

Ultrasound-Assisted Construction of Halogen-Bonded Nanosized Cocrystals That Exhibit Thermosensitive Luminescence

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Abstract: Multi-component organic nanocrystals that are comprised of two or more supramolecular building blocks can be used to extend the design and assembly scope of solid molecular materials. Herein, we report the use of ultrasonication to prepare halogen-bonded stilbene-based nano-cocrystals that exhibit different photoemis-

sion properties, including one- and two-phonon emission and fluorescence lifetimes, relative to those of macrodimensional crystals. The structural

Keywords: fluorescence • halogens • luminescence • nanocrystals • supramolecular chemistry

transformation from nano-cocrystals into nanocrystals upon heating results in a luminescence red-shift from greenish blue to yellow. The temperature-dependent ratiometric luminescence may allow such nano-cocrystals to be used as fluorescent sensors and thermosensitive materials.

Introduction

Organic π -conjugated nanocrystals have recently received much attention, owing to their promising optoelectronic applications in the fields of waveguides,^[1] light-emitting diodes,^[2] lasers,^[3] and chemical sensors.^[4] The size-dependent effect of such materials has also provided great opportunities to tune their emission for multiple-color displays.^[5] During the last few years, although a great deal of attention has been devoted to the synthesis of pure organic chromophore nanocrystals,^[6] the investigation of the optical properties of multi-component organic nanocrystals is still in its infancy.^[7] It is expected that the synthesis of photofunctional nanocrystals that are organized from two or more organic units (based on supramolecular synthesis)^[8] would greatly extend the design and assembly scope of solid organic materials, and result in unique photophysical properties.

Cocrystals are molecular solids that are composed of more than one neutral chemical species, which are held together by weak non-covalent interactions, such as hydrogen- and halogen-bonding interactions.^[9] This “cocrystal” ap-

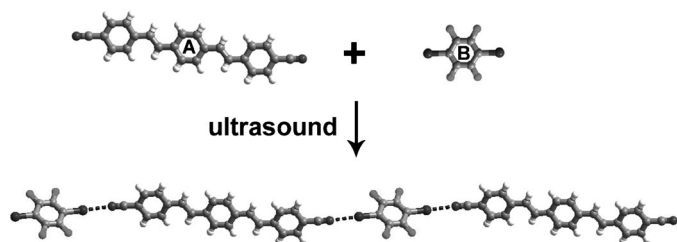
proach has received a great deal of recent attention, owing to its ability to allow the tuning and control of the physicochemical properties^[10] (e.g., bioavailability,^[10a] stored chemical energy,^[10b,c] photoemission,^[10d,e] and electronic behavior^[10f]) of organic solids, which is beneficial for the development of new types of medical, fluorescent, energetic, and semiconductor materials. Moreover, it has been reported that nanosized cocrystals (i.e., nano-cocrystals)^[11] exhibit different properties to their macroscopic counterparts, such as enhanced dissolution rates^[11a] and mechanical behavior,^[11b,d] which are advantageous for various applications, such as drug formulation. However, the luminescence and other optical properties of nano-cocrystals have as yet remained unexplored. Moreover, from the perspective of molecular recognition, although nano-cocrystals with hydrogen-bond-organized interactions have been successfully prepared,^[11] the formation of nano-cocrystals based on halogen-bonding interactions, as alternative supramolecular-bonding interactions,^[12a] has not yet been reported, which may be attributed to relatively weak interactions between the two building blocks.^[12b]

Herein, we demonstrate that nano-cocrystals that are sustained by halogen-bonding interactions can be synthesized by using a facile sonochemical method. 1,4-Bis-*p*-cyanostyrylbenzene (bpcb, **A**, Scheme 1), which exhibits high fluorescent quantum yields, and the co-former 1,4-diiodotetrafluorobenzene (**B**) were selected as the model compounds, owing to their ability to self-assemble through C $\equiv$ N $\cdots$ I halogen bonds.^[13a] Unlike cocrystals that are formed from hydrogen-bonded supramolecular synthons, the **A**·**B** (1:1) cocrystal is difficult to prepare by using conventional solution-based crystallization techniques, although it is readily accessible by using a mechanochemical (i.e., milling) method.^[13b] A typical SEM image of the mechanochemically obtained **A**·**B** cocrystal is shown in the Supporting Information, Figure S1,

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201203810>.



