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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.

1. Introduction

Thiophene-based π-conjugated oligomers[1] 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.

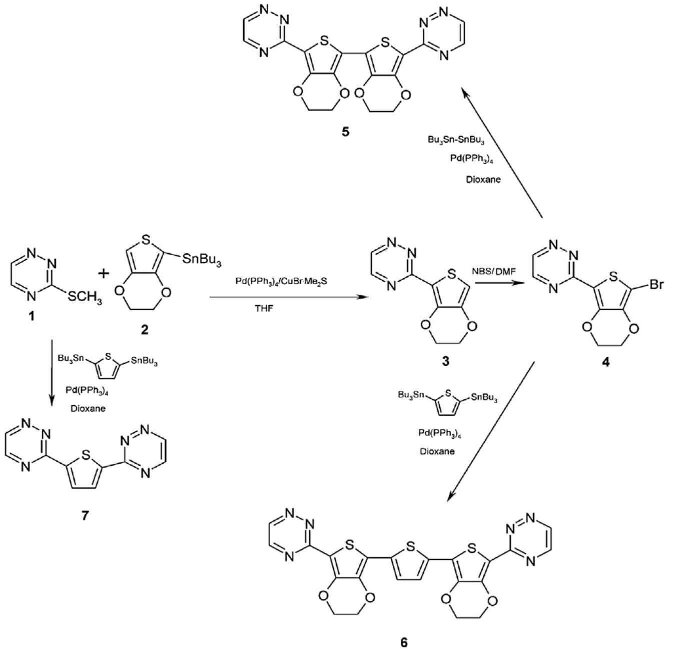
2. Results and discussion

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-ethylenedioxy-thiophene with *n*-BuLi and then *n*-Bu_3SnCl. This stannyl compound was then subjected to Stille coupling between 3-methylsulfanyl-1,2,4-triazine with $Pd(PPh_3)_4$ as catalyst and $CuBr\cdot Me_2S$ 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-ehylenedioxythiophen-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.



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

In the 3,4-ethylenedioxothiophene 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 parametersΔC_2[11,12] = 7.6(3)°, corresponding to the 2-fold axis symmetry bisecting bonds C11–C12, and ΔC_s[12] = 15.7(3)°, 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···N2^{i} 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 [101] using intermolecular C11–H111···O10^{ii} and C9–H9···N1^{iii} 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-ethylenedioxothiophene 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

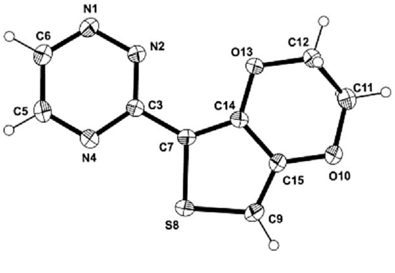


Fig. 1. A view of the X-ray molecular structure of **3** with atomic labelling and displacement ellipsoids (50% probability) of non-H atoms.

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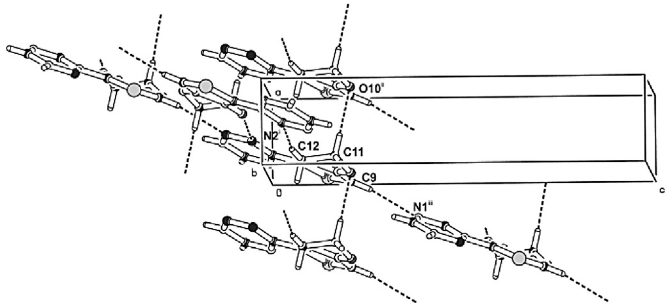

Fig. 2. The structural motif showing molecules connected by C–H ... X (X = N, O) hydrogen bonds in crystal of **3** (symmetry codes: *i* = 1−x, 1−y, −z; *ii* = 1 + x, y, z; *iii* = −1+x, 1/2−y, 1/2 + z).

emission spectra compared to **5** which is red shifted. Furthermore, the two EDOT units result in the emergence of a discernible fine structure due to a more rigid ground state geometry, similar to the effect observed by the Roncali group.[18] Comparing the UV–Vis absorption spectra of monomer **3** (302 nm) with 3-thiophen-2-yl-1,2,4-triazine (295 nm),[19] the presence of the EDOT ring only slightly increases the maximum absorption batochromically to lower energy.

