

Novel Second Harmonic Generation from Intermolecular Charge-transfer Complexes of Styrylpyridinium Tetraphenylborate

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Strong second harmonic light was observed for the first time from intermolecular ion-pair charge-transfer complexes of nitrostyrylpyridinium tetraphenylborate, the intensity of which decreased on irradiation at wavelengths longer than 370 nm to induce charge separation.

In second harmonic generation (SHG), which is a quadratic nonlinear optical effect, much attention has been paid to organic compounds owing to their larger optical nonlinearity as compared with inorganic compounds.¹ It has been shown experimentally and theoretically that the efficiency of the second-order nonlinearity depends on the intramolecular charge-transfer (CT) character. Particular emphasis has been placed on intramolecular CT compounds having both electron-donating and -accepting groups at the ends of a conjugated system. There is no direct evidence for SHG from intermolecular charge-transfer transitions, although there is one report on SHG which is suggested to be enhanced by a strong π interaction in crystals of 3-methyl-4-methoxy-4'-nitrostilbene, but the effect of intermolecular interaction remains unclear.² In the present communication, SHG from CT complexes of styrylpyridinium tetraphenylborate is reported for the first time, which is ascribed to the ion-pair CT transition between tetraphenylborate as electron donor and styrylpyridinium as electron acceptor.

1-Methyl-4-(4-nitrostyryl)pyridinium (NSTZ) salts were synthesized *via* three steps including aldol condensation of 4-substituted benzaldehyde and picoline, quaternization by methyl iodide and exchange of the counter anion from iodide to appropriate anions. The purity of these compounds was

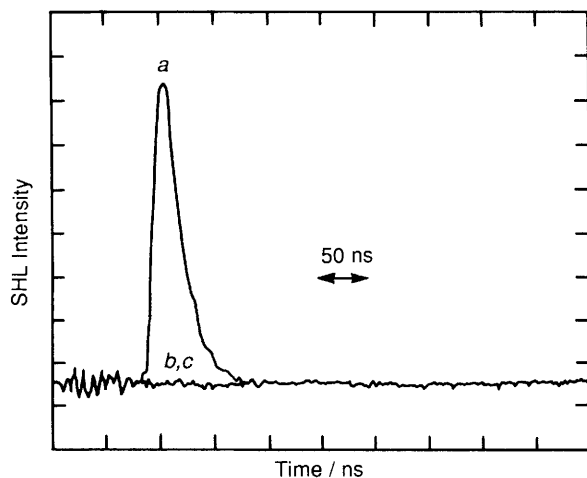
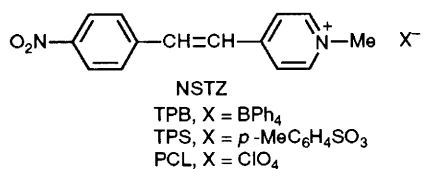


Fig. 1 The effects of counter anion on the second harmonic light (SHL) intensity from NSTZ crystalline powders: (a) TPB; (b) TPS; (c) PCL

confirmed by NMR and elemental analysis. The samples as crystalline powders were placed between two glass plates, and irradiated by an Nd-YAG laser pulse (1064 nm, 100 mJ cm⁻², 10 ns). Second harmonic light (SHL) was detected by a photomultiplier after passing through IR-cut glass filters and a monochromator. The signal was recorded by a computer-controlled storage-oscilloscope.

The SHL intensity from NSTZ markedly depended on the counter anion as shown in Fig. 1. Strong SHG about three times larger than that of urea was observed from the tetraphenylborate (TPB) salt, but SHG from the toluene-*p*-sulfonate (TPS) and perchlorate (PCL) salts were weaker than that from the TPB salt by four orders of magnitude. NSTZ ion has two electron-accepting sites: nitro and pyridinium groups, at opposite ends of the conjugated system. Since the electron-accepting abilities of the two groups are roughly the same one should expect a very small molecular hyperpolarizability for the NSTZ chromophore alone. Marder *et al.* reported that many TPS salts of styrylpyridinium compounds showed a noncentrosymmetric structure which is capable of SHG.³ The reason why the SHL intensity from NSTZ salts strongly depended on the counter anion is not considered to be due to the difference in orientation of the cation chromophore from the above results. A better explanation takes the interaction between the cation chromophore and its counter anion into consideration. The reflectance spectra in Fig. 2 showed that the TPB had a new absorption band ranging from 420 to 600 nm which is absent in TPS and PCL salts. The new absorption band in the TPB salt was assigned to a CT transition between the NSTZ chromophore as electron acceptor and the TPB anion as electron donor. A similar CT transition was also observed for 4,4'-bipyridinium TPB salt.⁴ The CT transition between the NSTZ cation and the TPB anion most probably enhanced the SHG from the TPB salt.

