Light-induced Intramolecular Electron Transfer from a Porphyrin linked to a *p*-Benzoquinone by a Rigid Spacer Group

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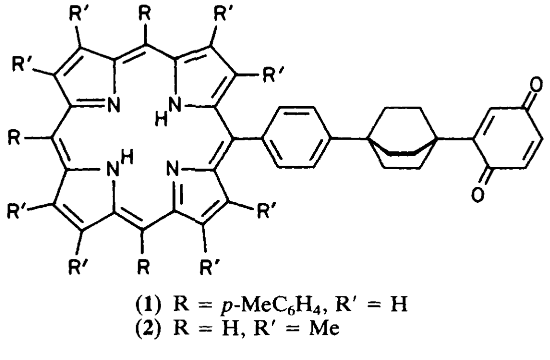
A model of the reaction centre in photosynthesis is described which consists of a tetra-arylporphyrin attached to a *p*-benzoquinone through a bicyclo[2.2.2]octane; fluorescence lifetime data suggest that visible light-induced intramolecular electron transfer between the porphyrin and the quinone is much less efficient than in previously reported linked porphyrin–quinone molecules and indicate that it is subject to a novel solvent effect.

It is well known that the primary photochemical step in photosynthesis consists of the transfer of an electron from the excited state of a porphyrin chromophore to an acceptor molecule to generate a transient radical–ion pair. The fundamental factors governing the efficiency of the light-induced electron transfer process and, of even greater practical interest, the factors which prevent the rapid back electron transfer in the charge separated species, are not well understood. In order to determine these factors there has been much effort expended in recent years on the synthesis of potentially photoactive donor–acceptor molecules; most of these consist of a porphyrin, acting as the light absorbing electron donor, and a chemically attached *p*-benzoquinone as the electron acceptor. The majority of the systems which have been reported to date[1] suffer from the disadvantage that the donor and acceptor parts of the molecule are attached by linkages that are quite flexible, so that the degree of separation of the donor and acceptor is not fixed. This complicates the interpretation of the light-induced electron transfer reactions in this series of compounds. Recently preliminary results have been reported for two types of rigidly linked porphyrin–quinone compounds which do not suffer from the problem of an unknown spacial relationship between the donor and acceptor. One of these consists of a tetra-arylporphyrin and a quinone attached to a tryptycene system,[2] and the other consists of an octamethylporphyrin attached to a quinone by a bicyclo[2.2.0]octane ring.[3] We have recently obtained results from a system comprising a tetra-arylporphyrin attached to a quinone by a bicyclo[2.2.0]octane ring which show important differences from the results previously reported. The system we have prepared is shown in structure (**1**).[†]

The u.v.–visible absorption spectrum of (**1**) in CH_2Cl_2 does not show any detectable interaction between the chromophores; the spectrum exhibits a normal porphyrin pattern (intense Soret band at 418 nm, and Q bands at 516, 551, 592, and 648 nm in CH_2Cl_2) superimposed upon a *p*-benzoquinone absorption at 246 nm. This is in contrast to the spectra obtained for the flexibly-linked porphyrin–quinone molecules previously prepared in this laboratory;[1] these molecules showed a broadening and a red shift of the porphyrin bands, which was used as evidence for ground-state interactions between the porphyrin and the quinone resulting from conformations of the molecule in which the quinone was folded back over the porphyrin ring. The rigid nature of the linkage between the porphyrin and quinone in (**1**) prevents this type of interaction. This interpretation is supported by the time-resolved fluorescent properties of (**1**). A single exponentially decaying fluorescent species was observed in several solvents (see Table 1) when (**1**) was excited in the Soret band, whereas for the flexibly linked compounds previously described,[1] two groups of emitting species were observed, one assigned to interacting conformations and the other to extended conformations.

The degree of light-induced electron transfer in (**1**) was determined by comparison of the fluorescence lifetime in various solvents with that of *meso*-tetra-*p*-tolylporphyrin as shown in Table 1. It is seen that the lifetime of the singlet excited state of (**1**) is shortened to the extent of between 0 and 13% only (depending on the solvent), as compared with tetratolylporphyrin. We assign this decrease in fluorescence lifetime to quenching of the excited state of the porphyrin in (**1**) by electron transfer to the quinone. The relative inefficiency of the quenching presumably reflects the nature of the linkage between the porphyrin and the quinone, and the magnitude of the separation between their chromophores [the centre-to-centre separation between the porphyrin and quinone in (**1**) is *ca.* 16 Å]. In contrast, Wasielewski and coworkers[2] have reported very efficient light-induced intramolecular electron transfer in a porphyrin–quinone held in a fixed orientation and distance by a tryptycene ring system where the centre-to-centre distance is approximately 10 Å; however, in this structure there is some possibility of overlap between the π-systems of the chromophores. In greater contrast, Joran *et al.* have found[3] from measurement of fluorescence intensity of compound (**2**), which is an octamethylporphyrin rigidly linked to a quinone by a bicyclo[2.2.0]octane ring system where the centre-to-centre distance is very similar to that in (**1**), that the electron transfer quenching of the porphyrin is much higher (in the order of 26% in benzene and 59% in propionitrile, see Table 1).

