



electron transfer (charge separation) between photosensitizer and  $C_{60}$ .<sup>11,12</sup>

Recently, we have designed and developed cyclic free-base porphyrin dimer **CPD** linked by butadiyne bearing four 4-pyridyl groups and its inclusion complex  $C_{60} \subset CPD$  with  $C_{60}$  (Fig. 1).<sup>13</sup> It was expected that  $C_{60} \subset CPD$  has favorable photochemical and electrochemical properties for PDT through the electrochemical measurements and the transient absorption spectroscopy, based on the fact that the singlet excited state  $C_{60}^1(CPD)^*$  undergoes intrasupramolecular electron transfer to give a completely charge-separated state  $C_{60}^{\cdot-} - CPD^{\cdot+}$ . Thus, in this work, to gain insight into the  $^1O_2$  generation properties of supramolecular complex of cyclic free-base porphyrin dimer with  $C_{60}$ , we evaluated the  $\Phi_{\Delta}$  and rate constant ( $K_{obs}$ ) of  $^1O_2$  generation for **CPD** and  $C_{60} \subset CPD$ . Here we reveal that cyclic free-base porphyrin dimer and its inclusion complex with fullerene  $C_{60}$  possess the ability to generate  $^1O_2$  under visible light irradiation, based on the kinetic and thermodynamic consideration concerning the electron transfer processes between the porphyrin dimer and  $C_{60}$ .

## Results and discussion

The cyclic free-base porphyrin dimer **CPD** in  $CH_2Cl_2/MeOH$  exhibits strong Soret band at around 420 nm and relatively weak Q band in the range 500–650 nm (Fig. 2,  $\lambda_{max}^{abs}/nm$  ( $\epsilon/M^{-1} cm^{-1}$ ) = 416 (708 000), 514 (31 200), 548 (7400), 587 (9000), 642 (2900)). The molar extinction coefficients ( $\epsilon$ ) of Soret and Q bands for **CPD** are higher than those of **H2PyP** ( $\lambda_{max}^{abs}/nm$  ( $\epsilon/M^{-1} cm^{-1}$ ) = 418 (419 000), 513 (19 200), 548 (6200), 588 (6000), 643 (3000))<sup>13e</sup> as an ABAB porphyrin monomer with two pyridyl groups and two phenyl groups. The fact is attributed to the porphyrin dimer structure of **CPD** with two porphyrin units. For the  $C_{60}$  inclusion complex  $C_{60} \subset CPD$ , it is difficult to obtain its exact absorption spectra because the 1 : 1 complex of **CPD** with  $C_{60}$  is in dissociation equilibrium in solution of  $10^{-5}$  to  $10^{-6}$  M concentration which is suitable for the measurement of photoabsorption spectra of porphyrins. In our previous work, however, we have demonstrated that upon addition of  $C_{60}$  to the solution of the cyclic porphyrin dimer, its Soret band was redshifted with a decrease in intensity, whereas its Q band was slightly redshifted but increased in intensity.<sup>13</sup>  $^1O_2$  generation by **CPD**,  $C_{60} \subset CPD$  or **H2PyP** in  $CH_2Cl_2/MeOH$  (=1/1, v/v) was evaluated by monitoring

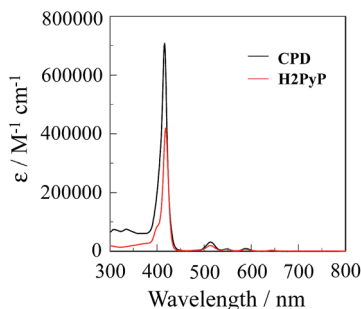


Fig. 2 Photoabsorption spectra of **CPD** and **H2PyP** in  $CH_2Cl_2/MeOH$ .

