

# Rotational and constitutional dynamics of caged supramolecules

Dirk Kühne<sup>a</sup>, Florian Klappenberger<sup>a</sup>, Wolfgang Krenner<sup>a</sup>, Svetlana Klyatskaya<sup>b</sup>, Mario Ruben<sup>b,c</sup>, and Johannes V. Barth<sup>a,1</sup>

<sup>a</sup>Physik Department E20, Technische Universität München, James-Frank-Strasse, D-85748 Garching, Germany; <sup>b</sup>Institut für Nanotechnologie, Karlsruhe Institute of Technology, D-76021 Karlsruhe, Germany; and <sup>c</sup>Strasbourg Institute of Material Physics and Chemistry, Centre National de la Recherche Scientifique, Unité Mixte de Recherche 7504, Université de Strasbourg, 23 Rue du Loess, 67034 Strasbourg, France

Edited by Julius Rebek, The Scripps Research Institute, La Jolla, CA, and approved October 5, 2010 (received for review June 24, 2010)

**The confinement of molecular species in nanoscale environments leads to intriguing dynamic phenomena. Notably, the organization and rotational motions of individual molecules were controlled by carefully designed, fully supramolecular host architectures. Here we use an open 2D coordination network on a smooth metal surface to steer the self-assembly of discrete trimeric guest units, identified as noncovalently bound dynamers. Each caged chiral supramolecule performs concerted, chirality-preserving rotary motions within the template honeycomb pore, which are visualized and quantitatively analyzed using temperature-controlled scanning tunneling microscopy. Furthermore, with higher thermal energies, a constitutional system dynamics appears, which is revealed by monitoring repetitive switching events of the confined supramolecules' chirality signature, reflecting decay and reassembly of the caged units.**

supramolecular dynamics | nanochemistry | surface architecture

The dynamics of molecular species can be controlled by carefully designed, fully supramolecular host architectures, provided either as discrete capsules or extended nanoporous networks. It was recognized in particular that unique rotary motion phenomena of single molecular species can be encoded by such conditions (1–5). Moreover, with the restriction to surface-confined systems it became possible to investigate molecular rotation and noncovalent assembly processes of individual molecules adsorbed at surfaces by atomic-scale scanning tunneling microscopy (STM) (6–12). However, the direct observation of dynamic supramolecular entities in controlled environments remained elusive although this objective represents a key issue of supramolecular science and constitutional dynamic chemistry (13–16). Herein we report dynamic phenomena at the supramolecular level, resulting from the nanoscale confinement of a multicomponent aggregate in an open 2D coordination network on a smooth metal surface. The presented nanopores steer the assembly and cage the realized discrete 2D-chiral trimeric dynamers, whose behavior is directly monitored by temperature-controlled STM. We visualized and analyzed quantitatively their rotary motions, whereby the collective nature of the system dynamics is demonstrated by following chirality-preserving individual reorientation events. The findings reveal opportunities for the field of surface-mounted rotors, limited to single molecular units so far (17–19). Furthermore, we infer constitutional dynamics from the switching of the chirality signature for increased thermal energies, reflecting the repetitive decay and reassembly of the caged supramolecules. With our observations, a demonstrator for the intricate collective dynamics of caged supramolecular dynamers is provided.

## Results and Discussion

For our investigations, we rely on the principles of surface-confined supramolecular chemistry, a versatile strategy for the fabrication of low-dimensional molecular architectures (20, 21). This methodology was notably employed to design regular nano-

porous networks presenting well-defined and tunable cavities (22–25). Specifically, we employed the cobalt-directed assembly of linear ditopic *para*-sexiphenyl-dicarbonitrile (NC-Ph<sub>6</sub>-CN) linkers to generate a highly regular array of well-defined host spaces on a smooth single crystal silver surface in (111) orientation under vacuum conditions (26). STM data of an exemplary network are depicted in Fig. 1*A*, revealing the high regularity of the template providing hexagonal pores with an enclosed van der Waals area of 24 nm<sup>2</sup>. The ideal stoichiometry for this room-temperature assembled network is given by a ratio of 3:2 of rod-like linkers and cobalt centers, respectively. However, upon increasing the surface concentration of the linkers at reduced temperatures (~145 K), they are captured in the network cavities because the energy barrier to migrate across the network rims is high enough to limit intercavity mass transport, which eventually sets in at  $T \sim 160$  K.

