A comparative study of third-order optical nonlinearity of symmetrical dipolar chromogenic probes and their enhancement by different metal ions

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We have investigated the two-photon absorption properties of three symmetrical NLO-phores, \textit{L}_1, \textit{L}_2 and \textit{L}_3, having different conjugation lengths as well as different binding sites like cryptand, crown ether and bipyridyl moiety. The TPA properties have been measured by a femtosecond laser at 800 nm, which is in the window of ‘\textit{in vivo}’ imaging. Upon metal ion binding, the TPA cross-section values are enhanced to different extents depending on the nature of metal ion and the overall architecture of the molecular system as well. The unique CT transition process after metal ion incorporation, along with various conjugation lengths of the NLO-phores, fully elucidates the structure-property relationship of the photophysical properties.

**Keywords:** Bioinorganic chemistry, Coordination chemistry, Optical nonlinearity, NLO-phores, Two photon absorption, Chromogenic probes

Molecules exhibiting optical nonlinearity are presently in great demand for various applications. Third-order optical nonlinearity can be related to two-photon absorption (TPA) that involves excitation of molecular species from the singlet ground state to the singlet excited state by simultaneous absorption of two photons. The efficiency of this process is determined by measuring the two-photon absorption cross-section ($\sigma^{(2)}$), value which is related to the imaginary part of the second hyperpolarizability. Molecules with large TPA cross-section are potentially useful in several areas of bio-photonics and materials science\textsuperscript{3}. Specifically, when the TPA cross-section of a molecule changes significantly in presence of a particular metal ion, it can be very useful for the detection and determination of static concentration of that ion in bio-systems for understanding various biological processes\textsuperscript{2}. Important classes of compounds capable of exhibiting large TPA cross-section values are organic molecules with symmetrical charge transfer possibilities. When a metal ion influences this charge transfer, modulation of the TPA activity can be achieved. Since intramolecular charge transfer (ICT) contributes strongly to the TPA capability, many two-photon chromophores have been reported in literature\textsuperscript{3}. These systems are built-up from electron donating and/or withdrawing groups bridged by π-conjugated systems. The present investigation deals with the design and synthesis of a versatile derivatizable set of TPA synths and their development towards TPA chromophores with large TPA cross-section ($\sigma^{(2)}$) values.

Zinc is an essential nutrient required in normal growth and development\textsuperscript{4} and for cellular processes such as DNA repair\textsuperscript{5} and apoptosis\textsuperscript{6}. This metal plays a key role in the synthesis of insulin and the pathological state of diabetes\textsuperscript{7}. On the other hand, many enzymatic reactions are mediated by Mg(II), while Ca(II) acts as an universal second messenger in cells\textsuperscript{8}. Therefore, trapping these metal ions by a suitable receptor for reporting their static concentration for various neurophysiological studies is an important research area of current interest.

Strategies have been evolved to append different D–π–A to suitable skeletons to have multi-polar systems. The present investigation deals with three conjugated dipolar chromogenic sensors, \textit{L}_1, \textit{L}_2 and \textit{L}_3, where the cryptand or crown ether receptors are exposed at the end of dipoles to have overall...
symmetrical D–π–D moieties with different conjugation length as well as different donor capabilities. Cryptands and crown ethers have been chosen as they bind biologically relevant alkali, alkaline-earth and transition metal ions with enhanced kinetic and thermodynamic stability. The NLO-phores, $L_1$, $L_2$ and $L_3$, are designed to have electronically independent D–π–A units, that after metallation form overall symmetrical D–π–D systems through the metal ion to exhibit large TPA cross-section values, ($\sigma^{(2)}$).

**Materials and Methods**

Reagent grade triethanolamine, salicylaldehyde, tris-(2-aminoethyl)amine, 1-fluoro-4-nitrobenzene, cesium chloride, 10 % Pd in activated charcoal, isophthalaldehyde, triphenylamine, 1-aza-18-crown-6, 2,2'-bipyridine-4,4'-dicarboxaldehyde and all the metal perchlorate salts were purchased from Aldrich Chemical Company (USA) and used as received without further purification. Reagent grade sodium borohydride, sodium hydroxide, potassium carbonate, anhydrous sodium sulfate, SOCl$_2$ and POCl$_3$ were received from SD Fine Chemicals (India). All the solvents were acquired from SD Fine Chemicals (India) and dried properly before use following literature methods. All the reactions were carried out under dinitrogen atmosphere. Chromatographic separation was done by column chromatography using 100-200 mesh silica gel obtained from Acme Synthetic Chemicals (India).

