

Electroabsorption spectra of push–pull porphyrins in solution and in solid films

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Dedicated to Professor Shunichi Fukuzumi on the occasion of his retirement

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ABSTRACT: Polarized electroabsorption (E-A) spectra of highly efficient porphyrin sensitizers (YD2 and YD2-oC8) have been measured in benzene solution. Polarized E-A spectra of these push–pull porphyrins embedded in poly(methyl methacrylate) films or sensitized on TiO₂ films are also observed. Based on the analysis of the E-A spectra, the magnitude of the electric dipole moment both in the ground state and in the lowest excited state have been evaluated in solution and in solid films. The electric dipole moment in the excited state of these compounds is very large on TiO₂ films, suggesting the interfacial charge transfer on TiO₂ surface following photoexcitation of porphyrin dyes. The electric dipole moment in the excited state evaluated from the E-A spectra is very different from the one evaluated from the electrophotoluminescence spectra on TiO₂, suggesting that the strong local field of TiO₂ films is applied to the fluorescing dyes attached to TiO₂ films.

KEYWORDS: Stark shift, electric dipole moment, dye-sensitized solar cell, push–pull porphyrins.

INTRODUCTION

Electric dipole moment, whose value reflects the molecular structure as well as electronic structure in each electronic state, is important not only as the fundamental physical parameter of molecules and molecular aggregates but also as the parameter which decides material functions such as nonlinear optical property or Kerr effect [1, 2]. In optoelectronic devices such as solar cell, charge separated character, that is, the magnitude of the electric dipole moment following photoexcitation is important because the primary process of dye-sensitized solar cell (DSSC) following photoirradiation is charge separation

in dye molecules. This kind information can be obtained from the measurements of electroabsorption spectra and electrophotoluminescence spectra [3–6], where plots of the field-induced change in absorption intensity and photoluminescence intensity are shown, respectively, as a function of wavelength or wavenumber. The effects of local electric fields on the optical properties, which may play an important role on DSSC [7–9], can be also obtained from the measurements of electroabsorption and electrophotoluminescence spectra. Hereafter, electroabsorption and electrophotoluminescence spectra are abbreviated to be E-A and E-PL spectra, respectively.

Porphyrins have a significant potential as sensitizers for highly efficient DSSC, owing to their photostability and high light-harvesting capabilities [10, 11]. In our previous paper [12], electric field effects on photoluminescence spectra, *i.e.* E-PL spectra, were reported for push–pull porphyrins YD2 and YD2-oC8, which give highly

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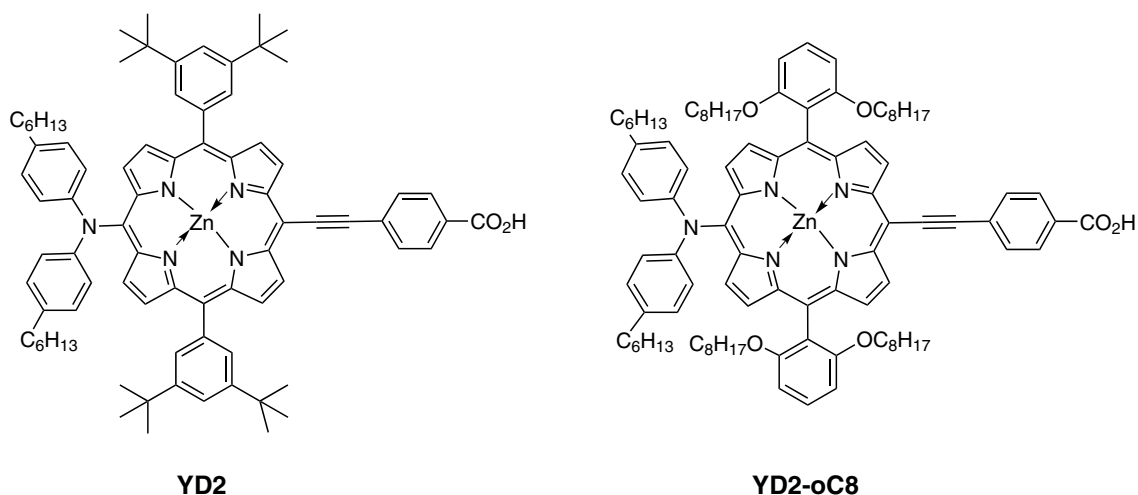


