Kinetics and Mechanisms of Photoinduced Reduction of Methylviologen by *N*-Alkyltetraphenylporphyrinatozinc(II) in Methanol

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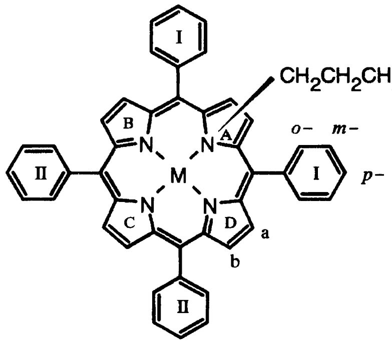
N-3-Bromopropyl-5,10,15,20-tetraphenylporphyrinato(1-)chlorozinc(II), [Zn(BrPrtpp)Cl], catalyzed the formation of a methylviologen radical cation ($MV^{+\bullet}$) on steady-state irradiation of degassed methanol solutions with visible light (>420 nm) in the presence of triethanolamine (TEOA). The initial rate (V_i) of the formation of $MV^{+\bullet}$ was of first order in the concentration of MV^{2+} and in the intensity of light and was independent of the concentration of TEOA above 0.025 M. Plots of V_i vs. the concentrations of [Zn(BrPrtpp)Cl] were curved. The fluorescence of [Zn(BrPrtpp)Cl]*, whose lifetimes are $\tau_1^s=0.7$ ns (48%) and $\tau_2^s=2.0$ ns (52%) in methanol at 25 °C, was not quenched by MV^{2+}. The excited triplet state of [Zn(BrPrtpp)Cl] ($\tau_0^t=3.2$ μs in MeOH) was efficiently quenched by MV^{2+} ($k_q=(6.0\pm0.6)\times10^7\ M^{-1}\,s^{-1}$ at 25 °C, 1 M=1 mol dm^{-3}). The thermal back electron-transfer reaction between $[Zn(BrPrtpp)Cl]^{+\bullet}$ and $MV^{+\bullet}$ was also observed ($k_b=(1.2\pm0.2)\times10^{10}\ M^{-1}\,s^{-1}$). On the basis of the steady-state irradiation kinetics and ns-laser flash photolysis, the quantum yield of the excited triplet state of [Zn(BrPrtpp)Cl] can be evaluated to be 0.98±0.02. [Zn(BrPrtpp)Cl] was found to be a more effective photocatalyst than [Zn(Prtpp)Cl] (HPrtpp=*N*-propyl-5,10,15,20-tetraphenylporphyrin) or [Zn(tpp)] (H_2tpp=5,10,15,20-tetraphenylporphyrin) under the present experimental conditions.

N-Alkylporphyrins have received considerable attention because of their biological significance, for example, as intermediate green pigments in the inactivation of hepatic cytochrome P-450 by a variety of substances, where the formation of *N*-substituted porphyrins includes a redox reaction as an important step. The redox reactions of *N*-alkylmetalloporphyrins have been studied during the last two decades. Although a number of studies of the photophysics and photochemistry of non-*N*-substituted porphyrins and methalloporphyrins have been reported, there have been very few studies of *N*-alkylporphyrins. Lavallee et al. reported fluorescence spectra of *N*-methylporphyrins and their zinc(II) complexes.[1—3] There has been no report of the photoinduced electron-transfer reaction of *N*-alkylmetalloporphyrins. Methylviologen (MV^{2+}) is the most effective mediator among bipyridinium salts in the catalytic photolysis of water under irradiation with visible light in the presence of a sensitizer such as tris(2,2′-bipyridine)ruthenium(II) and water-soluble Zn(II) porphyrins. In the latter case, the ground-state complexation between Zn(II) porphyrin and MV^{2+} inhibited the photoreduction of MV^{2+}.[4,5] Cationic Zn(II) porphyrins are therefore more effective in the formation of $MV^{+\bullet}$.[6] The *N*-alkylation of porphyrins results in distortion of the porphyrin plane by the sp^3 hybridization of one of the pyrrolenic nitrogens; the alkyl group is located perpendicular to the porphyrin plane.[1,7,8] The complexation between the *N*-alkylporphyrin and viologen is therefore expected to be reduced due to both steric hindrance and the distortion of the porphyrin plane.

In this work, we have found that *N*-3-bromopropyl-5,10,15,20-tetraphenylporphyrinato(1-)chlorozinc(II) ([Zn(BrPrtpp)Cl], **4**) catalyzes the formation of $MV^{+\bullet}$ on the steady-state irradiation of degassed methanol solutions with visible light (>420 nm) in the presence of triethanolamine (TEOA). We studied the photophysical and photochemical properties of [Zn(BrPrtpp)Cl] compared with those of [Zn(Prtpp)Cl] (**5**, HPrtpp = *N*-propyl-5, 10, 15, 20-tetraphenylporphyrin) and [Zn(tpp)] (H_2tpp = 5, 10, 15, 20-tetraphenylporphyrin) (Fig. 1).

Experimental

Materials. 1,1′-Dimethyl-4,4′-bipyridinium dichloride (Tokyo Kasei Kogyo Co., Ltd.) was recrystallized from ethanol. Methanol (Dotite Luminasol) was used for spectroscopic and kinetic measurements. H_2tpp and triethanolamine (reagent for FABMS) were purchased from Tokyo Kasei Kogyo Co., Ltd. 5,10,15,20-Tetraphenyl-



M = H; X = Br	HBrPrtpp (**1**)
M = H; X = H	HPrtpp (**3**)
M = ZnCl; X = Br	[Zn(BrPrtpp)Cl] (**4**)
M = ZnCl; X = H	[Zn(Prtpp)Cl] (**5**)

Fig. 1. Structures of *N*-alkylporphyrins.

porphyrinatozinc(II) ([Zn(tpp)]) was prepared by the reaction of H_2tpp with a 10-fold excess of $ZnCl_2$ in THF in the presence of 2,6-lutidine at 40 °C for 2 h under argon, followed by purification by alumina column chromatography. Other chemicals were of guaranteed reagent grade from Wako Chemical Industries, Ltd.

