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Synthesis and characterization of mono- and bis-D–π–A cryptand derivatives for second-order nonlinear optics and its modulation with different metal ion inputs†

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Two new classes of mono- and bis-D–π–A cryptand derivatives with a flexible and a rigid cryptand core have been synthesized. The linear and nonlinear optical properties of these molecules are probed. The three dimensional cavity of the cryptand moiety has been utilized to modulate the SHG intensity to different extents in solution with metal ion inputs such as Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II}. We also report that decomplexation events can be used to reversibly modulate their NLO responses.

Introduction

Nonlinear optical (NLO) materials have attracted increasing attention from chemists in recent years[1–3] as these materials are of enormous importance in the fields of telecommunications, optical data storage, information processing, and so on. Particularly, molecular engineering of multi-polar molecules has become the subject of intense research activity, due to several advantages they have over traditional dipolar molecules.[4] The multi-polar molecules can be designed to be quite transparent, yet they can exhibit large second order nonlinearity at no cost of transparency. Several studies on molecules with different symmetries (C_{2v}, D_2, C_3, D_3, and T) have been devoted addressing the usefulness and potential of these systems for nonlinear optics.[5–7] This approach was found to be highly efficient when four D–π–A units were incorporated in a calix[4]arene based system.[8] Similarly, this molecular engineering approach was successfully implemented in triphenylcarbinol[9] and binaphthyl[10] based systems with, respectively, three and two D–π–A units present in the building blocks. Recently, a β-cyclodextrin core incorporating seven D–π–A units was reported[11] to have excellent nonlinear optical properties. Earlier, we reported[12] that macrobicyclic cryptands can be efficiently utilized for designing molecules with quadratic NLO activity both at the molecular and the bulk levels.

Incorporation of switchability in NLO active molecules[13] would increase its utility manifold although very few molecules with such characteristics have been reported to date. The NLO based tunable materials are designed mainly using photoexcitation as the stimulus to carry out the structural changes at the molecular level.[14] Recently, reversible redox switching has been applied to design NLO active switchable compounds, with a Ru^{II} complex[15] and in octamethylferrocene linked to nitrothiophene *via* an ethenyl conjugated bridge.[16] Modulation of the NLO responses based on metal ion recognition events provides an alternative pathway. But, to best of our knowledge, only one example is available in the literature of a crown ether based molecule, where alkali and alkaline-earth metal ions irreversibly modulate its NLO property.[17] Transition metal ions provide a greater variety of electronic structure and geometry but surprisingly have not been utilized for NLO modulation in macrocyclic or macropolycyclic structures. A cryptand molecule[18] capable of including an ion or a neutral molecule inside its 3-D cavity, is attractive for modulation of the NLO property in the presence of guest molecules.

We report here, a new class of molecules (**B$_1$**–**B$_4$**), which have been synthesized by covalently linking two π–A units in two cryptand cores. The corresponding monomeric compounds (**M$_1$**–**M$_4$**) incorporating a single π–A unit have also been synthesized. The linear and nonlinear optical properties of these two sets of molecules are presented here. The effects of a flexible cryptand core (*ortho*-cryptand **L$_o$**) *vis-à-vis* a rigid core (*meta*-cryptand **L$_m$**) on the linear and nonlinear optical properties are also reported.

These bis- and mono-derivatized cryptands have, respectively, one and two secondary N atoms free for coordination with metal ions apart from a bridgehead N atom at each end of the cavity. This results in a larger residual electron density in the cavity of these molecules for metal ion binding compared to the tris–π–A functionalized cryptand molecules reported earlier.[12] Hence, these systems are suitable for modulating the NLO responses. We report for the first time, that recognition of different metal ions inside the 3-D cavity of either a mono- (**M$_1$**) or a bis-π–A functionalized (**B$_1$**) cryptand can be utilized for modulating its NLO response (Fig. 1). We also report that

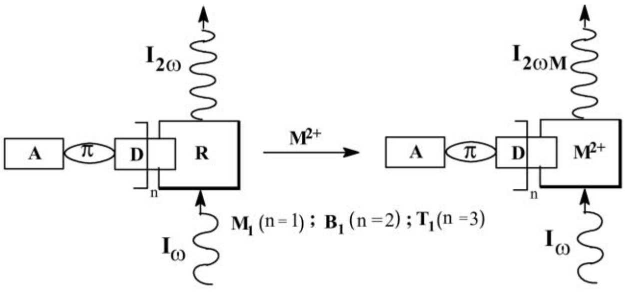

Fig. 1 Plan for switching of NLO responses in D–π–A functionalized cryptand molecules. R, receptor; D, donor; π, aromatic ring; A, acceptor; *n*, number of D–π–A units; M^{2+}, metal ions; I_{ω}, fundamental light; $I_{2\omega}$, second harmonic light; $I_{2\omega M}$, modulated second harmonic light.

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†Electronic supplementary information (ESI) available: 400 MHz ^{1}H-NMR and FAB mass spectra of compounds **M$_1$**–**M$_4$** and **B$_1$**–**B$_4$**. See http://www.rsc.org/suppdata/jm/b2/b203199j/

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its NLO property can be reversibly tuned by following metal ion complexation and decomplexation events.

