

torsion angles, were not investigated.

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Supplementary Material Available: Tables of total scattered intensities, calculated backgrounds for each plate, and averaged molecular intensities (11 pages). Ordering information is given on any current masthead page.

Photochemical Hydrogen Evolution via Singlet-State Electron-Transfer Quenching of Zinc Tetra(*N*-methyl-4-pyridyl)porphyrin Cations in a Zeolite L Based System

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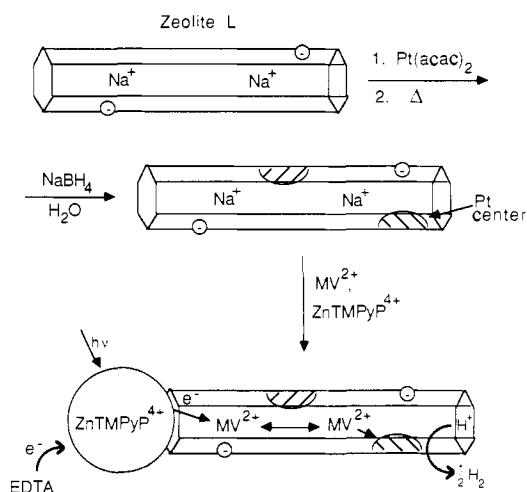
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Abstract: Molecular electron transport chains composed of EDTA, zinc tetra(*N*-methyl-4-pyridyl)porphyrin (ZnTMPyP⁴⁺), and methylviologen (MV²⁺), spatially organized by 1 μm diameter zeolite L particles, were studied. MV²⁺ ion exchanges into zeolite L to a maximum loading of 2.5–3.0 × 10⁻⁴ mol/g of zeolite, while the bulkier ZnTMPyP⁴⁺ adsorbs only onto the outer surface in approximately monolayer (8 × 10⁻⁶ mol/g) quantities. At pH 4.0, EDTA²⁻ is strongly adsorbed onto the ZnTMPyP⁴⁺-coated surface. When the composite is prepared from internally platinized zeolite L particles, hydrogen is evolved photochemically from water in pH 4.0, 2 × 10⁻³ M EDTA solution. The rate of hydrogen evolution depends on the MV²⁺ loading, no H₂ being evolved below 1.5 × 10⁻⁴ mol MV²⁺/g (ca. 0.4 MV²⁺ ion per large cavity). ZnTMPyP⁴⁺ shows a biphasic fluorescence decay when adsorbed on the zeolite L surface. The rapidly decaying component has a lifetime varying from <20 ps to 150 ps; the inverse lifetime (fluorescence decay rate) shows the same dependence on MV²⁺ loading as the hydrogen evolution rate. The slowly decaying fluorescence component and the time-resolved triplet-triplet absorbance are invariant with MV²⁺ loading. These observations are explained in terms of singlet-state electron-transfer quenching of ZnTMPyP⁴⁺ by MV²⁺. The triplet excited state reactivity of ZnTMPyP⁴⁺ is suppressed by a 200-mV positive shift of its redox potentials caused by adsorption onto the zeolite surface.

The study and development of molecular systems for light-to-chemical energy conversion are of both fundamental and practical importance. Among the best-studied artificial photosynthetic systems are homogeneous and heterogeneous (micelles, vesicles, etc.) fluids which employ a sensitizer, such as a polypyridyl-ruthenium complex or porphyrin, in conjunction with an electron relay (quencher) and a sacrificial electron donor or acceptor.¹ The excited state of the sensitizer must be sufficiently long-lived so that electron transfer to or from the quencher may occur on a diffusional time scale, i.e., in several nanoseconds or more. Thus, while metalloporphyrins have photophysical properties which make them desirable as sensitizers, in homogeneous solution their excited singlet states are not sufficiently long-lived for electron-transfer quenching.² In microstructurally organized media, singlet-state quenching of porphyrins and similar molecules may occur; for example, in the reaction center of *rhodospseudomonas viridis*,³ close juxtaposition of macrocyclic light absorbers and quenchers allows efficient electron-transfer quenching on a time scale of a few picoseconds.⁴ In special situations, man-made systems, in which the porphyrin is tethered covalently to an electron acceptor, show rapid singlet-state electron-transfer quenching.⁵ The synthesis of these molecules is generally quite challenging, however, and the formation of chemical products from the singlet-state reaction has been demonstrated only once.⁶

In this paper we describe a metalloporphyrin-based electron-transport chain which self-assembles by virtue of ion exchange and steric interactions with a zeolite L particle. The microstructure imposed by the zeolite permits zinc tetra(*N*-methyl-4-pyridyl)porphyrin, ZnTMPyP⁴⁺, to be held in sufficient proximity to a

Scheme I



methylviologen (MV²⁺) cation so that singlet-state electron-transfer quenching occurs on a subnanosecond time scale. With

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Table I. Loading of Zeolite L Powder^a with MV²⁺ and ZnTMPyP⁴⁺

no.	mol of MV ²⁺ used	mol of MV ²⁺ adsorbed	mol of ZnTMPyP ⁴⁺ adsorbed
1	1.36×10^{-4}	1.34×10^{-4}	8.4×10^{-6}
2	1.91×10^{-4}	1.84×10^{-4}	8.3×10^{-6}
3	2.69×10^{-4}	2.24×10^{-4}	8.1×10^{-6}
4	3.69×10^{-4}	2.99×10^{-4}	8.3×10^{-6}
5	0		8.3×10^{-6}

^a Amounts listed are per gram of zeolite L powder; solution volume was 60 mL/g; ZnTMPyP⁴⁺ adsorbed from a 15 mL solution containing 1.13×10^{-5} mol.

