Luminescent Materials

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A Cocrystal Strategy to Tune the Luminescent Properties of Stilbene-Type Organic Solid-State Materials**

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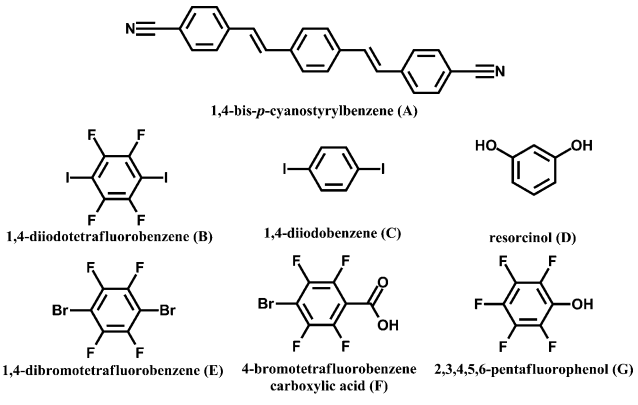
Organic solid-state chromophores have received much attention recently due to their promising optoelectronic applications in the fields of light-emitting diodes,[1] lasers,[2] sensors,[3] and two-photon fluorescent materials.[4] In terms of fundamental studies and practical applications, the ability to tune and control the luminescent color of an organic material is important to achieve multi-color displays and to meet the need of next generation light-emitting materials.[5] To obtain light-emission of an appropriate wavelength remains, however, a challenge.[6] Recent advances in organic fluorescent crystals have indicated that the intermolecular interactions or molecular stacking modes in the solid state play a key role in the observed bulk luminescent characteristics.[7] However, an effective strategy for tuning the luminescence of an organic solid by designing and controlling the orientation, interaction and stacking modes of molecules in a crystal structure remains a long-standing problem.

Cocrystals are molecular solids composed of at least two types of neutral chemical species.[8] Recently, cocrystal formation has received a great deal of attention as a means of modifying the properties of organic molecules in the solid state.[8c] Halogen- and hydrogen-bonding represent a large family of non-bonding interactions frequently used in the supramolecular cocrystal chemistry design of organic solids.[8a] Importantly, the modular structure of cocrystals allows the modification of and control over crystal structure by changing the direction and selective reorganization of halogen and hydrogen bonds within the crystal.[8d] By using halogen- and hydrogen-bonding interactions with a single chromophore molecule we have developed a cocrystallization strategy to prepare various crystalline materials with tunable fluorescent emission properties. The work, herein, is based on the expectation that by appropriate selection and design of the cocrystal components (co-formers) and of the interaction type (hydrogen- and/or halogen-bonding), the stacking of fluorescent molecules in the solid state can be finely controlled.

Phenylenevinylene and stilbene-type compounds have attracted considerable interest due to their excellent optical and electronic properties.[9] In this work, we have chosen a stilbene derivative, 1,4-bis-*p*-cyanostyrylbenzene (**A**, shown in Scheme 1 A), as a typical fluorescent model system. By selecting the co-formers with different potential halogen or hydrogen bond interaction modes with the cyano group in **A**, six cocrystal systems have been synthesized. We describe here how one-photon and two-photon fluorescence properties (such as fluorescence emission, lifetime and quantum yield) can be varied with respect to the pure **A** compound. These systems involve organic solids of the same chromophore molecule with changeable luminescence generated by the supramolecular cocrystal method. The method provides a facile way to design and develop new types of solid (both powder and single crystal) multi-color fluorescent organic materials.

Six representative compounds lacking visible solid-state fluorescence were chosen as the co-formers for **A** (compounds **B**–**G**, Scheme 1). The co-formers **B**, **C**, **E**, **F**, **G** provide functional groups common in typical supramolecular synthons, and can potentially assemble into one-dimensional



Scheme 1. Chemical structures of the fluorescent molecule (**A**, 1,4-bis-*p*-cyanostyrylbenzene) and its co-formers (**B**, 1,4-diiodotetrafluorobenzene; **C**, 1,4-diiodobenzene; **D**, resorcinol; **E**, 1,4-dibromotetrafluorobenzene; **F**, 4-bromotetrafluorobenzene carboxylic acid; **G**, 2,3,4,5,6-pentafluorophenol).

