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Synthesis and optical properties of some 3,4-(ethylenedioxythiophen-2-yl)-1,2,4-triazine derivatives

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ABSTRACT

A series of a hybrid oligomers with different combinations of thiophene, EDOT and 1,2,4-triazine rings have been synthesized and characterized. The synthesis of these alternated 1,2,4-triazine derivatives is reported using a straightforward palladium mediated Stille coupling reaction of 2-tri-*n*-butyltin-3,4-ethylenedioxythiophene with 3-methylsulfanyl-1,2,4-triazine. The molecular structure and the potential optoelectronic properties of the newly obtained compounds were characterized by UV–Vis absorption and emission spectra, X-ray analysis and theoretical calculations at the DFT level.

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1. Introduction

Thiophene-based π -conjugated oligomers¹ are subject to intensive work focused on their use as organic materials which find applications in different devices.² Oligothiophenes, due to their particular physical properties have received widespread attention as components of molecular electronic and optical devices.³ Although each type of device requires the optimization of specific properties such as absorption, emission spectrum, or luminescence efficiency, oxidation and reduction potential, in all cases the final output performance of the device strongly depends on the charge-transport efficiency of the active material. Most essential for this type of chain oligomer is the presence of a donor-acceptor system which is responsible for their π -conjugated system. Other thiophene oligomers explored as push-pull type systems employed the high electron donating character of the EDOT moiety which increases the HOMO energy level.⁴ Synthesis of EDOT incorporated oligothiophenes is well known.^{5,6} EDOT has been used as a building

block in several conjugated systems that incorporate unique properties such as electrochromic behavior, low band gap polymers and possess attractive properties, high stability, conductivity, transparency, as well as solubility in aqueous media. Several EDOT-based donor–acceptor conjugated polymers with small band gaps have been reported, including EDOT-pyridine,⁷ EDOT-thienopyrazine,^{8,9} and EDOT-benzothiadiazole,¹⁰ EDOT-benzimidazole,¹¹ EDOT-pyrrole.¹² The electronic properties of these donor–acceptor copolymers can be varied significantly by change the kind of the moieties. By inserting dialkoxybenzene group or fluorinated derivative in a separate study EDOT derivatives are excellent candidates for multicolor display applications. Incorporating viologen moieties or pendant groups appended along the backbone cause the redox state and the optical properties change too.¹³ A comprehensive understanding of the electronic structures and the electronic properties of these EDOT-based donor–acceptor alternating conjugated structures would help to further develop this and other classes of donor–acceptor copolymers for electronic applications.¹⁴

For this reason we focused our interest on the synthesis of EDOT-1,2,4-triazine derivatives which are not known to date. Currently, our publication is a continuation of our prior experience

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in the design of 1,2,4-triazine thienyl oligomers.¹⁵ Here we described the synthesis of a new series of EDOT-1,2,4-triazine oligomers in which the number and position of the EDOT group is changed. Furthermore, all donor groups were located at the inner position of the backbone oligomers. The structure and electronic properties of these various compounds were analyzed by X-ray methods, UV–Vis spectroscopy and theoretical calculations. The results are discussed with regard to the influence of the number and position of the EDOT group in the structure and electronic properties of the π -conjugated system.

2. Results and discussion

2.1. Synthesis

All oligomers were constructed from 3-methylsulfanyl-1,2,4-triazine **1** and the appropriate organic tin derivatives. The synthesis is presented in Scheme 1. EDOT is converted to monostannyl derivative **2** by treating 3,4-ethylenedioxythiophene with *n*-BuLi and then *n*-Bu₃SnCl. This stannyl compound was then subjected to Stille coupling between 3-methylsulfanyl-1,2,4-triazine with Pd(PPh₃)₄ as catalyst and CuBr·Me₂S as cofactor which is used to polarize the Pd–S bond in the rate-determining transmetalation step.¹⁶ 3-(3,4-Ethylenedioxythiophen-2-yl)-1,2,4-triazine (**3**) was treated with *N*-bromosuccinimide (NBS) to afford bromo derivative **4**. This main starting compound was reacted with hexa-*n*-dibutyltin to give dimer **5**. Reaction of 3-(7-bromo-3,4-ethylenedioxythiophen-2-yl)-1,2,4-triazine (**4**) in the next step with 2,5-dibutylstannyl-thiophene resulted in pentamer **6** with the thiophene ring in the centre. Tetramer **5** and pentamer **6** had very low solubility and for this reason electrochemical study of prepared oligomers could not be conducted.

2.2. X-ray analysis

In order to confirm the synthesis and proposed molecular structures of the investigated compounds, X-ray analysis of **3** as the model compound was performed. The structure and conformation

of the molecule **3** in the crystal is shown in Fig. 1.

