

Positioning of Single Co Atoms Steered by a Self-Assembled Organic Molecular Template

Wolfgang Krenner,^{*,†} Florian Klappenberger,[†] Dirk Kühne,[†] Katharina Diller,[†] Zhi-Rong Qu,[‡] Mario Ruben,^{‡,§} and Johannes V. Barth[†]

[†]Physik Department E20, Technische Universität München, James-Frank-Strasse, 85748 Garching, Germany

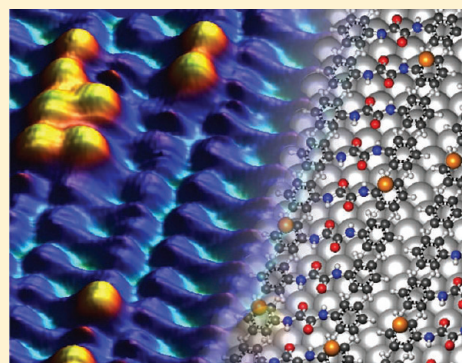
[‡]Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

[§]IPCMS-CNRS UMR 7504, Université de Strasbourg, 23 Rue du Loess, 67034 Strasbourg, France

S Supporting Information

ABSTRACT: The bonding and organization of cobalt atoms on a self-assembled organic molecular template are investigated by low-temperature scanning tunneling microscopy. In a first step, *N,N'*-diphenyl oxalic amide is deposited on the Ag(111) surface with submonolayer and monolayer coverage, leading to the formation of supramolecular nanogratings and a dense-packed layer, respectively. These templates are exposed to evaporated cobalt at different substrate temperatures in the range of 110 to 240 K. We find that Co always binds on top of the phenyl rings, and thus the realization of Co–phenyl complexes is preferred over metal cluster growth on the bare Ag(111) surface. In the case of the dense-packed template, a large fraction of the provided Co is engaged in the formation of well-defined, uniform monomeric Co-half-sandwich structures. At optimal temperatures in the 180–200 K range, the fraction of monomeric Co species on the template exceeds 80% of the total amount of Co deposited. The temperature-dependent adsorption behavior and monomer fraction are compared with calculations, simulating the site-selective positioning in the diffusionless limit by a hit-and-stick adsorption model. This analysis indicates that the organic template suppresses the clustering tendency inherent to diffusing Co atoms and allows the production of a monomer fraction as high as that for statistical growth in the low-coverage regime.

SECTION: Nanoparticles and Nanostructures



Single atoms on surfaces are possible units for future high-density magnetic data storage or spin computation applications. Therefore, in recent years, the organization and magnetic properties of single spin species have been under extensive investigation.^{1–7} Experiments have shown that the magnetic anisotropy energy, which leads to an alignment of the magnetization along specific spatial directions rather than randomly oscillating spins, depends strongly on the exact dimensionality, arrangement, and substrate used in these systems.^{8–15} Furthermore, the interaction between these spins gives rise to intriguing phenomena like the many-body Kondo effect and magnetocrystalline anisotropy.^{14–17} Extensive research toward ordered arrays of single-molecule magnets and their properties has also shown to provide a possible route toward the realization of molecular spintronics.^{18–22} As a whole, the field of research toward single magnetic species is limited by the level of control over the creation of magnetic objects. Therefore, for the realization of future magnetic nanodevices, the development of novel techniques to steer the formation of low-dimensional magnetic systems is a necessary prerequisite.

Recently, structures formed by bonding of Co dimers, residing axially on benzene or graphene, have been theoretically predicted to show huge magnetic anisotropies and were therefore proposed

as candidates for magnetic storage applications.^{23–25} In this work we explore the route toward the realization of such structures by employing a supramolecular engineering approach²⁶ to produce arrays of single magnetic atoms on top of a molecular template. Specifically, we used low-temperature scanning tunneling microscopy (STM) to investigate, first, the self-assembly of *N,N'*-diphenyl oxalic amide molecules^{27–29} on the Ag(111) surface and, second, the organization and bonding of Co atoms on the templated surface. The organic precursor forms, depending on coverage, nanogratings or a perfect dense-packed monolayer, on which Co adsorbs on top of the phenyl rings yielding Co-half-sandwich complexes,^{30–32} that is, compounds with a single magnetic metal atom and Co clusters. In the saturated organic layer case, the adsorption behavior depends on the substrate temperature during growth and the cobalt coverage, yielding high amounts of Co monomers. A comparison with the cluster distribution predicted for diffusionless growth by a simple statistical adsorption theory assuming a hit-and-stick behavior shows that the supramolecular template is hindering Co diffusion and cluster formation.

