

Short Note

4,4'-([2,2'-Bithiophene]-5,5'-diylbis(ethyne-2,1-diyl))bis(1-methylpyridin-1-ium) Iodide

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Abstract: Viologens are a highly advantageous class of compounds for the synthesis of functional materials. Owing to their versatile structure, they can embed additional conjugated moieties, thus representing a convenient platform, for example for organic semiconductors and other energy-related uses. A straightforward synthesis of an extended viologen containing a bithiophene is described here, together with its UV-visible absorption and fluorescence spectroscopy, showing multiple absorption and emission bands. Thanks to its ease of synthesis and optical properties, this organic salt appears to be of potential interest for various optoelectronic applications.

Keywords: viologen; fluorescent probe; Sonogashira reaction

1. Introduction

The thiophene motif is among the most frequently exploited ones in the construction of functional extended π -conjugated structures [1,2], both in small molecules and in polymers [3–5]; indeed, thiophene versatility, stability, ease of functionalization and the possibility to obtain both oligomers and polymers in a straightforward and controlled way make its derivatives suitable building blocks for an ever-growing variety of materials [6]. The field of organic semiconductors [7,8], in particular, greatly profits from oligo- and polythiophenes, thanks to their optoelectronic properties, such as luminescence, charge carrier mobility and tunability of the HOMO-LUMO energy gap, which can be adjusted by varying both the number of thiophene subunits and the chemical nature and position of substituents on the heteroaromatic rings. For these reasons, some of the most investigated applications of oligo- and polythiophenes are represented by organic light-emitting diodes (OLEDs) [9], organic field-effect transistors (OFETs) [10], organic solar cells (OSCs) and other photovoltaic applications [11,12], and conductivity-based sensors and biosensors [13,14].

Another extensively studied family of heterocycle-containing compounds finding many optoelectronic applications is represented by the so-called viologens [15,16], that is, quaternary 4,4'-bipyridinium salts, for which several readily accessible synthetic methods have been developed. These compounds are especially known for their redox properties and electrochromism, their electron-accepting capability and their ability to form charge-transfer complexes, therefore being of great interest for electrochromic devices, memory devices, energy storage and production, among others [17]. An interesting feature of viologens, besides the tunability of their physico-chemical properties by different functionalizations on both the carbon and nitrogen atoms of the pyridyl ring, is that they retain their characteristics even if the quaternarized pyridines are not directly connected, provided that conjugation through the spacer subunits is ensured, thus forming extended viologens that show a virtually limitless structural variability.

A very simple and efficient synthesis of a new extended viologen containing a bithiophene core, linked to the quaternary pyridinium rings by triple bonds, is presented here, to-



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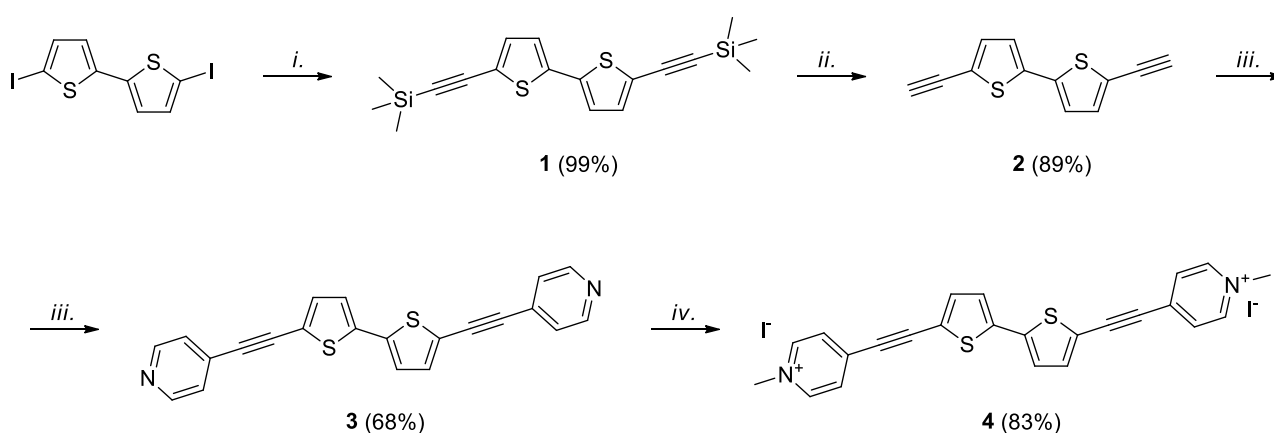