the photoabsorption spectral change of the known  $^1O_2$  scavenger 1,3-diphenylisobenzofuran (DPBF) accompanied by the reaction of DPBF with the generated  $^1O_2$ , that is, DPBF can trap  $^1O_2$  through its photooxidation.<sup>14</sup>  $CH_2Cl_2/MeOH$  was bubbled with air for 15 min. The air-saturated solution containing **CPD**,  $C_{60} \subset CPD$  or **H2PyP** and DPBF was irradiated with 509 nm ( $300 \mu W cm^{-2}$ ,  $\epsilon = 27\,300 M^{-1} cm^{-1} @ \lambda^{abs} = 509 nm$  for **CPD** and  $\epsilon = 17\,000 M^{-1} cm^{-1} @ \lambda^{abs} = 509 nm$  for **H2PyP**, respectively) obtained by passage of xenon light through monochromator. For both **CPD** and  $C_{60} \subset CPD$  as well as **H2PyP** the absorption band of DPBF at around 410 nm decreased with the increase in the photoirradiation time (Fig. 3), which indicate the reaction of DPBF with  $^1O_2$  generated upon the excitation of the porphyrin dimer. To gain insight into the effect of the cyclic porphyrin dimers on the efficiency of DPBF photooxidation, the changes in optical density ( $\Delta OD$ ) of DPBF are plotted against the photoirradiation time (Fig. 4a), and the slope ( $m_{sl}$ ) is used to estimate the  $\Phi_{\Delta}$  value for **CPD**,  $C_{60} \subset CPD$  and **H2PyP**. The  $m_{sl}$  value ( $-1.5 \times 10^{-2}$ ) of **H2PyP** is larger than those of **CPD** ( $-1.2 \times 10^{-2}$ ) and  $C_{60} \subset CPD$  ( $-9.8 \times 10^{-3}$ ). Moreover, it was revealed that the  $m_{sl}$  value of **CPD** is larger than that of  $C_{60} \subset CPD$ . Thus, the  $\Phi_{\Delta}$  values of **CPD**,  $C_{60} \subset CPD$  and **H2PyP** were estimated by the relative method using Rose Bengal (RB) ( $\Phi_{\Delta} = 0.80$ ,  $m_{sl} = -1.5 \times 10^{-2}$ , see Fig. S1†) in methanol<sup>15</sup> as the standard (Table 1). The  $\Phi_{\Delta}$  value of **CPD**,  $C_{60} \subset CPD$  and **H2PyP** is 0.62, 0.52 and 0.91 respectively, which is in good agreement with the  $m_{sl}$  value. This result suggests that as for the ABAB porphyrin monomer **H2PyP** the ISC efficiency from  $^1S^*$  to the  $^3S^*$  may be higher than in the cyclic free-base porphyrin dimer **CPD**. Moreover, it is worth noting that the  $\Phi_{\Delta}$  value of  $C_{60} \subset CPD$  is lower than that of **CPD**. Our previous work demonstrates that the decay of photoexcited

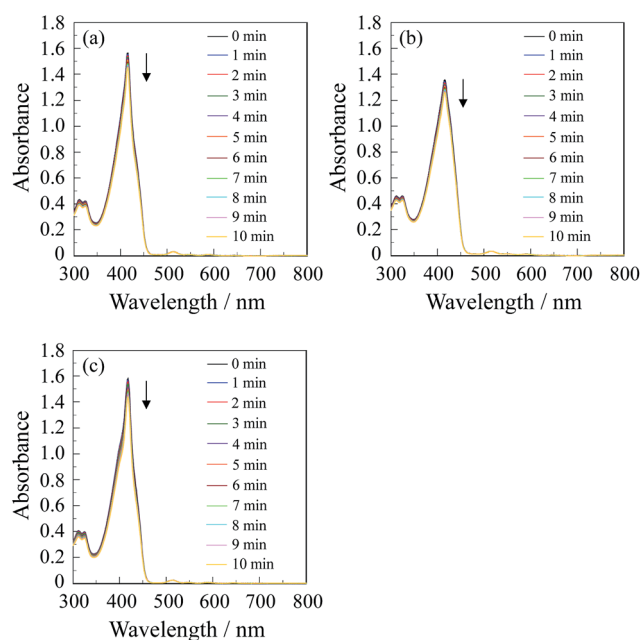
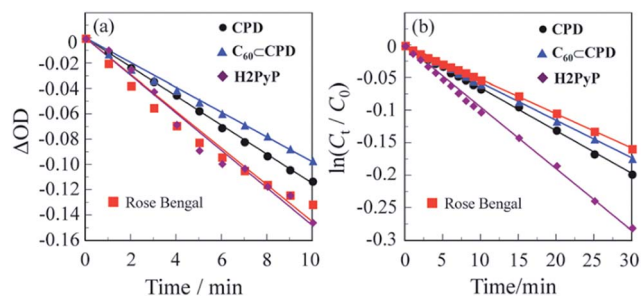


