The Dimensionality Transition between Three-Dimensional and Two-Dimensional Organic Microcrystals: Specific Symmetry and Selective Adhesion

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ABSTRACT: A three-dimensional–two-dimensional dimensionality transition of organic microcrystals was performed via elongated octahedrons, oblique octahedrons, diamond-like particles, and parallelograms using nonplanar 2,7-di(9*H*-carbazol-9-yl)spiro[fluorene-9,9'-xanthene] molecules. The specific crystal symmetry and selective adhesion of P123 on the {11–1}s facet are supposed to induce the morphological transition.

INTRODUCTION

Tailoring the morphology and dimensionality of micro/nanomaterials is critical in determining their properties, including electrical,¹ optical,^{2–4} plasmonics,^{5–7} magnetic,^{8,9} and catalytic^{10–12} performance. For inorganic particles, especially metal^{13–15} and metal chalcogenide^{16,17} micro/nanocrystals, tremendous growth mechanisms and methods have been proposed to efficiently forecast and control their size and shape under different conditions. However, the formation of organic crystals is more complicated than inorganic crystals to some extent: steric structures of organic molecules must be taken into consideration, which cannot be reduced to balls as inorganic counterparts usually do. Instead of simple close packing of balls, organic molecular arrangement is more like a compromise between the trend of 3D-packing volume minimization and the existent steric hindrance from molecular geometries. Recently, many efforts had been devoted to fabricate organic micro/nanomaterials of a variety of shapes, such as wires, belts, plates, and polyhedrons. For example, Hu et al. showed a 2D shape collection of heteroacene microcrystals with different growth rates of six lateral planes, including hexagons, elongated hexagons, rhombuses, and so on.¹⁸ There are also several reports on the manipulation of symmetric 3D morphologies including cubes, rhombic dodecahedra, octahedron, and cuboctahedron.^{19,20} Although these studies are encouraging, the uniqueness of organic crystals distinct from inorganic crystals may not be embodied adequately in terms of crystal symmetry and packing modes by using ordinary linear or planar molecules.

To fully understand the characteristic assembly of organic molecules, bulky molecules, especially cross-structured spiro-fluorenes, were served as the building blocks. Based on the 3D

steric architecture, the supramolecular interaction forces can be oriented to all directions, which lead to variable multidimensional morphologies.²¹ Furthermore, by jointing a planar supramolecular segment to the bulky molecular scaffold, the original 3D polyhedral particles can undergo a transformation to 2D nanosheets, which adopt an interdigital lipid bilayer-like (ILB) packing motif.^{22,23} Besides the molecular design strategy, here, we show a dimensionality transition of 2,7-di(9*H*-carbazol-9-yl)spiro[fluorene-9,9'-xanthene] (2,7-DCz-SFX) microcrystals with the selective coverage of a P123 surfactant. By precisely controlling the area decrease–increase of the eight exposed facets, a series of polyhedrons, including elongated octahedrons, oblique octahedrons, diamond-like particles, and parallelograms, have been generated in sequence during this gradual evolution from 3D to 2D. The unique symmetry of 2,7-DCz-SFX microcrystals is supposed to be the critical point for the morphology regulation, which provides benefit for the deeper understanding of the organic crystal symmetry, molecular assembly mode, and the strategy to fabricate organic polyhedral micro/nanocrystals.

RESULTS AND DISCUSSION

The chemical structure of the 2,7-DCz-SFX molecule is revealed in Figure 1a, which was prepared through the Ullmann-type coupling reaction between DBr-SFX and Cz. The synthetic process and the confirmation of chemical

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Figure 1. (a) Chemical structure and (b) molecular crystal structure of 2,7-DCz-SFX. (c) Single-crystal data of 2,7-DCz-SFX.

