

New Oligothiényl-imidazo-phenanthroline Chromophores for NLO Applications

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Abstract. A new series of oligothiényl-imidazo-phenanthrolines **3** were synthesised in good to excellent yields by condensation of 5,6-phenanthroline-dione **2** with formyl-thiophene derivatives **1** in the presence of ammonium acetate in glacial acetic acid. Furthermore, their solvatochromism and molecular optical nonlinearities were determined and comparatively studied. The experimental results indicate that phenanthrolines **3**, due to their moderate solvatochromic properties and good optical nonlinearities, could be used as suitable probes for the determination of solvent polarity and as nonlinear optical materials.

Introduction

Donor-acceptor π -conjugated organic materials have received much attention as they offer many new possibilities for devices combining unique optical, electrical and mechanical properties. In particular, chromophores bearing low aromaticity heterocycles along the conjugation path have been investigated and are considered as the most suitable for these applications. Heterocyclic imidazole 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 and good miscibility with high performance polymers. 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 [1-10]. 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. Oligothiophenes behave as very efficient electron relays almost comparable to polyenes, because of the lower resonance energy of thiophene compared to that of benzene, and have been shown to give larger contributions to β . Oligophenylenes attain a rapid saturation beyond the terphenyl unit, whereas oligothiophenes have a strong tendency to increase β with increasing number of thiophene units. 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 [11].

As a result of the optical and conductive properties, conjugated materials containing thiophene and imidazole heterocycles have found many applications including use as hole injection layers in OLED/PLEDs, in flexible light displays, solar cells, flat panel displays, field effect transistors, nonlinear optical materials, sensors, etc. [1-10]. Phenanthroline derivatives have been extensively used as ligands in both analytical and preparative coordination chemistry [12]. Furthermore the planarity and the extension of conjugation of the phenanthroline moiety with imidazole and oligothieryl units leads to an increase of the overall conjugation [13]. Due to the deficiency of electron density on the ring C atoms, the phenanthroline heterocycle acts also as an acceptor group. 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. Following our interest in heterocyclic derivatives for optical applications [14-21], we report in this communication the synthesis and characterization of the linear and nonlinear optical properties of NLO chromophores **3**, containing a functionalized oligothieryl π conjugated bridge linked to the imidazo-phenanthroline system, which is original and different from other related reports [1-6].

Results and discussion

Synthesis. Oligothieryl-imidazo-phenanthrolines **3** were synthesised with different thiophenic substituents at the 2-position of the imidazo-phenanthroline moiety in order to evaluate the effect of the nature of the π -conjugated bridge on the solvatochromic and nonlinear optical properties of chromophores **3**. Therefore, compounds **3** with either thienyl, bithienyl and terthienyl moieties (substituted with H or methoxy groups) linked to the imidazo-phenanthroline system, were synthesized in good to excellent yields (76-92%), by condensation of 5,6-phenanthroline-dione **2** with formyl-thiophene derivatives **1** [14] in the presence of ammonium acetate in refluxing glacial acetic acid [1] for 15 h (Scheme 1). The structures of the new phenanthrolines **3** were unambiguously confirmed by their analytical and spectral data (Table 1).

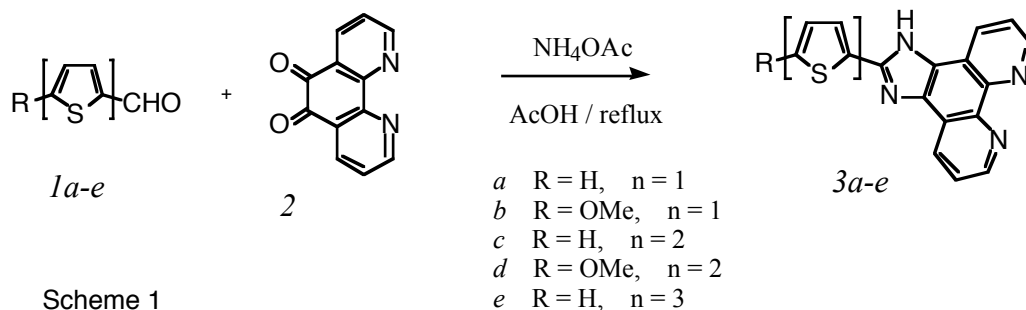


Table 1. Yields, spectroscopic data and linear^a and nonlinear optical data^a for phenanthrolines **3**.

