# ChemComm

#### COMMUNICATION

## **RSC**Publishing

View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2013, 49, 7614

Received 10th May 2013, Accepted 1st July 2013

DOI: 10.1039/c3cc43510e

www.rsc.org/chemcomm

### A 'two-point' bound zinc porphyrin-zinc phthalocyanine-fullerene supramolecular triad for sequential energy and electron transfer<sup>†‡</sup>

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A novel supramolecular triad composed of a zinc porphyrin-zinc phthalocyanine dyad and fullerenes has been assembled using a 'two-point' axial binding approach, and occurrence of efficient photoinduced energy transfer followed by electron transfer is demonstrated.

In natural photosynthesis, photon energy is efficiently funnelled with the help of antenna pigments to the reaction centre to generate charge separated states as a result of the occurrence of sequential energy and electron transfer events.<sup>1</sup> Inspired by this, there have been a number of artificial photosynthetic models capable of mimicking these events with an ultimate aim of converting light energy into solar fuels, as well as to build optoelectronic devices.2-4 Self-assembled assemblies are more appealing compared to covalently linked ones due to their close resemblance to natural systems. Additionally, although synthetically challenging, by introducing multiple modes of binding between the entities, the desired distance and orientation between the donor-acceptor entities could be achieved.<sup>2-4</sup> In this regard, a 'two-point' axial coordination approach was introduced by us to link a covalently linked porphyrin dimer to fulleropyrrolidine via metal-ligand axial coordination,<sup>5</sup> and photoinduced electron-transfer processes in relevant systems were demonstrated.<sup>6</sup> In the present study, we have extended this approach by employing a zinc porphyrin-zinc phthalocyanine (ZnP-ZnPc) dyad capable of undergoing singlet-singlet energy

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**Fig. 1** Structure of the zinc porphyrin–zinc phthalocyanine–fullerene triad held by a 'two-point' axial coordination binding approach.

transfer<sup>7</sup> and binding to an electron acceptor fullerene functionalized to possess two pyridine entities  $(C_{60}Py_2)$  via 'two-point' binding as shown in Fig. 1. Occurrence of sequential light induced energy and electron transfer events as probed spectroscopic and transient spectral studies is presented.

The synthesis of a ZnP–ZnPc dyad was carried out according to the procedure given in Scheme  $1^{7b}$  (see experimental details in ESI‡). Here, a *meta*-carboxy functionalized ZnP was used to react with hydroxy functionalized ZnPc. The *meta* derivative provided the necessary molecular orientation of the dimer to accommodate  $C_{60}Py_2$  *via* the two-point binding (*vide infra*).

Fig. 2a shows the absorption spectrum of the dyad along with the spectrum of a 1:1 mixture of ZnP and ZnPc in *o*-dichlorobenzene (DCB). A small red shift (1–2 nm) of the ZnP Soret and broadening of ZnPc bands were observed suggesting occurrence of some intramolecular interactions between the two entities of the dyad. Fig. 2b shows the fluorescence spectrum of the dyad along with that of the 1:1 mixture at the excitation at 425 nm corresponding to ZnP. The ZnP emissions at 600 and 650 nm were quenched over 80% of their values observed for the 1:1 mixture with the appearance of strong ZnPc emission at 700 nm indicating occurrence of intramolecular singlet excitation transfer in the dyad.<sup>7,8</sup> The excitation spectrum recorded for the dyad by holding the emission wavelength at 695 nm and scanning the excitation wavelength (Fig. S1 in ESI‡) revealed bands of both ZnPc and ZnP.

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 $<sup>\</sup>dagger$  In loving memory of Prof. Erach Talaty, a beloved teacher and dedicated researcher.

<sup>&</sup>lt;sup>‡</sup> Electronic supplementary information (ESI) available: Synthetic details and the mass spectrum of the ZnP–ZnPc dyad, experimental procedures and instrumentation, the excitation spectrum of the dyad, the femtosecond transient spectrum of  $C_{60}Py_2$  in DCB, and the nanosecond transient spectrum of the ZnP–ZnPc: $Py_2C_{60}$  triad in DCB. See DOI: 10.1039/c3cc43510e



**Scheme 1** Synthetic procedure adopted for the ZnP–ZnPc dyad (DMAE = N,N-dimethylaminoethanol, DCC = N,N'-dicyclohexyl-carbodiimide, DMAP = 4-(dimethylamino)pyridine).