The confined molecules are free to arrange within the pore in energetically favorable configurations. The outcome of such an experiment following the network exposure to an additional 0.1 monolayer linker concentration and subsequent cool-down to a temperature of 8 K is shown by the STM image reproduced in Fig. 1*B* (Fig. S14 is an overview image). Firstly, we note that the confined monomers are always attached to the network rim in a specific geometry, reflecting a surface templating effect and weak attractions between phenyl hydrogen and CN end groups. This arrangement is consistent with the structural motifs observed in pure organic lattices of linear dicarbonitrile linker molecules on the same surface (27, 28). Secondly, we identify a frequent trimeric arrangement reflecting the self-assembly of three caged linkers. Here a different threefold nodal bonding motif is encountered at the center of the trimeric unit, which must be understood as a consequence of the spatial confinement, because in organic layers exclusively fourfold nodal motifs exist (27, 28). Nevertheless, there is again a preferred registry of the supramolecular trimer with respect to the surface atomic lattice, i.e., the molecular backbones are oriented along close-packed  $\langle 110 \rangle$  directions and the terminating nitrogen atoms reside at threefold hollow sites (28) (compare Fig. 1*C* and Fig. S24). In addition, cavities exist that are either undecorated or host merely one molecule or arrangements of two or four guest molecules. Furthermore, Fig. 1*B* evidences that there are two mirror-symmetric configurations of the supramolecular trimer reflecting an organizational chirality (27, 28). These enantiomorphous species are designated  $\lambda$ - and  $\delta$ -rotator, respectively. Because these supramolecules will be shown to undergo thermally activated collective

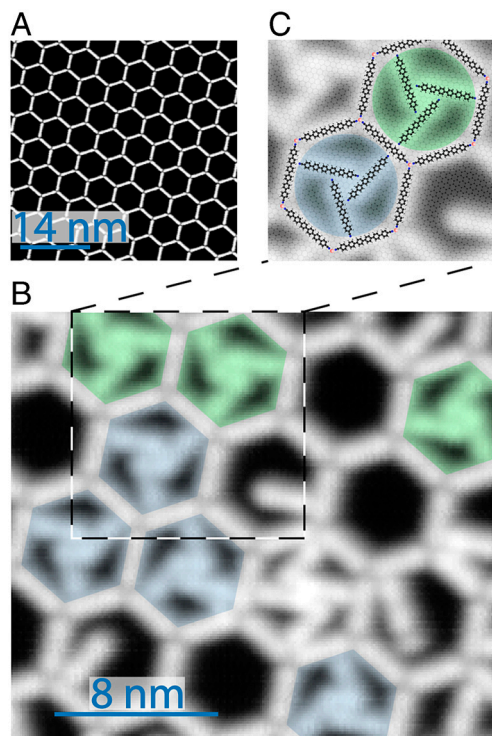
Author contributions: J.V.B. designed research; D.K., F.K., W.K., and S.K. performed research; S.K. and M.R. contributed new reagents/analytic tools; D.K. and W.K. analyzed data; and D.K., F.K., M.R., and J.V.B. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

<sup>1</sup>To whom correspondence should be addressed. E-mail: johannes.barth@ph.tum.de.

This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1008991107/-DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1008991107/-DCSupplemental).



