A Strategy for Constructing Photosynthetic Models: Porphyrin-containing Modules Assembled Around Transition Metals

Anthony Harriman
Center for Fast Kinetics Research, University of Texas at Austin, Austin, Texas 78712, USA

Jean-Pierre Sauvage
Laboratoire de Chimie Organo-minérale, Faculté de Chimie, Université Louis Pasteur, 1 rue Blaise Pascal, 67008 Strasbourg, France

1 Introduction

The photosynthetic process, and especially the rapid electron-transfer reactions occurring within protein-bound pigment complexes, has both fascinated and inspired scientists for many decades. Following from elegant biophysical investigations, including mutagenesis, and allowing for X-ray crystallography, much is now known about the intimate structure and reaction pathways of bacterial photosynthetic reaction centre (RC) complexes.[1,2] The main function of the RC is to generate an energy gradient, using successive electron-transfer (ET) processes to span the cytoplasmic membrane. During photosynthesis extremely long-lived, charge-separated states ($t_{1/2} > 1$ s) are formed, the redox sites being widely spaced (*ca.* 70 Å), with the unitary quantum efficiency for charge separation (CS) being achieved by virtue of a large expenditure of (photonic) energy. The cascade of ET steps that provides for long-range CS includes many individual reactions, each of which is sufficiently exergonic so as to be capable of competing with the inherent reverse ET process. This unique feature of the RC has been an important stimulant in the motivation for designing artificial molecular systems aimed at mimicking the structure and/or function of the bacterial photosynthetic RC. We note, with interest, that the initial (rapid) ET reaction occurs between large macrocyclic rings[1,2] and is followed by slower reactions that involve quinones and haems. In the latter case, ET occurs at the metal centre, not on the tetrapyrrolic ring, with the fastest reaction requiring 270 ns.

Synthetic models of the RC complex have advanced considerably in recent years, especially those based on covalently-linked porphyrin-quinone entities,[3–6] and many are able to mimic some of the essential features of the natural system.[7] We have concentrated on modelling the primary ET step between tetrapyrrolic nuclei that occurs within 3 ps in the RC complex,[8] despite the 17 Å centre-to-centre separation (Figure 1). In particular, we have shown how judicious incorporation of transition metals into the structure can influence the subsequent reactivity. Our basic strategy is illustrated in Figure 2 where it appears that transition metal centres can be used either to control the electronic properties of the bridge between donor and acceptor, and thereby modulate the rate of ET, or to assemble well-oriented structures containing terminal donor and acceptor porphyrinic subunits. Zinc(II) and gold(III) porphyrins have been selected as donor and acceptor, respectively, because of their highly favourable spectroscopic and electrochemical properties.[9] They represent acceptable, albeit crude, models for the bacteriochlorophyll special pair (primary donor) and bacteriopheophytin

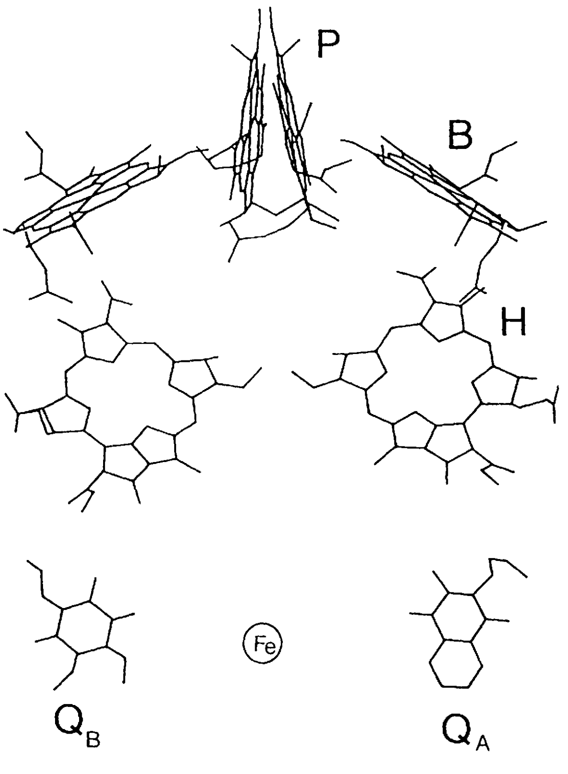
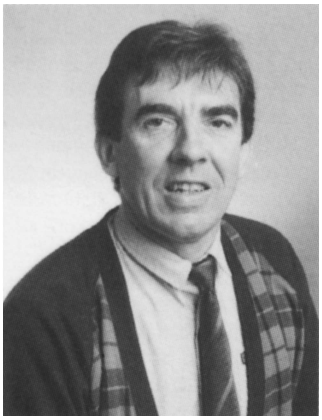


Figure 1 A fragment of the RC, as isolated from *Rhodopseudomonas viridis* with labels provided for the special pair of bacteriochlorophyll molecules (P) which acts as the primary electron donor, the accessory bacteriochlorophyll (B) which mediates ET, the bacteriopheophytin (H) which is the primary electron acceptor, the menaquinone (Q_A) which is an electron relay, and the ubiquinone (Q_B) which is the final electron acceptor. Note the presence of a non-haem iron atom and that ET involves only the labelled pigments (L branch). The unmarked bacteriochlorophyll and bacteriopheophytin molecules (M branch) do not appear as redox intermediates. See refs. 1 and 2 for original descriptions of the RC.



Jean-Pierre Sauvage was born in 1944 in Paris. After studying at Strasbourg University he did his PhD with J. M. Lehn on cryptates and spent some time as a post-doc with M. L. H. Green at Oxford. He is now a research director (CNRS) at the Faculty of Chemistry. His main scientific interests range from chemical topology (catananes and knots) to models of the photosynthetic reaction centre complex and one dimensional multicomponent transition metal complexes.

Anthony Harriman was born in 1949 in the West Midlands. After attending Wolverhampton Polytechnic he joined Sir George Porter's research group at the Royal Institution of Great Britain in 1974 before moving to the University of Texas at Austin in 1988. His major research interest is concerned with the development of artificial photosynthetic systems mostly based on metalloporphyrins and their exploration by transient spectroscopic techniques.