EDTA added as an electron donor, hydrogen is evolved photochemically from internal platinumized zeolite L containing ZnTMPyP⁴⁺ and MV²⁺. The preparation and operation of this compartmentalized photochemical system are shown in Scheme I. Here the hexagonal prisms are an idealization of the linear channels which run through zeolite L and bind MV²⁺. ZnTMPyP⁴⁺ is bound strongly to the zeolite outer surface but is size-excluded from the bulk. Substituting a more sterically hindered porphyrin, zinc tetra(trimethylamino)-4-phenylporphyrin (ZnTAPP⁴⁺), for ZnTMPyP⁴⁺ results in a system in which neither hydrogen evolution nor singlet-state quenching by MV²⁺ occurs. These observations may be explained in terms of a closely spaced and organized triad of molecules (EDTA²⁻, ZnTMPyP⁴⁺, MV²⁺) existing at the zeolite/solution interface.

Experimental Section

Materials. Zeolite L (ideal formula $K_6Na_3Al_9Si_{27}O_{72} \cdot 21H_2O$) was purchased as a powder from Union Carbide, Linde Molecular Sieves Division. The average particle diameter as determined by SEM was 1 μ m. ZnTMPyP⁴⁺, PdTMPyP⁴⁺, and ZnTAPP⁴⁺ were obtained as the chloride salts from Midcentury Chemicals (Posen, IL) and used as received. EDTA, methylviologen dichloride hydrate (Aldrich Chemical Co.), and platinum(II) acetylacetonate, Pt(acac)₂ (Sterm Chemical Co.) were also used as received. Spectrograde dichloromethane was obtained from Fisher Chemicals. All other materials and solvents were reagent grade and were obtained from commercial sources. Deionized water obtained from a Barnstead Nanopure system, resistivity 18.3 M Ω -cm, was used in all experiments.

Platinization of Zeolite L and Ion Exchange. Zeolite L was loaded with elemental Pt as described elsewhere.⁷ Briefly, the zeolite powder was equilibrated with Pt(acac)₂ dissolved in CH₂Cl₂ and rinsed with CH₂Cl₂ until none of the complex was detectable in the washings by UV-visible spectroscopy. The powder was heated at 250 °C to decompose the entrained complex, reduced with aqueous NaBH₄, and then washed with water. Elemental analysis showed that the platinum content of these samples was 0.001–0.004% by weight. Chemical tests⁷ established that Pt⁰ was deposited exclusively in the inner surface of the zeolite L particles.

MV²⁺ was ion exchanged into the zeolite as follows: 5 g of zeolite L was suspended in 200 mL water, and a weighed quantity of methylviologen dichloride hydrate dissolved in 50 mL of water was added dropwise with stirring. After 24 h of equilibration, the zeolite was filtered and washed copiously with water until the washings were free of viologen, or in the case of the most heavily loaded samples, the absorbance at 259 nm in the washings due to MV²⁺ was reduced to a value less than 0.05. The MV²⁺-exchanged platinumized zeolite was dried at 40 °C under flowing

nitrogen. Table I summarizes the quantities of MV²⁺ used in the equilibration step and the amount remaining in the zeolite.

The porphyrin sensitizers ZnTMPyP⁴⁺ and ZnTAPP⁴⁺ were adsorbed onto zeolite L by suspending 1 g of the latter in 15 mL of water containing 1.13×10^{-5} mol of porphyrin (chloride salt). The suspension was stirred for 12 h and then filtered and washed with water until the washings were colorless. The total washings were combined and analyzed spectrophotometrically to determine the porphyrin loading on the zeolite. Extinction coefficients for MV²⁺ and the porphyrins were obtained from the literature.^{8,9} Table I summarizes the porphyrin loading for various samples.

Instrumentation. UV-visible spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer. Fluorescence measurements were done on a Varian SF-30 spectrofluorimeter and/or SPEX Fluorolog. Laser flash photolysis and photon counting fluorescence experiments were done at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin. A Quantel YG481 Nd:YAG Q-switched laser which generates pulses of 10 ns duration at 532 nm and 0.2 at 355 nm was used for the flash photolysis experiments. The excitation beam was focused through a 1-cm solution and/or suspension and the analyzing light focused through a 1-mm pinhole at right angles. Path lengths of the analyzing beam were 0.5 or 1 cm. Samples were deaerated with nitrogen prior to the experiments. All spectra and kinetics were analyzed from at least five individual shots by procedures described elsewhere.¹⁰ Triplet quantum yields were determined by comparison with aqueous solutions, in which the ZnTMPyP⁴⁺ triplet yield was taken to be 0.9.⁹

