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Multi-component emission spectra in toluene–diamine systems

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Abstract

The fluorescence spectra of intermolecular and intramolecular toluene–amine and toluene–diamine systems were measured in THF. The fluorescence spectrum of toluene–*N*,*N*,*N*′,*N*′-tetramethyl-1,4-butanediamine (TMBD) mixtures was decomposed into four component bands with the shortest-wavelength band (band A) assigned to the excited toluene. Of the remaining bands, the short-wavelength (band B), the middle-wavelength (band C) and the long-wavelength band (band D) were assigned to a locally excited amine chromophore, an exciplex between toluene and an amino group, and an intramolecular excimer between two amino groups of the diamine, respectively. The fluorescence spectrum of toluene–TMBD mixtures in THF obtained upon nanosecond laser excitation showed a slight red shift with the time indicating that the contribution of band D increased with time. A reaction scheme and energy level diagram were proposed for this system. In toluene–dimethylethylamine mixtures bands A–C were observed. While for 4-phenyl-1-*N*,*N*-dimethylaminobutane bands A–C were also observed, for 3-phenyl-1-*N*,*N*-dimethylaminopropane only band C was observed. In toluene–*N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine mixtures, only bands A and D were observed, and for *N*,*N*,*N*′-trimethyl-*N*′-3-phenylpropyl-1,3-propanediamine bands C and D were observed. Emissions from intramolecular exciplexes and excimers in which two chromophores are separated by three methylene groups were predominantly observed.

Keywords: Fluorescence; Diamine; Exciplex; Excimer; Multi-component spectrum

1. Introduction

Several aromatic compounds show fluorescence quenching and exciplex emission in the presence of *tertiary* amines [1]. With naphthylalkylamines [2] and anthrylalkylamines [3] intramolecular exciplex formation has been observed. Formation of intramolecular exciplexes between phenyl and amino groups has also been observed in some ω-phenyl-α-(*N*,*N*-dimethylamino)alkanes [4–8]. Schryver et al. observed that in THF the emission of 4-phenyl-1-*N*,*N*-dimethylaminobutane (4-PDAB) at room temperature consisted of a broad structureless band at about 26,880 cm^{-1} and a shoulder at 35,000 cm^{-1}. The emission at 35,000 cm^{-1} was assigned to the toluene chromophore, and the broad band to the intramolecular exciplex and the locally excited state of the amino chromophore. The emission spectrum of 3-phenyl-1-*N*,*N*-dimethylaminopropane (3-PDAP) at room temperature consisted of a band with a maximum at 26,530 cm^{-1}; an emission from toluene chromophore was scarcely observed for this compound at room temperature. It was suggested that a back reaction occurred in which the exciplexes returns to the excited singlet state of the amine in these compounds. Interaction between an excited benzene and a ground-state saturated amine has been studied previously, and the formation of an exciplex and energy transfer from excited benzene to amine was observed in benzene–*N*,*N*-diethylmethylamine (DEMA) mixtures [9].

Intense fluorescence was observed for saturated *tertiary* amines in the excitation at the first absorption band [10–16]. Halpern et al. [17–20] investigated the structural effects on photophysical processes and intermolecular excimer formation in saturated *tertiary* amines. They also examined the fluorescence properties of members of the series $((CH_3)_2N(CH_2)_nN(CH_3)_2)$ and observed emission from an excited monomer and an intramolecular excimer for $n = 3$ (*N*,*N*,*N*′,*N*′-tetramethylpropane-1,3-diamine) and $n = 4$ (*N*,*N*,*N*’,*N*’-tetramethylbutane-1,4-diamine) [21]. Although there has been a considerable amount of work carried out on the emission of aromatic compound–saturated *tertiary* amine systems as mentioned above, almost no attention has been paid to the emission of aromatic compound–saturated diamine systems. As it is expected that many emission bands can be observed in intra- and intermolecular toluene and diamine systems, it would be interesting to know which bands are actually observed. In this study, spectroscopic properties

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of toluene–diamine mixtures and *N*,*N*,*N*′-trimethyl-*N*′-3-phenylpropyl-1,3-propanediamine (PPDA) were investigated in THF under conditions of steady-state illumination and pulsed laser excitation.

