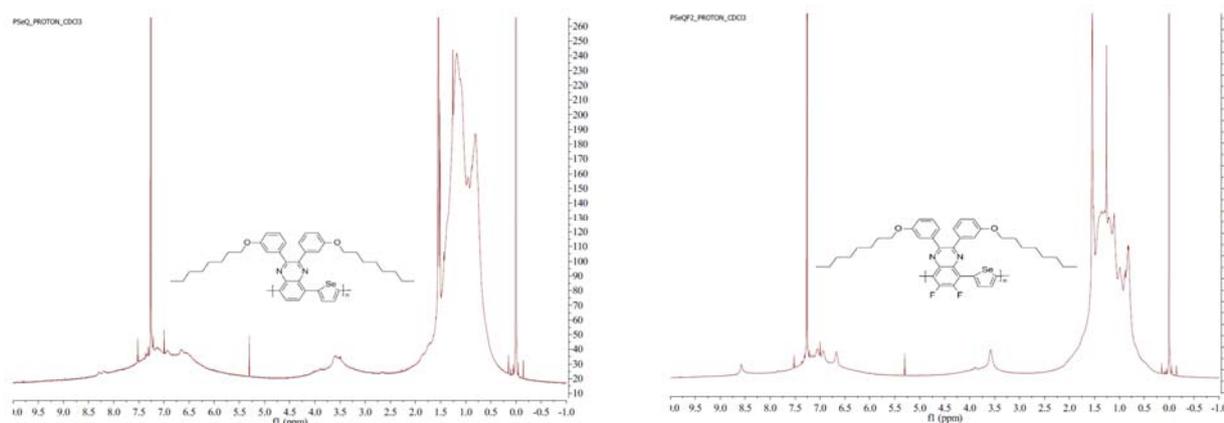
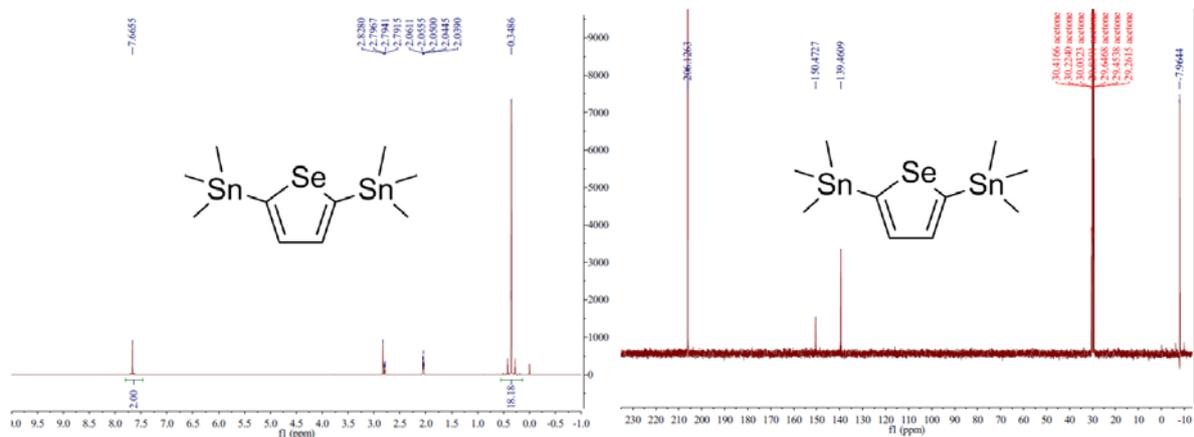
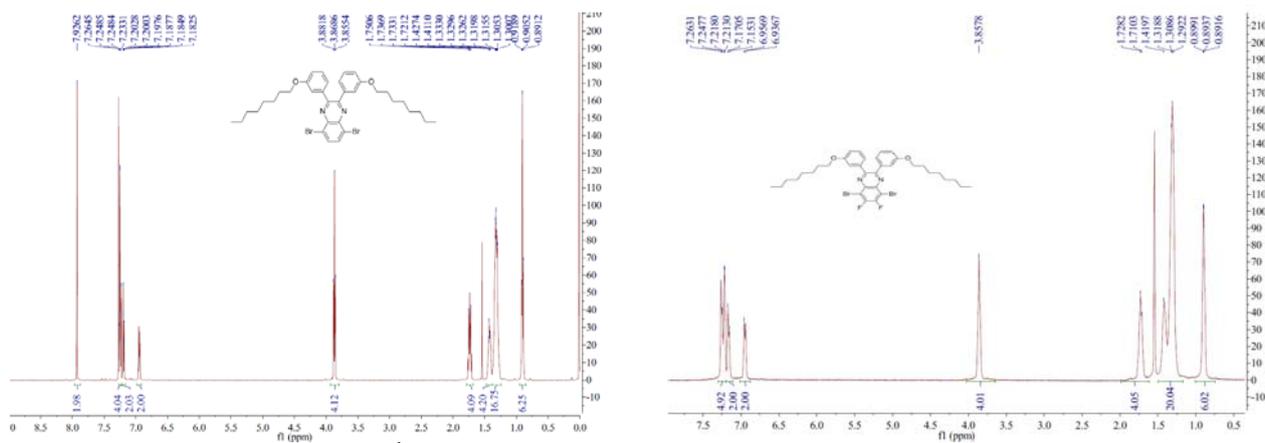


