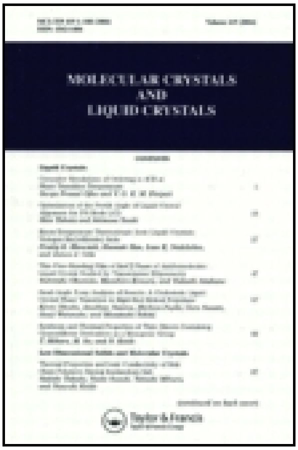


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Interaction of Phthalocyanine Studied by Electroabsorption in Near IR

Shuichi Yanagi [a], Akira Sakamoto [a], Tatsuo Wada [b], Jason P. Sokoloff [b], Minquan Tian [b], Keisuke Sasaki [b] & Hiroyuki Sasabe [b]

[a] Department of Material Sciences, Faculty of Science and Technology, Keio University, Yokohama, Kanagawa, 223, Japan

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

To cite this article: Shuichi Yanagi, Akira Sakamoto, Tatsuo Wada, Jason P. Sokoloff, Minquan Tian, Keisuke Sasaki & Hiroyuki Sasabe (1997): Molecular Interaction of Phthalocyanine Studied by Electroabsorption in Near IR, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 153-156

To link to this article: http://dx.doi.org/10.1080/10587259708032270

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 153–156
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR INTERACTION OF PHTHALOCYANINE STUDIED BY ELECTROABSORPTION IN NEAR IR

SHUICHI YANAGI†, AKIRA SAKAMOTO†, TATSUO WADA‡, JASON P. SOKOLOFF‡, MINQUAN TIAN‡, KEISUKE SASAKI† AND HIROYUKI SASABE‡
†Department of Material Sciences, Faculty of Science and Technology, Keio University, Yokohama, Kanagawa 223, Japan
‡Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

Abstract The linear and the nonlinear optical properties of soluble phthalocyanines in the condensed states were investigated by the absorption and the electroabsorption spectra. By a Kramers-Krönig analysis of the electroabsorption spectra, the wavelength of the maximum refractive index changes is located at around 980 nm for the casted polymer film doped with binuclear phthalocyanine.

INTRODUCTION

Binuclear phthalocyanines in which two phthalocyanine moieties share one benzene ring have a large red-shift of Q-band due to the extended π-conjugation in co-planar alignment of phthalocyanine rings. Since the Q-band of mononuclear phthalocyanine in monomeric state is located on around 700 nm,[1] hexa *tert*-butyl (*t*-bu: -C_4H_9) substituted binuclear metal-free phthalocyanine, $(H_2Pc)_2(t\text{-bu})_6$ shown in fig. 1, has the Q-band in the near IR which is corresponding to the widely used laser diode wavelength. Furthermore the third-order nonlinearities are expected to be enhanced through the extended of π-conjugation. We investigated the linear and the nonlinear optical properties of the poly(methyl methacrylate) (PMMA) films doped with $(H_2Pc)_2(t\text{-bu})_6$ by the absorption and the electroabsorption (EA) spectra.

EXPERIMENTAL

$(H_2Pc)_2(t\text{-bu})_6$/PMMA films for the EA measurements were prepared by spin-coating and casting. The EA measurements were performed under the sinusoidal electric field (140 Hz, 10^5 V/cm). Electromodulated signals were detected at the second harmonic frequency of an applied field. The details of the experimental procedures are reported in previous papers.[1,2]

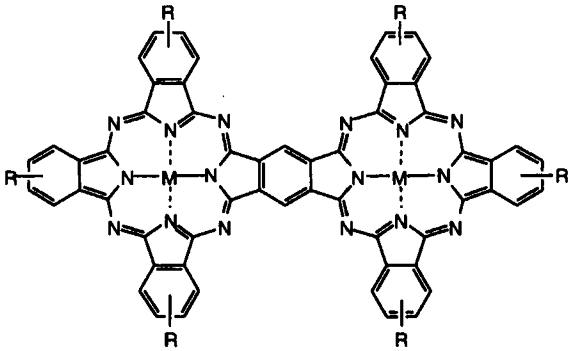
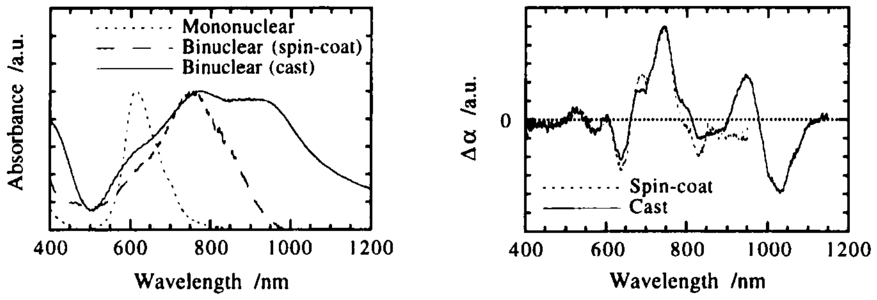