All the compounds were characterized by elemental analysis, NMR, and ESI-MS spectra. Both $^1$H-NMR (500 MHz) and $^{13}$C-NMR spectra (125 MHz) of the compounds were recorded on a JEOL JNM-LA400 FT spectrometer in CDCl$_3$ with tetramethylsilane as internal standard. Melting points were measured with an electrical melting point apparatus by PERFIT, India and are uncorrected. Elemental analyses were recorded on an Elementar Vario EL III Carlo Erba 1108 Elemental Analyser. The ESI-MS data were obtained in acetonitrile from a MICROMASS QUATRO Quadruple mass spectrometer. UV-vis spectra were recorded on a JASCO V570 UV-vis-NIR spectrophotometer in acetonitrile at 298 K.

**Measurement of two-photon absorption cross-section ($\sigma^{(2)}$)**

The TPA measurements were performed in acetonitrile using the open-aperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a 2 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane X). After passing through a $f = 10$ cm lens, the laser beam was focused to a 1 mm-quartz cell. As the position of the sample cell was varied along the laser-beam direction (z-axis), the transmitted laser beam from the sample cell was then probed with a Ge/PN photodiode (New Focus, 2033) used for reference monitoring. Details of the measurements are available elsewhere. The TPA measurements were performed where the linear absorption band was absent so that the one photon absorption did not affect the TPA resonance. It is to be noted that TPA measurements can vary with fluctuations in the power of the laser. In each case, the average of five measurements was taken.

**Synthesis of the NLO-phores**

The synthetic routes adopted for the NLO-phoric systems are given in Schemes 1-3.

**Synthesis of p-aminobenzene derivative of cryptand ($L_a$)**

The mono amino cryptand derivative ($L_a$) was synthesized and characterized following the reported method published earlier by our group. Typically, the mono nitro-derivative, $L_{m1}$ (1.362 g, 2 mmol) was taken in a two-necked round bottom flask with 50 mL absolute ethanol, purged with N$_2$ for a few minutes and 10 % Pd in activated charcoal (5 mol % per nitro group) was added, followed by dropwise addition of hydrazine hydrate (3 mL) over a period of 30 min. The mixture was refluxed for 3 h, filtered hot and the filtrate evaporated under reduced pressure almost to dryness. After shaking the remaining mass with 100 mL water to remove excess hydrazine hydrate, the desired amine was extracted with chloroform, dried over anhydrous Na$_2$SO$_4$ and finally evaporated to obtain a colorless solid.

**Synthesis of the NLO-phore, $L_1$**

This compound was synthesized by Schiff base condensation of $L_a$ with isophthalaldehyde in 2:1 molar ratio in dry ethanol. The desired product precipitated out after stirring the solution at room temperature for 24 h. The product was collected by filtration, washed twice with dry ethanol followed by diethyl ether and finally dried under vacuum.
(Scheme 1). Yield: 70%; m. pt.: 215°C; \(^1\)H-NMR (500 MHz, CDCl\(_3\), 25°C, TMS): \(\delta\): 1.68 (br, 4H), 2.42-2.47 (m, 8H), 2.54 (t, \(J = 5.7\) Hz, 4H), 2.89 (t, \(J = 4.6\) Hz, 4H), 2.93-2.97 (m, 4H), 3.07-3.15 (m, 8H), 3.26-3.29 (m, 4H), 3.45-3.49 (m, 4H), 3.62 (d, \(J = 13.4\) Hz, 4H), 5.13 (d, \(J = 13.4\) Hz, 4H), 6.46 (d, \(J = 8.7\) Hz, 4H), 6.68 (d, \(J = 8.4\) Hz, 4H), 6.83-6.89 (m, 10H), 7.05 (d, \(J = 6.9\) Hz, 4H), 7.14-7.23 (m, 12H), 7.93-7.95 (m, 2H), 8.57 (s, 2H);

