Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Organic Photovoltaic Cells with High Efficiencies for both Indoor and Outdoor Applications

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Experimental Section

Synthesis of HDO-4Cl

Synthesis of 3-methoxythieno[3,2-b]thiophene (compound 2）

A mixture of compound 1 (5.66 g), CuO (4.3g) and KI (222 mg) were dissolved in 90 mL sodium methoxide solution in methanol (5,4M) under the protection of argon atmosphere and heated at 100 °C for 20 h. The reaction mixture was cooled to room temperature and water was added, then the mixture was extracted by petroleum ether three times. After the combined organic phase was concentrated, silica gel column chromatography was carried out for further purification. The pure compound 2 was obtained as white solid (3.6g, yield 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 5.1 Hz, 1H), δ 7.17 (d, *J* = 5.1 Hz, 1H), δ 6.29 (s, 1H), δ 3.94 (s, 3H).

Synthesis of 3-(decyloxy)thieno[3,2-b]thiophene (compound 3）

To the solution of compound 2 (400 mg) in toluene (15mL), 1.48 g 1-decanol and 91 mg sodium p-toluenesulfonate were added. The solution was heated to reflux for 24 h under the protection of argon atmosphere. After cooling to room temperature, the solution was poured into water and exacted by dichloromethane three times. After the combined organic phase was concentrated, silica gel column chromatography was carried out for further purification. The pure compound 3 was obtained from silica gel column chromatography as colorless oil (530 mg, yield 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 5.2 Hz, 1H), δ 7.17 (d, *J* = 5.2 Hz, 1H), δ 6.27 (s, 1H), δ 4.08 (t, *J* = 6.8 Hz, 2H), δ 1.84 (m, 2H), δ 1.46 (m, 2H), δ 1.28 (m, 12H), δ 0.89 (t, *J* = 6.8 Hz, 3H).

Synthesis of (6-(decyloxy)thieno[3,2-b]thiophen-2-yl)trimethylstannane (compound 4）

The solution of compound 3 (3g) in tetrahydrofuran (100 mL) was cooled to -78 °C under an argon atmosphere. LDA (2M, 5.6 mL) was then added dropwise in the solution. The mixture was stirred for 1 h under that temperature. Trimethyhin chloride solution in hexane (11.2 mL, 1M) was injected to the mixture at one portion and then the mixed solution was stirred for another 1 h. After that, the reaction was quenched by water and extracted by diethyl ether three times. The combined organic phase was concentrated to give the crude compound 4 and the product was directly used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), δ 6.24 (s, 1H), δ 4.06 (t, *J* = 6.4 Hz, 2H), δ 1.82 (m, 2H), δ 1.47 (m, 2H), δ 1.28 (m, 12H), δ 0.89 (t, *J* = 6.4 Hz, 3H), δ 0.5-0.3 (m, 9H).

Synthesis of 4,7-bis(6-(decyloxy)thieno[3,2-b]thiophen-2-yl)-5,6-dinitrobenzo[c][1,2,5]thiadiazole (compound 5）

Compound 4 (4.4 g), 4,7-dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (1.47 g) and 200 mg $Pd(PPh_2)Cl_2$ was solved into 50 mL toluene under the protection of argon. The mixed solution was heated to reflux under 110 °C for 12 h. After the mixture cooled to the room temperature, water was added and the mixture was exacted by dichloromethane three times. The pure compound 5 was obtained from silica gel column chromatography as red solid (2.03 g, yield 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 2H), δ 6.43 (s, 2H), δ 4.10 (t, J = 6.3 Hz, 4H), δ 1.84 (m, 4H), δ 1.28 (m, 4H), δ 1.21 (m, 24H), δ 0.88 (t, J = 6.9 Hz, 6H).

Synthesis of 3,9-bis(decyloxy)-12,13-bis(2-hexyldecyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole (compound 6）

