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Small molecules containing rigidified thiophenes and a cyanopyridone acceptor unit for solution-processable bulk-heterojunction solar cells

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#### **Key Words**

Donor- $\pi$ -acceptor, Rigidified thiophenes, Cyanopyridone, Bulk-heterojunction solar cells

#### Abstract

We designed solution processable small molecules, 5-((5-(4two (diphenylamino)phenyl)thieno[3,2-*b*]thiophene-2-yl)methylene)-1-(2-ethylhexyl)- 4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (1) and 5-((6-(4-(diphenylamino)phenyl)-4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-d]pyrrol-2-yl)methylene)-1-(2-ethylhexyl)-4methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (2),consisting of a triphenylamine electron donating group and a cyanopyridone electron accepting group linked

by two different rigidified  $\pi$ -spacer thiophenes. Ultraviolet-visible absorption spectra revealed that the use of three fused rings (dithienopyrrole) as the conjugated  $\pi$ -spacer resulted in an enhanced intramolecular charge transfer transition and reduction of band gap, when compared with a non-fused bithiophene and two fused thiophenes (thienothiophene) analogues. Power conversion efficiencies (PCEs) of 2.39% and 2.14% were achieved for simple photovoltaic devices based on  $1/PC_{61}BM$  and  $2/PC_{61}BM$  under simulated AM 1.5 illumination (100 mW cm<sup>-2</sup>), respectively. It has been observed that the degree of conjugation of the central  $\pi$ -bridge was not a key factor for the enhancement of photovoltaic performance.

#### 1. Introduction

Bulk heterojunction (BHJ) organic solar cells have attracted a great deal of attention over the past two decades because of their promise of low-cost fabrication, ease of solution processability, light weight and potential application in flexible, large-area devices [1]. BHJ solar cells are comprised of an interpenetrating network of organic donor and acceptor domains, which is formed during their fabrication via solution processing. Traditionally, semiconducting polymers such as poly(3-hexylthiophene) (P3HT) as an electron donor material and a soluble fullerene derivative such as [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) as an electron acceptor material have been used [2–5]. However, recent reports of improved BHJ device performance as a result of using small molecules have attracted much attention [6–10]. Solution processable small molecules have a number of potential advantages over polymers such as high absorption coefficients, well defined structures, purification, high chemical stability and relatively straight-forward synthetic strategies. However, in common with polymeric structures, the design requirements of small molecules include a low optical band gap, broad absorption profile, high mobility, multiple reversible redox potentials and

appropriate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. It has been established that low band gap materials can be generated by incorporating an electron donor– $\pi$ -bridge–electron acceptor (D– $\pi$ –A or D–A) motif within the structure [11–16].

Reports of BHJ devices using small organic molecules as donor components have recently emerged that have utilized squaraine [17], oligothiophene [18], merocyanine dyes [19–20], diketopyrrolopyrrole derivatives [21], dibenzochrysene [22], and push-pull organic dyes [23– 25]. Progress in the field has resulted in devices exhibiting PCEs in the excess of 9% [26–30]. While this progress is encouraging, considerable scope still exists to develop novel lightharvesting materials that possess broad and efficient optical absorption, deep HOMO energy levels (-5.0 to -5.5 eV) and adequate solubility for thin film formation [9,10]. One successful strategy is the exploration of donor-acceptor molecules with a conjugated  $\pi$ -bridge. Such structures allow intramolecular charge transfer (ICT) transitions that broaden the absorption spectrum and narrow the optical band gap.

In our own studies of small molecule chromophores/charge transport materials based on a D– A design, we have previously shown that the use of a cyanopyridone acceptor fragment has a positive effect on the optoelectronic properties and material performance in devices [24,31]. However, while the reference dye **R1** (see Fig. 1) has almost ideal energy levels, according to the analysis by Brabec et al.[32], devices based on **R1** do not give the predicted power conversion efficiencies of 8%. This is due to low currents and low fill factors. We therefore set out to examine what is the effect of changing the chemistry of the central part of the molecule on their OPV performance. We have synthesized two examples 5-((5-(4-(diphenylamino)phenyl))thion[3,2-b]thiophene-2-yl)methylene)-1-(2-ethylhexyl)- 4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (**1**) and <math>5-((6-(4-(diphenylamino)phenyl))-

4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)methylene)-1-(2-ethylhexyl)-4-

methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (2) along with the reference dye (**R1**) such that all the materials have triphenylamine as a common donor and cyanopyridone as an acceptor fragment. All the molecular structures are shown in Fig. 1. In the reference dye, a non-fused bithiophene was used as the  $\pi$ -bridge and in this work, we examined the use of two fused thiophenes (thienothiophene) (target compound 1) and three fused rings (dithienopyrrole) (target compound 2) as alternative central cores. Our aim was to increase the absorbance of the compound at higher energy (fill in the gap around 400 nm) and we hypothesised that using more rigid cores might enhance the intermolecular interactions and therefore the fill factor of OPV devices. We know that thin films based on **R1** are largely amorphous and that device performance is not improved by thermal annealing [24]. By introducing more rigid groups, we hoped to improve charge transport.

