Supporting information for: Controlling Self-Assembly of Switchable Azobenzene Derivatives on Highly Oriented Pyrolytic Graphite at Ambient Conditions

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S1: Different adsorption induced isomers of AB, PABA, *meta*-ADB, *para*-ADB

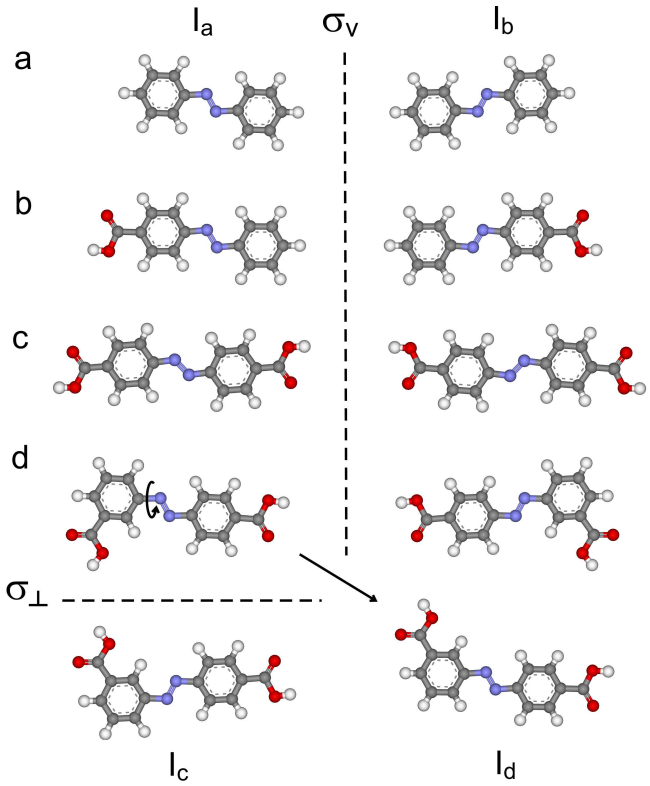

Figure S1: I_a indicates one adsorption induced isomer of AB (a), PABA (b), *para*-ADB (c) and *meta*-ADB (d). The other adsorption induced isomer (I_b) is obtained by a mirror operation of I_a using the vertical plane (indicated using σ_v). Assuming the adsorption plane as plane of the paper. For *meta*-ADB other adsorption induced isomers are possible; I_c obtained by a mirror operation of I_a with a plane indicated as $\sigma_\perp$; I_d is obtained by rotation of N–C bond (indicated using curly arrow in I_a).

S2: Synthetic details of *meta*-ADB

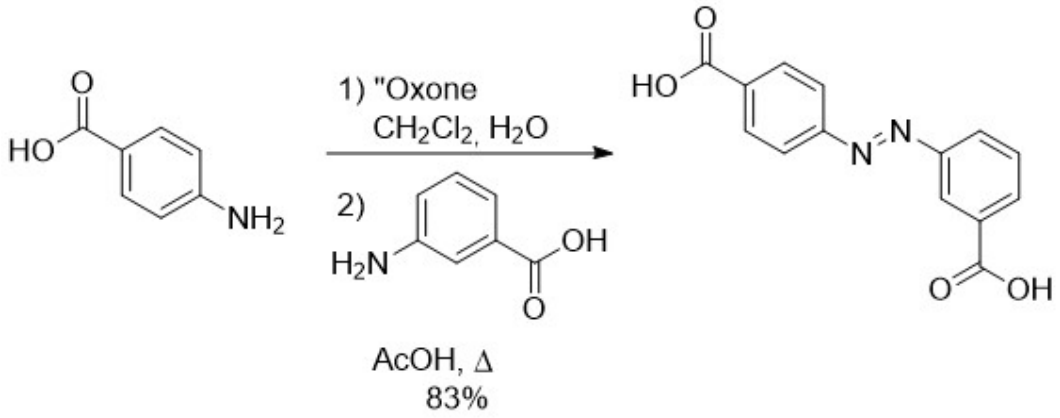

Figure S2: Synthetic scheme for meta-ADB.

p-Aminobenzoic acid (1.00 g, 7.29 mmol, 1.0 eq) was suspended in CH_2Cl_2(20 mL). 'Oxone' (9.00 g, 29.28 mmol, 4.0 eq) was dissolved in water (80 mL) and added to the reaction mixture. The reaction mixture was stirred for 3 hours at room temperature. The yellow precipitate was filtered, washed with water and the solvent was removed under reduced pressure to give the nitroso compound. p-Nitrosobenzoic acid (1.10 g, 7.28 mmol, 1.0 eq) and m-aminobenzoic acid (1.00 g, 7.29 mmol, 1.0 eq) were dissolved in acetic acid and refluxed for 8 hours. The orange red precipitate was filtered and washed with acetic acid. Crystallisation from acetic acid gave *meta*-ADB) (1.64 g, 6.06 mmol, 83 %) as orange powder.

1H-NMR: (500 MHz, DMSO-d6) δ = 13.31 (s, 2H), 8.41 (t, J = 1.7 Hz, 1H), 8.20-8.18(m, 1H), 8.17-8.15 (m, 3H), 8.03-8.01 (m, 2H), 7.77 (t, J = 7.8 Hz, 1H) ppm.