Table S1. Molar Masses, Optical and Electronic Properties

Polymer	GPC		UV-Vis	SWV – peak ^b			SWV – onset ^c			Estimated energies ^d		
	M_n (kDa)	M_w/M_n	E_g^{opt} (eV) ^a	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g^{elec} (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g^{elec} (eV)	E_{LUMO}^{opt} (eV)	E_{HOMO}^{opt} (eV)	E_{CT} (eV)
PTQ	46	2.6	1.75	-3.32	-5.69	2.37	-3.42	-5.50	2.08	-3.60	-5.35	1.16
PSeQ	37	9.7	1.65	-3.38	-5.84	2.46	-3.55	-5.45	1.90	-3.68	-5.33	1.14
PTQF2	49	2.5	1.80	-3.54	-6.31	2.77	-3.76	-6.04	2.28	-4.00	-5.80	1.62
PSeQF2	51	2.4	1.74	-3.47	-6.13	2.65	-3.65	-5.79	2.14	-3.85	-5.59	1.41
PC ₇₁ BM			1.70	-4.13	-6.52	2.39	-4.26	-6.39	2.13	-4.48	-6.18	

^a Determined by intersection of the tangent at inflection in the long-wavelength direction and baseline;

^b Determined from the first reduction and oxidation peak potentials respectively for LUMO and HOMO levels;

^c Determined by intersection of the tangents at inflection and baseline from the first reduction and oxidation potentials;

^d Estimated “effective” HOMO and LUMO levels and interfacial charge-transfer state energies according to the method used in the literature^{1c,5};

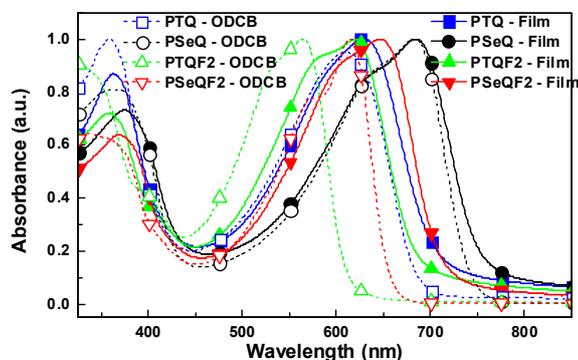


Figure S5. UV-Vis Absorption Spectra of Polymers in ODCB Solution and in Films

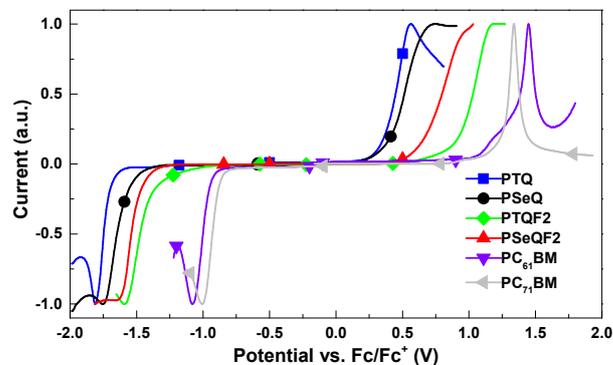
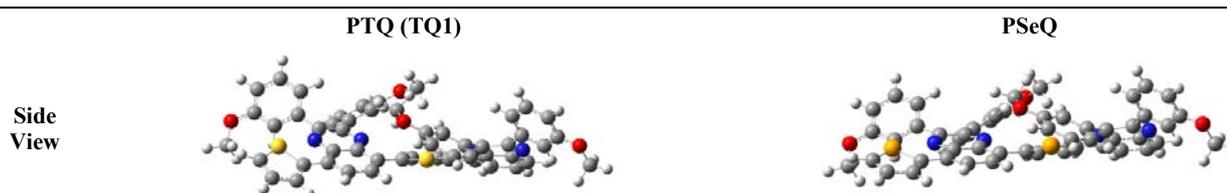


