Synthetic Model Approach to "Through-Bond" and "Through-Space" Electron Transfer Pathways

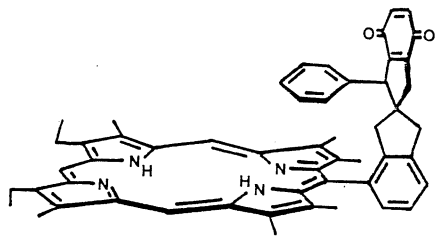
Suguru Higashida, Hirohito Tsue, Ken-ichi Sugiura, Takahiro Kaneda, Yoshinori Tanaka,†
Seiji Taniguchi,† Tadashi Okada,† and Yoshiteru Sakata*
The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki, Osaka 567
†*Department of Chemistry, Faculty of Engineering Science and Research Center for Extreme Materials, Osaka University, Machikaneyama, Toyonaka, Osaka 560*

(Received April 10, 1995)

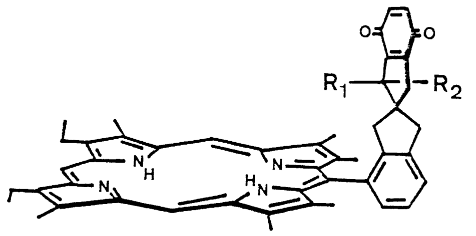
In order to understand electron transfer pathways through bond and through space, a covalently linked porphyrin-quinone molecule with an inserted phenyl ring between the redox pair was prepared. The inserted π-system is not used as a stepping stone in electron-transfer pathways.

Differentiation between "through bond" and "through space" electron transfer (ET) mechanism has been a big question in many ET systems especially long range ET in protein.[1] Even theoretical treatment for this problem have remained controversial.[2] It is generally accepted that ET takes place through bond in covalently linked D-A systems. Although there exist a few examples[3] of through-space mechanism for intramolecular ET, they are limited in macromolecules and no systematic models with well-defined structure have so far been reported to check this problem.

Here we report the synthesis of such a model **1s**, where a phenyl group is spatially inserted between an electron donor (porphyrin) and acceptor (benzoquinone) in **2**,[4] where the porphyrin and the quinone rings are fixed by a rigid spacer of spiro[3.3]nonane and by hindered rotation around a single bond between porphyrin and phenyl rings. For the energy minimized structure of **1s** by MM2 calculation the following results were obtained. (i) The shortest distance (edge-to-edge) between the porphyrin and the phenyl rings and between the phenyl and the quinone rings are 4.2 and 2.5 Å, respectively. (ii) Dihedral angles between the phenyl and porphyrin rings and between the phenyl and the quinone rings are 38.7° and 94.9°, respectively. (iii) The relative orientation and separation distance of the D-A pair in **1s** remained almost unchanged compared with those in **2**. If the both mechanisms of "through bond" and "through space" are operating, ET rate of **1s** is expected to be larger[5] than that of the reference compound **2**, because the inserted phenyl ring would accelerate ET by superexchange mechanism.

