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# Room Temperature Phosphorescence of 1-Bromo-4-(bromoacetyl)naphthalene Induced by Sodium Deoxycholate

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**Sodium deoxycholate (NaDOC) can induce 1-bromo-4-(bromoacetyl)naphthalene (BBAN) to undergo strong room temperature phosphorescence (RTP) without the removal of dissolved oxygen from the solution. RTP spectra, phosphorescence polarization and $^{13}C$ NMR results, along with the molecular modeling calculations, supported the conclusion that BBAN molecule was combined in a sandwich with two NaDOC molecules by a "back-to-back" hydrophobic interaction arising from the apolar faces of the NaDOC molecules, which provided BBAN with a rigid enough microenvironment to produce RTP.**

*Keywords*: Sodium deoxycholate; 1-Bromo-4-(bromoacetyl) naphthalene; Room temperature phosphorescence; Rigid environment; Polarization



## INTRODUCTION

Room temperature phosphorescence gives much more advantage over other luminescence methods, e.g. large Stokes shift, high signal-to-noise ratio, good selectivity and easily measurable luminescence lifetimes etc. [1,2], so it has been widely used in many fields, including pharmaceutical analysis, monitoring pesticide residues, studying protein structures and dynamics in conformation change as well as the interaction mechanisms of small molecule drugs with biological target molecules such as nucleic acid or proteins [3–6]. An ideal phosphorescent probe should exhibit some combination of spectroscopic and chemical properties, such as a high phosphorescence quantum yield, photochemical stability, and a reactive functional group for specific labeling of biomolecules. However, the availability of such phosphorescent probes is very limited. Turro and co-workers [7,8] have studied a series of lipophilic phosphorescent derivatives of bromonaphthoyl ketone that displayed valuable photophysical characteristics as outlined above. Bissell [9] and Brewster [10] have also described that some bromonaphthalene derivatives can emit phosphorescence with enhancement effects caused by the protection of cyclodextrin. Apart from these studies, Marriott *et al.* [11] have introduced a thiol-reactive phosphorescent probe: BBAN (Fig. 1). RTP of BBAN was studied in glycerol by purging nitrogen gas to remove the dissolved oxygen from the working solution. Herein we report the results of RTP of BBAN in sodium deoxycholate (NaDOC) aqueous solution, and it was found that NaDOC could induce BBAN to emit strong RTP without deoxygenation procedures. The resulting luminescence spectra and phosphorescence polarization indicated that NaDOC provided a rigid microenvironment for BBAN. The $^{13}C$ NMR measurements were conducted to investigate the interaction of the NaDOC media and the BBAN probe. The experimental results were combined with molecular modeling calculations to formulate a sandwich model for the NaDOC aggregate–probe complex.

## EXPERIMENTAL

### Materials

1-Bromonaphthalene, bromoacetoyl chloride, sodium deoxycholate (NaDOC, Fig. 1) and sodium taurodeoxycholate (NaTDOC, +98%), were used as received from Acros Organics Co. Aluminium chloride was purchased from Tianjin Tanggu

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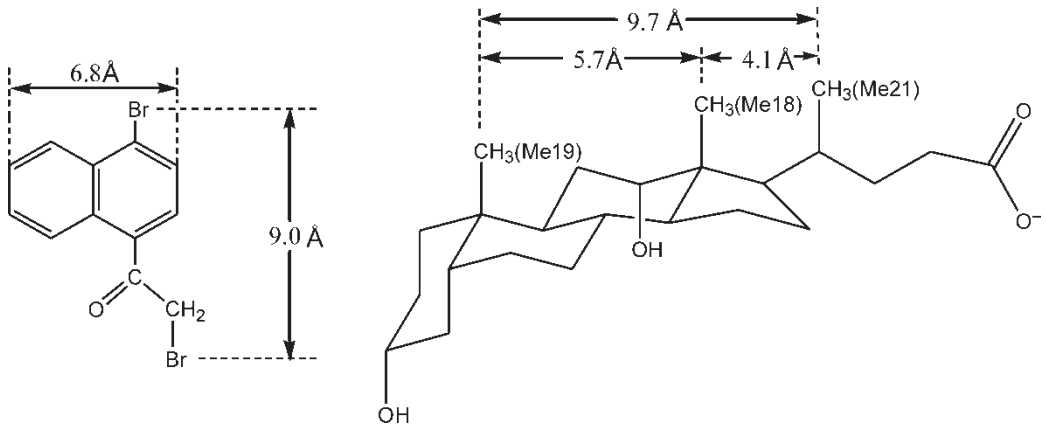


FIGURE 1 Molecular structures of BBAN probe (A) and sodium deoxycholate (B).

