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SURFACTANT PORPHYRINS LINKED TO RUTHENIUM OXIDE MICROCOLLOIDS: A MICROHETEROGENEOUS PHOTOREACTOR

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Summary. The synthesis of a series of porphyrins linked through bipyridines to RuO_2 microcolloids is described. These compounds were designed for use in water-in-oil microemulsions where the porphyrin, a one-electron photocatalyst localized in the organic phase, can transfer charge across the phase boundary to the RuO_2, a multi-electron dark catalyst localized in the aqueous phase. The redox behavior of these compounds has been characterized by cyclic voltammetry and their diffusion coefficients were measured by chronocoulometry. Fluorescence and phosphorescence measurements on these compounds are consistent with efficient photoelectron transfer from the excited singlet state of the porphyrin.

Introduction.

The molecular engineering of molecules for solar energy conversion has become increasingly popular in the last decade.[1] A successful photosynthetic system must include a chromophore which absorbs visible light, an electron transfer pathway that separates the electron-hole pair, and catalytic sites which effect the transformation of the electron and hole into reduced and oxidized products, respectively. The prevention of the back reaction (which degrades the light energy into heat) is one of the key problems in this area.

A large number of molecules have been designed which mimic some aspect of the natural photosynthetic reaction center.[1,2] Quinones have been covalently attached to porphyrins directly on the meso carbon,[3] by flexible linkages of various lengths,[4] and through a variety of rigid spacers.[5] In general, the competition between the rates of forward and back electron transfer is such that, at very short donor-to-acceptor (D-to-A) distances, one observes substantial fluorescence quenching but the lifetime of the redox product is too short to be measured. With increasing D-to-A distance the yield of redox product ($D^{+\cdot}$ $A^{-\cdot}$) decreases but its lifetime increases. The fluorescence quenching is also a function of spacer geometry, solvent, temperature, etc. Another common acceptor which has been attached to porphyrins is the viologen dication, MV^{2+}.[6] For a given length of flexible spacer, the lifetime of the charge separated state with this acceptor ($D^{+\cdot}$ $A^{+\cdot}$) is longer than that with a quinone ($D^{+\cdot}$ $A^{-\cdot}$), presumably because of the electrostatic repulsion between the two cation radicals. Some similar compounds have been designed around ruthenium polypyridines in place of the porphyrins,[7] while others have attached ruthenium polypyridines to porphyrins.[8] In any scheme such as this, the efficiency of energy conversion will be proportional to the rate at which the initially formed radical pair transfers charge on to the ultimate products relative to the rate at which the back electron transfer occurs. For research applications, the back electron transfer is often short circuited by the use of sacrificial donors or acceptors; for practical applications, however, this is not an option.

A more complex, and more biomimetic, system has been developed through the elegant work of Gust and Moore et al.[9] who linked a β-carotene with a porphyrin-quinone compound. The original photoelectron transfer from the porphyrin to the quinone is followed by a (dark) electron transfer from the carotene to the oxidized porphyrin, generating a long-lived charge separated state. Another strategy for increasing the yield of photoproducts, which is also important in biological systems, involves photoelectron transfer across a phase boundary,[4c,9b,10] e.g., in membranes, micelles or microemulsions, where the electrostatic field at the interface can present a barrier to the back electron transfer. In these cases, ideally, one photoproduct is soluble in the organic phase while the other is soluble in the aqueous phase.

In order to utilize the energy stored in the initially formed charge-separated species at a rate competitive with the back electron transfer, catalysts are usually required. This is especially true for the important multi-electron reactions such as the splitting of H_2O or the reduction of CO_2. The energy input required to perform such reactions is often inversely proportional to the number of electrons transferred per catalytic step. For example, the one electron oxidation of H_2O to hydroxyl radical occurs at 2.5 V (vs SSCE), the two electron oxidation to hydrogen peroxide occurs at 1.48 V, while the four electron oxidation directly to O_2 occurs at 0.94 V.[11] Thus, the kinetically simple reactions are often energetically difficult, and vice versa. Given the limited amount of energy available to a solar conversion system, multiple electron catalysts will often be needed to perform the desired redox reactions. Furthermore, it is important to keep the number of steps in the electron transfer chain to a minimum, since, to proceed at a useful rate, every step must involve a substantial decrease in free energy.

