Electronic Supplementary Information:

Synthesis of two-dimensional phenylene-boroxine networks through in-vacuo condensation and on-surface radical addition

Stefan Schlögl,[a,b] Thomas Sirtl,[a,b] Johanna Eichhorn,[a,b] Wolfgang M. Heckl,[a,b,c] and Markus Lackinger[a,b,c,*]

a) Department of Physics, TUM School of Education, Tech. Univ. Munich, Schellingstrasse 33, 80333 Munich, Germany
b) Deutsches Museum, Museumsinsel 1, 80538 Munich, Germany
c) Center for NanoScience (CeNS), Schellingstrasse 4, 80799 Munich, Germany
* Corresponding Author: E-mail: markus@lackinger.org, Tel: +49 89 2179 605

Table of content:

1. Experimental Details

All experiments were conducted with a home-built beetle type Scanning-Tunneling-Microscope at room temperature under ultra-high vacuum (UHV) conditions with a base pressure below 1×10^{-10}mbar. Lattice parameters and intermolecular distances were derived from STM topographs with an accuracy of ~5% after calibration with atomically resolved topographs of highly oriented pyrolytic graphite(001) (HOPG) and Ag(111) surfaces. Figure 2 was processed by a Gaussian 2×2 filter and correlation averaging.

Single crystal Ag(111) surfaces were prepared by cycles of Ne^+ ion-sputtering at 1 keV and electron-beam annealing at 550 °C for 50 minutes. The HOPG sample was cleaned by electron beam annealing up to 500 °C for 45 minutes. The cleanliness of the substrates was verified by STM imaging prior to deposition. All STM images have been recorded using a RHK electronics and XPM Pro 2.0.1.3 software.

The monomer 3,5-dibromophenylboronic acid (DBPBA) (CAS 117695-55-3, purity not specified) with the chemical formula $Br_2C_6H_3B(OH)_2$ and a molecular weight of 279.72 amu was obtained from Sigma Aldrich Germany. DBPBA was introduced into a home-built Knudsen cell and heated up to 190 °C for at least 1 h. During all deposition procedures the substrates were held at room temperature. The DBPBA sublimation temperature of 190 °C was determined by means of a Quartz Crystal Microbalance.

2. Raman spectra

Raman spectra were acquired from both a powder sample of thermally treated DBPBA and also a thin film of vacuum sublimed material with a confocal Raman microscope (alpha300 R, WITec GmbH, Ulm, Germany). All spectra were accumulated 10 times with an integration time of 1 s. An excitation laser power of 580 µW was used at a wavelength of $\lambda = 532$ nm. Using a 1800 mm^{-1} diffraction grating, the nominal resolution was 1.3 cm^{-1} per CCD-pixel. A ×100 microscope objective with a numerical aperture of 0.9 was used to efficiently collect the scattered photons. Since in the confocal geometry the signal arises from a spatially restricted volume of the sample (~400 nm lateral, ~ 1 µm vertical), probed volumes of powder sample and thin film are comparable.

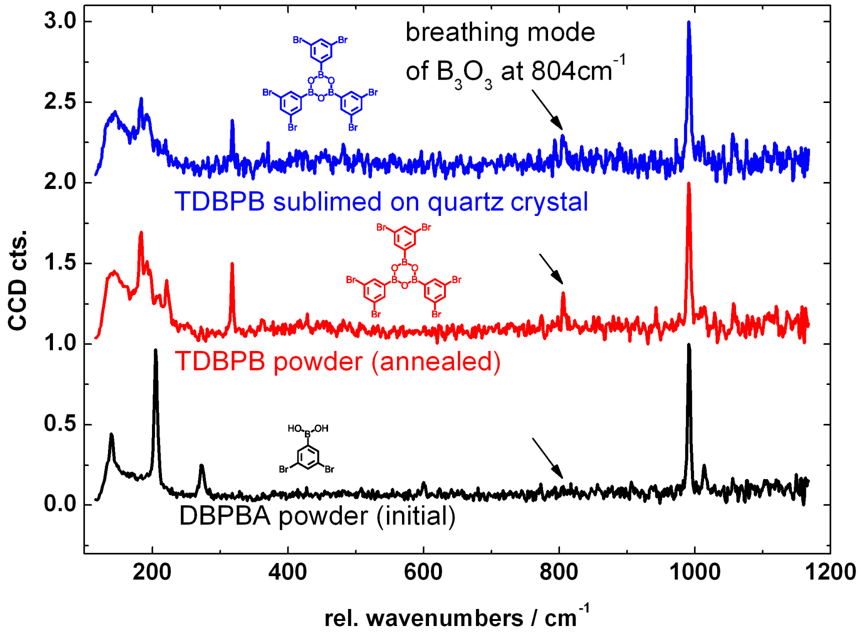

Figure S1: Raman spectra of untreated DBPBA (black), after thermal annealing at 190 °C for 120 minutes under vacuum conditions (red), and from a thin film deposited onto a quartz crystal microbalance located ~ 5 mm above the aperture of the Knudsen cell (blue). Both thermally treated and deposited materials exhibit new modes at ~317 cm^{-1} and ~804 cm^{-1} that are not present in the untreated DBPBA material. Also the bands around ~200 cm^{-1} are comparable for the thermally treated material and the thin film, but distinctly different from the unreacted starting material. The mode at ~317 cm^{-1} cannot be assigned, but the weak mode at ~804 cm^{-1} corresponds to the breathing mode of boroxine rings.[1] Its presence indicates the cyclocondensation of three DBPBA molecules into TDBPB.

