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Rotaxanes and other transition metal-assembled porphyrin arrays for long-range photoinduced charge separation

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Contents

Abstract

Bis-porphyrin conjugates have been synthesized for performing long-range photoinduced charge separation. The electron donor is a zinc(II) porphyrin in the excited state and the electron acceptor is a gold(III) porphyrin. These elements or their free-base analogs have been assembled following two different strategies. In a first approach, the porphyrinic subunits, separated by one or more 2,9-diphenyl-1,10-phenanthroline spacers, have been incorporated into rotaxane structures containing up to four threaded macrocycles by copper(I) templated synthesis. In a second approach, a triad having strictly controlled geometry has been prepared following a new gathering strategy. This triad, consisting of two porphyrinic moieties assembled via a central bis(phenyl-terpyridine)ruthenium(II) complex, uses coordination rather than covalent chemistry to interconnect the components. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Porphryins; Rotaxanes; Non covalent assemblies; Photochemistry; Electron transfer; charge separation

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1. Introduction

Photoinduced charge separation is a key process for conversion of light energy into chemical energy. This problem has been solved naturally by photosynthesis. For the last 15 years, studies, both theoretical and experimental, devoted to photosynthetic reaction centers [1–9] as well as to artificial donor–acceptor systems [10–19] have helped our understanding of the factors governing the efficiency of charge separation. Fig. 1 shows several artificial systems of increasing complexity that can be conceived for performing photoinduced charge separation at the molecular level. The simplest system is the diad (a). An electron donor in its excited state (D^*) is intramolecularly linked to an electron acceptor (A). Photoinduced charge separation occurs in a single step after light excitation. It is therefore obvious that in this system the recombination of charges will occur readily. To slow down this latter step, it is necessary to introduce an additional, charge stabilization step, in which the charges are moved apart from each other. This is realized in the simplest way by system (b), which is called a triad. Three components are required: a primary electron donor in its excited state (D^*_1), a secondary electron donor (D_2), and an electron acceptor (A). Other systems, containing three components, like D–A_1–A_2, can also be envisaged. The first two steps of (b) are similar to those of (a). The new step is the charge stabilization step. More complex systems, like the general polyad shown in (c), can be conceptually envisioned. Such systems suggest that, in order to observe an efficient charge separation, it is necessary to move the positive hole and the negative charge apart from each other as fast and as far as possible. In other words, charge separation must be fractioned over many fast elementary charge migration steps. In this paper, we shall present and discuss simple diad and triad systems based on porphyrin donors and acceptors.

2. Zn(II)/Au(III) bis-porphyrins and [2]-rotaxanes

A few years ago, we designed the 2,9-diphenyl-1,10-phenanthroline (dpp) bridged Zn(II)/Au(III) bis-porphyrin conjugate **1** (Fig. 1) [20]. The oblique geometry of

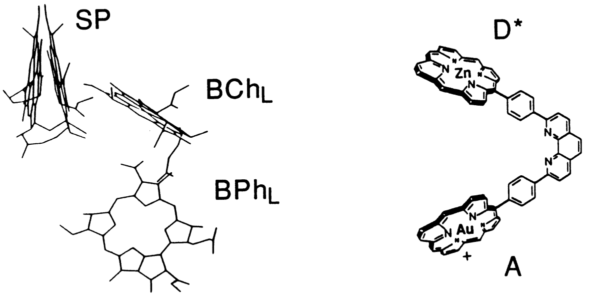

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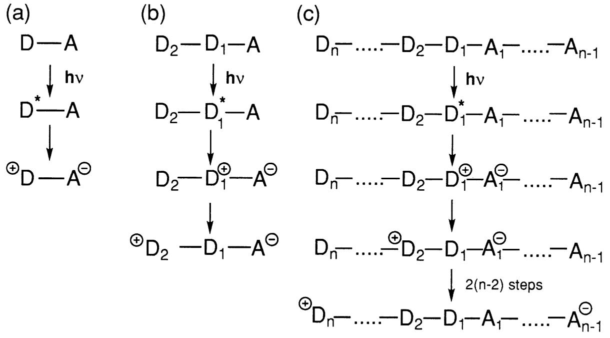
Fig. 1. A comparison between the tetrapyrrolic chromophoric triad of the photosynthetic reaction center (active branch) and bis-porphyrin conjugate **1**. Substituents of the porphyrins have been omitted for clarity.

