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Multiple photosynthetic reaction centres of porphyrinic polypeptide–Li⁺@C₆₀ supramolecular complexes†

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Multiple photosynthetic reaction centres have been successfully constructed using strong supramolecular complexes of free base porphyrin polypeptides with lithium ion-encapsulated C_{60} (Li⁺@C_{60}) as compared with those of C_{60}. Efficient energy migration and electron transfer occur in the supramolecular complexes.

Extensive effort has so far been devoted to mimicking light harvesting and charge separation processes in natural photosynthesis.[1–10] Multiporphyrin arrays have been employed as light-harvesting units.[11–17] Light-harvesting and charge-separation units have been combined by coordination bonds between metalloporphyrins and electron acceptor moieties bearing Lewis base ligands.[17–22] Thus, metal centres were required for the construction of supramolecular complexes between porphyrins acting as light harvesting units and electron acceptors containing Lewis base ligands for coordination to the metal centres.[17–22] As such there have been only a few reports on supramolecular complexes of free base porphyrin arrays and electron acceptors without Lewis base ligands, in which the binding is rather weak.[23] We report herein the construction of supramolecular complexes of free base porphyrin polypeptides ($P(H_2P)_n$: $n = 4$ and 8) with lithium ion-encapsulated C_{60} (Li⁺@C_{60})[24,25] (Fig. 1), in which binding is much stronger than the case of C_{60} in benzonitrile (PhCN). The photodynamics were studied by femtosecond and nanosecond laser-induced transient absorption and fluorescence lifetime measurements.
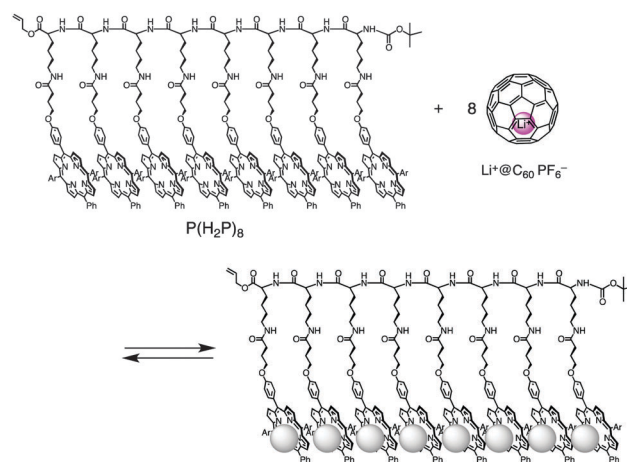
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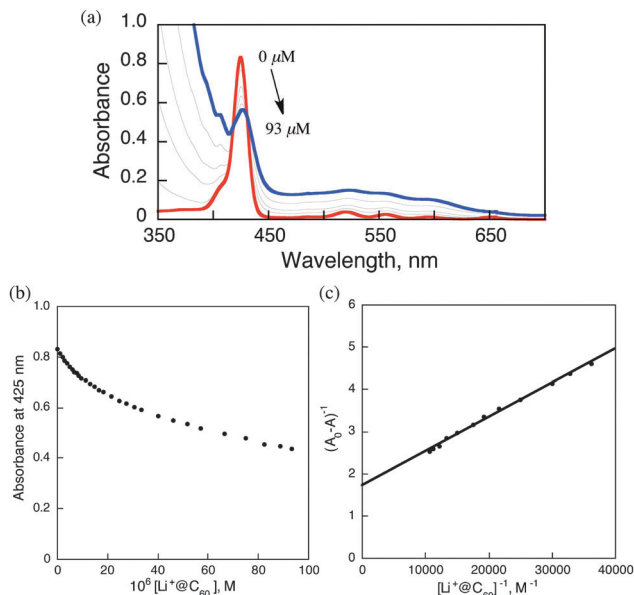
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Fig. 1 Supramolecular formation of peptide porphyrin oligomers with Li⁺@C_{60}. Ar = 3,5-di-*tert*-butylphenyl.