Received: May 19, 2011

Accepted: June 13, 2011

Published: June 13, 2011

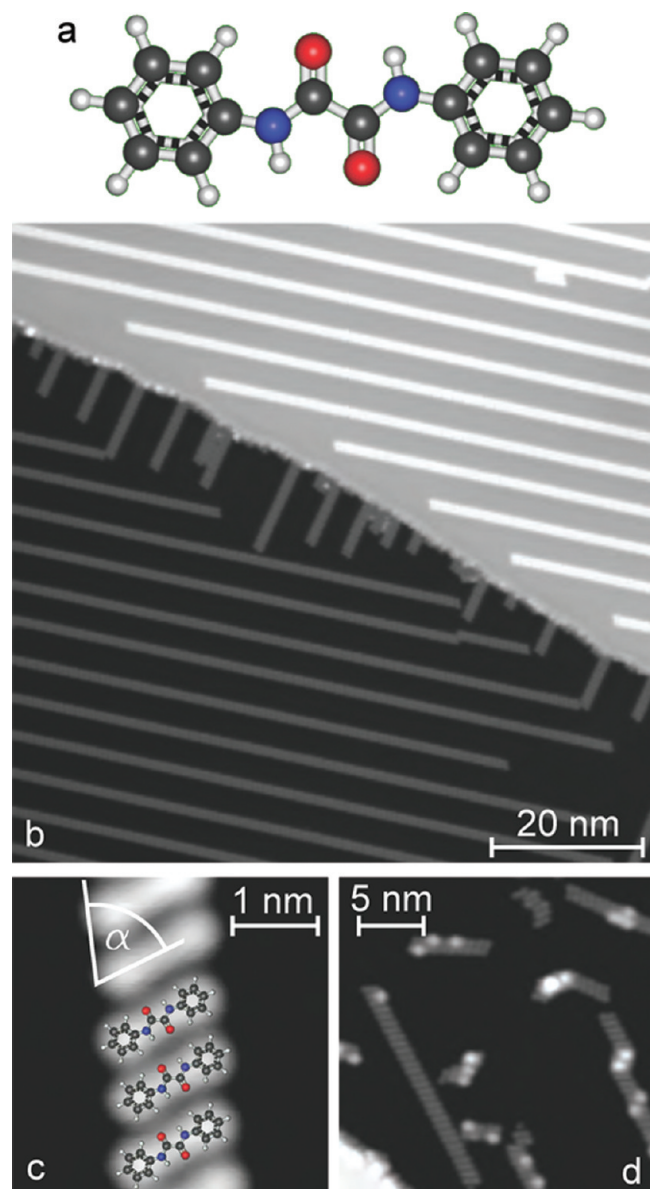


Figure 1. (a) Structure model of *N,N'*-diphenyl oxalic amide (H, white; C, black; O, red; N, blue). (b) Overview image of equally spaced molecular lines assembled on the Ag(111) surface. (Bias voltage: $V_B = -1.0$ V, tunneling current: $I_T = 0.1$ nA) (c) High-resolution image with molecular models superimposed. ($V_B = -0.3$ V, $I_T = 0.11$ nA). A single molecule is imaged as a dog-bone-like protrusion. This appearance originates from the two broader phenyl rings at the outer ends connected by a thinner waist. An arrangement of molecules forming pairs as a substructure of the nanowires is observed. This leads to $\alpha \approx 70^\circ$ between the nanowire direction and the molecular backbone. (d) Addition of Co at low temperatures ($T_{\text{dep}} = 130$ K) leads to adsorption on top of the phenyl rings instead of adsorbing to the silver surface. However, lines start to bend and break when Co is present ($V_B = -0.2$ V, $I_T = 0.1$ nA).

In the experiments, we prepared templates of organic *N,N'*-diphenyl oxalic amide molecules (Figure 1a) constructed via self-assembly. For molecule coverages below one monolayer (ML), an arrangement of approximately equally spaced lines of molecules (appearing brighter than the substrate) is observed (Figure 1b), similar to supramolecular gratings previously reported.^{33–35}

Pairs of molecules forming a substructure in the chains are encountered (Figure 1c). An angle of $\alpha \approx 70^\circ$ between the direction of the molecular nanowires and the long axis of molecules themselves as well as a slight tilt of the phenyl moiety with respect to the surface plane is observed in this case.^{28,29} However, recent theoretical work indicates a different bonding scheme as proposed in refs 28 and 29 for stabilizing the chain formation, which will be discussed in an upcoming publication.

Cobalt evaporation onto such a sample held at a deposition temperature (T_{dep}) of 130 K leads to a decoration of the molecules appearing as white dots on gray molecules, whereas no adsorption on the silver surface (black) is observed. (See Figure 1d.) In contrast, evaporation of Co onto the pristine surface without the organic template under similar conditions leads to the formation of clusters with a lateral size of several nanometers prevalently attached to the step edges.³⁶ Therefore, in our case, the presence of the molecular nanostructure suppresses the growth of large clusters and drastically reduces the size of the Co formations. The smallest objects are in the subnanometer regime and situated on either side on top of the nanowires but not in the center. However, there are also large clusters, frequently connected with breaking and bending of the molecular lines. (See Figure 1d.) The limited stability of the nanowires hence prevents the expression of regular nanostructures. By contrast, it was recently demonstrated by Decker et al.³⁷ that with a more stable template, namely, a self-assembled metal–organic network constructed from dicyanitrile–polyphenyl coordinated to Co centers,^{38,39} it is possible to create metal clusters on top of the template without destroying the molecular layer.

For a coverage of a saturated ML, a dense-packed arrangement of the molecules is observed. (See Figure 2a.) Even after evaporation of a sufficient amount of molecules onto a sample held at room temperature, no multilayer formation occurred. We conclude that excess molecules do not stick or merely remain transiently and desorb again under these conditions. Therefore, a perfect dense-packed ML covering the entire surface can easily be constructed. In this case, the supramolecular structure differs from the submonolayer (sub-ML) case in that no pairing occurs within the entire domain. The angle β between the nanowire direction and the molecular backbone amounts to $\beta \approx 80^\circ$. (See Figure 2b.) The packing theme resembles the structure also found in the bulk crystal.²⁹

When Co is deposited onto the organic ML, sub-nanometer-sized structures again evolve in a highly site-selective process. As evidenced in the high-resolution image in Figure 2c, the Co-induced nanostructures feature uniform structural characteristics. They are imaged as circular dots with an apparent diameter of ~ 6 Å and an apparent height below 1 Å, with the exact height depending on the experimental conditions, mainly the state of the tip and the bias voltage. Co atoms are positioned at the phenyl ring positions of the molecules. From the uniform shape and small size, we conclude that each dot actually represents a single Co atom. This interpretation is consistent with the amount of Co expected based on the flux calibration of the evaporator used in the experiments. The unoccupied part of a molecule hosting a Co atom is imaged with the same characteristics as the corresponding part of a molecule without Co attached. This observation indicates that the Co is residing on top of the phenyl ring. For the case of a Co atom positioned between the phenyl moiety and the Ag substrate, an uplift of the molecule would result, entailing a change in the appearance of the entire molecule, affecting the STM imaging of both phenyl moieties. Furthermore in such a

