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Supporting information

Introducing methoxy or fluorine on the conjugated side chain to reduce the voltage loss of organic solar cells

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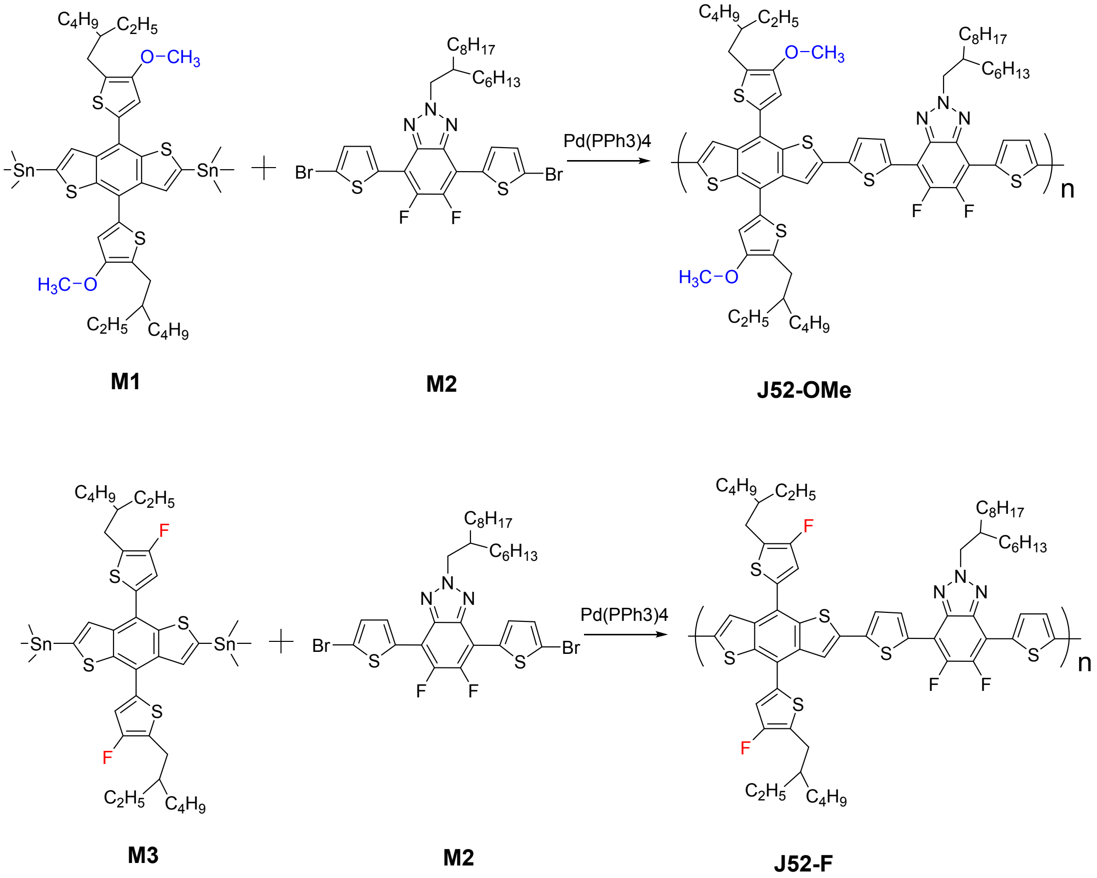
Materials and Synthesis.

All the reagents were purchased from commercial sources and used without further purification. Solvents were bought from the Beijing Chemical Plant. The monomers of M1, M2, M3 were synthesized according to the reported procedures.[1-2]



Scheme S1. Synthesis route of J52-OMe and J52-F.

