Enhancement of Quadratic Nonlinearity via Multiple Hydrogen-Bonded Supramolecular Complex Formation

Mily Bhattacharya, Ashoka G. Samuelson, and Puspendu K. Das*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

Received: March 19, 2007; In Final Form: May 1, 2007

The formation and quadratic nonlinearity of a multiple hydrogen-bonded 1:1 supramolecular complex **1·2** between the 2,6-diaminopyridine-based Λ-shaped molecule, **1**, and ferrocenyl barbituric acid, **2**, in solution have been investigated by the hyper-Rayleigh scattering (HRS) and NMR techniques. A 6-fold increase in the molecular hyperpolarizability (β) of the complex **1·2** over the sum of the molecular hyperpolarizabilities of the components **1** and **2** is seen. Such a significant enhancement in β is attributed to the alignment of the molecular dipoles of **1** and **2** in the 2D plane leading to the creation of a large dipole moment in the plane of the supramolecular complex. Depolarized HRS experiments led to the determination of the in-plane polarization components of β of the supramolecular complex **1·2**. The component of β in the direction of the dipole moment is large. This investigation exemplifies the role of multiple hydrogen bonds in stabilizing a 2D supramolecular architecture leading to a large enhancement of molecular nonlinearity.

Introduction

Various strategies have been suggested and adopted to optimize nonlinear optical (NLO) properties of molecules and materials which form the basis of all-optical data transmission, storage, and processing. One such strategy that has been frequently used in enhancing molecular nonlinearity is the increase in conjugation length.[1,2] However, practical use of such materials will have to be realized in macroscopic media such as in crystals, doped polymer films, Langmuir−Blodgett films, etc. In the light of such applications, the NLO effect generated in a collection of molecules has received greater emphasis. Several principles of aligning molecules in engineered molecule−molecule interactions with a specific spatial relationship to each other have been put forward.[3,4] Chromophore functionalized macromolecule matrices and self-assembled NLO chromophoric superlattices,[5] multichromophore assemblies,[6] macrocyclic chromophoric bundles,[7] monolayers, and multilayers formed by head-to-tail hydrogen bonds [8−12] have all been prepared and investigated for large second-order nonlinearity at the molecular level as well as in bulk.

Organizing molecules from random orientations in the gas phase or in dilute solutions to supramolecular assemblies in solution or in the solid state via noncovalent interactions with fixed orientation with interesting optical, NLO, and magnetic properties has become the preferred path[13−16] since chemical synthesis of covalently bound supramolecular structure can be formidable. In solution the approach that is vigorously pursued is the molecular recognition approach that uses the principles of the age-old "host−guest" chemistry. In this approach, a set of molecules possessing structurally and topologically well-defined hydrogen bond donor (D)−acceptor (A) motifs that promote the formation of supramolecules between molecules containing complementary, directional, and specific hydrogen bond forming pendant groups are added together. To impart stability to the engineered supramolecular network and for property optimization, multiple hydrogen bond formation is desired in this approach.

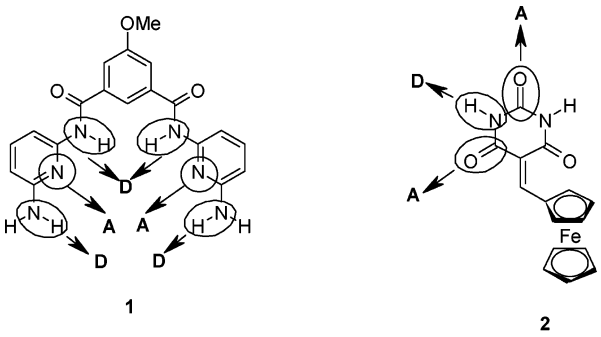
To realize large second-order nonlinearity in molecular and supramolecular complexes and assemblies, noncentrosymmetry is a major requirement both at the molecular level as well as in the assembled structure. The search toward noncentrosymmetric structures at the molecular level has led to the design and synthesis of Λ-shaped molecules[17,18] and chiral propeller-shaped molecules.[19,20] The ordering of noncentrosymmetric molecules in a noncentrosymmetric bulk arrangement is, however, not so trivial and requires a good knowledge of molecular engineering. In an attempt to develop such strategy, ionic species were allowed to form an inclusion complex with an amylose helix and doubling of molecular hyperpolarizability has been realized.[21] In a recent extension of the same strategy, stilbazolium chromophores with extended conjugation have been combined with amylose helices to form inclusion complexes and in certain cases the inclusion complex showed an order of magnitude increment in the hyperpolarizability.[5] However, this was not the general case and the authors concluded that the increase in conjugation length at the molecular level and inclusion in a helix to create noncentrosymmetic macroscopic arrangement are two independent engineering strategies and can be used independently to enhance molecular hyperpolarizability. Most recently Rashid et al.[22] have suggested that a 2:3 complex of β-cyclodextrin/*p*-nitroaniline forms a noncentrosymmetric crystal structure and has the potential for large nonlinearity.