3. LEED measurements

LEED experiments were carried out in an additional UHV system at a base pressure of 1×10^{-10} mbar. A LEED optics from Omicron NanoTechnology GmbH and control electronics from SPECS Surface Nano Analysis GmbH was used. Ag(111) single crystal surfaces were prepared by subsequent Ar^+ ion-sputtering and electron-beam annealing up to 550 °C for ~10 min. The thermal treatment of DBPBA and deposition parameters were similar to the STM experiments. LEED diffraction patterns were recorded with the sample at room temperature.

LEED experiments after room temperature deposition show rather broad reflections arranged in two rotational domains of a hexagonal lattice. Within the experimental error, the results are consistent with a commensurate $(2\sqrt{7}\times2\sqrt{7})R\pm19°$ structure that corresponds to a lattice parameter of 1.53 nm.

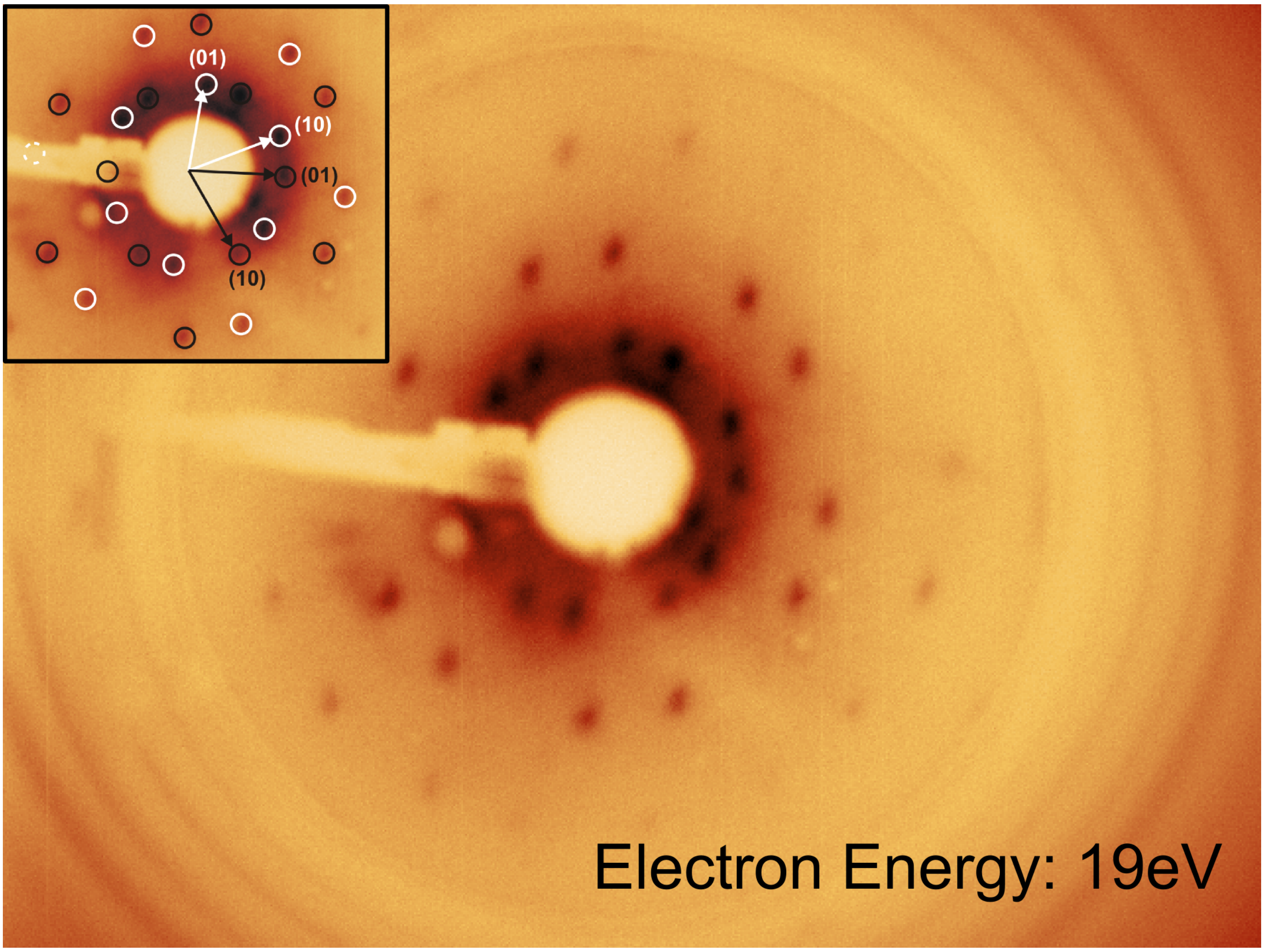

Figure S2: LEED diffraction pattern of an ordered TDBPB monolayer on Ag(111) acquired at an electron energy of 19.0 eV at room temperature. White and black circles in the inset assign the first and second order reflections to one of the two rotational domains. Numbers in parenthesis are the (hk) values of the respective reflections.

