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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 (${}^{1}O_{2}$) generation properties of supramolecular complexes of cyclic free-base porphyrin dimer with fullerene C₆₀, we evaluated the ${}^{1}O_{2}$ quantum yield (Φ_{Δ}) and rate constant (\mathcal{K}_{obs}) of ${}^{1}O_{2}$ generation for a cyclic free-base porphyrin dimer (CPD) linked by butadiyne bearing four 4-pyridyl groups and its inclusion complex ($C_{60} \subset CPD$) with C₆₀. We demonstrate that CPD and $C_{60} \subset CPD$ possess the ability to generate ${}^{1}O_{2}$ under visible light irradiation. Moreover, it was found that the Φ_{Δ} value of $C_{60} \subset CPD$ is lower than that of CPD. Based on the kinetic and thermodynamic consideration concerning the electron transfer processes between the porphyrin dimer and C₆₀, this work revealed that the lower Φ_{Δ} value of the C₆₀ inclusion complex would be attributed to the formation of the charge-separated state $c_{60}^{--}-CPD^{-+}$, leading to a low intersystem crossing (ISC) efficiency for the formation of the triplet excited state ${}^{3}(CPD)^{*}$.

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Introduction

Photosensitizers possessing the ability to generate singlet oxygen $({}^{1}O_{2})$ 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 ¹O₂ 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 $({}^{3}S^{*})$ to triplet oxygen $({}^{3}O_{2})$ produces ${}^{1}O_{2}$. Thus, to generate ³S* efficiency is one of the most effective strategies to give high $^{1}O_{2}$ quantum yield (Φ_{Λ}). 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 (H₂TPP) 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 C₆₀ dyads as well as boron dipyrromethene (BODIPY)-C₆₀ dyads exhibits a higher Φ_{Δ} value than each porphyrin or C₆₀, 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 ($C_{60} \subset CPD$) with C_{60} and ABAB porphyrin monomer H2PyP as a reference.

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electron transfer (charge separation) between photosensitizer and C₆₀.11,12

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} - **CPD** + Thus, in this work, to gain insight into the ¹O₂ 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 ${}^{1}O_{2}$ generation for CPD and $C_{60} \subset$ CPD. Here we reveal that cyclic free-base porphyrin dimer and its inclusion complex with fullerene C₆₀ possess the ability to generate ¹O₂ under visible light irradiation, based on the kinetic and thermodynamic consideration concerning the electron transfer processes between the porphyrin dimer and C₆₀.

Results and discussion

The cyclic free-base porphyrin dimer CPD in CH2Cl2/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 (ε) 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))^{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 C₆₀ 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 C₆₀ 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 ¹O₂ generation by CPD, C₆₀⊂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 CH₂Cl₂/MeOH.

the photoabsorption spectral change of the known ¹O₂ scavenger 1,3-diphenylisobenzofuran (DPBF) accompanied by the reaction of DPBF with the generated ${}^{1}O_{2}$, that is, DPBF can trap ${}^{1}O_{2}$ through its photooxidation.14 CH2Cl2/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 μ W cm⁻², $\varepsilon = 27$ 300 M⁻¹ cm⁻¹ (a) $\lambda^{abs} = 509$ nm for CPD and $\varepsilon =$ 17 000 M^{-1} cm⁻¹($a\lambda^{abs} = 509$ nm for H2PyP, respectively) obtained by passage of xenon light through monochromator. For both CPD and C₆₀⊂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 ¹O₂ 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 (Δ OD) of DPBF are plotted against the photoirradiation time (Fig. 4a), and the slope $(m_{\rm sl})$ is used to estimate the Φ_{Δ} value for CPD, C₆₀ \subset CPD and H2PyP. The $m_{\rm sl}$ value (-1.5 $\times 10^{-2}$) of H2PyP is larger than those of CPD (-1.2×10^{-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 Φ_{Δ} values of CPD, C₆₀ CPD and H2PyP were estimated by the relative method using Rose Bengal (RB) ($\Phi_{\Delta} = 0.80, m_{\rm sl} = -1.5 \times 10^{-2},$ see Fig. S1[†]) in methanol¹⁵ as the standard (Table 1). The Φ_{Δ} value of CPD, C₆₀⊂CPD and H2PyP is 0.62, 0.52 and 0.91 respectively, which is in good agreement with the $m_{\rm sl}$ 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 1.81.8 — 0 min (a) (b) ---- 0 min 1.6 1.6 1 min - 1 min 1.4 1.4 2 min 2 min 3 min 3 min 1.2 1.2 4 min 4 min



Fig. 3 Photoabsorption spectral changes for the photooxidation of DPBF (Abs. = ca. 1.0) using (a) CPD $(1.3 \times 10^{-6} \text{ M})$, (b) C₆₀ \subset CPD $(1.0 \times 10^{-6} \text{ M})$ 10^{-6} M) and (c) H2PyP (1.4×10^{-6} M) as photosensitizer under photoirradiation with 509 nm (300 μ W cm⁻²) in CH₂Cl₂/MeOH (=1/1, v/v).

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Fig. 4 (a) Plots of ΔOD for DPBF against the photoirradiation time for the photooxidation of DPBF using CPD, $C_{60} \subset CPD$, H2PyP or Rose Bengal as photosensitizers under photoirradiation with 509 nm (300 μ W cm⁻²) in CH₂Cl₂/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, $C_{60} \subset CPD$, H2PyP or Rose Bengal as photosensitizers under photoirradiation with visible light (>385 nm, 30 mW cm⁻²) in CH₂Cl₂/MeOH (=1/1, v/v).

