Supramolecular porphyrin–fullerene *via* 'two-point' binding strategy: Axial-coordination and cation–crown ether complexation†

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A highly stable porphyrin–fullerene conjugate with defined distance and orientation, was formed using a newly developed 'two-point' binding strategy involving axial-coordination and cation–crown ether complexation; photochemical studies performed in benzonitrile revealed efficient charge separation and slow charge-recombination in the supramolecular complex.

Employing multiple modes of binding in the design of supramolecular donor–acceptor dyads is a key factor for controlling the free rotation between the entities, and thereby providing the structural rigidity.[1] This approach provides information about the structure and orientation of the donor–acceptor pair, and minimizes the different degrees of electronic coupling due to the different wave function mixing, observed in flexibly linked donor–acceptor pairs. In this regard, several donor–acceptor systems covalently linked by rigid/multiple bonds and self-assembled with more than one modes of binding have been elegantly designed and studied using mainly porphyrins as donors and quinones as acceptors.[1]

Fullerenes have been recognized as good electron acceptors due to their 3-D structure, reduction potentials comparable to benzoquinone, and absorption spectra extending to most of the visible spectrum.[2] Also, studies performed on several covalently and noncovalently linked donor–fullerene dyads have shown that C_{60}, as an acceptor, accelerates charge separation and decelerates charge recombination. This novel property of fullerenes has been ascribed to the small reorganization energy (λ) of C_{60} in electron transfer reactions. Generally, the photoinduced charge separation occurs in the 'normal region' of the Marcus curve while charge recombination occurs in the 'inverted region' of the Marcus curve involving porphyrin–fullerene dyads.[2] This property has been effectively utilized in creating long-lived charge separation in a few covalently linked porphyrin–fullerene systems.[2d,3]

A few studies have focused on rigidly linked porphyrin–fullerene dyads by covalent attachment.[4] Our interest in this area of research has been to construct supramolecular porphyrin–fullerene dyads held by multiple modes of binding to restrict flexibility between the donor and the acceptor moieties.[5] Earlier, we developed 'two-point' binding strategies involving 'covalent-coordinate',[5a] 'coordinate-hydrogen bonding'[5b] and 'coordinate-coordinate bonding',[5c] and formed stable porphyrin–fullerene dyads and triads with defined distance and orientation. In the present study, we have devised another novel 'two-point' binding strategy which involves axial metal–ligand coordination and crown ether–cation complexation as binding modes (Chart 1). To achieve this, fullerene has been functionalized to possess a pyridine coordinating ligand and an alkyl ammonium cation, while zinc porphyrin has been functionalized with a benzo-18-crown-6 moiety. During self-assembly, the pyridine moiety is expected to coordinate to the metal center of zinc porphyrin[6a] while the ammonium cation is expected to bind the crown ether moiety of the porphyrin.[6b] As a result of the 'two-point' binding, highly stable complexes are expected to form allowing us to perform photochemical studies in a more polar solvent like benzonitrile which is otherwise not possible in a 'one-point' bound porphyrin–fullerene conjugates.[6a] Studies in polar solvents are important to promote charge separation and create long-lived charge separated states.[1,2]

The formation of the 'two-point' bound supramolecular complex was monitored by optical absorption and ^1H NMR studies. As shown in Fig. 1, addition of the functionalized fullerene to the porphyrin receptor in benzonitrile resulted in red shifted absorption bands with an isosbestic point at 417 nm. The binding constant, *K*, calculated from Scatchard method[6a] was found to be 4.4×10^4 mol^{-1} dm^3 suggesting stable self-assembled supramolecule formation even in a polar solvent. It may be mentioned here that using the 'one-point' axial-coordination approach a supramolecular complex in benzonitrile was not possible to form.[6a] ^1H NMR studies also revealed the presence of the two modes of binding. That is, the addition of functionalized porphyrin to a $CDCl_3$: CD_3OD (1 : 1 v/v) solution containing fulleropyrrolidine

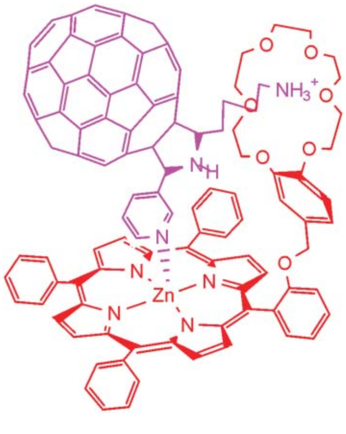

Chart 1

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† Electronic supplementary information (ESI) available: Experimental section involving the syntheses of porphyrin and fullerene derivatives, ^1H NMR spectra, fluorescence quenching data with Benesi–Hildebrand plot, and picosecond fluorescence decay plots of the dyads. See http://www.rsc.org/suppdata/cc/b4/b416736h/