Synthesis of *N*-3-Bromopropyl-5,10,15,20-tetraphenylporphyrin–Water (2/5) (1, HBrPrtpp·2.5 H_2O). A mixture of H_2tpp (5.09 g, 8.28 mmol), anhydrous K_2CO_3 (3.35 g, 24.2 mmol), and 1,3-dibromopropane (496 g, 2.45 mol) was heated in a sealed brown tube at 98 °C for 240 h under argon.[9,10] Excess 1,3-dibromopropane was removed with a rotary evaporator after filtration. The residue was dissolved in toluene and loaded on an alumina column (ϕ 3.8 cm×20 cm). A purple species was first eluted with toluene and identified as H_2tpp (recovered 3.82 g, 75%). The second green species was eluted with CH_2Cl_2 and rechromatographed on an alumina column (ϕ 3.8 cm × 8 cm). Elution with CH_2Cl_2 and recrystallization from CH_2Cl_2–MeOH gave HBrPrtpp·$2.5H_2O$ as a purple powder; yield 0.119 g (1.8%); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ=8.84 (2H, s, pyrrole C), 8.68 (2H, d, J=4.9 Hz, pyrrole B,D_a), 8.50 (2H, d, J=4.9 Hz, pyrrole B,D_b), 8.27 (4H, br, *o*-phenyl I), 8.15 (4H, br, *o*-phenyl II), 7.78—7.91 (6H, m, *m,p*-phenyl I), 7.75—7.82 (6H, m, *m,p*-phenyl II), 7.54 (2H, s, pyrrole A), 1.77 (2H, t, J=6.8 Hz, α-CH_2), −1.12—−1.09 (2H, m, β-CH_2), −4.33 (2H, t, J=5.8 Hz, γ-CH_2). IR (KBr) 3870, 3479, 1635, 1230, 1218, 1160, 1070, 1020, 1002, 964, 800, 757, 702, 669 cm^{-1}. UV-vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})) 429 (2.6×10^5), 530 (9.2×10^3), 570 (1.5×10^4), 614 (4.1×10^3), 676 (5.1×10^3). Found: C, 72.70; H, 4.76; N, 7.34%. Calcd for $C_{47}H_{35}N_4Br\cdot2.5H_2O$: C, 72.30; H, 5.16; N, 7.18%. The third green species was eluted with CH_2Cl_2 and identified as *N*-3-hydroxypropyl-5,10,15,20-tetraphenylporphyrin (**2**), which is a hydrolysis product of HBrPrtpp. Recrystallization from CH_2Cl_2–MeOH gave a purple powder; yield 0.053 g (0.8%); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ=8.73 (2H, s, pyrrole C), 8.58 (2H, d, J=4.4 Hz, pyrrole B,D_a), 8.39 (2H, d, J=4.4 Hz, pyrrole B,D_b), 8.20 (4H, br, *o*-phenyl I), 8.06 (4H, br, *o*-phenyl II), 7.70—7.77 (6H, m, *m,p*-phenyl I), 7.60—7.74 (6H, m, *m,p*-phenyl II), 7.41 (2H, s, pyrrole A), 1.90 (2H, t, J=6.2 Hz, α-CH_2), −1.43—−1.36 (2H, m, β-CH_2), −4.46 (2H, t, J=6.2 Hz, γ-CH_2). IR (KBr) 3850, 3457, 1633, 1225, 1150, 1030, 970, 790, 740, 690, 665 cm^{-1}. UV-vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})) 429 (3.2×10^5), 531 (1.1×10^4), 572 (1.9×10^4), 614 (5.8×10^3), 675 (7.1×10^3). Found: C, 81.60; H, 5.53; N, 7.94%. Calcd for $C_{47}H_{36}N_4O\cdot H_2O$: C, 81.71; H, 5.54; N, 8.11%. The green species which remained on the top of the column was not identified.

Synthesis of *N*-Propyl-5,10,15,20-tetraphenylporphyrin–Water (2/3) (3, HPrtpp·1.5H_2O). H_2tpp (5.02 g, 8.27 mmol) was dissolved in 1-iodopropane (349 g, 2.05 mol) containing 10.1 g of anhydrous K_2CO_3 (73.1 mmol) under argon. The mixture was heated at 98 °C for 24 h in a sealed brown tube. After filtration, 1-iodopropane was removed with a rotary evaporator. The residue was dissolved in toluene and was loaded on an alumina column (ϕ 3.8 cm × 8 cm). After the purple species (H_2tpp, recovered 2.37 g, 47%) was eluted with toluene, the green species was eluted with CH_2Cl_2 and rechromatographed on an alumina column (ϕ 3.8 cm × 8 cm). Recrystallization from CH_2Cl_2–MeOH gave a purple powder of HPrtpp·1.5H_2O; yield 0.020 g (0.35%); ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ=8.80 (2H, s, pyrrole C), 8.65 (2H, d, J=5.1 Hz, pyrrole B,D_a), 8.46 (2H, d, J=5.1 Hz, pyrrole B,D_b), 8.31 (4H, br, *o*-phenyl I), 8.14 (4H, br, *o*-phenyl II), 7.73—7.84 (6H, m, *m,p*-phenyl I), 7.71—7.78 (6H, m, *m,p*-phenyl II), 7.74 (2H, s, pyrrole A), −0.68 (3H, t, J=7.3 Hz, CH_3), −1.59—−1.52 (2H, m, CH_3CH_2), −4.47 (2H, t, J=6.6 Hz, N–CH_2). IR (KBr) 3850, 3590, 3210, 2960, 1634, 1240, 960, 790, 750, 700, 670 cm^{-1}. UV-vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})) 429 (2.5×10^5), 532 (8.3×10^3), 573 (1.4×10^4), 613 (4.2×10^3), 675 (4.6×10^3). Found: C, 82.19; H, 5.42; N, 8.02%. Calcd for $C_{47}H_{36}N_4\cdot1.5H_2O$: C, 82.55; H, 5.75; N, 8.19%. The green species which remained on the top of the column was not identified.