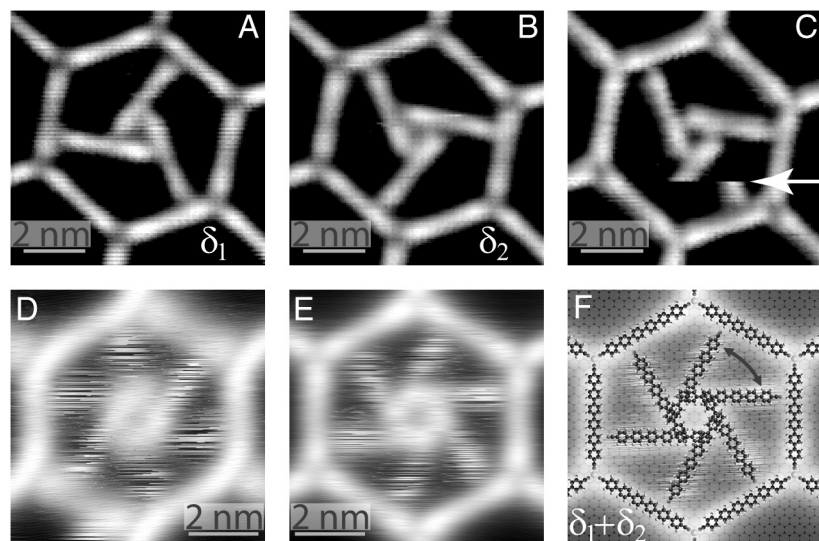
**Fig. 1.** Supramolecular chiral trimers in a nanoporous host lattice. (A) The template is provided by a regular 2D coordination network on a Ag(111) surface. The van der Waals area of the provided cavities is  $24 \text{ nm}^2$  ( $V_B = 0.5 \text{ V}$ ,  $I_T = 0.1 \text{ nA}$ ,  $T_{\text{sample}} = 8 \text{ K}$ ). (B) Self-assembled supramolecular trimers in two chiral configurations marked with blue and green hexagons named  $\lambda$ - and  $\delta$ -rotator, respectively ( $V_B = 2.0 \text{ V}$ ,  $I_T = 0.1 \text{ nA}$ ,  $T_{\text{sample}} = 29 \text{ K}$ ). (C) Structure model of the caged trimers that are stabilized by weak bonds between carbonitrile endgroups and phenyl moieties (H, C, N, and Co atoms in white, black, blue, and red, respectively).

motions and continuous changes in their constitution, they are recognized as *dynamers* (16).

Altogether, the situation reflects a two-level assembly of a 2D host network with caged supramolecular chiral guests, the shape of which is determined by the balance of intermolecular, molecule-surface, and host-guest interactions. Now, the metal-organic honeycomb nanomesh is thermally robust because of the underlying metal-ligand interactions that determine its structure (23, 24). By contrast, the lateral bonding of the guest system,

both regarding its internal structure and its attachment to the host cavity implies weaker, noncovalent interactions. In order to probe its response to thermal excitations, repeated STM measurements with increasing temperatures have been performed. Starting at  $T \sim 25 \text{ K}$ , we continuously imaged approximately 175 cavities during several days. At  $T \sim 60 \text{ K}$ , the first indications of thermal motions of the trimeric guest unit appeared. Importantly, they concern the entire supramolecular unit. Typical rotation events are visualized by the data series in Fig. 2 A–C concentrating on a single caged  $\delta$ -rotator. It is obvious that an orientation switching event occurred in the time interval between the recording of the images (Fig. 2A) and (Fig. 2B). This change corresponds to a transition between energetically equivalent, but geometrically different configurations with an identical chirality signature. The pertaining states are designated  $\delta_1$ ,  $\delta_2$  and  $\lambda_1$ ,  $\lambda_2$ , respectively.

A further chirality-conserving event occurred during the scanning of the rotator, i.e., within the measurement process. It is marked by an arrow in Fig. 2C and reveals that the time for the repositioning of the unit is much smaller than the interval for the recording of a line scan (164 ms). Furthermore, looking at well more than 1,000 rotator images, we found no indications of intermediate configurations of the rotator, suggesting that the orientational switching corresponds to a collective rotation of the entire supramolecular trimeric unit. This interpretation, in contrast to the principally existing possibility of sequential motions of individual molecular units in rapid succession, is supported by the fact that the elements of the supramolecular unit cannot be individually displaced between positions of different rotary configurations because of steric hindrance. The pertaining model shown in Fig. 2F (for more detailed views, see Fig. S3 B–D) reveals that the reason is the proximity of the carbonitrile groups and phenyl rings, i.e., the supramolecular bonding motif. A sequential motion would entail distances between molecular moieties falling locally below the van der Waals spheres of the constituents. The idea of a concerted rotational motion is further corroborated by observations at higher temperatures, where it is impossible to image a static rotator because of the increased rotation rates. Under these conditions, frizzled features are resolved in the cavities indicating rapid thermal motions (compare Fig. 2D and E). In agreement with earlier STM observations of single rotating molecules (10, 29–31), this imaging is ascribed to a unit rapidly rotating in arbitrary directions while residing on the average at the preferred surface orientations. With the present system, the envelope of the intracavity molecular features accordingly corresponds exactly to the superposition of the two distin-