In this paper, we report quadratic nonlinearity of a supramolecular complex **1·2** formed between a Λ-shaped molecule 5-methoxy-*N*,*N*′-bis(6-amino-2-pyridinyl)-1,3-benzenedicarboxamide (**1**) containing hydrogen bond donor and acceptor sites (D-A-D motif) in its inner core (Chart 1), and ferrocenyl barbituric acid (**2**) having the complementary A-D-A motif. The molecular hyperpolarizabilities (β) of the neutral, hydrogen-bonded host−guest complex **1·2** and the components have been measured by the hyper-Rayleigh scattering (HRS) technique in solution. Because of the perfect host−guest interaction between **1** and **2**, the binding constant of the complex is fairly large as estimated by both HRS and NMR methods. The host−guest interaction through multiple hydrogen bonds also makes the complex **1·2** achieve a close-packed structure that is conducive for chromophoric dipolar alignment and, thus, for enhancement of the second-order NLO property.

* Address correspondence to this author. Fax: 91-80-23601552. E-mail: pkdas@ipc.iisc.ernet.in.

10.1021/jp0721651 CCC: $37.00
Published on Web 05/26/2007

CHART 1: Chemical Structures of Hydrogen-Bonding Molecules Used in the Present Study



D: Hydrogen bond donor; **A**: Hydrogen bond acceptor

Experimental Section

The hyperpolarizability of the supramolecular complex **1·2** has been measured by the incoherent second harmonic Rayleigh scattering or hyper-Rayleigh scattering (HRS) technique in solution.[23,24] Experiments were performed with a setup described elsewhere.[25] A Q-switched Nd:YAG laser that delivers a fundamental beam at 1064 nm was used as the incident light source. The sample solutions (volume ca. 15−20 mL) were taken in a cylindrical glass cell of diameter 2.5 cm and the fundamental beam was focused by a glass plano-convex lens to a point 2−3 cm away from the center of the sample cell. The incident laser power was kept below 15 mJ/pulse. The incoherent, second harmonic scattered radiation at 532 nm was collected in a geometry perpendicular to that of the incident beam and dispersed through a monochromator (automated, Czerny-Turner type). The monochromator was operated either by using a manual hand scan module (HS1000) or by using GPIB interfaced "LABVIEW" software. A high gain visible photomultiplier tube (PMT) was used to detect the second harmonic signal. The output from the PMT was averaged over 512 laser shots and digitized on a digital storage oscilloscope and transferred to a PC. The quadratic power dependence of second harmonic light on the incident laser power was checked to guarantee that the scattering is a two-photon process. The monochromator was scanned through the second harmonic wavelength at 532 nm to check the contribution from two-photon fluorescence, if any (see the Supporting Information). We did not observe any significant two-photon fluorescence signal from the complexes. The external reference method[26] was employed to measure the first hyperpolarizabilities of the molecules used in this study, using pNA as the external reference. Stock solutions were prepared as follows: compound **1** (9.7 mg) was dissolved in 80 μL of dry DMSO and the volume was made up to maintain a concentration of 1.0×10^{-3} M. A solution of **1** (6 mL, 1.0×10^{-3} M) was added to compound **2** (31.2 mg). Compound **1**, that is, 5-methoxy-*N*,*N*′-bis(6-amino-2-pyridinyl)-1,3-benzenedicarboxamide, was synthesized from 5-methoxy 1,3-dicarbonyl dichloride and 2,6-diaminopyridine following a literature procedure[27,28] with a few modifications as were necessary (see the Supporting Information). All the solvents were commercially obtained and purified before use. All the absorption measurements were carried out in a Perkin-Elmer (Lambda 35) spectrometer.

