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Transition metal–assembled multiporphyrinic systems as models of photosynthetic reaction centre

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Contents

Abstract

A multicomponent system consisting of a zinc(II) porphyrin and a gold(III) porphyrinic module assembled via a central bis(phenyl-terpyridine) ruthenium(II) complex has been prepared following a new gathering strategy. Excitation into the zinc porphyrin moiety is followed by rapid stepwise intramolecular electron transfer leading to a relatively long-lived (33 ns), charge-separated state consisting of a zinc porphyrin radical cation and a neutral radical localized on the gold(III) porphyrin ring. The edge-to-edge separation beween the porphyrinic units is ca. 20 Å.

Keywords: Intramolecular electron transfer; Triad; Ruthenium(II) bis-terpyridine; Zn(II) porphyrin; Gold(III) porphyrin; Model of photosynthetic reaction centre

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1. Introduction

The most significant recent models of the photosynthetic reaction centre (RC) contain two or more porphyrins [1–4]. In agreement with the highly multichromo-

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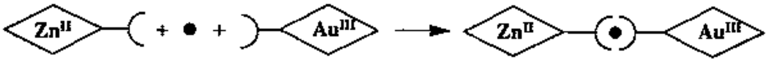

Scheme 1. A modular approach: the transition metal (●) collects two ligands (C) bearing a porphyrin unit.

phoric nature of the RC, as evidenced by its X-ray structure [5a], the initial electron transfer (ET) step occurs from bacteriochlorophyll to bacteriopheophytin [5b]. Until now, very few such systems have been constructed using non-covalent bonds, in spite of the attractive feature that such a modular approach displays (see, for example, Ref. [6]). Several multicomponent systems incorporating porphyrins attached to transition metal complexes have been reported [7–12], although no use was made of the potential ability of the metal to act as a gathering centre for two or more porphyrin modules.

A new, versatile strategy for constructing multiporphyrin assemblies involves using transition metals to collect ligands bearing a porphyrin unit [13]. This strategy, which uses coordination rather than covalent chemistry to interconnect the various components, offers several attractive features: (i) its high flexibility should allow easy preparation of multicomponent systems; (ii) good geometrical control should be possible. Such a route has now been used to make a porphyrin-based molecular triad consisting of differently metallated and substituted porphyrins. The synthetic principle is indicated in Scheme 1.

The use of 2,2′:6′,2″-terpyridine (terpy) as the chelate is indeed very appealing for the realization of Scheme 1 since substitution at its 4′ position leads to axially symmetric bis-terpyridine complexes. Ruthenium is the ideal central metal owing to its inertness towards substitution and to the electroactivity of its bis-terpy complexes. In fact, the role of the central ruthenium(II) ion is twofold: (i) to gather and orient the system so as to have two differently metallated and substituted porphyrins held rigidly at a fixed distance and (ii) to participate in electron transfer as a relay. The latter situation may arise because the $Ru(terpy)_2^{2+}$ unit can act as an efficient reductive quencher of a zinc porphyrin singlet excited state when both components are covalently linked [14].

The triad $\mathbf{1}^{3+}$ (Fig. 1) seems to fulfil most of the requirements necessary to perform long-range charge separation. $\mathbf{1}^{3+}$ contains both zinc etioporphyrin-like (donor) and gold(III) tetraarylporphyrin (acceptor) subunits. 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 favour electron transfer to the central $Ru(terpy)_2^{2+}$ unit. On the contrary the tetraarylporphyrin backbone metallated by a gold(III) centre is a better electron acceptor than the analogous gold(III) etioporphyrin.

2. Synthesis of the triad $\mathbf{1}^{3+}$

Triad $\mathbf{1}^{3+}$ was synthesised following a procedure analogous to that described previously for making symmetrical compounds [14]. The reference compounds

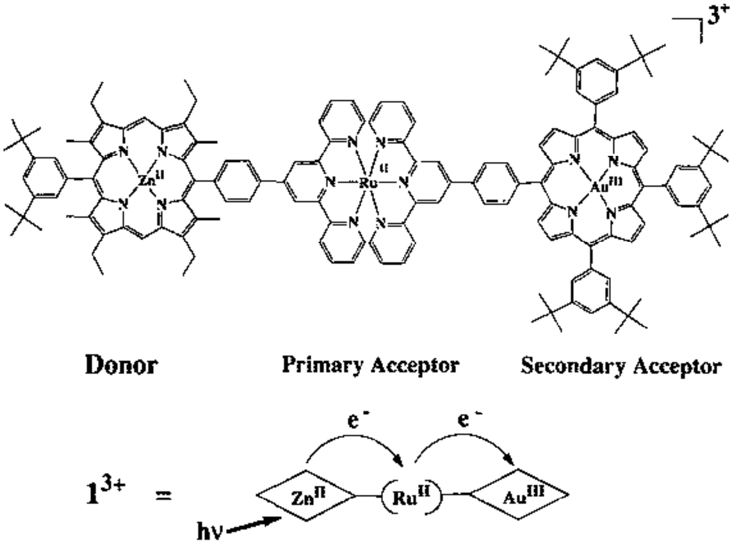

Fig. 1. The triad 1^{3+}.

together with the ligands 5^+ and 7 used for preparation of the triad are shown in Fig. 2.

