

2010

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This document is the authors' final version of the published article.

Link to published article: <http://dx.doi.org/10.1039/B926203B>

Citation

Zhang, Weifeng, Shing Chi Tse, Jianping Lu, Ye Tao, and Man Shing Wong. "Solution processable donor-acceptor oligothiophenes for bulk-heterojunction solar cells." *Journal of Materials Chemistry* 20.11 (2010): 2182-2189.

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Solution Processable Donor-Acceptor Oligothiophenes for Bulk-Heterojunction Solar Cells

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

5 First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

Novel p-type and low bandgap penta- and hexa-thiophenes asymmetrically endcapped with solubilizing triarylamine or triarylamine-substituted carbazole dendron and dicyanovinyl groups, namely, **PhNOF-OT(n)-DCN** and **G₂-OT(n)-DCN**, respectively where n = 5-6 for solution-
10 processable photovoltaic applications have been synthesized and investigated. With the incorporation of a solubilizing electron-donating group, the highly extended oligothiophenes are highly soluble in common organic solvents and solution-processable. Upon extending oligothiophene backbone, there is a strong increase in the absorption around 420 nm in addition to the intramolecular charge-transfer absorption (520 nm) which results in a strong spectral
15 broadening. The optical band-gap of these donor-acceptor oligothiophene thin-films greatly reduces to 1.85 eV. The solution-processed bulk heterojunction PV cells fabricated from these materials blended with PCBM as an acceptor showed a *PCE* up to 1.72 % with $V_{oc} = 0.79$ V in an as-fabricated device. Our findings also suggest that highly extended donor-acceptor oligomers can be useful for a p-type, low-bandgap semiconductor for solution-processable bulk heterojunction
20 PV cells.

Introduction

Organic photovoltaic (PV) cells, which directly convert sunlight into electricity, have drawn considerable attention from both academia and industry because of their promise as
25 low-cost, lightweight, renewable energy sources.¹ Heterojunction PV cells based on solution-processable conjugated p-type semiconducting materials blended with a soluble fullerene derivative, [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) offer advantages of facile and large-area
30 fabrication on flexible substrates by various printing or coating techniques or roll-to-roll process² affording high power conversion efficiencies (*PCE*) of greater than 6% recently.³ However, the structural characteristics including molecular weight, polydispersity, and regioregularity as well
35 as the purity of a polymer greatly affect its functional properties, the performance and the stability⁴ of the resulting devices. In addition to polymers, π -conjugated small molecules have been found attractive as alternative solution-processable p-type donor materials because of
40 monodispersity, ease of obtaining in high purity and reproducible properties. Nevertheless, the use of solution-processable small molecules for PV applications has drawn considerable attention.⁵ Recently, a *PCE* of 1.17% was obtained from a solution-processed BHJ solar cell using
45 anthracene-core donor and C₆₁-PCBM acceptor.⁶ In addition, a small molecule PV cell based on the blend of benzothiadiazole derivative and C₆₁-PCBM showed a *PCE* of 2.4% in the annealed device.⁷ A high *PCE* of 3.0% has very recently been demonstrated based on oligothiophene-diketopyrrolopyrrole and C₇₁-PCBM blend.⁸ To achieve a high efficiency heterojunction PV cell, it is fundamentally

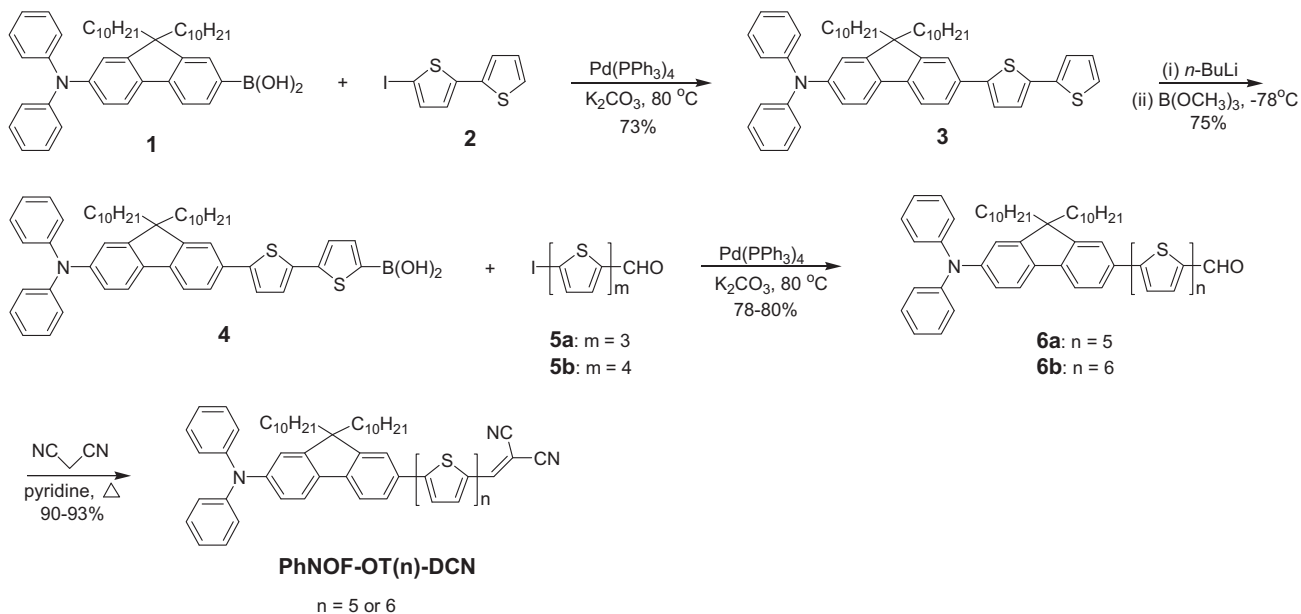
important to develop new p-type π -conjugated small molecules with a narrow energy bandgap to harvest more solar radiation and a high charge carrier mobility to transport
55 the photogenerated charges to the electrodes.⁹

Oligothiophenes endcapped with triarylamine and dicyanovinyl or tricyanovinyl groups, which exhibit low optical gap absorption and possess a large enough LUMO level offset with the PCBM acceptors for efficient exciton
60 dissociation, have shown to be useful for a high performance bilayer heterojunction photovoltaic cell.¹⁰ Nevertheless, these molecules were not suitable for solution processable bulk heterojunction PV cells. For application in solution processable bulk heterojunction PV cells, the materials need
65 to have good solubility and thin-film forming property.⁸ To promote the solution processable properties of small molecule donors, we have developed a novel series of highly extended oligothiophenes asymmetrically endcapped with a solubilizing triarylamine or triarylamine-substituted dendron and a
70 dicyanovinyl group as a p-type, low-optical-gap semiconductor for solution-processable bulk heterojunction PV cells. The use of a highly extended π -conjugated system not only lowers the optical bandgap and promotes strong π - π stacking of conjugated backbones but also increases the
75 absorption and broadens the absorption spectrum as compared to the lower homologues.

