

# Metal ion interaction with a novel anthracene pendant-armed fluorescent molecular probe. Synthesis, characterization, and fluorescence studies

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## Abstract

A new scorpionate system (**L**) containing an emissive anthracene pendant arm, derived of *O*<sup>1</sup>,*O*<sup>7</sup>-bis(2-formylphenyl)-1,4,7-trioxahep-tane and tren, has been synthesized and characterized. The sensing capability of **L** towards a range of metal ions has been studied. Protonation and complexation studies, using UV–Vis and fluorescent emission measurements, have been performed with alkaline and alkaline earth metal ions (M = Na(I), K(I), Li(I), Ca(II), Mg(II)), as well as transition and post-transition metal ions (M = Cr(III), Cu(II) and Zn(II), Cd(II), Hg(II) and Al(III)). An increase in the fluorescence emission (CHEF effect) was observed in methanol and in methanol/water mixtures in the presence of Cd(II) (5.0-fold), Zn(II) (4.5-fold), Cr(III) (2.0-fold) and Al(III) (1.8-fold); these results suggest a notable sensing ability of this new N<sub>3</sub>O<sub>4</sub> ligand for these metals; these experiments were also performed in the presence of large amounts of alkaline and alkaline earth metal ions.

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**Keywords:** Fluorescence probes; Anthracene; Macrocycles; Metal complexes

## 1. Introduction

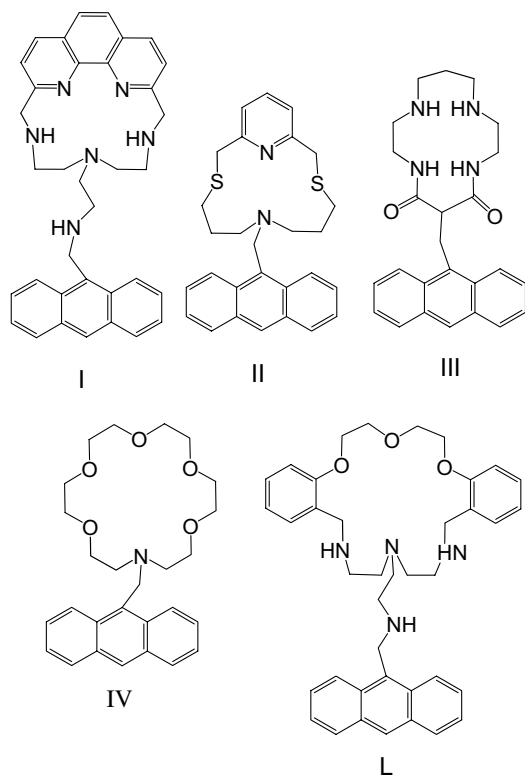
A considerable number of papers have focused on the use of anthracene containing compounds as protein photo cleavers [1], organic light-emitting diodes and materials [2], crystal engineering [3], molecular imprinted polymers [4], sensors and chemosensors [5]. Anthracene is one of the most employed chromophores due to its ability to induce PET (photoinduced electron transfer) processes. Czarnik and coworkers were among the pioneers in molecular

probes containing anthracene [6]. These abiotic receptors can be synthesized by covalently linking a fluorophore to a receptor unit [7]. Following this synthetic strategy many related molecules appropriate for metal ion and anion detection have been reported in the literature [8–10].

Scheme 1 depicts several scorpionate ligands containing anthracene which have been successfully used for metal ion chelation. The modification of the nature of the donor atoms in the macrocycle produces changes on the sensing capabilities of the ligands. In the polyaza phenanthroline ligand(I), Bencini and coworkers [11] have described a nice elementary molecular movement upon coordination with Zn(II); this system coordinates also Cd(II) and Hg(II), but no excimer formation between the phenanthroline and the anthracene moieties was observed. We have

