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Two-Dimensional Halogen-Bonded Porous Self-Assembled Nanoarchitectures of Copper β-Diketonato Complexes

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Abstract

Two novel copper β-diketonato Complexes with halogen atoms are synthesized. The length of complex arms is slightly different. Scanning tunneling microscopy (STM) shows that the two complexes self-assemble into porous two-dimensional nanoarchitectures at the solid-liquid interface on graphite. These arrangements are however stabilized by the formation of two different halogen synthons between neighboring molecules. These synthons are composed of four or two type-II halogen bonds. These observations reveal that a tiny modification of complex design can drastically affect the structure of two-dimensional halogen-bonded nanoarchitectures.

Introduction

Metal-containing organic species are promising building blocks to engineer novel nanoarchitectures for application in nanotechnology. β-diketonate ligands have for example been selected to create novel metalloligand complexes for the quest of molecular spin qubits.[1] To be used as molecular spin qubits, not only these complexes have to be synthesized but their collective arrangement has to be controlled to perform quantum logic operations. A rational synthetic design is thus required to govern β-diketonato complex electronic properties as well as their ability to form controlled nanostructures. β-diketonate ligands have also recently been used for the elaboration of nanoporous materials for anion exchange and scaffolding of selected anionic guests.[2] These β-diketonate based complexes are thus promising building blocks to engineer functionnal materials.

Molecular self-assembly offers unique possibilities for engineering two-dimensional (2D) nanoarchitectures on metal surfaces. The internal structure of these organic structures can be tailored at the atomic scale by exploiting intermolecular interactions.[3,4] Strong, selective and directional intermolecular interactions are required to stabilize the formation of porous organic nanoarchitecture and prevent molecules to form close-packed arrangements. Large self-assembled porous organic nanoarchitectures have thus been successfully engineered taking advantage of intermolecular hydrogen-bonds,[3,5–21] halogen-bonds,[13,22–38] metal-ligand[39–41] and organic-ionic compounds interactions.[42] Large cavities have been observed in the self-assembled molecular Sierpiński triangle fractals. These sophisticated structures have been achieved by exploiting intermolecular hydrogen-bonds,[43] metal-organic coordination interactions[43,44] and intermolecular halogen-interactions.[22] Zhang *et al.* showed that hydrogen-bond interactions appear wicker than metal-organic coordination interactions;[43] the largest Sierpiński triangle fractal motifs were achieved when the structures were stabilized by halogen-bonds[22] and metal-organic coordination interactions.[45] The halogen-bond is not only attracting interest for its high directionality and strength but also because of its potential for fine-tuning intermolecular interactions. X_2,[46–48] X_3,[22,49,50] X_4,[25,46,48,51] X_6[47] and X_∞[47] synthons have been observed in various two-dimensional arrangements. The strength of the halogen bond is however strongly depending of its geometry.[52] The high flexibility of this inter-molecular interaction combined with the tunability of the molecular building-block design offers multiple strategies to elaborate complicated self-assembled naoarchitectures with different internal structures.

In this paper the influence of molecular design on the self-assembly of two functionalised β-diketonato copper complexes at the 1-phenyloctane/graphite interface is investigated. The complex-**1** has one iodine atom at the end of its four arms, whereas the complex-**2** has a bromine atom and the length of its four arms is in addition longer. Scanning tunneling microscopy (STM) reveals that the two complexes self-assemble into halogen-bonded nanoarchitectures, having different the internal structure and different intermolecular biding.

Experimental

The synthesis of complex-**1** and complex-**2** is described in supplementary materials. Complex-**1** = cu(bipd)$_2$ with bipd = 1,3-bis(4-iodophenyl)propane-1,3-dione. Complex-**2** = cu(bbbpd)$_2$ with bbbpd = 1,3-bis(4'-bromo-[1,1'-biphenyl]-4-yl)propane-1,3-dione. The calculated Cu-O bond lengths for complex-1 and complex-2 were found to be 1.925 Å(ESI).

