Organic Semiconductors

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A General Method for Growing Two-Dimensional Crystals of Organic Semiconductors by "Solution-Epitaxy"

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Dedicated to the 60th anniversary of Institute of Chemistry, Chinese Academy of Sciences

Abstract: *Two-dimensional (2D) crystals of organic semiconductors (2DCOS) have attracted attention for large-area and low-cost flexible optoelectronics. However, growing large 2DCOS in controllable ways and transferring them onto technologically important substrates, remain key challenges. Herein we report a facile, general, and effective method to grow 2DCOS up to centimeter size which can be transferred to any substrate efficiently. The method named "solution-epitaxy" involves two steps. The first is to self-assemble micrometer-sized 2DCOS on water surface. The second is epitaxial growth of them into millimeter or centimeter sized 2DCOS with thickness of several molecular layers. The general applicability of this method for the growth of 2DCOS is demonstrated by nine organic semiconductors with different molecular structures. Organic field-effect transistors (OFETs) based on the 2DCOS demonstrated high performance, confirming the high quality of the 2DCOS.*

2D crystals are promising functional materials for next-generation electronics due to their long range order on the macroscopic scale in spite of being only a few atomic/molecular layers thick.[1–3] Graphene is the foremost 2D crystal,[4–6] and transition-metal dichalcogenides (MX_2, M = Mo, W; X = S, Se, Te, etc.),[7–9] and black phosphorus[10,11] are considered to be good alternatives with band gaps, for structural analogues of graphene. Two-dimensional crystals of organic semiconductors (2DCOS) have demonstrated unique advantages of 1) ideal band gaps and specific functions (electronic, optical, or magnetic) by molecular design,[12] 2) excellent flexibility, 3) solution processability,[13a,b] providing versatile routes, such as inkjet printing[13c] and solution-shearing[14] techniques, for large-area, low-cost electronics. However, over the past decade, research on 2DCOS is seriously hampered by the lack of understanding of, and absence of the corresponding technologies for, controllable crystal growth. By careful molecular design, Jiang et al. cast-assembled 2DCOS of 1,4-bis((5'-hexyl-2,2'-bithiophen-5-yl)ethynyl)benzene (HTEB) with length and width of hundreds micrometers and demonstrated that the charge transport in organic field-effect transistors (OFETs) could occur in single molecular layer near the gate insulator.[15] Zhang et al. grew fullerene 2DCOS with a lateral size of several micrometers,[16] and He et al. grew few-layer 2DCOS of dioctylbenzothienobenzothiophene (C8-BTBT) by van der Waals epitaxy up to 80 micrometers.[17] These results demonstrated the promising opportunity of preparing 2DCOS.[18] Herein, we report a novel approach of "solution epitaxy" to grow 2DCOS on water surface, wherein water surface acts as a molecularly flat and defect-free substrate.

Our method for growth of 2DCOS is depicted in Figure 1. Dozens of microliters of solution of molecular materials are dropped onto water surface (Figure 1 a), which then spread quickly over the whole water surface through surface tension (Figure 1 b). Then, the molecules of organic semiconductors begin to aggregate (Figure 1 c) through strong π–π molecular interactions, and evolve into micrometer-sized 2DCOS (Figure 1 d). Using the micrometer-sized 2DCOS as seed crystals, dropping new solution on them (Figure 1 e), causes epitaxial growth of the small 2DCOS, finally 2DCOS with sizes a millimeter or even over a centimeter are obtained (Figure 1 f). For better control of the crystal growth, it is crucial to choose a solvent and a solution concentration for this "solution-epitaxy" that avoids polycrystalline growth. Molecules capable of engaging in multi-molecular interactions, such as π–π, hydrogen bond, C–H–π or C–S bonds are also important.[19]

Figure 2 display images of optical, transmission electron microscopy (TEM), and selected-area diffraction pattern (SAED) of 2DCOS assembled through this method. The perylene 2DCOS up to several hundreds of micrometers are available as shown in Figure 2 a. The straight baseline and the sharp diffraction peaks in X-ray diffraction (XRD) pattern demonstrate the high quality of the 2DCOS (Figure S1 in the Supporting Information). The corresponding secondary diffraction peaks are also observed, manifesting the layer-by-