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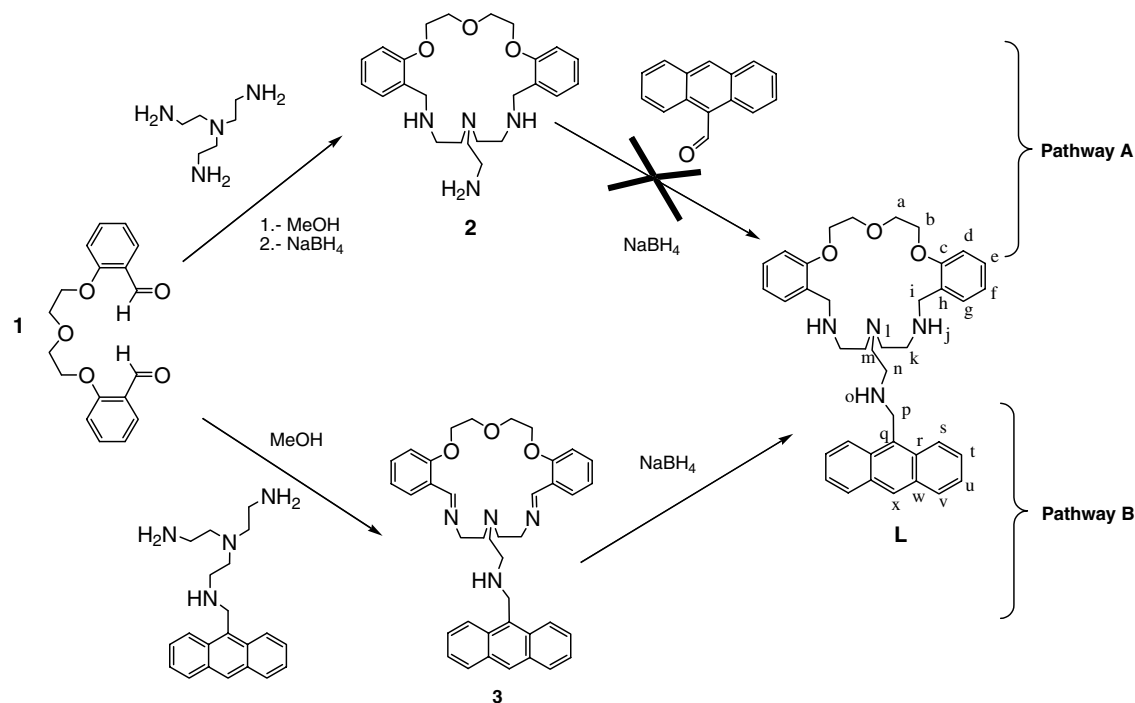
Scheme 1.

recently reported the interactions of Cu(II), Co(II), Ni(II), Zn(II) and Pd(II) with the thiaza macrocycle II [12]; the presence of sulfur atoms increases the affinity for soft metal ions. The oxa-aza system III is an elegant example of on/off behavior in the presence of Cu(II) and Ni(II) [13]; the N

containing ring is capable of incorporating the metal ion with simultaneous release of two amide protons, which provokes a photoinduced electron transfer process, resulting on the quenching of the fluorescence emission of the anthracene. When sufficient number of oxygen atoms are incorporated into the macrocycle skeleton, the interaction with alkaline and alkaline earth metal ions can be studied. de Silva and de Silva reported in the late eighties the system IV as fluorescent sensor for K(I) [14]. In the absence of the metal ion, the system is not emissive due to an electron transfer process from the tertiary amine nitrogen to the near excited anthracene fragment; complexation with K(I) restores the fluorescence by the involvement of the nitrogen lone pair.

We have recently reported macrocyclic ligand **2** (Scheme 2) derived from *O*<sup>1</sup>,*O*<sup>7</sup>-bis(2-formylphenyl)-1,4,7-trioxaheptane and tren containing an amine terminal pendant arm [15]. In the pH range 7–9, this ligand shows a 10-fold fluorescence emission increase in water solution in the presence of Zn(II). This result suggests that, in water solution, **2** is a good sensor for this metal ion of biological relevance. Fluorescence emission of system **2** complexed with Zn(II) was not affected in the presence of alkaline or alkaline earth metal ions. We have also reported the protonation and complexation reactions of **2** in the presence of Cd(II) and Cu(II) [15].

Herein we report the synthesis and characterization of a related new functionalized anthracene pendant armed macrocyclic ligand (**L**) and its protonation and complexation reactions. The interaction of **L** with alkaline and alkaline earth ions ( $M = \text{Na(I)}, \text{K(I)}, \text{Li(I)}, \text{Ca(II)}, \text{Mg(II)}$ ), and transition and post-transition ions ( $M = \text{Cr(III)}, \text{Al(III)}$ ),



Scheme 2.

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