Design and synthesis of 1,10-phenanthroline based Zn(II) complexes bearing 1D push–pull NLO-phores for tunable quadratic nonlinear optical properties

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Abstract

Three Zn(II) complexes bearing 1,10-phenanthroline and one-dimensional (1D) push–pull NLO-phores with various acceptor strength as well as π-conjugation length have been synthesized in high yields for two-dimensional (2D) nonlinear optical response. The quadratic optical nonlinearity of the ligands and the complexes are measured by the HRS technique. The ligands show small second-order optical nonlinearity (β) comparable to the standard, *para*-nitroaniline (*p*NA). However, upon complexation with Zn(II), each complex exhibits large β values showing the importance of metal ion in enhancing the optical nonlinear effect.
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1. Introduction

Synthesis of molecules displaying large second-order nonlinear optical (NLO) properties is of interest for their potential applications [1] in telecommunication, optical computing, optical data storage and so on. Efficiency of this property is determined by measuring the molecular first hyperpolarizability, β. At the molecular level, compounds likely to exhibit large β values must have polarizable electrons (i.e., π-electrons) spread over a large distance. Thus, organic dipolar compounds with extended π systems having terminal donor and acceptor groups are likely to exhibit large β values [2]. However, a major problem associated with these one-dimensional (1D) dipolar chromophores is the nonlinearity-transparency trade-off, such that the increase in the second-order hyperpolarizabil-

ity is accompanied by a bathochromic shift of the electronic transition, leading to undesirable dispersion, fluorescence and re-absorption effects [3]. Beside, the second-order molecular optical nonlinearity (β_{ijk}) of such classical dipolar push–pull NLO-phores is mostly one-dimensional in character and dominated by one hyperpolarizability β tensor component. Several design principles have been adopted during the past decade to circumvent these drawbacks by extending the charge transfer from one to higher dimensions (2D, 3D) [4]. Thus, recognition of molecules with multi-dimensional (*n*D) charge-transfer characteristics in nonlinear optics have triggered various synthetic research activities [5–7] with multi-polar molecules for second-order NLO applications. Compared to 1D dipolar NLO-phores, they offer several advantages such as increased β responses due to multi-dimensional β tensor components, easier non-centrosymmetric arrangements and an improved nonlinearity trade-off. Among the miscellaneous goals and strategies, one attractive approach is the

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design of compounds in which the assembly of several (identical or complementary) 1D NLO-phore leads to an improved optical response to the resulting multi-chromophoric compound with respect to its monomeric counterpart. There are few examples based on calix [4] arenes [8], β-cyclodextrin [9], polyamides [10], dendrimers [11] where 1D dipolar NLO-phores are incorporated via covalent linkages to show significantly large β values in comparison to the monomeric dipolar counterparts.

Metal ions being excellent templates, can gather organic 1D dipolar chromophores around to form predetermined 2D and 3D NLO-phores with various symmetries and charge-transfer dimension tunable by virtue of the coordinated metal center as well as the presence of polarizable d electrons can also contribute [12] to greater nonlinear activity (Scheme 1).

Other advantages of using metal complexes as NLO materials include higher damage threshold, fast response time and easy synthesis. Recent reports are available in the literature on Zn(II), Cu(I) and Ru(III) complexes of 4,4′-bis(dialkylaminostyryl)-[2,2′]-bipyridine ligands [13] with large β values of $140–340 \times 10^{-30}$ esu. As the Zn(II) ion usually prefers tetrahedral coordination geometry, it can serve as an excellent 3D template. We describe here the synthesis of three 1,10-phenanthroline based Zn(II) complexes (Fig. 1) for two-dimensional nonlinear optical response where 1D dipolar NLO-phores with different length of π-conjugation and acceptor strength are bonded

to the metal ion resulting in large enhancement of β values with respect to the corresponding 1D dipolar ligand.

2. Experimental section

Reagent grade 4-dimethylaminobenzoic acid (L_1), 4-(dimethylamino)cinnamic acid (L_2), 4-dimethylaminobenzaldehyde, *tert*-butyl-cyanoacetate and 1,10-phenanthroline monohydrate were acquired from Lancaster. Reagent grade zinc(II) acetate dihydrate was from SD Fine Chemicals, India. All these chemicals were used as received. All solvents (SD Fine Chemicals) were freshly distilled prior to use.

