ELECTRON TRANSFER REACTIONS IN MICROPOROUS SOLIDS

Progress Report

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B. **Publications resulting from DOE-supported work, 1990-present:**

1. **Manuscripts published or in press:**

a. J. S. Krueger, C. Lai, Z. Li, J. E. Mayer, and T. E. Mallouk, "Artificial Photosynthesis in Zeolite-Based Molecular Assemblies," in *Inclusion Phenomena and Molecular Recognition*, J. L. Atwood, Ed., Plenum (New York), 1990, pp. 365-378.

b. D. Rong, Y. I. Kim, H.-G. Hong, J. S. Krueger, J. E. Mayer, and T. E. Mallouk, "Electrochemistry and Photoelectrochemistry of Transition Metal Complexes in Well-Ordered Surface Layers," *Coord. Chem. Rev.*, 97, 237-248 (1990).

c. D. Rong, Y. I. Kim, and T. E. Mallouk, "Electrochemistry and Photoelectrochemistry of Pillared Clay-Modified Electrodes," *Inorg. Chem.*, 29, 1531-1535 (1990).

d. B. G. Maiya, T. E. Mallouk, G. Hemmi, and J. L. Sessler, "Effect of Substituents on the Spectral and Redox Properties of Cadmium(II) Texaphrins," *Inorg. Chem.*, 29, 3738-3745 (1990).

e. J. S. Krueger and T. E. Mallouk, "Redox Catalysis and Photochemistry in Zeolites," in *Kinetics and Catalysis in Microheterogeneous Media*, M. Grätzel and K. Kalyanasundaram, Eds., Marcel Dekker, New York, 1991, pp. 461-490.

f. Y. I. Kim, S. Salim, M. J. Huq, and T. E. Mallouk, "Visible Light Photolysis of Hydrogen Iodide Using Sensitized Layered Semiconductor Particles," *J. Am. Chem. Soc.*, 113, 9561-9563 (1991).

g. Y. I. Kim, R. L. Riley, M. J. Huq, S. Salim, A. N. Le, and T. E. Mallouk, "Zeolitic Materials as Organizing Media for Semiconductor-Based Artificial Photosynthetic Systems," in *Synthesis/Characterization and Novel Applications of Molecular Sieve Materials*, R. Bedard, Ed., Materials Research Society: Pittsburgh, 1991, pp. 145-156.

h. Y. I. Kim, R. L. Riley, E. H. Yonemoto, D. Rong, and T. E. Mallouk, "Self-Assembling Electron Transport Chains in Zeolites: Molecular Rectifiers and Photodiodes," *ACS Symposium Series 499* (Supramolecular Architecture), T. Bein, Ed., American Chemical Society: Washington, DC, 1992, pp. 333-346.

i. A. J. Bard and T. E. Mallouk, "Electrodes Modified with Clays, Zeolites, and Related Microporous Solids," in *Molecular Design of Electrode Surfaces*, R. W. Murray, Ed., Wiley, New York, 1992, pp. 271-312.

j. Y. I. Kim and T. E. Mallouk, "Dynamic Electron Transfer Quenching of the Tris(2,2'-bipyridyl)ruthenium(II) MLCT Excited State by Intrazeolitic Methylviologen Ions," *J. Phys. Chem.*, 96, 2879-2885 (1992).

k. E. H. Yonemoto, R. L. Riley, S. J. Atherton, R. S. Schmehl, and T. E. Mallouk, "Photoinduced Electron Transfer in Covalently Linked Ruthenium Tris(bipyridyl) - Viologen Molecules: Observation of Back Electron Transfer in the Marcus Inverted Region," *J. Am. Chem. Soc.*, 114, 8081-8087 (1992).

1. D. Rong and T. E. Mallouk, "Chemical Gating of a Molecular Bilayer Rectifier at Clay-Modified Electrodes," *Inorg. Chem.*, in press.

2. Manuscripts submitted for publication:

a. Y. I. Kim and T. E. Mallouk, "Sensitized Layered Metal Oxide Semiconductor Particles for Photochemical Hydrogen Evolution from Non-sacrificial Electron Donors," submitted to *J. Phys. Chem.*

b. E. S. Brigham, P. T. Snowden, Y. I. Kim, and T. E. Mallouk, "Electron and Energy Transfer as Probes of Interparticle Ion Exchange Reactions in Zeolite Y," submitted to *J. Phys. Chem.*

Several additional manuscripts, based on results described in the Progress Summary, are expected to be submitted in the near future.

