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Formation of Two Exciplexes in Cadmium-Photosensitized Reaction of Aliphatic Diamines

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Two emission bands have been observed during irradiation of mixtures of some aliphatic diamines and cadmium vapor with cadmium 326.1 nm radiation. From the temperature and pressure dependences of emission intensities of the two bands, we have concluded that they are assigned to two kinds of 1:1 exciplexes between an excited cadmium atom and a diamine molecule.

During the studies of the mercury- and cadmium-photosensitized reactions of ammonia, water, aliphatic amines, alcohols, and ethers,[1-3] it has been found that these molecules react with excited atoms to form elxciplexes and that such exciplexes fluoresce. From the relationship between the quantum yield of the luminescence, the wavelength at the peak of the emission band, and the rate constants for the exciplex formation and the structure of the substrates, it has been concluded that the emission is a charge-transfer band emitted by an excited complex in which hetero atoms in the substrates donate electrons to excited atoms.[4,5]

We have measured the cadmium-photosensitized emission of some diamines to examine the reactivity of compounds which have two hetero atoms, and observed two emission bands for N,N,N',N'-tetramethylethylenediamine(TMEDA) and N,N,N',N'-tetramethyl-1,3-propanediamine(TMPDA). In the present letter, we report briefly the cadmium-photosensitized emission of TMEDA, TMPDA, N,N'-dimethylpiperazine(DMP), and triethylenediamine(TEDA).

Apparatus and techniques were similar to those used previously.[6] The quartz cell was kept in an electric furnace whose temperature was varied from 230 to 300 °C. The spiral cadmium discharge lamp made of Pyrex was placed in another furnace kept at 280 °C. The 228.8 nm resonance line and lines longer than 400 nm were filtered out by a Pyrex plate and the Toshiba glass filter, UV-D33S. The 326.1 nm resonance line used excites Cd($^3P_1$) atoms from cadmium vapor.

TMEDA, TMPDA, DMP, and TEDA were obtained from commercial sources (G.R. grade). These diamines were used after drying by potasium hydroxide and repeated trap-to-trap distillation.

Figure 1 shows the emission spectra obtained in the cadmium-photosensitized reactions of TMPDA and TEDA at 300 °C. As is shown in Fig. 1, two emission bands are evident for TMPDA (broken lines show a tentative separation of two bands), while TEDA shows one emission band. The position and shape of the short-wavelength band (band I) of TMPDA are similar to those of the band of TEDA and of the bands reported for the excited cadmium-aliphatic amines system. The long-wavelength band (band II) has not been reported yet.

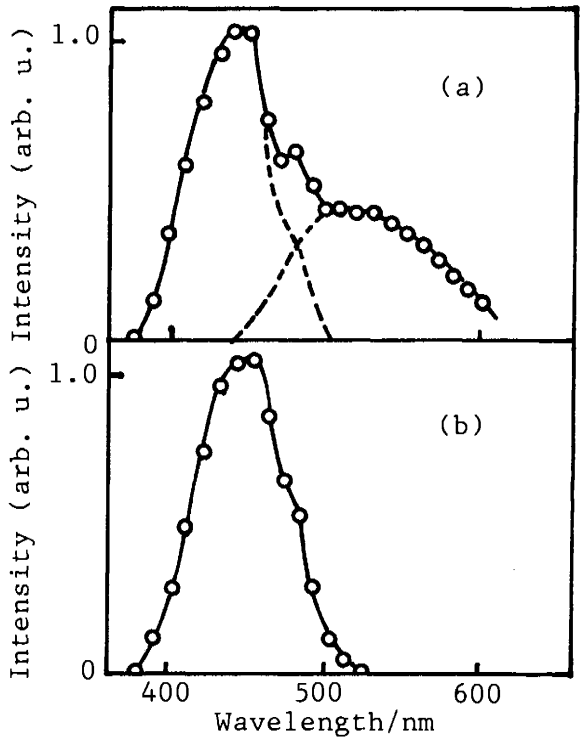


Fig. 1. Emission spectra for sensitized luminescence of TMPDA (a) and TEDA (b) at 300 °C.

The temperature dependence of the emission spectrum for TMPDA is shown in Fig. 2. The spectra obtained at 230, 260, and 300 °C have been adjusted to the same total intensity at two peaks. The profiles have an isosbestic point. This is characteristic of the superposition of just two basic functions which have same intensity at the isosbestic wavelength. The intensity of the band I increases and that of the band II decreases with increasing temperature. These findings show that two bands are ascribed to two different exciplexes (exciplex A for the band I and exciplex B for the band II) and that the equilibrium between two exciplexes shifts

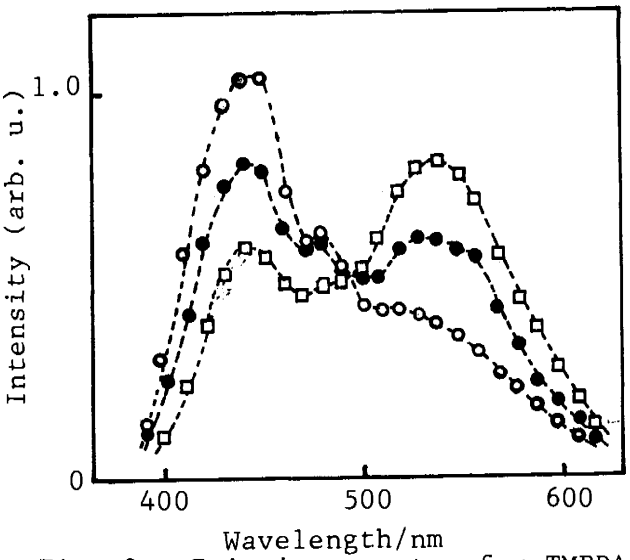


Fig. 2. Emission spectra for TMPDA at 230 (□), 260 (●), and 300 °C (○).