2. Experimental

N,*N*-Dimethylethylamine (DMEA), *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (TMPD) and *N*,*N*,*N*′,*N*′-tetramethyl-1,4-butanediamine (TMBD) were obtained from commercial sources (reagent grade) and used after drying with potassium hydroxide and trap-to-trap distillation. Toluene (T) was of reagent grade and purified by distillation over molecular sieves (4A 1/16). 3-PDAP and 4-PDAB were prepared from 3-phenylpropylamine and 4-phenylbutylamine, respectively, according to the method of Halpern [8]. ^{1}H NMR confirmed their structures and the products were purified by vacuum distillation. PPDA was prepared from *N*,*N*,*N*′-trimethyl-1,3-propanediamine (TMPDA) and 3-phenyl-propionaldehyde (PPA). To a solution containing TMPDA (4.1 g, 34 mmol) in 20 ml CH_2Cl_2, HCl (13.5 mmol, 5.5 ml of a 2.5 M solution in CH_3OH) was added, followed by PPA (1.0 g, 6.7 mmol), $NaBH_3CN$ (0.39 g, 5.9 mmol), and Aliquat 336 (1.8 g, 4.5 mmol). Approximately, 1 g of 4A molecular sieves was added, and the mixture was stirred at room temperature for 48 h. The mixture was centrifuged, the mother liquor acidified, and the solvent removed on a rotary evaporator. The residue was taken up with 10 ml of H_2O and extracted with 2-methylbutane. The extract was dried (with KOH) and after the solvent was removed, dried again (with CaH_2) and purified by vacuum distillation. The structure was confirmed by ^{1}H NMR. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.625 (quintet, $J = 7.6$ Hz, 2H), 1.789 (quintet, $J = 7.7$ Hz, 2H), 2.168 (singlet, 3H), 2.209 (singlet, 6H), 2.266 (triplet, $J = 7.8$ Hz, 2H), 2.330–2.379 (multiplet, 4H), 2.616 (triplet, $J = 7.8$ Hz, 2H), 7.158–7.191 (multiplet, 3H), 7.271 (triplet, $J = 7.8$ Hz, 2H). THF was of spectroscopic grade and was used as supplied.

The emission spectra were measured by a Simadzu spectrofluorophotometer, model RF 1500 (bandpass, 10 nm), at several temperatures. The wavelength dependence of the sensitivity of the detection system was determined using standard solutions of phenol [22], 2-naphthol [23] and *N*,*N*-dimethyl-*m*-nitroaniline [23]. Correction for wavelength dependence of the sensitivity of the detection system was found to be unnecessary in practice between 280 and 550 nm. Excitation was effected at 270 nm in each case, a wavelength at which the radiation is nearly exclusively absorbed by toluene (or phenyl group). The concentrations of 3-PDAP, 4-PDAB and PPDA were kept around 10^{-4} mol dm^{-3} to avoid intermolecular interaction. The solutions were degassed by four freeze–pump–thaw cycles. The temperature of the solution in the cell was varied from 293 to 343 K by circulating water around the cell. Absorption spectra were measured at room temperature by means of a Hitachi spectrophotometer, model U-3200.

For time-resolved fluorescence measurements, a pulsed Nd:YAG laser (Spectron SL803, $\lambda_{ex} = 266$ nm) was used. The time-resolution was about 10 ns. Fluorescence was detected at a perpendicular angle to the laser beam with a photomultiplier (Hamamatsu R-928). A Spex Minimate monochromator (20 cm in focal length: $\Delta\lambda = 20$ nm with 5 mm slit) was incorporated into the detection system, and the photomultiplier was placed behind the exit slit of the monochromator. Raw signals from the detector were first amplified by means of a PAR model 115 preamplifier. For the time-resolved measurements, the amplified signals were treated with a digital oscilloscope (Tektronix TDS 320) and the digitized output was stored and analyzed on a personal computer.

3. Results

3.1. Absorption spectra

Fig. 1 shows the absorption and emission spectra of THF solutions of toluene, DMEA and 4-PDAB. The absorption spectrum of PDAB is comparable to that of an equimolar mixture of toluene and DMEA, and shows no significant ground-state interaction between phenyl and amino groups in 4-PDAB. The absorption spectra of 3-PDAP and PPDA also show no significant ground-state interaction between phenyl and two amino groups. The absorption spectra of toluene–DMEA, TMPD and TMBD mixtures in THF also show no significant ground-state interactions between two chromophores.

