

Epitaxy-Induced Assembly and Enantiomeric Switching of an On-Surface Formed Dinuclear Organocobalt Complex

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Supporting Information

ABSTRACT: We report on the surface-guided synthesis of a dinuclear organocobalt complex, its self-assembly into a complex nanoarchitecture, and a single-molecule level investigation of its switching behavior. Initially, an organic layer is prepared by depositing hexakis((trimethylsilyl)ethynyl)-benzene under ultra-high-vacuum conditions onto Ag(111). After Co dosage at 200 K, low-temperature scanning tunneling microscopy (STM) reveals an epitaxy-mediated organization mechanism of molecules and on-surface formed organometallic complexes. The dinuclear complexes



contain two bis(η^2 -alkynyl) π -tweezer motifs, each stabilizing a single Co atom and express two enantiomers due to a conformation twist. The chirality is transferred to the two-dimensional architecture, whereby its Co adatoms are located at the corners of a 3.4.6.4 rhombitrihexagonal tessellation due to the systematic arrangement and anchoring of the complexes. Extensive density functional theory simulations support our interpretation of an epitaxy-guided surface tessellation and its chiral character. Additionally, STM tip-assisted manipulation experiments on isolated dinuclear complexes reveal controlled and reversible switching between the enantiomeric states *via* inelastic electron processes. After activation by bias pulses, structurally modified complexes display a distinctive Kondo feature attributed to metastable Co configurations.

KEYWORDS: cobalt alkynyl complex, surface tessellation, single-molecule switch, scanning tunneling microscopy

he rational design and synthesis of 2D-confined functional nanoarchitectures of well-defined optic, magnetic, and catalytic properties remain one of the key challenges toward the realization of future nanotechnology.¹⁻⁶ When targeting the controlled fabrication and embedding of magnetic nanoobjects, such as single atoms,⁷ small clusters,⁸ or single-molecule magnets,⁹ stepwise bottomup construction *via* templates under ultrahigh-vacuum (UHV) conditions provides a versatile route. One-atom thick sheets of graphene and boron nitride proved to be suitable templates for the trapping of metallic clusters¹⁰⁻¹⁴ at specific sites of the substrate-related Moiré lattices. Open-porous metal-organic coordination networks¹⁵ were employed for the selective decoration with transition-metal clusters¹⁶ and the confinement of single atoms.¹⁷ A self-assembled and highly ordered layer of diphenyl oxalic amide molecules was used to selectively bind

monomeric cobalt on top of benzene rings, thereby establishing a well-ordered Co superlattice. $^{18}\,$

Metal alkynyl complexes¹⁹ are attractive for various research fields, such as non-linear optics,²⁰ intramolecular charge transfer systems,²¹ and photovoltaics.²² Moreover, they constitute the key building block for metallopolymers, an emerging class of functional soft materials.²³

Despite their importance for functional materials, insight on interfacial alkynyl complexes is scarce, but a handful of first results demonstrate interesting prospects. Liu *et al.* reported the formation of surface-guided molecular wires stabilized by Agbisalkynyl coordination.²⁴ Polyyne-coupled dinuclear complexes proved that mixed valence state chemistry is operational

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on metallic surfaces.^{25,26} Ni–alkyne bonding facilitated the post-functionalization of an adaptable metal–organic network.²⁷

Recently, we reported the surface-guided formation of an original organocobalt complex from a precursor with one internal alkyne moiety. The established organometallic compound holds no counterpart in solution chemistry highlighting the intriguing phenomena triggered by the interfacial conditions.²⁸ Related organocobalt structures are highly relevant for chemical research and the development of synthesis protocols, where organocobalt compounds represent indispensable ingredients for numerous synthesis pathways based on the Pauson–Khand and Nicholas reaction and also the hydroformylation reaction.²⁹

Here, we investigated an organic species with six internal alkynes, thus bearing multiple organometallic binding sites. Exposing an organic template of self-assembled hexakis-((trimethylsilyl)ethynyl)benzene (HEB) molecules on Ag(111) to a beam of single Co atoms leads to the formation of mononuclear (C1) and dinuclear organocobalt complexes (C_2) , which arrange in a highly ordered two-dimensional (2D) nanoarchitecture representing a 3.4.6.4 tiling pattern. Utilizing the combination of high-resolution scanning tunneling microscopy (STM) and state-of-the-art density functional theory (DFT) modeling, we elucidate the structure of complexes and the intriguing surface tessellation. The chiral dinuclear complexes contain two bis(η^2 -alkynyl) π -tweezer motifs, $^{\rm 30,31}$ each stabilizing a single Co atom in a geometry that contrasts the more common scenario of σ -like metal-carbon bonding within alkynyl complexes.¹⁹

Furthermore, *via* a single-molecule level investigation of isolated C_2 , we achieved well-controlled and reversible twostate switching between chiral isomers attributed to conformational changes and demonstrate the appearance of a Kondo signature after tip-induced modification of the complex.

RESULTS AND DISCUSSION

Organic Layer. Within this study, we use the de novo synthesized six-fold symmetric alkyne derivative HEB (see Supporting Information (SI) and Figure S1 for synthetic details) with stochiometric formula $C_{36}Si_6H_{54}$. According to Figure 1a, the chemical structure is comprised of a central arene ring connected to six internal alkynes, each terminated by a trimethylsilyl group (TMS). Figure 1b-d shows different perspectives of a ball-and-stick molecular model established by geometry optimization via gas-phase DFT calculations. The calculated distances between adjacent alkynes are shown in the top view of the molecule (Figure 1c), the alkyne's bending flexibility is indicated by the out-of-plane (in-plane) angle $\varepsilon(\varphi)$ (Figure 1b,c), and free rotations of the TMS groups around σ bonds are indicated by the angle γ (Figure 1d). The mutual orientations of the six TMS groups induce chirality within surface-adsorbed molecules.

