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Heterosupramolecular chemistry

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The covalent and non-covalent assembly of nanocrystals and molecules in solution to yield heterosupermolecules possessing well defined heterosupramolecular functions is described. Also described is the organisation of heterosupermolecules into assemblies possessing addressable heterosupramolecular function. Strategies are considered that will permit the covalent and non-covalent assembly and organisation of a wide range of condensed phase and molecular components. Also considered are the possible longer term benefits of the development of a systematic chemistry of both condensed phase and molecular components, that is, a systematic heterosupramolecular chemistry.

1 Introduction

Conventionally, a supermolecule is distinguished from a large molecule as follows:[1] first, the molecular components of a supermolecule are non-covalently linked; secondly, the intrinsic properties of these molecular components largely persist; and thirdly, the properties of a supermolecule are not a simple superposition of the properties of the constituent molecular components, *i.e.* there exists a well defined supramolecular function.

With the widespread application of supramolecular concepts throughout chemistry, biology and physics, however, has come the need for a more inclusive definition.[2] Consequently, the term supermolecule is now also applied to covalently linked molecular components provided, as above, the properties of these constituent components largely persist and there exists a supramolecular function.

A more inclusive definition still has been adopted in discussing recent work directed toward the development of a chemistry of covalently and non-covalently assembled condensed phase and molecular components.[3] By analogy with a supermolecule, the properties of the constituent condensed phase and molecular components of a heterosupermolecule largely persist and there exists an associated heterosupramolecular function.

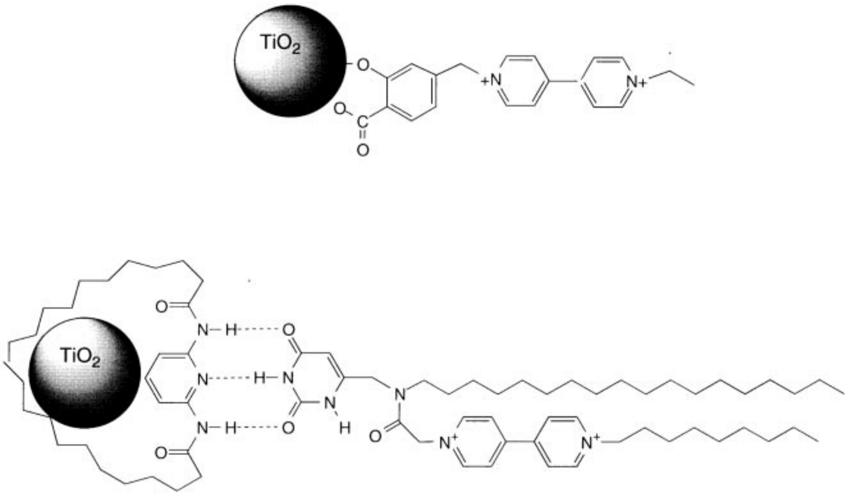
Scheme 1 shows two examples of heterosupermolecules, consisting of a covalently and non-covalently assembled condensed phase (TiO_2 nanocrystal electron donor) and molecular (viologen, electron acceptor) component,[4,5] prepared in this laboratory.

The covalent and non-covalent assembly in solution of heterosupermolecules possessing well defined heterosupramolecular functions is reviewed. Also reviewed is the covalent and non-covalent organisation of heterosupermolecules in solution to yield assemblies possessing addressable heterosupramolecular function. Strategies are considered that will permit the covalent and non-covalent assembly and organisation of a wide range of condensed phase and molecular components. Also considered are the possible long term benefits of developing a systematic chemistry of condensed phase and molecular components, *i.e.* a systematic heterosupramolecular chemistry.

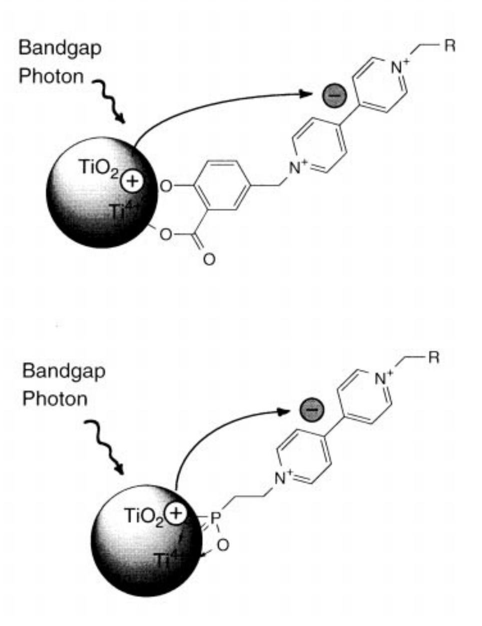
2 Covalent heterosupermolecules

The recent past has seen the synthesis of efficient sensitisers for use in regenerative photoelectrochemical cells.[6] Examples include ruthenium complexes containing bipyridine ligands derivatised by addition of carboxylic acid groups which are chemisorbed at the surface of the constituent nanocrystals of a nanostructured TiO_2 photoanode. It has been proposed that ligands containing such groups displace less basic solvent molecules and chelate Ti^{4+} sites at the surface of a TiO_2 nanocrystal.[7]

In this context, Moser and coworkers have studied the chemisorption of a series of model compounds at the surface of the constituent nanocrystals of a nanostructured TiO_2 film.[7e] They found salicylate is strongly adsorbed at a single Ti^{4+} site and is oriented normal to the substrate surface.



