

Supporting Information

Polymorphic Self-Assemblies of 2,7-Bis(decyloxy)-9-Fluorenone at the Solid/Gas Interface: Role of C–H···O=C Hydrogen Bond

*Kai Miao, Yi Hu, Bao Zha, Li Xu, Meiqiu Dong, Xinrui Miao, * Wenli Deng**

College of Materials Science and Engineering, South China University of Technology,

Guangzhou 510640, China

*Tel.: 020-22236708. E-mail: msxrmiao@scut.edu.cn, wldeng@scut.edu.cn

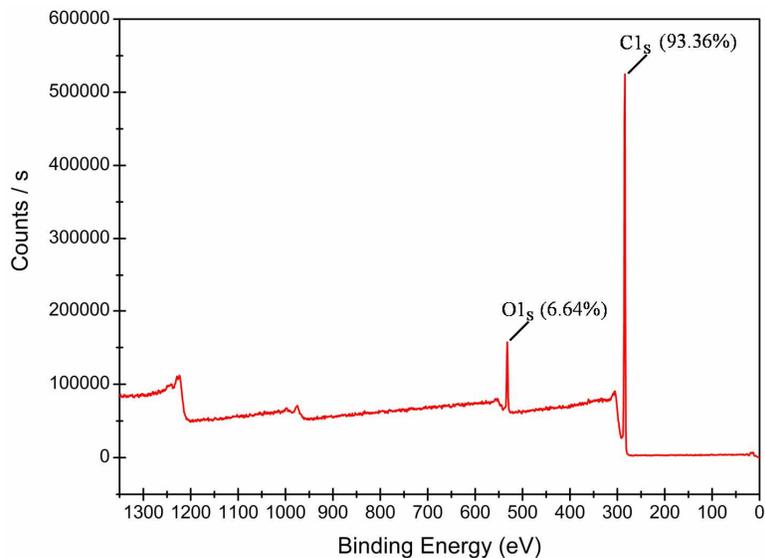


Figure S1. XPS survey spectrum of a BDF film on the HOPG surface after being dried in the vacuum oven for two days.

As can be seen in Figure S1, there is no detectable amount of chlorine element on the as-prepared BDF film according to the XPS results. Thus the possibility of dichloromethane molecules which co-crystallize with the BDF molecules through intermolecular interactions could be ruled out. In addition, other potential contaminations were avoided as well.

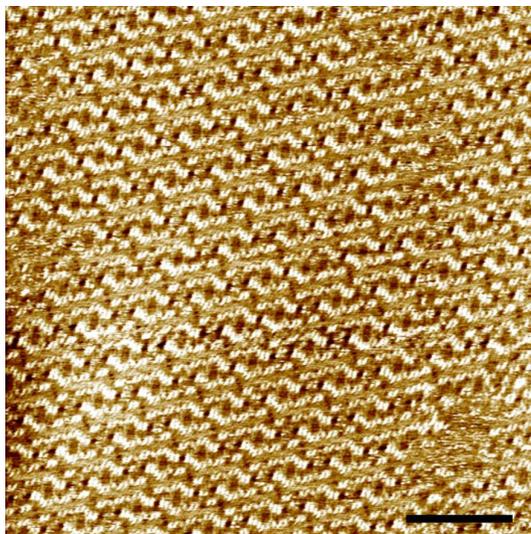


Figure S2. Large-scale image of the alternate pattern for BDF on the HOPG surface. $V_{\text{bias}} = 675 \text{ mV}$, $I_{\text{set}} = 560 \text{ pA}$; $C_{\text{BDF}} = 1.0 \times 10^{-6} \text{ mol L}^{-1}$. Scale bar = 16 nm.