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Supporting information for this article (details of the preparation and characterization for cocrystals) is available on the WWW under http://dx.doi.org/10.1002/anie.201106391.

chain structures with **A** through halogen- or hydrogen-bonding interactions;[8d] co-former **D** can potentially stack **A** molecules parallel with each other through hydrogen bonding interactions.[8b] The new cocrystal compositions were synthesized by employing the liquid-assisted grinding (LAG) method.[8d] Powder X-ray diffraction (PXRD) patterns of the as-prepared cocrystals (**1**: **A.B**; **2**: **A.C**; **3**: **3A.2D**; **4**: **A.E**; **5**: **A.F**; **6**: **A.2G**) and their co-former precursors are shown in Figure 1 and Figure S1 in Supporting Information (SI). It can

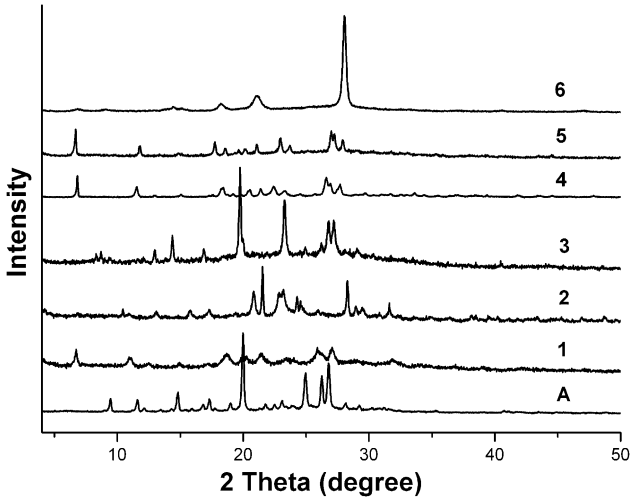

Figure 1. Powder XRD profiles of **1**–**6** and **A**.

be observed that the PXRD patterns of the as-prepared cocrystal products **1**–**6** are different from that of pure **A** and its co-former precursors, demonstrating that new compositions have formed. Moreover, we were not able to obtain these cocrystals directly by cocrystallization of appropriate cocrystal building blocks from solution, which may be attributed to the difference in the solubility between the two components.[8d] However, single crystals could be obtained by a seeding process using slow evaporation of chloroform solutions of the dissolved LAG produced cocrystal powders of **1**–**6**. It is noted that the PXRD profiles of the cocrystals **1**, **4** and **5** (Figure 1) are very similar, suggesting isostructurality and likely similar stacking arrangements. This we believe to be a consequence of the similar structures of the co-formers (**B**, **E** and **F**).

To study the thermal behavior of the cocrystals and their precursors, differential scanning calorimetry (DSC) was performed on the cocrystals **1**–**6**. Figure S2 in SI shows that the endotherms accompanying the decomposition of **1**–**6** occur at higher temperatures than those of the melting or decomposition of co-formers **B**–**G**. Thermogravimetric analysis (TGA) of cocrystals **1**–**6** show the weight losses before 270 °C are assigned to the decomposition of cocrystal with loss of the co-formers **B**–**G** (SI: Figure S3). These weight losses confirm the content ratios of the co-formers to **A** (1:1, 2:3 or 2:1) within the cocrystal. For example, cocrystal **1** shows a weight loss of ca. 52 % occurs at 235 °C, which matches the expected percentage content (55 %) of co-former **B** in the cocrystal **1** with a 1:1 ratio of **A** to **B**.

UV/Vis spectra (SI: Figure S4) demonstrate that the optical absorption characteristics of the as-prepared cocrystals are altered compared with pure **A**. This phenomenon can be further confirmed by observing these cocrystals under daylight (Figure 2 a), where it can be observed that the cocrystals (Figure 2 a: **1**–**6**) exhibit different colors compared with **A** (Figure 2 a: **A**). More interestingly, the as-prepared cocrystals have different fluorescence emission spectra (Figure 3) which range in color from blue to green to yellow (SI: Table S1). For example, compared with pure **A** which has a yellow emission color ($\lambda_{em}^{max} = 532$ nm; CIE 1931 color coordinates: (0.35, 0.60)), cocrystals **1**, **4** and **5** feature a strong blue-shift emission with the λ_{em}^{max} at 460, 462 nm and 468 nm, respectively. These solids have very similar fluorescent spectroscopic structures and their corresponding color coordinates of the fluorescence are located in the blue region (SI: Table S1). Cocrystal **6** shows a yellowish green emission (CIE 1931 color coordinates: (0.26, 0.51)) with the λ_{em} at 458, 486 and 525 nm, respectively. In addition, cocrystals **2** and **3**