Fig. 3 Photoabsorption spectral changes for the photooxidation of DPBF (Abs. = ca. 1.0) using (a) **CPD** ( $1.3 \times 10^{-6} M$ ), (b)  $C_{60} \subset CPD$  ( $1.0 \times 10^{-6} M$ ) and (c) **H2PyP** ( $1.4 \times 10^{-6} M$ ) as photosensitizer under photoirradiation with 509 nm ( $300 \mu W cm^{-2}$ ) in  $CH_2Cl_2/MeOH$  (=1/1, v/v).





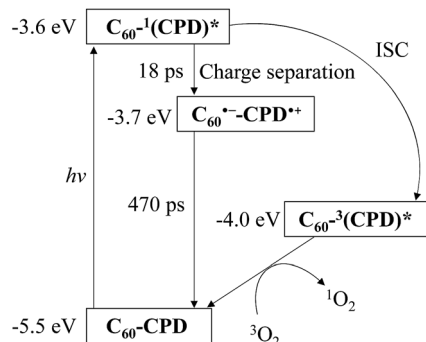
**Fig. 4** (a) Plots of  $\Delta OD$  for DPBF against the photoirradiation time for the photooxidation of DPBF using CPD,  $C_{60}\text{-CPD}$ , H2PyP or Rose Bengal as photosensitizers under photoirradiation with 509 nm ( $300 \mu\text{W cm}^{-2}$ ) in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v) and MeOH, respectively. (b) Plots of  $\ln(C_t/C_0)$  for DHN against the photoirradiation time for the photooxidation of DHN using CPD,  $C_{60}\text{-CPD}$ , H2PyP or Rose Bengal as photosensitizers under photoirradiation with visible light ( $>385 \text{ nm}$ ,  $30 \text{ mW cm}^{-2}$ ) in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v).

**Table 1**  $^1\text{O}_2$  quantum yield ( $\Phi_\Delta$ ) and first-order rate constant ( $K_{\text{obs}}$ ) for the photooxidation of DPBF and DHN in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v), respectively, using CPD,  $C_{60}\text{-CPD}$  or H2PyP as photosensitizer

Photosensitizer	$\Phi_\Delta^a$	$K_{\text{obs}}^b/\text{min}^{-1}$
CPD	0.62	$6.6 \times 10^{-3}$
$C_{60}\text{-CPD}$	0.52	$5.8 \times 10^{-3}$
H2PyP	0.91	$9.5 \times 10^{-3}$

<sup>a</sup>  $^1\text{O}_2$  quantum yield (relative decomposition rate of DPBF), with Rose Bengal (RB) as standard ( $\Phi_\Delta = 0.80$  in methanol,<sup>15</sup> see Fig. S1) and 3-diphenylisobenzofuran (DPBF) as  $^1\text{O}_2$  scavenger. <sup>b</sup> First-order rate constant for the reaction of DHN with  $^1\text{O}_2$  generated upon photoexcitation of the photosensitizer. The  $K_{\text{obs}}$  for RB is  $5.3 \times 10^{-3} \text{ min}^{-1}$  (see Fig. S2).

