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Electroabsorption spectra of a complex formed between tetraphenyl-porphyrin and fullerene in a polymer film☆

Md. Wahadoszamen [a], Takakazu Nakabayashi [a,b], Nobuhiro Ohta [a,b,*]

[a] *Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*
[b] *Research Institute for Electronic Science (RIES), Hokkaido University, Sapporo 060-0812, Japan*

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Dedicated to Professor Iwao Yamazaki.

Abstract

Electroabsorption spectra of a mixture of tetraphenylporphyrin (TPP) and fullerene (C_{60}) doped in a polymer film have been measured for both free-base porphyrin and its zinc analog with different concentrations of C_{60}. The absorption band whose peak is located in a wavelength region longer than the peak of the Soret band of TPP appears, as the concentration of C_{60} increases. This band is attributed to the absorption of a complex composed of TPP and C_{60}. Electroabsorption spectra show that a charge separation occurs upon photoexcitation to the absorption band of the complex located near the Soret band of TPP.

Keywords: Electroabsorption spectrum; Porphyrin; C_{60}; Charge-transfer complex

1. Introduction

The study of non-covalent supramolecular aggregates has exposed a promising area of investigation in the interdisciplinary research. The salient feature of such structures is their ability to offer a suitable environment for the electron- and energy-transfer processes that allow the conversion of solar energy to electrical or chemical energy [1,2]. Such aggregation phenomena together with their concomitant energy- and electron-transfer processes have attracted immense attention not only because of their pivotal role in some biological systems, such as natural photosynthesis, but also their outstanding contribution in material science [3–7].

Large π surfaces of both porphyrins (flat) and fullerenes (curved) coupled with their spectroscopic and electrochemical features, such as strong ground-state absorption throughout UV–vis spectral region, characteristic luminescence patterns and complementary electron donor–acceptor properties make them the excellent candidates for the construction of multi-component supramolecular systems displaying photoinduced electron transfer and/or energy transfer [8–14]. One of the most conspicuous features in the chemistry of fullerene is its small reorganization energy, especially towards electron-transfer reaction, which has expedited much the initial attempt of mimicking the reaction in photosynthetic reaction center by preparing a number of porphyrin-fullerene linked dyads and triads [15–20]. On the other hand, a number of observations based on the complex formation and cocrystalization between porphyrins and fullerenes and their derivatives have been reported recently [21–31]. Boyed et al. have concluded that the van der Waals attraction (dispersion forces) between a curved π surface of fullerene and a planer π surface of porphyrin is very favorable for a supramolecular recognition, in contrast to the traditional prerequisite of matching a concave host with a complementary convex guest [22]. Besides theses, cyclic dimers of free-base porphyrin and metalloporphyrin are found to form inclusion complexes with fullerene where the charge-transfer interaction plays a partial

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[*] Corresponding author.
E-mail address: nohta@es.hokudai.ac.jp (N. Ohta).

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role together with the van der Waals interaction [32,33]. In most of these observations, a complex formation between porphyrin and fullerene is characterized by the gradual shift of the Soret absorption band in the longer wavelength region.

In the present study, we have observed the gradual shift and broadening of the Soret absorption band of tetraphenyporphyrin, TPP, (both free and metal base) when the concentration of fullerene (C_{60}) mixed with a constant concentration of porphyrin (0.5 mol%) is increased from 0.5 to 2 mol% in a poly(methyl methacrylate) (PMMA) film. We have attributed this consequence to a complex formation between TPP and C_{60}. In order to investigate the electronic properties of this complex, the effect of external electric fields on the absorption of the complex has been examined in a PMMA film, based on the measurements of the electroabsorption spectra (plots of the field-induced change in absorption intensity as a function of wavelength/wavenumber).

2. Experimental

Commercially available free-base tetraphenylporphyrin (Wako Junyaku), zinc-tetraphenylporphyrin (Kanto Kagaku) and fullerene (Tokyo Kasei), detonated by H_2TPP, ZnTPP and C_{60}, respectively, were used without further purification. Commercially available PMMA (Aldrich) was purified by precipitation with a mixture of methanol and benzene and by extraction with hot methanol. The concentration of ZnTPP or H_2TPP doped in a PMMA film was fixed to be 0.5 mol% in the ratio to the monomer unit of PMMA, while the concentration of C_{60} was 0, 0.5, 1.0 or 2.0 mol% in a monomer unit of PMMA. Hereafter, the sample of a mixture of C_{60} having a concentration of X (=0, 0.5, 1.0 or 2.0 mol%) and porphyrin (0.5 mol%) is denoted by $ZnC_{60}(X)$ or $H_2C_{60}(X)$ for ZnTPP and H_2TPP, respectively. Hereafter, the monomer of free-base teraphenylporphyrin and its zinc compound is designated as H_2M and ZnM, respectively. Note that H_2M and ZnM correspond to H_2C_{60} (0) and ZnC_{60} (0), respectively.

A certain amount of toluene solution of PMMA containing each mixture was poured onto an ITO-coated substrate by a spin-coating technique. Then, the polymer film was dried in vacuo to eliminate toluene completely, and a semitransparent aluminium (Al) film was deposited on the dried polymer film by a vacuum vapor deposition technique. Al and ITO films were used as electrodes. The thickness of the polymer films was determined by using a thickness measurement system (Nanometrics, M3000).

All the optical spectra were measured at room temperature and under the vacuum condition. Steady-state absorption spectra were measured using spectrophotometer (U-3500, Hitachi). Electroabsorption (E–A) spectra were measured using electric-field modulation spectroscopy with the same apparatus as mentioned elsewhere [34,35]. Briefly, the converging light beam from JASCO FP 777 spectrofluorometer was collimated with a pinhole having a diameter of 1.4 mm and with a lens having a focal length of 20 cm, and then directed through a 10 mm aperture α-BBO prism (JDSU CASIX). The resulting polarized light was passed through the sample, which is placed in front of the photomultiplier and on the rotary stage which can provide different angles between the polarization direction of the incident beam and the direction of the electric field applied to the sample.