3.2. Emission spectra for intermolecular systems

The emission spectra by excitation at 270 nm of toluene in THF ($[T] = 1.0 \times 10^{-3}$ M) with DMEA at different

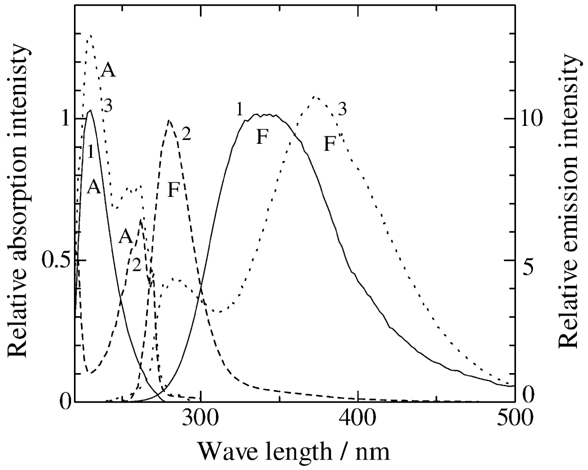

Fig. 1. Absorption (A) and emission (F) spectra of: (1) DMEA (1.0×10^{-3} M), (2) toluene (1.0×10^{-3} M) and (3) PDAB (1.0×10^{-3} M) in THF at room temperature.

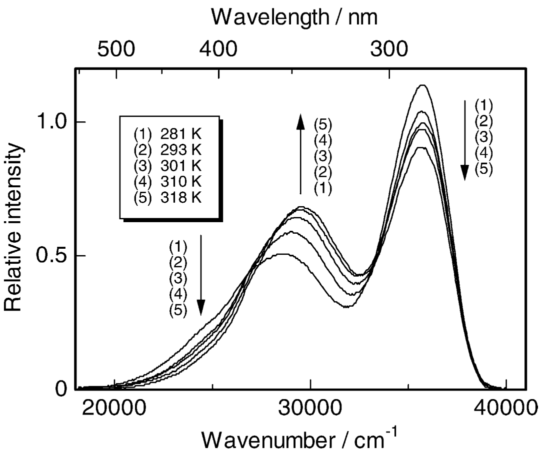

Fig. 2. Fluorescence spectra of a mixed solution of toluene (1.0×10^{-3} M) and DMEA (1.0×10^{-2} M) in THF at several temperatures, excited at 270 nm.

concentrations ([DMEA] = 0–5.0×10^{-2} M) showed that the emission intensity of toluene decreases and new emission bands appeared in a longer wavelength region and their intensities increased with increasing DMEA concentration. Fig. 2 shows the fluorescence spectra of a toluene–DMEA mixture in THF at several temperatures. As is shown in Fig. 2, the shape of the spectrum changed with temperature. When excited at 270 nm, a DMEA blank of equal concentration produced negligible emission. Since isosbestic points were not seen in these spectra, the spectrum seemed to consist of more than two component bands.

The emission spectra shown in Fig. 2 can be decomposed into three bands (bands A, B and C for short-, middle- and long-wavelength bands, respectively). Their shapes and positions are independent of temperature, but their relative intensities change with temperature. These findings indicate that the three bands can be ascribed to three different emitters and that their existence ratios change with temperature. The wavenumbers of the peaks and the half-widths of three bands are shown in Table 1. The table also shows the wavenumbers and the half-widths of the bands observed for pure DMEA, TMPD or TMBD.

Table 1
Wavenumbers of the peak (and bandwidths) of emission bands observed in THF (in 10^3 cm^{-1})[a]

System	Band A	Band B	Band C	Band D
DMEA		29.7 (5.1)		
TMPD				23.2 (5.8)
TMBD		29.0 (5.4)		23.5 (5.9)
Toluene–DMEA	35.7 (3.5)	29.6 (5.0)	26.8 (7.0)	
Toluene–TMPD	35.7 (3.4)			23.2 (5.8)
Toluene–TMBD	35.7 (3.5)	29.3 (5.4)	26.8 (6.2)	23.6 (6.0)
3-PDAP			26.7 (5.1)	
4-PDAB	35.1 (3.4)	29.4 (5.5)	26.0 (5.9)	
PPDA			27.4 (7.0)	23.6 (6.4)

[a] Bands A, B, C, and D are assigned to an excited toluene, an excited amine, an exciplex between phenyl and amino groups, and an excimer between two amino groups, respectively.

