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Note

Second harmonic generation in ferrocene based hydrogen bonded assemblies

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Abstract

Supramolecular assemblies formed by electron donors and acceptors might possess very large optical nonlinearity, even larger than the sum of the constituents if they form noncentrosymmetric networks. To probe this hypothesis we have functionalized barbituric acid, by condensing it with ferrocene carboxaldehyde to give **1**, a hydrogen bond donor–acceptor–donor (H_{DAD}). This molecule complements the hydrogen bond donor acceptor sites of 2,6-diaminopyridine (**2**) which is a hydrogen bond acceptor–donor–acceptor (H_{ADA}). 2,6-Diaminopyridine was further functionalized with acetyl ferrocene to give **3**, which forms complexes with **1**. Complex formation was studied using nuclear magnetic resonance spectroscopy. The second order nonlinear optical (NLO) response of these hydrogen bonded assemblies has been probed by hyper Rayleigh scattering (HRS) measurements and was found to be maximum when **1** was mixed with five equivalents of **3**. A plausible explanation for the formation of 1:5 complex was given on the basis of control experiments with **4**, a methylated analog of **1**, and the addition of a strong hydrogen bond acceptor solvent, methanol.

Keywords: Ferrocene; Hydrogen bonding; Nonlinear optics; Supramolecular assembly

1. Introduction

In recent years there has been considerable interest in the development of hydrogen bonded assemblies for unusual properties other than molecular recognition [1,2]. Large hyperpolarizablity exhibited by π-conjugated organic molecules with donor and acceptor moieties is often lost in the bulk due to a centrosymmetric crystal packing. If intermolecular hydrogen bonds can force the molecule to organize in a noncentrosymmetric fashion, second harmonic signal would remain unchanged or even increase tremendously [3]. Theoretical calculations on *p*-nitroaniline has shown that there is an increase in the value of β in going from the monomer to a dimer structure which is formed due to intermolecular hydrogen bonding between two *p*-nitroaniline molecules [4].

Barbiturates have been used as excellent hydrogen bond donors for macrocyclic receptors [5]. We report here the use of ferrocene based systems having complementary hydrogen bond donors–acceptors for second-order nonlinear optical (NLO) amplification. Analysis of the hydrogen bonding in ferrocene functionalized barbituric acid and 2,6-diaminopyridine has been carried out using ^{1}H-NMR studies. The hyperpolarizability of non hydrogen bonded systems has been studied in a similar way for comparison. Although, organometallic compounds are comparatively less explored in the area of nonlinear optics, several studies have been made on substituted ferrocenes [6,7]. Functionalization with ferrocene gives the advantage of tunability of donor–acceptor properties and increased polarizability.

2. Experimental

Ferrocenecarboxaldehyde and ferrocenoylchloride were prepared according to published literature meth-

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ods [8,9]. Other chemicals were purchased from Aldrich and Fluka and used as received. Thin layer chromatography (TLC) was carried out on aluminium sheets pre-coated with silica gel 60 F254 (Merck). Column chromatography was carried out using silica gel (60–120 mesh). The ^{1}H-NMR spectra were recorded on a Bruker ACF 200 FT NMR spectrometer or on a Bruker AM 400 MHz spectrometer and referenced against Me_4Si. The IR spectra of the complexes (Fig. 1) were recorded using a Bruker EQUINOX 55 spectrometer. Samples were examined as KBr pellets or as neat films.

2.1. Syntheses

2.1.1. Compound **1**

Barbituric acid (0.064 g, 0.5 mmol) and ferrocenecarboxaldehyde (0.107 g, 0.5 mmol) were dissolved in ethanol and refluxed until thin layer chromatography indicated completion of reaction (ca. 3 h). Then ethanol was removed under reduced pressure and the solid residue was purified by column chromatography (silica, CH_2Cl_2:CH_3OH = 9:1) giving the product as a blue powder. Yield = 77% Anal. Found (Calc.) for $C_{15}H_{12}N_2O_3Fe$ (**1**): C, 54.01 (55.59); H, 3.79 (3.73); N, 7.71 (8.64)%. IR data (cm^{-1}): 3192(w, br), 3118(w, br), 3039(w, br), 2841(w), 1738(s), 1705(m), 1649(s), 1533(vs), 1372(s), 847(w), 817(w). ^{1}H-NMR spectra ($CDCl_3$): 8.47 (s, 1H, CH=C), 7.71 (s, 1H, NH), 7.55 (s, 1H, NH), 5.33 (t, 2H, C_5H_4), 5.00 (t, 2H, C_5H_4), 4.30 (s, 5H, C_5H_5).