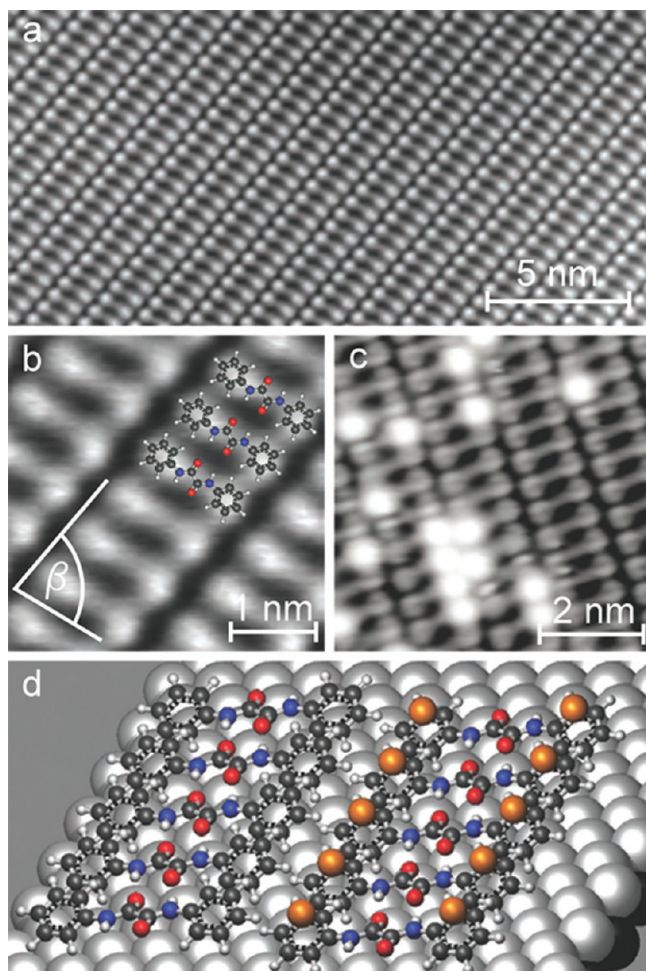


Figure 2. (a) Topographic image of a dense-packed ML of N,N' -diphenyl oxalic amides ($V_B = -1.25$ V, $I_T = 0.06$ nA). (b) High-resolution image with superimposed molecular model highlights the bonding scheme ($V_B = -0.31$ V, $I_T = 0.1$ nA). The molecules form two hydrogen bonds with each adjacent molecule, which leads to a bulk-like arrangement with $\beta \approx 80^\circ$. (c) Co atoms (bright protrusions) adsorb monomerically on top of the phenyl rings of the molecules without inducing defects in the organic template ($V_B = -0.98$ V, $I_T = 0.09$ nA). (d) 3D visualization of bare molecules (left row) and molecules with Co (orange) adsorbed on top (right row) in the ideal case of all phenyl rings being occupied by a single atom, thereby forming a dense-packed arrangement on the Ag(111) surface (silver spheres underneath).

case, the lateral bonding scheme would be affected, which is not supported by the data. Also, the possibility of the Co centers engaging in lateral metal–ligand interactions and connecting the reactive oxalic amide moieties must be excluded because major rearrangements of the lateral order scheme appear in such situations.^{40–42} Therefore, we conclude that uniform Co-half-sandwich structures^{30–32} are formed.

In contrast with the sub-ML grating, the saturated organic layer is stable enough to host high Co densities without a modification of its structure. This can be attributed to the high packing density increasing the stability due to more lateral intermolecular interaction and steric hindrance in contrast with the sub-ML regime.

However, defect and cluster formation cannot be eliminated completely. As shown in Figure 3a, the major part of the Co adsorbs monoatomically (imaged as yellow dots residing on the

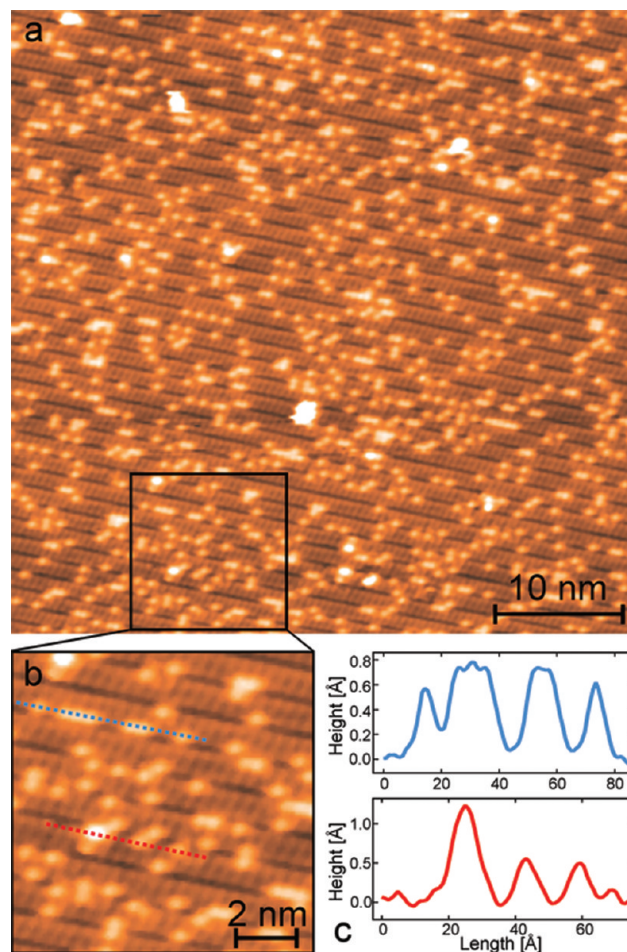


Figure 3. (a) Overview image of Co atoms adsorbed on the dense-packed ML (125 s Co at a flux of 0.0018 MLs/s, $T_{\text{dep}} = 180$ K, $V_B = 1.0$ V, $I_T = 0.1$ nA). Co monomers appear as yellow protrusions, whereas defects are imaged as white protrusions on the orange molecular template. In a zoomed in area of the sample (b) an enhancement in the apparent height ($\sim 30\%$, from ~ 0.6 to ~ 0.8 Å) for adatoms adsorbed on neighboring phenyl rings (blue dashed line) can be distinguished from the enhancement ($\sim 100\%$, from ~ 0.6 to ~ 1.2 Å) due to the presence of a dimer (red dashed line), as can be seen in the corresponding line scans (c).

molecular template depicted as orange, dog-bone-like protrusions), whereas defects, that is, clusters with more than one atom, appear as white regions with irregular shape and height.