We have attempted to design a system which incorporates a number of these considerations into a single molecule. We report here the synthesis and preliminary characterization of a surfactant-like porphyrin linked, through a bipyridine, to a ruthenium oxide microcolloid (Figure 1).

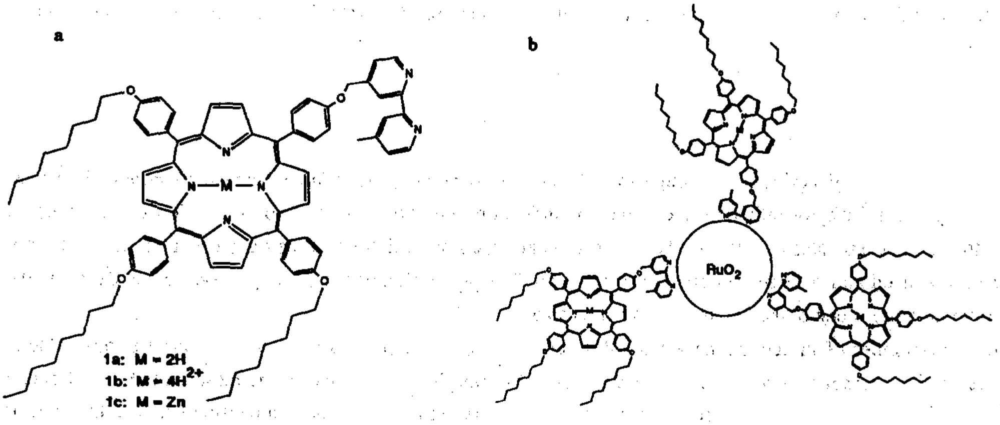

Figure 1. (a) Structure of the porphyrin-bipyridine compounds, **1a**, **1b**, and **1c**. (b) Schematic drawing of the porphyrin-bipyridine compounds complexed to a ruthenium oxide microcolloid.

This molecule was designed for use in water-in-oil microemulsions, where the porphyrin, in the organic phase, can transfer charge across the phase boundary to the RuO_2 catalyst in the aqueous phase. This couples a one electron photocatalyst to a multielectron dark catalyst by a single charge transfer step. It was also thought that charge transfer to a catalyst with a high density of states (relative to the porphyrin) might result in a further decrease in the rate of back electron transfer. A number of these compounds have been prepared and we describe their chemical, electrochemical, and photophysical properties.

Experimental.

Instrumental. Carbon and proton NMR spectra were measured with a General Electric GN-500 spectrometer. Fast atom bombardment (FAB) mass spectra were performed on a Finnigan TSQ 70 instrument with the sample in a 3-nitrobenzyl alcohol matrix. UV-visible spectra were taken on a Hewlett-Packard 8451A single beam spectrophotometer. Steady state fluorescence and phosphorescence spectra were measured on an SLM Aminco 500 C spectrofluorometer equipped with a phosphorimeter attachment. Electrochemical measurements were performed either with a Bioanalytical Systems (BAS) 100 Electrochemical Analyser or with a Princeton Applied Research 175 universal programmer, a Model 173 potentiostat and a Model 179 digital coulometer. The signal was recorded on a Houston Instruments 2000 X-Y recorder. A conventional single compartment electrochemical cell was used with a Pt disc working electrode of 0.026 cm^2 area, a Pt wire counter electrode and a $Ag/AgNO_3$ (0.1 M in acetonitrile) reference electrode.