Synthesis of the octaalkyl diaryl porphyrin terpy 7 was achieved in 20% yield following McDonald's methodology [15] using Lindsey's conditions [16]: acid-catalysed condensation of dipyrrylmethane 6 with aldehydes 2 and 3 in a molar ratio of 6:5:1 in dichloromethane [13].

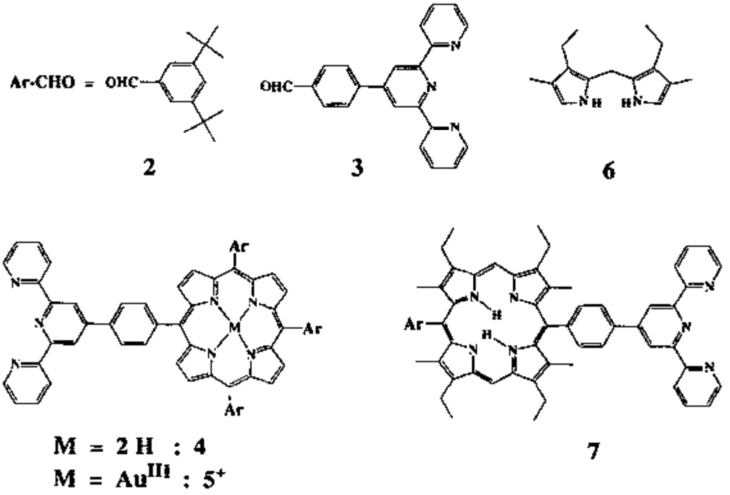

Fig. 2. Reference compounds and ligands 5^+ and 7.

The tetraarylporphyrin terpy **4** was prepared by reacting pyrrole with aldehydes **2** and **3** using two different sets of conditions. (1) Using Adler's conditions [17], a mixture of **2**, **3** and pyrrole in a ratio of 18:1:19 was refluxed in propionic acid giving **4** with 13% yield alfter purification by column chromatography. (2) Using Lindsey's conditions [16], a mixture of **2**, **3** and pyrrole in a molar ratio of 15:1:16 in dichloromethane containing trifluoroacetic acid was stirred at room temperature for 12 h. The resulting porphyrinogens were oxidised with tetrachloro-1,4 benzoquinone in refluxing dichloromethane. The crude product was purified by column chromatography, giving pure **4** in 9% yield. Metallation of the free porphyrin site of **4** with gold(III) was achieved using $KAuCl_4$ and NaOAc in refluxing acetic acid, affording $\mathbf{5}^+$ in 85% yield.

Stepwise formation of the asymmetrical ruthenium(II) complex $\mathbf{1}^{3+}$ from the molecular modules $\mathbf{5}^+$ and **7** was realized using a published procedure [14] (Fig. 3). In the first step, ligand $\mathbf{5}^+$ was reacted with $RuCl_3$, $3H_2O$ in refluxing ethanol to form $\mathbf{8}^+$, which was not isolated. In the second step, after dechlorination with $AgBF_4$, the reaction mixture was reacted with ligand **7** in refluxing ethanol. A pure sample of the triad $\mathbf{9}^{3+}$ was obtained in 35% yield by successive chromatography on silica gel eluting with an acetonitrile–water–aqueous saturated KNO_3 mixture.

Metallation of the free porphyrin site in $\mathbf{9}^{3+}$ was carried out with $Zn(OAc)_2$ in methanol. Compound $\mathbf{1}^{3+}$ was obtained as an orange solid in 88% yield. ^1H nuclear magnetic resonance and electron spectroscopy–mass spectroscopy spectra were in accordance with the postulated structure.

3. Electron transfer property of the triad $\mathbf{1}^{3+}$

The instruments and procedures used to obtain redox potentials, ground state absorption spectra, time-resolved luminescence spectra and laser flash photolysis data have been described previously [14].

Excitation of $\mathbf{1}^{3+}$ at 586 nm [18], where the zinc(II) porphyrin subunit is the dominant chromophore, gives rise to weak fluorescence having the same spectral profile as that recorded for the monomeric zinc porphyrin used as reference. The fluorescence lifetime in acetonitrile solution is only 50 ± 6 ps, compared with a value

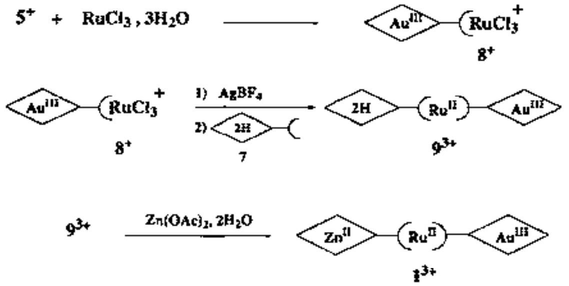

Fig. 3. Stepwise formation of the asymmetrical ruthenium(II) complex 1^{3+}.

