

Photoinduced Electron Transfer in a Zinc Phthalocyanine–Viologen Linked System

J. X. Liu, Q. Yu, Q. F. Zhou, and H. J. Xu*

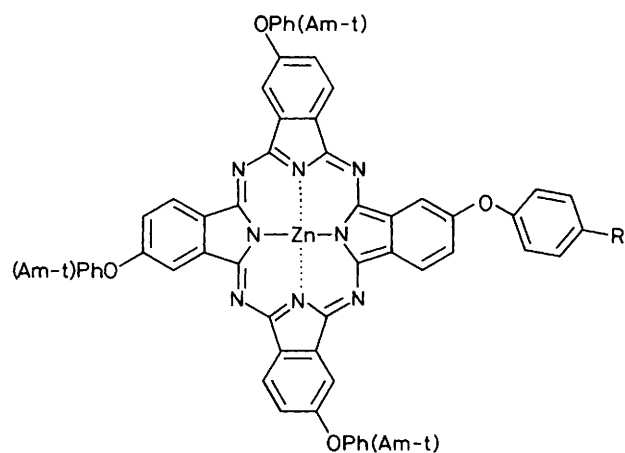
Institute of Photographic Chemistry, Academia Sinica, Bei Sha Tan, De Wai, Beijing 100012, People's Republic of China

The quenching of fluorescence of zinc phthalocyanine attached to viologen by a flexible chain has been studied and a long-living charge separated state was obtained in a dimethylformamide and water mixture by nanosecond laser photolysis.

A number of reaction centre models for artificial photosynthesis have been studied by the use of donor–acceptor linked systems.¹ An example is a porphyrin–quinone linked system for which charge-transfer states formed *via* singlet states are observed in the picosecond region.² In the case of a porphyrin–viologen linked system, charge separated states with lifetimes close to the μ s region have been reported by Porter³ and Matsuo.⁴ Our interest has centred on phthalocyanines which are known to undergo photoredox reactions⁵

and which have intense absorption bands in the 600–700 nm region so that they can collect more energy available in the solar spectrum. Previously, we have reported⁶ photoinduced redox reactions sensitized by metal phthalocyanines and their ability to photocatalytically cleave water.⁷ In this paper, phthalocyanine–viologen linked compounds (**II**) and (**III**) were prepared by coupling of *N*-butyl-4,4'-bipyridine to zinc 2,4-(4'-hydroxyphenoxy)-9,16,23-tri(*p*-t-amyloxy)-phthalocyanine compound (**I**) *via* 1,3-dibromopropane. Spectroscopic determination and nanosecond laser photolysis experiments were carried out and the photoinduced electron transfer characteristics were investigated. The structures of the model compounds are shown in Figure 1.

The parameters of electronic absorption spectra of compounds (**II**) and (**III**), characteristic of the spectra of metal phthalocyanines, are given in Table 1. Since the electronic absorption spectra of (**II**) and (**III**) are similar, there is no



(**I**) R = OH

(**II**) R = OEt

(**III**) R = O(CH₂)₃⁺N(C₆H₄)₂N⁺(CH₂)₃•Br⁻

(Am = amyl)

Figure 1

Table 1. Parameters of absorption spectra of (**II**) and (**III**) in DMF.

Compound	λ_{\max}/nm (log ϵ)
(II)	676 (5.33), 606 (4.66), 357 (4.99)
(III)	680 (5.13), 610 (4.65), 354 (4.85)

Table 2. Photophysical properties of covalently linked ZnPc–viologen compound (**II**) and (**III**) in DMF solution.