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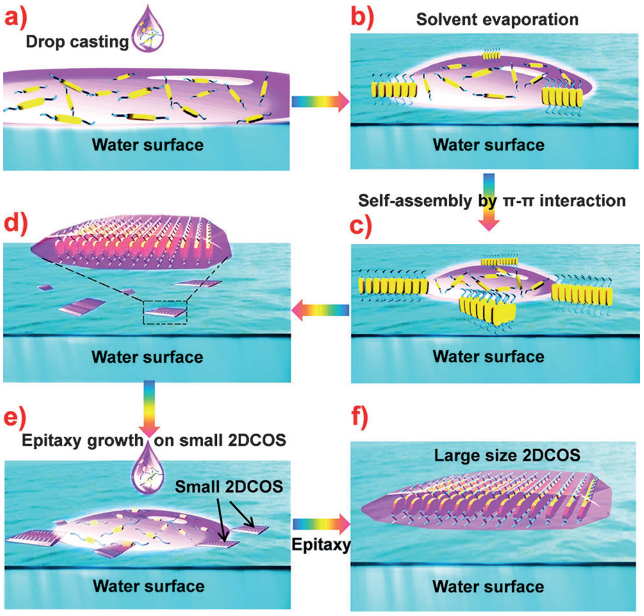

Figure 1. Schematic diagrams of growing 2DCOS, a) Dropping solution onto water surface, b) solvent evaporation resulting in molecular aggregation, c) molecular assembly by π–π interaction, d) self-assembled small 2DCOS on water surface, e) epitaxy growth based on small 2DCOS, f) large 2DCOS on water surface.

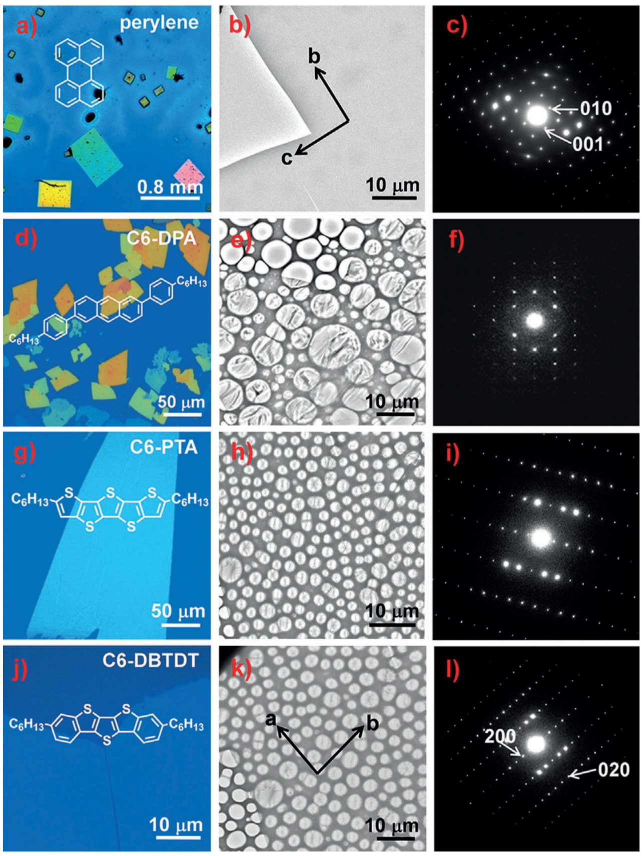

Figure 2. Characterization of micrometer sized 2DCOS. Optical microscopy images (left), TEM images (middle), SAED patterns (right) of 2DCOS of a)–c) perylene, d)–f) C6-DPA, g)–i) C6-PTA, and j)–l) C6-DBTDT.