Scheme 1 A covalently and non-covalently assembled heterosupermolecule.



Scheme 2 Light-induced electron transfer in covalently assembled heterosupermolecules.

Chemisorption of this molecule is also accompanied by development of a visible charge transfer absorption band.[8] It was concluded that salicylate could be used to covalently assemble a TiO_2 nanocrystal and a viologen molecule in solution.

Accordingly, salicylate–viologen molecules were synthesised and chemisorbed at the surface of the TiO_2 nanocrystals in a stable aqueous or ethanolic colloidal dispersion at pH 3.0.[4,9] As salicylate is adsorbed normal to the crystallite surface at a single Ti^{4+} site,[7e] and as dications are not adsorbed at the positively charged surface of the TiO_2 nanocrystals at pH 3.0,[10] it may be assumed that the viologen molecule is oriented normal to the nanocrystal surface as shown in Scheme 2. A series of such viologens, with more or less electron withdrawing moieties ($-R$), have been prepared.[9,11]

Recently, it has been found that ruthenium based complexes containing bipyridine ligands derivatised by addition of phosphonic acid groups are even more strongly chemisorbed at TiO_2.[12] Chemisorption is, as above, discussed in terms of the displacement of less basic solvent molecules and chelation of surface Ti^{4+} sites. Accordingly, the phosphonate–viologen molecules shown in Scheme 2 have also been synthesised.[9]

Bandgap excitation of these covalently assembled heterosupermolecules results in electron transfer from the TiO_2 nanocrystal (electron donor) to the viologen (electron acceptor), *i.e.* light-induced vectorial electron transfer.[4] As the first reduction potential of the viologen may be varied systematically by appropriate choice of a more or less electron withdrawing moiety $-R$, the rate of electron transfer may be determined as a function of the associated change in free energy change.[13] Although similar studies have previously been reported,[14] an unique advantage of the approach outlined above is that the separation and relative orientation of the TiO_2 nanocrystal and viologen molecule is known.

3 Covalent heterosupramolecular assemblies

The covalent assembly of a TiO_2 nanocrystal and a viologen molecule has been described. In a development of this approach salicylate–viologens have been chemisorbed, as shown in Scheme 3, at the surface of one of the constituent TiO_2 nanocrystals of a 4 μm thick nanostructured film supported on conducting glass.[4,15]

The TiO_2 nanocrystals of the heterosupramolecular assembly in Scheme 3 are in ohmic contact with each other and with the conducting support.[16] At sufficiently negative applied potentials, therefore, electrons occupy the available conduction band states of the nanostructured TiO_2 film and are transferred to the viologen molecules covalently linked to the surface of the nanocrystals (Scheme 4).[4,15] Under open circuit conditions, bandgap excitation of the heterosupramolecular assembly in Scheme III leads to formation of electron–hole pairs in the nanostructured TiO_2 film and, in the presence of a suitable hole scavenger, to the photogenerated conduction band electrons being transferred to the viologen molecules covalently linked to the surface of the nanocrystals (Scheme 4).[4,15] The associated heterosupramolecular functions are potential and light-induced electron transfer respectively.

Since electron transfer may be initiated either by applying a sufficiently negative potential or by bandgap excitation, the following question arises: can the effects of bandgap excitation be modulated potentiostatically?

As stated above, under open circuit conditions, bandgap excitation is followed by electron transfer from a TiO_2 nanocrystallite to a viologen (ON state). At sufficiently positive applied potentials, however, no electron transfer is observed following bandgap excitation (OFF state). This modulation effect, see Scheme 5, is attributed to the fact that at positive applied potentials the photogenerated conduction band electrons reduce vacant trap states in a nanocrystal rather than a covalently attached viologen.

This finding points to two general advantages of heterosupramolecular assemblies: first, that the function of the constituent heterosupermolecules of an assembly may be modulated if a bulk property of one or more of the condensed phase components may be modulated, and secondly, that if the property of the condensed phase component that is being modulated can be monitored, the modulation state of each heterosupermolecule may be inferred.

Finally, we note the following limitations of the above heterosupramolecular assembly: first, it is not an organised heterosupramolecular assembly, as a consequence of which, the constituent heterosupermolecules are not individually addressable; secondly, the constituent heterosupermolecules do not act fully independently, *i.e.* there is electron transfer between viologens adsorbed at the same or adjacent nanocrystals;[15] and thirdly, because the constituent condensed phase and molecular components are covalently linked, they may not be self-assembled.

