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Photoinduced energy transfer in ZnO–tetraphenylporphyrin systems

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ABSTRACT

The optical absorption and photoluminescence measurements were carried out for ZnO nanoparticle–tetraphenylporphyrin (TPP) systems made of four kinds of TPP's with and without *p*-aminophenyl groups. The ZnO particles were treated with L-cysteine in order to make a ZnO–(L-cysteine)–TPP binding. However, this binding was not formed because of an absence of the ZnO–(L-cysteine) binding. In the case of metal-free TPP's, the central hydrogen atoms of the TPP ring were replaced by a Zn atom during an aging of 2–4 weeks. An energy transfer from photoexcited ZnO to TPP occurs by a collision between ZnO and TPP in the dispersed medium.

1. Introduction

The optical properties of the assembled systems made of inorganic nanoparticles and organic molecules are gaining increasing interest for a wide range of biomedical applications, e.g. imaging [1–6], and photodynamic therapy [7–10]. A key phenomenon for such applications is the energy transfer from photoexcited nanoparticles to the organic molecules. Much effort is being made to obtain an efficient emission of the organic molecules by an energy transfer from the photoexcited nanoparticles [11–15].

In this Letter, the photoluminescence (PL) properties of ZnO nanoparticle–porphyrin systems are reported. ZnO is a direct band gap semiconductor with a band gap of 3.4 eV. ZnO nanostructures typically have a near-band-edge emission in the UV region and a defect-related visible emission in the blue to green region [10,16,17]. Because of its potential of non-toxicity, ZnO is a candidate for the materials applicable for biomedicine [2,3,10]. Porphyrin, on the other hand, is a well-known emitter of red light. The objective of the present study is to elucidate the PL properties and the energy transfer efficiency of the ZnO nanoparticle–porphyrin systems. A similar study of a ZnO nanoparticle–porphyrin system has recently been reported by Liu et al. using *meso*-tetra(*o*-aminophenyl) porphyrin (MTAP) [10]. They observed an efficient quenching of the ZnO emission and enhancement of the MTAP emission in the ZnO–MTAP system, which indicated that an energy transfer occurred from ZnO to MTAP with an efficiency of 83%. In the present study, four kinds of tetraphenylporphyrins (TPP) shown in Fig. 1, i.e. 5,10,15,20-tetraphenylporphyrin (H_2TPP), 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (H_2TPP(NH_2)), 5,10-bis(4-aminophenyl)-15,20-diphenylporphyrin (H_2TPP$(NH_2)_2$), and {5,10-bis(4-aminophenyl)-15,20-diphenylporphyrinato}zinc (II) (ZnTPP$(NH_2)_2$) are used instead of MTAP. Among these, H_2TPP(NH_2), H_2TPP$(NH_2)_2$ and ZnTPP$(NH_2)_2$ have one or two *p*-aminophenyl groups instead of four *o*-aminophenyls in MTAP. The different substitutional site of the amino group and the different number of aminophenyls may result in different energy transfer efficiencies and different emission properties.

Another important point of the present study is to elucidate the role of L-cysteine (HS–CH_2CH(NH_2)–COOH) which is a popular linker between inorganic nanoparticle and organic molecule. Liu et al. synthesized a ZnO–(L-cysteine)–MTAP conjugate assuming that L-cysteine is bound to the surface of the ZnO particles by a formation of Zn–S bonding. They made a chemical bonding between L-cysteine and MTAP by a reaction between the carboxyl group of L-cysteine and the amino group of MTAP resulting in a –(CO)–(NH)– bonding [10]. However, there is no clear evidence of the ZnO–(L-cysteine) and the (L-cysteine)–MTAP bondings. In the present study, it will be shown that L-cysteine is not bound to the ZnO particles. As a result, TPP's used in the present study are not bound to the ZnO particle. A collision-controlled energy transfer from ZnO to TPP will be reported.