composition are exhibited in the Supporting Information, Figures S1–S3. The corresponding thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements are shown in the Supporting Information (Figures S4 and S5) as well, indicating that the molecules can keep stable until 190 °C. According to the single-crystal data, the spatial structure of 2,7-DCz-SFX along with the locations of weak supramolecular forces were investigated as shown in Figure 1b. The molecular crystal structure presents a typical steric hindrance feature: the xanthene segment intersects almost vertically with the fluorene plane, connecting two carbazole wings (the corresponding dihedral angles are shown in Figure 1b). The supramolecular interaction sites are evenly spread over the SFX body and the Cz wings, acting as the intermolecular linkages for crystallization. The single-crystal data in Figure 1c indicates that the 2,7-DCz-SFX crystal belongs to monoclinic system with a $P2_1/n$ space group, which is common in organic crystals because of the anisotropic molecular packing. The concerning symmetry elements include the 2_1 axis and glide plane, resulting in central symmetry crystal characteristics.²⁴

2,7-DCz-SFX microcrystals were prepared using a typical reprecipitation method. A THF solution of 2,7-DCz-SFX (1 mM) was added into 2 mL deionized water with different P123 concentrations. Through scanning electron microscopy (SEM), it can be found that the morphology obtained in the absence of the surfactant is irregular as shown in Figure S6. In the case of 1 mg/mL P123, uniform elongated octahedrons are observed (Figure 2a), indicating the shape-modifying function of P123. With the increasing P123 concentration of 8 mg/mL, there is a slight change in the area ratios of the eight exposed facets of the octahedron, leading to the formation of oblique octahedrons (Figure 2b). This trend becomes more and more obvious with higher P123 concentration. When the P123 concentration reaches 16 mg/mL, diamond-like particles are generated via the tensile deformation of the octahedrons (Figure 2c). Although the shape has changed dramatically, the original eight facets still remain with four facets in the obverse side and the rest four facets in the reverse side. From Figure S7, it is clear that the four pairs of facets are antiparallel and centrosymmetric. With the upper and lower facets growing larger and larger, the microcrystals become thin gradually (Figure 2d, P123 concentration is 24 mg/mL) and eventually turn into 2D sheets (Figure 2e, P123 concentration is 32 mg/mL). The dimensional change is summarized in Figure S8 by measuring the length, width, and thickness of the 2,7-DCz-SFX microcrystals. During the whole 3D–2D transformation, 2,7-DCz-SFX microcrystals own the same crystal structure as the X-ray powder diffraction (XRD) patterns showing in Figure 2f.

Figure 2. SEM images of (a) elongated octahedrons prepared at $C_{2,7\text{-DCz-SFX}} = 1$ mM, $C_{\text{P123}} = 1$ mg/mL (2 mL), $V_{\text{THF}} = 1$ mL, aging time = 12 h; (b) oblique octahedrons prepared at $C_{2,7\text{-DCz-SFX}} = 1$ mM, $C_{\text{P123}} = 8$ mg/mL (2 mL), $V_{\text{THF}} = 1$ mL, aging time = 12 h; (c) diamond-like particles prepared at $C_{2,7\text{-DCz-SFX}} = 1$ mM, $C_{\text{P123}} = 16$ mg/mL (2 mL), $V_{\text{THF}} = 1$ mL, aging time = 12 h; (d) thin diamond-like particles prepared at $C_{2,7\text{-DCz-SFX}} = 1$ mM, $C_{\text{P123}} = 24$ mg/mL (2 mL), $V_{\text{THF}} = 1$ mL, aging time = 12 h; and (e) 2D rhombuses prepared at $C_{2,7\text{-DCz-SFX}} = 1$ mM, $C_{\text{P123}} = 32$ mg/mL (2 mL), $V_{\text{THF}} = 1$ mL, aging time = 12 h. (f) XRD patterns of these samples. The bottom line shows the standard powder spectrum simulated on the basis of the single-crystal data by DIAMOND software.

