

fluoropolymers. This is similar to the results<sup>8</sup> expected from radical or ionic polymerization.

All three polymers studied had unsaturated carbon sites and exhibited approximately the same rate of fluorine uptake (Figures 2 and 3). No shake-up satellites were observable on the fluorinated surfaces, suggesting that the carbon valencies are saturated.

For inert gas ions with kinetic energies of the order of 1 keV, the dominant mechanism which governs ion penetration depths into solids is nuclear-nuclear interactions,<sup>30,31</sup> i.e., billiard ball collisions, which can be treated by classical mechanics. Using LSS theory,<sup>32</sup> one can calculate the penetration depth of 1-keV F<sup>+</sup> ions treated as nonreactive billiard balls to be greater than 50 Å (depends on the polymer density). The XPS results indicate that the fluorinated film is less than one monolayer for F<sup>+</sup> and CF<sub>3</sub><sup>+</sup> bombardment and ~3 monolayers for the non-mass-selected bombardment. The result that the fluorinated films are significantly thinner than expected from LSS theory suggests that there is an additional stopping mechanism besides nuclear-nuclear interactions which is

operative and is the dominating mechanism for these systems. This additional stopping mechanism must be electronic interaction of the very reactive fluorine atoms with the carbon atoms to form chemical bonds, i.e., trapping in a product potential well.

### Conclusions

The experimental results show that very thin layers of fluoropolymers can be prepared on the surfaces of hydrocarbon polymers through the use of controlled fluorine-containing ion beams. The reaction produces fluorocarbons with specific bonding environments, e.g., -CHF- and -CF<sub>2</sub>-, rather than physically implanting the ions in nondiscrete environments. The specific fluorine environments appear to be insensitive to the type of unsaturated sites in the polymers used. Fluorination by mass-selected and non-mass-selected beams has shown that, at 1-keV kinetic energy, molecular ions are dissociated upon impact with the surface and the nascent fluorine atoms are the reactants. Consequently, the nature of the fluorine-carrying molecular ions used in the beam is significant only to the extent that the non-fluorine atoms in the beam may be deposited on the surface and block the reactive sites.

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## Perfluorinated "Mini" Micelles: Energy Transfer from Benzophenone and Determination of Aggregation Number

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The phosphorescences of Ru(bpy)<sub>3</sub><sup>2+</sup> and of benzophenone are readily observed in aqueous solutions containing sodium perfluorooctanoate (SPFO) micelles. The quenching of Ru(bpy)<sub>3</sub><sup>2+</sup> by nitrobenzene is employed to determine the aggregation number of SPFO micelles. A very small value of ~7 is found and indicates that SPFO forms "mini" micelles in contrast to typical hydrocarbon chain containing detergents which have aggregation numbers typically in the range of 50-100. From phosphorescence quenching and phosphorescence sensitization measurements, energy transfer from benzophenone triplets to 1,4-dibromonaphthalene in SPFO micelles was demonstrated to occur.

### Introduction

The observation of and study of luminescence phenomena and electronic energy transfer in conventional micelles have been reported frequently over the past decade.<sup>1-17</sup>

The overwhelming majority of publications in this field has involved conventional micelles composed of hydrocarbon backbones. Few studies of any type have been reported for micelles composed of perfluorinated carbon

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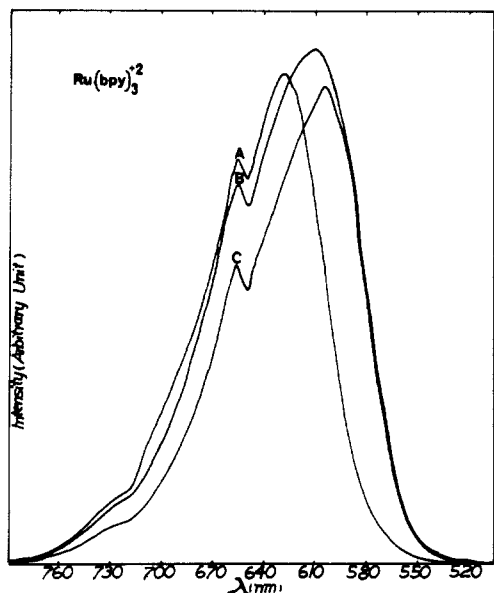
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**Figure 1.**  $\text{Ru}(\text{bpy})_3^{2+}$  emission spectra in different solvents: (A) 0.05 M SDS; (B)  $\text{H}_2\text{O}$ ; (C) 0.5 M SPFO. Concentration of  $\text{Ru}(\text{bpy})_3^{2+}$  are all ca.  $10^{-4}$  M.