In an HRS experiment, the second harmonic scattering signal, $I_{2\omega}$, generated from an ensemble of molecules in solution is quadratically dependent on the incident light intensity, I_ω, and can be written as

$$I_{2\omega} = gN\langle\beta^2\rangle I_\omega^2 \quad (1)$$

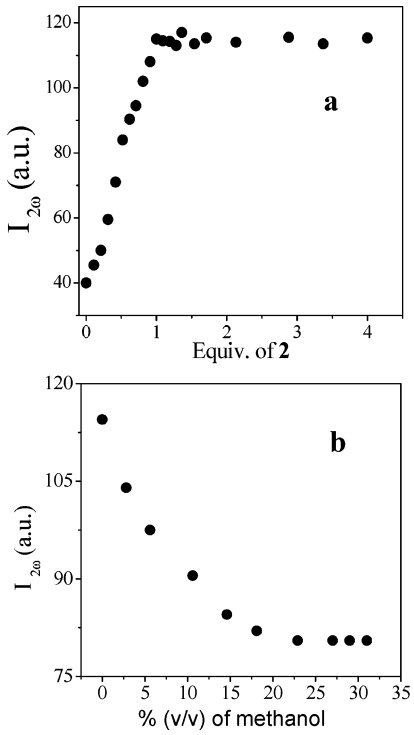


Figure 1. (a) The second-harmonic (SH) signal intensity from a solution of Λ-shaped compound **1** against equivalents of **2** added. (b) SH signal intensity vs percent (v/v) methanol added to the chloroform solution after **1·2** is formed.

where N is the number density and g is the geometrical factor, which accounts for the scattering geometry and the instrument factor, β is the molecular first hyperpolarizability, and $\langle\ \rangle$ indicates orientational averaging. It must be mentioned here that the second harmonic intensity, $I_{2\omega}$, depends on the various components of β, which is a tensor. For a two-component solute−solvent system where the intermolecular interaction is weak, eq 1 can be rewritten as[29]

$$\frac{I_{2\omega}}{I_\omega^2} = g(N_1\langle\beta_1^2\rangle + N_2\langle\beta_2^2\rangle) \quad (2)$$

However, if two molecules associate via noncovalent interaction, the second harmonic response is expected to be different from that of the summation of the responses of two individual chromophores. It may be higher or lower depending on the spatial disposition of individual molecular dipoles which will augment or reduce the β value of the complex.

Results and Discussion

HRS experiments were carried out to measure the first hyperpolarizability of the hydrogen-bonded molecular complex between the Λ-shaped **1** (host) and **2** (guest) in chloroform. The complex formation was monitored by titrating aliquots of **2** against a fixed concentration of **1** in solution. Figure 1a shows a second harmonic titration plot of **1** against **2**. The second harmonic intensity increases as small amounts of **2** are added to the solution containing **1** indicating the onset of complexation. The increment in the second harmonic signal is attributed to an increase in the scatterer size due to the formation of the supramolecular complex. The signal intensity reaches saturation after addition of exactly 1.0 equiv of **2** to the solution. No significant change in the second harmonic intensity was observed when more additional **2** was added to the solution. This implies that the stoichiometry of the complex is 1:1 and

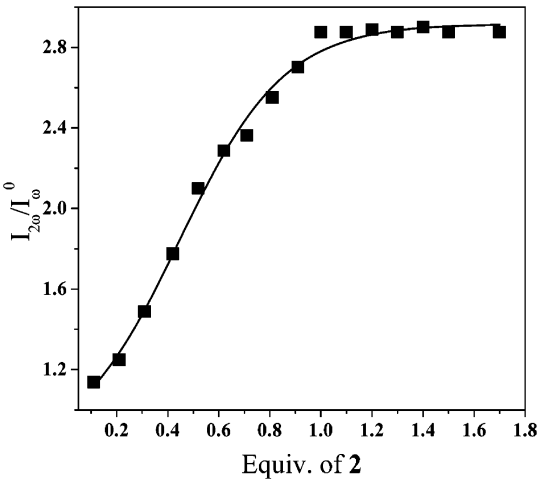


Figure 2. HRS titration data (squares) for compound **1** against **2** and the fit (smooth curve) to eq 5.

no further association of the **1·2** complex is taking place. To ascertain whether the increment in the second harmonic scattering signal is indeed from the hydrogen-bonded complex, small amounts of methanol were added to the complex at saturation. As methanol was added, a progressive decrease in the scattering signal was observed and at ~20% (v/v) methanol−chloroform composition, the second harmonic signal intensity fell to the base level (Figure 1b). This suggests that the complex is certainly hydrogen bonded and it falls apart with addition of methanol since methanol destabilizes the hydrogen-bonded complex by forming stronger hydrogen bonds with **1** and **2**.

