Photodissociation of Jet-Cooled Excimer in Molecular Clusters of 1-Cyanonaphthalene and Its Deuterated Compound

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The excimer formation and photodissociation in jet-cooled molecular clusters of 1-cyanonaphthalene (1-CNN) and its deuterated compound (1-CNN-d_7) were investigated. The jet-cooled excimer fluorescence was observed in the excitation cluster band ($n \geq 4$) of 1-CNN-d_7 as well as of 1-CNN. The excitation of the excimer at 700−750 nm results in a considerably strong depletion of the excimer fluorescence and a simultaneous fragment fluorescence of the clusters at 335−350 nm. An excimer depletion spectrum was observed at 700−750 nm from the wavelength dependence of the depletion laser of the fragment intensity. Comparison of the excimer depletion spectrum of the jet-cooled cluster with that of the transient absorption of the excimer in solution suggests that the excitation into the upper state of the excimer induces the photodissociation of the excimer and the simultaneous fluorescence of the fragment. Fluorescence decay times of the fragment by the excimer depletion were considerably larger than those of the monomer and smaller than the dimer's. The photodissociation mechanism of the excimer was discussed in terms of decay times of the fragment fluorescence and the unexpectedly stable dimer core of 1-CNN.

Introduction

Excimer and exciplex formations and fluorescence have, for a long time, been studied in solution and crystals. Saigusa and Itoh first reported the fluorescence of the excimer in the excited state of the van der Waals (vdW) dimer of fluorene in supersonic expansion.[1] Further, Itoh and Morita reported the excimer and exciplex fluorescence in 9-ethylfluorene and fluorene.[2] A few cases of excimer formation from jet-cooled vdW dimers were reported, though considerably numerous investigations of the jet-cooled exciplex were reported,[3−6] since the first observation of the exciplex from the vdW complex between 1-cyanonaphthalene (1-CNN) and triethylamine by Saigusa and Itoh.[7,8]

On the other hand, Syage and Wessel[9] and Wessel and Syage[10] reported the excitonic interactions in naphthalene clusters. Analysis of the resonance two-photon ionization spectra suggests that the tetramer geometry resembles bulk crystalline naphthalene. Ebata et al. reported the vdW dimer and trimer of 1-cyano-4-methylnaphthalene (4-MCNN) in supersonic expansion which exhibit only UV resonance fluorescence.[11] They suggested that the dimer and trimer have fairly rigid planar structures stabilized by strong dipole−dipole interaction. Further, Itoh et al. reported the first observation of the excimer fluorescence of jet-cooled molecular clusters in $(1\text{-CNN})_n$, $n \geq 4$, and its methyl-substituted compounds.[12] A little later, Saigusa et al. reported extensive studies on the excimer formation that occurs upon excitation of the small vdW clusters of naphthalene, $(C_{10}H_8)_n$, $n = 2-5$.[13,14] They extended their studies to the formation and photodissociation[15,16] dynamics of the jet-cooled excimer in naphthalene clusters.[15−17] On the other hand, we have reported that the excitation of the jet-cooled intramolecular exciplex in anthryl-$(CH_2)_3$-*N*,*N*-dimethylaniline systems leads to the photodissociation of the exciplex and the formation of the excited-state anthryl with very short fluorescence decay times.[18,19] This paper presents the excimer fluorescence depletion upon excitation of the upper state of the excimer in $(1\text{-CNN})_n$ and $(1\text{-CNN-}d_7)_n$, $n \geq 4$, and a simultaneous formation of fragment fluorescence of these clusters. The photodissociation mechanism of the excimer was discussed in terms of decay times of the fragment fluorescence and the unexpectedly stable dimer core of 1-CNN in comparison with those of naphthalene clusters.

Experimental Section

Materials and Procedures. 1-Cyanonaphthalene (Tokyo Kasei) was purified by vacuum distillation, repeated recrystallization, and vacuum sublimation. 1-Cyanonaphthalene-d_7 was prepared by bromination and cyanogenation of naphthalene-d_8 (C/S/N Isotopes Inc.). The structure and purity were confirmed by mass, elementary analysis, and NMR (270 and 500 MHz) spectroscopies. Melting point, mass, and elementary analysis are as follows: 1-cyanonaphthalene-d_7, mp 38.0 °C. Anal. Calcd for $C_{11}D_7N$: *m*/*z*, 160.2228; C, 82.45; D, 8.81; N, 8.75. Found: *m*/*z*, 160.1013; c, 82.51; D, 8.13; N, 8.63.