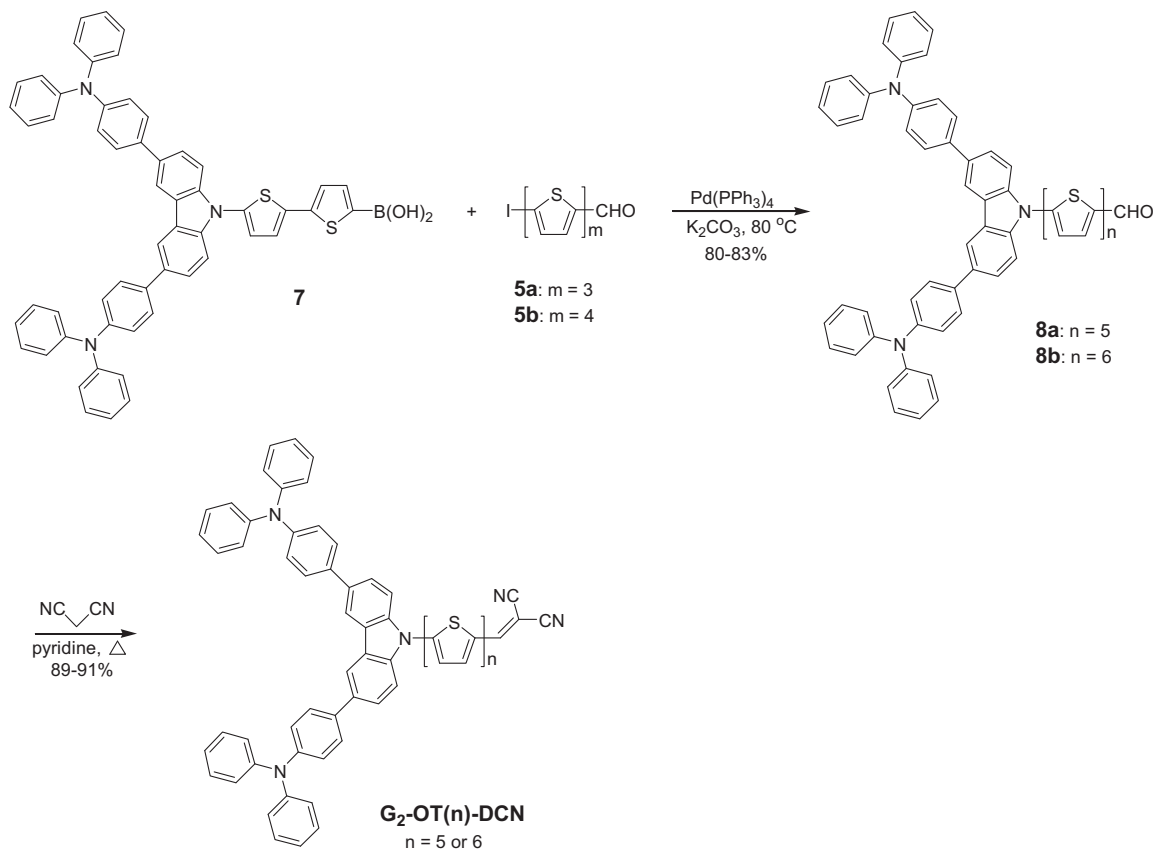
We report herein the synthesis and molecular properties of novel p-type and low bandgap penta- and hexa-thiophenes asymmetrically endcapped with solubilizing triarylamine or
80 triarylamine-substituted carbazole dendron and dicyanovinyl groups, namely, **PhNOF-OT(n)-DCN** and **G₂-OT(n)-DCN**, respectively where n = 5-6 for solution-processable photovoltaic applications. With the incorporation of a solubilizing electron-donating group, the highly extended

oligothiophenes are highly soluble in common organic solvents and solution-processable. The optical band-gap of these donor-acceptor oligothiophene thin-films greatly reduces to 1.85 eV. The solution-processed bulk heterojunction PV cells fabricated from these materials

blended with PCBM as acceptors showed a PCE up to 1.72 % with $V_{oc} = 0.79$ V in an as-fabricated device. Our findings also suggest that highly extended donor-acceptor oligomers can be used as a p-type, low-bandgap semiconductor for solution-processable bulk heterojunction PV cells.



Scheme 1 Synthesis of triarylamine dicyanovinyl asymmetrically disubstituted oligothiophenes, **PhNOF-OT(*n*)-DCN**, n = 5 or 6.



Scheme 2 Synthesis of triaryl-amino-substituted carbazole dendron and dicyanovinyl asymmetrically disubstituted oligothiophenes **G₂-OT(*n*)-DCN**, n = 5 or 6.

Table 1 Summaries of physical measurement of **PhNOF-OT(*n*)-DCN** and **G₂-OT(*n*)-DCN**.

