Inorganica Chimica Acta 363 (2010) 2824–2832

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

Debdas Ray, Amit Nag, Atanu Jana, Debabrata Goswami, Parimal K. Bharadwaj *

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

ARTICLE INFO

Article history:
Received 19 January 2010
Received in revised form 18 March 2010
Accepted 24 March 2010
Available online 27 March 2010

Dedicated to Animesh Chakravorty

Keywords:
Fluorescence
Optical nonlinearity
Sensor
Coumarin
DFT

ABSTRACT

Two coumarin derived dyes (compounds $\mathbf{L_a}$ 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, $\mathbf{L_a}$ 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.

1. Introduction

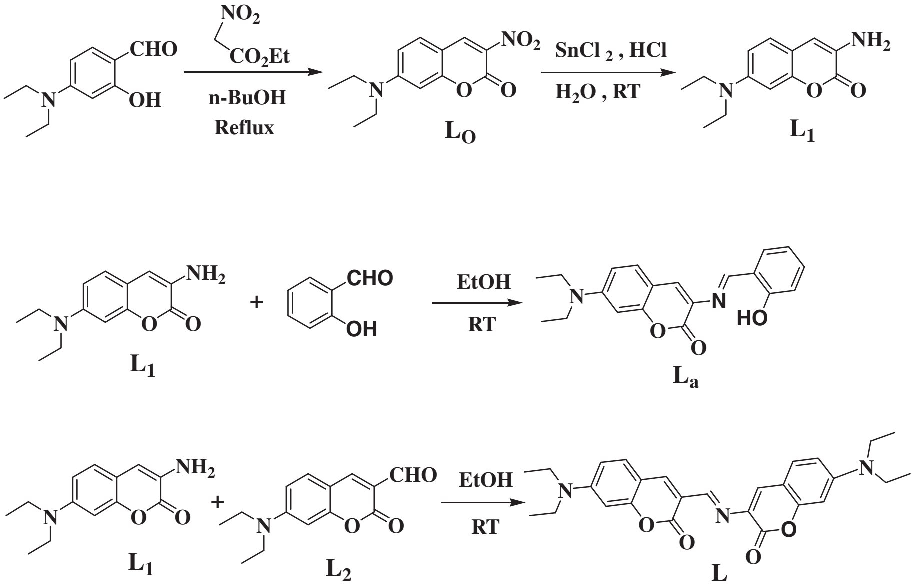
Search for new molecular two-photon absorbing materials is currently of great interest because of their potential applications in several areas of opto-electronics [1]. Two-photon absorption (TPA) sensing materials with two-photon fluorescence have many advantages over the commonly used one-photon fluorescence 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 ($\delta < 50$ GM, 1 GM = 1×10^{-50} cm^4 s photon^{-1} 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 π backbone are the most important factors affecting the molecular TPA activity [4]. These findings have led to molecules with D-π-D, A-π-D-π-A and D-π-A-π-D (D = donor, A = acceptor, π = π-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.

---

* Corresponding author. Tel.: +91 512 259 7034, fax: +91 512 259 7436.
E-mail address: pkb@iitk.ac.in (P.K. Bharadwaj).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.03.058



Scheme 1. Synthetic route for **L** and $\mathbf{L_a}$.

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 $\mathbf{L_a}$ (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 $\mathbf{L_a}$ 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, $\mathbf{L_1}$ and $\mathbf{L_2}$, are synthesized in several steps [17]. Synthesis of $\mathbf{L_a}$ can be achieved very easily in 80% yield by Schiff base condensation of 2-hydroxybenzaldehyde with $\mathbf{L_1}$. All synthesized compounds are characterized by NMR, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis. The zinc complex, Zn($\mathbf{L_a}$)(ClO_4) (**1**) is characterized by ESI-MS[1] and elemental analysis. The magnesium complex, Mg(**L**)$(ClO_4)_2$ (**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 $\mathbf{L_a}$ 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 isosbestic 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 $\mathbf{L_a}$ 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, $\mathbf{L_a}$ and Zn(II) is determined [17,19] from absorption and fluorescence titration data afford a value of $8.2 \times 10^4\ M^{-1}$.

Binding of Zn(II) to $\mathbf{L_a}$ 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 $\mathbf{L_a}$) 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 $\mathbf{L_a}$ are summarized in Table 1.

The ligand does not show any measurable TPA activity even at 10^{-1} M solution in the 740–860 nm wavelength region. The ligands (**L** and $\mathbf{L_a}$) belong to the D-π-A′-π-D (**L**) and D-π-A′ ($\mathbf{L_a}$) analogue since the NO_2 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_2 moiety converting **L** and $\mathbf{L_a}$ to a more strongly polarized D-π-A-π-D (**L**) and D-π-A ($\mathbf{L_a}$) units (Scheme 3) affording high TPA activity.

---

[1] Supporting Information.

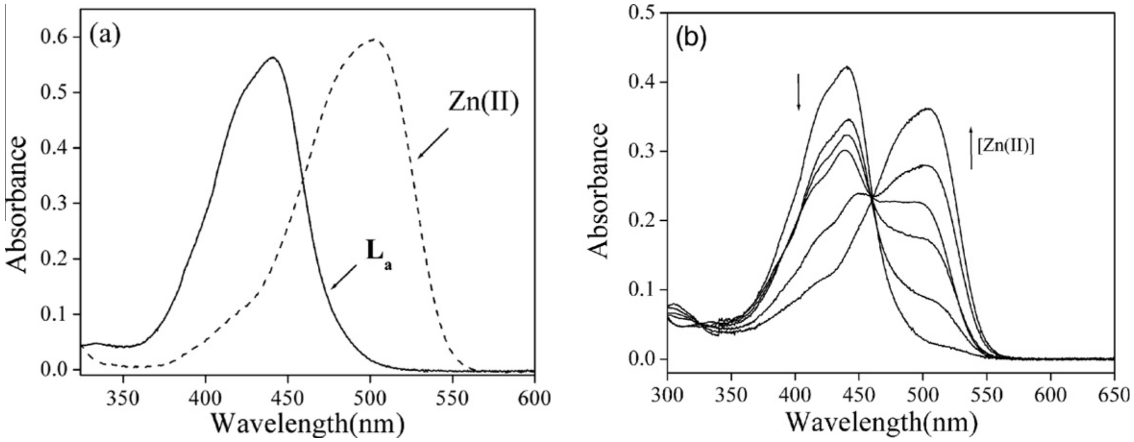


Fig. 1. (a) Absorption spectra of **L$_a$** (0.012 mM) alone and in presence of Zn(II) (0.12 mM) in ethanol. (b) Absorption spectra of **L$_a$** (0.01 mM) in ethanol at room temperature upon addition of increasing concentrations of Zn(II) ions (0–0.01 mM).