chains. We have applied luminescence methods that have provided important information on conventional micelles for the investigation of perfluorinated micelles, e.g., the quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  phosphorescence was employed to determine the aggregation number of perfluorinated micelles and electronic energy transfer from benzophenone triplets to 1,4-dibromonaphthalene was demonstrated.

### Experimental Section

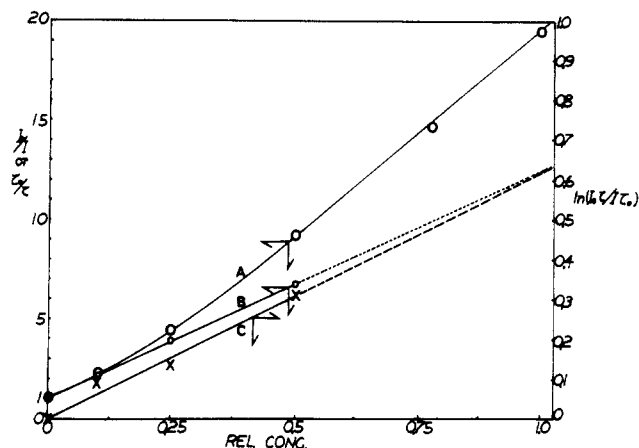
Benzophenone from Matheson Coleman and Bell was recrystallized twice from ethanol. 1,4-Dibromonaphthalene from Eastman Organic Chemicals was sublimed three times under vacuum. Perfluorooctanoic acid from ICN Pharmaceuticals, Inc. was sublimed three times under vacuum. A 0.5 M sodium perfluorooctanoate (SPFO) solution was prepared<sup>18</sup> by neutralizing the acid with the required amount of 1.0 N NaOH from Fischer Scientific Co.  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  was used as received from G. Frederick Smith Chemical Co. All other chemicals, whether spectrograde or not, were routinely checked for absorption or emission impurities. Solvents were subjected to further purification as needed. Water was first distilled from acidic  $\text{KMnO}_4$  and then redistilled twice.

Degassing was achieved by five freeze-and-thaw cycles under ca.  $10^{-5}$  torr vacuum. Emission spectra were taken on Hitachi-Perkin-Elmer fluorescence spectrophotometer (Model MPF-3L equipped with Osram 150-W xenon lamp and Hamamatsu R777 phototube) and were uncorrected.

Lifetimes and decay curves were taken on a single-photon-counting apparatus described previously.<sup>19</sup> Absorption spectra were recorded on a Cary spectrophotometer, Model 17.

### Results and Discussion

**Luminescence Quenching.  $\text{Ru}(\text{bpy})_3^{2+}$  Donor.** Although earlier studies<sup>18,20</sup> indicated the formation of SPFO micelles, we are unaware of any reported measurements of the aggregation number associated with these systems.



**Figure 2.** Quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  excited state as function of nitrobenzene concentration: (A)  $I_0/I$ ; (B)  $\tau_0/\tau$ ; (C)  $\ln [I_0\tau/(I\tau_0)]$  vs. nitrobenzene concentration. Concentration of  $\text{Ru}(\text{bpy})_3^{2+}$  is ca.  $1 \times 10^{-4}$  M. Highest concentration of nitrobenzene is  $4.2 \times 10^{-4}$  M. The dashed lines are extrapolated values. All samples are degassed at ca.  $10^{-5}$  torr for five cycles.

The luminescence method involving quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  phosphorescence<sup>1,5,8,9,11</sup> was employed to determine the aggregation number of SPFO micelles.

