Synthesis and Photochemical Properties of Porous Zirconium Viologen Phosphonate Compounds

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We recently reported stable, photoinduced charge separation in layered zirconium phosphonate viologen compounds ($Zr(O_3PCH_2CH_2(bipyridinium)CH_2CH_2PO_3)X_2$ (X = Cl, Br, I), ZrPV(X)). Here we report the synthesis and photochemical properties of porous versions of this material. Porosity can be built into the material by preparing a layered solid from a mixture of the large viologen bisphosphonic acid and a smaller phosphorus acid (i.e., $Zr(O_3P-R)_1(O_3PCH_2CH_2(bipyridinium)CH_2CH_2PO_3)_{0.5}C$; R = O⁻, OH, H, alkyl). These materials were characterized by powder X-ray diffraction and IR and NMR spectroscopies. The resulting structures are microporous and undergo photoreduction of the viologen at a faster rate than in ZrPV(X) compounds. Evidence for the porosity in these mixed materials is seen in the air sensitivity of the photoreduced species. Photoreduction of the viologen groups is observed only under anaerobic conditions, and the photoreduced solid is bleached immediately and quantitatively in the air. In contrast the close-packed analogs (ZrPV(X)) can be photoreduced and are moderately stable in the air. Detailed photophysical and isotopic labeling studies suggest that the mechanism for photoreduction of viologen in these materials is similar to that proposed for ZrPV(X).

Introduction

Photoinduced electron-transfer reactions in both homogeneous and heterogeneous media 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.[2] Both theoretical and experimental studies have shown that controlling the rates of forward and back electron transfers requires control of both electronic and structural properties of the system.[2] Heterogeneous systems have been used to accurately control the structural arrangement of molecular donors and acceptors.[3] These heterogeneous systems can provide the appropriate spatial organization to control the rates of electron transfer, leading to long-lived charge separation. Zeolites,[4] clays,[5] sol–gel glasses,[6] layered metal oxides,[7] semiconductor and metal colloids,[8]

synthetic monolayers,[9] and other molecular assemblies[10] 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.

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, I), ZrPV(X).[1,11] These layered compounds show efficient photoinduced charge transfer and form a charge-separated state which is long-lived and stable in the air. Photolysis of the zirconium viologen phosphonate compounds by solar radiation or a UV lamp leads to a blue solid. Spectroscopic

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studies indicate that the photoproduct is the dialkylviologen 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 color does not fade over several days. Transparent thin films of the same material can be prepared allowing the measurement of an accurate quantum yield. The viologen groups of ZrPV(Cl) are reduced with a quantum yield of 0.14 at 275 nm (this wavelength is λ_{max} in the photoaction spectrum).[11] The photoreduction of viologen in these materials has been attributed to charge transfer from the halide counterions. Different pathways are observed for the trapping of the halogen radicals formed in this process, depending on the identity of the halide. For films of ZrPV(Cl) the Cl• is trapped principally by an irreversible mechanism, while for ZrPV(Br) Br• trapping is highly reversible.[1,11]

The present report concerns the synthesis and study of porous versions of these photoreducible zirconium viologen phosphonates. Porous solids have been used for the assembly of interesting systems, which form long-lived charge-separated states on photolysis.[3,4a,b,12] In these materials, acceptors and donors are typically located on the inside and outside of zeolite particles, respectively. The zeolite in this case is an inert matrix, which spatially organizes acceptors and donors, facilitating photoinduced charge separation. In the class of materials reported here, porous solids have been prepared in which the acceptor groups themselves make up the porous matrix. Mixed phosphonate–phosphate and phosphonate–phosphite compounds have been prepared, in which the viologen bisphosphonate groups act to pillar the zirconium phosphonate lamellae, creating open space in the interlamellar gallery. In these materials the photoreduced viologen groups can be quantitatively oxidized by external substrates. For example, the photoreduced viologen groups of these porous materials are bleached quantitatively within seconds of exposure to air, contrary to ZrPV(Cl). These porous mixed materials are active photochemical matrices, whereas zeolites are inert. The syntheses and photophysical properties of these porous mixed phosphate–phosphonate and phosphite–phosphonate compounds will be described below.