A high-resolution image (Figure 3b) is used to exemplify the following analysis of cluster sizes based on their apparent height. The upper linescan across a line of monomers (blue) shows a maximal variation of the apparent height of atoms adsorbed along the phenyl ring chain of adjacent molecules of only 0.2 Å (Figure 3c, upper panel). The lower linescan across two monomers and a cluster (Figure 3b, red) displays an apparent height difference of ~ 0.6 Å, which can be clearly distinguished from the variations of the monomers. Clusters with characteristics as defined by the red linescan are assumed to consist of two Co atoms probably stacked upward on one another. Such a stacking was already demonstrated on the bare Ag(111) surface for Mn atoms by Klier et al.⁴³ Therefore, the protocols employed in our approach potentially yield the upright Co-dimers, as proposed by Xiao et al.^{23,25} and Cao et al.²⁵ in small numbers.

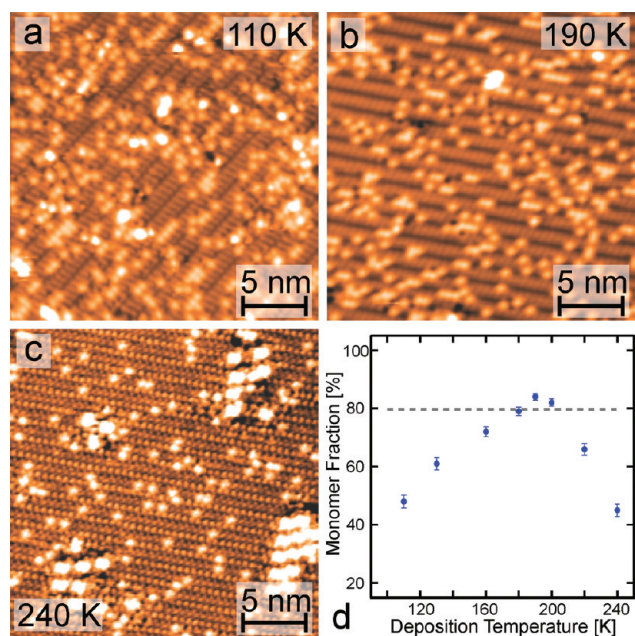


Figure 4. Exemplary topographs of samples with a constant Co coverage (0.23 MLs) evaporated at varying deposition temperatures (T_{dep} as indicated) onto the dense-packed organic template and monomer fraction analysis for the complete series of experiments. (a) At $T_{\text{dep}} = 110$ K, Co monomers (yellow) and defects of different size (white) cover the organic template (dark orange) ($V_{\text{B}} = 0.6$ V, $I_{\text{T}} = 0.05$ nA). (b) Under ideal growth conditions ($T_{\text{dep}} = 190$ K), monomeric Co dominates over a small number of defects that are characterized by a larger average size than in the previous case ($V_{\text{B}} = 0.4$ V, $I_{\text{T}} = 0.08$ nA). (c) For $T_{\text{dep}} = 240$ K, the number of monomers is smaller, and the defects are larger than those for lower temperatures. The defects have a tendency to assume a specific shape ($V_{\text{B}} = 0.9$ V, $I_{\text{T}} = 0.1$ nA). (a–c) Note that the change in the appearance of the molecular template is due to different imaging conditions and not due to a change in the molecular layer. (d) Monomer fraction is small ($\sim 40\%$) at both ends of the studied temperature range and increases monotonically toward the optimal growth temperature ($T_{\text{dep}} = 190$ K). The gray dashed line indicates the value expected for such a coverage from a simple hit-and-stick statistics. Under ideal deposition conditions, this value is nominally slightly exceeded.

However, with increasing coverage, the formation of higher concentrations of Co-dimers may become more likely. As is explained in the Supporting Information in further detail, we approximated larger clusters to be cone-shaped structures of several layers of Co stacking upward on several monomers adsorbed on neighboring phenyl rings. To evaluate the statistical error, we assumed an uncertainty for determining the flux calibration from the total amount of Co deposited in the experiments of 10%. (See the Supporting Information for details.)

Subsequently, we examined the ratio between monatomic Co adsorbates and defects in dependence of the substrate temperature during Co deposition (Figure 4). A series of experiments was carried out, wherein the total evaporated amount of Co was kept constant, whereas the sample temperature during metal evaporation was varied from 110 to 240 K. The nominal amount of Co was chosen to cover $\sim 23\%$ of the phenyl rings provided by the template if all Co atoms were adsorbed monatomically. Therefore, the samples had a Co coverage of 0.23 MLs, defining the metal ML corresponding to one Co atom per one phenyl ring of the organic template. For low temperatures, starting at 110 K (Figure 4a), a substantial amount of the

