JOC Article

Stable and Soluble Oligo(3,4-ethylenedioxythiophene)s End-Capped with Alkyl Chains

Mathieu Turbiez, Pierre Frère,* and Jean Roncali*

Groupe Systèmes Conjugués Linéaires, Laboratoire IMMO, UMR CNRS 6501 Université d'Angers, 2 Bd Lavoisier, 49000 Angers Cedex, France

pierre.frere@univ-angers.fr

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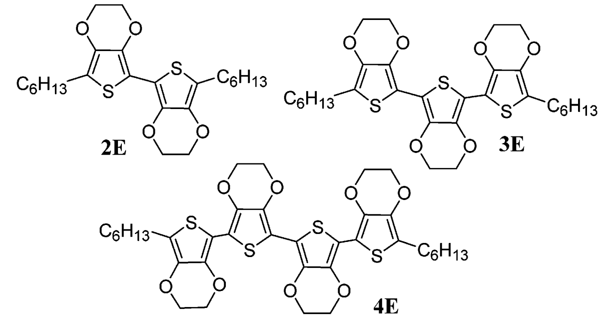
The synthesis of a new series of stable and soluble EDOT oligomers end-capped with *n*-hexyl groups is described. Optical and electrochemical results indicate that the synergy between the direct electron-releasing effects of the ethylenedioxy groups and the self-rigidification resulting from intramolecular interactions controls to a large extent the HOMO−LUMO gap.

The control of the structure and electronic properties of monodisperse π-conjugated oligomers with well-defined chemical structure is a subject of considerable interest.[1] Besides the modelization of the electronic properties of the parent polydisperse polymers,[1,2] these compounds are widely investigated as active materials for the fabrication of (opto)electronic devices such as field-effect transistors or light-emitting diodes.[1−3]

Further development of these fields implies the molecular engineering of new conjugated systems in order to optimize relevant properties such as π-electron delocalization, ionization potential, electron affinity, and energy gap.[4] The past few years have witnessed the emergence of the 3,4-ethylenedioxythiophene (EDOT) building block at the forefront of the chemistry of π-conjugated systems.[5] This rapid development is related to the unique combination of environmental stability, low oxidation potential, and moderate band gap of poly(EDOT).

Although co-oligomers based on the combination of EDOT moieties with various heterocycles such as thiophene, furane, bithiazole, or pyridine have recently been described,[6] the synthesis of EDOT oligomers remains so far limited to short-chain systems. The synthesis of the EDOT trimer was initally described by Reynolds and coworkers who pointed out the limited stability of this compound.[7] To reach stable EDOT-based oligomers, several groups have developed the synthesis of end-capped oligo-EDOT in which substitution of the terminal α-positions is used to prevent the oxidative coupling of the cation radical strongly activated by the ethylenedioxy group and which is thought to be a major source of instability. This approach led to the synthesis of ter-EDOTs end-capped by mesitylthio[8] and phenyl groups.[9]

CHART 1



In the continuation of our current interest in the molecular engineering of linear π-conjugated systems, we report here the synthesis of a new series of oligo-EDOTs (nEs) end-capped by *n*-hexyl groups (Chart 1). It is shown that this approach allows to develop stable and soluble EDOT oligomers without resorting to more bulky groups which might modify the electronic properties of the π-conjugated system.

The substitution of the EDOT or bis-EDOT cores by *n*-hexyl chains has been achieved by the *n*-BuLi/*n*-C_6H_{13}−Br sequence as shown in Scheme 1. The addition of bromohexane on the lithiated derivative of EDOT led to a mixture of EDOT (25%), monosubstituted **1** (40%), and

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* To whom correspondence should be addressed. Fax: 33(0)2 41 73 54 05.

(1) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377.

(2) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1998.

(3) (a) Mitschke, U.; Baüerle, P. *J. Mater. Chem*. **2000**, *10*, 1471−1507. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99−117.

(4) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

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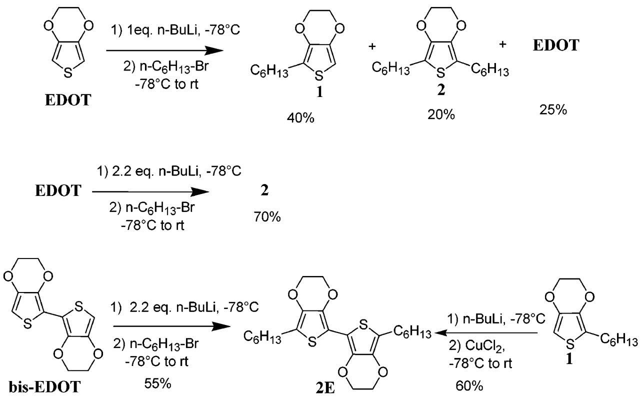
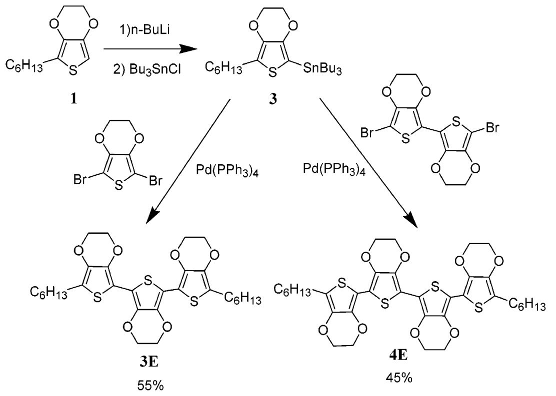
10.1021/jo0345493 CCC: $25.00

