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Supramolecular Chemistry

Molecular Tectonics on Surfaces: Bottom-Up Fabrication of 1D Coordination Networks That Form 1D and 2D Arrays on Graphite**

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In memory of Guy Ourisson

Molecular networks are periodic architectures formed upon mutual bridging between molecular construction units called tectons.[1–4] Such molecular assemblies are generated in the crystalline phase by self-assembly through molecular recognition processes, which take place between tectons bearing complementary interaction sites within their structure. So far, molecular tectonics has been mainly focused on the design and generation of molecular architectures in the crystalline phase. However, the control of spatial arrangements of molecular units on substrate surfaces is also a field of current interest.[5] In particular, the self-assembly of metal–ligand-based architectures at surfaces is a promising and versatile method for the fabrication of 2D metal-ion arrays.[6,7] Indeed, the correct choice of the ligand–metal pair made it possible to fabricate various thermodynamically stable nanoscale patterns of bipyridine-based complexes adsorbed on surfaces.[8] Scanning tunneling microscopy (STM) and spectroscopy can provide direct and quantitative insight into the nanoscale properties of supramolecular architectures by addressing and manipulating assemblies with a submolecular resolution.[9] Up to now, STM characterizations of metal–ligand self-assembly of terpyridine-based architectures have been focused on the study of single-molecule complexes that form self-organized monolayers,[10] gridlike assemblies,[6,11] or hexameric macrocycles.[12]

As stated above, although considerable effort has been devoted to the design and formation of 3D crystals composed of organic tectons and metal centers,[13] the use of a molecular tectonics approach for the generation of 2D crystalline metalloorganic patterns and arrays at surfaces has so far not been explored. Herein, we describe the design and the STM study of 1D coordination networks that form either 1D or 2D nanoscale arrays at surfaces. This bottom-up patterning is generated by self-assembly processes upon combining a directional, rigid, organic coordinating tecton bearing two differentiated coordination poles with suitable metal centers.

We focused on 1D coordination networks, which present translational symmetry in one direction of space of an assembling node that results from the formation of coordination bonds between organic units and metal centers. The design of such an arrangement may be based on the use of noncentric tectons bearing two coordination poles that offer different denticities. In particular, a combination of tectons which expose one monodentate and one tridentate coordination pole with metal centers offering four free coordination sites that occupy the corners of a square would match the requirement for the formation of directional 1D coordination networks (Figure 1). As concerns the metal center, one may envisage the use of either octahedral dicationic metals associated with two coordinating anions occupying the apical positions (Figure 1, top) or square-planar metal centers (Figure 1, bottom). In the crystalline phase, this strategy has been proven to be operational in the case of $CoCl_2$.[14–16]

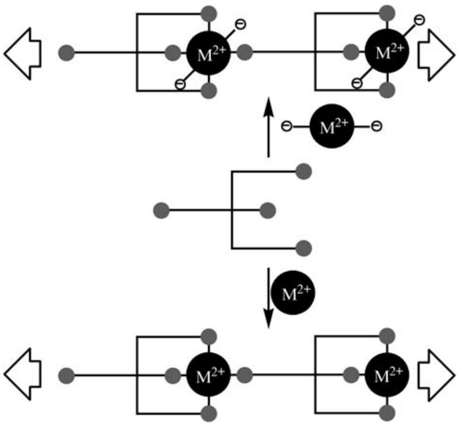

Figure 1. Schematic representation of the formation of directional 1D networks, based on the combination of an organic tecton bearing a monodentate and a tridentate coordination pole and either a neutral octahedral metal complex (top) or square-planar dicationic metal center (bottom), which offers four free coordination sites.