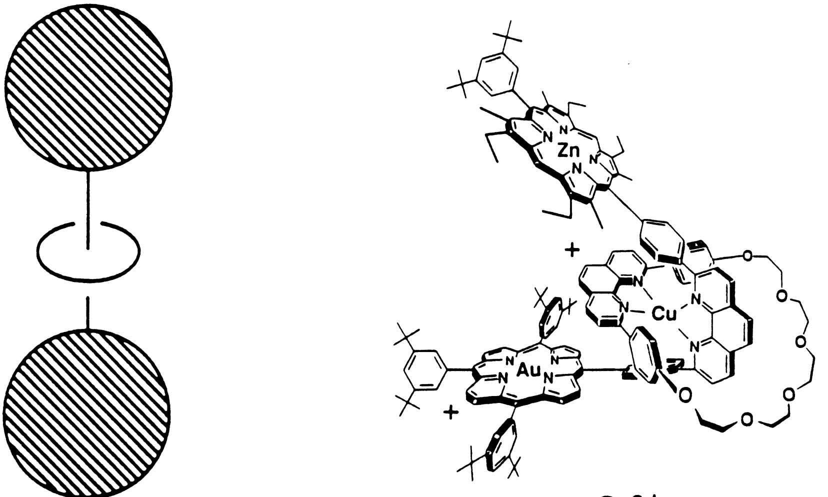


Scheme 1.

the two porphyrins was inspired by the mutual orientation of the so-called special pair (SP; primary donor in its excited state) and the bacteriopheophytin (BPh_L; primary acceptor) in the photosynthetic reaction center. A zinc(II) porphyrin (ZnP) and a gold(III) porphyrin (AuP^+) were selected as donor (D*) and acceptor (A) respectively, owing to favorable redox properties, and to well-arranged energy levels, i.e. in such a way that energy transfer from ^1ZnP to AuP^+ is not possible thermodynamically. Time-resolved fluorescence and transient absorption spectroscopy showed that forward electron transfer took place in 55 ps and charge recombination was delayed by a factor of 10 [21]. Presumably, electron transfer takes place via a through-bond pathway, the dpp bridge playing the role of a superexchange relay, similar to that of the accessory bacteriochlorophyll (BCh_L, Fig. 1) in the photosynthetic reaction center, according to several authors [4–7].

We then reasoned that lowering the energy level of the dpp LUMO, while keeping it above the HOMO of the zinc–porphyrin moiety in its excited state, would improve the superexchange effect. Practically, this could be done by coordination of the bridging phenanthroline to a transition metal. Copper(I) seemed to be a candidate of choice since it forms stable tetrahedral complexes with entwined dpp ligands. In order to circumvent dimerization of bis-porphyrin **1** in a $Cu(\mathbf{1})_2^+$ complex, which would introduce the unwanted possibility of interligand photoinduced electron transfer [22], we proposed to incorporate bis-porphyrin **1** (or, rather, an analog) in a rotaxane structure (Fig. 2): a macrocycle containing a dpp coordinating fragment is threaded onto a bis-porphyrin dumbbell. The target molecule is also represented in Fig. 2.

This strategy seemed viable, since it was shown earlier in our laboratory that the threading reaction, shown schematically in Fig. 3, was quantitative [23]. Indeed, structure C is a precursor to a rotaxane provided that the two extremities of the molecular thread are functionalized with bulky stoppers. Copper(I) is playing the role of a three-dimensional template, driving the threading of the macrocycle onto the molecular thread. Once it is removed, the macrocycle cannot escape from the dumbbell, provided that the stoppers are bulky enough, and a true rotaxane is obtained.



2 $^{2+}$

Fig. 2. A rotaxane (left) is made up of two components: a wheel (rota) and an axis onto which it is threaded. Two bulky stoppers prevent the breaking up of the system. A [2]-rotaxane contains one ring; an [*n*]-rotaxane contains $n-1$ rings.

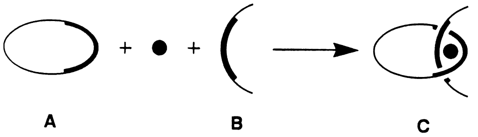


Fig. 3. The Cu(I)-directed threading reaction. A is a macrocyclic compound incorporating a dpp fragment (indicated by a thick line), B is a dpp-containing molecular thread and the black disk is Cu^+. C has a pseudo-rotaxane geometry.

The various steps leading to the copper(I)-complexed Zn(II)/Au(III) bis-porphyrin rotaxane **2**$^{2+}$ are summarized in Fig. 4 [24]. We shall start the description of the rotaxane construction from macrocycle **3** and gold–porphyrin **4**$^{+}$. Mixing equimolecular quantities of these compounds and $Cu(CH_3CN)_4BF_4$ leads to quantitative formation of prerotaxane **5**$^{2+}$, as expected. This complex, which is reactive via its aldehyde function, is treated with (3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrryl)-methane and 3,4-di-*tert*-butylbenzaldehyde in dichloromethane with trifluoroacetic acid as catalyst. Oxidation of the porphyrinogenic intermediate with tetrachloroquinone (chloranil) leads to the Cu(I)-complexed rotaxane in 19% yield. Next, the free-base porphyrinic stopper newly formed is metallated with zinc acetate, affording the target Cu(I)-complexed [2]-rotaxane **2**$^{2+}$.

