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Efficient Photoinduced Charge Separation in Layered Zirconium Viologen Phosphonate Compounds

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Abstract: Stable photoinduced charge separation has been observed in layered zirconium viologen phosphonate compounds, *i.e.* $Zr(O_3PCH_2CH_2(bipyridinium)CH_2CH_2PO_3)X_2$ (X = Cl, Br, I), ZrPV(X). Photolysis of these crystalline solids results in the formation of the blue viologen radical cation which is stable in air. Studies of these microcrystalline solids as well as related thin films are presented. Transparent thin films of ZrPV(Cl) were grown directly onto fused silica substrates from aqueous solution. Photoreduction of viologen in these thin-film samples is very efficient (quantum yield = 0.15), showing simple isobestic behavior in the electronic spectra. Contrary to the bulk solids, the photoreduced thin films are very air sensitive. Photophysical data is presented, which shows that the primary photoprocess involves a viologen-centered excitation, followed by oxidation of a halide anion. Subsequent reactions lead to the formation of a stable charge-separated state. Significant deuterium isotope effects ($k_H/k_D = 3$) for selectively labeled compounds suggest that the oxidized halide ions abstract hydrogen atoms from the methylene groups of ZrPV(Cl). NMR studies of these materials show that a number of different structural rearrangements are then involved in the formation of the ultimate charge-separated state. These structural rearrangements are most likely responsible for the longevity of the photoreduced states in ZrPV(Cl). Evidence is provided which shows that the photoreduction of viologen in ZrPV(Br) has a significant reversible component as well.

Introduction

Photoinduced electron-transfer reactions have been intensively studied, sparked by a desire to understand the key steps in natural photosynthesis and to develop artificial systems for the efficient storage and conversion of solar energy.[1] In these photochemical processes, chemical energy is stored in a charge-separated state ($D^+ A^-$). In a typical system charge separation involves a redox reaction between a photoexcited electron donor (D^*) and an electron acceptor (A), resulting in the production of the ion pair ($D^* + A \rightarrow D^+ A^-$). The efficiencies of these photoinduced electron-transfer processes for storing and converting solar energy into chemical energy are dependent on the rate of the thermal back-electron-transfer reaction ($D^+ A^- \rightarrow D + A$). A great deal of theoretical and experimental work has shown that controlling the rates of forward and back electron transfers requires control of both electronic and structural properties of the system.[1] The electronic properties of organic and molecular inorganic compounds can readily be tuned, but the spatial arrangements of these molecules are much more difficult to control. An approach used for controlling the spatial arrangement of molecular donors and acceptors involves heterogeneous systems, in which the donors and acceptors are incorporated into solid matrices.[2] These heterogeneous systems can provide the appropriate spatial organization of donors and acceptors to control the rates of electron transfer. Zeolites,[3] clays,[4] sol-gel glasses,[5] layered metal oxides,[6] semiconductor and metal colloids,[7] synthetic monolayers,[8] as well as other molecular assemblies[9] have been used for this purpose. Lifetimes of the photoinduced charge-separated states of hours have been achieved in these organizing systems, compared to nanosecond to microsecond lifetimes for the same donors and acceptors in solution.

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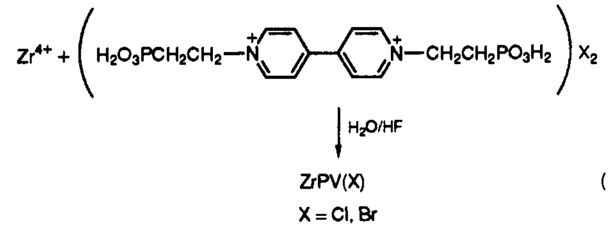
We have recently reported the preparation and photophysical properties of crystalline layered zirconium viologen phosphonate compounds, $Zr(O_3PCH_2CH_2(bipyridinium)CH_2CH_2PO_3)X_2$ (X = Cl, Br), ZrPV(X).[10] These layered compounds show very efficient photoinduced charge transfer and form a charge-separated state which is long-lived and stable in air. Photolysis of the colorless zirconium viologen phosphonate compounds by solar radiation or by a UV lamp leads to a blue solid which remains blue after the light source has been removed. Spectroscopic studies indicate that the photoproduct is the dialkyl viologen radical cation, produced in the interlamellar region of the zirconium phosphonate. In the air, the deep blue color fades over the course of several hours to a pale blue color, which persists indefinitely. Under anaerobic conditions the deep-blue does not fade over several days. The viologen is reduced with a quantum yield of >0.03 at 300 nm (this wavelength is λ_{max} in the photoaction spectrum). The photochemistry was attributed to charge transfer from the halide counterions, followed by trapping of the halide radicals. The remarkable stabilities of this charge-separated state in ZrPV(X) are believed to be due to structural features which allow for stabilization of the radicals due to delocalization and shielding from molecular oxygen.

We report here the synthesis, characterization, and photophysical properties of ZrPV(X) (X = Cl, Br, I) and related thin films. The thin films consist of multilayers of zirconium viologen phosphonate, grown on fused-silica slides. These films are transparent and thus render themselves more amenable to optical studies than the highly scattering bulk solids. Monitoring the photoreduction by electronic spectroscopy shows simple isobestic behavior. The photoreduction process in the thin films has a much higher quantum yield than was reported for the bulk solids. The mechanism for formation of the charge-separated states in these materials has both an irreversible and a reversible component. Insight into the details of the mechanism for formation of the charge-separated states has been gained through the study of both microcrystalline and thin-film samples of ZrPV(X) and will be discussed below.

Results and Discussion

Synthesis and Photophysical Studies of ZrPV(X) (X = Cl, Br, I). The syntheses of the chloride, bromide, and iodide compounds (ZrPV(X)) were achieved by slightly different methods. The chloride and bromide derivatives were prepared by the direct reaction of Zr^{4+} with the appropriate bisphosphonate salt, as shown in eq 1. The iodide salt was prepared by the reaction of Zr^{4+} with the tetraphenylborate salt of the viologen-bisphosphonate in the presence of a large excess of KI, eq 2. The tetraphenylborate ion is presumably too large to be taken into the ZrPV(X) lattice. All three compounds are microcrystalline, and narrow lines in both the ^{31}P CPMAS NMR and powder X-ray diffraction patterns (*e.g.* Figure 1) indicate that these materials are well-ordered. The proposed structure of these zirconium viologen phosphonate compounds is shown schematically in Figure 2.[10] The viologen groups are arranged between the inorganic zirconium phosphonate layers, as shown, with the halogen counterions present near the surfaces of the lamellae. The lines of the powder X-ray diffraction patterns for all of the compounds have identical 2θ values with differing relative intensities (see supplementary material). This indicates that the unit cell dimensions for each are identical, suggesting that the halide ions are not associated with the faces of the viologen groups. If the halide ions had been associated directly with the viologen groups, there should have been different unit cell parameters for Cl, Br, and I.



