# Electron transfer switching in supramolecular porphyrin–fullerene conjugates held by alkylammonium cation-crown ether binding†

Atula S. D. Sandanayaka,[a] Yasuyaki Araki,[a] Osamu Ito,[a] Raghu Chitta,[b] Suresh Gadde[b] and Francis D'Souza[b]

**Reversible switching between intra- to intermolecular electron transfer paths has been accomplished by adding and extracting potassium ions to the supramolecular porphyrin–fullerene conjugates formed by complexing porphyrin functionalized with a benzo-18-crown-6 entity and fullerene functionalized with an alkylammonium cation entity.**

Photoinduced electron transfer in donor–acceptor systems is one of the fast growing areas of research driven primarily by solar energy conversion and building molecular electronic devices.[1] Among the biomimetic donor–acceptor systems, porphyrin–fullerene systems[2] are one of the widely studied classes of compounds due to their rich photo- and redox chemistry. Both covalently linked and non-covalently linked via hydrogen bonds, van der Waals forces, electrostatic interactions, π–π stacking or metal–ligand coordination systems have been elegantly designed and studied.[2c] Fullerenes, owing to their spherical geometry require small reorganization energy in electron transfer reactions.[3] Consequently, in donor–acceptor systems, fullerenes accelerate forward electron transfer ($k_{CS}$) and slow down backward electron transfer ($k_{CR}$) resulting in the formation of long-lived charge-separated (CS) states,[4] a key factor for utilizing these compounds in building optoelectronic devices, logical gates, etc.

Recently, we demonstrated reversible switching of intra- to intermolecular electron transfer paths in supramolecular conjugates formed between porphyrins functionalized with one or four benzo-18-crown-6 entities as donors and pristine fullerene as acceptor.[5] Intramolecular charge-separation within the conjugates was blocked when potassium cations were included in the crown ether voids, allowing only intermolecular type electron transfer. Further, addition of 18-crown-6 to this solution extracted the potassium ions from the porphyrin-crown ether, thus restoring the initial intramolecular porphyrin–fullerene interactions. However, since the interactions between the porphyrin and fullerene were weak, addition effects of potassium cation and external crown-ether were not prominent. In the present investigation, we have employed fullerene functionalized with an alkylammonium cation, **1** (Scheme 1) instead of pristine fullerene. Here, compound **1** binds to porphyrins **2** primarily through the ammonium cation–crown ether binding resulting into efficient intramolecular photoinduced electron transfer.[6] As demonstrated in Scheme 1, addition of potassium cations to the porphyrin–fullerene conjugates would replace the secondary alkylammonium cation from the crown ether void, and under these conditions only intermolecular type interactions between the porphyrin and fullerene would mainly be observed. This process could be reversed by further addition of 18-crown-6 to the solution to extract the potassium cations from the conjugate. The present system is better defined as compared to the earlier reported system involving pristine fullerene,[5] because of the higher stability of the conjugates as a result of alkylammonium cation-crown ether binding.

Addition of **1** to a solution of porphyrin **2** revealed fluorescence quenching of porphyrin **2**[6] in benzonitrile (Fig. 1, spectra (i) and (ii)). Using the emission data obtained with changing the concentration of **1**, the binding constants ($K$) for the formation of the self-assembled supramolecular conjugates were obtained by constructing Benesi–Hildebrand plots and were found to be $\sim 10^4$ $M^{-1}$. The magnitude of the binding constants revealed stable self-assembly even in polar benzonitrile. The calculated Stern–Volmer constants, $K_{SV}$ were also found to be $\sim 10^4$ $M^{-1}$. On employing the excited-state lifetime of reference porphyrins, the intermolecular fluorescence quenching rate-constants, $k_q$, were evaluated to be $\sim 10^{11}$ $M^{-1}$ $s^{-1}$, which were three orders of
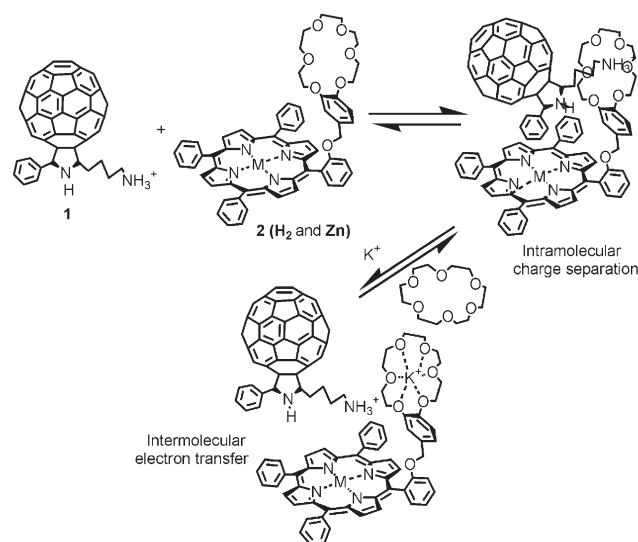


**Scheme 1** Structure of ammonium cation appended fullerene, **1** and its binding to benzo-18-crown-6 appended porphyrin, **2**, and potassium cation and 18-crown-6 induced reversible switching of inter- and intramolecular electron transfer processes.

