

electron transfer (charge separation) between photosensitizer and C_{60} .^{11,12}

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).¹³ 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 Φ_{Δ} 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, λ_{max}^{abs}/nm ($\epsilon/M^{-1} cm^{-1}$) = 416 (708 000), 514 (31 200), 548 (7400), 587 (9000), 642 (2900)). The molar extinction coefficients (ϵ) of Soret and Q bands for **CPD** are higher than those of **H2PyP** (λ_{max}^{abs}/nm ($\epsilon/M^{-1} cm^{-1}$) = 418 (419 000), 513 (19 200), 548 (6200), 588 (6000), 643 (3000))^{13e} 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.¹³ 1O_2 generation by **CPD**, $C_{60} \subset CPD$ or **H2PyP** in $CH_2Cl_2/MeOH$ (=1/1, v/v) was evaluated by monitoring

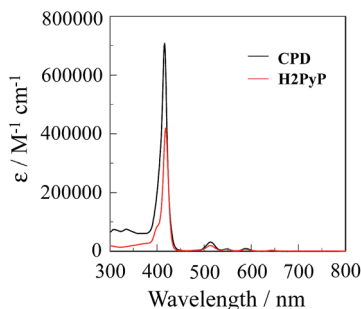


Fig. 2 Photoabsorption spectra of **CPD** and **H2PyP** in $CH_2Cl_2/MeOH$.

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.¹⁴ $CH_2Cl_2/MeOH$ 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 (ΔOD) of DPBF are plotted against the photoirradiation time (Fig. 4a), and the slope (m_{sl}) is used to estimate the Φ_{Δ} value for **CPD**, $C_{60} \subset CPD$ and **H2PyP**. The m_{sl} value (-1.5×10^{-2}) of **H2PyP** is larger than those of **CPD** (-1.2×10^{-2}) and $C_{60} \subset CPD$ (-9.8×10^{-3}). Moreover, it was revealed that the m_{sl} value of **CPD** is larger than that of $C_{60} \subset CPD$. Thus, the Φ_{Δ} 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 methanol¹⁵ as the standard (Table 1). The Φ_{Δ} 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 Φ_{Δ} value of $C_{60} \subset CPD$ is lower than that of **CPD**. Our previous work demonstrates that the decay of photoexcited

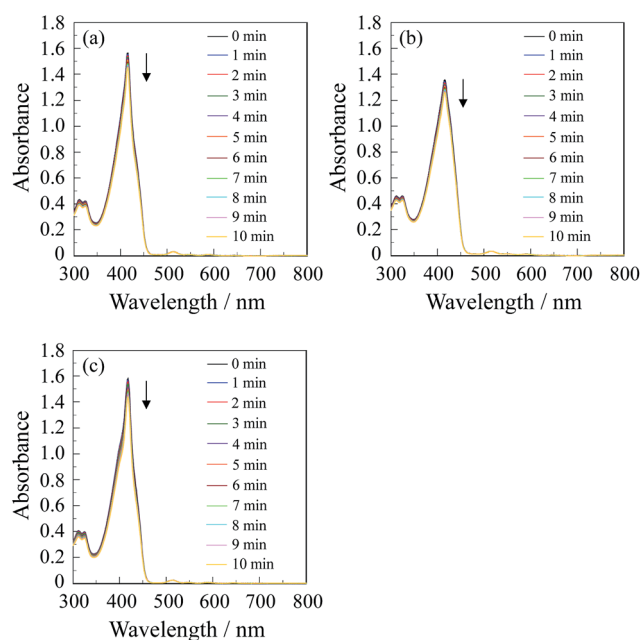


Fig. 3 Photoabsorption spectral changes for the photooxidation of DPBF (Abs. = ca. 1.0) using (a) **CPD** ($1.3 \times 10^{-6} M$), (b) $C_{60} \subset CPD$ ($1.0 \times 10^{-6} M$) and (c) **H2PyP** ($1.4 \times 10^{-6} M$) as photosensitizer under photoirradiation with 509 nm ($300 \mu W cm^{-2}$)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