Fig. 1. Molecular structure of YD2 and YD2-oC8

efficient photon energy conversion [13]. The molecular structures of these compounds are shown in Fig. 1. The dye-sensitized solar cell made of YD2-oC8 in a cobalt electrolyte attained efficiency more than 12% of power conversion [14]. Fluorescence of YD2 and YD2-oC8 is quenched in poly(methyl methacrylate) (PMMA) films by application of electric field, suggesting that the relaxation from the fluorescent state to a nonfluorescent charge-separated state is accelerated by electric field. The field-induced quenching becomes extremely large, when sensitized dyes are attached to TiO₂ films. Then, it was suggested that the electric field-induced quenching of fluorescence, which probably results from the field-induced charge separation to the nonfluorescent state, is related to the efficiency of the photon energy conversion in solar cells. It was also shown that the magnitude of the change in electric dipole moment following the fluorescence emission, which was evaluated from the E-PL spectra, is much larger in dyes attached to TiO₂ than that in dyes embedded in a PMMA film, suggesting that the charge-separated character of porphyrins is much larger on TiO₂ films than that in PMMA films. This observation further implies that the interfacial charge transfer occurs from the dyes to the TiO₂ surface as a result of the strong coupling between dyes and TiO₂ film.

The difference in electric dipole moment between the excited state and the ground state evaluated from the E-PL spectra was reported [12]. Hereafter, electric dipole moment and its change following optical transition are denoted by μ and $\Delta\mu$, respectively. E-PL spectra give the value of $\Delta\mu$ ($=|\Delta\mu|$) between the fluorescent relaxed state and the ground state, while E-A spectra give the $\Delta\mu$ value between the ground state and the photoexcited Franck-Condon state. Therefore, it seems to be very important to know whether the value of $\Delta\mu$ evaluated from the E-PL spectra is different from the one evaluated from the E-A spectra. If the exact value of μ ($=|\mu|$) can be obtained in each electronic state, further, a comparison among

different dyes can be made concerning the relation between the electric dipole moment and the solar energy conversion efficiency.

In the presence of electric fields, molecular reorientation occurs along the applied electric field, depending on the magnitude of μ of molecules. Then, the μ value both in the ground state and in the excited state can be obtained from the polarized E-A spectra in solution [15, 16]. In the present study, polarized E-A spectra of YD2 and YD2-oC8 have been measured in benzene solution. By evaluating the change in intensity of the E-A spectra resulting from the field-induced reorientation, the value of μ in the ground state of each molecule has been determined. The magnitude of $\Delta\mu$ following excitation into the lowest excited state of these compounds embedded in PMMA film or attached on TiO₂ films has been also evaluated, based on the measurements of the E-A spectra. By combining both results in solution and in solid films, the magnitudes of μ both in the ground state, *i.e.* μ_g , and in the lowest excited state, *i.e.* μ_e , have been evaluated. These magnitudes of μ of different porphyrin dyes obtained in PMMA and on TiO₂ films have been compared with each other to examine the role of the TiO₂ surface which plays in DSSC. The results of the E-A spectra are also compared with the ones obtained from the E-PL spectra reported in our previous paper [12].

THEORETICAL BACKGROUND

Energy levels and transition dipole moments of a molecule are influenced by an electric field. In the presence of an applied electric field (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.

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

As a result, optical spectra show a shift or/and a broadening upon the application of F . By assuming an isotropic distribution of the molecules in the absence of F , the intensity of the E-A spectrum at wavenumber $\bar{\nu}$, *i.e.* $\Delta A(\bar{\nu})$ can be expressed as the sum of the zeroth, first and second derivatives of the absorption spectrum as follows [23]:

$$\Delta A(\bar{\nu}) = (fF)^2 \left[A_\chi A(\bar{\nu}) + B_\chi \bar{\nu} \frac{d}{d\bar{\nu}} \left\{ \frac{A(\bar{\nu})}{\bar{\nu}} \right\} + C_\chi \bar{\nu} \frac{d^2}{d\bar{\nu}^2} \left\{ \frac{A(\bar{\nu})}{\bar{\nu}} \right\} \right] \quad (2)$$

where A_χ , B_χ and C_χ are coefficients. Note that χ represents the angle between the field direction and the polarization direction of the excitation light. If the field-induced change in transition moment is negligible, each coefficient can be expressed as follows [17]:

$$A_\chi = \frac{(3 \cos^2 \chi - 1)}{30k^2 T^2} \left[\mu_g^2 (3 \cos^2 \zeta - 1) + 3kT(\alpha_m - \bar{\alpha}) \right] \quad (3)$$

$$B_\chi = \frac{\Delta \bar{\alpha}}{2hc} + \frac{\mu_g \Delta \mu \cos \gamma}{3hckT} + \frac{(3 \cos^2 \chi - 1)}{15hc} \left\{ \frac{\mu_g \Delta \mu (3 \cos \zeta \cos \eta - \cos \gamma)}{kT} + \frac{3(\Delta \alpha_m - \Delta \bar{\alpha})}{2} \right\} \quad (4)$$

$$C_\chi = |\Delta \mu|^2 \left\{ \frac{5 + (3 \cos^2 \chi - 1)(3 \cos^2 \eta - 1)}{30h^2 c^2} \right\} \quad (5)$$

