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Dual Fluorescence and Excited-state Double Proton Transfer in the Dimer of 3,5-Dialkyl-4-hydroxybenzylidenemalononitrile

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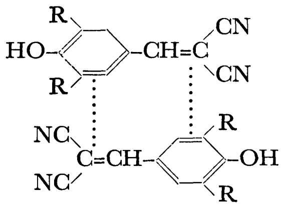
Dual fluorescence of the dimer of 3,5-dialkyl-4-hydroxybenzylidenemalononitrile (HO-BMN) was investigated by steady-state and nanosecond fluorescence spectroscopies. The dimerization of the compounds in 3-methylpentane (MP) solution was confirmed by concentration dependence of absorption and fluorescence spectra at low temperature (<150 K). While the MP solutions of the compounds are almost non-fluorescent at room temperature, the dimer exhibits a short-lived fluorescence ($\tau=4$—9 ns) at 450—520 nm and a long-lived fluorescence ($\tau=21$—34 ns) at 490—550 nm. The short-lived fluorescence was ascribed to a sandwich type dimer (D*) with a center of symmetry. An orientational relaxation leading to the double proton transfer reaction seems to occur in the excited state of the dimer. The long-lived fluorescence in the dimer was tentatively ascribed to the excited species (T*) generated by the double proton transfer reaction in D*. The excited-state proton transfer is discussed in terms of the effect of deuterium substitution of a 4-hydroxyl hydrogen upon fluorescence lifetimes of the dimer.

Taylor *et al.*,[1] and Ingham and El-Bayoumi[2] reported extensive studies of the hydrogen-bonded dimer formation in 3-methylpentane (MP) of 7-azaindole and the photoinduced double proton transfer reaction in the excited state of the dimer at low temperature. They observed a weak dimer fluorescence and a strong tautomer fluorescence generated by the double proton transfer reaction in the excited state. On the other hand, numerous investigations of dual fluorescence of aromatic hydrocarbons in nonpolar solvents consisting of the dimer and excimer fluorescence were reported.[3-5]

Recently, 3,5-dialkyl-4-hydroxybenzylidenemalononitrile (HO-BMN) was reported to be an active uncoupler of the oxidative phosphorylation,[6] and to show a remarkable pH dependence of absorption spectra.[7] The HO-BMN molecule exhibits an absorption band at 350—360 nm and a very weak fluorescence (almost non-fluorescent) in such a nonpolar solvent as MP. In strong hydrogen-bonding solvents, however, a proton transfer occurs from 4-hydroxy group to a proton acceptor to form an anion form of HO-BMN which reveals an absorption band at 450—460 nm and a corresponding fluorescence at 480—500 nm. Similar highly polar molecule, 3,5-dialkyl-4-methoxybenzylidenemalononitrile (MO-BMN) in MP solution exhibits very similar absorption band at 330—350 nm to that of the corresponding HO-BMN (a neutral form).[8] In MO-BMN, however, neither absorption (450—460 nm) nor fluorescence (480—500 nm) due to the anion form of HO-BMN was detected in such a highly polar solvent as alcohol. Recently, Itoh, *et al.*[9] reported the crystal structure of 3,5-di-*t*-butyl-4-hydroxybenzylidenemalononitrile (t-Bu$_2$-HO-BMN), and the excited-state proton transfer in the crystals. The crystalline t-Bu$_2$-HO-BMN exhibits a strong green fluorescence at 490—500 nm at low temperature, which was ascribed to the excited-state proton transfer between t-Bu$_2$-HO-BMN molecules in the crystals.

This paper describes the dimer formation of HO-BMN in the ground state in MP solution at low temperature, and dual fluorescence consisting of a short-lived fluorescence at 450—520 nm and a long-lived one at 490—550 nm. The former fluorescence in HO-BMN is ascribed to the dimer (D*) of the compound. The latter fluorescence is attributable to the excited species (T*) generated by the double proton transfer reaction in the excited state of the dimer,[10] while in MO-BMN to the excimer-type dimer by an orientational relaxation in D* as reported previously.[8] By taking account of the crystal structure, the structure of the dimer is proposed to be a sandwich-type dimer with a center of symmetry as follows:



R = *t*-butyl
t-pentyl
isopropyl
methyl

The dimer formation of these compounds seems to be attributable to an exciton interaction as well as a charge-transfer (CT) interaction between two component molecules in the dimer. Here, an orientational relaxation leading to the double proton transfer reaction maybe occur in the excited state of the dimer. In the HO-BMN dimer, the effect of deuterium substitution of a 4-hydroxyl hydrogen upon fluorescence lifetimes of the dimer (D*) was observed. The excited-state double proton transfer in the HO-BMN dimer is discussed in comparison with the orientational relaxation in the excited state of the MO-BMN dimer.

