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Evidence for Parallel Photoinduced Electron Transfer in Diquinone Substituted Porphyrins

Victor V. BOROVKOV,*,+ Akito ISHIDA, Setsuo TAKAMUKU, and Yoshiteru SAKATA*
The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 567

Fluorescence spectra and decay kinetics of diquinone substituted porphyrins were examined in a comparison with those of monoquinone substituted porphyrins. Fluorescence quenching of the diquinone molecules is larger than that of the monoquinones and the electron-transfer rate constants of the diquinones are larger than those of the monoquinones by a factor of two regardless of the rigidity of the spacer groups indicating the existence of the parallel electron-transfer mechanism in diquinones.

So far much attention has been concentrated on the fundamental problem of solar energy conversion in photosynthesis and a large number of artificial photosynthetic models have been developed.1-3) Most of the models, however, are consisted of a covalently linked pair of a donor and acceptor with 1:1 ratio, although formally there are two channels for electron transfer in natural photosynthetic reaction centers. There is only one example4) demonstrated some difference in photochemical properties between di- and mono-substituted capped porphyrin-quinones, which is interpreted in terms of an orbital symmetry effect.

In order to get further information on multi electron-transfer processes, we have synthesized diquinone substituted porphyrins **1** and **4** with rigid or flexible covalent spacers and studied their photochemical behaviors in comparison with those of monoquinone substituted porphyrins **2** and **5**. The model systems **1**, **2**, **4**, and **5** are distinguished by the number of quinone substituents (one in **2**, **5** and two in **1**, **4**) and by the nature of covalent bridges (rigid spiro type in **1**, **2** and flexible ester bridge in **4**, **5**). Based on molecular model considerations the center-to-center (or edge-to-edge) distances between porphyrin and quinone rings in the two rigid compounds **1** and **2** are the same, i.e. 12.5 Å (8.2 Å). For flexible compounds **4** and **5** it is quite difficult to determine exact distances which are widely varied from 3.4 Å (full folded conformation) to 14 Å (full linear conformation) due to spacial liability. On the basis of ^{1}H NMR analysis5-8) we assumed previously that for such structures with flexible covalent bonds between chromophores the conformational equilibrium is shifted to the folded form and for the diquinone derivatives both quinone moieties locate on the opposite sides of the porphyrin plane.

The synthesis9) of the rigid compounds **1**,10) **2**,11) and reference compounds **3** was performed by using the dipyrrolmethane cyclization method with Cl_3CCOOH12,13) as a catalyst. Diquinone porphyrin **1** was isolated as a mixture of α,α– and α,β–isomers, which show identical R_f values and could not be separated.

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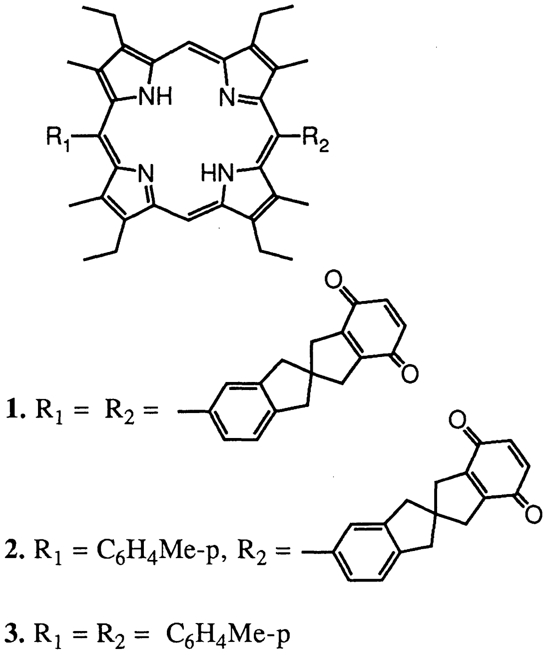
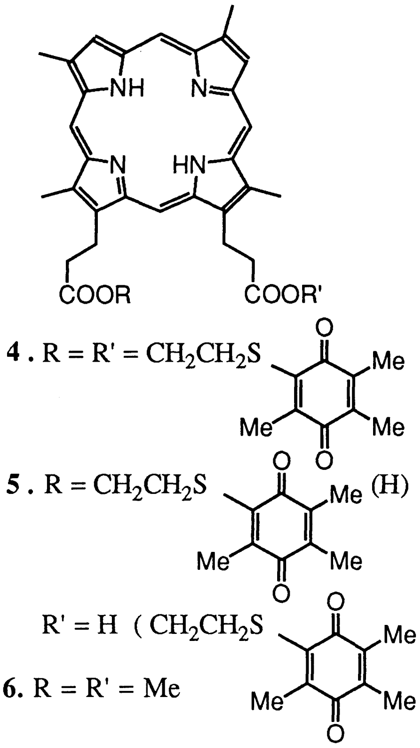
Obviously, their photochemical properties should be almost identical due to the similarity of energetic parameters and interchromophore distances. The porphyrin-quinone **4** was synthesized as described previously.6) The mono-substituted porphyrin **5** was obtained as a mixture of isomers at 13 and 17 substituted positions of porphyrin ring by the partial hydrolysis with 4 mol dm^{-3} HCl14) of diquinone derivative **4**.



