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Ultrafast Photoinduced Electron Transfer between Porphyrinic Subunits within a Bis(porphyrin)-Stoppered Rotaxane

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Abstract: A rotaxane has been built around a central copper(I) bis(1,10-phenanthroline) complex with gold(III) and zinc(II) porphyrins acting as terminal stoppers. Upon selective excitation of either porphyrin, rapid electron transfer occurs from the zinc porphyrin to the appended gold porphyrin. The copper(I) complex donates an electron to the resultant zinc porphyrin π-radical cation, and the ground-state system is restored by relatively slow electron transfer from the gold porphyrin neutral radical to the copper(II) complex. The rates of the various electron-transfer steps observed with the rotaxane are compared to those occurring in closely related systems, and it is concluded that the copper(I) complex mediates photoinduced electron transfer between the terminal porphyrinic subunits but not the reverse reaction. A qualitative understanding of the electron-transfer rate is presented in terms of a simple orbital energy diagram involving through-bond electron or hole transfer.

Photoinduced electron transfer between porphyrinic species is a well-studied phenomenon, mainly because of its direct relevance to the primary events occurring in bacterial photosynthetic reaction center complexes. Particular attention has been paid to molecular systems in which two dissimilar porphyrins are held apart by a covalently linked spacer function, giving rise to bis(porphyrins) with flexible[1–3] or constrained[4–6] geometries. For one specific bis(porphyrin) (**1**), comprised of gold(III) and zinc(II) porphyrinic subunits linked through a 1,10-phenanthroline spacer, the various electron-transfer pathways have been elaborated in considerable detail for excitation into either porphyrinic chromophore.[7] A further study[8] revealed that the rates of photoinduced electron transfer were increased significantly when two of these bis(porphyrins) were entwined (i.e., interlocked) into a tetrameric porphyrin ensemble by coordination of two 1,10-phenanthroline ligands to a central copper(I) cation (**2**). In attempting to rationalize the different rates of electron transfer found for this pair of molecular systems, several possible solutions have to be considered.[8] Thus, the presence of the copper(I) bis(1,10-phenanthroline) complex might alter the proximity of the porphyrin nuclei, change the thermodynamic properties of the system, or mediate photoinduced electron transfer within the same chelate via a superexchange mechanism. We now present experimental data obtained with a related bis(porphyrin) formed by constraining the accessory 1,10-phenanthroline ligand in a 30-membered macrocyclic ring, thereby forming a rotaxane (**3**) in which the porphyrin subunits act as stoppers.[9] Comparison of the rates of photoinduced electron transfer occurring in compounds **1**–**3** indicates that the copper(I) complex enhances the rate of forward electron transfer due to a superexchange mechanism.

Experimental Section

N,N-Dimethylformamide (DMF) (Aldrich spectroscopic grade) was fractionally distilled from CaH_2. Structures of compounds **1**–**3** are given in Figure 1; the synthesis of each compound has been described previously.[8–10] It should be noted that the substituents on the zinc porphyrin subunit are different for the rotaxane **3** than for the bis(porphyrin) **1** or the entwined ensemble **2**. This change in substitution pattern, which was made solely in order to simplify synthesis of the rotaxane,[9] causes small but significant shifts in absorption maxima and redox potentials for the zinc porphyrin subunit.

All experiments were made with freshly prepared, dilute solutions of the compound in deoxygenated DMF. Absorption spectra were recorded with a Hitachi U3210 spectrophotometer. Luminescence spectra were recorded with a Perkin-Elmer LS5 spectrofluorimeter and were corrected for wavelength responses of the detector.[11] Fluorescence quantum yields were measured relative to zinc tetraphenylporphyrin (ZnTPP) (Φ_f = 0.033).[12] Singlet excited-state lifetimes were measured by time-correlated, single-photon counting using a mode-locked Nd:YAG laser (Antares 76S) synchronously pumping a cavity-dumped Rhodamine 6G dye laser (Spectra Physics 375B/244). Glass cut-off filters were used to isolate fluorescence from scattered laser light. A Hamamatsu microchannel plate was used to detect emitted photons, for which the instrumental response function had an fwhm of 60 ± 10 ps. Data analyses were made according to O'Connor and Phillips using computer deconvolution to minimize reduced chi-square parameters.[13]

Flash photolysis studies were made with a frequency-doubled, mode-locked Quantel YG402 Nd:YAG laser (pulse width 30 ps). An alternative excitation wavelength was obtained by Raman shifting to 559 nm with benzene. Laser intensities were attenuated with crossed polarizers, and

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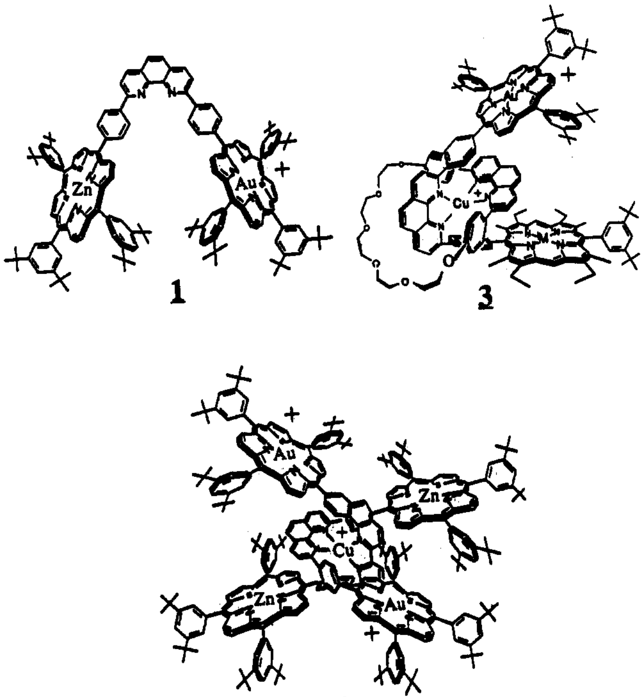

1

3

2

Figure 1. Structures of the compounds used in this study.

