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Multistep Electron Transfer in a Porphyrin–Ruthenium(II) Bis(terpyridyl)–Porphyrin Triad

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Natural photosynthesis generates an energy gradient using successive electron-transfer reactions to span a lipid membrane. Biomimetic model systems also have relied on successive electron-transfer steps to achieve long-range charge separation and to reduce the rate of reverse electron transfer.[1,2] Two distinct types of artificial photosynthetic systems have been devised which differ according to the electron-transfer sequence. Thus, donor–donor–acceptor (D_2–D_1–A) systems are known[3-6] in which the primary (light-induced) charge separation is followed by secondary (thermal) electron transfer according to

$$D_2\text{–}D_1\text{–}A \xrightarrow{h\nu} D_2\text{–}D_1^{+}\text{–}A^{-} \rightarrow D_2^{+}\text{–}D_1\text{–}A^{-} \qquad (1)$$

Alternative systems have utilized vectorial electron transfer among redox-graded electron acceptors to spatially separate the charges.[7,8]

$$D\text{–}A_1\text{–}A_2 \xrightarrow{h\nu} D^{+}\text{–}A_1^{-}\text{–}A_2 \rightarrow D^{+}\text{–}A_1\text{–}A_2^{-} \qquad (2)$$

Several systems have been extended by addition of ancillary chromophores, forming molecular tetrads[9] and pentads.[10] We now describe a new triad in which a central ruthenium(II) bisterpy (terpy = 2,2′:6′,2″-terpyridyl) complex[11] is used as spacer for a zinc(II)–gold(III) bisporphyrin. The central ruthenium(II) bisterpy complex also acts as an electroactive component in the two-step electron-transfer process. Thus, selective excitation of the zinc porphyrin subunit results in rapid electron transfer, first to the adjacent ruthenium(II) chelate and subsequently to the distant gold(III) porphyrin.

The triad **1** was synthesized by extension of the procedure described previously[12] and will be reported in full elsewhere. Each of the three chromophoric groups can be excited with partial selectivity at appropriate wavelengths. Thus, excitation of **1** in acetonitrile solution at 25 °C with light of 450 nm was followed by emission of phosphorescence displaying the characteristic spectral features of ruthenium(II) bisterpy.[13] The lifetime of this emission was found to be 200 ± 30 ps, compared to a value of 565 ± 25 ps recorded for ruthenium(II) bisterpy. The reduced lifetime observed for **1** is attributed to triplet energy transfer to the appended porphyrins,[14] which is exothermic in both cases.

Excitation of **1** with a 30-ps laser pulse at 532 nm, where the gold(III) porphyrin subunit is the dominant chromophore, resulted in formation of the triplet state of the gold(III) porphyrin subunit, as monitored by picosecond flash spectroscopy.[15] The resultant triplet lifetime was 1.5 ± 0.2 ns, which is identical to that measured for the corresponding monomeric gold(III) porphyrin under the same conditions. Similarly, the lifetimes of the triplet state of the zinc(II) porphyrin subunit, formed *via* energy transfer from the central ruthenium(II) bisterpy chelate, and the corresponding monomeric zinc porphyrin were both found to be 20 ± 5 μs. The porphyrin triplets in the triad **1**, therefore, remain unreactive toward intramolecular electron transfer. This is in marked contrast to the analogous system in which the porphyrins are separated by a 2,9-diphenyl-1,10-phenanthroline spacer function[15] or its corresponding copper(I)[16] and zinc(II)[17] complexes.

Excitation of **1** at 586 nm, where the zinc(II) porphyrin subunit is the dominant chromophore, gave rise to weak fluorescence having the same spectral profile as that recorded for the monomeric zinc porphyrin.[15] The fluorescence lifetime in acetonitrile solution was only 50 ± 6 ps, compared to a value of 2.2 ± 0.1 ns recorded for the corresponding monomer. Flash spectroscopy, using excitation at 586 nm with a 1-ps laser pulse, showed that the initially formed excited singlet state of the zinc porphyrin[15] decayed over about 50 ps to generate the zinc porphyrin π-radical cation. Decay of the excited singlet state, therefore, is attributed to intramolecular electron transfer to the adjacent ruthenium(II) bisterpy complex, for which there is a thermodynamic driving force of *ca.* 0.2 eV (Scheme 1). The same reaction occurs in the absence of the appended gold(III) porphyrin;[14] for this latter system rates of forward and reverse electron transfer, respectively, were 3.6×10^{10} s^{-1} and 5.0×10^{8} s^{-1}. In the triad, a second electron-transfer process followed in which the distant gold(III) porphyrin was reduced. The rate constant for this second step, derived by monitoring the growth of the reduced gold(III) porphyrin,[15] was found to be $\approx 6 \times 10^{8}$ s^{-1}. This latter process, which is attributed to an intramolecular charge-shift reaction (Scheme 1) and 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 $\approx 3 \times 10^{7}$ s^{-1} and leads to regeneration of the initial system.

