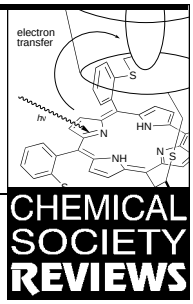
Photo-induced electron and energy transfer in non-covalently bonded supramolecular assemblies



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Covalently linked chromophore–quencher complexes are widespread in the area of transition-metal photochemistry and as models for photosynthesis. This review surveys recent examples of supramolecular complexes in which interacting chromophore and quencher fragments are instead held together by non-covalent interactions such as hydrogen bonding, aromatic π-stacking, hydrophobic interactions and labile metal–ligand coordinate bonds. The use of these methods to assemble multi-component photo-active complexes has led to the preparation of many highly sophisticated systems for energy transfer or charge separation which would not be accessible by 'conventional' synthetic methodology.

1 Introduction

The synthesis of polynuclear complexes containing photochemically active groups, such as metal polypyridyl complexes or metalloporphyrins, is one of the most widely studied topics in contemporary inorganic chemistry.[1] The impetus behind it is the possibility of harvesting solar energy. In nature, the energy of sunlight is harnessed during photosynthesis and used to drive the endothermic reaction sequence by which water and CO_2 are converted to sugars, and a great deal of effort is directed at understanding the primary events of photosynthesis in which absorption of light by chlorophyll is followed by a long-distance electron-transfer to a quinone group, generating a long-lived charge-separated state. There is also the possibility of preparing 'unnatural' systems by use of light-absorbing metal complexes which are not naturally occurring and therefore were not at nature's disposal during evolution. The ultimate idea is however the same: to use the light energy absorbed by the molecule to drive endothermic reactions, such as splitting of water to H_2 and O_2 which could be used as a fuel source.

Mike Ward took his BA at Robinson College in the University of Cambridge, and stayed put to do his PhD with Ed Constable on the coordination chemistry of multidentate pyridine-based ligands. He then went to Strasbourg for a year as a Royal Society post-doctoral fellow, to make catenates with Jean-Pierre Sauvage, before taking up his current position as a lecturer in the School of Chemistry at the University of Bristol. His research interests cover all aspects of the coordination chemistry of multidentate ligands, in particular the various forms of interaction (magnetic, electronic and photochemical) between metal centres in multinuclear complexes, and the design and synthesis of new ligands.

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The basis of these photochemically active compounds (chromophores) is that following absorption of a photon of light they enter a long-lived electronically excited state. Of course all chemical compounds are in principle capable of electronic transitions in which an electron is promoted from a ground state to a higher-energy state—usually a HOMO → LUMO transition—but in the vast majority of cases the excited state collapses very quickly back to the ground state, with evolution of heat as the electronic energy is converted to increased vibrational motion in the molecule. If the electronic excited state of the molecule survives for long enough however, there is the possibility that it can interact with another molecule before it is deactivated, and the reactions of molecules in their electronically excited state are completely different from those which they undergo in their ground state.[1,2] If no such interaction occurs then the excited state will be deactivated either thermally, or sometimes by emission of a photon (luminescence). Luminescent complexes are particularly useful in this area, as they tend to have long-lived excited states, and the loss of luminescence (quenching) is an obvious sign that the excited state complex is reacting with another group rather than undergoing radiative decay.

The two main mechanisms by which an electronically excited molecule can pass its energy on to another molecule (a 'quencher') are electron transfer and energy transfer. These are illustrated schematically in Fig. 1. It will be seen that promotion of an electron from a filled orbital to a higher-energy empty orbital means that in the excited state the molecule is simultaneously a stronger oxidising agent and a stronger reducing agent than it was in its ground state. The promoted electron is in a high-energy orbital and can transfer out to an electron-poor quencher; *i.e.* it acts as a reducing agent. Alternatively, the low-energy hole left by the promoted electron can accept an electron from an electron-rich quencher; *i.e.* the excited-state chromophore acts as an oxidising agent. The type of electron transfer that occurs depends on the nature of the species that is interacting with the excited-state chromophore. Energy transfer, in contrast, involves no net electron transfer; instead the excited-state energy of the chromophore is transferred to the quencher, which itself enters an electronically excited state. This is more likely to occur if the quencher has a low-energy excited state available and is not amenable to oxidation or reduction. These basic principles have been thoroughly and clearly described elsewhere, and the reader interested in the photophysical and photochemical principles which underlie the work described in this review is referred to these articles.[1,2]

In order to study the interactions between chromophores and quenchers under controlled conditions, very many molecules have been prepared in which these components are linked by a covalent bond. This allows reasonably precise knowledge of the distance between the two groups, their relative spatial orientation, and the nature of the pathway linking the two components which can act as a conduit for the electron or energy transfer. It has therefore been possible to relate the rate and efficiency of the interaction—such as electron transfer from chromophore to quencher after light absorption—to the distance between the components, the conformation of the bridge, the presence or

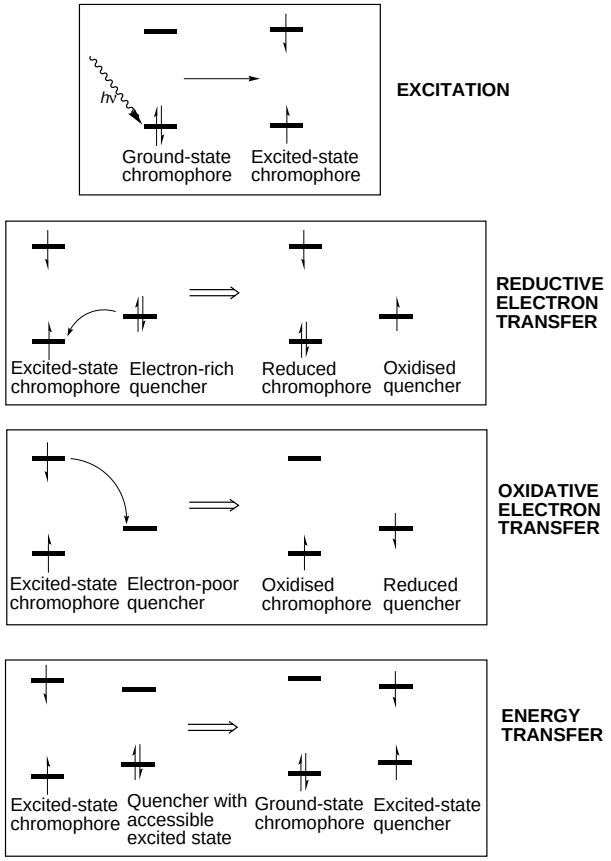


Fig. 1 Electron transfer and energy transfer quenching of a chromophore excited state

absence of direct orbital overlap between the components, and so on. Such studies have contributed a great deal to our understanding of the fundamental photophysical processes which it is desired to exploit further in solar energy harvesting, and there are many excellent reviews dealing with the preparations and properties of such systems.[3,4] A couple of illustrative recent examples of covalently linked chromophore–quencher systems are in Fig. 2.[5,6] The porphyrin (chromophore)—quinone (quencher) system is one of the most commonly studied because of its relevance to naturally occurring photosynthesis, in which the excited-state chlorophyll (a porphyrin complex) transfers an electron to a nearby quinone (an electron acceptor) following excitation by a photon of light.[3] The $[Ru(bipy)_3]^{2+}$ chromophore (bipy = 2,2′-bipyridine) is also a very popular system because of its particularly suitable photophysical characteristics, its high stability, and the ease with which it can by synthetically modified. Most of the examples in this article will involve one or other of these systems.[2,4]

