Hydrogen Bond Formations of 1-Aminoanthracene in the Ground and Excited Electronic States with Protic Solvent Molecules#

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The absorption and fluorescence spectra of 1-aminoanthracene (AA) in various solvents have been compared with those of 1-dimethylaminoanthracene (DMAA). This comparison has demonstrated that the amino group of AA in the ground electronic state acts as a proton-acceptor to form the A-type hydrogen bond with alcohol, while that of AA in the excited electronic state acts as a proton-donor to form the B-type one. In the cyclohexane–ethanol mixed solvent, the solute–solvent configuration for the fluorescing excited state of AA changes with the ethanol concentration; it keeps the same type of hydrogen bond with ethanol as that (A-type) in the ground electronic state in the lower ethanol concentrations up to 0.2% and exhibits an intramolecular-like rearrangement of the A-type hydrogen bond into the B-type one in the ethanol concentration range of 0.2—1%. This hydrogen bond rearrangement occurs in cooperation with a bulk reorientation of solvent molecules in the range of 1—100%. AA forms the hydrogen-donor-acceptor-type excimer in the nonpolar fluid matrix of MP (a 1 : 1 mixed solvent of methylcyclohexane and isopentane) at low temperature.

The electronic spectra of the aromatic compounds with the amino substituent have been reported to exhibit a characteristic spectral behavior in protic solvents which is different from that in aprotic solvents.[1—6] Sarpal and Dogra[3] have found that the absorption and fluorescence spectra of the amino substituted aromatic compounds in protic solvents are shifted depending on both the hydrogen-bonding ability and the polarity of the solvent, while those in aprotic solvents are simply red-shifted with increasing solvent polarity. Meech, O'Connor, and Phillips[7] have, however, considered that such a specific solute–solvent interaction as solute–solvent hydrogen bond has no significant contribution to the emission-spectral shift of 1-aminonaphthalene in polar solvents, the main contributors being an excited-state intramolecular reorganization of the amino substituent and a bulk relaxation of the solvent dipoles about the solute excited-state dipole moment.

1-Aminoanthracene (abbreviated hereafter as AA) emits an intense yellowish-green fluorescence. Many investigators have studied the photophysical nature of the absorption and emission spectra of AA.[8—15] Suzuki and Baba[8] have found that the lowest-frequency absorption band of AA in the isopentane–methylcyclohexane mixed solvent is markedly shifted to the red on cooling to liquid-nitrogen temperature in the presence of triethylamine. They have interpreted this marked red shift as due to the cooperation of the hydrogen bonding, which emerges between AA and triethylamine, and the solvent effect.

In this investigation we have measured the absorption and fluorescence spectra of AA and 1-dimethylaminoanthracene (abbreviated as DMAA) in various solvents to demonstrate the importance of specific solute–solvent interactions via the hydrogen bond in the ground and excited electronic states. In particular, the absorption and fluorescence spectra of AA and DMAA in the cyclohexane–ethanol mixed solvent have been measured at various ethanol concentrations to clarify the specific intermolecular relaxation process for the excited state of the solute hydrogen-bonded by solvent. In addition, we have studied an excimer formation of AA in a nonpolar fluid matrix at low temperature.

Experimental

Commercially available AA (Aldrich Chemical Company Inc.) was recrystallized three times from a 1 : 1 mixed solvent of ethanol and water after removal of the impurities in the sample solution

Dedicated to Dr. Yoshie Tanizaki, Professor Emeritus from Tokyo Institute of Technology, on the occasion of his 77th birthday.

by use of active charcoal. DMAA was synthesized as described,[16] its purity check and identification being performed by thin-layer chromatography and mass spectrometry. Methanol (Wako, guaranteed) was purified by distillation. Cyclohexane (Wako, guaranteed) was distilled after removal of benzene through a silica gel column. Diethyl ether (Wako, guaranteed) was dehydrated with a molecular sieve (Wako, 3A 1/16), refluxed with addition of sodium hydroxide, refluxed over sodium, and finally distilled. Isopentane (Wako, guaranteed) was distilled after reflux as for cyclohexane and removal of impurities through a silica gel column. Commercial ethanol (Wako, guaranteed), acetonitrile (Wako, spectrograde), and methylcyclohexane (Wako, spectrograde) were used as received.

A Shimadzu UV-360 spectrophotometer and a Hitachi F3010 fluorophotometer, both equipped with a cryostat, were used for the measurements of electronic absorption and fluorescence spectra, respectively.