Free base porphyrin polypeptide ($P(H_2P)_n$) were synthesised and characterised as reported previously.[18,26] Upon mixing a PhCN solution of Li⁺@C_{60} with that of $P(H_2P)_8$, the intensity of the Soret band decreased with an increasing concentration of Li⁺@C_{60} (Fig. 2a). A Soret band was slightly red-shifted from 425 to 427 nm by the addition of Li⁺@C_{60} to the solution. From the net absorption change at 425 nm in which the absorption due to Li⁺@C_{60} was subtracted, a linear Benesi–Hildebrand plot[27] was obtained as shown in Fig. 2b, indicating that each porphyrin unit of $P(H_2P)_8$ forms a 1:1 supramolecular charge-transfer complex with Li⁺@C_{60} independently with approximately the same binding constant of the unit of M⁻¹. The binding constant at 298 K was determined from the intercept and the slope in Fig. 2b to be 2.1×10^4 M⁻¹, which is significantly larger than that of C_{60} (5.3×10^3 M⁻¹).[28,29] The stronger binding of Li⁺@C_{60} as compared with C_{60} may result from the stronger electron acceptor ability of Li⁺@C_{60}, which facilitates the charge-transfer interaction as reported for the stronger charge-transfer binding of Li⁺@C_{60} with corannulene.[30] Similarly the binding constant of the supramolecular complex of $P(H_2P)_4$ was determined from the spectral

Fig. 2 (a) UV-vis absorption spectra of P(H₂P)₈ in the presence of various concentrations of Li⁺@C₆₀ in PhCN at 298 K; (b) absorption profile at 425 nm. (c) Benesi–Hildebrand plot for the determination of the association constant.
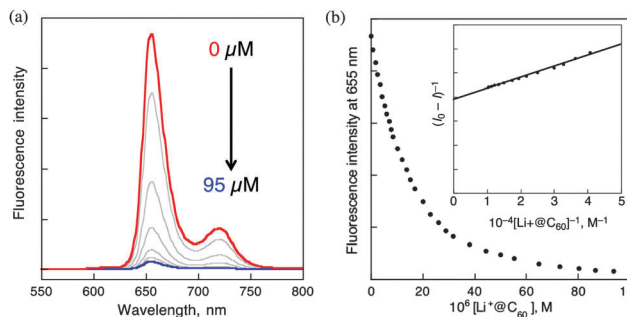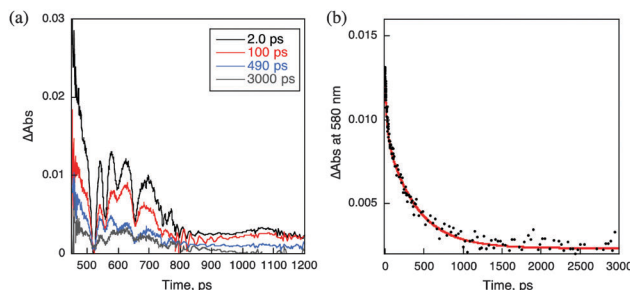

Fig. 3 (a) Fluorescence spectra of P(H₂P)₈ in the presence of various concentrations of Li⁺@C₆₀ in PhCN at 298 K; (b) fluorescence profile at 655 nm. Inset: Benesi–Hildebrand plot for the determination of the association constant.

titration to be 6.2×10^3 M^{-1} (Fig. S1 in the ESI†). In the case of P(H₂P)₂ and P(H₂P)₁, however, the spectral change was too small to be able to determine the binding constants accurately (Fig. S2 and S3 in the ESI†). The binding constants are summarised in Table 1. Thus, multiporphyrins may facilitate charge-transfer interactions through the encapsulation of Li⁺@C₆₀ by multiple porphyrins.

Fluorescence of P(H₂P)₈ was quenched by the addition of a PhCN solution of Li⁺@C₆₀ as shown in Fig. 3a. A Benesi–Hildebrand plot for fluorescence quenching (Fig. 3b) afforded the apparent binding constant of the supramolecular complex of P(H₂P)₈ with Li⁺@C₆₀ being 8.5×10^4 M^{-1}, which is significantly larger than the value determined from the absorption spectral titration (2.1×10^4 M^{-1}) (Fig. 2). Similarly the apparent binding constant of P(H₂P)₄ with Li⁺@C₆₀ was determined from the fluorescence quenching to be 1.6×10^4 M^{-1} (Fig. S4 in the ESI†), which is also larger than the value determined from the absorption spectral titration (Table 1). Such larger apparent binding constants determined from the fluorescence quenching than those determined from the absorption spectral titration

indicate that energy migration occurs between the singlet excited state of H₂P (^{1}H₂P*) and adjacent H₂P in P(H₂P)ₙ ($n = 4$ and 8).

