Photophysical and Photochemical Properties of Viologen-Linked N-Alkylporphyrin Diads and Their Metal Complexes

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A new type of viologen-linked or -bridged *N*-alkylporphyrin and metalloporphyrin diads was synthesized and characterized by ¹H NMR spectroscopy. Although the viologen moiety of free base diads linked with a methylene chain is flexible in solution, the insertion of metal ions results in the extended conformation, where the viologen moiety is located nearly perpendicular to the *N*-alkylporphyrin plane. The diad, having two porphyrin units bridged by a viologen moiety, is more rigid in conformation than the diad containing one porphyrin unit. The fluorescence quantum yields in the viologen-linked and -bridged *N*-alkylporphyrins become larger by insertion of H⁺, Mg²⁺, Al³⁺, and Si⁴⁺ into the *N*-alkylporphyrins. This may arise because the extended and orthogonal conformer due to the electrostatic repulsion between the viologen and the central metal ion decelerates the ET quenching of *N*-alkylporphyrin by the bound viologen unit.

Introduction

Porphyrins linked by viologen, which is a 4,4'-bipyridinium ion, have been synthesized to achieve an efficient electrontransfer (ET) quenching of the excited state of porphyrin or metalloporphyrin by viologen.¹ Since the first example of the covalently linked viologen-tetraphenylporphyrin was reported by Milgrom,² several types of viologen-linked porphyrin have been synthesized.^{3–8} The orientation between electron donor and acceptor is one of the important factors determining ET reaction rates.^{9,10} In some systems the fluorescence decay profiles are fitted to the sum of two exponentials, indicating the existence of two different conformers: the closed one, where viologen is close to the porphyrin ring, and the extended one, the viologen moiety of which is far away from the porphyrin plane.^{6b,7b} The closed conformer permits facile intramolecular ET reaction from the excited singlet-state of porphyrin to the bound viologen. All the porphyrins linked by electron donors or acceptors are non-N-substituted ones.

Porphyrins substituted at a pyrrolenic nitrogen atom, *N*-alkylporphyrins, are produced from the reactions of a number of xenobiotics with the detoxifying cytochrome P450 enzymes found in the liver and of hydrazines with hemoglobin and myoglobin in vivo, resulting in the ferrochelatase inhibition.¹¹ In addition to the biological significance of *N*-alkylporphyrins, their structural features are worthy of remark. The *N*-alkylation of porphyrins results in distortion of the porphyrin plane by the sp³ hybridization of one of the pyrrolenic nitrogens; the alkyl group is out-of-plane with respect to those unsubstituted pyrrolenic nitrogens.^{11–13}

An electronic coupling between the donor and acceptor orbitals with a π character must be weak in an orthogonal orientation for porphyrin, and the ET rate is expected to be slower than that for face-to-face interaction or the edge-to-edge cofacial one. We have designed two types of viologen-linked *N*-alkylporphyrins and their metal complexes. The first examples are the diads (10 and 11, Chart 1) whose viologen moiety is located nearly perpendicular to the porphyrin plane by not only the conformational characteristic N-alkyl bond but also the steric hindrance between the *N*-alkyl group and the relatively bulky four phenyl groups at meso positions. In the diad systems, the viologen unit is still able to wag and rotate around the bridging methylene group. Therefore, the excited singlet state after irradiation by light is expected to have two conformers corresponding to an extended and perpendicular form and a closed one, in the latter of which the viologen moiety is close to the porphyrin plane. The second model is a new type of viologen-bridged diad (14, Chart 2) to construct the orthogonal orientation between porphyrin and viologen by restricting the free rotation of the viologen unit. By inserting metal ions into the N-alkylporphyrin diads, the extended conformer must exist predominantly in solution due to charge repulsion between a central metal ion and the viologen moiety. In this work, we report the photophysical and photochemical properties of such models of electron donor and acceptor systems. The preliminary communications have been reported elsewhere.^{14,15}

Results and Discussion

Absorption Spectral Properties. Absorption spectra of viologen-linked diads and their metal complexes in MeCN are shown in Figures S1 and S2, and their numerical data are shown in Tables S1 and S2. In the viologen- and bipyridine-linked systems, the absorption due to the viologen unit appeared around 260 nm, where the absorption of the porphyrin moiety also exists. The ratios of the molar absorption coefficient (ϵ) of the

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Soret band to that of the band around 260 nm are (6-7):1 in diads and (8-9):1 in the viologen-bridged diads. The Soret maxima of the diads did not shift from that for the unlinked porphyrin (1) and the values of ϵ for the diads 10 and 14 are similar to and about twice that for the unlinked porphyrin (1), respectively. It is, therefore, suggested that the intramolecular $\pi - \pi$ interaction between porphyrin and viologen is very weak. The ground-state complexation between porphyrin and methyl viologen in solution caused a red shift in the Soret band.¹⁷ Zinc-(II) N-alkylporphyrins have partially resolved split Soret bands, arising from the lower symmetry of the porphyrin.¹¹ Lavallee et al. have reported that the absorption spectra and the structures of the N-alkylmetalloporphyrins of Mn(II), Fe(II), Co(II), Ni-(II), and Cu(II) are similar to those for the Zn(II) complexes.^{11–13} In the case of the other N-alkylmetalloporphyrins, such as Na-(I), Mg(II), Al(III), and Si(IV) complexes, Soret bands are not split but broad. The Q-bands are completely different from those for Zn(II) complexes; the first Q-band (around 680 nm) is the largest in intensity, although the second Q-band (around 610 nm) is the largest for the Zn(II) porphyrins. The largest in the first Q-band appears also in the monoprotonated species of the

free base *N*-alkylporphyrin, although its Soret band shifts slightly. It is suggested that these metal ions, except Zn(II), are only partially coordinated to three pyrrole nitrogens. The remaining pyrrole nitrogen is protonated. This is confirmed by ¹H NMR spectra of Al(III) and Si(IV) *N*-alkylporphyrins, where the N–H proton signal still appeared (see below). This is just as a "sitting-atop" complex that has been described for non-*N*-substituted porphyrins.¹⁸

Structural Features of Diads. Figure 1 shows a ${}^{1}\text{H}{-}{}^{1}\text{H}$ phase-sensitive NOESY NMR spectrum of the diad **10** at 34 °C in CD₃CN. The N–CH₂ proton signals in the bridged methylene group appeared at a high field (-4.64 to -4.55 ppm) due to the ring-current effect of the porphyrins and did not exhibit a triplet signal, but a multiplet one, suggesting the restriction of the free rotation of N–CH₂–CH₂ bonds. On the other hand, a triplet signal of –CH₂–N⁺ protons shows possible free rotation around the –CH₂–N⁺ bond. The signal for the two peripheral protons on pyrrole ring A bearing the *N*-alkyl group is shifted up field to 7.46 ppm in contrast to that for the opposite pyrrole ring C that has a similar chemical shift to that in the non-N-substituted H₂tpp, suggesting that this ring stays



Figure 1. Phase sensitive ${}^{1}H{-}^{1}H$ NOESY spectrum of the diad **10** in CD₃CN at 34 °C. Only the negative peaks are drawn. Open and closed signals indicate COSY and NOESY interactions, respectively.