[a]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Sendai, 980-8577, Japan.
E-mail: ito@tagen.tohoku.ac.jp
[b]Department of Chemistry, Wichita State University, 1845 Fairmount, Wichita, KS, 67260-0051, USA. E-mail: Francis.DSouza@wichita.edu
† Electronic supplementary information (ESI) available: Fluorescence decay profiles. See DOI: 10.1039/b610171b
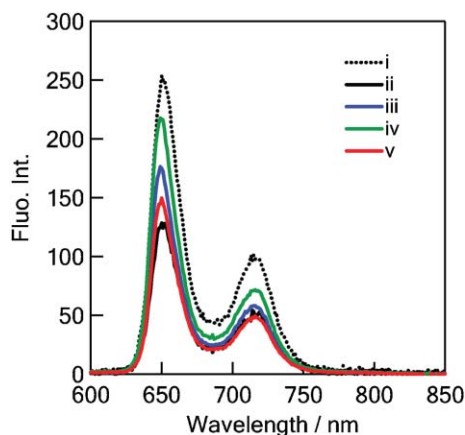
**Fig. 1** Fluorescence spectral changes observed for (i) **2**(H₂), (ii) **2**(H₂) + **1**, (iii) **2**(H₂) + **1** + K⁺ (1.0 mM), (iv) **2**(H₂) + **1** + excess K⁺ and (v) **2**(H₂) + **1** + K⁺ (1.0 mM) + 18-crown-6 (10 mM) in benzonitrile (concentrations of **2**(H₂) and **1** are 0.1 mM). $\lambda_{ex}$ = 420 nm.



**Fig. 2** Fluorescence decays for (i) **2**(Zn) (0.10 mM), (ii) **2**(Zn) (0.1 mM) + **1** (0.11 mM), (iii) **2**(Zn) (0.1 mM) + **1** (0.11 mM) + K⁺ (1.0 mM), (iv) **2**(Zn) (0.1 mM) + **1** (0.11 mM) + K⁺ (excess), and (v) **2**(Zn) (0.1 mM) + **1** (0.11 mM) + K⁺ (1.0 mM) + 18-crown-6 (10.0 mM) in benzonitrile.

magnitude higher than that expected for diffusion controlled-bimolecular quenching processes in benzonitrile ($\sim 5.0 \times 10^{9}$ M⁻¹ s⁻¹) suggesting that the intramolecular processes are responsible for the fluorescence quenching within the supramolecular conjugates.

Addition of potassium cations to the dyad solution resulted in restoring the quenched porphyrin emission for both the free-base and zinc derivative of **2**. Spectra (iii) and (iv) in Fig. 1 show the relatively strong fluorescence intensity upon addition of K⁺ to the solution of **2**(H₂) containing **1**. Nearly 85% of the quenched fluorescence was restored. These results suggest the dissociation of the supramolecular conjugates in which the ammonium cation in the crown ether cavity is replaced by the added K⁺. In order to check the reversibility of this process, pristine 18-crown-6 was added to the solution, as shown in spectrum (v) in Fig. 1, the fluorescence quenching was reproduced again as a proof of re-generation of the supramolecular conjugate. Here, the crown ether bound K⁺ was extracted by the added 18-crown-6 thus making room for the secondary alkylammonium cation functionalized fullerene to bind to the crown ether appended porphyrins.

The time-resolved fluorescence emission studies[7] also confirmed the reversible switching behavior. Time profiles (i) and (ii) in Fig. 2 show the emission decays of the crown ether appended porphyrin, **2**(Zn) in the absence and presence of **1** (see ESI† for the **2**(H₂)·**1** conjugate). Addition of 1.1 equivalents of fullerene derivatives to the porphyrins caused rapid decay in addition to slow decaying tail (Fig. 2(ii)). The porphyrin emission-decay in the dyads could be curve-fitted satisfactorily to a bi-exponential function. The short lifetimes were attributed to the quenching process within the supramolecular conjugates, while long lifetime components were attributed to the uncomplexed porphyrin emission. The quenching rates ($k^{S}_{q}$) evaluated from the short $\tau_{f}$ components in the usual manner employed in the intramolecular fluorescence quenching process[8] were found to be $1.7 \times 10^{9}$ and $2.6 \times 10^{9}$ s⁻¹, respectively for **2**(H₂)·**1** and **2**(Zn)·**1**, suggesting the occurrence of efficient electron transfer quenching process.

