

## Supporting Information

### All-Polymer Solar Cells Based on A Novel Narrow-Bandgap Polymer Acceptor with Power Conversion Efficiency Over 10%

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### Materials

The polymer donor PM6<sup>1</sup> and IC-Br<sup>2</sup> were synthesized according to the procedure reported in the literatures. PM6 exhibits a number average molecular weight (M<sub>n</sub>) of 38.9 KDa with a polydispersity index (PDI) of 2.0, measured by high temperature Gel permeation chromatography (GPC) with 1,2,4-trichlorobenzene as the eluent and polystyrene as a standard at 160 °C. The other chemicals and solvents were purchased from J&K, Alfa Aesar and TCI Chemical Co. respectively. The monomer MOITIC16-Br, and polymer PN1 were synthesized according to Scheme S1.

### MOIT16-CHO

Compound MOIT16 (1.00 g, 0.61 mmol) and 30 mL dry THF were mixed at -78 °C under argon protection, and 0.65 mL of nbutyllithium (1.52 mmol, 2.4 M in hexane) was slowly added dropwise. The reaction mixture was then stirred at -78 °C for 1 h and at RT for 1 h. Subsequently, N,N-dimethylformamide (0.30 mL) was added and the mixture was stirred overnight at RT. Then, the mixture was extracted with CHCl<sub>3</sub>, and the combined organic phase was washed with brine three times. The resulting crude compound was purified by using silica gel to give a yellow solid (620 mg, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS), δ(ppm): δ 9.88 (s, 2H), 7.93 (s, 2H), 7.64 (s, 2H), 7.18 (t, 4H), 6.85 – 6.73 (m, 12H), 3.74 (d,

8H), 1.70 (s, 4H), 1.23 (s, 96H), 0.85 (d, 24H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ),  $\delta(\text{ppm})$ :  $\delta$  182.55 (s), 159.69 (s), 154.01 (s), 149.64 (s), 146.06 (s), 145.66 (s), 144.41 (s), 143.21 (s), 141.75 (s), 140.03 (s), 136.40 (s), 129.60 (s), 120.03 (s), 118.14 (s), 114.98 (s), 113.19 (s), 71.11 (s), 37.81 (s), 31.82 (d), 31.20 (s), 29.98 (d), 29.94 – 29.46 (m), 29.31 (s), 26.99 – 26.57 (m), 22.65 (s), 14.09 (s). MALDI-TOF-MS  $m/z$ : $[M]$  calcd. for  $\text{C}_{110}\text{H}_{154}\text{O}_6\text{S}_4$ , 1700.68; found 1700.15.

### **MOITIC16-Br**

In a dry 50 mL flask, compounds MOIT16-CHO (0.30 g, 0.18 mmol), IC-Br (0.24 g, 0.88 mmol) and pyridine (1 mL) were added to a solution of 20 mL degassed  $\text{CHCl}_3$  under nitrogen and stirred vigorously at  $65^\circ\text{C}$  for 8 h. Then the mixture was poured into methanol (140 mL) and a precipitate was formed and collected. The resulting crude compound was purified by using silica gel to give a black solid (0.23g, 60%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS),  $\delta(\text{ppm})$ :  $\delta$  8.90 (s, 2H), 8.82 (s, 1H), 8.54 (d, 1H), 8.15 (s, 2H), 7.97 (s, 1H), 7.86 (d, 2H), 7.71 (d, 1H), 7.67 (s, 2H), 7.21 (t, 4H), 6.91 (s, 4H), 6.82 (t, 8H), 3.83 (s, 8H), 1.72 (s, 4H), 1.22 (d, 96H), 0.82 (dd, 24H). MALDI-TOF-MS  $m/z$ : $[M]$  calcd. for  $\text{C}_{134}\text{H}_{160}\text{Br}_2\text{N}_4\text{O}_6\text{S}_4$ , 2210.82; found 2211.2.