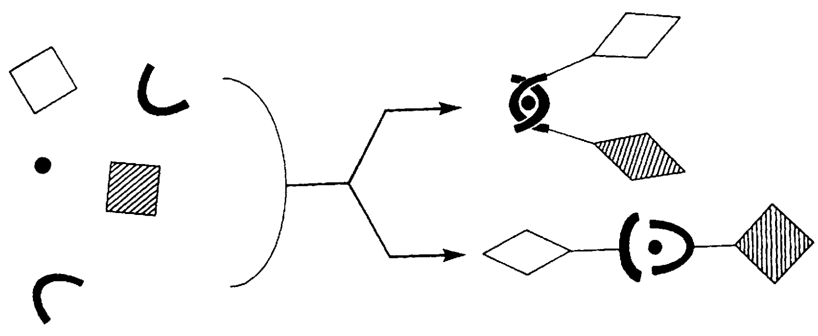
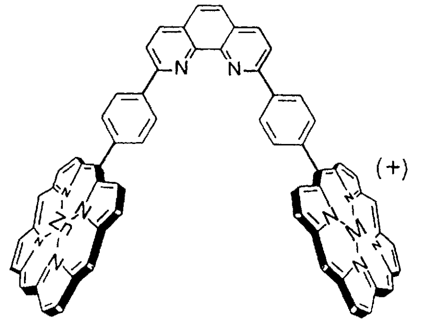


Figure 2 The principle whereby a transition metal centre (black dot) that coordinates to appropriate chelating ligands (solid arcs) can gather redox and/or photo active porphyrins (lozenges) into a single assemblage. Note the two porphyrin rings, which can differ by virtue of their substitution pattern and/or central metal cation, may be attached to the same ligand or to separate ligands. In both cases, formation of the central complex is essential. In the upper line, it will govern the electronic properties of the spacer connecting the two porphyrinic chromophores, whereas in the second case (bottom line) the metal will be the assembly point necessary for formation of the multicomponent molecular set.



1: M = 2H energy transfer
2: M = Au(III) electron transfer

Figure 3 Structure of the 2,9-diphenyl-1,10 phenanthroline bridged bis porphyrin illustrating the oblique arrangement of the porphyrin rings. Note the bis(3,5-*tert*-butyl)phenyl groups have been omitted from each of the vacant *meso*-positions for clarity of presentation. These substituents provide an important label for ^{1}H NMR studies and increase the solubility of the bis porphyrin in organic solvents. At least one of the porphyrin rings can be selectively excited with light of an appropriate wavelength while the nature of the second cation (M) controls the photochemistry that follows absorption of a photon by the zinc(II) porphyrin subunit.

(primary acceptor) present in the RC. It is important to realise that, for this pair of porphyrins, redox chemistry occurs exclusively at the macrocyclic ring and not at the metal centres. As such, bis-porphyrins formed from these modules differ from the well-studied analogues containing iron(III) or manganese(III) porphyrins.

Two types of asymmetric bis-porphyrins can be envisaged, namely (*i*) oblique structures having both porphyrin subunits attached to a single ligand,[10] giving a centre-to-centre separation of *ca.* 14 Å, and (*ii*) linear structures having only one porphyrin per ligand[11] and in which the centre-to-centre separation is *ca.* 30 Å. The synthetic approaches differ markedly for the two classes of bis-porphyrin but both involve isolation of a chelating ligand bearing the necessary functionality that permits subsequent construction of the porphyrin ring. The ligand has to remain sufficiently accessible for complexation with appropriate metal cations so as to form well-defined metal complexes of correct stoichiometry.

2 Oblique Bis-porphyrins

Oblique bis-porphyrins such as **1** and **2** (Figure 3) are obtained in multi-step procedures from 1,10-phenanthroline, with controlled metallation of the corresponding free-base porphyrin precursor.[12] The X-ray structure obtained for the corresponding bis-zinc (II) analogue[13] indicates a Zn^{II}–Zn^{II} separation of *ca.* 13.6 Å (Figure 4), the shortest porphyrin edge-to-edge separation being *ca.* 8.5 Å. Of course, the shortest through-bond (edge-to-edge) pathway exceeds even the centre-to-centre separation, and is estimated to be *ca.* 22 Å. The subsequent photochemistry of the bis-porphyrin is controlled by the choice of the second cation M, such that rapid energy- ($M = 2H^+$) or electron-transfer ($M = Au^{3+}$) processes dominate upon excitation of the appended zinc porphyrin. Energy transfer most likely proceeds *via* Forster-type dipole–dipole transfer,[14] as has been observed for many other covalently-linked bis-porphyrins having either alkyl or aryl bridges. With respect to photoinduced electron transfer, the oblique bis-porphyrin **2** is unique among model systems in that both porphyrin rings are photoactive, thereby permitting facile comparison of the photochemistry occurring *via* singlet and triplet excited states.[15,16]

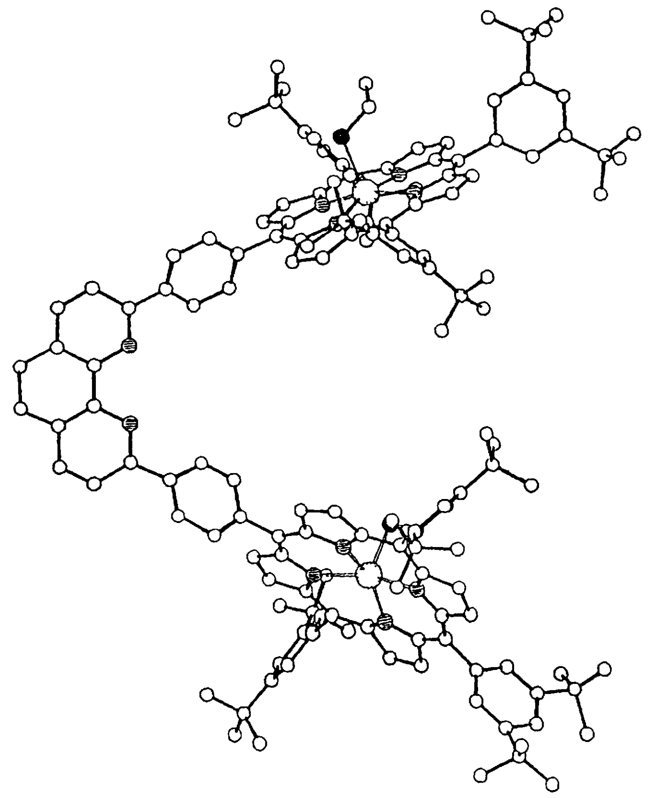


Figure 4 X Ray crystal structure obtained for the symmetrical bis zinc complex having the same organic backbone as **1** and **2**. It is assumed that the general geometrical features of the bis-porphyrin are only slightly dependent on the nature of the metals located in the coordination sites. The Zn···Zn interatomic distance is 13.7 Å in the present structure.

