Photoinduced electron transfer in multiporphyrin clusters and rotaxanes

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<u>Abstract</u> – A zinc(II) porphyrin and a gold(III) porphyrin
dimer bridged by a 2,9-diphenyl-1,10-phenanthroline (dpp)
spacer has been synthesized in order to mimic the array of
tetrapyrrolic chromophores in the bacterial photosynthetic
centres. The electronic properties of the dpp bridge have
been tuned by complexation of copper(I) either in a
homoleptic, entwined complex, or in a rotaxane complex
whose threaded ring is a dpp-containing macrocycle.
Photoinduced electron transfer between the zinc porphyrin
excited state and the gold porphyrin cation has been
studied by laser flash spectroscopy and its rate has been
shown to depend on the nature of the bridging species
lying in between the metal porphyrins : 55 ps in the dpp-
bridged dimer, and 1 ps only in the rotaxane copper(I)
complex.

INTRODUCTION

Photosynthesis is a fascinating process which has attracted formidable interest from various fields of science over several decades. The reason for this is at least twofold:

(i) the potential applications of artificial photosynthesis are of utmost importance, in relation with the conversion of light energy and cheap small molecules into chemical energy or high added-value chemicals.

(ii) natural photosynthesis represents the very essence of life. Synthetic chemists have tried to reproduce some of the functions of the natural photosynthetic apparatus using artificial molecular systems for many years (refs. 1, 2). They have also attempted to synthesize compounds expected to mimic the structural and geometrical properties of photosynthesis (refs. 1, 3), although a precise map of the photosynthetic Reaction Centre (RC) was not available till recently (refs. 4, 5).

The X-ray structure of the RC of *Rhodopseudomonas viridis* in 1984 by German researchers is with no doubt a major event (ref. 4). It not only confirmed or infirmed what the biologists already knew about the spatial arrangement of the various components of the RC, but it also inspired many research groups and thus initiated the design and synthesis of numerous multicomponent systems expected both to display structural analogy with the RC and to fulfill some of its photochemical and electron transfer functions.

Among the most relevant synthetic molecular systems proposed by various researchers in recent years, those containing two or more porphyrins are particularly promising (ref. 6). It is now well established that in the RC, electron transfer (ET) between tetrapyrrolic chromophores is indeed the primary charge separation step following

generation of the special-pair (SP) singlet excited state. This ET process occurs in ~3 ps with formation of bacteriopheophytin reduced state (BPh·¯ radical anion) (ref. 7). Subsequent electron transfer to a quinone is much slower (~200 ps). An important question is related to the exact function of the accessory bacteriochlorophyll BChl roughly located between the special pair and the primary acceptor bacteriopheophytin (ref. 8). Does it act as a real electron relay or is its rôle simply to catalyze electron transfer between the excited state of SP and BPh?

The design of our system was based on the following requirements :

(i) an oblique bis-porphyrin looked appealing since in the RC, the porphyrin-like nuclei are mostly organized in an oblique fashion to one another. The cytochrome part consists of 4 hemes and the transmembrane part contains 4 BChl's and 2 BPh's, the only pair of relatively closely lying and parallel rings being that of the SP (ref. 4).