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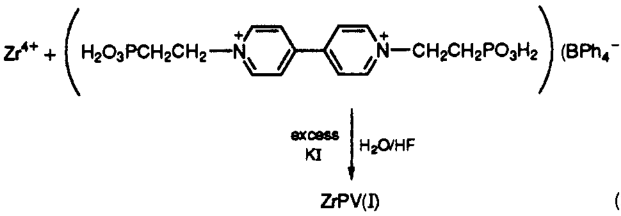

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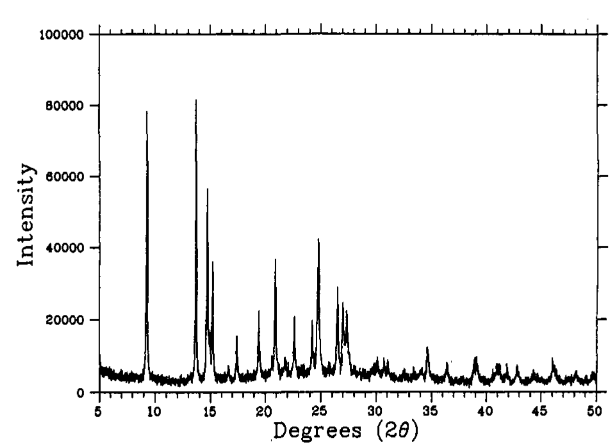

Figure 1. Powder X-ray diffraction pattern for ZrPV(Cl).

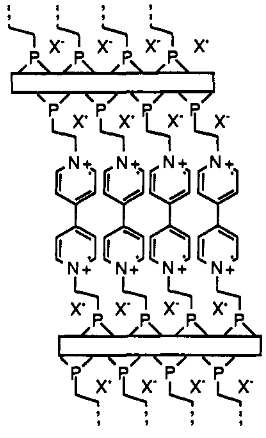

Figure 2. Structure of ZrPV(X).

Simultaneous photolysis of the chloride, bromide, and iodide zirconium viologen phosphonates shows that formation of the blue radical cation occurs at different rates in the order of Cl > Br > I. The relative rates of photoreduction of ZrPV(X) (estimated by photolysis of samples at 300 nm, while monitoring transmittance at 632 nm) are 1:0.82:0.67 for Cl/Br/I. This strong halide dependence suggests that the primary photoprocess involves the halide, which we proposed was a halide to viologen charge transfer.[10] The photoaction curves for ZrPV(Cl) and ZrPV(Br) are very similar (Figure 3), with λ_{max} for photoreduction of viologen at approximately 300 nm. Charge-transfer transitions in the electronic spectra of viologen halides shift as a function of the halide (heavier ions give lower energies).[10,11] If the primary photoprocesses were halide to viologen charge transfer, the maxima in the photoaction curves should also shift as a function

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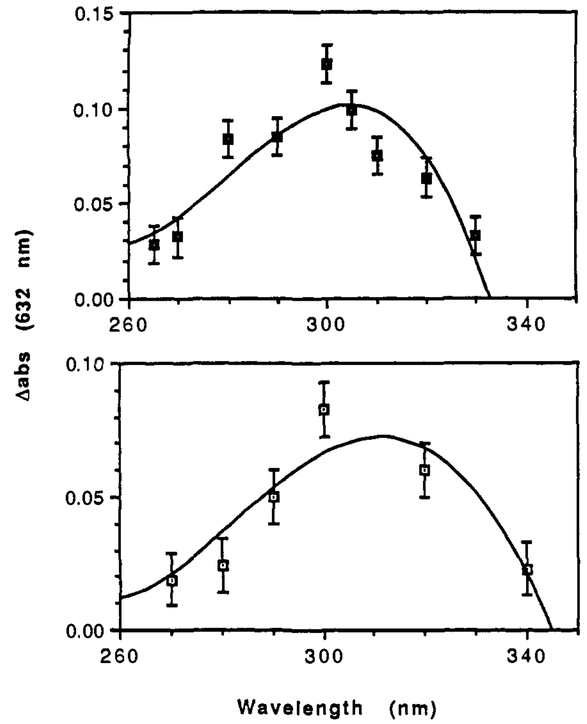
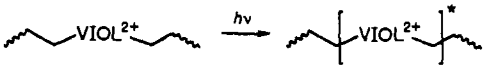


Figure 3. Photoaction spectra for powdered samples of ZrPV(Cl) (top) and ZrPV(Br) (bottom).

of the halide. The similarity of the photoaction spectra suggests that the photochemical step involves a viologen-centered transition (*i.e.* π–π^*), eq 3. This excited viologen is a potent oxidant and



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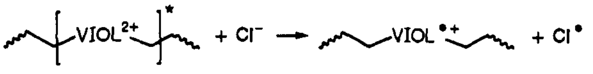

(4)

oxidizes the halide anion to give a charge-separated state composed of reduced viologen and the halogen radical, eq 4. This process would not be expected to show a strong halide ion dependence in the photoaction spectra, since the photochemical event is a viologen π–π^* transition.[12] A similar charge-separated state, albeit much shorter lived, can be formed by irradiation of dimethylviologen halides in aqueous solution.[11c,13] Ebbesen *et. al.*[13] proposed that the primary photoprocess in this aqueous system was excitation of the dimethylviologen acceptor, as suggested for ZrPV(X). A photoprocess similar to this one has also been proposed for viologen halides in polymer matrices.[9c,d]

In addition to photoreduction of viologen, these compounds also photoluminesce. When irradiated at 285 nm, the ZrPV(X) compounds luminesce at 340 nm. Again, the excitation curves for the chloride, bromide, and iodide complexes are identical. The lifetimes for all of these emitting states are less than 20 ns, suggesting that the emissive state is not a triplet. These observations are consistent with the observation of luminescence of methylviologen intercalated into clays (285-nm excitation gives 330-nm emission, lifetime = 3 ns),[14] which is due to excitation of a viologen-centered electronic transition.