Experimental

At the initial stage of the experiment, 3,5-di-*t*-butyl-4-hydroxybenzylidenemalononitrile was given by Prof. Y. Anraku (Department of Botany, The University of Tokyo). All of 3,5-dialkyl-4-hydroxybenzylidenemalononitrile were prepared by known procedures.[11] Pure samples were obtained by chromatography and recrystallization before use. Deuterium substitution of 4-OH hydrogen was performed by CH_3OD (CEA, deuterium grade 99.0%) in a vacuum system. After removing CH_3OD, 3-methylpentane was added through a vacuum system. Proton NMR gave an isotope purity of approximately 85—90%.

Solutions of samples were contained in rectangular quartz cells (1 cm) equipped with graded seals, and degassed by freeze-thaw cycles (several times) at 10^{-5} Torr. All of the optical absorption and fluorescence spectra were recorded by Hitachi 323 and MPF-4 spectrophotometers. Determination of their spectra at several temperatures was carried out by the method described previously.[12] The fluorescence lifetimes were determined by analyzing exponential decay curves measured by an oscilloscope, and by a coaxial N_2 laser as described previously,[13] and analyzed by a deconvolution method.[14]

Results and Discussion

Dimer Formation in the Ground State. The MP solution of *t*-Bu_2-HO-BMN shows an absorption band in the 340—360 nm region at room temperature, while shows considerable red-shift at low temperature (<150 K) as shown in Fig. 1. Figure 2 shows concentration dependence of absorption spectra of MP solutions of *t*-Bu_2-HO-BMN at 77 K. Here, a monomer-dimer equilibrium of *t*-Bu_2-HO-BMN in MP solution is assumed, and an association constant (K) can be written as follows:

$$K = [\mathrm{D}]/([\mathrm{C}]-2[\mathrm{D}])^2,$$

where [C] and [D] are concentrations of the monomer and dimer. If an absorption band at 400 nm is assumed to be owing to the dimer as shown in Fig. 2, an absorbance (A) at 400 nm is expressed as $A=\varepsilon[\mathrm{D}]l$, where ε is a molar extinction coefficient at this wavelength, and l is a light-path length. The following equation is obtained;[2,15]

$$[\mathrm{C}]/A = 2/\varepsilon + (1/\varepsilon K)^{1/2}(1/A)^{1/2}.$$

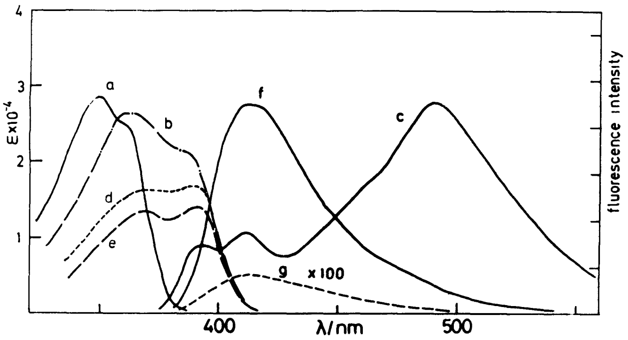


Fig. 1. Absorption spectra of an MP solution (concentration, 6×10^{-5} M) of *t*-Bu_2-HO-BMN at room temperature (a) and at 77 K (b). Fluorescence spectra of an MP solution (concentration, 2×10^{-6} M) of *t*-Bu_2-HO-BMN at 77 K excited at 360 nm (c) and the excitation spectra monitored at 455 nm (d) and at 530 nm (e). Fluorescence spectra of an MTHF solution of *t*-Bu_2-HO-BMN at 77 K (f) and at room temperature (g) (concentration, 2×10^{-6} M).

