

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51044785>

# Dithienothiophene (DTT)-Based Dyes for Dye-Sensitized Solar Cells: Synthesis of 2,6-Dibromo-DTT

ARTICLE *in* THE JOURNAL OF ORGANIC CHEMISTRY · MAY 2011

Impact Factor: 4.72 · DOI: 10.1021/jo2001484 · Source: PubMed

CITATIONS

45

READS

89

10 AUTHORS, INCLUDING:



**Samuel Lind**

University of Otago

10 PUBLICATIONS 303 CITATIONS

SEE PROFILE



**Keith C Gordon**

University of Otago

290 PUBLICATIONS 6,417 CITATIONS

SEE PROFILE



**David John Jones**

University of Melbourne

64 PUBLICATIONS 1,352 CITATIONS

SEE PROFILE



**Andrew B Holmes**

University of Melbourne

276 PUBLICATIONS 9,619 CITATIONS

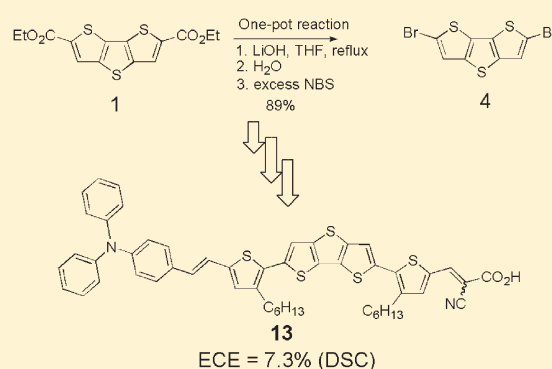
SEE PROFILE

## Dithienothiophene (DTT)-Based Dyes for Dye-Sensitized Solar Cells: Synthesis of 2,6-Dibromo-DTT

Tae-Hyuk Kwon,<sup>†</sup> Vanessa Armel,<sup>‡</sup> Andrew Nattestad,<sup>‡</sup> Douglas R. MacFarlane,<sup>\*,‡</sup> Udo Bach,<sup>\*,‡</sup> Samuel J. Lind,<sup>§</sup> Keith C. Gordon,<sup>§</sup> Weihua Tang,<sup>†</sup> David J. Jones,<sup>†</sup> and Andrew B. Holmes<sup>\*,†</sup><sup>†</sup>School of Chemistry, Bio21 Institute, University of Melbourne, Parkville, Vic 3010, Australia<sup>‡</sup>ARC Centre of Excellence for Electromaterials Science, Monash University, Clayton, Vic 3800, Australia<sup>§</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago, Dunedin, New Zealand

S Supporting Information

**ABSTRACT:** A one-pot synthesis of 2,6-dibromodithieno[3,2-*b*;2',3'-*d*]thiophene (dibromo-DTT, **4**) was developed. A key step was bromo-decarboxylation of DTT-2,6-dicarboxylic acid, obtained by saponification of the diester **1**. The donor–acceptor dye DAHTDDT (**13**), based on a central 2,6-bis[2'-(3'-hexylthienyl)]dithieno[3,2-*b*;2',3'-*d*]thiophene core (**9**), was prepared and incorporated in a dye-sensitized solar cell (DSC), which exhibited an energy conversion efficiency of 7.3% with  $V_{oc}$  of 697 mV,  $J_{sc}$  of 14.4 mA/cm<sup>2</sup>, and  $ff$  of 0.73 at 1 sun.



Recently, organic dye-sensitized solar cells (DSCs) have received considerable attention owing to their wide variety, high molar extinction coefficients of dyes, and potentially low cost of fabrication compared with those based on ruthenium dye sensitizers.<sup>1–17</sup> Some organic dyes exhibit impressive photovoltaic performances with high efficiency and good stability. Most organic sensitizers consist of a donor fragment (D), a  $\pi$ -conjugated linking segment, and an acceptor fragment (A) to achieve broad and intense absorption within the visible to near-IR spectrum. When designing dyes for high-efficiency DSCs, it is preferable to (i) employ a nonplanar structure to prevent self-aggregation, (ii) incorporate appropriate conjugation length for a broad absorption, (iii) use long alkyl chain substituents to minimize electron recombination, and (iv) aim for chemical and structural stability.

In this study, we employ a 2,6-bis[2'-(3'-hexylthienyl)]dithieno[3,2-*b*;2',3'-*d*]thiophene core unit **9** for the  $\pi$ -conjugated linking segment. This is due to the relatively high hole mobility exhibited by the fused thiophene core<sup>18</sup> in a variety of electronic and optical applications,<sup>4–7,19</sup> such as organic thin film transistors<sup>18,20–22</sup> and polymer solar cells.<sup>21</sup> Owing to the various useful applications of dithieno[3,2-*b*;2',3'-*d*]thiophene (DTT) in the optoelectronic field, the synthesis of DTT derivatives has received much attention.<sup>23–25</sup> However, many approaches still require multiple steps and harsh conditions.<sup>23,24</sup> For the purpose of a convenient synthesis and scale up of the DTT unit, we developed a synthesis of 2,6-dibromo-DTT **4** by a modification of the Hunsdiecker-type reaction (Scheme 1).<sup>26</sup>