Fig. 2 (a) Absorption (3.9  $\mu$ M each) and (b) emission (3.9  $\mu$ M each) spectrum of (i) ZnP–ZnPc dyad and (ii) 1:1 mixture of ZnP and ZnPc in DCB.  $\lambda_{ex}$  = 425 nm.

However, the ZnP bands were missing in the spectrum recorded for the 1:1 mixture providing evidence for the occurrence of excitation transfer in the dyad.

The supramolecular triad was formed by complexing  $C_{60}Py_2$  to the ZnP–ZnPc dyad. Fig. 3a shows spectral changes observed during titration of  $C_{60}Py_2$  to a solution of the ZnP–ZnPc dyad in DCB. A ZnP Soret band at 425 nm revealed characteristic features of axial coordination with diminished intensity accompanied by a red shift.<sup>6</sup> Similarly, the ZnPc band at 690 nm revealed diminished intensity in addition to three isosbestic points. The binding constant calculated from the spectral data using the Benesi–Hildebrand method<sup>9</sup> was found to be  $1.7 \times 10^5 \text{ M}^{-1}$  (Fig. 3b) which was over an order of magnitude higher than that reported for 'single-point' metal–ligand coordination.<sup>3b</sup> Further, a plot of the mole ratio revealed a break at 0.5 (Fig. 3c) confirming a 1:1 stoichiometry of the supramolecular triad involving binding of both metal centers to  $C_{60}Py_2$ .

Addition of  $C_{60}Py_2$  to the solution of the ZnP–ZnPc dyad quenched ZnPc emission almost quantitatively while such changes for the weak ZnP emission were minimal (Fig. 3d). To further understand this, additional computational and electrochemical



**Fig. 3** (a) Absorption spectral changes observed for C<sub>60</sub>Py<sub>2</sub> (3.7 mM, 2 µL each addition) binding to ZnP–ZnPc (3.9 µM) in DCB, (b) Benesi–Hildebrand plot to calculate the binding constant, (c) mole-ratio plot to establish the molecular stoichiometry, (d) fluorescence changes observed for binding of C<sub>60</sub>Py<sub>2</sub> to ZnP–ZnPc in DCB;  $\lambda_{ex} = 412$  nm corresponding to one of the isosbestic points.

studies were performed. Fig. 4a and b show B3LYP/6-31G\* optimized geometries<sup>10</sup> of the ZnP–ZnPc dyad and C<sub>60</sub>Py<sub>2</sub>. The two macrocycles of ZnP–ZnPc were tilted due to the *meta-substitution* of ZnP (dihedral angle = 96°). At least two geometries for the triad were possible owing to an extra connecting methylene group for one of the Py entities of C<sub>60</sub>Py<sub>2</sub> as shown in Fig. 4c and d. The structure shown in Fig. 4c is more stable by *ca.* 2.3 kJ mol<sup>-1</sup> compared to the one shown in Fig. 4d. The centre-to-centre distance between Zn and C<sub>60</sub> for the triad having C<sub>60</sub>-pyridine with connecting –CH<sub>2</sub>– was about 0.5 Å more than the one without a –CH<sub>2</sub>– fragment, both with a distance of 11.5 ± 0.5 Å.

Further free-energy calculations for charge-separation ( $\Delta G_{CS}$ ) were performed according to the Weller approach.<sup>11</sup> These values,



Fig. 4 B3LYP/6-31G\* optimized structures of the ZnP–ZnPc dyad (a),  $C_{60}Py_2$  (b) and the two forms of self-assembled triads (c) and (d).



Fig. 5 (a) Femtosecond transient spectra of the ZnP–ZnPc dyad at the indicated time intervals in DCB. The kinetic profiles of the 500 and 900 nm bands of <sup>1</sup>ZnP\* are shown in b and c, respectively.

determined from redox potential (Fig. S2 in ESI‡ for voltammograms) and singlet state energy of each zinc tetrapyrrole (2.06 eV for <sup>1</sup>ZnP\* and 1.83 eV for <sup>1</sup>ZnPc\*), were found to be -0.72 eV for <sup>1</sup>ZnPc\* and -0.58 eV from <sup>1</sup>ZnP\* originated electron transfer in the triad indicating dominance of ZnPc over ZnP in the electron transfer process.