13C-NMR: (125 MHz, DMSO-d6) δ = 166.7, 166.6, 154.1, 151.8, 133.2, 132.5, 132.3, 130.7, 130.1, 127.7, 122.8, 122.5 ppm.

ESI-MS (+): m/z: 271.17 [M-H]+

HRMS: m/z calcd. for $C_{14}H_{10}N_2O_4$ 271.07133 [M+H]+, found 271.07134 (Δm = 0.00001, error 0.04 ppm).

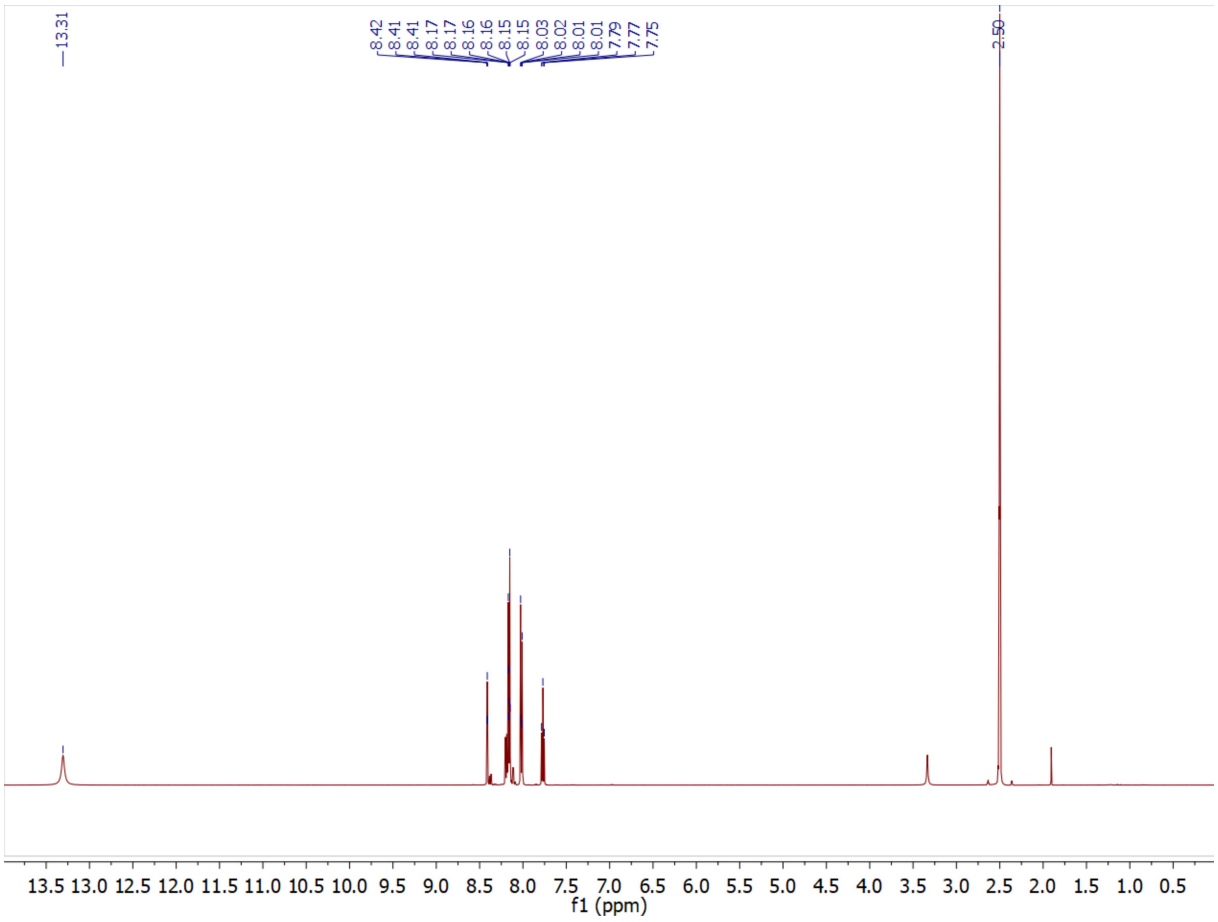

Figure S3: ^{1}H-NMR spectrum of meta-ADB.