Insertion of Zinc(II) into Porphyrins. A typical method is described for [Zn(BrPrtpp)Cl]·1.5H_2O (**4**). HBrPrtpp (0.040 g, 0.054 mmol) and $ZnCl_2$ (0.037 g, 0.27 mmol) were dissolved in 5 cm^3 of THF in the presence of 2,6-lutidine (0.0058 g, 0.054 mmol) under argon. The solution was stirred at 40 °C for 30 min. After THF was evaporated, the residue was dissolved in toluene and loaded on a silica-gel column (ϕ 2 cm×15 cm). Washing the column with toluene removed a trace amount of [Zn(tpp)]. A green species was eluted with CH_2Cl_2–acetone (v/v 50 : 1) and recrystallized from MeOH–H_2O; yield 0.020 g (43%): ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ=8.88 (2H, s, pyrrole C), 8.78—8.83 (4H, m, pyrrole B,D), 8.26 (4H, br, *o*-phenyl I), 8.19 (2H, s, pyrrole A), 8.10 (4H, br, *o*-phenyl II), 7.76—7.88 (4H, m, *p*-phenyl I,II), 7.65—7.76 (8H, m, *m*-phenyl I,II), 1.52 (2H, t, J=7.0 Hz, α-CH_2), −0.38—−0.53 (2H, m, β-CH_2), −4.46 (2H, t, J=7.0 Hz, γ-CH_2). IR (KBr) 3855, 3563, 3056, 1597, 1480, 1441, 1330, 1270, 1240, 1225, 1188, 1073, 1011, 990, 801, 754, 701 cm^{-1}. UV-vis (CH_3CN, λ_{max}/nm (ε/M^{-1} cm^{-1})) 330 (2.4×10^4), 436 (2.5×10^5), 446 (2.0×10^5), 560 (8.7×10^3), 610 (1.4×10^4), 657 (7.8×10^3); MeOH 325 (2.3×10^4), 431 (2.8×10^5), 444 (2.1×10^5), 557 (9.7×10^3), 604 (1.4×10^4), 651 (7.0×10^3). Found: C, 66.79; H, 4.13; N, 6.57%. Calcd for $C_{47}H_{34}N_4BrZnCl\cdot0.5H_2O$: C, 66.84; H, 4.18; N, 6.63%. The green species which remained on the top of the column was not identified.

[Zn(Prtpp)Cl]·$0.5H_2O$ (**5**) was obtained by the abovementioned method and recrystallization from MeOH gave a green powder; yield 0.025 g (61%). ^{1}H NMR (270 MHz, $CDCl_3$ TMS) $\delta=8.94$ (2H, d, $J=4.3$ Hz, pyrrole B,D_a), 8.93 (2H, s, pyrrole C), 8.85 (2H, d, $J=5.1$ Hz, pyrrole B,D_b), 8.34 (2H, br, *o*-phenyl I), 8.27 (2H, br, *o*-phenyl I), 8.16 (2H, s, pyrrole A), 8.14 (4H, br, *o*-phenyl II), 7.75—7.78 (12H, m, *m,p*-phenyl I,II), −0.90—−0.80 (5H, m, CH_3CH_2), −4.56 (2H, t, $J=6.8$ Hz, N–CH_2). IR (KBr) 3850, 3565, 3200, 1634, 1244, 1150, 1060, 1030, 1000, 700, 664 cm^{-1}. UV-vis (CH_3CN, λ_{max}/nm (ε/$M^{-1}\,cm^{-1}$)) 329 (2.4×10^4), 436 (2.6×10^5), 443sh (2.2×10^5), 560 (8.2×10^3), 611 (1.5×10^4), 656 (7.8×10^3); MeOH 326 (2.2×10^4), 432 (2.4×10^5), 443 (2.0×10^5), 558 (8.8×10^3), 606 (1.4×10^4), 650 (6.7×10^3). Found: C, 73.84; H, 4.73; N, 7.21%. Calcd for $C_{47}H_{35}N_4ZnCl\cdot0.5H_2O$: C, 73.73; H, 4.74; N, 7.32%.

Measurements. Fluorescence spectra were measured in degassed CH_3CN and MeOH solutions at 25 °C with a Hitachi 850 spectrofluorometer. The excitation wavelength was the Soret maximum. Fluorescence lifetimes were measured at 25 °C using a Horiba NAES-500 ns-fluorometer interfaced to an NEC PC-9801 RX personal computer. The excitation light below 420 nm was cut off with a glass filter. 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 ps-photon-counting streak camera system (Hamamatsu Photonics C2050/M1952/CCD temporal analyzer 3140-69)[11] was also used for fluorescence lifetime measurements of [Zn(BrPrtpp)Cl], where a mode-locked Nd:YAG laser (Coherent Antares 76-s) and a synchronously pumped dye laser (Coherent 701, Kiton Red dye) were used for excitation at 360 nm. T–T absorption spectra and the lifetimes of the excited triplet state were measured using ns-laser flash photolysis;[12] a XeCl excimer laser (Lambda physik EMG 53MSC) was used as a light source where the excitation wavelength was 308 nm, and a xenon lamp was used as a spectrum flash lamp. 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. ^{1}H 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.

Steady-State Irradiation Kinetics. A methanol solution in a quartz cell was degassed by repeated freeze-pump-thaw cycles in the dark. The degassed solution was irradiated with visible light from a 100-W tungsten lamp at 25 °C. Shorter wavelengths below 420 nm were cut off by a glass filter. The formation of $MV^{+\bullet}$ was monitored at 605 nm using a Shimadzu UV-200S spectrophotometer after shutting off the light. The initial rate of reaction (V_i) was obtained from the initial linear portion of the plots of the absorbance against time. The effects of the concentrations of Zn(II) porphyrin, MV^{2+}, and TEOA and the intensity of irradiated light (I_0) on V_i were examined under the concentrations where $[Zn(BrPrtpp)Cl]_0=0$—1.15×10^{-5} M, $[MV^{2+}]_0=0$—2.30×10^{-3} M, $[TEOA]_0=0$—0.10 M, and $I_0=0$—1.84×10^{-7} M s^{-1}. The light intensity absorbed in the solutions was determined by the use of potassium tris(oxalato)ferrate(III) trihydrate as an actinometer.[13] The iron(II) content was determined spectrophotometrically in the form of a tris(1,10-phenanthroline)iron(II) ion at 510 nm with a molar absorption coefficient of 1.11×10^4 $M^{-1}\,cm^{-1}$.

