Room Temperature Phosphorescence from Inclusion Complex of β-Cyclodextrin and 1-Bromonaphthalene in the Presence of Phenol and 1-Butanol

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In recent years, the study of cyclodextrin (CD) stablized luminescence properties has become an attractive field because of their unique characteristics. β-CD is one of the most commonly used media which have been proposed as appropriate hosts to form inclusion complexes with a variety of guest molecules that are incorporated totally or partially into the cavity.[1-8] 1-Bromonaphthalene (1-BrN) forms an inclusion complex in aqueous β-CD solution and exhibits very weak room temperature phosphorescence (RTP) without deoxygenation. This phenomenon was initially reported by Turro and coworkers for bromosubstituted naphthalene derivatives.[8-10] Various organic species, especially alcohols, have a significant influence on luminescence emission from the luminophor in the inclusion complex.[11-17] For alcohols, it has been suggested that the size and nonpolarity of the alcohol seem to be the predominant factors in determining the overall effect of the alcohol on the complex. In the presence of alcohol, relatively intense RTP of 1-BrN appears.[13] Furthermore, In the presence of alcohol and naphthalene (N) as the second and third guests, much more relatively intense RTP of 1-BrN was observed.[14] In the present study, the process of inclusion complex formation of β-CD and 1-BrN in the presence of phenol and 1-butanol (B) have been studied by the spectral changes. The purpose of this work is to help understanding how β-CD stabilize RTP emission, to evaluate the probability of expanding its application and eventually to apply it to the detection of analytically interested organic species.

Experimental Section

Chemicals. 1-BrN (C.P, Shanghai Reagent Corp.) was distilled under reduced pressure and dried with anhydrogen sodium sulfate, and then 5.0×10^{-3} mol/L stock solution of 1-BrN in methanol was prepared. Analytically pure phenol (Shanghai Reagent Corp.) was sublimated and a 0.1 mol/L stock solution of phenol was prepared in methanol. β-CD (Suzhou Garment Factory) was recrystallized twice from Milli-Q water. B (A.R, Shanghai Reagent Corp.) was distilled before use. Buffer solutions with pH value ranged from 1.0 to 13.0 were prepared, respectively. Milli-Q water was used throughout the experiment.

Apparatus. All steady state fluorescence and RTP measurements were performed on a Hitachi 850 fluorescence spectrofluorimeter equipped with a 150 W xenon lamp. The excitation and emission bandwidth of 5 nm and 10 nm were employed, respectively. The excitation wavelength was set at 296 nm. The scan speed of the monochromators was maintained at 120 nm/min. The quartz cell was stored in ethanol and rinsed thoroughly with water prior to use. CS501 super recycling water thermal heater (Chongqing Instruments Co.) was employed to keep the temperature constant during the experiment. CQ250 ultrasonic cleaner (Shanghai supersonic instruments Co.).

Procedures. An aliquot of 1-BrN solution was transferred into a 10 mL volumetric flask, β-CD, phenol and B were added. After dilution to the mark, the solution was allowed to stand in an ultrasonic vibrator for at least 24h and then was stored in refrigerator for another 24h. The sample was introduced into the sample compartment and fluorescence and RTP spectra were measured. All experiment was carried out in the temperature of 13 ± 0.2 °C.

Results and Discussion

Fluorescence and RTP Spectra. Inclusion complexes between β-CD and N or 1-BrN have been studied previously in aqueous solution by fluorescence and RTP measurement.[12-14] Figure 1 showed us the fluorescence spectra of 1-BrN and phenol in aqueous β-CD solution at different pH value. At pH = 1.0, the system appears only one fluorescence peak located at 330 nm with the weakest fluorescence intensity. When pH = 5.8, another structureless wide band peak appeared at 410 nm while the 330 nm peak maintained as similar as pH = 1.0. A great changes had taken place at pH = 13.0. The fluorescence peak red shifted about 5 nm, and its intensity was nearly as twice as that of at pH = 1.0 or pH = 5.8. All of the above shown that phenol only exhibits very significant fluorescence at higher concentrations and no RTP under the experimental conditions. However, 1-BrN gives rise to fluorescence and very weak phosphorescence at room temperature because of an internal heavyatom effect. Upon addition of the appropriate alcohol, as showed in Figure 2, relatively intense RTP from 1-BrN appears due to