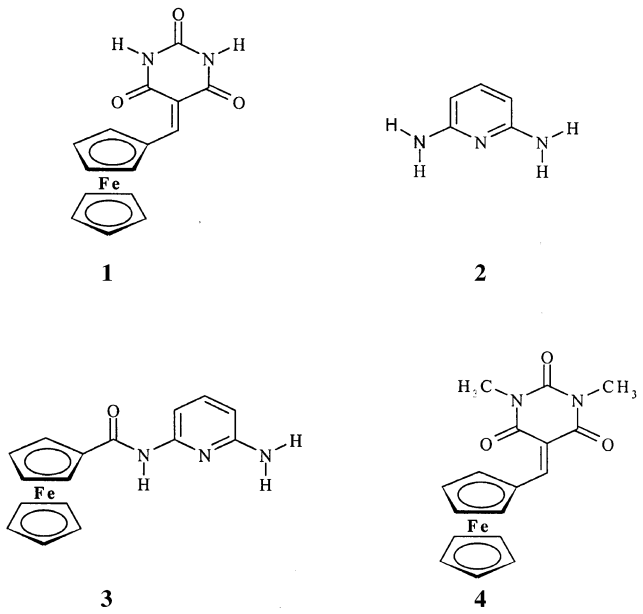

Fig. 1. Structures of compounds **1**–**4**.

2.1.2. Compound **3**

Ferrocenoyl chloride (0.27 g, 1.07 mmol) was dissolved in dry acetonitrile and added dropwise to a stirred solution of 2,6-diaminopyridine (0.11 g, 1.0 mmol) and triethylamine (0.1 g, 1.0 mmol). The mixture was stirred at room temperature (r.t.) for 18 h and then stirred at reflux temperature for 2 more hours. The deep red solution was filtered and solvent was removed by evaporation. The residue was purified by column chromatography using silica gel. Dichloromethane used as a elutant was mixed with increasing proportion of methanol (0–10%) to give the product as a red powder in 60% yield. Anal. Found (Calc.) for $C_{16}H_{15}N_3OFe$ (**3**): C, 59.88 (59.84); H, 4.99 (4.71); N, 12.89 (13.08)%. IR data (cm^{-1}): 3477(w, br), 3379(w, br), 3099(w), 2965(m), 2926(w), 1766(vs), 1712(s), 1672(m), 1615(s), 1525(m), 1454(s), 1244(vs), 822(s), 500(m). ^{1}H-NMR spectra ($CDCl_3$): 8.03 (s, 1H, –CONH), 7.66 (d, 1H, Py), 7.49 (t, 1H, Py), 6.27 (d, 1H, Py), 4.84–4.89 (m, 2H, C_5H_4), 4.44–4.47 (m, 2H, C_5H_4), 4.27 (s, 5H, C_5H_5).

2.1.3. Compound **4**

Compound **1** (0.162 g, 0.5 mmol) was dissolved in 5 ml dry dimethylformamide followed by addition of potassium carbonate (0.166 g, 1.2 mmol). After 5 min of stirring methyl iodide (0.075 ml, 1.2 mmol) was added into the reaction mixture. It was stirred for 8 h. The solvent was evaporated completely to give a residue which was washed with water to remove K_2CO_3 and then extracted with chloroform. The chloroform extractions were collected together and the solvent was removed completely to give **4**. The product was purified by chromatography. Yield: 36%. Anal. Found (Calc.) for $C_{17}H_{16}N_2O_3Fe$ (**4**): C, 58.21 (57.98); H, 4.39 (4.58); N, 7.88 (7.95)%. IR data (cm^{-1}): 2925(w), 2856(w), 1682(s), 1653(s), 1541(s), 1372(m), 825(w). ^{1}H-NMR spectra ($CDCl_3$): 8.45 (s, 1H, CH=C), 5.32 (t, 2H, C_5H_4), 4.90 (t, 2H, C_5H_4), 4.28 (s, 5H, C_5H_5), 3.40 (s, 3H, CH_3), 3.37 (s, 3H, CH_3). The compounds synthesized are depicted in Fig. 1.

