

Reversible On-Surface Metalation and Demetalation of Porphyrins in a Solvent-Free Ultrahigh-Vacuum Environment

Zewei Yi, Zhaoyu Zhang, Rujia Hou, Yuhong Gao, Yuan Guo, Yuanqi Ding, Lei Xie, Fei Song, Chi Zhang,* and Wei Xu*

Cite This: Cher	m. Mater. 2025, 37, 2806–2814	Read Online	
ACCESS	III Metrics & More	I Article Recommendations Supporting Information	
ABSTRACT: Con	trolling molecular interconversion	as reversibly is of great Au(111) Annealing in	22

ABSTRACT: Controlling molecular interconversions reversibly is of great interest in chemistry. Reversible molecular interconversions have been extensively realized on solid surfaces by the regulation of intermolecular noncovalent interactions and intramolecular covalent bonds. Among others, molecular reactions involving the reversible tuning of intramolecular covalent bonds have typically been induced by local manipulations on individual molecules using a scanning probe microscopy (SPM) tip. However, reversible control of on-surface molecular reactions in a global manner remains challenging. In this work, by a combination of scanning tunneling microscopy (STM) imaging, X-ray photo-



electron spectroscopy (XPS) measurements, and density functional theory (DFT) calculations, we report the reversible metalation and demetalation of porphyrin molecules on Au(111) in a controllable and global manner in a solvent-free ultrahigh-vacuum (UHV) environment by providing different atmospheres. The universality of such reactions involving the alkali metal Na was demonstrated by two types of porphyrins with different molecular backbones, while the on-surface metalation with the transition metal Co forming Co-porphyrin was found to be unidirectional. DFT calculations revealed the driving force for their different demetalation behaviors and further illustrated the critical role of extrinsic H atoms in the demetalation pathways. Our results represent a general strategy to reversibly steer the on-surface molecular metalation and demetalation, which should provide fundamental understanding of reversible molecular interconversions.

INTRODUCTION

Downloaded via TONGJI UNIV on April 30, 2025 at 05:17:53 (UTC). See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles

Reversible control of molecular interconversion is of great interest in chemistry as it allows the existence of bistable states triggered by a variety of external stimuli,¹⁻⁴ thereby enabling switchability for applications such as information processing and data storage.⁵ In general, these reversible molecular interconversions are responsive to the variation of ions in aqueous solutions^{6,7} or molecules in the gas phase.⁸ As for the situations on solid surfaces, scanning probe microscopy (SPM) under ultrahigh vacuum (UHV) conditions provides an appealing toolbox that assists in tracking the molecular conversion processes in situ⁹⁻¹¹ and to characterize multiple molecular states at the single-molecule or even single-bond level.^{12–15} Enormous efforts have been devoted to the control of reversible molecular interconversions on surfaces,¹⁶ mainly through the regulation of intermolecular noncovalent interactions and intramolecular covalent bonds. For instance, molecular structural transformations^{17,18} take advantage of the reorganization of components (including molecules, metals, etc.) via cleavage and reformation of intermolecular noncovalent bonds to achieve reversible interconversions. In addition, the chemisorption and desorption of gas molecules and atoms in the molecular systems, $^{19-22}$ along with varied intermolecular noncovalent interactions, generally leads to the reversible control of specific molecular states and properties.

On the other hand, due to the relative robustness of covalent bonds, molecular reactions associated with the tuning of intramolecular covalent bonds, such as tautomerization,^{23–25} skeletal rearrangement,^{26,27} dehydrogenation,^{28,29} and metalation/demetalation,^{30,31} have typically been induced by SPM manipulations locally on single molecules frozen at low temperatures. However, to the best of our knowledge, reversible regulation of on-surface molecular reactions in a well-controlled and global manner remains challenging and has been less reported. It is thus of general interest to establish a prototypical molecular system to demonstrate the reversible control of molecular reactions globally at the molecular level in real space.

Moreover, porphyrins, as a classical group of molecules with reversible reactions, i.e., metalation and demetalation, in which the two central protons can be replaced by a metal ion or in the reverse process, respectively, were selected as the model precursors. The reversible interconversion between porphyrins

Received:December 15, 2024Revised:April 2, 2025Accepted:April 2, 2025Published:April 9, 2025





Figure 1. Reversible metalation and demetalation based on H_2 TPP and Na in a repeatable manner. (a) Schematic illustration showing the reversible interconversion between H_2 TPP and Na-TPP with their proportions in each sample indicated, corresponding to the STM images directly below. H: white; C: gray; N: blue; Na: pink. (b) Large-scale and (c) close-up STM images showing the self-assembled H_2 TPP structure obtained after deposition of H_2 TPP and Na onto Au(111) held at RT, where Na was not involved in the assembly. (d) and (e) STM images showing the formation of metalated Na-TPP after annealing the above sample at 500 K. (f) and (g) Reverse demetalation back to H_2 TPP after annealing at 480 K in the atmosphere of atomic hydrogen at a pressure of 2.0×10^{-7} mbar. (h) and (i) Repeatable metalation after further annealing at 500 K to reform Na-TPP. The typical H_2 TPP and Na-TPP molecules are depicted by the white and green rectangles, respectively. The close-packed directions of Au(111) are indicated by the white arrows. Scanning conditions: V = -1.2 to -1.5 V, and I = 0.6-0.7 nA.