UV–Vis spectra calculated using the time dependent-density functional theory (TD-DFT) method for the excited state of molecules **3**–**7** in the gaseous phase and dichloromethane solution are presented in Table 1. As can be seen from Table 1, there are three bands at 275, 416 and 441 nm for **5**, four bands at 284, 346, 452 and 475 nm for **6** and two bands at 335 and 390 nm for **7** in the experimental spectra of compounds **5**–**7**. Theoretically calculated spectra showed that there is one broad band observed at 443 for **5**, 496 for **6** and 355 nm for **7** in the gas phase. In dichloromethane solution these bands are shifted to 466, 524, and 361 nm for **5**, **6** and **7**, respectively. The calculated absorption wavelengths for **3**, **5**–**7** are similar to within 20 nm in gaseous phase and 49 nm in dichloromethane solution to those recorded experimentally, maintaining the relative position of the bands. The calculated maxima absorption correspond to the electron transition from HOMO(-1) to LUMO(+1) and HOMO to LUMO(+1) in **3** and **4** and HOMO to LUMO in **5**–**7**. The relatively large values of oscillator strengths, with the largest for **5** and **6**, can indicate the strong intensity of absorption bands. Moreover, one can see that the oscillator strengths are increased in dichloromethane solution.

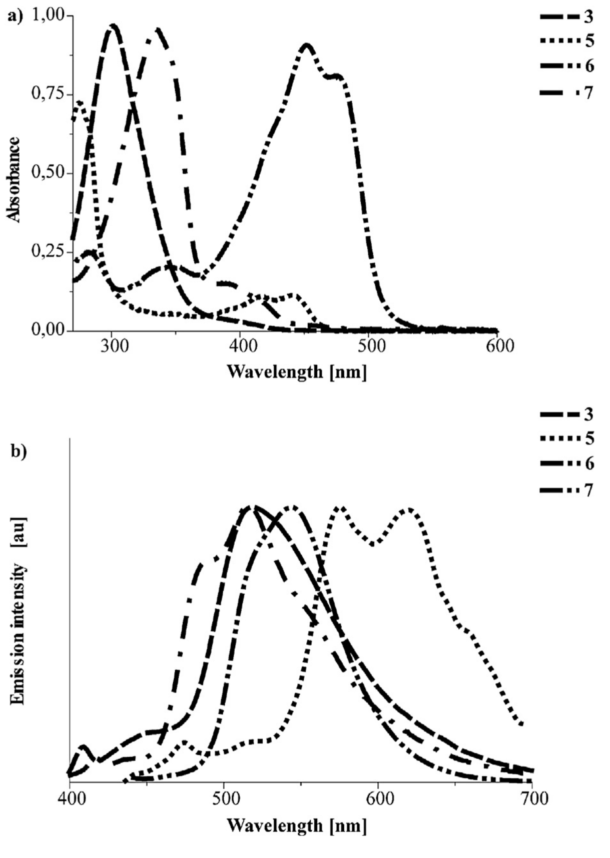

Fig. 3. Absorption a) and emission b) of obtained **3**, **5**–**7** oligomers detected in dichloromethane.