3. Analysis and measurements

Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer Model 1320; UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer in CH$_3$CN at 298 K. ^{1}H NMR spectra were recorded on a JEOL JNM-LA400 FT (400 MHz) instrument in CDCl$_3$ with Me$_4$Si as the internal standard. The electrospray mass spectra (ES-MS) were recorded on a MICROMASS QUATTRO Quadruple Mass Spectrometer. The samples, dissolved in acetonitrile were introduced into the ESI source through a syringe pump at the rate of 5 μl/min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. The spectra were collected in 6 s scans and the print outs were average spectra of 6–8 scans. 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.

4. Synthesis

Among the three ligands used in this study, the first two (i.e., L_1 and L_2) are commercially available (Lancaster). The ligand 4-dimethylamino-α-cyanocinnamic acid (L_3) was synthesized via Knoevenagel condensation as shown in Scheme 2.

Typically, to a 50 mL absolute ethanolic solution of 4-dimethylaminobenzaldehyde (0.6 g; 4 mmol) was added
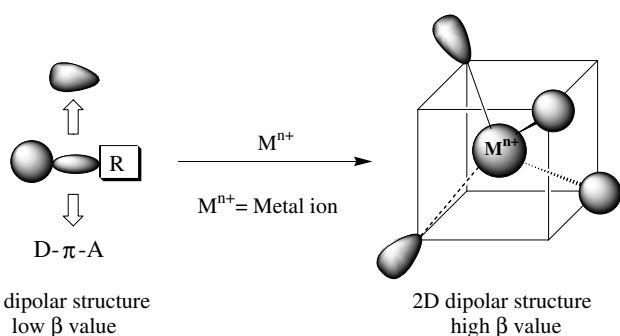
Scheme 1. A schematic representation of designing 2D dipolar structure through metal–ligand coordination for tunable NLO responses. R, receptor for metal ion; M^{n+}, Zn(II) ion.
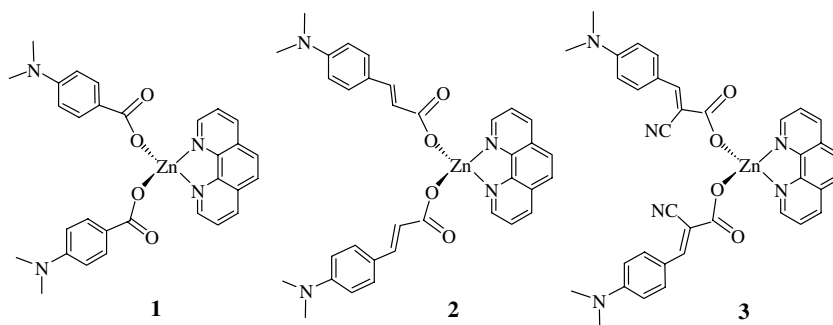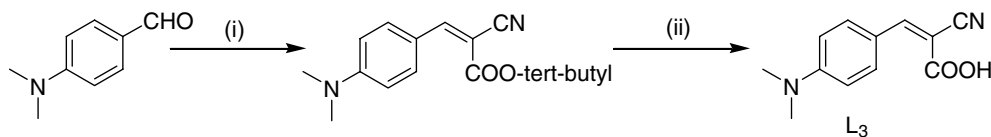

Fig. 1. Schematic representation of the Zn(II) complexes used in the study.

Scheme 2. Synthetic scheme for **L₃**. Reagents and conditions: (i) *tert*-butyl cyanoacetate, 2 drops of piperidine and absolute ethanol (ii) trifluoroacetic acid.

0.6 mL (4.4 mmol) of *tert*-butylcyanoacetate through a syringe all at a time followed by catalytic amount (2 drops) of piperidine. The orange yellow solid that appeared on stirring overnight at room temperature, was collected by filtration, washed thoroughly with ethanol and dried under vacuum. This solid was stirred for 2 h, with 3 mL of trifluoroacetic acid and then poured into 50 mL of water. The orange yellow solid that separated, was collected by filtration, washed with ethanol and finally dried under vacuum. Yield: 90%. Anal. Calc. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 62.88; H, 5.72; N, 13.08%.