Synthesis. Zinc-5,10,15-tris(4-octyloxyphenyl)-20-(4-hydroxyphenyl)-porphyrin. The free base was prepared by the method of Little[12] with the substitution of 4-octyloxybenzaldehyde (Aldrich) for 4-tolylaldehyde. It was purified by chromatography on SiO_2 in the dark (eluent, 1% MeOH in $CHCl_3$), metallated with $Zn(OAc)_2$ in $CHCl_3/MeOH$ and rechromatographed as before.

4-Bromomethyl,4'-methylbipyridine was prepared by the method of Lehn.[13]

ZnPB (1c). Zinc-5,10,15-tris(4-octyloxyphenyl)-20-(4-hydroxyphenyl)porphyrin (528 mg, 0.49 mmol) and 4-bromomethyl,4'-methylbipyridine (1.1 g, 4.2 mmol) were dissolved in dry DMF (90 ml) and toluene (10 ml) in the dark under N_2. K_2CO_3 (4 g) was added and the mixture was stirred for 3 d at 40° C. The crude product was precipitated by addition of $H_2O/MeOH$ (1:1), filtered, chromatographed on SiO_2 in the dark (eluent, 1% pyridine in $CHCl_3$) and recrystallized from $CHCl_3/MeOH$. The yield was 376 mg (61%). Mp 200-203° C. FAB *m/e* calcd for $C_{80}H_{86}O_4N_6Zn$ 1259, *m/e* found 1259. ^1H NMR (500 MHz, 3.5% D5-pyridine in $CDCl_3$) δ 0.94 (t, 9 H, J=7 Hz), 1.36 (m, 24 H), 1.61 (m, 6 H), 1.96 (m, 6 H), 2.45 (s, 3 H), 4.22 (t, 6 H, J=7 Hz), 5.40 (s, 2 H), 7.16 (m, 1 H), 7.24 (m, 6 H), 7.30 (m, 2 H), 7.59 (m, 1 H), 8.09 (m, 6 H), 8.11 (m, 2 H), 8.32 (m, 1 H), 8.60 (m, 1 H), 8.62 (m, 1 H), 8.78 (m, 1 H), 8.90 (m, 8 H). ^{13}C NMR (125.76 MHz, 3.5% D5-pyridine in $CDCl_3$) δ 14.02, 21.07, 22.58, 26.12, 29.19, 29.36, 29.41, 31.74, 68.12, 68.60, 112.15, 112.54, 119.08, 120.09, 121.59, 121.97, 122.76, 122.96, 123.16, 124.75, 131.21, 131.36, 131.40, 135.06, 135.25, 135.35, 135.44, 135.66, 148.86, 148.92, 149.08, 149.29, 149.42, 150.03, 150.16, 158.41.

ZnPBR 3:1(3c). 1a (251 mg, 0.21 mmol) was dissolved in 80 ml dry THF. $RuCl_3 \cdot 3H_2O$ (164 mg, 0.63 mmol) was dissolved in 30 ml dry MeOH and added to the porphyrin solution. The mixture was heated under reflux in the dark under N_2 for 5 h before being cooled to room temp. At this stage one ruthenium should be complexed to every bipyridine. The hydrolysis of the ruthenium chloride to the oxide was achieved by the addition of triethylamine (3 ml) and H_2O (3 ml); this was stirred overnight. The solution was then centrifuged for 15 min to remove small amounts of uncomplexed RuO_2. $Zn(OAc)_2$ was added to the supernatant which was briefly heated until metallation was complete (as observed by the visible absorption spectrum) and H_2O was added to induce crystallization of the product which was then filtered and dried *in vacuo*. The yield was 270 mg. XPS measurements showed peaks characteristic of Ru(IV) at binding energies of 281.6 and 285.7 eV.[14] Elemental analysis (Galbraith) showed a ruthenium to carbon ratio of 0.29 (by weight); the calculated ratio, assuming 3 ruthenium atoms per porphyrin, is 0.32. This is consistent with the small amounts of RuO_2 which were removed by centrifugation. Thus, the actual average ruthenium to porphyrin ratio was 2.6:1. This synthesis clearly led to a distribution of particle sizes and of stoichiometries. When we refer to RuO_2 microcolloids, it should be understood that this is an oversimplification. At very small particle sizes the stoichiometry is uncertain and these particles should perhaps be described as RuO_x clusters rather than microcolloids. Furthermore, they are presumably hydrated to some degree.

