

Photoinduced Electron Transfer in π -Donor-Capped Zn(II) Porphyrins and *N,N'*-Dimethyl-4,4'-bipyridinium Supramolecular Assemblies

Evgeny Kaganer, Ernesto Joselevich, and Itamar Willner*

*Institute of Chemistry and The Farkas Center for Light-Induced Processes,
The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

Zhangpin Chen, Maxwell J. Gunter, Throne P. Gayness, and Martin R. Johnson

Department of Chemistry, The University of New England, Armidale, NSW 2351, Australia

Received: September 18, 1997; In Final Form: November 19, 1997

π -Donor-polyoxyethylene-capped Zn(II)-porphyrins, **1–3**, form supramolecular complexes with *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+} , **4**. The association constants of the resulting adducts are 8×10^4 , 1×10^4 , and $1 \times 10^3 \text{ M}^{-1}$, respectively. The Zn(II)-porphyrins are quenched by MV^{2+} by two complementary routes that include internal electron-transfer quenching in the supramolecular complexes and diffusional electron-transfer quenching of the free chromophore.

Introduction

Substantial efforts have been directed over the past decade toward mimicking the vectorial photoinduced electron transfer and charge separation in the photosynthetic reaction center.^{1–3} One approach for modeling the photosynthetic reaction center includes the synthesis of covalently linked donor–acceptor diads,⁴ triads,^{5,6} and pentads.⁷ The electron-transfer products in these systems are generally stabilized against recombination by their spatial separation in the molecular arrays. Further stabilization of the photogenerated redox products in molecular triads was accomplished by the incorporation of the molecular assemblies in heterogeneous matrixes, such as zeolites⁸ or layered phosphates.⁹ Structural alignment and rigidification of the molecular arrays in these systems result in the stabilization of the redox products against back-electron transfer. Similarly, the formation of donor–acceptor supramolecular complexes between a molecular photosensitizer–acceptors triad and an electron donor was reported to result in the steric rigidification of the triad, leading to vectorial photoinduced electron transfer.¹⁰

A different approach for organizing photosensitizer–acceptor diads involves the noncovalent assembly of photosensitizer–acceptor supramolecular complexes. Complementary H bonds between functionalized photosensitizers and electron acceptors were reported to yield noncovalent photosensitizer–acceptor diads.¹¹ Structural alignment of donor–acceptor diads via the formation of inclusion complexes with cyclodextrins was reported to enhance the photoinduced charge separation.¹² Recently, we reported a novel approach to organize photosensitizer–acceptor diad and “polyad” assemblies via the application of octopus-like multireceptor photosensitizers that form supramolecular complexes with several electron-acceptor units by π -donor–acceptor interactions.¹³

We have shown that dialkoxybenzene receptor sites tethered to Ru(II)polypyridine complexes lead to the formation of receptor-modified photosensitizers.¹³ Formation of π -donor–

acceptor complexes between *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+} , or the bipyridinium cyclophane, cyclo[bis(*N,N'*-*p*-xylylene-4,4'-bipyridinium)], and the dialkoxybenzene receptor sites led to efficient electron-transfer quenching of the excited photosensitizers. Detailed analysis of the electron-transfer quenching and back-electron transfer revealed that the photosensitizer–electron acceptor assemblies behave as intact diads where the electron-transfer products recombine within the noncovalently linked complexes.

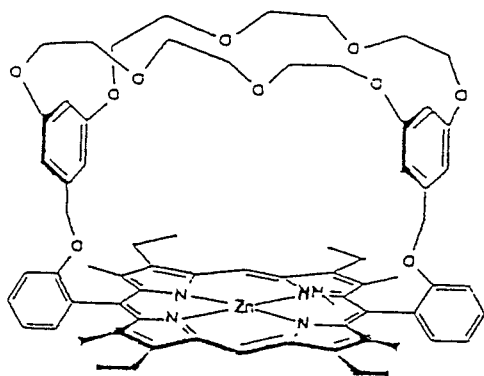
Substantial progress has been accomplished in recent years in the synthesis of π -donor-capped porphyrins and metalloporphyrins, i.e., Zn(II)-porphyrins.^{14,15} These porphyrins are capable of binding *N,N'*-dialkyl-4,4'-bipyridinium salts via π -donor–acceptor interaction, π – π interactions, and cation ligation. Indeed, the supramolecular complexes formed between bipyridinium salts and π -donor-capped Zn(II)-porphyrins were characterized spectroscopically and by ¹H-NMR methods and more recently by an X-ray crystal-structure determination.¹⁶ The well-established photoactivity of Zn(II)-porphyrins to stimulate electron transfer to bipyridinium salts^{17,18} suggests that the complexes formed between bipyridinium salts and π -donor-capped Zn(II)-porphyrins could represent interesting organized assemblies for photoinduced electron transfer. Here, we wish to report on the photophysical characterization of the supramolecular assemblies formed between the π -donor-polyoxyethylene-capped Zn(II)-porphyrins **1–3** and *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+} , **4**. We find that formation of the complexes prevents the intersystem crossing of the singlet to the triplet state owing to electron-transfer quenching of the excited state by MV^{2+} in the supramolecular assemblies.

Experimental Section

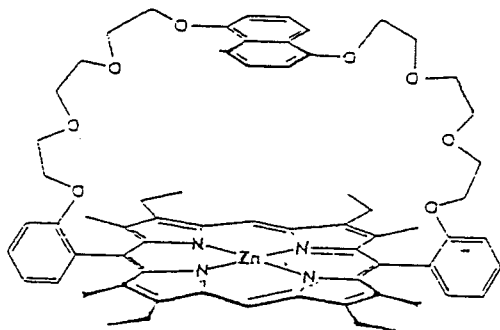
Absorption spectra were recorded with a Uvikon-860 (Kontron) spectrophotometer. Fluorescence spectra were recorded with a SFM-25 (Kontron) spectrofluorometer. Flash-photolysis experiments were carried out with a Nd:YAG laser (model GCR-150, Spectra Physics) coupled to a detection system (Applied Photophysics K-347) that included a monochromator

* To whom correspondence should be addressed. Telephone: 972-2-6585272. Fax 972-2-6527715. E-mail: willnea@vms.huji.ac.il.