TABLE 1: ¹H NMR Chemical Shifts for Bipyridinium Ring Protons of Diads in CD₃CN at 27 $^{\circ}$ C

	chemical shift ^a			
compd	2,6-bpy	3,5-bpy	3',5'-bpy	2',6'-bpy
10 10Zn 11 11Zn 14 14Zn	6.90 7.58 8.35 8.44 6.60 7.29, 7.58	7.41 7.83 8.07 8.16 7.20 7.29, 7.62	7.99 8.08 8.16 8.24	8.76 8.77 8.73 8.80

^a The internal standard of chemical shifts is TMS.

approximately in the plane of the macrocycle, whereas ring A is appreciably twisted from the plane.^{13,19} The proton signals of the pyrrole B,D_a and B,D_b are assigned to upfield and down-

field doublets, respectively, because the former protons have NOESY interactions with the *o*-phenyl I protons, for which NOESY cross-peaks were observed with pyrrole A protons. Table 1 summarizes the ¹H NMR chemical shifts for the bipyridinium ring protons of the diads. In the trimethylene bridged diads (10 and 10Zn), the proton signals for the bipyridinium ring (2,6-, 3,5-, 3',5'-, and 2',6'-bpy) appeared in this order from upper field, suggesting that the viologen moiety tends to locate out-of-plane with respect to the porphyrin plane. Insertion of Zn(II) into the free base diad 10 caused the changes in the proton signals, upfield for pyrrole C ring and downfield for 2,6- and 3.5-bpy, suggesting that the viologen moiety locates more apart from the central metal ion due to charge repulsion and/or steric requirement. On the other hand, the signals of the bipyridinium ring protons in the hexamethylene bridged diads (11 and 11Zn) appeared differently from those for 10 and 10Zn; the order of the signals from upper field is 3,5-, 3',5'-, 2,6-, and 2',6'-bpy, being similar to that for free bipyridinium ions. Therefore, the viologen moiety in 11 and 11Zn is free from the ring current of porphyrin.

The calculated structure of the diad **10** by MM2 (Figure 2) demonstrates that the closed form is more stable (a total energy, 1.4 kcal mol⁻¹) than the extended form (6.0 kcal mol⁻¹). On the other hand, the extended conformer is slightly more stable than the closed one for **10Zn** by 3 kcal mol⁻¹ (Figure 3). In the case of **11** and **11Zn**, the closed conformer of the viologen moiety apart from the porphyrin ring was obtained: 3.8 kcal mol⁻¹ for **11** (Figure 3) and 3.3 kcal mol⁻¹ for **11Zn**. These results are not inconsistent with the NMR data.

Figure 4 shows temperature-dependent ¹H NMR spectra of the viologen-bridged Zn(II) diad (**14Zn**). A considerably different ¹H NMR spectrum, compared with that for the diad **10Zn**, was observed for the protons of $-CH_2-N^+$ (δ 2.38–2.50), N-CH₂ (δ -4.70 to -4.60 and -4.60 to -4.50), the 2,6bipyridinium ring (δ 7.29 and 7.58), and the pyrrole rings (δ 8.40 and 8.86), whose signals were separated. These results suggest that the rotation of both viologen and trimethylene groups is significantly restricted. The calculated structure of **14Zn** based on MM2 (a total energy, 37 kcal mol⁻¹) is reasonable on the basis of the NMR data (Figure 5). The



Figure 2. Structural models of the diad 10 obtained by MM2 calculation: (left) an extended form; (right) a closed form.



Figure 3. Structural models of the diads 11 (left) and 10Zn (right) by MM2 calculation.



Figure 4. Temperature dependence of ¹H NMR spectra of the viologenbridged diad **14Zn** in CD₃CN.

orientation of viologen in the diads **10Zn** and **14Zn** is quite different from each other. The viologen unit of **10Zn** is capable of rotating around the methylene group $(-CH_2-N^+)$, because the proton signals of the methylene groups are not separated as those for **14Zn**. Intermediate properties in the conformation were observed for the free-base triad **14**. It is demonstrated from ¹H NMR measurements that the viologen moiety in **14** is more rigid than that in **10**.

Insertion of Si(IV) into the diad **10** changes drastically the ¹H NMR spectrum. The signal of the pyrrole C protons was shifted upfield by 0.35 ppm, whereas the other proton signals were shifted downfield; the extent of the shift was 0.25, 0.20– 0.23, 0.3–0.5, 0.54, 0.74, and 0.10 ppm for the pyrrole B,D ring, phenyl, bipyridinium, $-CH_2-N^+$, $-CH_2-$, and $N-CH_2-$



Figure 5. Structural model of the viologen-bridged diad 14Zn obtained by MM2 calculation.

protons, respectively. The N–H proton signal still appeared and was shifted downfield by ca. 1 ppm. These results strongly suggest that the extended conformer predominantly exists in the Si(IV) porphyrin due to the charge repulsion and that the pyrrole C ring is twisted from the plane. A molecular model based on MM2 demonstrates that the extended conformer is more stable than the closed one more than 5 kcal mol⁻¹ even in the hexamethylene-bridged **11Si** and that the N–H proton is twisted to the same side as the *N*-alkyl group, whereas the pyrrole C ring is at the opposite side. Insertion of Al(III) into the diad **10** also changed the ¹H NMR spectrum, but the changes in chemical shifts were within 0.2 ppm, suggesting that the conformational change of **10** on metalation by Al(III) is smaller than in the case of Si(IV).

Fluorescence Properties. Fluorescence data for *N*-alkylporphyrins and metalloporphyrins are summarized in Table 2. *N*-Alkylporphyrins have unique fluorescence properties com-

TABLE 2: Fluorescence Data for Viologen-Linked N-Alkylporphyrins and Their Metal Complexes in MeCN under Argon at 25 $^\circ \rm C$

compd	$\lambda_{ex}\!/\!nm$	$\lambda_{\rm em}/nm$	$\phi_{ m f}$	$\tau_{\rm f}/{ m ns}~({ m yield}/{ m \%})^a$
1	429	687, 745 (sh)	0.014	1.0 (100)
				$9.0 (100)^b$
$1H^+$	434	690, 745 (sh)	0.014	1.0 (100)
1Na	447	710	0.014	0.9 (100)
1Zn	436	668, 732	0.011	1.6 (100)
1Mg	448	710	0.014	0.9 (100)
1Al	450	715	0.014	1.0 (100)
1Si	450	713	0.015	1.0 (100)
2	429	687, 745 (sh)	0.020	<0.6 (25), 3.0 (75)
2Zn	436	669, 730	0.0058	1.1 (38), 1.9 (62)
3	429	687, 745 (sh)	0.016	<0.7 (20), 5.1 (80)
3Zn	436	668, 730	0.012	1.7 (100)
0	429	68/, /45 (sh)	0.0043	< 0.3 (87), 3.0 (13)
7	430	689, 745 (sh)	0.0049	<0.3 (72), 3.9 (28)
/Zn	430	608, 730	0.0081	1.4(100)
9	430	687, 745 (sll)	0.0049	< 0.7 (90), 3.1 (10)
10	429	087, 743 (SII)	0.0003	$(30, 20, 20)$ $(30)^{k}$
10 U +	121	600 745 (sh)	0.0028	2.0(70), 9.0(30)
1011 10No	434	710	0.0028	< 0.7 (100)
1013a	136	670 740 (sh)	0.0005	< 0.7 (100) $< 0.2 (85) 2.2 (15)^{\circ}$
10ZΠ 10Mσ	430	710	0.0000	< 0.2 (05), 2.2 (15) < 0.7 (100)
10Al	450	715	0.0024	< 0.7 (100)
105i	450	713	0.0074	0.9(100)
11	429	687, 745 (sh)	0.0009	< 0.4 (90), 3.5 (10)
	/	007,710 (01)	0.0007	$2.3(75), 5.9(25)^{b}$
11H ⁺	434	690, 745 (sh)	0.0094	<0.7 (100)
11Na	447	710	0.0017	< 0.7 (100)
11Zn	436	668, 740 (sh)	0.0023	$< 0.2 (30), 0.79 (60), 3.5 (10)^{c}$
11Mg	448	710	0.0046	< 0.7 (100)
11Aľ	450	715	0.012	0.8 (100)
11Si	450	713	0.014	1.0 (100)
12	430	717	0.0001	<0.5 (90), 5.4 (10)
14	430	687, 730 (sh)	0.0018	$<0.2(50), 1.1(50)^{c}$
				$2.9(50), 9.0(50)^{b}$
$14H^+$	434	690, 740 (sh)	0.0087	< 0.7 (100)
14Na	447	710	0.0027	< 0.7 (100)
14Zn	436	668, 730 (sh)	0.0024	< 0.2 (15), 1.3 (85)
14Mg	448	710	0.0055	< 0.7 (100)
14Al	450	715	0.013	0.9 (100)
14Si	450	713	0.014	1.0 (100)

^{*a*} By using a nanosecond-fluorometer. ^{*b*} In propylene glycol at 0 °C. ^{*c*} By using a picosecond-fluorometer.

