

Metal ion binding of photoactive poly-(arylene ethynylene) co-polymers

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ABSTRACT

The metal ion binding properties of three photoactive poly-(arylene ethynylene) co-polymers with potentially complexing units have been described. Upon protonation or complexation, the intensity of the luminescence typical of these conjugated polymers is completely quenched, due to the extended electronic conjugation of the polymer backbones. In the case of the formation of complexes with Yb³⁺ and Er³⁺, one of the studied polymers gives rise to an efficient sensitization of their typical metal centred NIR emission. This feature is of particular interest for the preparation of new materials that are the subject of active research for their possible applications in optical imaging and in optical amplification for telecommunication purposes.

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1. Introduction

A great development of electronic devices based on organic materials (molecular and polymeric), has taken place in the past few years, and their use, in place of the traditional inorganic semiconductors, has opened the way to industrial applications and consequently to a potential market [1,2]. The increasing interest toward organic materials is also due to their synthetic flexibility, the variety of their physical and chemical properties, the high compatibility with microelectronic technology and their low cost. In order to prepare efficient electroactive organic materials, an extended electronic conjugation, spanning along the entire molecular backbone, must be present. This characteristic induces suitable optoelectronic properties that can allow their use as molecular functional materials for many innovative applications, one of the most interesting being related to the development of chemical sensors [3].

The sensing ability of these materials is generated by a combination of two main effects that are cooperating to magnify the analytical response: (i) the electron density delocalized along the

molecular backbone – and relative properties – could be perturbed upon interaction with electron acceptor and/or donor groups (analytes); (ii) the conformational changes occurring in the molecular backbone upon interaction with an analyte may disrupt the π -overlap resulting in a decrease of the effective conjugation and thus affecting the related electronic properties. As a result of these interactions, assessable electric and optical signals can be generated.

In particular, the use of conjugated polymers for sensing purposes presents a considerable advantage: their excellent amplification ability. Due to the extended electronic conjugation of the polymer backbones, minor perturbations of the structural and electronic properties cause dramatic changes of their luminescence and/or conductivity responses, resulting in a high sensitivity. Often, it is sufficient that a single molecule of a given analyte is bound to one of the many receptor sites of a polymeric chain, to completely suppress the fluorescence of a whole polymeric chain. As a consequence, molecular recognition sites for specific analytes bound to a conjugated polymer amplify the sensing response compared to that of individual receptors. Moreover, the amplification ability of the conjugated polymers in sensor devices becomes especially relevant considering the often very small quantities of detectable analytes.

In addition, the possibility to modify organic compounds from a synthetic point of view, by introducing different functional groups, can open the way for the enhancement of the affinity of the sensing

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material towards a particular class of analytes, and consequently to modulate the selectivity of the resulting sensor. As a result of all these features, the use of conducting polymers in the field of chemosensing and biosensing has received much attention in recent years [4–7].

Poly-(arylene ethynylene)s (PAEs), polymers [2a,8,9] made of alternating aryl and ethynyl units, are currently representing one of the most important classes of materials to be used for sensing purposes, and recently Swager has reviewed different uses of PAEs as active element in the construction of sensors and biosensors based on colorimetric and fluorescence based methods [3].

In the framework of this research field, we have discovered and well exploited a new synthetic protocol named extended one pot (EOP), allowing a convenient access to PAEs of type $[-C\equiv C-A-C\equiv C-B-]_n$. In particular, this procedure is very effective in the introduction of different aromatic sub-structures (or “modules”) in the polymer sequence ($A=Ar$, $B=Ar'$) thus allowing numerous combinations of different structural motifs within the same polymer backbone. In this respect the A unit is generally a “module” impressing mechanical strength, chemical stability and processability (solubility, fusibility, filmability) to the polymer, while the B unit (or “module”) is chosen among the most suitable chemical structures to show sensing properties toward the material to be detected. This strategy has been called “The A - B modular approach” [10].

In the present work pyridine, phenanthroline and dithiophene moieties have been chosen as B units to be introduced in the polymeric backbone in order to obtain materials showing sensing properties toward proton and a range of heavy metal ions. As a term of blank reference a *co*-polymer containing a B “module” incapable of binding actions, such as the anthracene unit has been also prepared.