Results and Discussion

Fluorescence Properties. Fluorescence data for *N*-alkylporphyrins and Zn(II) complexes are summarized in Table 1. Red-shifts in the emission maxima and a considerable decrease in the fluorescence quantum yield were observed in *N*-alkylporphyrin and Zn(II) complexes compared with non-*N*-substituted porphyrins. Stokes' shifts between the $Q_x(0,0)$ absorption and $Q_x(0,0)$ fluorescence peaks in *N*-alkylporphyrins and Zn(II) complexes are larger than those for planar porphyrins: 258 cm^{-1} (HPrtpp), 236 cm^{-1} (HBrPrtpp), 274 cm^{-1} ([Zn(Prtpp)Cl]), 273 cm^{-1} ([Zn(BrPrtpp)Cl]), 71 cm^{-1} (H_2tpp), and 195 cm^{-1} ([Zn(tpp)]). This fact can be explained by the noncoplanarity of the porphyrin plane and a weaker ligand field than that of a typical planar metalloporphyrin. The low quantum yields of the fluorescence may arise from increased rates of radiationless decay processes (internal conversion and intersystem crossing). The internal conversion process is dependent on the vibrational wave function overlap (Franck–Condon factor) 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.[15] The quantum yield of the excited triplet state of [Zn(BrPrtpp)Cl] obtained in this work ($\phi=0.98$, vide infra) is larger than that of [Zn(tpp)] ($\phi=0.88$).[4] Therefore, the low quantum yield of the fluorescence of *N*-alkylporphyrinatozinc(II) arises mainly from the increased intersystem crossing rate. Although the fluorescence lifetimes of H_2tpp and [Zn(tpp)] have only one component, those of *N*-alkylporphyrins and Zn(II) complexes consist of two components except for [Zn(Prtpp)Cl]. The excited singlet state must have two conformers, because the alkyl chain is quite flexible. The fluorescence lifetimes of HBrPrtpp and [Zn(BrPrtpp)Cl] were shorter than those of HPrtpp and [Zn(Prtpp)Cl] because of the heavy atom effect of Br.[16] The change in the fluorescence intensity on adding free MV^{2+} was examined for HBrPrtpp, [Zn(Prtpp)Cl], and [Zn(BrPrtpp)Cl]. The fluorescence intensity of HBrPrtpp decreases with an increase in $[MV^{2+}]$ (up to 5.0×10^{-3} M), while no appreciable change was observed for [Zn(Prtpp)Cl] and [Zn(BrPrtpp)Cl]. The Stern–Volmer constant for the quenching of ^{1}(HBrPrtpp)* by MV^{2+} was 142 ± 12 M^{-1} at 25 °C in CH_3CN. This is in agreement with the fluorescence lifetime in the presence of MV^{2+} ($\tau=1.9$ ns at $[MV^{2+}]=4.0\times10^{-3}$ M with only one component). The quenching rate constant of ^{1}(HBrPrtpp)* by MV^{2+} is then evaluated to be $(4.7\pm0.4)\times10^{10}$ $M^{-1}\,s^{-1}$. Therefore, the fluorescence quenching by free MV^{2+} is important for free base porphyrins but not for Zn(II) porphyrins.

Table 1. Fluorescence Data for *N*-Alkylporphyrins and their Zinc(II) Complexes

Compound	Solvent	λ_{ex}/nm	λ_{em}/nm	ϕ_f	τ_1/ns (A_1/%)	τ_2/ns (A_2/%)	χ^2
H_2tpp	CH_3CN	419	650, 713	0.38	13.6 (100)[a]	—	—
[Zn(tpp)]	CH_3CN	421	602, 654	0.080	2.7 (100)[a]	—	—
HMetpp[b]	Ether	429	681, 755	0.014	—	—	—
[Zn(Metpp)Cl][b]	Ether	428	664, 725	0.011	—	—	—
HPrtpp	CH_3CN	429	687, 745sh	0.014	0.8 (47)	4.9 (53)	1.04
[Zn(Prtpp)Cl]	CH_3CN	436	668, 732	0.011	1.6 (100)	—	1.00
	MeOH	432	666, 730sh	0.011	1.9 (100)	—	1.05
HBrPrtpp	CH_3CN	429	687, 745sh	0.020	0.6 (25)	3.0 (75)	1.02
[Zn(BrPrtpp)Cl]	CH_3CN	436	669, 730	0.0058	1.1 (38)	1.9 (62)	1.20
	MeOH	431	666, 730sh	0.0057	0.7 (48)	2.0 (52)	1.03

a) In methylcyclohexane. Ref. 14. b) Ref. 2.

Excited Triplet State. There has been no report of phosphorescence from *N*-alkylporphyrin. We have observed a very weak phosphorescence spectrum of [Zn(Prtpp)Cl] with a maximum at 910 nm in an EtOH–MeOH glass (v/v 4 : 1) at 77 K. Phosphorescence from [Zn(BrPrtpp)Cl] was not detected under the same experimental conditions.

T–T absorption spectra of [Zn(Prtpp)Cl] and [Zn(BrPrtpp)Cl] in MeOH are shown in Fig. 2. The T–T absorption in the 450—500 nm region has two maxima at 475 and 490 nm, which are different from that of [Zn(tpp)] (a maximum at 460 nm in EtOH).[17] The lifetimes of the excited triplet states of [Zn(Prtpp)Cl] and [Zn(BrPrtpp)Cl] in MeOH and CH_3CN were determined using a ns-laser flash photolysis with excitation at 308 nm. Decay of ^{3}([Zn(Prtpp)Cl])* and ^{3}([Zn(BrPrtpp)Cl])* monitored at 470 nm was fitted to first-order kinetics over 98% of the decay, indicating that the T–T annihilation is not important for these two compounds. The lifetimes at 25 °C for [Zn(Prtpp)Cl] and [Zn(BrPrtpp)Cl] are 4.4 and 3.2 μs in MeOH and 7.9 and 2.7 μs in CH_3CN, respectively.

