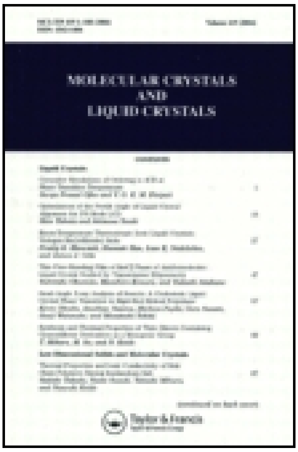

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 23 Sep 2006.

To cite this article: Hiroshi Sakaguchi , Toshihiko Nagamura , Masahiro Kodama , Nobuaki Nishiyama , Hirofumi Sakashita & Taku Matsuo (1994): Novel Second Harmonic Generation from Intermolecular Charge-Transfer Complexes of Styrylpyridinium Salts in the Crystalline State, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 255:1, 121-129

To link to this article: http://dx.doi.org/10.1080/10587259408029783

Mol. Cryst. Liq. Cryst. 1994, Vol. 255, pp. 121–129
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Printed in the United States of America

NOVEL SECOND HARMONIC GENERATION FROM INTERMOLECULAR CHARGE-TRANSFER COMPLEXES OF STYRYLPYRIDINIUM SALTS IN THE CRYSTALLINE STATE

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Abstract Novel second harmonic generation (SHG) was observed from the crystalline powder of the ion-pair charge-transfer (CT) complexes consisting of 1-methyl-4-(4-nitrostyryl)pyridinium as an acceptor and tetraphenylborate as a donor. The second harmonic light intensity dramatically decreased upon excitation of a CT band due to the photoinduced electron transfer from tetraphenylborate to styrylpyridinium moiety. These results strongly suggested that the CT transition in the ion-pair complexes would cause SHG. The crystalline structure of an ion-pair CT complex of 1-methyl-4-(4-cyanostyryl)pyridinium tetraphenylborate which also exhibited strong SHG was investigated to elucidate the mechanism of the SHG in the ion-pair CT complex system.

INTRODUCTION

Much interest has been paid to the development of the organic nonlinear materials with large second and third order optical nonlinearities because of the promising availability of these materials for the future photonic technologies such as optical computing.[1] In the case of quadratic optical nonliearities of organic compounds, many researches carried out so far have suggested that the intramolecular CT characteristics of the molecules could define their efficiencies.[2,3] While particular emphasis has been laid on the intramolecular CT compounds having both electron donating and accepting moieties at opposite ends of a conjugate system,[4,5] there have been no reports with respect to the SHG exploiting the intermolecular CT transition so far. We reported the SHG from an ion-pair CT complex for the first time by the use of 1-methyl-4-(4-nitrostyryl)pyridinium (abbreviated to NSTZ) as an electron acceptor and tetraphenylborate (abbreviated to TPB) as an electron donor.[6] In the present paper, the crystalline structure of an ion-pair CT complex of 1-methyl-4-(4-cyanostyryl)pyridinium (abbreviated to CSTZ) tetraphenylborate which also exhibited the strong SHG was investigated to explain the mechanism of SHG from ion-pair CT complexes.

EXPERIMENTAL

NSTZ and CSTZ salts were synthesized via three steps including ardole condensation of 4-substituted benzaldehyde and picoline, quaternization by methyliodide and the exchange of a counter anion from iodide to appropriate anions. The purity of these compounds was checked by NMR and elemental analysis. The sample for the SHG meaurement was prepared by inserting the crystalline powders between two glass slides. The samples were irradiated by an Nd-YAG laser pulse (1064 nm, 100 mJ/cm^2, 10 ns). The second harmonic light (SHL) was detected by a photomutiplier tube after passing through IR-cut glass filters and a monochromator. The signal was recorded by a computer-controlled storage-oscilloscope.

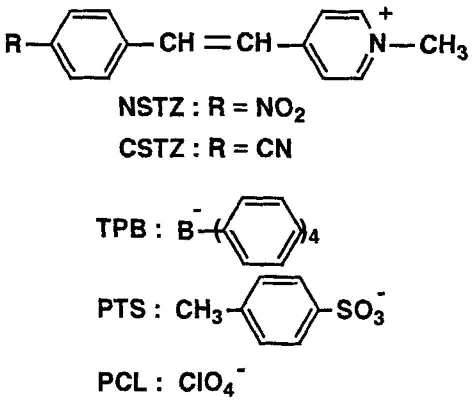

FIGURE 1 Chemical structures of the compounds.

