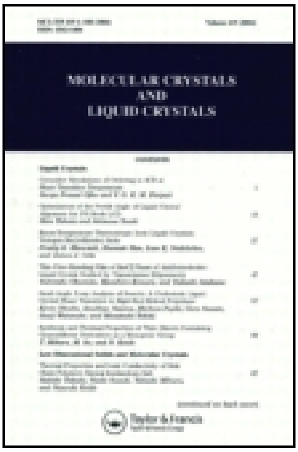

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Electroabsorption Spectra and Nonlinear Optical Susceptibility of Tetrakis Tert-Butyl Phthalo-Cyanine

Shuichi Yanagi [a] , Tatsuo Wada [b] , Jayant Kumar [c] , Hiroyuki Sasabe [b] & Keisuke Sasaki [a]

[a] Department of Material Sciences, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, 223, Japan

[b] Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama, 351-01, Japan

[c] Center for Advanced Materials, University of Massachusetts Lowell, 1, University Avenue, Lowell, MA, 01854, USA

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ELECTROABSORPTION SPECTRA AND NONLINEAR OPTICAL SUSCEPTIBILITY OF TETRAKIS TERT-BUTYL PHTHALOCYANINE

SHUICHI YANAGI, TATSUO WADA†, JAYANT KUMAR‡,
HIROYUKI SASABE† AND KEISUKE SASAKI

Department of Material Sciences, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan
†Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-01, Japan
‡Center for Advanced Materials, University of Massachusetts Lowell, 1, University Avenue, Lowell, MA 01854, USA

Abstract Absorption and electroabsorption measurements were performed on the substituted tetrakis *tert*-butyl metal-free phthalocyanine ($H_2Pc(t\text{-bu})_4$) solid solution. The complex third-order nonlinear susceptibilities were determined in poly(methyl methacrylate) films doped with $H_2Pc(t\text{-bu})_4$. The real and imaginary parts of $\chi^{(3)}(-\omega;\omega,0,0)$ were -5×10^{-13} and -4×10^{-13} esu, respectively, at 10 wt% doping of $H_2Pc(t\text{-bu})_4$. In guest/host system, the aggregation reduced the optical nonlinear susceptibilities rather than optical absorption coefficients.

INTRODUCTION

Phthalocyanines are known as a material which exhibits various opto-electronic responses and they are one of the most intensively investigated chromophores. Besides their unique optical properties, phthalocyanines have an advantage of being quite stable against thermal decomposition to fairly high temperatures,[1] which is very attractive for the practical application to optical devices. The intense absorption in the visible region, the Q band, results from the $a_{1u}\rightarrow e_g$ and $\pi\rightarrow\pi^*$ transition, generating an orbitally doubly degenerated state, *i.e.*, ^1E_u in metallophthalocyanine of D_{4h} symmetry. In the metal-free phthalocyanine, the symmetry is lowered to D_{2h} and the excited state is split into two components usually termed Q_x and Q_y. Interaction between adjacent phthalocyanine rings occurs through the coupling of electronic states.[2] The aggregation of phthalocyanine molecules can be observed in absorption spectra as a spectral broadening and multiple peaks. The electroabsorption (EA) measurements enables us to obtain the field induced change in absorption coefficient, $\Delta\alpha$, and hence the change in the complex index of refraction through Kramers-Kronig analysis[3] as shown in the following section. $\Delta\alpha$ depends quadratically on the applied field, and is related to the third-order nonlinear optical susceptibility, $\chi^{(3)}(-\omega;\omega,0,0)$.[4] Since the EA measurement is very useful method to investigate the nonlinear optical properties of molecular aggregation, we can discuss the effect of aggregation on third-order nonlinear optical responses of phthalocyanines by combining optical absorption with EA measurements. In this paper we will discuss these points for tetrakis *tert*-butyl metal free phthalocyanine, $H_2Pc(t\text{-bu})_4$ (Figure 1).

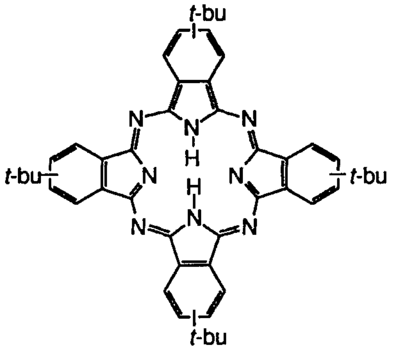

FIGURE 1 Structure of tetrakis *tert*-butyl metal free phthalocyanine.