Time-correlated photon-counting measurements were employed to determine fluorescence lifetimes. The excitation source consisted of a rhodamine-6G dye laser (Spectra Physics 574B) pumped by the second harmonic of a continuous wave Spectra Physics 3000 Nd:YAG oscillator. The latter was actively mode-locked at 81.66 MHz to yield 60-ps pulses at 12.5-ns intervals. The apparatus and technique have been described in detail by Rodgers.^{11,12} Fluorescence profiles were obtained for 100 s at a count rate between 17 000 and 18 000 counts per second. A Balzers K65 interference filter and 630-nm cutoff filter were positioned between the sample and the photomultiplier to minimize the collection of scattered light in single photon counting measurements. Control experiments carried out in the absence of adsorbed porphyrins showed that the scattered light was effectively eliminated. The fluorescence decay curves were deconvoluted by computer analysis¹⁰ against the instrument response function which represented the excitation profile. The excitation wavelength was in all cases at or near the maximum of the Q(1,0) band of the porphyrins. Appropriate neutral density filters were used in the excitation path to attenuate the incident beam to a desired level. Optical measurements were taken in 90% glycerol (10% water) or saturated sucrose solutions. The refractive indices of these solutions were well matched to the zeolite and minimized scattering. The samples were dispersed by sonication in the desired medium. In the steady-state and time-correlated fluorescence measurements a known amount of each zeolite sample was dispersed in 12 mL of the glycerol solution and measurements taken at right angles in a 1-cm cuvette.

Continuous irradiation and H₂ generation were carried out with a 1000 or 450 W high-pressure Xe arc lamp equipped with water jacket, focusing lenses, and appropriate UV cutoff filters. Light intensity was measured with a Scientech Disc Calorimeter power meter 36-0001. Radiation intensity was controlled when necessary by interposing a grid of appropriate transmittance between the lamp and the reaction cell. In all experiments the light intensity incident on the reaction vessel was 190 ± 5 mW. The irradiated area was kept close to 1 cm². Samples for photochemical hydrogen generation were prepared as follows: 100 mg of the zeolite composite (zeolite L powder with Pt⁰ and MV²⁺ in the cavities and metalloporphyrin adsorbed on the surface) was placed in a 8.5-mL Pyrex reaction vial and 5 mL of EDTA solution was added as the sacrificial donor. EDTA solutions of 2.0×10^{-3} , 1.5×10^{-3} , and 1.0×10^{-3} M were used. The pH was adjusted to 4.0 ± 0.1 with NaOH. In all cases a head space of 3.5 mL was maintained in the vial. A 7-mm Teflon-coated magnetic bar was also included for the purpose of agitating the suspension during irradiation. The vial was stoppered with a rubber septum. Samples were dispersed by sonication for 2–3 min and deoxygenated with an argon purge. The gas in the head space was analyzed by gas chromatography using a 13 \times 60/80 mesh molecular sieve column with argon as the carrier gas and a thermal conductivity detector.

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Table II. Photophysical Properties of ZnTMPyP⁴⁺ in Water, Saturated Sucrose Solution, and 90% Glycerol and on the Zeolite L Surface

property	H ₂ O	glycerol	on zeolite L	
electronic absorption	436 (11.25)	440 (16.1)	442 (5.7) ^b	
wavelength max, nm	562 (1.0)	564 (1.0)	568 (4.0)	
and (rel intensity)	602	604 (0.1)	608	
fluorescence emission	626 (1.6)	622 (1.93)	632 (1.1) ^b	
wavelength max, nm	666 (1)	658 (1.0)	672 (1)	
and (rel intensity)				
τ_F /ns, fluorescence lifetime	1.3 ^a	1.55	A_1 4.48 (τ_1) 0.15;	A_2 1.89 ^c (τ_2) 0.69 ^c
			A_1 2.71 (τ_1) 0.43;	A_2 1.61 ^d (τ_2) 1.55 ^d
			A_1 2.58 (τ_1) 0.24;	A_2 1.55 ^e (τ_2) 0.72 ^e
triplet state				
T-T absorption max (nm)	470	480	490	
τ_T , triplet lifetime	0.9 ms	0.59 ms	(τ_1) 0.10 ms ^f (τ_2) 1.5 ms ^e	
triplet yield	0.90 ^a	0.86	0.42 ^f	

^aReference 9. ^bThe relative intensities are dependent on loading. In these experiments the porphyrin loading was 8.3×10^{-6} mol/g of zeolite. ^cIn aqueous suspension; biphasic decay; τ_1 fast component, τ_2 slow component, $A_{1,2}$ preexponential factor. ^dSaturated sucrose. ^eIn 90% glycerol, biphasic decay. ^fThis value varies $\pm 5\%$ with ZnTMPyP⁴⁺ loading. Estimated error limits are as follows $Q_T \pm 0.05\%$, $E_{T-T} \pm 10\%$, $\tau_F \pm 10\%$, $\tau_T \pm 5\%$.

Analyses were done prior to illumination and at 3-h intervals during the period of illumination. The zeolite was recovered by centrifugation after irradiation and the contents of the supernatant solution were examined spectrophotometrically.

