CHEMISTRY LETTERS, pp. 1205-1208, 1988.

Synthesis of a Conformationally Restricted Quinone-linked Porphyrin

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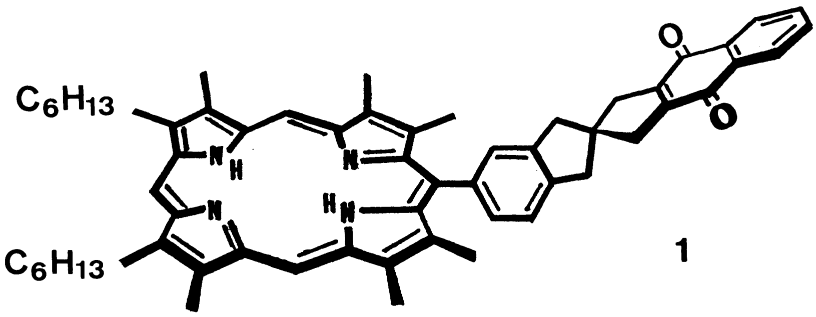
A porphyrin-quinone model compound connected by spiro-indane spacer was synthesized. The fluorescence of the model exhibited a singly decaying component with a lifetime of 1.89 ns, from which the rate of intramolecular photo-induced electron transfer was estimated to be 4.3 x 10^8 s^{-1}.

Recent crystallographic studies of the reaction center proteins from two photosynthetic bacteria have shown that the photo-active pigments are held in carefully controlled arrangements that optimize the efficiency of photon or electron transfers.[1,2] Characterization of these natural system has been aided by the synthesis of many different covalently linked porphyrin dimers and quinone-linked porphyrins.[3] A useful way to study photo-induced electron transfer reactions and the dependence of their rates on distance, orientation, and free energy is to synthesize model systems with known distances and orientations between the donors and acceptors.[4]



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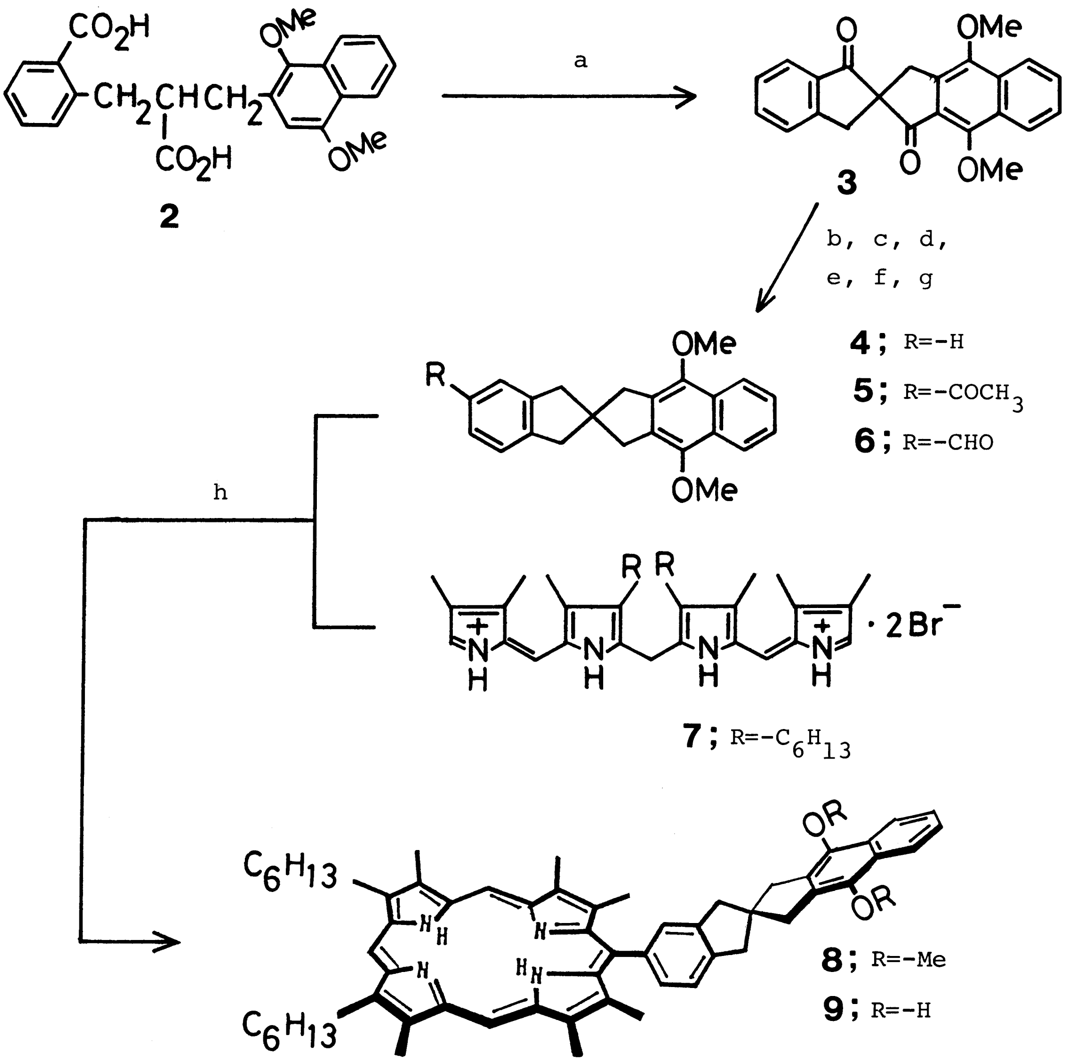
As a part of our program[5] aimed at the construction of porphyrin molecular system capable of being active as photosensitizer for charge separation, we have synthesized a novel quinone-linked porphyrin **1**, in which the quinone moiety is connected to the porphyrin through the spiro-indane spacer. The rigid spiro-indane bridge insures that the quinone part is separated by 14-15 Å (center to center) from the porphyrin macrocycle with the dihedral angle of ca. 20-40°. Interestingly this geometry well duplicates the natural situation of bacteriopheophytin and ubiquinone in photosynthetic reaction center of Rhodobactor sphaeroides R-26.[2)]