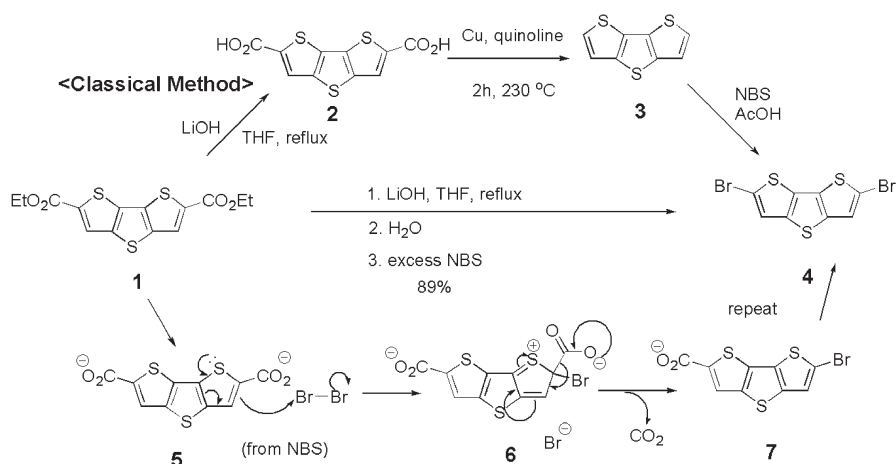
Recently thiophene-based dyes have been used for light-harvesting in DSCs.<sup>4–6</sup> However, as DTT-based dyes may not exhibit a broad absorption region,<sup>6</sup> modification of the structure through additional double conjugation by introduction of 3-hexylthiophene units can improve this situation. An additional benefit is the inhibition of electron recombination from the TiO<sub>2</sub> nanoparticle to the radical cation of the dye owing to the presence of the hexyl substituents. The final components of the light-harvesting dye, 2-cyano-3-[5-(6-[5-[2-(4-(diphenylamino)phenyl)vinyl][2'-(3'-hexylthienyl)]dithieno[3,2-*b*;2',3'-*d*]thien-2-yl)-4-hexylthien-2-yl]acrylic acid, DAHTDDT **13**, are the nonplanar triphenyl amine (TPA) donor unit (D) and an  $\alpha$ -cyanoacrylic acid group as the electron acceptor (A) to form a D- $\pi$ -A structure.

The synthesis of the dye DAHTDDT **13** is shown in Scheme 2. 2,6-Dibromo-DTT **4** can be prepared by bromination of DTT **3**, itself obtained by decarboxylation of the diacid **2** (overall yield 40% for three steps).<sup>23,24</sup> However, this classical method, although it gave a good yield, still required a three-step process and included the harsh preliminary decarboxylation step as outlined in Scheme 1. We now report an improved synthesis of the dibromo-DTT **4** by a one-pot bromo-decarboxylation of the DTT-2,6-diacid **5** (Scheme 1).<sup>27–31</sup> Conventional saponification

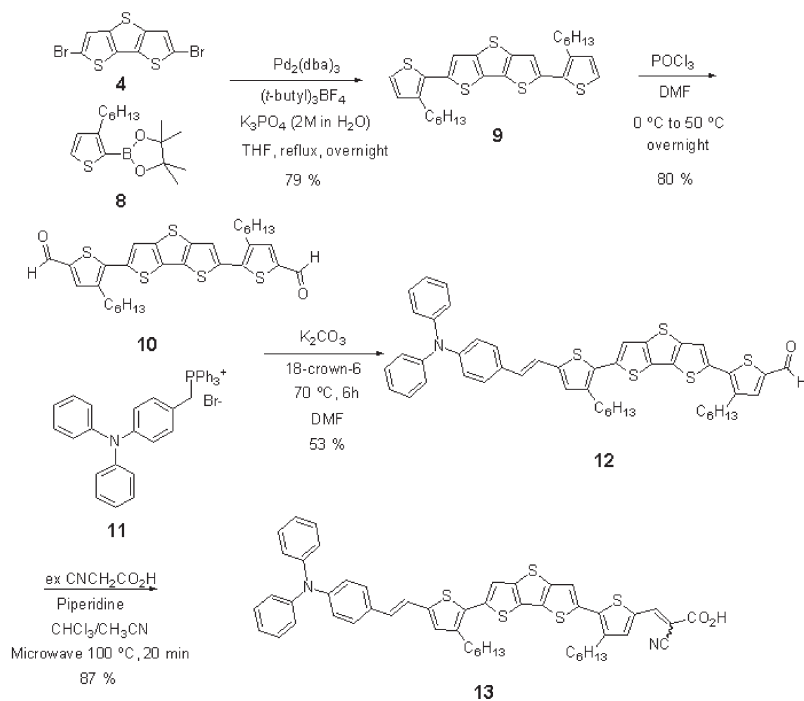
Received: January 24, 2011

Published: April 12, 2011

Scheme 1. Routes to Dibromo-DTT 4 from the Diester 1



Scheme 2. Synthesis of the Dye 13



of the diester **1** (heat to reflux in THF containing aqueous LiOH solution) followed by dilution of the cooled resulting slurry produced a solution of the dicarboxylate lithium salt. Treatment of this solution with an excess of solid NBS (>6 mol equiv) followed by stirring of the reaction mixture overnight at room temperature and extraction with dichloromethane gave the dibromo-DTT **4** in excess of 80% yield.