Scheme 1. The ultrasound-assisted formation of halogen-bond-assembled nano-cocrystals of 1,4-bis-p-cyanostyrylbenzene (bpceb, **A**) and its co-former, 1,4-diiodotetrafluorobenzene (**B**).

which shows that the aggregation of the organic particles is accompanied by a variation in the individual crystal sizes from the nanometer-scale to the micrometer-scale. This agglomeration and inhomogeneity in the particle size of the cocrystal may be attributed to the high concentration of heterogeneous interactions between the surfaces of the two adducts during the solid-phase reaction.

Results and Discussion

Structure and morphology: To guarantee the homogeneity of the particle size, a sonocrystallization approach was employed. Specifically, compounds **A** and **B** were separately dissolved in CH_2Cl_2 and MeOH, respectively, and then simultaneously injected into a sonicated solution of EtOH and water (1:5 v/v). After 1 min, the suspension was filtered or dispersed over a glass substrate. During such a process, we assumed that the energy for the formation of $\text{C}\equiv\text{N}\cdots\text{I}$ halogen bonds could be continuously supplied by the ultrasonic radiation; moreover, cocrystal **A**·**B** can rapidly nucleate, thereby resulting in a uniform particle size on the nanometer scale. XRD analysis of the obtained powder is shown in Figure 1. All of the reflections can be indexed to a monoclinic lattice with $P2_1/n$ symmetry. The main characteristic reflections appear at 6.72° (002, $d=1.26$ nm), 11.07° (110, $d=0.76$ nm), 12.73° (004, $d=0.67$ nm), 18.96° (111, $d=0.44$ nm), and 26.39° (024, $d=0.32$ nm), which fit well with the simulated crystal structure from cocrystal **A**·**B**. The lack of reflections of pristine **A** and **B** also confirms the phase purity of the product. Moreover, the cocrystal could not be formed without ultrasound treatment, thus confirming the key role of external perturbation in the molecular recognition between compounds **A** and **B**.

SEM was performed to estimate the particle size. Typical images of the nanoparticles that were filtered and extended over a glass slide are shown in Figure 2a and Figure 2b, respectively. The obtained cocrystals exhibit approximately spherical morphology with a uniform size of about 60–70 nm (Figure 2b, inset), thus demonstrating the formation of nano-dimensional **A**·**B** cocrystals.

Elemental analysis confirmed that the corresponding molecular formula of the cocrystal could be expressed as: $(\text{C}_{24}\text{H}_{16}\text{N}_2)_{1.046}(\text{C}_6\text{I}_2\text{F}_4)$. Energy-dispersive X-ray spectroscopy

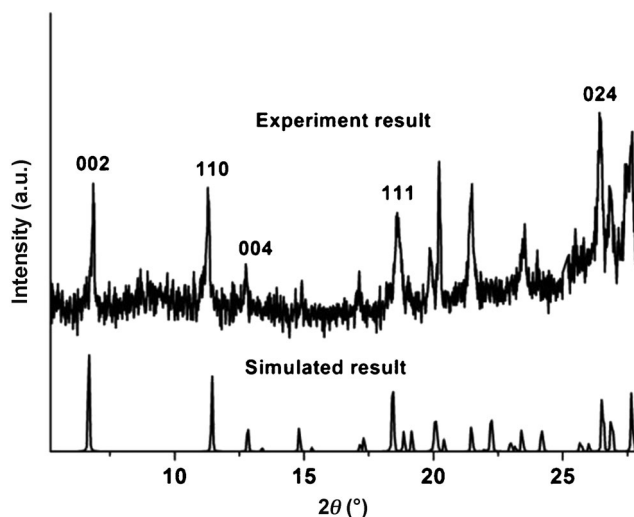


Figure 1. Powder XRD profile of **A**·**B** cocrystals, as prepared by using the ultrasound method, and the simulated single-crystal XRD pattern of the cocrystal.

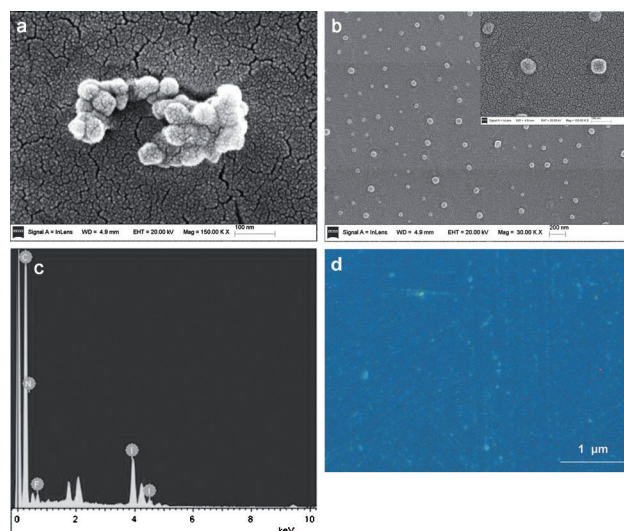


Figure 2. SEM images (a,b), EDX profile (c), and fluorescence microscopy image (d) of **A**·**B** nano-cocrystals; scale bar in (d): 1 μm .