layer growth of organic semiconducting molecules on substrate. The quality of the 2DCOS can be further evaluated by the full-width-at-half-maximum (FWHM) of the rocking curve (Figure S2). The narrow width testifies highly ordered alignment of planes in the out of-plane direction. The rocking curves at $2\theta = 8.79°$ shows FWHM at 0.029°, which is comparable with the values of dinaphtho[2,3-b:2′,3′-f]thieno-[3,2-b]thiophene (DNTT) crystals grown by physical vapor transport.[20] A bright-field TEM image of a randomly selected perylene 2DCOS on copper grid is shown in Figure 2b and its corresponding SAED is shown in Figure 2c. Typical TEM images of 2DCOS show uniform morphology. SAED at different parts show identical diffraction patterns (Figure S3), confirming the single crystalline nature of the 2DCOS. Lattice constants calculated from SAED patterns is $b = 10.7$ Å, $c = 11.5$ Å, which is consistent with that of the bulk crystal.[21] Interestingly, it is found that this method is wide applicable for assembling 2DCOS of other organic semiconductors, for example, C6-DPA (Figure 2d–f), C6-PTA (Figure 2g–i), and C6-DBTDT (Figure 2j–l), and very nice 2DCOS are obtained with smooth surfaces over tens of micrometers (as well as other compounds Figure S4,5) demonstrating the general applicability for 2DCOS growth. Powder XRD of the 2DCOS show intense peaks, for example, C6-DBTDT at $2\theta = 3.38°$, which correspond to d-spacing of 26.4 Å (Figure S6). Lattice constants calculated from SAED pattern (e.g., C6-DBTDT, $a = 4.1$ Å, $b = 10.9$ Å) are consistent with the data of bulk crystal[22] (Figure 2l). All of the diffraction patterns of SAED at different sites find no signs of noticeable polycrystalline diffraction and apparent angle rotation of the lattice direction throughout the entire domain (Figure S7). The results confirm that the thin film is a single crystal. C6-DBTDT adopts a herringbone packing motif with π–π overlap between adjacent molecules[23] (Figure S8). The π–π stacking distance is 3.545 Å. Moreover, short S–S contacts (3.530 and 3.793 Å) and S–C contacts (3.427 Å) exist in another direction and form a 2D network of intermolecular force. The strong 2D interactions may be the main driving force to grow large-area 2DCOS[24] and realize high-performance devices.[23] Atomic force microscopy (AFM) images show that the 2DCOS generally have a thickness of 3–5 nm (Figure S9). For example, the thickness of C6-DPA 2DCOS is 4.53 nm, C6-DBTDT is 5.01 nm, and PDIF-CN_2 is 4.91 nm. Considering the molecular length of C6-DPA at 29.8 Å, and that the molecules stand on a substrate, it suggests and 2–3 molecular layer 2DCOS for C6-DPA, C6-DBTDT, and PDIF-CN_2.

Epitaxy is a powerful method to grow high-order structures on crystal surfaces with accurate lattice matching. Seed-crystal-mediated-growth reportedly works effectively both for organic crystals, for example, the growth of copper phthalocyanine nanoribbon crystals) and graphene materials.[25,26] Pleasingly, we found that the small-size 2DCOS obtained on the water surface could be used as seed-crystals for new cycles of crystal growth by dropping the same organic solution on the small-size 2DCOS on the water surface (Figure 1e). As soon as the new solution is added, the small 2DCOS is etched a little by the new solution. Subsequent epitaxial growth from the small 2DCOS, gives large 2DCOS

(Figure 1 f). Indeed, such "solution-epitaxy" works effectively, over mm sized C6-DBTDT 2DCOS are obtained (Figure 3 a) as well as of C6-DPA and C6-PTA (Figure S10). Cross-polarized optical micrographs of individual C6-DBTDT 2DCOS were obtained. The uniform light extinction over 7 mm in the cross-polarized optical micrographs indicates the single-crystalline nature of the C6-DBTDT 2DCOS (Figure 3 b–c). The thickness of C6-DBTDT 2DCOS is 14.13 nm, suggesting the 2DCOS are 5–6 molecular layers (Figure 3 d). SAED of individual C6-DBTDT 2DCOS at different parts show identical diffraction patterns (Figure 3 e–i). It confirms that the single crystalline nature of the large-size 2DCOS.

2DCOS of perylene are obtained with size even near 1 cm (Figure 3 j). XRD results of the large 2DCOS and SAED of individual 2DCOS at different parts show identical diffraction patterns as identical as that of micrometer sized crystals (inset of Figure 3 j). All features of the large size 2DCOS are identical as those of small size 2DCOS, confirmed the high quality of the cm size 2DCOS. Finally, it should be addressed that a pre-requirement to apply the 2DCOS in electronic devices is to transfer them to solid substrates efficiently. Our 2DCOS can be easily transferred to any substrate due to their facile growth process (Figure S11). A substrate is inserted at an angle into the water just below the water surface. With water evaporation, the 2DCOS will fall on substrate automatically, and deposit the 2DCOS tightly and smoothly on substrate.

