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Heterosupramolecular optical write–read–erase device

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A covalently linked ruthenium tris(bipyridyl) complex and viologen have been chemisorbed at the surface of the constituent nanocrystals of a transparent nanostructured TiO_2 film supported on conducting glass. This resulting heterosupramolecular assembly, when incorporated as the working electrode in a sealed two-electrode cell, yields a device which can be written to using blue–green light, read using red light and erased by applying a voltage.

Chemists have long suggested that the covalent and non-covalent assembly of molecular components and their subsequent organization will yield devices based on supramolecular function addressable on the nanometer-scale.[1,2]

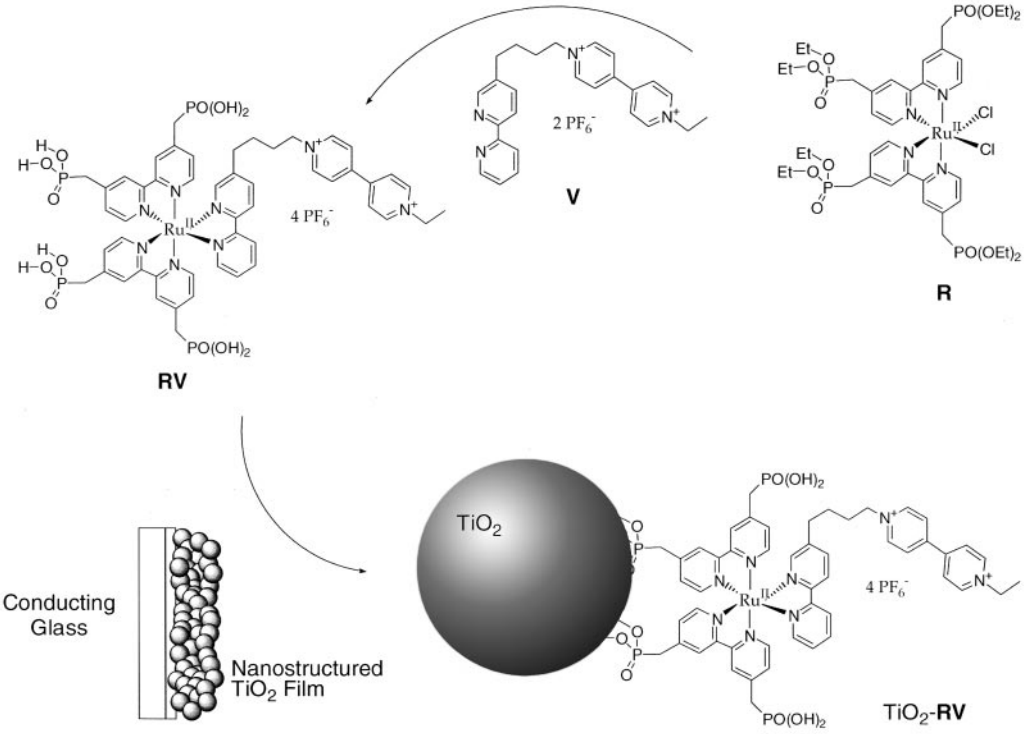
Recently, chemists have also begun to suggest that the covalent and non-covalent assembly of condensed phase and molecular components and their subsequent organization will yield devices based on heterosupramolecular function addressable on the nanometer-scale.[3,4]

There are a number of reasons why devices based on addressable heterosupramolecular function are of interest. First, greater functional diversity may be achieved because both condensed phase and molecular components are used to assemble heterosupermolecules; second, proven technologies from the electronics sector may be used to individually address the condensed phase component of each heterosupermolecule; and third, the functional state of each heterosupermolecule may be switched by modulating a bulk property of the condensed phase component.

The heterosupramolecular assembly denoted TiO_2–**RV** was prepared as shown in Scheme 1 by covalently linking two molecular components,[5,6] namely a ruthenium tris(bipyridyl) complex (**R**) and a viologen (**V**), and a condensed phase component,[7] namely a constituent nanocrystal of a transparent nanostructured TiO_2 (anatase) film supported on conducting glass.[8] This heterosupramolecular assembly was incorporated as the working electrode in a three-electrode cell.[9] The cell was filled with a mixed organic solvent containing the electrolyte tetrabutylammonium perchlorate (TBAP) and the sacrificial donor triethanolamine (TEOA). The reference and counter electrodes were platinum and conducting glass, respectively.

