Chinese Chemical Letters Vol. 15, No. 3, pp 339-342, 2004
http://www.imm.ac.cn/journal/ccl.html

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

Yu WANG, Wei Jun JIN*, Jian Bing CHAO, Li Ping QIN

Department of Chemistry, Shanxi University, Taiyuan 030006

Abstract: Sodium deoxycholate (NaDOC) could induce 1-bromo-4-(bromoacetyl) naphthalene (BBAN) to emit strong room temperature phosphorescence (RTP). Measurements of phosphorescence spectra, peak intensity and polarization were used to investigate the solubilization of BBAN as a function of NaDOC concentration.

Keywords: Sodium deoxycholate, 1-bromo-4-(bromoacetyl) naphthalene, room temperature phosphorescence.

Room temperature phosphorimetry has 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 such as pharmaceutical analysis, monitoring pesticide residue, studying the protein structure and dynamics in conformation change as well as interaction mechanism of small molecule drugs with biological target molecules such as nucleic acid, protein and so on[3-6]. An ideal phosphorescent probe should exhibit some combination of spectroscopic and chemical properties, such as high quantum yield and photochemical stability, reactive functional groups for specific labeling of biomolecules *etc.*. However, the availability of such phosphorescent probe was very limited. Turro and co-workers[7,8] studied a series of lipophilic phosphorescent derivatives of bromonaphthoyl ketone that displayed many photophysical characteristics as outlined above. According to those earlier studies, Marriott *et. al.*[9] introduced a thiol-reactive phosphorescent probe--BBAN, and RTP of BBAN was studied in glycecol by purging nitrogen to remove the dissolved oxygen from the solution. Herein we reported the RTP spectra of BBAN in aqueous solution of NaDOC, whose structure was shown in **Figure 1**. It was found that NaDOC could induce RTP of BBAN without deoxygenation, and polarization results further suggested that NaDOC provided a rigid enough microenvironment for the phosphor.

Experimental

1-Bromonaphthalene, bromoacetyl chloride, and sodium deoxycholate (NaDOC) were purchased from Acros Organics Co.. Aluminum chloride was from Tianjin Tanggu Dengzhong Chemical Plant. Ethanol (analytical reagent purchased from Tianjin Second

* E-mail: wjj1959@yahoo.com

Reagent Factory) was purified by distillation. All Other reagents were of analytical purity. Water was doubly distilled in a subboiling distiller.

The NMR spectra were measured on a DLX-300 spectrometer in $CDCl_3$. The chemical shifts were expressed using tetramethylsilane as an internal standard. The RTP spectra were collected with a LS-50B spectrofluorimeter (Perkin-Elemer Co.).

Procedure

The appropriate amount of ethanol solution of BBAN (2×10^{-3} mol/L) was transferred into a comparison tube of 10 mL, and then a proper volume of deoxycholate was added. The solutions were thoroughly mixed and placed for 6 h *prior to* measurement.

Synthesis of BBAN

The Friedel-Crafts acylation of 1-bromonaphathecene has been described previously[9]. Some modifications were made in this paper. Briefly, the reaction mixture was poured into HCl-ice and the product was extracted with ether. After evaporation, the product was purified by column chromatography over silica gel (160-200 mesh) by using hexane and ethyl acetate (1:1 V/V) as the eluent. The cream-colored BBAN crystal was recrystallized from cyclohexane. m.p. 62~64℃; ^{1}HNMR 4.53 ppm (s, 2H), 8.35(d, 1H, J=9.73 Hz) 8.58(d, 1H, J=9.76 Hz), 7.86(d, 1H, J=7.81 Hz), 7.74(d, 1H, J=7.81 Hz), 7.68(m, 2H, J=9.77 Hz).

Results and Discussion

NaDOC-RTP spectra of phosphorescent BBAN

According to the procedure above, RTP spectra of BBAN were obtained without deoxygenation and were shown in **Figure 2** for BBAN of 2×10^{-5}mol/L in NaDOC of 5 mmol/L.

Figure 1 Structure of NaDOC

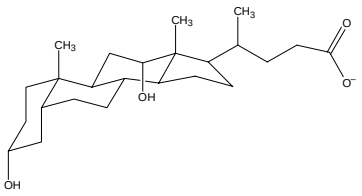
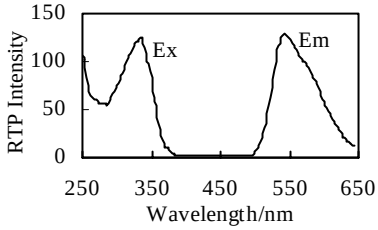


Figure 2 The RTP spectra of BBAN in NaDOC



BBAN could not produce phosphorescence in fully aqueous solution. Here sodium deoxycholate (NaDOC) induced BBAN to emit strong phosphorescence without deoxy- genation. No prompt fluorescence emission was observed for the same sample under steady-state illumination, which was confirmed by the previous reports[7,8] that the bromo- naphthyl ketone group possessed an efficient intersystem-crossing mechanism.

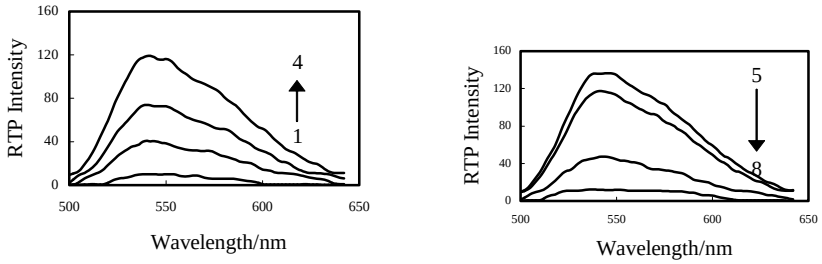
The experiments were also performed in sodium dodecyl sulfate (SDS) and sodium taurodeoxycholate (NaTDC), but no RTP of BBAN was observed without the removal of

oxygen, indicating that BBAN indeed dwelt in a much looser microenvironment than the rigid one that NaDOC provided.

