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The effects of positional isomers, protonation and solvent on the morphologies and photophysical properties of boron difluoride complex microcrystals⁺

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Positional isomers, protonation and solvent provide useful strategies for morphology-controllable fabrication of organic microcrystals. Among them, the solvent unprecedentedly induces a globate polyhedron morphology with unusual orange-red phosphorescence. The changes in morphology also induce interesting changes in the photophysical properties of boron difluoride organic microcrystals.

Organic micro/nanomaterials have drawn more and more attention due to their interesting properties and potential technological applications in many fields.¹ Organic micro/ nanostructures with various morphologies such as particles, rods, wires, sheets, cubes and fibers have been fabricated by using different approaches.² Among them, the reprecipitation method is considered as an effective and facile process to micro/nanomaterials prepare organic with unique morphology. However, the morphology/size-controllable fabrication of organic micro/nanomaterials is still a challenge when using this strategy. Therefore, there is increasing interest in developing preparation methods to control the morphology/size of organic micro/nanostructural materials, and further exploring the effects of morphology on their properties.

Organic microcrystals with various morphologies are easily self-assembled through supramolecular interactions.³ Other factors such as the substituted group, positional isomer, pH change, solvent, heat, light, and/or concentration also have important effects on the morphology/size of organic micro/ nanostructural materials.^{3,4} Tian *et al.* found that substituted groups on molecules are responsible for the final shape of the organic micro/nanostructures,⁵ and the corresponding nanoparticles and nanorods have been fabricated by either taking advantage of the different molecular structure characteristics or changing solvent quality. Varughese and Draper reported the influence of isomerism on the morphology of organic micro/nanocrystals.4b Very recently, we have discovered that the protonation and/or anion induced morphological changes in boron difluoride (BF₂) complex microcrystals²ⁿ and acid-base vapor can trigger a reversible morphological transformation with interesting "on/off" switching behaviors.⁶ Herein, two novel methyl-substituted BF₂ complexes were synthesized, which reveal the effects of the positional isomers of methyl groups on the morphologies. It is interestingly found that protonation (pH change) and solvent also have important influences on the morphologies. Especially, the solvent can even induce an unusual globate polyhedron morphology. We also demonstrate that morphologies exhibit obvious effects on the photophysical properties. The major purpose of this work is to unveil the fact that the morphological properties of organic microcrystals are tunable by appropriate factors such as positional isomers, protonation and solvent.

A 7,7' (or 8,8')-dimethyl-2,3'-biimidazo[1,2-*a*]pyridin-2'-one radical (Hdmbipo^{-•}, Scheme 1) was synthesized by a similar procedure to that of a 2,3'-biimidazo[1,2-*a*]pyridin-2'-one radical.⁷ The BF₂ complexes (BF₂-7,7'-dmbipo and BF₂-8,8'-dmbipo) were synthesized from the corresponding



Scheme 1 Synthesis of boron difluoride complexes and the corresponding hydrochlorides.

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Hdmbipo^{••} with BF₃·OEt₂ in DMF solution (Scheme 1). The protonated BF₂ complexes (BF₂-7,7'-dmbipoHCl and BF₂-8,8'-dmbipoHCl) were prepared from the corresponding BF₂-dmbipo by a dissolution–reprecipitation method in DMF (or DMSO)–HCl solution. The scanning electron microscopy (SEM) images reveal that BF₂-7,7'-dmbipo (termed microcrystal A) and BF₂-8,8'-dmbipo (termed microcrystal B) microcrystals present a one-dimensional (1D) rod-like morphology with an average diameter of 2.0 μ m (Fig. 1a) and a three-dimensional (3D) brick-like morphology with an average size of 24.3 μ m × 10.0 μ m × 5.7 μ m (Fig. 1b), respectively. The sharp peaks in the powder X-ray diffraction (PXRD) patterns confirm the microstructures of microcrystals A and B to be highly crystalline (Fig. S1, ESI†). The PXRD patterns indicate that microcrystals A and B possess various microstructures.

