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Dithienothiophene (DTT)-based dyes for dye-sensitized solar cells: synthesis of 2,6-Dibromo-DTT

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 bromodecarboxylation of DTT-2,6-dicarboxylic acid, obtained by saponification of the diester 1. The donor-acceptor dye DAHTDTT (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 Voc of 697 mV, Jsc of 14.4 mA/cm², and ff of 0.73 at 1 sun.

Keywords

cells, solar, sensitized, dye, dyes, dithienothiophene, dtt, dibromo, 6, 2, synthesis

Disciplines

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

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A one-pot synthesis of 2,6-dibromo-dithieno[3,2-*b*;2',3'-*d*]thiophene (dibromo-DTT **4**) was developed. A key step was bromodecarboxylation of DTT-2,6-dicarboxylic acid, obtained by saponification of the diester **1**. The donor-acceptor dye DAHTDTT (**13**) based on a central 2,6-bis[2'-(3'-hexylthiophenyl)]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/cm², 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.¹⁻¹⁷ Most organic sensitizers consist of a donor fragment (D), a π -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 non-planar structure to prevent self-aggregation, (ii) incorporate appropriate conjugation length for a broad absorption, (iii) use long alkyl chain substituents to minimize electron recombination, (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 π -conjugated linking segment. This is due to the relatively high hole mobility exhibited by the fused thiophene core¹⁸ in a variety of electronic and optical applications,^{4-7,19} such as organic thin film transistors^{18,20-22} and polymer solar cells.²¹ 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.²³⁻²⁵ However many approaches still require multiple steps and harsh conditions.^{23,24} 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 one-pot bromodecarboxylation reaction of the DTT-diacid **5**.

SCHEME 1. Routes to dibromo-DTT **4** from the diester **1**.

SCHEME 2. Synthesis of the dye **13**.

Recently thiophene-based dyes have been used for light-harvesting in DSCs.⁴⁻⁶ However, as DTT-based dyes may not exhibit a broad absorption region,⁶ 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 TiO₂ nanoparticle to the radical cation of the dye owing to the presence of the hexyl substituents. The final components of the light harvesting dye **DAHTDTT 13** are the nonplanar triphenyl amine (TPA) donor unit (D) and an α -cyanoacrylic acid group as the electron acceptor (A) to form a D- π -A structure.

The synthesis of the dye **DAHTDTT 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).^{23,24} 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).¹⁴ This method, followed standard saponification of the diester **6** (heat to reflux in aqueous THF containing NaOH), dilution of the cooled product slurry to dissolve the carboxylate salt, and addition of an excess of NBS (over 6 eq) followed by stirring overnight. Standard extraction with CH₂Cl₂ and basic work-up produced the dibromo-DTT **4** in over 80 % yield.

Without column purification, the dibromo-compound **4** was coupled under Suzuki conditions with 3-hexylthiophene-2-pinacolylboronate **8** in the presence of Pd₂(dba)₃, (*t*-butyl)₃P.HBF₄ and 2M K₃PO₄, 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**.⁶ 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.

FIGURE 1. UV/VIS and PL spectra of dye **13** in CH₂Cl₂ (0.02 mM).

The UV/VIS absorption spectrum of the dye **DAHTDTT 13** in CH₂Cl₂ (0.02 mM) showed a strong broad absorption maximum around 650 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 CH₂Cl₂ solutions (0.5 mM) with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) 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 more negative value than the level of the TiO₂ conduction band (CB) edge, (−0.5 V vs NHE) we can expect that the photo-excited state of the dye **13** can effectively inject electrons into the conduction band (CB) of TiO₂.

FIGURE 2. DFT-calculated electron densities of HOMO (bottom) and LUMO (top) orbitals of **13**.

Optimized Density Functional Theory (DFT) calculations were carried out utilizing Gaussian09 at the B3LYP/6-31G(d) level of theory.²⁶ As shown in Figure 2, the electron densities in the HOMO and LUMO of the dye are well separated. 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 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).⁶ For the titanium oxide different film thicknesses of the transparent and scattering layer were used as follows: 6 μm (6), 6 + 6 scattering layer μm (6 + 6s), 12 μm (12), and 12 + 6 scattering layer μm (12 + 6s) were studied as well as the effect of the co-adsorbent (DCA=3 α , 7 α -dihydroxy-5 β -cholic acid).

The device performances are summarized in Table 2, with optimal results shown in Figure 3 and 4. 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 TiO₂ surface.⁶ The binding mode and the number of dye molecules adsorbed onto the TiO₂ depend on the solvents. Adsorption of the dye **13** in

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 _{cal} (Exp)) ^a	LUMO _{cal} (Exp) ^a	Abs ($\epsilon \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$) ^b	PL ^b (λ_{max})	E_{ox} (V) vs NHE ^c	$E_{\text{o-o}}$ (V) vs (abs/Em) ^d	$E_{\text{ox}}-E_{\text{o-o}}$ (V) vs NHE
Dye 13	-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

^a HOMO = $-(E_{\text{onset}} \text{ vs Fc}^+/\text{Fc} - 4.8 \text{ eV})$, LUMO = HOMO + $E_{\text{o-o}}$. ^b 0.02 mM CH₂Cl₂ solution at 298 K. ^c Cyclic voltammetry measurement of the onset point of oxidation E_{ox} of the dye were measured in dry CH₂Cl₂ containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte, Ag/AgCl as a reference electrode, and glassy carbon as working electrode. Potentials calibrated with Fc⁺/Fc were converted normal hydrogen electrode (NHE) by addition of +0.63 V. ^d The $E_{\text{o-o}}$ transition energy was estimated from the intersection of the absorption and emission spectra.

