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Controlled Arrangement of Supramolecular Metal Coordination Arrays on Surfaces**

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The arrangement of special functional units with nanometer dimensions into defined molecular architectures on surfaces is one of the major goals in supramolecular, polymer, and material science in view of the potential applications of these systems in nanotechnology with regards to molecular information storage devices or functional surfaces.[1] This requires a precise control of the structures at very different length scales ranging from molecular size to micrometers. One promising approach for the construction of nanometric size objects comes from supramolecular chemistry.[1] It has been demonstrated in the last few years that information stored in molecular components can be read out by noncovalent interactions, for example, hydrogen-bonding[2] or metal-ligand[3] interactions, to assemble the final well-ordered architectures. Recently a new class of coordination arrays presenting a two-dimensional $[2 \times 2]$ grid-type architecture based on transition metal ions with octahedral coordination geometry was described (Figure 1a).[4, 5] These complexes were found to present interesting electronic, magnetic, and structural properties, such as electronic interactions between the metal centers and an antiferromagnetic transition at low temperatures[5, 6] (Figure 1b). They are formed by the spontaneous self-assembly of 4,6-bis(2′,2″-bipyridyl-6-yl)pyrimidine ligands[4] (or its functionalized derivatives[7]) and suitable metal ions such as Co^{II} (Figure 1a).[5]

Besides the design and synthesis of "isolated" grid units, the ordered and stable arrangement of such metallo-supramolecular architectures on surfaces or in thin films is of special

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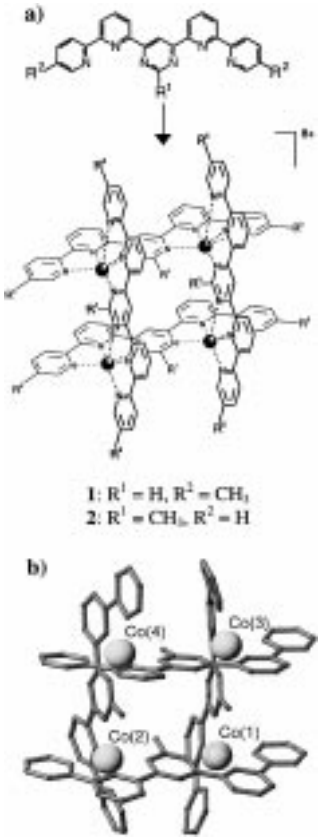

Figure 1. a) Schematic representation of the bis-terdentate ligands that lead to the formation of the $[2\times2]$ grid type complexes $[Co_4L_4]^{8+}$ **1** ($R^1=H$, $R^2=CH_3$) and **2** ($R^1=CH_3$, $R^2=H$); b) crystal structure of the $[Co_4L_4]^{8+}$ cation **2** (wireframe model) showing the gridlike arrangement of the four ligands and the four metal ions ($R^1=CH_3$, $R^2=H$).[5]

interest. Ordered layers of grids could provide materials with functional units smaller than quantum dots,[8] but with the additional advantage that they can be formed by spontaneous assembly, instead of microfabrication. It might be possible to inscribe patterns that could be read out nondestructively,[1, 3b] by addressing the metal ions photo- or electrochemically, to provide a basis for the construction of information storage devices.[9] Two approaches were recently described: a) hydroxy-terminated grids were organized on a water trough by using the Langmuir–Blodgett (LB) technique and then transferred onto substrates;[10] b) unfunctionalized ligands were self-assembled at the air–water interface.[11] However, both methods could not provide ordered monolayers of grids. Furthermore, images with molecular resolution of the grids within the layers could be obtained by using scanning tunneling microscopy (STM). Herein we describe two different methods for the preparation of highly ordered monolayers of grids on surfaces and the use of STM techniques to image and write with molecular resolution in monolayers of grids on solid surfaces. Technical aspects and diffusion parameters will be published elsewhere.[12]

