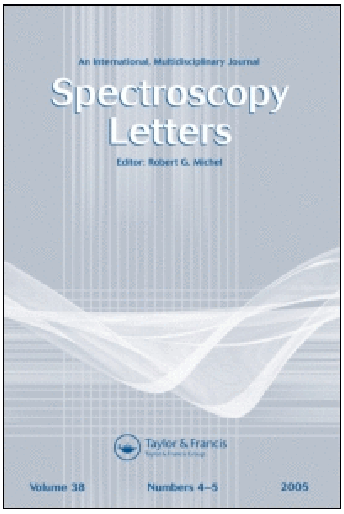

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A Novel Fluorescence Sensing Mode for Ions and Neutral Molecules Based on Ionic Micelle Mediated TICT Dual Fluorescence

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A Novel Fluorescence Sensing Mode for Ions and Neutral Molecules Based on Ionic Micelle Mediated TICT Dual Fluorescence

Keywords: Fluorescence sensing; TICT; Dual fluorescence; Ionic micelle mediation; Micelle interface electric field

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Abstract: According to the high sensitivity of TICT (twisted intramolecular charge transfer) emission to external electric field strength, a novel fluorescence sensing mode for ions and neutral molecules in aqueous solution was proposed by using ionic micelle mediated TICT dual fluorescence was proposed. In the sensing system the ionic micelle acts as electric field mediator for the TICT fluorophore. Examples were given for sensing potassium nitrate, sodium dodecylsulfate, and β-cyclodextrin by using sodium p-diethylaminobenzoate(SDEAB)/cetyltrimethylammoinum bromide(CTAB) micelle sensing system. Linear response of dual fluorescence intensity ratio Ia/Ib to analyte concentration with correlation coefficient higher than 0.99 was observed for three analytes.

Photoinduced twisted intramolecular charge transfer(TICT) state involves a complete charge separation [1], its dipole moment is thus much higher than that of ground state. As a consequent, the formation and emission of TICT state show a strong dependence on the strength of exerted electric field [2, 3]. Such a dependence would imply a potential application in fluorescence sensing, although there has been practically no such report in literature. We believe that the key point in employing this dependence in fluorescence sensing is to look for an electric field "mediator". Herein we report our first attempt to use this dependence in establishing a novel fluorescence sensing mode.

Based on previous work on the TICT in micelle from this laboratory[4-6], we propose that ionic micelle can be taken as the required electric field mediator. It is well established that there is net charge at ionic micelle interface. Thus the solubilized fluorophore looks like that it is in an electric field. Results have shown that the fluorescence intensity ratio of TICT typical dual fluorescence, Ia/Ib, serves as an indicating index for the strength of micelle interface electric field [4-6] Meanwhile, the high viscosity of micelle core makes it possible to anchor the solubilized fluorophore in micelle, allowing for a fixed mutual orientation of emission transition moment of fluorophore to micelle interface electric field. Therefore ionic micelle could serve as a good candidate for the electric field mediator. Through interacting with micelle and in turn altering the strength of electric field at micelle interface, both ions and neutral molecules in solution will be sensed by the TICT fluorescence.

Experimental

Sodium p-dimethylaminobenzoate (SDMAB) was prepared from p-dimethylaminobenzoic acid (DMABOA) which was synthesized from paminobenzoic acid (ABA) as described elsewhere [3-6]. Sodium p-diethylaminobenzoate (SDEAB) was synthesized by stirring ABA in ethyl iodide (distilled before use), followed by alkaline hydrolysis. The crude product was twice recrystallized from 95% ethanol. Cetyltrimethylammonium bromide (CTAB, an AR reagent from Shanghai the First Chemicals) was used after recrystallized from absolute ethanol. Potassium nitrate was a newly opened GR reagent from Shanghai the First Chemicals. Sodium dodecylsulfate (SDS) from Serva and β-cyclodextrin (β-CD) from Fluka were used as received. Water was twice deionized. Fluorescence spectra were recorded on either Shimadzu RF-5000 (output uncorrected spectrum) or Hitachi F-4500 (output corrected spectrum) fluorescence spectrophotometer.