Halpern and Frye [9] obtained three similar emission bands in benzene–DEMA in THF, and assigned them to benzene fluorescence (the short-wavelength band), amine fluorescence (middle-wavelength band) and the emission from the exciplex formed between an excited benzene molecule and an amine molecule (the long-wavelength band). The results obtained in this study are very similar to those obtained in the benzene–DEMA system, and show the formation of exciplex between excited toluene and amine and the energy transfer from excited singlet toluene to amine through the exciplex.

As is shown in Fig. 1, the absorption spectrum of DMEA appears at shorter wavelengths than that of toluene. It is well known that amines have pyramidal ground states and planar or near planar excited states. Large Stokes shifts of *tertiary* amines indicate that S_0 and S_1 potential surfaces are considerably displaced from each other with respect to the out-of-plane bending coordinate [24]. Further, fluorescence of *tertiary* amines is considerably red shifted, and is much broader in THF relative to that nonpolar solvents [9,25]. Fluorescence of DMEA has a maximum at 340 nm in THF (longer than that of toluene), as shown in Fig. 1. These effects make the singlet energy transfer from T^* to DMEA possible, and the nonvertical nature of this transfer would be clarified by the role of the exciplex.

Fig. 3 shows the fluorescence spectra of a toluene–TMPD mixture in THF at several temperatures. The spectra reveal two emission bands. The wavenumbers of the peaks and the half-widths are shown in Table 1. Judging from their shapes and positions, the short-wavelength band was assigned to an excited toluene and the long-wavelength band to an intramolecular excimer of the diamine (see Table 1). This indicates that the singlet energy transfer occurs from the excited toluene to one of the amino groups of the diamine, because TMPD shows mainly an emission band from an intramolecular excimer in THF upon the excitation of one of the amino groups [21]. In the toluene–TMPD system, fluorescence of

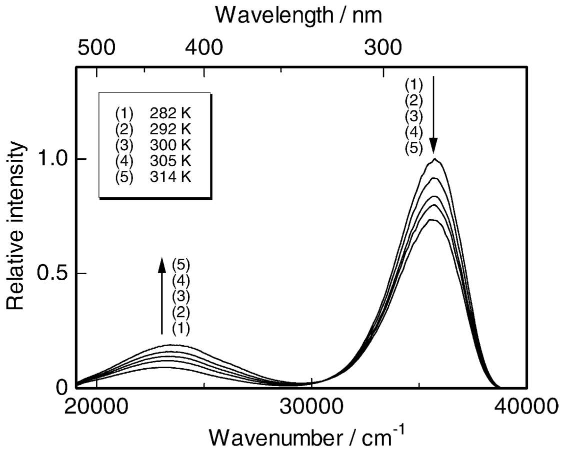

Fig. 3. Fluorescence spectra of a mixed solution of toluene (1.0×10^{-3} M) and TMPD (5.2×10^{-3} M) in THF at several temperatures, excited at 270 nm.

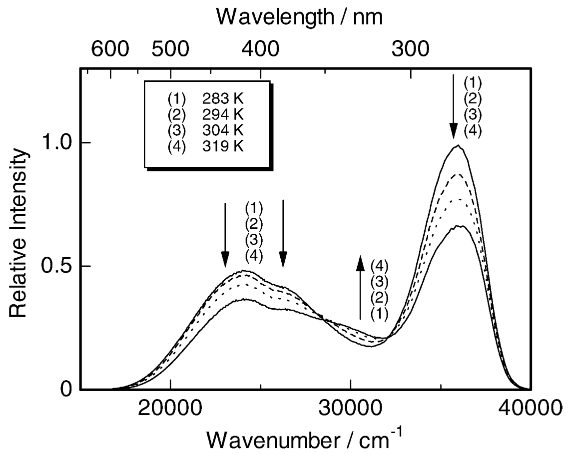

Fig. 4. Fluorescence spectra of a mixed solution of toluene (1.0×10^{-3} M) and TMBD (4.5×10^{-2} M) in THF at several temperatures, excited at 270 nm.

an amino group and the exciplex between toluene and amino groups were not observed.

