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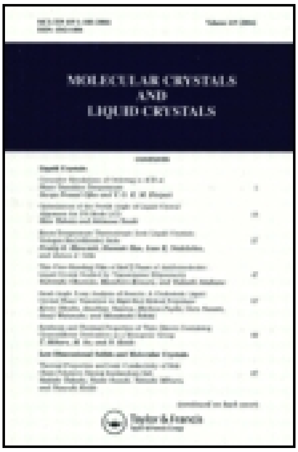

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Theoretical Study of Intramolecular Charge Transfer Turn-off Switching of N-(4-Dimethylaminobenzoyl) Thiourea Induced by Anion Recognition

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The development of colorimetric and fluorescence chemical sensors that have a function of in situ *selective sensing of biologically important anions is one of the significant issues in host-guest chemistry, and a large number of studies have been carried out in the field. The fluorescent chemical sensor, N-(4-Dimethylaminobenzoyl)thiourea (DMABTU; Chart 1) that has been reported by Wu* et al. *[1], has two emission wavelengths at* ca. *500 nm (stronger) and* ca. *350 nm (weaker)) in the absence of anions in chloroform solution. By the addition of anions such as acetate, the emission band at 500 nm decreases while the emission band at 350 nm increases. The broad emission band at around 500 nm was assigned to an intramolecular charge transfer (ICT) transition, and the narrow emission band at around 350 nm to a locally excited (LE) transition. However, a detailed theoretical analysis has not been performed yet on the turn-off switching mechanism of ICT induced by the anion recognition. Therefore, in this work, to clarify the ICT turn-off switching mechanism, we carried out a density functional theory (DFT) and time-dependent DFT (TDDFT) calculations on DMABTU in the ground (S_0) and excited (S_1) states. We obtained optimized structures of DMABTU-X^-(X^- = free, acetate) in S_0 and S_1, and also obtained potential-energy curves (PEC) with respect to a dihedral angle δ between the dimethylamino-group and phenyl-group planes. From the calculations, it was proved that the PEC of DMABTU is not quadratic but nearly flat between $\delta = 0\sim10$ degrees, and the potential minimums are located at $\delta =$* ca. *8∼9 degrees both in S_0 and S_1, while the PEC of DMABTU-AcO$^-$ is quadratic, and DMABTU-AcO$^-$ takes twisted structures ($\delta =$* ca. *12 degree in S_0 and $\delta =$* ca. *21 degree in S_1). These results suggest that ICT character of DMABTU is not a twisted ICT (TICT) but a planar ICT (PICT) state.*

Keywords Anion sensor; dimethylaminobenzene; PICT; thiourea; TICT

1. Introduction

The development of colorimetric and fluorescence chemical sensors that have a function of *in situ* selective sensing of biologically or environmentally important anions is one of the significant issues in host-guest chemistry, and a large number of studies have been

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carried out in the field [1–5]. In these anion sensors, urea/thiourea groups have been often employed as an anion receptor unit. An electronic structural change in urea/thiourea groups stimulated by the coordination of anions is transferred to a "signaling unit," leading to colorimetric or fluorescence changes.

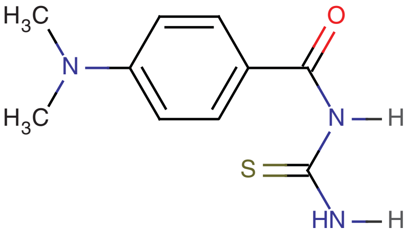

Chart 1. DMABTU

The fluorescent chemical sensor, N-(4-Dimethylaminobenzoyl)thiourea (DMABTU; Chart 1) that has been reported by Wu *et al.* [6], is one of such thiourea-based anion sensors. In DMABTU, N-(4-Dimethylaminobenzene) (DMAB) group, which is well known as a dual fluorescent chromophore, was considered to work as a signaling unit. Actually, DMABTU exhibited two emission bands at *ca.* 500 nm (stronger) and *ca.* 350 nm (weaker)) in the absence of anions in chloroform solution. By the addition of acetate anion (AcO^-), the emission band at 500 nm decreased in intensity while the emission band at 350 nm increased. The broad emission band at around 500 nm was assigned to an intramolecular charge transfer (ICT) transition, and the narrow emission band at around 350 nm to a locally excited (LE) transition because the longer wavelength fluorescence band showed pronounced dependence on the solvent polarity in the previous studies on DMAB compounds [7]. The ICT of DMAB-related compounds have been studied since long ago, and the molecular structure of ICT state has been discussed. For example, Grabowski *et al.* [8] have proposed a twisted ICT (TICT) state for 4-(Dimethylamino)benzonitrile (DMABN), in which dimethylamino (DMA) group is twisted from benzene-ring plane. In contrast, Zachariasse *et al.* [9] advocated a planar ICT (PICT) state for DMABN. Recently, Amatatsu has carried out a detailed theoretical analysis for the electronic excited states of DMABN, and proposed a united picture of TICT and PICT states [10].