2.2. ^{1}H-NMR experiment

Proton NMR titration experiments were carried out with a 1.01×10^{-3} M solution of compound **1** and 1.03×10^{-3} M solution of compound **3** in a 500 MHz NMR spectrometer to determine the nature of the hydrogen bonded complex formed [10]. Different molar ratios of compound **3** were added to a constant concentration of compound **1** in dry chloroform solution to ensure complete mixing in different NMR tubes. The solvent was then removed under vacuum and an equal amount of $CDCl_3$ was added to all the NMR tubes.

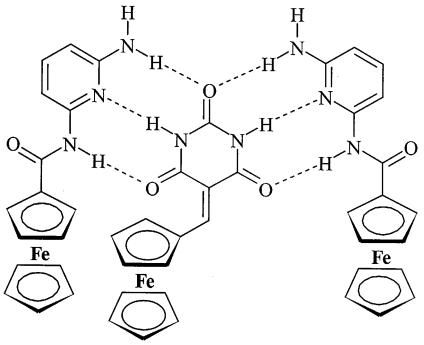

Fig. 2. Hydrogen bonded 1:2 complex of **1** and **3**.

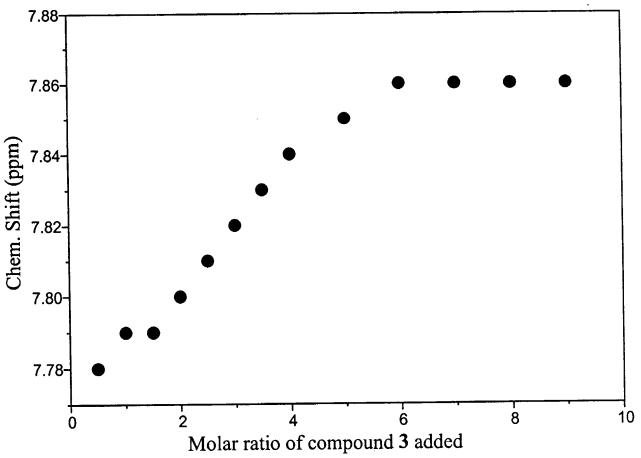

Fig. 3. Chemical shift of N–H proton on addition of molar quantities of **3** to **1**.

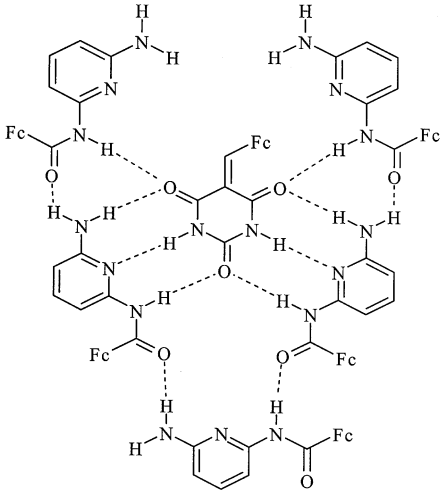

Fig. 4. Hydrogen bonded 1:5 complex of **1** and **3**.

2.3. Second harmonic measurement

Second harmonic scattering intensities at 532 nm were measured in chloroform solutions using 1064 nm light from a Q-switched Nd:YAG laser as the fundamental. Details about the experimental set-up may be found elsewhere [11]. Compounds **1** and **3** were mixed in various molar ratios in chloroform at micromolar concentrations and HRS measurements on them were carried out.