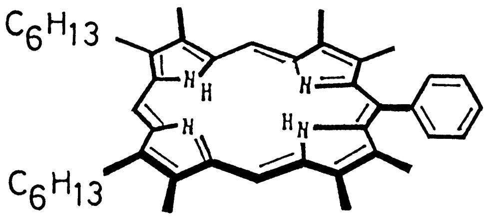
The synthesis of **1** is outlined in Scheme 1. Intramolecular Friedel Crafts acylation of dicarboxylic acid **2**[6)] with freshly prepared polyphosphoric acid afforded spiro-diketone **3** in 90% yield, which was reduced with ZnI_2-$NaCNBH_3$[7)] to **4** in 87% yield. The spiro-hydrocarbon **4** was regio-selectively acetylated to give **5** in 91% yield, which was transformed into aldehyde **6**[8)] in a usual reaction



Scheme 1. Synthetic scheme. (a) PPA, 100 °C. (b) ZnI_2, $NaCNBH_3$, $ClCH_2CH_2Cl$, 80 °C. (c) CH_3COCl, $AlCl_3$, 25 °C. (d) Br_2, NaOH, 5 °C. (e) CH_2N_2, 25 °C. (f) $LiAlH_4$, -78 °C. (g) PCC, CH_2Cl_2, 25 °C. (h) HBr, MeOH, reflux.

sequence involving haloform reaction, methylation with diazomethane, reduction with $LiAlH_4$, and oxidation with pyridinium chlorochromate in overall 35% yield. Acid-catalyzed condensation of 1,19-dideoxy-ac-biladiene **7**[9] with **6** (HBr/MeOH, 24 h, reflux) furnished dimethoxynaphthalene-linked porphyrin **8** in 48% yield.[10] Treating **8** with an excess of BBr_3 in dry CH_2Cl_2 gave **9**, which was immediately oxidized to **1** in CH_2Cl_2 with PbO_2. Chromatographic purification (silica gel, CH_2Cl_2) and recrystallization from CH_2Cl_2/methanol gave **1** in 95% yield.[11]

The absorption and fluorescence spectra of **1** are not perturbed by the linked quinone. However, the fluorescence quantum yield of **1** in CH_2Cl_2 is reduced to 0.19 as compared with that of 5-phenyl-substituted porphyrin **10** as a reference porphyrin, while the fluorescence intensity of **8** is the same as that of **10**. The fluorescence lifetimes (τ) of **1**, **8**, and **10** were determined in CH_2Cl_2 at 298 K by picosecond time-correlated single photon counting technique;[12] 1.89 ns (100%) for **1**, 10.33 ns (100%) for **8**, and 10.52 ns (100%) for **10**. Notably, the fluorescence of **1** exhibited a singly decaying component and the ratio (0.18) of τ(**1**)/ τ(**10**) was in good agreement with the ratio of the fluorescence quantum yields of **1** to **10**. These results indicate that the singlet excited state of the porphyrin in **1** is quenched by the linked quinone through a single conformation.



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The observed decrease in the fluorescence quantum yield and lifetime in **1** can be directly related to an electron-transfer rate constant by assuming that the sole additional deactivation pathway relative to **8** and **10** is electron transfer.[13] Taking the lifetime of **8** or **10** to define the natural fluorescence lifetime of the porphyrin, we can estimate the rate of electron transfer in **1** to be $4.3 \times 10^8\ s^{-1}$.

The authors thank Professor S. Hirayama of Kyoto Institute of Technology for measurement of pico second fluorescence lifetimes. This work was supported by the Grand-in-Aid for Scientific Research No. 62113003 from the Ministry of Education, Science and Culture.

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(Received April 28, 1988)