### **PN1**

MOITIC16-Br (224 mg, 0.10 mmol) and 2,5-bis(trimethylstannyl)thiophene (39.5 mg, 0.10 mmol) and dry toluene (10 mL) were added to a 25 mL double-neck round-bottom flask. The reaction container was purged with argon for 20 min, and then  $\text{Pd}(\text{PPh}_3)_4$  (10 mg) was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 12 h. The reactant was cooled down to room temperature and poured into MeOH (200 mL), then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol,

hexane, and chloroform. The polymer PN1 of 170 mg (Yield 77%) was recovered as solid from the chloroform fraction by precipitation from methanol, and was dried under vacuum.

## **Experimental Section**

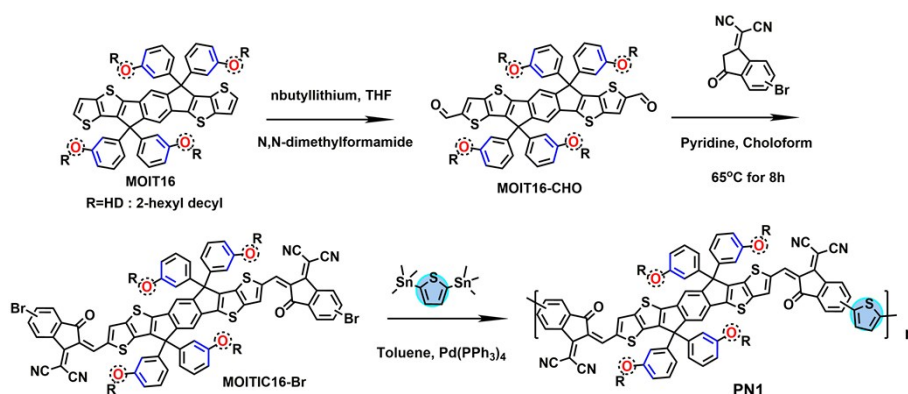
*Measurements:*  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured in  $\text{CDCl}_3$  on Bruker AV 400 MHz FT-NMR spectrometer. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. UV-vis absorption spectrum was recorded on a UV-Vis-NIR Spectrophotometer of Agilent Technologies Cary Series, in which the extinction coefficient was defined by the absorption intensity of the active layer with a thick of 1 cm (ca. 100 nm for PN1). Cyclic voltammetry (CV) was performed on a Zahner Zennium IM6 electrochemical workstation with a three-electrode system in 0.1 mol L<sup>-1</sup>  $\text{Bu}_4\text{NPF}_6$  acetonitrile solutions at a scan rate of 50 mV s<sup>-1</sup>. The three-electrode system included glassy carbon disk, platinum wire and Ag/Ag<sup>+</sup> electrode as the working electrode, counter electrode and reference electrode, respectively. The potential of the Ag/Ag<sup>+</sup> reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>), and the Ag/Ag<sup>+</sup> reference electrode possessed an energy level of 4.73 eV. The molecular weight of the polymer was measured by the GPC method with polystyrene as the standard and 1, 2, 4-trichlorobenzene as the solvent at 160 °C using Agilent Technologies PL-GPC220. Photoluminescence (PL) spectra were taken on an Edinburgh Instrument FLS 980. Thermogravimetric analysis (TGA) was measured on TGA/DSC 3+ from METTLER TOLEDO using STARe Software at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, where the Donor: PN1 films were prepared by the following processing

techniques for the TEM measurement: The Donor:PN1 films were spin-cast on the ITO/PEDOT:PSS substrates, and then the resulting substrates with the Donor:PN1 films were submerged in deionized water to make these Donor:PN1 films float onto the water/air interface, and finally the floated Donor:PN1 films were picked up on unsupported 200 mesh copper grids. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source.<sup>1</sup> Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. The crystal coherence length (CCL) was defined as  $CCL = 0.9 \times (2\pi/\text{FWHM})$  (Å), where FWHM is the full width at half maximum of the corresponding diffraction peak.