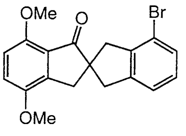


1s

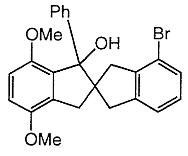


1a : $R_1=H$, $R_2=Ph$
2 : $R_1=R_2=H$

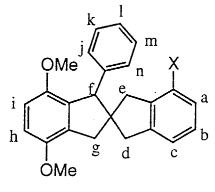
The introduction of a phenyl ring into the spacer unit was carried out by treatment of **3** with phenylmagnesium bromide in THF to give quantitatively diastereoisomeric alcohol **4**, which was reduced with a combination of triethyl- or triphenylsilane and trifuluoroacetic acid to give **5s** and **5a.** (Suffixes s and a mean that the Br and Ph groups are *syn* and *anti* with respect one another.) The stereochemistry was determined on the basis of ^{1}H NMR. Thus, all the protons of **5s** and **5a** were assigned by decoupling technique and the compound whose H_c proton resonates at higher field by 0.1 ppm due to the ring current effect of the facing phenyl ring was assigned to **5a**. Treatment of **5s** and **5a** with BuLi and DMF in THF gave **6s** and **6a**. The stereochemistry of these compounds was reconfirmed carefully by using nuclear Overhauser effect (NOE). Thus, for the compound **6a** NOE signals were observed for H_e, (H_f, H_g, and H_m), and (H_e and H_j) by irradiation of H_m, H_e, and H_f, respectively. These results clearly support the assignment of *anti* configuration for **6a**. Similar NOE experiments were somewhat difficult for **6s**, because of the overlapping of signals. However, the irradiation of the formyl proton gave an NOE signal for methylene protons which appeared at higher field by 0.1 ppm than the other methylene protons due to the ring current effect of the inserted phenyl ring and hence, could be assigned to H_e. When H_e protons were irradiated, weak NOE signals were observed for H_j protons, but not for H_f. The result also supports the stereochemistry of **6s**. The synthesis of **1s**[6] and **1a**[7] from **6s** and **6a**, respectively, was carried out in a manner similar to the synthesis of **2** and analogous compounds. NMR chemical shift differences between **1** and **2** were well explained by the assigned structure.



3



4



5: X=Br
6: X=CHO

Table 1. Fluorescence Lifetimes[a] and Charge Separation Rates[b] of **1**-**2**

	1s			**1a**			**2**		
	τ (ps)	τ_0 (ns)	k_{et} (s^{-1})	τ (ps)	τ_0 (ns)	k_{et} (s^{-1})	τ (ps)	τ_0 (ns)	k_{et} (s^{-1})
THF	260	14.9	3.8×10^9	110	16.6	9.0×10^9	280	17.5	3.5×10^9
DMF	280	16.7	3.5×10^9	110	16.2	9.0×10^9	260	17.5	3.8×10^9

[a] τ_0 is fluorescence lifetimes of the corresponding reference compound in which quinone ring is replaced by 1,4-dimethoxybenzene.
[b] Calculated using the equation $k_{et}=1/\tau - 1/\tau_0$.

Electronic spectra of **1s** and **1a** showed no special interaction between the donor and acceptor in the ground state. Redox potentials of **1**-**2** were measured in CH_2Cl_2 by differential pulse voltammetry and reversible one-electron oxidation and reduction peaks were observed. The values (vs. Ag/AgCl) are 896, -434 mV for **1s**, 880, -430 mV for **1a**, and 896, -456 mV for **2**. The results clearly show that exothermicity of **1s** and **1a** for ET reaction remains unchanged as compared with that of **2**. Fluorescence lifetimes of **1**-**2** and the corresponding references were measured by time-correlated single photon counting, and the values are summarized in Table 1. These results are in good agreement with the lifetime of the excited singlet states which were determined by analyzing the time dependence of the transient $S_n \leftarrow S_1$ spectra excited with a picosecond dye-laser systems at 590 nm. The lifetimes of **1**-**2** were used to calculate ET rates (k_{et}) in Table 1 by the equation $k_{et}=1/\tau - 1/\tau_0$ where τ and τ_0 are fluorescence lifetimes of the porphyrin-quinones and the corresponding reference compounds, respectively. From the table ET rates of **1s** and **2** are almost the same in two solvents. This clearly indicates that only through-bond mechanism is operating in the two compounds. One of the reason why the inserted phenyl ring does not act as a stepping stone in ET might be that the energy level of P^+-Ph^--Q (4.3 eV) is much higher than the excited singlet state energy of porphyrin (2.0 eV). It is quite surprising that **1a** has larger k_{et} value than those of **1s** and **2**. The reason for the rate acceleration is difficult to explain at this moment, but the difference in the reorganization energy by solvent may be responsible for the acceleration.[8]

In summary, through-space ET functions under the quite limited conditions to compete with overwhelmingly fast ET with through-bond pathways, when the both routes exist in covalently linked donor-acceptor systems.

