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# **Supporting Information**

Low Nonradiative Energy Losses within 0.2 eV in Efficient Non-fullerene All-Small-Molecule Organic Solar Cells

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### 1. Materials and Synthesis

Scheme S1. Synthetic routes acceptors and donors



Compound 1-1 and compound1-2 were purchased from Hyper Chemical Company. Compound 2-1, compound 2-2 and compound 2-3 were purchased from Wuxi Seniormaterial Company. Compounds 4-1, 4-2 and 4-3 were synthesized according the literature,<sup>1, 2</sup> Compounds 5 was synthesized through the methods described in the literature<sup>1, 3</sup>. Unless noted, all other solvents and chemical regents were purchased from commercial sources and used without further purification. All reagents and chemicals were purchased from J&K, Aladdin, Alfa and used as received. Solvents and other common reagents were obtained from the Tianjing KangKeDe company. Chloroform was dry before use.

**Compound 3-1 (BTP-C11-N2Cl):** Compound 1-1 (300 mg; 0.263 mmol) and compound 2-1 (586 mg, 2.103 mmol) were dissolved into dry chloroform (60 mL) in a three-neck flask. The solution was flushed with nitrogen for 20 min. After 0.8 mL

pyridine were added, the resulting solution was refluxed and stirred for 12 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water and extracted several times with chloroform. Then the solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to yield BTP-C11-N2Cl as black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.28 (s, 2H), 9.17 (d, J = 30.5 Hz, 2H), 8.34 (d, J = 27.5 Hz, 2H), 8.13 – 7.93 (m, 4H), 7.70 – 7.60 (m, 2H), 4.79 (d, J = 7.2 Hz, 4H), 3.28 (s, 4H), 2.32 – 2.21 (m, 2H), 2.15 (s, 2H), 2.01 (d, J = 5.3 Hz, 2H), 1.90 (d, J = 6.8 Hz, 4H), 1.78 – 1.45 (m, 20H), 1.45 – 0.72 (m, 49H), 0.72 – 0.40 (m, 9H). <sup>13</sup>C NMR (101 MHz, CDCl3)  $\delta$  187.87, 147.49, 145.38, 137.82, 136.75, 136.37, 136.33, 136.02, 135.84, 135.71, 134.10, 131.36, 131.34, 130.88, 130.54, 128.73, 124.93, 122.35, 113.61, 67.29, 66.89, 31.92, 31.63, 31.22, 30.61, 30.55, 30.45, 29.86, 29.68, 29.64, 29.54, 29.50, 29.35, 22.85, 22.69, 22.55, 14.13, 13.83. MALDI-TOF MS (m/z): 1160.113

**Compound 3-2 (BTP-C9-N2F):** was synthesized by similar procedure as compound 3-1 use compound 1-2 and compound 2-2. The final product was obtained as black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.18 (d, *J* = 9.2 Hz, 2H), 9.07 (d, *J* = 34.9 Hz, 2H), 8.39 (d, *J* = 23.6 Hz, 2H), 8.17 – 8.00 (m, 2H), 7.67 (dd, *J* = 37.2, 8.1 Hz, 2H), 7.52 – 7.44 (m, 2H), 4.88 (d, *J* = 5.1 Hz, 4H), 3.19 (s, 4H), 2.28 (s, 2H), 1.87 (s, 4H), 1.61 (s, 4H), 1.52 (d, *J* = 5.6 Hz, 4H), 1.42 – 1.20 (m, 36H), 1.06 (s, 12H), 0.89 – 0.72 (m, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 188.15, 165.43, 163.34, 161.60, 156.89, 154.56, 152.17, 147.72, 137.56, 136.66, 135.92, 133.16, 132.68, 132.22, 124.13, 120.25, 118.19, 113.92, 113.88, 112.38, 112.05, 111.57, 111.16, 104.30, 58.90, 55.80, 39.18, 31.88, 31.62, 30.50, 30.40, 29.85, 29.48, 29.32, 27.89, 25.49, 22.67, 14.12, 13.77. MALDI-TOF MS (m/z): 1572.099

