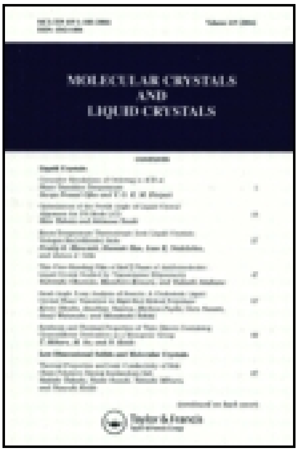

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INTERFACIAL ELECTRON TRANSFER FROM CdS CLUSTERS TO METALLOPORPHYRINS

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Abstract The efficiency of interfacial electron transfer from CdS clusters to ZnTPP and CdTPP in CH_3CN and 2-propanol increases with decreasing cluster size and in the presence of O_2. The excited singlet states of ZnTPP and CdTPP do not participate in the transfer process. Photoproducts of ZnTPP, formed in the presence of excited CdS, were monitored via their absorption and emission spectra. Interfacial electron transfer from CdS (e^-/h^+) was probed via the recombination luminescence of the cluster.

Keywords: Semiconductor clusters, CdS clusters, interfacial electron transfer, ZnTPP, metalloporphyrins

INTRODUCTION

Semiconductor clusters with diameters smaller than a critical one (D_{crit}), dependent upon the nature of the semiconductor under consideration, exhibit size-dependent optical and spectroscopic properties[1-5]. The photogenerated charge carriers (e^-/h^+ pairs) experience a "space confinement" in such clusters bringing about an increase in the energy of the lowest eigenstate of the e^-/h^+ pair and the effective band gap of the cluster. Size-dependent determinations of the band gap energy are in fair agreement with predictions from elementary theory[1,6-8]. Furthermore, interfacial electron tranfer depends upon the nature of defects and surface states as well as the size of the cluster[9-12]. The primary products of interfacial electron transfer are the acceptor radical ion ($R^{\dot{-}}$) and a positively charged cluster (radical ion). In the absence of back electron transfer the electron acceptor can be reduced to fairly stable products.

Negative ions of porphyrins and metalloporphyrins were obtained chemically in reactions of ZnTPP with sodium benzophenone ketyl in tetrahydrofuran leading to a sodium salt of $[ZnTPP^{\dot{-}}]$[13]. The Soret band of $[ZnTPP^{\dot{-}}]^{-}\bullet Na^{+}$ was shifted to

455 nm compared with 422 nm of ZnTPP. The dinegative anion, $[ZnTPP]^{2-}\bullet Na_2^+$, whose protonated form changes to tetraphenylphlorin with excess of methanol, was obtained with anthracene negative ions. These early observations were followed by electrochemical studies which led to the determination of the reduction potentials of ZnTPP, i.e. -1.32 and -1.73 V vs SCE in DMF[14], studies of formation of porphyrin radical ions by cyclic voltametry[15], formation of radical ions of metalloporphyrins[16] and many other studies. Electron transfer photoreactions in pophryins and metalloporphyrins were reviewed as early as in 1978[16,17]. Chemical photooxidation, on the other hand, of ZnTPP was achieved more recently in CH_2Cl_2 with $Fe(ClO_4)_3$ leading to the formation of appropriate radical ions, $ZnTPP^+.ClO_4^-$(λ_{max}=409 nm) and $ZnTPP^{2+}.2ClO_4^-$($\lambda_{max}\approx$350 nm)[18]. Radical cations of ZnTPP were also formed in flash photolysis studies of ZnTPP in the presence of BQH_2 and other electron acceptors with redox potential more negative than those of the excited singlet and triplet ZnTPP[19].

We have been studying interfacial electron transfer from CdS clusters to inorganic redox couples (Eu^{3+}, Yb^{3+}, Sm^{3+}, etc.). The low stability of the divalent ions formed makes it difficult to monitor the yield of electron transfer. In this brief paper we present preliminary results of light induced electron-transfer between excited CdS and ZnTPP. Due to the relative stability of the radical anions and cations of ZnTPP electron transfer can be monitored more easily.