In this paper, we report the facile synthesis and characterization of the optical, electrochemical and photovoltaic properties of small molecules **1** and **2**. The materials **1** and **2** were synthesized *via* the Knoevenagel condensation of the appropriate aldehyde with the active methylene group of the cyanopyridone acceptor and their chemical structures were confirmed by <sup>1</sup>H NMR spectroscopy and mass spectrometry. Knoevenagel condensation of the aldehyde groups present on the oligothiophenes is an efficient way of generating a double bond between the  $\pi$ -bridge and an acceptor unit. The use of such condensations is a common strategy to generate metal-free organic dyes for dye-sensitized solar cells [33]. However, the use of the same strategy to develop materials for BHJ photovoltaic devices has been limited [9,10]. In this report, we demonstrate the Knoevenagel condensation reaction between the aldehyde group present on a rigidified spacer and an aromatizable acceptor. To the best of our knowledge this is the first time that rigidified thiophenes have been used in conjunction with the aromatizable cyanopyridone acceptor.

#### **FIGURE 1 GOES HERE**

#### 2. Experimental

#### 2.1. Materials

All reagents and chemicals used, unless otherwise specified, were purchased from Sigma-Aldrich Co. The solvents used for reactions were obtained from Merck Speciality Chemicals (Sydney, Australia) and were used as received. 1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile and 6-(4-(diphenylamino)phenyl-4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-carbaldehyde were synthesized as per our previous reports [24,34].

#### 2.2. Spectroscopic measurements

Unless otherwise specified, all <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker AV400 spectrometer at 400 MHz and 100.6 MHz, respectively, or a Bruker AV200 spectrometer at 200 MHz and 50 MHz, respectively. Chemical shifts ( $\delta$ ) are measured in parts per million. Thin Layer Chromatography (TLC) was performed using 0.25 mm thick plates precoated with Merck Kieselgel 60 F<sub>254</sub> silica gel, and visualised using UV light (254 nm and 365 nm). Analytical high performance liquid chromatography (HPLC) analyses were performed using a Waters 2695 alliance system and Waters 2996 photodiode array detector scanning 190–700 nm using an Alltima HP C18 column at 30 °C with 95% acetonitrile and 5% tetrahydrofuran as mobile phase. Waters Empower 2 data management system was used for data processing. Melting points were measured using a Gallenkamp MPD350 digital

melting point apparatus and are uncorrected. Electron impact (EI) mass spectra were carried out on a ThermoQuest MAT95XP mass spectrometer using ionisation energy of 70 eV and employing PerFluoroKerosene (PFK) as a reference sample. Electro spray (ES) mass spectra were carried out on a Thermo scientific Q-Exactive FTMS. Atmospheric-pressure chemical ionization (APCI) experiments were carried out on a Thermo Scientific Q-Exactive FTMS, ionizing by APCI from an ASAP probe [35]. UV–Vis absorption spectra were recorded using a Hewlett Packard HP 8453 diode array spectrometer. Fluorescence spectra were measured using a Perkin Elmer LS50B fluorimeter.

#### 2.3. Electronic measurements

PESA measurements were recorded using a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on cleaned glass substrates. Electrochemical measurements were carried out using a PowerLab ML160 potentiostat interfaced via a PowerLab 4/20 controller to a PC running E-Chem For Windows version 1.5.2. The measurements were run in argon-purged dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The cyclic voltammograms were recorded using a standard three electrode configuration with a glassy carbon (2 mm diameter) working electrode, a platinum wire counter electrode and a silver wire pseudo reference electrode. The silver wire was cleaned in concentrated nitric acid followed by concentrated hydrochloric acid and then washed with deionised water. Cyclic-voltammograms were recorded with a sweep rate of 50 mV s<sup>-1</sup>. All the potentials were referred to the  $E_{1/2}$  of ferrocene/ferrocenium redox couple.

## 2.4. Device fabrication and characterization of photovoltaic devices

Indium tin oxide (ITO)-coated glass (Kintek, 15  $\Omega/\Box$ ) was cleaned by standing in a stirred solution of 5% (v/v) Deconex 12PA detergent at 90 °C for 20 minutes. The ITOcoated glass was then successively sonicated for 10 mins each in distilled water, acetone and isopropanol. The substrates were then exposed to a UV-ozone clean at room temperature for 10 minutes. UV/ozone cleaning of glass substrates was performed using a Novascan PDS-UVT, UV/ozone cleaner with the platform set to maximum height. The intensity of the lamp was greater than 36 mW/cm<sup>2</sup> at a distance of 10 cm. At ambient conditions the ozone output of the UV cleaner is greater than 50 ppm. Aqueous solutions of PEDOT/PSS (HC Starck, Baytron P AI 4083) were filtered (0.2 µm RC filter) and deposited onto glass substrates in air by spin coating (Laurell WS-400B-6NPP lite single wafer spin processor) at 5000 rpm for 60 sec to give a layer having a thickness of  $40 \pm 5$  nm. The PEDOT/PSS layer was then annealed on a hotplate in a glove box at 145 °C for 10 min. For OPV devices, the newly synthesized organic *p*-type materials and  $PC_{61}BM$  (Nano-C) were dissolved in individual vials by magnetic stirring. Blend ratios and solution concentrations were varied to optimize device performance. The solutions were then combined, filtered (0.2 µm RC filter) and deposited by spin coating onto the ITO-coated glass substrates inside a glove box. The coated substrates were then transferred (without exposure to air) to a vacuum evaporator inside an adjacent nitrogen-filled glove box. Samples were placed on a shadow mask in a tray. The area defined by the shadow mask gave device areas of exactly 0.2 cm<sup>2</sup>. Deposition rates and film thicknesses were monitored using a calibrated quartz thickness monitor inside the vacuum chamber. Layers of calcium (Ca) (Aldrich) and aluminium (Al) (3 pellets of 99.999%, KJ Lesker) having thicknesses of 20 nm and 100 nm, respectively, were evaporated from open tungsten boats onto the active layer by thermal evaporation at pressures less than  $2 \times 10^{-6}$ mbar. A connection point for the ITO electrode was made by manually scratching off a small

