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Intermolecular transitions observed by electric-quadrupole-resonant second-harmonic generation in a discotic liquid crystal of phthalocyanine

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Optical second-harmonic generation (SHG) spectra were obtained in the isotropic (Iso) and discotic (D) liquid crystal phases of a phthalocyanine derivative. In the D phase, a strong resonant peak due to an electric quadrupole transition was observed. In contrast, resonant peaks, in different spectral regions, with one or two orders of magnitude smaller intensities were observed in the Iso phase. The large spectral and intensity differences in the SHG spectra of both phases strongly indicate the existence of both resonant states due to intramolecular and intermolecular transitions. [S1063-651X(97)50912-3]

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In a usual electric dipole (ED) mechanism, second-harmonic generation (SHG) is forbidden in centrosymmetric systems [1]. However, SHG in centrosymmetric systems is allowed under higher-order mechanisms such as electric quadrupole (EQ), electric-quadrupole coupling (EQC), magnetic dipole (MD), and magnetic dipole coupling (MDC) mechanisms [2–7]. Actually, relatively strong SHG was observed in vacuum-deposited centrosymmetric films of phthalocyanines (Pc's) [6–11]. For a CuPc film, a $\chi^{(2)} = 4.5\times10^{-8}$ esu at 532 nm SH wavelength was reported [10]. In SHG spectroscopic studies, a resonance was observed at the SH wavelength 550 nm, which was attributed to an EQ resonant transition at the SH wavelength (EQ mechanism) [7]. This assignment was confirmed by the observation of the anisotropic SHG in epitaxial Pc films, which is allowed only in EQ and EQC mechanisms [8].

The electronic states of Pc have been widely studied [12]. Yamada *et al.* [7] assigned the resonant EQ transition to an intramolecular transition. However, Tokura *et al.* [13] suggested the existence of charge-transfer exciton bands based on electromodulation spectroscopy. Intramolecular and intermolecular transitions are seriously affected by molecular packing structures, i.e., stacking of π-conjugated macrocycles of Pc. Actually α- and β-form Pc crystals exhibit quite different electromodulation spectra [14]. In this respect, liquid crystals serve as an ideal system to study intramolecular and intermolecular transitions, since the intermolecular interaction critically changes between different liquid crystal phases. In this letter, we will show a drastic change in the SHG spectra of a Pc derivative in its discotic and isotropic phases, exemplifying the usefulness of liquid crystal systems for the study of electronic transitions.

The discotic liquid crystalline material, $H_2Pc(SC_{18}H_{37})_8$, was synthesized as will be described elsewhere [15] and shows the phase sequence; crystal-(57 °C)-discotic columnar (D)-(220 °C)-isotropic (Iso) in a heating process. The material was sandwiched between two clean glass substrates separated by about 3.8 μm. Without special treatment, we obtained nearly uniform alignment in which hexagonally packed columns of the D phase align along the glass surface normal.

The SHG spectra in the fundamental light range from 900 to 1400 nm were recorded by the system previously reported [7]. The p-polarized SH light generated by the s-polarized light with an incidence angle of 45° was detected in the transmission geometry. The sample temperature was kept at 15 °C higher and lower than the D-Iso transition temperature.

Figure 1(a) shows the linear absorption spectra in the Iso and D phases. In both phases, two peaks are seen; Q and B bands at about 680 nm and 470 nm, respectively. The insensitivity of these bands to the molecular condensed state (phase) suggests the dominance of intramolecular excitations. On the other hand, the SHG spectra exhibit a marked difference between the Iso and D phases, as shown in Fig. 1(b). In the D phase, a strong peak emerges at an SH wavelength of 560 nm (arrow b). Because of the resemblance of

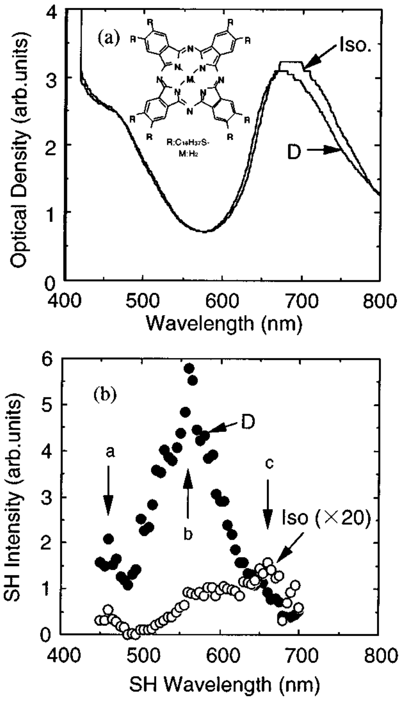

FIG. 1. Linear optical absorption spectra (a) and SHG spectra (b) in the Iso and D phases. The SH intensity in the Iso phase is magnified by 20 times. Three resonant peaks a, b, and c can be seen in (b). The Pc discotic liquid crystal used is also shown in (a).

