#### Tetrahedron 70 (2014) 2141-2150

Contents lists available at ScienceDirect

# Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# *N*-Alkyl- and *N*-aryl-dithieno[3,2-*b*:2',3'-*d*]pyrrole-containing organic dyes for efficient dye-sensitized solar cells



Tetrahedror

Akhil Gupta <sup>a,\*,†</sup>, Melissa M.A. Kelson <sup>b</sup>, Vanessa Armel <sup>c</sup>, Ante Bilic <sup>d</sup>, Sheshanath V. Bhosale <sup>b,\*</sup>

<sup>a</sup> Department of Materials Engineering, Faculty of Engineering, Monash University, Wellington Road, Clayton, 3800 Victoria, Australia <sup>b</sup> School of Applied Sciences, RMIT University, GPO Box 2476V, Melbourne, 3001 Victoria, Australia

<sup>c</sup> Department of Chemistry, Faculty of Science, Monash University, Wellington Road, Clayton, 3800 Victoria, Australia

<sup>d</sup> CSIRO Mathematics Informatics and Statistics, Bayview Avenue, Clayton, 3169 Victoria, Australia

# ARTICLE INFO

Article history: Received 15 October 2013 Received in revised form 21 January 2014 Accepted 3 February 2014 Available online 7 February 2014

Keywords: Donor- $\pi$ -acceptor Dithienopyrrole Dye-sensitized solar cells Knoevenagel condensation

### ABSTRACT

Two new organic sensitizers, 2-cyano-3-(6-(4-(diphenylamino)phenyl)-4-(2-ethylhexyl)-4H-dithieno [3,2-b:2',3'-d]pyrrol-2-yl)acrylic acid and 2-cyano-3-(6-(4-(diphenylamino)phenyl)-4-(4-(hexyloxy) phenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)acrylic acid, consisting of electron donating (triphenyl-amine) and electron accepting (cyanoacrylic acid) functionalities linked by two different rigidified  $\pi$ -spacers, *N*-alkyl- and *N*-aryl-dithieno[3,2-b:2',3'-d]pyrrole, were designed, synthesized and applied for dye-sensitized solar cells, respectively. The materials were successfully synthesized through Knoevenagel condensation reactions. Ultraviolet—visible absorption spectra revealed that the use of either of rigidified  $\pi$ -spacer resulted in similar charge transfer transition, however, enhanced spectral response was observed when compared with an oligothiophene analogue. In terms of their photovoltaic performance, new dyes outperformed the reference bithiophene sensitizer when tested with nitrile-based and ionic liquid-based electrolytes.

© 2014 Elsevier Ltd. All rights reserved.

# 1. Introduction

Over the past two decades, dye-sensitized solar cells  $(DSCs)^1$  have been the target of intensive research due to their capability to convert sunlight to electricity and a certified conversion efficiency of 11.1% has been reported by Y. Chiba et al.<sup>2</sup> One of the key material challenges in the DSC research is the development of efficient photosensitizer that can be produced at low cost. Traditionally, functional ruthenium(II)–polypyridyl complexes such as dye **N3** [Ru{(4,4'-CO<sub>2</sub>H)<sub>2</sub>bipy}<sub>2</sub>(NCS)<sub>2</sub>] and the doubly deprotonated analogue of **N3**, dye **N719** [(Bu<sub>4</sub>N)<sub>2</sub>[Ru{(4,4'-CO<sub>2</sub>H)<sub>2</sub>bipy}<sub>2</sub>(NCS)<sub>2</sub>]],<sup>3</sup> developed by Grätzel et al. are the most successful dyes with promising device characteristics. However, such complexes contain expensive ruthenium metal and require complex synthesis and tricky purification steps. On the other hand, continuous efforts for the design and development of organic sensitizers have helped to gradually narrow the performance gap between

organic and ruthenium-based sensitizers. Metal-free organic donor—acceptor dyes have achieved conversion efficiencies over 10% and the porphyrin sensitizers rival the ruthenium-based sensitizers with conversion efficiencies beyond 12%,<sup>4</sup> thus paying tributes to the advancement recently achieved in this field.

Key advantages with organic sensitizers (dyes) are that they have facile synthetic strategies and high absorption coefficients when compared to the dominant ruthenium-based dyes. One successful strategy to improve the performance of DSCs has been the design of typical 'donor-acceptor' (D- $\pi$ -A) modular organic dyes featuring triarylamine or its subsequent derivatives as donor fragments and cyanoacrylic acid as an acceptor fragment through the use of a central  $\pi$ -conjugated linker. This strategy with the variation of  $\pi$ -conjugated segments has attracted much attention and has led to a huge array of dyes that display promising energy conversion efficiencies.<sup>1d,5</sup> Such D– $\pi$ -A modular structures allow intramolecular charge transfer (ICT) transitions that broaden the absorption spectrum and narrow the optical band gap. There is, therefore, considerable synthetic interest in exploring new  $\pi$ conjugated linkers and in making molecules for efficient DSCs. Reports of DSC devices using such  $\pi$ -conjugated linkers have recently emerged that have utilized thieno[3,2-b]thiophene,<sup>6</sup> benzodiathiazole,<sup>7</sup> 3,4-ethylenedioxythiophene,<sup>8</sup> dithieno[3,2b:2',3'-d]thiophene,<sup>9</sup> dithieno[3,2-b:2',3'-d]pyrrole,<sup>10</sup> 4,4-bis(2-



<sup>\*</sup> Corresponding authors. Tel.: +61 3 9925 2680 (S.V.B); e-mail addresses: akhil. gupta@monash.edu, akhil.gupta@csiro.au (A. Gupta), sheshanath.bhosale@rmit. edu.au, bsheshanath@gmail.com (S.V. Bhosale).

 $<sup>^\</sup>dagger$  Present address: CSIRO Materials Science and Engineering, Bag 10, Clayton, 3169 Victoria, Australia.

<sup>0040-4020/\$ –</sup> see front matter @ 2014 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.tet.2014.02.002

ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b*']dithiophene,<sup>11</sup> phenoxazine<sup>12</sup> and fused bis-thiazole.<sup>13</sup> While this progress is encouraging, considerable scope still exists to develop new sensitizers that possess broad and efficient optical absorption, narrow band-gaps and adequate solubility for DSC fabrication.

