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Micro- and Nanocrystals of Organic Semiconductors

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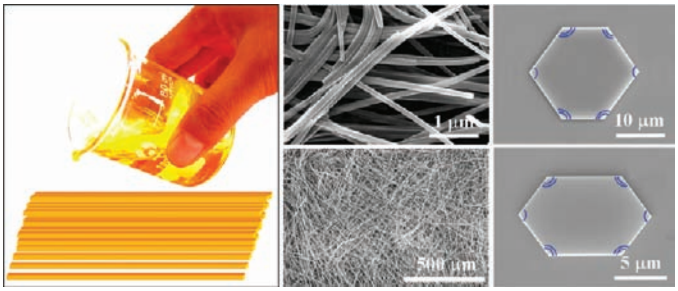
CONSPECTUS



Organic semiconductors have attracted wide attention in recent decades, resulting in the rapid development of organic electronics. For example, the solution processibility of organic semiconductors allows researchers to use unconventional deposition methods (such as inkjet printing and stamping) to fabricate large area devices at low cost. The mechanical properties of organic semiconductors also allow for flexible electronics. However, the most distinguishing feature of organic semiconductors is their chemical versatility, which permits the incorporation of functionalities through molecular design.

However, key scientific challenges remain before organic electronics technology can advance further, including both the materials' low charge carrier mobility and researchers' limited knowledge of structure−property relationships in organic semiconductors. We expect that high-quality organic single crystals could overcome these challenges: their purity and long-range ordered molecular packing ensure high device performance and facilitate the study of structure−property relationships.

Micro- and nanoscale organic crystals could offer practical advantages compared with their larger counterparts. First, growing small crystals conserves materials and saves time. Second, devices based on the smaller crystals could maintain the functional advantages of larger organic single crystals but would avoid the growth of large crystals, leading to the more efficient characterization of organic semiconductors. Third, the effective use of small crystals could allow researchers to integrate these materials into micro- and nanoelectronic devices using a "bottom-up" approach. Finally, unique properties of crystals at micro- and nanometer scale lead to new applications, such as flexible electronics.

In this Account, we focus on organic micro- and nanocrystals, including their design, the controllable growth of crystals, and structure−property studies. We have also fabricated devices and circuits based on these crystals. This interdisciplinary work combines techniques from the fields of synthetic chemistry, self-assembly, crystallography, and condensed matter physics. We have designed new molecules, including a macrocycle and polyaromatic compounds that self-assemble in a predictive manner into regular high-quality crystals. We have examined how the structure, particularly $\pi-\pi$ interactions, determines the crystal growth and how the external conditions affect the crystal morphology. We have developed new methods, such as the gold wire mask, the organic ribbon mask, and the gold layer stamp techniques, to fabricate high-performance devices based on the small crystals and investigate their anisotropic charge transport properties. In addition, we have demonstrated small-crystal organic circuits that function with high performance and ultralow power consumption. We expect that organic micro- and nanocrystals have a bright future in organic electronics.

Introduction

Inorganic semiconductor crystals like silicon are the fundamental blocks of today's modern electronics and microelectronics. Their counterparts, organic semiconductor crystals, have also attracted more and more attention with the rapid development of organic electronics since the 1990s, because the purity and long-ranged order

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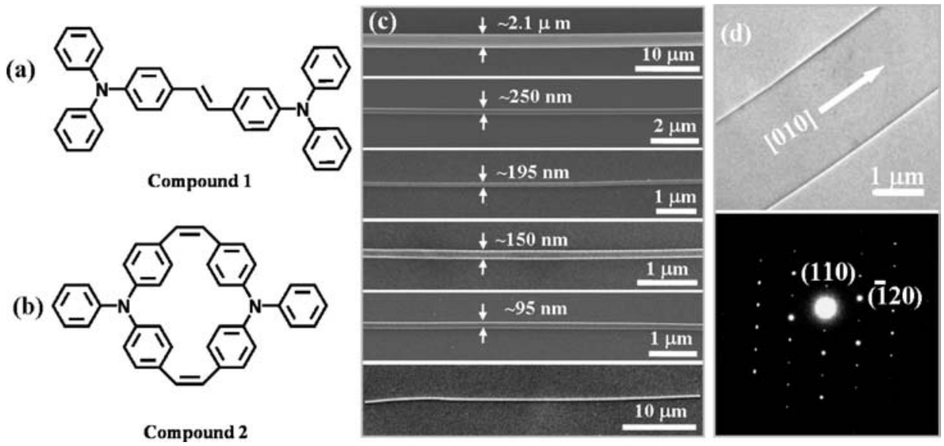


FIGURE 1. (a, b) Chemical structures of compounds **1** and **2**. Compound **1** forms amorphous films; compound **2** crystallizes efficiently. (c) SEM images of the nanometer- and micrometer-sized single-crystal ribbons of compound **2** grown by the physical vapor transport technique. (d) TEM image (top) and selected area electron diffraction (SAED) pattern (bottom) of an individual ribbon crystal. Adapted with the permission from ref 7. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

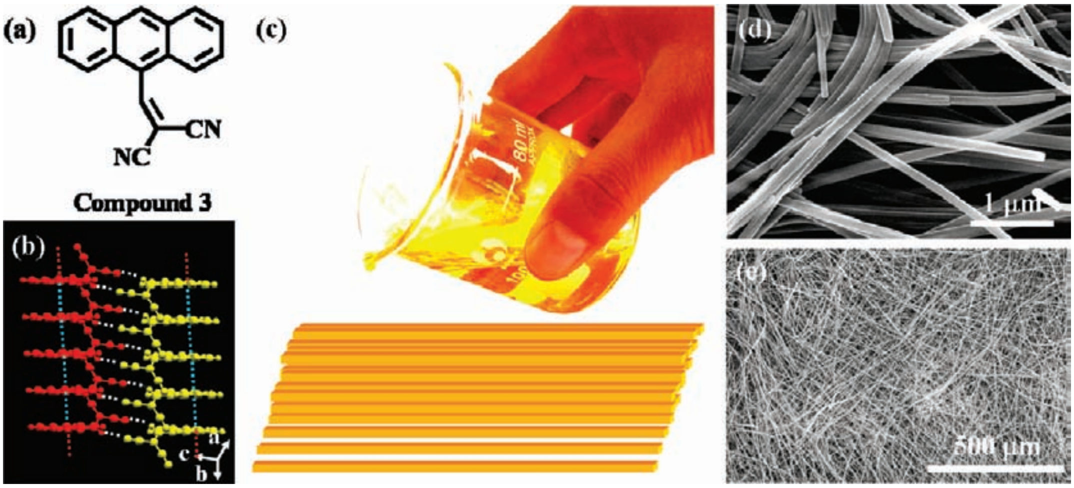


FIGURE 2. (a) Chemical structure of compound **3**, (b) dimers of **3** forming by hydrogen bonds between dicyanovinyl groups and anthracene rings and the packing of the dimers, (c) schematic for cast assembly of nanoribbons of compound **3**, (d, e) SEM images of the cast-assembled nanoribbon crystals. Adapted with permission from ref 16. Copyright 2008 American Chemical Society.

of organic crystals offer the convenience to study the intrinsic property of a material free from grain boundaries and the high quality of organic crystals ensures the high performance of their devices and circuits.[1−3] However, compared with inorganic crystals, organic crystals are much smaller, which poses great challenges for the fabrication of their devices and the exploration of their properties. Moreover, most conventional methods learned from inorganic materials are not applicable for the construction of devices based on organic crystals, especially the crystals at micrometer and nanometer size. For example, a focused ion beam (or electron beam) is found to damage the crystal surface easily during electrode deposition. The challenges, together with the urgent demand for rational material design, the controllable crystal growth, the understanding of the structure−properties relationships, and the application of crystals in devices and circuits, give organic semiconductor crystals an attractive prospect within sight. In this Account, examples are given to illustrate the bright future of this highly interdisciplinary research field.

Design of Organic Semiconductors

A prerequisite for high-performance devices and circuits lies with organic semiconductors with high mobility. Generally, high charge carrier mobility is expected in organic semiconductors with high crystallinity, which could be approached by tailoring the chemical structures of the compounds. Triphenylamine derivatives (TPA, e.g., compound **1**, Figure 1a) are widely used as hole-transport materials for optoelectronic applications such as in xerography and organic light-emitting diodes, which are typically nonplanar with asymmetric structures preventing the optimal packing and crystallization of molecules. As a consequence, they are amorphous in the solid state and exhibit low mobility.[4,5] In contrast, if the rotation of the phenyl groups of TPA derivatives could be restricted in which case the planarity of the molecules would be improved, then the crystallinity of the compound would also be improved. We recently reported on a new material with a macrocyclic structure, compound **2** (Figure 1b),[6] that bears a closed ring, and the steric structure is used to restrict the rotation of the phenyl groups. Indeed, compound **2** crystallizes easily as micro- and nanometer sized crystals as shown in Figure 1c,d,[7] which enables one to tailor the crystallinity of organic semiconductors through chemical design at the molecular level.