Results and Discussion

Synthesis of Porous Mixed Phosphate–Phosphonate and Phosphite–Phosphonate Compounds. The structural chemistry of zirconium phosphates and phosphonates has been studied by several groups.[13] These compounds are generally found to have layered structures. Each layer consists of a plane of metal atoms linked together by phosphate or phosphonate tetrahedra, with three oxygens of each tetrahedron bound to three different metal atoms. This arrangement forces the fourth group (organic for phosphonates, hydroxyl for phosphate) to lie above and below the inorganic layer. For metal phosphonates, the size of the organic group determines the
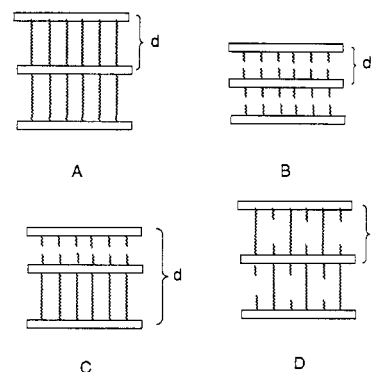
Figure 1. Possible products generated from the reaction of a bisphosphonate H_2O_3P–R–PO_3H_2; $R = \alpha,\omega$-alkyl) and a phosphorus acid H_2O_3P–R' (R' = OH, H, alkyl) with Zr^{4+}. d refers to the interlayer spacing.

interlayer spacing. Microporous zirconium phosphates, phosphites, and phosphonates have been prepared by the reaction of Zr^{4+} with two different acids (i.e., HO–PO_3H_2, H–PO_3H_2 or R–PO_3H_2, R = alkyl or aryl).[13b,14] The result is a layered solid in which the larger organic group now determines the interlayer repeat spacing. Alternatively, microporous solids have also been prepared by using a small phosphorus acid and a bisphosphonic acid which covalently links adjacent layers; the bisphosphonic acid then acts as a pillar holding the layers apart.[15]

Treatment of Zr^{4+} with a mixture of a bisphosphonic acid (i.e., H_2O_3P–R–PO_3H_2; $R = \alpha,\omega$-alkyl) and R'–PO_3H_2 (R' = OH, H, alkyl) will result in the formation of materials containing the mixture of acids (Figure 1). The possible products generated in these reactions include a mixture of pure zirconium bisphosphonate (A), the zirconium compound of the other phosphorus acid (i.e., $Zr(O_3P$–$R')_2$, B), mixed component materials in which both acids are contained within the same crystal or an amorphous material. The materials composed of an intimate mixture of the two acids can have two different crystalline forms. In one form the different acids are segregated into different layers (C), and in the other two, acids are mixed within a given layer (D), leading to a porous structure as shown in Figure 1.[16] The actual structures obtained can be evaluated by X-ray powder diffraction. A and B will have X-ray diffraction patterns identical to the authentic materials. C will give rise to an interlayer spacing that is the sum of those for A and B, while D will give an interlayer spacing which is close to that of A.

