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New roles of fused-ring electron acceptors in organic solar cells

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Materials

PTB7-Th was purchased from 1-material Inc. and PEIE (80% ethoxylated, M_w ~ 110,000 g mol^{-1}, and 37 wt% in water) and MoO_3 (99.5%) were purchased from Sigma-Aldrich. FOIC was synthesized according to our published procedure.[S1] ITO-coated glass substrates (sheet resistance = 15 Ω/square) were cleaned stepwise in detergent, water, acetone, and isopropyl alcohol in a ultrasonic bath for 30 min each and subsequently dried in an oven at 150 °C for 15 min.

Device fabrication

The procedure for fabricating inverted OSCs of ITO/ZnO/FOIC/PEIE/PTB7-Th:FOIC/MoO_3/Ag is as follows. ZnO thin film (*ca*. 30 nm) was spin-coated on the ITO cathode at a speed of 4000 rpm from a ZnO precursor solution, which is 0.1 mg mL^{-1} zinc acetate dihydrate solution containing mixed 2-methoxyethanol/ethanolamine (97:3 by volume), and annealed at 200 ºC for 30 min under ambient condition. Then, FOIC thin film was spin-coated on the ZnO layer from a dichlorobenzene solution (1 mg mL^{-1}) at an optimized speed of 2500 rpm. The resulting thickness of FOIC interlayer is estimated to be 0.51 nm based on the transparency of FOIC interlayer obtained in Fig. S5. The optimization data of this FOIC interlayer are shown in Table S4. PEIE thin film with a roughly estimated thickness of 1-2 nm was spin-coated onto the FOIC layer from a 2-methoxyethanol solution (an optimized concentration of 0.15 wt%) at an speed of 5000 rpm. The optimization data of PEIE interlayer are shown in Table S5. The PTB7-Th:FOIC thin films were spin-coated onto the PEIE layer for 60 s at a speed of 1500 rpm from a mixed solvent chloroform/ diphenyl ether (99.5:0.5 by volume) solution containing 5 mg mL^{-1} of PTB7-Th and 7.5 mg mL^{-1} of FOIC. The photoactive layers were dried in the vacuum for 1 h. Finally, 5 nm of MoO_3 and 100 nm of Ag were sequentially evaporated under high vacuum (*ca*. 10^{-5} Pa) through a shadow mask to define active area of solar cell (2 × 2 mm^2) and to form composite anode. The above fabrication procedure was applied to the OSCs of ITO/ZnO/PTB7-Th:FOIC/MoO_3/Ag and ITO/ZnO/PEIE/PTB7-Th:FOIC/ MoO_3/Ag. The thicknesses of photoactive layers were measured to be *ca*. 95 nm.

For fabricating reference inverted OSCs of ITO/CML/PTB7-Th/MoO_3/Ag, where CML = ZnO, ZnO/PEIE, and ZnO/FOIC/PEIE, the procedure is same as above mentioned, except that PTB7-Th thin films were spin-coated from a dichlorobenzene solution (15 mg mL^{-1}) at a speed of 1000 rpm. The thicknesses of PTB7-Th photoactive layer were measured to be *ca*. 95 nm. The electron-only devices with structure of ITO/CML/PTB7-Th:FOIC/Ca/Al, where CML = ZnO, ZnO/PEIE, and ZnO/FOIC/PEIE, were made using the same procedure as the OSCs. The PTB7-Th thin films for the transient PL characterization were spin-coated on the substrates from a dichlorobenzene solution (3 mg mL^{-1}) at a speed of 1000 rpm.

Measurements

The photovoltaic parameters of solar cells were obtained from the *J-V* measurements using a programmable Agilent B2912A sourcemeter under a 1 sun, AM 1.5G spectrum from an XES-70S1 solar simulator (AAA grade, 70 × 70 mm^2 photobeam size). The film thicknesses were measured using Bruker DektakXT stylus profiling system. The EQE, IQE, and reflectance spectra of inverted devices based on photoactive layer of PTB7-Th:FOIC were obtained using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The EQE spectra of inverted devices based on photoactive layer of neat PTB7-Th were characterized by a stanford SR830 lock-in amplifier, a SR570 current pre-amplifier, and a monochromator Newport cs260. A halogen lamp was used as the light source. The steady PL measurements were carried out on a Fluorolog-3 spectrofluorometer with an excitation wavelength of 325 nm. The transient PL spectra were obtained on a FLS980 lifetime spectrometer. The optical transparency was measured with a UV-vis spectrophotometer (PE lambda 950).