Highly oriented pyrolitic graphite was treated with diluted solutions of grids in acetone to obtain well-defined layers, and the surface architecture was investigated by STM. Two types of cobalt grids were used, differing in the position of the methyl groups (Figure 1): $[Co_4(L)_4](PF_6)_8$ (**1**, with $R^1=H$, $R^2=CH_3$) and $[Co_4(L)_4](AsF_6)_8$ (**2**, with $R^1=CH_3$, $R^2=H$). The key point for these experiments was the preparation of monodisperse solutions of grid molecules that did not contain aggregates of $[2\times2]$ complexes. As a consequence of the highly charged character of the grids they have a pronounced tendency to form clusters, which had to be controlled carefully. For the latter purpose sedimentation equilibrium analysis in an analytical ultracentrifuge was used.[13] Monodisperse solutions containing only the isolated grid units were obtained. Two different methods for the deposition of the grids from these solutions on the graphite surface were applied: 1) a drop of the solution was placed on a substrate that had already been scanned by STM, and after evaporation of the solvent the experiments were performed; 2) the substrate was dipped into the solution and scanned after evaporation of the solvent. By using method 1 monolayers of grid **1** could be prepared as shown in Figure 2a. The molecular pattern with nearly orthogonal periodicities of 1.35 nm × 2.6 nm is consistent with the size of the $[2\times2]$ Co^{II} grid **1** oriented normally to the surface (Figure 2b).[14] Furthermore, a periodicity of 0.6 nm could be observed, which correlates with the Co–Co distance within the grids (distance obtained from single-crystal X-ray data: 0.64 nm[5]). Investigation of the orientation of the molecular arrangement relative to the graphite lattice (Figure 2a, small picture) led to the assump-

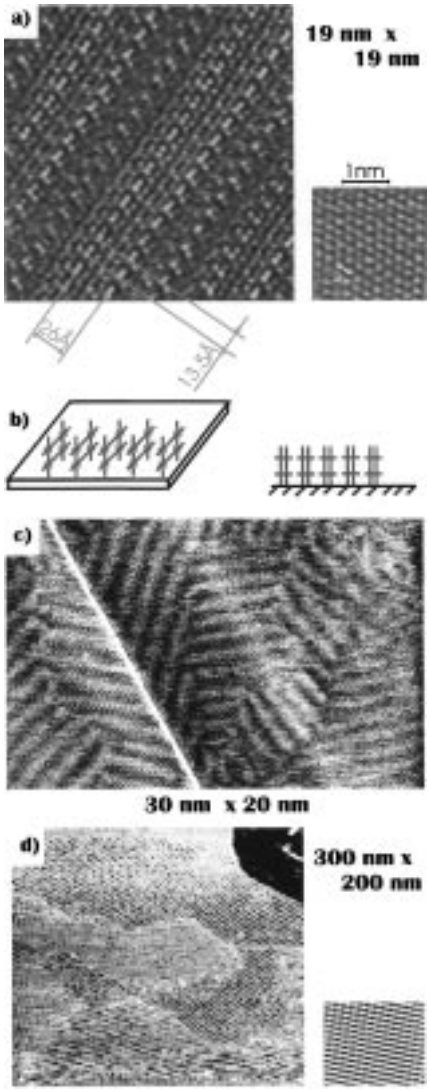

Figure 2. a) STM height image of grid **1** adsorbed by method 1. Height range of 0.5 nm, $I=8$ pA, $V=-50$ mV. The small picture shows an STM image of the underlying graphite lattice (side length 3 nm, $I=100$ pA, $V=-2$ mV). b) Tentative interpretation of the vertical arrangement of the grids on the surface. c) Domain structure of grid **1** adsorbed to graphite by method 1 (STM height image, height range of 0.5 nm, $I=8$ pA, $V=-50$ mV). d) Monolayer domain structure of grid **1** deposited by dipping of graphite into the solution (method 2). An uncovered area of graphite is visible in the upper right corner of the picture (STM height image, height range of 0.5 nm, $I=10$ pA, $V=-1$ V). The small picture shows a Fourier-filtered STM current image of the molecular arrangement (side length 25.2 nm; current range of 3 pA, $I=10$ pA, $V=-1$ V).