Dengzhong Chemical Plant. Ethanol and cyclohexane from the Second Reagent Factory of TianJin were purified by distillation. All other reagents were of analytical-reagent grade. Doubly distilled water was used for preparation of all the solutions.

### Apparatus

The $^{13}C$ NMR spectra were obtained on a DLX-300 spectrometer in $CDCl_3$ and $D_2O$, and the chemical shifts were expressed using tetramethylsilane as an internal standard. An LS-55 spectrofluorimeter (Perkin-Elmer Co.) was employed to obtain RTP spectra and polarization measurements. Molecular modeling software (CS Chem3D Version 6.0, MM2) was used to optimize the conformation of the NaDOC aggregates in the presence of BBAN.

### Procedures

An appropriate amount of BBAN ethanol solution of $2 \times 10^{-3}$ mol $L^{-1}$ was transferred into a comparison tube of 10 mL, and then a proper volume of sodium deoxycholate was added. The solutions were then allowed to equilibrate for 6 h prior to measurement.

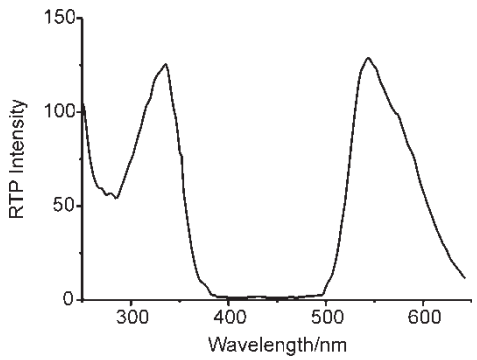


FIGURE 2 RTP spectra of BBAN in NaDOC solution (5 mmol $L^{-1}$).

### Synthesis of BBAN

The Friedel–Crafts acylation of 1-bromonaphthalene has been described in previous studies by Marriott *et al*. [11], and some modifications were made in this paper. In brief, bromoacetoyl chloride of 20 mmol was dissolved in dry dichloromethane of 20 mL at 5°C and then anhydrous aluminium chloride (20 mmol) was added to this solution in small portions with stirring at 0°C. 1-Bromonaphthalene (20 mmol) dissolved in 6 mL of cold dichloromethane was added dropwise and stirred for 30 min at 5°C followed by 2 h at 20°C. The reaction mixture was poured into HCl–ice and the product was extracted with diethyl ether. After evaporation, the residue was purified by column chromatography over silica gel (160–200 mesh) with hexane and ethyl acetate (1:1 V/V) as the eluent to remove the 1-bromonaphthalene. Recrystallization was done by using cyclohexane to produce 2 g of cream-colored BBAN crystals with a mp of 62–64°C. $^1H$ NMR (ppm) 4.53 (2H, s), 8.35 (1H, d), 8.58 (1H, d), 7.86 (1H, d), 7.74 (1H, d), 7.68 (2H, m).

## RESULTS AND DISCUSSION

### NaDOC-RTP Spectra of Phosphorescent BBAN

According to the procedures above, the spectra of BBAN were obtained without deoxygenation. The RTP spectra of BBAN ($2 \times 10^{-5}$ mol $L^{-1}$) in NaDOC are shown in Fig. 2, and the excitation and emission wavelengths used were 334 and 545 nm, respectively.