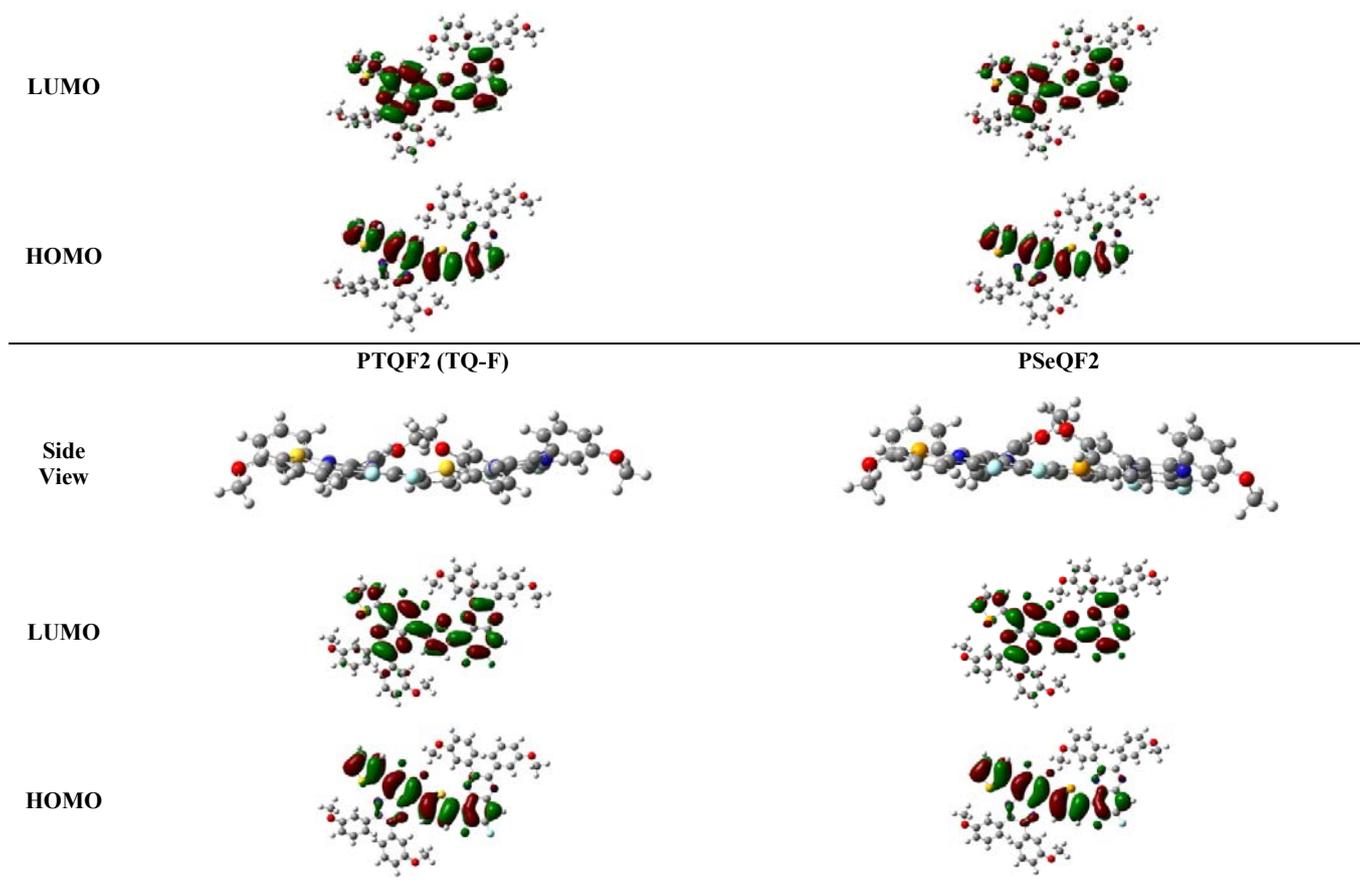
Figure S6. SWV of Polymers and PCBM

Theoretical Calculations

Quantum-chemical calculations by the density functional theory (DFT) at the B3LYP/6-31G(d) level⁶ using the Gaussian 09 program⁷ were employed to demonstrate the electronic structure of these polymers. For computational simplification, the alkoxy side chains on the quinoxaline unit were replaced with methoxy groups; and the backbones were simplified to two repeating units. All of the optimized molecular structures are in a stable local minimum of the ground state potential energy surface, and analytical second derivatives of the Hessian matrix were calculated at the same level of theory to ensure this. The optimized molecular geometries of the models and their calculated frontier orbitals are depicted in Table S2.

Table S2. Illustrations of the Frontier Orbitals for the Four Quinoxaline-Based Polymers and Their Molecular Geometries from Side View (Isovalue Surface 0.02 au) Evaluated at the B3LYP/6-31G* Level