The binding constant of the complex **1·2** was estimated from the HRS titration data by using a simple model[30,31] as illustrated below. Considering the following complex formation reaction

$$\mathbf{1} + \mathbf{2} \rightleftharpoons \mathbf{1{\cdot}2} \tag{3}$$

The association constant, K_a, for the above reaction can be written as

$$K_a = \frac{[\mathbf{1{\cdot}2}]}{[\mathbf{1}][\mathbf{2}]} \tag{4}$$

After considering the mass balance and the ratio of the second harmonic intensities in the presence ($I_{2\omega}$) and absence ($I^0_{2\omega}$) of **2** we can write

$$\frac{I_{2\omega}}{I^0_{2\omega}} = \left[1 + rm - \left\{\frac{1}{2}\left(1 + K_a - \frac{\beta^2_{\mathbf{1{\cdot}2}}}{\beta^2_{\mathbf{1}}}\right)\left[1 + m + \frac{1}{n}\right]\sqrt{\left(1 + m + \frac{1}{n}\right)^2 - 4m}\right\}\right] \tag{5}$$

where $m = [\mathbf{2}]_{add}/[\mathbf{1}]_{tot}$, $n = K_a[\mathbf{1}]_{tot}$, $[\mathbf{1}]_{tot}$ is the initial concentration of **1**, $[\mathbf{2}]_{add}$ is the concentration of **2** added to the solution, and $r = \beta^2_{\mathbf{2}}/\beta^2_{\mathbf{1}}$, where $\beta_{\mathbf{1}}$ and $\beta_{\mathbf{2}}$ are the first hyperpolarizabilities of compounds **1** and **2**, respectively. The values of the hyperpolarizability of the complex **1·2** and the association constant were determined by fitting eq 5 with the plot of $I_{2\omega}/I^0_{2\omega}$ vs m (Figure 2). The value of K_a obtained from the fit is $(1.3 \pm 0.9) \times 10^5\ M^{-1}$. The β values of the individual molecular subunits and the complex are given in Table 1. From the table, we find that while the β values of **1** and **2** are comparable, the β value of the complex **1·2** is much larger [$\beta_{complex} \approx 6 \times (\beta_{\mathbf{1}} + \beta_{\mathbf{2}})$] in comparison to that of the constituent molecules. The remarkable enhancement in the β value is possible if the formation of the complex leads to the alignment of the molecular dipoles in a particular direction. To ascertain that this increment in β is not caused by further self-assembly of the **1·2** complex in solution, ^{1}H NMR experiments were carried out independently to check the stoichiometry of the hydrogen-bonded complex of **1** and **2** in solution. The change in the chemical shift of the N-H proton of **1** was monitored as a function of the concentration of ferrocenyl barbituric acid (**2**) and the resulting ^{1}H NMR titration data are shown in Figure 3a. We observed that the chemical shift values of the N-H proton of **1** showed a continuous downfield shift and reached saturation at exactly 1.0 equiv of **2**. This clearly suggests that a strong hydrogen-bonded 1:1 complex of **1** with **2** is formed, which is in agreement with the HRS titration data. Figure 3b shows the Job plot of the NMR titration data between **1** and **2**. The Job plot exhibits a maximum at a mole ratio of 0.5 indicating that the stoichiometry of the complex is indeed 1:1. From the titration data, the association constant of the complex was estimated as $(5.0 \pm 2.5) \times 10^5\ M^{-1}$ by using the EQNMR[32] program. The values of K_a of the supramolecular

TABLE 1: First Hyperpolarizabilities and the Depolarization Ratios of 1, 2, and the 1:1 Hydrogen-Bonded Complex 1·2

molecules/ complex	$\langle\beta\rangle$,[a] $\times 10^{-30}$ esu	$D = I_{2\omega,Z}/I_{2\omega,X}$	$u = \beta_{ijj}/\beta_{iii}$	β_{iii}, $\times 10^{-30}$ esu	β_{ijj}, $\times 10^{-30}$ esu
1	45	0.22	−0.04	−111	4.6
2	55	0.28	−0.15	−139	21.5
1·2	550[b]	0.19	0.02	−1315	−28.4