Without column purification, the dibromo-compound **4** was coupled under Suzuki conditions with 3-hexylthiophene-2-pinacolyboronate **8** in the presence of  $\text{Pd}_2(\text{dba})_3$ , (*tert*-butyl) $_3\text{P}\cdot\text{HBF}_4$ , and 2 M  $\text{K}_3\text{PO}_4$ , to afford bis(3-hexylthiophenyl)-DTT **9** in 79% yield. Vilsmeier formylation gave the dialdehyde **10**, which underwent a mono-Wittig–Horner chain extension in 53% yield with the ylide derived from the known triarylamine-based phosphonium salt **11**.<sup>6</sup> Knoevenagel-type condensation of

the resulting aldehyde **12** with cyanoacetic acid (>20 equiv) in a microwave reactor gave the required dye **13** in 87% yield after purification by column chromatography.

The UV/vis absorption spectrum of the dye DAHTDTT **13** in  $\text{CH}_2\text{Cl}_2$  (0.02 mM) showed a strong broad absorption maximum around 490 nm ( $\epsilon_{\text{max}} > 30\,000$ ), with the PL emission maximum at 613 nm as shown in Figure 1.

Cyclic voltammetry measurements of the dye **13** in  $\text{CH}_2\text{Cl}_2$  solutions (0.5 mM) with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte are summarized in Table 1. Also included are the observed UV/vis and PL emission spectra and the DFT-calculated HOMO and LUMO energies.

The oxidation potential of the dye **13** (0.98 V versus NHE) is sufficiently positive compared with the reduction potential of

iodine/iodide (0.4 V versus NHE) that the photooxidized dye could be expected to be reduced efficiently by the iodine/iodide redox couple. The reduction potential of the dye ( $-1.29$  V vs NHE) was calculated from  $E_{\text{ox}} - E_{0-0}$  (V). As this is a more negative value than the level of the  $\text{TiO}_2$  conduction band (CB) edge ( $-0.5$  V vs NHE), we can expect that the photoexcited state of the dye **13** can effectively inject electrons into the conduction band (CB) of  $\text{TiO}_2$ .

Optimized Density Functional Theory (DFT) calculations were carried out utilizing Gaussian09 at the B3LYP/6-31G(d) level of theory.<sup>32</sup> The electron densities in the HOMO and LUMO of the dye are well separated (see ESI). The HOMO is generally located on the triphenyl amine unit while the LUMO is on the cyanoacetic acid group; this is a desirable feature for the required charge separation in dye-sensitized solar cells.

DSCs were constructed by using a sandwich configuration with an electrolyte composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.025 M lithium iodide, 0.04 M iodine, 0.05 M guanidinium thiocyanate (GuSCN), and 0.28 M *tert*-butylpyridine (TBP) in a dry acetonitrile/valeronitrile solvent mixture (v/v = 85/15).<sup>6</sup> For the titanium oxide different film thicknesses of the transparent and scattering layer were used as follows: 6  $\mu\text{m}$  (6), 6 + 6 scattering layer  $\mu\text{m}$  (6 + 6s), and 12 + 6 scattering layer  $\mu\text{m}$  (12 + 6s) were studied with the coadsorbent (DCA = 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid).

The device performances are summarized in Table 2, with optimal results shown in Figures 2 and 3. The dye **13** was adsorbed onto the titania from different solvents. The choice of solvent is crucial, and the device performance varied significantly according to the solvent system chosen. The difference in performance could be due to the interaction of the dye with the solvent, which can affect the photophysical and chemical properties of the dye on the  $\text{TiO}_2$  surface.<sup>6</sup> The binding mode and the number of dye molecules adsorbed onto the  $\text{TiO}_2$

depend on the solvents. Adsorption of the dye **13** in  $\text{CHCl}_3$  and EtOH solvent mixtures (1:1) yielded the highest device efficiency compared with  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{EtOH}$ , chlorobenzene, and chlorobenzene/EtOH (see ESI). Optimum devices were obtained by using the dye (0.2 mM) in  $\text{CHCl}_3/\text{EtOH}$  (1/1) solutions with overnight soaking on titania. Thus all devices were prepared in 0.2 mM  $\text{CHCl}_3/\text{EtOH}$  (1/1) solutions after overnight soaking.

Using a 6  $\mu\text{m}$  titania film with 10 mM DCA as coadsorbent, a device fabricated with dye **13** gave a short-circuit photocurrent density ( $J_{\text{sc}}$ ) of 12.2  $\text{mA}/\text{cm}^2$ , an open-circuit voltage ( $V_{\text{oc}}$ ) of 718 mV, and a fill factor ( $ff$ ) of 0.74, corresponding to an overall conversion efficiency ( $\eta$ ) of 6.5%. With a 6  $\mu\text{m}$  scattering layer (6 + 6s), an increase in  $J_{\text{sc}}$  from 12.2 to 12.6  $\text{mA}/\text{cm}^2$  was obtained. However, with a concomitant decrease in the fill factor from 0.74 to 0.71, the device efficiency with a 6 + 6s film (6.4%) was not significantly different from that of a 6  $\mu\text{m}$  film (6.5%). Using a 12  $\mu\text{m}$  transparent film with a 6  $\mu\text{m}$  scattering layer, 12 + 6s,  $J_{\text{sc}}$  significantly increased to 14.7  $\text{mA}/\text{cm}^2$  while  $V_{\text{oc}}$  slightly decreased to 698 mV and the fill factor was 0.70, leading to device efficiency improving to 7.1%. The  $J_{\text{sc}}$  of devices made with the dye **13** is slightly higher than that achieved for N719 (14.5  $\text{mA}/\text{cm}^2$ ) under the same conditions. Through further optimization, via an increase of coadsorbent (20 mM), the performance of the cell increased to 7.3% with  $V_{\text{oc}}$  of 697 mV,  $J_{\text{sc}}$  of 14.4  $\text{mA}/\text{cm}^2$ , and fill factor of 0.73.

