

## Structure and Solvent Dependence of the Exciplex Formation and Dissociation of Anthracene/*N,N*-Dimethylaniline Derivatives in *n*-Alkane Solvents

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The intermolecular exciplex formation and dissociation in solution has been widely chosen as a model system to study diffusion-influenced reactions, because two processes can be simultaneously studied by simply measuring the fluorescence lifetimes of monomer or exciplex.<sup>1</sup> The exciplex formation process is known to be a barrierless bimolecular reaction, but the exciplex dissociation process is an activated (barrier-crossing) unimolecular reaction. Therefore, it is expected that the exciplex formation and dissociation dynamics should be influenced in a different manner by the structure of the encounter pair. Among many exciplex forming molecules, anthracene/*N,N*-dialkylaniline pair has drawn considerable attention and its reaction process is relatively well known.<sup>2-8</sup> However, the effect of the encounter-pair structure on exciplex formation as well as dissociation has been rarely studied. Taylor *et al.*<sup>9</sup> have reported exciplex formation of pyrene with *N,N*-dimethylaniline and 3,5-di-*tert*-butyl-*N,N*-dimethylaniline. They observed that pyrene forms a sandwich-pair type exciplex with *N,N*-dimethylaniline, while it forms a localized pair type of exciplex with the other one in which two bulky *tert*-butyl group are attached to the meta position of the phenyl ring.

This work concerns dependence of anthracene exciplex formation and dissociation reactions on the structure of *N,N*-dimethylaniline (DMA) substituents in which alkyl groups are attached to the different positions of the phenyl ring of DMA. Inert alkyl group as a substituent was chosen, because it may change only the molecular structure of the electron donor without affecting the electronic state of aniline. The five DMA substituents used in this work are *N,N*-dimethyl-*o*-toluidine (DMOT), *N,N*-dimethyl-*m*-toluidine (DMMT), *N,N*-dimethyl-*p*-toluidine (DMPT), 4-*tert*-butyl-*N,N*-dimethylaniline (BDMA), and *N,N*,2,4,6-pentamethylaniline (PMA). In addition, solvent dependence of exciplex formation and dissociation has been examined. Medium viscosity was varied by using a series of homologous normal alkanes (*n*-hexane to *n*-hexadecane). The fluorescence lifetime was obtained by using the time-correlated single photon counting (TCSPC) system equipped with a hydrogen flash lamp and standard TCSPC electronics. The instrument response function of the system is *ca.* 1 ns. The undegassed solution was excited at 350 nm and the monomer emission decay was measured at 380 nm. All decay time constants were obtained by deconvoluting the instrument response function from the measured decay profiles. The anthracene concentration was maintained as low as  $3 \times 10^{-5}$  M to avoid energy transfer and excimer formation between themselves. The concentration of DMA derivatives was varied from  $5 \times 10^{-5}$  to  $5 \times 10^{-2}$  M.

Figure 1 shows the absorption spectra of DMA and its five derivatives. In the ultraviolet region, DMA has two absorption bands around 250 nm ( $S_2$ ) and 300 nm ( $S_1$ ) that con-

tain contribution arising from partial charge transfer of nitrogen lone pair electron to the phenyl ring.<sup>10</sup> Among the absorption spectra of DMA derivatives, DMMT is very similar to DMA. This is because substitution at meta position does not perturb the charge transfer process. Substitution at para position does not alter the position of the absorption band, but increases only the oscillator strength. Most significant change occurs with DMOT and PMA in which substitution was made at ortho position.

The steady-state emission spectra of monomer and exciplex contain information on reaction processes that are affected by differences in the electronic structures of DMA derivatives. For anthracene and DMA derivatives, the exciplex emission is not well separated from the monomer emission. So in Figure 2, plotted is the difference emission spectra which are obtained by subtracting anthracene fluorescence in the absence of electron donor from that in the presence of electron donor. The quencher concentration was 0.01 M. The negative and positive value are indicative of the fluorescence quenching of anthracene and the onset emission due to exciplex formation, respectively. The fluorescence emission spectra exhibit the similar aspect with the absorption characteristics, showing dependence on the substitution position. For example, most dramatic change occurs with DMOT and PMA. In fact, there is no exciplex emission with PMA, meaning that substitution at two ortho positions prohibits the exciplex