Experimental section

Materials and methods

Reagent grade 2,4-dinitrochlorobenzene (SD Fine Chem., India), 2-chloro-5-nitropyridine (Lancaster) and 1-fluoro-4-nitrobenzene (Fluka) were used without further purification. All the solvents were freshly distilled prior to use and all reactions were carried out under an N_2 atmosphere. Chromatographic purification was achieved by column chromatography using 100–200 mesh silica gel obtained from Acme Synthetic Chemicals.

The compounds were characterized by elemental analyses, ^{1}H NMR and FAB MS (positive ion). A JEOL JNM-LA400 FT (400 MHz) instrument was used for recording ^{1}H NMR spectra in $CDCl_3$ with Me_4Si as the internal standard. FAB MS (positive ion) data were recorded on a JEOL SX 102 /DA-6000 mass spectrometer using argon as the FAB gas at 6 kV and 10 mA with an accelerating voltage of 10 kV and the spectra were recorded at 298 K. Melting points were determined with an electrical melting point apparatus by PERFIT, India, and were uncorrected. UV–visible spectra were recorded on a Jasco V-570 spectrophotometer in $CHCl_3$ at 298 K. Elemental analyses were done either at the IIT Kanpur or at the CDRI, Lucknow.

NLO measurements

The hyper-Rayleigh scattering (HRS) technique was applied to carry out the second harmonic measurements in solution. In this experiment, 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.l. 22 cm) to a spot 8 cm away after passing through the glass cell containing the sample. A UV–visible sensitive photomultiplier tube (PMT) was used to collect the scattered light in the perpendicular direction. For wavelength discrimination, a monochromator (Triax MSL-T5AX2, 0.55 m) was used and no other collection optics were employed. The input power was monitored using a power meter. All data were collected at laser powers $\leqslant 24$ 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 $\boldsymbol{\beta}$ value for paranitroaniline (*p*NA) in CH_3CN by the external reference method[19] and a value of 21×10^{-30} esu was obtained. The monochromator was scanned at intervals of 2 nm to find if the signal at the second harmonic wavelength had any contribution from two- or multi-photon fluorescence in $\mathbf{M_1}$–$\mathbf{M_4}$ and $\mathbf{B_1}$–$\mathbf{B_4}$. It was found that the molecules did not show any two-photon fluorescence around 532 nm. The HRS titration experiments were carried out in dry MeCN, as the solvent and the metal perchlorates used were of the purest quality available. The $\boldsymbol{\beta}_{\text{excess}}$[17] values were determined by using excess metal ions (25 times) with respect to the free D–π–A cryptand derivatives. Blank experiments (without cryptand molecules) with metal ions were performed, which showed no contribution to the HRS intensity due to the metal salts.

Synthesis

To a suspension of the *o*-cryptand $\mathbf{L_o}$[20] (0.56 g, 1 mmol) in dry EtOH (40 mL) was added anhydrous K_2CO_3 (0.44 g, 2 mmol) and the reaction mixture was stirred for 10 min. Subsequently, a solution of 2,4-dinitrochlorobenzene (0.65 g, 1.8 mmol) in dry EtOH (10 mL) was added dropwise for 15 min and the reaction mixture was stirred at RT for 2 h and then refluxed for 4 h when the solution became yellow–orange in colour. After cooling to RT, the solvent was removed under vacuum and the yellow solid obtained was repeatedly washed with water (5 × 100 mL). The three components were separated by silica gel column chromatography. The tris-dinitro derivative ($\mathbf{T_1}$)[12] was eluted using chloroform : methanol in the ratio 99.5 : 0.5 (v/v) as the eluent.

$\mathbf{B_1}$. The second component $\mathbf{B_1}$ was subsequently eluted, using chloroform : methanol in a 98.5 : 1.5 (v/v) ratio. The product was isolated as a fine yellow crystalline solid. Yield 29%; mp 105 °C; ^{1}H NMR: δ 2.52 (br s, 6H), 2.70 (br s, 2H), 3.15–3.18 (m, 4H), 3.28–3.36 (m, 6H), 3.93 (s, 2H), 4.13 (br s, 4H), 4.29 (br s, 2H), 4.45 (s, 4H), 6.78–7.18 (m, 14H), 7.93 (d, J = 9.3 Hz, 2H), 8.54 (s, 2H); FAB MS (*m*/*z*) 892 (100%); Anal. Calcd for $C_{45}H_{49}N_9O_{11}$: C, 60.59; H, 5.54; N, 14.13. Found: C, 60.63; H, 5.63; N, 14.09.