The determination of heavy metal ions is of great scientific, medical and economic interest, since they cause significant adverse long-term health effects, even upon exposure to trace concentrations. Therefore, chemosensors capable to quantitatively detect these species could be employed in many fields such as in environmental control, in verifying the safety of drinking water and food and in monitoring many important industrial processes. Toward this goal the fundamental mechanisms ruling the energy and electron transfer related with the sensoristic properties of this class of conjugated polymers have been investigated and reported hereafter.

2. Experimental

The solvents used for photophysical measurements were dichloromethane, chloroform, and acetonitrile from Merck (UVA-SOL) without further purification. Absorption spectra in solution were recorded on a PerkinElmer Lambda 40 spectrophotometer. Uncorrected emission, corrected excitation spectra and excited-state lifetimes were obtained with a modular Edinburgh FLS920 with a Hamamatsu R928 as photomultiplier, equipped with a single-photon counting apparatus. Corrections for instrumental response, inner filter effects and phototube sensitivity were performed [11]. Concentration of the polymers were in the range 10^{-6} to 10^{-4} M in polymer repeating units; in our experimental conditions no aggregation was observed. Association processes were followed by monitoring changes in the UV-vis absorption or fluorescence spectra of ligand solutions titrated with increasing amounts of metal ions as perchlorate or triflate salts, as previously described [12].

The synthesis and characterization of polymers **P1–P4** have been already reported [10].

Molecular weights and polydispersity (MWD) of samples used in the present studies are reported in Table 1.

3. Results and discussion

The photophysical properties of the conjugated polymers **P1–P4** have been already reported in the literature [10]. The low energy absorption bands above 380 nm of the polymers **P1–P4** has been already attributed to delocalized π - π^* transitions, while the relatively weaker bands at higher energies has been attributed to a combination of delocalized and phenyl-localized π - π^* transitions [10]. In general, the conjugated polymers **P1–P4** present a very high fluorescence quantum yield and a very high absorption per repeating unit, two features that make these compounds very attracting as photoactive materials for sensors and labels [13]. On the other hand, the fluorescence bands have been attributed to localized states generated by the migration of excitations along the polymer main chains [4,14]. In particular, as mentioned in the introduction, the presence of possible coordinating units in three of them lead us to perform experiments in order to see the photophysical response of these materials in solution to the addition of protons and metal ions.

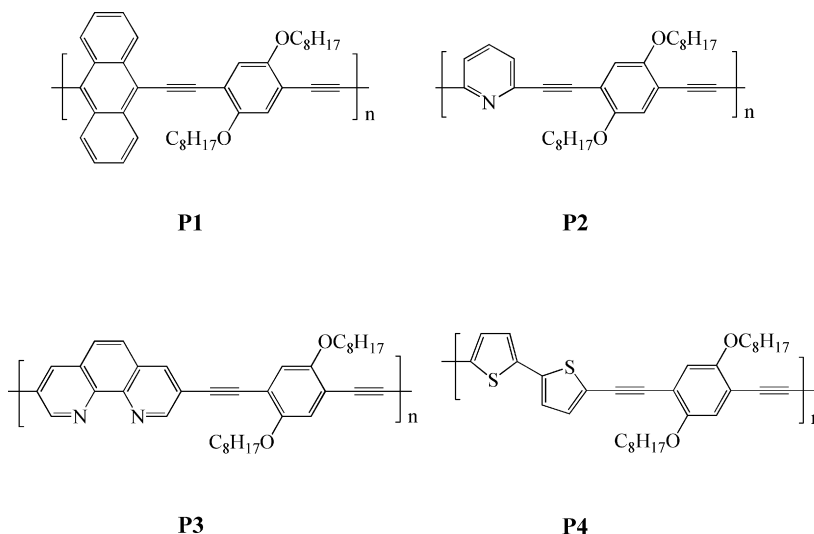


Table 1
Molecular weights for polymers **P1–P4**

Polymer	DP (M_w) ^a	DP (M_n) ^b	MWD ^c
P1	28	9	3.1
P2	15	8	1.8
P3	5	3	1.6
P4	23	10	2.2

^a Degree of polymerisation: calculated on the basis of the M_w value.