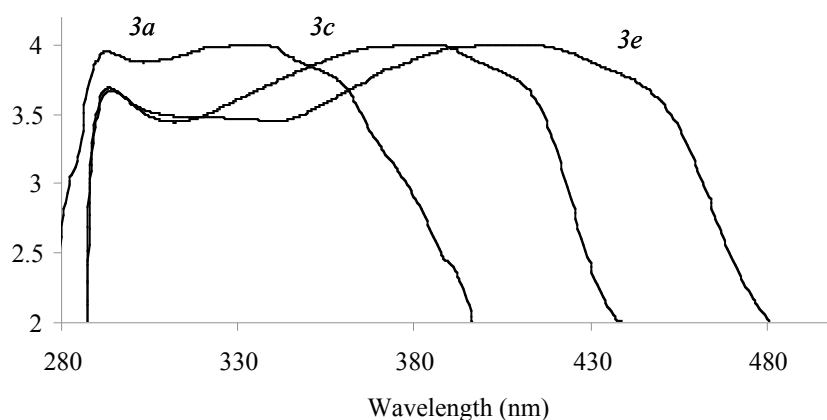
Entry	Compd.	R	n	Yield [%]	UV-Vis. λ_{max} [nm] ^a (log ϵ)	$\beta/10^{-30}$ [esu] ^b	$\beta_0/10^{-30}$ [esu] ^c	IR ν [cm ⁻¹]	δ_{H} [ppm] ^d
1	<i>3a</i>	H	1	90	336.5 (4.36)	39	21	3508	13.84
2	<i>3b</i>	OMe	1	92	346.0 (3.84)	116	60	3435	13.25
3	<i>3c</i>	H	2	88	383.5 (4.45)	54	23	3437	13.91
4	<i>3d</i>	OMe	2	76	393.0 (4.44)	172	68	3400	13.90
5	<i>3e</i>	H	3	83	411.5 (4.43)	319	109	3426	not visible
6	<i>pNA</i>	---	---	---	352.0	16.9	8.5	---	---

^a Experimental hyperpolarizabilities and spectroscopic data measured in dioxane solutions. ^b All the compounds are transparent at the 1064 nm fundamental wavelength. ^c Data corrected for resonance enhancement at 532 nm using the

two-level model with $\beta_0 = \beta [1 - (\lambda_{\max}/1064)^2][1 - (\lambda_{\max}/532)^2]$; damping factors not included 1064 nm. ^d For the NH proton of the imidazole ring for compounds **3** (300 MHz, DMSO-*d*₆).

UV-visible study. Electronic absorption spectra of chromophores **3** in dioxane solutions (10^{-4} M) showed an intense lowest energy charge-transfer absorption band in the UV-visible region. The position of this band was strongly influenced by the structure of the compounds, for example by the length of the π conjugated bridge and also by the electronic nature of the groups, (H or methoxy), that substituted the oligothieryl moiety at the imidazo-phenanthroline system (Table 1). The reason for the red shift in the investigated compound **3b** ($\lambda_{\max} = 346$ nm) relative to the unsubstituted thienyl-imidazo-phenanthroline **3a** ($\lambda_{\max} = 336.5$ nm) was the strong inductive and conjugative effect of the alkoxy substituent (Table 1, entries 1 and 2 respectively). In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption. Comparison of the electronic absorption spectra of thienyl-imidazo-phenanthroline **3a** ($\lambda_{\max} = 336.5$ nm) with bithienyl-imidazo-phenanthroline **3c** ($\lambda_{\max} = 383.5$ nm) and terthienyl-imidazo-phenanthroline **3e** ($\lambda_{\max} = 411.5$ nm) revealed that the increase of the number of thiophene units that constitutes the π conjugated bridge caused a dramatic red shift on the charge-transfer band (Figure 1). This observation clearly indicates that the incorporation of thiophene moieties in push-pull compounds enhances their charge-transfer properties. The increase of the β values, characteristic of the strength of the NLO response, is accompanied by an increase of the wavelength of the absorption maximum λ_{\max} in the UV-visible spectra, i.e. a decrease in the intramolecular charge transfer (ICT) values [16, 22].

Figure 1. UV-visible absorption spectra of compounds **3a**, **3c** and **3e** in dioxane.