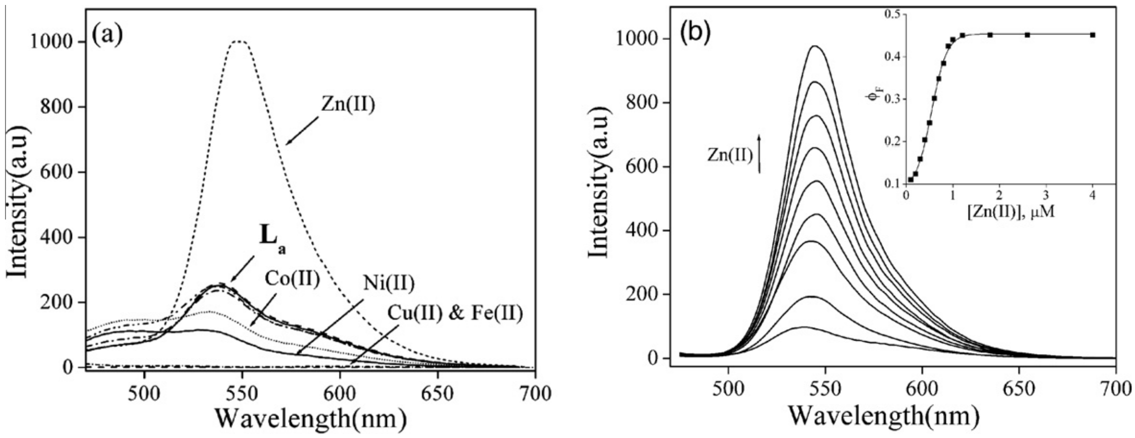
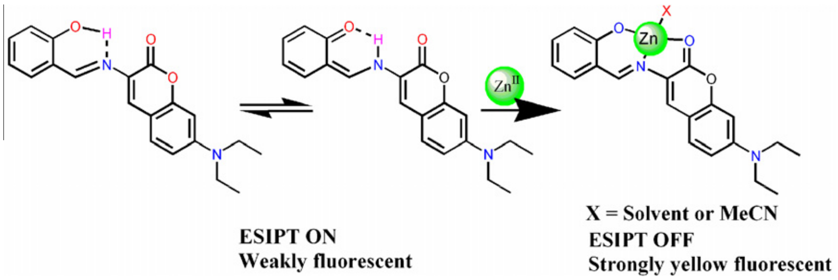


Fig. 2. (a) Fluorescence intensity change of **L$_a$** (0.25 μM) upon addition of various metal cations: 2.5 μM for Zn(II) and 25 μM for other metal ions in MeCN. (b) Fluorescence spectra (λ_{ex} = 460 nm) of **L$_a$** (1.2 μM) at room temperature upon addition of increasing amounts of Zn(II) ions (0–1.2 μM). Inset: Change of quantum yield upon addition of increasing [Zn(II)].



Scheme 2. Schematic representation of Zn(II)-induced fluorescence.

We also recorded the change in TPA cross-section values as a function of wavelengths for all the complexes of **L** and **L$_a$**. The TPA cross-section varies appreciably in the region, 760–860 nm for **L** in presence of Ca(II) or Mg(II) (Fig. 4a). Zinc complex of **L$_a$** also exhibit variation with wavelength (Fig. 4b).

Unfortunately, our experimental setup did not allow us to extend the measurements to higher wavelength beyond 900 nm. We have scanned the range, 740–900 nm and the maximum TPA cross-section values and their corresponding λ_{max} are shown in Table 1 separately. The results are graphically given in Fig. 4.

TPA titration experiment was carried out in 10^{-5} (M) acetonitrile solution at 860 nm. From the titration curve (Fig. 5) of ligand **L**, it is clear that upon addition of Mg(II) ion the TPA value gradually increases to a certain limit, and then further addition of the metal ion cannot change any significant TPA value, which indicates formation of 1:1 complex and saturation thereafter.

The increased fluorescence quantum yield [17] in [**L**·Mg(II)] complex is possibly the factor responsible for large two-photon action cross-section compared to the [**L**·Ca(II)] complex. The association constants of the complexes between ligands and metal cations

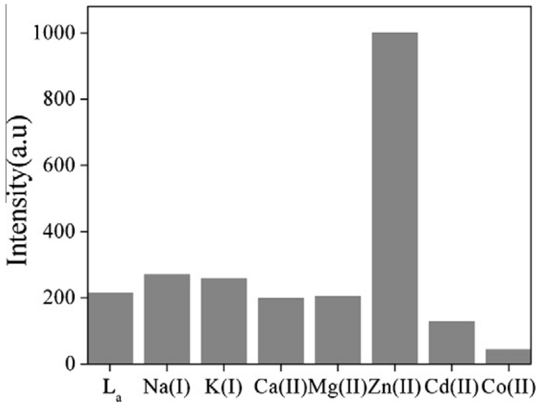


Fig. 3. The emission response of compound $\mathbf{L_a}$ (1 μM) to metal solutions (20 μM) in ethanol. Excitation was at 445 nm.

determined [17,19] from absorption and fluorometric titration data give K_s for Ca(II) and Mg(II) complexes of **L** as $6.0 \times 10^4\ M^{-1}$ and $1.1 \times 10^6\ M^{-1}$, respectively. Thus, complex stability constant data are consistent with the TPA values. When we take a different magnesium or zinc salt, the TPA values do not change.