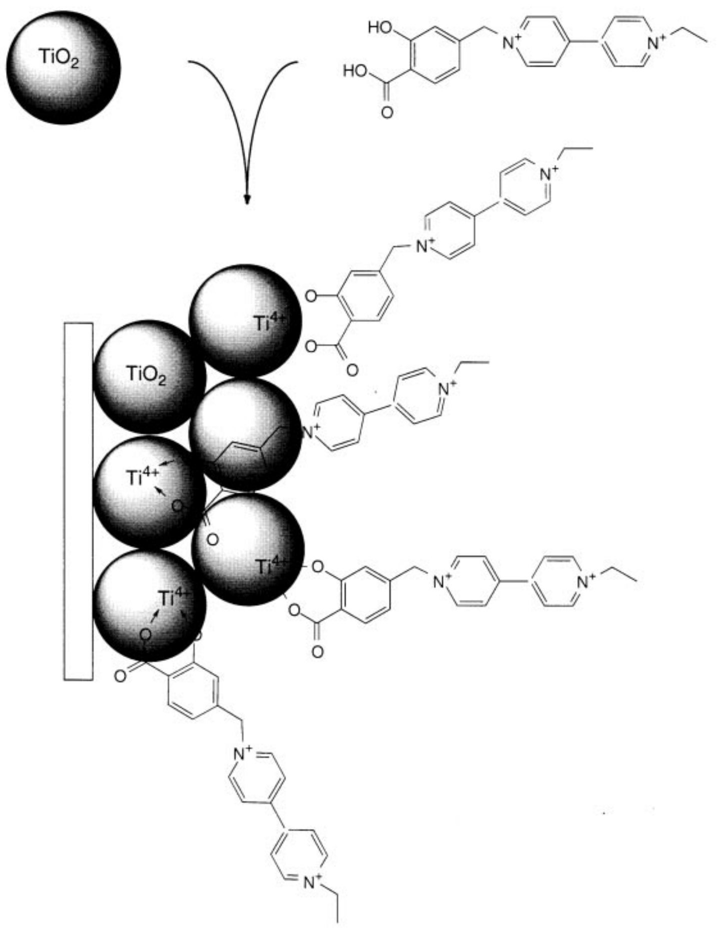
4 Non-covalent heterosupermolecules

The covalent assembly of a TiO_2 nanocrystal and a viologen molecule has been described in Section 2. An alternative approach is to non-covalently assemble these components.[5]

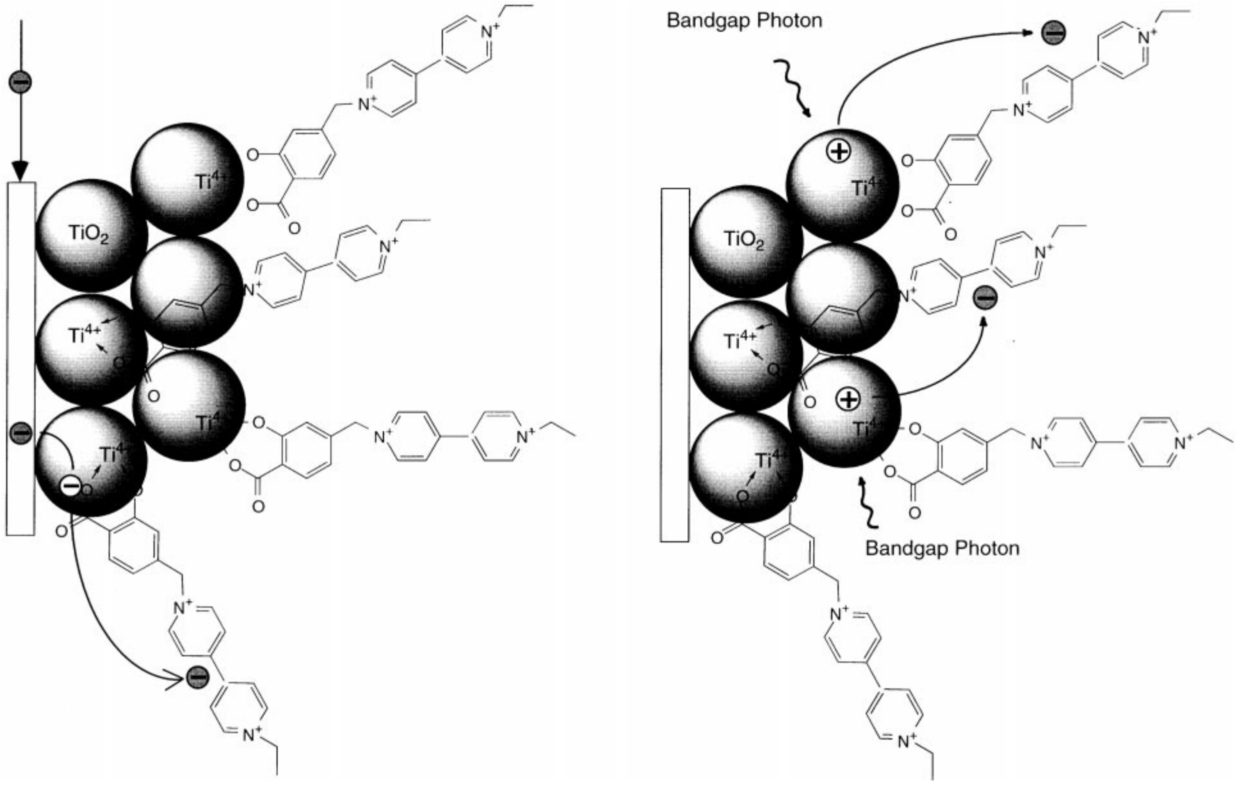
Toward this end, TiO_2 nanocrystals were prepared in the presence of the modified stabiliser shown in Scheme 6.[5,17] This stabiliser, whose synthesis has been described in detail elsewhere,[9,18] incorporates a diamidopyridine moiety which can recognise and selectively bind, by complementary hydrogen bonding, an uracil moiety.[19]

