



# Crystallization Mechanism of 9,9-Diphenyl-dibenzosilole from Solids

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Organic semiconductor (OSC) crystals have great potential to be applied in many fields, as they can be flexibly designed according to the demands and show an outstanding device performance. However, OSCs with the capacity of solid-state crystallization (SSC) are developing too slowly to meet demands in productions and applications, due to their difficulties in molecular design and synthesis, unclear mechanism and high dependence on experimental conditions. In this work, in order

## 1. Introduction

As high-performance organic field effect transistors (OFETs) have received more attention, processing methods of organic semiconductors (OSCs) electronic devices are gradually upgraded.<sup>[1,2]</sup> Among them, solid-state crystallization (SSC) shows great potentials for the simplification of post processing. Although some materials with the capacity of SSC have been reported,<sup>[3-6]</sup> difficulties such as molecule design, strong dependences on external stimuli, harsh post-process conditions like high temperature or vacuum, and the ambiguous mechanism, still limit their development. To deal with these problems, Guo group designed and synthesized a series of organic amphiphilic molecules with the capacity of SSC at room

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to solve the problems, we synthesized an organic semiconductor capable of SSC at room temperature by adjusting the relationship between conjugated groups and functional groups. The thermodynamic and kinetic properties have been studied to discover the model of film SSC. Moreover, it can be purposefully controlled to prepare the high-quality crystals, and their corresponding organic electronic devices were further fabricated and discussed.

temperature for the first time<sup>[7]</sup> and an evolutionary selection growth approach referring to the crystallization system in solution<sup>[8,9]</sup> was further proposed. This is the first exploration of the SSC mechanism. In this work, we further expand the SSC material system to common aromatic compounds with 9,9diphenyl-dibenzosilole (DPDBS). Taking advantages of the following two study methods:<sup>[9,10]</sup> thermodynamic method based on Differential Scanning Calorimeter analysis (DSC) and kinetic method based on in situ X-ray Diffraction (XRD) and ultraviolet–visible spectroscopy (UV-Vis), we summarized the crystallization principles and proposed a two–step evolutionary model for the film SSC system. Finally, OFET devices were fabricated with microcrystals and would be extend to further use.

## 2. Results and Discussion

## 2.1. Design and Synthesis of DPDBS

Functional OSC molecules usually consist of a semiconductor backbone and functional groups.<sup>[7,11]</sup> DPDBS selects dibenzosilole as a rigid  $\pi$ -backbone and it links to two rotatable benzenes by the single covalent bonds (the structure in Figure 1e and the synthetic route in Scheme S1). The molecular design of DPDBS is based on two considerations: 1) The  $\pi$ - $\pi$  interaction between the dibenzosilole groups facilitates crystallization,  $^{\left[ 12-14\right] }$  but the rigid nature of the  $\pi$  systems usually leads to a high phase transition temperature, which is detrimental to SSC at room temperature. 2) Adjusting degrees of freedom can optimize the phase transition temperature, which requires a precision balance between the rigidity of the  $\pi$ -systems and flexibility of functional groups. Accordingly, two benzene rings are grafted on the silicon atom of the silole as the functional groups. The single covalent bonds increase the degree of freedom by the rotation of the benzenes, so the phase transition temperature can be adjusted to the room temperature window (ca. 20-





**Figure 1.** The evolution model of film SSC. Stage 1: (a) A DPDBS amorphous film is spin–coated on the surface of a clean silicon wafer with a 300 nm  $SiO_2$  dielectric layer; (b) The metastable crystal precursor forms from the film; Stage 2: (c) High-quality rod-like crystals forms; (d) Crystals grown by absorbing residual solid films; (e) The molecular structure of DPDBS. Red and blue structures are the semiconductor backbone and the functional groups, respectively; (f) The devices were fabricated by placing gold films on both ends of the crystals grown from the solid film.

60 °C). Moreover, the volume of two benzene rings is comparable to that of dibenzosilole, and weak  $\pi$ - $\pi$  interaction between benzenes can also promote the self-assembly. It is proved by both thermodynamics and kinetics that DBDPS has the capacity of SSC at room temperature and we summarize the film SSC model as follows.

