

Space-Confined Strategy toward Large-Area Two-Dimensional Single Crystals of Molecular Materials

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S Supporting Information

ABSTRACT: Two-dimensional molecular crystals (2DMCs) are a promising candidate for flexible and large-area electronics. Their large-area production requires both low nuclei density and 2D crystal growth mode. As an emerging type of material, their large-area production remains a case-by-case practice. Here we present a general, efficient strategy for large-area 2DMCs. The method grows crystals on water surface to minimize the density of nuclei. By controlling the interfacial tension of the water/solution system with a phase transfer surfactant, the spreading area of the solvent increases tens of times, leading to the space-confined 2D growth of molecular crystals. As-grown sub-centimeter-sized 2DMCs floating on the water surface can be easily transferred to arbitrary substrates for device applications.

The 2D molecular crystals (2DMCs) are thin layers of periodically arranged organic molecules held together by weak interactions (i.e., hydrogen bonds, van der Waals interactions) in the 2D plane. They are attracting more and more attention in recent years due to their unique advantages compared with their inorganic counterparts (such as graphene and transition-metal dichalcogenides).¹ The building blocks, i.e., the organic molecules, can be tailor-made by synthesis with designed structures and desired properties.² Moreover, many organic molecules are soluble and solution process, such as printing, can be used for large-area low-cost production.³ As an emerging type of new material, 2DMCs are of critical importance for both fundamental studies and optoelectronic applications.⁴

In contrast to 1D molecular crystals (e.g., nanowires and nanoribbons) whose growth techniques and mechanisms have been well established,⁵ syntheses of 2DMCs have largely remained a case-by-case practice. Although molecular beam epitaxy (MBE) in a high vacuum or ultrahigh vacuum can be used to produce 2DMC,⁶ the high cost and the inability to transfer the crystal to target substrates pose myriad challenges for the fabrication of devices. It was not until recent years that several methods were developed for large-area 2DMCs. For example, Jiang et al. tried the solution casting method and millimeter-sized 2DMC of 1,4-bis((5'-hexyl-2,2'bithiophen-5-yl)ethynyl)benzene (HTEB) was obtained. The key was the unique structure of the molecule.⁷ He et al. reported the vapor phase epitaxial growth of dioctylbenzothienobenzothiophene

(C8-BTBT) with size up to 80 μm on graphene and hexagonal boron nitride (h-BN) substrates.⁸ Recently, Xu et al. demonstrated the growth of 2DMCs on water surface by "solution epitaxy".⁹ This method requires the epitaxial growth of crystals and thus good spreading of the solvent on water surface is a prerequisite.

Herein, we report the space-confined self-assembly (SCS) method for the simple yet effective production of sub-centimeter-sized free-standing 2DMCs (Figure 1). The SCS

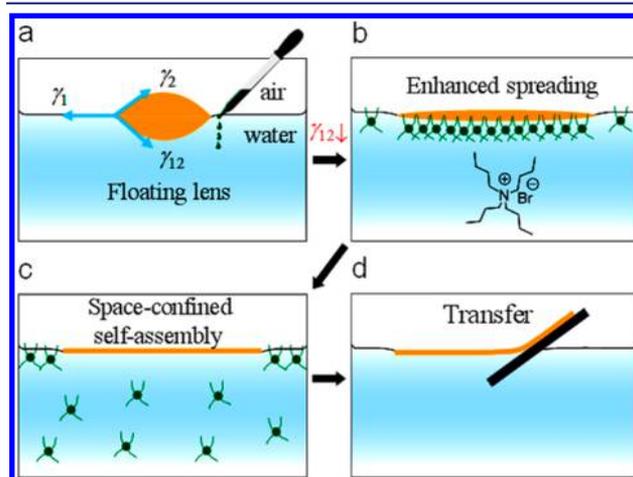


Figure 1. Sketches of the SCS method for the growth and transfer of 2DMC. (a) A floating lens was formed when a droplet of solution was placed on the surface of DI water. (b) Enhanced spreading with surfactant in the DI water. (c) 2D crystallization resulted in the growth of 2DMC. (d) Transfer of the 2DMC to target substrate.

method was designed to optimize the two key stages of crystallization for 2DMC: (i) minimized density of nuclei by using deionized water (DI water) as the liquid substrate^{9,10} and (ii) space-confined 2D crystal growth mode by enhanced spreading of the solution on water surface. The interfacial tension of the water/solution system was controlled with a phase transfer surfactant and the spreading area of the solvent was greatly increased, leading to the desired space-confined 2D growth mode for 2DMCs. Due to the controllable spreading of the solvent, the SCS method are universally applicable for water-immiscible organic solvents, including those with a

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density higher than water. (They cannot spread a large area on water surface and are postulated to be unsuitable for the growth of crystals on water surface.¹¹ One example is chlorobenzene, which we will use to show that the SCS method are general.)