deposited Co atoms is found to form clusters (irregular, white protrusions) instead of adsorbing as single atoms (yellow dots). The fraction of monatomic Co of the total amount of deposited metal atoms, from here on referenced to as monomer fraction (MF), is determined to be $\sim 50\%$. In this fraction, the total Co amount is the nominal amount calculated from the flux calibration and the evaporation time. With increasing sample temperature, the MF increases (Figure 4d) until a maximum is reached at $T_{\text{dep}} = 190$ K. An image recorded on a sample grown at $T_{\text{dep}} = 190$ K (Figure 4b) demonstrates that the majority of adsorbates appear as circular and uniform protrusions, whereas defects show a tendency toward increased size but clearly form less frequently. Under these optimal growth conditions, the MF peaks at $\sim 80\%$. For temperatures exceeding 200 K, cluster formation increases; therefore, the MF declines. As shown for 240 K, in Figure 4c, the number of single atoms (yellow protrusions) is strongly reduced, whereas the formation of clusters with rather similar shape and size (bright protrusions) is encountered, with the MF being reduced to $\sim 45\%$. The dependence of the MF on T_{dep} is displayed in Figure 4d, where the value for all samples of the series is given with blue dots. The curve exhibits a maximum at an optimal temperature $T_{\text{opt}} = 190$ K. With increasing temperature difference to T_{opt} , the MF decreases monotonically to lower as well as to higher temperatures. This behavior suggests two competing effects that govern the ordering process. On the basis of the comparison with the model value, we suggest the following scenario to govern the MF dependence. The MF at low temperature ($T_{\text{dep}} < T_{\text{opt}}$) is significantly less than the expectation value calculated in the hit-and-stick model, where a random bonding at phenyl moieties without diffusive displacements is posed. (See further discussion below and the Supporting Information for a detailed description of the calculation procedures.) This difference indicates spurious or hidden effects leading to cluster formation, with Co atoms possibly undergoing transient motion after their impact on the organic layer until the adsorption energy is dissipated. (Note that such effects have been rarely reported for metals^{44,45} and frequently involve precursor states in the adsorption process.⁴⁶) With increasing T_{dep} , fewer clusters evolve until at T_{opt} the model MF for Co monomers is reached, which can be reproduced within the simple hit-and-stick model. In the high-temperature regime ($T_{\text{dep}} > T_{\text{opt}}$), thermally activated processes mediate the formation of larger clusters, which are stable at these temperatures and to which the monomers may aggregate.

After optimizing the growth temperature, a series of samples was prepared with increasing Co coverage at $T_{\text{dep}} = 180$ K. The coverage was increased in three steps from 125 s deposition time, corresponding to 0.23 ML of Co, to 510 s, corresponding to 0.91 ML of Co. Exemplary topographs from this series of experiments are shown in Figure 5a–c. In Figure 5a, the majority of Co atoms adsorbs as single species (yellow protrusions on orange molecular template), whereas the amount of clusters (brighter protrusions) is comparably low. With increasing Co coverage (Figure 5b), the amount of monomers increases as well as the density of defects. At high Co density (0.91 ML in Figure 5c), it becomes difficult to make a clear distinction between monomers and other features. The result of a statistical analysis of the MF for the four coverages 0.23, 0.34, 0.47 (topograph not shown), and 0.91 MLs is reproduced in Figure 5d (blue dots). With increasing Co coverage, the MF decreases monotonically.

To gain further insight into the growth process, we simulated the distribution of atomic Co on the molecular precursor following a strict hit-and-stick process. In these calculations, we

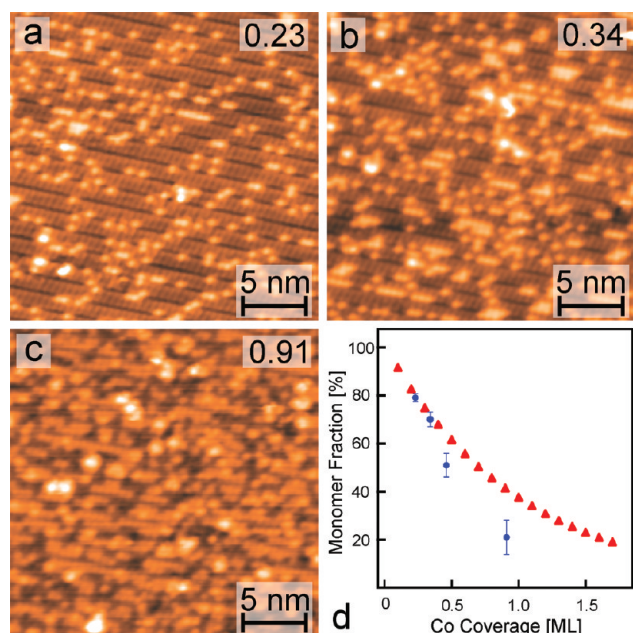


Figure 5. (a–c) Overview topographs of samples with increasing Co coverage and constant $T_{\text{dep}} = 180$ K. The fraction of a ML is indicated in the upper right corner of each image. With increasing coverage, an increase in Co atoms arranged in linear chains is observed ($V_B = 1.0$ V, $I_T = 0.1$ nA for all). (d) MF decreases with increasing coverage (blue dots, Co flux of 0.0018 MLs/s during deposition). The calculations (red triangles) following a hit-and-stick adsorption in the diffusionless limit show a deviation from experimental values (blue dots) for Co coverages exceeding ~ 0.4 MLs.

assumed that adsorbates do not perform any diffusion steps across the molecular precursor but rather directly stick to the first adsorption site encountered upon impact. As adsorption site, the area of a phenyl ring is taken into account, and sticking to this site is possible no matter whether the phenyl ring is still free or already occupied by a previous Co atom. In the model, the adsorption sites cover the full surface; that is, Co atoms hitting the central moiety of the organic building block are counted to the nearest adsorption place. By assuming a random statistical distribution for hitting the different adsorption sites, an expectation value for the MF was calculated. (For details, see the Supporting Information.) As shown in Figure 4d, the expected value for the MF from this simulation is $\sim 79\%$ (gray dashed line) for a coverage of 0.23 MLs of Co. The evolution of the MF depending on the Co coverage at 180 K is compared with the respective expectation values in Figure 5d.

Comparing the experimental results of the MF in dependence on the coverage to the statistical hit-and-stick analysis, it is found that for coverages up to 0.34 MLs the experimental MF can be reproduced with numerical predictions. However, for higher coverages, the fraction of Co monomers falls below the calculated value. This discrepancy is consistent with the hypothesis that the formation of stable clusters depends on the statistic probability of Co collision events, which in turn increases with coverage at identical temperatures.

