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# A small molecule with selenophene as the central block for high performance solution-processed organic solar cells



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## 1. Introduction

Organic photovoltaics (OPVs) have been considered a promising alternative solution for energy and environmental problems because of their attractive advantages such as low-cost, light weight, solution-processing and potential use in flexible devices [1–6]. With the rapid progress over the last few years, polymer-based photovoltaics (P-OPVs) have achieved power conversion efficiency (PCE) around 10% in single layer bulk-heterojunction (BHJ) solar cells [7–12]. Compared to the widely studied P-OPVs, while small molecule-based OPVs (SM-OPVs) have a late start, they have recently shown tremendous development [13,14]. This is based on several significant advantages such as relatively simple synthesis and purification, defined structures without batch-to-batch variations and easy control of energy levels by chemical structure design

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## ABSTRACT

A solution-processable A–D–A structure small molecule donor material called DRCN7T-Se with selenophene as the central block was synthesized. Conventional bulk-heterojunction solar cell devices based on DRCN7T-Se and  $PC_{71}BM$  were optimized by thermal annealing and an excellent power conversion efficiency of 8.30% was achieved under AM 1.5G irradiation (100 mW cm<sup>-2</sup>).

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[15–18]. With these developments, the PCE of single layer SM BHJ devices has made strides to over 9% [19–21].

We recently reported a small molecule donor material named DRCN7T for solution-processable BHJ solar cells [21]. Simply by changing the terminal groups from 3ethyl-2-thioxothiazolidin-4-one to 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile, a PCE performance of 9.30%, at an open circuit voltage ( $V_{oc}$ ) of 0.91 V, a short circuit current  $(J_{sc})$  of 14.87 mA/cm<sup>2</sup> and a fill factor (FF) of 68.7% was achieved for a DRCN7T-based device, which is attributed to the better structure with an optimized interpenetrating network and optimum crystalline fibrils. The results demonstrated that a delicate balance is needed for molecule design for high performance and some minor changes significantly affect device performance. Thus, based on previous work [22-25], it was considered that if Se was to replace S in the molecule DRCN7T, a better current might be expected for a higher overall performance since the unchanged overall molecular backbone structure would not have much effect on other factors such as  $V_{oc}$  or FF. Here, we report such a molecule, named DRCN7T-Se (Scheme 1), designed from DRCN7T by replacing the





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central thiophene unit with selenophene. Though, regrettably, no higher performance was obtained, an excellent PCE of 8.30% was achieved under AM 1.5G irradiation (100 mW cm<sup>-2</sup>) for solution-processed devices with  $PC_{71}BM$  as the acceptor.

# 2. Experimental

# 2.1. Materials and synthesis

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. The synthesis of DRCN7T-Se is outlined in Scheme 2. 5'-Bromo-3,4'-dioctyl-[2,2'-bithiophene]-5carbaldehyde (compound 3) and 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile (compound 4) were prepared according to the literature [21,26]. [6,6]-Phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) was purchased from American Dye Source, Inc. Other starting materials were all purchased from commercial suppliers and used without further purification.

# 2.1.1. 2,5-Bis(3-octylthiophen-2-yl)selenophene (compound 1)

A solution of Grignard reagent prepared from 2-bromo-3-octylthiophene (5.00 g, 18.2 mmol) in Et<sub>2</sub>O (20 mL) and Mg (2.60 g, 108.3 mmol) in Et<sub>2</sub>O (5 mL) under heating to reflux for 4 h with 1,2-dibromoethane as the entrainer was added using a dropping funnel to a stirred suspension of 2,5-dibromoselenophene (2.00 g, 6.9 mmol) and NiCl<sub>2</sub> (dppp) (70 mg, 0.13 mmol) in Et<sub>2</sub>O (30 mL) under argon atmosphere. The reaction mixture was refluxed for 17 h. The resulting reddish brown solution was poured into aq 2 N HCl (25 mL)/ice (50 g), and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic phases were dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent filtered and then removed to give a red oil, which was chromatographed on silica gel with hexane as eluent to yield 2,5-bis(3-octylthiophen-2-yl)selenophene as a red oil (2.2 g, 61%.).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21 (s, 2H), 7.15 (d, J = 5.1 Hz, 2H), 6.93 (d, J = 5.1 Hz, 2H), 2.79–2.72 (m, 4H), 1.69 (m, 4H), 1.24 (m, 20H), 0.92–0.81 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.30 (s), 139.40 (s), 132.91 (s),



Scheme 1. Chemical structure of DRCN7T-Se.

