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Zinc(II)- and Copper(I)-Mediated Large Two-Photon Absorption Cross Sections in a Bis-cinnamaldiminato Schiff Base

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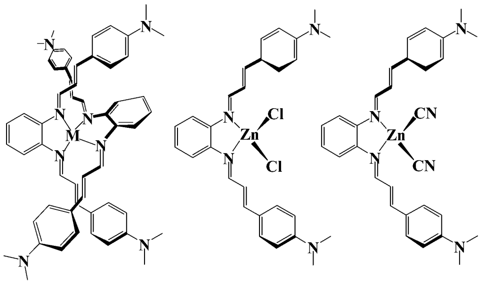
Molecules with large two-photon absorption cross sections (σ_2) have received increasing attention in recent years, due to their potential applications[1] in several areas of bio-photonics and materials science, such as two-photon fluorescence excitation microscopy,[1a] optical power limiting,[1b] three-dimensional optical data storage,[1c] two-photon up-conversion lasing,[1d] photodynamic cancer therapy,[1e] and so on. The two-photon absorption (TPA) process is a third-order nonlinear optical phenomenon, and the efficiency of this process is determined by measuring σ_2 values. The search for optimized molecular structures having large molecular TPA cross sections has led to molecules with donor−π-bridge−acceptor (D−π−A), 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. Upon excitation, a substantial symmetric intramolecular charge redistribution takes place in these molecules, resulting in high TPA cross sections.[2] To date, studies of the TPA phenomenon have focused mostly on dipolar[3] and quadrupolar,[4] dendrimer,[5] and (less so) octupolar[6] molecules. The results of these studies as well as theoretical calculations[7] reveal that the σ_2 value increases on proceeding from dipolar to three-fold symmetry (D_{3h}, D_3, T_d, or D_{2d}) octupolar compounds and also with increasing donor and acceptor strength.[8] However, syntheses of multipolar molecules having π-conjugated structural motifs incorporating donor and acceptor moieties require a lot of synthetic skill and generally afford very low yields of the desired products. Surprisingly, very little attention has been paid to coordination complexes for this purpose.

Metal ions, being powerful 3D templates, can assemble simple organic ligands in a variety of multipolar arrangements showing interesting electronic and optical properties and tunable by virtue of the coordinated metal center. This can induce a strong intraligand charge-transfer (ILCT) transition as well as a low-energy metal−ligand charge-transfer transition (MLCT). Metal complexes have high damage threshold and fast response time in comparison to organic compounds—properties that are important from the perspective of applications. Few organometallic complexes are reported in the literature that show σ_2 values in the range 10−2100 GM (1 GM $= 10^{-50}$ cm^4 s photon^{-1} molecule^{-1}).[8] Some reports are also available describing the effect of metal ions on TPA-active organic chromophores. Thus, Mg(II) was shown to lower the σ_2 values by 50% in an aza-crown ether connected to distyrylbenzenes in the D−π−A−π−D format.[9] On the other hand, Prasad and co-workers observed that the σ_2 values of 1,10-phenanthroline-based π-conjugated TPA chromophores increased from 165 GM to 578 GM upon their binding with Ni(II) ion.[10]

Herein, we report a Schiff base which does not have any two-photon absorption cross section at 890 nm, but when complexed with Zn(II) or Cu(I) ions to afford **1**−**4** (Scheme 1), it exhibits exceptionally high σ_2 values at the same wavelength, underlining the important role of the metal ion. Zn(II) ion is ubiquitous in biology, and measuring its concentration and imaging its spatial distribution in biosystems are of enormous importance. These metal ions, having no ligand field stabilization energy, prefer tetrahedral (T_d) coordination geometry and are excellent 3D templates. The σ_2 value of up to 10 736 GM, measured by a femtosecond open-aperture *Z*-scan technique, are among the highest values known for any coordination metal complexes to date.

Scheme 1. Schematic Representation of the Complexes

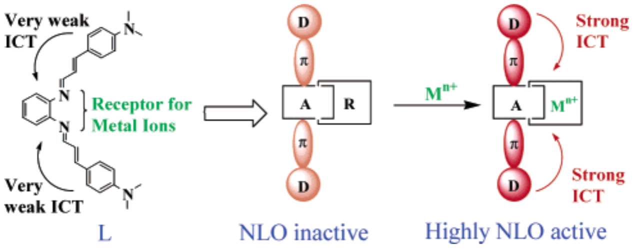


1. M = Zn(ClO$_4$)$_2$
2. M = Cu(BF$_4$)

3

4

Scheme 2. Plan for Metal-Mediated Third-Order Nonlinear Responses in D−π−A−π−D Schiff Base Ligand[a]



[a] R, receptor; D, donor; π, ethylenic conjugated moieties; M^{n+}, Zn(II) and Cu(I) ions.

The Schiff base ligand (**L**) belongs to the D−π−A−π−D analogue since the central diimine part possesses very weak electron-withdrawing character. Complexation with Zn(II) or Cu(I) enhances the electron-acceptor character of the central diimine moiety, converting **L** to a more strongly polarized D−π−A−π−D unit (Scheme 2) that makes these complexes potential candidates for third-order nonlinear responses.