Time-resolved fluorescence spectroscopy and transient absorption spectroscopy showed that now electron transfer between the Zn(II) porphyrin and the Au(III) porphyrin subunits took place within 1–2 ps [25]. The impressive increase of the

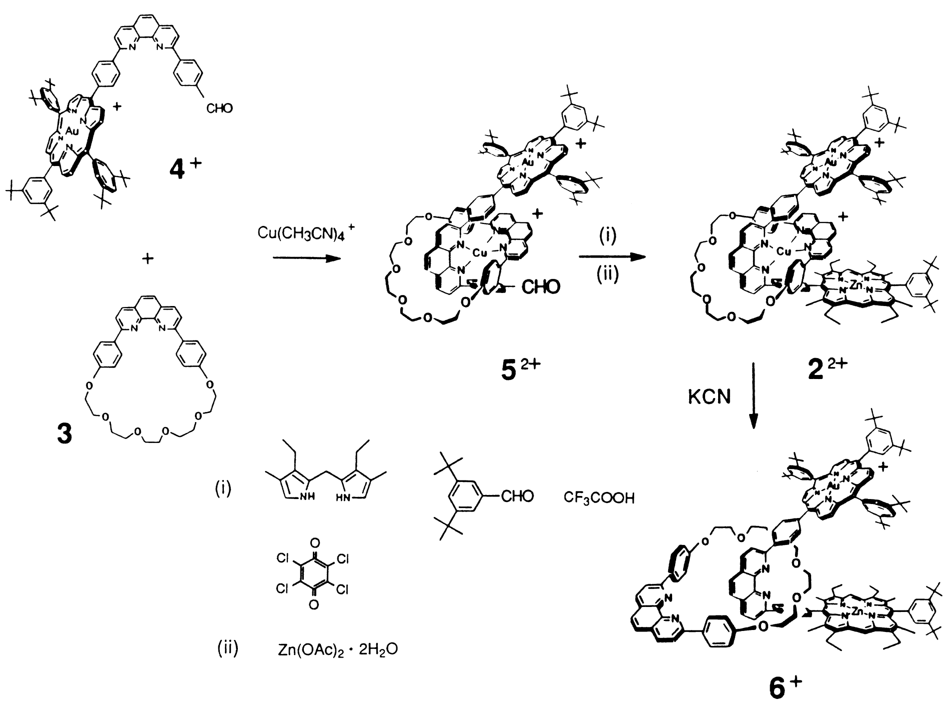


Fig. 4. The key steps leading to [2]-rotaxane $\mathbf{6}^+$. (i): (3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrryl)-methane, 3,5-di-*tert*-butylbenzaldehyde, CF_3CO_2H, CH_2Cl_2, Ar; chloranil, CH_2Cl_2, reflux; (ii) $Zn(OAc)_2 \cdot 2H_2O$, $CHCl_3$/MeOH reflux.

forward electron transfer rate is certainly due to an improved superexchange effect, as predicted, even taking into account the fact that the electron transfer process is slightly more exergonic in the case of rotaxane $\mathbf{2}^{2+}$ compared to bis-porphyrin **1**. Owing to the coordination of Cu(I), the dpp bridge is a better conducting medium. That this interpretation is correct is evidenced by the study of the copper-free rotaxane $\mathbf{6}^+$ (Fig. 4). Removal of Cu^+ was performed by treatment of $\mathbf{2}^{2+}$ with KCN. As evidenced by structural studies (^1H NMR), the free rotaxane has undergone a conformational rearrangement, the pentaethyleneoxy link now laying in between the two porphyrinic stoppers. More importantly, the dpp bridge is now decomplexed. As a matter of fact, the electron transfer phenomenon takes place in ca. 36 ps, a value which is closer to that found in the case of the bis-porphyrin conjugate **1** than to that of the Cu(I)-complexed rotaxane $\mathbf{2}^{2+}$. This finding agrees well with the role of the dpp bridge as a superexchange medium, through which the transferred electron may tunnel [26]. It should be stressed that when Cu(I) is replaced by Zn(II) in the rotaxane structure, the electron transfer is still much slower than in $\mathbf{2}^{2+}$, although the geometrical properties of both Cu(I)- and Zn(II)-complexed rotaxanes are virtually identical, as demonstrated by ^1H NMR studies. This observation is clear evidence for the electronic origin (superexchange) of the extremely fast electron transfer between the zinc porphyrin unit (singlet excited state) of $\mathbf{2}^{2+}$ and the Au(III) porphyrin component.

