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Modulation of SHG responses via supramolecular association/dissociation between two complementary cryptands

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Abstract

Two sets of complementary cryptands are investigated for supramolecular nitro–amino H-bonding interactions in solutions. The D-π-A cryptand and the unsubstituted cryptand forms 1:1 H-bonded structure. Its second harmonic generation capabilities in solution are explored by HRS titration experiments. Supramolecular assembly leads to spontaneous increase of the SHG intensity, which undergoes steady decrease on addition of MeOH due to the breakdown of the H-bonded structure. Thus, NLO responses can be reversibly modulated by applying such supramolecular principles.

Keywords: Cryptands; H-bonding interactions; Supramolecular assembly; SHG intensity

1. Introduction

Organic molecules with loosely held electrons such as those with π bonds can exhibit large optical nonlinearity [1]. The Traditional approach to the design of materials with enhanced molecular second-order NLO coefficients has been to use molecules with extended π-systems and significant molecular dipoles [2]. However, some of the drawbacks associated with dipolar molecules, such as unfavorable NLO efficiency/transparency trade-off and the tendency to adopt centrosymmetric packing in the solid state have led to the discovery of multipolar molecules for quadratic nonlinearity [3].

It is anticipated that materials, which combine NLO properties with switchability/tunability will find novel applications and are expected to become the materials of choice for the next generation of photonic devices [4]. Few reports are available on materials, where photoexcitation [5], metal ion recognition [6], and redox reactions [7] have been utilized as the stimuli for modulating the NLO activity. Modulation of NLO response by H-bonding interactions provides an attractive alternative pathway. Such interactions have been used to modulate the second harmonic intensity in a melamine–cyanuric acid complex [8] and in a ferrocene-based H-bonded assembly [9].

We have recently reported [10] that cryptands can exhibit quadratic NLO activity both at the molecular and at the bulk levels when functionalized with suitable π-A (acceptor) groups. Moreover, such systems offer NLO modulation by metal ion complexation and decomplexation events [11]. The self-assembly of supramolecular structures via molecular recognition between complementary H-bonding components has developed into a central theme for constructing well-defined arrangements of molecules in solution, in liquid crystals or in

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the solid state [12]. The nitro and amino groups form H-bonded structures, which are well documented in the crystal structures of NLO active nitro anilines [13] as well as in other organic structures [14]. Here, we demonstrate that the SHG intensity of a cryptand, functionalized with three π-A groups, can be modulated in solution on addition of the corresponding complementary parent cryptand ($\mathbf{L_{otn}}$ and $\mathbf{L_o}$) and ($\mathbf{L_{mtn}}$ and $\mathbf{L_m}$) (Fig. 1) due to the formation of H-bonded aggregation in solution. The effect of rigidity of the *meta*-cryptand core on the H-bonding formation and its effect on SHG responses are also investigated.

2. Experimental

2.1. Materials

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

2.2. Analysis and measurements

The compounds were characterized by elemental analyses, ^{1}H NMR and FAB mass (positive ion) spectroscopy. A JEOL JNM-LA400 FT (400 MHz) instrument was used for recording ^{1}H NMR spectra in $CDCl_3$ with Me_4Si the internal standard. FAB mass (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 unconnected.