Transmission electron microscopy (TEM) images further confirm the shapes of the oblique octahedron, the diamond-like particle, and the 2D sheet in Figure 3a–c. The corresponding selected-area electron diffraction (SAED) patterns in Figure 3d–f recorded respectively from $[11-1]$, $[011]$ and $[11-1]$ directions are attributed to the same monoclinic phase crystal structure identified by XRD. Combined SAED and XRD results together, the eight exposed faces can be indexed as (011) , $(0-1-1)$, (101) , $(-10-1)$, $(11-1)$, $(-1-11)$, (010) , and $(0-10)$. As the pair of opposite faces is identical due to the central symmetry of the microcrystals, the bounded faces can be summarized to be $\{11-1\}$ s, $\{011\}$ s, $\{101\}$ s, and $\{010\}$ s. The dihedral angles are calculated as $(11-1)/(011) = 101.69^\circ$, $(11-1)/(101) = 67.33^\circ$, and $(11-1)/(010) = 70.01^\circ$. Schematic models of the varying morphologies are drawn by WinXmorph as illustrated in Figure 3g according to the assigned facets. Obviously, the elongated/oblique octahedrons here fail to meet the criteria for real octahedrons in terms of symmetry and morphologies.²⁵ For example, $(11-1)$ and (010) belong to totally different families of crystal planes with different molecular packing motifs, although they look similar in the elongated octahedrons. Because of this distinctive crystal characteristic, the transition between 3D and 2D is available. This shape evolution is induced by the area variation of $\{11-1\}$ s, $\{011\}$ s,

Figure 3. TEM images of (a) the oblique octahedron, (b) the diamond-like particle, and (c) the thick 2D sheet. (d–f) Corresponding SAED patterns taken from a single polyhedron. (g) Schematic models for the polyhedra calculated by WinXmorph software based on the results of SAED and crystal parameters. (h) Surface free energies of crystal facets calculated by Material Studio.

{101}s, and {010}s, specifically, the increase of {11-1}s and the decrease of {011}s, {101}s, and {010}s, as shown in Figure 3g. The corresponding surface free energy in Figure 3h reveals that {11-1}s owns the highest surface free energy, which should grow the fastest until its disappearance according to the surface free energy minimizing principle.^{26,27} However, experimental facts did not obey this ideal assumption. This discrepancy was caused by many environmental factors, among which the involving of P123 surfactant should be the most important one.

The growth tendency toward 3D morphology originated from the aggregation of 2,7-DCz-SFX molecules in three

directions induced by supramolecular interactions. Figure 4a discloses a representative fragment of the 2,7-DCz-SFX molecular assembly viewed perpendicular to the *ac* plane, exhibiting the cross sections of several molecular columns. The column is an antiparallel packing chain of T-shaped 2,7-DCz-SFX molecules extending along the *b*-axis, as shown in Figure 4b. Therefore, the packing along the *a*-axis and *c*-axis is arranged in a staggered row, as illustrated in Figure S9. There are three kinds of dimers in the molecular arrangements with abundant supramolecular forces as shown in Figure 4c (detailed information of supramolecular forces is demonstrated in Figure S10).^{28,29} The column along the *b*-axis is assembled by dimer 1 as the yellow arrow indicates in Figure 4b. These columns connect each other in the forms of dimer 2 and dimer 3, as indicated by the red arrow and blue arrow in Figure 4a. With the interconnection in three dimensions, 2,7-DCz-SFX molecules reveal the growth potential of a 3D shape. However, the increasing concentration of P123 additives could induce a “planarity” growth behavior. The addition of large quantities of P123 was reported to modify succinic acid crystals from block-like crystals to needle-like crystals because the growth of the six side faces was inhibited.³⁰ In our case, the intrinsic difference of the largest {11-1}s and {010}s of pseudo-octahedron implies the dissimilarity of their adhesion strength with P123. To investigate the interaction of P123 with (11-1) and (010) planes, molecular dynamics (MD) simulations were performed in an aqueous solution environment (the calculation description is stated in the Supporting Information). The snapshot images of the simulation system illustrate the activities of P123 at the interface between solution and (11-1) (Figure 4d) or (010) (Figure 4e) faces. It is obvious that the P123 monomers are closer to the (11-1) plane, consistent with the binding energy results in Table S1. The stronger interactions between P123 and (11-1) plane can be attributed to the polar oxygen atom on the crystal faces (Figure 4f). Meanwhile, the nonpolar parts of carbazole on the (010) plane (Figure 4g) cannot interact effectively with P123.³¹ The strong inhibition of P123 on {11-1}s is supposed to be the reason of the augmentation of {11-1}s and the shape evolution from 3D to 2D.