#### 2.2. Two-Step Solid-State Crystallization Model

The evolutionary model of film SSC can be divided into two stages as shown in Figure 1. At the beginning, a solid film of the functional molecule DPDBS was spin-coated on a clean surface silicon wafer (Figure 1a). Thermally annealed at room temperature, metastable crystal precursors emerge at the nucleation sites (Figure 1b), which can be regarded as the mark of stage 1. For stage 2, the precursors were gradually developed into high–quality single crystals (Figures 1c). The crystals grow by grabbing functional molecules from the surrounding amorphous films and metastable precursors known as Ostwald Ripening (Figure 1d). Finally, an OSC single crystal device is fabricated by placing gold films at both ends of a single crystal as shown in Figure 1f.

#### 2.3. Thermodynamic Studies

The thermodynamic studies were conducted based on thermo gravimetric analysis (TGA) and DSC. It was found that in TGA the thermal decomposition temperature of DPDBS was above 200 °C (Figure S1), which guaranteed DPDBS a good stability at room temperature. The temperature range of DSC was set according to TGA, and the heating and cooling test were performed at a speed of  $10 \,^{\circ}$ C min<sup>-1</sup>. The results are shown in Figure 2a, and the temperature and enthalpy values of the thermodynamic transitions in the three heating and cooling cycles are summarized in Table 1. In general, the first cycle of



**Figure 2.** (a) DSC curves of three consecutive heating and cooling processes at a speed of 10 °C min<sup>-1</sup>. Inset shows a corresponding partially-enlarged DSC curves at the remperature range of the cold crystallization; (b) The temperature-related powder XRD based on DSC; (c) Index calculated powder XRD curve and the experimental powder XRD curves at 25 °C of the first and the second cycles; (d) Temperature-dependent evolutions for the average FWHM of the indexed 10 peaks in (c) in the second cycle. The red dashed line indicates the average FWHM value at 25 °C in the first cycle.

Table 1. Parameter summary of the phase transition in DSC.								
Cycle (n)	Heating Phase Transi- tion <sup>a)</sup>	T <sub>trans</sub> [°C]	Δ <i>H</i> [kJ mol <sup>-1</sup> ]	Cooling Phase Transi- tion <sup>a)</sup>	T <sub>trans</sub> [°C]	∆H [kJ mol <sup>-1</sup> ]		
1	Cr→IL	149.3	7.53	$IL{\rightarrow}Cr_{meta}$	68.5	-1.76		
2	$Cr_{meta} \rightarrow Cr$	58.7	-0.57					
	Cr→IL	149.0	9.53					
3	$Cr_{meta} \rightarrow Cr$	58.5	-2.77					
	Cr→IL	149.0	9.07					

" Cr: Stable crystal phase; IL: Isotropic liquid phase; Cr<sub>meta</sub>: Metastable polymorphic form which converts into the stable crystal phase.



DSC retains the stress during the processing. So, SSC analysis is based on the second and third heating and cooling cycles. In the second and third cycles, instead of the solidification peak in the cooling process, cold crystallization peaks appeared around 58.5 °C in the heating process. Their enthalpy values are -0.57 kJmol<sup>-1</sup> and -2.77 kJmol<sup>-1</sup>, which are much smaller than those of the melting peaks. The difference in enthalpy is caused by a similar range of the cold crystallization temperature and the room temperature window (ca. 20-60 °C), which leads to a slow crystallization at room temperature. Therefore, in addition to the exothermic peak during the heating process, another slow imperceptible exothermic process with a slow molecular self-assembly occurs during the entire cooling process and it will compensate for the difference in entropy. Moreover, the structural optimization happens at room temperature by SSC. In order to prove this point, powder XRD tests at different temperatures were carried out, as shown in Figure 2b. Firstly, a powder XRD of thermodynamic stable (long-time storage at room temperature) phase at 25 °C was conducted. Then it was tested at 25 °C again after melting at 180 °C, which produces the thermodynamic metastable phase without a long-time SSC (Figure 2b and 2c). It was found that there were diffraction patterns at both 25°C, but the intensities of the diffraction peaks decreased after melting compared to those before melting. It indicates that a certain degree of crystallization have been carried out, even no thermodynamic peaks were observed during the cooling process, and a further SSC was still in need to reach the initial thermodynamic stable phase. In order to find the SSC process, powder XRD was conducted from  $10\,^\circ\text{C}$  to  $85\,^\circ\text{C}$  in steps of  $10\,^\circ\text{C}.$  The average of their full widths at half maxima (FWHM) is a good parameter for describing degree of crystallization. The FWHM values were calculated by the program Jade according to the first ten peaks for their easy distinction. The 10 peaks below  $17^{\circ}$  were indexed as Figure 2c, and FWHM average statistics of the indexed peaks were calculated as shown in Figure 2d. It was found that the FWHM values decreased as the temperature increased from  $25^{\circ}$ C to  $85^{\circ}$ C, which means that the crystallinity is promoted by the cold crystallization in room temperature window. It is worth noting that the FWHM after the cold crystallization is  $0.1570^{\circ}$ , which is still bigger than  $0.1345^{\circ}$  obtained at room temperature before melting. It confirms the exsitence of a further SSC at room temperature.