1. $R_1 = R_2 =$

2. $R_1 = C_6H_4Me\text{-}p$, $R_2 =$

3. $R_1 = R_2 = C_6H_4Me\text{-}p$



4. R = R' = CH_2CH_2S

5. R = CH_2CH_2S (H)

R' = H (CH_2CH_2S)

6. R = R' = Me

Electronic spectra (Table 1) of **1**, **2**, **4**, and **5** are similar to those of corresponding reference porphyrins **3** and **6** without any changes and total spectrum is a superposition of porphyrin and quinone spectra. It indicates that there are no appreciable interactions between two chromophores in the ground state (S_0) that is typical for such model compounds.6-8,15,16)

Table 1. Absorption and Steady-State Fluorescence Spectroscopic Data for **1**-**6**

Compound	Soret band		β band		α band	
	λ_{max}/nm	λ_{ex}/nm	λ_{em}/nm	$I_{em} \times 10^{-2}$ a)	λ_{em}/nm	$I_{em} \times 10^{-2}$ a)
3	403.6	405	629	100	696	100
2	404.4	405	629	27	696	27
1	404.8	405	629	17	696	19
6	393.2	394	621	100	687	100
5	393.6	394	621	7.7	687	8.6
4	394.4	394	621	1.4	687	1.5

a) $\lambda_{em} > 560$ nm (by 0 - 560 filter), C = 10^{-6} mol/L, acetone.

Fluorescence intensities (Table 1) of all porphyrin-quinones **1**, **2**, **4**, and **5** are considerably quenched in comparison with those of **3** and **6** due to intramolecular electron transfer from the singlet exited state of porphyrin moiety to quinone electron acceptor. However, it was found as for rigid structures **1**, **2** and for flexible **4**, **5** the relative fluorescence yields of diquinone substituted porphyrins **1**, **4** are smaller than those of corresponding monoquinones **2** and **5**. Fluorescence decay kinetics of **1**, **2**, **4**, and **5** are well fitted by a sum of two exponential curves with short-lived component τ_1 and long-lived component τ_2 (Table 2). The τ_1 component dominates over than 80% for all porphyrin-quinones excepting mono-substituted porphyrin **5**. The τ_2 components of **1**, **2**, **4**, and **5** are close to the lifetimes of the single exponential fluorescence decay curves of **3** and **6**. Reasonable explanation for the τ_2 component is the presence of reduced form of quinone residues in **1**, **2**, **4**, and **5** and for flexible compounds **4** and **5** due to their conformation liability there is possibility of the presence of some conformations in which electron transfer does not take place. The τ_1 lifetimes related to intramolecular charge separation process were used to determine electron-transfer rate constants for **1**, **2**, **4**, and **5** (Table 2). It is remarkable to notice that k_{et} value of diquinone substituted porphyrins **1** and **4** is in approximately two times larger compared with those of the corresponding monoquinone-substituted porphyrins **2** and **5**, regardless of the rigidity of the spacer groups. This is in an agreement with decreasing of the steady-state fluorescence intensities in the diquinones than those in the monoquinones (Table 1). Since the energy gap of electron-transfer reactions and spacial structure of the corresponding pairs of mono- **2**, **5** and diquinone porphyrins **1**, **4** are almost the same, this phenomenon is clear evidence in favor of the parallel electron-transfer mechanism in diquinone substituted porphyrin models in contrast to mono-substituted derivatives due to the presence of the second quinone acceptor moiety. As far as our knowledge is concerned, this is the first example that showed experimentally the relationship between electron-transfer rates and the number of electron-transfer processes. The finding in this study will be useful in designing molecular devices for the achievements of efficient electron transfer.

