Room Temperature Phosphorescence of 1-Bromo-4-(bromoacetyl)naphthalene Induced Synergetically by β-Cyclodextrin and Brij30 in the Presence of Oxygen

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Received: December 18, 2003; In Final Form: April 21, 2004

Strong room temperature phosphorescence (RTP) of 1-bromo-4-(bromoacetyl)naphthalene (BBAN) is induced synergetically by β-CD and Brij30 without removal of oxygen dissolved in the solution because of the formation of ternary complex of β-CD, BBAN, and Brij30. Some factors that affect RTP intensity, such as standing time and ethanol etc., are also discussed. Sedimentation phenomena occur in the lactescent ternary system after enough standing time, and strong RTP from the suspended precipitates might indicate that the ternary complex exists as microcrystals in the measurement system. The proton nuclear magnetic resonance (^{1}H NMR) experimental results are consistent with the inclusion behavior of BBAN molecules. Chemical shift changes in H-5 of β-CD are larger than those in H-3, which indicates that the phosphor is included in the hydrophobic cavity at the narrower end. H-6 also witnesses relatively large changes in its chemical shifts, so the outside-exposed part of BBAN may be "locked" by the seven groups of methylol in the short section of the truncated cone molecule. NMR spectra also indicate that the alkyl chain of Brij30 is partially inserted into the β-CD cavity so as to enhance the rigidity of the cavity that BBAN dwells in, whereas the polar moiety lies outside of the cyclodextrin molecule at the narrower end. Additionally, ROESY spectra validate the reciprocity between Brij30 and β-CD. To further elucidate the so-called "synergetic effect", fluorescence measurements of solvatochromic probe 4-(dicyanomethylene)-2-methyl-6-[4-(dimethylamino)stryryl]-4*H*-pyran (DCM) are also conducted in the same microenvironment as that of BBAN, and the evident shifts to shorter wavelength of emission spectra imply that the BBAN resides in a more rigid environment with lower dielectric constant in the presence of both β-CD and Brij30 than exists when β-CD and Brij30 are present individually.

Introduction

Recent years have seen a tendency of ever-increasing interest in the effects of self-assemblied media on photochemical and photophysical properties of aromatic compounds. When the substances accumulate in molecular aggregates including micelles, microemulsion, and vesicles, or in cavities including cyclodextrins (CDs), calix[*n*]arenas, cage compounds, and other analogues, etc., they are often confined to a greater degree of organization compared with those in homogeneous solution, which may find use in mimicking phenomena occurring in biosystems as well as an application for energy storage.[1] In the field of supramolecular chemistry, owing to the natural characteristics in molecular structure, i.e., the amphiphilicity of combining the hydrophobic cavity with hydrophilic periphery, CDs are found to be of great importance as a highly organized host media. The hydrophobic cavity can serve as a selective container for organic molecules of proper size, and the hydrophilicity is really very convenient for the need of carrying out research works in aqueous solution. Room temperature phosphorescence induced by cyclodextrin (CD-RTP) was first introduced by Cline Love et al. in 1984,[2,4] and since then numerous investigations have exploited some interesting properties of cyclodextrins. CDs, especially β-CD for its low cost and high solubility in water, are employed to provide the included phosphors with a rigid enough microenvironment. However, in further investigations of CD-induced phosphorimetry, the removal of molecular oxygen produces some inconveniences, such as difficulties in adjusting the acidity caused by adding Na_2SO_3 as the chemical oxygen-scavenger,[3] time-consuming processes of nitrogen purging,[4] great efforts needed in producing "inert" gases of CO_2 or H_2 gases in situ[5] and so on. So, considerable effort has been expended to produce CD-RTP without deoxygenation. It is established that surfactants can cooperate with CDs to favor the improved environment for enhancing phosphorescence emission and influencing other photophysical characteristics.[1,6−10] So the synergetic effects are of interest for further study.[11] It is supposed that alkyl chains of guest molecules stick into the cavity of CDs, which produces a more rigid microenvironment for the luminophor. This greater rigidity restricts various molecular movements and reduces the effects of quenching.[12]