Figure 1 shows the  $\text{Ru}(\text{bpy})_3^{2+}$  phosphorescence emission spectra in  $\text{H}_2\text{O}$ , 0.05 M SDS (sodium dodecyl sulfate), and 0.5 M SPFO. The emission maximum in  $\text{H}_2\text{O}$  was found to be at 615 nm; the maxima in 0.05 M SDS and 0.5 M SPFO were found at 630 and 605 nm, respectively. The red shifting and band narrowing of  $\text{Ru}(\text{bpy})_3^{2+}$  emission in 0.05 M SDS relative to that in  $\text{H}_2\text{O}$  has been reported and ascribed<sup>21</sup> to the sensitivity of the emissive charge transfer triplet state of  $\text{Ru}(\text{bpy})_3^{2+}$  complex to the solubilization by SDS micelles. We attribute the blue shifting and band narrowing of  $\text{Ru}(\text{bpy})_3^{2+}$  emission in 0.5 M SPFO solution to solubilization of the complex by SPFO micelles. That blue shifting, rather than red shifting, is characteristic of the interaction of  $\text{Ru}(\text{bpy})_3^{2+}$  triplet state with fluorocarbon chains is supported by a recent report<sup>17</sup> in which a similar blue shift was observed for  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed into a perfluorosulfonate resin.

A further and convincing demonstration that  $\text{Ru}(\text{bpy})_3^{2+}$  is "totally" micellized by SPFO micelles follows from quenching efficiency discussed below. Two solutions,<sup>22</sup> each containing an equal amount of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Fe}(\text{CN})_6^{4-}$ , the former in pure water and the latter in an aqueous solution of 0.5 M SPFO, were employed for luminescence intensity quenching measurements. The efficiency of quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  phosphorescence of  $\text{Fe}(\text{CN})_6^{4-}$  in 0.5 M SPFO was found to be ca. 200-fold less than that in  $\text{H}_2\text{O}$ . The lifetimes of  $\text{Ru}(\text{bpy})_3^{2+}$  in  $\text{H}_2\text{O}$  and in 0.5 M SPFO were both found to be ca. 350 ns (aerated solution). The 200-fold decrease in quenching efficiency by  $\text{Fe}(\text{CN})_6^{4-}$  in 0.5 M SPFO clearly indicates that  $\text{Ru}(\text{bpy})_3^{2+}$  is effectively solubilized by SPFO micelles. Ionic micelles are known to carry a high density of charge on the surface, which shields the solubilizates from the approach of charged species carrying the same kind of charges as the micelles. Since both SPFO and  $\text{Fe}(\text{CN})_6^{4-}$  carry negative charges, and since  $\text{Ru}(\text{bpy})_3^{2+}$  is complexed with the SPFO micelles, the electrostatic repulsion due to the negatively charged micelle surface serves to greatly decrease the quenching efficiency of  $\text{Fe}(\text{CN})_6^{4-}$ .

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As an uncharged quencher, nitrobenzene was also found to be an effective quencher<sup>23</sup> of Ru(bpy)<sub>3</sub><sup>2+</sup> luminescence in 0.5 M SPFO solution. The results of a quenching study are shown in Figure 2. Two important features are seen from the intensity and lifetime quenching plot as functions of nitrobenzene concentration: (1) The intensity plot, i.e., A, is neither linear nor exponential over the range investigated. (2) The lifetime plot, i.e., B, is purely linear over the range investigated. Reference to the four limiting types of quenching in micelles<sup>9</sup> indicates that such behavior is diagnostic of case 2, for which quenching data are handled by

$$\frac{I_0}{I} = (1 + k_q \tau_0 [Q]_w) \exp\left(\frac{K[Q]}{1 + K[M]}\right) \quad (1)$$

$$\tau_0/\tau = 1 + k_q \tau_0 [Q]_w \quad (2)$$

where  $I_0$  and  $I$  are intensities of Ru(bpy)<sub>3</sub><sup>2+</sup> luminescence in the absence and presence of the quencher,  $\tau_0$  and  $\tau$  are lifetimes of Ru(bpy)<sub>3</sub><sup>2+</sup> triplet states in the absence and presence of the quencher,  $k_q$  is the quenching rate constant,  $[Q]$  is the total quencher concentration,  $[Q]_w$  is the quencher concentration in the aqueous phase,  $K$  is the association constant of the quencher with micelles, and  $[M]$  is the concentration of micelles. By dividing eq 1 by eq 2, eq 4 and 5 are obtained:

$$\frac{I_0}{I} \frac{\tau}{\tau_0} = \exp\left(\frac{K[Q]}{1 + K[M]}\right) \quad (3)$$