2. Experimental

$Zn(OAc)_2 \cdot 2H_2O$, 1-ethyl-3(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), *N*-hydroxysulfosuccinimide (sulfo-NHS), and diethylene glycol were purchased from Kanto Chemicals. H_2TPP, H_2TPP(NH_2) and H_2TPP$(NH_2)_2$ were synthesized by a literature procedure [18,19]. ZnTPP$(NH_2)_2$ was synthesized from H_2TPP$(NH_2)_2$ by adding excess amount of $Zn(OAc)_2 \cdot 2H_2O$ in a mixed solvent of chloroform and methanol (3:1) and refluxing.

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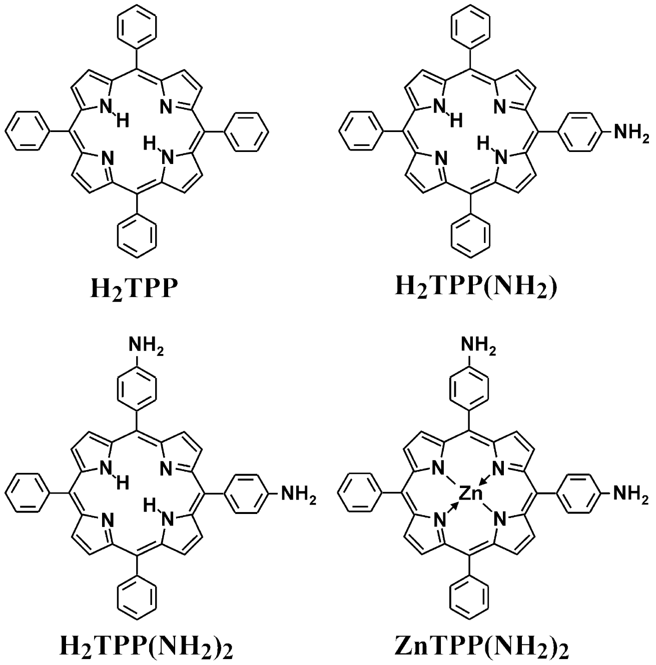

Fig. 1. The four types of porphyrins used in this study.

The synthesized $H_2TPP(NH_2)$, $H_2TPP(NH_2)_2$ and $ZnTPP(NH_2)_2$ were characterized by ^{1}H-nuclear magnetic resonance and Matrix-Assisted Laser-Desorption/Ionization Time-of-Flight (MALDI-TOF) Mass spectroscopies.

ZnO nanoparticles were synthesized by a reported method [10,16,17]. 3.8×10^{-4} mol of $Zn(OAc)_2{\cdot}2H_2O$ and 75 ml of diethylene glycol were mixed (Zn: 5.0×10^{-3} mol/L), and the mixture was heated under stirring and kept at 160 °C for 1 h. After this reaction, fluorescent ZnO nanoparticles were formed. Then, 30 ml of the ZnO dispersion in diethylene glycol (Zn: 1.5×10^{-4} mol) and an aqueous solution of L-cysteine (1.5×10^{-4} mol) were mixed, and the pH of the resultant dispersion was adjusted to 7 by adding NaOH aqueous solution. The mixture was heated to 60 °C for 48 h to form L-cysteine-treated ZnO particles (ZnO–LC). Then, the pH of the dispersion was again adjusted to 7.

The (ZnO–LC)–porphyrin system was prepared using the standard cross linking method [10,20,21]. 2.5×10^{-5} mol of EDC and 2.5×10^{-5} mol of sulfo-NHS were successively added to 5 ml of the ZnO–LC dispersion (Zn: 2.5×10^{-5} mol), and reacted for 15 min at room temperature. Then, 1.5×10^{-6} mol of the porphyrin was dissolved in a small amount of dimethylformamide for H_2TPP, and a small amount of diethylene glycol for $H_2TPP(NH_2)$, $H_2TPP(NH_2)_2$ and $ZnTPP(NH_2)_2$, and was added to the ZnO–LC dispersion treated with EDC and sulfo-NHS. The mixture was stirred for 3 h at room temperature. The pH of the resultant dispersion was adjusted to 7. Finally, the dispersion was diluted by 3 (or 21) times with diethylene glycol since it was too concentrated for optical absorption and PL measurements. The final concentrations of the Zn atoms and porphyrins were 1.7×10^{-3} (or 2.4×10^{-4}) mol/L and 1.0×10^{-4} (or 1.4×10^{-5}) mol/L, respectively. For the measurement of the excitation spectrum of the photoluminescence, the samples diluted by 21 times were used in order to get reliable excitation spectra.