^b Degree of polymerisation: calculated on the basis of the M_n value.

^c Molecular weight distribution (M_w/M_n). M_w and M_n values determined by GPC (THF, polystyrene standard).

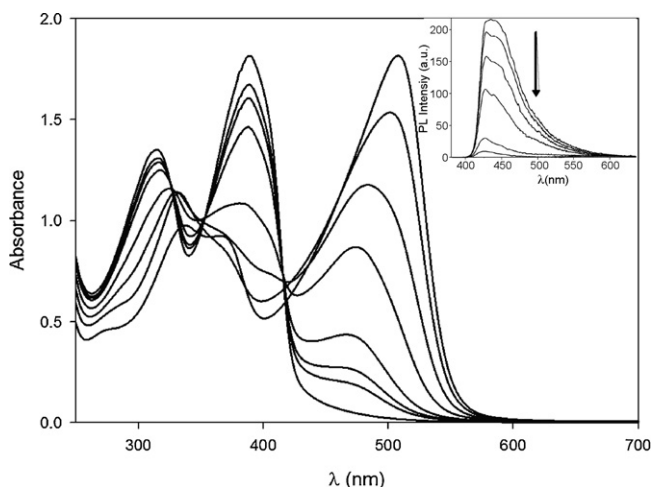


Fig. 1. Absorption spectra of **P2** 1.1×10^{-4} M (0.46 mg/L) in CH_2Cl_2 solution upon addition of an increasing amount of triflic acid. Inset: concomitant variations in the fluorescence spectra ($\lambda_{\text{exc}} = 315$ nm).

In this perspective, **P1** has been chosen to see if any response could be observed in a polymer without intrinsic coordinating units. In this case, the addition of an hundred-fold excess of Pb^{2+} , Hg^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} and of triflic acid did not cause any appreciable change neither in the absorption nor in the fluorescence spectrum. These results indicate that when the poly-(arylene ethynylene) *co*-polymers do not possess a coordinating unit, their affinity towards metal ions is very low also in apolar solvents, to such an extent that the effect of aspecific interactions can be neglected in these cases. These results are in agreement with those obtained with other amphiphilic poly-(arylene ethynylene) derivatives [15].

P2 was instead designed with the intent to obtain a material sensitive to the addition of protons, but with otherwise poor coordination capabilities, because of the steric hindrance caused by the

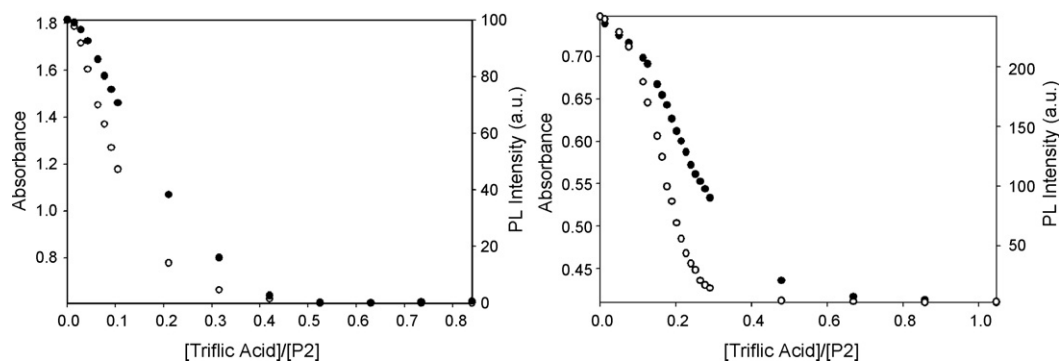


Fig. 2. Absorbance ($\lambda = 390$ nm, black circles) and fluorescence intensity ($\lambda_{\text{exc}} = 390$ nm; $\lambda_{\text{em}} = 420$ nm, white circles) profiles of a 1.1×10^{-4} M (0.46 mg/L) **P2** solution (a) or a 5.6×10^{-5} M (0.31 mg/L) **P3** solution (b) vs. added equivalents of protons.