The crystallographic studies of CSTZ-TPB salt were performed under the following procedures.[7] The yellow crystals of CSTZ-TPB were isolated by slow evaporation from the dimethylformamide (DMF) solution. The obtained crystal of CSTZ-TPB salt was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator, Cu Kα radiation. Cell parameters and intensity data were measured by using the ω-2θ scan technique. Cell parameters were defined from the setting angles of 16 reflections having $12.3 < \theta < 25.3°$. Successful refinement determined the space group as Ia. Intensity data were corrected for the background, Lorentz and polarization effects. Intensities of standard reflections decreased by 1.9 %, and a linear decay correction was applied. Analytical absorption corrections were also applied. The structure was solved by the direct methods using MULTAN 78 and was refined by weighted full-matrix least squares. Non-H atoms were refined anisotropically. H atoms were located by ΔFourier and were refined isotropically. The function minimized was $\Sigma w(|F_0| - |Fc|)2$ and weights were assigned as $w = 4 F_0^2 Lp [S^2(C + R^2B) + (0.02F_0^2)^2]^{-1}$ using Enraf-Nonius SDP system, where S = scan rate, C = total integrated peak counts, R = ratio of scan times to background counting times, B = total background counts, L = Lorentz-polarization factor. Of 2472 unique data, 2019 reflections having $I > 3\sigma(I)$ were used in the refinement. Final R = 0.043, wR = 0.065.

RESULTS AND DISCUSSION

The SHL intensity from the NSTZ salts was markedly dependent on the counter anions as shown in Fig. 2. Strong SHG about three times larger than that of urea was observed from the TPB salt. On the other hand, those from p-toluensulfonate (PTS) and perchlorate (PCL) salts were weaker by four orders of magnitude than that from the TPB salt. Murder et. al. investigated the effect of counter anions on the SHG from several kinds salts of styrylpyridinium ions with electron-donating groups.[8] The PTS salts of styrylpyridinium were reported to show the noncentrosymmetric crystal structure with high possibilities which enables SHG. According to the Murder's results, the PTS salt of NSTZ is expected to have the noncentrosymmetric crystal structure. Nevertheless it showed very weak SHG, which strongly suggeted that the hyperpolarizability of NSTZ chromophore was very small. The NSTZ chromophore has two electron accepting groups of nitro and pyridinium. Since the extent of an electron withdrawing nature is considered to be almost the same for these two groups,

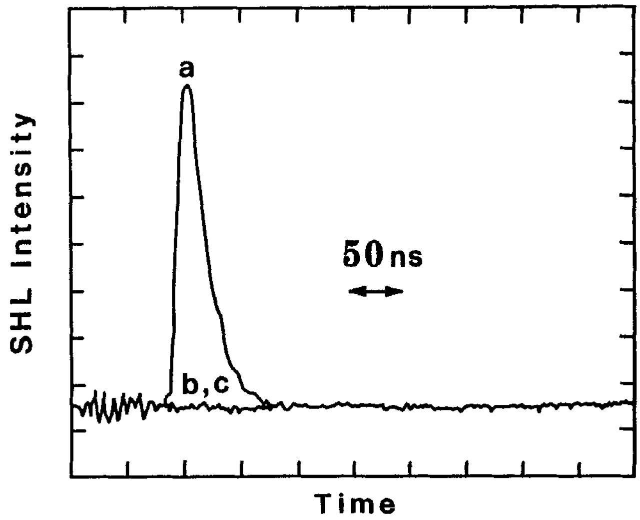

FIGURE 2 The effects of the counter anion on the second harmonic light (SHL) intensity from NSTZ crystalline powders: (a) TPB; (b) PTS; (c) PCL.