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gether with the description of its UV-visible absorption and fluorescence spectra; this water-soluble salt shows interesting light-absorption and emission features and thus presents a potential use as a fluorescent probe in applications such as fluorescence-based sensors.

2. Results and Discussion

The preparation of the extended viologen **4** was accomplished by a four-step synthesis (Scheme 1), starting from commercially available 5,5'-diiodo-2,2'-bithiophene, which could be easily functionalized through a palladium-catalyzed cross-coupling reaction, allowing for linkage with a great variety of conjugated moieties. In particular, the introduction of acetylenic units, afforded by the well-established Sonogashira reaction [18], appeared as a particularly favorable choice for a twofold reason: firstly, the widely investigated effectiveness of triple bonds in establishing conjugation and enabling electron transport [19,20]; and secondly, their linear geometry, allowing in principle the rotation of aromatic rings attached to the *sp* carbons, which could greatly affect both the structural and optical properties of compounds.



Scheme 1. Synthesis of product **4**; *i.* Pd(PPh₃)₄ (5 mol%), CuI (10 mol%), TMSA, toluene/*i*-Pr₂NH 7:3, r.t., 24 h; *ii.* KOH, THF/MeOH, r.t., 16 h; *iii.* 4-Iodopyridine, Pd(PPh₃)₂Cl₂ (20 mol%), CuI (10 mol%), THF/Et₃N, 60 °C, 24 h; *iv.* MeI, CH₂Cl₂, 40 °C, 24 h.

The synthesis then started with a palladium-copper-catalyzed reaction between 5,5'-diiodo-2,2'-bithiophene and the inexpensive building block trimethylsilylacetylene, according to a classic literature procedure [21], in a toluene/*diisopropylamine* mixture; the reaction gave the trimethylsilyl-protected bithiophene derivative **1**, obtained as a yellow solid with a nearly quantitative isolated yield (99%). This product was subsequently converted into the corresponding terminal diyne by stirring in the presence of KOH overnight at room temperature in a THF/MeOH mixture, affording 5,5'-diethynyl-2,2'-bithiophene **2** as a pale brown solid with 89% yield after aqueous workup and extraction with CHCl₃ followed by column chromatography.

The subsequent introduction of the pyridyl rings was achieved through iterated Sonogashira coupling between the dialkyne **2** and 2 equivalents of 4-iodopyridine, which led to the formation of 5,5'-bis(pyridin-4-ylethynyl)-2,2'-bithiophene **3**, obtained in 68% yield after chromatographic purification, as a bright yellow solid. This compound was finally converted into the corresponding quaternary bipyridinium salt **4** by methylation of the nitrogen atoms, carried out in CH₂Cl₂ at 40 °C with an excess of iodomethane. The expected product **4**, insoluble in the reaction medium, precipitated from the solution upon formation and was subsequently isolated by filtration of the mixture as a bright orange powder, in 83% yield; ¹H-NMR and ¹³C-NMR in DMSO-d₆ confirmed its identity and purity, without the need for further purification.

Although we did not perform 2D NMR experiments, the following signal assignments are proposed in the 1D spectra, on the basis of the predicted structure of the compound. The ¹H-NMR spectrum of **4** (Figure S1) shows a singlet at δ 4.33 ppm, attributable to the methyl groups attached to pyridine nitrogen atoms. As regards the pyridine hydrogen

signals, the protons in positions 2 and 3, involved in a second-order AA'XX' spin system, give multiplets at δ 9.00 and δ 8.25, respectively. The signals of protons on the thiophene rings can be easily detected as two doublets ($J = 3.9$ Hz) at δ 7.76 ppm and 7.67 ppm.