Another strategy to tune the crystallinity of organic semiconductors is to control molecular noncovalent interactions such as hydrogen bonds, electrostatic interactions, and $\pi-\pi$ stacking interactions for molecular packing.[8−11] Anthracene and its derivatives are selected as candidates because they exhibit good solubility and excellent optoelectronic properties.[12−15] A synthesized anthracene derivative is shown in Figure 2a (compound **3**),[16] which can easily form planar conjugated dimers due to the hydrogen-bonding interactions between the dicyanovinyl groups and the anthracene rings. With the $\pi-\pi$ interaction between neighboring dimers, a cofacial $\pi-\pi$ stacking along the *b* axis is formed and nice nanoribbons are generated by cast assembly (Figure 2b−e), which proves the effectiveness of hydrogen bonds for self-assembly. If the hydrogen bonds are eliminated by substituting cyano groups with methyl groups, no crystals are obtained, while upon resubstituting methyl groups with carboxylic groups, nanoribbon crystals are grown again. The significant variations of assembled products indicate the critical role of hydrogen bonds for organic semiconductor crystal engineering. The utility of other noncovalent interactions such as S···S interactions is also attractive to tune the solid-state structure of organic semiconductors. Oligothiophene and polycyclic aromatic hydrocarbons (PAH) are effective molecular scaffolds for organic semiconductors, but little work has concentrated on the crystal engineering of these materials. We synthesized an organic semiconductor, perylo[1,12-*b*,*c*,*d*]thiophene (compound **4**, Figure 3), with the introduction of one S atom into the PAH skeleton.[17] Short S···S contacts (3.51 Å) are found between the neighboring columns in its crystals, which drives the formation of ideal face-to-face molecular stacking along the *b* axis (Figure 3, top). Such molecular packing is totally different from the sandwich herringbone packing of its parent compound perylene (Figure 3, bottom), indicating the effective utility of weak intermolecular noncovalent interactions for the crystal engineering of organic semiconductors. A similar effect has also been observed in hexathiapentacene.[18]

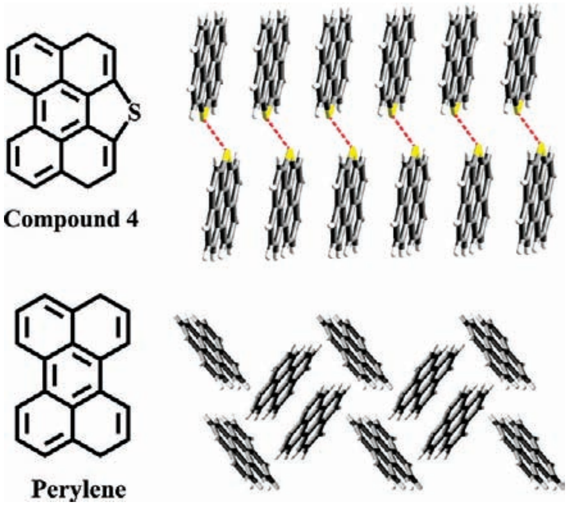
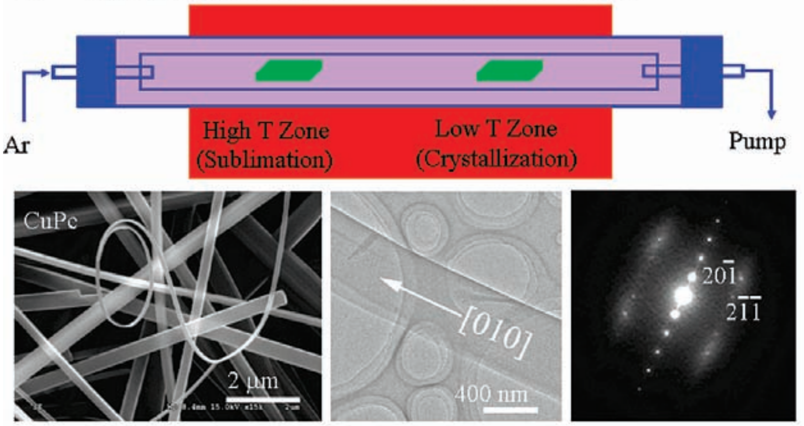


FIGURE 3. Molecular and crystal structures of perylene and compound **4**. Short S···S contacts are found between the neighboring columns in **4** crystals, which drive the formation of ideal face-to-face molecular stacking (top) rather than the sandwich herringbone packing of its parent compound perylene (bottom), indicating the effective utility of molecular weak interactions for the crystal engineering of organic semiconductors. Adapted with permission from ref 17. Copyright 2007 American Chemical Society.

Crystal Growth Methods

Crystal growth involves a variety of research fields such as surface science, crystallography, and condensed mater physics. Different from inorganic semiconductors, organic semiconductors are evaporated at low temperatures. Based on this, vapor-processed techniques such as physical vapor transport are developed for the growth of organic semiconductor crystals from the vapor phase,[19,20] which is usually carried out in a quartz tube by sublimating the starting material at a high-temperature zone and then crystallizing at a low-temperature zone (Figure 4a). This approach is widely used to grow crystals of oligomers and low molecular weight materials, such as CuPc and $F_{16}CuPc$.[21,22] Solution-processed techniques such as self-assembly have been newly developed for the growth of organic crystals (e.g., Figure 4b for an anthracene derivative). It is usually performed by cooling the solution, evaporating the solvent, or adding another solvent in which the organic semiconductor has lower solubility.[16,18,23−26] Compared with the vapor process, the solution process is easier to carry out. However, it requires organic semiconductors with good solubility in common solvents, which is not often the case and hence limits the application of this method. In addition, the solution process sometimes causes the doping of solvent molecules into the organic single crystals,[27,28] which may conceal

(a) Vapor process for the growth of micro and nanocrystals



(b) Solution process for the growth of micro and nanocrystals

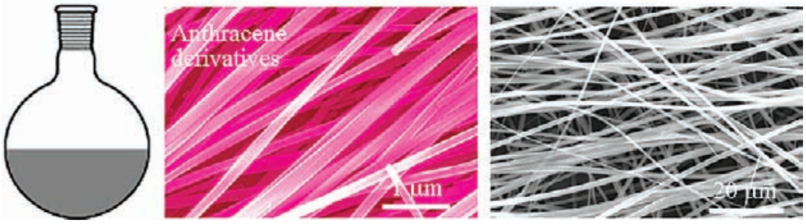


FIGURE 4. Crystal growth methods: (a) vapor process such as physical vapor transport technique, which is effective to grow crystals of oligomers and low molecular weight materials, such as CuPc; (b) solution processes such as self-assembly, which depends on the tuning and utilization of molecular interactions for self-assembly (e.g., for an anthracene derivative). Reproduced with permission from ref 33. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

the intrinsic properties of the organic semiconductors and lower the performance of their devices.

Control of Crystal Habit

The growth of organic crystals is controlled by both internal and external factors. Internal factors concern the molecular structure and inter- or intramolecular interactions in the solid state, while external factors mean the parameters for crystal growth. The crystallization of configurational isomers (such as compounds **5** and **6**[29] in Figure 5) is helpful to examine the internal factors because clear information of structural change on crystal habits can be obtained. By cast assembly, compound **5** tends to form micro- or nanometer-sized ribbons, while compound **6** self-assembles into diamond-like thin crystals (Figure 5). In compound **5**, strong $\pi-\pi$ interactions are found and are maximized along the [101] (or $[10\bar{1}]$) direction (Figure 6, top) so that the fastest crystal growth direction is along this direction. In compound **6**, an extensive network of $C-H\cdots\pi$ and $S\cdots\pi$ interactions are found within the $a-c$ plane of the crystal. In the direction perpendicular to the $a-c$ plane, that is, along the *b* axis, no strong intermolecular interaction is found (Figure 6, bottom). Obviously, when its molecules crystallize from solution, the fastest crystal growth direction is along the *a* and *c* axes, and thus two-dimensional diamond-like crystals are obtained. The distinctly different crystals of the two isomers confirm the importance of internal factors for the controllable growth of organic crystals.

