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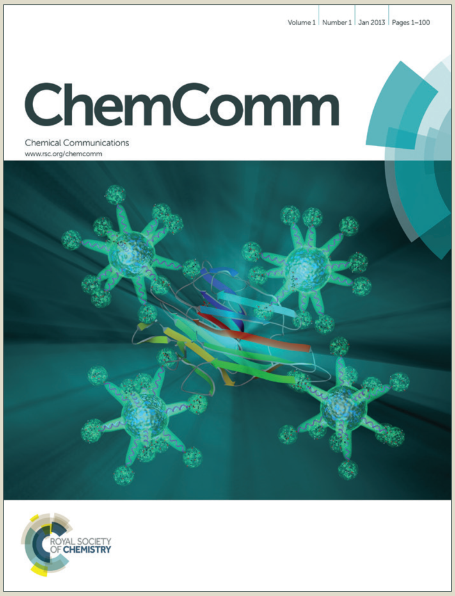

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Molecular tectonics based nanopatterning of interfaces with 2D metal-organic frameworks (MOFs)

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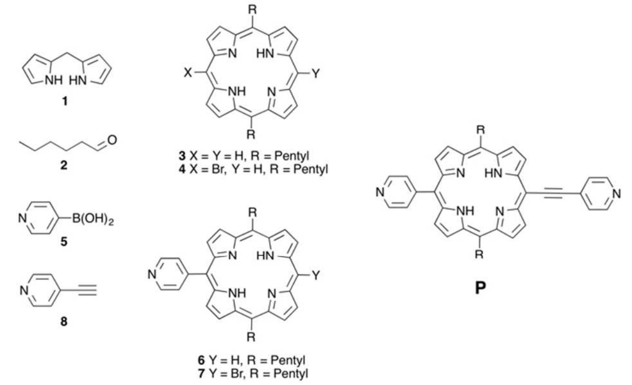
The nanostructuring of graphite surface with 2D coordination network, based on a combination of an acentric porphyrin tecton bearing two divergently oriented monodentate pyridyl units and $CoCl_2$ metallatecton, behaving as a four connecting node, was achieved at the solid-liquid interface and characterized by scanning tunnelling microscopy.

Achieving a control of surface patterning with sub-nanometer precision and long-range order is one among the greatest challenges in nanoscience.[1] Following the molecular tectonics approach[2] which deals with the design and construction of infinite periodic architectures in the crystalline phase, this may be attained *via* self-assembly of programmed molecular building blocks named tectons.[3] The latter bear within their structure specific and complementary recognition sites. Among various reversible intermolecular interactions, coordination bonding leading to robust coordination networks or metal-organic frameworks (MOFs) has been widely used to generate hybrid assemblies in the solid state.[4] These architectures may be generated through surface-assisted self-assembly processes between organic coordinating tectons and metal centres or metal complexes offering free coordination sites. Patterning surfaces with 2D architectures displaying nano-cavities with tuneable size may be of interest for generation of surface template 3D assemblies through layer-by-layer growth of MOFs.[5]

Molecular self-assembly can be monitored on the sub-nanometer scale by scanning tunnelling microscopy (STM). The latter is one among the most powerful tools to investigate the structure and dynamic properties of molecular assemblies at surfaces under various environmental conditions.[6] Many examples of diverse 2D coordination networks have been reported by using STM under ultra-high vacuum (UHV), including networks based on carboxylates,[7] carbonitriles,[8] pyridines,[9] and N-heterocyclic carbines.[10]Noteworthy while STM was already employed to monitor the formation of 1D MOFs at the solid-liquid interface,[12] to the best of our knowledge it was never employed to investigate 2D MOFs.



Scheme 1

Here we report on graphite surface nanopatterning with 2D coordination networks generated upon self-assembly between a porphyrin-based tecton with $CoCl_2$ metallatecton, as monitored in situ by STM at the solid-liquid interface.

