J. Am. Chem. Soc. **1993,** *115,* 7003–7004

Controlled Electron Transfer between Cyclodextrin-Sandwiched Porphyrin and Quinones

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Received January 12, 1993

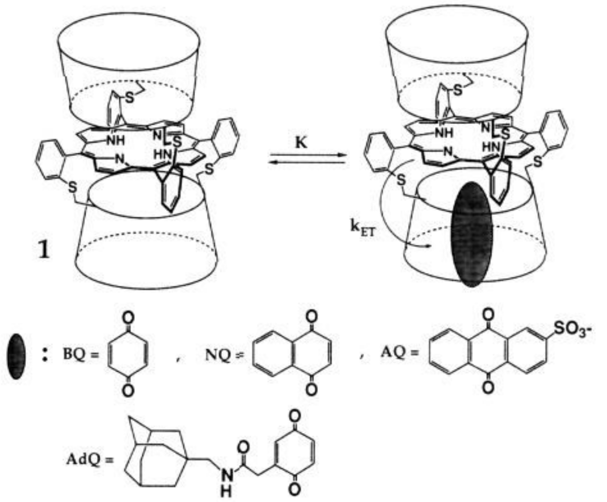

Figure 1. Cyclodextrin-sandwiched porphyrin and quinone derivatives.

Among various types of electron-transfer reactions, a photoinduced electron transfer between porphyrins and quinones has been attracting much attention from the viewpoint of biomimetics on the initial process of photosynthetic systems.[1] One recent interest in this field is the construction of self-assembling systems consisting of porphyrin and quinone components which mimic the characteristics of the natural photoreaction center.[2] We report here a unique porphyrin–quinone system which carried out specific electron-transfer reactions in an aqueous solution based on hydrophobic molecular recognition of quinone components. The system reported here shows highly specific binding toward quinone derivatives and clear relationships between electron transfer and binding compared with previous examples.[3]

We employed here cyclodextrin-sandwiched porphyrin (**1**)[4] and three types of quinones, benzoquinone (**BQ**), naphthoquinone (**NQ**), and anthraquinone-2-sulfonate (**AQ**), as the electron donor and acceptors, respectively (Figure 1). Specific binding of quinones **NQ** and **AQ** into the hydrophobic cavity of **1** is demonstrated by spectroscopic titration using Q-band absorption of **1** in a Sørensen's phosphate buffer solution (pH 9.0), which gave their association constants to be 7400 ± 300 and 22 000 ± 5000 M^{-1}, respectively.[5] Interestingly, addition of **BQ** under the same conditions results in no appreciable spectroscopic change corresponding to those observed for **NQ** and **AQ**. The sharp contrast of binding behavior between **BQ** and other quinones becomes more clear in the fluorescence quenching experiments. Stern–Volmer plots for the system consisting of **1** and these quinones are shown in Figure 2. Fluorescence from the porphyrin unit in **1** is quenched upon addition of **NQ** and **AQ**, and nonlinear saturation dependencies of their relative quantum yields on the concentrations of the quinones are observed. In contrast to these results, only very weak fluorescence quenching and a linear concentration dependency are observed when **BQ** is employed as the quencher. These observations suggest that **NQ** and **AQ** are bound into the hydrophobic cavity of the cyclodextrin unit of **1**, to result in effective photoinduced electron transfer within the complex, while complex formation between **BQ** and **1** is negligible or minor under the present conditions and, therefore, the intramolecular electron transfer in this system is ineffective. The conclusions are further supported by more interesting observations obtained from inhibition experiments using 1-adamantanecarboxylate (**Ad**), which is known to be a good substrate for cyclodextrin.[6] The association constant between **1** and **Ad** is estimated to be larger than 5×10^5 M^{-1} from spectroscopic titration. Fluorescence quenching observed for **NQ** and **AQ** ([**1**] = 6.1 μM) is completely suppressed in the presence of 240 μM **Ad**, and their concentration dependencies become identical with that of **BQ**, as shown in Figure 2. Thus, it is evident that the present photoinduced electron-transfer reactions from **1** to **NQ** and **AQ** proceed via reversible association between these components. Since the intermolecular interaction operating in these complexes is expected to be mostly a hydrophobic one, there is a very interesting possibility that the quenching ability of quinones may be controlled by addition of a hydrophobic attachment to quinones. This possibility is tested by using a new quinone

