Singlet oxygen generation properties of an inclusion complex of cyclic free-base porphyrin dimer and fullerene C₆₀†

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To gain insight into the singlet oxygen (1O₂) generation properties of supramolecular complexes of cyclic free-base porphyrin dimer with fullerene C₆₀, we evaluated the 1O₂ quantum yield (ΦΔ) and rate constant (Kobs) of 1O₂ generation for a cyclic free-base porphyrin dimer (CPD) linked by butadiyne bearing four 4-pyridyl groups and its inclusion complex (C₆₀−CPD) with C₆₀. We demonstrate that CPD and C₆₀−CPD possess the ability to generate 1O₂ under visible light irradiation. Moreover, it was found that the ΦΔ value of C₆₀−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 ΦΔ value of the C₆₀ inclusion complex would be attributed to the formation of the charge-separated state C₆₀$^–$/CPD$^+$, 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 (1O₂) have created considerable interest in recent years from the viewpoint of fundamental studies in photochemistry and their potential applications in photodynamic therapy (PDT). These photosensitizers generally produce 1O₂ through the following processes: initially the photosensitizer absorbs light (hν) 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 (3O₂) produces 1O₂. Thus, to generate 3S* efficiency is one of the most effective strategies to give high 1O₂ quantum yield (ΦΔ). 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 ΦΔ value of 0.6–0.7 (in benzene). Much effort in molecular design and development of porphyrin photosensitizers have been made to further improve the ΦΔ value so far.† Some researchers reported that porphyrin–fullerene C₆₀ dyads as well as boron dipyrromethene (BODIPY)–C₆₀ dyads exhibits a higher ΦΔ 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 (C₆₀−CPD) with C₆₀ and ABAB porphyrin monomer H₂PyP as a reference.
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 C60·CPD with C60 (Fig. 1).13 It was expected that C60·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 C60(1CPD)S undergoes intrasupramolecular electron transfer to give a completely charge-separated state C60−·CPD+. Thus, in this work, to gain insight into the 1O2 generation properties of supramolecular complex of cyclic free-base porphyrin dimer with C60, we evaluated the ΦΔ and rate constant (Ks) of 1O2 generation for CPD and C60·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, λmax/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 (εmax/nm (ε/M−1 cm−1) = 418 (419 000), 513 (19 200), 548 (6200), 588 (6000), 643 (3000))15 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 C60·CPD, it is difficult to obtain its exact absorption spectra because the 1 : 1 complex of CPD with C60 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 CH2Cl2/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 1O2, that is, DPBF can trap 1O2 through its photooxidation.14 CH2Cl2/MeOH was bubbled with air for 15 min. The air-saturated solution containing CPD, C60·CPD or H2PyP and DPBF was irradiated with 509 nm (300 µW cm−2, ε = 27 300 M−1 cm−1@λabs = 509 nm for CPD and ε = 17 000 M−1 cm−1@λabs = 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 (ΔOD) of DPBF are plotted against the photoirradiation time (Fig. 4a), and the slope (mΔ) is used to estimate the ΦΔ value for CPD, C60·CPD and H2PyP. The mΔ value (−1.5 × 10−2) of H2PyP is larger than those of CPD (−1.2 × 10−2) and C60·CPD (−9.8 × 10−3). Moreover, it was revealed that the mΔ value of CPD is larger than that of C60·CPD. Thus, the ΦΔ values of CPD, C60·CPD and H2PyP were estimated by the relative method using Rose Bengal (RB) (ΦΔ = 0.80, mΔ = −1.5 × 10−2, see Fig. S1†) in methanol15 as the standard (Table 1). The ΦΔ value of CPD, C60·CPD and H2PyP is 0.62, 0.52 and 0.91 respectively, which is in good agreement with the mΔ value. This result suggests that as for the ABAB porphyrin monomer H2PyP the ISC efficiency from 1S* to the 1S* may be higher than in the cyclic free-base porphyrin dimer CPD. Moreover, it is worth noting that the ΦΔ value of C60·CPD is lower than that of CPD. Our previous work demonstrates that the decay of photoexcited CPD and H2PyP in CH2Cl2/MeOH (=1/1, v/v).