The optoelectronic properties of the investigated oligothiophenes are strictly connected with electronic parameters as frontier orbitals energy and the energy gap being a difference of energy of LUMO and HOMO orbitals. These electronic parameters were theoretically calculated at the DFT/B3LYP/311++G(d,p) level for compounds **3**–**7** in the conformation of the molecules corresponding to the minimum energy (Fig. 4). The theoretically calculated minimum energy conformation for **3,** with a *trans* position of the S8 atom of the thiophene ring with respect to the N4 atom of 1,2,4-triazine system is different from that observed in the crystal. However, the energy difference between these conformations of 0.20 kcal/mol gives the possibility of coexistence of both conformers in 59:41 ratios in the gaseous phase at room temperature calculated using non-degenerated Boltzmann distribution. In the planar tetrameric molecule of **5** the two EDOT units are in the *trans* position relative to each other with the short intramolecular S···O interactions (S···O distance of 2.91 Å smaller than sum of the van der Waals radii of S and O atoms of 3.32 Å) stabilizing this conformation. Similar interactions are observed also in the pentameric planar structure of **6**, where two O atoms of different EDOT units interact with S atom of the central thiophene ring (S···O distances are 2.96 Å). In **7** the 1,2,4-triazine rings are in the opposite position in relation to the S atom of the thiophene ring.

Calculated surfaces of the frontier HOMO and LUMO orbitals, their energies and energy gaps are shown in Fig. 5. The HOMO and LUMO orbitals are concentrated practically on whole molecules of thiophene and 1,2,4-triazine as model compounds. Similar distribution of HOMO and LUMO orbitals is observed in **7** containing only thiophene and triazine rings. In the molecules of EDOT and other compounds **3**–**6** with EDOT units, only methylene CH$_2$ groups of the 3,4-ethylenedioxy ring from EDOT unit do not give contribution to the frontier HOMO and LUMO orbitals. It is noteworthy, that in molecules **5**, **6** and **7** having symmetrical structures, the same symmetry of frontier orbitals is maintained both in the shape and sign of the respective wave function.

The lowest value of energy gap of 2.72 eV is observed for compound **6**. The energy gap decreases with increasing the number of EDOT units from 4.09 eV for **3** and 3.95 eV for **4** with one EDOT unit, through 3.00 eV for **5** to 2.72 eV for **6** with two units and an additional thiophene ring in **6**. Decreasing of on the energy gap is mainly connected with the decreasing of energy of the LUMO orbital within the series of **3**–**6**. One can see that the bromination of the EDOT system in **4** does not significantly affect the energy gap in relation to **3**. Moreover, the lack of 3,4-ethylenedioxy unit in **7** gives a lower energy gap in compares to those observed in **3** and **4** and a greater energy gap in relation to that in **6** with the single thipohene ring and two EDOT units. The energy gap for the frontier orbitals calculated for compounds **3**–**7** are compared with those calculated for model 1,2,4-triazine, thiophene and EDOT molecules (Fig. 5). It is apparent that the incorporation of 1,2,4-triazine and thiophene

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Table 1
The experimental and calculated optical properties of compounds **3**–**7**.

Comp.	Experimental				The calculated with TD-DFT/B3LYP/6-311G++(d,p) in Vacuum/CH_2Cl_2			
	Λ^{em}_{max}[a] [nm]	Φ_{em}[b] [%]	Λ^{abs}_{max}[c] [nm]	E[d] [mol^{-1} cm^{-1}]	Λ^{abs}_{max}[e] [nm]	Energy [eV]	Osc. Strength (*f*)	Transition
3	519	3.41	302	2436	307/316	4.04/3.92	0.466/0.531	HOMO(-1)→LUMO(+1); HOMO→LUMO(+1)
4	–	–	–	–	314/319	3.95/3.88	0.258/0.246	HOMO(-1)→LUMO(+1)
					330/338	3.76/3.67	0.308/0.421	HOMO→LUMO(+1)
5	575, 619	1.97	275	6029	443/466	2.80/2.66	1.106/1.288	HOMO→LUMO
			416	853				
			441	882				
6	544	2.00	284	2490	496/524	2.50/2.37	1.546/1.723	HOMO→LUMO
			346	2020				
			452	9070				
			475	8070				
7	492sh, 516	0.24	335	1838	355/361	3.49/3.43	0.362/0.724	HOMO→LUMO
			390	290				