Compared with the previously reported device performance ( $\eta = 2.76\%$ ) of a similar dithienothiophene-based dye (*E*-2-cyano-3-[6-[2-(4-(diphenylamino)phenyl)vinyl]dithieno[3,2-*b*;2',3'-*d'*]thiophen-2-ylacrylic acid TTC2,<sup>6</sup> the efficiency of device made with dye **13** increases by a factor of ca. 2.6 under similar electrolyte composition and film thickness. Moreover, this efficiency reached 88% of the efficiency of devices made with N719 dye ( $\eta = 8.3\%$ ). Figure 2 shows the detailed current density versus voltage (*I*–*V*) curve at different light intensity: 10.3%, 38.5%, and 100% sunlight, respectively. Under 10.3% and 38.5% sunlight, the device efficiency reached 7.0% and 7.3%, respectively. The increase of short circuit current density with different film thickness is confirmed by using the incident photon-to-current conversion efficiency (IPCE) spectrum; the spectrum becomes broader in the sequence 6 < 6 + 6s < 12 < 12 + 6s. The IPCE spectrum of a device using dye **13** with 12 + 6s exhibits the broad absorption range starting from 800 nm and a higher plateau at 67% ( $\lambda = 495$  nm) (Figure 3).

In summary, we have developed a simple one-step synthesis of dibromo DTT (**4**) from diester DTT (**1**) in over 80% yield using a modified Hunsdiecker reaction for the DSC dye core unit. The organic DSC dye DAHTDTT (**13**) consisted of TPA and DTT coupled with hexylthiophene showing high efficiency of 7.3% with  $V_{\text{oc}}$  of 697 mV,  $J_{\text{sc}}$  of 14.4  $\text{mA}/\text{cm}^2$ , and  $ff$  of 0.73.

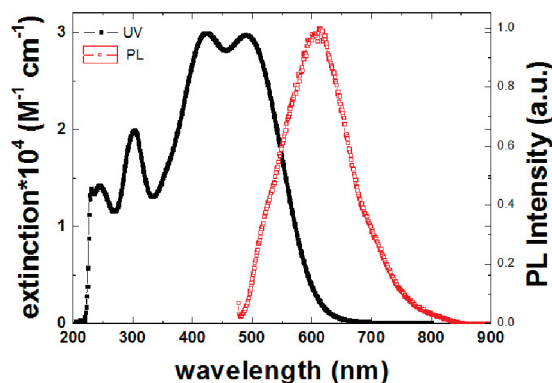


Figure 1. UV/vis and PL spectra of dye **13** in  $\text{CH}_2\text{Cl}_2$  (0.02 mM).

Table 1. DFT-Calculated HOMO and LUMO Energy Levels, the Experimentally Determined Values from the Electrochemically Measured Oxidation Potential and the Optical Bandgap, and UV/Vis Absorption and PL Emission Maxima in Dichloromethane Solution

entry	HOMO <sub>cal</sub> (exptl) <sup>a</sup>	LUMO <sub>cal</sub> (exptl) <sup>a</sup>	abs (nm)( $\epsilon \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$ ) <sup>b</sup>	PL <sup>b</sup> ( $\lambda_{\text{max}}$ )	$E_{\text{ox}}$ (V) vs NHE <sup>c</sup>	$E_{0-0}$ (V) vs (abs/Em) <sup>d</sup>	$E_{\text{ox}} - E_{0-0}$ (V) vs NHE
dye <b>13</b>	-4.67 (-5.15)	-2.75 (-2.88)	301 (2.0), 423 (3.0), 489 (3.0)	613 nm	0.98	2.27	-1.29

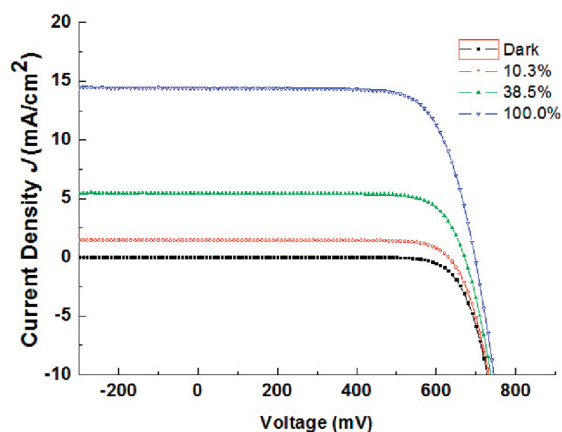
<sup>a</sup> HOMO =  $-(E_{\text{onset}} \text{ vs } \text{Fc}^+/\text{Fc} - 4.8 \text{ eV})$ , LUMO = HOMO +  $E_{0-0}$ . <sup>b</sup> 0.02 mM  $\text{CH}_2\text{Cl}_2$  solution at 298 K. <sup>c</sup> Cyclic voltammetry measurement of the onset point of oxidation  $E_{\text{ox}}$  of the dye was measured in dry  $\text{CH}_2\text{Cl}_2$  containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte, Ag/AgCl as a reference electrode, and glassy carbon as working electrode. Potentials calibrated with  $\text{Fc}^+/\text{Fc}$  were converted to normal hydrogen electrode (NHE) by addition of +0.63 V.<sup>6</sup> <sup>d</sup> The  $E_{0-0}$  transition energy was estimated from the intersection of the absorption and emission spectra.

