

3,4-Vinylenedioxythiophene (VDOT): a new building block for thiophene-based π -conjugated systems†

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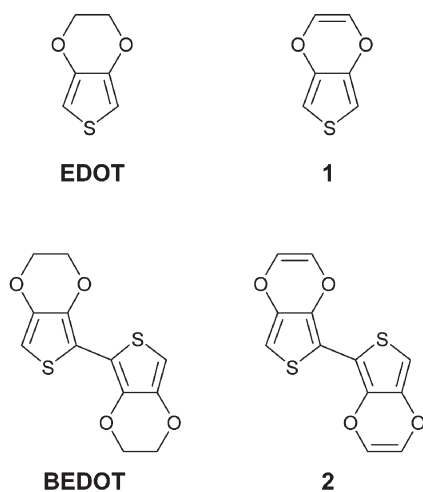
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The synthesis of the title compound and its use as a building block in π -conjugated systems are presented.

The last decade has witnessed the emergence of 3,4-ethylenedioxythiophene (EDOT) in the forefront of the chemistry of linear π -conjugated systems.^{1–8}

A combination of conductivity, optical transparency and stability has given rise to the development of multiple applications in the fields of anti-static coatings, electrolytic capacitors, or pre-treatment of the indium-tin oxide transparent electrodes used for the fabrication of (opto)electronic devices such as light-emitting diodes and solar cells.¹

At the molecular level, the strong electron-donating ether groups at the 3 and 4 positions of the thiophene ring lead at the same time to i) the prevention of linkage defects during polymerization, ii) an enhancement of the reactivity of the coupling α -positions and iii) the self-rigidification of the π -conjugated chain by non-covalent intramolecular sulfur–oxygen interactions.^{2,3}

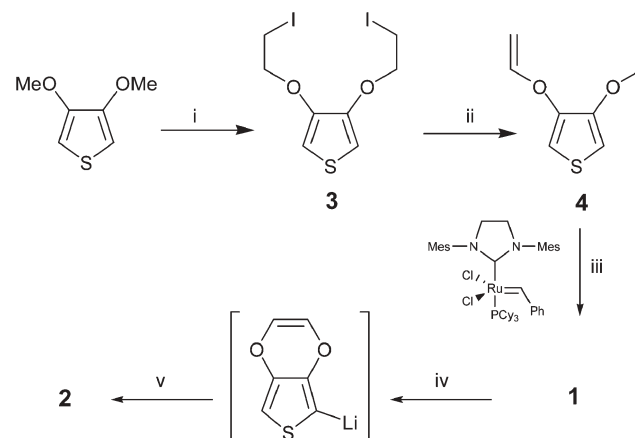


This unique conjunction of properties has given rise to a rich synthetic chemistry aiming at the development of new functional conducting polymers,^{2–7} and of various classes of molecular conjugated systems such as fluorophores, NLO-phores, tetrathiafulvalene analogues and oligomers.^{3,8}

Parallel to this wide use of the EDOT building block in molecular and polymeric functional π -conjugated systems,^{2,3} the development of new molecules or materials with original properties has been pursued by a different approach involving the modification of the chemical structure of the EDOT system itself.^{3–7} Examples of such work involve the lengthening of the alkylene bridge,^{2,4} the substitution of sulfur by selenium,⁵ or the replacement of one of the ether groups by a sulfide one.⁶ In this context we have recently reported the synthesis of 3,4-phenylenedioxythiophene (PheDOT) as a possible platform for the synthesis of planar soluble poly(EDOT) analogs.⁷

As a further step, we now report the synthesis of 3,4-vinylenedioxythiophene (VDOT) **1** in which the ethylene bridge of EDOT has been replaced by a vinyleno one.⁹ The dimer **2** has also been synthesized as a model compound and its structure analyzed by X-ray diffraction.