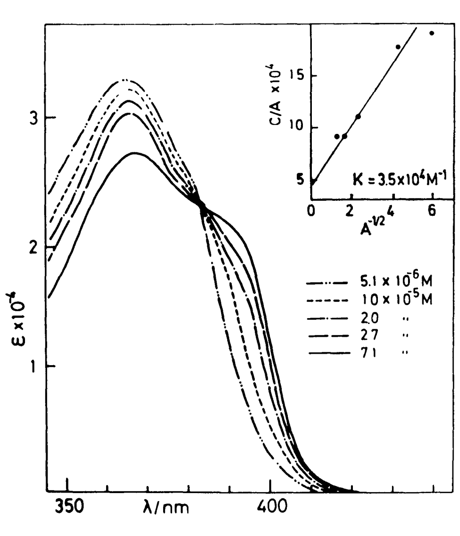


Fig. 2. Concentration dependence of absorption spectra of MP solutions of *t*-Bu_2-HO-BMN at 77 K, and plots of $[\mathrm{C}]/A$ *vs.* $A^{-1/2}$ (A, monitored at 400 nm).

An MP solution of considerable concentration of *t*-Bu_2-HO-BMN exhibits a strong green fluorescence at 77 K as shown in Fig. 1, while the solution is almost non-fluorescent at room temperature. Figure 1 also shows the fluorescence spectrum of this compound in 2-methyltetrahydrofuran (MTHF) at 77 K. The MTHF solution exhibits no significant temperature dependence of fluorescence and absorption spectra.[16] The green fluorescence in the MP solution markedly increases and a fluorescence spectrum at 400—430 nm decreases in intensity with increasing concentration of *t*-Bu_2-HO-BMN, as shown in Fig. 3. The excitation spectrum of the former fluorescence corresponds to an absorption band at 390 nm, while that of the latter to a band at 350—360 nm. Then, the fluorescence at 400—430 nm is tentatively ascribed to the monomer and the green one to the dimer of *t*-Bu_2-HO-BMN.[17] Intensity (I) of the green fluorescence may be proportional to the concentration of the dimer [D], though the green fluorescence consists of a short-lived fluorescence (D*) and a long-lived one (T*) as will be mentioned later. Therefore, the following equation is obtained for the monomer-dimer equilibrium;

$$[\mathrm{C}]/I = 2/q + (1/qK)^{1/2}(1/I)^{1/2},$$

where q is a constant including several experimental factors. Plots of $[\mathrm{C}]/A$ and $[\mathrm{C}]/I$ exhibit linear relationship against $(1/A)^{1/2}$ and $(1/I)^{1/2}$, respectively, as

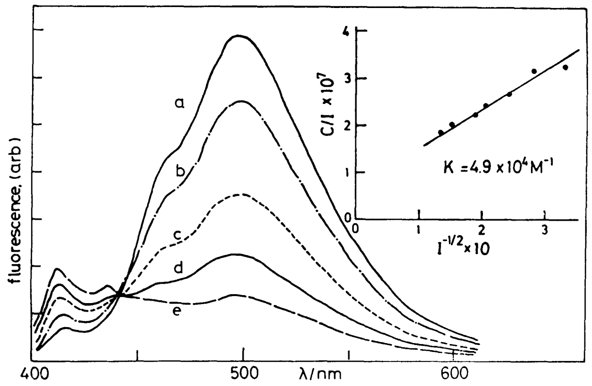


Fig. 3. Concentration dependence of fluorescence spectra of MP solutions of *t*-Bu_2-HO-BMN at 77 K (excited at 360 nm); concentrations of the compound are 9.6×10^{-6} (a), 8.5×10^{-6} (b), 5.1×10^{-6} (c), 3.6×10^{-6} (d), and 2.4×10^{-6} M (e). Plots of $[\mathrm{C}]/I$ *vs.* $I^{-1/2}$ at 77 K (I, monitored at 520 nm).

TABLE 1. FLUORESCENCE MAXIMA AND LIFETIMES OF D* AND T*, AND THE EFFECT OF DEUTERIUM SUBSTITUTION OF A 4-OH HYDROGEN AT 77 K
Equilibrium constants for the dimerization of dialkyl HO-BMN (MO-BMN) in MP at 77 K.

