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## Effect of anion binding on charge stabilization in a bis-fullerene-oxoporphyrinogen conjugate<sup>†‡</sup>

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Presence of strongly binding anion,  $F^-$  stabilizes the photoinduced charge-separated states of a bis-fullerene-substituted oxoporphyrinogen due to the large shift in the oxidation potential of the oxoporphyrinogen moiety upon anion binding through hydrogen bonding at its core.

Control of electron-transfer processes is an important issue in molecular species that may lead to their application in synthetic organic light-harvesting systems or molecular electronic devices.<sup>1-3</sup> Control of electron-transfer processes is often made possible by adding external ionic cofactors, which favor either charge separation or recombination.<sup>4</sup> For example, in the O<sub>2</sub> evolving complex of photosystem II (PSII), Ca<sup>2+</sup> and Cl<sup>-</sup> are known to be essential cofactors for efficient water oxidation.<sup>5</sup> In this context, we have previously reported a supramolecular oligochromophoric model system containing sites for binding of a reagent species and an anionic species (F<sup>-</sup>) in order to probe the effect of the binding of F<sup>-</sup> on the identities of products from photoinduced electron-transfer processes that occur within the resulting complex.<sup>6</sup> However, the effects of anionic species on photoinduced electron-transfer processes via the singlet excited state in covalently linked electron donor-acceptor systems, which are more chemically robust, have yet to be clarified.

We report herein the effect of binding of  $F^-$  to an appropriately structured tetrapyrrole chromophore, which is covalently linked with electron acceptor units, on the photoinduced electrontransfer (PET) processes *via* both the singlet and triplet excited states. The chemical structure of the subject molecule **1** contains two fulleropyrrolidine (C<sub>60</sub>) units substituted through 4,4'-biphenylmethylene groups at the nitrogen atoms of an oxoporphyrinogen (OxP) unit as depicted in Scheme 1. Both OxP

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and C<sub>60</sub> of the triad are usually considered electron-accepting agents<sup>2,6</sup> except that in this case the OxP unit is expected to be an electron donor given its ease of oxidation relative to the fulleropyrrolidine groups. Both OxP and C<sub>60</sub> components are fluorescent with the doubly substituted OxP being more strongly emissive.<sup>2,7</sup> Excitation of either of the entities is expected to induce photochemical processes in the triad. Significantly, the two imino hydrogens of the OxP unit possess the ability to bind anions with high stability<sup>8a</sup> resulting in modulation of the OxP unit redox properties.<sup>8b</sup> That is, the one-electron oxidation potential of the OxP unit, with four hemiquinone entities, is expected to exhibit large cathodic shifts upon binding of an anion. Consequently one should expect substantial changes in the energy levels which should alter the overall photochemical quenching processes. This phenomenon has been tested in the present study by using the newly synthesized model compound 1.

The synthetic details of **1** are given in ESI<sup> $\ddagger$ </sup>. Synthesis of bis(4-bromobenzyl)-substituted-OxP<sup>8</sup> was followed by Suzuki–Miyaura coupling with 4-formylphenylboronic acid to yield the bisformyl compound.<sup>9</sup> The latter was used as a substrate for the Prato reaction<sup>10</sup> yielding a bis-fullero-pyrrolidino-OxP triad, **1**.

Fig. 1a shows the optical absorption spectral changes of 1 during increasing addition of  $F^-$  in *o*-dichlorobenzene (DCB). The main peak of 1 corresponding to OxP entity located at 511 nm revealed diminished intensity with the concurrent appearance of two new bands at 603 and 756 nm. Isosbestic points at 309, 348 and 426 nm are observed suggesting the existence of only one equilibrium process in solution. The sharp peak at 430 nm of fulleropyrrolidine showed no visible effect upon addition of  $F^-$  in solution. Plots of mole ratio against absorbance change (Fig. 1c) suggest 1:1 complex



Scheme 1 Structure of the newly synthesized  $OxP(C_{60})_2$  triad, 1 to probe anion binding effect on charge separation.

