Relationship Between Electron Transfer and the Structure of a Quinone-linked Zinc Porphyrin with a Flexible Peptide Spacer

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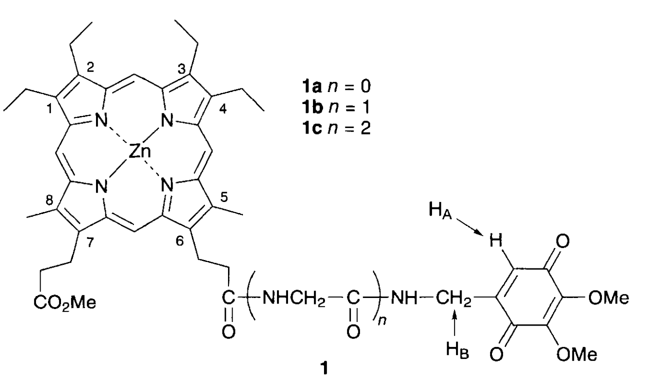
The solvent-dependent conformational change of the covalently linked porphyrin–peptide–quinone triad **1**, as determined by ^{1}H NMR and electronic absorption spectra, obviously reflects an intramolecular electron transfer reaction from the zinc porphyrin to quinone in both polar and nonpolar solvents.

Photoinduced electron transfer (ET) from zinc porphyrin to quinone is one of the most interesting reactions in chemistry and biochemistry for the elucidation of the ET mechanism in biological systems.[1] We have recently reported the intermolecular interaction of the face-to-face mode between modified porphyrin and ubiquinone analogues and the rapid ET reaction between these two components.[2] Here we describe the relationship between the structure of the covalently linked porphyrin–peptide–quinone triad **1** and the observed behaviour of intramolecular photoinduced ET in polar and nonpolar solvents.[3]

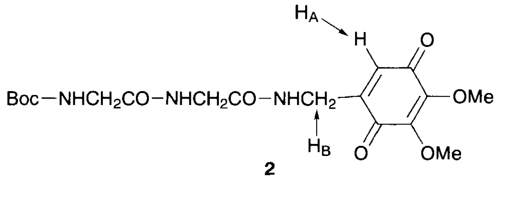
Compound **1** was designed as follows: firstly, the parent porphyrin has four ethyl groups at peripheral 1,2,3 and 4 positions to form a C_2-symmetrical structure to avoid the difficulty in separation of two isomers, which are afforded by the condensation reaction between native protoporphyrin and amino acid;[4] secondly, the peptide spacer between the porphyrin and quinone components brings about positional freedom for both electron donor and acceptor.[5]†

^{1}H NMR spectra of **1** at ambient temperature were observed in $CDCl_3$ and $[^2H_6]Me_2SO$, and all protons were unambiguously assigned by two-dimensional NMR. Table 1 displays the chemical shifts of the quinone (H_A) and methylene (H_B) protons of the spacer in **1** and **2**. Large upfield shifts of these protons in **1** owing to the diamagnetic ring current of porphyrin are found in $CDCl_3$. In contrast, the same proton resonances in $[^2H_6]Me_2SO$ are shifted only slightly upfield relative to **2**. Comparison of these results suggests that the quinone is situated so close to the porphyrin ring as to form a cofacial π–π interaction in the nonpolar solvent, although in polar solvents such as Me_2SO, no interactions are detected and the spacer seems to be extended.‡ Furthermore, the Soret band of **1** exhibits a red shift compared with 1,2,3,4-tetraethyl-5,8-dimethyl-6,7-dimethoxycarbonylethylporphyrin zinc complex **3** which has no quinone attached. The λ_{max} of **1c** shifts from 403 to 408 nm in CH_2Cl_2; however, a similar spectral change is not observed for **1** in Me_2SO. It is likely that the Me_2SO molecules impede the cofacial interaction by solvating the polar functions such as the amide groups and the quinone moiety of **1**.