4. Additional STM topographs

4.1. TDBPB deposited onto Ag(111) – without further thermal treatment

Deposition onto Ag(111) leads to non-covalent less well ordered TDBPB arrangements. The outer shape of the adsorbates and the six bright peripheral protrusions indicate adsorption of intact molecules, i.e. homolysis of all molecules does not occur for room temperature deposition onto Ag(111) without further thermal activation. Yet, occasionally observed dimers may already be covalently interconnected, as suggested by their relative spacing (see red arrow in Fig. S3). Also low concentrations of smaller impurities can also be discerned in the STM topographs. Their size and less symmetric appearance suggest that those impurities may be unreacted DBPBA monomers (see green arrow in Fig. S3).

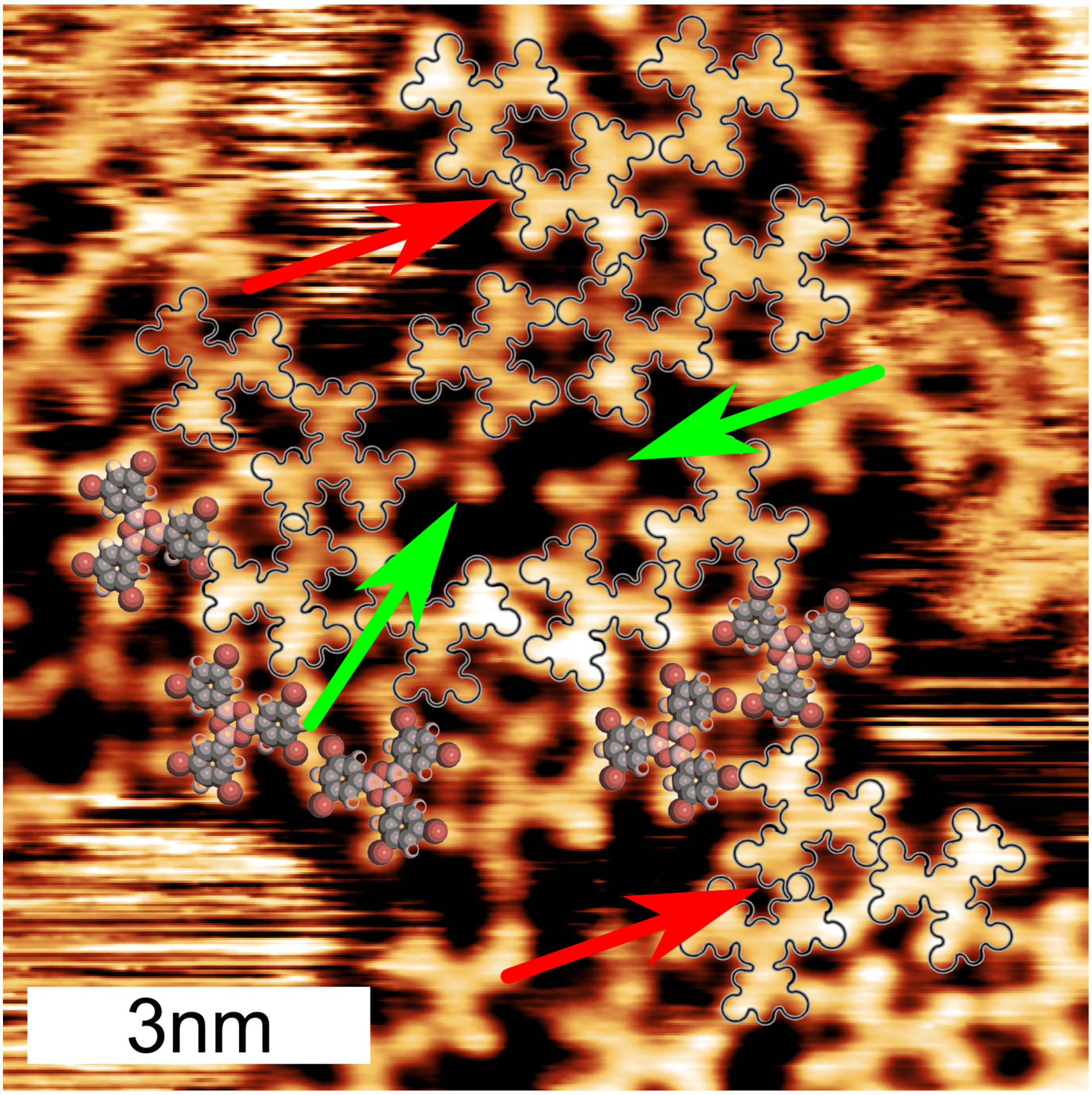

Figure S3: STM topograph of 1,3,5-tris(3,5-dibromophenyl)-boroxine TDBPB after deposition onto Ag(111) held at room temperature (+0.6 V, 60 pA). The apparent height of the molecules with respect to the substrate amounts to ~100 pm.

4.2. TDBPB deposited onto HOPG – without further thermal treatment

A close-up STM topograph of TDBPB deposited onto HOPG shows submolecular features, where the three-fold symmetry and six peripheral features can clearly be discerned. The 2 × 2 unit cell image has been processed by correlation averaging from an original 5 × 5 unit cell image using the software Image Metrology SPIP 5.1.2.

