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Dual fluorescence of 4-dimethylaminopyridine and its derivatives Effects of methyl substitution at the pyridine ring

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Abstract

Electronic absorption and emission spectra of 4-(dimethylamino)pyridine (DMAP), 3-methyl-4-(dimethylamino)pyridine (MDMAP), and 3,5-dimethyl-4-(dimethylamino)pyridine (TMAP = tetramethylaminopyridine) were measured in cyclohexane (nonpolar), chloroform (medium polar), and acetonitrile (highly polar) solutions. Intense charge transfer emission of DMAP was observed only in acetonitrile, while that of MDMAP and TMAP was observed in all the three solvents. Dynamics of excited electronic states of these molecules is discussed on the basis of steric hindrance between methyl groups at 3- and 5-positions of pyridine ring and dimethylamino groups.

Keywords: Intramolecular charge transfer; Dual fluorescence; Solvent effect; Dimethylaminopyridines

1. Introduction

It is well known that aromatic molecules having electron donor and acceptor parts, such as 4-(dimethylamino)benzonitrile (DMABN), show peculiar dual fluorescence with ordinary and large Stokes shifts in polar solvents. Since the first observation of the dual fluorescence for DMABN [1], its origin has been extensively investigated. It seems to be widely accepted that the dual fluorescence is ascribed to emissions from an initially prepared locally excited (LE) state and from a charge transfer (CT) state formed through the subsequent relaxation. Mechanism of CT state formation and molecular structure in CT state, however, have not been clearly elucidated. There has been no experimental technique to determine molecular structures in CT states directly, except for time-resolved vibrational spectroscopies [2–5]. Consequently, many models have been proposed for the mechanism of CT state formation.

Twisted intramolecular charge transfer (TICT) mechanism [6,7] has long been considered as the most plausible one to explain appearance of dual fluorescence, where twisting motion around the bond between donor and acceptor groups induces a charge separation. In the case of DMABN, for example, geometry in the LE state is considered to be almost planar as well as that in the ground electronic (S_0) state, whereas the dimethylamino group is considered to be nearly perpendicular to the cyanophenyl group in the TICT state.

In order to confirm the above TICT hypothesis, spectral behaviors of some derivatives of DMABN have been studied [8–13]. Pretwisted-model compounds, the dimethylamino group of which is in a twisted geometry against the cyanophenyl ring in their S_0 and LE states, show the CT emission even in nonpolar solvents. On the other hand, the CT emission is not observed for planar compounds when the internal rotations of the amino groups are restricted. These findings imply that the twisting motion around the amino–phenyl bond plays an important role for the CT emission.

Recently, however, another mechanism, planar intramolecular charge transfer (PICT), has been proposed for the dual fluorescence of DMABN [14–16]. This model assumes that the CT state is formed not with the torsional motion but with a change of conformation of the dimethylamino group from pyramidal ones in the S_0 and LE states to planar one in the CT state. This mechanism is supported by the following experimental results: (1) high efficiency of the CT formation is observed for the DMABN

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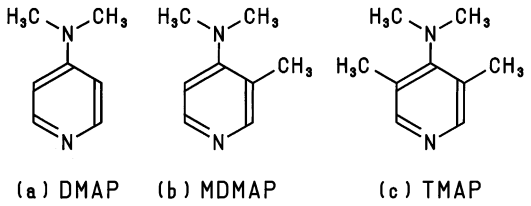

Fig. 1. Structural formulae of: (a) DMAP; (b) MDMAP; (c) TMAP.

derivatives with longer alkyl chains at the amino groups; (2) for the DMABN derivatives whose amino groups are part of heterocyclic rings with different sizes, the efficiency of CT formation decreases by increasing ring size; (3) dual emission is observed even in low temperature glass solutions where torsional motion is highly restricted.

Rehybridization by intramolecular charge transfer (RICT) and wagged intramolecular charge transfer (WICT) models have also been proposed to explain the source of dual fluorescence of DMABN. In the former model [17,18], charge transfer is accompanied by in-plane bending deformation of cyano group, while wagging motion of the dimethylamino group is considered to induce charge transfer in the latter model [19]. There are many other models proposed for the dual fluorescence of DMABN, such as the proton transfer model [20] and the excimer, exciplex and complex models [21–25].

