

Multicomponent Molecular Puzzles for Photofunction Design: Emission Color Variation in Lewis Acid–Base Pair Crystals Coupled with Guest-to-Host Charge Transfer Excitation

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Supporting Information

ABSTRACT: Simple yet ubiquitous multimolecular assembly systems with color-tunable emissions are realized by cooperative electron donor–acceptor interactions, such as the boron–nitrogen (B–N) dative bond as a Lewis acid–base pair and charge transfer (CT) interactions. These are ternary-component systems consisting of a naphthalenediimide derivative (NDI), tris(pentafluorophenyl)borane (TPFB), and aromatic molecules (guest) with an NDI:TPFB:guest ratio of 1:2:2. The crystal shows guest-dependent color-tunable emissions such as deep blue to orange when a guest molecule of benzene is replaced with other π -conjugated systems. A good correlation between the emission wavelength and ionization potential of the guest and electronic structure calculations indicated that the emission is due to the CT transition from the guest to the NDI. The present study suggests that a rational solution of multicomponent molecular puzzles would be useful for obtaining novel photofunctional solid-state systems.

Molecules have their own unique characteristics, but their hidden potential can be revealed when they are hybridized with other molecules. One example is an organic solid-state emissive material for which flexible color tuning has been achieved.^{1,2} Such a hybridized material is promising in the development of light-emitting displays, light sources, and chemosensors. Moreover, control of the crystal polymorph and multicomponent molecular solids (cocrystals, mixed crystals, salts, and complexes) has been successful for tuning the emission characteristics.^{3–12} A challenge in this field is being able to modulate the emission colors on demand by designing the molecular geometry and modes of assembly in the crystals. Although this should be conceptually easy, the performance of such organic-molecule-based materials is extremely sensitive to the assembly structure.^{13–15} The discovery of an effective strategy for molecular assembly is necessary to make further progress.

In terms of supramolecular chemistry and crystal engineering, porous crystalline materials (lattice inclusion crystals and

porous coordination polymers) are of great interest as platforms for solid-state emissive materials because of their color-tunable properties resulting from the host–guest chemistry inside the crystals.^{16–19} For example, Stalke and co-workers reported that crystals of anthracene derivatives bearing bulky substituents at the 9- and 10-positions include toluene molecules and showed tunable color emissions by accommodation and desorption of the guest molecules.¹⁶ Kitagawa and co-workers reported that porous coordination polymers, naphthalenediimides with ligands, show emission color changes upon inclusion of various aromatic guests inside the crystals.^{18,19} The emission color changes were attributed to the exciplex and/or the excited electronic charge transfer (CT) state formed by the host and aromatic guest molecules.

Inspired by the successful strategies above, we now report a cooperative multimolecular assembly system consisting of supramolecular acceptor hosts and guest donor molecules that lead to well-defined multicomponent crystals displaying guest-dependent color-tunable emissions. Our molecular design consists of the naphthalenediimide derivative *N,N'*-bis(pyrid-3-yl)-1,4,5,8-naphthalenediimide (NDI), tris(pentafluorophenyl)borane (TPFB), and a donor guest molecule (**Guest**) (Figure 1a). Mixtures of the ternary components formed supramolecular acceptor hosts (NDI–TPFB complexes) through selective complexations of boron–nitrogen dative bonds as Lewis acid–base pairs.²⁰ Encapsulation of two **Guest** molecules packed as a clathrate through CT interactions in the crystals then follows to form NDI:TPFB:Guest systems with a 1:2:2 ratio. These multimolecular assembly systems, suggestive of lattice inclusion phenomena of the crystal engineering technique,²¹ allow a novel design principle to arrange various donor guest molecules packed into acceptor host crystals with color-tunable emission properties. Although the chemistry of naphthalenediimides has been extensively studied in the fields of supramolecular materials such as ion channels, foldamers, catenanes, rotaxanes, metal–organic frameworks/porous coordination polymers, fluorescent aggregates, crystals, and

