TUTORIAL REVIEW

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Pushing around electrons: towards 2-D and 3-D molecular switches

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In the new age of molecular electronics there has been a great deal of speculation about ways to control the passage of electrons through organic-based wires using electro- or photo-active switches. However, the next stage development is envisaged as the added sophistication of *directionality* so that electron migration can be switched into 2 and 3 dimensions. This short *tutorial review* will set out how this realisation may be achieved and highlight examples where the idea of directionality in electron transfer has been put into practice.

Introduction

The incorporation of molecular-scale (nanoscale) components into real electronic devices has still not yet been fully realised, which is perhaps not too surprising considering that many physicochemical problems need to be solved, plus the silicon chip technology they have to overthrow is very well established.[1] The situation is not helped by the fact that the recent negative publicity on nanotechnology fuelled by an over exaggeration of 'nanobot' science is overshadowing the real benefits that this technology will surely offer in the near future. Even so, and putting all these negative issues aside, there is a healthy and intense research effort into the creation of working molecular-scale electroactive and photoactive devices.[2] One such area is that of molecular switching devices where electron flow along organic conduits is controlled by a relay so that information transfer is gated or switched 'on' and 'off'. There have been many excellent reviews[3–6] and chapters in books[7] on this topic and it is not the intention of this article to reiterate the numerous examples so far. Merely, here is shown a selection of assemblies to put across the common features and typical organic-based gates that have been used to date (Fig. 1).

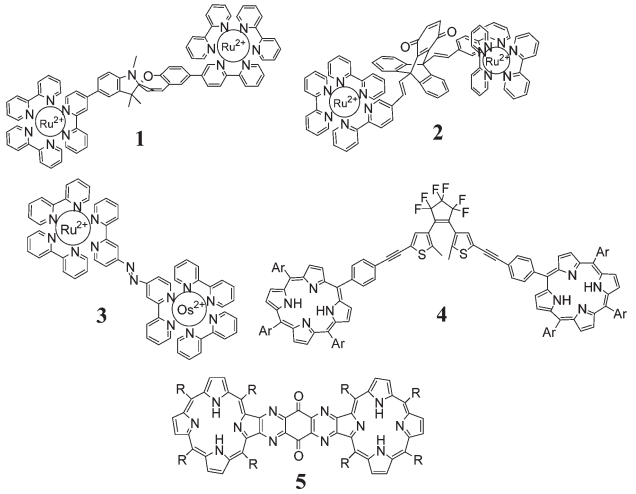

Fig. 1 Illustrations of some selected molecular switches developed to date.

In the examples **1–5** prepared by the groups of Belser,[4,8] Otsuki[9] Osuka,[10] and Crossley,[11] respectively, the two photoactive centres are separated by a unit which can be either photochemically or electrochemically activated. The perturbation of the central relay unit is what controls electron or energy migration from one end to the other. However, the common theme to the examples shown in Fig. 1 is a donor–bridge–acceptor motif which extends in a near linear fashion. Although not strictly correct this design motif can be considered control of electron direction in 1-D as illustrated in the cartoon (a) of Fig. 2. Within the diagram (a) the blue rectangle represents the switching portion which controls communication between the donor (D) and acceptor (A_1). If one takes this general idea a step further then theoretically the switch could contain a second acceptor (A_2) such that the molecular switch could be thought to operate in 2-D (Fig. 2b). Within this design motif the blue triangle is the gate which would now need to switch between 'on' and 'off' and control the electron flow direction. The resemblance of Fig. 1b to a turning point in a road has lead to the term T-junction to describe the assembly.[12] The final logical step in this thought process is to move into 3-D (Fig. 2c) in which the switch now incorporates three acceptors A_1 to A_3. The blue cube represents the gate which must now control electron migration in three directions. It is clear that creation of this final molecular-based switch is the most challenging, but

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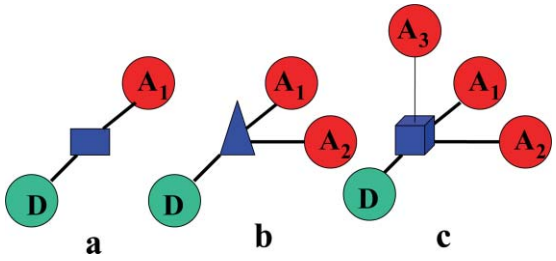

Fig. 2 Cartoon representation of 1-D (a), 2-D (b) and 3-D (c) molecular switches. Note: D and A correspond to donor and acceptor, respectively.

ultimately the most rewarding since the complexity of the system is now on a par with nature's molecular machinery.