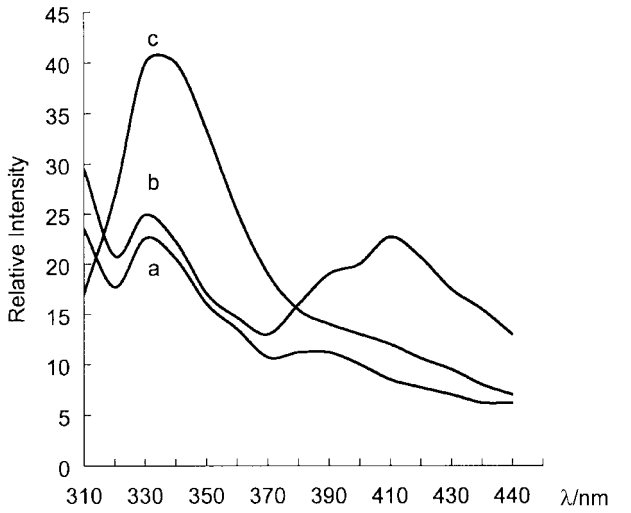

Figure 1. Fluorescence spectra of β-CD/1-BrN/phenol/B. a: pH = 1.0; b: pH = 5.8; c: pH = 13.0. [1-BrN] = 5.0×10^{-5} mol/L; [β-CD] = 1.0×10^{-2} mol/L; [phenol] = 3.0×10^{-4} mol/L; [B] = 0.7%. λ_{ex} = 296 nm.

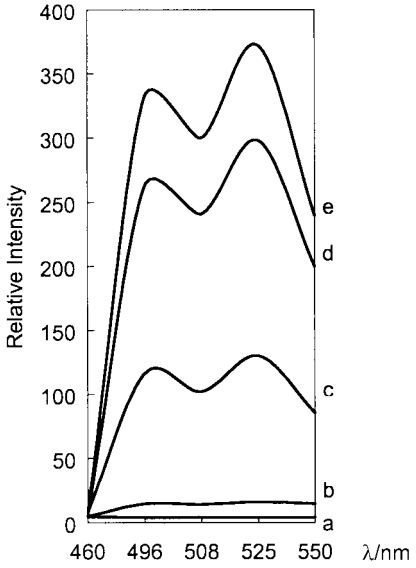

Figure 2. RTP spectra of 1-BrN. a. 1-BrN + phenol; b. β-CD+1-BrN; c. β-CD+1-BrN+phenol; d. β-CD+1-BrN+B; e. β-CD+1-BrN + B + phenol. [β-CD] = 1.0×10^{-2} mol/L; [B] = 0.7%; [1-BrN] = 5.0×10^{-5} mol/L; [phenol] = 3.0×10^{-4} mol/L. λ_{ex} = 296 nm.

the formation of the ternary β-CD: 1-BrN : alcohol complex. Our previous work shown that upon addition of N to the β-CD : 1-BrN complex, similar enhanced RTP is observed, because of the interaction between 1-BrN and N.[13] Furthermore, much more intense fluorescence of N and RTP of 1-BrN appears in the presence of N and B simultaneously. It reveals that N and B strikingly affect the microenvironment surrounding 1-BrN. There is more violent interaction between 1-BrN, N and B in the presence of both N and B than in the presence of N or B alone. The reasonable explanation is that 1-BrN, N and B are included in the β-CD cavity and formed greater rigidity inclusion complexes.[14] Additionally,

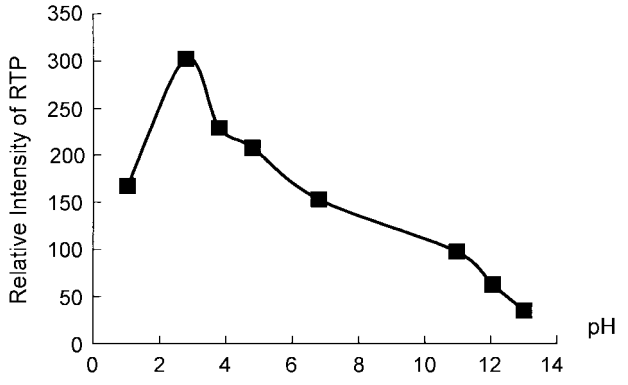

Figure 3. Effects of pH on RTP. [1-BrN] = 1.5×10^{-5} mol/L; [phenol] = 2.5×10^{-4} mol/L; [β-CD] = 1.0×10^{-2} mol/L; [B] = 0.7%.

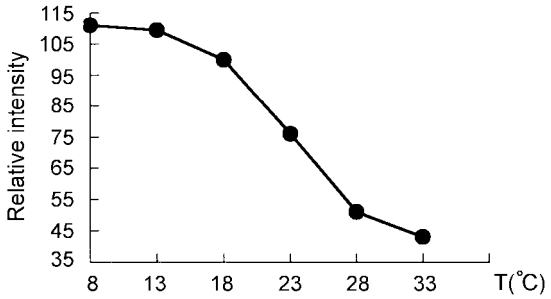

Figure 4. Dependence of RTP on temperature at pH = 2.8. [1-BrN] = 1.5×10^{-5} mol/L; [phenol] = 2.5×10^{-4} mol/L; [β-CD] = 1.0×10^{-2} mol/L; [B] = 0.7%.

