Electronic coupling in oblique bisporphyrins

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ABSTRACT

Rates of photoinduced electron transfer were measured for a bisporphyrin, comprised of gold(III) and zinc(II) porphyrinic subunits separated by a 2,9-diphenyl-1,10-phenanthroline spacer, in butyronitrile at various temperatures, solvents of differing polarity at ambient temperature, and frozen ethanol. Corresponding data were collected for rotaxanes formed by coordination of the phenanthroline to a metal complex and ring closure. Treating the data according to nonadiabatic electron transfer theory provides values for the extent of electronic coupling between porphyrins, total reorganization energy, and rate of electron transfer at zero activation free energy. These parameters are discussed in terms of the molecular architecture.

A. INTRODUCTION

Photoinduced electron transfer (ET) between porphyrin subunits has been studied extensively in recent years, mainly because of the relevance to natural and artificial photosynthesis. Several different sets of covalently linked bisporphyrins have been synthesized and the rates of intramolecular ET determined by ultrafast transient spectroscopy. By way of these and companion studies made with nonporphyrinic chromophores, and following from detailed theoretical treatments, many of the factors which serve to control the dynamics of ET processes have been elucidated. Particular interest has been given to molecular systems in which ET is mediated by orbitals on the connecting spacer moiety since such systems represent simple models for the protein-bound natural reaction centre complexes. Our work in this area has focussed on the design of systems for which the magnitude of electronic coupling between remote porphyrin subunits can be varied. This strategy permits modulation of the rate of ET by way of structural modification of the spacer function.

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B. METHODOLOGY

Our basic building block consists of the gold(III)/zinc(II) bisporphyrin shown in Figure 1 [1]. This compound has the two porphyrin rings separated by a 2,9-diphenyl-1,10-phenanthroline spacer such that the edge-to-edge (centre-to-centre) separation is ca. 8.5 Å (13.5 Å). Each porphyrin can be selectively excited and considerable evidence has been advanced to indicate that photoinduced ET occurs from zinc porphyrin (ZnP) to appended gold porphyrin (AuP^+) [1-5]. Direct excitation of the ZnP generates the excited singlet state whereas light absorption by the AuP^+ produces the corresponding excited triplet state. Both excited states react to give a common charge-transfer state.

$$^*(ZnP)\text{-}S\text{-}(AuP^+) \rightarrow (\cdot^+ZnP)\text{-}S\text{-}(AuP^\cdot)$$

$$(ZnP)\text{-}S\text{-}(AuP^+)^* \rightarrow (\cdot^+ZnP)\text{-}S\text{-}(AuP^\cdot)$$

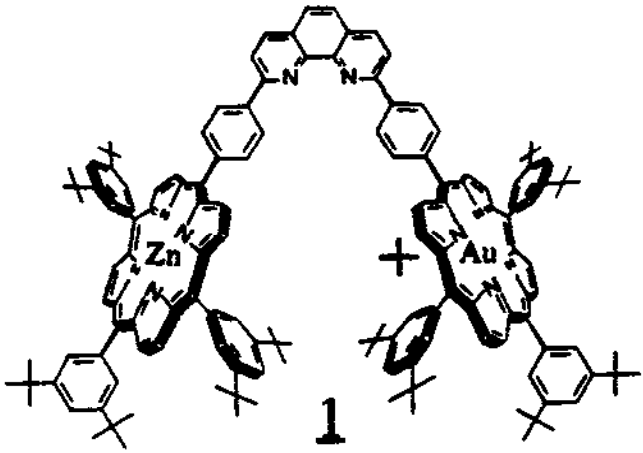

Figure 1. Structure of the bisporphyrin.

The rates of both ET processes have been measured under various conditions and used to quantify the magnitude of electronic coupling between the porphyrin subunits. It should be noted that ET via the ZnP involves through-bond electron transfer whereas ET via the triplet state of the AuP^+ involves through-bond hole transfer [3].