area of the active layers. A small amount of silver paint (Silver Print II, GC Electronics, part no.: 22-023) was then deposited onto all of the connection points, both ITO and Al. The completed devices were then encapsulated with glass and a UV-cured epoxy (Summers Optical, Lens Bond type J-91) by exposing to 365 nm UV light inside a glove box for 10 min. The encapsulated devices were then removed from the glove box and tested in air within 1 h. The OPV devices were tested using an Oriel solar simulator fitted with a 1,000W xenon lamp filtered to give an output of 100 mW/cm<sup>2</sup> at simulated AM 1.5. The lamp was calibrated using a standard, filtered silicon (Si) cell from Peccell Limited which was subsequently cross-calibrated with a standard reference cell traceable to the National Renewable Energy Laboratory. The devices were tested using a Keithley 2400 Sourcemeter controlled by labview software. Film thicknesses were determined using a Dektak 6M Profilometer.

## 2.5. Device fabrication and characterization of field effective transistors

A doped (N ~  $3 \times 10^{17}$  cm<sup>-3</sup>) silicon (Si) wafer was used as a substrate and as the gate electrode. Discrete bottom contact OFETs were fabricated on thermally grown smooth silicon dioxide (SiO<sub>2</sub>) (230 nm). Interdigitated source and drain electrodes were photolithographically patterned from a 50 nm sputtered gold layer. Channel length, L, of the devices was 20 µm and the channel width, W, was 2 mm. The SiO<sub>2</sub> layer was first cleaned with acetone, then with 2-propanol and finally treated with UV ozone. Device fabrication was completed by spin coating the organic semiconductor layers at 1500 rpm in the glove box from solutions in chloroform. The active layers consisted of pristine compounds or blends with PC<sub>61</sub>BM. Without any further treatment, completed devices were transferred (under airfree conditions) to another glove box fitted to probe the devices using a probe station. Electrical measurements were carried out using a Keithley 2612 dual channel SMU. The reproducibility of the organic field effect transistors (OFETs) preparation procedure was high with a confidence interval for the extracted mobility of ±15% of the values which have been

presented. The carrier mobility values presented in this work were generally averaged from measurements done on at least four devices on the same substrate.

#### 2.6. Synthesis

New compounds **1** and **2** were synthesized and characterized. The synthetic strategy for **1** and **2** is represented in schemes 1 and 2 respectively.



Scheme 1 Synthetic strategy for compound 1

#### 2.6.1 Synthesis of thieno[3,2-b]thiophene-2-carbaldehyde (S1)

Thieno[3,2-b]thiophene (3.00 g, 21.4 mmol) was taken in a 100 mL round bottom flask in ethylene dichloride (75.0 mL) and dimethylformamide (1.65 mL, 21.4 mmol) was

added at room temperature. The resulting reaction solution was cooled to 0 °C and POCl<sub>3</sub> (5.87 mL, 64.3 mmol) was added drop-wise. The reaction mixture was allowed to warm to room temperature and heated at reflux overnight. The reaction mixture was treated with a saturated solution of sodium acetate and the organic layer was separated. The organic layer was washed with water followed by brine, dried over anhydrous sodium sulphate and the solvent was evaporated *in vacuo* to give a crude dark yellow oil, which was purified by column chromatography on silica (hexane:ethyl acetate 9:1) to give the *title compound* **S1** (2.70 g, 75%) as a light yellow oil. R<sub>f</sub> (10% ethyl acetate/hexane) 0.45; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 25 °C, ppm)  $\delta$  10.05 (s, 1H), 8.33 (s, 1H), 8.00–7.99 (m, 1H), 7.57–7.55 (m, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C, ppm)  $\delta$  183.7, 145.9, 145.6, 139.4, 134.1, 129.3, 120.3; HRMS (APCI): calcd for C<sub>7</sub>H<sub>5</sub>OS<sub>2</sub> (M+H)<sup>+</sup> 168.9775; found 168.9776.

## 2.6.2 Synthesis of 5-iodothieno[3,2-b]thiophene-2-carbaldehyde (S2)

Compound **S1** (1.50 g, 8.93 mmol) was taken in a 100 mL round bottom flask in an acetic acid:chloroform 1:1 ( $\nu/\nu$ ) solvent mixture (50.0 mL) and *N*-iodosuccinimide (2.51 g, 11.2 mmol) was added at room temperature. The resulting reaction mixture was stirred overnight in the absence of light. The solid that formed in the reaction was collected by filtration and washed with hexane to obtain the *title compound* **S2** (1.00 g, 64%) as a light green solid. M. Pt.: 185–187 °C; <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 25 °C, ppm)  $\delta$  10.05 (s, 1H), 8.25 (s, 1H), 7.82 (s, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C, ppm)  $\delta$  183.7, 145.9, 144.9, 143.9, 129.3, 127.7, 83.5; HRMS (APCI): calcd for C<sub>7</sub>H<sub>4</sub>IOS<sub>2</sub> (M+H)<sup>+</sup> 294.8742; found 294.8743.

