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Synthesis of π-Conjugated 2,2:6′,2″-Terpyridine-Substituted Oligomers Based on 3,4-Ethylenedioxythiophene

Laure Fillaud, Gaëlle Trippé-Allard, and Jean Christophe Lacroix*

Nano-Electro-Chemistry group, Univ Paris Diderot, Sorbonne Paris Cité, ITODYS,
UMR 7086 CNRS, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France

lacroix@univ-paris-diderot.fr

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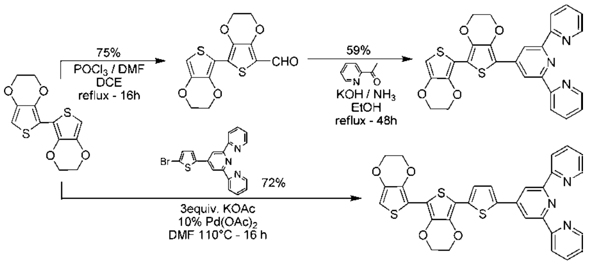
ABSTRACT



Dissymmetric π-conjugated monomers and oligomers incorporating 3,4-ethylenedioxythiophene (EDOT) units and bearing terpyridine end groups were synthesized in good yields through Vilsmeyer–Haak formylation followed by a reaction with 2-acetylpyridine in basic media or, for the longest oligomers, direct C–H bond arylation. They have a low HOMO–LUMO gap and are easily oxidized at low potentials. Upon complexation with cobalt(II) and iron(II) they yield new hybrid materials that can be used in various applications ranging from photovoltaics to spintronics.

Conjugated polymers and oligomers based on thiophene (T) are currently used in plastic and organic electronics as organic semiconducting materials to fabricate various devices such as field-effect transistors, light-emitting diodes, and organic solar cells.[1,2] Poly(3,4-ethylenedioxythiophene) (PEDOT) and functionalized EDOT oligomers are other widely used thiophene-based materials, characterized by a lower oxidation potential and a smaller intrinsic band gap.[3] Organometallic compounds incorporating π-conjugated oligomers as ligands are of considerable interest in various domains.[4] Cobalt complexes have, for instance, been recently used in Gratzel-type solar cells as alternatives to the usual iodine-based redox shuttle system. Photovoltaic yields as high as 12% have been reported.[5] Molecular spintronics is another growing research field in which organometallic compounds incorporating extended π-conjugated systems as ligands are used.[6]

In this paper, we will present the synthesis of several oligomers (and some monomers) combining EDOT and thiophene units, and bearing a terminal terpyridine (tPy) moiety. Using such ligands, cobalt(II) and iron(II) complexes have been obtained and characterized.

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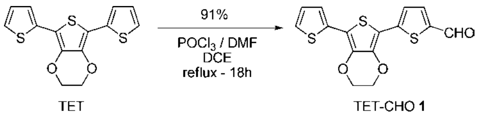
One of the most simple methods of preparing tPy oligomers is to convert a formyl oligomer by a one-pot reaction with 2-acetylpyridine in the presence of base.[7] Another possibility is to start from a short tPy-oligomer and then to increase the conjugation length.[8] We have employed both methodologies to prepare various oligomers bearing tPy.

Scheme 1. Formylation of Mixed Oligomer by Vilsmeyer–Haak Reaction



Several formyl oligomers were thus synthesized by Vilsmeyer–Haak formylation of the corresponding unsubstituted oligomers with phosphoryl chloride in DMF after adaptation of a reported procedure.[9] This method is the most useful since it is totally selective for the α-position of thiophene. The mixed and symmetric terthiophene TET, incorporating two thiophenes and one central EDOT unit, was converted in this manner to TET-CHO **1** in 91% yield (Scheme 1). Bithiophene, EDOT, and bi-EDOT were also transformed to their corresponding aldehydes by this method.

In order to study the influence of the position of EDOT in a terthienyl oligomer, we also prepared TTE-CHO **6** and ETT-CHO **7**. However, because of the lack of selectivity of the Vilsmeyer–Haak reaction, we were unable to obtain such dissymmetric formyl terthienyl oligomers by this approach. Another two-step strategy, depicted in Scheme 2, was therefore used. First, a short formyl oligomer was halogenated, and then this was coupled with another short oligomer via a Stille or Suzuki cross-coupling reaction. Thus, to prepare TTE-CHO **6**, bithienyl stannane, TT-$SnBu_3$,[10] and 2-bromo-5-formyl-EDOT **8**,[11] previously prepared according to reported procedures, were coupled by a Stille reaction in poor yield (17%). For ETT-CHO **7**, 2-formylbithiophene **3** was first iodinated by mercury oxide and iodine in 80% yield. Then, the resulting compound **9** gave ETT-CHO **7** by Suzuki reaction with boronic EDOT in satisfactory yield (63%).