The ZnO particles were observed with transmission electron microscopy (TEM, JEOL JEM-2010). Optical absorption spectra were measured using Shimazu UV-3100PC. PL spectra were measured using Ocean Optics USB2000 with an excitation light of 325 nm from a He–Cd laser. The optical absorption and PL measurements were performed using a 10 mm × 2 mm quartz sample cell. For the optical absorption measurement, the path length of the penetrating light through the sample was 2 mm. For the PL measurement, the path length of the excitation light was 10 mm, and the emitted light was detected at right angles to the excitation beam. The excitation spectra of the photoluminescence were measured on a HITACHI 850 Fluorescence Spectrophotometer using a 10 mm × 10 mm quartz sample cell.

3. Results and discussion

Fig. 2 shows the TEM image and the electron diffraction pattern of the ZnO nanoparticles without L-cysteine. It is observed that the ZnO particles are spherical with a diameter of typically 4 nm, which is as expected from a reported dependence of the particle size on the concentration of the starting material [17]. The electron diffraction pattern in Fig. 2 is attributed to ZnO, indicating that the ZnO particles are in a crystalline phase.

The optical absorption, PL, and excitation spectra of the ZnO–LC particles are shown in Fig. 3. The PL spectrum is similar to that reported by Liu et al. [10], and has a peak at 500 nm, indicating that the emission comes mainly from surface defects. The excitation spectrum of PL has a broad peak at 340 nm. The absorption spectrum has a tail in the visible region due to Rayleigh scattering, indicating that some sort of aggregation occurred. A TEM observation indicated that the size of the aggregates is typically 500 nm. After a centrifugation of the ZnO–LC dispersion, the supernatant showed

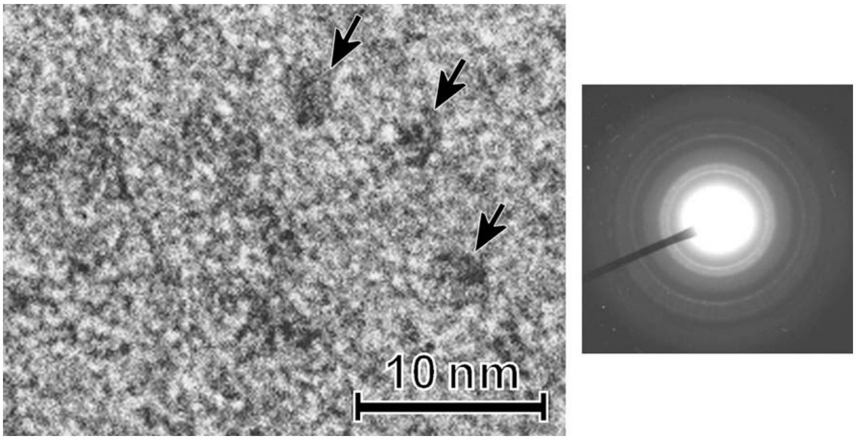

Fig. 2. TEM image and electron diffraction pattern of the ZnO nanoparticles without L-cysteine.

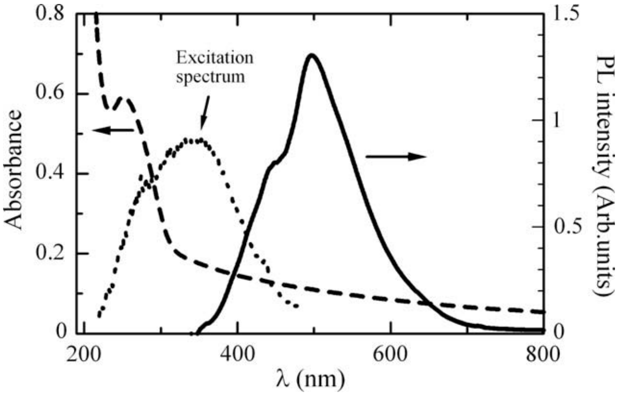

Fig. 3. Optical absorption and photoluminescence spectra of L-cysteine-treated ZnO nanoparticles dispersed in diethylene glycol. The excitation wavelength for the photoluminescence measurement was 325 nm. The excitation spectrum of the photoluminescence is also shown, which was measured for the 500 nm emission.

the identical optical absorption spectrum with the ZnO particles before the L-cysteine treatment. This clearly indicates that the aggregates are made of L-cysteine, and L-cysteine is not bound to the ZnO particles. It is noted that, after the treatment with EDC and sulfo-NHS, the ZnO–LC dispersion again became transparent with much smaller light scattering.