A mixed phosphate/viologen phosphonate, $Zr(PO)PV$-(X), was synthesized by treatment of a 2:1 ratio of orthophosphoric acid:viologen bisphosphonic acid with $ZrOCl_2$ in refluxing H_2O/HF. The powder X-ray diffraction pattern of the resulting product is shown in Figure 2. It shows no peaks attributable to ZrPV(X) or to zirconium hydrogen phosphate. This pattern is consistent with the formation of a new material where both –OH and
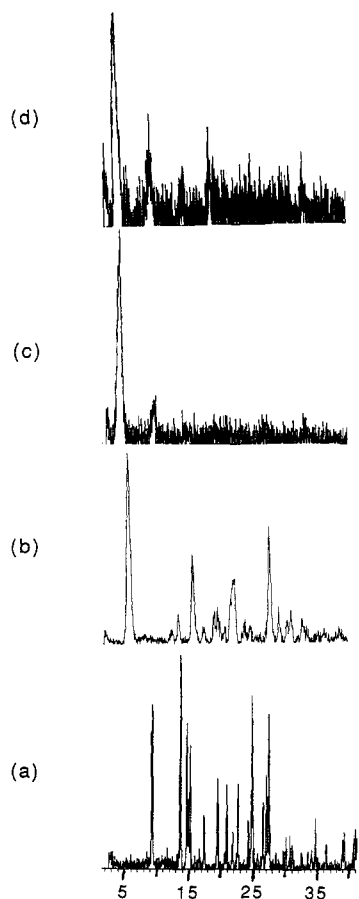
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(16) An alternate possibility for C has the layers of A and B separated into different regions of a given crystal, rather than regularly alternating as shown. The former possibility would given an X-ray pattern showing only lines due to A and B.
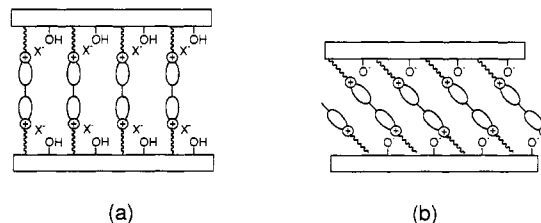
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Figure 2. X-ray powder patterns of (a) ZrPV(Cl), (b) Zr(PO)-PV(Cl), (c) Zr(PO)PV(Cl) prepared in 1 M HCl, and (d) Zr-(PH)PV(Cl).
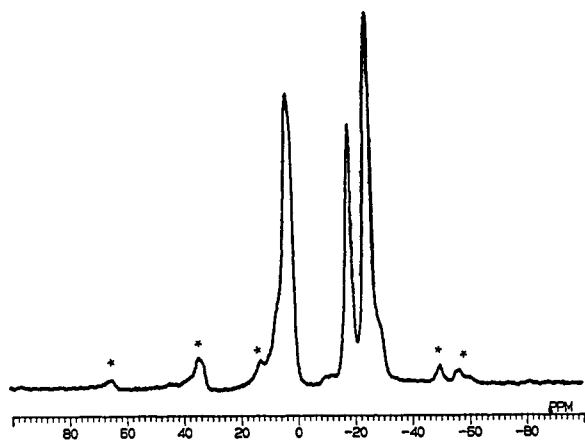
Figure 3. ^{31}P CPMAS solid-state NMR spectrum of Zr(PO)-PV(X). Asterisks indicate spinning side bands.

Figure 4. Proposed structures of Zr(PO)PV(X). ⊕-⊕ = viologen groups, ⌇⌇ = –CH$_2$CH$_2$–, and the bars represent the zirconium phosphonate lamellae.

viologen groups are found in the same layer, with an interlayer spacing of 13.6 Å. This spacing is smaller than would be expected for the bisphosphonate pillared material (models suggest a spacing of ca. 18 Å for ZrO$_3$PCH$_2$-CH$_2$(bipyridinium)CH$_2$CH$_2$PO$_3$). ^{31}P CPMAS NMR of this material shows the presence of three types of phosphorus (Figure 3). The resonance at 3.0 ppm is at the same frequency observed for ZrPV(X). The resonances at –18.6 and –24.5 ppm are due to protonated and deprotonated phosphate groups, respectively.[17] These data suggest that there are a mixture of two phases in this material. In one phase, the phosphate is protonated and halide counterions must be present to balance the charges on the viologen (Figure 4a). In the other phase, the phosphate is deprotonated and serves to balance the

charges on the viologen (Figure 4b). The latter structure fits the X-ray data the best.

The reactivity of this mixed material is consistent with the deprotonated phase being tightly packed as shown in Figure 4b and the protonated phase being porous in nature, Figure 4a. Refluxing the solid in HCl for several hours does not change the ratio of ^{31}P peaks in the CPMAS NMR spectrum due to protonated and deprotonated phosphate. Intercalation with HCl into the tightly packed deprotonated phase does not occur. However, the solid can be ion exchanged with KBr or KI. Ion-exchange with KI yiels an orange solid, consistent with formation of a viologen iodide charge-transfer salt. Therefore, the Zr-(PO)PV(X) phase which contains the halide counterions must be porous in order to allow for ion exchange. Ion exchange does not occur with the closely-packed pure-phase materials, ZrPV(X).