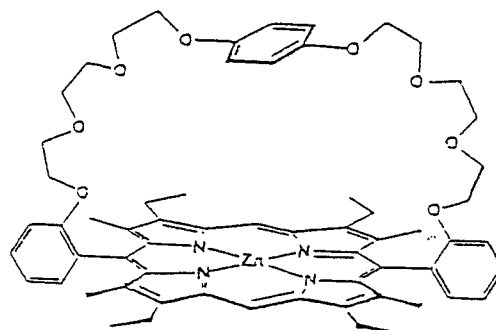
(1)



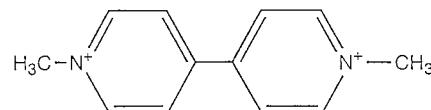
(2)



(3)



(4)



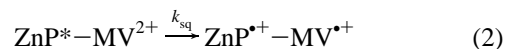
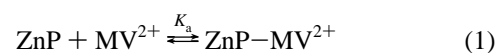
and photomultiplier linked to a digitizer (Tektronix 2430 A) and computer for data storage and processing. This flash-photolysis setup has a time resolution of >20 ns. Zinc porphyrins **2** and **3** were prepared as previously described.¹⁵ Compound **1** was prepared in an analogous manner and fully characterized; details of its synthesis and physical properties will be described elsewhere.^{16c} The association constants for **1** with MV^{2+} were determined by 1H -NMR methods as previously described.^{15,16a,b}

All photochemical measurements were performed in acetonitrile (Z.T. Baker, HPLC grade). All steady-state luminescence and time-resolved quenching experiments were performed in $1\text{ cm} \times 1\text{ cm}$ glass cuvettes that contained a solution of the respective photosensitizer in acetonitrile, 3.6×10^{-5} M (OD ≈ 0.6), and the appropriate concentration of the MV^{2+} . In the steady-state experiments, excitation of the chromophores was performed at $\lambda_{\text{ex}} = 542$ nm. For the time-resolved experiments a Nd:YAG laser, $\lambda_{\text{ex}} = 532$ nm, was used. The resulting triplet absorbance of the different photosensitizers was recorded at $\lambda_{\text{ab}} = 470$ nm. The recombination processes of the photogenerated photoproducts were characterized in acetonitrile in the presence of **1**, **2** or **3**, 3.6×10^{-5} M, and MV^{2+} at 5×10^{-5} , 6×10^{-5} , and 5×10^{-4} M, respectively. The triplet quantum yields (ϕ_{ST}) of **1–3** were determined by comparing the after-pulse triplet concentrations of isosbestic solutions of **1–3** and of aqueous eosin (Aldrich) as reference ($\phi_{\text{ST}} = 0.76$), all exhibiting an optical density of 0.45 AU at $\lambda_{\text{ex}} = 532$ nm. The triplet molar concentrations were calculated from the bleaching of the ground states, whose extinction coefficients are known. For all transient-absorption measurements, a pulse Xe arc lamp (ORC, 250W) was used. All samples were deaerated prior to the measurements by bubbling Ar for 20 min.

Results and Discussion

We have examined the photoinduced electron transfer and subsequent charge separation in a series of supramolecular systems consisting of the Zn-porphyrins **1–3** and N,N' -dimethyl-4,4'-bipyridinium, MV^{2+} , **4**. The Zn(II)-porphyrins are capped with π -donor dialkoxyarene units. The ability of dialkoxybenzene units to form donor–acceptor complexes together with the association of bipyridinium salts to metal porphyrins, and specifically Zn(II)-porphyrins, suggests that **4** could form supramolecular complexes with the different photosensitizers **1–3**. It is expected, however, that the structural features of the capped Zn(II)-porphyrin controls the binding features of the resulting donor–acceptor complexes. For example, it is well established that the association of MV^{2+} to a bis[dialkoxybenzene]cyclophane is enhanced compared with the binding affinity of MV^{2+} to dialkoxybenzene. Accordingly, MV^{2+} is anticipated to associate effectively to **1** since the electron acceptor is bound between two donor units.

Complexation of the Zn-porphyrins **1–3** to MV^{2+} is expected to yield internal, static, electron-transfer quenching of the excited singlet states of the chromophores (eqs 1 and 2):



Provided that the fluorescence intensity of the systems is proportional to the concentration of the free porphyrins, then the association constants K_a of the resulting complexes represent essentially the Stern–Volmer constants obtained by steady-state fluorescence quenching of the chromophores (eqs 3 and 4),