#### 2.6.3 Synthesis of 5-(4-(diphenylamino)phenyl)thieno[3,2-b]thiophene-2-carbaldehyde (S3)

Compound **S2** (1.00 g, 3.40 mmol), 4-(diphenylamino)phenylboronic acid (1.50 g, 5.10 mmol), sodium phosphate dodecahydrate (1.55 g, 4.08 mmol) and 10% Pd(C) (200 mg) were added together in a 250 mL round bottom flask and isopropanol (100 mL) was added at room temperature. The reaction mixture was heated to 80 °C for 24 h and the reaction progress was monitored by thin layer chromatography (hexane:ethyl acetate 9:1), which indicated the consumption of starting aldehyde. The mixture was cooled to room temperature, filtered through Celite (5.00 g) and eluted with dichloromethane. The solvent was removed and the residue was purified by flash chromatography eluted with 50% CHCl<sub>3</sub>/petroleum ether (60–80 °C) to afford the *title compound* **S3** (1.10 g, 78%) as a yellow solid. M. Pt.: 151–153 °C; R<sub>f</sub> (50% CHCl<sub>3</sub>/petroleum ether [60–80 °C]) 0.30; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, ppm)  $\delta$  9.93 (s, 1H), 7.88 (s, 1H), 7.51–7.48 (m, 2H), 7.42 (s, 1H), 7.31–7.27 (m, 4H), 7.15–7.13 (m, 4H), 7.10–7.06 (m, 4H); HRMS (APCI): calcd for C<sub>25</sub>H<sub>18</sub>NOS<sub>2</sub> (M+H)<sup>+</sup> 412.0824; found 412.0828.

2.6.4 Synthesis of 5-((5-(4-(diphenylamino)phenyl)thieno[3,2-b]thiophene-2-yl)methylene)1-(2-ethylhexyl)- 4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (1)

Compound **S3** (900 mg, 2.18 mmol) and 1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6tetrahydropyridine-3-carbonitrile (970 mg, 3.72 mmol) were added together in a 250 mL round bottom flask in chloroform (100 mL) and pyridine (340 mg, 4.36 mmol) was added to this mixture at room temperature. The resulting reaction mixture was heated at reflux overnight and the progress of reaction was monitored by thin layer chromatography (hexane:ethyl acetate 8:2), which indicated the complete consumption of starting compound **S3**. The reaction mixture was cooled and the solvent was evaporated *in vacuo* to give crude bluish-black oil, which was purified by flash chromatograph eluted with 50%

dichloromethane/pet ether (60–80 °C)  $\rightarrow$  100% dichloromethane to afford the *title compound* **1** (900 mg, 63%) as a shiny greenish-black powder. R<sub>f</sub> (100% dichloromethane) 0.40; HPLC (5% THF/ACN): 97%; M. Pt.: 208–213 °C; IR (thin solid film, cm<sup>-1</sup>) 2950, 2924, 2856, 2217, 1678, 1630, 1589, 1570, 1486, 1447, 1413, 1291, 1282, 1171, 783, 751, 694; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, ppm)  $\delta$  7.96 (s, 1H), 7.91 (s, 1H), 7.54–7.51 (m, 2H), 7.44 (s, 1H), 7.33–7.29 (m, 4H), 7.16–7.05 (m, 8H), 4.01–3.90 (m, 2H), 2.64 (s, 3H), 1.89–1.85 (m, 1H), 1.37–1.26 (m, 8H), 0.93–0.85 (m, 6H); <sup>13</sup>C NMR (200 MHz, CDCl<sub>3</sub>, 25 °C, ppm)  $\delta$  163.1, 160.9, 157.9, 156.3, 156.1, 149.4, 146.8, 144.7, 139.2, 138.4, 136.9, 129.5, 127.3, 126.3, 125.3, 124.1, 122.0, 116.2, 115.1, 114.3, 103.3, 44.0, 37.5, 30.5, 28.5, 23.8, 23.1, 18.9, 14.1, 10.6; HRMS (ESI): calcd for C<sub>40</sub>H<sub>37</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub> (*m/z*) 655.2322; found 655.2311.



Scheme 2 Synthetic strategy for compound 2

2.6.5 Synthesis of 5-((6-(4-(diphenylamino)phenyl)-4-(2-ethylhexyl)-4H-dithieno[3,2b:2',3'-d]pyrrol-2-yl)methylene)-1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6tetrahydropyridine-3-carbonitrile (**2**)

Compound 6-(4-(diphenylamino)phenyl-4-(2-ethylhexyl)-4*H*-dithieno[3,2-b:2',3'-d]pyrrol-2-carbaldehyde (700 mg, 1.24 mmol) and 1-(2-ethylhexyl)-4-methyl-2,6-dioxo-