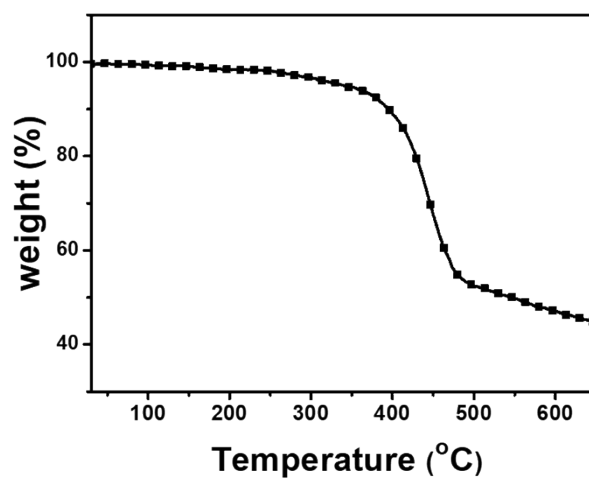
#### **Fabrication and characterization of all-polymer solar cells.**

The PSC devices structure was ITO/PEDOT:PSS/active layer/ZnO/Al. In an ultrasonic bath, the ITO-coated glass (10 Ω/sq) was cleaned with deionized water, acetone and isopropanol, respectively. After oxygen plasma cleaning for 10 min, and then a 30 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 °C for 15 min. In a nitrogen glove box containing less than 5 ppm moisture and oxygen, the active layers were then deposited atop the PEDOT:PSS layer by spin-coating a CB solution of PM6:acceptor (w:w, 1.5:1) with a blend concentration of 17 mg/mL. The thickness of the active layers was about 100 nm and controlled by adjusting the spin speed during the spin-coating process and measured by a KLA Tencor D-100 profilometer. The nanoparticle ZnO was then deposited on top of the active layer. Finally, 100 nm Al was evaporated on the photoactive layer under vacuum at a pressure of ca.  $4 \times 10^{-4}$  Pa, and through a shadow mask

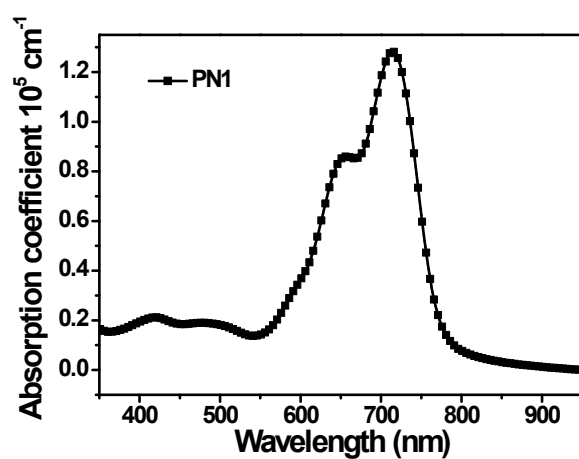
to determine the active area of the devices ( $\sim 2 \times 2 \text{ mm}^2$ ). The PCE values of the PSCs were measured under a illumination of AM 1.5G ( $100 \text{ mW/cm}^2$ ) using a SS-F5-3A solar simulator (AAA grade,  $50 \times 50 \text{ mm}^2$  photobeam size) of Enli Technology CO, Ltd. A  $2 \times 2 \text{ cm}^2$  monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO, Ltd. PCE statistics were obtained using 15 individual devices fabricated under the same conditions. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 of Enli Technology CO, Ltd. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell. To study the charge generation and dissociation processes of the PSCs, plots of the photocurrent ( $J_{ph}$ ) versus effective voltage ( $V_{eff}$ ) of the PSCs were measured. Here,  $J_{ph}$  and  $V_{eff}$  are defined as  $J_{ph} = J_L - J_D$  and  $V_{eff} = V_0 - V_{appl}$ , respectively, where  $J_D$  and  $J_L$  are the photocurrent densities in the dark and under the illumination, and  $V_{appl}$  is the applied bias voltage and  $V_0$  is the voltage at which  $J_{ph} = 0$ , respectively. The  $J_{ph}$  reaches the saturation current density ( $J_{sat}$ ) at high  $V_{eff}$  ( $\geq 2 \text{ V}$  in this case).