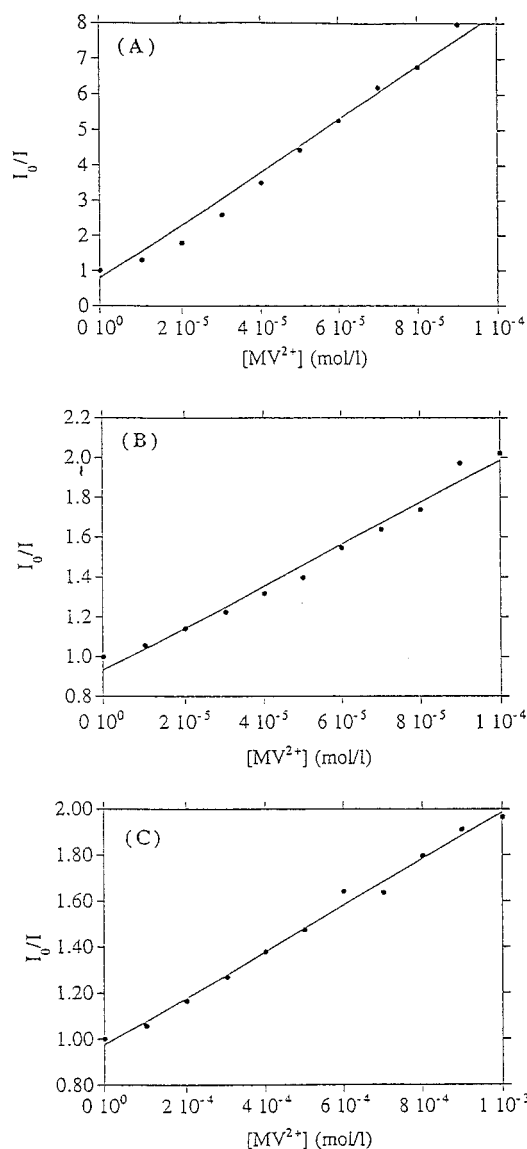


Figure 1. Stern–Volmer plots for (A) **1**, 3.6×10^{-5} M, (B) **2**, 3.6×10^{-5} M, (C) **3**, 3.6×10^{-5} M.

where I and I_0 represent the fluorescence intensities of the chromophore in the presence and absence of quencher (MV^{2+}), respectively.¹⁹

$$\frac{[ZnP-MV^{2+}]}{[ZnP]} = K_a[MV^{2+}] \quad (3)$$

$$\frac{I_0}{I} = 1 + K_a[MV^{2+}] \quad (4)$$

Figure 1 shows the steady-state Stern–Volmer plots for the quenching of the photosensitizers **1–3** by MV^{2+} . Table 1 summarizes the derived association constant for the respective supramolecular complexes. The association constant of the complex generated between **1** and MV^{2+} is substantially higher than the binding constants of the complexes formed with **2** and **3** ($K_a = 8 \times 10^4$ M⁻¹ compared with 1×10^4 and 1×10^3 M⁻¹, respectively).

Further insight into the features of the supramolecular assemblies formed between **1–3** and MV^{2+} is obtained by photophysical characterization of the systems using time-resolved laser experiments. Figure 2 shows the transient-absorption curves of the triplet states of the different Zn-

TABLE 1: Association Constants of the Supramolecular Assemblies Formed between Photosensitizers 1–3 and MV^{2+} and Kinetic Parameters Involved in the Photoinduced Electron Transfer in the Systems

photo-sensitizer	$10^6\tau_0$ (s ⁻¹)	$10^{-9}k_{dq}$ (M ⁻¹ s ⁻¹)	$10^{-9}k_{dr}$ (M ⁻¹ s ⁻¹)	K (M ⁻¹)
1	3.9	7.8 ^a (5.8) ^b	3.6	80000 ^c (87000) ^d
2	3.31	9.6 (9.7)	1.8	10000 (7000)
3	3.55	5.8 (7.2)	2.8	1000 (2000)

^a Determined from the shortening of the photosensitizer lifetime.

^b Determined by following the time-dependent evolution of $MV^{\bullet+}$ and using the equation

$$[MV^{\bullet+}](t) = \text{const} + [^3S^*](t=0) \frac{[S](t)}{[S](t=0)} \theta_{dq} \times (1 - e^{-k_{dq}[MV^{2+}]t})$$

^c Determined by steady-state fluorescence-quenching experiments.

^d Evaluated by determination of triplet concentration and using eq 17.

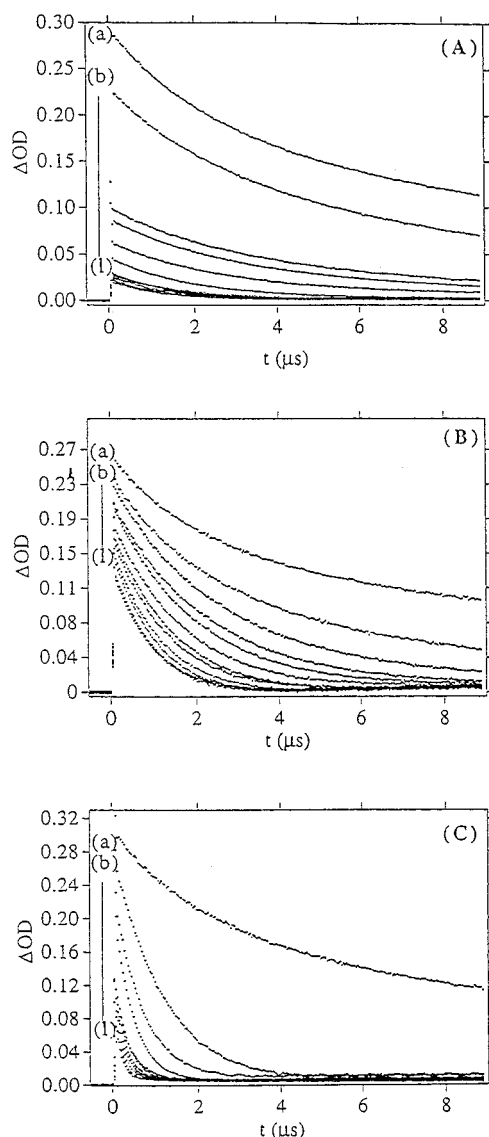
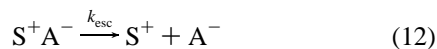


