Fluorescence Behavior Associated with a Possible Intercolumnar Charge-transfer Interaction in the Crystalline State of a Dyad Consisting of Mesitylene and 1,4-Dicyano-2-methynaphthalene Subunits

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ABSTRACT: Fluorescence (FL) properties of a novel donor–acceptor dyad, comprised of mesitylene and 1,4-dicyano-2-methynaphthalene (DCMN) subunits connected by an ether linkage, were elucidated. The dyad in cyclohexane exhibits FL arising from an intramolecular exciplex. In the crystalline state, the dyad does not emit light from intra- and inter-molecular exciplexes but rather displays FL that is nearly equivalent to that of 2-methoxymethyl-substituted DCMN. However, the emission spectrum of the crystalline dyad contains a shoulder in the long wavelength region, suggesting that weak intercolumnar charge-transfer interactions take place between columns consisting of the mesitylene and DCMN subunits.

An exciplex is an electronically-excited state complex comprised of two different molecules.¹ Mechanisms for inter-² and intra-molecular³ formations and the photo-physical⁴ and photo-chemical⁵ properties of a number of exciplexes in solution have been studied. On the other hand, exciplexes in the crystalline state have gained much less attention.

In a previous effort, we studied the fluorescence (FL) behavior of dyads containing a 1,4-dicyano-2-methynaphthalene (DCMN) electron acceptor tethered to 4-methyl-, 4-methoxy-, and 4,N,N-dimethylaniline⁶ donor subunits by an ether linkage (1a, 1b, and 1c, respectively, Chart 1). In the crystalline states of 1b and 1c, intermolecular exciplex (Fig. 1a)-derived FL occurs with respective maxima at λFL,C = 456 and 567 nm that are longer wavelengths than those in cyclohexane solutions. Intermolecular exciplexes of 1b and 1c were shown to have columnar structures in which p-substituted-toluene donor subunits are alternately stacked with the DCMN acceptor subunit of neighboring molecules.

Chart 1. Molecular Structures of Dyads 1a–c and 2 and the Acceptor Model 3

Table 1. Absorption, FL, and DR Properties in Cyclohexane Solutions (λAB,S, λFL,S, τFL,S, and ΦFL,S), KBr (λAB,R), and the Crystalline States (λFL,C, τFL,C, and ΦFL,C), and Stacking Manner of Donor and Acceptor Subunits in the Crystalline States of 1a–c, 2, and 3

<table>
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<th>λAB,S nm</th>
<th>λFL,S nm</th>
<th>τFL,S ns</th>
<th>ΦFL,S</th>
<th>λAB,R nm</th>
<th>λFL,C nm</th>
<th>τFL,C ns</th>
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<td>435</td>
<td>5.1</td>
<td>0.09</td>
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Figure 1. (a) Intermolecular exciplexes of 1b and 1c. (b) Locally-excited monomer and (c) intramolecular exciplex of 2. (d) Excited crystalline 2 involved in possible weak intercolumnar CT interactions and excited crystalline 3 in which CT interactions cannot take place. The mesitylene, DCMN, and ether subunits are shown in pink, blue, and orange, respectively.

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Dyads, comprised of the electron-donating arene and electron-accepting DCMN subunits, which exhibit exciplex FL at long wavelengths, have the potential of serving as crystalline emissive materials. However, when a dyad of this type contains a strong electron-donating moiety, FL quantum yields in the crystalline state ($\Phi_{FL,C}$) are low as a consequence of electron-transfer quenching of the emissive excited state that affords radical ion pairs. This phenomenon is exemplified by the observation that the $\Phi_{FL,C}$ of 1c is only 0.09 while that of 1b is 0.39.

As part of studying the design optimal dyads that exhibit long wavelength crystalline exciplex emission and high $\Phi_{FL,C}$, we investigated the FL properties of the novel dyad, 1,4-dicyano-2-(3,5-dimethoxytoluene)(dimethylnaphthalene) (2, Chart 1), which contains the low donating mesitylene as a donor and DCMN as an acceptor. The design of 2 took into account the expectation that the electron-donating ability of the mesitylene subunit is higher than that of the 4-methoxytoluene subunit in 1a yet lower than that of the 4-methoxynaphthalene subunit in 1b and the observation that the 4-methoxynaphthalene and DCMN subunits in the crystalline state of 1a do not stack alternately but rather are independently aligned in columns (Table 1). As a result, crystals of 1a exhibit FL at $\lambda_{FL,C} = 401$ nm, a wavelength that is shorter than that of 1a in cyclohexane. This observation indicates that FL from 1a does not arise from an intramolecular exciplex.

