Heterosupramolecular Chemistry: Self-Assembly of an Electron Donor (TiO_2 Nanocrystallite)–Acceptor (Viologen) Complex

Lucy Cusack, S. Nagaraja Rao and Donald Fitzmaurice*

Dedicated to Dr. Satoshi Ushioda on the occasion of his 65th birthday

Abstract: A TiO_2 nanocrystallite has been modified to recognise and selectively bind, by complementary hydrogen bonding, a uracil substrate incorporating a viologen moiety. Band-gap excitation of the self-assembled donor (TiO_2 nanocrystallite)–acceptor (viologen) complex results in electron transfer. Some implications of these findings for the self-assembly of functional nanostructures containing both condensed phase and molecular components are considered.

Keywords
electron transfer · heterosupermolecules · self-assembly · titanium oxide · viologens

Introduction

A heterosupermolecule is formed by linking a condensed phase and molecular components.[1] As is the case for a supermolecule, the properties of the constituent components largely persist[2] and an associated heterosupramolecular function is observed.[2] Specifically, a heterosupermolecule consisting of covalently linked TiO_2 nanocrystallite, viologen and anthraquinone components has been described,[3] and the associated heterosupramolecular function demonstrated, namely, light-induced vectorial electron flow.[4] The potentiostatic modulation of this function has also been demonstrated.[5] The potential advantages of heterosupramolecular chemistry in the construction of practical molecular devices have been noted.[5]

To date, the constituent components of a heterosupermolecule have been covalently linked.[1, 3–5] As a consequence, their self-assembly has been precluded.[6] Recently, however, TiO_2 nanocrystallites stabilised by the modified pyridine **I**[7] (Scheme 1, TiO_2–**I**) have been prepared. These nanocrystallites selectively bind, by complementary hydrogen bonding, the modified uracil (**II**) to form the heterosupermolecule TiO_2–(**I**+**II**).[8] In a further development of these studies, the self-assembly of the electron donor (TiO_2 nanocrystallite)–acceptor (viologen) heterosupramolecular complex TiO_2–(**I**+**III**) is reported.

Results and Discussion

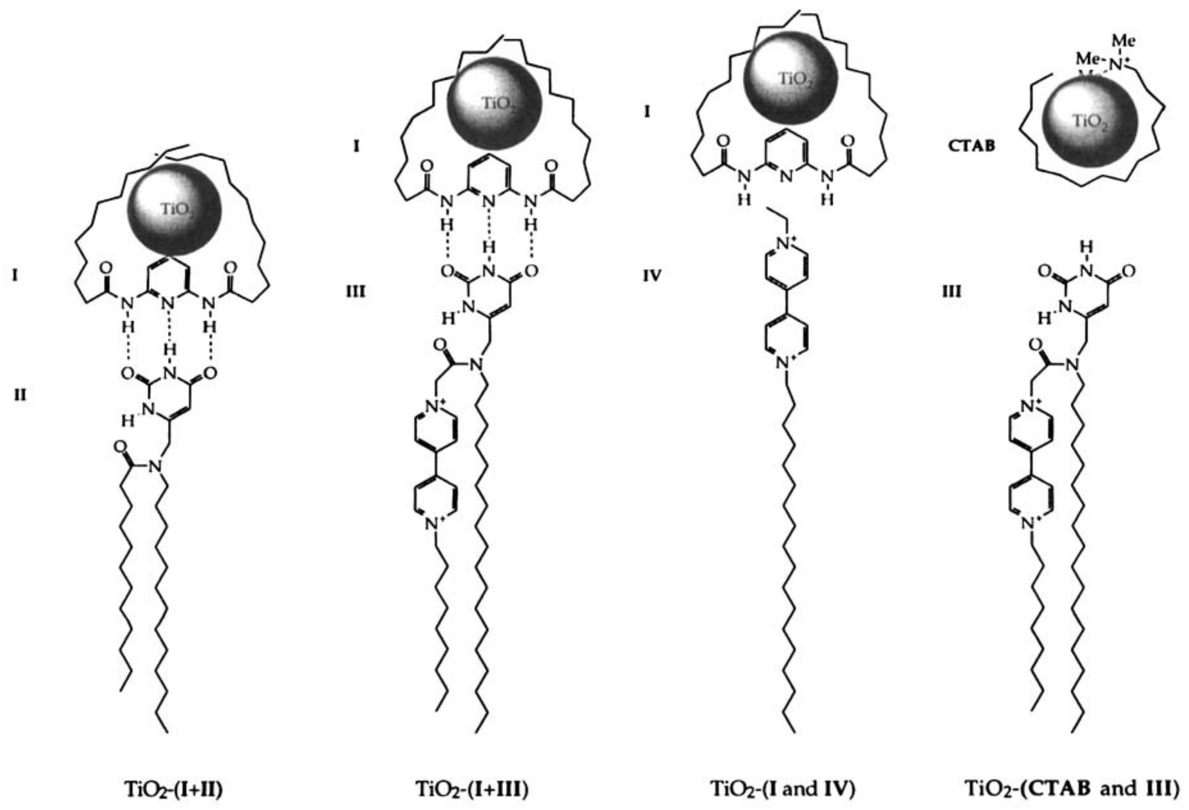
The ^1H NMR spectra recorded for TiO_2–**I**, **III** and TiO_2–(**I**+**III**) in $CDCl_3$/[D$_6$]acetone are shown in Figure 1 a–c. The amidic proton resonances of TiO_2–**I** are observed at $\delta = 8.67$. The amidic and imidic proton of **III** resonate at $\delta = 9.35$ and 9.70, respectively. For TiO_2–(**I**+**III**), the above resonances are observed at $\delta = 8.76$, 9.36 and 9.88, respectively. The basis for these assignments have previously been discussed in detail for TiO_2–(**I**+**II**).[8] The measured down-field shifts in the resonances assigned to the amidic protons of **I** and the imidic proton of **III** are consistent with self-assembly, by complementary hydrogen bonding, of the heterosupramolecular complex TiO_2–(**I**+**III**) (Scheme 1).[7–9] Also shown in Figure 1 are the ^1H NMR spectra in $CDCl_3$/[D$_6$]acetone recorded for a mixture of TiO_2–**I** and **IV**, denoted TiO_2–(**I** and **IV**), and a mixture of TiO_2–**CTAB** and **III**, denoted TiO_2–(**CTAB** and **III**). For TiO_2–(**I** and **IV**), the amidic proton resonances of TiO_2–**I** are observed at $\delta = 8.67$ both prior to and following addition of **IV**. This observation is consistent with the assertion that TiO_2–**I** and **IV** do not self-assemble to form a heterosupermolecule by complementary hydrogen bonding. Similarly, for TiO_2–(**CTAB** and **III**), the imidic proton resonance of **III** is observed at $\delta = 9.79$ prior to and following its addition to TiO_2–**CTAB**. This observation is again consistent with the assertion that TiO_2–**CTAB** and **III** do not self-assemble to form a heterosupermolecule by complementary hydrogen bonding.