ZnPBR 7:1 (4c). This was synthesized in the same manner as ZnPBR 3:1 but with a 7 fold excess of $RuCl_3$. Much larger amounts of RuO_2 were removed by centrifugation of this compound consistent with the ratio Ru/C = 0.35 found by elemental analysis, compared to the calculated ratio for a 7:1 compound, Ru/C = 0.73. This gives an average ruthenium to porphyrin ratio of 3.4:1.

ZnPBR 1:1 (2c) was prepared as ZnPBR 3:1 but with a stoichiometric amount of $RuCl_3$. Also, after the initial reflux, the solution was diluted with ether and washed with dilute HCl before the addition of triethylamine. This was to ensure the removal of any unreacted $RuCl_3$ before hydrolysis. Again, the measured Ru/C ratio (0.090) was smaller than that calculated for the 1:1 compound (0.105), giving a ruthenium to porphyrin ratio of 0.9:1.

The corresponding H_2PBR compounds (**2a, 3a, 4a**) were obtained by eliminating the metallation step in the synthesis. The H_4PBR^{2+} compounds (**2b, 3b, 4b**) were obtained by treatment of either the corresponding free base or zinc derivative with a strong acid.

Microemulsion. The anionic microemulsion consisted of xylene (60.8 wt%), n-pentanol (22.0 wt%), sodium dodecylsulfate (3.6 wt %) and H_2O (13.6 wt %) which gives water droplets ca. 100 Å in diameter.[15] The porphyrin-RuO_2 compounds are slightly soluble in pure xylene and insoluble in H_2O. They are quite soluble in this microemulsion which suggests that they are localized at the oil-water interface.

Results and Discussion.

Electrochemistry. The cyclic voltammogram (CV) of ZnPB (**1c**) in a 2:1 mixture of toluene and acetonitrile (Figure 2a) shows the two reversible oxidations and two reversible reductions characteristic of zinc tetrakis(methoxyphenyl)porphyrin.[16] Thus, the bipyridine group does not noticeably affect the electrochemistry of **1c**. Upon complexation to RuO_2, ZnPR 7:1 (**4c**), the two oxidation waves of the compound were practically unaffected while the reduction commenced at the same potential but was completely irreversible (Figure 2a). This behavior can be explained by assuming that the RuO_2 is not directly accessible to the electrode but that the porphyrin, upon reduction, can transfer an electron to the RuO_2. The CV of the 1:1 compound **2c** (not shown) was similar to both the 3:1 (**3c**) and the 7:1 (**4c**) compounds suggesting that, in this material also, the RuO_2 is not directly accessible to the electrode. This indicates that **2c** may exist as a dimer or a higher aggregate. This interpretation is further supported by the chronocoulometric results discussed below.

Figure 2b shows the CVs of the free bases, H_2PB (**1a**) and H_2PBR 7:1 (**4a**) in 1,2-dichloroethane (DCE). Again, the uncomplexed material **1a** shows the oxidation and reduction waves characteristic of tetrakis(methoxyphenyl)porphyrin.[16] In this case the reduction waves are slightly less reversible in the complexed species than in the starting material while the oxidation has become substantially less reversible. This indicates that the RuO_2 may transfer electrons to the oxidized porphyrin.