2.2. Theoretical studies

We employed a blend of quantum-chemical approaches to rationalize linear and nonlinear spectra of the compounds of interest. Geometry optimization has been carried out for the metal free ligands **L** and $\mathbf{L_a}$ and their corresponding metal complexes. All calculations were performed by the GAUSSIAN-03 program [21] using the B3LYP functional with a 6-31G* basis set. The observed optimized geometry of these molecules predicts that the free rotation around C=N bond is restricted by metal ion as input which leads to a planar configuration to the whole moiety. In case of *cis*-isomer there is less electronic delocalization due to tilted structure. While on addition of metal ion free rotation around C=N bond is stopped which leads a higher symmetry of charge delocalization in the metal complexes. This demonstrates an interesting point that the planar arrangement of this kind of compound has a marked influence upon their electronic properties.

Table 1
Linear and nonlinear spectroscopic data for **L**, $\mathbf{L_a}$ and their metal complexes.

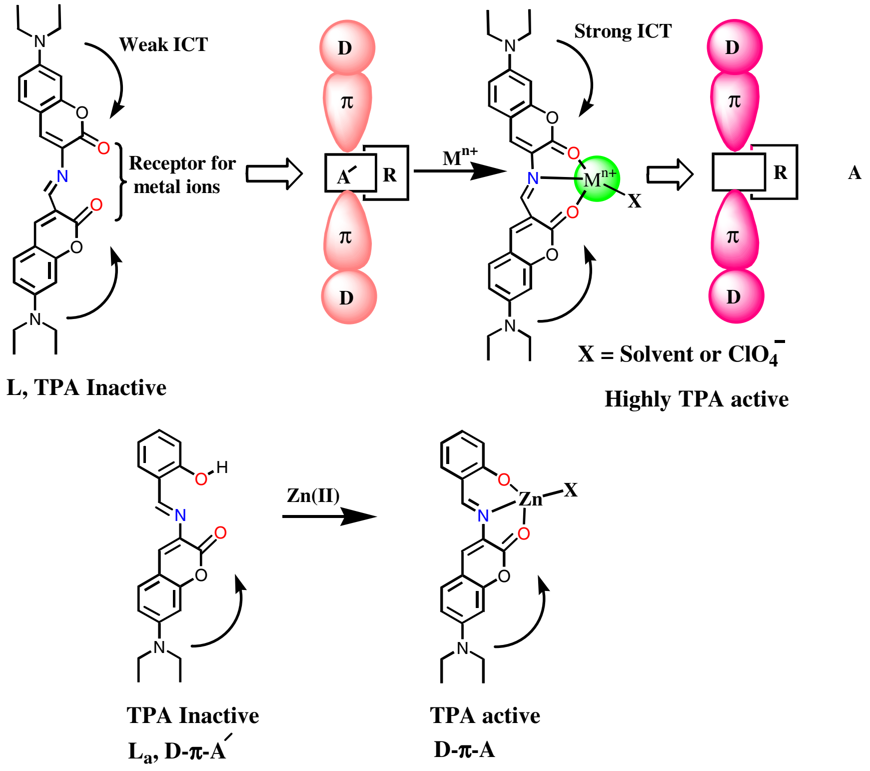
Compound	λ_{max} (nm)	λ_{em} (nm)	η	$^{a}\eta\delta_{max}$ (GM)	$^{b}\delta_{max}$ (GM)	K_s (M^{-1})
L	488		0.0003			
$\mathbf{L_a}$	445	535	0.08			
L + Mg(II)	555	602	0.176	453	2574	1.1×10^6
L + Ca(II)	510	596	0.010	5.5	550	6.0×10^4
$\mathbf{L_a}$ + Zn(II)	505	550	0.45	11.5	25.7[c]	8.2×10^4

Excitation wavelength for single photon fluorescence were 505 nm for [**L**·Mg(II)], 488 nm for [**L**·Ca(II)] and 460 nm for [$\mathbf{L_a}$·Zn(II)]. Fluorescence maxima was obtained by taking [**L**] = 0.8 μM, [$\mathbf{L_a}$] = 1 μM; [M^{n+}] = 10 μM. The quantum yield (η) is calculated by taking standard fluorescein in 0.1 N NaOH (η = 0.85).

[a] Two-photon action cross-section values at 800 nm for [$\mathbf{L_a}$.Zn(II)], 830 nm for Mg(II) and 840 nm for Ca(II) complex of **L**.

[b] Two-photon cross-section at 800 nm for [$\mathbf{L_a}$.Zn(II)], 830 nm for Mg(II) and 840 nm for Ca(II)complex of **L**. 1 GM = 1×10^{-50} cm^4 s $photon^{-1}$ molecule.

[c] Two-photon absorption cross-section at 10^{-3} M solution.



Scheme 3. Plan for cation-induced TPA response. D, donor; π, conjugated bridge; D′, weak donor; A, acceptor.

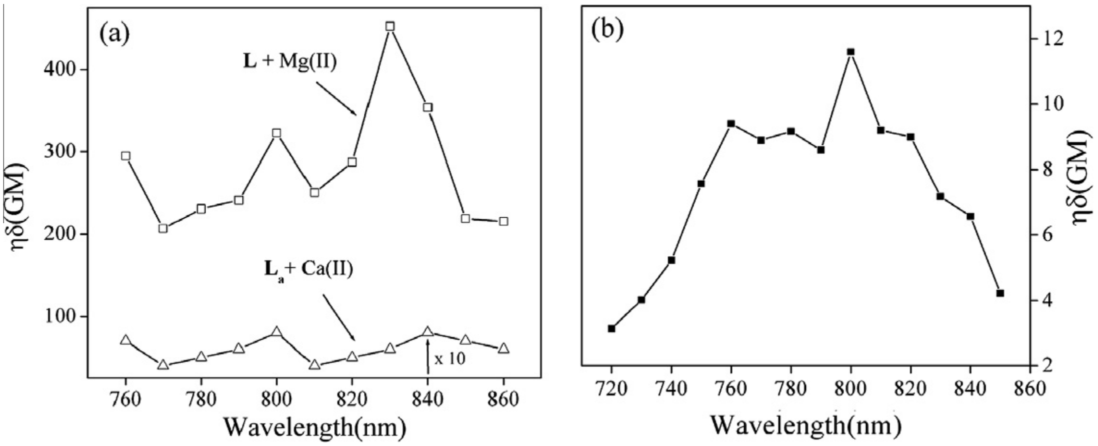


Fig. 4. Two-photon action spectra of (a) [**L**·Mg(II)] and [**L**·Ca(II)] complexes in MeCN ($\eta\delta$ values for [**L**·Ca(II)] complex is showing 10 times increment for clarity) (b) [$\mathbf{L_a}$·Zn(II)] complex in MeCN obtained using Rhodamin 6G as a reference.

