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INTERACTIONS OF TRANSITION-METAL-COMPLEX PHOTOSENSITIZERS WITH POLYMERS AND ORGANIZED MEDIA

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ABSTRACT

The interactions of luminescent platinum metal complexes with a variety of organized media, including micelles, cyclodextrins, and solid polymers, are described. In particular, Ru(II), Os(II), and Re(I) complexes with α-diimine ligands are discussed. Applications of these systems, including luminescence quantum counters, singlet oxygen generators, and a luminescent oxygen sensor, are described. Useful tools for studying these systems are described; these include a deuterium isotope method for measuring the degree of solvent exposure of bound sensitizers, excited-state-lifetime titrations for examining the compositions of systems, and spectral fitting and temperature profiles for probing excited state ordering and energies.

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INTRODUCTION

In 1971 the tris(2,2′-bipyridine)ruthenium(II) cation, $[Ru(bpy)_3]^{2+}$, was introduced as an energy-transfer photosensitizer [1]. This was the first metal complex that had lowest-lying charge-transfer (CT) excited states. Shortly afterwards it was also shown to be an excellent electron transfer quencher [2]. The numerous exemplary properties of this complex and its related Os(II), Ir(III), Rh(III), and Re(I) species are why they have largely supplanted traditional organic sensitizers in many fundamental and applied areas [3-10]. Indeed, $[Ru(bpy)_3]^{2+}$ has been referred to as the "inorganic biacetyl" since, for many years, biacetyl was the triplet sensitizer of choice.

One of several goals of this article will be to explain why these inorganic complexes have proved to be such powerful and useful probes and sensitizers. Further, we will describe both fundamental and practical applications of these complexes to studies of polymeric and organized media. We will describe tools and models that we have found to be particularly useful in accounting for the behavior of these systems. There has been an enormous amount of work on the photochemistry and photophysics of transition-metal-complex photosensitizers, and the interested reader is referred to several excellent reviews [3-6, 9, 10].

Transition-metal-complex photosensitizers have proved quite popular for a variety of reasons. They tend to be photochemically robust, can be tuned over a wide range of excited state energies and excited state oxidizing and reducing power, are soluble in a range of solvents, absorb intensely, emit intensely, and have long excited-state lifetimes in fluid solutions. Even with the same central metal ion, small variations in the ligands can radically alter the excited-state energies or redox properties.

In particular, the combination of long excited-state lifetimes and intense fluid solution emissions have made these particularly attractive as probes. For example, Ru(II) complexes with α-diimine ligands have excited-state lifetimes of hundreds of nanoseconds to above 5 μs in solution at room temperature. These long lifetimes make the decays quite easy to measure without elaborate equipment [11] (a $150 lifetime apparatus has been used [12]), and the long lifetimes make the decays particularly susceptible to environmental influences. Further, their luminescence quantum yields can be a few percent to almost 50%. With modern instrumentation, even yields of 0.001 would be useful for mechanistic and environmental studies.

We will discuss several practical applications of polymer-supported complexes: singlet oxygen ($^1O_2$) generators, oxygen sensors, and luminescence quantum counters. We describe tools for assessing the degree of solvent expo-

sure, selective excited-state quenching, probes of sensitizer environment on solid supported sensitizers, and surfactant or cyclodextrin titration coupled with nonlinear least-squares fitting. Finally, we show the extraordinarily high environmental sensitivity of these complexes by showing that the luminescent properties of a series of surfactant active Re(I) complexes can be radically altered by a normally electronically passive alkyl group.

SOLID-STATE SUPPORTS

We have utilized polymer-supported luminescent metal complexes for several practical applications. In each case, the polymer support provides a unique and different function.

Singlet-Oxygen Generators

Singlet oxygen is a pervasive and powerful synthetic tool, especially in organic chemistry [13-15]. Photochemically generated $^1O_2$ using homogeneously dispersed organic sensitizers has been widely used, but separation of products from the dyes has frequently been bothersome. Solid-polymer-supported organic dyes proved to be more convenient as the insoluble polymer could be removed by simple filtration after synthesis [13, 14]. Generally, the sensitizer was reusable. This same approach can be used with inorganic sensitizers. Further, in contrast to nonluminescent organic triplet sensitizers, the luminescence of the complexes provides a unique handle on probing the microstructure of the environment.

We have demonstrated that $Ru(bpy)_3^{2+}$ and related inorganic complexes were excellent homogeneous photochemical $^1O_2$ generators with efficiencies approaching 85% [16, 17]. This equals or exceeds the best organic dyes. To avoid the problems of covalently linking our complexes to polymer supports, we took advantage of the fact that the complexes bind essentially irreversibly to strong cation exchangers. Preparation was trivial; we added a solution of the complex to the solid exchanger and stirred it until the complex was extracted from the solution [18].

Using this cation-exchange-bound $Ru(bpy)_3^{2+}$, we found reasonable (20-50%) efficiency of $^1O_2$ formation in methanol solutions. However, the results were quite irreproducible and much lower than we would have expected on the basis of the homogeneous sensitization studies.

We traced the irreproducibility to the microscopic wetness of the polymer. Even with repeated extraction with dry methanol, the ion exchanger tena-

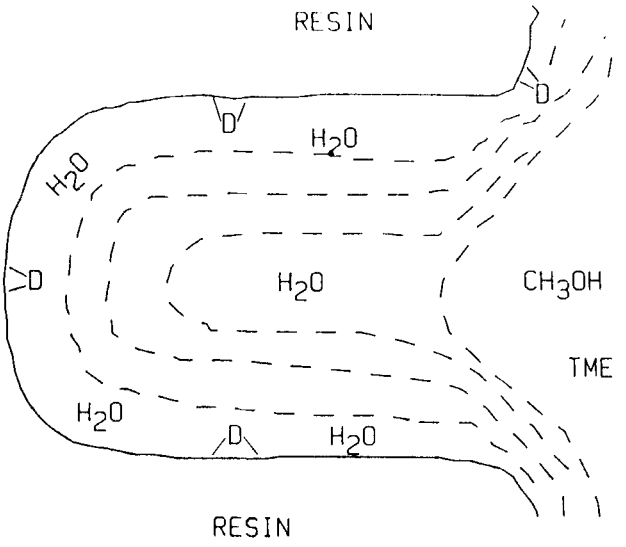


FIG. 1. Triphasic microheterogeneous model for ion-exchange-bound $Ru(bpy)_3^{2+}$ sensitizer. The dashed lines represent the methanol-water boundaries for different water loadings. D represents the bound photosensitizer. TME is the water-insoluble tetramethylethylene $^1O_2$ scavenger. Reprinted with permission from Ref. 18. Copyright 1983, American Chemical Society.

ciously held water. We developed the model of Fig. 1 to account for our results. In this model the hydrophilic complex is held on the surface of the exchanger. Without special treatment, the surface of the very hydrophilic exchanger represents a largely aqueous environment. When using water-insoluble reactants (e.g., tetramethylethylene), the $^1O_2$ generated by oxygen quenching of the complex must cross the aqueous barrier before it can escape into the methanol organic phase and be scavenged by the water-insoluble organic substrate. Our early low, irreproducible photooxygenation yields were caused by the facile decay of $^1O_2$ as it crossed the barrier and by the irreproducible removal of water by our methanol washing.