In a first step, the chemical vapor deposition (CVD) of HEB on the clean Ag(111) surface, kept at 450 K and in an UHV environment, was performed in order to grow a sub-ML molecular interface (see Figure S2 for preparation details). After transferring the sample to a LT-STM, the measurements show extended, homogeneous, and largely defect-free organic layers (Figure 2a), indicative of a high molecular mobility and weak intermolecular interactions allowing structural autocorrection mechanisms during the self-assembly process. The hexagonal symmetry and dense packing scheme of the islands is



Figure 1. (a) Chemical structure model of HEB. (b) DFTcalculated atomic ball-and-stick visualization of the molecular structure comprised of carbon (cyan), silicon (blue), and hydrogen (white) atoms. (c, d) Top and side view of calculated geometry.

rationalized by the predominance of attractive van der Waals interactions between bulky TMS end groups, leading to relatively weak molecular cohesion and adhesion, consistent with manipulation experiments (see Figure S2e). When superimposing a Ag(111) lattice model and molecular models to high-resolution STM data (Figure 2b), the six bright lobes surrounding a central void coincide with the six TMS-alkyne groups. Based on high-resolution STM imaging and the absence of Moiré-like effects in the STM contrast, we tentatively suggest a commensurate $\sqrt{31} \times \sqrt{31}$ R 8.9° adsorption structure, which reads in matrix notation:

$$\begin{pmatrix} \vec{a} \\ \vec{b} \end{pmatrix} = \begin{pmatrix} 6 & -1 \\ 1 & 5 \end{pmatrix} \begin{pmatrix} \vec{u} \\ \vec{v} \end{pmatrix}$$

where by \vec{u} and \vec{v} are the primitive vectors of Ag(111). As justified in the following analysis of organometallic units within Co-decorated organic islands (*cf.* Figures 2c,d and S3), we tentatively postulate that the molecules' centers adsorb on sixfold symmetric top sites. Besides this domain labeled α , a further domain orientation exists with its unit cell reading in

matrix notation: $\begin{pmatrix} 5 & 1 \\ -1 & 6 \end{pmatrix}$, as shown in Figure 2c. The existence

of this domain β is rationalized by a combination of the molecule's six-fold symmetry and alignment with respect to a crystallographic symmetry axis. A hexagonal contour enclosing a molecule with an associated line along opposite molecular lobes (Figure 2b,c) reveals that the orientation of the molecules is different in the two domains. We found a rotation of 8° with respect to the three mirror symmetry axes coinciding with the substrate's ($11\overline{2}$) directions (purple line representing one of them). Therefore, the molecular arrangement is chiral and is expressed in two enantiomorphous domains, which are distinguished by a 16° rotation of the unit cell.

Co Dosage at 12 K. To study the interaction of Co atoms with the organic template in the absence of molecular diffusion, cluster formation, or catalytic reactions, we performed an *in situ* Co dosage with the sample kept in the STM at temperatures below 12 K. Figure 2c presents a β domain decorated with Co,



Figure 2. Organic phase showing α (b) and β domains (a,c), which differ by the molecular alignment (black line with outlined molecule). Dense-packed and $[11\overline{2}]$ directions are indicated by stars and purple lines, respectively. (a) Large-scale STM image of a HEB island, and (b) high-resolution image with superimposed unit cell, molecular models, and tentative substrate registry. (c) Co-decoration of organic phase after *in situ* Co dosage at 12 K. Organometallic complexes with marked Co atoms (yellow dots) are color-coded according to their orientation. (d) Gas-phase DFT-calculated geometry of C₁ superimposed on the Ag(111) lattice, and zoomed-in images of the six orientations of C₁ observed in (c). Crossings of dashed circle and dashed lines mark hollow adsorption sites for Co center. Tunneling parameters V_v I_t : (a, c, d) -100 mV, 100 pA; (b) -10 mV, 49 pA.

where one can observe that the molecular domain structure described above remains preserved, however a new species is present within the matrix of unaltered HEB. This species appears in six different orientations (dashed outline). It is imaged with a characteristic depression on one side and two protruding lobes on the opposite side, and is denoted by C_1 . From large-scale STM topographs (see Figure S3a), we determined the coverage of Co in this sample to be approximately 0.002 ML, where one ML corresponds to one Co atom per Ag(111) surface atom. Putting this value in relation with the number of altered molecules, we infer that each C_1 hosts one Co atom. At such low dosage temperatures and Co concentrations, the organic template suppresses Co clustering, while at the same time intramolecular relaxation mediates the formation of the Co-bisalkyne geometry of C_1 .

Figure 2d shows high-resolution images of the six different orientations of C1, which are classified by three colored dashed lines. Interestingly, gas-phase DFT modeling reveals a siteselective interaction between a Co atom and a HEB molecule, hence rationalizing the formation of a C1 complex incorporating a Co-bis(alkynyl) tweezer-like binding motif. Albeit neglecting unavoidable geometrical adaptations during adsorption, the model helps in explaining the low-symmetry structure of the C_1 appearance in the STM images (see Figure S3b for a side view). The π -tweezer bonding is known for various transition metals³¹ and can afford stable interactions.³² Interestingly, reports on related cobalt complexes are rare.^{33,34} Without STM image simulations, one might expect the Co atom to sit at the brighter side of the complex. However, in accordance with observations for higher Co coverage (see below), we suggest that the Co atom causes the depression and attribute the counterintuitive STM contrast to a modified molecular conformation, where alkynes next to Co

spread apart, implying that non-interacting terminal groups are pushed upward (brighter appearance).

A closer look at the two protruding lobes of the C1 units (Figure 2d) reveals that one lobe appears brighter than the other, thus the complexes exhibit chirality. We define a C₁ unit to represent the 'R' enantiomer for the case that the brighter protrusion is on the right side of the dashed line when going from the cobalt atom toward the brighter side. Interestingly, when analyzing the handedness of the C_1 units within the β domain depicted in Figure 2c, it turns out that all complexes exhibit the same handedness (Figure 2d). Consistently, within an α domain, only the opposite handedness was observed (see Figure S3c). Based on the observation of six orientations of C_1 within organic domains, we propose its adsorption on a six-fold symmetric adsorption site (top site) and superimposed a gasphase DFT-calculated model, aligned according to the molecular orientation within β domains, on the Ag(111) registry (Figure 2d). The related situation for the α domain is depicted in Figure S3c. In both cases, six hollow sites are found very close to where the Co atom is expected from the gas-phase model (crossing of black dashed circle and dashed lines). Considering the tendency of Co atoms to adsorb at the hollow sites³⁵ along the periphery of the dashed circle (12 hollow sites), combined with a strong Co-bisalkyne π -tweezer binding motif (six binding sites for HEB), we can explain the six orientations of C_1 within the α domain and its six orientations within the β domain. Assuming that the minimal Co dosage at 12 K does not alter the epitaxy of the whole domain, this finding confirms our tentative model of the centers of HEB monomers adsorbing on top sites within the organic phase. The chiral configuration of the organocobalt complexes supposedly results from the interplay of the epitaxy with the underlying Ag(111) surface and the intermolecular interactions with the organic template. With the objective to establish two Co-

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bisalkyne motifs within one HEB unit (*i.e.*, a dicobalt complex), the Co dosage at 12 K was increased. However, instead of welldefined dicobalt complexes, we observe irregular Co clustering on the immobile molecular template. Consequently, the influence of the deposition temperature on the formation of organocobalt complexes was studied next.

