Electronic Supplementary Material (ESI) for ChemComm.

Anisotropic Growth of Thiophene-Based Layer on Si(111)-B

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Supplementary Information

1 Synthesis and Substrate Preparation

1.1 1,4-bis(2',2"-dithienyl)-2,5-bis(decyloxy)benzene, DTB10B

DTB10B molecule is based on a phenyl group surrounded by two dithenyl moities and two side alkyl chains in order to achieve the formation of supramolecular networks.

1,4-dibromo-2,5-bis(decyloxy)benzene and 2,2'-bithiophene-5-boronic acid pinacol ester molecules were purchased from Aldrich and used without further purification.

The 1,4-dibromo-2,5-bis(decyloxy)benzene (0.7g, 1.6 mmol) and 2,2'-bithiophene-5-boronic acid pinacol ester (1.0 g, 3.4 mmol) were dissolved in 40 mL of toluene. Then, an aqueous solution of K_2CO_3 (0.5 M, 6 mL) and $Pd(PPh_3)_4$ catalyst (42 mg, 0.03 mmol) were added. The resulting mixture was heated at reflux for 48 hours. Then, after cooling to room temperature, 60 mL of toluene were added, and the organic solution was washed three times with 100 mL of water. The solvent was removed under reduced pressure. The resulting solid is purified by column chromatography (silica gel, Dichloromethane/Hexane 1:3, Rf:0.5). The solid was recrystallized in acetone to give a pure yellow solid (700 mg, 67%).

^{1}H NMR (300 MHz, Chloroform-d) δ = 7.47 (d, J = 3.9 Hz, 2H), 7.23 (m, 6H), 7.18 (d, J = 3.9 Hz, 2H), 7.04 (t, J = 4.6 Hz, 2H), 4.12 (t, J = 6.6 Hz, 4H), 1.94 (q, J = 6.6 Hz, 4H), 1.57 (q, J = 6.6 Hz, 4H), 1.30 (m, 26H), 0.88 (t, J = 6.6 Hz, 6H).

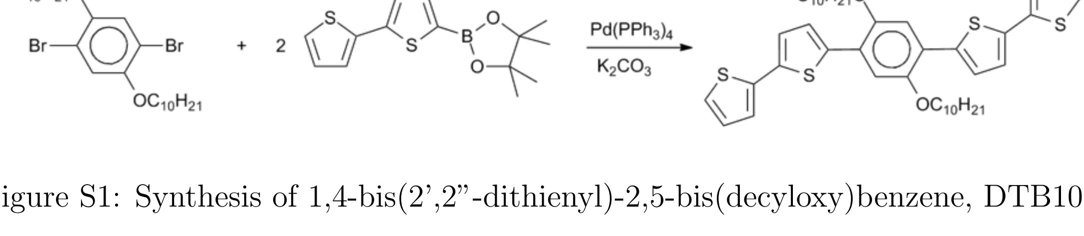

Figure S1: Synthesis of 1,4-bis(2',2"-dithienyl)-2,5-bis(decyloxy)benzene, DTB10B

1.2 Preparation of Si(111)-B surface

The Si(111)-B $\sqrt{3} \times \sqrt{3}$ R30° reconstruction surface is prepared by annealing of the (111) surface of a highly B-doped Si wafer (0.001 W·cm resistivity). Si(111) surface is carefully outgassed and cleaned in situ by a series of rapid heating up to 1200°C under a pressure lower than $5{\times}10^{-10}$ mbar. A thermal process (one hour at 800°C) activates the boron segregation at the surface and a maximum boron atom concentration of 1/3 monolayer (ML) can be obtained (one ML is referred to the Si(111) ideal surface atomic density with $7.8{\times}10^{14}$ atoms·cm^{-2}). In these conditions, the surface exhibits a perfect $\sqrt{3} \times \sqrt{3}$R30° reconstruction.

2 Instrumentation

STM experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure lower than $2{\times}10^{-10}$ mbar equipped with a variable temperature Omicron Scanning Tunneling Microscope (STM). STM images were acquired in a constant-current mode at room temperature or 100 K. 14,4"-dibromo-*p*-terphenyl molecules were deposited from a Quartz crucible at 135°C. The Si(111)-B substrate was kept at room temperature (RT) during the sublimation. Each image process was carried out by using WSXM software.[1] The artwork was produced with Blender.[2]