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Fig. 1 (a) Absorption spectra of 1 (7.5  $\mu$ M) upon increasing addition of F<sup>-</sup> (0.1–0.5 eq.). (b) Benesi–Hildebrand plot constructed to obtain the binding constant, and (c) mole ratio plot to obtain the molecular stoichiometry of the 1: F<sup>-</sup> complex in DCB.

formation. The binding constant evaluated by constructing a Benesi–Hildebrand plot<sup>11</sup> (Fig. 1b) is found to be  $5.8 \times 10^4 \text{ M}^{-1}$ , suggesting stable complex formation.

Both  $OxPR_2$  (R = alkyl or aryl)<sup>7</sup> and fulleropyrrolidine<sup>2</sup> are known to emit in the 720 nm region and this is also the case for the investigated compound **1**, albeit with much lower quantum yields. That is, a broad emission spanning the 600–850 nm range was observed for **1** (Fig. 2). The weak emission of fullerene is hidden under the relatively strong emission of OxP. Addition of F<sup>-</sup> further decreased the emission intensity resulting in formation of an almost non-emitting complex (>98% quenching) likely caused by occurrence of very efficient photochemical events.

Electrochemical studies are performed to probe the effect of anion binding on the redox potentials of 1 and their subsequent effect on the energy levels of photoinduced processes. The first oxidation of 1 is a reversible process located at  $E_{1/2} = 0.37$  V vs. Fc/Fc<sup>+</sup> in DCB (Fig. 3). The potential value is similar to that reported earlier for OxP(bz)<sub>2</sub> (bz = benzyl) derivative<sup>12</sup> lacking the fullerene suggesting that the site of oxidation involves the OxP unit. A second oxidation is also observed at higher anodic potentials ( $E_{1/2} = 0.58$  V). The fullerene reduction of 1 is located at  $E_{1/2} = -1.28$  V vs. Fc/Fc<sup>+</sup>, whereas the first reduction of OxP and the second reduction of fullerene are close and appeared at -1.56 and -1.64 V,



Fig. 2 Fluorescence spectra of 1 (7.5  $\mu$ M) on increasing addition of F<sup>-</sup> (0.1–0.5 eq.) in DCB;  $\lambda_{ex} = 509$  nm.



Fig. 3 Cyclic voltammograms of 1 in the absence (dark line) and presence (red line) of  $F^-$  in deaerated DCB containing 0.1 M (TBA)ClO<sub>4</sub>. Scan rate = 100 mV s<sup>-1</sup>.

respectively. Interestingly, addition of  $F^-$  revealed drastic changes in the oxidation potentials of the OxP entity. That is, addition of 1.1 eq. of  $F^-$  to a solution of 1 resulted in a cathodic shift of nearly 510 mV ( $E_{1/2} = -0.14$  V) as a result of  $F^-$  binding to the OxP unit. On the reduction side, the fullerene reduction underwent a small anodic shift of 60 mV ( $E_{1/2} = -1.22$  V) due to ion-pairing effect.<sup>13</sup> However, no appreciable shifts are seen for OxP reduction.

Free-energy calcuations for charge separation (CS) and charge recombination (CR) were performed according to Weller's approach.<sup>2b</sup> The driving forces for charge recombination  $(-\Delta G_{CR})$  and charge separation  $(-\Delta G_{CS})$  processes of 1 via the singlet excited state of OxP and C<sub>60</sub> are evaluated as 1.65 and 0.10 eV, respectively, taking into consideration that the energy of the singlet excited state of OxP and C<sub>60</sub> are 1.75 eV.<sup>7,15</sup> In case of 1: F<sup>-</sup>, the  $-\Delta G_{CR}$  value was determined to be 1.14 eV. The PET processes are exothermic from the singlet ( $-\Delta G_{CS} = 0.61$  eV) and triplet ( $-\Delta G_{CS} = 0.41$  eV) excited states of the OxP unit.

