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Acyclic donor–acceptor–donor chromophores for large enhancement of two-photon absorption cross-section in the presence of Mg(II), Ca(II) or Zn(II) ions

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ABSTRACT

Two new chromophores in the format, donor–acceptor–donor, have been synthesized in high yields from easily available starting materials. These compounds do not show any two-photon absorption (TPA) cross-section in the wavelength range, 780–900 nm when probed by the Z-scan technique with a femtosecond laser. However, in presence of Zn(II), Ca(II) or Mg(II) ion, each compound gives exceptionally large TPA cross-section in the same wavelength range.

1. Introduction

Molecules that exhibit optical nonlinearity are potentially important in for several technological applications. The two-photon absorption (TPA) process is a third-order nonlinear optical phenomenon and the efficiency of this process is determined by measuring TPA cross-section (σ_2) values. Molecules that have large σ_2 values are potentially useful in several areas of opto-electronics [1]. Both theoretical considerations and experimental results have revealed that the molecular charge transfer symmetry, strength of donor/acceptor groups, chromophore number density and length of conjugated π-backbone are important factors affecting molecular TPA activity [2]. These findings have led to molecules with symmetric donor–(π-bridge)–donor (D–π–D), acceptor–(π-bridge)–donor–(π-bridge)–acceptor (A–π–D–π–A), and donor–(π-bridge)–acceptor–(π-bridge)–donor (D–π–A–π–D) conjugated structural motifs. On excitation, a substantial symmetric intra-molecular charge re-distribution takes place in these molecules resulting [3] in high-TPA cross-section (σ_2). Both dipolar [4] as well as multi-polar [5,6] organic molecules show TPA activity although σ_2 value increases in proceeding from dipolar to multi-polar compounds keeping other parameters unaltered [7]. However, synthesis of multi-polar molecules can be difficult and generally affords low yields of the desired products. Metal ions can assemble simple organic ligands around to build a variety of multi-polar arrangements to tune the molecular NLO property [8] by the 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.

We report here synthesis of two organic compounds having D–π–A–π–D structural motif that have low TPA cross-section in the metal-free state. But in presence of biologically important metal ions such as Mg(II), Ca(II) and Zn(II), the TPA activity of the compounds increases highly. Zinc is an essential nutrient required for normal growth and development [9] and for cellular processes such as DNA repairs [10] and apoptosis [11]. This metal plays a key role in the synthesis of insulin and the pathological state of diabetes [12]. On the other hand, many enzymatic reactions are mediated by Mg(II), while Ca(II) acts as an universal second messenger in cells [13]. While several groups [14] studied TPA modulation by Zn(II), use of Mg(II) and Ca(II) for this purpose are fewer in number [15]. Few studies have been reported [16] in the literature on the TPA properties of ion-responsive chromophores such as calcium orange, calcium green-I, and calcium crimson with σ_2 values in the range of 1–30 GM in the unbound state. Upon binding of calcium ions, σ_2 values increase to 50–100 GM. On the other hand, Mg(II) was shown to lower the σ_2 value by 50% in an aza-crown ether connected to distyrylbenzene in D–π–A–π–D format [15a]. In a recent report, the σ_2 value of 1,10-phenanthroline-based π-conjugated TPA-chromophore was found to increase from 165 to 578 GM upon binding with Ni(II) ion [17]. Both reduction as well as enhancement of TPA can be utilized to inform binding of the guest. However, systems with TPA

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enhancement rather than reduction should be the choice for practical utility.

2. Experimental section

2.1. Analysis and measurements

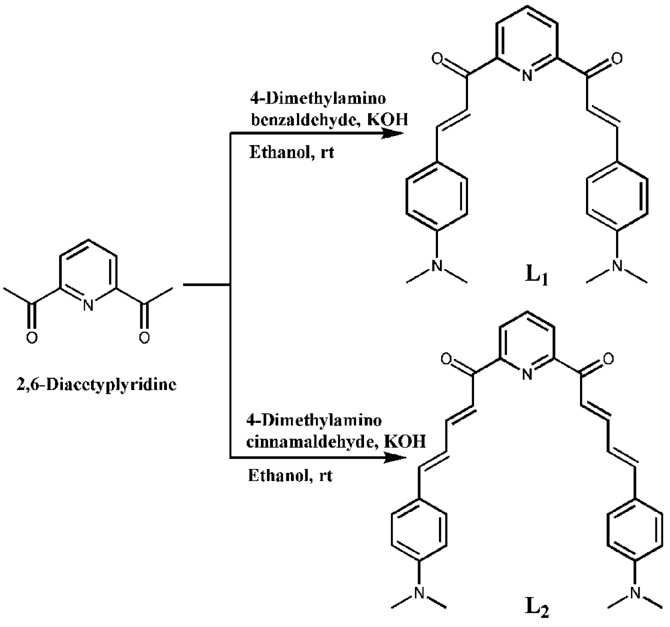
Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin-Elmer Model 1320; UV–visible spectra were recorded on a JASCO V-570 spectrophotometer in CH_3CN at 298 K in 10^{-5} M concentration. Steady-state fluorescence spectra were obtained with a Perkin-Elmer LS 50B Luminescence Spectrometer at 298 K. Fluorescence quantum yield was determined in each case by comparing the corrected spectrum with that of standard quinine sulphate [18] ($\phi = 0.54$ in 1N H_2SO_4); ^{1}H-NMR spectra were recorded on a JEOL JNM-LA400 FT (400 MHz) instrument in $CDCl_3$ with Me_4Si as the internal standard. The electrospray mass spectra (ESI-MS) were recorded on a MICROMASS QUATTRO quadruple mass spectrometer. Melting points were determined with an electrical melting point apparatus by PERFIT, India and were uncorrected. Microanalyses for the complexes were obtained from CDRI, Lucknow, India.

