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Transforming Surface Coordination Polymers into Covalent Surface Polymers: Linked Polycondensed Aromatics through Oligomerization of N-Heterocyclic Carbene Intermediates**

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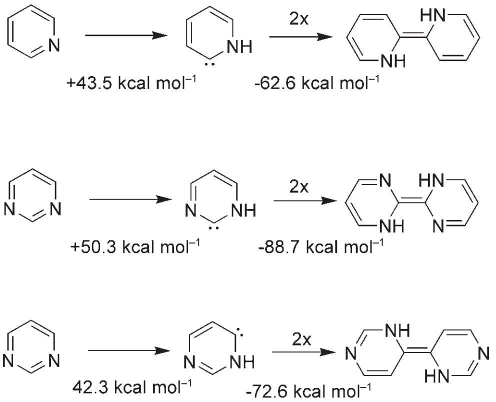
Dedicated to Lord Lewis of Newnham on the occasion of his 80th birthday

The carbene tautomers of pyridine, first postulated in 1937,[1] have recently begun to be systematically investigated both in the gas phase[2] and in the form of transition-metal-stabilized ligands.[3] Computational studies on the relative energies of the different tautomeric forms have revealed that the 2-carbene isomer (azacyclohexatriene-2-ylidene) in particular is more than 40 kcal mol^{-1} less stable than pyridine itself.[2,4] According to a DFT study (B3PW91/6-311G(d,p)), the potential Wanzlick-type dimerization[5] of two such carbenes would be -62.6 kcal mol^{-1} more stable than the two monomers but significantly disfavored ($+24.4$ kcal mol^{-1}) with respect to the dissociation into two pyridine molecules (Scheme 1). A similar trend is found for the carbene tautomers of pyrimidine, except that the dimerization appears to be less disfavored for both orientations ($+12$ kcal mol^{-1}).

Whereas the linkage of carbene tautomers of simple six-membered aromatic N-heterocycles thus appears unlikely, their integration into a polycyclic aromatic ring system changes this trend. We recently reported the synthesis of 1,3,8,10-tetraazaperopyrene (TAPP), which may be viewed as a perylene condensed with a pyrimidine ring at each end.[6] A DFT computational study on both the tautomerization and carbene dimerization of TAPP indicated that the formation of the tetraaminoethylene linkage would be significantly more favorable than for the monocyclic N-heterocycles and that the overall process might therefore be thermoneutral (Scheme 2). More significantly, this trend is enhanced in the formation of oligomers, which becomes an exothermic process for the generation of the trimer (-18.6 kcal mol^{-1} with respect to three molecules of TAPP) and even more so for higher oligomers.[7] This stabilization is thought to be due to conjugation of the tetraaminoethylene unit with the extended aromatic ring systems.



Scheme 1. Tautomerization of pyridine and pyrimidine to azacyclohexatriene-2-ylidene, diazacyclohexatriene-2-ylidene, and diazacyclohexatriene-4-ylidene, and the dimerization of the carbene species through di- and tetraaminoethylene linkages.

The low solubility of the parent compound TAPP in all common solvents precluded the investigation of such processes in solution. Moreover, their expected high activation barriers would have provided a potential practical obstacle. We therefore decided to study the reactivity of TAPP on metal surfaces, which allows the analysis of reaction products by surface-science techniques. Furthermore, the reduction of the organic molecules' degrees of freedom by adsorbing them on a (conducting) surface is thought to reduce the activation barrier involved in the concatenation of the poly-N-heterocyclic aromatic compounds[8] and thus to enhance their reactivity.[9]

Deposition of TAPP on a Cu(111) surface at submonolayer coverage at a sample temperature of 150 °C leads to the formation of a porous molecular network. The same network