The porphyrin core is a scaffold possessing unique opto-electronic properties that render them interesting for numerous applications including solar cells[13] and catalysis.[14] By using UHV technique, examples of 2D coordination networks based on combinations of porphyrin derivatives with a variety of metal centres have been reported.[9,15] Taking advantage of our previous studies[16] and works published by other groups[17] on crystal engineering of porphyrin based tectons, the porphyrin **P** (5,15-dipentyl-10-(4-yl-pyridine)-20-(4-yl-ethynylpyridin)porphyrin, Scheme 1) was designed and synthesise. It is an acentric tecton, based on a porphyrin core bearing in *trans meso* positions two monodentate 4-pyridyl coordination poles. The acentric nature of the tecton results from the difference in the connection of the coordinating sites to the opposite *meso* positions of the macrocyclic backbone. Indeed, whereas one of the two pyridyl units is directly connected to the porphyrin, the other one is linked through an ethynyl spacer. Furthermore, to enhance the affinity of the tecton for the graphite surface and to increase its solubility in organic solvents, the two remaining *meso* positions were equipped with pentyl side chains. The synthesis of tecton **P** (see ESI for details) was achieved by a multi-step procedure starting from the 5,15-dipentylporphyrin **3** (Scheme 1).[13] The latter was prepared upon reacting the dipyrromethane[19] **1** with hexanal **2** following a reported procedure.[16e] The monobromination of the porphyrin **3** using NBS in $CHCl_3$ afforded the compound **4** in 70% yield. The $Pd(PPh_3)_4$ catalyzed Suzuki coupling reaction between the compound **4** and 4-pyridine boronic acid **5**, afforded the monopyridyl derivative **6** in 60% yield. The latter was again brominated using NBS affording thus the precursor **7** in 96% yield. Finally, the second pyridyl moiety was intruded in 73% yield upon a copper free Sonogashira coupling reaction between **7** and 4-ethylpyridine **8** in the presence of $Pd_2(dba)_3$ and $As(Ph)_3$ as catalysts.[20] The free tecton **P** was characterized in the crystalline phase by X-Ray diffraction on single crystals (Fig. 1). The porphyrin core is almost planar. The pyridyl group directly connected to the porphyrin backbone is tilted 64° while the ethynylpyridyl is tilted by 40°. The overall tecton length corresponding to $N_{pyridyl}$-$N_{Ethynylpyridyl}$ distance is 17.95 Å.

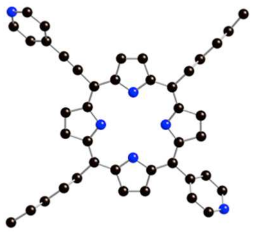


Figure 1. Crystal structure of the tecton **P**. H atoms and solvent molecules are omitted for clarity.

Noteworthy, owing to the acentric nature of the tecton **P**, in principle five different connectivity patterns (Fig. 2 a-e) may be envisaged for the formation of the 2D network resulting from the combination of the tecton **P** and $CoCl_2$. These connectivity patterns differ by combinations of the coordinating sites composing the assembling nodes *i.e.* [4 red and 4 blue] (a), [(3 red, 1 blue) and (3 blue, 1 red)] (b), [2 red and 2 blue in *trans* disposition] (c) and finally, [2 red and 2 blue in *cis* configuration] (d and e).

The packing of the free tecton **P** on HOPG surfaces was studied by STM at the solid-liquid interface, by applying a 4 µL drop of a 1 mM solution of **P** in 1-phenyloctane. Figure 3a shows a survey of the STM image displaying a monocrystalline region (Fig. 3b), which consists of a tens of nanometer-wide domain stable over several minutes. In this 2D crystal, molecules **P** are physisorbed in nearly planar conformation on the HOPG surface.

It is most likely, that due to the steric hindrance, the pyridyl ring connected directly to porphyrin backbone is not located in the plane containing the core of the tecton. The packing of tectons **P** is characterized by a unit cell with a = (1.5±0.2) nm, b = (1.6±0.2) nm, and α = (75±2)°, which leads to an area A = (2.3±0.3) nm^2, indicating that each unit cell contains a single tecton **P**. Considering the size of the unit cell, it appears that the pentyl side chains can be placed on the surface, although, since we have not resolved them, we do not have unambiguous confirmation of this feature.