Ionic surfactants are generally added to CD systems, which can be used without deoxygenation procedures and also ensure lucidity for the whole measurement system. As for the studies on nonionic detergents, few reports have dealt with measurements,[13−15] and involving ionic detergents, the explanation proposed for the interaction mechanism of CDs and guest molecules is usually based on the intuitive or empirical conjecture. The nonionic detergent Brij30, namely polyoxyethylene-(4)lauryl ether with the molecular formula $C_{12}H_{25}(OCH_2CH_2)_4$-OH, has a hydrophilic moiety and a long hydrophobic chain, so it usually forms micelles with the hydrophilic moiety extending into the bulky water phase and the tail groups aggregated together to form the hydrophobic core. The micelle has an obvious critical micelle concentration (CMC) of 40 μM in water,[16] and its solubilization sites include the micelle surface, palisade layer, and hydrophobic core.[17] Moreover, recent work has indicated that plots of RTP intensity vs temperature have a good linear relationship for solutions containing both β-CD and Brij30.[13] Now it is important to gain new insight into the interaction of β-CD and Brij30 in inducing RTP for the

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10.1021/jp037913a CCC: $27.50
Published on Web 05/29/2004

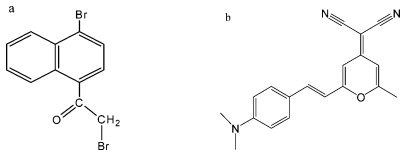

Figure 1. Schematic view of BBAN (a) and DCM (b).

development of a RTP temperature sensor[18] and also supramolecular chemistry devices.

Marriott et al.[19] reported that 1-bromo-4-(bromoacetyl) naphthalene (BBAN) as a phosphorescence probe is sensitive to the polarity of organic solvents. There is a need for the development of ideal phosphorescent probes that have the following spectroscopic and chemical properties: a high phosphorescence quantum yield, well-defined and excellent anisotropy at the excitation wavelength, relatively stable photochemical properties, dynamic sensitivity to the studied system, and so on. BBAN is undoubtedly an excellent probe to consider for use as phosphorescent monitor.[19,20] Herein is discussed a detailed study of the RTP of BBAN induced synergetically by Brij30 and β-cyclodextrin without deoxygenation. Moreover, we obtain the corresponding NMR results to support a proposed mechanism in the synergetic system concerned with different complexes in the similar condition of RTP sensing. As for more details in the varying polarity, 4-(dicyanomethylene)-2-methyl-6- [4-(dimethylamino)stryryl]-4*H*-pyran (DCM) is chosen as a useful solvatochromic probe to get further evidence about the microenvironmental properties of the ternary inclusion complex.

Experimental Section

1-Bromo-4-(bromoacetyl)naphthalene (BBAN), as shown in Figure 1a, is synthesized and purified by our group[20] according to the slightly modified procedure reported by Marriott et al.[19] BBAN stock solution of 1.0 mM is prepared by dissolving in ethanol. 4-(Dicyanomethylene)- 2-methyl-6-[4-(dimethylamino)-stryryl]-4*H*-pyran (DCM), as shown in Figure 1b, is used as received from Aldrich Co.. DCM is prepared as a 0.25 mM solution in ethanol. Brij30 is purchased from Acros Organics and used without further purification to prepare 100 and 10 mM aqueous solutions. β-CD is the product of the Guangdong Yunan Cyclodextrins Factory, and it is prepared into 10 mM aqueous solution after twice recrystallizing from ethanol. All the other reagents are of analytical-reagent grade. Water is doubly distilled in a sub-boiling quartz apparatus.

Typically, 100 μL of BBAN in ethanol solution is transferred into a comparison tube of 5 mL, and then a proper volume of β-CD solution is added to the same tube. The solutions are then allowed to equilibrate for 15 min prior to the addition of an appropriate volume of Brij30 aqueous solution, and then the final mixture is allowed to stand for about 1 h before making measurements. It is noteworthy that adequate shaking is carried out for even homogenization. For the measurement of fluorescence, 40 μL of DCM solution is transferred into one comparison tube. Then 4 mL of β-CD solution, 45 μL of Brij30, and water are added and fluorescence measurements are carried out after the solution stands for 1 h. All the other systems follow the same sequence of adding solution.

All the corrected RTP and fluorescence spectra are recorded on LS-55 luminescence spectrometer (Perkin-Elmer Co.) equipped with a pulsed xenon lamp. To produce RTP spectra, 335 nm was used as excitation for the phosphorescence spectra, and phosphorescence was observed at 575 nm for the excitation spectra. And the excitation and emission slits are set at 10 and 15 nm, respectively. The delay time and the gate width are set at 0.04 and 3 ms, respectively. Fluorescence measurements are generally carried through with the excitation and emission slits of 4 nm.

