Potentiostatic Modulation of the Lifetime of Light-Induced Charge Separation in a Heterosupermolecule

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A heterosupermolecule has been assembled by covalently linking a TiO_2 nanocrystal, a ruthenium complex, and a viologen. The associated heterosupramolecular function, long-lived light-induced charge separation, has been demonstrated. Potentiostatic modulation of this function has also been demonstrated. The reported findings and associated insights may find practical applications in the area of optical information storage.

Introduction

A supermolecule possesses the following attributes.^{1,2} First, the intrinsic properties of the linked molecular components are not significantly perturbed, and second, the properties of the supermolecule are not a simple superposition of the properties of the molecular components. That is, there exists a well-defined supramolecular function.

Upon replacement of a molecular component in a supermolecule by a condensed-phase component, a heterosupermolecule is formed.^{3–5} By analogy with a supermolecule, a heterosupermolecule possesses the following attributes. First, the intrinsic properties of the linked condensed-phase and molecular components are not significantly perturbed, and second, the properties of the heterosupermolecule are not a simple superposition of the properties of the condensed-phase and molecular components. That is, there exists a well-defined heterosupramolecular function.

An organized assembly of supermolecules offers the prospect of addressable supramolecular function (Scheme 1).⁶⁻⁸ By analogy, an organized assembly of heterosupermolecules offers the prospect of addressable heterosupramolecular function (Scheme 1). Both offer the prospect of devices based on function that is addressable on the nanometer scale.

With respect to devices based on supramolecular function addressable on the nanometer scale, an important objective is modulation of the functional state of the constituent supermolecules of an assembly. To fully meet this objective will require an ability to modulate a chemical or physical property of at least one of the molecular components of the supermolecules in the organized assembly. To date, modulation of the function of the constituent supermolecules of an organized assembly has been affected by modulating the properties of the assembly substrate or the contiguous medium.^{9–11} Neither approach has proved to be particularly effective.

With respect to devices based on heterosupramolecular function addressable on the nanometer scale, an equally important objective is modulation of the functional state of the constituent heterosupermolecules in an assembly. To fully meet this objective will require the ability to modulate a chemical or physical property of at least one of the constituent condensedphase or molecular components of the heterosupermolecules in the organized assembly. By comparison with a supramolecular assembly, therefore, the prospect of effective function modulation is more immediately envisaged. This is because modulation of a property of a nanometer-scale condensed-phase component is an increasingly realizable goal.^{12,13} Two approaches are envisaged.

The first approach involves organizing the heterosupermolecules of an assembly so that they build their own substrate (Scheme 2, top), termed an *intrinsic substrate*. Modulating a property of the intrinsic substrate, of necessity, modulates the same property of the condensed-phase component of each of the heterosupermolecules in the assembly. Since the function of a heterosupermolecule is determined by the properties of its components, effective function modulation is expected and has been observed.^{14–16} Furthermore, if the property of the intrinsic substrate can be monitored, then the modulation state of the heterosupermolecules in the assembly may be inferred.

The second approach involves organizing the heterosupermolecules of an assembly so that a property of a condensedphase component of each heterosupermolecule may be individually modulated (Scheme 2, bottom). With the advent of many new techniques for manipulating and characterizing condensed-phase matter on the nanometer scale,^{12,13} this is an increasingly realizable approach. Furthermore, if the property of the condensed-phase component can be monitored, then the modulation state of each heterosupermolecule in the assembly may be inferred.

The preparation and characterization of a heterosupermolecule consisting of a covalently linked TiO₂ nanocrystal, ruthenium complex (**R**), and viologen (**V**) components have recently been described (Scheme 3).¹⁶ Also described has been the covalent organization of these heterosupermolecules to form a heterosupramolecular assembly, denoted TiO₂–**RV**, in which effective function modulation via the intrinsic substrate formed by the TiO₂ nanocrystal components proved possible.

Specifically, the direction of light-induced electron transfer within the heterosupramolecular assembly was modulated by potentiostatically determining the quasi-Fermi level of the intrinsic substrate (Scheme 4) and, therefore, also the quasi-Fermi level of the TiO₂ nanocrystal component of each heterosupermolecule. At positive applied potentials, visible-light excitation of the **R** component results in electron transfer to the TiO₂ nanocrystal component (95%). At negative applied

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SCHEME 1

SCHEME 2



potentials, however, visible-light excitation of the **R** component results in electron transfer to both the TiO₂ nanocrystal (48%) and **V** components (52%).

Concerning the heterosupramolecular assembly TiO_2-RV , the following limitations were noted. First, modulation of the direction of light-induced electron transfer at negative applied potentials is partial. Attempts to fully modulate the direction of transfer, by applying still more negative potentials, proved unsuccessful because of desorption of the linked molecular components from the surface of the TiO₂ nanocrystal component at which they are adsorbed. Second, charge separation is shortlived. Attempts to inhibit back electron transfer, by addition of a sacrificial donor, proved unsuccessful because of the fact that electron transfer from the reduced V component to the oxidized R component is very fast (12 ps).

In the course of ongoing studies to address these limitations, the carboxylic acid groups used to link the TiO_2 nanocrystal and **R** components were replaced by phosphonic acid groups, in the expectation that this would prevent desorption of the molecular components at more negative applied potentials. Also, the length of the spacer group linking the **R** and **V** components was increased from one to four methylene groups, in the expectation that this would reduce the rate of back electron transfer.





TiO₂-RV

Covalent organization of these heterosupermolecules yields the heterosupramolecular assembly $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ (Scheme 5) for which the associated heterosupramolecular function, longlived light-induced charge separation, has been demonstrated. Potentiostatic modulation of this function has also been demonstrated. These findings and associated insights may find practical applications in the area of optical information storage.

Experimental Section

Preparation of Transparent Nanostructured TiO₂ Films. Transparent nanoporous nanocrystalline TiO₂ films (4 μm thick, 10 nm diameter nanocrystals) supported on fluorine-doped SnO₂ glass (0.5 μm, 8 Ω/square, supplied by Glastron) were prepared as described by Grätzel and co-workers.¹⁷ Briefly, a colloidal dispersion of TiO₂ nanocrystals was prepared by hydrolysis of titanium isopropoxide. The dispersion was autoclaved at 200 °C for 12 h, concentrated (160 g L⁻¹), and Carbowax 20000 (40 wt % equiv of TiO₂) added to yield a white viscous sol. This sol was spread on a conducting glass substrate masked with Scotch tape using a glass rod. The resulting gel film was fired in air at 450 °C for 12 h. All films were stored in a darkened vacuum desiccator until required for use.