A spectroscopic signature for the formation of radical ion pair species and kinetics of CS and CR are obtained from the transient absorption studies in the femtosecond and nanosecond time regimes by utilizing the 430 nm laser light, which selectively excites the OxP entity (Fig. 4). The femtosecond transient absorption spectrum of 1 and 1:  $F^-$  revealed absorption bands in the visible and near infrared (NIR) regions with maxima at 870 and 1000 nm due to  $OxP^{\bullet+}$  and  $C_{60}^{\bullet-}$  species,



**Fig. 4** Femtosecond transient absorption spectra of  $1: F^-$  in deaerated DCB;  $\lambda_{ex} = 430$  nm. The figure inset shows decay of the 1000 nm transient band corresponding to fullerene radical anion.



**Fig. 5** Nanosecond transient absorption spectra of  $1: F^-$  in deaerated DCB. Inset shows the time profile of the  $C_{60}^{\bullet-}$  at 1000 nm.

respectively, offering clear evidence for the occurrence of PET from the electron donating OxP to the electron accepting  $C_{60}$ .<sup>6,14</sup> The rate of CS *via* the singlet excited state is found to be very fast (~10<sup>12</sup> s<sup>-1</sup> ps). From fitting the decay of the radical ion pair species with clean first-order kinetics, the rates of charge recombination ( $k_{CR}$ ) were found to be 6.6 × 10<sup>10</sup> and 1.40 × 10<sup>10</sup> s<sup>-1</sup> for 1 and 1:F<sup>-</sup>, respectively. Using these  $k_{CR}$  values, lifetimes of the charge-separated states ( $\tau_{CS} = 1/k_{CR}$ ) *via* the singlet state were calculated to be 15 and 72 ps for 1 and 1:F<sup>-</sup>, respectively, revealing the effect of F<sup>-</sup> on stabilization of the charge-separated state.

Nanosecond transient absorption spectral studies provided evidence of PET from the triplet excited state of the OxP unit, taking into account the thermodynamic feasibility of electron transfer of  $1: F^-$  via the triplet state of OxP, as mentioned earlier. As shown in Fig. 5, the transient absorption spectrum exhibited peaks at 860 and 1000 nm due to  $OxP^{\bullet^+}$  and  $C_{60}^{\bullet^-}$ species.<sup>6,14</sup> The rate of CS from the triplet excited state was too fast to detect within the time resolution of the nanosecond laser pulse. By monitoring the decay of the  $C_{60}$  radical anion band,  $k_{CR}^{T}$  was determined as  $1.6 \times 10^5 \text{ s}^{-1}$ . Based on  $k_{CR}^{T}$ , the lifetime of the triplet CS state was evaluated as (6.3 µs), which is a relatively long-lived species compared to the widely investigated porphyrin–fullerene dyads in the literature.<sup>1,2</sup> The photochemical events via the singlet and triplet excited states of OxP are summarized as shown in Fig. 6.

In summary, we have synthesized a novel molecular triad comprised of a redox-active anion-receptor (OxP) and  $C_{60}$  entities. The OxP entity binds  $F^-$  through the imino-hydrogens



Fig. 6 Energy level diagram showing the electron transfer processes of  $1: F^-$  via the singlet and triplet OxP in deaerated DCB.

leading to a large cathodic shift of its oxidation potential. As a result, the donor-acceptor pair reveals very efficient PET from both the singlet and triplet excited states of OxP. Presence of  $F^-$  in the OxP pocket slows down the CR process thus generating the much desired long-lived CS state. Further studies to prolong the charge-separated state by means of multi-step charge migration in anion bound OxP containing polyads are in progress.