300 laser shots were averaged for each measurement. Solutions were adjusted to possess absorbances of ca. 0.4 at the excitation wavelength. Residual 1064-nm output from the laser was focused into 1/1 D_3PO_4/D_2O to produce a white light continuum for use as the analyzing beam. Variable delay times in the range 0–6 ns were selected in a random sequence, and transient differential absorption spectra were recorded with an Instruments SA UFS200 spectrograph interfaced to a Tracor Northern 6200 MCA and a microcomputer. Kinetic analyses were made by overlaying about 40 individual spectra and fitting data at selected wavelengths using computer nonlinear, least-squares iterative procedures.

Improved time resolution was achieved using a frequency-doubled, mode-locked Antares 76S Nd:YAG laser to pump a Coherent 700 dual jet (Rhodamine 6G) dye laser operated at 76 MHz. A Quantel Model RGA67-10 regenerative amplifier, a Quantel Model PTA-60 dye laser, and a Continuum SPA1 autocorrelator were used to obtain 3-mJ pulses at 586 nm having an fwhm of ca. 500 fs. The spectrometer was run at a frequency of 10 Hz, and data were acquired through a Princeton dual diode array spectrograph interfaced to a microcomputer. The detection setup and optical delay line were similar to those used for the 30-ps pulse width experiments; in both cases, the exciting and analyzing beams were almost collinear. Again, kinetic analyses were made by overlaying spectra collected at about 50 different delay times.

Redox potentials for one-electron oxidation or reduction of the porphyrinic subunits and the copper(I) complex were derived by cyclic voltammetry in deoxygenated DMF containing tetra-*n*-butylammonium perchlorate (0.2 M). A glassy carbon working electrode was used in conjunction with a Pt counter electrode and an SCE reference electrode. The peaks were assigned to particular processes on the basis of measurements made with the corresponding model compounds; the model compounds used throughout this study were gold(III) *meso*-tetrakis-(3,5-di-*tert*-butylphenyl)porphyrin,[7] zinc(II) *meso*-10,20-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin,[9] and copper(I) bis(2,9-diphenyl-1,10-phenanthroline).[8] Redox potentials corresponding to one- and two-electron reduction of the gold(III) porphyrinic subunit were well resolved from all other reduction processes and were found to be −0.49 ± 0.02 and −0.84 ± 0.03 V vs SCE for all three compounds. For **1**, redox potentials for one- and two-electron oxidation of the zinc(II) porphyrinic subunit were also well resolved and were found to be 0.82 ± 0.02 and 1.15 ± 0.03 V vs SCE. For comparison, the redox potentials for one- and two-electron oxidation of zinc(II) *meso*-tetrakis-(3,5-di-*tert*-butylphenyl)porphyrin were found to be 0.62 ± 0.03 and 0.95 ± 0.05 V vs SCE, respectively. The redox potential for one-electron reduction of the zinc(II) porphyrin subunit in **3** was found to be −1.55 ± 0.05 V vs SCE. The redox potential for one-electron oxidation of copper(I) bis(2,9-diphenyl-1,10-phenanthroline) in DMF was found[8] to be 0.58 ± 0.02 V vs SCE, and for **2** and **3** this oxidation peak overlaps that due to one-electron oxidation of the zinc(II) porphyrinic subunit. The overlapping peaks were resolved by computer convolution, using the peak shapes and currents recorded for the model compounds, in order to better estimate the peak separation. In this way, redox potentials for one-electron oxidation of the copper(I) complex and the zinc(II) porphyrinic subunit in **2**, respectively, were derived as 0.57 ± 0.05 and 0.81 ± 0.03 V vs SCE. The corresponding values for **3**, respectively, were derived as 0.54 ± 0.05 and 0.68 ± 0.03 V vs SCE. The difference in one-electron oxidation potentials derived for the zinc porphyrin subunits in **2** and **3** arises because of the varying nature of the substituents attached to the porphyrin nuclei. Indeed, the redox potentials for one- and two-electron oxidation of zinc(II) *meso*-10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin were found to be 0.64 and 0.95 V vs SCE, respectively.