We found that when we scrupulously removed the water by vacuum drying, the yields rose to about 80% and were quite reproducible. The dry polymeric sensitizer was resolvated with methanol and swelled to an extent comparable to when it was hydrated in water.

As further verification of this model, we exploited the great increase in ex-

cited state lifetime for $^1O_2$ in D_2O versus H_2O. We were able to increase the yields of the wet ion exchangers by almost a factor of 2 merely by using a deuterated water layer. The longer lifetime of the $^1O_2$ in the D_2O layer allowed a much higher percentage of the $^1O_2$ to diffuse across the barrier. This change of yield also allowed us to estimate the water barrier thickness as a function of the degree of hydration of the ion exchanger.

The deuterium isotope effect was quite useful for determining the microstructure of the media. This triphasic organization of the wet system might be exploited for carrying out selective reactions of materials that partition into the aqueous phase even in the presence of products or other reactants that are less favorably partitioned.

In this case the polymer is a highly solvent and gas-permeable but insoluble support. It is important, however, that the support not greatly quench the luminescence or the singlet-oxygen-generation efficiency will suffer.

Oxygen Analyzer

The quenching or deactivation of organic and inorganic complexes is well known. In particular, oxygen is a ubiquitous and efficient quencher of many excited states. Generally, this is an interference, and in many mechanistic or practical studies, oxygen has to be carefully removed. Within recent years this "problem" has been exploited to yield an oxygen sensor; the degree of quenching of the luminescence of organic species is determined by the oxygen concentration and has been used to quantitate oxygen concentrations. Initial attempts to use the sensor dissolved in the solvent proved impractical because excited states susceptible to oxygen quenching were generally equally prone to deactivation by a variety of materials in the solvent. However, by separating the luminescent probes from potential interferents by gas-permeable membranes, attractive luminescent-based oxygen sensors were developed [19, 20]. These organic-based systems do suffer from photodegradation and lack long enough lifetimes for an inexpensive and convenient lifetime-based sensor.

Our extensive work on oxygen quenching of metal-complex excited states [16-18] and their immobilization on polymers led us to believe that immobilization of our sensitizers in a suitable solvent-impervious, gas-permeable support might make a nearly ideal oxygen sensor [21].

After trying a number of supports and sensitizers, we found that $Ru(Ph_2phen)_3^{2+}$ (Ph_2phen = 4,7-diphenyl-1,10-phenanthroline) in a silicone rubber made an excellent oxygen sensor. Figure 2 shows the response of this sensor with both intensity and lifetime quenching data. The plots of I_0/I and τ_0/τ versus oxygen concentration in solution are linear and identical (Stern-

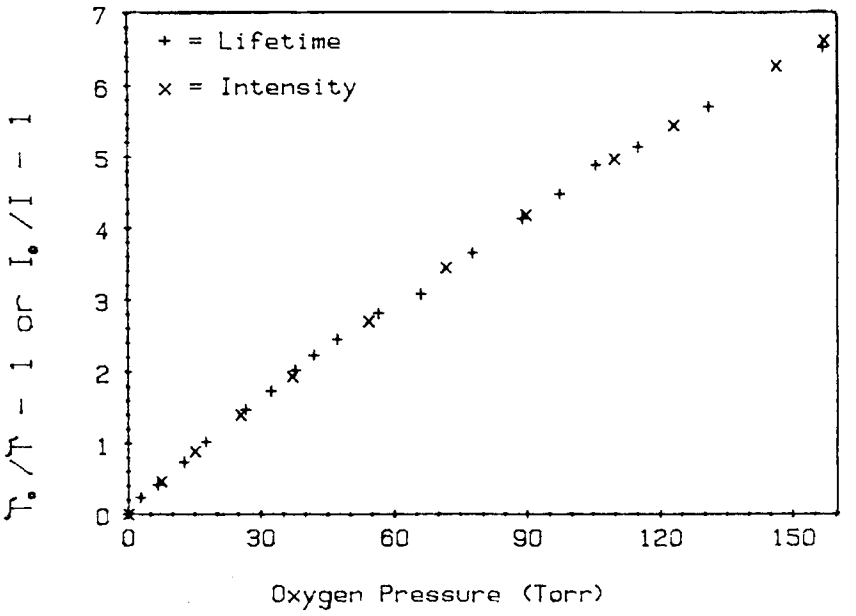


FIG. 2. Comparison of the lifetime and intensity responses of a $Ru(Ph_2phen)_3^{2+}$-silicone rubber luminescence oxygen sensor as a function of oxygen partial pressure. Reprinted with permission from Ref. 21. Copyright 1987, American Chemical Society.

Volmer quenching kinetics). We attribute the downward curvature to the presence of different local environments for the complex, each with a different quenching constant. The greater resistance of some sites to quenching causes the response to roll off at higher oxygen pressure. This phenomenon is quite common in solid-state luminescence sensors [19, 20]. However, for an analytically useful medium, the response need only be reproducible, which our sensor is. The agreement between intensity and lifetime measurements also means that either approach can be used.

$Ru(Ph_2phen)_3^{2+}$ has a 5-6 μs unquenched lifetime in silicone rubber. Precise lifetime measurements at this level are relatively easy and inexpensive. This compares with the few hundred nanoseconds for the best fluorescent organic sensors, which makes lifetime measurements much more expensive and difficult with the purely organic probes.

Figure 3 shows a primitive breathing monitor made with our sensor. The

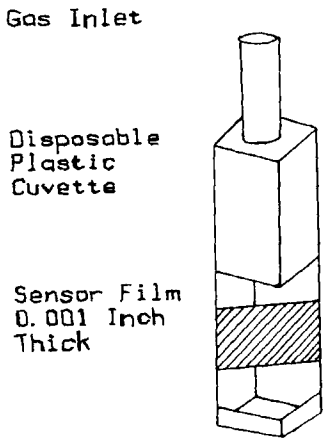


FIG. 3. Diagram of luminescence cell for monitoring oxygen concentrations. Gas flow through the tube at the top. The sensor film is 25 μm (0.001 in.) thick to decrease response time. Reprinted with permission from Ref. 21. Copyright 1987, Americal Chemical Society.

sensor film is 25 μm (0.001 in.) thick and is exposed to the gas flow on both sides to decrease the response time. Figure 4 shows the response to a switch in flow of gas over the sample between nitrogen and air. The response time is < 200 ms and may just equal the response time of the spectrofluorimeter. Figure 5 shows an even more interesting application—real-time monitoring of a breathing person. The high emission intensities are for exhalation and show the reduced oxygen concentration after exchange of air in the lungs. The profiles following the subject holding his breath are interesting. The oxygen concentration is clearly lower (higher emission intensity) on the first few exhalations because of the increased exchange time of the gas in the lungs. It takes several breaths for the lungs to reequilibrate, and the first few breaths are more rapid because of the buildup in CO_2 while the breath was being held.

Thus, polymer-immobilized metal complexes promise to be a very powerful and useful new class of luminescent sensors for a variety of applications. In particular, their long lifetimes, high luminescent yields, high photochemical stabilities, and flexibility for adding specific molecular features should lead to their extensive use. We are currently examining a variety of new systems and making fundamental studies on our current ones in order to characterize more fully and to design even more satisfactory sensors.