We are also interested in exploring the D $-\pi$ -A module for organic sensitizers and in this paper, we report the facile synthesis and characterization of the optical, electrochemical and photovoltaic properties of two new organic sensitizers 2-cyano-3-(6-(4-(diphenylamino)phenyl)-4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'd]pyrrol-2-yl)acrylic acid (coded as 1) and 2-cyano-3-(6-(4-(diphenylamino)phenyl)-4-(4-(hexyloxy)phenyl)-4H-dithieno[3,2*b*:2',3'-*d*]pyrrol-2-yl)acrylic acid (coded as **2**). These organic dyes feature *N*-alkyl- and *N*-aryl-dithieno[3,2-*b*:2',3'-*d*]pyrrole derivates and were synthesized via the Knoevenagel condensation of an appropriate aldehyde with active methylene group of the cyanoacrylic acid acceptor unit and their chemical structures were confirmed by <sup>1</sup>H NMR spectroscopy and mass spectrometry. We further set out to examine the effect of changing the chemistry of the central part of molecule will have on the DSC performance. New dyes **1** and **2** were synthesized along with a reference dye (**3**) such that all the materials have triphenylamine as a common donor and cvanoacrylic acid as an acceptor component. It is anticipated that these small variations within the structure of a target material can cause significant differences in photovoltaic properties.<sup>14–16</sup> All the molecular structures are shown in Fig. 1.

sensitizers is a desirable feature for the fabrication of DSC devices and both the dyes, **1** and **2**, fulfil this criterion. It is notable to mention that dye **2** is the first example where *N*-(4-(hexyloxy) phenyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole building block has been used for DSC applications. The use of such building block, or in fact any *para*-substituted *N*-aryl-dithieno[3,2-*b*:2',3'-*d*]pyrrole block, for DSC applications hasn't been reported in the literature,<sup>1d,5</sup> thus provides a strong incentive for its investigation. The design concept of **2** was further motivated by the generation of an organic sensitizer that has enhanced solubility, when compared with its structural analogue, and can be studied in various dye-baths, if required. Reference dye **3** was synthesized in our labs following the literature procedure.<sup>17</sup>

# 2.2. Optoelectronic properties

The ultraviolet–visible (UV–vis) spectral absorptivities of both the new dyes **1** and **2** were measured in chloroform solutions (Fig. 2) and compared with **3**. Both the dyes, **1** and **2**, exhibited similar absorption characteristics, while the molar extinction coefficient at absorption maximum of **1** is slightly higher than that of **2**, a finding that was consistent with the literature study of various oligomers based on dithieno[3,2-*b*:2',3'-*d*]pyrrole for organic electronic applications.<sup>18</sup> Absorption maxima ( $\lambda_{max}$ ) at 479 nm ( $\epsilon$ =48,080 M<sup>-1</sup> cm<sup>-1</sup>) for **1** and  $\lambda_{max}$  at 476 nm ( $\epsilon$ =37,600 M<sup>-1</sup> cm<sup>-1</sup>) for **2** were measured. This bathochromic shift



Fig. 1. Molecular structures of the investigated sensitizers 1, 2 and reference dye (3).

#### 2. Results and discussion

# 2.1. Synthesis and characterization

The new materials were designed by using dithieno[3,2-*b*:2',3'*d*]pyrrole as a central  $\pi$ -spacer, where alkyl and aryl substitutions were allocated on the nitrogen atom of pyrrole ring, thus generating **1** and **2**, respectively. Dyes **1** and **2** were synthesized by reacting the aldehyde precursors, 6-(4-(diphenylamino)phenyl-4-(2-ethylhexyl))-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-carbaldehyde

and 6-(4-(diphenylamino)phenyl-4-(4-(hexyloxy)phenyl)-4*H*dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-carbaldehyde, at reflux with cyanoacrylic acid in chloroform, respectively, in the presence of piperidine as base. Both the materials were purified by 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 soluble in a variety of conventional organic solvents such as chloroform, dichloromethane and acetonitrile. High solubility of organic



Fig. 2. Molar absorptivities of newly synthesized 1 (red) and 2 (blue) versus reference dye 3 (black) in chloroform solution.

for the solution spectra of **1** and **2** was observed as a result of using rigidified thiophenes as conjugated  $\pi$ -spacers when compared with oligothiophenes and can be attributed to the enhanced conjugation over the whole molecular backbone. Enhancement of the peak molar absorptivities for **1** and **2** was observed when compared with **3**.

Once adsorbed onto a TiO<sub>2</sub> surface, **1** and **2** show very similar light harvesting properties. However, an obvious red-shift of 25 nm remained for both the dyes **1** and **2**, when compared with **3**. Thus, the use of rigidified thiophene  $\pi$ -spacers can help to absorb a greater amount of the solar spectrum. When the dyes were adsorbed onto a TiO<sub>2</sub> film, a blue-shift of  $\lambda_{max}$  and an overall broadening of the absorption spectrum were observed. Such blue shifts of absorption spectra following adsorption on TiO<sub>2</sub> surface can be attributed to the deprotonation of carboxylic acid functionality. Thin film absorption spectra on mesoporous titania are represented in Fig. 3.



**Fig. 3.** Thin film absorption spectra of adsorbed dyes on  $TiO_2$ ; 1.2 µm thick  $TiO_2$  films sensitized with **1** (red), **2** (blue) and **3** (black) were used and the spectra were recorded in air. Sensitization of the films was performed using a 0.3 mM dye solutions in a chloroform and ethanol mixture (v/v 8:2) containing 5 mM chenodeoxycholic acid for 4 h.

Theoretical density functional theory (DFT) calculations using Gaussian 03 suite of programs<sup>19</sup> 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 triphenylamine and central rigidified conjugated spacers with considerable contribution from the former. LUMO was delocalized through the spacers and cyanoacrylic acid acceptor fragment with a sizable contribution from the latter (see Fig. 4). This spatially directed separation of HOMO and LUMO is an ideal condition for ICT between donor and acceptor fragments. It was observed that there was no contribution from the hanging phenyl functionality of 2 to either of the orbital densities, thus suggesting that the phenyl ring is out of plain and both the dyes, 1 and 2, can possess similar energy levels. The observation was consistent with the literature report of dithieno[3,2-b:2',3'-d]pyrrole derivatives for organic electronic applications.<sup>18c</sup>

Experimentally, cyclic voltammetry was carried out to determine the redox properties of **1** and **2** (see Fig. 5). The oxidation of **1** and **2** occurs at a half-wave potential of 0.34 eV and 0.36 eV versus ferrocene/ferrocenium (Fc/Fc+) internal reference, respectively. Both the dyes possess almost similar energy levels, a finding that is consistent with our theoretical calculations. However, reduction in optical band gap was observed for both the

dyes when compared with **3**. The respective HOMO levels of **1** and **2** were calculated to be 0.70 V and 0.72 V versus NHE, and were found to be sufficiently more positive than the iodine/iodide redox potential value, 0.4 V versus NHE,<sup>20</sup> indicating that the oxidized dye formed after electron injection can accept an electron from the iodide ions. Similarly, LUMO levels of **1** and **2** were calculated to be -1.33 V and -1.31 V versus NHE, respectively, and were found to be sufficiently more negative than the conduction band (CB) edge of the TiO<sub>2</sub> electrode (-0.5 to -0.7 V versus NHE)<sup>19</sup> indicating that the electrons from the excited dye can be injected to the CB of TiO<sub>2</sub>. The spectral properties of **1** and **2**, shown in Fig. 2, were combined with the electrochemical data in solution to calculate the  $E_{1/2}$ (D\*/D<sup>+</sup>) energy levels shown in Fig. 6.<sup>21</sup> The optical and electrochemical properties of **a** lt the materials are summarized in Table 1.

#### 2.3. Photovoltaic properties

All three dyes were used to construct DSCs and their performance under simulated sunlight and monochromatic light illumination was characterized. Identical TiO<sub>2</sub> films with a two-layer architecture (6 µm transparent TiO<sub>2</sub> with 30 nm average particle diameter+6 µm reflective TiO<sub>2</sub> layer with 400 nm average particle diameter) were used to construct all cells. A standard highperformance nitrile-based electrolyte and a non-volatile electrolyte based on the imidazolium ionic liquid were employed. In conjunction with the nitrile-based electrolyte, both 1 and 2 performed similarly, however, clearly outperformed reference dve 3. due to a higher short-circuit current and open-circuit voltage. The overall conversion efficiency difference of approx. 25% is surprising. given the similarities in dye design. For comparison, an N719 DSC was prepared by the same procedure. Table 2 summarizes their photovoltaic performances and Fig. 7 shows the photocurrent-voltage curves of solar cells presented in Table 2.