where c is the velocity of light, k is Boltzmann's constant, h is Planck's constant, T is temperature, μ_g and $\Delta \mu$ are the magnitudes of the ground state dipole moment and the change in electric dipole moment following photoexcitation, respectively. α_m is the polarizability in the ground state with respect to the direction of the transition dipole moment. $\bar{\alpha}$ represents the average of the trace of the polarizability tensor. ζ is the angle between μ and the transition dipole moment (d). γ is the angle between μ_g and $\Delta \mu$. η is the angle between $\Delta \mu$ and d . Then, the derivative components of the E-A spectra observed with $\chi = 54.7^\circ$ can be written as follows:

$$A_{54.7} = 0 \quad (6)$$

$$B_{54.7} = \frac{\Delta \bar{\alpha}}{2hc} + \frac{\mu \Delta \mu \cos \gamma}{3hckT} \quad (7)$$

$$C_{54.7} = \frac{|\Delta \mu|^2}{6h^2 c^2} \quad (8)$$

A comparison between Equations 3 and 6 shows that the magnitude of μ_g can be evaluated from the difference between the E-A spectra obtained with $\chi = 90^\circ$ and 54.7° . It is also noted that the temperature dependent term can be neglected even in the presence of F , if the molecules

are fixed. In the above discussion, the transition moment is assumed to be independent of the applied electric field. If the transition dipole moment itself is affected by F , the transition moment in the presence of F , d^F , can be written as:

$$d^F = d + X \cdot F + F \cdot Y \cdot F \quad (9)$$

where d is the transition dipole moment vector in the absence of F , and X and Y are the transition moment polarizability and hyperpolarizability tensors, respectively. In randomly distributed system, the coefficients of the zeroth and first derivative components of the E-A spectra observed with a magic angle of χ which results from X and Y can be given using the tensor components of X and Y as follows [18]:

$$A_{54.7} = \frac{1}{3|d|^2} \sum_{i,j} X_{ij}^2 + \frac{2}{3|d|^2} \sum_{i,j} d_i Y_{ij}^2 \quad (10)$$

$$B_{54.7} = \sum_{i,j} d_i X_{ij} \Delta \mu_j$$

The subscripts i and j refer to components of the vectors or tensors. Thus, the coefficient A_χ is not zero even with the magic angle of χ , if the transition moment is affected by F .

RESULTS AND DISCUSSION

E-A spectra of YD2 and YD2-oC8 in benzene solution observed for the Q-bands are shown in Fig. 2, together with the absorption spectrum. The E-A spectra were obtained with $\chi = 90^\circ$ and 54.7° (magic angle). As shown later, E-A spectra in solid films are independent of the angle of χ . In contrast with the E-A spectra in solid films, E-A spectra in solution observed with $\chi = 90^\circ$ and 54.7° are different from each other, which is attributed to the field-induced reorientation of the molecules in solution. As shown in Fig. 2, the difference in intensity of the E-A spectra is attributed to the band located in the longer wavelength region, which is called as Q1-band, and the difference in the next lowest band located in the wavelength region shorter than the Q1-band, which is called as Q2-band, is very small. Then, it is assumed that the difference is observed only for the Q1-band, and that this difference corresponds to the A_χ term of Equation 3. By assuming that the anisotropy of the polarizability is negligible, *i.e.* $\alpha_m = \bar{\alpha}$ and that the difference of the E-A spectra observed with $\chi = 90^\circ$ and 54.7° corresponds to the first term of Equation 3, the magnitude of μ_g of YD2 and YD2-oC8 is determined to be 2.9 and 5.1 D, respectively. Here, it is assumed that both the direction of the electric dipole moment in the ground state and the direction of the transition moment of the Q1-band are along the direction of the push-pull substituents, *i.e.* $\zeta = 0$. The negligible difference of the E-A intensity with different angles of χ for the Q2-band may indicate that the angle of ζ is close to the magic angle. The E-A