SCHEME 1



SCHEME 2



disubstituted derivative **2** (20%) of EDOT easily separated by distillation at low pressure. The formation of compound **2** was due to a proton exchange between **1** and the lithiated derivative of EDOT, followed by substitution with the halogen derivative. The beginning of the exchange reaction was observed at − 50 °C, which corresponds to the temperature at which the first substitution took place. Reaction of EDOT with 2 equiv of *n*-BuLi and an excess of bromohexane gave **2** in 70% yield. Compound **2E** was obtained either from the bis-EDOT[10] in 55% yield using the precedent method or in 60% yield from compound **1** by the oxidative coupling of the lithiated derivative in the presence of CuCl$_2$.

The synthesis of the oligomers **3E** and **4E** is depicted in Scheme 2. The *n*-BuLi/Bu$_3$SnCl sequence carried out on **1** led to the stannic derivative **3** which was quickly used for the next step after a flash chromatography. A two-fold Stille coupling between the stannic **3** and the dibromo derivatives of EDOT and bis-EDOT, obtained by action of 2 equiv of NBS on EDOT or bis-EDOT in DMF, gave **3E** and **4E** in 55% and 45% yield, respectively.

As expected, the solubility of the oligomers decreases with the lengthening of the conjugated chain. Nevertheless, **4E** is sufficiently soluble in THF or chloroform up to to concentrations around 10^{-1} and 10^{-2} mol·L^{-1}, respectively. It should be noticed that **3E** and **4E** slowly decompose in chlorinated solvents while the solution becomes purple.

TABLE 1. Optical[a] and Electrochemical[b] Data of Oligo-EDOTs

compd	λ_{max} (nm)	$E°_1$ (V)	$E°_2$ (V)	$\Delta E = E°_2 - E°_1$ (mV)
2T	322	1.20[c]		
3T	372	0.95	1.35[c]	400
4T	402	0.85	1.14	290
2E	333, 349	0.65[c]		
3E	390, 414	0.41	0.87[c]	460
4E	430, 459	0.22	0.61	390

[a] 10^{-5} mol·L^{-1} in CH$_2$Cl$_2$. [b] 10^{-4} mol·L^{-1} in 0.10 M Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ ref Ag/AgCl, v = 100 mV·s^{-1}. [c] Irreversible peak.

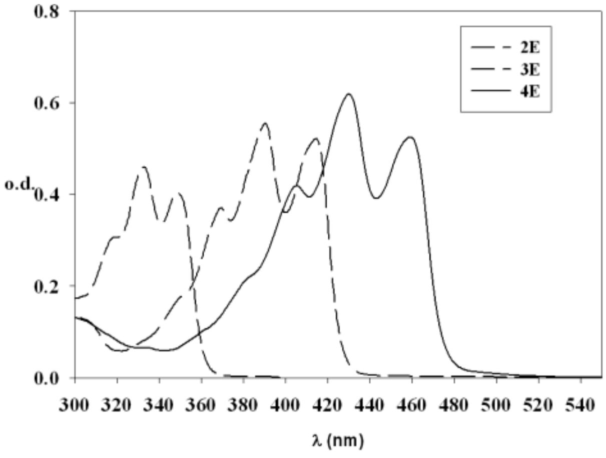


FIGURE 1. Electronic absorption spectra of oligomers 10^{-5} M in CH$_2$Cl$_2$

The optical and electrochemical data of the new oligomers are gathered in Table 1 and compared to those of the corresponding oligothiophenes (nTs) end-capped with *n*-hexyl groups.[11] Figure 1 presents the electronic absorption spectra of oligomers **2E**, **3E**, and **4E**.