Due to the excellent light harvesting properties at the peak absorption wavelengths of 1 and 2, most of the photons transmitted to mesoporous  $TiO_2$  layer are absorbed by the dyes (see Figs. 2 and 3). Consequently the peak incident photon-to-current conversion efficiency (IPCE) values at this wavelength give a good indication of the absorbed photon to electron conversion efficiencies, once corrected for transmission and reflection losses suffered in the FTO working electrode. The analysis of the IPCE measurements of these DSCs reveals a significantly higher peak IPCE of 1 (79.1%@495 nm) and 2 (83.9%@455 nm) compared to 3 (69.2%@440 nm), thus provides an indication that the superior performance of either of 1 or 2 can be rationalized in terms of either an increased electron injection efficiency or a reduced charge recombination rate. From the overlap integral of the IPCE curve with a standard AM 1.5G solar emission spectrum, short-circuit photocurrent densities of 10.5 mA/cm<sup>2</sup> and 11.5 mA/cm<sup>2</sup> were calculated for **1** and **2** (nitrilebased electrolyte), respectively, which is in excellent agreement of the measured photocurrent densities. Therefore there is negligible spectrum mismatch between our solar simulator and the standard AM 1.5G sunlight. Fig. 8 shows the IPCE spectra and Table 3 summarizes the measured IPCE values.

Overall, the use of rigidified thiophenes as conjugated  $\pi$ -spacers when compared with oligothiophenes resulted in around 25–30% increase in photocurrent density and ~25% increase in energy conversion efficiency, when compared with **R1**, thus promoting the use of rigidified moieties, such as *N*-alkyl- and *N*-aryl-dithieno[3,2-b:2',3'-d]pyrrole as an interesting structural concept for the design of high efficiency DSC sensitizers. Note that both the dyes, **1** and **2**, show light harvesting and electrochemical properties that are largely superior to **3**, and this does translate to higher conversion efficiency. Fig. 7 further summarizes the performance of these sensitizers in DSCs based on ionic liquid electrolytes, showing similar trends to the ones discussed for nitrile-based devices.



**Fig. 4.** Orbital density distribution for the HOMOs and LUMOs of **1** and **2**. DFT calculations were performed using Gaussian 03 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. 5. Cyclic voltammograms of 1 (red) and 2 (blue) in dichloromethane solution containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>; run at a sweep rate of 50 mV s<sup>-1</sup>.



Fig. 6. Diagram depicting the energy levels of iodide/triiodide electrolyte and new sensitizers 1 and 2.

Intensity modulated photovoltage and photocurrent spectroscopy (IMVS and IMPS)<sup>22</sup> in combination with charge extraction experiments were used to determine the electron lifetime and mean transit time of photoinjected charge carriers for acetonitrilebased electrolyte (see Fig. 9). Charge extraction measurements according to Duffy et al.<sup>23</sup> were used to determine the amount of charge stored in DSCs as a function of  $V_{oc}$  (see Fig. 9b). The results obtained through IMVS and charge extraction experiments were then combined to yield the electron lifetime as a function of charge stored in the DSC, as shown in Fig. 9a. The results clearly show an increase in electron lifetime for either **1-** or **2-**sensitized DSCs over devices sensitized with **3**. The IMPS results, shown in Fig. 9c, indicate that similar mean electron transit times were observed for all the dyes. This suggests that electron transport within the TiO<sub>2</sub> layer is comparable for all the dyes and electrolyte system.

# 3. Conclusions

We have reported the design, synthesis and characterization of two new organic dyes, 1 and 2, for use as photosensitizers in DSC devices. The dyes are bestowed with N-alkyl- and N-aryl-dithieno [3,2-b:2',3'-d] pyrrole units (1 and 2, respectively) as central  $\pi$ spacers, of which latter is the first example of such modification. Synthesis of 1 and 2 has been achieved in good yields and the dyes have been analytically characterized. On the basis of UV-vis absorption and cyclic voltammetry characterization, it has been found that either of the rigidified  $\pi$ -units appears to be more suitable than oligothiophenes in donor-acceptor dyes on the basis of its better conjugation and to effectively couple the triarylamine donor and cyanoacrylic acid acceptor functionalities. DSCs fabricated from 1 and 2 exhibit promising performance, clearly outperforming the reference dye **3**. Superior charge injection properties of **1** and **2** compared to **3** were proposed as the most likely reason for the enhanced photocurrent density and around 25% increase in energy conversion efficiency for nitrile-based and about 20% for ionic liquid-based electrolytes. These results provide strong incentive to apply these design concepts to novel generations of DSC sensitizers.

Further developments and exploration of this work is the subject of current research in our laboratories and we believe that new sensitizers will be designed with properties tailored toward their use in conjunction with alternative non-corrosive electrolytes such as cobalt-mediated and ferrocene.

Table 1	
Comparative optical and electrochemical properties of <b>1</b> , <b>2</b> and	13

Dye	Absorption (solution) $\lambda_{max}^{a}/onset/nm [\epsilon^{b}/(M^{-1} cm^{-1})]$	Absorption (film) $\lambda_{max}^{c}/nm$	Emission (solution) $\lambda_{max}^{a}/nm$	<i>E</i> <sub>HOMO</sub> <sup>d</sup> /eV	$E_{\rm bandgap}^{\rm e}/{\rm eV}$	<i>E</i> <sub>LUMO</sub> <sup>f</sup> /eV
1	479/610 [48,080]	427	623	-5.14	2.03	-3.11
2	476/610 [37,600]	427	629	-5.16	2.03	-3.13
3	460/580 [31,780]	402	680	-5.35	2.14	-3.29

<sup>a</sup> Absorption and emission spectra were measured in chloroform solutions  $(1.6 \times 10^{-5} \text{ M})$  at room temperature.

<sup>b</sup> The molar extinction coefficient at  $\lambda_{max}$  of the absorption spectra.

<sup>c</sup> Absorption spectra of the dyes adsorbed on TiO<sub>2</sub> electrodes. A 1.2 μm thick TiO<sub>2</sub> film was sensitized using a 0.3 mM dye solution in a chloroform and ethanol mixture (v/v 8:2) containing 5 mM chenodeoxycholic acid for 4 h.

<sup>d</sup> HOMO levels of the dyes were measured using cyclic voltammetry.

<sup>e</sup> Optical band gaps were estimated from the absorption onset in solution.

<sup>f</sup> LUMO levels were calculated from the optical band gaps and HOMO levels ( $E_{LUMO} = E_{bandgap} + E_{HOMO}$ ).

