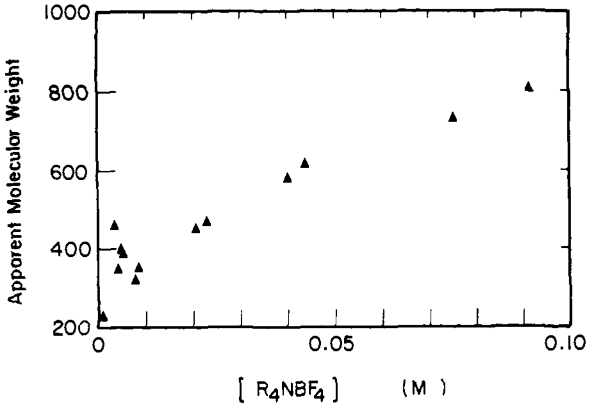
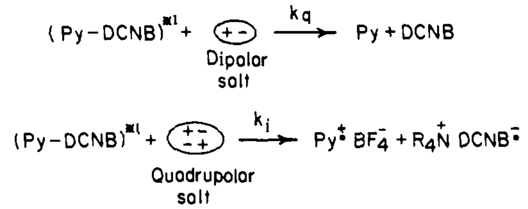


Figure 3. Plot of the apparent molecular weight of tetra-*n*-butylammonium tetrafluoroborate as a function of concentration in dimethoxyethane.

Scheme I



this concentration is sufficient to quench the exciplex emission significantly (Figure 1). However, the efficiency of Py$^{+\cdot}$ formation from quenched exciplexes increases at greater salt concentrations. This finding underscores and expands the exciplex emission quenching results; at low salt concentration the exciplex is quenched but gives Py$^{+\cdot}$ only inefficiently, while at higher salt concentration Py$^{+\cdot}$ is a major product. This nonlinear behavior may be traced to the self-association of R_4NBF_4.

The association of unionized salts to form quadrupoles and higher aggregates in nonpolar solvents is well-known.[9] Figure 3 shows a plot of the apparent molecular weight of R_4NBF_4 (determined by vapor pressure osmometry) as its concentration increases in DME solution. The molecular weight is seen to increase monotonically over the salt concentration range where nonlinear behavior is observed for the exciplex fluorescence quenching and for the yield of Py$^{+\cdot}$.

These observations are reasonably coupled and suggest that reaction of the exciplex with monomeric, dipolar salt results in quenching but not in radical ion formation and that the reaction of the exciplex with quadrupolar or aggregated salt gives radical ions in good yield, probably by an ion-pair exchange process. These concepts are illustrated for the case where the higher aggregates are represented as quadrupoles in Scheme I. This mechanism can account both qualitatively and quantitatively for the findings if $k_q > k_i$.

Finally, we confirmed that the radical ion pairs presumed to be formed from reaction of salt with the exciplex in nonpolar solvent give the same products as solvated ions formed in polar solvent, at least for one case. The electron-transfer-sensitized photooxidation of *trans*-stilbene by 9,10-dicyanoanthracene was used as a probe.[10] In acetonitrile this reaction gives benzaldehyde presumably by reaction of the stilbene radical cation. No oxidation is observed when this reaction is attempted in DME. However, addition of 0.035 M R_4NBF_4 to the DME solution leads to efficient formation of benzaldehyde. Similarly, when 1,4-dioxane is used as a solvent only a very low yield of Py$^{+\cdot}$ is detected by transient absorption spectroscopy even at high salt concentration. In this case benzaldehyde formation remains inefficient even when R_4NBF_4 is added to the reaction solution.

In sum, the quenching of exciplexes by R_4NBF_4 leads to ionic dissociation at high salt concentration where formation of quadrupoles and higher aggregates occurs. At low salt concentration, the exciplex is quenched but does not dissociate. This unusual behavior may be a useful probe for the intermediacy of ionic intermediates in photochemical processes.

Acknowledgment. This work was supported by the Office of Naval Research. We thank Dr. Peter Wolynes of this Department for some thoughtful suggestions.

Registry No. Py, 129-00-0; DCNB, 623-26-7; Bu_4NBF_4, 429-42-5.