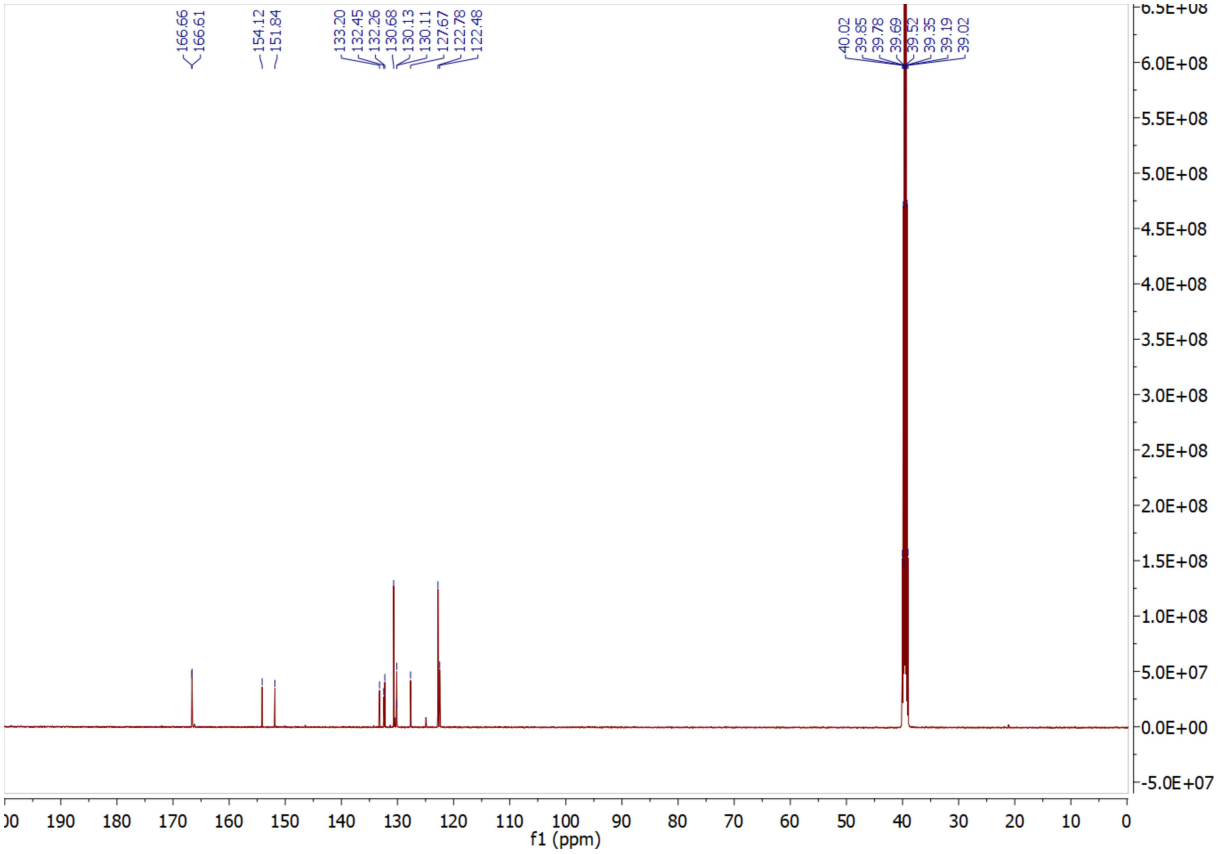

Figure S4: ^{13}C-NMR spectrum of meta-ADB.