### Table 2

Photovoltaic parameters of DSC devices under simulated AM 1.5G solar irradiation (100 mW  $\rm cm^{-2})^a$ 

Dye	Redox mediator	V <sub>oc</sub> <sup>b</sup> (mV)	J <sub>sc</sub> <sup>c</sup> (mA/cm <sup>2</sup> )	FF <sup>d</sup>	η <sup>e</sup> (%)
1	Nitrile-based electrolyte	762±5	10.6±0.10	0.75±0.01	6.1±0.10
2	Nitrile-based electrolyte	$741\pm7$	$11.4 \pm 0.20$	$0.74{\pm}0.01$	$6.2 {\pm} 0.05$
N719	Nitrile-based electrolyte	$814\pm2$	$12.0 \pm 0.10$	$0.72{\pm}0.01$	$7.0 {\pm} 0.10$
3	Nitrile-based electrolyte	$704{\pm}5$	$8.8{\pm}0.10$	$0.78{\pm}0.01$	$4.9{\pm}0.10$
1	Ionic liquid electrolyte	$724{\pm}1$	$10.0{\pm}0.1$	$0.75 {\pm} 0.01$	$5.5 \pm 0.1$
2	Ionic liquid electrolyte	701±2	$10.5 \pm 0.1$	$0.70 {\pm} 0.02$	$5.1 \pm 0.1$
N719	Ionic liquid electrolyte	$737\pm6$	9.3±0.2	$0.76 {\pm} 0.01$	$5.2 \pm 0.1$
3	Ionic liquid electrolyte	$665{\pm}2$	$9.1{\pm}0.1$	$0.74{\pm}0.00$	$4.5{\pm}0.1$

<sup>a</sup> The concentration of dye solutions was maintained at  $3 \times 10^{-4}$  M in chloroform/ ethanol (8:2), with 5 mM chenodeoxycholic acid as a co-adsorbate. The composition of nitrile-based electrolyte was 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M *tert*-butylpyridine, 0.05 M lithium iodide in a mixture of acetonitrile and valeronitrile (85:15, v/v); and ionic liquid electrolyte composition was 1-ethyl-3-methylimidazolium iodide/1,3dimethylimidazolium iodide/1-ethyl-3-methylimidazolium tetracyanoborate/lithium iodide/iodine/N-methylbenzimidazole in molar ratio (12:12:16:1:1.67:4). The effective area of devices was defined with the use of a metal mask to be 0.16 cm<sup>2</sup>. <sup>b</sup> Open-circuit voltage.

Open-circuit voltage

<sup>c</sup> Short-circuit photocurrent density.

<sup>d</sup> Fill factor.

<sup>e</sup> Power conversion efficiency.

Co. The solvents used for various reactions were obtained from Merck Speciality Chemicals (Sydney, Australia) and were used as such. 4-(2-Ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole was purchased from Luminescence Technology Corporation, Taiwan and was used as such. 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 (ppm). Thin layer chromatography (TLC) was performed using 0.25 mm thick plates precoated with Merck Kieselgel 60 F254 silica gel, and visualized using UV light (254 nm and 365 nm). Melting points were measured using a Gallenkamp MPD350 digital melting point apparatus and are uncorrected. Positive ion electron impact (EI) mass spectra were measured using a ThermoQuest MAT95XP mass spectrometer using ionization energy of 70 eV. High resolution mass spectra (atmospheric-pressure chemical ionization (APCI)) experiments were carried out on a Thermo Scientific O-Exactive FTMS, ionizing by APCI from an ASAP probe.<sup>24</sup> 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.



Fig. 7. Photocurrent–voltage characteristics of DSCs measured under simulated 100 mW cm<sup>-2</sup> AM 1.5G sunlight using 1 (red), 2 (blue), 3 (black) and N719 (green) for nitrile-based (left) and ionic liquid-based (right) electrolytes.

#### 4. Experimental section

#### 4.1. General methods

4.1.1. Reagents and methods. All the reagents and chemicals used, unless otherwise specified, were purchased from Sigma–Aldrich

4.1.2. Computational method and electrochemistry. Theoretical DFT calculations were carried out using Gaussian 03 suite of programs<sup>17</sup> and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. 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 Ver. 1.5.2. The measurements were



Fig. 8. Incident photon-to-current conversion efficiencies of DSCs sensitized with 1 (red), 2 (blue), N719 (green) and 3 (black) based on nitrile (left) and ionic liquid (right) electrolytes (same devices as reported in Table 2).

#### Table 3

Measured IPCEs of DSCs<sup>a</sup> sensitized with dyes reported in this study based on nitrilebased and ionic liquid-based electrolytes

Dye	Maximum IPCEs for nitrile-based electrolyte	Maximum IPCEs for ionic liquid-based electrolyte
1	79.1%@495 nm	76.7%@465 nm
2	83.9%@455 nm	75.2%@470 nm
N719	81.5%@530 nm	70%@525 nm
3	69.2%@440 nm	71.5%@445 nm

<sup>a</sup> Same devices as reported in Table 2.

wire pseudo reference electrode. The silver wire was cleaned in concentrated nitric acid followed by concentrated hydrochloric acid and then washed with deionized 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.

4.1.3. Solar cell assembly. The glass substrate used was 4 mm thick 10  $\Omega/\Box$  conductive FTO (fluorine doped tin oxide) glass with high transparency in the visible range purchased from Nippon sheet glass. Mesoporous  $4 \times 4$  mm TiO<sub>2</sub> films were printed



**Fig. 9.** IMVS and IMPS measurements performed on **1** (red), **2** (blue), **N719** (green) and **3** (black) sensitized DSCs for nitrile-based electrolyte (same devices as reported in Table 2). (a) Electron lifetime versus electron density. (b) Electron density as a function of V<sub>oc</sub>. (c) Mean charge transient time versus short-circuit current.

run in argon-purged dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The cyclic voltammograms were recorded using a standard threeelectrode configuration with a glassy carbon (2 mm diameter) working electrode, a platinum wire counter electrode and a silver using a commercial semi automatic screen printer and commercial 30 nm  $TiO_2$  screen printing paste (PST-30NR, JGC Catalysts and Chemicals). The scattering paste was prepared from 400 nm particles mixed 5 to 1 by weight with 30 nm particles and addition of 3.5 parts ethyl cellulose and 30.5 parts terpineol. After a first sintering process (500 °C), a TiCl<sub>4</sub> treatment was applied by immersing the films in a 40 mM aqueous TiCl<sub>4</sub> solution and heating at 70 °C for 30 min in a water saturated atmosphere. Prior to device assembly, the films were sintered again (500 °C), cooled to approximately 80 °C and immersed in a solution containing either of **1**. **2** or **3** (0.3 mM in a 8:2 mixture of chloroform and ethanol) for 6 h. The dved films were rinsed with absolute ethanol to remove non-attached dve from the films. Counter electrodes were prepared from 3 mm thick 15  $\Omega/\Box$  conductive FTO glass purchased from Nippon glass. A solution of chloroplatinic acid hexahydrate (10 mM) in ethanol was doctor bladed onto the pre-drilled substrate and pyrolyzed for 15 min at 450 °C. The dried working and counter electrodes were assembled using a 25 µm thick Surlyn gasket (Solaronix) of the dimensions  $5 \times 6$  mm. A pneumatic finger was used to apply pressure while heating through the counter electrode. The cells were then vacuum backfilled through a pre-drilled hole in the counter electrode. The backfilling hole was sealed at 150 °C using a square of aluminium backed Surlyn prepared by melting 25 µm Surlyn onto aluminium foil at 100 °C.

