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Intramolecular Charge Transfer Dual Fluorescence pH Sensing using *p*-Dibutylaminobenzoic Acid-b-cyclodextrin Inclusion Complex

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Abstract: The intramolecular charge transfer dual fluorescence of *p*-dibutylaminobenzoic acid-β-cyclodextrin inclusion complex showed a substantially higher sensitivity toward aqueous solution pH variation when compared with that of *p*-dibutylaminobenzoic acid alone, which established a new principle for direct CT fluorescence sensing in aqueous solution by using the CT fluorophore-cyclodextrin inclusion complex.

Keywords: pH sensing, dual fluorescence, intramolecular charge transfer, cyclodextrin inclusion complex, *p*-dibutylaminobenzoic acid.

It has been well known that the intramolecular charge transfer (CT) dual fluorescence of electron donor/acceptor *para*-substituted benzenes, such as *p*-dimethylaminobenzonitrile (DMABN), shows extremely high sensitivity towards the variations in the electron donating and/or accepting ability of the electron donor/acceptor and the solvent polarity change[1]. This makes the CT fluorophores important candidates for constructing fluorescent chemosensors. Directly employing the CT fluorescence for aqueous phase sensing, however, is not straightforward, since a serious problem arises from that the CT emission is heavily quenched by water molecules. Actually the CT fluorescence sensing so far has been mainly carried out in organic phase[2, 3], whereas that in aqueous phase has been limited[4, 5]. Ueno *et al.* [5] have reported a series of nice works on CT dual fluorescence sensing in aqueous solutions by attaching the CT fluorophore at the rim of cyclodextrin (CD). In that modified CD, the CT fluorophore stays in the non-polar CD cavity in the absence of analyte and is forced to protrude into the bulk aqueous phase when the analyte is present, thereby experiencing changed polarity and, as a consequence, showing varied CT dual fluorescence. Herein reported is an alternative strategy for direct CT fluorescence sensing in aqueous solution by using the CT fluorophore-cyclodextrin inclusion complex as the sensing species.

In our work on the CT of *p*-dialkylaminobenzoic acids in aqueous β-CD solution, we observed an enhanced CT emission when the fluorophore was included in the CD cavity. The observation of a positive correlation between the binding constant of the CT fluorophore-β-CD inclusion complex and the size of the alkyl substituent suggested

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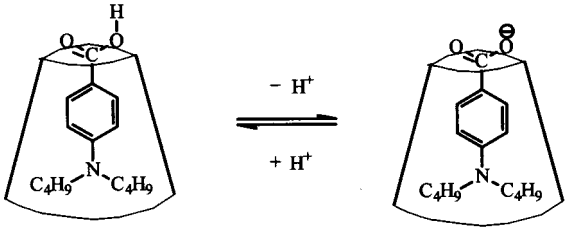
that in the *p*-dialkylaminobenzoic acid-β-CD inclusion complex the *N*, *N*-dialkylanilino moiety was included in the CD cavity while the carboxylic group pointed towards the aqueous phase. This promoted our decision to establish an alternative strategy for constructing aqueous solution CT dual fluorescence chemosensor by using the CT fluorophore-cyclodextrin inclusion complex. It was understood that in strongly bonded inclusion complex the CT fluorophore was afforded for a hydrophobic CD cavity microenvironment and therefore emitted CT fluorescence in aqueous solution, while its receptor site remained in the aqueous phase. The principle for this construction will be now described in this letter, for which the *p*-dibutylaminobenzoic acid-β-cyclodextrin inclusion complex was chosen for dual fluorescence pH sensing. The highly hydrophobic butyl sunstituents ensured a strong binding of the CT fluorophore toward the CD cavity while the carboxylic group protruding into the aqueous phase offered the possibility for pH sensing **(Scheme 1)**.