S3: Details of theoretical calculations of AB, PABA, *meta*-ADB and *para*-ADB

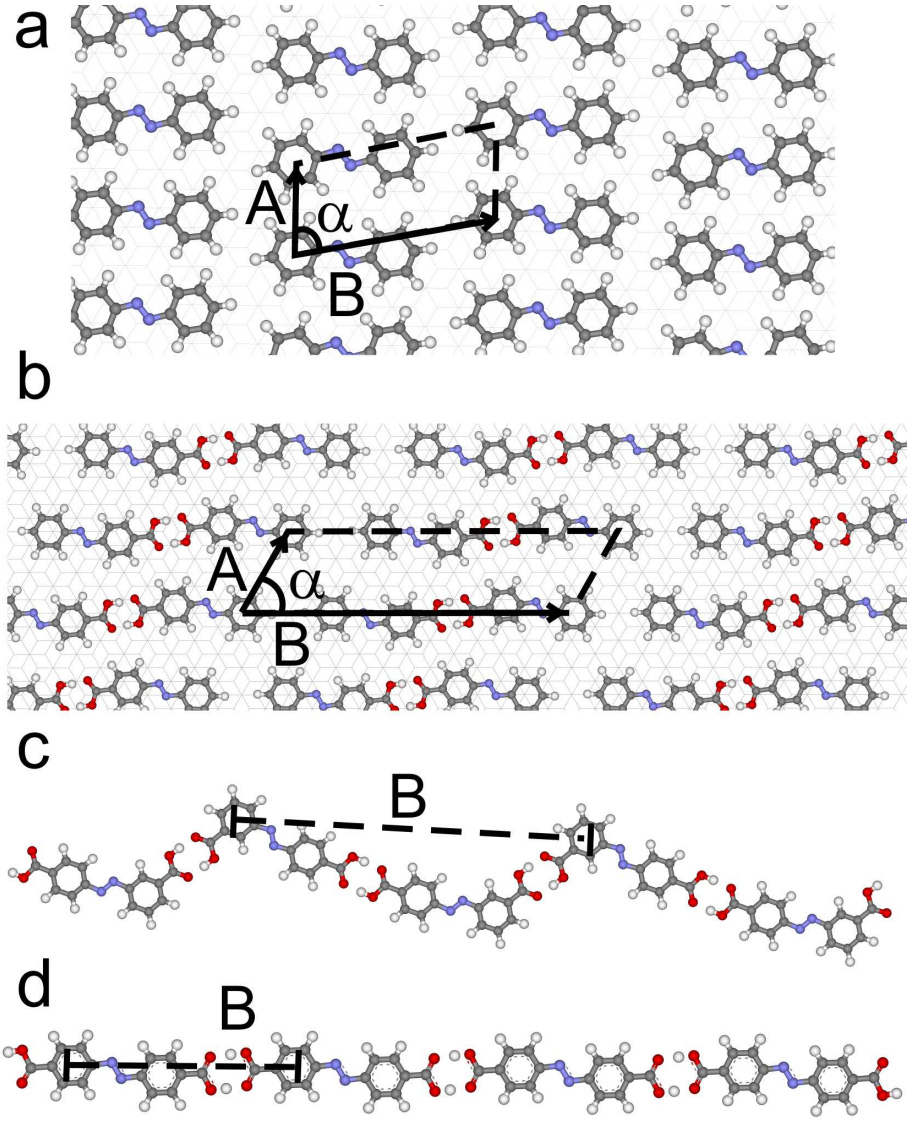

Figure S5

(a) Optimized AB molecular assembly on graphite bilayer. A free molecule of AB is optimized by density functional theory (DFT) at B3LYP/6-31g level using Gaussian 09. Using the optimized AB a unit cell on graphite is created based on the experimental input and optimized the pattern over bilayer graphite. The optimization is performed using DFT implemented in QuantumWise package. The bilayer was fixed during the optimization. The

optimization uses periodic boundary condition with DFT-PBE/GGA exchange correlation (pseudo potentials: H = 1.0, C = 4.0, N = 5.0, O = 6.0 and basis set: double zeta). The unit cell of the optimized pattern is indicated with unit vectors, $\overrightarrow{A}$ (0.6 nm) and $\overrightarrow{B}$ (1.3 nm). The angle between the unit vectors is α (78°). The relative orientation of the molecules clearly shows that the intermolecular interactions are mediated via van der Waals interaction along both compact directions. The experimental intermolecular distances along both compact directions are matching well with the simulations, however, the angle (α) is deviating. This leads to slightly different relative orientation of molecules in both theory and experiment. We are unable to reproduce the experimental observation due to the herringbone superstructure. (b) Optimized PABA dimer on bilayer graphite. A free dimer was optimized first and rest of the procedure is same as that for AB. The unit cell of the assembly is indicated with unit cell vectors $\overrightarrow{A}$ (0.8 nm) and $\overrightarrow{B}$ (2.9 nm) and the angle between the unit vectors is α (60°). As observed in the experiments, the assembly is mediated by dimers of molecules and the dimers are stabilized via cyclic carboxyl hydrogen bonds. (c) and (d) are chains of *meta*-ADB and *para*-ADB optimized by using DFT (B3LYP/6-31g) without any surface. The super-cells of these molecules are large and we have not attempted to optimize them on surface, due to limited computational resources. However, the calculations provide indications about the stability of the dimer chain. As observed, in experiment *meta*-ADB and *para*-ADB molecules are stabilized via cyclic carboxyl hydrogen bonded chains. Length of repeating unit in lateral direction is denoted by B, which is 2.9 nm and 1.6 nm for *meta*-ADB and *para*-ADB, respectively. These distances are comparable to the intermolecular distance indicated by $\overrightarrow{B}$ in the experiments for these molecules.

S4: Additional STM image of ultra-thin film of *meta*-ADB

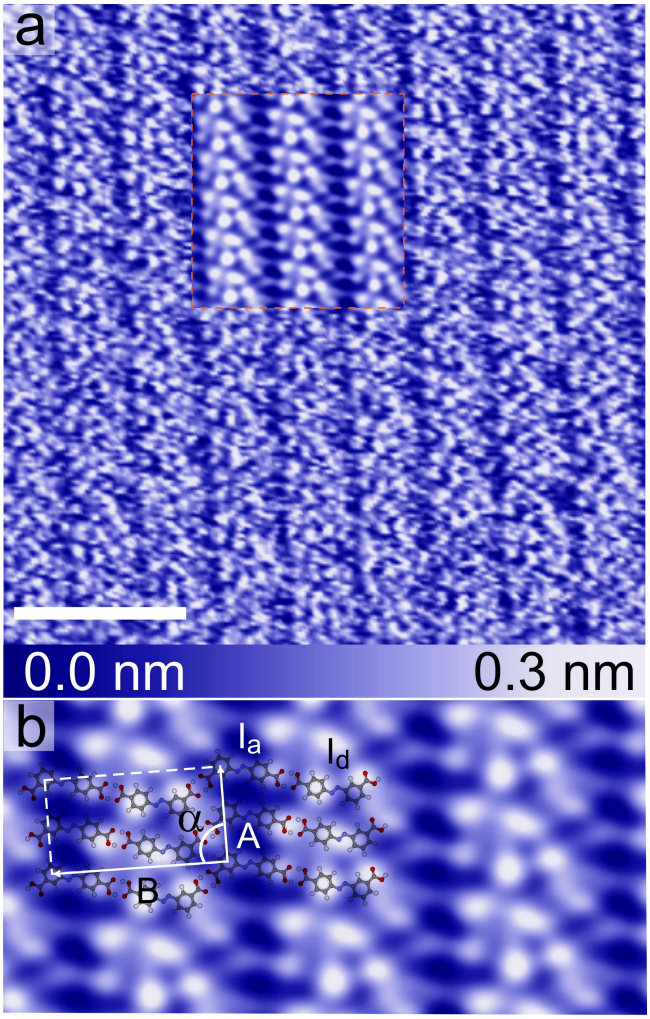

Figure S6

(a) STM topography (180 pA, 0.87 V, scale bar = 8 nm) of drop-casted ultra-thin film of *meta*-ADB molecules on HOPG (0001). Inset of (a) shows averaged image where the molecular orientation is clearly visible. Scaled *meta*-ADB molecules are overlaid on averaged STM image in (b). Two adjacent molecules interact through the carboxyl groups (cyclic hydrogen bond) of adjacent molecules and forms dimers and consequently form a hydrogen bonded chain of *meta*-ADB molecules. The unit cell of the assembly is indicated with unit cell vectors ($\overrightarrow{A} = 1.5 \pm 0.1$ nm and $\overrightarrow{B} = 3.2 \pm 0.1$ nm) and the angle between the unit vectors ($\theta = 90 \pm 2^{\circ}$). The isomers used in this case are different to that used in Figure 2f, indicating

that different islands are formed by the assembly of different adsorption induced isomers. As a consequence, the packing is also varying as evident from the unit cell parameters. I_d and I_a are adsorption induced isomers (SI S1).