The external factors are rather complicated. For the solution process of crystal growth, the influencing factors include the concentration, heat exchange, substrate, solvent, etc. For example, the difference between the concentration at the equilibrium temperature of the saturated solution and the concentration at the growth temperature will lead to a supersaturation, and crystals begin to nucleate and grow.[30,31] For the vapor process of crystal growth, for example, by the physical vapor transport method, the driving force can be expressed by the pressure ratio between the equilibrium vapor and the growth pressure, so factors such as temperature, vacuum level, carrier gas velocity, etc. are important for the growth of the crystals. For example, by control of the growth temperature (other conditions kept constant), typical crystals of compound **6** show three representative morphologies: hexagonal, elongated hexagonal and diamond-like products (Figure 7). Powder XRDs of the crystals prove that all samples exhibit identical diffraction peaks, confirming that the as-grown crystals share the same structure. The morphology variation suggests the importance of external factors for the controllable growth of organic semiconductor crystals.

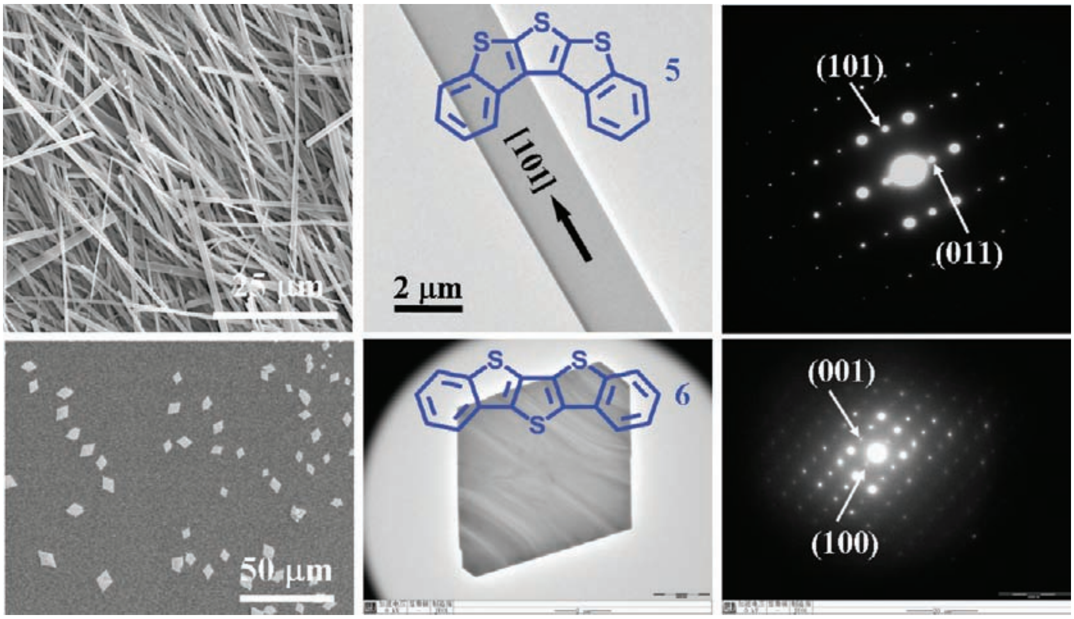


FIGURE 5. Self-assembled products of compound **5** (top) and compound **6** (bottom), and the corresponding SEM (left), TEM (middle) images, and SAED patterns (right) of the micro- and nanocrystals.

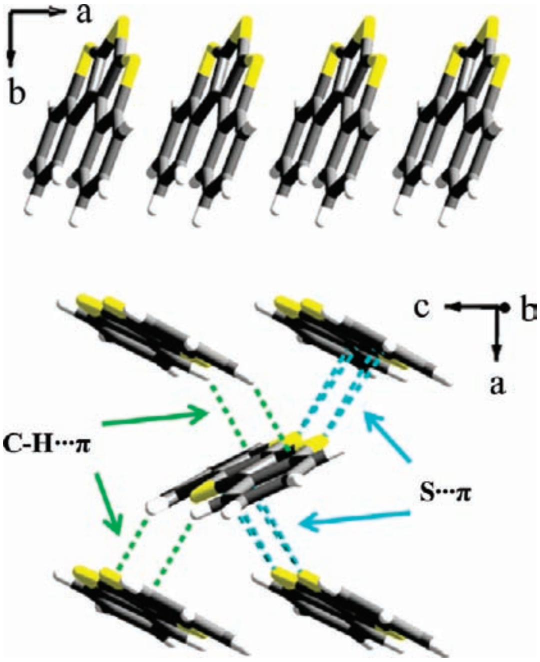


FIGURE 6. Different packing motifs and intermolecular interactions in isomers of compound **5** (top, viewed down the *c* axis) and **6** (bottom). In compound **5**, face-to-face $\pi-\pi$ stacking interactions are found, and in compound **6**, strong intermolecular interactions are found within the $a-c$ plane. The different intermolecular interaction modes explain the different self-assembled morphologies of the isomers.

Crystal Optoelectronic Devices

Device Fabrication. Devices based on organic single crystals are ideal to study the intrinsic properties of organic semiconductors. Controlling the growth of organic crystals for the fabrication of organic devices is a "bottom up" method, which integrates the requirements of nanoelectronics and organic electronics. One important challenge in this field is the high sensitivity of organic crystals to an electron beam or a focused ion beam, which limits the use of traditional microfabrication techniques for the fabrication of organic single-crystalline devices and circuits, as well as the investigation of optoelectronic properties of organic crystals.

Different nondestructive methods have been developed (Figure 8) to fabricate devices based on small organic crystals with bottom- or top-contact configuration.[1,32,33] Bottom-contact configuration (Figure 8a) is always adopted when organic crystals are unstable in vacuum (e.g., tetrathiafulvalene, TTF) or the deposition of a top electrode on them is difficult. It is also noticed that bottom-contact configuration sometimes causes contact problems due to the weak van der Waals force between electrode and crystal. In contrast, top-contact devices could work effectively to avoid this problem, for example, by using a copper grid or a Au microwire as a mask to deposit electrodes on a "small" organic crystal (Figure 8b).[7,21,22,25,26,34] But during the vacuum deposition of electrodes on the organic crystal, the thermal irradiation may also harm the organic crystal. In order to avoid thermal radiation damage and the filling of pinholes in the dielectric layer by metal atoms during electrode vacuum deposition, a mechanical technique was recently developed to paste electrodes onto crystals directly (Figure 8c).[35−38] A Au thin film deposited on a Si wafer is cut into small pieces (approximately 30 μm × 150 μm) by a sharp probe, and then a piece of the film is peeled off from the substrate by the probe and pasted

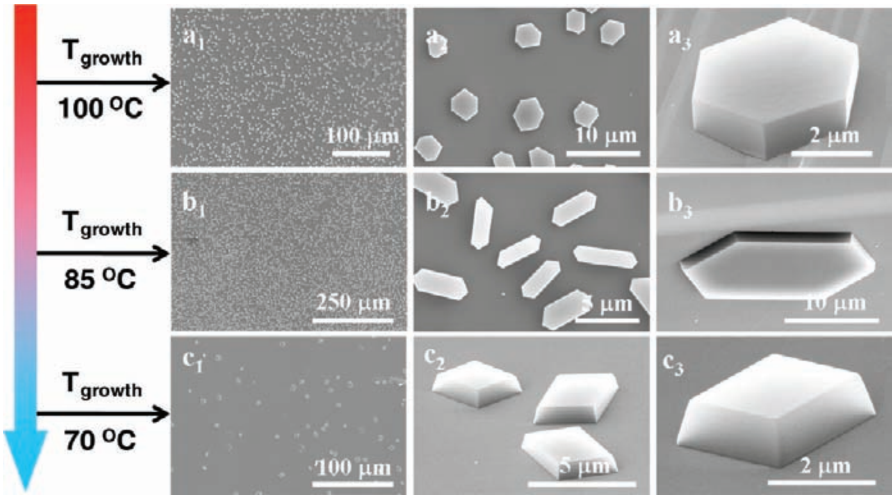
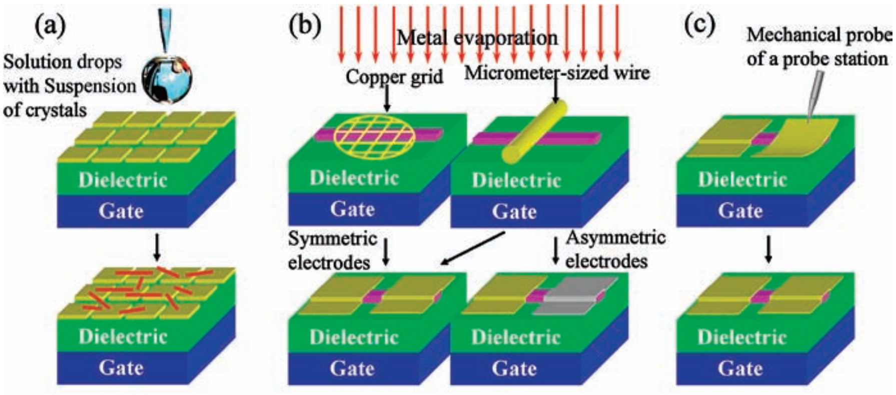


FIGURE 7. Crystal growth of compound **6** by controlling the growth temperature (other conditions kept constant) in the physical vapor transport system. Three representative morphologies are obtained, which indicates the importance of external factors for controlling the growth of organic crystals.