1a *n* = 0
1b *n* = 1
1c *n* = 2

1



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The solvent-dependent conformational change also reflects an intramolecular ET reaction from the zinc porphyrin to quinone.[6–8] The fluorescence spectra of **1** in CH_2Cl_2 are almost identical to those obtained in Me_2SO, but are more quenched. The relative fluorescence intensities of **1**, based on a spectrum of **3** as a standard, decrease with the decreasing number of glycine units in Me_2SO, as shown in Fig. 1; the relative intensities of **1c**, **1b** and **1a** are 42, 33 and 5%, respectively. In contrast, the fluorescence of **1** in CH_2Cl_2 is markedly quenched compared with **3**, and the observed relative intensities of the fluorescence emissions in CH_2Cl_2 are less than 10%.§ The rate constants, k_{ET}, of the ET reaction in Me_2SO increase with the decreasing number of glycine units in the spacer of **1**,¶ thus, the ET rate in Me_2SO exhibits a clear dependence on the distance between the porphyrin and quinone moieties: **1a**: $k_{ET} = 9.5 \times 10^9$; **1b** $k_{ET} = 1.2 \times 10^9$ **1c** $k_{ET} = 0.5 \times 10^9\ s^{-1}$ at 25 °C.‖ In contrast, this reaction in CH_2Cl_2 proceeds too fast to determine the fluorescence lifetime using sub-nanosecond-order instrument, and would be less sensitive to the length of the spacer between the porphyrin and quinone moieties. Thus, the efficiency of the fluorescence quenching of **1** in CH_2Cl_2 is explained by substantial formation of intramolecular face-to-face type interactions controlled by solvation.[9]

Both ^{1}H NMR and fluorescence measurements indicate flexibility of the peptide spacer between the zinc porphyrin and quinone. The present triad provides us with a suitable system for studying the mechanism of intramolecular ET relevant to conformational changes owing to solvent effects. Current efforts are being devoted to exploring further the physical properties of reconstituted myoglobin by the use of **1**.

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Table 1 ^{1}H NMR chemical shifts of the quinone parts at ambient temperature

		Solvent	
	Proton	$CDCl_3$[a] δ	$[^2H_6]Me_2SO$ δ
1a	H_A	3.140 (3.295)	6.144
	H_B	3.651 (0.564)	3.902
1b	H_A	3.117 (3.318)	6.124
	H_B	1.191 (3.024)	3.717
1c	H_A	3.825 (2.610)	6.387
	H_B	1.208 (3.007)	4.040
2	H_A	6.435	6.366
	H_B	4.215	4.024

[a] The results of upfield shifts of H_A and H_B based on **2** are given in parentheses.