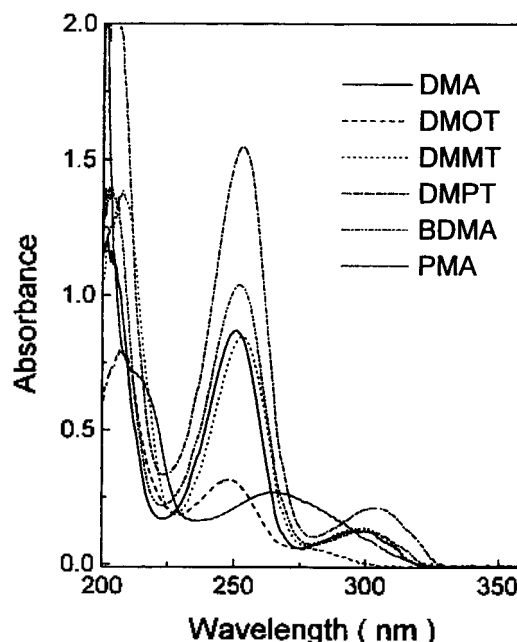
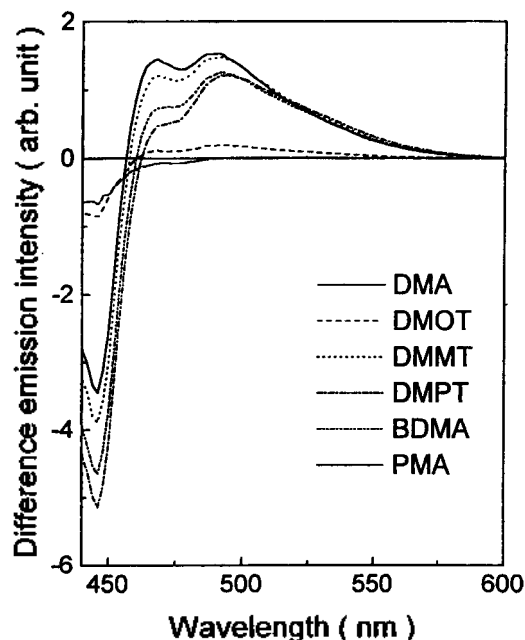


Figure 1. Absorption spectra of  $5 \times 10^{-5}$  M DMA and its derivatives in *n*-hexane solution.



**Figure 2.** Difference emission spectra of anthracene in the presence of DMA and its derivatives in *n*-hexane solution at 25 °C. The concentration of anthracene and DMA derivatives are  $5 \times 10^{-5}$  M and  $1 \times 10^{-2}$  M, respectively.

formation. This differences can be understood by comparing the structure of the substituted DMAs and potential surface for exciplex forming. The excited-state potential surface for exciplex formation is formed by the avoided crossing between the van der Waals interaction potential and the ion-pair state of the excited fluorophore and the ground state quencher.<sup>1</sup> By absorption measurement and oscillator strength calculation, it has been known that in sterically hindered aniline the resonance energy is proportional to the overlap integral of the orbitals of the amino group and of the phenyl ring.<sup>9,10</sup> Substitution at meta and para position does not affect the potential surface significantly. On the other hand, substitution at ortho position rotates the  $-N(CH_3)_2$  group of DMA due to steric hindrance, which should have an effect on the exciplex reaction potential. The difference emission spectrum of anthracene/DMA exciplex exhibits double peaks near 460

and 480 nm except for PMA with which the photoexcited anthracene does not form exciplex. The emission spectra of exciplex or excimer are usually structureless, due to the repulsive nature of the potential in the electronic ground state. In fact, the single emission peak of anthracene/DMA exciplex was observed around 500 nm in benzene solution at the concentration of *ca.* 0.1 M.<sup>4</sup> At the same concentration, we observed the maximum at somewhat shorter wavelength (*ca.* 460 nm) in *n*-hexane solution. When the quencher concentration is high, other side effects such as triplex formation and self quenching may occur, which makes the emission spectra more complex.

Lifetime measurement of anthracene at room temperature in the presence of DMMT, DMPT, and BDMA shows single exponential with the same time constant in the error range of  $\% \pm 5$ . This indicates that substitution at para position does not affect the potential surface of the exciplex formation. With these electron donors, the exciplex formation enthalpy is so high that the dissociation cannot occur during the lifetime of exciplex. Anthracene fluorescence decay in the presence of DMOT exhibits double exponential in all *n*-alkane solvents, indicating the exciplex dissociates indeed during the lifetime of the exciplex. This means the exciplex formation enthalpy for anthracene/DMOT is low compared with the anthracene/DMA or anthracene/DMMT. Table 1 shows the fluorescence decay data of anthracene in various *n*-alkane solvents in the presence of DMA, DMMT, and DMOT. The electron donor concentration [D] was fixed at 0.05 M.

As shown in the table, the electron donor, DMA and DMMT, show almost the same lifetime in all *n*-alkane solvents. For anthracene/DMA and anthracene/DMMT exciplex data, the exciplex formation rate constant is simply given by

$$k_f = (1/\tau_f - k_M)/[D] \quad (1)$$

where  $\tau_f$  is the lifetime of anthracene in the presence of the electron donor.  $k_M$  is the inverse of the fluorescence lifetime of anthracene in the absence of electron donor. The calculation shows solvent viscosity dependence of the exciplex formation rate constant for anthracene/DMA(DMMT) which decreases monotonously, for example, from  $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in *n*-hexane to  $2.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  in *n*-hexadecane. In the case of DMOT, two lifetime components increase as solvent viscosity increases. However, the relative amplitude