**Fig. 2.** Rotational motion of the caged supramolecular dynamer. (A and B) Sixty degree orientational switching between a stable  $\delta_1$  and  $\delta_2$  configuration with conservation of the chirality signature; images recorded with a time lap of 204 s ( $V_B = 1.0 \text{ V}$ ,  $I_T = 0.05 \text{ nA}$ ,  $T_{\text{sample}} = 64.4 \text{ K}$ ). (C) Orientation switching event while recording the topography at the position indicated with an arrow; the molecular units are exclusively imaged with positions reflecting preferred configurations ( $V_B = -1.0 \text{ V}$ ,  $I_T = 0.05 \text{ nA}$ ,  $T_{\text{sample}} = 64.8 \text{ K}$ ). (D and E) Rapid fluctuation of rotator states with event rates largely exceeding imaging frequency. The envelope of the intracavity molecular features with different chirality corresponds to a superposition of the two respective stable configurations (D,  $\lambda$ -rotator,  $V_B = -1.0 \text{ V}$ ,  $I_T = 0.1 \text{ nA}$ ,  $T_{\text{sample}} = 78.3 \text{ K}$ ; E,  $\delta$ -rotator,  $V_B = 0.2 \text{ V}$ ,  $I_T = 0.22 \text{ nA}$ ,  $T_{\text{sample}} = 81 \text{ K}$ ). (F) Model for the collective rotation superimposed on the data in E.



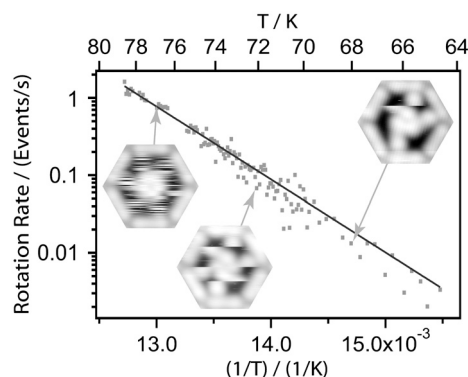
guishable rotator orientations (compare Fig. 2*A–F*). Importantly, this characteristic holds independently for both mirror-symmetric species (compare Fig. 2*D* and *E*), i.e., there is again chirality conservation in agreement with the notion of a supramolecular unit performing concerted motions. Thus, the hexagonal cavity dictates the shape of the self-assembly geometry and acts simultaneously as a supramolecular stator for the confined rotary motion of the dynamer exhibiting in this case only rotational, but no constitutional dynamics.

On the basis of the systematic temperature-controlled STM datasets, we performed a statistical analysis of the rotational switching event rates (details on the procedures are given in *Methods*; in short, they follow methodologies established for molecular surface diffusion, see ref. 32). The results are plotted in the Arrhenius representation reproduced in Fig. 3. They show the characteristics of a thermally activated process described by the well-known formula  $\Gamma_{\text{rot}} = A \exp[-E_{\text{rot}}/(kT)]$ , where  $\Gamma_{\text{rot}}$  represents the rotation rate,  $A$  the prefactor, and  $E_{\text{rot}}$  the rotational energy barrier. A corresponding fit to the data yields  $E_{\text{rot}} = 187 \pm 8$  meV and  $A = 1.3(\pm 0.8) \times 10^{12} \text{ s}^{-1}$ .