Fig. 2 Photoabsorption spectra of CPD and H2PyP in CH2Cl2/MeOH.

Fig. 3 Photoabsorption spectral changes for the photooxidation of DPBF (Abs. = ca. 1.0) using (a) CPD (1.3 × 10−6 M), (b) C60·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 CH2Cl2/MeOH (=1/1, v/v).
formation of $^3\text{C}_{60}^\ast$(CPD). Thus, on the basis of the photodynamics of the cyclic free-base porphyrin dimer and its inclusion complex with C$_{60}$, the lower $\Phi_a$ 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)$^\ast$ is in kinetically unfavorable compared to that of the charge-separated state C$_{60}^-$(CPD)$^\ast$.

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 photoperoxidation 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 photoperoxidation. CH$_2$Cl$_2$/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 photoperoxidation of DHN using CPD, C$_{60}$(CPD) or H$_2$PyP under photoperoxidation with the visible light in CH$_2$Cl$_2$/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 photoperoxidation time. The plots of $\ln(C_t/C_0)$ against the photoperoxidation time indicate that for CPD, C$_{60}$(CPD) and H$_2$PyP the $\ln(C_t/C_0)$ decreased almost linearly with the increase in the photoperoxidation time (Fig. 4b). Thus, this result indicates the $\ln(C_t/C_0)$ bears a linear relationship with the photoperoxidation time to provide the first-order rate constants ($K_{obs}$) for the photoperoxidation of DHN using the cyclic free-base porphyrin dimer or its inclusion complex with C$_{60}$ as the
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 H$_2$PyP (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 $1^O_2$ to produce 4-oxo-TEMPO as a stable nitroxide radical. When the air-saturated solution containing CPD, C$_{60}$:CPD or H$_2$PyP 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 H$_2$PyP 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](Image)

**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) H$_2$PyP 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$_2$Cl$_2$ solution containing CPD (2.5 × 10$^{-6}$ M), C$_{60}$:CPD (2.5 × 10$^{-6}$ M) or H$_2$PyP (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$_2$Cl$_2$ as low polar solvent was used because it was difficult to obtain a clear ESR signal in polar solvent such as CH$_3$Cl/MeOH (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 ($\Phi_\Delta$) and rate constant ($K_{obs}$) of $1^O_2$ generation for cyclic free-base porphyrin dimer CPD and its inclusion complex C$_{60}$:CPD with C$_{60}$. It was found that the $\Phi_\Delta$ value of C$_{60}$: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$_{60}$+−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 $1^O_2$ quantum yield**

Quantum yield ($\Phi_\Delta$) for singlet oxygen ($1^O_2$) generation by cyclic free-base porphyrin dimer CPD, its inclusion complex C$_{60}$:CPD with fullerene C$_{60}$ and H$_2$PyP in CH$_3$Cl/MeOH (1/1, v/v) was evaluated by monitoring the photoabsorption spectral change of the known $1^O_2$ 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. CH$_2$Cl$_2$/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 H$_2$PyP 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 H$_2$PyP) 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 $\Phi_\Delta$ values of CPD, C$_{60}$:CPD and H$_2$PyP. The $\Phi_\Delta$ values of CPD, C$_{60}$:CPD and H$_2$PyP were estimated by the relative method using Rose Bengal (RB) ($\Phi_\Delta$ = 0.80) in methanol as the standard. Therefore, the $\Phi_\Delta$ values were calculated according to the following eqn (1):

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

where $\Phi_\Delta$sam and $\Phi_\Delta$ref are the $1^O_2$ quantum yield of photosensitizer (CPD, C$_{60}$:CPD or H$_2$PyP) 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, C$_{60}$CPD and H$_2$PyP in CH$_2$Cl$_2$/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$_2$Cl$_2$/MeOH was bubbled with air for 15 min. The air-saturated solution containing the photosensitizer (2.5 x 10$^{-6}$ M for CPD and C$_{60}$CPD, 5.0 x 10$^{-6}$ M for H$_2$PyP and 2.5 x 10$^{-6}$ M for RB) and DHN (1.0 x 10$^{-4}$ M) 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 photooxidation of DHN with the photoradiation 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 the Lambert-Beer law ($A_{abs} = εtC_0$). 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 ($k_{abs}$).