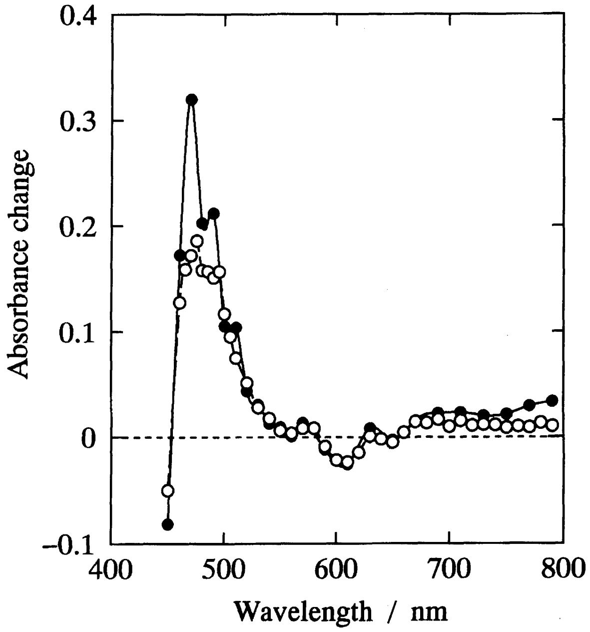


Fig. 2. T–T absorption spectra of ^{3}([Zn(Prtpp)Cl])* (○) and ^{3}([Zn(BrPrtpp)Cl])* (●) at 30 ns after irradiation of degassed MeOH solutions containing 3.0×10^{-6} M Zn(II) porphyrins.

In the presence of MV^{2+} the lifetimes of ^{3}([Zn(Prtpp)Cl])* and ^{3}([Zn(BrPrtpp)Cl])* became shorter: 4.1 and 2.9 μs at $[MV^{2+}]=5.0\times10^{-4}$ M and 3.8 and 2.7 μs at $[MV^{2+}]=1.0\times10^{-3}$ M in MeOH, respectively. Excitation of MV^{2+} in MeOH at 308 nm produced a small amount of $MV^{+\bullet}$, and the formation of $MV^{+\bullet}$ in the presence of [Zn(Prtpp)Cl] or [Zn(BrPrtpp)Cl] was complicated. The quenching of ^{3}([Zn(Prtpp)Cl])* or ^{3}([Zn(BrPrtpp)Cl])* by MV^{2+} was therefore analyzed at 470 nm, where the absorption of $MV^{+\bullet}$ is negligible. The quenching rate constants (k_q^t) of ^{3}([Zn(Prtpp)Cl])* and ^{3}([Zn(BrPrtpp)Cl])* by MV^{2+} in MeOH were evaluated to be $(3.5\pm0.2)\times10^7$ $M^{-1}\,s^{-1}$ and $(6.0\pm0.6)\times10^7$ $M^{-1}\,s^{-1}$ at 25 °C, respectively. The values of k_q^t are larger than that for the cationic non-*N*-substituted Zn(II) porphyrin (2.1×10^7 $M^{-1}\,s^{-1}$ in C_2H_5OH for 5-(1-methylpyridinium-4-yl-)-10,15,20-tris(4-tolyl)-porphyrinato(2-)zinc(II) ion).[6]

Thermal Back ET Reaction. After irradiation of [Zn(BrPrtpp)Cl] and MV^{2+} in MeOH with a 30 μs Xe flash lamp (λ>420 nm), the decay of $MV^{+\bullet}$ was followed at 400 nm, as is shown in Fig. 3. The decay of $MV^{+\bullet}$ was of second order, indicating that thermal back ET reaction between $[Zn(BrPrtpp)Cl]^{+\bullet}$ and $MV^{+\bullet}$ occurs. The rate constant of this process (k_b) was evaluated to be $(1.2\pm0.2)\times10^{10}$ $M^{-1}\,s^{-1}$ using a molar absorption coefficient of 4.3×10^4 $M^{-1}\,cm^{-1}$ at 400 nm for $MV^{+\bullet}$ [18] at several concentrations of MV^{2+}. Similarly, the value of k_b for [Zn(Prtpp)Cl] was determined to be $(2.6\pm0.3)\times10^{10}$ $M^{-1}\,s^{-1}$ at 25 °C in MeOH.

Steady-State Irradiation Kinetics. Figure 4 shows the change in absorbance during steady-state irradiation (λ>420 nm) of a degassed MeOH solution containing [Zn(BrPrtpp)Cl], MV^{2+}, and TEOA at 25 °C. It was observed that $MV^{+\bullet}$ accumulated while the absorption spectra of [Zn(BrPrtpp)Cl] did not change during the irradiation, indicating that [Zn(BrPrtpp)-

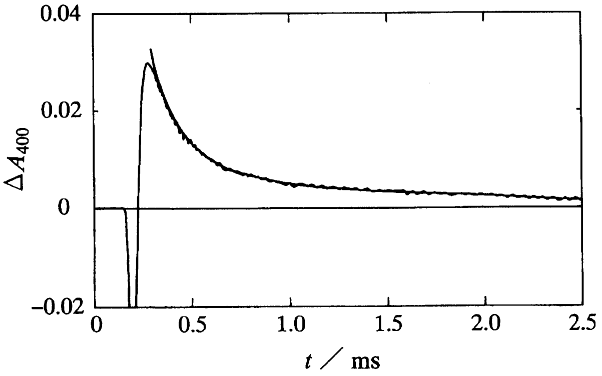


Fig. 3. The back ET reaction between [Zn(BrPrtpp)-Cl]$^{+\bullet}$ and MV$^{+\bullet}$ in degassed MeOH at [Zn(BrPrtpp)-Cl]$_0$=3.0×10^{-6} M and [MV^{2+}]$_0$=2.0×10^{-3} M. The data are averages of seven scans at 400 nm and are fitted to second-order decay kinetics.