(EDX, Figure 2c) also suggested that the ratio of **A** to **B** in the obtained solid was approximately the same as that of the idealized components (1:1) within the cocrystal. Under a fluorescence microscope with UV irradiation (365 nm), the nano-cocrystals showed a well-defined blue color with a homogeneous distribution over its entire area (Figure 2d).

Photophysical properties: One of the goals of this work was to compare the photophysical properties of the nano-cocrystals with these on the micrometer scale. Figure 3 A(a) shows a representative fluorescent spectrum of powdered **A**·**B** cocrystals that were prepared by using the grinding method; the dominant peak is located at 468 nm, whilst the secondary emission at 494 and 537 nm can be attributed to the

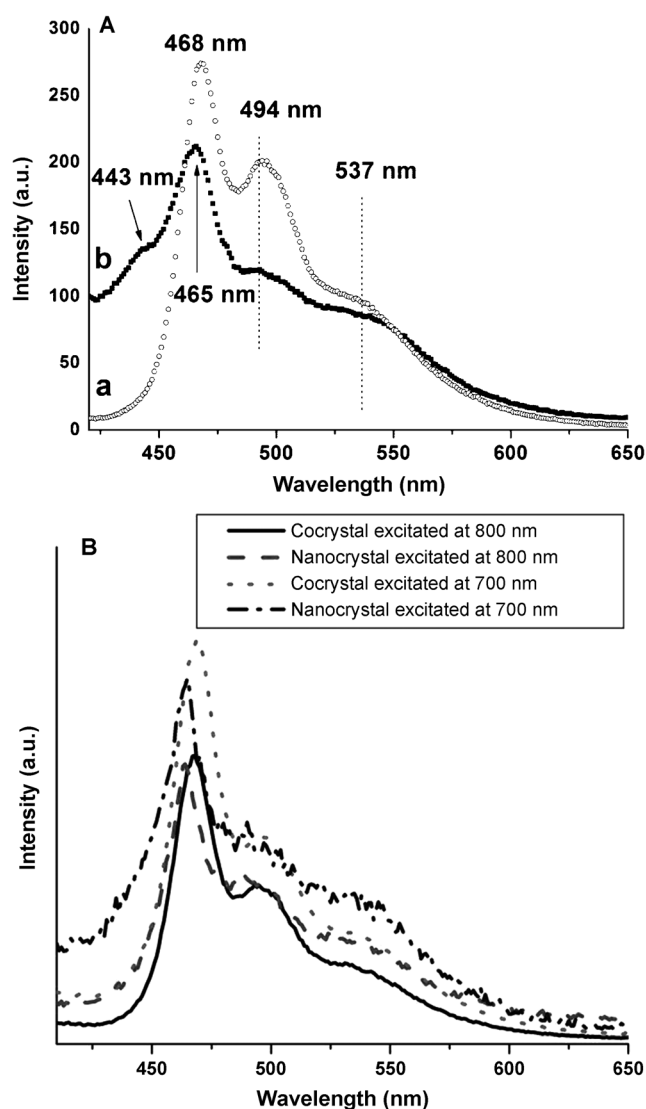


Figure 3. A) Fluorescence spectra of micro-sized (a) and nano-sized **A·B** cocrystals (b). B) Fluorescence spectra of **A·B** cocrystals, excited at 700 and 800 nm.

formation of an excimer and/or aggregation with the cocrystal. In the case of the nano-cocrystal sample (Figure 3 A(b)), the main peak undergoes a blue-shift of 3 nm. Such a phenomenon may be assigned to the size-effect of the nanoparticles: A decrease in size results in lattice softening and weaker interaction energies, thus further increasing the band gap.^[14] Moreover, a shoulder peak at 443 nm can also be resolved. Notably, the emission from a dilute solution of compound **A** appears at about 445 nm (see the Supporting Information, Figure S2); therefore, the emission from nano-cocrystal **A·B** at 443 nm very likely originates from the additional presence of molecules of monomer **A**. Such behavior is consistent with the fact that the relative amount of molecules of compound **A**, which lack strong π - π interactions, on the outer surface of the cocrystal further increase upon decreasing the particle size. Moreover, noting the up-conversion phenomenon of the stilbene compounds, the prepared

