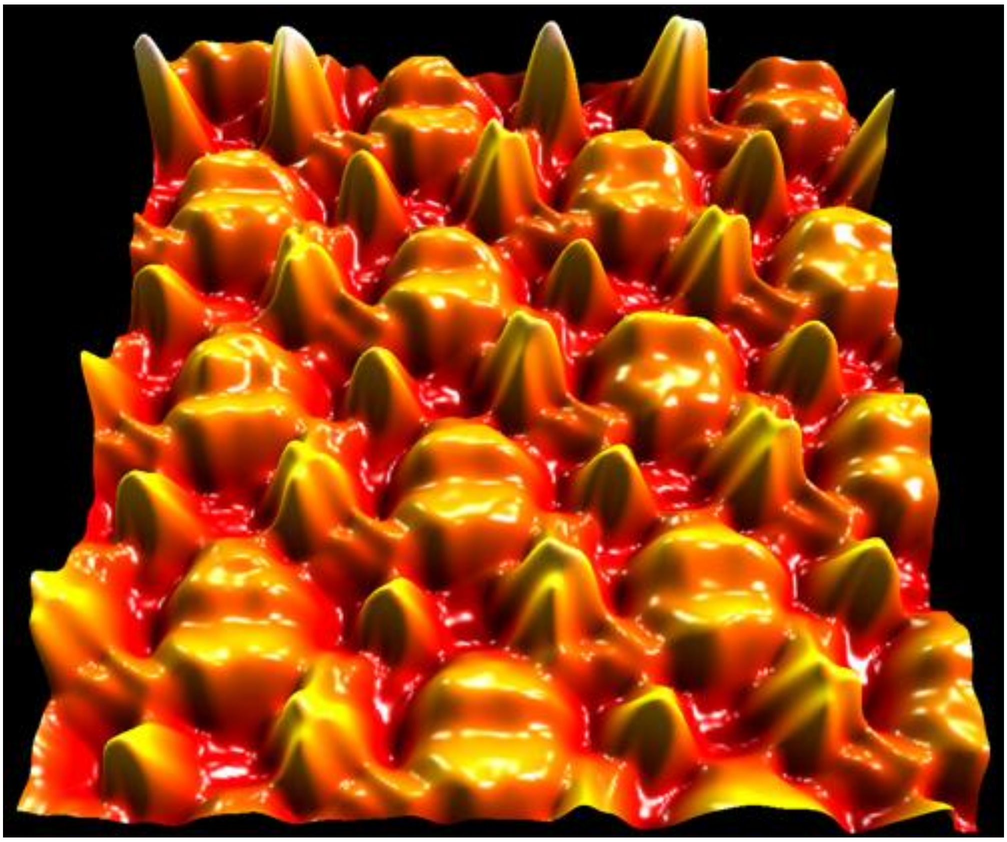
ChemComm

This article is part of the

Molecule-based Surface Chemistry web themed issue

Guest Editors include Steven De Feyter, Federico Rosei & Dmitrii Perepichka

Please visit the website to access the other articles in this issue:-
http://www.rsc.org/chemcomm/surfacechemistry



ChemComm

Dynamic Article Links

Cite this: *Chem. Commun.*, 2011, **47**, 12355–12357

www.rsc.org/chemcomm

COMMUNICATION

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

Stefan Schlögl,[ab] Thomas Sirtl,[ab] Johanna Eichhorn,[ab] Wolfgang M. Heckl[abc] and Markus Lackinger*[abc]

Received 30th June 2011, Accepted 10th October 2011
DOI: 10.1039/c1cc13896k

We report on covalent two-dimensional phenylene–boroxine hybrid-networks that were synthesized under ultra-high vacuum conditions from doubly functionalized monomers through thermally activated condensation prior to deposition and successive heterogeneously catalyzed radical addition on Ag(111). Structural properties were characterized *in situ* by high resolution Scanning-Tunneling-Microscopy (STM).