Results and Discussion

Ion Exchange in Zeolite L. A line drawing of the zeolite L pore structure is compared with those of the MV²⁺ and ZnTMPyP⁴⁺ cations in Figure 1. The structure of zeolite L^{13,14} contains Si, Al 12-rings which form one-dimensional channels running parallel to the crystallographic *c* axis; the window free diameter (in the plane of the 12-rings) is 7.1–7.8 Å, while the maximum free diameter (midway between the 12-rings) is about 13 Å. These channels are arranged in a hexagonal array with a center-to-center distance of 18.4 Å. The large cages are connected to their nearest neighbors in the *ab* plane via much smaller cages which are bounded by 8-rings and contain non-exchangeable cations.

Methylviologen has van der Waals dimensions¹⁵ of $6.3 \times 6.3 \times 13.4$ Å. Since MV²⁺ is longer than the cavity free diameter, it is unlikely that it tumbles freely in zeolite L. Electrochemical^{16,17} and NMR¹⁸ experiments show that MV²⁺ diffuses and reorients rapidly in hydrated zeolite Y but not in L, suggesting that the motion in L is restricted to rotations about the long molecular axis and longitudinal migration along the channels. Ion exchange of MV²⁺ for alkali cations in zeolite L takes place slowly, equilibrium being attained after 30 min or more with these ca. 1 μm diameter particles. It can be seen from Table I that the maximum loading of MV²⁺ is about $2.5\text{--}3.0 \times 10^{-4}$ mol/g, or 0.7–0.8 MV²⁺ ions per large cavity. The length of the cavity along the channel axis is 7.5 Å, so a certain degree of overcrowding or overlapping of the viologen aromatic rings in the cages is required at the highest loading level. At this loading level, motion of MV²⁺ is likely to be severely restricted.

The porphyrin molecules ZnTMPyP⁴⁺ and ZnTAPP⁴⁺ are far too large to enter the zeolite L channels but adsorb strongly by ion exchange onto the outer surface. Desorption of the porphyrin cations can be accomplished only by repeated back-exchange with saturated KCl or NaCl solutions. Observed porphyrin loadings (Table I) are consistent with approximately 2–3 monolayer coverage (1 monolayer = ca. 10^{-10} mol/cm²) of the zeolite outer surface, as calculated from the apparent (by SEM) surface area of the latter, 3×10^4 cm²/g. The outer surface area estimate is

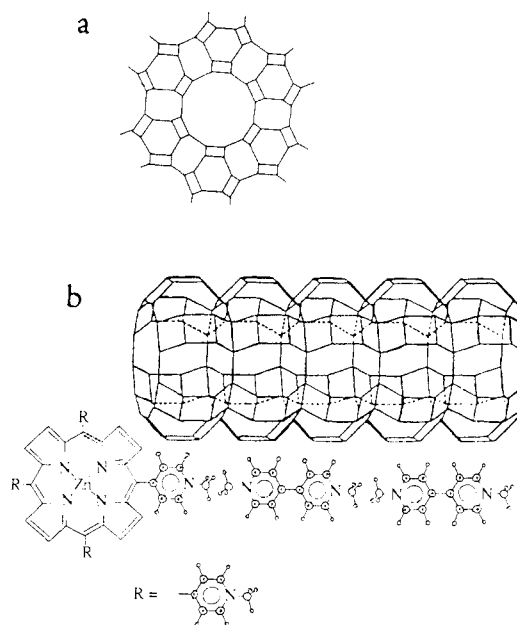


Figure 1. A perspective view of (a) zeolite L showing the one-dimensional channel circumscribed by twelve-membered rings and (b) the zeolite L main channel and the ZnTMPyP⁴⁺ and MV²⁺ ions.

a lower limit, as it is calculated as the geometrical surface area of an average spherical particle ($3/(\text{radius} \times \text{density})$) with a roughness factor of unity. The true roughness factor is probably at least 2–3, so the porphyrin coverage may actually be monolayer or submonolayer. Ion-pairing interactions of these surface-bound porphyrin cations with solution-phase anions are strong. For example, if ZnTMPyP⁴⁺ or MV²⁺-loaded or ZnTMPyP⁴⁺-loaded zeolite L is equilibrated with a 2.0×10^{-3} M EDTA solution at pH 4.0 and washed repeatedly with water, analysis for EDTA¹⁹ shows that 2.5×10^{-6} mol of EDTA is adsorbed per gram of zeolite. At this pH virtually all of the EDTA exists as the dianion, and the amount adsorbed onto the porphyrin-exchanged surface is in the monolayer range. Under the conditions of the photochemical experiments described below, i.e., in pH 4.0 EDTA solutions, a closely associated EDTA–porphyrin–MV²⁺ trimolecular electron transport chain is thus organized at the aqueous solution/zeolite interface.

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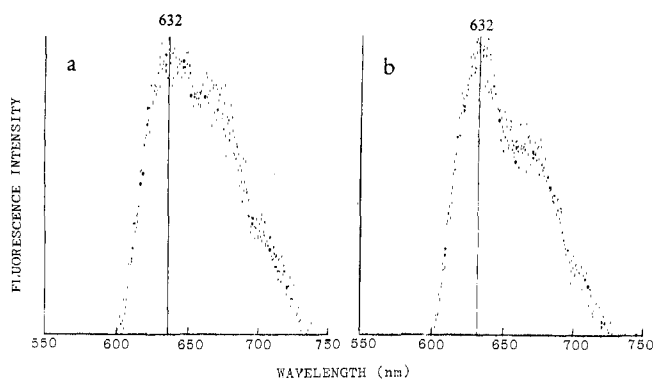


Figure 2. Fluorescence spectra in 90% glycerol of (a) ZnTMPyP⁴⁺ adsorbed on zeolite L and (b) ZnTMPyP⁴⁺ adsorbed on zeolite L containing 2.38×10^{-4} mol of MV²⁺/g.