pared with non-N-substituted porphyrins: red shifts in the emission maxima, a considerable decrease in the quantum yield, and larger Stokes' shifts between the $Q_x(0,0)$ absorption and $Q_x(0,0)$ fluorescence peaks.^{11,16} This fact can be explained by the noncoplanarity of the porphyrin plane. Conformationally distorted non-N-substituted porphyrins, such as dodecasubstituted porphyrins, have shown considerable decrease in the fluorescence quantum yield.²⁰ The low fluorescence quantum yields may arise from increased rates of radiationless internal conversion and intersystem crossing processes. The internal conversion process is dependent on the vibrational wave function overlap associated with a structural reorganization in the excited state, and the increased intersystem crossing rate results primarily from enhanced spin-orbit coupling in the nonplanar complexes. We have shown that the low quantum yield of the fluorescence of 1Zn or 2Zn arises mainly from the increased intersystem crossing rate.16

The fluorescence from the excited singlet state of $1 ({}^{1}(1)^{*})$ and its Zn(II) and Si(IV) porphyrins was quenched by free MV²⁺ in MeCN similar to non-*N*-substituted porphyrins.^{7b} A Stern– Volmer plot for the quenching of ${}^{1}(1)^{*}$ by MV²⁺ showed a saturation behavior, suggesting an exciplex formation between ${}^{1}(1)^{*}$ and MV²⁺. A new exciting spectral maximum appeared



Figure 6. Stern–Volmer plots for the fluorescence quenching of 1, 1Zn, and 1Si by MV^{2+} in degassed MeCN at 25 °C.

at 310 nm in the presence of excess MV^{2+} whose absorption maximum is 258 nm. The fluorescence of the Zn(II) and Si-(IV) complexes of **1** was also quenched by free MV^{2+} and the Stern–Volmer plots were linear for both Zn(II) and Si(IV) complexes (Figure 6). The intermolecular quenching rate constants were obtained to be $7.3 \times 10^9 M^{-1} s^{-1}$ for Zn(II) and $6.1 \times 10^9 M^{-1} s^{-1}$ for Si(IV): $\tau_0 = 1.6$ ns for **1Zn** and 1.0 ns for **1Si**. There is no appreciable formation of exciplex for the Zn(II) and Si(IV) complexes, arising from the charge repulsion between viologen and central metal ions.

Intramolecular Quenching by Linked Viologen. Fluorescence spectra of the diad 10 and its metal complexes in MeCN are shown in Figure 7 compared with those of the reference compounds 1 and 1Zn. The fluorescence-quantum yield (ϕ_f) and lifetime (τ_f) of the viologen-linked systems are both smaller than those of 1 and 1Zn, suggesting that the excited singlet state of the N-alkylporphyrin unit is quenched by the linked viologen through an intramolecular ET. The free energy change of the reaction can be estimated to be -0.55 and -0.42 eV for 10 and 10Zn, respectively, based on the redox potentials and the exciting energies: $E^{\circ}(MV^{2+}/MV^{\bullet+}) = -0.44 \text{ V}, E^{\circ}(10^{\bullet+}/$ ${}^{1}(10)^{*}$ = -0.99 V, and $E^{\circ}(10Zn^{+/1}(10Zn)^{*}) = -0.86$ V. Transient picosecond-absorption spectroscopy for the Zn(II) complexes, 1Zn, 10Zn, and 14Zn, are shown in Figures 8-10. The formation of a porphyrin radical cation (λ_{max} 470 nm (sharp) and 680 nm (broad)) after irradiation of light within 10-30 ps was confirmed (see Figures 8 and 9), although the absorption of a viologen radical cation (λ_{max} 600 nm) interfered with that of the porphyrin radical cation. The lifetimes of the singlet state were $\tau_s = 2.0$ ns for **1Zn**, $\tau_s < 14$ ps for **10Zn**, and $\tau_s^{-1} \approx 20$ ps (the fast phase) and $\tau_s^2 = 0.8$ ns (the slow phase) for 14Zn. An exciplex between zinc porphyrin and a viologen moiety may be formed. Then the porphyrin radical cation decayed rapidly, whose lifetime was ca. 50 ps for both 10Zn and 14Zn, and the amount of the radical cation intermediate for 14Zn was smaller than that for 10Zn. This is responsible for the fluorescence behavior that the lifetimes of these systems have two components, fast and slow (vide infra). The excited triplet state was gradually formed over several microseconds: T-T absorption maximum at 475 nm (broad).



Figure 7. Fluorescence spectra of the diad 10, its metal complexes, and the reference compounds 1 and 1Zn in degassed MeCN at 25 °C. Exciting wavelengths are Soret maxima.



Figure 8. Transient absorption spectra after excitation of $1Zn (3.0 \times 10^{-6} \text{ M})$ by picosecond-laser flash photolysis in Ar-saturated MeCN at 25 °C. The exciting wavelength is 532 nm.

The fluorescence lifetimes of the viologen-linked systems have two components (see Table 2). The lifetime for the fast component in MeCN was less than 0.2 ns, which is beyond the instrumental response. Therefore, the fluorescence lifetimes for 1, 10, 11, and 14 were also measured in propylene glycol. The lifetimes for the fast and slow component for 10 and 14 are shorter than and similar to that for the reference compound 1, respectively. The fast component might arise from a *closed* form (see Figure 2), where the viologen moiety is close to the porphyrin plane. The slow-fluorescence decay must occur in an extended and *perpendicular* form, where the electronic coupling between the porphyrin π -donor orbital and the viologen π -ac-



Figure 9. Transient absorption spectra after excitation of **10Zn** (3.0 \times 10⁻⁶ M) by picosecond-laser flash photolysis in Ar-saturated MeCN at 25 °C. The exciting wavelength is 532 nm.

ceptor orbital is weak. There are two possibilities in the ET pathway from donor and acceptor: a through-space mechanism and a through-bond one.²¹ If only the through-bond mechanism operated in the present system, the lifetimes for both closed and extended forms might not be different. Although the ET pathway is not clear at present, the coupling between the π -donor and π -acceptor orbitals in orthogonal orientation might be weaker than that in the closed orientation even by the through-bond mechanism. In the case of the hexamethylenebridged diad 11, the lifetimes for the fast and slow components are similar to and shorter than that for 10, respectively. The short lifetime for the slow component in 11 might arise because the viologen moiety of 11 is possible to locate close to the porphyrin plane due to flexibility of the hexamethylene chain. In the viologen-bridged zinc(II) diad 14Zn, the slow component becomes predominant (85%) in MeCN, reflecting the rigid ground-state conformation. In the case of the free-base diad 14, the closed form contributes to the fluorescence-decay process to greater extent than the extended one. The contribution of the slow-fluorescence lifetime for the triad is greater than that for the diad, which is confirmed by the transient absorption spectroscopy described above. The contribution of the slow component is in the order $10 \approx 10$ Zn < 14 < 14Zn, reflecting the rigidity of the bound viologen as predicted from NMR measurements.

Effect of typical metal ions of Na⁺, Mg²⁺, Al³⁺, and Si⁴⁺ on the fluorescence quantum yield was examined in MeCN (see Table 1 and Figure 7). The fluorescence maximum for these complexes appeared around 715 nm and the fluorescence quantum yields were in the order Na⁺ < Mg²⁺ < Al³⁺ < Si⁴⁺ for **10**, **11**, and **14**. Decrease in the fluorescence quantum yield, compared with the reference compound **1**, arises from the ET quenching by the bound viologen. Figure 11 shows the plots of relative fluorescence quantum yield for these metalloporphyrin diads (**10**, **11**, and **14**) and that for the unlinked porphyrin **1** against the effective charge on the metal ions (*z/r*). The Zn(II) porphyrins were not shown in Figure 11, because the structures of the Zn(II) porphyrins are different from those of the



Figure 10. Transient absorption spectra after excitation of **14Zn** (3.0 \times 10⁻⁶ M) by picosecond-laser flash photolysis in Ar-saturated MeCN at 25 °C. The exciting wavelength is 532 nm.