It is possible to state that the above stabiliser is physisorbed at the surface of a nanocrystal as the resulting dispersion, which otherwise flocculates on the time-scale of seconds, is stable on the time-scale of months. More quantitatively, ^1H NMR studies show that the methylene and methyl groups of this molecule interact with the surface of the TiO_2 nanocrystal at which it is adsorbed.

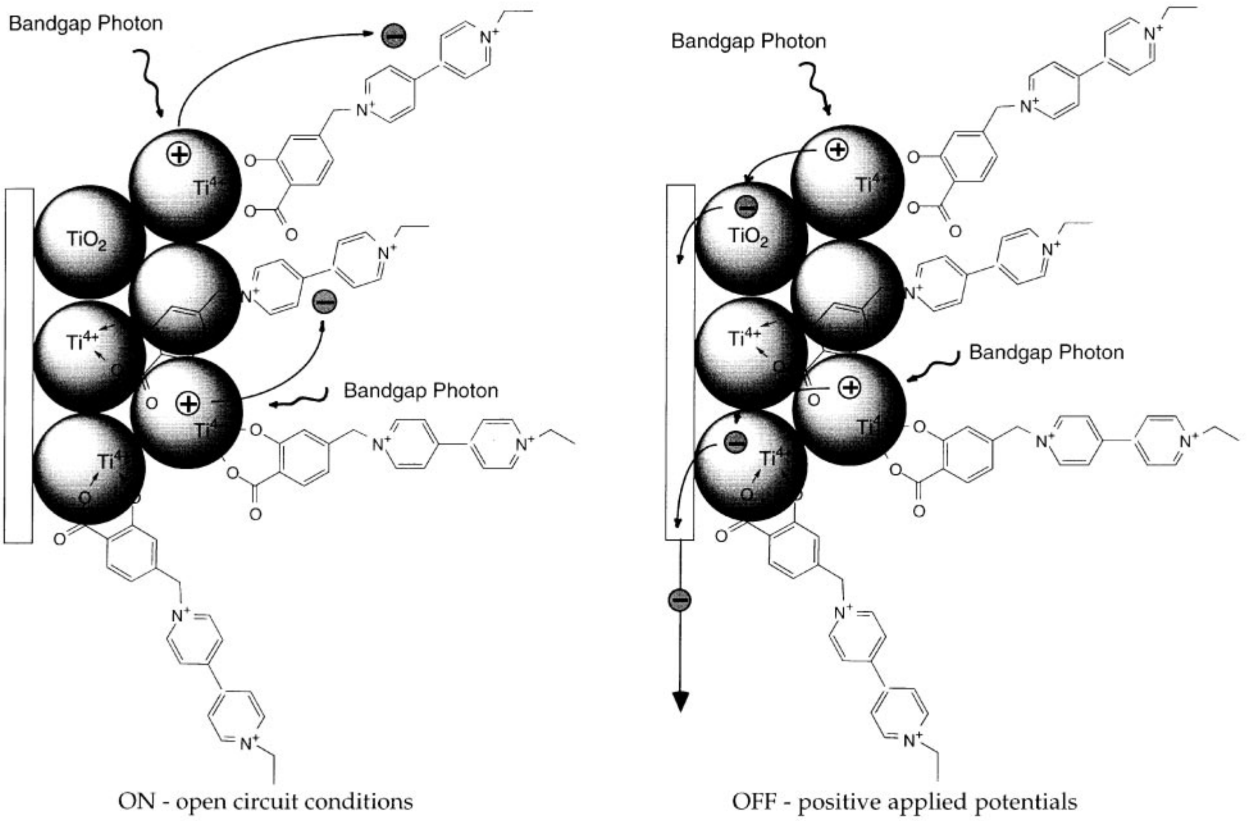
Also shown in Scheme 6 is a viologen molecule incorporating an uracil moiety. This is one of a series of compounds of the same general formula which have been prepared.[5,9] Having studied this series, it is possible to conclude the following: if



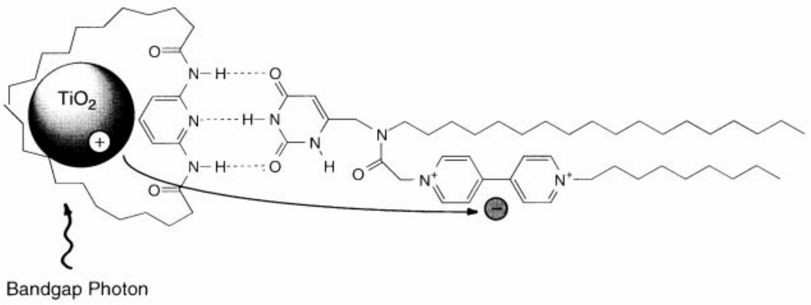
Scheme 3 A covalent heterosupramolecular assembly.