Co Dosage at 200 K. To investigate the influence of thermal activation on the formation and positioning of the complexes, we increased the sample temperature during Co dosage to a value (200 K), at which predeposited molecules are mobile. We prepared two samples with different stochiometric ratios (Co/HEB). Figure 3a-c refers to the low Co coverage,



Figure 3. Organocobalt phase, generated via Co dosage at 200 K, displaying α domain (d, e) and β domain (a). The Ag(111) closepacked directions are shown by stars. (a) Organocobalt island with a Co-HEB ratio of 0.64 together with superimposed unit cell, cobalt markers (yellow), and colored outlines marking the main axes (MA). Complexes with the same MA (color) appear on positions coinciding with points of a hexagonal lattice. (b) Magnified STM image of two complex species with same MA within the network: mononuclear complex C₁ (dashed outline) and dinuclear complex C₂ (solid outline) incorporating one and two Co atoms along their MA (drawn line). (c) Relative occurrence of C_1 (dashed) and C_2 (solid) for each MA (ensemble of 267 units) for low-coverage case. (d) STM image of organocobalt network with Co-molecule ratio 1.23. (e) Pristine molecule surrounded by six C₂ resembling windmill blades. (f) Relative occurrence of C_2 and C_1 (171 molecules evaluated) for high-coverage case. Tunneling parameters V_t, I_t: (a, b) 100 mV, 300 pA; (d) 100 mV, 100 pA; (e) 20 mV, 100 pA.

while the data shown in Figure 3d-f were obtained for the high Co coverage. Already at a low Co-molecule ratio (Figure 3a), one can observe the emergence of a new phase with a similar hexagonal packing scheme, but with a different unit cell containing both complexes and pristine molecules. The two domain orientations of this multicomponent phase differ from the organic phase by an $\sim 30^{\circ}$ rotation of the embedded units

(highlighted by hexagonal contours). The previously introduced α (β) notation is consistently reused for the organocobalt phase based on the fact that rotation of the organic α (β) unit cell by 31.3° [sum of R 8.9° and R 22.4° from Wood's notation for organic and organometallic adsorption phase (see above and below)] leads to the organometallic α (β) domain orientation.

In agreement with the *in situ* Co dosage at low temperature (cf. Figure 2c,d), the organometallic complexes appear in six orientations within one domain, which are classified by three 120° multiple main axes (MA); one of them shown for the C₁ orientation in Figure 3b (dashed line). For clarity, the MA of the complexes shown in Figure 3a,b,e are not depicted, but are inferred from the color scheme of their hexagonal contours. In addition to mononuclear C1 (dashed outline), a less frequent species (solid outline) is recognized exhibiting two bright lobes opposite to each other and two depressions along the main axis (Figure 3b) rotated by 90° with respect to the protrusions. Consistently with C_1 , which shows one depression, the second species is attributed to a dinuclear complex featuring two π tweezer binding motifs along the MA. Hence, the intramolecular STM contrast is tentatively ascribed to a downward pulling of alkynes next to Co atoms, while non-interacting moieties are pushed upward for steric reasons and thus appear very brightly. We denote this species C₂ and highlight all Co atoms of the recognized complexes by yellow markers for better apprehension of the STM image. Figure 3b shows two magnified sections with superimposed DFT molecular models (gas-phase DFT model for C1 and DFT model including surface for C_2), which represent two complexes with the same MA. With its Co atom having two possible adsorption sites along the MA, the C1 complex can assume two orientations with the same MA.

An intriguing observation is that all complexes displaying the same MA orientation (same color) represent one subset of hexagonal lattice points. Since there are three MA, each alignment of Co-HEB, *i.e.*, a term referring to both the C_1 and C_2 species, is assigned to one of three hexagonal lattices shifted against each other. When filling both the remaining "free" spots of the three hexagonal lattices and remaining voids with pristine molecules, a dense-packed domain structure is established.

A representative large-scale STM topograph of the highcoverage sample with twice the Co-molecule ratio is presented in Figure 3d. Compared to the previous case, pristine molecules mainly occupy sites (representing one hexagonal lattice) where complexes are not expected due to their site-selective adsorption behavior. Consistently with the preceding results, complexes only occupy three hexagonal lattices according to their MA, thus establishing a periodic nanostructure divided into four hexagonal lattices: a hexagonal lattice of pristine molecules, appearing without protruding features, coexistent with three fault-free hexagonal lattices embedding mainly C2 complexes (solid) and a few C_1 (dashed). A scenario where all six complexes surrounding one molecule are dinuclear is displayed in the close-up STM image of Figure 3e, whereby the positions of the Co atoms are given to guide the eye. The windmill-like motif is rationalized by three pairs of opposite complexes, where each pair reveals a different MA.

The relative occurrence of C_1 and C_2 within the molecular islands with low (high) Co coverage is displayed in the respective histogram in Figure 3f, representing an evaluation of 267 (173) molecules. The similar height of the three color-coded columns indicates that all three MA are equally probable



Figure 4. STM images with enhanced contrast displaying isolated C_2 conformers (α and β) and the organocobalt phase (α domain only). (a) Two STM images of isolated C_2 with same MA but opposite handedness. (b) High-resolution scrutinization of organocobalt domain with underlying Ag(111) lattice and superimposed molecular models. Co sites (yellow) and vacancies (black) of C_1 and C_2 coincide with fcc and hcp hollow sites. Co centers of complexes are connected by fcc and hcp triangles (color coded), which together with rhomboids (orange) and hexagons (red) span a chiral 3.4.6.4 surface tessellation pattern. (c) Adsorption model for windmill-motif (*cf.* Figure 3e) based on arranging molecules according to (b). Straight lines connecting opposite hollow sites (purple) coincide with MA orientations in (b) (purple-colored Co-Co axis). Tunneling parameters V_v I_i : (a) -10 mV, 30 pA; (b) -10 mV, 100 pA.

for C_1 (black fill with dashed outline) and C_2 (white fill with solid outline). In the case of low Co dosage, 40% of the molecules remain pristine, while the complexes primarily represent the C_1 species (dashed outline). At high Co dosage, however, only 26% are not complexed, while C_2 is the more abundant complex species (solid outline). The strong decrease of the C_1 species further hints to the incorporation of two Co atoms within the C_2 species.

As a result of this analysis, the ordering of complexes is independent of the Co coverage, *i.e.*, Co-HEB always occupies three of four hexagonal lattices of the domains, while HEB substituting the lack of Co-HEB does not show any preferential adsorption site. Hence, a rhombic region of four adjacent molecules within an organocobalt domain can contain $0 \le n \le$ 6 Co atoms. This implies that the strict ordering pattern is mainly ascribed to the adsorption behavior of the organocobalt complex. When increasing the Co/HEB ratio beyond 1.5, *i.e.*, the value of the ideal architecture (all complexes are dinuclear), we observed the complete dissolution of the mixed domains leaving behind scattered units, *i.e.*, isolated C_2 complexes and cluster-like structures containing Co and HEB in a highly irregular fashion (see Figure S4b). From the absence of openporous domains of complexes, we conclude that to induce and stabilize the formation of 2D organocobalt domains, at least one-fourth of all constituents must remain pristine HEB.