Laser flash photolysis studies carried out with **2** in acetonitrile solution at 25 °C have been used to elucidate the reaction pathway, together with rate constants for individual steps, following selective excitation of either porphyrinic subunit (Figure 5).[15] The excited states of both porphyrins (*i.e.*, singlet and triplet for the zinc porphyrin and triplet for the gold porphyrin) undergo intramolecular electron transfer to form a common radical pair, which persists for

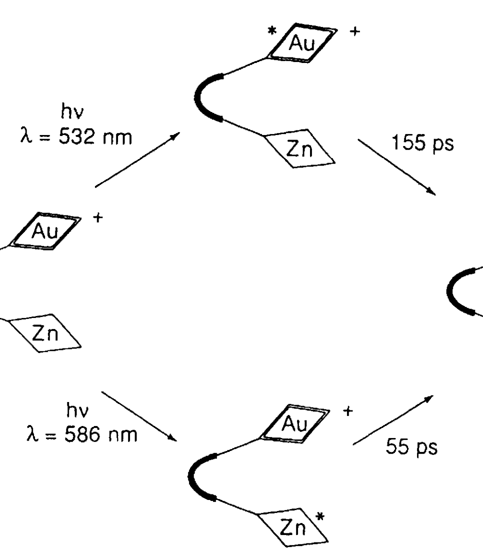


Figure 5 A pictorial representation of photoinduced electron transfer in the oblique zinc(II)–gold(III) bis-porphyrin **2**, following selective excitation into either porphyrin subunit, giving the lifetime of each intermediate species as measured by transient spectroscopic studies made in acetonitrile at 25 °C.

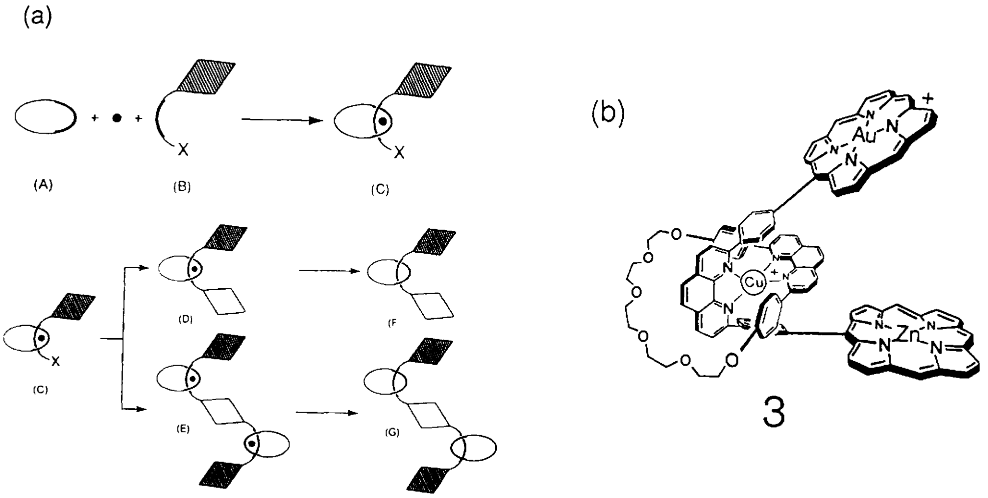
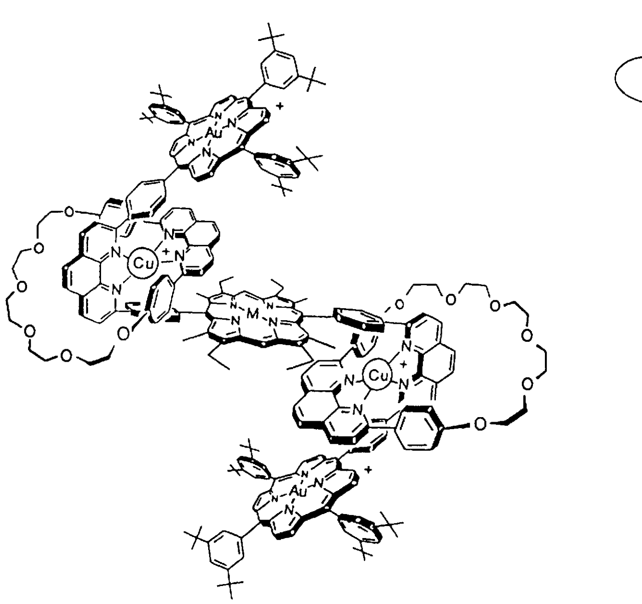


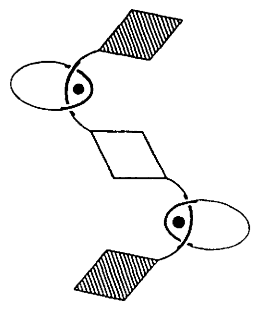
Figure 6 (a) Template synthesis of porphyrin stoppered [2]- and [3] rotaxanes. The macrocycle (A) incorporating a coordinating fragment (thick line) interacts with a metal centre (black dot) and an asymmetrical open chain chelate (B) bearing a single porphyrin and a precursor function (X) which is small enough to pass through the ring. After the threaded intermediate (C) is formed, the second porphyrin ring is subsequently constructed, giving rise to the transition metal complex-containing rotaxanes (D) and (E). Demetallation leads to the free-ligand rotaxanes (F) and (G) from (D) and (E), respectively. By applying the strategy described above [the hatched lozenge now represents a gold(III) porphyrin and the templating metal is a copper(I) cation], an asymmetrical bis porphyrin of type (F) is obtained (white lozenge symbolizing a free-base porphyrin). (b) This free coordination site can be metallated with zinc(II) to afford the [2] rotaxane **3**. Owing to the synthetic procedure necessary for assemblage of these rotaxanes, the porphyrinic subunits bear different substitution patterns. Note, the substituents on the porphyrin rings (see Figure 7) have been omitted for clarity of presentation while the overall charge on [2]-rotaxane **3** is +2.