The quality and potential application of the 2DCOS are examined by organic field-effect transistors (OFETs). Bottom-gate top-contact device configuration based on individual 2DCOS is adopted. Au stripes are stamped on 2DCOS as source and drain electrodes[27] and OTS-modified Si/SiO_2 (300 nm) is used as substrate (Figure S12). The carrier mobility is extracted from their saturated region characteristics by the equation of $I_{DS} = (W/2L)C_i\mu(V_G - V_T)^2$. All devices exhibit high performance with well-defined linear and saturation regimes at ambient conditions and room temperature (Figure 4, Figure S13,S14). For example, perylene OFETs possess an average mobility of 0.12 $cm^2V^{-1}s^{-1}$ and the highest mobility up to 0.18 $cm^2V^{-1}s^{-1}$ (Figure 4 a,b), among the best results of perylene based OFETs.[28] Similarly, the averaged mobility of C6-DPA reach 2.4 $cm^2V^{-1}s^{-1}$, and the maximum value is as high as 4.0 $cm^2V^{-1}s^{-1}$ (Figure 4 c,d),

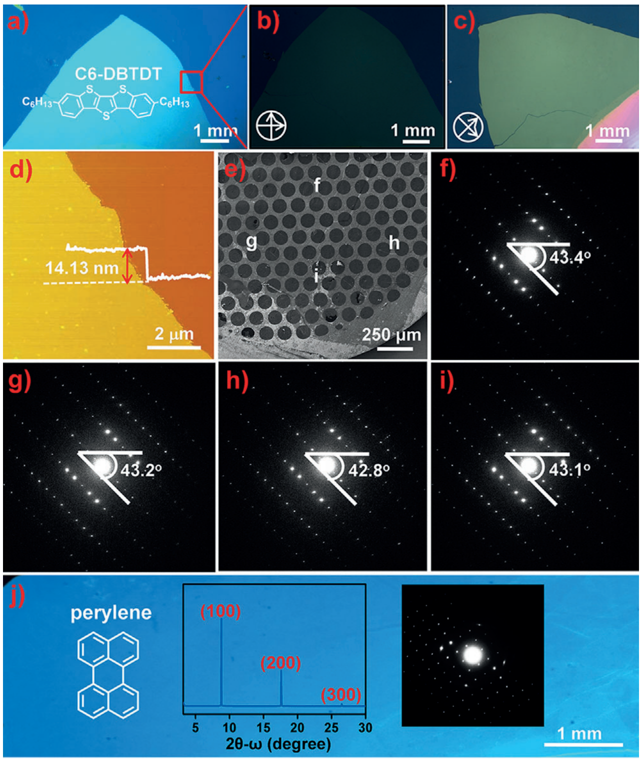

Figure 3. Characterization of mm and cm sized 2DCOS. a) Optical microscopy image of several mm sized 2DCOS of C6-DBTDT, b),c) Cross-polarized optical micrographs of the C6-DBTDT 2DCOS, and the uniform color change over the entire micrographs confirms that the 2DCOS is a single crystal, d) AFM image, indicating the thickness of 2DCOS at 14.13 nm, 5–6 molecular layers. e) SEM and f)–i) SAED of individual C6-DBTDT 2DCOS, the identical SAEDs at different parts of the 2DCOS in (e) confirming its single crystal nature, j) Optical microscopy image of cm sized 2DCOS (blue) of perylene, inset: XRD and SAED of the crystal.

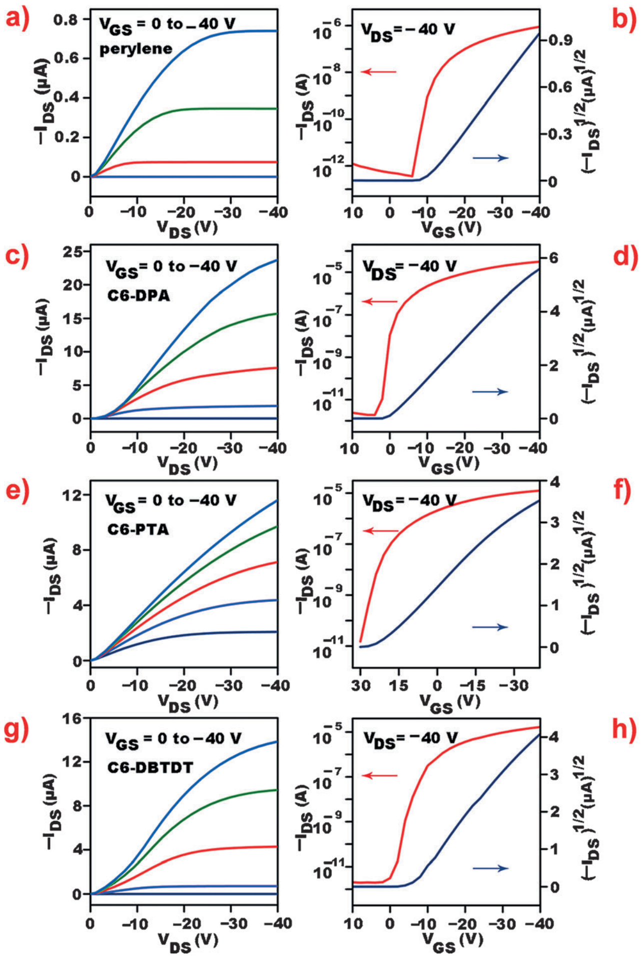

Figure 4. Transistor characteristics of the 2DCOS. Typical transfer and output characteristics of the OFETs based on the 2DCOS, a),b) perylene, c),d) C6-DPA, e),f) C6-PTA, g),h) C6-DBTDT on OTS SAM modified Si/SiO_2 substrates. The different colored lines in (a) (c) (e),and (g) correspond to the different gate voltages.