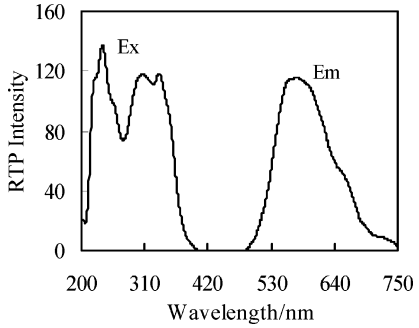

Figure 2. RTP excitation and emission spectra of BBAN in the synergetic system of Brij30 and β-CD ([BBAN] = 24 μM, [Brij30] = 0.9 mM, [β-CD] = 8 mM).

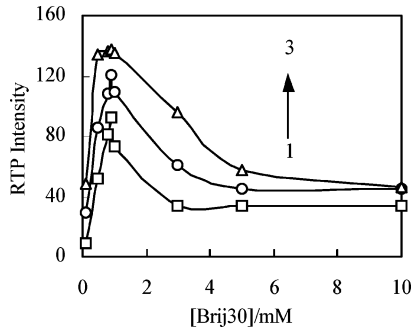

Figure 3. Effect of [Brij30] on BBAN phosphorescence (from 1 to 3, [β-CD] = 3, 6, 8 mM, [BBAN] = 24 μM).

All one-dimensional ^{1}H NMR spectra are acquired for solutions containing a binary solvent of deuterated acetone and D_2O (1:9, v/v), using a DRX-300 spectrometer. To achieve a suitable solibulization of both BBAN and β-CD, the stock solutions are prepared by combining both 10 mM β-CD and 20 mM Brij30 in D_2O and then adding 10mM of BBAN solubilized in CD_3COCD_3. The chemical shifts are expressed using tetramethylsilane as an internal standard. And the ROSEY spectroscopy of Brij30/β-CD complex is conducted at 25 °C.

Results and Discussion

RTP of the Three-Component Inclusion System. No RTP signals from BBAN are observed in the micellar Brij30 solution, and BBAN displays a very weak phosphorescence emission when it is individually included in the cavity of β-CD, in the presence of oxygen. However, synergetic effects are produced from mixing the two protective media of β-CD and Brij30 with BBAN, and RTP emission of BBAN is enhanced to a high enough degree. Thus, it can be inferred that the three-component inclusion complex, namely, β-CD/BBAN/Brij30 complex, really comes into existence. The excitation and emission spectra are shown as Figure 2 for the synergetic inclusion system.

Selection of Both the Brij30 and β-CD Concentrations. The variation in the RTP with Brij30 concentration is shown in Figure 3 for solution with different β-CD concentrations of 3, 6, and 8 mM. It can be seen that with the increase of [Brij30], RTP intensities sharply increase and reach a maximum value when [Brij30] is 0.9 mM, which is 22.5 times larger than the CMC value for Brij30,[16] and then decrease to a plateau. There is rather weak phosphorescence emission when the Brij30 concentration is more than 10 mM. As far as the plateau is concerned, a possible explanation is that the presence of β-CD

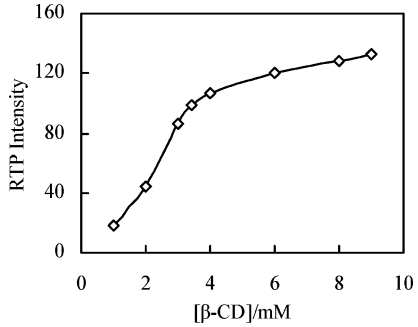

Figure 4. Effect of the concentration of β-CD on BBAN's phosphorescence ([BBAN] = 24 μM, [Brij30] = 0.9 mM).

might hinder the aggregation of Brij30 in forming micelles noted as $(Brij30)_n$, where n is the average number of Brij30 molecules per micelle. From Figure 3, it is approximately estimated that the delayed CMC value of Brij30 should be more than 0.9 mM in the presence of β-CD. Up to this concentration, Brij30 appears to be excessive for forming binary or ternary inclusion by β-CD or β-CD/BBAN, and then trends toward forming the micelles. So from the viewpoint of chemical equilibrium, BBAN tends to transfer from the β-CD/BBAN/Brij30 ternary complex into the Brij30 micellar regions with many solubilization sites where the final lower rigidity of the micelle microenvironment leads to some quenching of RTP, as can be seen in Figure 3.