Figure 2. Time-dependent photosensitizers triplet decays in the absence (a) and presence (b) → (i) of different concentrations of MV^{2+} : (A) **1**, 3.6×10^{-5} M, (a) $[MV^{2+}] = 0$, (b) → (i) sequential additions of MV^{2+} , 1×10^{-5} M; (B) **2**, 3.6×10^{-5} M, (a) $[MV^{2+}] = 0$, (b) → (i) sequential additions of MV^{2+} , 1×10^{-5} M; (C) **3**, 3.6×10^{-5} M, (a) $[MV^{2+}] = 0$, (b) → (i) sequential additions of MV^{2+} , 1×10^{-4} M. In all experiments $\lambda_{ex} = 532$ nm and triplet absorbance is followed at $\lambda = 470$ nm.

porphyrins upon addition of variable concentrations of MV^{2+} . The initial intensity of the triplet states absorbance decreases,

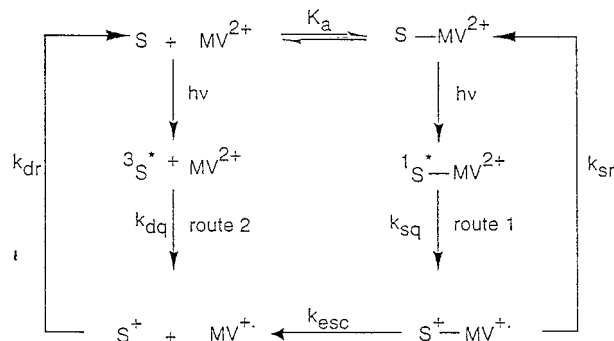
and the lifetimes of the triplet states are shortened as the concentration of MV^{2+} is increased. The initial absorbance of the triplet state is proportional to the triplet population in the systems. Hence, addition of MV^{2+} to the photosensitizers **1–3** reveals two general features. (i) Initial decay of the triplet intensity is decreased upon addition of MV^{2+} . This could imply the less efficient formation of the triplet states upon addition of MV^{2+} , i.e., due to rapid quenching of the singlet as a result of the formation of the complexes between the photosensitizer and MV^{2+} . (ii) Shortening of the triplet lifetime upon increasing the concentration of MV^{2+} . This is rationalized in terms of a diffusional electron-transfer quenching of the triplet states by the electron acceptor MV^{2+} . It should be noted that the most pronounced decrease in the triplet absorbance upon addition of MV^{2+} is observed for photosensitizer **1** (i.e., Figure 2A). This is consistent with the high affinity of **1** to form the noncovalent adduct with MV^{2+} as detected in the steady-state fluorescence experiments. The effective formation of the $[1-MV^{2+}]$ supramolecular assembly leads to internal quenching of the singlet chromophore and decrease in the triplet yield.

For quantitative analysis of the electron-transfer quenching and charge-separation processes in the resulting supramolecular complexes, we applied a kinetic model that assumes the processes summarized in eqs 5–13 and Scheme 1: (1) association and dissociation of the photosensitizer and electron-acceptor in the ground state (eq 5); (2) photoexcitation of the free photosensitizer (eq 6) and of the photosensitizer within supramolecular assembly (eq 7); (3) intersystem crossing (eq 8); (4) static-electron-transfer quenching within the supramolecular complex (eq 9); (5) diffusional electron-transfer quenching (eq 10); (6) static back-electron transfer of the redox products within the supramolecular assemblies (eq 11); (7) escape or dissociation of the redox products from the supramolecular assembly (eq 12); diffusional back-electron transfer of the photogenerated, separated, redox products (eq 13).



The main assumptions adopted in our analysis are the following: (a) The static quenching is much faster than intersystem crossing. That is, $k_{sq} \gg k_{isc}$; (b) The concentration of the electron acceptor is substantially higher compared with the concentration of the excited photosensitizer; (c) Diffusional quenching is faster than association; (d) Static quenching is faster than dissociation of the supramolecular adduct; (e) The triplet state of free photosensitizer that is formed undergoes only

SCHEME 1



natural and diffusional decay via quenching by MV^{2+} . Assumption a is supported by the fact that at high acceptor concentrations, where the photosensitizer is fully complexed, the triplet is essentially zero. Assumption b implies that the concentration of the electron acceptor is not significantly changed in the presence of the photosensitizer and can be regarded as constant. Assumptions c and d imply that electron transfer is faster than the dynamics of the formation or dissociation of the supramolecular complexes.

According to these assumptions, the time-dependent concentration decay of the triplet state of Zn(II)-porphyrin, ${}^3S^*$, is given by eqs 14 and 15,

$$\frac{d[{}^3S^*]}{dt} = k_D[{}^3S^*] + k_{dq}[{}^3S^*][A] \quad (14)$$

$$[{}^3S^*](t) = [{}^3S^*](0) e^{-kt} \quad (\text{where } k = k_D + k_{dq}[A]) \quad (15)$$

where k is the observed rate constant at each added concentration of MV^{2+} and k_D and k_{dq} are the radiative decay constant of ${}^3S^*$ and the diffusional rate constant of ${}^3S^*$ by the electron acceptor (MV^{2+}), respectively. Thus, by plotting the inverse triplet lifetimes ($1/\tau$) of the different photosensitizers at the variable concentrations of MV^{2+} , eq 16, the diffusional quenching rate constants, k_{dq} , could be elucidated. Figure 3 shows the analysis of the diffusional quenching rate constants, k_{dq} , of the photosensitizers **1–3** by MV^{2+} . The values of diffusional quenching rates are summarized in Table 1. The diffusional rate constants of all of the photosensitizers are close in their values.