The EPR spectrum of photoreduced ZrPV(Cl) is a single broad resonance (g = 2.005, line width = 8 G) at room temperature. On cooling, the resonance broadens (at 100 K, g = 1.998, line width = 22 G and at 10 K, g = 2.008, line width = 10 G), but no new signals appear. Reduced dimethylviologen in dilute solution gives a complex EPR spectrum, with hyperfine coupling to all of the hydrogen and nitrogen atoms in the molecule. The increased line width in the EPR spectra of reduced viologen in ZrPV(Cl) relative to the fluid solution can be due to electron transfer between reduced viologen and adjacent viologen groups. This effect would be expected to be significant in the close-packed ZrPV(Cl) lattice. Similar effects have been observed in related materials, in which the sample has a high concentration of viologen with a small percentage in the reduced form.[15] From the line widths of the solution and ZrPV(Cl) spectra, an electron-transfer rate of 3×10^7 M^{-1} s^{-1} was estimated for photoreduced ZrPV(Cl).[16] This rate is similar to those reported for dimethylviologen[15b] and other aromatic molecules.[17]

Samples of photolyzed ZrPV(X) show no evidence for either halogen radicals or $X_2^{\bullet -}$ ions in the EPR or UV/vis spectra.[13,18] The trapping of the halogen radicals must be involved in the stabilization of the charge-separated states in ZrPV(X), since back electron transfer from these open shell species (*i.e.* Cl$^\bullet$ and $Cl_2^{\bullet -}$) is very rapid.[11c] In addition to stabilizing the charge-separated state, this radical trapping may be responsible for the observed halide dependence in the photoreduction of these materials. The mechanism for radical trapping in ZrPV(X) will be discussed below.

Multilayer Thin Films of ZrPV(X). The materials described above are isolated as microcrystalline powders (particle size ≈ 1 μm). The powdered nature of these samples leads to severe scattering losses in optical studies, making their detailed photophysical study difficult. In order to overcome the scattering problems associated with powders, ZrPV(X) compounds have been grown as multilayer thin films on fused silica substrates. The phosphonate used to prepare ZrPV(X) is a bisphosphonic acid (*i.e.* H_2O_3P–R–PO_3H_2), making this material well suited to thin-film growth by the sequential growth method, reported first by Mallouk *et al.* for zirconium alkylphosphonates.[19] This film growth procedure involves several steps, shown in Scheme I for growth on a glass substrate. The substrate surface is first derivatized with phosphonate groups, as discussed below. When this derivatized substrate is treated with an aqueous solution of Zr^{4+}, the zirconium ions bind to the phosphonate groups on the surface, giving a zirconium-rich surface. The substrate is then removed from the Zr^{4+} solution, rinsed with water, and treated with a solution of a bisphosphonic acid. One of the phosphonate groups binds to the zirconium-rich surface, while the other is left uncoordinated. The result is that the surface is now rich in phosphonate groups. The substrate is removed from the solution of the bisphosphonic acid, rinsed thoroughly, and treated with a solution of Zr^{4+} again. Repeated sequential treatments with the bisphosphonic acid and zirconium solutions leads to layer-by-layer growth of a zirconium phosphonate film on both sides of the glass substrate simultaneously, see Scheme I. Thin films

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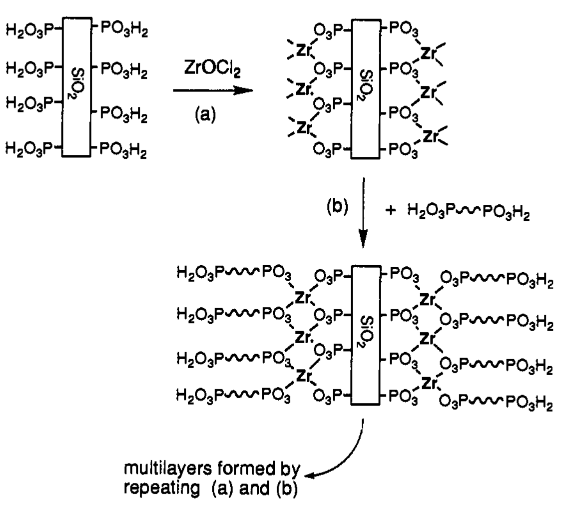
Scheme I



prepared in this way are transparent and well-ordered. The structure of a thin film formed in this way is very similar to that of the same material prepared in the bulk phase (*i.e.* microcrystalline $Zr(O_3P\text{-}R\text{-}PO_3)$).[19]

ZrPV(X), X = Cl, Br, thin films were grown on fused-silica slides by first treating the slides with $(EtO)_3SiCH_2CH_2CH_2NH_2$, followed by $POCl_3$.[20] This procedure leads to a phosphonate-rich surface, suitable for treatment with an aqueous solution of $ZrOCl_2$, Scheme I. The reaction of the zirconium-rich surfaces with $H_2O_3P\text{–}CH_2CH_2\text{–}$bipyridinium$\text{–}CH_2CH_2\text{–}PO_3H_2X_2$ is slow at room temperature. If the viologen bisphosphonate solution is heated to 85 °C, the reaction of the substrate is complete in 4 h (on the basis of UV spectroscopy). As the ZrPV(X) layers are deposited, a band at 270 nm grows in the UV spectrum of the sample. The incremental increase in absorbance at 270 nm is consistent with the reported extinction coefficient[21] (0.014 absorbance units per layer at 270 nm for ZrPV(Cl)), assuming a close-packed layer of the viologen bisphosphonate on the surface of the substrate. Katz also found that elevated temperatures were beneficial for film growth with related bisphosphonic acids.[20a] A plot of the absorbance at 270 nm as a function of the number of ZrPV(Cl) layers deposited on fused silica is shown in Figure 4. As expected for sequential film growth, the absorbance increases linearly with the number of layers deposited. Katz has recently reported very closely related thin films, formed with $H_2O_3P\text{–}(CH_2)_3\text{–}$bipyridinium$\text{–}(CH_2)_3\text{–}PO_3H_2$.[22]

UV photolysis of the multilayer thin film sample of ZrPV(X) in the air does not lead to any detectable coloration of the sample. If the sample is irradiated *in vacuo* or under Ar, however, the characteristic blue color of reduced viologen is observed almost immediately. Simple isobestic behavior is observed in this photoreduction of viologen, as shown in Figure 5. The UV band at 270 nm is bleached as the bands characteristic of the viologen radical cation grow in at 405 and 605 nm, indicating the direct transformation of the viologen dication to the singly reduced viologen radical cation. Exhaustive photolysis of the sample leads to reduction of >85% of the viologen groups in the thin film (on the basis of the absorbances at 405 and 605 nm). This corresponds to a very high concentration of reduced viologen in the interlamellar region of these materials. In aqueous solution the blue dimethylviologen radical cation is in equilibrium with a purple dimer ($K_{eq} = 6 \times 10^2$ M^{-1}).[23] The purple dimer shows a blue shift in both of the bands in the electronic spectrum (bands are observed at 380 and 540 nm).[24] Only bands due to the reduced viologen monomer are observed in the photoreduced thin films. The dimer is presumably not observed in the multilayer thin films due to the structural rigidity of the inorganic lamellae, preventing the reorientation of the viologen radical cations to form dimers.