4.1.4. Device fabrication. The dyes were tested in photovoltaic devices using standard titanium dioxide with a  $6 \,\mu m$  thick transparent layer of 30 nm sized particles and a 6 µm thick scattering layer of 400 nm sized particles on top of the transparent layer. A blocking layer TiO<sub>2</sub> of few nanometres were deposited prior to the screen printing of the transparent layer. The films were sintered for 30 min at 500 °C and cooled down to 80 °C before immersion of the films in a solution containing 0.3 mM dve with 5 mM chenodeoxycholic acid as co-adsorbant in a 8:2 mixture of chloroform and ethanol. The devices were sealed with a platinized FTO counter electrode using a hot-melt (Surlyn, DuPont). The devices were then filled with an electrolyte through a hole in the counter electrode. The hole was then sealed with a Surlyn disk and a thin glass to avoid the leakage of electrolyte. The composition of nitrile-based and ionic liquid-based electrolyte was 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M tertbutylpyridine, 0.05 M lithium iodide in a mixture of acetonitrile/ valeronitrile (85:15, v/v) and 1-ethyl-3-methylimidazolium iodide/ 1,3-dimethylimidazolium iodide/1-ethyl-3-methylimidazolium

tetracyanoborate/lithium iodide/iodine/*N*-methylbenzimidazole in molar ratio (12:12:16:1:1.67:4), respectively.

4.1.5. Device characterization. A sun simulator (Oriel) fitted with a filtered 1000 W xenon lamp was used to provide simulated solar irradiation (AM1.5, 1000 W m<sup>-2</sup>). Current-voltage curves were recorded using a Keithlev 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (Peccell Technologies). The photodiode was fitted with a colour filter provided by the supplier, to minimize the optical mismatch between the calibration diode and the dye-sensitized solar cells. The light intensity was adjusted by using a filter wheel equipped with a series of mesh filters. The IPCE was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 260) as a monochromatic light source. The illumination spot size was chosen to be slightly smaller than the active area of the DSC test cells. IPCE photocurrents were recorded under short-circuit conditions using a Keithley 2400 source meter. The monochromatic photon flux was quantified by means of a calibrated silicon photodiode (Peccell Technologies).

4.1.6. *IMVS and IMPS.* For IMPS and IMVS measurements, a red LED was modulated to a depth of ca. 2% using a Stanford lock-in amplifier (SR810) and purpose built LED driver with an adjustable DC offset. The illumination intensity was varied using a set of neutral density filters. All experiments were performed in an earthed Faraday dark-box to eliminate electrical noise at low light intensities. Photocurrents were measured using a battery powered current preamplifier (Stanford SR570) and photovoltages measured using a purpose built battery powered high impedance voltage follower (input impedance 1012  $\Omega$ ). The phase and amplitude of the resultant AC photocurrent (or photovoltage) were captured using the lock-in amplifier (SR810) under computer control (Labview). A charge extraction setup identical as in the literature<sup>21</sup> was used to determine the charge stored in the films.

# 4.2. Synthesis

Synthetic strategies for **1** and **2** are represented in Schemes 1 and 2, respectively.





Scheme 2. Synthetic scheme for 2.

4.2.1. Synthesis of 4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2-carbaldehyde (4). 4-(2-Ethylhexyl)-4H-dithieno[3,2-b:2',3'd]pyrrole (540 mg, 1.86 mmol) was taken in ethylene dichloride (25 mL) in a 100 mL round bottom flask followed by the addition of dimethylformamide (149.3 mg, 2.05 mmol) at room temperature. The resulting reaction solution was cooled to 0 °C and POCl<sub>3</sub> (0.51 mL, 5.58 mmol) was added drop wise. The reaction mixture was allowed to warm to room temperature and refluxed overnight. On the following day the reaction mixture was cooled down to room temperature and worked up with saturated sodium acetate solution and chloroform. The organic layer was washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and recovered to get crude yellow oil, which was purified by column chromatography on silica gel (10% ethyl acetate/hexane) to give the title compound 4 (540 mg, 76%) as a dark yellow oil; R<sub>f</sub> (10% ethyl acetate/hexane) 0.52; IR (thin solid film, cm<sup>-1</sup>) 2957, 2932, 2856 (-C-H str), 1652 (-C=O str), 1534, 1412, 1351, 1231, 1200, 1135;  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 9.86 (1H, s), 7.60 (1H, s), 7.36-7.35 (1H, m), 6.98-6.97 (1H, m), 4.10-4.04 (2H, m), 1.98–1.90 (1H, m), 1.35–1.19 (8H, m), 0.91–0.83 (6H, m).  $\delta_{\rm C}$ (100.6 MHz, CDCl<sub>3</sub>) 183.2, 149.7, 144.8, 140.2, 128.6, 123.4, 119.6, 115.1, 111.2, 51.6, 40.6, 30.8, 28.8, 24.2, 23.1, 14.1, 10.8; HRMS (APCI): M<sup>+</sup>, found 319.1061. C<sub>17</sub>H<sub>21</sub>NOS<sub>2</sub> requires 319.1059.

4.2.2. 4-(2-Ethylhexyl)-6-iodo-4H-dithieno[3,2-b:2',3'-d]pyrrole-2carbaldehyde (**5**). Compound **4** (450 mg, 1.41 mmol) was taken in 1:1 solvent mixture (25 mL) of acetic acid and chloroform in a 100 mL round bottom flask followed by the addition of *N*-iodosuccinimide (412 mg, 1.83 mmol) at room temperature. The resulting reaction mixture was stirred overnight at room temperature in the absence of light. The reaction mixture was worked up with water and chloroform and the organic layer was separated, washed with 20% sodium thiosulphate followed by water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and recovered to get *title compound* **5** as a dark brown oil (400 mg, 64%) that was used immediately; IR (thin solid film, cm<sup>-1</sup>) 2957, 2927, 2870 (-C-H str), 1649 (-C=0 str), 1532, 1406, 1351, 1224, 1183, 1133;  $\delta_{\rm H}$  (400 MHz, CDCl<sub>3</sub>) 9.86 (1H, s), 7.58 (1H, s), 7.17 (1H, s), 4.05–3.99 (2H, m), 1.93–1.87 (1H, m), 1.32–1.25 (8H, m), 0.91–0.85 (6H, m);  $\delta_{\rm C}$  (100.6 MHz, CDCl<sub>3</sub>) 183.2, 148.7, 144.3, 140.6, 122.7, 120.5, 119.6, 119.5, 111.1, 51.7, 40.6, 30.7, 28.7, 24.2, 23.1, 14.1, 10.8; HRMS (APCI): M<sup>+</sup>, found 445.0027. C<sub>17</sub>H<sub>20</sub>INOS<sub>2</sub> requires 445.0026.