As can be seen from Fig. 1, irradiation of TiO_2–**RV** at an applied potential of −0.45 V using the defocused blue–green output of an argon-ion laser leads to reduction of a significant fraction of the viologen components present in the assembly and to an absorption spectrum characteristic of the corresponding radical cation.[10,11] Furthermore the radical cations formed, which otherwise persist on the time-scale of hours, are completely reoxidized in <15 s at an applied voltage of +1.00 V.

A detailed mechanism has been proposed to account for these findings.[6] Briefly, at an applied potential equal to that of the conduction band edge of the TiO_2 nanocrystal, 95% of the electronically excited ruthenium complex components transfer an electron to the TiO_2 nanocrystal component,[5,12] while the



Scheme 1

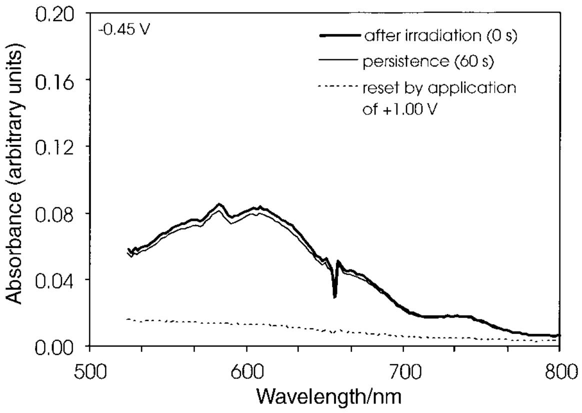


Fig. 1 Optical absorption spectra of TiO_2–**RV** at −0.45 V in MeCN–EtOH (70 : 30, v/v) containing TBAP (0.10 mol dm^{-3}) and TEOA (0.05 mol dm^{-3}) 0 s and 60 s after irradiation by the defocused blue–green output of an argon-ion laser (200 mW cm^{-2}, 1.0 cm^2 area, 3 s). Also shown is the spectrum of TiO_2–**RV** measured at −0.45 V following application of +1.00 V for 15 s.

other 5% transfer an electron to the viologen component.[5,13] Electrons transferred to the viologen component do not result in long-lived charge separation because back electron transfer from the reduced viologen component to the oxidized ruthenium complex is very fast (300 ps).[6,13,14] Of the 95% of electrons transferred to the TiO_2 nanocrystal component, *ca.* 80% of these are transferred back to the oxidized ruthenium complex component.[15] Oxidized ruthenium complex components that are not regenerated by back electron transfer from a TiO_2 nanocrystal are regenerated by electron transfer from the sacrificial donor TEOA.[14,15] The 20% of injected electrons which remain on the TiO_2 nanocrystal component occupy trap states and result in a localized shift of the quasi-Fermi level to more negative potentials.[16,17] These electrons, when transferred to the viologen component, result in long-lived charge separation. Application of a positive potential leads to emptying of intraband states that mediate reoxidation of the viologen component[18] and an electron transfer from the viologen component to the TiO_2 nanocrystal component is observed.[19]

These findings are significant because they suggest the optical write–read–erase device shown in Scheme 2.[20] In this device the heterosupramolecular assembly TiO_2–**RV** formed the working