To summarize, we demonstrated a novel approach toward the construction of arrays of single magnetic atoms. Co atoms were adsorbed on top of phenyl rings, provided by an organic template, namely, a dense-packed layer of N,N' -diphenyl oxalic amides. Monatomic Co-half-sandwich complexes and multiatomic Co

clusters with relative amounts of each depending on the sample temperature during evaporation are formed. The deposition conditions were optimized for high monomeric adsorption yields. The optimal temperature of the substrate was found to be in the range of 180–200 K. The complex behavior of the MF is interpreted to be a result of two competing effects, leading to the formation of small clusters at low temperatures and the statistic formation of stable large clusters at high temperatures, respectively.

The realized half-sandwich compounds bear interesting aspects for surface-confined metallocsupramolecular chemistry.^{47,48} They notably represent potential templates to create surface analogs to bis(benzene) organometallic sandwich complexes. In a similar way, we recently realized cerium–porphyrinato species by assembly and synthesis protocols on well-defined metal surfaces.⁴⁹ Employing an organic molecular template anchored on a surface may therefore prove to be a feasible route toward the construction of novel magnetic storage devices as proposed recently by theory.^{23–25}

In conclusion, our work demonstrates the possibility of creating hybrid organometallic surface nanoarchitectures constructed from single atoms using an organic molecular precursor, which acts as an ordered template for atomic organization. Structures constructed in this fashion may open up new possibilities for the realization of novel nanomagnetic or spintronic concepts, where by single atoms and their spins act as smallest functional units.

METHODS

All sample preparations and experiments were carried out in an UHV apparatus with a base pressure of $<10^{-10}$ mbar. The Ag(111) surface was prepared by repeated Ar^+ bombardment at an energy of 1 keV, followed by annealing to 750 K for ~ 10 min. The investigated molecular templates were formed by OMBE of N,N' -diphenyl oxalic amide molecules²⁷ from a quartz crucible, which was heated in a Knudsen cell held at ~ 417 K onto the Ag substrate held at room temperature (297 K). Thereafter, the samples were cooled to temperatures in the range of 110 to 240 K for Co deposition from an electron beam evaporator. After metal deposition, the sample temperature was held at growth temperature for several minutes before the samples were transferred into the home-built STM,⁵⁰ where data were recorded at ~ 14 K. In the STM images, molecules and Co adsorbates appear as protrusions and are depicted with bright colors, as described in the text.

ASSOCIATED CONTENT

S Supporting Information. Details on the statistical analysis of the Co monomer concentration and explanation of hit-and-stick modeling for statistical analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wkrenner@ph.tum.de. Phone: +49 89 12848. Fax: +49 89 12338.

ACKNOWLEDGMENT

Funding by the European Union via ERC Advanced Grant MolArt ($\circ 247299$) and the German Research Foundation

(DFG) through the TUM International Graduate School of Science and Engineering (IGSSE) and TUM Institute of Advanced Study (IAS) are gratefully acknowledged.