The dc component of the transmitted light intensity (I) was recorded by the personal computer following the analog-to-digital conversion. The ac component synchronized with the sinusoidal ac voltage applied to the sample (ΔI) was detected at the second harmonic of the modulation frequency of 40 Hz by using a lock-in amplifier (SR 830, SRS). A function generator (SG-4311, Iwatsu) combined with an amplifier was used to obtain the applied ac voltage. The field-induced change in absorption intensity (ΔA) as a function of wavelength was obtained with I and ΔI; $\Delta A = \Delta I/\ln 10\, I$. The field-induced change was multiplied by $2\sqrt{2}$ to convert it to an equivalent dc voltage. The applied field strength hereafter is denoted by $\boldsymbol{F}$, which was determined as the applied voltage divided by the sample thickness.

3. Theoretical background

Stark spectroscopy monitors spectral changes induced by an electric field in optical absorption and emission spectra of a molecule. When an external electric field is applied to a molecular system or molecular ensemble, the energy level of each molecule may be shifted, giving rise the spectral shift and/or broadening whose magnitudes depend respectively on the change in molecular polarizability ($\Delta\boldsymbol{\alpha}$) and the change in dipole moment ($\Delta\boldsymbol{\mu}$) between the ground state and the excited state. The theory of electric-field effects on molecular spectra in condensed phase has been developed in detail by Liptay and co-workers [36,37]. According to the theory, the field-induced change in absorption intensity (ΔA) of randomly oriented and spatially fixed molecules in rigid matrices, such as a PMMA polymer film, is given by [36,38]:

$$\Delta A(\nu) = (f\boldsymbol{F})^2 \left\{ \mathrm{A}A(\nu) + \mathrm{B}\nu \frac{\mathrm{d}[A(\nu)/\nu]}{\mathrm{d}\nu} + \mathrm{C}\nu \frac{\mathrm{d}^2[A(\nu)/\nu]}{\mathrm{d}\nu^2} \right\} \tag{1}$$

where $\boldsymbol{F}$ is the externally applied electric field, ν is the energy in wavenumber, and f is the internal field factor. The coefficients A, B and C depend on the molecular parameters, such as the transition polarizability and hyperpolarizability, and the difference in polarizability and in permanent electric dipole moment between the ground and excited electronic states for a particular electronic transition concerned. B and C are given by the following equations:

$$\mathrm{B} = \frac{\Delta\bar{\alpha}/2 + (\Delta\alpha_m - \Delta\bar{\alpha})(3\cos^2\chi - 1)/10}{hc} \tag{2}$$

$$\mathrm{C} = (\Delta\mu)^2 \frac{\left\{5 + (3\cos^2\xi - 1)(3\cos^2\chi - 1)\right\}}{30h^2c^2} \qquad (3)$$

where h represents Planck's constant and c represents the speed of light. Here, $\Delta\boldsymbol{\mu}$ and $\Delta\bar{\alpha}$ are the differences in electric dipole moment and molecular polarizability tensor, respectively, between the ground and excited states, which are given by:

$$\Delta\mu = |\Delta\boldsymbol{\mu}|, \quad \Delta\bar{\alpha} = \tfrac{1}{3}\mathrm{Tr}(\Delta\boldsymbol{\alpha}) \qquad (4)$$

$\Delta\alpha_\mathrm{m}$ denotes the diagonal components of $\Delta\boldsymbol{\alpha}$ with respect to the direction of the transition moment, χ is the angle between the direction of $\boldsymbol{F}$ and the electric vector of excitation light, and ξ is the angle between the direction of $\Delta\boldsymbol{\mu}$ and the transition dipole moment. Setting χ to magic angle ($\chi = 54.7°$) vanishes the angle dependence in the expression of B and C, allowing to obtain $\Delta\boldsymbol{\alpha}$ and $\Delta\boldsymbol{\mu}$ in a direct way. At the magic angle of $\chi = 54.7°$, B and C terms are reduced as:

$$\mathrm{B} = \frac{\Delta\bar{\alpha}/2}{hc} \qquad (5)$$

$$\mathrm{C} = (\Delta\mu)^2 \frac{5}{30h^2c^2} \qquad (6)$$

Thus, the second derivative contribution to the Stark effect yields information about the change in dipole moment between the ground state and photoexcited state of the molecule. It is worth mentioning that from the angle dependence of the second derivative contribution (in Eq. (3)), the angle ξ between $\Delta\boldsymbol{\mu}$ and the transition moment can be determined. On the other hand, if the change in molecular polarizability is significant upon photoexcitation, the first derivative contribution, i.e., the term B is dominant in the Stark shift line shape. Further, the zeroth derivative contribution must be considered as the Stark effect for the optical transition, if the transition moment of the molecule is perturbed by the external electric field.