The synthesis of VDOT is shown in Scheme 1. Transesterification of 3,4-dimethoxythiophene by 2-iodoethanol in the presence of *p*-toluenesulfonic acid led to 3,4-diiodoethoxythiophene **3** in 82% yield. Elimination of HI by reaction of **3** with *t*-BuOK in refluxing *t*-BuOH afforded the vinyl ether derivative **4** in 84% yield. Attempts to perform intramolecular metathesis using the 1st generation Grubbs catalyst failed leaving unreacted compound **4**. However, the use of the 2nd generation Grubbs catalyst led to compound **1** in 80% yield.^{10,11} The dimer **2** was prepared in 74% yield by oxidative coupling of the lithiated derivative of **1** in the presence of CuCl₂.†



Scheme 1 Reagents and conditions: i) 2-iodoethanol, PTSA, toluene, reflux; ii) *t*-BuOK, *t*-BuOH, reflux; iii) 2.5% mol. 2nd generation Grubbs catalyst, toluene, reflux; iv) *n*-BuLi, THF, -70 °C; v) CuCl₂.

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† Electronic supplementary information (ESI) available: Spectroscopic data of **3–4**, X-ray data for **2**, CV of poly(**2**) and theoretical calculations. See DOI: 10.1039/b513923f

Fig. 1 shows the structure of a single crystal of BVDOT **2** determined by X-ray diffraction. The π -conjugated system adopts a planar conformation allowing optimal π -electron delocalization. Thus, whereas for EDOT the ethylene chain induces a distortion of the bridge,¹² the fully planar structure of **2** leads to a herringbone packing mode with uniform stacks along the b axis and short intermolecular distances (~ 3.44 Å, see ESI). The two thiophene rings adopt an *anti* conformation with non-bonded S–O distances of 2.95 Å. This distance which is smaller than the sum of the van der Waals radii of the oxygen and sulfur atoms (3.25 Å) is indicative of non covalent intramolecular interactions which help to self-rigidify the conjugated structure, as already observed for many EDOT-containing conjugated systems.³

It is noteworthy that the S–O distance observed for **2** is slightly larger than that generally observed for EDOT-based systems, e.g. 2.92 Å for BEDOT.¹² This difference can be ascribed to a contraction of the six-membered ring associated with the change from an sp^3 to an sp^2 hybridization of the bridging carbons in **1**.

The UV-visible spectrum of compound **2** exhibits a broad band with λ_{\max} at 309 nm and two shoulders at 298 and 325 nm (Fig. 2). Comparison with the spectrum of BEDOT reveals a considerable loss of the resolution of the vibronic fine structure. This phenomenon and the concomitant 11 nm blue shift of λ_{\max} compared to BEDOT can be attributed to the simultaneous decrease of the electron releasing mesomeric effect of the oxygen

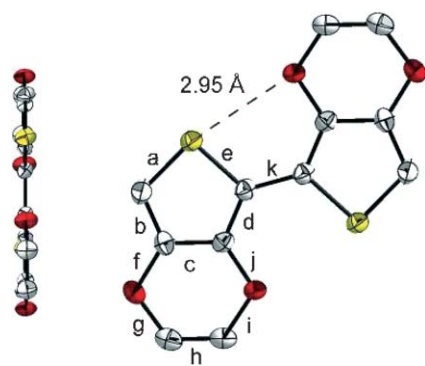


Fig. 1 ORTEP view of **2**.

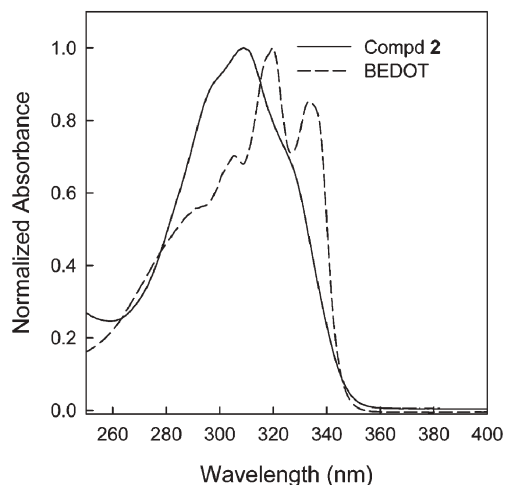


Fig. 2 Normalized UV-vis spectra of **2** and BEDOT in CH_2Cl_2 .