The synthesis of covalent two-dimensional organic materials is a challenging but promising goal in material science. Single layer graphene is the most abundant and best studied 2D organic material.[1] The inherent absence of an electronic band-gap gives rise to intriguing physics, yet, other envisaged applications require a band-gap that needs to be introduced by dopant side groups.[2] While graphene can meanwhile routinely be prepared by exfoliation of graphite or graphite oxide,[3] a bottom-up synthetic approach through polymerisation of organic monomers offers structural and chemical versatility.[4–6] On-surface synthesis of 2D covalent networks was accomplished through various types of polymerization reactions,[4] predominantly condensation[7–9] and radical addition of halogenated precursors.[10–12] Herein we demonstrate the synthesis of covalent hybrid-networks comprised of both phenyl and boroxine rings arranged on a hexagonal lattice. Boroxine rings (B_3O_3) are hexagonal, planar, and similar in size to phenyl rings.[13] In this respect it is interesting to study their interchangeability in covalent networks and the impact on structural properties.[14,15] Substitution of phenyl with boroxine rings is also known to modify material properties, *e.g.* renders polymeric materials flame retardant.[16,17] Synthesis of the proposed covalent hybrid-networks is based on 3,5-dibromophenylboronic acid (DBPBA). First, heating of DBPBA thermally activates condensation which yields less reactive TDBPB monomers that are then deposited onto Ag(111). Subsequent thermal annealing initiates the on-surface polymerization *via* radical addition (see Fig. 1 for a reaction scheme). To this end, the aromatic DBPBA monomer is doubly functionalized with two different functional groups: one boronic acid group for condensation and two bromine substituents for surface-mediated radical addition. On Ag(111) radical addition of brominated precursor molecules is kinetically suppressed at room temperature and thermal annealing is required to initiate the polymerization through homolysis of the bromine substituents.[12] On the other hand, the condensation of boronic acids can be thermally activated *in vacuo* without the need for a catalyst.[8] In the proposed reaction scheme, the cyclo-condensation of DBPBA molecules into TDBPB is the last synthesis step prior to deposition and carried out *in vacuo* by a mere thermal treatment at 190 °C. Boronic acids preferably react into boroxine rings through cyclo-condensation of three entities, whereby three H_2O molecules are released. Because DBPBA is only monofunctionalized for

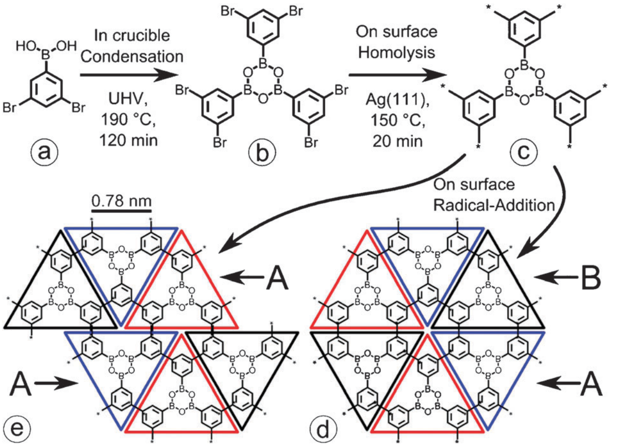


Fig. 1 Reaction scheme for synthesis of covalent phenylene–boroxine hybrid-networks from 3,5-dibromophenylboronic acid (DBPBA) monomers. First thermally activated condensation of (a) DBPBA in the crucible of a Knudsen cell results in (b) 1,3,5-tris(3′,5′-dibromophenyl)-boroxine (TDBPB). Deposition of TDBPB on Ag(111) and further thermal activation yield (c) surface-stabilized triphenylene–boroxine hexaradicals (TPBHR) that subsequently polymerize into covalent phenylene–boroxine networks through radical addition. Hereby the bromine substitution pattern of TDBPB allows for two different stackings: (d) ABAB and (e) AA.

---

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

† This article is part of the *ChemComm* 'Molecule-based surface chemistry' web themed issue.

‡ Electronic supplementary information (ESI) available: Experimental and calculational details; DFT results; LEED, NMR, additional STM, and Raman data. See DOI: 10.1039/c1cc13896k