Back-electron transfer proceeds mainly via redox chemistry involving the Cu^{2+}/Cu^{+} couple, according to Eq. (1):

$$^{+\cdot}\mathrm{PZn/Cu^{+}/PAu^{\cdot}} \xrightarrow{\text{fast (20 ps)}} \mathrm{PZn/Cu^{2+}/PAu^{\cdot}} \xrightarrow{\text{slow (2500 ps)}} \mathrm{PZn/Cu^{+}/PAu^{+}} \tag{1}$$

However, a small fraction (5%) of the charge separated (or rather charge shifted) state undergoes direct back-charge recombination [Eq. (2)]:

$$^{+\cdot}\mathrm{PZn/Cu^{+}/PAu^{\cdot}} \xrightarrow{\text{500 ps}} \mathrm{PZn/Cu^{+}/PAu^{+}} \tag{2}$$

The rate of this back-electron transfer is roughly the same as that obtained for bis-porphyrin **1**. This is not surprising, since in the case of this process, the superexchange effect cannot be operative, the gap between the HOMO of $PAu^{\cdot}$ and the LUMO of the bridging dpp being too high in energy.

3. Porphyrin-stoppered multirotaxanes

These results prompted us to elaborate the concept of multirotaxanes for performing long-range photoinduced charge separation. Let us synthesize a multirotaxane comprising a molecular dumbbell with several dpp chelating sites and stoppered by a zinc(II) and a gold(III) porphyrin, along which are threaded several coordinating macrocycles, each complexing a Cu^{+} cation. Within such a molecule, the forward electron transfer rate is expected to be more or less unchanged with respect to a single rotaxane; however, the direct back electron transfer rate should be considerably slowed down due to the increased distance between the donor and acceptor subunits, the superexchange effect being no longer operative, as explained above.

While such effects have not been proven yet, we present here the principles for construction of a rotaxane elaborated with two threaded macrocycles. In a preliminary experiment, we showed that threading of two macrocycles onto a bis-dpp-containing molecular string was straightforward for a variety of bridging units (alkyl, biphenyl, biphenylether) linking the two dpp chelating sites (Fig. 5) [27].

The precursors used and the synthetic strategy followed to prepare copper(I)-complexed bis-porphyrin-stoppered [3]-rotaxane $\mathbf{7}^{2+}$ are represented in Fig. 6.

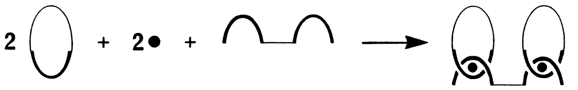


Fig. 5. Principle of metal-directed threading of two coordinating macrocycles onto a molecular thread containing two chelating sites. The black disc is a metal.