EXPERIMENTAL

Sample

The films of poly(methyl methacrylate) (PMMA) doped with various concentration of $H_2Pc(t\text{-bu})_4$ were prepared by casting on ITO glass substrates. Typical concentration ranges from 0.05 to 10wt%. The absorption measurements were performed by scanning spectrophotometer (SHIMADZU ; UV-3100PC) and the thickness of films was obtained by a stylus profilometer (Sloan ; Dektak IIA).

EA Measurement

Semitransparent gold was vacuum-deposited on the film surface as an electrode against ITO. Figure 2 shows the experimental setup used in this study. The light from tungsten lamp was monochromated by a grating monochromator and focused onto the sample. A photodiode behind the sample detected the transmitted light. An ac electric field (f=140 Hz) of ~ 10^5 V/cm was applied across the film. A lock-in amplifier tuned to second-harmonic frequency $2f$ of modulating field and detected small changes in the intensity of transmitted light, ΔI. These data were stored on a personal computer as a function of wavelength. The signals at the fundamental frequency f were disregarded as erroneous ones since no linear Stark effect was expected for centrosymmetric structure.[6] All measurements were performed at room temperature.

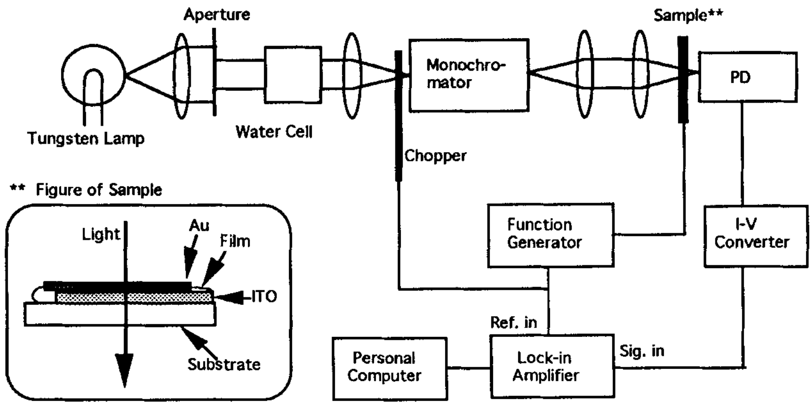

FIGURE 2 Experimental apparatus for electroabsorption spectra measurements.

Formulation

The data that we can directly obtain by EA measurements is ΔI/I, where I is an intensity of the transmitted light and ΔI is the field-induced change in I. The field-induced change in absorption coefficient, Δα, is given by

$$\Delta\alpha = -\frac{\Delta I/I}{d}, \tag{1}$$

where d is a thickness of the film. The absorption coefficient relates to the complex index of refraction, N=n+ik, through Kramers-Kronig relations[3]

$$\begin{aligned} n(\omega) &= \frac{1}{\pi}P\int_0^\infty \frac{c\alpha(\omega')}{\omega'^2-\omega^2}d\omega' - 1 \\ k(\omega) &= \frac{c\alpha(\omega)}{2\omega} \end{aligned} \tag{2}$$

where c is the light velocity and P represents the principal value of the integral. In principle, Eq. (2) requires knowledge of all the changes in absorption over the entire angular frequency ω. Since absorption changes are spectrally localized, it might be reasonable to assume that the change in absorption in other frequency region is negligible for the change in index of refraction. Then we can substitute $n(\omega) = n_0(\omega) + \Delta n(\omega)$, $k(\omega) = k_0(\omega) + \Delta k(\omega)$ and $\alpha(\omega) = \alpha_0(\omega) + \Delta\alpha(\omega)$ in Eq. (2). Assuming $\Delta\alpha$ is not zero only in the frequency range of $\omega_1<\omega<\omega_2$, Δn and Δk are given by following equation:[5]

$$\begin{aligned} \Delta n(\omega) &= \frac{1}{\pi} P \int_{\omega_1}^{\omega_2} \frac{c\Delta\alpha(\omega')}{\omega'^2 - \omega^2} d\omega' \\ \Delta k(\omega) &= \frac{c\Delta\alpha(\omega)}{2\omega} \end{aligned} \tag{3}$$

In the case that the field-induced changes of transmitted light depend quadratically on applied field, the complex third-order nonlinear susceptibility, $\chi^{(3)}(-\omega;\omega,0,0)$, can be calculated:[4]

$$\chi^{(3)}(-\omega;\omega,0,0) = \frac{N\Delta N}{2\pi F^2}, \tag{4}$$

where F is the applied field in statvolt/cm.