Figure 11. Plots of the relative fluorescence quantum yield vs zr^{-1} for the fluorescence of the diads **10**, **11**, and **14** and their metal complexes in degassed MeCN at 25 °C. The compound **1** and its metal complexes were used as references.

porphyrins of these typical metal ions (vide supra). This result indicates that the insertion of positive charged metal ions into *N*-alkylporphyrin decelerated the ET reaction and that in the case of **11Si** and **14Si** almost no quenching occurred. The ET rate might decrease in the extended and *perpendicular* conformation, being induced by electrostatic repulsion between the viologen moiety and a central metal ion. The redox potential of Al(III) and Si(IV) porphyrins ($E^{\circ}(MP^{\bullet+}/MP)$) becomes only 0.2 V higher than that of the free base porphyrin, which cannot explain the great deceleration of the ET reaction.



Figure 12. Absorption spectral changes after excitation of **10Zn** (3.0 \times 10⁻⁶ M) by a nanosecond-laser flash photolysis in degassed MeOH. The spectra were recorded at 0.03, 2, 4, 10, and 16 μ s after irradiation.



Figure 13. Decay of MV⁺⁺ after irradiation with a Xe flash lamp (a pulse width of 30 μ s) of the degassed MeCN solution of **10Zn** (3.0 × 10⁻⁶ M) in the presence of free MV²⁺ (1.0 × 10⁻³ M). The data are fitted to the second-order decay kinetics.

We have shown that the excited triplet state of 1Zn or 2Zn was intermolecularly quenched by free methyl viologen,16 similar to non-N-substituted Zn(II) porphyrins. In the case of the Zn(II) diad **10Zn**, transient nanosecond-laser spectroscopy showed that no radical-ion intermediate was detected (Figure 12) and the lifetime of the excited triplet state of 10Zn $(^{3}(10Zn)^{*})$ became shorter than that of 1Zn: $\tau^{t} = 3.0 \,\mu s \,(10Zn)$ and $\tau_0^t = 7.9 \ \mu s$ (1Zn) in MeCN and $\tau^t = 3.5 \ \mu s$ (10Zn) and $\tau_0^{t} = 4.4 \,\mu s$ (1Zn) in MeOH. The estimated free energy change for the back ET reaction of **10Zn**^{•+} with MV^{•+} is exothermic: $\Delta G^{\circ} = E^{\circ}(\mathrm{MV}^{2+}/\mathrm{MV}^{+}) - E^{\circ}(\mathbf{10Zn^{+}}/\mathbf{10ZnP}) = -0.44 - 1.05$ = -1.49 eV. Therefore, these results strongly suggest that the back ET reaction between the Zn(II) porphyrin radical cation and the linked viologen radical cation is much faster than the ET quenching of ${}^{3}(10Zn)^{*}$ by the linked viologen. The rate constants of the *intra*molecular quenching of ${}^{3}(10Zn)^{*}$ by the linked viologen are estimated to be $2.1 \times 10^5 \text{ s}^{-1}$ in MeCN and $5.9 \times 10^4 \text{ s}^{-1}$ in MeOH. These are smaller than those for the corresponding non-N-substituted Zn(II) porphyrins.^{3,6} This arises from the low driving force of the reaction: $\Delta G^{\circ} = E^{\circ}$ - $(MV^{2+}/MV^{\bullet+}) - \{E^{\circ}(10Zn^{\bullet+}/10ZnP) - E_{00}(^{3}(10Zn)^{*})\} =$ -0.44 - (1.05 - 1.48) = -0.01 eV. When free methyl viologen $(1.0 \times 10^{-3} \text{ M})$ was added into the solution of 10Zn (3.0 × 10^{-6} M) followed by irradiation of light with a Xe flash lamp (a 30 µs pulse width), both methyl viologen and Zn(II)porphyrin radical cations (λ_{max} 400 and 600 nm for the former and λ_{max} 470 and 680 nm for the latter) were detected and decayed over 15 ms with a second-order kinetics (Figure 13); the secondorder rate constants are 3.2 \times $10^9\,M^{-1}\,s^{-1}$ in MeCN and 5.8 \times 10⁹ M⁻¹ s⁻¹ in MeOH. This strongly suggests that the *intra*molecular ET quenching of $(10Zn)^*$ by the linked viologen competes with the *inter*molecular process in the presence of free MV²⁺.

Conclusions

The fluorescence quantum yields in the viologen-linked and -bridged *N*-alkylporphyrins become larger by insertion of H⁺, Mg^{2+} , Al^{3+} , and Si^{4+} into the *N*-alkylporphyrins. This may arise because the extended and orthogonal conformer due to the electrostatic repulsion between the viologen and the central metal ion decelerates the ET quenching of *N*-alkylporphyrin by the bound viologen unit.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphyrin (H₂tpp), 1,3dibromopropane, 1,6-dibromohexane, 1-iodopropane, nitromethane, 4,4'-bipyridine, and 3,4-dihydro-2H-pyrido[1,2-a]pyrimidin-2-one were purchased from Tokyo Kasei Kogyo Co., Ltd. and were used without further purification. Silver hexafluorophosphate was purchased from Aldrich Chemical Co., Inc. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), methanol (MeOH), acetonitrile (MeCN), and propylene glycol used were of Spectrosol (Dojindo Laboratory) for syntheses and spectroscopic measurements and were of Luminasol (Dojindo Laboratory) for luminescence and kinetic measurements. Activated alumina (Wako Chemical Industries, Ltd., 200 mesh), silica gel (Wakogel C-200), and Sephadex LH-20 (Pharmacia) were used for a column chromatography. Other chemicals were of guaranteed reagent grade from Wako Chemical Industries, Ltd. All of the solvents were dried by standard methods. 1,1'-Dimethyl-4,4'-bipyridinium perchlorate monohydrate ([MV]- $(ClO_4)_2 \cdot H_2O)$ and its hexafluorophosphate $([MV](PF_6)_2)$ were obtained from the corresponding chloride salt (Tokyo Kasei) by an anion exchange with sodium perchlorate and sodium hexafluorophosphate in water, respectively. 1-Methyl-4-(4pyridyl)pyridinium hexafluorophosphate ([mbpy]PF₆) were prepared by the reported method with slight modifications.²² 1,3-Diiodopropane and 1,6-diiodohexane were prepared by reacting the corresponding dibromoalkane with sodium iodide in acetone at room temperature.²³ Diphenyl(3-iodopropyl)sulfonium tetrafluoroborate ([Ph₂SprI]BF₄) and diphenyl(6-iodohexyl)sulfonium tetrafluoroborate ([Ph2ShxI]BF4) were prepared by reacting of diiodoalkane with diphenyl sulfide in nitromethane by the same method as reported in the literature.²⁴ 1,1"-Trimethylenebis(4-(4-pyridyl)pyridinium) hexafluorophosphate ([pdb]- $(PF_6)_2$) was prepared by treating the corresponding dibromide²⁵ with sodium hexafluorophosphate in water. N-(3-Propyl)-5,10,-15,20-tetraphenylporphyrin (HPrtpp·1.5H₂O, 1), N-(3-bromopropyl)-5,10,15,20-tetraphenylporphyrin (HBrPrtpp \cdot 2.5H₂O, 2), N-(3-hydroxypropyl)-5,10,15,20-tetraphenylporphyrin (HHOPrtpp-H₂O, **3**), and zinc(II) porphyrins ([Zn(Prtpp)Cl] •0.5H₂O (**1Zn**)

and $[Zn(BrPrtpp)Cl] \cdot 0.5H_2O$ (**2Zn**)) were prepared by the previously reported method.¹⁶