CHCl₃ and EtOH solvent mixtures (1:1) yielded the highest device efficiency compared with CHCl₃, CH₂Cl₂, CH₂Cl₂/EtOH, chlorobenzene, and chlorobenzene/EtOH (see ESI). Optimum devices were obtained using the dye (0.2 mM) in CHCl₃/EtOH (1/1) solutions with overnight soaking on titania. Thus all devices were prepared in 0.2 mM CHCl₃/EtOH (1/1) solutions after overnight soaking.

TABLE 2. Photovoltaic performance of cells fabricated using the dye **13**.

#	Thick (μm)	Coads (mM) ^a	V_{oc} (mV)	J_{sc} (mA/cm ²) ^b	ff	Effc (%)
1	6	0	700	11.0	0.73	5.6
2	6	10	718	12.2	0.74	6.5
3	6 + 6s ^b	10	720	12.6	0.71	6.4
4	12	10	705	13.3	0.70	6.6
5	12 + 6s	10	698	14.7	0.70	7.1
6	12 + 6s	20	697	14.4	0.73	7.3
N719 ^c	12 + 6s		780	14.5	0.73	8.3

^aCo-adsorbent is 3 α , 7 α -dihydroxy-5 β -cholic acid. ^b6s is 6 μm scattering layer. ^cElectrolyte for N719:0.6 M 1-butyl-3methyl imidazolium iodide, 0.03 M I₂, 0.10 M guanidinium thiocyanate (GuSCN), and 0.50 M *t*-butylpyridine (TBP) in the dry acetonitrile/valeronitrile (v/v=85/15).

FIGURE 3. The I - V curve of a DSC device using the titania layers 12 + 6s and standard electrolyte under various solar simulated light intensities.

Using a 6 μm titania film without any co-adsorbent, a device fabricated with dye **13** gave a short-circuit photocurrent density (J_{sc}) of 11.01 mA/cm², an open-circuit voltage (V_{oc}) of 700 mV, and a fill factor (ff) of 0.73, corresponding to an overall conversion efficiency (η) of 5.6%. With 10 mM DCA as co-adsorbent, the device efficiency was increased up to 6.5% (V_{oc} = 718 mV, J_{sc} = 12.2 mA/cm², ff = 0.74). These results indicate that the co-adsorbent prevents dye-aggregation thus improving electron injection yield.⁷ Adsorption of DCA usually leaves protons on the TiO₂ surface and hence

positively charges the surface. Thus the conduction band is shifted, resulting in low V_{oc} .^{7,8} However, in the present case an increase of 20 mV was observed, indicating that charge recombination was suppressed by DCA.⁷ With a 6 μm scattering layer (6 + 6s), an increase in J_{sc} from 12.2 to 12.6 mA/cm² 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 μm film (6.5%). Using a 12 μm film thickness, an increase of J_{sc} to 13.3 mA/cm² was observed as well as a loss in V_{oc} and a reduction in fill factor, resulting in a small increase in performance of the cells (6.6%). Using a 12 μm transparent film with a 6 μm scattering layer, 12 + 6s, J_{sc} significantly increased to 14.7 mA/cm² while V_{oc} remained the same (698 mV) and the fill factor was 0.70, leading to device efficiency improving to 7.1%. The J_{sc} of devices made with the dye **13** is slightly higher than that achieved for N719 (14.5 mA/cm²) under the same conditions. Through further optimization, via an increase of co-adsorbent (20 mM), the performance of the cell increased to 7.3% with V_{oc} of 697 mV, J_{sc} of 14.4 mA/cm² and fill factor was 0.73.

FIGURE 4. IPCE spectrum of devices fabricated using the dye **13** according to the film thickness of titania.

Compared with the previously reported device performance (η = 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-yl}-acrylic acid TTC2,⁶ 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 (η = 8.3%). Figure 3 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 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 the 800 nm and a higher plateau at 67% ($\lambda = 495$ nm) (Figure 4).

In summary, we have developed a simple one-step synthesis of dibromo DTT (**4**) from diester DTT (**1**) over 80% yield using one-pot bromo-decarboxylation for the DSCs dyes core unit. The organic DSCs dye DAHTDTT (**13**) consisted of TPA and DTT coupled with hexylthiophene showing high efficiency of 7.3% with V_{oc} of 697 mV, J_{sc} of 14.4 mA/cm², and ff of 0.73.

EXPERIMENTAL SECTION

Preparation of DAHTDTT (13). A solution of aldehyde **12** (80 mg, 0.09 mmol) in a mixture of acetonitrile (10 mL) and CHCl₃ (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 CH₂Cl₂ and the combined organic extracts were washed with 1N HCl, water, and brine solution. The organic layer was dried over MgSO₄. 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, m. p. 144 °C, $R_f = 0.56$ (10:1:0.1 CH₂Cl₂/MeOH/Acetic acid) after trituration with pet. spirits 40–60 °C and CH₂Cl₂. ¹H NMR (500 MHz, DMSO-*d*₆): δ 0.84 (6 H, t, $J = 7.0$ Hz), 1.28 (8 H, br m), 1.37 (4H, 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). ¹³C NMR (125 MHz, DMSO-*d*₆ at 50 °C): 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)+], 893.2 [60, (M+H)⁺], 894.2 [20, (M+2H)⁺]. m/z (EI): 892.2310. [M⁺]. Calcd. for C₅₂H₄₈N₂O₂S₅ 892.2319. FT-IR (neat cm⁻¹): 2921, 1684, 1569, 1507, 1492, 1391, 1276, 1173, 696.

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Supporting Information Available: Syntheses and spectra of **4**, **9**, **10**, **12**, and **13**; device fabrication; DFT calculations. This material is available free of charge via the internet at <http://pubs.acs.org>.

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