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## Notes and references

- (a) M. R. Wasielewski, Acc. Chem. Res., 2009, 42, 1910;
   (b) D. Gust and T. A. Moore, in The Porphyrin Handbook, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, Burlington, MA, 2000, vol. 8, pp. 153–190; (c) F. D'Souza, O. Ito, in Handbook of Porphyrin Science, ed. K. M. Kadish, R. Guilard and K. M. Smith, World Science Publishers, 2010, vol. 1, ch. 4, pp. 307–437.
- 2 (a) S. Fukuzumi and T. Kojima, J. Mater. Chem., 2008, 18, 1427;
  (b) V. Sgobba and D. M. Guldi, Chem. Soc. Rev., 2009, 38, 165;
  (c) L. Sanchez, M. Nazario and D. M. Guldi, Angew. Chem., Int. Ed., 2005, 44, 5374.
- 3 (a) H. Imahori, T. Umeyama and S. Ito, Acc. Chem. Res., 2009, 42, 1809; (b) P. V. Kamat, J. Phys. Chem. C, 2007, 111, 2834; (c) B. E. Hardin, E. T. Hoke, P. B. Armstrong, J.-H. Yum, P. Comte, T. Torres, J. M. J. Frechet, M. K. Nazeeruddin, M. Grätzel and M. D. McGehee, Nat. Photonics, 2009, 3, 667; (d) T. M. Figueira-Duarte, A. Gegout and J.-F. Nierengarten, Chem. Commun., 2007, 109.
- 4 (a) S. Fukuzumi, Prog. Inorg. Chem., 2009, 56, 49; (b) S. Fukuzumi, Bull. Chem. Soc. Jpn., 1997, 70, 1.
- 5 (a) C. F. Yocum, Coord. Chem. Rev., 2008, 252, 296; (b) J. P. McEvoy and G. W. Brudvig, Chem. Rev., 2006, 106, 4455; (c) L. M. Utschig and M. C. Thurnauer, Acc. Chem. Res., 2004, 37, 439.
- 6 F. D'Souza, N. K. Subbaiyan, Y. Xie, J. P. Hill, K. Ariga, K. Ohkubo and S. Fukuzumi, J. Am. Chem. Soc., 2009, 131, 16138.
- 7 Y. Xie, J. P. Hill, A. Lea Schumacher, A. S. D. Sandanayaka, Y. Araki, P. A. Karr, J. Labuta, F. D'Souza, O. Ito, C. E. Anson, A. K. Powell and K. Ariga, *J. Phys. Chem. C*, 2008, **112**, 10559.
- 8 (a) J. P. Hill, A. L. Schumacher, F. D'Souza, J. Labuta, C. Redshaw, M. R. J. Elsegood, M. Aoyagi, T. Nakanishi and K. Ariga, *Inorg. Chem.*, 2006, **45**, 8288; (b) A. L. Schumacher, J. P. Hill, K. Ariga and F. D'Souza, *Electrochem. Commun.*, 2007, **9**, 2751.
- 9 B. D. Palmer, A. M. Thompson, H. S. Sutherland, A. Blaser, I. Kmentova, S. G. Franzblau, B. Wan, Y. Wang, Z. Ma and W. A. Denny, J. Med. Chem., 2010, 53, 282.
- 10 M. Maggini, G. Scorrano and M. Prato, J. Am. Chem. Soc., 1993, 115, 9798.
- 11 H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 1949, 71, 2703.
- 12 J. P. Hill, I. J. Hewitt, C. E. Anson, A. K. Powell, A. L. McCarty, P. A. Karr, M. E. Zandler and F. D'Souza, *J. Org. Chem.*, 2004, 69, 5861.
- 13 D. Dubois, G. Moninot, W. Kutner, M. T. Jones and K. M. Kadish, J. Phys. Chem., 1992, 96, 7137.
- 14 M. E. El-Khouly, D. K. Ju, K.-Y. Kay, F. D'Souza and S. Fukuzumi, *Chem.-Eur. J.*, 2010, **16**, 6193.
- 15 D. M. Guldi and P. V., Kamat in Fullerenes: Chemistry, Physics and Technology, ed. K. M. Kadish and R. S. Ruoff, Wiley-Interscience, New York, 2000.