Results and Discussion

Experimental results obtained with both **1** and **2** in DMF have been reported in previous publications,[7,8] and little additional data are presented here.[14] The photophysical properties of **3** were measured under conditions that facilitate meaningful comparison with our earlier work. Interpretation of the transient spectroscopic changes follows the reasoning outlined previously.[7,8]

Excitation of the Rotaxane 3 via the Zinc(II) Porphyrin Subunit. Upon excitation at 586 nm, where only the zinc porphyrin subunit absorbs, extremely weak fluorescence could be observed. The fluorescence spectrum corresponded to emission from a zinc porphyrin,[12] and the excitation spectrum recorded over the visible region resembled that found for the corresponding monomeric zinc porphyrin. Comparing the fluorescence quantum yield with that observed for an optically-matched solution of the monomeric zinc porphyrin indicated that the degree of fluorescence quenching in **3** was >99%. The fluorescence decay profile, as recorded by time-correlated, single-photon counting techniques, could not be properly resolved from the instrument response function. The excited singlet state lifetime for the zinc porphyrin subunit in **3**, therefore, is presumed to be <10 ps.

Immediately after excitation of **3** with a 0.5-ps laser pulse at 586 nm, the characteristic differential absorption spectral features of the charge-transfer state[7,8] comprising zinc porphyrin π-radical cation and gold(III) porphyrin neutral radical were observed (Figure 2a). This state is formed upon electron transfer from the excited singlet state of the zinc(II) porphyrin to the appended gold(III) porphyrin; the reaction exothermicity ($\Delta G°$) for this reaction is estimated to be −1.01 eV.[15]

$$^{*}(\mathrm{ZnP})\text{–}\mathrm{Cu}^{+}\text{–}(\mathrm{AuP}^{+}) \rightarrow (^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^{+}\text{–}(\mathrm{AuP}^{\bullet}) \qquad (1)$$

The zinc porphyrin excited singlet state, which has a distinctive absorption spectrum[16] and which must be the precursor state for this process, could not be resolved under our experimental conditions. Upon monitoring at 660 nm, where the charge-transfer state has pronounced absorption relative to the excited singlet state, it was found that formation of the charge-transfer state followed the laser pulse profile (Figure 2b) and, therefore, the lifetime of the zinc porphyrin excited singlet state must be <1 ps.

Absorbance attributed to the charge-transfer state decayed with a lifetime[17] of 20 ± 5 ps to leave a residual species having

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(14) The new experimental data are as follows: (a) The rate constant for photoinduced electron transfer upon excitation into the gold(III) porphyrinic subunit in **2** has been remeasured using improved time resolution. (b) Reaction exothermicities were estimated previously from redox potentials measured for the corresponding monomeric porphyrins. These values have now been refined using redox potentials for compounds **1** and **2**.

(15) Calculated according to the following: $\Delta G° = -F(E_{red}° - [E_{ox}° - E_s])$ where $E_{red}°$ (=−0.49 V vs SCE) and $E_{ox}°$ (=0.68 V vs SCE) refer to the redox potentials for one-electron reduction and oxidation, respectively, of the gold(III) and zinc(II) porphyrinic subunits in **3**, and E_s (=2.18 eV) is the excitation energy of the zinc porphyrin excited singlet state, as determined from absorption spectroscopy.

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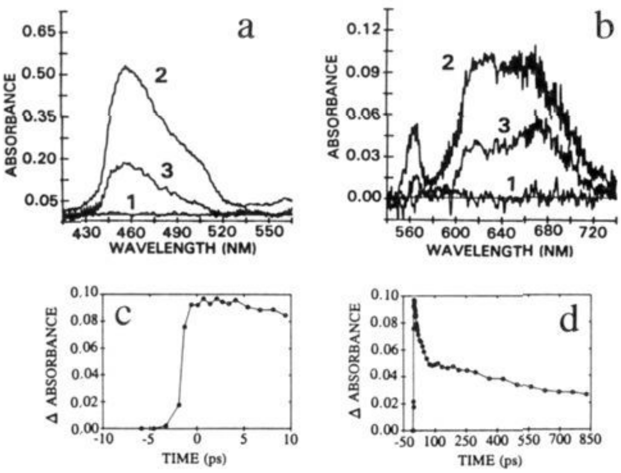


Figure 2. (a, b) Transient differential absorption spectra recorded after excitation of **3** in DMF with a 0.5-ps laser pulse at 586 nm at delay times of (1) 0, (2) 2, and (3) 50 ps. (c) Growth of the transient absorbance at 660 nm attributed to the charge-transfer state. (d) Decay profile recorded for the above experiment at 660 nm.

the characteristic differential absorption spectrum[7,8] of the gold(III) porphyrin neutral radical (Figure 2a). Deactivation of the charge-transfer state may involve direct reverse electron transfer between porphyrinic species ($\Delta G° = -1.17$ eV)[18]

$$(^{\bullet+}\text{ZnP})\text{–Cu}^{+}\text{–}(\text{AuP}^{\bullet}) \rightarrow (\text{ZnP})\text{–Cu}^{+}\text{–}(\text{AuP}^{+}) \tag{2}$$

and/or electron transfer from the central copper(I) complex to the zinc porphyrin π-radical cation ($\Delta G° = -0.14$ eV).[19]