**Table 2.** Photovoltaic Performance of Cells Fabricated with Use of the Dye 13

no.	thickness ( $\mu\text{m}$ )	coads. (mM) <sup>a</sup>	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	$ff$	eff (%)
1	6	10	718	12.2	0.74	6.5
2	6 + 6s <sup>b</sup>	10	720	12.6	0.71	6.4
3	12 + 6s	10	698	14.7	0.70	7.1
4	12 + 6s	20	697	14.4	0.73	7.3
N719 <sup>c</sup>	12 + 6s		780	14.5	0.73	8.3

<sup>a</sup> Coadsorbent is 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid. <sup>b</sup> 6s is 6  $\mu\text{m}$  scattering layer.

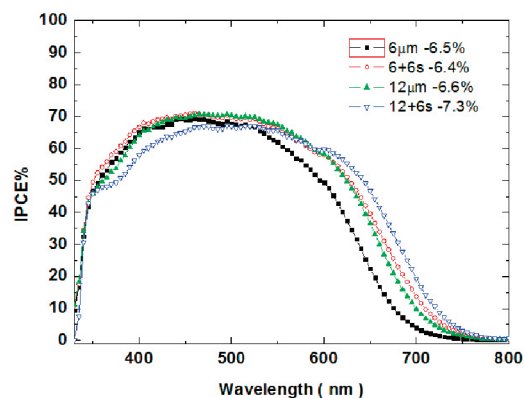
<sup>c</sup> Electrolyte for N719: 0.6 M 1-butyl-3-methyl imidazolium iodide, 0.03 M I<sub>2</sub>, 0.10 M guanidinium thiocyanate (GuSCN), and 0.50 M *tert*-butylpyridine (TBP) in the dry acetonitrile/valeronitrile (v/v = 85/15).

**Figure 2.** The  $I$ – $V$  curve of a DSC device, using the titania layers 12 + 6s and standard electrolyte under various solar simulated light intensities.

## EXPERIMENTAL SECTION

All reactions were performed with anhydrous solvent under an inert atmosphere (nitrogen or argon) unless stated otherwise. Silica gel was used for flash chromatography. Thin layer chromatography was performed on silica gel on glass (0.25 mm thick). <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy were carried out with a 500 MHz instrument. All high-resolution mass spectrometry experiments were conducted with use of a commercially available hybrid linear ion trap and Fourier-transform ion cyclotron resonance mass spectrometer, equipped with ESI. The microwave reaction was performed with a Biotage (Initiator EXP EU). The syntheses of the intermediates **1**, **8**, and **11** were carried out as previously reported.<sup>6,23,33</sup>

**One-Pot Bromo-Decarboxylation of Dithieno[3,2-*b*;2',3'-*d*]thiophene-2,6-dicarboxylic Acid Diethyl Ester (**1**) To Prepare the 2,6-Dibromodithieno[3,2-*b*;2',3'-*d*]thiophene (**4**).** To a suspension of DTT-diester **1** (3.4 g, 10 mmol) in the THF (40 mL) was added 40 mL of 1 M LiOH. After the reaction mixture had been heated under reflux for 3 h, water was added to give a clear brownish yellow solution. Excess solid *N*-bromosuccinimide (10.7 g, 60 mmol) was then added and the reaction mixture was stirred overnight at room temperature. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with saturated NaHCO<sub>3</sub> (aq), water, and brine, then dried with MgSO<sub>4</sub>. After the solvent was removed via rotary evaporator, the residue was precipitated with EtOH and then filtered to give the known dibromo-DTT **4** (3.1 g, 89% yield) as a white solid, mp 165 °C (lit.<sup>23</sup> mp 162–163 °C), whose spectroscopic data were identical with the reported values.<sup>23</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (2H, s).