Therefore, photolysis of the zinc porphyrin subunit results in electron transfer to the distant gold(III) porphyrin, corresponding to an edge-to-edge separation of *ca.* 20 Å. Electron transfer proceeds *via* reduction of the intervening ruthenium(II) bisterpy complex such that this species appears as a real, rather than a

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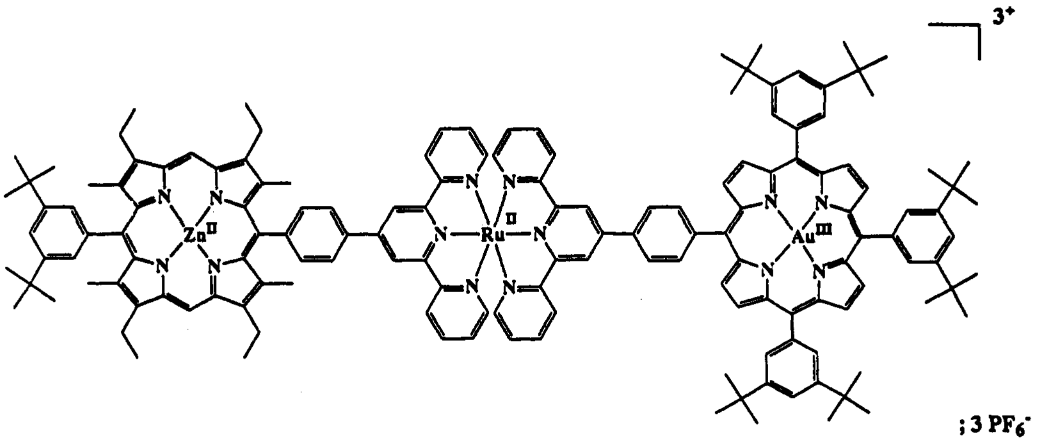
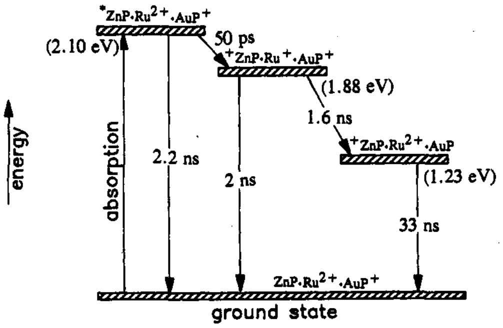
Chart 1



1

Scheme 1



virtual, intermediate in the electron-transfer pathway. The second electron-transfer step wastes *ca.* 0.6 eV but gives a 16-fold extension in the lifetime of the charge-transfer state.[14] Relative to the corresponding 1,10-phenanthroline-bridged bisporphyrin,[15] there is a 50-fold increase in the lifetime of the charge-tranfer state, probably due to the greatly increased separation. In the triad **1** the phenyl rings function as spacers to separate the redox-active subunits. Because of steric crowding, the phenyl ring that connects zinc porphyrin and ruthenium(II) bisterpy subunits lies almost orthogonal to the plane of the porphyrin nucleus whereas that between ruthenium(II) bisterpy and the gold porphyrin subunits can rotate more freely. The orientation of these phenyl rings might be a major contributor in controlling the rates of individual through-bond electron-transfer steps.[18]

The interesting features of this molecular triad[19] may be summarized as follows: (1) Rapid interporphyrin electron transfer occurs between linear, fixed-distance subunits having a center-to-center separation of *ca.* 30 Å. (2) The ultimate charge-separated state, which is formed with a quantum yield of *ca.* 0.6, retains approximately 1.2 eV out of a photonic energy input of 2.1 eV.[20] (3) Photoinduced electron transfer occurs in an ethanol glass at 77 K,[21] albeit at a slower rate (i.e., $k \approx 5 \times 10^8$ s^{-1}) than observed at room temperature (i.e., $k \approx 2 \times 10^{10}$ s^{-1}). (4) The modular synthetic approach is highly versatile and facilitates preparation of many different D–A$_1$–A$_2$ triads and higher order, linear oligomers. (5) The system exhibits a relatively small reorganization energy (i.e., 0.45 eV).[22] This feature, which arises from the precise molecular architecture of the triad, causes the maximal rates of electron transfer to occur at relatively low thermodynamic driving force (i.e., $\Delta G^\circ \approx -0.45$ eV) and favors rapid forward but slow reverse electron-transfer steps. (6) The central ruthenium(II) bisterpy complex appears not to enhance (i.e., superexchange) the rate of charge recombination between the ultimate redox partners, hence helping to ensure a long-lived charge-transfer state.

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[19] Full details regarding synthesis of the triad and the photophysical evaluation of **1**, together with closely related analogues, will be published later.

[20] Excited-state energies were determined as the intersection of absorption and fluoresence spectra, while redox levels were estimated from cyclic voltammetry studies carried out with appropriate model compounds.

[21] Measured by time-correlated, single-photon counting fluorescence spectroscopy as carried out in ethanol at 77 K.

[22] Derived by measuring the rates of electron transfer as a function of temperature and assuming the validity of the Marcus expression for nonadiabatic electron transfer.