It was found that BBAN could not produce phosphorescence in a completely aqueous solution. However, sodium deoxycholate (NaDOC) induced BBAN to emit strong RTP without deoxygenation. No prompt fluorescence emission was observed for the same sample under steady-state illumination, which confirmed the previous reports [7,8] that

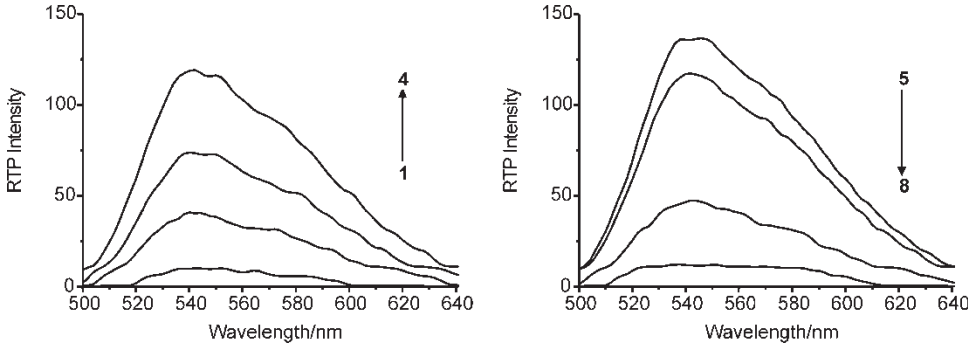


FIGURE 3 RTP spectra for BBAN (0.02 mmol $L^{-1}$) with increasing [NaDOC] values of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 mmol $L^{-1}$ corresponding to the waves numbered from 1 to 8.

the bromonaphthyl ketone group possesses an efficient intersystem crossing mechanism.

As comparative investigations, the experiments were also performed in sodium dodecyl sulfate (SDS) micelle media and NaTDC, but no RTP of BBAN without deoxygenation was observed, indicating that NaDOC provides a very rigid environment to protect the excited state of BBAN from molecular oxygen quenching, whereas the binding environment in SDS and NaDTC was more fluid.

### Effect of NaDOC Concentration on RTP Intensity

Relative RTP spectra of the BBAN probe as a function of the NaDOC concentration are shown in Fig. 3. The RTP intensity increased gradually with titration of NaDOC, and reached a maximum value when the NaDOC concentration was 5 mmol $L^{-1}$. Then, the RTP intensity dropped sharply and disappeared when the concentration of NaDOC was over 8 mmol $L^{-1}$. It is essential to provide an appropriately rigid microenvironment to ensure RTP emission in the micelle system. NaDOC is one of the most studied biological surfactants. It forms molecular aggregates in aqueous solution that are capable of solubilizing many lipid-soluble compounds. The aggregation of NaDOC has been investigated in many ways and it has been shown that NaDOC can exist as various clusters of different size containing NaDOC monomers, oligomers (dimers, trimers, tetramers, etc.), polymer-like (helical) aggregates together with nearly spherical aggregates [12,13]; aggregation in the lower concentration range resulted in the formation of oligomers. It is the "back-to-back" hydrophobic interactions among the non-polar faces of NaDOC molecules that tightly sandwiched the individual phosphorescent probe to provide a relatively isolated microenvironment to avoid quenching by water and molecular oxygen [14]; thus strong RTP signals were observed. With an increase in [NaDOC], the equilibrium shifted toward micelles of larger aggregation numbers, and a new type of aggregation might occur through exposed hydrophobic parts of these aggregates. However, the larger and looser helical aggregates of NaDOC are less rigid so that the phosphorescence decreased owing to lower protection from quenching. The concentration at the transition point of the RTP intensity of BBAN was consistent with the critical micelle concentration (CMC) of NaDOC (6.4 mmol $L^{-1}$) [14], indicating the changes that occur in the microenvironment in NaDOC solution.

### RTP Stability

The stability of phosphorescence was tested over a period of 9 h, and the corresponding results are shown in Fig. 4.

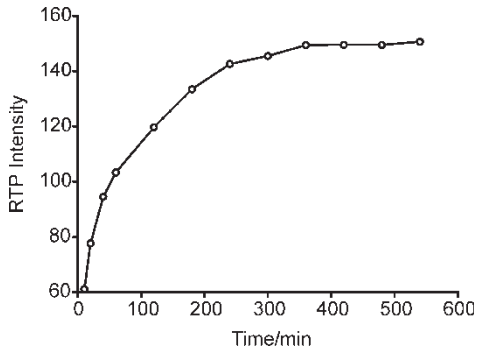


FIGURE 4 RTP intensity at different times.