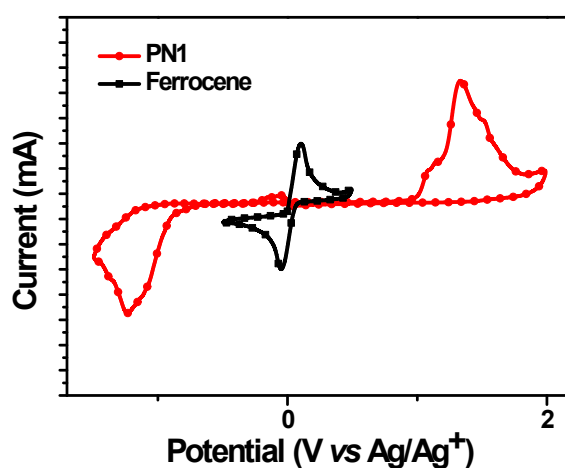
**Scheme S1.** Synthetic routes for the polymer acceptor PN1.



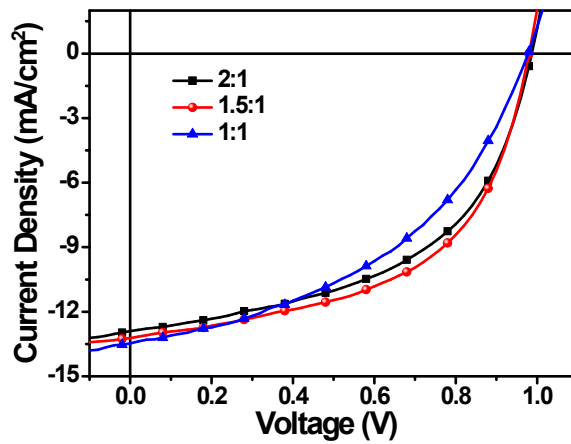
**Fig. S1.** Thermogravimetric analysis (TGA) curves of PN1.



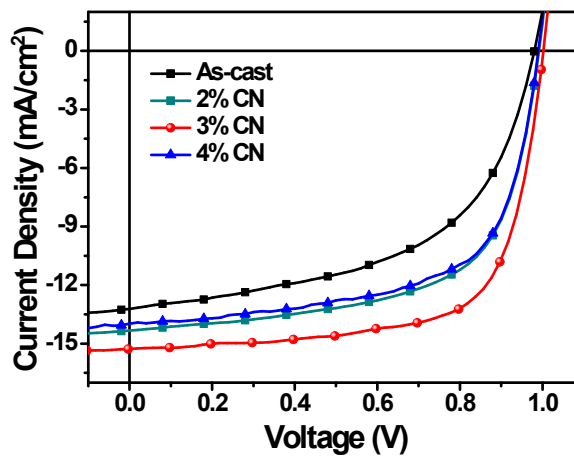
**Fig. S2.** The absorption coefficient of PN1 films.



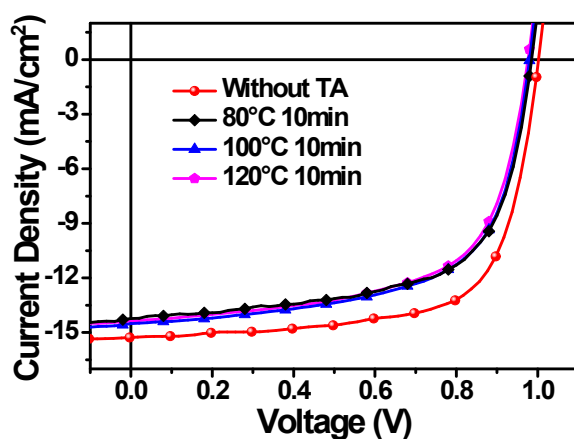
**Fig. S3.** Cyclic voltammograms of PN1 films on a glassy carbon electrode measured in a 0.1 mol/L  $\text{Bu}_4\text{NPF}_6$  acetonitrile solution at a scan rate of 50 mV/s.