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Binuclear Complexes of a Covalently Linked Porphyrin-Bipyridine Ligand

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In recent years there have been many attempts to devise synthetic systems capable of photochemical energy conversion analogous to photosynthesis.[1-3] Many of these have been based on the excited-state chemistry of metalloporphyrins[4] or tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$).[3-8] We present here the synthesis, electrochemical properties, and luminescence behavior of a novel binuclear complex containing a $Ru(bpy)_3^{2+}$ covalently linked across the face of a porphyrin at a distance of approximately 4 Å.[9] The fixed proximity of the two photochemically active centers results in a strong interaction which is reflected in both the luminescence and electrochemical properties of the complex.

The 5,5′-bis(3-hydroxypropyl)-2,2′-bipyridine (**1**) was prepared by the following route. Bromination of diol **2**[10] with HBr in acetic acid gave bis(bromomethyl)bipyridine **3**, which was alkylated by diethyl malonate to tetraester **4**. Decarboxylation of **4** to diester **5** in wet Me_2SO followed by $LiAlH_4$ reduction gave diol **1** in 21% overall yield from **2**. Reaction of diol **1** with the diacid chloride of mesoporphyrin II **6**[11] at high dilution in methylene chloride provided **7** (27%).[12] Reaction of **7** with $Ru(bpy)_2Cl_2$ in refluxing

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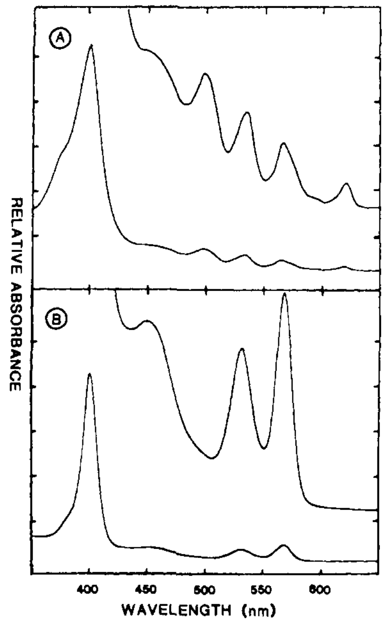
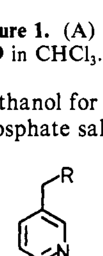
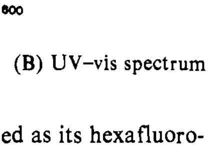


Figure 1. (A) UV–vis spectrum of **8** in $CHCl_3$. (B) UV–vis spectrum of **9** in $CHCl_3$.

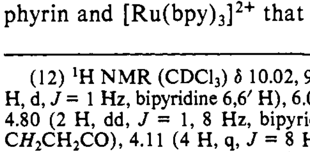
methanol for 48 h gave **8**, which was isolated as its hexafluorophosphate salt.[13]



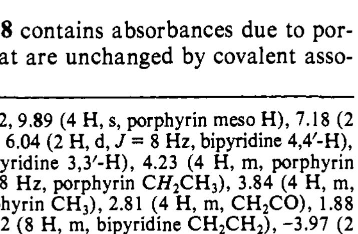
(1) R = CH_2CH_2OH
(2) R = OH
(3) R = Br
(4) R = $CH(CO_2Et)_2$
(5) R = CH_2CO_2Et



(6)



(7)



(8) M = 2H
(9) M = Zn

The UV–vis spectrum of **8** contains absorbances due to porphyrin and $[Ru(bpy)_3]^{2+}$ that are unchanged by covalent association (Figure 1A). Insertion of zinc into the porphyrin ($Zn(OAc)_2/CH_2Cl_2$, MeOH) yields the heterobinuclear complex **9**[14] and a further resolution of the spectral components (Figure 1B).

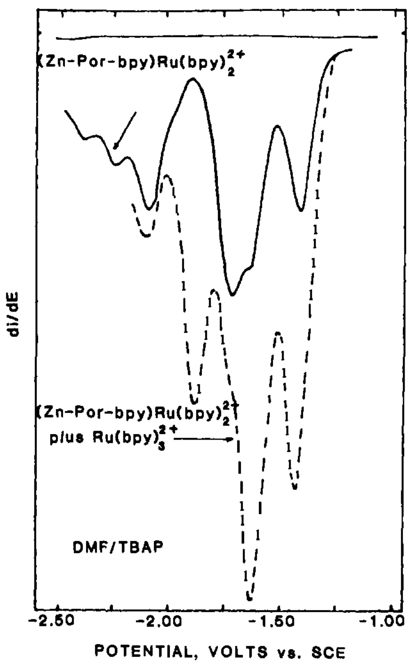


Figure 2. Differential-pulse polarogram of **9** in the cathodic potential region (—) showing six redox events. Spiking this sample with $Ru(bpy)_3^{2+}$ (---) clearly shows the first two waves to be Ru related, while the $Ru(bpy)_3^{0/1-}$ wave is not observed at the expected potential. The third and fourth wave are not affected by the spike and thus assigned to porphyrin redox chemistry. A dry DMF electrolyte containing 0.1 M TBAP was employed.[16]