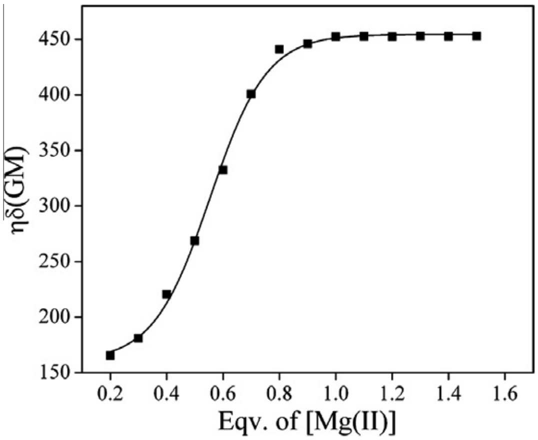


Fig. 5. Titration curve for the Mg(II) complex of $\mathbf{L_2}$ (10^{-5} M) in different metal ion concentrations (0–1.2) at 840 nm in MeCN solution.

Experimentally, we found that when free chromophores (**L** and $\mathbf{L_a}$) coordinate with metal ions, the magnitude of the TPA cross-section is increased. Compared to $\mathbf{L_a}$, the change is much more extensive in case of **L** (Table 1). The TPA cross-section is directly correlated with the extent of intramolecular charge transfer transition through π-conjugated bridge. Planar geometry of the complexes may also have significant contribution towards the nonlinear effects. For more intuitional analysis of the influence of the metal ion upon electronic property, we should consider the contours of some occupied and unoccupied frontier orbitals (Fig. 6).

From contour surface diagrams of **L** and its metal complex it is clear that in case of the free ligand, both the HOMO's and LUMO's are nearly completely localized upon the conjugated side arm of the ligand, indicating only a $\pi \rightarrow \pi^*$ electronic transition (i.e., intra-ligand charge transfer, ILCT). Metal ion only lowers the energy levels leading to the red shifting of absorption band and facilitate $\pi \rightarrow \pi^*$ electronic transition.

Again from the energy level diagrams of each of the compounds and their metal complex, it is also clear that the energy gap between HOMO and LUMO orbitals decreases significantly suggesting extensive electronic charge delocalization after complexation (Fig. 7) leading to more facile charge transfer transition and higher TPA values.

We also performed theoretical calculations to explain the origin of the peaks appear in UV–Vis spectra for **L**, $\mathbf{L_a}$ and their corresponding metal complexes using time-dependent DFT (TDDFT) method on the basis of optimized geometry in acetonitrile solvent. Our theoretically calculated OPA parameters are quite similar to the experimental results. The experimentally determined $\lambda_{\max}$ and the calculated values, the nature of the electronic transitions, corresponding oscillator strengths, major orbitals participate in transitions in case of free ligands and their corresponding metal complexes are given in Table 2.

3. Conclusion

In conclusion, we have reported the synthesis of a new magnesium responsive molecule in the format donor–acceptor–donor that exhibits large two-photon action cross-section measured by two-photon induced fluorescence technique in a femtosecond laser. Its TPA activity increases in presence of selective metal ions to different extents in consistent with their stability constant values. Interestingly, each of the ligand shows very high fluorescence increment upon metal binding. Fluorophores with large two-photon absorption cross-section are potentially important in TPLSM applications. Theoretical calculations carried out at the B3LYP/6-31G* formalism show that upon metal binding, charge delocalization increases significantly leading to higher TPA activity in the metal complexes. Further studies on similar systems are in progress in our laboratory.

4. Experimental

4.1. Materials

All reagent-grade chemicals were used without purification unless otherwise specified. Perchlorate salts of metal ions, 4-(diethylamino)salisaldehyde, diethylmalonate and nitroethylacetate were purchased from Aldrich (USA). Anhydrous stannous chloride, salicyldehyde and solvents were obtained from S.D. Fine Chemicals (India). All the solvents were purified prior to use. The syntheses of the compounds were achieved in several steps as illustrated in Scheme 1.

4.1.1. Physical measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 FT (400 MHz and 100 MHz, respectively) and JEOL ECX-500 instrument in $CDCl_3$. ESI mass spectra were recorded on a Q-TOF Premier micromass spectrometer. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. Melting points were determined with an electrical melting point apparatus by PERFIT,