Solutions of the complexes in 1-phenyloctane (Aldrich) were prepared. A droplet of the solutions was then deposited on a graphite substrate. STM imaging of the samples was performed at the liquid-solid interface using a Pico-SPM (Molecular Imaging, Agilent Technology) scanning tunneling microscope. Cut Pt/Ir tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the application FabViewer.[53]

Results

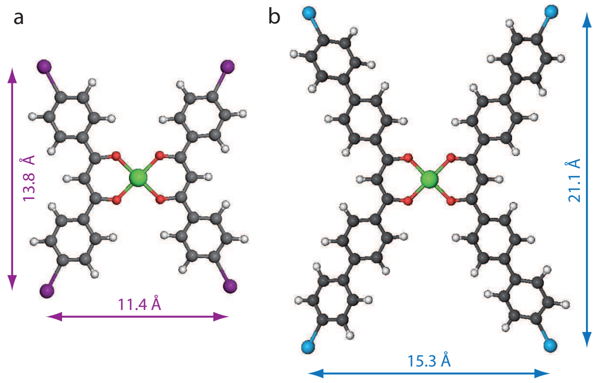

Figure 1: Scheme of the β-diketonato copper complexes, (a) $C_{30}H_{18}CuI_4O_4$ and (b) $C_{54}H_{34}Br_4Cu0_4$. Carbon atoms are gray, iodine atoms are purple, hydrogen atoms are white, oxygen atoms are red, copper atoms are green and bromine atoms are in blue, respectively.

The chemical structure of the two β-diketonato copper complexes complexes is presented in Figure 1. These 2-fold symmetry complexes are H-shaped complexes. The complex skeleton consists of a central copper atom connected to two acetylacetonate type ligands. Iodine or bromine atoms are located at the apex of the four complex arms. The iodine atom separations are 13.8 Å and 11.4 Å for the complex-**1** (Figure 1a), whereas the bromine separations are 21.1 Å and 15.3 Å for the complex-**2** (Figure 1b).

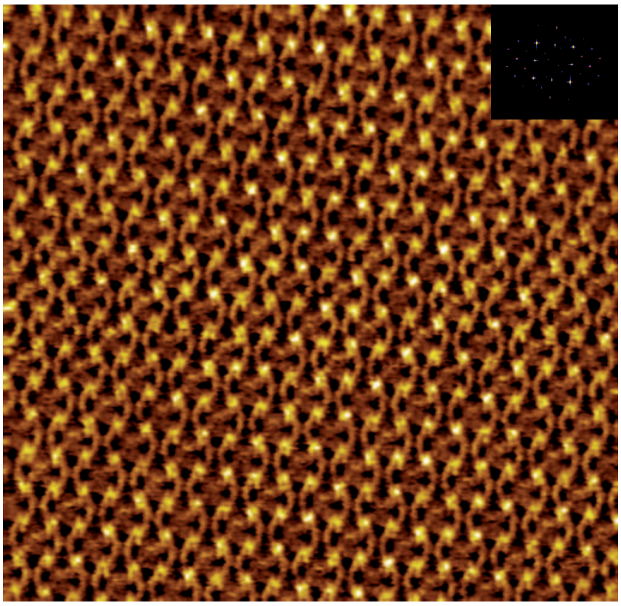

Figure 2: STM image of the complex-**1** self-assembled porous network at the 1-phenyloctane/graphite interface, 35×35 nm^2, V$_s$ = 0.55 V, I$_t$ = 9 pA. Inset: FFT of the STM image.

The STM image in Figure 2 shows the graphite surface after deposition of a droplet of complex-**1** in 1-phenyloctane. Molecules self-assemble into a large-scale 2D organic nanoarchitecture. Bright spots and dark areas are visible in the STM image. The fast Fourier transform of the STM image (inset) reveals that the unit cell of this arrangement has a nearly square-shape.

High resolution STM images of the complex-**1** self-assembly are presented in the Figure 3. The STM images in Figure 3a,b show that each molecule has four side-by-side neighbors. The bright features observed in the STM images correspond to squares composed of four bright spots. These bright spots are observed at the apex of molecular arms. It has been previously experimentally observed that halogen atoms, such as bromine and iodine, appear brighter than molecular carbon atoms in the STM images.[22,25,47] These bright spots therefore correspond to the molecular iodine atoms. The molecular arrangement is stabilized by X$_4$ synthons (highlighted with orange squares in Figure 3c). Two molecular orientations are observed in the organic nanoarchitecture, as it can