Results and Discussion

Solute-Solvent Interaction in Ground Electronic State. Figures 1a and 1b show the electronic absorption spectra of AA and DMAA in various solvents at room temperature. The most remarkable feature in Fig. 1a is that the first π–π^* band peak of AA in methanol is unshifted from that in cyclohexane; in contrast to that, the one in diethyl ether is most red-shifted. Considering that methanol is very polar and diethyl ether is the least polar, except for cyclohexane, among the solvents used here, as judged by relative dielectric constant (See Table 1), the above spectral feature is just opposite to the usual spectral shift of the π–π^* band due to solvent polarity. This phenomenon may be explained by some specific solute–solvent interaction mechanism, i.e., by the solute–solvent interaction via the hydrogen bond described below.

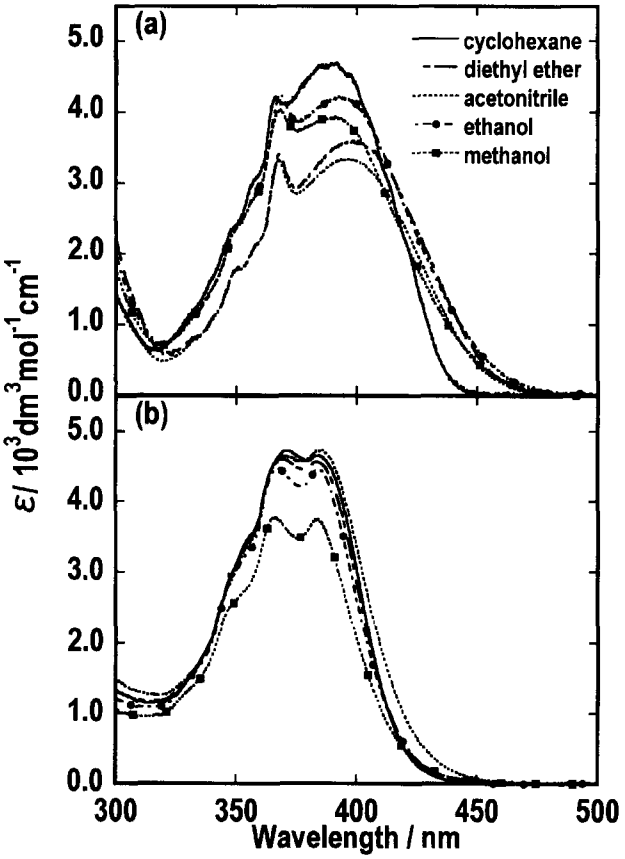


Fig. 1. The electronic absorption spectra of (a) AA and (b) DMAA in various solvents at room temperature.

Table 1. Relative Dielectric Constants of Solvents

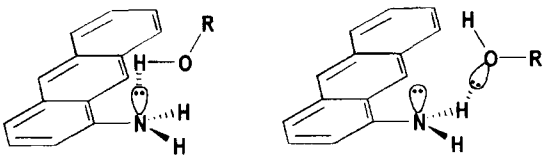
Solvent	Relative dielectric constant
Cyclohexane	2.0152
Diethyl ether	4.197
Ethanol	24.55
Methanol	32.6
Acetonitrile	35.94

The spectral feature in diethyl ether (Fig. 1a) is explained as follows. The oxygen atom of diethyl ether forms a hydrogen bond with the hydrogen atom of the amino group of AA. This hydrogen bond formation leaves a partial negative charge on the amino group to strengthen the migration ability of the p_π lone pair electrons of the amino group toward the aromatic ring of AA, inducing the largest red shift of the first π–π^* band of AA in diethyl ether.

The spectral feature in methanol (Fig. 1a) is explained as a result of cancellation of the solvent polarity effect and the solute–solvent hydrogen-bonding effect. Two possible structures A and B are shown below for the hydrogen bond formed between AA and alcohol (Chart 1). Structure B is equivalent to the hydrogen bond formed between AA and diethyl ether described above. In structure A, the p_π lone pair orbital on the amino group of AA is hydrogen-bonded to the hydrogen atom of alcohol, weakening the migration ability of the p_π lone pair electrons toward the aromatic ring of AA to induce the blue shift of the first π–π^* band of AA. The first π–π^* band of AA is expected to be red-shifted due to the solvent effect of a higher polar solvent methanol. This expected red shift happens to be cancelled by the blue shift of the band concerned, which is caused by the A-type hydrogen bond formation between AA and methanol.

The first band of AA in a less polar solvent ethanol is red-shifted from that in a more polar solvent methanol (Fig. 1a). This may be due to that an incomplete cancellation of the solvent polarity effect and the solute–solvent hydrogen-bonding effect just described above occurs for the case of AA in ethanol. That is, in the case of AA in ethanol having a weaker ability to donate a proton than methanol, the solvent polarity effect is considered to outweigh the solute–solvent hydrogen-bonding effect.