As regards the ^{13}C -NMR spectrum (Figure S2), a signal at δ 48.3 ppm is observed for the methyl groups, whereas the *sp* carbons of the triple bonds produce signals at 95.4 and 91.9 ppm. For the aromatic portion, the signal at δ 146.0 ppm is easily ascribed to carbons adjacent to nitrogen on the pyridyl rings, while the one at δ 128.8 ppm is attributable to those in position 3. The quaternary pyridyl carbon bearing the acetylene moiety afforded the signal at δ 138.0 ppm; lastly, the quaternary thiophene carbons produce signals at δ 119.9 and 140.9 ppm, for those attached to the triple bonds and those adjacent to the other thiophene ring, respectively, and the last two signals at δ 138.6 and 127.6 ppm are attributed to the C-H thiophene carbons.

The product resulted in being fairly soluble in H_2O and methanol; its UV-visible absorption spectrum (Figure 1) was measured in water solution ($c = 2.5 \times 10^{-4}$ M). It shows several intense absorption bands between 190 and 500 nm: the first and most intense of these has $\lambda_{\text{max}} = 193$ nm, with $\epsilon_{\text{max}} = 7988 \text{ M}^{-1}\text{cm}^{-1}$; then, two other bands in the UV region are present, with $\lambda_{\text{max}} = 225$ nm and 275 nm, respectively, and finally a large and intense absorption band in the visible region presents $\lambda_{\text{max}} = 444$ nm and $\epsilon_{\text{max}} = 6658 \text{ M}^{-1}\text{cm}^{-1}$.

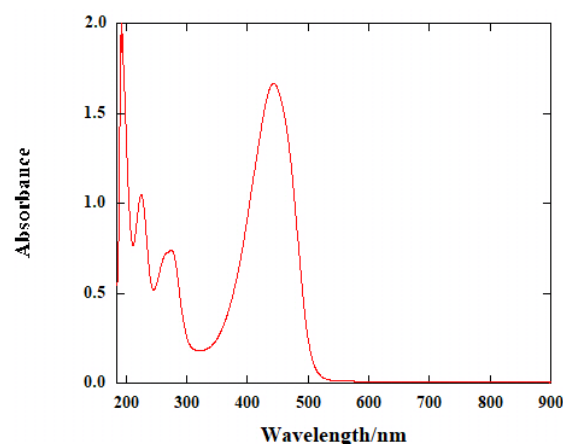


Figure 1. UV-visible absorption spectrum (H_2O , $c = 2.5 \times 10^{-4}$ M) of **4**.

Fluorescence spectra (Figure 2) of **4** were also measured in water solution, using the same concentration of the absorption one and two different λ of excitation, namely 225 and 275 nm, and they are characterized by multiple emission bands in the visible region, whose intensity depends on the λ_{exc} . In the spectrum obtained using $\lambda_{\text{exc}} = 225$ nm (Figure 2a), a very sharp peak with a maximum at $\lambda = 455$ nm can be seen, together with a peak of very modest intensity having a maximum at $\lambda = 494$ nm and another weak and large band between 500 and 645 nm. As for the spectrum corresponding to $\lambda_{\text{exc}} = 275$ nm (Figure 2b), besides showing a very weak band centered at about 395 nm, it is characterized by an intense convoluted band between 475 and 675 nm: it presents a sharp peak at $\lambda = 544$ nm, and another weaker peak can be identified with a maximum for $\lambda = 597$ nm.