The optical absorption spectra of the (ZnO–LC)–TPP systems are shown in Fig. 4, as well as the absorption spectra of the diethylene glycol solutions of the TPP's. It is noted that, for H_2TPP, a small amount of dimethylformamide was added because H_2TPP was not soluble to diethylene glycol. The absorption spectra of H_2TPP, $H_2TPP(NH_2)$ and $H_2TPP(NH_2)_2$ in diethylene glycol solution have four Q bands, i.e. $Q_x(0,0)$, $Q_x(1,0)$, $Q_y(0,0)$ and $Q_y(1,0)$ [22–24], where the numbers in (0, 0) and (1, 0) indicate the vibrational levels in the ground- or excited-state manifolds. The usual metal porphyrins have two Q bands of $Q(0,0)$ and $Q(1,0)$ [22,23,25]. The existence of four Q bands is due to the lower symmetry of the metal-free TPP's [22–24]. In the (ZnO–LC)–TPP systems, on the other hand, the Q bands of H_2TPP, $H_2TPP(NH_2)$ and $H_2TPP(NH_2)_2$ were altered significantly, especially by an aging after the sample preparation. After an aging of 2–4 weeks, only three absorption peaks were observed in the Q band region with the $Q_x(0,0)$ band disappeared, as shown in Fig. 4. Furthermore, the $Q_y(1,0)$ band became very weak. These features of the Q bands after the aging corresponds to those of the metal porphyrins, suggesting that the two central hydrogen atoms of H_2TPP, $H_2TPP(NH_2)$ and $H_2TPP(NH_2)_2$ were replaced by a Zn atom during the aging. This interpretation is confirmed by the absorption spectra of $ZnTPP(NH_2)_2$ in Fig. 4. Because of the higher symmetry of the Zn–substituted TPP compared to the metal-free TPP's, $ZnTPP(NH_2)_2$ has two Q-band peaks at 604 and 562 nm which are assigned to the $Q(0,0)$ and $Q(1,0)$ bands, respectively, and has a small peak at 520 nm. The (ZnO–LC)–$ZnTPP(NH_2)_2$ system does not show any aging effect in contrast to the (ZnO–LC)–(metal-free TPP) systems, indicating that the aging effect observed in the latter is related to the central hydrogen atoms of the metal-free TPP's. Furthermore, the peak positions and the line shape of (ZnO–LC)–$H_2TPP(NH_2)_2$ after the aging are identical with those of (ZnO–LC)–$ZnTPP(NH_2)_2$. This is a clear evidence of the substitution of the central hydrogen atoms of the metal-free TPP's by a Zn atom. The Zn atoms for the substitution most probably comes from the residual $Zn(OAc)_2$ in the system which is the starting material for the ZnO synthesis. This kind of substitution definitely occurs because $ZnTPP(NH_2)_2$ used in the present study was synthesized from $H_2TPP(NH_2)_2$ and $Zn(OAc)_2$ as explained in the experimental section.

Fig. 5 shows the PL spectra of the diethylene glycol solutions of the TPP's. The PL spectra of the metal-free TPP's, H_2TPP, $H_2TPP(NH_2)$ and $H_2TPP(NH_2)_2$ show two emission peaks at 649–670 nm and 714–724 nm which are assigned to the $Q_x(0,0)$ and $Q_x(0,1)$ bands, respectively [22,24]. The PL spectrum of $ZnTPP(NH_2)_2$, on the other hand, has two peaks at 618 and