or

$$\ln\left(\frac{\tau}{I} \frac{I_0}{\tau_0}\right) = \frac{K[Q]}{1 + K[M]} \quad (4)$$

where

$$K = [Q]_m / ([Q]_w [M]) \quad (5)$$

$[Q]_m$  is the quencher concentration in the micellar phase, and  $[Q]_m/[Q]_w$  is the partition ratio,  $P$ , of the quencher between the micellar and the aqueous phases. Hence

$$\ln\left(\frac{\tau}{I} \frac{I_0}{\tau_0}\right) = \frac{P}{1 + P} \frac{[Q]}{[M]} \quad (6)$$

A plot of  $\ln[\tau I_0/(I \tau_0)]$  against total quencher concentration  $[Q]$  is expected to yield a line with a slope equal to  $[P/(1 + P)](1/[M])$ .

Figure 2C shows a plot of eq 6 possessing a slope equal to 13.4. From solubilization studies, we find that in 0.5 M SPFO solution, the partition ratio,  $P$ , of nitrobenzene equals 13, which allows the calculation of  $[M]$  to be 0.069 M. Since

$$[M] = \frac{[\text{SPFO}] - \text{cmc}_{\text{SPFO}}}{N_{\text{SPFO}}} \quad (7)$$

where  $[\text{SPFO}]$  is the total SPFO monomer concentration,  $\text{cmc}_{\text{SPFO}}$  is the critical micelle concentration of SPFO micelles, and  $N_{\text{SPFO}}$  is the aggregation number of SPFO micelles. From the knowledge of 0.032 M as the  $\text{cmc}_{\text{SPFO}}$  (see next section),  $N_{\text{SPFO}}$  was then calculated to be 7! In a very recent publication,<sup>23</sup>  $N_{\text{SPFO}}$  was arbitrarily taken to be 20 for SPFO micelles in order to calculate the volume change on micelle formation.

This extraordinarily small aggregation number, together with the short fluorocarbon chain, is expected to make "mini" SPFO micelles loose and open to the interaction

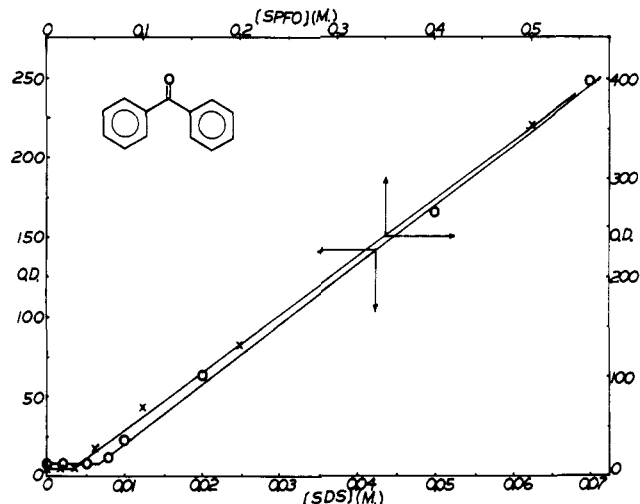


Figure 3. Solubility of benzophenone as function of SDS or SPFO monomer concentration. OD at 257 nm of benzophenone is monitored for both SDS (O) and SPFO (X) solutions. Variable path length cells were employed to achieve the experimental OD's.

of surrounding H<sub>2</sub>O molecules. This expectation is, indeed, supported by <sup>19</sup>F NMR experiments<sup>18</sup> which reveal that even the fluorine atoms believed to be at the very core of SPFO micelles are substantially "wetted" by water. The rate constants for quenching of Ru(bpy)<sub>3</sub><sup>2+</sup> by nitrobenzene were found to be  $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which is close to the reported value<sup>23</sup> of ca.  $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

*Triplet Energy Transfer Studies: Benzophenone Donor and 1,4-Dibromonaphthalene Acceptor.* Figure 3 shows the solubility curves of benzophenone in various concentrations of SDS and SPFO micellar solutions determined by monitoring the OD<sub>257</sub> of the solutions. Both curves show breaks at a certain detergent concentration, indicating their cmc's to be 0.007 M for SDS and 0.032 M for SPFO. Both values are close to published cmc values.<sup>18-25</sup>

Although aromatic ketones, such as benzophenone and acetophenone, are generally weakly or nonphosphorescent in normal organic solvents at room temperature,<sup>26</sup> benzophenone phosphorescence has been observed in benzene,<sup>27</sup> fluorocarbons,<sup>28</sup> isooctane,<sup>29</sup> carbon tetrachloride,<sup>30</sup> and water.<sup>31</sup> A major reason for the inability to observe phosphorescence from aromatic ketones in many organic solvents is ascribed to the severe quenching of the triplet state of aromatic ketones through hydrogen abstraction of the solvent molecules.