Based on these findings it was expected that band-gap excitation of the TiO_2 nanocrystallite in TiO_2–(**I**+**III**) would result in electron transfer to the viologen, whereas in TiO_2–(**I** and **IV**) and TiO_2–(**CTAB** and **III**) it would not. Transient and steady-state absorption experiments were performed to test this expectation.

---

[*] D. Fitzmaurice, L. Cusack, S. N. Rao
Department of Chemistry, University College Dublin
Belfield, Dublin 4 (Ireland)
Fax: Int. code +(1)706-2127
e-mail: dfitz@macollamh.ucd.ie

0947-6539/97/0302-0202 $ 15.00+.25/0



Scheme 1. TiO_2–(**I**+**II**) [8] and the three systems examined in this study.

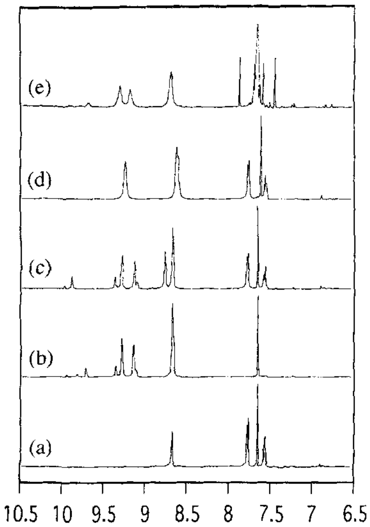


Figure 1. ^{1}H NMR spectra in a $CDCl_3$/[D_6]acetone mixture (1:1: *v*/*v*) at 20 °C: a) TiO_2–**I**; b) **III**; c) TiO_2–(**I**+**III**); d) TiO_2–(**I** and **IV**); e) TiO_2–(**CTAB** and **III**).

Figure 2 shows the μs and ms absorption transients and steady-state absorption spectra measured following band-gap excitation of TiO_2–**I** in chloroform/acetone. We note that:

1) The *μs transient* is not measurably dependent on the extent to which TiO_2–**I** is degassed.
2) While the ms transient for degassed TiO_2–**I** decays to about 50% of its initial amplitude between pulses, the same transient for aerated TiO_2–**I** decays fully.
3) While the visiblespectrum measured following band-gap irradiation of degassed TiO_2–**I** agrees with that reported for photogenerated electrons trapped in a TiO_2 nanocrystallite,[10, 11] no spectrum is measured for aerated TiO_2–**I** under the same conditions.
4) Based on the final amplitude of the ms transient for degassed TiO_2–**I** (0.0001 a.u.), an irradiation volume of 0.4 cm^3 (effective path-length of 0.7 cm) and a sample volume of 1.8 cm^3, one predicts a steady-state absorption of 0.003 a.u. at 600 nm.