In all, seven formyl oligomers were generated as intermediate compounds in the synthesis of tPy oligomers. They are listed in Table 1 along with their UV–visible spectroscopic properties and oxidation potentials.

Scheme 2. Synthesis of Formyl Oligomer from Dissymmetric Oligomer Based on Thiophene and EDOT

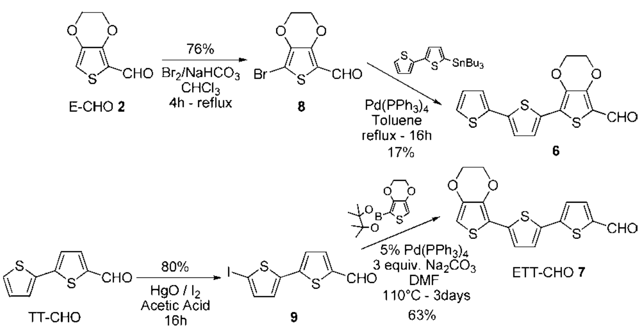
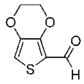
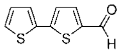
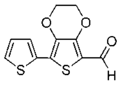
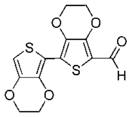
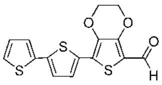
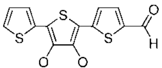
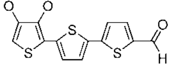


Table 1. Mixed T/E with Terminal Aldehyde Function

		Yield (%)	λ_{max} (nm)[a]	Eox (V vs. SCE)[b]
2 ECHO		69	290	1.66
3 2TCHO		65	348	1.48
4 TECHO		32	368	1.26
5 2ECHO		75	393	1.05
6 TTECHO		17	407	1.04
1 TETCHO		91	427	0.95
7 ETTCHO		63	409	0.92

[a] 10^{-5} M in ACN. [b] 10^{-3} M in 0.1 M $LiClO_4$/ACN, 100 mV·s^{-1}.

All compounds show a strong absorption band between 290 and 450 nm due to π–π* transitions. This band position is strongly influenced by several structural parameters such as the conjugation length. Indeed, formyl-EDOT **2** shows an absorption maximum below 300 nm; those incorporating two units (2T-CHO **3**, TE-CHO **4**, 2E-CHO **5**) have absorption maxima between 300 and 400 nm whereas those with three thiophene units absorb above 400 nm. The number of EDOT units is another important factor. When it increases (from zero for 2T-CHO **3** to one for TE-CHO **4**, and two for 2E-CHO **5**), a bathochromic shift is observed (20 nm for one EDOT and 45 nm for two EDOT). This behavior is due to the electron-donating

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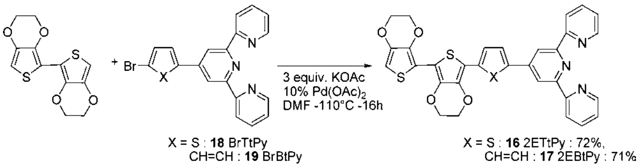
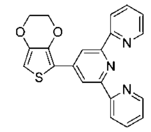
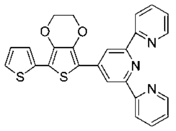
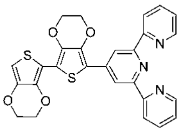
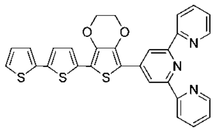
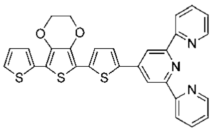
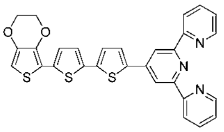
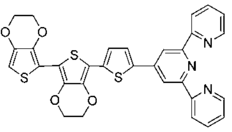
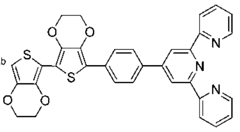
Scheme 3. Direct C–H Arylation of Thiophene-EDOT



