Supporting Information

Influence of Altering Chlorine Substitution Positions on Photovoltaic Property of Small Molecule Donors for All-Small-Molecule Organic Solar Cells

Keli Shi, ^a Beibei Qiu, ^{a,b}* Can Zhu, ^{b,c} Xinxin Xia, ^f Xiaonan Xue, ^d* Jinyuan Zhang, ^b* Yan Wan, ^g Shihua Huang, ^a Lei Meng, ^b* Xinhui Lu, ^f Zhi-Guo Zhang, ^e Yongfang Li^{b,c,h}

^a Key Laboratory of Solid State Optoelectronic Devices of Zhejiang Province, College of Physics and Electronic Information Engineering, Zhejiang Normal University, Jinhua, Zhejiang 321004, China
^b Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^c School of Chemical Science, University of Chinese Academy of Sciences, Beijing 100049, China

^d Frontiers Science Center for Transformative Molecules, In-situ Center for Physical Science, and

Center of Hydrogen Science, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

^{*e*} College of Materials Science and Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^f Department of Physics, The Chinese University of Hong Kong, New Territories, Hong Kong 999077, China

^g College of Chemistry, Beijing Normal University, Beijing 100875, China

^{*h*} Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China

* Corresponding authors:

qiubeibei@iccas.ac.cn (B. Qiu), louth@live.com (X. Xue), zhangjinyuan@iccas.ac.cn (J. Zhang), menglei@iccas.ac.cn (L. Meng)

Measurements and Instruments

¹H NMR and ¹³C NMR spectra were recorded on Bruker AVANCE 400 MHz NMR spectrometer at room temperature. The UV-vis absorption spectra were measured on a UH4150 Spectrophotometer (Direct Light Detector). Cyclic voltammogram (CV) measurements were conducted on a Zahner IM6e electrochemical workstation using sample film coated Platinum disk electrode as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. Fc/Fc⁺ redox couple was used as the reference for the calculation of the electronic energy levels of the donor and acceptor materials.

Fabrication and characterization of SM-OSCs

The SM-OSCs were fabricated with a conventional structure of ITO/PEDOT: PSS/small molecule: Y6/PDINO/AI. The PEDOT: PSS aqueous solution (Baytron P 4083 from H. C. Starck) was filtered through a 0.45 mm filter and spin-coat on precleaned ITO-coated glass at 5000 rpm for 30 s. Subsequently, the PEDOT: PSS film was baked at 150 °C for 20 min in air to give a thin film with a thickness of ~30 nm. A blend of the small molecule donor and Y6 acceptor was dissolved in chloroform (CHCl₃) with a total concentration of 22 mg/mL for 2 h and spin-coat at 2200~2500 rpm for 30 s onto the PEDOT: PSS layer. Then methanol solution of PDINO at a concentration of 1.0 mg mL⁻¹ was deposited atop the active layer at 3000 rpm for 30 s to afford a PDINO cathode buffer layer. Finally, the metal cathode AI was thermally evaporated under a shadow mask with a base pressure of approximately 10⁻⁵ Pa. The photovoltaic area of the device is 5 mm². The thermal annealing treatment of the SM-OSCs was performed at 120 °C for 10 min.

The *J-V* characteristics of the SM-OSCs were measured in a nitrogen glove box with a Keithley 2450 Source Measure unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450W xenon lamp and an air mass (AM) 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm⁻² by a Newport Oriel 91150V reference cell. The input photon to

converted current efficiency (IPCE) was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Measurement of charge carrier mobilities

The charge carrier mobilities were measured with the device structure of ITO/PEDOT: PSS/active layer/MoO₃/Ag for hole mobility and ITO/ZnO/active layer/PDINO/Al for electron mobility. The hole and electron mobilities are calculated according to the space charge limited current (SCLC) method equation: $J = 9\mu\varepsilon_{r}\varepsilon_{0}V^{2}/8d^{3}$, where J is the current density, μ is the hole or electron mobility, V is the internal voltage in the device, ε_{r} is the relative dielectric constant of active layer material, ε_{0} is the permittivity of empty space, and d is the thickness of the active layer.

Fabrication of the OFETs

OFETs were fabricated in a "bottom-gate top-contact" configuration on a highly doped n-type Si wafers with 300 nm thick SiO₂. The substrates were successively washed by deionized water, isopropyl alcohol, acetone and ethanol, and modified with octadecyltrichlorosilane (OTS) by vapor deposition. Then the thin small molecule films were spin-coated on the substrates from the solutions in chloroform (20 mg/mL) at a speed of 2000 rpm for 60s and annealed on a hotplate at 120 °C for 10 minutes. The patterned gold source-drain electrodes (80 nm) were deposited by vacuum evaporation and the channel length (*L*) and channel width (*W*) were 40 and 1400, respectively. The OFETs were measured in air by using a Keysight B1500A semiconductor characterization system. The mobility in the saturation region was calculated in the following equation: $I_{DS} = (W/2L) C_i \mu$ (V_{GS} - V_{th})². C_i is the capacitance per unit area of the insulator, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively.