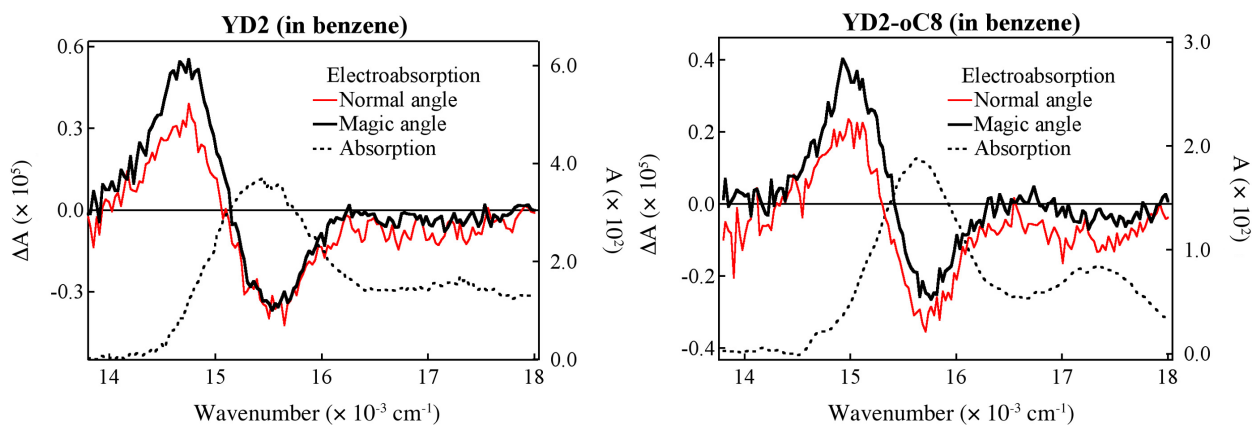


Fig. 2. Electroabsorption spectra of YD2 (left) and YD2-oC8 (right) in benzene solution observed for the Q-band region with $\chi = 90^\circ$ and 54.7° . The applied field strength was $0.16 \text{ MV}\cdot\text{cm}^{-1}$ in both cases

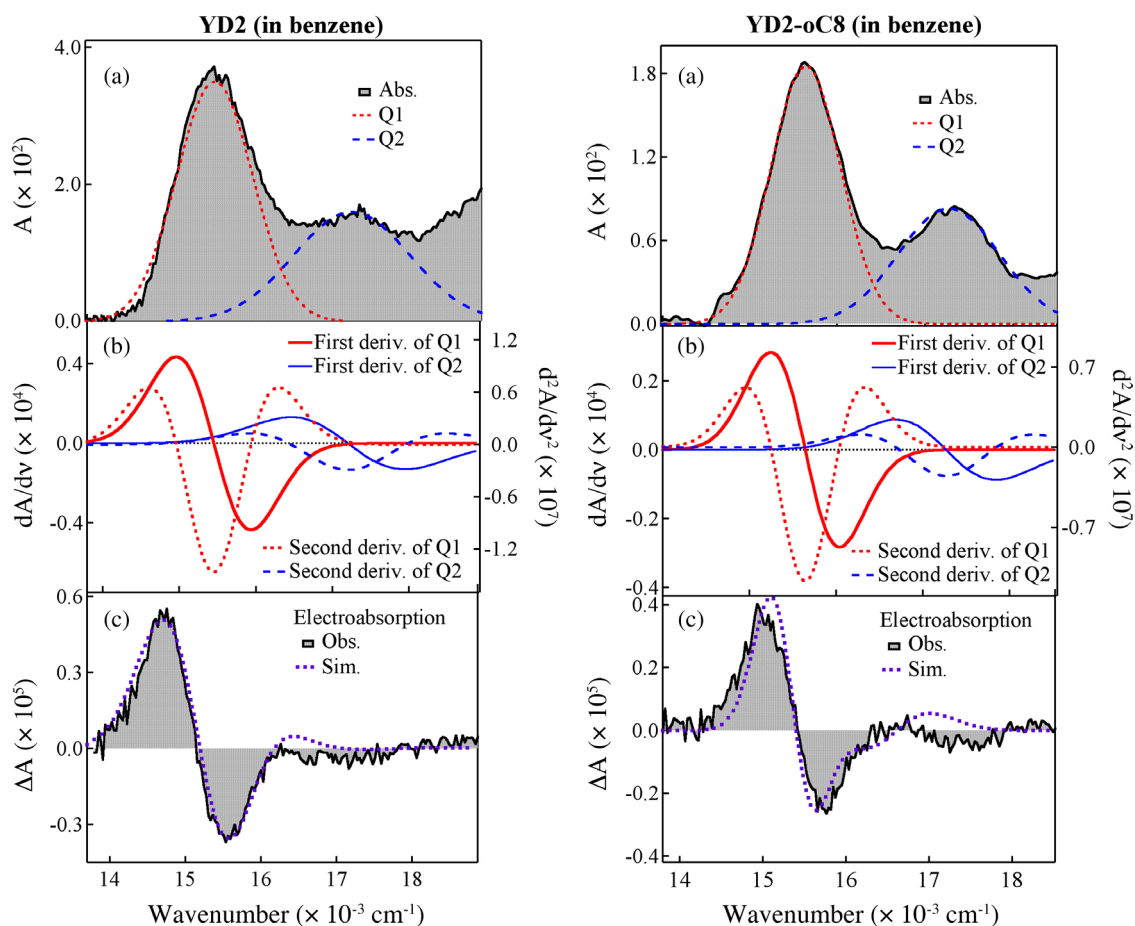


Fig. 3. The analysis of the E-A spectra of YD2 (left) and YD2-oC8 (right) observed with a magic angle of χ in solution with a field strength of $0.16 \text{ MV}\cdot\text{cm}^{-1}$. Absorption spectra (top), its first and second derivative spectra (middle) and E-A and simulated spectra (bottom)

spectra observed in solution with $\chi = 54.7^\circ$ are simulated by a linear combination of the zeroth, first and second derivative spectra, as shown in Fig. 3. From the second derivative component in the E-A spectra observed with the magic angle of χ , the magnitude of $\Delta\mu$ was evaluated to be 5.6 and 4.5 D, respectively, for the Q1-band of YD