	$\lambda_{\text{max}}^{\text{abs}}$ ^a / (10 ⁴ M ⁻¹ cm ⁻¹)	Optical gap ^{a,b} /eV	E _{1/2} ^{oxd} or E _p ^{oxd} ^c /V	E _p ^{red} ^c /V	HOMO ^d /eV	LUMO ^d /eV	Energy gap ^e /eV	T ^f /°C	T _{dec} ⁱ /°C
PhNOF-OT(5)-DCN	525 (5.73)	1.88	0.30, 0.42, 0.86	-1.44, -2.01	-5.10	-3.36	1.74	199 ^g	440
PhNOF-OT(6)-DCN	524 (6.55)	1.85	0.30, 0.39, 0.73	-1.41, -1.98	-5.10	-3.39	1.71	217 ^g	460
G₂-OT(5)-DCN	518 (5.17)	1.91	0.36, 0.49, 0.79	-1.55, -2.04	-5.16	-3.25	1.91	144 ^h	514
G₂-OT(6)-DCN	522 (5.42)	1.88	0.35, 0.48, 0.73	-1.55, -2.03	-5.15	-3.25	1.90	148 ^h	515

^ameasured in CHCl₃, ^bestimated from the absorption edge of thin-film. ^cdetermined by CV method using platinum disc electrode as a working electrode, platinum wire as a counter electrode and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution and ferrocene was used as an external standard, E_{1/2}(Fc/Fc⁺) = 0.49 V vs SCE. ^dcalculated from the first oxidation or reduction potential with ferrocene (4.8 eV vs vacuum).

^eEnergy gap = HOMO-LUMO. ^fdetermined by differential scanning calorimeter from re-melt after cooling with a heating rate of 10°C/min under N₂.

^gmelting point. ^hglass transition. ⁱdetermined by thermal gravimetric analyzer with a heating rate of 10°C/min under N₂.

Results and Discussion

The synthesis of novel triarylamine and dicyanovinyl asymmetrically disubstituted oligothiophenes is outlined in Scheme 1. By adapting the convergent approach used previously¹⁰, the palladium-catalyzed Suzuki cross-coupling of 7-diphenylamino-9,9-di-*n*-decylfluorenyl-2-boronic acid **1** and iodobithiophene **2** in the presence of Pd(PPh₃)₄ as a catalyst afforded the desired diphenylaminofluorenyl-substituted bithiophene **3** in 73% yield. Lithiation of **3** at -78 °C followed by quenching with trimethylborate and subsequently acid hydrolysis afforded the corresponding boronic acid **4** in a good yield. The palladium catalyzed Suzuki cross-coupling of 7-diphenylamino-9,9-di-*n*-decylfluorenyl-5'-bithiophene-5-boronic acid **4** with iodoter- or iodoquarter-thiophenecarboxaldehyde **5a** or **5b** afforded the desired diphenylaminofluorenyl-substituted penta- and hexathiophenecarboxaldehydes, **6a** and **6b**, respectively in good yields (78-80%). Condensation of these aldehydes **6a** or **6b**, with malononitrile in the presence of pyridine in refluxing chloroform afforded the desired donor-acceptor oligothiophenes **PhNOF-OT(*n*)-DCN**, *n* = 5 or 6 in excellent yields. Furthermore, the synthesis of novel triarylamine-substituted carbazole dendron and dicyanovinyl asymmetrically disubstituted oligothiophenes is outlined in Scheme 2. 5-{3,6-bis[4-(diphenylamino)-1-phenyl]carbazol-9-yl}-2-bithiophene-boronic acid, **7** was prepared according to the previously published protocol.^{5f} The palladium catalyzed Suzuki cross-coupling of boronic acid **7** with iodoter- or iodoquarter-thiophenecarboxaldehyde **5a** or **5b** afforded the desired triarylamine-substituted dendritic penta- and hexathiophenecarboxaldehydes, **8a** and **8b**, respectively in good yields (80-83%). Similarly, subsequent condensation of **8a** or **8b** with malononitrile afforded the triarylamine-substituted carbazole dendron and dicyanovinyl asymmetrically disubstituted oligothiophenes **G₂-OT(*n*)-DCN**, *n* = 5 or 6 in 89-91% yields. All the newly synthesized donor-acceptor oligothiophenes were fully characterized with ¹H NMR, ¹³C NMR, MALDI-TOF MS, and elemental analysis and found to be in good agreement with their structures.

The thermal behavior and stability of these donor-acceptor oligothiophenes were investigated by DSC and TGA analyses, respectively. The results are summarized in Table 1. The triarylamine-substituted oligothiophenes, **PhNOF-OT(*n*)-DCN** exhibit no apparent glass transition except a melting

transition (*T_m*) in the range of 199-217 °C; on the other hand, the dendron-substituted oligothiophenes, **G₂-OT(*n*)-DCN** show distinct and high glass transition temperatures with *T_g* > 144 °C suggesting that these dendrimers can form morphologically stable amorphous thin film. All the oligothiophenes exhibit an excellent thermal stability with *T_d* in the range of 440-515 °C. (Fig. 1)

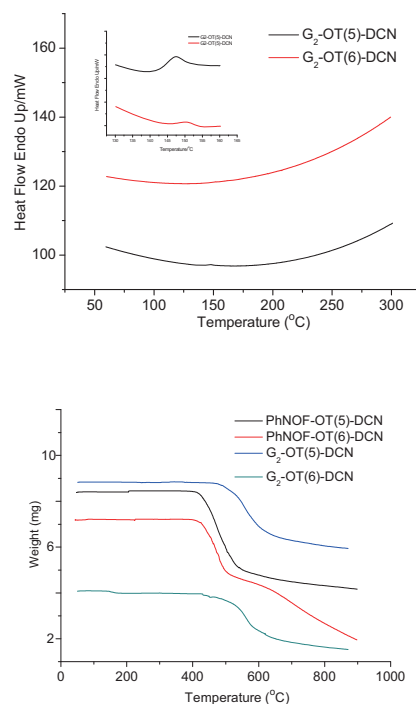


Fig. 1 (a) DSC traces of **G₂-OT(*n*)-DCN**. (b) TGA traces of **PhNOF-OT(*n*)-DCN** and **G₂-OT(*n*)-DCN**.