(ii) if intramolecular electron transfer between two porphyrin units is to be the main reaction occurring after light excitation, very precisely defined electrochemical properties for both components are required. In addition, the various excited state energy levels will also have to be positioned in a well controlled manner. The electron donor part will have to be a singlet excited state ($*^1D$). The acceptor porphyrin (A) will have to display a very high-lying singlet excited state *so as to avoid undesired energy transfer* from $*^1D$. In order to favour electron transfer, the acceptor porphyrin should, of course, be relatively easy to reduce and the singlet excited state of the donor ($*^1D$) must be a good reductant. These electronic properties can be governed by the nature of the metal centres introduced in the central coordination sites of each porphyrin. Surprisingly, the number of (M_1, M_2) metal couples fulfilling the requirements discussed above is very limited. For instance, a (Zn(II), 2H) couple will undergo fast energy transfer between the zinc porphyrin excited state and the free-base porphyrin (ref. 9). A (Zn(II), Fe (III)) couple is expected to afford electron transfer but the process will be complicated by the ability of Fe(III) to participate in the reaction as an electroactive centre (ref. 10). We selected zinc(II) and gold(III) as metals for the donor component and the acceptor subunit respectively. Both metal centres are electroinactive once complexed by a porphyrin and all the expected properties are in agreement with the objective (ref. 11). The (Zn(II), Au(III)) couple also displays an interesting property related to photoinduced electron transfer studies. If the porphyrin substituents are carefully chosen, a very convenient spectral window around 600 nm in the absorption spectrum allows to selectively excite the zinc containing tetrapyrrolic ring without significantly affecting the gold(III) porphyrin. It is worth noting that the (Zn(II), Au (III)) strategy is reminiscent
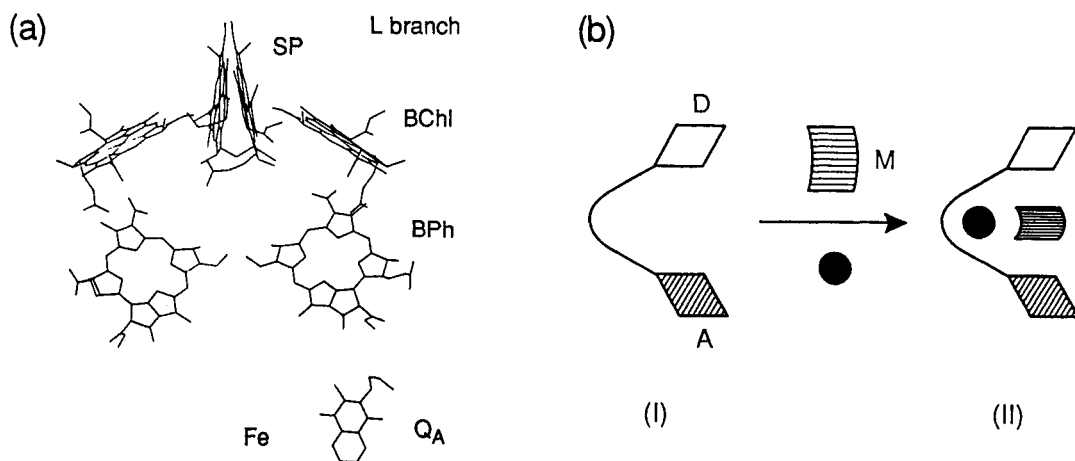

Fig. 1. (a) a fragment of the photosynthetic RC with the three important components : SP, BChl and BPh (ref. 4). (b) the principle of the modular approach. D and A are the donor and acceptor porphyrins respectively. M is an electron transfer mediator whose introduction between D and A can be realised via coordination to a metal centre (black circle) which will also bind the chelating part of the bis-porphyrin spacer. M could play the rôle of an electron gate, allowing the system to be switched between the non-mediated situation (I) and the mediated one (II).

of the photosynthetic RC. In Nature, energy transfer has been avoided by decreasing the energy level of the donor (SP : a porphyrin dimer instead of a porphyrin monomer) (ref. 12) whereas in our approach the same effect is obtained by raising the excited state level of the electron acceptor (gold(III) porphyrin).

(iii) *A modular approach* is particularly attractive in order to introduce chemical groups, supposed to play the rôle of the accessory bacteriochlorophyll, between D and A. The use of a chelate as spacer between both porphyrinic components should allow us to introduce chemical groups at will via coordination to a transition metal whose function could be both to serve as structural element (gathering centre) and to tune the electronic properties of the third component now lying between D and A. The principle is indicated in Figure 1 with the schematically represented fragment of the RC that it is supposed to mimic.

The gold(III) bis-porphyrin zinc (II)

Following a synthetic strategy related to the one used by Tabushi and Sasaki (ref. 13) for making other bis-porphyrins, compounds 1 and 2 of Figure 2 were obtained in multi-step procedures from 1,10-phenanthroline (refs. 9, 14).

