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Control of the CT interaction between electron-donor and -acceptor moieties of a 1,4-dicyanonaphthalene–arene dyad for intermolecular exciplex or excimer formation in crystals

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ABSTRACT

Colorless crystals of 1,4-dicyano-2-(4′-methoxybenzyloxy)methylnaphthalene (**2**), which is a 1,4-dicyano-2-methylnaphthalene (DCMN)–4-methylanisole (MA) dyad linked by an ether unit, selectively form a fluorescent intermolecular DCMN–MA exciplex (greenish blue, $\lambda_f^{\text{exciplex}} = 456$ nm). In contrast, 1,4-dicyano-2-(4′-methylbenzyloxy)methylnaphthalene (**3**), which is a DCMN–*p*-xylene dyad, forms a fluorescent intermolecular DCMN–DCMN excimer in the crystalline state (blue, $\lambda_f^{\text{excimer}} = 404$ nm). These findings demonstrate that a moderate charge transfer interaction takes place between the DCMN moiety of **2** and MA moieties of the adjacent molecules of **2**, which successfully facilitates the preparation of light-emissive organic crystals.

Inter-[1] and *intra*molecular[2] exciplexes have been studied in solution from the viewpoint of the mechanism of their formation, and their photophysical[3,4] and photochemical properties.[5] However, approaches to utilize the properties of exciplexes, especially their fluorescence, for luminescent organic single crystals[6] have rarely been explored despite potential organic functional materials in a variety of roles.[7] Recently, we explored[8] a new crystal architecture concept[9] in which charge transfer (CT) complexes in the crystalline state serve as the foundation of organic crystals that emit fluorescence via exciplexes. In the first test of this concept, we observed that the exciplex fluorescence of crystals of the 1,4-dicyano-2-methylnaphthalene (DCMN)–*N*,*N*-dimethyl-*p*-toluidine (DMT) dyad (**1**, Chart 1) was weak ($\Phi_f = 0.09$) as a consequence of the contribution of electron transfer quenching. This originated from the strong CT interaction between the DCMN and DMT moieties in the ground state. We believed that a potential solution to this problem would be to allow only moderate CT interaction between electron-donor (D) and -acceptor (A) moieties of a dyad in the crystals, thus, avoiding electron transfer quenching and leading the D and A moieties to preorient in a configuration suitable for exciplex formation when photoexcited.

In this work, we synthesized two new dyads: 1,4-dicyano-2-(4′-methoxybenzyloxy)methylnaphthalene (**2**)[10] and 1,4-dicyano-2-(4′-methylbenzyloxy)methylnaphthalene (**3**).[11] The former is a DCMN–4-methylanisole (MA) dyad linked by an ether unit, while the latter is a DCMN–*p*-xylene (XY) dyad. Herein, we present contrasting results for **2**, which forms a fluorescent intermolecular DCMN–MA exciplex in the crystalline state, and **3**, which forms a fluorescent intermolecular DCMN–DCMN excimer (Fig. 1). It is demonstrated that the moderate CT interaction between the DCMN and MA moieties of **2** in the crystals is an important factor in preparing light-emissive organic crystals.

Cyclohexane solutions of **2** and **3** (5.0×10^{-5} mol/L) are colorless under natural light, as shown in Figure 2a and c. UV–vis spectra of them (Fig. 3) exhibited intense absorption bands at 250–350 nm, which are nearly the same as those of DCMN,[9]

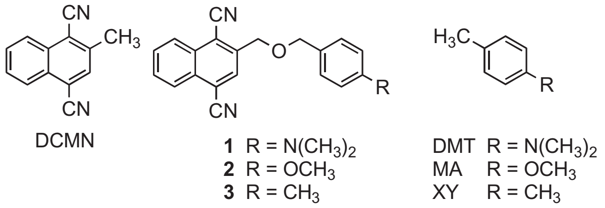

Chart 1. Structures of DCMN, **1**–**3**, DMT, MA, and XY.