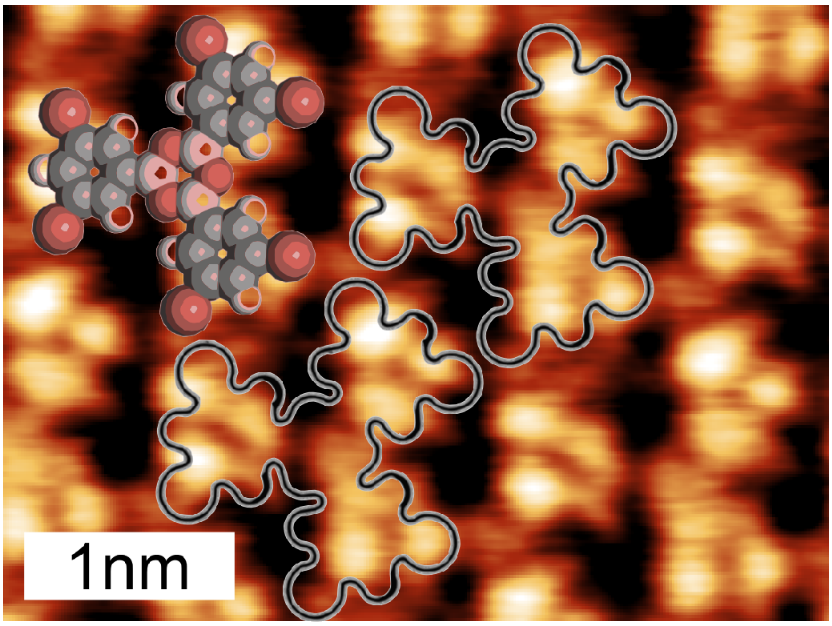

Figure S4: STM topograph of TDBPB deposited on HOPG showing the molecules in a hexagonal array with lattice constants of (1.5±0.1) nm and submolecular resolution.

4.3. TDBPB deposited on Ag(111) – after thermal treatment

Fig. S5 provides additional features of the polymerized phenylene-boroxine network:

- The blue arrows indicate a closed circle consisting of six combined phenylene-boroxine rings arranged around a centered hexaphenylene ring and arises from exclusive AB-stacking.
- The red arrows mark examples for AA-stacking, which consist of rings with five phenylene and one boroxine.
- Only two out of shown 30 rings are five-membered rings occasionally observed as linkers between smaller covalent aggregates (denoted by green arrows).