4. Results and discussion

Absorption spectra of mixtures of H_2TPP and C_{60}, i.e, $H_2C_{60}(0.5)$, $H_2C_{60}(1.0)$ and $H_2C_{60}(2.0)$, are shown in Fig. 1a, together with the absorption spectra of H_2TPP and C_{60} doped in a PMMA film. The thicknesses of the prepared samples were not the same, and the absorption spectra in Fig. 1 are obtained by normalizing the thicknes to be 0.25 μm. As mentioned below, the absorption spectra of $H_2C_{60}(X)$ or $ZnC_{60}(X)$ are considered to be a superposition of the spectra of TPP, C_{60} and complex formed between TPP and C_{60}. As the concentration of C_{60} increases, the intensity of the absorption band at 331 nm increases (see Fig. 1), but its peak position is independent of the C_{60} concentration, indicating that the band with a peak at 331 nm is assigned to C_{60} [39,40]. Since the absorption intensity of H_2TPP is very small at 331 nm, the absorption spectrum of C_{60} was subtracted from the observed absorption spectra by assuming that the intensity at 331 nm in $H_2C_{60}(X)$ is only due to C_{60} and that the shape of the absorption spectrum of C_{60} is not affected by a mixing of H_2TPP. The resulting spectra around the Soret band of H_2TPP are shown in Fig. 2a, together with the absorption spectrum of H_2M, i.e., the monomer spectrum of H_2TPP. The band shape and peak position depend on the C_{60} concentration, suggesting that the subtracted spectra of $H_2C_{60}(X)$ are regarded as a superposition of the spectra of the

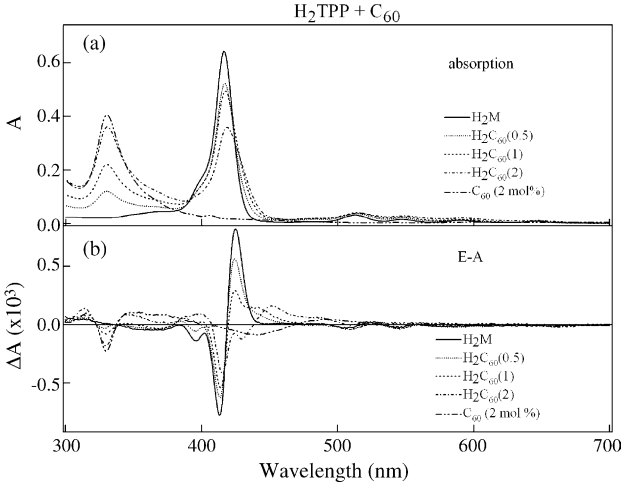

Fig. 1. Absoprtion spectra (a) and E–A spectra (b) of H_2TPP (H_2M), C_{60} and $H_2C_{60}(X)$ ($X = 0.5$, 1.0, 2.0 mol%) doped in a PMMA film in the region of 300–700 nm. The concentration of H_2TPP was 0.5 mol%. The absorption spectrum of C_{60} was obtained with a concentraion of 2 mol%. Applied field strength was 0.75 MV cm^{-1}. The thickness of the sample film is normalized to be 0.25 μm.

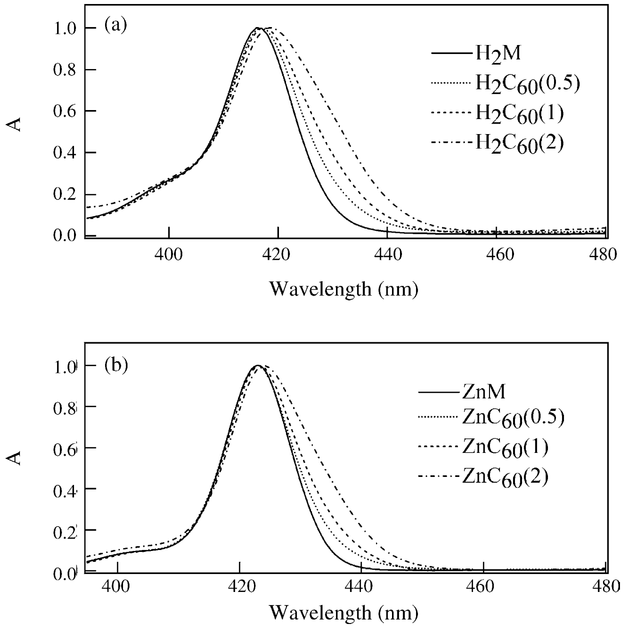

Fig. 2. Absorption spectra of $H_2C_{60}(X)$ (a) and $ZnC_{60}(X)$ (b), obtained by a subtraction of the absorption spectrum of C_{60} in the wavelength region around the Soret band of porphyrin, together with the spectrum of H_2M and ZnM. The maximum intensity is normalized to unity in every case.

