Supporting Information

Substrate Mediated Synthesis of 2D Covalent Organic Frameworks

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Contents

I. Experimental procedures

All experiments are carried out under UHV conditions (base pressure $<5.0 \times 10^{-10}$ mbar) at room temperature with two different STMs. One instrument is a commercial STM from Omicron whereas the other one a home-built beetle type STM as described elsewhere.[1] Both STMs are laterally calibrated by atomically resolved graphite images. 1,3,5-Tris(4-bromophenyl)benzene (TBB) is supplied by Sigma-Aldrich with a purity of 97% and extensively (>48 h) outgassed in UHV at 140°C. TBB is deposited from Knudsen cells with a crucible temperature in the range from 140 °C to 160 °C. The graphite surface is cleaned prior to experiments by annealing up to 500 °C for 30 minutes. Ag(110) and Cu(111) surfaces are cleaned by repeated cycles of sputtering and annealing. Cleanliness of the substrate is checked prior to evaporation by STM. During deposition, the substrate is held at room temperature. Thermal stability of 2D COFs is verified by annealing of a previously characterized sample and subsequent repeated STM measurements.

II. Additional STM data

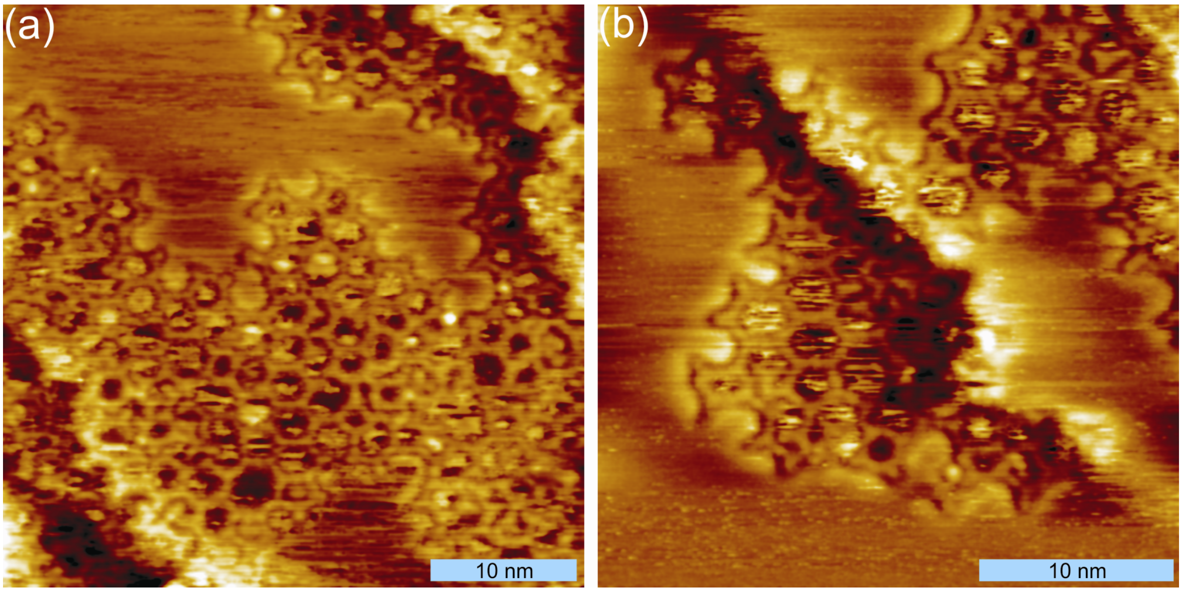

Figure S1. TBB evaporated on Ag(110) at 140 °C for 10 min **(a)** V = 1.2 V, I = 110 pA **(b)** V = 1,2 V, I = 123 pA. Both topographs show open-pore structures with high defect density. The contrast within the cavities can be attributed to coadsorbed molecules or split-off bromine atoms.