Since only DMABN and its derivatives have been studied extensively so far, detailed investigation of the similar substances seems to give more information. In the present study, electronic absorption and emission spectra of 4-(dimethylamino)pyridine (DMAP) and its two derivatives, 3-methyl-4-(dimethylamino)pyridine (MDMAP) and 3,5-dimethyl-4-(dimethylamino)pyridine (TMAP = tetramethylaminopyridine), have been measured in various solvents with different polarities. Structural formulae of the substances are shown in Fig. 1. Behaviors of the excited electronic states of the substances are studied in detail to elucidate the relation between molecular structure and efficiency of the CT-state formation. The dual fluorescence for DMAP in polar solvents has already been reported [26], suggesting that an electron transfer from the dimethylamino group to the pyridine ring results in the formation of CT state. Dimethylamino group and pyridine ring of MDMAP and TMAP cannot be coplanar due to steric hindrance between the dimethylamino group and the methyl groups at the 3- and 5-positions of pyridine ring. The effect of methyl substitution at the pyridine ring can be checked by examining behaviors of the excited electronic states of MDMAP and TMAP.

2. Experimental

DMAP (reagent grade) was purchased from Tokyo Kasei and was used after twice recrystallizations from 1:1 mixture of dichloromethane and heptane. MDMAP and TMAP were synthesized from 4-nitro-3-picoline-1-oxide and 3,5-lutidine, respectively, where the procedure reported in literature [27] was modified as follows. Infrared absorption, ^{1}H NMR, and mass spectra were measured to identify the synthesized samples.

MDMAP: chloro-substitution of 4-nitro-3-picoline-1-oxide (Tokyo Kasei, reagent grade) by treating with acetylchloride for 3 h under anhydrous conditions at 0°C gave 4-chloro-3-picoline-1-oxide (yield 86%), which was made to react with dimethylamine (50% aqueous solution) for 48 h at 125°C in an autoclave (pressure was approximately 9 atm) to yield 4-dimethylamino-3-picoline-1-oxide as a viscous liquid in 94% yield. Reduction by iron powder/acetic acid gave MDMAP, which was purified by a column chromatography (silica gel/chloroform or chloroform–methanol) and subsequent vacuum distillation; viscous liquid (boiling point, 76°C/1.2 Torr, yield: 49%, M^+: 136).

TMAP: oxidation of 3,5-lutidine (Tokyo Kasei, reagent grade) with acetic acid/hydrogen peroxide at 90°C and subsequent nitration with H_2SO_4–HNO_3 gave 4-nitro-3,5-lutidine-1-oxide as a yellow needle (melting point: 169.9–170.9°C, yield 49%). TMAP was obtained as a viscous liquid (boiling point, 75°C/0.6 Torr, yield by three steps: 38%, M^+: 150) via 4-chloro-3,5-lutidine-1-oxide, and 4-dimethylamino-3,5-lutidine-1-oxide through the similar procedure as the synthesis of MDMAP.

Cyclohexane (nonpolar solvent), chloroform (medium-polar solvent) and acetonitrile (highly polar solvent) were purchased from Kanto Kagaku (fluorescence grade) and used without further purification for solvents in measurements of electronic absorption and emission spectra.

Electronic absorption and emission spectra were measured, respectively, with a UV–VIS spectrophotometer (Shimadzu, UV-2200 or JASCO, U-best50) and a fluorescence spectrophotometer (Shimadzu, RF-5300PC or JASCO, FP-770), respectively. Quartz cells with a path length of 10 mm were used. All spectra were measured at a concentration of about 1×10^{-5} mol dm^{-3} at room temperature of about 25°C.

3. Results and discussion

In Fig. 2 are shown electronic absorption spectra of (a) DMAP; (b) MDMAP, and (c) TMAP in three solvents, i.e. cyclohexane, chloroform, and acetonitrile. The wavelengths of the absorption maxima ($\lambda_{a,max}$) are summarized in Table 1, where similar dependence of $\lambda_{a,max}$ on solvent appears in three compounds; $\lambda_{a,max}$ is shortest in cyclohexane, intermediate in acetonitrile, and longest in chloroform. This order is not equal to that of solvent polarity, when the dipole moment of solvent molecules, the dielectric constant, or the polarity parameter, E_T (30) [28–30], is chosen as an indicator of solvent polarity. Proton donating ability of solvent molecules, which is largest for chloroform and