While deposition at 12 K leads to statistically distributed C_1 orientations due to Co adsorption on an immobile molecular template, C_1 units formed at 200 K show a strong correlation between orientation and adsorption site due to the mobility of HEB and Co-HEB. From the observation that molecular deposition at 200 K leads to extended assemblies, we assume that the organocobalt phase requires the mobility of the onsurface formed complexes. Against the scenario that Co adatoms hop between molecular hosts speaks the ~30°

rotation of each unit within the new phase, compared to molecules of the pristine phase. Due to the strong distance dependency of electrostatic interactions, we exclude their influence on the highly selective positioning and alignments of Co-HEB. Combining the preferential adsorption of single Co adatoms at hollow sites together with the complexes' size and symmetry, and the selective bonding of Co atoms *via* alkyne— Co–alkyne bridges, the organization of the organocobalt domains is explained by the adsorption site-selective positioning of Co-HEB units on Ag(111).

Surface Tessellation. For a better understanding and atom-precise characterization of the intricate layer organization, we present high-resolution STM images with enhanced contrast for both isolated C₂ units (Figure 4a) and extended domains (Figure 4b). Isolated C₂ complexes coexist as a naturally formed species with 2D networks (see Figure S4). Due to the enhanced contrast for the complex depicted in Figure 4a, an uneven apparent height of the two lobes near to each Co position (yellow marker) is noticeable, whereby the two less protruding features are connected by a white line for simple identification. This α configuration is compared to a β C₂ unit, which reflects the same MA (purple line), however, it appears slightly rotated and the intramolecular contrast of the alkynes next to Co appears inverted (mirrored white line). From the different angles between the MA and the depicted lines, we identify the chiral character of the dinuclear organocobalt complexes, labeled α and β according to their mirror-symmetry with respect to the MA. The chiral signature could be interpreted as slightly different z-heights within each alkyne pair enclosing a Co atom, and it seems remarkable that both bisalkyne Co motifs of one complex display the same handedness. The existence of enantiomeric forms of the C2 complex demonstrates that chirality is present at the singlecomplex level and is not induced by the aggregation into a 2D domain only.

To establish a direct atomic-level comparison with the 2D organocobalt phase, an STM image with similar enhanced contrast is presented in Figure 4b together with the underlying Ag(111) lattice. First, a different apparent height of alkynes interacting with Co is identified for both C_1 and C_2 , and second, their bisalkyne Co motifs reflect the same chirality. Therefore, we conclude that this image shows an enantiopure domain in which the C_2 complexes correspond to the α conformer of Figure 4a. As expected, analyzing the enhanced STM contrast of an organometallic β domain reveals homochiral entities coinciding with single β conformers (see Figure S5). Both isolated and laterally embedded α (β) conformers exhibit the same molecular alignment with respect to their underlying $[11\overline{2}]$ directions, representing their mirrorsymmetric axes. There is approximately a 16° twist between α and β conformers. Compared to a racemic arrangement of these units,^{36,37} the organization within domains of homochiral complexes is assumed to promote a closer domain packing, which implies stronger van der Waals interactions and hence a gain in adsorption and free energy.

A closer look at the proposed model for the α domain (Figure 4b) reveals that molecules and complexes are aligned in such a highly ordered fashion and that all Co positions fall onto substrate hollow sites. The missing Co atoms with respect to the ideal structure (*cf.* Figure 3e) are marked as black circles. The two Co atoms belonging to one C₂ complex always occupy one fcc and one hcp hollow site. They are connected by purple lines in order to highlight the complex's MA. Interestingly, the

Co atom of C_1 is also located at either fcc or hcp hollow site, indicating that the presence of C_1 does not disturb the highly organized superlattice of incorporated Co atoms.

When linking the fcc (hcp) hollow sites of three adjacent complexes by an fcc (hcp) triangle and further connecting an fcc and hcp triangle by a rhomboid, a 3.4.6.4 tiling pattern³⁸ is clearly evident (lower part of Figure 4b). As highlighted by the colored polygons, one large hexagonal tile is surrounded by six triangles, three oriented upward (green) and three oriented downward (brown), and six rhomboids (orange). The unit cell contains one hexagon, two antiparallel triangles, and three 120° multiple rhomboids. The corners of the polygons are situated at hollow sites where Co is located. For the sake of completeness, we present the other handedness for the β domain (see Figure S5) and mention that both domains are mirror-symmetric with respect to the three MA (purple lines). As a note, we mention that the two-fold degenerate alignment of C₁ is attributed to the Co atom sitting at either fcc or hcp hollow site, however both configurations are not found with equal probability (see Figure S6).

The mathematical description of this structure dates back to Johannes Kepler, who deduced that the complete filling of an Euclidean plane with symmetric polygons can lead to just 11 tessellation structures.³⁹ Hitherto, numerous examples of surface tessellation have been reported, *e.g.*, a Kagomé lattice using dicarbonitrile linkers,⁴⁰ snub-square tiling within a lanthanide-based metal—organic framework,⁴¹ and a rhombitrihexagonal tiling in a solution-confined oligophenylene-ethylene-based Pd(II) complex;⁴² the latter motif is equivalent with our surface-confined tessellation pattern.

From a detailed analysis of both domains, we deduce a commensurate $\sqrt{129} \times \sqrt{129}$ R 22.4° superstructure with the α unit cell reading:

$$\begin{pmatrix} \vec{c} \\ \vec{d} \end{pmatrix} = \begin{pmatrix} 8 & 5 \\ -5 & 13 \end{pmatrix} \begin{pmatrix} \vec{u} \\ \vec{v} \end{pmatrix}$$

in matrix notation, where \vec{u} and \vec{v} are the primitive vectors of Ag(111), which were depicted in Figure 2b. The β unit cell reads in matrix notation: $\begin{pmatrix} 13 & -5 \\ 5 & 8 \end{pmatrix}$, as shown in Figure 3a and in the right part of Figure S5b. Consistent with our analysis of the organic phase, we encounter the pristine molecules' centers adsorbed at top sites, while the center of the complexes reside at bridge sites. The latter agrees with our symmetry consideration that both the STM appearance of Co-HEB and underlying bridge site share the same 120° multiple orientation and two-fold symmetric axis (MA).