S5: Statistical analysis of angle between 1D islands of AB and PABA

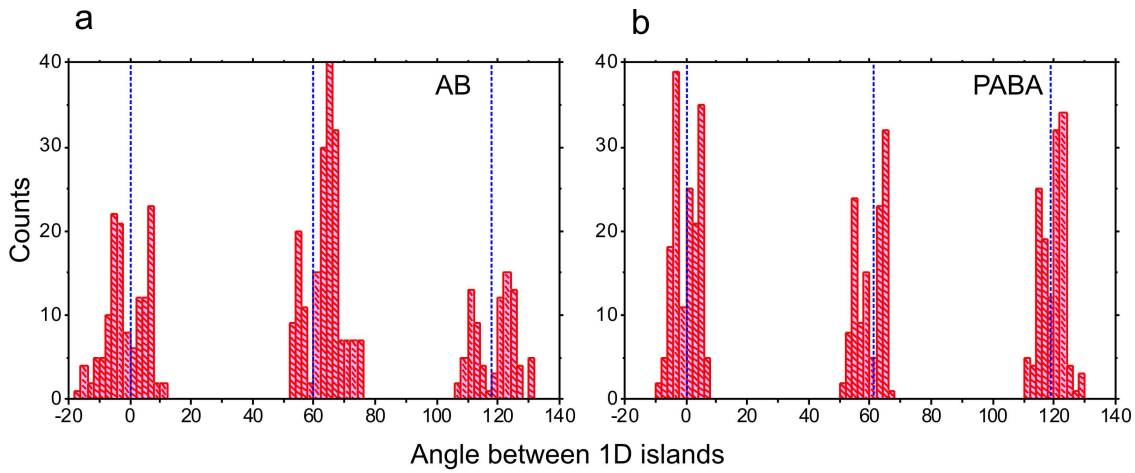

Figure S7: Statistical analysis of the angle between long edges of molecular islands of AB (a) and PABA (b). The analysis is performed by measuring the angle of rotation of all islands in an AFM image with respect to a randomly chosen island. The statistics will provide us all possible orientations of molecular islands with respect to each other. These angles are marked by magenta and white arrows is Figure 3a and 4a. AB shows six peaks at $\approx -5°$ and $6°, 55°$ and $65°, 111°$ and $123°$. These orientation are observed as three pairs and the pairs are separated by $\approx 60°$ with respect to an adjacent pair. The angle between the peaks in a pair is $\approx 11°$. The pairs indicate that the molecular islands are rotated by $\approx 5.5°$ with respect to the compact lattice of graphite (indicated using blue dashed line in Figure a). However, the broadness of each peak ($\approx 22°$) is rather high and suggesting that not all islands are satisfying a perfect registry with respect to graphite lattice. Strikingly for PABA six narrow peaks as three pairs at $\approx -4°$ and $3°, 55°$ and $64°, 115°$ and $123°$ are observed. The pairs are centred around $0°, 61°$ and $119°$ as in AB. The angle between the peaks in pairs is $8 \pm 1°$. Each molecular island is rotated by $4.0°$ with respect to the compact lattice directions of graphite, which are indicated using blue dashed lines in Figure b. The narrow peaks indicate a perfect registry of molecular islands with graphite lattice unlike AB. This also justifies the abundance of the 1D islands of PABA on HOPG.

S6: Additional AFM data of ultra-thin film of AB on HOPG (0001)