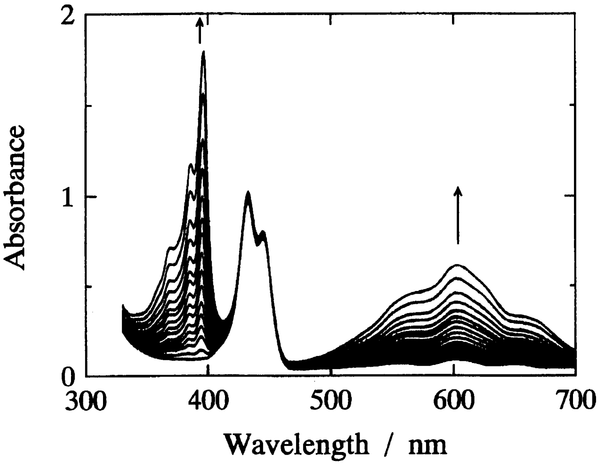


Fig. 4. Absorption spectral changes on steady-state irradiation (I_0=1.84×10^{-7} M s^{-1}) of the degassed MeOH solution containing 3.2×10^{-6} M [Zn-(BrPrtpp)Cl], 1.0×10^{-3} M MV^{2+}, and 0.05 M TEOA. Irradiation time intervals are 3 min for spectra No. 1 to 10 and 5 min for spectra No. 11 to 16.

Cl] acts as a homogeneous catalyst. Further, there is no evidence for the ground-state complexation between [Zn(BrPrtpp)Cl] and MV^{2+}.[19] Plots of the absorbance at 605 nm against the irradiation time at various concentrations of [Zn(BrPrtpp)Cl] are shown in Fig. 5. A small amount of MV$^{+\bullet}$ formed in the degassed MeOH or CH$_3$CN solution containing MV^{2+} and TEOA at 25 °C even in the dark. The rate of the formation of MV$^{+\bullet}$ is much slower in MeOH than in CH$_3$CN. Moreover, the formation of MV$^{+\bullet}$ in the solution containing MV^{2+} and TEOA during irradiation is negligible in the initial portion of the reaction under the conditions that [MV^{2+}]$_0$≤2.5×10^{-3} M and [TEOA]$_0$≤0.10 M at 25 °C in MeOH (see Fig. 5). The rate of the formation of MV$^{+\bullet}$ gradually decreased during the reaction due to an internal filter effect by the formation of MV$^{+\bullet}$. The initial rate of reaction (V_i) was therefore calculated from the data for the initial 10 min. The dependence of V_i on [Zn(BrPrtpp)Cl]$_0$, [MV^{2+}]$_0$, and I_0 are shown in Figs. 6, 7, and 8. Under the present experimental conditions, the values of V_i are proportional to I_0, although plots of V_i vs. [Zn(BrPrtpp)Cl]$_0$

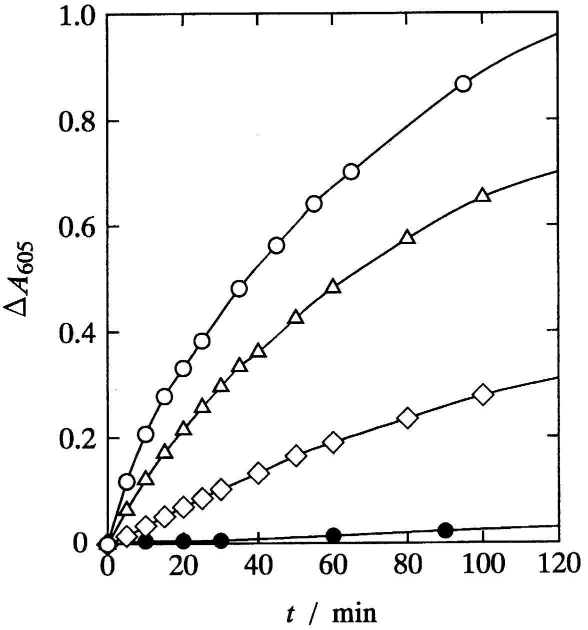


Fig. 5. Formation of MV$^{+\bullet}$ by the irradiation with visible light (I_0=1.84×10^{-7} M s^{-1}) of the degassed MeOH solution containing 1.0×10^{-3} M MV^{2+}, 0.05 M TEOA, and various concentrations of [Zn-(BrPrtpp)Cl]. ●: 0 M; ◇: 5.3×10^{-7} M, △: 2.1×10^{-6} M, and ○: 5.3×10^{-6} M.

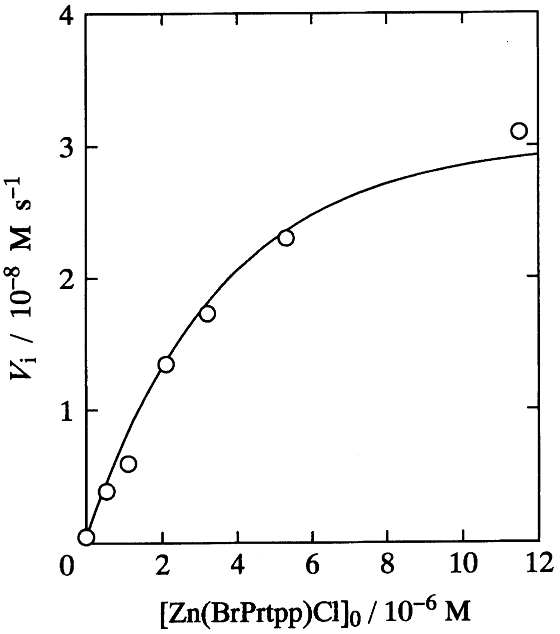


Fig. 6. Plots of V_i vs. [Zn(BrPrtpp)Cl]$_0$ for the formation of MV$^{+\bullet}$ under irradiation with visible light (I_0=1.84×10^{-7} M s^{-1}) at 25 °C in degassed MeOH solutions containing 1.0×10^{-3} M MV^{2+} and 0.05 M TEOA.