130.16 (s), 128.12 (s), 123.70 (s), 31.92 (s), 30.79 (s), 29.46 (dd), 22.72 (s), 14.15 (s).

# 2.1.2. 2,5-Bis(3-octyl-5-(tributylstannyl)thiophen-2-yl) selenophene (compound 2)

Under a N<sub>2</sub> atmosphere, n-BuLi (3.2 mL, 7.9 mmol) was added to a THF (30 mL) solution of compound 1 (1.40 g, 3.16 mmol) at -78 °C. After keeping it at this temperature for 30 min, this mixture was warmed to room temperature for another 30 min, and finally recooled to -78 °C for 2 h. Trimethyltin chloride (7.9 mL, 7.9 mmol, 1 M) was then added. This mixture was stirred overnight at room temperature and poured into water for extraction with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (2 × 100 mL) and dried over MgSO<sub>4</sub>. After the solvent had been removed under reduced pressure, the residue was purified by recrystallization from acetone to yield compound 3 (3.23 g, 93%).

#### 2.1.3. Compound DCH07T-Se

A solution of compounds 2 (1.20 g, 0.72 mmol) and 3 (0.8 g, 1.61 mmol) in toluene (30 ml) was degassed twice with argon followed by the addition of  $Pd(PPh_3)_4$  (0.025 g, 0.022 mmol). After stirring at 100 °C for 48 h under argon, the reaction mixture was poured into cold water and extracted with CHCl<sub>3</sub>. The organic layer was washed with water and then dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, the crude product was purified by silica gel using a mixture of dichloromethane and petroleum ether (3:1) as eluent to yield compound DCHO7T-Se (0.61 g, 62.5%) as a red solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.85 (s, 2H), 7.62 (s, 2H), 7.28 (s, 2H), 7.15 (s, 2H), 7.04 (s, 2H), 2.93–2.72 (m, 12H), 1.72 (s, 12H), 1.44 (s, 10H), 1.31 (t, 60H), 0.90 (dd, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 182.52 (s), 151.78–141.82 (m), 141.23 (s), 141.23 (s), 140.99 (d), 141.82–140.17 (m), 141.82–133.36 (m), 133.26 (s), 133.25–132.91 (m), 132.70 (d), 130.52 (s), 128.68 (d), 31.90 (d), 30.58 (d), 30.27 (s), 29.48 (ddd), 22.70 (s), 141.13 (s). MS (MALDI-TOF): calcd for  $C_{78}H_{112}O_2S_6Se$  [M]<sup>+</sup>, 1352.62; found, 1352.61.

#### 2.1.4. Compound DRCN7T-Se

Under the protection of argon, three drops of piperidine were added to a chloroform (50 ml) solution of DCHO7T-Se (0.50 g, 0.37 mmol) and compound 4 (0.70 g, 3.6 mmol). The resulting solution was stirred and refluxed for 48 h. The reaction mixture was then poured into cold water and extracted with CHCl<sub>3</sub>. The organic layer was washed with water and then dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, the crude product was purified by silica gel using chloroform as eluent. The crude solid was recrystallized from a mixed solvent of CHCl<sub>3</sub> and n-hexane three times to yield DRCN7T-Se as a black solid (0.51 g, 81.1%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (s, 2H), 7.29 (s, 4H), 7.18 (s, 2H), 7.05 (s, 2H), 4.32 (d, *J* = 7.2 Hz, 4H), 2.92–2.71 (m, 13H), 1.78–1.64 (m, 13H), 1.49–1.22 (m, 75H), 0.88 (t, *J* = 6.6 Hz, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.86 (s), 165.59 (s), 141.17 (s), 140.52 (s), 139.93 (s), 138.94 (s), 133.58 (s), 133.17 (s), 130.61 (s), 129.17 (s), 128.60 (s), 128.09 (s), 113.30 (d, *J* = 13.9 Hz), 112.32 (s), 55.45 (s),



Scheme 2. Synthesis of DRCN7T-Se.