Calculation and optical modeling

The total photocurrent density J_{ph} of inverted device is calculated via

$$J_{ph} = q\int_{300}^{1000} (1 - R(\lambda))\phi_{(sun)}(\lambda)d\lambda$$

where q is the elementary charge, R is the reflectance of device, and $\phi_{(\mathrm{sun})}$ is the AM 1.5 G solar spectrum in units of cm^{-2} s^{-1} nm^{-1}. The photocurrent loss due to the geminate recombination $J_{\mathrm{loss,\ gem}}$ is estimated by

$$J_{loss,gem} = q\int_{300}^{1000}(1-R(\lambda))(1-EQE(\lambda))\phi_{(sun)}(\lambda)d\lambda$$

The photocurrent loss due to the parasitic resistances $J_{\text{loss, par}}$ is calculated via

$$J_{loss,par} = J_{SC}\frac{R_S}{R_{SH}}$$

The optical modeling[S2] of inverted solar cells was done using a transfer matrix method. The frequency dependent refractive index (n) and extinction coefficient (k) of FOIC and PTB7-Th:FOIC thin flims are shown in Fig. S10.

Table S1 The total photocurrent density and photocurrent losses of the OSCs with structure of ITO/CML/PTB7-Th:FOIC/MoO_3/Ag

CML	total J_{ph} (mA cm^{-2})	$J_{\text{loss, gem}}$ (mA cm^{-2})	$J_{\text{loss, gem}}/J_{\text{ph}}$	$J_{\text{loss, par}}$ (mA cm^{-2})
ZnO	28.46	5.64	0.198	0.07
ZnO/PEIE	27.93	4.83	0.173	0.08
ZnO/FOIC/PEIE	29.04	4.45	0.153	0.08

Table S2 The photovoltaic parameters of the OSCs with structure of ITO/CML/PTB7-Th/MoO_3/Ag

CML	V_{OC} [a] (V)	J_{SC} [a] (mA cm^{-2})	FF [a]	PCE [a] (%)
ZnO	0.953±0.021	0.37±0.03	0.321±0.033	0.11±0.01
ZnO/PEIE	0.992±0.042	0.40±0.05	0.264±0.008	0.10±0.01
ZnO/FOIC/PEIE	0.995±0.030	0.99±0.09	0.270±0.006	0.24±0.02

[a] Average values with standard deviation for each structure were obtained from 20 devices.

Table S3 The photovoltaic parameters of the OSCs with structures of ITO/CML/PTB7-Th:FOIC/MoO_3/Ag.

CML	V_{OC} [a] (V)	J_{SC} [a] (mA cm^{-2})	FF [a]	PCE [a] (%)
ZnO	0.716±0.003 (0.711)	23.45±0.54 (24.36)	0.702±0.012 (0.701)	11.79±0.24 (12.15)
ZnO/IOIC2/PEIE	0.717±0.005 (0.723)	24.90±0.37 (24.36)	0.711±0.011 (0.729)	12.69±0.09 (12.84)
ZnO/IDIC/PEIE	0.713±0.004 (0.719)	24.07±0.75 (23.28)	0.703±0.020 (0.732)	12.05±0.14 (12.25)

[a] The photovoltaic parameters for the best-PCE devices are listed in the parentheses. Average values with standard deviation for each structure were obtained from 20 devices.

Table S4 The photovoltaic parameters of the OSCs with structure of ITO/ZnO/FOIC/PEIE/PTB7-Th:FOIC/MoO_3/Ag, where the FOIC interlayer is spin-coated at a speed of *x* rpm from a dichlorobenzene solution (1 mg mL^{-1}) and the PEIE interlayer is spin-coated at a speed of 5000 rpm from a 2-methoxyethanol solution (0.15 wt%). The speed of 2500 rpm is optimal to fabricate the FOIC interlayer.

x (rpm)	V_{OC} [a] (V)	J_{SC} [a] (mA cm^{-2})	FF [a]	PCE [a] (%)
2000	0.710±0.002	25.21±0.28	0.673±0.014	12.05±0.27
2500	0.720±0.002	25.04±0.66	0.707±0.010	12.75±0.22
3000	0.716±0.005	24.50±0.35	0.700±0.013	12.28±0.24
3500	0.717±0.009	24.21±0.33	0.683±0.006	11.86±0.13

[a] Average values with standard deviation for each structure were obtained from 20 devices.