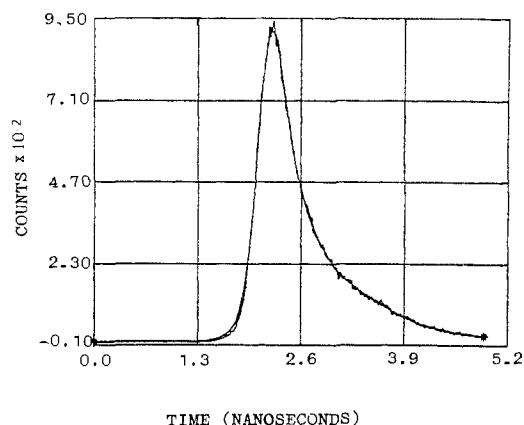


Figure 3. Fluorescence decay profile obtained from ZnTMPyP₄⁺ adsorbed on zeolite L in aqueous suspension. Fluorescence collected through Balzers K65 interference filter and 630 nm cutoff filter. Excitation in Q(1,0) band at 568 nm. A nonlinear least-squares fit to a biexponential decay is superimposed on the experimental data.

Spectral Properties. Absorption and emission spectra of ZnTMPyP⁴⁺ and ZnTAPP⁴⁺ in water are identical with those reported in the literature.⁹ In 90% glycerol or saturated aqueous sucrose solutions the three major absorption bands are red shifted approximately 2 nm; adsorption onto the zeolite L surface results in a further red shift of 2 nm in the Soret band and 2–4 nm in the Q bands. In terms of a band profile or shape, the Soret band is broadened by interaction with the zeolite.

Adsorption onto the zeolite surface results in marked changes in the fluorescence spectrum of ZnTMPyP⁴⁺ (Figure 2 and Table II). The emission maxima shift 10–15 nm to lower energy and the intensity of the 670 emission band increases relative to the 630 band (Figure 2a). The effect of methylviologen on the ZnTMPyP⁴⁺ emission spectrum is shown in Figure 2b. When the viologen or another large cation, e.g., tetramethylammonium (TMA⁺), was exchanged onto the zeolite prior to loading with ZnTMPyP⁴⁺, the relative intensities of the emission bands resemble those of solution-phase ZnTMPyP⁴⁺ (Table II). We tentatively ascribe this intensity shift to a lessening of the strength of interaction between the porphyrin cation and the anionic surface when viologen ions are present. This effect is interesting because it suggests that the viologen and surface porphyrin ions are held in sufficient proximity to interact electrostatically. The spectral shift occurs at relatively low (5×10^{-5} mol/g) MV²⁺ loading, where no (vide infra) detectable quenching of *ZnTMPyP⁴⁺ by MV²⁺ occurs.

The photophysical properties of ZnTMPyP⁴⁺ in homogeneous solution and on zeolite L are summarized in Table II. Fluorescence decays for ZnTMPyP⁴⁺ adsorbed on zeolite L were biphasic in water, 90% glycerol, and saturated sucrose solutions. A typical decay curve and double exponential fit are shown in Figure 3. Precautions were taken (see Experimental Section) to eliminate spurious single photon counting data arising from scattering of

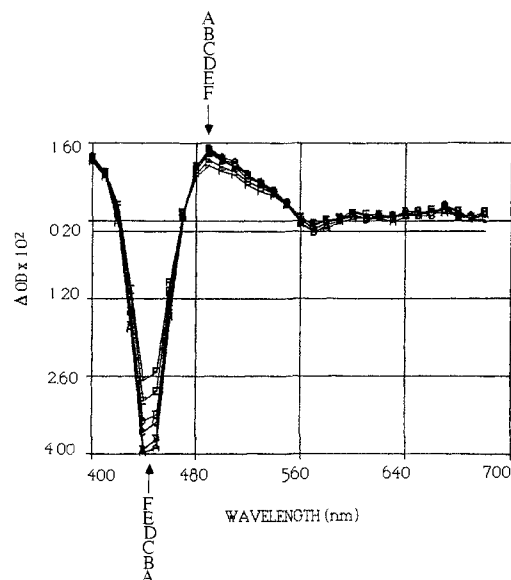


Figure 4. Triplet-triplet absorbance for ZnTMPyP⁴⁺ adsorbed on zeolite L containing 3.0×10^{-4} mol/g of MV²⁺ in 90% glycerol. A–F recorded 4, 10, 22, 37, 84.5, and 134 μ s after a 530-nm excitation pulse.