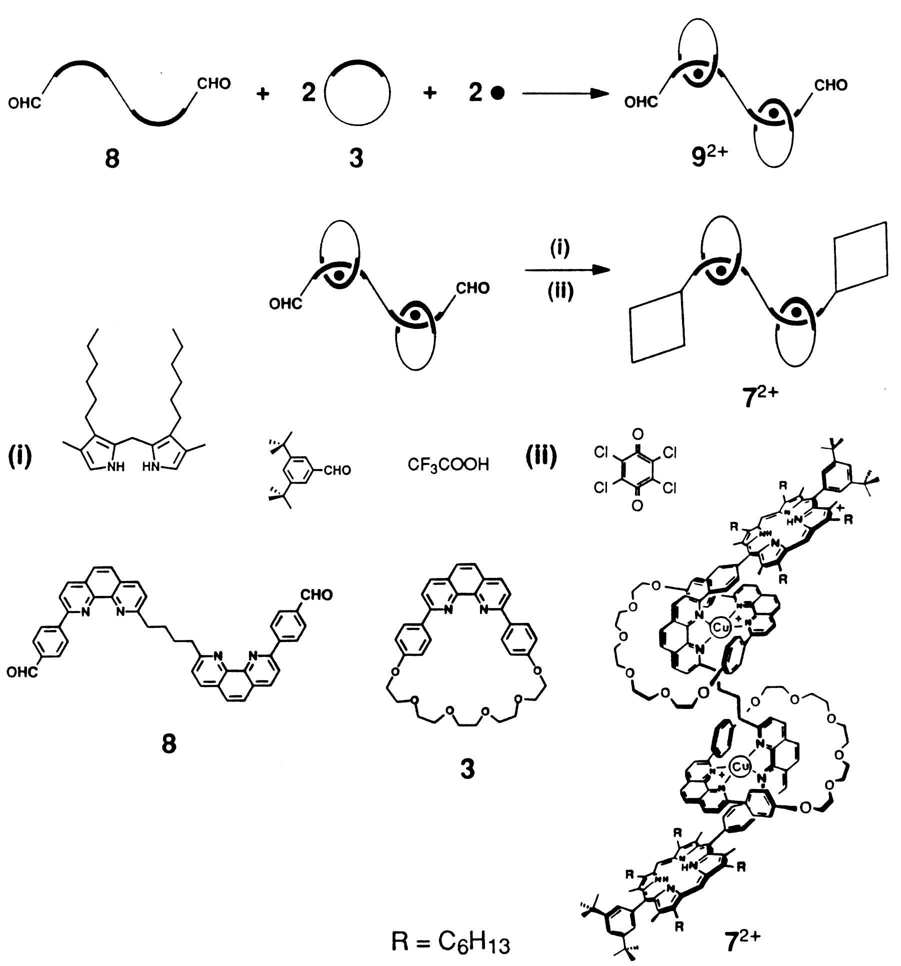


Fig. 6. Precursors and synthetic strategy for the preparation of 7^{2+}. The lozenges are porphyrins, the thick lines represent dpp coordinating sites and the circles are Cu(I) atoms. (i): (3,3′-dihexyl-4,4′-dimethyl-2,2′-dipyrryl)-methane, 3,5-di-*tert*-butylbenzaldehyde, CF_3CO_2H, CH_2Cl_2, Ar; (ii) chloranil, CH_2Cl_2, reflux.

After Cu(I)-directed threading of two macrocycles **3** onto the bis-dpp dialdehyde-ended molecular thread **8**, the resulting prerotaxane $\mathbf{9}^{2+}$ was reacted with (3,3′-dihexyl-4,4′-dimethyl-2,2′-dipyrryl)-methane and 3,5-di-*tert*-butylbenzaldehyde in conditions described earlier for the synthesis of rotaxane $\mathbf{2}^{2+}$. In the preparation of the multirotaxane, two porphyrins are constructed at the same time, yet affording the desired compound ($\mathbf{7}^{2+}$) in 34% yield, which is excellent considering the complexity of the molecule made and the number of various molecular fragments to be gathered and incorporated in its structure [28]. Such a molecule may be qualified as a [3]-rotaxane, since it is made up of three individual components which, after removal of copper(I), are only "mechanically" linked. The porphyrins were metallated with Zn(II).

In fact, there is another method for producing [3]-rotaxanes. Let us come back to the synthesis of [2]-rotaxane $\mathbf{2}^{2+}$ (Fig. 4). Suppose that 3,5-di-*tert*-butylbenzaldehyde is not involved in the porphyrin reaction formation. Then, two molecules of prerotaxane $\mathbf{5}^{2+}$ will dimerize at the newly formed porphyrin, as schematized in Fig. 7, affording [3]-rotaxane $\mathbf{10}^{4+}$.

Actually this compound was obtained, even in the presence of 3,5-di-*tert*-butylbenzaldehyde in the reaction medium, as a "by-product" of the synthesis of [2]-rotaxane $\mathbf{2}^{2+}$ [24]. The real molecule is represented in Fig. 8. It differs from [3]-rotaxane $\mathbf{7}^{2+}$ by the fact that it is made up of two merged dumbbells, each imprisoning a threaded macrocycle. It may be called "compartmental" [3]-rotaxane. Similarly, the reaction used for making [3]-rotaxane $\mathbf{7}^{2+}$ also produced a molecule resulting from the dimerization of two prerotaxane units: as schematized in Fig. 9, both terminal and bridging porphyrins are constructed at the same time, thus the presence of 3,5-di-*tert*-butylbenzaldehyde in the reaction medium is necessary.

The resulting molecule, $\mathbf{11}^{4+}$, represented also in Fig. 8, is a compartmental [5]-rotaxane [28]. Remarkably, its preparation yield, beside the synthesis of $\mathbf{7}^{2+}$, is 8%. This allows 50 mg of $\mathbf{11}^{4+} \cdot 4PF_6^-$ to be made relatively easily.

The philosophy of our approach to the problem of photoinduced charge separation is depicted in Fig. 10. First, a donor–acceptor dumbbell (I) was designed; then this dumbbell was incorporated in a [2]-rotaxane structure (II). The threaded ring complements the coordination of a copper(I) atom which improves the electronic conduction of the thread. Finally, since the distance between the donor and acceptor porphyrinic stoppers is increased in [3]-rotaxanes (III), two threaded rings are required. We have presented here only the synthesis of such a system. Selective metallation of the porphyrinic stoppers with Zn(II) and Au(III) will be presented in a future paper.

