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Supramolecular complex composed of a covalently linked zinc porphyrin dimer and fulleropyrrolidine bearing two axially coordinating pyridine entities†

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Received (in Corvallis, OR, USA) 26th May 2004, Accepted 26th July 2004
First published as an Advance Article on the web 8th September 2004

A zinc porphyrin dimer–fullerene supramolecular complex with a large association constant is assembled; efficient intramolecular photoinduced electron transfer from the singlet excited state of zinc porphyrin to the fullerene is observed.

Light induced electron transfer systems with efficient and long-lived charge separation are of great importance to develop artificial photosynthesis and molecular-level optoelectronics.[1,2] A number of covalently and non-covalently linked donor-acceptor systems have been prepared to further our understanding of the controlling factors such as molecular topology, distance, and orientation factors. In recent years, fullerenes as electron acceptors and porphyrins as electron donors have been realized to be important constituents owing to their rich redox, optical, and photochemical properties.[1,3] It is now well known that in contrast with the traditionally used two-dimensional aromatic electron acceptors, the fullerene in donor-acceptor dyads accelerates photoinduced charge separation and slows down charge recombination.[1f]

Recently, self-assembled supramolecular methodology using axial coordination, hydrogen bonding, crown ether-ammonium cation complexation, and rotaxane formation, has been successfully utilized to construct porphyrin-fullerene assemblies.[3a–c] Improved stability and control over the distance and orientation were achieved by utilizing multiple modes of binding, such as covalent-coordinate and coordinate-hydrogen bond formation in a few instances.[3d,e] In the present study we have adopted a 'two-point' coordinate bonding strategy for the construction of a highly stable porphyrin dimer–fullerene supramolecular complex. Here, a covalently linked zinc porphyrin dimer was self-assembled with fullerene functionalized with two pyridine entities (Chart 1). Construction of self-assembled supramolecular complexes bearing a dimer moiety of the donor bound to an electron acceptor entity is of particular interest since they mimic the components of the bacterial reaction center.[4]

The C_{60}bpy binds to the two porphyrin entities of the ZnP dimer leadng to the formation of a structure shown in Chart 1. The structure of the complex was established by UV-vis absorption and ^{1}H NMR spectra.[5] Job's method of continuous variation plots revealed formation of a 1:1 complex under a wide concentration range (0.1 to 10 μmol dm^{-3}). The binding constant was obtained from Scatchard methods[6] from the absorption data shown in Fig. 1. The calculated binding constant was found to be 1.8×10^5 (mol dm^{-3})$^{-2}$ which compared with a value of 1.45×10^4 (mol dm^{-3})$^{-2}$ for C_{60}bpy complexation with two zinc tetraphenylporphyrin (ZnTPP) monomers,[7a] and 7.0×10^3 mol^{-1} dm^3 for ZnTPP binding to fullerene bearing only one pyridine entity (C_{60}py).[7b] The very large binding constant for the coordination of bidentate C_{60}bpy to the ZnP dimer is due to the proximity effect of the ZnP dimer in contrast to ZnTPP monomer binding to C_{60}bpy, satisfying a 'two-point' coordinate bonding strategy. The ^{1}H NMR studies also revealed the bridging structure. That is, upon addition of C_{60}bpy to a solution of ZnP dimer (0.5 mmol dm^{-3}), the protons of both the pyridine entities of C_{60}bpy revealed high field shifts as a result of axial coordination to the zinc center. However, when the concentration of C_{60}bpy was close to that of the ZnP dimer, the complex started precipitating out of solution.