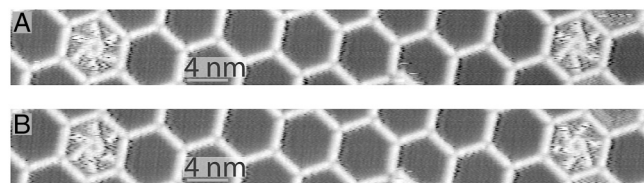
Thus, the strictly surface-confined self-assembly approach, using instructed molecular bricks, leads to the parallel construction of stator–rotator assemblies, which show inherently self-adaptation to the specific near-surface working conditions. The straightforward use of the self-assembly techniques in the architectural design cannot only provide direct access to functional surface structures, it also reflects the highly supramolecular design principles ubiquitous found in biological motors (e.g., rotary ATPase, linear kinesine, and myosine motors).

With substrate temperatures exceeding  $\sim 70$  K, intracavity chirality interconversion sets in as a rare event, as exemplified by the data reproduced in Fig. 4. Similar to the rotation events, these transitions are much faster than the instrumental scanning speed. Thus they cannot be visualized directly, but can be tracked by the change of the chirality of a rotator. In the presented case, a  $\lambda$ -rotator (Fig. 4*A*, trimer on the right) transforms into a  $\delta$ -rotator (Fig. 4*B*, trimer on the right). As a consequence, at even higher temperatures, the rotator STM appearance undergoes a qualitative change. Instead of frizzled features discussed above, a rather smooth, albeit slightly blurred envelope, of the intracavity molecular features occurs (Fig. 5*A*, recorded for  $T = 145$  K).

The appearance in 6-mm symmetry is understood as a consequence of averaging over many thermal motion processes that occur in the cavity during the recording of each individual scan line. At these conditions, the level of thermal excitation does not allow the caged molecules to migrate across the cavity rims, and accordingly they remain spatially confined. However, the unique chirality signature of the rotators observed at lower temperatures



**Fig. 3.** Arrhenius plot of dynamer rotation event rates. The data obey the expression  $E_{\text{rot}} = A \exp[-E_{\text{rot}}/(kT)]$ , the line fit yields  $A = 1.3(\pm 0.8) \times 10^{12} \text{ s}^{-1}$ ,  $E_{\text{rot}} = 187 \pm 8$  meV. Insets show exemplary STM images with a caged rotator in a single cavity at different temperatures (recorded with  $V_{\text{B}} = 2.0$  V,  $I_{\text{T}} = 0.1$  nA).

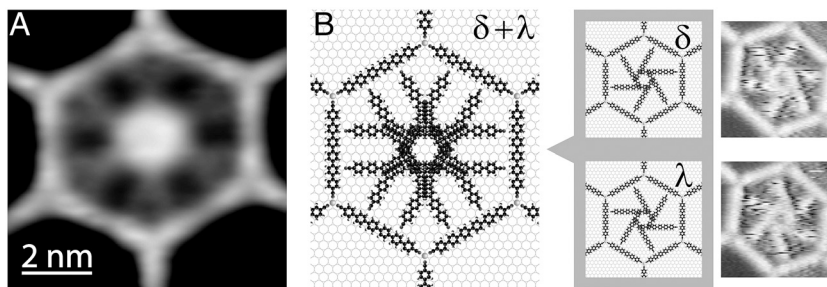


**Fig. 4.** Simultaneous observation of two dynamic caged rotators with equal (*A*) and opposite (*B*) handedness; images recorded with a time lap of 340 s ( $V_{\text{B}} = -2.07$  V,  $I_{\text{T}} = 0.05$  nA,  $T_{\text{sample}} = 90.5$  K). Between the two images of the same surface area, an intracavity chirality interconversion occurred as a rare event.