Preparation of Transparent Nanostructured Al₂O₃ Films. Transparent nanoporous nanocrystalline Al₂O₃ films (4 μ m thick, 14 nm diameter nanocrystals) supported on a microscope glass slide were prepared as described by Grätzel and co-workers.¹⁸ Briefly, the oxide powder (1 g) was ground in an agate mortar with dropwise addition of distilled water until a viscous paste





formed. Aqueous HCl (40 μ L, 1.0 mol dm⁻³) was added followed by manual grinding for 15 min. Water (4 mL) and Carbowax 20000 (0.25 g) were added and dissolved by stirring for several hours. Finally, Triton X100 surfactant (40 μ L) was added. This sol was spread on a conducting glass substrate masked with Scotch tape using a glass rod. The resulting gel film was fired in air at 450 °C for 12 h. All films were stored in a darkened vacuum desiccator until required for use.

Preparation of Transparent Nanostructured SnO₂:Sb Films. Transparent nanoporous nanocrystalline Sb-doped SnO₂ films (3 μ m thick, 5 nm diameter nanocrystals) supported on a fluorine-doped SnO₂ glass (0.5 μ m, 8 Ω /square, supplied by Glastron) were prepared as described by Fitzmaurice and coworkers.¹⁹ Briefly, Carbowax 20000 (0.38 g) was dissolved in an aqueous dispersion of Sb-doped SnO₂ colloid (5.0 g, 15 wt %, Alfa) with average particle size of 5 nm. Acetic acid (2 drops of a 2 mol dm⁻³ solution) was added under stirring, resulting in immediate formation of a gel-like paste. This paste was diluted by addition of water (1.5 mL) and was used to prepare a gel film on a conducting glass substrate that was allowed to air-dry for 30 min and was fired in air at 450 °C for 15 h.

Preparation of Linked Molecular Components. The molecular components used in the present study, $\mathbf{R}^{\mathbf{P}\mathbf{V}^{C1}}$ and $\mathbf{R}^{\mathbf{P}\mathbf{V}^{C4}}$, were prepared from the ligands shown in Schemes 6 and 7. All reagents were used as received from Aldrich. All solvents were Analar grade and also used as received.

All ligands and molecular components were characterized by ¹H NMR spectra recorded on a JEOL JNM-GX270 FT spectrometer. Optical absorption spectra were measured using a Hewlett-Packard 8452A diode array spectrometer. Optical emission spectra were measured using a Perkin-Elmer 3000 fluorescence spectrometer. All elemental analysis was performed by the Chemical Services Unit at University College Dublin.

I: 4,4'-Dicarboxy-2,2'-bipyridine. This reagent was prepared and characterized as described in detail elsewhere.²⁰

 $4 PF_6$







SCHEME 6^a



 a (i) K_2CrO_7/H_2SO_4; (ii) EtOH, H_2SO_4, reflux; (iii) NaBH_4, EtOH, RT; (iv) HBr, H_2SO_4; (v) P(OEt)_3.

II: 4.4'-Diethoxycarbonyl-2,2'-bipyridine. This reagent was prepared and characterized as described in detail elsewhere.²¹

III: 4,4'-Bis(hydroxymethyl)-2,2'-bipyridine. A solution of II (6.0 g, 22.1 × 10⁻³ mol) and sodium borohydride (2.5 g, 66.0×10^{-3} mol) in dry ethanol (300 mL) was stirred at room temperature for 3 h. Water (300 mL) was added dropwise, and the solution was stirred at room temperature overnight. The reaction mixture was extracted with ethyl acetate (4 × 250 mL). The combined organic layer was dried over MgSO₄ and evaporated to give the crude product, which was recrystallized from ethanol to yield 4.25 g (89%) of III. ¹H NMR (270 MHz, CDCl₃): δ (ppm) 4.62 (s, 4H), 7.27–7.29 (m, unr, 2H), 8.29– 8.30 (d, J = 0.7 Hz, 2H), 8.49–8.51 (d, J = 5.5 Hz, 2H). Calculated for C₁₂H₁₂N₂O₂: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.55; H, 5.73; N, 12.84.

IV: 4,4'-Bis(bromomethyl)-2,2'-bipyridine. **III** (4.0 g, 11.7 $\times 10^{-3}$ mol) was dissolved in a mixture of HBr (48%, 30 mL)



SnO2:Sb-RPVC4

SCHEME 7^a



^a (i) DMF, reflux; (ii) MeOH, reflux; 20% HCl reflux; (iii) MeOH, reflux; 20% HCl, reflux.

and concentrated H_2SO_4 (10 mL). The resulting solution was refluxed for 6 H and allowed to cool, and water (100 mL) was added. The pH was adjusted to 7.0 by addition of NaOH, and the resulting precipitate was filtered, washed with water, and air-dried. The aqueous filtrate was extracted with ethyl acetate (2 × 50 mL), the combined organic layer was washed with water (2 × 50 mL) and dried over MgSO₄, and the solvent was removed. The precipitate and the extracted product were combined to yield 3.5 g (88%) of **IV**. ¹H NMR (270 MHz, CDCl₃): δ (ppm) 4.51 (s, 4H), 7.37–7.40 (m, unr, 2H), 8.45– 8.46 (m, unr, 2H), 8.68–8.70 (m, unr, 2H). Calculated for $C_{12}H_{10}N_2Br_2$: C, 42.14; H, 2.95; N, 8.19. Found: C, 42.23; H, 2.97; N, 8.08.

L1: 4,4'-Bis(diethylmethylphosphonate)-2,2'-bipyridine. A solution of **VI** (3.0 g, 8.7 × 10⁻³ mol) in triethyl phosphite (30 mL) was refluxed for 3 h. The excess phosphite was removed by distillation under high vacuum. The crude product was purified by column chromatography on silica column (eluent: ethyl acetate/methanol 80/20), yielding 2.9 g (73%) of crystalline L1. ¹H NMR (270 MHz, CDCl₃): δ (ppm) 1.26–1.31 (t, *J* = 7.2 Hz, 12H), 3.21–3.29 (d, *J* = 22.2 Hz, 4H), 4.03–4.11 (q, *J* = 7.2 Hz, 8H), 7.31–7.35 (m, unr, 2H), 8.35–8.36 (m, unr, 2H), 8.61–8.63 (d, *J* = 4.5 Hz, 2H). Calculated for C₂₀H₃₀N₂O₆P₂: C, 52.63; H, 6.63; N, 6.14. Found: C, 52.37; H, 6.52; N, 6.42.