When a droplet of water-immiscible organic solvent is gently placed on water surface, the wetting behavior is determined by the spreading coefficient^{11b}

$$S = \gamma_1 - \gamma_2 - \gamma_{12} \quad (1)$$

where γ_1 , γ_2 and γ_{12} are the surface tension of water, solution and water/solution interface. If S is positive, wetting is total and the solvent spreads completely. If S is negative, wetting is partial. The latter case was observed for most water-immiscible organic solvents. In the case of partial wetting, a compact floating lens will form (Figure 1a), where disordered crystal domains are likely to appear, resulting in the 3D growth of numerous crystallites. Clearly, the formation of a compact lens is unfavorable for large-area 2DMCs and the spreading should be increased to confine the crystal growth within 2D.

As for a certain organic molecule dissolved in a solvent, γ_2 is fixed. According to eq 1, an increased spreading requires either an increased value of γ_1 and/or a decreased value of γ_{12} . The value of γ_1 is difficult to increase sustainably,¹² thus we focus on the reduction of γ_{12} . Surfactants have been widely used to change the surface and interfacial tension of solutions. To reduce γ_{12} effectively, the proper surfactant should concentrate more at water/solution interface than water surface. Typical surfactants such as sodium dodecyl sulfate (SDS) and hexadecyl trimethylammonium bromide (CTAB) adsorb at water surface and reduce γ_1 effectively.¹³ According to eq 1, S will become more negative and the lens will contract, which is unfavorable for 2D crystal growth (Figure S1). We turn our attention to phase transfer (PT) catalysts such as tetrabutyl ammonium bromide (TBAB). TBAB contains branched lipophilic butyl groups, which makes the compound soluble in organic solvent. It is also a polar ammonium salt, which makes the compound soluble in water as well. As a result, TBAB becomes one of the most commonly used PT catalysts, being employed in numerous bond forming, halogenation and oxidation reactions performed under liquid-liquid phase-transfer catalysis (PTC) conditions.¹⁴

Indeed, an enhanced spreading was observed when TBAB was used. It can be deduced that TBAB concentrates more at the water/solution interface and thus decreases γ_{12} effectively. The spreading property of perylene solution at water surface with different concentration of TBAB is shown in Figure 2a–d. (50 μ L of chlorobenzene solution with a perylene concentration of 0.5 mg/mL. Perylene is colored, so it is easy to check the spreading behavior.) The spreading area increased prominently as the concentration of TBAB increased from 0 to 10 mg/mL, with a maximal increment of 22 times compared with that on DI water. When the concentration of TBAB reached 15 mg/mL, the solution began to shrink, which was ascribed to the possibility that TBAB saturated at the water/solution interface and began to accumulate on water surface, causing the decrease of γ_1 and thus the shrink of the solution (Figure 2d).

After the evaporation of the solvent, thin crystals appeared on the water surface. Figure 3a,b shows typical photographs of free-standing 2DMCs floating on pure DI water and DI water with a TBAB concentration of 10 mg/mL, respectively. There were tens of small crystals on pure DI water with areas <1 mm². In sharp contrast, the SCS method produced only one large

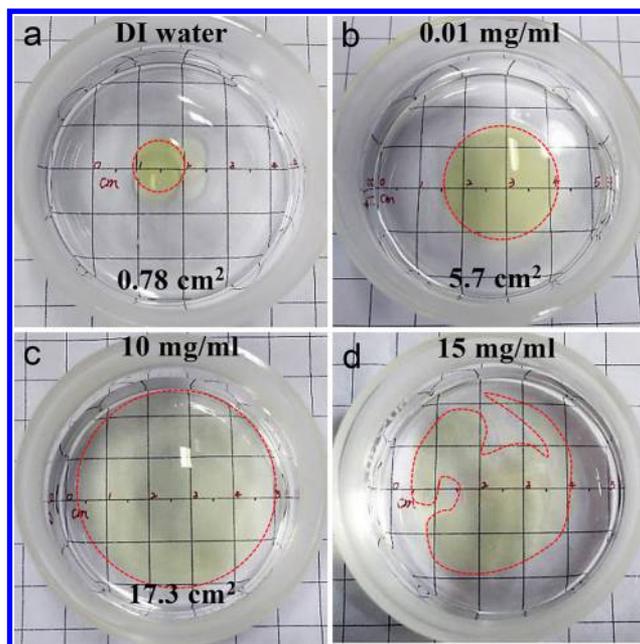


Figure 2. Photographs showing the change of spreading area when TBAB was added. The concentration of TBAB was shown on top and the corresponding spreading area on the bottom (except panel d).