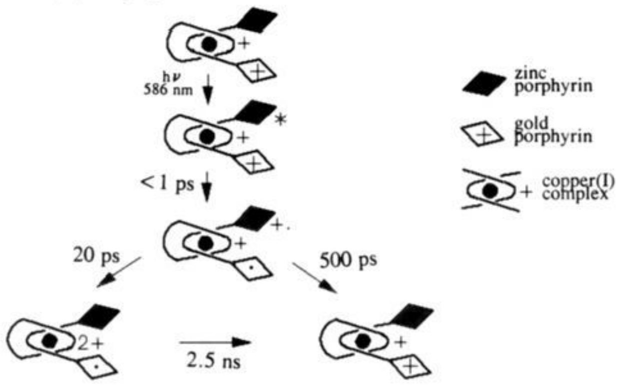
$$(^{\bullet+}\text{ZnP})\text{–Cu}^{+}\text{–}(\text{AuP}^{\bullet}) \rightarrow (\text{ZnP})\text{–Cu}^{2+}\text{–}(\text{AuP}^{\bullet}) \tag{3}$$

On the basis of differential extinction coefficients measured previously,[7,8] the latter process appears to be quantitative,[20] despite its minimal thermodynamic driving force. Indeed, using the rate constant for direct reverse electron transfer (reaction 2) derived following excitation into the gold(III) porphyrin subunit ($k_2 \approx 2 \times 10^9$ s^{-1}; see later), oxidation of the central copper(I) complex ($k_3 \approx 4.8 \times 10^{10}$ s^{-1}) should account for ca. 95% of the total decay of the intermediate charge-transfer state. The residual gold(III) porphyrin neutral radical decayed on a much longer time scale due to electron donation to the copper(II) complex ($\Delta G° = -1.03$ eV).[21]

$$(\text{ZnP})\text{–Cu}^{2+}\text{–}(\text{AuP}^{\bullet}) \rightarrow (\text{ZnP})\text{–Cu}^{+}\text{–}(\text{AuP}^{+}) \tag{4}$$

A more reliable estimate of the rate constant for reaction 4 ($k_4 = 4.0 \pm 0.8 \times 10^8$ s^{-1}) was obtained following excitation of **3** with a 30-ps laser pulse at 559 nm. The overall reaction sequence proposed for this system is given in Scheme I.

Scheme I. Pictorial Representation of the Reaction Sequence Initiated by Excitation of the Rotaxane **3** into the Zinc(II) Porphyrin Subunit



An alternative explanation involves electron abstraction from the central copper(I) complex by the excited singlet state of the zinc porphyrin.

$$^{*}(\text{ZnP})\text{–Cu}^{+}\text{–}(\text{AuP}^{+}) \rightarrow (^{\bullet-}\text{ZnP})\text{–Cu}^{2+}\text{–}(\text{AuP}^{+}) \tag{5}$$

There is a small thermodynamic driving force for this process ($\Delta G° = -0.09$ eV),[22] but the observed transient differential absorption spectra are inconsistent with formation of the zinc porphyrin π-radical anion.[23]

Excitation of the Rotaxane 3 via the Gold(III) Porphyrin Subunit. The gold(III) porphyrin subunit, like the corresponding monomeric gold(III) porphyrin,[24] does not luminesce in fluid solution at room temperature. Excitation of **3** with a 30-ps laser pulse at 532 nm, where the gold(III) porphyrin subunit absorbs about 80% of the total incident photons,[25] resulted in formation of the gold(III) porphyrin triplet excited state.[7,8] This species decayed within the laser pulse to form the charge-transfer state ($\Delta G° = -0.65$ eV),[26] as detected[7,8] by its characteristic transient differential absorption spectrum (Figure 3a,b).

$$(\text{ZnP})\text{–Cu}^{+}\text{–}(\text{AuP}^{+})^{*} \rightarrow (^{\bullet+}\text{ZnP})\text{–Cu}^{+}\text{–}(\text{AuP}^{\bullet}) \tag{6}$$

After deconvolution of the laser pulse, the lifetime of the gold(III) porphyrin excited triplet state was derived as 17 ± 4 ps, which can be compared to the value of 1.5 ± 0.2 ns measured for the corresponding monomeric porphyrin.[7,8]

The charge-transfer state was found to decay rapidly (Figure 3c), with a lifetime of 50 ± 6 ps (measured after deconvolution of the laser pulse), leaving a residual absorbance which was identified as the gold(III) porphyrin neutral radical by virtue of its differential absorption spectrum.[8] This latter species decayed relatively slowly, with a lifetime of 2.5 ± 0.7 ns, to re-form the ground state of **3**. As above, the rapid deactivation of the charge-transfer state is ascribed to a combination of direct reverse electron transfer (reaction 2) and oxidation of the central copper(I) complex by the zinc porphyrin π-radical cation (reaction 3). The

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(17) This is the average value measured at many different wavelengths across the spectral range.

(18) Calculated according to the following: $\Delta G° = -F(E_{ox}° - E_{red}°)$ where $E_{red}°$ (=-0.49 V vs SCE) and $E_{ox}°$ (=0.68 V vs SCE) refer to the redox potentials for one-electron reduction and oxidation, respectively, of the gold(III) and zinc(II) porphyrinic subunits in **3**.

(19) Calculated according to the following: $\Delta G° = -F(E_{ox}° - E_{cup}°)$ where $E_{ox}°$ (=0.68 V vs SCE) and $E_{cup}°$ (=0.54 V vs SCE), respectively, refer to the redox potentials for one-electron oxidation of the zinc(II) porphyrinic subunit and the copper(I) complex in **3**.