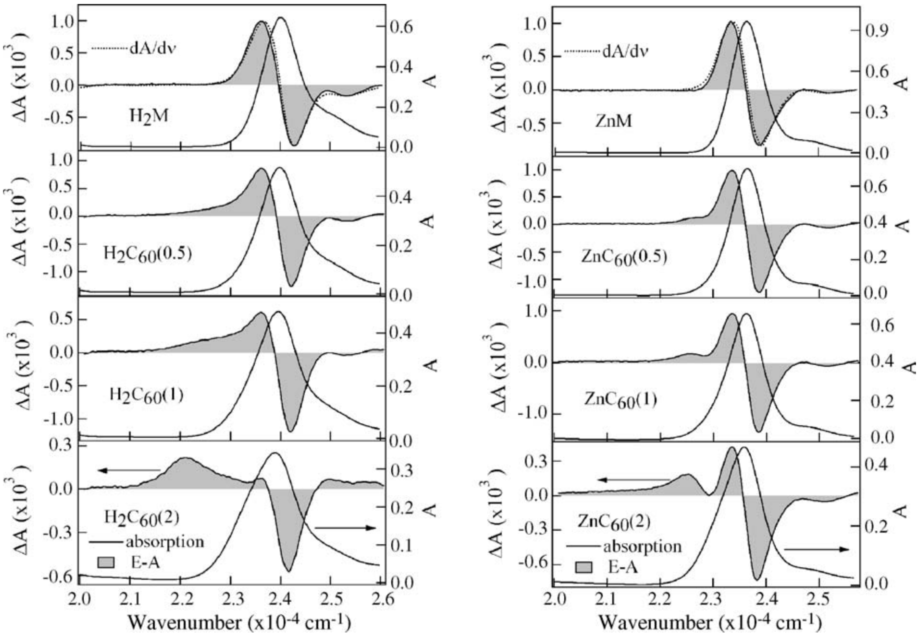

Fig. 3. E–A spectra of H_2C_{60}(X) (left) and ZnC_{60}(X) (right) obtained by a subtraction of the E–A spectrum of C_{60} in the wavelength region around the Soret band of porphyrin, together with the E–A spectra of H_2M and ZnM. The applied field strength was 0.75 MV cm^{-1}. The corresponding absorption spectrum is shown by a solid line in every case, and the first derivative of the absorption spectrum is shown by a dotted line for H_2M and ZnM.

H_2M and complex formed between H_2TPP and C_{60}. In the present study, we have focused our attention to the absorption bands located near the Soret band of TPP.

Similar experiments, as well as the analyses, were also done for the mixture between ZnTPP and C_{60}; the absorption spectrum of C_{60} was subtracted from the ones observed for ZnC_{60}(X). The subtracted absorption spectra of ZnC_{60}(X) near the Soret band of ZnTPP are also shown in Fig. 2b, together with the absorption spectrum of ZnM. The spectral shift and broadening are more pronounced in the mixtures of H_2TPP with C_{60} than those of ZnTPP and C_{60}. This is consistent with the experimental observation of Sun et al., who pointed out that C_{60} binds free-base porphyrin more strongly than metaleted porphyrin [29]. The interaction between porphyrin and fullerene is regarded as largely dominated by the van der Waals interaction, which may be influenced by other subtle interactions, such as electrostatic interaction or charge-transfer interaction. The incidence of the stronger CT for H_2TPP in the present study suggests that the electrostatic attraction between the electron-rich 6:6 ring-juncture bond of fullerene and the electropositive N–H center of porphyrin largely enhances the van der Waals interaction in H_2TPP/C_{60} system.

E–A spectra were obtained for H_2C_{60}(X), ZnC_{60}(X), H_2M, ZnM and C_{60} doped in a PMMA film. The results for H_2C_{60}(X), H_2M and C_{60} are shown in Fig. 1b. The E–A spectra both of C_{60} and of H_2TPP doped in a PMMA film are the same as the ones reported previously [39,40]. The E–A spectra of H_2C_{60}(X) or ZnC_{60}(X) are regarded as a superposition of the spectra of TPP, C_{60} and complex between TPP and C_{60}. The E–A spectrum of C_{60} was subtracted from the E–A spectrum of each mixture by employing the similar method as used in the normal absorption spectra; the subtraction factor was determined by using the E–A signal of C_{60} at 331 nm. The extracted E–A spectra around the Soret band of TPP are shown in Fig. 3 for both H_2C_{60}(X) and ZnC_{60}(X), together with the E–A spectra of H_2M and ZnM. Note that the E–A spectra of H_2M and ZnM are given by the first derivative of the absorption spectrum in shape (see Fig. 3), indicating that the change in molecular plarizability is significant upon optical transition in TPP monomer. Absorption spectra, as well as E–A spectra for both H_2TPP and ZnTPP, and for their mixtures with C_{60} were measured both under the magic angle cindition and under the normal incidence condition in χ, i.e., $\chi = 54.7$ and 90° in Eqs. (2) and (3). Note that the E–A spectra shown in Figs. 1 and 3 were obtained with $\chi = 54.7^\circ$. The absorption and E–A spectra, both for the monomer (H_2M or ZnM) and for the mixture (H_2C_{60}(X) or ZnC_{60}(X)), show only the increase in intensity on going from the normal incident condition to the magic-angle condition, as shown in Fig. 4. Note that the E–A spectra observed at the magic angle give the molecular parameters ($\Delta\boldsymbol{\mu}$ and $\Delta\boldsymbol{\alpha}$) in a direct manner (see Eqs. (5) and (6)). Apparently, the E–A spectra of both H_2C_{60}(X) and ZnC_{60}(X) in the Soret absorption region gradually change with an increase of the C_{60} concentration (see Fig. 3), indicating the external electric field effect on the absorption spectrum of the complex formed between TPP and C_{60}.

By comparing the spectral features of H_2C_{60}(X) and ZnC_{60}(X) at different concentrations of C_{60} with those of H_2M and ZnM, it can be easily envisioned that the absorption band of the complex is located contiguous to the Soret

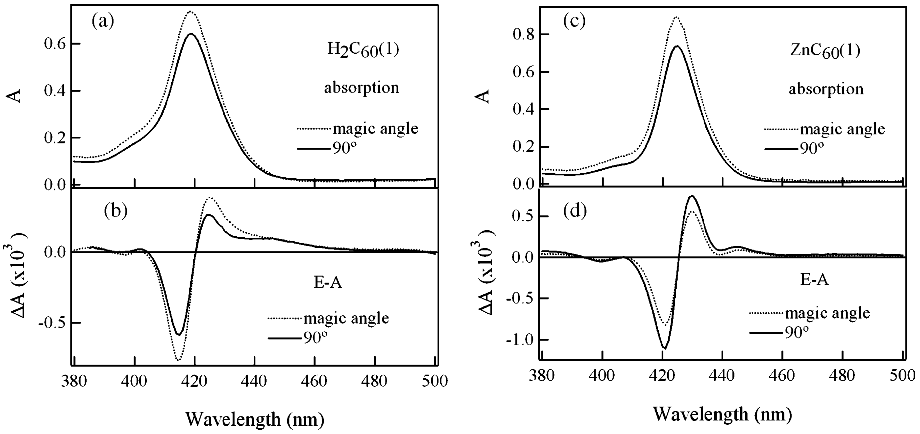

Fig. 4. Absorption spectra (a, c) and E–A spectra (b, d) of $H_2C_{60}(1)$ (a, b) and $ZnC_{60}(1)$ (c, d) observed with the magic angle (dotted line) and with 90° (solid line) for χ.