The above discussion would demonstrate that the amino



structure A
amino group: hydrogen acceptor
alchol: hydrogen donor

structure B
amino group: hydrogen donor
alchol: hydrogen acceptor

Chart 1.

group of AA in the ground electronic state acts as a proton-acceptor to form the A-type hydrogen bond with a protic solvent molecule such as alcohol. A further proof for this hydrogen bond formation is given from Figs. 2a and 2b, which show the absorption spectra of AA and DMAA in cyclohexane–ethanol mixed solvents at various concentration ratios. One can see from Fig. 2 that AA and DMAA both exhibit an isosbestic point over the concentration range of ethanol. This indicates that there exists an equilibrium between two light-absorbing chemical species, the one being the solute itself (AA or DMAA) and the other the solute hydrogen-bonding with ethanol. Since the dimethylamino group of DMAA cannot act as a proton-donor, the B-type hydrogen bond is ruled out from being common to AA and DMAA hydrogen-bonding with ethanol. Thus, it is further demonstrated from Fig. 2 that both AA and DMAA in the ground electronic state form the A-type hydrogen bond with ethanol in the mixed solvent.

It is noted from Fig. 1b that the peak positions for the first π–π^* band of DMAA in various solvents are almost invariant. Two reasons for this can be pointed out. First, the steric hindrance of the bulky dimethylamino group distorts the alignment of the p_π lone pair orbital on the dimetylamino group away from parallel to the p_π orbitals on the aromatic carbon ring of AA to weaken the conjugation ability of p_π lone pair orbital and the migration ability of the p_π lone pair electrons toward the aromatic ring, which in turn reduces both the solvent polarity and solute–solvent hydrogen-bonding effects described above. Second, DMAA does not form the B-type hydrogen bond with diethyl ether.

Solute–Solvent Interaction in Excited Electronic State. The fluorescence spectra of AA (Fig. 3a) and DMAA (Fig. 3b) in various solvents show much larger bathochromic shifts with increasing solvent polarity than the corresponding absorption spectra in Fig. 2, implying larger Stokes shifts with increasing solvent polarity; those in cyclohexane exhibit vibrational structure while those in other solvents are broad. These findings suggest that the Franck–Condon (abbreviated as FC) excited states of AA* and DMAA* in cyclohexane relax intramolecularly to fluorescing states (denoted as quasi-FC states) and these quasi-FC states fluoresce without any intermolecular relaxation, while those in other solvents relax to other fluorescing states via some intermolecular relaxation processes dependent on the solvent polarity. The energy difference between the fluorescing state in cyclohexane and those in other solvents is the stabilization energy due to the intermolecular relaxation process, whose magnitude is related to the extent of the red-shift of the fluorescence band in other solvents compared with that in cyclohexane.

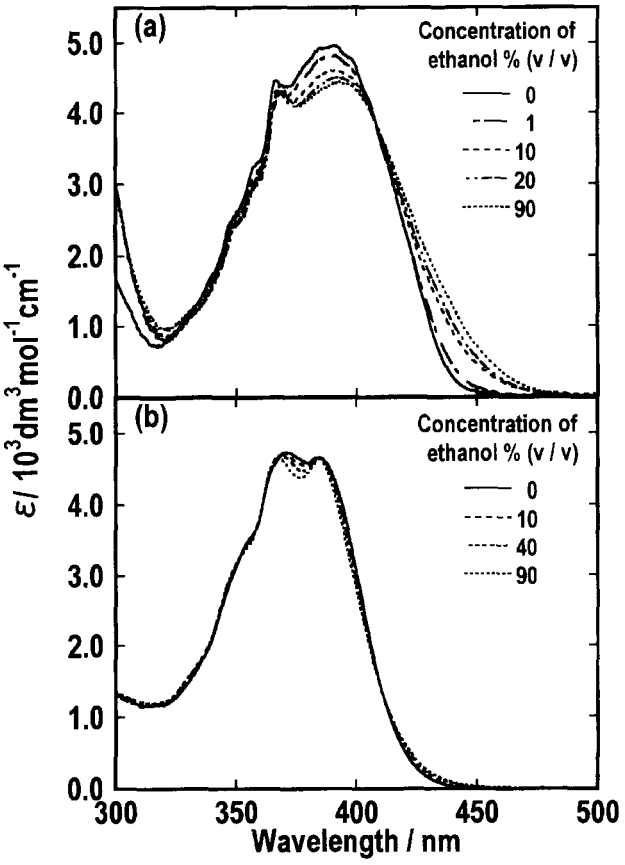


Fig. 2. The electronic absorption spectra of (a) AA and (b) DMAA in cyclohexane–ethanol mixed solvents at various mixing ratios.