The synthesis of polymers for J52-OMe and J52-F by the Stille coupling reaction was shown in Scheme S1. M1 (or M3) (0.4 mmol) and M2 (0.4 mmol) were added in a 100 mL two-neck round-bottom flask with 20 ml of toluene. After being followed vacuum and filled nitrogen for three times, the catalyst of $Pd(PPh_3)_4$ (0.017 mmol, 20 mg) was dissolved in the mixture. Then the mixture solution was purged with nitrogen for 10 min and stirred at 105 °C for 48 h. The reaction was injected blocking agent of tributyl(thiophen-2-yl)stannane and 2-bromothiophene six hours apart, respectively. 50 ml of ethanol was poured into the reaction solution, the precipitation was filtered and extracted in a Soxhlet extraction with methanol, hexane, dichloromethane, respectively. The solution extracted from dichloromethane was concentrated and added dropwise in the ethanol. Finally, the precipitate was collected and dried under vacuum to obtain reddish brown compound J52-OMe and reddish-brown compound J52-F.

J52-OMe yield: 94%; Mn = 23.2 kDa, Mw = 51.5 kDa, PDI = 2.22;

J52-F yield: 93%; Mn = 30.0 kDa, Mw = 69.9 kDa, PDI = 2.33;

Instruments and measurements

UV-Vis and CV characterization: UV-vis spectra were identified with a Lambda 950 spectrophotometer. Electrochemical CV was conducted on an electrochemical workstation (Chenhua, Shanghai) with a Pt disk coated with a molecular film, a Pt wire, and an Ag/AgCl electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1mol/L tetrabutylammonium phosphorus hexafluoride (Bu4NPF6) acetonitrile solution.

Device fabrication and measurements: The OPV devices were fabricated with a configuration of ITO/ PEDOT: PSS/ Blend films/ PDINO/ Al. A thin layer of PEDOT: PSS (40 nm) was spin-cast on pre-cleaned ITO-coated glass at 3000 rpm for 30s. After baking at 150℃ for 15 min, the substrates were transferred into glovebox. J52: JC2 (1:1.5), J52-OMe: JC2 (1:1.2) and J52-F: JC2 (1:1.5) were all dissolved in CF at a total concentration of 16mg mL^{-1} for around 1 h. Afterwards, the active layers were all spin-coated with a speed of 3000 rpm for 30 s. Subsequently, they were separately annealed at 170 °C, 150 °C and 130 °C for 10 min. The interlayer PDINO (1.0 mg mL^{-1}) was spin-coated at 3000 rpm for 30 s. Finally, Al (80 nm) metal top electrode was thermal evaporated onto the active layer under about 3×10^{-4} Pa. The active area of the device was 0.04 cm^2 defined by shadow mask. The *J-V* measurements were conducted in glove box using the solar simulator (SS-F5-3A, Enlitech). The light intensity was calibrated with the standard silicon solar cell (SRC-2020). The EQE measurements were performed with the integrated system (QE-R, QE-R3011, Enlitech).

s-EQE and EL measurements: s-EQE measurements were carried out by an integrated system (PECT600, Enlitech). EL measurements were carried out by applying external voltage/current sources through the devices (REPS, Enlitech). All devices were prepared at their optimal conditions. The external voltage was carefully applied to obtain appropriate current density range: J52: JC2, J52-OMe: JC2 and J52-F: JC2 were conducted at 0-1.4 V, 0-1.5 V and 0-1.26 V, respectively.

Transient absorption measurement: TAS was conducted using a commercial fs-TAS system (HELIOS, Ultrafast Systems). The 800 nm pulse from a Coherent Astrella regenerative amplifier (80 fs, 1 kHz, 2.5 mJ per pulse), seeded by a Coherent Vitara-s oscillator (35 fs, 80 MHz), was used to pump an optical parametric amplifier (Coherent, OperA Solo) to generate excitation pulse at 680 nm. The pump beam was chopped at 500 Hz with pump fluence at 56.6 μJ cm^{-2}, while a small fraction of the 800 nm output from the Astrella was fed to a sapphire crystal in the HELIOS for generating the white light continuum (WLC). A 750 nm short pass filter (SPF) was placed in the probe path before the sample to filter out the residual 800 nm in the WLC.

Carrier Mobilities: The carrier mobilities of the polymers were investigated by the space charge limited current (SCLC) method. The hole mobility of the blend films was measured with the device structure of ITO/PEDOT:PSS/active layer (~100 nm)/Au (80 nm) while the electron mobility of the blends was measured with the device structure of ITO/TiOx/active layer (~100 nm)/Al (80 nm).