Dialkyl HO-BMN	λ_{max}/nm$^{a)}$		τ/ns$^{b)}$		K/M^{-1}
	D*	T*	D*	T*	
t-Pe$_2$-HO-BMN	470	510	6(9)	34(34)	$5.1\times10^{4c)}$
t-Bu$_2$-HO-BMN	470	500	6(7—8)	32(32)	$3.5\times10^{4c)}$
i-Pr$_2$-HO-BMN	510	530	8(9)	25(25)	$4.9\times10^{4d)}$
Me$_2$-HO-BMN	515	547	7(8)	34(34)	$1.6\times10^{5e)}$
Me$_2$-MO-BMN$^{f)}$	490	505	4	21	4.8×10^{4}

a) Determined by time-resolved fluorescence spectra, error approximately ±5 nm. b) Determined by a computer deconvolution. Data in parenthese are those of the deuterium substituted samples of HO-BMN, error approximately ±5%. c) Determined by absorption spectra, monitored at 400 nm. d) Determined by absorption spectra, monitored at 410 nm. e) Determined by fluorescence spectra, monitored at 520 nm. f) Ref. 9.

shown in Figs. 2 and 3. Two straight lines confirm an assumption of the monomer-dimer equilibrium, and afford equilibrium constants; $K=4.9\times10^4$ M^{-1} from plots of the fluorescence spectra and $K=3.5\times10^4$ M^{-1} from those of the absorption spectra. Concentration dependence of absorption and fluorescence spectra of other alkyl HO-BMN in MP solutions also reveals the dimer formation at low temperature, whose equilibrium constants are summarized in Table 1. The absorption spectra of several concentrations of 3,5-dimethyl-4-methoxybenzylidenemalononitrile (Me$_2$-MO-BMN) in MP solutions at 77 K were reported to indicate the dimer formation of this compound. The equilibrium constant is also shown in Table 1 in comparison. An MP solution of Me$_2$-MO-BMN exhibits a strong green fluorescence in 460—500 nm at 77 K consisting of short and long components of decay. The former and the latter were ascribed to the dimer and the excimer fluorescence, respectively, as reported in the previous paper.

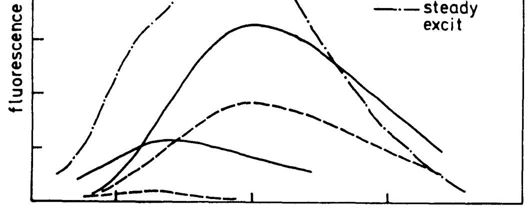


Fig. 4. A steady-state fluorescence and time-resolved fluorescence spectra of an MP solution of *t*-Bu$_2$-HO-BMN (3×10^{-5} M) at 77 K, which were depicted by a deconvolution method. The time indicated is virtually after a signal maximum of the fluorescence.

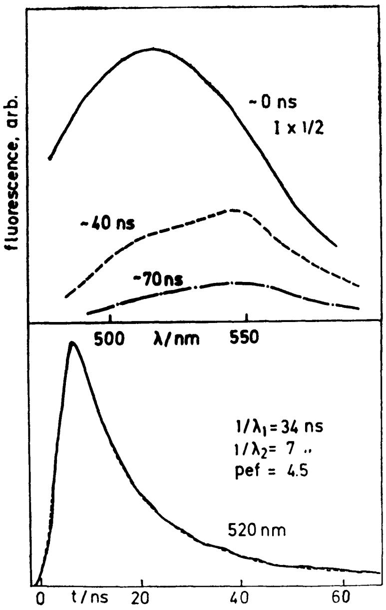


Fig. 5. Time-resolved fluorescence spectra and time evolution of fluorescence (at 520 nm) of an MP solution of Me$_2$-HO-BMN at 77 K; (——) and (——) are observed and simulated decay curves based on the obtained time constants and pre-exponential factor (pef), respectively. The time indicated in the time-resolved fluorescence spectra is virtually after a signal maximum of the fluorescence.

