

Design and Physico-Chemical Studies of “Two-Point” Bound Supramolecular Porphyrin-Fullerene Conjugates Formed by Cation-Crown Ether Complexation and Axial Co-ordination or π - π Interactions

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1. Introduction

Design of supramolecular donor-acceptor dyads employing different modes of binding and studies of their photo-induced electron transfer processes are of current interest in artificial photosynthesis. When constructing such dyads, fullerenes are appealing electron acceptors, while porphyrins are commonly used as electron donors. In several covalently and non-covalently linked donor-acceptor dyads, it has been shown that fullerenes accelerate the forward electron transfer (charge separation – k_{CS}) and slow down the back electron transfer (charge recombination - k_{CR}) and thus increase the lifetime of the charge separated state. Among such self-assembled dyads, those with defined distance and orientation are of major importance because of their structural rigidity and efficiency in intra or intermolecular electron transfer reactions. This approach provides information about the structure and orientation of the donor-acceptor pair, and minimizes the degrees of electronic coupling due to different wave function mixing observed in flexibly linked donor-acceptor pairs.

In this regard, porphyrins functionalized with one or four 18-crown-6 moieties and fullerene possessing an alkyl ammonium cation, a pyridine, or phenyl entities were synthesized.^{1, 2} As a result of crown ether-ammonium cation complexation, zinc pyridine co-ordination or π - π interactions, stable self-assembled “two-point” bound zinc porphyrin –fullerene conjugates with defined distance and orientation were formed. These complexes were characterized by ¹H NMR, ESI-MS. Evidence for the foregoing interactions was obtained from UV-Vis, fluorescence spectroscopy, and electrochemical studies.

2. Experimental, Results, and Discussion

Synthesis of porphyrin-fullerene derivatives

Synthesis of porphyrin derivatives: H₂-5-(2-Oxomethylbenzo-[18]-crown-6-phenyl)-10,15,20-triphenylporphyrin (**1**): This compound is prepared by refluxing H₂-5-(2-hydroxyphenyl)-10,15,20-triphenylporphyrin with 4'-chloromethylbenzo-[18]-crown-6 in presence of excess K₂CO₃ in DMF at ~80 °C. (Yield: ~85%). The remaining two porphyrins, H₂-5-(benzo-[18]crown-6-10,15,20-triphenylporphyrin (**2**) and H₂-5,10,15,20-Tetra-(benzo-[18]crown-6)-porphyrin (**3**) were prepared by refluxing required equivalents of 4'-formylbenzo-[18]-crown-6, benzaldehyde, pyrrole in propionic acid.

Fullerene derivatives (**4**) & (**5**): General procedure. A toluene solution containing C₆₀ (0.138 mmol), the appropriate aldehyde (0.69 mmol) and amino acid (0.406 mmol) was heated to reflux for 3h. The crude product was purified by column chromatography on silica gel. (Yield: ~ 60%). The required fullerene ammonium cations were synthesized according to published procedures.³ The structural integrity of all of the compounds is deduced from ¹H NMR, ESI mass in a CH₂Cl₂ matrix, optical absorption, emission, and electrochemical methods.

Ab initio B3LYP/3-21G() Modeling of porphyrin-fullerene Dyads*

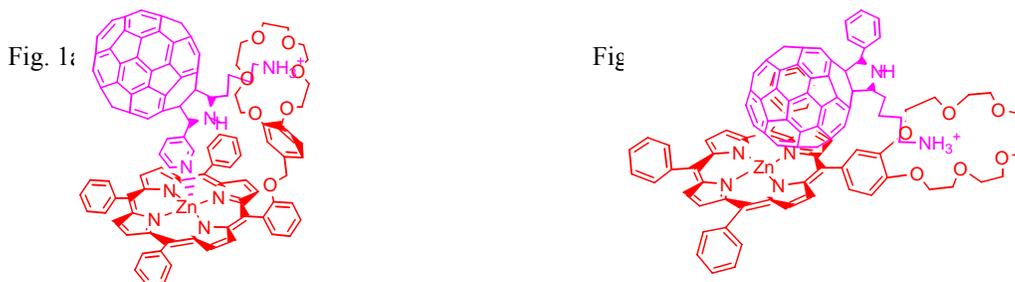
To gain insight into the geometry and electronic structure of the ‘two-point’ bound porphyrin-fullerene conjugates, computational studies were performed using density functional methods at the B3LYP/3-21G(*) level. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were found to be located entirely on the porphyrin and fullerene moieties in these dyads. The π - π type charge transfer interactions in the ground state of these dyads were confirmed by the partial delocalizations of HOMO and LUMO frontier orbitals on both the donor and acceptor entities.

Optical absorbance studies and ground state interactions

Evidence for the crown ether-ammonium cation complexation and zinc pyridine co-ordination or π - π interactions was obtained by UV-Visible spectroscopic studies. The binding constant, K , calculated by the Scatchard method was found to be $4.4 \times 10^4 \text{ mol}^{-1}\text{dm}^3$ suggesting a stable self-assembled supramolecular formation 1:4, (Fig. 1a) even in a polar solvent like benzonitrile. Evidence for π - π interactions was provided by a charge transfer band observed in the 725-825 nm region for the dyad 1:5 (Fig. 1b).

Steady state and time-resolved emission studies

Steady-state and time-resolved emission studies revealed efficient quenching of the zinc-porphyrin singlet excited state in these dyads, and the measured rates of charge separation, k_{CS} were found to be slightly better in the case of dyads held by axial co-ordination and crown ether-cation complexation. Nanosecond transient absorption studies provided evidence for the electron transfer reactions, and these studies also revealed charge stabilization in these dyads. Finally, the effect of axial ligation or π - π interactions between porphyrin and fullerene entities in these dyads was studied by externally co-ordinating pyridine to the porphyrin macrocycle. Under these conditions, the measured electron transfer rates revealed faster k_{CS} and slower k_{CR} as compared to those obtained in the absence of pyridine indicating charge stabilization in the studied dyads.



3. Conclusion

Design of ‘two-point’ bound systems involving crown ether-cation complexation and either axial coordination or π - π type interactions has yielded, highly stable, self-assembled zinc porphyrin-fullerene conjugates. Both steady-state and time-resolved emission studies revealed efficient quenching of the zinc-porphyrin singlet excited states in these dyads. The measured k_{CS} was slightly higher for the dyads formed by axial coordination and crown ether-cation complexation binding mechanism. Low k_{CS} values for the dyads involving π - π interactions and crown ether-cation complexation. Additional charge stabilization by eliminating the zinc-pyridine axial bond or by attenuating π - π interactions was achieved by the addition of pyridine.

4. Acknowledgements

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