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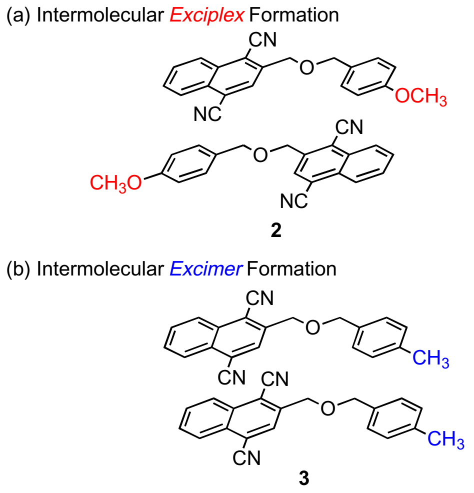

Figure 1. Schematic representation of intermolecular *exciplex* formation of **2** (a) and intermolecular *excimer* formation of **3** (b) in the crystals.

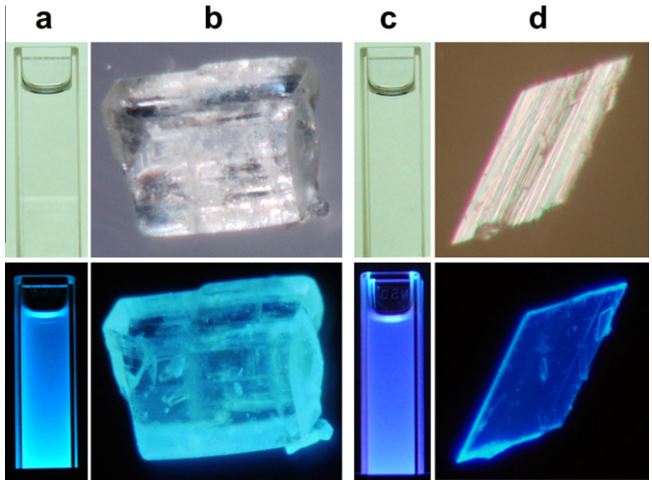

Figure 2. Photographs of **2** (a and b) and **3** (c and d) in cyclohexane and in the crystals under natural light (top) and under irradiation at 365 nm (bottom).

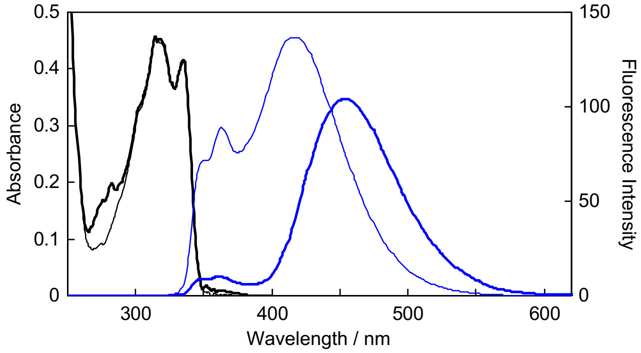

Figure 3. UV–vis spectra of **2** (black, bold) and **3** (black, thin) in cyclohexane (5.0×10^{-5} mol/L), and fluorescence spectra of **2** (blue, bold) and **3** (blue, thin) in cyclohexane (excitation wavelength 320 nm).

together with week absorptions at 350–370 nm.[12] These observations indicate that intramolecular CT complexes of **2** and **3** are not formed in cyclohexane. When the cyclohexane solution of **2** is irradiated with 320 nm light, fluorescence from the DCMN moiety is barely observed, but a greenish blue fluorescence is seen at 456 nm that is assignable to an intramolecular exciplex (Fig. 2a, bottom, Fig. 3, blue bold, $\Phi_f = 0.22$, fluorescence lifetime $\tau_f^{\text{exciplex}} = 33.7$ ns). This result contrasts with observations made in studies with **3** where a cyclohexane solution emits blue fluorescence (Fig. 2c, bottom) when photoexcited at 320 nm. The fluorescence spectrum of **3** (Fig. 3, blue thin) shows a monomer emission from the DCMN moiety at ca. 350 nm ($\tau_f^{\text{monomer}} = 1.4$ ns) and a typical intramolecular exciplex emission at 417 nm ($\tau_f^{\text{exciplex}} = 12.1$ ns). The total Φ_f for these two emissions is 0.25 (Table 1).