REFERENCES

- (1) Barth, J. V.; Costantini, G.; Kern, K. Engineering Atomic and Molecular Nanostructures at Surfaces. *Nature* **2005**, *437*, 671–679.
- (2) Iacovita, C.; Rastei, M. V.; Heinrich, B. W.; Brumme, T.; Kortus, J.; Limot, L.; Bucher, J. P. Visualizing the Spin of Individual Cobalt-Phthalocyanine Molecules. *Phys. Rev. Lett.* **2008**, *101*, 116602.
- (3) Meier, F.; Zhou, L.; Wiebe, J.; Wiesendanger, R. Revealing Magnetic Interactions from Single-Atom Magnetization Curves. *Science* **2008**, *320*, 82–86.
- (4) Schiffrin, A.; Reichert, J.; Auwärter, W.; Jahnz, G.; Pennec, Y.; Weber-Bargioni, A.; Stepanyuk, V. S.; Niebergall, L.; Bruno, P.; Barth, J. V. Self-Aligning Atomic Strings in Surface-Supported Biomolecular Gratings. *Phys. Rev. B* **2008**, *78*, 035424.
- (5) Serrate, D.; Ferriani, P.; Yoshida, Y.; Hla, S.-W.; Menzel, M.; von Bergmann, K.; Heinze, S.; Kubetzka, A.; Wiesendanger, R. Imaging and Manipulating the Spin Direction of Individual Atoms. *Nat. Nanotechnol.* **2010**, *5*, 350–353.
- (6) Jerratsch, J.-F.; Nilius, N.; Topwal, D.; Martinez, U.; Giordano, L.; Pacchioni, G.; Freund, H.-J. Stabilizing Monomeric Iron Species in a Porous Silica/Mo(112) Film. *ACS Nano* **2010**, *4*, 863–868.
- (7) Enders, A.; Skomski, R.; Honolka, J. Magnetic Surface Nanostructures. *J. Phys.: Condens. Matter* **2010**, *22*, 433001.
- (8) Gambardella, P.; Blanc, M.; Brune, H.; Kuhnke, K.; Kern, K. One-Dimensional Metal Chains on Pt Vicinal Surfaces. *Phys. Rev. B* **2000**, *61*, 2254.
- (9) Gambardella, P.; Stepanow, S.; Dmitriev, A.; Honolka, J.; de Groot, F. M. F.; Lingenfelder, M.; Sen Gupta, S.; Sarma, D. D.; Bencok, P.; Stanescu, S.; et al. Supramolecular Control of the Magnetic Anisotropy in Two-Dimensional High-Spin Fe Arrays at a Metal Interface. *Nat. Mater.* **2009**, *8*, 189–193.
- (10) Wende, H.; Bernien, M.; Luo, J.; Sorg, C.; Ponpandian, N.; Kurde, J.; Miguel, J.; Piantek, M.; Xu, X.; Eckhold, P.; et al. Substrate-Induced Magnetic Ordering and Switching of Iron Porphyrin Molecules. *Nat. Mater.* **2007**, *6*, 516–520.
- (11) Gambardella, P.; Rusponi, S.; Veronese, M.; Dhesi, S. S.; Grazioli, C.; Dallmeyer, A.; Cabria, I.; Zeller, R.; Dederichs, P. H.; Kern, K.; et al. Giant Magnetic Anisotropy of Single Cobalt Atoms and Nanoparticles. *Science* **2003**, *300*, 1130–1133.
- (12) Weiss, N.; Cren, T.; Epple, M.; Rusponi, S.; Baudot, G.; Rohart, S.; Tejeda, A.; Repain, V.; Rousset, S.; Ohresser, P.; et al. Uniform Magnetic Properties for an Ultrahigh-Density Lattice of Noninteracting Co Nanostructures. *Phys. Rev. Lett.* **2005**, *95*, 157204.
- (13) Pick, S.; Stepanyuk, V. S.; Klavysyuk, A. L.; Niebergall, L.; Hergert, W.; Kirschner, J.; Bruno, P. Magnetism and Structure on the Atomic Scale: Small Cobalt Clusters in Cu(001). *Phys. Rev. B* **2004**, *70*, 224419.
- (14) Hirjibehedin, C. F.; Lutz, C. P.; Heinrich, A. J. Spin Coupling in Engineered Atomic Structures. *Science* **2006**, *312*, 1021–1024.
- (15) Wahl, P.; Simon, P.; Diekhoner, L.; Stepanyuk, V. S.; Bruno, P.; Schneider, M. A.; Kern, K. Exchange Interaction between Single Magnetic Adatoms. *Phys. Rev. Lett.* **2007**, *98*, 056601.
- (16) Li, J. T.; Schneider, W. D.; Berndt, R.; Delley, B. Kondo Scattering Observed at a Single Magnetic Impurity. *Phys. Rev. Lett.* **1998**, *80*, 2893–2896.
- (17) Madhavan, V.; Chen, W.; Jamneala, T.; Crommie, M. F.; Wingreen, N. S. Tunneling into a Single Magnetic Atom: Spectroscopic Evidence of the Kondo Resonance. *Science* **1998**, *280*, 567–569.
- (18) Mannini, M.; Pineider, F.; Danieli, C.; Totti, F.; Sorace, L.; Sainctavit, P.; Arrio, M.-A.; Otero, E.; Joly, L.; Cezar, J. C.; et al. Quantum Tunneling of the Magnetization in a Monolayer of Oriented Single-Molecule Magnets. *Nature* **2010**, *468*, 417–421.
- (19) Mannini, M.; Pineider, F.; Sainctavit, P.; Danieli, C.; Otero, E.; Sciancalepore, C.; Talarico, A. M.; Arrio, M.-A.; Cornia, A.; Gatteschi, D.; et al. Magnetic Memory of a Single-Molecule Quantum Magnet Wired to a Gold Surface. *Nat. Mater.* **2009**, *8*, 194–197.
- (20) Gatteschi, D.; Cornia, A.; Mannini, M.; Sessoli, R. Organizing and Addressing Magnetic Molecules. *Inorg. Chem.* **2009**, *48*, 3408–3419.
- (21) Bogani, L.; Wernsdorfer, W. Molecular Spintronics Using Single-Molecule Magnets. *Nat. Mater.* **2008**, *7*, 179–186.
- (22) Rocha, A. R.; Garcia-Suarez, V. M.; Bailey, S. W.; Lambert, C. J.; Ferrer, J.; Sanvito, S. Towards Molecular Spintronics. *Nat. Mater.* **2005**, *4*, 335–339.
- (23) Xiao, R.; Fritsch, D.; Kuz'min, M. D.; Koepernik, K.; Eschrig, H.; Richter, M.; Vietze, K.; Seifert, G. Co Dimers on Hexagonal Carbon Rings Proposed as Subnanometer Magnetic Storage Bits. *Phys. Rev. Lett.* **2009**, *103*, 187201.
- (24) Xiao, R.; Fritsch, D.; Kuz'min, M. D.; Koepernik, K.; Richter, M.; Vietze, K.; Seifert, G. Prediction of Huge Magnetic Anisotropies of Transition-Metal Dimer-Benzene Complexes from Density Functional Theory Calculations. *Phys. Rev. B* **2010**, *82*, 205125.
- (25) Cao, C.; Wu, M.; Jiang, J.; Cheng, H.-P. Transition Metal Adatom and Dimer Adsorbed on Graphene: Induced Magnetization and Electronic Structures. *Phys. Rev. B* **2010**, *81*, 205424.
- (26) Barth, J. V. Molecular Architectonic on Metal Surfaces. *Annu. Rev. Phys. Chem.* **2007**, *58*, 375–407.
- (27) Meyer, R.; Seeliger, A. Über die Einwirkung von Oxaläther auf Aromatische Amidokörper. *Chem. Ber.* **1896**, *29*, 2640–2645.
- (28) Klappenberger, F.; Cañas-Ventura, M. E.; Clair, S.; Pons, S.; Schlickum, U.; Qu, Z. R.; Brune, H.; Kern, K.; Strunskus, T.; Wöll, C.; et al. Conformational Adaptation in Supramolecular Assembly on Surfaces. *ChemPhysChem* **2007**, *8*, 1782–1786.
- (29) Klappenberger, F.; Cañas-Ventura, M. E.; Clair, S.; Pons, S.; Schlickum, U.; Qu, Z. R.; Strunskus, T.; Comisso, A.; Wöll, C.; Brune, H.; et al. Does the Surface Matter? Hydrogen Bonded Chain Formation of an Oxalic Amide Derivative in Two and Three Dimensional Environment. *ChemPhysChem* **2008**, *9*, 2522–2530.
- (30) Zhang, X. Y.; Wang, J. L. Structural, Electronic, and Magnetic Properties of Co_n-Benzene_m Complexes. *J. Phys. Chem. A* **2008**, *112*, 296–304.
- (31) Pandey, R.; Rao, B. K.; Jena, P.; Blanco, M. A. Electronic Structure and Properties of Transition Metal-Benzene Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 3799–3808.
- (32) Pandey, R.; Rao, B. K.; Jena, P.; Newsam, J. M. Unique Magnetic Signature of Transition Metal Atoms Supported on Benzene. *Chem. Phys. Lett.* **2000**, *321*, 142–150.
- (33) Barth, J. V.; Weckesser, J.; Cai, C.; Günter, P.; Bürgi, L.; Jeandupeux, O.; Kern, K. Building Supramolecular Nanostructures at Surfaces by Hydrogen Bonding. *Angew. Chem., Int. Ed.* **2000**, *39*, 1230–1234.
- (34) Schiffrin, A.; Riemann, A.; Auwärter, W.; Pennec, Y.; Weber-Bargioni, A.; Cvetko, D.; Cossaro, A.; Morgante, A.; Barth, J. V. Zwitterionic Self-Assembly of L-Methionine Nanogratings on the Ag(111) Surface. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 5279–5284.
- (35) Pennec, Y.; Auwärter, W.; Schiffrin, A.; Weber-Bargioni, A.; Riemann, A.; Barth, J. V. Supramolecular Gratings for Tuneable Confinement of Electrons on Metal Surfaces. *Nat. Nanotechnol.* **2007**, *2*, 99–103.
- (36) Morgenstern, K.; Kibsgaard, J.; Lauritsen, J. V.; Laegsgaard, E.; Besenbacher, F. Cobalt Growth on Two Related Close-Packed Noble Metal Surfaces. *Surf. Sci.* **2007**, *601*, 1967–1972.
- (37) Decker, R.; Schlickum, U.; Klappenberger, F.; Zoppellaro, G.; Klyatskaya, S.; Ruben, M.; Barth, J. V.; Brune, H. Using Metal-Organic Templates to Steer the Growth of Fe and Co Nanoclusters. *Appl. Phys. Lett.* **2008**, *93*, 243102–1–3.
- (38) Schlickum, U.; Decker, R.; Klappenberger, F.; Zoppellaro, G.; Klyatskaya, S.; Ruben, M.; Silanes, I.; Arnau, A.; Kern, K.; Brune, H.; et al. Metal-Organic Honeycomb Nanomeshes with Tunable Cavity Size. *Nano Lett.* **2007**, *7*, 3813–3817.
- (39) Kühne, D.; Klappenberger, F.; Decker, R.; Schlickum, U.; Brune, H.; Klyatskaya, S.; Ruben, M.; Barth, J. V. High-Quality 2D Metal-Organic Coordination Network Providing Giant Cavities within Mesoscale Domains. *J. Am. Chem. Soc.* **2009**, *131*, 3881–3883.