The energy migration rate constant was determined by the fluorescence lifetime measurements of P(H₂P)₈ with Li⁺@C₆₀. The fluorescence of ^{1}P(H₂P)₈* exhibited a single exponential decay with the lifetime of 11 ns. In the presence of Li⁺@C₆₀, the decay of ^{1}P(H₂P)₈* is well analysed by three exponentials with lifetimes of 100 ps, 3.0 ns and 11 ns. The fast component corresponds to the lifetime of ^{1}H₂P* in the supramolecular complex with Li⁺@C₆₀. 95% of the fast component agrees with that predicted by the binding constant determined from the absorption spectral titration. The third component has the same lifetime as that without Li⁺@C₆₀, corresponding to the fluorescence lifetime of ^{1}(H₂P)₈*. The second component corresponds to energy migration between ^{1}H₂P* and the adjacent H₂P. 5% of the sum of the first and second components agrees with that predicted from the binding constant determined from fluorescence quenching.

Femtosecond laser-induced transient absorption spectra of P(H₂P)₈ were recorded in the absence and presence of Li⁺@C₆₀ (Fig. 4 and Fig. S10 in the ESI†). In each case, only the singlet–singlet absorption of ^{1}P(H₂P)₈* was observed, because H₂P was exclusively excited at the excitation wavelength (425 nm) in Fig. 4. The decay of ^{1}P(H₂P)₈* exhibits a fast component with a lifetime of 6 ps. A similar fast component was observed for ^{1}P(H₂P)₄* and ^{1}P(H₂P)₂* (Fig. S11 in the ESI†). In the case of P(H₂P)₁, however,

Table 1 Association constant (K, M^{-1}) of P(H₂P)ₙ with Li⁺@C₆₀ and C₆₀ in PhCN determined from UV-vis absorption and fluorescence spectral titration

Porphyrin	Li⁺@C₆₀		C₆₀[b]	
	UV-vis	FL	UV-vis	FL
P(H₂P)₁	—[a]	1.1×10^4	—[a]	—[a]
P(H₂P)₂	—[a]	1.1×10^4	—[a]	—[a]
P(H₂P)₄	6.2×10^3	1.6×10^4	$2.7 \times 10^{3\,b}$	$9.5 \times 10^{3\,b}$
P(H₂P)₈	2.1×10^4	8.5×10^4	$5.3 \times 10^{3\,b}$	$2.2 \times 10^{4\,b}$

[a] Too small to determine accurately. [b] Taken from ref. 28.

Fig. 4 (a) Transient absorption spectra of P(H₂P)₈ (5.2×10^{-6} M) with Li⁺@C₆₀ (2.0×10^{-5} M) in deaerated PhCN observed after femtosecond laser flash excitation. Excitation wavelength: 425 nm. (b) Decay time profile at 580 nm with a three-exponential decay curve fitting.

no fast component was observed (Fig. S6c in the ESI†). The ratio of the fast component increased upon increasing the number of H_2P in $P(H_2P)_n$. 96% of the fast component of $P(H_2P)_8$ decreased upon decreasing the laser intensity (Fig. 4b). These results indicate that the fast component results from the singlet–singlet annihilation of two $^1H_2P^*$ moieties in $P(H_2P)_n$ (n = 4 and 8).

In the presence of $Li^+@C_{60}$ (20 μM), the decay of $^1P(H_2P)_8^*$ exhibited three exponentials with lifetimes of 6 ps, 90 ps and 2 ns. The first fast component resulted from the singlet–singlet annihilation as observed without $Li^+@C_{60}$. The second component (90 ps) may result from electron transfer from $^1H_2P^*$ to $Li^+@C_{60}$ in the supramolecular complex. Because the transient absorption due to the charge-separated state ($H_2P^{\bullet+}$ and $Li^+@C_{60}^{\bullet-}$) was not observed in Fig. 4a, where only the singlet–singlet absorption of $^1H_2P^*$ is seen, back electron transfer may be much faster than the forward electron transfer. The third component may correspond to the energy migration between $^1H_2P^*$ and the adjacent H_2P, because its lifetime agrees with the lifetime of energy migration in the fluorescence lifetime measurements. In the presence of high concentration of $Li^+@C_{60}$ (120 μM), the component of electron transfer from $^1H_2P^*$ to $Li^+@C_{60}$ in the supramolecular complex increased. The three component decay was also observed for $P(H_2P)_4$ and $P(H_2P)_2$ with $Li^+@C_{60}$ (Fig. S11 and S12 in the ESI†). In the case of $P(H_2P)_1$, only single exponential decay with a lifetime of 11 ns was observed in the absence and presence of $Li^+@C_{60}$ because the binding of $Li^+@C_{60}$ to $P(H_2P)_1$ was negligible.