N-(3-Iodopropyl)-5,10,15,20-Tetraphenylporphyrin Hydrogen Tetrafluoroborate ([H₂IPrtpp]BF₄, 4) and N-(6-Iodohexyl)-5,10,15,20-tetraphenylporphyrin Hydrogen Tetrafluoroborate ([H₂IHxtpp]BF₄·CH₃C₆H₅, 5). Syntheses were carried out by the method of Setsune and Takeda.²⁶ The mixture of H₂tpp (5.13 g, 8.34 mmol) and [Ph₂SprI]BF₄ (10.5 g, 0.0238 mol) or [Ph₂ShxI]BF₄ (11.5 g, 0.0238 mol) was refluxed in 330 mL of 1,2-dichloroethane for 72 h under argon. After the solvent was removed, the residue was dissolved in dichloromethane (CH₂Cl₂) and the solution was loaded on a silica gel column (o.d. 3.8 cm \times 20 cm). A purple band was eluted with CH₂Cl₂ to recover H_2 tpp (4.00 g, 78%). The second green band was eluted with CH₂Cl₂-acetone (100:1 v/v), followed by a rechromatography on a silica gel column to yield 1.86 g (25%) of 4 and 2.14 g (28%) of 5. The excess amounts of diphenylsulfonium salts were eluted with acetone. A green band remained on the top of the column. 4: ¹H NMR (270 MHz, CDCl₃, 27 °C, TMS) δ 8.89 (d, J = 4.1 Hz, 2H, pyrrole B,D_a), 8.77 (s, 2H, pyrrole C), 8.70 (d, J = 4.1 Hz, 2H, pyrrole B,D_b), 8.39 (br, 4H, o-phenyl I), 8.21 (br, 4H, o-phenyl II), 7.70-7.92 (m, 12H, *m*-, *p*-phenyl I, II), 7.67 (s, 2H, pyrrole A), 1.30 (t, J =5.4 Hz, 2H, -CH₂I), -2.54 (br, 1H, NH), -1.38 to -1.19 (m, 2H, -CH₂-), -4.91 (br, 2H, N-CH₂-). Anal. Calcd for C₄₇H₃₆N₄IBF₄: C, 64.85; H, 4.17; N, 6.44. Found: C, 65.05; H, 4.16; N, 6.34. 5: ¹H NMR (270 MHz, CDCl₃, 27 °C, TMS) δ 8.89 (d, J = 6.6 Hz, 2H, pyrrole B,D_a), 8.64 (s, 2H, pyrrole C), 8.43 (d, J = 6.6 Hz, 2H, pyrrole B,D_b), 8.33 (br, 4H, o-phenyl I), 8.25 (br, 4H, o-phenyl II), 7.67-8.02 (m, 12H, *m*-, *p*-phenyl I, II), 7.79 (s, 2H, pyrrole A), 2.67 (t, J = 7.0 Hz, 2H, α -CH₂I), 1.02–1.13 (m, 2H, β -CH₂–), 0.06–0.17 (m, 2H, γ -CH₂-), -0.60 to -0.49 (m, 2H, δ -CH₂-), -1.69 to -1.59 (m, 2H, ϵ -CH₂-), -5.08 (br, 2H, N-CH₂-). Anal. Calcd for C₅₀H₄₂N₄IBF₄·CH₃C₆H₅: C, 68.14; H, 5.02; N, 5.58. Found: C, 68.56; H, 4.93; N, 5.96.

N-(3-Iodopropyl)-5,10,15,20-tetraphenylporphyrin (HIPrtpp, 6) and N-(6-Iodohexyl)-5,10,15,20-tetraphenylporphyrin (HIHxtpp, 7). Compound 4 (0.983 g, 1.13 mmol) or compound 5 (1.14 g, 1.13 mmol) was treated with 3,4-dihydro-2H-pyrido-[1,2-a]pyrimidin-2-one (0.184 g, 1.24 mmol) in 20 mL of CH₂-Cl₂ at room temperature for 1 h. The solution was filtrated and evaporated to dryness. The residue was dissolved in toluene, and the solution was loaded on an alumina column (o.d. 2.0 $cm \times 15$ cm). The purple band was eluted with CH₂Cl₂. After the solvent was evaporated, the residue was recrystallized from CH_2Cl_2 -MeOH to give a purple powder: yield, 0.816 g (92%) for **6** and 0.876 g (94%) for **7**. **6**: ¹H NMR (270 MHz, CDCl₃, 34 °C, TMS) δ 8.81 (s, 2H, pyrrole C), 8.65 (d, J = 4.8 Hz, 2H, pyrrole B,D_a), 8.47 (d, J = 4.8 Hz, 2H, pyrrole B,D_b), 8.26-8.45 (br, 4H, o-phenyl I), 8.13-8.20 (br, 4H, o-phenyl II), 7.75-7.85 (m, 12H, m-, p-phenyl I, II), 7.52 (s, 2H, pyrrole A), 1.44 $(t, J = 7.1 \text{ Hz}, 2H, -CH_2I), -2.2 \text{ (br, NH)}, -1.09 \text{ (quintet,})$ 2H, J = 6.4 and 7.1 Hz, $-CH_2$ -), -4.40 (t, J = 6.4 Hz, 2H, N-CH₂-). Anal. Calcd for C₄₇H₃₅N₄I: C, 72.12; H, 4.51; N, 7.16. Found: C, 72.47; H, 4.56; N, 7.11. FAB-MS (3nitrobenzyl alcohol (3-NBA)): m/z (rel intensity, %) 783 {-[HIPrtpp]⁺, 100]. 7: ¹H NMR (270 MHz, CDCl₃, 34 °C, TMS) δ 8.79 (s, 2H, pyrrole C), 8.64 (d, J = 4.9 Hz, 2H, pyrrole B,D_a), 8.45 (d, J = 4.9 Hz, 2H, pyrrole B,D_b), 8.26-8.40 (br, 4H, o-phenyl I), 8.10-8.17 (br, 4H, o-phenyl II), 7.73-7.85 (m, 12H, m-, p-phenyl I, II), 7.45 (s, 2H, pyrrole A), 2.67 (t, J = 6.8 Hz, 2H, α -CH₂I), 1.02–1.13 (m, 2H, β -CH₂–), 0.08– 0.16 (m, 2H, γ -CH₂-), -0.47 to -0.59 (m, 2H, δ -CH₂-), -1.49 to -1.57 (m, 2H, ϵ -CH₂-), -4.48 (br, 2H, N-CH₂-). Anal. Calcd for C₅₀H₄₁N₄I: C, 72.81; H, 5.01; N, 6.79. Found: C, 73.44; H, 5.15; N, 6.74. FAB-MS (3-NBA): *m*/*z* (rel intensity, %) 825 {[HIHxtpp]⁺ 100}.

5,10,15,20-Tetraphenyl-N-[3-(4-(4-pyridyl)pyridinio)propyl]porphyrin Bromide ([HBpyPrtpp]Br·3H₂O, 8). Compound 2 (0.080 g, 0.10 mmol) and 4,4'-bipyridine (0.319 g, 2.04 mmol) were dissolved in 3 mL of DMF, and the solution was heated at 75-80 °C for 46 h under argon. DMF was evaporated, and the residue was washed with cold toluene. The desired compound was further purified by a Sephadex LH-20 column chromatography (o.d. 2.0 cm \times 5.0 cm) with MeCN as an eluent. Recrystallization from CH₂Cl₂-toluene gave a purple powder 8 (0.057 g, 63%). 8: ¹H NMR (270 MHz, CDCl₃, 34 °C, TMS) δ 8.84 (s, 2H, pyrrole C), 8.69 (d, J = 5.9 Hz, 2H, 2',6'-bpy), 8.48 (d, J = 3.7 Hz, 2H, pyrrole B,D_a), 8.32 (d, J =3.7 Hz, 2H, pyrrole B,Db), 8.17-8.27 (br, 4H, o-phenyl I), 8.01-8.08 (br, 4H, o-phenyl II), 7.69-7.82 (m, 12H, m-, *p*-phenyl I, II), 7.52 (s, 2H, pyrrole A), 7.10 (d, J = 5.9 Hz, 2H, 3',5'-bpy), 6.93 (d, *J* = 5.1 Hz, 2H, 3,5-bpy), 6.82 (d, *J* = 5.1 Hz, 2H, 2,6-bpy), 2.53 (t, J = 5.5 Hz, 2H, $-CH_2-N^+$), -0.71 to .62 (m, 2H, $-CH_2-$), -4.77 to -4.71 (m, 2H, N-CH₂-). Anal. Calcd for C₅₇H₄₃N₆Br·3H₂O: C, 72.37; H, 5.22; N, 8.88. Found: C, 72.43; H, 4.80; N, 8.73. Application of the same method to HIPrtpp gave an iodide ([HBpyPrtpp]I· CH₃C₆H₅, 9). Yield: 0.081 g (79%). Anal. Calcd for C₅₇H₄₃N₆I· CH₃C₆H₅: C, 74.56; H, 4.99; N, 8.15. Found: C, 74.31; H, 4.90; N, 8.49.

