Supporting information for

Porous graphenes: Two-dimensional polymer synthesis with atomic precision

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Synthesis and characterization of CHP

Detailed information on the synthesis and characterization of CHP can be found in the publication by Pisula et. al.[1]

The onset of CHP coupling towards polymer networks

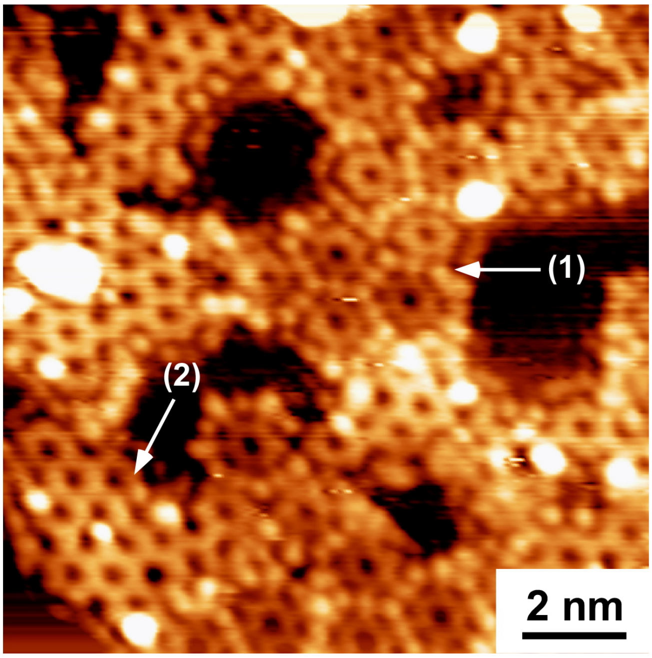

Fig. S1 STM image (-1.5 V, 30 pA) obtained after room-temperature deposition of CHP on Ag(111) and a 5-min post-annealing step at 575 K. Arrow (1) points to domains of unreacted molecules surrounded by iodine atoms, and (2) marks covalently bonded species.

Figure S1 shows an STM image recorded after CHP deposition on Ag(111) at room temperature and post-annealing the surface at 575 K for 5 min. Two different species can be discerned in the image. Arrow (1) points to a domain of unreacted molecules. This is evident by comparison with Fig. 2, which shows CHP molecules deposited on Ag(111) at room temperature. In addition, the above STM image shows bright spherical features around unreacted CHP molecules, which are assigned to iodine atoms (*cf.* Fig. 2). On the other hand, arrow (2) in Fig. S1 marks a domain of reacted, *i.e.* covalently bonded molecules. This is evident by the characteristic honeycomb structure, which is obvious in Fig. 3 for the fully developed polyphenylene network. Furthermore, analysis of the periodicity of the honeycomb structure gives a pore-to-pore distance of 7.4 Å, in excellent agreement with the value of 7.45 Å predicted by AM1 calculation[2] (see also the next section). In summary, STM images such as the one showed above give clear evidence for CHP aryl–aryl homo-coupling under the applied experimental conditions. They also show that under the above mentioned conditions the reaction proceeds slowly, and that unreacted molecules can still be identified after a 5-min annealing step. Polymerization is found to be completed after annealing for 5 min at temperatures above 575 K, and to result in fully developed polyphenylene networks as shown in Fig. 3. However, desorption of chemisorbed iodine, the byproduct of the coupling reaction, is only observed at temperatures above 825 K, in agreement with previous work.[3]

AM1 calculations of CHP and the polyphenylene network

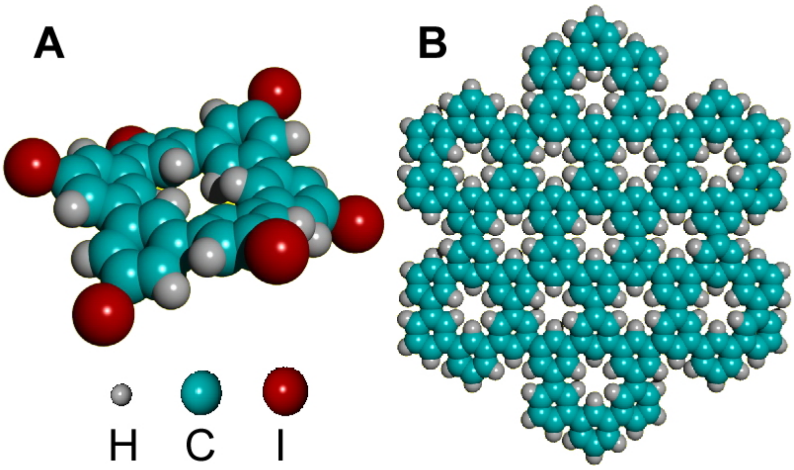

Fig. S2 Calculated structures by using the AM1 level of theory. (A) Perspective view of the optimized structure of the free CHP molecule. (B) Top view of the optimized structure of a fraction of the polyphenylene network obtained by six-fold homocoupling of CHP.

Figure S2 displays the results of structure optimizations at the AM1 level of theory. Figure S2A shows a perspective of the CHP molecule after structure optimization *in vacuo*. Intramolecular H···H repulsion results in an energetically most favourable “puckered” conformation for gas-phase CHP, with a twist angle of 37° between adjacent phenyl groups. In Fig. S2B we present the optimized structure of a fraction of the CHP polyphenylene network, which was determined without taking into account the Ag(111) substrate. The calculated pore-to-pore distance of 7.45 Å is in excellent agreement with the experimental observation of 7.4 Å. The calculated structure exhibits a phenyl–phenyl twisting of about 20°, *i.e.* significantly less than the free CHP molecule. For both, the surface-adsorbed CHP molecules and the surface-supported polyphenylene network, van der Waals interaction with the Ag(111) surface is expected to significantly reduce the phenyl–phenyl twist angle and to lead to essentially planar molecular conformations.

References

1. W. Pisula, M. Kastler, C. Yang, V. Enkelmann and K. Mullen, *Chem.-Asian J.*, 2007, **2**, 51-56.
2. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902-3909.
3. G. J. Szulczewski and J. M. White, *Surf. Sci.*, 1998, **399**, 305-315.