in comparison with that of β-CD : 1-BrN : N : B complex, under the same experimental condition, more than eight times intensive RTP emission was observed when phenol replaced N in this experiment. It is reasonable for us to attribute this change to the formation of β-CD : 1-BrN : phenol : B inclusion complex, furthermore, the hydrogen bonding interaction between β-CD and phenol.[18]

Influence of pH on RTP. Figure 3 showed us the influence of pH on RTP of the inclusion complex. The strongest RTP emission was observed at pH = 2.8. Additionally, from Figure 1 and Figure 3, an identical result was obtained that stronger fluorescence emission was observed under higher pH value and stronger RTP emission was observed under lower pH value. And this experimental result gives a strong support to that hydrogen bonding between β-CD and phenol is a dominant cause to enhance the RTP of β-CD : 1-BrN : phenol : B inclusion complex.

Influence of temperature on RTP. Figure 4 showed us the influence of temperature on RTP of the inclusion complex. It is evident that temperature influence RTP of inclusion complex of β-CD : 1-BrN : phenol : B greatly. RTP intensity decreased remarkably with the increase of the temperature. So, all experiment had to be carried out in the temperature of 13 ± 0.2 °C.

Influence of phenol and B on fluorescence and RTP. 1-BrN is a bromosubstituted N derivative and exhibits fluorescence and weak RTP without deoxygenating in aqueous β-

CD solution due to the internal heavy atom effect. Upon addition of B to β-CD : 1-BrN complex, relatively intense RTP of 1-BrN appears because of a ternary β-CD : 1-BrN : B complex formed and B occupied more room in the cavity of β-CD that made the complex more rigid and protected 1-BrN far from the quenchers in bulk system.[13] Upon addition of phenol to β-CD : 1-BrN complex, a similar RTP phenomenon is observed, though RTP is still weak under this circumstance as shown in Figure 2. However, this implies that there is significant interaction between 1-BrN and phenol. Like B, it is possible that phenol is incorporated into the cavity together with 1-BrN and is responsible for RTP enhancement. It can be seen from Figure 2, in the presence of B, addition of phenol resulting in much more intense characteristic RTP of 1-BrN was observed. At a given phenol concentration, a similar result was obtained by addition of B to the same system. This suggests that phenol and B have significant effects on the microenvironment surrounding 1-BrN and there is also interaction between phenol and B. One plausible explanation is that complexation takes place. The β-CD : 1-BrN : phenol or β-CD : 1-BrN : B complex still has enough open space inside the cavity and this extra space can be filled by B or phenol to modify the microenvironment inside the cavity as a third component. Consequently, it is reasonable to assume that 1 : 1 : 1 : 1 β-CD : 1-BrN : phenol : B complex formed in aqueous solution in view of the dimensions of the β-CD cavity. Because additional guest molecules occupy more space inside the cavity and are more conductive to a better fit, the more rigid microenvironment provides more effective protection form quenchers for RTP. Hence, more enhanced RTP is observed. On the other hand, the interaction of hydrogen bonding between β-CD and phenol is another reason why the RTP intensity was much more stronger than that of β-CD : 1-BrN : N : B. However, it should be noted that in the present case, a higher concentration of phenol and B, such as 3.0×10^{-5} mol/L for phenol and 0.7% for B, is needed in order to form β-CD : 1-BrN : phenol : B complex in comparison with that of phenol in the β-CD : 1-BrN : phenol complex and that of B in the β-CD : 1-BrN : B complex. For example, intense RTP was observed from β-CD : 1-BrN : B when concentration of B was 0.2% in the published paper.[13] These results provide significant evidence for the formation of 1 : 2 β-CD : 1-BrN complex or β-CD : phenol complex at a higher 1-BrN or phenol concentration in the absence of the second and third components.

The analytical properties of 1-BrN. As mentioned above, the remarkable enhancement in RTP of 1-BrN in the presence of phenol and B suggests that it is of analytical interest to estimate the limits of detection for 1-BrN when direct RTP is employed. A linear relationship between RTP intensity and 1-BrN concentration was obtained in the range 0.0 to 1.0×10^{-5} mol/L for 1-BrN. Based on signal-to-noise of three, the limit of detection is calculated as 7.57×10^{-7} mol/L for 1-BrN.

Conclusion

The ability of β-CD complexation to prevent 1-BrN interaction with quenchers in aqueous solution in the presence of phenol and B has been investigated by fluorescence and RTP. Three important conclusions may be drawn from this work. Firstly, as similar as to N, phenol can also be used as a second guest like alcohol.[13] amines[15,16] and nitrile.[17] Secondly, the ability of phenol or B as a third guest to effectively modify β-CD inclusion is further explained in the presence of B or phenol. Thirdly, hydrogen bonding played an important role in the system to obtain strong enhanced RTP. The spectral information presented here seems to suggest that both phenol and B participate in the complex as the second and third guests and hydrogen bonding that significantly enhance RTP from 1-BrN.

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