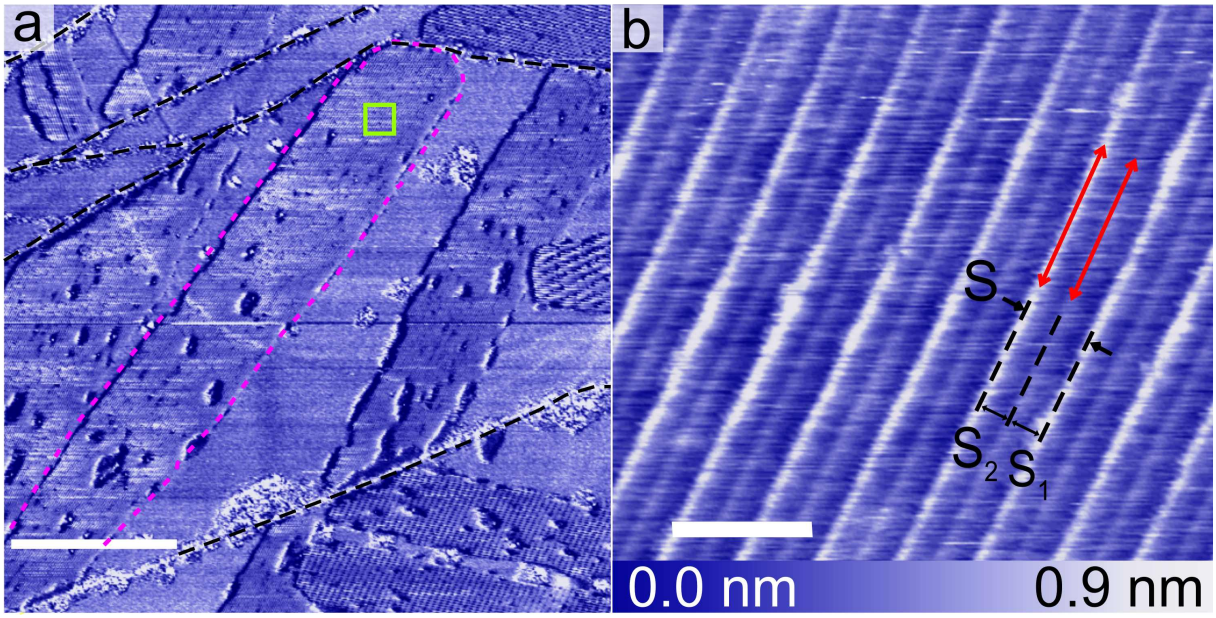

Figure S8: (a) AFM phase image (scale bar = 400 nm) of ultra-thin film of AB on HOPG (0001). One molecular island is marked with magenta dashed line. Step edges are marked with black dashed line. (b) High resolution (scale bar = 12 nm) of a section (marked with green box in a) of an island. Alternate bright and less bright molecular rows and the spacing between these rows are marked as S_1 ($\approx$ 3.4 nm) and S_2 ($\approx$ 3.0 nm). The super periodicity of the pattern is indicated using S (6.4 nm). These distances are correlating with STM (Figure 2b) and interpreted to be originating from the herringbone arrangement of molecules. Red double headed arrows indicate the herringbone rows.

S7: AFM topography of phase image shown in Figure 4

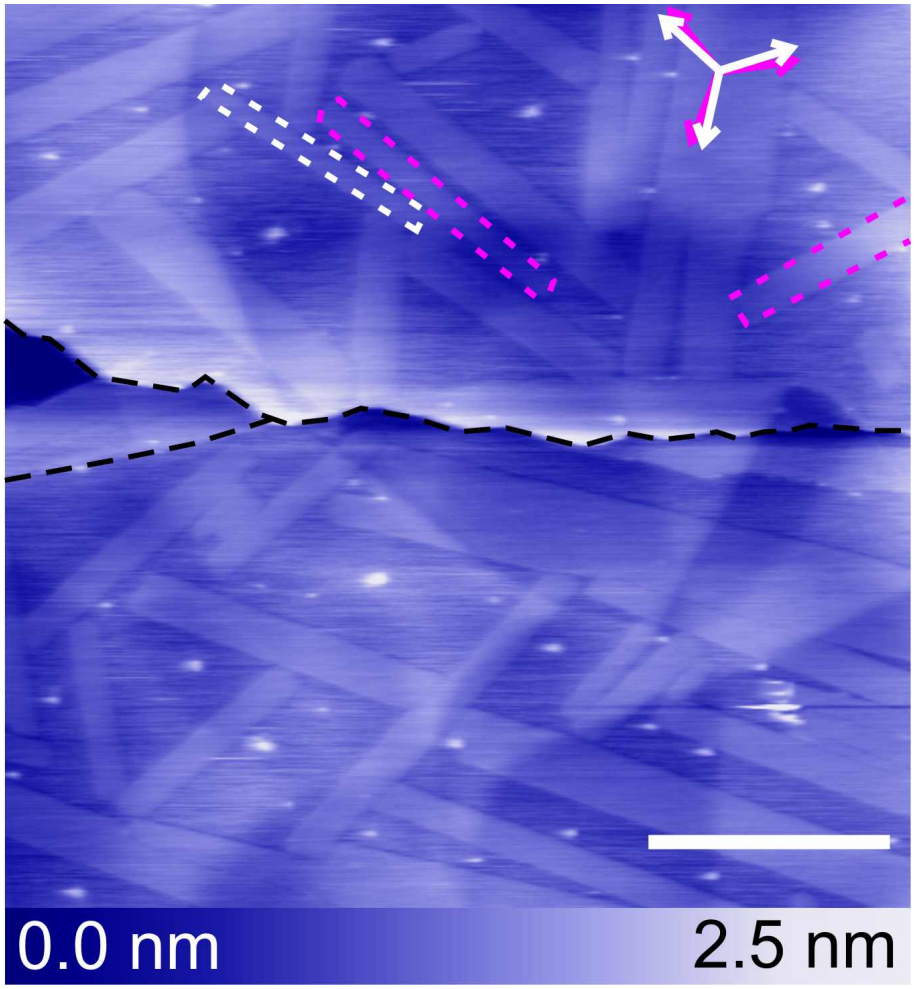

Figure S9: AFM topography (scale bar = 800 nm) of the phase image produced in Figure 4. A molecular island is marked with dashed magenta line. All possible growth directions of the molecular islands are indicated using white and magenta arrows.