Compound	(II)	(III)
ϕ_f	0.24	0.078
τ_f/ns	4.2	3.4
$Q_S/\%$	—	65.7
$Q_D/\%$	—	19.0
K_{et}/s^{-1}	—	5.6×10^7

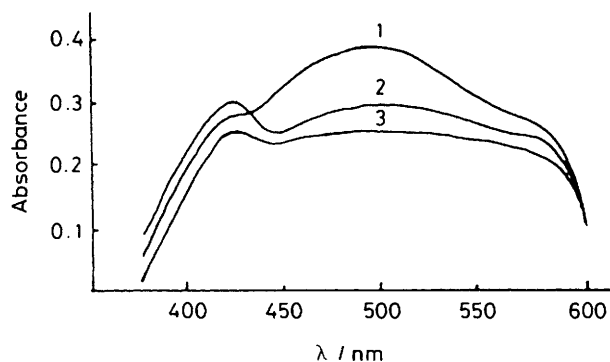


Figure 2. Transient difference absorption spectra of compound (III) (5.0×10^{-5} M) in 9:1 DMF-water at room temperature; 1—20 ns, 2—5.4 μ s, 3—100 μ s after 355 nm excitation.

indication of ground state complexation between zinc phthalocyanine (ZnPc) and the viologen of compound (III) in dimethylformamide (DMF). Furthermore, the fluorescence from the phthalocyanine moiety is appreciably quenched and the singlet excited state lifetime of ZnPc was reduced by the pendant viologen. The relative fluorescence quantum yields (ϕ_f) and fluorescence lifetimes (τ_f) measured in DMF solution at sufficiently low chromophore concentration (1.0×10^{-6} M), to suppress intermolecular interaction, and percentage quenching determined according to equations (1) and (2) are summarized in Table 2.

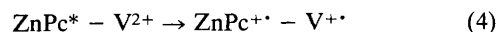
$$\% \text{ quenching } Q_S = (1 - \phi_f / \phi_f^{\text{ZnPc}}) \times 100 \quad (1)$$

$$\% \text{ quenching } Q_D = (1 - \tau_f / \tau_f^{\text{ZnPc}}) \times 100 \quad (2)$$

It is indicated that the percentage quenching calculated from fluorescence quantum yield measurements is more than three-fold larger than those calculated from fluorescence lifetime determinations. The observed difference in Q values is suggested to come from static quenching. It is assumed that, upon excitation, a random distribution of geometries of compound (III) is formed. When the fluorophore is adjacent to the viologen at the moment of excitation it is immediately deactivated, which accounts for the static portion of the quenching. The lifetime measurements were used to confirm that the portion of quenching was dynamic, which was responsible for the electron transfer process. The rate constant of electron transfer is calculated from equation (3) and is also included in Table 2.

$$K_{et}^s = 1/\tau_f - 1/\tau_f^{\text{ZnPc}} \quad (3)$$

Laser flash photolysis studies in 9:1 (v/v) DMF-water solution showed transient absorption spectra recorded at room temperature. The spectral shape observed 20 ns after 355 nm excitation (curve 1) in Figure 2 is different from that observed 5.4–100 μ s after excitation (curves 2 and 3). The broad transient absorption spectrum in the 400–600 nm region with a peak around 480 nm (curve 1) is assigned to the excited triplet state of ZnPc.⁸ A remarkable change observed between 5.4 and 100 μ s is the appearance of a new sharp band which has a peak at 410 nm. The absorption curve 2 can be interpreted in terms of superposition of absorption of $V^{+\cdot}$ with λ_{max} at 410 nm and the radical cation of ZnPc ($\text{ZnPc}^{+\cdot}$) with λ_{max} at 520 nm, which is buried in the triplet absorption of $^3\text{ZnPc}^*$ (* = excited state). After 100 μ s, curve 3 retains the feature of $V^{+\cdot}$ absorption and a rather broad band is observed in the 450–550 nm region. This broad band is mainly attributed to the triplet state of ZnPc. The difference in the transient absorption strongly indicates that appreciable photo-induced intramolecular electron transfer took place in the ZnPc-viologen linked system, giving redox-ion intermediates (equation 4). The nature of the photoactivated precursor ZnPc^*



cannot be specified at present. However, it is quite likely that the observed radical ion is generated *via* a triplet pathway, since none of the singlet linked ion pairs has been reported to survive beyond 1 μ s.⁹ It is conceivable that there may be some degree of charge separation from a singlet excited state photoreaction, but our experimental limitations preclude its observation.

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