Results and Discussion

Theoretically, the fluorescence intensity, I, depends on the external electric field strength, E, according to equation (1) [2, 3]:

$$I = I_0 (1 + K \bullet E^2) \qquad (1)$$

where I_0 is fluorescence intensity at zero electric field, K is a constant depending on mutual orientation of emission transition moment of fluorophore versus external electric field and the difference between the dipole moment of excited state and that of ground state, larger difference leading to a higher K value. Thus on employing an ionic micelle to establish a more sensitive TICT sensing system, one should choose a TICT fluorophore with a higher TICT state dipole moment and a relatively fixed orientation to micelle interface electric filed. Based on the characteristics of interaction of solubilized molecule with micelle, i.e. hydrophobic and electrostatic [4], one can empirically select a TICT fluorophore holding opposite charge to micelle interface, allowing for a strong association of fluorophore with micelle.

As an example, the cationic CTAB micelle as electric field mediator and SDMAB and SDEAB as TICT fluorophores were examined by TICT typical dual fluorescence. Figure 1 presents curves of intensity ratio of TICT emission band to LE band, Ia/Ib [4, 5], of SDMAB and SDEAB, versus CTAB concentration in aqueous solution. It is observed that for both TICT fluorophores the variations are "S"-shaped with break point at the same position corresponding to critical micelle concentration (CMC) of CTAB. It is important to noted that the Ia/Ib ratio is independent of the CTAB concentration both before and after micelle formation. Thus the Ia/Ib ratios in these two regions represent those of SDMAB or SDEAB in aqueous and micellar phases, respectively. The leveling of Ia/Ib after micelle formation indicates that Ia/Ib ratio of TICT fluorophore does not depend on micelle concentration and/or the amount of fluorophore that is solubilized in micellar phase.

It is obvious as shown in Figure 1 that Ia/Ib ratio of SDEAB is higher than that of SDMAB in either aqueous or micellar phase, indicating that the Ia/Ib ratio of sodium p-dialkylaminobenzoate increases with lengthening alkyl group. Similar observation has been reported for p-dialkylaminobenzonitrile [7] in organic solvents. More appreciable change of Ia/Ib from aqueous phase to micellar phase for SDEAB than for SDMAB indicates that the dipole moment of the TICT state of SDEAB is higher than that of SDMAB. From this point of view, SDEAB is a better TICT fluorophore than SDMAB for to establish a sensing system by using CTAB micelle. At the same time, because of the longer alkyl substitution at amino group in SDEAB, a stronger hydrophobic interaction of SDEAB

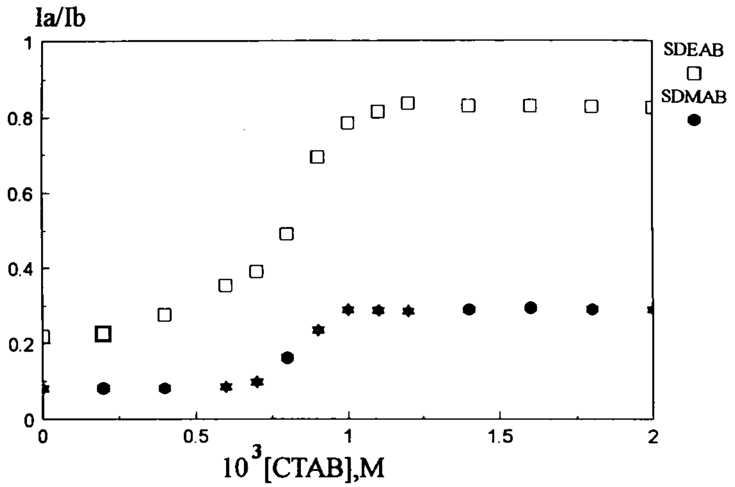

Figure 1 Ratio Ia/Ib of SDEAB and SDMAB vs CTAB concentration
[SDEAB]:2.5X10^{-5}M. [SDMAB]:2.5X10^{-5} M

than SDMAB with CTAB micelle can be expected. Thus the total interaction of SDEAB with CTAB micelle is stronger than that of SDMAB [4]. Therefore, a TICT fluorescence sensing system can be established by incorporating SDEAB into CTAB micelle.