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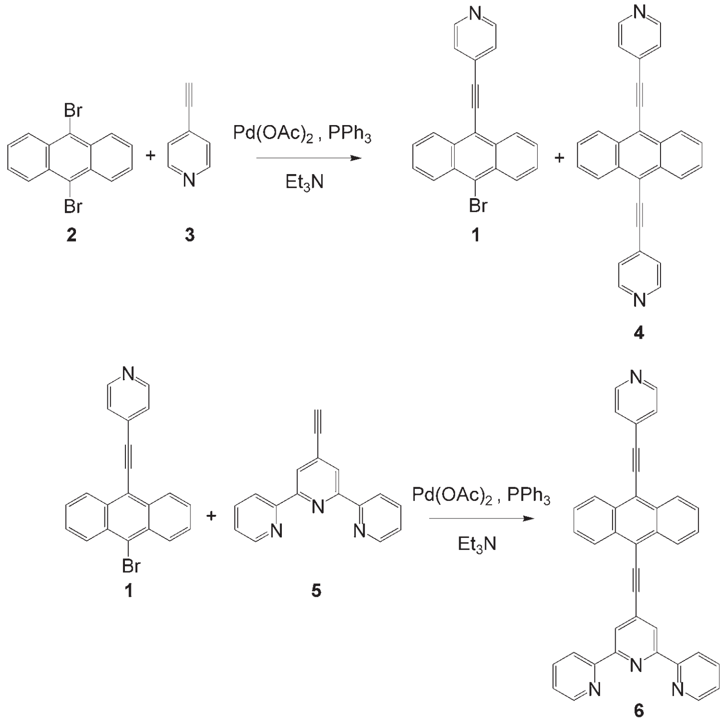

Scheme 1. Synthesis of tecton **6**.

The design of the tecton **6** (Scheme 1) was based on the use of an anthracene moiety as a platform, and pyridine and terpyridine units as the two different coordination poles. Both the pyridine and terpyridine units were connected to the backbone at their 4-positions. The linkage between the monodentate and tridentate coordination poles and anthracene was achieved at positions 9 and 10 by ethenyl groups. This connectivity pattern was chosen because it leads to an inline disposition of the two coordinating poles. The choice of the ethenyl spacer was motivated by the fact that such a unit, by avoiding atropoisomerism, would lead to a flat yet π-conjugated construction unit well-suited to physisorption within self-assembled architectures on a graphite surface.

The synthesis of compound **6** was sequential and based on two palladium-catalyzed C–C coupling reactions. The starting material was 9,10-dibromoanthracene (**2**; Scheme 1). The condensation of **2** with 4-ethynylpyridine (**3**), prepared according to published procedures,[17] in Et_3N in the presence of $Pd(OAc)_2$ and PPh_3 afforded compound **1** in 34 % yield. As expected, this reaction also led to the formation of the symmetrical double-condensation product **4** (25 % yield).[18] The latter, based on the anthracene core and bearing two pyridine moieties, is a bis(monodentate) unit and might also be of interest for the generation of either discrete or infinite networks when combined with appropriate metal centers. The reaction between compound **1** and 4-ethynylterpyridine (**5**), synthesized according to the literature,[19] in Et_3N with $Pd(OAc)_2$ and PPh_3 as catalysts afforded the desired compound **6** in 80 % yield.

The solid-state structure of the free tecton **6** was investigated by X-ray diffraction on a single crystal. The crystal (monoclinic, *C*2/*c*) is composed of **6** and two disordered chloroform molecules. All C–C and C–N bond lengths are in agreement with expected and reported values. Compound **6** exhibits an almost flat conformation (Figure 2 a). The pyridine ring is almost coplanar with the anthracene unit (0.7° tilt angle). The central pyridine unit of the terpyridine moiety is also coplanar with the anthracene spacer. However, the other two pyridine units are in a *trans* conformation and tilted with respect to the central pyridine (NCCC dihedral angle of −17°). Molecules of compound **6** are packed along the *b* axis with the same orientation, thus leading to arrangement along this direction. The lateral packing of molecules in the XOY plane is achieved in *syn*-parallel mode, thus affording a polar sheet. As a result of the antiparallel packing of molecules along the *c* axis, the overall arrangement is apolar. Consequently, the head-to-tail-type disposition of molecules along the *c* axis leads to parallel and face-to-face packing of the pyridine and terpyridine units, with a centroid-to-centroid distance between consecutive units of approximately 3.93 Å (Figure 2 b).