3. Results and discussion

Barbituric acid moiety has two sets of H_{ADA} sites for hydrogen bonding. Similarly the 2,6-diaminopyridine unit has H_{DAD} sites for hydrogen bonding. So one barbituric acid unit can bind two molecules of 2,6-diaminopyridine to form a hydrogen bonded complex with a total of six hydrogen bonds (Fig. 2). Compound **1** shows two different chemical shifts for the –NH– protons at 7.66 and 7.55 ppm. On addition of 2,6-diaminopyridine moiety the signal corresponding to the –NH– protons in **1** started shifting downfield. A maximum shift to 7.80 and 7.72 ppm, respectively, were observed when five equivalents of compound **3** were added to one equivalent of compound **1**. The positions of the amide proton and the amine proton in compound **3** which take part in the hydrogen bonding with barbituric acid, also shifted downfield. The –CONH– and $-NH_2$ protons shifted from 7.78 to 7.88 ppm and 4.30 to 4.40 ppm, respectively. A plot of the chemical shift of the –CONH– proton versus molar ratio of compound **3** added to **1** is shown in Fig. 3. Addition of excess **3** (more than five equivalents), does not change the chemical shift position. From Fig. 3 it is clear that the increase of the chemical shift with molar ratios of **3** is not smooth, a discontinuity occurs at the point where two equivalents of the 2,6-diaminopyridine derivative are added. This suggests the formation of the expected 1:2 complex in addition to other complexes of different composition. The supramolecular structure of the 1:2 hydrogen bonded complex is shown in Fig. 2. The chemical shift of the pyridine ring protons and the cyclopentadienyl ring protons remain practically unchanged during the titration experiment. The NMR titration of compounds **3** with **4** produced no changes in the chemical shift of the –CONH– and $-NH_2$ protons of **3**. Crowding due to the bulky methyl group prevents compound **3** from interacting with compound **4** to form a hydrogen bonded complex. Thus, from the NMR titration experiments it is clear that a 1:2 and a 1:5 hydrogen bonded complexes are formed in solution. A possible structure for the 1:5 complex is suggested in Fig. 4. Such unsymmetrical arrangements are what we trust would lead to large second harmonic generation.

The hyper-Rayleigh scattering (HRS) technique in solution has been used for probing the formation of the self-assembled hydrogen bonded aggregates. This technique has been employed in the past to measure the formation and destabilisation of supramolecular assembly between melamine and cyanuric acid in solution [12]. The intensity of the second harmonic scattered light at 532 nm generated from the incident light (1064 nm)

depends linearly on the concentration of the nonlinear optical chromophores present in solution. The commonly used organic solvents generally produce little second harmonic light, and for a fixed solute concentration, the scattered light intensity will increase with increasing chromophore size. Thus supramolecular structure formation should lead to an enhancement of second harmonic intensity. Fig. 5 displays the increase in the second harmonic intensity as a 1.0×10^{-5} M solution of **1** in chloroform was titrated with **3**. To a solution of complex **1**, aliquots of complex **3** (0.25×10^{-5} M) were added until the total amount of complex **3** exceeded the ratio 1:5. The SHG intensity increased slowly with the addition of **3** and reached a maximum when the ratio was 1:5. Surprisingly further addition of **3** led to the reduction in the second harmonic intensity. The scattering intensity of compound **3** alone in solution at the same concentration (6.5×10^{-5} M) was less than half of that of the 1:5 complex. This indicates that the increase in the HRS intensity is not due to the increase in the concentration of compound **3**. Further confirmation of the hydrogen bonded assembly present in solution was obtained by

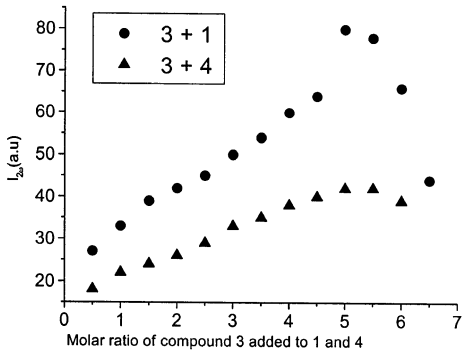

Fig. 5. Measurement of scattering intensity ($I_{2\omega}$) on addition of **3** to **1** and **4** to **1**.