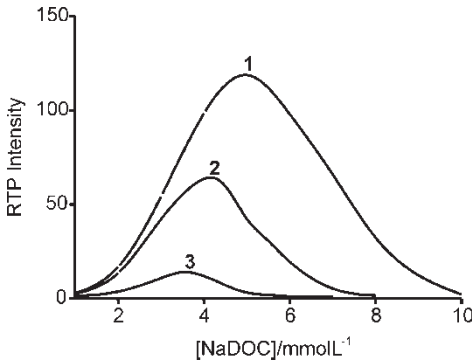


FIGURE 5 RTP spectra for a 0.02 mM solution of BBAN in the presence of NaCl; [NaCl] = 10, 20, 30 mmol $L^{-1}$ (curves 1 to 3).

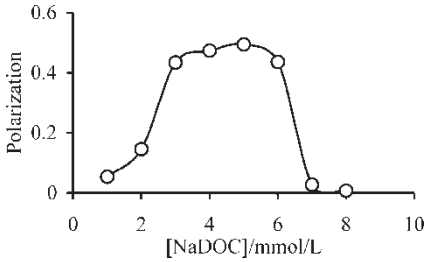


FIGURE 6 Effect of varying the concentrations of NaDOC on the phosphorescence polarization of BBAN ($2 \times 10^{-5}$ mol $L^{-1}$).

The experiments showed that the phosphorescence intensity of BBAN in NaDOC increased on standing, and no significant change was observed after 6 h, which might indicate that the interaction might have reached a stable and rigid state after a relatively slow process between the probe molecules and NaDOC aggregates. As the binding interaction of the probe molecules and NaDOC might be weakly non-convalent forces (including hydrophobic forces, Van der Waals forces and probably hydrogen bonding), the whole adjustment process between the probe and the stabilizing medium leading to the optimal conformation could take quite a long time, which would seem to be about 6 h from our results. Moreover, as for the reactive bromoacetyl group of BBAN and NaDOC, we thought it possible that there might be some reactions that could be useful in the synthesis and organization of imitative biomembrane-conjugating phosphorescent probes. This work is still being carried out in our laboratory. However, no signals indicating any reaction could be observed under our present experimental conditions.



## Effect of NaCl on RTP

Metal cations are known to enhance the aggregation of bile salts and lower their CMC values [15]. Figure 5 shows that the RTP intensities obviously decreased with an increasing concentration of NaCl, and the concentration of NaDOC corresponding to the highest RTP intensity decreased, which further indicated that the presence of NaCl might lower the CMC of NaDOC, speed up the aggregation process and increase the size of the aggregates.

## Measurement of RTP Polarization

Phosphorescence signals can usually be observed only under the conditions of a rigid medium and with the removal of dissolved oxygen, but BBAN produced RTP in NaDOC aqueous solution without deoxygenation. The RTP intensity and phosphorescence polarization of BBAN changed with an increase in the concentration of NaDOC. Figure 6 shows that the phosphorescence polarization values decreased sharply when the NaDOC concentration was over its CMC of 6.4 mmol $L^{-1}$, indicating a change in the microenvironment of the phosphorescent probe. Above the CMC, the microenvironment rigidity of the BBAN molecules in NaDOC system decreased, leading to a decrease in the RTP intensity.

## NMR Measurements

The binding interaction of BBAN and NaDOC (4 mmol $L^{-1}$) was also examined using $^{13}C$ NMR spectroscopy. When BBAN was added, the Me18 and Me19 signals were most affected by the solubilized