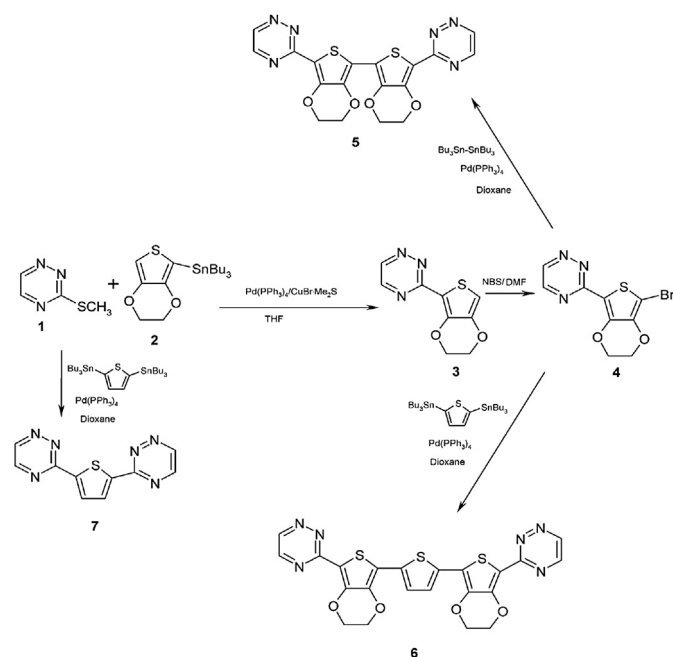
In the 3,4-ethylenedioxythiophene fused ring system the thiophene ring is planar to within 0.004(2) Å. The six-membered partially saturated dioxane ring is nonplanar and it adopts an intermediate conformation between a half-chair and sofa. This conformation is confirmed by the asymmetry parameters $\Delta C_2^{11,12} = 7.6(3)^\circ$, corresponding to the 2-fold axis symmetry bisecting bonds C11–C12, and $\Delta C_5^{12} = 15.7(3)^\circ$, corresponding to the mirror plane passing through C12 and C15 atoms.¹⁷ The 1,2,4-triazine ring is planar to within 0.007(3) Å and has the geometry typical for the π -electron system. The torsion angle N4–C3–C7–S8 of 6.0(3)° shows the *cis* position of the S8 atom of the thiophene ring with respect to the N4 atom of 1,2,4-triazine system.

In the crystal structure of **3** (Fig. 2), molecules form a three-dimensional network via weak intermolecular C–H ... X (X = N, O) hydrogen bonds. The inversion related molecules form molecular dimers through a pair of intermolecular C12–H122...N2ⁱ hydrogen bonds [C12–H122 = 0.97, H122...N2 = 2.43, C12...N2 = 3.362(3) Å, C12–H122...N2 = 162° and *i* = 1–x, 1–y, –z]. These molecular dimers related by *a* translation and *c*-glide planes are linked into molecular chains in the directions [100] and [010] using intermolecular C11–H111...O10ⁱⁱ and C9–H9...N1ⁱⁱⁱ hydrogen bonds, respectively [C11–H111 = 0.97, H111...O10 = 2.53, C11...O2 = 3.454(4) Å, C11–H111...O10 = 158° and *ii* = 1 + x, y, z; C9–H9 = 0.93, H9...N1 = 2.58, C9...N9 = 3.497(3) Å, C9–H9...N1 = 168° and *iii* = –1 + x, 1/2 – y, 1/2 + z]. Additionally, the thiophene rings of the 3,4-ethylenedioxythiophene system belonging to the translation-related molecules overlap each other and form molecular stacks in [100] direction, with centroid-to-centroid separation of 3.9062(14) and 3.9060(14) Å between the thiophene ring at (x, y, z) position and the translation-related thiophene ring at (–1 + x, y, z) and (1 + x, y, z) positions, respectively. The respective π – π distances of 3.5946(10) and 3.5947(10) Å are close to van der Waals distance of about 3.4 Å for the overlapping π -aromatic ring systems.

2.3. Spectroscopy

UV–Vis absorption spectra recorded for compounds **3**, **5**–**7** are shown in Fig. 3. Electronic absorption and fluorescence emission spectra of the oligomers were investigated in dichloromethane, and the results are listed in Table 1.

The data for the bis-3,4-ethylenedioxythiophene-based 1,2,4-triazine ring end-capped tetramer **5** and pentamer **6** with the thiophene ring in the middle of the 3,4-ethylenedioxythiophene 1,2,4-triazine ring end-capped were compared (see Fig. 3). These oligomers have practically the same wavelength λ_{max} 450 nm, but the bands have different intensity. Again, the fluorescence emission spectra reveal a smaller Stokes shift for **6** than for **5**. On the other hand the thiophene ring in **6** does not influence the wavelength



Scheme 1. Synthesis of π -conjugated oligomers **5**–**7**.

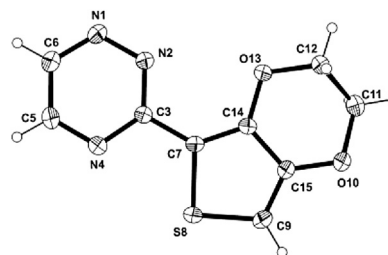


Fig. 1. A view of the X-ray molecular structure of **3** with atomic labelling and displacement ellipsoids (50% probability) of non-H atoms.

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