It is the aim of this short review to set out how this realization of moving into 2-D and 3-D may be achieved, and highlight examples where the idea of directionality in electron transfer has been put into practice. Examples are also included where energy transfer migration is affected. It is worth noting that although energy transfer results in the movement of energy from one part of a molecule to another, a mutual exchange of electrons (Dexter mechanism) *via* HOMO/LUMO orbitals of a bridge are required in this process. Thus, one can imagine that perturbation of these orbitals could be used to direct energy flow. A question arises as to whether one should consider systems where control of fluorescence resonance energy transfer (FRET) is achieved. Within FRET the dipole–dipole (Förster) mechanism operates and so there is no mutual exchange of electrons involving the linking bridge. Hence, examples are not included here but in Further Reading those working in this area are given since it has been possible to switch FRET on and off.

The starting point of this review, however, will be to take a look at Nature and see what lessons can be learnt and what design criteria could be taken from natural systems.

2 Nature shows the way–electron directionality in photosynthetic reaction centre complexes

As eluded to earlier, natural systems already have the upper hand in their ability to direct and control the passage of electrons along what appear complex pathways. The most noteworthy example of this phenomenon is the unidirectional electron transfer exhibited in photosystem II by the reaction centre complex of the purple bacteria *Rhodopseudomonas viridis* (Fig. 3).[13] The working machinery of the complex consists of two quasi-symmetrical cofactors encased in a protein matrix. The 'special-pair' of porphyrins shown in green at the top of Fig. 3, are the collection point for a photon from the nearby light-harvesting ring. Straddled ether side of the special pair are two porphyrinic relays which lead to electron acceptor quinone moieties.† Despite the fact that the two relays are almost identical, electron transfer proceeds (as shown) preferentially along the L-branch. It is believed that electron migration proceeds in this manner because of a difference in the dielectric constant between the L and M branches.[14] This subtle dielectric asymmetry is enough to favourably stabilise the charge-separated species in the L-branch over the M-branch. It is interesting to note that the unidirectionality of electron transfer displayed in photosystem II is not shared by the analogous photosystem I which has a similar dual branch

† The quinone Q_B is the termination point for electron transfer in PSII and because of its mobility migrates out of the membrane to be replaced by a new quinone acceptor. In PSI iron–sulfur clusters act as terminal acceptors, and the quinone unit serves only as an intermediary in electron transfer.

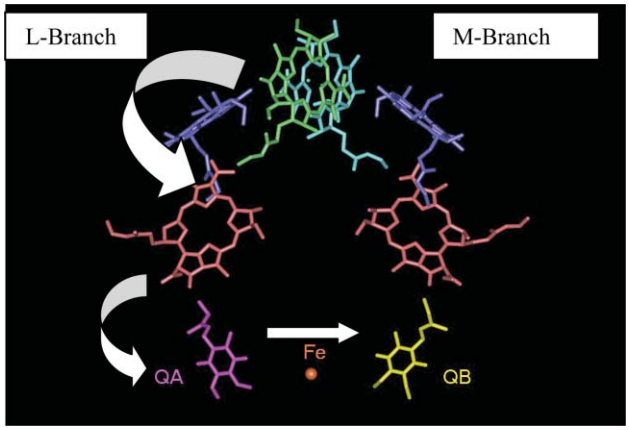

Fig. 3 Spatial arrangement of the co-factors in the photosynthetic reaction centre complex of the purple bacteria *Rhodopseudomonas viridis*. Note: the arrows depict the preferential electron flow along the L-branch of the co-factors. (Reproduced in part with permission of Dr R. Wheeler.)

electron transfer pathway.[15] Evidently nature only uses directional electron transfer when required! We can, however, take note that it is the local environment that influences the electron migration in PSII, and perhaps that this effect could be taken on board when designing artificial systems.

3 Moving into 2-D and 3-D: What is required?

The simple cartoon pictures of Fig. 2 hide the complexity of what is required if one is to create molecular switches that operate in 2 and 3 dimensions. It is clear that the switch portion is the key, although if we are to prove that electrons travel in specific directions then this must be readily detected. For a start this could be achieved by ensuring that A_1 through A_3 are different, and that electron arrival is signalled by different means such as a colour change or fluorescence alterations. Of course, there is one problem with the outlined designs, and it relates to a property which is going to work against operation of our multi-dimension switch. That is through-space communication of, for example, D and A_2 (Fig. 2b) *via* the interdispersed solvent molecules.[16] Thus we could imagine that for a system to stand a chance of working, the through-bond communication between D and A_1 would need to be greater than the through-space interaction of D and A_2. However, this problem could work to our advantage if the switching action also leads to a change in separation between subunits, since electronic coupling critically depends on distance.[17]

Clearly, the final hurdle to overcome in all these design systems is how to make all the switching systems behave in a coherent manner at a controllable interface. Hence, switching devices will be required to act on surfaces or within macroscopic materials.

