# **Supporting Information**

# Naphthodifuran-Based Zigzag-Type Polycyclic Arene with Conjugated Side

# **Chains for efficient photovoltaics**

Hongjian Peng<sup>a</sup>, Xiangfeng Luan<sup>a</sup>, Liuliu Feng<sup>a</sup>, Jun Yuan<sup>a\*</sup>, Zhi-Guo Zhang<sup>b</sup>, Yongfang Li<sup>b</sup> and Yingping Zou<sup>a\*</sup>

a. College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China. E-mail: yingpingzou@csu.edu.cn(Y.Zou); amani323@sina.com (J.Yuan)

b. Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

#### Characterization

NMR spectra were recorded using a Bruker AV-500 spectrometer in deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts were reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. Molecular weights and polydispersity indices of the polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3 and HT4) using THF (HPLC grade) as eluent at a flow rate of 1.0 mL/min at 35 °C. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K/min under nitrogen. UV-Vis absorption spectra were recorded on SHIMADZU UV-2600 spectrophotometer. For the solid state measurements, polymer solution in chloroform was spin-coated on quartz plates. The cyclic voltammetry was recorded with a computer controlled CHI660E electrochemical workstation using polymer films on platinum electrode (1.0  $cm^2$ ) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile at a scanning rate of 50 mV·s<sup>-1</sup>. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. The morphologies of the polymer/PC<sub>71</sub>BM blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 5 µm scanner. Transmission electron microscope (TEM) measurements were performed in a JEM-2100F. The crystal structures of the power were confirmed using x-ray power diffraction (XRD, Rigaku-TTRⅢ).

# Fabrication and characterization of polymer solar cells.

The PSCs were fabricated with an indium tin oxide (ITO) glass as positive electrode and a ETLs/Al as negative electrode. Patterned ITO glass with a sheet resistance of 10  $\Omega$ /sq was purchased from CSG HOLDING Co. LTD. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. Then PEDOT:PSS (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)) (Baytron PVP Al 4083, Germany) was filtered through a 0.45 µm poly(tetrafluoroethylene) (PTFE) filter and spin coated at 3000 rpm for 40 s on the ITO substrate. Subsequently, PEDOT: PSS film was baked at 150 °C for 15 min in the air, and the thickness of the PEDOT:PSS layer is about 40 nm. The polymers and PC<sub>71</sub>BM (10 mg/mL for polymers) were dissolved in o-DCB and 0.25% volume ratio of 1,8diiodooctane (DIO, Sigma Aldrich) overnight and spin-cast at 2500 rpm for 90 s onto the PEDOT:PSS layer. The thickness of the photoactive layer is about 110 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisting of ETLs (~15 nm) capping with Al (~40 nm) was thermal evaporated under a shadow mask with a base pressure of ca.  $10^{-5}$  Pa. The active area of the PSCs is 5 mm<sup>2</sup>. The ETLs were simply prepared by spin-coating its water/ethanol solution (1 mg mL<sup>-1</sup>) on photoactive layer at 3000 rpm for 30 s at room temperature, no thermal annealing or any other post-treatment was performed. Finally, top electrodes were deposited in a vacuum onto the active layer.

Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW cm<sup>-2</sup> (Oriel 67005, 500 W), calibrating by a standard silicon cell. *J-V* curves were recorded with a Keithley 236 digital source meter. A xenon lamp with AM 1.5 filter was used as the white light source and the optical power was 100 mW cm<sup>-2</sup>. The EQE measurements of PSCs were performed by Stanford Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. All of these fabrications and characterizations were conducted in a glove box.

# Materials and synthesis

Tetrakis(triphenylphosphine)palladium(Pd(PPh<sub>3</sub>)<sub>4</sub>),bis(triphenylphosphine)palladium(II),dichloride(PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>), n-butyllithium (n-BuLi) and Sn(CH<sub>3</sub>)<sub>3</sub>Cl were obtained from J&K, and they were all used as received. Toluene was dried over  $P_2O_5$  and freshly distilled prior to use. All other reagents and solvents were purchased commercially as analytically pure and used without further purification. 1,5-Bis (2,2-diethoxyethoxy) naphthalene (1), 1,5-dibromo-4,8-bis(2,2diethoxyethoxy)naphthalene (2), 5,10-dibromonaphtho[1,2-b:5,6-b']difuran (3) were synthesized according to previous literatures.<sup>1</sup> M2 and M3 were prepared according to the reported procedures. <sup>2-4</sup>

# (4-((2-ethylhexyl)oxy)phenyl) tributyl stannane

1-Bromo-4-((2-ethylhexyl)oxy)benzene (8.85 g, 31 mmol) was dissolved in 50 mL of dry THF and cooled to -78 °C. n-BuLi (13.65 mL, 2.5 M solution in hexane) was added under N<sub>2</sub> and stirred for 1h. To this solution, 11.11 g (34.13 mmol) of tributyltinchloride was added dropwisely at -78 °C. The temperature was slowly raised to room temperature and stirred overnight. The reaction mixture was quenched with water and then extracted with dichloromethane. Removal of the solvent and dried under vacuum at 50 °C overnight to give a pale yellow oil and the product was used directly in the next step without further purification.

