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Spectroscopic characterization of intramolecular charge transfer of sodium 4-(*N*,*N*-dimethylamino)naphthalene-1-sulfonate

Li-Rong Lin [a,*], Wen-Liang Yang [a], Guang-Le Zheng [a], Yun-Bao Jiang [a,b]

[a] *Department of Chemistry, Xiamen University, Xiamen 361005, China*
[b] *The MOE Laboratory of Analytical Sciences of Xiamen University, Xiamen 361005, China*

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Abstract

In this paper, a new dual fluorescent *N*,*N*-dimethylaminonaphthalene derivative, sodium 4-(*N*,*N*-dimethylamino)naphthalene-1-sulfonate (SDMDNS), was reported. It was found that SDMDNS emits dual fluorescence only in highly polar solvent water but not in organic solvents such as methanol, dioxane and acetonitrile. Only a single broad band emission at ca. 420 nm was observed in the short wavelength region in organic solvents. The dual fluorescence of SDMDNS in water was found at 423 and 520 nm, respectively. Introduction of organic solvent as ethanol into aqueous solution of SDMDNS leads to blue shift of the long-wavelength emission, and this was evidently supported by introduction of cyclodextrin or surfactant in the aqueous solution. It indicates that a highly polar solvent was required to bring out dual fluorescence; furthermore, the short wavelength fluorescence is emitted from locally excited (LE) state and the long wavelength fluorescence is emitted from charge transfer (CT) state. The pH dependence of the dual fluorescence of SDMDNS demonstrates that the neutral form of the molecular has a higher ratio of CT band intensity to LE band. Temperature effect on the excited state of SDMDNS was also examined and gave stabilization enthalpy ($-\Delta H$) of the CT reaction 8.7 kJ mol^{-1}.

Keywords: Intramolecular charge transfer; Dual fluorescence; Sodium 4-(*N*,*N*-dimethylamino)naphthalene-1-sufonate

1. Introduction

Since Lippert et al. [1] first reported the dual fluorescence of 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN), a huge amount of dual fluorescent *N*,*N*-dimethylaniline (DMA) derivative with electron acceptor at the *para* position of the donor have been investigated and the two emission bands were assigned to the locally excited (LE) state and the charge transfer (CT) state, respectively [2–9]. Aminonaphthalenesulfonates, such as 1-dimethylamino-5-naphthalene sulfonate (dansyl) and 1-anilino-8-naphthalene sulfonate (ANS), are important fluorescent probes in biological assays and chemical probe [10,11]. In spite of the fact that the emissive state of these aminonaphthalene sulfonates is reportedly of charge transfer character, these sulfonates gave off only single-band emission. Therefore, searching for dual fluorescent amine substituted aromatic sulfonates would be significant in demonstrating their charge transfer mechanism and developing direct and efficient fluorescent probes.

From founding that *p*-(*N*,*N*-dimethylamino)benzenesulfonate (SDMAS), sulfonic acid derivative of DMA, shows dual fluorescence in polar water [12], our attempt was made to sodium 4-(*N*,*N*-dimethylamino)naphthalene-1-sulfonate, sulfonic acid derivative of 4-(*N*,*N*-dimethylamino)naphthalene-1-cyano which shows dual fluorescence. In the present paper, the fluorescence spectra of the newly synthesized sodium 4-(*N*,*N*-dimethylamino)-naphthalene-1-sulfonate (SDMDNS) (Scheme 1) in several different solvents are reported. Dual fluorescence was observed in polar solvent water, β-cyclodextrin and cetyltrimethylammonium bromide surfactant aqueous solution.

2. Experimental

SDMDNS was synthesized from the reaction of sodium 4-aminonaphthalene-1-sulfonate with CH_3I in alkaline solution [13]. The product was identified by H^1 NMR.

* Correspondence author.
E-mail address: linlr@jingxian.xmu.edu.cn (L.-R. Lin).

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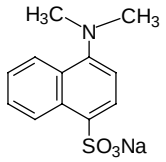


Scheme 1. Molecular structure of SDMDNS.