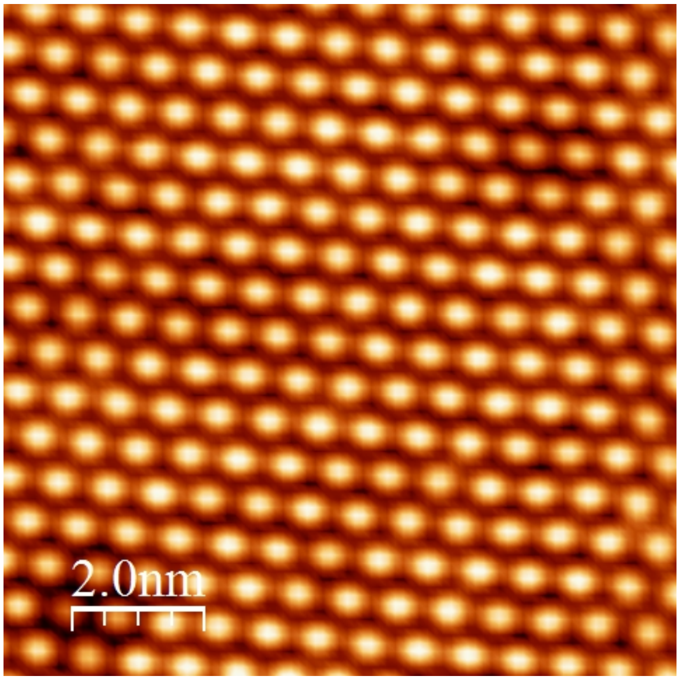

Figure S2: STM image of a clean Si(111)-B surface. Measurement conditions: I=0.2 nA, V = 2.6 V, 10 nm × 10 nm

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[1] I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A. M. Baro, Rev. Sci. Instrum. 2007, 78, 013705.

[2] http://www.blender.org

3 Computations

3.1 DFT Calculations

The DFT calculations were performed with the NWChem package[3] and the B3LYP hybrid functional.[4] The geometry of the gas phase ground state of DTB10B was fully optimized without any symmetry constraints with a 6-31G quality basis sets on all atoms with the quasi-Newton method until a gradient convergence factor better than 10^{-5} Hartree/Bohr was reached.

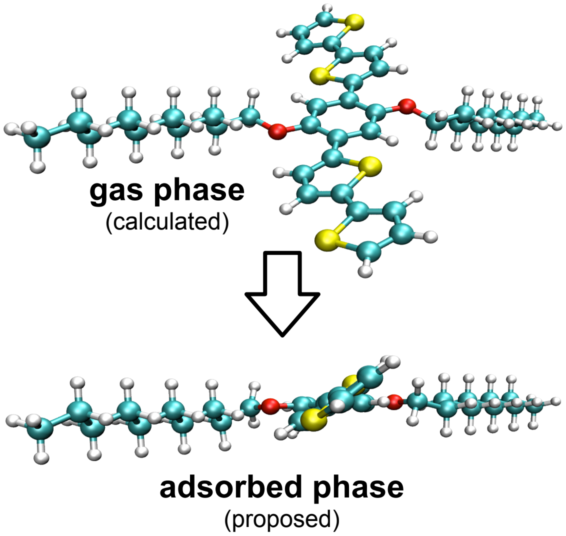

Figure S3: Optimized geometry for gas phase DTB10B molecule obtained at DFT/B3LYP/6-31G level, and the subsequent planarization upon its adsorption on the Si(111)-B surface. The geometry of the adsorbed phase was not optimized but was adjusted during STM simulations to reproduce the main experimental STM features.

3.2 STM simulations

The STM simulations were carried out within the Flex-STM module[5] now included in our in-house SPAGS-STM software[6]. For the STM simulations, we used standard Hamiltonian derived from extended Hückel theory[7] in conjunction the Tersoff-Hamann[8] level of theory to compute the tunneling current. All the simulated STM images were computed in topographic mode, or in other words in a constant current mode.

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[3] M. Valiev, E. Bylaska, N. Govind, K. Kowalski, T. Straatsma, H. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. Windus, *et al.*, Comput. Phys. Commun. 2010, 181, 1477.

[4] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.

[5] N. Boulanger-Lewandowski, A. Rochefort, Phys. Rev. B, 83, 2011, 115430.

[6] B. Janta-Polczynski, J. Cerda, G. Éthier-Majcher, K. Piyakis, A. Rochefort, J. Appl. Phys. 104, 2008, 023702.

[7] G. Landrum, YAeHMOP; Yet Another Extended Hu´uckel Molecular Orbital Package, Cornell University, Ithaca, NY, 1995.

[8] J. Tersoff, D. R. Hamann, Phys. Rev. Lett. 50, 1983, 1998.