To obtain the purely open structure of the phosphate/viologen phosphonate, the synthesis was carried out in 1 M HCl. The X-ray pattern for this material shows the presence of a single phase (d = 18.5 Å, Figure 2) consistent with the porous structure shown in Figure 4a. This material is readily exchangeable with KI, resulting in the formation of an orange solid. The absence of lines associated with this phase in the powder X-ray diffraction pattern of Zr(PO)PV(X) (Figure 4b) suggests that either the porous phase in that material is amorphous or the domain size is small enough that the lines are not observed.

A mixed phosphite/phosphonate, Zr(PH)PV(X), was synthesized by treatment of Zr^{4+} with a 2:1 mixture of phosphorous acid:viologen bisphosphonate. The X-ray powder pattern of the product is shown in Figure 2. The X-ray powder pattern shows the presence of both ZrPV-(X) and a new phase (d = 18 Å), but no Zr(O$_3$PH)$_2$ (d = 5.5 Å). The powder pattern of the new phase is very similar to that of the sample of Zr(PO)PV(X) prepared in 1 M HCl. The ^{31}P CPMAS NMR spectrum shows only two types of phosphorous (one phosphonate at 5.5 ppm and one phosphite at –9.5 ppm). Both X-ray and NMR data are consistent with a mixed-component material, whose structure is similar to the porous structure shown in Figure 4a. The phosphite/viologen phosphonate is readily ion-exchanged with Br$^-$ and I$^-$ (generating yellow and orange solids, respectively), indicating that the structure is indeed porous.

Zr(PH)$_x$(PV(X))$_y$ was synthesized by using various ratios of phosphorous acid:viologen bisphosphonates. It was found that the crystallinity depends heavily upon this ratio. The least crystalline material results when a 6:1 ratio is used. Pure Zr(O$_3$PH)$_2$ is not observed in the X-ray patterns of any of the materials.

(17) The difference in chemical shifts (5.9 ppm) is similar to that reported for protonated and deprotonated zirconium hydrogen phosphate. MacLachlan, D. J.; Morgan, K. R. *J. Phys. Chem.* **1990**, *94*, 7656–7661.

Other porous materials were synthesized using a variety of different phosphonic acids. These include H_2O_3P-R; R = $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-CH_2CH_2COOH$, $-CH_2C_6H_5$, $-C_6H_5$, $-CH_2Cl$, and $-CH_2CH_2Br$. These compounds have the general formula $Zr(O_3P-R)_1(O_3PCH_2-CH_2(bipyridinium)CH_2CH_2PO_3)_{0.5}Cl$. All give X-ray powder patterns which are consistent with a mixed-component porous material (Figure 1D; see supplementary material). Most of these materials also show lines attributable to ZrPV(X) in their powder patterns.

Photolysis of Zr(PO)PV(X) and Zr(PH)PV(X). Photolysis of these two mixed-component materials with a mercury arc lamp in the presence of oxygen does not result in any color change of the material. This result is expected based upon the proposed porous structures. Photolysis of ZrPV(X) results in permanent color change in the presence of air because the reduced viologen is generated inside the crystals and is protected from air oxidation.[1] In the mixed-component materials, however, the porous structure would not prevent oxygen from diffusing into the material and bleaching the photoreduced viologen. The deprotonated phase of Zr(PO)PV(X) phase should be a more closely packed structure; however, there are no halide ions present in this phase. If the halide counterions are indeed necessary for forming the charge-separated state, as suggested previously,[1,11] this close-packed phase should not undergo photoreduction.

When oxygen is excluded, however, the viologen groups of Zr(PO)PV(X) and Zr(PH)PV(X) are reduced on photolysis, giving a blue solid (Figure 5). Side-by-side comparisons of ZrPV(Cl), Zr(PO)PV(Cl), and Zr(PH)PV-(Cl) show that photoreduction of the mixed materials are faster and more complete than in ZrPV(X). Simultaneous photolysis of ion-exchanged Zr(PO)PV(X) and Zr(PH)-PV(X) show different rates of photoreduction, which follow the trend Cl > Br > I as is observed in ZrPV(X). This halide ion dependence supports the proposal that the deprotonated phase of Zr(PO)PV(X) is not photoactive, since this phase should not be influenced by changing the halide ions. Contrary to the pure viologen materials, the mixed-component materials are rapidly and completely bleached when exposed to oxygen.

