

Electron Transfer in Porphyrin-Fullerene Dyads

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1. Introduction

Study of light-induced electron transfer between donor-acceptor dyads to develop artificial photosynthetic systems to harvest solar energy is an area of current interest.¹⁻³ For constructing these dyads, fullerenes are appealing as electron acceptors due to their unique structure, low reduction potentials, and absorption spectra extending over the visible spectral range.³ Porphyrins are used as electron donors because of their well-understood photochemical properties and structural similarity to the naturally occurring chlorophyll molecules.^{2,3} Because of the three-dimensional structure, fullerenes in donor-acceptor dyads accelerate forward electron transfer (k_{CS}) and slow down the backward electron transfer (k_{CR}). This results in the much desired long-lived charge-separated states for light energy harvesting applications.³ Several donor-fullerene dyads have been synthesized and studied to verify the formation of long-lived charge-separated states and also to probe the effect of distance and orientation factors.¹⁻³ Recently, porphyrin-fullerene supramolecular triads, tetrads, and pentads have been synthesized and studied.¹⁻³

In the present investigation, a series of novel porphyrin-fullerene dyads have been synthesized (Figure 1), and the photo-induced electron transfer reactions have been probed by a variety of physico-chemical techniques. The present investigations successfully demonstrate mimicry of the primary events of the photosynthetic reaction center by using the porphyrin-fullerene model compounds.

2. Experimental, Results, and Discussion

Synthesis of Porphyrin-Fullerene, MPo~C₆₀ (M = 2H, Zn or Mg) Dyads

The synthesis of free-base porphyrin-C₆₀ (H₂Po~C₆₀) and ZnPo~C₆₀ is given elsewhere.⁴ A sample of H₂Po~C₆₀ (80 mg) was dissolved in 30 mL of CH₂Cl₂ and 20 eq. of triethylamine and 10 eq. of MgBr₂·O(Et)₂ were added. The mixture was stirred for 30 min at room temperature. The course of the reaction was monitored by absorption spectroscopy. The mixture was diluted with CH₂Cl₂, washed with 5% NaHCO₃, and dried over anhydrous Na₂SO₄. The desired compound, MgPo~C₆₀ was obtained after purification on a silica gel (9:1 toluene: CHCl₃). The structural integrity of all of the compounds is deduced from ¹H NMR, ESI mass spectrometry in a CH₂Cl₂ matrix, optical absorption and emission spectroscopy, and electrochemical methods.

Ab initio B3LYP/3-21G() Modeling of MPo~C₆₀ (M = 2H, Zn and Mg) Dyads*

To gain better insight on the molecular and electronic structure, computational studies were performed using density functional methods at the B3LYP/3-21G(*) level. The B3LYP methods have been quite successful in predicting the geometry and electronic structure of the supramolecular dyads and triads.⁵ The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were found for each the dyads. From the computational studies, the MPo~C₆₀ dyads revealed a closely spaced MP and C₆₀ entities as shown in Figure 2. The donor-acceptor distances were calculated for the dyads.

Cyclic Voltammetry Studies and Electron Transfer Driving Forces

Electrochemical studies were performed to measure the redox properties, which gave information about interactions between the porphyrin and fullerene entities in the ground states. The cyclic voltammograms of the MPo~C₆₀ dyads (M = Mg, Zn and 2H) were recorded in 0.1 M (n-Bu)₄NClO₄ in *o*-dichlorobenzene. All three of the porphyrins revealed two one-electron oxidations. The magnitudes of the $E_{1/2}$ values depended on the metal ion present in the porphyrin cavity, following the order MgP < ZnP < H₂P.

From the electrochemical data, the driving forces for charge separation ($-\Delta G_{CS}$)⁶ and charge recombination ($-\Delta G_{CR}$) were calculated according to Equations (1) and (2):

$$-\Delta G_{CS} = E_{0,0} - (-\Delta G_{CR}) \quad (1)$$

$$-\Delta G_{CR} = E_{ox} - E_{red} - \Delta G_s \quad (2)$$

where E_{ox} is the first oxidation potential of the porphyrin (P^{0/+}), E_{red} is the first reduction potential of the fullerene (C₆₀^{0/-}), $E_{0,0}$ is the energy of the 0-0 transition between the lowest excited state and the ground state of the porphyrin as evaluated from the

fluorescence peaks of $\text{MgPo}\sim\text{C}_{60}$. These $E_{0,0}$ values are respectively, 2.03 eV for $^1\text{MgP}^*$, 2.07 eV for $^1\text{ZnP}^*$, and 1.90 eV for $^1\text{H}_2\text{P}^*$. Negative values of ΔG_{CS} were found to follow the order: $\text{MgPo}\sim\text{C}_{60} < \text{ZnP}\sim\text{C}_{60} < \text{H}_2\text{P}\sim\text{C}_{60}$ in *o*-dichlorobenzene, indicating the expected higher exothermicity for electron transfer via the excited singlet states of the $\text{MgPo}\sim\text{C}_{60}$ compared to its zinc and free-base porphyrin analogs.

Next, ultra-fast time resolved femto-second spectroscopy and nanosecond transient absorption spectral investigations were carried out to determine the rates of charge separation and charge recombination, and lifetime of the radical ion-pairs.⁴ The measured rates were found to be very efficient, $k_{\text{cs}} \sim 10^9 \text{ s}^{-1}$ with almost unit quantum yield. The measured rates of charge recombination, k_{cr} were $\sim 10^6 \text{ s}^{-1}$, which were 3 orders of magnitude smaller than the k_{cs} values. These results suggest charge-stabilization in the dyads and the measured lifetimes of the radical ion-pairs were found to be in the order of microseconds.

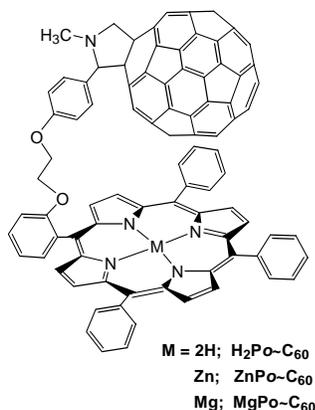


Figure 1. Structure of porphyrin-fullerene dyad

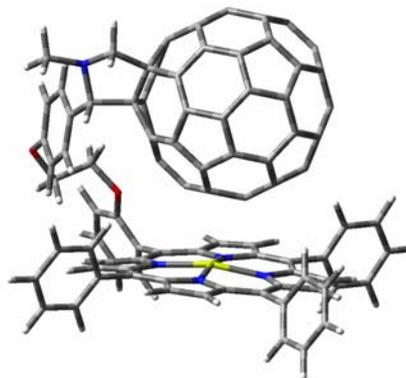


Figure 2. Ab initio B3LYP/3-21G(*) optimized geometries of $\text{MgPo}\sim\text{C}_{60}$

3. Conclusion

The results of the present investigations demonstrate that the porphyrin-fullerene dyads are suitable candidates for building solar energy harvesting devices. They undergo efficient charge separation as determined from their rates of forward electron transfer and quantum yields. They also yielded the much desired long-lived radical ion-pairs on the order of microseconds.

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5. References

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