Room Temperature Phosphorescence pH Switch
Based on Photo-induced Electron Transfer

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Abstract: In this paper, photoinduced electron transfer(PET) phosphoroionophore, N-(1-bromo-2-naphthylmethyl)-diethanolamine (BND) was synthesized and its phosphorescent characteristics were studied. The experimental results showed that strong phosphorescence could be observed in β-cyclodextrin aqueous solution only at low pH value. This system combined AND and NOT function to produce a three-input inhibit (INH) logic gate.

Keywords: Room temperature phosphorescence, pH switch, photoinduced electron transfer, N-(1-bromo-2-naphthylmethyl)diethanolamine, β-cyclodextrin, logic gate.

As an important aspect in supramolecular chemistry, the design of photoresponsive sensors and switches has gained increasing interests and has been developed rapidly over the past decades[1,2]. With high sensitivity and convenience, fluorescence was often used to design optical sensors and switches for protons, such as fluorescence PET proton switches[3-5], pH sensors[6,7], logic gates[8,9] and so on. It is noteworthy that room temperature phosphorescence (RTP) has many advantages over fluorescence, *e.g.*, large Stokes shift, higher signal to noise ratio, good selectivity and easily measurable luminescence lifetimes[10] *etc.*, and it can be found as a helpful complementary method of fluorescence sensing. However, there are few reports dealing with the applications of phosphorescence in this field. Herein we investigated a room temperature phosphorescence pH switch based on PET, and it was found that the system exhibited a logic function of inhibit.

Experimental

Reagents and apparatus

1-Bromo-2-methylnaphthalene, N-bromosuccinimide, benzoylperoxide, diethanol -amine were purchased from Acros Organics Co.. Quinine bisulfate was the product of Shanghai Second Reagent Factory. β-Cyclodextrin, obtained from Guangdong Yunan Huanhujing Factory, was recrystallised from boiling water and then washed with ethanol. 1-Bromo-2-bromomethylnaphthalene (BBMN) was synthesized according to the

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literature[11].   All other reagents were of analytical grade.

NMR spectra were measured on a DLX-300 spectrometer in CDCl$_3$ and the chemical shifts were expressed using tetramethylsilane as an internal standard.   Mass spectra were measured on a PolarisQ GC-MS spectrometer.   The UV-2602 spectro- photometer was from Shanghai Unico Co., and RTP spectra were carried out with a LS-55 spectrofluorimeter from Perkin-Elemer Co..   The excitation and emission slits were set at 10 nm and 15 nm, respectively, and the gate time and the delay time were 2 ms and 0.1 ms.

Synthesis of BND

To 50 mL of CHCl$_3$ were added 3.1 g of 1-bromo-2-bromomethylnaphthalene, 4 mL of diethanolamine and 1.4 g of K$_2$CO$_3$.   After stirring for 6 hrs at room temperature, the reaction mixture was washed thrice with water.   The organic layer was dried over anhydrous MgSO$_4$, followed by the evaporation of the solvent in vacuum.   The crude product was recrystallized from carbon tetrachloride as white crystals (BND).   M.p. 65-66   MS *m/z* 324(M+1) ^{1}HNMR δ_H(CDCl$_3$,ppm) 7.46-8.31(m,6H,Ar), 4.03(s,2H, ArCH$_2$), 3.61(t,4H,J=5.489Hz,CH$_2$O), 2.77(t,4H,J=5.489Hz,NCH$_2$CH$_2$O), 2.5(s,2H, OH)

An aliquot portion of the stock solution of BND, appropriate volume of acid, base and β-cyclodextrin solution were in turn pipetted into 10 mL comparison tube.   After dilution to its final volume with water, the system was shaken thoroughly for homogeneity.   The prepared sample was transferred to a quartz cuvette and deoxy- genated by bubbling high purity nitrogen for 2 minutes *prior to* phosphorescence measurement.   Phosphorescence quantum yield was determined with the standard value of 0.55 at the excitation wavelength of 313 nm[12,13] for quinine bisulfate in 0.05 mol/L H$_2$SO$_4$.

Results and Discussion

Luminescence excitation and emission wavelength

Based on the procedures above, RTP spectra were obtained with the excitation and emission wavelengths of 288 nm and 533 nm, respectively.   Under the same condition, the phosphorescence intensity of BND was weaker than that of 1-bromo-2-methyl-naphthalene due to PET process from amine to phosphor, occurring in BND.

