Photoinduced Electron Transfer Reactions *through* Dendrimer Architecture

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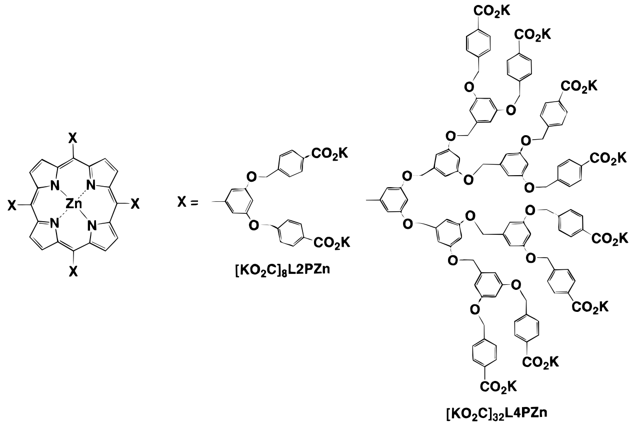
Long-range photochemical interactions between chromophores have attracted interest in relation to the initial stage of photosynthesis,[1] and special attention has been focused on the design of noncovalently assembled donor−acceptor arrays.[2] Recently, we have reported the first example of a dendritic metalloporphyrin, in which the zinc porphyrin functionality is covalently encapsulated by an aryl ether dendrimer framework with methoxy groups on the exterior surface,[3] on the basis of Fréchet's convergent approach.[4,5] Dendrimers are well-defined, highly branched macromolecules with uniform molecular weight, bearing a unique three-dimensional shape with nanoscopic size depending on the interior functionality and the number of generations.[6]

Herein we report the first photoreactive dendritic metalloporphyrin having noncovalently assembled electron-acceptor molecules on the exterior surface and describe a long-range photoinduced electron transfer *through* dendrimer architecture.[7] Here, water-soluble dendritic zinc porphyrins with two different numbers of generations ($[KO_2C]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$, $n = 2, 4$) were newly synthesized: Alkaline-mediated coupling of 5, 10, 15, 20-tetrakis(3′,5′-dihydroxyphenyl)porphine with methoxycarbonyl-terminated aryl ether dendritic bromides[8] gave $[MeO_2C]_{2^{(n+1)}}\mathrm{L}n\mathrm{PH_2}$ ($n = 2$ and 4), which were metalated with $Zn(OAc)_2$,[9] followed by hydrolysis of the exterior MeO_2C− groups with KOH.[8] Dialysis of the reaction mixture for 2 days in fresh water to remove excess KOH, followed by evaporation to dryness, gave $[KO_2C]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ as a purple powder.[10]



$[KO_2C]_8$L2PZn

$[KO_2C]_{32}$L4PZn

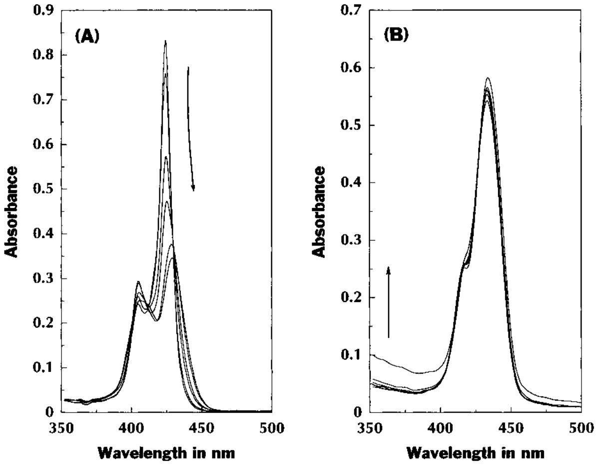


Figure 1. Spectral changes upon titration of (A) $[KO_2C]_8$L2PZn (2.0 μM, aqueous borate buffer at pH 9.2) and (B) $[KO_2C]_{32}$L4PZn (2.9 μM, aqueous phosphate buffer at pH 7.2) with methyl viologen (MV^{2+}) at 20 °C. $[MV^{2+}]$: 0, 1, 5, 10, 50, and 100 μM for $[KO_2C]_8$L2PZn; 0, 1, 10, 100, 1000, and 20 000 μM for $[KO_2C]_{32}$L4PZn.

The electronic absorption spectrum is informative of the interior environment of $[KO_2C]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$. In CH_2Cl_2, the zinc porphyrin Sorets of $[MeO_2C]_{32}$L4PZn (428.5 nm) and $[MeO_2C]_8$L2PZn (425.8 nm) were not much different from each other.[9] In contrast, in aqueous media, $[KO_2C]_{32}$L4PZn showed the Soret band at 433.8 nm, while that of $[KO_2C]_8$L2PZn was blue-shifted by 9.8 nm from that of $[KO_2C]_{32}$L4PZn.[10] Interestingly, a clear hypochromicity was observed for $[KO_2C]_{32}$L4PZn upon increasing the ionic strength or lowering the pH of the solution: When KCl was added to aqueous $[KO_2C]_{32}$L4PZn (2.6 μM), the Soret band absorbance was decreased from 0.49 to 0.34 with increasing [KCl] from 0 to 5.3 M. Similarly, upon addition of AcOH to aqueous $[KO_2C]_{32}$L4PZn (2.2 μM) [pH 6.2 → 5.2], the absorbance at the Soret band was decreased from 0.42 to 0.30. The observed hypochromicity is attributable to the shrinkage of the hydrophobic dendrimer framework as a consequence of the decrease in ionicity of the exterior surface.