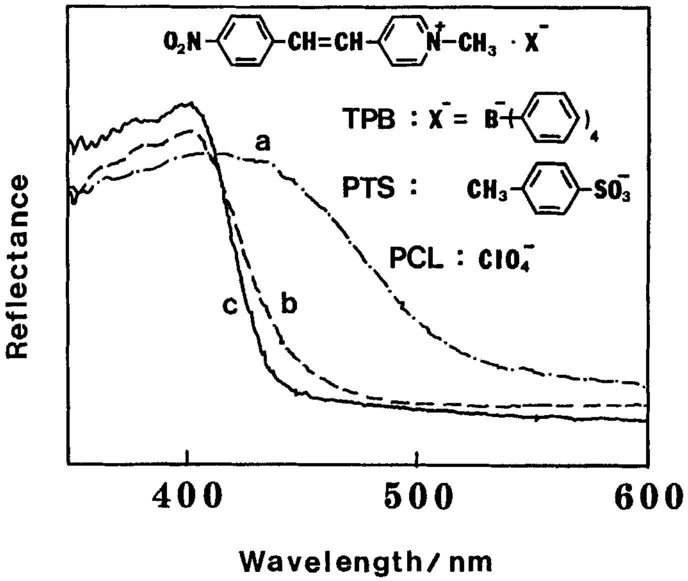

FIGURE 3 The reflectance spectra of NSTZ crystalline powders with (a) TPB; (b) PTS; (c) PCL as counter anions.

very small molecular hyperpolarizability of the NSTZ chromophore can be expected. The reason why the SHL intensity from the NSTZ salt strongly depended on the counter anions is then probably owing to the CT interaction between the cation chromophore and the counter anion. The reflectance spectra showed that the TPB salt exhibited an absorption band ranging from 420 nm to 600 nm which was absent in the PTS and the PCL salts as shown in Fig. 3. This additional absorption band shown in the TPB salt was ascribed to a CT transition between the NSTZ chromophore as an electron acceptor and the TPB anion as an electron donor. The similar CT transition was also observed for 4,4'-bipyridinium-TPB salt.[9] The CT transition between NSTZ and TPB is thus supposed to enhance the SHG from a TPB salt.

The crystalline powder of the NSTZ-TPB salt showed the photochromism. The color of the NSTZ-TPB salt changed from yellow to blue with exposure of a Xe lamp at wavelength longer than 370 nm which corresponds to the CT band of NSTZ-TPB salt. Such photochromism is caused by the photoinduced electron transfer from the TPB to the NSTZ in the crystalline powders to form the radical of NSTZ.[10] This reaction is an irreversible process because the oxidized TPB is decomposed to triphenylboron and a phenyl radical.[11] The SHL intensity decreased dramatically to 6 % of that before irradiation as shown in Fig. 4. The SHL intensity after exposure of light normalized by taking into account for the absorption of NSTZ radical and scattering factor at the wavelength of second harmonics of 532 nm was estimated to 11.4% of that before irradiation. The reason for the tremendous decrease of the SHL intensity might be ascribed to two reasons. The first reason is the change of the phase-matching condition of SHG before and after the excitation at a CT band of NSTZ-TPB salt due to a change of the refractive indexes of the crystal. The second is the change of second order nonlinear susceptibility before and after the exposure of light. Although the exact mechanism is unknown at the present time, the molecular hyperpolarizability of NSTZ-TPB salt after the irradiation of a CT band would be expected to decrease markedly because of the disappearance of CT interaction which enhanced the SHG. We reported that the SHL intensity from ruthenium complex decreased by UV laser irradiation due to the change of molecular hyperpolarizability on going from the ground state to the excited state.[12-14]

The CSTZ-TPB salt showed a CT band ranging from 400 nm to 500 nm in acetone which was absent in the case of the PTS and PCL salt of CSTZ. The CSTZ-TPB salt showed the strong SHG which was 5.3 times larger than that of urea in the crystalline powders. The SHL intensity from the CSTZ-TPB salt was not affected by the photo irradiation at a CT absorption band while an tremendous decrease was observed in the case of the NSTZ-TPB salt. The CSTZ-TPB salt was found not to exhibit a photochromism in both solution and crystalline state when it was irradiated at a CT absorption band in contrast to a remarkable color change in NSTZ-TPB salts as mentioned above. This result strongly suggests that the back electron transfer from the radical of CSTZ to that of TPB after the photoinduced electron transfer occurs so fast prior to the decomposition of the TPB radical. This seems to be the reason for the fact that there were no effects of the photo irradiation at a CT band of CSTZ-TPB salt on the SHL intensity.