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D. Progress Summary

1. Project Objectives

The basic thrust of our DOE-funded research program involves the use of microporous solids (zeolites, clays, layered and tunnel structure oxide semiconductors) as organizing media for artificial photosynthetic systems. The purpose of the microporous solid in this work is twofold. First, it induces spatial organization of photoactive and electroactive components (sensitizers, semiconductor particles, electron relays, and catalysts) at the solid-solution interface, enhancing the quantum efficiency of charge separation and separating physically the ultimate electron donor and acceptor in the electron transport chain. Second, since the microcrystalline solid admits only molecules of a certain charge and size, it is possible to achieve permanent charge separation by sieving chemical photoproducts (e.g., H_2 and I_3^- , or H_2 and O_2) from each other. Spectroscopic and electrochemical methods are used to study the kinetics of electron transfer reactions in these hybrid molecular/solid state assemblies.

a. Structures of Microporous Solids. Several kinds of molecular sieve materials have been used in this work as microcrystalline "scaffolding" for molecular and semiconductor-based electron transport chains. Non-conductive solids, such as clays and zeolites, have one-, two-, or three-dimensional channel systems with window openings of molecular dimensions. Figure 1 shows some representative materials. The largest pore materials, zeolite Y and pillared montmorillonite, will admit solvent molecules and also small electroactive molecules, such as viologens, metallocenes, metal ammine complexes,

and polycyclic aromatics. Larger molecules such as substitution-inert $M(\text{bpy})_3^{2+}$ ($M = \text{Ru}, \text{Os}$) and metalloporphyrins are size-excluded from the internal volume. While $M(\text{bpy})_3^{2+}$ are too large to fit through the 12-ring pore openings of zeolite Y, they can nevertheless be encapsulated in the supercages by "ship in a bottle" syntheses. For $M=\text{Ru}$, this entails ion exchange with a smaller complex ($\text{Ru}(\text{NH}_3)_6^{3+}$) and subsequent thermal treatment with bpy ¹. For $M=\text{Co}$, the complex is sufficiently labile that it can be exchanged in from aqueous solution, dissociating and re-assembling inside the zeolite². Smaller pore materials such as zeolite A and sodalite are also interesting, because of their potential for sieving small molecule products of photochemical reactions, e.g., halogens or O_2 from H_2 .

Figure 1. Structures of zeolites Y, A, sodalite, and mordenite.

Another very interesting class of microporous solids are sheet and tunnel structure alkali transition metal oxides. Some representative structures are shown in Figure 2. These materials share some of the molecular sieving and cation-exchange properties of zeolites and clays, but have semiconducting frameworks. While in most cases they absorb light only in the ultraviolet, they can be sensitized in the visible by adsorbing molecular

photosensitizers, and in this case the solid acts not only as the organizing medium but also as one of the components of the electron transport chain. Again, the frameworks are typically anionic, so they can be exchanged with electroactive/photoactive cations of appropriate size. Both one-dimensional (tunnel structure) and two-dimensional (sheet structure) oxides of this type are available. The renewal proposal contains some possible synthetic approaches to semiconducting three-dimensional molecular sieve frameworks.

Figure 2. Hollandite ($\text{A}_{0.25}\text{MO}_2$, A=alkali, M=Mg,Ti,Nb,etc.) and KTiNbO_5 structures.

b. General Schemes for Light-Induced Charge Separation. Figure 3 shows three schematic designs, which we have explored with DOE support, for multicomponent photochemical assemblies in microporous solids. In one an electron transport chain containing two, three, or four molecular components assembles at the zeolite-solution interface through ion-exchange reactions and size-exclusion effects. The ultimate electron donor in the system shown is either size excluded or of the wrong charge type (i.e., anionic) to enter the channel system of a large-pore zeolite such as Y or mordenite. The sensitizer, typically a $\text{Ru}(\text{bpy})_3^{2+}$ derivative, is also size-excluded but covalently tethered to a viologen dication that can enter the micropores at the solution/solid interface. If desired a fourth component (a viologen acceptor) can be exchanged into the bulk of the zeolite, although to date this strategy has not resulted in longer-lived charge separation than the three-component donor-sensitizer-acceptor system.

Figure 3. Three schemes for interfacial charge separation using zeolitic materials.

The second scheme involves growing small platinum clusters and oxide semiconductor particles (TiO_2 or Nb_2O_5) inside a linear channel zeolite, typically mordenite. Exchange of an electron relay, methylviologen (MV^{2+}) into the zeolite and photolysis in the presence of an anionic sacrificial donor results in hydrogen evolution, via the electron transport pathway shown. The third scheme involves sensitization of a wide-bandgap layered metal oxide semiconductor (LMOS) with a visible dye. In experiments to date a carboxylated $\text{Ru}(\text{bpy})_3^{2+}$ derivative has been used. Metal catalyst clusters grown inside the structure catalyze the reduction of water using visible light. The most striking feature of this system is that it operates with *non-sacrificial* electron donors (I^- being the most effective one studied to date), because the layered solid sieves the oxidized donor

from the interlayer space where the catalyst particles are located. More detailed descriptions of each of these systems are given in the following sections.