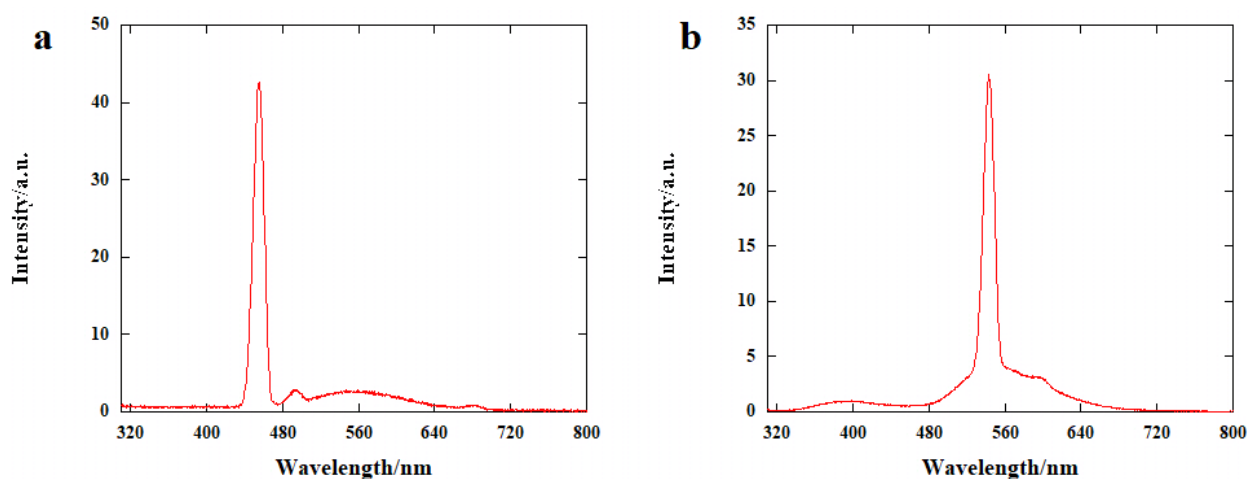


Figure 2. Fluorescence spectra (H_2O , $c = 2.5 \times 10^{-4}$ M) of **4**, with (a) $\lambda_{\text{exc}} = 225$ nm and (b) 275 nm.

3. Materials and Methods

All the reagents were purchased from Merck and TCI and used as received unless otherwise stated. Dry solvents were distilled according to standard procedures: tetrahydrofuran was distilled over Na/benzophenone, triethylamine and diisopropylamine were distilled over KOH, and dichloromethane was distilled over P_2O_5 . Reactions and chromatographic separations were monitored by thin layer chromatography (TLC) on 0.25 mm silica gel plates (Merck Kieselgel 60 F254) and revealed under a UV lamp ($\lambda = 254$ nm). Column chromatography was carried out on silica gel Merck-Kieselgel 60 (0.063–0.20 mm, 70–230 mesh) as a stationary phase.

^1H and ^{13}C -NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using 5 mm tubes and chloroform- d (CDCl_3) and dimethyl sulfoxide- d_6 ($\text{DMSO}-d_6$) as solvents. Spectral data of compounds **1** and **2** are in agreement with literature ones [22].

The UV-Vis spectrum was acquired with a Shimadzu (Japan) UV2600 UV-vis spectrophotometer, while fluorescence spectra were measured on a Cary Eclipse (Varian) spectrofluorometer using SUPRASIL quartz cells (10×10 mm).

Synthesis of 5,5'-bis(trimethylsilyl)ethynyl-2,2'-bithiophene (1): In a flame-dried Schlenk tube under argon atmosphere, 4 mL of a degassed and anhydrous 7:3 toluene/ $i\text{-Pr}_2\text{NH}$ mixture are introduced, followed by 400 mg (0.957 mmol) of 5,5'-diiodo-2,2'-bithiophene. Then, 55 mg (0.048 mmol) of $\text{Pd}(\text{PPh}_3)_4$, 18 mg (0.096 mmol) of CuI and 0.32 mL (2.31 mmol) of trimethylsilylacetylene are added, and the mixture is stirred for 24 h at room temperature. After that, the solvents are evaporated under vacuum, and the residue is purified by column chromatography in hexane in order to afford 350 mg (0.956 mmol) of pure **1** (99%) as a yellow solid. ^1H -NMR (CDCl_3 , 400 MHz) δ 7.13 (d, 2H, $J = 3.8$ Hz), 7.02 (d, 2H, $J = 3.8$ Hz), 0.28 (s, 18H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 138.0, 133.5, 123.8, 122.5, 100.5, 97.2, -0.2 .

