



Electroabsorption and electrophotoluminescence spectra of some subphthalocyanines



Kamlesh Awasthi^a, Kosuke Nakamura^b, Hirohiko Kono^{b,*}, Nagao Kobayashi^{b,*}, Nobuhiro Ohta^{a,*}

^a Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0020, Japan

^b Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

ARTICLE INFO

Article history:

Received 26 November 2013

In final form 21 February 2014

Available online 28 February 2014

ABSTRACT

Electric field effects on the electronically excited states have been investigated for two subphthalocyanines, F-SubPc and T-SubPc, which have the electron-withdrawing and electron-donating substituents, respectively. In contrast with T-SubPc, the directions of the electric dipole moment in the excited states S_1 and S_2 of F-SubPc are found to be very different from that in the ground state S_0 . The S_1 and S_2 states of T-SubPc show a prominent charge-transfer character, suggesting that T-SubPc is a suitable candidate as the dye in photovoltaic cells. Electrophotoluminescence spectra suggest that the intersystem crossing from S_1 to T_1 is enhanced by electric fields.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Subphthalocyanines (SubPcs), which are phthalocyanine (Pc) analogues with lower symmetry, are nonplanar, cone-shaped aromatic macrocycles composed of three diimino-isoindoline units N -fused around a boron center [1,2]. These compounds show strong absorption and strong emission in the visible region, which makes SubPcs promising chromophores with potential application in optoelectronic devices including organic photovoltaic cells and nonlinear optics [3–9], in photosynthetic models for studying energy- and electron-transfer processes [10–13], and in photodynamic therapy (PDT) [14]. These compounds have a reduced tendency to aggregate, as well as a higher solubility than phthalocyanine [15], leading to high emission quantum yields, efficient solar energy conversion, and manageable treatment.

The charge-separated character of photoexcited molecules, that is, the magnitude of the electric dipole moment in the excited state, is particularly important for electron injection in dye-sensitized solar cells from molecules to the semiconductor surface [16], and in bilayer cells from electron donor to acceptor [17,18]. It is also noted that the change in direction of the electric dipole moment following absorption is applicable to a molecular switching device [19]. It is known that a strong electric field develops at both metal/organic interfaces and organic heterojunctions [20]. Therefore, it is important to know how the dynamics of the excited

state is influenced by electric fields, which can be examined from the electrophotoluminescence measurements, where field-induced change in photoluminescence spectra is obtained. Note that the photoluminescence process competes with nonradiative processes including energy transfer and electron transfer [21]. Electric field effects on optical spectra are also applicable for optical storage [22,23] and for field-sensitive holographic storage devices [24,25].

In the present study, we have measured the electroabsorption spectra and the electrophotoluminescence spectra of two subphthalocyanine compounds doped in a PMMA film, which have different peripheral substituent from each other, that is, electron-donating substituent (*tert*-butyl) and electron-withdrawing substituent (fluorine) in the isoindole rings, respectively. Hereafter, ‘electroabsorption’ and ‘electrophotoluminescence’ are abbreviated as E–A and E–PL, respectively. Based on the results of the E–A spectra, the magnitude of the changes in the electric dipole moment and in the molecular polarizability following photoexcitation has been evaluated for the subphthalocyanines having different peripheral substituents. By combining the experimental results with the theoretical calculation, the electric dipole moment and the molecular polarizability in each electronic state have been evaluated. The field-induced change in excitation dynamics of those two compounds have also been discussed, based on the E–PL spectra.

2. Experimental

Fluorosubphthalocyanine and tertiary butyl subphthalocyanine, denoted by F-SubPc and T-SubPc, respectively, having the molecular structures shown in Figure 1, were prepared as described in

* Corresponding authors. Fax: +81 22 795 7720 (H. Kono), +81 22 795 7719 (N. Kobayashi), +81 11 706 9410 (N. Ohta).

E-mail addresses: hirohiko-kono@m.tohoku.ac.jp (H. Kono), nagaok@m.tohoku.ac.jp (N. Kobayashi), nohta@es.hokudai.ac.jp (N. Ohta).