The room temperature solution ($CHCl_3$) luminescence spectra of **7** and **8** show two peaks at 622 and 688 nm upon irradiation into any of the porphyrin absorptions. The emission is shifted to 578 and 626 nm in the binuclear complex **9**. Interestingly, no $[Ru(bpy)_3]^{2+}$ emission is observed from either complex **8** or **9** independent of the excitation wavelength. This observation is confirmed by excitation spectroscopy, which only reproduced the porphyrin absorption peaks for both **8** and **9**. The mechanism of this efficient ruthenium-quenching process is currently under investigation. Note that the quenching process does not lead to a porphyrin emissive excited state. Mixtures, 1:1, of **7** and $[Ru(bpy)_3]^{2+}$ do not indicate any quenching of the $[Ru(bpy)_3]^{2+}$ MLCT excited state.[15] Thus the behavior of compounds **8** and **9** is a result of the intimate association of the porphyrin and bipyridal complexes.

Similarly the electrochemistry[16] of **9** indicates site–site interactions. The complexes were investigated by using cyclic voltammetry and differential-pulse polarography in dry DMF/0.1 M tetra-*n*-butylammonium perchlorate electrolyte. Compounds **7**–**9** yielded an oxidation wave at approximately +0.7 V vs. SCE typical of porphyrin oxidation to the radical cation, whereas **8** and **9** yielded a second oxidation wave at +1.16 V vs. SCE as expected for the $[Ru(bpy)_3]^{2+/3+}$ couple. Cyclic voltammetry of **7** in dry acetonitrile electrolyte suggests that this latter potential may also be associated with the oxidation of the porphyrin ring to the dication. Unmetalated **7** produced two quasi-reversible reduction waves with half-wave values of −1.57 and −2.04 V vs. SCE. Addition of the Ru center to the system caused the appearance

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[12] ^1H NMR ($CDCl_3$) δ 10.02, 9.89 (4 H, s, porphyrin meso H), 7.18 (2 H, d, J = 1 Hz, bipyridine 6,6′ H), 6.04 (2 H, d, J = 8 Hz, bipyridine 4,4′-H), 4.80 (2 H, dd, J = 1, 8 Hz, bipyridine 3,3′-H), 4.23 (4 H, m, porphyrin CH_2CH_2CO), 4.11 (4 H, q, J = 8 Hz, porphyrin CH_2CH_3), 3.84 (4 H, m, OCH_2), 3.70, 3.56 (12 H, s, porphyrin CH_3), 2.81 (4 H, m, CH_2CO), 1.88 (6 H, t, J = 8 Hz, CH_2CH_3), 0.82 (8 H, m, bipyridine CH_2CH_2), −3.97 (2 H, s, NH); mass spectrum $(M + H)^+$ 803, calcd mass (M) for $C_{50}H_{54}N_6O_4$, 802; UV–vis spectrum λ_{max} = 399 nm (ϵ 1.4 × 10^5), 496 (1.2 × 10^4), 530 (9.2 × 10^3), 566 (5.9 × 10^3), 620 (3.9 × 10^3).

[13] ^1H NMR ($CDCl_3$) δ 10.47, 10.27, 10.26, 10.14 (4 H, s, porphyrin meso H), 7.98–6.25 (20 H, m, bipyridine H, alkylated bipyridine 6,6′,4,4′-H, 4.85–3.85 (14 H, m, alkylated bipyridine 3,3′-H, CH_2CH_2CO, CH_2CH_3, OCH_2), 3.82, 3.75, 3.71, 3.67, (12 H, s, porphyrin CH_3), 3.56–2.90 (4 H, m, CH_2CO), 1.85 (6 H, m, CH_2CH_3), 0.90 (8 H, m, bipyridine CH_2CH_2), −3.85 (2 H, m, NH); mass spectrum $(M + H)^+$ 1216, calcd mass (M) for $C_{70}H_{70}N_{10}O_4Ru$, 1215; UV–vis spectrum λ_{max} = 400 nm (ϵ 1.9 × 10^5), 450 (2.2 × 10^4), 496 (1.9 × 10^4), 530 (1.4 × 10^4), 566 (1.1 × 10^4), 620 (8.7 × 10^3). **8** is a mixture of two diasteriomers due to the combined chiralities of the octahedral metal complex and the strapped porphyrin (planar chirality). This is seen in the NMR of **8** which shows four equivalent singlets due to the porphyrin meso Hs and four due to the porphyrin CH_3 groups.