A mixture of compound 4 (1.5 g) and triethyl phosphite (10 mL) were dissolved in o-dichlorobenzene (o-DCB, 6 ml) under the protection of argon atmosphere and heated at 180 °C to reflux for 18 h. After cooling to room temperature, the reaction mixture was extracted by dichloromethane three times. Then, the combined organic phase was dried (Na_2SO_4), filtered, and concentrated. A solution of the residue, 1-bromo-2-hexyldecane (2.8 g), K_2CO_3 (1.02 g) and KI (600 mg) in DMF (40 mL) was purged with argon for 30 min and then the mixture was placed in 80 °C oil bath for several hours to complete the reaction. After the mixture cooled to the room temperature, water was added and the mixture was exacted by dichloromethane three times. After the combined organic phase was concentrated, the crude product was further purified by silica gel column chromatography to yield the target compound as orange oil (840 mg, yield 38%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.29 (s, 2H), δ 4.54 (d, J = 7.2 Hz, 4H), δ 4.16 (t, J = 6.3 Hz, 4H), δ 2.05 (m, 2H) δ 1.89 (m, 4H), δ 1.50 (m, 4H), δ 1.29-0.89 (m, 72H), δ 0.83 (t, J = 7.2 Hz, 12H), δ 0.69 (t, J = 7.2 Hz, 6H).

Synthesis of 3,9-bis(decyloxy)-12,13-bis(2-hexyldecyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (compound 7）

To a mixture solvent of POCl3 (1 mL) and anhydrous DMF (1mL), the solution of compound 6 (500 mg) in dry 1,2-Dichloroethane (10 mL) was slowly added under the protection of argon. After stirring at 80 °C for 4 h, the mixture was dropwise added into $NaHCO_3$ aqueous solution and stirring for 0.5 h. The mixture was extracted with chloroform twice. After the combined organic phase was concentrated by rotary evaporation, the pure compound 7 was obtained from silica gel column chromatography as orange solid (377 mg, yield 72%). ^1H NMR (300 MHz, $CDCl_3$) δ 10.11 (s, 2H), δ 4.69 (t, J = 6.4 Hz, 4H), δ 4.59 (d, J = 7.6 Hz, 4H), δ 1.94 (m, 4H) δ 1.54 (m, 2H), δ 1.50 (m, 4H), δ 1.29-0.89 (m, 72H), δ 0.83 (m , 12H), δ 0.63 (m, 6H).

Synthesis of HDO-4Cl

To a mixture of compound 7 (200 mg) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (200 mg) in 10 mL chloroform, pyridine (0.5 mL) was added at room temperature under an argon atmosphere. Then, the reaction was stirred for 10 hours at room temperature. The mixture was directly purified by silica gel column chromatography by using dichloromethane as the eluent to yield the product as a black solid (230 mg, yield 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 2H), δ 8.66 (s, 2H), δ 7.88 (s, 2H), δ 4.78 (t, J = 6.4 Hz, 8H), δ 2.14 (t, J = 6.0 Hz, 2H), δ 2.03 (m, 4H) δ 1.54 (m, 2H), δ 1.50 (m, 4H), δ 1.29-0.89 (m, 72H), δ 0.83 (m , 12H), δ 0.63 (m, 6H).

Instruments and Measurements

A Bruker 400 or 300 spectrometer was used to measure the ^1H spectra of compounds at room temperature. Absorption spectra and molecular energy levels of the small molecular acceptors were measured on a Hitachi UH4150 UV-Vis spectrophotometer and a CHI650D Electrochemical Workstation, respectively. For the molecular energy level measurements, glassy carbon disk, Pt wire, and a Ag/Ag^+ electrode as the working electrode, counter electrode, and reference electrode, respectively. 0.1 M Bu_4NPF_6 acetonitrile solution was used as an electrolyte, and ferrocene/ferrocenium was used as an external standard and measured in parallel. The HOMO and LUMO levels were calculated according to the equation, HOMO/LUMO = $-e\,(\varphi_{ox}/\varphi_{red} + 4.80 - \varphi_{Fc/Fc+})$ (eV). The AFM height and phase images were acquired on a Bruker Nanoscope V AF microscope in tapping mode. Two-dimensional grazing incidence wide-angle X-ray scattering

(GIWAXS) data were obtained at the PLS-II 9AU-SAXS beam line of Pohang Accelerator Laboratory. The electron mobilities were measured by the space charge limited current (SCLC) method, with a device architecture of ITO/ZnO/neat film/Al. The mobilities were obtained by taking the dark current−voltage curves in the range 0−6 V. The emission spectra and light intensity of the LED light source were measured by a Fiber Optics Spectrometer (Maya2000 Pro, Ocean Optics).