about 600 ps before undergoing charge recombination (CR) to reform the original species. The radical pair is formed from the excited singlet state of the zinc porphyrin in *ca.* 55 ps ($\Delta G^\circ = -0.75$ eV, edge-to-edge distance = 8.5 Å) compared to *ca.* 3 ps for the corresponding process in the RC complex ($\Delta G^\circ = -0.39$ eV, edge-to-edge distance = 9.5 Å).[17] Furthermore, whereas the rate of the primary ET reaction occurring in the RC complex is essentially independent of temperature,[18] **2** exhibits both a significant activation energy in solution ($E_a = 0.009$ eV)[19] and a 110-fold decrease in rate of ET on moving from fluid solution at 25 °C to a frozen glass at 77 K.[20] Under the latter conditions, the radical pair could be detected by EPR spectroscopy.

Detailed mechanistic studies[19] were found consistent with photoinduced ET between the terminal porphyrin subunits in **2** occurring *via* orbitals localized on the bridging 1,10-phenanthroline spacer. At first glance, we might find the rate of ET in **2** surprisingly slow if the process involves superexchange with the aromatic bridge since ET through such moieties can be rapid.[21] In contrast, the protein medium surrounding the reactants in the RC may involve a substantial attenuation factor,[17] causing the rate of ET to depend critically on separation distance. For **2**, there was no indication that CR within the radical pair involved a superexchange mechanism and, in fact, this process might occur through the intervening space occupied by solvent molecules. This being so, it was considered that the rate of the forward ET step, but not that of CR, could be modulated by varying the energy of the LUMOs and/or HOMOs on the spacer moiety. The latter situation can be realised by incorporating the bridging 1,10-phenanthroline ligand into a [2]-rotaxane (Figure 6).[22] Synthesis of the [2]-rotaxane **3** relies critically on the templating role of Cu^I ions, a strategy used successfully to prepare molecular knots[23] and other such exotica,[24] with the same reaction favouring formation of the corresponding [3]-rotaxane **4** (Figure 7).[25]

Following selective excitation[26] into the zinc(II) porphyrinic subunit of the [2]-rotaxane **3** the corresponding radical pair was formed in *ca.* 1 ps, a 55-fold increase in the rate of ET relative to the corresponding bis-porphyrin **2**. In competition with CR, the zinc porphyrin π-radical cation oxidizes the central Cu^I complex (Figure 8) before the original ground-state species is restored. By removal of the copper(I) cation from [2]-rotaxane **3**, giving rise to **5**, and





4 M = 2H

Figure 7 Structure of the copper(I) containing [3] rotaxanes having a central octaalkyl diphenyl porphyrin and terminal gold(III) tetraaryl porphyrins. Note, substituents on the zinc(II) and gold(III) porphyrins are the same as for the corresponding [2] rotaxane illustrated in Figure 6(b). The [3]-rotaxane **4** is obtained in 32% yield while the same reaction affords the corresponding [2] rotaxane **3** in 25% yield. The overall charge on compound **4** is +4

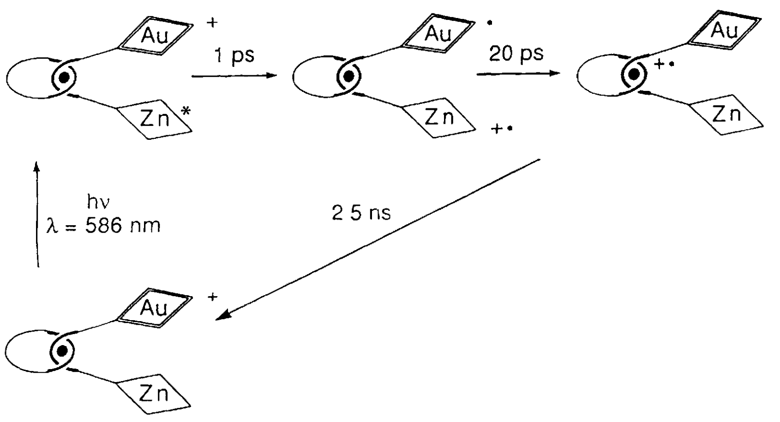
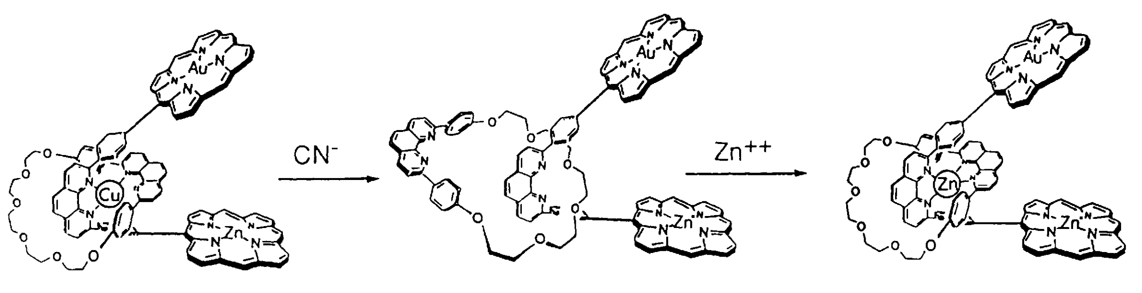


