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Direct Fluorescence Sensing of Metal Ions in Aqueous Solution Using Intramolecular Charge Transfer Emission from Aggregates of Pentaerythrityl Tetra(*p*-dimethylaminobenzoate)

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Abstract: Pentaerythrityl tetra(*p*-dimethylaminobenzoate) (PTDMAB) was synthesized and shown to emit in water-rich aqueous dioxane solutions the intramolecular charge transfer fluorescence that was sensitive to the presence of metal ions.

Keywords: Intramolecular charge transfer, aggregation, fluorescence sensing, pentaerythrityl tetra-(*p*-dimethylaminobenzoate), alkaline metal ions.

In spite of the fact that fluorescence sensing in aqueous solution under photo-induced electron transfer (PET) mechanism has been well documented[1,2], direct sensing in aqueous solution using the charge transfer (CT) emission is scarce. This is mainly because of the high dipole moment of the CT state[3] and the high polarity of water molecules that lead to heavy quenching of the CT emission in aqueous solution. It has been shown that organic molecules of high hydrophobicity, *e.g.* bearing long alkyl chain, aggregate in aqueous solution to form aggregates that afford a non-polar inner microenvironment[4]. We hence decided to develop direct CT fluorescence sensing systems for aqueous solutions using molecular aggregates for shielding the CT state from water molecule quenching. Here we report our first attempt in this regard for sensing metal ions using the aggregates of pentaerythrityl tetra(*p*-dimethylaminobenzoate) (PTDMAB) bearing four emissive CT fluorophores *p*-dimethylaminobenzoate (**Scheme 1**)[5].

PTDMAB was designed to have high hydrophobicity that allows aggregation in aqueous solution and to bear multi-ester structural framework in the ester derivatives of calixarenes that affords metal ion binding sites[6,7]. Fluorescence spectra of PTDMAB in water-dioxane binary solvents of varying water volume fraction, Φ, were recorded (**Figure 1a**). It was found that with increasing water content the CT emission (originally observed in pure dioxane at 440 nm) was red-shifted and quenched, till Φ of 0.40, when no CT emission could be observed, and the CT emission was suddenly recovered at 420 nm, Φ 0.6. This is the sign of the aggregation of PTDMAB at this

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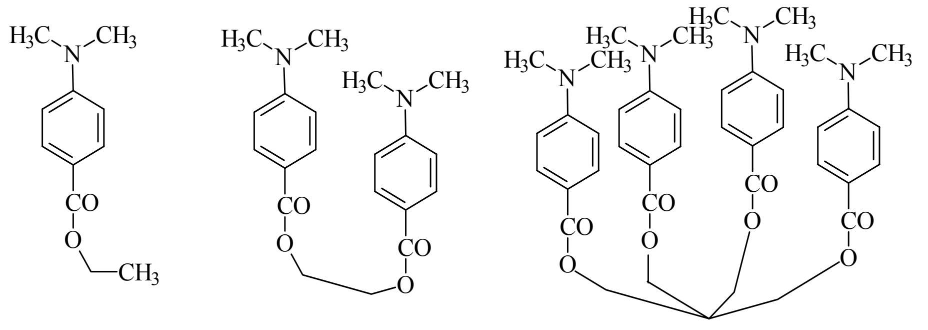
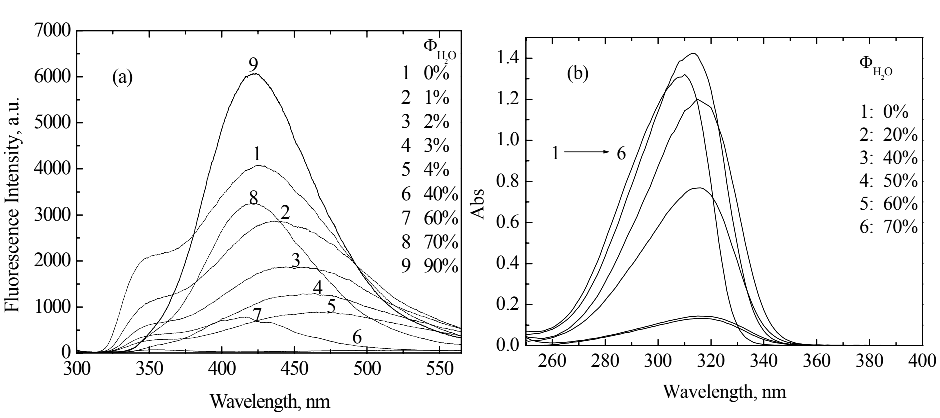
solvent composition. It was noted that after aggregation the intensity ratio of the CT to LE (locally excited state) emission, I_a/I_b, at a value of *ca.*10 remained almost constant and was much higher than that in pure dioxane in which I_a/I_b value of 2 was found, see **Figure 1a**. The blue shifted CT emission observed in the aggregates against that in pure dioxane suggested that the CT fluorophores in the aggregates were indeed shielded from highly polar water molecules. The diester derivative of PTDMAB, *i.e.* EGDMAB (**Scheme 1**), was also found to aggregate at Φ of 0.7 with the CT emission at 420 nm. The mono-ester derivative without a long alkyl chain, EDMAB (**Scheme 1**), however, did not show any evidence of aggregation and the CT emission was completely quenched at water volume fraction higher than 0.4. Aggregation of PTDMAB or EGDMAB in water-dioxane binary solvents was also shown dramatic variations in the absorption spectrum, (see **Figure 1b)**, whereas those of EDMAB did not aggregate at all.