Table 1 ¹O₂ quantum yield (Φ_{Δ}) and first-order rate constant (K_{obs}) for the photooxidation of DPBF and DHN in CH₂Cl₂/MeOH (=1/1, v/v), respectively, using CPD, C₆₀ \subset CPD or H2PyP as photosensitizer

Photosensitizer	${\varPhi_\Delta}^a$	$K_{\rm obs}^{\ \ b}/{\rm min}^{-1}$
CPD C ₆₀ ⊂CPD H2PyP	0.62 0.52 0.91	$6.6 imes 10^{-3}\ 5.8 imes 10^{-3}\ 9.5 imes 10^{-3}$
CPD C ₆₀ ⊂CPD H2PyP	0.62 0.52 0.91	6.6×10^{-5} 5.8×10^{-5} 9.5×10^{-5}

^{*a*} ¹O₂ quantum yield (relative decomposition rate of DPBF), with Rose Bengal (RB) as standard ($\Phi_{\Delta} = 0.80$ in methanol,¹⁵ see Fig. S1) and 3diphenylisobenzofuran (DPBF) as ¹O₂ scavenger. ^{*b*} First-order rate constant for the reaction of DHN with ¹O₂ generated upon photoexcitation of the photosensitizer. The K_{obs} for RB is 5.3 × 10⁻³ min⁻¹ (see Fig. S2).

state of $C_{60} \subset CPD$ 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} ⁻⁻-CPD⁺ (*ca.* -3.7 eV).¹³ c_{60} ⁻⁻-CPD⁺⁺ 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



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

formation of ${}^{3}C_{60}^{*-}(CPD)$. 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 chargeseparated 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 chargeseparated state c_{60}^{--} -CPD⁻⁺.

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 $C_{60} \subset CPD$ 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, $C_{60} \subset CPD$ 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, $C_{60} \subset CPD$ 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 C₆₀ 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) C₆₀ \subset 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 CH₂Cl₂/MeOH (=1/1, v/v).

photosensitizer (Table 1). Obviously, the higher $K_{\rm obs}$ 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 $K_{\rm obs}$ values of **CPD** and $C_{60} \subset$ **CPD** are lower than that of **H2PyP** ($9.5 \times 10^{-3} \text{ min}^{-1}$). It is worth noting here that the $K_{\rm obs}$ value ($6.6 \times 10^{-3} \text{ min}^{-1}$) of **CPD** is greater than that ($5.8 \times 10^{-3} \text{ min}^{-1}$) of **CeD**. Therefore, this result demonstrates that **CPD** exhibits more efficient photosensitizing ability due to the effective ISC compared to $C_{60} \subset$ **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 ${}^{1}O_{2}$ to produce 4-oxo-TEMPO as a stable nitroxide radical. 16 When the air-saturated solution containing **CPD**, $C_{60} \subset$ **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 ${}^{1}O_{2}$ under visible light irradiation.



Fig. 7 The ESR spectra of 4-oxo-TEMPO which is formed by the reaction of 4-oxo-TEMP with ${}^{1}O_{2}$ 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 CH₂Cl₂ 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 CH₂Cl₂ as low polar solvent was used because it was difficult to obtain a clear ESR signal in polar solvent such as CH₂Cl₂/MeOH (=1/1, v/v).

Conclusions

To investigate singlet oxygen (${}^{1}O_{2}$) generation properties of cyclic free-base porphyrin dimer and its inclusion complex with fullerene C_{60} , we evaluated the ${}^{1}O_{2}$ quantum yield (Φ_{Δ}) and rate constant (K_{obs}) of ${}^{1}O_{2}$ generation for cyclic free-base porphyrin dimer **CPD** and its inclusion complex $C_{60} \subset CPD$ with C_{60} . It was found that the Φ_{Δ} value of $C_{60} \subset CPD$ 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}^{--} **CPD**⁺, 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}^{--} -**CPD**⁺ is favorable for ${}^{1}O_{2}$ generation. Consequently, this work demonstrates that the cyclic free-base porphyrin dimer and its supramolecular complex with C_{60} possess the ability to generate ${}^{1}O_{2}$ under visible light irradiation.

Experimental

Evaluation of ¹O₂ quantum yield

Quantum yield (Φ_{Δ}) for singlet oxygen $({}^{1}O_{2})$ generation by cyclic free-base porphyrin dimer CPD, its inclusion complex $C_{60} \subset CPD$ 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 ¹O₂ scavenger 1,3-diphenylisobenzofuran (DPBF) accompanied by the reaction of DPBF with the generated ${}^{1}O_{2}$, that is, DPBF can trap ${}^{1}O_{2}$ through its photooxidation. CH2Cl2/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, C60 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, $C_{60} \subset$ CPD or H2PyP) and DPBF was irradiated with 509 nm (300 μ 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, $C_{60} \subset$ CPD and H2PyP. The Φ_{Δ} values of CPD, $C_{60} \subset CPD$ and H2PyP were estimated by the relative method using Rose Bengal (RB) ($\Phi_{\Delta} = 0.80$) in methanol as the standard. Therefore, the ${}^{1}\Phi_{\Delta}$ values were calculated according to the following eqn (1):

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

where $\Phi_{\Delta \text{sam}}$ and $\Phi_{\Delta \text{ref}}$ are the ${}^{1}\text{O}_{2}$ quantum yield of photosensitizer (CPD, $C_{60} \subset \text{CPD}$ 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 $L = 1 - 10^{-4}$ ("A" is the absorbance at the photoirradiation wavelength).

Photosensitizing ability

Photosensitizing ability of CPD, C₆₀ 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 1,5dihydroxynaphthalene (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 airsaturated solution containing the photosensitizer (2.5 \times 10^{-6} M for CPD and C₆₀ \subset CPD, 5.0 \times 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 $(A_{\text{DPBF}} = \varepsilon cl)$. 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}) .

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), C₆₀ \subset **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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