Table 1
Fluorescence properties of **2** and **3** in cyclohexane and in the crystals

Dyad	Solvent	$\lambda_f^{\text{monomer}}$ (nm)	$\lambda_f^{\text{exciplex}}$ (nm)	$\lambda_f^{\text{exciplex}}$ (nm)	λ_f
2	Cyclohexane[a]	361	456	Nd[b]	0.22
	Crystals	Nd[b]	456	–	0.39
3	Cyclohexane[a]	363	417	Nd[b]	0.25
	Crystals	Nd[b]	–	404	0.29

[a] 5.0×10^{-5} mol/L.
[b] Not detectable.

Dyad **2** is colorless under natural light in the crystalline state as well as in cyclohexane solution (Fig. 2b, top) and it displays greenish blue fluorescence when irradiated at 365 nm (Fig. 2b bottom). As shown in Figure 4, fluorescence of **2** in the crystalline state has a maximum at 456 nm with $\Phi_f = 0.39$ that is higher than that in cyclohexane (0.22) and matches that of the exciplex fluorescence band of **2** in cyclohexane (see Fig. 3 and Table 1). X-ray crystallographic analysis shows that the DCMN and MA moieties of **2** are coplanar with each other and that **2** intermolecularly stacks with MA and DCMN moieties of the adjacent molecules (Fig. 5).[13] Thus, the intermolecular face-to-face overlap between DCMN and MA moieties of **2** in the crystalline state results from CT interaction in the ground state in which the CT transition dipole moments cancel each other, as shown in Figure 5.

Similarly to crystals of **2**, crystals of **3** are colorless and emit blue fluorescence (Fig. 2d, bottom) at 404 nm upon excitation at 320 nm ($\Phi_f = 0.29$, Fig. 4, blue thin). However, an X-ray crystallographic analysis clearly shows that differences exist in the crystalline states of **2** and **3**. Namely, effective π-stacking takes place between the DCMN moiety of one molecule **3** and the DCMN moiety of an adjacent molecule **3** (Fig. 6).[13] This observation suggests that the blue fluorescence of crystals of **3** results from an intermolecular DCMN–DCMN excimer.[14] Note that the CT interaction between the DCMN and XY moieties of **3** is evidently inefficient compared to the DCMN–DCMN interaction.

In conclusion, we have successfully prepared light-emissive organic crystals ($\Phi_f = 0.39$) with the crystal architecture concept utilizing the CT interaction of the DCMN–MA dyad of **2**. We have found that the moderate CT interaction between the D (MA) and A (DCMN) moieties in the crystals is an important factor in the

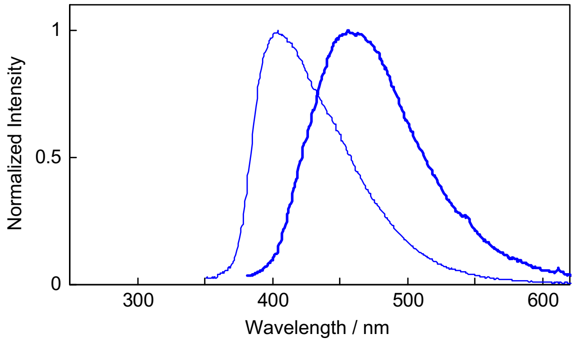

Figure 4. Fluorescence spectra of crystals of **2** (blue bold) and **3** (blue thin) (excitation wavelength 320 nm).