Crystals were dispersed on bottom-contact electrodes via drop-casting, spin-coating, or spraying coating from the solution with the suspension of crystals.

One copper grid or one single micrometer-sized wire was applied as the shadow mask. By multi-movement of the micrometer-sized wire, the channel length was decreased and asymmetric electrode devices could be fabricated.

A technique was developed to make drain and source electrodes with mechanical process. Thin Au layers were transferred onto the micro /nanometer sized crystal as electrodes.

FIGURE 8. Techniques for the fabrication of devices based on organic micro- and nanocrystals: (a) bottom-contact configuration with predeposited electrode arrays on substrates, dropping solution on the electrodes for crystallization; (b) shadow mask technique by employing a copper grid or a Au microwire as the mask for electrode deposition to make symmetrical and asymmetrical electrodes; (c) Au-layer stamping technique, in which thin Au layers are mechanically transferred and pasted on an individual crystal as the electrodes. Reproduced with permission from ref 33. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

onto the organic crystal as source or drain electrode. The "cold" electrode circumvents the disadvantages of thermal evaporation and thus ensures high device performance. Moreover, this technique needs only a few instruments and hence is very appropriate for fundamental study of organic crystals. Principally, this method may also be applicable to a variety of metals of different work functions to meet the needs of different energy levels from the organic semiconductors. It should be pointed out that this "pick and paste" method should only apply to relatively thin crystals because thick crystals will contribute to vertical contact resistance.

Structure−Property Relationship. Structure−property studies are prerequisites to understand the fundamental properties of organic materials and their corresponding molecular structure and device properties. High mobility is expected when conjugated molecules have strong interactions with neighboring molecules to maximize the overlap of π molecular orbits, for example, the cofacial $\pi-\pi$ stacking structure.[39] However, so far, lots of organic semiconductors that exhibit high mobility (e.g., pentacene[40,41]) adopt the edge-to-face herringbone structure with reduced intermolecular electronic couplings. It is imperative to estab-

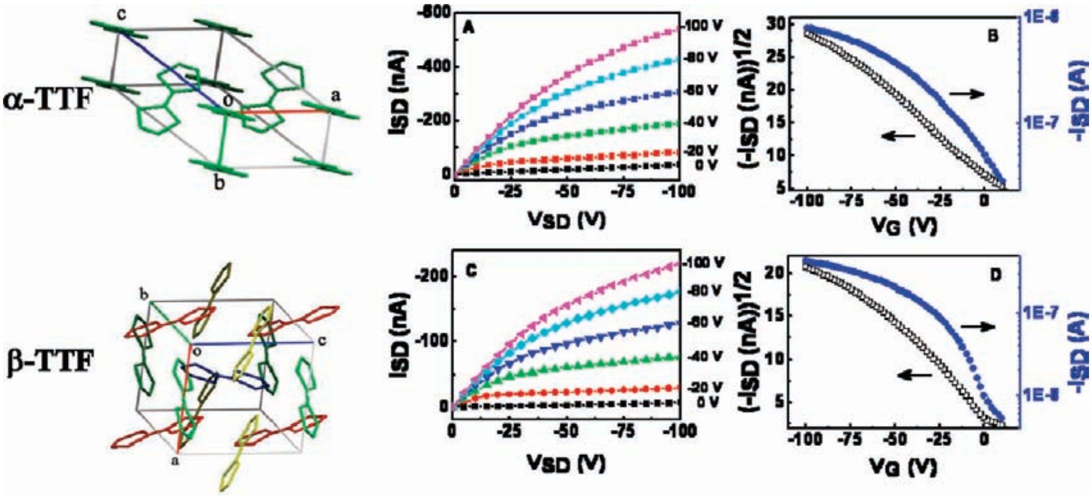


FIGURE 9. Crystal structures of α- and β-TTF and typical output and transfer characteristics of the transistors based on α- and β-TTF crystals. The maximum field-effect mobility of α-TTF is as high as 1.20 $cm^2/(V\ s)$, while that of β-TTF is only about 0.23 $cm^2/(V\ s)$. The different charge transport properties indicate the importance of phase control for high-performance devices. Adapted with permission from ref 43. Copyright 2007 American Institute of Physics.

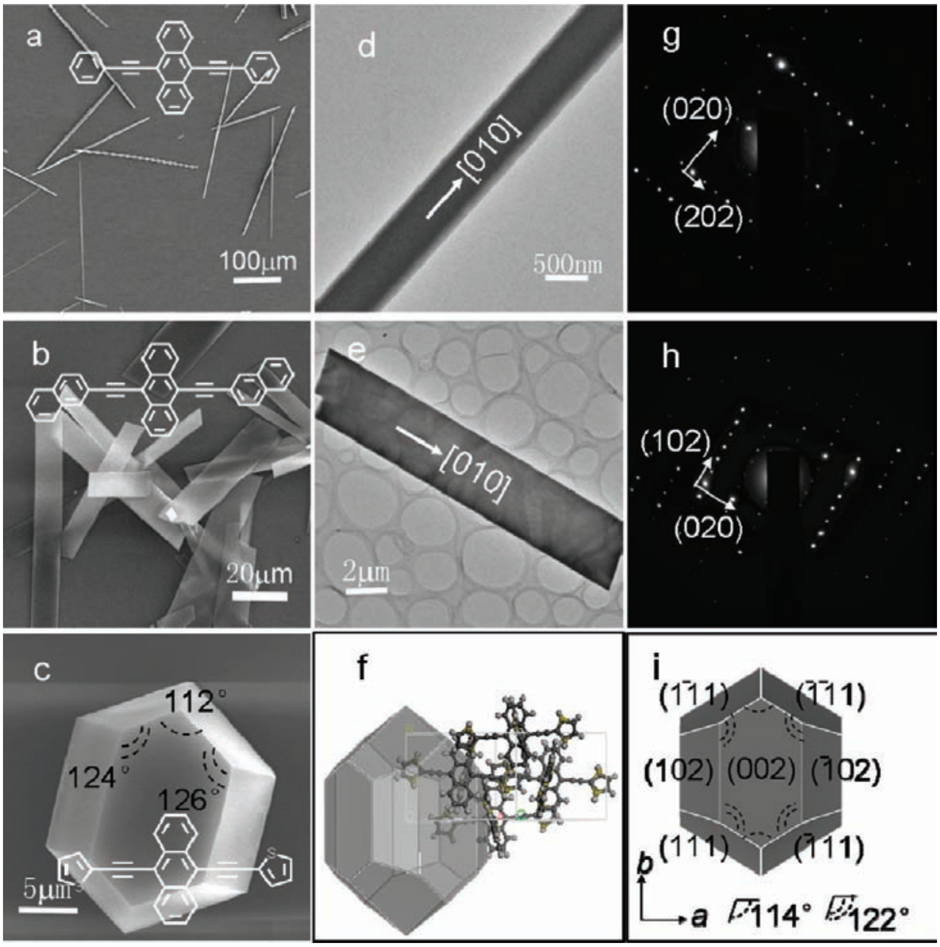


FIGURE 10. SEM and TEM images and SAED patterns of an individual crystal of compounds **10a**, **10b**, and **10c**: (a, d, g) compound **10a**; (b, e, h) compound **10b**; (c, f, i) compound **10c**. The corresponding transistors based on individual crystals exhibit mobility up to 0.73 $cm^2/(V\ s)$ for **10a**, 0.52 $cm^2/(V\ s)$ for **10b**, and 10^{-5} $cm^2/(V\ s)$ for **10c**, indicating the significant roles of $\pi-\pi$ interaction (**10a** > **10b** > **10c**) for morphology (1D → 2D → 3D) and mobility control (**10a** > **10b** > **10c**). Adapted with permission from ref 44. Copyright 2009 American Chemical Society.