The purpose of this review is to look at some recent examples of chromophore–quencher systems in which the two components are associated by non-covalent interactions. Whilst conventional chemical synthesis relies on manipulation of covalent bonds, the recently emerging area of supramolecular chemistry relies on weaker non-covalent interactions such as metal–ligand coordinate bonds, hydrogen-bonding, aromatic π-stacking, hydrophobic interactions and so on to control the assembly of large, structurally sophisticated species whose preparation would be way beyond the scope of more conventional synthetic methods.[7,8] There are two principal reasons for the use of weaker interactions of this type to control the assembly of chromophore–quencher systems. The first is ease and diversity of synthesis. The covalently linked systems can be very difficult to prepare and are limited in that the assembly of the molecule is irreversible; it is not usually possible to undo the components and reassemble them in a different way. Each synthesis is therefore a difficult, one-off process. Being able to prepare the component parts, mixing them together, and letting a collection of non-covalent interactions assemble the components for you has obvious appeal. The second reason is that nature relies on supramolecular methods of assembly. In the photosynthetic reaction centre for example the complex array of components is not held together by covalent bonds between them; rather, the components are held in a spatially well-defined arrangement by the surrounding protein, with a collection of weak non-covalent interactions between them which suffice to

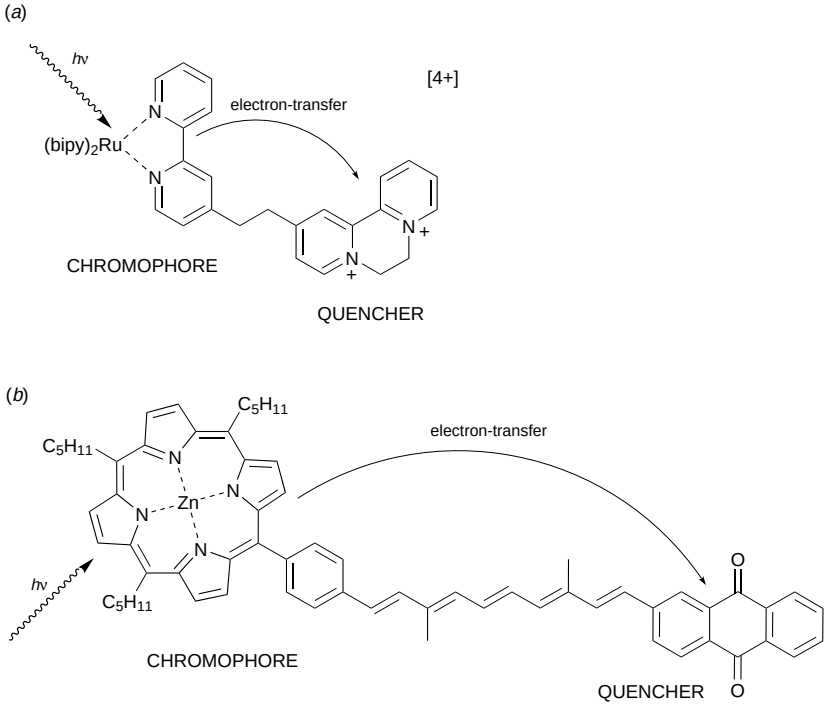


Fig. 2 Examples of covalently linked chromophore–quencher assemblies, based on (*a*) a polypyridyl–Ru^{II} chromophore and a viologen-type quencher (ref. 5), and (*b*) a porphyrin chromophore and a quinone quencher (ref 6).

mediate the energy or electron-transfer processes as well as holding the components in place.[9]

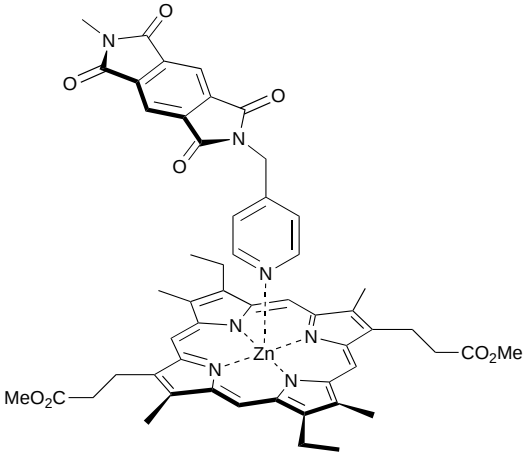
Accordingly, the last few years has seen a surge of interest in use of supramolecular methods to synthesise chromophore–quencher complexes, both as models for the naturally occurring photosynthetic reaction centres and to explore new 'unnatural' systems for light-harvesting. A selection of these form the subject of this review, and are subdivided according to the type of interaction responsible for linking the components:[8] coordinate bonds; hydrogen bonds (by far the largest category); hydrophobic interactions; aromatic π-stacking; and, finally, combinations of two or more types of interaction.

2 Components linked by coordinate bonds

Coordinate bonds (dative bonds between ligand lone-pairs and metals) may be crudely subdivided into two types; those involving a kinetically inert metal centre and those involving a kinetically labile metal centre. The former are essentially like covalent bonds in that, once formed, they are more or less permanent and the ligands are not involved in equilibria between bound and unbound states. With kinetically labile metals however monodentate ligands may exchange rapidly, so association by such an interaction is easily reversible and more akin to *e.g.* supramolecular association *via* hydrogen-bonding, and these are the examples of interest for our purposes.

Most examples of chromophore–quencher assembly *via* labile coordinate bonds involve axial ligation of pyridine ligands to zinc–porphyrin units. The association constant K for such complexes is *ca.* 10^3–10^4 dm^3 mol^{-1}. The principle is illustrated by complex **1**, in which a pyromellitimide group with a pendant pyridyl group is axially ligated to a zinc(II)–porphyrin fragment.[10] This is a 'donor–spacer–acceptor' assembly, so-called because in this case the excited state of the porphyrin unit acts as an electron donor, the pyridyl group is the spacer, and the pyromellitimide acts as an electron-accepting quencher. Simply adding an excess of the free pyromellitimide–pyridyl ligand to a solution of the zinc–porphyrin complex results in complete loss of the characteristic luminescence of the porphyrin fragment, because assembly of the five-coordinate complex **1** allows electron-transfer to occur from the excited-state porphyrin to the pyromellitimide, with a rate constant k_{ET} of 2.1×10^{10} s^{-1}. The same principle has been exploited in complex **2**, in which a quinone electron-acceptor is tethered between two Zn^{II}–porphyrins by two axial pyridyl ligands.[11] In this case the 'two-point' binding of the electron-acceptor means that the association constant between the two components is much higher (10^7 dm^3 mol^{-1}), so simply mixing the two components results in more or less complete association even at the low concentrations typically used for spectroscopic studies. The electron-transfer rate constant k_{ET} was found to be 1.6×10^{10} s^{-1}, a similar value to that for **1** which reflects the similar nature of the electron-donor and the comparable separation between chromophore and quencher.