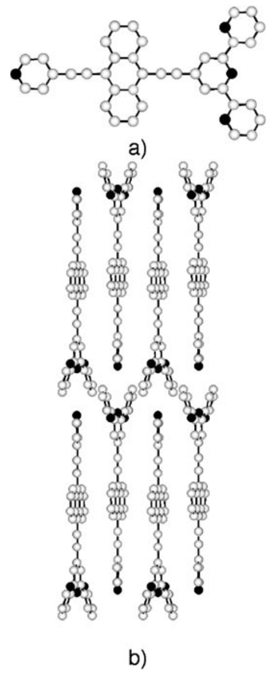

Figure 2. a) A portion of the solid-state structure of tecton **6** (black N, gray C) and b) packing of consecutive units. Hydrogen atoms are not represented for clarity. For bond distances and angles, see text.

Figure 3 shows ordered 2D monolayers formed by assembly of the tecton **6** onto a graphite surface. The monolayer displays a polycrystalline structure (Figure 3 a), which consists of hundreds of nanometer-wide domains that are stable over several minutes. Bright rods, tilted by about 35° with respect to the *b* axis of the unit cell (see black arrows in Figure 3 b), are observed. The unit cell dimensions, estimated from the smaller-scale image (Figure 3 b), are $a = (3.2 \pm 0.2)$ nm, $b = (2.60 \pm 0.15)$ nm, and $\alpha = (89 \pm 3)°$, which lead to an area $A = (8.32 \pm 1.0)\ \mathrm{nm}^2$. In the inset of Figure 3 b, the Corey–Pauling–Koltun (CPK) molecular structure has been added on top of the STM zoom image, thus providing evidence for a zigzag

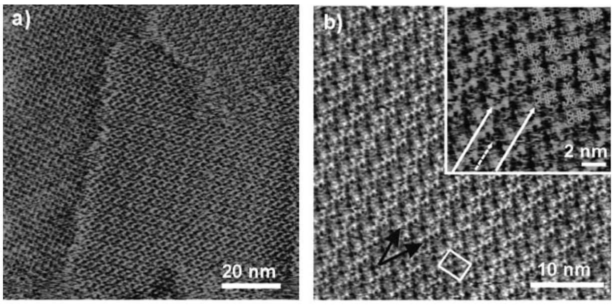

Figure 3. a, b) STM images of the pure ligand **6**. Tip bias (V_{tip}) = 745 mV; average tunneling current (I_t) = 36.0 pA. The inset in (b) shows a zoom image. See text for further details.

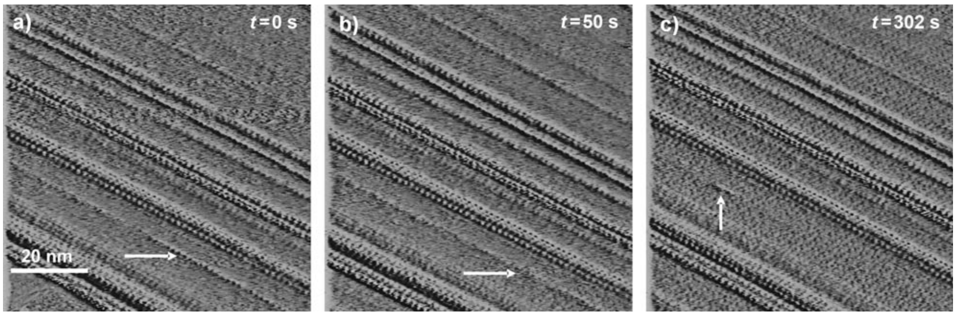

Figure 4. a–c) Time-resolved STM images of the uncharged network formed by ligand **6** and $CoCl_2$. The arrows indicate a given 1D network that disassembles over time. V_{tip} = 705 mV; I_t = 13.0 pA.