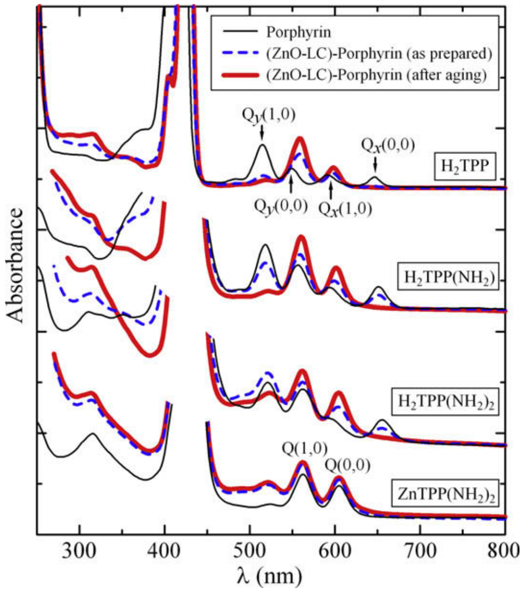

Fig. 4. Optical absorption spectra of the diethylene glycol solutions of the four types of tetraphenylporphyrins, H_2TPP, $H_2TPP(NH_2)$, $H_2TPP(NH_2)_2$ and $ZnTPP(NH_2)_2$ (Thin solid lines), and (ZnO–LC)–porphyrin systems dispersed in diethylene glycol (Broken lines: as prepared. Thick solid lines: after an aging of 2–4 weeks). The very strong B-band absorption peak of the porphyrins at $400\text{ nm} < \lambda < 450\text{ nm}$ was omitted in the figure. The four Q bands of the metal-free porphyrins in the solution are assigned to $Q_x(0,0)$, $Q_x(1,0)$, $Q_y(0,0)$ and $Q_y(1,0)$. On the other hand, the two Q bands of the (ZnO–LC)–(metal-free porphyrin) after aging, as well as those of $ZnTPP(NH_2)_2$, are assigned to $Q(0,0)$ and $Q(1,0)$ of Zn–substituted porphyrins.

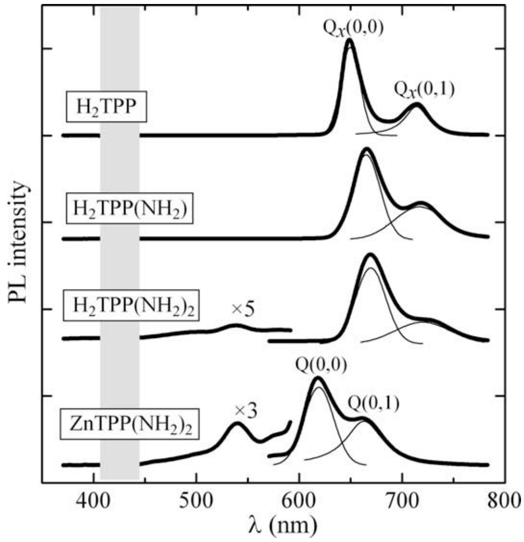

Fig. 5. Photoluminescence spectra of the diethylene glycol solutions of the four types of tetraphenylporphyrins, H_2TPP, $H_2TPP(NH_2)$, $H_2TPP(NH_2)_2$ and $ZnTPP(NH_2)_2$. Excitation wavelength: 325 nm. Each spectrum consists of two spectral components, denoted by thin solid curves, which are assigned to the $Q_x(0,0)$ and $Q_x(0,1)$ bands for the metal-free porphyrins, and $Q(0,0)$ and $Q(0,1)$ for $ZnTPP(NH_2)_2$. For $410\text{ nm} < \lambda < 445\text{ nm}$, no reliable luminescence measurement was possible because of a re-absorption of the emitted light by the porphyrins due to very strong B-band absorption.

664 nm which are assigned to the $Q(0,0)$ and $Q(0,1)$ bands, respectively [25]. For $H_2TPP(NH_2)_2$ and $ZnTPP(NH_2)_2$, a small peak at 540 nm is also observed with a long tail down to 400 nm, the origin of which is unknown. As will be shown later, the intensity of this unknown emission becomes larger in the (ZnO–LC)–TPP systems.