(20) At 460 and 660 nm, the zinc porphyrin π-radical cation and the gold(III) porphyrin neutral radical possess almost identical molar extinction coefficients, while there are negligible differential absorption changes associated with oxidation of the central copper(I) complex. (The latter was established by controlled potential spectroelectrochemistry.) Direct reverse electron transfer restores the prepulse base line, whereas reduction of the zinc porphyrin π-radical cation by electron transfer from the central copper(I) complex should lower the absorbance by approximately 50%. The observed absorption changes correspond to a 50 ± 5% decrease in the initial absorbance attributed to the charge-transfer state. The uncertainty in this measurement is expected to be ca. 10%.

(21) Calculated according to the following: $\Delta G° = -F(E_{cup}° - E_{red}°)$ where $E_{red}°$ (=-0.49 V vs SCE) and $E_{cup}°$ (=0.54 V vs SCE) refer to the redox potentials for one-electron reduction and oxidation, respectively, of the gold(III) porphyrinic subunit and the copper(I) complex in **3**.

(22) Calculated according to the following: $\Delta G° = -F([E_{red}° + E_s] - E_{cup}°)$ where $E_{red}°$ (=-1.55 V vs SCE) and $E_{cup}°$ (=0.54 V vs SCE) refer to the redox potentials for one-electron reduction and oxidation, respectively, of the zinc(II) porphyrinic subunit and the copper(I) complex in **3**, and E_s is the excitation energy.

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(25) This value was estimated using molar extinction coefficients at 532 nm measured for the corresponding monomers.

(26) Calculated according to the following: $\Delta G° = -F([E_{red}° + E_t] - E_{ox}°)$ where $E_{red}°$ (=-0.49 V vs SCE) and $E_{ox}°$ (=0.68 V vs SCE) refer to the redox potentials for one-electron reduction and oxidation, respectively, of the gold(III) and zinc(II) porphyrinic subunits in **3**, and E_t (=1.82 eV) is the excitation energy of the gold(III) porphyrin excited triplet state, as determined from phosphorescence spectroscopy for the corresponding monomer.

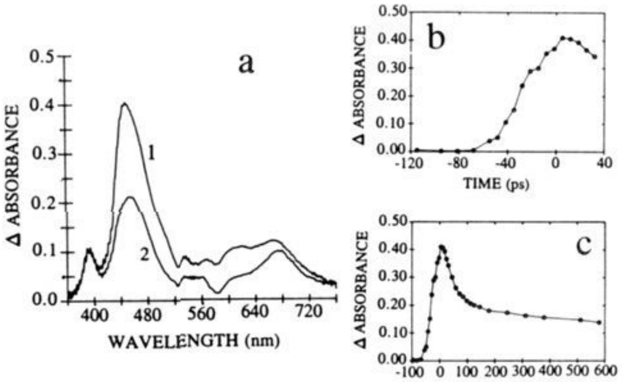
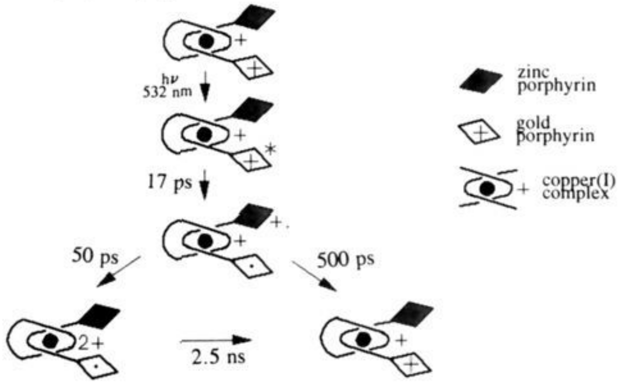


Figure 3. (a) Transient differential absorption spectra recorded after excitation of **3** in DMF with a 30-ps laser pulse at 532 nm at delay times of (1) 5 and (2) 100 ps. (b) Growth of the transient absorption at 660 nm attributed to the charge-transfer state. (c) Decay profile recorded for the above experiment at 660 nm.

Scheme II. Pictorial Representation of the Reaction Sequence Initiated by Excitation of the Rotaxane **3** into the Gold(III) Porphyrin Subunit



yield of the gold(III) porphyrin neutral radical which escaped direct electron transfer was estimated[20] from the transient absorption spectral changes to be 90%. Thus, direct reverse electron transfer ($k_2 \approx 2.0 \times 10^9$ s^{-1}) accounts for only 10%, and electron abstraction from the central copper(I) complex ($k_3 \approx 1.8 \times 10^{10}$ s^{-1}) is the dominant decay route, despite its much lower thermodynamic driving force. The residual gold(III) porphyrin neutral radical decays over several nanoseconds due to electron donation to the copper(II) complex (reaction 4), as indicated in Scheme II.