Femtosecond transient absorption spectral studies were performed to probe mechanistic and kinetic details of energy and electron transfer events. The acceptor,  $C_{60}Py_2$ , upon excitation by the 393 nm laser light revealed formation of  ${}^{1}C_{60}Py_2^*$  at 900 nm that decayed at a rate of  $2.3 \times 10^9 \text{ s}^{-1}$  to populate  ${}^{3}C_{60}Py_2^*$  at 700 nm (Fig. S3 in ESI‡).<sup>12</sup> The ZnP–ZnPc dyad upon excitation by the 393 nm laser revealed initial population of  ${}^{1}ZnP^*$  with characteristic transient peaks at 500 and 950 nm with a rate constant  $>5 \times 10^{12} \text{ s}^{-1}$ ; these peaks decayed to populate  ${}^{1}ZnPc^*$  at 830 nm (Fig. 5) within 1.5 ps. The rate of singlet energy transfer was close to that reported recently for the ZnP–ZnPc dyad with a *para* linkage<sup>7b</sup> revealing very small influence from the mode of porphyrin substitution (*meta versus para*).

The supramolecular triad formed upon binding of  $C_{60}Py_2$  revealed features confirming the occurrence of photoinduced electron transfer. As shown in Fig. 6, excitation of the triad at 393 nm had features of singlet–singlet energy transfer from <sup>1</sup>ZnP\* to ZnPc at a rate not much different from that of the ZnP–ZnPc dyad. However, the newly formed <sup>1</sup>ZnPc\* underwent photoinduced electron transfer with the coordinated fullerene to produce the ZnP–ZnPc<sup>•+</sup>–C<sub>60</sub><sup>•-</sup> radical ion-pair state as witnessed from the appearance of a fullerene radical anion peak at 1000 nm. The ZnPc radical cation band at 840 nm overlapped with the <sup>1</sup>ZnPc\* band at 820 nm.<sup>13</sup> These radical ion-peaks persisted for about 3 ns indicating formation of



**Fig. 6** (a) Femtosecond transient absorption spectra of the  $ZnP-ZnPc:Py_2C_{60}$  triad at the indicated time intervals in DCB. The kinetic profiles of absorbance at (b) 900 nm and (c) 1000 nm are at the right hand side panel.

relatively long-lived charge-separated states. The lifetime of the charge-separated state was determined from the decay curve of absorbance at 1000 nm due to the  $C_{60}^{\bullet-}$  moiety to be 1.7 ns (Fig. 6c). Additional nanosecond transient studies performed revealed the absence of transient features of the charge separated species indicating occurrence of charge recombination well before the 10 ns detection limit of the instrument (Fig. S4 in ESI<sup>‡</sup>).

In summary, using a 'two-point' axial binding approach, we have assembled a novel triad comprised of a ZnP–ZnPc dyad and  $C_{60}$  to probe sequential photoinduced energy and electron transfer events. The two-point binding approach resulted in a triad of defined shape and relatively high stability. Free-energy calculation suggested that electron transfer from <sup>1</sup>ZnPc\* is energetically more favorable than that from the <sup>1</sup>ZnP\* in the triad although the acceptor ( $C_{60}$ ) was disposed at an almost equal distance. Consequently, efficient energy transfer from <sup>1</sup>ZnP\* to ZnPc in the triad followed by formation of a ZnP–ZnPc•<sup>+</sup>– $C_{60}$ •<sup>-</sup> radical ion-pair was witnessed in the triad. These findings prove to be significant for future design of tetrapyrrole donor–nanocarbon acceptor hybrids for wide-band capture and efficient light energy harvesting.

FD acknowledges support from the NSF (Grant No. 1110942). SF and K.O. acknowledge support from Grants-in-Aid (No. 20108010 to S.F. and 23750014 to K.O.) from MEXT, Japan, and KOSEF/MEST through the WCU project (R31-2008-000-10010-0), Korea. The computational work was completed utilizing the Holland Computing Center of the University of Nebraska.

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