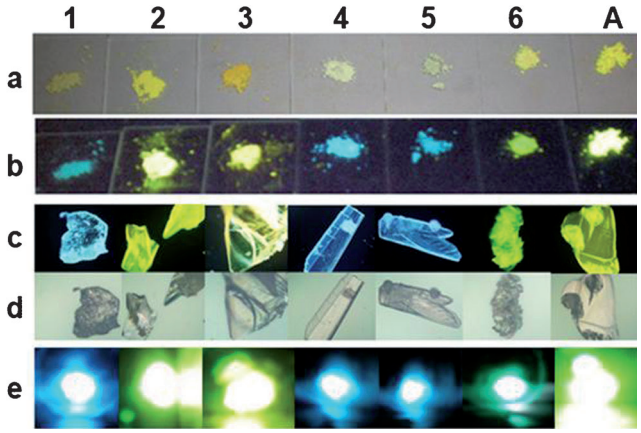

Figure 2. Photographs of solid-state cocrystal samples (from left to right: **1**–**6**) and **A**. a) and b) the powder samples under daylight and UV (365 nm); c) and d) the single crystal samples under UV (365 nm) and daylight observed by fluorescence microscope multiplied by 50-fold; e) two-photon luminescence under 800 nm laser.

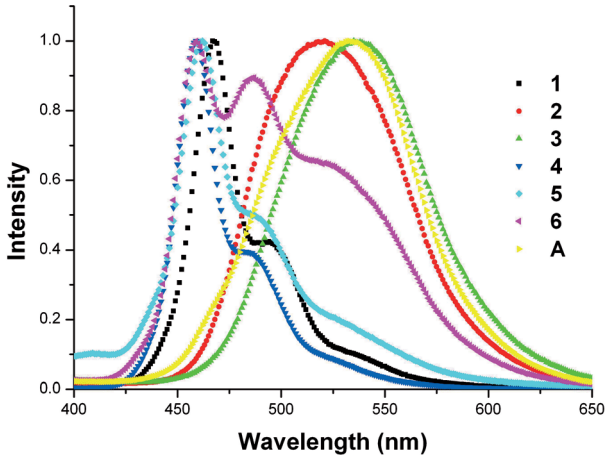

Figure 3. Normalized fluorescence spectra (excited at 360 nm) for cocrystals **1**–**6** and pure **A**.

show blue and red-shift emission of 13 and 5 nm respectively, compared with pure **A**. Irradiating the cocrystals with UV light (Figure 2b) also reveals that these solid powders show multi-color luminescence, which can be clearly detected visually. Additionally, the cocrystals also exhibit variable photoluminescence quantum yields (PLQYs) in the range from 4.9% (**6**) to 25.9% (**4**), illustrating that the PLQY values can also be tuned by this cocrystal strategy. Transparent single crystals of cocrystals **1**–**6** can be obtained (Figure 2d) which show nearly unchanged light-emitting properties compared with their powder forms, demonstrating tunable emission can also be obtained from single crystals (Figure 2c).

To obtain further insight into the photophysical properties and excited-state information of fluorescence for these solids, the fluorescence lifetimes were measured and the corresponding fluorescence decay curves are shown in Figure S5 in the SI. The fluorescence lifetimes of cocrystals **1**, **4** and **5** (with low-wavelength emission) are less than 1 ns, whereas for cocrystals **2**, **3** and pure **A** (with long-wavelength emission) the values are in the range 13.35–20.67 ns (SI: Table S1). In particular, cocrystal **6** shows a clear difference in the fluorescence lifetime when the fluorescence decay is monitored at 490 (0.34 ns) and 530 nm (4.55 ns). These facts suggest that the stacking arrangement of the molecules in cocrystals **2** and **3**, and pure **A** may favor the formation of aggregates (or excimers) which are responsible for the longer fluorescence lifetime and long-wavelength emission.[10]

We noted that the stilbene compound can be a two-photon absorption and emissive chromophore. Thus two-photon-excited fluorescence measurements were also made. Upon excitation by 800 nm laser light, cocrystals **1**–**6** and **A** exhibit strong two-photon fluorescence without obvious red- or blue-shift emission compared with those excited at 360 nm UV light (SI: Figure S6), illustrating that the same emission process from one-photon and two-photon excited states to the ground state are involved. Taking cocrystal **1** as an example, the emission spectrum features two main narrow peaks at 470 and 497 nm (Figure 4). The emission intensity shows a nearly quadratic increase as a function of the incident energy: the full widths at half-maximum (fwhm, inset in Figure 4) of the spectra decrease dramatically from 78 to 55 nm upon increasing pump energy, although the fwhm of the spectra are still far from the criterion of a laser action. As a result, the as-prepared solid-state samples can also serve as two-photon fluorescent materials with a tunable emission from blue to yellow when excited at a single wavelength of 800 nm. This is further visualized in Figure 2e.