When lower-generation $[KO_2C]_8$L2PZn (2.0 μM) (Figure 1A) was titrated with methyl viologen (MV^{2+}), a positively charged electron acceptor, the spectrum was dramatically changed upon increment of $[MV^{2+}]$ from 0 to 100 μM. This was also the case when $[KO_2C]_8$L2PZn was titrated with a negatively charged acceptor such as naphthalenesulfonate (NS^-), but the spectral change required much higher acceptor concentration (~10^4 μM). In sharp contrast, the spectrum of higher-generation $[KO_2C]_{32}$L4PZn (2.9 μM) remained virtually intact through increase in acceptor concentration up to 2×10^4 μM (Figure 1B). Therefore, it is evident that lower-generation $[KO_2C]_8$L2PZn takes an open architecture, so that the interior zinc porphyrin functionality is directly interactive with MV^{2+} and even electrostatically repulsive NS^- (Scheme 1A). In contrast, the zinc porphyrin within higher-generation $[KO_2C]_{32}$L4PZn is

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(9) UV−vis (CH_2Cl_2) λ_{max} (nm) for $[MeO_2C]_8$L2PZn, 425.8, 554.0, 595.0; for $[MeO_2C]_{32}$L4PZn, 428.5, 555.0, 596.0.

(10) UV−vis (water) λ_{max} (nm) for $[KO_2C]_8$L2PZn (pH 7.0), 424.0 (log $\epsilon = 5.72$), 556.4, 596.0; for $[KO_2C]_{32}$L4PZn (pH 9.0), 433.8 (log $\epsilon = 5.28$), 557.8, 598.2.

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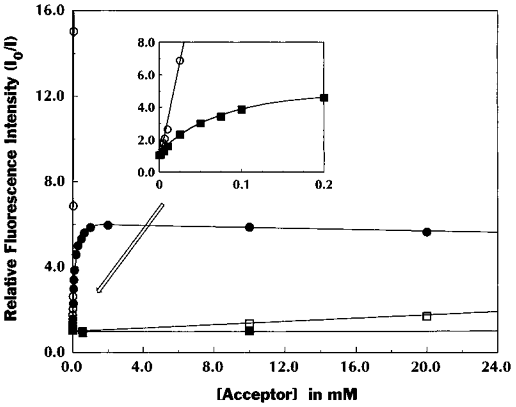

Figure 2. Stern−Volmer plots for the $[\mathrm{KO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ ($n = 2$ [2.0 μM], aqueous borate buffer at pH 9.2, $\lambda_{\mathrm{ext}} = 411 \pm 2$ nm; $n = 4$ [2.9 μM], aqueous phosphate buffer at pH 7.2, $\lambda_{\mathrm{ext}} = 432 \pm 2$ nm) and acceptor (methyl viologen [$\mathrm{MV^{2+}}$], naphthalenesulfonate [$\mathrm{NS^-}$]) systems at 20 °C. The fluorescence intensity was monitored at 660 nm (○, $[\mathrm{KO_2C}]_8\mathrm{L2PZn/MV^{2+}}$; □, $[\mathrm{KO_2C}]_8\mathrm{L2PZn/NS^-}$; ●, $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn/MV^{2+}}$; ■, $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn/NS^-}$).

Scheme 1

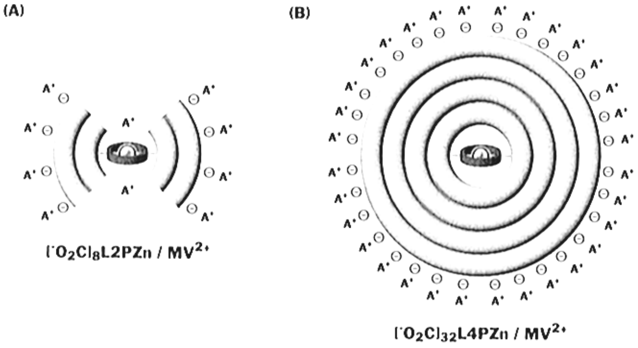

Table 1. Fluorescence Lifetimes (τ) of $[\mathrm{KO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ ($n = 2, 4$)[a]

run	$[\mathrm{KO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ n	[$\mathrm{MV^{2+}}$] (M)	$\tau_1{}^b$ (ns)	$A_1{}^b$ (%)	$\tau_2{}^b$ (ns)	$A_2{}^b$ (%)
1	2	0	0.9	54	1.8	46
2	4	0	1.5	88	3.0	12
3	4	0.39	0.3	95	1.5	5

[a] In deoxygenated aqueous borate buffer (pH 9.2) for $[\mathrm{KO_2C}]_8\mathrm{L2PZn}$ (77 μM) and aqueous phosphate buffer (pH 7.2) for $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ (41 μM) at 25 °C using a Hamamatsu picosecond fluorescence-measuring system model C4780 equipped with a LN120C2 $\mathrm{N_2}$ laser-pumped dye laser (Coumarin 540A). [b] From $I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ using the single-photon-counting data at 600−680 nm; the deviations are within 0.02 ns.

sterically shielded by the dendritic cage from the access of the acceptor molecules.