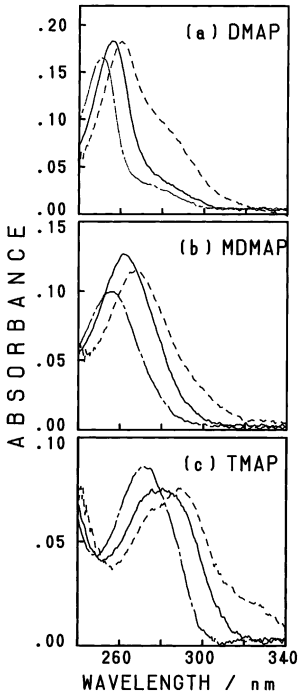

Fig. 2. Electronic absorption spectra of: (a) DMAP; (b) MDMAP; (c) TMAP in acetonitrile (—); chloroform (- - -); cyclohexane solutions (- · - · -).

smallest for cyclohexane [30,31], presumably affects the solvent dependence of $\lambda_{a,max}$.

A shoulder appears at the longer wavelength side of the main band of the electronic absorption band of DMAP. Since, the relative intensity of the shoulder against the main band depends on solvent, they are possibly assigned to different species. We assume that the shoulder is due to DMAP protonated or hydrogen-bonded with solvent molecule at the pyridine nitrogen or at the amino nitrogen. This assumption is supported by the experimental fact that only one absorption band is observed at the position of the shoulder when DMAP is dissolved in water saturated with CO_2 [32], where hydrolysis of CO_2 makes the solution acid to protonate DMAP easily.

The shoulder appears clearly in chloroform which has the highest proton donating ability [30,31], while in acetonitrile and cyclohexane with less or no proton donating ability, respectively, the shoulders are so weak that they look like tails of main bands. The shoulders (or tails) of MDMAP and TMAP are not clear presumably because broader main bands hide the shoulders, or because methyl groups at 3- and 5-positions of pyridine ring block the interaction of solvent molecule with the dimethylamino group of solute molecule.

Cazeau-Duboroca et al. claimed that DMAP, which is pretwisted in the ground electronic state by forming hydrogen-bonded complex with residual water in the solvent, shows the anomalous dual fluorescence [26]. We found, however, that the fluorescence excitation spectrum of DMAP in acetonitrile measured by probing the CT emission at 440 nm is completely identical with the electronic absorption spectrum in the same solvent. This fact reveals that hydrogen-bonded DMAP shows the dual fluorescence as well as nonhydrogen-bonded DMAP: neither hydrogen-bonding nor protonation is needed for the CT state formation. Since the CT emission is observed by exciting at either the main band or shoulder band, we inquire here neither the origin of the shoulder band nor the effect of hydrogen-bonding and protonation any more.

In Fig. 3, emission spectra of (a) DMAP; (b) MDMAP, and (c) TMAP are shown in the similar manner as in Fig. 2. Each spectrum was measured by exciting the solution at the absorption maximum. Wavelengths of CT emission maxima ($\lambda_{CT,max}$) are summarized in Table 1.

The emission spectrum of DMAP in acetonitrile consisted of dual fluorescence. Wavelengths of the emission maxima were 344 and 441 nm. They are attributable to LE and CT emissions, respectively. Only weak LE emission at the shorter wavelengths was observed in cyclohexane, while very weak LE emission and perhaps CT emission with less intensity than the LE emission were observed in chloroform. CT emissions of MDMAP and TMAP were observed in all solvents, while no distinct LE emission was observed except for TMAP in acetonitrile; inconspicuous structures around 300–350 nm for TMAP in acetonitrile might be due to LE emission.

The $\lambda_{CT,max}$ shifts to the longer wavelength as the polarity of solvent increases; shortest in cyclohexane, intermediate in chloroform, and longest in acetonitrile. Emission intensity also depends on the solvent polarity. More intense CT emission was observed in the solvent with higher polarity as shown in Fig. 3.

Irrespective of the intensity of CT emission, LE emissions of these compounds were found to be very weak. This is

Table 1
Electronic absorption maxima ($\lambda_{a,max}$) and CT emission maxima ($\lambda_{CT,max}$) of DMAP, MDMAP and TMAP

Solvent	DMAP		MDMAP		TMAP	
	$\lambda_{a,max}$ (nm)	$\lambda_{CT,max}$ (nm)	$\lambda_{a,max}$ (nm)	$\lambda_{CT,max}$ (nm)	$\lambda_{a,max}$ (nm)	$\lambda_{CT,max}$ (nm)
Cyclohexane	251	–[a]	256	379	273	388
Chloroform	260	~410[b]	270	400	290	400
Acetonitrile	256	441	260	435	282	431

[a] Not observed.
[b] Very weak.