An alternative explanation involves electron abstraction from the central copper(I) complex by the excited triplet state of the gold(III) porphyrin ($\Delta G° = -0.79$ eV).[27]

$$(\mathrm{ZnP})\text{–}\mathrm{Cu}^{+}\text{–}(\mathrm{AuP}^{+})^{*} \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^{2+}\text{–}(\mathrm{AuP}^{\bullet}) \qquad (7)$$

The transient differential absorption spectra recorded after decay of the gold(III) porphyrin excited triplet state are inconsistent with reaction 7 being the sole process,[28] but we cannot exclude the possibility that this reaction makes a significant contribution to the overall deactivation of the triplet. Previously, using an entwined tetrameric gold(III) porphyrin analogue of **2**, k_7 was found[8] to be 5.9×10^9 s^{-1}. We might expect, therefore, that reaction 7 accounts for about 10% of the decay of the gold(III) porphyrin excited triplet state. The relatively slow rate of reaction 7 is attributed to an unusually high reorganization energy associated with formation of a coordinatively-unsaturated copper(II) complex.[29]

Comparison of the Electron-Transfer Rates for the Three Systems. A compilation of the various electron transfer rate constants measured for compounds **1**–**3** is given in Table I; kinetic data for compounds **1** and **2** are from previous studies.[7,8] Thermodynamic data have been calculated[18,19,21,26] from redox potentials measured for the compounds in DMF and are uncorrected for any changes in Coulombic forces which accompany electron transfer.[30] The rate constants can be ascribed to five distinct electron transfer steps: namely, photoinduced electron transfer between porphyrinic subunits following excitation into either gold(III) (k_6) or zinc(II) (k_1) porphyrin, reverse electron transfer between the primary products (k_2), electron abstraction from the copper(I) complex by the zinc porphyrin π-radical cation (k_3), and reduction of the resultant copper(II) complex by the gold(III) porphyrin neutral radical (k_4). We now compare the rates of these reactions according to the molecular architecture housing the bis(porphyrin).

The rates of both reactions that lead to reoxidation of the gold(III) porphyrin neutral radical are independent of the nature of the compound, and the average values for k_2 and k_4, respectively, are $1.6 \pm 0.4 \times 10^9$ and $4 \pm 1 \times 10^8$ s^{-1}. Both reactions are relatively slow and dissipate large amounts of energy (Table I), although there is no reason to suppose that they fall within the Marcus "inverted" region.[31] The reaction exothermicities are comparable for all three compounds. The copper(I) complex exerts no significant effect on the rate of direct reverse electron transfer. That $k_2 > k_4$ is in accord with the relative reaction exothermicities and the notion that reduction of the copper(II) complex, which is initially formed as a coordinatively-unsaturated species, may involve a high reorganization energy.[29]

The rate of reduction of the zinc(II) porphyrin π-radical cation by the copper(I) complex is significantly faster in the rotaxane **3** than in the entwined porphyrin ensemble **2**. This observation holds true regardless of which porphyrin is initially excited and regardless of the slightly higher reaction exothermicity associated with **2**. We tentatively attribute this disparity in rates to slight differences in the stereochemistry of the compounds. It is also noteworthy that, for both **2** and **3**, k_3 far exceeds k_2, although the reaction exothermicity for reaction 3 is very much less than that for reaction 2. The faster rate for reaction 3 may arise because of the closer proximity of the reactants and/or because electron transfer occurs via a different route. One further point in this respect concerns the observation that k_3 shows a slight dependence on the identity of the porphyrin excited state. Thus for the rotaxane **3** there is a 3-fold increase in k_3 when the zinc porphyrin π-radical cation is formed by way of the zinc porphyrin excited singlet state compared to when the gold(III) porphyrin excited triplet state is the precursor.[32] The origin of this effect is unclear, the only apparent difference being the spin multiplicity of the precursor excited state.

The most profound difference in reactivity between the bis(porphyrin) **1** and the copper(I) complex containing ensembles

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(27) Calculated to the following: $\Delta G° = -F([E_{\mathrm{red}}° + E_{\mathrm{t}}] - E_{\mathrm{cup}}°)$ where $E_{\mathrm{red}}°$ (=−0.49 V vs SCE) and $E_{\mathrm{cup}}°$ (=0.54 V vs SCE) refer to the redox potentials for one-electron reduction and oxidation, respectively, of the gold(III) porphyrinic subunit and the copper(I) complex in **3**, and E_{t} is the excitation energy.

(28) In particular, the differential absorption spectral changes associated with oxidation of the central copper(I) complex are insignificant compared to those arising from the porphyrinic species. The resultant copper(II) complex exhibits a weak absorption band centered at 670 nm with an extinction coefficient of ca. 800 M^{-1} cm^{-1}. The transient differential absorption spectral changes observed after decay of the triplet state were entirely consistent with transformation of the charge-transfer state into the gold(III) porphyrin neutral radical.

(29) (a) Kirchhoff, J. R.; Gamache, R. E.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380. (b) Palmer, C. E. A.; McMillin, D. R.; Kirmaier, C.; Holten, D. *Inorg. Chem.* **1987**, *26*, 3167.

(30) In most cases, there is no net change in electronic charge. The exceptions are those reactions involving the central copper complex.

(31) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.

(32) The disparity in k_3 values for the entwined ensemble **2** is about 10-fold, although the experimental uncertainty is greater than that for **3**. Current EPR and magnetic field experiments in frozen alcohol are aimed at resolving the nature of this effect.