L2: 4-((1'-Ethyl-4,4'-bipyridinediium-1-yl)methyl)-4'-methyl-2,2'-bipyridine) Dihexafluorophosphate. This ligand was prepared and characterized as described in detail elsewhere.¹⁶

L3: 5-((1'-Ethyl-4,4'-bipyridinediium-1-yl)-butyl)-2,2'-bipyridine) Dihexafluorophosphate. This ligand was used as received from Prof. Stoddart and co-workers, then at the University of Birmingham and now at the University of California at Los Angeles. The preparation and characterization of this ligand has been described in detail elsewhere.²²

P: cis-Dichloro-bis(4,4'-bis(diethylmethylphosphonate)-2,2'bipyridine)ruthenium(II). Ruthenium trichloride (0.092 g, 0.44 \times 10⁻³ mol) and **L1** (0.380 g, 0.83 \times 10⁻³ mol) were heated at 120 °C in *N*,*N*-dimethylformamide (40 mL) for 8 h with continuous bubbling of nitrogen. The solvent was removed by distillation under high vacuum, and the resulting product was purified on a silica column (eluent: methanol/acetone 40/60), yielding 0.144 g (32%) of crystalline **P**. Calculated for RuC₄₀H₆₀N₄O₁₂Cl₂P₄•4H₂O: C, 41.78; H, 5.91; N, 4.87. Found: C, 41.39; H, 5.71; N, 4.58. Absorption (EtOH): 392 and 498 nm. Emission (EtOH): none.

 $R^{P}V^{C1}$: Bis(4,4'-dimethylphosphonic-2,2'-bipyridine)-(4-((1'ethyl-4,4'-bipyridinediium-1-yl)-methyl)-4'-methyl-2,2'-bipyridine)ruthenium(II) Tetrahexafluorophosphate. **P** (0.074 g, 0.07 \times 10^{-3} mol) and L2 (0.035 g, 0.07×10^{-3} mol) were refluxed in methanol (10 mL) for 16 h. The solvent was removed under vacuum, and the compound was precipitated from water (10 mL) with ammonium hexafluorophosphate and extracted into nitromethane $(2 \times 5 \text{ mL})$. The nitromethane was removed under vacuum, and the resulting phosphonate ester was refluxed in HCl (20%, 15 mL) for 16 h. The solvent was removed under vacuum, and the resulting crude product was precipitated from water (10 mL) using ammonium hexafluorophosphate and extracted into nitromethane $(2 \times 5 \text{ mL})$. The crude product was purified on a Sephadex LH20 column (eluent: neutral water) to yield 0.040 g (35%) of **R^PV^{C1}**. ¹H NMR (270 MHz, CD₃-CN): δ (ppm) 1.50–1.55 (t, J = 7.3 Hz, 3H), 2.31 (s, 3H), 3.15-3.21 (d, J = 18.1 Hz, 8H), 4.55-4.65 (q, J = 7.3 Hz, 2H), 6.02 (s, 2H), 7.06-7.20 (m, unr, 4H), 7.46-7.84 (m, unr, 8H), 8.26-8.50 (m, unr, 8H), 8.73-8.78 (m, unr, 2H), 8.95-8.97 (d, J = 6.2 Hz, 2H), 9.06–9.09 (d, J = 5.9 Hz, 2H). Calculated for RuC₄₈H₅₂N₈F₂₄O₁₂P₈: C, 33.18; H, 3.02; N, 6.45. Found: C, 33.66; H, 3.11; N, 6.32. Absorption (MeCN): 470 nm ($\epsilon = 13 \ 100 \ \text{mol}^{-1} \ \text{cm}^{-1}$). Emission (EtOH): none.

 $R^{P}V^{C4}$: Bis(4,4'-dimethylphosphonic-2,2'-bipyridine))(5-((1'ethyl-4,4'-bipyridinediium-1-yl)butyl)-2,2'-bipyridine)ruthenium-(II) Tetrahexafluorophosphate. **P** (0.060 g, 0.05 × 10⁻³ mol) and **L3** (0.035 g, 0.05 × 10⁻³ mol) were refluxed in methanol (10 mL) for 16 h during which a color change to orange was observed. The solvent was removed under vacuum, and the resulting phosphonate ester was refluxed in HCl (20%, 15 mL) for 16 h. The solvent was removed under vacuum, and the crude product was precipitated from water (10 mL) using ammonium hexafluorophosphate and extracted into nitromethane (2 × 5 mL). The crude product was purified on a Sephadex LH20 column (eluent: neutral water) to yield (48%) 0.045 g of **R**^PV^{C4}. ¹H NMR (270 MHz, CD₃CN): δ (ppm) 1.19–1.21 (t, J = 7.3 Hz, 3H), 1.49–1.51 (m, unr, 2H), 1.81–1.83 (m, unr, 2H), 2.52–2.55 (m, unr, 2H), 3.16–3.20 (d, J = 21.5 Hz, 8H), 4.60–4.66 (m, unr, 4H), 7.20–7.41 (m, unr, 4H), 7.57–8.03 (m, unr, 8H), 8.23–8.49 (m, unr, 11H), 8.99–9.09 (m, unr, 4H). Calculated for RuC₅₀H₅₆N₈F₂₄O₁₂P₈: C, 34.01; H, 3.20; N, 6.35. Found: C, 33.84; H, 3.44; N, 6.46. Absorption (MeCN): 466 nm ($\epsilon = 14$ 200 mol⁻¹ cm⁻¹). Emission (EtOH): none.

Preparation of Heterosupramolecular Assemblies. A transparent nanostructured TiO₂, Al₂O₃, or SnO₂:Sb film was immersed in an ethanolic solution (typically 2×10^{-4} mol dm⁻³, pH 3.0) of $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ for 2 h. The resulting heterosupramolecular assemblies denoted TiO₂- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$, TiO₂- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, Al₂O₃- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$, Al₂O₃- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, and SnO₂:Sb- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ were washed thoroughly with ethanol and stored in a darkened vacuum desiccator until required for use.

Potential-Dependent Optical Absorption Spectroscopy. A heterosupramolecular assembly formed the working electrode of a closed three-electrode single-compartment cell. The counter electrode was a platinum wire and the reference electrode a Ag|AgCl|saturated KCl(aq) electrode connected via a salt bridge. All spectra and electrochemical measurements were undertaken in an electrolyte solution prepared from a mixture of dry MeCN/ EtOH (70/30 by volume) and containing tetrabutylammonium perchlorate (TBAP, 0.1 mol dm⁻³) and triethanolamine (TEOA, $0.05 \text{ mol } \text{dm}^{-3}$). All solutions were degassed by bubbling with argon for 15 min. Potential control was provided by a Solatron SI 1287 potentiostat controlled by a Lab View program running on a Power Macintosh. The above cell was incorporated into the sample compartment of a Hewlett-Packard 8452A diode array spectrometer. Unless otherwise stated, all spectra were recorded 3 s after application of the indicated potential against a background measured at 0.00 V. Importantly, the reported spectra show no temporal evolution before, during, or after measurement. The blue-green (all lines) output (200 mW cm^{-2}) of a Coherent Ar-ion laser (Innova 70-5) was used as an excitation source (irradiated area 1 cm²). Unless otherwise stated, all spectra were recorded 3 s after irradiation against a background measured at 0.00 V. As above, the reported spectra show no temporal evolution before, during, or after measurement.