Transient absorption spectroscopy

A Ti: sapphire amplifier (Astrella, Coherent) supplied laser beams centered at 800 nm with

pulse duration of ~40 fs, pulse repetition rate of 1 kHz, and a maximum pulse energy of 7 mJ. The output of the amplifier was split into two streams of pulses. One was used to drive an optical parametric amplifier (Topas C, Light Conversion) to obtain the pump beam. Residual stream was directed into an ultrafast spectroscopic system (HARPIA-TA, Light Conversion) to generate the white light continuum probe beam. In the spectrometer, the pump chopped at 500 Hz frequency was spatially and temporally overlapped with the probe beam on the sample. Excitation energy of the pump pulse was set to 2 μ J/cm² to avoid singlet-singlet annihilation. The film samples for TA measurements were prepared by spin coating the blended materials on thin quartz plates. The TA treated samples were then annealed in nitrogen atmosphere at120 °C for 10 min prior to measurement.

Experimental Section

Materials: Compound Y6 was commercially available from Solarmer Materials Inc. Compound1a, 1b and 2 were synthesized according to the previous literature. Pd(PPh₃)₄ was obtained from J&K chemical Co. Toluene was dried over Na/benzophenone and freshly distilled prior to use. The other chemicals, solvents and materials used in this work were all commercially available and used without further purification.



Scheme S1. Synthetic routes of small molecules: SM1-α-Cl and SM1-β-Cl.

Synthesis of SM1- α -Cl: A solution of 1a (146 mg, 0.15 mmol) and 1b (280 mg, 0.375 mmol) in dry toluene (12 mL) was degassed several times with argon followed by the addition of Pd(PPh₃)₄ (30 mg). After stirring at 110 °C for 36 h under argon, the mixture was poured into water and extracted with CHCl₃. The residue was purified by silica gel chromatography using a mixture of petroleum and dichloromethane ether (1:1) as eluent to afford compound SM1- α -Cl as a black solid (148 mg, 49%). ¹H NMR (400 MHz, CDCl₃) δ : 8.19 (s, 2H), 7.60 (s, 2H), 7.56 (s, 2H), 7.30 (d, J = 3.9 Hz, 2H), 7.19 (s, 2H), 7.14 (d, J = 3.9 Hz, 2H), 7.13 (s, 2H), 4.27-4.16 (m, 4H), 2.88-2.67 (m, 12H), 1.78-1.62 (m, 14H), 1.48-1.22 (m, 76H), 0.97-0.83 (m, 30H).

¹³C NMR (101 MHz, CDCl₃) δ: 163.20, 145.81, 141.46, 141.31, 140.62, 139.99, 138.82, 138.16, 138.01, 137.39, 135.36, 134.50, 133.06, 130.70, 128.99, 128.68, 128.24, 126.45, 125.79, 122.60, 118.64, 115.88, 97.91, 68.80, 38.79, 31.92, 31.89, 31.86, 30.48, 30.32, 30.23, 29.65, 29.61, 29.53, 29.46, 29.41, 29.31, 29.26, 28.93, 28.19, 23.76, 22.95, 22.68, 14.12, 14.06, 11.02.

Synthesis of SM1- β -Cl: SM1- β -Cl was synthesized with similar method as that described above for the synthesis of SM1- α -Cl, and a black solid was obtained (146 mg, 49%).

¹H NMR (400 MHz, CDCl₃) δ: 8.19 (s, 2H), 7.59 (s, 2H), 7.56 (s, 2H), 7.30 (d, J = 3.9 Hz, 2H), 7.25 (s, 2H), 7.15 (d, J = 2.8 Hz, 4H), 4.27-4.15 (m, 4H), 3.00-2.89 (m, 4H), 2.88-2.72 (m, 8H), 1.80 (dt, J = 15.3, 7.6 Hz, 4H), 1.70 (dd, J = 12.2, 6.2 Hz, 10H), 1.50-1.24 (m, 76H), 0.96-0.83 (m, 30H). ¹³C NMR (101 MHz, CDCl₃) δ: 163.20, 145.82, 141.47, 141.32, 140.62, 139.61, 138.78, 138.18, 138.06, 137.35, 135.35, 135.15, 134.49, 133.05, 130.69, 128.76, 128.25, 128.16, 126.46, 122.51, 122.14, 118.58, 115.89, 97.91, 68.80, 38.79, 31.88, 31.86, 30.54, 30.48, 30.32, 30.23, 29.71, 29.65, 29.53, 29.46, 29.41, 29.31, 29.29, 29.27, 28.93, 28.05, 23.76, 22.96, 22.69, 14.12, 14.06, 11.02.