1,2,5,6-tetrahydropyridine-3-carbonitrile (550 mg, 2.20 mmol) were added together in a 100 mL round bottom flask in chloroform (70.0 mL) and pyridine (147 mg, 1.86 mmol) was added to this mixture at room temperature. The resulting reaction mixture was heated at reflux overnight and the solvent was evaporated off to give a crude dark black solid that was purified by flash chromatograph eluted with 100% dichloromethane to afford the *title* compound 2 (550 mg, 55%) as a shiny black powder. Rf (100% DCM) 0.50; HPLC (5% THF/ACN): 96%; M. Pt.: 137–140 °C; IR (thin solid film, cm<sup>-1</sup>) 2950, 2924, 2856, 2217, 1678, 1630, 1589, 1570, 1486, 1447, 1413, 1291, 1282, 1171, 783, 751, 694; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C, ppm) δ 7.95 (s, 1H), 7.79 (s, 1H, bd), 7.54–7.52 (m, 2H), 7.33–7.27 (m, 4H), 7.15-7.10 (m, 7H), 7.06-7.04 (m, 2H), 4.09-4.06 (m, 2H), 3.98-3.80 (m, 2H), 2.59 (s, 3H), 2.01–1.95 (m, 1H), 1.89–1.83 (m, 1H), 1.40–1.24 (m, 16H) 0.95–0.81(m, 12H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C, ppm) δ 163.2, 161.5, 157.9, 153.8, 152.5, 148.8, 146.9, 146.1, 144.5, 136.1, 134.5, 129.5, 127.5, 126.7, 125.6, 125.1, 123.8, 122.5, 115.8, 114.3, 113.7, 105.1, 100.6, 51.4, 43.9, 40.3, 37.4, 30.6, 30.6, 28.6, 28.5, 24.1, 23.8, 23.1, 22.9, 18.9, 14.1, 13.9, 10.7, 10.6; HRMS (ESI): calcd for C<sub>50</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub> (*m/z*) 806.3683; found 806.3646.

## 3. Results and discussion

#### 3.1. Synthesis and characterization

The materials **1** and **2** were synthesized by reacting the aldehyde precursors, 5-(4-(diphenylamino)phenyl)thieno[3,2-b]thiophene-2-carbaldehyde and 6-(4-(diphenylamino)phenyl-4-(2-ethylhexyl)-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-carbaldehyde, at reflux with 1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile in

chloroform, respectively, in the presence of pyridine as a base. Both the materials were purified through column chromatography. These solids were characterized spectrally and their physical properties were investigated. The materials were prepared in moderate to high yields and were found to be highly soluble in a variety of conventional organic solvents such as chlorobenzene, chloroform, dichloromethane and toluene. High solubility of organic materials is an essential criterion for the fabrication of solution-processable organic photovoltaic devices and newly designed materials **1** and **2** fulfil this criterion. Synthetic details of **R1** have been reported previously [24].

#### 3.2. Optical properties

The ultraviolet-visible (UV–Vis) spectra of both the new materials 1 and 2 were measured in chloroform solutions (Fig. 2) and compared with **R1**. Dye 2 had a significantly higher extinction coefficient and absorption maximum when compared with 1 or **R1**. This bathochromic shift for the solution spectrum of 2 was observed as a result of using dithienopyrrole as the conjugated  $\pi$ -spacer when compared with either two fused thiophenes or a non-fused bithiophene, and can be attributed to the extended conjugation for ICT over the whole molecular backbone. On the contrary, dye 1 exhibited 19 nm of blue shift in the solution spectrum when compared with **R1**. Overall, the absorption profile was not broadened, but it was red-shifted. Absorption maximum ( $\lambda_{max}$ ) at 571 nm ( $\varepsilon = 61,011 \text{ M}^{-1} \text{ cm}^{-1}$ ) with onset at 706 nm for 1 and  $\lambda_{max}$  at 621 nm ( $\varepsilon = 101,621 \text{ M}^{-1} \text{ cm}^{-1}$ ) with onset at 730 nm for **2** were measured. Peak molar absorptivity for **1** and **R1** were similar, whereas we found ~65% enhancement to the peak molar absorptivity of **2** when compared with **1** or **R1**. We further realized that dye **1** may exert solvatochromism for which it is showing inferior absorption maximum in chloroform, and we decided to conduct its solution spectra in other solvents such as ethyl acetate (EA) and tetrahydrofuran (THF). The blue shift of 19 nm

which was observed for the solution spectrum of **1** in chloroform was reduced to about 5 nm in both the new solvents when compared with **R1**. However, considering the empirical solvent polarity parameter  $E_T(30)$  we realized that EA and THF have similar  $E_T(30)$  values. We decided to choose some more solvents and to compare the solution spectra of **1** and **R1** to elucidate solvatochromism. The solution spectra of **1** and **R1** were studied in acetonitrile (ACN) and dimethylformamide (DMF). We observed that the absorption maxima difference of **1** and **R1** was about 5 nm in both the ACN and DMF solvents, thus indicating that dye **1** certainly exerts solvatochromism. The comparative absorption spectra of dyes **1** and **R1** are depicted in Figures 2a and 2b.

# FIGURE 2 GOES HERE FIGURE 2a GOES HERE FIGURE 2b GOES HERE

Absorption spectra of **1** and **2** as pristine films (equimolar solutions of **1** and **2** spun at 3000 rpm for 1 minute) were measured on glass substrates (Fig. 3). Generally, for a given compound, the thin film absorption spectrum will exhibit a bathochromic shift as compared to its solution spectrum. This was true for **2** where we observed a broader spectrum with onset extension in comparison to its solution spectrum. So the use of three fused rings as the conjugated  $\pi$ -spacer could help to absorb a greater amount of solar spectrum. However, film spectra of **1** indicated a blue shift of about 70 nm when spun-cast from its chloroform solution. The same observation was found with the use of other solvents such as chlorobenzene. An explanation to this absorption spectrum modification towards blue shift can be suggested based on the destruction of ordering of crystal packing.