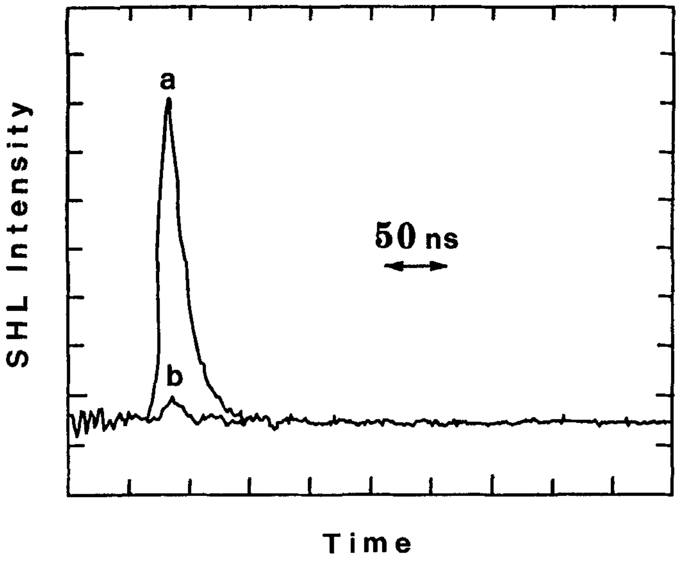

FIGURE 4 The SHL intensity from NSTZ-TPB salt (a) before and (b) after irradiation (> 370 nm).

The crystallographic studies of the ion-pair CT complex of NSTZ-TPB and CSTZ-TPB were investigated to elucidate the detailed mechanism of the SHG from the ion-pair CT complexes. The space group of the NSTZ-TPB crystal which was formed by slow evaporation from DMF solutions was considered to be Ia or $I_{2/a}$ from its x-ray diffraction data. But it could not be defined exclusively because the NSTZ-TPB crystal had a poor quality for the crystallographic studies. On the other hand, the single crystal of CSTZ-TPB salts good enough for the definition of the crystal structure was easily formed via slow evaporation from DMF solutions. The molecular arrangement of CSTZ-TPB indicates a charge transfer interaction between CSTZ chromophore and

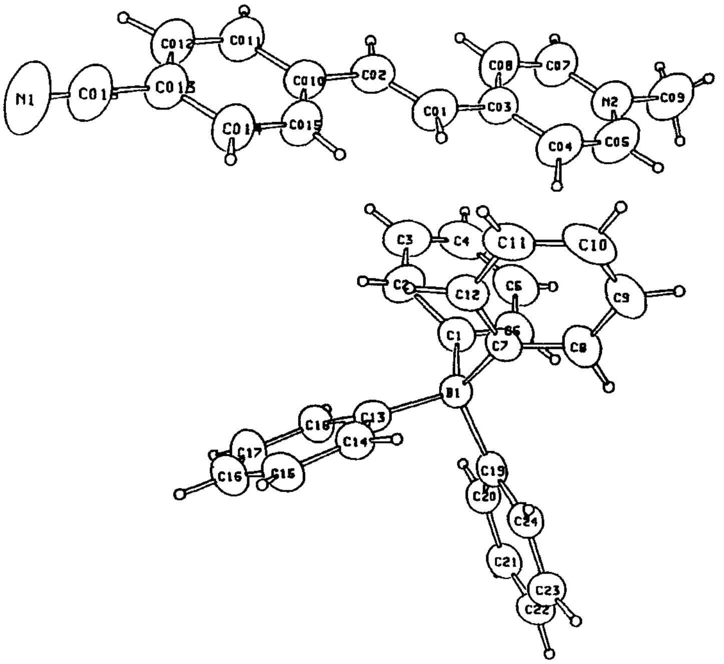

FIGURE 5 Molecular arrangement of CSTZ-TPB salt.