this spectra to the spectra for vacuum-deposited Pc films, this peak is attributed to the EQ resonant transition at the SH wavelength (EQ mechanism) [7]. On the other hand, the SHG intensity is considerably reduced in the Iso phase. Note the magnification of 20 times for the Iso data in Fig. 1. The peaks at 460 and 660 nm (arrows *a* and *c*) are obvious. In the previous SHG spectra of vacuum-deposited Pc films, these peaks were out of the measured SHG wavelength range (505 nm to 655 nm) [7]. These two peaks are attributed to ED resonant transitions at the SH wavelengths, since they are located at *B* and *Q* bands in the linear absorption spectra. Among the higher-order mechanisms, both MDC and EQC mechanisms allow such a resonance [7]. Moreover, the anisotropic SHG study in epitaxial Pc films showed the significant contribution of EQ and/or EQC mechanisms [8]. Hence, the resonant peaks *a* and *c* are attributed to the ED transitions at the SH wavelengths via EQC mechanisms.

The most striking result mentioned so far is the large difference of the SH intensity in the Iso and *D* phases. For the peaks *a*, *b*, and *c* in the *D* phase, SH intensities are 77, 123, and 16 times as large as those in the Iso phase, respectively. In order to clarify the reason for this large difference, we first examine whether or not the large difference of the SH intensities in the Iso and *D* phases can be explained only by the molecular orientational change. For this purpose, we use the oriented gas model only taking account of an intramolecular transition.

We consider two molecular condensed states: in the Iso phase, molecules are randomly oriented (K_h symmetry) while in the *D* phase, the average direction of the Pc's macrocycle normal, *z* axis, is parallel to the substrate surface normal, *Z* axis, ($D_{\infty h}$ symmetry) [16]. For EQC and EQ mechanisms, the effective nonlinear polarizations in the laboratory coordinates are expressed as

$$P_{\mathrm{eff}}=P-\nabla\cdot Q, \tag{1}$$

$$P_i=\sum \Delta_{ijkl}E_j\partial_k E_l, \tag{2}$$

$$Q_{ij}=\sum \Lambda_{ijkl}E_k E_l, \tag{3}$$

where Δ and Λ are the nonlinear susceptibilities for EQC and EQ mechanisms, respectively, P the nonlinear polarization and Q the nonlinear electric quadrupole polarization. For $D_{\infty h}$ and K_h symmetries, the effective nonlinear polarizations in the $s\rightarrow p$ condition are expressed as [6]

$$P_1^{\mathrm{eff}}=(\Delta_{1212}-2\Lambda_{1122})E_2\partial_1 E_2, \tag{4}$$

$$P_3^{\mathrm{eff}}=(\Delta_{3232}-2\Lambda_{3322})E_2\partial_3 E_2. \tag{5}$$

According to the oriented gas model, neglecting the local field factors [17], Δ and Λ are expressed as

$$\Delta_{ijkl}=\frac{N\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\,\sin\,\theta\int_0^{2\pi}d\psi F(\phi,\theta,\psi)R_{ii'}R_{jj'}R_{kk'}R_{ll'}\delta_{i'j'k'l'}}{\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\,\sin\,\theta\int_0^{2\pi}d\psi F(\phi,\theta,\psi)}, \tag{6}$$

$$\Lambda_{ijkl}=\frac{N\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\,\sin\,\theta\int_0^{2\pi}d\psi F(\phi,\theta,\psi)R_{ii'}R_{jj'}R_{kk'}R_{ll'}\lambda_{i'j'k'l'}}{\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\,\sin\,\theta\int_0^{2\pi}d\psi F(\phi,\theta,\psi)}, \tag{7}$$

where N is the number density of molecules, $F(\phi,\theta,\psi)$ is an orientational distribution function for Euler angles (ϕ,θ,ψ), R is the rotation matrix $R(\phi,\theta,\psi)$ given in Ref. [18], δ and λ are molecular hyperquadrupole polarizabilities in molecular coordinates for EQC and EQ mechanisms, respectively. For Pc molecules, we assume the D_{4h} molecular symmetry. The independent components of δ and λ in D_{4h} symmetry are given in Ref. [8].