In contrast to the $^1O_2$ generator, the polymer must be highly gas perme-

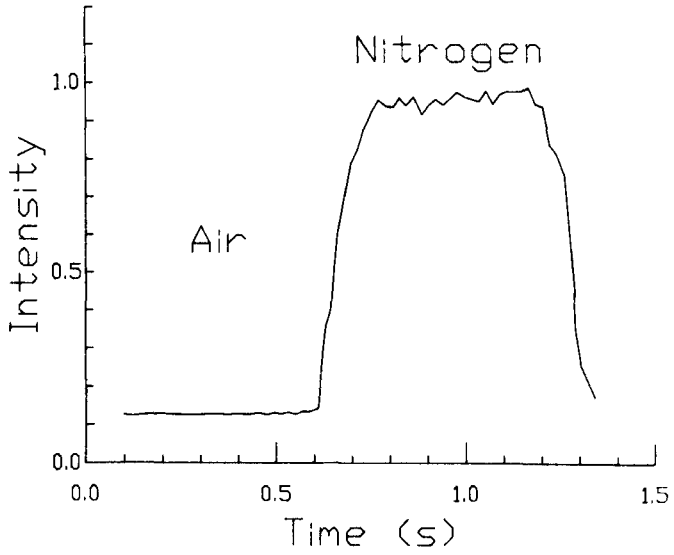


FIG. 4. Luminescence response of the sensor of Fig. 3 to a step change in the oxygen concentration (air to nitrogen to air). The response time may be limited by the spectrofluorimeter. Reprinted with permission from Ref. 21. Copyright 1987, American Chemical Society.

able but not be penetrated by the solvent. Solvent penetration will alter the probe properties and make calibration dependent on environment. Furthermore, good solvents for the probe will leach the probe out and destroy the sensor. Again, it is important that the support dissolve the probe well and not greatly quench the luminescence.

Luminescent Quantum Counters

Excluding some low-sensitivity thermal detectors, most optical detectors have responses that are constant in neither energy nor photon units with respect to wavelength [22-24]. The photomultiplier, the most sensitive detector, is one of the worst offenders in this regard. This variation of sensitivity with wavelength has made accurate intensity measurements over a range of wavelengths quite difficult.

Bowen developed a very clever device called a quantum counter [25] that overcame some of the shortcomings of traditional detectors.

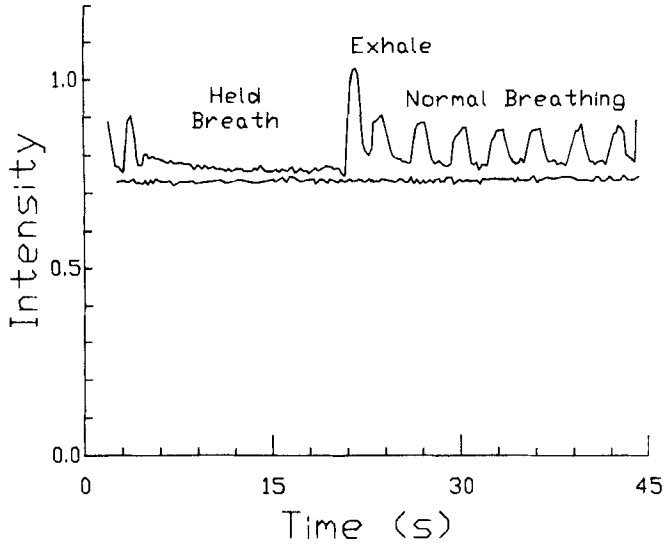


FIG. 5. Response of the sensor of Fig. 3 to a breathing subject. The baseline is for an equilibrated sample in the spectrofluorimeter. Normal breathing would correspond to the rightmost three breaths. Reprinted with permission from Ref. 21. Copyright 1987, American Chemical Society.

His counter consisted of an optically dense dye which was viewed by a conventional detector. If the dye absorbed all of the incident light and had a quantum efficiency and emission spectrum that was independent of wavelength, then the combination yielded a device with a quantum flat response (i.e., equal response for equal number of photons) over the operating range of the dye.

The most popular dye has been Melhuish's Rhodamine B in a variety of organic solvents. It has a relatively flat response from 250-600 nm [23, 26]. Its response is not perfectly flat (4.2% maximum spread for 350-600 nm), depends on the solvent and concentration [22-24], and the need to handle a solution is a further inconvenience. We have shown that traditional organic quantum-counter dyes can be supported in polymer matrices with only little loss in performance [27]. This avoids the difficulties of handling solution, evaporation, bubbles, leakage, etc.

More recently, however, we have shown that $Ru(bpy)_3^{2+}$ in a polymer support has nearly perfect quantum-counter properties [28]. Figure 6 shows

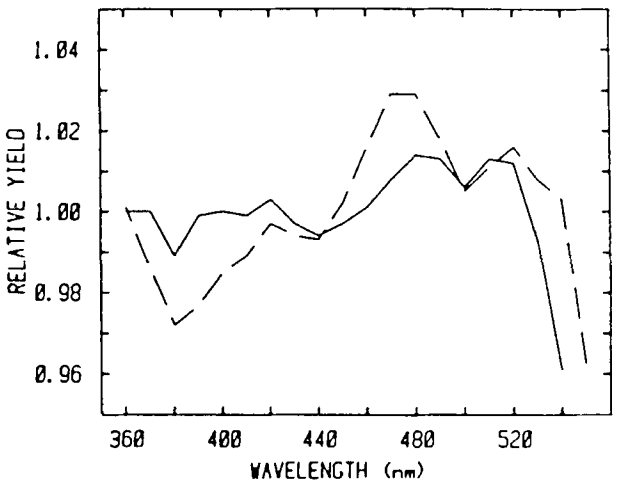


FIG. 6. Relative photon responses of $Ru(bpy)_3^{2+}$ in PVA (solid line) and PVP films (broken line). The falloff in response at 540 and 550 nm for the PVA and PVP films, respectively, is due to sample transmission. Note the very expanded response scale. Reprinted with permission from Ref. 28. Copyright 1981, American Chemical Society.

the response of poly(vinyl alcohol) (PVA)-supported $Ru(bpy)_3Cl_2$. The response is the flattest we have ever seen; it is at the limits of our resolution. The spectral range is somewhat limited, but other platinum-metal complexes can improve this range. It is our belief that, in the future, the best luminescent quantum-counter systems will be polymer-supported inorganic species.

The polymer in this case functions as a solvent for the probe and protection from oxygen quenching. A rigid low-oxygen-diffusion polymer reduces or eliminates oxygen quenching, which would otherwise reduce the quantum-counter sensitivity. PVA and poly(vinylpyrrolidone) both meet this criterion although the more limited solubility in the PVP makes the sensor less satisfactory because of lower absorbance in the red and reduced range.

ORGANIZED MEDIA

Organized media have been used to affect the rates and outcomes of numerous chemical, photochemical, and photophysical processes. For example,

micelles can organize reactants, alter photochemical product distributions, retard energy-wasting back reactions, and enhance product-formation efficiencies in energy-conversion schemes. Cyclodextrins can organize reactants and protect luminescent species from environmental deactivation.