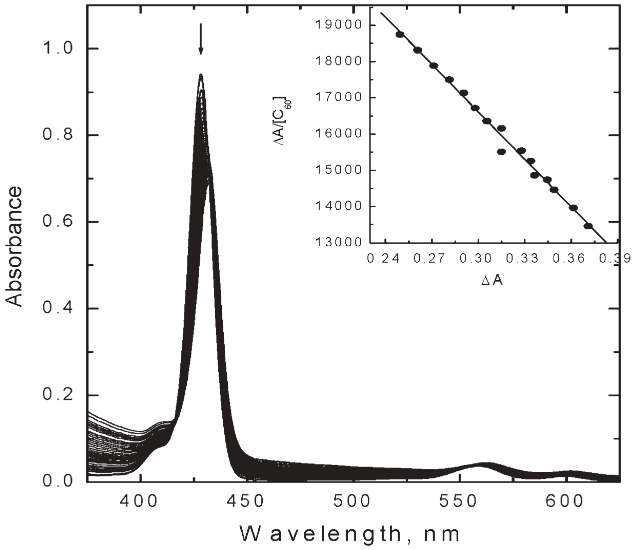

Fig. 1 Spectral changes observed during the titration of the zinc porphyrin receptor (1.42×10^{-6} mol dm^{-3}) with functionalized fullerene in Chart 1 (0.20 eq. each addition) in benzonitrile. Figure inset shows the Scatchard plot.

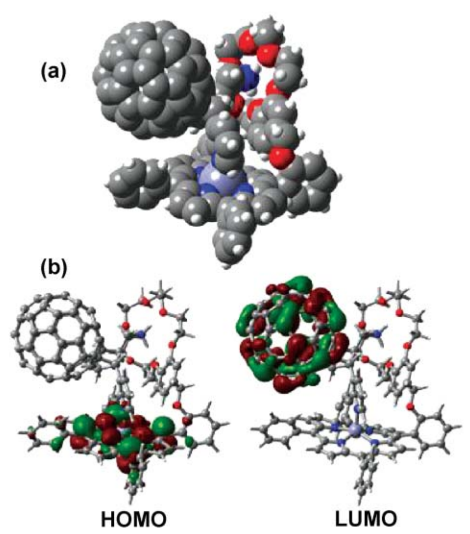

Fig. 2 (a) The B3LYP/3-21G(*) optimized structure, (b) HOMO, and LUMO of the self-assembled *via* axial-coordination and cation–crown ether complexation zinc porphyrin–fullerene supramolecular complex.

revealed shielding of pyridine protons initially located at 9.11, 8.59, 8.45 and 7.60 ppm up to 3 ppm indicating formation of zinc–nitrogen coordinate bond. The crown ether protons located in the range 3.56–2.28 ppm revealed a small deshielding and appeared in the range 3.62–3.02 ppm up on cation–crown ether complexation (see ESI).† Results of the steady-state fluorescence revealed efficient quenching of the porphyrin emission (>90%) upon addition of the functionalized fullerene (see ESI).† The Stern–Volmer quenching constant calculated from the emission data was found to be 4 orders of magnitude higher than that expected for intermolecular quenching process indicating the occurrence of intramolecular photochemical events. The K calculated using Benesi–Hildebrand analysis of the emission data was found to be 4.5×10^4 mol^{-1} dm^3, which agreed well with the absorption data.

DFT studies using B3LYP/3-21G(*) basis set[7] have been performed to visualize the geometry and electronic structure of the 'two-point' bound porphyrin–fullerene conjugate. As shown in Fig. 2a, the optimized structure revealed the presence of both zinc–pyridine coordinate bond and ammonium cation–crown ether complex. The center-to-center and the edge-to-edge distances between the porphyrin and C_{60} moieties were found to be 10.1 and 4.51 Å, respectively. The Zn–N distance of the newly formed coordinate bond was found to be 2.1 Å which is comparable to the Zn–N distance determined earlier by X-ray studies on a 'one-point' axial bound zinc porphyrin–C_{60} dyad.[8] Two sets of N–O bond distances, 2.80 and 3.00 Å, respectively, were found for the ammonium cation–crown ether complex. The smaller N–O bonds represent the presence of N–H···O type hydrogen bonding. The fullerene was oriented in such a way that the center of C_{60}, center of porphyrin, and the nitrogen of the ammonium cation, roughly formed an equilateral triangle. The gas phase dissociation energy for the complex, calculated as the energy difference between the dyad and the sum of the energies of the individual porphyrin and fullerene moieties, was found to be 489 kJ mol^{-1}. This energy is nearly four times larger than that reported earlier for porphyrin–fullerene conjugate bound only by a coordinate bond.[6a] As shown in Fig. 2b, the frontier HOMO and LUMO were found to be located entirely on the porphyrin and fullerene moieties. That is, the existence of ammonium cation–crown ether complex did not perturb the electronic structure of the donor and acceptor entities of the conjugate.

