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Singlet oxygen generation properties of an inclusion complex of cyclic free-base porphyrin dimer and fullerene C_{60}†

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To gain insight into the singlet oxygen ($^1O_2$) generation properties of supramolecular complexes of cyclic free-base porphyrin dimer with fullerene C_{60}, we evaluated the $^1O_2$ quantum yield (Φ_Δ) and rate constant (K_{obs}) of $^1O_2$ generation for a cyclic free-base porphyrin dimer (**CPD**) linked by butadiyne bearing four 4-pyridyl groups and its inclusion complex (**C_{60}⊂CPD**) with C_{60}. We demonstrate that **CPD** and **C_{60}⊂CPD** possess the ability to generate $^1O_2$ under visible light irradiation. Moreover, it was found that the Φ_Δ value of **C_{60}⊂CPD** is lower than that of **CPD**. Based on the kinetic and thermodynamic consideration concerning the electron transfer processes between the porphyrin dimer and C_{60}, this work revealed that the lower Φ_Δ value of the C_{60} inclusion complex would be attributed to the formation of the charge-separated state $C_{60}^{\cdot-}$-**CPD**$^{\cdot+}$, leading to a low intersystem crossing (ISC) efficiency for the formation of the triplet excited state ^{3}(**CPD**)*.

Introduction

Photosensitizers possessing the ability to generate singlet oxygen ($^1O_2$) have created considerable interest in recent years from the viewpoint of fundamental studies in photochemistry and their potential applications in photodynamic therapy (PDT).[1–6] These photosensitizers generally produce $^1O_2$ through the following processes: initially the photosensitizer absorbs light ($h\nu$) to generate the singlet excited state of the photosensitizer ($^1S^*$), then the photoexcited sensitizer ($^1S^*$) undergoes intersystem crossing (ISC) to generate the triplet excited state ($^3S^*$). Subsequent energy transfer from the photoexcited sensitizer ($^3S^*$) to triplet oxygen ($^3O_2$) produces $^1O_2$. Thus, to generate $^3S^*$ efficiency is one of the most effective strategies to give high $^1O_2$ quantum yield (Φ_Δ). In particular, porphyrin dyes have been regarded as promising candidates for photosensitizers as a result of their strong Soret (400–500 nm) and moderate Q band (500–700 nm) absorption properties, as well as their electrochemical, photochemical and thermal stabilities. The typical photosensitizer, free-base tetraphenylporphyrin (H_2TPP) exhibits Φ_Δ value of 0.6–0.7 (in benzene).[7] Much effort in molecular design and development of porphyrin photosensitizers have been made to further improve the Φ_Δ value so far.[7–11] Some researchers reported that porphyrin–fullerene C_{60} dyads as well as boron dipyrromethene (BODIPY)-C_{60} dyads exhibits a higher Φ_Δ value than each porphyrin or C_{60}, which is attributed to the formation of long-lived triplet excited state ($^3S^*$) by the effective ISC due to intramolecular energy transfer or

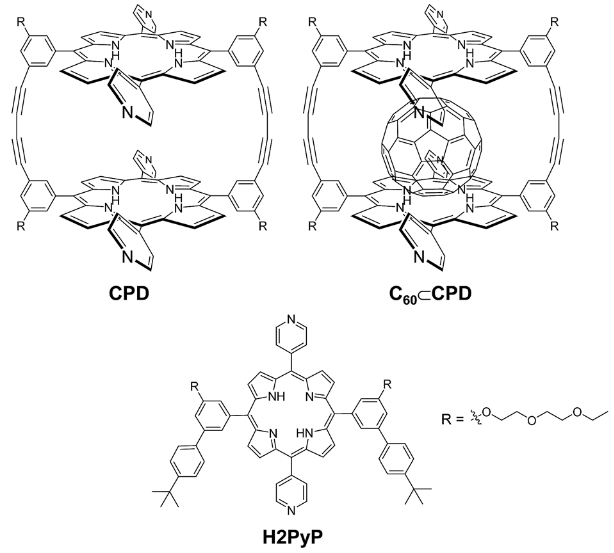

Fig. 1 Chemical structures of cyclic free-base porphyrin dimer (**CPD**) linked by butadiyne bearing four 4-pyridyl groups, its inclusion complex (**C_{60}⊂CPD**) with C_{60} and ABAB porphyrin monomer **H2PyP** as a reference.