2 and YD2-oC8. By combining μ_g and $\Delta\mu$ thus obtained, the magnitudes not only of μ_g but also of μ_e in the excited state reached by the Q1-band excitation are determined by assuming that the electric dipole moment in the excited state is larger than that in the ground state. The results are shown in Table 1.

Table 1. Magnitudes of $\Delta\mu$ following absorption to the Q1-band, μ_g and μ_e of YD2 and YD2-oC8 in benzene, in PMMA film and on TiO₂ film evaluated from the E-A spectra^a

	YD2	YD2-oC8
$\Delta\mu$ (D)		
in benzene	5.6	4.5
in PMMA	3.2 (8.6) ^b	4.0 (7.0) ^b
on TiO ₂	8.3 (41.3) ^b	12.5 (77.3) ^b
μ_g (D)		
in benzene	2.9	5.1
μ_e (D)		
in benzene	8.5	9.6
in PMMA	6.1	9.1
on TiO ₂	11.2	17.6

^aInternal field factor (f) is assumed to be unity, and errors are regarded as $\pm 15\%$ in all values. ^bThe magnitude of $\Delta\mu$ estimated from the E-PL spectra [10].

Polarized E-A spectra of YD2 and YD2-oC8 embedded in a PMMA film or attached on TiO₂ films were obtained both with $\chi = 90^\circ$ and 54.7° . The results of YD2-oC8 are shown in Fig. 4. Both spectra are essentially the same, indicating that the consideration on the field-induced orientation is not necessary in solid films. Then, the temperature dependent term in Equations 3, 4 and 7 can be neglected in solid films. As shown in Fig. 4, however, the integration of the E-A spectra along the wavenumber from 14000 cm⁻¹ to 18000 cm⁻¹, that is, along the Q1 and G2-bands, gives nonzero value, *i.e.* positive value, indicating that the absorption intensity of the Q1-band increases in the presence of F . As mentioned above, this value does not come from the field-induced reorientation. Then, the field-induced increase of the absorption intensity is attributed to the change in transition moment,

that is, the transition moment polarizability, *i.e.* $A_{54.7}$ given in Equation 10, is not negligible. It is noted that the integrated intensity relative to the absorption intensity is ~ 0.00015 with a field strength of 0.1 MV.cm⁻¹. This value is proportional to the square of the applied electric field, and the field-induced increase in absorption intensity with a field strength of 1.0 MV.cm⁻¹ is expected to be about 1.5%. As in the case of E-A spectra in solution, the E-A spectra of porphyrin dyes in solid film obtained with $\chi = 54.7^\circ$ are analyzed by a linear combination of the zeroth, first and second derivatives of the absorption spectra, by assuming that absorption spectra are composed by the Q1 and Q2-bands. The results are shown in Figs 5 and 6, respectively, for YD2 and YD2-oC8. In the present study, the attention is paid only to the Q1-band, and the magnitude of $\Delta\mu$ following excitation into the Q1-band was obtained, based on the second derivative component of absorption spectra in the E-A spectra. The results are shown in Table 1.

The $\Delta\mu$ values in PMMA are roughly the same as the ones obtained in solution. On the other hand, the $\Delta\mu$ values on TiO₂ are much larger than the ones in PMMA or in solution. E-PL spectra also show that the magnitudes of $\Delta\mu$ of both YD2 and YD2-oC8 attached on TiO₂ films are much larger than that obtained in PMMA films (see Table 1). These results imply that the charge separated state of YD2 and YD2-oC8 is extended over TiO₂ surface, as we have already suggested in our previous paper [12]. Also the value of $\Delta\mu$ both of YD2 and of YD2-oC8 on TiO₂ obtained from the E-PL spectra are much larger than that obtained from the E-A spectra on TiO₂. This result may suggest that the local field produced by the TiO₂ surface on which excited molecules of porphyrins are attached is much larger than the field produced by the TiO₂ surface to which the ground state molecules of porphyrins are simply attached. It is noted that the internal field factor was assumed to be unity in the results shown in Table 1.