Cyclodextrin Complexes

We turn now to the alteration of excited-state properties by formation of cyclodextrin (CD) inclusion complexes. Based on the earlier observations that CD binding to organic molecules could radically alter their photophysics and photochemistry [29], we made a comprehensive study of the interactions of β-CD with Ru(II) photosensitizers to determine whether we could form CD inclusion complexes and what effect inclusion would have on their photophysics and photochemistry [30].

We have tested $Ru(II)L_2L'$ complexes, where L and L′ are 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or their substituted analogs, for binding with β-CD. We find that with β-cyclodextrin there is no binding for phen, bpy, or any of the methyl-substituted analogs including Me_4phen. Apparently the complexes are too nearly spherical and do not project enough into the bulk of the medium for the CD to find a binding site. If, however, L′ is a phenyl-substituted bpy or phen, the phenyl group provides a suitable "hook" for formation of a CD inclusion complex.

Formation of these transition-metal complex inclusion complexes turned out to be very easy to monitor. The excited-state lifetimes are quite sensitive to the presence of the CD, and excited-state lifetime titration curves can be used to determine the binding constants. Figure 7 shows a titration curve for $Ru(phen)_2((SO_3Ph)_2phen)$. In this case there are two potential binding sites, one on each of the sulfonated phenyl groups. In the absence of oxygen (A), the very clearly biphasic titration curve demonstrates unambiguously the presence of CD binding to each of the two phenyl groups. The solid line is the best fit to an equilibrium model involving two binding constants where *D, *D(CD), and $*D(CD)_2$ each have a different excited-state lifetime.

Figure 7(B) shows the same complex in the presence of air. The changes in τ are much greater and monotonically upwards. This curve can be fitted with a model involving only *D and *D(CD). If we had only performed the air-saturated experiment, we would have been misled into believing that only the first binding was significant and that steric interactions blocked the second binding. The best-fit curve for the air-saturated solution was obtained by using the same binding constants that were used for fitting the deoxygenated solution. The excellent agreement supports the dual binding model.

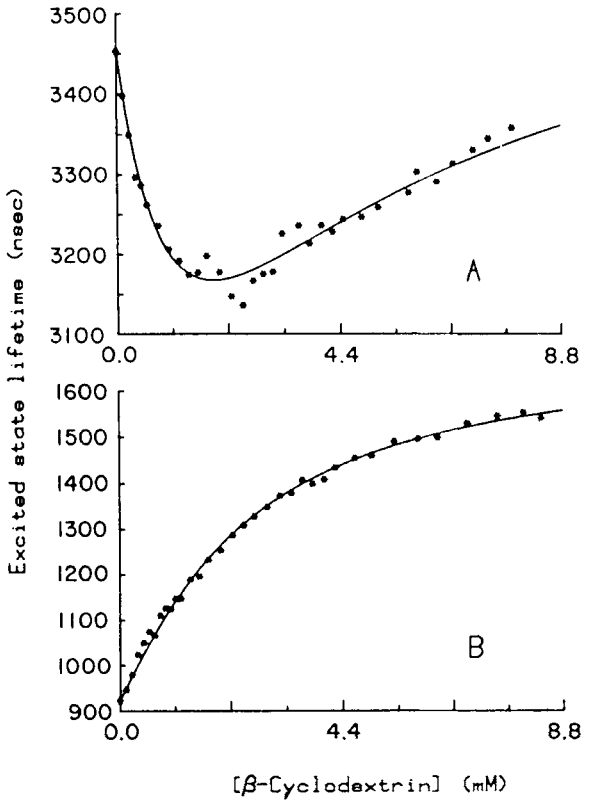


FIG. 7. Lifetime titration curve of $(phen)_2 Ru(PhSO_3)_2 phen$ by β-cyclodextrin in water. (A) Nitrogen bubbled; (B) aerated. The asterisks represent the experimental points, and the solid lines are the best fit of the data using a single and double CD-binding model with a common set of equilibrium constants for each plot. Reprinted with permission from Ref. 30. Copyright 1985, Americal Chemical Society.

From these two curves we are able to determine the oxygen-quenching constants for *D, *D(CD), and $*D(CD)_2$. Surprisingly, we found that addition of only one CD typically reduced the bimolecular oxygen-quenching constant by a factor of 3. This was especially surprising since the molecular models showed that a single CD covered or shielded only a relatively small portion of the surface of the complex. Thus, assuming that the molecule

could be treated as if excitation were uniformly distributed over the surface, we had expected only a 15-20% decrease in quenching.

In retrospect, the reason for the large reduction in oxygen-quenching constant was quite clear. There are charge-transfer excited states that arise from promotion of an electron from the Ru(II) to the phen ligand and to the phenyl-substituted ligand. The phenyl-substituted ligand gives rise to a CT state that is lower in energy than the one arising from electron promotion to the phen. Thus, the lowest excited state in the complex is the one localized in the phenyl-substituted ligand. Formation of an inclusion complex with CD will shield that very portion of the molecule where the excitation is resident and have a disproportionate effect on the quenching constant. In other words, CD is a selective shielding agent in this case and does not waste its shielding ability on the unexcited portion of the complex.

Micelles

In order to apply sensitizers or probes, one needs to understand the basic interactions of the sensitizer with the surfactant, membrane, or macromolecule. We have examined the interactions of luminescent metal complexes with a variety of charged and uncharged micelles. In addition to exploiting the charge or structure to enhance or reduce quenching interactions, we were interested in using the complexes to probe the details of the micelle-sensitizer structure. We have developed several new tools, including methods for estimating the degree of bulk solvent exposure of the bound photosensitizers, assessing binding alterations of relative state energies, and detecting and determining the relative importance of premicellar aggregates. These methods all rest on the susceptibility of the excited state properties to relatively subtle changes in environment.

Selective Shielding

Micelles are particularly useful for limiting or accelerating access of quenchers or products of photochemical reactions with reactive species. One example from our own group involved the binding of $Ru(II)L_3$ complexes to neutral Triton micelles. The binding region was to the aromatic hydrocarbon core with part of the sensitizer in the wet polyethylene oxide region.

Since our sensitizers are not bound strongly to the micelles, there was a range of Triton concentrations over which both bound and unbound sensitizers were present in the solution. On adding the quencher Cu^{2+}, we found that the luminescence-decay curves were given by the sum of two exponentials; one

lifetime was independent of $[Cu^{2+}]$ while the other decreased with increasing quencher concentration and followed normal Stern-Volmer quenching kinetics. With increasing Triton concentration, the preexponential factor of the quenched component decreased [31].

We concluded that the bound form was protected by the overlayer of poly(ethylene oxide), which excluded the very hydrophilic quenchers, such as Cu^{2+} and Fe^{3+}. The free form was quenched by normal bimolecular kinetics. By using a sufficiently high concentration of Triton or a very hydrophobic, strongly binding sensitizer, virtually all the sensitizer could be sequestered on the micelle and protected from quenching.

We have shown similar results for protection from $HgCl_x^{2-x}$ ($x = 2, 3, 4$) quenchers of $Ru(II)L_3$ complexes by binding to sodium lauryl sulfate (NaLS) micelles. Protection in this case was largely by electrostatic repulsion of the negatively charged quenchers or by shielding of the complex by the large surrounding bulk of the micelle. A model for electron-transfer quenchers on micelles was developed and successfully applied to the data [32].