Synthesis of 5,5'-diethynyl-2,2'-bithiophene (2): In a flame-dried round-bottom flask under argon atmosphere, 350 mg (0.956 mmol) of **1** are dissolved in 5 mL of anhydrous THF, and a solution of 325 mg (5.8 mmol) of anhydrous KOH in 2.5 mL of CH_3OH is added; the reaction mixture is stirred at room temperature overnight; then, CHCl_3 is added, and the solution is extracted with water (2×10 mL) and brine (2×10 mL). The organic phase is dried over anhydrous Na_2SO_4 and concentrated under vacuum, after which the crude product is purified by column chromatography in hexane, affording 183 mg (0.854 mmol) of pure **2** as a pale brown solid (89%). ^1H -NMR (CDCl_3 , 400 MHz) δ 7.19 (d, 2H, $J = 3.8$ Hz), 7.05 (d, 2H, $J = 3.8$ Hz), 3.44 (s, 2H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ 138.1, 134.0, 123.9, 121.5, 82.7, 76.7.

Synthesis of 5,5'-bis(pyridin-4-ylethynyl)-2,2'-bithiophene (3): In a flame-dried Schlenk tube under argon atmosphere, 183 mg (0.854 mmol) of **2** are dissolved in 10 mL of a degassed and anhydrous 1:1 THF/ Et_3N mixture; then, 120 mg (0.171 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 16 mg (0.086 mmol) of CuI and 528 mg (2.59 mmol) of 4-iodopyridine are added. The mixture is

stirred for 24 h at 60 °C, after which it is cooled, washed with a saturated NH₄Cl solution, and the aqueous phase is washed with ethyl acetate (5 × 15 mL). The combined organic phases are dried over anhydrous Na₂SO₄ and concentrated under vacuum; then, the crude product is purified by column chromatography (1:1 → 2:8 hexane/ethyl acetate) in order to afford 214 mg (0.581 mmol) of pure **3** as a yellow solid (68%). ¹H-NMR (CDCl₃, 400 MHz) δ 8.65 (m, 4H), 7.38 (m, 4H), 7.28 (d, 2H, J = 4.4 Hz), 7.15 (d, 2H, J = 4.4 Hz); ¹³C-NMR (CDCl₃, 100 MHz) δ 149.8, 139.1, 134.3, 130.8, 125.2, 124.5, 121.6, 92.1, 87.0.

Synthesis of 4,4'-(2,2'-bithiophene)-5,5'-diylbis(ethyne-2,1-diyl)bis(1-methyl-1-pyridinium) diiodide (4): In a flame-dried Schlenk tube, 214 mg (0.581 mmol) of **3** are dissolved in 15 mL of anhydrous CH₂Cl₂, and 2.5 mL (40.0 mmol) of CH₃I are added under argon atmosphere. The mixture is stirred at 40 °C for 24 h, after which it is cooled to room temperature and filtered under vacuum; the solid is washed with portions of CH₂Cl₂ and dried for 1 h under suction in order to yield 316 mg (0.484 mmol) of pure **4** as a dark orange solid (83%). ¹H-NMR (DMSO-*d*₆, 400 MHz, Figure S1) δ 9.00 (m, 4H), 8.25 (m, 4H), 7.76 (d, 2H, J = 3.9 Hz), 7.67 (d, 2H, J = 3.9 Hz), 4.33 (s, 6H); ¹³C-NMR (DMSO-*d*₆, 100 MHz, Figure S2) δ 146.0, 140.9, 138.6, 138.0, 128.8, 127.6, 119.9, 95.4, 91.9, 48.3.

4. Conclusions

A new bithiophene-containing extended viologen with acetylene moieties has been synthesized in four steps, with a total yield of 50%, and its light absorption and emission in H₂O solution have been studied by UV-visible absorption and fluorescence spectroscopy. They show intense and composite absorbance and emission bands, especially in the visible range; this compound thus exhibits potential as a candidate in fluorescence-related applications.

Supplementary Materials: ¹H (Figure S1) and ¹³C NMR (Figure S2) spectra of the title compound can be downloaded.

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