



Synthesis, characterization and optical properties of novel oligothiophenes bearing pyrene units attached via well defined oligo (ethylene glycol) spacers



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ABSTRACT

Two new thiophene monomers bearing pyrene units attached via di(ethylene glycol) and tetra(ethylene glycol) spacers were synthesized, 3-methyl-4-(diethoxy) thiophene (**M2**) and 3-methyl-4-(tetraethoxy) thiophene (**M4**). These monomers were linked to thiophene and bithiophene via a Suzuki coupling reaction to give the corresponding terthiophenes and quaterthiophenes: [3,3-(di (diethoxypyrene)), 4,4''dimethyl-2,2':5'2''-terthiophene (**TT2**)], [3,3-(di(tetraethoxypyrene)), 4,4''dimethyl-2,2':5'2''-terthiophene (**TT4**)], [3,3''-di(diethoxypyrene), 4,4''methyl-2,2':5':2'':5'',2'''-quaterthiophene (**QT2**)], and [3,3'''-di(tetraethoxypyrene), 4,4''methyl -2,2':5':2'':5'',2'''-quaterthiophene (**QT4**)]. The obtained oligothiophenes were characterized by ¹H, ¹³C NMR spectroscopies and MALDI-TOF mass spectrometry. The optical properties of these compounds were studied by absorption and fluorescence spectroscopy. The absorption spectra of these compounds exhibited a broad absorption band at $\lambda_{\max} = 350$ nm arising from the $S_0 \rightarrow S_2$ transition of the pyrene group. This broadening is an indication of the presence of pyrene–pyrene interactions in the ground state. A discrete band at $\lambda = 385$ nm due to the $S_0 \rightarrow S_1$ transition ($n-\pi^*$) of the oligothiophene backbone was also observed. The emission spectra of oligomers **TT2**, **TT4**, **QT2** and **QT4** showed a “monomer emission” band at $\lambda_M = 379$ –450 nm followed by an intense excimer emission band at $\lambda_E = 570$ nm due to intramolecular pyrene–pyrene interactions. The effect of the flexible spacer length as well as that of the oligomer backbone influences significantly the formation of pyrene–pyrene complexes.

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1. Introduction

Polythiophenes have been widely studied in the last 25 years because they show reasonably good stability, ease of structural modification, controllable optical properties and electrochemical behaviour [1–3]. Nevertheless its applications were limited because of its insolubility in many organic solvents, due to its extended π -conjugated structure [4]. Oligothiophenes are very promising for the development of novel organic electronic materials. For instance, the conducting properties of tetramers and hexamers have allowed the development of organic semiconductors and light-emitting diodes [5,6]. Oligothiophenes also show chromic effects similar to those found for their corresponding polymers [7,8]. Later, alkyl chains have been incorporated into

the thiophene units in order to get monomers able to give soluble polymers. The incorporation of alkoxy groups into polythiophenes increases significantly their conductivity without diminishing their solubility in organic solvents [9,10].

It is very well known that π -conjugated oligomers are considered as promising materials since their optical and electrical properties make them excellent prospects for the elaboration of optoelectronic devices such as OFETs [11], OLEDs [12], electro-optic modulators and photovoltaic cells [13]. In oligothiophenes, the high conjugation degree causes a red-shift of the absorption and emission transition bands to the visible range, a significant reduction of the oxidation potentials as well as a high stabilization of the resulting radical-cation species, which is helpful for the elaboration of electronic materials [14].

On the other hand, pyrene is a fluorescent probe that has been widely used for polymer labeling because it easily forms excimers. Moreover, pyrene has a longer singlet lifetime than other chromophores, which facilitates the excimer formation. The main

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photophysical properties of pyrene excimers have been studied in detail by Winnik [15]. An excimer emission band appears if an excited-state molecule associates with a ground-state molecule after which the photon is delocalized over the conjugate to show a net change in the fluorescence spectral profile. The resulting photophysical properties give us useful information about the conjugated geometry, internal stacking and long distance pyrene–pyrene interactions.

In a previous work Aso et al. [16] improved the emission properties of oligothiophenes modified it with pyrene units at the 2- or 3-positions (Fig 1a). The insertion of pyrenes has the advantage of not only enhancing the fluorescence but also the thermal stability and charge-transport capability of the oligothiophene films.

Moggia et al. [17] prepared pyrene-substituted oligothiophene derivatives (Fig 1b) in order to study the influence of the pyrene groups on the opto-electronic properties. Spectroscopic studies in solution show that the introduction of the pyrene moieties induces a significant extension of electronic conjugation and, consequently, a reduction of the gap value.

In our research group, we have synthesized and characterized different series of π -conjugated polymers and oligomers bearing pyrene units in their structure [18]. We studied the effect of the internal stacking in the optical and photophysical properties [19–22]. Very recently, we carried out the incorporation of pyrene units into dendritic molecules bearing porphyrin and fullerene moieties in order to study the fluorescence energy transfer phenomenon (FRET) as a function of the distance between the donor (pyrene) and the acceptor group (porphyrin or fullerene) [23–25]. We reported also a series of polythiophenes containing pyrene groups attached via alkyl chains. These polymers exhibited good thermal stability and showed the presence of non parallel intramolecular pyrene–pyrene interactions [26].