Solvent-Exposure Studies

The CT excited state lifetimes of platinum metal complexes are sensitive to vibrational deactivation via OH vibrations of the solvent. Thus, altering the OH vibrations in contact with the complex by isotopic substitution to OD will reduce vibrational deactivation of the excited state and increase the lifetime. This deuterium isotope effect can be used to determine the fraction of the surface of a bound complex that is directly in contact with a bulk OH-containing solvent. This approach was introduced by Windsor and Kropp for rare-earth complexes in solution [33] and later extended to determining the solvent exposures of rare-earth ions bound to proteins [34]. We have developed an analogous approach for determining solvent exposures of our photosensitizers. Subject to several quite reasonable assumptions, the necessary equation is [35, 36]

$$F = \frac{\tau_{H(m)}^{-1} - \tau_{D(m)}^{-1}}{\tau_{H(s)}^{-1} - \tau_{D(s)}^{-1}}, \tag{1}$$

where F is the fractional surface of the bound sensitizer that is exposed to the bulk solvent, $\tau_{H(s)}$ and $\tau_{D(s)}$ are the lifetimes of the sensitizer in surfactant-free pure H_2O and pure D_2O, respectively, and $\tau_{H(m)}$ and $\tau_{D(m)}$ are the lifetimes of the micelle-bound sensitizer in pure H_2O and pure D_2O, respectively.

Thus, to determine F, one need only measure the excited-state lifetime of the probe in pure H_2O, in a medium containing the binding agent in H_2O, in pure D_2O, and in a medium containing the binding agent in D_2O. The crucial experimental requirement is that the probe have an appreciably different lifetime in H_2O and D_2O.

Qualitatively, it is easy to see how this works. Consider two limiting cases. First, if the probe is bound only loosely and the bulk water solvent freely covers most of the complex's surface, then the change in the excited-state lifetime of the bound form will be the same on going from H_2O to D_2O, regardless of whether the probe is bound or free. In other words, the complex feels a very similar water environment regardless of whether it is bound or not. On the other hand, if the probe is completely sequestered in the micelle, then it experiences no change in environment on going from H_2O to D_2O, and the lifetime of the bound probe will be unaffected.

For binding of a large series of homo- and heterochelated Ru(II) complexes ($Ru(II)L_3$ and $Ru(II)L_2L'$) to NaLS and Triton X-100, we found that the degree of solvent exposure was about 1/3. The simplest interpretation is that one of the three ligands was exposed to water while the rest were shielded. F did decrease, however, as the hydrophobicity of the ligands increases; this was to be expected as the complex tried to draw away as much as possible from the bulk water solvent.

We have also applied this technique to measuring F values for the cyclodextrin inclusion complexes. These results showed one limitation of the method. We found F values near or above unity for the inclusion complexes—an unrealistic result. However, in contrast to the micelle studies where we were replacing water with nonquenching, non-OH-containing solvent, in the CD work we were replacing water OH with some OH from the exposed face of the CD. These facial CD OH groups are exchangeable with D_2O and can quench appreciably, but they will have quenching rates different from those of the water OH groups; our simple equation would then fail. Thus, for Eq. (1) to work, it is important to compare media in which the OH quencher species are of the same type for both the bound and free sensitizer.

Lifetime Surfactant Titrations

Important to any application of micelle-bound sensitizer is an understanding of the species present and their photophysical properties. Such systems have turned out to be more complicated than one might have originally thought.

We have found that luminescence titrations with different complexes and

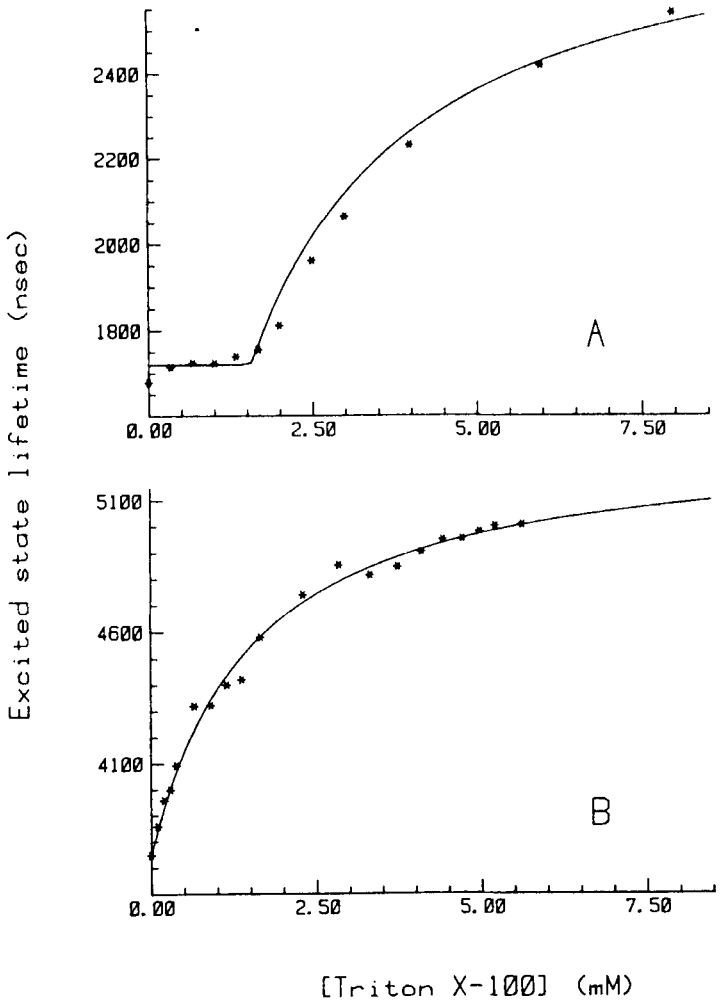


FIG. 8. Luminescence-lifetime titration curves for $Ru(4,7\text{-}Me_2phen)_3^{2+}$ (A) and $Ru((SO_3Ph)_2phen)_3^{4-}$ by Triton X-100. The asterisks are the experimental points, and the solid lines are the best fit to the model in the text assuming that premicellar aggregation is absent. Reprinted with permission from Ref. 37. Copyright 1983, American Chemical Society.

surfactants yielded titration curves with a variety of shapes. Generally, the shape began to change rapidly even below the critical micelle concentration (CMC) of the surfactant, indicating some form of premicellar interaction with the probe. Additional changes were observed through the CMC, and frequently a plateau was observed above the CMC.

To account for these diverse titrations, we developed the following simple model [37-39]:

$$*D \longrightarrow D + h\nu \text{ or } \Delta, \quad \tau_D$$

$$*D + nS \rightleftharpoons *DS_n, \quad \tau_{DS},$$

$$*D + M \rightleftharpoons *DM, \quad \tau_{DM},$$

where S is the free surfactant, M is the micelle, $*DS_n$ is a complex between *D and the free surfactant, *DM is the micelle-bound probe, and τ_D, τ_{DS}, and τ_{DM} are the lifetimes of the free, surfactant aggregate, and micelle complex, respectively.