The variation in electron transfer quenching with solvent for



(**1**) R = *p*-MeC_6H_4, R' = H
(**2**) R = H, R' = Me

[†] Compound (**1**) was prepared by a sequence involving treatment of 1-hydroxy-4-iodobicyclo[2.2.2]octane[4] with $BF_3 \cdot Et_2O$ in refluxing toluene to give 1-(*p*-tolyl)-4-iodobicyclo[2.2.2]octane in 65% yield, which was converted into 1-(*p*-tolyl)-4-(2,5-dimethoxyphenyl)bicyclo[2.2.2]octane in 44% yield by reaction with 1,4-dimethoxybenzene and aluminium trichloride in carbon disulphide. Oxidation with cerium(III) ammonium nitrate in 50% aq. acetic acid (60 °C, 3 h)[5,6] gave 1(*p*-formylphenyl)-4-(1,4-benzoquinonyl)bicyclo-[2.2.0]octane in 40% yield. This was converted[7] into (**1**) by condensation with pyrrole and 4-methylbenzaldehyde.

Table 1. Fluorescence lifetimes and electron transfer rate constants.

Solvent	Dielectric constant	Refractive index	τ_1[a]	τ_2[b]	k_{ct}[c]	Φ_{ct}[d]
Dibutyl ether	3.04	1.3992	12.39 ± 0.05	12.37 ± 0.06	*ca.* 0	*ca.* 0
2-Methyltetrahydrofuran	7.6	1.4060	11.80 ± 0.05	12.03 ± 0.05	1.6 ± 0.5	0.019 ± 0.006
CH_2Cl_2	9.1	1.4242	7.89 ± 0.03	8.99 ± 0.04	15.3 ± 0.6	0.122 ± 0.005
Butan-1-ol	17.8	1.3993	10.09 ± 0.06	11.84 ± 0.05	14.6 ± 0.9	0.148 ± 0.007
Acetone	20.7	1.3587	11.64 ± 0.06	11.97 ± 0.06	2.4 ± 0.6	0.028 ± 0.007
Acetonitrile	37.5	1.3441	11.42 ± 0.05	11.45 ± 0.05	*ca.* 0	*ca.* 0
Benzene[e]	2.27	1.5011	17		15	0.26
Propionitrile[e]	27.2	1.3659	18		33	0.59

[a] Fluorescence lifetime of (**1**) (in ns) measured by the method of time correlated single photon counting on a Photochemical Research Associates Model 3000 nanosecond lifetime fluorometer. [b] Fluorescence lifetime of the unlinked model compound, 5,10,15,20-tetratolylporphyrin (in ns) measured as in footnote (a). [c] The electron transfer rate constant k_{ct} ($s^{-1} \times 10^6$). Calculated using the formula $k_{ct} = 1/\tau_1 - 1/\tau_2$. [d] Quantum yield of electron transfer, $\Phi_{ct} = k_{ct} \times \tau_1$. [e] Data for compound (**2**) taken from ref. 3. Φ_{ct} is calculated as in footnote (d) using values of τ_1 from ref. 3.

(**1**) shows an unusual pattern in that it is maximised for solvents of intermediate polarity rather than those of greatest polarity. Using a formulation based upon the Onsager reaction field model for solute–solvent interactions[8] it can be shown that a correlation exists between the solvation energy of the charge separated state of (**1**) and the observed quenching rate constant. This relationship depends in part on the solvent dielectric but is more strongly dependent on the solvent refractive index. This can be seen in qualitative form for (**1**) in Table 1. For other linked porphyrin–quinone systems which we have examined, the relationship is more quantitative if solvents are used which are more closely related in structure.[9] The variation with solvent of the electron transfer efficiency and rate is very different from that observed for compound (**2**);[3] in (**2**) the efficiency is increased from 26 to 59% in going from benzene to propionitrile whereas for (**1**) the electron transfer efficiency drops to zero in acetonitrile.

The inefficiency of electron transfer quenching in (**1**) and its solvent dependence suggest that in the natural photosynthetic system the nature of the matrix (corresponding to the solvent in our study) supporting the chlorophyll-electron acceptor is critical and indicate that the donor–acceptor pair needs to be held at a closer distance than is present in (**1**). These conclusions are not, however, in agreement with those indicated by the results obtained by Joran *et al.*[3] One possible reason for the different electron transfer efficiencies of (**1**) and (**2**) may be the different substitution pattern on the porphyrin rings and their effect upon the conformation of the phenyl linking group relative to the plane of the porphyrin ring.

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