Nanosecond laser-induced transient absorption spectra of $P(H_2P)_8$ with $Li^+@C_{60}$ (40 μM) at the excitation wavelength of 532 nm are shown in Fig. 5, where the transient absorption band at 730 nm due to the triplet excited state of $Li^+@C_{60}$ ($^3Li^+@C_{60}^*$) is observed together with the absorption band at 1035 nm due to $Li^+@C_{60}^{\bullet-}$.[25] The decay of the absorption at 730 nm coincides with the appearance of $Li^+@C_{60}^{\bullet-}$ (Fig. S13 in the ESI†). Thus, electron transfer from $P(H_2P)_8$ to $^3Li^+@C_{60}^*$ occurs to produce the triplet charge-separate (CS) state of $P(H_2P)_8^{\bullet+}$ and $Li^+@C_{60}^{\bullet-}$. The transient absorption due to $P(H_2P)_8^{\bullet+}$ is overlapped with that of $^3Li^+@C_{60}^*$ in the 600–700 nm region. The photoexcitation of 532 nm resulted in the excitation of $Li^+@C_{60}$ leading to the formation of $^3Li^+@C_{60}^*$ via intersystem crossing. The decay of the absorbance at 1035 nm due to $Li^+@C_{60}^{\bullet-}$ obeyed first-order kinetics with the lifetime of 210 μs (Fig. 5b). Thus, back electron transfer from $Li^+@C_{60}^{\bullet-}$ to $P(H_2P)_8^{\bullet+}$ occurs in the supramolecular complex. The lifetime is long because of the spin-forbidden back electron transfer in the triplet CS state.

Similarly the triplet CS states derived from $^3Li^+@C_{60}^*$ were observed for $P(H_2P)_n$ (n = 4, 2, and 1) with $Li^+@C_{60}$ (Fig. S14–S16 in the ESI†). The rate constants of electron transfer from $^1H_2P^*$ to $Li^+@C_{60}$ and the energy migration in the supramolecular complexes of $P(H_2P)_n$ with $Li^+@C_{60}$ are summarised in Table 2 together with the lifetimes of the triplet CS states. The CS lifetime increases upon increasing the number of H_2P in $P(H_2P)_n$. Such an increase in the CS lifetime may result from the charge migration between $H_2P^{\bullet+}$ and the adjacent H_2P in $P(H_2P)_n^{\bullet+}$. The energy diagram of photoexcitation of $P(H_2P)_n$ with $Li^+@C_{60}$ is given
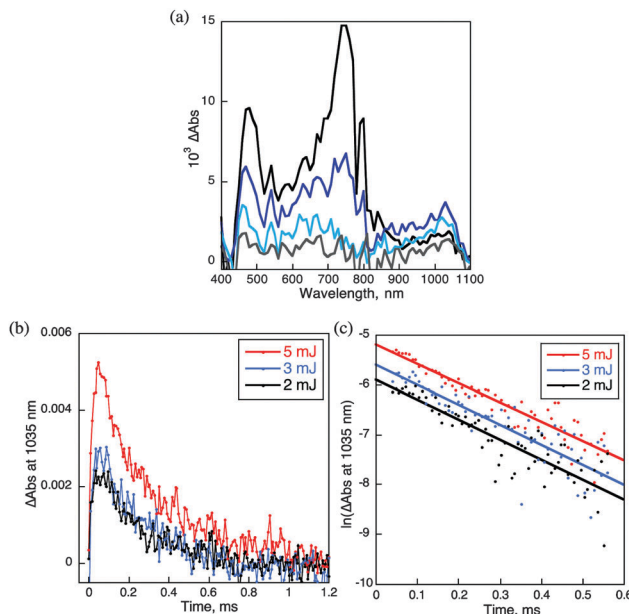

Fig. 5 (a) Transient absorption spectra of $P(H_2P)_8$ (2.6×10^{-6} M) with $Li^+@C_{60}$ (4.0×10^{-5} M) in deaerated PhCN observed after nanosecond laser flash excitation taken at 8 (black), 32 (blue), 96 (sky blue) and 200 μs (gray). Excitation wavelength: 532 nm. (b) Decay time profile at 1035 nm with the different laser pulse intensities (2–5 mJ pulse^{-1}). (c) First-order plots.