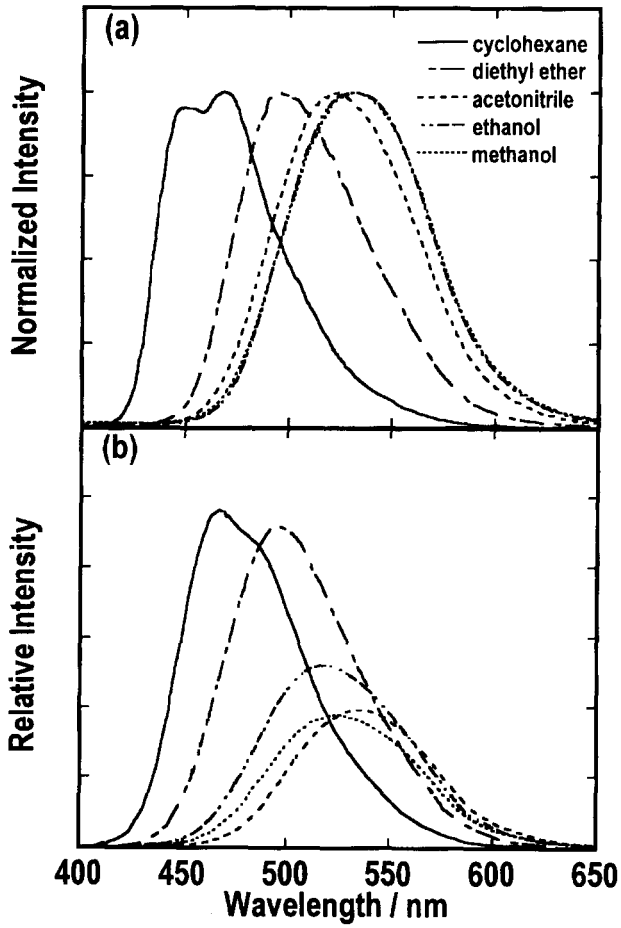


Fig. 3. The fluorescence spectra of (a) AA and (b) DMAA in various solvents at room temperature.

The magnitude of the stabilization energy or of the red shift of the fluorescence band is seen from Fig. 3 to be approximately proportional to the solvent polarity; it increases in the order of diethyl ether < ethanol < methanol < acetonitrile for DMAA* (Fig. 3b) and diethyl ether < acetonitrile < ethanol ≈ methanol for AA* (Fig. 3a). According to the relative dielectric constants of solvents in Table 1, the above order of increasing magnitude of bathochromic band shifts for DMAA* in various solvents is considered to be in fair proportion to polarities of solvents. Thus the intermolecular relaxation processes for DMAA* can be considered to be simply induced by a solvent molecule reorientation due to dipole (solvent)–dipole (DMAA*) interaction. The reversed order of acetonitrile < alcohol for AA* reflects that, in the case of AA* in alcohol, a specific relaxation process is taking place accompanying some extra structural change to a more stable solute–solvent configuration in which the AA* molecule in the fluorescing excited state is specifically interacting with the alcohol molecule. Taking into account that this specific interaction causes an enhanced red shift of the fluorescence band of AA* and is not able to occur between DMAA* and alcohol, we propose that the B-type hydrogen bond is formed between fluorescing AA* and alcohol. This proposal, coupled with the previous demonstration that AA in the ground electronic state forms the A-type hydrogen bond with alcohol, claims that the FC excited state of AA* forming the A-type hydrogen bond with alcohol is forced to relax into fluorescing AA*, forming the B-type hydrogen bond with alcohol. That is, it is proposed that the hydrogen bond rearrangement of A-type into B-type is taking place in the course of a specific relaxation process for AA* in alcohol.