which is 7 times higher than that of C6-DPA polycrystalline films (Figure S15). OFETs of C6-PTA 2DCOS exhibit averaged mobility of $0.63\ cm^2V^{-1}s^{-1}$, and the maximum value is as high as $1.3\ cm^2V^{-1}s^{-1}$ (Figure 4e,f), which is about 28 times higher than that of PTA thin films ($0.045\ cm^2V^{-1}s^{-1}$).[29] The averaged mobility of C6-DBTDT devices is around $1.6\ cm^2V^{-1}s^{-1}$, with the maximum value as high as $2.8\ cm^2V^{-1}s^{-1}$ (Figure 4g,h). Moreover, minor hysteresis and bias stress effects are observed in these devices (e.g., Figure S16), indicating the negligible charge traps between the 2DCOS and gate dielectric. The summary of all device performance is given in Table 1,[30] demonstrating the high performances of the devices and high quality of the 2DCOS.

Table 1: Transistor performance of different kind 2DCOS.[a]

Materials	μ_{ave} ($cm^2V^{-1}s^{-1}$)	μ_{max} ($cm^2V^{-1}s^{-1}$)	On/off ratio	V_T[V]
C8-BTBT	6.9[2.6]	11.2	9×10^6–5×10^7	−1.7–−8.9
C6-DPA	2.4[0.92]	4.0	4×10^6–8×10^7	−0.2–−1.5
C6-DBTDT	1.6[0.64]	2.8	3×10^6–1×10^7	−3.3–−14.7
C6-PTA	0.63[0.33]	1.3	2×10^5–1×10^6	16–23
perylene	0.12[0.04]	0.18	3×10^5–1×10^6	−3.3–−17.4
DH6T	0.011[0.0013]	0.012	1×10^4–2×10^5	−0.4–−9.8
Ph-Ant	0.45[0.14]	0.62	9×10^5–7×10^6	−5.4–−14.9
PFIF-CN_2	0.03[0.012]	0.04	1×10^5–9×10^5	3.9–15
DFH4T	8.5×10^5 [$2.7\times10^{--15}$]	1.2×10^{-4}	1×10^3–5×10^3	2.3–7.6

[a] The mobilities are estimated from the saturation regime. The average mobilities are calculated using data from 5–8 devices. The standard deviation of the mobilities is given in square brackets.

In summary, we develop a facile and low cost method to grow uniform, large-area and high quality 2DCOS. By "solution-epitaxy" growth crystal on water surface, 2DCOS with size of centimeter size are obtained with thickness of molecular layers. The general applicability of this novel method for 2DCOS growth has been demonstrated by nine organic semiconductors with different molecular configurations. The as-grown 2DCOS can be transferred to any substrate facilely by inserting substrate at an angle into the water. OFETs based on the 2DCOS exhibit high performance, confirming the high quality and potential application of the 2DCOS. Our methodology provides a convenient route to assemble large scale and high quality 2DCOS with novel structure and function for their applications in flexible- and opto-electronics.

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Keywords: 2D materials · organic crystals · organic electronics · organic field-effect transistors · self-assembly

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Communications

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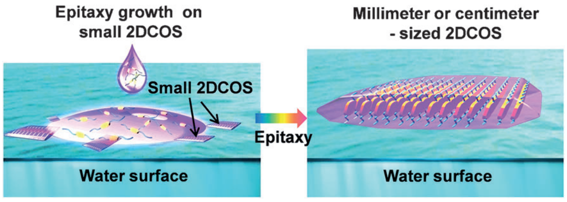
A General Method for Growing Two-Dimensional Crystals of Organic Semiconductors by "Solution-Epitaxy"



Water of crystallization: A novel method named "solution epitaxy" for the growth of 2D crystals of organic semiconductors (2DCOS) is based on the self-assemble micrometer-sized 2DCOS on water surface, and then epitaxial growth of them into centimeter sized 2DCOS with thickness of several molecular layers.

