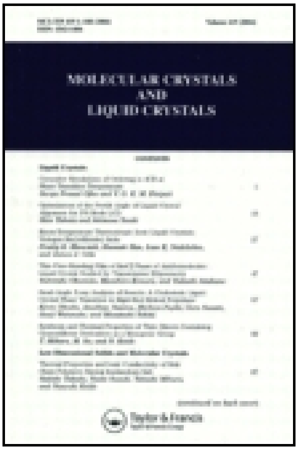

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Evidence of Intermolecular Interaction Effect on Nonlinear Optical Properties of Copper Phthalocyanine

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ABSTRACT In some organic molecular aggregates and crystals, intermolecular interaction effects play an essential role in the nonlinear optical (NLO) properties. Here, we report on the experimental results on copper phthalocyanine films, which demonstrate a significant intermolecular interaction effects on NLO properties. Results of third-harmonic generation and electro-absorption measurements are presented and discussed.

INTRODUCTION

Much effort have been made on the research and development of nonlinear optical (NLO) organic materials showing large quadratic and cubic NLO susceptibilities. In the case of quadratic NLO crystals, the basic NLO properties are predominantly determined by the electronic orbitals localized within the constituent molecules.[1] The molecular orientation effect is important in crystal, but intermolecular interaction in the excited states is thought to play a minor role. However, in case of cubic NLO organic substances, the cubic NLO properties are largely dependent on the electronic excited states more or less delocalized over several constituent molecules. In this paper, we *demonstrate an example of the intermolecular interaction effect in* the NLO properties of copper phthalocyanine (Cu-Pc) films.

ELECTRONIC STRUCTURE OF Cu-Pc

Phthalocyanines (Pc's) have been received extensive studies for their remarkable opto-electronic properties as organic photo-conductors. Recently, interest has been also aroused in the NLO properties by the finding that some Pc's show cubic NLO susceptibility comparable to these of conjugated polymers.[2,3] High chemical stability of Pc films is favorable for the NLO application, but there is a complexity associated with the polymorphism of crystal structures.

The effect of intermolecular interaction in different polymorphic forms of Pc's has been argued before from the electro-absorption measurement of α- and β-form Pc's.[4] It is tempting, then to investigate the same effect on the NLO properties of Pc's. In this study, we deal with copper-phthalocyanine (Cu-Pc) films, having either α- or β-form. Structure parameters of α- and β-form CuPc are listed in Table 1. (The α-form crystal structure has not been well characterized as yet, due to the difficulty in growing single crystal.)

For the convenience of later discussion a schematic energy diagram for Pc's is depicted in Fig. 1. The lowest molecular excitation is doubly degenerated π-π^* transitions. In crystal, they form molecular exciton levels, F_1 and F_2, by the intermolecular interaction. Besides, intermolecular charge-transfer (CT) excitations take place between adjacent Pc molecules on a stack. In the centro-symmetric α- and β-from Pc's, these CT excitations are classified as either optically allowed symmetric(s)-CT exciton or forbidden antisymmetric(a)-CT exciton.[5] Actual excitations are hybridized states between the molecular and CT excitons as shown in Fig. 1(c).

EXPERIMENTAL PROCEDURE

Reagent-grade Cu-Pc powders purchased from Tokyo Kasei Co. were

	d_1/Å	d_2/Å	Φ/degrees
α-Form	3.8	3.4	28
β-Form	4.8	3.3	46

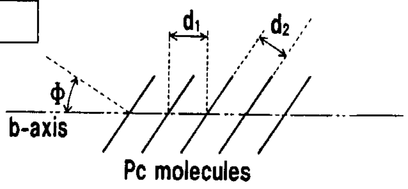


TABLE 1 Structure parameters of α-form[6] and β-form [7] Cu-Pc.

purified by two-times of sublimation procedure. Thin α-form Cu-Pc films were obtained by vacuum deposition of these powders on a slide grass substrate under pressure of $5X10^{-6}$ Torr. The β-form films were obtained by thermal annealing of α-form films at 630 K in a vacuum. Assignment of α- and β-forms was made by optical absorption and X-ray diffraction measurements. Typical film thickness was 0.1 μm.

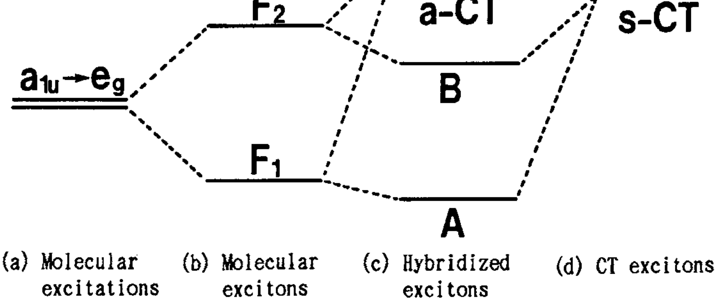
Measurements of electro-absorption (EA) and third-order harmonic generation (THG) were made on α- and β-form Cu-Pc films both at room temperature. In the EA measurements, an AC field (1KHz) of 50 KV/cm was applied across the gap of two aluminum electrodes deposited on the sample surface. Modulated second-harmonic signals were detected by a lock-in amplifier. The EA spectra of $\Delta I/I$ were measured as a function of photon energy.