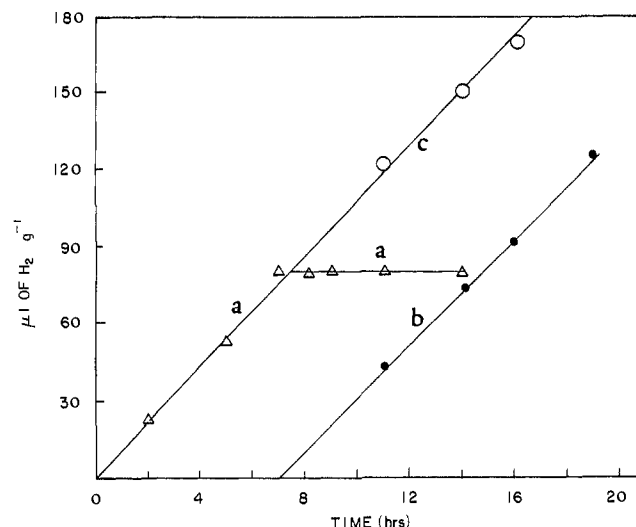


Figure 5. Dependence of H₂ photoproduced with time: (a) linear increase and production ceases after 8 h; (b) obtained with the same sample in a fresh solution of EDTA. The time axis is displaced to coincide with the break in (a); (c) curve obtained by adding linear regions of (a) and (b).

the incident laser flash. Fast (150–430 ps) and slow (700–1600 ps) decays were observed in all three media (Table II). Triplet-triplet absorption spectra of ZnTMPyP⁴⁺ adsorbed on zeolite L also showed biphasic decay (fast component 0.10 ms, slow component 1.5 ms, Table II) and shifting of the major peak to 490 nm (Figure 4), compared to 470 nm in water and 480 nm in 90% glycerol. No effect of viologen loading on the triplet-triplet spectrum or decay rates could be detected within experimental error.

Photochemical Hydrogen Generation. Hydrogen evolution was observed in pH 4.0 aqueous EDTA solutions containing the zeolite L composite (ZnTMPyP⁴⁺, MV²⁺-exchanged, platinumized zeolite L powder) at 30 ± 3 °C. The exact pH was not critical; solutions in the pH range 3.8–4.3 gave essentially the same hydrogen evolution rate. A pH of 4 was chosen in order to allow sufficient driving force (0.21 V) for the reduction of water by MV⁺ and to minimize acid decomposition of the zeolite. When any element of the electron transport chain (EDTA, ZnTMPyP⁴⁺, MV²⁺, Pt, or visible illumination) was left out, only traces of hydrogen were observed after 8 h of irradiation. No hydrogen was evolved thermally when the porphyrin/viologen/platinumized zeolite com-

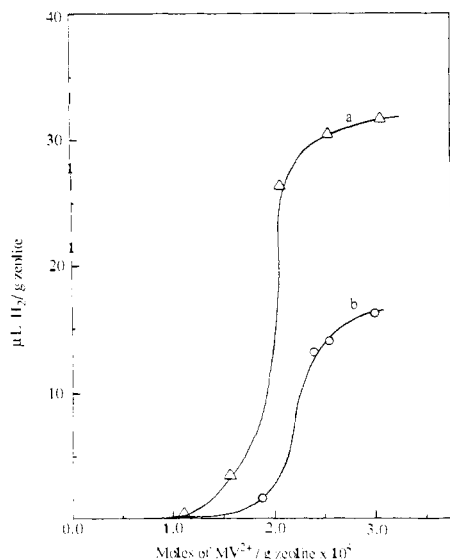


Figure 6. Dependence of H_2 photoproduced within the first 3 h on the amount of MV^{2+} in the zeolite: (a) Pt loading 0.004% by weight; (b) Pt loading 0.0015% by weight.

posite was incubated in the dark in EDTA solution at 30–35 °C.

Figure 5 shows a plot of H_2 produced vs. time for 100 mg of the zeolite containing 8×10^{-6} mol/g of $ZnTMPyP^{4+}$, 2.5×10^{-4} mol/g of MV^{2+} , and 0.0015 wt % Pt irradiated in 5 mL of 2.0×10^{-3} M EDTA solution. The rate of hydrogen production is constant with time and does not vary with EDTA concentration until the latter is almost used up. After 7–8 h, no more hydrogen is produced and titration of the supernatant solution¹⁹ shows that less than one-tenth of the EDTA initially present remains. Addition of the centrifugally separated composite to a fresh EDTA solution, or addition of solid Na_2EDTA to the original solution, results in renewed hydrogen evolution at the original rate. The amount of EDTA consumed is in excess by a factor of 5–6 of that required by stoichiometry (i.e., 2 mol of EDTA per mol of H_2); the reasons for this effect are not understood at present but may be attributed at least in part to reduction of oxygen remaining in the zeolite at the beginning of the experiment, loss of hydrogen during sampling, adsorption, and complexation of EDTA.

Analysis of the supernatant solution by graphite furnace atomic absorption spectroscopy, after 16 h of irradiation, shows that the soluble aluminum concentration (presumably leached from the zeolite as the EDTA complex) is $1-2 \times 10^{-4}$ M. X-ray powder diffraction patterns of zeolite L and the zeolite composite dried after irradiation are superimposable. The X-ray results confirm that the zeolite structure remains intact throughout the experiment; interestingly, there is no evidence in the powder patterns for ordering of the MV^{2+} ions, even at the highest loading level (3.0×10^{-4} mol/g of zeolite) of the latter.