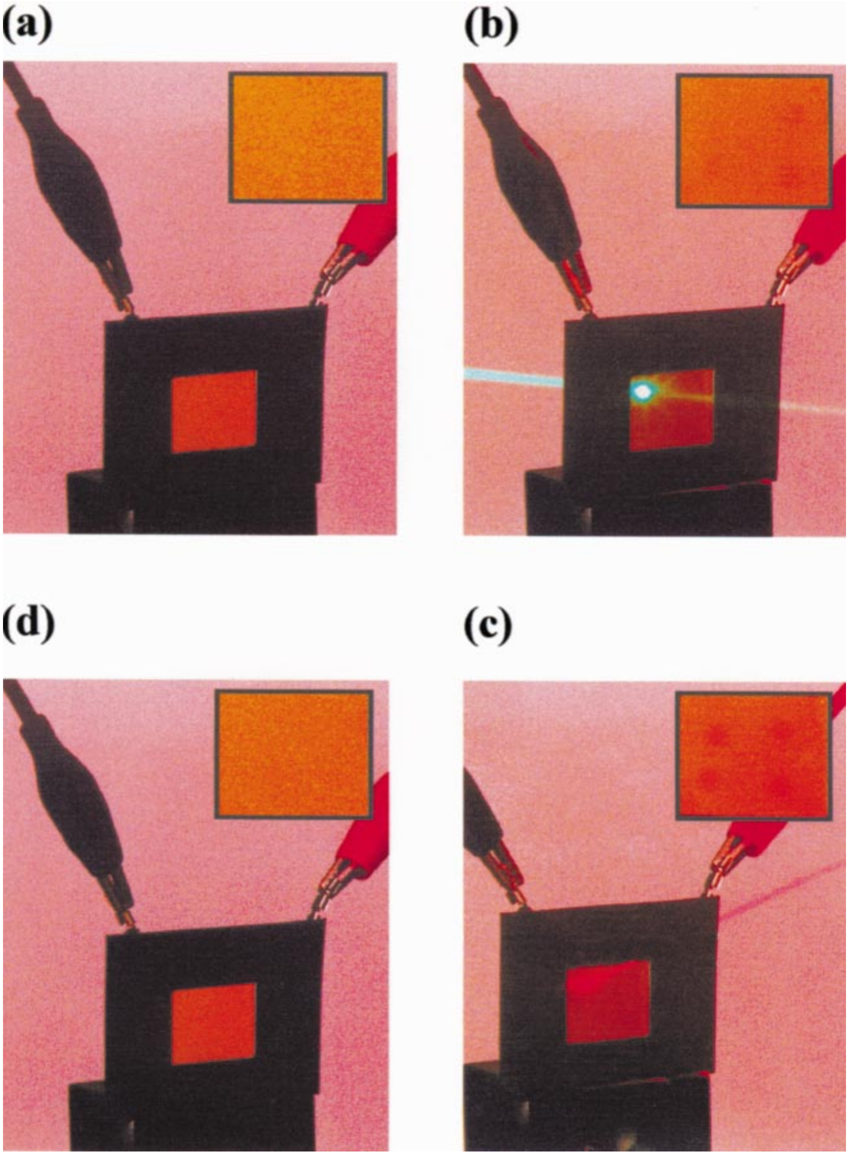
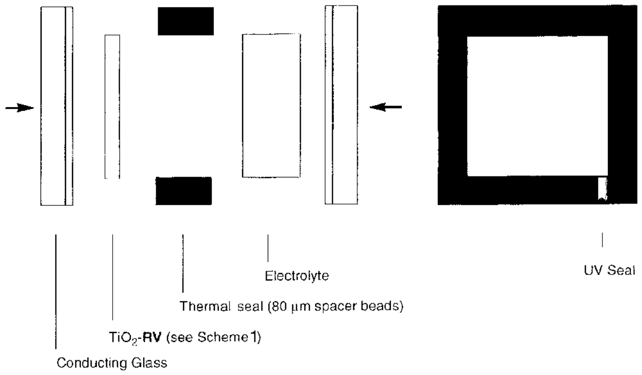


Fig. 2 A sealed two-electrode device incorporating the heterosupramolecular assembly in Scheme 1, namely TiO_2–**RV**, (a) prior to writing (open circuit), (b) being written to using the defocused blue–green output of an Ar-ion laser (open circuit, 70 mW cm^{-2}, 0.5 cm^2 area, 3 s), (c) being read using the defocused red output of a He–Ne laser (open circuit, 5 mW cm^{-2}, 0.5 cm^2 area) and (d) having being erased following application of +1.0 V for 15 s.



Scheme 2

electrode of a sealed two-electrode cell. The cell was filled with an organic solvent containing the electrolyte TBAP and the sacrificial donor TEOA. The counter electrode was conducting glass.

As can be seen from Fig. 2, under open circuit conditions it is possible to write a well defined pattern, consisting of four spots, to the device using the defocused green–blue output of an Ar-ion laser.[21] Visual inspection establishes these spots are the same size as the area irradiated by the defocused laser beam, while optical absorption spectroscopy establishes that the appearance of these spots is due to formation of the radical cation of the viologen component. As can also be seen from Fig. 2, this pattern, which persists for up to 1 h under open circuit conditions, may be read using the defocused red output of a He–Ne laser.[22] Importantly the red laser source does not write to the device as it does not absorb light at this wavelength. The pattern shown in Fig. 2 may be fully erased by applying a voltage of +1.0 V for 15 s.[23] Furthermore, so long as this voltage continues to be applied, irradiation with the green–blue output of an Ar-ion laser no longer results in a pattern being written to the device. This corresponds to an off state. Clearly, these findings are consistent with those presented in Fig. 1 and the mechanism proposed to account for them.