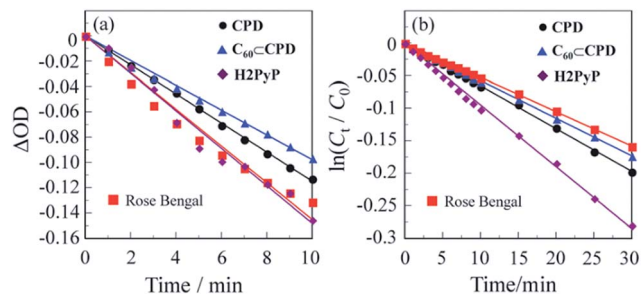


Fig. 4 (a) Plots of ΔOD for DPBF against the photoirradiation time for the photooxidation of DPBF using CPD, $C_{60}\text{-CPD}$, H2PyP or Rose Bengal as photosensitizers under photoirradiation with 509 nm ($300 \mu\text{W cm}^{-2}$) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (=1/1, v/v) and MeOH, respectively. (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 mW cm^{-2}) in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (=1/1, v/v).

Table 1 $^1\text{O}_2$ quantum yield (Φ_Δ) and first-order rate constant (K_{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	Φ_Δ^a	$K_{\text{obs}}^b/\text{min}^{-1}$
CPD	0.62	6.6×10^{-3}
$C_{60}\text{-CPD}$	0.52	5.8×10^{-3}
H2PyP	0.91	9.5×10^{-3}

^a $^1\text{O}_2$ quantum yield (relative decomposition rate of DPBF), with Rose Bengal (RB) as standard ($\Phi_\Delta = 0.80$ in methanol,¹⁵ see Fig. S1) and 3-diphenylisobenzofuran (DPBF) as $^1\text{O}_2$ scavenger. ^b First-order rate constant for the reaction of DHN with $^1\text{O}_2$ generated upon photoexcitation of the photosensitizer. The K_{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 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 eV).¹³ $c_{60}^{\cdot-}\text{-CPD}^{\cdot+}$ 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 eV), in addition, the $C_{60}^3(\text{CPD})^*$ would undergo energy transfer to C_{60} , leading to the

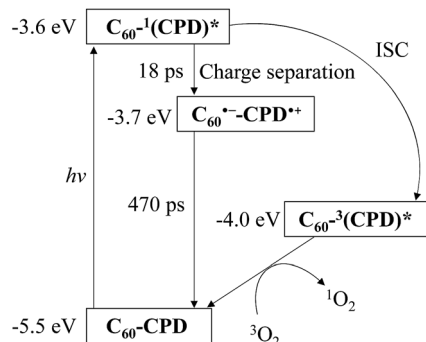


Fig. 5 The photodynamics of $C_{60}\text{-CPD}$ and $^1\text{O}_2$ generation.

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 Φ_Δ 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 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_{obs}) for the photooxidation of DHN using the cyclic free-base porphyrin dimer or its inclusion complex with C_{60} as the