S8: AFM images of 1D islands of *meta*-ADB on HOPG (0001)

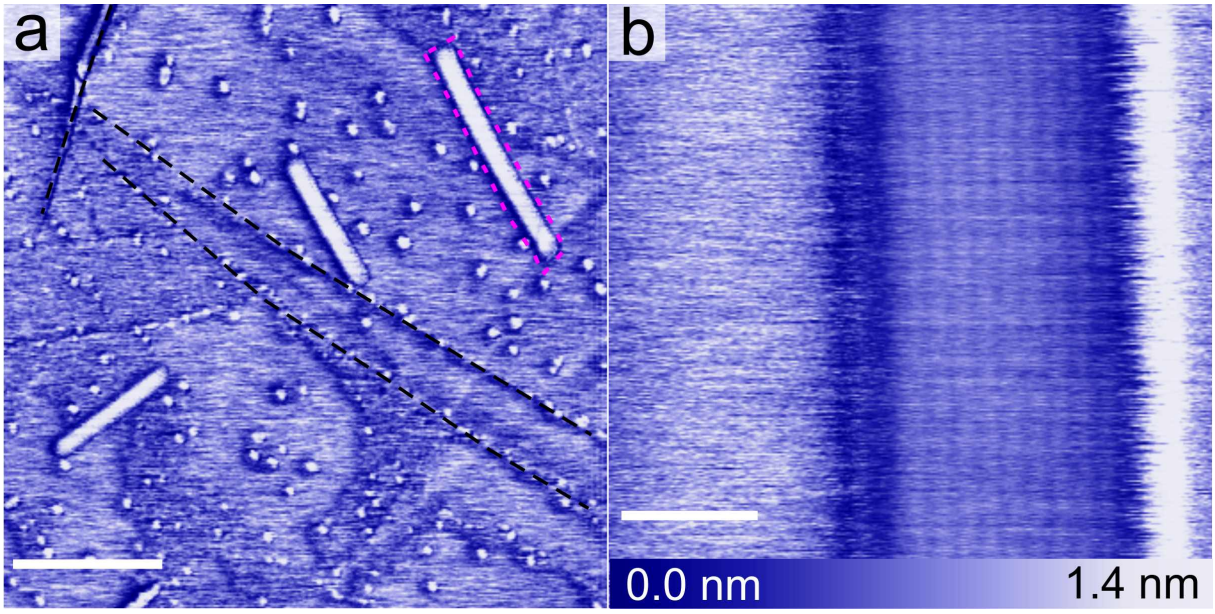

Figure S10: (a) AFM phase image (scale bar = 450 nm) of ultra-thin film of *meta*-ADB on HOPG (0001). 1D islands of molecules are marked with magenta dashed line. These islands following lattice direction of surface (3-fold orientation). (b) High resolution AFM topography (scale bar = 40 nm) of part of a 1D island. Molecular rows are visible as line like features and are extending over the entire length of the island. The spacing between these molecular rows are $\approx$ 6.4 nm.

S9: AFM and STM image of ultra-thin film of *para*-ADB on HOPG (0001)