band of the porphyrin monomer. Accordingly, the absorption and E–A spectra of $H_2C_{60}(X)$ and $ZnC_{60}(X)$ shown in Figs. 2 and 3 are regarded as a superposition of the TPP monomer and the complex spectra. The absorption spectrum, as well as the E–A spectrum of the complex, was extracted and simulated by using the following assumptions: (1) absorption and E–A spectra of the monomer species which exist in $H_2C_{60}(X)$ and $ZnC_{60}(X)$ are the same in shape as the ones of H_2M and ZnM irrespective of the difference of X, and the subtraction of the monomer spectrum from the mixture yields the spectrum of the complex; (2) absorption and E–A spectra of the complex which exists in $H_2C_{60}(X)$ and $ZnC_{60}(X)$ are independent of the C_{60} concentration; (3) the mixture spectrum can be reproduced by a linear combination of the monomer spectrum and some Gaussian curves. Two Gaussian curves, each of which gives the same shape at different concentrations of C_{60} were obtained, i.e., G_1 and G_2 in $H_2C_{60}(X)$ and G_1' and G_2' in $ZnC_{60}(X)$, as shown in Fig. 5. The relative intensity between G_1 and G_2 or between G_1' and G_2' was the same at different concentrations of C_{60}. A sum of these two Gaussian curves, i.e. $(G_1 + G_2)$ in $H_2C_{60}(X)$ and $(G_1' + G_2')$ in $ZnC_{60}(X)$, was supposed to give the absorption spectrum of the complex. The simulated absorption spectrum of the complex, as well as its first and second derivatives, is shown in Fig. 5.

E–A spectra of the complex between TPP and C_{60} are considered to be obtained by subtracting the E–A spetrum of the TPP monomer from the spectrum of $H_2C_{60}(X)$ or $ZnC_{60}(X)$. At first, the subtraction of the E–A spectum of H_2M or ZnM was done by assuming that the E–A spectrum of the TPP

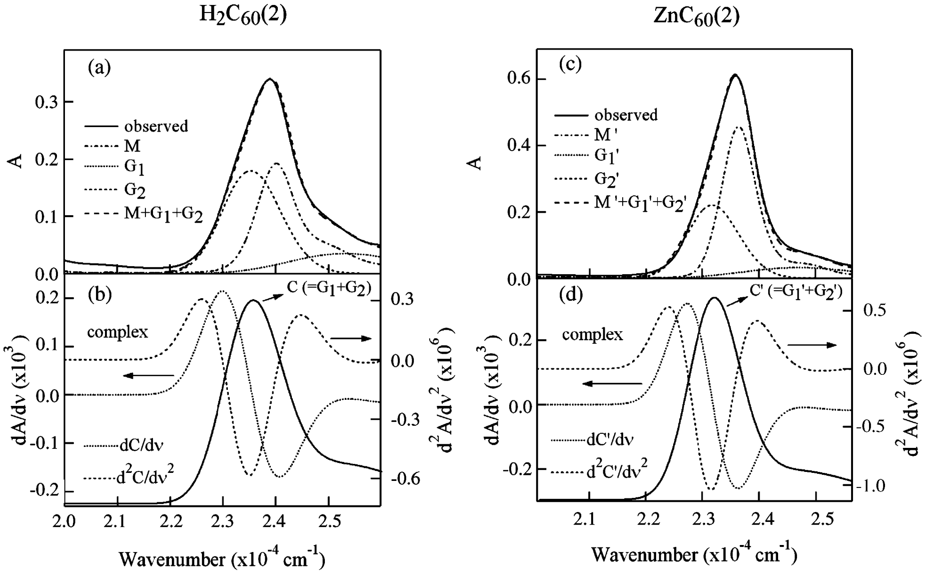

Fig. 5. Absorption spectrum of $H_2C_{60}(2)$ and $ZnC_{60}(2)$ where the absorption spectrum of C_{60} was subtracted, and its decomposition to the TPP monomer spectrum (M and M′) and two Gaussian shapes, G_1 and G_2 in the left and G_1' and G_2' in the right (a, c). Extracted absorption spectra of the complex formed by TPP and C_{60}, i.e., C $(=G_1 + G_2)$ and C′ $(=G_1' + G_2')$, and their first and second derivative spectra (b, d). The sum of the monomer spectrum and two Gaussians is also shown by a broken line in (a) and (c).

monomer is independent of the C_{60} concentration; the intensity of the E–A spectrum of the monomer relative to the absorption spectrum of the TPP monomer was assumed to be the same as the one observed for H_2M or ZnM. The extracted E–A spectra thus obtained were tried to be simulated by a linear combination of the zeroth, first and second derivatives of the absorption spectrum of the complex, i.e., $G_1 + G_2$ in $H_2C_{60}(X)$, as mentioned below. The simulation was done by assuming that the second derivative of C (=$G_1 + G_2$) is dominant and that the contribution of the first derivative of C is minor (see Fig. 6b), and then the simulation was done by assuming the equal contribution for both the first and second derivatives of C (see Fig. 6c). In both cases, the extracted spectra could not be reproduced by a linear combination of the first and second derivatives of the absorption spectrum of the complex. Even when the first derivative of C is assumed to be dominant, the extracted E–A spectrum could not be reproduced (not shown). Thus, the extracted E–A spectra of the complex which were obtained by assuming that the E–A spectrum of the TPP monomer is independent of the C_{60} concentration could not be reproduced by a simulation.