Most of the materials reported here turn blue on photolysis, however, two samples were observed to turn purple. The purple color is observed for the phosphite when the synthesis was carried out with a 2:1 ratio of phosphorous acid to viologen and for the phosphate which was prepared as the solely porous phase (synthesis in 1 M HCl). The spectra obtained by diffuse reflectance for the purple solids (λ_{max} = 405, 450, 600 nm) is consistent with the formation of viologen dimers; see Figure 5.[18] There is no evidence for dimer formation in ZrPV(X) or in analogous thin films.[11] Dimers are presumably formed in these two compounds because the yield for photoreduction is high and the open structure of the porous solid allows the viologen radicals to adapt the correct configuration for dimer formation.

Photolyzed Zr(PO)PV(X) and Zr(PH)PV(X) are EPR active. They both show a peak (g = 2.0003; width = 14 G), similar to ZrPV(X). This is expected because the viologen radicals should still be close enough to undergo rapid electron exchange with adjacent diamagnetic viologen compounds.[19] The purple materials also show some paramagnetism, indicating that there must still be isolated
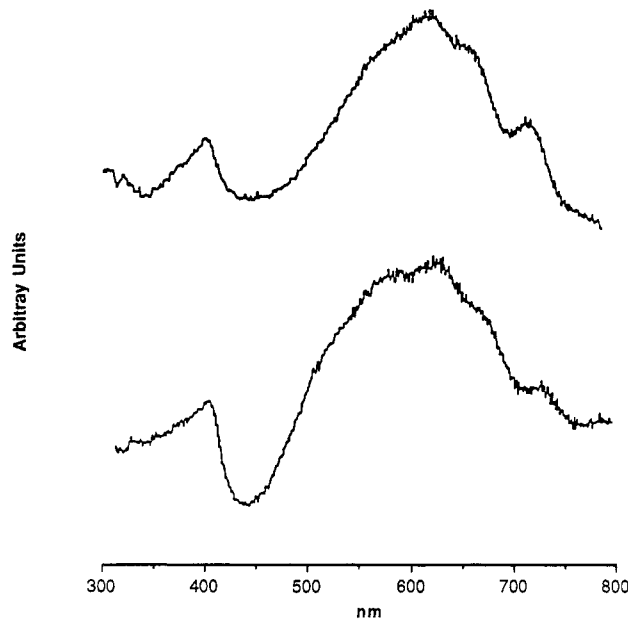
Figure 5. Diffuse reflectance spectra of photolysed blue Zr-(PO)PV(X) (top) and purple Zr(PH)PV(Cl) (bottom).

monomer present, since the dimer is EPR silent. This is also consistent with the absorption spectrum which shows the presence of both monomer and dimer.

The photoaction spectra for these porous materials is similar to that of ZrPV(X) with maximum efficiency for photoreduction occurring at approximately 300 nm. The primary photochemical event has been proposed to be a viologen-centered transition, followed by thermal electron transfer from the halide counterions.[11] The porous solids also exhibit luminescent properties similar to ZrPV(X) (excitation at 285 nm leads to emission at 340 nm). However, the luminescence is observed only under anaerobic conditions for the porous solids, whereas ZrPV(X) fluoresces in the presence of oxygen.