Effect of NaDOC concentration on RTP spectra

Relative RTP spectra of BBAN as a function of NaDOC concentration were shown in **Figure 3**. The RTP intensities of BBAN increased gradually with the titration of NaDOC, and reached the maximum value when [NaDOC] was 5 mmol/L. Then, RTP intensity dropped sharply and disappeared when [NaDOC] was over 8 mmol/L.

Figure 3 RTP spectra for BBAN of 0.02 mmol/L with the increasing [NaDOC] of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 mmol/L



It was essential to provide an appropriate rigid microenvironment to ensure RTP emission in the micelle system. NaDOC was one of the most studied biological surfactants. It formed molecular aggregates in aqueous solution capable of solubilizing many water insoluble compounds. The aggregation of NaDOC had been investigated in many ways. It was pointed out that for NaDOC there existed various clusters of different size inclusive of NaDOC monomers, oligomers (dimmers, trimers, tetramers…), polymer-like (helical) aggregates and nearly spherical aggregates as a funtion of [NaDOC][10,11]. Among nonpolar faces of the NaDOC molecules, the individual phosphorescent probe was tightly sandwiched through "back-to-back" hydrophobic interactions, which protected it from quenching owing to water and molecular oxygen and made RTP signals stronger. With the increase of [NaDOC], the equilibrium was shifted toward micelles of larger aggregation number, and a new type of aggregation might occur through exposing hydrophilic parts of these aggregates. However, the larger and looser helical aggregates of NaDOC were less rigid so that the phosphorescence of BBAN decreased owing to the less protection. The concentration at the transition point of RTP intensity was consistent with the CMC of NaDOC (6.4 mmol/L)[12], indicating that the microenvironment of NaDOC solution was changed (**Figure 5**).

Effect of NaCl on RTP

Metal ions are known to speed the aggregation of bile salts and lower their critical micelle concentration (CMC) values. **Figure 4** showed that RTP intensities obviously decreased with the increase of [NaCl] and [NaDOC] corresponding to the highest RTP

intensity was descending, which indicated that NaCl might lower the CMC of NaDOC, speed the aggregation process and increase the size of the aggregates.

Measurement of phosphorescence polarization

Usually RTP signals could be observed only in a rigid medium devoid of oxygen, and BBAN emitted RTP in NaDOC aqueous solution without deoxygenation. **Figure 5** showed that RTP polarization values decreased sharply when the NaDOC was over CMC (6.4 mmol/L), indicating the change of microenvironment of phosphorescent probe. Over CMC, the microenvironment rigidity of NaDOC decreased so much that the RTP intensity decreased.

Figure 4 Effect of NaCl on RTP spectra for BBAN (0.02mmol/L) with the increasing [NaCl] of 0, 10, 30 mmol/L from 1 to 3.

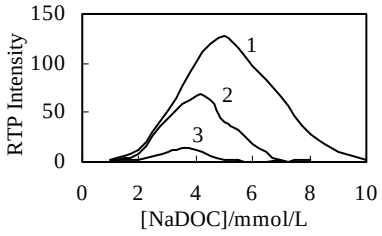
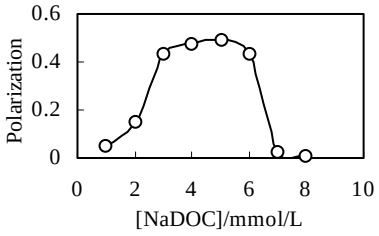


Figure 5 Effect of the concentration of NaDOC on RTP polarization of BBAN (2×10^{-5}mol/L)



Acknowledgment

This work was financially supported by the National Natural Science Foundation of China and the Youth Foundation of Shanxi province (China).

References

1. T. Vo-Dihn, *Room Temperature Phosphorimetry for chemical Analysis*, Wiley/Interscience, New York, **1984**.
2. A. Sanz-Medel, *Anal. Chim. Acta*, **1993**, *283*, 367.
3. A. S. Carretero, C. C. Blanco, B.C. Diaz, *et. al.*, *Talanta*, **1999**, *50*, 401.
4. L. F. Capitan-Vallvey, M. D. Fernandez Romos, R. Avidad, *et. al.*, *Anal. Chim. Acta*., **2001**, *440*, 131.
5. W. J. Jin, C. S. Liu, *Anal. Chem.*, **1993**, *65*, 863.
6. W. Yuan, W. J. Jin, C. Dong, *Chem. J. Chin. Univ.*, **2001**, *22*, 922.
7. J. D. Bolt, N. J. Turro, *Photochem. Photobiol*, **1982**, *5*, 305.
8. N. J. Turro, T. Okubo, C. J. Chung, *J. Am. Chem. Soc*., **1982**, *104*, 1789.
9. G. Merriott, T. M. Jovin, Y. Y. Marriott, *Anal. Chem*., **1994**, *66*, 1490.
10. G. Conte, R. Di Blasi, E. Giglio, A. Parretta, *et. al.*, *J. Phys. Chem.*, **1984**, *88*, 5720.
11. Y. B. Jiang, J. S. Hu, J. G. Xu, *Chem. J. Chin. Univ.*, **1993**, *14*, 966.
12. J. M. Roe, B. W. Barry, *J. Collid and Interface Science*, **1985**,*107*, 398.

Received 5 March, 2003