Recovery of the fluorescence decay was observed when K⁺ was added to the supramolecular conjugates of the crown ether appended porphyrin–fullerene, as shown in the time profiles (iii)
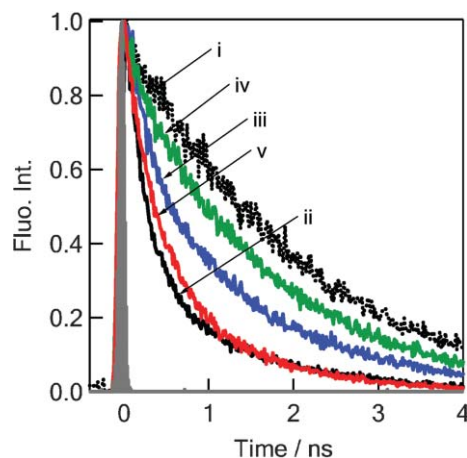
and (iv) in Fig. 2, suggesting destabilization of the supramolecular conjugates by the insertion of K⁺ into the crown ether voids (see Scheme 1). Under these conditions, the fractions of the fast fluorescence decay part decreased with K⁺ addition; the $(\tau_{f})_{complex}$ values also became long, recovering up to 80% to the initial value of porphyrin in the absence of **1**. In a control experiment, the fluorescence emission of K⁺ complexed porphyrins, **2** in the absence of fullerene, **1** was measured, but no acceleration of the fluorescence decay was observed for **2**·K⁺ (see ESI†). As shown in the fluorescence time profile (v) in Fig. 2, addition of 18-crown-6 re-accelerated the recovered fluorescence decay even in the presence of K⁺, indicating re-establishment of the supramolecular conjugate. This observation indicates that the addition of excess of 18-crown-6 eliminates most of the K⁺ in the cavity of crown ether attached porphyrin, changing the fluorescence quenching path from inter- to intramolecular route. Under these conditions, the quenching efficiency is slightly less than the original quenching probably due to some complexation of ammonium cation to the added crown ether.

Nanosecond transient absorption spectra[9] recorded after 550 nm laser irradiation offered evidence for electron transfer quenching mechanism and additional proof of switching mechanism. As shown in Fig. 3(a), the spectra of **1**·**2**(H₂) supramolecular conjugate revealed a peak at 1020 nm corresponding to the formation of fulleropyrrolidine anion radical ($C_{60}^{\bullet-}$). Although the absorption peak of the porphyrin radical cation was covered by the strong absorptions of the triplet states of the porphyrin and fullerene, the radical ion-pair may be generated as a product due to fluorescence quenching *via* the singlet excited state of the porphyrin. Therefore, the fluorescence quenching can be attributed to a charge-separation process; that is, $k^{S}_{q} = k^{S}_{CS}$.

The initial part of the time profile of the 1020 nm peak followed the first-order decay as shown in the inset of Fig. 3(a) suggesting the occurrence of intramolecular charge-recombination process of the radical ion-pair. The $k_{CR}$ values were evaluated to be $\sim 2.0 \times 10^{7}$ s⁻¹, which are nearly two orders of magnitude smaller than the $k_{CS}$ values suggesting charge stabilization in the supramolecular conjugates. Addition of K⁺ decreased the intensity of the $C_{60}^{\bullet-}$
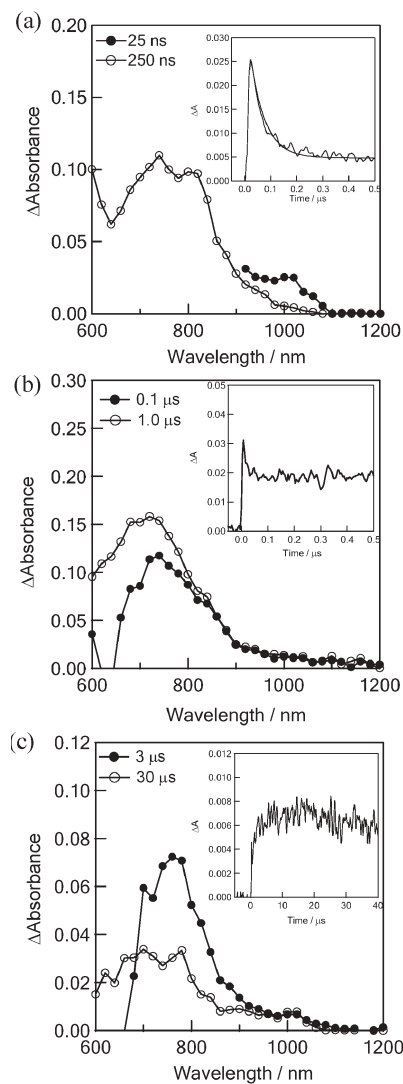
**Fig. 3** Nanosecond transient absorption spectra of (a) **2**(H$_2$) (0.10 mM) in the presence of **1** (0.11 mM), (b) added excess K$^+$ (1.00 mM), (c) **2**(H$_2$) (0.10 mM) in the presence of **1** (0.3 mM) and excess K$^+$ (1.00 mM) after the 550 nm laser irradiation in Ar-saturated benzonitrile at time intervals shown in the figure. Inset: the time profiles of the fullerene anion radicals monitored at 1020 nm.