N-[3-(1-Methyl-4,4'-bipyridinio)propyl]-5,10,15,20-tetraphenylporphyrin Hexafluorophosphate ([HMVprtpp](PF₆)₂· $3H_2O$, 10) and N-[6-(1-Methyl-4,4'-bipyridinio)hexyl]-5,10,-15.20-tetraphenylporphyrin Hexafluorophosphate ([HMVhxtpp](PF₆)₂·0.5CH₃C₆H₅, 11). A DMF solution (6 mL) of compound 2 (0.188 g, 0.241 mmol) or compound 6 (0.189 g, 0.241 mmol) with [mbpy]PF₆ (1.14 g, 3.61 mmol) was heated at 75-80 °C for 48 h under argon. DMF was evaporated, and the residue was washed with cold water and toluene to remove unreacted [mbpy]PF₆ and compound 2 or 6, respectively. The crude product was purified by Sephadex LH-20 column chromatography (o.d. $2.0 \text{ cm} \times 10 \text{ cm}$). Only one purple band was eluted with MeCN. Removal of MeCN and washing with cold MeOH gave a purple powder. Yield: 0.124 g (0.106 mmol, 44%) for 10 and 0.117 g (0.116 mmol, 48%) for 11. The protonated green species of 10 and 11 were sometimes obtained after washing with cold water; then they were further deprotonated by using 3,4-dihydro-2*H*-pyrido[1,2-*a*]pyrimidin-2-one, followed by the purification with Sephadex LH-20 column chromatography described above. 10: ¹H NMR (270 MHz, CD₃-CN, 35 °C, TMS) δ 8.83 (s, 2H, pyrrole C), 8.76 (d, J = 6.8Hz, 2H, 2',6'-bpy), 8.59 (d, J = 4.8 Hz, 2H, pyrrole B,D_a), 8.59 $(d, J = 4.8 \text{ Hz}, 2\text{H}, \text{pyrrole B}, D_b), 8.32-8.40 \text{ (m, 4H, }o\text{-phenyl})$ I), 8.12-8.22 (m, 4H, *o*-phenyl II), 7.99 (d, J = 6.8 Hz, 2H, 3',5'-bpy), 7.88-7.94 (m, 6H, m-, p-phenyl I), 7.76-7.84 (m, 6H, *m*-, *p*-phenyl II), 7.55 (s, 2H, pyrrole A), 7.41 (d, J = 6.8Hz, 2H, 3,5-bpy), 6.90 (d, J = 6.8 Hz, 2H, 2,6-bpy), 4.40 (s, 3H, N⁺-CH₃), 2.32 (t, J = 6.6 Hz, 2H, $-CH_2-N^+$), -0.66 to -0.57 (m, 2H, $-CH_2$ -), -2.3 (br, NH), -4.64 to -4.55 (m, 2H, N-CH₂-). Anal. Calcd for C₅₈H₄₆N₆P₂F₁₂•3H₂O: C, 59.49; H, 4.48; N, 7.18. Found: C, 59.51; H, 3.99; N, 7.07. FAB-MS (3-NBA): *m/z* (rel intensity, %) 827 {[HMVprtpp]⁺, 100}, 414 {[HMVprtpp]²⁺, 30}. **11**: ¹H NMR (270 MHz, CD₃CN, 34 °C, TMS) δ 8.77 (s, 2H, pyrrole C), 8.73 (d, J = 6.8 Hz, 2H, 2',6'bpy), 8.59 (d, J = 4.8 Hz, 2H, pyrrole B,D_a), 8.35 (d, J = 6.8Hz, 2H, 2,6-bpy), 8.38 (d, J = 4.8 Hz, 2H, pyrrole B,D_b), 8.258.60 (m, 4H, *o*-phenyl I), 8.14–8.22 (m, 4H, *o*-phenyl II), 8.16 (d, J = 6.8 Hz, 2H, 3',5'-bpy), 8.07 (d, J = 6.8 Hz, 2H, 3,5-bpy), 7.79–7.88 (m, 6H, *m*-, *p*-phenyl I), 7.72–7.83 (m, 6H, *m*-, *p*-phenyl II), 7.40 (s, 2H, pyrrole A), 4.32 (s, 3H, N⁺– CH₃), 3.90 (t, J = 7.7 Hz, 2H, α -CH₂–N⁺), 1.05–1.14 (m, 2H, β -CH₂–), -0.07 to +0.09 (m, 2H, γ -CH₂–), -0.66 to -0.53 (m, 2H, δ -CH₂–), -1.62 to -1.54 (m, 2H, ϵ -CH₂–), -2.0 (br, NH), -4.57 to -4.49 (m, 2H, N–CH₂–). Anal. Calcd for C₆₁H₅₂N₆P₂F₁₂•0.5CH₃C₆H₅: C, 64.28; H, 4.68; N, 6.97. Found: C, 64.42; H, 4.37; N, 7.15. FAB-MS (3-NBA): *m/z* (rel intensity, %) 869 {[HMVhxtpp]⁺, 100}, 435 {[HMVhxtpp]²⁺, 48}.

5,10,15,20-Tetraphenyl-N-[3-(1'-(3-(4-(4-pyridyl)pyridinio)propyl)-4,4'-bipyridinio)propyl]porphyrin Hexafluorophosphate ([HPdbPrtpp](PF₆)₃·0.5CH₂Cl₂, 12). A DMF solution (15 mL) of compound 2 (0.145 g, 0.186 mmol) or compound 6 (0.153 g, 0.186 mmol) with $[pdb](PF_6)_2$ (2.39 g, 3.71 mmol) was heated at 75-80 °C for 48 h under argon. After DMF was evaporated, the residue was washed with cold water to remove excess [pdb](PF₆)₂ and then with cold toluene to remove compound 2 or 6. The resulting purple solid was dissolved in MeCN, and the solution was purified by Sephadex LH-20 column chromatography (o.d. 2.0 cm × 4.0 cm). Recrystallization from CH₃CN-CH₂Cl₂ gave a purple powder 12 (0.183 g, 66%). 12: ¹H NMR (270 MHz, CD₃CN, 34 °C, TMS) δ 9.13 (d, J = 6.6 Hz, 2H, 2",6"-bpy), 9.07 (d, J = 6.6 Hz, 2H, 2',6'-bpy), 9.03 (d, J = 6.6 Hz, 2H, 2''',6'''-bpy), 8.90 (d, J =6.6 Hz, 2H, 3", 5"-bpy), 8.85 (d, J = 4.8 Hz, 2H pyrrole B,D_a), 8.75 (s, 2H, pyrrole C), 8.55-8.60 (m, 4H, o-phenyl I), 8.39 (d, J = 6.6 Hz, 2H, 3^{'''},5^{'''}-bpy), 8.25–8.34 (m, 4H, *o*-phenyl II), 8.17 (d, *J* = 6.6 Hz, 2H, 3',5'-bpy), 8.00-8.13 (m, 6H, *m*-, p-phenyl I), 8.04 (s, 2H, pyrrole A), 7.86-7.98 (m, 6H, m-, *p*-phenyl II), 7.82 (d, J = 4.8 Hz, 2H pyrrole B,D_b), 7.75 (d, J = 6.6 Hz, 2H, 3,5-bpy), 7.36 (d, J = 6.6 Hz, 2H, 2,6-bpy), 4.86 (t, J = 8.8 Hz, 2H, $\alpha'' - CH_2 - N^+$), 4.83 (t, J = 8.1 Hz, 2H, N⁺-CH₂-(α')), 2.72-2.86 (m, 2H, -CH₂-(β')), 2.13 (t, J = 7.3 Hz, 2H, α -CH₂-N⁺), -0.69 to -0.58 (m, 2H, β -CH₂-), -5.13 to -5.08 (m, 2H, N-CH₂-). Anal. Calcd for C₇₀H₅₇N₈P₃F₁₈•0.5CH₂Cl₂: C, 56.92; H, 3.93; N, 7.53. Found: C, 56.76; H, 3.51; N, 7.77.