[a] Experimental emission maximum.
[b] Fluorescence yield.
[c] Experimental absorption maximum.
[d] Molar absorptivity.
[e] Calculated absorption maximum.

rings into the EDOT system significantly reduces the energy gap for the compounds **3**–**7** in comparison to those observed for the starting systems, making the final compounds as materials with interesting optoelectronic properties. The energy gap depends on the electric structure getting the band gap larger for azine derivatives. This correlation is observed for pyrrole derivatives with energy gaps around 2.68 eV[20] and they range from 1.94 eV to 3.07 eV for azines and polyazines.[21] Thus these kinds of compounds are not promising as organic conductors, and are proposed as light-emitting diodes.

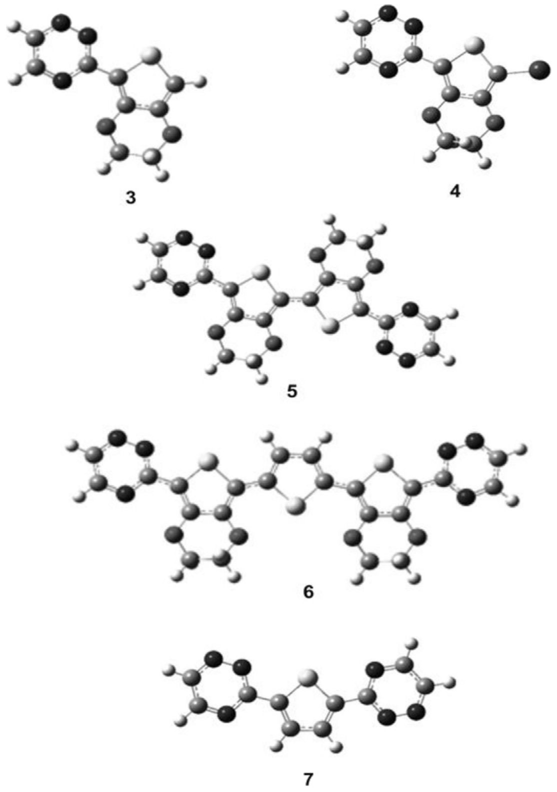

Fig. 4. A view of molecules **3**–**7** in conformation corresponding to the minimum energy calculated at the DFT/B3LYP/311++G(d,p) level.

Fluorescence lifetimes of compounds **3**, **5**, **6**, and **7** have been measured in dichloromethane at the corresponding maxima of the stationary emission spectra (see Table 2). The decays have bi-exponential character although the shorter time component (τ_1) is dominant in all cases (amplitudes of 90–99%). Thus, it is assigned to the lifetime of these compounds in their dominant form in solution. The values of τ_1 are relatively short, being 0.4, 0.2, and 0.3 ns for **3**, **5**, and **7**, respectively. Such short values correspond well with generally low fluorescence quantum yields of these compounds (Φ_{em} in Table 1). The shortest lifetime of $\leq$0.1 ns was obtained for **6**. In this case, the decay practically follows the temporal resolution of our experimental system, thus only the upper limit for τ_1 value can be determined. This compound has five subunits interconnected by formally single –C–C– bonds, making it very floppy. This may open some non-radiative channels of deactivation, shortening the observed fluorescence lifetime. The longer time components (τ_2) have values of 2.5, 1.2, 1.1, and 3.3 ns, for **3**, **5**, **6**, and **7**, respectively. Their contributions in the fluorescence decays are much smaller (1–10%). We suggest that these lifetimes can be due to some rotamers possibly existing in the solution, but we cannot completely exclude a minor population of *N*-protonated forms. More detailed spectroscopic studies are planned to verify these suggestions.