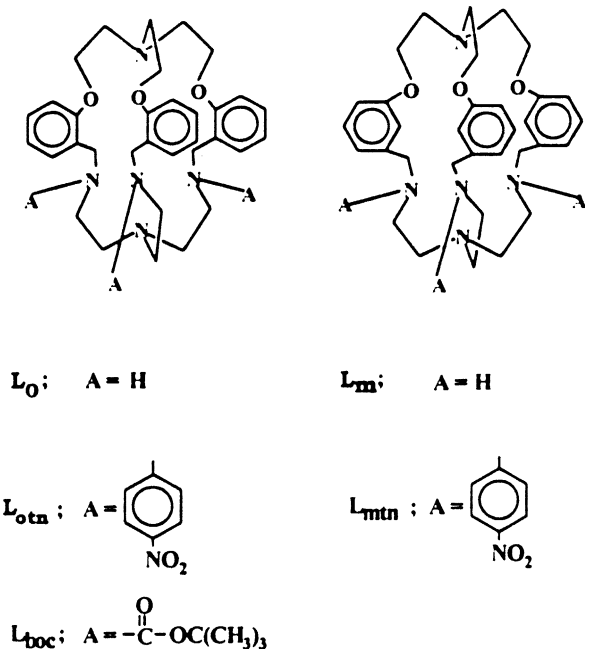


Fig. 1. Structure of the cryptands headgroups ($\mathbf{L_o}$ and $\mathbf{L_{otn}}$) and ($\mathbf{L_o}$ and $\mathbf{L_{otn}}$) investigated for H-bonding experiments.

2.3. NLO measurements

The HRS technique was employed to carry out 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. An UV–Vis 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 was employed. The input power was monitored using a power meter. All data were collected at laser powers $\leq$24 mJ/pulse, 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 pNA in $CHCl_3$ by the external reference method [15a] and a value of 18×10^{-30} e.s.u. was obtained which was close to the reported value of 16.4×10^{30} e.s.u. for this compound [15b]. 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 the compounds. It was found that the molecules did not show any two-photon fluorescence around 532 nm. The HRS titration experiments were done in dry chloroform as the solvent.

2.4. Synthesis

o-N_5O_3 ($\mathbf{L_o}$) [16] and *m*-N_5O_3 ($\mathbf{L_m}$) [17] were synthesized as reported earlier from our laboratory. $\mathbf{L_{otn}}$. To a solution of *ortho*-cryptand $\mathbf{L_o}$ (0.56 g, 1 mmol) in dry DMSO (15 mL) was added anhydrous K_2CO_3 (0.44 g, 3.2 mmol). Subsequently 1-fluoro-4-nitrobenzene (0.45 g, 3.2 mmol) in dry DMSO (15 mL) was added dropwise in 30 min and the reaction mixture was allowed to stir at 70 °C for 48 h. The reaction mixture was then poured into cold water (250 mL). The yellow solid separated, was collected by filtration and washed thoroughly with water (5×100 mL). The trisubstituted product was purified by column chromatography (SiO_2, 100–200 mesh, Hexane/EtOAc, 4:1) and recrystallized from MeCN to obtain a bright yellow crystalline solid. Yield: 92%; m.p. 230 °C.

Characterization: ^{1}H NMR: δ 2.78 (s br, 6H), 3.07 (s br, 6H), 3.56 (s br, 6H), 4.29 (s br, 6H), 4.85 (s, 6H), 6.44 (d, $J = 9.3$ Hz, 6H), 6.53–7.23 (m, 12H), 7.74 (d, $J = 9.3$Hz, 6H). ^{13}C NMR: 50.22, 51.12, 51.25, 53.79, 63.96, 110.20, 111.45, 120.88, 124.54, 125.46, 125.86, 128.19, 136.89, 151.49. and 155.69 ppm. FAB-MS (*m/z*) 923 (70%); Anal. Calcd. for $C_{51}H_{54}N_8O_9$: C, 66.36; H, 5.89; N, 12.14. Found: C, 66.39; H, 5.97; N, 12.01%.

L_{mtn}. This was synthesized in a similar manner as used for **L_{otn}** except that the cryptand **L_m** was used in place of **L_o**. Yield: 91%; m.p. 165 °C.

Characterization: ^{1}H NMR: δ 2.59 (t, $J = 6.2$ Hz, 6H), 3.06 (t, $J = 4.6$ Hz, 6H), 3.35 (t, $J = 6.2$ Hz, 6H), 3.97 (t, $J = 4.6$ Hz, 6H), 4.44 (s, 6H), 6.48 (d, $J = 9.4$ Hz, 6H), 6.56 (s, 3H), 6.66–7.18 (m, 9H), 8.03 (d, $J = 9.4$ Hz, 6H). ^{13}C NMR: 49.49, 53.07, 55.15, 57.10, 68.76, 110.79, 113.56, 114.06, 118.64, 126.28, 130.07, 137.66, 137.99, 152.93, 159.89 ppm. FAB-MS (*m/z*) 923 (30 %) Anal. Calcd. for $C_{51}H_{54}N_8O_9$: C, 66.36; H, 5.89; N, 12.14. Found: C, 66.51; H, 5.94: N, 12.06%.

