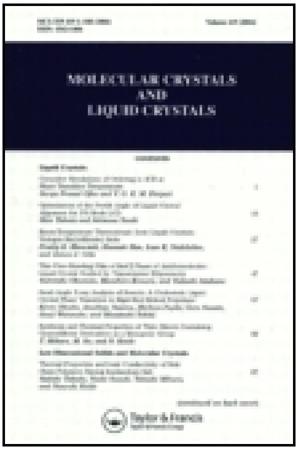

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Anisotropy of Transient Absorption Change in Aggregate Metallophthalocyanine with Two-Dimensional Transitions

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Anisotropy of Transient Absorption Change in Aggregate Metallophthalocyanine with Two-Dimensional Transitions

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Anisotropy of transient absorption change in phase-I aggregate vanadylphthalocyanine was investigated in terms of the influence of intermolecular interaction on dimensionality. It was found that, depending on the wavelength and the nature of interaction, the two-dimensionality of the molecule can be reduced to one-dimensional in aggregates.

Keywords: two-dimensional molecule; intermolecular interaction; aggregation; anisotropic transient absorption change

In order to design a functional molecular system, it is essential to understand the structure-to-property relation. For example, anisotropy in nonlinear optical properties is governed by the symmetry of the molecule through the dimensionality of its electronic structure. This relation is also very important in terms of material characterization and application, such as the optical Kerr-gate measurement and all-optical switches.

In the case of photoinduced absorption change measured by pump-

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probe method, randomly oriented molecules with one-dimensional (1-D) character present a polarization dependence of 3:1. Here the polarization dependence is the ratio of the responses at the probe polarization parallel to the pump polarization and perpendicular to it. On the other hand, molecules with two-dimensional (2-D) character such as metallophthalocyanines present a different anisotropy. Here we define a 2-D molecule as a molecule with twofold degenerate transitions. Polarization dependence of fluorescence and pump-probe response in a 2-D system was reported to be initially 8:1 (i.e., fluorescence anisotropy r=0.7) and 4:3 (i.e. r=0.1) after in-plane relaxation[1,2]. Recently, we have shown that the initial polarization ratio in transient absorption change is governed by the nature of the probe transition, and that 4:3 ratio can be observed as an initial polarization dependence[3]. We have also reported anisotropy of electroabsorption in metallophthalocyanines to show a specific polarization dependence of 0:1[4], reflecting their 2-D character.

In an aggregate of a 2-D molecule, it can be expected that intermolecular interaction affects to the dimensionality of the system. In metallophthalocyanines, a "slipped stack" structure is generally observed, in which each phthalocyanines are stacked so that the molecular planes are parallel to each other and that the stacking axis is oblique to the normal of molecular plane. This can introduce asymmetry in the molecular plane, resulting in nondegenerate intermolecular exciton-exciton interactions[5]. In addition, those slipped stack columns are closely packed, resulting in an intermolecular interaction which has a rather "coplanar" character. This can also lead to 1-D character, depending on the arrangement of stacks. In this paper, we report polarization dependence of transient absorption change in an aggregate of vanadylphthalocyanine, a 2-D molecule, showing a 1-D character at certain wavelengths due to intermolecular exciton-exciton interaction.

In the experiment, a soluble vanadylphthalocyanine derivative, VOPc(t-bu)$_{1.1}$ (t-bu stands for tertiary butyl group), was doped in polystyrene (PS) at a concentration of 10 wt% and spin-coated on fused silica substrates to form phase-I aggregate thin films. Transient absorption change was measured using a subpicosecond pump-probe measurement setup. The light source was a Ti-sapphire laser with a Ti-sapphire regenerative amplifier, which provides about 20 μJ/pulse output with a temporal width of 250 fs operating at 1 kHz. The probe beam was a spectral continuum at wavelengths from 450 nm to longer than 1 μm. Polarizer and half-wave plate combinations were used to control polarization and intensity of pump and probe.

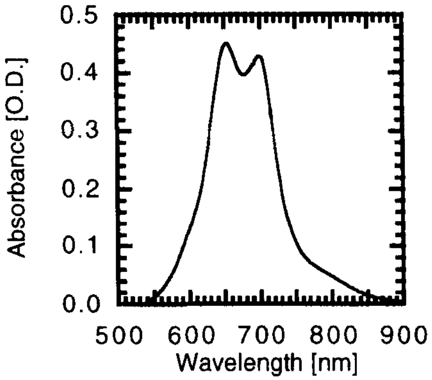

FIGURE 1 Absorption spectrum of a phase-I $\mathrm{VOPc}(t\text{-bu})_{1.1}$/polystyrene film.

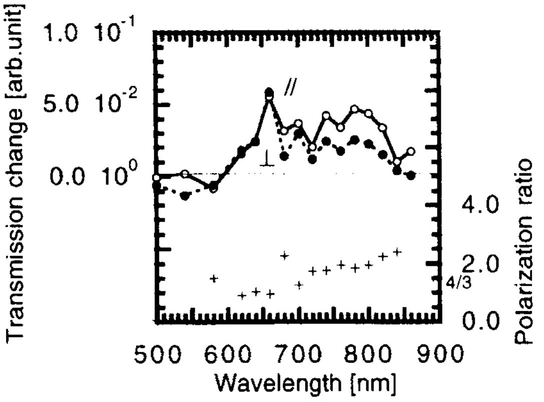

FIGURE 2 Transient absorption changes (top) and their polarization ratio (bottom) of a phase-I $\mathrm{VOPc}(t\text{-bu})_{1.1}$/polystyrene film. o (//) and • (⊥) stand for polarization configurations where the pump and probe polarizations are parallel and perpendicular, respectively, to each other. Polarization ratio (+) is the ratio of // and ⊥. The dotted line in the bottom trace shows 4/3 ratio which is specific to a 2-D system.

Figure 1 shows linear absorption spectrum. It is a typical phase-I VOPc absorption spectrum with two main peaks at 650 nm and 700 nm, the latter attributed to monomeric Q-band absorption and the former to the blue-shifted Q-band transitions due to cofacial intermolecular exciton-exciton interaction.

Figure 2 shows transient absorption spectra and its polarization dependence of the same sample at a pump wavelength of 760 nm and a delay of 5 ps. The polarization ratio is close to 4:3 between 580 to 660 nm which corresponds to the absorption band peaking at 650 nm. In phase-I packing, VOPc molecules are stacked without large slip, resulting into rather symmetric cofacial interaction. Therefore, this blue-shifted component keeps 2-D character. On the other hand, the polarization ratio at longer wavelength than 720 nm is about 2:1, suggesting rather 1-D character. At this wavelength region, there is a shoulder in the absorption spectrum. This might be attributed to a red-shifted Q-band transition due to coplanar intermolecular interaction, possibly between neighboring molecular stacks. It might be less symmetric, resulting into 1-D response. This feature is consistent with anisotropy of electroabsorption response already reported[4]. These results suggest that the influence of the intermolecular interaction depends on the wavelength.

In conclusion, it has been experimentally demonstrated that intermolecular exciton-exciton interaction due to aggregation affects to the dimensionality of an aggregate of a 2-D molecule. Depending on wavelength, the dimensionality of aggregate system varies between 2-D and 1-D. For further investigation, transient absorption measurement of evaporated and spin-coated films in phase-I and II is in progress.

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