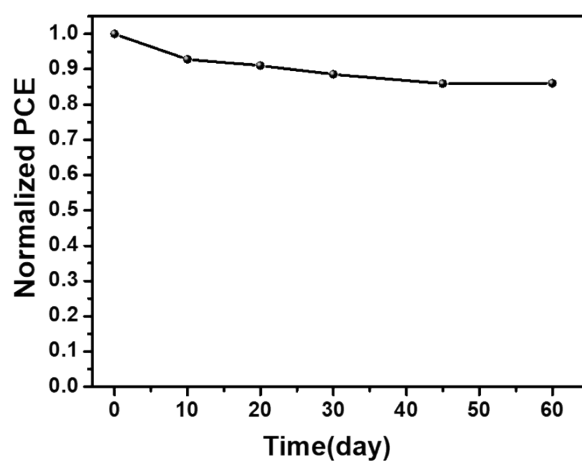
**Fig. S4.** The  $J$ - $V$  characteristics of the all-PSCs based on PM6:PN1 at different D/A weight ratios without post under the irradiation of AM 1.5G, 100 mW/cm<sup>2</sup>.



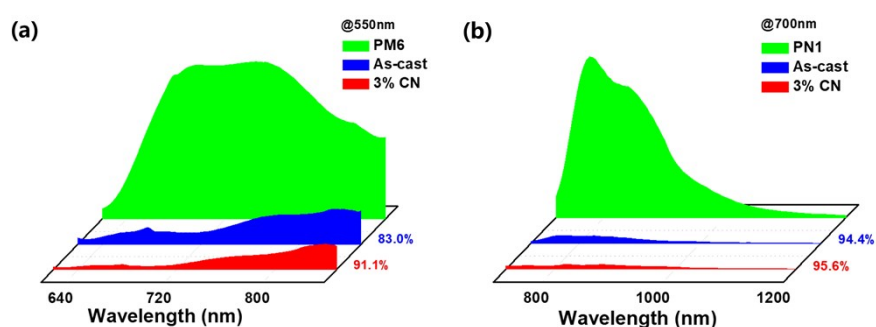
**Fig. S5.** The  $J$ - $V$  characteristics of the all-PSCs based on PM6:PN1 with different contents of CN under the irradiation of AM 1.5G, 100 mW/cm<sup>2</sup>.



**Fig. S6.** The  $J$ - $V$  characteristics of the all-PSCs based on PM6:PN1 (1.5:1, w/w) with 3%CN at different annealing temperature, under the irradiation of AM 1.5G, 100 mW/cm<sup>2</sup>.

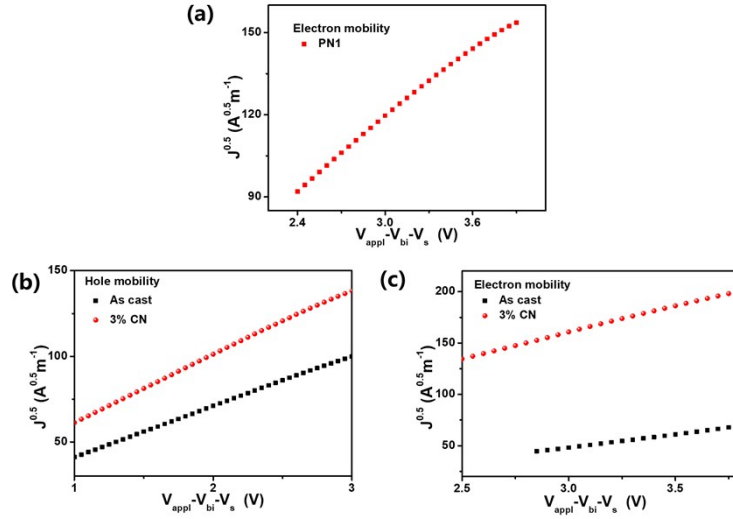


**Fig. S7.** Storage stability of the optimized devices.



**Fig. S8.** (a) and (b) the PL spectra of PM6, PN1 and the related blend films (excited at 550 nm for PM6, and 700 nm for PN1 and the related blend films).