In order to elicit this information, we have used conventional nonadiabatic ET theory to formulate the rate constant for the ET process (k):

$$k = (4\pi^2/h)|V|^2(FCWD)$$

$$FCWD = [4\pi\lambda_S k_B T]^{-1/2}\sum_{w=0}^{\infty}(e^{-S}S^w/w!)\exp\{-[\lambda_S + \Delta G^\circ + whcv)^2/4\lambda_S k_B T]\}$$

$$S = \lambda_V/hcv$$

Here, V is the electronic matrix coupling element, λ_S and λ_V respectively are the solvent and nuclear reorganization energies, ΔG° is the reaction exergonicity, and ν is a single skeletal vibration of 1500 cm^{-1}. Measurement of k as a function of temperature gives rise to V and λ ($\lambda = \lambda_S + \lambda_V$) while measuring k in solvents of differing polarity permits evaluation of the rate of ET at zero activation free energy change (k_o). The latter parameter facilitates direct comparison of ET rates for different bisporphyrins without having to correct for variations in thermodynamic properties of individual systems.

C. RESULTS

Temperature-dependence studies carried out with the bisporphyrin 1 in butyronitrile (BuCN) solution allowed calculation of V and λ for reaction via ZnP (Table 1) and AuP^+ (Table 2) subunits [3]. Similar studies made with solvents of differing polarity at room temperature provided the data required to determine k_o (Tables 1 and 2). Related studies were made in frozen ethanol glasses but it was found that ET occurred only via the ZnP subunit [5]. The derived parameters are collected in Table 2. Studies were made also with the bisporphyrin-stoppered rotaxanes 2-4 whose structures are shown in Figure 2 [4]. Again, the derived parameters are compiled in Tables 1 and 2.

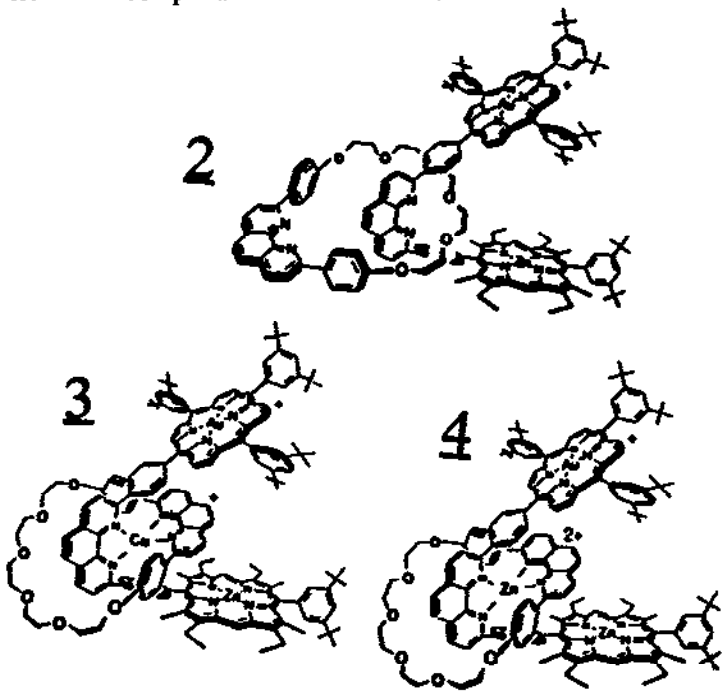

Figure 2. Structures of the rotaxanes 2-4.

TABLE 1. ET parameters for excitation into the ZnP subunit

Compound	Solvent	V (cm^{-1})	λ (eV)	$k_o/10^{10}$ (s^{-1})	δE_{AB} (eV)
1	BuCN	85	1.67	16	0.73
1	EtOH glass	0.5	0.09	0.02	1.44
2	BuCN	30	0.89	5	0.50
3	BuCN	180	0.80	60	0.15
4	BuCN	60	0.80	16	0.55

TABLE 2. ET parameters for excitation into the AuP^+ subunit

Compound	Solvent	V (cm^{-1})	λ (eV)	$k_o/10^{10}$ (s^{-1})	δE_{AB} (eV)
1	BuCN	110	1.53	56	0.65
2	BuCN	12	0.93	2	0.65
3	BuCN	100	0.73	19	0.60
4	BuCN	34	0.75	6	0.63

D. DISCUSSION

According to our theoretical model, the rate constant for ET (k) should depend on the square of the electronic matrix coupling element (V). In order to avoid complications arising from differing reaction exergonicities, we have used k_o to express the rate constant values. The experimental data are in good agreement with this prediction (Figure 3); data collected for both singlet and triplet excited states fit on a common plot. This relationship establishes that ET steps for the various bisporphyrins are well explained in terms of conventional nonadiabatic ET theory.