2. Donor-Acceptor Diads and Triads

We have studied light-induced electron transfer in donor-sensitizer-acceptor systems using laser flash photolysis/transient absorbance techniques²⁻⁵. The rates of electron transfer in covalently linked $\text{Ru}(\text{bpy})_3^{2+}$ -viologen diads were studied as a function of reaction energetics and donor-acceptor distance in three different media: in fluid solution, as guest molecules in β -cyclodextrin (β -CD) hosts, and as components of larger (triad and tetrad) assemblies at the zeolite/solution interface.

a. Ruthenium Polypyridyl/Viologen Donor-Acceptor Molecules. At the heart of zeolite-based photochemical "reaction centers" studied by us and others^{1b-e,6} are photosensitizers such as $\text{Ru}(\text{bpy})_3^{2+}$ and metalloporphyrins⁷, which transfer electrons to viologen acceptors. $\text{Ru}(\text{bpy})_3^{2+}$ -viologen donor-acceptor pairs possess several endearing qualities, such as photostability in water, high visible extinction coefficient, and large free energy content in the charge-separated state, that have made them very popular in both homogeneous and heterogeneous artificial photosynthetic systems⁸ since the first report of their electron transfer reaction in 1974⁹. Interestingly, while quenching of the $\text{Ru}(\text{bpy})_3^{2+}$ excited state by MV^{2+} can occur with practically unit quantum efficiency, the yield of charge-separated products in this system is typically low, on the order of 10-30% in aqueous media¹⁰. Because we found similar quantum yields for charge separation in zeolite-based systems^{5,11}, we undertook a study to understand the rates of forward and back electron transfer, and consequently cage-escape yields, in this system as a function of potentially variable parameters such as reaction energetics and intermolecular distance.

A series of covalently linked donor/acceptor molecules, shown below, was prepared. By changing groups R and R', the free energy dependence of the rate constants k_f and k_b was studied for $n=1-2$. The forward and back reactions occur in the normal and Marcus inverted rate regions, respectively⁴. While direct measurements of inverted region

electron transfer rates had not been made previously for ruthenium polypyridyl-viologen donor-acceptor pairs, this result is not unexpected in light of recent work by Elliott¹² and Hoffman¹³ on related systems, in which inverted region back transfer could be inferred.

What is more interesting is the distance dependence of electron transfer rates^{5b} for the series $n = 1-8$, $R = \text{methyl}$, $R' = \text{H}$, shown in Figure 4. Both $\ln k_f$ and $\ln k_b$ vary linearly with the number of carbon atoms in the spacer chain up to $n = 4$. For $n \geq 5$ only k_f can be measured, since k_b is much larger than k_f . For these longer chain compounds $\ln k_f$ is roughly constant with n . In the presence of β -CD, the long-chain compounds are complexed and forced into a conformation in which the donor and acceptor ends of the molecule are held apart. In this extended conformation, the $\ln k_f$ points fall roughly onto the line defined by the $n=1-4$ points without β -CD. These results indicate that electron transfer through the saturated spacer is the dominant pathway for the $n=1-4$ molecules, and that the through-solvent pathway becomes important only for the longest chains.

An unusual feature of these $\ln k$ vs. distance plots (the distance being calculated for the extended conformation of the flexible spacer) is the apparently stronger variation of k_f with distance than k_b . The slope of the lines is the damping factor β , where it is assumed that the rate constant varies exponentially with distance, i.e. $k = k_0 \exp[-(r-r_0)\beta]$. Previous studies by Miller and coworkers give almost exactly the same β for electron transfer in both directions through saturated spacers¹⁴. The issue of the distance dependence of the rate constant in such systems is a complex one, as recent quantum mechanical calculations

Figure 4. Distance dependence of electron transfer rates in Ru(bpy)₃²⁺-MV²⁺ diads.

support superexchange models involving many parallel pathways for electron transfer^{15,16}. These models predict a slightly weaker distance dependence if the predominant pathway is hole superexchange, rather than electron superexchange (back and forward transfer, respectively), but also predict that for long spacer chains most pathways will be mixed electron/hole. Indeed, these models do not necessarily even imply a linear dependence of $\ln k$ on distance as did earlier models based on exclusively McConnell-type (i.e., nearest-neighbor coupling) pathways¹⁷.