As for DMABTU, ICT (TICT or PICT) state of DMABTU seems to be inhibited by the AcO^- recognition. However, a detailed theoretical analysis has not been performed yet on this turn-off switching mechanism of ICT induced by the anion recognition. Therefore, in this work, to clarify the ICT turn-off switching mechanism of DMABTU, we carried out density-functional-theory (DFT) calculations on DMABTU in the ground (S_0) and excited (S_1) states.

2. Methods

For the DFT calculations, the ωB97XD density functional [11], which includes long-range dispersion empirically, was employed. Dunning's correlation consistent double-zeta basis set (cc-pVDZ) [12] was used on all the atoms. Furthermore, a diffuse function (aug-cc-pVDZ) was augmented to the thiourea-group atoms (N, H) to improve long-range interactions due to hydrogen bonding with the anion. Potential-energy curves about the dihedral angle (δ) between the DMA group and benzene-ring plane was calculated under

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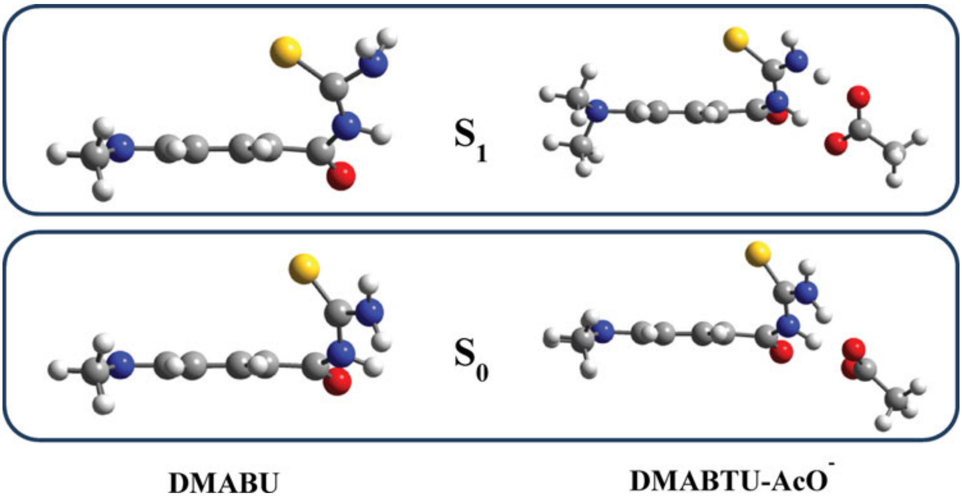

Figure 1. Optimized molecular structures of DMABTU and DMABTU-AcO- in S_0 and S_1.

the condition that the potential energy was minimized for the other degrees of freedom. Vertical-transition energies and their oscillator strengths from S_0 to S_1 (absorption) and from S_1 to S_0 (fluorescence) were calculated by using the TDDFT method with an optimized structure in S_0 and S_1, respectively. All the above mentioned calculations were carried out with the Gaussian 09 package in Hokkaido University information initiative Center.

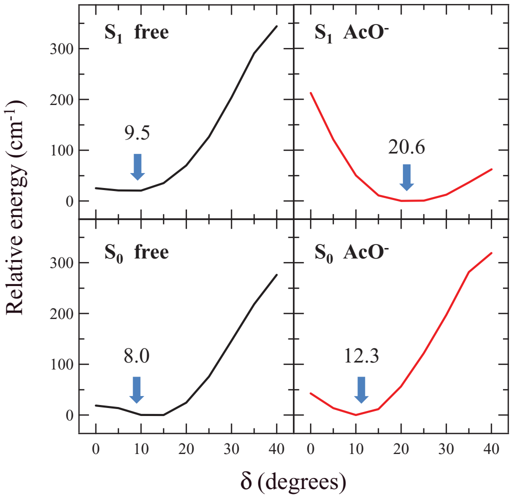

Figure 2. The potential energy curves of DMABTU (left) and DMABTU-AcO- (right). The lower panel: in the ground state (S_0). The upper panel: in the excited state (S_1). δ is a dihedral angle between DMA and benzene planes.