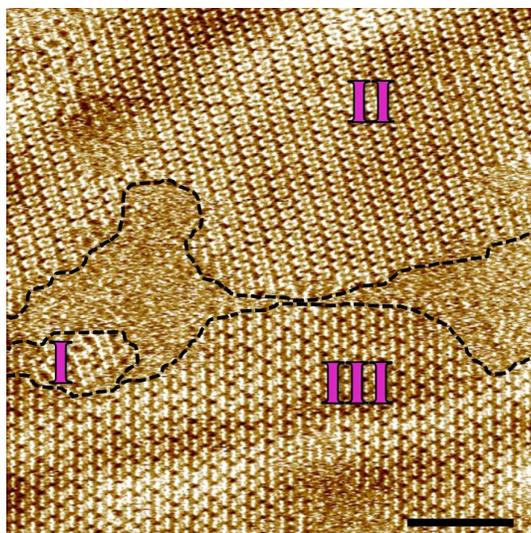


Figure S3. Large-scale image showing the coexistence of the alternate pattern (I), tetramer pattern (II) and trimer-I pattern for BDF on the HOPG surface. $V_{\text{bias}} = 653 \text{ mV}$, $I_{\text{set}} = 575 \text{ pA}$; $C_{\text{BDF}} = 6.0 \times 10^{-6} \text{ mol L}^{-1}$. Scale bar = 24 nm.

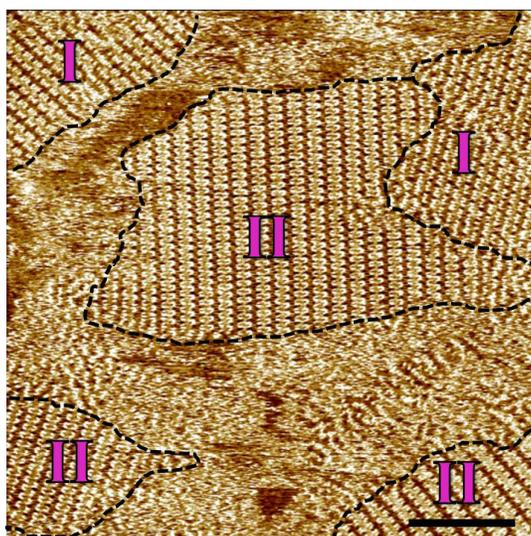


Figure S4. Large-scale image showing the coexistence of trimer-I pattern (I) and tetramer pattern (II) for BDF on the HOPG surface. $V_{\text{bias}} = 679 \text{ mV}$, $I_{\text{set}} = 533 \text{ pA}$; $C_{\text{BDF}} = 1.2 \times 10^{-5} \text{ mol L}^{-1}$. Scale bar = 24 nm.

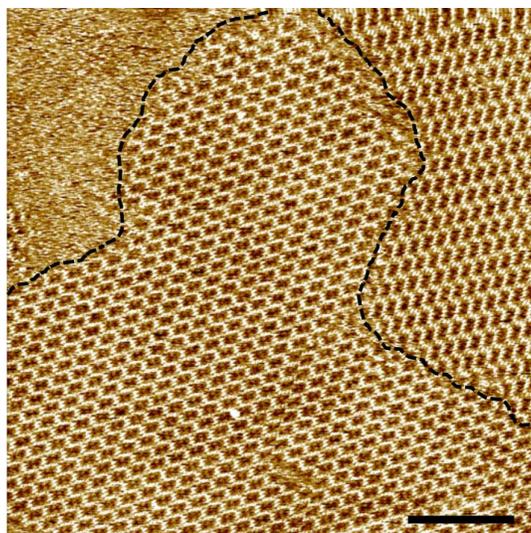


Figure S5. Large-scale image of the wave-like pattern for BDF on the HOPG surface. $V_{\text{bias}} = 665 \text{ mV}$, $I_{\text{set}} = 527 \text{ pA}$; $C_{\text{BDF}} = 2.0 \times 10^{-5} \text{ mol L}^{-1}$. Scale bar = 24 nm.