The absorption spectra of these donor-acceptor oligothiophenes measured in chloroform and DMSO as shown in Fig. 2 are composed of three broad and structureless absorption bands, a weak to strong absorption in the range of 310-330 nm corresponding to the *n*→*π** transition of arylamine moiety of triarylamine-based donating group, a moderate to strong absorption around 410-420 nm corresponding to the transition of the extended oligothiophene core, and the long wavelength absorption ($\lambda_{\text{max}}^{\text{abs}}$) around 520 nm corresponding to the intramolecular charge-transfer (ICT) transition. The $\lambda_{\text{max}}^{\text{abs}}$ remains fairly constant for **PhNOF-**

OT(*n*)-DCNs and shifts slightly to a longer wavelength for **G₂-OT(*n*)-DCNs** when the oligothiophenyl core extends from five to six indicating the approach of the effective conjugation length for the series. It is worth mentioning that in addition to ICT, the enhancement of the absorption around 420 nm upon extending oligothiophene backbone gives rise to a strong spectral broadening. These oligomers also exhibit inverted solvatochromic effect upon an increase in polarity of solvent. There is no observable fluorescence emission upon irradiating at $\lambda_{\text{max}}^{\text{abs}}$ which is attributed to the strong charge-transfer character of these donor-acceptor oligothiophenes. These oligomers showed pronounced peak broadening and red shifts of ~40 nm of absorption cutoff upon formation into thin films which is attributed to the planarization of aryl rings and the presence of interchain interactions in the solid state, resulting in the optical band gap reducing to 1.85 eV.

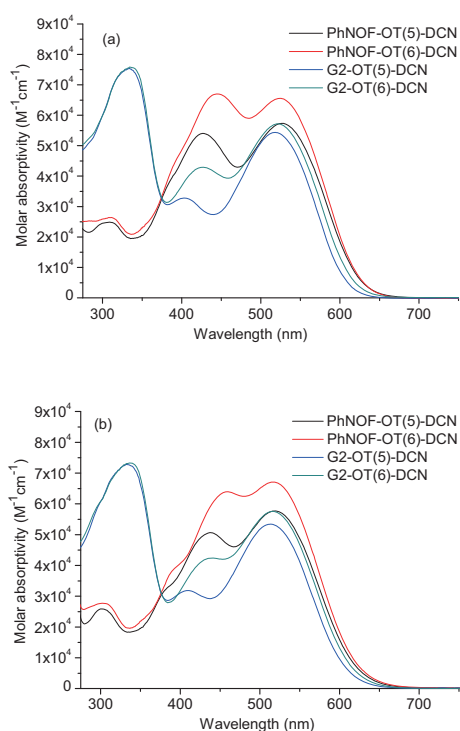


Fig. 2 Absorption spectra of **PhNOF-OT(*n*)-DCN** and **G₂-OT(*n*)-DCN** in (a) chloroform and (b) DMSO.

Both **PhNOF-OT(*n*)-DCNs** and **G₂-OT(*n*)-DCNs** exhibit very similar electrochemical redox behavior. All the oligothiophenes showed three oxidation waves with E_{oxd1} at 0.30-0.35 V, E_{oxd2} at 0.39-0.48 V, and E_{oxd3} at 0.73-0.86 V ($E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.49$ V vs SCE) corresponding to the sequential removal of electrons from the arylamino group(s), the oligothiophene core or the interior carbazole moieties, and the oligothiophene core, respectively. (Fig. 3) They also exhibit two reduction waves ($E_{\text{red1}} = -1.50$ V and $E_{\text{red2}} = -2.00$ V vs Fc/Fc^+) corresponding to the reductions of dicyanovinyl

group and the reduction of oligothiophene core, respectively. Hence, the HOMO and LUMO levels of these oligothiophenes were estimated to be ~ -5.2 eV and ~ -3.3 eV, respectively based on CV data.

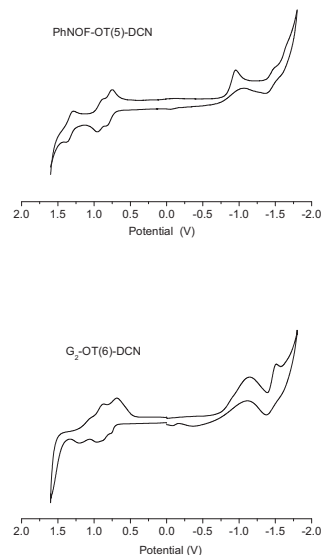


Fig. 3 CV traces of **PhNOF-OT(5)-DCN** and **G₂-OT(6)-DCN**.

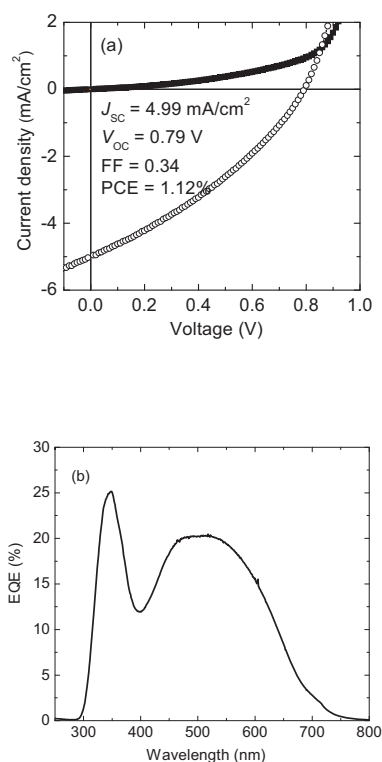


Fig. 4 (a) *J-V* characteristics of **G₂-OT(6)-DCN:PCBM (1:2)**-based PV cells (b) the EQE curves of the corresponding PV cells.

Table 2 Summary of PV device performance with device structure of ITO / PEDOT:PSS / oligomer:PCBM / LiF (0.95 nm) / Al (130 nm).