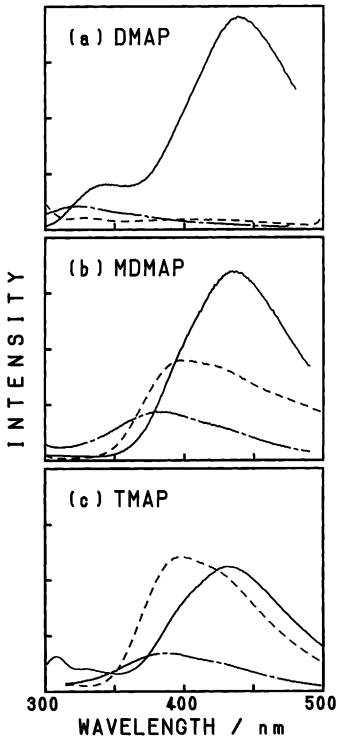

Fig. 3. Emission spectra of: (a) DMAP; (b) MDMAP; (c) TMAP in acetonitrile (—), chloroform (- - -) and cyclohexane solutions (- · - · -) measured by exciting at $\lambda_{a,max}$.

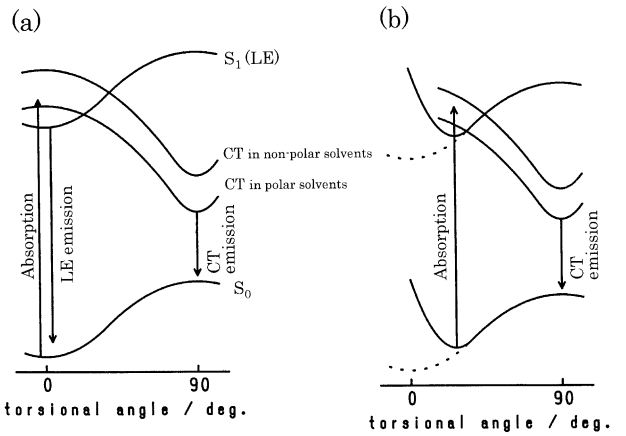

Fig. 4. Schematic potentials of DMAP and its derivatives. Horizontal axis shows the torsional angle between the dimethylamino group and pyridine ring. (See text).

presumably because intersystem crossing from the LE states to the triplet states is fast as in the case of pyridine and methyl pyridines [33]. Intersystem crossing of DMAP and its derivatives might be faster than radiative decay (fluorescence), but slower than charge transfer.

The above experimental results give important information on the origin of dual fluorescence of DMAP and its derivatives. The RICT model proposed for DMABN, in which the CT state formation is accompanied by in-plane bending deformation of the cyano group, cannot be applied for DMAP, because pyridine ring of DMAP has no substituent group at the opposite position of the dimethylamino group. The PICT model might also be excluded, because CT emission is well observed for MDMAP and TMAP where the methyl groups at 3- and 5-positions prevent the molecules to be planar: it is improbable that the molecules in the CT state are planar.

Dual fluorescence of DMAP and its derivatives, therefore, is considered to be due to the WICT or TICT state formation. Although it is quite possible that steric hindrance between the dimethylamino group and the methyl groups at the 3- and 5-positions force the dimethylamino group to wag or twist against the pyridine ring, there exists no experimental information to conclude which deformation is preferable. In order to get more information, calculation of the structure of TMAP in the S_0 state was performed with the molecular orbital calculations (GAUSSIAN 98, B3LYP/6-31G* [34]). The calculation results show that the dimethylamino group and the pyridine ring of TMAP are not in a wagged position, but in a twisted position. The dihedral angle between the pyridine ring and the dimethylamino group is about 55°. This result suggests that the long wavelength fluorescence of TMAP is due to the TICT-state formation, although the structures of TMAP in the LE and CT states have not been calculated. It is improbable that the structures of S_0 and CT states are, respectively, twisted and wagged; if it is the case, the Franck–Condon factor of transitions from CT to S_0 should be small, and the intense CT emission could not be expected.