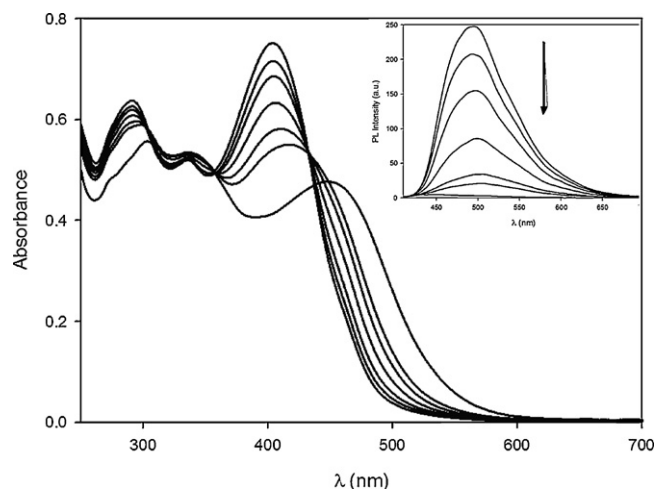


Fig. 3. Absorption spectra of **P3** 5.6×10^{-5} M (0.31 mg/L) in CH_2Cl_2 solution upon addition of an increasing amount of triflic acid. Inset: concomitant variations in the fluorescence spectra ($\lambda_{\text{exc}} = 400$ nm).

bulky substituents on the 2 and 6 positions of the pyridine rings. Addition of triflic acid to a dichloromethane solution of **P2** causes, in fact, dramatic changes in the absorption and in the fluorescence spectra. In particular, the lowest energy absorption band almost disappears, while a new very intense absorption band shows up at 510 nm (Fig. 1).

As far as the emission spectra is concerned, the addition of triflic acid leads to a quenching of the fluorescence (Fig. 1, inset). From a quantitative point of view, it is very interesting to note that upon addition of only 0.2 equiv. of acid per repeating unit the fluorescence decreases to a 13% of the initial intensity, and the complete quenching is observed after the addition of only 0.4 equiv. of acid (Fig. 2).

It is worth to note that for other conjugated polymers containing pyridine units, a red-shift [16] or no perturbation [17] had been observed increasing the concentration of protons in solution. A very similar quantitative pattern can be observed plotting the variations of one of the absorption maxima (Fig. 2). The absence of isosbestic points in the absorption spectrum (Fig. 1) and the presence of inflection points in the titration curves (Fig. 2a) indicate the coexistence of multiple equilibria, as expected because of the presence of many basic centres per single chain. Addition of Zn^{2+} , Hg^{2+} , and Cu^{2+} ions that are typically coordinated by not hindered pyridine derivatives, did not cause any appreciable change neither in the absorption nor in the fluorescence spectrum, indicating that **P2** is not able to coordinate such cations in these experimental conditions. On the contrary, **P3** contains five phenanthroline ligands

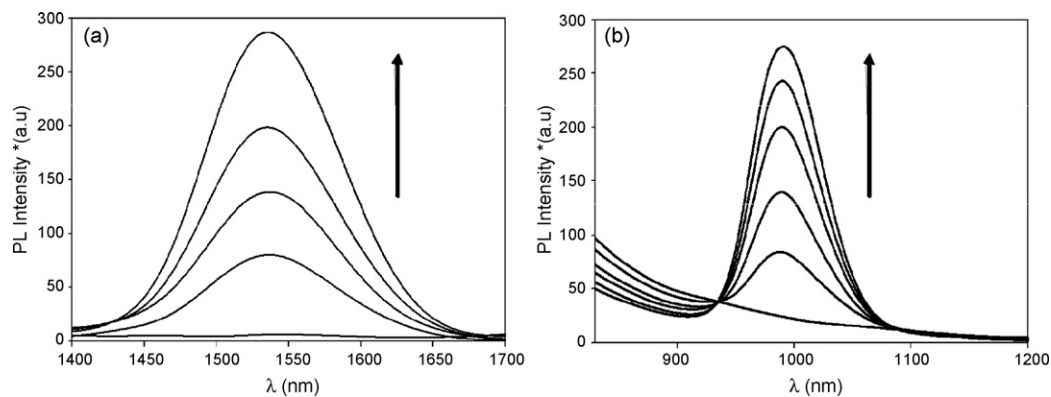


Fig. 4. Room temperature emission ($\lambda_{\text{exc}} = 400 \text{ nm}$) spectra of a $5.6 \times 10^{-5} \text{ M}$ (0.31 mg/L) CH_2Cl_2 solution of **P3** upon addition of increasing amounts of $\text{Er}(\text{NO}_3)_3$ (a) or $\text{Yb}(\text{NO}_3)_3$ (b).