Figure 4. Molecular packing and supramolecular interactions of 2,7-DCz-SFX microcrystals viewed from the (a) *b*-axis and (b) *c*-axis. (c) Three kinds of concerned dimer units. The arrows in panels (a) and (b) with different colors indicate the growth directions based on these dimers. The snapshot of the simulation system of the simplified P123 monomers ($x = y = z = 2$) interacting with the (d) (11-1) and (e) (010) facets. The red background is made up by H₂O molecules, and the other scattered molecules are P123 monomers. The structure exposed in (f) (11-1) and (g) (010) facets. Color code: carbon atoms, blue; nitrogen atoms, yellow; oxygen atoms, red.

CONCLUSIONS

In conclusion, a series of sequential morphology transition between 3D and 2D is achieved using 2,7-DCz-SFX molecules, including elongated octahedrons, oblique octahedrons, diamond-like particles, and parallelograms. The crystal symmetry of the pseudo-octahedrons is distinct from real octahedrons, which enables the surfactant adsorption difference of the crystal faces and induces the precise manipulation of the microcrystal shapes. This work may help to understand deeply the crystal symmetry of organic crystals and their transformation behaviors.

EXPERIMENTAL SECTION

Materials. 2,7-DCz-SFX was synthesized by condensation of carbazole with 2,7-dibromospiro[fluorene-9,9'-xanthene] in high yields, and the corresponding detailed synthesis process is shown in Figure S1. All chemicals were purchased from J&K Scientific Co., Ltd. and were used without further purification unless otherwise stated. Poly (ethyleneglycol)-block-poly-(propyleneglycol)-block-poly-(ethylene glycol) (P123) was purchased from Sigma-Aldrich and used without further purification. Ultrapure water was obtained from the Millipore S. A. 67120 apparatus (France) with a resistivity of 18.2 MΩ cm.

Preparation of Micro/Nanocrystals and Single-Crystal Structures. The microcrystals were fabricated through a classical reprecipitation method. Typically, a 2,7-DCz-SFX compound (0.66 mg) dissolved in THF (1 mL) was injected into 2 mL different concentrations of a Pluronic 123 (P123) aqueous solution under vigorous stirring for 5 min, following aging at room temperature for 12 h to stabilize the nanostructures. Then, the nanocrystals with distinct morphologies can be formed in the mixed solution. At last, the nanocrystals underwent centrifugation and were washed with pure water at least four times. Single-crystal data of 2,7-DCz-SFX was obtained by solvent diffusion method; tetrahydrofuran and isopropanol are the good solvent and the poor solvent, respectively. Crystal data for CCDC: 1949939 contained the supplementary crystallographic data for this paper.

Characterization. ^1H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. Field emission scanning electron microscopy images were obtained using a Hitachi S-4800 scanning electron microscope at the accelerating voltage of 5 kV. For the preparation of the SEM samples, a drop of 10 μL as-prepared dispersion was deposited onto a freshly cleaned wafer with the solvent evaporating completely. The transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) studies were performed in a JEM 2010F JEOL and operated under an accelerating voltage of 120 kV. The TEM samples were made by placing a drop of 5 μL as-prepared dispersion gently onto the carbon-coated copper grid. Samples for X-ray diffraction (XRD) measurements were prepared by depositing a drop of a suspension onto the Si slide with the solvent evaporating completely. XRD spectra were recorded on a Bruker D8 X-ray diffractometer with Cu KR radiation ($\lambda = 1.54050 \text{ \AA}$). The operating 2θ angle ranges from 5 to 30 $^\circ$ with a step length of 0.025 $^\circ$. The single-crystal data collection was performed at around 100 or 298 K on a Bruker 2000 CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All structures were solved by direct methods using SHELXS-2015

and refined against F2 using SHELXL-2015. The surface free energy ($E_{\text{surf}}^{\text{[hkl]}}$) calculations were performed using the Forcite and Morphology modules of Materials Studio Software.