Scheme 4 Potential and light-induced electron transfer in a covalent heterosupramolecular assembly.



Scheme 5 Potential modulation of light-induced electron transfer in a covalent heterosupramolecular assembly.



Scheme 6 Light-induced electron transfer in a non-covalently assembled heterosupermolecule.

the two alkane chains contain much less than 25 methylene groups, the viologen molecule is not soluble in chloroform. If, however, the viologen molecule contains much more than about 25 methylene groups, micellisation is observed in chloroform at the concentrations necessary to enable characterisation of the resulting heterosupermolecule by ^{1}H NMR and IR.

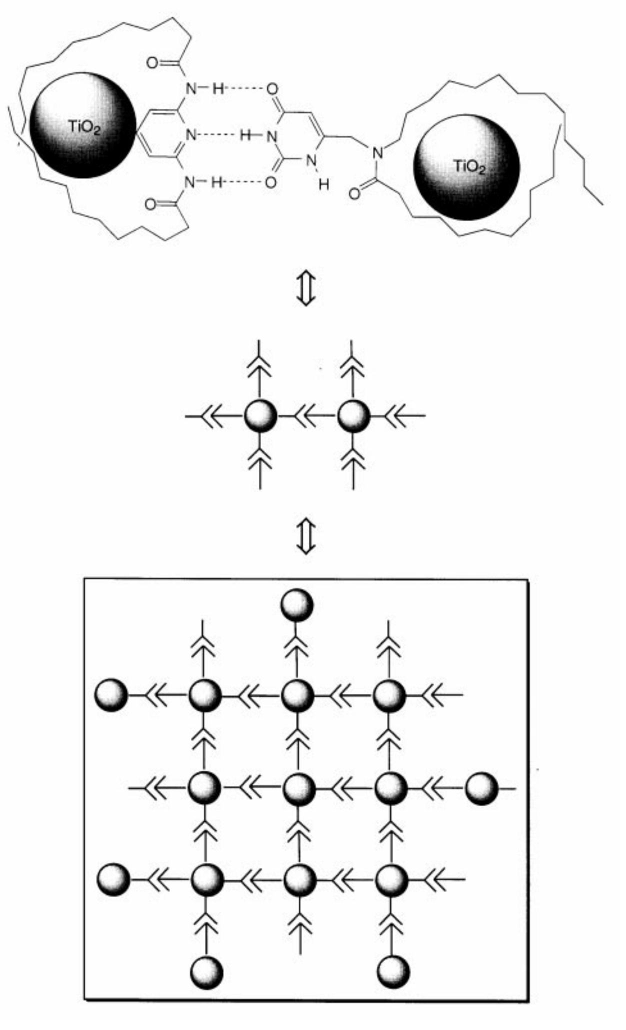
On mixing a colloidal TiO_2 nanocrystal dispersion prepared in the presence of the stabiliser incorporating a diamidopyridine moiety with a solution of the viologen molecule incorporating an uracil moiety, the former recognises and selectively binds the latter as shown in Scheme 6.[5] Bandgap excitation of a TiO_2 nanocrystal is followed by electron transfer to the non-covalently bound viologen molecule.[5] The associated heterosupramolecular function is, therefore, light-induced vectorial electron transfer.

Briefly, these studies have been extended to permit the non-covalent assembly of two TiO_2 nanocrystals. As before, TiO_2 nanocrystals were prepared in the presence of the modified stabiliser incorporating a diamidopyridine moiety.[5,17] However, TiO_2 nanocrystals were also prepared in the presence of the modified stabiliser incorporating an uracil moiety.[5,17] On mixing, these nanocrystals recognise and selectively bind each other as shown in Scheme 7.[5] Further, these nanocrystals self-organise to form an extended array in solution.[5] Evidence for ordering of the nanocrystals in these arrays has been obtained.

5 Non-covalent heterosupramolecular assemblies

A covalent heterosupramolecular assembly of TiO_2 nanocrystals and viologen molecules has been described in Section 3. In a development of these studies a non-covalent organised assembly of TiO_2 nanocrystals and viologen molecules has been prepared.

The phosphonic acid in Scheme 8 was synthesised.[9] The long alkane chain ensures this molecule is sufficiently hydrophobic to be deposited as a close-packed monolayer using Langmuir–Blodgett (LB) techniques. The phosphonic acid head group ensures irreversible attachment of the deposited monolayer to the constituent nanocrystals of a TiO_2 substrate,[12] see below. Also synthesised was the viologen shown in Scheme 8.[9] This molecule contains two alkane chains each



Scheme 7 Non-covalent assembly of an organised nanocrystal assembly.

equal in length to that of the phosphonic acid, ensuring that this molecule is also sufficiently hydrophobic that it may be deposited as a close-packed monolayer using LB techniques.