$\mathbf{M_1}$. The third product was isolated as a bright yellow crystalline solid using a chloroform : methanol ratio of 95.5 : 4.5 (v/v). Yield 32%; mp 145 °C; ^{1}H NMR: δ 2.42–2.51 (m, 4H), 2.64–2.75 (m, 4H), 2.89–2.94 (m, 2H), 3.23–3.26 (m, 4H), 3.35–3.41 (m, 4H), 3.62 (d, J = 13 Hz, 2H), 3.91 (d, J = 13 Hz, 2H), 4.23–4.26 (m, 6H), 4.48 (s, 2H), 5.33 (br, 2H), 6.82–6.99 (m, 8H), 7.1 (d, J = 9.4 Hz, 1H), 7.22–7.28 (m, 4H), 8.07 (dd, J = 9.4 Hz, J = 2 Hz, 1H), 8.54 (d, J = 2 Hz, 1H); FAB MS (*m*/*z*) 726 (100%); Anal. Calcd for $C_{39}H_{47}N_7O_7$:C, 64.54; H, 6.53; N, 13.51. Found: C, 64.62; H, 6.61; N, 13.42.

Synthesis of $\mathbf{B_2}$ and $\mathbf{M_2}$

To a suspension of $\mathbf{L_o}$ (0.56 g, 1 mmol) in 40 mL of dry *N*-methyl-2-pyrrolidone (NMP), was added freshly distilled Et_3N (0.32 g, 2 mmol). Subsequently, a solution of 2-chloro-5-nitropyridine (0.51 g, 1.8 mmol) in dry NMP (15 mL) was added dropwise in 20 min and the reaction mixture was stirred at RT for 24 h and for a further period of 30 h at 70 °C for completion of the reaction. It was then poured into cold water (200 mL). The pale yellow solid separated was collected by filtration and washed repeatedly with water (5 × 100 mL). This mixture of tris-, bis- and mono-nitropyridine derivatives of $\mathbf{L_o}$ was passed through a silica gel column. The tris-nitropyridine derivative ($\mathbf{T_2}$)[12] was first to separate as a bright yellow crystalline solid, using chloroform : methanol in a 99 : 1 ratio (v/v) as the eluent.

$\mathbf{B_2}$. This was eluted out with a chloroform : methanol ratio of 97.5 : 2.5 (v/v). Evaporation of the solvent afforded a golden yellow crystalline solid. Yield 24%; mp 115 °C; ^{1}H NMR: δ 2.58 (br s, 2H), 2.73–2.75 (m, 6H), 3.11–3.14 (m, 2H), 3.24 (br s, 4H), 3.62 (br s, 4H), 3.91 (s, 2H), 4.12–4.25 (m, 6H), 4.82 (br s, 4H), 6.07 (d, J = 8.8Hz, 2H), 6.71–7.23 (m, 12H), 7.85 (d, J = 8.8 Hz, 2H), 8.81 (d, J = 2.7Hz, 2H); FAB-MS (m/z) 804 (100%); Anal. Calcd for $C_{43}H_{49}N_9O_7$: C, 64.24; H, 6.14; N, 15.68. Found: C, 64.33; H, 6.23; N, 15.58.

$\mathbf{M_2}$. The mono-derivative being the most polar, was last to come out using chloroform : methanol in 93.5 : 6.5 ratio (v/v) as the eluent. This product was isolated as a pale yellow crystalline solid. Yield 31 %; mp 160 °C; ^{1}H NMR: δ 2.50–2.52 (m, 4H), 2.64–2.66 (m, 2H), 2.76–2.79 (m, 2H), 2.93–2.94 (m, 2H), 3.21–3.23 (m, 4H), 3.32–3.35 (m, 2H), 3.58–3.62 (m, 4H), 3.93 (d, J = 13 Hz, 2H), 4.17–4.22 (m, 4H), 4.32–4.34 (m, 2H), 4.74 (s, 2H), 5.29 (br s, 2H), 6.39 (d, J = 9.4 Hz, 1H), 6.82–7.32 (m, 12H), 8.09 (dd, J = 9.4 Hz, J = 2.4 Hz, 1H), 8.94 (s, 1H); FAB MS (*m*/*z*) 682 (100%); Anal. Calcd for $C_{38}H_{47}N_7O_5$: C, 66.94; H, 6.95; N, 14.38. Found: C, 67.04; H, 6.99; N, 14.29.

Synthesis of $\mathbf{B_3}$ and $\mathbf{M_3}$

To a suspension of $\mathbf{L_o}$ (0.56 g, 1 mmol) in dry DMSO (30 mL) was added anhydrous K_2CO_3 (0.44 g, 3.2 mmol). 1-Fluoro-4-nitrobenzene (0.45g, 3.2 mmol) in dry DMSO (15 mL) was added dropwise in 20 min and the reaction mixture was stirred at RT for 24 h and then at 70 °C for 48 h. The reaction mixture was then poured into cold water (200 mL). The bright yellow solid that separated was collected by filtration and washed thoroughly with water (5 × 100 mL). The tris-substituted product ($\mathbf{T_3}$) was first to separate using chloroform : methanol in the ratio 99.75 : 0.25 (v/v) as the eluent in a silica gel column.