The initial triplet absorbance in the decay curves shown in Figure 2 relates to the triplet concentration of the different photosensitizers at the respective MV^{2+} concentrations. The decrease in the triplet concentration at any MV^{2+} concentration compared with the triplet concentration in the absence of MV^{2+} relates directly to the fraction of photosensitizer that is associated with MV^{2+} and statically quenched within the complex. The initial triplet absorbance relates, however, to the concentration of the free photosensitizer. Accordingly, one can relate the initial absorbance values of the triplet photosensitizer and the association constants in terms of eq 16:

$$\frac{[{}^3S^*](t=0, [A]=0) - [{}^3S^*](t=0, [A]_i)}{[{}^3S^*](t=0, [A]_i)} = K_a[A] \quad (16)$$

$$\frac{[{}^3S^*](t=0, [A]=0)}{[{}^3S^*](t=0, [A]_i)} = 1 + K_a[A]_i \quad (17)$$

where $[{}^3S^*](t=0, [A]=0)$ and $[{}^3S^*](t=0, [A]_i)$ represent the triplet concentrations or initial triplet intensity in the absence of MV^{2+} and at any MV^{2+} concentration $[A]_i$, respectively.

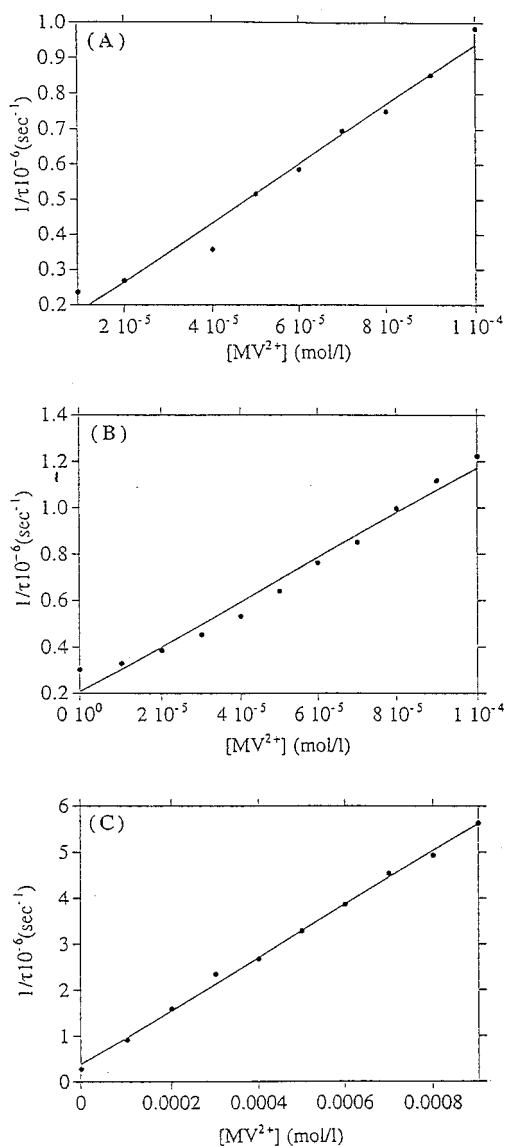


Figure 3. Triplet lifetime of different photosensitizers, 3.6×10^{-5} M, at different quencher (MV^{2+}) concentrations: (A) 1; (B) 2; (C) 3.

Figure 4 shows the analysis of the transients shown in Figure 2 according to eq 17, where the slopes of the different lines represent the association constants of MV^{2+} to the various photosensitizers. The derived values of K_a are also given in Table 1. We find excellent agreement between the association constant values extracted from the steady-state fluorescence-quenching experiments and the values obtained by analysis of the time-resolved triplet-decay curves. It should be noted that our results complement nicely the association-constant values determined for the complexes formed between 1–3 and MV^{2+} by $^1\text{H-NMR}$.^{15,16} In these experiments, titration of the respective Zn(II)-porphyrins with MV^{2+} was carried out and the chemical-shift changes of the Zn(II)-porphyrin or MV^{2+} , compared with those of the pure components, $\Delta\delta_{\text{obs}}$, were used to elucidate the respective association constants.^{16a,b} For example, for 1, $K_a > 2 \times 10^5 \text{ M}^{-1}$, for 2, $K_a = 2 \times 10^4 \text{ M}^{-1}$, and for 3, $K_a = 1.6 \times 10^3 \text{ M}^{-1}$. We have previously shown that the association constants are particularly solvent-dependent. The values quoted for 2 and 3 were determined by $^1\text{H-NMR}$ methods in dimethylformamide- d_7 , while that for 1 was in $\text{CDCl}_3/\text{CD}_3\text{COCD}_3$. The values obtained in this work were measured in acetonitrile.

The association constant values of MV^{2+} to the dialkoxybenzene-capped Zn-porphyrins 1–3 are exceptionally high

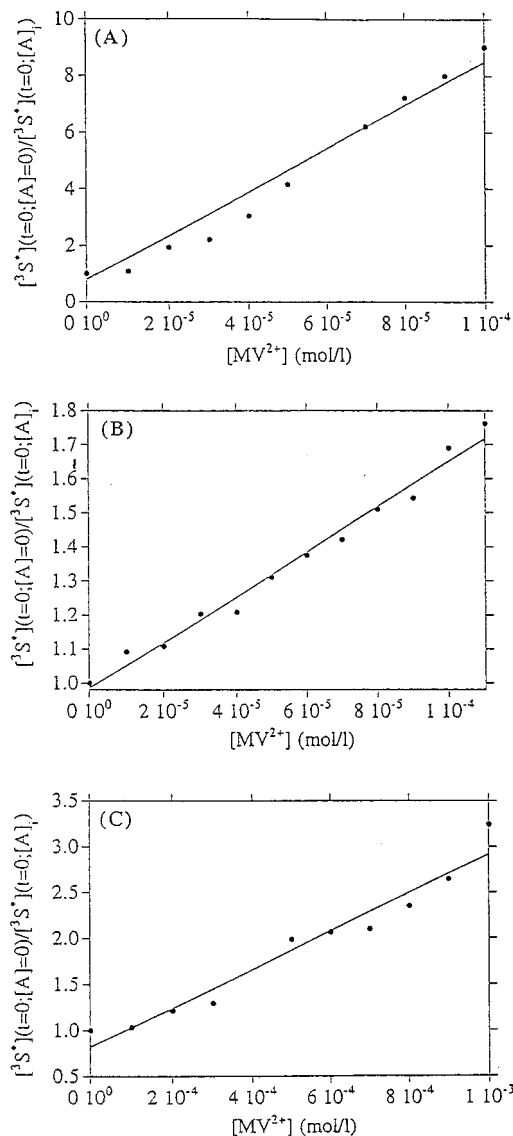


Figure 4. Plot of the ratio of photosensitizer triplet concentrations in the absence and presence of quencher at variable concentrations of MV^{2+} : (A) 1, 3.6×10^{-5} M; (B) 2, 3.6×10^{-5} M, (C) 3, 3.6×10^{-5} M.