\(^1^3\)C-NMR (125 MHz, CDCl\(_3\), 25°C, TMS): \(\delta\): 47.2, 51.1, 53.7, 54.9, 55.5, 60.5, 65.9, 66.7, 67.2, 111.6, 111.7, 111.9, 120.4, 120.9, 122.6, 126.8, 127.9, 128.7, 128.9, 129.8, 132.5, 156.1, 157.7; ESI-MS: (m/z): 1399.82 (100%) [M + H]\(^+\); Anal. (%): Calcd for C\(_{86}\)H\(_{102}\)N\(_{12}\)O\(_6\): C, 73.79; H, 7.34; N, 12.01. Found: C, 73.90; H, 7.67; N, 11.83.

Synthesis of bis(4-formylphenyl)phenyamine

This compound was synthesized from triphenylamine following literature procedure\(^{11}\). Yield: 25%; m. pt.: 140°C; \(^1\)H-NMR (500 MHz, CDCl\(_3\), 25°C, TMS): \(\delta\): 7.16-7.18 (m, 6H), 7.25 (t, \(J = 5.8\) Hz, 1H), 7.38 (t, \(J = 6.1\) Hz, 2H), 7.76 (d, \(J = 6.7\) Hz, 4H), 9.88 (s, 2H); \(^1^3\)C-NMR (125 MHz, CDCl\(_3\), 25°C, TMS): \(\delta\): 122.8, 126.4, 127.2, 130.2, 131.4, 145.6, 152.1, 190.6; ESI-MS: (m/z): 302.12 (100%) [M + H]\(^+\); Anal. (%): Calcd for C\(_{20}\)H\(_{15}\)NO\(_2\): C, 79.72; H, 5.02; N, 4.65. Found: C, 79.81; H, 5.17; N, 4.28.

Synthesis of the NLO-phore, \(L_2\)

The NLO-phore, \(L_2\), was synthesized by Schiff base condensation of \(L_a\) with bis(4-formylphenyl) phenyamine in 2:1 molar ratio in dry ethanol. The desired product precipitated out on stirring at room temperature for 24 h. The product was collected by filtration, washed twice with dry ethanol followed by diethyl ether and finally dried under vacuum (Scheme 2). Yield: 75%; m. pt.: 190°C; \(^1\)H-NMR (500 MHz, CDCl\(_3\), 25°C, TMS): \(\delta\): 1.69 (br, 4NH), 2.38-2.52 (m, 8H), 2.89-2.96 (m, 8H), 3.08-3.16 (m, 8H), 3.27-3.29 (m, 4H), 3.46-3.50 (m, 4H), 3.61 (d, \(J = 13.3\) Hz, 4H), 3.98-4.06 (m, 8H), 4.09-4.13 (m, 8H), 4.37 (s, 4H), 5.14 (d, \(J = 13.3\) Hz, 4H), 6.44 (d, \(J = 8.8\) Hz, 4H), 6.68 (d, \(J = 8.4\) Hz, 4H), 6.82-6.89 (m, 10H), 7.03-7.37 (m, 20H), 7.70-7.75 (m, 6H), 7.79 (d, \(J = 8.4\) Hz, 1H), 8.43 (d, \(J = 13.7\) Hz, 2H);

\(^1^3\)C-NMR (125 MHz, CDCl\(_3\), 25°C, TMS): \(\delta\): 51.1, 53.6, 54.9, 55.5, 60.5, 66.7, 67.2, 111.7, 111.9, 120.3, 120.9, 122.4, 123.5, 125.1, 126.6, 126.8, 127.8, 128.7, 128.9, 129.4, 129.7, 129.9, 131.4, 156.1, 157.7; ESI-MS: (m/z): 1566.89 (100%) [M+H]\(^+\); Anal. (%): Calcd for C\(_{98}\)H\(_{111}\)N\(_{13}\)O\(_6\): C, 75.11; H, 7.14; N, 11.62. Found: C, 74.81; H, 7.47; N, 11.88.
Synthesis of $L_n$