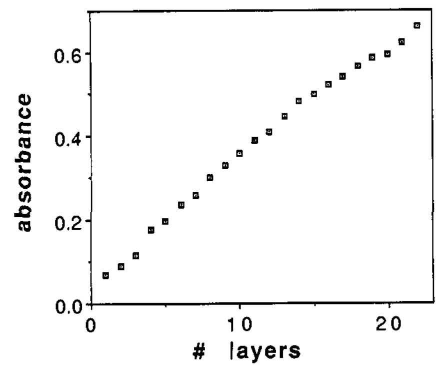


Figure 4. Measured absorbance at 270 nm as a function of the number of layers of ZrPV(Cl) deposited on a fused silica substrate. Note that layers are deposited on both sides of the glass slide, so that what is labeled ten layers is actually a total of twenty layers.

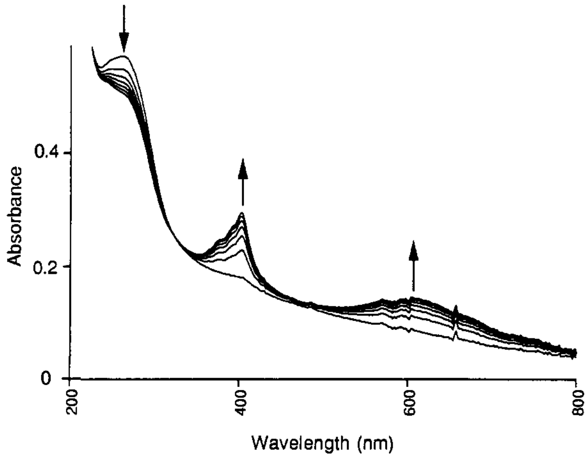


Figure 5. Electronic spectra of a multilayer film of ZrPV(Cl) as it was irradiated with a low intensity UV light (254 nm). Spectra were taken at three minute intervals. Up and down arrow indicate the bands which increase and decrease over time, respectively.

The electronic spectra of the thin films as well as the air sensitivity of the photoreduced samples suggest that these multilayer thin films are not as tightly packed as microcrystalline samples of ZrPV(X). The UV band of the thin film is very close to that of dimethylviologen in aqueous solution (265 nm), which has been assigned to a $\pi\text{–}\pi^*$ transition.[11,13,25] Microcrystalline ZrPV(Cl) is bathochromically shifted by 30 nm relative to a thin film of the same material. The bathochromic shift is expected for tightly packed viologens, due to interactions of the π systems of adjacent viologens. Also consistent with a more open lattice for the thin films is the oxygen sensitivity of the photoreduced thin films. Treating a photoreduced film with air leads to complete bleaching within a matter of seconds, while the microcrystalline materials require hours to days. Oxygen appears to freely diffuse through the thin film. Related zirconium bisphosphonate thin films also show a high permeability to small molecules (*i.e.* Cl$^-$).[26]

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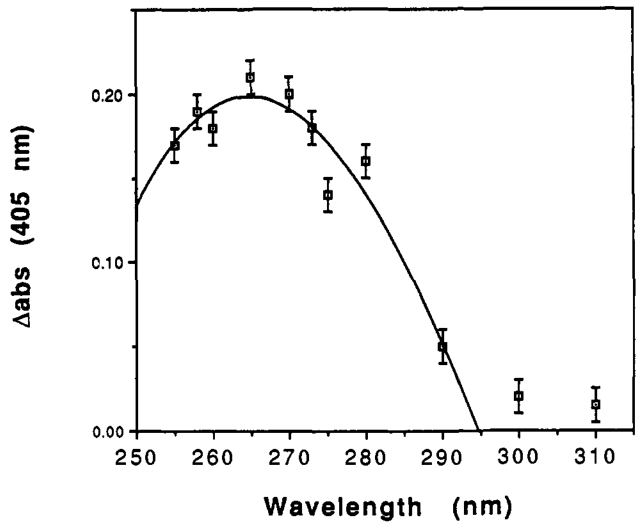

Figure 6. Photoaction spectrum for a ten layer thick film of ZrPV(Cl) on fused silica. Photolysis time at each wavelength was 20 seconds.

No luminescence is observed for the thin-film samples. The luminescence observed in the powdered samples is fairly weak. This process may not be observed in thin films simply due to the small amount of ZrPV(Cl) in the thin-film sample, leading to emission too weak to be observed by the fluorimeter.

The photoaction spectrum of the multilayer thin-film sample of ZrPV(Cl) is qualitatively similar to that of the powdered solids, Figure 6. A peak in the photoaction spectrum is observed at 265 nm. Photoreduction of viologen in these thin-film samples of ZrPV(Cl) is an efficient process, with a measured quantum yield of 0.15 for reduction of viologen at 275 nm (10-nm band-pass). The peak at 265 nm is very similar to the λ_{max} observed in the electronic spectrum of the thin film. This observation is consistent with the primary photoprocess being excitation of the viologen group, followed by oxidation of a halide ion by the excited viologen, as described above.