The magnitude of μ of YD2-oC8 is larger than that of YD2 both in the ground state and in the excited state, as shown in Table 1. The long alkoxy chains attached at

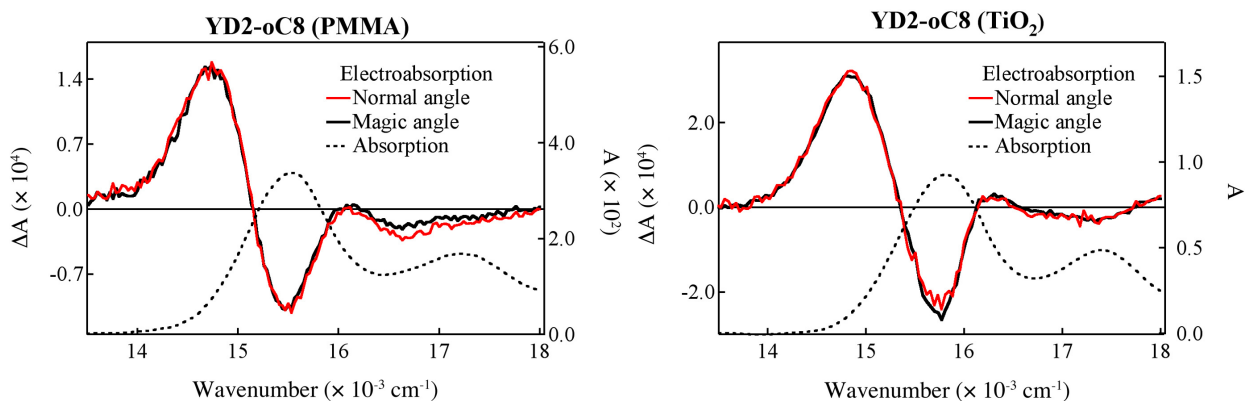


Fig. 4. E-A spectra in the Q-band region of YD2-oC8 embedded in a PMMA film (left) and attached on TiO₂ films (right) with $\chi = 90^\circ$ and 54.7° . The field strength was 1.0 and 0.1 MV.cm⁻¹, respectively

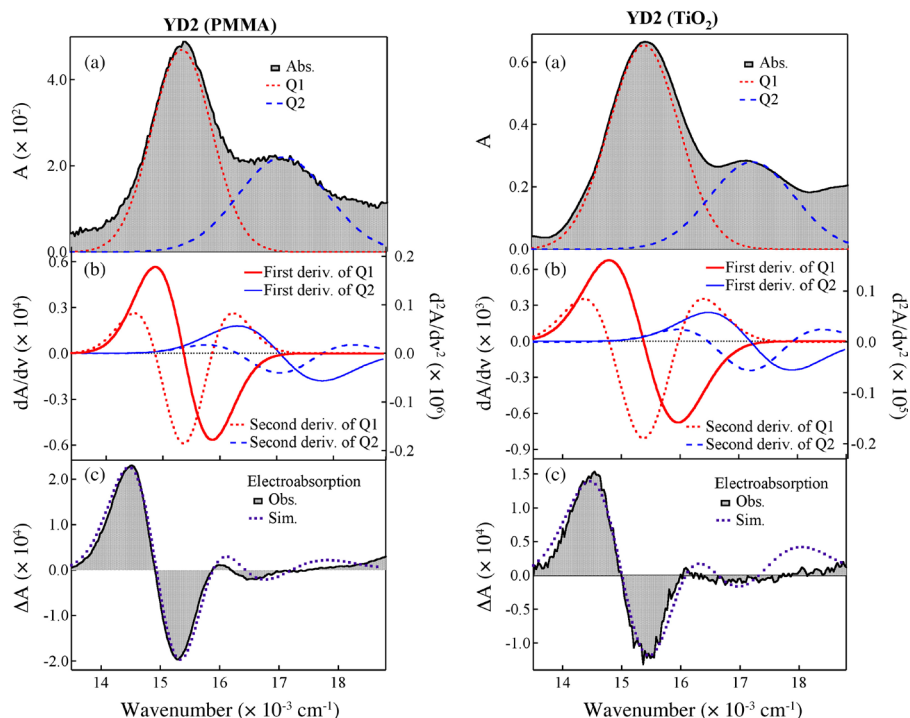


Fig. 5. The analysis of the E-A spectra of YD2 embedded in a PMMA film (left) and attached to TiO_2 films (right) observed with a magic angle of χ with a field strength of 1.0 and 0.1 $\text{MV}\cdot\text{cm}^{-1}$, respectively. Absorption spectra (top), its first and second derivative spectra (middle) and E-A and simulated spectra (bottom)