We want to know in more detail how the above-described hydrogen bond rearrangement and the solvent molecule reorientation are taking place in the course of the specific relaxation process for AA* in alcohol. So we have investigated the dependence of the specific relaxation process on the ethanol concentration or the polarity of the cyclohexane–ethanol mixed solvent by measuring the fluorescence spectra of AA* along with DMAA* in that mixed solvent at various concentration ratios; the spectra are seen in Figs. 4a and 4b, respectively. All the excitation spectra of AA and DMAA in the cyclohexane–ethanol mixed solvent have almost completely reproduced the corresponding absorption spectra in Figs. 2a and 2b, respectively. Judging from apparent band shapes, we observe at least three types of fluorescence spectra, which correspond to the ethanol concentrations of 0, 0.2, and 1%, in Fig. 4a, while we find only two types, corresponding to the ethanol concentrations of 0 and 4%, in Fig. 4b. This implies that there exist at least three fluorescing chemical species for AA* in the mixed solvent, but only two fluorescing ones for DMAA* in the mixed solvent. In accordance with this, the fluorescence spectra of AA* and DMAA* in the mixed solvent are, as evident from Fig. 4, strange enough to exhibit respectively complex three-stage and two-stage spectral changes depending on ethanol concentrations. In contrast, the absorption spectra of AA and DMAA in the same mixed solvent exhibit simple spectral changes show-

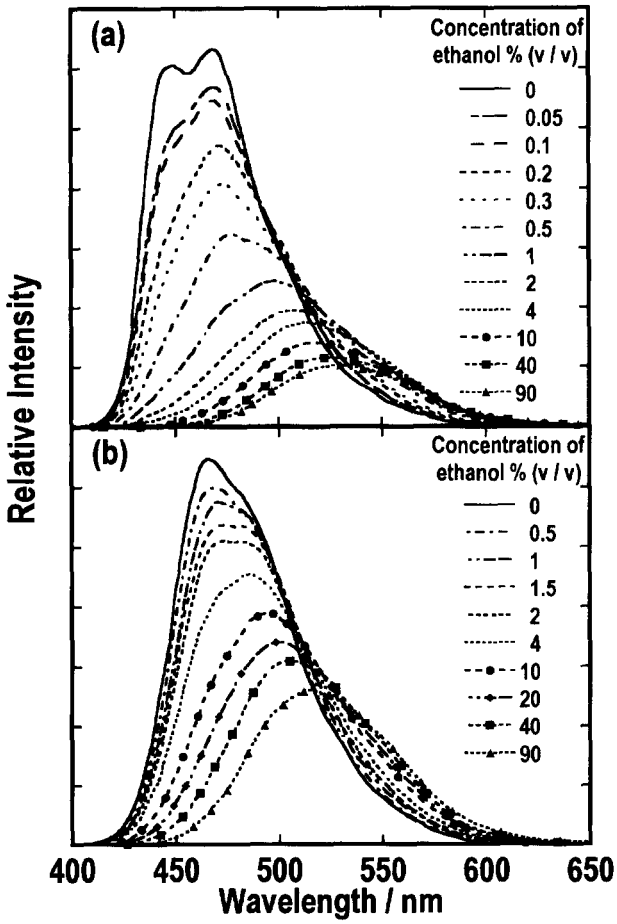


Fig. 4. The fluorescence spectra of (a) AA and (b) DMAA in cyclohexane–ethanol mixed solvents at various mixing ratios.

ing isosbestic points over the whole ethanol concentration ranges with slight band shifts (Fig. 2). In the first stage spectral changes in the lower ethanol concentration ranges of 0—0.2% (Fig. 4a) and 0—1.5% (Fig. 4b), both the fluorescence spectra of AA* and DMAA* show isoemissive points at 493 and 500 nm with slight band shifts. These observations indicate that, at lower ethanol concentrations just mentioned, there exists an equilibrium between two fluorescing chemical species, the one being the quasi-FC-excited solute itself (AA* or DMAA*) existing in cyclohexane and the other the electronically-excited solute hydrogen-bonding with ethanol. Since AA and DMAA in the ground electronic state are both demonstrated to form the A-type hydrogen bond with ethanol in the mixed solvent, the latter would be the quasi-FC-excited solute (AA* or DMAA*) forming the A-type hydrogen bond with ethanol in the mixed solvent. It has, therefore, been demonstrated that, at lower ethanol concentrations, the quasi-FC state of AA* fluoresces without any intermolecular relaxation process, keeping the same type of hydrogen bond as that (A-type) of AA in the ground electronic state. In the second (0.2—1% ethanol concentration) and third stage (1—100% ethanol concentration) spectral changes in Fig. 4a, and in the second stage (1.5—100% ethanol concentration) one in Fig. 4b, the fluorescence spectra of AA* and DMAA*