$\mathbf{B_3}$. This compound was next to come out using chloroform : methanol in a 99 : 1 ratio (v/v) as the eluent. The product was isolated as a bright yellow crystalline solid. Yield 30%; mp 138 °C; ^{1}H NMR: δ 2.53–2.56 (m, 4H), 2.61–2.69 (m, 6H), 3.08–3.23 (m, 4H), 3.43 (br s, 4H), 3.83 (s, 2H), 4.05–4.07 (m, 4H), 4.18–4.29 (m, 2H), 4.76 (br s, 4H), 6.30 (d, J = 8.8 Hz, 4H), 6.63–7.22 (m, 12H), 7.83 (d, J = 8.8 Hz, 4H); FAB MS (*m/z)* 802 (100%); Anal. Calcd for $C_{45}H_{51}N_7O_7$: C, 67.39; H, 6.41; N, 12.23. Found: C, 67.48; H, 6.48; N, 12.16.

$\mathbf{M_3}$. This was finally separated using chloroform : methanol in a 96 : 4 ratio (v/v) as the eluent. The product was isolated as a bright yellow crystalline solid. Yield 21%; mp 175 °C; ^{1}H NMR: δ 2.45–2.66 (m, 6H), 2.84–2.89 (m, 4H), 3.02–3.16 (m, 6H), 3.65 (d, J = 13.4 Hz, 4H), 3.98 (d, J = 3.8 Hz, 4H), 4.16–4.27 (m, 4H), 4.89 (d, J = 13.6 Hz, 2H), 6.31 (d, J = 9.5 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 6.83–6.95 (m, 5H), 7.18–7.26 (m, 5H), 8.0 (d, J = 9.3 Hz, 2H); FAB MS (*m/z*) 681 (100%); Anal. Calcd for $C_{39}H_{48}N_6O_5$: C, 68.80; H, 7.11; N, 12.34. Found: C, 68.91; H, 7.23; N, 12.28.

The compounds $\mathbf{B_4}$ and $\mathbf{M_4}$ were synthesized following the procedure adopted for the synthesis of $\mathbf{B_1}$ and $\mathbf{M_1}$ by using $\mathbf{L_m}$[21] instead of $\mathbf{L_o}$. The crude product was passed through a silica gel column and the tris-derivative ($\mathbf{T_4}$) was eluted using chloroform : methanol in a 99.5 : 0.5 ratio (v/v) as the eluent.

$\mathbf{B_4}$. This compound was next separated with chloroform : methanol in a 98.5 : 1.5 ratio (v/v) as the eluent and isolated as a golden yellow crystalline solid. Yield 28%; mp 107 °C; ^{1}H NMR: δ 2.53–2.60 (m, 8H), 3.07–3.25 (m, 10H), 3.56 (s, 2H), 3.88–3.89 (m, 2H), 4.01–4.08 (m, 4H), 4.24 (s, 4H), 6.51 (s, 2H), 6.66–6.88 (m, 10 H), 7.19–7.27 (m, 2H), 8.02 (dd, J = 9.3 Hz, J = 2.7 Hz, 2H), 8.59 (d, J = 2.9 Hz, 2H); FAB MS (*m/z)* 892 (100%); Anal. Calcd for $C_{45}H_{49}N_9O_{11}$: C, 60.59; H, 5.54; N, 14.13. Found: C, 60.63; H, 5.59; N, 14.06.

$\mathbf{M_4}$. This mono-derivative was separated finally with chloroform : methanol in a 95.5 : 4.5 ratio (v/v) as the eluent and isolated as a bright yellow crystalline solid. Yield 33%; mp 130 °C; ^{1}H NMR: δ 2.47–2.67 (m, 6H), 2.86–2.92 (m, 4H), 3.01–3.16(m, 8H), 3.67 (d, J = 12.7 Hz, 2H), 3.9–4.07 (m, 8H), 4.15 (d, J = 12.4 Hz, 2H), 6.54–6.83 (m, 9H), 6.98 (d, J = 7.3 Hz, 2H), 7.22–7.29 (m, 2H), 8.02 (dd, J = 9.5 Hz, J = 2.7 Hz, 1H), 8.53 (d, J = 2.7 Hz, 1H); FAB MS (*m/z*) 726 (100%); Anal. Calcd for $C_{39}H_{47}N_7O_7$: C, 64.54; H, 6.53; N, 13.51. Found: C, 64.60; H, 6.59; N, 13.46.

Results and discussions

Synthesis

With the aim of tailoring the electron density to different extents inside the 3-D cavity of the cryptand, we have adopted a new synthetic strategy whereby functionalized cryptand molecules with varying numbers of π–A units are formed in one pot following the aromatic nucleophilic substitution (ArSN) reactions[22] (Scheme 1 and Scheme 2). In this strategy, the hassles of multi-step protection and deprotection of amines can be avoided and mono-, bis- and tris-π–A functionalized cryptands can be formed in one pot by simple variation of the stoichiometry of the reactants. This is summarized in Table 1 for $\mathbf{M_1}$, $\mathbf{B_1}$ and $\mathbf{T_1}$.