The experimental setup and procedures of fluorescence spectroscopy of the pulsed supersonic free jet were completely the same as those described in the previous papers.[19−21] The 10 Hz pulse supersonic free jet backed by He (2−3 atm) was excited at 10−12 mm downstream of a nozzle by an excimer laser pumped dye laser (Lambda Physik Compex 102/FL 3002). The setup and procedures of the photodissociation of the excimer were similar to those of fluorescence hold burning depletion spectroscopy.[19−21] An excimer laser pumped dye laser (Lambda Physik EMG 53MSC/FL 2002) was used as an photodissociation laser pulse of the excimer. A digital oscilloscope (Tektronix TDS 520) for detecting of fluorescence signal in the photodis-

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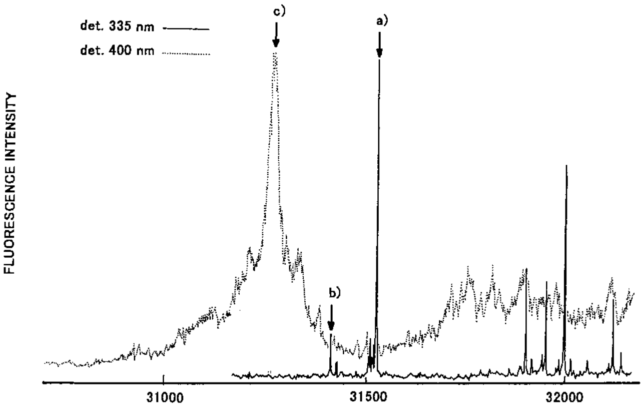

Figure 1. Fluorescence excitation spectrum of jet-cooled 1-CNN-d_7. Fluorescences were detected at 335 nm (—) and at 400 nm (- - -). The origin bands of the monomer and dimer and the cluster $(1\text{-CNN})_n$ band (mostly $n = 4$) are indicated by (**a**), (**b**), and (**c**), respectively.

sociation of the excimer was triggered by a dissociation laser pulse, and the output of signal was processed by a personal computer. The errors of the decay times are approximately 10%.[19,20]

Results and Discussion

Excimer Fluorescence in the Jet-Cooled Clusters of 1-CNN-d_7 in Comparison with Those of 1-CNN. In the previous papers,[11] the formation of molecular clusters of 1-CNN and its methyl-substituted compounds was reported in supersonic expansion. The molecular clusters $n \geq 4$ in $(1\text{-CNN})_n$ exhibit the excimer fluorescence for the first time, though the vdW dimer and trimer of these compounds exhibit only UV resonance fluorescence.[11] The dimer and trimer were suggested to be fairly rigid coplanar structures, and the clusters $n \geq 4$ were proposed to resemble bulk crystalline structures which lead to the full or partial overlap of π-electron system exhibiting the excimer fluorescence.[12] Figure 1 shows UV and excimer fluorescence excitation spectra of jet-cooled 1-CNN-d_7. A strong band at 31 520 cm^{-1} in the UV fluorescence excitation spectrum is the origin band of this compound, which shows an approximately 90−110 cm^{-1} red shift from that (31 416 cm^{-1}) of undeuterated compound (1-CNN), and a weak band at 31 403 cm^{-1} may be ascribed to the dimer on the analogy of the dimer of 1-CNN.[11,12] In the >400 nm fluorescence excitation spectrum, a strong band at 31 283 cm^{-1} observed on the broad band system seems attributable to the mostly $n = 4$ cluster band in attenuated nozzle temperature, though broad bands due to some higher clusters $n > 4$ may be superimposed in the higher nozzle temperature, as mentioned in the previous papers.[12] The size of the clusters was examined by the vapor pressure dependence of the intensities of these fluorescence excitation spectra. Figure 2 shows the excimer fluorescence spectra in the excitations of the cluster bands together with UV fluorescence spectra due to $n = 1$ and 2.