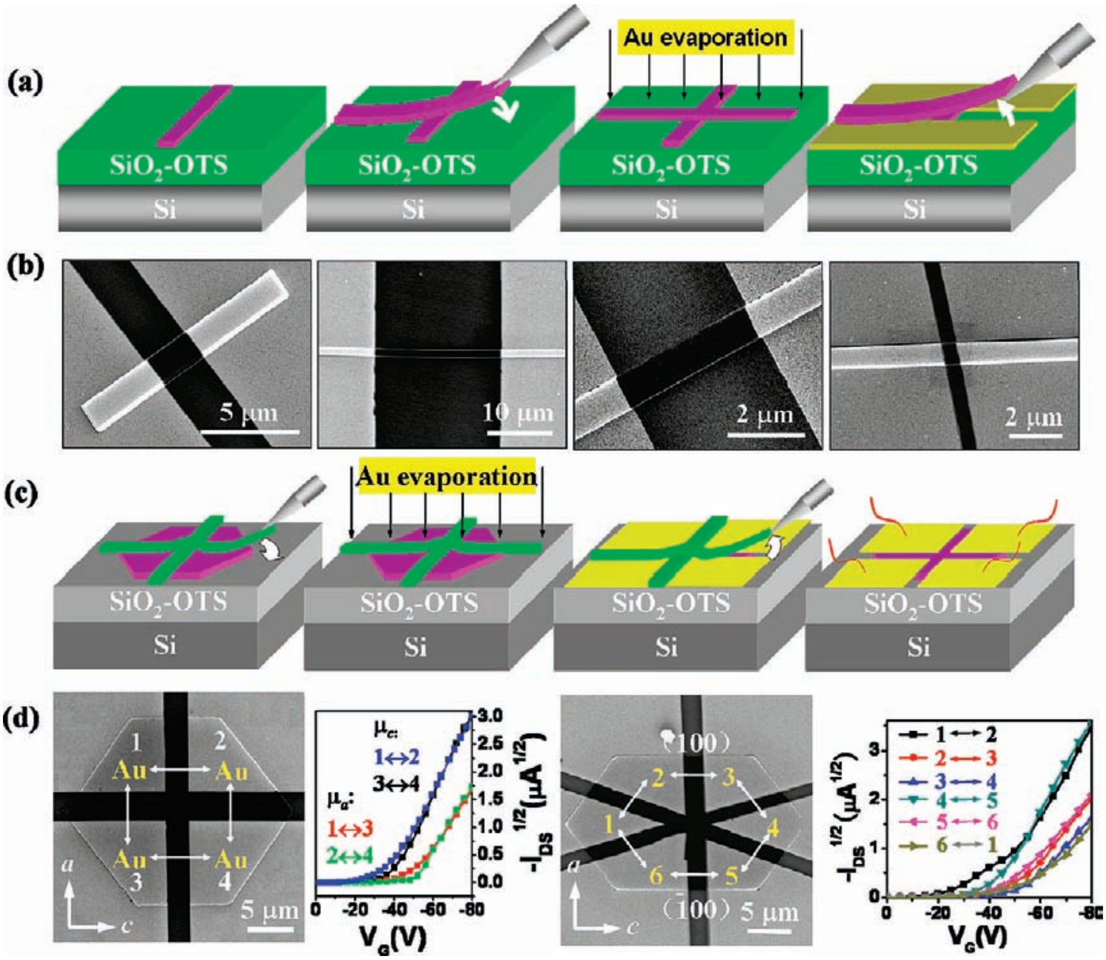


FIGURE 11. (a) Schematics for the fabrication of crystal devices using an individual organic micro- or nanoribbon as the mask, (b) SEM images of the fabricated devices with different channel length based on an individual organic micro- or nanocrystal using the "organic ribbon mask technique", (c) schematics for the deposition of multielectrodes on an individual organic micro- and nanocrystal by using the "two-dimensional organic ribbon mask" technique, and (d) SEM images and transfer characteristics of the devices' transport along different crystal axes (left) and different crystal surfaces (right). Adapted with permission from refs 12 and 51. Copyrights 2008 and 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

lish the structure–property relationship of organic semiconductors explicitly.

TTF and its derivatives have become one of the most studied heterocyclic systems since its discovery.[42] It is well-known that TTF crystals have two phases: α-TTF, which belongs to the space group $P2_1/c$ with two molecules at centrosymmetric sites of the unit cell, and β-TTF, which belongs to the space group $P1$ with four symmetry-inequivalent molecules at the centrosymmetric sites of the unit cell (Figure 9).[43] Crystals of α-TTF can be grown from *n*-heptane solution, while β-TTF can be obtained by using chlorobenzene as solvent. Single-crystal transistors based on α- and β-TTF (Figure 9) suggest that the maximum field-effect mobility of the α phase is as high as 1.20 cm^2/(V s) while that of the β phase only about 0.23 cm^2/(V s), which is assigned to the strong π–π stacking and the S···S intermolecular interactions of α-TTF.[43] The results provide direct evidence of the structure–property relationships of TTF crystals.

Cruciform molecules are another kind of ideal candidate for the examination of the structure–property relationship due to their unique structures with two distinct molecular axes perpendicular to each other. As shown in Figure 10, the selected molecules have anthracene as one axis and the substituents on the 9,10 positions of the anthracene ring as another axis. The results demonstrate that the cruciform molecules are easily crystallized as micro- and nanocrystals via a simple solution drop-cast process, forming one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) crystals. The corresponding transistors based on individual crystals exhibit mobility up to 0.73 cm^2/(V s) for **10a**, 0.52 cm^2/(V s) for **10b**, and 10^{-5} cm^2/(V s) for **10c**, indicating the significant roles of π–π interac-

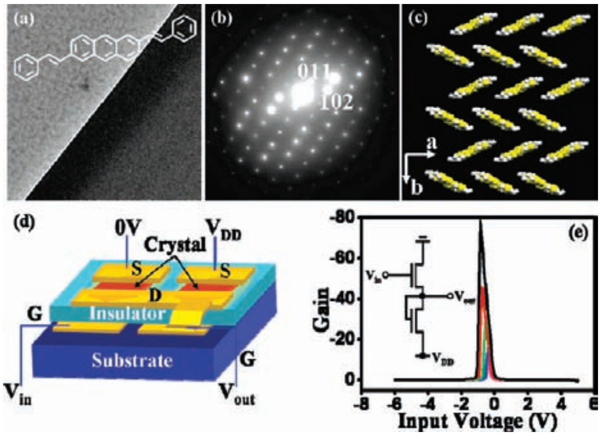


FIGURE 12. (a) Molecular structure and TEM image of individual crystal of DPV-Ant, (b) SAED patterns of the crystal, (c) crystal packing in the crystal of DPV-Ant, (d) schematic inverters based on DPV-Ant single crystals integrating with two top-contact p-type single-crystal transistors, and (e) corresponding voltage gains of the inverters. Adapted with permission from ref 52. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

tion (**10a** > **10b** > **10c**) for morphology (1D → 2D → 3D) and mobility control (**10a** > **10b** > **10c**).[44]

Molecular aggregation controlled properties are also vivid examples for the study of structure−property relationship. For example, nanocoils of an anthracene derivative in J-aggregates with slight $\pi-\pi$ overlap exhibit no photoresponse activity, but its nanoribbons in H-aggregates with relatively strong $\pi-\pi$ overlap exhibit good photoresponse ability,[45] which shows the close relationship between molecular structure, solid-state morphology, and properties of organic semiconductors.