Linear and nonlinear optical properties

The UV spectra of $\mathbf{M_1}$–$\mathbf{M_4}$ and $\mathbf{B_1}$–$\mathbf{B_4}$ were recorded in CH_3CN and are shown in Fig. 2. The broad and intense absorption band exhibited by these molecules in the near ultraviolet region are attributable to the charge-transfer transition from the donor amino N atom to the acceptor nitro group. This absorption band shows a hypsochromic shift for the bis-π–A substituted cryptands compared to the corresponding mono-π–A substituted ones. This shift is maximum in the case of $\mathbf{B_3}$, which shows (Fig. 2) a blue shift of 11 nm of the charge-transfer band compared to that exhibited by $\mathbf{M_3}$. Moreover, the intensity of this band is higher for the bis-derivatives compared to the mono-derivatives, that makes the molecules ($\mathbf{B_1}$–$\mathbf{B_4}$) particularly noteworthy as they show much better transparency compared to ($\mathbf{M_1}$–$\mathbf{M_4}$). Further, changing the core from $\mathbf{L_o}$ to $\mathbf{L_m}$, a hypsochromic shift in the charge-transfer band is observed—$\mathbf{M_4}$ showing a 7 nm blue shift with respect to $\mathbf{M_1}$ while $\mathbf{B_4}$ shows a shift of 11 nm with respect to $\mathbf{B_1}$.

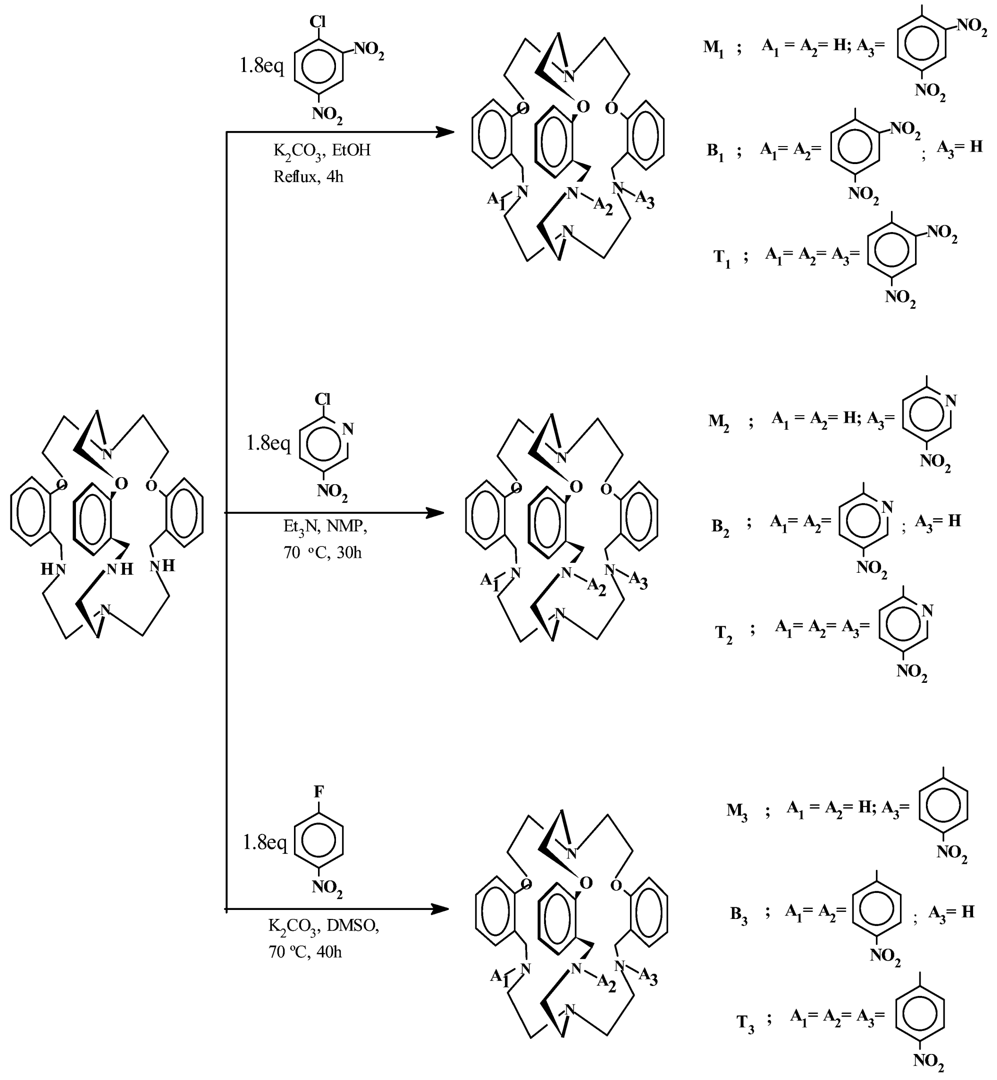
The first hyperpolarizabilities ($\boldsymbol{\beta}$) of the compounds are determined by the hyper-Rayleigh scattering (HRS) technique[23] in CH_3CN. The corresponding static hyperpolarizability values ($\boldsymbol{\beta}_0$) are derived from the well known two-state model.[24] The values are summarized in Tables 2 and 3. It is observed that covalent linking of multi-chromophoric units around a cryptand core is beneficial for maintaining a good transparency/nonlinearity trade-off.