nano-cocrystals were also excited at 700 and 800 nm by using a Xe lamp as an excitation source^[15] on a standard spectrofluorimeter (Figure 3B). Compared with the micro-sized sample of cocrystal **A·B**, which was prepared by using the grinding method, the emission spectra for the nano-cocrystal exhibit a sharp main band with a blue-shift of 3 nm. For the samples that were prepared by using both the grinding and ultrasound methods, no obvious red- or blue-shifts occurred compared to the samples that were excited with 360 nm UV light, thus demonstrating that the same emission processes from one-photon- and two-photon-excited states to the ground state are involved. Analysis of the fluorescence decays (Figure 4) reveals that the fluorescence life-

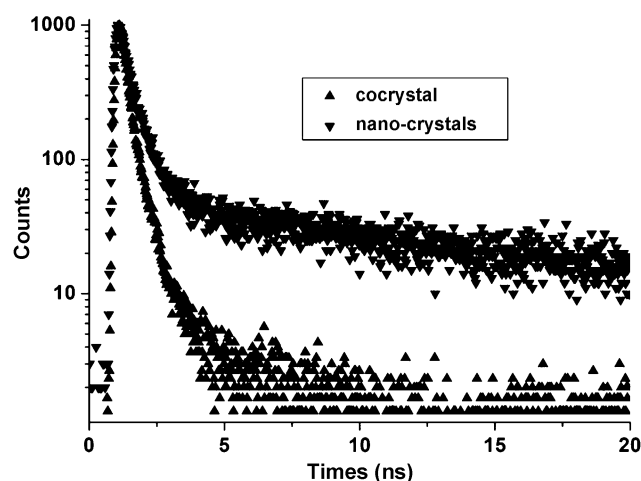


Figure 4. Comparison of the fluorescence-decay profiles for nanosized and micro-sized cocrystals.

time of the nano-cocrystals is prolonged to 0.50 ns compared to that of the micro-sized cocrystals (0.33 ns). This increase is related to the de-aggregation of the cocrystals, which decrease the excited-state nonradioactive relaxation, owing to excitonic coupling between the cocrystal particles.^[2] To the best of our knowledge, although size-dependent optical properties have largely been reported in both inorganic and purely organic nanomaterial systems,^[16] very few studies have focused on such multicomponent organic nanocrystals.

The prepared nano-cocrystal also displayed interesting temperature-dependent luminescence behavior: On heating the **A·B** nano-cocrystal from 30 to 110 °C, the luminescence intensity of the photoemission peaks at 494 and 537 nm gradually increased, with a concomitant disappearance of the shoulder peak at 443 nm (Figure 5 A). When the temperature increased to 150 °C, the fluorescence emission at around 532 nm became dominant. The emission intensity also increases upon further increasing the temperature within the range 150–240 °C, thus suggesting enhanced fluorescence quantum yields. The intensity ratio of I_{465}/I_{532} systematically decreases from 3.15 to 0.43 across the whole temperature range (Figure 5 A, inset). Therefore, the nano-cocrystal undergoes an obvious color change from greenish