Time-dependent DFT (TD-DFT) calculations⁸ were performed to assess the excited-state vertical transition energies and oscillator strengths based on the optimized molecular geometries at the same level of theory. We find that for all the polymers, all the transitions in the visible region correspond to $\pi-\pi^*$ transitions. In particular, the lowest excitations are all dominated by the HOMO \rightarrow LUMO transitions as can be seen from Figure S7. The band gap narrowing effect of selenium substitution is observed (i.e. from PTQ to PSeQ or from PTQF2 to PSeQF2). We also see a double enhancement in the oscillator strengths for the dominant absorption through the incorporation of fluorine atoms and selenium atoms, in agreement with the UV-Vis absorption spectroscopy.

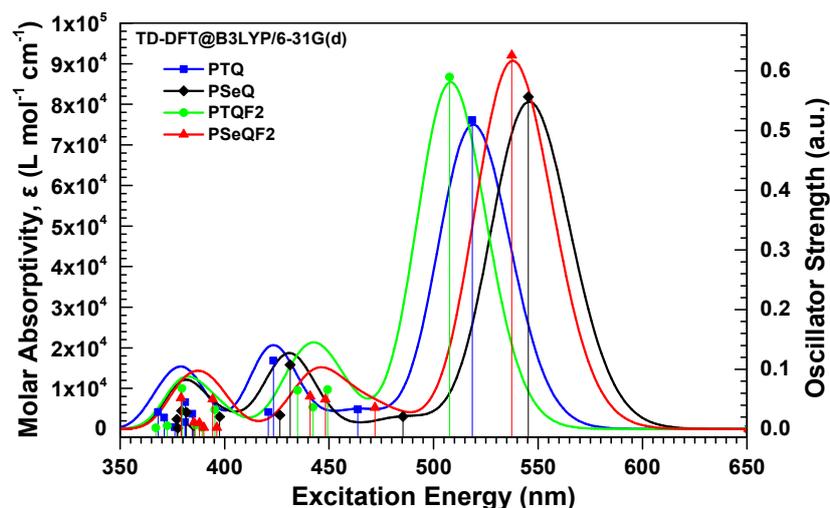


Figure S7. Simulated Absorption Spectra (the Full Width at Half-Maximum of the Gaussian Curves for Convolution = 1500 cm^{-1}) by TD-DFT at the B3LYP/6-31G(d) Level with Singlet Excitations

