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Contrasting Intermolecular and Intramolecular Exciplex Formation of a 1,4-Dicyano-2-methylnaphthalene−*N,N*-Dimethyl-*p*-toluidine Dyad

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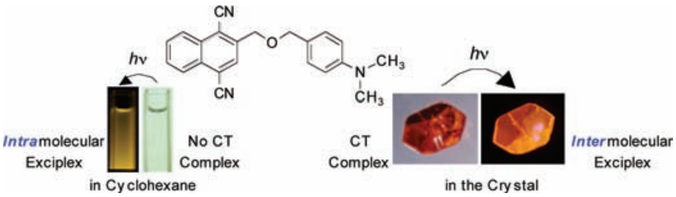
ABSTRACT



An intramolecular exciplex is formed upon excitation of the cyclohexane solution of the 1,4-dicyano-2-methylnaphthalene−*N,N*-dimethyl-*p*-toluidine dyad, but little if any intramolecular CT complex exists in the ground state of this substance in solution. In contrast, in the crystalline state, the dyad forms an intermolecular mixed-stack CT complex in the ground state and an intermolecular exciplex when it is photoexcited.

Inter-[1] and intramolecular[2] exciplexes are often observed in solution. Their formation mechanism and photophysical and -chemical properties[3] have been studied in terms of molecular structure[4] and solvent effects.[5] Very recently, exciplex emission resulting from charge recombination of the electron-hole in organic elctroluminescence devices is becoming the focus of attention.[6] However, approaches to the utilizing of exciplex emission rarely have been tried on luminescent organic single crystals, although luminescent organic crystals attract much attention due to their potential applications to a variety of organic functional materials.[7]

Hirayama found that linking a donor (D) and an acceptor (A) with a three-carbon methylene chain, as represented by D-$(CH_2)_3$-A, results in effective formation of an intramolecular exciplex through conformational change leading to charge-transfer (CT) processes (Hirayama rule).[8] Although most exciplexes are observed in the solution phases, some exciplexes are observed in the crystalline or solid states.[9] For instance, Becker et al. found an intramolecular anthracene−ethylene exciplex generated by photoexcitation of a lepidopterene in the crystals.[10] To the best of our knowledge, however, few studies have been conducted on molecules which form inter- and intramolecular exciplexes

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in both the crystalline and solution states,[11] though the formation of excimers in the crystalline state is relatively common.[12]

Crystal engineering of CT complex is a very interesting research field, because an exquisite packing of D and A can be readily achieved in the crystalline state.[13] We think of idea that we apply the crystal engineering of CT complex to preparing luminescent organic crystals, in which a face-to-face alignment of D and A forms emissive exciplex. Therefore, in this work, we designed and synthesized a new dyad, 1,4-dicyano-2-[4′-(*N*,*N*-dimethylamino)benzyloxy]-methylnaphthalene (**1**, Figure 1), and studied its optical properties in solution and the crystalline or solid states. In this paper, we present the results of studies that show that an intermolecular exciplex is formed in crystals of **1** while, as expected, dyad **1** forms an intramolecular exciplex in cyclohexane solution (Figure 2). In addition, observations made in this effort clearly demonstrate that the intermolecular exciplex of **1** in the crystalline state results directly from excitation of a ground-state intermolecular CT.

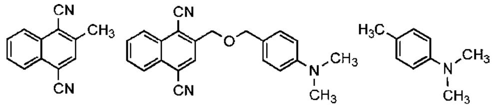

Figure 1. Chemical structures of DCMN, **1**, and DMT.

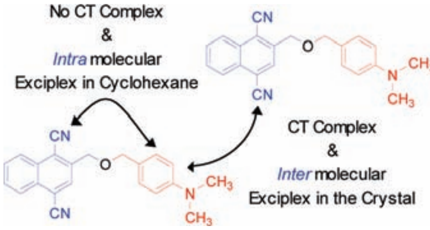

Figure 2. Schematic for the formation of CT complexes and intermolecular and intramolecular exciplexes of **1**.

