

LONG-LIVED CHARGE-SEPARATED STATES OF ZINC CHLORIN-C₆₀ DYADS

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One of the most fundamental steps in photosynthesis and light-to-chemical energy conversion is photoinduced charge separation in the photosynthetic reaction center. Toward this end, a number of electron donor-acceptor (D-A) linked systems have been designed and the photodynamics has been examined in order to mimic photosynthetic charge separation. The lifetime of the charge-separated (CS) state in natural photosynthetic reaction center is as long as 1 second.

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 formation of an unusually long-lived radical ion pair.^{1,2}

We report herein the synthesis and electron transfer (ET) properties of new zinc chlorin-C₆₀ dyads (ZnCh-C₆₀) having the short spacer linked at different positions as shown in Figure 1.

The rate constants for formation of the CS state 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. The back electron transfer (BET) rate (k_{BET}) was determined from the disappearance of the absorption band at 790 nm due to ZnCh⁺ in ZnCh⁺-C₆₀⁻. The decay of the absorption band at 790 nm observed using different laser power obeys first-order kinetics with the same slope. This indicates clearly

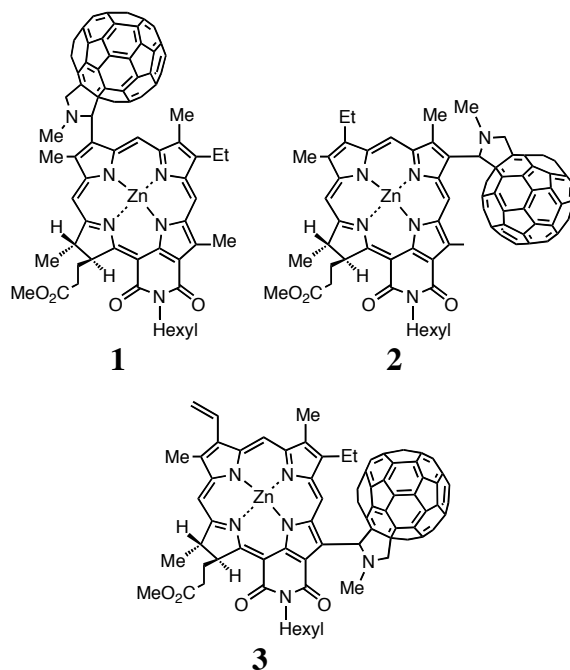


Figure 1. Chemical structures of ZnCh-C₆₀.

that the decay of the CS state is ascribed to intramolecular BET rather than intermolecular BET. The k_{BET} value is determined as $4.3 \times 10^3 \text{ s}^{-1}$ for **1**, $1.7 \times 10^3 \text{ s}^{-1}$ for **2** and $7.1 \times 10^3 \text{ s}^{-1}$ for **3**. The lifetimes of the CS states are 230, 600 and 140 μs at 25 °C, respectively.

The ESR spectra were measured under photoirradiation of ZnCh-C₆₀ in frozen PhCN. The ESR spectrum consists of two characteristic signals, one of which is attributable to an organofullerene radical anion with the g value (2.0007) smaller than the free spin value (2.0023) and the other to the zinc chlorin radical cation with a higher g value (2.0033).^{1,2} The disappearance of the ESR signal intensity obeyed first-order kinetics under the experimental conditions where a low concentration of ZnCh-C₆₀ ($1.0 \times 10^{-5} \text{ M}$) was employed to avoid intermolecular decay of the CS state.

The lifetime of the CS state of **1** at -150 °C is as long as 120 s, which is the longest CS lifetime ever reported for donor-acceptor linked systems.

In summary, we have successfully shown that intramolecular electron transfer from the singlet excited state of zinc chlorin to fullerene occurs efficiently in the dyad with a short linkage to attain an ultra-long lived CS state without loss of energy which is inevitable in multi-step electron transfer processes.

References

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