Transmembrane Electron Transfer catalysed by Manganese Porphyrin-linked Quinones with Various Carbon Chain Lengths

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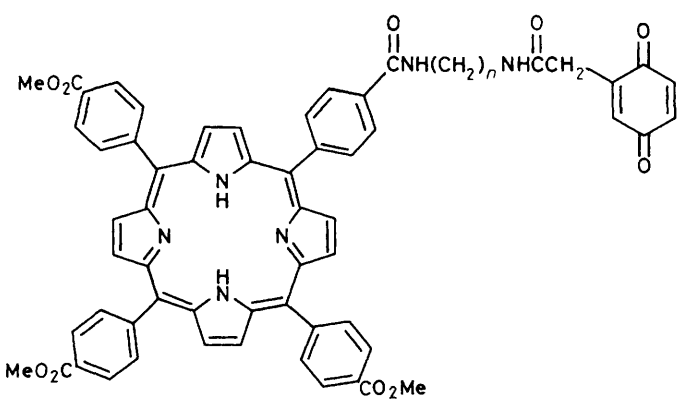
An enhanced rate of transmembrane electron transfer across a lipid bilayer catalysed by a manganese porphyrin-linked quinone $MnP(CO_2Me)_3$-C_n-Q (n = 2, 3, 4, or 6) has been observed when n = 2, and a parallel quenching study of the free porphyrin-linked quinone has shown the crucial effect of the linkage length on the electron transfer from porphyrin to quinone.

The use of chemical models whose structure and 3-dimensional relationship are well understood can be very helpful in studying the effect of distance and orientation in the electron transfer reactions of photosynthesis and other biological processes. Porphyrin pigments and quinones play a key role in bacterial photosynthetic reactions, and the preparation of porphyrin-linked quinones which are capable of light induced intramolecular electron transfer reported have been in the search for a model for the reaction centre.[1—7] However, there has been little study of the ground state electron transfer from porphyrin to quinone in order to provide insight into the effect of distance and orientation so that a vectorial electron transfer system can be constructed in the phospholipid bilayer. We report transmembrane electron transfer as catalysed by (**2**) and the parallel quenching study of (**1**), where the length of the linkage between the compounds has a crucial effect on the transmembrane electron transfer. Compounds (**1**) and (**2**) were prepared by the following synthetic sequence. Commercially available 2,5-dimethoxyphenylacetic acid was converted to its methyl ester and treated with diaminoalkane [$NH_2(CH_2)_nNH_2$; n = 2, 3, 4, or 6] in methanol at reflux overnight to give *N*-(2,5-dimethoxyphenylacetyl)-1,*n*-diaminoalkane (**3**) (n = 2, 3, 4, or 6) as described previously.[8d] 5-(*p*-Carboxyphenyl)-10,15,20-tri(*p*-methoxyphenyl)porphyrin, $P(CO_2Me)_3CO_2H$, was prepared by the condensation of pyrrole with a mixture of *p*-methoxyphenylaldehyde and 4-carboxybenzaldehyde in refluxing propionic acid, followed by chromatographic separation (silica gel, 5% acetone–chloroform) of the monocarboxy porphyrin and polycarboxy porphyrin.[8] The monocarboxy porphyrin was converted to its acid chloride, $P(CO_2Me)_3COCl$ with thionyl chloride and treated with (**3**) in chloroform at reflux overnight to give the porphyrin-linked dimethoxyphenyl compound (**4**). The ^1H n.m.r. spectra of (**4**), isolated by silica gel chromatography (10% acetone–chloroform) unambiguously support the assigned structure.† Conversion of the dimethoxyphenyl portion of (**4**) to the corresponding hydroquinone (QH_2) compounds was achieved by treatment with boron tribromide at low temperature under standard conditions.[2] The ^1H n.m.r. spectra and elemental analyses of the compounds, $P(CO_2Me)_3$-C_n-QH_2 (**5**), isolated by column chromatography, confirmed that the desired transformation had occurred.† In particular, the methoxy groups present in the dimethoxyphenyl portion of (**4**) were absent from the ^1H n.m.r. spectrum of (**5**). Treatment of (**5**) with PbO_2 in CH_2Cl_2 gave the corresponding quinone, (**1**). The course of the oxidation was followed by u.v.–vis spectroscopy as described previously.[2,7]‡ The preparation of a manganese porphyrin complex, was accomplished by addition of a saturated solution of tris(pentane-2,4-dionato)manganese (III) in pyridine at reflux overnight. The fluorescence spectrum of (**1**) in CH_2Cl_2–10% EtOH shows normal porphyrin fluorescence. Some quenching of the porphyrin fluorescence occurred where the fluorescence