(40) Klyatskaya, S.; Klappenberger, F.; Schlickum, U.; Kühne, D.; Marschall, M.; Reichert, J.; Decker, R.; Krenner, W.; Zoppellaro, G.; Brune, H.; et al. Surface-Confined Self-Assembly of Di-carbonitrile Polyphenyls. *Adv. Funct. Mater.* **2011**, *21*, 1230–1240.

(41) Marschall, M.; Reichert, J.; Weber-Bargioni, A.; Seufert, K.; Auwärter, W.; Klyatskaya, S.; Zoppellaro, G.; Ruben, M.; Barth, J. V. Random Two-Dimensional String Networks Based on Divergent Coordination Assembly. *Nat. Chem.* **2010**, *2*, 131–137.

(42) Clair, S.; Pons, S.; Fabris, S.; Baroni, S.; Brune, H.; Kern, K.; Barth, J. V. Monitoring Two-Dimensional Coordination Reactions: Directed Assembly of Co-Terephthalate Nanosystems on Au(111). *J. Phys. Chem. B* **2006**, *110*, 5627–5632.

(43) Kliewer, J.; Berndt, R.; Minár, J.; Ebert, H. Scanning Tunnelling Microscopy and Electronic Structure of Mn Clusters on Ag(111). *Appl. Phys. A: Mater. Sci. Process.* **2006**, *82*, 63–66.

(44) Negulyaev, N. N.; Stepanyuk, V. S.; Niebergall, L.; Bruno, P.; Auwärter, W.; Pennec, Y.; Jahnz, G.; Barth, J. V. Effect of Strain Relaxations on Heteroepitaxial Metal-on-Metal Island Nucleation and Superlattice Formation: Fe on Cu(111). *Phys. Rev. B* **2009**, *79*, 195411.

(45) Brune, H. Microscopic View of Epitaxial Metal Growth: Nucleation and Aggregation. *Surf. Sci. Rep.* **1998**, *31*, 125–229.

(46) Barth, J. V. Transport of Adsorbates at Metal Surfaces: From Thermal Migration to Hot Precursors. *Surf. Sci. Rep.* **2000**, *40*, 75–149.

(47) Barth, J. V. Fresh Perspectives for Surface Coordination Chemistry. *Surf. Sci.* **2009**, *603*, 1533–1541.

(48) Lin, N.; Stepanow, S.; Ruben, M.; Barth, J. V. Surface-Confined Supramolecular Coordination Chemistry. *Top. Curr. Chem.* **2009**, *287*, 1–44.

(49) Écija, D.; Auwärter, W.; Vijayaraghavan, S.; Seufert, K.; Bischoff, F.; Tashiro, K.; Barth, J. V. Assembly and Manipulation of Rotatable Cerium-Porphyrinato Sandwich Complexes on a Surface. *Angew. Chem., Int. Ed.* **2011**, *50*, 3872–3877.

(50) Clair, S. Ph.D. Thesis, Ecole Polytechnique Federale de Lausanne, 2004.