In naphthalene clusters $(C_{10}H_8)_n$, Saigusa et al.[13,14] reported that the excimer fluorescence was observed in the excitations of the vibronic band of the dimer ($n = 2$) and trimer ($n = 3$) with some excess vibrational energies as well as in the excitation of the $n = 4$ cluster band, 8_0^1. However, Ebata et al.[11] reported that no excimer fluorescence but only UV resonance fluorescence was observed even in the vibronic band excitations of the dimer with excess vibrational energy up to 587 cm^{-1} in 4-MCNN. The higher vibronic level excitation of the dimer results in the intramolecular vibrational redistribution (IVR) and a small amount of vibrational predissociation. In 1-CNN and 1-CNN-d_7, the excimer fluorescence was observed only in the excitations of the respective cluster bands ($n \geq 4$, 31 190 and 31 283 cm^{-1}), while only UV resonance fluorescence was observed even in the excitations of vibronic levels of the dimer and trimer, as mentioned above. The remarkable different features in the dimer and trimer between naphthalene and 1-CNN series may be attributable to the transition characters of these compounds. Both L(b) and L(a) bands in 1-CNN may be much greater in intensity than the respective bands of naphthalene, and then the 1-CNN clusters ($n = 2$ and 3) seem to have fairly rigid structures stabilized by the dipole−dipole interaction. Therefore, it seems that no transformation in the excited state takes place from the rigid dimer/trimer structures to the excimer conformation favorable for the charge resonance interaction even in the higher vibronic band excitations.

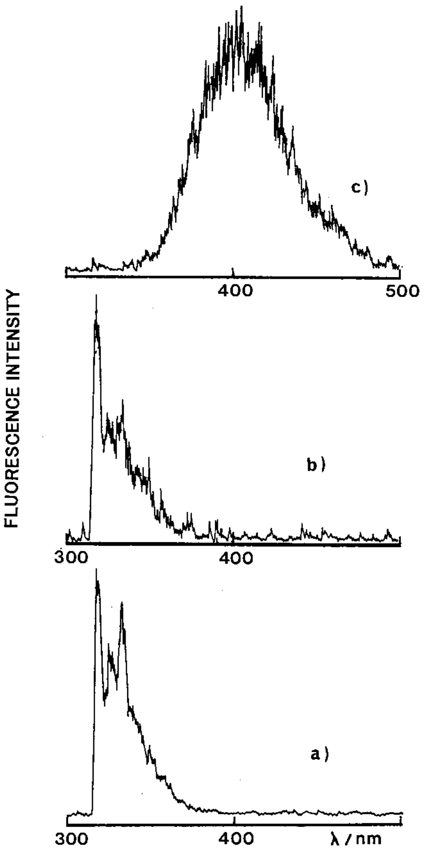

Figure 2. Dispersed fluorescence spectra of the monomer and cluster of jet-cooled $(1\text{-CNN-}d_7)_n$. Spectra were obtained in the excitations at 31 520 cm^{-1} (**a**, $n = 1$), 31 403 cm^{-1} (**b**, $n = 2$), and 31 283 cm^{-1} (**c**, mostly $n = 4$).

Photodepletion of Excimer Fluorescence Leading to Fragment Fluorescence. Figure 3 shows the excimer fluorescence decay curves in the excitation of the cluster band (31 283 cm^{-1}) $(1\text{-CNN-}d_7)_4$ and the time-resolved photodissociation of the excimer subjected to a 730 nm depletion laser pulse with a 50−100 ns delay time. The wavelength of the depletion laser pulse corresponded to the transient absorption spectrum, which was observed at 700−800 nm in hexane solution at room temperature as will be mentioned later. A pronounced depletion on the excimer fluorescence decay curve was observed. Figure 3 also shows a simultaneous formation of UV fluorescence at the same time as the excimer depletion. The facts suggest that the excitation ($S_n \leftarrow S_1$) into the upper energy level of the excimer results in the depletion of the excimer and the simultaneous formation of the fragment excited state of the excimer.