To rationalize the emergence of the apparent windmill-like tiling motifs, *i.e.*, a pristine molecule surrounded by six complexes (*cf.* Figure 3e), Figure 4c displays the Ag(111) lattice with superimposed molecules, which are positioned and oriented corresponding to the α domain's registry in Figure 4b. Since we encounter a pair of hollow sites, one fcc and one hcp site, in close proximity to the Co positions of the gas-phase configuration of the complex (purple line), we suspect that the MA of complexes is determined by the favorable Co epitaxy and aligns accordingly, *i.e.*, perpendicular to the connection of the two substrate atoms forming the bridge site. Assuming that the orientation of the complex is correlated with its adsorption site, the intriguing surface tessellation pattern can be explained. In the case of a dense-packed molecular matrix and sufficient

Co atoms, three-fourths of the molecules can form two-fold symmetric complexes, which will be centered at bridge sites. The remaining one-fourth of molecules is necessary to complete the remaining voids with the six-fold symmetric precursors' centers located on top sites, which would be unfavorable for the complexes. As a note, the significant asymmetry of the π -tweezer Co bonding following from this simplified model (Figure 4c) may imply intramolecular relaxation due to flexible bending of interacting alkynes and slight displacements of Co with respect to the deeper lying hollow sites. Regarding the ability of isolated C2 to express enantiomeric states (cf. Figure 4a) and 120° multiple orientations (colored outlines in Figure S4), we conclude based on comparison with Figure 4b that the isolated and incorporated complex exhibits the same adsorption behavior. An adsorption model for a single C₂ unit is shown in Figure S8d (left column).

DFT Results for the Organocobalt Phase. For a characterization of the extended supramolecular tessellation from a theoretical point of view, state-of-the-art DFT calculations including the Ag(111) substrate were performed. The input of this DFT calculation is based on positioning Co adatoms on a molecular lattice according to the experimentally observed organocobalt phase. To check reproducibility, the calculations were carried out with two different approximations of the exchange and correlation term (see Methods section). Both the revPBE+D3 and B86r-vdW-DF2 treatment provide very similar results, therefore only the results with the former procedure are presented.

A visualization of the lowest-energy geometry of the organocobalt phase is presented in Figure 5. To facilitate comparison with the experimentally observed structure (Figures 4a,b and Figure S5a,b), the Ag atoms in Figure 5b,c are represented by red (instead of gray) spheres. Notably, the DFT calculations corroborate the on-surface formation of dinuclear compounds with a Co–Co distance of 7.76 Å (Figure 5b). It is worth mentioning that this distance is close to twice the Co–arene distance (3.96 Å) of the gas-phase DFT model of C₁ (*cf.* Figure 2d), which suggests a minor influence of the Ag(111) surface on the Co–arene distance during C₁ \rightarrow C₂ conversion.

The DFT structure of the organocobalt domain has a unit cell with six Co atoms (yellow) and four molecules (white outline in Figure 5c), which agrees well with the observed α domain (*cf.* Figure 4b). Consistent with experiment, molecules without Co atoms are centered on top adsorption sites, while complexes are centered at bridge sites, thus establishing the observed windmill-like motifs (*cf.* Figures 3e and 4c). With the Co atoms preferentially binding close to fcc (hcp) hollow sites and representing the corners of superimposed brown (green) triangles, the experimentally observed tessellation pattern is fully reproduced.

To elucidate the arrangement of substrate atoms below the organocobalt phase, Figure 5a shows the topmost Ag atoms of a five-layer Ag(111) slab with a color coding and scaling according to labeled z-height intervals, whereby z = 0 defines the topmost layer. The Ag atoms with the lowest (highest) z values are exclusively encountered below the complexes, *i.e.*, two red (blue) Ag atoms along the Co–Co axis (perpendicular to it). The Ag atom below each alkyne-Co-alkyne motif is indented (red), while the Ag atom below each non-interacting TMS-alkyne moiety of C₂ is protruding (blue). Since the surface corrugation of the topmost Ag(111) layer is absent



Figure 5. DFT modeling of surface-supported C_2 and pristine molecules within the α domain. (a) DFT representation emphasizing the corrugation of the topmost Ag(111) layer, as indicated by *z*-height intervals and scaled spheres representing indented (red) and protruding (blue) Ag atoms. Diameter of Co atoms is reduced in (a) and (b) for better visibility of substrate atoms. (b) Top view of single surface-supported C_2 . (c) DFT model highlighting the varying *z*-height of the Si atoms by scaled spheres (blue) within the unit cell (white outline). The superlattice of embedded Co atoms is grouped by fcc and hcp triangles. Numeric values are in Å.

below the HEB molecules, we assume that it originates from the embedded Co atoms of the complexes. We consider that the complexes are pulled down *via* Co atoms, by which a strong interaction between alkynes and Ag atoms is only present for complexed HEB. For each complex, the d orbitals of each of the two protruding Ag atoms (blue) might strongly hybridize with the out-of-plane π orbitals of the overlying alkyne. The remaining four alkynes' in-plane π orbitals are supposed to strongly hybridize with the d orbitals of Co instead, wherefore the Ag atom below each alkyne-Co-alkyne motif (red) is lowered. The periodicity and distribution of the surface corrugation (0.58 Å height difference between blue and red spheres) agrees with the STM contrast observed in Figure 3e, where the complexes' non-interacting moieties show the strongest brightness, while the darkest contrast is found at the Co sites.

From the increased surface-molecule interaction of Co-HEB, we expect its lowering compared to HEB. Indeed, when comparing the physical heights of all carbon atoms (SI Figure S7b), the interacting C(sp) atoms of Co-HEB are lowered by 0.65 Å compared to the C(sp) atoms of HEB. As a consequence of this alkyne-Co-alkyne anchoring at hollow sites, the arene ring ($C(sp^2)$ atoms) of Co-HEB is lowered by 0.26 Å. These molecular conformations brought about by the incorporation of Co atoms are caused by a strong bending of the alkynes next to Co (see Figure S7a).

Comparing the heights of the Si atoms, as illustrated by the scaled diameters of prominent blue spheres within the unit cell of Figure 5c, one notices the equal z-height of the six Si atoms of pristine HEB. On the contrary, for C₂, the two Si atoms of the TMS-alkyne-Co-alkyne-TMS binding motifs systematically display different heights, which implies a non-uniform alkyne-Co-alkyne interaction and is visible by strong bending deformations of the respective moieties. Consequently, the DFT calculation confirms the formation of an enantiopure organocobalt domain and rationalizes the chiral character of C₂ by the bending of the two alkynes next to Co. Although the physical heights of the simulation image cannot be directly related to the STM image contrast of Figure 4b, it should be mentioned that the TMS-alkyne being closer to Co appears brighter in the STM contrast, while the DFT image represents it with a smaller Si height than the less interacting moiety of the alkyne-Co-alkyne motif. The fact that the TMS groups of HEB appear less bright than the non-interacting TMS groups of Co-HEB is not reflected within the DFT visualization of the Si and C heights (Figures 5c and S7b), but is explained by the corrugation of topmost Ag atoms below the complexes (see above). Since the STM contrast reflects a convolution of both the z-height and electronic density of states, this discrepancy can be related to electronic effects contributing to the STM appearance.