#### 2.4. Kinetic Studies

Thermodynamic studies have demonstrated the capacity of the functional molecule DPDBS for SSC at room temperature. However, compared to the bulk materials in thermodynamic studies, the object of the kinetic study is two-dimensional solid film. In order to exclude the effect of residual solvent, the twodimensional solid film was directly subjected to X-ray photoelectron spectroscopy (XPS), electron ionization mass spectrum (EI-MS) and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) after spincoated with DPDBS solution in chloroform. As shown in Figure S2, S3 and S4, no chlorine signals prove that the film had no chloroform after spin-coated, so SSC is inherent to the material rather than effects of solvent doping. Moreover, the kinetic studies need to be based on crystallography. So single crystals were obtained by a solution method, and the crystal structures by XRD structure analysis are summarized in Figure S5 and Table S1. The film was subjected to a film XRD, immediately after spin-coated with the 5 mg mL<sup>-1</sup> DPDBS solution in chloroform. It was found that a diffraction peak appeared at 9.6° after about 40 min. As shown in Figure 3a, the



**Figure 3.** (a) Time evolution of film XRD patterns showing the transition of crystalline phases in a 5 mg mL<sup>-1</sup> DPDBS film sample at room temperature (25 °C). The peak at 9.6°, is indexed as (012). Colour scales from blue (low intensity) to red (high intensity). (b) Peak intensities extracted from the peaks of 9.6°, which can be divided into two stages (Stage 1: light red; Stage 2: purple); (c) and (d) are SEM images of films (5 mg mL<sup>-1</sup> solution spin-coating at 3000 rpm) annealed at room temperature (25 °C) for 6 h and 24 h, respectively; (e) The ideal crystal morphology calculated from the single crystal structure.



diffraction peak can be indexed as (012). Extracting the intensity of the diffraction peak (012) in Figure 3b, it was found that the entire process of SSC evolution can be divided into two stages according to the growth rate of the diffraction intensity: Stage 1 (0-6 h, red region) and Stage 2 (6-72 h, purple region). Scanning electron microscope (SEM) observations of the two stages were carried out. It was found that at the end of stage 1 (6 h, Figure 3c), on the surface of the substrate was mainly metastable crystal. At this time, metastable crystals as the crystal precursor of Stage 2 had a weak diffraction intensity, which had begun to form a crystal morphology, but the upper surface was undulating and the edges were rough. At 24 h (Figure 3d) crystal precursor had grown into prismatic crystals with high quality, which is in agreement with the ideal crystal morphology (Figure 3e) calculated from the single crystal structure. Therefore, it can be considered that the two stages of SSC are consistent with the model mentioned above: Stage 1: metastable crystal precursors form rapidly; Stage 2: metastable crystals finally grow into molecular crystals with a good morphology.

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Furthermore, *in-situ* time-dependent film self-growth kinetics based on polarized optical microscopy (POM) was conducted and presented in Figure 4. At the moment of 00:00, the field showed the amorphous spin-coated film with the front edge of the metastable crystal appearing at the bottom. The frontier spread upward at a rate of about 0.17  $\mu$ m min<sup>-1</sup>, which could be classified as Stage 1 of SSC (01:53). Then at 03:58, a nucleus appeared inside the metastable phase, where a well-structured crystal developed at the nucleus, and Stage 2 started. As time went (5:42, 7:59, 9:52), the frontier of the first-stage metastable phase gradually rose up to the top of the field of view, while SSC continued in the metastable phase as the number of nucleus in the second stage gradually increased, and the crystals with stronger diffraction intensity gradually grew

into bigger size and complete shape. On the other hand, wellformed crystals were formed at the sacrifice of the surrounding film and metastable crystal precursors. As shown in Figure S6, the growth of dendritic crystals absorbed molecules of surrounding films or metastable crystals as the material source, which lead to their shrink and disappearance known as Oswald Ripening. The experimental phenomenon was in great agreement with SSC model.