Oligothiophene systems exhibit outstanding opto-electronic properties arising from their well defined conjugated backbone

and the chromophores attached to it [27]. Indeed, the molecular architecture of the oligomers can be modified by changing the conjugated backbone length or by the incorporation of photoactive chromophores such as pyrene. This strategy is very useful to modulate their optical and photophysical properties in order to develop luminescent materials [28–30].

Here, we describe the synthesis, characterization and optical properties of a series of oligothiophenes [terthiophenes (**TT2**, **TT4**) and quaterthiophenes (**QT2**, **QT4**)], where TT means Terthiophene, QT means Quaterthiophene, 2 and 4 indicate the presence of di (ethylene glycol) and tetra(ethylene glycol) chains, respectively. These oligothiophenes bearing pyrene units attached via di (ethylene glycol) and tetra(ethylene glycol) spacers (Fig 2) were prepared in order to study the influence of the geometry of the molecules on the optical properties and the formation of excimers. Monomers and oligomers were characterized by ^1H and ^{13}C NMR spectroscopies and MALDI-TOF mass spectrometry. Finally their optical properties of were studied by absorption and fluorescence spectroscopy.

2. Experimental work

2.1. Apparatus

^1H NMR and ^{13}C NMR spectra of all the compounds were carried out in CDCl_3 solution, using a Bruker Avance 400 spectrometer, operating at 400 MHz and 100 MHz for ^1H and ^{13}C , respectively. MALDI-TOF mass spectra of the oligomers were recorded using dithranol as matriz, on a Bruker Daltonics flexAnalysis

Absorption spectra of the oligomers in CHCl_3 solution (spectrometric grade, concentration $1 \times 10^{-5}\text{M}$) were scanned on a Varian Cary 1 Bio UV/vis spectrophotometer model 8452A using quartz cells with a width of 1 cm. Steady state fluorescence spectra were recorded on a Photon Technology International LS-100 steady-state system with a pulsed Xenon flash lamp as the

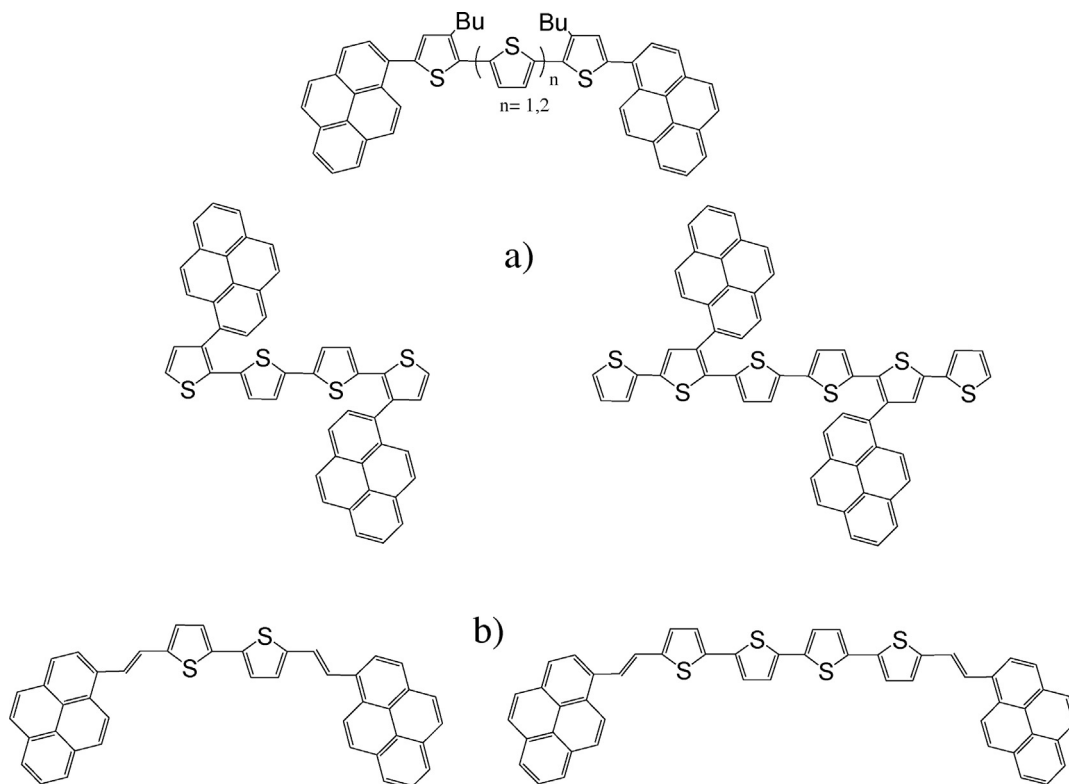


Fig. 1. (a) Chemical structure of pyrene-modified oligothiophenes, (b) pyrene-modified oligothiophenes Moggia.

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