In **1** and **2**, the shortest through-space route between chromophore and quencher is also the through-bond pathway, since the chain of atoms linking the chromophore and quencher lies more or less on the straight line between them. It is therefore not possible to tell whether the electron-transfer in these systems is occurring through space or whether it requires the chain of bonds to act as a 'wire'. In **3** however this ambiguity is removed. Axial coordination of the two pyridyl groups of one component (upper in the diagram) to the Zn^{II}–porphyrin centres of the other (lower) results in a close spatial approach of the free-base porphyrin chromophore and naphthalene–diimide quencher fragments.[12] The through-space separation of the components is at most 10 Å, whereas the through-bond distance around the ring is about 35 Å. As with **2**, the two-point binding which holds the complex together results in a high association constant, of about 3×10^8 dm^3 mol^{-1}. The assembly of the complex results in a loss of about 70% of the fluorescence



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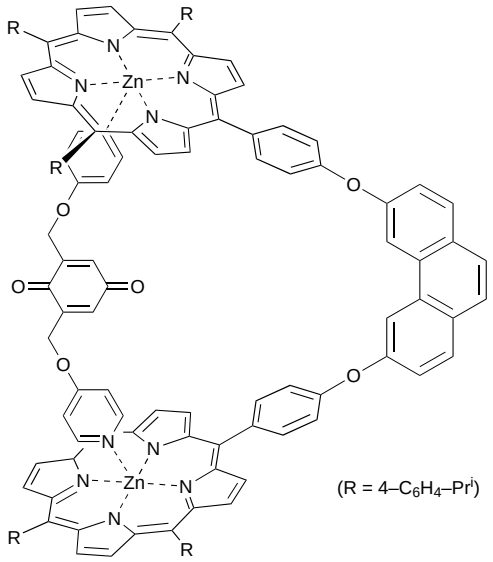

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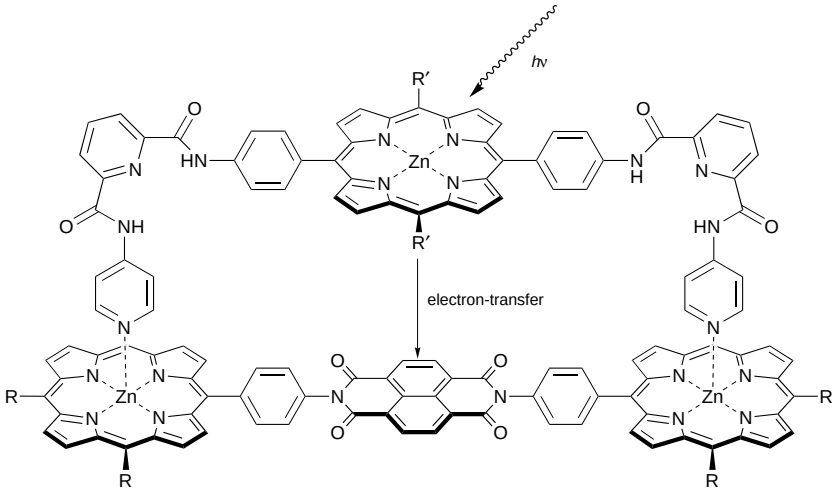
intensity from the free-base porphyrin of the upper component. In other words, following excitation, 70% of the excited-state free-base porphyrin units are quenched by electron-transfer to the naphthalene–diimide electron acceptor, and this electron transfer occurs through space (or, more accurately, through the solvent molecules occupying the cavity between the two components).

3 Components linked by hydrogen bonds

3.1 Hydrogen bonds as an interface for electron or energy transfer

Hydrogen bonding has been by far the most popular method for supramolecular assembly of chromophore–quencher groups over the last few years. This is because of its two principal characteristics; its directionality and its selectivity.[8] The directional features of hydrogen bonds mean that when two components are associated *via* hydrogen-bonding, it is possible to know the separation between the components and, in some cases, their relative orientation. In this respect hydrogen bonds behave like the coordinate bonds described above, and unlike some of the weaker non-covalent interactions described below. The selectivity, particularly in multiply hydrogen-bonded systems, means that considerable control can be exerted over the association process by careful use of exactly complementary components, and this is apparent in the examples described below. Although the strength of an individual hydrogen bond is relatively weak (of the order of 10 kJ mol^{-1}), multiple hydrogen

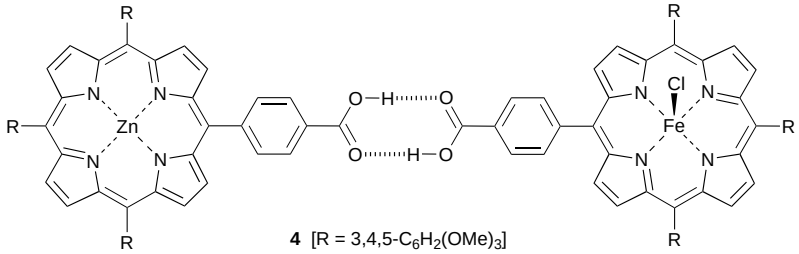


3 (R, R′ = substituted aryl groups)

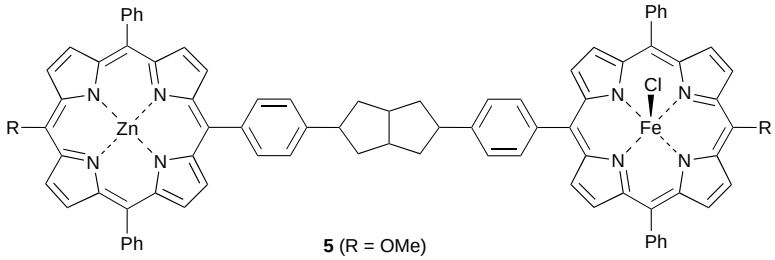
bonds can be much stronger, typically of the order of 50 kJ mol^{-1} or more, which is beginning to approach the strength of the weakest covalent or coordinate bonds.

For hydrogen bonding to be of any use in this area it is necessary that the bond can act as an effective conduit for electron transfer or energy-transfer in addition to its structural properties. Complexes **4** and **5** were compared to evaluate this.[13] In **4**, the Fe^{III}–porphyrin centre acts as an electron acceptor following excitation of the Zn^{II}–porphyrin centre, and k_{ET} is 8.1×10^9 s^{-1} across the double hydrogen bond formed by association of carboxylic acids. In **5**, with a saturated carbon covalent bridge, k_{ET} is 4.3×10^9 s^{-1}. Somewhat surprisingly, therefore, the double hydrogen-bond interface between components is more effective at mediating electron-transfer than an interface of comparable length composed of carbon–carbon σ bonds.

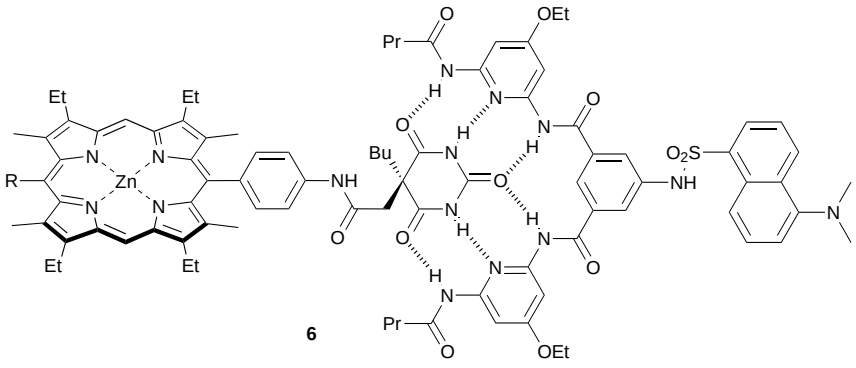
Complex **6** is a nice example of a carefully designed multiple hydrogen bond between two complementary components.[14] The pendant barbiturate group attached to the porphyrin forms six hydrogen bonds with the exactly complementary bis(diamidopyridine) receptor to which is attached a fluorescent dansyl (dimethylaminonaphthalene–sulfonyl) group. The multi-point hydrogen-bonding ensures a very strong association ($K = 10^6$ dm^3 mol^{-1}), and in the associated complex the fluorescence of