Spectrophotometric analysis of the aqueous phase after 8 h of irradiation shows that significant quantities of $ZnTMPyP^{4+}$ and MV^{2+} have not leached from the zeolite—their concentrations in solution are less than 2×10^{-7} and 2×10^{-5} M, respectively. It seems unlikely, therefore, that $ZnTMPyP^{4+}$ and MV^{2+} present in the solution phase can be contributing to the observed hydrogen evolution. Adding excess $ZnTMPyP^{4+}$ to the solution phase actually decreases the hydrogen evolution rate, probably as a consequence of increased light absorption by the solution. When $ZnTAPP^{4+}$ is substituted for $ZnTMPyP^{4+}$, no hydrogen evolution is detected. This negative result is interesting because it is known²⁰, and has been confirmed in our experiments, that the triplet excited state of $ZnTAPP^{4+}$ is quenched efficiently by MV^{2+} in aqueous solution and evolves hydrogen copiously in the presence of EDTA and colloidal or silica-supported Pt. This result argues strongly

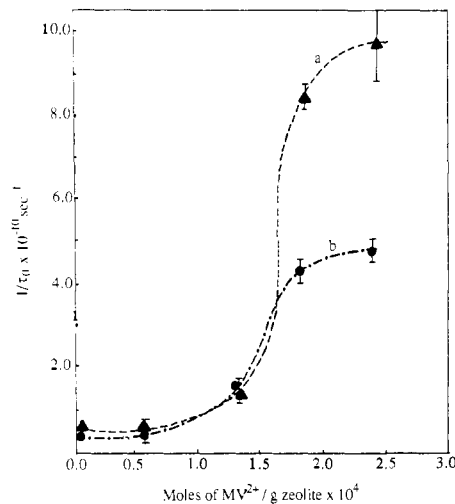


Figure 7. Plot of the inverse of singlet-state lifetime (fast component) of $ZnTMPyP^{4+}$ as a function of MV^{2+} loading within the zeolite cavities: (a) an aqueous suspension; (b) saturated sucrose.

against the participation of solution-phase porphyrins or MV^{2+} in hydrogen photoproduction with Pt incorporated inside the zeolite.

The rate of H_2 evolution monitored in the first 3 h of irradiation depends in an unusual manner on the amount of MV^{2+} exchanged into the zeolite. The curve is sigmoidal (Figure 6) with practically no H_2 evolved at loading levels below 1.5×10^{-4} mol of MV^{2+} /g of zeolite. At this loading (0.4 viologen/large cavity), there is sufficient room in the structure (Figure 1) for a “comfortable” fit of one viologen in every 2 cages. The MV^{2+} ions need not overlap in the channels and probably are able to avoid close contact with the surface $ZnTMPyP^{4+}$ ions. At higher loadings the MV^{2+} and $ZnTMPyP^{4+}$ ions are forced to interact more closely, and the H_2 evolution rate increases sharply. The rate of hydrogen evolution is dependent on the amount of platinum loaded into the zeolite, but the shape of the rate vs. MV^{2+} loading curve is the same: significant hydrogen evolution only results when the viologen ions are forced together so that there are close MV^{2+} – MV^{2+} and MV^{2+} – $ZnTMPyP^{4+}$ contacts.

Fluorescence Lifetimes and Singlet-State Reactivity. A surprising result is obtained when the fluorescence decay rate of $ZnTMPyP^{4+}$ on zeolite L is monitored as a function of MV^{2+} loading. As noted above, this decay is biphasic. The rate of decay of the slow component is invariant with MV^{2+} loading, but the rapidly decaying component shows a sigmoidal rate dependence (Figure 7). Interestingly, the fluorescence decay rate and the hydrogen evolution rate, plotted against the same abscissa (Figures 6 and 7), are nearly superimposable. We can reason that the fast decay comes from a porphyrin ion which interacts strongly with the zeolite surface. Close juxtaposition of a MV^{2+} ion, caused by overcrowding of the bulk ($>1.5 \times 10^{-4}$ mol of MV^{2+} /g), results in singlet-state electron-transfer quenching on a 10–100-ps time scale. The more sterically hindered $ZnTAPP^{4+}$ shows no hydrogen evolution and no dependence of fluorescence decay rate on viologen loading. This result suggests that singlet-state quenching of $ZnTMPyP^{4+}$ by MV^{2+} may occur because of close positioning of the methylpyridinium group of the two molecules. On the basis of the structure of $ZnTMPyP^{4+}$ we speculate that this contact occurs between the methylpyridinium groups (see Figure 1). That is, $ZnTMPyP^{4+}$ may adsorb onto the surface with one or two methylpyridinium groups sticking into the channels, and some degree of π -overlap may exist between these groups and MV^{2+} . Such an arrangement is less likely with $ZnTAPP^{4+}$ because of the bulkiness of the trimethylaminophenyl group, so rapid electron-transfer quenching by MV^{2+} is not possible. In fluid solution $ZnTAPP^{4+}$ and MV^{2+} may orient relative to each other in any fashion, allowing close contact of their π -electron systems and rapid electron-transfer quenching.²⁰

A lower limit for the hydrogen evolution quantum yield in the $ZnTMPyP^{4+}$, MV^{2+} -platinized L system is 0.003% (calculated