**Fig. S9.**  $J^{1/2}$ - $V$  plots of (a) the PN1 pure film, (b) hole-only devices based on copolymer: PN1 blends, (c) the electron-only devices based on copolymer: PN1 blends.

**Table S1.** Photoovltaic performance parameters of the all-PSCs based on PM6:PN1 at different D/A weight ratios without post under the irradiation of AM 1.5G, 100 mW/cm<sup>2</sup>.

D:A [w/w]	$V_{oc}$ [V]	$J_{sc}^a$ [mA cm <sup>-2</sup> ]	FF	PCE <sup>b</sup> [%]
2:1	0.99	12.9/12.5	0.52	6.6 (6.4)
1.5:1	0.98	13.2/13.1	0.54	7.0 (6.9)
1:1	0.98	13.5/13.3	0.45	5.9 (5.6)

<sup>a</sup>The integral  $J_{sc}$  in parentheses from the EQE curves. <sup>b</sup>The average PCEs in parentheses from 15 devices.

**Table S2.** Photoovltaic performance parameters of the all-PSCs based on PM6:PN1 with different contents of CN under the irradiation of AM 1.5G, 100 mW/cm<sup>2</sup>.

D:A [w/w]	CN	$V_{oc}$ [V]	$J_{sc}^a$ [mA cm <sup>-2</sup> ]	FF	PCE <sup>b</sup> [%]
1.5:1	As-cast	0.98	13.2/13.1	0.54	7.0 (6.9)
	2%CN	0.99	14.3/13.7	0.63	8.9 (8.5)
	3%CN	1.00	15.2/14.7	0.69	10.5 (10.2)
	4%CN	0.99	14.0/13.5	0.64	8.8 (8.5)

<sup>a</sup>The integral  $J_{sc}$  in parentheses from the EQE curves. <sup>b</sup>The average PCEs in parentheses from 15 devices.

**Table S3.** Photoovltaic performance parameters of the all-PSCs based on PM6:PN1 (1.5:1, w/w) with different annealing temperature, under the irradiation of AM 1.5G, 100 mW/cm<sup>2</sup>.

Conditions	$V_{oc}$ [V]	$J_{sc}^a$ [mA cm <sup>-2</sup> ]	FF	PCE <sup>b</sup> [%]
Without TA	1.00	15.2/14.7	0.69	10.5 (10.2)
80 °C for 10 min	0.99	14.7/13.3	0.65	9.4 (9.2)
100 °C for 10 min	0.98	14.5/13.5	0.63	8.6 (8.4)
120 °C for 10 min	0.98	14.4/13.3	0.63	8.3 (8.0)

<sup>a</sup>The integral  $J_{sc}$  in parentheses from the EQE curves. <sup>b</sup>The average PCEs in parentheses from 15 devices.

**Table S4.** Charge mobilities of the device active layers measured by SCLC method.

Treatments	$\mu_h$ (cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup> )	$\mu_e$ (cm <sup>2</sup> v <sup>-1</sup> s <sup>-1</sup> )	$\mu_h/\mu_e$
PN1		$9.39 \times 10^{-4}$	
PM6:PN1 <sup>a</sup>	$6.92 \times 10^{-4}$	$4.06 \times 10^{-4}$	1.71
PM6:PN1 <sup>b</sup>	$9.82 \times 10^{-4}$	$9.62 \times 10^{-4}$	1.02

<sup>a</sup>W/O, <sup>b</sup>3%CN+TA

## References

1. M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, *Adv. Mater.*, 2015, **27**, 4655-4660.
2. J. Wilbuer, G. Schnakenburg and B. Esser, *Eur. J. Org. Chem.*, 2016, **14**, 2404-2412.