The experimental results can be well explained with the TICT model by considering two factors; one is the solvent effect and the other is the torsional angle between the dimethylamino group and the pyridine ring. These two factors affect the energies of three electronic states, i.e. S_0, LE and CT states. Schematic potential diagrams for explanation of the effects are shown in Fig. 4, which are essentially same with those for DMABN found in literature [15,35]. Fig. 4(a) represents the diagram for DMAP, while Fig. 4(b) does for MDMAP and TMAP. The horizontal axis depicts the torsional angle, and the vertical axis shows the energy of the system, where only the relative positions of potential curves are shown.

Firstly, the solvent effect is considered in detail. Since molecules in the S_0 and LE states have similar dipole moments, the solvent effects for their states are expected to be similar. Then, bands in electronic absorption spectra show only a small shift when solvent polarity is changed. On the other hand, molecules in the CT state have larger dipole moments than those in the S_0 and LE states. Therefore, the relative energy of the CT state against the LE state depends on the solvent polarity. This means that the CT state is greatly stabilized in polar solvents. For DMAP in a nonpolar solvent such as cyclohexane, energy of the CT state is higher than that of the LE state; the molecule excited to the

LE state cannot relax to the CT state. Only weak LE emission and no CT emission is observed for DMAP in cyclohexane. In the polar solvents such as acetonitrile, energy of the CT state goes down to be lower than that of the LE state. Consequently, molecules excited to the LE state relax to the CT state, resulting in the observation of the CT emission.

The change of the spectroscopic behaviors on going from DMAP to MDMAP and TMAP is explained in terms of the second factor, i.e. steric hindrance between the methyl groups on the pyridine ring and the dimethylamino group. DMAP has no steric hindrance and is almost planar in the S_0 and LE states. Potential minima of the states are at 0° as shown in Fig. 4(a). The potentials of MDMAP and TMAP are deformed by methyl substitution at the 3- and 5-positions of pyridine ring as shown in Fig. 4(b), where the potentials of DMAP are also shown by dashed curves. Energies at 0° are relatively high for MDMAP and TMAP because of the steric hindrance. Potential minima move to twisted positions; twisting deformation moderates the steric hindrance. Consequently, MDMAP and TMAP are twisted even in the S_0 and LE states where energies of MDMAP and TMAP are higher than those of DMAP in the respective states.

Energies of the S_0 and LE states of MDMAP and TMAP are appreciably different from those of DMAP. On the other hand, energies of the CT states of MDMAP and TMAP are similar to that of DMAP, because steric hindrance affects only a little the energies and structures of the CT states whose equilibrium structures are twisted irrespective of the existence of the steric hindrance due to the methyl groups at 3- and 5-postions of pyridine ring. Then the energies of the CT states of MDMAP and TMAP become relatively lower than those of the respective LE states. The circumstance makes it possible for MDMAP and TMAP to form the CT states even in the cyclohexane solutions.

The first factor, i.e. solvent effect, is effective on MDMAP and TMAP as well as on DMAP. The CT states are more stabilized in a solvent with higher polarity, and the energies decrease with respect to those of S_0 and LE states, resulting in the red shift of the CT band and the higher efficiency of CT formation (stronger CT emission) in polar solvents.

The spectroscopic behavior of MDMAP and TMAP can be explained by the TICT model, which could be valid for the source of dual fluorescence of DMAP, MDMAP and TMAP as well as in the case of DMABN and its derivatives. In order to support this explanation, more experimental evidence is useful; for example, some experiments for compounds with longer alkyl chains at amino group, spectroscopic investigation of the compounds in the low temperature glass solutions and time-resolved measurements of vibrational spectra of the CT states.

It should be also noted that all the similar molecules as DMABN and DMAP do not necessarily form TICT-type CT states. It has been known that a similar aromatic compound having electron donor and acceptor groups shows intramolecular CT emission although its structure is fixed to a planar position [36]. In this case, the original state of the CT emission is not TICT-type. Therefore, common explanation for a problem to obtain remains unresolved.

Measurements and analysis of laser-induced fluorescence excitation and single vibronic dispersed-fluorescence spectra of DMAP, MDMAP and TMAP in supersonic jets are now in progress in our laboratory to elucidate the mechanism of CT state formation more clearly. The determination of the detailed structure of these compounds by high resolution spectroscopy or electron diffraction technique is also planned. The results of these experiments will be reported in separate papers in future.

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