Table S5 The photovoltaic parameters of the OSCs with structure of ITO/ZnO/FOIC/PEIE/PTB7-Th:FOIC/MoO_3/Ag, where the FOIC interlayer is spin-coated at a speed of 3000 rpm from a dichlorobenzene solution (1 mg mL^{-1}) and the PEIE interlayer is spin-coated at a speed of 5000 rpm from a 2-methoxyethanol solution (*x* wt%). The concentration of 0.15 wt% is optimal to fabricate the PEIE interlayer.

x (wt%)	V_{OC} [a] (V)	J_{SC} [a] (mA cm^{-2})	FF [a]	PCE [a] (%)
0.1%	0.713±0.003	23.93±0.41	0.699±0.021	11.92±0.21
0.125%	0.710±0.003	23.80±0.43	0.695±0.021	11.74±0.17
0.15%	0.716±0.005	24.50±0.35	0.700±0.013	12.28±0.24
0.2%	0.722±0.002	24.06±0.70	0.695±0.023	12.07±0.14
0.3%	0.721±0.003	24.14±0.67	0.690±0.018	12.01±0.16

[a] Average values with standard deviation for each structure were obtained from 20 devices.

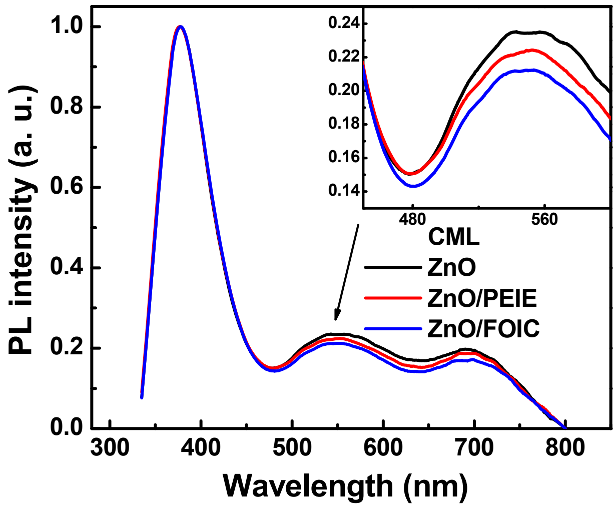

Fig. S1 The steady PL spectra of ZnO, ZnO/PEIE, and ZnO/FOIC deposited on the quartz glass.

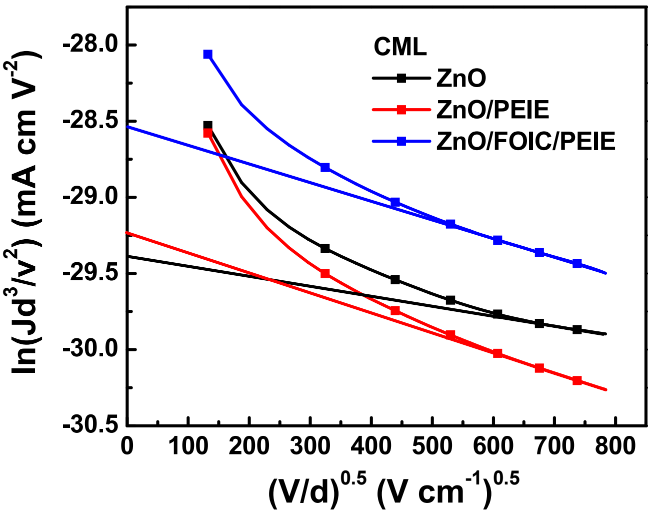

Fig. S2 *J-V* characteristics measured under dark for electron-only devices with structure of ITO/CML/PTB7-Th:FOIC/Ca/Al.