3. Conclusions

Various hybrid oligomers based on the different combination of 1,2,4-triazine, thiophene and EDOT rings have been synthesized and characterized. The X-ray analysis of **3** as the model compound confirmed the synthesis pathway and the molecular structures of the investigated compounds. The conformational analysis performed at DFT/B3LYP/311++G(d,p) level showed that the self-rigidifying effect is associated with noncovalent intramolecular S ⋯ O interactions observed for the tetrameric and pentameric model systems stabilizing their planar conformation. The UV–Vis spectroscopic analysis and theoretical calculations showed that incorporation of 1,2,4-triazine and thiophene rings to the EDOT system significantly reduces the energy gap for the compounds **3**–**7** making these compounds materials with interesting optoelectronic properties.

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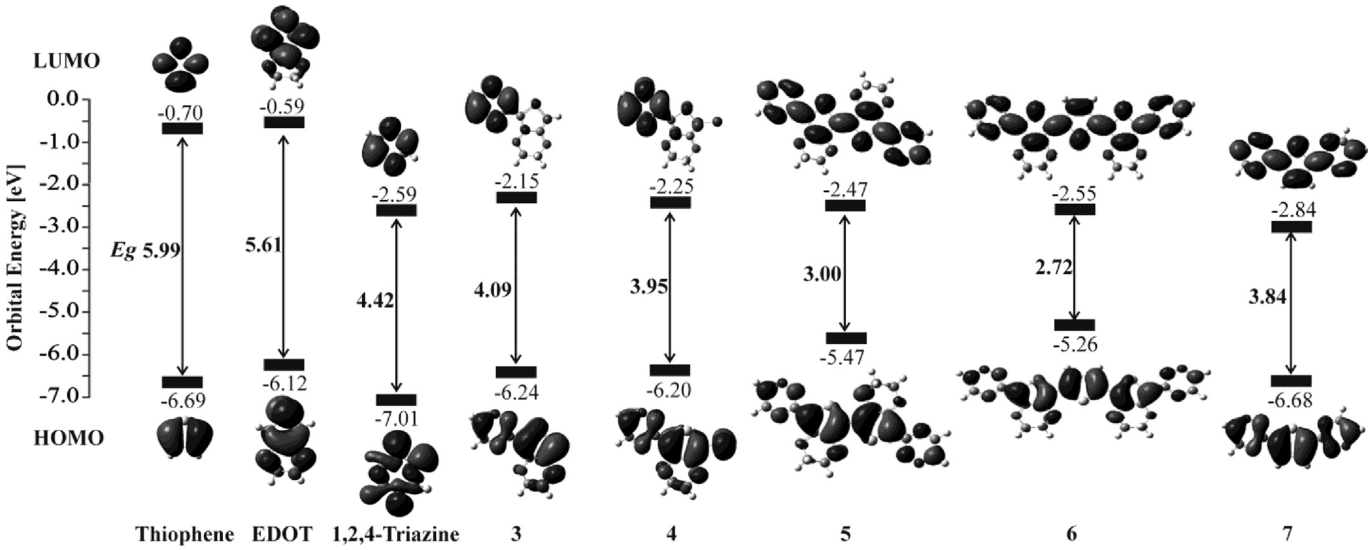

Fig. 5. Schematic drawings of the HOMO and LUMO orbitals of thiophene, EDOT and compounds **3**–**7**, calculated using the DFT/B3LYP/6-311++G(d,p) method.

Table 2
The experimental lifetime of compounds **3**, **5**–**7**.

Compound	Λ^{em} [nm]	τ_1 [ns]	Amplitude [%]	τ_2 [ns]	Amplitude [%]
3	510	0.4	93	2.5	7
5	580	0.2	90	1.2	10
6	530	≤0.1[a]	98	1.1	2
7	510	0.3	99	3.3	1

[a] Upper limit determined by temporal resolution of the experimental setup.

3.1. General methods

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were determined at 400 and 100 MHz respectively on a Varian Gemini spectrometer. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. Mass spectra were obtained using AMD 604 (AMD Intectra GmbH, Germany) and GC/MS QP 5050 Shimadzu (30 m × 0.25 mm ID-BPX 5 0.25 mm) spectrometers. Thin layer chromatography (TLC) was carried out on aluminium sheets percolated with silica gel 60 F_{254} (Merck). Column chromatography separations were performed using Merck Kieselgel 60 (0.040–0.060 mm). Solvents were dried and distilled according to standard procedures. All reagents were purchased from Aldrich and used as received.