Fig. 4 shows the fluorescence spectra of a toluene–TMBD mixture in THF at several temperatures. The shape of the spectrum changes with temperature. This indicates that the spectrum consists of several bands. The shortest-wavelength band is well separated and can be assigned to the fluorescence of toluene, like toluene–DMEA system. Fig. 5 shows a decomposition of the emission spectrum obtained by subtracting the toluene band from the total fluorescence spectra of the toluene–TMBD mixture at 294 K into three Gaussian curves. Their peak wavenumbers and half-widths are shown in Table 1. The spectra obtained at other temperatures could be also separated into four component bands. Their shapes and positions are independent of temperature, but their relative intensities change with temperature. The four emission bands are those from an excited toluene (band A), an excited amine (band B), an exciplex between toluene and one of the amino groups (band C) and an intramolecular excimer of diamine (band D). Therefore, in this system we could observe all of the possible emission bands.

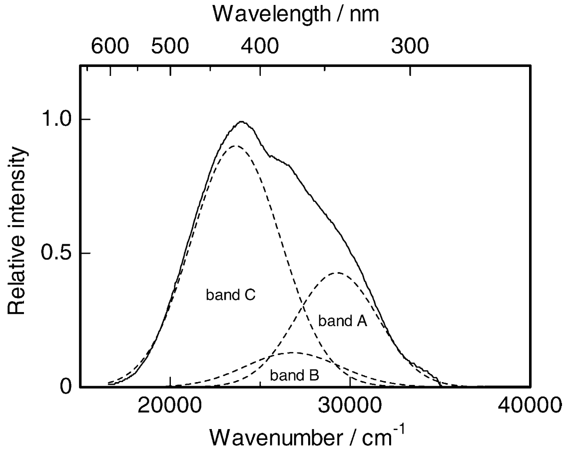

Fig. 5. Decomposition of the emission spectrum obtained by subtracting the toluene band for toluene–TMBD at 294 K into three Gaussian curves.

Upon the nanosecond laser excitation ($\lambda_{ex} = 266$ nm) of the toluene–TMBD mixture in THF at room temperature, broad emission spectra were obtained. Fig. 6 shows the time dependence of the spectral shape. The fluorescence spectrum of the toluene–TMBD system shows a slight red shift with time during the rise and decay of the spectrum (10–24 ns). The red shift of the spectrum can be explained by the increase in the contribution of band D with time, as discussed below.

3.3. *Emission spectra for intramolecular system*

The emission spectrum of 4-PDAB in THF ([4-PDAB] = 1.0×10^{-3} M, $\lambda_{ex} = 270$ nm) was found to change with temperature and to decompose into three component bands (Table 1). Three bands are assigned to the fluorescence of toluene, that of the amino group, and the emission from an intramolecular exciplex. When a 3-PDAP solution in THF ([3-PDAP] = 1.0×10^{-3} M) is excited at 270 nm, only an emission band at 375 nm was observed (the fluorescence

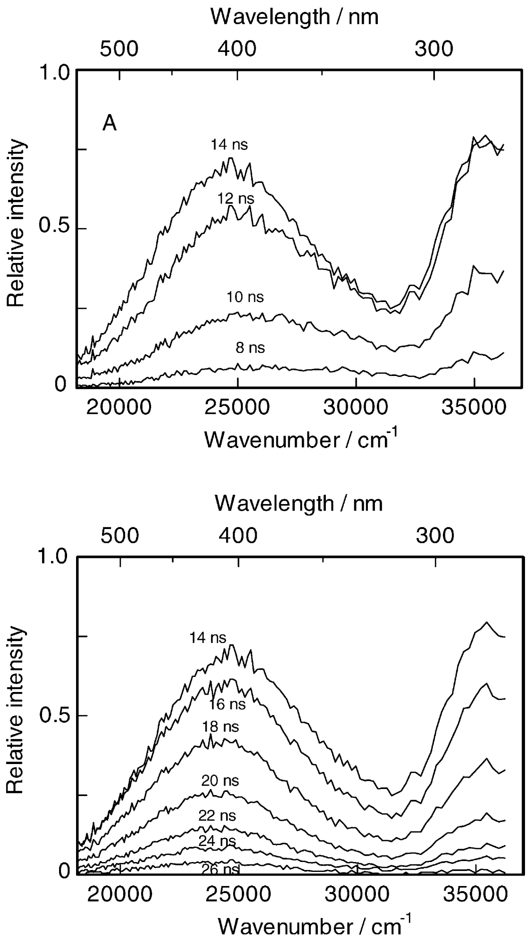

Fig. 6. Time dependence of the fluorescence spectral shape of a toluene (1.1×10^{-3} M)–TMBD (3.9×10^{-3} M) mixture following 266 nm excitation: A, rise and B, decay.