We have searched for benzophenone phosphorescence in various micellar solutions, e.g., SDS, HDTBr, HDTCl, Brij 35, and SPFO solutions, with negative results for all solutions tried, except one: SPFO solutions. The finding was further checked by phosphorescence quenching by these surfactant monomers in aqueous solution. While SPFO monomer does not quench benzophenone phosphorescence, SDS monomer, as an example of hydrocarbon surfactant, quenches with a rate constant of as high as  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>32</sup> Benzophenone ketyl radical absorption has been

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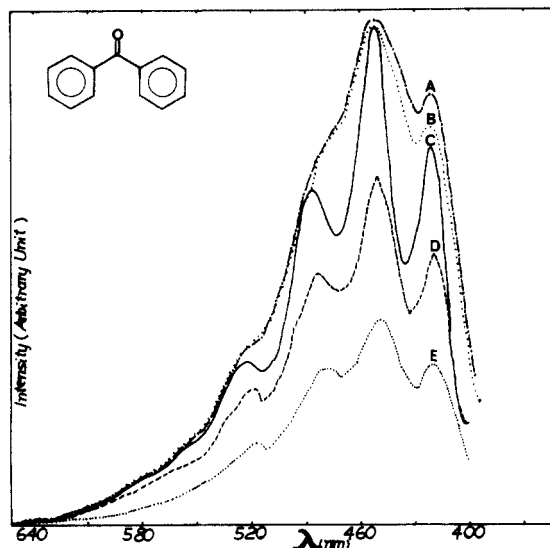
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**Figure 4.** Benzophenone phosphorescence spectra in different solvents at room temperature. Arbitrary intensity units: (A) 0.5 M SPFO; (B)  $\text{H}_2\text{O}$ ; (C) isooctane; (D) perfluorocyclohexane and water-saturated perfluorocyclohexane; and (E) acetonitrile.

observed in the latter solution.<sup>32</sup> Of course, such a deactivation is not possible for SPFO micelles, which do not possess any available hydrogen atoms.

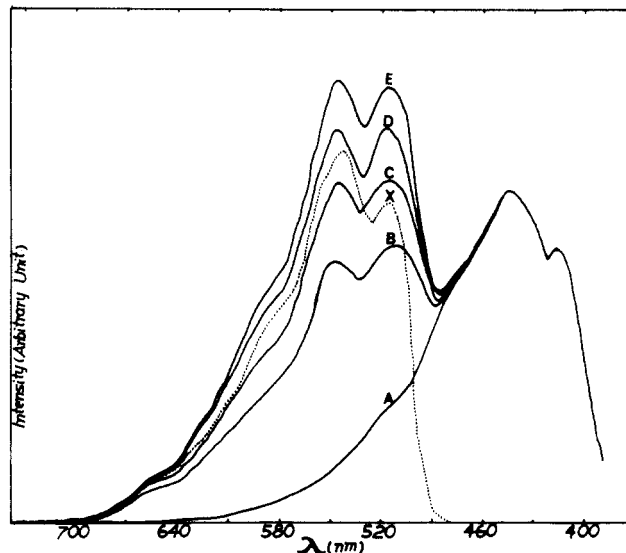
Figure 4 shows the benzophenone phosphorescence spectra in SPFO micelles and in various fluid solvents at room temperature. Although there is little or no shift in the emission spectrum, a significant loss of vibrational fine structure is observed when solvent polarity increases (isooctane to acetonitrile to SPFO to  $\text{H}_2\text{O}$ ). The loss of vibrational fine structure in benzophenone phosphorescence as solvent polarity increases has also been reported<sup>33</sup> in other systems.