[a] The measured hyperpolarizabilities were calibrated with respect to a standard *p*-nitroaniline solution. The β value of *p*-nitroaniline in chloroform was found to be 17×10^{-30} esu.[26] [b] The β value of the complex is estimated to be $(550 \pm 50) \times 10^{-30}$ esu with K_a from HRS and $(640 \pm 160) \times 10^{-30}$ esu with K_a from NMR experiments.

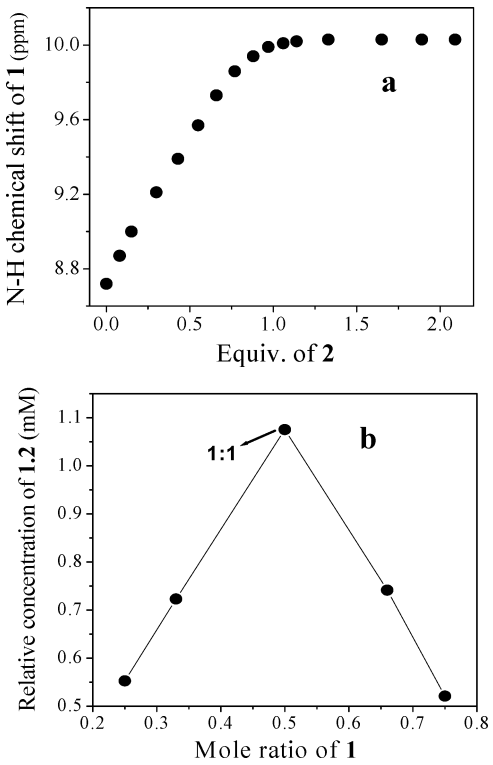


Figure 3. (a) Chemical shifts of the N-H protons of **1** vs equivalents of **2** added to the solution. (b) Job plot of the NMR titration data of **1·2**.