4 Pseudo-rotaxane, cyclophane and catenated electron transfer directors

It is clearly not an easy task to mimic the subtle alteration of environment observed in the reaction centre complex, which drives preferential electron transfer. The local non-covalent interactions of the vast protein coating are too complex to imitate in a model system. Hence, focusing on one type of interaction and utilising it, is an easier and a more profitable approach. In the following examples the use of π–π interactions to influence the redox properties of electron acceptors is discussed as a way of altering rates of electron transfer along dual pathways.[18] The model assemblies (Fig. 4) are based on

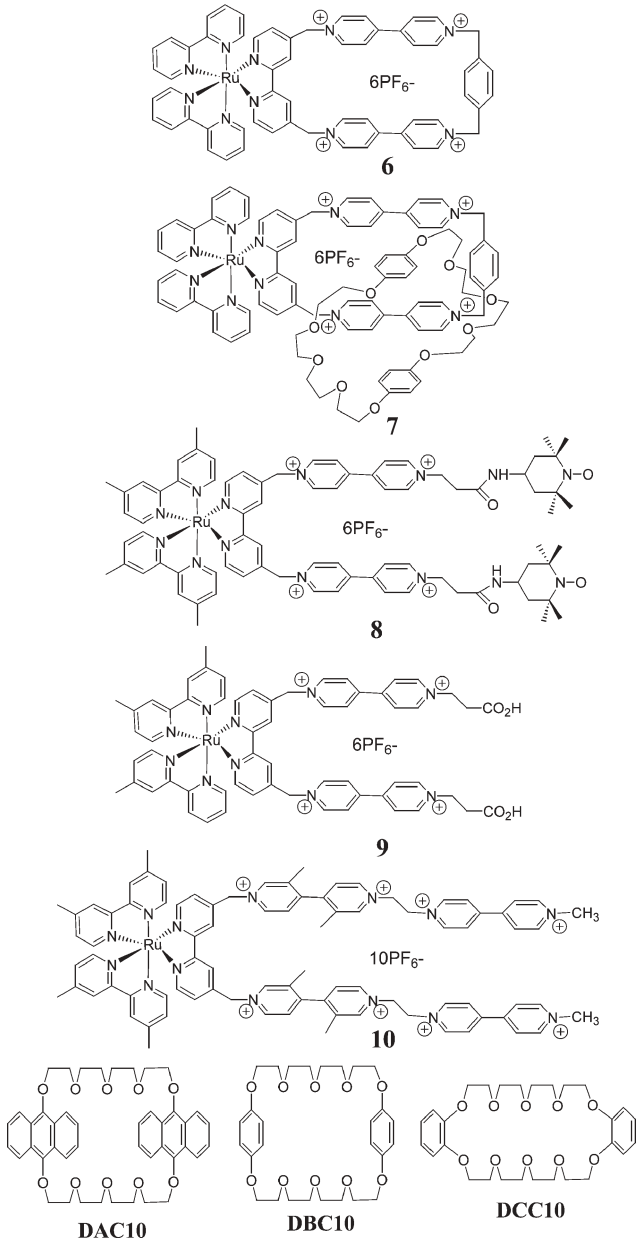

Fig. 4 Examples of ruthenium(II) polypyridyl assemblies capable of forming catenane, cyclophane and psuedo-rotaxane structures with the shown crown ethers.

the topologically interesting catenane and pseudo-rotaxane structures. Catenanes represent a class of compounds in which two rings are interlocked but can mutually rotate since no covalent bond links them together. Pseudo-rotaxanes are their counterparts where a 'bead' is able to slip onto a 'thread' and reside at a specific site through non-covalent interactions.[19] For all the compounds **6–10** the photoactive centre is the ruthenium(II) 2,2′-bipyridyl (Rubipy) site and the electron acceptors are the *N*,*N*-bipyridinium (viologen) units. Hence, light activation of the 'Rubipy' core will lead to electron transfer to the viologen acceptors. In **6** the two viologen units are identical and so one would expect that there is an equal probability that either group is reduced in the photoinduced electron transfer event. On the other hand the crown polycycle in **7** wraps preferentially around one of the viologen units. This does two things; first, the encased viologen is protected from the surrounding solvent, and second the reduction potential of the viologen is made more negative with respect to 'open' one. To understand why this later point is significant one must look at the Marcus equation[20] for understanding electron transfer events.

$$k_{et} = \frac{2\pi V^2}{h\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (1)$$

$$\Delta G^* = \frac{(\lambda + \Delta G^{o})^2}{4\lambda}$$

The rate of an electron transfer process (k_{et}) depends upon a number of parameters including the electronic coupling element V, total reorganization energy λ and the activation energy ΔG^*, which itself is related to the thermodynamic driving force ΔG° (eqn. (1)). In the Marcus normal region k_{et} increases with the thermodynamic driving force and reaches a maximum when $\Delta G^{\circ} = \lambda$, after this k_{et} decreases and is the portion of the graph called the inverted region.