ability of the ethylenedioxy group on the thiophene ring, which decreases the HOMO–LUMO gap of the molecules. The EDOT position on the formylterthiophene also affects the absorption maximum. When EDOT is located in the center of the terthiophene, its electron-donating ability is stronger than when it is far from the aldehyde function. For TTE-CHO **6** and ETT-CHO **7**, intramolecular S···O interactions are less numerous than for TET-CHO **1**. Because of this, the TET-CHO **1** oligomer possesses a more rigid structure, inducing a higher bathochromic effect, than TTE-CHO **6** or ETT-CHO **7**.[12] An electrochemical study was also performed on these formyl oligomers. All compounds were oxidized with an irreversible peak whose position changed with the structure. The electrochemical behavior depends on the same structural parameters as the UV–visible spectroscopic properties. E_{ox} decreases when the conjugation chain increases: the irreversible oxidation peak is at 1.66 V/SCE for E-CHO **2**, whereas it is around 1 V for formyl-terthiophene **6** (TTE-CHO) and decreases to 0.9 V when the distance between the EDOT and the formyl groups increases (TET-CHO **1** and ETT-CHO **7**). Moreover, the number of EDOT units exerts a marked effect. E_{ox} decreases by 0.21 V when the number of EDOTs goes from one (TE-CHO **4**) to two (2E-CHO **5**).

Formyl oligomers were then used as reactants to achieve a terpyridine chelating group. Starting from formyl oligomers, 2,2′:6′,2″-terpyridine (tPy) derivatives were synthesized by a one-pot synthesis reported by Constable.[7b,13] The formyl oligomer was heated at reflux for at least 16 h with a slight excess of 2-acetylpyridine (2.03 equiv) in a basic medium (KOH/NH_3/ethanol). The corresponding terpyridine was readily obtained by filtration. Thus, E-tPy **10**, TE-tPy **11**, 2E-tPy **12**, TTE-tPy **13**, TET-tPy **14**, and ETT-tPy **15** were obtained starting from E-CHO **2**, TE-CHO **4**, 2E-CHO **5**, TTE-CHO **6**, TET-CHO **1**, and ETT-CHO **7**, respectively, with yields between 28% and 66%.

Table 2. Mixed T/E Oligomer-tPy

		Yield (%)	λ_{max} (nm)	Eox (V vs. SCE)
10 EtPy[a]		46	288,315	1.52
11 TEtPy[a]		66	398	1.05
12 2EtPy[a]		59	458	0.88
13 TTEtPy		28	411	0.82
14 TETtPy[a]		52	411	0.79
15 ETTtPy[a]		61	252,274,398	0.74
16 2ETtPy[b]		72	289,315,330,420	0.75
17 2EBtPy[b]		71	277,316,329	0.74

[a] 10^{-5} M in CH_3CN. [b] 10^{-3} M in 0.1 M $LiClO_4/CH_3CN$, scan rate 100 mV·s^{-1}.

An alternative to the use of formyl oligomers to synthesize terpyridine oligomers is to couple a terpyridine unit with an aryl or a heteroaryl group. In this context, examples with Stille[14] and Suzuki[15] reactions are the most reported. In the past few years, direct C–H arylation has became more and more popular,[16] and Borghese[17] developed a new method to prepare oligomers based on EDOT. In this method, EDOT or its derivatives react with a halogeno-arene in the presence of palladium acetate. Thus, the synthesis of organometallic precursors, required in the usual cross-coupling reactions, is avoided. Among its numerous advantages, direct C–H arylation allows, depending on the reagent in excess, the synthesis of both symmetrical and unsymmetrical oligomers. Nevertheless, the few reported examples of monoarylation leading to

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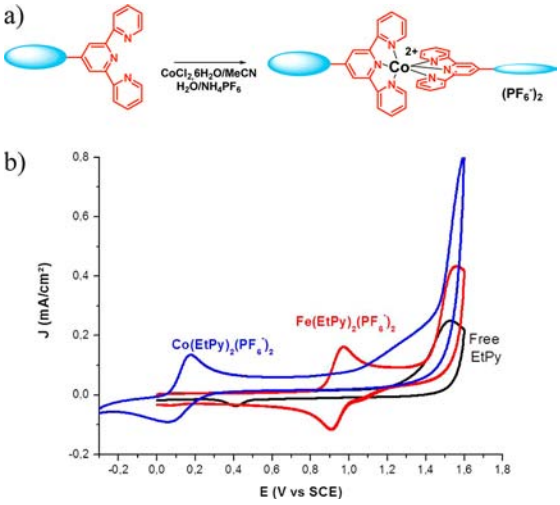

