



# Coumarin derived chromophores in the donor–acceptor–donor format that gives fluorescence enhancement and large two-photon activity in presence of specific metal ions

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## ABSTRACT

Two coumarin derived dyes (compounds **L<sub>a</sub>** and **L**) have been synthesized in high yields by Schiff base condensation. On probing with a femtosecond laser, none of these compounds show any two-photon activity in the wavelength range, 760–860 nm. However, **L<sub>a</sub>** in presence of Zn(II) and **L** in presence of Mg(II), exhibit large two-photon absorption as well as emission in the same wavelength range. Theoretical calculations at the B3LYP functional with 6-31G\* and LanL2DZ mixed basis set under DFT formalism support experimental results.

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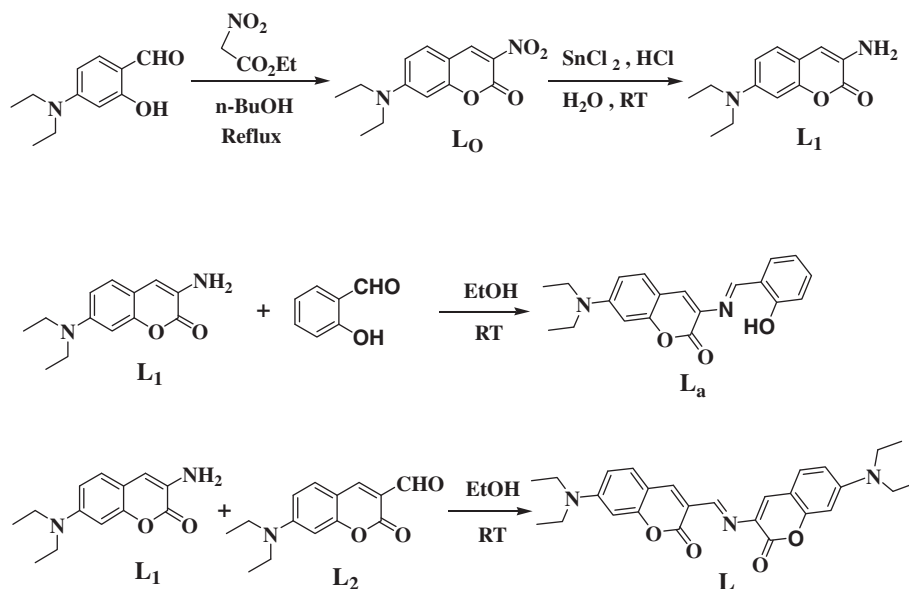
## 1. Introduction

Search for new molecular two-photon absorbing materials is currently of great interest because of their potential applications in several areas of opto-electronics [1]. Two-photon absorption (TPA) sensing materials with two-photon fluorescence have many advantages over the commonly used one-photon fluorescence materials. These include exclusive confinement of the excitation to the focal volume with high 3D resolution and reduced photobleaching by virtue of the low-energy NIR excitation with greater depths of penetration for biological applications. However, most of the fluorescent probes presently used for two-photon laser scanning microscopy are Mag-fura-2, Magnesium Green (MgG), and Oregon green 488 BAPTA-1 (OG) based on fluorescein or benzofuran as the fluorophore having small two-photon cross-sections ( $\delta < 50 \text{ GM}$ ,  $1 \text{ GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ ) [2]. Therefore, more efficient two-photon probes with large TPA cross-section are required for biological application. The selectivity and sensitivity demonstrated in these sensing materials is still need to be improved. Both theoretical considerations and experimental results led to the molecules with high TPA activity as the ones where donor and acceptor groups are symmetrically disposed resulting in a substantial symmetric intramolecular charge re-distribution

upon excitation [3]. These studies also reveal that the effect of molecular charge transfer symmetry, donor/acceptor group strength, chromophore number density and length of the conjugated  $\pi$  backbone are the most important factors affecting the molecular TPA activity [4]. These findings have led to molecules with D- $\pi$ -D, A- $\pi$ -D- $\pi$ -A and D- $\pi$ -A- $\pi$ -D (D = donor, A = acceptor,  $\pi$  =  $\pi$ -bridge) conjugated structural motifs. Metal ions can assemble organic ligands around to build a variety of multi-polar arrangements to tune the molecular NLO property [5] by virtue of inducing a strong intra-ligand charge transfer (ILCT) as well as low-energy metal-ligand charge transfer (MLCT) transitions. If large increment of TPA cross-section of organic molecules upon metal binding can be achieved, its scope in various opto-electronic applications can be increased. This can also be useful in reporting on the static concentration of a metal ion *in vivo* for understanding biological processes. Recently, a few fluorescence materials sensitive to metal ions working on the two-photon excited fluorescence principle, appeared in the literature [6]. The use of Mg(II) and Ca(II) for this purpose are fewer in number [7].

The development of fluorescence chemosensors with high selectivity and sensitivity for biologically important analytes has emerged as an important area of contemporary research [8]. In this respect, detection of Mg(II) in presence of Ca(II), Na(I), and K(I) as well as biologically relevant transition-metal ions is of particular significance. Mg(II) is one of the most abundant divalent ions in the cell and plays a crucial role in cell proliferation and cell death.