Since the redox potentials for the two viologens of catenane **7** are different, the driving forces for electron transfer are not equal and so the k_{et} values predicted from eqn. (1) are quite different. Specifically, the k_{et} value for electron transfer to the encapsulated viologen is smaller than the corresponding value of k_{et} for reduction of the 'open' viologen. The derived selectivity for the directional electron transfer is an impressive 85% in favour of the exposed viologen.[18] A number of assumptions are made in the analysis, these being that V and λ are similar for both viologens. Time-resolved transient absorption experiments carried out on **6** and **7** have shown that the rate of forward electron transfer is fast ($k_{for} \sim 6 \times 10^{10}$ s^{-1}), and as required is occurring in the normal Marcus region. Unfortunately, it is not possible spectroscopically to distinguish between the two viologens and unequivocally confirm the selectivity in the electron transfer process.

In similar related work to the above, the supramolecular entities **8–10** have been studied. Evidently, for outlined systems to direct electron flow the communication between the two acceptors must be negligible. This has been shown to be true using EPR experiments and looking for an interaction between the two TEMPO (2,2′,6,6′-tetramethylpiperidine *N*-oxide) units of **8**. In fluid solution above 5 °C there is no evidence for electron spin exchange.[21] Follow up work has focused on **9** and **10** and in particular looking at the influence on the charge-separated lifetime upon binding the various crown ethers to the viologen unit. For example, complexation of **DBC10** to **9** led to a dramatic increase in lifetime of the charge-separated state by a factor of 2×10^4. A more modest 5500-fold increase in the lifetime of the charge-separated state was observed upon complexation of **DCC10** to **10**. The impressive observed changes can be attributed to a decrease in the reorganization energy, λ, at the viologen acceptor site, because of the presence of the crown polycycle.[22]

In a step in the direction of actually using a protein matrix to influence electron transfer events Himachi and co-workers[23] have studied the catenated assembly **11** in cytochrome b_{562} and myoglobin by cofactor reconstitution. Within the assembly the zinc porphyrin (ZnP) moiety or 'Rubipy' site can act as an electron donor, whereas the viologen cyclophane is the electron

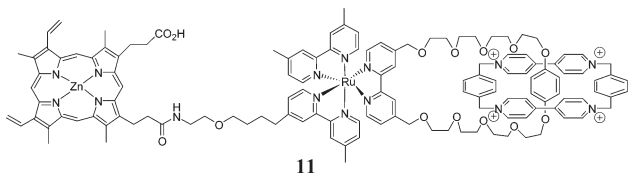

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Fig. 5 An illustration of a triad molecular array containing a ruthenium(II) polypyridyl catenane and a porphyrin electron donor.

acceptor. Although there is no directionality in the electron transfer event in the assembly it is interesting to note that the protein matrix greatly influences which state of the ZnP takes part in charge separation. For example, excitation of ZnP when the assembly is in the protein matrix leads to direct electron transfer from the triplet state of the porphyrin to the cyclophane electron acceptor. Without the protein the electron transfer event within **11** takes place *via* the singlet state of the porphyrin. Furthermore the lifetime of the charge-separated state depends greatly on whether or not the assembly is encased in the protein matrix. It can be argued that these outlined systems do not contain a switching system to allow complete control of electron migration. However, workers are attempting to manipulate the positioning of the crown ether polycycle in catenanes and rotaxane assemblies by both photochemical and electrochemical means.[24] Thus, the combination of these two research efforts in the future could bode well for the creation of true dimensional electron director switches.

