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Porphyrin-containing [2]-Rotaxanes: Metal Coordination Enhanced Superexchange Electron Transfer between Noncovalently Linked Chromophores

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In the photosynthetic reaction center (RC) of bacteria, charge separation proceeds via a series of electron-transfer steps between porphyrin-like components and quinones.[1] Numerous synthetic models have been proposed but, contrary to the RC, the various chromophores are, in general, covalently bound.[2] In a few examples, coordination bonds[3] or hydrogen bonds[4] have been utilized to assemble the electron donor and the acceptor. Recently, mechanical links have also been used.[5] The present report is concerned with the photochemical study of the two rotaxanes represented in Figure 1,[5a] abbreviated as $\mathbf{(ZnP)_2/Ag^+/AuP^+}$ and $\mathbf{(ZnP)_2//AuP^+}$, in which the reactants are assembled via coordination bonds and mechanical links, respectively. In particular, we could monitor the formation of the charge transfer state, $\mathbf{(ZnP)(ZnP^{\bullet+})/Ag^+/AuP^\bullet}$ or $\mathbf{(ZnP)(ZnP^{\bullet+})//AuP^\bullet}$, in both compounds, and determine its lifetime. Interestingly, the central silver(I) complex of $\mathbf{(ZnP)_2/Ag^+/AuP^+}$ enhanced the rate of electron transfer from ZnP to the excited triplet ^{3}AuP$^+$, probably via a superexchange mechanism.

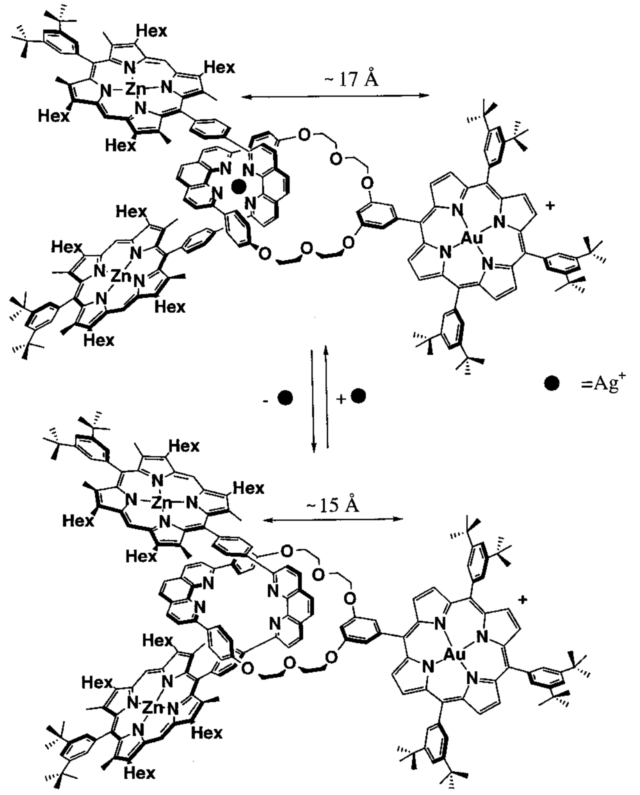

Figure 1. Structure of rotaxanes $\mathbf{(ZnP)_2/Ag^+/AuP^+}$ and $\mathbf{(ZnP)_2//AuP^+}$.

Selective excitation of the ZnP unit at 575 nm in DMF solution at room-temperature resulted in photoinduced electron transfer from the singlet excited-state ^{1}ZnP to the ground-state AuP$^+$:

$$\mathbf{(ZnP)(^1ZnP)//AuP^+} \xrightarrow{\Delta G^\circ = -0.89\ \text{eV}} \mathbf{(ZnP)(ZnP^{\bullet+})//AuP^\bullet} \quad (1)$$

The reaction led to a decrease in fluorescence yield and lifetime of the ^{1}ZnP unit compared to those of the ZnP model porphyrin ($\tau = 2.0$ ns, this work), and the transient absorption spectra revealed the expected features[6] of an initial singlet excited-state ^{1}ZnP that was almost quantitatively converted to the charge-transfer state $\mathbf{(ZnP)(ZnP^{\bullet+})//AuP^\bullet}$. Back-electron transfer followed, as seen by the complete decay of all transient absorption changes, reforming the ground-state molecules within 30 ns:

$$\mathbf{(ZnP)(ZnP^{\bullet+})//AuP^\bullet} \xrightarrow{\Delta G^\circ = -1.25\ \text{eV}} \mathbf{(ZnP)_2//AuP^+} \quad (2)$$