per chain and they are substituted in the 3 and 8 positions. This causes a much less steric hindrance around the two coordinating nitrogen atoms that are able, in this case, to interact also with metal ions. The changes in the absorption spectra upon addition of triflic acid to a solution of **P3** are reported in Fig. 3 that clearly shows how protonation causes a bathochromic shift of the band peaking at 400 nm, and a concomitant decrease of its intensity.

It is to note that the typical band of the protonated form of **P3** is at higher energy and presents a lower intensity as compared with the band observed for the protonated form of **P2**. The protonation process leads, at the same time, to a complete quenching of the fluorescence band (Fig. 3). Also in this case, the complete quenching occurs after the addition of only 0.4 equiv. of acid per repeating unit, although it is to note that the intensity is fivefold reduced after the addition of only 0.2 equiv., a behaviour that is very similar to the one showed by **P2** (Fig. 3). In the case of **P3**, also the addition of several metal ions induces noticeable changes in its photophysical properties. In particular, we added Zn^{2+} , Cu^{2+} , and Hg^{2+} because of their relevance in environmental analysis, and Tb^{3+} , Eu^{3+} , Yb^{3+} , and Er^{3+} to see if it were possible to induce in the polymer an antenna-like behaviour populating the luminescent metal-centred excited state typical of each of these lanthanide complexes. In all cases, the addition of the metal ion caused a bathochromic shift of the band peaking at 400 nm, similar to the one observed upon the addition of triflic acid and almost independent on the metal ion added. At the same time, in all cases the polymer own fluorescence was completely quenched, in general upon the addition of one metal ion every 10 phenanthroline units. Interestingly, at 77 K **P3** shows a phosphorescence band at ca. 600 nm, this band is not quenched by the addition of Zn^{2+} , Cu^{2+} , Hg^{2+} , and Tb^{3+} even in large excess. On the other hand, at room temperature the addition of Yb^{3+} and Er^{3+} ions induces the appearance of a new luminescence band with maximum at 980 and 1530 nm, respectively (Fig. 4). These new luminescence bands can be attributed, thanks to their typical energy, to a metal centred transition. It is to note that the excitation spectra with $\lambda_{\text{em}} = 980$ and 1530 nm for Yb^{3+} and Er^{3+} , respectively, are proportional to the absorption spectra of the complexed polymer. These results clearly support the occurrence of a very efficient energy transfer process from the polymer chain to the metal ions. These luminescence bands can be observed also at 77 K, together with the disappearance of the typical phosphorescence of the conjugated polymer. In these experimental conditions it has also been possible to observe the metal centred luminescence of the Eu^{3+} ions, and also in this case the excitation spectrum matches the absorption one (Fig. 5). On the contrary, at room temperature the addition of europium ions causes only the decrease of the fluorescence intensity of **P3**, without any sensitization of the metal centred luminescence.

To understand the reasons why the protonation of **P2** and **P3** and the complexation of the latter polymer lead to the complete quenching of the polymer own fluorescence it is important to consider that this effect is observed also when energy transfer and reductive or oxidative electron transfer processes involving the complexed species cannot occur, as in the case of H^+ , Zn^{2+} , and Cd^{2+} , since these species do not usually introduce low energy metal (proton)-centred or charge separated excited state into the molecule [18].