As shown in Figure 3a,b, cyclohexane solutions of **1** and DCMN are colorless under natural light. The absorption spectrum of **1** in cyclohexane (Figure 4, black and bold) is virtually the sum of the spectra of DCMN (black and solid) and DMT (black broken line) and exhibits intense absorptions at 250−350 nm and weak absorptions at 350−400 nm.[14] These findings indicate that an intramolecular CT complex of **1** is hardly formed in cyclohexane, even though the strong acceptor DCMN is interlinked with the strong donor DMT.

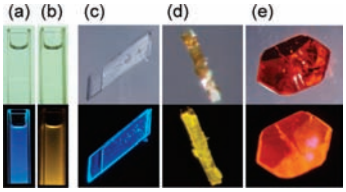

Figure 3. Photographs of DCMN (a and c) and **1** (b, d, and e) in cyclohexane and in crystals under natural light (top) and under light at 365 nm (bottom).

When a cyclohexane solution of DCMN (5.0×10^{-5} mol/L) is excited with 320-nm light, blue fluorescence is observed at ca. 350 nm (Figure 3a, bottom, and Figure 4, blue) with a quantum yield (Φ_f) of 0.29 and a fluorescence lifetime (τ_f^{MONO}) of 3.7 ns. When DMT is added to the DCMN solution ($[DMT] = 5.0 \times 10^{-3}$ mol/L), a weak emission band corresponding to an intermolecular exciplex between DCMN and DMT is observed at 526 nm along with an intense monomer emission from the singlet excited DCMN at ca. 350 nm. On the other hand, excitation of a *dilute* cyclohexane solution of dyad **1** (5.0×10^{-5} mol/L) at 320 nm leads to significantly decreased emission from the DCMN moiety ($\lambda_{em}^{MONO} = 354$ nm, $\tau_f^{MONO} = 3.7$ ns) and orange fluorescence ($\lambda_{em}^{EX} = 550$ nm, $\Phi_f = 0.05$, $\tau_f^{EX} = 13.7$ ns; Figure 3b, bottom, and Figure 4, red). The fluorescence, which is

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similar to that of the intermolecular exciplex of DCMN and DMT in cyclohexane, is assigned to an intramolecular exciplex involving the DCMN and DMT moieties of **1**.

Although a cyclohexane solution of **1** is colorless under natural light (see Figure 3b), needle crystals of **1** (from 1:3 $CHCl_3-CH_3OH$, mp 160−161 °C) are yellow under natural light (Figure 3d). Interestingly, prisms of **1** (evaporatively recrystallized from CH_3OH solution of the yellow needles, mp 165−166 °C) are red (Figure 3e). For comparison purposes, columnar crystals of DCMN are essentially colorless (Figure 3c). These observations suggest that an interaction takes place between the DCMN and DMT moieties in both yellow needles and red prisms of **1**. Actually, a diffuse reflection spectrum of the red prisms of **1** in a KBr pellet, obtained after Kubelka−Munk transformation, contains a broad and structureless band in the 350−550 nm region (Figure 5, black bold line). A similar band is not observed for DCMN (Figure 5, black thin line). This finding indicates that CT interaction between the DCMN and DMT moieties occurs in the red prisms of **1**.

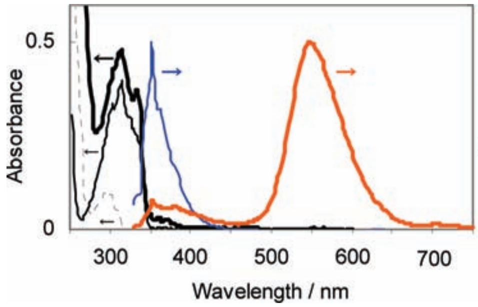


Figure 4. Absorption spectra of **1** (black, bold), DCMN (black, solid), and DMT (black, broken) in cyclohexane (5.0×10^{-5} mol/L) and fluorescence ($\lambda_{ex} = 320$ nm) spectra of **1** (red) and DCMN (blue) in cyclohexane.