4.2.3. 6-(4-(Diphenylamino)phenyl-4-(2-ethylhexyl))-4H-dithieno [3,2-b:2',3'-d]pyrrole-2-carbaldehyde (6). Compound 5 (843 mg, 1.89 mmol), 4-(diphenylamino)phenylboronic acid (927 mg, 3.21 mmol), sodium phosphate dodecahydrate (1686 mg, 4.72 mmol) and 10% Pd(C) (640 mg) were mixed in isopropanol (100 mL) in 250 mL RB flask at room temperature. The mixture was heated to 80 °C in oil bath for 24 h and the reaction progress was monitored by thin layer chromatography (hexane/ethyl acetate 8:2), which indicated the consumption of starting aldehyde. The reaction mixture was filtered off and the solvent was recovered to get crude oil, which was subjected to column chromatography on silica gel (hexane/ethyl acetate 9:1) to get title compound 6 (700 mg, 66%) as an orange oil. NMR spectrum of compound 6 is consistent with NMR spectrum of the reported literature of similar analogue;  $^{10c}$   $R_f$  (10% ethyl acetate/hexane) 0.30; IR (thin solid film, cm<sup>-1</sup>) 3036, 2958, 2917, 2849 (-C-H str), 1650 (-C=O str), 1587, 1508, 1492 (Ar-C=C str), 1278, 1260, 1213, 1029, 802; δ<sub>H</sub> (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 9.86 (1H, s), 7.65 (1H, s), 7.58–7.54 (2H, m), 7.35–7.28 (4H, m), 7.19–7.02 (9H, m), 4.15-4.11 (2H, m), 2.06-1.96 (1H, m), 1.38-1.21 (8H, m), 0.97-0.87 (6H, m);  $\delta_{C}$  (100.6 MHz, CDCl<sub>3</sub>) 185.1, 148.3, 140.1, 129.5, 129.3, 129.2, 127.7, 126.6, 126.5, 126.4, 124.9, 123.6, 123.2, 122.9, 121.9, 116.3, 115.9, 47.5, 40.5, 34.9, 29.5, 28.7, 23.1, 14.0, 10.6; HRMS (APCI): M<sup>+</sup>, found 562.2108. C<sub>35</sub>H<sub>34</sub>N<sub>2</sub>OS<sub>2</sub> requires 562.2107.

4.2.4. 2-Cyano-3-(6-(4-(diphenylamino)phenyl)-4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)acrylic acid (**1**). Compound **6** (480 mg, 0.85 mmol) was taken in 1:1 solvent mixture (25 mL) of chloroform and acetonitrile in a 100 mL RB flask at room temperature. Cyanoacetic acid (217 mg, 2.55 mmol) was added at room temperature followed by the addition of piperidine (0.08 mL, 0.85 mmol) and the resulting red solution was refluxed overnight. Solvent was removed and the residue was dissolved in ethyl acetate and washed with 2 N HCl followed by water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and recovered to get crude solid, which was subjected to column chromatography on silica gel (chloroform/methanol 8:2) to get *title compound* **1** (270 mg, 51%) as a deep red solid: mp 278–283 °C; Rf (20% methanol/chloroform) 0.29; IR (thin solid film, cm<sup>-1</sup>) 3434 (br d), 3063, 3028, 2957, 2927, 2872, 2208, 1590, 1516, 1493, 1447, 1363, 1320, 1246, 1186, 826, 793, 753, 696;  $\delta_{\rm H}$  (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) 8.19 (1H, s), 7.82 (1H, s), 7.60-7.56 (3H, m), 7.31-7.27 (4H, m), 7.06-7.01 (6H, m), 6.96-6.94 (2H, m), 4.13-4.11 (2H, m), 1.94-1.87  $(1H, m), 1.25 - 1.14 (8H, m), 0.80 (3H, t, 17.5 Hz), 0.74 (3H, t, 16.8 Hz); \delta_{C}$ (100.6 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) 165.3, 149.4, 147.6, 147.4, 145.4, 144.4, 144.1, 144.0, 134.4, 130.3, 129.2, 126.9, 124.9, 124.1, 123.7, 121.0, 120.0, 119.6, 113.2, 107.9, 51.1, 40.0, 30.4, 28.3, 23.9, 23.1, 14.4, 10.9; HRMS (EI): M<sup>+</sup>, found 629.2197. C<sub>38</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub> requires 629.2165.

4.2.5. 4-(4-(Hexyloxy)phenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (7). 3,3'-Dibromo-2,2'-bithiophene (2.00 g, 6.17 mmol) was added in toluene (100 mL) in a 250 mL round bottom flask followed by the addition of sodium-tert-butoxide (1.42 g, 14.8 mmol) at room temperature. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane (97.9 mg, 0.12 mmol) was added to this reaction mixture followed by the addition of 1,1'-bis(diphenylphosphino)ferrocene (266 mg, 0.48 mmol) ligand at room temperature. The resulting reaction mixture was stirred for 15 min followed by the addition of 4-(hexyloxy)aniline (1.19 g, 6.17 mmol) at room temperature. Reaction mixture was heated to reflux overnight and the solvent was evaporated under reduced pressure to get crude solid, which was subjected to column chromatography on silica (hexane/dichloromethane 9:1) to get *title compound* **7** (1.60 g, 73%) as a white solid; mp 87–90 °C;  $R_f$  (10% CH<sub>2</sub>Cl<sub>2</sub>/hexane) 0.77; IR (thin solid film, cm<sup>-1</sup>) 2949, 2928, 2857 (Ar –C-H str), 1516, 1468, 1405 (Ar –C=C str), 1290, 1246, 814, 692; δ<sub>H</sub> (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.50–7.46 (2H, m), 7.19-7.17 (2H, m), 7.12-7.10 (2H, m), 7.06-7.02 (2H, m), 4.02 (2H, t), 1.85-1.77 (2H, m), 1.51-1.45 (2H, m), 1.39-1.34 (4H, m), 0.94-0.89 (3H, m); δ<sub>C</sub> (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 157.7, 144.6, 132.7, 124.3, 123.4, 116.2, 115.6, 112.2, 68.6, 31.7, 29.4, 25.8, 22.8, 13.9; HRMS (APCI): M<sup>+</sup>, found 355.1061. C<sub>20</sub>H<sub>21</sub>NOS<sub>2</sub> requires 355.1059.

4.2.6. 4-(4-(Hexyloxy)phenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2carbaldehyde (8). Compound 7 (600 mg, 1.69 mmol) was added to ethylene dichloride (25 mL) in a 100 mL round bottom flask followed by the addition of dimethylformamide (129 mg, 1.77 mmol) at room temperature. The resulting reaction solution was cooled to 0 °C and POCl<sub>3</sub> (0.46 mL, 5.07 mmol) was added drop wise. The reaction mixture was allowed to warm to room temperature and refluxed overnight. Reaction mixture was cooled down and worked up with saturated sodium acetate solution and chloroform. The organic layer was washed twice with water followed by brine, dried over Na<sub>2</sub>SO<sub>4</sub> and recovered to yield title compound 8 (350 mg, 54%) as a yellow solid, which was used as such for the next step; mp 104-106 °C; IR (thin solid film, cm<sup>-1</sup>) 2929, 2856 (-C-H str), 1653 (-C=O str), 1511, 1467, 1407 (Ar–C=C str), 1356, 1292, 1247, 1143, 833, 801, 713;  $\delta_{\rm H}$  (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 9.84 (1H, s), 7.74 (1H, s), 7.50–7.46 (2H, m), 7.43–7.42 (1H, m), 7.13-7.11 (1H, m), 7.09-7.05 (2H, m), 4.03 (2H, t), 1.85-1.78 (2H, m), 1.51–1.46 (2H, m), 1.39–1.34 (4H, m), 0.94–0.90 (3H, m);  $\delta_{C}$ (100.6 MHz, CDCl<sub>3</sub>) 183.2, 158.4, 148.7, 144.1, 140.7, 131.7, 128.8, 124.8, 124.5, 120.8, 116.4, 115.8, 112.1, 68.6, 31.7, 29.4, 25.8, 22.8, 14.2; HRMS (APCI): M<sup>+</sup>, found 383.1009. C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub>S<sub>2</sub> requires 383.1008.