Table 2 Rate constants of intra- and intermolecular photoinduced electron transfer (k_{ET} and k_{et}) and lifetimes ($\tau(CS)$) and quantum yields ($\Phi(CS)$) of the charge-separated state

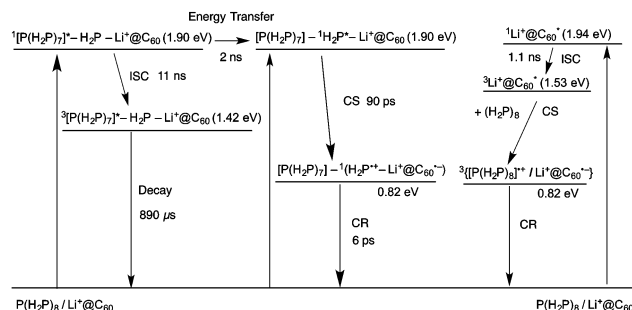| Porphyrin	$P(H_2P)_1$	$P(H_2P)_2$	$P(H_2P)_4$	$P(H_2P)_8$
k_{ET}, s^{-1}	7.7×10^5	6.7×10^4	9.5×10^4	1.5×10^5
k_{et}, M^{-1} s^{-1}	1.7×10^9	1.8×10^9	8.0×10^8	1.5×10^8
$\tau(CS)$, μs	—^{a}	—^{a}	160	210
$\Phi(CS)$	0.70	0.34	0.16	0.13

^{a} Bimolecular decay in the radical ion pair.

in Scheme 1. The energies of the excited state of porphyrin and $Li^+@C_{60}$ were determined by UV-vis, fluorescence and phosphorescence spectral measurements. The energy of the CS state was determined to be 0.82 eV in PhCN from the one-electron oxidation potential of porphyrin (+0.96 V vs. SCE) and reduction potential of $Li^+@C_{60}$ (+0.14 V vs. SCE) by the electrochemical measurements (DPV; see Fig. S17 in the ESI†). Femtosecond laser excitation of the supramolecular complex of $P(H_2P)_8$ with $Li^+@C_{60}$ at 425 nm resulted in electron transfer from H_2P to the bound $Li^+@C_{60}$ to produce the singlet CS state and energy transfer from $^1H_2P^*$ to the adjacent H_2P, followed by electron transfer to $Li^+@C_{60}$, when it is bound H_2P. The singlet CS state decays rapidly to the ground state. Nanosecond laser excitation at 532 nm resulted in the formation of the singlet excited state of excess $Li^+@C_{60}$, followed by intersystem crossing to produce $^3Li^+@C_{60}^*$, to which intermolecular electron transfer occurs from H_2P to produce the triplet CS state with a long lifetime because of the spin-forbidden back electron transfer to the ground state.

In conclusion, free base porphyrin polypeptides ($P(H_2P)_n$; n = 4 and 8) form supramolecular complexes with $Li^+@C_{60}$ in PhCN,

Scheme 1 Reaction course of photoinduced charge separation and charge recombination in the supramolecular complex between $P(H_2P)_8$ and $Li^+@C_{60}$ with the values of energy levels.

in which the binding is much stronger than C_{60}. Efficient energy migration occurs between porphyrins in $P(H_2P)_n$. Although the lifetimes of the singlet CS states were too short to be detected, the triplet CS states derived from $^3Li^+@C_{60}$ had long lifetimes because of the spin-forbidden back electron transfer. The triplet CS lifetime becomes longer upon increasing the number of H_2P due to the charge migration among porphyrins. The present study provides valuable insight into the energy and electron transfer in multiple reaction centres.