Molecular Dynamics Simulations. All the all-atom MD simulations were based on a GROMOS54a7 force field¹ created by ATB² and were carried out using the Gromacs-4.6.7 software package.³ The time step was 2 fs, and the total run time was 10 ns NVT for the equilibrium MD simulation. We used the relaxed system as a starting configuration. As it is prior to system relaxation MD, energy minimization was carried out with a composite protocol of steepest descent using termination gradients of 100 kJ/mol nm. The Nosé–Hoover thermostat⁴ was used to maintain the equilibrium temperature at 298 K, and periodic boundary conditions were imposed on all three dimensions. The particle mesh Ewald method^{5,6} was used to compute long-range electrostatics within a relative tolerance of 1×10^{-6} . A cut-off distance of 1.2 nm was applied to real-space Ewald interactions. The same value was used for van der Waals interactions. The LINCS algorithm⁷ was applied to constrain bond lengths of hydrogen atoms. A leap-frog algorithm⁸ was used with a time step of 2 fs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.9b03962>.

Crystal data for CCDC: 1949939 (CIF)

Synthesis of 2,7-DCz-SFX and additional data and results (PDF)

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[§]S.-S.W. and R.R. contributed equally to this work. S.-S.W. and R.R. conceived and designed the experiments. R.R. carried out most of the experiments and data analysis. H.Z. performed the SEM and TEM, Y.-R.L. and X.H. performed the SAED and XRD, and Y.Y. and Y.W. provided the molecules. W.H. and L.-H.X. discussed the results and commented on the manuscript. S.-S.W. and R.R. wrote and revised the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Shan, L.; Liu, D.; Li, H.; Xu, X.; Shan, B.; Xu, J.-B.; Miao, Q. Monolayer Field-Effect Transistors of Nonplanar Organic Semiconductors with Brickwork Arrangement. *Adv. Mater.* **2015**, *27*, 3418–3423.
- (2) Yang, B.; Xiao, J.; Wong, J. I.; Guo, J.; Wu, Y.; Ong, L.; Lao, L. L.; Boey, F.; Zhang, H.; Yang, H. Y.; Zhang, Q. Shape-Controlled Micro/Nanostructures of 9,10-Diphenylanthracene (DPA) and Their Application in Light-Emitting Devices. *J. Phys. Chem. C* **2011**, *115*, 7924–7927.
- (3) Wang, X.; Li, H.; Wu, Y.; Xu, Z.; Fu, H. Tunable Morphology of the Self-Assembled Organic Microcrystals for the Efficient Laser Optical Resonator by Molecular Modulation. *J. Am. Chem. Soc.* **2014**, *136*, 16602–16608.
- (4) Chandrasekhar, N.; Chandrasekar, R. Reversibly Shape-Shifting Organic Optical Waveguides: Formation of Organic Nanorings, Nanotubes, and Nanosheets. *Angew. Chem., Int. Ed.* **2012**, *51*, 3556–3561.
- (5) Niu, Y.; Yeung, L. K.; Crooks, R. M. Size-Selective Hydrogenation of Olefins by Dendrimer-Encapsulated Palladium Nanoparticles. *J. Am. Chem. Soc.* **2001**, *123*, 6840–6846.