Results and Discussion

I. Photophysical Properties of $\mathbb{R}^{P}V^{C1}$ and $\mathbb{R}^{P}V^{C4}$. Shown in Figure 1 are the optical absorption spectra of $\mathbb{R}^{P}V^{C1}$ and $\mathbb{R}^{P}V^{C4}$ in a MeCN/EtOH (70/30 by volume) solution (1 × 10⁻⁴ mol dm⁻³) containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³). Also shown in Figure 1 are the optical absorption spectra of $\mathbb{R}^{P}V^{C1}$ and $\mathbb{R}^{P}V^{C4}$ in a MeCN/EtOH (70/30 by volume) solution (1 × 10⁻⁴ mol dm⁻³) containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) following irradiation by the blue-green output of an argon-ion laser (200 mW cm⁻², 15 s).

In both cases, the following bands are observed between 350 and 800 nm and may be assigned to the **R** component:²³ a weak band at about 360 nm assigned to a metal-centered (MC) d-d transition; a strong band at 460 nm (broad) assigned to a spin-



Figure 1. Optical absorption spectra of (a) $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C}1}$ and (b) $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C}4}$ (1 $\times 10^{-4}$ mol dm⁻³) in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and following irradiation by the all-lines output of an argon-ion laser (200 mW cm⁻², 15 s).

allowed metal-to-ligand charge transfer (MLCT) $d-\pi^*$ transition; and finally, a long-wavelength tail extending to about 600 nm assigned to a spin-forbidden MLCT $d-\pi^*$ transition. No bands that may be assigned to the V component are observed. In short, the optical absorption spectra of $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ and **R** are indistinguishable.

The band that dominates the visible absorption spectrum of $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ is the spin-allowed MLCT transition of the **R** component at 460 nm. It has been shown for a complex similar to the **R** component that the excited state, in which an electron is localized on one of the bipyridine ligands,²⁴ is formed in less than 300 fs²⁵ and is largely triplet in nature.²³ It should be noted that the above electron, although initially localized on one of the three bipyridine ligands, hops between these ligands on the picosecond time scale.²⁶ If the **R** component is not linked to a V component, the excited state undergoes radiative decay with a lifetime of about 600 ns to give rise to an emission spectrum with a maximum at 660 nm.²⁴ If, however, the **R** component is linked to a V component, as is the case in $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C}\mathbf{I}}$ and $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C4}}}$, the electron is transferred when localized on the bipyridine ligand linked to V component and no emission is observed.24,27,28

For a supermolecule closely related to $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{I}}}$, a rate constant of $1.38 \times 10^{11} \text{ s}^{-1}$ for electron transfer to the \mathbf{V} component, corresponding to a lifetime of 7 ps, and a rate constant of 8.38 $\times 10^{10} \text{ s}^{-1}$ for electron transfer from the reduced \mathbf{V} component to the oxidized \mathbf{R} component, corresponding to a lifetime of 12 ps, have been measured by Mallouk and co-workers.²⁷ For a supermolecule closely related to $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C4}}}$, a rate constant of 6.55 × 10⁸ s⁻¹ for electron transfer to the **V** component, corresponding to a lifetime of 1500 ps, and a rate constant of 3.24 × 10⁹ s⁻¹ for electron transfer from the reduced **V** component to the oxidized **R** component, corresponding to a lifetime of 300 ps, have also been measured by Mallouk and co-workers.²⁷ A similar value for the rate constant for electron transfer to the **V** component (6.2 × 10⁸ s⁻¹) has been measured by Balzani and co-workers.²²

It should be noted that inferring the rate constants for electron transfer from the V component to the R component in both $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C1}}}$ and $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C4}}}$ from those measured for closely related complexes is based on the assumption that the small structural differences between these complexes do not, as may be the case for supermolecules assembled using flexible linkers, result in significant differences in the rates of intramolecular electron transfer.

Clearly, irradiation under these conditions does not lead to a measurable change in the optical absorption spectrum of either **R^PV^{C1}** or **R^PV^{C4}**. However, this finding is not unexpected, since the rate constants for back electron transfer from the reduced V component to the oxidized R component in R^PV^{C1} and R^PV^{C4} are 8.38×10^{10} s⁻¹ and 3.24×10^9 s⁻¹, respectively, and since the estimated diffusion-limited rate constant for electron transfer by the sacrificial donor TEOA to the oxidized R component is about 5×10^4 s⁻¹. Under these conditions, electron transfer by the reduced V component to the oxidized R component in $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ is 6 and 5 orders of magnitude faster than electron transfer by the sacrificial donor to the oxidized R component, respectively. This, in turn, ensures that only 1 in 10^6 and 10^5 photons absorbed the **R** component and leads to long-lived reduction of a V component in $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, respectively. Consequently, no significant change in the absorption spectrum is measured, the estimated upper limits for change of absorbance being between 0.001 and 0.0001, respectively.

If, however, the \mathbb{R}^{PVC4} solution in Figure 1 was irradiated for 15 min, a long-lived absorption spectrum (not shown) that may be assigned to the radical cation of the V component is measured.²⁷ It is noted that the absorbance increase measured at 600 nm (0.05) was in good agreement with that expected (about 0.06). Furthermore, Balzani and co-workers have shown that continuous irradiation of an ethanolic solution of a closely related supermolecule (3 × 10⁻⁵ mol dm⁻³), also containing TEOA (1 × 10⁻² mol dm⁻³), with a tungsten lamp (150 W, λ > 350 nm) results in the long-lived formation of the reduced form of the viologen.²² In both cases, the reduced form of the V component persists until oxygen enters the irradiated solution.

II. Photophysical Properties of $Al_2O_3 - R^PV^{C1}$ and $Al_2O_3 - R^PV^{C4}$. The linked **R** and **V** components, R^PV^{C1} and R^PV^{C4} , were chemisorbed at the surface of the constituent Al_2O_3 nanocrystals of a nanostructured film to yield the heterosupramolecular assemblies $Al_2O_3 - R^PV^{C1}$ and $Al_2O_3 - R^PV^{C4}$, respectively.

Shown in Figure 2 are the optical absorption spectra of $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ and $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and following irradiation by the blue-green output of an argon-ion laser (200 mW cm⁻², 15 s).

Clearly, the absorption spectra of $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ are not significantly different from those of $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ in solution. Furthermore, no visible emission is detected from either $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$. Equally clearly, irradiation with the blue-green output of an Ar-ion laser (200



Figure 2. Optical absorption spectra of (a) $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ and (b) $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and following irradiation by the all-lines output of an argon-ion laser (200 mW cm⁻², 15 s).

mW cm⁻²) for 15 s does not lead to a measurable change in the optical absorption spectrum of either $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$. These findings, however, are not unexpected, since the band gap of Al_2O_3 is so large (about 9 eV) that there are no conduction band states isoenergetic with the electronically excited state of the **R** component of either $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$.¹⁸ Consequently, photoexcitation of the **R** component is followed by electron transfer to the linked **V** component and, as was the case for and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ in solution, followed in turn by electron transfer from the reduced **V** component to the oxidized **R** component.