3.1.1. Synthesis of 3-(3,4-ethylenedioxothiophen-2-yl)-1,2,4-triazine (*3*)

To a round bottom flask were added 3-methylsulfanyl-1,2,4-triazine (**1**) (0.30 g, 2.39 mmol) in THF (20 ml). To the mixture was added $Me_2S\cdot CuBr$ (1.21 g, 5.79 mmol) and 2-tri(*n*-butyl)tin-3,4-ethylenodioxythiophene (**2**) (0.65 g, 6.22 mmol) and $Pd(PPh_3)_4$ (0.14 g, 5 mol %). The mixture was refluxed under argon for 24 h, then the solvent was evaporated under vacuum. To the residue hexane was added and the precipitate was filtered. The precipitate was dissolved in AcOEt and extracted with brine. Organic layers were dried under $MgSO_4$. The solvent was evaporated and crude product was purified by column chromatography using silica gel and dichloromethane:acetone (100:1) to give 0.38 g (71%) **3** as orange crystals, mp 167–168 °C. IR (KBr) cm^{-1}: 1053, 1071, 1454, 3085. ^{1}H NMR ($CDCl_3$) δ ppm: 4.28 (br s, 2H, -OCH_2), 4.45 (br s, 2H, -OCH_2), 6.64 (s, 1H, CH), 8.58 (br s, 1H, CH), 9.01 (br s, 1H, CH). ^{13}C NMR ($CDCl_3$) δ ppm: 64.14, 65.45, 106.07, 113.47, 142.45, 144.10, 145.86, 148.26, 161.66. HR ESI $(M+H)^+$ $C_9H_8N_3SO_2$ calcd 222.03317, found 222.03333.

3.1.2. Synthesis of 3-(7-bromo-3,4-ethylenedioxythiophen-2-yl)-1,2,4-triazine (*4*)

To a round bottom flask 3-(3,4-ethylenedioxythiophen-2-yl)-1,2,4-triazine (**3**) (0.70 g, 3.19 mmol) in anhydrous DMF (10 ml) and NBS (0.58 g, 3.19 mmol) were added. The mixture was stirred for 24 h at room temperature. The reaction was monitored on TLC until disappearance of the substrate. To the reaction mixture ice water was poured into. The precipitate was filtered then on silica gel using dichloromethane to give yellow crystals 0.48 g (51%) (**4**) mp 191–192 °C. IR (KBr) cm^{-1}: 1054, 1082, 1521, 3088. ^{1}HNMR ($CDCl_3$) δ ppm: 4.37 (dt, *$J_1 = 2.4$ Hz*, *$J_2 = 4.0$ Hz*, 2H, -OCH_2), (dt, *$J_1 = 2.4$ Hz*, *$J_2 = 4.0$ Hz*, 2H, -OCH_2), 8.52 (d, *$J = 2.0$ Hz*, 1H, CH), 8.98 (d, *$J = 2.0$ Hz*, 1H, CH). ^{13}C NMR ($CDCl_3$) δ ppm: 64.62, 65.41, 95.61, 113.64, 140.83, 143.42, 145.87, 148.27, 161.18. HR ESI $(M+H)^+$ $C_9H_7N_3O_2S_1Br$ calcd 301.94164, found 301.94126.