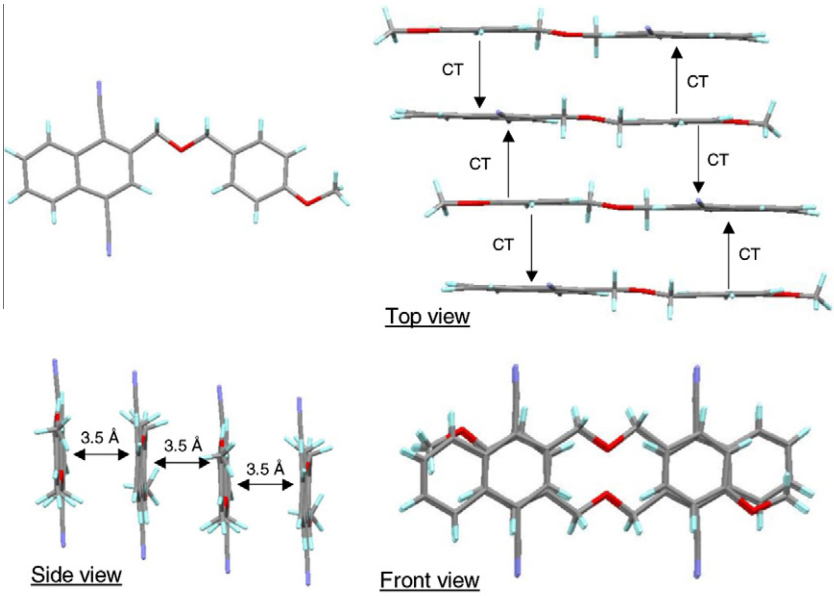

Figure 5. Molecular geometry (top left) and crystal structure of **2**.

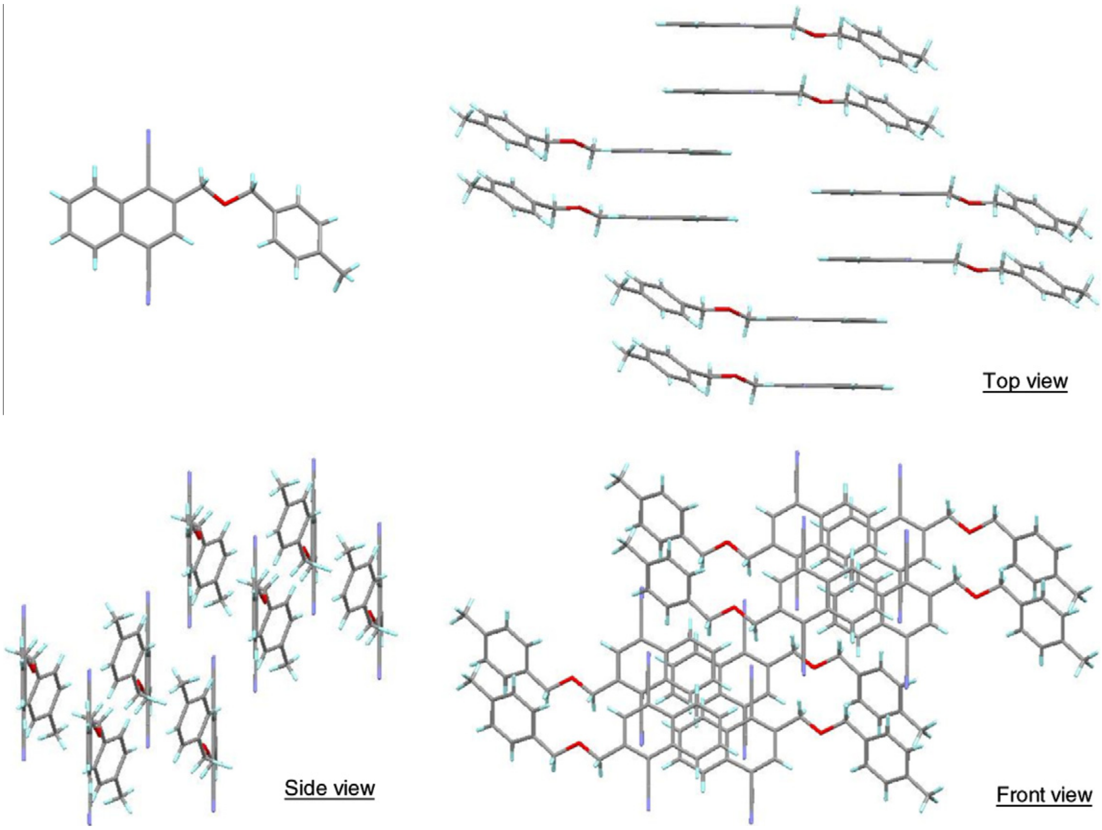

Figure 6. Molecular geometry (top left) and crystal structure of **3**.

preparation of light-emissive organic crystals. The moderate CT interaction avoids electron transfer quenching on excitation and leads the D and A moieties to preorient in a configuration suitable for exciplex formation. In the case of **2**, the emission of the organic crystals is attributed to the exciplex fluorescence. In this sense, not only are the electron-donating and electron-accepting properties of the D and A moieties in the ground state important;[17] but those in the excited state are also crucial and controlling. Further studies, aimed at generalization and quantification of the crystal architecture concept, are now in progress.