Whereas the UV−vis absorption spectra of nTs are known to present a broad and structurless absorption band which reflects the conformational disorder in the conjugated backbone, the spectra of nEs exhibit a well-resolved fine structure with three distincts maxima. As shown in Figure 1, the vibronic fine structure persists with the lengthening of the conjugated chain. The lowest energy band, the main absorption band, and the higher energy band are equally spaced by 1300−1400 cm^{-1}, which is consistent with a C═C stretching mode in the heteroaromatic moieties, strongly coupled to the electronic structure. This behavior is indicative of a strong rigidification of the π-conjugated system. We have recently demonstrated that this self-rigidification process results from the development of intramolecular S···O interactions between adjacent EDOT moieties (Scheme 3).[12]

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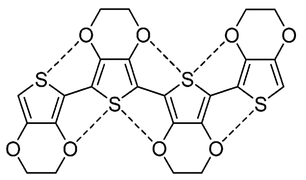
(10) Bis-EDOT was obtained by coupling of monolithiated EDOT in the presence of CuCl$_2$. See refs 6a, 7, and: Akoudad, S.; Roncali, J. *Synth. Met.* **1998**, *93*, 114.

(11) **2T** was obtained by coupling of monolithiated EDOT in the presence of CuCl$_2$. For **3T**, see: Raimundo, J. M.; Levillain, E; Gallego-Planas, N.; Roncali, J. *Electrochem. Commun.* **2000**, *2*, 211. For **4T**, see: Garnier, F.; Hajlaoui, R.; Kassmi, A. El, Horowitz, G., Laigre, L.; Porzio, W.; Armanini, M.; Provasoli, F. *Chem. Mater.* **1998**, *10*, 3334−3339.

SCHEME 3



These interactions are clearly apparent in the X-ray structure of compound **3E** (Figure 2). The three EDOT units adopt an anti conformation, and short S···O distances $d_1 = 2.91$ Å and $d_2 = 3.11$ Å are observed. These values, considerably shorter than the sum of the van der Waals radii of sulfur and oxygen (1.85 Å + 1.50 Å = 3.35 Å), confirm the self-rigidification of the conjugated system by noncovalent intramolecular interactions. Despite the substitutions on the β positions of the thiophene rings, the deviations from the coplanarity are about 9° and 16°. Such interactions which stabilize the trans conformation of the molecule have also been observed in the X-ray crystallographic structure of bis-EDOT derivatives.[12] The molecules stack along the *a* axis, and each column is separated in the *b* axis by the hexyl chains. The shortest distances between the carbon atoms of the conjugated systems are 3.68 and 3.85 Å indicating that the molecules are only separated by the conventional van der Waals contact.

As shown in Table 1, replacement of the thiophene rings by EDOT moieties results in a large bathochromic shift of the absorption and hence in a narrowing of the HOMO−LUMO gap. This red shift is due to a synergy of electronic and structural effects of the oxygen atoms of the EDOT units. In addition to the electron-releasing character of the ethylenedioxy groups which raises the HOMO level, the planarization and rigidification of the π-conjugated system contributes to enhance the π-electron delocalization.

The electrochemical properties have been analyzed by cyclic voltammetry. Unlike bis-EDOT derivatives end-capped with phenyl or mesitylthio groups which were reversibly oxidized to the cation radical, compound **2E** presents an irreversible oxidation peak at 0.65 V even with a scan rate up to 1.0 V·s^{-1}. A detailed analysis of the voltammograms suggests that the evolution of the radical cation might correspond to a dimerization process which would be less hindered by the hexyl chains than by the bulky phenyl and mesitylthio groups. The lengthening of the conjugated chain stabilizes the radical cation and allows to reach the dication state. Thus, trimer **3E** presents a first reversible oxidation wave followed by a second irreversible peak while the tetramer **4E** shows two reversible one-electron oxidation processes corresponding to the formation of cation radical and dication. For **4E**, a strong deformation of the voltammogram was observed even at low concentration in dichloromethane, due to the adsorption of the oxidized states on the platinum electrode. A mixture of CH_3CN/CH_2Cl_2 limits this phenomenon and allows us to clearly identify the two reversible oxidation processes (Figure 3).

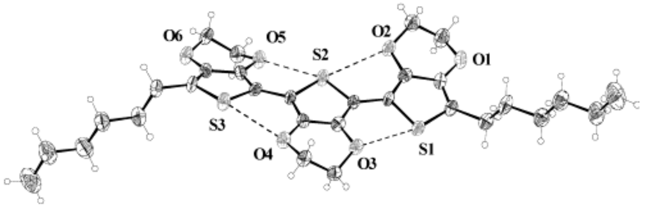


FIGURE 2. Molecular structure of trimer **3E**. Intramolecular S- - -O interactions are indicated by dotted lines