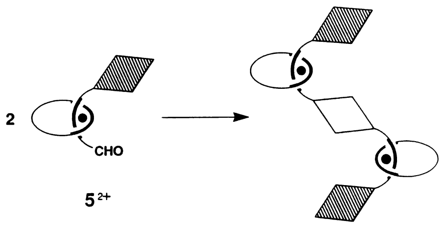
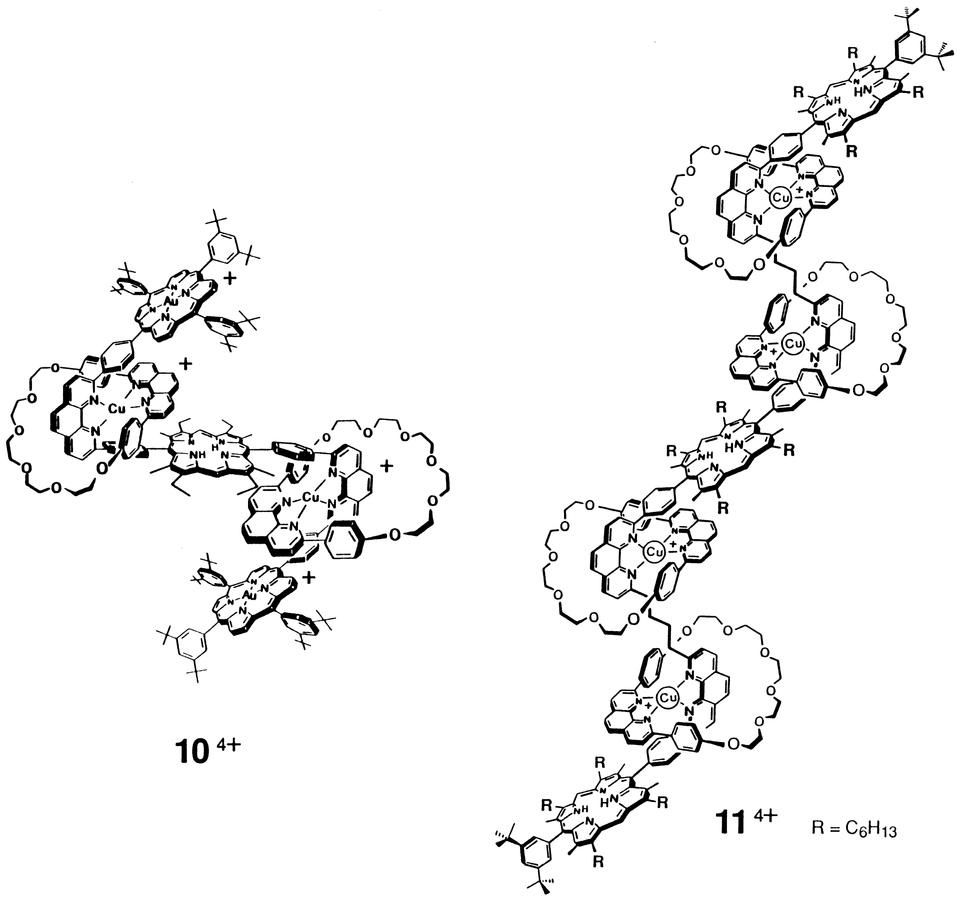


Fig. 7. Formation of compartmental [3]-rotaxane $\mathbf{10}^{2+}$. The lozenges are porphyrins, the thick lines represent dpp coodinating sites and the black disks are Cu(I) atoms. Same experimental conditions as in Fig. 4.



10^{4+}

11^{4+} R = C_6H_{13}

Fig. 8. Chemical structures of the compartmental [3]- and [5]-rotaxanes 10^{2+} and 11^{4+}.

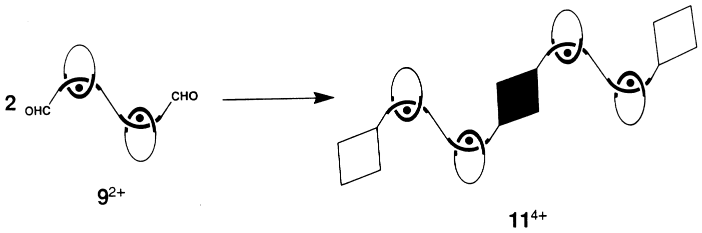


Fig. 9. Formation of compartmental [5]-rotaxane 11^{4+}. The lozenges are porphyrins, the thick lines represent dpp coodinating sites and the circles are Cu(I) atoms. Same experimental conditions as in Fig. 6.