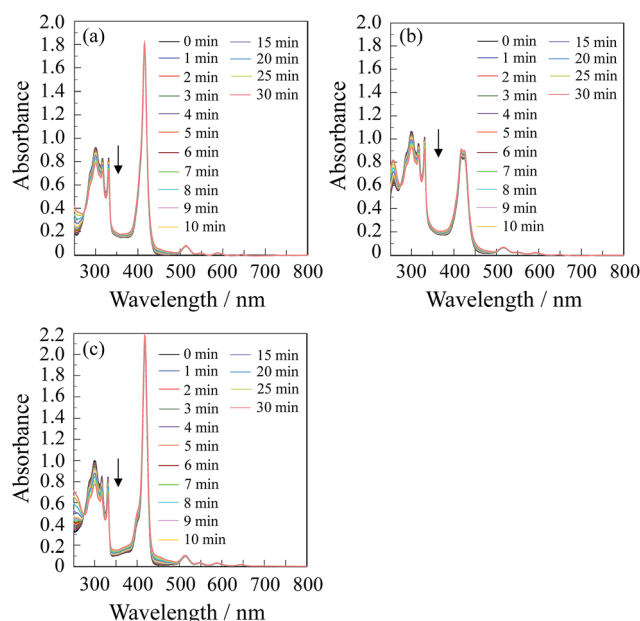
state of  $C_{60}\text{-CPD}$  has two steps (Fig. 5): the first step has a lifetime of 18 ps, which corresponds to the disappearance of the singlet excited state of  $C_{60}^1\text{(CPD)}^*$  (*ca.*  $-3.6 \text{ eV}$ ), that is,  $C_{60}^1\text{(CPD)}^*$  undergoes intrasupramolecular electron transfer to give a completely charge-separated state  $C_{60}^{\cdot-}\text{-CPD}^{\cdot+}$  (*ca.*  $-3.7 \text{ eV}$ ).<sup>13</sup>  $C_{60}^{\cdot-}\text{-CPD}^{\cdot+}$  decays with a lifetime of 470 ps to the ground state. The singlet excited state  $C_{60}^1\text{(CPD)}^*$  has a slower ISC to its triplet excited state  $C_{60}^3\text{(CPD)}^*$  (*ca.*  $-4.0 \text{ eV}$ ), in addition, the  $C_{60}^3\text{(CPD)}^*$  would undergo energy transfer to  $C_{60}$ , leading to the



**Fig. 5** The photodynamics of  $C_{60}\text{-CPD}$  and  $^1\text{O}_2$  generation.

formation of  $^3C_{60}^*\text{(CPD)}$ . Thus, on the basis of the photodynamics of the cyclic free-base porphyrin dimer and its inclusion complex with  $C_{60}$ , the lower  $\Phi_\Delta$  value of the  $C_{60}$  inclusion complex would be attributed to the formation of charge-separated state, leading to low ISC efficiency because the ISC is in kinetically competition with the intrasupramolecular electron transfer, that is, the formation of triplet excited state  $^3\text{(CPD)}^*$  is in kinetically unfavorable compared to that of the charge-separated state  $C_{60}^{\cdot-}\text{-CPD}^{\cdot+}$ .

In order to evaluate the photosensitizing ability of the cyclic free-base porphyrin dimer and its inclusion complex with  $C_{60}$ , the  $\ln(C_t/C_0)$  is plotted against the photoirradiation time, where  $C_t$  is a concentration of 1,5-dihydroxynaphthalene (DHN) at the reaction time ( $t$ ) and  $C_0$  is the initial concentration of DHN before photoirradiation.  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v) were bubbled with air for 15 min. The air-saturated solution containing CPD or  $C_{60}\text{-CPD}$  and DHN was irradiated with visible light ( $>385 \text{ nm}$ ,  $30 \text{ mW cm}^{-2}$ ) obtained by passage of xenon light through a 385 nm long path filter. The photoabsorption spectral changes for the photooxidation of DHN using CPD,  $C_{60}\text{-CPD}$  or H2PyP under photoirradiation with the visible light in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v) are shown in Fig. 6. Evidently, the absorption band of DHN at around 300 nm decreased with the increase in the photoirradiation time. The plots of  $\ln(C_t/C_0)$  against the photoirradiation time indicate that for CPD,  $C_{60}\text{-CPD}$  and H2PyP the  $\ln(C_t/C_0)$  decreased almost linearly with the increase in the photoirradiation time (Fig. 4b). Thus, this result indicates the  $\ln(C_t/C_0)$  bears a linear relationship with the photoirradiation time to provide the first-order rate constants ( $K_{\text{obs}}$ ) for the photooxidation of DHN using the cyclic free-base porphyrin dimer or its inclusion complex with  $C_{60}$  as the