(and the corresponding reaction for the Ag$^+$ rotaxane). The fluorescence decay traces (single photon counting) representing the forward electron transfer (reaction 1) did not follow single-exponential kinetics. Presumably the polyether chain of the macrocycle allows some flexibility, thus leading to the presence of different conformations. Good fits were obtained with a sum of two exponentials with lifetimes of 80 ps (35%) and 570 ps (65%). The transient absorption decay curves at 460−660 nm were well fitted with a sum of three exponentials, two representing the forward reaction 1 and one representing the recombination (reaction 2). The lifetimes obtained from the fits were 80 ps (35%) and 570 ps (65%) for reaction 1, in agreement with the fluorescence data, and ∼10 ns for the subsequent recombination reaction 2. The rate constants calculated for the forward electron transfer are given in Table 1. For the Ag$^+$-containing rotaxane, the corresponding values were very similar (see Table 1). Thus, the insertion of Ag$^+$ resulted only in a slight decrease of the forward electron-transfer rate and no significant effect on the recombination. One may therefore conclude that electron transfer to the Ag(phen)$_2{}^+$ moiety ($\Delta G^\circ = -0.7$ eV[7]) was not significant. Furthermore, the results show that rotation of the macrocycle in $\mathbf{(ZnP)_2//AuP^+}$, bringing the reactants in close proximity, does not occur.

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[6] (a) The transient spectra of the excited- and charge-transfer states of the porphyrins are similar (see ref 8b−d), but the latter are smaller in magnitude. Thus, at all wavelengths (450−660 nm) the forward reaction, reaction 1 or 3, was seen as a decay of the transient absorption. Note also, e.g., the 500 nm shoulder and the 620 nm peak in the ^{3}AuP$^+$ spectrum (after 40 ps in Figure 2) that are absent in the charge-transferred state spectrum (after 4 ns). (b) Brun, A. M.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8657 and references therein. (c) Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1989**, *111*, 6500. (d) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451.

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Table 1. Summary of Forward Electron-Transfer Rate Constants

	$\mathbf{k_{ET}}$ (s^{-1}) (rel. amplitudes)[a]			
	ZnP excitation		AuP^+ excitation	
$(ZnP)_2//AuP^+$	1.2×10^{10}	1.3×10^9	1.1×10^{10}	5×10^8
	(35%)	(65%)	(40%)	(60%)
$(ZnP)_2/Ag^+/AuP^+$	1.2×10^{10}	1.1×10^9	2.0×10^{10}	2.0×10^9
	(35%)	(65%)	(40%)	(60%)

[a] $k_{ET} = 1/\tau - 1/\tau_0$, where τ and τ_0 are the excited-state lifetimes in the rotaxane and the model porphyrin.

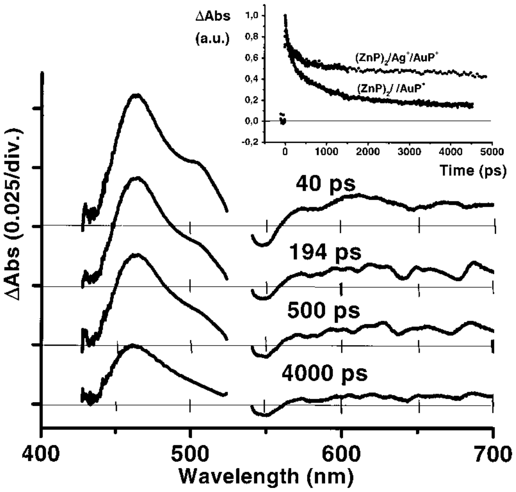

Figure 2. Difference absorption spectra at various times after excitation of $\mathbf{(ZnP)_2/Ag^+/AuP^+}$ with a 150 fs laser pulse[9] at 528 nm (in DMF at room temperature). The inset shows the decay of the 470 nm absorption from the initially formed $^3AuP^+$ as it is converted to the charge-transfer state. On a longer time scale recombination to the ground state occurs (τ = 10 ns) as seen by the complete decay of all transient absorption.

