

The Effect of Separation Distance on the Fluorescence Quenching for Zinc Porphyrin/Viologen Systems

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Fluorescence from zinc porphyrins is quenched by methyl viologen in rigid media due to electron transfer. The volume of the quenching sphere depends upon the medium with the radius changing from 11.2 Å in ethanol at 80 K to 14.8 Å in decalinol at 298 K. These radii correspond to the average centre-to-centre separation distance at which the rate of electron transfer equals the rate of nonradiative decay of the singlet excited state of the porphyrin. Attaching the viologen to the porphyrin via a short, flexible chain leads to efficient fluorescence quenching, especially in rigid media where the porphyrin and viologen are held in quite close proximity (ca. 6 Å apart).

Introduction

In recent years there have been several notable attempts to study the rate of an adiabatic electron transfer process as a function of the distance separating the reactants. According to classical theory [1, 2], the rate (k) should decrease exponentially with increasing separation distance (r)

$$k = \nu \exp(-\alpha r) \quad (1)$$

where ν is the frequency factor having a high temperature maximum of ca. 10^{13} s^{-1} and the constant α is normally given a value of ca. 1.1 \AA^{-1} [3]. Several advances in the theoretical description of such processes have been made [4, 5] but an experimental study is rendered difficult by the need to have a well-defined geometric arrangement of donor and acceptor species. Most work in this field has been carried out in rigid matrices and has relied heavily on luminescence quenching measurements which have shown that fast electron transfer can occur over distances of ca. 15 Å [6–9]. More elaborate studies have been reported by Verhoeven [10] and Miller [11] and their coworkers using rigid spacers to separate acceptor and donor moieties and, again, it was demonstrated that efficient electron transfer could occur over 15 Å or so.

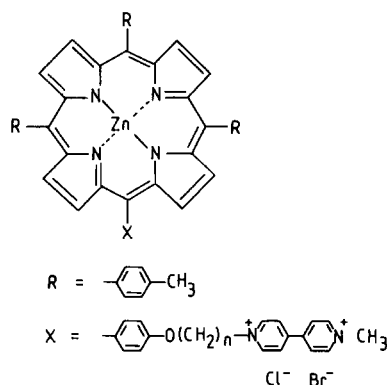


Fig. 1. Structures for the covalently-linked zinc porphyrin/viologen compounds.

In a previous paper [12], we reported on the photoinduced electron transfer processes in zinc porphyrins covalently-linked to a single viologen unit. The linkage was a flexible hydrocarbon chain of various chain lengths as shown in Fig. 1. Inefficient fluorescence quenching was observed for these molecules in ethanol solution at 298 K and we raised the assumption that the short excited singlet state lifetime ($\tau_S \sim 1 \text{ ns}$) precluded any significant diffusion so that the excited singlet state witnessed only the random distribution of geometries present at the moment of excitation. Consequently, the fluorescence quenching rate constant is the average k from eqn. 1 taken over the entire span of available r values. In this paper, we attempt to specify the average distribution of geometries somewhat more clearly by repeating the fluorescence quenching experiments in rigid media.

Experimental

The compounds used in this study were prepared and purified as described previously [12]. Ethanol (Burroughs AR grade) and decalinol (Aldrich Chemicals) were used as received. Luminescence measurements were made with a Perkin Elmer MPF 4 spectrofluorimeter using the optically dilute method [13].