Dyad 2 was synthesized using mesitylene and 2-methyl-naphthalene employing a method that is similar to that used for preparation of 1a-c. The results of cyclic voltammetry measurements show that 2 in CH$_3$CN is oxidized at $E^{\circ}_{1/2} = +1.98$ V vs SCE, showing that the electron-donating ability of the mesitylene subunit in 2 is approximately halfway between those of the 4-methyl- and 4-methoxytoluene subunits in 1a ($E^{\circ}_{1/2} = +2.04$ V) and 1b ($+1.64$ V), respectively. This conclusion is supported by the results of density functional theory calculations (B3LYP/6-31G* level), which show that the energy levels of the HOMOs ($E_{HOMO}$) of 1a, 1b, and 2 are $-6.38$, $-5.91$, and $-6.26$ eV, respectively.

The UV–Vis absorption spectrum of 2 in cyclohexane contains absorption maxima at $\lambda_{A_{LS}} = 318$ and 334 nm (Table 1 and Fig. 2a), which are nearly the same as those in the spectrum of 3, a model DCMN acceptor (Chart 1). This finding indicates that charge-transfer (CT) interactions between the mesitylene and DCMN subunits in 2 do not occur in the ground state. In contrast to 3, which has a FL maximum at $\lambda_{FL,S} = 362$ nm (excitation at $\lambda_{EX} = 320$ nm), 2 has an emission with a major and longer wavelength band at $\lambda_{FL,S} = 407$ nm and a minor band at 362 nm (Fig. 2b). Moreover, the FL of 2 does not show a significant dependence on concentration, suggesting that the respective FL bands at 362 and 407 nm are associated with a locally-excited monomer (Fig. 1b) and intramolecular exciplex (Fig. 1c).

Crystallization of 2 from CH$_3$CN gave single crystals that exhibit blue FL under 254-nm light (Fig. 3a). The results of X-ray crystallography, show that 2 adopts an extended molecular geometry (Fig. 3b), suggesting that it cannot readily form an intramolecular exciplex upon photoexcitation in its crystalline state. Additionally, molecules in crystals of 2 are aligned in a columnar structure (Fig. 3c), in which the mesitylene and DCMN subunits are independently assembled in respective columns. No face-to-face overlap between the mesitylene and DCMN subunits exist in crystals of 2, indicating that 2 does not form intramolecular exciplexes in its crystalline state. The observations suggest that more effective CT interactions than those that exist between the mesitylene and DCMN subunits of 2 would be required for creation of a packing structure with alternately-stacked donor and acceptor. The threshold strength of the CT interactions could be an important consideration in designing organic semiconductors based on CT crystals.

The diffuse reflection (DR) spectrum of 2 in KBr, obtained after employing the Kubelka–Munk transformation, contains a peak at $\lambda_{DR} = 335$ nm (Table 1 and Fig. 4a), which is similar to that in the DR spectrum of 3. This finding shows that the DCMN subunit does not participate in electronic interactions with the mesitylene subunit in.
the ground state of 2 in its crystalline state. The FL wavelength of 2 in the crystalline state ($\lambda_{FLC} = 443$ nm) is similar to that of 3 (435 nm, Fig. 4b). Moreover, 2 and 3 have nearly identical FL lifetimes (Table 1, $\tau_{FL}$) and quantum yields ($\Phi_{FL}$). Thus, it appears that the DCMN fluorophore is the major contributor to the FL of 2 in the crystalline state.

Although the crystal packing structure of 3 has not been elucidated, FL from crystals of 2 and 3 likely originate from excited species that exist in independently-stacked DCMN columns (acceptor) (Figs. 1d and 3c), which we refer to as intercolumnar CT interactions.

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REFERENCES AND NOTES

8. For the details, contact the corresponding author.
10. Crystal information file can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC-1052873) via www.ccdc.cam.ac.uk/data_request/cif.