2.2. TPA measurements

TPA cross-section values of these samples are measured by open aperture Z-scan technique. All measurements are done at 1×10^{-5} M concentration in freshly purified CH_3CN solvent using 1 mm long quartz cells. Each solution is allowed to stand for 1 h before measurements. Our femtosecond experimental scheme involves mode-locked coherent Mira titanium: sapphire laser (Model 900) which is pumped by a coherent Verdi frequency doubled Nd:vanadate laser. The model 900 Mira is tunable from 740 to 900 nm and its repetition rate is 76 MHz. We employ blanking [19] by using a mechanical chopper (model SR540), whose frequency is optimized and set to 560 Hz to allow equal ratio of illuminating to blanking of 1 ms. Here, we used 780–900 nm wavelength regions for all the measurements. Using a 20 cm focal length lens, the beam is focused into a 1 mm long cell filled with sample, where it easily produces GW-level intensity at the focal point of the lens while maintaining the cell length to be less than the Rayleigh range (thin sample limit) [20]. The observed nonlinear absorption coefficient values (β) have been calculated by fitting the measured transmittance values to the following [21] expression: $T(z) = 1 - \beta I_0 L/[2(1+z^2/z_0^2)]$, where β = nonlinear absorption coefficient, I_0 = on-axis electric field intensity at the focal point in absence of the sample, L = sample thickness, z_0 = Rayleigh range ($z_0 = \pi\omega_0^2/\lambda$), where ω_0 = is the minimum spot size at the focal point. The β values are calculated by curve fitting of the measured open-aperture traces with the above equation. The TPA cross-section values measured in G.M. ($1\,GM = 1 \times 10^{-50}\,cm^4$. s. $photon^{-1}$ $molecule^{-1}$) in the region, 780–900 nm where neither the ligands nor their complexes show any single-photon absorption. We have taken the known value of σ_2 for Rhodamine-6G as the reference for calibrating our measurement technique [22].

2.3. Materials

All reagent-grade chemicals were used without purification unless otherwise specified. Perchlorate salts[1] of Zn(II), Ca(II) and Mg(II), 2,6-diacetylpyridine, 4-(dimethylamino)benzaldehyde and 4-(dimethylamino)cinnamaldehyde were purchased from Aldrich. Solvents were received from S. D. Fine Chemicals (India) and they were purified prior to use. The syntheses of the compounds were achieved following a published procedure [23,24] as shown in Scheme 1.



Scheme 1. Synthesis of compound $\mathbf{L_1}$ and $\mathbf{L_2}$.

3. Results and discussion

3.1. Synthesis and characterization

The compounds can be readily synthesized in a single step in high yields by aldol condensation. Both are characterized (Table 1) by elemental analysis, ESI-mass and ^{1}H-NMR spectra [24]. Once isolated, they are found to be stable in air and soluble in common organic solvents.

3.2. Electronic spectroscopy

3.2.1. Single-photon absorption

Both one- and two-photon measurements were carried out in MeCN with perchlorate salt of Zn(II), Ca(II) or Mg(II) as input to either ligands and the data are collected in Table 2. The ligand $\mathbf{L_1}$ exhibits two absorption bands with λ_{max} at 263 and 418 nm that are, respectively, the localized excitation and ILCT transitions. The ILCT band is significantly red-shifted with increased ε_{max} upon complexation with a metal ion, the extent of red-shift depends on the nature of the metal ion (Table 2 and Fig. 1a). Ligand $\mathbf{L_2}$ shows the corresponding bands at λ_{max} of 290 and 437 nm. Like in the previous case, the ILCT band red-shifts upon metal complexation (Fig. 1b). The red-shift of the ILCT band causes color change on complexation with a metal ion that is perceptible to the naked-eye [24] and is due to stabilization of the excited state. Both for $\mathbf{L_1}$ and $\mathbf{L_2}$ each of the metal ions gives a well-defined isosbestic point indicative of the presence of an unique complex in equilibrium with the free ligand [24]. Job's plot of the complexes determined from the UV–vis data can be fitted to a 2:1 stoichiometry. This result has also been confirmed by ESI-MS data of the free ligands and their metal complexes [24]. The binding constants of the

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[1] **Caution**! Metal perchlorates may form explosive mixtures with organic compounds. They should be handled carefully and in small quantities.