[14] Mass spectrum $(M)^+$ 1278, calcd mass (M) for $C_{70}H_{68}N_{10}O_4Ru$ Zn, 1278; UV–vis spectrum λ_{max} = 480 nm (ϵ 2.0 × 10^5), 450 (2.2 × 10^4), 538 (1.7 × 10^4), 574 (1.8 × 10^4).

[15] At a series of concentrations ranging from 10^{-7} to 10^{-3} M.

[16] Electrochemical experiments were carried out by using a PAR 174 electrochemical analyzer. A standard three-electrode cell employing platinum working electrodes and counterelectrodes with an Ag/Ag^+ (acetonitrile) reference electrode was employed. The system was protected from water and air by a dry nitrogen purge and rigorously dried electrolyte.

of four reduction waves (−1.51, −1.68, −1.99, and −2.11 V vs. SCE). A comparison of the electrochemistry of $Ru(bpy)_3^{2+}$ with compound **7** suggests that the most positive wave is associated with both the $Ru(bpy)_3^{2+/1+}$ couple and the formation of the porphyrin radical anion. The second wave correlates with the $Ru(bpy)_3^{1+/0}$ redox couple and the third wave with the $Ru(bpy)_3^{0/1-}$ system. The most negative wave is therefore assigned to the formation of the porphyrin dianion. Addition of Zn to the porphyrin ring **9** leads to the appearance of six quasi-reversible reduction waves, the differential-pulse polarogram of which is shown in Figure 2. The first two waves are similar to those found in **8** and are believed to be associated with the first two reductions of the Ru complex since addition of Zn is expected to cause a negative shift in the porphyrin reduction waves. Interestingly, the wave at −1.99 V vs. SCE observed for both $[Ru(bpy)_3]^{0/1-}$ and complex **8** is not observed; rather two new waves at −2.27V and −2.39V vs. SCE are noted. Presumably one of these waves is associated with the third Ru reduction. The remaining two waves (−1.76 and −2.12 V vs. SCE) are associated with the Zn-porphyrin system. Spectroscopic experiments are currently being employed to unambiguously identify these waves. Yet, it is remarkable to note that the $Ru(bpy)_3^0$ species is stabilized to an extent of 350 mV (~8 kcal/mol) with respect to the $Ru(bpy)_3^{1-}$ species by the presence of the zinc porphyrin.

Acknowledgment. Acknowledgement is made by ADH to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are also very grateful to Dr. Steve Unger of the Squibb Institute for Medical Research for obtaining mass spectral data.

Registry No. 1, 92642-08-5; **2**, 63361-65-9; **3**, 92642-09-6; **4**, 92642-10-9; **5**, 92642-11-0; **6**, 92669-33-5; **7**, 92642-12-1; **8**, 92642-05-2; **9**, 92642-07-4.

Magnetic Field Effect on the Photosensitized Oxidation Reaction of 1,3-Diphenylisobenzofuran in SDS Micellar Solutions

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We wish to report a very significant magnetic field (MF) effect on the anthraquinone (AQ)-photoinduced oxidation reaction of 1,3-diphenylisobenzofuran (DPBF) in sodium dodecyl sulfate (SDS) micellar solution. Photoirradiation of the 330-nm absorption band of AQ and DPBF in aerated SDS micellar solution results in the formation of *o*-dibenzoylbenzene (DBB),[1] while DPBF itself is photostable in deaerated micellar solution. A typical UV spectral change during photolysis of the solution is shown in Figure 1a.[2] The bands at 330 and 410 nm are mainly due to AQ and DPBF, respectively. Since DPBF photoreacts very slowly in the aerated micellar solution without AQ, the oxidation of DPBF is mostly photosensitized by AQ. Further, a laser flash photolysis of this micellar solution[3] shows a remarkable quenching of anthrasemiquinone (AQH·) transients by oxygen in the micelle (apparent quenching rate, (1–2) × 10^6 s^{-1}),[4] which implies a possible participation of hydroperoxy radical ($HO_2\cdot$) in the present oxidation of DPBF, though DPBF is generally accepted as a singlet oxygen trap.[5]