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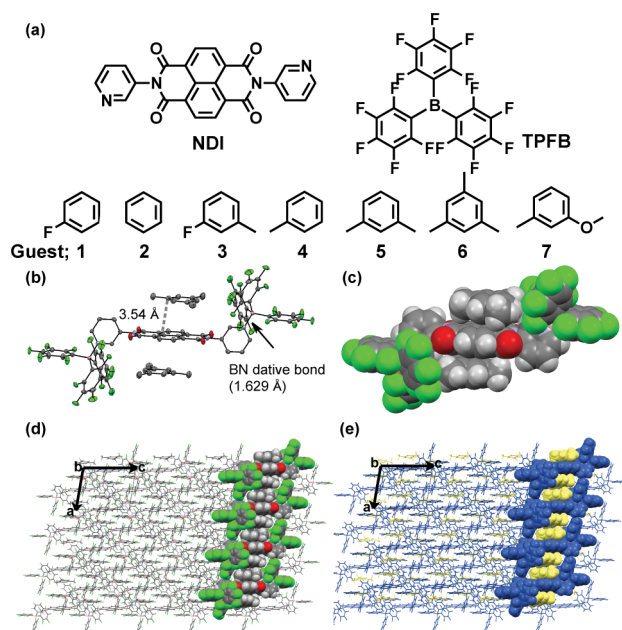


Figure 1. (a) Chemical structure of the multicomponent crystal motif used in this study. (b) Crystal structure of **C6** showing displacement ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. The crystal (**C6**) is composed of **NDI**, **TPFB**, and mesitylene (**6**) in a 1:2:2 molar ratio. The length of the B–N dative bond between the pyridyl moiety of **NDI** and **TPFB** is 1.629 Å. The interplanar distance between **NDI** and **6** is 3.54 Å. (c) As in (b), but as a space-filling model including hydrogen atoms. (d) Crystal packing viewed from the *b* axis, showing that one-dimensional columns are formed in the crystal. (e) As in (d), but with the color changed to show the supramolecular host acceptor (blue) and guest donor (yellow).

gelators,^{18,19,22} to the best of our knowledge this report is the first systematic approach demonstrating naphthalenediimide-based multicomponent crystals yielding multicolor emissions.

In a typical preparation, **NDI** (50 mg, 1 equiv) and **TPFB** (125 mg, 2 equiv) are mixed in hot **Guest** (**1–7**) (10 mL, excess as solvent), and then the mixture is cooled to ambient temperature to obtain multicomponent crystals (**C1–C7**) in high yields (ca. 80%).

The structural features of the compounds are essentially the same, as was successfully revealed by single-crystal X-ray structure analyses and powder X-ray diffraction (PXRD) measurements. Figure 1b–e shows the structure of **C6** as a typical example. For the other compounds, see Figure S1 and Tables S1–S3 in the Supporting Information (SI). It is evident that the crystals contain supramolecular complexes between one **NDI** and two **TPFB**s linked by B–N dative bonds as Lewis acid–base pairs with two **Guest** molecules accommodated in the void space to form **NDI:TPFB:Guest** systems with a 1:2:2 ratio. The three C₆F₅ substituents of **TPFB** are arranged in a propeller-like fashion and act as bulky substituents, enabling the accommodation of two **Guest** molecules sandwiching the **NDI** moiety in a face-to-face manner. This is suggestive of inclusion phenomena of the crystal engineering technique. The B–N dative bond length of the **C6** crystal is 1.629 Å, and the interplanar distance between **NDI** and mesitylene (**6**) is 3.54 Å, resulting in the formation of a CT complex between the π -electron-deficient **NDI** and π -electron-rich **Guest** molecules in the crystals. These results indicate that cooperative electron donor–acceptor interactions (e.g., B–N dative bonds and CT

interactions) play an important role in forming multicomponent molecular crystals. As shown in Figure 1e, a supramolecular **NDI–TPFB** complex (blue) acts as a host acceptor (A) and a **Guest** molecule (yellow) acts as a donor (D), and these are arranged in an alternating donor–acceptor–donor (D–A–D) fashion to form a one-dimensional (1D) crystal lattice. Hirshfeld surface analysis^{23–25} was used to gain additional insight into the close-contact interactions to illustrate the connectivity of the intermolecular interactions of the superstructure of the crystals (Figure S2 in the SI). In the case of **C6**, the results indicated that a fluorine atom in **TPFB** participates in hydrogen bonding through C(arene)–H...F contacts (2.385 Å),²⁶ which may play an important role in the formation of the 1D crystal lattice. Furthermore, the molar ratios of the multicomponent crystals (**C1–C7**) were confirmed as **NDI:TPFB:Guest** = 1:2:2 by elemental analyses (Table S4 in the SI). Thermogravimetric analyses of the multicomponent crystals (**C1–C7**) (Figure S3 in the SI) supported the inclusion of the **Guest** molecules.