Fabrication and characterization of the OSC devices

ITO-coated glass substrates were cleaned by a surfactant scrub and washed by water, acetone and isopropanol, successively. Then, substrates were treated under UV-ozone for 15 minutes. A 10 nm thick layer of PEDOT:PSS was spin-coated on top of the ITO as an anode interlayer, and annealed for 15 min at 150 ℃. For HD-4Cl based devices, the donor (D) and acceptors (A) were fully dissolved in chloroform (CF) at a polymer weight concentration of 7.5 mg/mL with a D: A mass ratio of 1:1.2, and 0.3% (v/v) 1,8-iodooctane (DIO) was used as solvent additive. For HDO-4Cl based devices, he donor (D) and acceptors (A) were fully dissolved in chloroform (CF) at a polymer weight concentration of 7.5 mg/mL with a D: A mass ratio of 1:1.6, and 1 % (v/v) Benzyl Ether (DBE) was used as solvent additive. The thickness of the active layers was about 110 nm as measured by a Bruker Dektak XT profilometer. Active layer films were thermally annealed at 100 ℃ for 10 min, and then PFN-Br was spin-coated on the top. Finally, about 80 nm Al were thermally evaporated onto the active layer under high vacuum, giving an area of 9 mm^2. Except for the spin-coating of anode interlayer PEDOT:PSS, the other preparation processes were all carried out in a nitrogen-filled glove box. Standard AM1.5G spectrum (100 mW·cm^{-2}) were used in the measurements of the photovoltaic performance of the PSC devices, and a NIM (National Institute of Metrology, China) calibrated cell was used as a reference. An integrated quantum efficiency measurement system named QE-R3011 (Enli Technology Co. Ltd., Taiwan) was used to record the EQE spectra of the devices, which was calibrated with a crystal silicon photovoltaic cell before use.

DFT calculation

The molecular geometries were optimized by Gaussian 09 with a functional of B3LYP and a basis set of 6-31G(d,p).[1] The long alkyl chains were replaced by methyl or ethyl for saving computation time. The dimmer conformation was optimized on the B3LYP/6-31G(d,p) calculation level combining with the Grimmer D3 version dispersion correction. Via employing the basis set superposition error (BSSE) function in the Gaussian 09, the combining energies of the optimized dimmer can be provided.

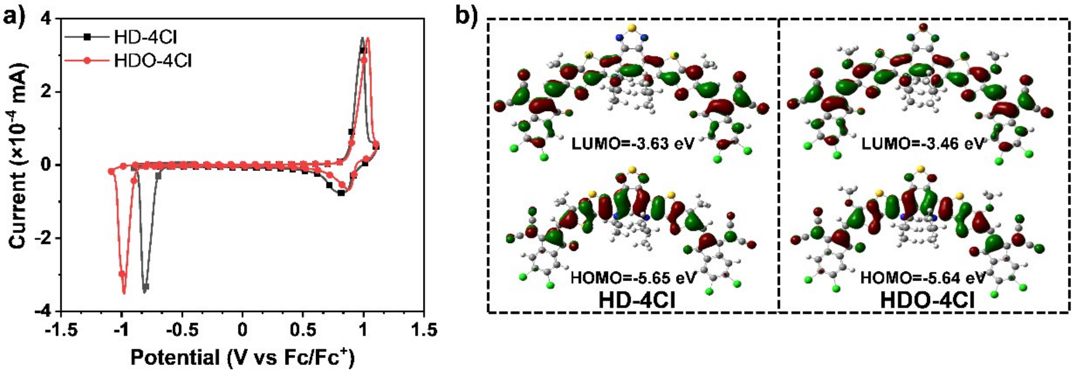

Figure S1. a) Cyclic voltammetry plots and **b)** Calculated energy levels of HD-4Cl and HDO-4Cl.

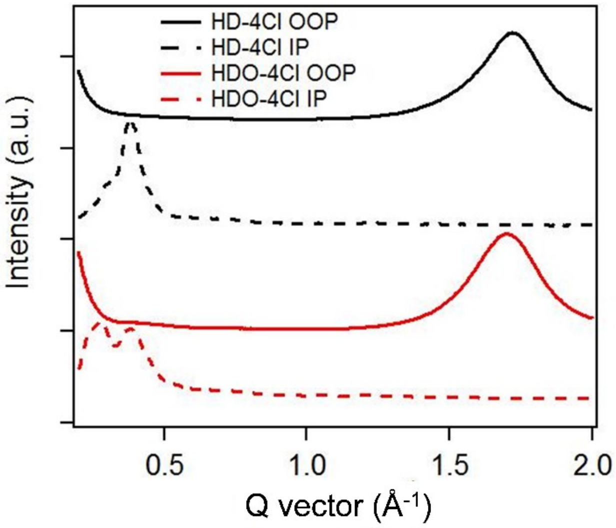

Figure S2. Extracted 1D profiles along the IP and OOP directions of the neat films.