Actually, it is important to note that it is not necessarily the rate constant, but rather the electronic coupling matrix element $V(r)$, that is expected to vary exponentially with

distance in most of these models. Since the solvent reorganization energy is smaller at short D-A distances and larger at longer D-A distances, the distance dependence of the rate constant is larger than that of $|V(r)|^2$ in the normal region, and weaker than that of $|V(r)|^2$ in the Marcus inverted region. This effect actually explains the different apparent β 's in Figure 4 quantitatively. Corrected for the variation in reorganization energy, plots of $\ln|V(r)|^2$ vs. distance give a single β for both the forward and back reactions. That this behavior has not been observed before is apparently a consequence of the fact that distance-dependent rate data have not been previously collected for a homologous D-A series in which forward and back transfer are in the normal and inverted regions, and in which the rates are sufficiently similar that both can be measured for the same molecule. Previous studies of very similar molecules by Elliott and coworkers did not show this effect, primarily because the back electron transfer rates are too fast to measure directly¹⁸. This finding has an important implication for the design of artificial photosynthetic systems, namely that long D-A distances will enhance k_b relative to k_f if the former is in the inverted region. The effect should be most pronounced in polar media, where the outer-sphere reorganization energy is large, and less important in nonpolar media.

One final interesting point that arose from this study is that the cage escape yield for $\text{Ru}(\text{bpy})_3^{2+}$ and viologen derivatives does not show a recognizable dependence on the energetics of the back reaction, despite the fact that the rate data for covalently linked D-A complexes show that the back reaction is inverted. The data suggest that geometric factors are dominant, since the bulkiest viologen studied (benzylviologen) has the highest cage escape yield for all $\text{Ru}(\text{bpy})_3^{2+}$ derivatives. The $\text{Ru}(\text{bpy})_3^{2+}$ /benzylviologen pair has a cage escape yield of 77% in acetonitrile solution, significantly higher than has been reported for any ruthenium polypyridyl/viologen combination in homogeneous media.

b. Zeolite-Based Donor-Acceptor Systems. Photochemical charge separation between $\text{Ru}(\text{bpy})_3^{2+}$ and MV^{2+} at the zeolite/solution interface was studied in two ways. One entailed simply exchanging $\text{Ru}(\text{bpy})_3^{2+}$ onto the surface, and MV^{2+} into

the bulk of large-pore zeolites (Y, L, mordenite)¹¹. The other involved the donor-acceptor molecules described above, ion-exchanged onto the external surface of the same materials^{2,5b}.

For the $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}$ pair on/in large-pore zeolites, the quenching and charge separation behavior are remarkably similar to that expected for a fluid solution. Linear Stern-Volmer plots were derived from time-resolved emission and transient diffuse reflectance data, consistent with a dynamic electron transfer quenching mechanism. The same behavior was found in the absence of an external solvent phase, where there is still a significant intrazeolitic water content. In this case, the apparent diffusion coefficient for MV^{2+} was approximately half the value found in aqueous zeolite suspensions. Quantum yields for formation of photoproducts were 6-9 %, and the lifetime of the charge-separated $\text{Ru}(\text{bpy})_3^{3+} - \text{MV}^{+\bullet}$ state was in the range of tens of microseconds.

Covalently linked $\text{Ru}(\text{bpy})_3^{2+}-(\text{CH}_2)_n-\text{MV}^{2+}$ diads exchanged onto the surface of these zeolites showed markedly different behavior. First, the quantum yield for formation of the charge-separated state depended strongly on n , consistent with solid state NMR data² that showed a large fraction of the complex in a "folded" conformation on the zeolite surface for short chains ($n = 2, 3$), and a predominantly extended conformation (i.e., viologen end inside the channel) for $n \geq 4$. The quantum yield for charge separation actually peaks at $n = 4 - 5$, since for longer chains the forward electron transfer becomes slower than alternative pathways of MLCT state decay.

For cases where charge separation is observed, the lifetime is on the order of hundreds of microseconds, i.e. ten times longer than the zeolite-bound $\text{Ru}(\text{bpy})_3^{3+} - \text{MV}^{+\bullet}$ pair, in which the latter is free to diffuse. This behavior is difficult to rationalize, given the fixed D-A distance and the rapidity of the back reaction in fluid solution, unless electron exchange between neighboring diad molecules can occur. In this case, charge transport diffusion can separate the electron and hole to much larger distances, and since the molecules cannot physically diffuse, the charge separated lifetime might be expected to be

unusually long. Attempts to study this system at very low loading, in which there would be no neighboring D-A molecules, have been frustrated by signal-to-noise limitations in our present transient diffuse reflectance apparatus.

c. Zeolite-Based Donor-Sensitizer-Acceptor Triads. By adding a solution-phase electron donor, or an intrazeolitic electron acceptor, to these diads, a trimolecular D-S-A or S-A-A' system can be formed. These studies have been carried out as a prelude to more complex systems, described in the renewal proposal, in which the ultimate electron donor is part of a separate solid phase, and an intermediate electron donor "shuttle" carries electrons from it to the diad bound at the zeolite/solution interface.