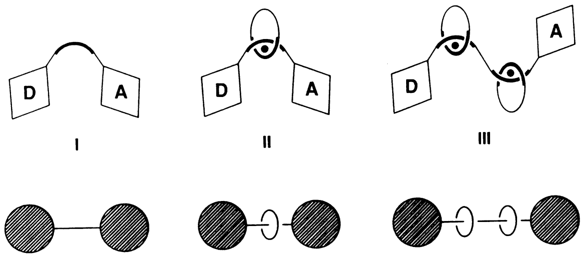


Fig. 10. From a donor–acceptor bis-porphyrin dumbbell to a donor–acceptor bis-porphyrin-stoppered [3]-rotaxane.

4. Porphyrin-containing one-dimensional systems using ruthenium bis-terpyridine as assembling complex

As demonstrated previously, copper(I) is a very efficient transition metal for tuning the electronic properties of the bridge in rotaxanes used as models of primary electron transfer in the photosynthetic reaction center. We would now like to expand the role of the metal complex and use it as an assembling center. This strategy, which uses coordination rather than covalent chemistry to interconnect the various components, offers several attractive features: notably (i) its high flexibility should allow easy preparation of multicomponent systems; (ii) good geometrical control should be possible. The general concept and the synthetic principle are illustrated in Fig. 11.

The role of the transition metal is manifold: (i) to gather and orient the system so as to have metallated porphyrins held rigidly at a fixed distance and to have non-symmetrical systems able to undergo electron or energy transfer; (ii) to modulate the electronic coupling between the donor and acceptor porphyrins; (iii) to form a complex which could act as a relay in electron transfer or as an antenna in energy transfer.

The ligand to be attached to each porphyrin and the binding mode used to assemble the two modules into the final conjugates are selected so as to facilitate strict stereochemical control, especially with regard to the distance between the porphyrins.

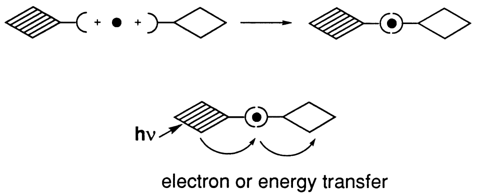


Fig. 11. Strategy used to assemble asymmetrical bis-porphyrins around a central transition metal cation (black dot). The basic module consists of a porphyrin (lozenge) covalently attached to a chelate (arc of a circle). Provided the transition metal complex is resistant to ligand exchange processes, stepwise electron transfer can be envisaged after selective illumination of a porphyrin ring.

12^{3+}

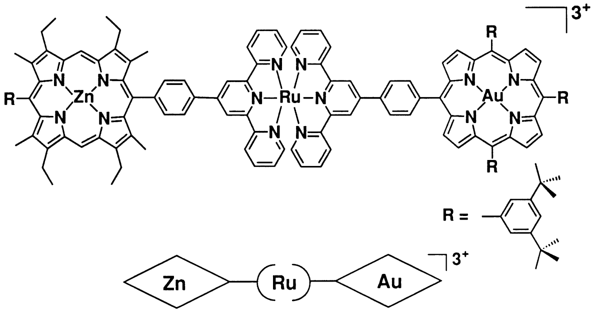


Fig. 12. The triad.

In order to perform long-range charge separation, the triad **12**$^{3+}$ represented in Fig. 12 has been prepared [29,30]. It should be noted that it contains two differently substituted porphyrins, a zinc etioporphyrin-like (donor) and a gold(III) tetraarylporphyrin (acceptor) as [2]-rotaxane **2**$^{2+}$. The $-CH_3$ and $-CH_2CH_3$ substituents located at the periphery of the tetrapyrrolic donor increase the electron donating ability of the singlet excited state (^{1*}PZn) and thus favours electron transfer to the central Ru(tpy)$_2^{2+}$ unit. On the other hand, the tetraarylporphyrin metallated by a

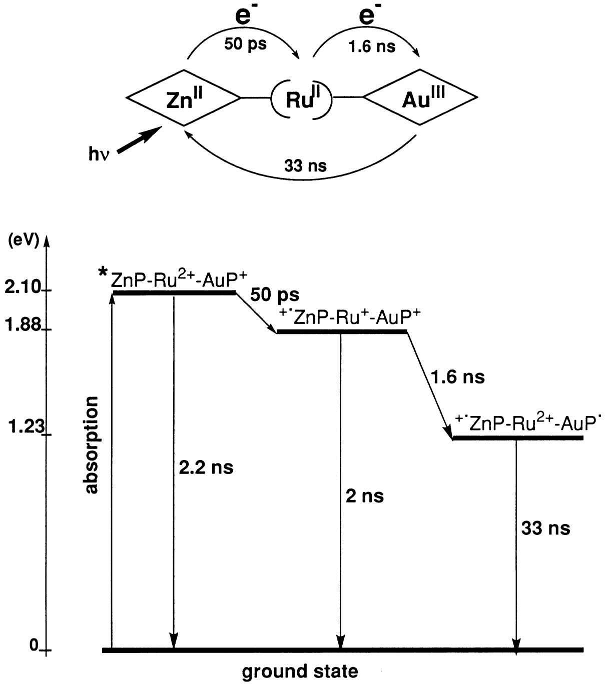


Fig. 13. Energy level diagram showing the electron transfer sequence for the triad.

gold(III) center is a better electron acceptor than the analogous gold(III) etioporphyrin.