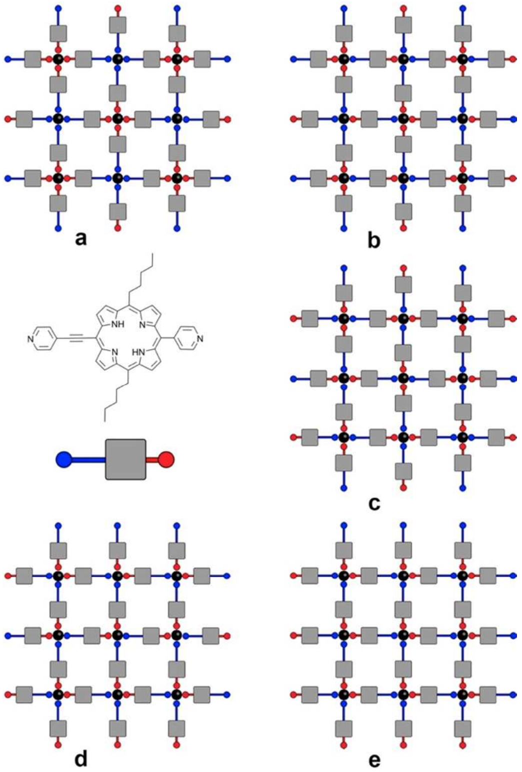


Figure 2. Schematic representation of different possible 2D coordination networks which may be formed upon combining the neutral acentric tecton **P** with neutral $CoCl_2$ salt (black sphere). The grey square represents the porphyrin core, whereas the red and the blue segments correspond to the pyridyl unit directly connected to the porphyrin backbone and the ethynyl pyridyl moiety respectively. Chloride anions occupying the two apical positions on the octahedron around the Co(II) cation are not presented for clarity.

The supramolecular motif is further stabilized by molecule-HOPG van der Waals interactions, and by molecule-molecule van der Waals contacts and dipole-dipole interactions. Noteworthy, the ordered monolayers of **P** were monitored only upon using well-defined experimental conditions, i.e. by applying to the HOPG surface 1 mM solutions in 1-phenyloctane.

STM was also used to probe both *the in situ* and *ex situ* formation of 2D coordination networks on HOPG. As a first attempt, *in situ* experiments have been carried out by addition of 1 equivalent of $CoCl_2 \times 2H_2O$, on top of a pre-existing monolayer of **P**. To this end, a 2 µL drop of 2 mM solutions (isopropanol:1-phenyloctane, 1:99 *vol:vol*) was deposited on top of a monolayer of **P** formed by applying a 4 µL drop of a 1 mM solution of **P** in 1-phenyloctane on the HOPG surface.

Unfortunately, this strategy failed and only disordered structures were observed by STM. It seems that the rather high adsorption energy of the tecton **P** on the surface prevent the binding of Co(II) by **P** which requires successive desorption of molecules, complexation and re-adsorption. We then performed *ex situ* experiments by simultaneous co-deposition of 4 µL of a 1 mM solution of **P**, and 2 µL drop of 2 mM solutions of $CoCl_2 \times 2H_2O$ (isopropanol:1-phenyloctane, 1:99 *vol:vol*) on top of a freshly prepared HOPG surface. After solvent evaporation (24 h at room temperature) the sample surface was gently rinsed with the a 1:1 mixture of $CHCl_3$ and isopropanol, in order to remove the excess of free tecton **P**, cobalt salt and $[\mathbf{P}(CoCl_2)]_n$ fragments not directly adsorbed on the HOPG surface.