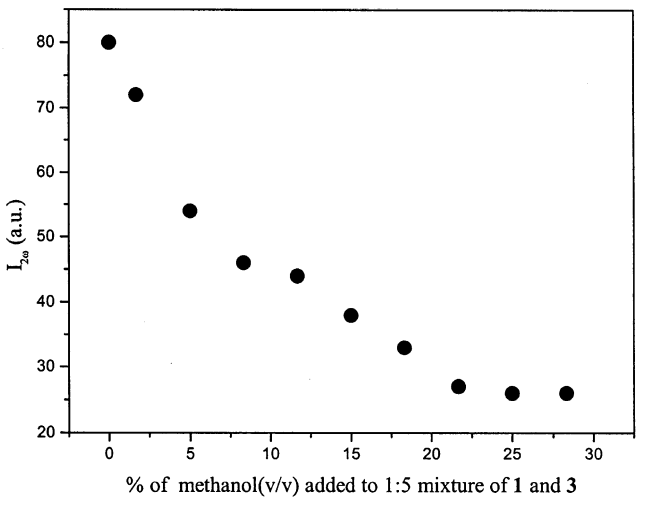

Fig. 6. Measurement of scattering intensity on addition of methanol to the 1:5 complex of **1** and **3**.

controlled addition of methanol [13]. Methanol was added in a stepwise fashion to the 1:5 complex in solution to find out if the dramatic increase in the second harmonic scattered light intensity is indeed due to hydrogen bonded complex formation. Fig. 6 shows the disappearance of the strong second harmonic signal as methanol was added to the chloroform solution of 1:5 complex of **1** and **3**. Addition of small amounts (12% v/v) of methanol brought the intensity from 80 down to 44 mV and with further addition of methanol the second harmonic intensity ($I_{2\omega}$) decreased slowly until coming to a constant value (26 mV). The complex was completely destroyed when methanol concentration reached 20% (v/v). The stepwise decrease in $I_{2\omega}$ with the addition of methanol can be explained as follows. In the 1:5 complex, the three 2,6-diaminopyridine moieties are bound very weakly by two hydrogen bonds. The rapid decrease of the scattering intensity is perhaps due to the removal of these weakly bound units. In the 1:2 complex, the 2,6-diaminopyridine unit is connected by three hydrogen bonds and because of a greater stability of this complex, the second harmonic intensity decreases slowly. This is consistent with the fact that the stability of hydrogen bonded complex increases with (a) increasing number of hydrogen bonds and (b) the effectiveness of the hydrogen bond. The stability also depends on the arrangement of the hydrogen bond donor and hydrogen bond acceptor groups. After a methanol–chloroform ratio of 20:80 (v/v), the hydrogen bonded structure of the complex is completely destroyed and the signal intensity reaches a constant value.

Similar titration experiments were attempted with compound **3** added to compound **4** in a stepwise fashion until the molar ratio of **3** exceeded five times that of **4**. No sharp increase in the second harmonic light intensity was observed in this case (Fig. 5). The linear increase in the SHG intensity is accounted for by the increase in concentration of compound **3**. On the contrary, formation of a hydrogen bonded assembly would result in a drastic enhancement of $I_{2\omega}$. A decrease in the second harmonic intensity with increasing amounts of **3** beyond 1:5 mole ratio between **1** and **3** deserves a comment. One of the possibilities is that after formation of the unsymmetrical 1:5 complex, addition of **3** results in the formation of more symmetrical structures which scatter less.

4. Conclusion

In this paper we have shown that the ferrocene based hydrogen bonded supramolecular structures can be exploited for second harmonic generation. Barbituric acid is a versatile template for making organometallic substrates with hydrogen bond donors and acceptors positioned in an unsymmetrical fashion. While the 1:5 complex formed by the two substrates, **1** and **3** are quite unexpected, the large increase in the second har-

monic scattering light intensity demonstrates the value of hydrogen bonding in designing large supramolecular assemblies for efficient second harmonic generation.

Acknowledgements

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