4 [R = 3,4,5-$C_6H_2(OMe)_3$]



5 (R = OMe)



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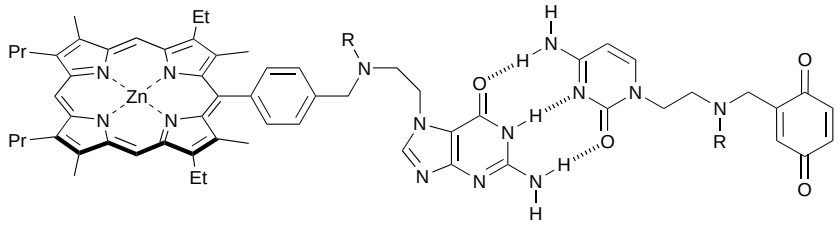
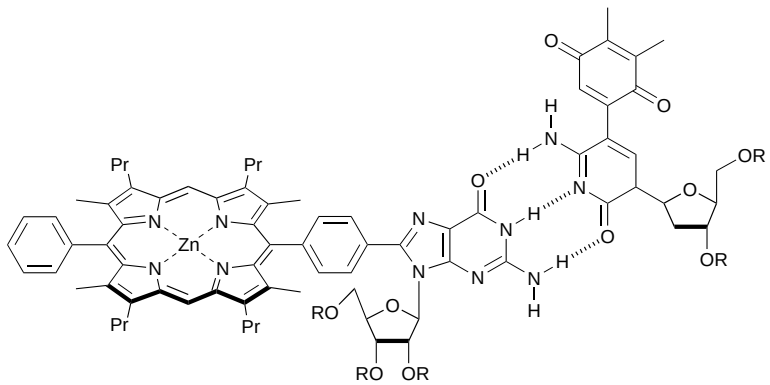
the dansyl group is almost completely quenched by efficient energy-transfer to the porphyrin fragment.

Complexes **7**–**9** are all examples of complexes in which the electron-donor [a Zn^{II}–porphyrin] is associated with an electron acceptor *via* a triple hydrogen bond. For **7** and **8**, the electron acceptor is a quinone and the interface is a cytosine–guanine hydrogen bond of the type which occurs in double-stranded nucleic acids. Complex **8** is however more conformationally rigid than **7**, which gives a better-defined inter-component separation, and therefore allows a better understanding of the intercomponent electron-transfer pathway which occurs in both cases.[15] Whereas the electron-transfer in **7** ($k_{ET} = 4 \times 10^8\ s^{-1}$) could occur in part by diffusional encounter between the components which transiently brings them spatially close together, in **8** the electron-transfer ($k_{ET} = 8 \times 10^8\ s^{-1}$) most likely occurs through the hydrogen bonded bridge. Complex **9** uses a different mode of hydrogen bonding to link the components; here the quinone associates with the hydroxy groups of a calixarene group pendant from the Zn^{II}–porphyrin, but in such a way that it is held spatially close (9 Å) to the porphyrin core.[16] The inter-component electron-transfer ($k_{ET} = 8 \times 10^8\ s^{-1}$) is therefore more likely to be through space or through the intervening solvent, rather than taking the much longer through-bond route (*cf.* complex **3**). The assembly **10** is an example of a multi-chromophore (as opposed to a chromophore–quencher) assembly of porphyrin units *via* triple cytosine–guanine hydrogen-bonds, and rapid inter-component energy-transfer between components was observed [from the Zn^{II}–porphyrin unit which has the higher-energy excited state, to the free-base porphyrin unit which has the lower-energy excited state].[17] This is of particular relevance to attempts to model the behaviour of the primary light-absorption process of the photosynthetic reaction centre, which contains an array of several light-harvesting porphyrin units.[9]

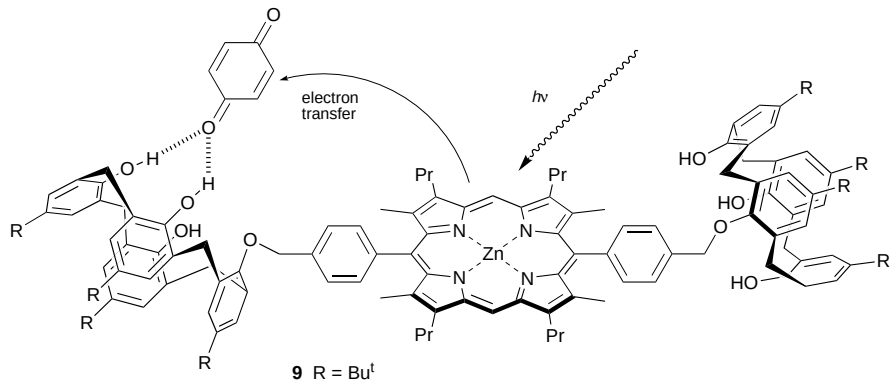
The use of metal–polypyridyl complexes with pendant hydrogen-bonding substituents has lagged behind the use of porphyrin complexes but is beginning to be developed. The author's group in Bristol have prepared complexes **11**–**14**, in which luminescent Ru^{II} or Os^{II} tris-bipyridyl cores are functionalised with the nucleobases adenine, thymine, cytosine or guanine respectively.[18] It is well-known that excitation of a $[Ru(bipy)_3]^{2+}$-type chromophore can result in energy-transfer to an $[Os(bipy)_3]^{2+}$ chromophore if the two components are directly attached.[4] Complexes **11**–**14** were prepared to see if a similar result could be obtained across a hydrogen bond. Thus, mixing components **11** and **12** results in association but with a rather small stability constant ($K \approx 10^2\ dm^3\ mol^{-1}$), which means that only a fraction of one percent of the components associate at the concentrations normally used for spectroscopic studies; the properties of the associated pair are difficult to detect in the presence of large excesses of the free component parts. However, use of the pair **13** and **14**, with the triple cytosine–guanine hydrogen-bond replacing the weaker double adenine–thymine hydrogen bond, overcomes this: the associa-



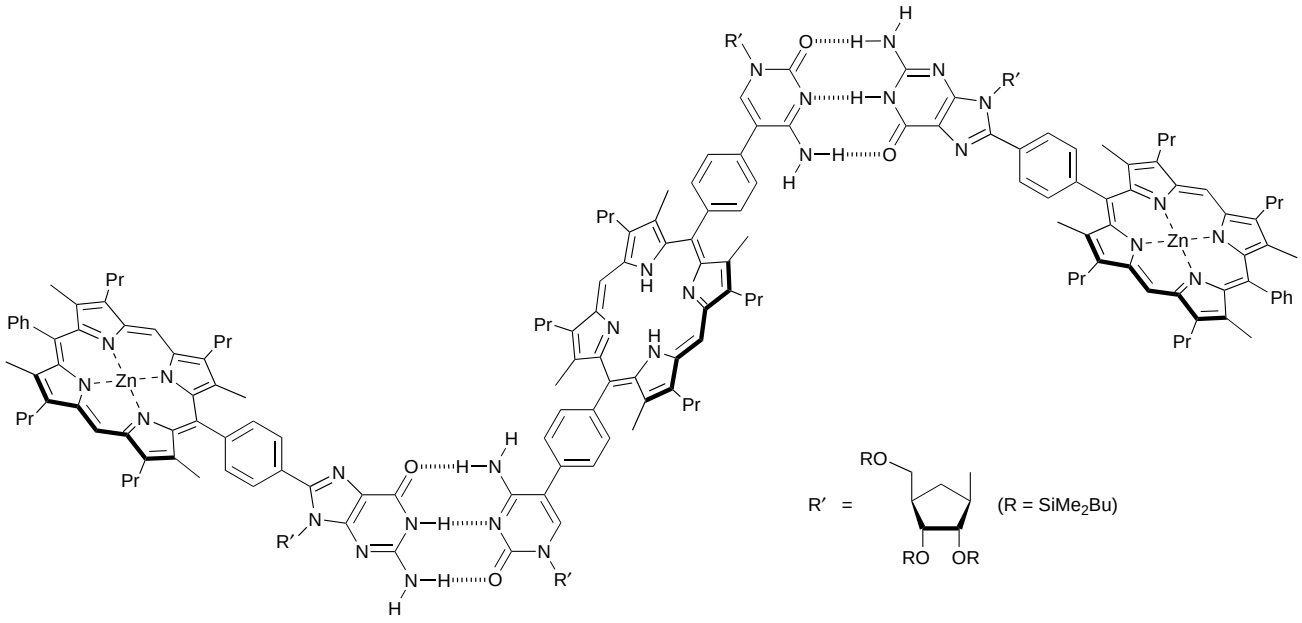
7 [R = $CH_2C_6H_4O(CH_2)_2O(CH_2)_2OCH_3$]