4.1. [Zn(phen)(L₁)₂] (1)

A methanolic solution (15 mL) containing 4-dimethylaminobenzoic acid (**L₁**), (0.33 g; 2 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.22 g; 1 mmol) and 1,10-phenanthroline monohydrate (0.2 g; 1 mmol) were allowed to stir for 24 h at room temperature. An off-white solid separated which was collected by filtration, washed with methanol and finally dried under vacuum. The same product is obtained on using different molar ratios of the reactants signifying stability of the product under the reaction conditions. Yield: 80%. ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 2.72 (s, 12H), 6.24 (d, $J = 8.79$, 4H), 7.55–7.52 (m, 1H), 7.60 (d, $J = 8.79$, 4H), 7.64–7.62 (m, 1H), 7.69 (bs, 2H), 8.26 (d, $J = 8.03$, 2H), 9.06 (bs, 2H); ES-MS (*m/z*): 572(35%) [M−H]⁺. Anal. Calc. for $C_{30}H_{28}N_4O_4Zn_1$: C, 62.78; H, 4.92; N, 9.76. Found: C, 62.88; H, 5.01; N, 9.85%. IR (KBr phase): 3082vw, 2911vw, 2814vw, 1605vs, 1523s, 1475m, 1441s, 1396vs, 1362vs, 1318m, 1194vs, 782vs, 611s cm⁻¹ (vw, very weak; w, weak; m, medium; s, strong; vs, very strong).

4.2. [Zn(phen)(L₂)₂] (2)

This compound was isolated in a similar manner taking 4-dimethylamino cinnamic acid (**L₂**) (0.38 g; 2 mmol) in place of **L₁** keeping other reactants unchanged. The yellow solid was collected by filtration, washed thoroughly with methanol and dried under vacuum. Yield: 85%. ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 2.72 (s, 12H), 5.88 (d, $J = 15.87$, 2H), 6.21 (d, $J = 8.55$, 4H), 6.9 (d, $J = 8.79$, 4H), 7.05 (d, $J = 15.87$, 2H), 7.59 (bs, 2H), 7.67 (bs, 2H), 8.26 (d, $J = 7.79$, 2H), 8.95 (bs, 2H); ES-MS (*m/z*): 625(20%) [M−H]⁺. Anal. Calc. for $C_{34}H_{32}N_4O_4Zn_1$: C, 65.23; H, 5.15; N, 8.95. Found: C, 65.33; H, 5.23; N, 9.07%. IR (KBr phase): 3070vw, 2892vw, 2806vw, 1631vs, 1606vs, 1527vs, 1429vs, 1362vs, 1252vs, 1225s,

1181vs, 1064w, 985vs, 946m, 864vs, 813vs, 728vs, 704s cm⁻¹ (vw, very weak; w, weak; m, medium; s, strong; vs, very strong).

4.3. [Zn(phen)(L₃)₂] (3)

Synthesis of this complex is also accomplished following a similar procedure taking 4-dimethylamino-α-cyanocinnamic acid (**L₃**), (0.43 g; 2 mmol) in place of **L₂**. The bright yellow solid that separated upon stirring overnight was collected by filtration, washed with methanol and dried under vacuum. Yield: 87%. ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 2.86 (s, 6H), 2.98 (s, 6H), 6.47 (d, $J = 9.03$, 2H), 6.55 (d, $J = 9.03$, 2H), 7.65 (d, $J = 8.79$, 4H), 7.85–7.78 (m, 4H), 7.96 (s, 2H), 8.41 (d, $J = 6.79$, 2H), 9.21 (bs, 2H); ES-MS (*m/z*): 675(18%) [M−H]⁺. Anal. Calc. for $C_{36}H_{30}N_6O_4Zn$: C, 63.96; H, 4.47; N, 12.43. Found: C, 64.11; H, 4.55; N, 12.57%. IR (KBr phase): 3108vw, 2905w, 2207vs, 1769m, 1601vs, 1526vs, 1351vs, 1235s, 1182vs, 945m, 814s, 719vs, 544m cm⁻¹ (vw, very weak; w, weak; m, medium; s, strong; vs, very strong).