The photophysical properties of the multicomponent crystals **C1–C7** highlight the uniqueness of the compounds. The UV–vis diffuse-reflectance spectra of **C1–C7** and a guest-free crystal (**GF**) were conducted using an integrating sphere. As shown in Figure 2a, a strong absorption band appears in the visible region (>400 nm to 550 nm). This may be attributed to the CT complex between the **NDI** and **Guest** molecules in the crystalline state. This assignment was also supported by density functional theory (DFT) calculations (see Figures S11–S13 and Table S7 in the SI). The CT absorption band of our multicomponent crystalline systems is more intense than the previously reported CT absorption bands of naphthalenediimide–aromatic molecule systems in the solution phase²⁷ and inside porous coordination polymers.^{18,19} The highly ordered arrangement of the **NDI** and **Guest** in the crystals may contribute to the strong CT absorption in the ground state (see Figure S10 in the SI).

The multicomponent crystals **C1–C7** also show surprisingly unique photoluminescence characteristics, reflecting the type of **Guest** molecule. Under UV light irradiation of a common wavelength ($\lambda_{\text{ex}} = 370$ nm), luminescence color variation was achieved, as shown in Figure 2b. Deep blue (**C1**), blue (**C2**), cyan (**C3**, **C4**), green (**C5**), green-yellow (**C6**), and orange (**C7**) emissions were observed in the crystals (Figure 2d). It is important to note that the emissions occur with high quantum yields (Φ_{PL}) of 31.3% for **C3**, 20.2% for **C4**, 26.3% for **C5**, and 10.5% for **C6** in the crystalline state (Table 1).

The interesting and practically important photoluminescence properties of the multicomponent crystals may be ascribed to the host–guest interactions. The guest-free crystal yielded negligibly weak emissions ($\Phi_{\text{PL}} < 0.5\%$) under UV light irradiation (Figure S8 in the SI). The relationship between the emission energy of the multicomponent crystal and the ionization potential (IP) of the **Guest** molecule is shown in Figure 2c. The linear correlation indicates that the CT complexation between **NDI** and **Guest** dominates the photoluminescence from the crystals.^{18,19,27} Moreover, to obtain further insight into the photophysical properties and excited-state information on the emissions for these crystals, the lifetimes were measured, and the corresponding emission decay curves are shown in Figure S9 in the SI. The average lifetimes (τ_{av}) of the multicomponent crystals **C1–C7** are in the range of 4.2–24.9 ns (Table 1 and Table S5 in the SI). These results indicate that the photoluminescence of **C1–C7** is a

