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A New Approach to Study of Solvent Effect on Intramolecular Electron Transfer

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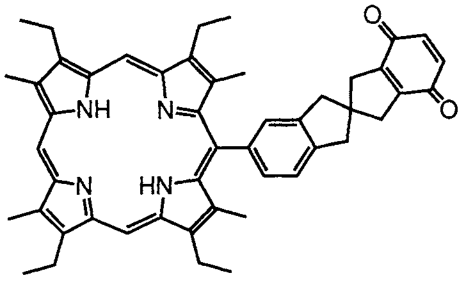
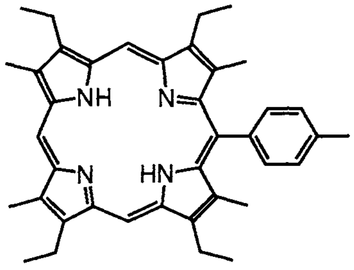
An electron-transfer process in a porphyrin-quinone model compound was studied by steady-state and nanosecond time-resolved fluorescence spectroscopy in thirteen solvents with different polarity (ε_s values ranged from 4.3 to 46.7). Electron-transfer rate constants (k_{et}) and fluorescence quenchings were strongly dependent on the polarity of solvents. The parabolic dependence of $\ln k_{et}$ on optical and static dielectric constant term ($1/\varepsilon_{op} - 1/\varepsilon_s$) was observed for applied solvents.

Photoinduced electron-transfer reactions play an important role in natural biological and chemical processes. In order to understand more deeply these processes various donor-acceptor model compounds[1-3] have been synthesized and studied. Generally, the efficiency of electron transfer depends upon several factors, such as structure of donor-acceptor pair, free energy change between singlet excited (^{1}S) and charge-separated states, and medium effect. Although the role of all factors has been intensively studied[1-4] and experimentally provided data agreed well, in many cases with theoretical predictions, one of the most difficult problem is the investigation of solvent dependence on electron transfer due to ignoring of solvation effect or introduction of correction terms leading to overestimation and some errors. In some cases[5-8] the role of solvent effect has not been detected or was too small or deviated from theory rather large.

Now we report a new approach to study on electron-transfer processes in different solvents with medium and strong polarity using a rigid model compound of porphyrin-quinone **P-Q**,[9] which is quite similar to the previous synthesized models[10,11] with the same intramolecular distances between chromophores. As a reference compound meso-substituted tolyl porphyrin **P** was employed.



P-Q



P

Electronic spectra of **P-Q** in all the solvents used in this study show that there are no appreciable

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Table 1. Fluorescence Lifetimes and Electron-Transfer Rate Constants for **P-Q** and **P** for different solvents

Solvent	Dielectric constant		Lifetime τ_1 b) of P-Q / ns	Quantum yield ϕ_1 c) of τ_1 / %	Lifetime τ_2 b) of P-Q / ns	Quantum yield ϕ_2 c) of τ_2 / %	Lifetime τ_{ref} b,d) of P / ns	k_{et} e) / $10^8 s^{-1}$
	static ε_s	optical ε_{op} a)						
1. Et_2O	4.34	1.83	4.88	97.2	18.1	2.8	16.2	1.43
2. EtOAc	6.02	1.88	3.32	96.0	16.1	4.0	16.8	2.42
3. n-BuCl	7.39	1.97	3.46	85.6	7.2	14.4	15.4	2.24
4. THF	7.58	1.97	3.41	71.8	16.6	28.2	17.6	2.36
5. MTHF	7.6	1.97	3.18	72.5	15.4	27.5	16.6	2.54
6. CH_2Cl_2	8.93	2.02	1.08	97.5	9.99	2.5	11.9	8.42
7. $(CH_2Cl)_2$	10.36	2.08	1.13	97.1	11.0	2.9	13.0	8.08
8. n-PrCN	20.3	1.91	2.52	91.6	12.0	8.4	17.3	3.39
9. acetone	20.7	1.84	3.33	85.1	15.5	14.9	16.7	2.40
10. n-EtCN	27.21	1.87	2.95	80.6	16.4	19.4	17.5	2.82
11. DMF	36.71	2.04	2.05	74.9	17.0	25.1	17.3	4.30
12. MeCN	37.5	1.81	3.21	96.1	10.9	3.9	17.6	2.55
13. DMSO	46.7	2.18	1.29	94.3	10.4	5.3	17.0	7.16

a) Optical dielectrical constants were calculated from proper refractive indexes n using the equation $\varepsilon_{op} = n^2$.

b) $\lambda_{em} > 560$ nm (by O - 56O filter), C = 10^{-6} mol/L.