Table I. Rate Constants and Reaction Exothermicities for the Various Electron Transfer Steps Described for the Multicomponent Systems

compd	reaction	k^d	$k/10^8$ (s^{-1})	$\Delta G°$ (eV)
1	${}^*(\mathrm{ZnP})\text{–}(\mathrm{AuP}^+) \rightarrow ({}^{\bullet+}\mathrm{ZnP})\text{–}(\mathrm{AuP}^\bullet)$	1	178	–0.75
1	$({}^{\bullet+}\mathrm{ZnP})\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}(\mathrm{AuP}^+)$	2	17	–1.31
1	$(\mathrm{ZnP})\text{–}(\mathrm{AuP}^+)^* \rightarrow ({}^{\bullet+}\mathrm{ZnP})\text{–}(\mathrm{AuP}^\bullet)$	6	76	–0.51
2	${}^*(\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+) \rightarrow ({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet)$	1	3300	–0.76
2[a]	$({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^{2+}\text{–}(\mathrm{AuP}^\bullet)$	3	50	–0.24
2[b]	$({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^{2+}\text{–}(\mathrm{AuP}^\bullet)$	3	5	–0.24
2	$({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+)$	2	11	–1.30
2	$(\mathrm{ZnP})\text{–}\mathrm{Cu}^{2+}\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+)$	4	5	–1.06
2[c]	$(\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+)^* \rightarrow ({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet)$	6	300	–0.52
3	${}^*(\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+) \rightarrow ({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet)$	1	>10 000	–1.01
3[a]	$({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^{2+}\text{–}(\mathrm{AuP}^\bullet)$	3	480	–0.14
3[b]	$({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^{2+}\text{–}(\mathrm{AuP}^\bullet)$	3	180	–0.14
3	$({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+)$	2	20	–1.17
3	$(\mathrm{ZnP})\text{–}\mathrm{Cu}^{2+}\text{–}(\mathrm{AuP}^\bullet) \rightarrow (\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+)$	4	4	–1.03
3	$(\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^+)^* \rightarrow ({}^{\bullet+}\mathrm{ZnP})\text{–}\mathrm{Cu}^+\text{–}(\mathrm{AuP}^\bullet)$	6	530	–0.65

[a] Singlet charge-transfer state. [b] Triplet charge-transfer state. [c] Rate constant measured in this study. [d] Refers to the reaction number given in the text.

2 and **3** concerns the relative rates of photoinduced electron transfer. Regardless of which porphyrinic subunit is excited, the rate of photoinduced electron transfer is very much faster in **2** than in **1**, despite the almost identical reaction exothermicities. We have suggested previously[8] that this rate enhancement may arise from a greater proximity between the porphyrinic subunits or because the copper(I) complex mediates electron transfer via a superexchange mechanism. These rates are even faster in **3** than in **2**, due in part to higher reaction exothermicities (Table I) which arise because the zinc(II) porphyrinic subunit in **3** is easier to oxidize and has a higher excited singlet state energy. Even so, the rates of photoinduced electron transfer found for the rotaxane **3** are extremely fast, especially when one considers that electron transfer occurs over an edge-to-edge separation of ca. 8.5 Å.[33]

Since **3** consists of only two porphyrinic subunits and since the mutual arrangement of these two porphyrin nuclei[33] is not expected to differ significantly from that in the bis(porphyrin) **1**, it is tempting to invoke a superexchange effect to account for the huge difference in photoinduced electron-transfer rates found for **1** and **3**. There are at least two distinct ways for this to happen. Firstly, the copper(I) complex might modulate the energy of the relevant HOMO or LUMO orbitals on the bridging unit; this would be significant if electron transfer occurs through the spacer moiety.[34] Secondly, the accessory 1,10-phenanthroline residue contained in the 30-membered macrocyclic ring of the rotaxane **3** could participate in electron transfer since it is most probably interspersed between the two porphyrin rings which undergo forward and reverse electron transfer. This latter situation, which is reminiscent of the bacterial photosynthetic reaction center complex,[35,36] would be significant if electron transfer proceeded through space. The presence of an accessory 1,10-phenanthroline residue and a central copper(I) complex is common to both **2** and **3**.

Further work is needed to resolve the details of the various electron-transfer pathways. We note, however, that the relative rates of electron transfer observed for the three compouds can be qualitatively explained in terms of a simple orbital energy diagram[37] of the type displayed in Figure 4. Here, the energies of the donating and accepting orbitals on the zinc(II) and gold(III) porphyrins are compared to the energies of the LUMO and HOMO on the 2,9-diphenyl-1,10-phenanthroline spacer moiety.[38] For reaction to proceed via electron transfer through the LUMO of the spacer moiety, it is important to minimize the energy gap (B_-) between the donating orbital and the LUMO. Conversely, for reaction to proceed via hole transfer through the HOMO of the spacer moiety, it is important to minimize the energy gap (B_+) between the accepting orbital and the HOMO. The energy gaps have been calculated[39] for each of the electron-transfer reactions and are collected in Table II.