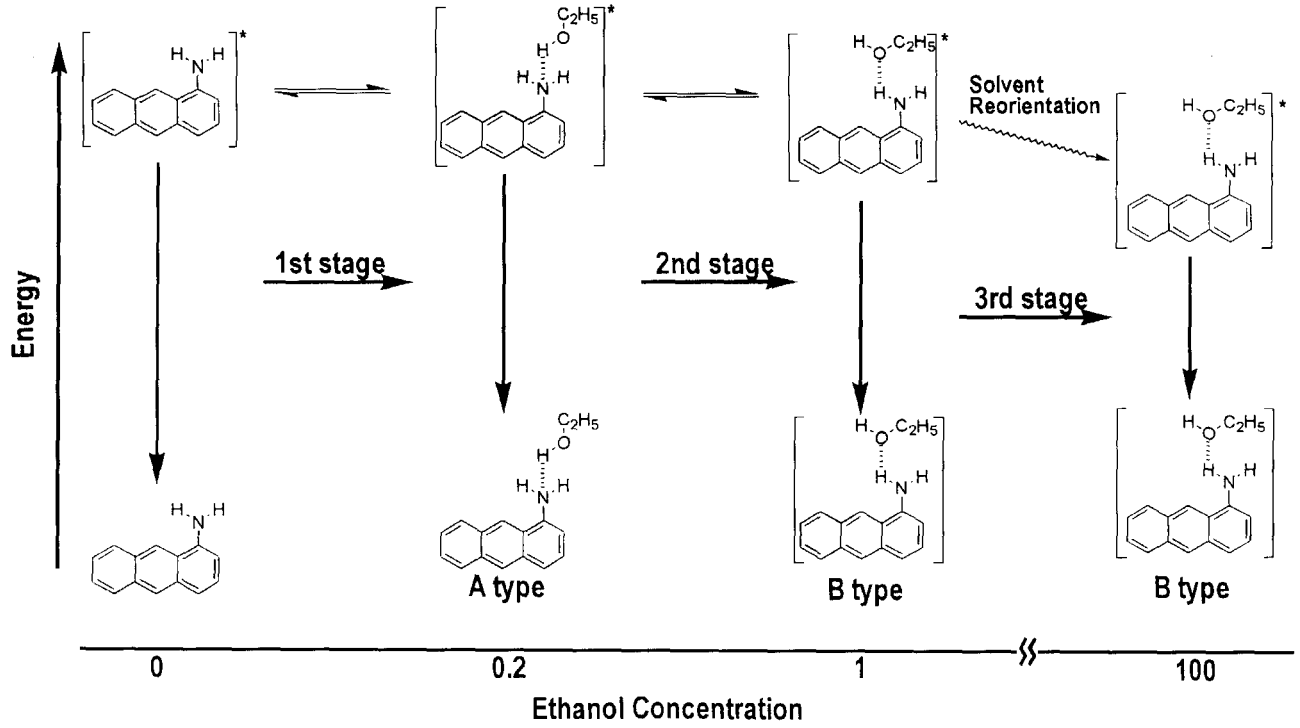


Fig. 5. A proposed mechanism for the emission of AA in the mixed solvent of cyclohexane and ethanol.

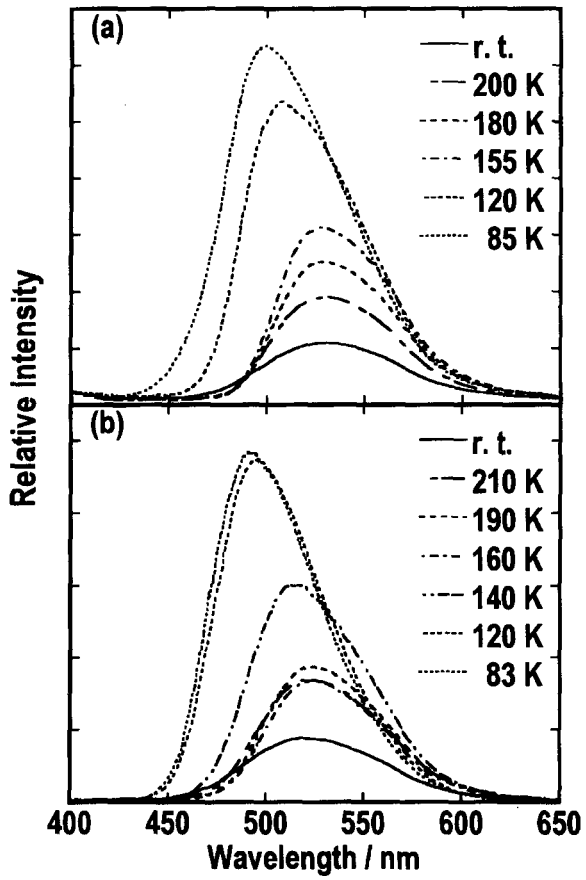


Fig. 6. The temperature dependence of the fluorescence spectra of (a) AA and (b) DMAA in ME (a 1 : 1 mixed solvent of methanol and ethanol).