EXPERIMENTAL

Nonstoichiometric CdS clusters were prepared in CH_3CN and 2-propanol using the method of "arrested precipitation"[20]. Details are given elsewhere[11]. Colloidal suspensions of 2×10^{-4}M CdS with 8×10^{-4}M Cd^{2+} in CH_3CN are characterized by an emission maximum at 530-535 nm and a band gap energy (Eg), determined from plots of $\{\alpha(h\nu)\}^2$ vs $h\nu$(eV), equal to 3.05eV. Another preparation of 1×10^{-4} M CdS with 9×10^{-4} M Cd^{2+} excess in CH_3CN was characterized by $(\lambda_{em})_{max}\approx$530-540 nm and Eg≈3.0eV. Two different preparations of CdS clusters in 2-propanol, namely 2×10^{-4} M CdS with 5×10^{-4} M Cd^{2+} excess and 3×10^{-4} M CdS with 7×10^{-4} M Cd^{2+} excess, were characterized by $(\lambda_{em})_{max}$=535-540 nm, Eg=3.05eV and $(\lambda_{em})_{max}$=570-580 nm Eg≈2.9 eV, respectively. Zinc tetraphenylporphyrin was prepared from H_2TPP (chlorin free) and zinc acetate using methods from the literature[21]. Cadmium tetraphenylporphyrin was prepared as a complex in solution in the presence of excess Cd^{2+} and was characterized spectroscopically.

RESULTS AND DISCUSSION

The recombination luminescence of CdS in CH_3CN and in 2-propanol, excited at 364±1 nm, is quenched considerably by ZnTPP and to a less extent by CdTPP. The quenching efficiency of a given electron acceptor (i.e. ZnTPP) increases with decreasing cluster size (larger Eg value and blue-shifted emission spectrum). The value of Eg is predicted to increase with decreasing size of the cluster[1].

$$Eg=E_G + \hbar^2\pi^2/8R^2(1/m_e^*+1/m_h^*)-1.8e^2/\varepsilon R + \text{other terms} \qquad (1)$$

were Eg is the band gap energy of a cluster with radius R, E_G is the band gap energy of the bulk semiconductor and m_e^*, m_h^* the effective masses of the electron and hole in the cluster. Clusters of CdS with similar particle size are quenched by ZnTPP and CdTPP to a different extent and to a less extent in the absence of O_2. The recombination luminescence of CdS was monitored at the emission maximum of CdS clusters under consideration. The fluorescence of ZnTPP and CdTPP, excited at 546 nm, is not quenched by CdS clusters. Luminescence quenching of excited CdS clusters, $CdS(e^-/h^+)$, by ZnTPP and CdTPP cannot be described by the Stern-Volmer law at higher [ZnTPP] and [CdTPP] implying the participation of static rather than dynamic interactions. The initial slopes of Stern-Volmer plots (not shown), attributed to dynamic interactions at $[Q]\rightarrow O$,

$$I_F^O/I_F^Q=\{1 + (k_Q\tau)\ [Q]\}\ \exp\ [K[Q]] \qquad (2)$$

are summarized in Table 1. ($k_Q\tau$ and K values).

TABLE 1 Stern-Volmer initial slopes of the recombination luminescence quenching of CdS clusters by metalloporphyrins. $k_Q\tau(CdS\ \ e^-/h^+)/M^{-1}$ and K/M^{-1} (in parentheses)

SAMPLE	λ em (nm)	Eg (eV)	ZnTPP Deaerated	ZnTPP Aerated	CdTPP Aerated
$2x10^{-4}M$ CdS; $8x10^{-4}M\ Cd^{2+}$ in CH_3CN.	530-535	3.05	$1.0x10^5$ ($1.0x10^5$)	$1.5x10^5$ ($1.4x10^5$)	$5.0x10^4$ ($5.2x10^4$)
$1x10^{-4}M$ CdS; $9x10^{-4}M\ Cd^{2+}$ in CH_3CN.	535-540	3.0	-	$1.3x10^5$ ($1.3x10^5$)	-
$2x10^{-4}M$ CdS; $5x10^{-4}M\ Cd^{2+}$ in 2-propanol.	535-540	3.05	-	$6.0x10^4$ ($6.0x10^4$)	-
$3x10^{-4}M$ CdS: $7x10^{-4}M\ Cd^{2+}$ in 2-propanol.	570-580	2.9	-	$2.0x10^4$ ($3.0x10^4$)	-