absorption at 1020 nm (Fig. 3(b)) suggesting destruction of the supramolecular conjugate. Under these conditions, the non-decaying component at 1020 nm can be attributed to the triplet absorption tail. As shown in Fig. 3(c), further addition of fullerene, **1** in the presence of K$^+$ resulted in the concomitant acceleration of the decays of the triplet absorption accompanied by the slow rise of the C$_{60}{}^{\bullet-}$, characteristic of the occurrence of intermolecular electron transfer *via* the triplet excited states. On further addition of excess 18-crown-6, the increase of the quick rise–decay time profile at 1020 nm was recovered, indicating the occurrence of the charge-separation within the recovered supramolecular conjugate.

In summary, reversible switching of electron transfer paths in supramolecular porphyrin–fullerene conjugates held by crown ether–alkylammonium cation binding has been successfully demonstrated. The intra- to intermolecular switching was achieved by the addition of potassium cations which dissociated the crown ether–alkylammonium complex, while inter- to intramolecular switching was achieved by the addition of 18-crown-6 to extract the potassium ions of the porphyrin–crown entity. The employed porphyrin–fullerene donor–acceptor pairs were proved to be suitable for this type of applications because of the generation of relatively long-lived charge-separated states, which allows easy switching and monitoring of such processes. Further studies along this line are in progress.

## Notes and references

1 (*a*) J. S. Connolly and J. R. Bolton, in *Photoinduced electron transfer*, ed. M. A. Fox and M. Channon, Part D, Elsevier, New York, 1988; (*b*) D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 1993, **26**, 198; (*c*) M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435; (*d*) M. D. Ward, *Chem. Soc. Rev.*, 1997, **26**, 365.

2 (*a*) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; (*b*) D. M. Guldi, *Chem. Commun.*, 2000, 321; (*c*) M. D. Meijer, G. P. M. van Klink and G. van Koten, *Coord. Chem. Rev.*, 2002, **230**, 141; (*d*) M. E. El-Khouly, O. Ito, P. M. Smith and F. D'Souza, *J. Photochem. Photobiol. C.*, 2004, **5**, 79; (*e*) H. Imahori and S. Fukuzumi, *Adv. Funct. Mater.*, 2004, **14**, 525; (*f*) L. Sánchen, M. Sierra, N. Martin, A. J. Myles, T. J. Dale, J. Rebek, Jr., W. Sietz and D. M. Guldi, *Angew. Chem., Int. Ed.*, 2006, **45**, 4637.

3 *Fullerene and Related Structures*, ed. A. Hirsch, Springer, Berlin, 1999, vol. 199.

4 H. Imahori, K. Hagiwara, T. Akiyama, M. Akoi, S. Taniguchi, T. Okada, M. Shirakawa and Y. Sakata, *Chem. Phys. Lett.*, 1996, **263**, 545; D. M. Guldi and K.-D. Asmus, *J. Am. Chem. Soc.*, 1997, **119**, 5744.

5 F. D'Souza, R. Chitta, S. Gadde, M. E. Zandler, A. L. McCarty, A. S. D. Sandanayaka, Y. Araki and O. Ito, *J. Phys. Chem. B*, 2006, **110**, 4338.

6 For syntheses details, see: F. D'Souza, R. Chitta, S. Gadde, M. E. Zandler, A. L. McCarty, A. S. D. Sandanayaka, Y. Araki and O. Ito, *Chem. Eur. J.*, 2005, **11**, 4416.

7 Time-resolved fluorescence spectra were measured by single-photon counting method using a second-harmonic generation (SHG, 410 nm) of a Ti:sapphire laser [Spectra–Physics, Tsunami 3950-L2S, 1.5 ps full width at half-maximum (fwhm)] and a streak scope (Hamamatsu Photonics, C4334-01) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source and a detector, respectively.

8 F. D'Souza, G. R. Deviprasad, M. E. El-Khouly, M. Fujitsuka and O. Ito, *J. Am. Chem. Soc.*, 2001, **123**, 5277.

9 Nanosecond transient absorption measurements were carried out using 550 nm laser light of a Nd:YAG laser (fwhm 6 ns) as an excitation source. For transient absorption spectra in the near-IR region (600–1200 nm), monitoring light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). All the samples in quartz cells (1 × 1 cm) were deaerated by bubbling argon through the solution for 15 min.