L_{boc}. To a solution of the *ortho*-cryptand **L_o** (0.56 g, 1 mmol) in dry DCM (25 mL), was added dropwise a solution of di-*tert*-butyl dicarbonate (0.69 g, 3.2 mmol) in dry DCM (25 mL) at 5 °C over a period of 30 min. The reaction mixture was stirred at RT for 8 h. Subsequently, the solvent was removed under vacuo and the white solid obtained was repeatedly washed with water (5×50 mL). The solid was further purified by recrystallization from DCM–Hexane (1:5) to give a white crystalline solid. Yield: 94%; m.p. 89 °C.

Characterization: ^{1}H NMR: δ 1.38 (s, 27H), 2.28–2.63 (m, 6H), 3.01–3.34 (m, 12H), 4.10 (s, 6H), 4.47–4.53 (m, 6H), 6.77–7.24 (m, 12H). FAB-MS (*m/z*) 860 (100%) Anal. Calcd. for $C_{48}H_{69}N_5O_9$: C, 67.03; H, 8.08; N, 8.14. Found: C, 67.14: H, 8.01; N, 8.21%.

3. Results and discussions

The cryptand **L_o** has three sets of secondary amino protons as donor sites for H-bonding with the complementary cryptand **L_{otn}**, which has three sets of nitro groups, acting as the H-bonding acceptor sites.. Thus, on titration (in dry $CDCl_3$) with **L_{otn}**, the N–H protons of the cryptand **L_o** shows a maximum downfield shift of 0.12 ppm at 1:1 molar ratio, as expected on the basis of their involvement in hydrogen bonding with the oxygen of the nitro groups. A plot of the chemical shift of the NH protons vs. the molar ratio of the compound **L_{otn}** added to **L_o** is shown in Fig. 2. The methylene protons, phenyl protons, and the protons of the nitrobenzene ring remain practically unchanged during the titration experiment. Addition of excess of **L_{otn}** does not change the chemical shift position of the amino protons of **L_o**. As a control experiment, the NMR titration of **L_o** with

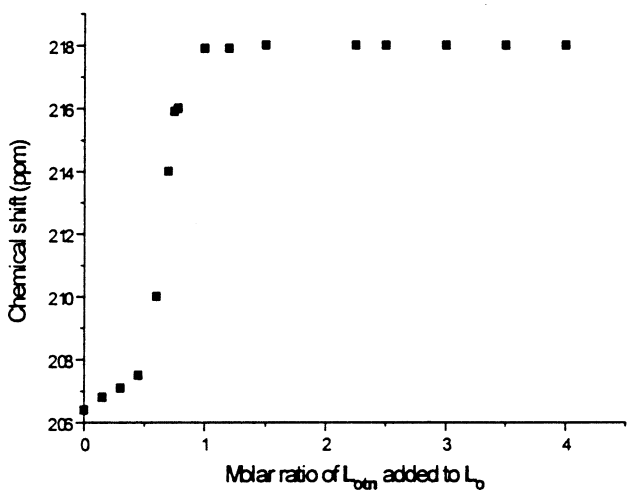
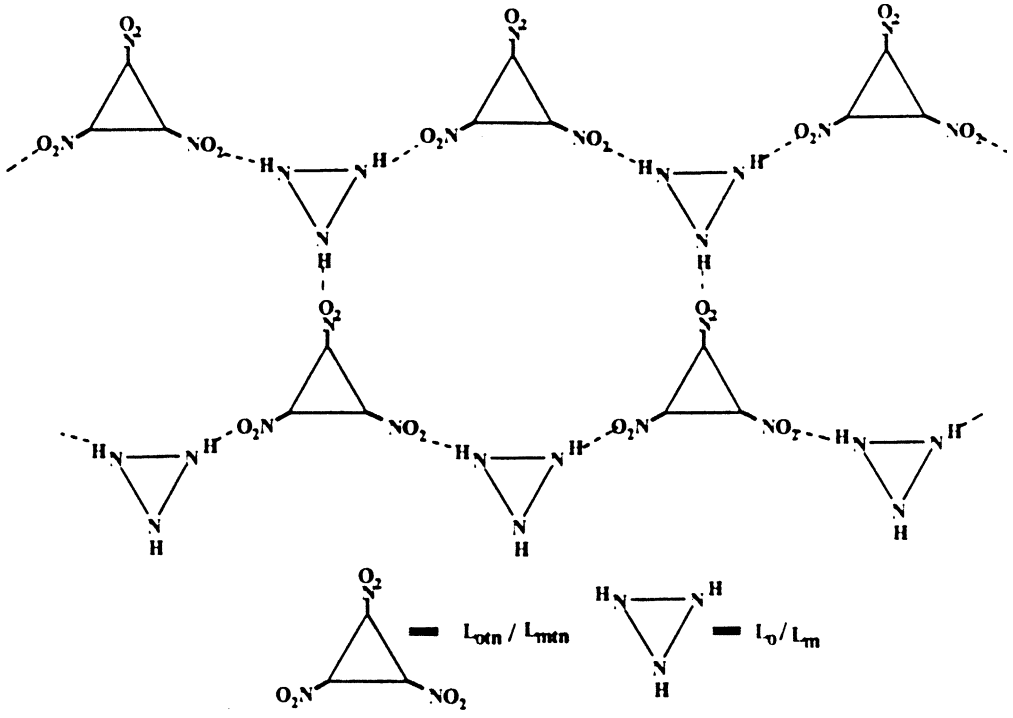