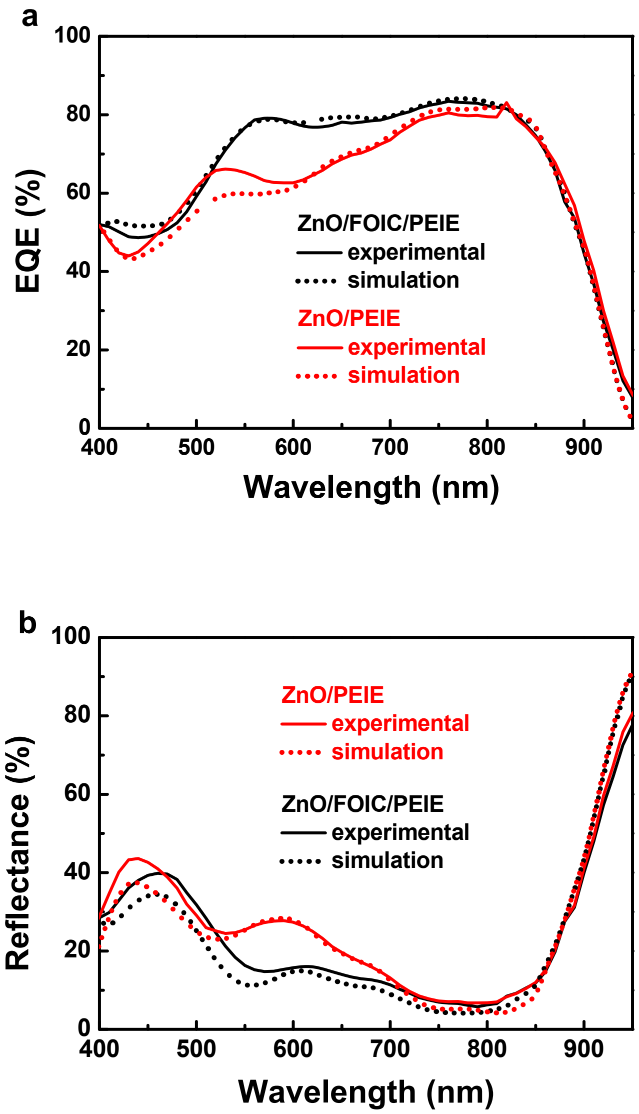

Fig. S3 Experimental and TM model simulated (a) EQE and (b) reflectance of the solar cells based on ZnO/PEIE and ZnO/FOIC/PEIE.

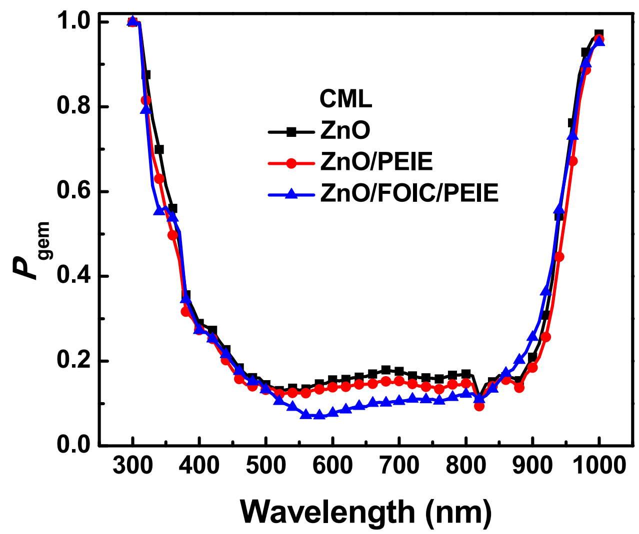

Fig. S4 The proportion of geminate recombination (P_{gem}) versus wavelength curves of the OSCs with structures of ITO/CML/PTB7-Th:FOIC/MoO_3/Ag.

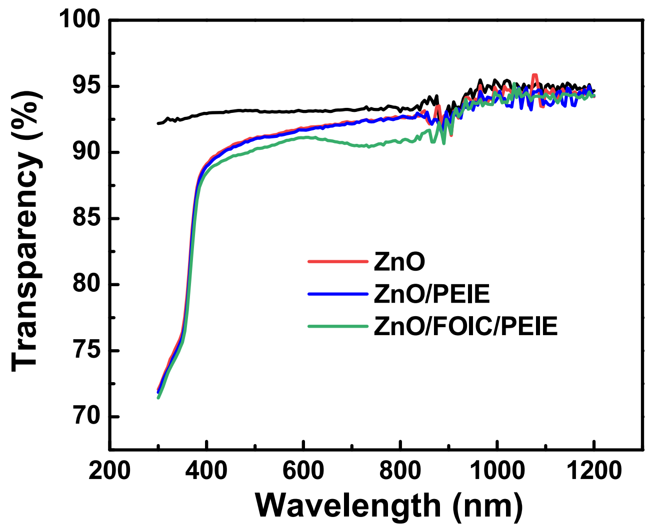

Fig. S5 Optical transparency curves of ZnO, ZnO/PEIE, and ZnO/FOIC/PEIE deposited on the quartz glass. The black curve of transparency for quartz glass is listed for reference.