To a solution of mono-aza crown ether, $L_c$, (0.26 gm, 1 mmol) in dry DMSO (10 mL), was added anhydrous Na$_2$CO$_3$ (0.21 g, 2 mmol). Subsequently, 1-fluoro-4-nitrobenzene (0.16 mL, 1.5 mmol) in dry DMSO (10 mL) was added dropwise in 15 minutes and the reaction mixture was allowed to stir at 90 °C for 36 h. The reaction mixture was then poured into ice water (150 mL). The yellow solid which separated out was collected by filtration and washed thoroughly with water (5 × 100 mL). The mono-substituted product ($L_n$) was purified by column chromatography (SiO$_2$ 100-200 mesh) with CHCl$_3$ as the eluent and finally recrystallized from MeCN to obtain a bright yellow crystalline solid. Yield: 45 %; m pt.: 85 °C; ¹H-NMR (500 MHz, CDCl$_3$, TMS): δ: 3.40-3.96 (m, 24H), 6.72 (d, $J$ = 9.5 Hz, 2H), 8.05 (d, $J$ = 9.4 Hz, 2H); ¹³C-NMR (125 MHz, CDCl$_3$, TMS, 25 °C) δ: 53.8, 69.5, 70.6, 116.2, 117.9, 137.5, 140.9; Anal. (%): Calcd for C$_{48}$H$_{38}$N$_6$O$_7$: C, 65.90; H, 6.97; N, 9.23.

Synthesis of $L_p$

The mono-nitro derivative ($L_p$) obtained above was reduced using Pd in activated charcoal and hydrazine hydrate in ethanol under refluxing condition for 2 h. Ethanol was then evaporated under vacuum and the colorless semi-solid was extracted with CHCl$_3$ mixture. This product was used in the next step without further purification. Yield: 45 %; ¹H-NMR (500 MHz, CDCl$_3$, TMS, 25 °C) δ: 3.5-3.69 (m, 24H), 3.86 (b, 2H), 6.48-6.75 (m, 4H); ¹³C-NMR (125 MHz, CDCl$_3$, TMS, 25 °C) δ: 52.3, 67.8, 70.5, 111.5, 125.7, 137.8, 150.3; Anal. (%): Calcd for C$_{38}$H$_{38}$N$_6$O$_7$: C, 56.24; H, 7.34; N, 7.29. Found: C, 56.38; H, 7.31; N, 7.11.

Synthesis of the NLO-phore, $L_3$

The semi-solid $L_p$ was allowed to undergo Schiff base condensation by stirring overnight at room temperature with 2,2′-bipyridine-4,4′-dicarboxyaldehyde in dry ethanol. The yellow mass formed was collected by filtration, washed twice with dry ethanol followed by diethyl ether and finally dried under vacuum (Scheme 3). This compound was directly used for analysis and further studies. Yield: 60 %; m. pt.: 120 °C; ¹H-NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ = 3.66-3.77 (m, 48H), 6.73 (d, $J$ = 9.2 Hz, 2H), 7.17 (d, $J$ = 8.8 Hz, 2H), 7.27 (d, $J$ = 6.9 Hz, 2H), 7.32 (d, $J$ = 8.7 Hz, 2H), 7.87 (d, $J$ = 6.5 Hz, 2H), 8.56 (s, 1H), 8.61 (s, 1H), 8.74-8.80 (m, 2H), 8.83 (d, $J$ = 5.8 Hz, 2H); ¹³C-NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ = 48.5, 51.5, 68.8, 69.7, 70.9, 111.9, 120.9, 121.9, 122.6, 123.3, 145.0, 147.9, 150.0, 152.1, 154.7, 156.8; ESI-MS: (m/z): 885.45 (100 %) [M + H]$^+$; Anal. (%): Calcd for C$_{48}$H$_{38}$N$_6$O$_7$: C, 65.14; H, 7.29; N, 9.50. Found: C, 65.90; H, 6.97; N, 9.23.