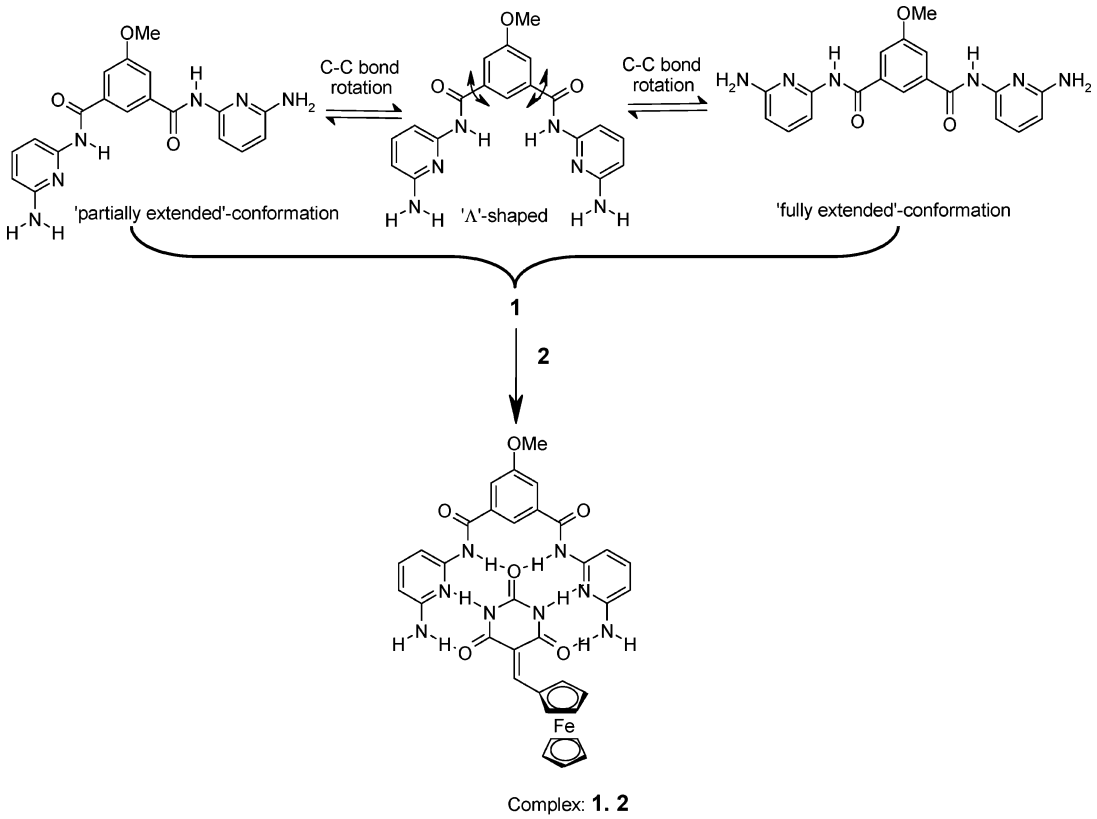


Figure 4. Various possible conformations of **1** in solution and a possible structure of the supramolecular complex.

complex **1·2** obtained from the two methods (HRS and NMR) are in good agreement with each other.

Structure of the Supramolecular Complex 1·2. Rotation around the C−C bonds of the Λ-shaped molecule **1** is possible in solution, which gives rise to a large number of conformations. Molecule **1** can have a partially extended structure where one of the C−C bonds has been rotated by 180° holding the other C−C bond fixed on the molecular plane *xy* or a fully extended structure where both the C−C bonds have been rotated by 180° as shown in Figure 4. Therefore, the β value of **1** in the case of unpolarized excitation and detection in the HRS setup in the laboratory frame will be the tumbling average of β weighted by all the possible conformations in solution that exist in equilibrium with each other. When **2** is added to the solution containing **1**, a supramolecular complex **1·2** is generated, stabilized by the formation of six hydrogen bonds, which is likely to lock the two molecules in a planar structure as shown in Figure 4 barring the peripheral hydrogen atoms.

To gain further insight into the structure of the supramolecular complex **1·2**, HRS measurements were carried out with a linearly polarized excitation beam and polarization resolved detection of the second harmonic scattered light. The total HRS intensity, using linearly polarized light along the *X* direction in the laboratory fixed frame, *XYZ*, is given by

$$I_{2\omega} = GI_{\omega}^2 N\langle\beta^2\rangle = GI_{\omega}^2 N[\langle\beta_{XXX}^2\rangle + \langle\beta_{ZXX}^2\rangle] \qquad (6)$$

Analysis of the HRS signal (traveling in the *Y* direction) at two perpendicular directions gives[33]

$$I_{2\omega,Z} = GN\langle\beta_{ZXX}^2\rangle I_{\omega,X}^2 \qquad (7)$$

as the intensity of the *Z*-polarized second harmonic radiation, and

$$I_{2\omega,X} = GN\langle\beta_{XXX}^2\rangle I_{\omega,X}^2 \qquad (8)$$

as the intensity of the *X*-polarized second harmonic radiation. The macroscopic depolarization ratio (*D*) in the lab fixed frame gives the degree of polarization of HRS signal along a particular direction and is defined as $D = I_{2\omega,Z}/I_{2\omega,X}$. If we now define the molecular β components in the molecule fixed frame *ijk*, then the dominant in-plane molecular hyperpolarizability tensors β_{iii} and β_{ijj} are related to the anisotropy ratio *u*, as $u = \beta_{ijj}/\beta_{iii}$, which, in turn, is related to the macroscopic depolarization ratio (*D*) by

$$D = \frac{\langle\beta_{ZXX}^2\rangle}{\langle\beta_{XXX}^2\rangle} = \frac{3 - 2u + 11u^2}{15 + 18u + 27u^2} \qquad (9)$$

D is obtained from the polarization resolved HRS measurements and the value of *u* is found from solving eq 9. Between the two values of *u* found from eq 9, the value that is less than 1 is retained since the dipole moment along the molecular *i*-axis is assumed to be larger for all the individual molecules and the complex. From the value of *u* and the measured value of β with unpolarized excitation and detection, it is possible to get the in-plane components of the molecular hyperpolarizability tensors of the supramolecular complex **1·2**, since

$$\langle\beta^2\rangle = \frac{\beta_{iii}^2}{105}(18 + 16u + 38u^2) \qquad (10)$$

The negative value of β_{iii}, along the molecular *i*-axis (going from the acceptor to the donor) is generally retained for a dipolar molecule. The molecular components of β for the complex **1·2** and those of the individual components are listed in Table 1. The data reveal that the values of *D* and *u* are the lowest for the supramolecular complex compared to the components. We find a large, more than an order of magnitude enhancement in the component, β_{iii}, implying that the molecular dipoles of the individual components in the complex align in a particular direction (*X*-axis in the laboratory frame) giving rise to a large

net dipole moment of the complex. Such a rigid complex structure leads to partial coherence to the incoherent scattering process (HRS), which is reflected in the large β value of the supramolecular complex.