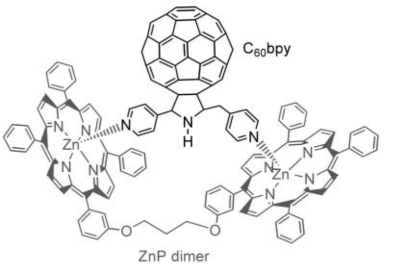

Chart 1

The geometry and the electronic structure of the supramolecular complex were visualized by performing *ab initio* calculations at the B3LYP/3-21G(*) level.[8] In the optimized structure (Fig. 2a), the two ZnP rings were aligned in a V-shape with an angle of 70°. No steric hindrance was observed. The distance of the center of the C_{60} to the nearest zinc atom was found to be 10.3 Å while the Zn–Zn distance was found to be 13.8 Å. As predicted, the HOMOs formed two sets of degenerate orbitals and were alternately located exclusively on the ZnP entities while the LUMO was located on the C_{60} entity. The lack of delocalization of the HOMOs on both the ZnP entities is suggestive of little or an absence of intramolecular interactions between the two ZnP entities of the dimer.

Both steady-state (Fig. 1 inset) and time-resolved fluorescence spectra of ZnP dimer in the presence of C_{60}bpy revealed quenching

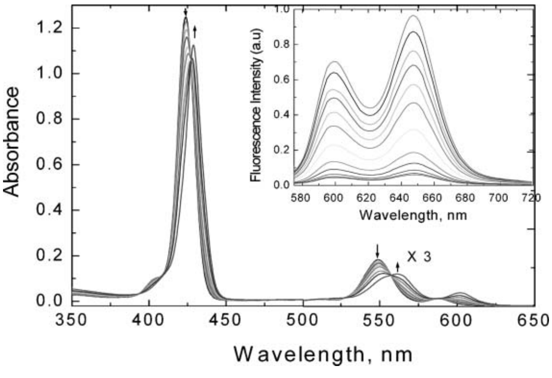

Fig. 1 Spectral changes observed during the titration of ZnP dimer (1.88 μmol dm^{-3}) with C_{60}bpy (each 0.1 eq. addition) in *o*-dichlorobenzene. Figure inset shows the steady state fluorescence spectra of ZnP dimer (1.88 μmol dm^{-3}) in the presence of C_{60}bpy (0.15 eq. each addition) in *o*-dichlorobenzene. Excitation = 550 nm.

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† Electronic supplementary information (ESI) available: Experimental section, syntheses of the studied compounds, and Job's plots. See http://www.rsc.org/suppdata/cc/b4/b407985j/

DOI: 10.1039/b407985j

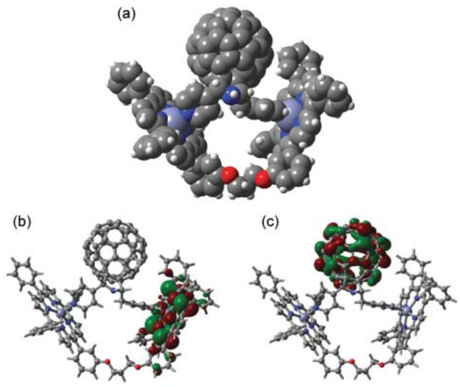

Fig. 2 (a) The B3LYP/3-21G(*) optimized structure, (b) HOMO, and (c) LUMO of the supramolecular complex.

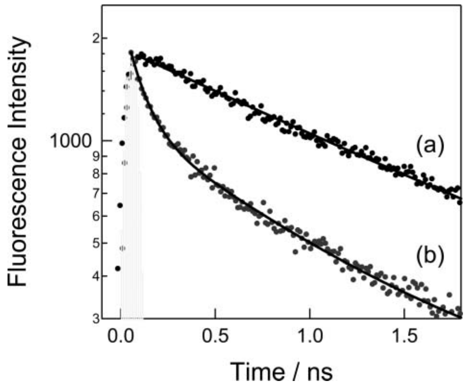

Fig. 3 Fluorescence decay time-profile (log scale) of (a) ZnP dimer and (b) ZnP dimer–C_{60}bpy (1 : 2.5) in *o*-dichlorobenzene; initial intensity was normalized. Excitation = 400 nm.