atoms towards the bithiophenic π -conjugated system, and of the self-rigidification by non-covalent S–O interactions. The former point is consistent with the lengthening of bonds f and j and the shortening of bonds g and i in the structure of compound **2** compared to BEDOT (see ESI).¹²

Optimization of the geometry of compounds **1** and **2** (Density Functional Theory at the B3LYP/6-31G* level) has been performed using Gaussian 98. As expected, both molecules **1** and **2** are perfectly planar and the latter exhibits short S–O distances (2.96 Å) in agreement with crystallographic results. The energy of the HOMO, LUMO levels of **1**, **2**, EDOT and BEDOT and their difference are listed in Table 1.

The HOMO level of **1** (-5.34 eV) is higher than that of EDOT (-5.80 eV) due to the effective contribution of the electron-rich vinylene bridge to the HOMO orbital. Comparison of the two dimers reveals the reverse effect since the HOMO level of **2** is lower than that of BEDOT by 0.36 eV. On the other hand, the LUMO level of **2** is lower than that of BEDOT which explains the very close values of the HOMO–LUMO gaps calculated for the two molecules.

The cyclic voltammograms (CVs) of **1** and **2** show an irreversible oxidation peak at 1.38 V and 1.20 V, respectively (Table 1). Comparison with EDOT and BEDOT under the same conditions shows that compound **1** is a stronger electron-donor than EDOT while the reverse situation is found for the dimers in agreement with theoretical calculations.

All attempts to electropolymerize VDOT remained unsuccessful. This behaviour suggests that similarly to the PheDOT cation radical⁷ the density of unpaired electron at the linking positions is too low to ensure efficient polymerization. In contrast, application of recurrent potential scans with a positive limit set at the foot of the oxidation wave of BVDOT **2** led to the emergence of a new redox system at lower potential characteristic of straightforward electropolymerization (Fig. 3). The CV of poly(BVDOT) in a monomer-free electrolytic medium shows a quasi-reversible redox system with an anodic peak potential at 0.40 V (see ESI). This value, which is 0.31 V higher than that for poly(BEDOT),¹³ suggests that poly(BVDOT) has a higher ionization potential than poly(BEDOT) and that the neutral state should therefore be more stable in air. A scan towards negative potentials reveals an irreversible cathodic wave peaking at -1.80 V. The difference between the onset for oxidation and reduction gives a roughly estimated bandgap E_g of 1.70 eV.

Fig. 4 shows a set of electronic absorption spectra corresponding to a spectroelectrochemical analysis of a film of poly(BVDOT) on bulk platinum. The spectrum of the undoped polymer shows a λ_{\max} at 530 nm, while the low energy absorption edge at 740 nm leads to an E_g value of 1.67 eV comparable to that of

Table 1 CV data, HOMO, LUMO and HOMO–LUMO gap

	Epa (V) ^a	HOMO (eV) ^b	LUMO (eV) ^b	Gap (eV) ^b
EDOT	1.50	-5.80	-0.04	5.76
VDOT 1	1.38	-5.34	-0.24	5.10
BEDOT	0.90	-4.86	-0.80	4.06
BVDOT 2	1.20	-5.22	-1.13	4.09

^a V vs. Ag/AgCl, 1 mM in 0.10 M Bu_4NPF_6/CH_2Cl_2 , scan rate 100 mV/s, Pt working electrode. ^b Calculated by DFT method at B3LYP/6-31G* level of theory.

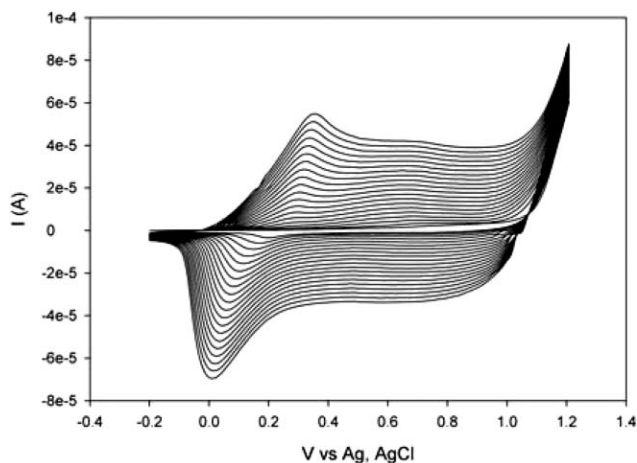


Fig. 3 Potentiodynamic electropolymerization of **2**, 10 mM in 0.10 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$, scan rate 50 mV s^{-1} .