Organic solvents were purified by standard procedures and were checked to have no fluorescent impurity at the excitation wavelength used for samples. β-cyclodextrin (β-CD, Suzhou Gourmet Factory) was used after recrystallized three times. Cetyltrimethylammonium bromide (CTAB, received from Shanghai Reagent Co.) was recrystallized in ethanol. Water was deionized and twice distilled.

Corrected fluorescence spectra were taken on Hitachi F-4500 fluorescence spectrophotometer using excitation wavelength of 320 nm. Absorption spectra were recorded on Shimadzu UV-2501PC UV-Vis record spectrophotometer. pH values of aqueous solutions were measured on Metler Toledo 320 pH-meter.

3. Results and discussions

3.1. The fluorescence spectroscopic characteristic of SDMDNS in different solvents

Fig. 1 is the fluorescence spectra of SDMDNS in representative solvents of different polarity. It is found that SDMDNS emits dual fluorescence in strongly polar water solvent, with two bands peaked at 423 and 520 nm, respectively. While in polar organic solvents such as methanol (MeOH), ethanol (EtOH), 1,4-dioxane (DiOX), tetrahydrofuran (THF) and acetonitrile (ACN), SDMDNS only gave off a wide single-band emission at around 420 nm, in methanol, ethanol (perhaps in acetonitrile) the spectrum is especially broad. That band slightly shifts to the red with increasing polarity, demonstrates that the emissive state has a dipole moment higher than the ground state. The fluorescence emission behavior of SDMDNS in water and organic solvents is apparently similar to that of sodium *p*-(*N*,*N*-dimethylamino)benzen-sulfonate (SDMAS) [12]. With SDMAS, the dual fluorescence was assigned to the DMABN family molecules, then the dual fluorescence of SDMDNS can be assigned to the 4-(*N*,*N*-dimethylamino)naphthalene-1-cyano family molecules, that is to say, the two emission bands were emitted from the locally excited (LE) state (short wavelength band) and the charge transfer (CT) state (long wavelength band), respectively. This assignation is supported by the concentration dependence of the dual fluorescence in water, solvent polarity dependence of the fluorescence spectrum in water–EtOH binary mixtures and the observation of the dual fluorescence of SDMDNS in β-cyclodextrin and CTAB aqueous solution, respectively.

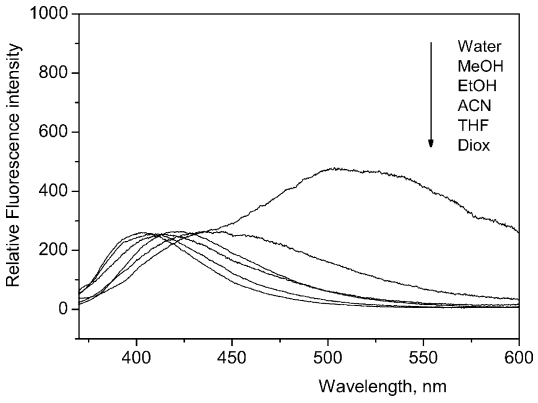


Fig. 1. Fluorescence spectra of SDMDNS in water and organic solvents.

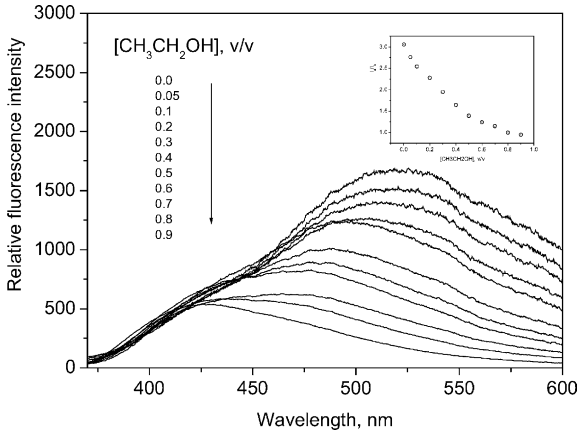


Fig. 2. Fluorescence spectra of SDMDNS change with the variation of ethanol content in ethanol–water binary solvents. The inset is the I_a/I_b value with variation of ethanol content.