Fig. 6 shows the PL spectra of the (ZnO–LC)–TPP systems. Again, the spectra of the metal-free TPP's showed a drastic change by the aging. After an aging of 2–4 weeks, the $Q_x(0,1)$ emission at ~720 nm disappeared. Instead, a new peak grew up at 603–615 nm. This aging effect is consistent with the substitution of the central hydrogen atoms of the metal-free TPP by a Zn atom discussed above, and the two emission peaks at ~610 and ~660 nm after the aging are assigned to the $Q(0,0)$ and $Q(0,1)$ bands, respectively, of the Zn–substituted TPP's. On the other hand, the PL spectrum of (ZnO–LC)–$ZnTPP(NH_2)_2$ in Fig. 6 does not show any aging effect. This again confirms that the alteration of the PL spectra of the metal-free TPP's by the aging is due to the generation of the Zn–substituted TPP's. The PL spectra of $H_2TPP(NH_2)_2$ and $ZnTPP(NH_2)_2$ have relatively large peaks at 540 and 577 nm besides the $Q(0,0)$ and $Q(0,1)$ bands at 616 and 660 nm. In the case of $H_2TPP(NH_2)_2$, these peaks grew up by the aging. The 540 nm peak seems to also exist in the PL spectra of (ZnO–LC)–H_2TPP and (ZnO–LC)–$H_2TPP(NH_2)$ although the intensity is extremely weak. It is noted that the ZnO–$H_2TPP(NH_2)$ and ZnO–$H_2TPP(NH_2)_2$ systems *without* L-cysteine gave nearly identical optical absorption and PL spectra with the systems having L-cysteine. This supports our conclusion that TPP's are not bound to the ZnO particles because L-cysteine is not bound to ZnO.

In order to investigate the origin of the peaks observed in Fig. 6, the excitation spectrum of PL was measured for (ZnO–LC)–$H_2TPP(NH_2)$ and (ZnO–LC)–$H_2TPP(NH_2)_2$, and the results for the latter are shown in Fig. 7. The excitation spectrum of the 616 nm emission is very close to the optical absorption spectrum shown in Fig. 4. The 660 nm emission showed a similar excitation spectrum. These results are as expected since the two emission peaks at 615 and 661 nm are attributed to the Zn–substituted porphyrin. The emission peaks at 540 and 577 nm, on the other hand, show totally different excitation spectra which have three main peaks at 320, 490, and 520 nm, and have no contribution from the B-band of the porphyrin at around 420 nm, which is shown in Fig. 7 for the 580 nm emission. Thus, the emissions at 540 and 577 nm are not the usual porphyrin emissions. The three peaks at 320, 490, and 520 nm in the excitation spectrum of the 580 nm emission are also observed in the absorption spectrum of the (ZnO–LC)–$H_2TPP(NH_2)_2$ system in Fig. 4 although the 490 nm peak in the absorption spectrum is extremely weak. The origin of these new emission peaks is unknown at present.

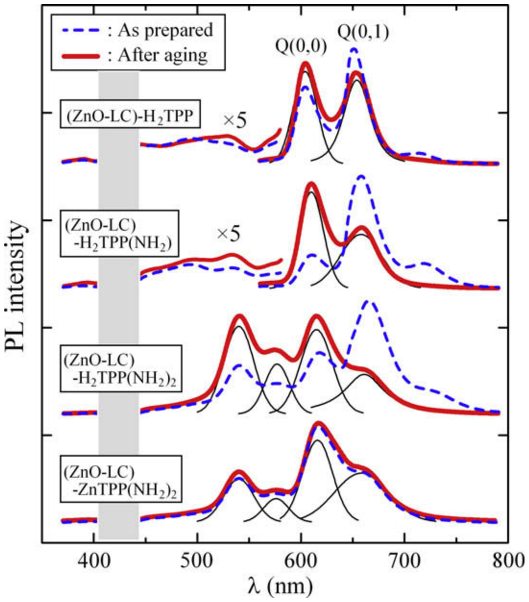

Fig. 6. Photoluminescence spectra of (ZnO–LC)–porphyrin systems dispersed in diethylene glycol. Thick solid lines: after an aging of 2–4 weeks. Excitation wavelength: 325 nm. Thin solid lines are the spectral components of each emission spectrum. The two spectral components at 603–615 nm and 655–660 nm of the (ZnO–LC)–(metal-free porphyrin) after aging, as well as those of (ZnO–LC)–$ZnTPP(NH_2)_2$, are assigned to the $Q(0,0)$ and $Q(0,1)$ bands, respectively, of Zn–substituted porphyrins. The ZnO emission with a peak at 500 nm is overlapped in each spectrum.