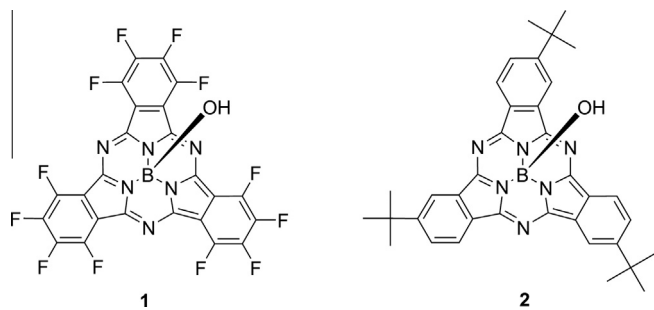


Figure 1. Molecular structures of F-SubPc (1) and T-SubPc (2).

previous studies [26,27]. Poly(methyl methacrylate), denoted as PMMA, (Aldrich, averaged MW = 120000) was purified by precipitation with a mixture of benzene and methanol and by extraction with hot methanol solution. Sample films of F-SubPc and T-SubPc embedded in PMMA were deposited on indium-tin-oxide (ITO)-coated silica substrates by spin coating from toluene solution in which a mixture of SubPc and PMMA with a weight ratio of 1 to 20 was dissolved. The thickness of the sample film, measured with an interferometric microscope (Nano Spec/AFT-010-0180, Nanometric), was typically 0.5 μm . A semitransparent aluminum (Al) film was further deposited on the sample film by vacuum vapor deposition.

Absorption measurements were performed with a Hitachi U-3500 spectrophotometer. E–A and E–PL spectra, that is, plots of the field-induced change in absorption intensity and photoluminescence (PL) intensity, respectively, as a function of wavelength or wavenumber, were obtained at the second harmonic of the modulation frequency (40 Hz) of the applied electric field with the same apparatus as reported in our previous papers [28–30]. Hereafter, applied electric field is denoted by F , and its strength is represented by the *rms* value. In the E–A measurements, a convergent light beam from a Xenon lamp of a Jasco FP-777 spectrofluorometer, i.e., the excitation light dispersed by the monochromator installed in the spectrofluorometer, was collimated and directed through an α -barium borate polarization prism (CASIX, JDSU) and through the sample slide to a photomultiplier. The dc component was collected directly using a computer, and the ac component, synchronized with the modulation frequency of the applied voltage, was recorded by a lock-in amplifier (Stanford Research System, SR830), as described previously [28–30].

E–PL spectra were measured under vacuum conditions at 295 K with a Jasco FP777 spectrofluorometer combined with a lock-in amplifier system. Unpolarized emission was monitored with excitation at wavelengths where the field-induced-change in absorption intensity was negligible. The PL intensity at zero field and its field-induced change are represented by I_F and $\Delta I_F (=I_{F \neq 0} - I_{F=0})$, respectively. The observed change in the total emission intensity in the presence of F is ascribed to the field-induced change in the emission quantum yield.

3. Results and discussion

Figure 2 shows the absorption spectra of F-SubPc and T-SubPc doped in a PMMA film. Strong absorption bands are observed with peaks at 575 and 305 nm in F-SubPc and at 568 and 309 nm in T-SubPc. These two bands correspond to the Q and B (Soret) band of phthalocyanine, respectively [31,32]. The oscillator strength of the Q band, i.e., f_{osc} , was estimated from the absorption spectrum in benzene solution to be 0.50 and 0.43 for F-SubPc and T-SubPc, respectively, based on $f_{osc} = 4.32 \times 10^{-9} n^{-1} \int \epsilon(\nu) d\nu$ [33], where $\epsilon(\nu)$ is the molecular extinction coefficient at wavenumber ν and

n is the refractive index of solvent. E–A spectra of F-SubPc and T-SubPc in PMMA observed with a field strength of 1.0 MV cm^{-1} are shown in Figures 3 and 4, respectively. These E–A spectra were obtained at the magic angle $\chi (=54.7^\circ)$; χ is the angle between the direction of applied electric field and the electric vector of the incident light.