However, as revealed by the changes in the absorption spectra, the complexation processes cause a change in the electronic density, leading to a lower energy excited state centred on the polymeric structure. This singlet excited state, that is clearly not emissive, it is likely to have a charge transfer character, since part of the electronic density of the electron rich not complexed units can be transferred, upon absorption of a photon, to the electron poor complexed species. It is important to note that in the case of typically quenching ions such as Cu^{2+} , more efficient energy- or electron-transfer processes involving the metal ion cannot be ruled out. Fig. 3 shows that in general the protonation of only one unit in **P3** is sufficient to quench the luminescence of the whole polymer, leading to signal amplification effect. As indicated by Zhou and Swager [19] the origin of this effect is the facile energy migration throughout the polymer: an exciton is delocalized over many chromophores in the polymeric receptor, and it is enough that only one of the receptors binds to the analyte, for the fluorescence of the whole chain to be totally quenched and, as a consequence, an enhanced effect is observed. In the case of addition of metal ions to

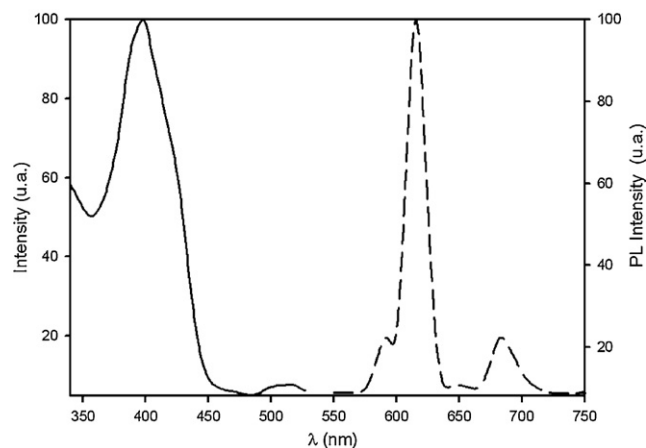


Fig. 5. Emission ($\lambda_{\text{exc}} = 400 \text{ nm}$) and excitation ($\lambda_{\text{em}} = 615 \text{ nm}$) spectra of a $5.6 \times 10^{-5} \text{ M}$ (0.31 mg/L) CH_2Cl_2 solution of **P3** at 77 K after the addition of one equivalent of $\text{Eu}(\text{NO}_3)_3$ per repeating unit.

P3, one single ion is able to quench 10 repeating units, and this can be attributed to the formation of a complex in which each metal ion is surrounded by two different polymeric chains.

The formation of complexes emitting in the NIR region is in turn of interest because materials presenting high luminescence in this spectral region can find applications in optical imaging, and in the constructions of optical amplifiers and light emitting diodes [20–23]. The observation of sensitized NIR emission in the case of the complexation of Yb^{3+} and Er^{3+} ions, is proven by the correspondence of the excitation spectrum with the absorption spectrum of the complexed species. This feature is of particular interest in this context, especially since the examples of conjugated polymers luminescent in the NIR region are to date quite rare [24]. As observed for many molecular coordination compounds [25], the sensitization process can occur through the triplet state centred on the polymer structure, since this is the lowest excited state observed when Zn^{2+} (no metal centred excited state) and Tb^{3+} (higher energy metal centred excited state) are coordinated. The lack of any luminescence at room temperature for the Eu^{3+} complexes can be due, in turn, to the presence of a charge separated state, involving the reduction of the metal ions, as already observed in many molecular complexes of this kind [25].

As far as the fluorescence of **P4** is concerned it is affected only by the addition of mercury ions; in this case, however, only a weak decrease of the intensity could be observed, accompanied by very small changes in the absorption spectrum. These results are very similar to those obtained with polythiophene containing thymine moieties [26], but in comparison with the results obtained with **P3**, a much lower affinity and no signal amplification had been observed. This indicates that one of the repeating “modules” of the conjugated polymer has to present good complexing properties, in order to obtain suitable materials for practical applications.

4. Conclusions

In this paper we have described the metal ion binding properties of four photoactive poly-(arylene ethynylene) *co*-polymers, without (**P1**) or with (**P2–P4**) good complexing units. Upon protonation of **P2** and upon protonation or complexation of **P3**, the intensity of the typical luminescence of these conjugated polymers is completely quenched, with a noticeable amplification effect, a very valuable feature for the design and preparation of efficient chemical sensors [13,19,27]. Furthermore, the observation of efficiently sensitized NIR emission upon addition of Yb^{3+} and Er^{3+} ions to a solution of **P3** is very interesting for the preparation of new materials with luminescence properties in this spectral region, because of their importance in optical imaging and in optical amplification for telecommunication purposes.

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