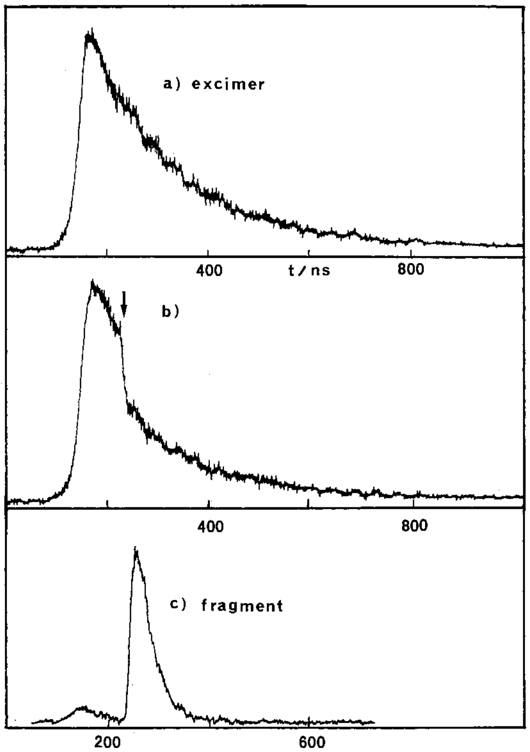

Figure 3. Typical time-resolved photodissociation of the excimer fluorescence (**a** and **b**, detected at 400 nm) and the fragment UV fluorescence signal (**c**, detected at 335 nm) for the jet-cooled $(1\text{-CNN})_n$ cluster. The excimer fluorescence decay curves were obtained by excitation of the cluster band (31 283 cm^{-1}, mostly $n = 4$). The dissociation laser pulse (730 nm) is indicated by an arrow. The UV fluorescence was not detected by the dissociation laser pulse without the cluster band (31 283 cm^{-1}) band excitation.

The action spectra of the excimer photodissociation in 1-CNN and 1-CNN-d_7 were obtained by monitoring UV fragment fluorescence intensity ratios versus attenuated laser power. No significant deuterated effect of the depletion spectra was observed. The photodissociation action spectra of the jet-cooled excimer exhibit a broad spectrum peaked at ~730 nm. On the other hand, a transient absorption spectrum of hexane solution of 1-CNN at room temperature was observed at the 710−760 nm region, whose solution really exhibits the concentration-dependent excimer fluorescence at 380−430 nm with decay time of ~18 ns. The photodissociation spectrum of the excimer of the jet-cooled clusters is essentially consistent with the transient absorption spectrum ($S_n \leftarrow S_1$) in solution, though the former in gas phase is blue-shifted approximately 10−20 nm from the latter in solution.[22] Further, it was observed that variable delay plots of the UV fragment fluorescence intensities correspond to the decay time of the excimer fluorescence in supersonic expansion. The facts indicate that the excitation of the excimer to the upper excited state induces the photodissociation of the excimer and that the fragment fluorescence arises from the dissociation of the excimer.

Saigusa et al.[15−17] reported the photodissociation dynamics of the naphthalene excimer producing the excited state of the monomer fragment. On the other hand, we have reported that the excitation of jet-cooled intramolecular exciplex in anthryl-$(CH_2)_3$-*N*,*N*-dimethylaniline systems leads to the photodissociation of the exciplex and the formation of the excited-state anthryl with very short fluorescence decay times.[18,19] It was proposed that the anthryl fluorescence with very short decay times emits from certain vibrational states of the upper energy levels in anthryl moieties, which were generated by the photodissociation of the exciplex.

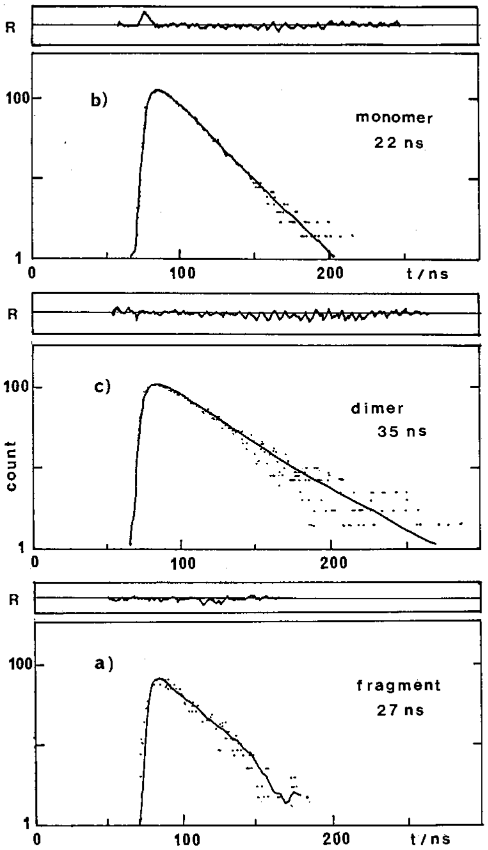

Figure 4. Typical decay analysis of the UV fragment fluorescence (**a**, 335 nm) by the photodissociation of the excimer, in comparison with those of the monomer (**b**) and dimer (**c**) fluorescence.