The excitation spectra of SDMDNS in water obtained by monitoring the short and long wavelength fluorescence are found identical and similar to the absorption spectrum (data not shown). This observation shows that the two emissive states of SDMDNS in water have the same origin of excitation. Concentration dependence of SDMDNS fluorescence spectra in water shows that both emission bands intensity increase with increasing concentration, the intensity ratio of the two bands (long wavelength to short wavelength), I_a/I_b, remains constant over the studied concentration of 1.0×10^{-5} to 1.0×10^{-4} mol l^{-1}. Hence, it follows that the long wavelength emission is not due to the excimer formation.

The presence of the two excited states and the relationship between them were further supported by solvent polarity effect which was examined in an attempt to demonstrate the ICT character of the emissive state of the long wavelength fluorescence in water. Fig. 2 shows the fluorescence spectra of SDMDNS in water–EtOH binary solvents, in which the LE band is normalized. It can be found that, with the EtOH content decreasing, the long wavelength band is red shifted and the intensity enhanced. The enhancement in the long wavelength band is directly reported in the set of Fig. 2, in which I_a/I_b is plotted against EtOH content by volume

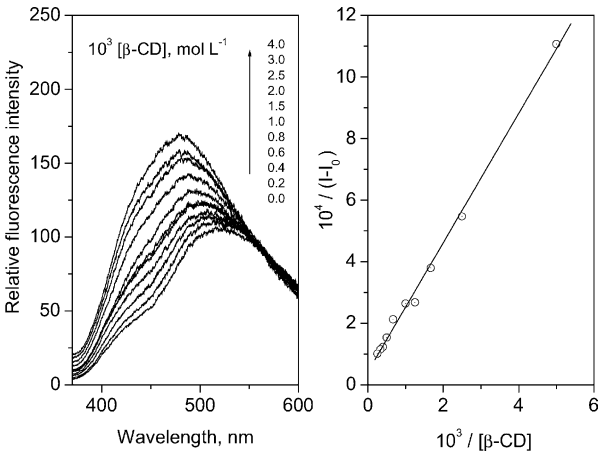


Fig. 3. Fluorescence spectra of SDMDNS in β-CD aqueous solution (left) and the Benesi–Hidebrand plots for the reciprocal of (I–I_0) vs. the reciprocal of β-CD concentration (right).

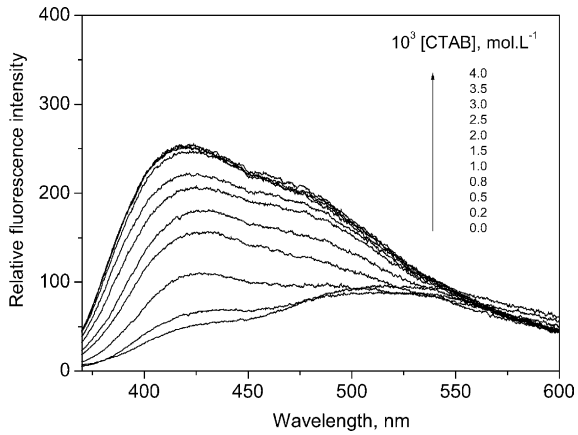


Fig. 4. Fluorescence spectra of SDMDNS in different concentration of CTAB aqueous solution.

in the binary mixtures, where I_a/I_b was determined by the ratio of fluorescence intensity at the maximum wavelength of CT band to that of LE band (the data of intensity of LE band, I_b, is read by fixed at 423 nm and the data of CT band, I_a, is read at the highest intensity of the broad CT band assumed that the spectrum is subtracted by the LE band, of which spectrum is obtained by process of the last and bottom spectrum of Fig. 2 as the LE band and CT band is overlay). The red shifted in the long wavelength band of SDMDNS with increasing solvent polarity clearly points to the charge transfer character of the emissive state, as also found with the well-established CT dual fluorescent molecules. The long wavelength emission of SDMDNS in water should really be assigned to a CT state.