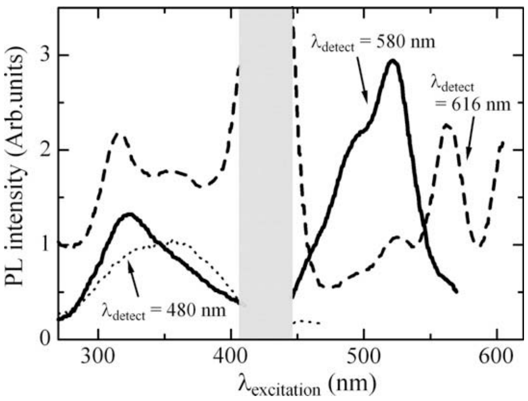

Fig. 7. The excitation spectra of the photoluminescence of (ZnO–LC)–$H_2TPP(NH_2)_2$ in diethylene glycol after an aging of 1 week. The detection wavelengths (λ_{detect}) were 480, 580, and 616 nm. For 410 nm < λ < 445 nm, no reliable measurement was possible because of an extremely small penetration depth of the excitation light in the sample due to the very strong B-band absorption of the porphyrin.

Now, the intensity of the ZnO emission of the (ZnO–LC)–TPP systems is examined. In the PL spectra in Fig. 6, the ZnO emission is observed at around 500 nm. This is confirmed by the excitation spectrum of the 480 nm emission, which is shown in Fig. 7 for (ZnO–LC)–$H_2TPP(NH_2)_2$. The excitation spectrum of the 480 nm emission is close to that of the ZnO emission shown in Fig. 3. The intensity of the ZnO emission could be obtained from the emission intensity at 500 nm for (ZnO–LC)–H_2TPP and (ZnO–LC)–$H_2TPP(NH_2)$. However, for (ZnO–LC)–$H_2TPP(NH_2)_2$ and (ZnO–LC)–$ZnTPP(NH_2)_2$, an emission of unknown origin and unknown intensity is overlapped in the 500 nm region as is evident from the solution spectra of $H_2TPP(NH_2)_2$ and $ZnTPP(NH_2)_2$ in Fig. 5, so that the intensity of the ZnO emission could not be obtained for these systems. The emission intensities of the ZnO for (ZnO–LC)–H_2TPP and (ZnO–LC)–$H_2TPP(NH_2)$ in Fig. 6, were substantially smaller than the intensity for the ZnO–LC without TPP shown in Fig. 3. It is noted, however, that the light power absorbed by ZnO is not the same for the two cases of with and without TPP, so that a correction must be made for the light power absorbed by ZnO, which was carried out using the values of the absorbance at 325 nm in Figs. 3 and 4. Then, the energy transfer efficiency Φ was calculated using the following equation [10,11].

$$\Phi = 1 - \frac{I_{DA}}{I_D}, \qquad (1)$$

where I_{DA} and I_D are the emission intensities of ZnO (energy donor) with and without TPP (energy acceptor) for the same absorbed light power. The estimated values of Φ for (ZnO–LC)–H_2TPP and (ZnO–LC)–$H_2TPP(NH_2)$ are summarized in Table 1. Two features are observed. (1) The values of Φ for (ZnO–LC)–H_2TPP and (ZnO–LC)–$H_2TPP(NH_2)$ are nearly the same. (2) Φ is smaller for the diluted samples. In the case of (ZnO–LC)–H_2TPP, the porphyrin ring cannot be bound to the ZnO particle because H_2TPP does not have any

Table 1
Energy transfer efficiency Φ of the ZnO–porphyrin systems in diethylene glycol.