TABLE 1: Origin Bands (cm^{-1}) of Monomer, Dimer, Trimer, and Clusters (Mostly $n = 4$) in Jet-Cooled 1-CNN-d_7 and 1-CNN

	monomer	dimer	trimer	cluster ($n = 4$)
1-CNN-d_7	31 520	31 403	31 276	31 283
1-CNN	31 416	31 298	31 180	31 190

Decay times of the fragment UV fluorescence by the excimer photodissociation as well as those of the monomer and dimer of 1-CNN and 1-CNN-d_7 were determined. The determination of these decay times was performed severaltimes, and almost the same results were obtained in the respective species. The typical decay analysis (1-CNN-d_7) is shown in Figure 4. The fluorescence decay times of the monomer and dimer of 1-CNN-d_7 are considerably smaller than the respective decay times of 1-CNN, though no significant deuterium substitution effect was detected in the excimer decay times. These decay times together with those of the fragment fluorescence are summarized in Table 2. As mentioned above, Saigusa et al. proposed that the excited-state monomer was generated by the photodissociation of the naphthalene excimer in supersonic expansion. In 1-CNN-d_7 clusters, it is noteworthy that the decay times of the UV fragment fluorescence are larger than those of the monomer but smaller than the dimer's. These decay features of the fragment fluorescence were also observed in the excimer photodissociation in the 1-CNN clusters. The dispersed fluorescence spectrum of the fragment was examined to detect for the excimer photodissociation. However, since the fragment fluorescence spectrum was too weak and very congested, it was difficult to determine whether monomer or dimer was responsible for the photo fragment of the excimer by fluorescence spectra. In this case, multiphoton ionization (MPI) mass detection of the fragments might be expected. However, the MPI mass detection was impossible in this excimer photodissociation experiment at the present stage because of our insufficient equipment. The ionization potential of 1-CNN (Ip = 8.61 eV) is greater than the two-photon energy of the origin band region of the monomer and clusters (31 416 cm^{-1} → 3.94 eV). The cluster formation of (1-CNN)$_n$, $n = 2-9$, was detected by one-color two-photon ionization using a 248 nm (KrF, 9.98 eV) excimer laser; however, no size-selected excitation spectrum of the clusters was obtained, as reported in the previous paper.[12b]

If the excited-state monomer may be generated by the photodissociation of the excimer, the fragment decay time may be identical with that of the monomer or somewhat smaller than the monomer's. The observed decay times of the fragment fluorescence of the excimer photodissociation in 1-CNN (30−31 ns) and 1-CNN-d_7 (26−28 ns) were both larger than the respective decay times of the monomer (24−26 ns in 1-CNN and 22 ns in CNN-d_7) but smaller than the dimer's (47 and 35 ns). As mentioned above in the exciplex photodissociation,[18,19] the fragment fluorescence with very short decay times emits from certain vibrational states of the upper energy levels in anthryl moieties. Taking account of results of the photodissociation of the exciplex, the excited-state dimer may be a possible candidate for the observed fragment fluorescence in the excimer photodissociation of (1-CNN)$_4$, as will be mentioned later.

Mechanism of the Excimer Formation and Photodissociation. As reported in the previous papers, the excimer fluorescence obtained from jet-cooled clusters of (1-CNN)$_n$, mostly $n = 4$, extremely resembles the excimer fluorescence in the crystals and also that generated from the ground-state dimer in the rigid solution at 77 K.[12] Further, the excimer fluorescence and transient absorption spectra were observed in the concentrated hexane solution at room temperature. The X-ray crystallography of methyl-substituted 1-CNN exhibiting the excimer fluorescence demonstrates the partially overlapped head-to-tail structure facing π-electron systems. Therefore, full or partial overlap between two π-electron systems may be required for the excimer formation even in the jet-cooled clusters. However, the jet-cooled dimer and trimer of 1-CNN (1-CNN-d_7) exhibited no excimer fluorescence but only UV resonance fluorescence even in the excitations of vibronic bands of the dimer and trimer. The dimer and trimer were suggested to have stable rigid structures due to the strong dipole−dipole interaction in (1-CNN)$_n$, $n = 2-3$.[11] The facts suggest that no transformation from the rigid planar dimer and trimer structures to the full or partially overlapped π-electron configuration takes place in their excited states. These are completely different from the vdW dimer and trimer in naphthalene clusters and also from the fluorene dimer.[1,2] The excited-state transformation of the naphthalene dimer/trimer to the excimer takes place in the higher vibronic energy levels, as reported by Saigusa et al.[13,14] These different features between 1-CNN and naphthalene clusters demonstrate that the structure transformation in the excited state of the rigid dimer and trimer to the excimer configuration is very difficult in comparison with the case of naphthalene clusters, as mentioned above.