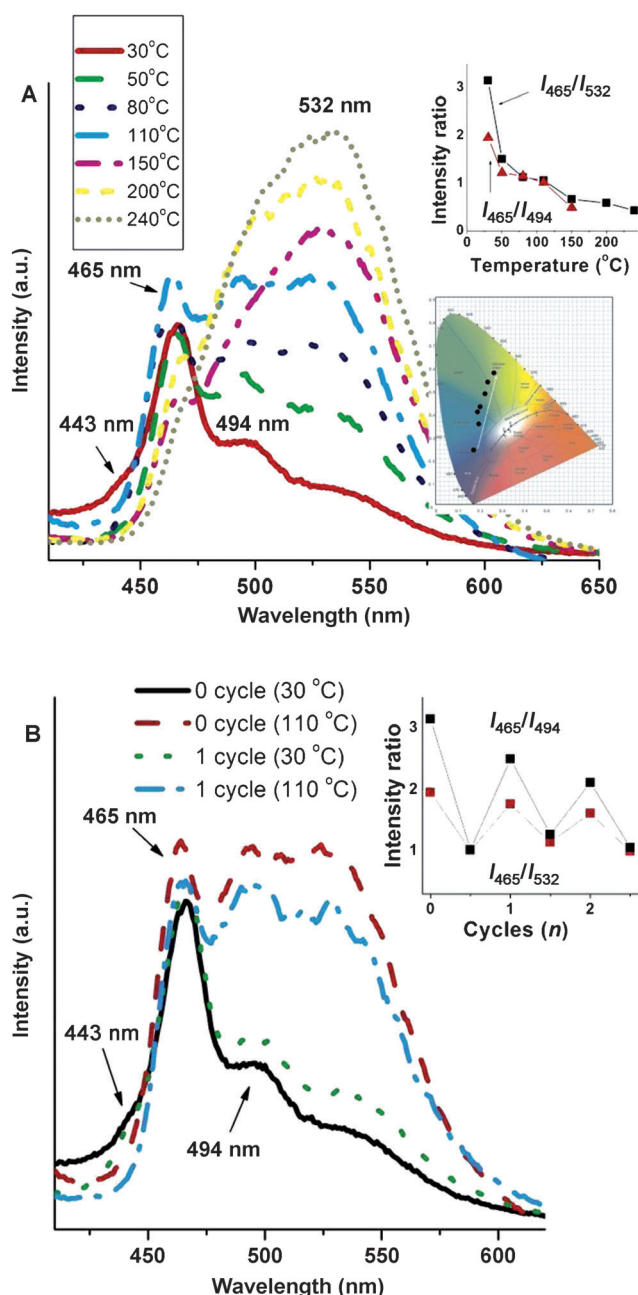


Figure 5. A) Fluorescence spectra of the nano-cocrystals within the temperature range 30–240 °C (insets show the fluorescence-intensity ratios at I_{465}/I_{494} and I_{465}/I_{532} and the dependence of the color coordinates on temperature). B) Changes in the fluorescence spectra over two heating/cooling cycles (insets show the reversible response of the intensity ratio at I_{465}/I_{494} and I_{465}/I_{532} over three consecutive cycles).

blue (color coordinates: (0.171, 0.250)) through green and yellow (color coordinates: (0.259, 0.560)) on heating the sample from 30 to 240 °C, as shown in Figure 5 A, inset, and Table 1. The change in luminescence may be related to a structural transformation of the nano-cocrystal **A-B**. It was also found that the change in the luminescence color of the nano-cocrystal could be reversed within the temperature range 30–110 °C. When the nano-cocrystal was cooled to

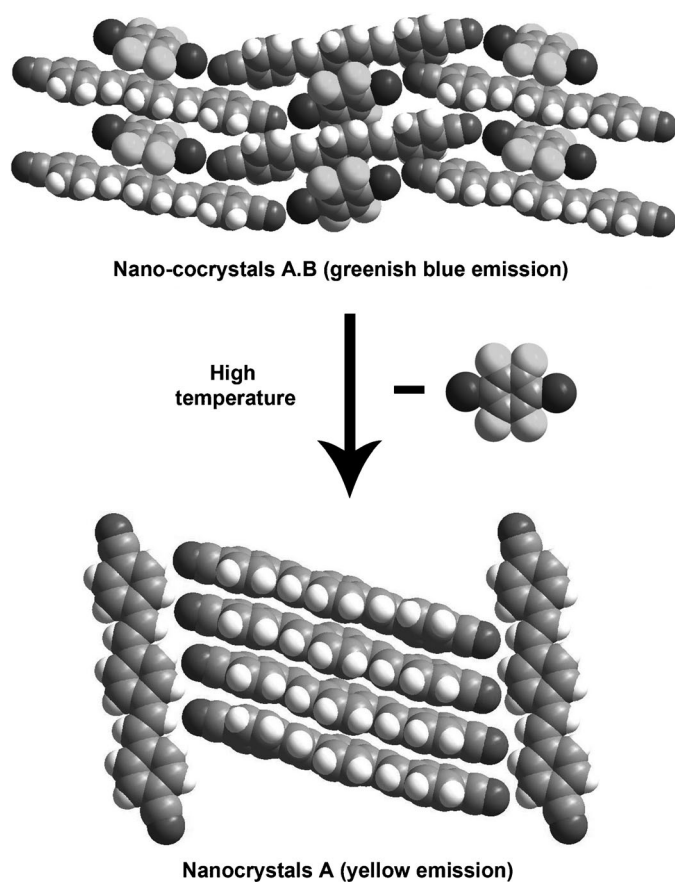
Table 1. Fluorescence-color coordinates of the nano-cocrystal at different temperatures.