Transport Anisotropy. The charge transport anisotropy of organic bulk crystals can be examined with the elastomeric transistor stamp technique,[46,47] painting graphite electrodes technique,[48] predeposited radial shape electrodes,[49,50] etc. However, it is a great challenge to study the transport anisotropy of organic micro- or nanocrystals by these techniques. We have developed the "organic ribbon mask" technique to deposit electrodes on "small" organic crystals. The channel length of the devices can be scaled down to nanometer level (Figure 11a,b), which opens a new cost-effective and facile way to fabricate organic single-crystal devices with a short conducting channel without the need of photo- or electron beam lithography.[12] Moreover, based on this technique, a "two-dimensional organic ribbon mask" technique is further approached, so that multielectrodes can be fabricated based on an individual microcrystal.[51] An exemplified device with four electrodes along the *c* and *a* directions of an individual hexagonal crystal of compound **6** is shown in Figure 11c,d. The mobility along the *c* direction is found to be 0.6−1.8 cm^2/(V s) and that along the *a* direction 0.1−0.5 cm^2/(V s). The mobility ratio of anisotropy is around 2.3−2.5. And the anisotropy of different crystal planes shows that mobilities along conduction channels of 1 ↔ 2 and 4 ↔ 5 (equivalent directions, μ_c) are moderately higher than that along conduction channels of 2 ↔ 3, 5 ↔ 6, 3 ↔ 4, and 6 ↔ 1 (equivalent directions, μ_{ac}). The results agree well with the fact that the closer the molecular packing, the higher the mobility.[51]

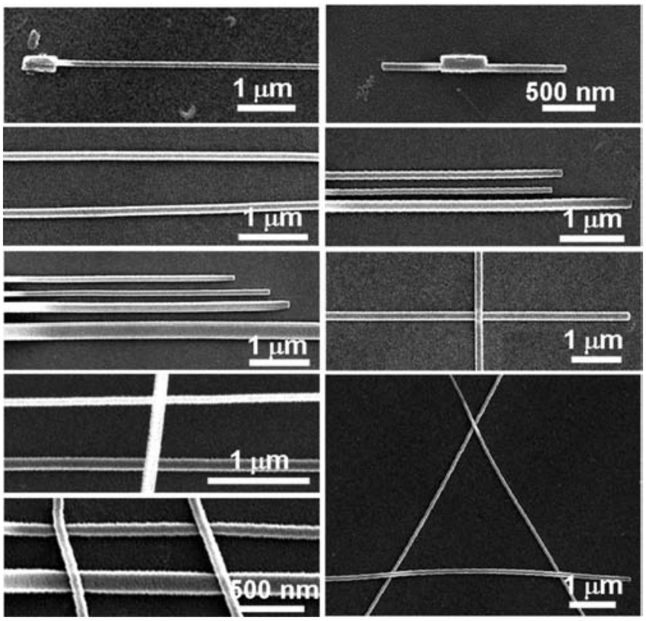


FIGURE 13. Patterning organic single-crystalline nanoribbons on substrate by epitaxial growth of the crystal along the long axis of crystal seeds, by controlling the orientation of the crystal seeds, single-crystal nanoribbons with various architectures can be obtained. Reproduced with permission from ref 55. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

Circuits of Organic Crystals

The high performance of organic crystals and devices ensures the high performance of their corresponding circuits, such as complementary inverters. Here, a kind of high-performance digital inverter integrating by only p-type organic single-crystal transistors is introduced.[52] The used organic semiconductor is an anthracene derivative (DPV-Ant), which possesses facile synthesis procedures, high-performance thin-film transistors, and high stability in air.[13,14] Single crystals of the compound are grown by the physical vapor transport technique (Figure 12a−c), and transistors based on individual crystals are fabricated by the "organic ribbon mask" technique. The devices exhibit mobility at 1.6−4.3 cm^2/(V s) along the *a* direction. Digital inverters consisting of two top-contact p-type single-crystal transistors are fabricated as shown in Figure 12d with ideal transfer curves and excellent logic-level conservation with voltage gain maximum to 80.[52]

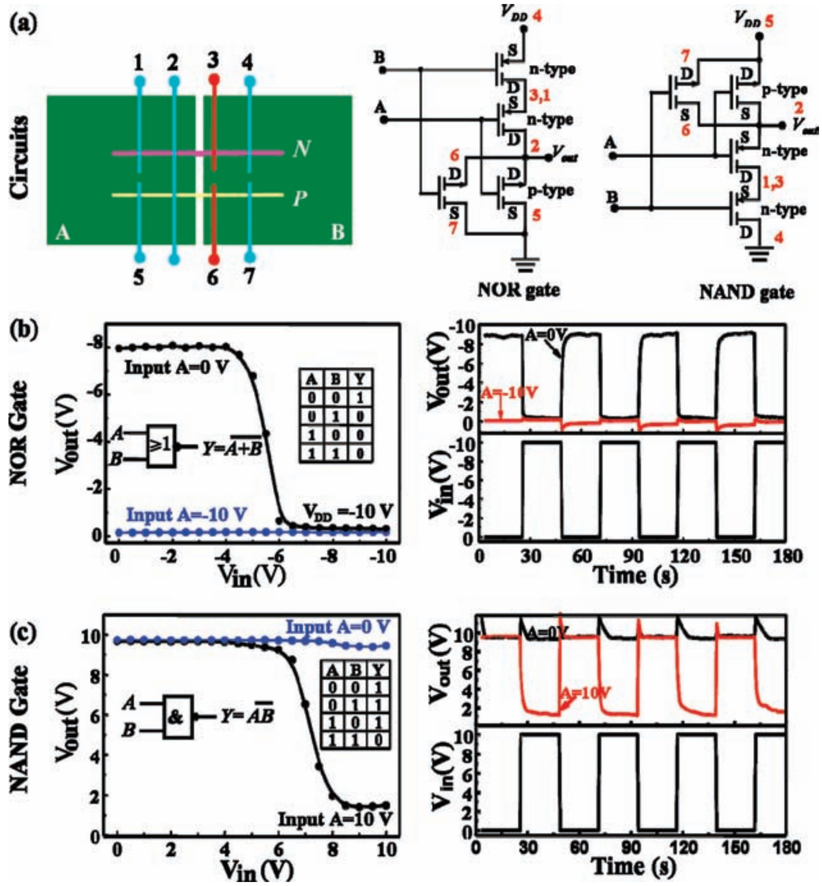


FIGURE 14. Organic single-crystal logic circuits of NOR and NAND by using nanoribbons of CuPc, F_{16}CuPc, and SnO_2−Sb as building blocks: (a) circuit and schematics of logic circuits of NOR and NAND; (b) transfer and dynamic switching characteristics of an NOR gate at $V_{DD} = -10$ V; (c) transfer and dynamic switching characteristics of an NAND gate at $V_{DD} = 10$ V. Adapted with permission from ref 56. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

For the fabrication of more complex circuits, it is important to pattern organic crystals on substrates[32,53,54] to avoid the disadvantages of handpicking process of organic crystals and give intimate contacts between the gate insulator and organic semiconductor. A novel method for this target is developed to *in situ* pattern organic single-crystalline nanoribbons on a SiO_2 surface (Figure 13)[55] by epitaxial growth of the crystal along the long axis of crystal seeds. By control of the orientation of the predeposited seeds, single-crystal nanoribbons with various architectures can be obtained (Figure 13), which presents the prospect of integrated circuits based on organic single crystals. Cross-bar circuits of organic single-crystalline nanoribbons are demonstrated as shown in Figure 14, wherein the used single crystals are CuPc (p-type) and F_{16}CuPc (n-type), and electrodes are single-crystal nanoribbons of Sb-doped SnO_2.[56] Two n-type and two p-type transistors with independent gate electrodes and gate insulators compose the circuits, which can perform multiple functions in different connection configurations. Diverse functions such as inverter and OR, AND, and NOR logic gates can be achieved by the cross-bar circuits. For example, through the connections of the ends of the single crystals as shown in Figure 14, the NOR and NAND circuits are accomplished nicely. Such circuits exhibit very low operational voltage (<10 V), low current (static current <4 pA), and ultralow power consumption (<40 pW).[56]

Conclusions

Micro- and nanocrystals of organic semiconductors have attracted particular attention in recent years. Remarkable progress includes the design of new molecules self-assembling in a predictive manner into regular high-quality crystals, the elucidation of how the internal structures determine the crystal growth and how the external conditions affect the crystal morphology, the probing of the optoelectronic properties of organic single crystals with the design and use of new facile methods, the microscopic description of the structure−property relationship, and the nice demonstration of devices and circuits based on the micro- and nanocrystals. The development of materials science, the increasing demand for miniaturization of organic electronic devices, crystallography, organic semiconductors, condensed matter physics, and nanoelectronics all point to the cross-disciplinary role of micro- and nanocrystals of organic semiconductors.

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FOOTNOTES

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REFERENCES

1 Reese, C.; Bao, Z. Organic Single-Crystal Field-Effect Transistors. *Mater. Today* **2007**, *10*, 20–27.

2 Reese, C.; Bao, Z. Organic Single Crystals: Tools for the Exploration of Charge Transport Phenomena in Organic Materials. *J. Mater. Chem.* **2006**, *16*, 329–333.