packing motif that may result from a different orientation of molecule **6** on the XOY plane with respect to the surface underneath. The two different rows are marked by solid and dashed white arrows (Figure 3b, inset). As expected from π–π interactions between the rather flat conjugated compound **6** and the substrate, in both cases the molecules are adsorbed preferentially parallel to the basal plane of the underlying graphite plane. The observed packing of unit cells containing two molecules is probably favored by both intra- and intermolecular weak N···H–C hydrogen bonds.[20] The lower contrast of the molecules along the dotted lines, if compared to those along the solid lines, can be a result of either different positioning of molecules along the z axis (that is, different distances from the surface) or different conformers of **6** that possess a lower degree of planarity.[21] In both cases, the overlap between the π orbitals of compound **6** and the substrate varies, thus leading to changes in the detected tunneling currents.

According to previous observations on the crystalline phase of structurally related tectons,[14–16] the combination of the neutral tecton **6** with $CoCl_2$ should lead to the formation of neutral 1D coordination networks on the graphite surface. The generation of the network results from the binding of the Co^{II} center, which adopts the octahedral coordination geometry and offers four free coordination sites occupying the corners of a square (the two apical positions being occupied by two Cl^- anions), with one terpyridine and one pyridine coordinating pole belonging to consecutive tectons **6** (Figure 1, top). This coordination mode defines the assembling node, which, upon translation into one direction of space, leads to the 1D network.

Figures 4 and 5a show STM images of a film prepared by physisorption of a solution containing the neutral tecton **6** and neutral $CoCl_2$ complex on graphite. Perfectly straight nanostructures with a length up to 400 nm were observed. At a smaller scale (Figure 5a), these 1D nanostructures are made of aligned and regularly spaced circular spots separated by (1.70 ± 0.15) nm. Given the high electron densities of the Co^{II} metal centers, it is most likely that these spots correspond to the Co ions complexed by tecton **6**. However, such spots are not laterally correlated. In fact, these 1D nanostructures grow either as single anisotropic nano-objects or as tightly packed parallel wires separated by a variable distance (see white arrows in Figure 5a). Time-resolved STM mapping made it possible to highlight a dynamic exchange between the 1D nanostructures and a 2D monolayer adsorbed at the solid/liquid interface, the latter consisting most probably of the pure ligand **6**. In particular, on the several seconds timescale, the neutral 1D networks formed upon mutual bridging between tectons **6** and $CoCl_2$ complexes (indicated by white arrows in Figure 4) disassemble into the 2D monolayer. This disappearance of the 1D nanostructure can be a consequence of either its desorption in the supernatant solution or a disassembly process occurring directly at the surface. Given the different spacing between repeating motifs, that is, (1.70 ± 0.15) nm intermetal distance along the 1D network, and the b axis of the unit cell for the pure tecton **6** mentioned above (b = (2.60 ± 0.15) nm), it is most likely that a desorption–readsorption process takes place during the disappearance of 1D networks. The high shape persistence of the 1D nanostructures is determined by the directionality of the coordination bonds formed between the Co metal center and tecton

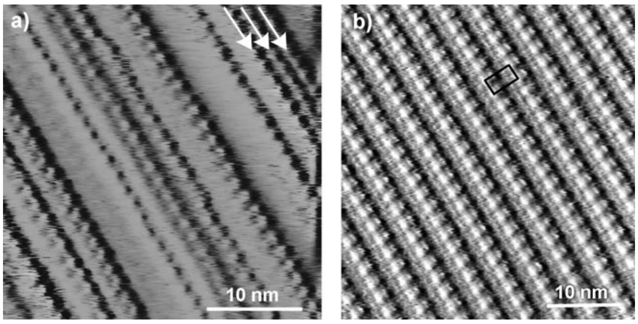

Figure 5. STM images of the network generated upon combining tecton **6** with a) $CoCl_2$ and b) Pd^{II}. Image (a) shows the formation of laterally uncorrelated 1D nanostructures, while (b) displays the parallel packing of 1D networks that leads to the generation of a 2D nanoscale array. a) V_{tip} = 705 mV; I_t = 13 pA; b) V_{tip} = 983 mV; I_t = 13.6 pA.