#### 4,9-bis(4-((2-ethylhexyl)oxy)phenyl)naphtho[1,2-b:5,6-b']difuran(4)

Above obtained (4-((2-ethylhexyl)oxy)phenyl)tributyl stannane was added to a solution of 3 (0.62 g, 1.69 mmol) in anhydrous toluene (20 mL). The mixture was purged with nitrogen for 20 min and bis(triphenylphosphine)palladium(II) dichloride (0.24 g, 0.34 mmol) was then added. The reaction was heated at 100 °C for 24 h. The mixture was poured into water and extracted with dichloromethane. The solvent was removed in vacuum and the crude product was further purified by column chromatography on silica gel using petroleum ether/dichloromethane (4:1, v/v) as the eluent to obtain a white solid (0.62 g, 61.3 %).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.65 (s, 2H), 7.48 (d, J = 0.7 Hz, 2H), 7.45 (d, J = 8.3 Hz, 4H), 7.04 (d, J = 8.3 Hz, 4H), 6.83 (d, J = 0.7 Hz, 2H), 3.99 (d, J = 5.8 Hz, 4H), 1.83 (dq, J = 12.2, 6.0 Hz, 2H), 1.64 – 1.35 (m, 16H), 1.04 – 0.93 (m, 12H).

# (4,9-bis(4-((2-ethylpentyl)oxy)phenyl)naphtho[1,2-b:5,6-b']difuran-2,7-

#### diyl)bis(trimethyl)stannane (M1)

4,9-Bis(4-((2-ethylhexyl)oxy)phenyl)naphtho[1,2-b:5,6-b']difuran 4 (1.06 g, 1.62 mmol) was added to anhydrous tetrahydrofuran (80 mL) in a three-necked flask under a nitrogen atmosphere. The solution was cooled to -78 °C and n-butyllithium (2.36 mL, 2.4 M, 5.68 mmol) was added dropwisely. The mixture was stirred at -78 °C for 1h, and then trimethyltin chloride (6.48 mL, 1.0 M, 6.48 mmol) was added in one portion. The cooling bath was removed and the reaction mixture was stirred at ambient temperature overnight. Finally it was poured into 100 mL iced water and extracted by dichloromethane. The organic layer was washed by water three times, then dried by anhydrous MgSO<sub>4</sub> and evaporated to give a crude product. The residue was further purified by recrystallization from methanol to afford the target compound 7a as pale yellow solid (0.78 g, 50.9%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 (s, 2H), 7.42 – 7.40 (m, 4H), 7.01 – 6.99 (m, 4H), 6.98 (s, 2H), 3.97 (dd, J = 5.6, 1.8 Hz, 4H), 1.82 (dq, J = 12.2, 6.1 Hz, 2H), 1.69 – 1.36 (m, 16H), 1.04 – 0.93 (m,

# 12H), 0.32 – 0.15 (m, 18H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.65, 158.38, 154.61, 136.02, 132.32, 131.02, 130.96, 123.61, 121.78, 117.88, 117.44, 113.46, 113.26, 70.62, 70.23, 39.57, 30.69, 30.64, 29.18, 24.02, 23.97, 23.13, 14.15, 11.22.

#### Synthesis of PzNDFP-BT

M1 (0.14 g, 0.15 mmol), M2 (0.11 g, 0.15 mmol) were added to anhydrous toluene (12 mL) in a two-necked flask. The mixture was purged with nitrogen for 20 min, then Pd(PPh<sub>3</sub>)<sub>4</sub> (15 mg) was added into the flask. The mixture was refluxed for 24 h at 110 °C and then cooled down to room temperature. Then the reaction mixture was poured into methanol (200 mL) slowly. The resulting precipitate was filtered through a filter parer, which was then subjected to Soxhlet extractions with methanol, hexane and acetone. Finally the polymer was extracted from the chloroform fraction by rotary evaporation. The dark - purple solid was obtained (0.115 g, yield: 64%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.45 (s, 2H), 7.52 (s, 2H), 7.13 (s, 4H), 7.69-6.75 (br, 8H), 4.29-3.86 (br, 8H), 2.21–1.92 (m, 2H), 1.54-0.89 (m, 58H).

# Synthesis of PzNDFP-ffQx

**PzNDFP**–*ff***Qx** was synthesized by the similar method starting from M1 (0.14 g, 0.15 mmol) and M3 (0.14 g, 0.15 mmol). Finally, the green-black solid was obtained (0.128 g, yield: 62%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.03 (s, 2H), 7.45 (s, 2H), 6.92 (s, 4H), 7.75-6.52 (br, 14H), 4.39-3.62 (br, 8H), 2.31–1.72 (m, 4H), 1.54-0.89 (m, 56H).