The ligand **L** is synthesized in ~90% yield as a yellow solid by Schiff base condensation of *o*-phenylenediamine with 4-(dimethylamino)cinnamaldehyde in ethanol. The octupolar complexes **1** and **2** are readily obtained as deep red solids by treating Zn(ClO$_4$)$_2$·6H$_2$O in dichloromethane and [Cu(MeCN)$_4$]BF$_4$ in acetonitrile respectively with 2 equiv of **L**. Similarly, the dipolar complexes **3** and **4** are isolated as red solids by treating 1 equiv of **L** with ZnCl$_2$·2H$_2$O and Zn(CN)$_2$ respectively in dichloromethane/methanol (1:1) at room temperature. Only **4** can be isolated in single-crystal form, and its structure is confirmed by X-ray crystallography,[11] while the other structures are characterized by ES-MS as well as

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Table 1. Linear and Nonlinear Spectroscopic Data for **L**, **1**−**4**

compd	$\lambda_{\text{max abs}}$ (nm)	$\epsilon \times 10^4$ (mol L^{-1} cm^{-1})	σ_2 (GM)[a]	T_d (°C)
L	378	4.62		160 (mp)
1, $Zn(L)_2(ClO_4)_2$	493	15.45	10736	240
2, $Cu(L)_2(BF_4)$	461	8.49	10198	260
3, $ZnCl_2(L)$	448	8.15	1769	220
4, $Zn(CN)_2(L)$	446	6.85	1700	210

[a] The errors are ±1%. See Supporting Information.

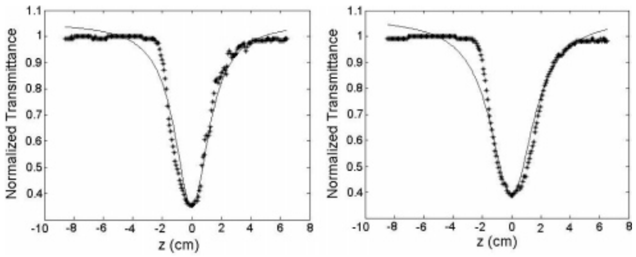

Figure 1. Open-aperture *Z*-scan traces of **1** and **2**. Solid lines are the best fits to the experimental data.

^{1}H NMR spectroscopy. All four complexes show satisfactory elemental analysis. These complexes possess good thermal stability and decompose above 200 °C.[11]

The linear and nonlinear spectroscopic data[11] of **L** and **1**−**4** are summarized in Table 1. The ligand **L** exhibits a broad absorption band with λ_{max} at 378 nm which is a combination of $\pi-\pi^*$ and ILCT transitions. This band is significantly red-shifted upon complexation with Zn(II) and Cu(I), where the amount of red-shift is sensitive to the structure of the complexes. This is attributable to the change in the electronic properties of **L** into a more strongly polarized D−π−A−π−D unit (Scheme 2). The nonlinear optical measurements were performed in the near-infrared region since it is clear from the UV−vis spectra[11] that the Schiff base (**L**) and all the metal complexes (**1**−**4**) are transparent in this region.

The TPA cross section (σ_2) values were measured by using a standard open-aperture *Z*-scan technique[12] for 1-cm-long quartz sample cells. We have used 100-fs pulses at 890 nm with 76-MHz repetition rate from a mode-locked tunable Coherent Mira titanium: sapphire laser (model 900) which is pumped by a Coherent Verdi frequency-doubled Nd:vanadate laser. By using a 20-cm lens for our experiments, GW level laser intensities are easily produced at the focus, which induces TPA in the sample. All of the compounds were measured at 5×10^{-4} M solution concentration in dichloromethane solvent. The solvent itself does not show any TPA activity under the experimental conditions. We have calculated the observed nonlinear absorption coefficient values (β)[13] by fitting our measured transmittance values to the following expression: $T(z) = 1 - \beta I_0 L/[2(1 + z^2/z_0^2)]$, where β is a nonlinear absorption coefficient, I_0 is the on-axis electric field intensity at the focal point in the absence of the sample, L is the sample thickness, and z_0 is the 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 the measured open-aperture traces with the above equation. Figure 1 shows the open-aperture traces of **1** and **2**. We have taken rhodamine 6G, for which the σ_2 value is known in the literature,[14] as the reference for calibrating our measurement technique.

Free ligand **L** does not show any nonlinear absorption behavior at 890 nm. In contrast, significant nonlinear absorption performance is observed for each of the complexes **1**−**4** at the same wavelength. While the TPA cross sections of dipolar complexes **3** and **4** are quite similar, those of **1** and **2** are nearly 6 times higher. The increased chromophore number densities[15] in **1** and **2** with octupolar structure[16] may be responsible for the large TPA cross sections compared to those of the other two structurally related dipolar complexes. The σ_2 of **1** is larger than that of **2**, which can be attributed to the greater acceptor strength of Zn(II) in comparison to Cu(I), leading to an increased ILCT in **L**.[7]

In conclusion, we have adopted a very simple strategy to induce exceptionally large σ_2 values on a Schiff base through metal complexation whose magnitude depends on the structure of the complex. The high thermal stability as well as high TPA cross sections make theses complexes potential candidates for NLO applications. Further studies are in progress on other systems in our laboratory.

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Supporting Information Available: Crystallographic data of **4** (CIF); synthesis, spectroscopic characterization, and UV−vis spectra of **L** and **1**−**4**; open-aperture *Z*-scan traces of **2**, **3**, and rhodamine 6G; TGA analysis of **1**−**4**; complete ref 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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