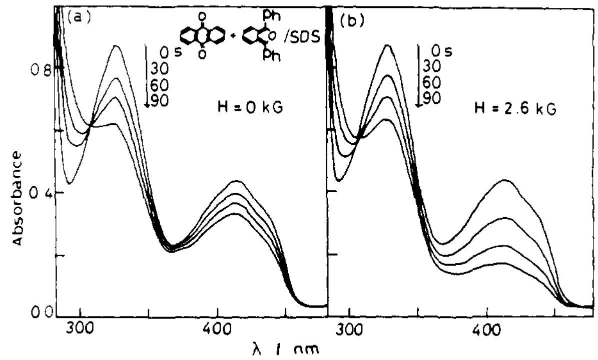

Figure 1. Magnetic field effect on the UV spectral change of the photolysis of the 0.4 M SDS micellar solution containing AQ (1 × 10^{-4} M) and DPBF (2 × 10^{-5} M) (see text): (a) 0 kG; (b) 2.6 kG.

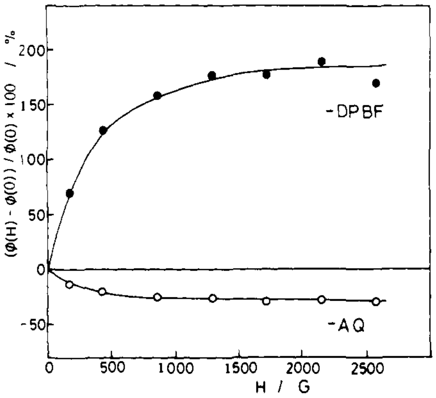

Figure 2. Magnetic field dependence of the relative quantum yield, ϕ, of disappearance of DPBF and AQ in the SDS micellar solution (see text).

Figure 1b shows the MF effect (2.6 kG) on the UV spectral change during the photolysis. The field significantly enhances the rate of disappearance of the 410-nm band (i.e., the quantum yield of disappearance of AQ), while it slightly decreases that of the 330-nm band (i.e., the disappearance of AQ). Figure 2 shows the MF dependence of the relative quantum yield, ϕ, of disappearance of DPBF and AQ determined from the spectral changes.[6] The change of the yield, $Q(H)$, at magnetic field H is defined as follows:

$$Q(H) = 100(\phi(H) - \phi(0))/\phi(0) \qquad (1)$$

The Q value of DPBF increases significantly up to ~1 kG and then slowly, while that of AQ decreases up to ~1 kG and is almost constant at higher field. At 2.6 kG, the Q values of DPBF and AQ are 180% and -30%, respectively.

AQ and DPBF are almost completely micellized. Taking into account the concentration of the solution,[7] coexistence of AQ and DPBF in the same micelle is infeasible. Therefore no direct reaction between AQ and DPBF in a micelle may occur. A proposed reaction mechanism is as follows:

$$AQ \xrightarrow{h\nu} {}^1AQ \rightarrow {}^3AQ \rightarrow {}^3\overline{AQH\cdot\cdot S} \qquad (2)$$

---

[1] The 0.8 M SDS micellar solutions containing AQ and DPBF were irradiated with a 500-W xenon-arc lamp equipped with a $NiSO_4$–$CuSO_4$ aqueous solution filter and a glass filter (Toshiba, UV-D33S) (λ_{max}, 330 nm). Photoproducts in the solution were extracted with ethyl acetate and benzene, followed by the liquid chromatography. A main product was assigned to DBB by melting point, mass, and NMR measurements.

[2] Typically, 3 mL of aerated 0.4 M SDS micellar solution of AQ (1 × 10^{-4} M) and DPBF (2 × 10^{-5} M) in a 1-cm square quartz cell placed at the center of an electromagnet was irradiated with a 330-nm light.[1]

[3] For experimental setup, see ref 8a.

[4] Concentrations of oxygen are estimated to be 3 × 10^{-4} M in water and 1 × 10^{-3} M in the micelle: Matheson, I. B. C.; King, A. D., Jr. *J. Colloid Interface Sci.* **1978**, *66*, 464.

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[6] ϕ of DPBF was determined from the initial intensity change at 440 nm upon irradiation. ϕ of AQ was similarly determined from the change at 328 nm, after correcting the intensity due to DPBF.

[7] The concentration of the SDS micelle is estimated to be 6.5 × 10^{-3} M: Turro, N. J.; Yakta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951.