The compound $\mathbf{M_4}$ shows the maximum $\boldsymbol{\beta}$ value amongst $\mathbf{M_1}$–$\mathbf{M_4}$ combined with a good transparency. The static hyperpolatizability ($\boldsymbol{\beta}_0$) value of this compound is 1.8 times that of *p*NA. The compounds $\mathbf{B_1}$–$\mathbf{B_4}$ exhibit 30–40% higher $\boldsymbol{\beta}$ values than the corresponding $\mathbf{M_1}$–$\mathbf{M_4}$. This is significant as higher $\boldsymbol{\beta}$ values shown by $\mathbf{B_1}$–$\mathbf{B_4}$ are accompanied by greater transparency in the visible region. Similar observations have been made[8a] in case of multichromophoric calixarenes, which show better transparency and higher $\boldsymbol{\beta}$ values for the bis-derivatives compared to the corresponding mono-derivatives. The compound $\mathbf{B_4}$ shows the highest $\boldsymbol{\beta}$ value amongst all the compounds studied and its $\boldsymbol{\beta}_0$ is almost 2.5 times greater than the reference compound *p*NA. The greater rigidity of the $\mathbf{L_m}$ core as found from the solid-state structures,[20] results in a higher $\boldsymbol{\beta}$ value accompanied by greater transparency ($\mathbf{M_4}$, $\mathbf{B_4}$) compared to the corresponding ($\mathbf{M_1}$, $\mathbf{B_1}$) with the less rigid $\mathbf{L_o}$ core.[21]

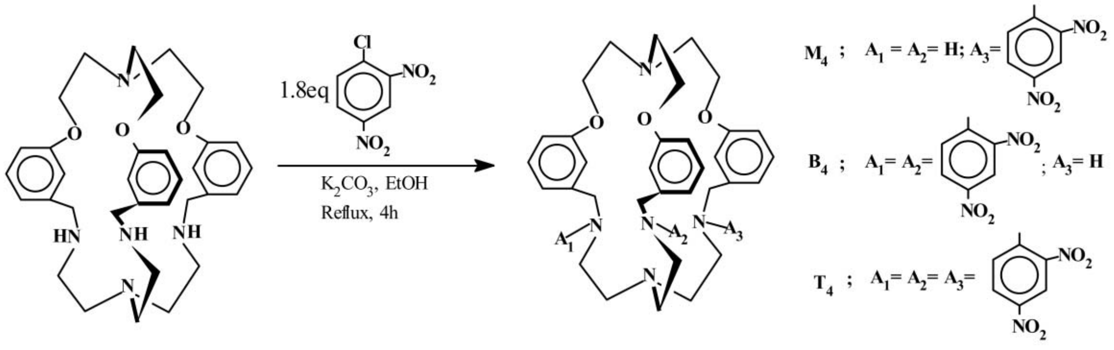
Modulation of linear and non linear optical property

The unsubstituted cryptand derivative $\mathbf{L_o}$ has versatile complexation properties[25] with transitions as well as heavy metal ions, which have earlier been characterized crystallographically.[20] This prompted us to investigate the modulation of linear and nonlinear optical properties of the π–A functionalized $\mathbf{L_o}$ molecules, $\mathbf{M_1}$ and $\mathbf{B_1}$, with different metal ions.

The alkali metal ions such as Li^I, Na^I, and K^I or the alkaline earth metal ions such as Mg^{II} and Ca^{II} do not show any changes in the absorpton spectra, since they occupy the upper part of the cryptand core and are thus unable to communicate with the D–π–A chromophore units. Addition of a metal ion such as Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} induces anti-auxochromic shifts in the absorption spectra of the functionalized cryptand molecules, as these metal ions are in direct communication with the D–π–A chromophore units. On gradual addition of a metal ion, the absorption spectra show a well-defined isosbestic point, suggesting a 1 : 1 stoichiometry with the π–A functionalized cryptand. Compound $\mathbf{M_1}$ exhibits a maximum blue shift in the



Scheme 1 Formation of mono-, bis- and tris-π–A functionalized cryptands with the *ortho*-cryptand core $\mathbf{L_o}$



Scheme 2 Formation of mono-, bis- and tris-π–A functionalized cryptands with the *meta*-cryptand core $\mathbf{L_m}$

Table 1 Synthesis of $\mathbf{M_1}$, $\mathbf{B_1}$ and $\mathbf{T_1}$ by varying the stoichiometry of the reactants

Entry	Donor/equivalents of *o*-cryptand) $\mathbf{L_o}$	π–A/equivalents of 2,4-dinitrochlorobenzene	Yield (%)		
			Mono $\mathbf{M_1}$	Bis $\mathbf{B_1}$	Tris[12] $\mathbf{T_1}$
1	1	1	44	20	18
2	1	1.4	39	24	22
3	1	1.8	32	29	25
4	1	2.4	24	32	34
5	1	3.0	—	—	92

