

Spectroscopic and photophysical studies of a naphthalene-based emissive probe for metal cations



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ABSTRACT

A comprehensive photophysical characterization of a bis-naphthalene derivative, **L**, was carried out in acetonitrile, using UV–Vis absorption, steady-state and time-resolved emission spectroscopy. It was found that in the 250–400 nm region, the absorption spectra showed two bands with maxima at ~220 nm and ~292 nm whereas the emission spectrum showed a band settled between 300 and 550 nm. A detailed time-resolved investigation (in the ps and ns time domain) showed that the fluorescence decay of **L** in dichloromethane was bi-exponential indicative of the presence of a ground-state equilibrium involving two species: monomeric (absorption of a single naphthalene unit) and dimeric. Upon addition of Cu²⁺, Zn²⁺, Cd²⁺ or Hg²⁺ metal cations in acetonitrile a quenching of the fluorescence emission was observed. From time-resolved data, it is shown that the fluorescence contribution of the species with the longest decay time was sensitive to the explored metal ions.

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Metal cations are important for the functioning of the organism; however, when in excess they can cause serious health problems. In particular, excess of copper can cause severe health problems such as irritation, headaches, dizziness, nausea and diarrhea when ingested in small (yet excessive) amounts and ultimately can lead to liver, kidney damage and even death in large amounts. In turn, zinc in excess is associated with epilepsy, Alzheimer's and Parkinson's diseases, ischemic stroke and infantile diarrhea [1]. Accumulation of mercury in the body is responsible for several complications such as prenatal brain damage, serious cognitive and motion disorders and Minamata's disease [2] while cadmium can lead to kidney disease, lung damage and fragile bones.

The main source of these metals occurs through contaminated water and food due to pollution of soils and ground-waters. Due to the harmful effects of these metals (and others) and with the ultimate goal of finding analytical sensors with wide applicability, capable of detecting selectively small amounts of metal cation, preferably cheap and

recoverable for subsequent application, more accurate ways to detect and determine their concentrations have been the subject of recent investigations.

Molecular scale sensors (probes) emerge within this type of molecules; they consist of compounds that when interact with a given analyte cause a chemical change which in turn induces a change in a measurable property. Depending on the measurable property, the probe can be classified as electrochemical, electronic, optic, etc. From these, particular attention must be given to the optic sensors, i.e., sensors that cause changes in optical parameters such as absorption, luminescence (fluorescence and/or phosphorescence) and refractive index. Within these parameters, inducing changes in the fluorescence emission is one of the advantages since fluorescence spectroscopy is highly sensitive, it is easily performed [3], does not require a reference nor the analyte is consumed [4], has a quick response [5] and different assays can be designed based on different aspects of the fluorescence output (lifetime, intensity, anisotropy and energy transfer) [4].

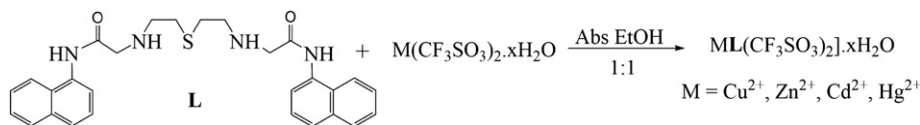
The interaction of a ligand to an analyte can induce several changes as (red or blue) shifts of the maxima band (from the absorption or/and emission spectra) which can induce color changes in the visible region, quenching or enhancement of the fluorescence spectra, appearance or disappearance of bands, etc. This changes can be caused by different mechanisms such as photoinduced electron or charge transfer (PET or PCT) [6,7], excimer or exciplex formation [8–10], fluorescence

Abbreviations: A. C., autocorrelation; L, ligand; M, metal; ps, picosecond; TCSPC, time-correlated single photon counting.

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Scheme 1. Synthetic route of the metal complexes derived from **L**.

resonance energy transfer (FRET) [11], internal charge transfer (ICT) [12, 13], and excited state intramolecular proton transfer (ESIPT) [14,15,16].

The synthesis of chemical probes highly sensitive and selective to the detection of transition metals (M) such as Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} ions has increasingly attracted the attention of several scientific fields [17] in particular medicine and environment [18].

Among the various methods for detecting cations, fluorescence spectroscopy is a technique widely used both for its versatility [6], high sensitivity and selectivity [7,19]. Indeed, the detection ability is associated with the interaction between the unit responsible for the selective binding of ions – ionophore – and the unit which regulates the signal transduction – fluorophore, which may result in an increase/decrease in the fluorescence intensity of the probe [6]. Several factors make fluorescence one of the most important ways for understanding the mechanisms of chemical events in the scope of recognition, among these are the possibility of studying it analytically, since this technique (i) is highly sensitive, (ii) does not consume the analyte, and (iii) does not require a reference [20]. The applications of fluorophores based on the naphthalene chromophore range from biological markers to the development of detection systems and materials for light-emitting diodes. The naphthalene structure has a low molecular weight and its (spectroscopic and photophysical) properties strongly depend on the number, type and position of substituent groups in the ring. Although the unsubstituted naphthalene is poorly fluorescent ($\phi_F = 0.23$ in cyclohexane) [21], if electron donor and acceptor groups are placed, for example, in positions 2 and 6 of the naphthalene ring, a significant increase in fluorescence is obtained by intramolecular charge transfer [22].