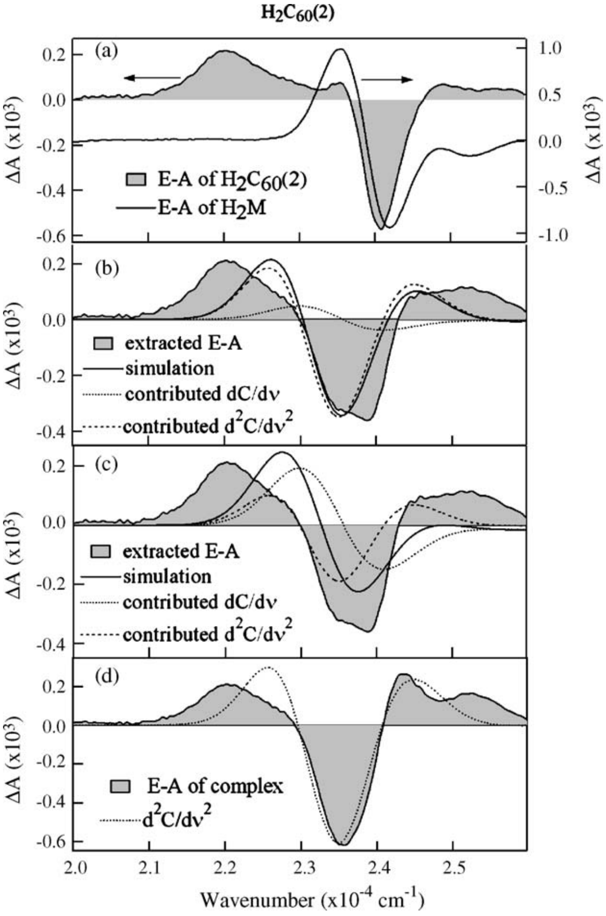

Fig. 6. (a) E–A spectra both of $H_2C_{60}(2)$ where the E–A spectrum of C_{60} was subtracted and of H_2M, (b) and (c) E–A spectrum of the complex between H_2TPP and C_{60} extracted by assuming that the E–A spectrum of the TPP monomer is independent on the concentration of C_{60}, together with the spectrum simulated by a sum of the first and second derivative components given in the figure, (d) E–A spectrum of the complex extracted by subtracting the monomer E–A spectrum multiplied by a weighted factor, together with the second derivative of the absorption spectrum of the complex. Simulation was done in (b) with a dominant contribution of the second derivative and a minor contribution of the first derivative of the absorption spectrum, while the simulation was done in (c) with the equal contribution for both the first and second derivative components.

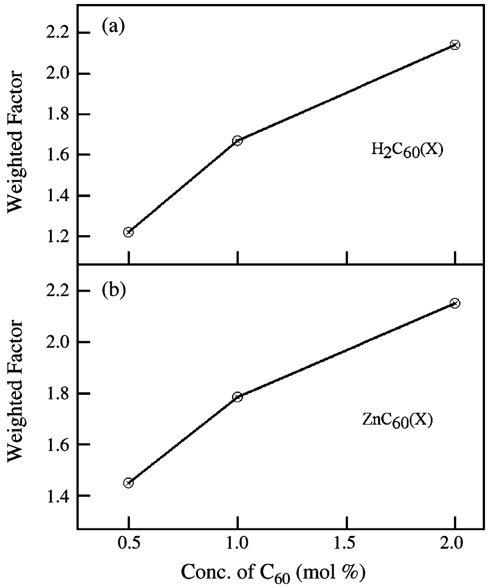

Fig. 7. Plots of the weighted factor used in the subtraction of the E–A spectrum of the TPP monomer from the E–A spectra of $H_2C_{60}(X)$ or $ZnC_{60}(X)$ as a function of the C_{60} concentration; H_2TPP (a) and ZnTPP (b).

A disagreement between the extracted E–A spectrum of complex and the simulated spectrum could be reduced with an increase of the weighted factor of the E–A spectrum of the TPP monomer used for the subtraction. Actually, we gradually increased the weighted factor, and in each time, we tried to simulate the resulting E–A spectrum by a linear combination of the first and the second derivatives of the absorption spectrum of complex, i.e., ($G_1 + G_2$) in $H_2C_{60}(X)$. By using such a try-and-error method, we could obtain the E–A spectrum which could be reproduced quite well by a linear combination of the first and second derivatives of the extracted absorption spectrum of complex, as shown in Fig. 6d. The weighted factor used for the subtraction is plotted in Fig. 7 against the concentration of C_{60}. The weighted factor increases monotonically, as the concentration of C_{60} increases. As shown in Fig. 6d, the extracted E–A spectrum of the complex is very similar in shape to the second derivative, and the magnitude of $\Delta\boldsymbol{\mu}$ for the absorption band of the complex located around the Soret band of TPP was evaluated to be 3.3 D with Eq. (6). This value was obtained with a Lorentz field correction; f in Eq. (1) was assumed to be 1.87 [41]. The angle between $\Delta\boldsymbol{\mu}$ and the direction of the transition dipole was evaluated to be 70°, based on the analysis of the angle (χ) dependence of the E–A spectrum (see Eq. (3)).