Table 1. Calculated fluorescence ($S_1 \rightarrow S_0$) wavelength (energy), oscillator strength, and orbital composition of DMABTU and DMABTU-AcO$^-$

Species	Wavelength/nm (energy/eV)	f	Orbital	CI/%
DMABTU	694 (1.79)	0.0013	LUMO→HOMO	28
			LUMO→HOMO-1	18
DMABTU-ACO$^-$	503 (2.47)	0.011	LUMO→HOMO	49

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3. Results and Discussion

Optimized structures of DMABTU and DMABTU-AcO$^-$ in S_0 and S_1 are drawn in Fig. 1. In all the electronic and coordination states, thiourea group was out of benzene-ring plane. On the other hand, the geometry of DMA group showed pronounced dependence on the coordination of AcO$^-$. The potential energy curves (PEC) against δ are displayed for DMABTU and DMABTU-AcO$^-$ in Fig. 2; the locations of potential minimum obtained by full geometry optimization are indicated by arrows. In the case of DMABTU, DMA group was nearly planar to the benzene ring, that is, δ was 8.0 (S_0) and 9.5 (S_1) degrees. In contrast, DMA group was rather twisted against benzene plane in DMABTU-AcO$^-$, that is, δ was 12.3 (S_0) and 20.6 (S_1) degrees, respectively. The PECs are nearly flat around zero degree in DMABTU both in S_0 and S_1, but abrupt in DMABTU-AcO$^-$ in S_0 and especially in S_1. These results ensures that DMABTU takes a nearly planar and DMABTU-AcO$^-$ a twisted structure.

The calculated fluorescence and absorption wavelengths of the lowest excited state (S_1) and corresponding oscillator strengths and orbital compositions (squares of CI coefficient) of DMABTU and DMABTU-AcO$^-$ are summarized in Table 1 and 2, respectively. From Table 2, it was found that absorption intensity and its wavelength does not change very much ($f = 0.012 \rightarrow 0.015$; $\lambda = 341$ nm $\rightarrow$ 324 nm) from DMABTU to DMABTU-AcO$^-$, although the fluorescence intensity and its wavelength given in Table 1 showed noticeable changes ($f = 0.0013 \rightarrow 0.011$; $\lambda = 694$ nm $\rightarrow$ 503 nm) from DMABTU to DMABTU-AcO$^-$. From the orbital analysis described in later section, the fluorescence transition of DMABTU and DMABTU-AcO$^-$ has an ICT and a LE character, respectively. In Table 3, the calculated and experimental fluorescence wavelengths are summarized for ICT

Table 2. Calculated absorption ($S_0 \rightarrow S_1$) wavelength (energy), oscillator strength, and orbital composition of DMABTU and DMABTU-AcO$^-$

Species	Wavelength/nm (energy/eV)	f	Composition	CI/%
DMABTU	341(3.64)	0.012	HOMO-1→LUMO	22
			HOMO-1→LUMO+2	12
			HOMO→LUMO	10
DMABTU-AcO$^-$	324(3.82)	0.015	HOMO→LUMO	32
			HOMO→LUMO+3	10

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Table 3. Calculated and experimental fluorescence wavelengths of LE and ICT fluorescence

	Wavelength/nm		
	Calculated	Experimental[a]	Calc./exp.
ICT (DMABTU)	694	500	1.39
LE(DMABTU-AcO$^-$)	503	360	1.40

[a] These experimental values are taken from Ref. 1.

(DMABTU) and LE (DMABTU-AcO$^-$) transitions. The ratios (scaling factors) of experimental/calculated emission wavelengths were very close between LE and ICT bands (Table 3), and hence it can be said that calculations reproduce experimental results fairly well. On the basis of these results obtained from calculations, vertical absorption/fluorescence-transition wavelengths and their orbital changes are illustrated for DMABTU in Fig. 3 and for DMABTU-AcO$^-$ in Fig. 4, respectively. In DMABTU, the Franck-Condon (FC) S_1 state, which has the same geometrical structure with S_0, relaxes to the stable S_1 state. The FC S_1 state and the relaxed S_1 state have noticeably different electronic character: π electron in the FC S_1 state moves to the thiourea group in the stable S_1 state. Since the vertical transition from the relaxed S_1 state to S_0 state is of CT character, the lowest excited state of DMABTU may be easily affected by solvent. In contrast, the FC S_1 state and the