**Compound 3-3 (BTP-C9-N4F):** was synthesized by similar procedure as compound 3-1 use compound 1-2 and compound 2-3. The final product was obtained as black solid. <sup>1</sup>H NMR <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.22 (s, 2H), 9.08 (s, 2H), 8.34 (s, 2H), 7.82 (dd, J = 19.1, 10.9 Hz, 4H), 4.86 (d, J = 6.3 Hz, 4H), 3.23 (t, J = 7.1 Hz, 4H), 2.24 (s, 2H), 1.94 – 1.85 (m, 4H), 1.53 (t, J = 10.6 Hz, 4H), 1.26 (d, J = 27.7 Hz, 24H), 1.20 – 0.94 (m, 28H), 0.89 (t, J = 6.6 Hz, 6H), 0.73 (td, J = 14.4, 7.3 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  187.75, 169.90, 160.12, 153.98, 147.43, 145.41, 143.15, 137.88, 136.38, 135.73, 135.38, 134.10, 133.50, 132.53, 130.95, 125.45, 123.25,

122.13, 117.74, 116.37, 116.05, 115.69, 115.43, 113.71, 67.15, 55.84, 39.23, 31.87, 31.63, 31.24, 30.53, 30.43, 29.85, 29.48, 29.32, 28.06, 27.92, 25.53, 22.90, 22.86, 22.67, 22.53, 22.51, 14.12, 14.09, 14.07, 13.83, 13.79, 8.70. MALDI-TOF MS (m/z): 1608.106

Compound 6-1 (ZR1-C2): Compound 4-1 (200mg, 0.14mmol) and compound 5 (282mg, 1.3mmol) were dissolved in dry CHCl<sub>3</sub> (30 mL). After 3 drops of piperidine was added, the resulting solution was refluxed and stirred for 12 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, and extracted several times with chloroform. The organic phases were combined, washed with brine, and dried over anhydrous magnesium sulfate. Then the solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (CHCl3) to yield ZR2-C2 as black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 (s, 2H), 7.22 (dd, J = 11.9, 3.5 Hz, 4H), 7.18 – 7.01 (m, 6H), 6,86-6.84 (m, 2H), 4.10 - 3.90 (m, 4H), 3.14 - 2.97 (m, 4H), 2.82 - 2.63 (m, 4H), 1.85 (dd, J = 15.1, 6.8 Hz, 4H), 1.67-1.62 (m, 8H), 1.58 – 1.24 (m, 66H), 0.96 – 0.86 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl3) δ 191.71, 167.07, 148.73, 143.79, 143.16, 141.89, 139.43, 139.25, 136.40, 136.10, 133.96, 132.22, 129.40, 128.99, 128.67, 126.67, 125.87, 124.45, 122.77, 119.54, 115.90, 44.62, 37.16, 35.98, 33.66, 33.29, 32.05, 32.00, 31.26, 30.27, 30.12, 29.95, 29.63, 29.50, 29.03, 27.97, 26.81, 26.44, 23.30, 22.83, 22.54, 14.33, 14.24, 14.01. MALDI-TOF MS (m/z): 1839.0

**Compound 6-2 (ZR1-C3):** was synthesized by similar procedure as compound 6-1 use compound 4-2 and compound 5. The final product was obtained as black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (s, 2H), 7.21 (d, J = 2.8 Hz, 4H), 7.19 – 6.96 (m, 6H), 6.91 (s, 2H), 4.08 – 4.00 (m, 4H), 3.04 (t, J = 7.2 Hz, 4H), 2.75 (s, 4H), 1.85 (dt, J = 14.8, 7.4 Hz, 4H), 1.67-1.65 (m, 8H), 1.52 – 1.26 (m, 70H), 0.90-0.85 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl3)  $\delta$  191.83, 167.20, 143.90, 143.21, 142.05, 139.56, 136.60, 136.34, 134.16, 133.98, 132.41, 130.21, 129.60, 129.13, 128.68, 126.94, 126.10, 124.70, 123.02, 119.80, 116.10, 44.71, 33.86, 33.37, 33.20, 31.97, 31.34, 30.91, 30.20, 29.91, 29.45, 29.05, 28.87, 26.82, 26.45, 23.24, 22.79, 14.20. MALDI-TOF MS (m/z): 1879.3