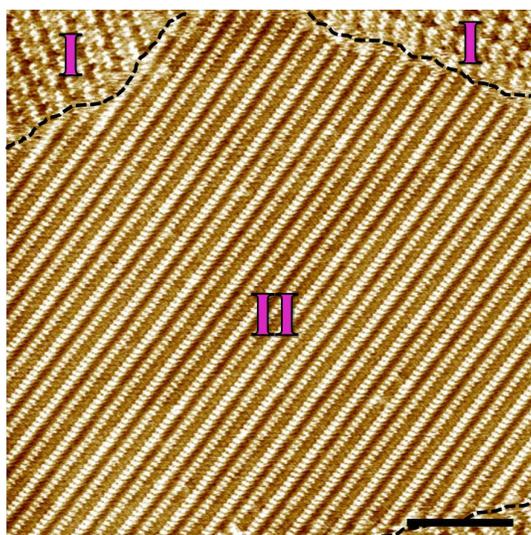


Figure S6. Large-scale image showing the coexistence of trimer-I pattern (I) and linear lamella pattern (II) for BDF on the HOPG surface. $V_{\text{bias}} = 679 \text{ mV}$, $I_{\text{set}} = 533 \text{ pA}$; $C_{\text{BDF}} = 1.2 \times 10^{-5} \text{ mol L}^{-1}$. Scale bar = 16 nm.

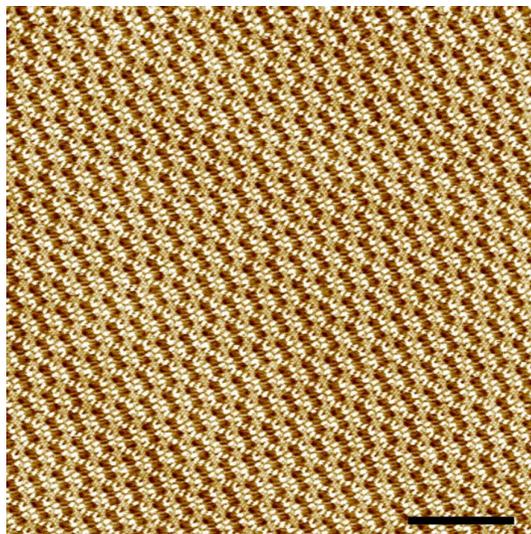


Figure S7. Large-scale image of the wave-like pattern for BDF on the HOPG surface. $V_{\text{bias}} = 665 \text{ mV}$, $I_{\text{set}} = 527 \text{ pA}$; $C_{\text{BDF}} = 2.0 \times 10^{-5} \text{ mol L}^{-1}$. Scale bar = 24 nm.

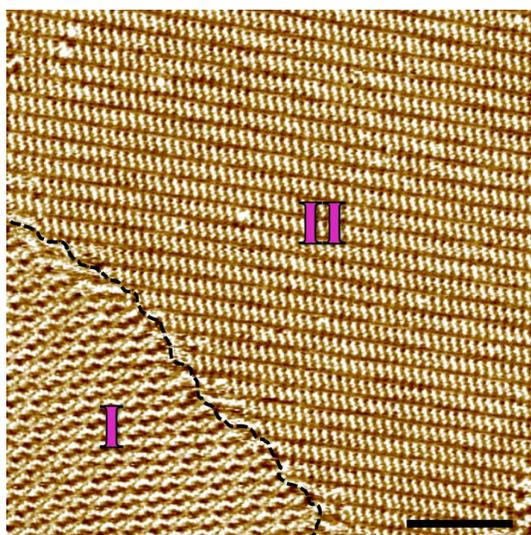


Figure S8. Large-scale image showing the coexistence of S-like pattern (I) and trimer-II pattern (II) for BDF on the HOPG surface. $V_{\text{bias}} = 641 \text{ mV}$, $I_{\text{set}} = 577 \text{ pA}$; $C_{\text{BDF}} = 6.0 \times 10^{-4} \text{ mol L}^{-1}$. Scale bar = 20 nm.