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tion that two ligands lie along that main direction and another two ligands are oriented normal to the graphite surface. A view of a larger area showing the boundaries between different domains is shown in Figure 2c.[14] The period of the superstructure observed is compatible with the period of the molecular arrangement (the different periods of superstructure have been observed with values from two to five periods of molecular rows): the 120° angle between strips of superstructure in neighboring domains corresponds to the hexagonal graphite lattice. By using the dipping deposition (method 2) a domain structure with grain boundaries was observed (Figure 2d, the edge of the film is visible in a defect area in the upper right corner of the picture). The molecular lattice values are comparable to the values obtained by the first method of sample preparation.

Deposition of grid **2** gave a layer that showed a molecular periodicity of the adsorbed grid molecules on the graphite surface different from grid **1**. A monolayer with periodicities of 2.5 nm × 2.4 nm was found (Figure 3a). These findings correspond to an adsorption of the grids parallel to the surface (Figure 3b). A large area image with boundaries between different domains could also be obtained in this case (Figure 3c). The differences in the orientation of the grids in the two cases may result from a number of contributions, in particular the packing, the different position of the methyl groups, and the interaction with the counterions. For a first attempt at interpreting the fine pattern in the STM images we performed local electron density calculations (Figure 4).[15] The calculated electron density distributions were in good agreement with the distribution determined by the STM technique.

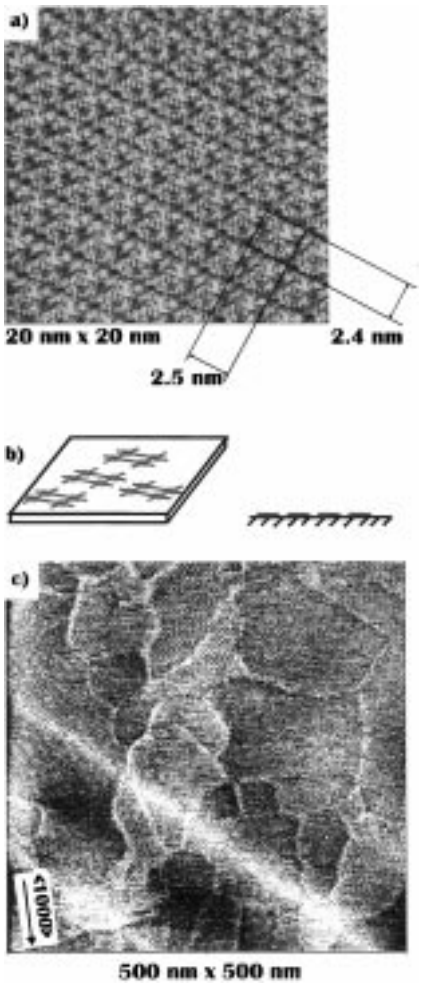

Figure 3. a) STM height image of grid **2** deposited on graphite by method 1 (height range of 0.5 nm, $I = 8$ pA, $V = -50$ mV); b) tentative interpretation of the horizontal arrangement of the grids on the surface; c) domain structure of grid **2** adsorbed to graphite by method 1.

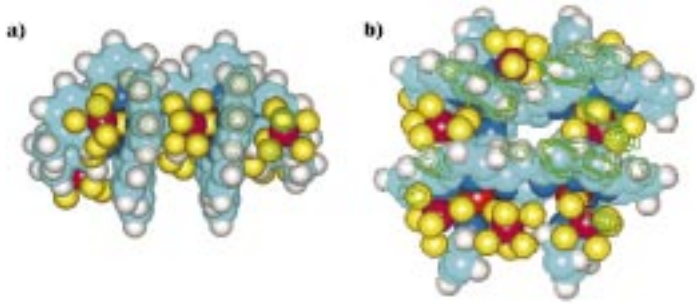

Figure 4. Schematic representation of the local electron density distribution: a) green circles represent the contours of equal electron density over grid **1** with a plane offset of 7.8 Å relative to the center of the cation; b) green circles represent contours of equal electron density over grid **2** with a plane offset of 16 Å relative to the third graphite plane.[15]

As first experiments of molecular manipulation of such ordered metallo-supramolecular architectures on surfaces and in order to determine the exact position of the grids we performed the extraction of single grids from the monolayer. A single grid **1** could be removed by a short negative voltage pulse (Figure 5a, $V_{tip} = -0.5$ V, 1 ms). The dimensions of the hole correspond to the size of the cation (Figure 5b). In contrast positive voltage pulses did not affect the STM images. An extension of this manipulation process resulted in larger holes (Figure 5c, here three grids are missing).