**Compound 6-3 (ZR1-C4):** was synthesized by similar procedure as compound 6-1 use compound 4-3 and compound 5. The final product was obtained as black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.75 (s, 2H), 7.20 (d, J = 2.6 Hz, 4H), 7.14-7.06 (m, 6H), 6.89 (s, 2H), 4.06 – 4.00 (m, 4H), 3.07 (t, J = 7.2 Hz, 4H), 2.74 (s, 4H), 1.91 – 1.83 (m, 4H), 1.68-1.63 (m, 8H), 1.60 – 1.27 (m, 74H), 0.91 – 0.86 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl3)  $\delta$  191.77, 167.12, 148.44, 143.85, 143.16, 141.94, 139.42, 136.15, 133.98, 129.56, 128.67, 126.72, 126.02, 124.56, 122.87, 119.68, 115.93, 44.66, 37.48, 33.78, 33.52, 33.42, 32.39, 32.05, 32.00, 31.28, 30.56, 29.93, 29.61, 29.47, 29.03, 26.83, 26.79, 26.43, 23.27, 22.79, 22.53, 14.29, 14.01. MALDI-TOF MS (m/z): 1894.1

#### 2. Fabrication and Characterization

## Molecular properties characterization

<sup>1</sup>H NMR was obtained on a Bruker Avance III 400 NMR Spectrometer (operating at 400 MHz, using CDCl<sub>3</sub> as solvent using tetramethylsilane as internal standard). Mass spectra were measured by Bruker microflex MALDI-TOF mass spectrometer. The UV-vis absorption was measured by Shimadzu UV-3600 spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted an electrochemical workstation (VMP3 Biologic, France) with a Pt disk coated with blend film, a Pt plate, and an Ag<sup>+</sup>/Ag electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1 mol/L tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution. The experiments were calibrated with the standard ferrocene/ferrocenium (Fe) redox system and assumption that the energy level of Fe is 4.8 eV below vacuum.

### **Device Fabrication**

The photovoltaic devices were fabricated with a conventional structure of glass/ITO/PEDOT:PSS/active layer/Ag architecture. The 1.5cm×1.5cm ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent solution, DI water, ethanol and isopropyl alcohol for 20 min respectively. A hole transporting layer of PEDOT:PSS was spin-coated at 3500 r.p.m. onto the ITO surface before baking at

150 °C for 15 min. Subsequently, the weighted amount of donors and acceptors with a weight ratio of 1:0.5 were dissolved in chloroform at a concentration of 15mg/mL and stirred at 50°C for approximately 30 min before spin-coated upon PEDOT:PSS inside nitrogen-filled glove box. Finally, a layer of 160 nm Ag layer was deposited on top of active layer via vacuum vapor deposition (cal.  $1 \times 10-5$  Pa), serving as top electrode. Hole and electron mobility measurements blend films were realized by space-charge limited current (SCLC) method with the following devoice structures: ITO/PEDOT:PSS/active layer/ MoOx/Ag for holes and ITO/ZnO/active layer/PFN-Br/Al for electrons. The active layers for these two devices were spin-coated under the same condition as that of optimized solar cells

#### Photovoltaic performance Characterization

J–V curves measurements were conducted under AM 1.5 G (100mWcm–2) by Newport Thermal Oriel 91159A solar simulator, with Newport Oriel PN 91150 V Sibased solar cell as light intensity calibration reference. Signals of J–V measurements were recorded by a Keithley 2400 source-measure unit. EQE tests were conducted by Oriel Newport system (Model 66902) with a standard Si diode.

The current density-voltage (J-V) curves in the range of 0-5 V were obtained by a Keithley 2420 Source-Measure Unit in the dark. Mobility could be calculated by fitting the results in the equation:

$$J = \frac{9}{8L^3} \varepsilon_r \varepsilon \mu V^2 exp \left( 0.89 \sqrt{\frac{V}{E_0 L}} \right)$$

where J is the current density, L is the thickness of active layer,  $\mu$  is the constant mobility,  $\varepsilon_0\varepsilon_r$  is the dielectric permittivity of the active layer and V is the internal voltage in the device.  $V = V_{appl} - V_r - V_{bi}$ , where  $V_{appl}$  is the voltage applied to the device,  $V_r$  is the voltage drop caused by the contact resistance and series resistance across the electrodes, and  $V_{bi}$  is the built-in voltage resulting from the relative work function difference of the two electrodes.