8 (R = $SiMe_2Bu^t$)



9 R = Bu^t



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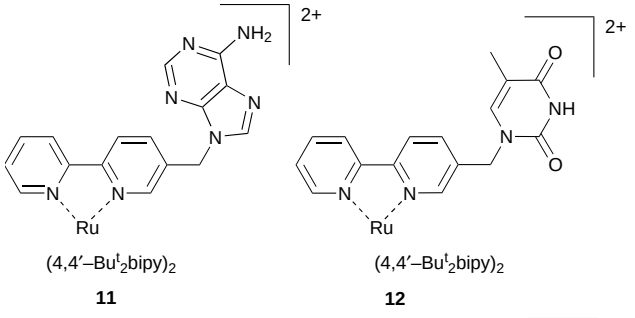

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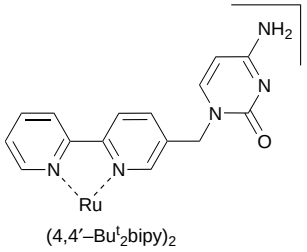

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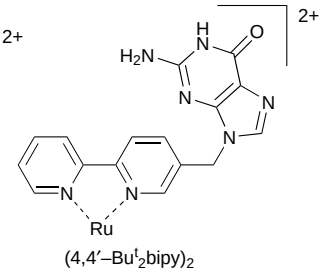

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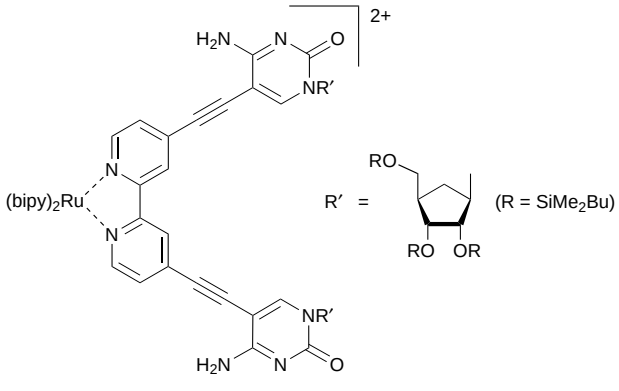

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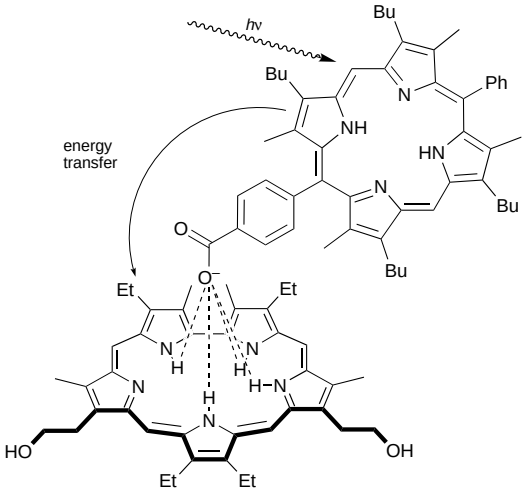
tion constant K is *ca*. 6000 dm^3 mol^{-1} in CH_2Cl_2, and in the associated pair the luminescence of the Ru^{II} energy-donor is quenched. Along similar lines, Sessler has prepared complex **15** for possible attachment by hydrogen-bonding to porphyrin chromophores.[19]

An associative interaction related to hydrogen bonding is the salt bridge between a deprotonated carboxylate and a protonated 'sapphyrin' pentapyrrolic macrocycle in assembly **16**.[20] Here, the anion is effectively 'chelated' by the four protons, and the geometry of this interaction serves to ensure that the two components must be mutually perpendicular. The pathway linking them is therefore clearly defined; in particular face-to-face association, which could provide an alternative energy-transfer pathway and thereby complicate interpretation of the results, is not possible. Excitation of the porphyrin fragment resulted in nearly complete (96%) energy-transfer across the salt bridge to the sapphyrin, with a rate constant of 1.8×10^9 s^{-1}. The particular appeal of this system is that simple anions (sulfate, phosphate *etc*.) could be used to direct the assembly of large numbers of luminescent chromophores by formation of multiple salt-bridge interactions of this type.

As an alternative to the molecular components described in all of the above examples, a small 'nanocrystallite' of the semiconductor TiO_2 (diameter about 22 Å) has been used as an electron-donor. Irradiation of the TiO_2 fragment at 355 nm results in promotion of an electron across the band gap, from the valence-band to the conduction band. Charge-separation has therefore resulted, giving a high-energy electron and a low-energy hole (*cf*. Fig. 1 which depicts the analogous situation for an individual molecule). In complex **17**, a particle of TiO_2 is encapsulated by a diamidopyridine derivative containing long alkyl chains which attach to the TiO_2 surface by adsorption.[21] The diamidopyridine forms a triple hydrogen-bond with the complementary uracil-based component to which a doubly alkylated 4,4′-bipyridyl fragment (a viologen) is attached. Viologen groups are good electron acceptors, and following irradiation of the TiO_2 particle, electron-transfer to the viologen occurs across the triple hydrogen-bond. Several control experiments showed that the hydrogen-bond is essential for the electron-transfer to occur; no electron-transfer either through space or by diffusional encounter of the donor and acceptor components was detected.

3.2 Proton-coupled electron-transfer

Because hydrogen bonds involve (by definition) protic functional groups, they are also appropriate for studying proton-coupled electron-transfer in which inter-component proton transfer accompanies electron transfer, with the electron



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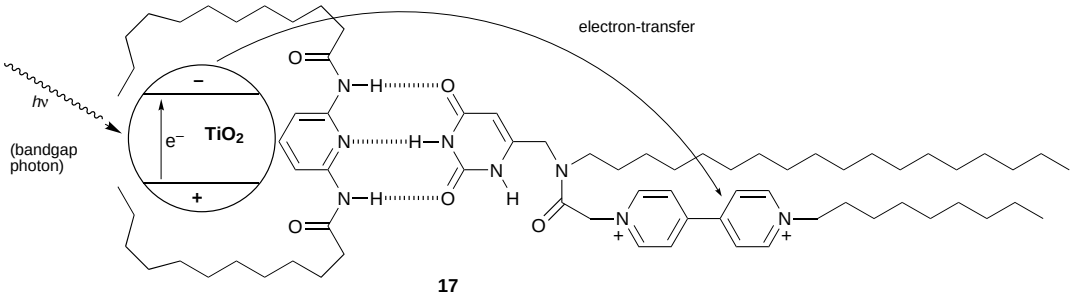