Upon excitation at the zinc porphyrin Soret in aqueous media, $[\mathrm{KO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ ($n = 2, 4$) emitted fluorescences at 610 and 660 nm. We found that the fluorescences are quenched by $\mathrm{MV^{2+}}$, but the profiles differ dramatically depending on the number of generations. The Stern−Volmer plots for the $[\mathrm{KO_2C}]_8\mathrm{L2PZn{-}MV^{2+}}$ system (Figure 2, ○) showed a highly efficient fluorescence quenching even at a low [$\mathrm{MV^{2+}}$]. In contrast, for higher-generation $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ (●), the fluorescence quenching was clearly saturated at [$\mathrm{MV^{2+}}$] > 1000 μM, where the ratio I_0/I was almost constant at 5.5−6.0. Considering the result in Figure 1B, this saturation behavior indicates the assembly of $\mathrm{MV^{2+}}$ molecules via electrostatic force on the negatively charged dendrimer surface (Scheme 1B).[11] On the other hand, when negatively charged $\mathrm{NS^-}$ was employed in place of $\mathrm{MV^{2+}}$, only $[\mathrm{KO_2C}]_8\mathrm{L2PZn}$ (□) showed a fluorescence quenching, while no quenching occurred for $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ (■) even at a high [$\mathrm{NS^-}$].

The fluorescence quenching of $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ by $\mathrm{MV^{2+}}$ (Figure 2, ●) is obviously the result of a long-range photoinduced electron transfer *through* the dendrimer framework: When the zinc porphyrin Soret of the $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn/MV^{2+}}$ system was continuously irradiated in the presence of triethanolamine as a sacrificial donor, the solution turned blue, where the absorption due to the methyl viologen radical ion appeared at 605 nm.[12] Table 1 shows the fluorescence lifetimes of $[\mathrm{KO_2C}]_8\mathrm{L2PZn}$ (run 1) and $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ (run 2), where the fluorescence decay profiles were satisfactorily analyzed by the double-exponential equation. The fluorescence of lower-generation $[\mathrm{KO_2C}]_8\mathrm{L2PZn}$ decayed biphasically, where an abnormally short-lived component (0.9 ns) was detected in addition to a normally decaying one (1.8 ns). This is possibility due to the aggregation of $[\mathrm{KO_2C}]_8\mathrm{L2PZn}$, as indicated by the presence of a blue-shifted Soret[13] at 404.0 nm (Figure 1A).[14] In contrast, the fluorescence of higher-generation $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ showed a normal decay profile with the lifetime of 1.5 ns. In the presence of $\mathrm{MV^{2+}}$, the fluorescence lifetime of $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ was definitely shortened (run 3). Taking into account the negligible donor−acceptor complexation at the ground state (Scheme 1B) together with the saturation behavior in the fluorescence quenching (Figure 2, ●), the rate constant (k_{ET}) for the electron transfer *through* the dendrimer framework was estimated, using the equation $k_{\mathrm{ET}} = (\tau_{[\mathrm{MV^{2+}}]})^{-1} - (\tau_{[\mathrm{none}]})^{-1}$, to be 2.6×10^9 s^{-1}.

In conclusion, the long-range photoinduced electron transfer *through* an aryl ether dendrimer framework was demonstrated for a water-soluble dendritic zinc porphyrin bearing noncovalently assembled electron-acceptor molecules on the exterior surface. The electron transfer properties of higher-generation homologues ($n \geq 5$) and the stability of the resulting radical ion pair as a function of the dendrimer size are subjects worthy of further investigation.

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Supporting Information Available: Analytical data of $[\mathrm{MeO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PH_2}$, $[\mathrm{HO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$, and $[\mathrm{KO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ ($n = 2, 4$), UV−vis spectral changes for titration of $[\mathrm{KO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ ($n = 2, 4$) with $\mathrm{NS^-}$, fluorescence decay curves of $[\mathrm{KO_2C}]_{2^{(n+1)}}\mathrm{L}n\mathrm{PZn}$ ($n = 2,4$) and $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn/MV^{2+}}$, and UV−vis spectral profile with experimental conditions for photoreduction of $\mathrm{MV^{2+}}$ with triethanolamine sensitized by $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) The fluorescence quenching was completely inhibited upon addition of $\mathrm{K^+}$ (KCl, 8 mM) to an aqueous solution of a mixture of $[\mathrm{KO_2C}]_{32}\mathrm{L4PZn}$ (2.6 μM) and $\mathrm{MV^{2+}}$ (3.7 μM).

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