Figure 8 A pictorial representation of photoinduced electron transfer in the copper(I) containing [2]-rotaxane **3** having terminal zinc(II) and gold(III) porphyrins, following selective excitation into the zinc(II) porphyrin subunit, giving the lifetime of each intermediate species as measured by transient spectroscopic studies made in acetonitrile at 25°C. Note, the central copper(I) cation is represented by a black dot and carries a positive charge

subsequent insertion of a zinc(II) cation to form **6** (Figure 9),[27] it was possible to establish a good correlation between the rate of the forward ET process and the reciprocal of the energy gap between the relevant orbitals on the porphyrin excited state and on the bridging ligand. Noteworthy, ^{1}H NMR investigations[25] provided unambiguous evidence that [2]-rotaxanes **3** and **6** possess the same geometry, thus facilitating comparison of the two systems solely in terms of their electronic properties. This finding is entirely consistent with a superexchange mechanism involving molecular orbitals resident on the bridging 1,10-phenanthroline moiety. The rate of CR was hardly affected by these changes in molecular architecture. As such, this strategy permits design of systems capable of rapid forward ET but relatively slow CR. It should be noted that, for synthetic convenience, the nature of the zinc porphyrin donor present in the [2]-rotaxanes differs somewhat from that used in the simple bis-porphyrin. This change affects the driving force for the various ET steps and, because of adjacent alkyl substituents on the pyrrole rings, forces the connecting phenyl ring to become essentially orthogonal to the plane of a porphyrin ring.

Despite the slightly larger edge-to-edge separation and smaller driving force (ΔG°), the rate of the primary ET step in the RC complex is much faster than that found for **2** at 25 °C. The electronic coupling matrix element estimated for the RC complex ($V \approx 25\ \mathrm{cm}^{-1}$)[28] is also significantly smaller than the corresponding value ($V = 85\ \mathrm{cm}^{-1}$)[19] measured for **2**. However, the high rate of ET characteristic of the RC complex arises because the driving force is comparable to the total reorganization energy (λ) associated with ET, such that the activation energy is close to zero and reaction occurs at the apex of a Marcus-type energy-gap profile. [Note, in its simplest form, the activation free energy change may be expressed as $\Delta G^* = [(\lambda + \Delta G^\circ)^2/4\lambda]$, where λ is the reorganization energy accompanying electron transfer and ΔG° is the thermodynamic driving force for electron transfer. This expression holds well for ET in the normal (*i.e.*, $-\Delta G^\circ < \lambda$) region but needs to be modified to allow for high frequency quantum modes, usually represented by a single (average) vibrational frequency, when applied to ET in the inverted region.] For **2**, this is not the case ($-\Delta G^\circ \approx 0.5\lambda$) and ET occurs well within the 'normal' region of the Marcus-type parabola. Indeed, the activationless rate of ET (*i.e.*, $-\Delta G^\circ = \lambda$) for **2**, extrapolated from temperature and solvent dependence studies,[19] corresponds to a lifetime for the excited state of the zinc porphyrin of *ca.* 6ps. For the copper(I) [2]-rotaxane **3** we note that $-\Delta G^\circ \approx \lambda$ so that, as for the RC complex, the rate of ET is at a maximum. It should be noted, however, that although formation of the radical pair in the [2]-rotaxane **3** occurs on the same time scale as forward ET in the RC complex the inherent rate of CR ($k = 2 \times 10^9\ \mathrm{s}^{-1}$, $\Delta G^\circ \approx -1.2$ eV) in these various bis-porphyrins[27] is much faster than that found in natural RC complexes ($k = 2 \times 10^7\ \mathrm{s}^{-1}$ $\Delta G^\circ = -0.9$ eV). This situation most probably arises because CR for the RC complex ($-\Delta G^\circ \approx 3.6\lambda$) occurs well



3 **5** **6**

(1 ps) (36 ps) (28 ps)

Figure 9 Sequential removal of copper(I) from [2]-rotaxane **3** with cyanide ions, giving rise to **5**, and insertion of zinc(II) into the vacant coordination site so as to form the zinc(II) containing porphyrin stoppered [2]-rotaxane **6**. Lifetimes for the zinc porphyrin excited singlet state, as quenched by intramolecular electron transfer to the gold(III) porphyrin, are provided for each of the [2]-rotaxanes. Note, substituents on the porphyrin rings, which are the same as shown on Figure 7, have been omitted for clarity of presentation while the overall charge on **6** is +3.

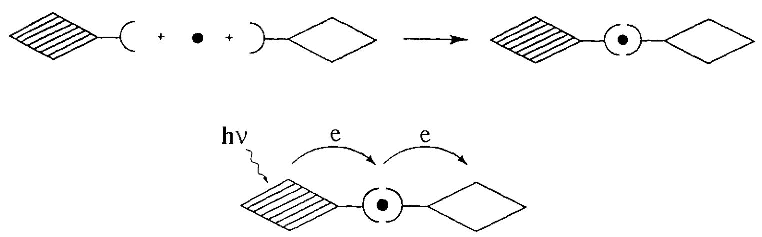


Figure 10 Strategy used to assemble asymmetrical bis porphyrins around a central transition metal cation (black dot). The basic module consists of a porphyrin (lozenge) covalently attached to a chelate (arc of a circle). Provided the transition metal complex is resistant to ligand-exchange processes, stepwise ET can be envisaged after selective illumination of a porphyrin ring.

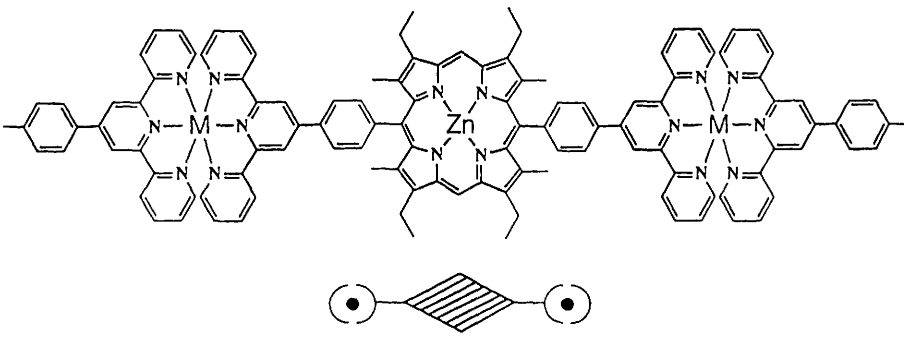
within the Marcus inverted region whereas that for the model systems ($-\Delta G^\circ \approx 1.3\lambda$) is much closer to the apex. {Note, when considering ET reactions occurring deep within the inverted region it is necessary to allow for the magnitude of the electron–vibrational coupling strength [$S_C = \Delta_C^2/2$, where Δ_C is the change in equilibrium configuration for the particular (*i.e.*, averaged) vibrational mode expressed in units of the root-mean-square displacement at the zero-point energy]. For the RC, S_C is small so that the rate of ET should decrease rapidly with increasing driving force. For isolated porphyrinic subunits, however, $S_C \approx 0.5$—1 such that the inverted effect is less pronounced and the rate of CR will decrease more gradually with increasing driving force.}