It should be noted that extended irradiation of $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $Al_2O_3 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ for 15 min with the blue-green output of an Ar-ion laser (200 mW cm⁻²) results, as was the case for $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ in solution, in a measurable absorption by the radical cation of the **V** component.

In short, the behavior of $Al_2O_3 - R^PV^{C1}$ and $Al_2O_3 - R^PV^{C4}$ and R^PV^{C1} and R^PV^{C4} in solution is the same.

III. Photophysical Properties of $TiO_2 - R^P V^{C1}$ and $TiO_2 - R^P V^{C4}$. The linked **R** and **V** components, $R^P V^{C1}$ and $R^P V^{C4}$, were chemisorbed at the surface of the constituent TiO_2 nanocrystals of the nanostructured TiO_2 film to yield the heterosupramolecular assemblies $TiO_2 - R^P V^{C1}$ and $TiO_2 - R^P V^{C4}$, respectively.

Shown in Figure 3 are the optical absorption spectra of TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and



Figure 3. Optical absorption difference spectra of (a) $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and (b) $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ in a MeCN/EtOH (70/30 by volume) solution (1 $\times 10^{-4}$ mol dm⁻³) containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and following irradiation by the all-lines output of an argon-ion laser (200 mW cm⁻², 15 s). The reference spectra were measured prior to irradiation and are shown as insets.

following irradiation by the blue-green output of an argon-ion laser (200 mW cm⁻², 3 s).

As may be seen from Figure 3 (insets), the absorption spectra of $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ are not significantly different from those of the linked molecular components $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ in solution. Furthermore, no visible emission is detected from either $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ or $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$.

As may also be seen from Figure 3, irradiation of either $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ or $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ does result in a significant change in the measured absorption spectrum at wavelengths longer than 520 nm. No such similar change is observed for $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ or for $Al_2O_3-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ and $Al_2O_3-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ under similar conditions (see Figures 1 and 2). These spectral changes, which in the absence of oxygen are long-lived, may readily be assigned to formation of the radical cation of the **V** component.²⁷

These findings, together with those for $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$ and $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$ and for Al₂O₃- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$ and Al₂O₃- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{4}}}$, strongly suggest that the conduction band and trap states of the TiO₂ nanocrystal component participate in reduction of the V component of TiO₂- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$ and TiO₂- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$. Specifically, irradiation of $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$, $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$, Al₂O₃- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$, or Al₂O₃- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{4}}}$ for 15 s does not result in long-lived formation of the radical cation of V, while irradiation of TiO₂- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$ and TiO₂- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$ and TiO₂- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{4}}}$ under the same conditions does. On this basis, it may be asserted that the conduction band and trap states of the TiO₂ nanocrystal, known to be isoenergetic with the electronically excited state of the **R** component,³¹ participate in reduction of the V component of TiO₂- $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{4}}$.



Figure 4. Potential dependence of absorbance by (a) $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ and (b) $\text{TiO}_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ at 600 nm in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³). The reference absorbance was that measured at 0.00 V.

If the above is the case, we can state the following. First, to fully account for these findings, it will be necessary to have a quantitative description of the trap and conduction band state energetics of the TiO₂ nanocrystal component. Second, if the occupancy of these state may be controlled by the potential applied to the constituent TiO₂ nanocrystal component of TiO₂– $\mathbf{R}^{P}\mathbf{V}^{C1}$ and TiO₂– $\mathbf{R}^{P}\mathbf{V}^{C4}$, then the extent to which visible-light irradiation results in long-lived charge separation may be potentiostatically modulated.

IV. Potential-Dependent Optical Absorption Spectroscopy of $\text{TiO}_2-\mathbf{R}^{P}\mathbf{V}^{C1}$ and $\text{TiO}_2-\mathbf{R}^{P}\mathbf{V}^{C4}$. The condensed-phase and molecular component energetics of $\text{TiO}_2-\mathbf{R}^{P}\mathbf{V}^{C1}$ and $\text{TiO}_2-\mathbf{R}^{P}\mathbf{V}^{C4}$ in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) were elucidated by potential-dependent optical absorption spectroscopy.

As may be seen from Figure 4, on sweeping the applied potential to $\text{TiO}_2-\mathbf{R}^{P}\mathbf{V}^{C1}$ and $\text{TiO}_2-\mathbf{R}^{P}\mathbf{V}^{C4}$ from 0.00 to -1.50 V the following is observed: a gradual increase in absorbance between -0.35 and -0.65 V, an increase in absorbance between -0.65 and -0.75 V, a decrease in absorbance between -0.75 and -0.95 V, and an increase in absorbance at -1.20 V. During the reverse sweep the following is observed: a decrease in absorbance between -1.50 and -1.20 V, an increase in absorbance between -0.95 and -0.95 and -0.75 and -0.75 V, and -1.20 V, an increase in absorbance between -0.95 and -0.75 V, an essentially constant absorbance between -0.75 and -0.35 V, and a gradual decrease in absorbance between -0.35 and 0.00 V. It should be noted, as discussed in section VI, that the residual absorbance at 0.00 V eventually decreases to zero.

SCHEME 8



In a similar experiment for an unmodified nanostructured TiO_2 film (not shown), the absorbance measured at 600 nm remained constant between 0.00 and -1.20 V, although there was a sharp increase in absorbance at -1.20 V. The reverse sweep showed a decrease in absorbance between -1.50 and -1.20 V. No other absorbance changes were observed.

The potential-dependent optical absorption spectroscopy and band energetics of nanostructured TiO₂ films have previously been studied in a range of protic and aprotic solvents.³² On this basis, the reversible increase in absorbance observed at applied potentials more negative than -1.20 V is assigned to the accumulation of electrons in available states of the conduction band. Also on this basis, the potential of the conduction band edge at the semiconductor-liquid electrolyte interface (SLI) is determined to be -1.20 V, while, consistent with the measured onset for band gap absorption (380 nm), the potential of the valence band edge at the SLI is determined to be +2.06 V. Furthermore, it is known that there are two populations of intraband states in nanostructured TiO₂ films.³⁰ The first of these lies about 0.5 eV below the conduction band edge and is assigned to surface Ti^{IV} atoms. The second lies about midgap, i.e., about 1.63 eV below the conduction band edge, and is assigned to surface peroxy species. From the above and from the known half-wave potentials of the R and V components in $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4},33}$ an energy level diagram may be constructed (Scheme 8).