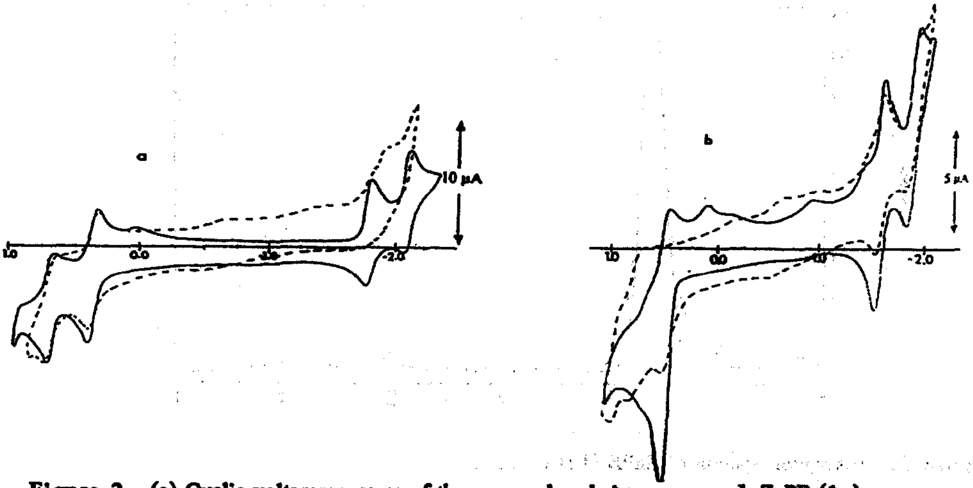

Figure 2. (a) Cyclic voltammograms of the uncomplexed zinc compound, ZnPB (**1c**) ——— and the complexed compound, ZnPBR 7:1 (**4c**) - - - - - - in a 2:1 mixture of toluene and acetonitrile. (b) Cyclic voltammograms of the uncomplexed free base H_2PB (**1a**) ——— and the complexed free base H_2PBR 7:1 (**4a**) - - - - - - in dichloroethane. Scan rate is 200 mV/s. Potentials are vs. $Ag/AgNO_3$ (0.1 M). Cathodic currents are plotted upwards.

In order to obtain an approximate size of these compounds in solution, chronocoulometry[17] was employed to measure the diffusion coefficients[18] of the complexed species, **2c**, **3c**, and **4c** in DCE. The uncomplexed starting material, **1c**, and zinc tetraphenylporphyrin (ZnTPP) were run as comparisons. The data is given in Table 1. The measured diffusion coefficient of ZnTPP in DCE, $D = 6.7 \times 10^{-6}$ cm^2/s, compares well with that measured for MgTPP in CH_2Cl_2, $D = 6.1 \times 10^{-6}$ cm^2/s.[19] The three octyloxy chains and the bipyridine group on compound **1c** reduce the diffusion coefficient to almost half that of ZnTPP, $D = 3.6 \times 10^{-6}$ cm^2/s. Complexation to RuO_2 further decreases the diffusion coefficient but not by a great deal. This indicates that the complexed species probably exist as very small aggregates. Furthermore, the 1:1 compound is not qualitatively different from the 3:1 and 7:1 species, suggesting that it probably exists as a dimer rather than as a single porphyrin complexed to a single oxoruthenium molecule.

Table I. Ruthenium to Porphyrin Ratio and Diffusion Coefficients in Dichloroethane of the Complexes and Related Porphyrins.

Compound	Ru/Por ratio (exptl.)	D x 10^{-6}, cm^2/s
ZnTPP	——	6.7
ZnPB (1c)	——	3.6
ZnPBR 1:1 (2c)	0.9 : 1	2.9
ZnPBR 3:1 (3c)	2.6 : 1	2.6
ZnPBR 7:1 (4c)	3.4 : 1	2.5