from B to A with temperature. From the similarity of the position and shape of the band I to those of the bands for aliphatic amines as mentioned above, the exciplex A is ascribed to a 1:1 exciplex similar to those formed between an excited cadmium atom and an amine molecule.

Figure 3 shows the dependences of the relative emission intensities at 420 and 540 nm on TMPDA pressure. As Fig. 3 shows, the intensities increase rapidly with increasing TMPDA pressure in the low pressure region and then level off to a constant value. The intensities are constant at higher pressures than 200 Pa ($I_{420}/I_{540} \approx 2.1$). Figure 4 shows the relationship between the emission intensities at 420 and 540 nm and the exciting light intensity. Both emission intensities increase linearly with increasing the exciting light intensity to which the stationary concentration of an excited cadmium atom is considered to be proportional. These findings show that two exciplexes have the same composition (Cd : Diamine = 1:1).

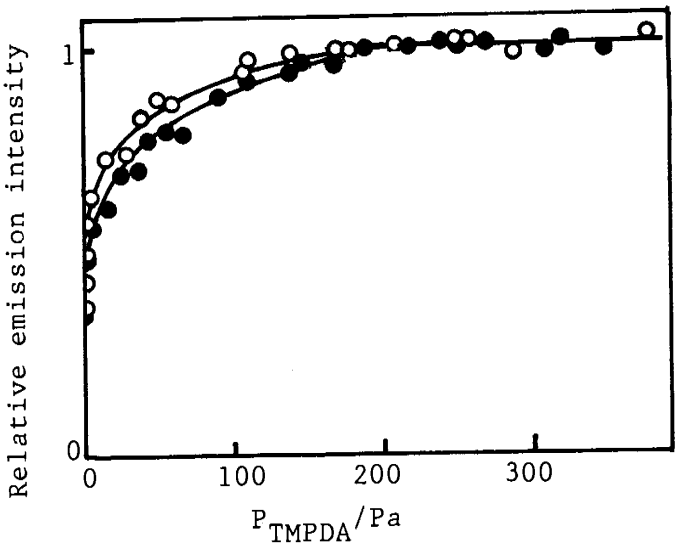


Fig. 3. Pressure dependence of emission intensities for TMPDA at 300 °C and at 420 (○) and 540 nm (●).

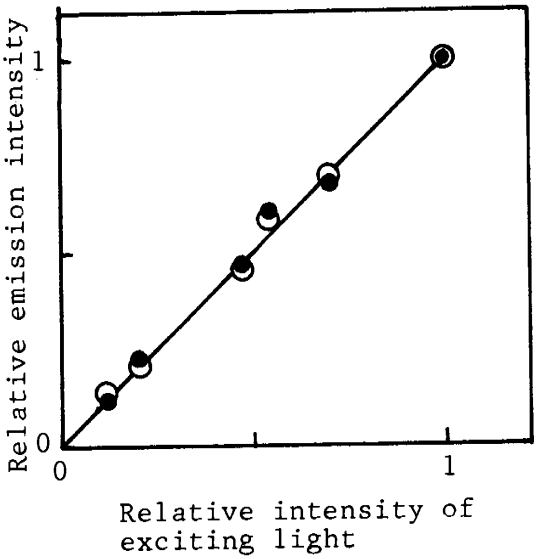


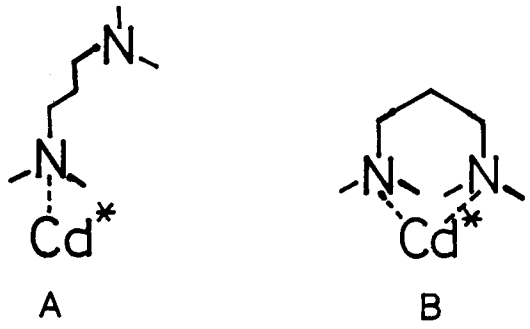
Fig. 4. Dependence of emission intensities for TMPDA at 420 (○) and 540 nm (●) on intensity of exciting light.

We have briefly examined the emission spectra for other diamines and obtained the following results; (1) DMP and TEDA have only the band I. (2) TMEDA and TMPDA have both of the bands I and II (Table I).

A possible explanation is that the bands I and II are from the exciplexes A and B shown for TMPDA in Scheme 1, respectively. For DMP and TEDA, the formation of such a cyclic exciplex as exciplex B seems to be difficult, judging from their rigid structures.

Table 1. Wavelength at the peak of the emission bands

Diamines	λ_{max}/nm	
	I	II
TMEDA	460	530
TMPDA	440	510
DMP	450	—
TEDA	450	—



A B

Scheme 1.

Further studies with several other related compounds are in progress.

References

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