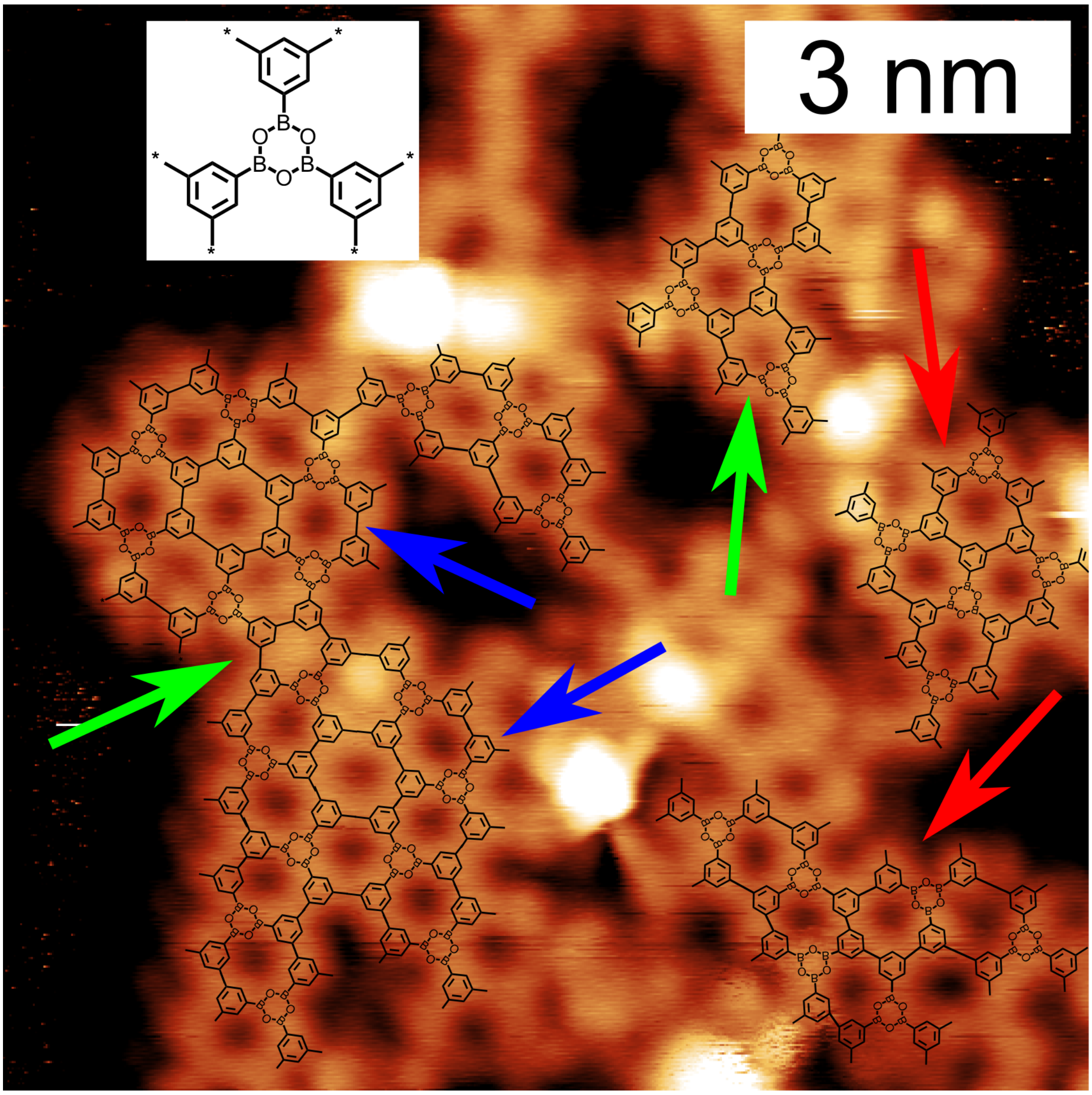

Figure S5: STM topograph of 1,3,5-tris(3,5-dibromophenyl)-boroxine TDBPB after deposition onto Ag(111) and annealing at elevated temperatures (+0.6 V, 60 pA). AB and AA stacking are indicated by blue and red arrows, respectively, while green arrows highlight five membered rings.

5

5. DFT results

5.1. Lattice parameter and electronic structure of p6mm phenylene-boroxine networks

DFT simulations were conducted of regular phenylene-boroxine networks with p6mm symmetry that would result from exclusive ABAB stacking. The simulations employ a gradient corrected (GGA) functional PW91[2] with plane wave basis set as implemented in the CASTEP code.[3] The substrate influence could be neglected, because for covalent networks molecule-molecule interactions are significantly stronger than molecule-substrate interactions. Total energies per unit cell were calculated as a function of lattice parameter for a hexagonal unit cell with periodic boundary conditions. The minimum total energy per unit cell was found for a lattice parameter of 1.55 nm (as shown in Fig. S6(a)). This lattice parameter of the p6mm unit cell corresponds to a distance of 0.775 nm between adjacent pores. The electronic structure (cf. Fig. S6(b)) of the p6mm network exhibits a HOMO-LUMO energy gap of ~2.8 eV and negligible dispersion in k-space, indicating localized immobile electrons. Yet, since DFT is known to underestimate band gaps,[4] the actual HOMO-LUMO gap might be larger.

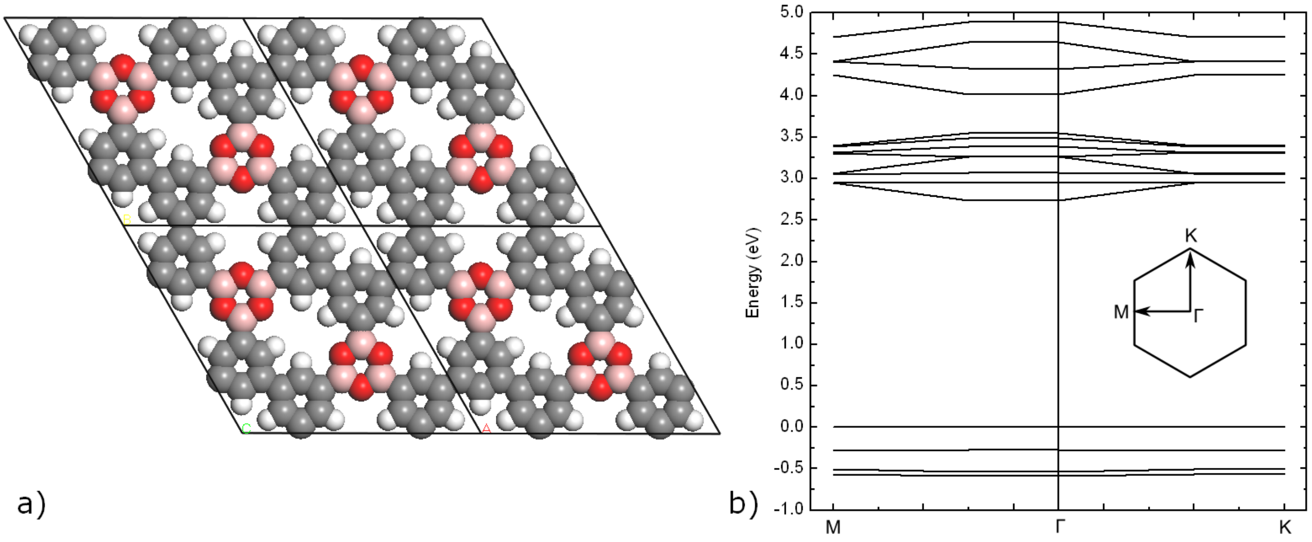

Figure S6: (a) Model of the covalent network with optimized lattice parameter: hexagonal lattice parameters a=b=1.55 nm and periodic boundary conditions. (b) DFT CASTEP calculations of the electronic structure yield a HOMO-LUMO energy gap of 2.8 eV and the absence of dispersion in k-space.