A difference between the DFT structure and the model derived above from our STM observations is that the molecules are slightly rotated with respect to the experimental α domain configuration. This might be due to a limited accuracy of the DFT results in reproducing the delicate balance between Agalkyne and alkyne-Co-alkyne interactions.

Single-Molecule Manipulations on C₂. To inspect the structural integrity and conformational flexibility of isolated complexes, we performed single-molecule manipulation experiments. The STM image in Figure 6a shows isolated C₂ units together with small close-packed islands. Interestingly, at both low and high Co concentrations, single C₂ entitites coexist with assembled structures (see Figure S4a,b). The histogram in the inset is based on counting isolated C₂ species according to their MA. It reveals that all three orientations coexist with nearly equal probability within the evaluated region of 200×200 nm².

Figure 6b depicts STM images before and after a 120° rotation induced by the STM tip. For this purpose, we centered the tip on C_2 , opened the feedback loop, and approached the tip from the set point ($V_t = -10 \text{ mV}$, I = 50 pA) until current spikes indicated a rotation of C_2 , in response to the increased tunneling current (typically at I = 20 nA). The similarity of the molecular features before and after the rotation implies the



Figure 6. STM-tip manipulations on isolated C_2 complexes. (a) STM image illustrating isolated C_2 units distributed over a Ag(111) terrace. Inset: Histogram of MA orientations. (b) STM images after tip manipulation showing a 120°-rotated species. (c) Sequence showing a tip-assisted displacement of C_2 (along the depicted line) and associated rotation by 120°. Tunneling parameters for imaging V_{ν} I_t: (a-c) -10 mV, 50 pA.

preservation of the chemical structure of C_2 upon this kind of manipulation, thus demonstrating the robustness of the C_2 complex.

The complexes' stability toward high tunneling currents, as long as the bias voltage remains low, was further used to demonstrate their cohesion and intactness toward lateral displacements. Figure 6c presents STM images of the complex before and after the lateral movement along the marked line. This displacement was achieved by approaching the tip until reaching $I_t = 25$ nA and dragging the complex along the path of the tip with respect to a fixed reference mark (white line). While attemps in manipulating pristine molecules resulted in molecular adsorption on the tip, isolated complexes could easily be moved without triggering any structural modification, as evident from the consecutive STM images. The latter implies a stronger interfacial coupling for Co-HEB compared to HEB. The 120° rotation of the complex after the manipulation hints to a correlation between its MA and adsorption site. Also the 120° rotation of a C₂ unit embedded in an organocobalt domain was achieved (see Figure S8). In this case, a significant increase in the measured height of the entire complex is evident. We tentatively assign it to a geometric lifting and rationalize it by an unfavorable adsorption site for this complex. Therefore, when, after rotation of the complex, its migration to a nearby hollow site with favorable [112] orientation is sterically hindered by the surrounding molecules, the complex is stuck in an unfavorable configuration where Co atoms cannot reach the preferred hollow sites, presumably lifting the whole unit.

Kondo Signature of Activated Complexes. Complexes incorporating multiple magnetic metal centers^{9,43,44} are discussed as promising candidates for nanomagnets, spintronic, and quantum computing devices.^{45–47} The focus lies particularly on surface-supported molecular magnets expressing long magnetic lifetimes^{48–50} and remarkable hysteresis characteristics.⁵¹ Accordingly, we explored the properties of isolated complexes regarding potential magnetic behavior. Initially, we performed scanning tunneling spectroscopy (STS) measurements on isolated C₂ units, which do not show a Kondo feature. Then, we applied a stronger manipulation procedure than before, in order to alter the interaction between Co atoms and alkynes: the STM images I and II of Figure 7a were obtained after applying a bias pulse of -2 V for a duration of 10 ms on top of the left bright lobe



Figure 7. Kondo features in activated C₂ species. (a) Activation of pristine complex (upper panel) by a bias pulse (-2 V, 10 ms) with the tip positioned above a bright lobe. Occurrence of one (two) frizzled spot(s) (red outline) in activated species I and II, along with a reduced brightness of one (two) protrusion(s), and a rotation of HEB. (b) Low-bias dI/dV spectra on pristine Ag(111) (black) and C₂ [green: spectrum on pristine complex acquired at position of green marker in the inset in (b), and red: spectrum acquired within red circle of configuration I in (a)]. The Fano fit (blue) was carried out with q = 0.27, $x_0 = 1.9$ mV, $T_{\rm K} = 23$ K. Tunneling parameters for imaging V_v I_t : (a, b) STM and STS set point: -20 mV, 100 pA. STS set point parameters: -20 mV, 100 pA (120 pA for Kondo spectrum), $\Delta z = -90$ pm before sweep, $V_{\rm mod} = 1$ mV rms, f = 933.5 Hz, T = 1.2 K.

(upper image). The structurally modified complex I is characterized by a slight rotation, one remaining protrusion, and a grainy frizzled feature (red outline) located between two alkynes. The manipulation experiments were repeated for different complexes and show that configuration I is highly reproducible. Occasionally, a voltage pulse on a protrusion triggered the emergence of a strongly rotated compound with two grainy frizzled features, as identified by two outlined spots in configuration II. A further voltage pulse on configuration II converted it back to I, identifying the latter as more stable.

Interestingly, the frizzled features of the I and II variants in Figure 7a appear at different locations compared to the Co sites of the initial structure above. We attribute them to loosely bound Co atoms losing their initial binding sites and changing to a metastable binding configuration, in which they partially follow the STM tip. In configuration I, one of the two Co atoms has undergone this site change, while in configuration II, both Co atoms have changed their adsorption sites. While the transformation from I to II is reversible, we could not convert the activated complex to pristine C_2 .