Results and Discussion

One photon absorption spectra

The UV-vis absorption spectra for $L_1$, $L_2$, and $L_3$ and their metal complexes were recorded in 10$^{-5}$ M acetonitrile solution. The ligand $L_1$ exhibits a strong band at ~400 nm along with a shoulder at 340 nm attributable to the ligand-centered π→π* electronic transitions (ILCT). This band makes a significant red-shift (~100 nm) and becomes more intense in presence of a metal ion (Fig. 1a). This is due to the fact that after encapsulating the metal ion, the cryptand becomes an efficient acceptor of electron and an overall electronic charge delocalization takes place within two ends causing a red-shift in the absorption spectra. The absorbance changes as a function of Zn(II) metal ion concentration has been studied (Supplementary Data Fig. S13a). Upon gradual addition of Zn(II) ion, intensity of the band at
500 nm increases with a gradual decrease of the 400 nm band. The spectrophotometric titration of $L_1$ with Zn(II) reveals that two metal ions bind the two cryptand moieties. Similarly, the metal-free $L_2$ exhibits a strong band around 415 nm along with a shoulder near 334 nm. Both these bands are due to the ligand based intramolecular $\pi \rightarrow \pi^*$ charge transfer from the N donor of the cryptand moiety. Due to extension of the length of $\pi$-conjugation bridge, the bands in the case of $L_2$ are red-shifted compared to those of $L_1$. Upon addition of Zn(II) metal ion, the cryptand becomes a strong acceptor and two bands are observed whose positions as well as $\epsilon_{\text{max}}$ values are sensitive to the concentration of the metal ion. As shown in Fig. S13c, a distinct band around 530 nm becomes gradually intense while at the same time the 415 nm band decreases in intensity. Intensity of the 530 nm band reaches the maximum upon addition of 2 equivalents of Zn(II) ion. Since such charge-transfer bands are weak in the case of $L_1$, it indicates that the donor-acceptor interaction is larger for $L_2$/Zn(II) compared to $L_1$/Zn(II).

The absorption spectra (Fig. 2) of $L_3$ are somewhat complicated in nature. In the metal-free state, it shows three bands at 241, 303 and 418 nm, which are red-shifted upon addition of a metal ion. In presence of alkali metal ions, the absorption spectra remain almost the same as that of the free chromophore, while addition of an alkaline earth metal ion causes noticeable red-shift of the 418 nm band. This feature is consistent with the stronger binding of Mg(II)/Ca(II) ions into the aza-crown ether cavity than Na(I)/K(I) ions. The Zn(II) ion behaves like the alkaline earth metal ions in this case.

**Binding constant determination of metal complexes**

The binding constants ($K_s$) were determined from the variation of intensity of absorption at proper wavelengths for all the chromophores. The concentration of chromophores was $1 \times 10^{-5} \text{ M}$ and that of a metal ion was varied from $1 \times 10^{-6} \text{ M}$ to $3 \times 10^{-5} \text{ M}$. The absorption spectral changes upon gradual addition of metal ions, Zn(II) or Mg(II), are displayed in Figs S13 (Supplementary data). The binding constants for 1:2 complexation of the complexes were measured by taking the data at a particular wavelength using the following equation (Eq. 1),

$$\frac{A_0}{A_0 - A} = \frac{A_0}{A_0 - A_{\text{Complex}}} + \frac{A_0}{K_s [M]^2 (A_0 - A_{\text{Complex}})}$$

where $A_0$ is the absorbance of free ligand, $A$ is the observed absorbance at different metal ion concentration, $A_{\text{complex}}$ is the maximum absorbance of metal-ligand complex and $[M]$ is the metal ion concentration.

When $A_0/(A_0 - A)$ is plotted against $1/[M]^2$, the binding constant, $K_s$, can be obtained by the intercept/slope ratio. In every case, the calculated values show good correlation coefficients ($\geq 0.99$). Here, for the complexation of chromophores $L_1$, $L_2$
and $L_3$ with Zn(II) perchlorate salts, the log $K_s$ values were found to be 9.66, 9.81 and 9.10 respectively, and for the Mg(II) complex of $L_3$ the log $K_s$ value is 9.23. These higher stability constant values arise from the 'macrocyclic effect'.