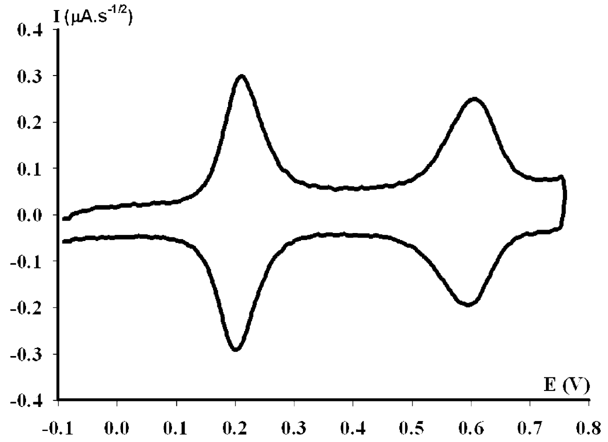


FIGURE 3. Deconvoluted cyclic voltammogramm of **4E**, 10^{-4} mol·L^{-1} in 0.10 M Bu_4NPF_6 in 1:2 $CH_2Cl_2-CH_3CN$, ref Ag/AgCl, v = 100 mV·s^{-1}.

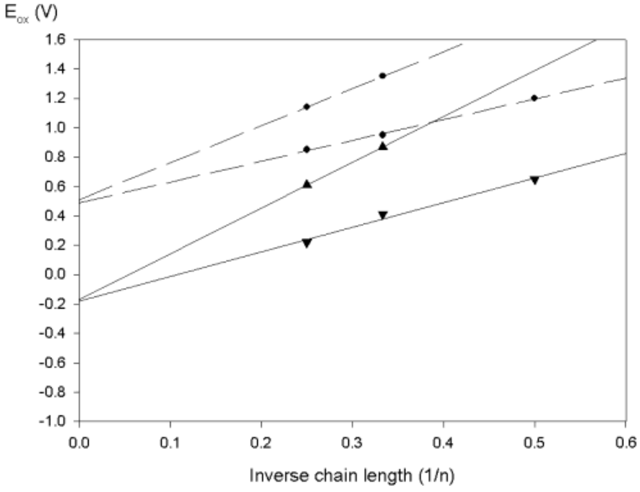


FIGURE 4. Evolution of E_{ox} of nEs (triangles) and nTs (circles) as a function of the reciprocal number of thiophene rings.

The chain length dependence of the redox potentials of nTs and nEs is summarized in Figure 4. As expected, the variation of the oxidation potentials correlates with the reciprocal number of thiophene or EDOT rings. The lower values of E_{ox} and the steeper slopes observed for nEs reflect the combined electron-releasing and rigidification effects of the ethylenedioxy groups. Extrapolation of the oxidation potential to an infinite chain leads to a predicted oxidation potential of ca. −0.20 V vs Ag/AgCl for an ideal poly-EDOT. This value, ca. 0.20 V less positive than the actual oxidation potential of poly-EDOT

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[12] (a) Raimundo, J. M.; Blanchard, P.; Frère, P.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali, J. *Tetrahedron Lett.* **2001**, *42*, 1507−1510. (b) Leriche, P.; Turbiez, M.; Monroche, V.; Blanchard, P.; Skabara, P. J.; Roncali, J. *Tetrahedron Lett.* **2003**, *44*, 649−652.

(~0.0V), can be attributed to the electron-releasing effect of the *n*-hexyl chains.

For both the nTs and nEs series, the plots corresponding to the first and second oxidation potentials converge to a common value for an infinite conjugated chain length. However, and contrary to the results reported for oligo-EDOTs end-capped by phenyl groups, access to the dication state is more difficult in the nEs series than for the nTs one. This is confirmed by the larger value of $\Delta E = E_2 - E_1$ observed for the trimers and tetramers. This result, indicative of an increase of the Coulombic repulsion between the positive charges in the dication of nEs, shows that the combined electron-releasing effect of the ethylenedioxy groups and terminal alkyl chain tend to relocalize the positive charges toward the middle of the conjugated chain. Such a behavior has already been observed for extended tetrathiafulvalene analogues built around EDOT[13] or bis-EDOT[12b] spacers.

Conclusion

To summarize, a new series of stable and soluble oligo-EDOT end-capped by *n*-hexyl chains has been synthesized and characterized. The association of the electronic and structural effects of the ethylenedioxy groups leads to a self-rigidified π-conjugated system with lower energy gap than the corresponding oligothiophene analogues. Work aiming at the realization of electronic and optoelectronic devices based on these systems is now underway and will be reported in future publications.

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Supporting Information Available: Detailed experimental procedures and characterizations of all compounds, crystal data of **3E**, and copies of ^{1}H NMR and ^{13}C NMR spectra of compounds **1**, **2E**, **3E**, and **4E**. X-ray data for **3E** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Akoudad, S.; Frère, P.; Mercier, N.; Roncali, J.; *J. Org. Chem.* **1999**, *64*, 4267−4272.