Effect of pH on phosphorescence emission

The effect of pH on RTP intensity was investigated and pH was adjusted by adding appropriate volume of trihydroxymethyl aminomethane and H$_2$SO$_4$.   As shown in **Figure 1**, when the pH value increased, the phosphorescence of BND was quenched gradually because the PET process was thermodynamically favored from the teriary amine to the excited chromophore(*naph).   And under acid condition, the oxidation potential of the phosphor was raised with the protonation process of its tertiary amine part, so PET process was inhibited and phosphorescence survived.   At pH 3.44, RTP reached the maximum.

Figure 1 RTP spectra (a) of BND in β-CD aqueous solution under different acidities
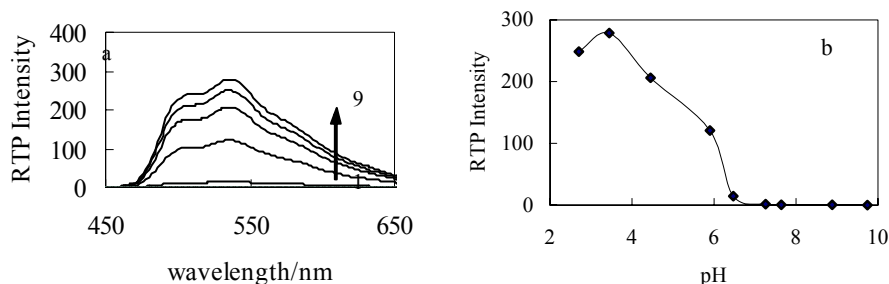
[BND] was 1.0×10^{-5} mol/L and [β-CD] was 8×10^{-3} mol/L. From 1 to 9, pH values were 9.47, 8.88, 7.64, 7.26, 6.47, 5.90, 4.45, 2.70, 3.44, respectively

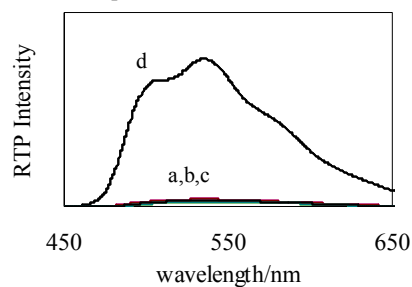**Table 1** Phosphorescence quantum yield of BND at different pH values

pH	11.60	10.22	9.74	8.88	7.64	7.26
Quantum yield	0	0	0	0.0002	0.0003	0.0056
pH	6.47	5.90	4.45	3.84	3.44	2.70
Quantum yield	0.0071	0.0676	0.1201	0.1290	0.1671	0.1332

However, at lower pH RTP intensity slightly decreased, which could be probably attributed to increase of solubility of phosphor from β-CD cavity to water bulk after strong protonation. Besides, RTP quantum yield of BND under different acidities were listed in **Table 1**, under basic condition the quantum yields were near to zero due to the process of PET while under acid condition the quantum yield increased and reached the maximum value at pH 3.4. That is, RTP intensity in this system fell in two reverse states of ON-OFF by adjusting acidity. The experimental results further indicated that BND could be used as a phosphorescent pH switching.

Logic gate function of BND

The logic gate function of BND was also investigated. Oxygen, proton, and β-CD could be regarded as three inputs and RTP emission as one output, respectively. It was only when H^+ and β-CD were simultaneously present in the condition of deoxygenation that strong phosphorescence was generated as shown in **Figure 2**. The PET quenching process was blocked by H^+ and β-CD inputs with dioxygen as a third input that disabled the device, *i.e.* the compound was basically an AND gate with a third input inverted through a NOT function(**Table 2**). So it was obvious that RTP characteristics of BND under different input conditions was suitable to act as logic gates of INH, which might have potential implication to molecular computation[14].

Figure 2   Phosphorescence spectra of BND after deaeration under different input conditions.

a: blank; b: H⁺; c: β-CD; d: H⁺and β-CD

Table 2   The truth table of BND

IN₁ (H⁺)	IN₂ (β-CD)	IN₃ (O₂)	OUT (λₑₘ=533nm)
0	0	0	0
0	1	0	0
1	0	0	0
1	1	0	1
0	0	1	0
0	1	1	0
1	0	1	0
1	1	1	0

This digit is coded by the transmitted light intensity output at 533 nm when high (1) or low (0).

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