When an ionic or neutral analyte is introduced to the sensing system, it will interacts with micelle, leading to several effects one micelle that makes it possible to be sensed. One effect is the decrease in electric field strength at micellar interface [8, 9], which can be indicated by TICT emission variation according to equation(1). The others include changes in CMC, average aggregation number (N), micellar phase polarity, and viscosity which could also lead to change in TICT emission.

Reports from this laboratory have shown that micellar phase viscosity, when compared to polarity, plays a relatively minor role in TICT behavior in micelle [4-6]. The variations of CMC and/or N in the presence of an additive will result in a change in micelle concentration as shown by equation (2),

$$[M] = (Ct - CMC) / N \qquad (2)$$

where [M] is micelle concentration and Ct the total surfactant concentration In appropriately selected system, such as that in the present work, the Ia/Ib ratio of a TICT fluorophore is independent of micelle concentration. Under these circumstances, only the additive induced changes in micellar interface electric field and micellar phase polarity will be sensed by the TICT dual fluorescence.

Figure 2 shows the response of the TICT dual fluorescence of SDEAB/CTAB micelle system to potassium nitrate. Although both the intensities of LE and TICT emission bands decrease with increasing potassium nitrate concentration, the decrease in that of TICT band is much faster, as can be more clearly seen in Figure 3 in which the Ia/Ib ratio is plotted versus [KNO_3]. The variation of LE band intensity could be due to the slightly higher dipole moment than that of ground state and to the change in molecular absorption coefficient and excitation efficiency. We use Ia/Ib as sensing index could thus directly and precisely measure the response of TICT emission to micelle interface electric field variation because of the presence of an analyte. In addition, the possible vibration in the excitation source energy can be corrected by taking Ia/Ib ratio. The TICT band position that is strongly sensitive to medium polarity [1, 3-7, 10, 11] was observed not to shift upon introduction of potassium nitrate, indicating that no change in the polarity has been induced. One may also argue that the variation of TICT dual fluorescence in the presence of an analyte, especially of an anion, could be due to the expelling of TICT