TPB counter anion in such a way that one of the four benzene rings of TPB overlaps with a pyridinium ring of CSTZ as shown in Fig. 5. The similar π-π interaction also appeared in the single crystal of 4-4'-bipyridinium-TPB CT complex.[15] The space group of CSTZ-TPB salt is Ia in which the molecules in the crystalline state take a noncentrosymmetric configuration to enable the SHG. The orientation of CT dipoles of CSTZ-TPB lacks a centrosymmetry in the crystalline structure as shown in Fig. 6. It was thus made sure that the ion-pair CT interaction could cause the SHG. There could be considered another reason for SHG due to the intramolecular electronic transition in the CSTZ chromophore because CSTZ moieties are also aligned noncentrosymmetrically in the crystalline structure. However CSTZ chromophre has two electron accepting groups of pyridinium and cyano grourps at opposite sites of its structure. Its absorption band exists at the wavelength shorter than 350 nm indicating little delocalization. Therefore it might be expected to have a very small quadratic optical nonlinearity. Ion-pair CT transition between CSTZ and TPB in the crystal is most probably the main reason for strong SHG from the crystalline state of its ion-pair CT comlex.

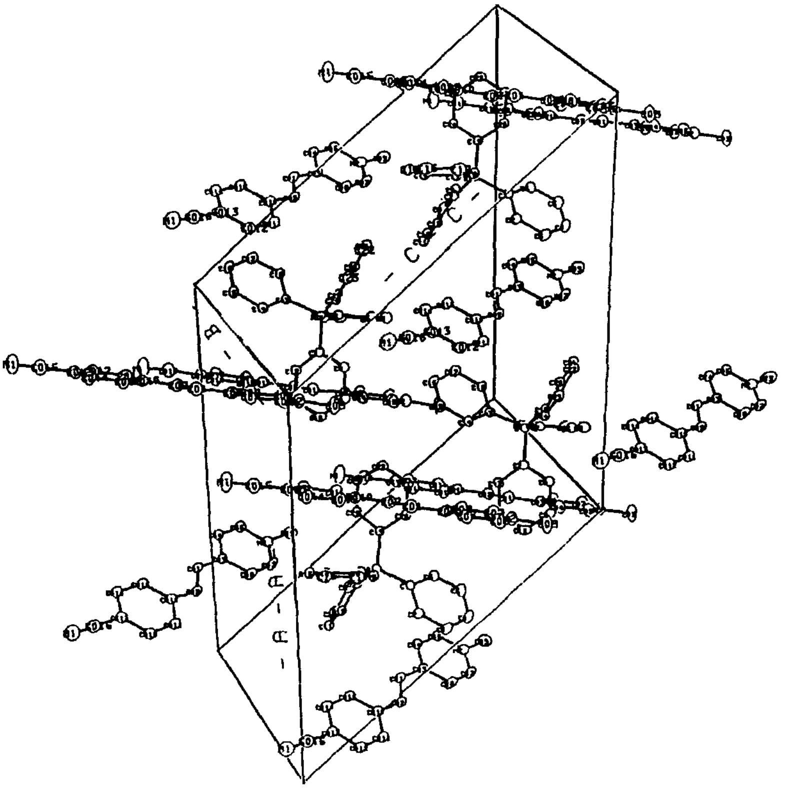

FIGURE 6 Crystal structure of CSTZ-TPB salt.

Conclusion

Novel second harmonic generation was observed from the crystalline powder of the ion-pair charge-transfer complexes of NSTZ-TPB and CSTZ-TPB showing ion-pair CT absorpion. The SHL intensity from the NSTZ-TPB salt dramatically decreased with exposure of light at a CT band due to the photoinduced electron transfer from TPB to NSTZ. These results strongly suggested that the CT transition in the ion-pair complex cause SHG. The single crystal of an ion-pair CT complex of CSTZ-TPB showed a noncentrosymmetric structure in which the CT dipoles between CSTZ and TPB take a polarizable configuration. This is the first example of the SHG from CT complex and its photochemical control.

Acknowledgment

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 01790426) from the Ministry of Education, Science and Culture, Japan. The crystallographic studies were performed by using the automatic 4-axis x-ray diffractometer at the Center of Advanced Instrumental analysis, Kyushu University.

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