Fig. S1 <sup>1</sup>H NMR spectrum of 4,9-bis(4-((2-ethylhexyl)oxy)phenyl)naphtho[1,2-b:5,6-b']difuran



**Fig. S2** <sup>1</sup>H NMR spectrum of (4,9-bis(4-((2-ethylpentyl)oxy)phenyl)naphtho[1,2-b:5,6-b']difuran-2,7-diyl)-bis(trimethyl)stannane



**Fig. S3** <sup>1</sup>C NMR spectrum of (4,9-bis(4-((2-ethylpentyl)oxy)phenyl)naphtho[1,2-b:5,6-b']difuran-2,7-diyl)-bis(trimethyl)stannane



Fig. S4 <sup>1</sup>H NMR spectrum of PzNDFP-BT



Fig. S5 <sup>1</sup>H NMR spectrum of PzNDFP-ffQx



Fig. S6 TGA curves of the polymers with a heating rate of 20K min<sup>-1</sup>



Fig. S7 XRD patterns of polymer:PC71BM blend films without or with DIO

Polymer	M <sub>n</sub>	$M_{ m w}$	PDI	Yield	
	(kDa)	(kDa)		(%)	
PzNDFP-BT	13	24	1.85	64	
PzNDFP- <i>ff</i> Qx	12	23	1.92	62	

Table S1 Molecular weights and thermal properties of the copolymers.

**Table S2** The device parameters of PSCs based on polymer:  $PC_{71}BM$  with different cathode and ratio DIO under illumination of AM 1.5G,100 mW cm<sup>-2</sup>.

 $T_d$ 

(°C)

314

339

Active layer	V <sub>oc</sub> (V)	$J_{\rm sc}$ (mA cm <sup>-</sup> <sup>2</sup> )	FF (%)	PCE (%)
<b>PzNDFP-BT</b> :PC <sub>71</sub> BM (1.5:1) <sup>a</sup>	0.87	6.18	36	1.9
<b>PzNDFP-BT</b> :PC <sub>71</sub> BM (1.5:1) <sup>a</sup> (0.25% DIO)	0.88	9.53	53	4.5
<b>PzNDFP-BT</b> :PC <sub>71</sub> BM (1.5:1) <sup>a</sup> (0.5% DIO)	0.86	8.93	55	4.2
<b>PzNDFP-BT</b> :PC <sub>71</sub> BM (1:1) <sup>a</sup>	0.88	7.50	34	2.2
PzNDFP-BT:PC <sub>71</sub> BM (1:1) <sup>a</sup> (0.25% DIO)	0.85	9.82	61	5.1
<b>PzNDFP-BT</b> :PC <sub>71</sub> BM (1:1) <sup>c</sup>	0.87	7.38	36	2.3
<b>PzNDFP-BT</b> :PC <sub>71</sub> BM (1:1.5) <sup>a</sup>	0.85	7.38	33	2.1
<b>PzNDFP-BT</b> :PC <sub>71</sub> BM (1:1.5) <sup>a</sup> (0.25% DIO)	0.86	11.1	72	6.9
PzNDFP-BT:PC <sub>71</sub> BM (1:1.5) <sup>b</sup> (0.25% DIO)	0.86	11.2	71	6.8
<b>PzNDFP-</b> <i>ff</i> <b>Qx</b> :PC <sub>71</sub> BM (1.5:1) <sup>a</sup>	0.82	4.19	53	1.8
PzNDFP-ffQx:PC71BM (1.5:1) <sup>a</sup> (0.25%DIO)	0.75	9.97	38	2.8
PzNDFP-ffQx:PC71BM (1:1) <sup>a</sup>	0.83	3.98	55	1.8
PzNDFP-ffQx:PC71BM (1:1) <sup>a</sup> (0.25% DIO)	0.79	10.92	45	3.9
<b>PzNDFP-ffQx</b> :PC <sub>71</sub> BM (1:1.5) <sup>a</sup>	0.87	5.59	59	2.9
<b>PzNDFP-ffQx</b> :PC <sub>71</sub> BM (1:1.5) <sup>a</sup> (0.25% DIO)	0.83	12.21	55	5.6

<sup>a</sup>The cathode interlayer is PDINO.

<sup>b</sup>The cathode interlayer is ZrAcac.

°With thermal annealing at 90 °C for 10 min.

## References

1. Li, S.; Yuan, Z.; Deng, P.; Sun, B.; Zhang, Q. *Polymer Chemistry* **2014**, 5, (7), 2561.

2. Liu, B.; Chen, X.; Zou, Y.; Xiao, L.; Xu, X.; He, Y.; Li, L.; Li, Y. *Macromolecules* **2012**, 45, (17), 6898-6905.

3. Ding, P.; Zhong, C.; Zou, Y.; Pan, C.; Wu, H.; Cao, Y. *The Journal of Physical Chemistry C* **2011**, 115, (32), 16211-16219.

4. Jiang, J.-M.; Lin, H.-K.; Lin, Y.-C.; Chen, H.-C.; Lan, S.-C.; Chang, C.-K.; Wei, K.-H. *Macromolecules* **2014**, 47, (1), 70-78.