5.2. Structural properties of a single TDBPB molecule

Thermal treatment of DBPBA results in cyclo-condensation of three molecules into 1,3,5-tris(3,5-dibromophenyl)-boroxine (TDBPB) molecules. An experimental proof of this hypothesis was accomplished by deposition of the product molecule onto unreactive substrates and subsequent STM imaging. In order to obtain precise theoretical dimensions of TDBPB molecules for overlaying them to the STM topographs, geometry optimized DFT calculations of isolated molecules were conducted using Gaussian03 with a B3LYP functional and a 6-31G* basis set applying standard convergence criteria.[5] The geometry optimized TDBPB molecule is essentially planar, although the substrate was neglected and no additional constraints have been applied. The results are depicted in Fig. S7 and show that boroxine and phenyl rings in this compound are almost similar in size, with deviations below 1 %.

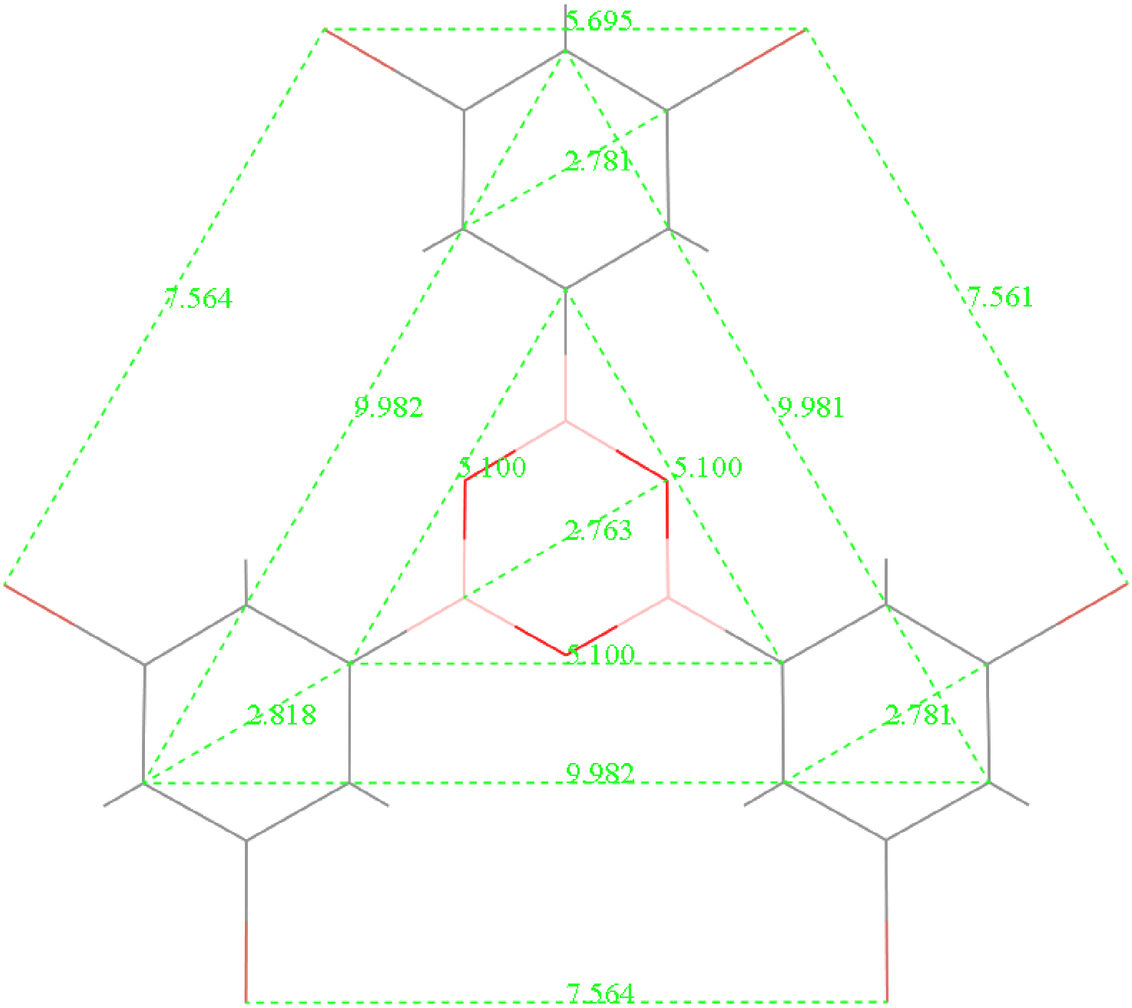

Figure S7: DFT geometry optimized structure of TDBPB molecules in the gas phase. All distances are given in Å and indicate nearly equal diameters of ~2.8 Å for phenyl and boroxine rings, respectively. Based on these calculations, we anticipate that size differences between boroxine and phenyl rings are indistinguishable in STM measurements.

6. NMR data of untreated and thermally treated DBPBA

Proton 1H-NMR spectra were acquired with a JEOL ECP-270 spectrometer at frequencies of 270 MHz and a sample temperature of 298 K. The molecules were dissolved in Methanol-D4 and no additional standard has been used. The data was processed using the Delta 5.0.1 Software from JEOL and standard FFT settings.

The proton peak of the free boronic acid group is observed for the initial DBPBA molecules (Fig. S8), but is absent in the NMR spectra of the thermally treated TDBPB molecules (Fig. S9) indicating thermally activated condensation. A comparison of the proton peaks for unreacted and treated molecules suggests a high yield of the thermally activated reaction.