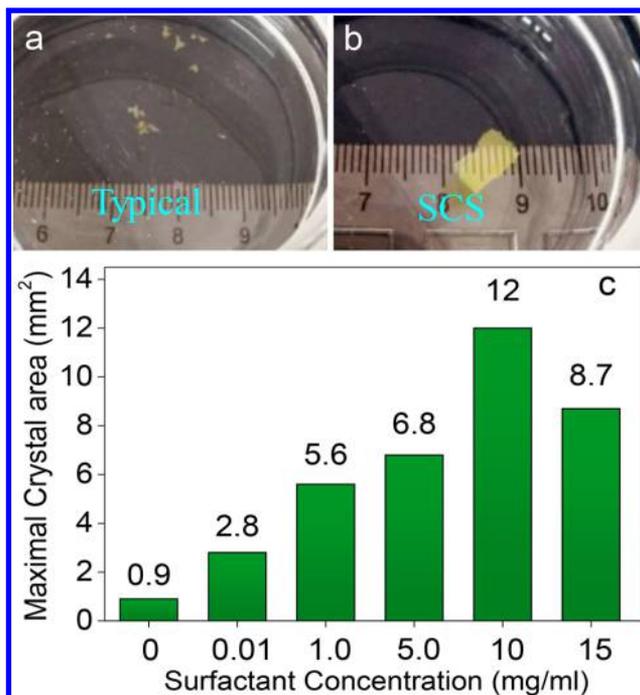


Figure 3. Photographs of crystals grown by the typical (a) and by the SCS (b) method, respectively. (c) Maximal crystal area as a function of the concentration of the surfactant.

crystal with an area of ~ 40 mm², which was 40 times larger than crystals produced by the typical method.¹⁵ The crystals floating on water surface can be transferred to target substrates easily by dipping the target substrate into the water and fishing the crystals from below.¹⁶ The maximal crystal area counted for a typical growth and transfer (on SiO₂/Si wafer) showed prominent increase when the TBAB concentration varied from 0 to 10 mg/mL, reaching 12 mm² at an optimal TBAB concentration of 10 mg/mL (Figure 3c). Judging from Figure

3c, an optimal TBAB concentration was 10 mg/mL, which coincided with the optimal TBAB concentration for maximal spreading area (Figure 2c). On the basis of the above results, we deduced that an improved spreading area resulted in the self-assembly of larger 2DMCs, proving the effectiveness of the SCS method (the SCS method hereafter means DI water with TBAB concentration of 10 mg/mL).

Polarized optical microscopy (POM) images were taken to check the structure of the crystals produced by the SCS method (Figure 4a,b, e,f and i,j). Three archetype organic semi-

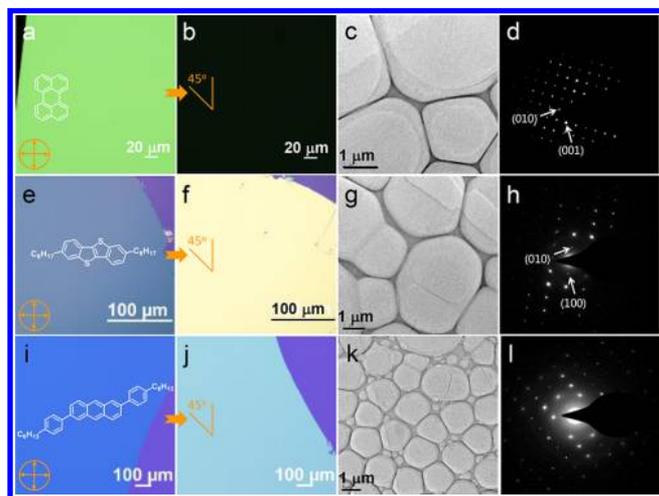


Figure 4. (a,b), (e,f), (i,j) POM images of 2DMCs of three archetype organic semiconductors. The inset showed the chemical structure of the semiconductors. (c,d), (g,h), (k,l) TEM and the corresponding SAED patterns of the 2DMCs.