To explore the relationship between the tunable emission of the cocrystal systems and their crystal structures, X-ray single crystal diffraction measurements were performed on the cocrystals **1**–**5** with typical blue or red-shift emission to compare with the pure **A**. A previous crystal structure analysis has revealed an asymmetric unit consisting of three independent molecules. The molecular packing of these molecules is ladder-like where two of the three independent molecules act as the rungs and interact with each other via π–π interactions (average central distance: 3.79 Å), while the third molecule interacts with the rungs via C(arene)-H···N≡C hydrogen bonds. This stacking structure corresponds to strong

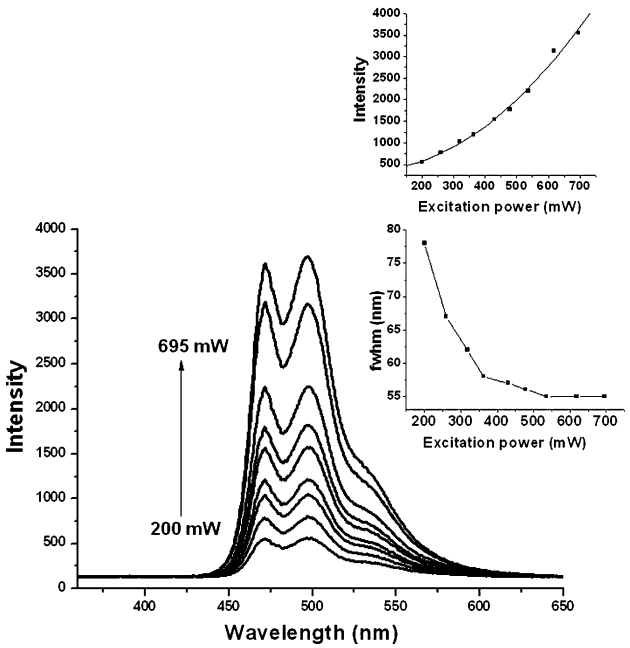

Figure 4. Two-photon fluorescence spectra of the cocrystal **1** excited by 800 nm laser under different pump intensity. Insets show the changes in intensity at 470 nm and fwhm with increasing pump intensity.

intermolecular interactions, facilitating the formation of molecular aggregates. Upon assembly of **A** with co-former **B** to give cocrystal **1**,[12] C≡N···I halogen bonds form between the iodine in co-former **B** and the nitrogen in **A** (cocrystal **1**, Figure 5). This stacking mode results in the separation between the **A** molecules being enlarged by ca. 2.2-fold compared with pure **A** crystal, and the molecules of **A** are no longer stacked on top of each other, resulting in the deaggregation of the **A** molecule in the crystal, in agreement with the blue-shift by 64 nm of the fluorescence compared to pure **A**. Moreover, no obvious change in the intramolecular

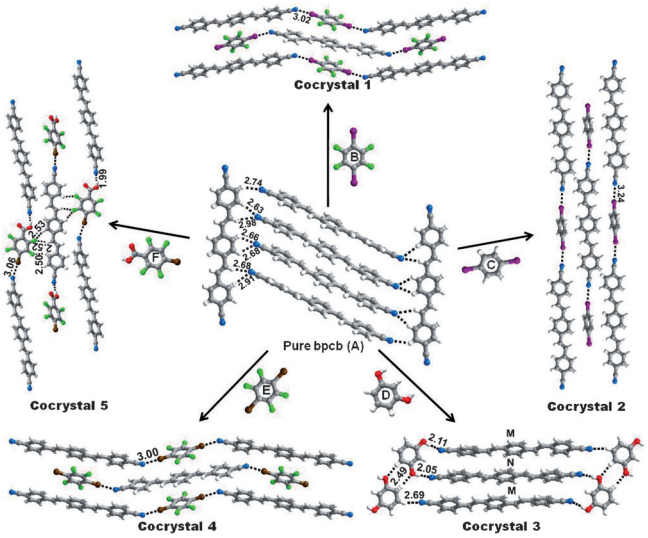

Figure 5. Crystal structures of **A**, cocrystal **1**–**5** (**A** assembled with co-former **B**, **C**, **D**, **E** and **F**, respectively).