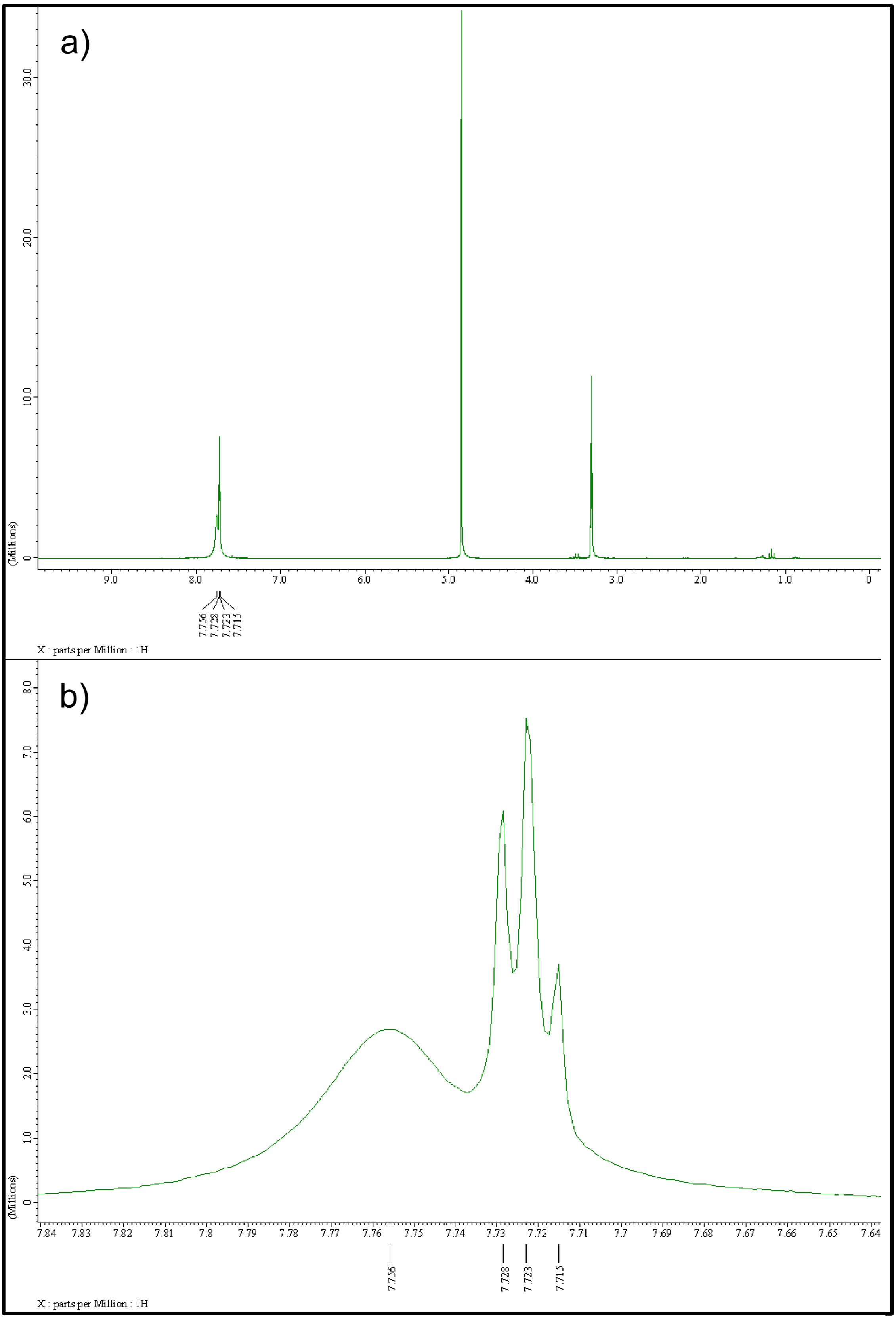

Figure S8: (a) NMR spectra of untreated DBPBA (^{1}H NMR, 270 MHz, CD_4O): δ_H 7.756 (OH), 7.728 (CH), 7.723 (CH), 7.715 (CH), 7.756 (OH). Small residues of undeuterated solvent molecules account for the peaks at 4.8 ppm and 3.3 ppm. (b) Close-up of (a). The broad peak centered at δ=7.756 (OH) can be assigned to the protons of the free boronic acid group, while the remaining multiplet originates from the aromatic protons.