In summary, it is possible to write to the proof-of-principle device whose construction is described using blue–green light and to read the same device using red light. Furthermore, by applying a sufficiently positive potential the device may be reset.

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8 Transparent nanostructured TiO_2 films (10 mm × 10 mm active area, 4 µm thick, 10 nm diameter nanocrystals) were prepared on fluorine doped SnO_2 glass (10 mm × 20 mm substrate area, 0.5 mm, 8 Ω $\square^{-1}$, supplied by Glastron).[7] A ruthenium tris(bipyridyl) complex and viologen were covalently linked and irreversibly chemisorbed at the surface of a constituent nanocrystal of the nanostructured TiO_2 film (5×10^{-4} mol dm^{-3} in methanol, 24 h).[5,6] The extinction of the ruthenium complex component was determined (14 200 dm^3 mol^{-1} cm^{-1}, 460 nm) and used to calculate the concentration of adsorbed molecular components (2.5×10^{16} cm^{-2}, projected (geometric) area not including surface roughness).[6]

9 The reference and counter electrodes were Ag/AgCl/saturated KCl (aq) and Pt, respectively. The electrolyte, continuously degassed by bubbling with argon, was an acetonitrile–ethanol mixture (73 : 30, v/v) containing added tetrabutylammonium perchlorate (TBAP, 0.10 mol dm^{-3}) and triethanolamine (TEOA, 0.05 mol dm^{-3}). Potential control was provided by a Solatron SI 1287 potentiostat. Optical absorption spectra were measured using a Hewlett–Packard 8452A diode array spectrophotometer against a background recorded at 0.00 V.

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11 Prior to irradiation, 20% of the viologen components on TiO_2–**RV** are reduced at an applied potential of −0.45 V. Following irradiation using the defocused blue–green (488 and 514 nm) output of an argon-ion laser (200 mW cm^{-2}, 1 cm^2 area, 3 s) the absorbance at 610 nm increased by 0.085 absorbance units owing to formation of the radical cation of the viologen component. Using the extinction coefficient for the radical cation of the viologen component as given in ref. 10, it is estimated that a further 14% of the viologen components are reduced. The combined percentage, 34%, is in excellent agreement with that observed prior to irradiation at an applied potential of −0.60 V (32%).[6]

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20 A transparent nanostructured TiO_2 film (25 mm × 25 mm active area, 4 µm thick, 10 nm diameter nanocrystals) was prepared on fluorine doped SnO_2 glass (30 mm × 30 mm substrate area, 0.5 mm, 8 Ω $\square^{-1}$, supplied by Glastron).[7] The linked ruthenium tris(bipyridyl) complex and viologen, **RV**, was irreversibly chemisorbed at the surface of a constituent nanocrystal of the nanostructured TiO_2 film (5×10^{-4} mol dm^{-3} in methanol, 24 h) to yield the heterosupramolecular assembly TiO_2–**RV**.[5,6] A conducting glass counter electrode (30 mm × 30 mm substrate area, 0.5 mm, 8 Ω $\square^{-1}$, supplied by Glastron) was mounted over the working electrode and sealed using a proprietary adhesive supplied by Donnelly Mirrors (Ireland) Ltd. The above adhesive, which contained 80 µm polystyrene beads to maintain a constant separation between the working and counter electrodes, was cured at 130 °C for 1 h. One corner of the device was kept free of adhesive to permit subsequent introduction, by vacuum back filling under argon, of the following electrolyte: acetonitrile–ethanol (73 : 30, v/v), TBAP (0.10 mol dm^{-3}) and TEOA (0.05 mol dm^{-3}). Finally, this opening was sealed using proprietary UV rapid-cure adhesive, again supplied by Donnelly Mirrors (Ireland) Ltd. The device was connected to a Thompson Electrochem Ministat 251, configured to act as a precision voltage source.

21 The device in ref. 20 was written to using the defocused blue–green (488 and 514 nm, 8 mm diameter) output of an argon-ion laser (70 mW cm^{-2}, 0.5 cm^2 area, 3 s).

22 The device in ref. 20 was read using the defocused red (633 nm) output of He–Ne laser (5 mW cm^{-2}, 0.5 cm^2 area, 3 s).

23 A voltage of +1.00 V was applied to the device in ref. 20 for 15 s. The working electrode was biased positive with respect to the counter electrode.

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