To prepare the heterosupramolecular assembly shown in Scheme 8, a close-packed monolayer of TiO_2 nanocrystals is first deposited, using LB techniques, on a conducting glass substrate. A close-packed mixed monolayer of the phosphonic acid and the viologen (ratio of 12:1) is then deposited, also using LB techniques, on the nanocrystal monolayer. Detailed characterisation confirms the deposited molecular monolayer has the structure shown.[20] On this basis it is possible to assert that there is a single viologen associated with each nanocrystal, that each viologen has a well defined orientation with respect to that nanocrystal, and that electron transfer between adjacent viologens is not significant.

Each TiO_2 nanocrystal of the organised heterosupramolecular assembly in Scheme 8 is in ohmic contact with the conducting support.[16] Upon application of a sufficiently negative potential, therefore, electrons occupy the available conduction band states of a nanocrystal and are transferred to the viologen molecule non-covalently linked to the surface of the same nanocrystal, see Scheme 9.[4,15] Under open circuit conditions, bandgap excitation of the organised heterosupramolecular assembly in Scheme 8 leads to formation of electron–hole pairs in a nanocrystal and, in the presence of a suitable hole scavenger, to photogenerated conduction band electrons being transferred to the viologen molecules non-covalently linked to the surface of the nanocrystal, see also Scheme 9.[4,15] The associated heterosupramolecular functions are potential and light-induced electron transfer, respectively.

Since electron transfer may be initiated either by applying a sufficiently negative potential or by bandgap excitation, the following question again arises: can the effects of bandgap excitation be modulated potentiostatically?

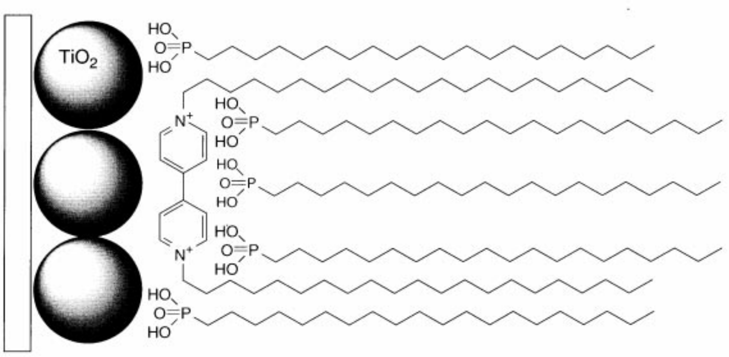
As stated above, under open circuit conditions bandgap excitation is followed by electron transfer from a TiO_2 nanocrystallite to a viologen (ON state). At sufficiently positive applied potentials, however, no electron transfer is observed following bandgap excitation (OFF state). This modulation effect, see Scheme 10, is again attributed to the fact that at positive applied potentials the photogenerated conduction band electrons reduce vacant trap states in a nanocrystal rather than a covalently attached viologen.

Finally, we note the following limitations of the covalent heterosupramolecular assembly have been addressed: first, an organised heterosupramolecular assembly has been prepared, as a consequence of which the constituent heterosupermolecules are individually addressable; secondly, the constituent heterosupermolecules act fully independently, *i.e.* there is no electron transfer between viologens adsorbed at adjacent nanocrystals;[15] and thirdly, because the constituent condensed phase and molecular components are non-covalently linked, they may be self-assembled.

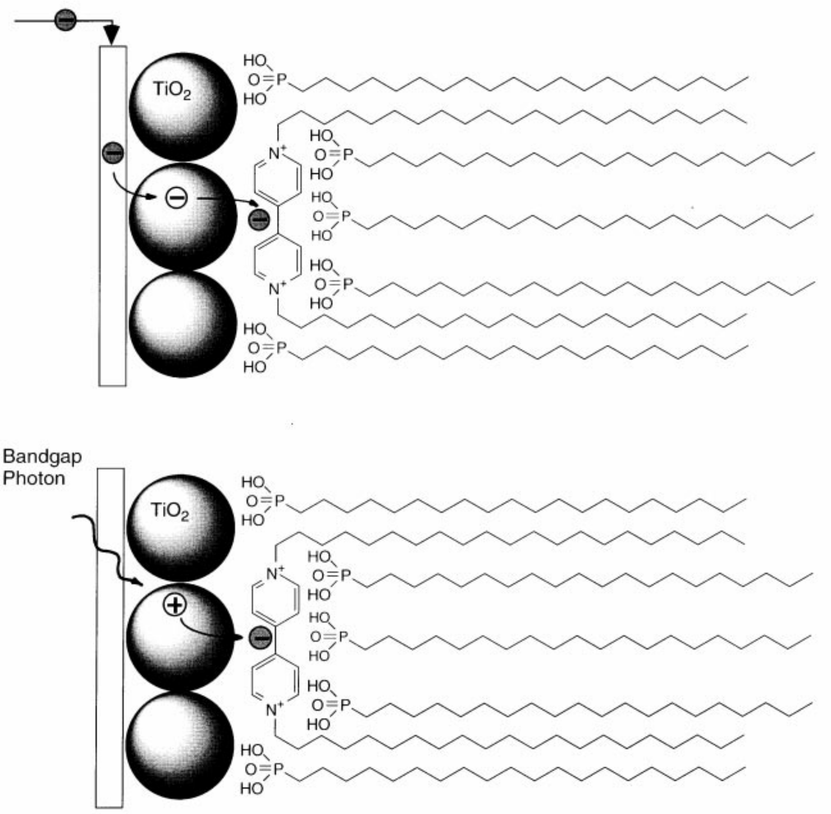
6 Current and future studies

Current and future work in this area will be directed toward the preparation and synthesis of a wider range of condensed phase and molecular components and their incorporation into heterosupermolecules and organised assemblies of heterosupermolecules possessing novel and diverse functions. Outlined below are two examples of work ongoing in the laboratory.