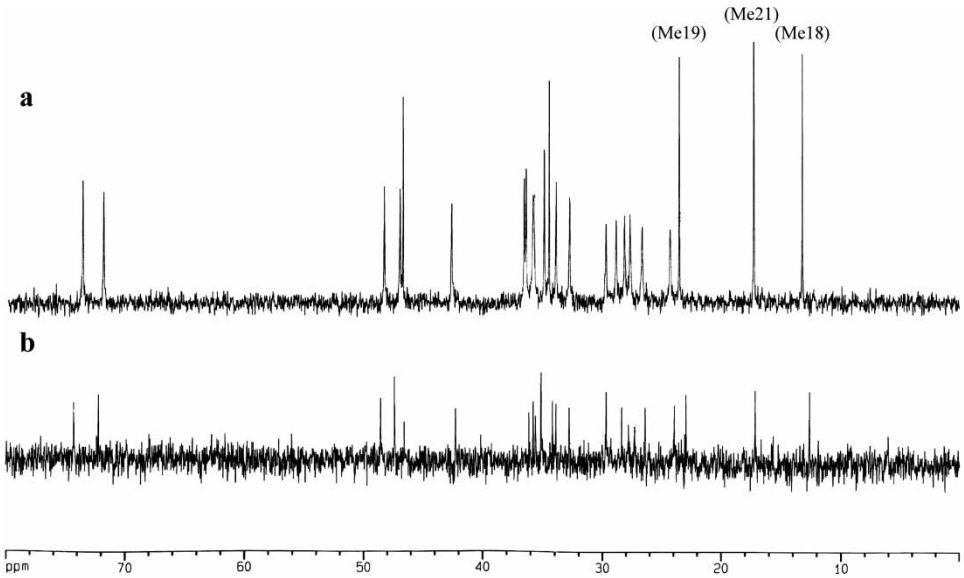


FIGURE 7 $^{13}C$ NMR spectral changes of NaDOC (4 mmol $L^{-1}$) without BBAN (a) and in the presence of $2 \times 10^{-5}$ mol $L^{-1}$ BBAN (b) in $D_2O$ at 298 K.

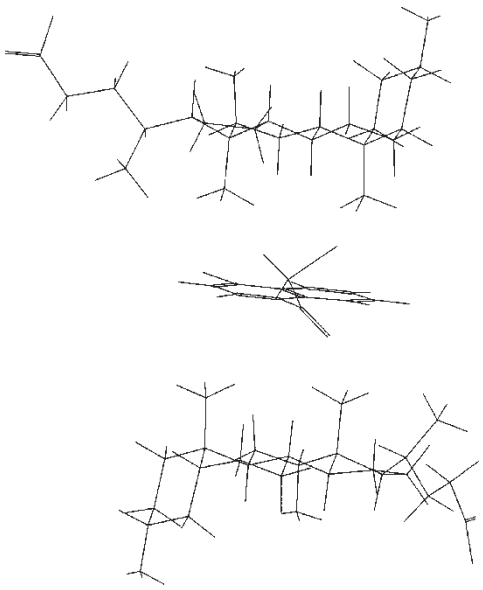

FIGURE 8 Sandwich model for BBAN solubilized in an NaDOC dimer.

BBAN, and underwent a significant upfield shift by 0.6 and 0.65 ppm, as shown in Fig. 7. The results support the previous report that through "back-to-back" hydrophobic interactions arising from the nonpolar faces of the NaDOC molecules, the individual phosphorescent probes were tightly inserted between the bulky hydrophobic bile salt surfaces [14].

### Molecular Modeling Study

Using molecular modeling methods, it was possible to estimate the size of the NaDOC aggregates and propose reasonable structures for the probe–NaDOC complexes. The molecular structures of the BBAN probe and NaDOC monomer are shown in Fig. 1. On the basis of the experimental results and the molecular modeling studies, a "sandwich" dimer model for BBAN in NaDOC was proposed, and the optimal conformation is illustrated in Fig. 8 where BBAN is sandwiched between two NaDOC monomers. The aromatic ring surface is just covered by the two monomers and is fairly well protected from the bulk aqueous solution. This would account for the experimental observation that BBAN emits strong RTP without deoxygenation. In this model, the methyl groups and the hydrogen atoms on the hydrophobic surface of the NaDOC molecule become involved in the hydrophobic interaction with the probe. Therefore, the NaDOC molecule is slightly distorted to achieve maximal contact with the BBAN molecule. This model is supported by NMR studies, which showed that C18 and C19 of the methyl groups in the NaDOC molecule (Fig. 1B) are most affected by the solubilized BBAN.

## CONCLUSION

Our experimental results demonstrate that NaDOC can effectively induce the RTP of BBAN without the removal of dissolved oxygen from the solution. This observation shows that the interior structure of the NaDOC aggregate is rigid and also efficient in shielding the excited state of BBAN from oxygen quenching. The results have been interpreted in terms of a model in which the basic unit is a sandwich complex of BBAN in an NaDOC dimer.

### *Acknowledgements*

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