$1 : M_1 = M_2 = 2H \; ; \; n=0$

$2 : M_1 = M_2 = Zn \; ; \; n=0$

$3 : M_1 = Zn, M_2 = 2H \; ; \; n=0$

$4^+: M_1 = Zn, M_2 = Au(III) \; ; \; n=1$
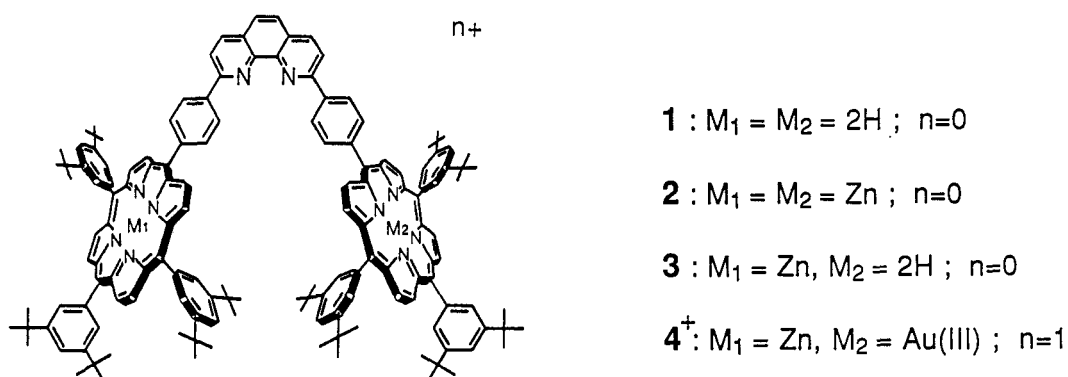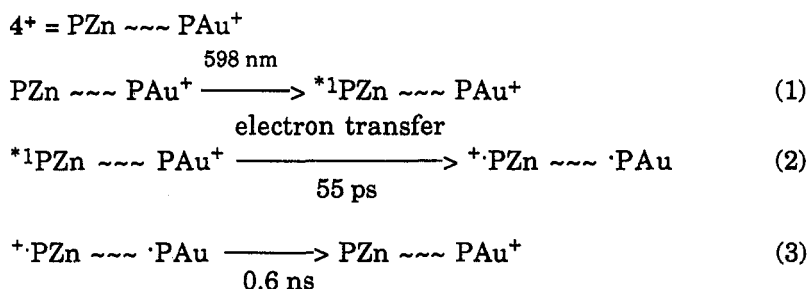
Fig. 2. The 2,9-diphenyl-1,10-phenanthroline bridged bis-porphyrins synthesized.

Controlled metallation of 1 afforded 3. By taking advantage of the extreme stability of Au(III) porphyrins, the other non-symmetrical compound 4^+ could be obtained (ref. 15). The electrochemical and spectrochemical properties of 4^+ were as expected, with in particular a spectral window around 600 nm allowing us to selectively excite the zinc(II) containing component (PZn).

Time-resolved fluorescence measurements and transient absorption spectroscopy clearly evidenced formation of a charge shift product after excitation of PZn (ref. 11). Electron transfer from the singlet excited state part ($*^1PZn$) onto the acceptor part (PAu^+) occurs in 55 ps. It generates the diradical ($^{+\cdot}PZn \sim\sim\sim \, \cdot PAu$) according to the following sequence of reactions :

$$4^+ = PZn \sim\sim\sim PAu^+$$

$$PZn \sim\sim\sim PAu^+ \xrightarrow{\quad 598 \text{ nm} \quad} *^1PZn \sim\sim\sim PAu^+ \qquad (1)$$

$$*^1PZn \sim\sim\sim PAu^+ \xrightarrow[\quad 55 \text{ ps} \quad]{\text{electron transfer}} {}^{+\cdot}PZn \sim\sim\sim \cdot PAu \qquad (2)$$

$$^{+\cdot}PZn \sim\sim\sim \cdot PAu \xrightarrow[\quad 0.6 \text{ ns} \quad]{} PZn \sim\sim\sim PAu^+ \qquad (3)$$

Of course, fast recombination is observed (equation (3)). It is worth noting that the charge separation step (1) is significantly slower than in the RC (55 ps as compared to 3 ps) in spite of a slightly shorter edge-to-edge distance. An X-ray structure study of the

symmetrical compound **2**, which is likely to be strongly analogous to **4⁺**, showed that the edge-to-edge separation between the two oblique porphyrins is ~8.6 Å (ref. 16) whereas the corresponding distance in the RC (SP to BPh) is 9.5 Å (refs. 4, 12).