Results and Discussion

As a model, consider the fluorescence quantum yield (ϕ_F) of zinc tetraphenylporphine (ZnTPP) in a rigid matrix (either ethanol at 80 K or decalinol at 298 K) containing various concentrations of methyl viologen (MV^{2+}). The dependence of ϕ_F upon the concentration of MV^{2+} can be expressed in the form [5]

$$\frac{\phi_F}{\phi_F^0} = (\exp(-(MV^{2+})V)) \quad (2)$$

where the concentration of MV^{2+} is expressed in molecules per unit volume and V refers to the volume of the capture sphere.

$$V = \frac{4}{3} \pi (R_t^3 - R_o^3) \quad (3)$$

Here, the average reaction radius R_t is equated to the distance at which the electron transfer rate k equals the reciprocal of the excited state lifetime and

$$R_o = R_A + R_D \quad (4)$$

where R_A and R_D are the molecular radii of acceptor and donor respectively ($R_o \sim 7 \pm 1 \text{ \AA}$) [12]. Plots of $\ln(\phi_F/\phi_F^0)$ vs. (MV^{2+}) were linear (Fig. 2), at least up to concentrations of MV^{2+} in the region of 0.3 mol dm^{-3} , and there was no evidence for ground state interactions from absorption spectroscopy. From the plots, the effective reaction radii (R_t) for frozen ethanol at 80 K and decalinol at 298 K were found to

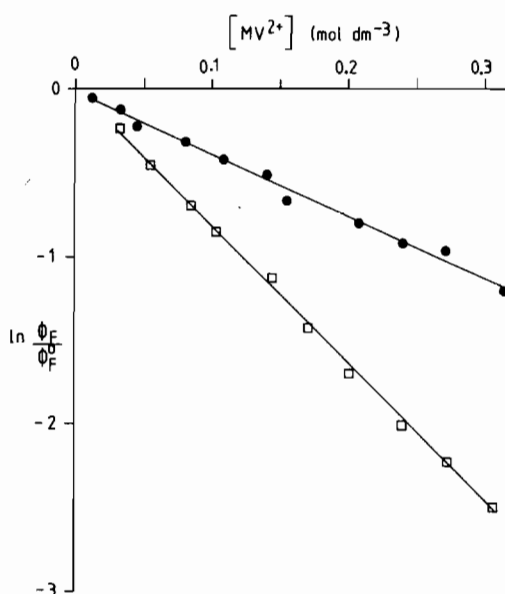


Fig. 2. Quenching of fluorescence from ZnTPP upon addition of MV^{2+} in frozen ethanol at 80 K (●) and decalinol at 298 K (□).

be (11.2 ± 0.4) and $(14.8 \pm 0.3) \text{ \AA}$ respectively. With $R_o \sim 7 \text{ \AA}$, these values mean that the rate of intermolecular electron transfer equals the rate of non-radiative deactivation of the excited singlet state at edge-to-edge separation distances of 4.2 \AA and 7.8 \AA respectively for frozen ethanol and decalinol. The concentrations of MV^{2+} required to reduce ϕ_F by 50% were 0.18 and $0.084 \text{ mol dm}^{-3}$ respectively for ethanol glass at 80 K and decalinol at 298 K.

For an isolated donor/acceptor pair, eqn. 1 can be rewritten to give

$$R_t = R_o + \alpha^{-1} \ln \nu \tau_S \quad (5)$$

and with $\tau_S = 1.7 \text{ ns}$ the frequency factor ν can be evaluated for each system. The average values found from the quenching plots were $\nu = (6.0 \pm 0.5) \times 10^{10} \text{ s}^{-1}$ for ethanol at 80 K and $\nu = (3.1 \pm 0.3) \times 10^{12} \text{ s}^{-1}$ for decalinol at 298 K. This latter case approaches the high temperature limit for an adiabatic process. Since the ν values are dependent upon thermodynamic parameters and the two environments are quite dissimilar, the observed differences in ν cannot be ascribed simply to a temperature effect.

In frozen ethanol, phosphorescence from ZnTPP could be seen clearly and the yield was found to decrease with increasing concentration of MV^{2+} . However, the reduction in phosphorescence followed quite closely the magnitude of the drop in ϕ_F so that there appears to be no real quenching of the triplet excited state under such conditions. In ethanol solution at 298 K, MV^{2+} does quench the triplet excited state of ZnTPP but the thermodynamic driving force for electron transfer is minimal [12] and freezing the solution might be sufficient to make the reaction thermodynamically unfavourable.