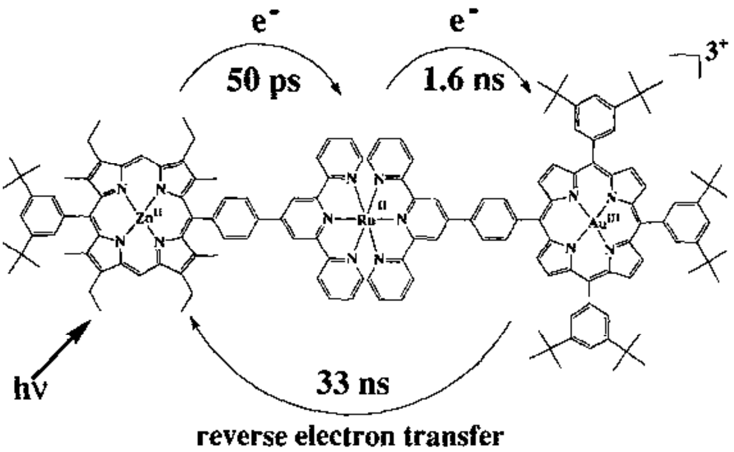

Fig. 4. Stepwise electron transfer in the triad after excitation of the zinc porphyrin.

photoactive components arranged along an axis. The edge-to-edge separation between the porphyrin rings is fixed as 20 Å. Selective excitation of the zinc porphyrin subunit results in rapid ET first to the adjacent ruthenium(II) complex and subsequently to the neighbouring gold(III) porphyrin (Fig. 4). The original ground state system is restored by relatively slow interporphyrin electron transfer.

The interesting features of this molecular triad may be summarised as follows: (i) rapid interporphyrin ET 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.

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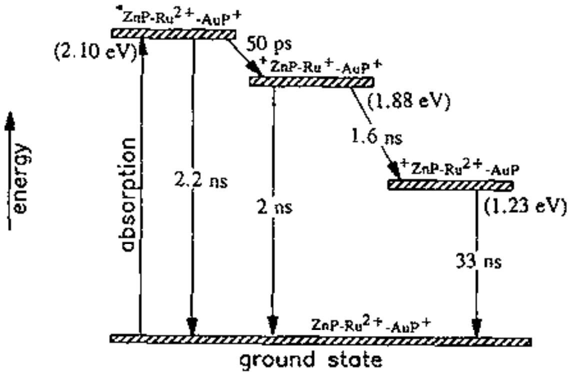

Scheme 2. Energy level diagram.

of 2.2 ± 0.1 ns recorded for the corresponding reference. Laser flash spectroscopy, using excitation at 586 nm with a 1 ps pulse, shows that the initially formed excited singlet state of the zinc porphyrin decays over about 50 ps to generate the zinc porphyrin π radical cation. Decay of the excited singlet state, therefore, is attributed to intramolecular ET to the adjacent Ru(II) bis-terpy complex, for which there is a thermodynamic driving force of ca. 0.2 eV (Scheme 2). The same reaction occurs in the absence of the appended gold(III) porphyrin [14]; for the latter system, rates of forward and reverse electron transfer respectively were $3.6 \times 10^{10}\ s^{-1}$ and $5.0 \times 10^{8}\ s^{-1}$.

In the triad, a second ET process follows in which the distant gold(III) porphyrin is reduced. The rate constant for this second step, derived by monitoring the growth of the reduced gold(III) porphyrin, is found to be $6 \times 10^{8}\ s^{-1}$. The latter process, which is attributed to an intramolecular charge shift reaction (Scheme 2) and for which there is a thermodynamic driving force of ca. 0.6 eV, is in competition with reverse ET to restore the ground state. Subsequent charge transfer between the terminal porphyrinic subunits occurs with a rate constant of $3 \times 10^{7}\ s^{-1}$ and leads to regeneration of the initial system. Therefore, photolysis of the zinc porphyrin subunit results in ET to the distant gold(III) porphyrin, corresponding to an edge-to-edge separation of ca. 20 Å. ET proceeds via reduction of the intervening Ru(II) bis-terpy complex such that this species appears as a real, rather than a virtual, intermediate in the ET pathway.

4. Conclusions

Using a modular approach based on the gathering of two terpy ligands at a metal centre, each terpy bearing a different metalloporphyrin, it was possible to make multicomponent molecular systems having strictly controlled geometry. Because of the axial symmetry of a bis-terpy complex, and the use of aromatic spacers, the bis-porphyrin ruthenium bis-terpy triad described here is a rigid ensemble of electro and

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