The fact that benzophenone phosphorescence is well structured in "dry" and water-saturated perfluorocyclohexane as in some other organic solvents indicates that, when solubilized by SPFO micelles, benzophenone molecules experience mainly an aqueous environment. This is not surprising considering the small size of the SPFO micelles, with their monomer chain length of 8 carbons and aggregation number of 7. As pointed out in the previous section,  $^{19}\text{F}$  NMR results<sup>18</sup> are also in accord for SPFO micelles which possess a small, loose, and open structure. The phosphorescence lifetime of benzophenone in SPFO micelles was found to be 22  $\mu\text{s}$ , which is close to the extrapolated value of 40  $\mu\text{s}$  which is found for benzophenone in infinite dilute aqueous solution.

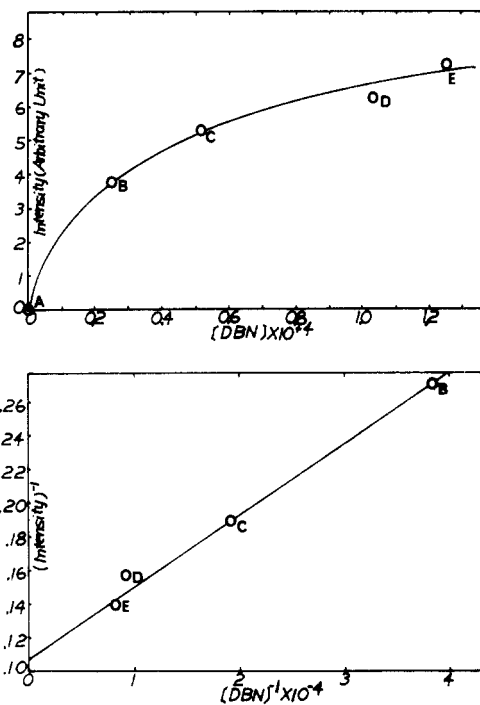
The possibility of energy transfer from benzophenone to 1,4-dibromonaphthalene (1,4-DBN) was investigated in 0.5 M SPFO micelles. 1,4-DBN was chosen because its triplet state lies about ca. 7 kcal/mol below that of benzophenone and because its phosphorescence is readily observable in micellar solution.<sup>34</sup>

Figure 5 shows the results in 0.5 M SPFO solution that were saturated with  $\text{CCl}_4$  and which contained benzophenone and 1,4-dibromonaphthalene. Evidently,  $\text{CCl}_4$  is able to slightly "swell" SPFO micelles, since the solubility of 1,4-DBN was doubled.

As can be seen from Figure 5, the emission at ca. 545 nm increases as concentration of 1,4-DBN increases. A subtraction spectrum, X, reveals this emission to be from



**Figure 5.** Energy transfer from benzophenone to 1,4-DBN in 0.5 M SPFO solution saturated with  $\text{CCl}_4$ . Excitation is carried out at 355 nm. All samples contain  $1.2 \times 10^{-3}$  M benzophenone and different amount of 1,4-DBN: (A) 0; (B)  $2.6 \times 10^{-5}$ ; (C)  $5.2 \times 10^{-5}$ ; (D)  $1.04 \times 10^{-4}$ ; and (E)  $1.24 \times 10^{-4}$  M, respectively. They are degassed at ca.  $10^{-4}$  torr for 5 cycles. X is the emission spectra after subtracting a from e after normalizing at 450 nm.



**Figure 6.** 1,4-DBN phosphorescence intensity as function of DBN concentration. Upper: phosphorescence intensity as function of 1,4-DBN concentration. Lower: phosphorescence intensity reciprocal as function of 1,4-DBN concentration reciprocal. Data points are taken from Figure 5.

1,4-DBN phosphorescence.<sup>34</sup> The fact that the 1,4-DBN emission comes from the excitation of benzophenone is confirmed by the observation that, under the same experimental conditions, a saturated solution of 1,4-DBN in  $\text{CCl}_4$  saturated 0.5 M SPFO solution did not emit at all. Also it can be seen from Figure 5 that, within experimental error, there is little change in benzophenone emission at 450 nm. This is reasonable because of the low concentration of 1,4-DBN, which is at most  $1.24 \times 10^{-4}$  M. However, due to much higher phosphorescence quantum yield of 1,4-DBN than that of benzophenone in this system,

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every act of energy transfer from benzophenone is "magnified" through 1,4-DBN phosphorescence.