#### **FIGURE 3 GOES HERE**

#### 3.3. Energy levels

Experimental estimation of the HOMO and LUMO energies of compounds 1 and 2 using Photo Electron Spectroscopy in Air (PESA) and UV–vis spectrometry indicated that the band gaps of these materials are all in the range required of donor materials for BHJ devices and are significantly narrower in magnitude than 1.8 eV measured for P3HT (see Fig. 4 for the energy level diagram). HOMOs for all the compounds were found to be similar. By comparison with **R1**, the LUMO of 1 was raised by 0.16 eV as a result of a wider band-gap. However, the LUMO of 2 was the deepest of all due to the extended red-shift in the film absorption spectrum when compared with 1 or **R1**. The optical and electrochemical properties of all the materials are summarized in Table 1.

**FIGURE 4 GOES HERE** 

## Table 1

Comparative optical and electronic properties

Dye	Absorption	Absorption	Emission	$E_{\rm HOMO}$	$E_{\rm bandgap}$	ELUMO
	(solution)	(film)	(solution)	eV <sup>c</sup>	$eV^d$	eV <sup>e</sup>
	$\lambda_{max}^{a}/onset/nm$	$\lambda_{max}^{b}/onset/nm$	$\lambda_{\max}^{a}/nm$			
	$[\varepsilon/(M^{-1}cm^{-1})]$					
1	571/706	512/722	744	-5.40	1.72	-3.68
	[61,011]					
2	621/730	614/834	720	-5.40	1.49	-3.91
	[101,621]					
R1	590/722	584/790	800	-5.40	1.57	-3.83
	[61,028]					

<sup>a</sup> Absorption and emission spectra were measured in chloroform solution.

<sup>b</sup> Absorption spectra of thin solid films spin-cast (equimolar solutions of **1** and **2** spun at 4000 rpm for 1 minute) from chloroform solutions.

<sup>c</sup> HOMO levels of the dyes were measured using PESA on thin solid films on glass.

<sup>d</sup> Energy band gaps were estimated from the absorption onset in thin solid films.

<sup>e</sup> LUMO levels were calculated from the optical band gaps (film) and HOMO levels ( $E_{LUMO}$ =

 $E_{\text{bandgap}} + E_{\text{HOMO}})$ 

Electrochemistry experiments revealed that both the compounds 1 and 2 undergo reversible oxidation processes, thus suggesting their suitability as p-type materials in BHJ devices (see Fig. 5). Cyclic voltammograms indicated that the oxidation of 1 and 2 occurred at a half-wave potential of around 0.1 eV versus ferrocene/ferrocenium (Fc/Fc+) internal reference

(ferrocene potentials: 0.32 eV and 0.24 eV), a finding consistent with the HOMO energy levels estimated using PESA.

#### **FIGURE 5 GOES HERE**

#### 3.4. Density functional theory calculations

Density functional theory (DFT) calculations using the Gaussian 09 suite of programs [36] and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory indicated that the HOMO electron densities of **1** and **2** were homogeneously populated over the triphenylamine and central fused conjugated spacers with considerable contribution from the former. The HOMO was more delocalized over the whole molecular backbone when compared with **R1**. The LUMO was delocalized through the spacers and cyanopyridone acceptor fragments with a sizable contribution from the latter (see Fig. 6).

## **FIGURE 6 GOES HERE**

Furthermore, we thought to elucidate the nature of ICT using time-dependent DFT calculations (TD-DFT). TD-DFT calculations were carried out using the optimized ground state geometries of **1** and **2** at the B3LYP/6-311G(d,p) level of theory. The TD-DFT calculations provide excitation energies and oscillator strengths (denoted by f) of the lowest singlet states. The computed absorption spectra (see Fig.7) show the first transition peak at 619.39 nm and 589.63 nm, respectively, for **1** and **2**. The first peak is quite clearly described as HOMO  $\rightarrow$  LUMO transition: Excited State 1: 2.0017 eV 619.39 nm f=0.9932, 173(HOMO)  $\rightarrow$  174(LUMO) 0.70535; Excited State 1: 2.1028 eV 589.63 nm f=1.4739,

 $215(\text{HOMO}) \rightarrow 216(\text{LUMO}) \ 0.69822$ , for **1** and **2**, respectively. Consequently, the subsequent analysis of the transition density matrix via natural transition orbitals (NTOs), produces a pair of NTOs with a very similar character as the corresponding HOMO/LUMO pair (see Fig. 8).