Conclusion

In this paper, we have investigated the complex formation and the resulting quadratic nonlinearity of a supramolecular complex **1·2** assembled by a proper alignment of molecular dipoles of a Λ-shaped molecule **1** and another dipolar molecule, **2**, in a multiple hydrogen-bonded 2-D supramolecular structure in solution. Such a "lock and key" design leads to a large enhancement of the second-order nonlinearity. This enhancement is due to the fact that the multiple intermolecular hydrogen bond formation reduces the dimensionality of the supramolecular complex from 3 to 2 in comparison to the various possible conformations that the complex could take. The intermolecular hydrogen bonds restrict the possible rotations of the C−C bonds and align the individual molecular dipoles in a manner conducive for large dipolar architecture in 2D. We infer that by a rational design of molecular chromophores with suitable positioning of multiple hydrogen-bonding D-A-D motifs, it is possible to build a supramolecular array where large dipolar polarization is created leading to large optical nonlinearities.

Acknowledgment. M.B. thanks CSIR, New Delhi for a Senior Research Fellowship. Funding from the Indo-French Center for Promoting Academic Research, New Delhi and Ministry of Human Resources Development, New Delhi is gratefully acknowledged. We thank Sampa Ghosh for helping us with the depolarized HRS measurements.

Supporting Information Available: The details of synthesis and characterization of compound **1** and plots of wavelength scans, power dependence, and the change in second harmonic intensity as a function of number density of the compounds (Figures S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Zyss, J.; Chemla, D. S. *Nonlinear optical properties of organic molecules and crystals*; Zyss, J., Chemla, D. S., Eds.; John Wiley: New York, 1987; Vols. I and II.

(2) Marder, S. R.; Sohn, J. E.; Stucky, G. D. *Materials for nonlinear optics*; ACS Symp. Ser. No. 455; Americal Chemical Society: Washington, D.C., 1991.

(3) Terenziani, F.; Mongin, O.; Katan, C.; Bhatthula, B. K. G.; Blanchard-Desce, M. *Chem. Eur. J.* **2006**, *12*, 3089.

(4) Heath, J. R.; Ratner, M. A. *Phys. Today* **2003**, *56*, 43.

(5) Perez-Moreno, J.; Asselberghs, I.; Zhao, Y.; Song, K.; Nakanishi, H.; Okada, S.; Nogi, K.; Kim, Oh-K.; Je, J.; Matrai, J.; De Maeyer, M.; Kuzyk, M. G.; Clays, K. *Proc. SPIE* **2005**, *5935*, 59350B/1.

(6) Datta, A.; Terenziani, F.; Painelli, A. *Chem. Phys. Chem.* **2006**, *7*, 2168.

(7) Liao, Y.; Firestone, K. A.; Bhattacharjee, S.; Luo, J.; Haller, M.; Hau, S.; Anderson, C. A.; Lao, D.; Eichinger, B. E.; Robinson, B. H.; Reid, P. J.; Jen, A. K.-Y.; Dalton, L. R. *J. Phys. Chem. B* **2006**, *110*, 5434.

(8) Khan, R. U. A.; Kwon, O.-P.; Tapponnier, A.; Rashid, A. N.; Günter, P. *Adv. Funct. Mater.* **2006**, *16*, 180.

(9) Rashid, A. N.; Gunter, P. *Org. Electron.* **2004**, *5*, 147.

(10) Facchetti, A.; Beverina, L.; van der Boom, M. E.; Dutta, P.; Evmenenko, G.; Shukla, A. D.; Stern, C. E.; Pagani, G. A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 2142.