has disappeared and a mirror-symmetric superposition figure prevails. The high number of cavities featuring identical envelopes is consistent with the number occupied by the trimeric dynamers at lower temperatures. This figure can be constructed from the superposition of all four possible rotator configurations ( $\lambda_1$ ,  $\lambda_2$ ,  $\delta_1$ , and  $\delta_2$ ) combining both dynamic imaging features for rotators with different chirality (see Fig. 5*B*). The fact that the overall dynamic envelope of the confined linkers can be constructed this way confirms that this interconversion of rotor chirality, necessarily requiring a transient decay and reassembly of the rotator unit, occurs regularly at the employed temperatures. Thus, we recognize a clear indication for constitutional dynamics (16), i.e., there is a repetitive dissociation and reconstitution of the caged trimeric unit. In turn, the conservation of chirality throughout a large number of rotation events indicates that the collective rotary dynamics, i.e., *not* involving decay and reassembly, persists over periods of time between the constitutional changes. In the temperature window  $90.7 \pm 0.4$  K, we measured a rate of  $\Gamma_{\text{chir}} \approx 1.8 \times 10^{-3} \text{ s}^{-1}$  for intracavity chirality switches (see Fig. 4). The corresponding rotation rate is  $56.5 \text{ s}^{-1}$  as extrapolated from the Arrhenius fit. Assuming a Markov process, where every second decay of the trimeric unit actually leads to a chirality switch, the ratio of rotation to decay rates is determined to be approximately  $1.6 \times 10^4$ . Using the same prefactor for both rotation and decay, the activation barrier for the latter is estimated to be  $E_{\text{decay}} = kT \ln[A/(2\Gamma_{\text{chir}})] \approx 260$  meV.

In the course of our systematic studies, there were no hints on a correlated occupation or dynamics of guest species in neighboring cavities, although this point can unfortunately not be conclusively addressed with the datasets at hand. Note that in several previous studies addressing single-molecule rotational motions in 2D superlattices correlations could also not be found for species confined in separate network cavities (9, 10). For an interesting example of a nanoporous template with communicating cavities, see ref. 33; however, with this system, the flexibility of the constituting porphyrins plays an important role. A potential pathway that could mediate a correlated dynamics is given by the indirect electronic interactions due to surface state scattering on the network and confined objects, which has been exploited to steer the alignment of adatoms in supramolecular gratings on the same substrate in the past (34, 35). However, with these systems, there was similarly no evidence for a correlated translational motion or lateral organization in adjacent 1D furrows (34, 35), presumably because there is little crosstalk between areas separated by molecular rims (34–36).

Finally, we briefly comment on the nature and dynamics of single, dimeric, and tetrameric guest arrangements. The data reproduced in Fig. S4 shows a single trimeric dynamer with adjacent cavities comprising the other species. At the employed conditions (temperature in the 60–61 K range), the monomers are already highly mobile and the filled cavity shows a streaky interior indicative of rapid motions. In contrast, the rates for the thermal motions of dimers and tetramers are comparable to that of the trimer; thus thermally induced rearrangements of the confined supramolecules can be monitored. However, a detailed



**Fig. 5.** Constitutional dynamics expressed in chirality switching of the caged trimeric unit. The blurred STM imaging is a result of intracavity decay and reassembly proceeding in parallel with rapid rotational motion of the caged dynamer. (A) The envelope of the intracavity molecular features reflects a superposition of the two enantiomers ( $\delta$  and  $\lambda$ ) of the chiral rotator ( $V_B = 0.5$  V,  $I_T = 0.1$  nA,  $T_{\text{sample}} = 145$  K), as demonstrated by the model in B.

data analysis reveals that these motions frequently comprise both rotary and translatory steps, i.e., there are frequent structural changes of the supramolecular units. Consequently their dynamics cannot be described by the straightforward terms used for the trimer concerted rotary motions and constitutional rearrangements.

## Conclusion

In conclusion, we demonstrated the bottom-up construction of caged supramolecular dynamers. Using a tailored nanoporous network as a template, we developed a hierarchic organization to generate collective motion and assembly phenomena with noncovalently designed chiral units. The realized supramolecular dynamers exert complex, concerted rotations, which have been directly monitored and quantitatively analyzed at the single-molecule level. In order to gain improved control over 2D supramolecular stator–rotator systems, e.g., achieving directionality, or changing the energy supply from heat to photons or electrons, the synthesis and incorporation of responsive rotator units is envisioned. Furthermore, the observed chirality switching events of the caged trimeric units reflect a constitutional dynamics of the system, i.e., there is direct evidence of a dynamic chemistry at the supramolecular level. Our findings demonstrate the remarkable potential of surface-confined self-assembled nanoporous architectures by exploiting massively parallel fabrication concepts (20–25) to control dynamic phenomena of supramolecular species, here mechanically, but prospectively also concomitant electronic or magnetic dynamic features, e.g., mechanoelectronic coupling of molecular motion with dynamic electron confinement.