RESULTS AND DISCUSSION

Absorption Spectra

Figure 3 shows the absorption spectra for PMMA films doped with $H_2Pc(t\text{-bu})_4$ normalized by the peak value. Film thickness ranges from 4 to 11μm.

Mononuclear species of phthalocyanine generally shows no sign of intermolecular aggregation in common organic solvents at concentrations below 1×10^{-5} M at room temperature.[2] At higher concentration, however, intermolecular aggregation can occur. In Figure 3(e), the concentration of $CHCl_3$ solution is 1×10^{-5} M and then the spectra represent non-aggregated or "monomeric" state. On the other hand, pure $H_2Pc(t\text{-bu})_4$ film obtained by spin-coating of $CHCl_3$ solution without PMMA shows the fully aggregated state.

The absorption spectra changed dramatically in solution and solid states. The peak located on the high energy side of phthalocyanine-doped film grows with concentration. According to the study of binuclear metal-free phthalocyanine linked via 4-*tert*-butyl-*o*-catecholate reported by Dodsworth et.al.,[2] the first peak at 656nm corresponds to the Q-band of binuclear absorption, and peaks at 682nm and 714nm correspond to the Q-band of mononuclear absorption. Latter two peaks in Q-band may be superimposed and form a broad envelope, as shown in Figure 3(b)-(d), because two independent mononuclear species can form a cofacial aggregation in the film. The changes of absorption spectra in different concentrations are regarded as the changes of aggregation fraction. That is, the contribution of aggregation overcomes monomeric contribution to the absorption spectra at higher concentrations.

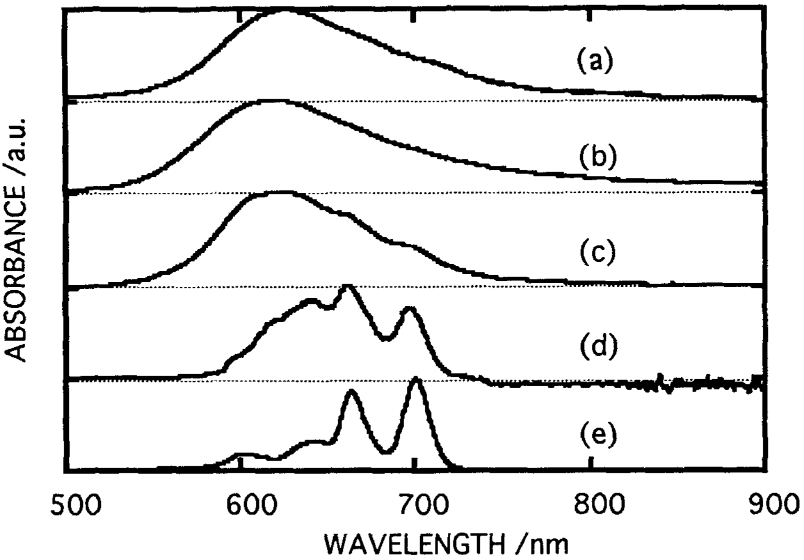

FIGURE 3 Absorption spectra of PMMA film doped with various concentration of $H_2Pc(t\text{-}bu)_4$: (a) pure $H_2Pc(t\text{-}bu)_4$ film, (b) 5wt% doping, (c) 0.5wt% doping, (d) 0.05wt% doping, and (e) 1×10^{-5}M $CHCl_3$ solution as a reference.

Electroabsorption Spectra

Figure 4 shows the EA spectra of PMMA films doped with $H_2Pc(t\text{-}bu)_4$. The field induced signals of 0.05wt% doped film were so small that the amplitude of EA spectrum was set 10 times in this figure. The field applied for 0.05wt%, 0.5wt% and 5wt% doping films were 7.0×10^5 V/cm, 5.0×10^5 V/cm and 3.0×10^5 V/cm, respectively. The thickness of 0.05wt%, 0.5wt% and 5wt% doping films were 4.9μm, 8.0μm and 4.0μm, respectively.