compared with the association constants of the π -donor–acceptor complexation between MV^{2+} and a dialkoxybenzene unit. For example, in a previous study we reported²⁰ that the association constant of MV^{2+} to a dialkoxybenzene unit tethered to a Ru(II)-tris[bipyridine] complex in water is $K_a = 28 \text{ M}^{-1}$. In the present systems, we find that the association constants of the resulting supramolecular complexes are 10^2 – 10^3 -fold higher. It is also interesting to note the pronounced difference in the association constant values within the series of three photosensitizers. For example, the association constant of MV^{2+} to 1 is ca. 10-fold higher than that of 3. The capped dialkoxyarene-Zn(II)-porphyrins 1–3 include several modes to associate MV^{2+} . The dialkoxyarene sites provide π -donor units for the formation of π -donor–acceptor complexes with MV^{2+} . The well-established affinity of MV^{2+} with dibenzo crown ethers suggests that the polyoxyethylene bridges provide an additional stabilization of the pyridinium cation of the electron acceptor.²¹ In photosensitizer 1, two crown ether chains and an additional benzo group, when compared to 2 and 3, are available for binding of MV^{2+} .

The Zn(II)-porphyrin seems to provide an additional site for the stabilization of the bipyridinium complex via π -donor–

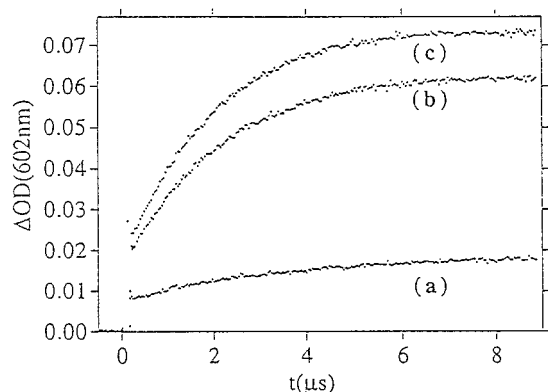


Figure 5. Absorbance evolution at $\lambda = 602$ nm upon photoexcitation of the different photosensitizers in the presence of $[MV^{2+}] = 5 \times 10^{-5}$ M: (a) **1**, 3.6×10^{-5} M; (b) **2**, 3.6×10^{-5} M; (c) **3**, 3.6×10^{-5} M.

acceptor interactions.²² Presumably, all of these interactions operate synergetically leading to the high association constants between MV^{2+} and the photosensitizers **1–3**. Realizing the different interactions that stabilize the supramolecular complexes between **1–3** and MV^{2+} , one can discuss the different association constants of the complexes in the series of photosensitizers. Photosensitizer **1** exhibits two dialkoxybenzene π -donor sites for the complexation of MV^{2+} . The complex in which MV^{2+} is sandwiched between two π -donor units is known to reveal a substantially higher association constant than the unimolecular MV^{2+} - π -donor complex. In the other photosensitizers, i.e., **2** and **3**, a single π -donor unit is present. Thus, we suggest that the complexation of MV^{2+} between two π -donor sites and the cooperative stabilization of the complex by the crown ether site leads to the high binding affinity of MV^{2+} to **1**. Preliminary X-ray studies support the suggested donor-acceptor interactions between MV^{2+} and the different Zn(II)-porphyrins.²³ For the complex formed between **1** and MV^{2+} , we find that the electron acceptor (MV^{2+}) is positioned between the two dialkoxybenzene units at an equidistance of ca. 3.5 Å. For the complex between **2** and MV^{2+} , we find that the electron acceptor MV^{2+} is positioned between the planes generated by the dialkoxynaphthalene and Zn(II)-porphyrin units. The distance separating MV^{2+} and the dialkoxynaphthalene is ca. 3.5 Å.

A further aspect that can be addressed relates to the formation of electron-transfer products as a result of the diffusional and static quenching of the excited photosensitizer by MV^{2+} and the recombination of the photogenerated redox. Figure 5 shows the transient absorbance changes at $\lambda = 602$ nm, characteristic of the N,N' -dimethyl-4,4'-bipyridinium radical cation, $MV^{\bullet+}$, upon excitation of the photosensitizers **1–3**. Note that the absorbance changes are followed within a short time scale. We see that the absorbance of $MV^{\bullet+}$ increases instantaneously upon excitation of the photosensitizers and then the $MV^{\bullet+}$ absorbance gradually increases with time and after ca. 6 μ s it levels off to a constant value. The yield of charge-separated $MV^{\bullet+}$ in the presence of **2** or **3** is ca. 5-fold higher than that formed in the presence of **1**. The time-dependent increase in the absorbance of $MV^{\bullet+}$ followed upon excitation of the different systems follows pseudo-first-order kinetics, since the concentration of MV^{2+} is much higher than the concentration of the excited state of photosensitizers. The derived observed rate constants for photosensitizers **1–3** are 5.8×10^9 , 9.7×10^9 , and 7.2×10^9 $M^{-1} s^{-1}$, respectively. These values coincide with the bimolecular diffusional rate constants of the triplet states of **1–3** by $MV^{\bullet+}$ (eq 10). Thus, the time-dependent increase in the $MV^{\bullet+}$ absorbance, curves a–c, Figure 5, originates from the triplet-