The analysis of the E–A spectra of $ZnC_{60}(X)$ was done by a similar fashion to the one mentioned above for $H_2C_{60}(X)$. Fig. 8 shows the results for $ZnC_{60}(2)$. Fig. 5 represents the

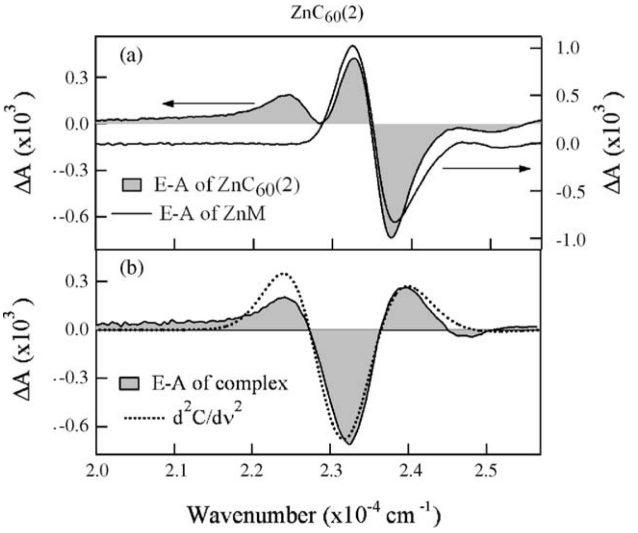

Fig. 8. (a) E–A spectra of ZnM and $ZnC_{60}(2)$, (b) extracted E–A spectrum of the complex formed by a mixture of ZnTPP and C_{60}, and the second derivative of the extracted absorption spectrum of the complex.

absorption spectrum of $ZnC_{60}(2)$ together with the simulated constituents; M′, G_1' and G_2', where M′ is the contribution of the monomer absorption, i.e., ZnM, and G_1' and G_2' are two Gaussian curves whose peaks are located respectively to the shorter and longer wavelength regions relative to the peak of ZnM. As shown in Fig. 5, a sum of these two Gaussian curves, i.e., C′ (=$G_1' + G_2'$) is attributed to the absorption spectrum of the complex between ZnTPP and C_{60}. As in the case of $H_2C_{60}(X)$, the E–A spectrum of C′ shown in Fig. 8b was extracted by subtracting the E–A spectrum of ZnM from the E–A spectrum of $ZnC_{60}(2)$, where the weighted factor was chosen in such a way that the extracted E–A spectrum could be reproduced by a linear combination of the first and the second derivatives of C′. The magnitude of $\Delta\boldsymbol{\mu}$ of the complex between ZnTPP and C_{60} following excitation into the band located around the Soret band of TPP was evaluated from the analysis of the contribution of the second derivative to be 3.0 D with a Lorentz field correction (see Eq. (6)). The angle between $\Delta\boldsymbol{\mu}$ and the direction of the transition dipole was evaluated to be 65° from the angle (χ) dependence of the E–A spectrum. As already mentioned, there is no doubt that the Stark shift of the Soret band of ZnM, as well as H_2M results from $\Delta\boldsymbol{\alpha}$, in contrast with the complex between TPP monomer and C_{60}.

The weighted factor employed for the subtraction of the E–A spectrum of the ZnTPP monomer was plotted against the concentration of C_{60} (see Fig. 7). A monotonic increase of the weighted factor with an increase of the C_{60} concentration is observed, not only in $H_2C_{60}(X)$, but also in $ZnC_{60}(X)$, suggesting that the local field becomes stronger with increasing the C_{60} concentration; the actual field operated to the sample in PMMA, which is usually different from the externally applied electric field, becomes stronger, as the C_{60} concentration increases.

5. Conclusion

E–A spectrum of the complex formed between H_2TPP or ZnTPP and C_{60} in the wavelength/wavenumber region around the Soret band of TPP is very similar to the second derivative of the absorption spectrum, indicating that the change in dipole moment ($\Delta\boldsymbol{\mu}$) is significant following the optical transition of the complex. This indicates that a charge separation occurs following excitation into the absorption band of the complex between TPP and C_{60} located near the Soret band of TPP. The magnitude of the change in dipole moments for the complexes of H_2TPP and ZnTPP with C_{60} has been evaluated from the E–A spectra to be 3.3 and 3.0 D, respectively. The similar incident was observed in the case of meso–meso linked porphyrin arrays [42], where the nonzero value of $\Delta\boldsymbol{\mu}$ was attributed to the photoinduced charge transfer along the linked porphyrin array. The angle between the transition dipole and $\Delta\boldsymbol{\mu}$ has been evaluated to be 70° in the complex of $H_2TPP + C_{60}$ and 65° in the complex of $ZnTPP + C_{60}$ by comparing the E–A spectra obtained with the magic angle and with 90° for χ.

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References

[1] B. O'Regan, M. Gratzel, Nature 353 (1991) 737.
[2] G. Steinberg-Yfrach, J.-L. Rigaud, E.N. Durantini, A.L. Moore, D. Gust, T.A. Moore, Nature 392 (1998) 479.
[3] D.M. Kaschak, J.T. Lean, C.C. Waraksa, G.B. Saupe, H. Usami, T.E. Mallouk, J. Am. Chem. Soc. 121 (1999) 3435.
[4] C.A. Bignozzi, R. Argazzi, C. Chiorboli, F. Scandola, R.B. Dyer, J.R. Schoonover, T.J. Meyer, Inorg. Chem. 33 (1994) 1652.
[5] J. Barber, Nature 333 (1988) 114.
[6] W. Kühlbrandt, Nature 374 (1995) 497.
[7] G. Decher, Science 277 (1997) 1232.
[8] K. Kalyanasundaram, Photochemistry of Polypiridene and Porphyrin Complexes, Academic Press, London, 1992.
[9] M.R. Wasielewski, Chem. Rev. 92 (1992) 435.
[10] L. Flamigni, F. Barigelletti, N. Armaroli, J.-P. Collin, J.-P. Sauvage, J.A.G. Williams, Chem. Eur. J. 4 (1998) 1744.
[11] A.W. Jensen, S.R. Wilson, D.I. Schuster, Bioorg. Med. Chem. 4 (1996) 767.
[12] D.M. Guldi, Chem. Commun. (2000) 321.
[13] N. Armaroli, F. Diederich, C.O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten, J.-P. Sauvage, Chem. Eur. J. 4 (1998) 406.
[14] H. Imahori, Y. Sakata, Adv. Mater. 9 (1997) 537.
[15] H. Imahori, K. Hagiwara, T. Akiyama, M. Aoki, S. Taniguchi, T. Okada, M. Shirakawa, Y. Sakata, Chem. Phys. Lett. 263 (1996) 545.
[16] D. Kuciauskas, S. Lin, G.R. Seely, A.L. Moore, T.A. Moore, D. Gust, T. Drovetskaya, C.A. Reed, P.D.W. Boyd, J. Phys. Chem. 100 (1996) 15926.