For K_h, $F(\phi,\theta,\psi)d\phi d\theta d\psi=\sin\,\theta d\phi d\theta d\psi$. Then we obtain

$$\Delta_{1212}=\Delta_{3232}=N[\tfrac{1}{5}(\delta_{1111}+\delta_{1212})+\tfrac{1}{5}(\delta_{1313}+\delta_{3131}-\delta_{3311})], \tag{8}$$

$$\Lambda_{1122}=\Lambda_{3232}=N[-\tfrac{2}{15}(\lambda_{1111}+\lambda_{1212})+\tfrac{2}{15}(\lambda_{1133}-2\lambda_{1313})]. \tag{9}$$

For $D_{\infty h}$, on the other hand, the general expression for $F(\phi,\theta,\psi)d\phi d\theta d\psi$ is given by $F(\theta)d\phi d\theta d\psi$, where $F(\theta)$ is expressed by series of Legendre polynomial about θ, the angle between *z* and *Z* axes. By assuming that the orientation is perfect, we use the δ function for $F(\theta)$. Thus, we obtain

$$\Delta_{1212}=N[\tfrac{1}{2}(\delta_{1111}+\delta_{1212})+\tfrac{1}{4}\delta_{1133}], \tag{10}$$

$$\Delta_{3232}=N[\delta_{3131}], \tag{11}$$

$$\Lambda_{1122}=N[-\tfrac{1}{2}(\lambda_{1111}+\lambda_{1212})-\tfrac{3}{4}\lambda_{3311}], \tag{12}$$

$$\Lambda_{3322}=N[\lambda_{3311}]. \tag{13}$$

For the molecular hyperquadrupole polarizabilities, we assume that every component including *z* (3) in any subscripts is much smaller than the others, because the Pc molecule is a two-dimensional π-electron system. This assumption leads to the following simple relations:

$$\frac{\Delta_{1212}(D_{\infty h})}{\Delta_{1212}(K_h)}=2.5, \tag{14}$$

$$\frac{\Delta_{3232}(D_{\infty h})}{\Delta_{3232}(K_h)}=0, \tag{15}$$

$$\frac{\Lambda_{1122}(D_{\infty h})}{\Lambda_{1122}(K_h)}=3.75, \tag{16}$$

$$\frac{\Lambda_{3322}(D_{\infty h})}{\Lambda_{3322}(K_h)}=0. \tag{17}$$

Equations (14)–(17) together with Eqs. (8) and (9) suggest that the SHG in the D phase can be larger than that in the Iso phase through the different Δ_{1212} and Λ_{1122} components in the two phases. The estimated ratios of the SH intensities in the D and Iso phases are 6.25 and 14.06 for the EQC and EQ mechanisms, respectively. The experimentally obtained ratios, however, are 77 and 16 for the EQC peaks a and c, respectively, and 123 for the EQ peak b. Thus, the disagreement is serious, particularly for the a and b peaks. The disagreement becomes larger, if we take into account the non-δ-functional distribution of $F(\theta)$ and Δ_{3232} and Λ_{3322}. Therefore, we can conclude that the SHG spectra cannot be interpreted within the framework of intramolecular excitation, although Yamada *et al.* [7] interpreted the resonant peak by the intramolecular EQ transition.

It is suggested that intermolecular excitations, like charge-transfer (CT) excitons, play an important role in the transition of Pc [13,14]. Tokura *et al.* [13] proposed the existence of hybridized exciton states originating from molecular excitons and CT excitons. The eigenstates of the CT excitons are symmetric and antisymmetric combinations of CT excitations to adjacent molecules on the same discotic stack. The antisymmetric CT exciton is ED forbidden and is not mixed with the molecular excitons. In contrast, the symmetric exciton is hybridized with the molecular excitons. The antisymmetric CT exciton is expected to exist at the higher energy tail of the Q band. Hence, the resonant peak b, which shows a large difference in the Iso and D phases, can be attributed to a resonant EQ transition to the antisymmetric CT exciton state. On the other hand, the resonant peak c is attributable to a resonant ED transition to the hybridized exciton state. This assignment is consistent with the fact that the difference of the SH intensities in the Iso and D phases is small and can essentially be explained using the oriented gas model. The fairly large difference of the SH intensities at the a peak also suggests the dominance of the intermolecular (CT) excitation. However, it is not easy to discuss the details of this region because of the existence of many electronic states in this region.

In conclusion, the SHG spectra were measured for a Pc derivative in the Iso and D phases. The two-orders-of-magnitude difference of the SH intensity between the Iso and D phases cannot be interpreted by the oriented gas model, suggesting a significant contribution of intermolecular excitations to the SH resonance effect. In the present work, the usefulness of using liquid crystals for the study of electronic transitions is suggested.

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