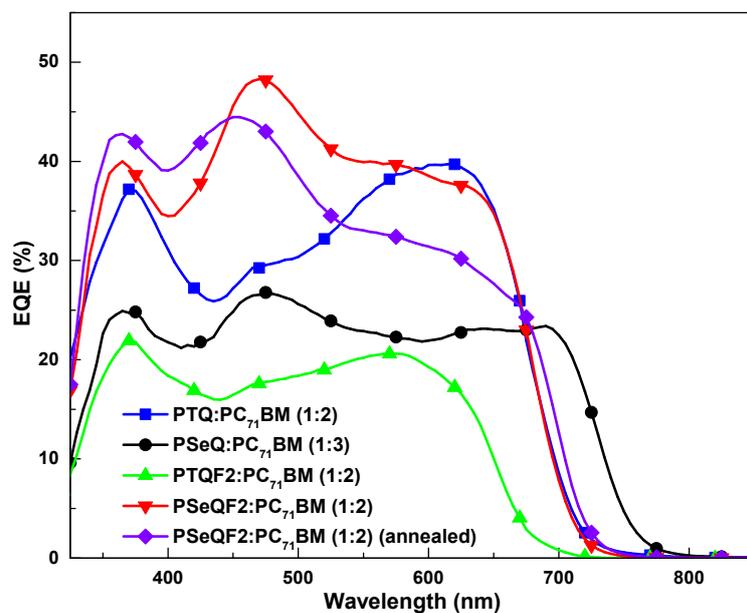


Figure S8. EQE curves of the polymer:PC₇₁BM based BHJ PSCs.
The PTQ and PTQF2 curves are reproduced from Ref. 1c.

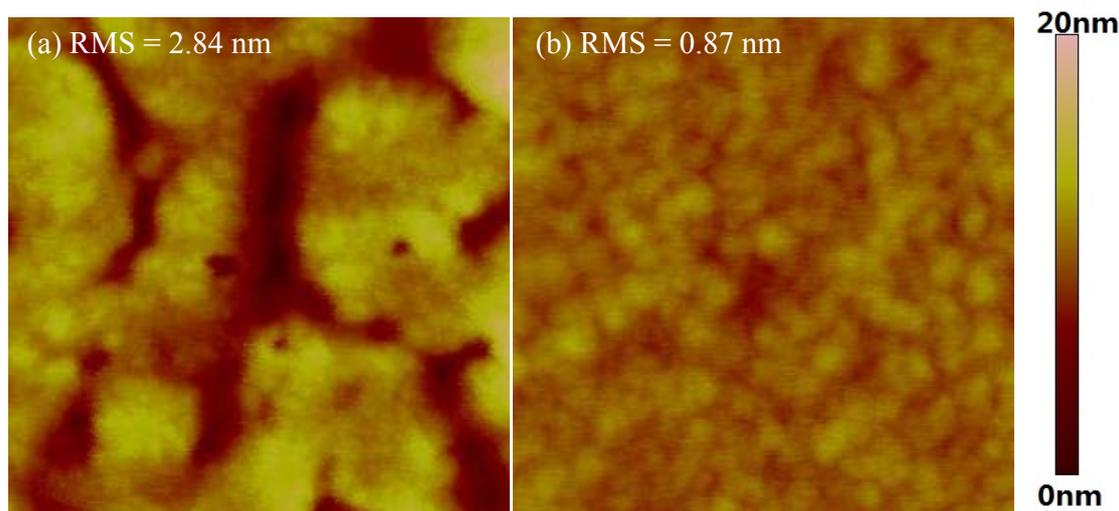


Figure S9. AFM Images (Size: 1 μm \times 1 μm) of the Active Layers from
(a) 1:3 (wt/wt) PSeQ:PC₇₁BM and (b) 1:2 (wt/wt) PSeQF2:PC₇₁BM

References

1. (a) E. Wang, L. Hou, Z. Wang, S. Hellström, F. Zhang, O. Inganäs and M. R. Andersson, *Adv. Mater.*, 2010, **22**, 5240–5244; (b) E. Wang, L. Hou, Z. Wang, Z. Ma, S. Hellström, W. Zhuang, F. Zhang, O. Inganäs and M. R. Andersson, *Macromolecules*, 2011, **44**, 2067–2073; (c) R. Kroon, R. Gehlhaar, T. T. Steckler, P. Henriksson, C. Müller, J. Bergqvist, A. Hadipour, P. Heremans and M. R. Andersson, *Sol. Energy Mater. Sol. Cells*, 2012, **105**, 280–286.
2. (a) V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, **298**, 97–102; (b) N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910; (c) C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367–2371.
3. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edn., John Wiley & Sons, New York, 2001.

4. Q. Hou, Y. Q. Chen, H. Y. Zhen, Z. F. Ma, W. B. Hong, G. Shi and F. L. Zhang, *J. Mater. Chem. A*, 2013, **1**, 4937–4940.
5. D. Veldman, S. C. J. Meskers and R. A. J. Janssen, *Adv. Funct. Mater.*, 2009, **19**, 1939–1948.
6. (a) C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (c) W. J. Hehre, Ditchfie.R and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261; (d) P. C. Harihara and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
7. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, Editon edn., 2010.
8. M. E. Casida, *J. Mol. Struct.: THEOCHEM*, 2009, **914**, 3–18.