#### **FIGURE 7 GOES HERE**

#### FIGURE 8 GOES HERE

#### 3.5. Photovoltaic properties

Because of their appropriate optoelectronic properties, solubility and good film forming capabilities, **1** and **2**, were incorporated as *p*-type semiconducting components with the soluble fullerene derivative  $PC_{61}BM$  as the *n*-type semiconductor in BHJ photovoltaic devices and were compared with reference dye **R1**. BHJ architectures typically deliver higher device power conversion efficiencies by maximising the surface area of the interface between the donor and acceptor materials in the active layer. For both the compounds, **1** and **2**, the device structure used was ITO/PEDOT: PSS (38 nm)/active layer/Ca (20 nm)/Al (100 nm) where the active layer was a solution-processed blend of either of **1** or **2** and the solubilised fullerene  $PC_{61}BM$ . This was done by spin coating mixtures of the appropriate dye with  $PC_{61}BM$  in chlorobenzene under ambient conditions in 1:1 or 1:4 ratios without subsequent annealing. The optimum layer thickness was found to be in the range of about 60 nm. It was interesting to see that the BHJ devices based on **1** and **2** were copper-red and blue, respectively (Fig. 9). The best photovoltaic devices based on compound **1** gave a PCE ( $\eta$ ) of 2.39% with 1:4 donor:acceptor blend ratio whereas for compound **2**, the optimized blend

ratio was found to be 1:1 under which the device afforded 2.14% PCE. The respective current-voltage (J-V) curves are shown in Fig. 9.

For organic BHJ solar cells, it is documented that  $V_{oc}$  is proportional to the energy difference between HOMO of donor component and LUMO of the acceptor component [37,38]. This initial screen for the efficacy of target compounds **1** and **2** showed  $V_{oc}$  of 0.83 and 0.81V respectively. These values are consistent with the measured HOMO values and in-line with the similar HOMO of **R1**. Device performance showed that with compound **1** we have significantly improved the *FF* but the current is slightly reduced by comparison with **R1**. For compound **2**, the *FF* is comparable to **R1** and the device results are also comparable. However, the devices based on compound **2** showed a higher photocurrent than either of **1** or **R1** when compared for 1:1 blend, a finding that is consistent with the observed red-shift in the absorbance for compound **2** when compared with **1** or **R1**. Table 2 represents the comparative photovoltaic performance data.

#### Table 2

Dye	Testing	Blend film	V <sub>oc</sub>	$J_{\rm sc}$	FF	Efficiency
	conditions @	thickness	(mV)	(mA/cm <sup>2</sup> )		(η%)
	4000 rpm					
1	1:1 PC <sub>61</sub> BM <sup>a</sup>	64	830	5.36	0.45	2.00
1	1:4 PC <sub>61</sub> BM <sup>a</sup>	56	830	5.44	0.53	2.39
2	1:1 PC <sub>61</sub> BM <sup>a</sup>	62	810	7.33	0.36	2.14
2	1:4 PC <sub>61</sub> BM <sup>a</sup>	53	740	5.14	0.33	1.27
R1	1:1 PC <sub>61</sub> BM <sup>a</sup>	55	872	6.77	0.38	2.25
<mark>R1</mark>	1:4 PC <sub>61</sub> BM <sup>a</sup>	<mark>65</mark>	<mark>822</mark>	<mark>5.64</mark>	0.32	<mark>1.50</mark>

Comparative BHJ solar cells performances

a BHJ devices with specified weight ratio. Device structure is ITO/PEDOT: PSS (38 nm)/active layer/Ca(20 nm)/Al (100 nm) with an active layer thickness of around 60 nm.

#### **FIGURE 9 GOES HERE**

The incident photon to current conversion efficiency (IPCE) curves of the best BHJ devices based on these small molecules under monochromatic light are shown in Fig. 10. For dye 1, the IPCE curve is blue-shifted relative to the thin film absorption spectrum. The IPCE shows a maximum of ~42% at 505 nm. By contrast, the IPCE spectrum of compound 2 shows a broad response covering 400–800 nm, with a maximum value of ~41% at 640 nm. The IPCE measurements reported here are comparable to the film absorptions of 1 and 2 which indicate that the current arises mainly from the *p*-type donor material.

#### **FIGURE 10 GOES HERE**

With regards to the processing conditions of blend solutions, we [22] and others [6] have shown in previous studies that there exists a strong effect of solvent and the degree of crystallization on the cell performance. Attempts to fabricate the devices using low boiling solvents, such as chloroform, resulted in very poor photovoltaic performance. This was mainly due to poor film quality. The finding that the OPV devices comprising **1** and **2** perform better with high-boiling solvents is significant as the use of high-boiling solvents is preferable from a processing point of view.

To gain an insight into the effective charge carrier mobilities in active blends, we examined

the field effect mobility,  $\mu_{e,h}$ , of charge carriers in devices fabricated using **1** and **2** from their corresponding OFETs. In this study, bottom gate bottom contact OFETs were fabricated by depositing the organic semiconductor from solution by spin casting onto a lithographically patterned substrate (see experimental for details). To our surprise, we were unable to measure either hole or electron mobilities for the blend films, both being  $\leq 10^{-7}$  cm<sup>2</sup>/Vs. We did find a hole mobility of the order of  $1.2 \times 10^{-6}$  cm<sup>2</sup>/Vs for **1** in its pristine state while no mobility was observed for **2** in its pristine state. This unbalanced charge carrier transport, unlike polymer BHJ [39] may be responsible for the lower *FF* values observed in the present system. For **R1**, hole mobility of the order of  $1.8 \times 10^{-6}$  cm<sup>2</sup>/Vs was observed in its pristine state with no electron mobility.