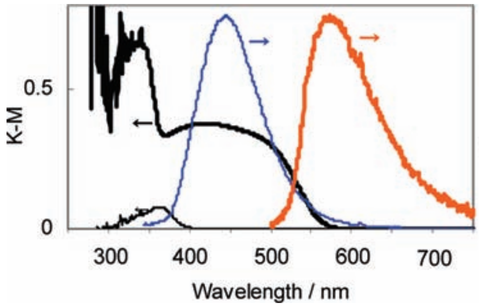


Figure 5. Diffuse reflection and fluorescence ($\lambda_{ex} = 320$ nm) spectra of colorless columnar crystals of DCMN (black thin and blue) and red prism crystals of **1** (black bold and red) in KBr.

Columnar crystals of DCMN display typical blue fluorescence upon excitation at 365 nm (Figure 3c, bottom). Also, a broad emission band at ca. 450 nm is produced by excitation of columnar crystals of DCMN ($\Phi_f = 0.49$; Figure 5, blue), which is referred to aggregation of DCMN in the crystals. In contrast, yellow needles of **1** emit yellow fluorescence ($\Phi_f = 0.10$; Figure 3d bottom) at 550 nm, being in good agreement with the exciplex fluorescence in cyclohexane (see the Supporting Information). The corresponding red prisms show orange fluorescence ($\Phi_f = 0.09$; Figure 3e, bottom) upon excitation at 365 nm.

The red prisms of **1** fluoresce in the 500−750 nm region ($\lambda_{em}^{EX} = 567$ nm; Figure 5, red), a band that is associated with exciplex fluorescence. In fact, X-ray crystallographic analysis of the red prisms[15,16] shows that the DCMN moiety in **1** is twisted by 106° from the plane of the DMT moiety (Figure 6),[17] and it is successfully stacked with the DMT moiety of an adjacent molecule of **1**. The DCMN moiety of this "adjacent molecule" is further stacked with the DMT moiety of another molecule of **1**, as shown in Figure 6. Thus, intermolecular face-to-face overlap between the DCMN and DMT moieties of **1** in the red prisms results in formation of

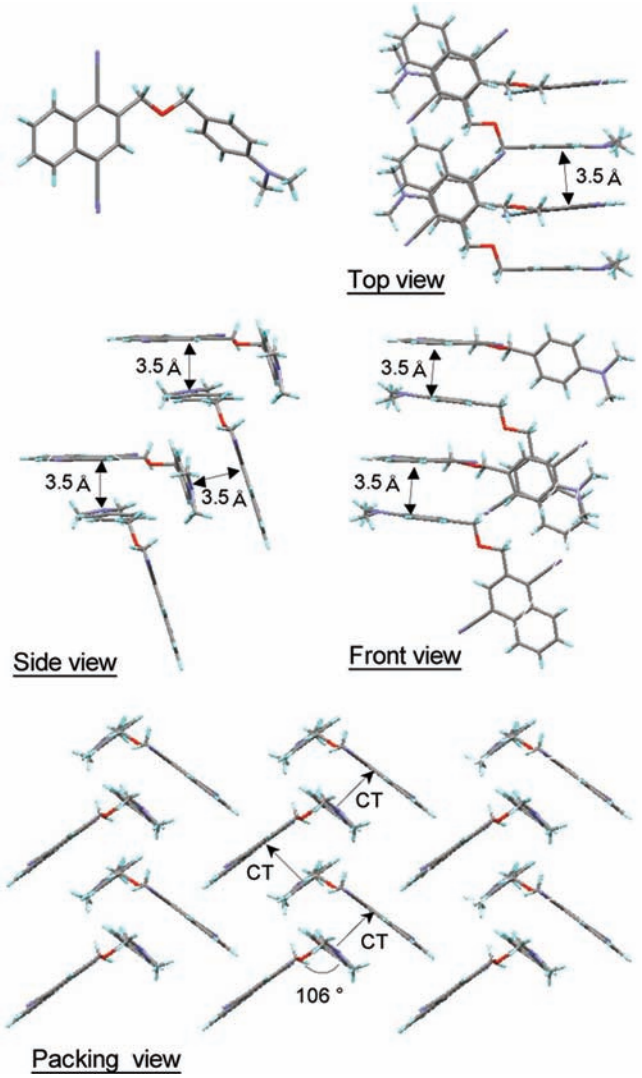
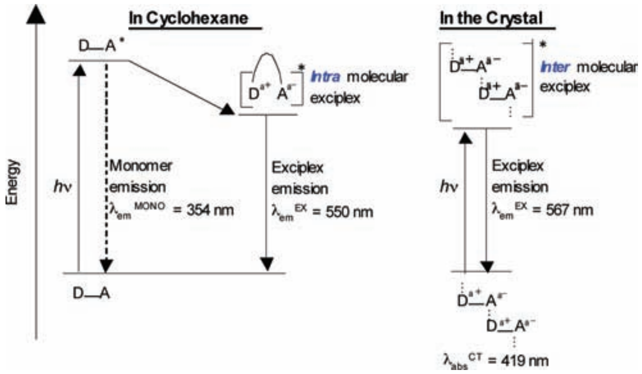