5. NLO measurements

Second, harmonic measurements in solution were carried out by the hyper-Rayleigh scattering (HRS) technique [14]. The fundamental (1064 nm) of a Q-switched Nd:YAG laser (Spectra Physics, DCR-3G, 8 ns) beam was focused by a biconvex lens (f.1. 10 cm) to a spot 5 cm away after passing through the glass cell containing the sample. The scattered light in the perpendicular direction was collected by a UV–Vis sensitive photomultiplier tube (PMT). For wavelength discrimination, a monochromator (Czerny Turner 0.25 m) was used and no other collection optics was employed. The input power was monitored using a power meter. All data were collected at laser power ⩽24 mJ pulse⁻¹ that is below the threshold for stimulated Raman, self-focusing/self-defocusing, Brillouin scattering, and dielectric breakdown. The experimental set-up was first standardized by measuring the β value for *para*-nitroaniline (pNA) in CH₃CN by the external reference method [15] and a value of 22.1×10^{-30} e.s.u. was obtained that was close to the reported value for this compound. The monochromator was scanned at intervals of 2 nm to find if the signal at the second harmonic wavelength has any contribution from two or multi-photon fluorescence in **L₁**, **L₂**, **L₃** and **1**–**3**. In fact, it was found that all the compounds do not have any two-photon fluorescence around 532 nm. All the complexes showed excellent stability under laser

irradiation and no sign of decomposition could be detected. Blank experiments (without ligands) with metal ions were performed, that showed no contribution to the HRS intensity due to the metal salts. Fig. 2 displays the plots of $I_{2\omega}/I_{\omega}^2$ vs. number density of **1**, **2** and **3** as well as reference standard pNA. From the ratio of the two slopes (i.e., ratio of slope of compound and pNA) in Fig. 2a and b, the β value of **1**, **2** and **3** was determined by external reference method.

6. Results and discussion

All the complexes are stable in air and their solubility in common organic solvents. The IR spectra of complexes **1**–**3** show that the coordination geometry around the Zn(II) ion are almost same for all the complexes. Although the carbonyl stretching frequency of complexes **1** and **3** are 1605 cm^{-1} and 1601 cm^{-1}, respectively whereas in case of complex **2** it is 1631 cm^{-1} attributable to the more symmetric binding nature [16a] of the carboxylate to the Zn(II) ion in complex **2**. The cyano group in complex **3** remains non-interacting with the metal and shows a strong peak at 2207 cm^{-1}. Metal-coordinated cyano groups show [16b] the stretching frequency above 2250 cm^{-1}. The thermal analysis data obtained on the complexes [17] show that each complex is stable at least up to 250 °C that make them potentially useful as NLO materials. The complexes were characterized by ^{1}H NMR, IR and ES-Mass spectroscopy as well as by elemental analysis [17]. The UV–Vis spectral data of the three ligands and corresponding Zn(II) complexes recorded in dry CH$_3$CN are displayed in Fig. 3. The ligands exhibit intraligand charge transfer absorption in the near UV-region. The peak position is quite sensitive to the length of conjugation as well as acceptor strength and shifts monotonously to higher wavelengths as the conjugation length and acceptor strength increases. On complexation with Zn(II), a small blue-shift is observed (Fig. 3) in each case offering better transparency compared to the ligands.

The molecular first hyperpolarizabilities of **L$_1$**–**L$_3$** and their Zn(II) complexes are collected in Table 1. The corre-
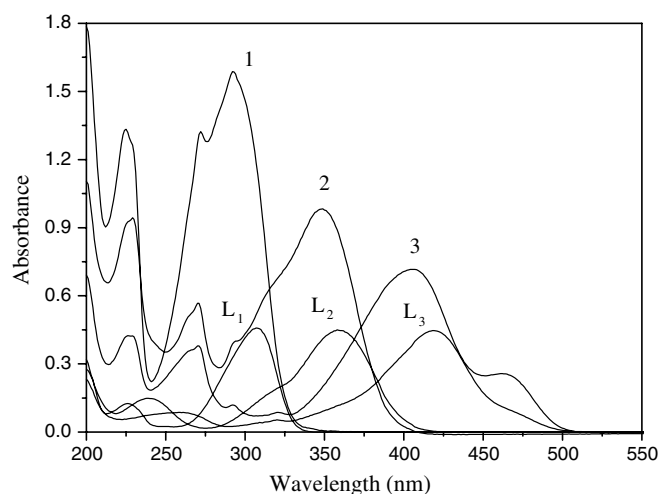

Fig. 3. Absorption spectra of the ligands and their Zn(II) complexes in CH$_3$CN (conc. 1×10^{-5} M).

sponding β_0 static values are derived from the well-known two-state model [18] and are listed as well. The first hyperpolarizability (β) for **L$_1$**–**L$_3$** are slightly lower comparable to that of the standard, pNA (Table 1) although the trend shows that the β value increases with higher conjugation and acceptor strength causing greater polarization of the entity which can stabilize the charge-separated form much more as expected [2e,19].