Because microcrystals A and B were fabricated under the same conditions, the factors such as solvent, pH, and temperature, *etc.* are not responsible for the formation of different morphologies. Instead, the positional isomeric methyl groups have a profound effect on the morphologies of microcrystals A and B. The morphology variations of micro/nanocrystals as a function of steric hindrance, π - π stacking, and hydrogen bonding are known in the literature, although the manipulation of morphology by altering the molecular geometry only has a limited success.^{8,4b} Thus, a rational and simple approach to fabricate organic microcrystal materials is highly desirable for understanding the various factors that influence the morphologies. Two isomers exhibit different steric hindrance and molecular geometries (Scheme 1), and these in turn are reflected in the morphologies. BF₂-7,7'-dmbipo should possess a longer molecular size compared to BF2-8,8'dmbipo (Scheme 1). Thus, BF2-7,7'-dmbipo molecules with a "linear" geometry were self-assembled into 1D rod-like microcrystal A, whereas BF₂-8,8'-dmbipo molecules with a relatively "rectangular" geometry were constructed into 3D brick-like microcrystal B. This change in morphology can therefore be attributed to the different interactions at the supramolecular level brought about by the variation of the methyl group positions in the molecules. Moreover, compared to BF2-7,7'dmbipo, the larger steric hindrance of the methyl groups in BF₂-8,8'-dmbipo is also an important factor in the formation of the 3D brick-like morphology. The observed steric effects could hinder the formation of 1D nanostructures, and thus the formation of thin platelets and nanoparticles have been reported instead.^{9,4b} Therefore, the results reveal that the morphology of the organic small molecular microcrystals can be facilely tuned by varying the isomer or the steric hindrance.

Interestingly, when microcrystals A and B were dissolved in DMF-HCl solution by the dissolution-reprecipitation method, the resulting microcrystals C (BF₂-7,7'-dmbipoHCl) and D (BF₂-8,8'-dmbipoHCl) disclose a flower-like morphology composed of two-dimensional (2D) microsheets (Fig. 2a) and a 1D microstrip morphology (Fig. 2b), respectively. The sharp peaks in the PXRD patterns also confirm the microstructures of microcrystals C and D to be highly crystalline (Fig. S1, ESI†). From the SEM images, one can see that the thickness (about 100 nm) of the microsheets (Fig. 2a) is thinner than that of the microstrips (thickness of about 160 nm, Fig. 2b). The above results reveal that the protonation (pH change) and/or Cl⁻ anion can also trigger morphological changes.²ⁿ



Fig. 1 SEM images of 1D microrods of microcrystal A (a) and 3D microbricks of microcrystal B (b).



Fig. 2 SEM images of flower-like microcrystal C composed of 2D microsheets (a) and 1D microstrips of microcrystal D (b).

The exact mechanism for the protonation and/or Cl^- anion induced morphology is still not clear, but we can hypothesize that the Cl^- anions were selectively adsorbed on a specific crystal facet due to the electrostatic attraction, resulting in the anisotropic growth which gives the microsheets and the microstrips of microcrystals C and D, respectively.

Moreover, when microcrystal B was dissolved in DMSO-HCl solution, the resulting microcrystal E (BF₂-8,8'dmbipoHCl) reveals an unusual zero-dimensional (0D) globate polyhedron morphology with an average diameter of 22.8 μ m (Fig. 3), which is also crystalline as confirmed by the PXRD pattern (Fig. S1, ESI[†]). To our knowledge, the globate polyhedron morphology has not been reported in organic microcrystals. Obviously, when DMSO was used as a solvent under the same conditions for the fabrication of microcrystal D, the resulting microcrystal E displayed a quite different morphology from microcrystal D. It is noteworthy that the solvent is the only difference in the reaction conditions for the preparation of such two kinds of morphologies by the reprecipitation method. As a result, the different morphologies of microcrystals D and E are ascribed to the solventinduced morphological changes.⁴ It is well known that polar solvents have a stronger interaction with polar molecules. The use of DMF as a solvent led to the formation of 1D microstrips of microcrystal D (Fig. 2b), owing to the relatively low polarity of the DMF, while the reaction in DMSO which has a higher polarity¹⁰ resulted in the unique globate polyhedron morphology of microcrystal E (Fig. 3), attributable to the stronger interaction between the "rectangular" BF2-8,8'dmbipoH⁺ cation and DMSO which both have a higher polarity. However, when DMSO was used as a solvent for the preparation of the BF2-7,7'-dmbipoHCl microcrystal, a flower-like morphology similar to that of microcrystal C was also obtained, possibly because DMSO which has a higher polarity did not exhibit an effective interaction with the "linear" BF2-7,7'-dmbipoH⁺ cation which has a lower polarity, unlike in the case of the preparation of the BF2-8,8'-dmbipoHCl microcrystal.