Active layer	Thin Thickness (nm)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%) ^{a,b}	EQE_{max} (%)
PhNOF-OT(5)-DCN : PCBM (1:2)	85	2.94	0.93	0.17	0.47	37
	160	4.97	0.83	0.28	0.97	47
	106	4.16	0.79	0.31	1.03	40
PhNOF-OT(5)-DCN : PCBM (1:4)	147	5.41	0.79	0.40	1.72	43
	81	1.78	0.79	0.52	0.73	18
PhNOF-OT(6)-DCN : PCBM (1:2)	102	1.96	0.75	0.52	0.76	17
	110	4.30	0.54	0.32	0.63	11
G₂-OT(5)-DCN : PCBM (1:2)	100	3.90	0.81	0.35	1.11	28
	160	4.99	0.79	0.34	1.12	25
G₂-OT(6)-DCN : PCBM (1:2)	103	3.26	0.52	0.33	0.56	27
	141	3.68	0.66	0.35	0.84	26

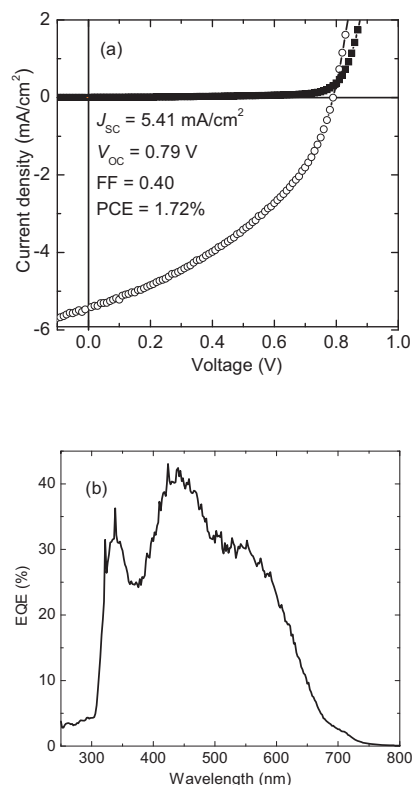
^a J_{sc} and PCE have been calibrated using external quantum efficiency measurement. ^bUnder simulated AM 1.5 solar irradiation of 100 mW/cm² for as-fabricated devices.

5 The potential of these highly extended oligothiophenes as hole-transporting light-absorbing materials in solution-processable photovoltaic cells was explored. The bulk heterojunction PV cells with device structure of ITO / PEDOT:PSS / oligomer:PCBM / LiF (1 nm) / Al (120 nm) were fabricated by the spin-casting of PEDOT:PSS layer and then blend of oligomer:PCBM layer followed by vacuum deposition of LiF and Al as the cathode. The PV response of these devices were measured under the AM 1.5 simulated solar illumination at an irradiation intensity of 100 mW/cm². 15 The results of the device performance are summarized in Table 2. Most of the devices have relatively large V_{oc} (~ 0.8 V) because of the low-lying HOMO levels of these oligothiophenes (~ -5.2 eV) resulting in larger differences to the LUMO level of PCBM. The devices with thicker active 20 layer have better PCEs and fill factors. By increasing the film thickness from 100 nm to 160 nm, devices fabricated with 1:2 **G₂-OT(6)-DCN**:PCBM ratios exhibit significant increase in J_{sc} and PCE up to 1.12% with V_{oc} of 0.79 V. (Figure 4) It is known that the carrier mobility of a blended film is greatly 25 influenced by the donor:acceptor ratio. **G₂-OT(6)-DCN**:PCBM-based devices with a ratio of 1:4 exhibit decreases in J_{sc} , V_{oc} and thus, PCE . In sharp contrast, devices fabricated with 1:4 **PhNOF-OT(5)-DCN**:PCBM ratios exhibit dramatic enhancement in J_{sc} (to 5.41 mA/cm²) and FF (= 30 0.40) with a PCE up to 1.72%. (Figure 5) The external quantum efficiency (EQE) measurements show that the **PhNOF-OT(5)-DCN**-based device exhibits a very broad photoresponse range from 300 nm to 680 nm which corresponds well to the UV-vis absorption spectra of the films 35 and the maximum EQE reaches 43% at 424 nm. Our findings highlight the potential of this class of materials promising for further device optimization in high performance PV applications.

Conclusions

40 In summary, a novel series of solution-processable, p-type, low-optical-gap semiconductors based on penta- and hexathiophenes asymmetrically endcapped with triarylamine or triarylamino-substituted dendron and dicyanovinyl groups has been synthesized. Highly extended oligothiophene backbone 45 results in strong spectra boardening which is advantageous to

light harvesting. The **PhNOF-OT(5)-DCN**:PCBM-based device exhibits a high PCE of 1.72% with V_{oc} = 0.79 V and EQE_{max} = 43%. Our findings also suggest that highly extended donor-acceptor oligomers can be useful as a p-type, low 50 bandgap semiconductor for solution-processable bulk heterojunction PV cells. Further device optimization to enhance the efficiency of these oligomer-based PV cells is still in progress.

**Fig. 5** (a) J - V characteristics of **PhNOF-OT(5)-DCN**:PCBM (1:4)-based PV cells (b) the EQE curves of the corresponding PV cells.

Experimental

General procedures and requirements

All the solvents were dried by the standard methods wherever needed. ^1H NMR spectra were recorded using a Bruker-400 NMR spectrometer and referenced to the residual CHCl_3 7.26 ppm. ^{13}C NMR spectra were recorded using a Bruker-400 NMR spectrometer and referenced to the CDCl_3 77 ppm. Mass Spectroscopy (MS) measurements were carried using fast atom bombardment on the API ASTER Pulsar I Hybrid Mass Spectrometer or matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) technique. Elemental Analysis was carried on CARLO ERBA 1106 Elemental Analyzer. Thermal stabilities were determined by thermal gravimetric analyzer (PE-TGA6) with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under N_2 . The glass transition and melting transition were extracted from the second run DSC traces which were determined by differential scanning calorimeter (PE PYRIS Diamond DSC) with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under N_2 . All absorption measurements were performed with Varian Cary 100-UV-Vis spectrophotometer. The half-wave potential ($E_{1/2}$) or peak potential (E_p) vs F_C^+/F_C were estimated by cyclic voltammetric method (Voltammetric Analyzer CV-50W) using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar bridge connecting to the oligomer solution dissolved in CH_2Cl_2 using 0.1 M of Bu_4NPF_6 as a supporting electrolyte with a scan rate of 100 mV/s and all the potential were calibrated with ferrocene as an external standard.