On this basis, the μs transient in Figure 2a is assigned to long-lived electrons trapped in the TiO_2 *nanocrystallite of* TiO_2–**I**. Finally, as there is no measurable absorption by the molecular component **I** at 355 nm, no transients are measured for **I**.

Also shown in Figure 2 are the μs and ms absorption transients and steady-state absorption spectra measured following band-gap excitation of TiO_2–(**I**+**III**) in chloroform/acetone. We note that:

1) The μs transient is not measurably dependent on the extent to which TiO_2–(**I**+**III**) is degassed.
2) While the ms transient for degassed TiO_2–(**I**+**III**) rises initially within the laser pulse and slowly during 10 ms, the ms transient for aerated TiO_2–(**I**+**III**) rises only within the laser pulse.
3) While the ms transient for degassed TiO_2–(**I**+**III**) decays to about 80% of its initial amplitude, the same transient for aerated TiO_2–(**I**+**III**) decays fully.
4) The visible spectrum measured following band-gap irradiation of degassed TiO_2–(**I**+**III**) agrees well with that reported for the radical cation of viologens[12] and, as expected, is offset from the baseline by about 0.003 a.u. due to the presence of long-lived electrons trapped in the TiO_2 nanocrystallites of TiO_2–**I**.[10, 11] In contrast, no spectrum is measured for aerated TiO_2–(**I**+**III**) under the same conditions.
5) Based on the final amplitude (0.0015 a.u.) of the ms transient for degassed TiO_2–(**I**+**III**), an irradiation volume of 0.4 cm^3 and a sample volume of 1.4 cm^3, one predicts a steady-state absorption of about 0.06 a.u. at 600 nm.