5 Metal-based complexes

In the previous examples it was the direction of an electron transfer event that was controlled to some extent. In this section the idea of directing an energy transfer process will be discussed. The multitopic polypyridine complexes **12** and **13** (Fig. 6) incorporate a photoactive 'Ru-terpy' core which is

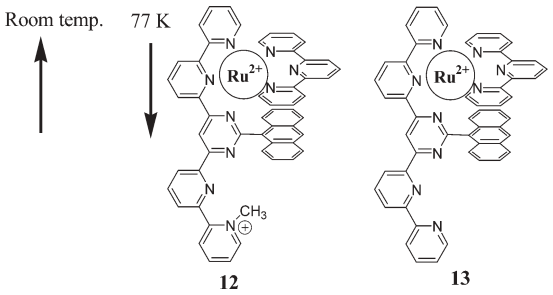

Fig. 6 Illustrations of ruthenium(II) polypyridyl complexes used to control the direction of photoinduced energy transfer. The arrows depict the direction of energy transfer at the two different temperatures.

adjacent to an anthracene (An) unit.[25] Energy transfer from the 'Ru-terpy' core to the anthracene unit occurs when the compounds are held in a rigid matrix at 77K. In fluid solution at room temperature the direction of the energy transfer process is reversed. This alteration in energy transfer direction can be attributed to the relative positioning of the ^{3}MLCT and ^{3}An energy levels, and changes in thermal population of these two states. That is, at room temperature thermal activation of the uphill energy transfer to the ^{3}MLCT takes place. At the low temperature the ^{3}MLCT state is poorly populated and the energy collected is funnelled out *via* the anthracene unit. In these two examples it is clear that a metal-based system incorporating another photoactive subunit may hold the key to directional energy transfer. Illustrated in Fig. 7 are two more recent examples where alterations in energy flow direction has been proposed. The compound **14** is highly multifunctional comprising a coumarin–Ruterpy–azo–Osterpy linear array.[26] The critical part of the array is the azo segment which can undergo a one-electron redox process. When the azo unit is in the reduced state excitation of the coumarin leads to energy transfer to the Ruterpy site followed by energy transfer to the Osterpy unit. Thus, there is coherent energy migration along the molecular array. This process is stopped when the azo subunit is oxidised back to its neutral form, since now a quenching trap is introduced.

Spiropyrans are an interesting class of compounds whose

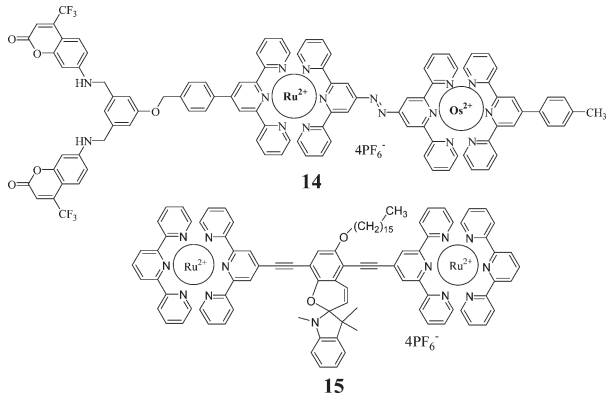

Fig. 7 Polypyridyl complexes designed to control energy transfer flow.

properties differ dramatically when opened up into their merocyanine form. A recent development has seen the incorporation of a spiropyran unit into the connector linking two Ruterpy subunits to form complex **15**. It is well established that the electron in the ^{3}MLCT excited state of ruthenium(II) complexes incorporating a 4′-ethynylene-2,2′:6′,2″-terpyridine ligand delocalises onto the acetylene portion.[27] Thus, in the 'closed' form the electron in the excited state would be expected to migrate between the two metal centres. In the 'open' form, however, an alternative pathway for the electron is introduced as depicted in Fig. 8. The study of systems based on **15** are at a

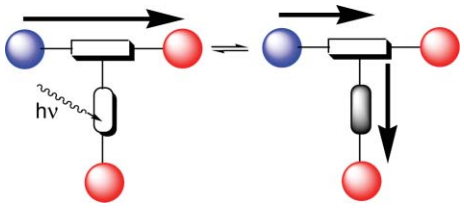

Fig. 8 Proposed operation of a T-junction relay by light activation of a spiropyran unit.

very early stage of development, but preliminary results are encouraging and support the opening/closing of the T-junction.[12]

6 Bi-directional organic donor–acceptor compounds

Control of electron direction is not confined to complex looking molecules, but can be exhibited by carefully designed relatively simple looking organic compounds (Fig. 9). Particularly good examples of this are the compounds **16a** and **16b** studied by de Silva and Rice,[28] which have shown to undergo unidirectional electron transfer. Numerous aminoalkyl derivatised fluorophores are weakly luminescent as a result of efficient quenching, because of rapid photoinduced electron transfer (PET) from the amine group to the fluorophore. Upon protonation of the amine unit there is a dramatic increase in luminescence intensity since PET is inhibited. Compounds **16a** and **16b** are isomers and theoretically there are two possible PET pathways provided for the fluorophore by the dialkylaminoethyl side chains. Using pH-dependent fluorescence experiments it was shown that protonation of the distal nitrogen of the 4-substituent had a much greater effect on fluorescence recovery when compared to protonation of the distal nitrogen of the 9-substituent. Thus, the preferred electron transfer direction for PET is (as shown in Fig. 9) from the distal nitrogen of the 4-substituent. More recently, work by Marcus and Gao[29] has put these observations on a firm theoretical footing using the series of compounds **16–19**. The initially