The photoreduction of viologen groups in ZrPV(Cl) has been proposed to involve charge transfer from chloride ions to photoexcited viologen groups. The chloride radicals are then trapped in either a reversible or an irreversible reaction. The latter process involves hydrogen atom abstraction from phosphonate methylene groups by the chloride radicals.[20] A similar process could be envisaged for Zr(PH)PV(X), in which a halide radical could abstract a hydrogen atom from the phosphite (O_3P-H) as well as from the alkyl chain of the viologen (see Scheme 1). It has been recently reported that the related phosphorus based radical ($^2-O_3P^\bullet$), generated by H atom abstraction from phosphorous acid at pH = 11, reduces viologen at near diffusion-controlled rates in solution to give ^-O_3P.[21] Thus in the photoreduction of Zr(PH)PV(Cl) a single photon would give rise to 2 equiv of reduced viologen (see Scheme 1). This would explain the faster rate of photoreduction which is observed for the porous phosphite/phosphonate as compared to ZrPV(X). This mechanism would be supported by a primary deuterium isotope effect when deuterium is substituted for the phosphite hydrogen. Zr-

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(20) Evidence for this hydrogen atom abstraction was obtained by measuring the quantum yield for photoreduction of $Zr(O_3PCR_2-CR_2(viologen)CR_2CR_2PO_3)Cl_2$ for R = H and D. The measured quantum yields are 0.15 and 0.05, respectively, giving a k_H/k_D of 3. See ref 11.

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(PD)PV(X) was prepared by first treating phosphorus acid with D_2O to generate D_2O_3PD and then preparing the mixed phosphite/phosphonate in the normal manner in D_2O solvent. The product obtained has the same X-ray powder pattern as the perprotio analog. The rate of photoreduction for each sample ($h\nu$ = 300 nm) was estimated by monitoring transmission of a He–Ne laser through a degassed aqueous suspension of each solid. The rate of photoreduction was 3–4 times faster for the perprotio than for the deuterio sample, supporting the proposal that hydrogen atom abstraction from the phosphite is involved in this photoreduction. This deuterium isotope effect is similar to that found for ZrPV(X) materials.[20]

A further piece of evidence in favor of hydrogen atom abstraction from phosphorus in the photoreduction of Zr-(PH)PV(Cl) comes from ^{31}P NMR of dissolved solids. When an exhaustively irradiated sample of Zr(PH)PV-(Cl) is dissolved in HF/D_2O three ^{31}P resonances are observed. Signals at 21 and 5 ppm are observed, due to the bisphosphonic and phosphorous acids, respectively. A signal at 0 ppm is also observed, which is due to orthophosphoric acid. Hydrogen atom abstraction, followed by oxidation of phosphorous acid leads to orthophosphoric acid in aqueous solution.[21] ^{31}P NMR of solutions from dissolution of Zr(PH)PV(Cl) which has not been irradiated shows only signals at 21 and 5 ppm.

We have demonstrated that porous solids can be prepared of the general formula, $Zr(O_3P-R)(O_3PCH_2-CH_2(\text{viologen})CH_2CH_2X_2)_{0.5}$, R = OH, H, alkyl, X = halide. These solids are microporous and undergo photochemical reduction of viologen upon ultraviolet irradiation. The porous nature of the solids make it possible to ion exchange other electron donors and/or anions for the halide ions, which may allow the photochemistry to be pushed into the visible region of the solar spectrum. The photochemically reduced viologens in these solids may be useful as size- and shape-selective reductants, since the pore size may be controlled by the choice of the R group. In addition, we are currently working on incorporating colloidal metal particles into these materials. These metal particles could act as catalysts for the reduction of substrates, which are not reduced by the viologen radical cation for kinetic reasons (e.g., the reaction of $2H^+$ to H_2).

Experimental Section

General Methods. ^{31}P solid-state NMR spectra were recorded on a JEOL 270-MHz spectrometer (109 MHz) equipped with a 7-mm magic angle spinning (MAS) probe from Doty Scientific. High-power ^1H decoupling, cross polarization (CP), and MAS were employed for all ^{31}P spectra. A 50-kHz field strength was used for both ^1H decoupling and cross polarization; spinning speeds were approximately 3.5 kHz. ^{31}P signals were externally referenced to 85 wt % H_3PO_4 (downfield shifts positive). ^{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.

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 (Cu Kα radiation). Fluorescence measurements were obtained on a Perkin-Elmer 2850 luminescence spectrometer. Diffuse reflectance spectra was obtained with a Cary 14 spectrophotometer. EPR spectra were obtained on a Bruker ESP 300/ER 200 D Series spectrometer (100-kHz field modulation). All chemicals were purchased from Aldrich and used without further purification unless otherwise noted.