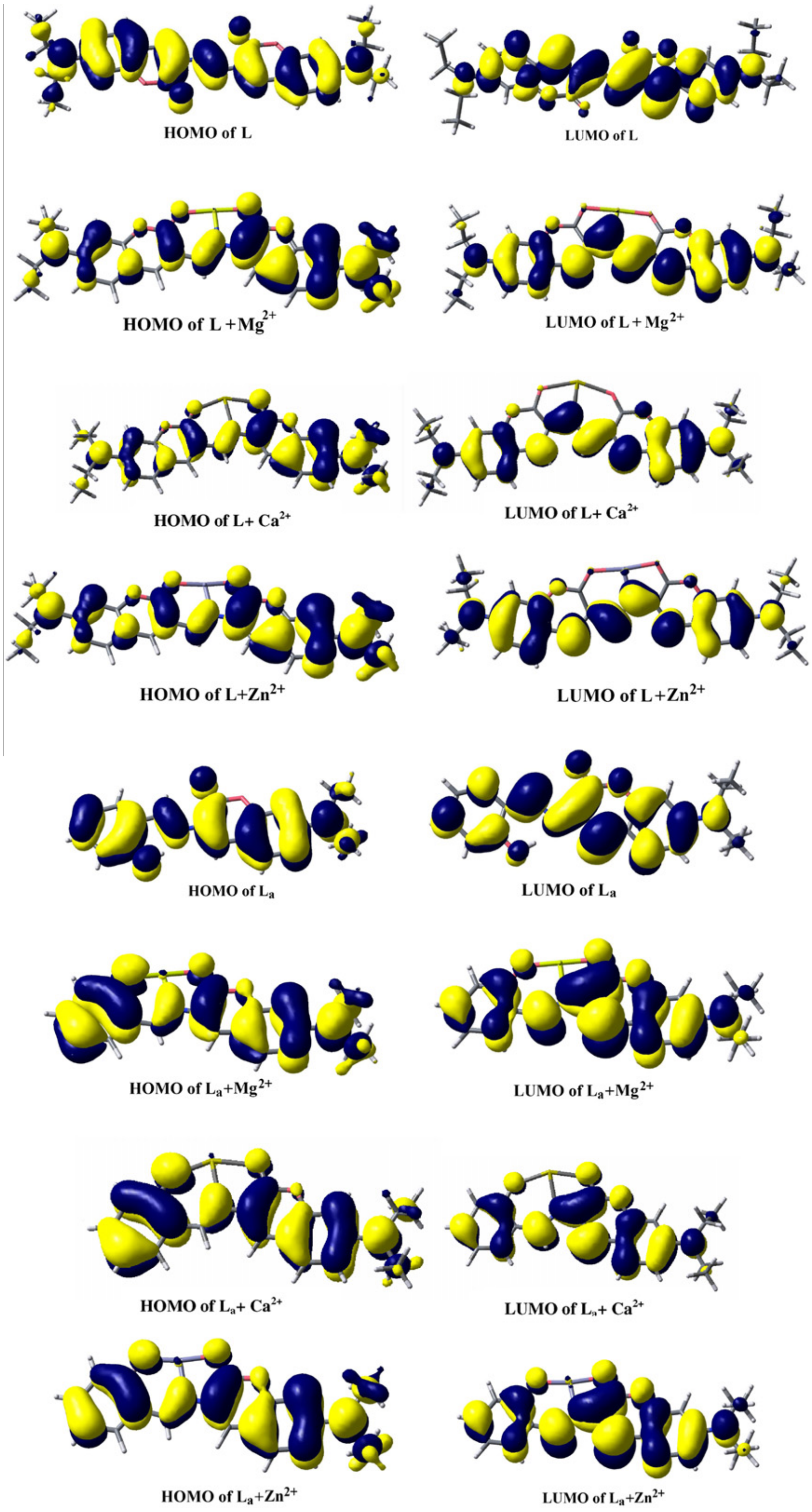


Fig. 6. Contour surfaces of HOMO and LUMO of **L** and $\mathbf{L_a}$ and their corresponding Mg(II), Ca(II) and Zn(II) complexes.

India and were uncorrected. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer at 293 K and the average of three measurements was taken. The deviations in molar absorption coefficients were in the last digit only. Steady-state fluorescence spectra were obtained using a Perkin–Elmer LS 50B Luminescence Spectrometer at 293 K with excitation and emission band-pass 5 nm. Fluorescence quantum yields in each case were determined by comparing the corrected spectrum with that standard Fluorescein [22] (η 0.85 in 0.1(N) NaOH) taking the area under the total emission. The fluorescence measurements in solutions were carried out at $\sim 10^{-6}$ M concentration unless otherwise specified. The complex association constant K_a was determined [17,19] from

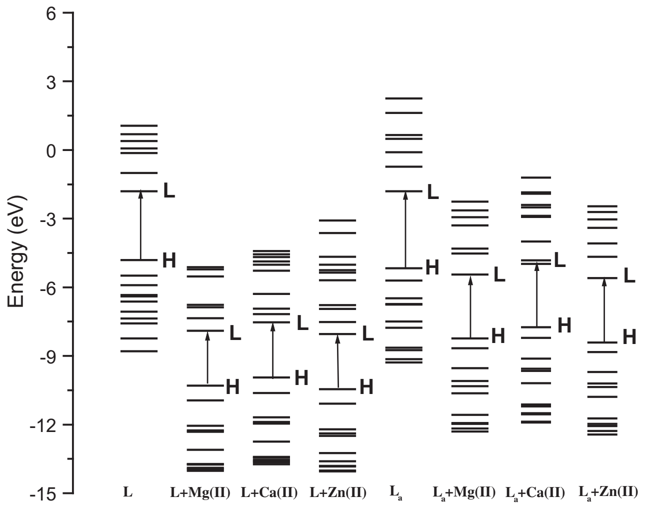


Fig. 7. B3LYP/6-31G* predicted molecular orbital energy levels for metal free ligands and their corresponding Mg(II), Ca(II) and Zn(II) complexes.

the change in absorbance or fluorescence intensity resulting from the titration of dilute solutions (~10^{-5}–10^{-6} M) of **L** and **L_a** against metal ion concentration. The reported values gave good correlation coefficients (⩾0.99).

4.2. Two-photon fluorescence studies

Two-photon absorption cross-section values of these samples are measured by two-photon induced fluorescence technique. All measurement is done in freshly purified MeCN solvent. Because of the limited sensitivity of our experimental setup, we have been able to work only with relatively concentrated solutions, typically in the range of 1×10^{-3}–1×10^{-5} M for both the reference and the investigated chromophore. No aggregate formation was observed in solution, even at such a high concentration. Our femtosecond experimental scheme involves mode-locked coherent Mira titanium: sapphire laser (Model 900) which is pumped by coherent Verdi frequency doubled Nd: vanadate laser. We employ blanking in our measurements by using a mechanical chopper MC1000A, Thorlabs Inc. at 50% duty cycle. Our z-scan setup is already described in detail elsewhere [23].