The SCLC model is described by modified Mott-Gurney law:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

where J stands for current density, ε_0 is the permittivity of free space (8.85×10^{-12} C V^{-1} m^{-1}), ε_r is the relative dielectric constant of the transport medium (assuming that of 3.0), μ is the carrier mobility, and L is the thickness of the active layer. V is the internal potential in the device, and $V=V_{app}-V_{bi}$, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (the V_{bi} values of hole-only and electron-only devices were all selected as 0 V).

AFM characterization: AFM height images were obtained on a Multimode 8HR at the tapping mode.

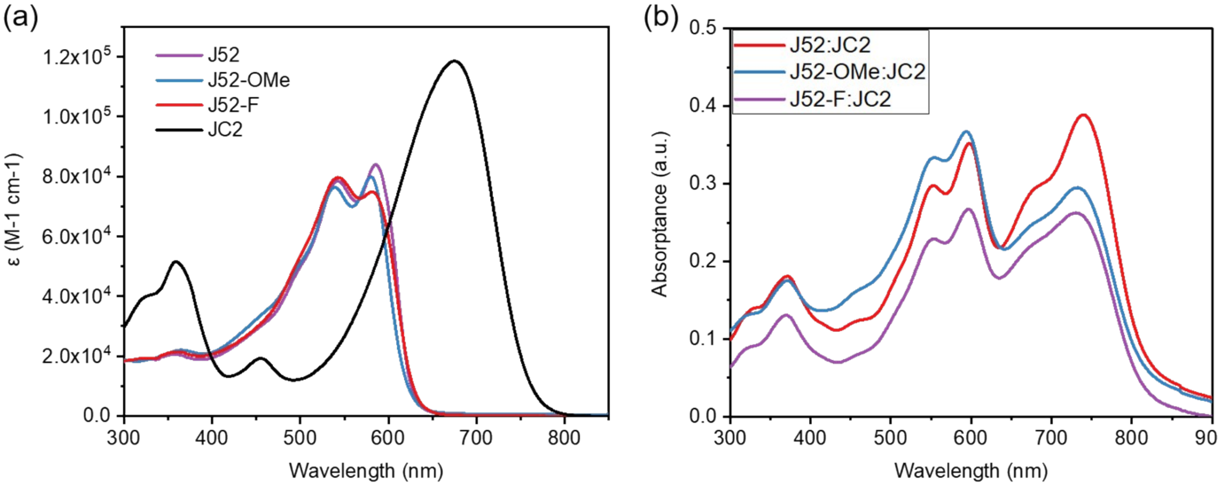


Figure S1. (a) The absorption spectra of polymers and JC2 in dilute chloroform solution. (b) The blend films absorption spectra, which were fabricated in their optimal device conditions. The calculated absorption coefficients of J52: JC2, J52-OMe: JC2 and J52-F: JC2 blend films are 3.50×10^4 cm^{-1}, 3.57×10^4 cm^{-1} and 2.67×10^4 cm^{-1}, respectively.

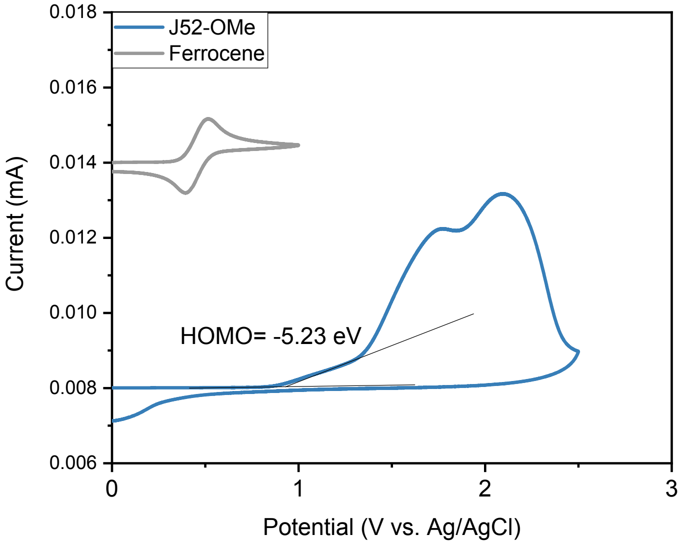


Figure S2. Cyclic voltammogram curves of J52-OMe and Fc/Fc$^+$ couple in 0.1M Bu$_4$NPF$_6$ acetonitrile solution *vs.* Ag/AgCl.