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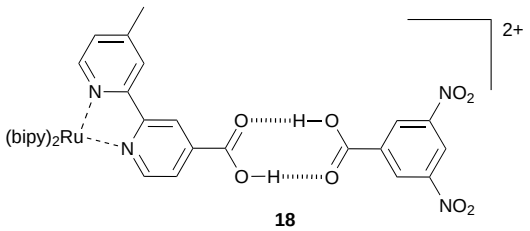
transfer and the proton transfer both mediated by the same interface. Coupling of proton transfer and electron transfer is common in many simple redox processes, such as the $2e/2H^+$ reduction of quinone (Q) to hydroquinone (benzene-1,4-diol, H_2Q), or the $2e/2H^+$ reduction of metal–oxo complexes [$L_nM{=}O$] to aqua complexes [$L_nM{-}OH_2$]. In biological systems it is of fundamental importance during photosynthesis. Absorption of light results in a charge-separation process, *i.e.* generation of an electron on one side of the membrane and a positive hole on the other side. The electron is used to reduce $NADP^+$ to NADPH on one side of the membrane, a process which also consumes protons. The hole is used ultimately to oxidise water to O_2 on the other side of the membrane, a process which also liberates protons. The resulting proton imbalance generates a thermodynamic gradient which is the driving force for production of adenosine triphosphate (ATP).

In the particular case of photoinduced electron transfer, where the transfer is initiated by electronic excitation of one component, the coupling of proton motion to electron transfer has recently been demonstrated in a few cases. In complex **18**, there is a symmetrical double hydrogen-bond between the carboxylic acid substituents attached to the Ru^{II} fragment (electron donor in its excited state) and the dinitrobenzene (electron acceptor). In complex **19** in contrast the bridge is asymmetric, between a protonated amidinium group attached to the Ru^{II} complex and a deprotonated carboxylate on the electron acceptor.[22] Two pieces of evidence suggest that the photoinduced electron-transfer is indeed coupled to proton transfer. Firstly, although the thermodynamic driving force for electron transfer is significantly less for system **18** than for **19**, the intramolecular electron transfer rate is faster (k_{ET} = 8.0×10^6 s^{-1} and 4.3×10^6 s^{-1}, respectively) which is the opposite of what would be expected. This is because for **18** the double proton transfer is overall symmetrical [Fig. 3(*a*)] and therefore does not result in any charge redistribution in the bridge. Consequently there is no need for the solvent interactions around the bridge to change, and the activation energy barrier is



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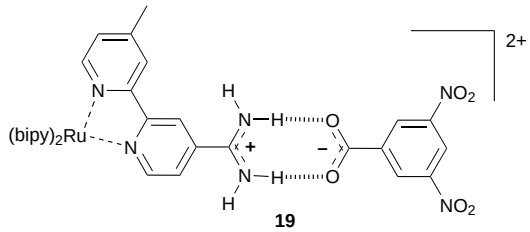

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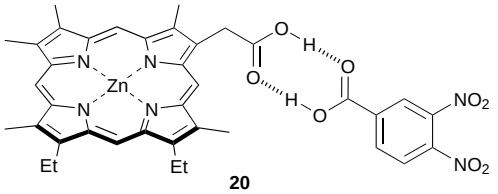

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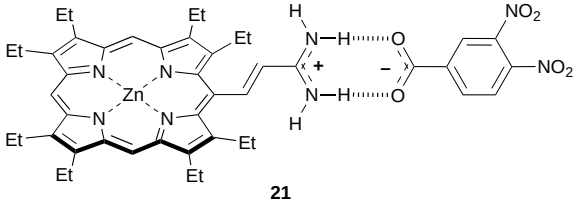

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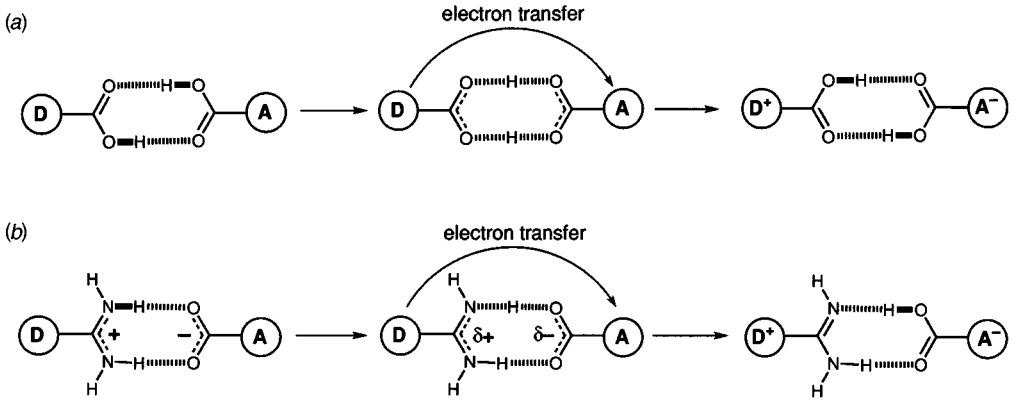


Fig. 3 Examples of proton-coupled electron transfer, in which (*a*) double proton exchange within a carboxylic acid dimer results in no charge redistribution within the bridge (*cf.* complex **18**), and (*b*) single-proton transfer from amidinium to carboxylate results in a redistribution of charge within the bridge (*cf.* complex **19**). The bonds indicated in bold are those directly involved in the proton transfer.

low. In contrast, the proton transfer in **19** results in a charge redistribution in the bridge, [Fig. 3(*b*)], which in turn requires changes in solvation. This imposes an activation energy barrier on the proton transfer and therefore, since the two processes are coupled, the electron transfer is also slowed. The second piece of evidence comes from the kinetic isotope effect; replacement of the H atoms in the hydrogen-bonded bridges of **18** and **19** by D atoms slows down the k_{ET} values by a factor of about 1.4 in each case. This means that cleavage of the O–D bond (for **18**) or the N–D bond (for **19**) is involved in the rate-determining step; if no movement of the protons occurred with the electron transfer then substitution of H for D would not affect the rates. Systems such as **20** and **21** with porphyrins as the electron-donors have also been studied and show similar behaviour;[23] in **20**, deuteration of the hydrogen-bonded bridge slowed down the photo-induced electron transfer by a factor of about 1.7.

Why should proton motion be coupled to electron transfer at all? For example, in **19** it is easy enough to see why the proton transfer should be hindered (because of the change in solvation of the components required to stabilise the charge redistribution), but why should that also slow the electron-transfer rate? The answer to this is that the strength of the electronic interaction between the electron donor and acceptor groups is strongly dependent on the position of the H atoms in the hydrogen bond. The equilibrium O–H···O arrangement for a hydrogen-bond is not optimal for acting as a conduit for electron-transfer; it has been estimated that the electron-transfer rate is about four times faster if the hydrogen bond is in the symmetrical O···H···O arrangement, which corresponds to the transition state between the O–H···O and O···H–O extremes. The electron transfer will therefore occur just at the instant that the hydrogen bond is converting from one extreme to the other, which accounts for the experimental observations described above for complexes **18** to **21**.[24]

