A Novel Porphyrin with Weak Fluorescence due to Intramolecular Electron Transfer Quenching

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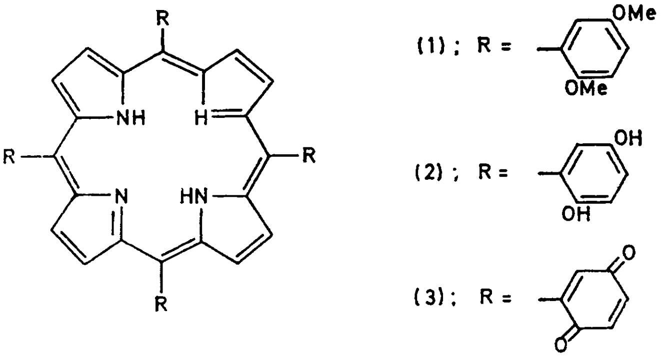
Summary A porphyrin bearing benzoquinone substituents at its *meso* positions has been synthesised; its electronic absorption and emission spectra suggest extensive intramolecular charge transfer.

The primary photochemical reaction of photosynthesis is thought[1] to involve electron transfer from a photoexcited chlorophyll molecule to a quinone. As part of a study[2] of the rates of analogous processes, we have synthesised compound (**3**)† which has benzoquinone units at the *meso* positions of the porphyrin ring. Its precursor (**1**)† was made from the appropriate aldehyde by standard methods.[3]



$$(\mathbf{1}) \xrightarrow{\text{i, BBr}_3\text{; ii, H}_2\text{O}} (\mathbf{2}) \xrightarrow{\text{DDQ}} (\mathbf{3})$$

(DDQ = Dichlorodicyanobenzoquinone)

The u.v.–visible absorption spectrum of (**3**) (Figure; A and C) shows a broadened Soret (B) absorption band which extends to beyond 700 nm. This feature seems previously to have been recognised only in *allo*-[4] or *hyper*-[5] metalloporphyrins, where it is attributed to ring → metal charge transfer. In the case of (**3**) we attribute the broadening to (intramolecular) porphyrin → quinone charge-transfer states. Addition of excess of acid to a porphyrin reversibly forms the di-*N*-protonated porphyrin dication, whose spectrum broadly resembles that of the neutral species.[5] In the case of (**3**), addition of acid should also enhance any intramolecular electron-transfer to the quinone substituents.[6] On the present view, this should lead to a further broadening of the absorption bands. Thus the extraordinarily broadened Soret band of the dication of (**3**) (Figure: B) is consistent with extensive intramolecular charge transfer.

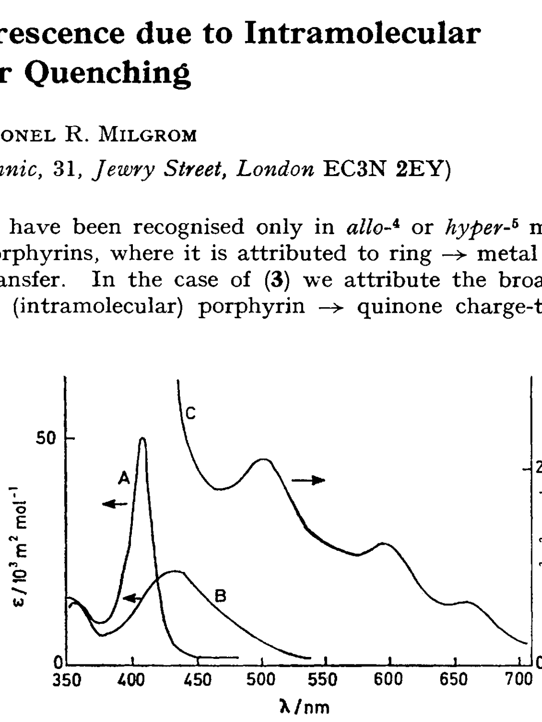


FIGURE. Decadic extinction coefficient of solutions in $CHCl_3$ of (**3**) *vs.* wavelength: (A) and (C) in the absence and (B) in the presence of excess of CF_3CO_2H.

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† Satisfactory elemental analyses were obtained.

We were unable to detect fluorescence emission from degassed benzene solutions of (**3**) over the range 550—800 nm. This means that its fluorescence quantum yield under these conditions must be less than 10^{-3}. The decadic extinction coefficient of the 660 nm band (*ca.* 300 $m^2 mol^{-1}$; $CHCl_3$ solution; making allowance for the tail of the B band absorption) suggests[7] a radiative lifetime of *ca.* 100 ns for any corresponding fluorescence. Therefore the overall pseudounimolecular rate constant for radiationless deactivation must exceed $10^{10} s^{-1}$. This is at least an order of magnitude greater than those found for tetra *meso*-aryl porphyrins under similar conditions[8] and is presumably dominated by an intramolecular electron-transfer contribution.

Added in proof: Extensive but incomplete quenching of fluorescence has recently been reported for tetraphenylporphyrin bearing a benzoquinone substituent on one of the aryl rings.[9]

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