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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}⊂CPD** with C_{60} (Fig. 1).[13] It was expected that **C_{60}⊂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}⊂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^{abs}_{max}/nm (ε/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^{abs}_{max}/nm (ε/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}⊂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}⊂CPD** or **H2PyP** in CH_2Cl_2/MeOH (=1/1, v/v) was evaluated by monitoring 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}⊂CPD** or **H2PyP** and DPBF was irradiated with 509 nm (300 μW cm^{-2}, ε = 27 300 M^{-1} cm^{-1}@λ^{abs} = 509 nm for **CPD** and ε = 17 000 M^{-1} cm^{-1}@λ^{abs} = 509 nm for **H2PyP**, respectively) obtained by passage of xenon light through monochromator. For both **CPD** and **C_{60}⊂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}⊂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}⊂CPD** (-9.8×10^{-3}). Moreover, it was revealed that the m_{sl} value of **CPD** is larger than that of **C_{60}⊂CPD**. Thus, the Φ_Δ values of **CPD**, **C_{60}⊂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[15] as the standard (Table 1). The Φ_Δ value of **CPD**, **C_{60}⊂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}⊂CPD** is lower than that of **CPD**. Our previous work demonstrates that the decay of photoexcited

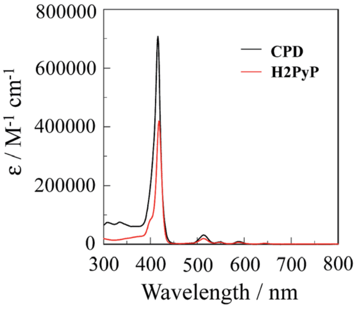

Fig. 2 Photoabsorption spectra of **CPD** and **H2PyP** in CH_2Cl_2/MeOH.

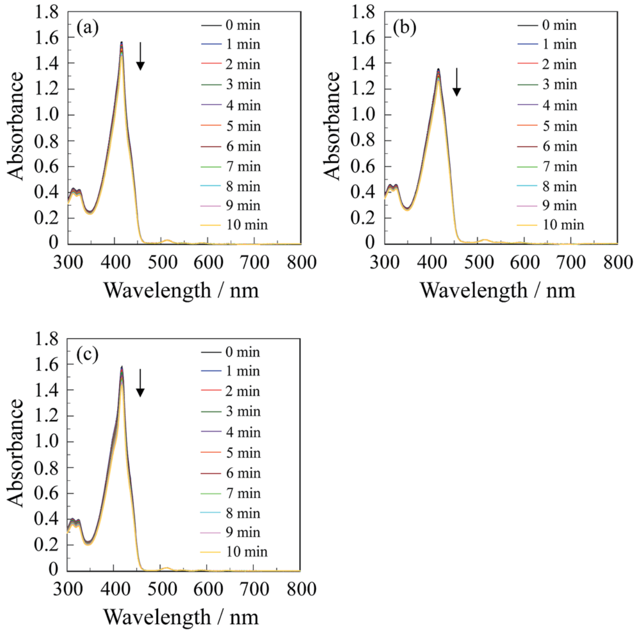

Fig. 3 Photoabsorption spectral changes for the photooxidation of DPBF (Abs. = *ca.* 1.0) using (a) **CPD** (1.3×10^{-6} M), (b) **C_{60}⊂CPD** (1.0×10^{-6} M) and (c) **H2PyP** (1.4×10^{-6} M) as photosensitizer under photoirradiation with 509 nm (300 μW cm^{-2}) in CH_2Cl_2/MeOH (=1/1, v/v).

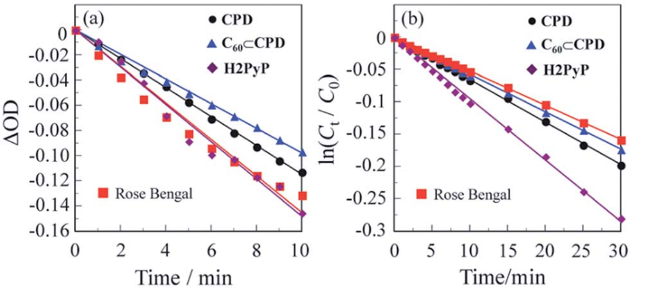

Fig. 4 (a) Plots of ΔOD for DPBF against the photoirradiation time for the photooxidation of DPBF using **CPD**, **C_{60}⊂CPD**, **H2PyP** or Rose Bengal as photosensitizers under photoirradiation with 509 nm (300 μW cm^{-2}) in CH_2Cl_2/MeOH (=1/1, v/v) and MeOH, respectively. (b) Plots of ln(C_t/C_0) for DHN against the photoirradiation time for the photooxidation of DHN using **CPD**, **C_{60}⊂CPD**, **H2PyP** or Rose Bengal as photosensitizers under photoirradiation with visible light (>385 nm, 30 mW cm^{-2}) in CH_2Cl_2/MeOH (=1/1, v/v).