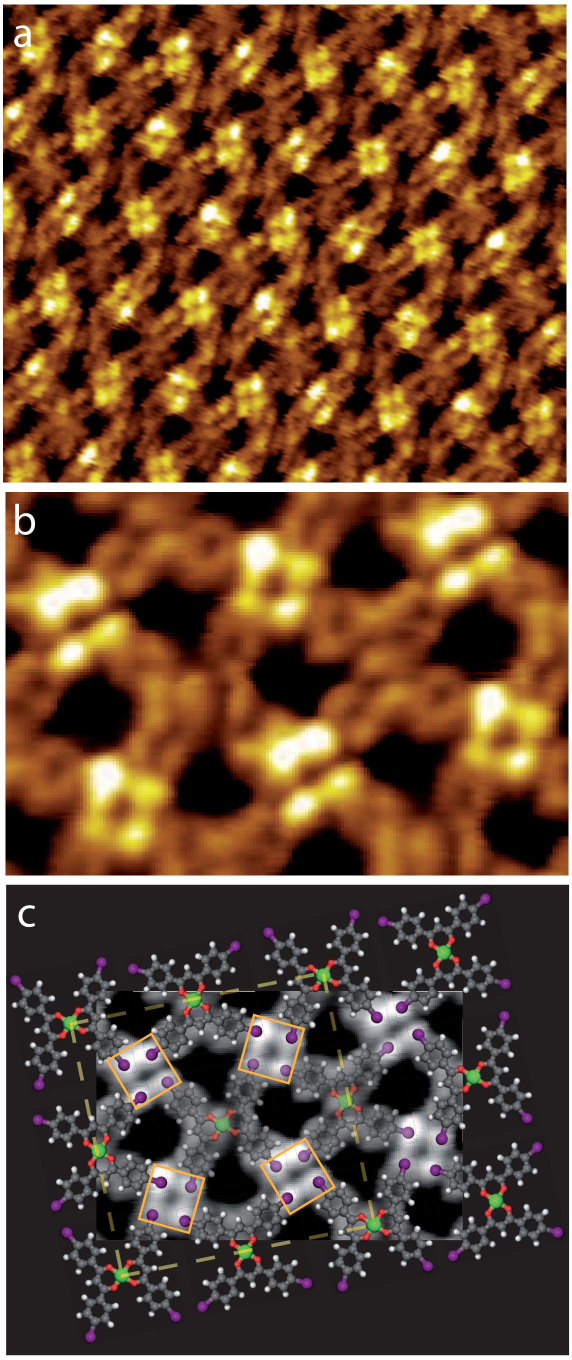

Figure 3: High resolution STM images of the complex-**1** self-assembled porous network, (a) 10×8 nm^2, V_s = 0.95 V, I_t = 9 pA, (b) 5×3 nm^2, V_s = 0.95 V, I_t = 9 pA. (c) Assembly model with the STM image in (b) placed underneath as a guide for the eyes. X_4 synthons are highlighted with orange squares.

be observed in the high resolution STM image presented in Figure 3b. Molecular closest neighbors are rotated by 90°. The model of the complex-**1** self-assembly is presented in Figure 3c. As a guide for the eyes, the STM image presented in Figure 3b has been placed underneath the schemes of the molecules, Figure 3c. The network unit cell, containing two molecules and corresponding to the FFT image in Figure 2-inset, is represented by dashed yellow lines in Figure 3c. The unit cell of this porous structure is a square with 3.4±0.1 nm unit cell constants. The molecular architecture is stabilized by halogen$\cdots$halogen interactions between neighboring molecules, forming X_4 synthons. The angle between I-C groups of neighboring molecules is ∼95 °.