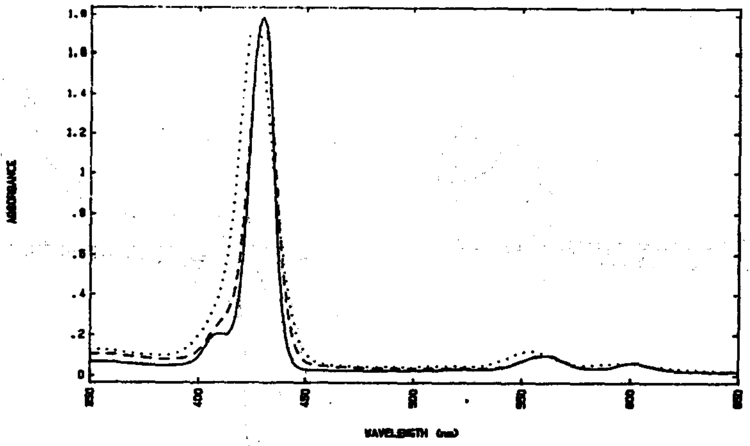

Figure 3. Absorption spectra of ZnPB (1c) in the microemulsion ———— ; ZnPBR 3:1 (3c) in the microemulsion - - - - - - - ; and 3c in dichloroethane ·······.

Absorption Spectra. The absorption spectrum of the RuO_2 complexed species depended slightly on the way in which they were purified. Spectra taken directly from the reaction mixture, after hydrolysis but before the material was precipitated, were identical to the spectrum of the precursor porphyrin and its fluorescence was quenched as much, or more, than the purified material (see below). However, to prepare the compound free from solvents and remaining salts, it was necessary to precipitate it from solution. This precipitation, or chromatography on SiO_2 or cellulose, resulted in a broadening of the Soret band and a slightly sloping baseline in the absorption spectrum, presumably due to some aggregation and/or some complexation of the porphyrin chromophore with the RuO_2. This effect was diminished when the material was dissolved in coordinating solvents such as THF and pyridine or in the microemulsion relative to non-coordinating solvents such as DCE. Figure 3 shows the absorption spectrum of ZnPBR 3:1 in DCE and in the microemulsion relative to that of ZnPB in the microemulsion.

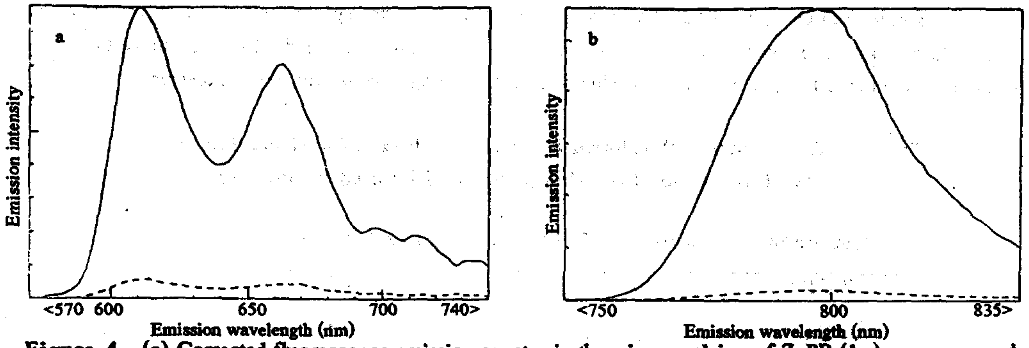

Figure 4. (a) Corrected fluorescence emission spectra in the microemulsion of ZnPB (1c) ———— and ZnPBR 3:1 (3c) - - - - - - . Excitation was at 560 nm. (b) Corrected phosphorescence emission spectra in a methyltetrahydrofuran glass at 77 K of ZnPB (1c) ———— and ZnPBR 7:1 (3c) - - - - - - . Excitation was at 556 nm.