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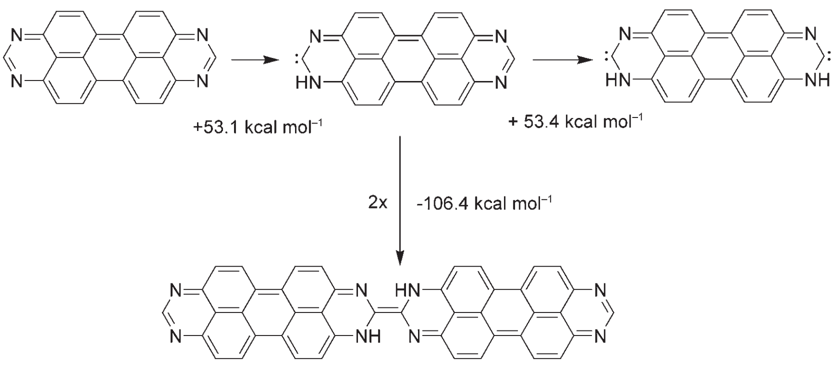
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the authors.



Scheme 2. Single and double tautomerization of TAPP and the formation of a TAPP dimer.

is obtained if the substrate is annealed at 150 °C after deposition of TAPP at ambient temperature (Figure 1 a). Low-energy electron diffraction (LEED) measurements established the dimensions of the approximately rectangular unit cell of TAPP, which is commensurate with the Cu substrate (17.9 Å × 16.8 Å, angle = 89.4°).[10] The network itself is assigned as a coordination polymer in which the organic dye molecules coordinate to Cu atoms through the lone pairs of their nitrogen atoms (Figure 1 b). Similar coordination networks of potential "ligands" have been reported previously.[11] The observed overall N-Cu-N separation of 4 Å for the metal-coordinating linkage is as expected from Cu coordination chemistry.[10,12]

The coordination network is stable up to about 190 °C. Above this temperature, the long-range order of the surface structure is lost, and, after annealing the sample at a temperature of about 250 °C, the formation of oligo- and polymeric chains is observed. The length of the chains varies but not their width, which corresponds to the width of a single molecule (Figure 1 c). Furthermore, the orientation of the chains, some of which display marked curvature, appears not to be determined by the substrate lattice structure. This finding gave a first indication that the interaction between the monomers in the chains dominates over the bonding to the metal surface.

The chain structure is particularly apparent after the annealing of surfaces with very low initial coverage of TAPP (Figure 2 a). A representative high-resolution STM image (STM = scanning tunneling microscopy) of a TAPP chain recorded at 4 K is displayed in Figure 2 b. Altogether, 16 images were used to determine the distance between the centroids of adjacent monomer units in the chain. This distance, which was found to be 1.23 ± 0.12 nm, is in good agreement with the value calculated by DFT methods for the TAPP oligomers in the gas phase (1.27 nm) and provided a first indication of the type of polymer formation predicted above and displayed in Figure 2 c. Another indication is provided by X-ray photoelectron spectroscopy (XPS) measurements. They revealed that the coordination network exhibits one N 1s peak, whereas the chains show an additional peak at a slightly lower energy.[13]

An important consequence of the covalent linkage of the N-heterocyclic aromatic molecules on the metal surface and