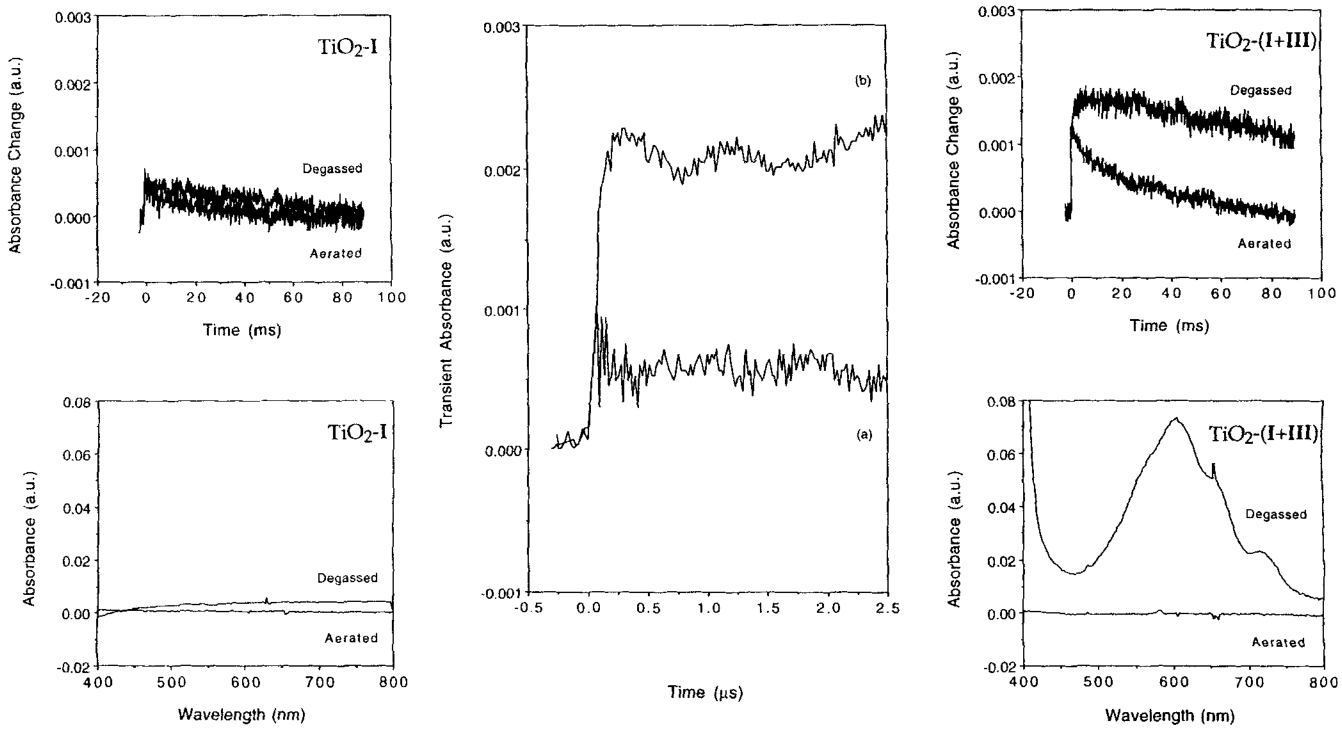


Figure 2. a) Transient absorption at 600 nm for degassed $\mathrm{TiO_2}$–**I** in a chloroform/acetone mixture (1:1: *v*/*v*) at 20 °C on the μs timescale following band-gap excitation at 355 nm (average of 10 pulses of 5 ns duration at 2 mJ per pulse). Also shown are the absorption transients for degassed and aerated $\mathrm{TiO_2}$–**I** in a chloroform/acetone mixture (1:1: *v*/*v*) at 20 °C on the ms timescale (average of 100 pulses of 5 ns duration at 2 mJ per pulse) (top left) and the corresponding absorption spectra measured following irradiation (bottom left). b) and spectra on the right: as above for $\mathrm{TiO_2}$–(**I**+**III**).

On this basis, the μs transient in Figure 2b is assigned to radical cation of **III** and to long-lived electrons trapped in the $\mathrm{TiO_2}$ nanocrystallite of $\mathrm{TiO_2}$–(**I**+**III**). The slow component of the ms transient for degassed $\mathrm{TiO_2}$–(**I**+**III**) is assigned to the radical cation of **III** formed by diffusion to $\mathrm{TiO_2}$–**I**.[13] It is noted that the contribution by trapped electrons to the measured transient for degassed $\mathrm{TiO_2}$–(**I**+**III**) may be accurately deduced from the transient measured for degassed $\mathrm{TiO_2}$–**I**. Finally, as there is no measurable absorption by the molecular components **I** or **III** at 355 nm, no transients are measured for **I**, **III** or (**I**+**III**).

Figure 3 shows the μs and ms absorption transients and steady-state absorption spectra measured for $\mathrm{TiO_2}$–(**I** and **IV**) in chloroform/acetone. We note that:

1) The μs transient is not measurably dependent on the extent to which $\mathrm{TiO_2}$–(**I** and **IV**) is degassed.
2) While the ms transient for degassed $\mathrm{TiO_2}$–(**I** and **IV**) rises within the laser pulse and slowly during 10 ms, the ms transient for aerated $\mathrm{TiO_2}$–(**I** and **IV**) rises only within the laser pulse.
3) While the ms transient for degassed $\mathrm{TiO_2}$–(**I** and **IV**) decays to about half its maximum amplitude, the same transient for aerated $\mathrm{TiO_2}$–(**I** and **IV**) decays fully and agrees well with that for aerated $\mathrm{TiO_2}$–**I**.
4) The visible spectrum measured following band-gap irradiation of degassed $\mathrm{TiO_2}$–(**I** and **IV**) agrees well with that reported for the radical cation of viologens,[12] and is offset from the baseline by about 0.003 a.u. due to the presence of long-lived electrons trapped in the $\mathrm{TiO_2}$ nanocrystallites of $\mathrm{TiO_2}$–**I**.[10, 11] In contrast, no spectrum is measured for aerated $\mathrm{TiO_2}$–(**I** and **IV**) under the same conditions.
5) Based on the difference of the final amplitudes of the ms transients (0.0005 a.u.), an irradiation volume of 0.4 $\mathrm{cm^3}$ and a sample volume of 1.4 $\mathrm{cm^3}$, one predicts a steady-state absorption of 0.02 a.u. at 600 nm for degassed $\mathrm{TiO_2}$–(**I** and **IV**) by reduced **IV**.

On this basis, the μs transient in Figure 3a is assigned to electrons trapped in a $\mathrm{TiO_2}$ nanocrystallite and to the radical cation of **IV** formed by diffusion to the surface of $\mathrm{TiO_2}$–**I**.[13] Finally, as there is no measurable absorption by the molecular components **I** or **IV** at 355 nm, no transients are measured for **I**, **IV** or (**I** and **IV**).

Also shown in Figure 3 are the μs and ms absorption transients and steady-state absorption spectra measured for $\mathrm{TiO_2}$–(**CTAB** and **III**) in chloroform/acetone. Qualitatively, they agree with those measured for $\mathrm{TiO_2}$–(**I** and **IV**) although, the following quantitative differences are noted: Firstly, the ms transients for degassed and aerated $\mathrm{TiO_2}$–(**CTAB** and **III**) decay more slowly.[14] Therefore, while the visible spectrum measured following band-gap irradiation of degassed $\mathrm{TiO_2}$–(**CTAB** and **III**) agrees well with that reported for the radical cation of viologen,[12] it is offset from the baseline by about 0.006 a.u., twice the value for degassed $\mathrm{TiO_2}$–(**I** and **IV**), owing to the presence of longer-lived electrons trapped in the $\mathrm{TiO_2}$ nanocrystallites of $\mathrm{TiO_2}$–**I**.[10, 11] Consistent with the above and in contrast to aerated $\mathrm{TiO_2}$–(**I** and **IV**), a spectrum is measured for aerated $\mathrm{TiO_2}$–(**CTAB** and **III**), which agrees well with that reported for photogenerated long-lived electrons trapped in $\mathrm{TiO_2}$ nanocrystallites.[10, 11] Secondly, based on the difference of the final amplitudes of the ms transients (0.0005 a.u.), an irradiation volume of 0.4 $\mathrm{cm^3}$ and a sample volume of 1.4 $\mathrm{cm^3}$, one predicts a steady-state absorption of 0.02 a.u. at 600 nm for degassed

