



Synthesis and characterization of novel (oligo)thienyl-imidazo-phenanthrolines as versatile π -conjugated systems for several optical applications

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ABSTRACT

A series of new heterocyclic chromophores **3–6** were synthesized in moderate to excellent yields by condensation of 5,6-phenanthroline-dione with formyl-thiophene derivatives **1–2** in the presence of ammonium acetate in glacial acetic acid. These chromophores possess an (oligo)thienyl π -conjugated system attached to an imidazo-phenanthroline moiety. These derivatives were evaluated concerning their solvatochromic properties, thermal stabilities, and molecular optical nonlinearities.

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1. Introduction

The design and synthesis of organic chromophores as nonlinear optical (NLO) materials has been the focal point of a large amount of recent research in great part due to the potential advances in the fields of optical communication, information processing, frequency doubling and integrated optics that could be realized by materials, which display strong second order optical nonlinearities together with robust material properties.¹ Donor–acceptor substituted heteroaromatic compounds have attracted widespread interest because it has been experimentally and theoretically demonstrated that they increase the second-order molecular NLO properties of push–pull chromophores with respect to the corresponding aryl analogues. It has also been demonstrated that the electron density of the π -conjugated system plays a major role in determining second-order NLO response.² Electron excessive/deficient heterocycles act as auxiliary donors/acceptors when they are connected to donating/withdrawing groups, and the increase of donor/acceptor strength leads to substantial increase in β values.³

Oligothiophenes behave as very efficient electron relays almost comparable to polyenes; thiophene has a lower resonance energy than that of benzene, and oligothiophenes have been shown to produce larger values of the molecular hyperpolarizability, β . The larger nonlinearities were attributed to the bathochromic effect of sulfur, the partial decrease of aromatic character, and an increased π -overlap between the thiophene units. Oligophenylenes attain a rapid saturation beyond the terphenyl unit, whereas oligothiophenes have a strong tendency to increase β as the number of thiophene units increases. Aside from the electron transmission efficiency, another merit of oligothiophenes is their inherent stability from which thiophene-based donor (D)–acceptor (A) chromophores should benefit.⁴ Moreover, these push–pull systems are also excellent solvent polarity indicators due to their positive solvatochromism.^{4b–e,g–j} This type of compounds can therefore be applied in electro-optical devices.¹

Triaryl(heteroaryl)-imidazole^{2e,5} and benzimidazole⁶ based chromophores have received increasing attention due to their distinctive linear and nonlinear optical properties and also due to their excellent thermal stability in guest–host systems. Imidazole derivatives can be further substituted on the nitrogen atom so that the electron density of the chromophore can be changed. This functionalization will remove the possibility of tautomerism and

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introduces a new potentially useful chemical variable for the optimization of NLO activity of the chromophore (e.g., introduction of groups with suitable electronic properties). The imidazole ring can be easily tailored to accommodate functional groups, which allows the covalent incorporation of the NLO chromophores into polyamides leading to NLO side chain polymers.^{5a,d,7} For the practical application of second-order NLO materials, not only a high hyperpolarizability but also good thermal stability is required. In this respect, promising candidates are (benz)imidazole derivatives,^{5,6} as well as conjugated (oligo)thiophenes.⁴ Despite all these promising properties for NLO applications, only a few publications concerning the synthesis and characterization of NLO chromophores based on triaryl(heteroaryl)-imidazoles can be found in the available literature.^{2e,5a–e,h,m}

Due to their optoelectronic properties, aryl-imidazo-phenanthrolines play important roles in materials science and medicinal chemistry.^{8–10} Therefore, they have found application as ligands for the synthesis of metal complexes of ruthenium(II), copper(II), cobalt(II), nickel(II), manganese(II), and several lanthanides especially for nonlinear optical (NLO) applications,^{8a–c,g} while in medicinal chemistry they are important building blocks for the synthesis of proton, anion, and cation sensors⁹ or as ligands for ruthenium(II) and platinum(II) complexes with important and diverse biological applications such as probes of DNA structure or new therapeutic agents due to their capacity to bind or interact with DNA.¹⁰

New material properties can be achieved when new conjugated systems are composed by different heterocyclic nuclei, which allow the fine tuning of important physical and/or photophysical properties. As a result of the optical and conductive properties, conjugated materials containing thiophene, imidazole, and phenanthroline heterocycles have found many applications including those described above.^{4,5,8–10}

Owing to synthetic difficulties, most of the NLO imidazoles developed so far, namely 2,4,5-triaryl(heteroaryl)-imidazoles, only possess short conjugation pathways (spacers) such as phenyl, thienyl or thiazolyl.^{2e,5a–e,h,m} Our approach to the design of new π -conjugated systems for several potential optical applications is based on the use of electron-rich five-membered heteroaromatics such as thiophenes and imidazoles in the conjugation pathway, combined with electron deficient heterocycles such as phenanthroline, which also acts as an acceptor group due to the deficiency of electron density on the ring C atoms. Furthermore, the planarity and the extension of conjugation of the phenanthroline moiety with imidazole and oligothieryl units lead to an increase of the overall conjugation. Additionally to the structural characteristics described above they exhibit also high thermal stabilities making them interesting for several applications in materials chemistry.^{2e,11}

