

## An unconventional helical push-pull system for solar cells

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### ARTICLE INFO

#### Keywords:

Push-pull chiral system  
Tetrathiahelicene  
Dye-sensitized solar cells

### ABSTRACT

The synthesis, photophysical and electrochemical characterization, theoretical calculations and photovoltaic studies of a push-pull dye with an unconventional nonplanar tetrathiahelicene  $\pi$ -spacer between the donor-acceptor groups, are reported. The molecule exhibits suitable HOMO LUMO levels to be used in DSSC. The presence of the donor-acceptor helical architecture allows the internal charge transfer and subsequent electron injection to the conduction band of  $\text{TiO}_2$  leading to the good photocurrent value of  $4.6 \text{ mA cm}^{-2}$ .

### 1. Introduction

Tetrathiahelicenes (7-THs), formed by thiophene and benzene rings *ortho*-fused in an alternating fashion, belong to an intriguing class of chiral helical-shaped molecules, that have reached a high degree of appeal thanks to the association of synthetic challenges to manifold applications in different areas of science [1]. The configurationally fixed helical arrangement confers them a peculiar topology and chirality, and has a strong impact on the electronic structure of the  $\pi$ -conjugated system, thus providing unique electronic and optical properties suitable for applications in optoelectronics [2], biomolecular recognition [3], and asymmetric catalysis [4]. The regioselective functionalization of the  $\alpha$ -position(s) of the terminal thiophene ring(s) allows the introduction of a variety of substituents [5], which can further modulate specific properties, including electronic properties. At the same time the helical system can exhibit even a high degree of flexibility depending on the nature and dimension of substituents present on the terminal aryl rings [6]. In light of these considerations it is therefore quite surprising that the 7-TH has never been used as a  $\pi$ -linker in push-pull dyes for applications in dye-sensitized solar cells (DSSCs). In this paper we describe the first example of a push-pull dye in which the 7-TH scaffold has been used as the  $\pi$ -spacer between a donor and an acceptor group, and we investigate the photophysical and electrochemical properties. In addition, we also performed theoretical calculations and photovoltaic (PV) studies to assess their performance

as helical-based push-pull dye.

We designed the novel helical dye system **1** (Fig. 1), that could fulfil the requirements as an organic donor- $\pi$ -acceptor DSSC sensitizer, being constituted by: *i*) the thiahelicene scaffold as stable and  $\pi$ -conjugated-bridge spacer; *ii*) the triarylamine moiety connected to the heteroaromatic spacer by a vinylene linkage as a donor group; *iii*) the cyanoacrylic acid moiety as an electron acceptor and anchoring group for the covalent grafting to the  $\text{TiO}_2$  surface. Two *n*-propyl chains are incorporated into the dye **1** to improve solubility and alleviate aggregation. As this regard, the non-planarity of the helical system along with the presence of the bulky triarylamine group should also disturb possible adverse  $\pi$ -stacking events, suppressing the aggregation of the dye molecules on the  $\text{TiO}_2$  surface.

### 2. Experimental section

#### 2.1. General methods

All commercially available reagents and solvents were used without further purification unless otherwise noted. Tetrathia[7]helicene-based aldehydes **2** and **6** were prepared according to literature [5d]. The phosphonium salt **3** was prepared as previously reported [7]. Thin-layer chromatography (TLC) was performed with Aldrich silica gel 60 F254 precoated plates, and plates were visualized with short-wave UV light (254 and 366 nm). Column chromatography was carried out with

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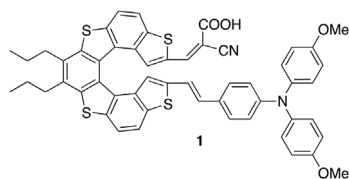


Fig. 1. Structure of dye 1.