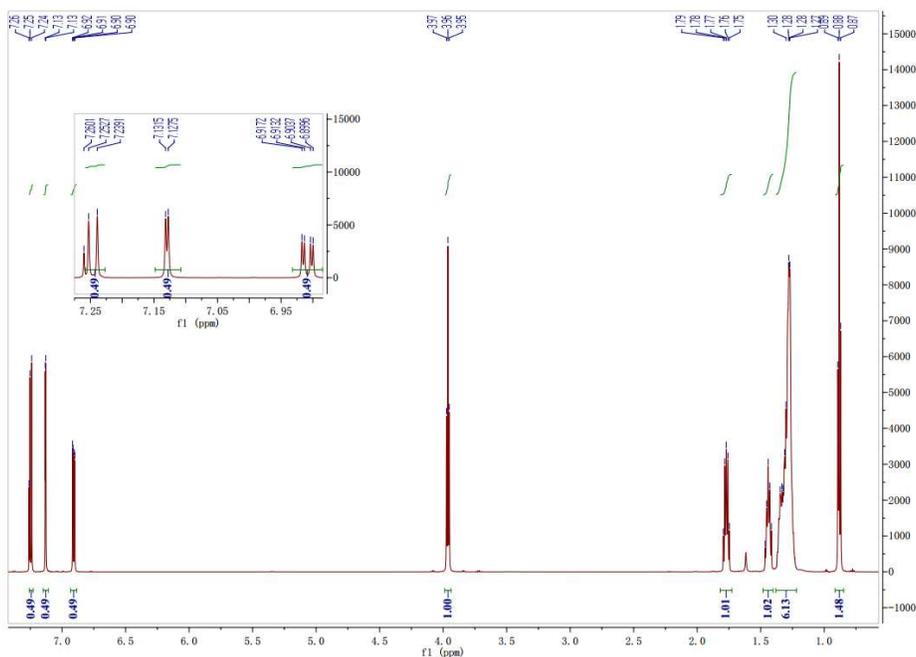


Figure S9 ^1H -NMR Spectrum of BDF (600 MHz, CDCl_3 , ppm): δ 7.24 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 2.4$ Hz, 2H), 6.91 (dd, $J = 8.2, 2.4$ Hz, 2H), 3.96 (t, $J = 6.6$ Hz, 4H), 1.75–1.79 (m, 4H), 1.42–1.47 (m, 4H), 1.27–1.35 (m, 24H), 0.88 (t, $J = 6.8$ Hz, 6H).

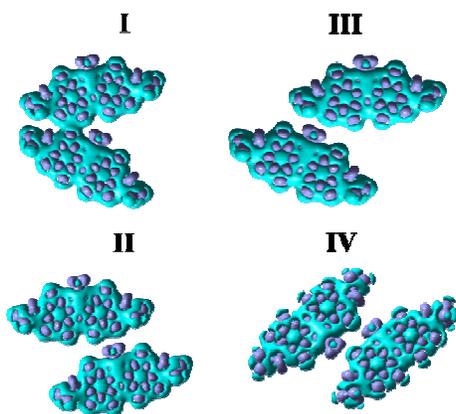


Figure S10. 3D deformation charge density maps in the plane for all BDF dimer configurations. Positive surface are shown in purple mesh, and negative surface are shown in blue mesh.

Table S1. Lattice Parameters of All Experimentally Observed BDF Polymorphs at the Solid/Gas Interface

Pattern	N	Unit parameters			S (nm ²)	S _m (nm ² per
		<i>a</i> (nm)	<i>b</i> (nm)	γ (°)		
Alternate	22	7.1 ± 0.2	8.6 ± 0.3	51 ± 2	47.45	2.16
Tetramer	4	1.8 ± 0.2	4.6 ± 0.2	85 ± 1	8.25	2.06
Trimer-I	6	2.7 ± 0.2	4.5 ± 0.1	80 ± 1	11.97	1.99
Wave-like	6	3.6 ± 0.1	3.3 ± 0.2	85 ± 2	11.83	1.97
Linear	2	0.9 ± 0.1	4.2 ± 0.2	88 ± 1	3.78	1.89
S-like	7	4.2 ± 0.1	3.4 ± 0.1	58 ± 1	12.11	1.73
Trimer-II	3	2.0 ± 0.1	1.7 ± 0.2	83 ± 2	3.37	1.13

N refers to the number of molecules within each unit; S refers to the area of each unit; S_m refers to the area occupied by each molecule;