## Methods

The synthesis of the rod-like NC-Ph<sub>6</sub>-CN molecule as well as the Co-directed honeycomb network assembly have been described in a previous publication (see ref. 26). All experiments were performed under ultrahigh vacuum conditions using a home-built liquid-He-cooled low-temperature STM with cryoshields (37). The employed Ag(111) substrate was prepared by standard procedures (cycles of Ar<sup>+</sup> sputtering and annealing) to obtain extended flat terraces separated by monoatomic steps. The linkers were deposited from a quartz crucible in an organic molecular beam epitaxy source at 572 K, with the substrate kept at 300 K. Submonolayer molecular films were subsequently exposed to a beam of Co atoms for coordination assembly, whereby the linker to metal ratio was adjusted to 3:2. The Co-coordinated assembly was cooled down and an additional 0.1 monolayer concentration of linker molecules were added at 144 K (coverages are given with respect to the saturated monolayer coverage of a purely organic layer as defined in ref. 28). Following the preparation, the sample was transferred in situ and STM data were acquired at  $T = 8$ –150 K. During the measurements, the tunneling parameters were in the high-resistance regime of 20 G $\Omega$  to avoid tip-induced motions.

The rotation rates were determined by counting the number of rotations within a hexagonal cavity and dividing this number by the time it took to scan the cavity. For low temperatures, rotation events rarely happened. In this case, their number was divided by the accumulated time, which elapsed while scanning the hexagonal cavity in between the occurrence of rotation events.

**ACKNOWLEDGMENTS.** This work was supported by International Graduate School of Science and Engineering and Institute of Advanced Study at Technische Universität München, European Research Council Advanced Grant MolArt ( $\epsilon$ 247299).