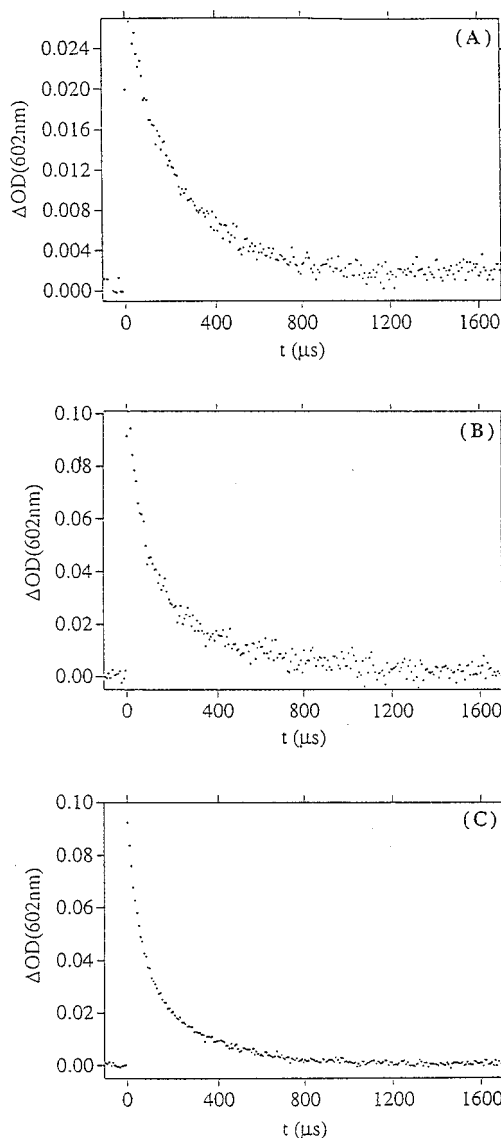


Figure 6. Time-dependent decay of $MV^{\bullet+}$ (followed at $\lambda = 602$ nm) photogenerated by the excitation of the different photosensitizers: (A) **1**, 3.6×10^{-5} M. (B) **2**, 3.6×10^{-5} M. (C) **3**, 3.6×10^{-5} M.

state electron-transfer quenching of the photosensitizers by MV^{2+} . The immediate increase in the $MV^{\bullet+}$ absorbance may be attributed to the static electron-transfer quenching of the singlet excited states of the photosensitizers **1–3** within the photosensitizer- MV^{2+} supramolecular assemblies followed by the escape of the reduced photoproduct $MV^{\bullet+}$ from the complex structure (eqs 9 and 12). Note, however, that not all of the reduced photoproduct escapes the supramolecular structures and part of it recombines within these assemblies (eq 11). It should also be noted that the instantaneous absorbance change at $\lambda = 602$ nm does not reflect the net absorbance of escaped $MV^{\bullet+}$. At this wavelength, the triplet states of **1–3** exhibit a residual absorbance, and thus, the net absorbance of $MV^{\bullet+}$ is lower than the observed values. Thus, the photogenerated free $MV^{\bullet+}$ is mainly formed by electron-transfer quenching of the triplet Zn-porphyrins by MV^{2+} and, to some extent, from the escape of $MV^{\bullet+}$ from the supramolecular systems where the singlets of Zn-porphyrins are quenched.

The $MV^{\bullet+}$ generated by the two routes undergoes back-electron transfer with the oxidized Zn-porphyrin photosensitizers (eq 13). Figure 6 shows the transient decay curves of $MV^{\bullet+}$ as a result of the recombination (followed at $\lambda = 602$ nm). Note

that in these curves the time scale of the recorded transients is substantially longer than the time scale shown in Figure 1. Thus, in the latter traces, the initial absorbance at $\lambda = 602$ nm essentially describes the rapid formation of MV^{2+} by the static and diffusional routes as described earlier. The decaying transients of MV^{2+} (Figure 6) follow second-order kinetics. The back-electron-transfer rate constants were calculated to be $k_{dr} = 3.6 \times 10^9$, 1.8×10^9 , and $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the systems that include the photosensitizers **1–3**, respectively.

Conclusions

The present study addressed the formation of supramolecular complexes between a series of dialkoxybenzene- and dialkoxyarene-capped Zn(II)-porphyrins and *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+} . We find that these complexes exhibit remarkably high association constants (1×10^3 to $8 \times 10^4 \text{ M}^{-1}$). The high affinity of the MV^{2+} to the Zn(II)-capped porphyrins can be attributed to π -donor-acceptor interactions with the dialkoxyarene units, π - π interactions with the Zn-porphyrin units, and electrostatic interactions with the polyoxyethylene bridges. Formation of the high-affinity complexes between MV^{2+} and the Zn-porphyrins results in effective static quenching of the excited chromophores at very low quencher concentration.

Acknowledgment. The research at The Hebrew University of Jerusalem was supported by the James Frank Minerva Foundation.