**Figure 3.** IPCE spectrum of devices fabricated with use of the dye 13 according to the film thickness of titania.

**2,6-Bis[2'-(3'-hexylthienyl)]dithieno[3,2-*b*;2',3'-*d*]thiophene (**9**).** To a degassed solution of dibromo DTT **4** (4.3 g, 12.0 mmol), 2-(3-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**), and HP(*tert*-butyl)<sub>3</sub>BF<sub>4</sub> (0.72 mmol, 0.06 equiv, 208 mg) in THF (100 mL) was added Pd<sub>2</sub>(dba)<sub>3</sub> (0.36 mmol, 0.03 equiv, 329 mg), then the mixture was stirred at 60 °C overnight. After being cooled to room temperature, the reaction mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, then dried with MgSO<sub>4</sub>. After the solvent was removed via rotary evaporator, the residue was purified by column chromatography on silica gel eluting with petroleum spirits 40–60 °C to give compound **9** (5.0 g, 79% yield) as an orange solid after drying under high vacuum, *R*<sub>f</sub> 0.50 (petroleum spirits 40–60 °C), whose spectroscopic data were identical with the reported values.<sup>23</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.89 (6H, t, *J* = 6.5 Hz), 1.30–1.33 (8H, m), 1.39–1.41 (4H, m), 1.68 (4H, q, *J* = 7.5 Hz), 2.82 (4H, q, *J* = 8.0 Hz), 6.98 (2H, d, *J* = 5.0 Hz), 7.24 (2H, d, *J* = 5.0 Hz), 7.30 (2H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.1, 22.6, 29.2, 29.3, 30.7, 31.7, 119.3, 119.3, 124.4, 130.1, 130.6, 130.6, 136.9, 140.4, 140.9; *m/z* (ESI) 528.6 [M<sup>+</sup>], calcd for C<sub>28</sub>H<sub>32</sub>S<sub>5</sub> 528.1.

**2,6-Bis[2'-(3'-hexyl-5'-formylthienyl)]dithieno[3,2-*b*;2',3'-*d*]thiophene (**10**).** To a solution of **9** (400 mg, 0.75 mmol) in dry DMF (30 mL) at 0 °C was added dropwise POCl<sub>3</sub> (0.4 mL, 4.6 mmol). The reaction was stirred at this temperature for 30 min, and then the temperature was raised to 70 °C and the mixture was stirred for 12 h. The reaction mixture was poured into cold water and neutralized with NaOH (1 N), followed by extraction with CHCl<sub>3</sub>. The combined organic layers were washed with water and brine, then dried with MgSO<sub>4</sub>. After the solvent was removed via rotary evaporator, the residue was purified by column chromatography with petroleum spirits 40–60 °C and CHCl<sub>3</sub> (v/v = 4/1 to 1/4) to give the dialdehyde compound **10** (350 mg, 80% yield) as an orange crystalline solid after trituration with petroleum spirits 40–60 °C and CH<sub>2</sub>Cl<sub>2</sub>, mp 133 °C, *R*<sub>f</sub> 0.28 (1:2 petroleum spirits 40–60 °C/CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.90 (6 H, t, *J* = 7.0 Hz), 1.32–1.35 (8 H, br m), 1.41–1.44 (4H, br m), 1.69–1.75 (4H, m), 2.86 (4 H, t, *J* = 7.5 Hz), 7.48 (2 H, s), 7.63 (2 H, s), 9.86 (2 H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.3, 22.8, 29.4, 29.7, 30.6, 31.8, 114.8, 121.0, 131.9, 136.5, 139.1, 140.9, 141.2, 142.5, 182.7; *m/z* (EI) [rel intensity] 584.1 [100, (M)<sup>+</sup>], 585.1 [95, (M + H)<sup>+</sup>], 586.1 [40, (M + 2H)<sup>+</sup>]; *m/z* (EI) 584.1002 [M<sup>+</sup>], calcd for C<sub>30</sub>H<sub>32</sub>O<sub>2</sub>S<sub>5</sub> 584.1006; FT-IR (neat cm<sup>-1</sup>): 3822, 3676, 2931, 1658, 1431, 1244, 1154.

**5-(6-[5-[2-(4-(Diphenylamino)phenyl)vinyl]]2'-(3'-hexylthienyl)]dithieno[3,2-*b*;2',3'-*d*]thien-2-yl)-4-hexylthiophene-2-carbaldehyde (**12**).** To a suspension of a solution of compound **10** (186 mg, 0.32 mmol) in DMF (10 mL) containing anhydrous K<sub>2</sub>CO<sub>3</sub> (88 mg, 0.64 mmol) and 18-crown-6 (7 mg, 0.025 mmol) at a



temperature of 70 °C was added dropwise a solution of phosphonium salt **11** (210 mg, 0.35 mmol) in DMF (10 mL) over 3 h. The reaction mixture was stirred for a further 3 h. It was then cooled and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with water and brine solution. The organic phase was dried over MgSO<sub>4</sub>, then purified by column chromatography on silica gel eluting with petroleum spirits 40–60 °C/dichloromethane (v/v 4/1 to 1/4) to give alkene **12** (140 mg, 53%) as a red solid, mp 50 °C, *R*<sub>f</sub> 0.40 (2:1 petroleum spirits 40–60 °C/CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.83 (6 H, br t), 1.26 (8 H, br m), 1.36 (4 H, br m), 1.60–1.66 (4 H, br m), 2.71 (2 H, t, *J* = 8.0 Hz), 2.79 (2 H, t, *J* = 8.0 Hz), 6.78 (1 H, d, *J* = 16 Hz), 6.82 (1 H, s), 6.94–6.98 (5 H, m), 7.04 (4 H, d, *J* = 8.5 Hz), 7.18–7.21 (5 H, m), 7.23 (1 H, s), 7.25 (1 H, s), 7.39 (1 H, s), 7.54 (1 H, s), 9.77 (1 H, s); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 15.3, 31.9, 32.0, 33.3, 34.4, 120.8, 121.1, 121.6, 123.3, 124.9, 125.3, 126.5, 126.6, 127.1, 127.9, 128.3, 129.3, 130.3, 131.3, 131.6, 131.7, 132.9, 133.3, 137.2, 140.0, 141.6, 143.0, 143.1, 143.9, 144.8, 149.4, 184.6; *m/z* (EI) [rel intensity] 825.2 [100, (M)<sup>+</sup>], 826.2 [55, (M + H)<sup>+</sup>], 827.2 [20, (M + 2H)<sup>+</sup>], 828.2 [10, (M + 2H)<sup>+</sup>]; *m/z* (EI) 825.2258 [M<sup>+</sup>], calcd for C<sub>49</sub>H<sub>47</sub>NOS, 825.2261; FT-IR (neat cm<sup>-1</sup>) 2926, 2853, 1664, 1590, 1506, 1492, 1422, 1328, 1281, 1241, 1154, 821, 752, 696.