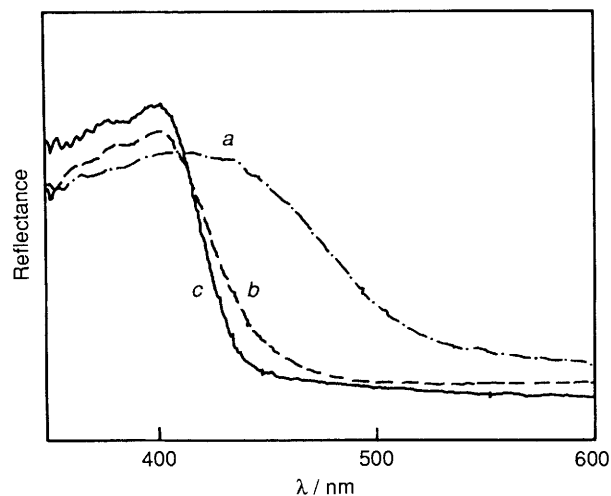


Fig. 2 The reflectance spectra of NSTZ crystalline powders with (a) TPB; (b) TPS; (c) PCL as counter anions

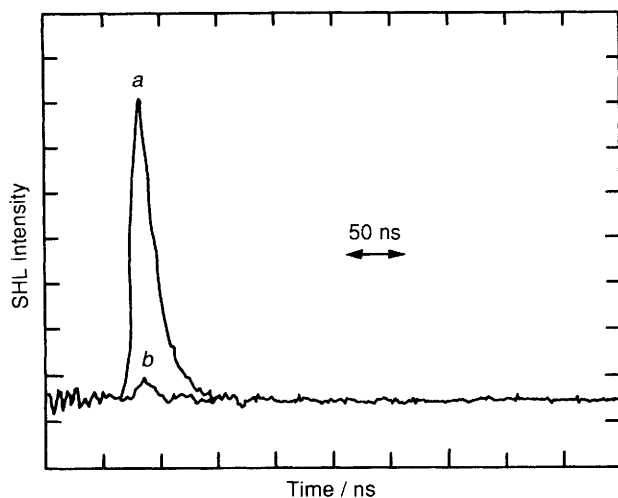


Fig. 3 The change of the SHL intensity from NSTZ-TPB salt (a) before and (b) after irradiation (>370 nm) *in vacuo*

The crystalline powder of the TPB salt showed photochromism, changing from yellow to blue on steady photoirradiation with a Xe lamp at wavelengths longer than 370 nm. Such photochromism was ascribed to the photoinduced electron transfer from TPB to NSTZ in the crystalline powders to form an NSTZ radical. This reaction was irreversible because the oxidized TPB was decomposed to triphenylboron and phenyl radicals.⁵ The photoinduced electron transfer was confirmed by observing the EPR signal after irradiation of the TPB salt of NSTZ. The SHL intensity of the powdered sample dramatically decreased upon CT excitation to only 6% of that before irradiation as shown in Fig. 3.

A semi-transparent KBr disk containing the TPB salt was prepared in order to obtain quantitative information about the decrease of SHL intensity on CT excitation. The fundamental laser beam (1064 nm) was incident on the KBr disk at right angles to the disk plane, and the transmitted SHL from the sample was detected. The decrease in SHL intensity as evaluated by the KBr disk method (transmitted light) was almost the same as that by previous powder method (reflected

light). The absorption coefficient at 532 nm and scattering coefficient was measured so as to estimate the decrease of SHL intensity due to the absorption by NSTZ radical and scattering from the KBr disk. The corrected value of the SHL intensity on CT excitation was 11.4% of that before irradiation. The marked decrease of SHL intensity can be ascribed to two reasons: (i) the change in phase-matching conditions of SHG before and after UV excitation due to a change in refractive indices; and (ii) the change in second-order non-linear susceptibility which is dominated by molecular hyperpolarizability. At the present time, the exact mechanism is unknown. We recently reported that the SHL intensity from a ruthenium-bipyridine complex decreased on UV laser irradiation.⁶ The observation was explained as being due to the smaller hyperpolarizability of the excited state than that of the ground state. The molecular hyperpolarizability of NSTZ-TPB before and after CT excitation is expected to change markedly because the CT transition of ion pairs, which contributed to SHG, diminished after charge separation by photoinduced electron transfer. These discussions are in agreement with the previous suggestion that the SHG occurs by a CT transition in the ion-pair of the TPB salt.

In conclusion, strong SHG was observed from an ion-pair charge-transfer complex for the first time. The mechanism for SHG was ascribed to a charge-transfer transition between NSTZ and TPB. The decrease of SHL intensity by CT excitation supports such mechanism.

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