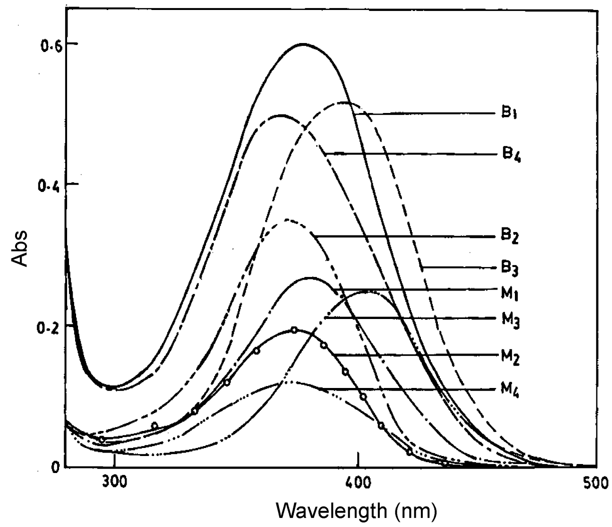


Fig. 2 UV spectra of $\mathbf{M_1}$–$\mathbf{M_4}$ and $\mathbf{B_1}$–$\mathbf{B_4}$ (1×10^{-5} M) in MeCN

Table 2 Results of hyper-Rayleigh scattering measurements on $\mathbf{M_1}$–$\mathbf{M_4}$ in MeCN (λ = 1064 nm, T = 298 K)

	pNA	M_1	M_2	M_3	M_4
λ_{max}	357	379	375	403	372
$\beta/10^{-30}$esu	21	19	26	26	27
$\beta_0/10^{-30}$esu	10	12	17	16	18

Table 3 Results of hyper-Rayleigh scattering measurements on $\mathbf{B_1}$–$\mathbf{B_4}$ in MeCN (λ = 1064 nm, T = 298 K)

	*p*NA	B_1	B_2	B_3	B_4
λ_{max}	357	377	370	392	366
$\beta/10^{-30}$esu	21	25	29	32	34
$\beta_0/10^{-30}$esu	10	16	20	20	23

presence of Cu^{II} ions (21 nm) with respect to the metal-free cryptand. Similarly, $\mathbf{B_1}$ shows a maximum blue shift in the presence of Cu^{II} ions (30 nm) (Fig. 3). These results indicate that intramolecular charge-transfer (ICT) from the amine (donor) to the nitro (acceptor) within the conjugated unit is hindered to the maximum extent as the nitrogen lone pair interacts with the Cu^{II} ion. The tris-dinitro substituted cryptand ($\mathbf{T_1}$) shows no change in the absorption spectra with any of the metal ions. This is expected, as the 3-D cavity in $\mathbf{T_1}$ is deficient of electron density, since all the three N atoms are conjugated with the π–A chromophores and thus lose their coordination abilities. It has been known from our earlier studies[21b] on the Ni^{II} complex with $\mathbf{L_0}$ that the metal ion can be removed from the cavity by adding NaCN as the more stable $[Ni(CN)_4]^{2-}$ complex. So, addition of NaCN to either of the Ni^{II} complexed π–A functionalized cryptands, results in the restoration of the position and absorbance of the metal-free $\mathbf{M_1}$ or $\mathbf{B_1}$. This result provides an ample scope for reversible modulation of the NLO property.

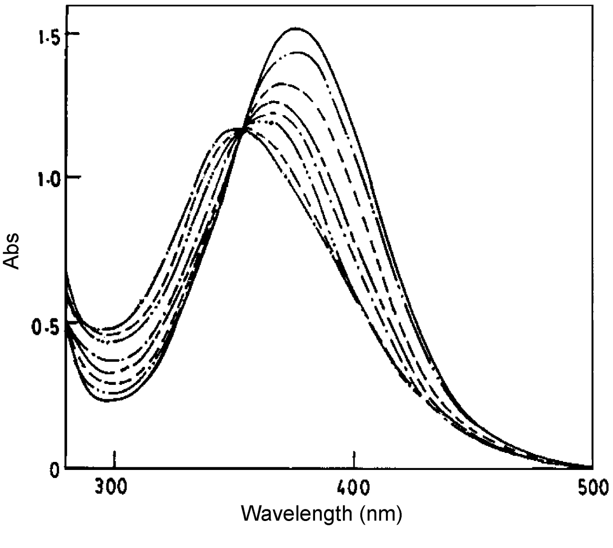


Fig. 3 Effect of Cu^{II} addition on the UV spectra of $\mathbf{B_1}$: (——) metal-free cryptand $\mathbf{B_1}$ (5×10^{-5} M); (— ·· —) Cu^{II} (2.5×10^{-5} M); (– – –) Cu^{II} (5×10^{-5} M); (— - —) Cu^{II} (1.6×10^{-4} M); (— · —) Cu^{II} (5×10^{-4} M); (— ··· —) Cu^{II} (8×10^{-4} M); (———) Cu^{II} (1.6×10^{-3} M); (— · —) Cu^{II} (5×10^{-3} M).

