A Raman Spectroscopic Study of Merocyanine Aggregates of a ^{15}N-Isotopomer of 6-Nitro-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline]. A Direct Evidence for the Association through the NO_2-Bridges

Hiroyasu Sato,*[†,††] Akiyoshi Matsuzaki,[†] Satoru Nishio,[†] Motohiro Yoshimi,[†] Katsutoshi Yamamoto,[†] and Hideo Tomioka[†]
[†]*Department of Chemistry for Materials, Faculty of Engineering, Mi'e University, Tsu 514*
[††]*Institute for Molecular Science, Myodaiji, Okazaki 444*

(Received April 24, 1996)

A Raman spectroscopic study on large-sized merocyanine aggregates prepared by the irradiating a $^{15}NO_2$-isotopomer of 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6-nitro BIPS) with UV light in a cyclohexane solution strongly indicates the association of merocyanine monomers through the NO_2-bridges.

Spiropyrans constitute an important class of organic photochromic compounds.[1] Some spiropyrans including 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (6-nitro BIPS) are noted for aggregate formation under UV irradiation in nonpolar solvents. Krongauz and coworkers[2] reported formation of "quasicrystals" for some spiropyrans including 6-nitro BIPS. Present authors[3,4] found that prolonged UV irradiation in nonpolar solvents leads to the formation of large-sized (10–100 μm) aggregates which precipitate out of the solution. The aggregates were featured with a broad absorption band covering the 450–700 nm range.[3,4] The resonance Raman spectrum of the aggregates[3,4] was very similar to that of the corresponding merocyanine (monomers) obtained by Takahashi et al.[5] with time-resolved Raman spectroscopy. Most of the bands were very close in their positions and relative intensities to those in the spectrum of Takahashi et al. These authors attributed those bands to transient species having trans-trans-cis (TTC), CTC, TTT and CTT configurations with respect to the three C-C partial double bonds of the merocyanine skelton. According to them, in non-polar solvents the polar TTC configuration is converted with time to CTC and TTT, then to CTT, resulting in an equilibrium of these four configurations. In polar solvents the conversion of TTC is so rapid that the other three are in equilibrium even after 200 ns after UV irradiation. As remarked in Ref. 4, the band profile of the aggregates, though precipitated out of cyclohexane solutions, compared well with that of the transient monomer in acetonitrile (composed of CTC, TTT and CTT), rather than that in cyclohexane at 2 ms after excitation (composed of TTC, TTT and CTT). This indicates that the environment within the solid aggregate is highly polar, comparable with that in acetonitrile. The spectrum of the aggregates has, however, three extra bands at 1541/1532, 1281 and 1199 cm^{-1}, which were not found for merocyanine monomers.[6] They were attributed to the structure peculiar to the aggregates. A structure of the aggregates was assumed, in which a large number of merocyanine monomers are linked together through the NO_2-bridges, as exemplified in Figure 1. (One of resonance hybrid structures is shown.) The extra bands at 1281 (and/or 1199) and 1532 cm^{-1} were assigned to N-O and N=O stretching modes of the bridging NO_2 moiety. However, their decisive assignments have awaited a $^{15}NO_2$-isotope study.

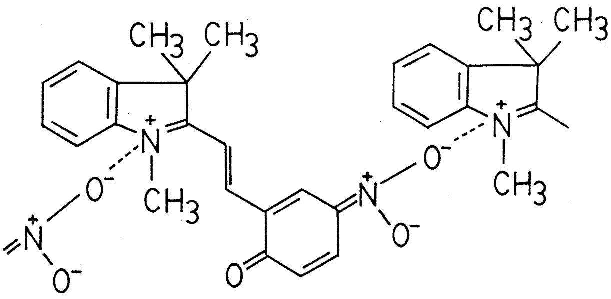

Figure 1. A probable structure of aggregates of 6-nitro BIPS linked together through NO_2-bridges.

Yuzawa et al.[7] reported in their recent publication Raman spectra of transients I, II and III appearing sequentially when they UV-irradiated 6-nitro BIPS in cyclohexane. The transient III was attributed to dimeric species. The spectrum of the aggregates in our study is distinct from these spectra.

In the present Letter, a $^{15}NO_2$-isotopomer of the spiropyran was prepared, and Raman spectra of the aggregates were measured to obtain more insight on the structure of the aggregates.

Preparation of 6-nitro [$^{15}NO_2$] BIPS was made by the procedure of Berman et al.[8] Nitro[$^{15}NO_2$]salicylaldehyde was prepared using nitric-^{15}N acid (Aldrich, 98 atom% ^{15}N), in a 11.8% yield. It was then coupled with 1,3,3-trimethyl-2-methylene-indoline in a 45.1% yield. Purities of the intermediate and final product were examined by NMR measurements using a JEOL JNM-EX270 NMR spectrometer.

Merocyanine aggregates of 6-nitro [$^{15}NO_2$] BIPS were prepared as those of ordinary sample. Briefly, a cyclohexane solution (5.0 mmol dm^{-3}) was UV-irradiated with a Ushio UXL-150D xenon short arc lamp for more than 1 hour. Solid material obtained was washed with portions of cyclohexane until the washing solution was no more colored on the UV irradiation. Then the solid material was used for spectral measurements.