$^{1}O_2$ 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$_2$Cl$_2$ solution containing CPD (2.5 x 10$^{-6}$ M), C$_{60}$CPD (2.5 x 10$^{-6}$ M) or H$_2$PyP (5.0 x 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 $^{1}O_2$, was clearly observed as a characteristic 1 : 1 : 1 triplet (Fig. 7).

**Notes and references**

1 J. F. Lovell, T. W. B. Liu, J. Chen and G. Zheng, *Chem. Rev.*, 2010, **110**, 2839.

2 M. C. DeRosa and R. J. Crutchley, *Coord. Chem. Rev.*, 2002, **233–234**, 351.

3 M. Pawlicki, H. A. Collins, R. G. Denning and H. L. Anderson, *Angew. Chem., Int. Ed.*, 2009, **48**, 3244.

4 K. A. Leonard, M. I. Nelen, L. T. Anderson, S. L. Gibson, R. Hilf and M. R. Detty, *J. Med. Chem.*, 1999, **42**, 3942.

5 J. M. Dąbrowski and L. G. Arnaut, *Photochem. Photobiol. Sci.*, 2015, **14**, 1765.

6 T. Patrice, *Photodynamic Therapy*, Royal Society of Chemistry, 2003.

7 (a) R. Bonnett, *Chem. Soc. Rev.*, 1995, **24**, 19; (b) M. Ethirajan, Y. Chen, P. Joshi and R. K. Pandey, *Chem. Soc. Rev.*, 2011, **40**, 340.

8 (a) J. P. Belair, C. J. Ziegler, C. S. Rajesh and D. A. Modarelli, *J. Phys. Chem. A*, 2002, **106**, 6445; (b) P. C. Lo, J. D. Huang, D. Y. Y. Cheng, E. Y. M. Chan, W. P. Fong, W. H. Ko and D. K. P. Ng, *Chem.–Eur. J.*, 2004, **10**, 4831; (c) A. Karotki, M. Khurana, J. R. Lepock and B. C. Wilson, *Photochem. Photobiol.*, 2006, **82**, 443; (d) L. Delanaye, M. A. Bahri, F. Tifibel, M.-P. Fontaine-Aupart, A. Mouithys-Mickalad, B. Heine, J. Piette and M. Hoebeke, *Photochem. Photobiol. Sci.*, 2006, **5**, 317; (e) M. Morone, L. Beverina, A. Abbatto, F. Silvestri, E. Collini, C. Ferrante, R. Bozio and G. A. Pagani, *Org. Lett.*, 2006, **8**, 2719; (f) M. Khurana, H. A. Collins, A. Karotki, H. L. Anderson, D. T. Cramb and B. C. Wilson, *Photochem. Photobiol.*, 2007, **84**, 1441.

9 (a) A. P. Thomas, P. S. S. Babu, S. A. Nair, S. Ramakrishnan, D. Ramaiah, T. K. Chandrashekar, A. Srinivasan and M. R. Pillai, *J. Med. Chem.*, 2012, **55**, 5110; (b) H. Hirakawa, Y. Nishimura, T. Arai and S. Okazaki, *J. Phys. Chem. B*, 2013, **117**, 13490; (c) H. Horiuichi, M. Hosaka, H. Mashio, M. Terata, S. Ishida, S. Kyushin, T. Okutsu, T. Takeuchi and H. Hiratsuka, *Chem.–Eur. J.*, 2014, **20**, 6054; (d) Y. Q. Yu, E. M. Rodríguez, R. Naccache, P. Forgione, G. Lamoureux, F. Sanz-Rodriguez, D. Schegelman and J. A. Capobianco, *Chem. Commun.*, 2014, **50**, 12150; (e) D. Yao, V. Hugues, M. Blanchard-Desce, O. Mongin, C. O. Paul-Roth and F. Paul, *New J. Chem.*, 2015, **39**, 7730.