[17] H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, Y. Sakata, J. Am. Chem. Soc. 118 (1996) 11771.
[18] T.D.M. Bell, T.A. Smith, K.P. Ghiggino, M.G. Ranasinghe, M.J. Shephard, M.N. Paddon-Row, Chem. Phys. Lett. 268 (1997) 223.
[19] H. Imahori, K. Tamaki, D.M. Guldi, C. Luo, M. Fujitsuka, O. Ito, Y. Sakata, S. Fukuzumi, J. Am. Chem. Soc. 123 (2001) 2607.
[20] H. Imahori, K. Tamaki, Y. Araki, T. Hasobe, O. Ito, A. Shimomura, S. Kundu, T. Okada, Y. Sakata, S. Fukuzumi, J. Phys. Chem. A 106 (2002) 2803.
[21] M.M. Olmstead, D.A. Costa, K. Maitra, B.C. Noll, S.L. Phillips, P.M. Van Calcar, A.-L. Balch, J. Am. Chem. Soc. 121 (1999) 7090.
[22] P.D.W. Boyd, M.C. Hodgson, C.E.F. Rickard, A.G. Oliver, L. Chaker, P.J. Brothers, R.D. Bolskar, F.S. Tham, C.A. Reed, J. Am. Chem. Soc. 121 (1999) 10487.
[23] T. Da Ros, M. Prato, D. Guldi, E. Alessio, M. Ruzzi, L. Pasimeni, Chem. Commun. (1999) 635.
[24] N. Armaroli, F. Diederich, L. Echegoyen, T. Habicher, L. Flamigni, G. Marconi, J.-F. Nierengarten, New J. Chem. (1999) 77.
[25] D. Sun, F.S. Tham, C.A. Reed, L. Chaker, M. Burgess, P.D.W. Boyd, J. Am. Chem. Soc. 122 (2000) 10704.
[26] T. Ishii, R. Kanehama, N. Aizawa, M. Yamashita, H. Matsuzaka, K. Sugiura, H. Miyasaka, T. Kodama, K. Kikuchi, I. Ikemoto, H. Tanaka, K. Marumoto, S. Kuroda, J. Chem. Soc. Dalton Trans. (2001) 2975.
[27] D.V. Konarev, I.S. Neretin, Y.L. Slovokhotov, E.I. Yudanova, N.V. drichko, Y.M. Shul'ga, B.P. Tarasov, L.L. Gumanov, A.S. Batsanov, J.A.K. Howard, R.N. Lyubovskaya, Chem. Eur. J. 7 (2001) 2605.
[28] M. Kimura, Y. Saito, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, J. Am. Chem. Soc. 124 (2002) 5274.
[29] D. Sun, F.S. Tham, C.A. Reed, L. Chaker, P.D.W. Boyd, J. Am. Chem. Soc. 124 (2002) 6604.
[30] S.R. Wilson, S. MacMahon, F.T. Tat, P.D. Jarowski, D.I. Schuster, Chem. Commun. (2003) 226.
[31] D. Balbinot, S. Atalick, D.M. Guldi, M. Hatzimarinaki, A. Hirsch, N. Jux, J. Phys. Chem. B 107 (2003) 13273.
[32] K. Tashiro, T. Aida, J.-Y. Zheng, K. Kinbara, K. Saigo, S. Sakamoto, K. Yamaguchi, J. Am. Chem. Soc. 121 (1999) 9477.
[33] K. Tashiro, T. Aida, J. Inclu. Phenom. Macrocycl. Chem. 41 (2001) 215.
[34] S. Umeuchi, Y. Nishimura, I. Yamazaki, H. Murakami, M. Yamashita, N. Ohta, Thin Solid Films 311 (1997) 239.
[35] E. Jalviste, N. Ohta, J. Chem. Phys. 121 (2004) 4730.
[36] W. Liptay, in: E.C. Lim (Ed.), Excited States, 1, Academic Press, New York, 1974, p. 129.
[37] R. Wortmann, K. Elich, W. Liptay, Chem. Phys. 124 (1988) 395.
[38] G.U. Bublitz, S.G. Boxer, Ann. Rev. Phys. Chem. 48 (1997) 213.
[39] N. Ohta, T. Tanaka, I. Yamazaki, Res. Chem. Intermed. 27 (2001) 61.
[40] Y. Iwaki, N. Ohta, Chem. Lett. 894 (2000).
[41] N. Ohta, M. Koizumi, S. Umeuchi, Y. Nishimura, I. Yamazaki, J. Phys. Chem. 100 (1996) 16466.
[42] N. Ohta, Y. Iwaki, T. Ito, I. Yamazaki, A. Osuka, J. Phys. Chem. B. 103 (1999) 11242.