Excited-state Double Proton Transfer in HO-BMN Dimer. Nanosecond time-resolved fluorescence spectra of an MP solution of *t*-Bu$_2$-HO-BMN at 77 K shown in Fig. 4 demonstrate that the green fluorescence consists of two fluorescence spectra; a short-lived fluorescence ($\tau_D=6$ ns, $\lambda_{max}=470$ nm) and a long-lived fluorescence ($\tau_T=32$ ns, $\lambda_{max}=500$ nm). The dual fluorescence of the dimer was also observed in other dialkyl HO-BMN (3,5-di-*t*-pentyl, 3,5-diisopropyl- and 3,5-dimethyl HO-BMN). Figure 5 shows time-resolved fluorescence spectra and decay curve of an MP solution of Me$_2$-HO-BMN at 77 K. Table 1 summarizes the fluorescence maxima determined by time-resolved fluorescence spectra and lifetimes in the dimers of these compounds at 77 K. The excitation spectra of the short-lived and long-lived fluorescence are identical each other, and corresponding to the dimer absorption band. The spectral behavior in the case of *t*-Bu$_2$-HO-BMN is shown in Fig. 1. From the large Stokes shift of the long-lived fluorescence, the fluorescence may be tentatively ascribed to the excited species (T*) generated from the excited state of the HO-BMN dimer (D*), while the short-lived one to the dimer.

The photochemical reaction scheme of the excited state of the dimer (D*), and the excited species T* generated from D* is as follows:

$$\begin{tikzcd}[column sep=small]
D \arrow[rr, "h\nu"] & & D^* \arrow[rr, shift left, "k_3"] \arrow[dl, "k_1"'] \arrow[dr, "k_2"] & & T^* \arrow[ll, shift left, "k_4"] \arrow[dl, "k_5"'] \arrow[dr, "k_6"] & \\
 & D + h\nu' & & D \quad T + h\nu'' & & T
\end{tikzcd}$$

Time-depedent concentrations of D* and T* are expressed by the following equations;[18,19)]

$$[\mathrm{D}^*] = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t), \qquad (1)$$

$$[\mathrm{T}^*] = c_3 \exp(-\lambda_1 t) - c_3 \exp(-\lambda_2 t), \qquad (2)$$

$$\lambda_{1,2} = \frac{1}{2}[k_1+k_2+k_3+k_4+k_5+k_6 \mp (\{k_1+k_2+k_3-(k_4+k_5+k_6)\}^2+4k_3k_4)^{1/2}].$$

Since two fluorescence decay curves of D* and T* at a certain wavelength overlap each other, actual decay curves at several wavelengths were analyzed by the following equation:

$$[\mathrm{D}^*] + [\mathrm{T}^*] \propto \exp(-\lambda_1 t) + (c_2-c_3)\exp(-\lambda_2 t)/(c_1+c_3).$$

Here, if $k_3 \gg k_4$, and k_4 is negligible, fluorescence lifetimes of D* and T* were determined to be 6 ns and 32 ns from λ_2 and λ_1, respectively. If a pre-exponential factor (pef), $(c_2-c_3)/(c_1+c_3)$ is obtained to be negative, T* should show the fluorescence rise. Unfortunately, the fluorescence rise of T* was not significant as shown in Fig. 6, because the D* fluorescence overlaps on the decay curve of T* even at 600 nm.

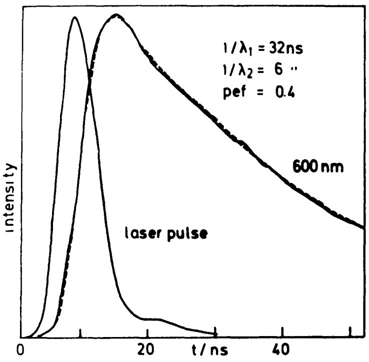


Fig. 6. Time evolution of fluorescence observed at 600 nm of an MP solution of *t*-Bu_2-HO-BMN at 77 K, and a computer simulation (-----) from time constants and pre-exponential factor obtained (concentration, 2×10^{-5} M).