Notes and references

1 (a) *Anoxygenic Photosynthetic Bacteria*, ed. R. E. Blankenship, M. T. Madigan and C. E. Bauer, Kluwer Academic Publisher, Dordecht, 1995; (b) *Molecular Level Artificial Photosynthetic Materials*, ed. G. J. Meyer, Wiley, New York, 1997.
2 (a) R. A. Wheeler, *Introduction to the Molecular Bioenergetics of Electron, Proton, and Energy Transfer, ACS Symposium Series*, 2004, vol. 883, pp. 1–6; (b) W. Leibl and P. Mathis, *Electron Transfer in Photosynthesis. Series on Photoconversion of Solar Energy*, 2004, vol. 2, p. 117.
3 D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2009, **42**, 1890.
4 (a) G. Bottari, G. de la Torre, D. M. Guldi and T. Torres, *Chem. Rev.*, 2010, **110**, 6768; (b) V. Sgobba and D. M. Guldi, *Chem. Soc. Rev.*, 2009, **38**, 165.
5 M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910.
6 S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2283.
7 (a) F. D'Souza and O. Ito, *Chem. Commun.*, 2009, 4913; (b) F. D'Souza and O. Ito, *Coord. Chem. Rev.*, 2005, **249**, 1410.
8 S. Fukuzumi, K. Saito, K. Ohkubo, T. Khoury, Y. Kashiwagi, M. A. Absalom, S. Gadde, F. D'Souza, Y. Araki, O. Ito and M. J. Crossley, *Chem. Commun.*, 2011, **47**, 7980.
9 (a) T. Kojima, T. Honda, K. Ohkubo, M. Shiro, T. Kusukawa, T. Fukuda, N. Kobayashi and S. Fukuzumi, *Angew. Chem., Int. Ed.*, 2008, **47**, 6712; (b) S. Fukuzumi, T. Honda, K. Ohkubo and T. Kojima, *Dalton Trans.*, 2009, 3880; (c) T. Kojima, K. Hanabusa, K. Ohkubo, M. Shiro and S. Fukuzumi, *Chem. – Eur. J.*, 2010, **16**, 3646.
10 S. Fukuzumi, in *Functional Organic Materials*, ed. T. J. J. Müller and U. H. F. Bunz, Wiley-VCH, 2007, pp. 465–510.
11 (a) T. Tanaka and A. Osuka, *Chem. Soc. Rev.*, 2015, **44**, 943; (b) H.-W. Jiang, T. Tanaka, H. Mori, K. H. Park, D. Kim and A. Osuka, *J. Am. Chem. Soc.*, 2015, **137**, 2219.
12 (a) N. Aratani, D. Kim and A. Osuka, *Acc. Chem. Res.*, 2009, **42**, 1922; (b) J. Yang, M.-C. Yoon, H. Yoo, P. Kim and D. Kim, *Chem. Soc. Rev.*, 2012, **41**, 4808.
13 (a) T. Miyatake and H. Tamiaki, *Coord. Chem. Rev.*, 2010, **254**, 2593; (b) S. Sengupta and F. Würthner, *Acc. Chem. Res.*, 2013, **46**, 2498; (c) T. S. Balaban, *Acc. Chem. Res.*, 2005, **38**, 612.
14 H.-J. Son, S. Jin, S. Patwardhan, S. J. Wezenberg, N. C. Jeong, M. So, C. E. Wilmer, A. A. Sarjeant, G. C. Schatz, R. Q. Snurr, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 862.
15 (a) I. Cohen-Ofri, M. van Gastel, J. Grzyb, A. Brandis, I. Pinkas, W. Lubitz and D. Noy, *J. Am. Chem. Soc.*, 2011, **133**, 9526; (b) J. L. R. Anderson, C. T. Armstrong, G. Kodali, B. R. Lichtenstein, D. W. Watkins, J. A. Mancini, A. L. Boyle, T. A. Farid, M. P. Crump, C. C. Moser and P. L. Dutton, *Chem. Sci.*, 2014, **5**, 507–514; (c) F. A. Tezcan, B. R. Crane, J. R. Winkler and H. B. Gray, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 5002; (d) T. Koshiyama, M. Shirai, T. Hikage, H. Tabe, K. Tanaka, S. Kitagawa and T. Ueno, *Angew. Chem., Int. Ed.*, 2011, **50**, 4849.