This simple model has successfully fit the titrations for all combinations of cationic, anionic, and neutral sensitizers and surfactants that we have examined so far. Figure 8 shows two titration curves with Triton X-100. We show data for a rather hydrophilic $Ru(4,7\text{-}Me_2phen)_3^{2+}$ and a more hydrophobic $Ru((SO_3Ph)_2phen)_3^{4-}$. In these cases there is little evidence for a premicellar aggregation, and association with S is ignored. Only above the CMC, which can be altered by the presence of the probe, does micelle formation and efficient association occur. The delay before the curve starts to rise is caused by the failure to form micelles below the CMC. The hydrophobic complex does, however, induce early micelle formation, and there is no delay. Other systems require inclusion of the DS_n species for a satisfactory fit [39].

These titration curves are essential to a full understanding of any photophysics, photochemistry, or kinetics of these systems where the surfactant concentration can be below the CMC. We have, for example, been able to follow changes in oxygen-quenching constants as the composition of the solution changes from premicellar aggregates to micelle-bound species.

Spectral Fitting and Temperature Effects

The emission spectra, quantum yields, and lifetimes of many of our probes can be radically altered in a micellar environment. For example, $Ru(II)L_3$ probes on NaLS show considerable spectral sharpening, large emission red shifts,

and increases in lifetime and quantum yield. $Rubpy_3^{2+}$ exhibits a bright yellow-orange emission in pure deoxygenated water with a yield of 0.042 and lifetime of 580 ns. On micellization of the complex in aqueous NaLS, the emission becomes dull red, sharpens appreciably, and the yield and lifetime increase to 0.055 and 800 ns, respectively [40]. We were curious about the origin of these spectral changes. As we will show, temperature dependence studies and spectral fitting have provided, at least in part, some of the answers [40].

The luminescence properties of many of the probes are temperature sensitive. This sensitivity has been attributed to thermal deactivation of the CT-emitting states via a relatively low-lying metal localized *dd* excited state. The energy gap between the emitting state and the deactivating *dd* state can be measured from the temperature dependence of the excited-state lifetime. Changes in local environment can alter not only the state energy of the emitting level, but also its energy relative to the deactivating *dd* state.

We have measured thermal deactivation parameters for a number of $Ru(II)L_3$ and $Ru(II)L_2L'$ species in NaLS micelles. We find that the emitting CT state drops in energy on micellization. Because of the energy gap law for radiationless transitions, one would expect that the quantum yield and lifetime should decrease, but in fact, both increase. We were able to show that this is caused mainly by a decreased thermal deactivation of the emitting state via the *dd* state. The CT state energy is quite sensitive to environment, while the metal localized *dd* state is not. Micellization lowers the CT state energy, but leaves the *dd* largely unaffected. This combination results in a lower rate of deactivation via the *dd* and higher luminescence yields and lifetimes even though direct deactivation to the ground state is more efficient.

These results predict that the photochemical stability of these probes should be improved because of the less efficient deactivation via the photoactive *dd* state. Experiments are in progress to test this hypothesis.

Spectral fitting shows that the significant sharpening of the emission spectra on micellization is a result, not of narrower bands as we had originally assumed, but of suppression of one of the enabling vibrations. The homogeneous-medium spectra were composed of two different vibrational progressions, while the micellized spectra were predominantly due to one. This loss of a vibrational progression results from restricted motion on the micelle that prevents distortion of the complex along one of the intermolecular coordinates with a concomitant loss of intensity in that vibration. The effect is similar to that caused by freezing the complex in a rigid glass.

Conclusions

Our methodologies have proved invaluable for assessing the local environment around bound sensitizers, the effect of microenvironment on such fea-

tures as relative excited-state ordering, and the determination of the nature and distribution of aggregates both above and below the CMC. This information is essential for the rational design of new sensitizers or probe systems with optimal properties.

INTRAMOLECULAR INTERACTIONS

Since most of our sensitizers were cationic, electrostatic interactions generally blocked binding. We wished to generate a series of new luminescent sensitizers that could be anchored to cationic micelles. We designed a series of sensitizers of the form

$$fac\text{-}Re(bpy)(CO)_3NC(CH_2)_nCH_3^+, \quad n = 0\text{-}17.$$

We reasoned that, as the alkyl-chain tail became longer, the hydrophobic interactions of the tail would drive the complex into the micelle. Indeed, this prediction was borne out. For $n > 5$, tight micelle binding to CTAB appears to occur. However, a much more interesting phenomenon presented itself. Even in the absence of surfactants, this class of materials exhibits a large and totally unexpected perturbation of the excited-state properties with increasing chain length. This effect occurred for a variety of solvents ranging from the very polar water to the nonpolar toluene [41-43].

Figure 9 shows the excited state lifetime for $Re(bpy)(CO)_3NC(CH_2)_nCH_3^+$ as a function of n. The lifetime is constant up to about $n = 7$, where it abruptly rises to a new plateau at $n = 13$. The upper plateau has a lifetime that is about double the short chain one. We attribute this novel behavior to an intramolecular solvent effect. The different chain-length tails can fold over and displace solvent molecules from the bpy face. This alteration of solvent environment around the excited Re-bpy portion of the molecule affects the decay paths and, thus, the decay time. For small n, the chains cannot fold over onto the bipyridine face and there is no dependence on n. For intermediate chain lengths, the alkyl chain can fold over and displace solvent molecules from the bpy face. At $n = 13$, complete displacement of solvent from the one bpy face is achieved; lengthening the alkyl chain to $n = 17$ provides little additional coverage. Molecular models fully bear out this picture of the conformations (Fig. 10).

Further, if this model is correct, then anything that alters the degree of foldback should also alter the decay paths. The hydrophobicity of the hydrocarbon tail should allow it to form facile CD complexes. Formation of inclusion complexes would affect the environment of the chromophore and affect

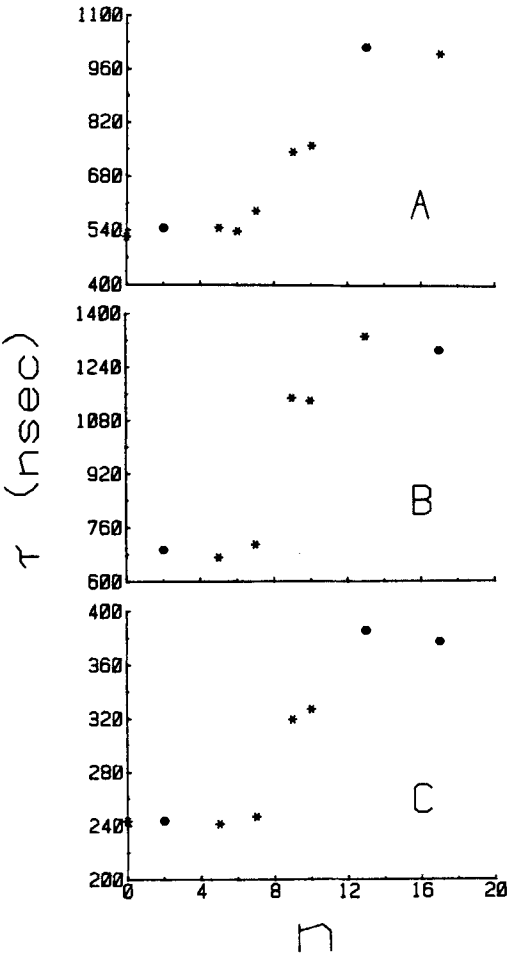


FIG. 9. Excited-state lifetime of $Re(bpy)(CO)_3NC(CH_2)_nCH_3^+$ versus n in deoxygenated acetonitrile (A), toluene (B), and pyridine (C) at 298 K. Reprinted with permission from Ref. 40. Copyright 1986, American Chemical Society.

the decay paths including oxygen quenching. This was borne out by experiments. Both α- and β-cyclodextrin can pry the alkyl chain off of the bpy and alter both the lifetimes and the oxygen quenching constants.