In the first example, the stabilisers incorporating a diamidopyridine and an uracil moiety and incorporating at least one thiol group have been synthesised.[9] These stabilisers are strongly chemisorbed at the surface of a silver or gold nanocry-



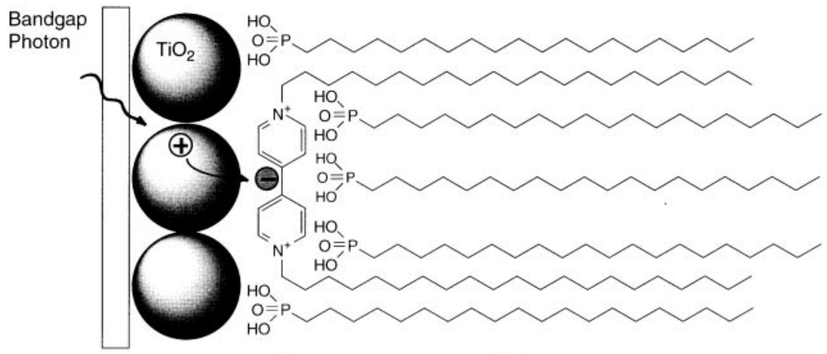
Scheme 8 A non-covalently organised heterosupramolecular assembly.



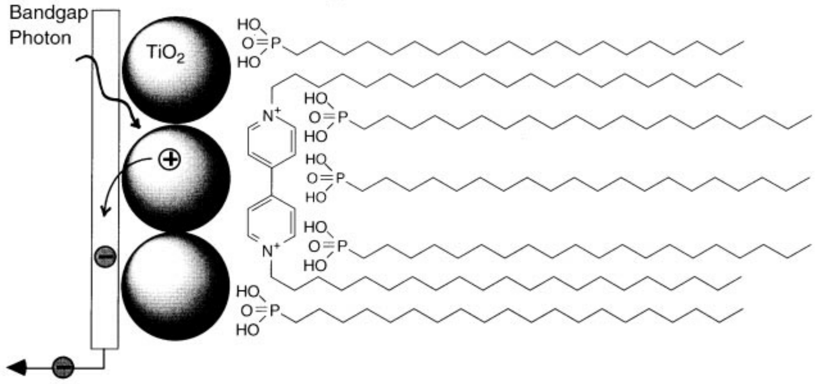
Scheme 9 Potential and light-induced electron transfer in a non-covalent organised heterosupramolecular assembly.

stals prepared in their presence.[21] These nanocrystals recognise and selectively bind each other to form a heterosupermolecule consisting of two non-covalently assembled condensed phase components, see Scheme 11. Because the above stabilisers are chemisorbed at the surface of a given nanocrystal, exchange of stabilisers between Au and Ag nanocrystals is not possible, and it is predicted that the resulting nanocrystal assemblies will have Au and Ag nanocrystals in alternating lattice sites.[22]

The second example relates to the non-covalent assembly of heterosupermolecules in a wide range of polar solvents. Toward