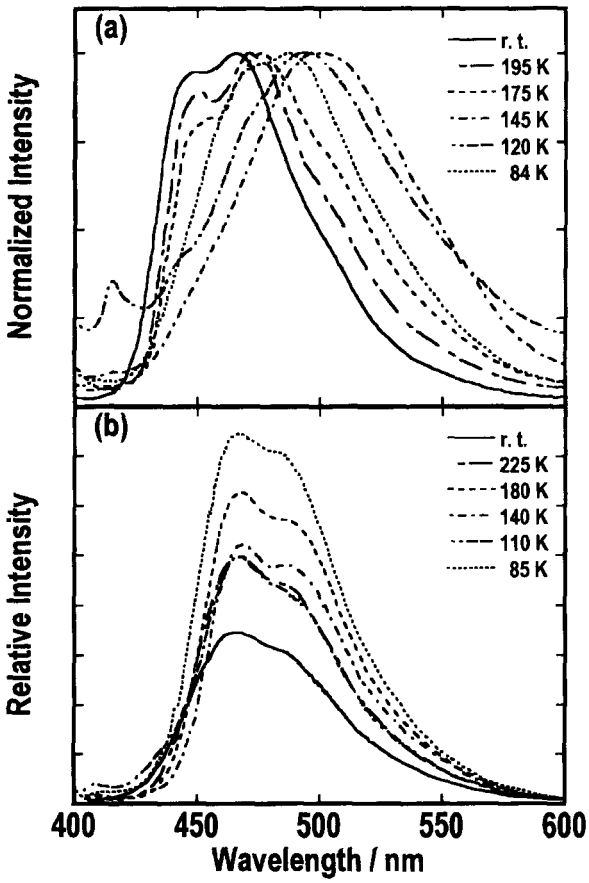


Fig. 7. The temperature dependence of the fluorescence spectra of (a) AA and (b) DMAA in the nonpolar fluid (until down to 145 K) matrix of MP (a 1 : 1 mixed solvent of methylcyclohexane and isopentane).

exhibit no isoemissive point and show bathochromic shifts which become larger with increasing ethanol concentrations. This observation suggests that the extra hydrogen bond rearrangement is a complex process exhibiting no equilibrium between two fluorescing chemical species. It is noteworthy that the third stage spectral change for AA* in Fig. 4a behaves just like the second stage one for DMAA* in Fig. 4b, both keeping broad band shapes. This yields the following two claims: First, the second stage spectral change for AA* in Fig. 4a corresponds mainly to the extra hydrogen bond rearrangement process, which does not appear for the case of DMAA*, i.e., to the process that the quasi-FC state of the A-type AA* rearranges directly into the B-type fluorescing AA*; second, the third stage one to the solvent molecule reorientation process, i.e., to the process that the fluorescing AA* of B-type emerged after the second stage relaxes into a more stable one via the solvent molecule reorientation. That is, the intermolecular relaxation process for AA* in the mixed solvent is considered to be triggered by the extra hydrogen bond rearrangement process, followed by the solvent molecule reorientation process.

According to the above discussion, the mechanism for the emission of AA* in the mixed solvent of cyclohexane and ethanol is considered to be dependent on the ethanol concentrations, as proposed in Fig. 5. The hydrogen bond rearrangement concerned is considered to be an intramolecular reorganization, which is made possible by small changes in the solute environment and begins to emerge at relatively lower ethanol concentrations, while the solvent molecule reorientation is a bulk relaxation developing at higher ethanol concentrations. The driving force for the hydrogen bond rearrangement originates from the fact that the electronic transition of AA induces a significant decrease in the π-electron density on the nitrogen atom of the amino group and results in lower proton-accepting and higher proton-donating abilities of the amino group of AA*.

The temperature dependences of the fluorescence spectra of AA and DMAA in ME (a 1 : 1 mixed solvent of methanol and ethanol) are similar to each other (Fig. 6). That is, while both the fluorescence spectra of AA and DMAA in ME are scarcely shifted on cooling from 298 to 155 K, they are gradually blue-shifted with no isoemissive point on going from 155 to 85 K. This finding, along with the observation that both the excitation spectra of AA and DMAA in ME are unshifted on cooling down to 85 K and reproduce approximately the respective absorption spectra, can be interpreted to mean that the blue shifts in question are due to the fact that the bulk relaxation of the solvent molecule reorientation is continuously restricted because of decreasing fluidity of ME on cooling down to 85 K. This interpretation is in accordance with the proposed emission mechanism in Fig. 5 and enables us to understand the fact that the fluorescence spectrum at 85 K in Fig. 6a coincides in peak position with that at 1% ethanol concentration in Fig. 4a, both corresponding to the final stage of the intramolecular-like hydrogen bond rearrangement process, i.e., the initial stage of the solvent molecule reorientation process. The same interpretation as this one was given for the blue shift of the fluorescence spectrum of 1-aminonaphthalene in polar solvent at lower temperatures.[7]