In spite of the internal consistency of this model, we were puzzled at the magnitude of the effect. Low-temperature results revealed that increasing the chain length could actually invert the lowest excited states in the molecules. For short alkyl chains, which cannot interact with bpy, the broad structureless emission was virtually all CT, but as n increased above 5, the emission shifted to a highly structured one characteristic of a ligand-localized π-π^* phosphorescence.

Thus, we attribute the very large intramolecular solvent effect to a perturbation of the relative energies of a CT and a π-π^* triplet state that are in close proximity. The well-known solvatochromism of such states is brought about in this case by changes in the microenvironment of the CT state. It is this perturbation of the interaction between the two states and the relative importance of their decay pathways that accounts for the large chain-length dependence. As further support of this interpretation, we have synthesized the series

$$cis\text{-}Os(bpy)_2(CO)NC(CH_2)_nCH_3^{2+}, \quad n = 0\text{-}21.$$

In this series the CT states are much lower in energy than the π-π^* triplet state, and small perturbations of the CT state energy on foldback should have a minimal effect. Indeed, we see almost no differences in the excited state lifetime as a function of n for this series [44].

CONCLUSIONS

We have tried to convey some of the rich and fascinating spectroscopy, photochemistry, and photophysics of platinum metal complexes and their interactions with polymers and organized media. In particular, we have shown relatively simple systems that yield important new applications. We have developed some rules and methods for examining and predicting micromechanistic interactions of metal complex sensitizers with organized media. We have shown examples of radical alteration of sensitizer properties in some important and useful ways. We have shown that these systems can be extraordinarily sensitive to extremely subtle changes in local environment. The great sensitivity of the Re(I) complexes to such small factors as the length of alkyl

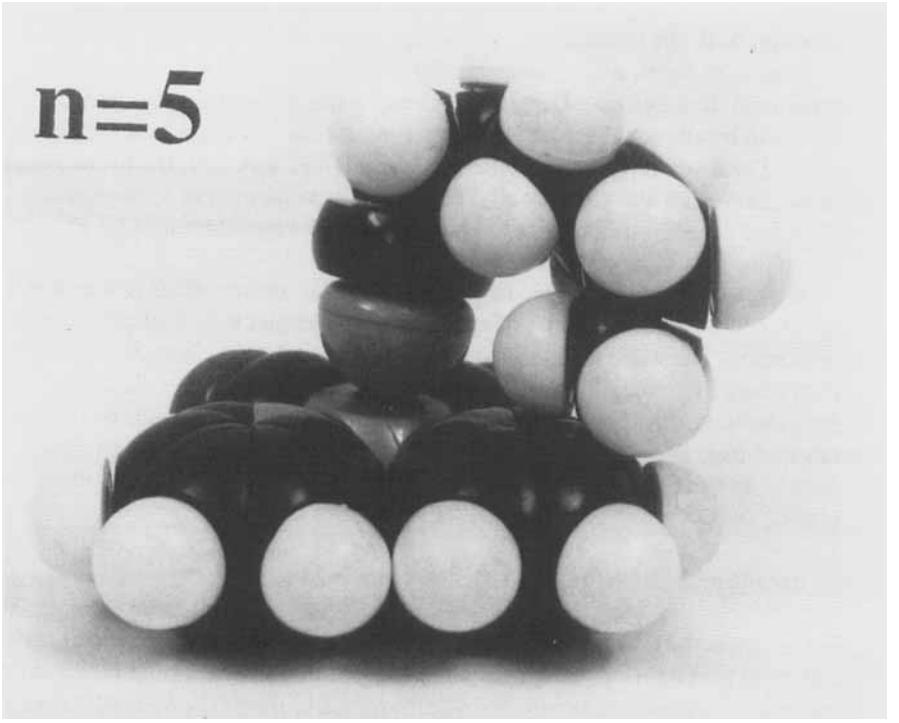
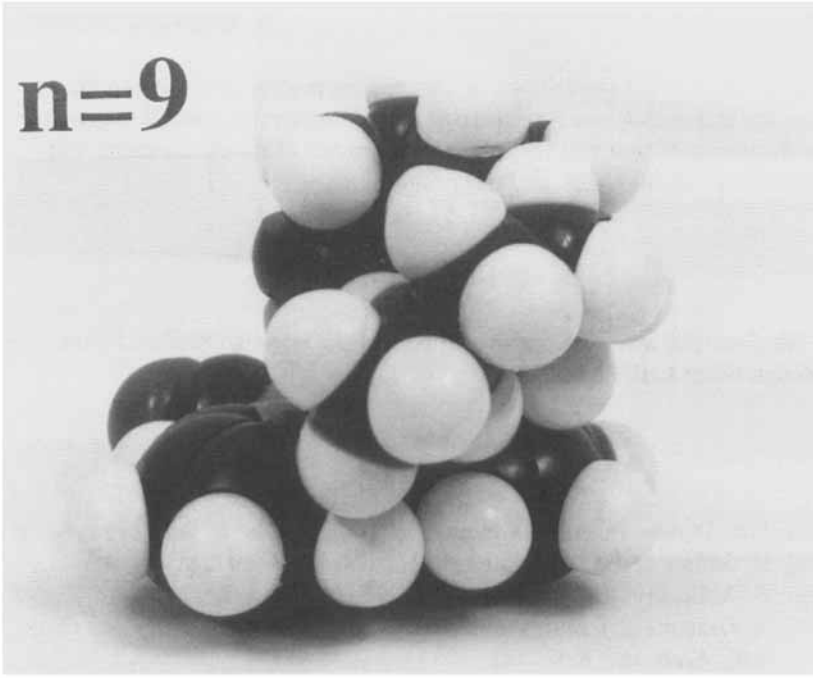


FIG. 10. Space-filling models of $Re(bpy)(CO)_3NC(CH)_2)_nCH_3^+$ as a function of n, showing the maximum overlap between the alkyl chain and the bpy ligand.