Figure 6. Molecular geometry (top, left) and crystal structure of the red prisms of **1**.

an intermolecular one-to-one mixed-stack ground state CT complex that has a transition dipole moment continuously oriented in a zigzag manner. The results clearly demonstrate that emission from the red prisms of **1** is a consequence of an intermolecular exciplex occurring between the DCMN and DMT moieties aligned in a face-to-face orientation through CT interactions.

Scheme 1. Simplified Energy Diagrams of Intra- and Intermolecular Exciplex Formation of **1** in Cyclohexane and in the Crystals, Respectively[a]



[a] Key: A, DCMN moiety; D, DMT moiety.

Scheme 1 shows simplified energy diagrams for intra- and intermolecular exciplex formation for **1** in cyclohexane solution and the crystalline state. Photoexcitation of a cyclohexane solution of dyad **1**, in which its ground state does not participate in strong CT interactions, results in production of an exciton that, prior to monomer emission from the DCMN moiety, forms an intramolecular exciplex through a pathway involving a conformational change and CT. In contrast, in the crystalline state **1** exists in an infinite intermolecular CT ground-state complex that is capable of directly forming an intermolecular exciplex when photoexcited.

In conclusion, we have found that a dyad **1** hardly forms a CT complex in the ground state but that it produces an intramolecular exciplex between the DCMN and DMT moieties in cyclohexane in accord with the Hirayama rule. In contrast, crystals of the dyad **1** form an intermolecular mixed-stack, one-to-one CT complex in the ground state. The observations made in this effort clearly demonstrate that the intermolecular exciplex, generated by excitation of crystals of **1**, arises directly from the ground state CT complex, in which the DCMN and DMT moieties are immobilized in a face-to-face manner by intermolecular CT interactions. In addition, the studies have shown that the difference in color between the yellow needles and the red prisms would be due to a difference in their crystal structures. We are now in the process of investigating the effects of crystal strucure on the formation of the intermolecular exciplex of **1** and the mechanism for the formation of inter- and intramolecular exciplexes of **1** in crystals and various solutions.

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Supporting Information Available: Synthetic details and optical and electrochemical properties of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The weak absorption between 350−400 nm may indicate a feeble CT interaction of the DCMN and DMT moieties of **1** in the ground state. However, solvent effects on absorption spectrum are not significant. See the Supporting Information.

(15) Crystallographic data of the red prisms (mp 165−166 °C) of **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 752019.

(16) Many efforts to obtain a satisfactory single crystal for X-ray crystallographic analysis of the yellow needles (mp 160−161 °C) of **1** were unsuccessful, but are still continued and will be published elsewhere.

(17) The molecular geometry determined with X-ray crystallographic analysis was also supported by density function theory calculation B3LYP/6-31G(d,p).