OPV Device Fabrication and Testing

ITO-coated glass substrates ($15\ \Omega/\square$) were patterned by conventional wet-etching process using an acid mixture of HCl (6 N) and HNO_3 (0.6 N) as the etchant. The active area of each solar cell was $5 \times 7\text{ mm}^2$. After patterning, the substrates were rinsed in deionized water, and then ultrasonicated sequentially in acetone ($20\text{ }^\circ\text{C}$) and 2-propanol ($65\text{ }^\circ\text{C}$). Immediately before device fabrication, the ITO substrate was treated in a UV-ozone oven for 15 min. Subsequently, a poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) thin film (50 nm) was spin-coated at 5000 rpm from its aqueous solution onto the treated substrate, and then baked at $140\text{ }^\circ\text{C}$ under nitrogen for 30 min. The active layer composed of the blend of oligomer and PCBM at various ratios was then spin-coated on top of PEDOT-PSS from chlorobenzene solutions for 60 s. The thickness of the resulting film was measured with a Dektak III surface profilometer. The device fabrication was completed by the vacuum deposition of LiF (1 nm) and Al cathode (120 nm). The solar cells with no protective encapsulation were subsequently tested in air under air mass (AM) 1.5 simulated solar illumination (100 mW/cm^2 , Sciencetech, Model SF150). Current-voltage (I-V) characteristics were recorded using a computer-controlled Keithley 2400 source meter.

2-[9,9-Bis(*n*-decyl)-2-diphenylamino-7-fluorenyl]-bithiophene (3). To a 100 mL round bottom flask was added 1.4 g (2.13 mmol) of boronic acid **1**, 5-iodo-2,2'-bithiophene **2** (746 mg , 2.56 mmol), 100 mg of $\text{Pd}(\text{PPh}_3)_4$, 5 mL of 2 M

K_2CO_3 and 40 mL of THF. The mixture was heated to $80\text{ }^\circ\text{C}$ and stirred for overnight under N_2 . After cooling to room temperature, the mixture was poured into water and extracted with DCM ($3 \times 20\text{ mL}$). The combined organic phase was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using PE/DCM as eluent affording the desired product as a colorless crystalline solid (1.2 g , 73%). Mp: $72\text{--}74\text{ }^\circ\text{C}$. ^1H NMR (400 MHz , CDCl_3): δ 7.54-7.60 (m, 3 H), 7.49 (d, $J = 0.8\text{ Hz}$, 1 H), 7.20-7.27 (m, 6 H), 7.17 (d, $J = 4.0\text{ Hz}$, 1 H), 7.10-7.12 (m, 5 H), 6.99-7.04 (m, 4 H), 1.80-1.95 (m, 4 H), 1.05-1.27 (m, 28 H), 0.86 (t, $J = 2.8\text{ Hz}$, 6 H), 0.67-0.69 (m, 4 H). ^{13}C NMR (100 MHz , CDCl_3): δ 152.3, 151.4, 147.9, 147.2, 144.0, 140.6, 137.6, 136.1, 135.7, 132.0, 129.1, 127.8, 124.6, 124.5, 124.2, 123.8, 123.5, 123.4, 123.2, 122.5, 120.4, 119.6, 119.4, 119.2, 55.1, 40.2, 31.9, 29.9, 29.7, 29.6, 29.5, 29.3, 23.8, 22.6, 14.1. MS (MALDI-TOF): m/z 778.1 (M^+).

5-[9,9-Bis(*n*-decyl)-2-diphenylamino-7-fluorenyl]-2-pentathiophenecarboxaldehyde (6a). To a dry 100 mL two-neck flask containing 2.0 g (2.57 mmol) of **3** and 30 mL of dry THF was dropwise added 2.4 mL (3.9 mmol) of 1.6 M of *n*-butyl lithium under N_2 at $-78\text{ }^\circ\text{C}$ while maintaining a good stirring. After stirring for 1 h, trimethyl borate (0.45 mL , 4.0 mmol) was added in one portion. The reaction mixture was then stirred for 1 h at $-78\text{ }^\circ\text{C}$. When the mixture was naturally warmed to $-30\text{ }^\circ\text{C}$, water and HCl (3 M) were added. Then the solution mixture was poured into water and extracted with EA ($3 \times 50\text{ mL}$). The combined organic phase was dried over anhydrous sodium sulfate, filtered and evaporated to dryness under $35\text{ }^\circ\text{C}$. The crude product was purified by silica gel column chromatography using DCM and PE/EA as eluent affording the desired product, 5-[9,9-bis(*n*-decyl)-2-diphenylamino-7-fluorenyl]-2-bithiopheneboronic acid (**4**) as a green solid (1.58 g , 75%). The product was directly used in the next coupling reaction without further purification. To a 100 mL round bottom flask was added 300 mg (0.36 mmol) of boronic acid **4**, 100 mg (0.25 mmol) of aldehyde (**5a**), 50 mg of $\text{Pd}(\text{PPh}_3)_4$, 2 mL of 2 M K_2CO_3 and 20 mL of THF. The mixture was heated to $80\text{ }^\circ\text{C}$ and stirred for overnight under N_2 . After cooling to room temperature, the mixture was poured into water and extracted with DCM ($3 \times 20\text{ mL}$). The combined organic phase was dried with anhydrous sodium sulfate, filtered and evaporated to dryness. The crude product was purified by silica gel column chromatography using PE/DCM as eluent affording the desired product as a red solid (205 mg , 78%). Mp: $145\text{--}147\text{ }^\circ\text{C}$. ^1H NMR (400 MHz , CDCl_3): δ 9.86 (s, 1 H), 7.67 (d, $J = 4.0\text{ Hz}$, 1 H) 7.54-7.60 (m, 3 H), 7.49 (d, $J = 1.2\text{ Hz}$, 1 H), 7.23-7.28 (m, 7 H), 7.17 (d, $J = 4.0\text{ Hz}$, 1 H), 7.09-7.14 (m, 10 H), 6.99-7.03 (m, 3 H), 1.81-1.96 (m, 4 H), 1.07-1.25 (m, 28 H), 0.86 (t, $J = 2.8\text{ Hz}$, 6 H), 0.67-0.70 (m, 4 H). ^{13}C NMR (100 MHz , CDCl_3): δ 182.4, 152.3, 151.5, 147.9, 147.3, 146.7, 144.5, 141.6, 140.8, 138.8, 137.4, 137.0, 136.9, 135.6, 135.5, 135.2, 135.1, 134.5, 131.8, 129.2, 127.0, 125.2, 124.8, 124.7, 124.6, 124.3, 124.1, 124.0, 123.9, 123.5, 123.4, 122.6, 120.4, 119.6, 119.5, 119.2, 55.1, 40.2, 31.9, 29.9, 29.6, 29.5, 29.3, 23.8, 22.7, 14.1. MS

(MALDI-TOF): m/z 1052.2 ($M^+ + 1$).

