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Intramolecular charge transfer dual fluorescence of *p*-dimethylaminobenzoates

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Abstract

A series of ester, *p-N,N*-dimethylaminobenzoates ($(CH_3)_2NC_6H_4COOR$, $R = n\text{-}C_nH_{2n+1}$, $n = 1, 2, \ldots, 8$), were synthesized and their fluorescence spectra were recorded. Intramolecular charge transfer (CT) dual fluorescence was found in common organic solvent or in water with cetyltrimethylammonium bromide (CTAB) micelle. The fluorescence intensity ratio of CT band to normal band (I_{CT}/I_{LE}) was decreased dramatically with the increasing of carbon number of R group when the carbon number of R group were 1–3, but the dependence was not obvious when the carbon number of R group were 4–8. Oppositely, the I_{CT}/I_{LE} was increased with increasing of carbon number of R group in water with CTAB micelle.

Keywords: p-N,N-Dimethylaminobenzoate; Dual fluorescence; Organic solvent; CTAB micelle

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1. Introduction

Recent years, the study of the intramolecular charge transfer (CT) dual fluorescence has been an active area in theoretical and practical research [1]. The investigations of the charge transfer process and the properties of CT dual fluorescence have attracted much attention for their potential applications in fluorescence probe, et al. It is well know that *p*-(*N,N*-dimethylamino)benzonitrile and *p*-(*N,N*-dimethylamino)benzoic acid are typical molecules with intramolecular charge transfer dual fluorescence, which containing both electron-donor and electron-accepter group [2–4]. Many new molecules which contain *N,N*-dialkyl group and different electron-withdrawing group ($-CF_3$, –CHO, $-CONH_2$ and –COOH [5–8]) have been synthesized and examined. The research result showed the similar profile of dual fluorescence can be observed in molecules with quite different electron-acceptor substituents, and the position of the CT emission band were affected by electron-acceptor strength. The red-shifts of CT emission band were observed along with the increasing of electro-drawing ability of electron-acceptor group. Moreover, the relative positions and intensities of the dual emission were dependent on the solvent polarity and viscosity [9–11].

In the paper, a series of ester, *p-N,N*-dimethylaminobenzoates ($(CH_3)_2NC_6H_4COOR$, $R = n\text{-}C_nH_{2n+1}$, $n = 1, 2, \ldots, 8$) (DMABE), were synthesized. As comparing with acid, $(CH_3)_2NC_4H_6COOH$, the esters can avoid acidic dissociation and specific hydrogen bonding between the electron acceptor and solvent [12,13]. The properties of dual fluorescence of DMABE in organic solvents and in water with cetyltrimethylammonium bromide (CTAB) micelle were examined. The research results were helpful to understand the CT photophysical processes.

2. Experimental

p-N,N-Dimethylaminobenzoates ($(CH3)_2NC_6H_4COOR$, $R = n\text{-}C_nH_{2n+1}$, $n = 1, 2, \ldots, 8$), were synthesized by reaction of *p-N,N*-dimethylaminobenzoic acid with corresponding alkyl alcohol (Scheme 1). The synthesis of the esters, *p-N,N*-dimethylaminobenzoates ($n = 1, 2, 3$), were carried out with refluxing in corresponding alkyl alcohol. The synthesis of the other esters ($n = 4, 5, 6, 7, 8$) was

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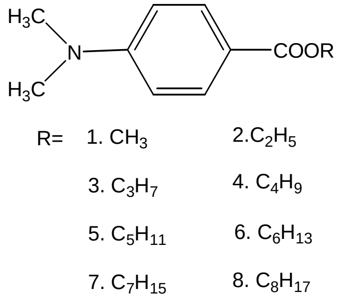

Scheme 1. Chemical structures of *p*-dimethylaminobenzoates.

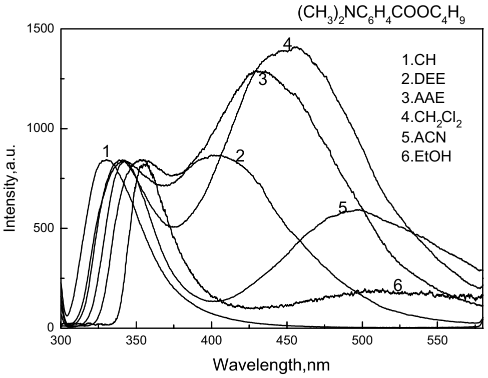

Fig. 1. Fluorescence spectra of butyl *p*-dimethylaminobanzoate in solvents of varied polarity. Solvents are cyclohexane (CH, 1), diethyl ether (DEE, 2), ethyl acetate (AAE, 3), dichloromethane (CH_2Cl_2, 4), acetonitrile (ACN, 5) and ethanol (EtoH, 6), respectively.

refluxed in the benzene solvent. The products were characterized by IR data and NMR data.