UV-Vis also confirmed the SSC properties of DPDBS. The film sample and the solution sample were simultaneously placed at room temperature for 72 h before UV-Vis tests. As shown in Figure S7a, the DPDBS solution started a spectral absorption at a wavelength of 338 nm and the band gap was calculated as 3.67 eV. But the solid sample, as shown in Figure S7b, exhibited spectral absorption all over the entire UV-Vis range, and maintained strong absorption close to the detection utmost. The reason why the solid film absorption curve goes out of shape may be that the spectral absorption moves toward the high field as the molecular arrangement goes denser by SSC. On the other hand, the formation of the crystals may increase the thickness of the film, so that the UV-Vis transmittance is further reduced. Furthermore, we performed a time-dependent UV-Vis of solid film and found it in complete agreement with the designed model and the other test results (Figure 5). In 0-6 h, the absorption was slightly enhanced as the DPDBS functional molecule underwent preliminary SSC from the initial disorder state to form a metastable crystal phase at stage 1. As molecules were arranged more closely, the vibration and rotation were gradually weakened, and the photoelectron transition ability was enhanced. The intensities of the two characteristic absorption bands (E<sub>2</sub> band at ca. 200 nm and B band at ca. 300 nm) of the aromatic compounds were gradually increased. The initial absorption position gradually moved toward the long wavelength field. After 6 h, Stage 2 started and



Figure 4. Time-dependent film self-growth kinetics based on POM. White arrows indicate the growing direction and the front edge of metastable crystal phase in Stage 1; Yellow arrows indicate the nuclei and the stable crystal growing in Stage 2.

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**Figure 5.** Time-dependent film self-growth kinetics conducted by UV-Vis at room temperature (25 °C). The white dashed line indicates the UV-Vis curve at 6 h.  $E_2$  band at ca. 200 nm and B band at ca. 300 nm are characteristic peaks of aromatic compounds and marked in the corresponding wavelength.

the functional molecules further crystallized, which made the intensities of the B band and the  $E_2$  band to grow even faster than those of Stage 1.

## 2.5. Electrical Performance of SSC Microwires

By SSC with high-concentration samples for over 72 h, we clearly observed the formation of single-crystal microwires with the length up to 0.5 mm from solid films as shown in the POM image (Figure 6a). The single-crystal microwires were further evaluated by SEM (Figure 6a inset) and atomic force microscope (AFM, Figure 6b and 6c), showing a width of ca.  $4 \,\mu m$  and a height of ca. 150 nm with straight and smooth edges and flat surface. The places that thickness changed were stepped. Figure 6d demonstrates a highly aligned microwire array of DPDBS after spontaneous growth in the glove box for a week. It offers possibility of further preparation for single crystal device arrays. We fabricated OFETs based on highly aligned microwires. Typical output and transfer characteristics for an OFET (channel length L: 16.7 µm and channel width W: 6.7 µm) are presented (Figure 6e and 6f). The obtained hole mobility is ca.  $0.15 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  with a high on/off ratio of ca.  $10^5$ . A statistical investigation based on over 30 individual devices revealed an average mobility of ca. 0.1  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ . Compared with the single crystal devices obtained by thermal annealing or solvent annealing, the performance of BPBDS OFET devices via SSC is not ideal. It may be due to the relatively poor performance of dibenzosilole as the semiconductor backbone compared to BTBT,<sup>[15]</sup> pentacene<sup>[16]</sup> and other common semiconductors with high performance. On the other hand, the semiconductor molecules in the single crystal structure do not achieve tight  $\pi$ - $\pi$  stacking (Figure S5), which also results in poor OFET performances. However, the successful design and synthesis of DPDBS semiconductor with SSC properties provide experimental experience for functional material synthesis methodology. The optimization of the material design deserves intensive further



**Figure 6.** (a) POM of a single crystal microwire. The inset shows SEM morphology; (b) AFM image showing the morphologies of a single crystal microwire; (c) Height profile of the single crystal at the white line in (b); (d) POM image of a single crystal array; (e) Output characteristics of a microwire single crystal OFET. Inset shows the POM of a single device. Scale bar: 50  $\mu$ m. Channel length *L*: 16.7  $\mu$ m and channel width *W*: 6.7  $\mu$ m. Gate voltage ( $V_{GS}$ ) ranged from 0 to -60 V in -10 V steps. (f) Transfer characteristics with the source-drain voltage ( $V_{DS}$ ) of -60 V.



studies to achieve OSC materials with the better performance in future.