Two different electron transfer sequences occur when solution-phase electron donors are used in these systems. For short-chain molecules ($n = 4,5$) where quenching of the MLCT state by the viologen is fast, the sequence of electron transfer is $\text{Ru}(\text{bpy})_3^{2+}$ to MV^{2+} , followed by donor to $\text{Ru}(\text{bpy})_3^{3+}$. Figure 5 shows spectra obtained with the $n = 5$

Figure 5. Transient diffuse reflectance spectra for $\text{Ru}(\text{bpy})_3^{2+}$ -(CH_2)₅- MV^{2+} /Zeolite Y acetonitrile suspensions with and without the solution phase donor PMZ^+ .

compound. The two spectra show clearly the sequence of electron transfer events and formation of the $\text{PMZ}^{2+ \cdot}/\text{Ru}(\text{bpy})_3^{2+} - \text{MV}^{+ \cdot}$ charge separated state, which decays on a timescale of ca. 200 μs . With long-chain compounds ($n = 7,8$) in which intramolecular electron transfer quenching is slow relative to the lifetime of the MLCT state, anionic, solution-phase electron donors can quench the excited state of the diad molecule. Subsequent electron transfer from the $\text{Ru}(\text{bpy})_3^+$ moiety to MV^{2+} occurs rapidly even through the long spacer because of the much higher driving force for this reaction, relative to the $\text{Ru}(\text{bpy})_3^{2+ \cdot} - \text{MV}^{2+}$ electron transfer. Both $\text{W}(\text{CN})_8^{4-}$ and $\text{Mo}(\text{CN})_8^{4-}$ are good electron donor quenchers for $\text{Ru}(\text{bpy})_3^{2+ \cdot}$, and give the $\text{M}(\text{CN})_8^{3-}/\text{Ru}(\text{bpy})_3^{2+} - \text{MV}^{+ \cdot}$ charge separated state in 10-15% quantum yield with the $n = 7,8$ compounds on zeolites Y and L.

3. Sensitized Oxide Semiconductors

Oxide semiconductor particles offer several advantages, relative to small molecules, as electron relays in artificial photosynthetic systems. Among the most important are their better chemical and photochemical durability, and the high rate and quantum efficiency of electron injection from carboxylated $\text{Ru}(\text{bpy})_3^{2+}$ photosensitizers¹⁹. To date we have explored two strategies (Fig. 4) for preparing sensitizer-oxide semiconductor-catalyst composite materials for photochemical hydrogen evolution.

A general reaction scheme for these systems is shown in Figure 6. A chemically reversible electron donor, such as I^- , is used to replace the electron injected from the LUMO of the photosensitizer into the semiconductor conduction band, and a catalyst (such as Pt) on the semiconductor particle converts $\text{e}^- + \text{H}^+$ to molecular hydrogen. Overall, the thermodynamically uphill reaction (1) is driven by light of energy $h\nu$. A very basic design problem is that oxidized and reduced products are made in the same region of space. Since the reverse of (1) is favorable by $nF\Delta E_0'$, the free energy stored in the photolysis reaction,

it will *always* occur if the oxidized and reduced products are not prevented from contacting the catalyst simultaneously. This problem can be overcome using the molecular sieving properties of zeolitic materials.

Figure 6. Energetics of a sensitized semiconductor/catalyst system for photochemical decomposition of HX.

a. Linear Channel Zeolites. We have developed a new "ship in a bottle" technique for depositing Pt^0 clusters exclusively within the pore network of linear channel zeolites L and mordenite²⁰. The fact that the external surface is completely free of Pt^0 is essential to blocking the reverse of (1), since the oxidized donors are excluded on the basis of their charge and/or size from the internal volume but are free to recombine with H_2 at any external catalyst sites. The non-occurrence of the reaction of H_2 with $\text{Fe}(\text{CN})_6^{3-}$ establishes the selectivity of Pt^0 siting in these materials. Impregnation of Pt^0 -mordenite with TiCl_4 or $\text{Ti}(\text{O}-i\text{Pr})_4$ and subsequent pyrolysis leaves both internally and externally sited TiO_2 clusters with an average particle size of 10-15 Å, estimated from the blueshift in bandgap absorption onset. The fraction of the channel volume occupied by TiO_2 can be gauged by BET measurements and MV^{2+} sorption; both measurements show that most of the semiconductor is inside the zeolite.