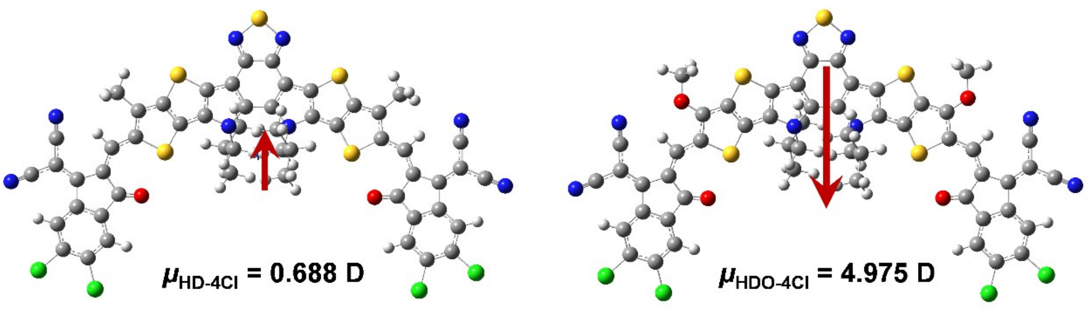

Figure S3. Calculated diploe moments (μ) of HD-4Cl and HDO-4Cl.

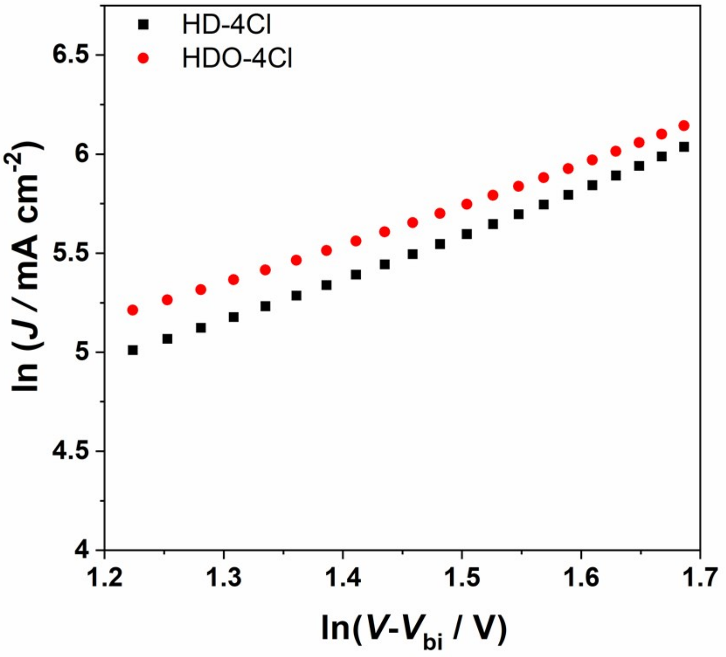

Fig S4. *J-V* characteristics of the SCLC regions of the electron-only devices.

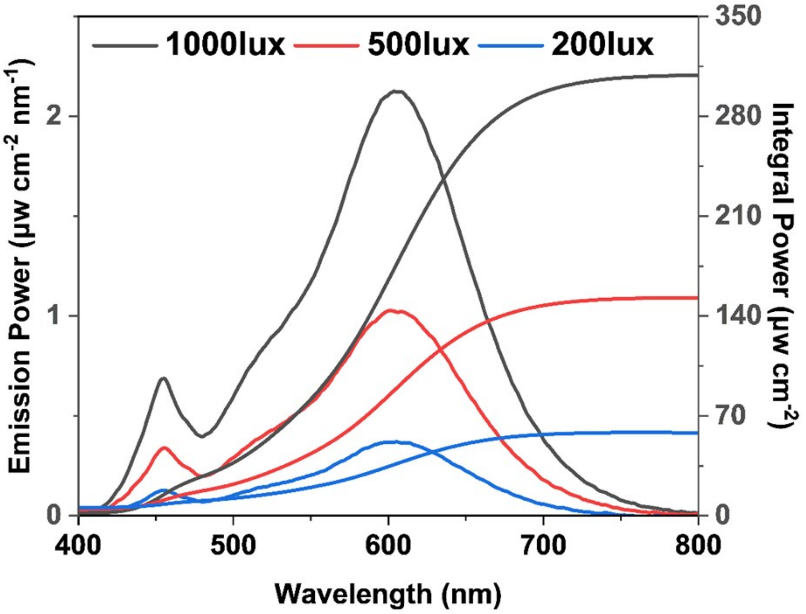

Figure S5. Emission power and integrated power spectra of the LED 2700 K with different intensities.