NMR of Photolyzed Materials. NMR spectroscopy was used to look for changes in the composition of ZrPV(X) on photolysis. An exhaustively photolyzed sample of ZrPV(Cl) was dissolved in D_2O/HF and its solution NMR spectrum recorded. The spectra of dissolved samples were used, because new signals could be obscured by the relatively broader lines of the solid-state NMR spectrum compared to a solution spectrum and also because solution samples will eliminate the broadening due to paramagnetic species generated on photolysis. The ^{31}P spectrum shows a very weak signal near 0 ppm, in addition to a large signal at 21.9 ppm due to the viologen bisphosphonic acid. Considering the active wavelengths for the photoreduction of these materials, the small size of the new signal is not surprising. The UV light needed to photoreduce the solid should be scattered or absorbed by the first few hundred angstroms of each crystal, leaving the bulk of the solid unphotolyzed. To determine if the surface layers of the crystals are in fact screening the bulk of the crystal from UV light, thin films of ZrPV(Cl) were grown on the surfaces of silica gel particles.[27] In this way the unreacted core of the ZrPV(Cl) crystal could be replaced by an inert matrix (*i.e.* SiO_2), which will not give a ^{31}P NMR signal. A sample of the thin film material (five layers) on silica gel was dissolved with D_2O/HF without photolysis and shows only a single ^{31}P resonance at 21.9 ppm, identical to the case of an authentic sample of the viologen bisphosphonate. A sample of the supported material was then photolyzed exhaustively under argon to give a deep-blue solid and the sample dissolved in HF/D_2O in the air. The ^{31}P NMR spectrum of this sample shows phosphoric acid (0.0 ppm) in addition to the viologen bisphosphonic acid, Figure 7. The ^{31}P resonance centered at 21.9 ppm is significantly broader than that observed for the unphotolyzed material and consists of at least two different species. The reduced viologen in this sample was oxidized by O_2. To be certain that the phosphoric acid was not coming from a byproduct of this oxidation step, a sample was treated with Br_2 prior to dissolution with HF/D_2O rather than oxygen. This bromine-oxidized sample gave a ^{31}P spectrum very similar to that of the O_2-treated material. We have been unable to get a useful ^{13}C spectrum of these samples. Weak signals for the parent viologen bisphosphonate are observed, but no new resonances are detected. The proton spectrum only shows the parent viologen bisphosphonate as well as a small amount of the singly substituted bipyridyl species. A good portion of the spectrum is obscured, however, by the proton impurity in the D_2O solvent.

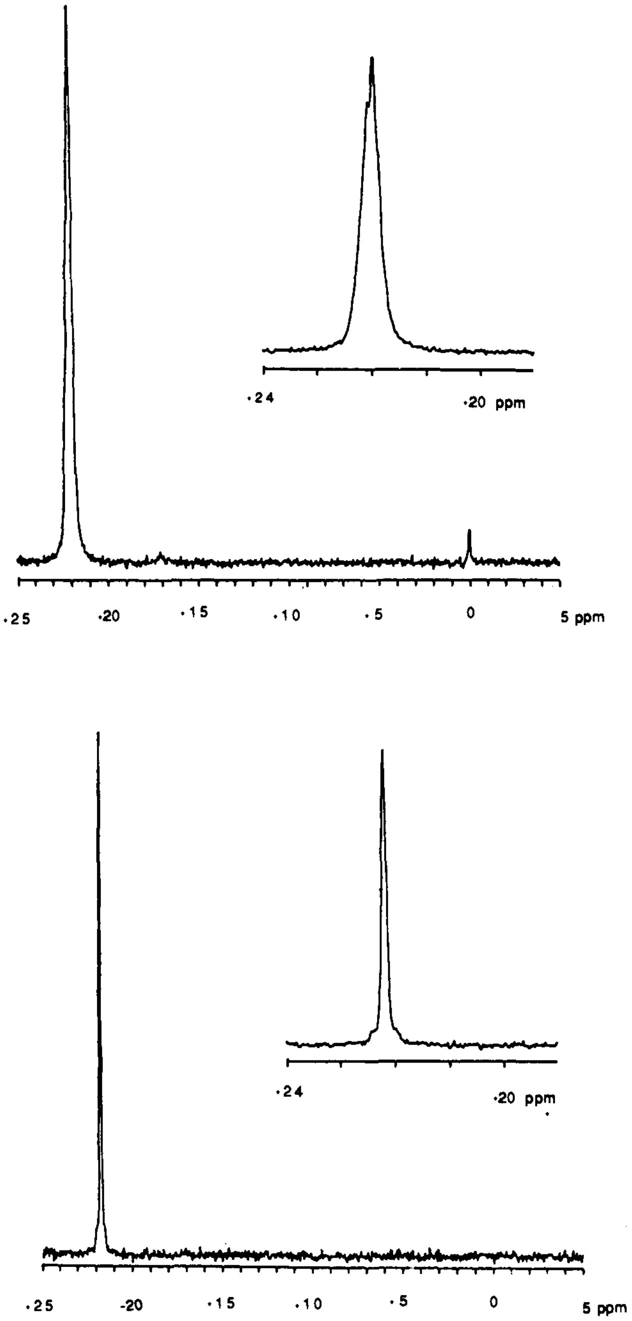

Figure 7. ^{31}P NMR spectra of a thin film of ZrPV(Cl) grown on silica gel before (bottom) and after (top) photolysis. Films were removed from the silica support by washing the solid with HF/D_2O. The NMR spectra shown are for these D_2O solutions.

Mechanism of Charge Separation. The halide dependence in the photoreduction of viologen in ZrPV(X) (Cl > Br > I) suggests

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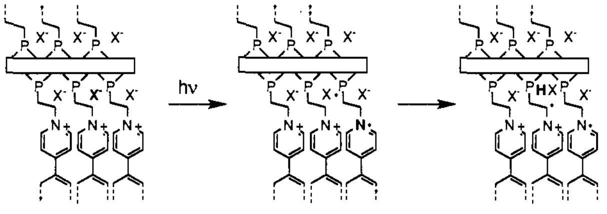
[27] Hong, H.; Sackett, D. D.; Mallouk, T. E. *Chem. Mater.* **1991**, *3*, 521–527.

Scheme II



that the halogen is involved in the photochemical reaction. However, the similarity of the photoaction spectra for the different halide compounds indicates that the halide is not involved in the primary photoprocess. What's more, the typical involvement of the halide ions in a system such as this would be to facilitate an intersystem crossing to a triplet state. This intersystem crossing would be most effective for the heaviest anions. The fact that the luminescent lifetimes for the Cl, Br, and I compounds are all very short (<20 ns) suggests that a heavy-atom effect is not present in these materials. An alternate explanation for the observed trend involves the reactions leading to a stable photoreduced state. It was proposed above that for ZrPV(X), photolysis leads to reduced viologen and halogen radicals. The observed halide ion dependence could be the result of differing efficiencies for trapping these radicals, since no evidence for any open-shell molecules other than reduced viologen is seen in the EPR and electronic spectra of ZrPV(Cl). One mechanism for trapping the halide radicals involves abstraction of a hydrogen atom from the α-methylene of a neighboring viologen alkyl chain, as shown in Scheme II. This is a benzylic carbon, and the radical formed should be stabilized by delocalization onto the bipyridinium. The rate of this hydrogen atom abstraction by chlorine atoms should be faster than that for bromine atoms,[28] as observed for the photoreduction of ZrPV(X).