To examine the physical microstructure of the surface we used atomic force microscopy (AFM) in tapping mode. Figure 11 displays the topographic and phase images of 1:4 blends of **1** and **2** with PC<sub>61</sub>BM. **1** appears to have a worm-like morphology with larger domains and better phase separation with surface roughness of ~ 2.8 nm, whereas blend films of **2** are fairly smooth, with a roughness of ~ 0.33 nm. This difference in morphology is like the origin of why the devices of **1** outperform those of **2**, even though **1** has a lower extinction coefficient and  $\lambda_{max}$ . Compound **1** displays superior morphological properties that had a greater effect on efficiency than the light absorption properties of that dye. The presence of two ethylhexyl substituents on **2** may be hindering the formation of favourable microstructure due excessive compatibility of **2** with PC<sub>61</sub>BM. The use of shorter alkyl groups on the dithienopyrrole may improve its performance by decreasing its solubility.

#### FIGURE 11 GOES HERE

#### 4. Conclusions

In conclusion, we have demonstrated the use of D– $\pi$ –A small molecules containing rigidified  $\pi$ -spacer thiophenes in organic solar cells. The new materials **1** and **2** using thienothiophene and dithienopyrrole respectively as  $\pi$ -spacers were soluble in common organic solvents and were applied as *p*-type semiconducting components along with the *n*-type material PC<sub>61</sub>BM in BHJ photovoltaic devices. By comparison with a reference dye using bithiophene as the  $\pi$ -spacer (**R1**), compound **1** shows a larger band gap, similar extinction coefficient and blue shifted absorption in solution and thin films whereas **2** had a significantly smaller band gap, a large red-shift in absorbance and a larger extinction coefficient suggesting greater visible light harvesting capacity. When these compounds were used in BHJ devices, better performance was observed with **1**. Efforts are ongoing to further improve the power conversion efficiency of devices and future studies will look at exploiting the fused thiophenes unit in higher efficiency D– $\pi$ –A materials.

#### Acknowledgements

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## LIST OF FIGURES



Fig. 1. Molecular structures of the newly designed (1 and 2) and reference (R1) materials



Fig. 2. UV–vis absorption spectra of 1 and 2 in chloroform solution



**Fig. 2a.** UV–Vis absorption spectra of **1** and **R1** in ethyl acetate (EA) and tetrahydrofuran (THF) solutions



**Fig. 2b.** UV–Vis absorption spectra of **1** and **R1** in acetonitrile (ACN) and dimethylformamide (DMF) solutions



Fig. 3. Normalized UV–vis absorption spectra of 1 and 2 in thin solid films, spin-cast from their chloroform solutions



Fig. 4. Energy level diagram depicting the band gaps of 1, 2 and R1 in comparison with P3HT and  $PC_{61}BM$  (Note: This does not represent a device structure).

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**Fig. 5.** Cyclic-voltammograms of **1** and **2** run in dichloromethane at a sweep rate of 50 mV sec<sup>-1</sup> showing reversible oxidation processes



**Fig. 6.** Orbital density distribution for the HOMOs and LUMOs of **1** (upper) and **2** (lower). DFT calculations were performed using Gaussian 09 suite of programs and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. The *calculated* HOMO/LUMO energy levels (vs Vac scale) are also shown.



Fig. 7. The computed absorption spectra of 1 (upper) and 2 (lower) showing the first transition peak at 619.39 nm and 589.63 nm respectively.



**Fig. 8.** A pair of NTOs with a very similar character as the corresponding HOMO/LUMO pair



**Fig. 9.** Characteristic current density vs voltage (*J*–*V*) curves for the best BHJ devices based on **1** and **2** in blends with PC<sub>61</sub>BM under simulated sunlight (100 mW cm<sup>-2</sup> AM 1.5 G). Device Structure is: ITO/PEDOT: PSS (38 nm)/Active layer/Ca (20 nm)/Al (100 nm). For **1** the active layer was 56 nm thick with w: w = 1: 4, for **2** the active layer was 62 nm thick with w:w = 1:1.



Fig. 10. Comparative incident photon to current efficiencies (IPCEs) (solid lines) and absorption spectra of blends (on top of films of PEDOT:PSS) (dotted lines) for 1 and 2 respectively. IPCE data are for the best devices described in Table 2.



Fig. 11. AFM images of 1:4 blend films with  $PC_{61}BM$  spin-cast from chlorobenzene at 2500 rpm atop annealed ITO/PEDOT:PSS substrates. Topographic images (a) as-cast, RMS ~ 2.8 nm of 1:PC\_{61}BM and (b) as-cast, RMS ~ 0.33 nm of 2:PC\_{61}BM. Phase images (c) as-cast for 1:PC\_{61}BM and (d) as-cast for 2:PC\_{61}BM. Scan size for all images was 10  $\mu$ m × 10  $\mu$ m. Thermal annealing conditions of ITO/PEDOT:PSS substrate: 110 °C for 10 min.

## **Figure captions**

Fig. 1. Molecular structures of the newly designed (1 and 2) and reference (R1) materials

Fig. 2. UV-vis absorption spectra of 1 and 2 in chloroform solution

Fig. 2a. UV-vis absorption spectra of 1 and R1 in ethyl acetate and THF solutions

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## **Research Highlights:**

- Use of rigidified thiophenes in conjunction with aromatizable cyanopyridone acceptor
- Linkage of rigidified thiophenes to aromatizable acceptor for spectral red-shift
- Two fused thiophenes display better film morphology comparing to three fused heterocycles incorporating thiophenes

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