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Scheme 1. Synthetic route for **L** and **L<sub>a</sub>**.

It also participates in the modulation of signal transduction, various transporters, and ion channels [9–11]. On the other hand, Zn(II) is an essential nutrient required for normal growth and development [12] and for cellular processes such as DNA repair [13] and apoptosis [14]. This metal plays a key role in the synthesis of insulin and the pathological state of diabetes [15].

Herein, our discussion is focused on two coumarin-derived ligands **L** and **L<sub>a</sub>** (Scheme 1). Our interest in coumarin derivatives as fluorescence signaling systems stems from the fact that they have large Stokes shift upon metal binding as well as visible excitation and emission wavelengths [16]. Previously, we reported the bis-coumarin [17] derivative **L** acts as a fluorescence signaling system selectively for Mg(II). It is shown here that the free ligand **L<sub>a</sub>** exhibits low fluorescence due to excited-state intramolecular proton transfer (ESIPT) [18] but specifically in presence of Zn(II) ion high fluorescence is observed due to blockage ESIPT. We also report the TPA activity of the ligands in the metal-free state as well as in presence of metal ions. To support the experimental findings, DFT calculations are also carried out.

## 2. Results and discussion

The ligand **L** is synthesized by Schiff base condensation of two coumarin derivatives. The coumarin derivatives, **L<sub>1</sub>** and **L<sub>2</sub>**, are synthesized in several steps [17]. Synthesis of **L<sub>a</sub>** can be achieved very easily in 80% yield by Schiff base condensation of 2-hydroxybenzaldehyde with **L<sub>1</sub>**. All synthesized compounds are characterized by NMR, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis. The zinc complex, Zn(**L<sub>a</sub>**)(ClO<sub>4</sub>) (**1**) is characterized by ESI-MS<sup>1</sup> and elemental analysis. The magnesium complex, Mg(**L**)(ClO<sub>4</sub>)<sub>2</sub> (**2**), has also been synthesized and characterized by ESI-MS [17].

### 2.1. Electronic spectroscopy

All UV–Vis and fluorescence measurements are carried out in acetonitrile at room temperature while metal perchlorates are used as source of metal ions. The single photon absorption as well as fluorescence behavior of bis-coumarin derivative (**L**) alone and

in presence of the metal ions are described in our earlier report [17]. Metal free ligand **L<sub>a</sub>** shows an absorption maximum at 445 nm with a shoulder at lower wavelength due to intramolecular charge transfer (ICT) transitions [17]. On addition of Zn(II), these bands are appreciably red-shifted (Fig. 1a). An isobestic point is observed at 460 nm (Fig. 1b) on recording the spectra with varying concentrations of Zn(II) ion, indicating 1:1 complex formation.

Metal-free **L<sub>a</sub>** shows weak emission in MeCN when excited at 445 nm and no emission enhancement is observed upon addition of metal ions like Na(I), K(I), Ca(II) or Mg(II). Also, no enhancement in emission is observed in presence of first-row transition metal ions except for Zn(II) which leads to a large emission enhancement with a slight red-shift of the emission band (Fig. 2a). The fluorescence quantum yield steadily increases (Fig. 2b) upon addition of Zn(II). The maximum is reached upon addition of 1.2 equiv. of the metal ion. Association constant of the complex between ligand, **L<sub>a</sub>** and Zn(II) is determined [17,19] from absorption and fluorescence titration data afford a value of  $8.2 \times 10^4 \text{ M}^{-1}$ .

Binding of Zn(II) to **L<sub>a</sub>** prevents excited-state intramolecular proton transfer (ESIPT) [18] between the enol-imine and the keto-enamine forms (Scheme 2) leading to enhancement. Changing the solvent to EtOH or MeCN afford similar results. Emission responses of the ligand in presence of different metal ions are shown in Fig. 3 in the form of a bar diagram.

The nonlinear optical measurements were performed in the near-infrared region since it was clear from the UV–Vis spectra that the Schiff base (**L** and **L<sub>a</sub>**) and their metal complexes are transparent in this region. Two-photon absorption properties of Zn(II), Ca(II) and Mg(II) complexes are measured by two-photon induced fluorescence technique [20]. The solvent itself does not show any TPA activity under experimental conditions. The linear and nonlinear spectroscopic data of **L** and **L<sub>a</sub>** are summarized in Table 1.

The ligand does not show any measurable TPA activity even at  $10^{-1} \text{ M}$  solution in the 740–860 nm wavelength region. The ligands (**L** and **L<sub>a</sub>**) belong to the D- $\pi$ -A'- $\pi$ -D (**L**) and D- $\pi$ -A' (**L<sub>a</sub>**) analogue since the NO<sub>2</sub> site possesses very weak electron-withdrawing character. Addition of a metal ion like Ca(II), Mg(II) or Zn(II) results in significant two-photon action cross-section (Table 1). Complexation with Ca(II), Mg(II) or Zn(II), enhances the electron-acceptor character of the NO<sub>2</sub> moiety converting **L** and **L<sub>a</sub>** to a more strongly polarized D- $\pi$ -A- $\pi$ -D (**L**) and D- $\pi$ -A (**L<sub>a</sub>**) units (Scheme 3) affording high TPA activity.

<sup>1</sup> Supporting Information.

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