condensation, the reaction does not yield interconnected networks as for diboronic acids,[13] but larger 1,3,5-tris(3′,5′-dibromophenyl)-boroxine molecules (TDBPB, see Fig. 1(b)). This "in-crucible synthesis" is feasible, because cyclo-condensation of the boronic acid functionality is preferred over sublimation, whereby thermal sublimation of the free boronic acid DBPBA is essentially not possible. Instead a relatively high experimentally determined sublimation temperature of 190 °C indicates thermal sublimation of the larger threefold-symmetric TDBPB monomer that already features both phenyl and boroxine rings. Since bromine functionalities are not known to react at these relatively low temperatures without the presence of a catalyst, further polymerization reactions in the crucible are not expected, but thermal sublimation of intact molecules. The thermal "in-crucible synthesis" of TDBPB was verified by comparative Raman spectroscopy and NMR of the initial and thermally treated DBPBA compound (see ESI‡ for spectra and details). In additional experiments a DBPBA filled crucible was used to deposit organic molecules onto graphite(001) as well as onto Ag(111), with both substrates held at room temperature. These experiments further substantiate the thermally activated condensation of DBPBA into TDBPB and its subsequent deposition. On inert graphite(001) substrates well-ordered self-assembled trigonal monolayers with a lattice parameter of (1.50 ± 0.10) nm were observed. In the STM topograph shown in Fig. 2(a) threefold symmetric molecular entities can be identified, whose size and symmetry are consistent with intact TDBPB molecules. Moreover, six peripheral protruding spherical features can be discerned and are assigned to the bromine substituents of intact TDBPB. In the proposed structural model, cyclic halogen–halogen–halogen bonds between three bromine substituents with experimental bromine–bromine distances of (0.45 ± 0.10) nm stabilize the self-assembled monolayer (Fig. 2(b)). Halogen bonds are attractive anisotropic electrostatic interactions between Cl, Br, or I subsitutents that originate from a non-spherical charge distribution at the halogen with a negative ring and a positive end cap.[18,19] Trigonal cyclic arrangements optimize electrostatic interactions and were similarly found in both 3D and 2D structures.[18,20] Experimental Br–Br distances here are larger than those found in bulk crystals (0.36 nm) and hint towards a surface influence. STM measurements of TDBPB deposited onto Ag(111) reveal a less well ordered arrangement of threefold symmetric molecules (Fig. S3, ESI‡). Again, size and symmetry of the molecules and the discernible bromine substituents suggest deposition of TDBPB rather than the precursor material DBPBA. Albeit some monomers are already interconnected and some contrast features point toward deposition of a low fraction of unreacted DBPBA monomers, the great majority of TDBPB molecules remains intact upon deposition onto Ag(111) held at room temperature and the bromine substituents are not cleaved off. Although the intermolecular arrangements exhibit only short-range order, molecular aggregates are likewise stabilized by halogen-bonds similar to the monolayers on graphite. LEED measurements of similarly prepared samples show a hexagonal pattern of rather broad reflections. The LEED pattern is consistent with two orientational domains of $(2\sqrt{7}\times2\sqrt{7})$ ± R19° that corresponds to a lattice parameter of a = 1.53 nm (Fig. S2, ESI‡). Yet, the diffraction pattern most likely does not arise from long-range ordered monolayers, but from short range order, where TDBPB dimers adopt a preferred intermolecular distance of 1.5 nm and a preferred orientation with respect to the substrate. The LEED lattice parameter is consistent with the nearest-neighbor distance in STM measurements of less-well ordered samples. Although in the STM experiments, the deposition rate was varied from 0.02–0.1 monolayer per minute, no long-range ordered monolayers were obtained on Ag(111), maybe because of DBPBA impurities and first covalent interlinking reactions.

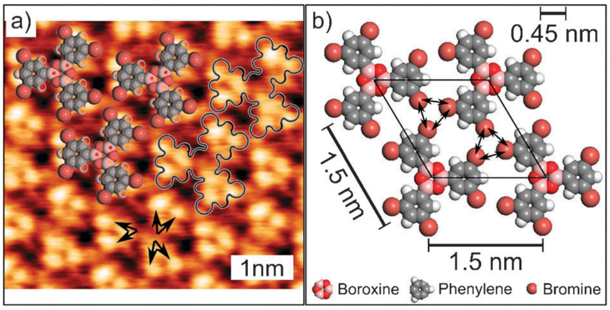


Fig. 2 Self-assembled TDPBP monolayer on graphite(001). (a) STM topograph (+0.60 V, 40 pA, correlation-averaged); as evident from the scaled overlay, size and symmetry of the molecular entities are consistent with threefold-symmetric TDBPB molecules and six peripheral bromines of one molecule are highlighted by black arrows. (b) Tentative model of the TDBPB monolayer, where molecules interact through cyclic halogen–halogen–halogen bonds (indicated by black arrows).