3.1.3. Synthesis of 7,7′-bis-1,2,4-triazin-3-yl-2,2′- 3,4-ethylenedioxythiophene (*5*)

To a round bottom flask 3-(7-bromo-3,4-ethylenedioxythiophen-2-yl)-1,2,4-triazine (**4**) (0.30 g, 1.00 mmol) was added in anhydrous dioxane (18 ml). After 5 min hexa-*n*-butylditin (0.37 g, 0.71 mmol) and$Pd(PPh_3)_4$ (0.02 g, 1.8 mol %) were added. The reaction mixture was refluxed under argon for 24 h. The solvent was evaporated and the crude product was crystallized from DMF to give orange crystals 0.11 g (50%) (**5**) mp > 400 °C. IR (KBr) cm^{-1}: 1032, 1074, 1517, 3076. ^{1}H NMR (CF_3COOH, C_6D_6) δ ppm: 4.32–4.34 (m, 4H, -OCH_2), 4.43–4.45 (m, 4H, -OCH_2), 8.38 (d, *J = 2.0 Hz*, 2H, CH), 8.59 (d, *J = 2.0 Hz*, 2H, CH). ^{13}C NMR (CF_3COOH, C_6D_6) δ w ppm: 65.64, 67.69, 107.62, 126.60, 141.66, 144.24, 149.51, 155.62, 159.79. HR ESI $(M+H)^+$ $C_{18}H_{13}N_6$ O_4S_2 calcd 441.04342, found 441.045369.

3.1.4. Synthesis of 2,5-bis-(3,4-ethylenedioxythiophen-2-yl)-7,7′-1,2,4-triazin-3-yl-thiophene (*6*)

To a round bottom flask 3-(7-bromo-3,4-ethylenedioxythiophen-2-yl)-1,2,4-triazine (**4**) (0.30 g, 1.00 mmol) in anhydrous dioxane (18 ml) hexa-*n*-butylditin (0.43 g, 0.70 mmol) and $Pd(PPh_3)_4$ (0.12 g, 4.2 mol %) were added. The mixture was refluxed under argon for 24 h. The solvent was evaporated and the crude product was crystallized from DMF to give 0.22 g (83%) **6** as dark orange crystals mp > 350 °C. IR (KBr) cm^{-1}: 1055, 1081, 1523, 3076. ^1H NMR (CF_3COOH, C_6D_6) δ ppm: 4.47 (br s, 4H, -OCH_2), 4.61 (br s, 4H, -OCH_2), 7.60 (br s, 2H, CH), 8.58 (br s, 2H, CH), 8.92 (br s, 2H, CH). Very low solubility does not allow getting ^{13}C NMR data. IR (KBr) cm^{-1}: 3076, 1523, 1081 (C-O-C), 1055 (C-S-C). HR ESI $(M)^+$ $C_{22}H_{14}N_6O_4S_3$ calcd 522.02332, found 522.02344.

3.1.5. *Synthesis of 2,5-bis-1,2,4-triazin-3-yl-thiophene (**7**)*

To a round bottom flask 3-methylsulfanyl-1,2,4-triazine(0.3 g, 2.36 mmol) in THF (20 ml), $Me_2S\cdot CuBr$(1.09 g, 5.21 mmol), 3,5-bis-tri(n-butyl)tinthiophene (0.72 g, 1.16 mmol) and$Pd(PPh_3)_4$ (0.14 g, 5 mol%) ware added. The reaction mixture was refluxed under argon for 24 h. After this time the solvent was evaporated. Hexane was added and the precipitate filtered. The crude product was dissolved in EtOAc and washed with brine. Organic layer was dried under $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography using dichloromethane:acetone (5:1). Dark yellow crystals were obtained in 49% (0.14 g), mp 315–317 °C. IR (KBr) cm^{-1}: 980, 1050, 1385, 2985. ^1H NMR ($CDCl_3$) δ ppm: 8.26 (s, 2H, CH), 8.63 (d, $J = 2.4$ *Hz*, 2H, CH), 9.14 (d, $J = 2.4$ *Hz*, 2H, CH). Very low solubility does not allow getting ^{13}C NMR data. HR ESI $(M+H)^+$ $C_{10}H_7N_6S_1$ calcd 243.04474, found 243.04482.