FIGURE 1 Structure of the binuclear phthalocyanine $(H_2Pc)_2(t\text{-bu})_6$; R = *tert*-butyl ($-C_4H_9$), M = H_2.

RESULTS AND DISCUSSIONS

Figure 2 shows the absorption and the EA spectra of 1 wt% $(H_2Pc)_2(t\text{-bu})_6$/PMMA films prepared by spin-coating and casting. The absorption spectrum of the PMMA film of 1 wt% doped with tetrakis *tert*-butyl metal-free phthalocyanine ($H_2Pc(t\text{-bu})_4$) is included in fig. 2 (a). In the case of the mononuclear species, the dominant feature of the linear absorption spectra was a large blue-shift of the Q-bands (620 nm) as compared to a monomeric solution (around 700 nm)[1], which can be attributed to the interaction between co-facially aligned molecules.[1,3] On the other hand, $(H_2Pc)_2(t\text{-bu})_6$/PMMA films have the major absorption peak located close to 800 nm with a shoulder absorption around 620 nm. The additional long wavelength component located on around 980 nm was observed in the casted film, which is considered to be due to the molecular aggregation occurred in the casting process.

In the wavelength region from 400 nm to 900 nm (Region I), the EA spectral features of spin-coated and casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA films were almost same, suggesting similarities of the electronic states in the both films. Therefore the additional long wavelength component in the casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA film has no significant effect on the electronic state of the Region I and we can discuss independently about the Region I and the wavelength region from 900 nm to 1200 nm (Region II). The electromodulated signals of the casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA film in the Region II are considered to be purely caused by the additional long wavelength absorption component. When we assume the additional long wavelength absorption component of the casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA film to be a gaussian, the EA spectral feature in the Region II is well reproduced by the first-derivative of a gaussian. The absorption components which affect on the EA spectrum as the first-derivative are known to be caused by the Frenkel excitons.[4] Therefore the absorption located on around 1000 nm is expected to be caused by the intermolecular interaction between adjacent co-planar $(H_2Pc)_2(t\text{-bu})_6$ molecules.

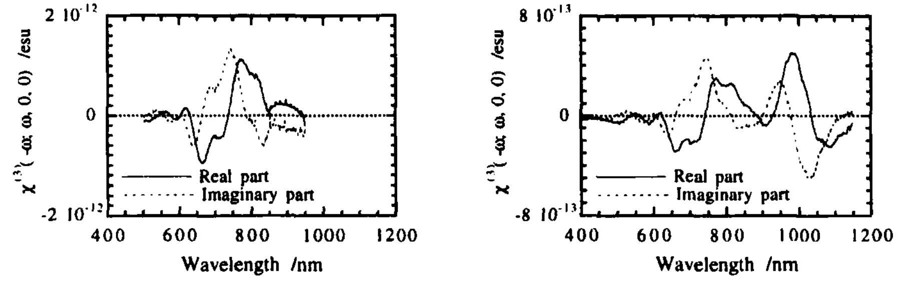


(a). Absorption spectra. (b). Electroabsorption spectra.

FIGURE 2 Absorption and electroabsorption spectra of the spin-coated and casted 1 wt% $(H_2Pc)_2(t\text{-bu})_6$/PMMA films; absorption spectrum of 1 wt% $H_2Pc(t\text{-bu})_4$/PMMA film is included in (a).