For the THG measurement, the sample film was irradiated by a pulsed laser beam, obtained from a lithium niobate difference-frequency generator, in which two laser beams from a Q-switched YAG laser and a dye laser, pumped by the second harmonic light of the YAG laser, were mixed. The $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ values were estimated by a standard Maker's fringe method.

EXPERIMENTAL RESULTS AND DISCUSSIONS

In figure 2, we show the EA and NLO susceptibility spectra observed on α- and β-form Cu-Pc films. The photon energies in parenthesis indicate the fundamental photon energy in the THG measurements. The $|\chi^{(3)}|$ values of β-form Cu-Pc film are of the order

FIGURE 1 Schematic energy diagram of phthalocyanine crystal (from ref. [5]).



of $10^{-12} \sim 10^{-11}$ esu in the fundamental photon energy region investigated, but for the α-form film, the third-harmonic light intensities were comparable to these of the glass substrate, so that reliable estimation of the NLO susceptibility was not so easy because of the interference effect by the substrate. In Fig. 2(c), two experimental points are shown, but they represent approximate values. What we can say safely here is that the NLO response is nearly one order of magnitude smaller in the α-form than the β-form. Looking at the $|\chi^{(3)}|$ spectra of the β-form film, one finds that the $|\chi^{(3)}|$ spectra of β-form film resemble in shape to absorption spectrum of the same film. The $|\chi^{(3)}|$ data are lacking before 1.7 eV, as an appropriate laser was not available in this region, but the $|\chi^{(3)}|$ spectrum shows the maximum value of 1×10^{-11} esu at 1.73 eV, where the absorption peak is located. The second peak of $|\chi^{(3)}|$ spectrum at 1.95 eV is also coincident with the second absorption peak. This indicates that the NLO response on this region is predominantly determined by the three-photon resonance effect.

The EA spectra of α- and β-form Cu-Pc films shown in Fig. 2(a,b) provide additional information on the NLO properties of these films. In

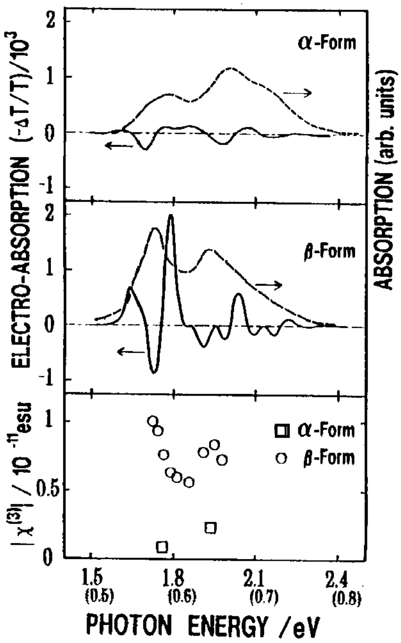


FIGURE 2 Absorption and electro-absorption spectra (upper) and experimental $|\chi^{(3)}(-3\omega\,;\,\omega,\,\omega,\,\omega)|$ values (lower) of α- and β- form phthalocyanine films at room temperature.

fact, third-order susceptibility $|\chi^{(3)}(-\omega;\omega, 0, 0)|$ which is related to the experimental EA spectra by $\mathrm{Im}\chi^{(3)}(-\omega:0, 0, \omega)=(\Delta\varepsilon_2/3\varepsilon_0E^2)$ (1), where $\Delta\varepsilon_2$ is the field-induced change in the imaginary part of complex dielectric function ε under an field of E. It is immediately noticed that the EA signals in the β-form film are appreciably larger than that of the α-form film. This means that the third-order NLO susceptibility $\chi^{(3)}(-\omega;0, 0, \omega)$, given by eq. (1), is larger for the β-form than the α-form, which is consistent with the THG results.

Now, with above-mentioned experimental results in mind, we shall briefly discuss on the possible implication of the results in view of energy level scheme of Pc crystals shown in Fig. 1. Most important point revealed by this study is the following: The absorption spectra are not so different between the α- and β-form seen in the top of Fig.1, but there are remarkable difference between the two forms in the NLO response as detected by THG and EA measurements. In general, the NLO response is thought to be enhanced by the one-dimensional exciton effect, that is, by the contribution of the CT exciton as shown in Fig. 1, whereas the ordinary absorption is predominated by intramolecular electronic excitations. The large NLO susceptibilities in the β-form CuPc seems to indicate a larger contribution of the CT exciton character, as compared with more localized excited states in the α-form CuPc It has been argued before that the higher energy part of absorption spectra in both form Pc's is predominated by the CT-like excitations and their phonon sidebands. However, according the present results, more careful examination seems to be necessary on the nature of electronic excitations involved in the linear and nonlinear optical processes of both form films.

SUMMARY

We have measured the $|\chi^{(3)}|$ values of Cu-Pc films, for the first time to our knowledge, in the resonance region with the exciton absorption bands in both α- and β-forms. The $|\chi^{(3)}|$ values were found to be significantly dependent on the molecular packing structure, the $|\chi^{(3)}|$ value in the β-form being appreciably larger than the α-form. This is consistent with the electro-absorption data; the field-modulated signals in the β-form film are nearly one order of

magnitude lager than those of the α-form. These results seem to require reexamination of previous interpretation of the exciton states in the polymorphic Pc crystals.

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