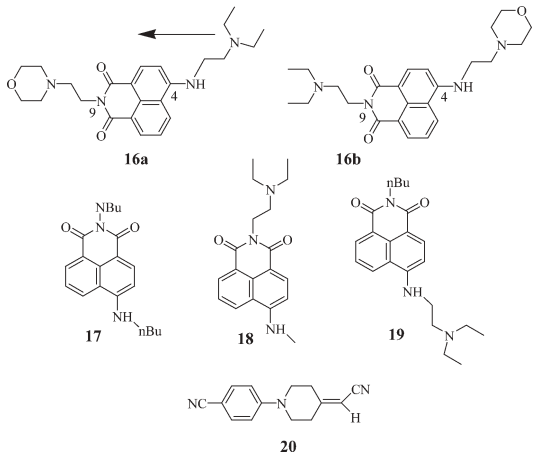

Fig. 9 Organic compounds used in studies for promoting directional electron transfer (**16–19**) and a trichromophoric array (**20**).

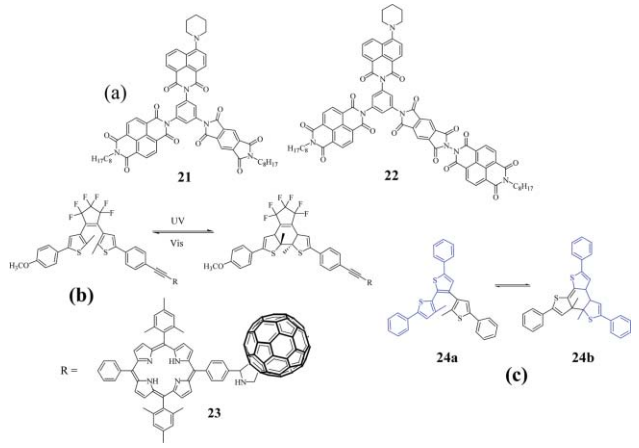

Fig. 10 Illustrations of organic-based directional femtosecond optical switches (a), dithienylethene–porphyrin–fullerene photonic switch (b) and a molecular re-router (c): Note the arrows depict the direction of electron migration in (a) and the blue colouration indicates the preferred electron delocalisation pathway in (c).

proposed reason for the directional electron transfer in **16a/b** was assigned to generation of an internal electric field. Specifically, excitation of the naphthalimide first generates a charge-separated state consisting of a delta positive on the 4-N and a delta negative on the dicarboximide. Hence, this internal electric field directs the 'hole' to the distal nitrogen of the 4-substituent. Marcus *et al.* have, however, proposed a simpler explanation based on calculations of the electronic coupling elements of the orbitals involved. Extended Hückel calculations reveal that a much larger electronic coupling element exists for electron transfer from the distal nitrogen attached to the 4-position, when compared to the distal nitrogen anchored at the 9-position.

The compound **20** (Fig. 9) is another example where directionality in an electron transfer event is an issue, and it consists of two cyano-based electron acceptors and donor in a A_1–D–A_2 linear fashion.[30] Within the molecule there exists a competition between electron transfer mechanisms using the σ-bond framework or the π-way. The central donor portion of **20** is part of the initially formed excited state and so electron transfer can occur in two directions. Detailed time-resolved measurements have shown that in diethyl ether and acetonitrile two charge-transfer states (σ-CT and π-CT) are formed by electron migration through the sigma- and pi-bonds, respectively. These two states are in fact generated immediately upon excitation of **20**, and it is interesting to note that electron exchange between the states occurs preferentially in one direction.

In the examples discussed so far there has been no real mention of the timescale for the switching of an electron transfer event. The work by Wasielewski and co-workers[31] has focused on this aspect, especially with their branched donor–acceptor arrays (**21–22**) that display femtosecond optical switching of the electron transport direction (Fig. 10a). Both the compounds comprise a 4-(*N*-piperidinyl)-1,8-napthalenediimide (ANI) electron donor attached in various fashions to 1,8:4,5-naphthalenediimide (NI) and pyromellitimide (PI) electron acceptors. Selective excitation of the ANI unit with a femtosecond laser pulse leads to directional one-electron reduction of the near-by NI unit. A subsequent selective excitation of this radical anion with a second femtosecond pulse creates the excited $*NI^-$ species. This energetic species reduces the PI acceptor of the other branch. It is worth noting that under normal conditions the electron transfer process NI^- to PI is thermodynamically uphill, and so the second laser pulse is essential for the branch switching to occur. In the more complex array **22** the generation of PI^- can lead to a cascade of the electron down the branch.