Temperature [°C]	Color coordinates
30	(0.171, 0.250)
50	(0.193, 0.363)
80	(0.189, 0.416)
110	(0.192, 0.427)
150	(0.221, 0.498)
200	(0.231, 0.543)
240	(0.259, 0.560)

30 °C for 3 min, the emission spectra partially recovered its original position, together with the associated reverse fluorescence-color changes. Figure 5 B shows the typical spectroscopic changes over two consecutive heating/cooling cycles and the ratio of I_{465}/I_{494} and I_{465}/I_{532} can be readily repeated at least three times, as shown in the Figure 5 B, inset. As previously reported, the thermosensitive ratiometric emission between different wavelengths from a solid-state nanocrystal is seldom observed compared with solution-state systems.^[17] Based on the response of the fluorescence-intensity ratios I_{465}/I_{494} and I_{465}/I_{532} to temperature, this nano-cocrystal could serve as a new type of molecular temperature sensor or molecular thermometer.

To further investigate the possible temperature-dependent structural transformation of the nano-cocrystal, in situ high-temperature powder XRD experiments were performed on the nano-cocrystal sample, as shown in the Supporting Information, Figure S3 A. It can be observed that the (002) and (004) reflections systematically move to a higher 2θ angle upon increasing the temperature from 30 °C to 150 °C, with a gradual decrease in their peak intensity. This result indicates an expansion of the lattice spacing in the $\langle 00l \rangle$ direction and a decrease in the crystallinity of the nano-cocrystal, which may be related to an increase in the $C\equiv N\cdots I$ distance and a weakening of the halogen bond; this process can be regarded as the pre-disassembly of such a 1D supramolecular polymer (see the Supporting Information, Figure S4 A). In addition, similar lattice-expansion behavior can also be observed in the $\langle 110 \rangle$ and $\langle 111 \rangle$ directions, which is related to an increase in the distance between **A** molecules and either adjacent co-former **B** or parallel neighboring **A** molecules (see the Supporting Information, Figure S4 B and S4 C). These structural changes demonstrate that the interactions between the chromophore and its co-former and the aggregation of pure **A** molecules weaken, which can further modify the emission behavior of the crystal. Moreover, it was also observed that a contraction in the (00 l) and (110) basal spacing occurred on cooling the cocrystal powder (see the Supporting Information, Figure S3 B), thus suggesting that the halogen-bond interactions can be restored by the heating/cooling treatment within the temperature range 30–100 °C, which is responsible for the reversed luminescent change, as described above. By further increasing the temperature, the characteristic reflections of the pure **A** crystal gradually appear at about 19.29°, 24.18°, and 25.35°, accompanied by a decrease in the intensities of the

peaks that correspond to the nano-cocrystal. This result is due to the decomposition of the nano-cocrystal and to its transformation into nanocrystals of compound **A**, which is consistent with the irreversible change in the luminescence at higher temperatures. Moreover, upon heat treatment at 200 °C, the obtained **A** crystal maintains its nanometer dimensions, as shown in the Supporting Information, Figure S5. Such structural transfer from nano-cocrystal **A·B** into nanocrystal **A** has seldom been observed in the literature. It can be expected that, based on a structure- and fluorescence-transfer mechanism (Scheme 2) with a predictable decomposition temperature of the nano-cocrystal, these as-prepared samples can find potential applications as a new type of thermosensitive materials.



Scheme 2. Mechanism for the structural transformation from **A·B** nano-cocrystals into **A** nanocrystals.

Theoretical calculations: To better understand the difference in energy levels, electronic structure, and fluorescence characteristics between the **A·B** nano-cocrystal and the pure **A** system, periodic density functional theoretical (PDFT) calculations were performed on an individual molecule of compound **A**, the crystal structure of compound **A**, and cocrystal **A·B**. Frontier-orbital analyses (Figure 6 and the Supporting Information, Figure S6) show that the electron densities of

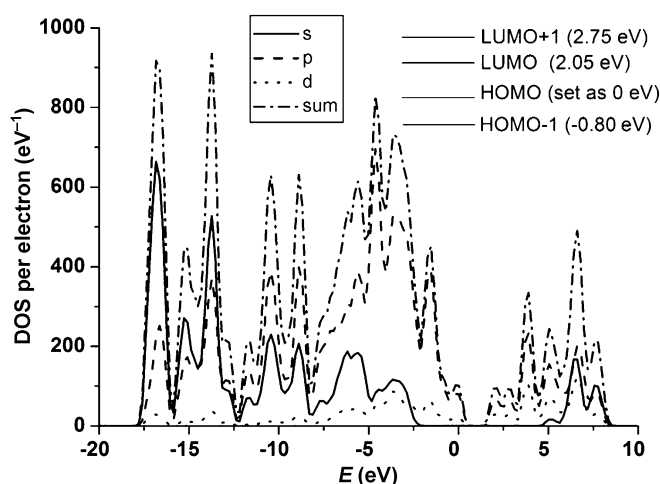


Figure 6. Total and partial electronic densities of states (TDOS and PDOS) for pure compound **A**. The energy gap between the HOMO and the LUMO is about 2.05 eV.