Fig. 2. A plot of the chemical shift of the NH protons vs. the molar ratio of the compound **L_{otn}** added to **L_o**.

the tris-boc derivative, **L_{boc}** produces no change in the chemical shift of the NH protons of **L_o**. A possible supramolecular assembled network of the complementary cryptands through H-bonding interactions is shown in Scheme 1.

To explore the NLO modulation properties of the π-A functionalized cryptand moiety, the HRS titration experiments [18] were carried out. A 1 mM solution of **L_{otn}** in dry $CHCl_3$ is titrated with **L_o**. In each step, 0.2 mmol of solid **L_o** is added into the solution. As the complex formation took place with the addition of **L_o**, the SHG intensity increased almost linearly and reached a maximum (a factor of three with respect to the initial value) at 1:1 molar ratio (Fig. 3). The SHG intensity remains nearly constant even after addition of a large excess of **L_o**. Further, the NLO titration experiments carried out with the *meta*-cryptand core (**L_{mtn}** and **L_m**), showed similar results underlining the fact that rigidity of the cryptand core has no effect on the formation of the H-bonded supramolecular network. Thus, the H-bonding between the cryptand molecules are solely dependent on the terminal nitro groups and amino H-atoms.

The intensity of the second harmonic light scattered at 532 nm generated from the incident 1064 nm light depends linearly on the concentration of the NLO chromophores present in the solution. The solvent (dry $CHCl_3$) produces negligible second harmonic light on its own. For a fixed solute concentration, the scattered light intensity is expected to increase with increasing chromophore size. In the present case, therefore, the formation of supramolecular aggregation of the cryptands results in spontaneous and rapid increase of the SHG intensity. Similar results were reported earlier [8] in case of melamine–cyanuric acid H-bonded supramolecular complex.



Scheme 1. A possible supramolecular asembled network of the complementary cryptands through H-bonding interactions.