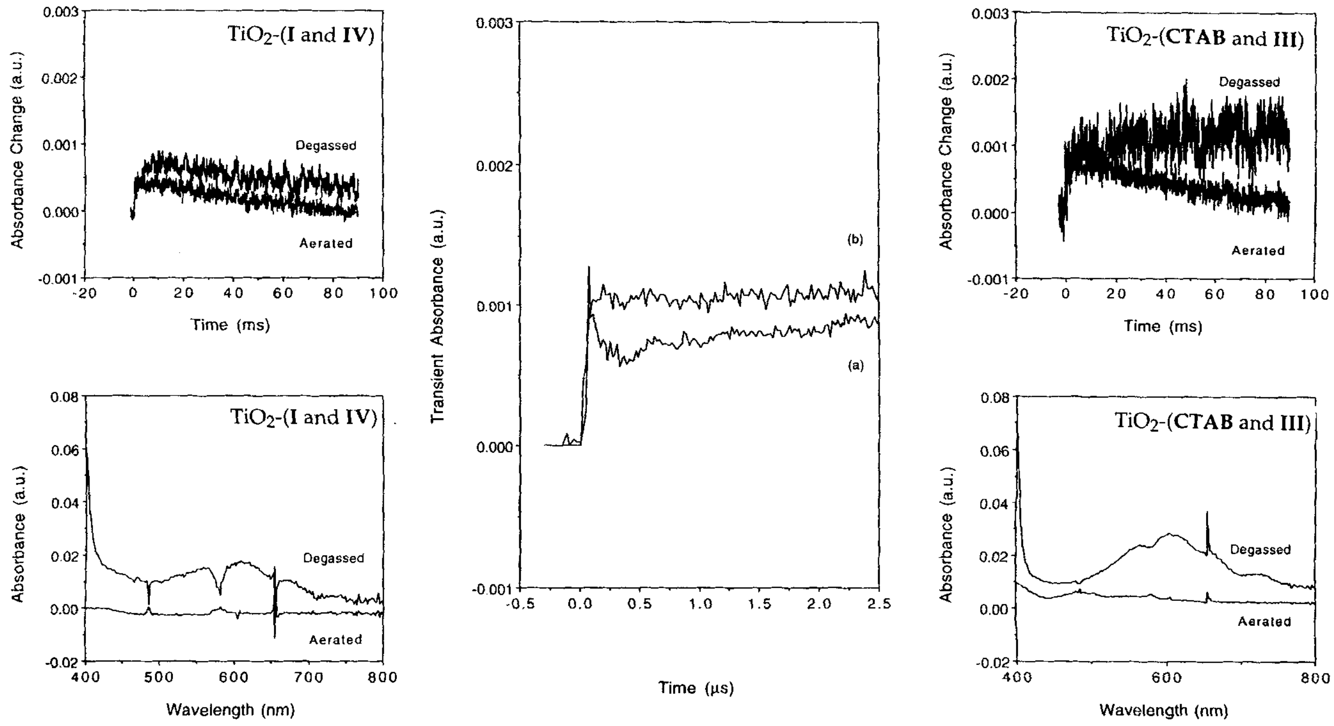


Figure 3. a) Transient absorption at 600 nm for degassed TiO_2–(**I** and **IV**) in a chloroform/acetone mixture (1:1: *v*/*v*) at 20 °C on the μs timescale following band-gap excitation at 355 nm (average of 10 pulses of 5 ns duration at 2 mJ per pulse). Also shown are the absorption transients for degassed and aerated TiO_2–(**I** and **IV**) in a chloroform/acetone mixture (1:1: *v*/*v*) at 20 °C on the ms timescale (average of 100 pulses of 5 ns duration at 2 mJ per pulse) (top left) and the corresponding absorption spectra measured following irradiation (bottom left). b) and spectra on the right: as above for TiO_2–(**CTAB** and **III**).

TiO_2–(**CTAB** and **III**) by reduced **III**. On this basis, the μs transient in Figure 3 b is assigned to electrons trapped in a TiO_2 nanocrystallite and to the radical cation of **III** formed by diffusion to the surface of TiO_2–**CTAB**. Finally, as there is no measurable absorption by the molecular components **CTAB** or **III** at 355 nm, no transients are measured for **CTAB**, **III** or (**CTAB** and **IV**).