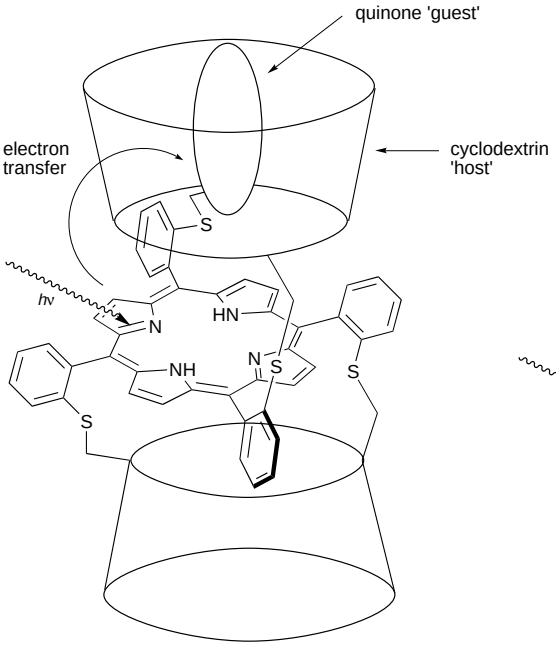
4 Components linked by hydrophobic interactions

Non-polar compounds tend to aggregate in polar solvents, particularly water, to minimise unfavourable solute–solvent interactions; this is responsible in part for the formation of micelles when detergents (with long hydrophobic tails) are added to water. This is a weak and directionally non-specific process but can be sufficient to permit components to associate to a sufficient extent to allow an electronic interaction between them which would not occur otherwise. An elegant example is provided by complex **22**, which contains a cyclodextrin 'bowl' attached to each face of a porphyrin chromophore.[25] Cyclodextrins are basically hollow cylindrical molecules with a conical taper, whose hydrophobic interiors provide a suitable refuge for small non-polar molecules to hide from a polar solvent.[8] In the presence of various hydrophobic quinone derivatives in water, quenching of the porphyrin luminescence was observed by electron transfer ($k_{ET} \approx 10^9$ s^{-1}) to the quinone held in the cyclodextrin cavity. Quinones without hydrophobic substituents, which did not enter the cavity, did not cause any quenching of the porphyrin excited state.

The excited state of the fluorescent pyrene derivative **23** is very efficiently quenched by the nucleosides 2′-deoxythymidine (dT), 2′-deoxycytidine (dC) and 2′-deoxyguanosine (dG) in aqueous solution, by an electron-transfer process in each case.[26] The extent of quenching is much greater than would be expected to arise from random collisional encounter of the chromophore and quencher, which is ascribed to association of the components to give a non-covalently bonded [chromophore···quencher] complex. Although hydrogen-bonding and aromatic π-stacking between the components is feasible, the principal reason for this association is thought to be a hydrophobic interaction, since both chromophore and quencher components contain hydrophobic domains. Interestingly, quenching by dC and dT shows a substantial kinetic isotope effect when H_2O as the solvent is replaced by D_2O, indicating the presence of a proton-coupled electron-transfer as the quenching step. Note that hydrogen bonding between these components is not thought to be significant; the proton transfer in this instance comes from the solvent (*cf.* complexes **18**–**21** in which proton coupling arose from shifts in the positions of the protons within the hydrogen bond). Non-protonated dC and dT are poor electron acceptors, and without assistance would not be able to accept an electron from the excited state of **23** as their reduction potentials are too negative; they are thermodynamically incapable of quenching **23** in non-polar organic solvents. However when protonated the positive charge makes them much easier to reduce, so the electron-transfer quenching that is observed can only occur if it is coupled to simultaneous protonation by the solvent to stabilise the reduced nucleoside. The solvent therefore plays two roles in the quenching; a kinetic one (driving the components together by a hydrophobic interaction) and a thermodynamic one (making the electron-transfer process energetically favourable by permitting simultaneous proton transfer).

5 Components linked by aromatic stacking interactions

The tendency of planar aromatic systems to 'stack' in an approximately parallel face-to-face arrangement (*cf.* the structure of double-stranded DNA) has been known for a long time. Although its origins are still not completely understood, this type of interaction offers a well-established way of promoting self-assembly in supramolecular complexes.[8] The interaction is known to be considerably strengthened when one of the



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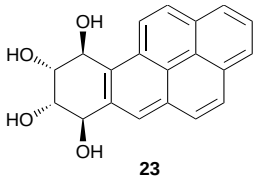

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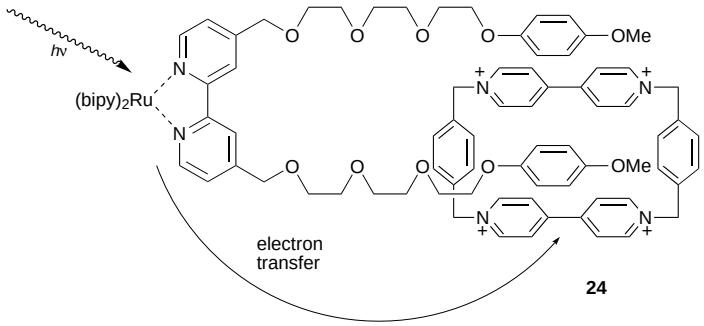

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aromatic systems is electron-poor and the other electron-rich, such that there is an electrostatic donor–acceptor component to the interaction and therefore some degree of charge transfer between the components.

Complex **24** contains a tris(bipyridyl)-ruthenium(II) chromophore to which is appended dialkoxyphenyl substituents.[27,28] A cyclic electron-acceptor (BXV^{4+}) containing two viologen-based groups can associate with these by a π-stacking interaction between the electron-rich dialkoxyphenyl and the electron-poor methylviologen aromatic rings. The association constant K is 1200 $dm^3\ mol^{-1}$ in water. This association provides an intramolecular pathway for photoinduced electron transfer from the excited-state of the ruthenium chromophore to the methylviologen [*cf.* Fig. 2(*a*), displaying the same components but covalently linked]. Following excitation, electron-transfer to the BXV^{4+} quencher affords the photo-product $Ru^{3+}\cdots(BXV^{\cdot})^{3+}$, which is particularly long-lived (*ca.* 1 μs) because electrostatic repulsion between the oxidised Ru^{3+} and the reduced $(BXV^{\cdot})^{3+}$ prevents the back-transfer of an electron which would regenerate the $Ru^{2+}\cdots(BXV)^{4+}$ ground-state. Viologen-based acceptors have been incorporated into supramolecular assemblies with porphyrin-based electron-donors in the same way (*e.g.* complex **25**).[29]

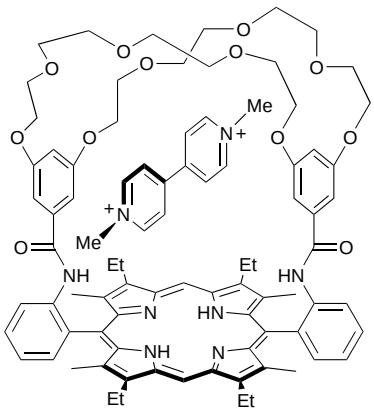
Assembly of chromophore and quencher components using π-stacking has also been achieved *via* intercalation of the component parts into DNA strands. Compounds with externally directed planar aromatic groups may bind to DNA by insertion of the aromatic group between the parallel base-pairs. Complexes **26** and **27** can intercalate into DNA by virtue of their dipyridophenazine (**26**) or phenanthrenequinone–diimine (**27**) groups.[30] The Ru^{II} complex **26** is the chromophore; the Rh^{III} complex **27** is capable of quenching the luminescence of ruthenium-based chromophore by accepting an electron from the photo-excited state. In the presence of DNA, both components bind strongly by intercalation with association constants of $K > 10^6\ dm^3\ mol^{-1}$, and on excitation of the chromophore, rapid electron transfer to the quencher is observed over distances as long as 40 Å. This electron transfer occurs through the stacked array of 25 or more aromatic heterocycles in the DNA strand and is very fast ($k_{ET} > 10^9\ s^{-1}$).