The (1-CNN)$_n$ clusters, mostly $n = 4$, may possess an unsymmetric structure, and the dimer core in the clusters seems to be the nearly overlapped π-electron system pertinent to the excimer. In the dimer core structure in the cluster (1-CNN)$_4$, the other two molecules may play an important role as a kind of solvent molecule. These two molecules seem to rend the dimer core to make the overlapped π-electron system favorable to the excimer formation. The transient absorption band of the excimer is considered as a transition from the excimer state into an upper state. The lower (Ψ_1) and upper (Ψ_2) excimer states of 1-CNN are expressed by a linear combination of the molecular exciton state $\Phi_\pm$ and the charge resonance state $\Phi_\pm$(CR). The molecular exciton state may originate from the monomer S_1 state, since the $S_1 \leftarrow S_0$ band of 1-CNN has a considerably large molar extinction coefficient ($\epsilon_{\mathrm{MeOH}} = 2220$) due to the C═N group in comparison with a forbidden band of naphthalene (^1L_b). The $\Phi_\pm$ and $\Phi_\pm$(CR) are the symmetric and antisymmetric combinations of the molecular exciton and charge resonance states, respectively. The excimer excitation by the transient absorption band corresponds to the $\Psi_2 \leftarrow \Psi_1$ transition. The upper excimer state, Ψ_2, may be considerably repulsive or a weakly bound state. In the naphthalene excimer, the photodissociation of the excimer producing the excited state of the monomer fragment provided an evidence of the significant contribution of the repulsive resonance state in the upper excimer state.

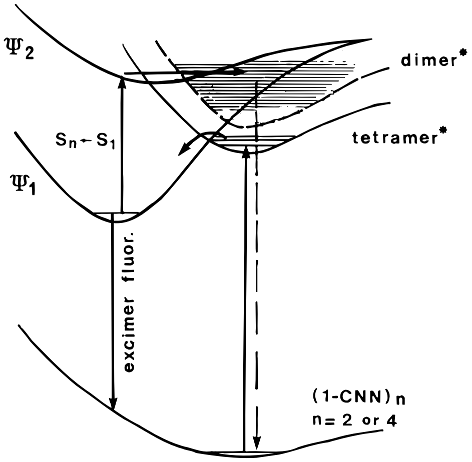

Figure 5. Schematic potential energy curve illustrating the formation and photodissociation of the excimer generated from the 1-CNN clusters. The potential energy curves of the dimer may be on a different energy surface from the others.

In the excitation of the excimer to the upper state, $\Psi_2 \leftarrow \Psi_1$, it is likely that the inter- and/or intramolecular vibrational energy redistribution takes place in the cluster (1-CNN)$_4$, which results in the formation of the upper excimer state of the dimer core as well as evaporation of two 1-CNN molecules that surrounded the dimer core. The energy levels of the upper excimer state in the dimer core may correspond to the higher vibrational continuum of the Ψ_1 excimer state and also that of the rigid dimer in the S_1 state. The geometrical transition followed by the electronic relaxation seems to occur from the upper excimer state to the higher vibrational states of the dimer S_1 state, whose schematic illustration is shown in Figure 5. As mentioned above, if the 1-CNN monomer is generated from the upper state of the excimer, the excimer fragment fluorescence decay time of 1-CNN and 1-CNN-d_7 may be similar to those of the respective monomer or smaller than them. However, the observed fragment decay times were between those of the monomer and the dimer, as summarized in Table 2. Therefore, we propose tentatively that the excimer fragment may be the excited-state dimer and the dimer fluorescence with short decay times emits from a certain vibrational state of the upper energy levels in the dimer. Further, the deuterium substitution effects on the decay times of the fragment fluorescence generated by the excimer photodissociation may be discussed in terms of the

TABLE 2: Fluorescence Decay Times (ns) of Monomer, Dimer, and Photodissociation Fragment of the Excimer[a]

	monomer	dimer	photodissociation fragment
1-CNN-d_7	22−23	35	27
1-CNN	26	48	30−31

[a] Errors of decay times are approximately 5%.

role of level density in the cross section between the higher excimer state (Ψ_2) and the higher vibrational state of the dimer.[18,19]

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