Scheme 1



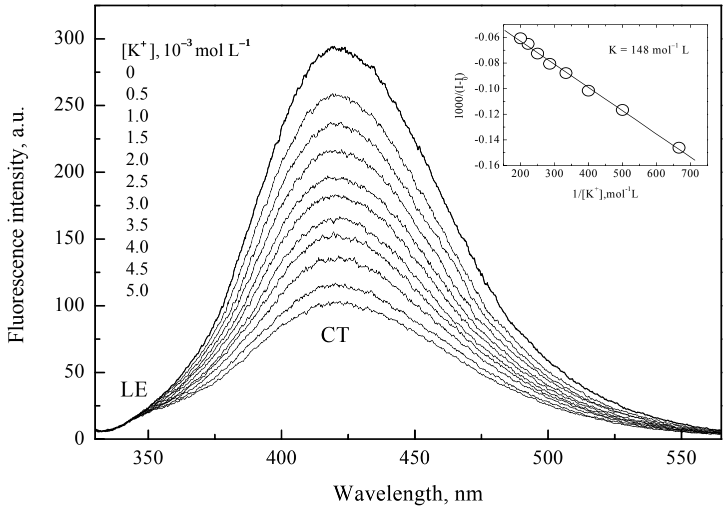
EDMAB EGDMAB PTDMAB

Figure 1 (a) Fluorescence spectra and (b) absorption spectra of PTDMAB in water-dioxane binary solvents of varied water volume fraction, Φ. [PTDMAB] = 7.5×10^{-6} mol L^{-1}.



The sensing possibility to alkaline metal ions of the CT emission from PTDMAB aggregates in aqueous dioxane solution of Φ 0.80 and 0.95 was examined. **Figure 2** shows the fluorescence spectra of PTDMAB in Φ 0.80 solutions as a function of K^+ concentration. Indeed, a sensitive response was found in the CT emission, while no shift in the CT band position was noted. The latter observation means that the response is not due to the change in electron withdrawing ability of the electron acceptor in the presence of metal ion. Double reciprocal plot[8] (inset in **Figure 2**) afforded a binding constant of K^+ with the aggregates of 148 mol^{-1} L. Response toward Li^+, Na^+ and Ca^{2+} was also found, with binding constants of 54.2, 29.4, and 133 mol^{-1} L, respectively. In Φ 0.95 solutions similar sensing behavior was found and the binding constants were evaluated as 252, 148, 333, and 185 mol^{-1} L for Li^+, Na^+, K^+, and Ca^{2+}, respectively, which are in general higher than those found in Φ 0.80 solution. Despite the difference in the binding constants, it is hard at this stage to conclude if there is response selectivity among the tested metal ions.

Figure 2 Fluorescence spectra of PTDMAB in 80% H_2O-dioxane mixture in the presence of K^+. Inset is the double reciprocal plot for the binding of K^+ to PTDMAB aggregates.



The contribution to the sensing of the calixarene-rim like binding framework present in PTDMAB was evidenced by the fact that the aggregates formed by EGDMAB in the same aqueous dioxane solution showed practically no response to metal ions. This should also suggest that the binding of metal ion in the PTDMAB aggregates is within each PTDMAB molecule but not between two or more PTDMAB molecules. This observation indicated that the presence of multi-ester groups in *p*-dimethylaminobenzoate derivatives was necessary for the sensing of alkaline metal ions. We suppose that the response of the CT fluorescence to metal ions in aqueous solutions is due to the influence of the electrostatic interactions[9] among the highly dipolar CT states within the aggregates, resulting from the binding of metal ions to the multi-ester moiety in PTDMAB molecule.

Electric conductivity experiments were carried out to confirm that PTDMAB indeed binds with metal ion (data not shown). In water-dioxane binary solvents ($\Phi = 0.9$) the apparent mobility of K^+ in the presence of PTDMAB was found to be lower than that in the absence of PTDMAB. This is a clear indication of the binding of PTDMAB to K^+ that results in decreased mobility of K^+. The mobility of K^+, however, remains unchanged in the presence of EGDMAB aggregates, which is in agreement with the observations that the fluorescence of EGDMAB aggregates in water-dioxane mixtures showed no response to metal ions.

In conclusion, we showed that the CT emission in aqueous solution could be ensured *via* aggregation of the CT fluorophore containing molecules and the CT emission could be directly employed in sensing metal ions in aqueous solution. Supported by the rich knowledge of supramolecular chemistry, the direct charge-transfer fluorescence sensing principle outlined here would find extended applications in fluorescent sensing through sophisticated design of the sensor molecules.

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References and Notes

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