Organic solvents were purified before use and were checked to have no fluorescent impurity at the used excitation wavelength. Cetyltrimethylammonium bromide (AR, Shanghai) was used as received.

Corrected fluorescence spectra and the absorption spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer and Beckman DU-7400 absorption spectrophotometer, respectively. Quantum yields of the aerated sample solutions were measured using quinine sulfate as the standard (0.546 in 0.5 mol l^{-1} H_2SO_4 [14]). IR data were acquired from Nicolet Avatar FT-IR 360 spectrometer. AM1 calculations were carried out using GAUSSIAN 94 software [15].

3. Results and discussion

3.1. Some characterizations and absorption spectra of the eaters

The series of esters were characterized by IR and the IR data of carbonyl (>C=O) in different esters didn't appear obvious change (Table 1). The dipolar moments of ground-state of the esters were calculated and about 3.88±0.2 D (Table 1). That suggested the ground-state structures of these esters were similar, thereby ensuring the comparability of the electron acceptors in these esters.

The absorption of these esters in common organic solvents were measured. It was found that the maximum absorption wavelengths of the esters in acetonitrile (ACN) hardly appeared any change (Table 1). The similar phenomenon was found in other solvents.

3.2. The fluorescence spectra of the esters in organic solvents

The fluorescence spectra of the esters were recorded in several solvents with different polarity. The excitation wavelength was located at 300 nm and the concentration of these esters was lower about 1×10^{-5} mol l^{-1}. Fig. 1, as an example, showed the emission spectra of butyl *p*-*N*,*N*-dimethylaminobenzoate in different organic solvents. It was found that the esters emitted mainly short-wavelength fluorescence with a tail extending to beyond 450 nm in non-polar solvent, cyclohexane (CH). The dual fluorescence was revealed in polar solvents and could be readily assigned to the locally excited (LE) state and the charge transfer state, respectively. In agreement with some reported observations [3], the LE emission of at around 345 nm showed very weak dependence on solvent polarity, whereas the CT emission showed red-shifts with the increasing of solvent polarity.

In addition, the fluorescence spectra showed apparently variation with different R group. Fig. 2 displayed the fluorescence spectra of different esters in CH_2Cl_2. It was observed that the CT emission of some esters (R = $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$) in CH_2Cl_2 were gradually blue-shifted and

Table 1
The IR stretching frequencies of the carbonyl double bonds, the absorption and fluorescence spectral parameters of *p*-dimethylaminobenzoates in ACN and the ground-states dipole moments

R	$\nu_{c=0}$ (IR, cm^{-1})	λ_{abs} (max, nm)	$\lambda_{CT}/\lambda_{LE}$ (nm)	I_{CT}/I_{LE}	Total quantum yield	μ_g (D)
–CH3	1701.2	309	500.8/349.8	10.21	0.02897	3.99
$-C_2H_5$	1699.6	308	497.6/347.2	5.36	0.01673	3.90
$-C_3H_7$	1702.3	308	496.8/344.6	0.35	0.03819	3.88
$-C_4H_9$	1703.0	309	497.6/343.8	0.71	0.03502	3.88
$-C_5H_{11}$	1703.0	309	495/343.2	0.68	0.04383	3.87
–C6	1703.0	308	497.6/343.8	0.85	0.03541	3.88
–C7	1701.1	308	500.8/345.8	1.02	0.04470	3.84
–C8	1704.0	308	498.2/343.2	0.97	0.05114	3.86

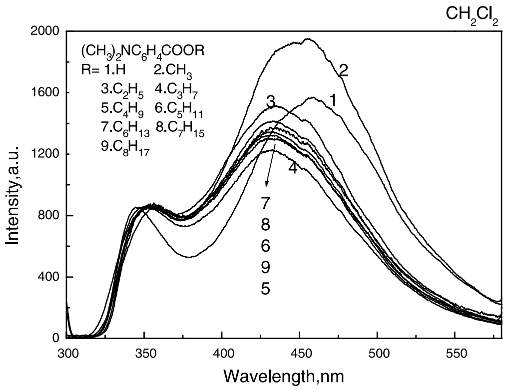

Fig. 2. Fluorescence spectra of *p*-dimethylamonobenzoates in CH_2Cl_2.

the ratio of fluorescence intensity of CT emission to LE emission (I_{CT}/I_{LE}) were sharply decreased, but the CT emission of other esters ($R = –C_4H_9$ to $R = –C_8H_{17}$), showed little change on either fluorescence wavelength or ratio of fluorescence intensity (I_{CT}/I_{LE}). Similar phenomena were observed in other polar solvents and were shown in Fig. 3.