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

d) Quantum yield ϕ of τ_{ref} exponent was 100% in all solvents.

e) Electron-transfer rate constants were calculated using the equation $k_{et} = 1/\tau_1 - 1/\tau_{ref}$.

chromophore interactions in the ground state.[10-12] The absorption bands for **P-Q** and **P** are shifted by a maximum value of 6 nm depending upon solvents. Fluorescence spectra of **P-Q** and **P** are also affected by solvation effect shifting the maximum of α and β emission bands by 10-12 nm and changing the ratio between intensities of α and β emission bands by 1.7 times. The fluorescence intensities of **P-Q** are considerably quenched in comparison with those of **P** due to intramolecular electron transfer from the singlet excited state of porphyrin moiety to the quinone electron acceptor. In general, the relative fluorescence yields of **P-Q** decrease with an increase of solvent polarity, however some deviations were observed. Fluorescence decay kinetics of **P-Q** in all the solvents are well fitted by the sum of two exponential curves with a short-lived component τ_1 related to intramolecular electron transfer and a long-lived component τ_2, apparently, due to the presence of reduced form of quinone residue,[10] while the decay curves of P are single exponential in all the solvents with corresponding τ_{ref} (Table 1). The lifetime τ_1 and electron-transfer rate constant k_{et} calculated from τ_1 and τ_{ref} values are strongly dependent upon solvent effect. However, taking into account only static dielectric constants ε_s of solvents some discrepancy in k_{et} values (Table 1) could not be easily explained. On the other hand Marcus theory [13-17] for "outer-sphere" electron-transfer reactions predicts that k_{et} value exponentially depends on free energy change (ΔG) and reorganization energy (λ) by the equation

$$k_{et} = \nu_{et} \cdot \exp[-(\Delta G + \lambda)^2/4\lambda RT]$$

where ν_{et} is the frequency factor. However, usual treatment of experimental data in a simple plot of ln k_{et} against ΔG is rather difficult when different solvents are used due to considerable overestimation of correction terms, sometimes by as much as twice,18) for medium polar ($\varepsilon_s < 9$) solvents. We suggest to apply both dielectric and optical constants (ε_s and ε_{op}, respectively) for the study of solvent effect on electron transfer, because λ linearly depends on $1/\varepsilon_{op} - 1/\varepsilon_s$ term, if structural organization of donor-acceptor pair does not change due to solvation effect according to the equation:

$$\lambda = \lambda_{in} + e^2(1/2r_P + 1/2r_Q - 1/2R_{PQ})\cdot(1/\varepsilon_{op} - 1/\varepsilon_s)$$

where λ_{in} is "inner-sphere" reorganization energy, r_P and r_Q are the radii of porphyrin and quinone, respectively, and R_{PQ} is the center-to-center distance between P and Q. Applied our approach we have got clear parabolic dependence19) of ln k_{et} versus $1/\varepsilon_{op} - 1/\varepsilon_s$ term for thirteen different solvents (Fig. 1). Bolton et al.20) also observed that quenching rate constants depend in part on ε_s but are more strongly dependent on the solvent refractive index n. On the basis of our approach we treated several experimental data published previously6,8,20,21) and observed similar dependence. Probably these findings are general for electron-transfer reactions in different solvents and may be useful tool for the study of solvent dependence and for calculation of correction term for different solvents.

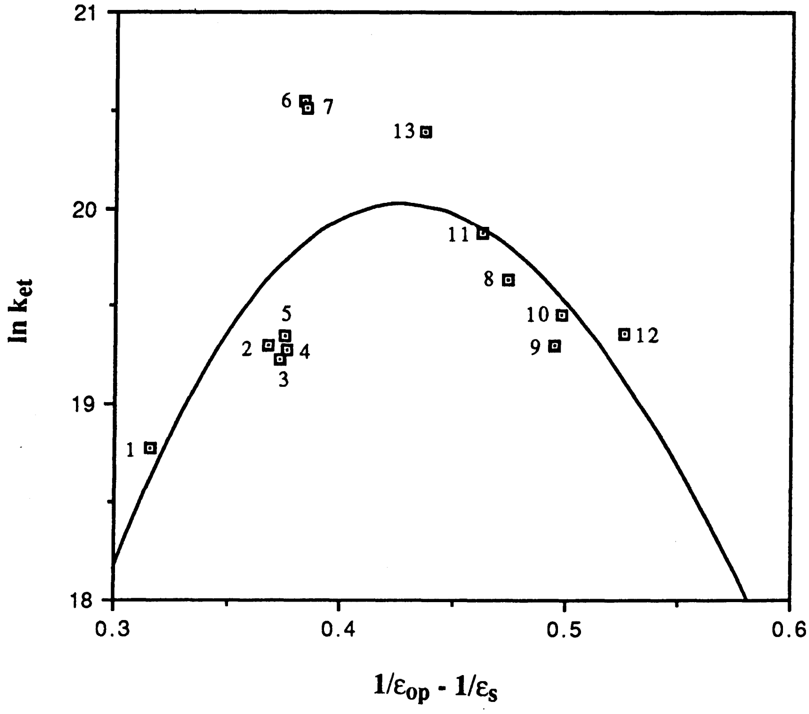

Fig. 1. Plot of ln k_{et} versus $1/\varepsilon_{op} - 1/\varepsilon_s$ values for all the solvents. The number of proper point corresponds to the number of solvent in Table 1.

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