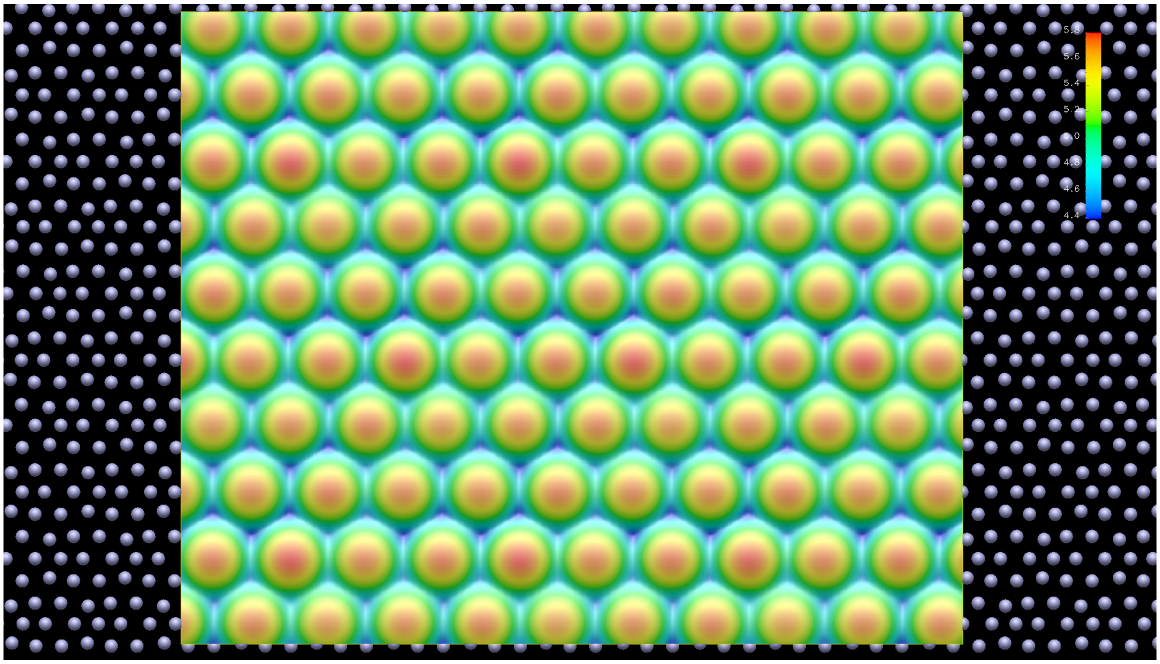

Figure S4: Calculated topographic STM image for the Si(111)-B surface containing 5733 atoms, dimension of the Si(111)-B model = 13.8 nm × 13.6 nm × 0.5 nm. STM simulations conditions: EHT Hamiltonian, Tersoff-Hamann method, I = 0.1 nA, V = 2 V, scanned zone = (6.7 × 11.5) nm^2, resolution = 0.01 nm.