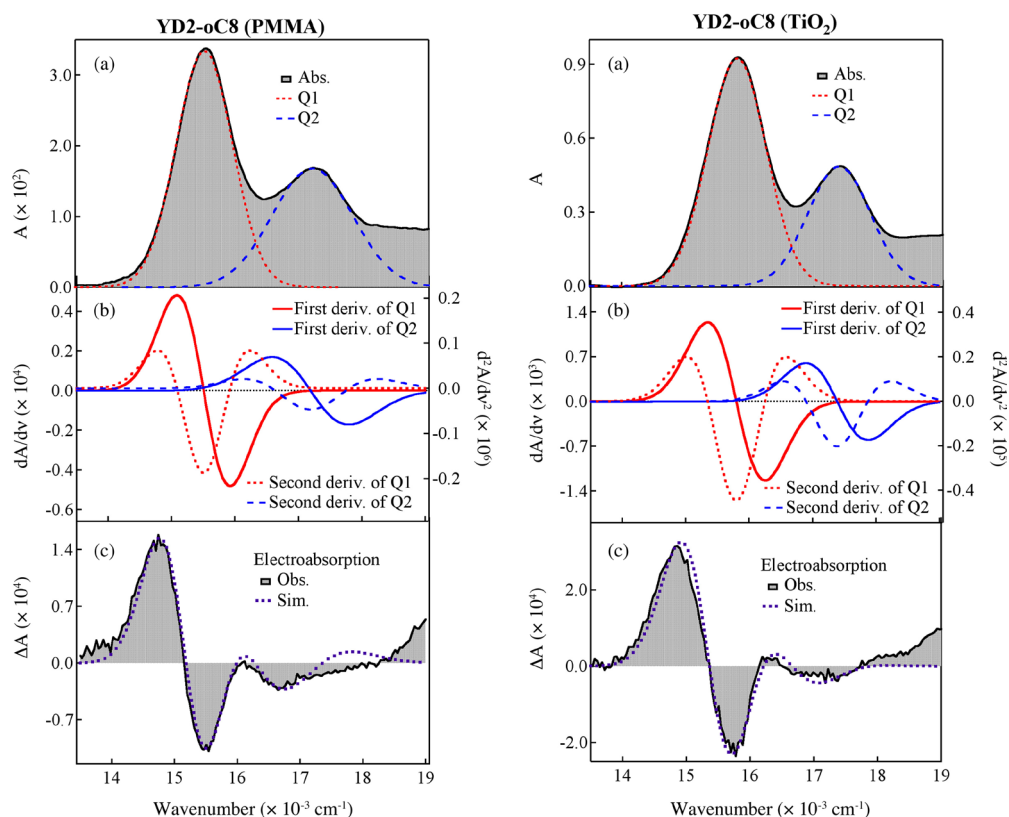


Fig. 6. The analysis of the E-A spectra of YD2-oC8 embedded in a PMMA film (left) and attached to TiO_2 films (right) observed with a magic angle of χ with a field strength of 1.0 and 0.1 $\text{MV}\cdot\text{cm}^{-1}$, respectively. Absorption spectra (top), its first and second derivative spectra (middle) and E-A and simulated spectra (bottom)

the *ortho*-positions of the *meso*-phenyls of the porphyrin seems to reduce the planarity between porphyrin and phenyls, which may play a role to increase the polar character of YD2-oC8 both in the ground state and in the excited state, in comparison with YD2. The substitution of the long alkoxy chains at the *ortho*-position may also protect the dye aggregation of the porphyrin cores. Then, the high performance of DSSC with YD2-oC8 may result from the large value of μ in the excited state and also from the protection of the porphyrin cores from the dye aggregation.

EXPERIMENTAL

Solution sample of YD2 or YD2-oC8 was prepared with benzene as a solvent. Anhydrous benzene (Wako Chem.) was used without further purification. The sample was circulated through sandwich-type cell by using a peristaltic pump with a constant low flow rate. The liquid cell consisted of two ITO-coated quartz windows and a polymer spacer (6 μm). The schematic illustration of the solution cell is shown in Fig. 7. ITO layers were used as the semitransparent electrodes. A silicon-dioxide film was coated on the ITO layer as an insulator film with a thickness of 0.58 μm . AC voltage (4 kHz) was applied to the liquid cell. The strength of the applied electric field was evaluated from the applied voltage divided by the gap between two electrodes of the cell, which was evaluated from interferogram. Hereafter, applied electric field is represented as F . The sample solution was used at ambient pressure at room temperature.

The synthetic details of YD2 and YD2-oC8 are reported elsewhere [19–21]. For the YD2: PMMA or YD2-oC8: PMMA thin films, the porphyrin embedded in PMMA was deposited on an ITO-coated quartz substrate with a spin-coating technique from toluene solution in which a mixture of porphyrin and PMMA (weight ratio = 1:40) was dissolved. The thickness of the sample was $\sim 0.5 \mu\text{m}$ measured with an interferometric microscope (Nano Spec/AFT-010-0180, Nanometric). A semitransparent Al film was further deposited on the sample film with vacuum vapor deposition. The scheme of the solid sample of porphyrins embedded in PMMA is shown in Fig. 8.