If a hydrogen atom abstraction is the key step in the photoreduction of ZrPV(X), it should be possible to observe a kinetic isotope effect when deuterium is substituted into the appropriate positions. A deuterated version of the ZrPV(Cl) compound was prepared from $H_2O_3PCD_2CD_2$–bipyridinium–$CD_2CD_2PO_3H_2$. The powder X-ray diffraction pattern and NMR spectra for this material are identical to those of the perprotio material. Side-by-side photolyses of deuterated and nondeuterated ZrPV(Cl) with a low-intensity UV light show a much slower rate of color change with the deuterated material. The rate of photoreduction of these materials by 300-nm irradiation was monitored by transmittance of a HeNe laser (632 nm) through an aqueous slurry. The k_H/k_D estimated by this method is 3 ± 1, confirming that a hydrogen atom abstraction is involved in the photoreduction of ZrPV(Cl). The kinetic isotope effect in multilayer thin films was also examined. Twelve-layer thin films were grown in the normal manner with $H_2O_3PCD_2CD_2$–bipyridinium–$CD_2CD_2PO_3H_2$ and with the perprotio bisphosphonic acid. The observed quantum yields for photoreduction of viologen in these samples were 0.15 ± 0.01 and 0.05 ± 0.01 for the perprotio and deuterated films, respectively. These values give a k_H/k_D of 3 ± 1 for photoreduction of the thin films, suggesting that hydrogen atom abstraction is also involved in photoreduction in the thin films of ZrPV(Cl).

Studies are currently underway to determine the fate of the α-methylene radical, formed by H atom abstraction. NMR spectra of the photolyzed thin films (*vide supra*) suggest several routes may be possible for trapping this radical species. A process which would explain the formation of phosphate on photolysis involves a structural rearrangement at phosphorus. In this rearrangement, a homolytic bond cleavage of the P–C bond results in the formation of a vinyl bipyridine derivative and phosphorus-(IV) radical species [$Zr(O_3P—CH_2\dot{C}H—VIOL— \rightarrow Zr(O_3P^\bullet + CH_2{=}CH—VIOL—$]. It has been recently reported that the P(IV) radical obtained by hydrogen atom abstraction from phosphorous acid ($^\bullet PO_3^{2-}$) will reduce dimethylviologen at near diffusion controlled rates in aqueous solution.[29] The analogous reduction in this system leads to the formation of a second equivalent of reduced viologen and a phosphorus(V) species (O_3P^+). On dissolution in H_2O the phosphorus(V) species will hydrolyze to give phosphoric acid, consistent with the ^{31}P NMR studies discussed above. A second radical trapping process could involve chloride radicals formed photochemically. A low steady-state concentration of chlorine radicals would be expected under photolytic conditions. Combination of one of these chlorine radicals with the carbon-based radical would lead to a phosphonate with a chloro substituent on the β carbon. If radicals are generated at the α-methylenes of two adjacent viologen groups, they could readily couple. Both this dimerization and trapping by Cl$^\bullet$ would lead to a slight shift in the ^{31}P resonance, relative to that of the parent viologen bisphosphonate, consistent with the observed spectrum. Structural rearrangements such as these are most likely responsible for the longevity of the photoreduced states in these materials.

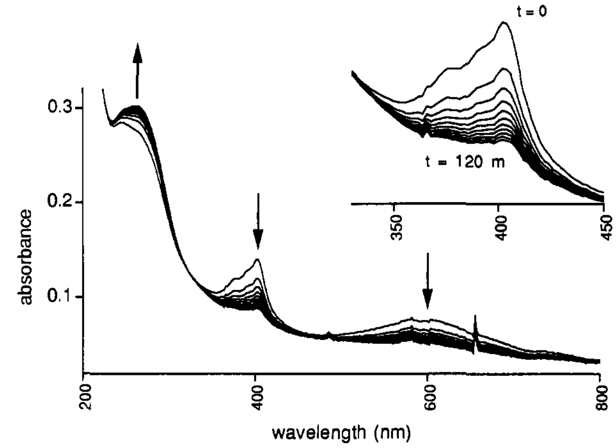


Figure 8. Electronic spectra of a ten layer film of ZrPV(Br) (in vacuo), which was irradiated with a low intensity UV lamp (254 nm). Spectra were recorded immediately on removing the lamp and then at 12 minute intervals for two hours. Up and down arrow indicate the bands which increase and decrease over time, respectively.

The mechanism proposed above for trapping the photogenerated halide radicals suggests that the photoreduction processes in these materials are completely irreversible. Experiments carried out with ZrPV(Br) thin films demonstrate that a substantial reversible component is active in its photoreduction, leading to the formation of charge-separated states. Exhaustive photolysis of a ZrPV(Br) thin film leads to reduction of the viologen groups. When the UV light is removed, the blue color of reduced viologen gradually fades. The intensities of the bands due to reduced viologen decrease over 2 h to *ca.* 10% of their original values (*e.g.* see Figure 8) but do not fade completely. The same behavior is observed on repeated photolyses of these films. Under identical conditions a ZrPV(Cl) film shows a higher degree of photoreduction and does not show significant bleaching of the reduced viologen bands over 2 h. The explanation for why ZrPV(Br) and ZrPV(Cl) films behave differently may involve a difference in the rates of hydrogen atom abstraction by the two halogen radicals. Hydrogen atom abstractions by chlorine atoms are much faster than those by bromine atoms,[27] so chlorine atoms should be much more rapidly trapped by hydrogen atom abstraction than bromine atoms. Hydrogen atom abstraction by bromine atoms may be slow enough to allow a reasonable steady-state concentration of Br atoms to be formed under photolytic conditions. These bromine atoms could diffuse away from the reduced viologen and combine

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with other bromine atoms to give Br_2 or react with Br^- to give $Br_2^{\bullet -}$. The larger size of these Br_2 molecules would slow their diffusion back through the lattice relative to that of bromine atoms, significantly slowing the rate of back electron transfer but not preventing it. Some hydrogen atom abstraction would be expected for ZrPV(Br), which would account for the reduced viologen that does not fade thermally. A process similar to this one has also been proposed for the photochromism observed for viologen halides in polymer matrices.[9c,d]

Conclusions. Long-lived charge-separated states can be formed photochemically in layered zirconium viologen phosphonates. Similar photochemistry has been observed for both microcrystalline and thin-film samples of this material, with a measured quantum yield of 0.15 for formation of the charge-separated state in the thin films. Evidence has been provided which suggests that the mechanism for formation of charge-separated states in these materials involves both irreversible and reversible components. An irreversible component is proposed to involve hydrogen atom abstraction by photochemically formed halide radicals, followed by structural rearrangements. We are currently studying these structural rearrangements in more detail, as well as examining the reversible mechanism for formation of the charge-separated state in greater detail. Optimization of this reversible process may make it possible to use these materials for efficient conversion and storage of photochemical energy.

