Second Harmonic Generation in Inclusion Complexes

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Second harmonic generation in inclusion complexes between dimethyl β-cyclodextrin and nitroaniline derivatives having a non-centrosymmetric crystal structure occurs.

Recently, organic molecular crystals have been of interest because of their large optical nonlinearities and high optical damage threshold.[1,2] It was reported that aromatic molecules, possessing donor–acceptor pairs, exhibit very large optical nonlinearities.[3] However, most aromatic molecular crystals, such as *p*-nitroaniline (*p*-NA), possess a centrosymmetric crystal structure, which forbids second harmonic generation (S.H.G.).[4] Various methods have been proposed for overcoming this limitation including the addition of bulky substituents in an asymmetric manner,[5] or the introduction of chiral substituents[6] or ion pairs[7] onto the *p*-NA.

This communication describes a new method of removing crystalline centrosymmetric geometry in aromatic derivatives for S.H.G. by forming inclusion complexes between cyclodextrin and the aromatic derivative, using dimethyl β-cyclodextrin (dimethyl β-CD) as the host molecule. *p*-Nitroaniline (*p*-NA), 2-hydroxy-4-nitroaniline (HNA), and *N*-methyl-4-nitroaniline (*N*MNA) were chosen as the guest molecules.

To investigate whether dimethyl β-CD can form inclusion complexes with nitroaniline derivatives, the dissociation constants (*K*) for *P*-NA, HNA, and *N*MNA were measured by u.v. spectral titration.[8] Estimated dissociation constants (*K*) for the experimental samples are listed in Table 1. Dimethyl β-CD complexes with *p*-NA, *N*MNA, and HNA are stable in H_2O because the constants are small.

Fine crystals of the dimethyl β-CD complex were precipitated from an aqueous solution containing dimethyl β-CD and nitroaniline derivatives in a 1 : 1 molar ratio. The solubility of

Table 1. Estimated dissociation constants (K) for the dimethyl β-CD complexes.

Guest molecule	Dissociation constant $(K)/\text{M}^{-1}$
HNA	1.5×10^{-4}
p-NA	2.6×10^{-4}
*N*MNA	3.7×10^{-4}

Table 2. S.H.G. intensity ratio compared to urea for crystals of three dimethyl β-CD complexes, three nitroaniline derivatives, and dimethyl β-CD.

Compound	Guest	Complex
HNA	0	2
p-NA	0	4
*N*MNA	0	5.5
Dimethyl β-CD	<0.1	

the dimethyl β-CD complex decreases markedly as the solution temperature increases. Therefore, crystals were precipitated by maintaining the temperature at 80 °C.[9] The precipitated crystals were confirmed to be the dimethyl β-CD complex by *X*-ray diffraction and i.r. spectra. None of the *X*-ray diffraction peaks of a physical mixture of dimethyl β-CD and *p*-NA are seen in the *X*-ray pattern of the precipitated crystal. Therefore, the precipitated crystal is different from crystals of the physical mixture. The i.r. spectrum of the precipitated crystals had absorption peaks originating from dimethyl β-CD and *p*-NA. It can thus be concluded that an inclusion complex between dimethyl β-CD and *p*-NA is formed. For HNA and *N*MNA, the same results were obtained from *X*-ray diffraction and i.r. spectra.

S.H.G. intensity in these dimethyl β-CD complexes was measured by the powder method[10] using a Nd YAG laser (λ 1.064 μm). Grain sizes of the complex powders were in the range 105—124 μm. Table 2 lists the S.H.G. intensity ratio compared to urea for the three different dimethyl β-CD complexes, the three nitroaniline derivatives, and dimethyl β-CD. Although the S.H.G. intensity ratio of dimethyl β-CD and *p*-NA is below 0.1 and 0 respectively, the dimethyl β-CD complex with *p*-NA has a ratio of 4 : 1 compared to urea. This indicates that the formation of the dimethyl β-CD complex destroys the centrosymmetric crystal structure.

The dimethyl β-CD–*N*MNA complex had the largest S.H.G. intensity, while the complex with HNA had the lowest S.H.G. intensity of the three complexes. The optical nonlinearity of *N*MNA is larger than that for *p*-NA because of electron donation by the *N*-methyl group. Conversely, the optical nonlinearity of HNA is less than that of *p*-NA owing to the presence of the hydroxy group, which disturbs the intramolecular charge transfer between the NO_2 and NH_2 radicals.[1] Therefore, if organic molecules having larger optical nonlinearity can serve as guests, inclusion complexes with larger S.H.G. intensities can be obtained.

In conclusion, S.H.G. has been observed in dimethyl β-CD complexes where the nitroaniline guest compounds (*p*-NA, *N*MNA, and HNA) have a centrosymmetric crystal structure. Since there is a wide variety of host and guest molecule combinations possible for the formation of inclusion complexes, this method should have a wide application for research into organic materials suitable for nonlinear optics.

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