References and Notes

1 G. McLendon, *Acc. Chem. Res.*, **21**, 160 (1988); G. McLendon, *Chem. Rev.*, **92**, 481 (1992); J. R. Winkler and H. B. Gray, *Chem. Rev.*, **92**, 369 (1992).

2 A. Kuki and P. G. Wolynes, *Science*, **236**, 1647 (1987); D. N. Beratan, J. N. Betts, and J. N. Onuchic, *Science*, **252**, 1285 (1991); P. Siddarth and R. A. Marcus, *J. Phys. Chem.*, **97**, 6111 (1993)

3 M. Tanaka, H. Yoshida, and M. Ogasawara, *J. Phys. Chem.*, **95**, 955 (1991); C. J. Murphy, M. R. Arkin, Y. Jenkins, N. D. Ghatlia, S. H. Bossmann, N. J. Turro, and J. K. Barton, *Science*, **262**, 1025 (1993).

4 Y. Sakata, H. Tsue, Y. Goto, S. Misumi, T. Asahi, S. Nishikawa, T. Okada, and N. Mataga, *Chem. Lett.*, **1991**, 1307; H. Tsue, S. Nakashima, Y. Goto, H. Tatemitsu, S. Misumi, R. J. Abraham, T. Asahi, Y. Tanaka, T. Okada, N. Mataga, and Y. Sakata, *Bull. Chem. Soc. Jpn.*, **67**, 3067 (1994); Y. Sakata, H. Tsue, M. P. O'Neil, G. P. Wiederrecht, and M. R. Wasielewski, *J. Am. Chem. Soc.*, **116**, 6904 (1994).

5 Assuming the participation of the inserted phenyl ring in ET and using the simple equation presented by Beratan et al.,[2] the ET rate of **1s** is estimated to be larger by 14% than that of **2**.

6 **1s**: ^{1}H NMR (270 MHz, $CDCl_3$) δ -3.30 (br. s, 2H), 1.85 (t, J=7.6 Hz, 6H), 2.00 (d, J=17.0 Hz, 1H), 2.29 (d, J=17.0 Hz, 1H), 2.38 (s, 3H), 2.47 (s, 3H), 2.76 (d, J=18.2 Hz, 1H), 3.10 (d, J= 18.2 Hz, 1H), 3.29 (d, J= 15.7 Hz, 1H), 3.41 (d, J=15.7 Hz, 1H), 3.52 (s, 3H), 3.54 (s, 3H), 3.62 (s, 3H), 3.63 (s, 3H), 4.06 (m, 4H), 4.23 (s, 1H), 6.4-6.7 (m, 5H), 6.56 (d, J=10.1 Hz), 6.67 (d, J=10.1 Hz, 1H), 7.56 (t, J=7.3 Hz, 1H), 7.61 (d, J=7.3 Hz, 1H), 7.79 (d, J=7.3 Hz, 1H), 9.92 (s, 1H), 10.11 (s, 1H), 10.13 (s, 1H) MS (FAB) 777 (M^++2).

7 **1a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.86 (t, J=8.0 Hz, 6H), 2.3-2.5 (m, 2H), 2.47 (s, 3H), 2.56 (s, 3H), 2.7-3.0 (m, 4H), 3.54 (s, 3H), 3.57 (s, 3H), 3.62 (s, 3H), 3.63 (s, 3H), 3.93 (s, 1H), 4.05 (q, J=8.0 Hz, 4H), 6.19 (d, J=10.0 Hz, 1H), 6.30 (d, J=10.0 Hz, 1H), 6.9-7.0 (m, 1H), 7.3-7.4 (m, 3H), 7.47 (d, J=7.5 Hz, 1H), 7.58 (t, J=7.5 Hz, 1H), 7.9-8.0 (m, 1H), 9.92 (s, 1H), 10.14 (s, 1H), 10.15 (s, 1H). MS (FAB) 805(M^+).

8 Electron transfer rates for charge recombination process were obtained by analyzing the time dependence of the transient absorption spectra in THF and benzene. The relative ratio of back ET rates for **1**-**2** is similar to that of forward ET shown in Table 1.