Facile synthesis of metal-free organic dyes featuring a thienylethynyl spacer for dye sensitized solar cells☆

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ABSTRACT

In this article, we report the facile synthesis of metal-free dyes **6** and **7**, their solution-based optical and redox properties and their use as sensitizers in dye-sensitized solar cells (DSSCs). Our studies indicate that the addition of the second thiophene unit in dye **7**, decreases the oxidation and reduction potential and consequently the band gap of the molecule compared to **6**. Furthermore, increasing the length of the conjugated spacer also affects on the properties of the DSSCs, with dye **7** providing a higher power conversion efficiency compared to **6** (η = 4.49 versus 3.23%).

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1. Introduction

Dye-sensitized solar cells (DSSCs) are attracting significant academic and commercial interest as possible lower-cost alternatives to conventional solid-state photovoltaic devices [1,2]. The nature of the photosensitizer plays an important role in DSSCs, as it has a profound influence on both the power conversion efficiency as well as the stability of the cells. Organic dyes have attracted much interest in recent years as they offer several advantages over their ruthenium-based brethren including bespoke structural modification through rich synthetic protocols, lower cost large-scale production, reduced environmental and toxicity issues and high molar extinction coefficients [3—7]. One of the main goals in this area has been focused upon improving the power-conversion-efficiency of these systems through structural modification [8]. In general, these systems feature donor (D) and acceptor (A) systems separated by a π-conjugated bridge (D−π−A). For example, triphenylamine derivatives have been commonly utilized as the electron donor (D), whilst a cyanoacrylic acid moiety acts as the electron acceptor (A) and anchoring unit in the D−π−A structure [9]. Various π-conjugated bridges, such as benzene, thiophene and benzothiadiazole, have been introduced to broaden their absorption towards the near-infrared region. Interestingly, studies have shown that in addition to optimizing the optical properties of the dye, increasing the number of thiophene π-bridging units tends to result in an increase in power conversion efficiency [10]. Another important goal is to develop systems that may be accessed through short and simple synthetic routes for more widespread implementation in lower cost applications [11].

In this study, we report the facile synthesis of two organic dyes (**6** and **7**, Scheme 1), which can be conveniently prepared in two steps from commercially available thiophene derivatives **1** and **2** and alkyne **3**. The dyes have been designed to investigate the effect of increasing conjugation through the addition of thiopehene units has on the properties of the dyes. Importantly, the acetylene linker

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Scheme 1. Reagents and conditions: (a) Pd/C 10%, CuI, Ph₃P, K₂CO₃, DME: H₂O; (b) cyanoacetic acid, piperidine, CH₃CN.

group has been included to provide a planar linker moiety [12–14] and as a handle for further synthetic manipulation [15]. We have investigated the influence the number of thiophene units has on the optical, redox and DSSC properties of dyes **6** and **7**. This study has revealed that the addition of the second thiophene unit in compound **7** plays an important role in modulating the optical and redox properties of this system compared to **6**. Furthermore, increasing the conjugation between the D and A units in this way also results in improved efficiency of the DSSCs (**6** η = 3.23%; **7** η = 4.49%).

2. Experimental

2.1. Materials

All reactions were undertaken under a nitrogen atmosphere. Solvents were purified using a PureSolv solvent purifier system. Compounds **1**, **2** and **3** were purchased from either Aldrich or TCI, and were used without further purification.

2.2. Characterization

NMR spectroscopy was undertaken on a Bruker AVIII (400 MHz) spectrometer. Chemical shifts are reported in ppm and are relative to tetramethylsilane. UV–vis spectra were recorded on a Perkin–Elmer Lamda 25 instrument. Band gaps (E_g) were estimated using the absorption edge of the longest wavelength absorption (λ) using $E_g = 1240/\lambda$. Cyclic voltammetry measurements were undertaken using a CH Instruments 440a electrochemical analyzer using a platinum disc working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode. Ferrocene was used as an internal standard and all redox couples are reported versus the ferrocene/ferrocenium (Fc/Fc⁺) redox couple adjusted to 0.0 V. The solutions were prepared using dry dimethylformamide (DMF) containing electrochemical grade tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The solutions were purged with nitrogen gas for 3–4 min prior to recording the electrochemical data. The HOMO/LUMO energies were estimated from the oxidation and reduction waves, respectively, using a HOMO energy for ferrocene of −4.8 eV [16].

2.3. Computation

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed using a Gaussian '09 software package [17]. The geometry of dyes **6** and **7** was optimized using the B3LYP method with the 6−31 + G(d) basis set. The optimized structures have been classified as local minima on their respective potential energy surfaces according to their vibrational frequencies. None of the vibrational frequencies in the optimized geometries generated negative frequencies in their ground state. To introduce the effect of solvent, the electronic states of both organic dyes in acetonitrile were also calculated by means of the Tomasi's Polarized Continuum Model (PCM).

2.4. Synthesis

2.4.1. Compound **4**

5-Bromo-2-thiophenecarboxaldehyde **1** (0.50 g, 2.30 mmol), 10% Pd/C (0.07 g, 0.07 mmol), CuI (0.13 g, 0.68 mmol), Ph₃P (0.47 g, 1.80 mmol) and K₂CO₃ (0.50 g, 3.6 mmol) were dissolved at room temperature in a 1:1 mixture of water (15 mL) and DME (15 mL). The mixture was degassed with N₂ for 5 min and stirred for 30 min under N₂. Then 4-ethynyl-N,N-dimethylaniline **3** (0.50 g, 3.40 mmol) was added to the mixture. The reaction mixture was heated under reflux overnight. The mixture was then cooled and DCM (80 mL) was added and the organic layers were separated, dried over MgSO₄ and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO₂; toluene/DCM, 9:1) to give **4** as an orange solid (0.37 g, 63%); mp. 147–149 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.84 (s, 1H), 7.64 (d, J = 3.9 Hz, 1H), 7.41 (d, J = 8.9 Hz, 2H), 7.22 (d, J = 3.9 Hz, 1H), 6.65 (d, J = 8.9 Hz, 2H), 3.02 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 182.2 (C̲=O), 150.7 (C̲−N), 142.7 (C̲−H), 136.3 (C̲−H), 134.4 (C̲−C), 132.9 (2 × C̲−H), 131.2 (C̲−H), 111.6 (2 × C̲−H), 108.1 (C̲−C), 100.3 (C̲≡C), 80.6 (C̲≡C), 40.0 (2 × C̲−N) ppm; IR (film) ʋ 2807, 2182, 1656, 1229 cm⁻¹; HRMS m/z (EI+) calculated for C₁₅H₁₃NOS 255.0718 found 255.0708.

2.4.2. Compound **5**

5-Bromo-2,2′-bithiophene-5′-carboxaldehyde **2** (0.50 g, 1.83 mmol), 10% Pd/C (0.06 g, 0.06 mmol), CuI (0.10 g, 0.55 mmol), Ph₃P (0.40 g, 1.50 mmol) and K₂CO₃ (0.40 g, 2.90 mmol) were dissolved at room temperature in a 1:1 mixture of water (15 mL) and DME (15 mL). The mixture was degassed with N₂ for 5 min and stirred for 30 min under N₂. Then 4-ethynyl-N,N-dimethylaniline **3** (0.40 g, 2.75 mmol) was added to the mixture. The reaction mixture was heated under reflux overnight. The mixture was then cooled and DCM (80 mL) was added and the organic layers were separated,