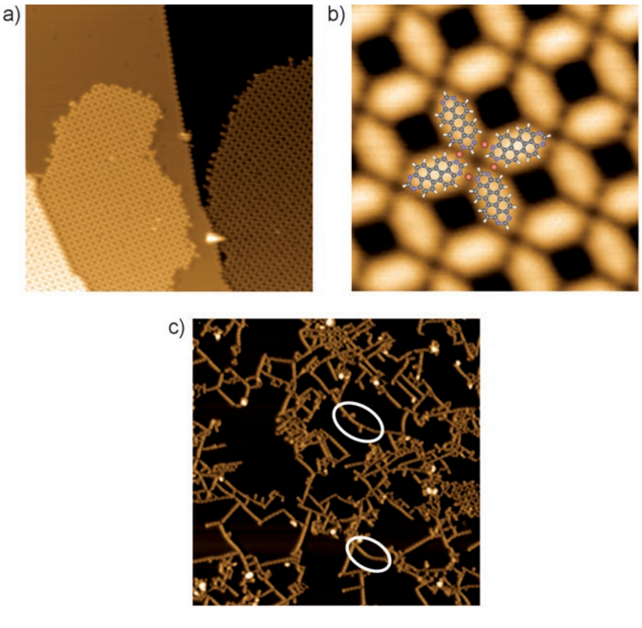


Figure 1. STM images of a submonolayer of TAPP deposited on Cu(111): a) TAPP assembles in a porous network after annealing at 150 °C (70 × 70 nm^2, 1.4 V/20 pA). b) Proposed structure of the surface coordination network (5.3 × 5.3 nm^2, 0.4 V/20 pA). c) After annealing at approximately 250 °C, the polymeric chains appear (80 × 80 nm^2, 1 V/90 pA). The areas highlighted by the ellipses show that the molecules do not only arrange along the principal directions of the Cu surface, which is a first indication for a dominating intermolecular interaction. The junctions between the chains have variable angles and can be explained by copper atoms bound to the side of a chain in a bipyridyl-type coordination on the one hand and to an N-heterocyclic end of a second oligo(TAPP) chain on the other.

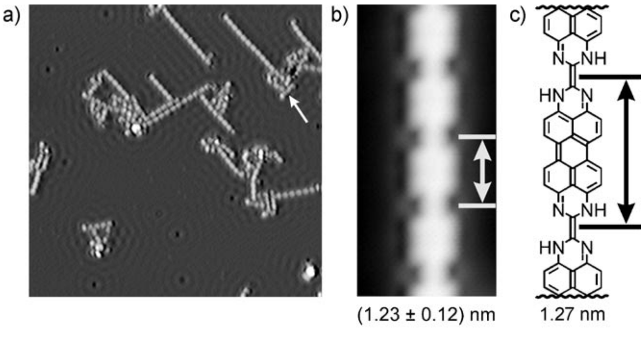


Figure 2. a) STM image of the TAPP chains obtained from low monomer surface coverage (50x50 nm^2, 0.1 V/20 pA). The chain formation seems to depend on molecular clusters or surface defects that nucleate the growth (white arrow). Owing to the low tunneling voltage used to acquire this STM image, standing wave patterns in the Shockley surface state of Cu(111) as they arise from scattering at chains as well as defects can be observed.[16] b) High-resolution STM image of a TAPP chain (2.4 × 5 nm^2, 0.1 V/20 pA). The distance between the monomers was determined by STM to be (1.23 ± 0.12) nm. c) Schematic model for the TAPP chains. For calculations in the gas phase, the distance indicated by the arrow amounts to 1.27 nm.

thus the strong bonding interactions between the monomeric units is the possibility to mechanically manipulate whole chain sections with the aid of the STM tip.[14] To this end, the following manipulation sequence was applied, the tunneling parameters being set to 1.2 V/20 pA during this sequence: First, the STM tip was placed next to the chain, the feedback loop subsequently switched off, and the tip slowly moved towards the surface by approximately 0.7 nm and then retracted to its initial position. The success of this procedure was checked by imaging the same region again. The manipulation was repeated consecutively 19 times, and the movement of the tip had a repulsive effect upon the chain. The recorded images have been combined in a movie, which is provided in the Supporting Information. In Figure 3, four of these 19 images are displayed which clearly show that the manipulation has left the chain intact, thereby illustrating its flexibility as a whole. This finding provides additional support for the assumption of strong bonding between the tautomerized TAPP molecules, irrespective of the interaction with the substrate.

An interesting combination of covalent and coordination polymeric structures is observed when two chains are aligned next to each other in a parallel arrangement, as exemplified in Figure 4. The protrusions (black arrow) that can be observed between the two parallel chains may be interpreted as Cu atoms interconnecting the chains by the formation of square-planar metal complexes between the Cu atoms and the nitrogen donor functions of the TAPP units.