Aldrich silica gel (70–230 mesh). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 25 °C using Bruker AC-300 MHz, Bruker Avance III 400 MHz, Bruker AMX-500 MHz and Bruker Avance 600 MHz spectrometers. Chemical shifts ( $\delta$ ) were reported in parts per million calibrated against the residual protonated solvent resonances ( $^1\text{H}$ :  $\delta = 2.05$  ppm,  $^{13}\text{C}$ :  $\delta = 29.92$  ppm for  $(\text{CD}_3)_2\text{CO}$ ;  $^1\text{H}$ :  $\delta = 2.50$  ppm,  $^{13}\text{C}$ :  $\delta = 39.51$  ppm for  $\text{DMSO}-d_6$ ). High-resolution mass spectra (HRMS) were recorded using a Bruker Daltonics ICR-FTMS (Fourier transform ion cyclotron resonance mass spectrometry) APEX II. The elemental analyses were recorded with a Perkin-Elmer 2400.

## 2.2. Syntheses

### 2.2.1. Synthesis of intermediate 4

A solution of **3** (120 mg, 0.18 mmol) in DMF (4 mL) was slowly added, under stirring at room temperature, to a suspension of **2** (117 mg, 0.21 mmol),  $\text{K}_2\text{CO}_3$  (50 mg, 2.1 mmol), 18-crown-6 ether (9.5 mg, 0.036 mmol) in DMF (4 mL). The resulting reaction mixture was stirred at room temperature for 16 h. The mixture was then poured into water (10 mL), and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (4  $\times$  15 mL). The resulting organic layer was washed with water (2  $\times$  10 mL), dried over anhydrous sodium sulphate, and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using hexane and  $\text{AcOEt}$  (9:1 v/v) as eluent to give compound **4** (95 mg, 67%) as an orange solid.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  9.36 (s, 1H), 8.47 (d, 1H,  $J = 8.6$  Hz), 8.39 (d, 1H,  $J = 8.8$  Hz), 8.18 (s, 2H), 7.43 (s, 1H), 7.22 (d, 2H,  $J = 8.8$  Hz), 7.05 (m, 4H), 6.94 (m, 4H), 6.68 (d, 2H,  $J = 8.7$  Hz), 6.62 (d, 1H,  $J = 16$  Hz), 6.47 (s, 1H), 6.43 (d, 1H,  $J = 16$  Hz), 3.76 (s, 6H), 3.16 (m, 4H), 1.84 (m, 4H), 1.14 (t, 6H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (150 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  185.1 (CHO), 157.7 ( $\text{C}_q$ , 2C), 150.1 ( $\text{C}_q$ ), 143.7 ( $\text{C}_q$ ), 142.1 ( $\text{C}_q$ ), 141.4 ( $\text{C}_q$ ), 141.3 ( $\text{C}_q$ ), 141.0 ( $\text{C}_q$ ), 140.98 ( $\text{C}_q$ ), 137.8 ( $\text{C}_q$ ), 137.5 ( $\text{C}_q$ ), 136.9 ( $\text{C}_q$ ), 136.7 ( $\text{C}_q$ ), 136.4 (CH), 135.9 ( $\text{C}_q$ ), 134.2 ( $\text{C}_q$ , 2C), 133.6 ( $\text{C}_q$ ), 133.3 ( $\text{C}_q$ ), 131.7 (CH), 131.1 ( $\text{C}_q$ ), 130.6 (CH), 129.2 ( $\text{C}_q$ ), 129.1 ( $\text{C}_q$ ), 128.53 (CH), 128.49 ( $\text{C}_q$ ), 128.2 (CH, 4C), 128.0 (CH), 124.2 (CH), 124.0 (CH), 122.6 (CH), 122.2 (CH), 120.4 (CH), 119.8 (CH), 119.3 (CH), 115.9 (CH, 3C), 115.8 (CH), 56.0 ( $-\text{OCH}_3$ , 2C), 35.2 ( $\text{CH}_2$ , 2C), 24.3 ( $\text{CH}_2$ , 2C), 15.1 ( $\text{CH}_3$ , 2C). HRMS (ESI, positive mode)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{51}\text{H}_{41}\text{NO}_3\text{S}_4$  843.1969, found 843.2075.