Figure 1. (a) General scheme for complexation of cobalt(II) with π-conjugated 2,2:6′,2″-terpyridine oligomers. (b) Electrochemical response of EtPy **10** (black), Co(EtPy)$_2$(PF$_6^-$) **20** (blue), and Fe(EtPy)$_2$(PF$_6^-$) **22** (red). C = 1.0×10^{-3} M in 0.1 M LiClO$_4$/CH$_3$CN, scan rate 100 mV·s^{-1}.

unsymmetrical derivatives gave poor to moderate yields (35 to 55%) after 8 to 12 h of reaction.[18] Catellani et al.[19] achieved satisfactory yields (72−82%) by increasing the reaction time (24 h). Terpyridine oligomers 2ETtPy **16** and 2EBtPy **17** were synthesized according to this methodology (Scheme 3). First, 2-bromothienylterpyridine BrTtPy[13] **18** and 2-bromophenylterpyridine BrBtPy[20] **19** were prepared according to reported procedures. A slight excess of bi-EDOT (1.3 equiv) with the bromo-arene-terpyridine in DMF in the presence of KOAc and Pd(OAc)$_2$ was heated at 80 °C for 1 h. Thus, 2ETtPy **16** and 2EBtPy **17** were isolated in yields around 70%, and ^{1}H NMR revealed no trace of symmetrical compounds.

The UV−visible spectra of the various molecules show a strong absorption band between 288 and 458 nm due to $\pi-\pi^*$ transitions (Table 2). The maximum absorption position is influenced by the same parameters as in the formyl oligomers. The conversion of aldehyde to tPy has an additional bathochromic effect (λ_{max} = 368 and 398 nm for TE-CHO **4** and TE-tPy **11**, respectively), and band multiplicity appears due to the terpyridine function.[21] A preliminary electrochemical study was performed on these tPy oligomers. They present an irreversible oxidation peak, ranging from 0.74 to 1.52 V/SCE, which depends on the structure and the number of EDOT moieties. Each tPy oligomer has an oxidation potential lower than that of the corresponding formyl oligomer, with the tPy group being less electron-withdrawing than the aldehyde functional group.

As an example of new hybrid materials with metallic cores incorporating tPy oligomers, we have synthesized two complexes by reacting E-tPy **10** with CoCl$_2$·6H$_2$O and FeCl$_2$·6H$_2$O, followed by anion exchange, to yield [Co(E-tPy)$_2$][PF$_6$]$_2$ **20** and [Fe(E-tPy)$_2$][PF$_6$]$_2$ **22**, respectively. The Co(E-tPy)$_2$][PF$_6$]$_2$ **20** paramagnetic complex has been studied using NMR (see Supporting Information (SI)). The terpyridine signal appears before 100 ppm, which indicates that this complex is low-spin at rt.[22] Similar results were obtained with [Co(2EB-tPy)$_2$][PF$_6$]$_2$ **21** (see SI).

Figure 1 compares the electrochemical properties of Co(E-tPy)$_2$ **20** and [Fe(**E-tPy**)$_2$] **22** with that of E-tPy **10**. The three systems exhibit an irreversible oxidation peak corresponding to E-tPy **10** oxidation at 1.5 V/SCE. Reversible signals corresponding to the Co(III)/Co(II) and Fe(III)/Fe(II) redox couples are observed at 0.15 and 0.95 V/SCE, respectively. The 0.15 V value for [Co(E-tPy)$_2$]-[PF$_6$]$_2$ **20** is close to the standard redox potential of several cobalt-based shuttles used in Gratzel-type solar cells. Note also that the redox potential corresponding to Co(III)/Co(II) in [Co(2EB-tPy)$_2$][PF$_6$]$_2$ is around 0.2 V and does not seem to be strongly affected by the oligomer length. Such compounds could also present spin transition properties around or above rt, as seen with analogous cobalt(II) complexes.[23]

In the present paper, we have obtained, in good yields, dissymmetric π-conjugated oligomers incorporating 3,4-ethylenedioxythiophene units and bearing terpyridine. They have a low HOMO−LUMO gap and are oxidized at low potentials. The shortest oligomers have been complexed with cobalt(II) and iron(II). They yield new hybrid materials that can be used in various applications ranging from photovoltaics to spintronics.

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Supporting Information Available. Synthesis procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.