- (6) Orendorff, C. J.; Sau, T. K.; Murphy, C. J. Shape-Dependent Plasmon-Resonant Gold Nanoparticles. *Small* **2006**, *2*, 636–639.
- (7) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. Photoinduced Conversion of Silver Nanospheres to Nanoprisms. *Science* **2001**, *294*, 1901–1903.
- (8) Deng, H.; Li, X.; Peng, Q.; Wang, X.; Chen, J.; Li, Y. Monodisperse Magnetic Single-Crystal Ferrite Microspheres. *Angew. Chem., Int. Ed.* **2005**, *44*, 2782–2785.
- (9) Yue, M.; Li, C.; Wu, Q.; Ma, Z.; Xu, H.; Palaka, S. A facile synthesis of anisotropic SmCo₅ nanochips with high magnetic performance. *Chem. Eng. J.* **2018**, *343*, 1–7.
- (10) Bell, A. T. The Impact of Nanoscience on Heterogeneous Catalysis. *Science* **2003**, *299*, 1688.
- (11) Narayanan, R.; El-Sayed, M. A. Shape-Dependent Catalytic Activity of Platinum Nanoparticles in Colloidal Solution. *Nano Lett.* **2004**, *4*, 1343–1348.
- (12) Huang, X.; Tang, S.; Mu, X.; Dai, Y.; Chen, G.; Zhou, Z.; Ruan, F.; Yang, Z.; Zheng, N. Freestanding palladium nanosheets with plasmonic and catalytic properties. *Nat. Nanotechnol.* **2011**, *6*, 28–32.
- (13) Zhang, H.; Jin, M.; Xiong, Y.; Lim, B.; Xia, Y. Shape-Controlled Synthesis of Pd Nanocrystals and Their Catalytic Applications. *Acc. Chem. Res.* **2013**, *46*, 1783–1794.
- (14) Tao, A.; Sinsermsuksakul, P.; Yang, P. Polyhedral Silver Nanocrystals with Distinct Scattering Signatures. *Angew. Chem., Int. Ed.* **2006**, *45*, 4597–4601.
- (15) Lin, H.-x.; Lei, Z.-c.; Jiang, Z.-y.; Hou, C.-p.; Liu, D.-y.; Xu, M.-m.; Tian, Z.-q.; Xie, Z.-x. Supersaturation-Dependent Surface Structure Evolution: From Ionic, Molecular to Metallic Micro/Nanocrystals. *J. Am. Chem. Soc.* **2013**, *135*, 9311–9314.
- (16) Zhou, J.; Lin, J.; Huang, X.; Zhou, Y.; Chen, Y.; Xia, J.; Wang, H.; Xie, Y.; Yu, H.; Lei, J.; Wu, D.; Liu, F.; Fu, Q.; Zeng, Q.; Hsu, C.-H.; Yang, C.; Lu, L.; Yu, T.; Shen, Z.; Lin, H.; Yakobson, B. I.; Liu, Q.; Suenaga, K.; Liu, G.; Liu, Z. A library of atomically thin metal chalcogenides. *Nature* **2018**, *556*, 355–359.
- (17) Heine, T. Transition Metal Chalcogenides: Ultrathin Inorganic Materials with Tunable Electronic Properties. *Acc. Chem. Res.* **2015**, *48*, 65–72.
- (18) Li, R.; Zhang, X.; Dong, H.; Li, Q.; Shuai, Z.; Hu, W. Gibbs–Curie–Wulff Theorem in Organic Materials: A Case Study on the Relationship between Surface Energy and Crystal Growth. *Adv. Mater.* **2016**, *28*, 1697–1702.
- (19) Zhang, X.; Dong, C.; Zapfen, J. A.; Ismathullakhan, S.; Kang, Z.; Jie, J.; Zhang, X.; Chang, J. C.; Lee, C.-S.; Lee, S.-T. Polyhedral Organic Microcrystals: From Cubes to Rhombic Dodecahedra. *Angew. Chem., Int. Ed.* **2009**, *48*, 9121–9123.