- Rebek J, Jr (2009) Molecular behavior in small spaces. *Acc Chem Res* 42:1660–1668.
- Kitagawa H, Kobori Y, Yamanaka M, Yoza K, Kobayashi K (2009) Encapsulated-guest rotation in a self-assembled heterocapsule directed toward a supramolecular gyroscope. *Proc Natl Acad Sci USA* 106:10444–10448.
- Rosi NL, et al. (2003) Hydrogen storage in microporous metal-organic frameworks. *Science* 300:1127–1129.
- Horiike S, Shimomura S, Kitagawa S (2009) Soft porous crystals. *Nat Chem* 1:695–704.
- Akutagawa T, et al. (2009) Ferroelectricity and polarity control in solid-state flip-flop supramolecular rotators. *Nat Mater* 8:342–347.
- Gimzewski JK, et al. (1998) Rotation of a single molecule within a supramolecular bearing. *Science* 281:531–533.
- Lin N, Dmitriev A, Weckesser J, Barth JV, Kern K (2002) Real-time single-molecule imaging of the formation and dynamics of coordination compounds. *Angew Chem, Int Ed* 41:4779–4883.
- Kühnle A, Linderth TR, Hammer B, Besenbacher F (2002) Chiral recognition in dimerization of adsorbed cysteine observed by scanning tunneling microscopy. *Nature* 415:891–893.
- Schull G, et al. (2006) Single-molecule dynamics in a self-assembled 2D molecular sieve. *Nano Lett* 6:1360–.
- Wintjes N, et al. (2007) A supramolecular multiposition rotary device. *Angew Chem, Int Ed* 46:4089–4092.
- Tomba G, et al. (2007) Structure and energetics of diphenylalanine self-assembling on Cu(110). *J Phys Chem A* 111:12740–12748.
- Grill L, et al. (2007) Rolling a single molecular wheel at the atomic scale. *Nat Nanotechnol* 2:95–98.
- Lehn JM (2002) Toward complex matter: Supramolecular chemistry and self-organization. *Proc Natl Acad Sci USA* 99:4763–4768.
- Rowan SJ, Cantrill SJ, Cousins GRL, Sanders JKM, Stoddart JF (2002) Dynamic covalent chemistry. *Angew Chem, Int Ed* 41:898–952.
- García-Garibay MA (2005) Crystalline molecular machines: Encoding supramolecular dynamics into molecular structure. *Proc Natl Acad Sci USA* 102:10771–10776.
- Lehn JM (2007) From supramolecular chemistry towards constitutional dynamic chemistry and adaptive chemistry. *Chem Soc Rev* 36:151–160.
- Kottas GS, Clarke LI, Horinek D, Michl J (2005) Artificial molecular motors. *Chem Rev* 105:1281–1376.
- Browne WR, Feringa BL (2006) Making molecular machines work. *Nat Nanotechnol* 1:25–35.
- Balzani V, Credi A, Venturi M (2008) Molecular machines working on surfaces and at interfaces. *ChemPhysChem* 9:202–220.
- Barth JV (2007) Molecular architectonic on metal surfaces. *Annu Rev Phys Chem* 58:375–407.
- Lin N, Stepanow S, Ruben M, Barth JV (2009) Surface-confined supramolecular coordination chemistry. *Top Curr Chem* 287:1–44.
- Theobald JA, Oxtoby NS, Phillips MA, Champness NR, Beton PH (2003) Controlling molecular deposition and layer structure with supramolecular surface assemblies. *Nature* 424:1029–1031.
- Stepanow S, et al. (2004) Steering molecular organization and host-guest interactions using tailor-made two-dimensional nanoporous coordination systems. *Nat Mater* 3:229–233.
- Schlickum U, et al. (2007) Metal-organic honeycomb nanomeshes with tunable cavity size. *Nano Lett* 7:3813–3817.
- Madueno R, Räisänen MT, Silien C, Buck M (2008) Functionalizing hydrogen-bonded surface networks with self-assembled monolayers. *Nature* 454:618–621.
- Kühne D, et al. (2009) High-quality 2D metal-organic coordination network providing giant cavities within mesoscale domains. *J Am Chem Soc* 131:3881–3883.
- Schlickum U, et al. (2008) Chiral kagomé lattice from simple ditopic molecular bricks. *J Am Chem Soc* 130:11778–11782.

28. Kühne D, et al. (2009) Self-assembly of nanoporous chiral networks with varying symmetry from sexiphenyl-dicarbonitrile on Ag(111). *J Phys Chem C* 113:17851–17859.
29. Maksymovych P, Sorescu DC, Dougherty DB, Yates JT, Jr (2005) Surface bonding and dynamical behavior of the CH<sub>3</sub>SH molecule on Au(111). *J Phys Chem B* 109:22463–22468.
30. Gao L, et al. (2008) Constructing an array of anchored single-molecule rotors on gold surfaces. *Phys Rev Lett* 101:197209-1–4.
31. Baber AE, Tierney HL, Sykes ECH (2008) A quantitative single-molecule study of thioether molecular rotors. *ACS Nano* 2:2385–2391.
32. Barth JV (2000) Transport of adsorbates at metal surfaces: From thermal migration to hot precursors. *Surf Sci Rep* 40:75–149.
33. Spillmann H, et al. (2006) A two-dimensional porphyrin-based porous network featuring communicating cavities for the templated complexation of fullerenes. *Adv Mater* 18:275–279.
34. Pennec Y, et al. (2007) Self-assembled molecular superlattices for tunable confinement of electrons on metal surfaces. *Nat Nanotechnol* 2:99–103.
35. Schiffrin A, et al. (2008) Self-aligning atomic strings in surface-supported biomolecular gratings. *Phys Rev B* 78:035424-1–7.
36. Klappenberger F, et al. (2009) Dichotomous array of chiral quantum corrals by a self-assembled nanoporous kagomé network. *Nano Lett* 9:3509–3514.
37. Clair S, et al. (2004) STM study of terephthalic acid self-assembly on Au(111): Hydrogen-bonded sheets on an inhomogeneous substrate. *J Phys Chem B* 108:19392–19397.