**Table 1.** Fluorescence decay time (ns) of anthracene in the presence of DMA, DMMT, and DMOT in *n*-alkane solvents at 22 °C

<i>n</i> -alkane	viscosity (cP) <sup>a</sup>	None	DMA <sup>b</sup>	DMMT	DMOT <sup>c</sup>
hexane	0.292	3.40	0.70	0.69	0.86(0.54) 4.94(0.46)
heptane	0.390	3.46	0.83	0.82	0.91(0.54) 5.12(0.46)
octane	0.514	3.65	0.96	0.95	1.15(0.55) 5.70(0.45)
nonane	0.667	3.86	1.11	1.11	1.28(0.59) 6.36(0.41)
decane	0.854	4.05	1.27	1.21	1.48(0.63) 7.22(0.37)
undecane	1.082	4.22	1.39	1.39	1.35(0.69) 7.79(0.31)
dodecane	1.358	4.31	1.49	1.57	1.65(0.70) 8.48(0.30)
tridecane	1.689	4.44	1.73	1.72	1.73(0.74) 9.34(0.26)
tetradecane	2.081	4.53	1.81	1.75	2.00(0.73) 9.53(0.27)
pentadecane	2.544	4.64	2.06	2.01	2.05(0.77) 10.70(0.23)
hexadecane	3.087	4.71	2.11	2.10	2.35(0.78) 11.29(0.22)

<sup>a</sup> Viscosity was taken from Ref. 11. <sup>b</sup> Decay of anthracene in DMA fits double exponential, but the amplitude of the second component is negligibly small compared with the first component (< 3%). Only the decay time of the major component is given in the table. <sup>c</sup> The numbers given in parenthesis are relative amplitudes of two decay components.

change of two components is also correlated because both processes, exciplex formation and dissociation, occur for anthracene/DMOT pair in the excited state. The detailed work on exciplex formation and dissociation processes for anthracene/DMOT which depend on solvent viscosity as well as temperature is in progress.

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## A Two-Dimensional Network of a Melamine-Formaldehyde Monolayer

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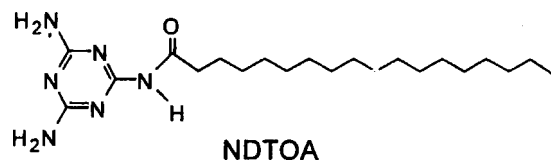
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The network structure is important for molecularly-thin films such as the Langmuir-Blodgett (LB) film in order to improve the intrinsic fragility and to make their technological applications possible. In particular, for selective permeations of gases or biomolecules through the LB films which covered the pores of substrate membranes, the mechanical stability of the LB films should be importantly taken into account.<sup>1</sup> Crosslinking of the LB films is an alternative breakthrough for the stability improvement. For examples, crosslinked monolayers have been obtained by polycondensation of octadecylureas<sup>2</sup> and amino acid esters.<sup>3</sup> Bauer *et al.*<sup>4</sup> carried out crosslinking of hydroxy moieties with epichlorohydrin in a lipid monolayer. Jones *et al.*<sup>5</sup> have prepared monolayers from crosslinkable polymers with a vinyl side group and made network structure from the LB film by UV irradiation. Kunitake *et al.* have reported stabilization of monolayers and LB films by electrostatic interaction of ionic polymers with oppositely-charged amphiphiles<sup>6</sup> and by covalent crosslinking of ionically interacting polymers.<sup>7</sup> We have also used the technique of polyion complexation at the air-water interface in order to prepare stable LB films on porous substrates.<sup>8</sup> However, two-dimensionally crosslinked monolayer films of thermosetting resins have not been reported as yet.

We report a monolayer network of a melamine resin produced by the LB method. As the spreading molecule, N-(4,6-diamino-1,3,5-triazin-2-yl) octadecanamide (NDTOA) was synthesized from the condensation reaction of melamine and



stearic acid. The chemical structure of NDTOA was confirmed by IR, <sup>1</sup>H NMR, and elemental analysis. The chloroform solution (1 mM) of NDTOA was spread to monolayer on water subphase. The surface pressure-area ( $\pi$ -A) isotherms (Figure 1) show the formation of stable monolayers, *i. e.*, the collapse pressure of monolayer raised up to 60 mN/m. The monolayer shows condensed phase, which is attributed to the strong H-bonds of amino and amide groups of NDTOA. When the pH of water subphase was controlled to acidic (pH=2.2) or basic (pH=11.1) by adding 0.1 M aq. HCl or NaOH, the molecular area increased (Figure 1a). The charge repulsion between the molecules and the increase of hydration extent at the low or high pH are thought to be related to the area expansion. When NDTOA was spread on 1% aq. formaldehyde subphase, the  $\pi$ -A isotherm (Figure 1b) showed very expanded phase. This means that the N-hydroxymethylation of melamine amino groups occurs at the air-water interface, *i. e.*, two-dimensional reaction between formaldehyde and amino group of melamine moiety proceeds on the water surface. A spontaneous increase of surface pressure was also found from the NDTOA monolayer on the aq.