Therefore, it is appropriate to choose the peak value as the optimum concentration for Brij30, namely 0.9 mM. In Figure 4, in the presence of Brij30, RTP intensities increase sharply with the addition of β-CD. In the concentration range of β-CD from 4.0 to 9.0 mM, the degree of enhancement grows slower and slower. Measurements of RTP at higher concentrations of β-CD are impossible because of the β-CD solubility limit. It must be the stable inclusion that occurs among BBAN, β-CD, and Brij30. β-CD is an amphiphilic molecule possessing both a hydrophobic cavity and a hydrophilic outside, and Brij30 contains a lauryl chain connecting polyoxygenethenyl and the hydroxyl group; so the inference is reasonable that BBAN is solubilized into the β-CD cavity together with the long alkyl chain of Brij30. Therefore, BBAN is experiencing a sufficiently rigid enough microenvironment to produce strong RTP emission, which will be discussed further in later parts.

The inclusion of β-CD, BBAN, and Brij30 can be further discussed. If the inclusion complexes contain no more than one β-CD molecule per BBAN molecule, the interactions concerned can be written as follows:

$$\beta\text{-CD} + \text{BBAN} \overset{K_1}{\rightleftharpoons} \beta\text{-CD/BBAN} \quad (1)$$

$$\beta\text{-CD/BBAN} + \text{Brij 30} \overset{K_2}{\rightleftharpoons} \beta\text{-CD/BBAN/Brij 30} \quad (2)$$

$$\beta\text{-CD} + \text{Brij 30} \overset{K_3}{\rightleftharpoons} \beta\text{-CD/Brij 30} \quad (3)$$

$$n\text{Brij 30} \overset{K_4}{\rightleftharpoons} (\text{Brij 30})_n \quad (4)$$

$$\beta\text{-CD/BBAN/Brij 30} + (\text{Brij 30})_n \overset{K_5}{\rightleftharpoons} \beta\text{-CD/Brij 30} + (\text{Brij 30})_n\text{/BBAN} \quad (5)$$

Now, consider the following deviation, in which C refers to β-CD, B refers to BBAN, R refers to Brij30, and R_n refers to Brij30 micelles. K_1, K_2, K_3, K_4, and K_5 are the binding constants for reactions 1−5, respectively. Equation 6 is the conservation equation for BBAN.

$$[B]_0 = [B] = [C/B] + [C/B/R] + [B/R_n] \quad (6)$$

Solution of the binding constant expressions for [C/B], [C/B/R], [C/R], and $[B/R_n]$ and substitution into eq 6 gives

$$[B]_0 = [B] + K_1[C][B] + K_1K_2[C][B][R] + K_1K_2K_5[B][R_n]/K_3 \quad (7)$$

Under the experimental conditions of the work described herein, $[C]_0$ is much larger than [B]. Combining this inequality with the binding constant expressions for eqs 1 and 2, it is true that

$$[C][B][R] = K_1K_2[C][B][R] + K_1K_2\,[C]_0[B][R] \quad (8)$$

Combing eqs 7 and 8 gives

$$[C][B][R] = K_1K_2[C]_0[R][B]_0/(1 + K_1[C]_0 + K_1K_2[C]_0[R] + K_1K_2K_5[R_n]/K_3) \quad (9)$$

If the RTP emission is predominantly from the triplet-state ternary inclusion complex, then from eq 9 it is seen that a plot of emission intensity vs [β-CD] should be asimple hyperbola but not an S-shaped curve. In Figure 4, the deviation from a simple hyperbola in the curve shape might be due tof the two following factors. First, when there exist the complexes containing n ($n > 1$) cyclodextrin molecules, eq 9 contains a $[C]_0^n$ term and mathematically the plot of emission intensity vs $[C]_0$ will be sigmoid. Second, the submicronic particles formed by β-CD and its various complex forms consequentially increase the RTP intensity because the suspended particles in solution enhance the rigidity of the microenvironment where BBAN dwells, effectively retarding oxygen quenchig. Combined with the previous results,[2,21] herein it is supposed that the latter factor plays a vital role in leading to the deviation of the curve. However, more work is needed to prove the speculation.

Effect of Ethanol. Owing to the poor solubility of BBAN in water, ethanol is employed to prepare the stock solution of the phosphor. The experimental data indicate that ethanol has an insignificant impact on luminescence intensity when ethanol is limited within the volume proportion from 0.5% to 2% in the working solution. So it is unnecessary to remove ethanol prior to further studying RTP emission.