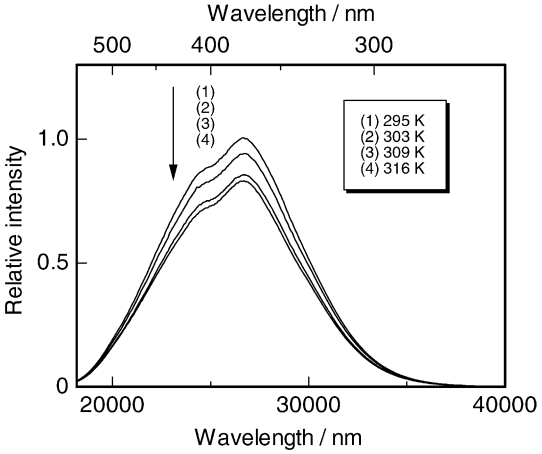

Fig. 7. Fluorescence spectra of PPDA (1.1×10^{-3} M) in THF at several temperatures, excited at 270 nm.

of toluene was scarcely observed). This band was assigned to the intramolecular exciplex (Table 1). These findings for 3-PDAP and 4-PDAB are consistent with the results observed at room temperature for these compounds by De Schryver and coworkers [6,7].

The emission spectra of PPDA in THF at several temperatures are shown in Fig. 7. The spectrum shape of PPDA did not change with temperature and could be decomposed into two Gaussian curves. Judging from their positions and shapes, these two bands were assigned to an intramolecular exciplex between phenyl and an amino group, and an intramolecular excimer between two amino groups (Table 1). The relative intensities of the bands were independent of temperature.

4. Discussion

As mentioned above, in the toluene–TMBD system four component bands were observed. The part of emission spectra between 16,000 and 33,000 cm^{-1} obtained at various times after excitation shown in Fig. 6 can be separated into three component bands whose shapes and positions are consistent with the bands B–D shown in Fig. 5. Fig. 8 shows the time dependence of the proportions of bands B–D to the sums of the intensities of these bands ($I_{\mathrm{total}} = I(\mathrm{band\,B}) + I(\mathrm{band\,C}) + I(\mathrm{band\,D})$); which are the integrated intensities of bands B, C and D, respectively). As is shown in Fig. 8, the intensity of band B decreases nearly parallel with that of band C, while the intensity of band D increases with time. These findings show that TMBD having an excited amino group, and the intramolecular exciplex may coexist in a near equilibrium, while the intramolecular excimer between two amino groups is produced with the consumption of these two excited species. To explain the experimental results obtained for this system, the following set of reactions was considered:

$$\mathrm{T} + h\nu \rightarrow \mathrm{T}^*, \quad I_0 \tag{1}$$

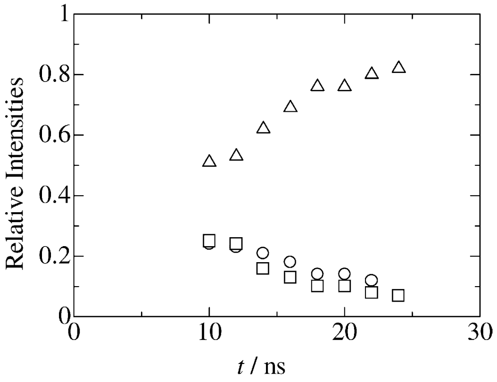

Fig. 8. Temperature dependence of the intensity ratios of band B (○), band C (□) and band D (△) to the total intensity ($I_{\mathrm{total}} = I(\mathrm{band\,B}) + I(\mathrm{band\,C}) + I(\mathrm{band\,D})$) for a toluene ($1.1 \times 10^{-3}$ M)–TMBD (3.9×10^{-3} M) mixture in THF.