16 (a) R. A. Miller, N. Stephanopoulos, J. M. McFarland, A. S. Rosko, P. L. Geissler and M. B. Francis, *J. Am. Chem. Soc.*, 2010, **132**, 6068; (b) L. S. Witus and M. B. Francis, *Acc. Chem. Res.*, 2011, **44**, 774.
17 (a) Y. S. Nam, T. Shin, H. Park, A. P. Magyar, K. Choi, G. Fantner, K. A. Nelson and A. M. Belcher, *J. Am. Chem. Soc.*, 2010, **132**, 1462; (b) M. Endo, M. Fujitsuka and T. Majima, *Chem. – Eur. J.*, 2007, **13**, 8660.
18 (a) S. Fukuzumi and K. Ohkubo, *J. Mater. Chem.*, 2012, **22**, 4575; (b) S. Fukuzumi, K. Ohkubo and T. Suenobu, *Acc. Chem. Res.*, 2014, **47**, 1455.
19 S. Fukuzumi, K. Saito, K. Ohkubo, V. Troiani, H. Qiu, S. Gadde, F. D'Souza and N. Solladié, *Phys. Chem. Chem. Phys.*, 2011, **13**, 17019.
20 (a) A. Takai, C. P. Gros, R. Guilard and S. Fukuzumi, *Chem. – Eur. J.*, 2009, **15**, 3110–3122; (b) A. Takai, C. P. Gros, J.-M. Barbe and S. Fukuzumi, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12160; (c) A. Takai, C. P. Gros, J.-M. Barbe and S. Fukuzumi, *Chem. – Eur. J.*, 2011, **17**, 3420.
21 S. Fukuzumi, K. Saito, K. Ohkubo, T. Khoury, Y. Kashiwagi, M. A. Absalom, S. Gadde, F. D'Souza, Y. Araki, O. Ito and M. J. Crossley, *Chem. Commun.*, 2011, **47**, 7980.
22 (a) Y. Pareek and M. Ravikanth, *RSC Adv.*, 2014, **4**, 7851; (b) V. S. Nair, Y. Pareek, V. Karunakaran, M. Ravikanth and A. Ajayaghosh, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10149.
23 (a) M. Tanaka, K. Ohkubo, C. P. Gross, R. Guilard and S. Fukuzumi, *J. Am. Chem. Soc.*, 2006, **128**, 14625; (b) A. Takai, M. Chkounda, A. Eggenspiller, C. P. Gros, M. Lachkar, J.-M. Barbe and S. Fukuzumi, *J. Am. Chem. Soc.*, 2010, **132**, 4477.
24 S. Aoyagi, E. Nishibori, H. Sawa, K. Sugimoto, M. Takata, Y. Miyata, R. Kitaura, H. Shinohara, H. Okada, T. Sakai, Y. Ono, K. Kawachi, K. Yokoo, S. Ono, K. Omote, Y. Kasama, S. Ishikawa, T. Komuro and H. Tobita, *Nat. Chem.*, 2010, **2**, 678.
25 (a) Y. Kawashima, K. Ohkubo and S. Fukuzumi, *Chem. – Asian J.*, 2015, **10**, 44; (b) S. Fukuzumi, K. Ohkubo, Y. Kawashima, D. S. Kim, J. S. Park, A. Jana, V. M. Lynch, D. Kim and J. L. Sessler, *J. Am. Chem. Soc.*, 2011, **133**, 15938.
26 (a) N. Solladié, A. Hamel and M. Gross, *Tetrahedron Lett.*, 2000, **41**, 6075; (b) F. Aziat, R. Rein, J. Peon, E. Rivera and N. Solladié, *J. Porphyrins Phthalocyanines*, 2008, **12**, 1232.
27 H. Benesi and J. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.
28 T. Hasobe, K. Saito, P. V. Kamat, V. Troiani, H. Qiu, N. Solladié, K. S. Kim, J. K. Park, D. Kim, F. D'Souza and S. Fukuzumi, *J. Mater. Chem.*, 2007, **17**, 4160.
29 The characterization of a highly ordered structure as shown in Fig. 1 was carried out by microscopic measurements of thin film.[28]
30 M. Yamada, K. Ohkubo, M. Shionoya and S. Fukuzumi, *J. Am. Chem. Soc.*, 2014, **135**, 13240.