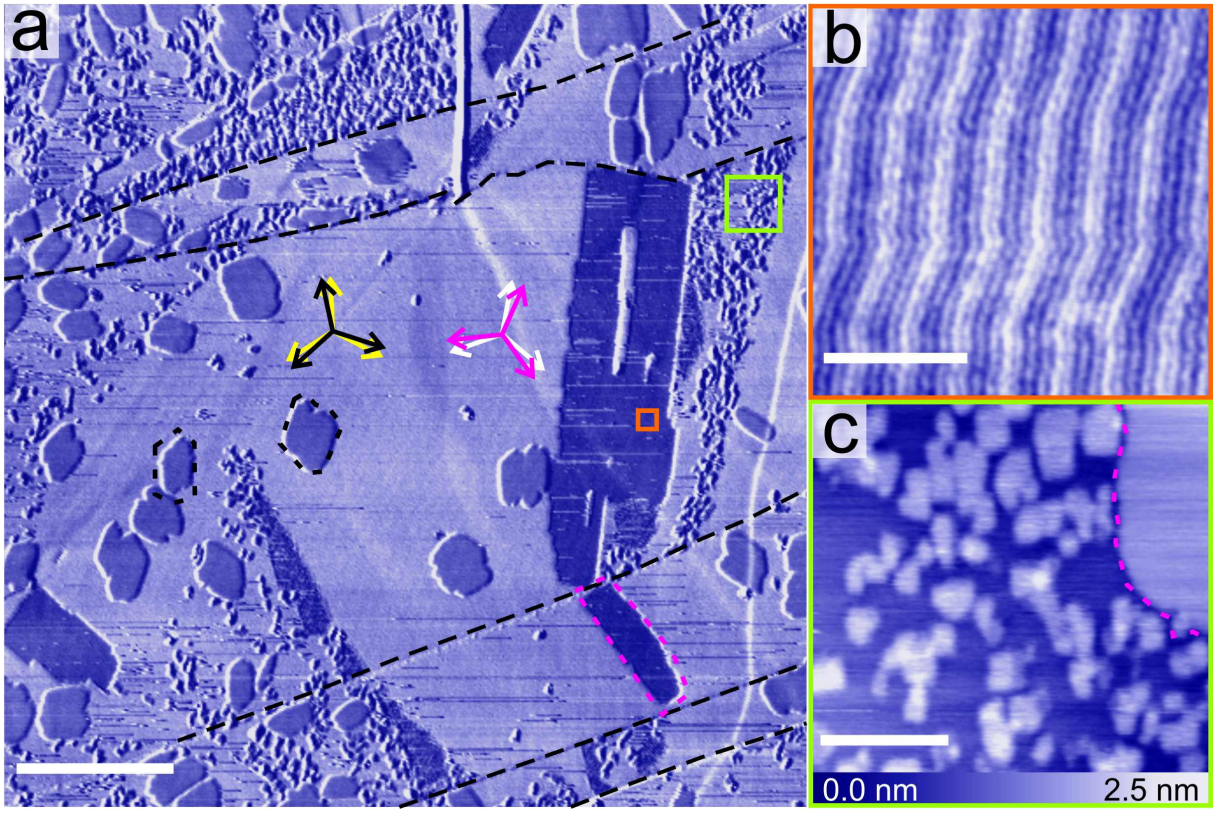

Figure S11

(a) AFM phase image (scale bar = 500 nm) of drop-casted ultra-thin film of *para*-ADB molecules on HOPG (0001). Few terrace edges are marked by black dashed lines. Three types of crystalline islands are observed : 1). Crystalline islands growing upto a few hundreds of nm. These type of islands are marked by black dashed lines. The edges of these types of islands are well defined and has uniform height profile. Black and yellow arrows show the orientation of one of the growth facets and are seemingly aligned with three fold graphite lattice directions. This indicates that they are crystalline in nature. 2). Long crystalline islands growing to a few μm (appearing as dark). An orange box is placed on one of such islands and further high resolution of the area is shown in Figure S11b (scale bar = 18 nm). The line like contrast originates from molecular rows and are spaced $\approx$ 1.5 nm, which matches

with the length of a *para*-ADB molecule. The islands are showing typical growth directions as marked with magenta and white arrows. The growth preference (six orientations for the long edge of islands) indicates that the islands are aligned to a three fold graphite lattice direction. 3). Smaller crystallites with size ranging to only a few tens of nm (marked in green box). High resolution AFM topography of these smaller crystallites are shown in Figure S11c (scale bar = 60 nm). The uniform height of these islands is the indication of the crystalline nature.

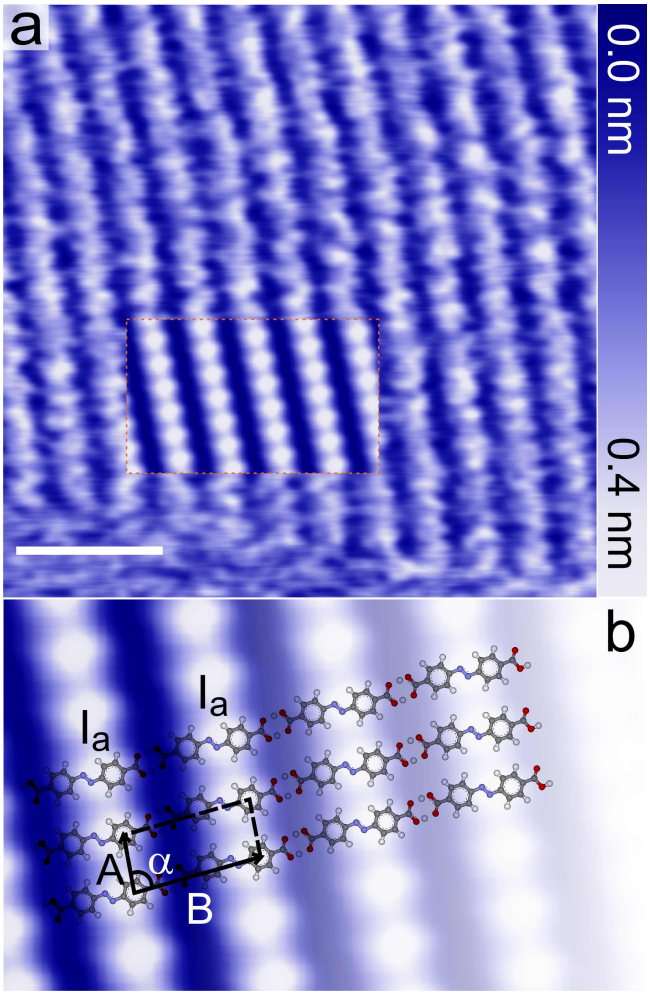

Figure S12: (a) As measured STM topography (scale bar = 5.0 nm, 150 pA, 0.86 V) of drop-casted ultra-thin film of *para*-ADB molecules on HOPG (0001). Inset of (a) shows averaged image where the molecular orientation is clearly visible. Scaled para-ADB molecules are overlaid on averaged STM image in (b). Two adjacent molecules interact through the carboxyl groups (cyclic hydrogen bond) of adjacent molecules and forms dimers and consequently form a hydrogen bond chain of *para*-ADB molecules. The unit cell of the assembly is indicated with unit cell vectors ($\overrightarrow{A} = 0.8 \pm 0.1\,\text{nm}$ and $\overrightarrow{B} = 1.6 \pm 0.1\,\text{nm}$) and the angle between the unit vectors ($\theta = 85 \pm 2°$). The distance $\overrightarrow{B}$ is matching with the spacing of molecular rows observed in AFM indicating its origin. I_a is a adsorption induced isomer SI S1