40.64 (s), 31.89 (d, J = 3.7 Hz), 30.65 (s), 30.14 (s), 29.94–29.14 (m), 22.70 (s), 14.17 (d, J = 8.3 Hz). MS (MALDI-TOF): calcd for C<sub>94</sub>H<sub>122</sub>N<sub>6</sub>O<sub>2</sub>S<sub>8</sub>Se [M]<sup>+</sup>, 1702.66; found, 1702.64. Anal. calcd. For C<sub>94</sub>H<sub>122</sub>N<sub>6</sub>O<sub>2</sub>S<sub>8</sub>Se: C: 66.28%, H: 7.22%, N: 4.93%; found: C: 66.32%, H: 7.14%, N: 4.65%.

#### 2.2. Characterization

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400 Spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) were performed on a Bruker Autoflex III LRF200-CID instrument. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409PC instrument under a purified nitrogen gas flow with a 10 °C min<sup>-1</sup> heating rate. UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer. All CV measurements were carried out at room temperature with a conventional three-electrode configuration using glassy carbon as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s<sup>-1</sup>. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation potential and the onset reduction potential, using the equation  $E_{\text{HOMO}} = -(4.8 + E_{\text{onset}}^{\text{ox}})$ ,  $E_{\text{LUMO}} = -(4.8 + E_{\text{onset}}^{\text{ox}})$ .

Atomic force microscopy (AFM) was performed using a Multimode 8 atomic force microscope in the tapping mode. Transmission electron microscopy (TEM) was performed on Philips Tecnai  $G^2$  F20 at 200 kV. The specimen for TEM examination was prepared by spin casting the blended solution on an ITO/PEDOT:PSS substrate, then floating the film on water, and transferring it to TEM grids.

SCLC hole-only mobility was measured using a diode configuration with the ITO/PEDOT:PSS/donor:PC<sub>71</sub>BM/Au device structure by taking the dark current density in the range 0-4 V and fitting the results to a space charge limited form, where SCLC is described by the equation below:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0 V^2}{8L^3} \exp\left(0.89\beta\sqrt{\frac{V}{L}}\right)$$

where *J* is the current density, *L* is the film thickness of the active layer,  $\mu_0$  is the hole or electron mobility,  $\varepsilon_r$  is the relative dielectric constant of the transport medium,  $\varepsilon_0$  is the permittivity of free space (8.85 × 10<sup>-12</sup> F m<sup>-1</sup>), *V* (=*V*<sub>appl</sub> – *V*<sub>bi</sub>) is the internal voltage in the device, where *V*<sub>appl</sub> is the applied voltage to the device and *V*<sub>bi</sub> is the built-in voltage due to the relative work function difference of the two electrodes.

### 2.3. Solar cell fabrication and testing

The devices were fabricated with the structure glass/ ITO/PEDOT:PSS/donor:acceptor/PFN/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatments in detergent, deionized water, acetone, and isopropyl alcohol under ultra-sonication for 15 min each and subsequently dried by a nitrogen blow. A thin layer of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45 µm) was spin-coated at 3000 rpm onto an ITO surface. After baking at 150 °C for 20 min, the substrates were transferred to an argon-filled glove box. Subsequently, an active layer was spin-coated from blended chloroform solutions with DRCN7T-Se and PC<sub>71</sub>BM blends and then annealed different temperature for 10 min with a series of concentration. The substrate was then removed and a PFN layer was spin-coated on it as described to the literature [7,21]. Finally, an 80 nm Al layer was deposited under high vacuum ( $< 2 \times 10^{-4}$  Pa). The effective area of cells was 4 mm<sup>2</sup> as defined by shallow masks. Current density-voltage (J-V) curves of the photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under simulated illumination of 100 mW cm<sup>-2</sup> AM 1.5G irradiation using an Oriel 96000 solar simulator, calibrated with a standard Si solar cell. The average PCE was obtained using 20 devices under the same conditions. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer. External Quantum Efficiency (EQE) values of the devices were obtained using a lock-in amplifier (SR810, Stanford Research Systems). The encapsulated devices were illuminated by monochromatic light from a 150 W xenon lamp passing through an optical chopper and a monochromator. The photon flux was determined by a calibrated standard silicon photodiode.

#### 3. Results and discussion

# 3.1. Synthesis and thermal stability

As described in Scheme 2, the aldehyde intermediate, DCHO7T-Se, was made from 2,5-bis(3-octyl-5-(tributylstannyl)thiophen-2-yl)selenophene and 5'-bromo-3,4'-dioctyl-[2,2'-bithiophene]-5-carbaldehyde by Still coupling. The desired molecule, DRCN7T-Se was obtained by Knoevenagel condensation of DCHO7T-Se with the electron-deficient unit 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile. The thermogravimetric analysis (TGA) plot shown in Fig. 1 suggests that DRCN7T-Se exhibits good stability with a decomposition temperature of 370 °C under a N<sub>2</sub> atmosphere.