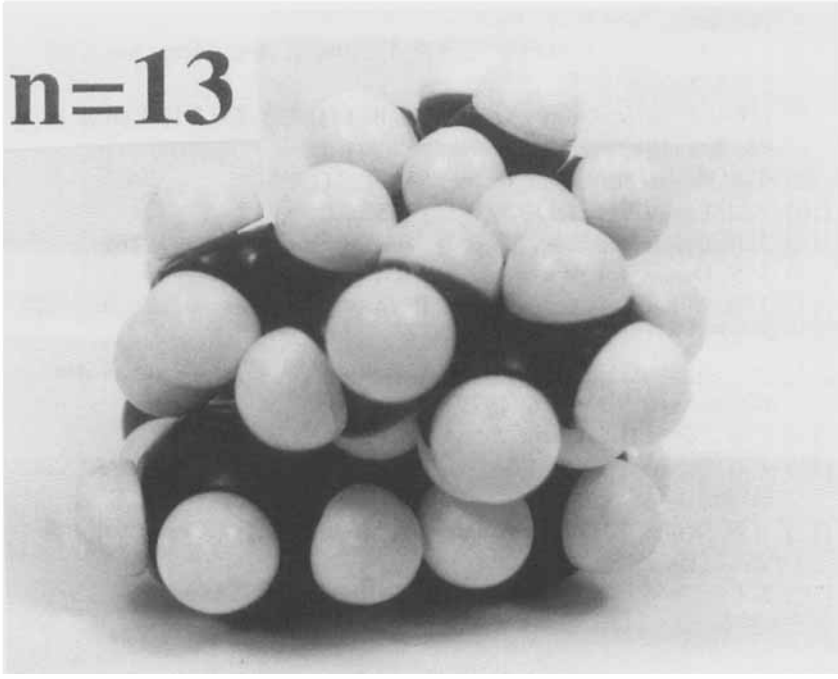


FIG. 10 B and C

chain, well removed spatially from the emitting portion of the complex, promises interesting new spectroscopy and photophysics. Our ultimate goals are the design of new sensitive site-specific probes of the environment and structure of micelles, CDs, and macromolecules.

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REFERENCES

[1] J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc., 93,* 1800 (1971).
[2] H. Gafney and A. W. Adamson, *Ibid., 94,* 8238 (1972).
[3] G. A. Crosby, *Acc. Chem. Res., 8,* 231 (1975).
[4] M. Grätzel (ed.), *Energy Resources through Photochemistry and Catalysis,* Academic, New York, 1983.
[5] K. Kalyanasundaram, *Coord. Chem. Rev., 46,* 159 (1982).
[6] K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems,* Academic, New York, 1987.
[7] C. V. Kumar, J. K. Barton, and N. J. Turro, *J. Am. Chem. Soc., 107,* 5518 (1985).
[8] (a) R. J. Watts, *J. Chem. Educ., 60,* 834 (1983). (b) J. N. Demas, *Ibid., 60,* 803 (1983) and other articles in issue.
[9] T. J. Meyer, *Pure Appl. Chem., 58,* 1193 (1986).
[10] A. J. Lees, *Chem. Rev., 87,* 711 (1987).
[11] J. N. Demas and C. M. Flynn Jr., *Anal. Chem., 48,* 353 (1976).
[12] J. N. Demas, *J. Chem. Educ., 53,* 657 (1976).
[13] J. R. Williams, G. Ortor, and L. R. Unger, *Tetrahedron Lett., 46,* 4603 (1973).
[14] A. P. Schaap, A. L. Thayer, K. A. Zaklika, and P. C. Valenti, *J. Am. Chem. Soc., 101,* 4016 (1979).
[15] C. S. Foote, *Acc. Chem. Res., 1,* 104 (1968).
[16] J. N. Demas, R. P. McBride, and E. W. Harris, *J. Phys. Chem., 80,* 2248 (1986).
[17] J. N. Demas, E. W. Harris, and R. P. McBride, *J. Am. Chem. Soc., 99,* 3547 (1977).
[18] S. Buell and J. N. Demas, *J. Phys. Chem., 87,* 4675 (1983).

[19] J. I. Peterson, R. V. Fitzgerald, and D. D. Buckhold, *Anal. Chem., 56,* 62 (1984).
[20] N. Z. Opitz and D. W. Lubbers, *Adv. Exp. Med. Biol., 169,* 899 (1984).
[21] J. R. Bacon and J. N. Demas, *Anal. Chem., 59,* 2780 (1987).
[22] D. G. Taylor and J. N. Demas, *Ibid., 51,* 712, 717 (1979).
[23] J. N. Demas, in *Photoluminescence Spectrometry* (K. D. Mielenz, ed.), Academic, New York, 1982, p. 195
[24] J. N. Demas, T. D. L. Pearson, and E. Cetron, *Anal. Chem., 57,* 51 (1985).
[25] E. J. Bowen, *Proc. R. Soc. London, Ser. A., 154,* 349 (1936).
[26] W. H. Melhuish, *N. Z. J. Sci. Technol., Sect. B., 37,* 142 (1955).
[27] K. Mandel, T. D. L. Pearson, and J. N. Demas, *Anal, Chem., 52,* 2184 (1980).
[28] K. Mandel, T. D. L. Pearson, and J. N. Demas, *Inorg. Chem., 20,* 786 (1981).
[29] M. L. Bender and M. Komiyama, *Reaction Structure: Concepts in Organic Chemistry,* Vol. 6, Springer-Verlag, Berlin, 1978, Vol. 6.
[30] J. I. Cline III, W. J. Dressick, J. N. Demas, and B. A. DeGraff, *J. Phys. Chem., 84,* 94 (1985).
[31] S. Snyder, D. Raines, P. T. Reiger, J. N. Demas, and B. A. DeGraff, *Langmuir, 1,* 548 (1985).
[32] W. J. Dressick, B. L. Hauenstein Jr., J. N. Demas, and B. A. DeGraff, *Inorg. Chem., 23,* 1107 (1984).
[33] J. L. Kropp, M. W. Windsor, *J. Phys. Chem., 71,* 477 (1967).
[34] W. DeW. Horrocks Jr., and D. R. Sunick, *Acc. Chem. Res., 14,* 384 (1981).
[35] B. L. Hauenstein Jr., W. J. Dressick, S. L. Buell, J. N. Demas, and B. A. DeGraff, *J. Am. Chem. Soc., 105,* 4251 (1983).
[36] W. J. Dressick, B. L. Hauenstein Jr., T. B. Gilbert, J. N. Demas, and B. A. DeGraff, *J. Phys. Chem., 88,* 3337 (1984).
[37] K. Mandel, B. L. Hauenstein, J. N. Demas, and B. A. DeGraff, *Ibid., 87,* 328 (1983).
[38] B. L. Hauenstein Jr., W. J. Dressick, T. B. Gilbert, J. N. Demas, and B. A. DeGraff, *Ibid., 88,* 1902 (1984).
[39] (a) S. W. Snyder, MS Thesis, University of Virginia, 1985. (b) S. W. Snyder, J. N. Demas, and B. A. DeGraff, Manuscript in Preparation.
[40] W. J. Dressick, J. I. Cline III, J. N. Demas, and B. A. DeGraff, *J. Am. Chem. Soc., 108,* 7567 (1986).
[41] G. A. Reitz, W. J. Dressick, J. N. Demas, and B. A. DeGraff, *Ibid., 108,* 5344 (1986).

[42] G. A. Reitz, MS Thesis, University of Virginia, 1987.
[43] G. A. Reitz, J. N. Demas, B. A. DeGraff, and E. M. Stephens, *J. Am. Chem. Soc., 111,* 5051 (1988).
[44] L. Mayes, J. N. Demas, and B. A. DeGraff, Submitted.

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