By use of this energy level diagram, the potential-dependent spectroscopy of $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ may be accounted for. It has been established that there is a population of surface $\mathrm{Ti}^{\mathrm{IV}}$ states at -0.70 V and that the half-wave potential for the first reduction of the V component is -0.41 V.³³ It has also been established, by optical absorption spectroscopy (not shown), that the increase in absorbance at 600 nm between -0.35 and -0.75V is due to formation of the radical cation of the V component in $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ and $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$.²⁹ On this basis, it is concluded that reduction of the V component is mediated by surface $\mathrm{Ti}^{\mathrm{IV}}$ states. 34 It should be noted that only 38% and 45% of V components are reduced in $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C}\mathbf{1}}$ and $TiO_2 \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, respectively, suggesting that the orientation of the molecular components with respect to the nanocrystal component may be important. These values have been calculated as follows. In the case of $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C}\mathbf{1}}$ the absorbance by the **R** component at 470 nm in Figure 3a is 0.54. From the measured extinction coefficient of **R** at 470 nm (13 100 mol cm^{-1}) the

surface concentration of $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ was calculated to be 2.5 \times 10¹⁶ molecules cm^{-2} (geometric). From the known extinction of the radical cation of the V component at 600 nm (10 400 mol cm⁻¹) an absorbance of 0.59 is expected if all V components are reduced. The measured absorbance at 600 nm in Figure 4a is 0.19, indicating that 38% of all viologens are reduced. In the case of TiO_2 -**R**^P**V**^{C4} the absorbance by the **R** component at 470 nm in Figure 3b is 0.50. From the measured extinction coefficient of **R** at 470 nm (14 200 mol cm⁻¹) the surface concentration of $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ was calculated to be 2.0 \times 10¹⁶ molecules cm^{-2} (projected area). From the known extinction of the radical cation of the V component at 600 nm (14 000 mol cm^{-1}) an absorbance of 0.49 is expected if all V components are reduced. The measured absorbance at 600 nm in Figure 4b is 0.22, indicating that 45% of all viologens are reduced.

It has been established that there is a population of surface Ti^{IV} states at -0.70 V and that the half-wave potential for the second reduction of the V component is -0.81 V.³³ It has also been established, by optical absorption spectroscopy, that the decrease in absorbance at 600 nm between -0.75 and -0.95 V is due to formation of the neutral dication of the V component in $TiO_2 - \mathbf{R}^{P} \mathbf{V}^{C1}$ and $TiO_2 - \mathbf{R}^{P} \mathbf{V}^{C4}$. On this basis, it is concluded that second reduction of the V component is also mediated by surface Ti^{IV} states.³⁴

At still more negative potentials, that is, more negative than -1.20, there is a sharp increase in absorbance that may be assigned, by examination of the corresponding absorption spectrum (not shown),³² mainly to accumulation of electrons in the available states of the conduction band. By comparison with the findings outlined above for an unmodified nanostructured TiO₂ film, it is concluded that there is no change in the potential of the conduction band edge at the SLI following adsorption of $\mathbf{R}^{P}\mathbf{V}^{C1}$ and $\mathbf{R}^{P}\mathbf{V}^{C4}$ to form the heterosupramolecular assemblies TiO₂- $\mathbf{R}^{P}\mathbf{V}^{C1}$ and TiO₂- $\mathbf{R}^{P}\mathbf{V}^{C4}$, respectively.

When the applied potential is reversed, the filled conduction band states are emptied, leading to a sharp decrease in absorbance between -1.50 and -1.20 V. Subsequently, the intraband states are emptied, leading to a sharp increase in absorbance, as the neutral diradical of the V component in $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ is reoxidized to form the highly colored radical cation. Because the concentration of intraband trap states is small at potentials more positive than -0.41 V, the half-wave potential for the first reduction of the V component, this process is kinetically limited and the absorbance assigned to this species persists for some minutes even at 0.00 V (see also section VI).

The findings that chemisorption of $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{1}}}$ and $\mathbf{R}^{\mathbf{P}\mathbf{V}^{\mathbf{C}\mathbf{4}}}$ at the surface of the TiO₂ nanocrystal film to form TiO₂- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, respectively, does not affect the energy of the valence or conduction bands of the TiO2 nanocrystal components are consistent with previously reported findings.³² However, these and closely related studies have also established that chemisorption of the R component via phosphonic acid groups at surface Ti^{IV} atoms result in their promotion into the conduction band and elimination as trap sites.^{32,34,35} From Figure 3 the concentrations of adsorbed RPV^{C1} and RPV^{C4} are estimated to be 2.5 \times 10^{16} molecules cm^{-2} (projected area) and 2.1 \times 10¹⁶ molecules cm⁻² (projected area), respectively. This finding implies, assuming a surface roughness of 100017 and a concentration of Ti^{IV} surface states of 2×10^{13} Ti^{IV} sites per cm² (absolute area),³⁶ that most of the available surface states are occupied, as might have been expected from the relatively slow rates of oxidation and reduction. Langmuir-Blodgett

studies have shown that molecules similar to the ruthenium complex component in $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ occupy an area of 85 Å² (absolute) at the air-water interface.³⁷ On this basis, the extent of loading in TiO₂- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ is estimated to 22% and 18%, respectively.

V. Potential-Dependent Light-Induced Charge Separation in TiO₂- $\mathbb{R}^{P}V^{C1}$ and TiO₂- $\mathbb{R}^{P}V^{C4}$. As discussed in section III, irradiation of TiO₂- $\mathbb{R}^{P}V^{C1}$ and TiO₂- $\mathbb{R}^{P}V^{C4}$ under the stated conditions at the open-circuit potential results in long-lived formation of the radical cation of the V component. Furthermore, it is likely that the conduction band and trap states of the TiO₂ nanocrystal component mediated this process. As discussed in section IV, the occupancy of the conduction band and trap states of the TiO₂ nanocrystal component may be controlled potentiostatically. Taken together, these findings suggested that the effect of irradiation of TiO₂- $\mathbb{R}^{P}V^{C1}$ and TiO₂- $\mathbb{R}^{P}V^{C4}$ might be modulated potentiostatically.

For this reason $\text{TiO}_2-\mathbf{R}^{\mathbf{P}\mathbf{V^{C1}}}$ and $\text{TiO}_2-\mathbf{R}^{\mathbf{P}\mathbf{V^{C4}}}$ in a MeCN/ EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) were irradiated at different applied potentials by the green-blue output of an argon-ion laser (200 mW cm⁻², 3 s). The potential dependence of the effect of irradiation of on TiO₂- $\mathbf{R}^{\mathbf{P}\mathbf{V^{C4}}}$ is shown in Figures 5 and 6.

At an applied potential of 0.00 V, irradiation of TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ leads to reduction of 14% and 8% of the V components, respectively. It should be noted, however, that radical cations formed are not long-lived. At an applied potential of -0.45 V, irradiation of TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ leads to reduction of 20% and 14% the V component, respectively. Furthermore, the radical cations formed are longer-lived. At an applied potential of -0.60 V, 32% and 26% of the V components of TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ are reduced, a fraction that is not increased by irradiation. It should be noted, as discussed in section IV, that at an applied potential as negative as -0.75 V only 38% and 45% of the V components were reduced in TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, respectively.