Table 2. Fluorescence Lifetimes and Electron-Transfer Rate Constants for **1-6**

Compound	Lifetime a) τ_1/ns	Quantum yield ϕ_1 b) of τ_1 exponent/ %	Lifetime a) τ_2/ ns	Quantum yield ϕ_2 b) of τ_2 exponent/ %	k_{et} c)/ $10^9 s^{-1}$
3	-	-	14.2	100	-
2	3.38	83.3	12.1	16.7	0.25
1	1.63	83.9	12.9	16.1	0.54
6	-	-	17.4	100	-
5	0.77	44.1	14.6	55.9	1.23
4	0.41	97.9	14.8	2.1	2.37

a) $\lambda_{em} > 560$ nm (by O - 560 filter), C = 10^{-6} mol/L, acetone.

b) Relative quantum yield ϕ_i was calculated by the equation $\phi_i = a_i\tau_i/\Sigma a_i\tau_i$.

c) Electron transfer rate constants were calculated using the equation $k_{et}=1/\tau_1 - 1/\tau_2$ (τ_2 of **3** or **6**).

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9) Synthesis of **1-3** will be reported elsewhere.

10) **1**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 10.22(2H, s, meso H), 7.87(2H, d, J=7.5 Hz, arom H), 7.86(2H, s, arom H), 7.54(2H, d, J=7.5 Hz, arom H), 6.76(2H, s, quinone H), 4.03(8H, q, J=7.5 Hz, $C\mathit{H}_2CH_3$), 3.34(4H, s, spiro CH_2), 3.23(4H, s, spiro CH_2), 3.13(4H, d, J=17.0 Hz, spiro CH_2), 3.06(2H, d, J=17.0 Hz, spiro CH_2), 2.53(12H, s, CH_3), 1.78(12H, t, J=7.5 Hz, $CH_2C\mathit{H}_3$), -2.42(2H, br. s, NH); MS (FAB) 979($(M+6H)^+$, 43%), 978($(M+5H)^+$, 46), 977($(M+4H)^+$, 95), 976($(M+3H)^+$, 100), 975($(M+2H)^+$, 62), 974($(M+H)^+$, 57), 973(M^+, 16).

11) **2**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 10.22(2H, s, meso H), 7.95(2H, d, J=7.5 Hz, arom H), 7.87(1H, d, J=7.5 Hz, arom H), 7.86(1H, s, arom H), 7.54(3H, d, J=7.5 Hz, arom H), 6.75(2H, s, quinone H), 4.03 (4H, q, J=7.5 Hz, $C\mathit{H}_2CH_3$), 4.02(4H, q, J=7.5 Hz, $C\mathit{H}_2CH_3$), 3.33(2H, s, spiro CH_2), 3.22(2H, s, spiro CH_2), 3.12(2H, d, J=17.1 Hz, spiro CH_2), 3.04(2H, d, J=17.1 Hz, spiro CH_2), 2.72(3H, s, CH_3), 2.52 (6H, s, CH_3), 2.51(6H, s, CH_3), 1.78(6H, t, J=7.5 Hz, $CH_2C\mathit{H}_3$), 1.77(6H, t, J=7.5 Hz, $CH_2C\mathit{H}_3$), -2.42 (2H, br. s, NH); MS (FAB) 820($(M+4H)^+$, 67%), 819($(M+3H)^+$, 100), 818($(M+2H)^+$, 50), 817($(M+H)^+$, 28), 816 (M^+, 6).

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