System	Diluted by three times	Diluted by 21 times
	$\left(\begin{array}{l}\mathrm{Zn}: 1.7\times10^{-3}\ \mathrm{mol/L}\\ \mathrm{Porphyrin}: 1.0\times10^{-4}\ \mathrm{mol/L}\end{array}\right)$	$\left(\begin{array}{l}\mathrm{Zn}: 2.4\times10^{-4}\ \mathrm{mol/L}\\ \mathrm{Porphyrin}: 1.4\times10^{-5}\ \mathrm{mol/L}\end{array}\right)$
(ZnO–LC)–H_2TPP[a]	69 ± 6%	33 ± 15%
(ZnO–LC)–H_2TPP(NH_2)[a]	59 ± 5%	29 ± 17%
ZnO–H_2TPP(NH_2)[b]	60 ± 5%	37 ± 12%

[a] ZnO–LC denotes the ZnO nanoparticles treated with L-cysteine.

[b] Without L-cystine.

amino groups. The above two features clearly indicate that the energy transfer in the (ZnO–LC)–H_2TPP and (ZnO–LC)–H_2TPP(NH_2) systems is due to the collisions between the ZnO particle and TPP. Table 1 also shows the results for the ZnO–H_2TPP(NH_2) system without L-cysteine. It is observed that L-cysteine does not affect the energy transfer efficiency, which is as expected because L-cysteine does not work as a linker between ZnO and TPP.

The present energy transfer from ZnO to porphyrin may be explained by the Förster's mechanism [13]. In the Förster's theory, the energy transfer rate k_{ET} obeys the following relationship.

$$k_{ET} = \int_0^\infty I_D(\lambda)\varepsilon_A(\lambda)\lambda^4\,d\lambda/R^6, \tag{2}$$

where $I_D(\lambda)$ is the emission spectrum of the energy donor, $\varepsilon_A(\lambda)$ is the absorption coefficient of the energy acceptor, R is the distance between the donor and the acceptor. In the present system, the emission spectrum of ZnO shown in Fig. 3 overlaps with the strong B-band absorption of the TPP's shown in Fig. 4, while the emission spectra of the TPP's shown in Fig. 5 do not have any overlap with the absorption spectrum of ZnO shown in Fig. 3. Thus, the direction of the energy transfer is expected to be from ZnO to TPP, as observed in the present experiment. In the present system, the ZnO particles and TPP can move in the dispersion, so that the energy transfer can occur when they are in close proximity to each other. The effective distance at which the transfer occurs is unknown.

Generally, there can be another mechanism of the luminescence quenching, which is the photoinduced electron transfer from electron donor to acceptor. In the present system, the LUMO level of TPP's is ~3.3 eV calculated from the reported ionization potential of 5.2 eV [26] and the optical HOMO–LUMO gap of ~1.9 eV. On the other hand, the conduction band edge of ZnO locates at 4.4 eV [27]. Thus, the electron transfer is possible from the LUMO level of TPP's to the conduction band of ZnO, resulting in the luminescence quenching of TPP's. However, no substantial quenching of the TPP emission was observed in the present systems. This may be another evidence that the present TPP's are not bound to the ZnO particles.

4. Conclusions

Photoluminescence properties of the (ZnO–LC)–porphyrin systems dispersed in diethylene glycol were studied using four kinds of tetraphenylporphyrins, H_2TPP, H_2TPP(NH_2), H_2TPP$(NH_2)_2$ and ZnTPP$(NH_2)_2$. The central hydrogen atoms of the metal-free TPP's were replaced by Zn atom by an aging of 2–4 weeks, which altered the *Q*-band features of the TPP's significantly. For (ZnO–LC)–H_2TPP$(NH_2)_2$ and (ZnO–LC)–ZnTPP$(NH_2)_2$, new emission bands were generated at 540 and 577 nm, the origin of which is unknown at present. The energy transfer efficiency from the photoexcited ZnO to the porphyrin was the same for (ZnO–LC)–H_2TPP, (ZnO–LC)–H_2TPP(NH_2) and ZnO–H_2TPP(NH_2), and the efficiency became smaller by diluting the system by adding diethylene glycol. This clearly indicates that the energy transfer occurs by the collisions of the ZnO particles with porphyrins in the dispersion. ZnO and TPP do not bound with each other because L-cysteine is not bound to the ZnO particles.

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