**Fig. 6** Photoabsorption spectral changes for the photooxidation of DHN ( $1.0 \times 10^{-4} \text{ M}$ ) using (a) CPD ( $2.5 \times 10^{-6} \text{ M}$ ), (b)  $C_{60}\text{-CPD}$  ( $2.5 \times 10^{-6} \text{ M}$ ) and (c) H2PyP ( $5.0 \times 10^{-6} \text{ M}$ ) as photosensitizer under photoirradiation with visible light ( $>385 \text{ nm}$ ,  $30 \text{ mW cm}^{-2}$ ) in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v).



photosensitizer (Table 1). Obviously, the higher  $K_{\text{obs}}$  values of the cyclic free-base porphyrin dimer and its inclusion complex with  $C_{60}$  relative to RB (see Fig. S2†) are due to the contribution of the strong Soret band of the cyclic free-base porphyrin skeleton, although the  $K_{\text{obs}}$  values of CPD and  $C_{60}\text{CPD}$  are lower than that of H2PyP ( $9.5 \times 10^{-3} \text{ min}^{-1}$ ). It is worth noting here that the  $K_{\text{obs}}$  value ( $6.6 \times 10^{-3} \text{ min}^{-1}$ ) of CPD is greater than that ( $5.8 \times 10^{-3} \text{ min}^{-1}$ ) of  $C_{60}\text{CPD}$ . Therefore, this result demonstrates that CPD exhibits more efficient photosensitizing ability due to the effective ISC compared to  $C_{60}\text{CPD}$ .

In addition, we performed an electron paramagnetic resonance (EPR) method with 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TEMP) as the spin-trapping agent, which can react with  $^1\text{O}_2$  to produce 4-oxo-TEMPO as a stable nitroxide radical.<sup>16</sup> When the air-saturated solution containing CPD,  $C_{60}\text{CPD}$  or H2PyP and 4-oxo-TEMP was irradiated with visible light ( $>385 \text{ nm}$ ,  $30 \text{ mW cm}^{-2}$ ) obtained by passage of xenon light through a 385 nm long path filter, for both the free-base porphyrin dimer and its inclusion complex with  $C_{60}$  as well as H2PyP the ESR spectra of 4-oxo-TEMPO were clearly observed as a characteristic 1 : 1 : 1 triplet (Fig. 7). Consequently, this work demonstrated that the cyclic free-base porphyrin dimer and its inclusion complex with  $C_{60}$  possess the ability to generate  $^1\text{O}_2$  under visible light irradiation.