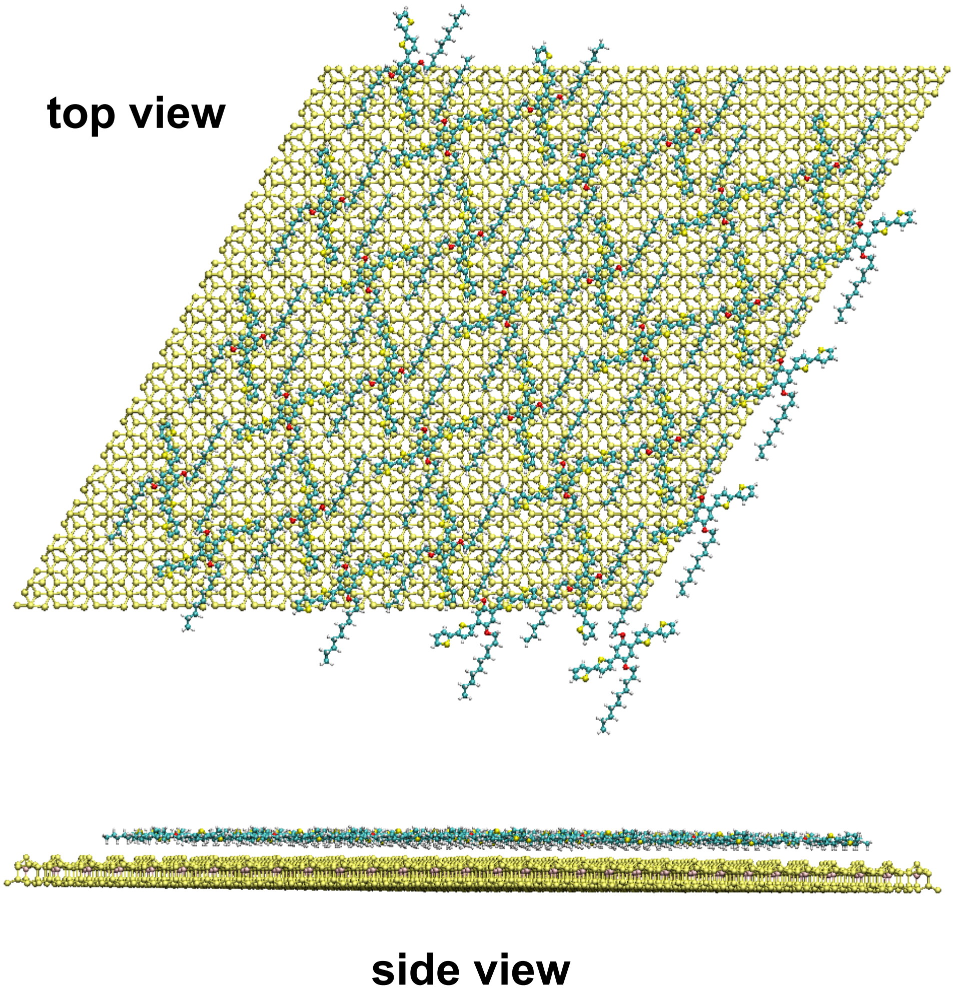

Figure S5: Molecular model used for the STM simulations of the DTB10B/Si(111)-B system. Although this supercell contains 6592 atoms, no periodic boundary conditions were applied in the STM simulation; every single atoms can be manually displaced or its chemical nature changed, while a new STM image can be subsequently evaluated.

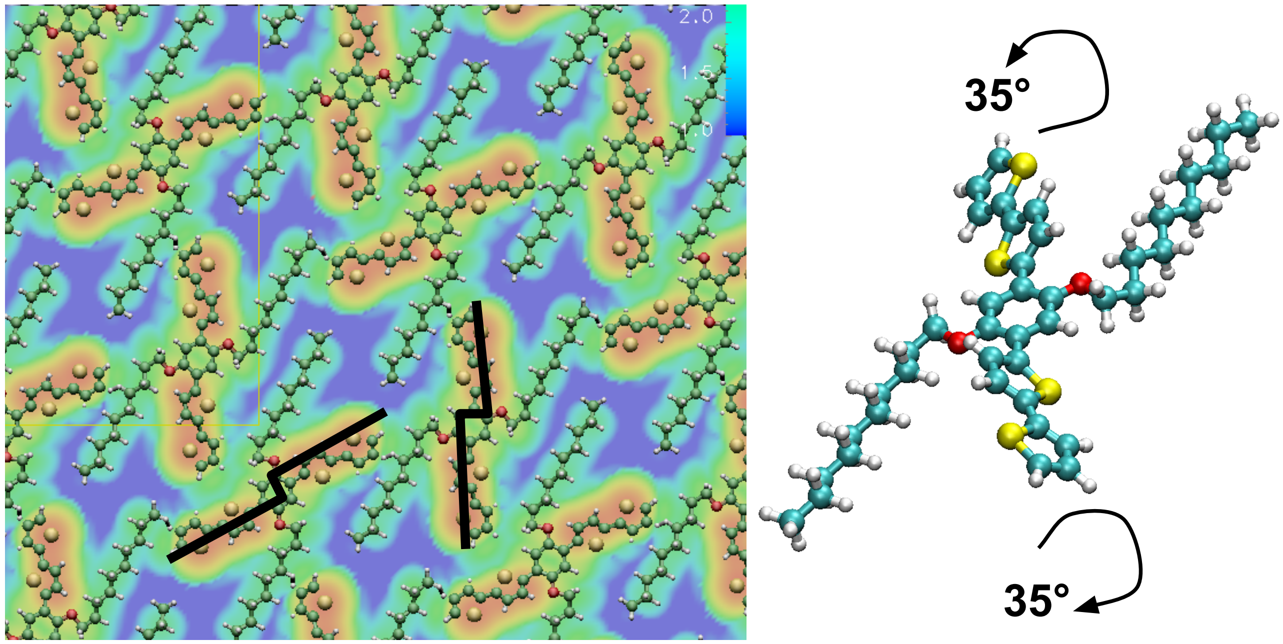

Figure S6: STM simulation of adsorbed DTB10B where the two thiophene units each side of the central benzene ring are rotated by 35° and -35° with respect to the central benzene ring. This clearly shows the influence of thiophene rotation on the resulting simulated STM image. STM simulations conditions: EHT Hamiltonian, Tersoff-Hamann method, I = 0.1 nA, V = -1.5 V, resolution = 0.01 nm.