# **Morphology Characterization**

Transmission electron microscopy (TEM) images were obtained by a Tecnai G2 F20 UTWIN TEM instrument. Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were conducted at XEUSS SAXS/WAXS equipment. Atomic force microscopy (AFM) images of the blend films were obtained from the devices directly on a VEECO Dimension 3100 atomic force microscope working under tapping mode.

## 3. Tables and Figures

**Table S1.** Optimized photovoltaic parameters of devices under the illumination ofAM 1.5 G, 100 mW/cm².

Active layers	$V_{OC}(V)$	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
ZR1: Y6	0.861	24.34	68.44	14.34
ZR1-C2: Y6	0.842	23.27	70.45	13.80
ZR1-C3: Y6	0.844	24.55	72.92	15.12
ZR1-C4: Y6	0.852	23.57	69.23	13.90

**Fig. S1.**  $J^{1/2}$ -V curves of (a) electron-only and (b) hole-only devices. (c)  $J_{ph}$  versus  $V_{eff}$  curve of optimized devices.



**Fig. S2.** GIWAXS pattern for pristine (a) ZR1-C3, (b) BTP-C11-N2Cl, (c) BTP-C9-N2F and (d) BTP-C9-N4F. (e) In-plane and (f) out-of-plane line cuts of the corresponding 2D-GIWAXS pattern.



Fig. S3. GIWAXS pattern for (a) ZR1-C3: BTP-C11-N2Cl, (b) ZR1-C3: BTP-C9-N2F, and (c) BTP-C9-N2F blend films without thermal annealing. (d) In-plane and (e) out-of-plane line cuts of corresponding GIWAXS pattern.



Table S2. Summarized GIWAXS data of pristine films.

Materials	(010)				_	(100)			
	q	d-spacing	FWHM	CCL		q	d-spacing	FWHM	CCL
ZR1-C3	1.772	3.546	0.130	42.986		0.272	23.068	0.026	215.161
BTP-C11-N2Cl	1.719	3.656	0.368	15.290		0.389	16.170	0.107	52.053
BTP-C9-N2F	1.725	3.643	0.367	15.247		0.399	15.764	0.080	69.988
BTP-C9-N4F	1.726	3.639	0.370	15.095		0.393	15.990	0.099	56.737

D: A	(010)					(100)				
	q	d-spacing	FWHM	CCL		q	d-spacing	FWHM	CCL	
ZR1-C3:	1.754	3.582	0.182	30.704		0.267	23.496	0.047	119.233	
BTP-C11-N2Cl										
ZR1-C3:	1.762	3.566	0.185	30.291		0.268	23.487	0.052	107.746	
BTP-C9-N2F										
ZR1-C3:	1.760	3.569	0.187	29.826		0.270	23.268	0.045	123.335	
BTP-C9-N4F										

Table S3. Summarized GIWAXS data of blend films.

Fig. S4. EL quantum efficiency of optimal blend films at different injected currents.





a) <sup>1</sup>H NMR spectrum of BTP-C11-N2Cl.



b) <sup>1</sup>H NMR spectrum of BTP-C9-N2F.



c) <sup>1</sup>H NMR spectrum of BTP-C9-N4F.



d) <sup>1</sup>H NMR spectrum of ZR1-C2



e) <sup>1</sup>H NMR spectrum of ZR1-C3



f) <sup>1</sup>H NMR spectrum of ZR1-C4

Figure S6. <sup>13</sup>C NMR



a) <sup>13</sup>C NMR spectrum of BTP-C11-N2Cl.



b) <sup>13</sup>C NMR spectrum of BTP-C9-N2F.



c) <sup>13</sup>C NMR spectrum of BTP-C9-N4F.



d) <sup>13</sup>C NMR spectrum of ZR1-C2



e) <sup>13</sup>C NMR spectrum of ZR1-C3



f) <sup>13</sup>C NMR spectrum of ZR1-C4

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