At higher quencher concentrations the exponential part(static interactions) of Eq(2) becomes more significant. Semilog plots of $(I_F)^Q_{cds}/I^0_F)_{cds}$ vs [Q], shown in Fig. 1 lead to straight lines, with one notable exception. The recombination luminescence quenching of CdS(e^-/h^+) is attributed to electron transfer of e^-_{CB} to the appropriate electron acceptor. The criterion for such electron transfer process is:

$$\Delta G_{el.tr}=E^0(CdS^+/CdS(e^-/h^+)) - E^0(Q/Q^-) - e^2/\varepsilon R < O \qquad (3)$$

where R is the distance between donor and acceptor in the precursor ion-pair. The lack of quenching of the florescence emission of ZnTPP(CdTPP) by CdS implies $E^0(CdS/CdS^-)<E^0(ZnTPP^+/ZnTPP^*)$, i.e. the redox potential of CdS is more negative than the redox potential of ZnTPP*. Similarly, recombination luminescence quenching of CdS(e^-/h^+) by ZnTPP and CdTPP implies $E^0(CdS^+/CdS(e^-/h^+))<E^0(ZnTPP/ZnTPP^-)$.

Electron transfer from the conduction band of CdS to ZnTPP and CdTPP is accompanied by drastic changes in both the absorption and emission spectra of ZnTPP and CdTPP. The characteristic absorption bands of the metalloporphyrin (Soret and Q-bands) nearly disappear and are replaced by new weak bands at 450-500 nm, 640 nm and in the UV region. Typical absorption spectra of ZnTPP, irradiated at 365 nm in the presence of CdS are shown in Fig. 2. In the presence of O_2 the photodamage brought about on ZnTPP in the presence of excited CdS is enhanced. The lack of well defined isosbestic points is indicative of the existence of different photochemical mechanisms in deaerated and air saturated systems. It should be pointed out that ZnTPP irradiated under similar conditions in the absence of CdS clusters remained totally unchanged.

The luminescence spectra of the photoproducts of ZnTPP formed in the presence of CdS are totally different from those of ZnTPP. They are strongly dependent upon the excitation wavelength. Emission spectra of ZnTPP-CdS samples in CH_3CN (λ_{exc}=546) consist of a strong broad emission band at about 600 nm (slightly blue-shifted from 603 nm) and an extremely weak and broad band at about 650 to 655 nm (Fig. 3). The latter emission band becomes very strong, very broad and slightly red-shifted under excitation at 365 nm. Under the same excitation conditions the emission band at about 600 nm becomes very weak (approximately 1/5 of that at 655 nm following 3 hours irradiation at 365 nm). It is apparent that more than one photoproduct are produced. Although the primary reduction product is expected to be $ZnTPP^{\cdot-}$ or $ZnTPPH^{\cdot}$ with a Soret band at about 455 nm [13], the final reduction

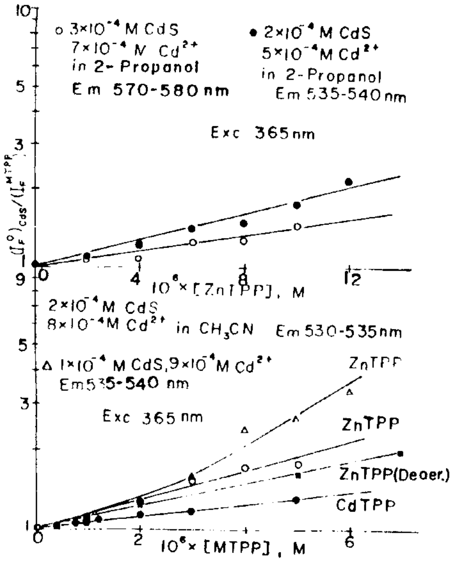

Fig. 1 Semilog plots of recombination luminescence quenching of CdS clusters by metalloporphyrins