6 Components linked by a combination of interactions

The examples above were chosen to illustrate the individual non-covalent interactions between chromophore and quencher species which can promote energy transfer or electron transfer. In many cases however a combination of interactions is used to achieve the desired association, and the examples in this section illustrate some examples of the careful use of several types of interaction in concert to achieve assembly between components.

In complex **28** the two hydroxy groups on one side of the porphyrin plane provide a means of selectively binding *para*-quinones in such a fashion that face-to-face aromatic π-stacking of the quinone with the porphyrin also occurs, although most of the strength of the interaction is thought to arise from the hydrogen bonds. The two-point hydrogen bonding results in association constants of the order of 100 $dm^3\ mol^{-1}$ (in chloroform solution) for a variety of *para*-quinones.[31] Complex **29** is an extension of this principle in which four-point hydrogen bonding between the convergent hydroxynaphthyl substituents on the zinc–porphyrin and 2,3,5,6-tetramethoxy-*p*-benzoquinone is strong ($K = 2.5 \times 10^5\ dm^3\ mol^{-1}$ in toluene) and highly specific; other *para*-quinones are bound much less strongly.[32] In both cases very fast (picosecond timescale) and efficient electron transfer occurs from the photo-excited porphyrin to the quinone, resulting in complete quenching. In **30** the quinone quencher binds to the chromophore *via* a double hydrogen-bond with a peripheral hydroquinone group, which again also results in face-to-face π-stacking of the two aromatic fragments.[33]

A different type of approach to the assembly of components is exhibited by **31**, which contains covalently-linked chromophore (zinc–porphyrin) and quencher (quinone) units linked by a covalent bridge.[34] The molecule has a U-shaped structure, in which the chromophore and quencher components are separated by about 9 Å (centre-to-centre) on either side of the central



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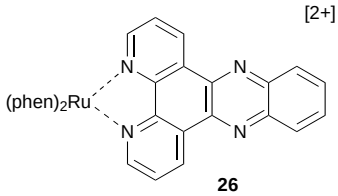

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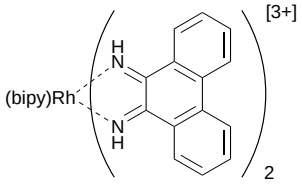

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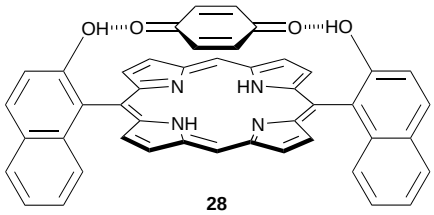

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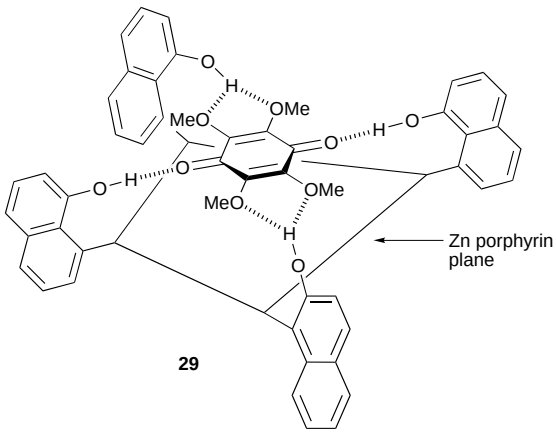
(ethyl substituents on octaethylporphyrin core omitted for clarity)



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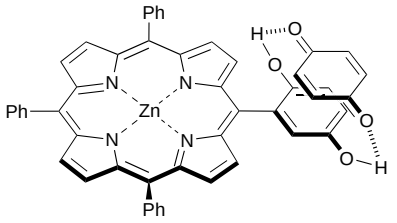
cavity. The size and shape of the cavity are ideal for the binding of an aromatic guest molecule. Dihydroxybenzene derivatives bind within the cavity of **31** by a combination of aromatic π-stacking with the porphyrin and quinone fragments on either side of the cleft, and hydrogen bonding to the amide carbonyl groups at the bottom of the cleft. The presence of an aromatic guest in the cleft greatly increases the efficiency of electron-transfer between chromophore and quencher. In CCl_4, very little electron-transfer across the cleft from chromophore to quencher could occur. The much longer pathway around the covalent bond system of the molecule could be discounted. On addition of hexyl-3,5-dihydroxybenzoate however, 75% of the luminescence intensity from the porphyrin unit was quenched, because incorporation of the aromatic guest into the cleft provided a facile pathway for electron-transfer, across the π-stacked system of aromatic groups (*cf.* electron-transfer through the stacked aromatic nucleobases of DNA).[30]

As a final example, complex **32** is particularly elegant because formation of the chromophore–spacer–quencher assembly relies on three types of non-covalent interaction, all mediated by the macrocyclic receptor unit.[35] The quinone quencher is held in this macrocyclic receptor by a combination of hydrogen bonding to the amide protons and π-stacking with the phenyl rings in the cyclic framework ($K \approx 3000$ dm^3 mol^{-1}). The whole quencher–receptor assembly was then attached to the axial position of a zinc–porphyrin chromophore *via* coordination of the peripheral pyridyl group of the macrocyclic receptor. The complex, therefore, relies on a combination of metal–ligand coordinate bonds, π-stacking, and hydrogen bonding to assemble the components in a very specific way. Efficient quenching of the porphyrin luminescence by the quinone occurs within this assembly, by photo-induced electron transfer from porphyrin to quinone; this quenching is much more efficient than that which occurs between the porphyrin unit and free quinone by diffusion in solution.

7 Conclusion

Supramolecular methods clearly offer great promise for the assembly of high-nuclearity, structurally sophisticated complexes; nature uses such methods all the time, and synthetic chemists have started to use them more and more in the last few years. The application of such methods to the assembly of



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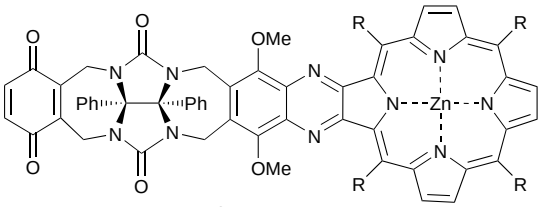

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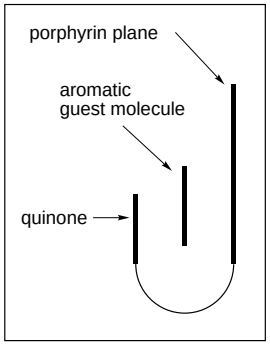

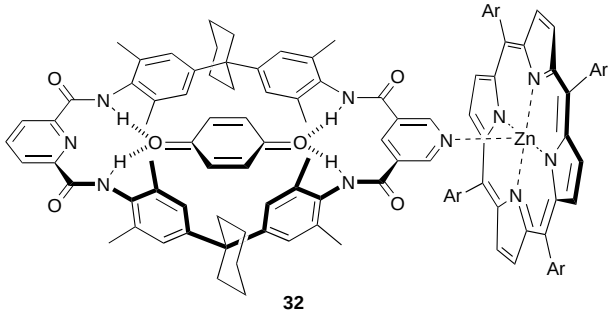

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photochemically active molecules, both for understanding natural photosynthetic processes and for the preparation of 'unnatural' systems for light-harnessing, is catching up rapidly and offers immense scope for further development.

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