3 Linear Bis-porphyrins

Having demonstrated, by virtue of [2]-rotaxane **3** being a reasonable model for primary ET in the RC complex, the efficacy of transition metal ions like Cu^I towards tuning the electronic properties of the bridge, it is opportune to expand the role of the metal complex. Thus, the transition metal cation used to modulate electronic coupling between donor and acceptor can be employed also as a template, capable of gathering and orienting the two porphyrinic components.[29] The ligand to be attached to each porphyrin and the binding mode used to assemble the two modules into the final conjugate were selected so as to facilitate strict stereochemical control, especially with regard to the distance between the various electro- and photo-active components. It was further considered that unidimensional structures were particularly well adapted to accommodate multistep ET reactions, eventually leading to long-lived and spatially-remote CS states. Although there have been several reports[30–34] describing porphyrin–metal complex dyads it was decided that linear, rigid structures could be achieved most readily using 2,2′:6′,2″-terpyridine as the chelating ligand. This required access to novel materials bearing appropriate functional groups.

The general strategy for making these one-dimensional multicomponent molecular systems is illustrated in Figure 10. In principle, a single complexation step should facilitate assembly of a bis-porphyrin by gathering two relatively simple (porphyrin-containing) molecular modules around the central transition metal. In addition to serving as a bridge between the terminal porphyrins, the metal complex so formed could also act as an electron relay. Indeed, in the corresponding mono-porphyrinic dyads **7** and **8** (Figure 11) it was observed[35] that fluorescence from the porphyrin was extensively quenched due to rapid electron transfer to the appended metal complex. The presence of a phenyl ring between porphyrin and terpyridyl ligand plays a crucial role since, by decoupling the reactants, it slows down the rate of CR from fs to ns timescales. For example, with ruthenium(II) bis-(4′-phenylterpyridyl) as spacer, CR is sufficiently slow (*i.e.*, 2 ns) to permit engineering of triads in which successive ET steps can compete with CR (Figure 10).[11] In these latter triads, excitation into the terminal zinc porphyrin results in ET to the central ruthenium(II) bis-terpyridyl complex, followed by secondary ET to the appended gold(III) complex (Figure 12).[36] Consequently, ET occurs by two consecutive steps over a Zn^{II}–Au^{III} separation of *ca.* 30 Å, rate constants for individual steps, as determined from laser flash photolysis studies, are indicated in Figure 13. It is interesting to compare the lifetime of 33 ns measured for the ultimate charge-separated state in the triad with the value of 2 ns found for that in the corresponding ruthenium(II)-containing dyad since this illustrates the advantage of using a multistep ET pathway. Light absorbed by the central ruthenium(II) complex in **9** is transferred to the appended porphyrins, most likely *via* a Dexter-type electron-exchange mechanism.

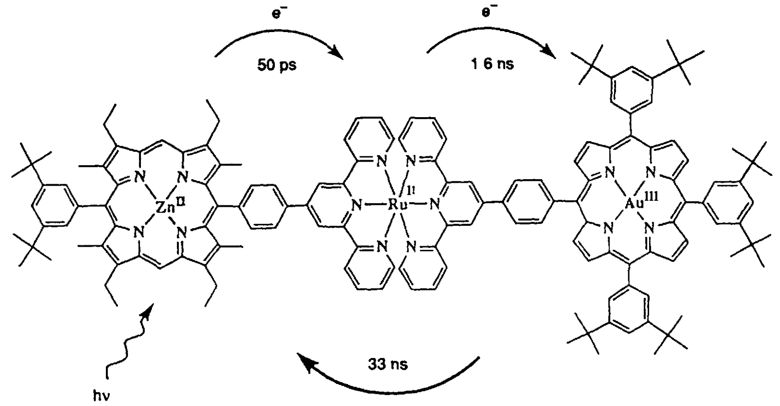
In triad **9**, the primary ET step leading to reduction of the central Ru^{II} complex ($\Delta G^\circ = -0.25$ eV, edge-to-edge separation ≈ 7 Å) requires 50 ps at 25 °C and is essentially quantitative.[36] This relatively slow rate of ET arises because of an almost orthogonal alignment of the bridging phenyl ring, which restricts electronic coupling between the reactants ($V = 12\ \mathrm{cm}^{-1}$), and from the fact that ET occurs well within the 'normal' region ($-\Delta G^\circ \approx 0.5\lambda$). However,



7 M = Rh(III)

8 M = Ru(II)

Figure 11 Structures of the photoactive dyads 7 and 8 containing zinc(II) porphyrin and rhodium(III) bis-terpyridyl subunits A bridging phenyl ring can be used electronically to decouple the redox-active subunits, as can be seen by examination of the relevant rate constants for charge separation (k_{cs}) and charge recombination (k_{cr}) measured in acetonitrile solution for 7 ($k_{cs} \approx 3 \times 10^{11}$ s^{-1}, $k_{cr} \approx 8 \times 10^{9}$ s^{-1}) and the analogue not having the bridging phenyl ring ($k_{cs} \approx 2 \times 10^{12}$ s^{-1}, $k_{cr} > 4 \times 10^{12}$ s^{-1}) The tripartite compound 7 is classified as a dyad, rather than a triad, since it contains only two different redox centres Note that rhodium(III) can be replaced by ruthenium(II) with only a slight modification in the observed rates of electron transfer



9

Figure 12 Structure of the bis-porphyrin-containing triad 9 with the time scales of important ET steps being indicated The central ruthenium(II) bis-terpyridyl complex serves to gather and orient the terminal porphyrins and to act as a redox intermediate in the ET pathway leading to formation of an inter-porphyrin radical pair This complex is not involved as a redox intermediate in interporphyrin charge recombination