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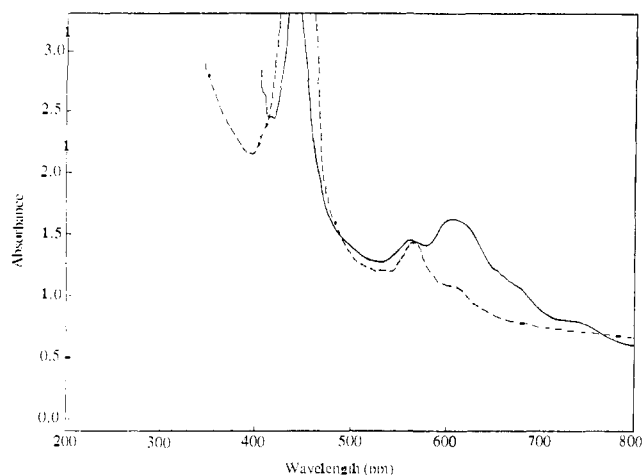
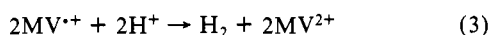
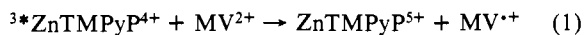


Figure 8. Spectrum in 5 mL of glycerol of 0.05 of zeolite composite containing 2.38×10^{-4} mol of MV^{2+} within the cavities and 8.2×10^{-6} mol of $ZnTMPyP^{4+}$ on the surface per gram: (—) before irradiation; (---) after irradiation.

as H_2 molecules/2 incident photons, uncorrected for scattering, reflectance, absorption spectrum of $ZnTMPyP^{4+}$, etc.). The quantum yield is low because back electron transfer from MV^+ to $ZnTMPyP^{5+}$ is undoubtedly fast and efficient. Competing with the back-reaction are processes that result ultimately in hydrogen evolution—electron transfer from adsorbed EDTA to $ZnTMPyP^{5+}$, and migration of reducing equivalents along the viologen chains to the Pt^0 aggregates contained within the zeolite structure. Evidence that the latter process is occurring in competition with the back reaction is shown in Figure 8. In this experiment a $ZnTMPyP^{4+}$, MV^{2+} -exchanged zeolite L sample containing no platinum was suspended in 90% glycerol with no EDTA present and irradiated continuously for 10 h. The absorbance spectrum after irradiation shows bleaching of the porphyrin Soret band (decreased absorbance at 440 nm) and the growth of absorbances at 550 and 602 nm attributable to the reduced viologen cation MV^+ . The dependence of hydrogen evolution rate on platinum loading (Figure 6) is further evidence that charge transport into the zeolite via the viologens is competing to some extent with the back reaction.

The observation of singlet-state reactivity in this system and the lack of triplet-state chemistry are at first surprising. In homogeneous solution, and in heterogeneous media such as micelles, the long-lived $ZnTMPyP^{4+}$ triplet state is reactive^{1,5} according to reactions 1–3. Reaction 1, however, is only weakly



exoergic⁹ (by ca. 10 mV) in aqueous solution. The analogous

${}^3ZnTAPP^{4+}$ reaction is exoergic by 230 mV.²⁰ Adsorption of these porphyrins onto the surface of zeolites is known to shift their ground-state redox potentials to more positive values by ca. 200 mV.^{17,21} The $MV^{2+/+}$ potential is relatively unaffected by exchange into zeolite Y.^{17,22} Because changes in the fluorescence and triplet-triplet absorbance spectra of $ZnTMPyP^{4+}$ and the phosphorescence spectrum of $PdTMPyP^{4+}$ are small (<0.05 eV shifts) when these ions are adsorbed onto zeolite L, we can assume that the triplet state potentials (i.e., $E_{1/2}$ for the ${}^3ZnTMPyP^{4+}/ZnTMPyP^{5+}$ couple) will also shift by ca. +200 mV. Reaction 1 then is endoergic and is not expected to occur. The analogous $ZnTAPP^{4+}$ reaction will be weakly exoergic or endoergic on zeolite L, depending on the magnitude of the anodic shift. Triplet-state quenching of $ZnTAPP^{4+}$ may still be further retarded, however, by unfavorable steric effects. The energetics for singlet-state quenching of either porphyrin adsorbed on zeolite L by MV^{2+} are favorable because the singlet-triplet energy difference is ca. 0.4 eV/molecule. The MV^{2+} -quenching reactions are thus exoergic by ca. 150 and 350 mV for ${}^1ZnTMPyP^{4+}$ and ${}^1ZnTAPP^{4+}$, respectively.

Conclusions

Molecular level organization of an electron donor–metalloporphyrin–quencher assembly by zeolite L has been demonstrated. Under visible illumination this compartmentalized, integrated system produces hydrogen from water via singlet-state electron-transfer quenching of the porphyrin molecule. The high degree of microstructural order in this system forces the porphyrin and viologen quencher into close proximity, making singlet-state quenching possible. Spatial separation of the hydrogen evolution catalyst and oxidized donor molecules may permit the use of nonsacrificial, solution-phase donors in this and similar zeolite-based systems; such nonsacrificial donors have been employed with very limited success in homogeneous systems.^{23,24} The zeolite-based composite self-assembles by ion exchange from simple, commercially available components; more complex interfacial assemblies, designed to maximize the quantum yield for electron-hole separation, may be envisioned.

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