Photophysical and Photochemical Properties of C_{60}-linked Dendritic Multi-zincporphyrin Arrays

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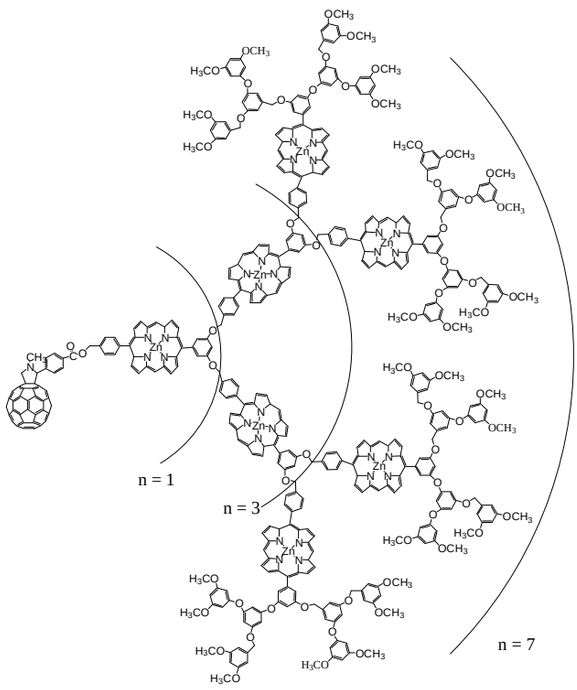
Photochemical and photophysical properties of C_{60}-linked dendritic multi-zincporpyrins (scheme 1) have been investigated by measuring the fluorescence lifetimes and transient absorption spectra with changing the generation of dendritic multi-zincporphyrins. Fluorescence lifetimes of the zincporphyrin moiety become short in various solvents, suggesting that intramolecular electron-transfer takes place from the singlet excited states of zincporphyrin moiety to the connected C_{60} moiety. The fluorescence lifetimes of $1P_{Zn}$-C_{60} are shorter than those of $3P_{Zn}$-C_{60} and $7P_{Zn}$-C_{60}, in which latter two nP_{Zn}-C_{60} showed similar fluorescence lifetimes, suggesting that the charge-separation takes place from the singlet excited states of zincporphyrin moiety at the first- and second-generations. In the charege-separation rate constants and the quantum yields are almost similar with changing solvent polarity from anisole and THF to benzonitrile.

In anisole, absorption of the radical anion of the C_{60} moiety decayed quickly during the ns-laser pulse, showing the lifetimes of the radical ion-pair are as short as ca. 10 ns. In THF and benzonitrile, slow rises of the radical anion of the C_{60} moiety were observed in the nanosecond time scale. In such case, the charge-recombination rates of the radical ion-pair states are as slow as ca.10^6 s^{-1}. The longest lifetime of the radical ion-pair was observed for $7P_{Zn}$-C_{60} in benzonitrile (ca. 500 ns) compared with $3P_{Zn}$-C_{60} (ca. 400 ns) and $3P_{Zn}$-C_{60} (ca. 400 ns). The lifetimes of the ion-pairs in THF are slightly shorter than those in benzonitrile. The activation energies of the slow charge-recombination process were evaluated to be ca. 7, ca. 8, and ca. 10 kcal mol^{-1} for first-, second-, and third-generations, respectively. The higher activation energy may be caused by the delocalization of the radical cation (hole) in whole prophyrin moieties even in $7P_{Zn}$-C_{60}.



Scheme 1. C_{60}-linked dendritic multiporphyrin arrays (nP_{Zn} -C_{60}).

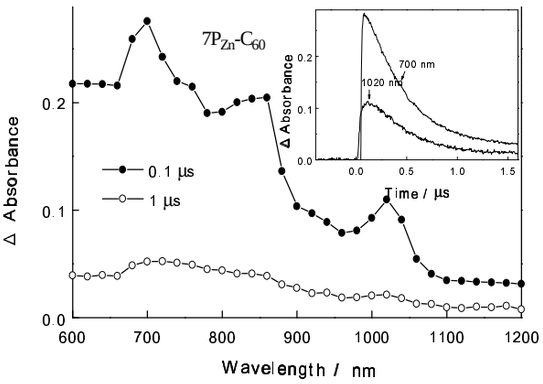


Figure 1. Nano-second transient absorption spectra of $7P_{Zn}$-C_{60} in benzonitrile observed by the laser excitation with 532 nm light in Ar-saturated solution. Inset: Time profiles at 700 nm for triplet state of and at 1000 nm of radical anion of C_{60} moiety.

References

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2) Imahori, H.; Tamaki. K.; Guldi, D. M.; Luo, C.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607.

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