**2-Cyano-3-[5-(6-[5-[2-(4-(diphenylamino)phenyl)vinyl]-2'-(3'-hexylthienyl)]dithieno[3,2-*b*;2',3'-*d*]thien-2-yl)-4-hexylthien-2-yl]acrylic Acid DAHTDTT (**13**).** A solution of aldehyde **12** (80 mg, 0.09 mmol) in a mixture of acetonitrile (10 mL) and CHCl<sub>3</sub> (10 mL) with an excess of cyanoacetic acid (153 mg, 1.8 mmol) and piperidine (0.1 mL) was heated to 100 °C in a microwave reactor for 20 min. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic extracts were washed with 1 N HCl, water, and brine solution. The organic layer was dried over MgSO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography on silica gel eluting with dichloromethane/methanol/acetic acid (in the volume proportions 10/1/0 to 10/1/0.1) to give the organic dye **13** (70 mg, 87% yield) as a dark solid, mp 144 °C, *R*<sub>f</sub> 0.56 (10:1:0.1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH/Acetic acid) after trituration with petroleum spirits 40–60 °C and CH<sub>2</sub>Cl<sub>2</sub>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 0.84 (6 H, t, *J* = 7.0 Hz), 1.28 (8 H, br m), 1.37 (4 H, br m), 1.62–1.67 (4 H, br m), 2.75 (2 H, t, *J* = 7.5 Hz), 2.83 (2 H, t, *J* = 7.5 Hz), 6.88–6.93 (3 H, m), 7.02–7.07 (6 H, m), 7.11 (1 H, s), 7.24 (1 H, d, *J* = 16 Hz), 7.32 (4 H, t, *J* = 7.5 Hz), 7.47 (4 H, d, *J* = 8.5 Hz), 7.66 (1 H, s), 7.89 (1 H, s), 7.90 (1 H, s), 8.36 (1 H, s); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub> at 50 °C) δ 14.6, 22.7, 29.1, 29.2, 29.3, 29.6, 30.1, 30.4, 31.7, 31.8, 117.5, 120.2, 120.4, 122.6, 123.3, 124.1, 125.0, 128.3, 128.8, 128.9, 129.7, 130.3, 130.7, 131.2, 131.7, 134.0, 135.2, 138.1, 141.0, 141.3, 142.0, 142.8, 142.9, 143.0, 143.7, 147.5, 147.6, 147.6, 164.0; *m/z* (EI) [rel intensity] 892.2 [100, (M)<sup>+</sup>], 893.2 [60, (M + H)<sup>+</sup>], 894.2 [20, (M + 2H)<sup>+</sup>]; *m/z* (EI) 892.2310 [M<sup>+</sup>], calcd for C<sub>52</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub>S<sub>5</sub>, 892.2319; FT-IR (neat cm<sup>-1</sup>) 2921, 1684, 1569, 1507, 1492, 1391, 1276, 1173, 696.

## ■ ASSOCIATED CONTENT

**S** Supporting Information. Spectra of **5**, **10**, **12**, and **13**, device fabrication, and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [aholmes@unimelb.edu.au](mailto:aholmes@unimelb.edu.au) (A.B.H.), [douglas.macfarlane@monash.edu](mailto:douglas.macfarlane@monash.edu) (D.R.M.), and [udo.bach@sci.monash.edu.au](mailto:udo.bach@sci.monash.edu.au) (U.B.).

## ■ ACKNOWLEDGMENT

We thank the Australian Research Council, the Australian Government [DIISR ISL (CG10059)], and the Victorian State

Government DPI (SERD) and DBI (VSA SPF) Program VICOSC for financial support. We thank Drs. Joseph Frey and Michael Armitage (University of Cambridge) for their early observations on the bromodecarboxylation reactions of DTT-carboxylic acids.