(11) (a) Facchetti, A.; Annoni, E.; Beverina, L.; Morone, M.; Zhu, P.; Marks, T. J.; Pagani, G. A. *Nat. Mater.* **2004**, *3*, 910. (b) Zhu, P.; Kang, H.; Facchetti, A.; Evmenenko, G.; Dutta, P.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 11496. (c) Saadeh, H.; Wang, L.; Yu, L. *J. Am. Chem. Soc.* **2000**, *122*, 546. (d) Cai, C.; Müller, B.; Weckesser, J.; Barth, J. V.; Tao, Y.; Bosch, M. M.; Kundig, A.; Bosshard, C.; Biaggio, I.; Günter, P. *Adv. Mater.* **1999**, *11*, 745.

(12) Johal, M. S.; Cao, Y. W.; Chai, X. D.; Smilowitz, L. B.; Robinson, J. M.; Li, T. J.; McBranch, D.; Li, D. Q. *Chem. Mater.* **1999**, *11*, 1962.

(13) (a) Lehn, J.-M. *Science* **2002**, *295*, 2400. (b) Reinhoudt, D. N.; Crego-Calama, M. *Science* **2002**, *295*, 2403. (c) Ikkala, O.; Brinke, G.-T. *Science* **2002**, *295*, 2407. (d) Hollingsworth, M. D. *Science* **2002**, *295*, 2410. (e) Kato, T. *Science* 2410. (f) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.

(14) Zyss, J.; Nicoud, J. F.; Coquillay, M. J. *Chem. Phys.* **1984**, *81*, 4160.

(15) Mohanalingam, K.; Nethaji, M.; Das, P. K. *J. Mol. Struct.* **1996**, *378*, 177.

(16) Gangopadhyay, P.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2451.

(17) Moylan, C. R.; Ermer, S.; Lovejoy, S. M.; McComb, I.-H.; Leung, D. S.; Wortmann, R.; Krdmer, P.; Twieg, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 12950.

(18) Ostroverkhov, V.; Petschek, R. G.; Singer, K. D.; Twieg, R. J. *Chem. Phys. Lett.* **2001**, *340*, 109.

(19) Dhenaut, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; Bozec, H. L. *Nature* **1995**, *374*, 339.

(20) Brunel, J.; Mongin, O.; Jutand, A.; Ledoux, I.; Zyss, J.; Blanchard-Desce, M. *Chem. Mater.* **2003**, *15*, 4139.

(21) Clays, K.; Olbrechts, G.; Munters, T.; Persoons, A.; Kim, O.-K.; Choi, L.-S. *Chem. Phys. Lett.* **1998**, *293*, 337.

(22) Rashid, A. N.; Kirschbaum, K.; Shoemaker, R. K. *J. Mol. Struct.* **2006**, *785*, 1.

(23) Terhune, R. W.; Maker, P. D.; Savage, C. M. *Phys. Rev. Lett.* **1965**, *14*, 681.

(24) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980.

(25) Sri Ranjini, A.; Das, P. K.; Balaram, P. *J. Phys. Chem. B* **2005**, *109*, 5950.

(26) Kodaira, T.; Watanabe, A.; Ito, O.; Matsuda, M.; Clays, K.; Persoons, A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3039.

(27) Chang, S.-K.; van Engen, D.; Fan, E.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 7640.

(28) Kahnberg, P.; Lager, E.; Rosenberg, C.; Schougaard, J.; Camet, L.; Sterner, O.; Nielsen, E. O.; Nielsen, M.; Liljefors, T. *J. Med. Chem.* **2002**, *45*, 4188.

(29) Clays, K.; Persoons, A.; De Mayer, L. *Adv. Chem. Phys.* **1994**, *85*, 455.

(30) Sri Ranjini, A. Ph.D. Thesis, Indian Institute of Science, 2005.

(31) Das, P. K. *J. Phys. Chem. B* **2006**, *110*, 7621.

(32) EQNMR version 2.1 was used to calculate the K_a value of the complex **1·2** from the change in the chemical shift of N-H proton. The freeware was developed by Prof. M. J. Hynes, Chemistry Department, National University of Ireland, Galway, Ireland.

(33) (a) Heesink, G. J. T.; Ruiter, A. G. T.; van Hulst, N. F.; Bölger, B. *Phys. Rev. Lett.* **1993**, *71*, 999. (b) Brasselet, S.; Zyss, J. *J. Opt. Soc. Am. B* **1998**, *15*, 257.