Stability of the Synergetic System. The lactescent system is prepared according to the above-mentioned procedures in a comparison tube, and the solution is placed for a certain interval of time before each measurement. More precipitation occurs during the succeeding hours, and weaker RTP signals are detected from clearer supernatant. So it is noteworthy that before measurements, the lactescent system should be vigorously shaken for homogeneous dispersion. The resulting delaminated solution can produce intense RTP emission, which indicates that the ternary complex exists as microcrystals. Though the solution looks cloudy as previously reported,[2] the reproducible, good quality phosphorescence spectra can be observed and RTP intensity does not show remarkable change during the measurement time. Within 22 h, there is a rather small increase in phosphorescence for the setting system, as shown in Figure 5. The degree of inclusion will be enhanced after enough dynamic binding interaction between BBAN and β-CD during the standing course. The standing time of 1 h is enough to get a satisfactory RTP signal.

NMR Data. Figure 6 shows the relative positions of protons of interest in the β-CD molecule.[23] To confirm the inference

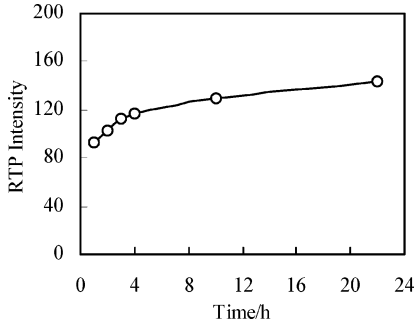

Figure 5. Effect of standing time ([BBAN] = 24 μM, [Brij30] = 0.9 mM, [β-CD] = 8 mM).

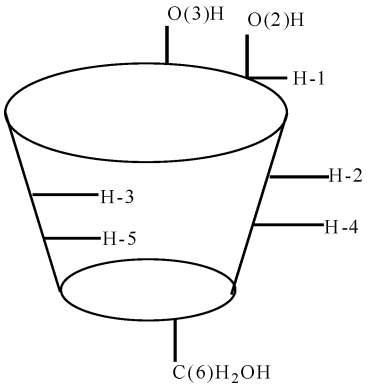

Figure 6. Representative localization of the "external" and "internal" protons in the β-CD molecule.

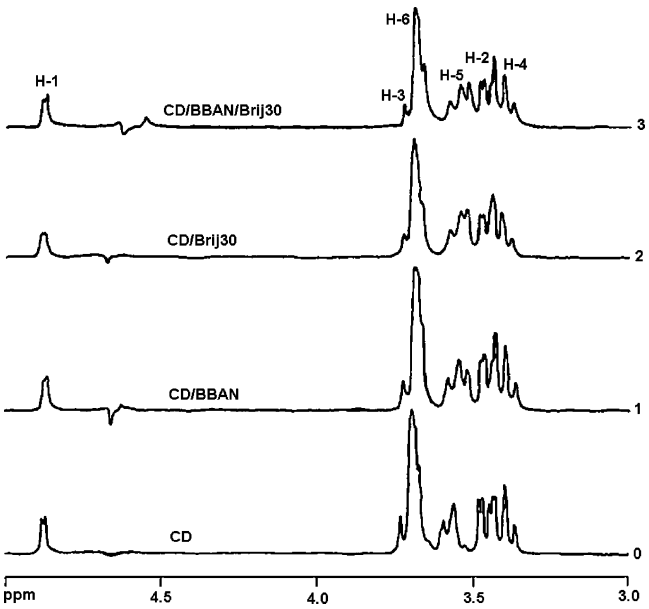

Figure 7. One-dimensional NMR spectra of β-CD and its different complexes ([BBAN] = 1 mM, [β-CD] = 5 mM, [Brij30] = 5 mM, in the mixed solvent of D_2O and CD_3COCD_3 with the volume proportion 1:9).

on the interaction model of the ternary inclusion complex (vide supra), ^{1}H NMR spectra in D_2O are obtained as the additional evidence. The corresponding ^{1}H NMR spectra are shown in Figure 7, where the negative peaks around 4.7 ppm are due to suppression of the peak due to residual H_2O in the solvent. The change of chemical shifts of various relevant protons in the β-CD is listed in Table 1. It is seen that in the binary system of β-CD and BBAN, $\Delta\delta_1$ of H-3, H-5, and H-6 displayed a larger change, and H-1 a smaller. In the binary system of β-CD and Brij30, $\Delta\delta_2$ of H-5 is larger than that of H-3, H-4, and H-6. In the ternary of β-CD/BBAN/Brij 30, the change is very similar