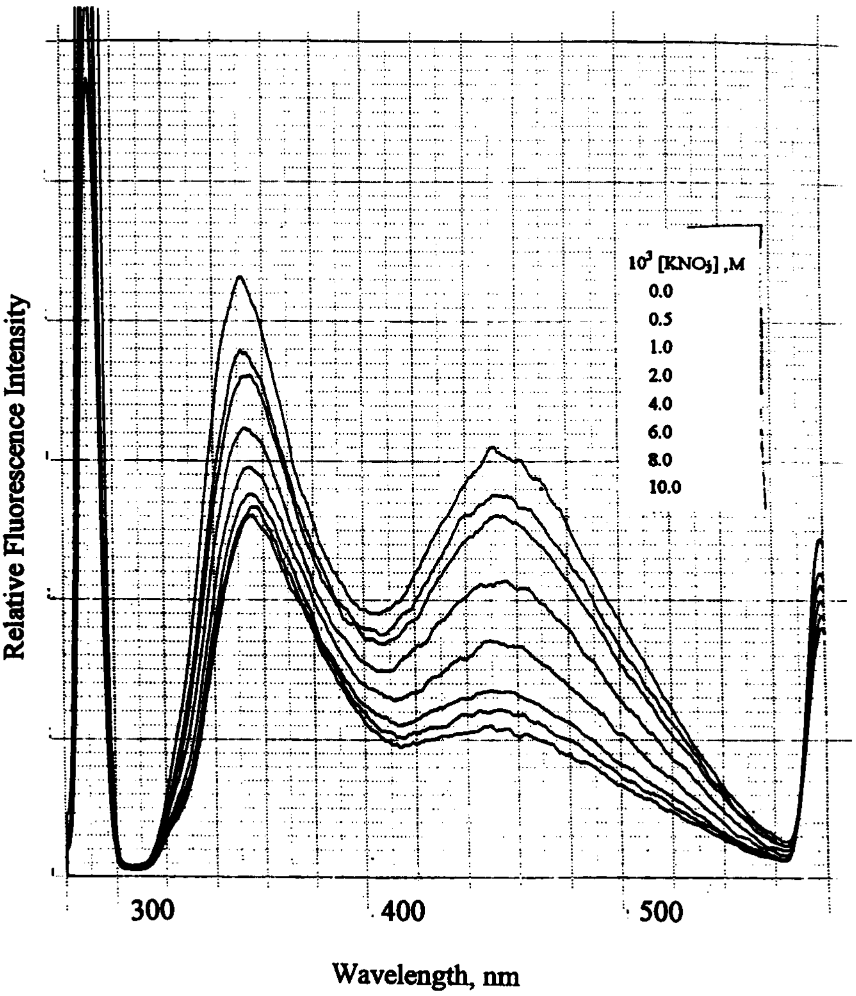

Figure 2 Fluorescence spectra of SDEAB in CTAB micellar solution as a function of potasium nitrate concentration

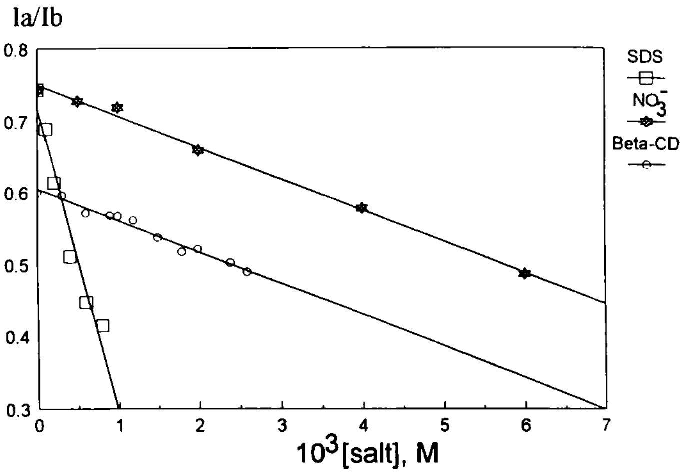

Figure 3 linear dependence of Ia/Ib of SDEAB in CTAB micelle on concentration of ion or neutral molecule [SDEAB]=2.5×10^{-5}M. [CTAB]=0.0025 M

fluorophore out of micelle. This could be the case, but no change in the Ia/Ib ratio will be induced since we showed in above paragraph that Ia/Ib ratio in micellar solution does not depend on the amount of TICT fluorophore that is solubilized in micellar phase, see also Figure 1. Thus the variation of the TICT dual fluorescence is only due to the change in electric field at micellar interface, making the sensing mode solidly backed. Similar results were observed in sensing for several other ionic and neutral molecules. Figure 3 shows typical response of Ia/Ib ratio of SDEAB/CTAB micelle system to the concentrations of several ions and neutral molecule. (It should be pointed out that data for SDS and KNO_3 were taken on Shimadzu RF-5000 while those for β-CD on Hitachi F-4500 of corrected spectrum mode. This would account for the difference between these two groups of data shown in Figure 3.) Nice linear dependence with a correlation coefficient higher than 0.99 were obtained, showing a promising application of the present novel sensing system in analytical chemistry.

Acknowledgments

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