Photonic switching of photoinduced electron transfer has also been reported by Gust and Moore[32] using the diethienylethene–porphyrin–fullerene system **23**. When the compound **23** is in the open form the porphyrin excited state donates an electron to the C_{60} moiety to form a charge-separated P^+–$C_{60}^{-\bullet}$ state. However, irradiation of **23** with UV light closes the switch portion and now the porphyrin excited state is quenched by energy transfer to the dithienylene unit in about 2ps.

To conclude this review a very recent example by Kawai *et al.*[33] of a molecular re-router **24a/b** is highlighted as a highly promising switching unit. In the 'open' form of the 2,2′-3,3″-terthiophene derivative (**23a**) the π-conjugation of the molecule (shown in blue) is associated with dithiophene segment. Upon ring closure to form **23b** the π-conjugation is re-routed to the other side of the molecule. Although still at a very early development stage this switching unit should be ideal for controlling electron delocalisation pathways in more complex arrays, especially if the terminal phenyl groups are functionalised with donor/acceptor groups.

7 Outlook

From the examples outlined in this review it is hoped that the reader is convinced that multicomponent molecular-scale assemblies and simple organics offer the opportunity to study directional electron and energy transfer. There is a still a long way to go before the likes of true 2-D and 3-D molecular switches emerge and real materials are realised. The use of crystal engineering may play a big part in the creation of such materials. Indeed, there are encouraging signs that this method could be applicable as highlighted in a recent review by Sato[34] on optically switchable molecular solids. For example, the complex $[Fe(pap)_2]ClO_4$ (Fig. 11) forms a one-dimensional network in which multiple π–π stacking takes place. The material undergoes light-induced spin state trapping in which the Fe(III) high-spin state is photogenerated from the Fe(III) low-spin ground state. It will be interesting to see if a cross fertilization of ideas from this field of study and molecular-scale switches can be put to use to create truly multi-dimensional operational materials.

8 Further reading

In this short review it has not been possible to put in the contribution of all the workers in the field of electron transfer in multifunctional arrays. Interested readers are pointed

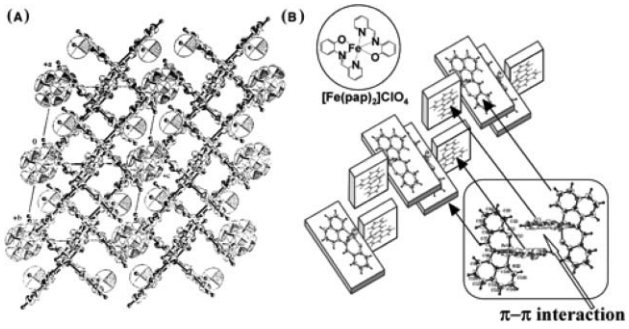

Fig. 11 Crystal packing diagram of $[Fe(pap)_2]ClO_4.H_2O$ (A) and an illustration of the π-stacking of the molecules (B). Reprinted with permission from ref. 34. Copyright 2003 American Chemical Society.

towards other papers by workers cited in this review and researchers such as Holton, Bocian and Lindsey,[35] Yagi,[36] Tian,[37] and Otsuki[38] for further inspirational contributions to the field.