The apparent metal coordination is observed in equivalent positions on the outside of such double-stranded coordination bands (as indicated by the white arrows in Figure 4). This arrangement is thought to be favored by a dehydrogenation of the NH groups after formation of the chains, similar to the thermal dehydrogenation previously established by us for 4,9-diaminoperylene-3,10-diimine (DPDI) molecules on Cu surfaces.[15] The polymeric N-heterocycles are thus rendered ligands with multiple chelating metal-binding sites.

Herein, we have demonstrated that thermally induced C–C coupling reactions of polycyclic heteroaromatic compounds may be used to generate electronically highly delocalized polyaromatic chains. The reaction is thought to occur through the tautomerization of the N-heterocyclic end units to carbene intermediates, which couple according to a Wanzlick-type dimerization. While the tautomerization itself is precedented in the coordination sphere of transition metals,[3] this is the first time that such chemistry has been employed for the construction of covalent surface structures. It provides an additional tool in the current quest for new methods for controlled covalent linkage and polymerization of organic monomers on crystal surfaces.[17]

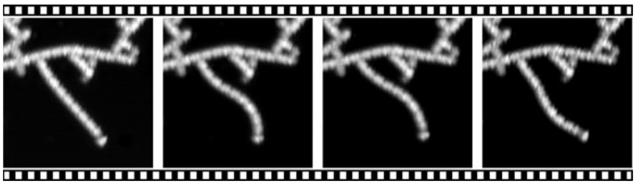


Figure 3. Consecutive STM images of the same area (16×16 nm^2, 1.2 V/20 pA). The STM tip was used in proximity to the sample to induce lateral motion of the chain between each of the micrographs displayed. These four images (taken from a sequence of nineteen images, see movie in the Supporting Information) demonstrate the successful and reversible bending of a chain that stays intact during the process. The degree of bending and the elasticity of the system are remarkable.

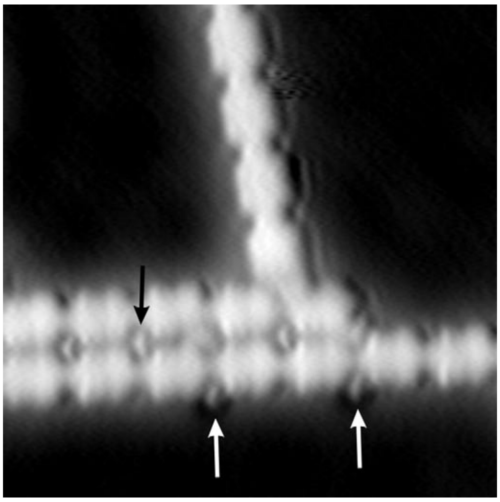


Figure 4. STM image of a double-stranded band of TAPP chains (8×8 nm^2, 0.1 V/20 pA) held together by Cu coordination. The protrusions (black arrow) are interpreted as Cu atoms connecting two parallel TAPP chains by coordination of their nitrogen atoms. Likewise, the protrusions highlighted by white arrows indicate metal coordination at the border of this double-stranded band.

Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) system, consisting of different chambers for sample preparation and characterization, at a base pressure of 10^{-10} mbar. The Cu(111) single crystal was prepared by subsequent cycles of sputtering with Ar^+ ions and annealing at 500 °C. The molecules were deposited onto the Cu surface from a glass crucible that was heated inside a commercial evaporator (Kentax UHV equipment) while the rate was controlled by a quartz crystal microbalance. The sample was analyzed with LEED at room temperature and with a commercial LT-STM instrument (Omicron NanoTechnology GmbH) at 77 K and 4 K using the Nanonis SPM control system (Nanonis GmbH). The bias voltage was applied to the tip. The free software WSxM[18] was used for data processing of the STM images.

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