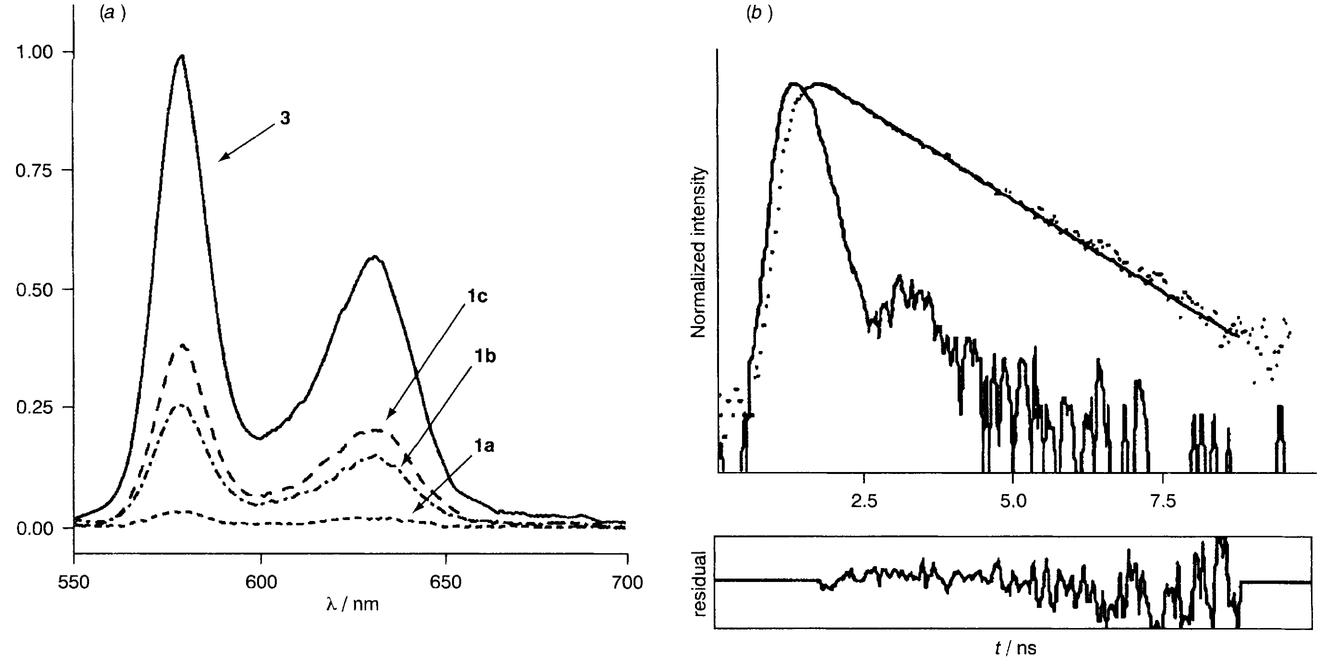

Fig. 1 (*a*) Normalized fluorescence spectra obtained of **1** and **3** in Me_2SO at 25 °C with excitation wavelengths at 539–540 nm. (*b*) Fluorescence decay profiles obtained in the range 560–760 nm from 3×10^{-6} mol dm^{-3} solutions of **1c** at room temperature in Me_2SO: excitation wavelength at 544 nm by N_2 dye laser.

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Footnotes

† Compounds **1a–c** were characterized by 500 MHz ^1H NMR and high resolution mass spectral data. Experimental details for the syntheses and characterizations of these compounds will be provided in a forthcoming paper.

‡ The proton resonances of the methylene spacer in the free base of **1** shows similar large upfield shifts to those observed for the zinc complex of **1**: the chemical shifts of protons H_A and H_B in **1c** are δ 4.153 and 1.594, respectively. The contribution from the coordination of the quinone moiety to the zinc atom seems not to be crucial for the cofacial interaction.

§ Fluorescence quenching of **3** was not observed in the presence of equimolar amounts of 2,3-dimethoxy-5-methyl-*p*-benzoquinone.

¶ The rate constants of the ET reaction, k_{ET}, were determined from analyses of the following fluorescence decay profiles: **1a** $\tau = 0.1$; **1b** $\tau = 0.6$; **1c** $\tau = 1.0$; **3** $\tau = 2.0$ ns at 25 °C in Me_2SO; $k_{ET} = (1/\tau_1) - (1/\tau_3)$. τ_1 and τ_3 are the fluorescence lifetimes of **1** and **3**, respectively.

|| The ET rate constant k_{ET} is given by $k_{ET} = \nu \exp(-ar_{ee})$, where ν is Frank–Condon term and r_{ee} is the distance between donor and acceptor. Plot of ln k_{ET} *vs.* the distance from edge-to-edge of porphyrin–quinone **1a–c** shows the linear realtionship (coefficient of correlation $r = 0.97$, $a = 0.43$ Å^{-1}, $\nu = 7.7 \times 10^{10}$).[6] The distances r_{ee} of the most extended conformation of **1a–c** are estimated to be 5.4, 8.8 and 12.3 Å, respectively, from CPK molecular models.

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