Porphyrin-linked quinone (**1**) $P(CO_2Me)_3$-C_n-Q (n = 2, 3, 4, 6) (**2**) $MnP(CO_2Me)_3$-C_n-Q

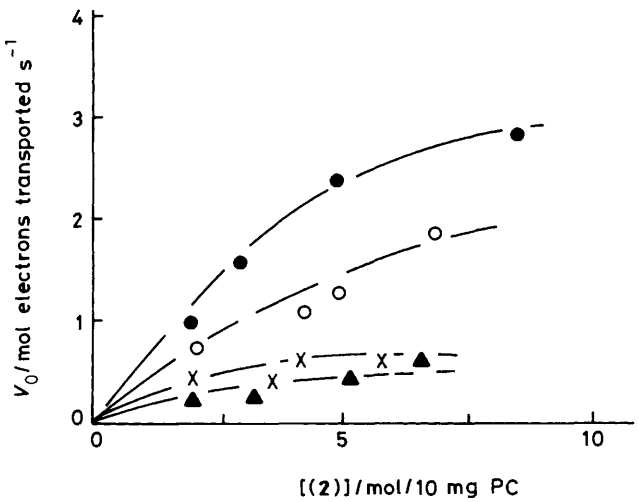


Figure 1. Initial rates of electron transfer catalysed by manganese porphyrin-linked quinone, $MnP(CO_2Me)_3$-C_n-Q(**2**) (n = 2, 3, 4, or 6) at 25 °C. ● n = 2, ○ n = 3, × n = 4, ▲ n = 6.

† More detailed synthetic and analytical data will be reported elsewhere.

‡ The absorption spectra at 260—280 nm showed that in aqueous solution (**1**) was present as a mixture of the quinone and hydroquinone forms. Considering the ratio between the two forms, no significant difference between the length of the methylene groups in the compounds was observed.

yields of (**1**) were decreased in comparison to the unlinked porphyrin (**3**), where the highest quenching was observed when the linkage length (n) of the compounds was 2. Quenching occurred in the following order, $n = 2 \geqslant n = 3 > n = 4 > n = 6$. Similar quenching results for porphyrin-linked quinones with a varying number of methylene groups was reported by us and others,[2,6] in which higher quenching also occurred when $n = 2$ or 3. In addition, when the porphyrin-linked quinone complexes were reduced with $NaBH_4$, no fluorescence quenching was observed, consistent with a charge separation mechanism in which the quinone accepts an electron from the porphyrin in its excited singlet state.[4—6]‡

Electron transport from an external reducing agent (reduced 5,5′,7,7′-indigotintetrasulphonic acid, $ITSAH_2$, 1×10^{-5} M) to potassium ferricyanide (0.1 M) trapped within an egg yolk phosphatidylcholine (PC) liposome was measured anaerobically at pH 7.0 (0.4 M imidazole buffer) as catalysed by (**2**) incorporated in the vesicle bilayer.[9] The oxidized form of the dye, ITSA, has an intense absorbance band at λ 600 nm. The intensity and position of this band allowed us to measure the rate of the electron transport reaction with minimal spectroscopic interference from components of the model system. The initial rate of electron, transfer (V_0) was determined from the initial slope of the change of absorbance band at 600 nm. Figure 1 shows plots of V_0 *vs.* concentration of (**2**) incorporated in the PC, where the rate depends on the number of methylene groups (n = 2, 3, 4, or 6) in the compounds. A significantly enhanced rate was observed, particularly when $n = 2$, indicating that the length of the linkage in the compounds has a crucial effect on the electron transfer. This effect is consistent with the fact that the highest fluorescence quenching of (**1**) was observed when $n = 2$. These results indicate that intramolecular electron transfer from porphyrin to quinone plays an important role in transmembrane electron transfer. This series of compounds is the first reported system in which an incremental effect of the distance between porphyrin and quinone in transmembrane electron transfer has been observed.

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