In accordance to the steady-state fluorescence behaviour, the picosecond time-resolved emission studies[9] revealed quenching of porphyrin emission upon supramolecular complex formation. The measured lifetime of the supramolecular complex was found to be 280 ps which compared with a value of 1980 ps of the donor, zinc porphyrin receptor (see ESI†). The rate of charge separation, k_{CS}, calculated from the fluorescence lifetimes and the usual procedure adopted for intramolecular dyads[10] was found to be 3.1×10^9 s^{-1} and the charge separation quantum yield, Φ_{CS}, was found to be 0.86, indicating the occurrence of efficient electron transfer.[11]

Direct evidence for charge separation in the supramolecular complex was obtained from nanosecond transient spectral studies[12] which also allowed us to determine the rate of charge recombination. As shown in Fig. 3, the transient absorption spectra obtained by 550 nm laser irradiation, revealed a band at 1020 nm corresponding to the $C_{60}^{-\cdot}$.[5a] In addition, $ZnP^{+\cdot}$ at 640 nm as a shoulder; intense bands at 840 nm and 700 nm corresponding to $^3ZnP^*$ and $^3C_{60}^*$, respectively, generated from $^1ZnP^*$ and $^1C_{60}^*$ *via* intersystem crossing and/or present as free species were observed. The rate of charge recombination, k_{CR}, calculated by monitoring the decay of the 1020 nm band (Fig. 3 inset) was found to be 2.1×10^7 s^{-1}. It may be mentioned here that the long-time measurements of the tail of the 1020 nm band with different laser powers yielded lifetimes of 8.7–9.7 $\times$ 10^3 s^{-1}, which was attributed to the tail of the triplet decay of the fullerene entity. For these long-time measurements, the first order decay fitting was more than 90% satisfied suggesting little or no contributions from the second order intermolecular type events occurring in solution. From the kinetic data, the calculated ratio of

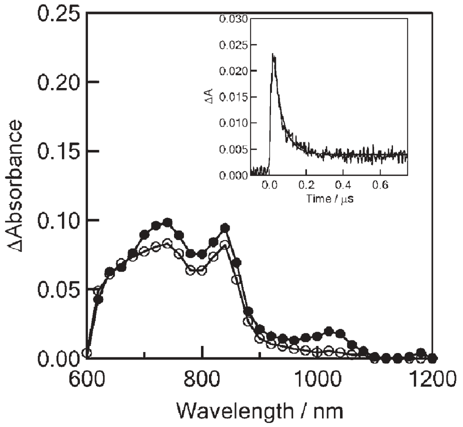

Fig. 3 Nanosecond transient absorption spectra of the zinc porphyrin–fullerene supramolecular complex (0.1 mmol dm^{-3}) in benzonitrile at 30 ns (filled circle) and 300 ns (open circle) after the 550 nm laser irradiation. Inset: Absorption time profile at 1020 nm.

the forward to backward electron transfer rates, k_{CS}/k_{CR} was found to be 150, indicating ion-pair formation in the rigidly held porphyrin–fullerene supramolecular complex.

An examination of the electron transfer kinetic data presented here for the self-assembled zinc porphyrin–fullerene by the newly developed 'axial-coordination and cation–crown ether complexation' two-point binding approach; compared to the earlier reported[5] zinc porphyrin–fullerene dyads assembled by either 'covalent-coordinate', or 'coordinate-hydrogen bonding' or 'coordinate-coordinate' binding mechanisms, suggested that utilizing multiple modes of binding not only results in dyads held by defined distance and orientation, but also improves the overall electron transfer aspects. That is, the k_{CS} and Φ_{CS} values become comparable to that of the covalently linked zinc porphyrin–fullerene dyads in literature.[2] Additionally, k_{CR} becomes slower generating relatively long-lived charge separated states. The charge recombination process can be slowed down further by introducing second electron donor, *viz*. *N*,*N*-dimethylaminophenyl group on the fullerene moiety.[5b]

In summary, we have assembled a porphyrin–fullerene conjugate using a 'two-point' binding strategy involving 'axial-coordination, and ammonium cation–crown ether complexation'. As a result of the adopted 'two-point' binding, a stable porphyrin–fullerene conjugate with defined distance and orientation was obtained which led us to perform the spectral and photochemical studies in a more polar solvent like benzonitrile. Picosecond time-resolved emission and nanosecond transient absorption studies revealed efficient quenching of porphyrin singlet emission, and a comparison of the measured rates of k_{CS} and k_{CR} revealed charge stabilization in the supramolecular complex.

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9 Time-resolved fluorescence spectra were measured by a 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.

10 The k_{CS} and Φ_{CS} were calculated using: $k_{CS}{}^{singlet} = (1/\tau_f)_{complex} - (1/\tau_f)_{ZnP}$, ${}^*\Phi_{cs}{}^{singlet} = [(1/\tau_f)_{complex} - (1/\tau_f)_{ZnP}]/(1/\tau_f)_{complex}$.

11 The free energy changes for charge separation, ΔG_{CS} and charge recombination, ΔG_{CR} calculated from the first oxidation potential of ZnP and the first reduction potential of C_{60}, singlet energy of the ZnP, and the Coulomb energy (ref. 6*a*), were found to be exothermic with values of -0.71 and -1.32 eV, respectively.

12 Nanosecond transient absorption measurements were carried out using SHG (532 nm) of Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. For transient absorption spectra in the near-IR region (600–1600 nm), monitoring light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). All the samples in a quartz cell (1 × 1 cm) were deaerated by bubbling argon through the solution for 15 min.