**Fig. 1.** Thermogravimetric analysis (TGA) plot of DRCN7T-Se with a heating rate of  $10 \degree C \min^{-1}$  under N<sub>2</sub> atmosphere.



**Fig. 2.** (a) Cyclic voltammogram (CV) of DRCN7T-Se in dichloromethane with 0.1 M Bu4NPF6. (b) UV–vis absorption spectra of the DRCN7T-Se solution (in CHCl<sub>3</sub>) and film.

# 3.2. Optical absorption and electronic properties

The HOMO and LUMO energy levels of DRCN7T-Se were estimated from a cyclic voltammogram to be -5.05 and -3.43 eV with an electrochemical band gap of 1.62 eV, which is shown in Fig. 2a. The LUMO difference between DRCN7T-Se and PC<sub>71</sub>BM is 0.47 eV, which is larger than 0.3 eV and ensures efficient exciton dissociation [27,28]. UV-vis absorption spectra for DRCN7T-Se in a chloroform solution and in a thin film spin-coated on a quartz

Table 1				
Electronic and optical absorption da	ta of compounds	DRCN7T a	nd DRCN71	-Se

Compounds	is CV <sup>b</sup>		UV-vis (solution)			UV-vis (pristine film)			
	HOMO (eV)	LUMO (eV)	$E_{g}^{CV}(eV)$	$\lambda_{\max}$ (nm)	$\varepsilon (\lambda_{max}) (L \text{ mol}^{-1} \text{ cm}^{-1})$	$\lambda_{\max}$ (nm)	$\varepsilon (\lambda_{\rm max}) ({\rm cm}^{-1})$	$\lambda_{onset} (nm)$	$E_{\rm g}^{ m opt}\left({ m eV} ight)$
DRCN7T <sup>a</sup> DRCN7T-Se	$-5.08 \\ -5.05$	-3.44 -3.43	1.64 1.62	530 533	$\begin{array}{c} 8.2\times10^4\\ 6.2\times10^4\end{array}$	621 616	$\begin{array}{c} \textbf{7.4}\times \textbf{10^4} \\ \textbf{7.0}\times \textbf{10^4} \end{array}$	764 765	1.62 1.62

<sup>a</sup> Data from Ref. [21].

<sup>b</sup> Data obtained from CH<sub>2</sub>Cl<sub>2</sub> solution.

substrate are shown in Fig. 2b. The DRCN7T-Se solution has an absorption peak at 533 nm with an absorption coefficient of  $6.2 \times 10^4 \,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$ . The peak shows an 83 nm red shift to 616 nm with a maximum absorptivity of  $7.0 \times 10^4$  cm<sup>-1</sup> in the solid state. The optical band gap of DRCN7T-Se estimated from the onset of film spectrum is 1.62 eV. All the electrochemical and optical absorption data of DRCN7T and DRCN7T-Se are summarized in Table 1. From this table, we were disappointed to find that the replacement of thiophene with selenophene in the central unit of the DRCN7T did not produce the expected red-shift in the UV-vis spectra of both the solution and the film. Compared with DRCN7T, its HOMO, and LUMO energy levels and absorption range are almost the same as those of DRCN7T, and the absorption coefficients of its solution and pristine film are even slightly decreased.

#### 3.3. Photovoltaic performance

The photovoltaic performance of DRCN7T-Se as the donor was evaluated using a similar method to that for DRCN7T. BHJ devices were fabricated using different donor/acceptor (D/A) weight ratios of DRCN7T-Se and PC<sub>71</sub>BM, with a conventional device structure of ITO/ PEDOT-PSS/donor:acceptor/PFN/Al using the solution spin-coating process. The best result was obtained from a CHCl<sub>3</sub> solution for a D/A ratio of 1:0.8 with a donor concentration of  $10 \text{ mg mL}^{-1}$ , where the actives layer thickness was around 120 nm. These devices were further optimized by fine-tuning the thermal treatment conditions [29,30]. All the current density-voltage (I-V) curves are shown in Fig. S1 and the corresponding data are summarized in Table S1 from which it can be seen that with an increase of annealing temperature, the  $V_{\rm oc}$  of the best device drops step-by-step from 0.939 V to 0.906 V, while J<sub>sc</sub> and FF both increase initially and then decrease. These changes in  $V_{oc}$ ,  $J_{\rm sc}$  and FF agree with our previous work and could be due to the increased saturation dark current, crystal size and phase size caused by the higher annealing temperature [31]. The best device performance was achieved when the active layer was annealed at 100 °C for 10 min, with a  $V_{oc}$  of 0.913 V, a  $J_{sc}$  of 13.06 mA/cm<sup>2</sup>, a FF of 69.6%, and a PCE of 8.30%, which are typical of high-performance small molecule organic photovoltaics [19-21,32-35].