4.3. Synthesis

4.3.1. 7-Diethylamino-3-nitro-chromene-2-one L_0

1.4 g (7.24 mmol) of 4-diethylamino-salicylaldehyde, 0.80 ml (7.96 mmol) of ethylnitroacetate, 0.1 ml piperidine and 0.2 ml glacial acetic acid were taken in 20 ml of *n*-BuOH and the reaction mixture was refluxed for 12 h. Orange solids were formed while cooling. The solids were filtered and washed with *n*-BuOH (2 × 10 ml) and finally dried in vacuum, which affords an orange solid (1.7 g, 90% Y). m.p. 170 °C. ν_{max}/cm^{-1} 1745 (C=O); δ_H (400 MHZ, $CDCl_3$) 1.25 (t, 6H, *J* = 7.2 Hz, CH_3), 3.47 (q, 4H, *J* = 7.1 Hz, CH_2), 6.46 (s, $1H_{ar}$), 6.68 (dd, 1H, *J* = 9.2, 2.6 Hz, H_{ar}), 7.42 (d, 1H, *J* = 9.0 Hz, H_{ar}), 8.70 (s, $1H_{ar}$). ^{13}C NMR (100 MHz, $CDCl_3$,) 12.4, 45.5, 96.9, 106.2, 111.1, 132.5, 138.1, 143.2, 154.5, 156.5, 158.8. *Anal.* Calc. for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38; N, 10.68. Found: C, 59.29; H, 5.44; N, 10.93%.

4.3.2. 3-Amino-7-diethylamino-chromene-2-one L_1

In a 100 ml round-bottomed flask $SnCl_2.2H_2O$ (10 mmol) and 20 ml 15% HCl were taken. To it compound **L_0** (1 g, 4.3 mmol)

Table 2
The OPA data for compounds **L**, **L_a** and their corresponding metal complexes.

Molecules	Experimental λ_{max} (nm)	Theoretical λ_{max} (nm)	Transitions	f_{os}	Major contributions
L	488	470	$S_0 \rightarrow S_1$	1.959	H → L (66%)
	360–400	388	$S_0 \rightarrow S_2$	0.078	H-1 → L (54%)
	Band	377	$S_0 \rightarrow S_3$	0.003	H-1 → L (37%) H → L+1 (49%)
L + Mg^{2+}	555	546	$S_0 \rightarrow S_1$	1.410	H → L (63%)
	450	468	$S_0 \rightarrow S_2$	0.403	H → L+1 (60%) H-1 → L (31%)
L + Ca^{2+}	510	546	$S_0 \rightarrow S_1$	1.334	H → L (80%)
		536	$S_0 \rightarrow S_2$	0.0013	H → L+1 (99%)
		478	$S_0 \rightarrow S_3$	0.3999	H-1 → L (20%) H → L+2 (69%)
L + Zn^{2+}	560	543	$S_0 \rightarrow S_1$	1.391	H → L (63%) H → L+1 (12%)
	440	468	$S_0 \rightarrow S_2$	0.409	H → L+1 (60%)
		433	$S_0 \rightarrow S_3$	0.004	H-1 → L (48%) H → L+1 (21%)
L_a	440	425	$S_0 \rightarrow S_1$	1.259	H → L (64%)
	335	344	$S_0 \rightarrow S_2$	0.019	H-1 → L (67%)
		334	$S_0 \rightarrow S_3$	0.039	H → L+1 (66%)
L_a + Mg^{2+}	490	489	$S_0 \rightarrow S_1$	0.574	H → L (59%)
		434	$S_0 \rightarrow S_2$	0.453	H-1 → L (61%) H → L (21%)
	370–400	380	$S_0 \rightarrow S_3$	0.007	H → L+2 (67%)
	Band	377	$S_0 \rightarrow S_4$	0.081	H-2 → L (14%) H → L+1 (64%)
L_a + Ca^{2+}	449	530	$S_0 \rightarrow S_1$	0.0038	H-1 → L+1 (3%) H1 → L+1 (96%)
		531	$S_0 \rightarrow S_2$	0.536	H-1 → L (9%) H → L (77%)
		432	$S_0 \rightarrow S_3$	0.0009	H-1 → L+1 (96%) H → L+1 (3%)
		431	$S_0 \rightarrow S_4$	0.454	H-1 → L (79%) H → L (5%)
L_a + Zn^{2+}	505	480	$S_0 \rightarrow S_1$	0.627	H → L (58%)

was added portion wise and the solution was stirred at RT for 6 h. Then 5 M NaOH solutions were added to neutralize the excess acid. The aqueous phase was extracted with ethyl acetate (3 × 30 ml). The organic layer was dried with anhy. Na_2SO4 and evaporated to dryness. A yellow semi solid came, which was directly used for the next step without any characterization.

4.3.3. Compound $\mathbf{L_a}$

A mixture of 3-amino-7-diethylamino-chromene-2-one (0.5 g, 1.48 mmol), salicylaldehyde (0.22 ml, 2.15 mmol), in dry ethanol (20 ml) was stirred overnight at room temperature under N_2 atmosphere. A yellow precipitate appeared, which was filtered and washed with ethanol (4 × 10 ml). It was dried under vacuum to afford a yellow crystalline solid (0.51 g, 70.8% Y). mp 180 °C. ν_{max}/cm^{-1} 1703 (C=O) and 1616 (C=N). δ_H (500 MHz, $CDCl_3$) 1.22 (t, 6H, J = 6.5 Hz, CH_3), 3.43 (q, 4H, J = 6.7 Hz, CH_2), 6.56 (s, $1H_{ar}$), 6.67 (s, $1H_{ar}$), 6.9 (t, 1H. J = 7 Hz, H_{ar}), 6.97 (t, 1H, J = 7 Hz, H_{ar}), 7.34 (d, 1H, J = 8.5 Hz, H_{ar},), 7.40 (d, 1H, J = 7.5 Hz, H_{ar}), 7.26 (s, $1H_{ar}$), 7.65 (s, $1H_{ar}$), 9.57 (s, 1H, C=NH), 13.34 (s, 1H, OH). m/z 337.13 ($\mathbf{L_a}$, 100%) (ESI). *Anal.* Calc. for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N,8.33. Found: C, 71.69; H, 6.01; N, 8.34%.