The bis-porphyrin copper(I) rotaxane

Following the approach of Figure 1(b), it was clear that the dpp part of the molecule (dpp = 2,9-diphenyl-1,10-phenanthroline) could be utilized for introducing a chemical group between PZn and PAu⁺. We first made and studied a tetraporphyrinic compound constructed by entwining two fragments **4⁺** via coordination to copper(I) (ref. 17). Very fast electron transfer between *¹PZn and PAu⁺ was observed, indicating that the central copper(I) complex part of the molecule could indeed participate in the process and facilitate electron transfer. However, since the compound contained two PZn units and two PAu⁺ components, it was not absolutely certain which porphyrins were involved in the electron transfer : PZn and PAu⁺ belonging to the same chelate **4⁺** or incorporated in two different fragments **4⁺**.

In order to remove any ambiguity, it was decided to construct a bis-porphyrin rotaxane, so that the two partners of the electron transfer reaction could be identified with certainty. The strategy followed and the actual sequence of reactions carried out are described in Figures 3 and 4 respectively (ref. 18).
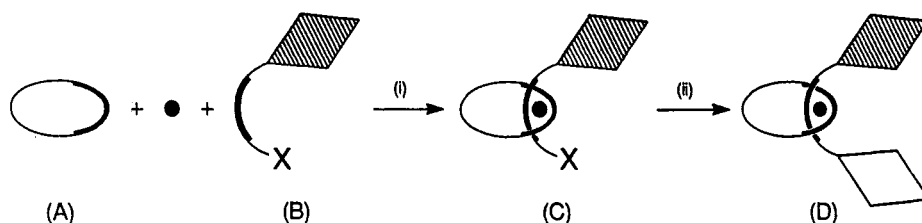

Fig. 3. i, The macrocycle (A) incorporating a coordinating fragment (thick line) interacts with a metal centre (black circle) and a non-symmetrical open chain chelate (B) bearing one porphyrin and a precursor function X to form the threaded intermediate (C); ii, the second porphyrin ring is then constructed affording the transition metal complex-rotaxane (D).

As shown by data collected in Table 1, the three components of **9²⁺** behave as three electrochemically independent species. It can be noted that the gold(III) porphyrin unit is a good electron acceptor (PAu⁺/PAu° : E° = -0.49 V vs. SCE in CH₃CN). In addition, the oxidized donor part, ⁺·PZn, is a sufficiently strong electron acceptor to be thermodynamically able to abstract an electron from the copper(I) complex core, Cu(dpp)₂⁺.

Time-resolved fluorescence measurements showed that the singlet excited state of the PZn unit is extremely rapidly quenched. More informative were the transient absorption spectroscopic measurements performed after selective excitation of PZn. *The electron transfer products PZn⁺· and PAu· were formed in about 1 ps*, (ref. 19) i.e. slightly faster than in the natural system and thus significantly faster than in **4⁺** itself (55 ps). This observation, schematically summarized on Figure 5, tends to indicate that the Cu(dpp)₂⁺ central part of the rotaxane **9²⁺** strongly facilitates electron transfer between *¹PZn and PAu⁺.

TABLE 1. Redox potentials and selected absorption spectral data for complex **9²⁺**.

Redox potentials (V *vs.* SCE, CH₃CN)			Visible absorption spectrum λ, nm (ε, mol.l⁻¹.cm⁻¹)	
PZn⁺/PZn	Cu(dpp)²⁺/Cu(dpp)⁺	PAu⁺/PAu	Soret	Q bands
0.68	0.54	-0.49	413 (678000)	538 (32000), 573 (9600)

5⁺ + **6**

+ $Cu(CH_3CN)_4^+$

5⁺

7²⁺

1)