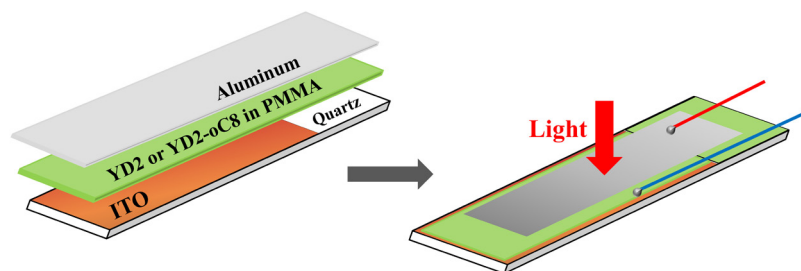


Fig. 8. Schematic illustration of the solid sample of YD2 or YD2-oC8 embedded in PMMA film. ITO and Al films were used as the electrodes

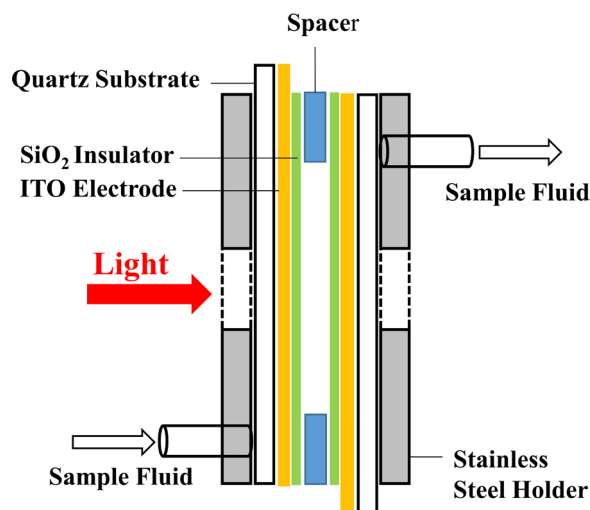


Fig. 7. Design of the solution cell used in the present study for the E-A measurements

TiO₂ nanoparticles (NP) were prepared according to the conventional synthetic procedure reported by Grätzel and co-workers [22, 23], and then prepared as a paste for screen printing according to the procedure reported elsewhere [24]. The TiO₂ NP was coated on a TiCl₄ treated FTO glass substrate (TEC 7, Hartford) to obtain a film with the thickness $\sim 15 \mu\text{m}$. For the porphyrin/TiO₂ thin films, the porphyrin adsorbed on transparent TiO₂ layer on FTO glass substrate with thickness $\sim 3 \mu\text{m}$ and then a PMMA thin film $\sim 0.5 \mu\text{m}$ was deposited on the TiO₂ film as an insulator. Furthermore, there was an Al film deposited on the PMMA thin film. ITO/FTO and Al films were served as electrodes in solid samples.

E-A spectra were obtained using electric field modulation spectroscopy. Both home-made E-A spectrometer and the commercially available E-A spectrometer (JASCO EMV-200) were used. Details of these apparatus are described elsewhere [5, 6, 15, 16]. Briefly, the modulated transmitted light intensity from the sample detected by the photomultiplier was sent to an amplifier, and then ac and dc signals were separated. The dc signal (I), which corresponds to the total intensity of the transmitted light, was recorded by an analog-to-digital converter. The ac signal (ΔI) was detected by a lock-in

amplifier at the second harmonic of the modulation frequency of the applied voltage. Then, the field-induced change in absorbance, ΔA , was obtained by the following equation: $\Delta A = -(2\sqrt{2}/\ln 10)\Delta I/I$. The electric field was determined in every case, as the ratio of applied voltage divided by the distance between two electrodes, *i.e.* between ITO and ITO films in solution and between ITO/FTO and Al films in solid films.

CONCLUSION

Electroabsorption (E-A) spectra of push–full porphyrins, YD2 and YD2-oC8, have been measured in solution. Based on the polarization dependence of the E-A spectra, which results from the field-induced reorientation of dye molecules, electric dipole moment in the ground state and the magnitude of the change in electric dipole moment following excitation into the Q1-band of these compounds have been obtained. E-A spectra of these compounds embedded in PMMA films or attached on TiO₂ films are also observed, and the corresponding magnitudes of the change in electric dipole moment following excitation into the Q1-band were also obtained in solid films. The large electric dipole moment in the excited state of the porphyrins on TiO₂ probably correspond to the high energy conversion of the DSSC constructed using these porphyrin sensitizers. The electric dipole moment in the excited state of the dyes on TiO₂ evaluated from the E-A spectra are very different from those evaluated from the E-PL spectra, suggesting that the strong local field of TiO₂ films is applied to the fluorescing dyes attached to TiO₂ films.

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