The *J*–*V* curves and the corresponding parameters for DRCN7T and DRCN7T-Se based solar cells under their best performance conditions are given in Fig. 3a and Table 2, respectively. From the table, we can see that compared to the DRCN7T-based device, the smaller  $J_{sc}$  of the DRCN7T-Se based device is the main reason for its inferior performance. This smaller  $J_{sc}$  is supported by the external

quantum efficiency (EQE) spectrum. As shown in Fig 3b, the best device based on DRCN7T-Se gives a lower EQE than that of DRCN7T over the entire solar spectrum. Because these two compounds have similar optical abilities (Figs. 2b and S2), the distinct differences in  $J_{sc}$  and EQE may possibly be due to the difference of morphology.

Therefore, atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to



**Fig. 3.** (a) *J*–*V* curves and (b) EQE spectrum of DRCN7T and DRCN7T-Se based devices under best performance condition.

Table 2

Typical parameters of DRCN7T and DRCN7T-Se based devices under best performance conditions.  $J_{cal}$  is the calculated current from EQE measurements.

Donor/ PC <sub>71</sub> BM	$V_{\rm oc}\left({\rm V} ight)$	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	J <sub>sc</sub> (mA/cm <sup>2</sup> )
DRCN7T <sup>a</sup>	0.910	14.87	68.7	9.30	14.37
DRCN7T-Se	0.913	13.06	69.6	8.30	12.46

<sup>a</sup> Data from Ref. [21].

 Table 3

 Summary of the AFM, TEM and SCLC hole-only mobility data under best performance conditions.

Donor/PC71BM	AFM roughness (RMS)	TEM domain size (nm)	Hole mobility $(cm^2 V^{-1} s^{-1})$
DRCN7T <sup>a</sup> DRCN7T-Se	0.68 0.74	10 19	$\begin{array}{c} 5.9\times 10^{-4} \\ 2.3\times 10^{-4} \end{array}$

<sup>a</sup> Data from Ref. [21].

study the films of donor/PC71BM blends. From AFM measurements (Table 3), the root-mean-square (RMS) surface roughness for DRCN7T and DRCN7T-Se films under the optimum conditions are 0.68 and 0.74, respectively. These two roughness values are small and quite close, indicating that the two films have a similar high quality surface morphology. The TEM images (Fig. 4) show a clearer picture of the morphology structure. The light regions are the donor domains because of the relatively low electron scattering density [36]. A noteworthy point is that the DRCN7T-Se/ PC71BM mixture with the best performance consists of fiber-like domains with a diameter of  $\sim$ 20 nm, while the average fibril diameter of the best performing DRCN7T film is around 10 nm (comparable to the exciton diffusion length [37]). As we know, a larger domain may impair exciton diffusion to the D/A interface and lead to a lower  $I_{sc}$ [31]. Moreover, a DRCN7T-Se based film has a less continuous interpenetrating network than DRCN7T does, that is



**Fig. 4.** Transmission electron microscope (TEM) images: (a) DRCN7T and (b) DRCN7T-Se based devices with the best performance. The scale bar is 200 nm.

bad for charge transport and could further reduce  $J_{sc}$ . This was supported by space charge-limited current (SCLC) measurements. The SCLC hole mobility for the DRCN7T-Se based device with the best performance is  $2.3 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which is much smaller than the value of  $5.9 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> obtained for DRCN7T.

# 4. Conclusions

In summary, a new solution-processable A–D–A structure small molecule donor molecule DRCN7T-Se containing selenophene as the central block unit and 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile as the electrondeficient group was designed and synthesized. After finetune the donor/acceptor weight ratio, film thickness and thermal annealing condition, a power conversion efficiency of 8.30% was obtained. Though a considerable PCE was achieved, its worse performance than that of the previously corresponding molecule DRCN7T is probably due to the larger diameter of its fibril-like domains.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2015.01.035.

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