When performing dI/dV spectroscopy above a frizzled feature of the activated configuration I (red outline, Figure 7a), we observed a strong Kondo resonance. The low-bias STS spectrum exhibiting a dip-like structure is shown in Figure 7b together with dI/dV spectra on pristine Ag(111) and C₂, both revealing a featureless shape (STS data obtained at 1.2 K). We suggest that the dip feature indicates the existence of a magnetic moment that is screened by the surrounding electrons, giving rise to a many body state.⁵² The shape of the Kondo resonance shown in Figure 7b has been reproduced on many activated C₂ species (configuration I) with different STM tips. It was fitted by the Fano equation:

$$dI/dV \propto \frac{(q\Gamma + E - E_0)^2}{\Gamma^2 + (E - E_0)^2}$$

where E_0 and Γ are the position and temperature-dependent half width at half-maximum of the Kondo feature and q is the shape parameter giving different weight to the interfering quantum-tunneling paths. After eliminating thermal broadening and modulation voltage (root-mean-square values $V_{\rm rms}$) broadening by the formula:

$$\Gamma(T) = \sqrt{(3.5k_{\rm B}T)^2 + (\sqrt{6}\,eV_{\rm rms})^2 + 2(k_{\rm B}T_{\rm K})^2} \tag{1}$$

with $k_{\rm B}$ and e being respectively the Boltzmann constant and the elementary charge, 53,54 the obtained Kondo temperature reads $T_{\rm K}$ = 23 K. This value is remarkably lower than for isolated Co atoms on the Ag(111) surface (95 K).⁵⁵ The diminished value could be related to Co-alkyne orbital interactions weakening the Co-surface bond and thus the Kondo screening, which originates from the delocalized cloud of surface electrons. Configuration II (two grainy spots), which was rarely observed, also expressed a Kondo signature on both sides, but with different Kondo temperatures. Embedded C2 entities within organocobalt domains can also be similarly activated to display a Kondo signature above the frizzled feature of configuration I. The observed Kondo resonance on STM tipmanipulated C2 complexes reveals a chemical fingerprint of incorporated Co atoms, which further consolidates our interpretation of an on-surface formed dinuclear organocobalt complex.

Conformer Switching. The creation of single-molecule switches and molecular motors, which are powered by the tunneling electrons of a STM tip^{56–59} or the STM tip's electrical field,^{60,61} bears promising potential for nanoelectronic devices. Furthermore, STM represents an exquisite tool to identify switching between enantiomeric states of surface-adsorbed chiral molecules, *e.g.*, the vibration-induced switching of propene.⁶²

Intrigued by the existence of the different conformer states (α and β) of the C₂ complexes, we explored the possibility to switch between C₂ enantiomers with the aid of the STM tip. The STM image in Figure 8a displays two isolated C₂ units, which, according to the brightness of the four alkynes next to Co, are recognized as β and α conformers (compare with Figure 4a). When imaging the α complex with an elevated tunneling bias ($V_t = 100 \text{ mV}$), we observe a fuzzy appearance of isolated C₂ (right panel of Figure 8a). In subsequent imaging with low bias voltage (~20 mV), the same complex again appears stable and with a clearly discernible enantiomeric state. Accordingly, we attribute the fuzziness of the high-bias image to tip-induced switching between the α and β conformers. It seems to occur within a significantly smaller time scale compared to the acquisition time of the STM image.

To determine the critical bias voltage of this drastic transition in the appearance behavior, we recorded dI/dV spectra. They are displayed in Figure 8b and show two regimes separated by a threshold of ±40 mV. For bias voltages below the threshold, a stable signal with either low or high conductance is present, whereas beyond the threshold, a fluctuating signal is observed. The latter is assigned to repreated switching between the two enantiomeric states causing low and high conductance at the same tip position (*cf.* Figure 8c).

For better characterizing the switching behavior, we recorded a series of spectra over all of the TMS-alkyne groups involved in organometallic bonding (markers in Figure 8c), which are referred to as TMS 1, 2, 3, 4 in Figure 8c–f. At these four locations, we recorded time traces of the tip height changes with a closed feedback-loop, such as the example shown in Figure 8d. For each of these traces, we assign the abrupt



Figure 8. STM and STS results qualifying isolated C₂ as a chiral complex. Dashed vertical lines indicate the voltage at which STM images and time sequences were recorded. (a) STM topograph at -20 mV allows the differentiation of the α and β conformer, while the adjacent STM image at 100 mV appears frizzled. (b) Two subsequent dI/dV spectra obtained at spots marked in a) exhibit a symmetric threshold at ± 40 mV and two-state fluctuations above it. (c) Enhanced contrast STM images before and after switching the chiral state, where marked molecular lobes flipped their brightness contrast. (d) $\Delta z(t)$ spectrum on top of a marked lobe for a bias voltage above threshold. Abrupt changes between plateaus indicate switching events. (e) Logarithmic plot of switching rate as a function of the bias voltage for TMS 1, 2, 3, 4 (markers). (f) Controlled switching by applying a short bias pulse while monitoring z-height below the threshold voltage. Tunneling parameters for imaging V_v , I_t : (a) -20 mV, 100 pA; inset: 100 mV, 300 pA; (c) -10 mV, 300 pA. STS set point parameters: (b) 100 mV, 300 pA, $V_{mod} = 1$ mV rms, f = 733.5 Hz, T = 4.5 K. Time sequences at T = 1.2 K: (d) -40 mV, 30 pA; (e) 30 pA; (f) -10 mV, 50 pA.

changes between plateaus of different z-height (offset Δz) to switching events between enantiomeric states and determine the switching rate by dividing the number of events by the acquisition time (10 s). The dependence of the switching rate on the bias voltage is shown for each of the four TMS-alkyne groups (markers) and at a constant tunneling current of 40 pA (Figure 8e). For all moieties, the logarithmic scale implies that an exponential trend is present for bias voltages above a threshold of about ± 40 mV. The absence of the switching below the threshold value for both polarities is consistent with the behavior apparent in the STS spectra of Figure 8b. Hence, the switching is associated with an electron-driven process exciting molecular vibrations. To determine whether an event is triggered by only one electron,58 the dependence of the switching rate on the tunneling current was studied. From the associated double-logarithmic representation together with a linear fit revealing a slope being slightly higher than unity (see Figure S9), we cannot exclude that the switching is caused by a higher-order electron process.

To control the switching process without triggering multiple switching events, a short bias voltage pulse (-75 mV and 45)ms) was employed while acquiring z(t). As shown in Figure 8f, the apparent edge due to the pulse coincides with a jump in z_i indicating a controlled single switching event. Recording STM images before and after such switching demonstrates that a single switching event suffices to reproducibly alter between the two enantiomeric states of a C₂ unit. Within the interacting TMS-alkyne moieties (marked molecular lobes in Figure 8c), diagonally opposite lobes appear with the same brightness, while adjacent lobes reveal an apparent height difference. Hence, we assume that the out-of-plane bending (oscillation) of these intramolecular lobes is coupled. For each switching process, all four interacting groups change z-height, whereby two diagonally opposite lobes oscillate in phase, while two adjacent moieties express opposite conformation states during this synchronous two-state switching.