The resonance Raman spectra of the aggregates were measured in KBr discs (weight ratio of the aggregate to KBr = 1:200) on a JASCO CT-80D double monochromator equipped with a Hamamatsu R-649 photomultiplier/CT-1050 photon counting unit. The exciting light (514.5 nm) was obtained form a Spectra-Physics Model 165 argon ion laser. The sample was rotated in the measurements to avoid deterioration due to the prolonged exposure to laser light.

The observed Raman spectrum of the ^{15}N-isotopomer is shown in Figure 2(curve a), in comparison with that of ordinary sample (curve b). Three peaks with asterisks in (b) at

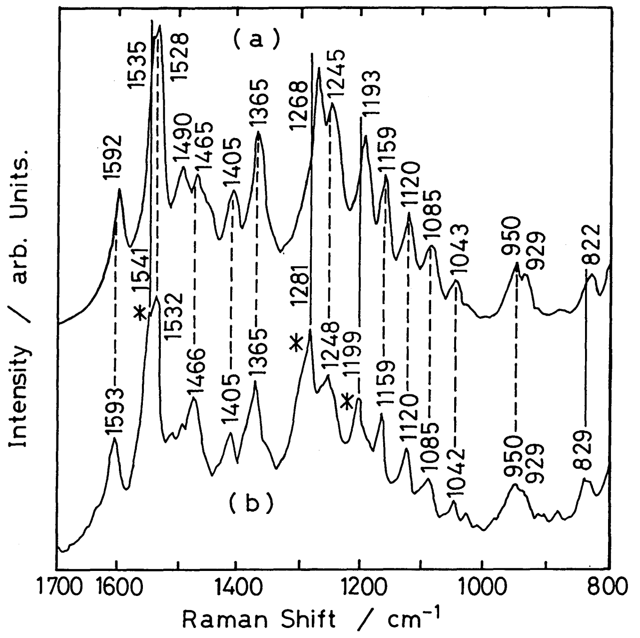

Figure 2. Raman spectra of aggregates. (a) $^{15}NO_2$–isotopomer, (b) ordinary sample.

1541/1532, 1281 and 1199 cm^{-1} shift to 1535/1528, 1268, and 1193 cm^{-1}, respectively, while remaining bands fall within ±3 cm^{-1} of original positions. These three bands are those present only for the aggregates and have been attributed to vibrational modes associated with the NO_2 bridge.[4,6] The observed shift supports the idea.

It is a natural conjecture to assign these three bands to two N–O stretching and one C–N stretching (in C–NO_2) modes. The 1541/1532-cm^{-1} band is located in the usual wavenumber range for the antisymmetric NO_2 stretching mode. The 1281-cm^{-1} band can be related to symmetric NO_2 stretching mode, in light of the report of Miyata et al.[9] on aggregate formation of photomerocyanines of amphiphilic spiropyrans in LB films. They observed a downward wavenumber shift of the symmetric NO_2 stretching band of spiropyran at 1340 cm^{-1} to 1295 cm^{-1} for photomerocyanine and eventually to split peaks at 1280 and 1250 cm^{-1} in the aggregate, while the corresponding shift of the antisymmetric stretching mode was very small, e.g. 1520 cm^{-1} to 1518 cm^{-1}. The shift of the band at 1541/1532 cm^{-1} (1535/1528 cm^{-1} for the $^{15}NO_2$-species) and that at 1281 cm^{-1} (1268 cm^{-1} for the $^{15}NO_2$-species) are in further, definitive support of the assignments of these bands to stretching modes within the NO_2 moiety, although some N=O and N–O stretching character must be associated with the 1541/1532 and 1281-cm^{-1} bands, respectively.[10] The remaining 1199-cm^{-1} (1193 cm^{-1} for the $^{15}NO_2$-species) band can be assigned to C–NO_2 stretching mode, though it must be coupled strongly with the NO_2 symmetric stretching mode. The 829-cm^{-1} band, attributable to NO_2 deformation, shifts to 822 cm^{-1} for the $^{15}NO_2$-species. These findings strongly indicate the association of merocyanine monomers through the NO_2-bridges in the large-sized aggregates found in our study.

References and Notes

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6 The 1199-cm^{-1} band which appeared in Figure 3 of Ref. 4 was erraneously listed as 1190 cm^{-1} in text and Table II of Ref. 4. In Ref. 4, the lower-wavenumber member (at 1532 cm^{-1}) of the closely located doublet (1541, 1532 cm^{-1}) was assigned to the aggregate. In light of the present experiment, however, the whole doublet may be associated with the aggregate structure, although the band due to the CTT skelton must be overlapped. Little can be said on structures between 1480–1500 cm^{-1}.
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10 One of the anonymous referees pointed out the possibility that the 1541/1532-cm^{-1} band has a contribution from the C=N$^+$ stretching mode in the C=N$^+$(–O$^-$)$_2$ structure shown in Figure 1. This is certainly an interesting point to be discussed. The structure shown in Figure 1 is one of three types of resonance hybrid structures given in Ref. 5 (the other two are with C–NO_2 structures). In the time-resolved Raman study of a similar compound, 6-nitro-8-methoxy BIPS, Albert et al. (J.L. Albert, J.P. Bertigny, J. Aubard, R. Dubest, and J.E. Dubois, J. chim. phys., 82, 521 (1985)) ruled out the presence of a C=N$^+$ double bond by the absense of bands in the 1650–1700 cm^{-1} range. This is the case also for our aggregates, which indicates that aggregation does not lead to any appreacible increase in the relative importance of the resonance hybrid structure shown in Figure 1, in comparison with the corresponding merocyanine monomers.