- (20) Kang, L.; Fu, H.; Cao, X.; Shi, Q.; Yao, J. Controlled Morphogenesis of Organic Polyhedral Nanocrystals from Cubes, Cubooctahedrons, to Octahedrons by Manipulating the Growth Kinetics. *J. Am. Chem. Soc.* **2011**, *133*, 1895–1901.
- (21) Lin, Z.-Q.; Sun, P.-J.; Tay, Y.-Y.; Liang, J.; Liu, Y.; Shi, N.-E.; Xie, L.-H.; Yi, M.-D.; Qian, Y.; Fan, Q.-L.; Zhang, H.; Hng, H. H.; Ma, J.; Zhang, Q.; Huang, W. Kinetically Controlled Assembly of a Spirocyclic Aromatic Hydrocarbon into Polyhedral Micro/Nanocrystals. *ACS Nano* **2012**, *6*, 5309–5319.
- (22) Wang, S.-S.; Rong, R.; Jin, L.-Z.; Yang, S.-S.; Li, Y.-X.; Zhang, H.; Xiong, Y.-W.; Sun, L.-T.; Cao, H.-T.; Xie, L.-H.; Huang, W. Variable Segment Roles: Modulation of the Packing Modes, Nanocrystal Morphologies and Optical Emissions. *Nanoscale* **2018**, *10*, 13310.
- (23) Li, Y.-X.; Wang, S.-S.; Yu, Y.; Zhang, H.; Wang, W.-Y.; Yang, R.-Q.; Xie, L.-H.; Liu, F.; Lin, Z.-Q.; Shi, N.-E.; Sun, L.-T.; Huang, W. SMART Design of a Bulk-Capped Supramolecular Segment for the Assembly into Organic Interdigital Lipid Bilayer-Like (ILB) Nano-sheets. *Small* **2018**, *14*, 1703151.
- (24) Glazer, M.; Burns, G.; Galzer, A. N. *Space Groups for Solids State Scientists*; Academic Press: 2016, pp. 432.
- (25) Jones, D. K.; Kerwin, B.; Zhao, W.; Gavvalapalli, N. Aryl amphiphile shape-directors for shape-controlled synthesis of organic semiconductor particles. *Chem. Commun.* **2019**, *55*, 1306–1309.
- (26) Loi, M. A.; Da Como, E.; Dinelli, F.; Murgia, M.; Zamboni, R.; Biscarini, F.; Muccini, M. Supramolecular organization in ultra-thin films of α -sexithiophene on silicon dioxide. *Nat. Mater.* **2005**, *4*, 81.
- (27) Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J. Y.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. Inkjet printing of single-crystal films. *Nature* **2011**, *475*, 364.
- (28) Cao, H.-L.; Zhou, J.-R.; Cai, F.-Y.; Lü, J.; Cao, R. Two-Component Pharmaceutical Cocrystals Regulated by Supramolecular Synthons Comprising Primary N...H...O Interactions. *Cryst. Growth Des.* **2019**, *19*, 3–16.
- (29) Lü, J.; Perez-Krap, C.; Trouselet, F.; Yan, Y.; Alsmail, N. H.; Karadeniz, B.; Jacques, N. M.; Lewis, W.; Blake, A. J.; Coudert, F.-X.; Cao, R.; Schröder, M. Polycatenated 2d hydrogen-bonded binary supramolecular organic frameworks (sofs) with enhanced gas adsorption and selectivity. *Cryst. Growth Des.* **2018**, *18*, 2555–2562.
- (30) Klapwijk, A. R.; Simone, E.; Nagy, Z. K.; Wilson, C. C. Tuning Crystal Morphology of Succinic Acid Using a Polymer Additive. *Cryst. Growth Des.* **2016**, *16*, 4349–4359.
- (31) Gupta, K. M.; Yani, Y.; Poornachary, S. K.; Chow, P. S. Atomistic Simulation To Understand Anisotropic Growth Behavior of Naproxen Crystal in the Presence of Polymeric Additives. *Cryst. Growth Des.* **2019**, *19*, 3768–3776.