## ■ REFERENCES

- (1) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474.
- (2) Oyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, 2903.
- (3) Ning, Z. J.; Tian, H. *Chem. Commun.* **2009**, 5483.
- (4) Qin, H.; Wenger, S.; Xu, M.; Gao, F.; Jing, X.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 9202.
- (5) Yang, H. Y.; Yen, Y. S.; Hsu, Y. C.; Chou, H. H.; Lin, J. T. *Org. Lett.* **2010**, *12*, 16.
- (6) Tian, H. N.; Yang, X. C.; Chen, R. K.; Zhang, R.; Hagfeldt, A.; Sunt, L. C. *J. Phys. Chem. C* **2008**, *112*, 11023.
- (7) Wang, Z. S.; Cui, Y.; Dan-Oh, Y.; Kasada, C.; Shinpo, A.; Hara, K. *J. Phys. Chem. C* **2007**, *111*, 7224.
- (8) Neale, N. R.; Kopidakis, N.; van de Lagemaat, J.; Grätzel, M.; Frank, A. J. *J. Phys. Chem. B* **2005**, *109*, 23183.
- (9) Zeng, W. D.; Cao, Y. M.; Bai, Y.; Wang, Y. H.; Shi, Y. S.; Zhang, M.; Wang, F. F.; Pan, C. Y.; Wang, P. *Chem. Mater.* **2010**, *22*, 1915.
- (10) Bessho, T.; Zakeeruddin, S. M.; Yeh, C.-Y.; Diau, E. W.-G.; Grätzel, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6646.
- (11) Paek, S.; Choi, H.; Lee, C. W.; Kang, M. S.; Song, K.; Nazeeruddin, M. K.; Ko, J. *J. Phys. Chem. C* **2010**, *114*, 14646.
- (12) Ko, S.; Choi, H.; Kang, M. S.; Hwang, H.; Ji, H.; Kim, J.; Ko, J.; Kang, Y. *J. Mater. Chem.* **2010**, *20*, 2391.
- (13) Lin, L. Y.; Tsai, C. H.; Wong, K. T.; Huang, T. W.; Hsieh, L.; Liu, S. H.; Lin, H. W.; Wu, C. C.; Chou, S. H.; Chen, S. H.; Tsai, A. I. *J. Org. Chem.* **2010**, *75*, 4778.
- (14) Li, R. Z.; Liu, J. Y.; Cai, N.; Zhang, M.; Wang, P. *J. Phys. Chem. B* **2010**, *114*, 4461.
- (15) Fischer, M. K. R.; Wenger, S.; Wang, M. K.; Mishra, A.; Zakeeruddin, S. M.; Grätzel, M.; Bäuerle, P. *Chem. Mater.* **2010**, *22*, 1836.
- (16) Zhang, G. L.; Bala, H.; Cheng, Y. M.; Shi, D.; Lv, X. J.; Yu, Q. J.; Wang, P. *Chem. Commun.* **2009**, 2198.
- (17) Daenke, T.; Kwon, T.-H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. *Nat. Chem.* **2011**, *3*, 211.
- (18) Li, X. C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206.
- (19) Wang, L.; Chen, Q.; Pan, G. B.; Wan, L. J.; Zhang, S. M.; Zhan, X. W.; Northrop, B. H.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 13433.
- (20) Zhang, L.; Tan, L.; Wang, Z. H.; Hu, W. P.; Zhu, D. B. *Chem. Mater.* **2009**, *21*, 1993.
- (21) Zhan, X. W.; Tan, Z. A.; Zhou, E. J.; Li, Y. F.; Misra, R.; Grant, A.; Domercq, B.; Zhang, X. H.; An, Z. S.; Zhang, X.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem.* **2009**, *19*, 5794.
- (22) He, M. Q.; Li, J. F.; Sorensen, M. L.; Zhang, F. X.; Hancock, R. R.; Fong, H. H.; Pozdin, V. A.; Smilgies, D. M.; Malliaras, G. G. *J. Am. Chem. Soc.* **2009**, *131*, 11930.
- (23) Frey, J.; Bond, A. D.; Holmes, A. B. *Chem. Commun.* **2002**, 2424.
- (24) We thanks Drs. J. Frey, S. Proemmel, and M. Armitage for first developing this method in the synthesis of DTT. See; Frey, J.; Proemmel, S.; Armitage, M. A.; Holmes, A. B. *Org. Synth.* **2006**, *83*, 209.
- (25) Chen, M. C.; Chiang, Y. J.; Kim, C.; Guo, Y. J.; Chen, S. Y.; Liang, Y. J.; Huang, Y. W.; Hu, T. S.; Lee, G. H.; Facchetti, A.; Marks, T. J. *Chem. Commun.* **2009**, 1846.
- (26) A reviewer has drawn our attention to the electrophilic variation of the Hunsdiecker reaction of electron-rich aromatic and heteroaromatic carboxylic acids.<sup>27–31</sup> This process suffers the limitation of further electrophilic substitution reactions in the aromatic ring.
- (27) Janz, K.; Kaila, N. *J. Org. Chem.* **2009**, *74*, 8874.

- (28) Camps, P.; Lukach, A. E.; Pujol, X.; Vazquez, S. *Tetrahedron* **2000**, *56*, 2703.
- (29) Grovenstein, E.; Henderson, U. V. *J. Am. Chem. Soc.* **1956**, *78*, 569.
- (30) Johnson, R. G.; Ingham, R. K. *Chem. Rev.* **1956**, *56*, 219.
- (31) Koo, B. S.; Kim, E. H.; Lee, K. J. *Synth. Commun.* **2002**, *32*, 2275.
- (32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian09*; Gaussian, Inc., Pittsburgh, PA, 2003.
- (33) Kong, H.; Lee, D. H.; Kang, I. N.; Lim, E.; Jung, Y. K.; Park, J. H.; Ahn, T.; Yi, M. H.; Park, C. E.; Shim, H. K. *J. Mater. Chem.* **2008**, *18*, 1895.