5-[9,9-Bis(*n*-decyl)-2-diphenylamino-7-fluorenyl]-2-hexathiophenecarboxaldehyde (6b). The synthetic procedure of compound **6a** was followed using 300 mg (0.36 mmol) of boronic acid **4**, 121 mg (0.25 mmol) of aldehyde **5b**, 50 mg of Pd(PPh₃)₄, 2 mL of 2 M K₂CO₃ and 20 mL of 1, 4-dioxane. The crude product was purified by silica gel column chromatography using PE/DCM as eluent affording the desired product as a red solid (227 mg, 80 %). Mp: 162-164 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.86 (s, 1 H), 7.68 (d, $J = 3.6$ Hz, 1 H), 7.54-7.60 (m, 3 H), 7.49 (d, $J = 1.2$ Hz, 1 H), 7.23-7.29 (m, 7 H), 7.18 (d, $J = 4.0$ Hz, 1 H), 7.10-7.15 (m, 12 H), 6.99-7.03 (m, 3 H), 1.81-1.96 (m, 4 H), 1.07-1.25 (m, 28 H), 0.86 (t, $J = 2.8$ Hz, 6 H), 0.67-0.70 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 182.4, 152.3, 151.5, 147.9, 147.3, 146.7, 144.4, 141.6, 140.8, 138.7, 137.4, 137.0, 136.9, 136.7, 136.5, 135.6, 135.5, 135.2, 134.6, 131.9, 129.2, 127.0, 125.2, 124.8, 124.7, 124.6, 124.5, 124.4, 124.3, 124.1, 123.9, 123.4, 122.5, 120.4, 119.6, 119.5, 119.2, 55.1, 40.2, 31.9, 29.9, 29.6, 29.5, 29.3, 23.8, 22.6, 14.1. MS (MALDI-TOF): m/z 1134.3 ($M^+ + 1$).

PhNOF-OT(5)-DCN. To a 100 mL round bottom flask containing 210 mg (0.20 mmol) of **6a** and 10 mL of CHCl₃ was added 0.40 g (6.1 mmol) of malononitrile and 0.8 mL of pyridine at room temperature. The solution was heated to refluxing and stirred for overnight under N₂. After cooling to room temperature, the reaction mixture was poured into water, neutralized with 0.1 M HCl, and extracted with CHCl₃ (3 × 20 mL). The combined organic phase was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The crude product was purified by silica gel column chromatography using PE/DCM as eluent and further precipitated by CHCl₃/Et₂O, washed with methanol and dried in vacuum affording the desired product as a black red solid (204 mg, 93 %). ¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 1 H), 7.54-7.62 (m, 4 H), 7.49 (d, $J = 1.2$ Hz, 1 H), 7.35 (d, $J = 4.0$ Hz, 1 H), 7.23-7.29 (m, 6 H), 7.09-7.18 (m, 11 H), 6.99-7.03 (m, 3 H), 1.83-1.94 (m, 4 H), 1.07-1.27 (m, 28 H), 0.86 (t, $J = 7.2$ Hz, 6 H), 0.67-0.70 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 152.3, 151.5, 149.8, 148.8, 147.9, 147.3, 144.5, 140.9, 140.2, 140.1, 137.5, 137.1, 135.5, 135.4, 135.0, 134.6, 133.5, 133.3, 131.8, 129.2, 128.1, 125.6, 124.8, 124.7, 124.6, 124.3, 124.2, 124.1, 123.9, 123.4, 122.6, 120.4, 119.6, 119.5, 119.1, 114.2, 113.5, 75.9, 55.1, 40.2, 31.9, 29.9, 29.6, 29.5, 29.3, 23.9, 22.6, 14.1. HRMS (MALDI-TOF): calcd: For C₆₉H₆₉N₃S₅: 1099.4089; Found: 1089.4092. Anal calc. for C₆₉H₆₉N₃S₅: C 75.30, H 6.32, N 3.82; found: C 75.36, H 6.33, N 3.84.

PhNOF-OT(6)-DCN. The synthetic procedure of **PhNOF-OT(5)-DCN** was followed using 226 mg (0.20 mmol) of **6b**, 0.40 g (6.1 mmol) of malononitrile, 0.8 mL of pyridine and 10 mL of CHCl₃. The crude product was purified by silica gel column chromatography using PE/DCM and precipitated by CHCl₃/Et₂O affording the desired product as a black red solid (212 mg, 90 %). ¹H NMR (400 MHz, CDCl₃): δ 7.74 (s, 1 H),

7.55-7.63 (m, 4 H), 7.49 (s, 1 H), 7.35 (d, $J = 4.0$ Hz, 1 H), 7.23-7.29 (m, 6 H), 7.09-7.18 (m, 13 H), 6.99-7.03 (m, 3 H), 1.81-1.95 (m, 4 H), 1.07-1.25 (m, 28 H), 0.86 (t, $J = 6.8$ Hz, 6 H), 0.67-0.70 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 153.3, 151.5, 149.8, 148.8, 147.9, 147.3, 144.4, 140.8, 140.1, 137.4, 136.8, 136.6, 135.6, 13.5, 135.3, 134.7, 133.5, 133.4, 131.8, 129.2, 128.2, 125.6, 124.9, 124.8, 124.7, 124.6, 124.4, 124.3, 124.1, 123.9, 123.4, 122.6, 120.5, 119.6, 119.5, 119.2, 114.2, 113.5, 75.9, 55.1, 40.2, 31.9, 30.9, 29.9, 29.6, 29.5, 29.3, 23.9, 22.7, 14.1. HRMS (MALDI-TOF): calcd: For C₇₃H₇₁N₃S₆: 1181.3966; Found: 1181.4034. Anal calc. for C₇₃H₇₁N₃S₆: C 74.13, H 6.05, N 3.55; found: C 74.42, H 6.07, N 3.71.