Table II. Energy Gaps for the Various Electron Transfer Steps between Porphyrinic Species Assuming Reaction Proceeds by Way of the Spacer Moiety

compd	$k/10^8$ (s^{-1})	$\Delta G°$ (eV)	B_- (eV)	B_+ (eV)
		Electron Transfer from *ZnP		
1	178	–0.75	0.76	2.44
2	3300	–0.76	0.40	2.39
3	>10 000	–1.01	0.15	2.39
		Electron Transfer from *AuP$^+$		
1	76	–0.51	2.82	0.62
2	300	–0.52	2.46	0.57
3	530	–0.65	2.33	0.57
		Direct Reverse Electron Transfer		
1	17	–1.31	1.51	1.13
2	11	–1.30	1.16	1.08
3	20	–1.17	1.16	1.22

The calculated energy gaps indicate to us that reaction from the first excited singlet state of the zinc porphyrin should proceed by way of electron transfer through the LUMO of the spacer. There is a relatively small energy gap for this process (B_-) in each case, and the magnitude of the gap decreases with increasing rate of electron transfer. However, the gold(III) porphyrin triplet is

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[33] Chardon-Noblat, S.; Guilhem, J.; Mathis, P.; Pascard, C.; Sauvage, J.-P. In *Photoconversion Processes for Energy and Chemicals*; Hall, D. O., Grassi, G., Eds.; Elsevier: London, 1989; p 90.

[34] We treat the bridging 2,9-diphenyl-1,10-phenanthroline moiety as a single (i.e., homogeneous) π-system without allowing for the linking bonds. Osuka *et al.*[6] have observed that the rate of electron transfer through aromatic spacers depends only on the separation distance and not on orientation or number of connecting bonds. Helms *et al.*[5b] have argued in favor of a more complex picture in which the connecting bonds play a significant role.

[35] (a) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385. (b) Deisenhofer, J.; Epp, O.; Miki, K.; Michel, H. *Nature* **1985**, *318*, 618. (c) Deisenhofer, J.; Michel, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 829.

[36] (a) Ogrodnik, A.; Remy-Richter, N.; Michel-Beyerle, M. E. *Chem. Phys. Lett.* **1987**, *135*, 576. (b) Bixon, M.; Jortner, J.; Michel-Beyerle, M. E.; Ogrodnik, A.; Lersch, W. *Chem. Phys. Lett.* **1987**, *140*, 626. (c) Plato, M.; Mobius, K.; Michel-Beyerle, M. E.; Bixon, N.; Jortner, J. *J. Am. Chem. Soc.* **1988**, *110*, 7279. (d) Marcus, R. A. *Chem. Phys. Lett.* **1987**, *133*, 471. (e) Won, Y.; Friesner, R. A. *Biochim. Biophys. Acta* **1988**, *975*, 9.

[37] Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746.

[38] Cyclic voltammetry studies in DMF showed the redox potentials for one-electron reduction and oxidation, respectively, for 2,9-diphenyl-1,10-phenanthroline to be –2.00 ± 0.05 and 1.95 ± 0.07 V vs SCE. Coordination to a copper(I) cation raises the reduction potential to –1.65 ± 0.05 V vs SCE but has little effect on the oxidation potential, which is located at 1.90 ± 0.07 V vs SCE. It should be noted that the copper(I) complex has a metal-centered oxidation process at 0.58 V vs SCE, but we have used the ligand-centered oxidation reaction as representing the HOMO of the spacer moiety. For further details about the electrochemistry of these and related complexes, see: Dietrich-Buchecker, C.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 7791.

[39] Redox levels are obtained by electrochemical measurements and use the excited-state energies calculated elsewhere in this paper. It should be noted that electron transfer and hole transfer, respectively, correspond to formation of $({}^{\bullet+}\mathrm{ZnP})\text{–}(\mathrm{S}^-)\text{–}(\mathrm{AuP}^+)$ and $(\mathrm{ZnP})\text{–}(\mathrm{S}^+)\text{–}(\mathrm{AuP}^\bullet)$ virtual states.

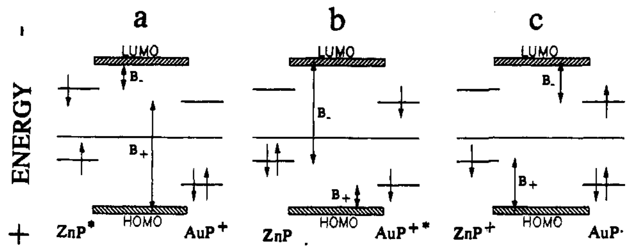

Figure 4. Orbital energy level diagrams for (a) photoinduced electron transfer from the excited singlet state of the zinc porphyrin, (b) photoinduced electron transfer from the excited triplet state of the gold(III) porphyrin, and (c) direct reverse electron transfer. Values for the energy gaps (B_- and B_+) are collected in Table II.

more likely to react via hole transfer through the HOMO of the spacer. There is a modest reduction in the size of the energy gap (B_+) upon coordination of a copper(I) cation to the bridging 2,9-diphenyl-1,10-phenanthroline moiety, which is accompanied by an increase in the rate of electron transfer. For both photoinduced electron-transfer steps, there are increases in reaction exothermicity for **3** relative to **2**, arising from the different substituents on the zinc porphyrin subunit, which enhance the rates of reaction for **3**.

The rate of direct reverse electron transfer (i.e., reaction 2) remains insensitive to the molecular architecture, within experimental limits. There are relatively large energy gaps for both electron and hole transfer, but the smallest energy gap for each compound is of comparable magnitude. The slow rates observed appear to be consistent with the large energy gaps, and there seems to be no preferred pathway for this process. Overall, it appears that rates of electron transfer between porphyrinic species are well explained in terms of the simple superexchange model involving electron or hole transfer through orbitals of the spacer moiety, as displayed in Figure 4. The role of the accessory 1,10-phenanthroline residue present in **2** and **3** will be addressed separately using a more appropriate molecular system.

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