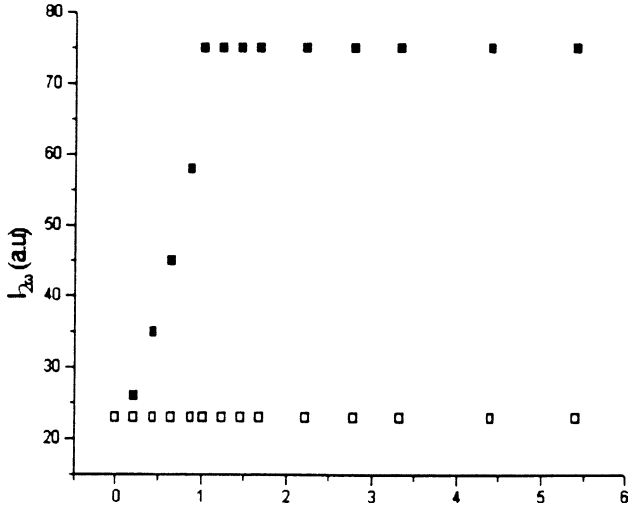


Fig. 3. SHG intensity of 1 mM solution of compound $\mathbf{L_{otn}}$ in $CHCl_3$ plotted against millimoles of (■) $\mathbf{L_o}$ or (□) $\mathbf{L_{boc}}$.

The first hyperpolarizability, β of the compounds investigated were measured by HRS in $CHCl_3$. Compound $\mathbf{L_o}$ and $\mathbf{L_{otn}}$ has (β of 6 and 19×10^{-30} e.s.u., while $\mathbf{L_m}$ and $\mathbf{L_{mtn}}$ has β of 7 and 27×10^{-30} e.s.u., respectively. As there is a 3-fold increase in the SHG responses for the 1:1 H-bonded complexes for both of the complementary cryptands ($\mathbf{L_o}$:$\mathbf{L_{otn}}$) and ($\mathbf{L_m}$:$\mathbf{L_{mtn}}$), a value of 32 and 46×10^{-30} e.s.u. can be estimated for the corresponding 1:1 complexes since, $I_{2w}/I_w{}^2$ is proportional to β^2.

Control experiments were performed with compound $\mathbf{L_{boc}}$ to ascertain that the increase in SHG intensity was due to H-bonded aggregation through the nitro and amino groups. Thus, when one equivalent of $\mathbf{L_{boc}}$ was added in portions to a 1 mM solution of $\mathbf{L_{otn}}$, no increase in the SHG intensity was observed.

The SHG intensity decreased steadily as methanol was added stepwise to the 1:1 complex. The reduction of I_{2w} was slow up to about 4% (v/v) of methanol. Thereafter, the signal intensity decreases rapidly before returning to the base value (Fig. 4). The rapid decrease

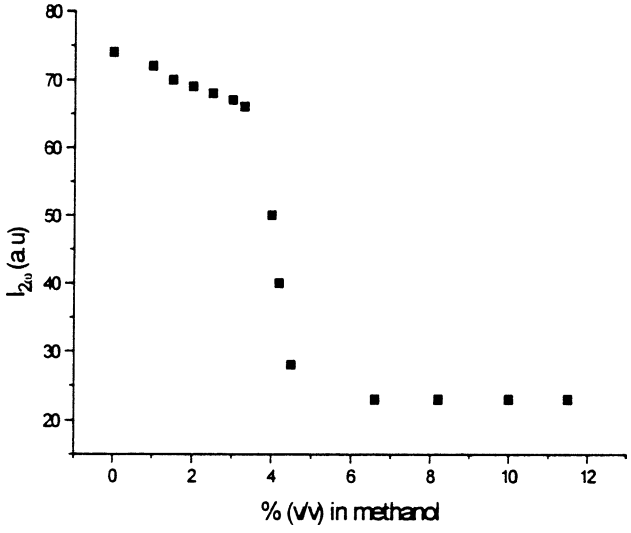


Fig. 4. SHG intensity of a 1:1 complex of compound $\mathbf{L_{otn}}$, and $\mathbf{L_o}$ is plotted against % methanol (of the total volume).

in the scattering intensity is due to the removal, of the weakly bound cryptand units as methanol now competes with to form hydrogen bonds with each separately.

4. Summary

In this paper, we have shown that modulation of the SHG intensity can be achieved in a reversible manner in π-A functionalized aza cryptands through the supramolecular complex formation in solution and its dissociation by changing the solvent characteristics. This represents the first such study carried out on cryptand-based H-bonded structures to modulate the NLO responses. The large increase in the intensity of the second harmonic scattering light of the supramolecular complexes demonstrates the value of hydrogen bonding in designing supramolecular assemblies for efficient SHG effects.

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