2) Chloranil

CHO, CF_3CO_2H

6

8²⁺: M = 2H
9²⁺: M = Zn
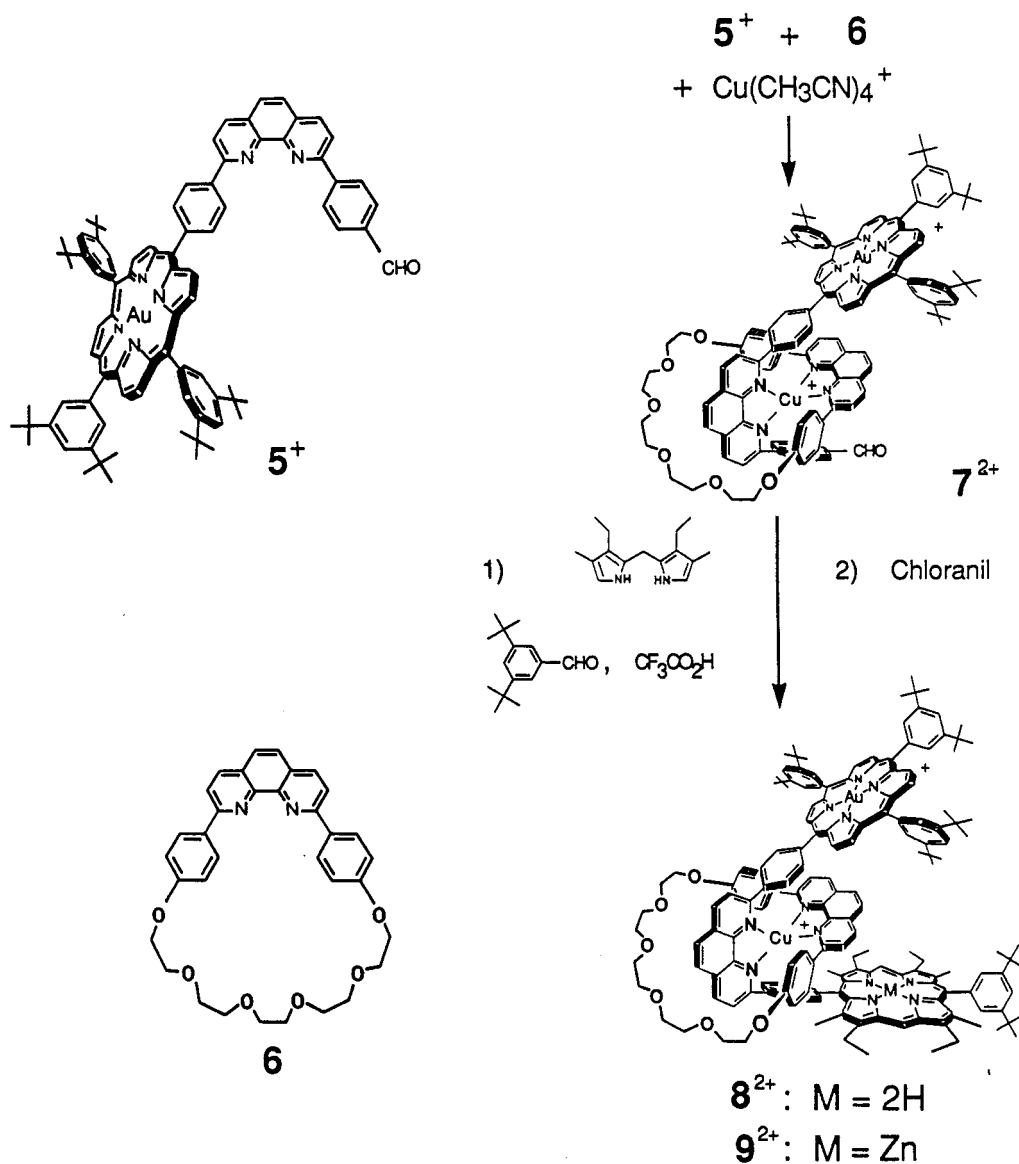
Fig. 4. Precursors and sequences of reactions leading to Cu(I) rotaxane **9²⁺**.
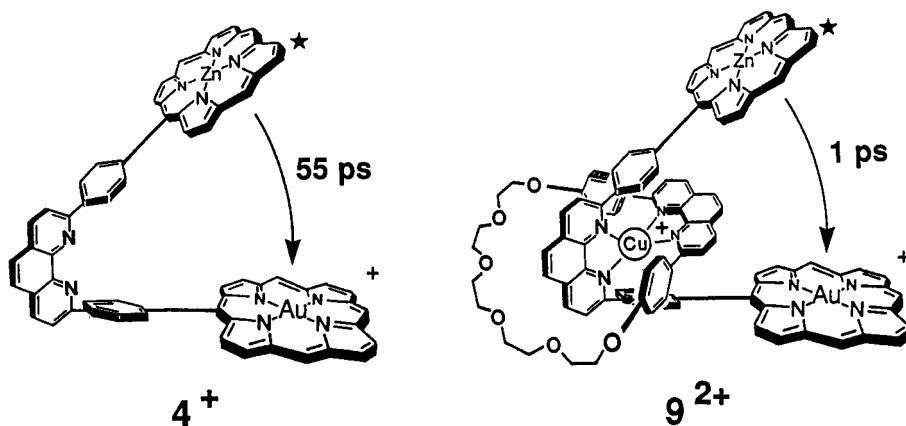
55 ps