The photoluminescence (PL) spectrum of microcrystal A displays a broad emission band in the range of 400–675 nm

with one strong emission peak at 506 nm and one shoulder at ca. 436 nm (Fig. 4), indicating that it might emit greenwhite light (Fig. 5a). However, microcrystal B only emits green light (Fig. 5b), as indicated by its PL spectrum with an emission peak at about 511 nm (Fig. 4). Moreover, the protonated microcrystals C and D reveal obviously blue-shifted PL spectra, with microcrystal C having an emission peak at 447 nm (Fig. 4), meaning that it emits blue light (Fig. 5c), and microcrystal D having a strong emission peak at 455 nm, as well as two shoulders at 483 and 575 nm (Fig. 4), implying that it emits blue-white light (Fig. 5d). Unprecedentedly, microcrystal E exhibits an obviously red-shifted PL spectrum with an emission peak at about 622 nm (Fig. 4), meaning that it emits orange-red light (Fig. 5e). Moreover, microcrystal E also emits orange light when illuminated with ambient light (Fig. 5f), due to its maximum excitation wavelength at about 455 nm (Fig. S2, ESI[†]). The detailed emission mechanism for microcrystals A-E is not clear at present; however, as aggregation-induced emission, their emission mechanism can be ascribed to morphology-dependent luminescence.¹¹ Take microcrystals C and D for example, the phosphorescent nature of microcrystals A-E is confirmed by the microsecondorder decay lifetime in the solid state (Fig. S3, ESI[†]). The different phosphorescent colors of microcrystals A-E should be ascribed to their various morphologies owing to the morphology-dependent luminescence.¹¹ Especially, the globate polyhedron induced orange-red phosphorescence is very unusual, probably attributable to the 0D morphology and/or the lower crystalline state of microcrystal E. Both Ito et al.¹² and Sagara et al.¹³ have reported that red-shifted emission in luminescent materials is related to the amorphous state and that the crystalline state is responsible for the blue-shifted emission. The red-shifted emission of microcrystal E would be supported by its PXRD pattern with a lower crystalline state, compared to microcrystals A-D (Fig. S1, ESI†).



Fig. 3 SEM image of globate polyhedra of microcrystal E.



Fig. 4 Normalized PL spectra of microcrystals A (a), B (b), C (c), D (d) and E (e).



Fig. 5 Photographs of microcrystals A (a), B (b), C (c), D (d) and E (e) under 365 nm UV lamp irradiation, and microcrystal E under ambient light irradiation (f).

The phosphorescence quantum yield (PHQY) of microcrystals A–E is 8.7 \pm 0.9%, 5.6 \pm 0.6%, 22.4 \pm 2%, 13.8 \pm 1% and 2.1 \pm 0.2%, respectively, upon excitation at 365 nm.^{14,2n} Interestingly, microcrystal C shows a higher PHQY, which should be ascribed to the local field enhancement effect induced by the anisotropic microsheet structure $2^{n,15}$ in the flower-like morphology (Fig. 2a) and/or the thinner sheet thickness (about 100 nm). Moreover, the lower PHOY of microcrystal E could be due to its 0D morphology and larger diameter (about 22.8 µm, Fig. 3). The various PHQYs of microcrystals A-E should be attributed to their different morphology/size effects.²ⁿ On the other hand, microcrystals A-E display interesting near-infrared (NIR) absorption characteristics with multiple absorption bands from 1180 nm to 2500 nm (Fig. S4-S6, ESI⁺), which can be looked as aggregationinduced NIR absorption.¹⁶ Interestingly, compared to microcrystals A and B (Fig. S4, ESI⁺), microcrystals C and D reveal an enhanced NIR absorption (Fig. S5, ESI†). Especially, microcrystal C shows an absorption intensity in the NIR region (above 2000 nm) that is even higher than that in the UV-vis region (~408 nm). Such an enhanced NIR absorption is also ascribed to the morphological anisotropy of the 2D microsheets and 1D microstrips. It should be noted that compared to microcrystals A-D, microcrystal E exhibits not only fewer NIR absorption bands, but also a lower absorption intensity in the NIR region (Fig. S6, ESI⁺). This phenomenon should be attributed to its "isotropical" 0D globate polyhedron morphology and larger diameter.

In conclusion, we have achieved the *in situ* syntheses of 1D microrods and 3D microbricks of BF₂-dmbipo microcrystals tuned by the positional isomeric methyl groups, from which morphology-controllable flower-like microcrystals composed of 2D microsheets and 1D microstrips were respectively fabricated through protonation by the dissolution-reprecipitation method. Unprecedentedly, DMSO as solvent can even induce a globate polyhedron morphology which is the first reported in organic microcrystals. The changes in morphology induce distinctive changes in the photophysical properties. Significantly, the 2D microsheets in the flower-like microcrystal exhibit higher PHQY (22.4 \pm 2%) and enhanced NIR absorption, which are attributed to the morphological anisotropy effects of the 2D microsheets. Interestingly, the globate polyhedron microcrystal reveals orange-red phosphorescence and lower NIR absorption, due to its "isotropical" 0D globate polyhedron morphology. The importance of this work evidences the fact that the positional isomers, protonation and solvent can tune morphological properties. Our results could also be helpful for searching novel organic micro/nanomaterials with potential applications.

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