The third-order nonlinear susceptibility, $\chi^{(3)}(-\omega; \omega, 0, 0)$, can be obtained by a Kramers-Krönig analysis of the EA spectrum, since the electromodulated absorption changes are caused by the DC Kerr effect.[5,6] Figure 3 shows the $\chi^{(3)}(-\omega; \omega, 0, 0)$ spectra of 1 wt% $(H_2Pc)_2(t\text{-bu})_6$/PMMA films calculated from the EA spectra shown in fig. 1 (b). The magnitude around 1×10^{-12} esu of $\chi^{(3)}(-\omega; \omega, 0, 0)$ maximum of the spin-coated 1 wt% $(H_2Pc)_2(t\text{-bu})_6$/PMMA film is larger than that of 1 wt% $H_2Pc(t\text{-bu})_4$/PMMA film (around 2.5×10^{-13} esu[1]). This enhancement of $\chi^{(3)}(-\omega; \omega, 0, 0)$ are expected to be the result of the expansion of π-conjugate systems. However, in spite of the same doped concentration, in the Region I the magnitude of the $\chi^{(3)}(-\omega; \omega, 0, 0)$ of the casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA film is about half of that of the spin-coated one. The half magnitude of $\chi^{(3)}(-\omega; \omega, 0, 0)$ can be explained by the decrease in the numbers of the molecules to response on the nonlinearities at the Region I, resulting the increase in the numbers of the molecules to response on the nonlinearities at the Region II.

The wavelength of the maximum of the real part of $\chi^{(3)}(-\omega; \omega, 0, 0)$ ($\mathrm{Re}\chi^{(3)}$) of spin-coated $(H_2Pc)_2(t\text{-bu})_6$/PMMA film was located on 770 nm. Since the wavelength of maximum of the $\mathrm{Re}\chi^{(3)}$ of $H_2Pc(t\text{-bu})_4$/PMMA film was located on 670 nm, the red-shift of the $\mathrm{Re}\chi^{(3)}$ maximum wavelength was achieved by 100 nm with the co-planar interaction. Furthermore the over 300 nm red-shift was achieved for the casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA film, because the wavelength of maximum of the $\mathrm{Re}\chi^{(3)}$ was located on 980 nm due to the intermolecular interaction between adjacent co-planar $(H_2Pc)_2(t\text{-bu})_6$ molecules. A Kramers-Krönig analysis of the EA spectra indicates that the refractive index change of 3×10^{-5} in the 5 wt% $(H_2Pc)_2(t\text{-bu})_6$/PMMA film can be obtained at around 980 nm under the applied field of 6×10^5 V/cm.



(a). Spin-coated film. (b). Casted film.

FIGURE 3 Third-order nonlinear susceptibility spectra of the $(H_2Pc)_2(t\text{-bu})_6$/PMMA films.

SUMMARY

The electroabsorption measurements were performed for the spin-coated and the casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA films. The comparison of the absorption and the electroabsorption spectra between the spin-coated and the casted films revealed that the origin of the absorption located on around 1000 nm is caused by the intermolecular interaction between co-planar aligned phthalocyanines. A Kramers-Krönig analysis of the EA spectra indicates the wavelength of the maximum refractive index changes is located at around 980 nm for the casted $(H_2Pc)_2(t\text{-bu})_6$/PMMA film. By the higher order intermolecular interaction, the maximum refractive index change can be further red-shifted making them of interest for telecommunication device applications.

REFERENCES

1. S. Yanagi, T. Wada, J. Kumar, H. Sasabe and K. Sasaki, Mol. Cryst. Liq. Cryst., 255, 167 (1994).
2. T. Wada, S. Yanagi, H. Kobayashi, J. Kumar, K. Sasaki and H. Sasabe, SPIE Proc., 2143, 172 (1994).
3. M. Kasha, H. R. Rawls and M. A. El-Bayoumi, Pure & Appl. Chem., 11, 371 (1965).
4. L. Sebastian, G. Weiser and H. Bässler, Chem. Phys., 61, 125 (1981).
5. S. D. Phillips, R. Worland, G. Yu, T. Hagler, R. Freedman, Y. Cao, V. Yoon, J. Chiang, W. C. Walker and A. J. Heeger, Phys. Rev., B40, 9751 (1989).
6. J. S. Weiner, D. A. B. Miller and D. S. Chemla, Appl. Phys. Lett., 59, 842 (1987).