In contrast to isolated C_{2} , it was not possible to switch the chirality of C₂ units embedded in the 2D organocobalt phase. According to our interpretation, a switching process represents an interconversion of the complex's handedness, which is accompanied by a rotation of the molecule (Figure 8c). Presumably, this process is prohibited due to steric interactions with the surrounding molecules in the densely packed chiral architecture, which represents a conglomerate phase. The switching of isolated Co-HEB shows the relationship between its two chiral states and the respective unit cell orientation of assembled domains. Both the isolated compound as well as the unit cell of the organic and organocobalt conglomerate phase reveal a twist of ~16° between α and β . During $\alpha \leftrightarrow \beta$ switching, the Co atoms along the MA of the isolated C_2 may remain at fixed locations or rotate (together with their molecular host) symmetrically to the complex's underlying bridge site. The latter scenario would be more consistent with the observed 120° multiple rotations of the Co–Co axis (MA) (cf. Figure 6b,c).

CONCLUSIONS

In summary, we have presented a systematic STM and DFT study of an on-surface synthesized dinuclear organocobalt complex, which was accomplished by the well-defined incorporation of Co atoms into a multitopic alkyne derivative on a smooth metal surface. The organometallic building blocks self-assemble into a 2D nanoarchitecture, whose incorporated Co atoms express a 3.4.6.4 surface tessellation. Atom-precise STM imaging and extensive DFT calculations unraveled the decisive role of the surface registry on the formation of the chiral tiling pattern. Tip manipulation experiments on isolated complexes demonstrated their conformational flexibility enabling reversible two-state switching between enantiomers and deepened our understanding of the structural properties of the 2D phase. A Kondo feature at modified complexes provided a chemical fingerprint for the incorporated Co atoms.

Our results open up new ways to generate nanoobjects with multiple spin-centers embedded within custom-designed molecular backbones, which is specifically interesting taking into account the extraordinary capabilities of the alkyne moiety to develop conjugated electronic states, as already demonstrated within a plethora of structures.^{21,63–65} The STM tipactivated configuration of such complexes could represent an alternative approach toward nanomagnetism where wide tunability of the magnetic behavior is expected. Combining multinuclear alkynyl complexes with on-surface coupling

reactions^{66–68} could afford extended spin systems with a prospect for quantum information manipulation at the single-molecule level. Our results bear fruitful perspectives for interfacial organometallic chemistry and provide useful prospectives toward the atom-precise fabrication of functional interfacial nanoarchitectures with transition metal centers in well-defined environments.

METHODS

All sample preparations and STM measurements were carried out in the UHV environment of the preparation and STM chamber of a commercial Joule-Thompson scanning tunneling microscope (www. specs.de) with a base pressure below 1×10^{-10} mbar. The Ag(111) sample was cleaned by repeated cycles of Ar+ sputtering (0.9 kV, 10 μ A emission) for 25 min (min) and subsequent annealing at 760 K for 15 min. The powder of purified HEB molecules (synthesized by Zhi Chen, Ruben group at Karlsruhe Institute of Technology) was thoroughly degassed and evaporated at a crucible temperature of 430 K, which caused a strong darkening of the initially yellow powder. The organic phase was prepared by CVD on the clean Ag(111) sample kept at 300 or 450 K. Co was sublimated from a thoroughly degassed Co wire of 99.995% purity (Alfa Aesar), which was wound around a tungsten wire that was thermally heated by a current. For the in situ deposition, an evaporator was placed in front of the cryostat's evaporation gate, which was opened for a certain time with the sample always staying below 12 K. For deposition at 200 K, the sample was placed by a precooled manipulator in front of an additional evaporator installed in the preparation chamber. During Co deposition, the power supply provided a voltage and current of $V_d = 1.7$ V, $I_d = 6.4$ A (1.2 V, 8.1 A) for the in situ (ex situ) deposition. The STM topographs were mainly acquired at liquid helium temperature (~4.5 K), and if not stated otherwise, the constant current mode was used. Spectroscopic and manipulation measurements were mainly conducted at 1.2 K with an etched tungsten tip that was sputtered, Ag-coated by field-emission and prepared by soft indentations on the smooth Ag(111) surface, until a clear signature of the surface state was present. For dI/dVspectroscopy, an external lock-in amplifier was used at a frequency of f= 733.5 and 933.5 Hz and modulation voltage of V_{mod} = 1 mV rms (low-bias spectra).

We performed the DFT calculations within the Kohn–Sham scheme. We used the TurboMole code in the gas-phase (isolated cluster) calculations and the QuickStep module⁶⁹ in the CP2K⁷⁰ package for the surface calculations. In the calculations with TurboMole, we employed the def2-TZVPP Gaussian basis set, expanded the electronic wave functions, and the Perdew–Burke–Ernzenhof (PBE)⁷¹ generalized gradient approximation (GGA) as the approximation for the exchange–correlation functional. Furthermore, we included the D3 dispersion correction⁷² in order to be more consistent with the calculations at the surface, even if, in the gas phase molecule, this is not relevant.

In the CP2K calculations, we employed two different approximations to the exchange-correlation term: a revised-PBE (revPBE)⁷³ GGA together with the D3 dispersion correction and a density functional that contains an explicit non-local term for the London dispersions. In the latter, we employ the vdW-DF2⁷⁴ form with the revised B86 gradient dependent or GGA part of the exchange functional. The wave functions in the Gaussian projector wave (GPW) method in QuickStep were expanded in the MOLOPT-DZVP basis set⁷⁵ and the density up to 700 Ry, with a value of 60 Ry for the REL_CUTOFF parameter. Only the Γ point was used to approximate the integral over the first Brillouin zone. 32 Å was the length of the cell along the surface normal, leaving more than 16 Å vacuum between the molecules and the opposite site of the slab. The occupation numbers were broadened using the Fermi-Dirac distribution, corresponding to an effective temperature of 500 K. We used the equilibrium lattice constant of 4.1074 Å obtained with the rB86-vdW-DF2 exchangecorrelation functional in both cases. The geometry is very similar to the two treatments of the exchange and correlation effects (revPBE

+D3 and B86r-vdW-DF2). Therefore, we only report one DFT treatment, *i.e.*, the revPBE+D3 results.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b06114.

Synthetic details of HEB molecule. Preparation details on surface-adsorbed organic phase. Large-scale STM image on in situ Co dosage at 12 K, along with 'S' enantiomers (C_1) within α domain and related adsorption model. Large-scale STM images for optimal (excessive) Co concentration dosed at 200 K, resulting in extended organocobalt domains (phase dissolution). STM results showing surface tessellation for both organocobalt domains and derived adsorption models. Two-fold degenerate alignment of the C1 species based on STM results evincing the coexistence of both domains within the same Ag(111) terrace. DFT-modeled visualization depicting physical heights of all carbon atoms within the organocobalt phase. Single-molecule rotation of C2 within a molecular island and adsorption model for a single C_2 unit. Switching statistic for isolated C_2 , *i.e.*, double-logarithmic presentation of switching rate versus current (PDF)

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Notes

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