Two-photon absorption spectra

The femtosecond Z-scan measurements were carried out at 800 nm, which is within the window of minimum cell damage for in vivo studies. The $\sigma^{(2)}$ values as well as other photophysical data for the chromophores $L_1$, $L_2$, $L_3$ and their corresponding metal complexes are collected in Table 1. In every case, the metal-free chromophores show comparatively much smaller TPA cross-section values, $\sigma^{(2)}$, which increases enormously upon complexation.

The open-aperture Z-scan traces for the chromophores $L_1$, $L_2$, $L_3$ and their corresponding metal complexes were studied (Supplementary Data Fig. S14). As the length of $\pi$-conjugation bridging the two cryptand moieties in $L_1$ and $L_2$ is increased, the TPA cross-section values are also increased. These observations are also directly related to the OPA spectra, where $L_2$ gives stronger intraligand charge transfer (ILCT) intensity compared to $L_1$.

It should be noted that double cryptand-linked molecules show relatively larger TPA cross-section values than those of single cryptand-linked molecules. Although single and double cryptand-linked molecules have similar absorption spectra, the TPA cross-section values of double cryptand-linked molecules $L_1$ and $L_2$ are enhanced significantly. In other words, due to the enhanced CT transition of symmetric D--$\pi$--D system, $L_1$ and $L_2$ have relatively larger TPA cross-section values than the single cryptand-linked molecules. Moreover, after metal complexation, $L_1$, $L_2$, and $L_3$ show higher TPA cross-section values ($\sigma^{(2)}$) than metal-free cases. The increment is much more significant (11100 GM) in the case of $L_2$ with Zn(II) metal ion.
In the case of \( L_3 \), the situation is quite interesting. The aza-crown ether moiety can bind with alkali and alkaline earth metals whereas the bipyridine moiety has the affinity to bind transition metal ions. During measurements, 2 equivalents of alkali and alkaline earth metal ions along with 0.5 equivalent of Zn(II) were used for 1 equivalent of \( L_3 \). In presence of alkali and alkaline earth metals as input, the \( \sigma^{(2)} \) values are not changed significantly as compared to the free dye. Interestingly, after addition of 0.5 equivalent of Zn(II) to \( L_3 \), the \( \sigma^{(2)} \) value showed a marked increase (Table 1). However, greater \( \sigma^{(2)} \) values are observed when alkali/alkaline earth metal ion is added in presence of Zn(II) (Table 1). Binding of Zn(II) to the dye not only increases the acceptor power of the bipyridine moiety but also increases the number of NLO-phores around Zn(II) from one to two. In contrast, binding of alkali/alkaline earth metal ion to the macrocycle leads to small changes in its electronic distribution.

Theoretical calculation of our previous findings reveals that the TPA cross-section value is directly correlated with the extent of intramolecular charge transfer transition through \( \pi \)-conjugation bridge as well as the frontier molecular orbitals \(^{10}\), especially HOMO\(−1\), HOMO, LUMO and LUMO+1 which play a significant role in electronic transition during two-photon absorption process. Here, in every case, the increased intramolecular charge transfer transition triggered by a metal ion is a major factor in the enhancement of TPA cross-section values as compared with metal-free chromophores \(^{11}\).

**Conclusions**

The third-order optical nonlinearity of three symmetrical chromophores are measured in femtosecond regime, which gives information on the directional electron flow induced by metal ion and its effect on TPA cross-section values. A deeper understanding of the effect of donor-acceptor strength in branching units of dipolar entities on linear and nonlinear optical properties has been achieved by using dipolar chromophores. In particular, by modifying the metal ion coordination site and lengthening the conjugated branches, larger TPA cross-section values can be attained. The TPA cross-section values increase with extinction coefficients of the one photon absorption spectra. As the absorption spectra remain unchanged with alkali metal binding, the TPA values are found to be smaller compared to the cases of other metal ions used. These studies of structure/property relationships provide insight into the molecular mechanism of two-photon absorption processes with a focus on the degree of intramolecular symmetric charge redistribution in molecules of \( A−\pi−D−\pi−A \) structural motifs.

**Supplementary Data**

Characterization of the NLO-phores \( L_1−L_3 \) including \(^1\)H-NMR, \(^{13}\)C-NMR and ESI-MS associated with this article may be obtained from the corresponding author on request.

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<th>Comp.</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
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<td>( L_1 )</td>
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