Further to classify the CT state of SDMDNS in polar water, the dual fluorescence of SDMDNS in β-cyclodextrin and CTAB surfactant was examined, respectively. In aqueous solution, cyclodextrin or surfactant can provide two different microenvironments with incorporated molecule [14,15]. Hence, cyclodextrin and surfactant are ideal system to control the ICT process of various ICT molecules [16,17]. Fig. 3 (left) is the fluorescence spectra of SDMDNS in β-cyclodextrin aqueous solution. It can be clearly seen that both the LE band and CT band are blue-shifted with increasing the concentration of β-CD. It indicates that SDMDNS is incorporated into the β-CD hydrophobic cavity [14]. According to Bensi–Hidebrand method [18], using the equation of

$$\frac{1}{I - I_0} = \frac{1}{A} \times \frac{1}{K_f[\beta\text{–CD}]_0} + \frac{1}{A}$$

where, I and I_0 are the fluorescence intensities on addition of β-CD and without β-CD, A is the instrumental factor, K_f is equilibrium constant for the formation of 1:1 complex in the ground state. Plotting the $1/(I - I_0)$ versus $1/[\beta\text{-CD}]$ obtains a straight line (as shown in Fig. 3 (right)), a 1:1 stoichiometry inclusion complex between SDMDNS and β-CD is formed. From the intercept and slope of the line, it is calculated the binding constant of SDMDNS/β-CD with 202 l mol^{-1}. The result that the variation of I_a/I_b of SDMDNS in β-CD aqueous solution decreases gradually with increasing β-CD concentration, and then keeps constant, further proves that CT character of SDMDNS is required highly polar. This is what SDMDNS molecule similar to SDMABS. The more evident control of dual fluorescence of SDMDNS was to put it in CTAB aqueous solution. Fig. 4 is the spectra of SDMDNS in different concentration of CTAB aqueous solution. It can be easily seen the change of the relative intensity of the dual fluorescence of SDMDNS in CTAB aqueous solution. Both the LE and CT bands are blue-shifted and enhanced with the addition of CTAB solution. The relative intensity ratio of I_a/I_b was plotted against CTAB concentration and the results are shown in Fig. 5 (left). Below the critical micelle concentration (CMC) of CTAB, I_a/I_b decreases with increasing the CTAB solution; after the CMC of CTAB, the I_a/I_b keeps constant, it indicates that SDMDNS incorporated into the stern layer of the CTAB after CMC via static electric and hydrophobic interaction [19]. In β-CD or CTAB aque-

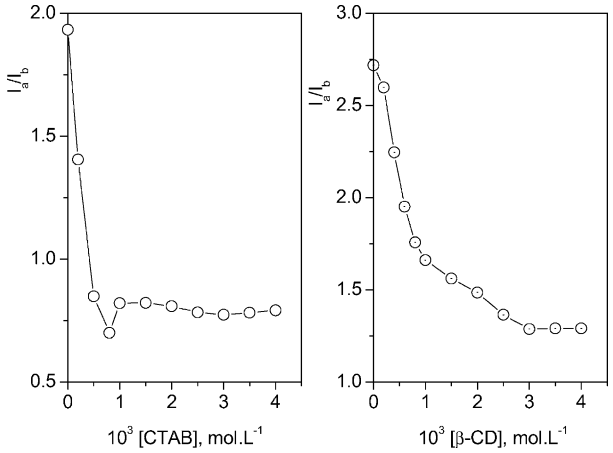


Fig. 5. The variations of I_a/I_b of SDMDNS vs. β-CD concentration (right) and CTAB concentration (left).