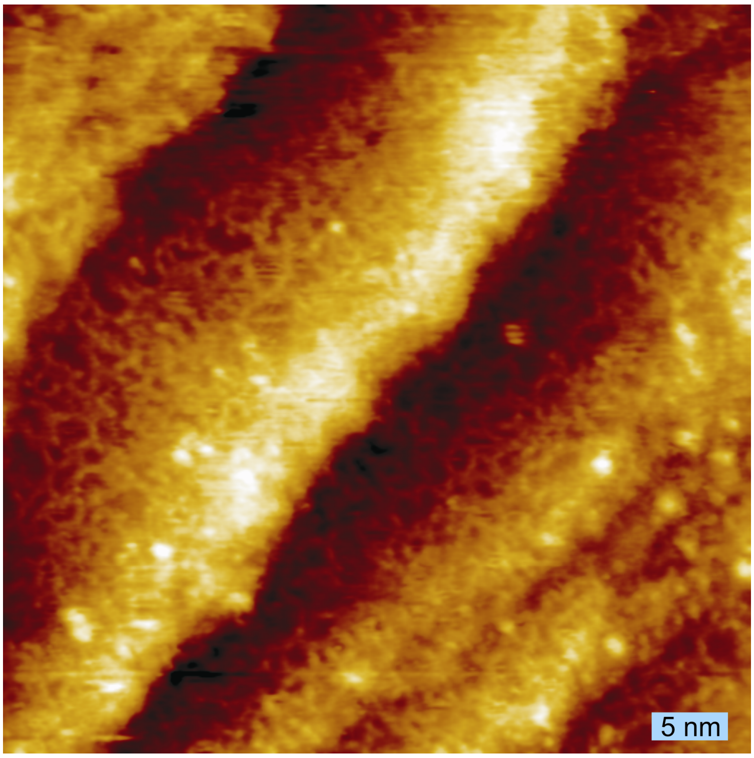

Figure S2. TBB evaporated on Cu(111) and annealed to 400 °C for 20 min (V = 1.3 V, I = 170 pA). The formerly covalent network is degraded and no ordered structure can be observed.

III. Forcefield and DFT calculations

The geometry of covalent organic frameworks is optimized by means of molecular mechanics simulations, conducted with the Cerius^2 (Version 4.5, MSI) software package and the Dreiding forcefield.[2] Periodic boundary conditions are applied to a hexagonal lattice with p6 symmetry and the lattice parameter is varied in order to find the minimum energy configuration. Free standing monolayers, i.e. without substrate influence are simulated. An energy difference of $< 2\times10^{-5}$ kcal/mol between single steps serves as a convergence criteria in all calculations.

The minimum energy is found for a lattice parameter of 2.21(2) nm (cf. Fig. S3) in agreement with the experimentally deduced value of 2.2 nm. Fig. S3 depicts the calculated values for the total energy as a function of lattice parameter. This lattice parameter corresponds to a distance of 1.28 nm between adjacent molecules.

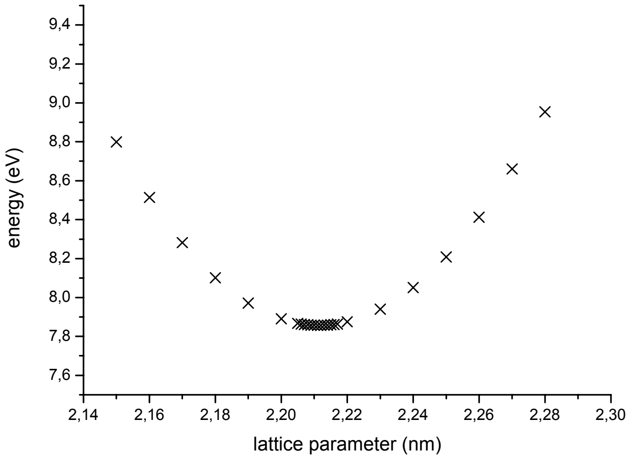

Figure S3. Calculated energy per unit cell for the geometry optimized framework as a function of lattice parameter according to molecular mechanics simulations. The isolated monolayer is fixed to p6 symmetry. A lattice parameter of 2.21(2) nm yields the minimum energy.

The geometry of an ideal hexagonal 2D COF is also optimized by density functional theory (DFT) calculations implemented in the Gaussian03 software package.[3] For this purpose, the B3LYP functional with 6-31G(d) basis set is used. Periodic boundary conditions are employed, the substrate is neglected. The input geometry is that of the previously force-field optimized geometry with p6 symmetry. Lattice parameter and angle are allowed to vary. Standardized convergence criteria as preset in Gaussian03 are used. The structure optimization yields lattice parameter of 2.245 nm and 2.243 nm and an angle of 120.02°. Adjacent phenyl rings are tilted by ~60° with respect to each other because of steric hindrance. Since the rotational barrier for a biphenyl is relatively low, interaction with the substrate is likely to cause planar adsorption as experimentally observed in the STM topographs.

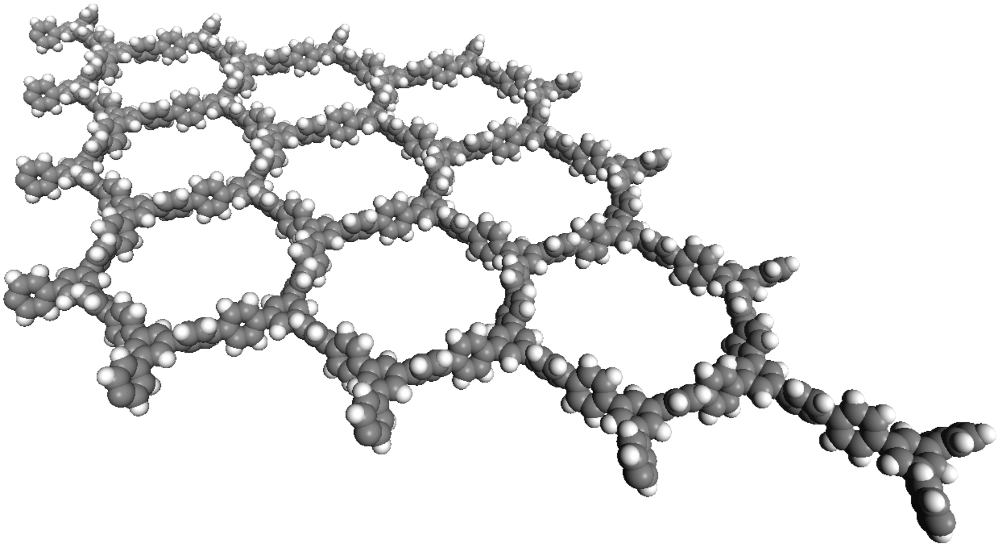

Figure S4. Model of an ideal hexagonal covalent organic framework. The geometry corresponds to the output of the DFT calculation with the above stated lattice parameters. Phenyl rings are tilted by about 60° with respect to each other.