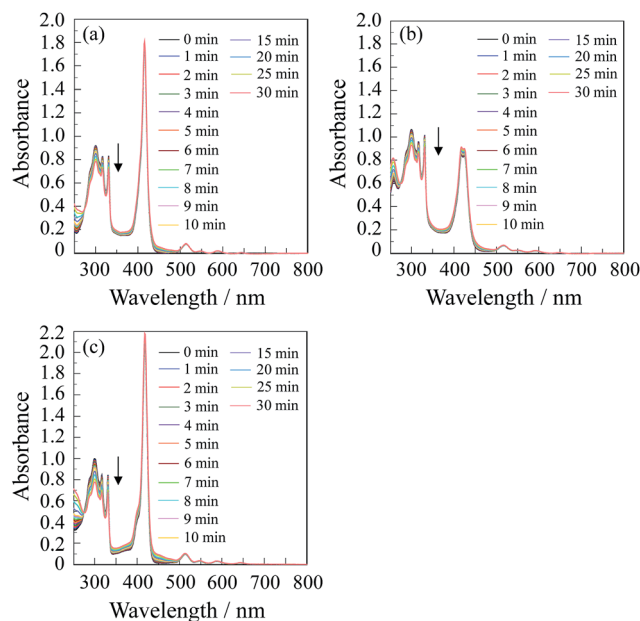


Fig. 6 Photoabsorption spectral changes for the photooxidation of DHN ($1.0 \times 10^{-4} \text{ M}$) using (a) CPD ($2.5 \times 10^{-6} \text{ M}$), (b) $C_{60}\text{-CPD}$ ($2.5 \times 10^{-6} \text{ M}$) and (c) H2PyP ($5.0 \times 10^{-6} \text{ M}$) as photosensitizer under photoirradiation with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



photosensitizer (Table 1). Obviously, the higher K_{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_{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_{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.¹⁶ 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 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.

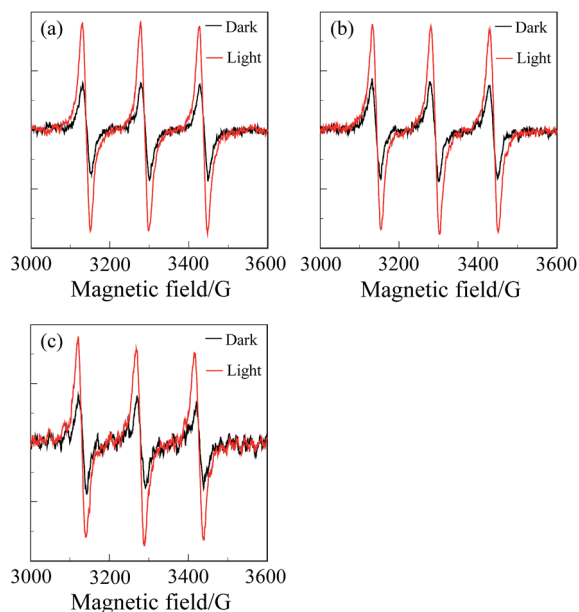


Fig. 7 The ESR spectra of 4-oxo-TEMPO which is formed by the reaction of 4-oxo-TEMP with $^1\text{O}_2$ which was generated by (a) CPD, (b) $C_{60}\text{CPD}$ and (c) H2PyP under irradiation with visible light (temperature 298 K, microwave power 1 mW, microwave frequency 9.439 GHz, and field modulation 0.2 mT at 100 kHz). The air-saturated CH_2Cl_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 mW cm^{-2} for 1 h) obtained by passage of xenon light through a 385 nm long path filter, where CH_2Cl_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 (Φ_{Δ}) and rate constant (K_{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 Φ_{Δ} value of $C_{60}\text{CPD}$ is lower than that of CPD. The lower Φ_{Δ} 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 (Φ_{Δ}) 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 (ΔOD) of DPBF are plotted against the photoirradiation time, and the slope is used to estimate the Φ_{Δ} values of CPD, $C_{60}\text{CPD}$ and H2PyP. The Φ_{Δ} 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_{sam} and m_{ref} are the slope of the difference (ΔOD) in the change in the absorption maximum wavelength of DPBF (around 410 nm) which are plotted against the photoirradiation time, L_{sam} and L_{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, C₆₀C-CPD and H2PyP in CH₂Cl₂/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. CH₂Cl₂/MeOH was bubbled with air for 15 min. The air-saturated solution containing the photosensitizer (2.5×10^{-6} M for CPD and C₆₀C-CPD, 5.0×10^{-6} M for H2PyP and 2.5×10^{-6} M for RB) and DHN (1.0×10^{-4} M) was irradiated with visible light (>385 nm, 30 mW cm⁻²) 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 ($A_{\text{DPBF}} = \epsilon c l$). 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_{obs}).

¹O₂ 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 CH₂Cl₂ solution containing CPD (2.5×10^{-6} M), C₆₀C-CPD (2.5×10^{-6} M) or H2PyP (5.0×10^{-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⁻² 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 ¹O₂, was clearly observed as a characteristic 1 : 1 : 1 triplet (Fig. 7).

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