The above findings, and those in section IV, are consistent with the following mechanism for long-lived light-induced charge separation (Scheme 9). At 0.00 V absorption of a visible photon by the **R** component of either $TiO_2 - \mathbf{R}^P \mathbf{V}^{C1}$ or $TiO_2 - \mathbf{R}^P \mathbf{V}^{C1}$ **R**^P**V**^{C4} results in electron transfer to a conduction band state of the TiO₂ nanocrystal component with 95% efficiency.¹⁶ In the presence of the added sacrificial donor TEOA a significant fraction of the injected electrons, about 20% under the reported conditions,³⁸ are not transferred back to the oxidized **R** component but occupy the available trap states at the surface of the TiO_2 nanocrystal component. In short, there is a shift of the quasi-Fermi level to a potential that is sufficiently negative to reduce the V components in both $TiO_2 - \mathbf{R}^{\mathbf{P}V^{C1}}$ and $TiO_2 - \mathbf{R}^{\mathbf{P}V^{C1}}$ **R^PV^{C4}**. Furthermore, since the radical cation of the viologen component is formed only where the heterosupramolecular assembly is irradiated, the shift of the quasi-Fermi level to more negative potentials is apparently localized. At an applied potential of 0.00 V, trap states are being filled more quickly than they are being emptied under irradiation. Once irradiation ceases, however, these trap states are gradually emptied, resulting in the slow reoxidation of the reduced viologen components.

At an applied potential of -0.45 V, irradiation of both TiO₂-**R**^P**V**^{C1} and TiO₂-**R**^P**V**^{C4} leads to reduction of a larger fraction of the **V** components, while the resulting radical cations are longer-lived. These findings, however, are entirely consistent with the mechanism proposed above for light-induced charge



Figure 5. Optical absorption difference spectra of $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ at (a) 0.00 V, (b) -0.45 V, and (c) -0.60 V in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and immediately following irradiation by the all-lines output of an argon-ion laser (200 mW cm⁻², 3 s) and 60 s later. The reference spectra were measured prior to irradiation.

separation at 0.00 V. Specifically, as a more negative potential is applied to the TiO₂ nanocrystal component of TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, more of the surface Ti^{IV} states are filled initially and irradiation results in a localization of the quasi-Fermi level to still more negative potentials. This, in turn, results in a larger fraction of the V components in TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ and TiO₂– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ being reduced. Furthermore, once irradiation ceases, only those trap states at potentials more negative than the potentiostatically applied potential, -0.45 V, are emptied. As a consequence, there are no empty surface Ti^{IV} states available to mediate back electron transfer from the reduced



Figure 6. Optical absorption difference spectra of $TiO_2 - \mathbf{R}^{\mathbf{P}V^{C4}}$ at (a) 0.00 V, (b) -0.45 V, and (c) -0.60 V in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and

0.00 V, (b) -0.45 V, and (c) -0.60 V in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and immediately following irradiation by the all-lines output of an argon-ion laser (200 mW cm⁻², 3 s) and 60 s later. The reference spectra were measured prior to irradiation.

viologen component in $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ or $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ to the TiO_2 nanocrystal component and charge separation is long-lived.

At an applied potential of -0.60 V, irradiation of either $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ or $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$ does not result in an increase in the intensity of the absorption spectrum assigned to the radical cation of the V components. Again, this finding is entirely consistent with the mechanism proposed. Specifically, at sufficiently negative applied potentials all those V components with the requisite geometry have been reduced and optically pumping the quasi-Fermi potential to more negative potentials will not result in an increase in the fraction of viologen components that are reduced.



TiO2-RPVC4 : At Open Circuit or Negative Applied Potentials



TiO2-RPVC4 : At Positive Applied Potentials

It will be noted that the findings presented do not preclude a mechanism where the photoinjected electrons are transferred directly to an oxidized **R** component formed by light-induced electron transfer to the **V** component to which it is covalently linked. In this context, it is noted that there is increasing evidence to support the view that the rate of electron transfer to the oxidized **R** component increases significantly as the concentration of electrons present in the nanostructured TiO₂ film increases.³⁸ As a consequence, more detailed time-resolved studies are necessary and are being undertaken.³⁹

It should also be noted that direct electron transfer by the electronically excited **R** component, even at negative applied potentials, does not lead to long-lived charge separation. This is because, as has been discussed in detail above, back electron transfer from the reduced **V** component to the oxidized **R** component is between 5 and 6 orders of magnitude faster than electron transfer from the sacrificial donor.

VI. Charge Recombination Kinetics in $TiO_2-R^PV^{C1}$ and $TiO_2-R^PV^{C4}$. As discussed above, irradiation of $TiO_2-R^PV^{C1}$ or $TiO_2-R^PV^{C4}$ at an applied potential of -0.45 V results in electron transfer from the photoexcited **R** component to the TiO_2 nanocrystal component. This, in turn, results in a localized shift of the quasi-Fermi level to more negative potentials and to electron transfer from the TiO_2 nanocrystal component to the V component. Reduction of the V component yields the visible spectrum characteristic of the corresponding radical cation and, more specifically, an increase in the absorbance measured at 600 nm.

By subsequent monitoring of the decrease in the absorbance measured at 600 nm, the rate of reoxidation of the reduced V component in $TiO_2-\mathbf{R}^{P}\mathbf{V}^{C1}$ and $TiO_2-\mathbf{R}^{P}\mathbf{V}^{C4}$ at -0.45 V can



Figure 7. Natural logarithm of the absorbance at 600 nm at the indicated applied potential plotted against elapsed time for (a) TiO_2 - $\mathbf{R}^{P}\mathbf{V}^{C1}$ and (b) $TiO_2-\mathbf{R}^{P}\mathbf{V}^{C4}$ in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) following irradiation by the all-lines output of an argon-ion laser (200 mW cm⁻², 3 s) at -0.45 V. The reference spectra were measured prior to irradiation.

TABLE 1: Rate Constants for Reoxidation of Radical Cation of Viologen Components in $TiO_2-R^PV^{C1}$ and $TiO_2-R^PV^{C4}$

	applied potential		
	+1.00 V	0.00 V	-0.45 V
$TiO_2 - \mathbf{R}^{\mathbf{P}} \mathbf{V}^{C1}$ $TiO_2 - \mathbf{R}^{\mathbf{P}} \mathbf{V}^{C4}$	$\begin{array}{c} 1.7\times 10^{-3}{\rm s}^{-1}\\ 34.0\times 10^{-3}{\rm s}^{-1} \end{array}$	$\begin{array}{c} 1.5\times10^{-3}{\rm s}^{-1}\\ 5.8\times10^{-3}{\rm s}^{-1}\end{array}$	$\begin{array}{c} 0.5\times10^{-3}\mathrm{s}^{-1}\\ 1.0\times10^{-3}\mathrm{s}^{-1} \end{array}$

be measured (see Figure 7). Similar measurements were performed in which $TiO_2-\mathbf{R}^{\mathbf{P}\mathbf{V}^{C1}}$ and $TiO_2-\mathbf{R}^{\mathbf{P}\mathbf{V}^{C4}}$ were irradiation at -0.45 V and the rate of decay of the radical cation formed measured at applied potentials of 0.00 and +1.00 V. The decay of the absorbance assigned to the radical cation of the viologen component is monoexponential, with the corresponding first-order rate constants being given in Table 1.