In the presence of F , the shift of the transition energy (ΔE) is related to the difference in dipole moment ($\Delta\mu$) and molecular polarizability ($\Delta\alpha$) between the excited state and the ground state (S_0);

$$\Delta E = -\Delta\mu \cdot F - F \cdot \Delta\alpha \cdot F/2 \quad (1)$$

where $\Delta\mu$ and $\Delta\alpha$ are given by $\mu_e - \mu_g$ and $\alpha_e - \alpha_g$, respectively, with the electric dipole moment and molecular polarizability in S_0 (μ_g, α_g) and in the excited state (μ_e, α_e). When the distribution of absorbers or emitters is isotropic and the molecules are immobilized in the films, the change in absorption intensity or photoluminescence intensity in the presence of F , i.e., $\Delta A(\nu)$ and $\Delta I_{PL}(\nu)$, observed at the second harmonic of the modulation frequency can be expressed as a sum of the zeroth-, first- and second-derivatives of the absorption intensity ($A(\nu)$) and photoluminescence intensity ($I_{PL}(\nu)$) as follows [34–38]:

$$\Delta A(\nu) = (fF)^2 \left[AA(\nu) + B\nu \frac{d}{d\nu} \left\{ \frac{A(\nu)}{\nu} \right\} + C\nu \frac{d^2}{d\nu^2} \left\{ \frac{A(\nu)}{\nu} \right\} \right] \quad (2)$$

$$\Delta I_{PL}(\nu) = (fF)^2 \left[A'I_{PL}(\nu) + B'\nu^3 \frac{d}{d\nu} \left\{ \frac{I_{PL}(\nu)}{\nu^3} \right\} + C'\nu^3 \frac{d^2}{d\nu^2} \left\{ \frac{I_{PL}(\nu)}{\nu^3} \right\} \right] \quad (3)$$

where f is the internal field factor. Coefficients A and A' correspond to the field-induced change in absorption intensity and PL intensity, respectively. Coefficient A depends on the field-induced change in transition dipole moment, and A' comes from the field-induced change in emission quantum yield. Coefficients B and C , as well as B' and C' , correspond to the spectral shift and the spectral broadening of the absorption and emission spectra, respectively, which mainly results from $\Delta\alpha$ and $\Delta\mu$, respectively, between S_0 and excited states. These coefficients with the magic angle of χ are given as follows:

$$B = \Delta\bar{\alpha}/2hc, \quad C = |\Delta\mu|^2/6h^2c^2 \quad (4)$$

where $\Delta\bar{\alpha}$ is the average of the trace of $\Delta\alpha$, h is Planck's constant, and c is velocity of light. If the magnitude of $\Delta\mu$ following the optical absorption is significant, the presence of an electric field will broaden an isolated transition, giving rise to the E–A spectrum, the shape of which is the second derivative of the absorption spectrum. If the magnitude of $\Delta\bar{\alpha}$ is significant, the shape of the E–A spectrum is the first derivative of the absorption spectrum, resulting from the spectral shift upon application of F . The values of $|\Delta\mu|$ ($\equiv \Delta\mu$) and $\Delta\bar{\alpha}$ can be obtained from an analysis of the derivative parts of the E–A spectra.

3.1. Electroabsorption spectra

As shown in Figures 3 and 4, E–A spectra of both F-SubPc and T-SubPc are very similar in shape to the second derivative of the absorption spectra, indicating that the field-induced change in absorption spectrum comes mainly from $\Delta\mu$ following the optical transition to the excited states. Actually, the observed E–A spectra could be simulated by a linear combination of the first and second derivatives of each absorption band, except for the band located at wavenumbers above 34000 cm^{-1} , where a shoulder of the B band is observed. The fact that the zeroth derivative component is negligible indicates that the field-induced change in transition moment is negligible in both compounds. From the first and second

Download English Version:

<https://daneshyari.com/en/article/5380985>

Download Persian Version:

<https://daneshyari.com/article/5380985>

[Daneshyari.com](https://daneshyari.com)