Experimental Section

General Methods. FTIR spectra were obtained on a Nicolet 730 FTIR spectrometer. Powder X-ray diffraction (XRD) patterns were obtained by using a Scintag PAD-V diffractometer (CuKα radiation). Fluorescence measurements were obtained on a Perkin Elmer 2850 luminescence spectrometer. UV–visible spectra of solutions and thin films were obtained on a Hewlett Packard 8452A diode array spectrometer. Diffuse reflectance spectra were obtained with a Cary 14 spectrophotometer. ^{13}C and ^{31}P solid-state NMR spectra were recorded on a JEOL 270-MHz spectrometer (67.9 and 109 MHz for ^{13}C and ^{31}P, respectively) equipped with a 7-mm magic angle spinning (MAS) probe from Doty Scientific. High-power ^{1}H decoupling, cross polarization (CP), and MAS were employed for all ^{13}C and ^{31}P spectra. A 50-kHz field strength was used for both ^{1}H decoupling and cross polarization; spinning speeds were approximately 3.5 kHz. ^{13}C signals were referenced to TMS (downfield shifts positive) by using adamantane as a secondary external reference. ^{31}P signals were externally referenced to 85 wt % H_3PO_4 (downfield shifts positive). Proton decoupled ^{31}P solution NMR spectra were obtained on a Bruker WM-250 NMR spectrometer equipped with a broad band probe (109 MHz for ^{31}P) and were externally referenced to H_3PO_4. ^{1}H and ^{13}C solution NMR were obtained on a GE QE-300 NMR spectrometer.

Fluorescence lifetime measurements for ZrPV(X) were obtained with an excimer pump dye laser (Questek 2420 and Lambda Physik 2002E, respectively) with a pulse duration of 10 ns (frequency doubled using BBO to obtain 280-nm excitation, band pass = 0.4 cm^{-1}). The UV radiation was used to excite the compound which had been deposited on a mirror. Fluorescence from the compound was collected by a lens at 90° to the incident radiation and focused at the entrance slit of an Oriel Model 7420 single monochromator. Output from the monochromator was detected by a General Electric GL931A PMT (rise time = 2 ns) and recorded by a Biomation 8100 transient recorder interfaced to a Nicolet 1170 signal averager system. The detected decays were shorter than the estimated 20-ns maximum time resolution of the apparatus.

Unless otherwise noted, all chemicals were purchased from Aldrich Chemical Co. and used without further purification.

Synthesis of Viologen Bisphosphonates. The viologen bisphosphonate dichloride and dibromide compounds [$H_2O_3PCH_2CH_2$(bipyridinium)$CH_2CH_2PO_3H_2)X_2$, (X = Cl, Br)] were synthesized as reported elsewhere.[10] (^{1}H NMR (D_2O) 9.1 (d), 8.5 (d), 4.2 (m), 2.0 (m) ppm; ^{13}C NMR (D_2O) 151, 147, 128, 58, 30 ppm; ^{31}P NMR (D_2O) 17.8 (s) ppm; IR (KBr) 3112, 3014, 1640, 1555, 1506, 1443, 1358, 1281, 1175, 1112, 1020, 936, 816, 485 cm^{-1}.)

The Viologen bisphosphonate bis(tetraphenyl borate) salt [($H_2O_3PCH_2CH_2$(bipyridinium)$CH_2CH_2PO_3H_2$)(BPh_4)$_2$] was prepared by dissolving viologen bisphosphonate dichloride in a minimum amount of H_2O and adding this solution to a saturated solution of sodium tetraphenylborate.[30] The orange solid was filtered and washed with H_2O and air-dried. ^{1}H NMR (D_2O) 9.1 (d), 8.5 (d), 7.4(t), 7.2 (m), 7.0 (m), 4.2 (m), 2.0 (m) ppm.

Viologen octadeuterio bisphosphonate [($H_2O_3PCD_2CD_2$(bipyridinium)$CD_2CD_2PO_3H_2)X_2$] was prepared by procedures very similar to those used for the perprotio analogue. Reaction of perdeuterio-1,2-dibromoethane with triethyl phosphite at elevated temperatures affords the tetradeuterio diethyl bromoethyl phosphonate [$(EtO)_2P(O)CD_2CD_2Br$], which was purified by distillation. ^{1}H NMR (acetone) 4.1 (m), 1.3 (t). Octadeuterio viologen bisphosphonate was prepared by the reaction of this tetradeuterio compound with 4,4′-bipyridine, as described previously.[10] ^{1}H NMR (D_2O) 9.1 (d), 8.5 (d) ppm; IR (KBr) 3112, 3021, 1637, 1548, 1499, 1443, 1178, 1069, 1034, 994, 817 cm^{-1}.

Zirconium Phosphonate Viologen Chloride, (ZrPV(Cl)). $ZrOCl_2{\cdot}8H_2O$ (0.92 g) was dissolved in approximately 50 mL of H_2O, and 0.484 g of 50% HF (Fisher) was added. Viologen bisphosphonate dichloride (1.3 g) was dissolved in 50 mL of H_2O and added to the aqueous zirconium solution. The solution was heated to reflux for 7 days. The resulting crystalline white solid was filtered and washed with H_2O, methanol, and acetone and air-dried. ^{13}C NMR (CPMAS) 147, 129, 66, 29 ppm; ^{31}P NMR (CPMAS) 7.9 ppm; IR (KBr) 3126, 3056, 1640, 1563, 1506, 1450, 1393, 1161, 1119, 1055, 872, 802, 767, 717, 569, 478 cm^{-1}. Total weight loss on heating to 1000 °C:[31] calc, 50.2%; obs, 50.1%.

Zirconium Phosphonate Viologen Bromide (ZPV(Br)). The bromide compound was prepared in a similar manner. $Zr(SO_4)_2$ (0.533 g) was dissolved in 50 mL of H_2O and 0.317 g of 50% HF was added. Viologen phosphonate dibromide (1 g) was dissolved in 50 mL of H_2O, and this solution was added to the aqueous zirconium solution. The solution was refluxed for 7 days, and the resulting white solid was isolated in the same manner as that for the chloride compound. ^{31}P NMR (CPMAS) 8.9 ppm; IR (KBr) 3112, 3014, 1640, 1555, 1506, 1443, 1358, 1281, 1175, 1112, 1020, 936, 816, 485 cm^{-1}. Total weight loss on heating to 1000 °C:[31] calc, 57.3%; obs, 57.5%.