$$\mathrm{T}^* \rightarrow \mathrm{T} + h\nu_{\mathrm{A}}, \quad k_{0\mathrm{r}} \tag{2}$$

$$\mathrm{T}^* \rightarrow \text{other reaction}, \quad k_{0\mathrm{n}} \tag{3}$$

$$\mathrm{T}^* + \mathrm{DA} \rightarrow \mathrm{TDA}^*, \quad k_1 \tag{4}$$

$$\mathrm{TDA}^* \rightarrow \mathrm{T} + \mathrm{DA} + h\nu_{\mathrm{C}}, \quad k_{2\mathrm{r}} \tag{5}$$

$$\mathrm{TDA}^* \rightarrow \text{other reaction}, \quad k_{2\mathrm{n}} \tag{6}$$

$$\mathrm{TDA}^* \rightleftarrows \mathrm{DA}^* + \mathrm{T}, \quad k_3, k_{-3} \tag{7}$$

$$\mathrm{DA}^* \rightarrow \mathrm{DA} + h\nu_{\mathrm{B}}, \quad k_{4\mathrm{r}} \tag{8}$$

$$\mathrm{DA}^* \rightarrow \text{other reaction}, \quad k_{4\mathrm{n}} \tag{9}$$

$$\mathrm{DA}^* \rightleftarrows \mathrm{DA}^{**}, \quad k_5, k_{-5} \tag{10}$$

$$\mathrm{DA}^{**} \rightarrow \mathrm{DA} + h\nu_{\mathrm{D}}, \quad k_{6\mathrm{r}} \tag{11}$$

$$\mathrm{DA}^{**} \rightarrow \text{other reaction}, \quad k_{6\mathrm{n}} \tag{12}$$

Here, T and DA denote toluene and TMBD, TDA* is the exciplex between toluene and TMBD, DA* and DA** are TMBD having an excited amino group and the intramolecular excimer between two amino groups. The following equations for the intensities of the emission bands were derived by a steady-state treatment based on the assumption that a fast equilibrium between TDA* and DA* is attained, as mentioned above:

$$\frac{I(\mathrm{band\,B})}{I(\mathrm{band\,C})} = \frac{k_{4\mathrm{r}}}{k_{2\mathrm{r}}}\frac{K_3}{[\mathrm{T}]} \tag{13}$$

$$\frac{I(\mathrm{band\,D})}{I(\mathrm{band\,B})} = \frac{k_{6\mathrm{r}}}{k_{2\mathrm{r}}}\frac{k_5}{k_{-5} + k_6} \tag{14}$$

where I(band B), I(band C) and I(band D) are the integrated intensities of bands B, C and D, respectively; $k_6 = k_{6\mathrm{r}} + k_{6\mathrm{n}}$ and K_3 the equilibrium constant expressed as follows:

$$K_3 = \frac{[\mathrm{T}][\mathrm{DA}^*]}{[\mathrm{TDA}^*]} \tag{15}$$

If the values of $k_{2\mathrm{r}}$ and $k_{4\mathrm{r}}$ and [T] are independent of the temperature, the value of $\Delta H_3°$ for the equilibrium between TDA* and DA* can be obtained from the slope of the straight-line plots of ln[I(band B)/I(band C)] vs. 1/T. The value obtained was 42 kJ mol^{-1}. It is difficult to see how the values of k_{2r} and k_{4r} can vary with the temperature. Since the ratio of k_{4r}/k_{2r} is the ratio of the rate constants for similar radiative processes, this ratio is expected to be little dependant on temperature. [T] is also almost independent of the temperature in the range used here, because we used the same solution at different temperatures.

A semiquantitative energy level diagram for toluene–TMBD system is shown in Fig. 9. Levels shown by the dashed lines show the Franck–Condon excited and ground states of the amino group and those for the configurations of the exciplex and the intramolecular excimer (reached directly via absorption and emission of the light). Levels shown by the solid lines show geometrically relaxed ground (pyramidal) and excited (planar) states of the amine and relaxed states of the exciplex and the excimer. Since DA* and DA** are not in equilibrium as mentioned above, we could not obtain the value of ΔH_5° from the temperature dependence of the ratio of I(band D)/I(band B). The value of ΔH_5° shown in Fig. 9 was from Ahmed and Yamamoto [25]. The enthalpy change between TDA* and DA*, and that between DA* and DA**, and the light energies for the absorption by toluene and for the emissions from T*, TDA*, DA* and DA** are shown in Fig. 9. This diagram is similar in part to that proposed for benzene–DEMA by Halpern and Frye [9].

