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Long-lived Colored Merocyanine Conformers in the Aggregates Formed on UV Irradiation of Spiropyran.
A Raman Spectroscopic Study

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Resonance Raman spectra of the aggregate formed on the UV irradiation of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6-nitro BIPS) in nonpolar solvents revealed the presence of long-lived colored merocyanine conformers.

Spiropyrans constitute an important class of photochromic compounds.[1,2] UV irradiation of the uncolored form (spiropyran) produces transient colored species (merocyanine). Among various spiropyrans known to date, 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6-nitro BIPS) is one of those frequently studied. Recently Takahashi et al.[3] have made a time-resolved resonance Raman study on 6-nitro BIPS in several solvents, and obtained the spectra of colored transient species. They assigned several bands in the transient spectra to a few conformers having merocyanine-like structures. 6-Nitro BIPS is known for the formation of an aggregate on UV irradiation in nonpolar solvents (cf. "quasicrystals" reported by Krongauz et al.[4]). Although the color due to merocyanine fades out immediately in nonpolar solvents, it persists for a long time (more than days) in the aggregate. We measured resonance Raman spectra of the long-lived colored species incorporated in the aggregate and compared them with the transient spectra of Takahashi et al.,[3] in order to know their molecular conformations. 1',3',3'-Trimethylspiro[2H-1-benzopyran-2,2'-indoline] (BIPS) and 8-nitro BIPS were studied for comparison.

6- and 8-Nitro BIPS, BIPS (Tokyo Kasei), heptane (Wako), cyclohexane

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m- and p-xylene, ethyl ether and carbon tetrachloride (Nacalai) were used as received.

Nondegassed solutions of 6-nitro BIPS in either of these solvents (5 x 10^{-3} mol dm^{-3}) were irradiated by an Ushio 135W xenon lamp at room temperature. After a substantial amount of colored aggregate was formed (irradiation for 30 min or more), irradiation was stopped. Colorless supernatant was decanted. (Irradiation of this supernatant gave the color of merocyanine.) Precipitate was washed repeatedly with portions of a small amount of the solvent until no coloration was observed on irradiation of the wash solution. Then the precipitate was used as the sample of the aggregate. 8-Nitro BIPS gave only a small amount of aggregate on UV irradiation. BIPS did not give any aggregate.

Morphologies of the aggregate of 6-nitro BIPS observed by electron microscope depended on the solvent used, for example, ca. 10 μm dendrites and ca. 10 μm x 100 μm needles from cyclohexane and m-xylene, respectively. These aggregate particles were much larger compared to "quasicrystals" (0.1-0.4 μm in diameter) obtained by Krongauz et al.[4)] X-ray diffraction patterns of these aggregates showed a sharp peak at 2θ = 16.5°, indicating the essentially crystalline nature.

Raman spectra of the aggregate of 6-nitro BIPS were measured on KBr discs (aggregate/KBr = 1/40). Excitation laser wavelength was 514.5 nm from a Spectra Physics 165 Ar^+ laser. The laser power

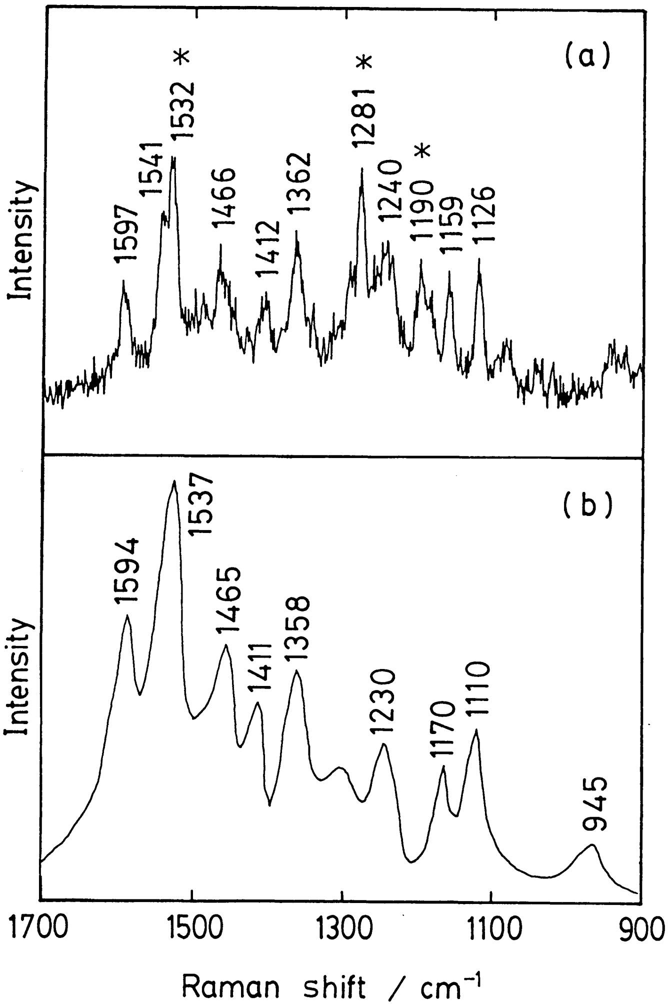

Fig. 1. (a) Resonance Raman spectrum of the aggregate of 6-nitro BIPS, (in KBr disc, for asterisks see text) in comparison with (b) transient Raman spectrum of 6-nitro BIPS in acetonitrile (2 ms after irradiation), adapted from Takahashi et al. (Ref. 3).

was 0.1 - 0.5 W. A double monochromator (Jasco CT-80D) equipped with a Hamamatsu R649/C1050 photomultiplier/photon counting unit was used. A rotating sample cell was used to avoid the deterioration of the sample dye during the measurements.