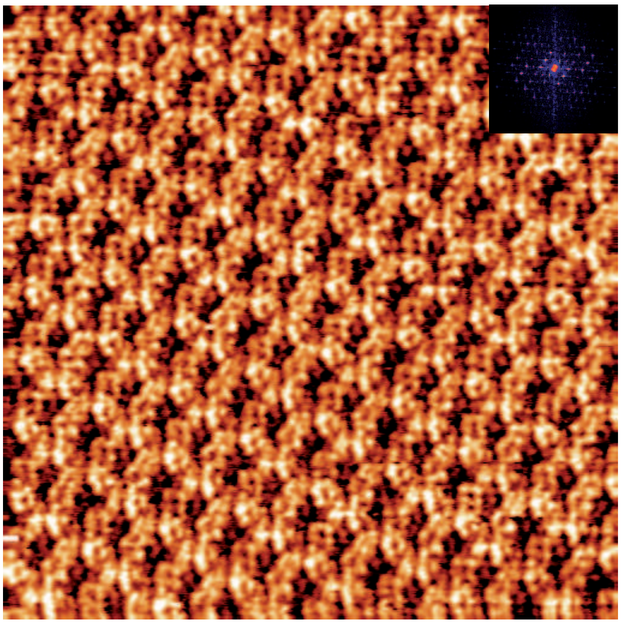

Figure 4: STM image of the complex-**2** self-assembled porous network at the 1-phenyloctane/graphite interface, 27×27 nm^2, V_s = 0.95 V, I_t = 9 pA. Inset: FFT of the STM image.

The STM image in Figure 4 shows the graphite surface after deposition of a droplet of complex-**2** in 1-phenyloctane. Molecules self-assemble into a large-scale 2D organic nanoarchitecture. The fast Fourier transform of the STM image (inset) reveals that the unit cell of this arrangement has a nearly rectangular shape.

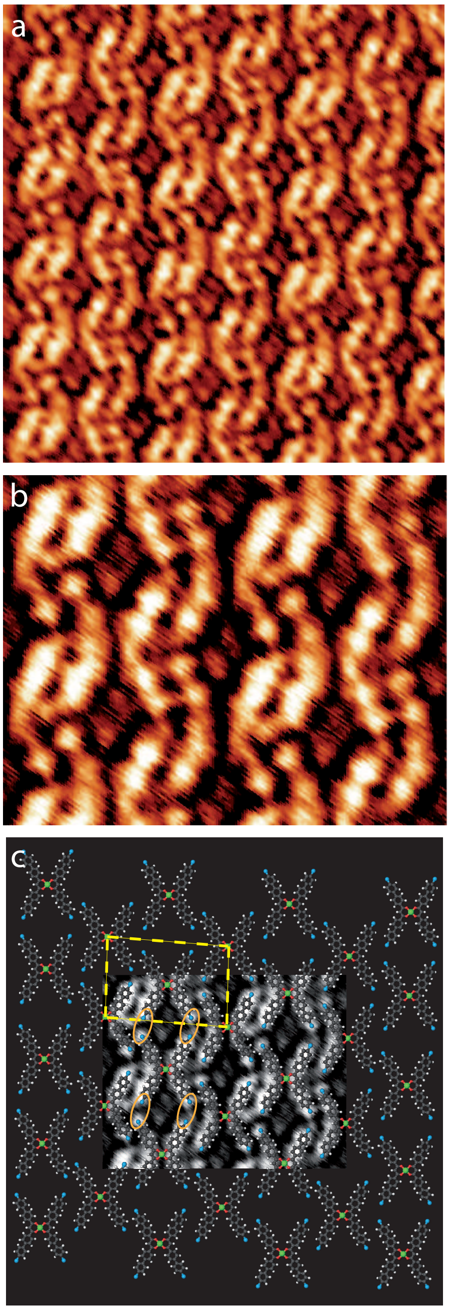

Figure 5: High resolution STM images of the complex-**2** self-assembled porous network, (a) 15×15 nm^2, V_s = 0.95 V, I_t = 9 pA, (b) 8×6 nm^2, V_s = 0.95 V, I_t = 9 pA. (c) Assembly model with the STM image in (b) placed underneath as a guide for the eyes. X_2 synthons are highlighted with orange ellipses.