the HOMOs and the LUMOs were distributed over the whole π -conjugated chain of molecule **A**, thus suggesting that no intramolecular energy transfer appeared during the photoexcitation process for the pure **A** molecule, as shown in Figure 7. The calculated energy gap is about 2.05 eV.

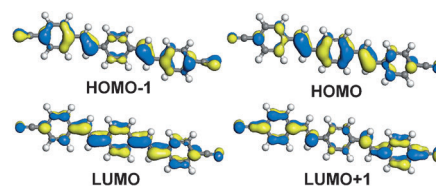


Figure 7. Frontier-orbital-distribution profiles (HOMO-1, HOMO, LUMO, LUMO+1) for pure compound **A**. The blue/yellow colors denote $\pm$ electronic wavefunctions.

Total electronic densities of states (TDOS) and partial electronic densities of states (PDOS) analysis (see the Supporting Information, Figures S7 and S8) revealed that the energy gap decreased to 1.70 eV upon the formation of crystalline **A**. Moreover, intermolecular energy transfer can also be observed between the HOMO and the LUMO of the crystal unit cell (see the Supporting Information, Figure S9), thus demonstrating the presence of strong molecular aggregation. For cocrystal **A·B**, TDOS, PDOS, and energy-band analysis (see the Supporting Information, Figures S10 and S11) showed that the sample had a band gap of 1.94 eV at the *G* point (0,0,0) in the first Brillouin zone. The difference between this theoretical value and that of pure compound **A** (0.24 eV) is close to the strong red-shift in the luminescence of nano-crystal **A**, formed from the decomposition of nano-cocrystal **A·B**, which was determined from the experimental luminescence results to be 0.32 eV. The frontier-orbital distribution further shows that electronic densities in co-former **B** are populated in most of the HOMO-1 and in part of the

HOMO (Figure 8). This result can be attributed to the strong electron-withdrawing effect of the fluorine atoms in co-former **B**, which decreases the electron density in mole-

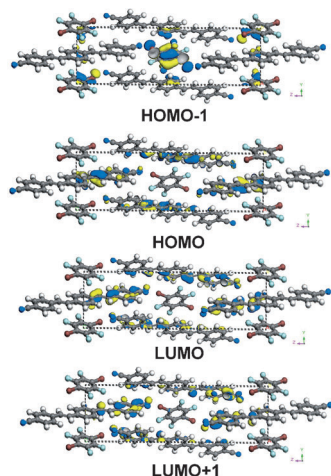


Figure 8. Frontier-orbital-distribution profiles (HOMO–1, HOMO, LUMO, LUMO+1) in the crystal structure of cocrystal **A·B** (the blue/yellow colors denote $\pm$ electronic wavefunctions).

cule **A** in the crystal. Therefore, it can be concluded that co-former **B** not only tunes the aggregation and packing of chromophore molecule **A** through halogen-bond interactions, but that it also adjusts the frontier-orbital distribution, the energy gaps, and the electronic structure in the nano-cocrystal. Both of these effects give rise to the difference in luminescence between nano-cocrystal **A·B** and nanocrystal **A**.

Conclusion

In summary, we have demonstrated that nano-cocrystals that are sustained through halogen-bonding interactions can be prepared by using an ultrasound-assisted crystallization method. The resulting nano-cocrystals exhibit different optical properties (such as one- and two-photon luminescence emission and fluorescence lifetimes) compared with their micrometer-sized analogues and, thus, present new insights into the size-dependent luminescence effects of multi-component organic nanocrystals. These nano-cocrystals also show reversible changes in their luminescence within the temperature range 30–110°C. A structural transfer from nano-cocrystal **A·B** into nanocrystal **A** above 200°C results in an irreversible luminescence red-shift from greenish blue to yellow and the temperature-dependent ratiometric luminescence suggests that such nanocrystals can be potentially used as fluorescent antiforgery devices. Theoretical calculations demonstrate that the introduction of the co-formers can change both the geometric and electronic structures of the chromophore in the cocrystal, which provides new insight into the structure–property relationships in the nano-

cocrystal solids. Owing to the diversity and versatility of the modular cocrystal approach,^[8] it is expected that the strategy presented herein can be readily extended and employed for the construction of other nano-cocrystal systems with intriguing optical properties. We also anticipate that halogen-bond design and assembly principles based on molecular recognition and nano-cocrystal-to-nanocrystal transformation can provide considerable flexibility and potential applications in the fabrication of other new types of luminescent materials that are sensitive to heat stimuli.^[18]