The results of photolysis experiments with and without intrazeolitic MV^{2+} , in the presence of a sacrificial electron donor (TEOA) are shown in Figure 7. The fact that some

Figure 7. Hydrogen evolution from 0.1 g mordenite/Pt(0.1%)/TiO₂ (10.6%, from Ti(O-iPr)₄/RuL₃²⁺(2.5 × 10⁻⁶ mol/g) in 8 mL 10 mM TEOA at pH 4.0. Visible illumination, $\lambda \geq 400$ nm, intensity < 20 mW).

Table I. Electrochemically Reversible Electron Donors

	E_o' (V vs. SCE)
Fe(CN) ₆ ⁴⁻	0.20
Mo(CN) ₈ ⁴⁻	0.55
W(CN) ₈ ⁴⁻	0.26
Os(CN) ₆ ⁴⁻	0.40
I ⁻	0.29
Cytochrome C	0.01
0.51
0.16
0.16

hydrogen is generated in the absence of the MV^{2+} relay indicates that a fraction of the TiO_2 connects the externally sited RuL_3^{2+} ($L = 4,4'$ -dicarboxy-2,2'-bipyridine) sensitizer with the internally sited Pt^0 .

A screening of available non-sacrificial donors (Table I) has shown that none are effective with this system. The problem arises because the conduction band-edge potential of TiO_2 is almost exactly the same as the H_2/H^+ potential, and therefore the TiO_2 can mediate electron transfer in both directions. Once it is impregnated with TiO_2 , the platinized zeolite catalyzes the reduction of $Fe(CN)_6^{3-}$ by H_2 and related recombination reactions in the dark. Referring to Fig. 6, it can be seen that what is needed in this system is a semiconductor with a sufficiently negative conduction bandedge potential that injection of electrons at the H^+/H_2 potential does not occur. The flatband potential of TiO_2 is essentially coincident with $E_0'(H^+/H_2)$. However, preliminary experiments involving Nb_2O_5 (prepared by pyrolysis of $NbCl_5$) in place of TiO_2 give hydrogen evolution with the anionic N,N' -dialkyl-4-methoxyaniline derivative shown in Table I. This result adds support to the hypothesis that the problem in the TiO_2 case is one of band energetics. Unfortunately, in the case of Nb_2O_5 almost all of the semiconductor is externally sited, resulting in a low (ca. 0.5%) quantum efficiency. An obvious strategy for improving this situation is to try other precursors that might give internally sited Nb_2O_5 , or other semiconductors with appropriately positioned conduction bandedge potentials.

b. Layered Metal Oxide Semiconductors. Layered alkali transition metal oxides represent a solution to the problem described above, in which the zeolitic framework is itself a wide bandgap semiconductor with an appropriate conduction bandedge potential. Especially interesting materials in this regard are the alkali niobates and titanoniobates, such as $K_4Nb_6O_{17}$ and $KTiNbO_5$. These solids contain essentially two-dimensional semiconducting, anionic sheets of edge- and corner-sharing MO_6 octahedra interleaved with alkali cations. The physical properties of these compounds resemble those of layered van der Waals solids of high charge density, such as micas and layered double hydroxides.

These solids can be internally platinized through a series of ion-exchange and oxidation-reduction reactions, and then acid-exchanged so as to be able to adsorb RuL_3^{2+} on their external surface. Again, it is possible to deposit the platinum catalyst exclusively on the inside, at sites inaccessible to anionic or size-excluded oxidized donor molecules. Continuous photolysis of the acid-exchanged, internally platinized, sensitized semiconductor $\text{K}_{4-x}\text{H}_x\text{Nb}_6\text{O}_{17}\cdot n\text{H}_2\text{O}/\text{RuL}_3^{2+}$ in KI solution results in the formation of H_2 and I_3^- . These are formed in a 1/1 mole ratio, in keeping with the stoichiometry of HI photolysis. Control experiments show that only traces of hydrogen are formed in the absence of iodide, and that none is produced with visible light excitation in the absence of photosensitizer. The good news vis a vis this system is that it represents the first photocatalyst for visible light splitting of a molecule HX. The bad news is that at present the quantum yield is only 0.3 %²¹.

We have conducted a detailed investigation of the mechanisms of charge separation and recombination in sensitized $\text{K}_{4-x}\text{H}_x\text{Nb}_6\text{O}_{17}\cdot n\text{H}_2\text{O}$ and related oxide semiconductors. Flash photolysis studies have shown that charge separation involves electron injection from the sensitizer, followed by rapid reduction of the oxidized sensitizer by I^- . The I^- initially formed in this process is very rapidly converted to $\text{I}_2^{\cdot-}$, which then forms I_3^- in a second-order reaction. Transient spectra do not show any evidence for geminate recombination between $\text{I}_2^{\cdot-}$ and the oxidized sensitizer, or for the formation of a geminate charge-transfer complex of these ions. Tests for dark recombination of I_3^- and H_2 with these materials are negative, indicating that once chemical products are formed, they do not recombine. Apparently the low quantum efficiency for formation of chemical products is a consequence of recombination between conduction band electrons and I_3^- .