The present results demonstrate a simple entry to controlled arrangements of metallo-supramolecular grids on surfaces. Monodomains of regularly packed layers of adsorbed grids with defect free areas up to 0.5 mm^2 were observed, which amounts to a sort of spontaneous two-dimensional crystallization. The arrangement of molecules, as observed by STM with molecular resolution, displays excellent stability and reproducibility of the structure period. Two different molecular orientations on the surface could be observed. This result indicates that it may be possible to control the surface architectures through the introduction of specific substituents at given locations in the ligand. Single grids could be removed from the ordered surface architecture in a controlled way. Investigations in the direction of generating stable metallo-supramolecular architectures on surfaces and performing reversible molecular manipulations are being pursued.

Experimental Section

The 4,6-bis(2′,2″-bipyridyl-6-yl)pyrimidine ligand and its derivatives were synthesized as described in references [4, 7]. The reaction of equimolar quantities of the molecules and Co^{II} acetate in refluxing methanol led exclusively to the formation of the tetranuclear complexes (isolated as PF_6 or AsF_6 salts and recrystallized from acetone/diethyl ether).[5]

For the ultracentrifuge experiments, solutions of the complexes in acetone with a sample concentration of 0.2 mg mL^{-1} and 40 mM NH_4PF_6 were used.

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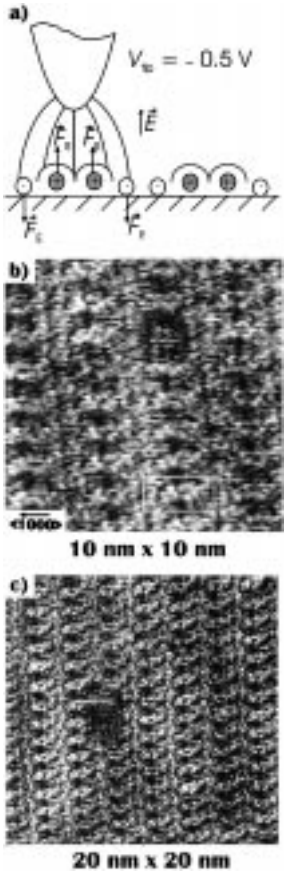

Figure 5. Single cation extraction experiments from the monolayer of grid **1** by pulse voltage with $V = -0.5$ V (STM height image, height range of 0.5 nm, $I = 8$ pA, $V = -50$ mV). a) Schematic representation of the method; b) removal of one grid; c) removal of three grids.

The grids were stirred vigorously for approximately one week before measurement. Sedimentation equilibrium experiments were performed in a Beckman Optima XL-A ultracentrifuge: An-60 Ti rotor, rotor speed 40000 rpm, rotor temperature 20 °C, titanium double sector centerpieces (BASF AG, Ludwigshafen), polyethylene gaskets.[13] The absorbance of the samples as a function of radius $A(r)$ were recorded at 430 nm and evaluated assuming ideal sedimentation behavior.[16]

Sample preparation**:** Two different methods were applied for deposition on the graphite surface: 1) A drop of the dilute solution in acetone ($c = 0.1$ g L^{-1}) was placed on a freshly cleaved surface of highly oriented pyrolitic graphite (HOPG) after the surface had already been scanned by STM under conditions that allowed an atomic resolution of the graphite surface structure. A potential of $V = \pm 50$ mV and -1 mV (bias voltage) was applied to the substrate in different experiments (scan rate: 20–60 nm s^{-1}; tunneling current set point 1–15 pA). The tip was retracted from the surface to a distance of 2 mm when the solution was added. After about 20 s the acetone had evaporated, the tip was moved back to the surface, and scanning of the sample under the above conditions could be started. 2) A freshly cleaved piece of graphite was dipped into a dilute solution ($c = 0.01$ g L^{-1}) and extracted at a rate of 1 mm min^{-1}.

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