Table 4 Summary of data for modulating NLO responses in D–π–A cryptands with metal ions

D–π–A cryptand	Metal ion input	$\Delta\lambda$/nm	$\beta_{excess}/10^{-30}$esu	Modulation of β (%)
$\mathbf{M_1}$	—		19	
	Ni	−11	13	32
	Cu	−21	10	47
	Zn	−8	13	32
	Cd	−10	12	37
$\mathbf{B_1}$	—		25	
	Ni	−19	15	40
	Cu	−30	10	60
	Zn	−8	16	36
	Cd	−9	14	44

In agreement with the UV–vis studies, addition of an alkali or an alkaline-earth metal ion does not change the HRS signal intensity for $\mathbf{M_1}$ and $\mathbf{B_1}$. However, a substantial decrease in the β values can be observed on addition of a transition metal ion (Table 4). As expected from the absorption spectral studies, Cu^{2+} modulates the β value to the maximum extent of 47% and 60% for $\mathbf{M_1}$ and $\mathbf{B_1}$, respectively. Further exploration of the NLO modulation by titration experiments shows that a progressive decrease in SHG intensity occurs with the amount of the added metal ion. A 1 : 1 stoichiometry is also confirmed from these titration experiments (Fig. 4). As expected, a maximum decrease in SHG intensity is observed with Cu^{II} ion both in the case of $\mathbf{M_1}$ and $\mathbf{B_1}$ to the extent of 63% and 80%, respectively. This modulation depends on the different extents of ICT in the metal-free and metal-bound states. Thus, a variety of metal ions can be used to modulate the NLO property to different extents in these systems. The maximum decrease in SHG intensity both in the case of $\mathbf{M_1}$ and $\mathbf{B_1}$ with Cu^{II} ion is noteworthy as Cu^{II} can readily tune its geometry according to the need of the preorganized binding sites of these π–A functionalized cryptand molecules, compared to the other

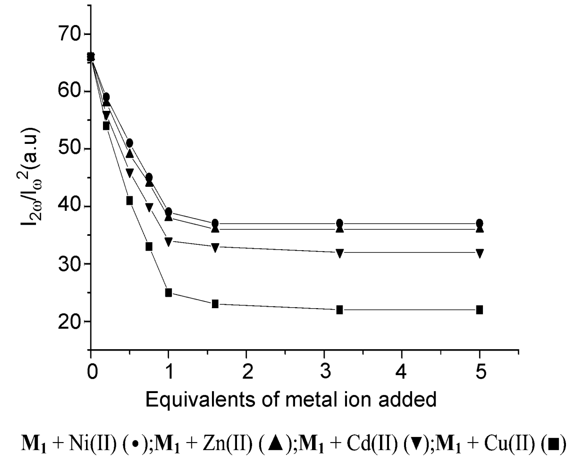


Fig. 4 Plot of HRS signal ($I_{2\omega}/I_{\omega}^2$) of $\mathbf{M_1}$ as a function of concentration of different metal ion inputs.

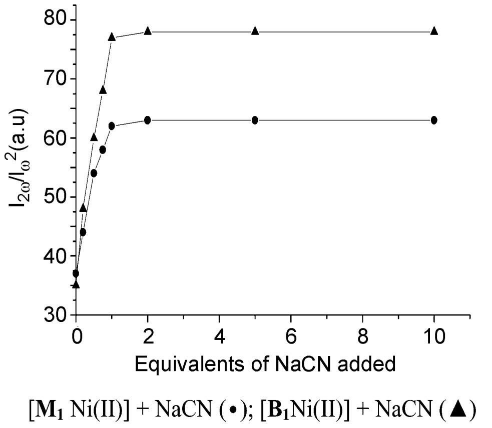


Fig. 5 Plot of HRS signal ($I_{2\omega}/I_\omega^2$) of Ni^{II} complexed D–π–A cryptand $\mathbf{M_1}$ and $\mathbf{B_1}$ as a function of added NaCN concentration.

metal ions such as Ni^{II}, Zn^{II}, and Cd^{II}, which prefer higher coordination numbers.[26]

Addition of $Ni(H_2O)_6(ClO_4)_2$ to $\mathbf{M_1}$ and $\mathbf{B_1}$, decreases the SHG intensity by 44% and 60%, respectively, due to formation of the Ni^{II} complexes. However, when NaCN is added to these complexes, the SHG intensity gradually increases until it reaches almost the value of the metal-free cryptand due to removal of all of Ni^{II} as the more stable $[Ni(CN)_4]^{2-}$ complex (Fig. 5). Thus, complexation/de-complexation events can be utilized to reversibly modulate the SHG activity in these D–π–A cryptand molecules. The extent of SHG modulation achieved with different metal ions is significantly larger (up to 80%) than that reported by Houbrechts *et al.*[17] with crown ether-based molecules (up to 35%) and alkali or alkaline-earth metal ions as modulating agents.

Conclusion

In conclusion, we have shown that a simple and straightforward synthetic strategy can be utilized for having mono- and bis-D–π–A cryptand molecules with NLO activity. The bis-derivatives as well as the compounds with the more rigid core ($\mathbf{L_m}$) show favorable transparency/nonlinearity trade-off. Moreover, it has been shown for the first time, that a cryptand cavity can modulate the NLO property with different metal ions, and to larger extents compared to the reported crown ether-based molecule. The free secondary amines in these molecules can be readily functionalized with long alkyl chains to have a new generation of cryptand-based amphiphilic molecules which will have potential use for device fabrication. We are presently engaged in research along these lines.

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