Solute–Solute Interaction in Excited Electronic State. AA has properties of both hydrogen-donor and hydrogen-acceptor; in contrast to that, DMAA has properties of hydrogen-acceptor alone. Therefore, measuring the fluorescence spectra of AA in a nonpolar fluid medium at low temperatures, we have the possibility to observe the fluorescence from the hydrogen-donor-acceptor-type excimer, while there is no possibility to observe such an excimer fluorescence for DMAA.

Figure 7 shows the fluorescence spectra of AA and DMAA in the nonpolar fluid (until down to 145 K) matrix of MP (a 1 : 1 mixed solvent of methylcyclohexane and isopentane) measured at various low temperatures. It is evident from

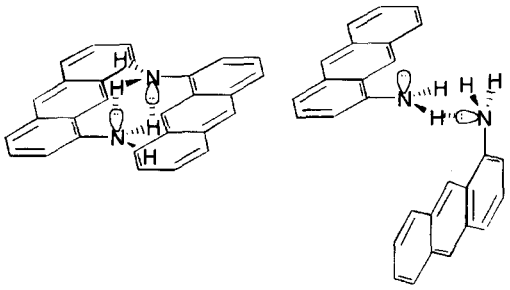


Chart 2.

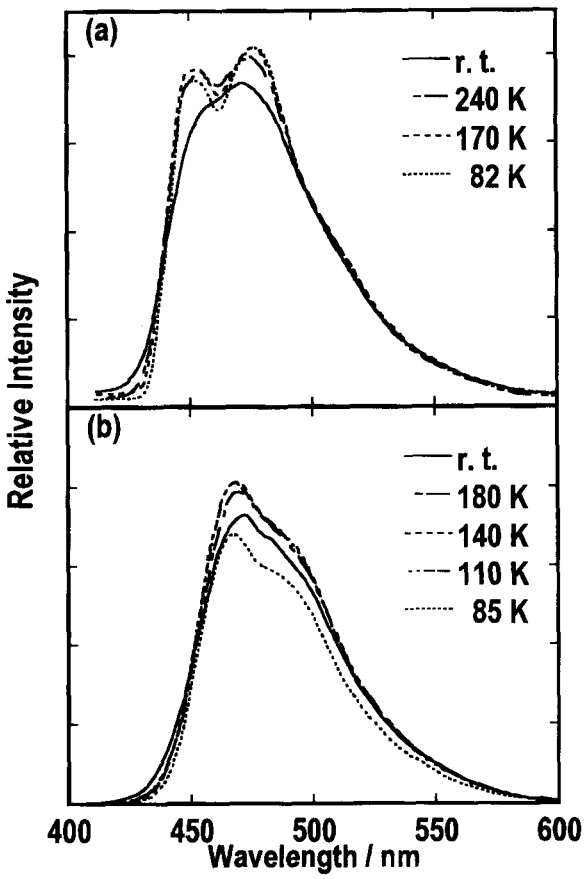


Fig. 8. The temperature dependence of the fluorescence spectra of (a) AA and (b) DMAA in the polyethylene film.

this figure that AA* in MP exhibits a vibronically structured fluorescence spectrum at room temperature and a largely red-shifted broad one at 145 K, while DMAA* in MP shows no such specific change in the fluorescence spectrum on cooling, the vibronically structured band shape and band position being unchanged (Chart 2). Coupled with the observation that both the excitation spectra of AA and DMAA in MP exhibit no specific change on lowering the temperature and reproduce approximately the respective absorption spectra, the largely red-shifted broad fluorescence band observed for AA* in MP at 145 K is considered to be assigned to the above-mentioned excimer [AA–AA]* formed from AA* interacting with AA. The structure of this excimer [AA–AA]* is considered to be as shown below. This structure includes both the A- and B-type hydrogen bonds as indicated.

No specific temperature dependence is observed for both the fluorescence bands of AA* (Fig. 8a) and DMAA* (Fig. 8b) in the polyethylene film which is a nonpolar rigid medium. The reason is as follows: since solute molecules disperse monomolecularly in the polyethylene film, no interaction between solute molecules can occur even at low temperatures.

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