Scheme 1



We have shown that the binding constant of *p*-dialkylaminobenzoic acid with β-CD increased from 350 mol^{-1} L for *p*-dimethylaminobenzoic acid (DMABOA), through 2700 mol^{-1}L for *p*-diethylaminobenzoic acid (DEABOA), to 5750 mol^{-1}L for *p*-dibutylaminobenzoic acid (DBABOA), and further increasing of the alkyl substituent size did not strengthen very much the binding. Thus two butyl substituents were considered to be good enough for a strong binding and to require as low as possible CD concentration for a saturated inclusion. In aqueous solution without β-CD, the CT dual fluorescence of DBABOA, as expected, was heavily quenched (**Figure 1a**). Although the emission showed weak response toward solution pH variation, the changes in both the total intensity and the dual fluorescence intensity ratio were very minor (**Figure 2**). In the presence of 1.0×10^{-3} mol L^{-1} of β-CD, however, the CT fluorescence was substantially enhanced and blue shifted that reflected the inclusion of the CT fluorophore in the non-polar CD cavity (**Figure 1b**). It was found that the CT dual fluorescence of the DBABOA-β-CD inclusion complex showed greatly enhanced sensitivity toward pH variations, which could be seen clearly in **Figure 2**. It should be pointed out that in aqueous solution without β-CD the fluorescence emission of DBABOA was very weak, the measurements of both the total fluorescence intensity and the CT to LE (the locally excited state) intensity ratio were therefore with high uncertainty. As the fluorescence in DBABOA-β-CD inclusion complex was greatly enhanced, using the inclusion complex as the sensing species also ensured better analytical performance.

Figure 1 Corrected fluorescence spectra of DBABOA in solutions of varying pH in the absence (a) and presence (b) of $1.0x10^{-3}$ mol L^{-1} β-CD. The excitation wavelength was 290nm.

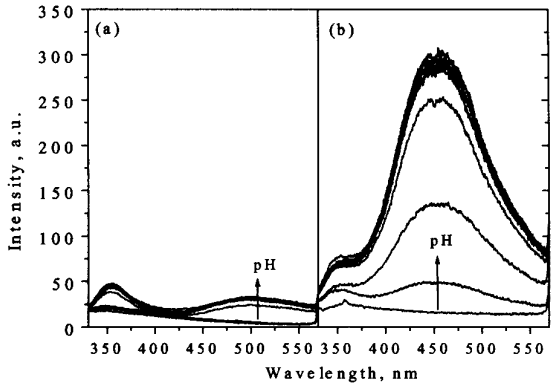
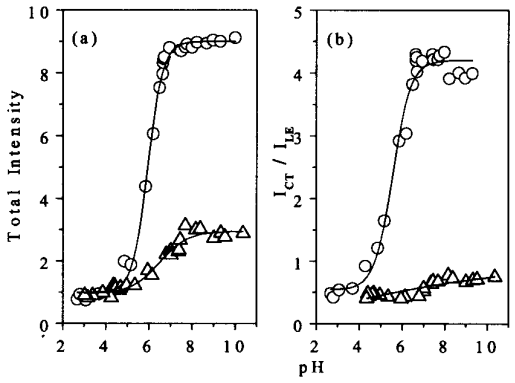


Figure 2 pH titration curves for the CT dual fluorescence of DBABOA and DBABOA-β-CD systems. [β-CD] = $1.0x10^{-3}$ mol L^{-1}.



It was found from **Figure 2** that the sensing occurred over pH range of *ca*.4.5 to 6.5 at around the pK_a of the acid (pK_a for DMABOA, 5.0)[6], both in the presence and absence of β-CD. This means that on one hand the sensing is due to the acid dissociation and on the other hand that the carboxylic group stays in aqueous phase. It should also be noted that while the intensity and the CT to LE intensity ratio of DBABOA in cyclodextrin solution showed substantial enhancements at pH around the pK_a there was no change in the CT emission wavelength. This means that at higher pH when DMABOA may exist in its anionic form the inclusion complex remained undestroyed. We therefore confirmed the new CT fluorescence sensing principle by using the CT fluorophore-cyclodextrin inclusion complex that ensures both enhanced CT emission and accessible

receptor for sensing event to occur. As the CT to LE intensity ratio can be employed as the sensing index (**Figure 2b**) a ratiometric assay was established.

Based on this principle it is believed that new CT dual fluorescence molecular recognition systems could be developed if suitable receptors are attached to the CT fluorophore. We are currently working within this framework.

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