To the best of our knowledge, this is the first report on the synthesis and evaluation of the solvatochromic and optical (linear and nonlinear) properties of (oligo)thienyl-imidazo-phenanthroline derivatives. We are aware of only one article that reports the synthesis of a thienyl-imidazo-phenanthroline derivative in which the thiophene ring was linked to the imidazo-phenanthroline moiety through its position 3. This compound was used as ligand on the synthesis of a polypyridyl ruthenium complex as effective coating agent for the synthesis of gold or silver nanocomposites.^{8f}

Following our interest in heterocyclic derivatives for several optical applications (e.g., NLO, OLED's, etc.)^{4b–e,g–k,12} we now report the synthesis and characterization of the thermal and optical properties of the new π -conjugated systems **3–6**, containing a functionalized oligothieryl π -conjugated bridge linked to the imidazo-phenanthroline system, which is original and different from other related reports.^{8–10}

2. Results and discussion

2.1. Synthesis

2.1.1. Synthesis of formyl-(oligo)thiophenes **1–2**

The formylation of thiophene and oligothiophene derivatives is usually achieved through two methods: the Vilsmeier reaction,^{4a,b,13} (or by a modified procedure of the Vilsmeier formylation using DMF/POCl₃ in dichloroethane¹⁴) or by metalation followed by formylde lithiation using DMF.^{4a,b,15} More recently, palladium catalyzed cross-coupling reactions, have also been used in the synthesis of formyl-functionalized (oligo)thiophenes.^{4c,d,hi}

In order to compare the effect of the electronic nature of one or two imidazo-phenanthroline moieties on the optical properties of linear or angular oligothieryl-imidazo-phenanthrolines **3–6**, formyl-oligothiophenes **1–2** containing one or two formyl groups were used as precursors of phenanthrolines **3–6**. Compounds **1b,e,f** and **2b** were prepared using two different methods of synthesis: metalation followed by reaction with DMF (**1b** and **2b**) or through Suzuki cross-coupling reactions (**1e,f**).

Therefore, 5-formyl-2-methoxythiophene **1b** was synthesized using our recently reported procedure.^{4b} The metalation of 2-methoxythiophene was carried out using 1.2 equiv of *n*-BuLi in dry ether at 0 °C for 1 h. Subsequently, the organolithium derivative was converted to the corresponding formylthiophene by addition of 1.2 equiv of DMF followed by refluxing the mixture for 1 h, with a 73% yield.

Recently, we have demonstrated that 5-alkoxy- and 5-*N,N*-dialkylamino-2,2'-bithiophenes are selectively lithiated at the α -position of the thiophene ring giving only the mono-formylated derivatives, 5'-formyl-5-alkoxy- or 5'-formyl-5-*N,N*-dialkylamino-2,2'-bithiophenes, when equimolar amounts of bithiophene and DMF were used.^{4b} In order to obtain the diformyl bithiophene **2b** an excess of the metalation reagent (2 equiv) and also of DMF (2 equiv) were used. Instead of the diformyl derivative **2b**, as the only product, we obtained a mixture of two compounds (confirmed by TLC and ¹H NMR). The metalation of 5-methoxy-2,2'-bithiophene using 2 equiv of *n*-BuLi in dry ether at 0 °C for 1 h followed by reaction with 2 equiv of DMF by refluxing the mixture for 1 h produced a mixture of the two formylated derivatives: 5'-formyl-5-methoxy-2,2'-bithiophene^{4b} in 42% yield and 5-methoxy-4,5'-diformyl-2,2'-bithiophene **2b** in 31% yield. The methoxy group in phenyl or benzyl derivatives is known as a moderately strong *ortho* directing substituent with electron withdrawing properties in metalation reactions.^{15d,16} In 5-methoxy-2,2'-bithiophene **2b**, the methoxy group also demonstrated an *ortho* directing effect on the thiophene ring. Consequently, formylation at position 4 of the bithiophene moiety, *ortho* to the methoxy group was also observed for 5-methoxy-2,2'-bithiophene giving the diformylated derivative **2b**.

Compounds **1a** and **1c** were commercially available. The synthesis of 5'-formyl-2-methoxy-2,2'-bithiophene **1d** and 4-formyl-5-piperidino-2,2'-bithiophene **2a** has been reported by us, recently, through metalation followed by reaction with DMF or through Vilsmeier formylation.^{4b}

2.1.2. Synthesis of (oligo)thienyl-imidazo-phenanthrolines **3–6**

Mono- or diformyl (oligo)thiophenes **1–2** with the formyl group at α , β or α and β positions of the thiophene ring were used as precursors of linear and angular phenanthrolines **3–6** in order to evaluate the effect of the position of the phenanthroline group on the optical properties of these chromophores. Therefore, compounds **3–6** with either thienyl, bithienyl or terthienyl moieties (substituted with H, alkoxy or *N,N*-dialkylamino donor groups) linked to the imidazo-phenanthroline system were synthesized in moderate to excellent yields (41–92%, Table 1)

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