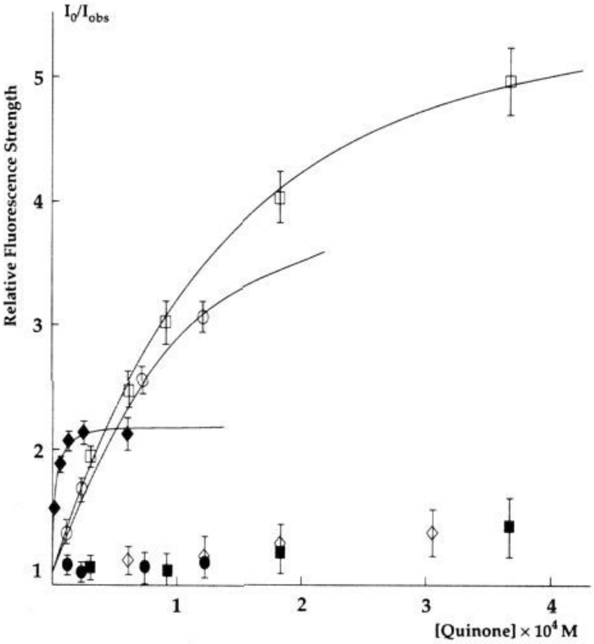

Figure 2. Stern–Volmer plots for the systems consisting of **1** (6.1 μM) and quinones in Sørensen's phosphate buffer (5 mM, pH 9.0) at 23 °C. The excitation wavelength was 524 nm, and the fluorescence intensity was monitored at 654 nm (□, **NQ**; ■, **NQ** + **Ad** (240 μM); ○, **AQ**; ●, **AQ** + **Ad** (240 μM); ◇, **BQ**; ◆, **AdQ**).

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(5) Since **1** has two equivalent cyclodextrin binding sites, a 1:2 complex formation model may be logically expected for the present binding process. The spectroscopic changes in titration experiments, however, show clear isosbestic points, and it is not possible to differentiate 1:1 and 1:2 complex formation processes. Therefore, the association constants are tentatively estimated on the basis of the 1:1 complex formation model.

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Table I. Fluorescence Lifetimes and Electron-Transfer Rate Constants of the Self-Assembling Systems Consisting of 1 and Quinones[a]

quinone	τ_1 (ns)	τ_2 (ns)	$(A_1/A_2)[Q]$ (μM)[b]	k_{ET} (s^{-1})[c]
none	3.2 ± 0.2			
NQ	3.2 ± 0.3	0.5 ± 0.1	200 ± 50	2×10^9
AQ	3.2 ± 0.2	0.7 ± 0.1	40 ± 20	1×10^9
AdQ	3.7 ± 0.3	0.7 ± 0.2	10 ± 5	1×10^9

[a] In the aqueous Sørensen's phosphate buffer (5 mM) pH 9.0 and at 23 °C. All samples were degassed by freeze–pump–thaw, and the measurements were carried out under Ar atmosphere. The lifetime data were obtained on a Hamamatsu picosecond fluorescence lifetime measuring system type C4780 equipped with a N_2 laser-pumped dye laser (cumalin 500), LN120C1, PRA LASER INC. The concentration of **1** was kept at 6.0 μM, and the several sets of time-resolved fluorescence data (λ_{ex} = 517 nm) were collected at the concentration range from 0 to 3 mM quinones. Data were satisfactorily analyzed by the double exponential equation, $I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, using the single-photon-counting data of 690 – 750 nm. [b] The slope of the (A_1/A_2) vs $[\text{quinone}]^{-1}$ plot. Assuming the present model, the values of $(A_1/A_2)[Q]$ should correspond to those of K_{ass}^{-1} for each quinone. [c] The electron-transfer rate constant derived from $k_{ET} = \tau_1^{-1} - \tau_2^{-1}$.