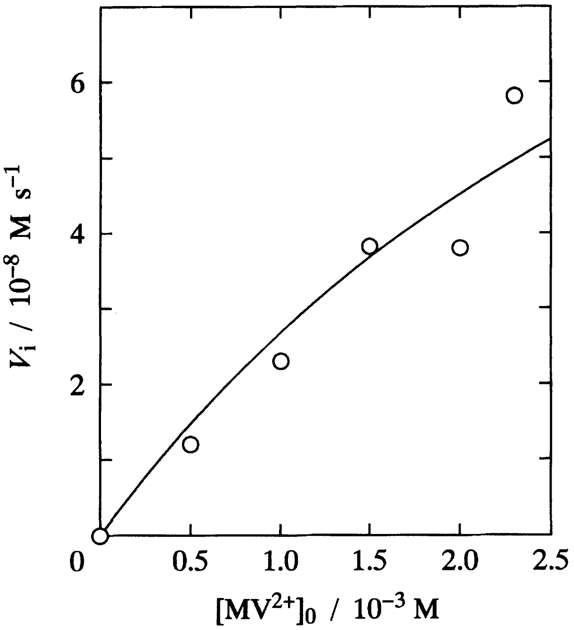


Fig. 7. Plots of V_i vs. $[MV^{2+}]_0$ for the formation of $MV^{+\bullet}$ under irradiation with visible light ($I_0 = 1.84\times10^{-7}$ M s^{-1}) at 25 °C in degassed MeOH solutions containing 5.3×10^{-6} M [Zn(BrPrtpp)Cl] and 0.05 M TEOA.

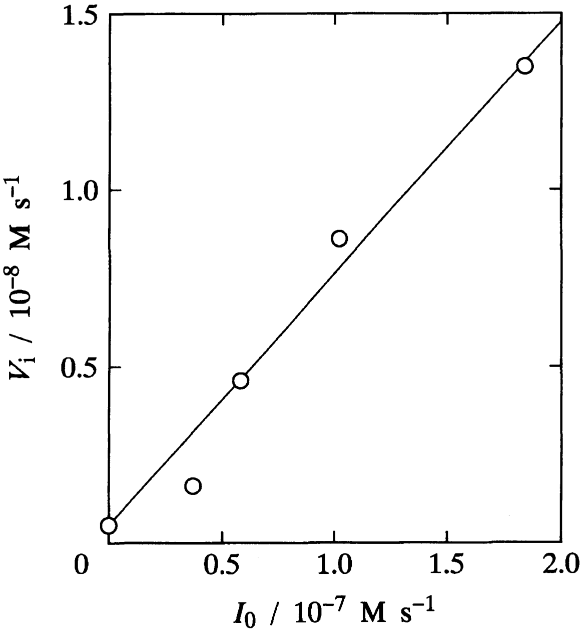


Fig. 8. Plots of V_i vs. I_0 for the formation of $MV^{+\bullet}$ at 25 °C under irradiation with visible light at 25 °C in degassed MeOH solutions containing 2.1×10^{-6} M [Zn(BrPrtpp)Cl], 1.0×10^{-3} M MV^{2+}, and 0.05 M TEOA.

and vs. $[MV^{2+}]_0$ are both curved. Moreover, V_i was independent of $[TEOA]_0$ over the range from 0.025 to 0.10 M.

Mechanisms of Photocatalytic Reaction. All the results are accounted for by the following reaction mechanism, which has been proposed for the oxidative quenching of the excited triplet state of Zn(II) porphyrins:[20]

$$\mathrm{ZnP} \xrightarrow{h\nu} {}^3(\mathrm{ZnP})^*, \quad I_a\phi \tag{1}$$

$$ {}^3(\mathrm{ZnP})^* \xrightarrow{k_0^t} \mathrm{ZnP}, \tag{2}$$

$$ {}^3(\mathrm{ZnP})^* + \mathrm{MV}^{2+} \xrightarrow{k_q^t} \mathrm{ZnP}^{+\bullet} + \mathrm{MV}^{+\bullet}, \tag{3}$$

$$\mathrm{ZnP}^{+\bullet} + \mathrm{MV}^{+\bullet} \xrightarrow{k_b} \mathrm{ZnP} + \mathrm{MV}^{2+}, \tag{4}$$

and

$$\mathrm{ZnP}^{+\bullet} + \mathrm{TEOA} \xrightarrow{k_5} \mathrm{ZnP} + \mathrm{TEOA}^{+\bullet}. \tag{5}$$

The excited singlet state of ZnP was not quenched by MV^{2+} for [Zn(BrPrtpp)Cl] and [Zn(Prtpp)Cl]. Therefore, the ET quenching occurs from the excited triplet state of ZnP. The values of k_b are $(1.2\pm0.2)\times10^{10}$ $M^{-1}s^{-1}$ and $(2.6\pm0.3)\times10^{10}$ $M^{-1}s^{-1}$ for the [Zn(BrPrtpp)Cl] and [Zn(Prtpp)Cl] systems, respectively. The initial rate of reaction was independent of $[TEOA]_0$ above 0.025 M and $MV^{+\bullet}$ accumulated. Reaction 5 must therefore be much faster than reaction 4 ($k_5 > 1\times10^6$ $M^{-1}s^{-1}$). On the basis of the steady-state assumption for ${}^3(ZnP)^*$ and $ZnP^{+\bullet}$, the following rate law can be derived:

$$V_i = \mathrm{d}[\mathrm{MV}^{+\bullet}]/\mathrm{d}t = k_q^t I_a\phi[\mathrm{MV}^{2+}]/(k_0^t + k_q^t[\mathrm{MV}^{2+}]), \tag{6}$$

where I_a and ϕ are the light intensity absorbed and the quantum yield of the excited triplet state of ZnP, respectively. From Lambert–Beer's law, I_a correlates to I_0 and the concentrations of ZnP according to Eq. 7:

$$I_a = I_0\{1-\exp(-\gamma[\mathrm{ZnP}])\}, \tag{7}$$

where γ is a constant containing the molar absorption coefficient (ε) of ZnP and the optical path length (l). Therefore, Eq. 6 can be represented as Eq. 8:

$$V_i = k_q^t I_0\phi[\mathrm{MV}^{2+}]\{1-\exp(-\gamma[\mathrm{ZnP}])\}/(k_0^t + k_q^t[\mathrm{MV}^{2+}]). \tag{8}$$

