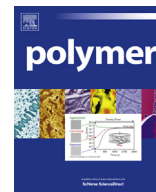




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Oligo-thiophene tethered 1,10-phenanthroline as N-chelating moiety. Electrochemical and optical characterization of the π -conjugated molecule and of the relevant conducting polymer and metallopolymers

Paola Manca, Serafino Gladiali, Daniela Cozzula ¹, Antonio Zucca, Gavino Sanna, Nadia Spano, Maria I. Pilo*

Dipartimento di Chimica e Farmacia, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

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ABSTRACT

The synthesis and characterization of a new highly conjugated molecule, 4-(2,2':5',2''-terthien-3'-ethynyl)-1,10-phenanthroline (TAF4) is reported. The new compound features an expanded π -conjugation as compared with the analogue 2,2':6',2''-terpyridine derivative (4'-(2,2':5',2''-terthien-3'-ethynyl)-2,2':6',2''-terpyridine) we have recently reported. The electrochemical polymerization of TAF4 allows to obtain the corresponding conducting polymer PTAF4. Electrochemical and spectroscopic characterization were performed on both the original tether TAF4 and the polymer, and the results are compared with related structures bearing different spacers and nitrogen substituents. PTAF4 shows a remarkable lowering of band gap value that is consequent on the nature both of the spacer and of the substituent on the terthiophene fragment.

Furthermore, the synthesis and characterization of the Ru(II) complex, $[\text{Ru}(\text{TAF4})_3][\text{PF}_6]_2$, and of the corresponding metallopolymers, are reported.

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1. Introduction

Conjugated materials have attracted particular attention in the past few decades, because of their properties and practical applications. Interest is motivated by their suitability in photophysical, optical and electronic devices. In particular polythiophenes (PT) are an important class of conducting polymers (CPs) because of their structural versatility and thermal stability of both neutral and doped forms [1]. For this reason synthesis, electrochemical and spectroscopic properties and electronic transport mechanism of oligo- and polythiophenes have been widely studied and many structure–property relationships have been elucidated up to date. The key of their versatility lies in the possibility of introducing different substituents on the heterocyclic ring, the nature and the position of the functionalization being tools for a high tunability. In

the last decades, many efforts have been devoted to the derivatization of thiophene in 3 or 4 position, with a wide variety of aryl substituents [2–5].

Furthermore, π -conjugated polymers containing chelating ligands are a subject of high interest, because they allow the electronic, optical and catalytic properties of metal complexes to be coupled with non-linear optical properties, electronic conductivity, luminescence and processability of conducting polymers [6,7]. In particular polypyridine complexes of ruthenium(II) received the greatest attention by groups working on photoinduced electron and energy transfer [8], because $[\text{Ru}(\text{bipy})_3]^{2+}$ (bipy = 2,2'-bipyridine) is the best known and most studied photoluminescent transition-metal complex [9]. An obvious alternative to bipyridine-derivatives is 1,10-phenanthroline (phen), and the photochemistry of copper(I) bis(phenanthroline) complexes has been investigated [10] to make them suitable for practical applications such as light harvesting for photovoltaic cells.

Since phen is a ligand with a π -conjugated condensed structure, it looks as an excellent candidate for the inclusion in conducting polymers. Its rigid structure provides for the enhanced stability of

* Corresponding author. Tel.: +39 079 229578; fax: +39 079 229559.

E-mail address: mpilo@uniss.it (M.I. Pilo).

¹ Present address: CAT Catalytic Center ITMC, RWTH Aachen University, Woringerweg 1, 52074 Aachen, Germany.

phen chelate complexes [11] and the planarity of the heterocyclic scaffold favours a more efficient electronic transport along the backbone. In spite of these favourable features π -conjugated polymers with 1,10-phenanthroline have not received much attention thus far.

Introduction of suitable substituents onto the phenanthroline skeleton proved successful in shifting the fluorescence emission at short wavelength into the visible region, and in increasing the quantum efficiency of some complexes [12]. The majority of the reported examples involve double substitution mainly in 3,8 [13–16], in 2,9 [9] or 4,7 [17] positions of the phenanthroline framework. Quite few examples report single substitution in 4 position [18,19], and to our knowledge no cases are reported of such substitution with heterocycles like thiophene.

Our research is focused on the electrochemical synthesis of conducting polythiophenes made up with a terthiophene (as polymerizing unit) and with an N-chelating moiety, connected through different spacers. We previously used 2,2'-6',2''-terpyridine (terpy) as a metal-binding unit and we bridged it to terthiophene with both saturated [20] or unsaturated [21] spacers. The more interesting electrochemical and optical properties were observed in the latter arrangement, that is in the case of 4'-(2,2':5',2''-terthien-3'-ethynyl)-2,2':6',2''-terpyridine, TAT (chart 1) [22]. At the same time, ruthenium(II) complexes of TAT [23] revealed luminescence properties, exhibiting an extraordinary long excited state lifetime [24].

