

SMALL REORGANIZATION ENERGY OF INTRAMOLECULAR ELECTRON TRANSFER IN BACTERIOCHLORIN-, CHLORIN-, AND PORPHYRIN-C₆₀ DYADS

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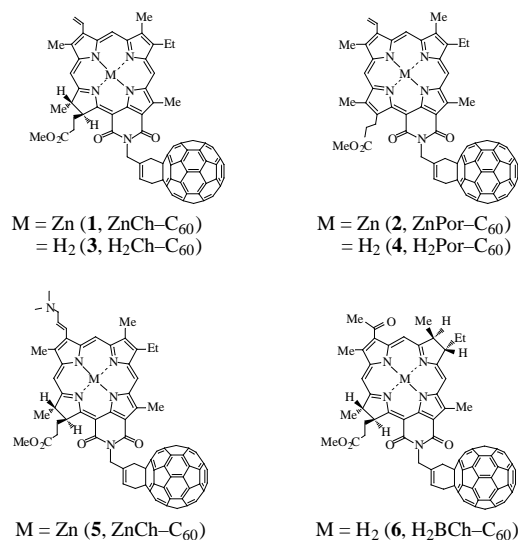
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The Marcus theory of electron transfer (ET) provides a valuable guide for controlling and optimizing the efficiency of charge separate (CS) vs charge recombination (CR) processes. In particular, the rate of CR can be markedly slowed down by shifting deep into the inverted region of the Marcus parabola, where the driving force ($-\Delta G^0_{ET}$) is larger than the total reorganization energy (λ) of ET.¹ Extensive efforts have been directed toward establishing the driving force dependence of the ET rate, and thereby probing the inverted region of the Marcus curve in donor-acceptor couples.

Recently we have reported photochemical and electrochemical properties of chlorin-C₆₀ or porphyrin-C₆₀ dyads having the same short spacer between the macrocycle and the fullerene. The photoexcitation of a zinc chlorin-C₆₀ dyad results in an unusually long-lived radical ion pair.²

We report herein ET properties of six dyads (bacteriochlorin-, chlorin-, and porphyrin-C₆₀) having the same short spacers as shown below.



The rate constants for formation of the CS process in these dyads were determined by fluorescence lifetime measurements of the dyads and unlinked compounds. The CR rate constants were studied using laser flash photolysis. The photoexcitation of the zinc chlorin-C₆₀ dyad results in formation of the long-lived radical ion pair, which has absorption spectra maxima at 790 and 1000 nm. Photoexcitation of the other dyads (free-base bacteriochlorin, free-base chlorin-C₆₀, zinc porphyrin-C₆₀ and free-base porphyrin-C₆₀ dyad) leads to formation of ion pairs which decay quickly to the triplet excited states of the chlorin or porphyrin moiety via the higher lying radical ion pair states as is expected from the redox potentials.

The driving force dependence in the intramolecular ET rate constants for the dyads is shown in Figure 1. The photoinduced ET processes in the dyads are located in the normal region of the Marcus parabola ($\Delta G^0_{ET} > -\lambda$) whereas the back electron transfer (BET) process from C₆₀^{•-} to ZnCh⁺ is in the inverted region ($\Delta G^0_{BET} < -\lambda$). In the inverted region, the k_{BET} value decreases with decreasing λ value. The solvent reorganization energy is expected to decrease with decreasing the donor-acceptor distance.¹ Thus, the small λ value (0.51 eV) in the present dyad systems with the short spacers leads to the small k_{BET} value as compared to the value of any other D-A dyad system containing a porphyrin, chlorin or bacteriochlorin as the donor and C₆₀ as the acceptor.

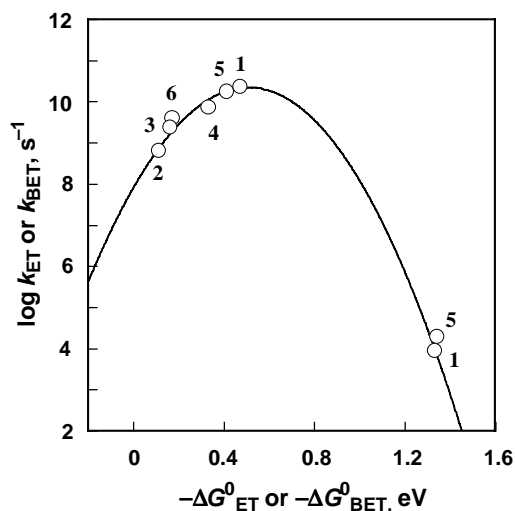


Figure 1. Driving force ($-\Delta G^0_{ET}$ or $-\Delta G^0_{BET}$) dependence of intramolecular ET rate constants (k_{ET} or k_{BET}) in C₆₀-linked dyads in PhCN. The curves represent the best fit to eq 1; $\lambda = 0.51$ eV and $|V| = 7.8$ cm⁻¹.

$$k_{ET} = \left(\frac{4\pi^3}{h^2 \lambda k_B T} \right)^{1/2} |V|^2 \exp \left[-\frac{(\Delta G^0_{ET} + \lambda)^2}{4 \lambda k_B T} \right] \quad (1)$$

References

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