conductors were used, i.e., Perylene, C8-BTBT and C6-DPA, whose structures are given in the inset of Figure 4a,e,i, respectively. These crystals showed smooth surfaces with sharp edges. The color of the entire film changed simultaneously from bright to dark when rotating the substrate along an axis perpendicular to the substrate, indicating the absence of any grain boundaries in the film, i.e., the whole film checked was a single crystal. The thickness of the 2DMCs can be tuned from several nanometers (i.e., several molecular layers) to several hundred of nanometers, depending on the concentration of the solution (Figure S2). X-ray diffraction (XRD, Figure S3) of all 2DMCs exhibited sharp diffraction peaks, indicating the high-quality of the 2DMCs. More importantly, all crystals produced by both methods showed identical diffraction peaks, indicating that these crystals shared the same structure. It was clear that the TBAB molecule was not incorporated into the crystal lattice. Bright-field transmission electron microscopy (TEM) images of randomly selected 2DMCs on copper grid are shown in Figure 4c,g,k. All 2DMCs were uniform in contrast. Selected-area electron diffraction (SAED) data on different positions of each 2DMC exhibited the same set of diffraction spots, confirming the single crystalline nature of the 2DMCs (Figure 4d,h,l).

The charge transport properties of the 2DMCs grown by both methods were probed by organic field-effect transistors (OFETs). A top-contact (Au source and drain electrodes) bottom-gate configuration was adopted (Figure 5a). Figure 5b shows a device array based on a sub-centimeter-sized 2DMC grown by the SCS method. All devices exhibited high mobility with well-defined linear and saturation regimes at ambient

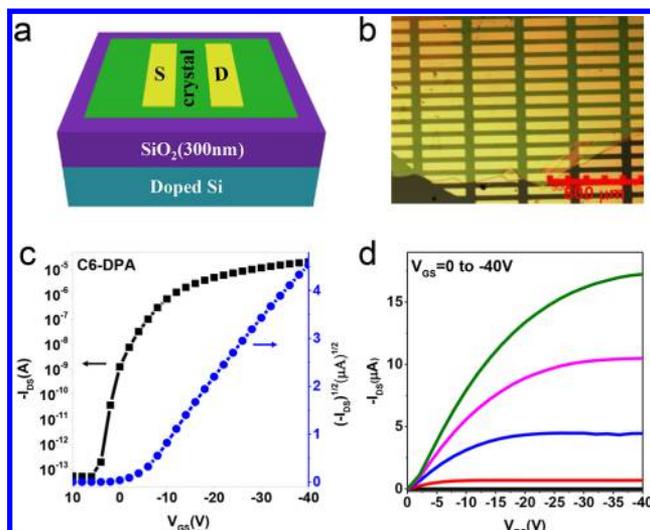


Figure 5. (a) Sketch of the structure of the OFET. (b) Optical microscope image of one OFET array based on a piece of 2DMC. (c,d) Typical transfer and output curves of the OFETs based on 2DMCs grown by the SCS method.

conditions and little mobility differences were found between crystals grown by the typical and the SCS method (Figure S4). Take C6-DPA as an example, the highest mobility (average mobility over 20 devices) for 2DMCs produced by both the typical and the SCS method was 1.44 (0.98) and 1.41 (0.99) $\text{cm}^2/(\text{V s})$, respectively. The high-mobility indicated the potential application of as-prepared 2DMCs in high-performance optoelectronic devices.

In conclusion, a simple yet effective method, i.e., the SCS method, was developed to grow large-area free-standing 2DMCs. By controlling the surface and the interfacial tension of the air/water/solution system with a phase transfer surfactant, space-confined 2D crystallization were realized and sub-centimeter-sized 2DMCs were produced on water surface. As-grown free-standing 2DMCs could be easily transferred to arbitrary target substrates. OFETs based on the 2DMCs showed high performance, confirming the high-quality nature of the 2DMCs. Bearing in mind the structural versatility of organic semiconductors, the one-step production of large-area free-standing 2DMCs combined with the easy transfer may open up a new field of organic van der Waals heterostructures or even organic superlattices for both fundamental studies and optoelectronic applications.¹⁷

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b01997.

Experimental methods, spreading behaviors using SDS and CTAB as the surfactants, AFM images and section analysis of the 2DMCs, XRD, statistical mobilities and average mobilities of the 2DMCs (PDF)

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Notes

The authors declare no competing financial interest.

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