1 ps

4⁺

9²⁺

Fig. 5. A pictorial representation of photoinduced electron transfer between *¹ZnP
and AuP⁺ in bis-porphyrin **4⁺** and Cu(I) rotaxane **9²⁺** (substituents omitted).

(a)   (b)
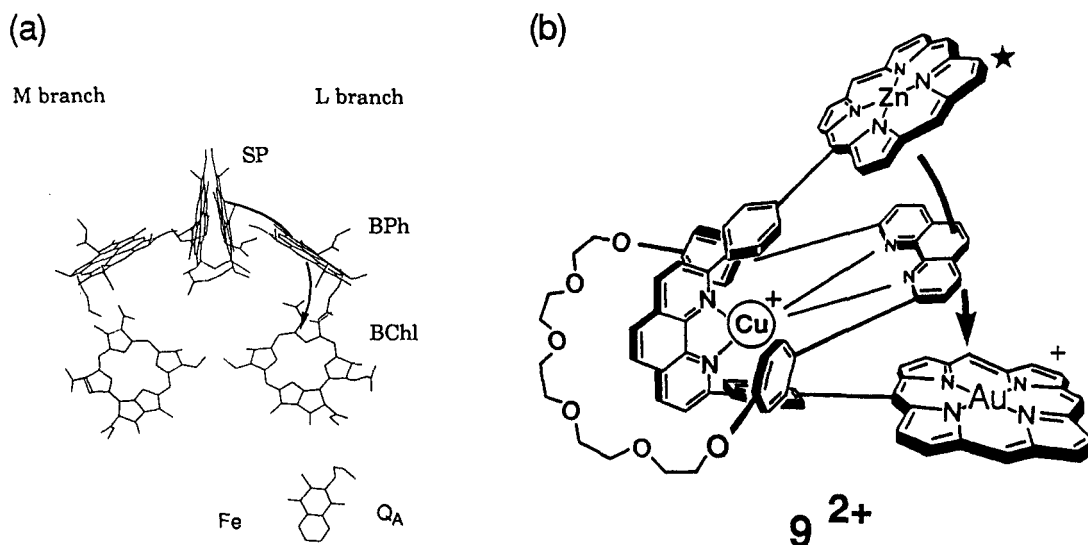
M branch   L branch

Fig. 6. a) Hypothetical superexchange function of the accessory bacteriochlorophyll (Bchl) in the RC. b) Could the central complexed phenanthroline play the same rôle in the bis-porphyrin Cu(I) rotaxane 9^{2+}? Substituents are omitted for clarity.

By analogy with the function of the accessory bacteriochlorophyll in the RC, a superexchange mechanism could be invoked to account for the fast ET in 9^{2+} (ref. 8), the complexed 1,10-phenanthroline nucleus interspersed between PZn and PAu+ playing the same rôle as BChl. This hypothesis is represented in Figure 6.

Interestingly, the electron gate function of the central complex could be put in action by removing the copper(I) metal and, either reintroducing it, or incoporating another metal like Zn^{2+} (refs. 20, 21). As expected, the central metal-free rotaxane turned out to undergo slower electron transfer than its copper(I) complex (36 ps) (ref. 21).

Noteworthy, the back-reaction leading to the initial state PZn~~~~PAu+ (equation (3)) is not affected by the presence of the central metal, again in accordance with a superexchange mechanism. By taking advantage of this observation and by constructing multi-rotaxanes incorporating several electron transfer mediators separating the two end-attached porphyrins (PZn and PAu+), it should be possible to carry out very long-range charge separation with a slow recombination rate.

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