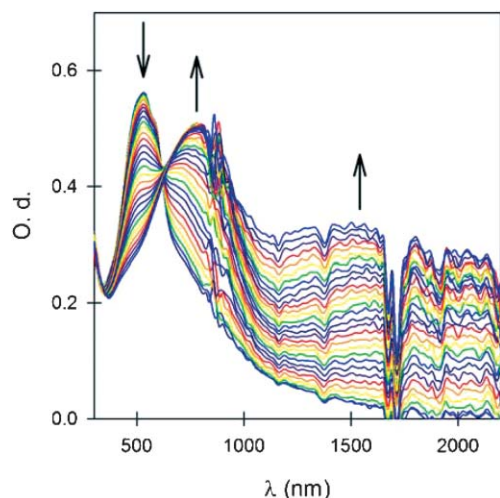


Fig. 4 Spectroelectrochemistry of poly(**2**) in 0.10 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ – Applied voltages from -0.1 to 1.2 V .

poly(BEDOT),¹³ Application of progressively higher potentials produces the bleaching of the visible absorption band and the emergence of two new transitions around 850 and 1500 nm characteristic of the polaron state. Similarly to poly(PheDOT),⁷ a further increase of the applied potential does not lead to the appearance of the characteristic bipolaron state transition.

To summarize, 3,4-vinylenedioxythiophene has been synthesized by ring-closing metathesis. The X-ray data for the dimer reveal a more compact crystal structure than that of BEDOT consistent

with stronger π -intermolecular interactions. This property associated with the higher oxidation potential of **2** and its polymer suggests that VDOT-based extended π -conjugated systems should exhibit a better environmental stability than their EDOT analogs.⁸ Work aiming at the synthesis of such VDOT-based oligomers is now in progress.

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Notes and references

‡ Spectroscopic data for **1–2**: **1**: colorless oil; $^1\text{H NMR}$ (CDCl_3): 6.27 (s, 2H), 5.93 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3): 139.3, 125.2, 101.2; EIMS calcd for $\text{C}_6\text{H}_4\text{O}_2\text{S}_2$: 139.99; found: 139.99. Anal. for $\text{C}_6\text{H}_4\text{O}_2\text{S}_2$. Found (Calcd): C, 51.41 (51.42); H, 2.95 (2.88); **2**: white solid; mp 214°C ; $^1\text{H NMR}$ (CDCl_3): 6.24 (s, 2H), 6.05 (d, $^3J = 3.8 \text{ Hz}$, 2H), 5.96 (d, $^3J = 3.6 \text{ Hz}$, 2H); $^{13}\text{C NMR}$ (CDCl_3): 138.5, 135.0, 125.4, 125.1, 109.9, 100.0; Maldi-tof MS calcd for $\text{C}_{12}\text{H}_6\text{O}_4\text{S}_2$: 277.99; found 277.98. Anal. for $\text{C}_{12}\text{H}_6\text{O}_4\text{S}_2$. Found (Calcd): C, 51.41 (51.79); H, 2.53 (2.17).

§ Crystal data for **2**: $\text{C}_6\text{H}_3\text{O}_2\text{S}$, $M = 139.14$, Monoclinic, $P21/n$, $a = 7.000(1) \text{ \AA}$, $b = 4.8894(6) \text{ \AA}$, $c = 15.815(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 94.88(2)^\circ$, $\gamma = 90^\circ$, $V = 539.32(93) \text{ \AA}^3$, $Z = 4$, $R1 = 0.0446$, $wR2$ (all data) = 0.0963. CCDC 285541. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513923f

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