3.2. *X-ray structure determinations*

X-ray data for **3** were collected on a Bruker SMART APEX II CCD diffractometer; crystal sizes 0.25 × 0.14 × 0.003 mm, CuKα ($\lambda = 1.54178$ Å) radiation, ω scans, $T = 293(2)$ K, absorption correction: multi-scan SADABS,[22] $T_{min}/T_{max} = 0.8479/1.000$. The structure was solved by direct methods using SHELXS-2013/1[23] and refined by full matrix least squares with SHELXL-2014/7.[23] The H atoms were positioned geometrically and treated as riding on their parent C atoms with C–H distances of 0.97 Å (CH_2) and 0.93 Å (aromatic). All H atoms were refined with isotropic displacement parameters taken as 1.5 times those of the respective parent atoms. The final refinement cycles gave an R value of 0.077. However, the analysis of Fo/Fc differences suggested that the crystal of **3** used in X-ray analysis can be twinned. The twin law was found using ROTAX (Version 26th November 2001[24]). The crystal is a two component twin with a ratio of 0.93:0.07, where the components are related by a 2-fold axis in [100] direction. The continuation of the process of refinement with the appropriate BASF and TWIN instructions of SHELXL gave the final R value of 0.037. All calculations were performed using WINGX version 2014.1 package.[25] CCDC-1481455 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

Crystal data for **3**: $C_9H_7N_3O_2S$, $M_r = 221.24$ $gmol^{-1}$, monoclinic, space group $P2_1/c$, $a = 3.9061(1)$, $b = 13.4957(3)$, $c = 17.3856(4)$ Å, $\beta = 90.189(2)°$, $V = 916.49(4)$ Å^3, $Z = 4$, $D_{calc} = 1.603$ gcm^{-3}, $F(000) = 456$, $\mu(\text{Cu } K\alpha) = 3.016$ mm^{-1}, $T = 293(2)$K, 5636 measured reflections (θ range 2.54–66.56°), 1598 unique reflections ($R_{int} = 0.035$) final $R = 0.037$, $wR = 0.096$, $S = 1.035$ for 1457 reflections with $I > 2\sigma(I)$, $\Delta\rho_{max} = +0.200$ and $\Delta\rho_{min} = -0.223$ eÅ^{-3}.

3.3. *Computational details*

The theoretical calculations were performed at the DFT/B3LYP/311++G(d,p)[26,27] level using the Gaussian 03 program.[28] The structures were fully optimized without any symmetry constraints and the initial geometries were built from the crystallographic data of **3**. The conformational analysis was performed for molecules of all investigated compounds **3**–**7**. The surfaces of the potential energy were searched in order to find local energy minima. The conformations of molecules **3**–**7** in the energy minima were checked using frequency calculations. Calculated energies were corrected for the zero-point energy (ZPE). UV–Vis spectra electronic transitions excitation absorbance and oscillator strength were performed in gas phase and dichloromethane solution (The Polarizable Continuum Model; PCM[29]) using TD-DFT method.[30] The visualization of theoretical calculation results was made using GaussView 4.1.[31]

3.4. *Fluorescence lifetime measurements*

Spectral quality dichloromethane (Merck) was used as purchased. The lifetimes were measured by means of the Time-Correlated Single Photon Counting (TCSPC) technique using home-build setup. It consists of TimeHarp 100 computer card (PicoQuant) for signal processing, sub-nanosecond pulsed LED (282 nm) and LD (375 nm) excitation sources with controller (PicoQuant), and CM110 single monochromator (Spectral Products) supported by glass filter GG400 (Schott). The instrument response function (IRF) of the setup was collected as a scatter signal at the excitation wavelength, and it typically had a half-width of ~0.4 and ~0.7 ns, for 375 and 282 nm excitation, respectively. Analytical exponential function was re-convoluted with the IRF and then fitted to the experimental decay. The quality of the fits was characterized in terms of weighted residuals distribution and reduced $\chi 2$ values. The final limit of time resolution after deconvolution was assessed as ~0.1 ns.

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