Acknowledgments

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10. Preparation of **2**: A solution containing 1,4-dibromo-2-(4′-methoxybenzyloxy)methylnaphthalene (2.2 g, 2.7 mmol), NaCN (0.53 g, 11 mmol), Pd(PPh_3)$_4$ (0.64 g, 0.55 mmol), and CuI (0.21 g, 1.1 mmol) in propionitrile (7 mL) was stirred at reflux for 2 h and cooled to room temperature. After addition of EtOAc (60 mL), the mixture was filtered through a Celite pad, washed with water and brine, and the solvent was concentrated in vacuo. The resulting dark-brownish residue was subjected to silica-gel chromatography with hexane–EtOAc (9:1), giving 0.88 g of crude **2** as pale yellow powder in 99% yield. Recrystallization from CH_3OH gave a pure **2** as colorless columns. Mp 110–111 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 3.74 (s, 3H, OCH_3), 4.60 (s, 2H, CH_2), 4.88 (s, 2H, CH_2), 6.92 (AA′BB′, J = 8 Hz, 2H), 7.35 (AA′BB′, J = 8 Hz, 2H), 7.94–8.00 (m, 2H), 8.22–8.27 (m, 2H), 8.34 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 55.1 (OCH_3), 68.8 (CH_2), 72.1 (CH_2), 112.7, 113.7 (2C), 113.7, 114.8 (CN), 116.3 (CN), 125.3, 125.4, 129.5, 129.6 (2C), 130.4, 130.4, 130.8, 131.3, 132.4, 142.6, 158.9; UV–vis (cyclohexane) λ_{max} 315 nm (ε = 9123 mol^{-1} L cm^{-1}); IR (diamond ATR) ν 2216 cm^{-1} (CN); Anal. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.70; H, 4.79; N, 8.53.
11. Dyad **3** (colorless columns) were prepared from 1,4-dibromo-2-(4′-methylbenzyloxy)methylnaphthalene in 53% by a similar procedure described for **2**: mp 124–125 °C (MeOH); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 2.29 (s, 3H, CH_3), 4.63 (s, 2H, CH_2), 4.89 (s, 2H, CH_2), 7.17 (AA′BB′, J = 8 Hz, 2H), 7.30 (AA′BB′, J = 8 Hz, 2H), 7.94–8.00 (m, 2H), 8.21–8.27 (m, 2H), 8.35 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 20.8 (CH_3), 69.0 (CH_2), 72.3 (CH_2), 112.7, 113.7, 114.8 (CN), 116.3 (CN), 125.3, 125.4, 128.0 (2C), 128.9 (2C), 130.4, 130.4, 130.8, 131.3, 132.4, 134.6, 137.0, 142.5; UV–vis (cyclohexane) 314 nm (ε = 9038 mol^{-1} L cm^{-1}); IR (diamond ATR) ν 2218 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.61; H, 5.05; N, 8.93.
12. The feeble absorption at 350–370 nm might indicate a very weak CT interaction of the DCMN and DMT moieties of **2** in the ground state in cyclohexane.
13. Crystallographic data of **2** and **3** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 782829 and 782830.
14. Itoh et al.[15] and Hutten et al.[16] reported that conjugated nitrile compounds show intermolecular π-stacking in the crystals and form excimers when photoexcited.
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17. Anodic peak potentials (E_{ap}) and cathodic peak potentials (E_{cp}) of **1**, **2**, and **3** are as follows. $E_{ap}(\mathbf{1})$ = +0.84 V versus SCE (irrev.), $E_{ap}(\mathbf{2})$ = +1.69 V (irrev.), $E_{ap}(\mathbf{3})$ = +2.31 V (irrev.), and $E_{cp}(\mathbf{1}) \sim E_{cp}(\mathbf{2}) \sim E_{cp}(\mathbf{3}) \sim -1.3$ V (rev.). These values were measured on the ALS model 600C electrochemical analyzer by cyclic voltammetry (Pt electrode, scan rate 100 mV/s) in CH_3CN containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.