Table 1
Linear and nonlinear optical data

Compound	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	β (10^{-30} esu)	β_0 (10^{-30} esu)	T_d (°C)[a]
pNA (standard)	340	22.1	11.7	–
L$_1$	307 (45,781)	10.2	6.2	–
L$_2$	358 (44,959)	16.7	8.1	–
L$_3$	417 (44,479)	20.2	6.6	–
1	292 (158,733)	49.0	31.3	300
2	349 (98,256)	82.7	41.5	260
3	404 (71,577)	107.9	39.2	260

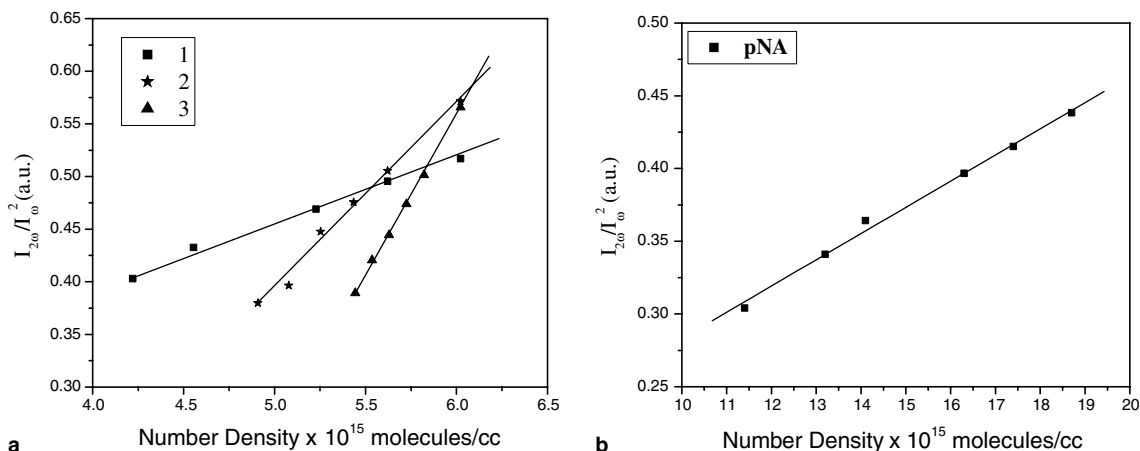[a] Decomposition temperature.

Fig. 2. (a) Plots of $I_{2\omega}/I_{\omega}^2$ vs. number density of **1**, **2** and **3**. (b) A plot of $I_{2\omega}/I_{\omega}^2$ vs. number density of reference standard pNA.

The absorption spectra of the Zn(II) complexes show blue shift with a broadening compare to its monomeric counterparts L_1–L_3 that can attributable from several interactions between the 1D NLO-phores such as electrostatic or π–π cofacial interactions [20], excitanic coupling [21], hindered solvation or aggregation effects within the Zn(II) complex. As the harmonic wavelength is far enough from the $\lambda_{cut-off}$ for the ligands as well as their Zn(II) complexes, any contribution of two-photon-induced fluorescence to the HRS signal can be considered as negligible. Table 1 shows that **2** possesses higher β value compared to **1** whereas **3** exhibits the highest β value among the three. The Zn(II) ion organizes two 1D NLO-phores ligands around leads to strong dipolar interactions enhancing the polarizability of the complex unit which can significantly affect in the marked increase of the β values of the complexes compared to the 1D chromophores underlying the importance of metal ions in modulating the optical nonlinearity.

7. Conclusion

In conclusion, we have shown that a simple synthetic strategy to obtained 2D dipolar Zn(II) complexes from 1D push–pull NLO-phoric ligands via metal-template effect with very large second-order optical nonlinearity (β values). The monomeric 1D dipolar ligands themselves do not exhibit any significant β values but readily form complexes with Zn(II) ion resulting various 2D dipolar structures that shows significantly high β values in comparison to the monomeric 1D dipolar counterparts underlying the importance of the Zn(II) ion in the spontaneous self-organization of the 1D dipolar NLO-phores within the complexes. The high thermal stability and large optical nonlinearity of these complexes offer them potential candidate as a NLO materials. We are presently working with metal mediated second as well as third-order nonlinear optical properties where the metal ions are taken from both the transition and the inner transition series.

Acknowledgements

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