References and Notes

- (1) (a) Willner, I.; Willner, B. *Top. Cur. Chem.* **1991**, 159, 157. (b) Gust, D.; Moore, T. A. *Top. Curr. Chem.* **1991**, 159, 103.
- (2) (a) Bard, A. J. *Science* **1980**, 207, 139. (b) Meyer, T. J. *Acc. Chem. Res.* **1989**, 22, 163.
- (3) (a) Grätzel, M., Ed. *Energy Resources Through Photochemistry and Catalysis*; Academic Press: New York, 1983. (b) Gust, D.; Moore, T. A.; Moore, A. L.; Seely, G.; Liddell, P.; Barrett, D.; Harding, L. O.; Ma, X. C.; Lee, S. J.; Gao, F. *Tetrahedron* **1989**, 45, 4867. (c) Willner, I.; Willner, B. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., von Bülow, G., Eds.; Wiley: New York, 1995; Vol. 20, p 217.
- (4) (a) Connolly, J. S.; Bolton, J. R. In *Photoinduced Electron Transfer*, Part D; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Section 6.2. (b) Cooley, L. F.; Headford, C. E. L.; Elliott, E. M.; Kelley, D. F. *J. Am. Chem. Soc.* **1988**, 110, 6673.
- (5) (a) Gust, D.; Moore, T. A. *Science* **1989**, 244, 35. (b) Moore, T. A.; Gust, D.; Moore, A. L.; Bensasson, R. V.; Seta, P.; Bienvenue, E. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Boston, 1987; p 283. (c) Gust, D.; Moore, T. A. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Boston, 1987; p 267. (d) Wasielewski, M. R.; Gains, G. L., III; Wiederrecht, G. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1993**, 115, 10442.
- (6) (a) Sanders, G. M.; van Dijk, M.; van Veldhuizen, A.; van der Plas, M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1131. (b) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, 107, 5562. (c) Mecklenburg, S. L.; Peek, B. M.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, 109, 3297. (d) Danielson, E.; Elliott, C. M.; Mesket, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, 109, 2519. (e) Johnson, D. G.; Niemczyk, M. P.; Minsek, D. W.; Wiederrecht, G. P.; Svec, W. A.; Gains, G. L., III; Wasielewski, M. R. *J. Am. Chem. Soc.* **1993**, 115, 5692.
- (7) (a) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 849. (b) Gust, D.; Moore, T. A.; Moore, A. L.; Lee, S.-J.; Bittersmann, E.; Luttrull, D. K.; Rehms, A. A.; DeGraziano, J. M.; Ma, X. C.; Gao, F.; Belford, R. E.; Trier, T. T. *Science* **1990**, 248, 199.
- (8) Yonemoto, E. H.; Kim, Y. I.; Schmehl, R. H.; Wallis, J. O.; Shoulders, B. A.; Richardson, B. R.; Haw, J. F.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, 116, 10557.
- (9) (a) Vermuelen, L. A.; Thompson, M. E. *Nature* **1992**, 358, 656. (b) Ungashe, S. B.; Wilson, W. L.; Katz, H. E.; Scheller, G. R.; Putrinski, T. M. *J. Am. Chem. Soc.* **1992**, 114, 8717.
- (10) Zahavy, E.; Seiler, M.; Marx-Tibbon, S.; Joselevich, E.; Willner, I.; Dürr, H.; O'Connor, D.; Harriman, A. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1005.
- (11) (a) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, 115, 10418. (b) Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, 114, 388. (c) Turró, C.; Chang, C. K.; Leroy, G. E.; Cukier, R. I.; Nocera, D. G. *J. Am. Chem. Soc.* **1992**, 114, 4013. (d) Sun, L.; von Gersdorff, J.; Niethammer, D.; Tian, P.; Kurreck, H. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 2318.
- (12) Yonemura, H.; Nakamura, M.; Matsuo, T. *Chem. Phys. Lett.* **1989**, 155, 157.
- (13) (a) Kropf, M.; Joselevich, E.; Dürr, H.; Willner, I. *J. Am. Chem. Soc.* **1996**, 118, 655. (b) David, E.; Kaganer, E.; Joselevich, E.; Dürr, H.; Willner, I. *J. Am. Chem. Soc.* **1997**, 119, 7778.
- (14) (a) Gunter, M. J.; Johnston, M. R. *Tetrahedron Lett.* **1990**, 31, 4801. (b) Gunter, M. J.; Johnston, M. R. *Tetrahedron Lett.* **1992**, 33, 1771.
- (15) (a) Gunter, M. J.; Johnston, M. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1163. (b) Gunter, M. J.; Hockless, D. C. R.; Johnston, M. R.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1994**, 116, 4810.
- (16) (a) Gunter, M. J.; Johnston, M. R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1009. (b) Gunter, M. J.; Johnston, M. R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 995. (c) Gunter, M. J.; Chen, Z.; Jeaynes, T. P.; Turner, P. To be published.
- (17) Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982**, 44, 83.
- (18) (a) Harriman, A. *J. Photochem.* **1985**, 29, 139. (b) Parmon, V. N.; Lymar, S. V.; Tevetkov, L. M.; Zamaraev, K. I. *J. Mol. Catal.* **1983**, 21, 353.
- (19) The relation expressed in eq 4 is valid only if the supramolecular complex $ZnP-MV^{2+}$ has no singlet emission or its excited lifetime is very short. This is supported by the fact that the singlet excited state of $ZnP-MV^{2+}$ is quenched within the laser pulse width, <5 ns (cf. Figure 2).
- (20) Seiler, M.; Dürr, H.; Willner, I.; Joselevich, E.; Doron, A.; Stoddaart, J. F. *J. Am. Chem. Soc.* **1994**, 116, 3399.
- (21) (a) Philp, D.; Stoddaart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1154. (b) Amabilino, D. B.; Stoddaart, J. F. *Chem. Rev.* **1995**, 95, 2725.
- (22) (a) Shelnutt, J. A. *J. Am. Chem. Soc.* **1981**, 103, 4275. (b) Okura, I.; Aono, S.; Takeuchi, M.; Kusunoki, S. *Bull. Chem. Soc. Jpn.* **1982**, 55, 3637. (c) Okura, I.; Kusunoki, S.; Aono, S. *Inorg. Chim. Acta* **1983**, 77, 99. (d) Leighton, P.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2385. (e) Leighton, P.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1984**, 856.
- (23) Gunter, M. J. Unpublished results.