3.3. Fluorescence spectra of the esters in water with CTAB (2.0 × 103 M) micelle

In order to understand profoundly the CT emission responding to the electron-acceptor strength or the environmental effects, we investigated their fluorescent spectra in water with cetyltrimethylammonium bromide micelle, after the critical micelle concentration (CMC) [16]. Fig. 4 showed the fluorescence spectra of the esters in water with CTAB (2.0×10^{-3} M). It can be founded that the local emission (LE) of methyl *p*-*N*,*N*-dimethylaminobenzoate ($(CH_3)_2NC_6H_4COOCH_3$) was more red-shifted than the other esters. The result could be attributed to aggregates of methyl ester in water. Other esters which contain more large R group could easily embed into CTAB micelle that destroy the aggregated state of esters in water [17]. So the intensity ratio of CT emission to LE emission was gradually increased with the increasing of chain length of R group. The results demonstrated the increasing of stabilization of the CT state with the interactions between the esters and the micelle. The interactions may be hydrophobic interaction and electron interaction between –COOR group and micelle [17].

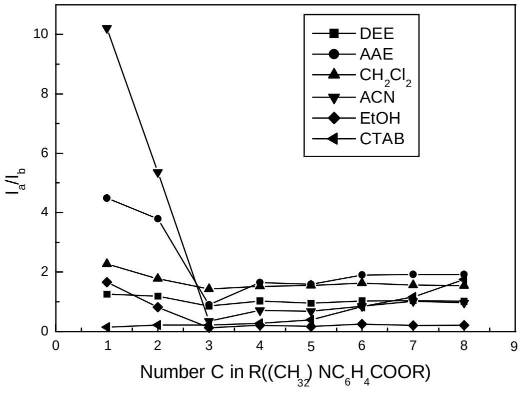

Fig. 3. Plots of I_{CT}/I_{LE} vs. number C in R ($(CH_3)_2NC_6H_4COOR$).

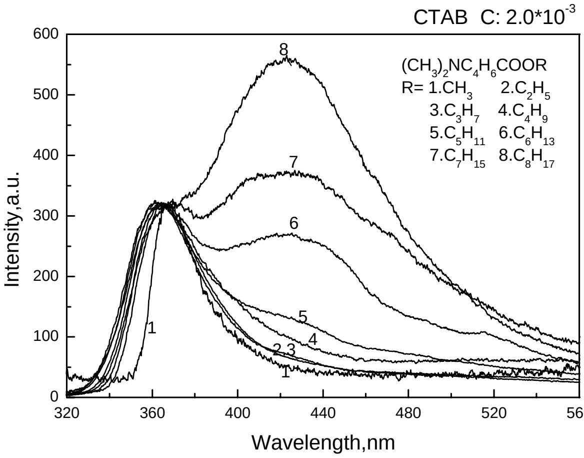

Fig. 4. Fluorescence spectra of *p*-*N*,*N*-dimethylaminobenzoates in an aqueous solvent in the presence of CTAB (2.0×10^{-3} M).

4. Conclusions

A series of esters, *p*-*N*,*N*-dimethylaminobenzoates ($(CH_3)_2NC_6H_4COOR$, $R = C_nH_{2n+1}$, $n = 1, 2, \ldots, 8$), were prepared. The IR data and the ground-states dipole moments showed that the ground-state structures of these esters were similar. The CT dual fluorescence were observed in different medium. In organic solvent, the position of CT emission of some esters ($n = 1, 2, 3$) was blue-shifted and the I_{CT}/I_{LE} were decreased alone with the increasing of the chain length of R group, but the CT emission of other esters ($n = 4, 5, 6, 7, 8$) were very similar. In water with cetyltrimethylammonium bromide (CTAB) micelle, the I_{CT}/I_{LE} was increased with the increasing of the length of R group.

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