3 de Boer, R. W. I.; Gershenson, M. E.; Morpurgo, A. F.; Podzorov, V. Organic Single-Crystal Field-Effect Transistors. *Phys. Stat. Sol. A* **2004**, *201*, 1302–1331.

4 Shirota, Y.; Kageyama, H. Charge Carrier Transporting Molecular Materials and Their Applications in Devices. *Chem. Rev.* **2007**, *107*, 953–1010.

5 Shirota, Y. Photo- and Electroactive Amorphous Molecular Materials - Molecular Design, Syntheses, Reactions, Properties, and Applications. *J. Mater. Chem.* **2005**, *15*, 75–93.

6 Song, Y. B.; Di, C. A.; Yang, X. D.; Li, S. P.; Xu, W.; Liu, Y. Q.; Yang, L. M.; Shuai, Z. G.; Zhang, D. Q.; Zhu, D. B. A Cyclic Triphenylamine Dimer for Organic Field-Effect Transistors with High Performance. *J. Am. Chem. Soc.* **2006**, *128*, 15940–15941.

7 Li, R. J.; Li, H. X.; Song, Y. B.; Tang, Q. X.; Liu, Y. L.; Xu, W.; Hu, W. P.; Zhu, D. B. Micrometer- and Nanometer-sized, Single-Crystalline Ribbons of a Cyclic Triphenylamine Dimer and Their Application in Organic Transistors. *Adv. Mater.* **2009**, *21*, 1605–1608.

8 Briseno, A. L.; Mannsfeld, S. C. B.; Jenekhe, S. A.; Bao, Z.; Xia, Y. Introducing Organic Nanowire Transistors. *Mater. Today* **2008**, *11*, 38–47.

9 Kovacs, A.; Szabo, A.; Hargittai, I. Structural Characteristics of Intramolecular Hydrogen Bonding in Benzene Derivatives. *Acc. Chem. Res.* **2002**, *35*, 887–894.

10 Desiraju, G. R. Hydrogen Bridges in Crystal Engineering: Interactions without Borders. *Acc. Chem. Res.* **2002**, *35*, 565–573.

11 Desiraju, G. R. The $C-H\cdots O$ Hydrogen Bond: Structural Implications and Supramolecular Design. *Acc. Chem. Res.* **1996**, *29*, 441–449.

12 Jiang, L.; Gao, J. H.; Wang, E. J.; Li, H. X.; Wang, Z. H.; Hu, W. P.; Jiang, L. Organic Single-Crystalline Ribbons of a Rigid “H”-type Anthracene Derivative and High-Performance, Short-Channel Field-Effect Transistors of Individual Micro/nanometer-Sized Ribbons Fabricated by an “Organic Ribbon Mask” Technique. *Adv. Mater.* **2008**, *20*, 2735–2740.

13 Klauk, H.; Zschieschang, U.; Weitz, R. T.; Meng, H.; Sun, T.; Nunes, G.; Keys, D. E.; Fincher, C. R.; Xiang, Z. Organic Transistors Based on Di(phenylvinyl)anthracene: Performance and Stability. *Adv. Mater.* **2007**, *19*, 3882–3887.

14 Meng, H.; Sun, F.; Goldfinger, M. B.; Gao, F.; Londono, D. J.; Marshal, W. J.; Blackman, G. S.; Dobbs, K. D.; Keys, D. E. 2,6-Bis[2-(4-pentylphenyl)vinyl]-anthracene: A Stable and High Charge Mobility Organic Semiconductor with Densely Packed Crystal Structure. *J. Am. Chem. Soc.* **2006**, *128*, 9304–9305.

15 Meng, H.; Sun, F.; Goldfinger, M. B.; Jaycox, G. D.; Li, Z.; Marshall, W. J.; Blackman, G. S. High-Performance, Stable Organic Thin-Film Field-Effect Transistors Based on Bis-5′-alkylthiophen-2′-yl-2,6-anthracene Semiconductors. *J. Am. Chem. Soc.* **2005**, *127*, 2406–2407.

16 Jiang, L.; Fu, Y. Y.; Li, H. X.; Hu, W. P. Single-Crystalline, Size, and Orientation Controllable Nanowires and Ultralong Microwires of Organic Semiconductor with Strong Photoswitching Property. *J. Am. Chem. Soc.* **2008**, *130*, 3937–3941.

17 Sun, Y. M.; Tan, L.; Jiang, S. D.; Qian, H. L.; Wang, Z. H.; Yan, D. W.; Di, C. G.; Wang, Y.; Wu, W. P.; Yu, G.; Yan, S. K.; Wang, C. R.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. High-Performance Transistor Based on Individual Single-Crystalline Micrometer Wire of Perylo[1,12-*b*,*c*,*d*]thiophene. *J. Am. Chem. Soc.* **2007**, *129*, 1882–1883.

18 Briseno, A. L.; Mannsfeld, S. C. B.; Lu, X.; Xiong, Y.; Jenekhe, S. A.; Bao, Z.; Xia, Y. Fabrication of Field-Effect Transistors from Hexathiapentacene Single-Crystal Nanowires. *Nano Lett.* **2007**, *7*, 668–675.

19 Laudise, R. A.; Kloc, C.; Simpkins, P. G.; Siegrist, T. Physical Vapor Growth of Organic Semiconductors. *J. Cryst. Growth* **1998**, *187*, 449–454.

20 Kloc, C.; Simpkins, P. G.; Siegrist, T.; Laudise, R. A. Physical Vapor Growth of Centimeter-Sized Crystals of α-Hexathiophene. *J. Cryst. Growth* **1997**, *182*, 416–427.

21 Tang, Q. X.; Li, H. X.; He, M.; Hu, W. P.; Liu, C. M.; Chen, K. Q.; Wang, C.; Liu, Y. Q.; Zhu, D. B. Low Threshold Voltage Transistors Based on Individual Single-Crystalline Submicrometer-Sized Ribbons of Copper Phthalocyanine. *Adv. Mater.* **2006**, *18*, 65–68.

22 Tang, Q. X.; Li, H. X.; Liu, Y. L.; Hu, W. P. High-Performance Air-Stable n-Type Transistors with an Asymmetrical Device Configuration Based on Organic Single-Crystalline Submicrometer/Nanometer Ribbons. *J. Am. Chem. Soc.* **2006**, *128*, 14634–14639.

23 Briseno, A. L.; Mannsfeld, S. C. B.; Shamberger, P. J.; Ohuchi, F. S.; Bao, Z.; Jenekhe, S. A.; Xia, Y. Self-Assembly, Molecular Packing, and Electron Transport in n-Type Polymer Semiconductor Nanobelts. *Chem. Mater.* **2008**, *20*, 4712–4719.

24 Lim, J. A.; Lee, H. S.; Lee, W. H.; Cho, K. Control of the Morphology and Structural Development of Solution-Processed Functionalized Acenes for High-Performance Organic Transistors. *Adv. Funct. Mater.* **2008**, *19*, 1515–1525.

25 Kim, D. H.; Lee, D. Y.; Lee, H. S.; Lee, W. H.; Kim, Y. H.; Han, J. I.; Cho, K. High-Mobility Organic Transistors Based on Single-Crystalline Microribbons of Triisopropylisilylethynl Pentacene via Solution-Phase Self-Assembly. *Adv. Mater.* **2007**, *19*, 678–682.

26 Kim, D. H.; Han, J. T.; Park, Y. D.; Jang, Y.; Cho, J. H.; Hwang, M.; Cho, K. Single-Crystal Polythiophene Microwires Grown by Self-Assembly. *Adv. Mater.* **2006**, *18*, 719–723.

27 Ji, H. X.; Hu, J. S.; Wan, L. J.; Tang, Q. X.; Hu, W. P. Controllable Crystalline Structure of Fullerene Nanorods and Transport Properties of an Individual Nanorod. *J. Mater. Chem.* **2008**, *18*, 328–332.

28 Ji, H. X.; Hu, J. S.; Tang, Q. X.; Song, W. G.; Wang, C. R.; Hu, W. P.; Wan, L. J.; Lee, S. T. Controllable Preparation of Submicrometer Single-Crystal C_{60} Rods and Tubes through Concentration Depletion at the Surfaces of Seeds. *J. Phys. Chem. C* **2007**, *111*, 10498–10502.

29 Gao, J. H.; Li, R. J.; Li, L. Q.; Meng, Q.; Jiang, H.; Li, H. X.; Hu, W. P. High-Performance Field-Effect Transistor Based on Dibenzo[*d*,*d*′]thieno[3,2-*b*:4,5-*b*′]dithiophene, an Easily Synthesized Semiconductor with High Ionization Potential. *Adv. Mater.* **2007**, *19*, 3008–3011.