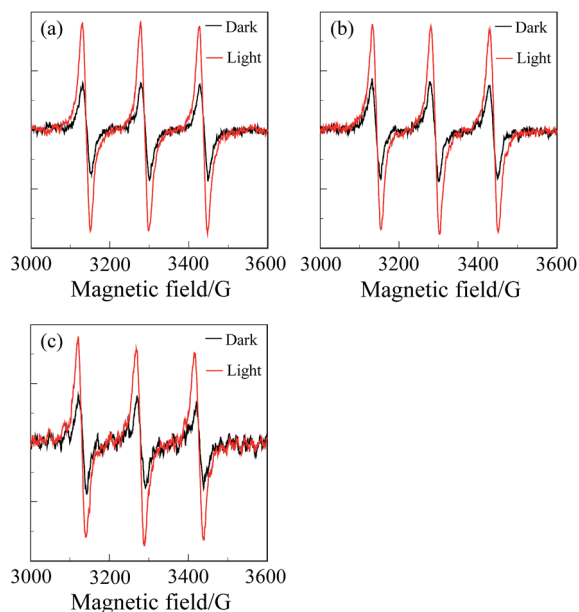


Fig. 7 The ESR spectra of 4-oxo-TEMPO which is formed by the reaction of 4-oxo-TEMP with  $^1\text{O}_2$  which was generated by (a) CPD, (b)  $C_{60}\text{CPD}$  and (c) H2PyP under irradiation with visible light (temperature 298 K, microwave power 1 mW, microwave frequency 9.439 GHz, and field modulation 0.2 mT at 100 kHz). The air-saturated  $\text{CH}_2\text{Cl}_2$  solution containing CPD ( $2.5 \times 10^{-6} \text{ M}$ ),  $C_{60}\text{CPD}$  ( $2.5 \times 10^{-6} \text{ M}$ ) or H2PyP ( $5.0 \times 10^{-6} \text{ M}$ ) as the photosensitizer and 4-oxo-TEMP (50 mM) as the spin-trapping agent was irradiated with visible light ( $>385 \text{ nm}$ ,  $30 \text{ mW cm}^{-2}$  for 1 h) obtained by passage of xenon light through a 385 nm long path filter, where  $\text{CH}_2\text{Cl}_2$  as low polar solvent was used because it was difficult to obtain a clear ESR signal in polar solvent such as  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v).

## Conclusions

To investigate singlet oxygen ( $^1\text{O}_2$ ) generation properties of cyclic free-base porphyrin dimer and its inclusion complex with fullerene  $C_{60}$ , we evaluated the  $^1\text{O}_2$  quantum yield ( $\Phi_{\Delta}$ ) and rate constant ( $K_{\text{obs}}$ ) of  $^1\text{O}_2$  generation for cyclic free-base porphyrin dimer CPD and its inclusion complex  $C_{60}\text{CPD}$  with  $C_{60}$ . It was found that the  $\Phi_{\Delta}$  value of  $C_{60}\text{CPD}$  is lower than that of CPD. The lower  $\Phi_{\Delta}$  value of the  $C_{60}$  inclusion complex would be attributed to the formation of charge-separated state  $c_{60}^{\cdot-}\text{CPD}^{\cdot+}$ , leading to low intersystem crossing (ISC) efficiency for the formation of triplet excited state  $^3(\text{CPD})^*$ , although it was expected that the formation of  $c_{60}^{\cdot-}\text{CPD}^{\cdot+}$  is favorable for  $^1\text{O}_2$  generation. Consequently, this work demonstrates that the cyclic free-base porphyrin dimer and its supramolecular complex with  $C_{60}$  possess the ability to generate  $^1\text{O}_2$  under visible light irradiation.

## Experimental

### Evaluation of $^1\text{O}_2$ quantum yield

Quantum yield ( $\Phi_{\Delta}$ ) for singlet oxygen ( $^1\text{O}_2$ ) generation by cyclic free-base porphyrin dimer CPD, its inclusion complex  $C_{60}\text{CPD}$  with fullerene  $C_{60}$  and H2PyP in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (=1/1, v/v) was evaluated by monitoring the photoabsorption spectral change of the known  $^1\text{O}_2$  scavenger 1,3-diphenylisobenzofuran (DPBF) accompanied by the reaction of DPBF with the generated  $^1\text{O}_2$ , that is, DPBF can trap  $^1\text{O}_2$  through its photooxidation.  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  was bubbled with air for 15 min. The absorbance of DPBF was adjusted to around 1.0 in air-saturated solvent. Concentration of CPD,  $C_{60}\text{CPD}$  or H2PyP was adjusted with an absorbance of ca. 0.03 at the irradiation wavelength (509 nm). The air-saturated solution containing the photosensitizer (CPD,  $C_{60}\text{CPD}$  or H2PyP) and DPBF was irradiated with 509 nm ( $300 \mu\text{W cm}^{-2}$ ) obtained by passage of xenon light through monochromator. The photoabsorption spectral change of DPBF with the photoirradiation was monitored with an interval of 1 min up to 10 min. The absorption band of DPBF at around 410 nm decreased with the increase in the photoirradiation time. The changes in optical density ( $\Delta\text{OD}$ ) of DPBF are plotted against the photoirradiation time, and the slope is used to estimate the  $\Phi_{\Delta}$  values of CPD,  $C_{60}\text{CPD}$  and H2PyP. The  $\Phi_{\Delta}$  values of CPD,  $C_{60}\text{CPD}$  and H2PyP were estimated by the relative method using Rose Bengal (RB) ( $\Phi_{\Delta} = 0.80$ ) in methanol as the standard. Therefore, the  $^1\Phi_{\Delta}$  values were calculated according to the following eqn (1):