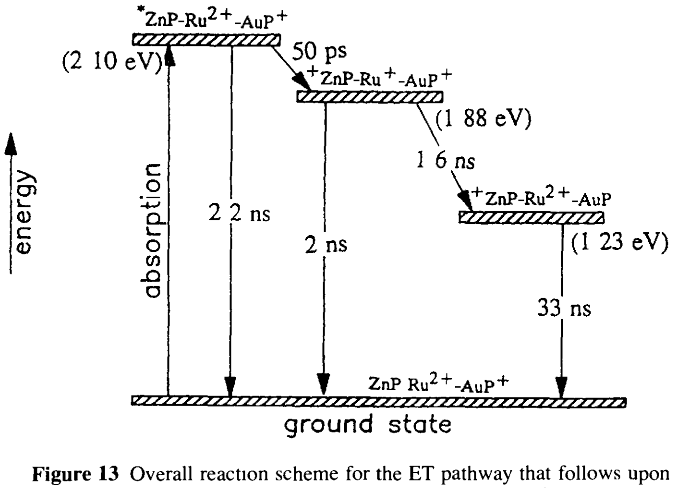


Figure 13 Overall reaction scheme for the ET pathway that follows upon illumination of the zinc(II) porphyrin subunit in triad 9 The various energy levels are obtained from spectroscopic and electrochemical measurements while the lifetime for each ET step has been determined by transient spectroscopy

primary CR is also slow because reaction occurs deep in the inverted region ($-\Delta G^\circ \approx 4\lambda$) and this permits secondary ET, resulting in reduction of the gold(III) porphyrin to occur with a yield of *ca* 60% Interporphyrin CR occurs over an edge-to-edge separation of *ca* 20 Å and takes place on the same time scale ($k \approx 3 \times 10^7$ s^{-1} $\Delta G^\circ = -1\ 2$ eV) as primary CR in the RC complex, despite the much larger separation that prevails for the model system Again, this situation can be explained in terms of a Marcus-type energy gap profile since CR in the triad ($-\Delta G^\circ \approx 1\ 7\lambda$) is expected to occur near to the apex It is interesting to note that in the corresponding triad having a free-base porphyrin in place of the zinc porphyrin the initial light-induced ET reaction still takes place despite an unfavourable driving force ($\Delta G^\circ \approx 0$ eV) In this case, interporphyrin CR is slower ($k \approx 1 \times 10^7$ s^{-1} $\Delta G^\circ = -1\ 4$ eV) than found for 9 It is also noteworthy that for 9 the interporphyrin radical pair survives for several microseconds in an ethanol glass at 77 K

4 Conclusion

We have indicated that photoinduced ET between terminal porphyrins can occur across an interspersed metal complex, the latter species appearing as a virtual or real redox intermediate, over distances relevant to the RC complex (Figure 14) Our model systems developed to date, although capable of high rates of ET, do not possess optimal thermodynamic properties with respect to the mutual relationship between ΔG° and λ which is an integral feature

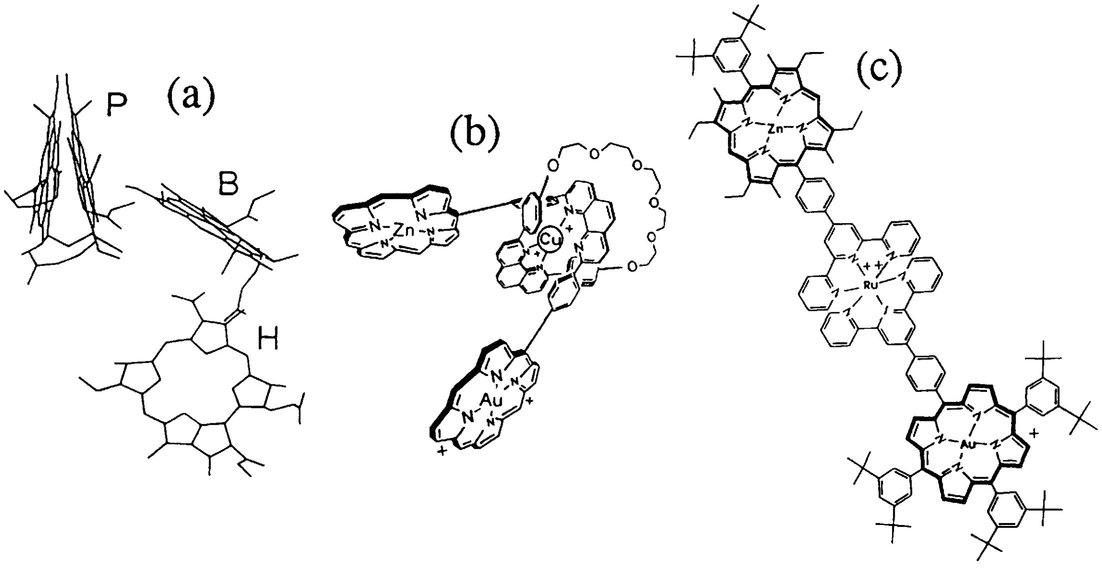


Figure 14 Comparison of natural and artificial porphyrin assemblages (a) Fragment of the RC showing the primary electron donor (P) and acceptor (H), together with the bridging bacteriochlorophyll (B) (b) Corresponding porphyrin stoppered [2]-rotaxane **3** where the donor is a zinc porphyrin, the acceptor is a gold(III) porphyrin, and the copper(I) bis 1,10-phenanthroline complex serves as the bridge (c) Bis-porphyrin based triad **9** where the donor is a zinc porphyrin, the acceptor is a gold(III) porphyrin, and the interspersed ruthenium(II) bis-terpyridyl complex provides the bridge Only in the latter case does the bridge also act as a redox intermediate in the forward ET process

of the RC Future model systems will need to take better advantage of this relationship in order to maximize rates of CS and, at the same time, minimize rates of CR It is also apparent that close attention must be given to the preferred orientation of any bridging phenyl rings since this can influence the extent of electronic coupling between appended redox-active subunits Indeed, the inadvertent positioning of alkyl substituents on the tetrapyrrolic macrocycle may make a major contribution to this effect, we have, however, demonstrated the necessity for such bridges Even so, triads such as **9** can be considered as belonging to a family of molecules that represents a genuine modular approach to construction of multicomponent molecular arrays having a logical and well-defined arrangement of the subunits, as in the RC, and which allows for a cascade of ET events The availability of a gradient of redox centres is an important, if not essential, aspect of designing molecular systems capable of circumventing CR and, thereby, realizing long-lived, widely-spaced CS states[37,38] The modular approach advocated here represents a viable and highly versatile alternative to the common, and successful, practice of using only covalent bonding to assemble giant arrays It provides new opportunities for the construction of elaborate molecular architectures that closely resemble the RC complex In particular, the methodology can be readily adapted to synthesize higher-order oligomers possessing quinoid and/or haem-like redox centres that could serve to extend the ET sequence so as to cover many redox partners