### 2.2.2. Synthesis of dye 1

Cyanoacetic acid (18.0 mg, 0.21 mmol) and piperidine (2 mg, 0.5 mmol) were added to a solution of **4** (41 mg, 0.05 mmol) in a mixture of THF (1 mL) and  $\text{CH}_3\text{CN}$  (10 mL) at room temperature. The resulting mixture was then stirred at reflux for 5 h. The solvents were removed under reduced pressure. The residue was taken up with an aqueous solution of HCl (0.1 M, 6 mL), the solid was filtered and washed with hexane and  $\text{CH}_3\text{CN}$ , and dried under vacuum to afford **1** (27 mg, 60%) as a red solid.  $^1\text{H}$  NMR (600 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  8.39 (m, 2H), 8.14 (m, 2H), 7.72 (s, 1H), 7.32 (s, 1H), 7.22 (d, 2H,  $J = 8.6$  Hz), 7.05 (d, 4H,  $J = 8.8$  Hz), 6.93 (d, 4H,  $J = 8.8$  Hz), 6.67 (d, 2H,  $J = 8.5$  Hz), 6.63 (d, 1H,  $J = 16$  Hz), 6.45 (s, 1H), 6.43 (d, 1H,  $J = 16$  Hz), 3.75 (s, 6H), 3.12 (m, 4H), 1.82 (m, 4H), 1.13 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  163.9 ( $\text{C}_q$ ), 157.5 ( $\text{C}_q$ , 2C), 154.5 (CH), 149.9 ( $\text{C}_q$ ), 147.2 (CH), 143.3 ( $\text{C}_q$ ), 141.4 ( $\text{C}_q$ ), 141.2 ( $\text{C}_q$ , 2C), 141.1 ( $\text{C}_q$ ), 140.8 ( $\text{C}_q$ ), 137.7 ( $\text{C}_q$ ), 137.5 (CH), 137.4 ( $\text{C}_q$ ), 136.7 ( $\text{C}_q$ ), 136.6 ( $\text{C}_q$ ), 135.2 ( $\text{C}_q$ ), 134.7 ( $\text{C}_q$ ), 134.1 (CH), 134.0 ( $\text{C}_q$ ), 133.3 ( $\text{C}_q$ ), 132.4

( $\text{C}_q$ ), 131.5 (CH), 130.9 ( $\text{C}_q$ ), 129.4 (CH), 129.2 ( $\text{C}_q$ ), 128.9 ( $\text{C}_q$ ), 128.4 (CH), 128.0 (CH, 4C), 124.0 (CH), 123.7 (CH), 122.9 ( $\text{C}_q$ ), 121.9 (CH), 120.3 (CH), 119.7 (CH), 119.2 (CH), 117.1 (CH), 116.5 ( $\text{C}_q$ ), 116.1 (CH), 115.8 (CH, 2C), 102.9 ( $\text{C}_q$ ), 55.8 ( $-\text{OCH}_3$ , 2C), 35.0 ( $\text{CH}_2$ , 2C), 24.1 ( $\text{CH}_2$ , 2C), 15.0 ( $\text{CH}_3$ , 2C). HRMS (ESI, positive mode)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{54}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_4$  910.2027, found 910.2064. Elemental anal. Found: C, 71.68; H, 4.38; N, 2.74%; molecular formula  $\text{C}_{54}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_4$  requires C, 71.18; H, 4.65; N, 3.07%. UV-vis (DCM),  $\lambda_{\text{max}}$  [ $\epsilon$  ( $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )]: 424 [5.14] nm.