Figure S1. Thin film absorption spectra of (a) SM1- α -Cl: Y6 and (b) SM1- β -Cl: Y6 blend films with or without thermal annealing treatment.



Figure S2. Absorption coefficients of small molecules SM1- α -Cl and SM1- β -Cl.



Figure S3. DFT calculations at the B3LYP/6-31G (d, p) level of SM1-α-Cl and SM1-β-Cl.



Figure S4. Cyclic voltammograms of small molecules SM1-α-Cl and SM1-β-Cl.



Figure S5. TGA curves of small molecules SM1-α-Cl and SM1-β-Cl.



Figure S6. *J-V* characteristics in the dark for hole mobility measurement of SM1-α-Cl and SM1-β-Cl.



Figure S7. *J-V* characteristics in the dark for hole mobility measurement of small molecule: Y6 blend films with or without TA treatment: (a) SM1- α -Cl: Y6 and (b) SM1- β -Cl: Y6.



Figure S8. *J-V* characteristics in the dark for electron mobility measurement of small molecule: Y6 blend films with or without TA treatment: (a) SM1- α -Cl: Y6 and (b) SM1- β -Cl: Y6.



Figure S9. *J-V* characteristics of as cast SM-OSCs based on SM1-α-Cl: Y6 and SM1-β-Cl: Y6.



Figure S10. (a) GIWAXS patterns: (i) As cast SM1- α -Cl film, (ii) As cast SM1- β -Cl: Y6 film. (b) Corresponding line-cut profiles.



Figure S11. TEM images of neat small molecule donor films: (i) SM1-α-Cl film, (ii) SM1-β-Cl film.

(a) As-cast films. (b) TA treated films at 120 $^{\rm o}{\rm C}$ for 10 min.



Figure S12. ¹H NMR of small molecule SM1-α-Cl.



Figure S13. ¹³C NMR of small molecule SM1-α-Cl.



Figure S14. ¹H NMR of small molecule SM1-β-Cl.



Figure S15. ¹³C NMR of small molecule SM1-β-Cl.

Table S1. Photovoltaic parameters of the as cast SM-OSCs based on small molecule: Y6 (2.2:1).

A	V_{oc}	J_{sc}	FF	PCE
Active layer	(V)	(mA cm ⁻²)	(%)	(%)
SM1-α-Cl: Y6	0.950	0.88	20.1	0.17
SM1-β-Cl: Y6	0.964	0.35	21.0	0.07

Table S2. Summary of SCLC charge mobilities of the neat donor films and blend films.

Active lay	yer	Condition	μ_h (×10 ⁻⁴ cm ² V ⁻¹ s ⁻¹)	$\mu_{e}(\times 10^{-4} \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1})$
SM1-α-0	C1	As cast	0.76	/
SM1-β-0	C1	As cast	2.95	/
$SM1 \approx C1$	VG	As cast	0.36	0.08
SM1-a-CI:	10	TA	1.69	3.01
SM1 B C1	V6	As cast	0.84	0.08
Sw11-p-CI: 10	10	TA	3.33	2.83

Active layer	$\mu_{ m h}$	$V_{th}(V)$	I_{on}/I_{off}
SM1-α-Cl	6.2×10 ⁻⁴ cm ² V ⁻¹ s ⁻¹	-1.8	10 ² ~10 ³
SM1-β-Cl	2.4×10 ⁻³ cm ² V ⁻¹ s ⁻¹	-17.3	10 ² ~10 ³

Table S3. Summary of OFET charge mobilities of the small molecule donor films.

Table S4. Summary of the GIWAXS parameters for the neat small molecular films.

film	direction	diffraction	q (Å-1)	d-spacing (Å)	FWHM (Å-1)	Coherence length (Å)
SM1-α-Cl	In plane	(010)	1.709	3.677	0.102	56.082
	Out of plane	(100)	0.311	20.203	0.026	220.117
SM1-β-Cl	In plane	(010)	1.732	3.628	0.155	36.916
	Out of plane	(100)	0.297	21.156	0.032	179.581
SM1-α-Cl: Y6	In plane	(010)	1.708	3.679	0.162	35.310
	Out of plane	(100)	0.316	19.883	0.028	204.966
SM1-β-Cl: Y6	In plane	(010)	1.730	3.632	0.178	32.145
	Out of plane	(100)	0.291	21.592	0.029	195.735