5-{3,6-bis[4-(diphenylamino)-1-phenyl]carbazol-9-yl}-2-pentathiophenecarboxaldehyde (8a). The synthetic procedure of compound **6a** was followed using 430 mg (0.5 mmol) of boronic acid **7**, 161 mg (0.4 mmol) of aldehyde **5a**, 40 mg of Pd(PPh₃)₄, 3 mL of 2 M K₂CO₃ and 20 mL of THF. The crude product was purified by silica gel column chromatography using PE/DCM as eluent affording the desired product as a red solid (362 mg, 83 %). Mp: 298-300 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.86 (s, 1 H), 9.88 (s, 1 H), 8.32 (d, $J = 1.2$ Hz, 2 H), 7.67-7.70 (m, 3 H), 7.61 (d, $J = 8.4$ Hz, 6 H), 7.24-7.29 (m, 11 H), 7.13-7.16 (m, 18 H), 7.02-7.05 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 182.4, 147.7, 146.7, 146.6, 141.7, 141.3, 138.6, 137.5, 137.4, 136.7, 136.2, 136.0, 135.8, 135.4, 135.1, 134.7, 134.1, 129.3, 127.9, 126.9, 125.6, 125.3, 125.2, 124.7, 124.67, 124.61, 124.3, 124.2, 124.1, 122.8, 122.5, 118.3, 110.6. MS (MALDI-TOF): m/z 1092.1 ($M^+ + 1$).

5-{3,6-bis[4-(diphenylamino)-1-phenyl]carbazol-9-yl}-2-hexathiophenecarboxaldehyde (8b). The synthetic procedure of compound **6b** was followed using 430 mg (0.5 mmol) of boronic acid **7**, 145 mg (0.30 mmol) of aldehyde **5b**, 3 mL of 2 M K₂CO₃ and 20 mL of 1, 4-dioxane. The crude product was purified by silica gel column chromatography using PE/DCM as eluent affording the desired product as a red solid (281 mg, 80 %). Mp: 302-305 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.87 (s, 1 H), 8.32(d, $J = 1.6$ Hz, 2 H), 7.68-7.71 (m, 3 H), 7.61 (d, $J = 8.4$ Hz, 6 H), 7.24-7.30 (m, 11 H), 7.13-7.21 (m, 20 H), 7.02-7.05 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 182.4, 147.7, 146.7, 146.6, 141.6, 141.3, 138.7, 137.4, 137.3, 136.8, 136.2, 136.0, 135.8, 135.3, 135.2, 134.6, 134.0, 129.3, 127.9, 127.0, 125.6, 125.4, 125.2, 124.7, 124.6, 124.57, 124.52, 124.3, 124.2, 124.1, 122.8, 122.4, 118.3, 110.6. MS (MALDI-TOF): m/z 1174.3 ($M^+ + 1$).

G₂-OT(5)-DCN. The synthetic procedure of compound **PhNOF-OT(5)-DCN** was followed using 160 mg (0.146 mmol) of **8a**, 400 mg (6.1 mmol) of malononitrile, 0.7 mL of pyridine and 10 mL of CHCl₃. The crude product was purified by silica gel column chromatography using PE/DCM and precipitated by CHCl₃/Et₂O affording the desired product as a black solid (149 mg, 89 %). ¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, $J = 1.2$ Hz, 2 H), 7.72 (s, 1 H), 7.69 (dd, $J = 8.8$ Hz, $J = 1.6$ Hz 2 H), 7.61 (d, $J = 8.4$ Hz, 7 H), 7.35 (d, $J = 4.0$ Hz, 1 H), 7.23-7.29 (m, 10 H), 7.12-7.20 (m, 18 H), 7.05 (t, $J = 7.4$

Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 148.8, 147.8, 146.8, 141.3, 140.1, 140.0, 137.6, 137.3, 136.4, 135.9, 135.8, 135.1, 135.0, 134.1, 133.7, 133.5, 129.3, 128.2, 127.9, 125.7, 125.4, 125.0, 124.9, 124.8, 124.7, 124.4, 124.3, 124.2, 122.8, 122.6, 118.4, 114.3, 113.5, 110.6, 76.1. HRMS (MALDI-TOF): calcd: For C₇₂H₄₅N₅S₅: 1139.2273; Found: 1139.2288. Anal calc. for C₇₂H₄₅N₅S₅: C 75.82, H 3.98, N 6.14; found: C 75.87, H 3.99, N 6.03.

G₂-OT(6)-DCN. The synthetic procedure of compound **PhNOF-OT(5)-DCN** was followed using 170 mg (0.144 mmol) of **8b**, 400 mg (6.1 mmol) of malononitrile, 0.7 mL of pyridine and 10 mL of CHCl₃. The crude product was purified by silica gel column chromatography using PE/DCM and precipitated by CHCl₃/ Et₂O affording the desired product as a black solid (161 mg, 91 %). ¹H NMR (400 MHz, CDCl₃): δ 8.32 (d, *J* = 1.2 Hz, 2 H), 7.74 (s, 1 H), 7.70 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2 H), 7.59-7.62 (m, 7 H), 7.36 (d, *J* = 4.0 Hz, 1 H), 7.25-7.30 (m, 10 H), 7.12-7.21 (m, 20 H), 7.02-7.06 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ 149.8, 148.7, 147.7, 146.7, 141.2, 140.1, 140.0, 137.4, 137.3, 136.4, 136.0, 135.7, 135.6, 135.0, 134.9, 134.0, 133.6, 133.4, 129.3, 128.1, 127.9, 125.6, 125.2, 124.8, 124.7, 124.5, 124.3, 122.8, 122.4, 118.3, 114.2, 113.5, 110.6, 75.8. HRMS (MALDI-TOF): calcd: For C₇₆H₄₇N₅S₆: 1221.2150; Found: 1221.2121. Anal calc. for C₇₆H₄₇N₅S₆: C 74.66, H 3.87, N 5.73; found: C 74.77, H 3.99, N 5.58.

Acknowledgement

This work was financially supported by Hong Kong Research Grant Council, GRF, HKBU 202408.

Notes and references

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† Electronic Supplementary Information (ESI) available: [physical characterization and spectra of new compounds]. See DOI: 10.1039/b000000x/

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