conformation of the chromophore is observed in the cocrystal. Therefore, by introduction of the co-former, the stacking fashion of the chromophore within the original organic crystal has been changed, and thus the solid-state luminescent properties can be further tuned. Similar stacking is also observed in cocrystal **4** (Figure 5), further confirming their isostructurality. In cocrystal **2** (Figure 5),[12] the long-axes of **A** are parallel (central distance between two neighboring **A** molecules: 6.05 Å), and C≡N···I halogen bonds (3.24 Å) are formed between **A** and the co-former **C**, which builds a one-dimensional supramolecular polymer. This stacking mode is also beneficial to the formation of chromophore excimer, and the enlargement of the molecular distance results in a blue-shift emission of 13 nm, compared to that of pure crystalline **A**. For cocrystal **3**, two C≡N···H−O hydrogen bonds and one C≡N···H−C hydrogen bond are formed between the **A** molecule (labeled as M and N) and co-former **D**, respectively. The close stacking aggregation of the **A** allows for the formation of excimer-like emission, which is similar to that of pure **A**: an observation consistent with cocrystal **3** showing similar yellow luminescence to that of pure **A**. For cocrystal **5**, the arrangement of two cocrystal building blocks is similar to that of cocrystal **1**; as expected, the **A** molecules and co-former **F** are assembled via both halogen (distance: 3.06 Å) and hydrogen bonding (distance: 1.99 Å). Within the structure of **5**, co-former **F** exhibits orientational disorder, which may be assigned to the similar interaction intensity of halogen and hydrogen bonding within the crystal. In addition, although currently we could not obtain the crystal structure of cocrystal **6** due to its relative weak crystallinity, we expect that the structure will be assembled by two O−H···N≡C hydrogen bonds between the -OH groups in the two co-former **G** molecules and the two N≡C groups at the two ends of **A**.

To investigate the non-covalent interactions within the cocrystals, their FT-IR spectra were recorded. Compared with the characteristic vibration band of the cyano group in pure **A** at 2213 cm^{-1}, the values in the cocrystals are systematically shifted to higher frequencies by approximately 3 to 30 cm^{-1} (for cocrystals **2** and **6**, respectively; see SI: Figure S7). This indicates that the strength of the halogen or hydrogen bond interactions between **A** and the co-formers influences the vibrational properties of **A**. Particularly, the cyano group in cocrystals **3** and **5** have two different vibrational absorption maxima located at 2221, 2231 and 2224, 2235 cm^{-1}, respectively, which is consistent with the fact that cocrystals **3** and **5** feature two different sets of non-covalent interactions. For example, the vibrational absorption maxima at 2224 and 2235 cm^{-1} with nearly the same absorption intensity in cocrystal **5** are assigned to the C≡N···Br halogen-bonding and C≡N···HOOC hydrogen-bonding interaction at the two ends of the **A** molecule, respectively. For the cocrystal **3**, two N≡C vibrational bands correspond to the two types of hydrogen bonds between **A** and co-former **D** within the cocrystal.

In summary, the optical properties (such as UV/Vis absorption, luminescence emission, color, lifetime, quantum yield) in an organic solid chromophore can be finely modified by supramolecular cocrystal formation. The resulting powder and single crystals exhibit multi-color emission from blue through green to yellow as well as strong two-photon luminescence. Crystal structure analysis demonstrates that the introduction of the co-formers can change the geometric arrangement of the chromophore in the cocrystal, which present new insight into the structure-property relationship of these cocrystal systems. Due to the diversity and versatility of the cocrystal approach, we anticipate that the strategy developed here can be readily employed to tune the emission colors of organic solid chromophores for other luminescent systems, providing considerable flexibility and potential applications for the design of various new types of organic luminescent materials.

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[12] CCDC 824986 (**1**), 824987 (**2**), 824988 (**3**), 839000 (**4**), 839001 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Structure solution and refinement were conducted using Ser-92, SHELX-97 and X-Seed.[13]

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