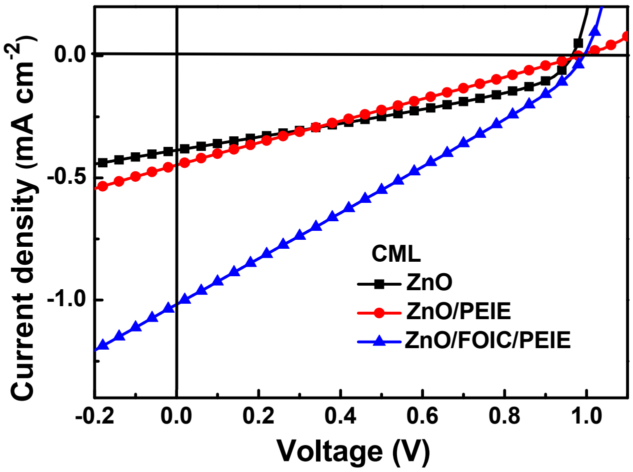

Fig. S6 *J*-*V* characteristics of the OSCs with structures of ITO/CML/PTB7-Th/MoO_3/Ag.

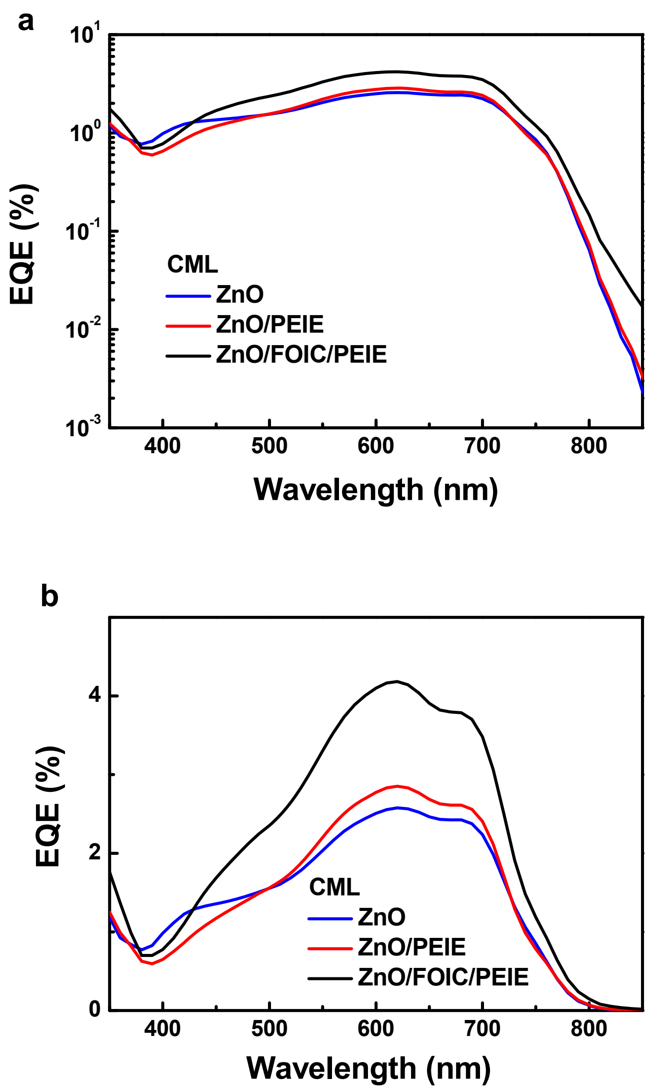

Fig. S7 (a) Semilogarithmic and (b) linear scale EQE spectra of the OSCs with structure of ITO/CML/PTB7-Th/MoO_3/Ag.