The crystal structure of *t*-Bu_2-HO-BMN demonstrated that the molecule is almost planar and packed along the b axis with a spacing of 3.69 Å in a monoclinic unit cell, as reported in a previous paper.[9)] Two molecules packed along the b axis are considered to be a sandwich-type dimer with a center of symmetry. Therefore, the structure of the dimer in solution may be similar to that in the crystals. In the excited state of the dimer, an orientational relaxation maybe occur eeading to the formation of the excited species T*. Here, it is likely that the double proton transfer reaction is involved in the orientational relaxation in the excited state of the dimer. On the other hand, there seems to be a possibility that the excited species T* might be ascribed to an ordinary excimer-type dimer, where no proton transfer is involved. However, this was excluded by the effect of deuterium substitution of a 4-OH hydrogen of HO-BMN upon fluorescence lifetimes of D*. Fluorescence lifetimes of D* and T* in several dialkyl HO-BMN and their deuterium substituted HO-BMN at 77 K were determined and analyzed by computer simulation mentioned above. The results are summarized in Table 1. All of fluorescence lifetimes of D* somewhat increase by deuterium substitution of 4-OH protons, while those of T* remain almost unaltered. The significant effects of deuterium substitution upon fluorescence quantum yield or proton transfer rate in 2-naphthol,[20)] 2-naphthylamine, and carbazol[21)] were reported by several investigators. El-Bayoumi and his coworkers[2,22)] reported that the rate constant (k_3) of the double proton transfer in 7-azaindole dimer was decreased by deuterium substitution. In the excited-state proton transfer reaction reported here, increases of fluorescence lifetimes and pre-exponential factor (pef) mentioned above may be attributable to the effect of the deuterium substitution upon the proton transfer rate constant k_3.

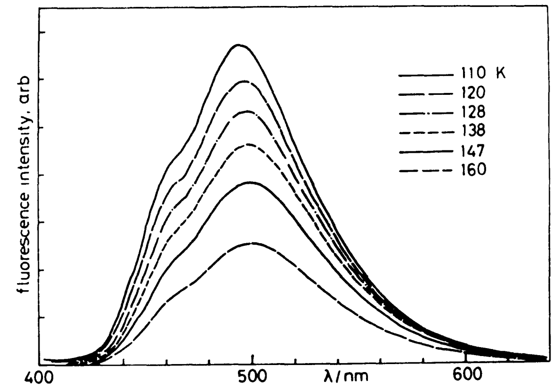
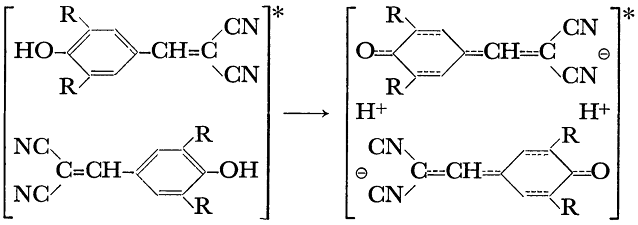


Fig. 7. Temperature dependence of fluorescence spectra of an MP solution of *t*-Bu_2-HO-BMN (concentration, 5×10^{-5} M) excited at 390 nm.

On the other hand, an MP solution of considerable concentration of *t*-Bu_2-HO-BMN reveals temperature dependence of fluorescence spectra, as shown in Fig. 7. The D* fluorescence at 450—490 nm decreases in intensity slightly more than the T* fluorescence at 480—550 nm with increasing temperature (77 K to 150 K). Since most of molecules are virtually present as dimers trapped in the MP matrix, and since no monomer fluorescence is detected under these conditions, the temperature dependence suggests that there seems to be very small activation barrier between these two fluorescent states. However, the energy was too small to be estimated from the fluorescence spectra. The fact is compared with the results in Me_2-MO-BMN (0.9 kcal mol^{-1}) reported previously.

The structure of the dimers of dialkyl-HO-BMN is conclusively considered to be a sandwich type with a center of symmetry from the crystal structure reported previously. The dimer formation of nonpolar molecules such as anthracene and tetracene may be attributable to the exciton interaction as well as the charge transfer (or charge resonance) interaction. In the highly polar molecules reported here, the charge transfer character between two component molecules in the dimer seems to increase in the excited state. Further, it is likely that an orientational relaxation from the short-lived dimer state to the fluorescent excimer occurs in the excited state. Here, the simultaneous double proton transfer reaction leading to the formation of T* may occur in the orientational relaxation process in the excited state dimer of HO-BMN as follows:



The effect of deuterium substitution of the 4-hydroxyl hydrogen upon fluorescence lifetimes of D* confirms the excited-state proton transfer reaction. On the other hand, the difference of fluorescence band maxima between D* and T* (E*) was observed to be somewhat greater in the HO-BMN dimer than in the MO-BMN dimer as seen in Table 1. Further, the activation barrier of D* to T* seems to be smaller in the HO-BMN system than that of D* to E* in the MO-BMN system, as mentioned above. These results of the fluorescence behavior are instructive for understanding of the electronic structure of T* as well as E*, though it is not obvious at this stage.

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