4.2.7. 4-(4-(Hexyloxy)phenyl)-6-iodo-4H-dithieno[3,2-b:2',3'-d]pyrrole-2-carbaldehyde (**9**). Compound **8** (350 mg, 0.91 mmol) was added to a 1:1 solvent mixture (25 mL) of acetic acid and chloroform in a 100 mL round bottom flask followed by the addition of Niodosuccinimide (266 mg, 1.18 mmol) at room temperature. The resulting reaction solution was stirred overnight at room temperature in the absence of light. The reaction mixture was worked up with water and chloroform, and the organic layer was separated, washed with 20% sodium thiosulphate followed by water, brine. dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and recovered to get *title compound* **9** (360 mg, 78%) as a dark brown solid that was used as such for the next step; mp 63–65 °C; IR (thin solid film, cm<sup>-1</sup>) 2954, 2926, 2851 (-C-H str), 1652 (-C=O str), 1511, 1467 (Ar-C=C str), 1407, 1277, 1248, 1091, 1019, 799; δ<sub>H</sub> (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 9.84 (1H, s), 7.71 (1H, s), 7.46-7.42 (2H, m), 7.33 (1H, s), 7.08-7.05 (2H, m), 4.03 (2H, t, J 6.6 Hz), 1.84–1.78 (2H, m), 1.50–1.46 (2H, m), 1.39–1.34 (4H, m), 0.94-0.90 (3H, m);  $\delta_{C}$  (100.6 MHz, CDCl<sub>3</sub>) 183.2, 158.6, 147.8, 143.7, 141.0, 131.2, 124.9, 123.7, 121.4, 120.8, 120.7, 115.9, 115.7, 68.7, 31.7, 29.3, 25.8, 22.8, 14.2; HRMS (APCI): M<sup>+</sup>, found 508.9977. C<sub>21</sub>H<sub>20</sub>INO<sub>2</sub>S<sub>2</sub> requires 508.9975.

4.2.8. 6-(4-(Diphenylamino)phenyl)-4-(4-(hexyloxy)phenyl)-4H-di*thieno*[3,2-*b*:2',3'-*d*]*pyrrole*-2-*carbaldehyde* (**10**). Compound (760 mg, 1.49 mmol) and 4-(diphenylamino)phenylboronic acid (731 mg, 2.53 mmol) were added in 1:1 solvent mixture (40 mL) of tetrahydrofuran and dimethoxyethane in a 100 mL round bottom flask followed by the addition of potassium carbonate (617 mg, 4.47 mmol) at room temperature. The reaction suspension was stirred for 30 min followed by the addition of tetrakis(triphenylphosphine)palladium(0) (85.5 mg, 0.07 mmol) at room temperature. The resulting yellow suspension was refluxed overnight and solvent was evaporated off to get crude solid, which was subjected to column chromatography on silica (hexane/ethyl acetate 9:1) to afford title compound 10 (400 mg, 43%) as a yellowish-orange solid; mp 59–61 °C;  $R_f$  (10% ethyl acetate/hexane) 0.32; IR (thin solid film, cm<sup>-1</sup>) 2917, 2849 (-C-H str), 1653 (-C=O str), 1587, 1509, 1492 (Ar-C=C str), 1409, 1280, 1248, 1028, 833, 753;  $\delta_{\rm H}$  (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 9.86 (1H, s), 7.65 (1H, s), 7.53-7.47 (2H, m), 7.35-7.00 (17H, m), 4.11-4.07 (2H, m), 2.02-1.96 (2H, m), 1.38-1.29 (6H, m), 0.97-0.90 (3H, m); δ<sub>C</sub> (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 183.1, 158.4, 148.3, 147.4, 140.7, 131.5, 129.5, 129.2, 128.8, 127.7, 126.5, 124.9, 124.8, 124.7, 123.6, 122.9, 121.9, 116.3, 115.8, 112.1, 99.7, 68.7, 31.7, 29.8, 25.8, 22.8, 13.9; HRMS (APCI): M<sup>+</sup>, found 626.2055. C<sub>39</sub>H<sub>34</sub>IN<sub>2</sub>O<sub>2</sub>S<sub>2</sub> requires 626.2056.

4.2.9. 2-Cyano-3-(6-(4-(diphenylamino)phenyl)-4-(4-(hexyloxy)phenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)acrylic acid (2). Compound 10 (400 mg, 0.64 mmol) was added in 1:1 solvent mixture (20 mL) of chloroform and acetonitrile in a 100 mL RB flask at room temperature. Cyanoacetic acid (218 mg, 2.56 mmol) was added at room temperature followed by the addition of piperidine (0.03 mL, 0.32 mmol), and the resulting red solution was refluxed overnight. Solvent was removed and the residue was dissolved in ethyl acetate and washed with 2 N HCl followed by water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and recovered to get crude solid, which was subjected to column chromatography on silica (chloroform/methanol 8:2) to get title compound 2 (150 mg, 34%) as a deep cherry powder; mp 250–254 °C; R<sub>f</sub> (20% methanol/chloroform) 0.35; IR (thin solid film, cm<sup>-1</sup>) 3447 (br d), 3028, 2929, 2858, 2209, 1590, 1512, 1493, 1369, 1326, 1278, 1247, 1167, 832, 753, 696;  $\delta_{\rm H}$ (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) 8.20 (1H, s), 7.78 (1H, s), 7.59-7.57 (2H, m), 7.53-7.51 (2H, m), 7.47 (1H, s), 7.30-7.26 (4H, m), 7.07-7.04 (4H, m), 7.02-6.99 (4H, m), 6.92-6.90 (2H, m), 3.97 (2H, t, J 6.5 Hz), 1.72-1.65 (2H, m), 1.42-1.35 (2H, m), 1.29-1.24 (4H, m), 0.85-0.82 (3H, m); δ<sub>C</sub> (100.6 MHz, CD<sub>3</sub>SOCD<sub>3</sub>) 165.2, 157.9, 147.8, 147.7, 147.3, 146.2, 144.0, 143.3, 135.2, 131.6, 130.3, 130.2, 128.8, 127.3, 125.0, 124.9, 124.2, 123.4, 122.5, 119.8, 116.2, 114.9, 108.0, 104.6, 68.7, 31.6, 29.3,

25.8, 22.7, 14.6; HRMS (EI): M<sup>+</sup>, found 693.2101. C<sub>42</sub>H<sub>35</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub> requires 693.2114.

# Acknowledgements

A.G. would like to acknowledge the Flexible Electronics Theme of CSIRO Future Manufacturing Flagship, Monash University, Clavton and RMIT University. Melbourne Australia for providing equipment support. A.G. would further like to thank Dr. Jo Cosgriff and Dr. Carl Braybrook from Materials Science and Engineering, CSIRO Clayton VIC 3169 for MS analysis. S.V.B. acknowledges financial support from the Australian Research Council under a Future Fellowship Scheme (FT110100152) and the School of Applied Sciences (RMIT University) for the facilities. A.B. thanks CSIRO for support through the Julius Career Award. The use of the NCI National Facility supercomputers at the ANU is gratefully acknowledged.

# Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.02.002.

### **References and notes**

- 1. (a) O'Regan, B.; Grätzel, M. Nature 1991, 353, 737–740; (b) Grätzel. M. I. Photochem. Photobiol., C: Photochem. Rev. **2003**, 4, 145–153; (c) Grätzel, M. Nature 2001, 414, 338-344; (d) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Chem. Rev. 2010, 110, 6595-6663.
- 2. Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. Jpn. J. Appl. Phys., Part 2 2006, 45, L638-L640.
- 3. (a) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Baker, R. H.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. J. Am. Chem. Soc. 1993, 115, 6382-6390; (b) Nazeeruddin, M. K.; Pechy, P.; Renouard, T.; Zakeeruddin, S. M.; Baker, R. H.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. J. Am. Chem. Soc. **201**, 123, 1613–1624; (c) Na-zeeruddin, M. K.; Angelis, F. D.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. J. Am. Chem. Soc. 2005, 127, 16835–16847.
- **4.** (a) Zeng, W.; Cao, Y.; Bai, Y.; Wang, Y.; Shi, Y.; Zhang, M.; Wang, F.; Pan, C.; Wang, P. *Chem. Mater.* **2010**, *22*, 1915–1925; (b) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, Md. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Science 2011, 334, 629-633.
- 5. Mishra, A.; Fischer, M. K. R.; Bäuerle, P. Angew. Chem., Int. Ed. 2009, 48, 2474–2499.
- (a) Zhang, G.; Bala, H.; Cheng, Y.; Shi, D.; Lv, X.; Yu, Q.; Wang, P. Chem. Commun. 2009, 2198-2200; (b) Xu, M.; Li, R.; Pootrakulchote, N.; Shi, D.; Guo, J.; Yi, Z.; Zakeeruddin, S. M.; Grätzel, M.; Wang, P. J. Phys. Chem. C 2008, 112, 19770–19776; (c) Zhang, G.; Bai, Y.; Li, R.; Shi, D.; Wenger, S.; Zakeeruddin, S. M.; Grätzel, M.; Wang, P. Energy Environ. Sci. 2009, 2, 92–95.
- 7. Velusamy, M.; Thomas, K. R. J.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. Org. Lett. 2005, 7, 1899-1902.

- 8. Liu, W.-H.; Wu, I.-C.; Lai, C.-H.; Lai, C.-H.; Chou, P.-T.; Li, Y.-T.; Chen, C.-L.; Hsu, Y.-Y.; Chi, Y. Chem. Commun. 2008, 5152-5154.
- (a) Qin, H.; Wenger, S.; Xu, M.; Gao, F.; Jing, X.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. J. Am. Chem. Soc. 2008, 130, 9202–9203; (b) Chen, R.; Yang, X.; Tian, H.; Sun, L. J. Photochem. Photobiol., A 2007, 189, 295–300; (c) Chen, R.; Yang, X.; Tian, H.; Wang, X.; Hagfeldt, A.; Sun, L. Chem. Mater. 2007, 19, 4007-4015.
- (a) Polander, L. E.; Yella, A.; Teuscher, J.; Baker, R. H.; Curchod, B. F. E.; Astani, N. 10 A.; Gao, P.; Moser, I.-E.; Tavernelli, I.; Rothlisberger, U.; Grätzel, M.; Nazeeruddin, Md. K.; Frey, *J. Chem. Mater.* **2013**, *25*, 2642–2648; (b) Sahu, D.; Padhy, H.; Patra, D.; Yin, J.-F.; Hsu, Y.-C.; Lin, J.-T. 'S.; Lu, K.-L.; Wei, K.-H.; Lin, H.-C. Tetrahedron **2011**, 67, 303–311; (c) Xu, M.; Zhang, M.; Pastore, M.; Li, R.; De Angelis, F.; Wang, P. Chem. Sci. **2012**, 3, 976–983.
- 11. Xiang, W.; Gupta, A. ,; Kashif, M. K.; Duffy, N.; Bilic, A.; Evans, R. A.; Spiccia, L.; Bach. U. ChemSusChem 2013. 6. 256–260.
- Tian, H.; Yang, X.; Cong, J.; Chen, R.; Liu, J.; Hao, Y.; Hagfeldt, A.; Sun, L. Chem. 12 *Commun.* **2009**. 6288–6290.
- 13. Dessì, A.; Consiglio, G. B.; Calamante, M.; Reginato, G.; Mordini, A.; Peruzzini, M.; Taddei, M.; Sinicropi, A.; Parisi, M. L.; Fabrizi de Biani, F.; Basosi, R.; Mori, R.; Spatola, M.; Bruzzi, M.; Zani, L. *Eur. J. Org. Chem.* **2013**, 1916–1928. Tian, H.; Yang, X. C.; Chen, R. K.; Zhang, R.; Hagfeldt, A.; Sun, L. *J. Phys. Chem. C*
- 14 2008, 112, 11023-11033.
- Wan, Z. Q.; Jia, C. Y.; Zhang, J. Q.; Duan, Y. D.; Lin, Y.; Shi, Y. J. Power Sources 2012, 15 199, 426-431.
- 16. Tian, H.; Yang, X. C.; Cong, J. Y.; Chen, R. K.; Teng, C.; Liu, J.; Hao, Y.; Wang, L.; Than, T., Tang, A. C., Cong, J. H., 2010, 84, 62–68.
  Zhang, F.; Luo, Y. H.; Song, J. S.; Guo, X. Z.; Liu, W. L.; Ma, C. P.; Huang, Y.; Ge, M.
- F.; Bo, Z.; Meng, Q. B. Dyes Pigments 2009, 81, 224-230.
- 18. (a) Pappenfus, T. M.; Hermanson, B. J.; Helland, T. J.; Lee, G. G. W.; Drew, S. M.; Mann, K. R.; McGee, K. A.; Rasmussen, S. C. Org. Lett. 2008, 10, 1553-1556; (b) Rasmussen, S. C.; Evenson, S. J. *Prog. Polym. Sci.* **2013**, *38*, 1773–1804; (c) Evenson, S. J.; Pappenfus, T. M.; Delgado, M. C. R.; Wohlers, K. R. R.-; Navarretec, J. T. L.; Rasmussen, S. C. Phys. Chem. Chem. Phys. 2012, 14, 6101–6111.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 03, Revision C.02; Gaussian: Wallingford, CT, 2004
- (a) Hagfeldt, A.; Grätzel, M. Chem. Rev. 1995, 95, 49-68; (b) Listorti, A.; O'Regan, 20. B.; Durrant, J. R. Chem. Mater. 2011, 23, 3381-3399.
- 21. Tian, H. N.; Jiang, X.; Yu, Z.; Kloo, L.; Hagfeldt, A.; Sun, L. C. Angew. Chem., Int. Ed. 2010, 49, 7328-7331.
- 22 Fisher, A. C.; Peter, L. M.; Ponomarev, E. A.; Walker, A. B.; Wijayantha, K. G. U. J. Phys. Chem. B 2000, 104, 949-958.
- 23. Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U. Electrochem. Commun. 2000, 2, 658-662.
- 24. McEwen, C. N.; McKay, R. G.; Larsen, B. S. Anal. Chem. 2005, 77, 7826-7831.