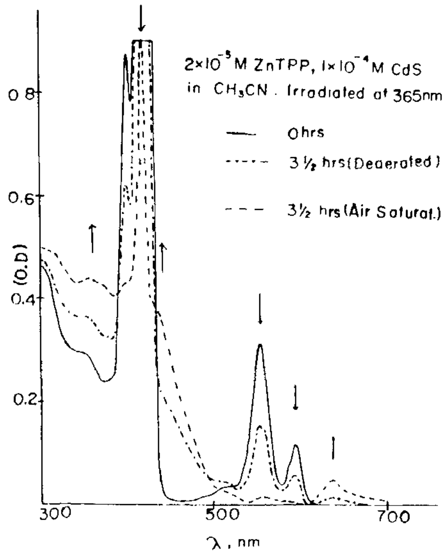

Fig. 2 Absorption spectra of non-irradialed and UV-irradiated CdS-ZnTPP mixtures.

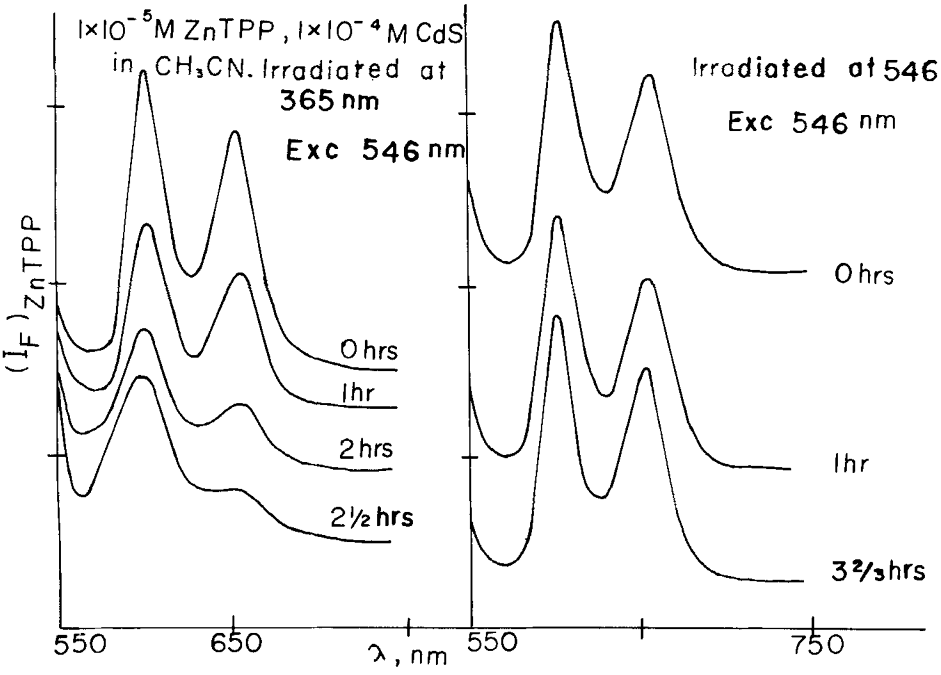

Fig. 3 Luminescence spectra of ZnTPP irradiated at different time intervals at 365 and 546 nm in the presence of CdS clusters.

product is more likely to be tetraphenylphlorin with a weak absorption band at 600-640 nm, weak UV absorption and emission at 655-660 nm. In addition, the role of O_2^-, formed via an electron-transfer process from CdS(e^-/h^+) to O^2, is not clear at this time. The intensity of recombination luminescence is about 20% lower than that of deaerated systems. Whether O_2 mediates electron transfer from CdS(e^-/h^+) to ZnTPP, leads to oxidation products, or both remains to be determined.

Studies are underway leading to quantitative photodamage of ZnTPP and CdTPP in deaerated and air saturated systems in the presence of CdS clusters. A larger scale production of photoproducts is required, at short irradiation times, for a successful NMR product identification. In addition, several other metalloporphyrins (different redox potentials) are being used to probe the size-dependence of interfacial electron transfer.

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