$$\Phi_{\Delta\text{sam}} = \Phi_{\Delta\text{ref}} \times [(m_{\text{sam}}/m_{\text{ref}}) \times (L_{\text{ref}}/L_{\text{sam}})] \quad (1)$$

where  $\Phi_{\Delta\text{sam}}$  and  $\Phi_{\Delta\text{ref}}$  are the  $^1\text{O}_2$  quantum yield of photosensitizer (CPD,  $C_{60}\text{CPD}$  or H2PyP) and RB, respectively,  $m_{\text{sam}}$  and  $m_{\text{ref}}$  are the slope of the difference ( $\Delta\text{OD}$ ) in the change in the absorption maximum wavelength of DPBF (around 410 nm) which are plotted against the photoirradiation time,  $L_{\text{sam}}$  and  $L_{\text{ref}}$  are the light harvesting



efficiency, which is given by  $L = 1 - 10^{-A}$  ("A" is the absorbance at the photoirradiation wavelength).

### Photosensitizing ability

Photosensitizing ability of CPD, C<sub>60</sub>C-CPD and H2PyP in CH<sub>2</sub>Cl<sub>2</sub>/MeOH was evaluated by plotting the  $\ln(C_t/C_0)$  against the photoirradiation time, where  $C_t$  is a concentration of 1,5-dihydroxynaphthalene (DHN) at the reaction time ( $t$ ) and  $C_0$  is the initial concentration of DHN before photoirradiation. CH<sub>2</sub>Cl<sub>2</sub>/MeOH was bubbled with air for 15 min. The air-saturated solution containing the photosensitizer ( $2.5 \times 10^{-6}$  M for CPD and C<sub>60</sub>C-CPD,  $5.0 \times 10^{-6}$  M for H2PyP and  $2.5 \times 10^{-6}$  M for RB) and DHN ( $1.0 \times 10^{-4}$  M) was irradiated with visible light ( $>385$  nm,  $30$  mW cm<sup>-2</sup>) obtained by passage of xenon light through a 385 nm long path filter. The photooxidation of DHN with the photoirradiation was monitored by following the decrease in the photoabsorption at around 300 nm with an interval of 1 min up to 10 min and then an interval of 5 min up to 30 min. The concentration ( $C_t$ ) of DHN at the reaction time ( $t$ ) was calculated based on Lambert-Beer law ( $A_{\text{DPBF}} = \epsilon cl$ ). The  $\ln(C_t/C_0)$  decreased almost linearly with the increase in the photoirradiation time due to the photooxidation of DHN, that is, the slope was used to estimate the rate constants ( $K_{\text{obs}}$ ).

### <sup>1</sup>O<sub>2</sub> detection by EPR spin-trapping method with 4-oxo-TEMP

The EPR spectra were recorded on a JEOL JES-RE1X spectrometer under the following experimental conditions: temperature 298 K, microwave power 1 mW, microwave frequency 9.439 GHz, and field modulation 0.2 mT at 100 kHz. The air-saturated CH<sub>2</sub>Cl<sub>2</sub> solution containing CPD ( $2.5 \times 10^{-6}$  M), C<sub>60</sub>C-CPD ( $2.5 \times 10^{-6}$  M) or H2PyP ( $5.0 \times 10^{-6}$  M) as the photosensitizer and 4-oxo-TEMP (50 mM) as the spin-trapping agent was irradiated with visible light ( $>385$  nm,  $30$  mW cm<sup>-2</sup> for 1 h) obtained by passage of xenon light through a 385 nm long path filter. The ESR spectrum of 4-oxo-TEMPO which is formed by the reaction of 4-oxo-TEMP with <sup>1</sup>O<sub>2</sub>, was clearly observed as a characteristic 1 : 1 : 1 triplet (Fig. 7).

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