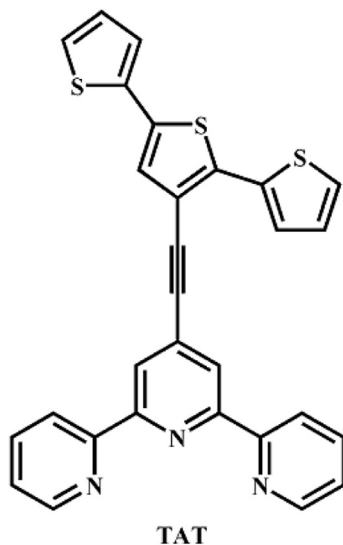
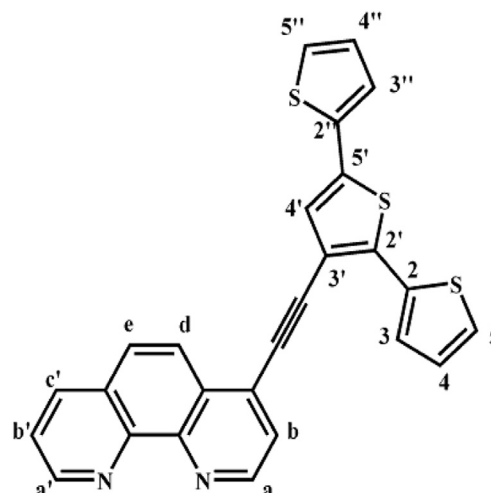


Chart 1. Structure of 4'-(2,2':5',2''-terthien-3'-ethynyl)-2,2':6',2''-terpyridine, TAT.

These results provide evidence that the unsaturated spacer is responsible for the improvement of electrochemical and luminescent behaviour, enabling the communication between the π -conjugated systems. We consider TAT as a starting point to further improve the conjugation extent, through the replacement of the terpyridine moiety with 1,10-phenanthroline, connected through 4 position to the ethynyl-terthiophene moiety.

Here we report the synthesis and characterization of 4-(2,2':5',2''-terthien-3'-ethynyl)-1,10-phenanthroline (TAF4) (chart 2). The electrochemical polymerization of TAF4, leading to the corresponding conducting polymer PTAF4, was also performed, and the electrochemical and optical characterization of the film is reported, together with the comparison with PTAT. Furthermore, the synthesis and the optical and electrochemical characterization of the Ru(II) complex with TAF4 ($[\text{Ru}(\text{TAF4})_3][\text{PF}_6]_2$) is reported.



TAF4

Chart 2. Structure of 4-(2,2':5',2''-terthien-3'-ethynyl)-1,10-phenanthroline, TAF4.

2. Experimental

2.1. Materials and measurement

All chemicals were purchased from Aldrich. 3'-(ethynyl)-2,2':5',2''-terthiophene (ET) was synthesized as previously reported [21]. 4-Cl-1,10-phenanthroline (4-Cl-phen) was available in our laboratory as a side-product of the preparation of the 2-chloro analogue [25]. $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ was obtained according to reference [26]. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in CD_2Cl_2 solution on a Varian VXR 300 or on a Bruker Avance III 400 spectrometer. The ^1H and ^{13}C chemical shifts are referred to the solvent signal at 5.32 ppm and 53.84 ppm, respectively [27]. IR spectra were recorded on a JASCO FT/IR-480 Plus by using KBr disks in the range 4000–400 cm^{-1} . Melting points were determined with a BÜCHI 530. Elemental analyses were performed on a Perkin–Elmer 240B analyser. Electrochemical characterizations were performed with an Autolab PGSTAT12 (Ecochemie) potentiostat/galvanostat interfaced with a PC under GPES software. All electrochemical tests were carried out in a single-compartment three-electrode cell, at room temperature, under Ar atmosphere. A 2 mm diameter Pt disk electrode was used as the working electrode, an aqueous Ag/AgCl with suitable salt bridge was the reference electrode, and a graphite rod was the auxiliary electrode. The working electrode was polished subsequently with 1 and 0.3 μm alumina powder and then rinsed with distilled water in an ultrasonic bath for 5 min before use. All the experiments were carried out in CH_3CN (Aldrich, anhydrous, 99.8% pure, packaged under nitrogen) and in CH_2Cl_2 (Aldrich, anhydrous, >99.8%, packaged under nitrogen), using 0.1 M tetraethylammonium hexafluorophosphate (TEAPF_6 , Fluka, puriss, electrochemical grade >99%) as supporting electrolyte. The UV-Vis spectra were recorded using a Hitachi U-2010 UV-visible spectrophotometer. The film thickness (d) was estimated assuming a proportional relationship between d and the electrodeposition charge Q_{dep} , that is $d \text{ (nm)} = \alpha Q_{\text{dep}} \text{ (mC/cm}^2\text{)}$, with $\alpha = 2.5 \text{ nm cm}^2/\text{mC}$ [28]. Scanning electron microscopy (SEM) analysis was performed on LEO 1530 instrument. Doping levels (x) were calculated according to the equation $x = Q_{\text{CV}}/(Q_{\text{dep}} - Q_{\text{CV}})$ [29], where Q_{CV} is the charge obtained integrating p- or n-doping wave and Q_{dep} is the charge passed during the electropolymerization process.

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