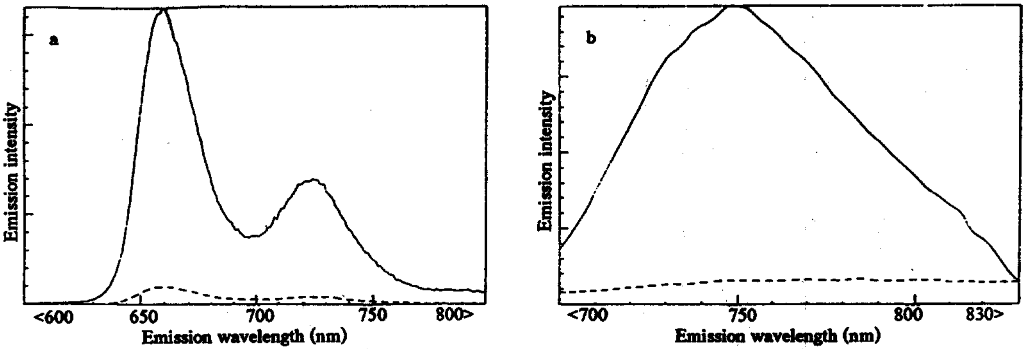

Figure 5. (a) Corrected fluorescence emission spectra in dichloroethane of H_2PB (**1a**) ———— and H_2PBR 7:1 (**4a**) - - - - - - - ; Excitation was at 520 nm. (b) Corrected fluorescence emission spectra in a dichloroethane/trifluoroacetic acid mixture of H_4PB^{2+} (or H_6PB^{4+}) (**1b**) ———— and H_4PBR^{2+} 7:1 (**4b**) - - - - .- - - . Excitation was at 692 nm.

Fluorescence and phosphorescence. The fluorescence emission intensity of ZnPB was greatly quenched by complexation to RuO_2. The extent of fluorescence quenching was independent of the solvent (microemulsion, THF, pyridine or DCE) and of the amount of RuO_2 complexed: ZnPBR 7:1, 3:1 and 1:1 were all quenched by ca. 95% relative to the starting material. The fluorescence of the 1:1 complex was measured after washing with HCl but before hydrolysis, i.e., when the complexed species was presumably $RuCl_3$. This compound exhibited no measurable fluorescence. This indicates that at this stage of the synthesis no uncomplexed porphyrin exists. After the addition of triethylamine and H_2O, the compound showed the usual 95% quenching relative to the starting material. Figure 4a shows the fluorescence of ZnPB in the microemulsion compared to that of ZnPBR 3:1.

There are three obvious mechanisms for fluorescence quenching in these compounds: electron transfer, energy transfer and the external heavy atom effect. Given the lack of noticeable absorption by the RuO_2, energy transfer can be ruled out. If the fluorescence were being quenched by spin-orbit coupling due to the ruthenium atoms, one would expect an increase in the quantum yield for triplet formation and a decreased triplet lifetime.[20] We have compared the phosphorescence efficiency of the uncomplexed compound, ZnPB, to that of ZnPBR 7:1 in a methyltetrahydrofuran glass at 77 K. The phosphorescence is quenched to the same degree (95%) as the fluorescence (Figure 4b). Preliminary time resolved measurements on ZnPBR 7:1 have shown that the phosphorescence lifetime is > 1ms.[21] These results are consistent with fluorescence quenching by electron transfer from the singlet state of the porphyrin to the RuO_2. The formation and decay of the triplet state is not noticeably affected by the presence of the RuO_2.

The fluorescence of H_2PBR 7:1 (**4a**) in DCE relative to H_2PB (**1a**) is shown in Figure 5a. The extent of fluorescence quenching in the free base (94%) is very similar to that seen in the zinc derivative. The extent of quenching in THF and pyridine is similar to that in DCE. Attempts to measure the fluorescence lifetime in pyridine of H_2PBR 7:1 by single photon counting showed that it was beyond the limits of our resolution, i.e., $\tau_f < 0.7$ ns, while for the unsubstituted compound, H_2PB, $\tau_f = 10.2$ ns.[23]