Zirconium Phosphonate Viologen Iodide (ZPV(I)). $Zr(SO_4)_2$ (0.317g) was dissolved in 65 mL of H_2O, and 50% HF (0.189 g) was added. Viologen bisphosphonate bis(tetraphenylborate) (0.567 g) was slurried in 65 mL of H_2O, and NaI (2 g) was added. The slurry was added to the aqueous zirconium solution and heated to reflux for 7 days. The resulting yellow solid was isolated in the usual manner. The solid was further purified by stirring in boiling water to remove any excess viologen bisphosphonate tetraphenylborate which might remain. The resulting off-white solid was filtered and washed in the usual manner. ^{31}P NMR (CPMAS) 9.3 ppm; IR (KBr) 3126, 3056, 1640, 1563, 1506, 1450, 1393, 1112, 830, 802, 738, 548, 428 cm^{-1}.

Synthesis of Deuterated ZrPV(Cl). Deuterated ZrPV(Cl) was prepared as described above, except that the deuterated viologen bisphosphonate dichloride was used. IR (KBr) 3125, 3049, 1638, 1555, 1506, 1444, 1169, 1061, 705, 542 cm^{-1}. Thermal analysis: calc, 49.4%; obs, 49.4%.

Preparation of Thin Films. Thin films of ZrPV(Cl) and ZrPV(Br) were grown using methodology developed by Mallouk[19] and Katz.[20] Fused-silica slides were cleaned in a 1:3 solution of 30% H_2O_2 and concentrated H_2SO_4 at room temperature for 1 h. Dry slides (200 °C for 1 h) were refluxed in a solution composed of 2% (3-aminopropyl)triethoxysillane (purchased from Hüls America Inc.) in octane for 20 min. The slides were rinsed with octane and acetonitrile and then phosphorylated by treatment with an acectonitrile solution of $POCl_3$ and 2,6-lutidine (10 mM in each) for 12 h at room temperature. The slides were then rinsed with water and zirconated in a 65 mM solution of $ZrOCl_2$ for 3 h at room temperature. Multilayers of ZrPV(X) (X = Cl, Br) were produced by alternate dippings in 6 mM viologen bisphosphonic acid, ($H_2O_3PCH_2CH_2$(bipyridinium)$CH_2CH_2PO_3H_2)X_2$, at 80 °C for 4 h and $ZrOCl_2$ solution at room temperature for 1 h. Films were thoroughly rinsed with deionized water between dippings. UV–vis absorption measurements were taken after phosphonic acid treatments. These measurements were typically taken at 284 nm. The measured extinction coefficient for the viologen bisphosphonate is 24 000 M^{-1} cm^{-1} at 260 nm. Viologen octadeuterio bisphosphonate thin films were prepared in the same manner as that described above.

Preparation and ^{31}P NMR Study of Multilayer Films on Silica Gel. Five monolayers of zirconium phosphonate were grown on silica gel

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(31) Burwell, D. A.; Thompson, M. E. *Chem. Mater.* **1991**, *3*, 730.

following the method of Mallouk.[32] Silica gel (1.75 g) was added to a filtered solution containing 9.4 g of $ZrOCl_2{\cdot}8H_2O$ in 500 mL of Millipore-filtered H_2O. The slurry was heated at 65 °C for 2 days and then filtered and washed with copious amounts of H_2O. The solid was slurried in H_2O again and stirred for 1 h and then filtered and washed again. The slurry, filtration, and washing was repeated a total of three times. The resulting solid was then added to a solution containing 445 mg of viologen bisphosphonate dichloride and 400 mL of H_2O, and this solution was stirred at 25 °C for 2 days. The solid was filtered and washed three times as described above. The procedure was repeated four times at room temperature, resulting in five layers of zirconium phosphonate viologen. Samples were prepared for NMR study by suspending 0.3 g of the coated silica gel in 3 mL of D_2O and adding the minimum amount of concentrated HF (3–5 drops) to dissolve all of the solid. NMR spectra were recorded as described above.

Photophysical Measurements for Microcrystalline ZrPV(X). The photoaction curves for the ZrPV(X) were obtained by irradiating each of the samples as an aqueous suspension in a 1-mm quartz cuvette. Photolysis was carried out with a 200-W Hg/Xe lamp equipped with a monochromator. Detection of the viologen radical was achieved by measuring the change in transmittance of a helium–neon laser (633 nm). The change in transmittance was plotted as a function of time. A plot of the change in transmittance vs time is linear at first but gradually approaches a saturation point. This is a result of the inability of the ultraviolet light to penetrate deep into the sample, due to the highly scattering nature of the microcrystalline material. The only data points considered were those on the linear portion of the curve. Formation of product was calculated as change in absorbance (–log of transmittance) corrected for lamp intensity and time of irradiation.

The samples for the measurement of the deuterium isotope effect in the photoreduction of ZrPV(Cl) were prepared as described above for the photoaction curves. Both the deuterated and nondeuterated samples were irradiated with the Hg/Xe lamp with the monochromator set at 300 nm. The change in transmittance for each was calculated and plotted vs time as described above.

Photophysical Measurements on Multilayer Thin-Film Samples. Slides with 10–12 layers (abs ≈ 0.4–0.5 at 265 nm) were used for photoaction and quantum yield measurements. All photophysical measurements were performed with the samples under vacuum (*ca.* 10^{-4} Torr). The photoaction spectra for ZrPV(Cl) films were generated by photolysis with a 200-W Hg/Xe arc lamp equipped with a monochromator (band-pass set to 10 nm). The amount of reduced viologen generated after a given photolysis time was determined by measuring the change in transmittance at 405 and 605 nm ($\epsilon_{405} = 40\,000$ M^{-1} cm^{-1}, $\epsilon_{605} = 13\,000$ M^{-1} cm^{-1}).[21] The light source for the transmittance measurements was the Hg/Xe lamp, and the intensity was measured using a Newport Instruments Si radiometer positioned behind the sample. The reduced viologen concentrations were corrected for changes in lamp intensity as a function of wavelength. Quantum yields were determined at 275 nm using the same procedure as above. The lamp intensity for the quantum yields was determined using a ferrioxalate actinometer.[33]

Acknowledgment. The authors would like to thank Andrew Bocarsly and T. Andrew Ronneberg for helpful discussions and Mr. Martin Mason for help with the fluorescence lifetime measurements. Financial support for this project has come from the National Science Foundation (Grant DMR-9113002) and the Princeton Materials Institute.

Supplementary Material Available: Powder X-ray diffraction patterns for ZrPV(X) and a listing of 2θ and relative intensity values (4 pages). Ordering information is given on any current masthead page.

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