### 2.2.3. Synthesis of dye 5

Cyanoacetic acid (48 mg, 0.58 mmol) and piperidine (4 mg, 0.046 mmol) were added to a solution of **6** (60 mg, 0.116 mmol) in THF (6 mL) at room temperature. The resulting mixture was then stirred at reflux for 5 h. The solvent was removed under reduced pressure. The residue was taken up with  $\text{CH}_2\text{Cl}_2$  and an aqueous solution of HCl (0.2 M). The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ , and the resulting organic layer was washed with water, dried over anhydrous sodium sulphate, and filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography using  $\text{CH}_2\text{Cl}_2$  and MeOH (9:1 v/v) as eluent to give compound **5** (55 mg, 82%) as an orange solid.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.19–8.07 (m, 4H), 7.28 (s, 1H), 7.19 (d, 1H,  $J = 5.5$  Hz), 6.86 (s, 1H), 6.41 (d, 1H,  $J = 5.5$  Hz), 3.01 (m, 2H), 2.90 (m, 2H), 1.67 (m, 4H), 1.01–0.98 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  163.1 ( $\text{C}_q$ ), 140.5 (CH), 139.4 ( $\text{C}_q$ ), 139.2 ( $\text{C}_q$ ), 138.2 ( $\text{C}_q$ ), 136.3 ( $\text{C}_q$ ), 136.0 ( $\text{C}_q$ ), 135.6 ( $\text{C}_q$ ), 135.1 ( $\text{C}_q$ ), 134.9 ( $\text{C}_q$ ), 134.0 ( $\text{C}_q$ ), 132.4 ( $\text{C}_q$ ), 132.0 (CH), 131.9 ( $\text{C}_q$ ), 130.5 ( $\text{C}_q$ ), 130.1 ( $\text{C}_q$ ), 127.3 ( $\text{C}_q$ ), 127.0 ( $\text{C}_q$ ), 125.8 (CH), 124.0 (CH), 121.7 (CH), 121.6 (CH), 121.3 (CH), 119.0 (CH), 118.2 ( $\text{C}_q$ ), 111.0 ( $\text{C}_q$ ), 33.6 ( $\text{CH}_2$ , 2C), 23.8 ( $\text{CH}_2$ , 2C), 14.4 ( $\text{CH}_3$ , 2C). MS (EI)  $m/z$ : 537  $[\text{M} - \text{CO}_2]^+$ . HRMS (ESI, positive mode)  $m/z$ :  $[\text{M} - \text{CO}_2]^+$  calcd for  $\text{C}_{31}\text{H}_{23}\text{NS}_4$  537.0713, found 537.0405. Elemental anal. Found: C, 66.23; H, 4.27; N, 2.30%; molecular formula  $\text{C}_{32}\text{H}_{23}\text{NO}_2\text{S}_4$  requires C, 66.06; H, 3.98; N, 2.41%. UV-vis (DCM),  $\lambda_{\text{max}}$  [ $\epsilon$  ( $10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ )]: 434 [2.3] nm.

## 2.3. Optical and electrochemical measurements

UV-vis spectra of compounds **1** and **5** were recorded with a V-570 Jasco spectrophotometer.

Cyclic voltammetry (CV) studies were performed at potential scan rates typically ranging 0.05–2  $\text{V s}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  solutions 0.0005 M and 0.00075 M, deaerated by  $\text{N}_2$  bubbling, with tetrabutylammonium perchlorate TBAP 0.1 M as the supporting electrolyte, at 298 K. The ohmic drop has been compensated by the positive feedback technique. The experiments were carried out using an AUTOLAB PGSTAT potentiostat (EcoChemie, The Netherlands) run by a PC with GPES software. The working electrode was a glassy carbon (GC) one (AMEL, diameter = 1.5 mm) cleaned by diamond powder (Aldrich, diameter = 1  $\mu\text{m}$ ) on a wet cloth (STRUERS DP-NAP); the counter electrode was a platinum wire; the reference electrode was an aqueous saturated calomel electrode (SCE), having in our working solvent ( $\text{CH}_2\text{Cl}_2$ ) a difference of  $-0.495 \text{ V}$  vs. the  $\text{Fc}^+|\text{Fc}$  couple (the inter-solvental redox potential reference currently recommended by IUPAC) and inserted in a double bridge in order to prevent water and/or chloride leakage. The HOMO and LUMO values were estimated with the formula: HOMO (LUMO) =  $-e [E_p, I_a \text{ vs } \text{Fc}^+|\text{Fc} (E_p, I_c \text{ vs } \text{Fc}^+|\text{Fc}) + 4.8]$ , where  $e$  is the unitary charge,  $E_p$ ,  $I_a$  and  $E_p$ ,  $I_c$  are the first oxidation and reduction peaks, respectively and +4.8 is the recommended value to be consistent with the absolute value for the normal hydrogen electrode.

## 2.4. Computational studies

The equilibrium geometry of **1** has been optimized using density functional theory (DFT) employing the  $\omega\text{B97XD}$  [8] exchange-correlation functional in combination with the cc-pVDZ basis set [9]. The

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