(Fig. 3). As predicted from the binding constant value, the quenching was found to be very efficient, that is, by the addition of 2.5 eq. of C_{60}bpy over 97% of the initial fluroescence intensity of ZnP dimer was quenched. From Fig. 3, it is clear that the supramolcular complex is weakly fluorescent, suggesting efficient charge separation within the supramolecular complex.[9] The time-resolved fluorescence of ZnP dimer revealed a single exponential decay with a lifetime of 1880 ps. Addition of 2.5 eq. C_{60}bpy, accelarated the decay process and the decay curve could satisfactorily be fitted to a biexponential decay. The measured lifetimes were found to be 260 ps (47%) and 1840 ps (53%). The rate of charge separation calculated from the fast decaying component was found to be 3.3×10^9 s^{-1} and the charge separation quantum yield, Φ_{CS} was found to be 0.86, indicating efficient charge separation.

Nanosecond transient absorption spectral studies on the supramolecular ZnP dimer-C_{60}bpy complex revealed evidence for the charge-separated quenching pathway and permitted us to evaluate the the rate of charge recombination. Fig. 4 shows the transient absorption spectra for the supramolecular complex after 565 nm laser irradiation at two time intervals. Spectral features at 6 ns after the laser pulse corresponding to the anion radical of fulleropyrrolidine were observed at 1020 nm and ZnP dimer cation radical at 480 nm.[3a] The figure inset shows the decay time profile for the anion radical at its peak maximum. The sharp rise and decay with maximum at 6 ns clearly suggests the occurrence of an intramolecualar event. The rate of charge-recombination, k_{CR} obtained from these decay curves was found to be $\sim 2 \times 10^8$ s^{-1} and $\sim 1.8 \times 10^8$ s^{-1} at room teperature (23 °C) and −10 °C, respecively, in *o*-dichlorobenzene indicating fairly rapid charge recombination.

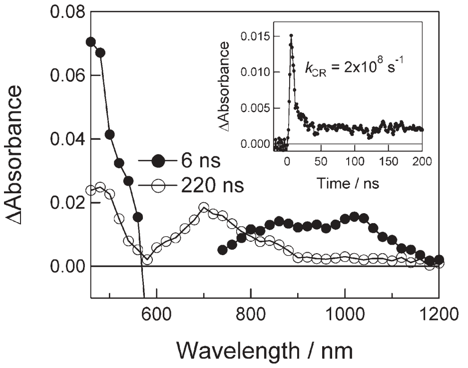

Fig. 4 Transient absorption spectra of ZnP dimer–C_{60}bpy complex (ZnP dimer:C_{60}bpy = 0.1:0.25 mmol dm^{-3}) in *o*-dichlorobenzene at 6 ns (filled circle) and 220 ns (open circle) after the 565 nm laser irradiation. Inset: absorption time profile at 1010 nm.

In summary, we have assembled a stable, self-assembled supramolecular complex, as a photosynthetic reaction center mimic, *via* a 'two-point' axial ligand coordination approach using a covalently linked zinc porphyrin dimer and fulleropyrrolidine functionalized with two pyridine entities. Steady-state and time-resolved fluorescence studies revealed efficient charge separation while evidence for charge-separated state and rate of charge-recombination were obtained from nanosecond transient absorption studies.

The authors are thankful to the donors of the Petroleum Research Fund administered by the American Chemical Society, National Institutes of Health (GM 59038 to FD), Japan Ministry of Education, Science, Technology, Culture and Sports (Primary area 417), for support of this work.

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5 See ESI† for the instruments and methods used.

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9 The free-energy changes for charge separation, ΔG_{CS} and charge recombination, ΔG_{CR} calculated from the first oxidation potential of the zinc porphyrin dimer and the first reduction potential of fullerene, singlet energy of the zinc porphyrin dimer, and the Coulomb energy (ref. 3*a*) were found to be exothermic with values of −0.84 eV and −1.27 eV respectively.