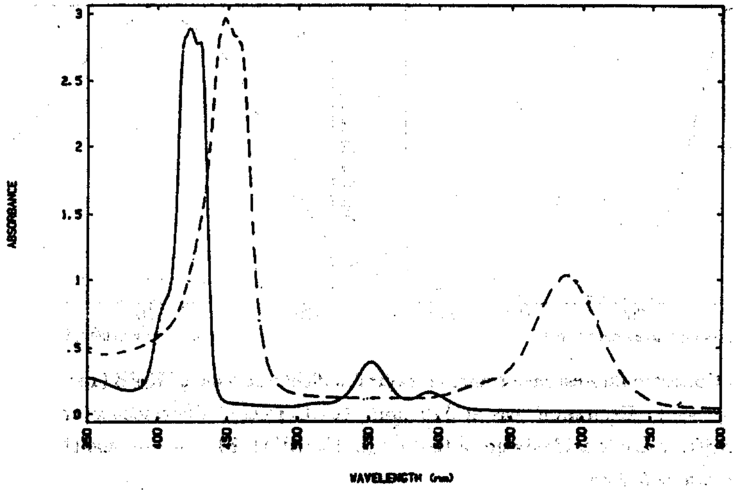

Figure 6. Absorption spectra of ZnPBR 7:1 (4c) in dichloroethane ———— and H_4PBR^{2+} 7:1 (4b) in a dichloroethane/trifluoroacetic acid mixture - - - - - - .

The excited singlet state of ZnPB is a rather strong reducing agent, having an excited state oxidation potential of ca. -1.4 V vs. SCE. The fluorescence lifetime of the uncomplexed material is estimated to be ca. 2.7 ns.[24] If the fluorescence is quenched by 95% due to electron transfer, we can estimate a rate constant for electron transfer, $k_{et} \approx 7 \times 10^9$ s^{-1}.[20] We have not yet measured the rate of the back electron transfer which, in contrast to the forward electron transfer, should be dependent on the environment, e.g., a microemulsion or a pure solvent.[10] The excited singlet state of H_2PB is a weaker reducing agent than that of the zinc derivative. Its excited state oxidation potential is estimated to be ca. -1.0 V.[24] It is a slightly stronger oxidizing agent than ZnPB, having an excited state reduction potential of ca. 0.7 V vs. SCE, while that of ZnPB is ca. 0.6 V.[24] These differences may account for its slower rate of electron transfer relative to the zinc derivative: if its fluorescence lifetime of 10.2 ns is 94% quenched by electron transfer, this leads to $k_{et} \approx 1.5 \times 10^9$ s^{-1}.

The fluorescence of the diacid derivative, H_4PBR^{2+} 7:1 in DCE containing trifluoroacetic acid is also substantially quenched (ca. 90%) relative to the uncomplexed form, either H_4PB^{2+} or H_6PB^{4+} (Figure 5b). The oxidation potential of the diacid form of octaethylporphyrin, H_4OEP^{2+}, is ca. 1 V positive of the corresponding zinc derivative, ZnOEP.[16] Assuming that a similar trend holds for the tetraphenylporphyrins, the excited state of H_4PBR^{2+} 7:1 should be a strong oxidizing agent (reduction potential of ca. 1.5 V vs. SCE) while that of ZnPBR 7:1 is a strong reducing agent. Furthermore, the absorption spectra of the two species together make an almost perfect match to the solar spectrum (Figure 6) absorbing practically all wavelengths from 350 - 800 nm. This is an intriguing combination of properties for a solar energy conversion system. However, a great deal of work still remains to be done on the characterization of these compounds.

Conclusions.

A set of microheterogeneous photosystems has been described which consists of free base, diacid, and zinc porphyrins attached to RuO_2 particles. The measured diffusion constants suggest that these systems are of molecular dimensions. Electrochemical, fluorescence and phosphorescence measurements indicate that charge is efficiently transferred from the excited singlet state of the porphyrin to the RuO_2.

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