Although the features of EA spectra show the same tendency in all concentrations, the peaks at 580nm and 650nm in the concentrations of 0.05wt% and 0.1wt% shift to red in comparison with those in higher concentrations. This behavior may indicate that the effects of aggregation appeared in the EA spectra.[7] On the other hand, the peak located in the region of 710-720nm shows no shift in all concentrations. The change of the peak ratio of 580-650nm to that of 710-720nm was also observed. From the changes of absorption spectra, it is suggested that these peak shifts and changes of the ratio are caused by the difference in the aggregation states. Therefore we can conclude that EA spectra of PMMA films doped with $H_2Pc(t\text{-bu})_4$ show the same aggregation and monomeric contributions as the absorption spectra. Unfortunately we could not measure the EA spectra below 0.05wt% because of the small electric field induced signals. It is quite difficult to obtain the information of non-aggregated state in EA measurements.

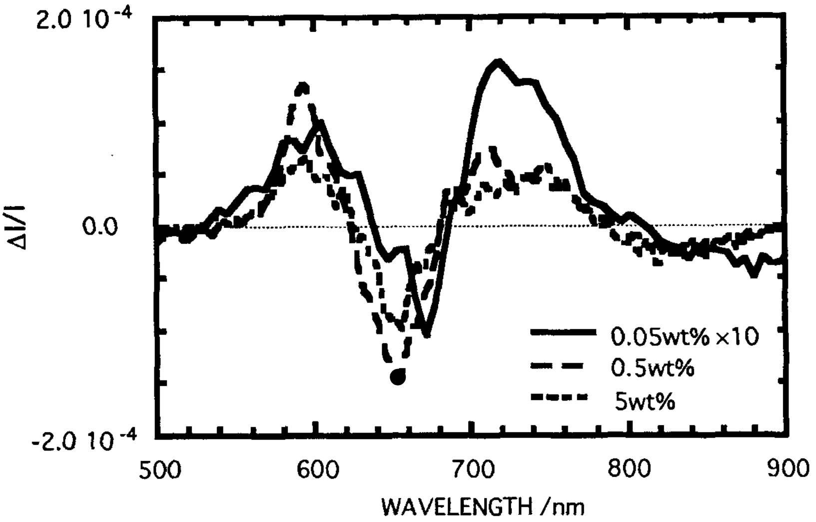

FIGURE 4 Electroabsorption spectra of PMMA films doped with $H_2Pc(t\text{-bu})_4$ at various concentrations.

Third-Order Nonlinear Optical Susceptibility

Since the field induced changes ΔI/I depend quadratically on the applied field F in all the measurements, they are regarded as the term of third-order nonlinear susceptibility $\chi^{(3)}(-\omega;\omega,0,0)$. So we can calculate the complex $\chi^{(3)}$ by Eq.(4). Figure 5 shows the real part of $\chi^{(3)}$ spectra calculated from the EA spectra. The magnitude and profile of imaginary part were almost the same as those of real part and EA spectra, respectively.

The peak shifts and the changes of the ratio were also observed in $\chi^{(3)}$ spectra. These behaviors were caused by the difference in the aggregated states. Since the aggregation was observed in the absorption spectra of 0.05wt% doped-PMMA film, the eminent change in the profiles of $\chi^{(3)}$ spectra is expected.

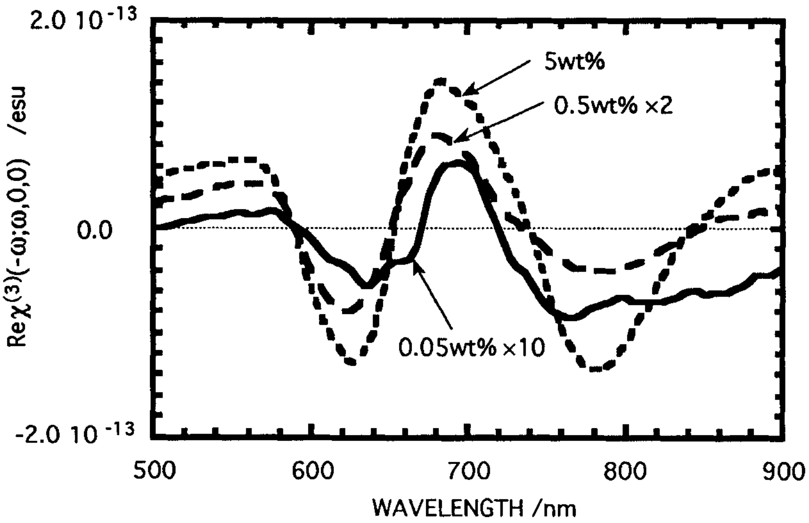

FIGURE 5 Spectra of the real part of third-order nonlinear optical susceptibility in PMMA films doped with $H_2Pc(t\text{-bu})_4$ at various concentrations.