Because of its bromine substitution pattern and its planar structure, TDBPB is a well suited monomer for the synthesis of hexagonal phenylene–boroxine hybrid-networks through surface-mediated polymerization. While annealing of TDBPB monolayers up to 200 °C for 10 min on graphite(001) only leads to thermally induced desorption, annealing on Ag(111) (10 min at 130 °C) activates the dehalogenation reaction aided by the catalytic properties of the surface,[10,12,21] whereby triphenylene–boroxine hexaradicals (TPBHR) are generated (Fig. 1(c)). Subsequently, these radicals polymerize through radical addition into covalent networks directly on the surface (Fig. 3(a) and (b)). As illustrated in the reaction scheme the polymerization of hexaradicals can proceed in two different stereochemical arrangements (Fig. 1(d) and (e)). Two adjacent monomers can interlink *via* two covalent intermolecular bonds. Since the monomers possess a triangular footprint this means they adjoin at their bases. Exclusive formation of these two-fold covalent interconnects would result in a periodic covalent network with ABAB stacking and *P6mm* symmetry as depicted in Fig. 1(d). However, radical addition is also possible in a way that one monomer forms two covalent bonds with two different monomers on one side of its triangular footprint. Continuation of this binding motif into extended two dimensional networks yields AA stacking (Fig. 1(e)), where the tips of the triangles are aligned with the center of the baseline in the row above. The resulting periodic network would still exhibit a hexagonal arrangement of boroxine and phenyl rings, but would possess considerably lower symmetry (*P2mg*). In the experiment random stacking is expected, since the polymerization cannot be controlled, and consequently a less regular distribution of boroxine rings within the hexagonal network. Polymerization, *i.e.* the formation of covalent networks upon thermal treatment is unambiguously verified by

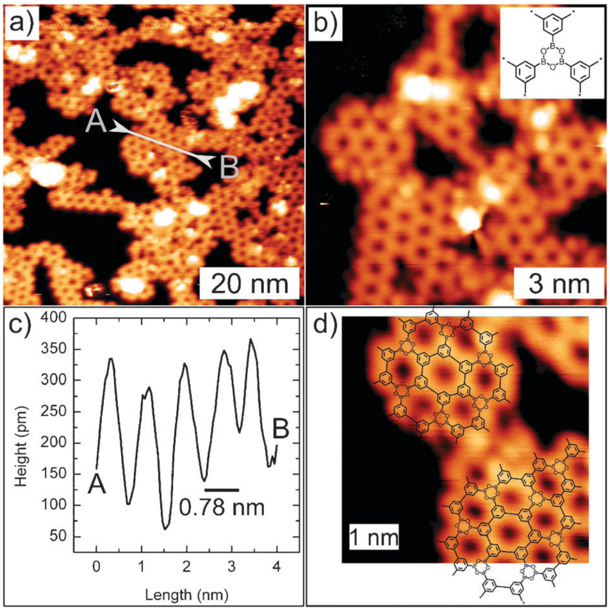


Fig. 3 (a) Overview and (b) close-up STM topographs (+0.7 V, 50 pA) of annealed TDPBP monolayers on Ag(111). Thermally activated dehalogenation and radical addition yield covalent networks. (c) Line-profile along A–B in image (a); it indicates a lattice parameter, *i.e.* interpore distance, of (0.78 ± 0.10) nm. (d) Close-up of covalent networks with molecular overlay. The aggregate is formed by exclusive AB stacking.

comparison of precise experimental STM derived structure parameters with theoretical values. The line-profile in Fig. 3(c) indicates a spacing between adjacent six-membered rings of (0.78 ± 0.10) nm. This value is in perfect agreement with the 0.78 nm as obtained from geometry optimized DFT calculations of the *P6mm* structure (*cf.* ESI‡).

The DFT calculations also yield an approximative value of 2.8 eV for the HOMO–LUMO energy gap. The electronic states do not exhibit a significant dispersion in k-space. This means that electrons are localized with low mobility and almost infinite effective mass. Similar hexagonal networks that only consist of phenylene rings show a less flat dispersion relation. Comparison of those structurally similar networks denotes effective electronic decoupling through boroxine rings[22] (details can be found in ESI‡).

The covalent phenylene–boroxine networks do not exhibit long-range order. Yet, in covalent networks that were synthesized from structurally much simpler tritopic monomers as for instance tribromophenylbenzene[12,21] non-ideal strained covalent rings composed of more or less than six monomers occur with densities comparable to those of ideal rings. In polymerized TDBPB networks strained rings are only observed occasionally (*cf.* ESI‡). Apparently, their formation becomes less likely due to the complex bond topology of the six-fold bromine-substituted monomer. Although the polymerized TDBPB networks exhibit mostly regular rings, the resulting domain size is comparatively small. Different azimuthal orientations to the substrate impair coherent interconnection into long-range ordered networks. In contrast to covalent networks from simple tritopic monomers, now vacancies can be observed (see Fig. S5, ESI‡). Around these vacancies, the hexagonal lattice is preserved and just one monomer is missing, leading to AA stacking.