10 (a) M. Prein and W. Adam, *Angew. Chem., Int. Ed.*, 2014, **53**, 6938; (b) H. Shimoroi, F. Kodaira, S. Matsugo, S. Kawabata and A. Osuka, *Chem. Lett.*, 2005, **34**, 322; (c) L. G. Arnaut, M. M. Pereira, J. M. Dąbrowski, E. F. F. Silva, F. A. Schaberle, A. R. Abreu, L. B. Rocha, M. M. Barsan, K. Urbanska, G. Stoeche and C. M. A. Brett, *Chem.–Eur. J.*, 2014, **20**, 5346; (f) F. Hammerer, G. García, S. Chen, F. Roys, S. Achelle, C. Fiorini-Debuisschert, M.-P. Telulade-Fichou and P. Maillard, *J. Org. Chem.*, 2014, **79**, 1406; (g) J. Schmitt, V. Heitz, A. Sour, F. Bolze, F. Tani, J.-F. Nicoud, L. Flamigni and B. Ventura, *Angew. Chem., Int. Ed.*, 2015, **54**, 169.

11 M. E. Milanesio, M. G. Alvarez, V. Rivarola, J. J. Silber and E. N. Durantini, *Photochem. Photobiol.*, 2005, **81**, 891.

12 (a) L. Huang, X. Yu, W. Wu and J. Zhao, *Org. Lett.*, 2012, **14**, 2594; (b) A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.*, 2013, **42**, 77; (c) L. Huang, X. Cui, B. Therrien and J. Zhao, *Chem.–Eur. J.*, 2013, **19**, 17472.

13 (a) H. Nobukuni, Y. Shimazaki, H. Uno, Y. Naruta, K. Okubo, T. Kojima, S. Fukuzumi, S. Seki, H. Sakai, T. Hasobe and F. Tani, *Chem.–Eur. J.*, 2010, **16**, 11611; (b) H. Nobukuni, T. Kamimura, H. Uno, Y. Shimazaki, Y. Naruta and F. Tani, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 862; (c) K. Sakaguchi, T. Kamimura, H. Uno, S. Morii, S. Ozako, H. Nobukuni, M. Ishida and F. Tani, *J. Org. Chem.*, 2014, **79**, 2980; (d) T. Kamimura, K. Okubo, Y. Kawashima, H. Nobukuni, Y. Naruta, F. Tani and S. Fukuzumi, *Chem. Sci.*, 2013, **4**, 1451; (e) T. Kamimura, K. Okubo, Y. Kawashima, S. Ozako, K. Sakaguchi, S. Fukuzumi and F. Tani, *J. Phys. Chem. C*, 2015, **119**, 25634; (f) Y. Ooyama,
K. Uenaka, T. Kamimura, S. Ozako, M. Kanda, T. Koide and F. Tani, *RSC Adv.*, 2016, **6**, 16150.

14 K. Golinick and A. Griesbeck, *Tetrahedron*, 1985, **41**, 2057.

15 W. Wu, J. Sun, X. Cui and J. Zhao, *J. Mater. Chem. C*, 2013, **1**, 4577.

16 (a) Y. Yamakoshi, N. Umezawa, A. Ryu, K. Arakane, N. Miyata, Y. Goda, T. Masumizu and T. Nagano, *J. Am. Chem. Soc.*, 2003, **125**, 12803; (b) S. Oriana, S. Aroua, J. O. B. Söllner, X.-J. Ma, Y. Iwamoto and Y. Yamakoshi, *Chem. Commun.*, 2013, **49**, 9302.