The analysis of the above results was then plotted in Figure 6, from which an overall energy transfer rate constant of  $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was obtained for this system.

### Conclusion

The aggregation number of SPFO micelles is deduced to be very much smaller than that of conventional micelles. However, the "mini" micelles of SPFO are capable of solubilizing organic substrates such as benzophenone, nitrobenzene, and 1,4-dibromonaphthalene. In addition to solubilization, other features of conventional micelles are exhibited: protection from quenching by species possessing the same charge as the micelle surface, and enhanced quenching by quenchers solubilized in micelles containing energy donors. Should an aggregate of less than

10 units be termed a micelle at all? We think that the essential empirical characteristics of a micelle are its ability to enhance solubility of hydrophobic substance in aqueous solutions and to organize the solubilized species into a microscopically small space of the order of the dimensions of a sphere whose radius is roughly that of a detergent unit. Our results indicate that solutions of SPFO micelles in water display these characteristics.<sup>35</sup>

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(35) A referee has pointed out that the  $\text{Ru}^{\text{II}}$  complex could be causing aggregation to form a 7:1 SPFO/ $\text{Ru}^{\text{II}}$  complex. If this were true, our aggregation number would refer only to the complex and not to the "native" micelle in the absence of  $\text{Ru}^{\text{II}}$ .

## Origin of Multiple Phosphorescence Emission from *p*-Chlorobenzaldehyde in Polycrystallized Methylcyclohexane-*d*<sub>14</sub> at 4.2 K

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The dual phosphorescence spectra of *p*-chlorobenzaldehyde in polycrystalline methylcyclohexane is shown to originate from different guest sites in the crystalline matrix, by narrow band excitation and lifetime experiments.

### Introduction

Coupling between closely spaced molecular electronic states, although widely studied<sup>1-4</sup> with extensive attention having been paid to molecules with  $n\pi^*$  and  $\pi\pi^*$  states, is still controversial. The different sensitivity of  $\pi\pi^*$  and  $n\pi^*$  states to substituent and environmental perturbation allows modulation of the state spacing and further allows state switching.

Recently, a solid solution of *p*-chlorobenzaldehyde (PCB) in polycrystallized methylcyclohexane (MCH) was shown to constitute a favorable system for studying coupling effects on the triplet states since the solute triplet state sequence and spacing depends on the cooling rate of the solution and also on deuterium labeling of the matrix.<sup>5,6</sup>

In perdeuterated MCH (MCH-*d*<sub>14</sub>), PCB phosphorescence exhibited two types of spectra related to the existence of two crystalline phases of the host:<sup>5</sup> the  $\alpha$  phase, which occurs for moderate cooling rates (e.g., from 300 to 77 K in less than 10 min) and the  $\beta$  phase which is uniquely observed only for very slow cooling (e.g., from 300 to 77

K in more than 1 h). In nondeuterated MCH, the  $\beta$  phase is not observed in either intermediately or slowly cooled samples.

Phosphorescence of PCB in the  $\beta$  phase yields a single phosphorescence spectrum. However, phosphorescence of PCB in the  $\alpha$  phase in both MCH and MCH-*d*<sub>14</sub> gives rise to multiphosphorescence emission. The spectrum has been interpreted as either an intramolecular dual phosphorescence originating from two independent  $^3n\pi^*$  and  $^3\pi\pi^*$  states only weakly coupled by phonon interaction, or dual emission due to different sites.<sup>6</sup>

In this paper we report narrow band phosphorescence spectra and phosphorescence lifetime experiments which definitively prove that the dual emission of PCB and PCB-*d* in the MCH  $\alpha$  phase is due to a multisite mechanism. Moreover, phosphorescence excitation spectra monitored by narrow band observation provides compelling evidence for this interpretation.

### Experimental Details

*p*-Chlorobenzaldehyde and its deuterium derivative, PCB-*d*<sub>1</sub> (aldehyde hydrogen deuterated), had the same origin as in our previous studies. Perdeuterated methylcyclohexane (MCH-*d*<sub>14</sub> Merck Sharp and Dohm, 99.15% D was used without further purification. The degassed samples were sealed in 4-mm i.d. Pyrex tubes and cooled by being lowered into a dewar containing liquid nitrogen.

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