As the optical absorption at 355 nm of the nanocrystallite in TiO_2–**I** nm is 0.1 a.u., the pulse energy is 2 mJ, the cross-sectional area for irradiation is 0.4 cm^2 and assumed reflection losses are 20%, it is estimated that six electron–hole pairs are generated in each TiO_2 nanocrystallite. From the initial amplitude of the μs transient in Figure 2 b for degassed TiO_2–(**I** + **III**) and the known extinction coefficient for the reduced form of viologen,[12] it is estimated that one radical cation of **III** is formed per particle. That is, the charge separation efficiency is about 6% with the majority of the photogenerated electron–hole pairs being lost by recombination or trapping.[10, 11] From the initial amplitudes of the μs transients for degassed TiO_2–(**I** and **IV**) and TiO_2–(**CTAB** and **III**), equal to that for degassed TiO_2–**I**, it is clear that no radical cations of **IV** and **III** are formed within the laser pulse, although, as for TiO_2–(**I** + **III**), they are subsequently formed on the ms timescale by diffusion. It is noted that the molecular components of TiO_2–(**I** + **III**), TiO_2–(**I** and **IV**) or TiO_2–(**CTAB** and **III**) may undergo oxidative degradation under prolonged irradiation in the absence of a suitable hole scavenger.[15] However, no evolution of the transients was observed in Figures 2 or 3 that might be attributed to oxidative photodegradation of the molecular components.

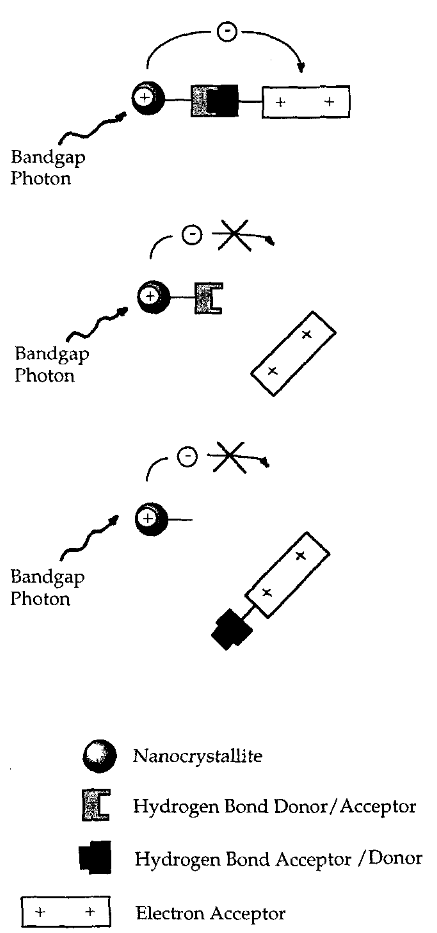
Conclusions

In short and as represented pictorially in Scheme 2 (top), TiO_2–**I** containing a diaminopyridine moiety recognises and selectively binds the modified viologen **III** containing a uracil moiety. Light-induced vectorial electron flow is observed for the resulting donor–acceptor complex. There is ample precedent for electron transfer over long distances in supermolecules and their organised assemblies.[16] In the absence of a uracil moiety (Scheme 2, middle) the modified nanocrystallite TiO_2–**I** does not recognise or selectively bind the viologen **IV**. Similarly, in the absence of a diaminopyridine moiety (Scheme 2, bottom) the modified nanocrystallite TiO_2–**CTAB** does not recognise or selectively bind the modified viologen **III**. In neither of these last two cases is direct light-induced electron transfer to the viologen moiety observed. Our current studies are directed toward modifying the surface of a TiO_2 nanocrystallite to selectively bind another condensed-phase component.[17] Looking further to the future, analogous approaches involving many condensed phase and molecular components may be envisaged and offer the prospect of self-assembling complex heterosupramolecular structures.

Experimental Procedure

TiO_2 nanocrystallites ($d = 22 \pm 2$ Å and $\lambda_{onset} = 360$ nm) were prepared in $CDCl_3$ in the presence of **I** or **CTAB** to form the stable sols denoted TiO_2–**I** or TiO_2–**CTAB** respectively [18].

I and **II** have been prepared and characterised previously [7,8]. A summary of their ^1H NMR spectra is given.



Scheme 2. Pictorial representation of TiO_2-(**I**+**III**), TiO_2-(**I** and **IV**) and TiO_2-(**CTAB** and **III**).

I ($CDCl_3$): $\delta = 0.88$ (t, 6H, $J = 7.0$ Hz), 1.25–1.74 (m, 36H), 2.36 (t, 4H, $J = 7.6$ Hz), 7.52 (s, 2H, -NH amidic), 7.69 (t, 1H, $J = 8.2$ Hz), 7.88 (d, 2H, $J = 8.2$ Hz).