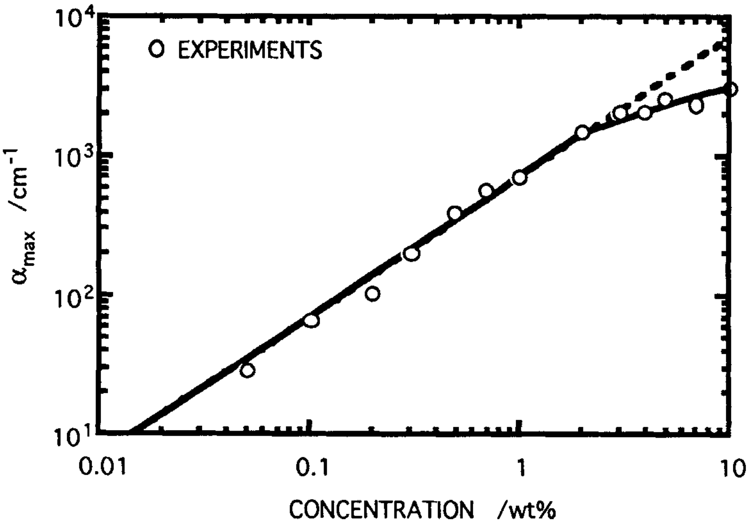

FIGURE 6 The concentration dependence of absorption coefficients. Solid line; interpolation of experimental data. Dashed line; linear extrapolation.

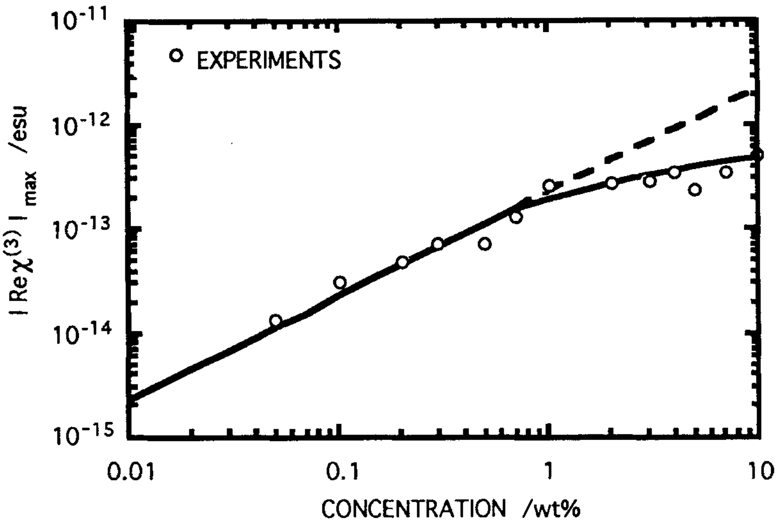

FIGURE 7 The concentration dependence of Re$\chi^{(3)}$ values. Solid line; interpolation of experimental data. Dashed line; linear extrapolation.

Figures 6 and 7 show the concentration dependence of absorption coefficients and $\chi^{(3)}$ values, respectively. The absorption coefficients and $\chi^{(3)}$ values at a peak were not proportional to the concentration. The apparent saturation was observed in both cases. While the absorption coefficient saturated at around 2wt% doping in Figure 6, $\chi^{(3)}$ values at peak began to saturate at even 0.5wt% doping . The concentration dependence of $\chi^{(3)}$ values was much sensitive to molecular aggregation. The aggregation reduces the absorption coefficient and $\chi^{(3)}$ values by *ca.* 0.4 and 0.2, respectively.

CONCLUSION

From the absorption measurements, it was found that the molecular aggregation of $H_2Pc(t\text{-bu})_4$ can easily occur in doped-PMMA films. This aggregation is attributed to the cofacial interaction between adjacent phthalocyanine rings. The absorption spectrum is considered to be superimposed by the aggregation and monomeric contributions. We estimated the complex $\chi^{(3)}(-\omega;\omega,0,0)$ from the electroabsorption spectra. At the concentration of 10wt%, the real and the imaginary parts of $\chi^{(3)}(-\omega;\omega,0,0)$ were -5×10^{-13} esu and -4×10^{-13} esu, respectively. Molecular aggregation of $H_2Pc(t\text{-bu})_4$ in solid solution affected rather $\chi^{(3)}(-\omega;\omega,0,0)$ values than absorption coefficients.

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