1,1'-Bis[3-(5,10,15,20-tetraphenylporphyrinyl)propyl]-4,4'bipyridinium Dibromide ([(HP)₂MV]Br₂·3CH₂Cl₂·(CH₃)₂-NCOH, 13) and Hexafluorophosphate ([(HP)₂MV](PF₆)₂· 5H₂O, 14). Method A. To the DMF solution (3 mL) of compound 2 (0.120 g, 0.154 mmol) was added 4,4'-bipyridine (9.6 mg, 0.061 mmol) in DMF (0.26 mL) over 9 h with stirring at 75–80 °C under argon. After 39 h, DMF was evaporated and the residue was washed with cold toluene to remove unreacted 2 and 4,4'-bipyridine. Further purification by Sephadex LH-20 column chromatography (o.d. 2.0×6.0 cm) with MeCN and recrystallization from CH₂Cl₂-toluene yielded a purple powder (0.025 g, 10%).

Method B. The mixture of compound **8** (0.070 g, 0.078 mmol) with compound **2** (0.159 g, 0.204 mmol) in DMF (6 mL) was heated at 75–80 °C for 48 h under argon with stirring. After DMF was evaporated, the residue was washed with cold toluene and further purified by Sephadex LH-20 column chromatography with MeCN. Recrystallization from CH₂Cl₂– toluene gave a purple powder **13** (0.062 g, 49%). Using compound **6** instead of **2** gives the corresponding iodide of **13**. The bromide or iodide salt was converted to a hexafluorophosphate with silver hexafluorophosphate in MeCN to give a purple powder **14** (0.066 g, 95%). **13**: Anal. Calcd for C₁₀₄H₇₈N₁₀-Br₂·3CH₂Cl₂·(CH₃)₂NCOH: C, 67.56; H, 4.69; N, 7.88.

Found: C, 67.30; H, 4.88; N, 8.44. **14**: ¹H NMR (270 MHz, CD₃CN, 34 °C, TMS) δ 8.77 (d, J = 6.6 Hz, 4H, pyrrole B,D_a), 8.67 (s, 4H, pyrrole C), 8.42–8.55 (m, 8H, *o*-phenyl I), 8.12–8.18 (m, 8H, *o*-phenyl II), 7.88–8.07 (m, 12H, *m*-, *p*-phenyl I), 7.96 (s, 4H, pyrrole A), 7.65–7.92 (m, 12H, *m*-, *p*-phenyl II), 7.40 (d, J = 6.6 Hz, 4H, pyrrole B,D_b), 7.20 (d, J = 6.0 Hz, 4H, 3,5-bpy), 6.60 (d, J = 6.0 Hz, 4H, 2,6-bpy), 2.15 (t, J = 8.1 Hz, 4H, $-CH_2-N^+$), -0.70 to -0.60 (m, 4H, $-CH_2-$), -4.65 to -4.45 (m, 4H, N– CH_2-). Anal. Calcd for C₁₀₄H₇₈N₁₀-P₂F₁₂·5H₂O: C, 68.27; H, 4.85; N, 7.65. Found: C, 68.34; H, 4.61; N, 7.76. FAB-MS (3-NBA): m/z (rel intensity, %) 812 {[[(HP)₂MV]²⁺ - [Htpp(CH₂)₃]⁺]⁺, 100}, 1468 {[(HP)₂MV]⁺, 9; 17 in 1-thioglycerol}.

Insertion of Zinc(II) into Porphyrins. A typical method is described for chloro{[3-(1-methyl-4,4'-bipyridinio)propyl]-5,-10,15,20-tetraphenylporphyrin}zinc(II) ([ZnCl(MVprtpp)](PF₆)₂· 0.5CH₃C₆H₅, **10Zn**). Compound **10** (0.078 g, 0.067 mmol) and zinc(II) chloride (0.091 g, 0.67 mmol) were dissolved in 5 mL of THF including 2,6-lutidine (7.4 mg, 0.069 mmol), and the mixture was heated at 40 °C for 40 min under argon with stirring. After THF was evaporated, the residue was washed with cold water and then with cold toluene. The resulting purple powder was dissolved in MeCN and purified by Sephadex LH-20 column chromatography with MeCN. Recrystallization from CH₂Cl₂-toluene gave a purple powder (0.054 g, 64%). The same method as previously described in the literature¹⁶ was used for the synthesis of compound 7Zn. 10Zn: ¹H NMR (270 MHz, CD₃CN, 35 °C, TMS) δ 8.93 (d, J = 4.8 Hz, 2H, pyrrole B,D_a), 8.87 (s, 2H, pyrrole C), 8.77 (d, J = 4.8 Hz, 2H, pyrrole B,D_b), 8.77 (d, J = 6.8 Hz, 2H, 2',6'-bpy), 8.38 (s, 2H, pyrrole A), 8.22-8.32 (m, 4H, o-phenyl I), 8.05-8.10 (m, 4H, o-phenyl II), 8.08 (d, J = 6.8 Hz, 2H, 3',5'-bpy), 7.79-8.02 (m, 6H, m-, *p*-phenyl I, II), 7.83 (d, J = 6.8 Hz, 2H, 3,5-bpy), 7.58 (d, J =6.8 Hz, 2H, 2.6-bpy), 4.37 (s, 3H, N⁺-CH₃), 2.36 (t, J = 7.3Hz, 2H, $-CH_2-N^+$), -0.26 to -0.15 (m, 2H, $-CH_2-$), -4.63to -4.57 (m, 2H, N-CH2-). Anal. Calcd for C58H45N6-ZnClP₂F₁₂•0.5CH₃C₆H₅: C, 58.49; H, 3.91; N, 6.65. Found: C, 57.95; H, 3.97; N, 6.39. FAB-MS (3-NBA): m/z (rel intensity, %) 926 {[[ZnCl(MVprtpp)]²⁺ - H⁺]⁺, 100}, 1072 $\{[ZnCl(MVprtpp)]^{2+} \cdot PF_6^{-}, 40\}$. 11Zn $([ZnCl(MVhxtpp)](PF_6)_2 \cdot PF_6^{-}, 40]$ 0.5CH₃C₆H₅): ¹H NMR (270 MHz, CD₃CN, 34 °C, TMS) δ 8.97 (d, J = 4.8 Hz, 2H, pyrrole B,D_a), 8.89 (d, J = 4.8 Hz, 2H, pyrrole B,D_b), 8.84 (s, 2H, pyrrole C), 8.80 (d, J = 6.8 Hz, 2H, 2',6'-bpy), 8.25, 8.62 (br, 4H, o-phenyl I), 8.44 (d, J = 6.8Hz, 2H, 2,6-bpy), 8.28 (s, 2H, pyrrole A), 8.24 (d, *J* = 6.8 Hz, 2H, 3',5'-bpy), 8.16 (d, *J* = 6.8 Hz, 2H, 3,5-bpy), 8.09 (br, 4H, o-phenyl II), 7.83-7.91 (m, 6H, m-, p-phenyl I,II), 4.37 (s, 3H, N⁺-CH₃), 3.98 (t, J = 7.7 Hz, 2H, α -CH₂-N⁺), 1.08-1.20 (m, 2H, β -CH₂-), 0.05-0.17 (m, 2H, γ -CH₂-), -0.83 to -0.71 (m, 2H, δ -CH₂-), -0.92 to -0.86 (m, 2H, ϵ -CH₂-), -4.69 to -4.63 (m, 2H, N-CH₂-). Anal. Calcd for C₆₁H₅₁N₆ZnClP₂F₁₂· 0.5CH₃C₆H₅: C, 59.37; H, 4.25; N, 6.44. Found: C, 59.86; H, 3.96; N, 6.35. FAB-MS (3-NBA): *m/z* (rel intensity, %) 966 $\{[ZnCl(MVhxtpp)]^{2+} - H^{+} - 2H]^{+}, 100\}, 968 \{[ZnCl (MVhxtpp)]^{2+} - H^+], 90\}, 1114 \{[ZnCl(MVhxtpp)]^{2+} PF_6^-,$ 32}. **3Zn** ([ZnCl(HOPrtpp)]•0.5H₂O): ¹H NMR (270 MHz, CDCl₃, 34 °C, TMS) δ 8.94 (d, J = 5.1 Hz, 2H, pyrrole B,D_a), 8.86 (d, J = 5.1 Hz, 2H, pyrrole B,D_b), 8.84 (s, 2H, pyrrole C), 8.53-8.63 (br, 4H, o-phenyl I), 8.21 (s, 2H, pyrrole A), 8.10-8.20 (br, 4H, o-phenyl II), 7.70-7.90 (m, 12H, m-, p-phenyl I, II), 1.83 (t, J = 6.0 Hz, 2H, $-CH_2OH$), -0.67 to -0.57 (m, 2H, $-CH_2-$), -4.46 (t, J = 7.3 Hz, 2H, N $-CH_2-$). Anal. Calcd for C₄₇H₃₅N₄OZnCl·0.5H₂O: C, 72.22; H, 4.64; N, 7.17. Found: C, 72.22; H, 4.72; N, 6.96. **7Zn** ([ZnCl(IHxtpp)]•H₂O):