Further evidence for this mechanism was gained from a study of hydrogen evolution from $\text{M}_{4-x}\text{H}_x\text{Nb}_6\text{O}_{17}\cdot n\text{H}_2\text{O}$, $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$, in which the size of the hydrated alkali metal modulates the interlayer spacing of the semiconductor²². It was found that the hydrogen evolution rate varied monotonically with the inverse of the layer

spacing, indicating that electron tunnelling between layers is the rate-limiting step in hydrogen evolution. We are currently studying the incorporation of spacer ions that will enhance the mobility of electrons between layers, and the use of non-electroactive adsorbates that can block access of I_3^- to the surface. We are also investigating the possibility of overcoming the two-dimensional conductivity problem by using other microporous oxide semiconductors, such as hollandite, which have three-dimensional tunnel structures.

4. Zeolite A-Based Inorganic "Z-Schemes"

While visible light is capable, thermodynamically, of driving energetically demanding reactions such as water or HX ($X = Br, Cl$) photolysis on a one-photon-per-electron basis, in practice no such systems exist. Nature uses a biphotonic Z-scheme to drive a similarly endoergic reaction, the conversion of CO_2 and water to carbohydrates and oxygen. Small-pore zeolites provide a potential means of organizing inorganic components, such as small semiconductor particles and electron relays, into biphotonic assemblies that might carry out such photolysis reactions. The general energetic scheme for these composite materials is shown in Figure 8. While several formidable problems,

Figure 8. Biphotonic Z-scheme for HX photolysis based on two semiconductor particles and electron relay O/R.

such as possible electron-hole recombination pathways and a requirement for matching redox levels and spectral properties of various components, attend the construction of workable systems, we have nevertheless begun to examine materials that could serve as useful components.

Because the zeolitic solid used in the construction of this system must sieve X_2 and H_2 , a small pore material is required, with window openings of ca. 2-3 Å. Candidate host solids include sodalite (2.3 Å), zeolite A (3.3 - 5.1 Å), and layered alkali transition metal oxides such as $K_4Nb_6O_{17} \cdot 3H_2O$ (ca. 3 Å). Our initial efforts in this area centered on sodalite, a salt-bearing tectosilicate of formula $Na_6Al_6Si_6O_{24} \cdot 2MX \cdot nH_2O$, where MX is normally a sodium salt, such as NaCl or NaOH. In the latter case, neutralization of NaOH with H_2S and subsequent exchange with Cd^{2+} gives CdS-loaded sodalite. Treatment of this solid with size-excluded aqueous Br_2 removes CdS from the external surface, leaving small clusters on the inside that have an absorption onset of ca. 320 nm. This extreme blueshift (relative to bulk CdS, which has an absorption onset of 515 nm), larger than that observed for CdS tetramers in the sodalite cages of larger pore zeolites²³, is consistent with the formation of very small (possibly monomeric or dimeric) CdS clusters.

Because the absorption of CdS is shifted into the UV in sodalite, and also because of the inherent difficulty in assembling "ships" through a 2.3 Å "bottleneck", a different approach was taken in subsequent experiments. The window opening in zeolite A is conveniently variable, depending on the cation with which it is exchanged. In the Na^+ (4 Å) form, it can be loaded with atomic Te at 500°C. Subsequent exchange with K^+ effectively traps the Te inside, by reducing the pore opening to 3 Å. Subsequent exchange with Cd^{2+} , followed by hydrogen reduction at 200°C and treatment with aqueous $KHCO_3$ gives encapsulated CdTe clusters that are remarkably air- and water-stable²⁴. The absorption spectrum of this material shows an exciton band at ca. 430 nm and a bandgap absorption onset of 390 nm, consistent with a particle size of approximately 8 Å. This is consistent with siting of $(CdTe)_n$ aggregates either in the large α -cages, or in the smaller

sodalite cages, provided there is electronic coupling between neighboring clusters in the latter.

We have made preliminary attempts to construct a biphotonic system (Fig. 8) with this material, using $\text{Ti}(\text{O-iPr})_4$ as a precursor to extrazeolitic TiO_2 and Ag^+ as an electron relay. In the absence of CdTe, flash photolysis experiments show that $\text{Ag}_n^{(n-1)+}$ species are formed by electron transfer from photoexcited TiO_2 . However, in the presence of CdTe, a broad red emission (500 - 700 nm) is observed. By analogy to previous studies of Ag_2S -CdS particles by Henglein and coworkers²⁵, we attribute this luminescence to carrier trapping and recombination at the Ag/CdTe interface. This result suggests that Ag^+ will not be an appropriate electron relay in this system.