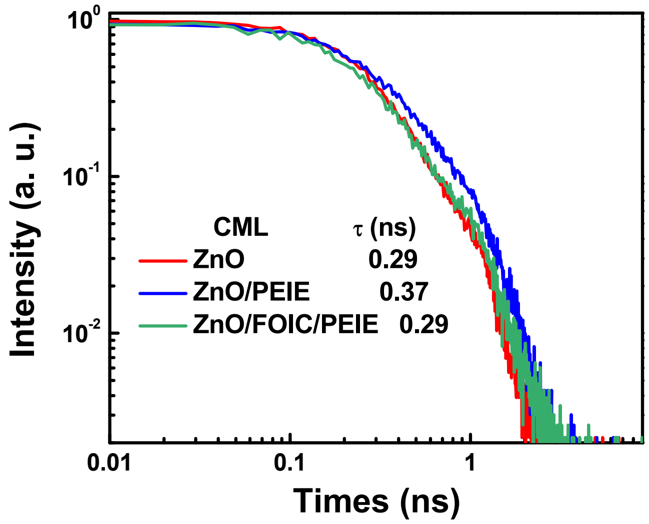

Fig. S8 Transient PL spectra of PTB7-Th on ZnO, ZnO/PEIE, and ZnO/FOIC/PEIE substrates.

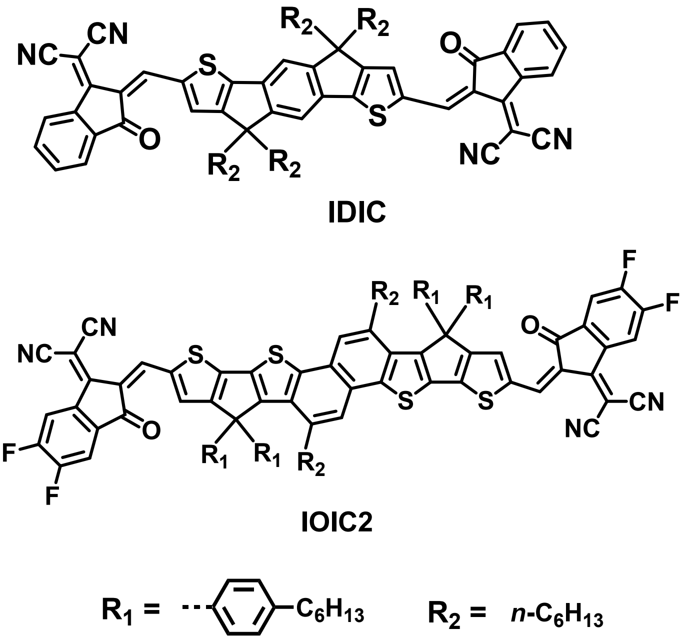

Fig. S9 The molecular structures of IDIC and IOIC2.

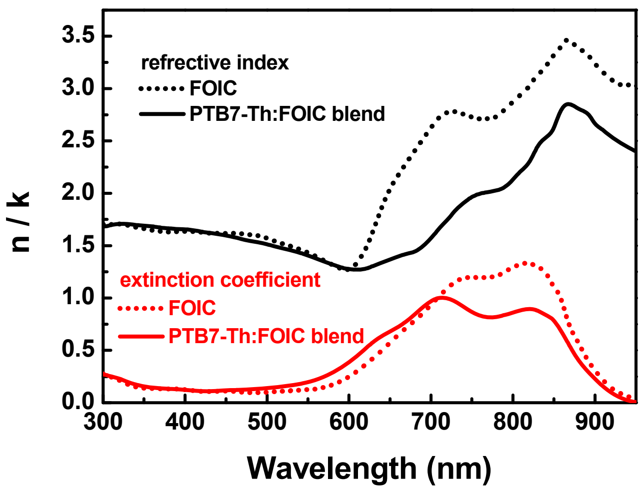

Fig. S10 Dielectric functions of FOIC and PTB7-Th:FOIC blend.

References

S1 T. Li, S. Dai, Z. Ke, L. Yang, J. Wang, C. Yan, W. Ma and X. Zhan, *Adv. Mater.* 2018, **30**, 1705969.

S2 L. A. A. Pettersson, L. S. Roman, O. Inganas, *J. Appl. Phys.* 1999, **86**, 487.