¹H NMR (270 MHz, CDCl₃, 34 °C, TMS) δ 8.95 (d, J = 5.1Hz, 2H, pyrrole B,D_a), 8.86 (d, J = 5.1 Hz, 2H, pyrrole B,D_b), 8.85 (s, 2H, pyrrole C), 8.50-8.60 (br, 4H, o-phenyl I), 8.20-8.31 (br, 4H, o-phenyl II), 8.19 (s, 2H, pyrrole A), 7.76-7.89 (m, 12H, *m*-, *p*-phenyl I, II), 2.64 (t, J = 6.8 Hz, 2H, α -CH₂I), 0.99-1.10 (m, 2H, β -CH₂-), 0.15-0.24 (m, 2H, γ -CH₂-), -0.75 to -0.67 (m, 2H, δ -CH₂-), -0.87 to -0.81 (m, 2H, ϵ -CH₂-), -4.58 (t, J = 7.3 Hz, 2H, N-CH₂-). Anal. Calcd for C₅₀H₄₀N₄IZnCl·H₂O: C, 63.71; H, 4.49; N, 5.94. Found: C, 63.41; H, 4.22; N, 5.86. **14Zn** ([(ZnClP)₂MV](PF₆)₂•3H₂O): ¹H NMR (270 MHz, CD₃CN, 34 °C, TMS) δ 8.80-8.95 (m, 8H, pyrrole B,D), 8.68 (br, 4H, *o*-phenyl I), 8.40 (d, J = 8.8Hz, 4H, pyrrole C), 8.28 (br, 4H, o-phenyl I), 8.10 (br, 8H, o-phenyl II), 7.97 (br, 4H, pyrrole A), 7.80-8.00 (m, 24H, m-, *p*-phenyl I,II), 7.62 (d, J = 6.0 Hz, 4H, 3,5-bpy), 7.58 (d, J =6.0 Hz, 2H, 2- or 6-bpy), 7.29 (d, J = 6.0 Hz, 2H, 2- or 6-bpy), 2.38-2.50 (m, 4H, $-CH_2-N^+$), -0.18 to -0.13 (m, 4H, $-CH_2$ -), -4.60 to -4.50 (m, 2H, N- CH_2 -), -4.70 to -4.60 (m, 2H, N-CH₂-). Anal. Calcd for $C_{104}H_{76}N_{10}Zn_2Cl_2P_2F_{12}$. 3H₂O: C, 62.10; H, 4.11; N, 6.96. Found: C, 62.14; H, 3.88; N, 7.08. FAB-MS (3-NBA): m/z (rel intensity, %) 911 $\{[(ZnClP)_2MV]^{2+} - [ZnCl(tpp(CH_2)_3)]^+ - H]^+, 100\}, 1667$ $\{[(ZnClP)_2MV]^+, 30\}.$

Insertion of Na(I), Mg(II), Al(III), and Si(IV) into Porphyrins. Metalloporphyrins were prepared in situ by adding NaPF₆, MgCl₂·6H₂O, AlCl₃·6H₂O, and SiCl₄ in slight excess in MeCN. The 1:1 complex formation was confirmed by a molar ratio method at Soret band maxima for Na⁺, Mg²⁺, Al³⁺, and Si⁴⁺ ions.²⁷ An attempt to isolate these metalloporphyrins as a solid was unsuccessful; removal of excess metal ions gave a mixture of metalloporphyrin with free-base porphyrin. A small amount of water was added into MeCN due to the lower solubility of the metal salts except for NaPF₆ and SiCl₄. The water content of the sample solution was less than 0.055 M.

Measurements. Fluorescence spectra were measured in degassed MeCN and MeOH solutions at 25 °C with a Hitachi 850 spectrofluorometer. The fluorescence quantum yield was determined by using that of 1 as a standard compound.¹⁶ The excitation wavelength was the Soret maximum. Fluorescence lifetimes were measured at 25 °C using a Horiba NAES-500 nanosecond-fluorometer. Glass filters were used for cutting off the exciting light (B390 (HOYA)) and the emission (U330 (HOYA), L42 (TOSHIBA), and Y51 (HOYA)). The fluorescence was detected by a single-photon counting system and analyzed as the sum of two exponential components after deconvolution of the instrument response function. A picosecondphoton-counting streak scope system (Hamamatsu Photonics C4780) was also used for fluorescence lifetime measurements of compounds 14, 10Zn, 11Zn, and 14Zn, where an N₂/dye laser was used for excitation at 430 nm (a 300 ps pulse width and 10 μ J/pulse). T-T absorption spectra and the lifetimes of the excited triplet state were measured using nanosecond-laser flash photolysis;²⁸ a XeCl excimer laser was used as a light source where the excitation wavelength was 308 nm, and a Xe lamp was used as a spectrum flash lamp. Time-resolved difference absorption spectra over a delay time ranging from 0-6000 ps were measured using a picosecond-laser spectroscopy system,²⁹ where a mode-locked Nd³⁺:YAG laser (Continuum PY61C-10, fwhm = 17 ps, 10 Hz) was used for excitation at 532 nm. Conventional pulse flash photolysis was also carried out for a slow reaction using a Photal RA-412 pulse flash apparatus with a Xe flash lamp (a 30 μ s pulse width). ¹H NMR spectra were measured with a JEOL JNM-GX270 FT NMR spectrometer. UV-vis and IR spectra were recorded with a Shimadzu UV-240 spectrophotometer and a Perkin-Elmer 1740 FT IR spectrometer, respectively. FAB-MS spectra were measured with a JEOL JMS-HX100 double focusing mass spectrometer in a 3-nitrobenzyl alcohol matrix. Cyclic voltammetry was done in an N2-saturated MeCN solution containing 0.05 M tetrabutylammonium perchlorate ([Bu₄N]ClO₄) with a Yanako Model P-900 instrument. A three-electrode system (BAS Inc.) was used with a Pt auxiliary electrode and a glassy carbon or a Pt working electrode against an Ag/AgClO₄ reference electrode. The potentials were converted to the values vs a saturated calomel electrode (SCE). MM2 calculations for molecular modeling were carried out with a CAChe system.

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Supporting Information Available: Absorption spectral data for N-alkylporphyrins and their zinc(II) complexes in MeCN (Table S1), absorption spectral data for viologen-linked N-alkylmetalloporphyrin diads in MeCN (Table S2), absorption spectra of the viologen-linked diads 10 and 14 and their Zn(II) complexes in MeCN (Figure S1), and absorption spectra of the metal complexes of viologen-linked diad 10 in MeCN (Figure S2). This information is available free of charge via the Internet at http://pubs.acs.org.

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(27) When the free-base porphyrin exists in excess over metal ions, a sandwich type of metalloporphyrins (metal ion:porphyrin = 1:2) was rapidly formed for Na⁺, Mg²⁺, Zn²⁺, Al³⁺, and Si⁴⁺. Detailed results for the sandwich-type metalloporphyrins will be reported elsewhere.

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