Selective excitation of the AuP^+ unit at 528 nm is expected to generate the AuP^+ triplet within a few ps,[6b,8] and our transient absorption spectra after 40 ps displayed the corresponding features with maxima around 460 and 620 nm[6b] (Figure 2). Electron transfer from the ground-state ZnP to the triplet $^3AuP^+$ followed, as monitored by the transient absorption changes (Figure 2), forming the same charge-transfer products as in reaction 1:

$$\mathbf{(ZnP)_2//{}^3AuP^+} \xrightarrow{\Delta G^\circ = -0.50\ \mathrm{eV}} \mathbf{(ZnP)(ZnP^{\bullet+})//AuP^\bullet} \quad (3)$$

(with the corresponding reaction for the Ag^+ rotaxane). The product yield was lower than with ZnP excitation, presumably because the slower electron transfer (Table 1) competes less favorably with the decay to the ground state (the lifetime of the $^3AuP^+$ model porphyrin was 2.0 ns). Back-electron transfer according to reaction 2 reformed the ground-state molecules also in this case. A sum of three exponentials gave a good fit to the transient absorption decay curves, with lifetimes 90 ps (40%) and 1000 ps (60%) for the forward reaction 3 in $\mathbf{(ZnP)_2//AuP^+}$, and ~10 ns for the recombination reaction. In contrast to the excited ^1ZnP, the $^3AuP^+$ triplet does not emit at room temperature, but its absorption signature (the shoulder at 500 nm and the peak at 630 nm) remained visible after a few hundred ps, showing that both the two fastest components reflected the forward reaction 3. The calculated electron-transfer rate constants are given in Table 1. The lifetime of the back reaction 2 was ~10 ns, in agreement with the results from ZnP excitation. Interestingly, however, the effect of Ag^+ coordination on the forward reaction was now significant and opposite to that when the ZnP was excited. That is, the forward reaction was now *faster* for $\mathbf{(ZnP)_2/Ag^+/AuP^+}$ than for $\mathbf{(ZnP)_2//AuP^+}$, giving lifetimes of 50 ps (40%) and 400 ps (60%) for the former (cf. Table 1). More markedly, also the yield of charge-transfer products was much higher when Ag^+ was coordinated, as seen from the higher absorption signal at the end of the trace (Figure 2, inset). This was mainly due to an increase in the rate of the slower component of the forward reaction, since the fast component was twenty times faster than the $^3AuP^+$ decay to the ground-state already without Ag^+. Thus, from the increase in charge-transfer rate and yield, it is clear that the coordination of Ag^+ enhanced the rate of electron transfer between the porphyrins (reaction 3), despite the larger interchromophoric distance.

Alternative reactions cannot explain the higher reaction rates observed in $\mathbf{(ZnP)_2/Ag^+/AuP^+}$. Excitation, oxidation, and reduction of the $Ag(phen)_2^+$ unit[7] by $^3AuP^+$ can all be ruled out on thermodynamic grounds. Energy transfer to form the singlet ^1ZnP is also endoergonic. Formation of the triplet ^3ZnP is exoergonic, but its lifetime is relatively long in this rotaxane[10] so that an absorption *increase* with time would have been observed around 450−480 nm. Finally, the enhanced rate cannot be explained by a simple Ag^+-induced structural change that would bring the reactants closer to each other, because then the reaction from the excited ^1ZnP would also have been faster.

Instead, we propose that the coordination of Ag^+ increased the reaction rate in a superexchange mechanism[11,12] involving the bridging structure of the rotaxane between the porphyrin units. Coordination of Ag^+ will certainly increase the electronic coupling between the phenanthrolines that link the macrocycle and the dumbbell ”rod” together. For electron transfer from ^1ZnP, the mediating orbitals would presumably be the LUMO of the link (“electron-transfer pathway”[12,13]). For the reaction starting from ^3AuP instead, the HOMO of the link are more likely to dominate (“hole transfer pathway”[12,13]). From our results it would seem that only the “hole transfer pathway” is enhanced by coordination of Ag^+. A difference between HOMO and LUMO coupling is not surprising, given the complicated, asymmetric electronic structure of the rotaxanes. This is in contrast to previously reported systems with only repeated units of hydrocarbon sigma bonds between the reactants, in which a symmetric HOMO/LUMO mediation was observed.[13]

There was no significant effect of Ag^+ on the recombination (reaction 2), within experimental error. We note that the ~10 ns lifetime of the charge-transfer state is the longest so far in this series of rotaxanes,[3a] and the charge-transfer yield is still >80% in the Ag^+ rotaxane, irrespective of excitation wavelength.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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