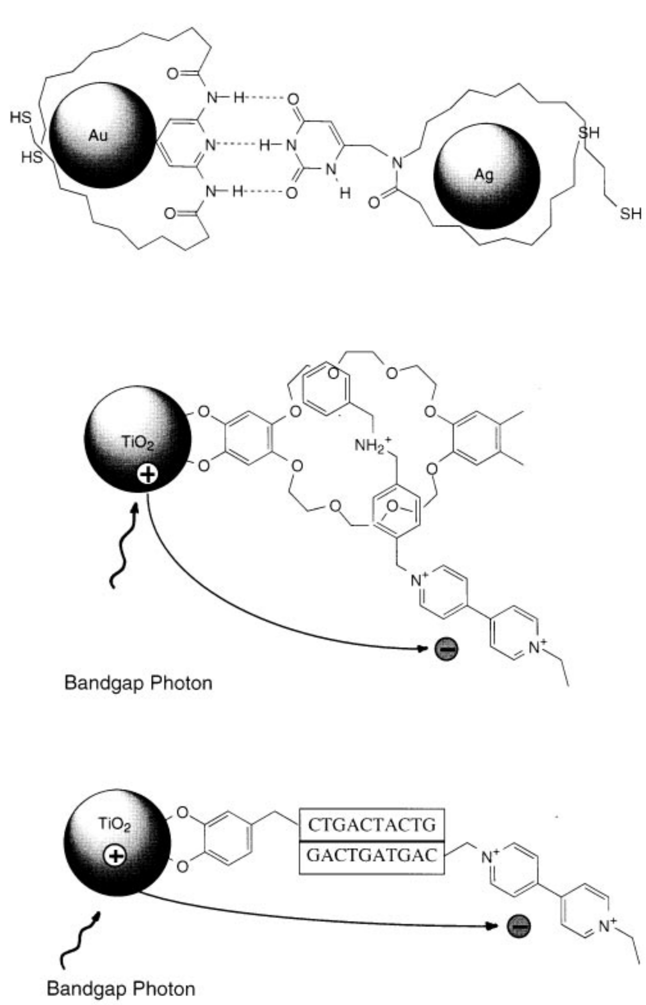


ON - open circuit conditions



OFF - positive applied potentials

Scheme 10 Potential modulation of light-induced electron transfer in a non-covalent organised heterosupramolecular assembly.



Scheme 11 Current and future studies in heterosupramolecular chemistry.

this end, a series of receptor-substrate pairs known to associate in polar solvents are being investigated (Scheme 11). The first, based on a crown ether–ammonium cation receptor–substrate pair may be used to self assemble heterosupermolecules in moderately polar solvents.[23] Specifically, this recognition–substrate pair will be used to assemble Au and Ag nanocrystals in acetonitrile.[24] The second, based on non self-complementary DNA oligomers may be used to assemble heterosupermolecules in polar solvents.[25] Specifically, this recognition-substrate pair will be used of assemble Au and Ag nanocrystals in water.[26]

7 Why a systematic heterosupramolecular chemistry?

The self-assembly and self-organisation of complex nanometer-scale structures in solution is an important objective of materials chemistry and physics. The importance of this objective is a result of the desire to be able to programme the bottom-up assembly in solution of materials with ever more precisely defined chemical and physical properties. In the longer term, it is expected that it will be possible to assemble nanometer-scale devices in solution and to organise these devices into addressable arrays.

It must be accepted, however, that progress in respect of the latter has, to date, been very limited for approaches based solely on the assembly and organisation of supermolecules. It is in this context that we have sought to develop a systematic chemistry, termed heterosupramolecular chemistry, of covalently and non-covalently assembled and organised condensed phase and molecular components whose intrinsic properties largely persist but which possess well defined functions. This is because the use of both condensed phase and molecular components offers three important advantages over the use, as characterised by conventional solid state chemistry, of only condensed phase components or, as characterised by conventional supramolecular chemistry, of only molecular components.

First, the use of both condensed phase and molecular components will permit the assembly and organisation of nanometer-scale structures possessing novel functions that could not be achieved if only condensed phase or molecular components are used. In this context, recent advances in the preparation of nanocrystallites of a wide range of materials possessing well defined sizes, surface properties and crystal structures have been important.[6,27] Also of importance have been the development of strategies for linking molecules, typically capping groups or sensitiser molecules, to the surface of these nanocrystallites.[6,27] Further, conventional supramolecular chemistry continues to provide an ever increasing number of receptor–substrate pairs that can be used to self-assemble and self-organise the condensed phase and molecular components of a heterosupermolecule or heterosupramolecular assembly.[28]

Secondly, as stated above, progress toward realisation of practical nanometer-scale devices based on organised assemblies of supermolecules has been slow. A reason for this has been the difficulties encountered in identifying substrates capable of modulating supramolecular function and providing information concerning modulation state of the assembly. The incorporation of condensed phase components in nanometer-scale devices, however, offers general advantages in this respect. Specifically, as the function of a heterosupermolecule in an assembly is dependent on the properties of its constituent condensed phase components, modulation of a bulk property of condensed phase components will, of necessity, modulate the function of the heterosupermolecules in the assembly. Importantly, in this respect, modulation of the property of a nanometer-scale condensed phase component is increasingly a realisable goal.[27] Further, if the property of the condensed phase component which is being modulated can be monitored, then the modulation state of each heterosupermolecule may be inferred.

Thirdly, the use of both condensed phase and molecular components will permit heterosupermolecules and heterosupramolecular assemblies possessing novel architectures to be self-assembled and self-organised in solution. That this will be necessary is increasingly apparent. For example, Grätzel and coworkers have described a stable and efficient regenerative photoelectrochemical cell for the conversion of solar energy to electrical energy.[6] Innovative aspects of the Grätzel cell include the use of ruthenium complexes as sensitisers whose absorption spectra overlap well the solar emission spectrum and the use of 10 μm thick nanoporous nanocrystalline semiconductor films with a surface roughness of >1000 as photoanodes. Central to the efficient operation of the Grätzel cell is the fact that the sensitiser molecules, as a consequence of their being adsorbed directly at the photoanode, are effectively stacked and the probability of an incident visible photon being absorbed is close to unity. It is important to note that while the above light-harvesting strategy is clearly based on that of green plants, its practical implementation utilises a heterosupramolecular assembly and that implementation of the same strategy using only condensed phase or molecular components has not proved possible.

In the future it is likely that solid state and synthetic chemistry will evolve into a seamless continuum of activities which may be usefully discussed in the framework of a systematic heterosupramolecular chemistry.

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