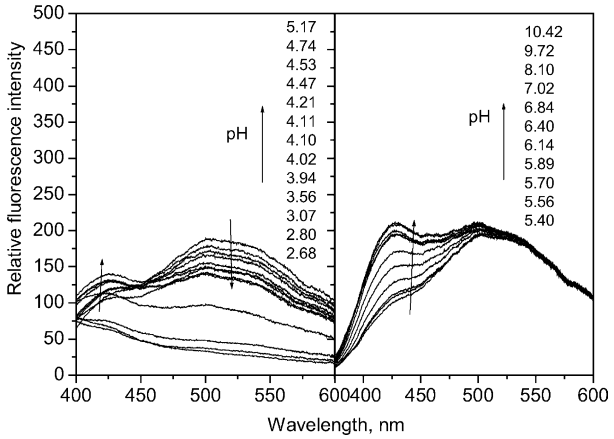


Fig. 6. Fluorescence spectra of SDMDNS change with pH values in aqueous solution.

ous solution, it can be seen that the dual fluorescence of SDMDNS is a result of the non-polar microenvironments from β-CD or CTAB, which are different from organic solvent.

3.2. pH dependence of the dual fluorescence of SDMDNS

Fig. 6 shows the dual fluorescence emission of SDMDNS in aqueous solution at different pH values. It can be seen that when the pH value below 3.56, the CT and LE intensities are decreased with decreasing pH value because of the molecule of SDMDNS totally protonated, whereas when pH value between 3.94 and 5.17, the CT emission is quenched and the LE band is slightly enhanced with the increasing the pH value. After pH value becomes higher than 5.17 but lower than 7.02, the CT band is slightly blue-shifted and enhanced while the LE band is blue-shifted and enhanced dramatically, and the dual fluorescence spectrum almost does not change after pH higher than 7.02. The total fluorescence intensity was plotted against the pH value as shown in Fig. 7(a). It was found that there are two pH break points in the curve. The first pH break point at pH 3.60 is the pK^*_{a1} of the sulfonic acid of SDMDNS in excited state which is the same as

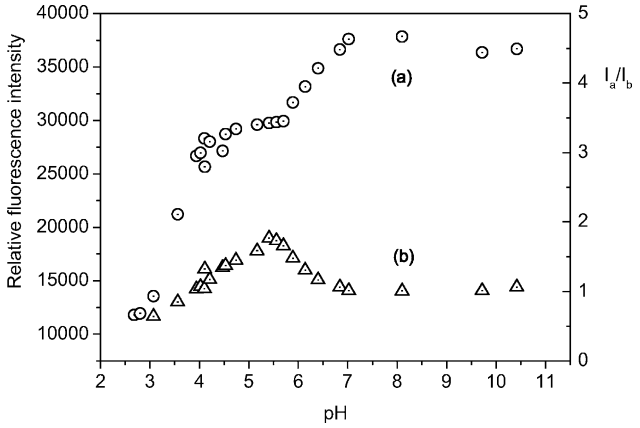
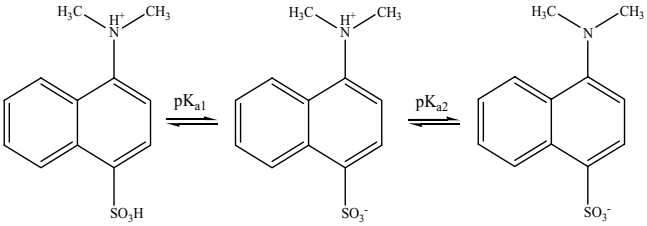


Fig. 7. The variation of fluorescence intensity and I_a/I_b of SDMDNS with pH value.



Scheme 2. The dissociated equilibrium of SDMDNS in aqueous solution.

in ground state pK_{a1} (as shown in Scheme 2) value of SDMDNS [20]. The second pH break point at pH 6.50 is the pK^*_{a2} of the amino of SDMDNS which is the same with the pK_{a2} of SDMDNS in ground state, because the pK_{a2} of SDMDNS detected by absorption spectra is also around 6.50 (see Fig. 8). These results indicate that the first and second dissociation of protonated SDMDNS in excited state is much slower than fluorescence in the acid or conjugate base form of SDMDNS. Furthermore, the neutral form of SDMDNS has a higher I_a/I_b value. Thus, the variation of I_a/I_b of SDMDNS at different pH values is as shown in Fig. 7(b) divided by three regions: (i) when SDMDNS existed mainly in acid and neural forms (pH < 5.17), the I_a/I_b ratio increases with increasing pH values; (ii) when SDMDNS existed mainly in neutral and base form (5.17 < pH < 7.02), the I_a/I_b ratio decreases with increasing pH values; (iii) when SDMDNS existed mainly in base form (pH > 7.02), the I_a/I_b keeps constant.