TABLE 1: ^{1}H Chemical Shifts Corresponding to β-CD in Complexes at the Presence of Different Components

	δ_0/ppm	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_3$
H-1	4.872	−0.004	−0.002	−0.001
H-2	3.482	−0.001	−0.002	−0.001
H-3	3.733	−0.009	−0.008	−0.010
H-4	3.430	−0.001	−0.005	−0.009
H-5	3.595	−0.014	−0.020	−0.019
H-6	3.699	−0.011	−0.007	−0.010

[a] δ_0 indicates the chemical shifts of cyclodextrin protons in β-CD, and $\Delta\delta_i = \delta_i - \delta_0$ ($i = 1-3$), where 1−3 correspond to the respective CD protons in solutions of β-CD + BBAN, β-CD + Brij30, and β-CD + BBAN + Brij30.

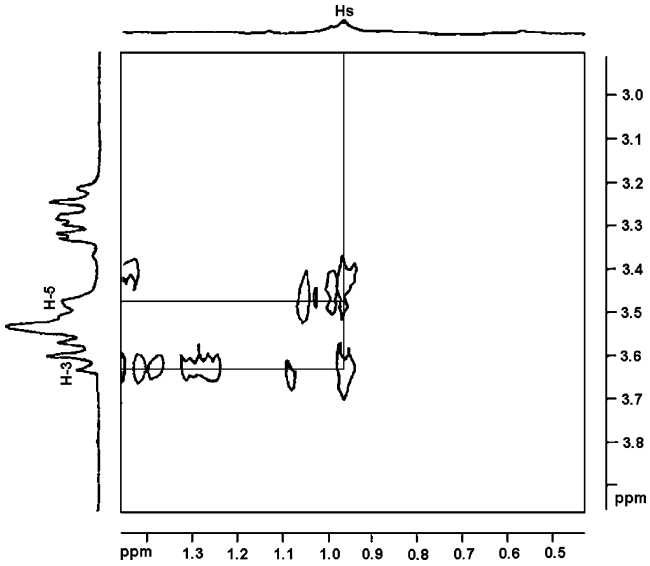

Figure 8. Partial contour plot of a ROESY spectrum of β-CD/Brij30 complex showing the cross-peaks between the protons of Brij30 and cyclodextrin at 25°C(300 MHz).

to that of $\Delta\delta_2$. On the whole, the change of chemical shifts showed the following order: $\Delta\delta$(H-5) > $\Delta\delta$(H-3) ~ $\Delta\delta$(H-6) > $\Delta\delta$(H-4) > $\Delta\delta$(H-1) ≈ $\Delta\delta$(H-2).

Generally speaking, it is the van der Waals interaction between host and guest molecules that induces a shielding of the inner protons of the glucose units of β-CD. In all investigated cases the largest change of H-5 chemical shift may indicate that the proton directly contacts the BBAN molecule and thus experiences the magnetic environment in another status. Assuming that the strength of interaction between BBAN and all protons of β-CD is the same for the same separation distance, it can be concluded that the inclusion of Brij30 in the cavity causes BBAN to be strictly confined to close to the smaller end of β-CD. Also, the seven methylol groups in the narrower opening of the truncated cone molecule play an important role in stabilizing the inclusion complex, whereas this function of the methylols is often neglected.

Two-dimensional ROESY studies are also carried out to estimate the inclusion behaviors of the Brij30/β-CD complex. Figure 8 shows a spatial contour plot of the ROESY spectrum for the β-CD system. The protons of alkyl chains in Brij30 molecules give cross-peaks with H-3 and H-5 protons of β-CD, and other protons do not appear to produce cross-linking peaks. This indicates that Brij30 inserts into the hydrophobic cavity of cyclodextrin with the hydrophobic parts. It is also important to understand the binary system of β-CD/BBAN by the change in the ROESY spectrum. Unfortunately, under our experimental conditions, no distinct peaks are given for pure BBAN due to its poor solubility in the mixed solvents of CD_3COCD_3 and D_2O