For a superexchange (i.e., through-bond) ET process, V can be expressed as: $V = (\beta_A\beta_B)/\delta E_{AB}$ where β_A and β_B refer, respectively, to electronic coupling factors between inital state and spacer and between spacer and final state while δE_{AB} is the energy gap between the initial state and the spacer. These latter values have been determined from electrochemical measurements and are compiled in Tables 1 and 2. It is seen that the nature of the bisporphyrin affects the magnitude of the δE_{AB} value and, in turn, this can modulate the rate of ET for that particular step. Assuming that the $\beta_A\beta_B$ term remains constant throughout the series, we would expect to observe

a linear correlation between k_o and $(1/\delta E_{AB})^2$. As can be seen from Figure 4, even after omission of the data determined in a frozen ethanol glass [5], there is no obvious correlation between the rate of ET and the energy gap. This finding demonstrates that the molecular architecture influences the $\beta_A\beta_B$ parameters and thereby alters the rates of photoinduced ET.

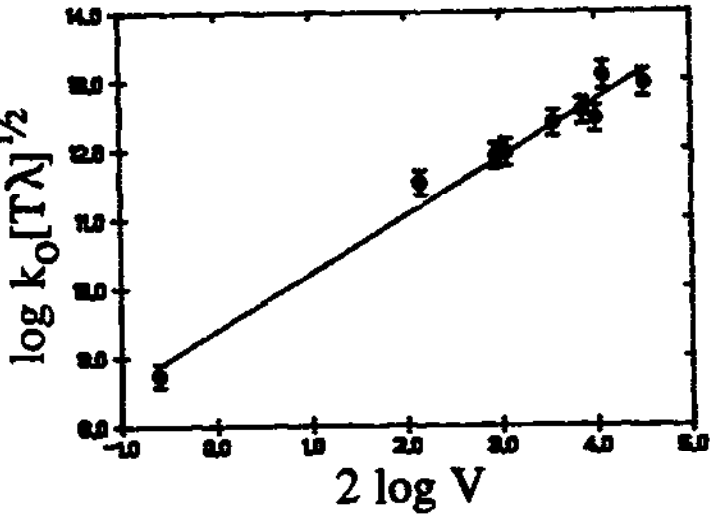

Figure 3. Correlation between k_o and electronic matrix coupling element.

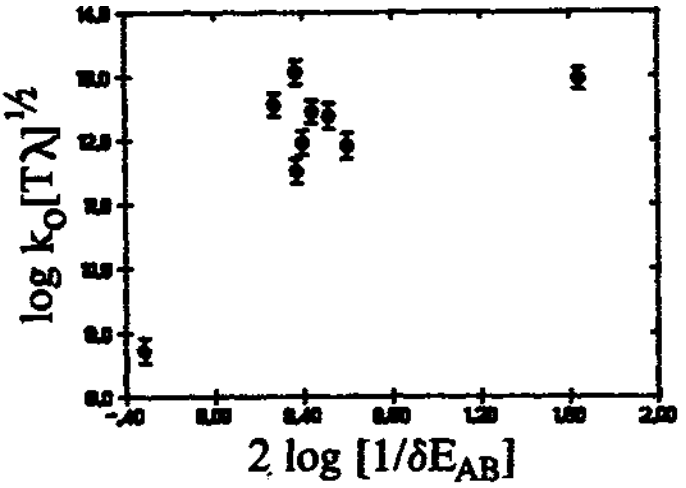

Figure 4. Correlation between k_o and energy gap.

E. REFERENCES

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