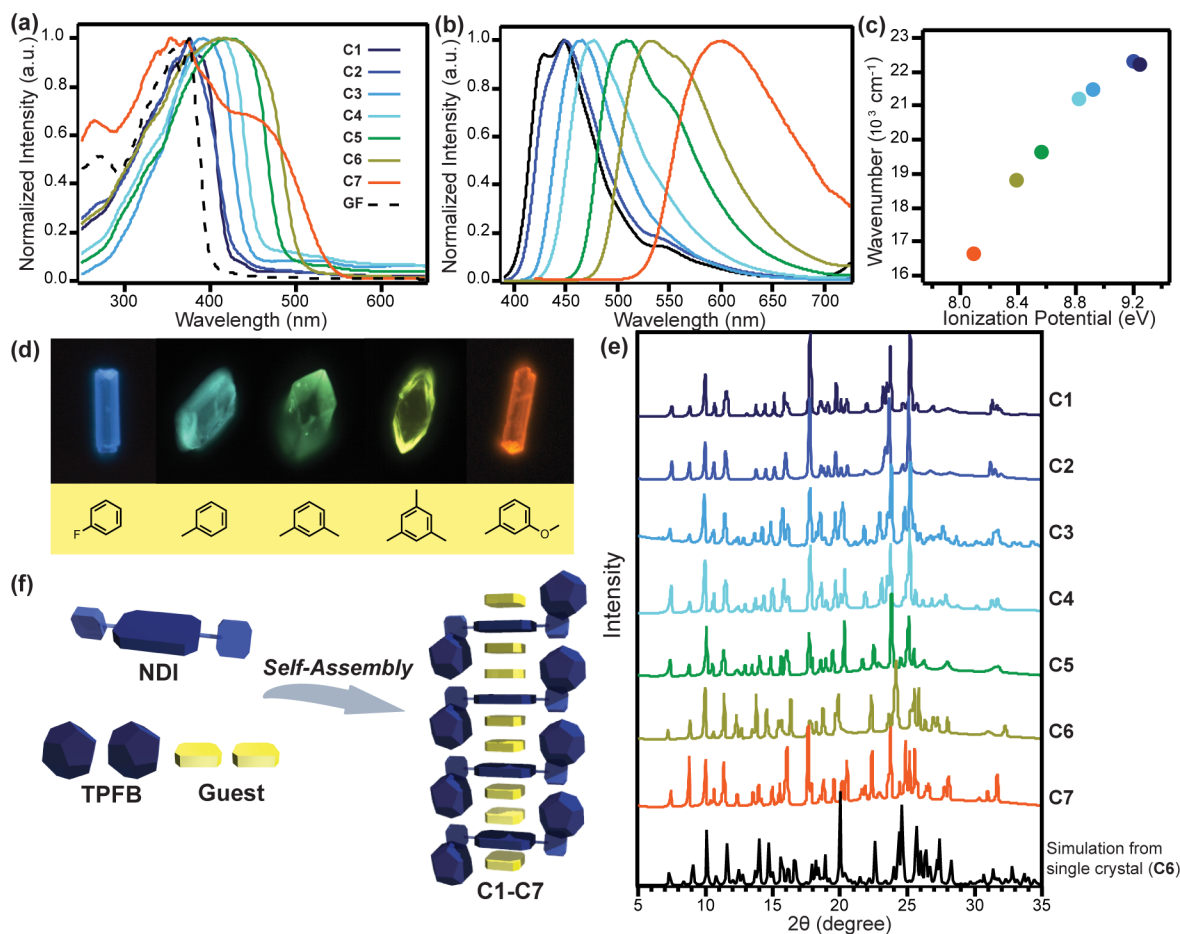


Figure 2. (a) Height-normalized UV-vis diffuse-reflectance spectra of C1–C7 and a guest-free crystal (GF). (b) Height-normalized emission spectra of multicomponent crystals C1–C7. Excitation at 370 nm. (c) Relationship between the emission energies of the inclusion crystals (C1–C7) and the ionization potentials of the Guest molecules (1–7). The linear correlation implies that the CT complexation dominates the emission. (d) Fluorescence microscopy images of C1 (deep blue), C4 (cyan), C5 (green), C6 (green-yellow), and C7 (orange). Excitation at 330–380 nm, emission at >420 nm. (e) PXRD patterns of C1–C7 and the simulated pattern from the single-crystal structure of C6. (f) Schematic illustration of the formation of multicomponent crystals C1–C7. Cooperative intermolecular interactions, B–N dative bonds, and CT interactions play important roles in the formation of the crystals.

Table 1. Photophysical Properties of C1–C7 in the Crystalline State

no.	guest molecule	IP of guest (eV) ^a	λ_{em} (nm)	Φ_{PL} (%) ^b	τ_{av} (ns) ^c
C1	fluorobenzene	9.20	448	8.0	5.4
C2	benzene	9.24	450	16.6	6.6
C3	<i>m</i> -fluorotoluene	8.91	466	31.3	14.0
C4	toluene	8.83	472	20.2	14.1
C5	<i>m</i> -xylene	8.56	509	26.3	24.9
C6	mesitylene	8.41	531	10.2	14.5
C7	<i>m</i> -methylanisole	8.10	600	1.5	4.2

^aThe ionization potential (IP) values were taken from refs 28 and 29.

^bAbsolute photoluminescence quantum yields (Φ_{PL}) were determined using a calibrated integrating sphere system with excitation at 370 nm for C1 and C2 and at 400 nm for C3–C7. ^cThe fluorescence lifetime values of C1–C7 in the crystalline state were measured at their emission peaks with excitation at 365 nm.

fluorescence emission resulting from the excited electronic CT states of the crystals.

In conclusion, we have demonstrated that cooperative electron donor–acceptor interactions (e.g., B–N dative bonds and CT interactions) effectively form multicomponent crystals

C1–C7 showing deep-blue to orange light emissions upon UV light irradiation. The unique photoluminescence colors originate from the excited-state CT interactions between the NDI and Guest molecules in the crystalline state, and the emission color is tunable depending on the donor ability (ionization potential) of the Guest molecule. Hirshfeld surface analysis clearly indicates that intermolecular C(arene)–H...F hydrogen bonding participates in the formation of the 1D crystal lattice to form a superstructure. These highly reliable multicomponent molecular assembly systems, suggestive of lattice inclusion phenomena of the crystal engineering technique, have opened up the design principle of arranging luminescent excited electronic CT state combinations packed into a host framework with guest molecules. The results obtained here are expected to help guide the development of crystal structure predictions with optoelectronic solid-state materials.^{14,30}

■ ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures for the preparation of the multicomponent crystals; optical, X-ray diffraction, and thermogravimetric analyses; and DFT calculations. The

Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04178. CCDC-1053317 (C1), CCDC-1053318 (C2), CCDC-1053321 (C3), CCDC-1053322 (C4), CCDC-1053323 (C5), CCDC-1053324 (C6), and CCDC-1053325 (C7) contain the supplementary crystallographic data for this paper. These data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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