3.3. Temperature effect on the excited state of SDMDNS

The temperature dependence of SDMDNS in excited state was also examined. Fig. 9 is the dual fluorescence spectra of SDMDNS as a function of temperature, both the LE and the CT emission are enhanced and blue-shifted with the elevation of temperature. According to Stevens–Ban's plot [21], $\ln(I_a/I_b)$ against the reciprocal of the absolute temperature ($1/T$), a straight line was obtained (as shown in the inset of Fig. 9). Hence, the stabilization enthalpy ($-\Delta H$) of SDMDNS CT reaction was measured as 8.7 kJ mol^{-1}.

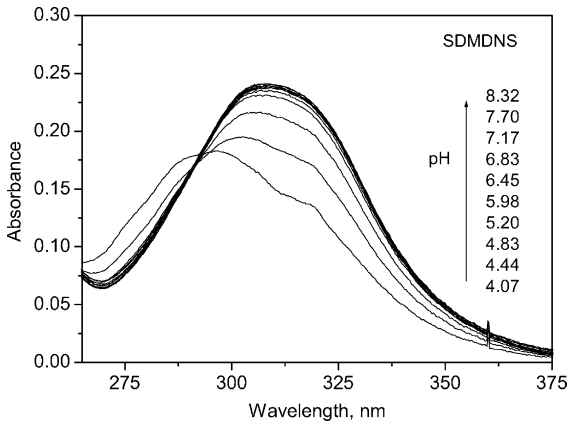


Fig. 8. The absorption spectra of SDMDNS as a function of pH value.

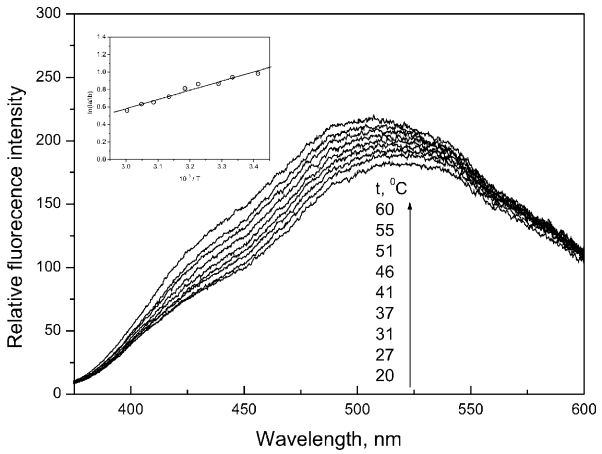


Fig. 9. Fluorescence spectra of SDMDNS change with temperature. The inset is the plots of $\ln(I_a/I_b)$ with the reciprocal of T.

4. Conclusions

We reported a new dual fluorescent 1,4-(*N*,*N*-dimethylamino)naphthalene derivative, sodium 1,4-(*N*,*N*-dimethylamino)naphthalene-sulfonate (SDMDNS). It was found that SDMDNS only showed dual fluorescence in polar solvent water, β-cyclodextrin or surfactant such as CTAB aqueous solution. Steady-state fluorescence measurements demonstrated that, with SDMDNS in water, the long wavelength band at ca. 520 nm was emitted from a charge transfer state while the short wavelength band at 423 nm from the LE state. The pH dependence of SDMDNS fluorescence demonstrates that the neutral form of SDMDNS molecule has a relative higher ratio of CT band intensity to LE band. And the temperature effect on the excited state of SDMDNS gave the CT reaction stabilization enthalpy ($-\Delta H$) 8.7 kJ mol^{-1}.

It is significant to be able to observe in water the dual fluorescence of SDMDNS with appreciable CT emission. This would no doubt make it a good candidate as a protein fluorescence probe because the currently available important aminonaphthalenesulfonate–protein probes only give single-band emission, thereby able to offer message on protein structural change via CT fluorescence variation.

Acknowledgements

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