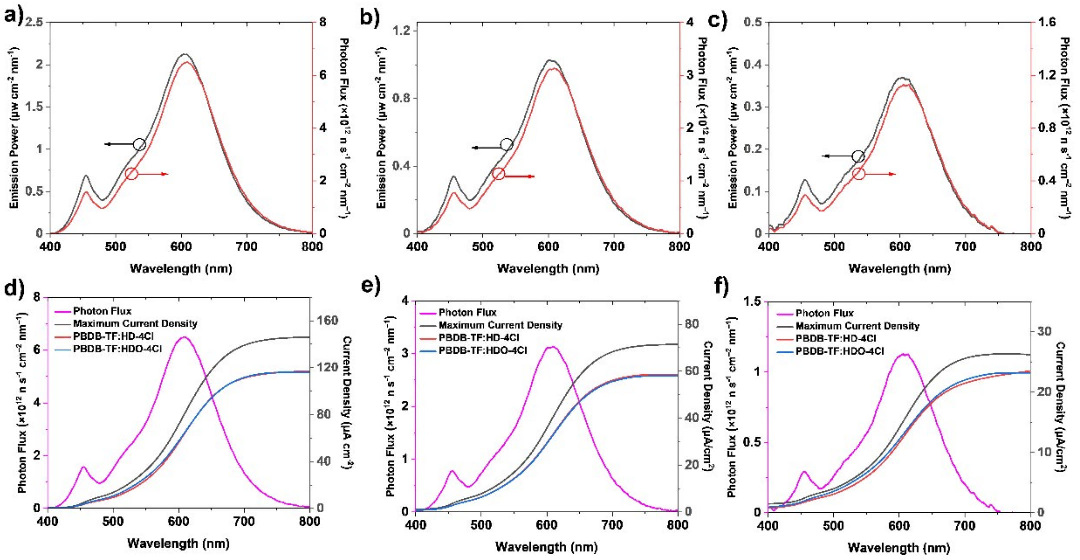

Figure S6. Emission power and the calculated photo flux of LED 2700K with **a)** 1000 lux, **b)** 500 lux and **c)** 200 lux. Photon flux, theoretically maximum integral current density, integral current density of PBDB-TF:HD-4Cl and PBDB-TF:HDO-4Cl based on EQE data under LED 2700K with **d)** 1000 lux, **e)** 500 lux and **f)** 200 lux.

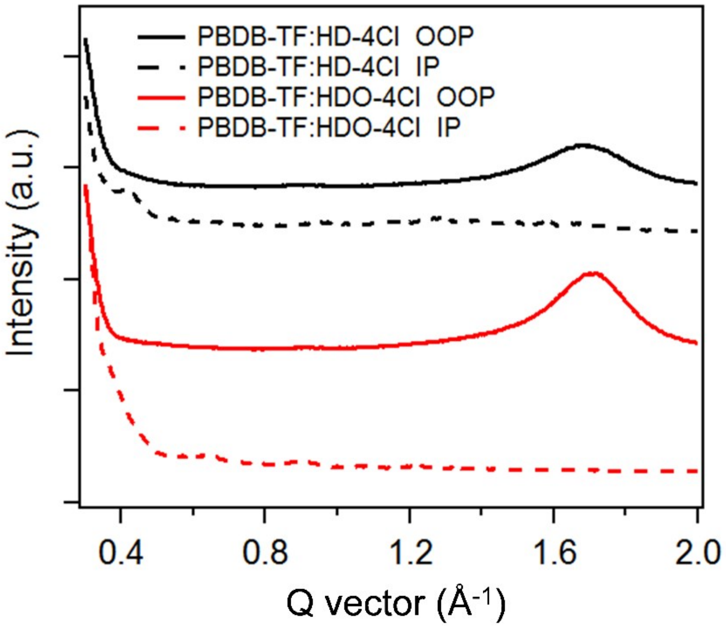

Figure S7. Extracted 1D profiles along the IP and OOP directions of the blends.