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References

1 A. C. Benniston and P. R. Mackie, in *Handbook of Nanostructured Materials and Nanotechnology: Concise Edition*, Ed. H. S. Nalwa, Wiley & Sons, San Diego, California, 2001, p. 693.
2 P. F. Barbara, *Acc. Chem. Res.*, 2001, **34**, 409 and reviews within.
3 H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, 85.
4 A. Beyeler and P. Belser, *Coord. Chem. Rev.*, 2002, **230**, 29.
5 L. Fabbrizzi and L. Prodi, *Chem. Soc. Rev.*, 1995, **24**, 197.
6 J.-P. Launay, *Chem. Soc. Rev.*, 2001, 386.
7 J. M. Lehn, in *Supramolecular Chemistry: Concepts and Perspectives*, VCH, 1995.
8 M. Querol, B. Nunzion and P. Belser, *Polyhedron*, 2003, **22**, 655.
9 J. Otsuki, M. Tsujino, T. Iizaki, K. Araki, M. Seno, K. Takatera and T. Watanabe, *J. Am. Chem. Soc.*, 1997, **119**, 7895.
10 A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake and M. Irie, *J., Org. Chem.*, 2001, **66**, 3913.
11 K. Sendt, L. A. Johnston, W. A. Hough, M. J. Crossley, N. S. Hush and J. R. Reimers, *J. Am. Chem. Soc.*, 2002, **124**, 9299.
12 A. Amini, K. Bates, A. C. Benniston, D. J. Lawrie and E. Soubeyrand-Lenoir, *Tetrahedron Lett.*, 2003, **44**, 8245.
13 J. Deisenhofer, O. Epp, R. Miki, R. Huber and H. Michel, *J. Mol., Biol.*, 1984, **180**, 385; J. Deisenhofer, O. Epp, R. Miki, R. Huber and H. Michel, *Nature*, 1985, **318**, 618.
14 M. A. Steffen, K. Lao and S. G. Boxer, *Science*, 1994, **264**, 810.
15 This is still a debatable issue but recent experiments support the idea that both pathways are used in PSI. See M. Guergova-Kura, B. Boudreaux, A. Joliot, P. Joliot and K. Redding, *Proc. Nat. Acc. Sci. USA*, 2001, **98**, 4437.
16 N. J. Head, A. M. Oliver, K. Look, N. R. Lokan, G. A. Jones and M. N. Paddon-Row, *Angew. Chem. Int. Ed.*, 1999, **38**, 3219.
17 M. N. Paddon-Row, *Acc. Chem. Res.*, 1994, **27**, 18.
18 A. C. Benniston, A. Harriman and P. R. Mackie, *Angew. Chem. Int. Ed.*, 1998, **37**, 354.
19 For reviews on catenanes and pseudorotaxanes see: D. Amabalino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.
20 For a concise review of Marcus theory see: G. Grampp, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 691.
21 S. H. Bossmann, M. F. Ottaviani, D. van Loyen, H. Dürr and C. Turro, *Chem. Commun.*, 1999, 2487.
22 V. Schild, D. van Loyen, H. Dürr, H. Bouas-Laurent, C. Turro, M. Wörner, M. R. Pokhrel and S. H. Bossmann, *J. Phys. Chem. A*, 2002, **106**, 9149.
23 Y.-Z. Hu, H. Takashima, S. Tsukiji, S. Shinkai, T. Nagamune, S. Oishi and I. Hamachi, *Chem.-Eur. J.*, 2000, **6**, 1907.
24 A. C. Benniston, *Chem. Soc. Rev.*, 1996, **25**, 427.
25 S. Serroni, S. Campagna, R. P. Nascone, G. S. Hanan, G. J. E. Davidson and J.-M. Lehn, *Chem.-Eur. J.*, 1999, **5**, 3523.
26 T. Akasaka, T. Mutai, J. Otsuki and K. Araki, *J. Chem. Soc., Dalton, Trans.*, 2003, 1537.
27 A. Harriman and R. Ziessel, *Coord. Chem. Rev.*, 1998, **171**, 331.
28 A. P. de Silva and T. E. Rice, *Chem. Commun.*, 1999, 163.
29 Y. Q Gao and R. A. Marcus, *J. Phys. Chem. A*, 2002, **106**, 1956.
30 S. Depaemelaere, F. C. De Schryver and J. W. Verhoeven, *J. Phys., Chem. A*, 1998, **102**, 2109.
31 A. S. Lukas, S. E. Miller and M. R. Wasielewski, *J. Phys. Chem. B*, 2000, **104**, 931.
32 P. A. Liddell, G. Kodis, A. L. Moore, T. A. Moore and D. Gust, *J., Am. Chem. Soc.*, 2002, **124**, 7668.
33 T. Kawai, T. Iseda and M. Irie, *Chem. Commun.*, 2004, 72.
34 O. Sato, *Acc. Chem. Rev.*, 2003, **36**, 692.
35 D. Holton, D. F. Bocian and J. S. Lindsey, *Acc. Chem. Res.*, 2002, **35**, 57.
36 S. Yagi, M. Ezoe, I. Yoeekura, T. Takagishi and H. Nakazumi, *J. Am., Chem. Soc.*, 2003, **125**, 4068.
37 (*a*) J. Gan, H. Tian, Z. Wang, K. Chen, J. Hill, P. A. Lane, M. D. Rahn, A. M. Fox and D. D. C. Bradley, *J. Organomet. Chem.*, 2002, **645**, 168; (*b*) H. Tian, T. Xu and K. Chen, *J. Chem. Soc., Perkin Trans. 2*, 1999, 545.
38 J. Otsuki, A. Suka, K. Yamazaki, H. Abe, Y. Araki and O. Ito, *Chem. Commun.*, 2004, 1290.