## 3. Conclusion

In summary, this project designed and synthesized an organic semiconductor molecule DPDBS with the capacity of SSC at room temperature as the target. Through thermodynamic studies based on DSC and kinetic studies based on *in-situ* XRD, POM and UV-Vis, it confirmed the material with designed properties, and validated the two-step solid film crystallization model proposed in the work. It provides an experimental basis to expansion of non-classical crystallization system. The OFET electronics were constructed with the products of SSC. Next, we will continue to optimize the SSC molecular structure to obtain OSC materials with superior performance.

[CCDC 1949203 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.]

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# Conflict of Interest

The authors declare no conflict of interest.

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- [1] Y. Diao, L. Shaw, Z. Bao, S. C. B. Mannsfeld, Energy Environ. Sci. 2014, 7, 2145.
- [2] Y. Wen, Y. Liu, Y. Guo, G. Yu, W. Hu, Chem. Rev. 2011, 111, 3358.
- [3] J. E. Koskela, V. Liljeström, J. Lim, E. E. Simanek, R. H. A. Ras, A. Priimagi, M. A. Kostiainen, J. Am. Chem. Soc. 2014, 136, 6850.
- [4] H. Nakano, T. Takahashi, T. Kadota, Y. Shirota, Adv. Mater. 2002, 14, 1157.
- [5] E. Uchida, R. Azumi, Y. Norikane, Nat. Commun. 2015, 6, 7310.
- [6] G. Liu, J. Liu, H. Sun, X. Zheng, Y. Liu, X. Li, H. Qi, X. Bai, K. A. Jackson, X. Tao, J. Am. Chem. Soc. 2015, 137, 4972.
- [7] H. Chen, M. Li, Z. Lu, X. Wang, J. Yang, Z. Wang, F. Zhang, C. Gu, W. Zhang, Y. Sun, J. Sun, W. Zhu, X. Guo, *Nat. Commun.* **2019**, *10*, 3872.
- [8] A. Rao, H. Cölfen, Chem. Rec. 2018, 18, 1203.
- [9] J. J. De Yoreo, P. U. P. A. Gilbert, N. A. J. M. Sommerdijk, R. L. Penn, S. Whitelam, D. Joester, H. Zhang, J. D. Rimer, A. Navrotsky, J. F. Banfield, A. F. Wallace, F. M. Michel, F. C. Meldrum, H. Cölfen, P. M. Dove, *Science* 2015, 349, aaa6760.
- [10] J. Chung, I. Granja, M. G. Taylor, G. Mpourmpakis, J. R. Asplin, J. D. Rimer, *Nature* 2016, 536, 446.
- [11] E. C. P. Smits, S. G. J. Mathijssen, P. A. van Hal, S. Setayesh, T. C. T. Geuns, K. A. H. A. Mutsaers, E. Cantatore, H. J. Wondergem, O. Werzer, R. Resel, M. Kemerink, S. Kirchmeyer, A. M. Muzafarov, S. A. Ponomarenko, B. de Boer, P. W. M. Blom, D. M. de Leeuw, *Nature* **2008**, *455*, 956.
- [12] W. W. H. Wong, J. F. Hooper, A. B. Holmes, Aust. J. Chem. 2009, 62, 393.
- [13] H. Li, Z. Wang, C. Song, Y. Wang, Z. Lin, J. Xiao, R. Chen, C. Zheng, W. Huang, *J. Mater. Chem. C* **2014**, *2*, 6946.
- [14] J. Yin, R. F. Chen, S. L. Zhang, H. H. Li, G. W. Zhang, X. M. Feng, Q. D. Ling, W. Huang, J. Phys. Chem. C 2011, 115, 14778.
- [15] H. Chen, N. Cheng, W. Ma, M. Li, S. Hu, L. Gu, S. Meng, X. Guo, *ACS Nano* **2016**, *10*, 436.
- [16] C. Liu, T. Minari, X. Lu, A. Kumatani, K. Takimiya, K. Tsukagoshi, Adv. Mater. 2011, 23, 523.

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