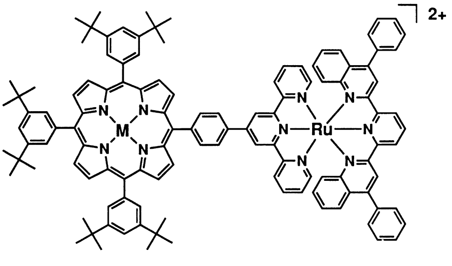
Excitation of the terminal zinc porphyrin in the triad results in electron transfer to the central ruthenium(II) bis-terpyridine complex, followed by secondary electron transfer to the appended gold(III) porphyrin (Fig. 13). Electron transfer occurs by two consecutive steps over a porphyrin center-to-center distance of ca. 30 Å.

Rate constants for individual steps, as determined from laser photolysis studies [30], are indicated in Fig. 13. The primary electron transfer step leading to reduction of the central Ru(II) complex ($\Delta G^\circ = -0.25$ eV) requires 50 ps and is essentially quantitative. A second electron transfer process follows in which the distant gold(III) porphyrin is reduced. The rate constant for this second step is found to be 6×10^8 s^{-1}. This process, for which there is a thermodynamic driving force of ca. 0.6 eV, is in competition with reverse electron transfer to restore the ground state. Subsequent charge transfer between the terminal porphyrinic subunits occurs with a rate constant of 3×10^7 s^{-1} and leads to regeneration of the initial system.

The interesting features of this molecular triad may be summarized as follows: (i) rapid interporphyrin electron transfer between linear, fixed-distance subunits; (ii) the ultimate charge separated state, which has a lifetime of 33 ns, retains almost 60% (1.2 eV) of a photonic input of 2.1 eV; and (iii) the modular synthetic approach is highly versatile, facilitating preparation of many different D–A_1–A_2 triads and higher order, linear oligomers.

In an attempt to improve the performance of such systems, we have designed a new ruthenium(II) complex, Ru(ttpy)(bpqpy)$^{2+}$ [where ttpy is 4′-p-tolyl-2,2′:6′,2″-terpyridine and bpqpy is 2,6-bis(4′-phenyl-2′-quinolyl)pyridine], which has a low-energy excited state and is easy to reduce [31]. Then, we have covalently linked this ruthenium complex (Ru) to tetraaryl porphyrins [a free base, PH_2 and a zinc(II) species, PZn] which are less electron-rich but more chemically and photochemically robust than etioporphyrins. The schematic formulae of the investigated compounds are shown in Fig. 14.

The photoinduced processes which occur on excitation of **13**$^{2+}$ and **14**$^{2+}$ diads have been investigated in butyronitrile fluid solution at room temperature [32] and



M = 2H : **13**$^{2+}$

M = Zn : **14**$^{2+}$

Fig. 14. Schematic formulae of the investigated diads.

in rigid matrix at 77 K [31]. In both diads at low temperature, the lowest singlet excited state of the porphyrin moiety (S_1) is quenched by energy transfer to give the triplet metal-to-ligand charge transfer excited state of the Ru complex (^{3}MLCT), which in turn is quenched by energy transfer to yield the triplet excited state of the porphyrin moiety (T_1). At room temperature, for the diad **14**$^{2+}$ the deactivation of S_1 occurs mainly by electron transfer to give a charge separated state ($^{\cdot +}$PZn–Ru$^-$) which then deactivates to the T_1 excited state of the porphyrin moiety. In the case of **13**$^{2+}$ the level of the charge separated state lies slightly above S_1. As a consequence, only a fraction (ca. 30%) of the S_1 excited states are quenched by electron transfer, the remaining part being quenched by energy transfer to give the ^{3}MLCT excited state of the ruthenium-based moiety.

To improve the efficiency of the electron transfer reaction and to slow recombination, we envisage some modifications in the design of such systems. Firstly, we plan to use acceptors [iridium(III) bis-terpyridine could be a good candidate] with a higher excited state energy level to inhibit the energy transfer processes which compete with the desired electron transfer reaction in the latter system (**13**$^{2+}$). Secondly, other parameters such as the number of components, the nature of connectors between them, and the exergonicity of each individual electron transfer step are very important features and will contribute to the lifetime of the photoinduced charge separated state. These long-term research projects are part of a more general theme on the construction of non-covalently assembled multiporphyrins and the study of their electron transfer properties.

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