The fluorescence quantum yields were determined, under identical conditions to the above, for the ZnP/ MV^{2+} covalently-linked systems and the values are given in Table I. Comparison of these values with Fig. 2 allows estimation of the effective concentration of MV^{2+} for the linked systems (Table I) and the relatively high values observed show the benefits of attaching the acceptor close to the donor. The fluorescence quenching data can be used also to estimate the average k for electron transfer, assuming a nonrandom distribution of geometries, according to

$$\frac{\phi_F}{\phi_F^0} = \frac{k_{NR}}{k_{NR} + k} \quad (6)$$

where $k_{NR} = \tau_S^{-1}$. If this assumption is valid, then the derived k values (Table I) can be used to determine the average separation distance between viologen and porphyrin if it is further assumed that the thermodynamic parameters are identical for free and linked systems. Although experimental support for this latter assumption is not available, the average

TABLE I. Fluorescence Quenching Parameters for the Covalently-linked Porphyrin/viologen Compounds in Rigid Media.

Compound	ϕ_F/ϕ_F^0	$10^{-8} \times k/s^{-1}$	$r/\text{\AA}$	'Effective' (MV^{2+})/mol dm ⁻³
Ethanol at 80 K				
n = 1	0.79	1.5	5.4	0.05
n = 2	0.64	3.3	4.7	0.12
n = 4	0.60	4.0	4.6	0.14
n = 6	0.57	4.4	4.5	0.15
Decalinol at 298 K				
n = 1	0.31	13.2	7.0	0.14
n = 2	0.21	22.4	6.6	0.19
n = 4	0.09	60.0	5.7	0.29
n = 6	0.13	39.2	6.0	0.24

edge-to-edge separation distances have been calculated and they are collected in the Table I.

The derived separation distances for both systems depend upon chain length and longer chains favour more efficient fluorescence quenching. In this respect, the behaviour observed in rigid media differs significantly from that found in fluid solution where shorter chains exhibited more efficient quenching [12]. In rigid media the average separation distances are around 4–7 Å and, within experimental limitations, the longer chains give shorter separation distances. This suggests that the molecules reside within cavities in the rigid media which favour a folded conformation that brings porphyrin and viologen into close proximity. The chains appear to be extended in fluid solution [12] and, because of the ensuing greater separation distances, fluorescence quenching is less efficient than in rigid media at the same temperature. Such findings suggest that electron transfer is primarily 'through space' rather than 'through bond'.

Unlike with the free reactants, the linked systems showed a small but definite phosphorescence quenching effect. This triplet quenching was essentially independent of chain length, within experimental error, and corresponded to an average quenching sphere radius of 12 Å. The difference between linked and free systems might be due to small changes in the thermodynamic parameters or it might be due to the shorter average separation distances found with the linked systems.

This work has confirmed that by attaching the viologen near the porphyrin via a short flexible chain it is possible to attain a high local concentration of viologen and, therefore, quench the singlet excited state of the porphyrin. The average distance separating the two reactants depends upon the nature of the linkage and the type of medium used. In rigid media, medium length chains (n = 4 or 6) lead to the most effective fluorescence quenching and, at room

temperature, the average separation distance is *ca.* 6 Å. Under these conditions, the rate of electron transfer is high ($k \sim 5 \times 10^9 \text{ s}^{-1}$) and it competes with nonradiative decay of the excited singlet state. The use of rigid media enhances the efficiency of fluorescence quenching, possibly by favouring folded conformations, relative to fluid solution so that it is possible to obtain quite high fluorescence quenching at low concentration of quencher without the need for diffusional encounters. Similar benefits could be obtained by using a protein to site chromophore and quencher, as found in natural photosynthesis, and there have been a few reports describing the use of such media [14, 15].

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