Acknowledgement We are deeply indebted to our many colleagues whose efforts made possible the work described herein and, in particular, we appreciate the significant contributions made by Anne Brun, Jean-Claude Chambron, Sylvie Chardon-Noblat, Jean-Paul Collin, Valérie Heitz, and Fabrice Odobel Financial support from CNRS, NSF, NATO and NIH is gratefully acknowledged

5 References

1 J Deisenhofer and H Michel, *Angew Chem Int Ed Engl* 1989, **28**, 829
2 R Huber, *Angew Chem Int Ed Engl* 1989, **28**, 848
3 J S Connolly and J R Bolton, in *Photoinduced Electron Transfer*, ed M A Fox and M Chanon, Elsevier, Amsterdam, 1988, Part D, p 303
4 D Gust and T A Moore, *Science*, 1989, **244**, 35
5 K Maruyama and A Osuka, *Pure Appl Chem* , 1990, **62**, 1511
6 M R Wasielewski, *Chem Rev* 1992, **92**, 435
7 W W Parson, in *New Comprehensive Biochemistry Photosynthesis*, ed J Amesz, Elsevier, Amsterdam, 1987, p 43
8 J L Martin, J Breton, A J Hoff, A Migus and A Antonetti, *Proc Natl Acad Sci USA*, 1986, **83**, 957
9 J C Chambron, S Chardon-Noblat, A Harriman, V Heitz and J P Sauvage, *Pure Appl Chem* , 1993, **65**, 2343
10 V Heitz, S Chardon-Noblat and J P Sauvage, *Tetrahedron Lett* , 1991, **32**, 197
11 F Odobel and J P Sauvage, *New J Chem* , 1994, **18**, 1139
12 S Chardon Noblat and J P Sauvage, *Tetrahedron*, 1991, **47**, 5123
13 C Pascard, J Guilhem, S Chardon Noblat and J P Sauvage, *New J Chem* , 1993, **17**, 331
14 S Chardon-Noblat, J P Sauvage and P Mathis, *Angew Chem Int Ed Engl* , 1989, **28**, 593
15 A M Brun, A Harriman, V Heitz and J P Sauvage, *J Am Chem Soc* 1991, **113**, 8657
16 A M Brun, S J Atherton, A Harriman, V Heitz and J P Sauvage, *J Am Chem Soc* , 1992, **114**, 4632
17 S Franzen, R F Goldstein and S G Boxer, *J Phys Chem* , 1993, **97**, 3040
18 G R Fleming, J L Martin and J Breton, *Nature (London)*, 1988, **333**, 190
19 A Harriman, V Heitz and J P Sauvage, *J Phys Chem* 1993, **97**, 5940
20 A Harriman, V Heitz, M Ebersole and H van Willigen, *J Phys Chem* , 1994, **98**, 4982
21 A Osuka, K Maruyama, N Mataga, T Asahi, I Yamazaki and N Tamai, *J Am Chem Soc* 1990, **112**, 4958
22 J C Chambron, V Heitz and J P Sauvage, *J Chem Soc Chem Commun* 1992, 1131
23 C O Dietrich-Buchecker and J P Sauvage, *Angew Chem Int Ed Engl* 1989, **28**, 189
24 A Livoreil, C O Dietrich-Buchecker and J P Sauvage, *J Am Chem Soc* 1994, **116**, 9399
25 J C Chambron, V Heitz and J P Sauvage, *J Am Chem Soc* , 1993, **115**, 12378
26 J C Chambron, A Harriman, V Heitz and J P Sauvage, *J Am Chem Soc* 1993, **115**, 6109
27 J C Chambron, A Harriman, V Heitz and J P Sauvage, *J Am Chem Soc* 1993, **115**, 7419
28 M Plato, K Mobius, M E Michel-Beyerle, M Bixon and J Jortner, *J Am Chem Soc* , 1988, **110**, 7279
29 F Odobel, J P Sauvage and A Harriman, *Tetrahedron Lett* 1993, **34**, 8113
30 A D Hamilton, H D Rubin and A B Bocarsly, *J Am Chem Soc* , 1984, **106**, 7255
31 E S Schmidt, T S Calderwood and T C Bruice, *Inorg Chem* 1986, **25**, 3718
32 M Gubelmann, A Harriman, J M Lehn and J L Sessler, *J Phys Chem* 1990, **94**, 308
33 N M Rowley, S S Kurek, M W George, S M Hubig, P D Beer, C J Jones, J M Kelly and J A McCleverty, *J Chem Soc Chem Commun* 1992, 497

34 J. L. Sessler, V. Capuano and A. K. Burrell, *Inorg. Chim. Acta*, 1993, **204**, 93.
35 J. P. Collin, A. Harriman, V. Heitz, F. Odobel and J. P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 5679.
36 A. Harriman, F. Odobel and J. P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 5481.
37 D. Gust, T. A. Moore, P. A. Liddell, G. A. Nemath, L. R. Makings, A. L. Moore, D. Barrett, P. J. Pessiki, R. V. Bensasson, M. Rougée, C. Chachaty, F. C. De Schryver, M. Van der Auweraer, A. R. Holzwarth and J. S. Connolly, *J. Am. Chem. Soc.*, 1987, **109**, 846.
38 M. R. Wasielewski, G. L. Gaines, M. P. O'Neil, W. A. Svec and M. P. Niemczyk, *J. Am. Chem. Soc.*, 1990, **112**, 4560.