6 and the rigidity of the latter. The parallel packing of the 1D networks might suggest that the graphite substrate lattice or step edges dictate the relative orientation of the networks assembled at the surface. This is a well-known behavior, which has been ascribed to the greater reactivity of step edges of graphite. Notably, grid-type architectures based on bis(terpyridine) ligands combined with cobalt also adsorb on graphite step edges.[11c] As a result of the nonplanarity of the octahedral assembling node, the ligand backbones cannot be fully planar to the graphite surface, thus leading to partial overlap of the π orbitals of tecton **6** and the graphite. As a consequence, it is most likely that the 1D networks are stabilized by interactions with the step edges of graphite rather than by side-to-side packing interactions.

On the other hand, the use of the Pd^{II} cation, by design, yields a polycationic 1D network. Indeed, because of the dicationic nature of palladium, its binding by the neutral tecton **6** generates a charged square-planar assembling node formed by the palladium center and one terpyridine and one pyridine unit belonging to consecutive tectons **6**. Figure 5b shows a STM image of the straight, laterally correlated, parallel 1D networks obtained by self-assembly of the ligand **6** with Pd^{II} on graphite. As in the case of $CoCl_2$, the spots observed along the rows can be attributed to the metal centers as a result of their high electron density. The spots form a 2D crystalline layer characterized by the unit cell $a=(4.0\pm 0.2)$ nm, $b=(2.00\pm 0.15)$ nm, and $\alpha=(91\pm 3)^\circ$, which leads to a surface area $A=(8.0\pm 1.0)\ \mathrm{nm}^2$ (see black rectangle in Figure 5b). Each unit cell contains one molecule of tecton **6** and one Pd^{II} cation. The 1D cationic networks are formed along the b axis through interconnection of palladium cations by neutral tectons **6**. The lateral correlation between the 1D networks forming the crystalline layer suggests a cooperative process that takes place during the generation of 1D networks assembled on graphite. The unit cell area (normalized for a single unit composed of one tecton **6** and one palladium cation) of approximately 8.0 nm^2 is larger than that determined for the free tecton **6** (about 4.16 nm^2), which suggests possible packing within the monolayer of BF_4^- counterions between polycationic 1D networks. This packing mode seems reasonable because it avoids repulsive interactions between positively charged 1D networks. Furthermore, the formation of a 2D monolayer made of parallel and regular dispositions of the 1D networks on the graphitic surface may also be attributed to the planar disposition of the assembling node, and thus the 1D networks favoring π-stacking interactions between the polycationic 1D networks and the surface.

Notably, in both cases shown above, the STM characterization of physisorbed metal–ligand complexes at the solid/liquid interface reveals 1D coordination networks with lengths over a few hundreds of nanometers. Such lengths are comparable to those observed on straight structures made of dry metallo-supramolecular complexes of bis(terpyridine) derivatives with Fe^{II} stabilized by alkane lamellae ($\approx$200 nm long) self-assembled on graphite, as revealed by atomic force microscopy investigations.[22]

In conclusion, by STM studies at the graphite/solution interface, we have demonstrated the possibility of designing flat, coordinating construction units capable of forming persistent 1D coordination networks in the presence of metal cations. Depending on the overall charge of the network and thus on the nature of the tectons used, either 1D or 2D arrays that expose metal centers in preprogrammed locations, with an Ångstrom resolution, may be obtained. We are currently investigating the generation of molecular networks on surfaces using the molecular building block reported here, and its analogues, with a variety of other metal centers. Finally, given the multifunctional character of these architectures, which incorporate a metal center and an optically active unit (that is, anthracene), future studies will be addressed toward the exploitation of their unique optical properties.

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