Solvatochromic study. Donor-acceptor substituted oligothiophenes have been known to demonstrate strong solvatochromic behavior [15-16]. In order to investigate if compounds **3** could act as suitable probes for the determination of solvent polarity, we carried out a study of the absorption spectra of compounds **3** in five selected solvents of different solvation character. The wavelength maxima λ_{\max} and wavenumber maxima ν_{\max} of compounds **3** are listed in Table 2 and were compared with π^* values for each solvent, determined by Kamlet and Taft [23]. Compounds **3** exhibited positive solvatochromism with respect to their CT absorption band, that is, the position of the absorption maximum shifted to longer wavelengths as the polarity of the solvent increased due to a great stabilization of the excited state relative to the ground state with the increase of polarity of the solvent. In view of the moderate solvatochromism, the good correlation with π^* values for the 5 solvents investigated and the long wavelength absorption in the visible range, compounds **3b** ($\Delta\nu_{\max} = 930$ cm^{-1}) **3c** ($\Delta\nu_{\max} = 752$ cm^{-1}) and **3e** ($\Delta\nu_{\max} = 821$ cm^{-1}) appear to be quite reliable solvent polarity indicating dyes.

Table 2. Solvatochromic data [λ_{\max} (nm) and ν_{\max} (cm^{-1}) of the charge-transfer band] for compounds **3** in various solvents with π^* values by Kamlet and Taft [23].

Solvent ^a	π^* ^b	Compound									
		<i>3a</i>		<i>3b</i>		<i>3c</i>		<i>3d</i>		<i>3e</i>	
		λ_{\max}	ν_{\max}	λ_{\max}	ν_{\max}	λ_{\max}	ν_{\max}	λ_{\max}	ν_{\max}	λ_{\max}	ν_{\max}
EtOH	0.54	333.0	30030	354.0	28248	377.0	26525	389.0	25706	406.0	24630
dioxane	0.55	336.5	29717	346.0	28902	383.5	26075	393.0	25445	411.5	24301
CHCl ₃	0.76	337.0	29673	348.0	28736	381.0	26246	391.0	25575	410.0	24390
DMF	0.88	336.0	29761	356.5	28050	386.0	25906	393.0	25445	419.0	23866
DMSO	1.00	337.0	29673	357.5	27972	388.0	25773	394.0	25380	420.0	23809

^a Solvents used as received. ^b The correlation coefficient r obtained for the linear solvation energy relationship with π^* values by Kamlet and Taft was $r = 0.9492$ for *3b* (without ethanol), $r = 0.8987$ for *3c* and $r = 0.9329$ for *3e*.

Nonlinear optical study. We used the hyper-Rayleigh scattering (HRS) method [24-25] to measure the first hyperpolarizability β of phenanthrolines **3**. *p*-Nitroaniline (*p*NA) was used as standard [26-27] in order to obtain quantitative values. The static hyperpolarizability β_0 values were calculated using a very simple two-level model neglecting damping [28-30]. They are therefore only indicative and should be treated with caution. From Table 1 it is obvious that the increase of the donor strength of the group substituted on the thiophenic or bithiophenic moieties resulted both in red-shifted absorption maxima and enhanced β values for phenanthrolines *3b* and *3d* (R= OMe), compared to derivatives *3a* and *3c* (R=H) (Table 1, entries 1-4). Comparison of the β values for *3a* (39×10^{-30} esu), *3c* (54×10^{-30} esu) and *3e* (319×10^{-30} esu) showed that the increase of the number of thiophenic nuclei linked to the imidazo-phenanthroline moiety lead to larger nonlinearities (Table 1, entries 1, 3 and 5 respectively). In comparison with oligophenylenes, oligothiophenes behave as very efficient electron relays almost comparable to polyenes, because of the lower resonance energy of thiophene compared to that of benzene. Oligothiophenes have a strong tendency to increase β with increasing number of thiophene units [11, 16].

Conclusions

In summary, we have synthesized new oligothieryl-imidazo-phenanthrolines **3** in good to excellent yields. The solvatochromic and NLO properties of chromophores **3**, substituted with different thienyl moieties, functionalized by groups with different electronic character, have been evaluated and it was obvious that the electronic nature of these groups and the number of thiophenic units of the π conjugated bridge had significant influence on the solvatochromic and NLO properties. In particular we have shown that phenanthrolines **3** had good molecular nonlinearities especially derivatives *3d-e* as their β values were 10-19 times higher than that of the well known *p*NA molecule. The experimental results obtained for donor-acceptor compounds **3** indicate that these new heterocyclic materials could find application in nonlinear optics.

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