4.3.4. Compound **1**

$Zn(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol) dissolved in 5 ml of dry MeCN was added to a solution of ligand in dry MeCN (5 ml) with stirring under N_2 atmosphere. After stirring for 30 min the dark red solution was filtered. Diethyl ether was allowed to diffuse into the filtrate, which precipitated the desired complex as a red solid. It was collected by filtration and dried under vacuum. Yield ~50%. m/z 501.2443 (**1**, 100%) (ESI). *Anal.* Calc. for $C_{20}H_{19}ClN_2O_7Zn$: C, 48.02; H, 3.83; N, 5.60. Found C, 48.10; H, 3.88; N, 5.51%.

CAUTION! Care should be taken when using the potentially explosive metal perchlorate salts.

Acknowledgments

Financial support received from DRDO & DST, New Delhi, India (to P.K.B.), is gratefully acknowledged. D.G. thanks DST, MCIT (India) and international SRF program of Welcome Trust (UK) for the financial grant. D.R. thanks CSIR for SRF and A.N. thanks UGC for SRF and A.J. thanks CSIR for SRF.

References

[1] (a) R.H. Kohler, J. Cao, W.R. Zipfel, W.W. Webb, M.R. Hansen, Science 276 (1997) 2039;
(b) B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.-Y.S. Lee, D.M. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.L. Wu, S.R. Marder, J.W. Perry, Nature 398 (1999) 51;
(c) J.D. Bhawalkar, G.S. He, P.N. Prasad, Opt. Commun. 119 (1995) 587;
(d) J.H. Strickler, W.W. Webb, Adv. Mater. 5 (1993) 479;
(e) Q. Zheng, G.S. He, T.-C. Lin, P.N. Prasad, J. Mater. Chem. 13 (2003) 2499;
(f) J.D. Bhawalkar, N.D. Kumar, C.F. Zhao, P.N. Prasad, J. Clin. Laser. Med. Surg. 15 (1997) 201.
[2] R.P. Hauhland (Ed.), The Handbooks – A Guide to Fluorescent Probes and Labeling Technologies, 10th ed., Molecular Probes, Eugene, OR, 2005.
[3] .M. Albota, D. Beljonne, J.-L. Brédas, J.E. Ehrlich, J.-Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S.R. Marder, D. McCord-Maughon, J.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, C. Xu, Science 281 (1998) 1653.
[4] (a) S.-J. Chung, K.-S. Kim, T.H. Lin, G.S. He, J. Swiatkiewicz, P.N. Prasad, J. Phys. Chem. B 103 (1999) 10741;
(b) M. Rumi, J.E. Ehrlich, A.A. Heikal, J.W. Perry, S. Barlow, Z. Hu, D. McCord-Manghon, T.C. Parker, H. Röckel, S. Thayumanavan, S.R. Marder, D. Beljonne, J.-L. Brédas, J. Am. Chem. Soc. 122 (2000) 9500;
(c) W.J. Yang, D.Y. Kim, M.-Y. Jeong, H.M. Kim, Y.K. Lee, X. Fang, S.-J. Jeon, B.R. Cho, Chem.-Eur. J. 11 (2005) 4191;
(d) X.M. Wang, D. Wang, G.Y. Zhou, W.T. Yu, Y.F. Zhou, Q. Fang, M.H. Jiang, J. Mater. Chem. 11 (2001) 1600;
(e) L. Antonov, K. Kamada, K.Ohta, F.S. Kamounah, Phys. Chem. Chem. Phys. 5 (2003) 1193;
(f) J. Yoo, S.K. Yang, M.-Y. Jeong, H.C. Ahn, S.-J. Jeon, B.R. Cho, Org. Lett. 5 (2003) 645;
(g) B.R. Cho, K.H. Sou, S.H. Lee, Y.-S. Song, Y.-K. Lee, S.-J. Jeon, J.H. Choi, H. Lee, M. Cho, J. Am. Chem. Soc. 123 (2001) 10039.
[5] (a) S.D. Bella, Chem. Soc. Rev. 30 (2001) 355;
(b) B.J Coe, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 9, Elsevier, Pergamon, Oxford, UK, 2004, p. 621;
(c) E. Cariati, M. Pizzotti, D. Roberto, F. Tessore, R. Ugo, Coord. Chem. Rev. 250 (2006) 1210.
[6] (a) H.C. Ahn, S.K. Yang, H.M. Kim, S. Li, S.-J. Jeon, B.R. Cho, Chem. Phys. Lett.. 410 (2005) 312;
(b) H.M. Kim, M.-Y. Jeong, H.C. Ahn, S.J. Jeon, B.R. Cho, J. Org. Chem. 69 (2004) 5749;
(c) M. Taki, J.L. Wolford, T.V. O'Halloran, J. Am. Chem. Soc. 126 (2004) 712;
(d) S. Charier, O. Ruel, J.-B. Baudin, D. Alcor, J.-F. Allemand, A. Meglio, L. Jullien, Angew. Chem., Int. Ed. 43 (2004) 4785;
(e) M.H.W. Werts, S. Gmouh, O. Mongin, T. Pons, M. Blanchard-Desce, J. Am. Chem. Soc. 126 (2004) 16294;
(f) R. Bozio, E. Cecchetto, G. Fabbrini, C. Ferrante, M. Maggini, E. Menna, D. Pedron, R. Ricco, R. Signorini, M. Zerbetto, J. Phys. Chem. A 110 (2006) 6459;