IV. Thermogravimetric analysis

In an inert atmosphere, approximately 50 mg of TBB are heated with a rate of 1 °C per minute and the weight loss recorded. Degradation sets in at about 250 °C and is largely completed at ~375 °C. A residual of 4% of the original weight of sample remains. The temperature range for deposition by means of vacuum sublimation is 140° - 160°C as indicated by the colored bar in Fig S5 and is significantly lower than the decomposition temperature. Thus, the conclusion that intact molecules arrive at the surface can be drawn.

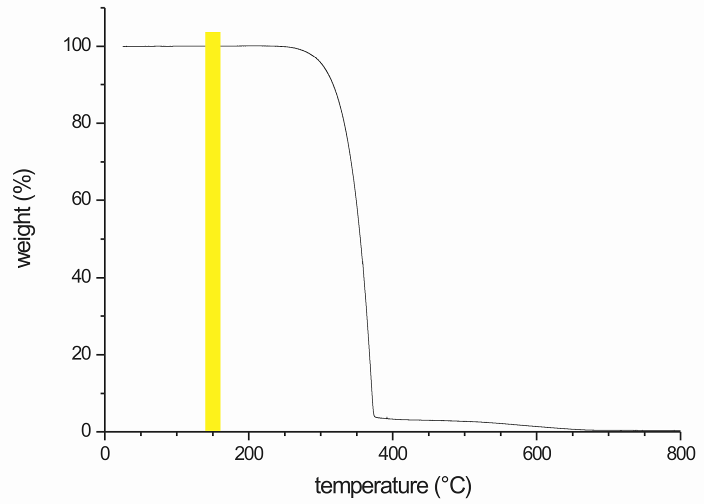

Figure S5. Thermogravimetric analysis of TBB. The colored area indicates the temperature range applied for thermal sublimation.

V. UV/Vis spectra

In order to support the hypothesis that TBB molecules remain intact upon vacuum sublimation, UV/Vis spectroscopy is conducted with n-hexane as solvent. A quartz glass cuvette with an optical path length of 1 mm is used. Unsubstituted 1,3,5-triphenylbenzene (TPB) serves as a control substance. Because of its significantly higher solubility, TPB solutions are diluted by a factor 30, whereas for TBB saturated solutions are used. Three different TBB solutions are prepared and compared: TBB as provided, TBB sublimated once onto the shutter, TBB residuals from the crucible of the Knudsen cell.

In the wavelength range from 200 nm to 500 nm, all absorption spectra exhibit two main peaks (see Fig. S6). For all three TBB solutions these two peaks are centered at the same wavelength, namely λ_1=206 nm and λ_2=260 nm. While for unsubstituted TPB the peak at longer wavelength is slightly blue-shifted and centered at λ_2=250 nm, thereby demonstrating the influence of the Br substitution. Because for all three TBB solutions the shape of the spectra and the peak positions remain the same, we conclude that both thermally sublimed molecules and molecules from the crucible which were held at a temperature of 140 °C - 160 °C for extended amounts of time remain intact.

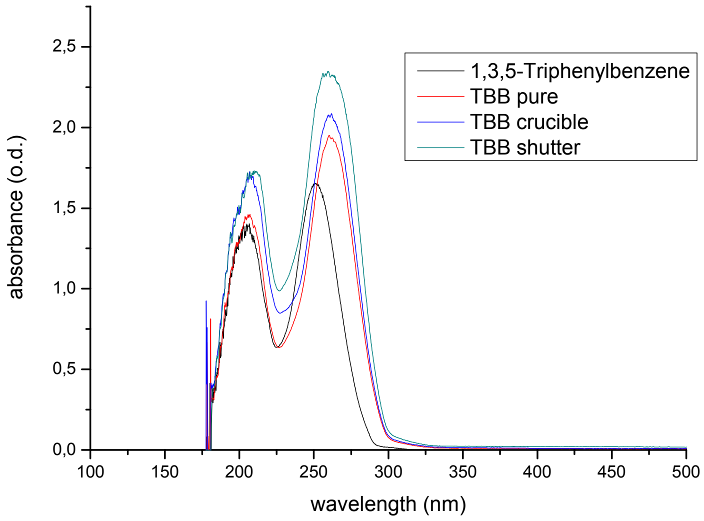

Figure S6. UV/Vis absorption spectra of TBB (saturated solutions) and 1,3,5-Triphenylbenzene (1:30 diluted solutions) in n-hexane

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(2) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, *94*, 8897-8909.

(3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian, Inc., Wallingford CT* **2004**.