High resolution STM images of the complex-**2** self-assembly are presented in the Figure 5. In contrast with complex-**1** arrangement, the STM images in Figure 5a,b reveal that only one molecular orientation is now observed in the organic nanoarchitecture. Each complex-**2** has two side-by-side neighbors and not four as the complex-**1**. Complex-**2** are forming parallel rows and neighboring rows are shifted along their axis by half a complex-length. The complex arrangement is stabilized by X_2 synthons, that can be observed in the molecular rows. The X_2 synthons are highlighted with orange ellipses in Figure 5c. There is no halogen interaction between complexes of neighboring rows, the complex arms of neighboring rows are arranged side-by-side. This configuration is therefore maximizing intermolecular van der Walls interactions. The model of the complex-**2** self-assembly is presented in Figure 5c. As a guide for the eyes, the STM image presented in Figure 5b has been placed underneath the schemes of the molecules, Figure 5c. The network unit cell, containing two molecules and corresponding to the FFT image in Figure 4-inset, is represented by dashed yellow lines in Figure 5c. The unit cell of this porous structure is a parallelogram with 4.1 ± 0.1 nm and 2.6 ± 0.1 nm unit cell constants and an angle of $93\pm1^\circ$ between the axes. The molecular architecture is stabilized along the molecular row by halogen$\cdots$halogen interactions, forming X_2 synthons. The angle between Br-C groups of neighboring molecules is $\sim127^\circ$.

Discussion

The design of complex-**1** and complex-**2** is very similar. The length of complex-**2** arms is increased by the insertion of one additional phenyl ring in comparison with the complex-**1** arm, Figure 1. STM shows that the two H-shaped complexes self-assemble into 2D porous nanoarchitectures stabilized by intermolecular halogen interactions at the 1-phenyloctane/graphite interface. Two molecular orientations are observed in the complex-**1** arrangement. Neighboring molecules are rotated by 90 ° in comparison of each other. In contrast, only one orientation is observed in the complex-**2** arrangement. The complex-**1** arrangement is in addition stabilized by X_4 halogen synthons, whereas the complex-**2** arrangement is stabilized by X_2 halogen synthons. The angle between the complex halogen-carbon covalent bond (X-C) of neighboring complexes is different in the complex-**1** X_4 synthon and the complex-**2** X_2 synthon. This angle is 95° in the X_4 synthon, whereas it is 127° in the X_2 synthon. Bui $et\ al.$ previously showed that the strength of the halogen$\cdots$halogen interaction depends of the C-X$\cdots$X-C binding angle.[52] The halogen$\cdots$halogen interaction strength is similar to van der Waals interactions when the C-X$\cdots$X-C angle is 180°. This interaction is called a Type-I halogen interaction. In comparison the strength of the halogen$\cdots$halogen interaction is stronger and is similar to the one of a hydrogen-bond when the C-X$\cdots$X-C angle is 90±30°. This bond is called a type-II halogen interaction (it should be noticed that only the Type-II halogen interaction is considered as a "true" halogen-bonds by the IUPAC Recommendations 2013[54]). The high resolution STM images in Figure 3 and Figure 5 are thus revealing that the X_4 synthon as well as X_2 synthon are only composed of Type-II halogen interactions (halogen-bonds only). The STM images are showing that the complex-**1** nanoarchitecture is only stabilized by halogen-bonds, but the complex-**2** arrangement is also stabilized by intermolecular van der Walls interactions, i.e. neighboring complex arms are arrangement side-by-side. These observations reveals that a tiny modification of the complex design can drastically affect its arrangement.

The graphite surface was selected because it is expected to weakly interact with the molecules. Molecules are usually strongly interacting with semiconducting surfaces but less with conductive and metal surfaces. However when molecules with halogen atoms are deposited on metal surfaces, dehalogenation through Ullmann coupling may already occur at room temperature. Halogen-bonded intermolecular interactions can therefore be investigated on graphite surface,[25,46,55,56] whereas noble metal surfaces are promising surfaces to engineer on-surface synthesized covalent nanoarchitectures.[47,57]

Conclusion

To summarize, the influence of complex design on H-shaped copper β-diketonato complex self-assembly at the 1-phenyloctane/graphite interface was investigated using scanning tunneling microscopy. Complexes self-assemble into different porous halogen-bonded nanoarchitectures. STM revealed that the geometry of the halogen synthons stabilizing these nanoarchitetcture is drastically influence by the complex design. These observations show that halogen$\cdots$halogen bonds are promising intermolecular binding to control and tune two-dimensional arrangement of molecular magnet on flat surfaces. This opens up new opportunities for engineering tailored organic magnetic nanoarchitectures at the nanometer scale.

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Supporting Information Available

Preparation and synthesis of the Ligands and complexes and the computational details for the optimization of the complex geometry are presented in the supporting information.

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