In summary, we show that a covalent hybrid-network consisting of both phenyl and boroxine rings can be synthesized entirely in UHV from a comparatively simple monomer. The employed monomer was doubly functionalized with both boronic acid groups and bromine substituents for condensation and radical addition reactions, respectively. We find that vacuum sublimation of even comparatively small boronic acids is not possible, because increasing the crucible temperature up to the sublimation point already thermally activates self-condensation. Then again, the preferred and reliable self-condensation of boronic acids into boroxine rings can also serve as a design principle for carrying out the last synthesis step in the crucible of the Knudsen cell and deposit more complex monomers from abundantly available, structurally simpler precursor molecules.

We thank Dr A. M. Gigler for Raman measurements and S. Hug and Prof. B. V. Lotsch for NMR measurements. Funding by the Nanosystems-Initiative Munich (NIM) cluster of excellence, Elitenetzwerk Bayern (St. S.) and Verband der Chemischen Industrie (T.S.) is gratefully acknowledged.

Notes and references

1 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.
2 J. Wintterlin and M. L. Bocquet, *Surf. Sci.*, 2009, **603**, 1841–1852.
3 H. C. Schniepp, J. L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville and I. A. Aksay, *J. Phys. Chem. B*, 2006, **110**, 8535–8539.
4 A. Gourdon, *Angew. Chem., Int. Ed.*, 2008, **47**, 6950–6953.
5 D. F. Perepichka and F. Rosei, *Science*, 2009, **323**, 216–217.
6 J. Sakamoto, J. van Heijst, O. Lukin and A. D. Schlüter, *Angew. Chem., Int. Ed.*, 2009, **48**, 1030–1069.
7 C. H. Schmitz, J. Ikonomov and M. Sokolowski, *J. Phys. Chem. C*, 2009, **113**, 11984.
8 S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf, E. Lægsgaard, F. Besenbacher and T. R. Linderoth, *Angew. Chem., Int. Ed.*, 2008, **47**, 4406.
9 N. A. A. Zwaneveld, R. Pawlak, M. Abel, D. Catalin, D. Gigmes, D. Bertin and L. Porte, *J. Am. Chem. Soc.*, 2008, **130**, 6678–6679.
10 M. Bieri, M. Nguyen, O. Gröning, J. Cai, M. Treier, K. Ait-Mansour, P. Ruffieux, C. Pignedoli, D. Passerone, M. Kastler, K. Müllen and R. Fasel, *J. Am. Chem. Soc.*, 2010, **132**, 16669–16676.
11 L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. Peters and S. Hecht, *Nat. Nanotechnol.*, 2007, **2**, 687–691.
12 R. Gutzler, H. Walch, G. Eder, S. Kloft, W. M. Heckl and M. Lackinger, *Chem. Commun.*, 2009, 4456–4458.
13 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170.
14 M. J. Farrall and J. M. J. Frechet, *J. Org. Chem.*, 1976, **41**, 3877–3882.
15 J. Pellon, L. H. Schwind, M. J. Guinard and W. M. Thomas, *J. Polym. Sci.*, 1961, **55**, 161–167.
16 A. L. Korich and P. M. Iovine, *Dalton Trans.*, 2010, **39**, 1423–1431.
17 A. B. Morgan, J. L. Jurs and J. M. Tour, *J. Appl. Polym. Sci.*, 2000, **76**, 1257–1268.
18 E. Bosch and C. L. Barnes, *Cryst. Growth Des.*, 2002, **2**, 299–302.
19 S. L. Price, A. J. Stone, J. Lucas, R. S. Rowland and A. E. Thornley, *J. Am. Chem. Soc.*, 1994, **116**, 4910–4918.
20 H. Walch, R. Gutzler, T. Sirtl, G. Eder and M. Lackinger, *J. Phys. Chem. C*, 2010, **114**, 12604–12609.
21 M. O. Blunt, J. C. Russell, N. R. Champness and P. H. Beton, *Chem. Commun.*, 2010, **46**, 7157–7159.
22 D. Armstrong and P. Perkins, *J. Chem. Soc. A*, 1967, 790–792.