The emission bands for the other systems can be explained using the energy diagram in Fig. 9. For the toluene–DMEA mixture, the emission bands from the states corresponding to T*, TDA* and DA* were observed. The value of ΔH_3° for the equilibrium between the exciplex and the excited amine was found to be 28 kJ mol^{-1}, a value somewhat smaller than that for the toluene–TMBD system. For the toluene–TMPD mixture, emissions from the excited toluene and the intramolecular excimer of TMPD were observed. This finding is consistent with the tendency for TMPD to show exclusively the emission from the intramolecular excimer by the excitation of the amino group.

Hirayama [26] measured fluorescence spectra for a variety of diphenyl- and triphenylalkanes, and observed the emissions from intramolecular excimers only for compounds in which phenyl groups are separated by exactly three carbon atoms. For donor–acceptor systems with short linear chain polymethylene spacers, the intramolecular exciplex fluorescence intensity has a maximum for chain lengths of three carbon atoms, similar to that observed by Hirayama for intramolecular arene–arene excimer formation [26]. These findings are called “$n = 3$ rule” [27], and the above finding for PDAP can be explained by this rule. The light energy of the emission from the excimer of TMPD is somewhat smaller than that of TMBD showing that the value of ΔH_5° for TMPD must be larger than that for TMBD. This also shows that the intramolecular excimer of TMPD is more stable, and that the population of this state must be larger compared with toluene–TMBD system.

Only the emission from the intramolecular exciplex between phenyl and amino groups was observed for 3-PDAP, again seeming to come from the “$n = 3$ rule”. For 4-PDAB, three emission bands were observed, consistent with the results reported by De Schryver and coworkers [6,7]. The value of ΔH_3° obtained for 4-PDAB (43 kJ mol^{-1}) is similar to that for toluene–TMBD system. For PPAB, two emission bands were observed and were assigned to the intramolecular exciplex and the intramolecular excimer. The stabilization

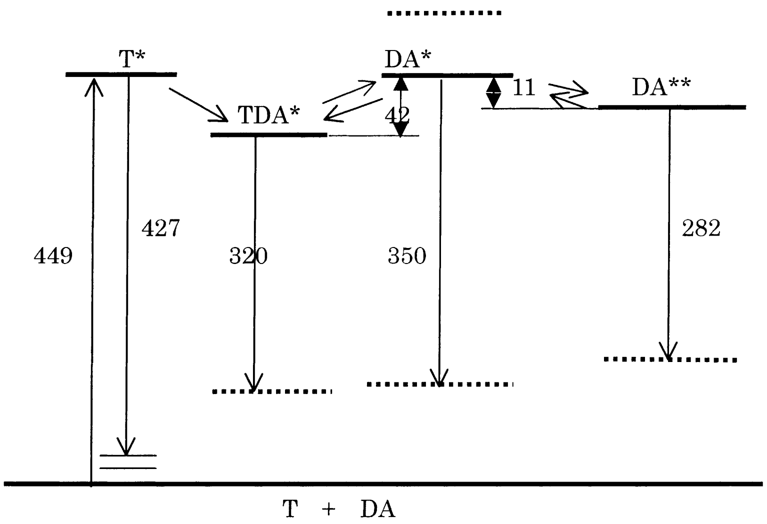

Fig. 9. Schematic representation of the potential-energy level diagram of the toluene–TMBD system: (- - -) the Franck–Condon excited and ground states (reached directly via absorption and emission of light) of the amino groups and the Franck–Condon ground states for the configurations of the exciplex and the excimer; (—) geometrically relaxed ground (pyramidal) and excited (planar and near planar) states of the amino groups and relaxed states of the exciplex and excimer. Figures show energy differences in kilojoules per mole. T and DA denote toluene and TMBD, respectively, TDA* is the exciplex between toluene and TMBD, DA* and DA** are TMBD having an excited amino group and the intramolecular excimer between two amino groups, respectively.

of these exciplex and excimer are also explained by “$n = 3$ rule”. As noted above, the shape of the spectrum does not change with temperature, indicating that the energy level of the exciplex is similar to that of the excimer for this compound.

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