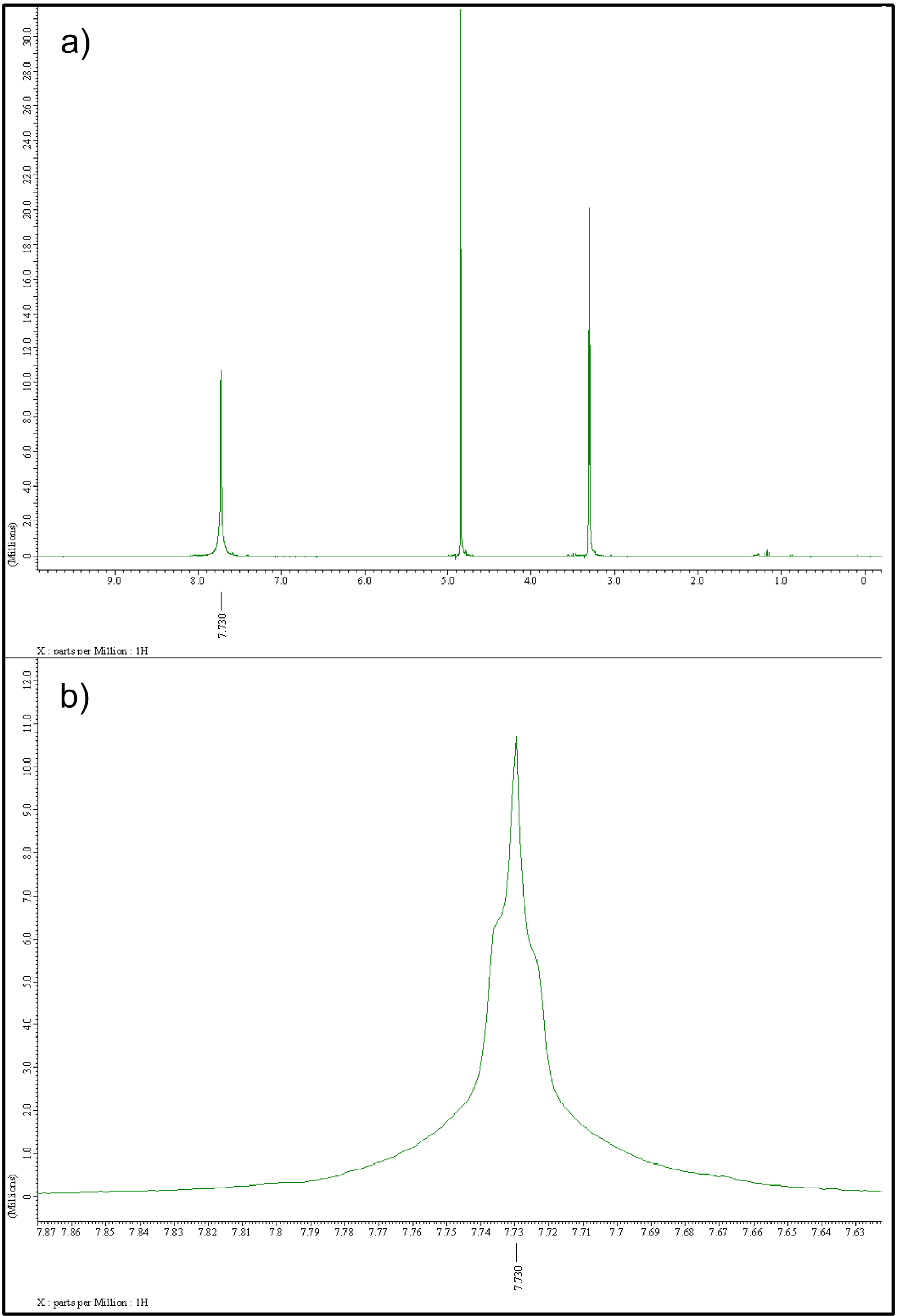

Figure S9: (a) NMR spectra of thermally treated DBPBA (190 °C, 120 minutes) (^{1}H NMR, 270 MHz, CD_4O): δ_H 7.730 (CH), 7.756 (OH)). Again, undeuterated solvent molecules account for the peaks at 4.8 ppm and 3.3 ppm. (b) Close-up of (a). The broad peak at δ=7.756 (OH) is absent after thermal treatment, indicating the condensation of DBPBA into TDBPB.

References:

1. J. Goubeau and H. Keller, *Z. Anorg. Allg. Chem.*, 1953, **272**, 303-312.
2. J. Perdew and Y. Wang, *Physical Review B*, 1992, **45**, 13244-13249.
3. M. Segall, P. Lindan, M. Probert, C. Pickard, P. Hasnip, S. Clark and M. Payne, *J. Phys.: Condens. Matter*, 2002, **14**, 2717-2744.
4. A. J. Cohen, P. Mori-Sanchez and W. Yang, *Science*, 2008, **321**, 792-794.
5. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, , J. R. C. M. A. Robb, G. Scalmani, V. Barone, B. Mennucci, , H. N. G. A. Petersson, M. Caricato, X. Li, H. P. Hratchian, , J. B. A. F. Izmaylov, G. Zheng, J. L. Sonnenberg, M. Hada, , K. T. M. Ehara, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, , O. K. Y. Honda, H. Nakai, T. Vreven, J. A. Montgomery, Jr., , F. O. J. E. Peralta, M. Bearpark, J. J. Heyd, E. Brothers, , V. N. S. K. N. Kudin, T. Keith, R. Kobayashi, J. Normand, , A. R. K. Raghavachari, J. C. Burant, S. S. Iyengar, J. Tomasi, , N. R. M. Cossi, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, , C. A. V. Bakken, J. Jaramillo, R. Gomperts, R. E. Stratmann, , A. J. A. O. Yazyev, R. Cammi, C. Pomelli, J. W. Ochterski, , K. M. R. L. Martin, V. G. Zakrzewski, G. A. Voth, , J. J. D. P. Salvador, S. Dapprich, A. D. Daniels, , J. B. F. O. Farkas, J. V. Ortiz, J. Cioslowski, and a. D. J. Fox, *Gaussian, Inc., Wallingford CT, 2010*.