Experimental Section

Experimental details: *Reagents.* 1,4-bis-*p*-cyanostyrylbenzene (**A**), 1,4-diiodotetrafluorobenzene (**B**), CH₂Cl₂, and MeOH were purchased from Sigma Chemical Co. Ltd and used without further purification.

Preparation of the nano-cocrystal system. In a typical ultrasound-assisted experiment, dilute solutions of compounds **A** (5×10^{-5} mol) and **B** (5×10^{-5} mol) in CH₂Cl₂ (10 mL) and MeOH (10 mL), respectively, were simultaneously injected into a solution of EtOH and water (1:5 v/v) under ultrasonic conditions (frequency: 40 kHz, power: 50 W). After 1 min, the suspension was filtered or extended on a glass substrate (79% yield). Elemental analysis (%) calcd for (C₂₄H₁₆N₂)_{1.046}(C₆I₂F₄): found: C 49.81, H 2.36, 3.98. EDX analysis gave the content of elemental C and N atoms as 66.54% and 4.97%, respectively, and the calculated ratio of **A** to **B** was about 1.2, which was approximately consistent with the nominal ratio of 1:1.

Instrumentation. Powder X-ray diffraction (XRD) and in situ temperature-dependent XRD were performed on a PANalytical X-Pert PRO MPD powder X-ray diffractometer by using CuK α radiation ($\lambda = 0.154184$ nm) at 30 kV, 40 mA, with a scanning rate of 10°min^{-1} and $2\theta = 5\text{--}30^\circ$. Solid-state one- and two-photon fluorescence spectra were recorded on a Shimadzu RF-5301PC fluorospectrophotometer at excitation wavelengths of 360, 700, and 800 nm. Upon excitation at 700 and 800 nm, a light filter was used to eliminate frequency doubling at 350 and 400 nm, respectively. The width of both the excitation and emission slits was 3 nm. The fluorescence decays were measured on a LifeSpec-ps spectrometer by laser excitation at 372 nm and the lifetimes were calculated by using the F900 Edinburgh instruments software. The 1931 CIE color coordinates were measured on an HORIBA Jobin–Yvon FluoroMax-4 spectrofluorimeter that was equipped with an F-3018 integrating sphere. The fluorescence images were obtained on an Olympus U-RFLT50 fluorescence microscope. The morphology was investigated by using a scanning electron microscope (SEM Hitachi S-3500) that was equipped with an EDX attachment (EDX Oxford Instrument Isis 300) at an accelerating voltage of 20 kV. Elemental analysis was carried out on a Perkin–Elmer Elementarvario elemental analyzer.

Periodic density functional theory (PDFT) calculations: The PDFT method was performed by using the Dmol3^[19] module with the Material Studio software package.^[20] Molecule **A** and the crystal structures of pure **A** and cocrystal **A·B** were selected as the initial models, which were optimized by using the Perdew–Wang (PW91)^[21] generalized gradient approximation (GGA) method with the double numerical basis sets and the polarization function (DNP). The SCF convergence criterion was within 1.0×10^{-5} Hartree/atom and the convergence criterion of the structure optimization was 1.0×10^{-3} Hartree/bohr. The Brillouin zone (BZ) was sampled by $1 \times 1 \times 1$ *k* points and test calculations revealed that a higher number of *k* points did not affect the results.

Acknowledgements

We are grateful to the National Natural Science Foundation of China, the 973 Program (2009CB939802), the 111 Project (B07004), and the Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT, IRT1205). Support from the Royal Society (Newton International Fellowship to D.K.B.), the Pfizer Institute of Pharmaceutical Materials Science (to A.D.), the Herchel Smith Fund (to G.O.L.), the EPSRC, and the INTERREG IVA 2 Mers Seas Zeeën Cross-border Co-operation Programme 2007–2013 (to B.P.) are acknowledged.

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Received: October 25, 2012

Revised: March 9, 2013

Published online: April 24, 2013