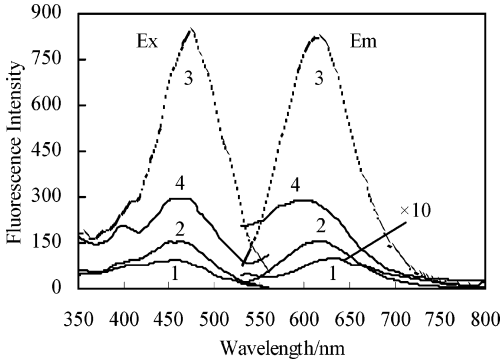

Figure 9. Fluorescence spectra of DCM in different media ([DCM] = 2 μM, [Brij30] = 0.9 mM, [β-CD] = 8 mM): (1) in aqueous solution, λ_{ex} = 456 nm; (2) in β-CD media, λ_{ex} = 462 nm; (3) in micellar Brij30, λ_{ex} = 474 nm; (4) in synergetic system of β-CD and Brij30, λ_{ex} = 470 nm.

TABLE 2: Comparison of Fluorescence Maximum Wavelength of DCM in Different Media with Ref. 26

media	dielectric constant (20 °C)	λ_{max}/nm
chloroform[a]	4.8	566
methyl methacrylate[a]		583
β-CD/Brij30[b]		596
Brij30[b]		612
β-CD[b]		618
methanol[a]	33.6	619
water[b]	80.4	632

[a] Reference 26. [b] Results in Figure 9.

with the same ratio, so it is impossible for us to investigate the cross-peaks for the complex of BBAN/β-CD. But Figure 8 is really instructive for our speculation that the cavity of β-CD can certainly provide a rigid enough microenvironment.

Probing the Microenvironment of the Synergetic Effects by Fluorescence. DCM is a very important solvatochromic probe that is sensitive to the polarity and viscosity of its surrounding and finds wide applications in biological fields.[24,25] Fluorescence spectra of DCM correspondingly shift to the blue region with the decrease of the dielectric constant of the system. And it has been reported that DCM was used to monitor the latex microenvironment, where RTP signals of 1-bromonaphthalene can be detected because the high viscosity within the particles retards oxygen diffusion.[26] As mentioned above, strong RTP signals can be obtained in the presence of both β-CD and Brij30, with respect to the case of β-CD or Brij30. From this point, it is reasonably speculated that BBAN dwells in a more rigid microenvironment. Under the assumption that both DCM and BBAN bind in a very similar fashion in the cyclodextrin cavity, DCM is used here to probe the appointed microenvironment to gain further evidence for our speculation.

It is very clear from the emission spectra shown in Figure 9 and Table 2 that there is a consecutive shift to shorter wavelength when DCM is in the water, β-CD, Brij30 micelle, and β-CD/Brij30 solution, respectively. The change in spectral wavelengths indicates that DCM gradually experiences quite different microenvironments of different polarities, i.e., in the β-CD/DCM/Brij30 ternary system, DCM experiences a microenvironment with lower dielectric constant, higher microviscosity, and less molecular oxygen than when placed in the presence of simple Brij30 micelles or β-CD. It is the noncovalent interactions, the foundation of supramolecular chemistry, that apparently produce the so-called "synergetic effects" when the ternary system comes into existence, regardless of whether the guest molecule is phosphorescent BBAN or fluorescent DCM. So it can be also rationally consider that BBAN has the same microenvironment with the DCM molecule under the investigated conditions. That is, β-CD and Brij 30 indeed synergetically induce BBAN to display intense RTP emission in the presence of oxygen, which may find wider uses in future investigation.

Conclusions

In this paper the application of different spectroscopic methods including RTP, NMR, and fluorescence has provided a relatively comprehensive understanding of the synergetic effect by which BBAN emits strong phosphorescence in the presence of oxygen. Combining RTP spectra with NMR data, we suppose that BBAN is included in the cavity of β-CD, close to the narrower end. Besides, the seven methylol groups may further stabilize the complex. Brij30 acts as a space-regulating molecule to enhance the stability of the complex of β-CD/BBAN and hinder the diffusion of molecular oxygen to quench the phosphor. And the experimental results are consistent with the twice rigidization mechanism of "inclusion complexation−suspension microcrystallization" proposed by Jin et al.,[22] which was also further proved by Nazarov et al.[21]

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (No. 20345004) and the Natural Science Foundation of Shanxi Province (No. 20031018). We also appreciate very much the reviewer's valuable suggestions and advice on this paper.

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