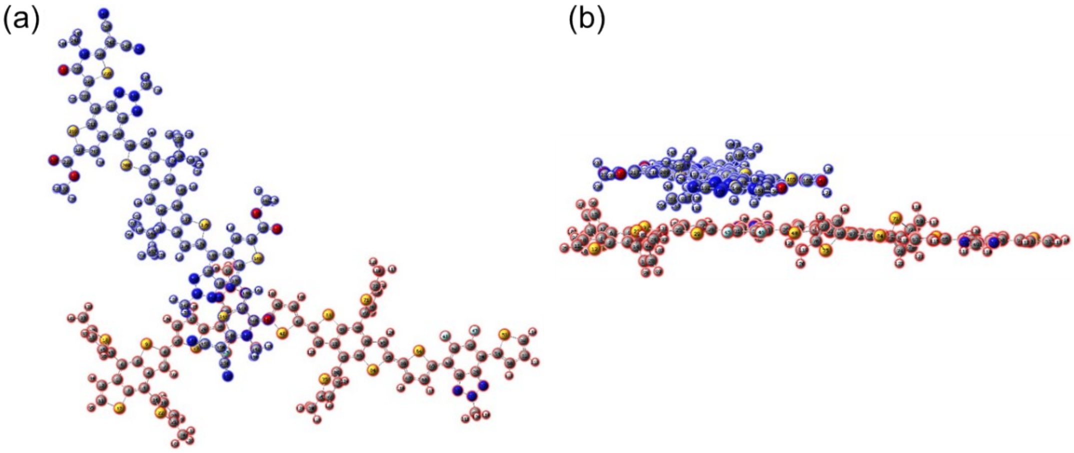


Figure S3. Initial geometry of the J52/JC2 complex with the benzene ring of in the middle BTA of J52 parallel to the rhodamine plane of JC2 and the inter-plane distance was set to 3.5 Å. (a) Top view and (b) side view.

Table S1. The photovoltaic performance of J52-X (X=H, OMe, F): JC2 under different donor: acceptor weight ratio. Note that the interlayer of J52:JC2 was used Ca.

Blends	D:A	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
J52:JC2	1:1	0.847	17.16	58.7	8.54
	1:1.5	0.847	17.56	60.0	8.91
	1:2	0.840	16.95	60.8	8.60
J52-OMe:JC2	1:1	0.995	16.92	56.4	9.49
	1:1.2	0.982	16.26	61.1	9.76
	1:1.5	0.987	15.50	59.0	9.03
J52-F:JC2	1:1.2	0.993	15.88	62.7	9.89
	1:1.5	0.991	18.05	63.9	11.44
	1:1.8	0.992	15.59	63.0	9.74

Table S2. The photovoltaic performance of J52-X (X=H, OMe, F): JC2 under different annealing temperature.

Blends	TA (℃)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
J52:JC2	130	0.836	17.88	60.4	9.03
	150	0.837	17.95	64.6	9.70
	170	0.850	19.04	63.5	10.27
	190	0.846	16.19	64.3	8.81
J52-OMe:JC2	130	0.982	16.26	61.1	9.76
	150	0.986	18.33	61.8	11.18
	170	0.981	16.94	62.9	10.45
	190	0.994	14.25	59.3	7.97

J52-F:JC2	110	0.994	15.71	62.2	10.40
	130	0.991	18.05	63.9	11.44
	150	0.987	14.31	68.1	9.62
	170	0.995	14.13	68.4	8.46

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(2) Bin, H.; Zhang, Z.-G.; Gao, L.; Chen, S.; Zhong, L.; Xue, L.; Yang, C.; Li, Y. Non-Fullerene Polymer Solar Cells Based on Alkylthio and Fluorine Substituted 2d-Conjugated Polymers Reach 9.5% Efficiency. *J. Am. Chem. Soc.* **2016**, *138* (13), 4657-4664.