The Raman spectrum of the aggregate (formed in cyclohexane solution, irradiation for 30 min) is shown in the upper panel (a) of Fig. 1. Similar spectra were obtained for the aggregate formed by irradiation in heptane, p-xylene, ethyl ether, and carbon tetrachloride. In the lower panel (b), the transient resonance Raman spectrum of 6-nitro BIPS reported by Takahashi et al.[3)] (in acetonitrile, 2 ms after irradiation) is reproduced for comparison. There is a general similarity not only in band positions but also in relative intensities between the two spectra, except for three bands with asterisks (1532, 1281, and 1190 cm^{-1}) which are found only in the aggregate. Takahashi et al.[3)] reported transient Raman spectra in three solvents. In cyclohexane the spectra changed with time (25 μs - 2 ms) after UV photoexcitation. In acetonitrile and methanol the spectra did not exhibit time dependence over the time period 200 ns to 2 ms. Among the spectra of transient species in the three solvents observed at 2 ms after UV irradiation, a good coincidence was observed in band frequencies although relative intensities of the bands differed considerably. The spectrum of the aggregate measured in the present study compares well with the transient spectrum in acetonitrile, rather than that in cyclohexane (2 ms). Raman spectra of the uncolored (spiropyran) form of BIPS and 6- and 8-nitro BIPS were measured using rotating KBr discs (dye : KBr = 1 : 10). 6- and 8-Nitro BIPS gave bands near 1335 and 1520 cm^{-1} which were not found for BIPS. These bands must be due to symmetric and antisymmetric stretching modes (ν_s and ν_{as}) of nitro group, respectively. These two bands do not show up in the spectrum of the aggregate.

Takahashi et al.[3)] assigned some of the bands they observed to three conformations of transoid merocyanine: 1537, 1465, and 1358 cm^{-1} bands to cis-trans-trans (CTT), CTC, and TTT, respectively, with respect to the three C-C partial double bonds in the merocyanine skelton. All of these bands are observed in the spectrum of the

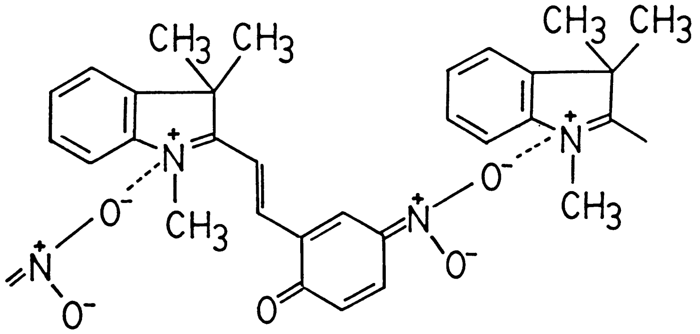

Fig. 2. A propable structure of the aggregate of 6-nitro BIPS. (One of resonance hybrid structures is shown.)

aggregate. This strongly suggests that the aggregate contains these three transoid merocyanines. The Raman bands found only for the aggregate (1532, 1281, 1190 cm^{-1}) must be due to some conformations characteristic to the aggregate. In view of the experimental finding that the aggregate is formed for 6-nitro BIPS, in smaller extent for 8-nitro BIPS, and not for BIPS, the nitro group must play an essential role in the aggregate formation. The presence of a nitro group at the 6-position in the benzopyran ring gives rise to the contribution of aci-nitro form in the resonance hybrid structure of the transient species,3) which increases the resonance stabilization energy and yields the possibility of coordination via the nitro group. From these considerations, the plausible molecular conformations in the aggregate are those containing the coordinated aci-nitro structure in which two N-O bonds are not equivalent. One of these conformations which corresponds to the CTT configuration of the three C-C partial double bonds in the merocyanine skelton is shown in Fig. 2. The aggregate must also contain the CTC and TTT conformations. Then the aggregate is presumably a mixture of several types of crystallites composed of these conformers, or a composite of these crystallites in amorphous matrix containing more than one of these conformers and spiropyran. When one considers the above together with the absence of the ν_s and ν_{as} of NO_2 ($\approx$1335 and $\approx$1520 cm^{-1}, respectively) in the aggregate, the bands at 1281 (and/or 1190) and 1532 cm^{-1} are most probably assigned as the N-O and N=O stretching modes of asymmetric nitro group contained in the coordinated aci-nitro structure.

In conclusion, the present Raman spectroscopic study strongly suggests that the aggregate of 6-nitro BIPS contains long-lived transoid merocyanine conformers which are coupled each other by the coordination via the NO group in the aci-nitro structure.

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