Table 1 $^1O_2$ quantum yield (Φ_Δ) and first-order rate constant (K_{obs}) for the photooxidation of DPBF and DHN in CH_2Cl_2/MeOH (=1/1, v/v), respectively, using **CPD**, **C_{60}⊂CPD** or **H2PyP** as photosensitizer

Photosensitizer	Φ_Δ^{a}	K_{obs}^{b}/min^{-1}
CPD	0.62	6.6×10^{-3}
C_{60}⊂CPD	0.52	5.8×10^{-3}
H2PyP	0.91	9.5×10^{-3}

[a] $^1O_2$ 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 $^1O_2$ scavenger. [b] First-order rate constant for the reaction of DHN with $^1O_2$ generated upon photoexcitation of the photosensitizer. The K_{obs} for RB is 5.3×10^{-3} min^{-1} (see Fig. S2).

state of **C_{60}⊂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}(CPD)*** (*ca.* −3.6 eV), that is, **C_{60}-^{1}(CPD)*** undergoes intrasupramolecular electron transfer to give a completely charge-separated state **$C_{60}^{\cdot -}$-CPD$^{\cdot +}$** (*ca.* −3.7 eV).[13] **$C_{60}^{\cdot -}$-CPD$^{\cdot +}$** decays with a lifetime of 470 ps to the ground state. The singlet excited state **C_{60}-^{1}(CPD)*** has a slower ISC to its triplet excited state **C_{60}-^{3}(CPD)*** (*ca.* −4.0 eV), in addition, the **C_{60}-^{3}(CPD)*** would undergo energy transfer to C_{60}, leading to the formation of **$^3C_{60}$*-(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}(CPD)*** is in kinetically unfavorable compared to that of the charge-separated state **$C_{60}^{\cdot -}$-CPD$^{\cdot +}$**.

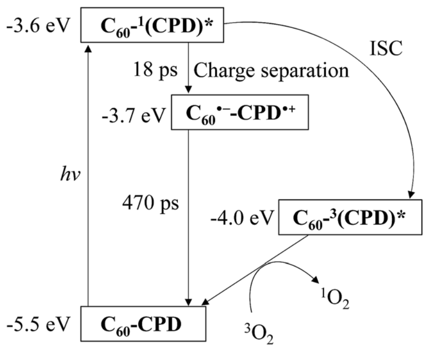

Fig. 5 The photodynamics of C_{60}⊂CPD and $^1O_2$ generation.

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. CH_2Cl_2/MeOH (=1/1, v/v) were bubbled with air for 15 min. The air-saturated solution containing **CPD** or **C_{60}⊂CPD** and DHN 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 photoabsorption spectral changes for the photooxidation of DHN using **CPD**, **C_{60}⊂CPD** or **H2PyP** under photoirradiation with the visible light in CH_2Cl_2/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}⊂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

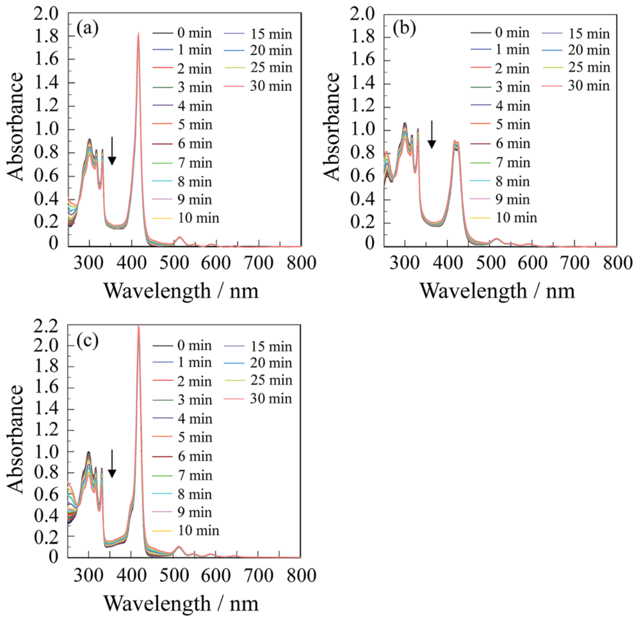

Fig. 6 Photoabsorption spectral changes for the photooxidation of DHN (1.0×10^{-4} M) using (a) **CPD** (2.5×10^{-6} M), (b) **C_{60}⊂CPD** (2.5×10^{-6} M) and (c) **H2PyP** (5.0×10^{-6} M) as photosensitizer under photoirradiation with visible light (>385 nm, 30 mW cm^{-2}) in CH_2Cl_2/MeOH (=1/1, v/v).