Phosphate/Viologen Phosphonate (Zr(PO)PV(X)).

Scheme 1
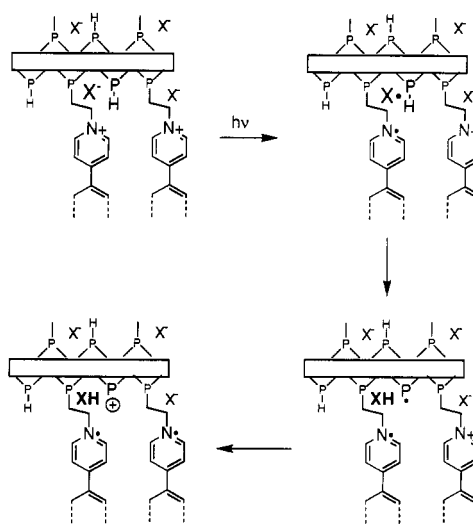
HF (0.189 g) was added. Viologen bisphosphonate dichloride (0.25 g) and 85% phosphoric acid (0.129 g) were dissolved in 25 mL of H_2O, and this solution was added to the aqueous zirconium solution. The reaction was heated to reflux for seven days and the white crystalline product isolated by filtration. The solid was washed with water, methanol, and acetone before air drying. IR (cm^{-1}), 3126, 3056, 1633, 1562, 1499, 1450, 1217, 1055, 816, 738, 647, 612, 520, 471. ^{31}P NMR (ppm) 3.0, –18.6, –24.5. Powder X-ray, 2θ (Å) 6.5 (13.49), 12.98 (6.82), 14.06 (6.29), 16.34 (5.42), 17.78 (4.98), 19.62 (4.52), 19.82 (4.48), 22.14 (4.01), 22.64 (3.92), 28.15 (3.17), 29.49 (3.03), 30.74 (2.91), 31.39 (2.85), 33.18 (2.70).

Phosphite/Viologen Phosphonate (Zr(PH)PV(Cl). $ZrOCl_2\cdot 8H_2O$ (0.724 g) was dissolved in 50 mL of H_2O, and 50% HF (0.389 g) was added. Viologen bisphosphonate dichloride (0.5 g) and phosphorous acid (0.184 g) were dissolved in 50 mL of H_2O, and this solution was added to the aqueous zirconium solution. The reaction was heated to reflux for 7 days, and the white crystalline product isolated by filtration. The solid was washed with water, methanol, and acetone before air drying. IR (cm^{-1}) 3126, 3056, 2436, 1633, 1555, 1499, 1443, 1386, 1210, 1161, 1048, 830, 731, 548. ^{31}P NMR (ppm) 5.5, –9.5. Powder X-ray, 2θ (Å) 4.74 (18.6), 9.74 (9.1), 14.53 (6.09), 19.00 (4.67).

Deuterated Phosphite/Viologen Phosphonate (Zr(PD)-PV(Cl)). Deuterated phosphite/viologen phosphonate was prepared as described above except that deuterated phosphorous acid was first prepared by stirring phosphorous acid in D_2O (monitoring exchange by NMR) prior to precipitation with zirconium. IR (cm^{-1}) 3126, 3056, 1781, 1732, 1633, 1555, 1499, 1450, 1048, 823, 781, 555.

Measurement of Photoreduction Rates. The photoaction curves for the ZrPV(X) pure phase materials were obtained by irradiating samples of an aqueous suspension of each in a 1-mm quartz cuvette. Each sample was irradiated with a mercury/xenon lamp equipped with a monochromator. Detection of viologen radical was achieved by measuring the change in transmittance of a helium–neon laser (633 nm), and the change plotted as a function of time. The change in transmittance vs time plot is linear at first but gradually approaches a saturation point which is a result of the inability of the UV light to penetrate completely through the sample. The only data points considered were those on the linear portion of the curve. Formation of product was calculated as change in absorbance (–log transmittance) corrected for lamp intensity at a given wavelength and time of irradiation.