An emissive molecular probe bearing two naphthalene units at the extremities was already investigated in the past by some of us [23]. The probe interaction with cations (such as Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+}) and anions (F^- , Cl^- , Br^- , I^- and CN^-) was explored in DMSO where it showed to be remarkably selective for Cu^{2+} and to interact with CN^- and F^- .

Following our research interest on the design of new emissive compounds [20,24–27] and metal complexes [28–30], in this work, the photophysical properties of another symmetric probe **L**, with two naphthalene units in the extremities as well, were described together with its interaction (aiming chemoselectivity) with Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} metal ions in acetonitrile.

Compound **L** was synthesized according to the method previously reported by us [31]. Molecular probe **L** was found to be soluble in dichloromethane, dimethylsulfoxide, N,N'-dimethyl formamide, acetonitrile, ethanol, cyclohexane and dioxane and insoluble in water. In the solid state, **L** presents a brown color but within the concentrations of ligand in the solvents used, the solution is colorless.

The presence of seven, properly positioned, donor atoms ($\text{N}_4\text{O}_2\text{S}$) in the ligand structure of **L** (Scheme 1) should give strong recognition ability towards different metal ions. In that case, the coordination ability of ligand **L** towards hydrated triflate salts of Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} was explored. For the preparation of the complexes $[\text{ML}(\text{CF}_3\text{O}_3\text{S})_2] \cdot x\text{H}_2\text{O}$, ligand **L** (1 eq) and $\text{M}(\text{CF}_3\text{O}_3\text{S})_2 \cdot x\text{H}_2\text{O}$ (1 eq) ($\text{M} = \text{Cu}^{2+}$, Zn^{2+} , Cd^{2+} and Hg^{2+}) were mixed in absolute ethanol. After 4 h, the solvent was partially removed to ca. 5 mL and diethyl ether was infused into the residue resulting in the formation of a powdery precipitate that was separated by centrifugation and discarded [32]. The solid metal complexes were isolated from the evaporation of the remaining solutions. The complexes were characterized by elemental analysis, IR and MALDI-MS spectra [33]. MALDI-MS spectra of the metal complexes display peaks that

confirm the formation of these species. In the IR spectra of the complexes, the band due to the $[\nu(\text{C}=\text{O})]$ and $[\nu(\text{N}-\text{H})]$ stretching modes is shifted to higher wavenumbers when compared to its position in the spectrum of the free ligand (IR (cm^{-1}): $\nu = 1430$ ($\text{C}=\text{C}$), 1666 ($\text{C}=\text{O}$), 2980 ($\text{N}-\text{H}$)) [31]. Both effects suggest that in solid state the carbonyl and the amine groups presented on compound **L** could be involved in the coordination to the metal ion.

Fig. 1 shows the (normalized) absorption and fluorescence (excitation and emission) spectra of ligand **L** in acetonitrile [34]. Due to its miscibility with water, we select acetonitrile as solvent for the development of the spectroscopic studies of **L**. A single band is observed in the absorption which matches (maxima at the same wavelength) with the excitation spectra collected at $\lambda_{\text{em}} = 350$ nm. However, the excitation spectrum is broader, clearly mirroring the presence of dimers or higher order aggregates. Very interesting is also to note that the excitation spectra when collected at $\lambda_{\text{em}} = 450$ nm, presents an “absorption” band between 300 and 425 nm (Fig. 1). This is indicative that at longer emission wavelengths the absorption (although with a small molar extinction value) of a dimer is likely to be present. Indeed when exciting at the tail of the absorption band (330 nm) the obtained emission spectra are different than when excitation is at $\lambda_{\text{exc}} = 290$ nm, see Fig. 1 (right hand panel).

The spectral and photophysical properties of **L** are summarized in Table 1 and include the molar extinction coefficient (ϵ), the fluorescence quantum yield (ϕ_F) and the radiative (k_R) and radiationless (k_{NR}) rate constants in several solvents.

In view of the values in Table 1, it can be seen that the ϕ_F value is low, indicating that the fluorescence is not an efficient route for the deactivation of the excited state of **L**, which is further attested by the small k_F value and high k_{NR} value; moreover, although there are some differences in the ϕ_F and τ_F values, the main deactivation is made through the radiationless deactivation channel ($k_{\text{NR}} \gg k_F$). This, however, is not limited to observing the interaction of this fluorescent ligand with metal cations.

A more detailed observation shows, however, that the absorption spectrum of **L** is red-shifted and broader when compared with naphthalene itself [35].

The presence of a dimer becomes more evident in the fluorescence decay obtained with excitation at 281 nm and collected at 340 nm and 500 nm (*data not shown*). In this case the global (simultaneous) analysis of the decays at 340 and 500 nm leads bi-exponential decays with the same decay times at different pre-exponential factors. It is worth reminding that the pre-exponential factors mirror the concentration at time zero of the associated species: the monomer and the dimer. Since the monomer emits preferentially at shorter wavelengths and the dimer at longer ones, the decay times should therefore be associated with monomeric (shorter decay component) and dimeric species (longer decay component). In addition, the absence of rising components (rise-time) suggests that the dimeric species is not formed in the excited state, but is already present in the ground state.

Upon the addition of the metal ions Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} to an acetonitrile solution of **L** [36], the vibronic progression of the monomer band (Fig. 2) changes, which is indicative of the formation of a complex involving the metal M and the ligand **L** (with its absorption beneath the emission spectra of the monomer).

Indeed, upon addition of different metal cations (M), a shift towards lower wavelengths in the absorption spectra likely due to a photoinduced charge transfer involving the metal and the ligand, MLCT [with

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