derivative (**AdQ**) which is prepared from (2,5-dihydroxyphenyl)-acetic acid and 1-adamantanemethylamine.[7] The new quinone **AdQ**, as expected, shows very high affinity toward **1** ($K > 5 \times 10^5$ M^{-1}) and exhibits effective fluorescence quenching for **1**, which forms a striking contrast with the quenching behavior of **BQ** (See Figure 2). Although it is difficult to detect radical species directly by ESR under the same conditions as those for quenching experiments because of the high dielectric nature of the aqueous solvent, ESR measurement of the present system in a frozen form showed photoinduced radical formation. Irradiation of the frozen solution (pH 8.8) of **1** (4.4×10^{-5} M) and **AdQ** (4.6×10^{-5} M) with a 500-W Xe lamp through a 470-nm cutoff filter at −134 °C for 5 min induced a single-line ESR signal (g = 2.0027), which may be assigned to a mixture of the porphyrin cation radical and the quinone radical anion.[3a,8]

Based on these results, we further analyze present electron-transfer reactions by means of time-resolved fluorescence spectroscopy. The fluorescence decay profile of **1** is a clean single exponential with $\tau_s = 3.2 \pm 0.2$ ns without quinones[9] and becomes biphasic in the presence of **NQ**, **AQ**, and **AdQ**. The obtained lifetimes are summarized in Table I. The lifetimes for long-lived (τ_1) and short-lived (τ_2) components determined for the each system remained constant, but the relative contribution of the short-lived component increases with increasing concentration of the quinone. The observed τ_1 values agree with the intact lifetime of **1** (τ_s) within experimental error. Assuming the simplest model where the electronic interaction between quinone and porphyrin components at the ground state is negligibly weak,[10] the rate constants of the intramolecular electron transfer (k_{ET}) are evaluated to lie in 10^9 s^{-1} order in all cases (see Table I). The estimated k_{ET} values are quite reasonable for this type of rate constants compared with previously reported examples,[2b,11] though there is an interesting difference between present and other models: the quinone approaches the porphyrin from its out-of-plane direction in the present system but from the in-plane one in other systems (Figure 3).

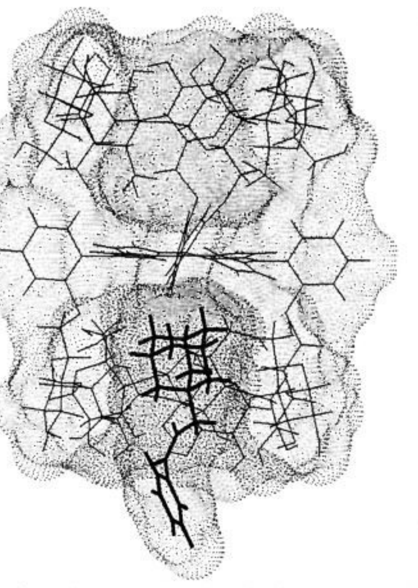

Figure 3. One of possible structures of the **1·AdQ** complex optimized by molecular mechanics calculations using NMRGRAPH, Molecular Simulations Inc. Dots show the solvent-accessible surfaces of **1** and **AdQ**.

The system reported here is suitable for systematic investigations of electron-transfer reaction in systems with no covalent bonds, because it is possible in the present system to design binding sites and reaction sites in substrates separately. Further investigations along this line are now underway.

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(7) The NMR and mass spectra of **AdQ** are satisfactory for the expected structure: ^{1}H NMR ($CDCl_3$, TMS) δ 1.37–2.10 (m, 15H), 2.97 (d, 2H), 3.37 (s, 2H), 5.90 (br s, 1H), 6.78–6.90 (m, 3H), MS m/z found 313.1647, calcd. 313.1677 for $C_{19}H_{23}NO_3$.

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