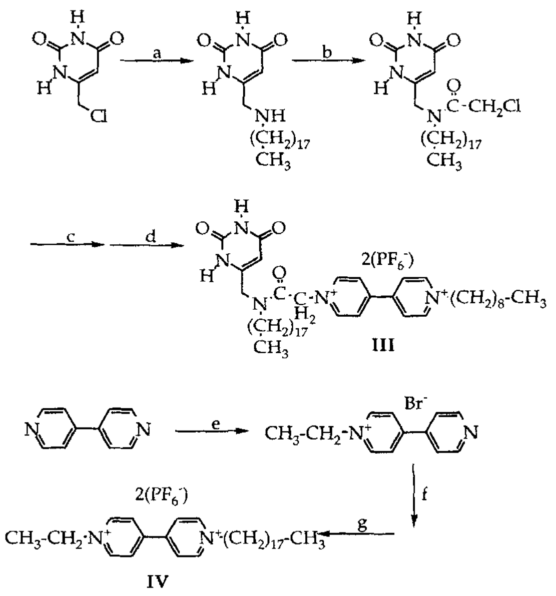
II ($CDCl_3$): $\delta = 0.88$ (t, 6H, $J = 7.0$ Hz), 1.26–1.58 (m, 40H), 2.36 (t, 2H, $J = 7.8$ Hz), 4.16 (s, 2H), 5.52 (s, 1H); 8.14 (s, 1H, -NH amidic); 9.51 (s, 1H, -NH imidic).

III·$(PF_6)_2$ and **IV**·$(PF_6)_2$ were synthesised as shown in Scheme 3 and characterised by elemental analysis and ^1H NMR.

III·$(PF_6)_2$: Calculated C, 52.42; H, 7.10; N, 6.95. Found: C, 52.02; H, 7.02; N, 6.83. ^1H NMR ($[D_6]$acetone): $\delta = 0.86$ (t, 6H, $J = 6.7$ Hz), 1.28–1.39 (m, 46H), 3.60 (t, 2H, $J = 7.8$ Hz), 4.52 (s, 2H), 5.00 (t, 2H, $J = 7.6$ Hz), 5.52 (s, 1H), 6.32 (s, 2H), 7.5 (brs, 1H, -NH amidic), 8.87–8.91 (dd, 4H, $J = 5.1$, 2.0 Hz), 9.35 (d, 2H, $J = 7.3$ Hz), 9.49 (d, 2H, $J = 7.1$ Hz), 9.90 (s, 1H, NH imidic).

IV·$(PF_6)_2$: Calculated C, 49.44; H, 6.92; N, 3.85. Found: C, 50.00; H, 7.11; N, 3.84. ^1H NMR ($[D_6]$acetone): $\delta = 0.88$ (t, 3H, $J = 6.6$ Hz), 1.28–1.32 (m, 32H), 1.80 (t, 3H, $J = 7.4$ Hz), 4.96 (q, 4H, $J = 7.4$ Hz), 8.85 (dd, 4H, unresolved coupling), 9.43 (d, 2H, unresolved coupling), 9.46 (d, 2H, unresolved coupling). **CTAB** was used as supplied without further purification. A summary of its ^1H NMR spectrum ($CDCl_3$): $\delta = 0.88$ (t, 3H, $J = 6.6$ Hz), 1.25–1.36 (m, 28H), 1.78 (m, 2H), 3.50 (s, 9H).

General procedure: A solution of the required molecular component, either **III** or **IV**, was prepared in acetone or $[D_6]$acetone and added to an equal volume of TiO_2–**I** or TiO_2–**CTAB** in chloroform or $CDCl_3$. The final (particle) concentration of TiO_2 nanocrystallites was 4×10^{-7} mol dm^{-3}. The final (molecular) concentration of **I**, **III**, **IV** and **CTAB** was, in each case, 4×10^{-4} mol dm^{-3}. It is noted, that under these conditions, about 70% of **I** or **CTAB** are adsorbed at the nanocrystallite surface [8]. The above sols were studied by ^1H NMR and transient optical absorption spectroscopy at 20 °C. All NMR spectra were recorded on either a JEOL JNM-GX270 FT or Varian 500 FT spectrometer. All absorption transients were recorded, unless otherwise stated, at 600 nm following pulsed excitation at 355 nm (5 ns, 2 mJ pulse^{-1}) of a rigorously degassed samples contained in a vacuum-tight 1 cm by 1 cm quartz cell. The transient absorption spectrometer, a double-beam laser-based system capable of measuring absorption changes of 5×10^{-5} absorbance units, has been described in detail elsewhere [19]. Transients reported on the µs timescale are the average of ten measurements, those reported on the ms timescale are the average of one hundred measurements. Absorption spectra were measured using a Hewlett-Packard 8452A diode array spectrophotometer.