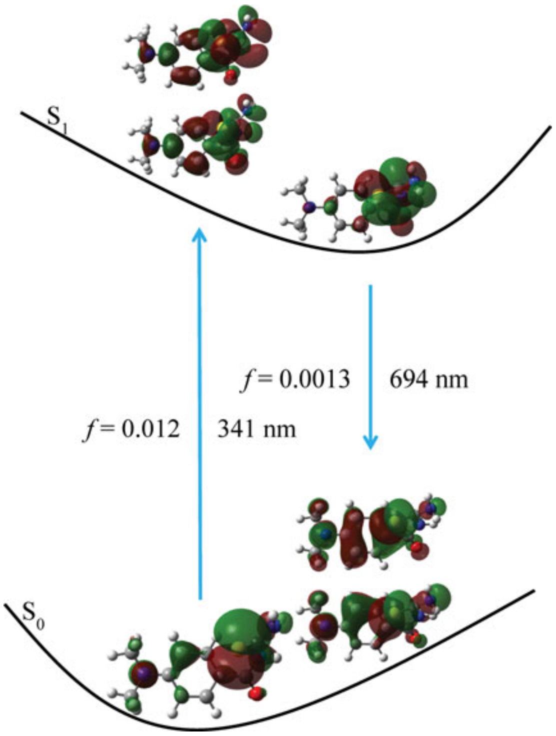

Figure 3. Orbital configurations related to $S_0 \rightarrow S_1$ (absorption) and $S_1 \rightarrow S_0$ (fluorescence) transitions of DMABTU.

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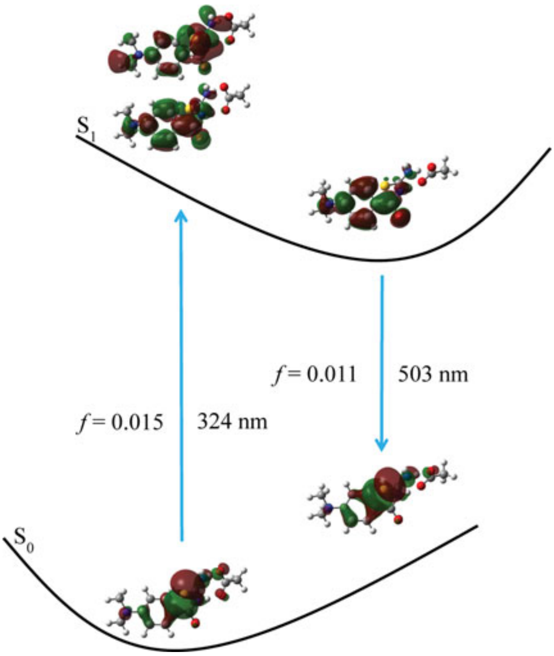

Figure 4. Orbital configurations related to $S_0 \rightarrow S_1$ (absorption) and $S_1 \rightarrow S_0$ (fluorescence) transitions of DMABTU-AcO$^-$.

stable S_1 state of DMABTU-AcO$^-$ have nearly the same electronic character: π-electron on the benzene ring does not move. Furthermore, the vertical transition from the relaxed S_1 state to S_0 state is of LE character; the lowest excited state of DMABTU-AcO$^-$ will not be affected very much by solvent. The ICT process mainly takes place from benzene to thiourea in DMABTU, and this ICT process is inhibited by the AcO$^-$ coordination to the thiourea group in DMABTU-AcO$^-$. Twisting of DMA group may not be directly related to the ICT process in DMABTU. This is very different case from the ICT process of DMABN.

Conclusions

Geometrical optimization and orbital analysis showed that (1) Franck-Condon S_1 state of DMABTU seems to be ICT state, (2) however, the relaxed (or stable) S_1 state has an ICT character clearly, (3) the ICT state of DMABTU is not TICT but rather PICT, (4) Franck-Condon and relaxed S_1 states of DMABTU-AcO$^-$ have a similar electronic structure, (5) ICT character of the relaxed (or stable) S_1 state of DMABTU-AcO$^-$ is very small although the DMA group is twisted ($\delta = 20.6$ degree). The ICT process mainly takes place from benzene to thiourea in DMABTU, and this ICT process is inhibited by the AcO$^-$ coordination to the thiourea group in DMABTU-AcO$^-$.

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