5. Electrochemistry of Aluminosilicate Modified Electrodes

Electrochemical techniques were used to study charge transfer reactions at solution/zeolite and solution/clay interfaces. In particular the rates of intrazeolitic electron transfer and interparticle exchange of electroactive ions, which are relevant to the design of zeolite-based photochemical systems, were investigated. An interesting effect that was discovered in the course of these experiments was chemical "gating" (through pH changes) of electron transfer at pillared clay/polyelectrolyte interfaces.

a. Zeolite Y. Electrochemical studies of electron transfer to and from molecules exchanged into large-pore zeolites support two possible charge transport mechanisms. In one it is assumed that intrazeolitic electron transfer is slow, and that oxidation or reduction of a zeolite-bound ion is preceded by exchange into the solution phase²⁶. A second possible mechanism involves charge transport diffusion via intrazeolitic electron exchange, with concomitant motion of charge-balancing cations in and out of the zeolite. We have carried out two sets of experiments that support the latter mechanism. Hydrophobic electroactive cations such as trimethylammonium methylferrocene, FcR^+ , can be exchanged into zeolite Y at a loading of ca. one ion per supercage, but are invisible electrochemically at

zeolite Y modified electrodes in aqueous electrolytes at low ionic strength². Exchange of a monolayer of $\text{Os}(\text{bpy})_3^{2+}$ ions onto the external surface of the zeolite results in large anodic waves that can be attributed to mediated oxidation of bulk FcR^+ by surface $\text{Os}(\text{bpy})_3^{2+}$. This behavior is consistent with interfacial electron transfer between FcR^+ and $\text{Os}(\text{bpy})_3^{2+}$, and subsequent intrazeolitic charge transfer diffusion of the $\text{FcR}^{+/2+}$ couple.

In contrast, intrazeolitic $\text{Co}(\text{bpy})_3^{2+}$ cannot be oxidized by surface $\text{Os}(\text{bpy})_3^{3+}$, despite the fact that the driving force for this reaction is higher than in the FcR^+ case. Normally charge transport diffusion in chemically modified electrodes occurs by a combination of physical diffusion of molecules and electron exchange between them. We might imagine that physical diffusion of $\text{FcR}^{2+/+}$ could be reasonably rapid, but that $\text{Co}(\text{bpy})_3^{3+/2+}$ would move very slowly within the zeolite. The latter complex must dissociate in order to move between supercages, and the oxidized form (a d^6 complex) does not dissociate readily. An additional complicating factor is the need to move charge compensating ions into and out of the zeolite as the entrained complex is oxidized and reduced.

In a second set of experiments, the rates of ion exchange between zeolite particles were studied for surface ($\text{Os}(\text{bpy})_3^{2+}$) and bulk (MV^{2+}) ions²⁷. The technique used was luminescence quenching of $\text{Ru}(\text{bpy})_3^{2+}$, which was either grown inside the zeolite supercages by the ship-in-a-bottle technique, or ion exchanged onto the external surface. Under conditions (0.1 - 3 mM electrolyte concentration) mimetic of most electrochemical and photochemical experiments involving similar ions in zeolite Y, the timescales of these exchange reactions are on the order of minutes. While this result argues for an intrazeolitic electron transfer mechanism in these supramolecular systems, it should be noted that the rate of interparticle exchange is still sufficiently rapid to ensure equilibration (i.e., equal concentrations of exchangeable ions in all particles) in a matter of hours. This finding places some limitations on possible designs for systems which might contain one set of ions on some particles and another set on others (e.g., electron donors and acceptors,

respectively). Such systems would rapidly equilibrate to a more homogeneous one in which all particles contained donors and acceptors.

b. Pillared Montmorillonite. Previous experiments carried out with zeolite- and clay-modified electrodes have shown that molecular rectifiers and photodiodes can be made to self-assemble by ion exchange of appropriate photoactive and redox-active molecules²⁸. An interesting question in these systems is whether current flow can be "gated" (i.e., switched on and off) with a chemical signal. We have found that cationic metalloporphyrins, which mediate electron transfer to smaller cationic molecules exchanged into the bulk of the pillared clay, can be switched from an effectively conductive to non-conductive state, reversibly, via axial ligation²⁹. This effect has now been demonstrated with amine ligation of cobalt porphyrins, and with protonation/deprotonation of the hydroxide ligand of cationic iron porphyrins. These changes in axial ligation alter by several orders of magnitude the rate of electron transfer cross-reactions between the metalloporphyrin and electroactive ions within the clay galleries. Since the latter are held at sites too remote from the electrode for direct electron transfer, the current is effectively switched off when the porphyrin is in the "slow" ligation state, and on again when it is in the "fast" state.

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