From the findings summarized in Table 1, it is evident that, in the case of both $\text{TiO}_2-\mathbf{R}^{\mathbf{P}\mathbf{V}^{C1}}$ and $\text{TiO}_2-\mathbf{R}^{\mathbf{P}\mathbf{V}^{C4}}$, the rate of reoxidation of the **V** component increases at more positive applied potentials. Again, this is consistent with the mechanism proposed above and is explained by the availability of a larger number of empty surface Ti^{IV} states at more positive potentials capable of mediating electron transfer.^{5,29}

From the findings summarized in Table 1, it is also evident that at a given applied potential the rate of reoxidation of the V component in $\text{TiO}_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C1}}$ is significantly slower than that of the same component in $\text{TiO}_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$. It should be noted that this result is consistent with the findings discussed in section III. It is tentatively suggested that this be accounted for by the



Figure 8. Optical absorption difference spectra of SnO_2 :Sb- $\mathbb{R}^{\mathbf{P}}\mathbf{V}^{C4}$ at (a) 0.00 V, (b) -0.45 V, and (c) -0.60 V in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and immediately following irradiation by the all-lines output of an argonion laser (200 mW cm⁻², 3 s). The reference spectra were measured prior to irradiation under the above conditions. The spectrum of SnO₂: Sb- $\mathbb{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ measured at the open-circuit potential under the above conditions is shown as an inset.

reduced configurational freedom of the V component in $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ compared with that of the same component in $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$.

It should be noted that it is not possible to say whether there is transfer of electrons between adjacent viologens in TiO_2 - $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C1}$ and $TiO_2-\mathbf{R}^{\mathbf{P}}\mathbf{V}^{C4}$. However, it should also be noted that while this may affect the absolute rate constants measured by providing a pathway by which electrons localized on a viologen component can migrate to a surface state that mediates their transfer to the TiO₂ nanocrystal component, the proposed mechanism and the proposed interpretation of the effect of the applied potential are appropriate in either case.

VII. Potential-Dependent Light-Induced Charge Separation in $SnO_2:Sb-R^PV^{C4}$. Further support for the proposed mechanism was obtained by comparing the effect of applied potential on light-induced charge separation in $SnO_2:Sb-R^PV^{C4}$.

Shown in Figure 8 are the optical absorption spectra of SnO₂: Sb- $\mathbb{R}^{P}V^{C4}$ in a MeCN/EtOH (70/30 by volume) solution containing the electrolyte TBAP (0.10 mol dm⁻³) and the sacrificial donor TEOA (0.05 mol dm⁻³) prior to and following irradiation by the blue-green output of an argon-ion laser (200 mW cm⁻², 3 s) at the indicated applied potentials.

Regardless of the applied potential, irradiation of SnO₂:Sb– $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ does not lead to a measurable increase in the absorbance assigned to the radical cation of the **V** component. This finding, however, is not unexpected, since the electrons injected into the SnO₂:Sb nanocrystal component move freely throughout the nanostructured film in the absence of low-energy states capable of acting as traps.¹⁸ That is, an injected electron can either be transferred back to the oxidized **R** component or be quickly diffused toward the back contact, as a consequence of which there is no significant localized shift of the quasi-Fermi level to more negative potentials and no detectable light-induced reduction of the **V** component.

Conclusions

A heterosupermolecule has been assembled by covalently linking a TiO₂ nanocrystal, a ruthenium complex, and a viologen. The covalent organization of these heterosupermolecules yields a heterosupramolecular assembly TiO₂ $-\mathbf{R}^{P}\mathbf{V}^{C4}$.

The associated heterosupramolecular function, long-lived lightinduced charge separation, has been demonstrated.

A mechanism, supported by detailed studies of $TiO_2 - \mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ and the closely related heterosupramolecular assemblies Al2O3- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$ and \mathbf{SnO}_{2} :Sb- $\mathbf{R}^{\mathbf{P}}\mathbf{V}^{\mathbf{C4}}$, has been proposed. In summary, electron transfer directly from the **R** component to the TiO_2 nanocrystal component results, upon trapping of the injected electron in a surface Ti^{IV} state, in a localized shift of the quasi-Fermi level to more negative potentials and in electron transfer to the V component. Charge separation is long-lived because the sacrificial donor in solution competes with electron transfer from the TiO_2 nanocrystal component to the oxidized **R** component and because electron transfer from the reduced V component to the oxidized sacrificial donor does not occur. If electrons are transferred directly from the R component to the V component, charge separation is not long-lived because the sacrificial donor in solution does not compete with electron transfer from the reduced V component to the oxidized R component.

Because the electron transfer that results in long-lived lightinduced charge separation is from a surface Ti^{IV} state to the V component, potentiostatic control of the occupancy of these states has been used to modulate the effect of irradiation. In summary, at an applied potential of -0.45 V the surface Ti^{IV} states are potentiostatically filled to a potential just positive of the potential at which the V component is reduced. As a consequence, irradiation leads to reduction of a significant fraction of these components. Furthermore, since there are no empty surface Ti^{IV} states at potentials positive of the potential at which the V component is oxidized, charge separation is longlived. At an applied potential of 0.00 V, however, the surface Ti^{IV} states are potentiostatically filled to a potential significantly positive of the potential at which the V component is reduced and irradiation leads to reduction of a substantially smaller fraction of these components. Furthermore, since there are empty surface Ti^{IV} states at potentials positive of the potential at which the V component is oxidized, charge separation is not longlived. At an applied potential of +1.00 V no reduction of the V component is observed upon irradiation, while any previously reduced V component is rapidly reoxidized. In short, the above heterosupramolecular assembly may be written using green light at -0.45 V, read using red light, and erased by application of +1.00 V.

It is important to note the limitations of the above heterosupramolecular assembly. First, it is not an organized heterosupramolecular assembly, as a consequence of which the constituent heterosupermolecules are not individually addressable. Second, the constituent heterosupermolecules most probably do not act fully independently, i.e., there is likely electron transfer between viologens adsorbed at the same or adjacent nanocrystals. Third, because the constituent condensed-phase and molecular components are covalently linked, they may not be selfassembled.

Nevertheless, the findings reported here demonstrate that effective function modulation may indeed be achieved by organizing the condensed-phase components of a heterosuper-molecule to form an intrinsic substrate. In the near future, optical write—read—erase devices based on the above heterosupramolecular assembly will be described.⁴⁰

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