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}⊂CPD** are lower than that of **H2PyP** (9.5×10^{-3} min^{-1}). It is worth noting here that the K_{obs} value (6.6×10^{-3} min^{-1}) of **CPD** is greater than that (5.8×10^{-3} min^{-1}) of **C_{60}⊂CPD**. Therefore, this result demonstrates that **CPD** exhibits more efficient photosensitizing ability due to the effective ISC compared to **C_{60}⊂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 $^1O_2$ to produce 4-oxo-TEMPO as a stable nitroxide radical.[16] When the air-saturated solution containing **CPD**, **C_{60}⊂CPD** or **H2PyP** and 4-oxo-TEMP was irradiated with visible light (>385 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 $^1O_2$ under visible light irradiation.

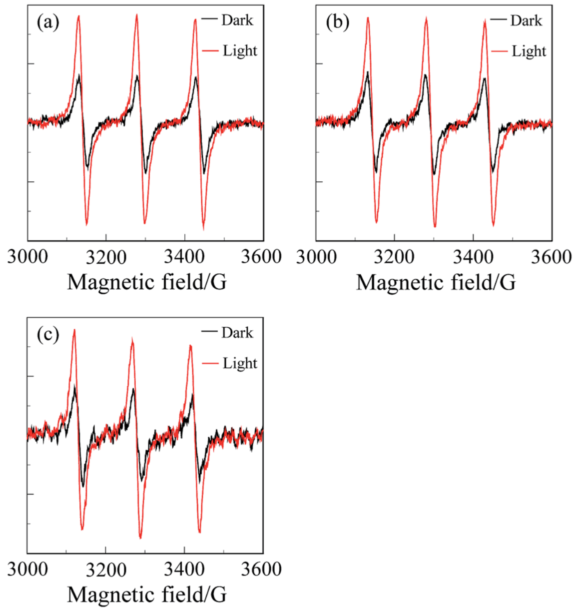

Fig. 7 The ESR spectra of 4-oxo-TEMPO which is formed by the reaction of 4-oxo-TEMP with $^1O_2$ which was generated by (a) **CPD**, (b) **C_{60}⊂CPD** and (c) **H2PyP** under irradiation with visible light (temperature 298 K, microwave power 1 mW, microwave frequency 9.439 GHz, and field modulation 0.2 mT at 100 kHz). The air-saturated CH_2Cl_2 solution containing **CPD** (2.5×10^{-6} M), **C_{60}⊂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, 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 CH_2Cl_2/MeOH (=1/1, v/v).

Conclusions

To investigate singlet oxygen ($^1O_2$) generation properties of cyclic free-base porphyrin dimer and its inclusion complex with fullerene C_{60}, we evaluated the $^1O_2$ quantum yield (Φ_Δ) and rate constant (K_{obs}) of $^1O_2$ generation for cyclic free-base porphyrin dimer **CPD** and its inclusion complex **C_{60}⊂CPD** with C_{60}. It was found that the Φ_Δ value of **C_{60}⊂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 $C_{60}^{\cdot-}$-**CPD**$^{\cdot+}$, leading to low intersystem crossing (ISC) efficiency for the formation of triplet excited state ^{3}**(CPD)***, although it was expected that the formation of $C_{60}^{\cdot-}$-**CPD**$^{\cdot+}$ is favorable for $^1O_2$ generation. Consequently, this work demonstrates that the cyclic free-base porphyrin dimer and its supramolecular complex with C_{60} possess the ability to generate $^1O_2$ under visible light irradiation.

Experimental

Evaluation of $^1O_2$ quantum yield

Quantum yield (Φ_Δ) for singlet oxygen ($^1O_2$) generation by cyclic free-base porphyrin dimer **CPD**, its inclusion complex **C_{60}⊂CPD** with fullerene C_{60} and **H2PyP** in CH_2Cl_2/MeOH (=1/1, v/v) was evaluated by monitoring 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. CH_2Cl_2/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}⊂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}⊂CPD** or **H2PyP**) and DPBF was irradiated with 509 nm (300 μW 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}⊂CPD** and **H2PyP**. The Φ_Δ values of **CPD**, **C_{60}⊂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):

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

where $\Phi_{\Delta\mathrm{sam}}$ and $\Phi_{\Delta\mathrm{ref}}$ are the $^1O_2$ quantum yield of photosensitizer (**CPD**, **C_{60}⊂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**, **C_{60}⊂CPD** and **H2PyP** in CH_2Cl_2/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_2Cl_2/MeOH was bubbled with air for 15 min. The air-saturated solution containing the photosensitizer (2.5×10^{-6} M for **CPD** and **C_{60}⊂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 ($A_{\mathrm{DPBF}} = \varepsilon cl$). 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_{obs}).

$^1O_2$ 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_2Cl_2 solution containing **CPD** (2.5×10^{-6} M), **C_{60}⊂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 $^1O_2$, was clearly observed as a characteristic 1 : 1 : 1 triplet (Fig. 7).

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