Scheme 3. Reaction conditions for synthesis of **III** and **IV**: a) Octadecylamine, *i*PrOH, reflux, N_2; b) chloroacetic anhydride, pyridine–chloroform, RT; c) 4-nonylbipyridinium bromide, acetonitrile, reflux; d) methanolic ammonium hexafluorophosphate; e) excess ethyl bromide (neat), RT; f) octadecyl bromide, acetonitrile, reflux; g) as in (d).

Acknowledgements: This work was supported by a grant from the Commission of the European Union under the Joule III programme (Contract JOR 3-CT 960107). The authors thank D. Harris of Cell Media for the cover design.

Received: June 13, 1996 [F 478]

---

[1] X. Marguerettaz, R. O'Neill, D. Fitzmaurice, *J. Am. Chem. Soc.* **1994**, *116*, 2628.
[2] a) J.-M. Lehn, *Supramolecular Chemistry*, VCH: Weinheim, **1995**. b) V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood: New York, **1991**; Chapt. 3.
[3] X. Marguerettaz, D. Fitzmaurice, *J. Am. Chem. Soc.* **1994**, *116*, 5017.
[4] X. Marguerettaz, G. Redmond, S. N. Rao, D. Fitzmaurice, *SPIE Proceedings Series* **1994**, *2255*, 793.
[5] X. Marguerettaz, G. Redmond, S. N. Rao, D. Fitzmaurice, *Chem. Eur. J.* **1996**, *2*, 420.
[6] a) D. Philp, J. F. Stoddart, *Synlett* **1991**, 445. b) J. S. Lindsey, *New J. Chem.* **1991**, *15*, 153. c) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312.
[7] M.-J. Brienne, J. Gabard, J.-M. Lehn, *J. Chem. Soc. Chem. Commun.* **1989**, 1868.
[8] L. Cusack, S. N. Rao, J. Wenger, D. Fitzmaurice, *Chem. Mater.* in press.
[9] a) B. Feibush, A. Fiueroa, R. Charles, K. Onan, P. Feibush, B. Karger, *J. Am. Chem. Soc.* **1986**, *108*, 3310. b) B. Feibush, M. Saha, K. Onan, B. Karger, R. Giese, *ibid.* **1987**, *109*, 7531. c) A. Hamilton, D. Van Engen, *ibid.* **1987**, *109*, 5035. d) A. Bisson, F. Carver, C. Hunter, J. Waltho, *ibid.* **1994**, *116*, 10292.
[10] a) A. Henglein, *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 246. b) D. Duonghong, J. Ramsden, M. Grätzel, *J. Am. Chem. Soc.* **1982**, *104*, 2977. c) U. Kolle, J. Moser, M. Grätzel, *Inorg. Chem.* **1985**, *24*, 2253. d) G. Rothenberger, J. Moser, M. Grätzel, N. Serpone, D. Sharma, *J. Am. Chem. Soc.* **1985**, *107*, 8054.

0947-6539/97/0302-0206 $ 15.00+.25/0

[11] There is apparently general agreement that the spectrum of trapped holes does not extend to wavelengths longer than about 450 nm: a) D. Bahnemann, A. Henglein, J. Lilie, L. Spanhel, *J. Phys. Chem.* **1984**, *88*, 709. b) O. Micic, Y. Zhang, R. Cromack, A. Trifunac, M. Thurnauer, *J. Phys. Chem.* **1993**, *97*, 7277.

[12] a) B. Kok, H. Rurainski, O. Owens, *Biochem. Biophys. Acta* **1965**, *109*, 347. b) P. Trudinger, *Ananl. Biochem.* **1970**, *36*, 222. c) T. Wantanabe, K. Honda, *J. Phys. Chem.* **1982**, *86*, 2617.

[13] H. Frei, D. Fitzmaurice, M. Grätzel, *Langmuir* **1990**, *6*, 198.

[14] L. Cusack, X. Marguerettaz, S. N. Rao, J. Wenger, D. Fitzmaurice, unpublished results. The detailed reasons for the slower rate of decay of the transient assigned to long-lived trapped electrons in TiO_2-(**CTAB** and **III**) as compared with TiO_2-(**I** and **IV**) will be discussed here and supported by detailed NMR studies.

[15] Ethanol has been shown to act as an efficient hole scavenger in a number of studies: H. Finklea in *Semiconductor Electrodes* (Ed. H. Finklea), Elsevier, New York, **1988**, p. 113.

[16] a) C. Chidsey, *Science* **1991**, *251*, 919. b) H. Finklea, D. Hanshew, *J. Am. Chem. Soc.* **1992**, *114*, 3173. c) G. Cleland, B. Horrocks, A. Houlton, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 4001.

[17] R. Rizza, L. Cusack, D. Fitzmaurice, submitted for publication.

[18] N. Kotov, F. Meldrum, J. Fendler, *J. Phys. Chem.* **1994**, *98*, 2735.

[19] D. Fitzmaurice, M. Eschle, H. Frei, J. Moser, *J. Phys. Chem.* **1993**, *97*, 3806.