30 Sunagawa, I. *Crystals Growth, Morphology, and Perfection* Cambridge University Press: New York, 2005.

31 Liu, Y. L.; Ji, Z. Y.; Tang, Q. X.; Jiang, L.; Li, H. X.; He, M.; Hu, W. P.; Zhang, D. Q.; Wang, X. K.; Wang, C.; Liu, Y. Q.; Zhu, D. B. Particle-Size Control and Patterning of a Charge-Transfer Complex for Nanoelectronics. *Adv. Mater.* **2005**, *17*, 2953–2957.

32 Liu, S.; Wang, W. M.; Briseno, A. L.; Mannsfeld, S. C. B.; Bao, Z. Controlled Deposition of Crystalline Organic Semiconductors for Field-Effect-Transistor Applications. *Adv. Mater.* **2009**, *21*, 1217–1232.

33 Tang, Q. X.; Jiang, L.; Tong, Y. H.; Li, H. X.; Liu, Y. L.; Wang, Z. H.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. Micrometer- and Nanometer-Sized Organic Single-Crystalline Transistors. *Adv. Mater.* **2008**, *20*, 2947–2951.

34 Xiao, S.; Tang, J.; Beetz, T.; Guo, X.; Tremblay, N.; Siegrist, T.; Zhu, Y.; Steigerwald, M.; Nuckolls, C. Transferring Self-Assembled, Nanoscale Cables into Electrical Devices. *J. Am. Chem. Soc.* **2006**, *128*, 10700–10701.

35 Tan, L.; Zhang, L.; Jiang, X.; Yang, X. D.; Wang, L. J.; Wang, Z. H.; Li, L. Q.; Hu, W. P.; Shuai, Z. G.; Li, L.; Zhu, D. B. A Densely and Uniformly Packed Organic Semiconductor Based on Annelated β-Trithiophenes for High-Performance Thin Film Transistors. *Adv. Funct. Mater.* **2009**, *19*, 272–276.

36 Tan, L.; Jiang, W.; Jiang, L.; Jiang, S. D.; Wang, Z. H.; Yan, S. K.; Hu, W. P. Single Crystalline Microribbons of Perylo[1,12-*b,c,d*]selenophene for High Performance Transistors. *Appl. Phys. Lett.* **2009**, *94*, 153306.

37 Tang, Q. X.; Tong, Y. H.; Li, H. X.; Ji, Z. Y.; Li, L. Q.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. High-Performance Air-Stable Bipolar Field-Effect Transistors of Organic Single-Crystalline Ribbons with an Air-Gap Dielectric. *Adv. Mater.* **2008**, *20*, 1511–1515.

38 Tang, Q. X.; Tong, Y. H.; Li, H. X.; Hu, W. P. Air/Vacuum Dielectric Organic Single Crystalline Transistors of Copper-hexadecafluorophthalocyanine Ribbons. *Appl. Phys. Lett.* **2008**, *92*, 083309.

39 Coropceanu, V.; Cornil, J.; daSilvaFilho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. L. Charge Transport in Organic Semiconductors. *Chem. Rev.* **2007**, *107*, 926–952.

40 Mattheus, C. C.; Dros, A. B.; Baas, J.; Meetsma, A.; de Boer, J. L.; Palstra, T. T. M. Polymorphism in Pentacene. *Acta. Cryst. Sect. C* **2001**, *C57*, 939–941.

41 Roberson, L. B.; Kowalik, J.; Tolbert, L. M.; Kloc, C.; Zeis, R.; Chi, X. L.; Fleming, R.; Wilkins, C. Pentacene Disproportionation during Sublimation for Field-Effect Transistors. *J. Am. Chem. Soc.* **2005**, *127*, 3069–3075.

42 Mas-Torrent, M.; Hadley, P.; Bromley, S. T.; Ribas, X.; Tarres, J.; Mas, M.; Molins, E.; Veciana, J.; Rovira, C. Correlation between Crystal Structure and Mobility in Organic Field-Effect Transistors Based on Single Crystals of Tetrathiafulvalene Derivatives. *J. Am. Chem. Soc.* **2004**, *126*, 8546–8553.

43 Jiang, H.; Yang, X. J.; Cui, Z. D.; Liu, Y. C.; Li, H. X.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. Phase Dependence of Single Crystalline Transistors of Tetrathiafulvalene. *Appl. Phys. Lett.* **2007**, *91*, 123505.

44 Wang, C. L.; Liu, Y. L.; Ji, Z. Y.; Wang, E. J.; Li, R. J.; Jiang, H.; Tang, Q. X.; Li, H. X.; Hu, W. P. Cruciforms: Assembling Single Crystal Micro- and Nanostructures from One to Three Dimensions and Their Applications in Organic Field-Effect Transistors. *Chem. Mater.* **2009**, *21*, 2840–2845.

45 Zhang, Y. Q.; Chen, P. L.; Jiang, L.; Hu, W. P.; Liu, M. H. Controllable Fabrication of Supramolecular Nanocoils and Nanoribbons and Their Morphology-Dependent Photoswitching. *J. Am. Chem. Soc.* **2009**, *131*, 2756–2757.

46 Sundar, V. C.; Zaumseil, J.; Podzorov, V.; Menard, E.; Willett, R. L.; Someya, T.; Gershenson, M. E.; Rogers, J. A. Elastomeric Transistor Stamps: Reversible Probing of Charge Transport in Organic Crystals. *Science* **2004**, *303*, 1644–1646.

47 Podzorov, V.; Menard, E.; Borissov, A.; Kiryukhin, V.; Rogers, J. A.; Gershenson, M. E. Intrinsic Charge Transport on the Surface of Organic Semiconductors. *Phys. Rev. Lett.* **2004**, *93*, 086602.

48 Zeis, R.; Besnard, C.; Siegrist, T.; Schlockermann, C.; Chi, X.; Kloc, C. Field Effect Studies on Rubrene and Impurities of Rubrene. *Chem. Mater.* **2006**, *18*, 244–248.

49 Reese, C.; Bao, Z. High-Resolution Measurement of the Anisotropy of Charge Transport in Single Crystals. *Adv. Mater.* **2007**, *19*, 4535–4538.

50 Lee, J. Y.; Roth, S.; Park, Y. W. Anisotropic Field Effect Mobility in Single Crystal Pentacene. *Appl. Phys. Lett.* **2006**, *88*, 252106.

51 Li, R. J.; Jiang, L.; Meng, Q.; Gao, J. H.; Li, H. X.; Tang, Q. X.; He, M.; Hu, W. P.; Liu, Y. Q.; Zhu, D. B. Micrometer-Sized Organic Single Crystals, Anisotropic Transport, and Field-Effect Transistors of a Fused-Ring Thienoacene. *Adv. Mater.* **2009**, *21*, 4492–4495.

52 Jiang, L.; Hu, W. P.; Wei, Z. M.; Xu, W.; Meng, H. High-Performance Organic Single-Crystal Transistors and Digital Inverters of an Anthracene Derivative. *Adv. Mater.* **2009**, *21*, 3649–3653.

53 Briseno, A. L.; Mannsfeld, S. C. B.; Ling, M. M.; Liu, S. H.; Tseng, R. J.; Reese, C.; Roberts, M. E.; Yang, Y.; Wudl, F.; Bao, Z. Patterning Organic Single-Crystal Transistor Arrays. *Nature* **2006**, *444*, 913–917.

54 Briseno, A. L.; Aizenberg, J.; Han, Y. J.; Penkala, R. A.; Moon, H.; Lovinger, A. J.; Kloc, C.; Bao, Z. Patterned Growth of Large Oriented Organic Semiconductor Single Crystals on Self-Assembled Monolayer Templates. *J. Am. Chem. Soc.* **2005**, *127*, 12164–12165.

55 Tang, Q. X.; Li, H. X.; Song, Y. B.; Xu, W.; Hu, W. P.; Jiang, L.; Liu, Y. Q.; Wang, X. K.; Zhu, D. B. In Situ Patterning of Organic Single-Crystalline Nanoribbons on a SiO_2 Surface for the Fabrication of Various Architectures and High-Quality Transistors. *Adv. Mater.* **2006**, *18*, 3010–3104.

56 Tang, Q. X.; Tong, Y. H.; Hu, W. P.; Wan, Q.; Bjørnholm, T. Assembly of Nanoscale Organic Single-Crystal Cross-Wire Circuits. *Adv. Mater.* **2009**, *21*, 4234–4237.