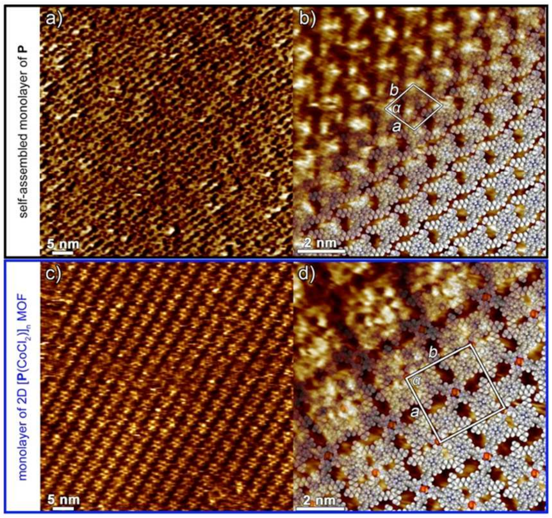


Figure 3. STM current image of a monolayer of the free tecton **P**: a) Survey image, b) Zoom-in image with proposed molecular packing motif. STM current image of a monolayer of 2D $[\mathbf{P}(CoCl_2)]_n$ architecture: c) Survey image, d) zoom-in with proposed molecular packing motif. Scanning parameters (a-d): average tunnelling current (I_t) = 25 pA, tip bias (V_t) = 650 mV. The zoom-in images without the overlaying models are shown in the ESI.

To increase the imaging resolution, a drop of non-solvent, *i.e.* 1-phenyloctane, was added to screen the tip-sample contact from condensing water vapours, and the surface was analysed by STM. Figure 3c portrays a large scale STM image of $[\mathbf{P}(CoCl_2)]_n$ monolayer. The monolayer displays a polycrystalline structure (Fig. 2c) consisting of hundreds of nanometers sized domains. The molecular packing is characterized by the unit cell a = b = (3.1±0.2) nm, and angle α = (90±2)°, which leads to an area A = (9.6±0.6) nm^2 (white square in Fig. 3d), where each unit cell contains four tecton **P** coordinated to a Co(II) centre. As expected, since each tecton **P** bears two divergently oriented monodentate sites and each Co centre behaves as a four connecting node, a 2D coordination network is generated through binding of Co(II) cations by four pyridyl units belonging to four different tectons **P**. Noteworthy, the procedure used to generate the network on the surface does not lead to the metallation of the porphyrin core by Co cation. The results obtained indicate, that the binding of Co(II) by **P** may only take place in the supernatant solution. Indeed, owing to the packing morphology of the free tecton **P** on the surface, *i.e.* parallel lamellar arrangement, the binding of Co(II) by four tectons **P** must lead to reshuffling of **P** molecules within the crystalline domain, which is energetically disfavoured in tightly packed monolayers.

Interestingly, as stated above, owing to the acentric nature of the tecton **P**, five different types of 2D networks may be formed (Fig. 2). When taking into account the metrics of the tecton **P** (blue fragment corresponding to a shorter distance between the porphyrin centroid and the coordinating N atom resulting from the direct connection of the pyridyl moiety to the *meso* position and the red fragment to a longer distance owing to the presence of the ethynyl spacer), one would expect different metrics for the unit cells corresponding to the different arrangements depicted in Fig. 2. Indeed, among the five possible connectivity modes, only the [4 red and 4 bleu] (Fig. 2a) 2D network would display perfect square geometry, whereas for the other cases, a rhomboidal geometry would be expected. Experimentally, the unit cell parameters determined by the STM investigation correspond to square type geometry and thus the formation of the 2D network of the type (a) presented in Fig. 2, highlighting the selective nature of the complexation process in the presence of the solid substrate, where the structures with: i) the highest degree of symmetry, and ii) smallest unit cell area, i.e. the structure with the highest packing density, are favoured.

In summary, by mastering principles of molecular tectonics at surfaces, we have formed and monitored by STM for the first time 2D MOFs at the solid-liquid interface. These architectures resulted from mutual interconnection of porphyrin based acentric tectons **P** bearing two divergently oriented pyridyl units and $CoCl_2$ metallatecton behaving as a four connecting node. STM imaging revealed a dramatic change between the packing of the free tecton **P** physisorbed on the surface and the formation of a periodic 2D architecture. The generation of infinite molecular patterns on graphite surface using other porphyrin based tectons and metal centres is currently under investigation.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [experimental details, full characterisation of new compounds, NMR spectra]. Experimental crystallographic data: CCDC 995030. See DOI: 10.1039/b000000x.

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