(g) Y. Tian, C.-Y. Chen, C.-C. Yang, A.C. Young, S.-H. Jang, W.-C. Chen, A. K.-Y. Jen, Chem. Lett. 20 (2008) 1977.
[7] (a) S.J.K. Pond, O. Tsutsumi, M. Rumi, O. Kwon, E. Zojer, J.-L. Brédas, S.R. Marder, J.W. Perry, J. Am. Chem. Soc. 126 (2004) 9291;
(b) H.M. Kim, P.R. Yang, M.S. Seo, J.-S. Yi, J.H. Hong, S.-J. Jeon, Y.-G. Ko, K.J. Lee, B.R. Cho, J. Org. Chem. 72 (2007) 2088;
(c) H.M. Kim, C. Jung, B.R. Kim, S.-Y. Jung, J.H. Hong, Y.-G. Ko, K.J. Lee, B.R. Cho, Angew. Chem., Int. Ed. 46 (2007) 3460.
[8] (a) J.F. Callan, A.P. de Silva, D.C. Magri, Tetrahedron 61 (2005) 8551;
(b) K. Komatsu, Y. Urano, H. Kojima, T. Nagano, J. Am. Chem. Soc. 129 (2007) 13447;
(c) Y. Zhang, X. Guo, W. Si, L. Jia, X. Qian, Org. Lett. 10 (2008) 473;
(d) J. Kim, T. Morozumi, H. Nakamura, Org. Lett. 9 (2007) 4419;
(e) Q. Wu, E.V. Anslyn, J. Am. Chem. Soc. 126 (2004) 14682;
(f) T. Gunnlaugsson, J.P. Leonard, N.S. Murray, Org. Lett. 6 (2004) 1557;
(g) M. Royzen, Z. Dai, J.W. Canary, J. Am. Chem. Soc. 127 (2005) 1612;
(h) J.L. Bricks, A. Kovalchuk, C. Trieflinger, M. Nofz, M. Büschel, A.I. Tolmachev, J. Daub, K. Rurack, J. Am. Chem. Soc. 127 (2005) 13522;
(i) Y. Xiang, A. Tong, Org. Lett. 8 (2006) 1549.
[9] [a] R.P. Haugland (Ed.), The Hand Books – A Guide to Fluorescent Probes and Labeling Technologies, 10th ed., Molecular Probes, Eugene, OR, 2005;
(b) A. Hartiwig, Mutat. Res. 475 (2001) 113.
[10] (a) B. O'Rourke, P.H. Backx, E. Marban, Science 257 (1992) 245;
(b) H.C. Politi, R.R. Preston, Neuroreport 14 (2003) 659;
(c) L.-J. Dai, G. Ritchie, D. Kerstan, H.S. Kang, D.E.C. Cole, G.A. Quamme, Physiol. Rev. 81 (2001) 51.
[11] (a) C. Schmitz, A. Perraud, C.O. Johnson, K. Inabe, M.K. Smith, R. Penner, T. Kurosaki, A. Fleig, A.M. Scharenberg, Cell 113 (2003) 191;
(b) F.I. Wolf, A. Torsello, A. Fasanella, A. Cittadini, Mol. Aspects Med. 24 (2003) 11.
[12] (a) J.J.R.F de Silva, R.J.P Williams, The Inorganic Chemistry of Life, 2nd ed., Oxford University Press, New York, 2001;
(b) R.J.P. Williams, J.J.R.F. de Silva, Coord. Chem. Rev. 200 (2000) 247;
(c) B.L. Vallee, K.H. Falchuk, Physiol. Rev. 73 (1993) 79.
[13] (a) E. Ho, B.N. Ames, Proc. Natl. Acad. Sci. USA 99 (2002) 16770;
(b) H. Daiyasu, K. Osaka, Y. Ishino, H. Toh, FEBS Lett. 503 (2001) 1.
[14] A.Q. Troung-Tran, J. Carter, R.E. Ruffin, P.D. Zalewski, Biometals 14 (2001) 315.
[15] A.B. Chausmer, J. Am. Coll. Nutr. 17 (1998) 109.
[16] (a) N.C. Lim, C. Brückner, Chem. Commun. (2004) 1094;
(b) S.R. Trenor, A.R. Shultz, B.J. Love, T.E. Long, Chem. Rev. 104 (2004) 3059;
(c) N.C. Lim, J.V. Schuster, M.C. Porto, M.A. Tanudra, L. Yao, H.C. Freake, C. Brückner, Inorg. Chem. 44 (2005) 2018.
[17] D. Ray, P.K. Bharadwaj, Inorg. Chem. 47 (2008) 2252.
[18] (a) M.M. Henary, C.J. Fahrni, J. Phys. Chem. A 106 (2002) 5210;
(b) H.N.C. Lim, N.C. Freake, C. Brückner, Chem.-Eur. J. 11 (2005) 38;
(c) R.-C. William, S.Z. Jimena, C.-F. Elisa, P. Jorge, J. Phys. Chem. A 111 (2007) 6241;
(d) S.K. Sahoo, R.K. Bera, M. Baral, B.K. Kanungo, J. Photochem. Photobiol. A 188 (2007) 298. and references therein.
[19] (a) S. Fery-Forgues, M.-T. Le Bries, J.-P. Guetté, B. Valeur, J. Phys. Chem. 92 (1988) 6233;
(b) B.P. Bag, P.K. Bharadwaj, J. Phys. Chem. B 109 (2005) 4377.
[20] C. Xu, W.W. Webb, J. Opt. Soc. Am. B 13 (1996) 481.
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong,

C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision C.02, Gaussian Inc., Wallingford CT, 2004
[22] (a) C.A. Parker, W.T. Ress, Analyst 85 (1960) 587;
(b) T. Gabe, Y. Urano, K. Kikuchi, H. Kojima, T. Ngano, J. Am. Chem. Soc. 126 (2004) 3357.
[23] (a) S. Das, A. Nag, D. Goswami, P.K. Bharadwaj, J. Am. Chem. Soc. 128 (2006) 402;
(b) A. Nag, S. Singh, D. Goswami, Chem. Phys. Lett. 430 (2006) 420;
(c) A. Nag, A.K. De, D. Goswami, J. Phys. Conf. Ser. 80 (2007) 012034.