Equation 8 is consistent with all the results obtained in this work. The curve in Fig. 6 is fitted to Eq. 8, where γ $(=\varepsilon l)=2.8\times10^5$ M^{-1} and $k_q^t I_0\phi[MV^{2+}]/(k_0^t + k_q^t[MV^{2+}])=3.0\times10^{-8}$ M s^{-1}. Using the values of k_q^t $(=6.0\times10^7$ $M^{-1}s^{-1})$, k_0^t $(=3.1\times10^5$ $s^{-1})$, I_0 $(=1.84\times10^{-7}$ $M^{-1}s^{-1})$, and $[MV^{2+}]$ $(=1.0\times10^{-3}$ M) for [Zn(BrPrtpp)Cl], the quantum yield (ϕ) for ${}^3([Zn(BrPrtpp)Cl])^*$ can be evaluated to be 1.0. From the plots of V_i vs. $[MV^{2+}]_0$, the value of ϕ was determined to be 0.96 (see the solid curve in Fig. 7). The ϕ value of 0.98 was obtained from the linear dependence of V_i on I_0 (Fig. 8). These two values are in good agreement with that obtained from the $[Zn(BrPrtpp)Cl]_0$ dependency. The value of ϕ $(=0.98\pm0.02)$ is larger than that for non-*N*-substituted Zn(II) porphyrins.[4,20]

Steady-state irradiation kinetics was also briefly carried out for [Zn(Prtpp)Cl] and [Zn(tpp)]. Under the same experimental conditions as in Fig. 7 where $[MV^{2+}]_0=1.0\times10^{-3}$ M, the values of V_i were 2.1×10^{-8} $M\,s^{-1}$ and 3.1×10^{-9} $M\,s^{-1}$ for [Zn(Prtpp)Cl] and [Zn(tpp)], respectively. The photocatalytic abilities under the present experimental conditions are in the following order: [Zn(BrPrtpp)Cl] (1.0) > [Zn(Prtpp)Cl] (0.90) ≫ [Zn(tpp)] (0.13). Pileni has reported the rate constants of the quenching of $^3([Zn(tpp)])^*$ by MV^{2+} in C_2H_5OH ($k_q^t=7.0\times10^8$ $M^{-1}\,s^{-1}$ and $k_0^t=5.0\times10^4$ s^{-1}).[21] Therefore, we can compare the efficiency of the $MV^{+\bullet}$ formation, $k_q^t\phi[MV^{2+}]/(k_0^t+k_q^t[MV^{2+}])$, for these Zn(II) porphyrins. The values of $k_q^t\phi[MV^{2+}]/(k_0^t+k_q^t[MV^{2+}])$ at $[MV^{2+}]_0=1.0\times10^{-3}$ M are 0.16, 0.13, and 0.82 for [Zn(BrPrtpp)Cl], [Zn(Prtpp)Cl], and [Zn(tpp)], respectively. Therefore, the difference in V_i for [Zn(BrPrtpp)Cl] and [Zn(Prtpp)Cl] arises from that in the value of $k_q^t\phi[MV^{2+}]/(k_0^t+k_q^t[MV^{2+}])$. However, the low photocatalytic ability of [Zn(tpp)] cannot be explained by this term. We must consider the other two factors. The first is the ground-state complexation of [Zn(tpp)] with MV^{2+}. In the case of [Zn(BrPrtpp)Cl] and [Zn(Prtpp)Cl], the ground-state complexation with MV^{2+} is negligible. When $[MV]Cl_2$ (up to 3.0×10^{-2} M) was added to the MeOH solution of [Zn(tpp)], the absorption spectrum in the Soret region changed with an isosbestic point at 423 nm. Although we could not observe a distinct Soret maximum for the complex of [Zn(tpp)] with MV^{2+} due to the limited solubility of $[MV]Cl_2$ in MeOH, this spectral change can be attributed to the ground-state complexation of [Zn(tpp)] with MV^{2+}.[5,22] Reciprocal plots of the absorbance change vs. the concentration of MV^{2+} in the Soret region gave straight lines. The formation constant of the ground-state complex was obtained from intercept/slope ($K=40\pm4$ M^{-1}). This value is much smaller than those for anionic Zn(II) porphyrins and is larger than those for cationic Zn(II) porphyrins in water.[22,23] Under the present experimental conditions ($[ZnP]=5.3\times10^{-6}$ M and $[MV^{2+}]_0=1.0\times10^{-3}$ M), 96% of [Zn(tpp)] exists in free [Zn(tpp)]. Therefore, the low catalytic ability of [Zn(tpp)] cannot be explained by only the ground-state complexation. The second factor is the absorption efficiency term of $\{1-\exp(-\gamma[ZnP])\}$. When $\lambda>420$ nm and $[ZnP]=5.3\times10^{-6}$ M, the values of this term are 0.77, 0.72, and 0.11 for [Zn(BrPrtpp)Cl], [Zn(Prtpp)Cl], and [Zn(tpp)], respectively. Therefore, the low photocatalytic ability of [Zn(tpp)] arises mainly from the low absorption efficiency of [Zn(tpp)] under irradiation with light at $\lambda>420$ nm. The merits of the use of N-alkylporphyrinatozinc(II) in the photoreduction of methylviologen are summarized: (i) no ground-state complexation with viologen (thereafter longer lifetime of the charge separation state), which may be efficient at high concentrations of ZnP and MV^{2+}, and (ii) the use of visible light at longer wavelengths.

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