and metalloporphyrins has been demonstrated to be wellcontrolled in aqueous solutions and at the solid/liquid interface by tuning the properties of the medium (typically pH),^{6,7,32,33} where the metals and hydrogens in the ionic states can be reversibly exchanged depending on the chemical equilibrium. On the contrary, in a solvent-free UHV environment, on-surface metalation reactions of porphyrins to form metalloporphyrins have been extensively explored with successful incorporation of most metal elements,³⁴⁻³⁷ while the reverse demetalation reaction has not been achieved yet, leaving the underlying mechanisms on surfaces elusive. In addition, the irreversible on-surface transmetalation of metalloporphyrins,^{38,39} i.e., the exchange of central metals, has been shown to be feasible depending on their relative stability, indicating the potential of dynamic properties for the realization of reversible reactions.

Herein, by a combination of scanning tunneling microscopy (STM) imaging, X-ray photoelectron spectroscopy (XPS) measurements, and density functional theory (DFT) calculations, reversible metalation and demetalation of porphyrin molecules were achieved on Au(111) in a controllable and global manner by providing different atmospheres in a solvent-free UHV environment. Based on 2H-tetraphenylporphyrin (abbreviated as H_2TPP) and alkali metal Na, the metalation process forming Na-TPP was realized by annealing in vacuum, while the reverse demetalation back to H_2TPP was obtained after annealing in the atmosphere of atomic hydrogen. Such a reversible interconversion reaction was shown to be highly repeatable. In addition, by changing the molecular backbone to the 2H-tetrapyridylporphyrin (H_2TPyP), the universality of the reversible on-surface metalation and demetalation in the

presence of Na was demonstrated. Furthermore, in the case of the transition metal Co, the metalation process to form cobalttetraphenylporphyrin (CoTPP) was found to be unidirectional, with the reverse demetalation inaccessible. DFT calculations further validated that the different demetalation behaviors were driven by the variation of the total energies of different binding structures of H atoms and metal atoms (Na and Co) on porphyrin molecules on Au(111). Moreover, the critical role of extrinsic H atoms in the demetalation pathways of Naporphyrins was also demonstrated. Our results represent a model case study of reversible on-surface molecular reaction in a controllable and global manner, which should provide fundamental understanding of the reversible control of molecular interconversions based on covalent interactions.

METHODS

All the STM experiments were performed in an ultrahigh vacuum (UHV) chamber (with a base pressure of 1.0×10^{-10} mbar), equipped with a variable-temperature, fast-scanning "Aarhus-type" STM using electrochemically etched tungsten (W) tips.^{40,41} The Au(111) substrate was cleaned by Ar⁺-ion sputtering and annealing at 800 K for repeated cycles. After thorough degassing, the H₂TPyP (purchased from Macklin, with a labeled purity of >97%) and NaCl (purchased from Bidepharm, purity >99.9%) were sublimated by homemade Knudsen-cells at 650 and 830 K, respectively. The H₂TPP (purchased from Macklin, with a labeled purity of >99%) and CoTPP (purchased from Bidepharm, with a labeled purity of >98%) were sublimated by using a commercial molecular evaporator at 510 K, separately. The purchased CoTPP contains approximately 40% of H₂TPP as determined by STM characterization, similar to the previous report.⁴² The alkali metal sodium (Na, from SAES Getters) was sublimated via conventional resistance heating after fully degassing. The STM images shown in Figures 3, S2, and S3 were

recorded at room temperature (300 K), and the others were recorded at 100-150 K. Unless otherwise noted, the annealing duration time in different atmospheres to achieve the metalation or demetalation of porphyrins was all 10 min. All the STM images were further smoothed to eliminate noise. All the statistics were performed based on over 1000 molecules in nonrepetitive regions on each sample.

The XPS experiments were performed at the beamline 20U (BL20U) of Shanghai Synchrotron Radiation Facility (SSRF), which provides photons in the energy range of 10–150 keV. A HiPP-2 hemispherical analyzer is equipped with a base pressure of better than 1.0×10^{-9} mbar. The N 1s spectra were collected at the photon energy of 600 eV with a pass energy of 200 eV, and the Au core level spectra were used for calibration. The employed photon energy of the X-ray is safe to avoid the degradation or decomposition of the samples.⁴³

The atmosphere of atomic hydrogen was created by using a homebuilt hydrogen cracker with a hot W filament as reported,⁴⁴ which was heated by the current flow (P = 60 W). Hydrogen gas was dosed through a leak valve at a pressure of $2.0 \pm 0.3 \times 10^{-7}$ mbar and passed first through the nearby hydrogen cracker and then into the preparation chamber. In this way, hydrogen molecules were cracked into atomic hydrogen. In addition, the ion gauge was always on during our experiments to monitor the pressure, which has also been proven to be able to convert molecular hydrogen into atomic hydrogen.^{45,46}

The calculations were performed in the framework of DFT by using the Vienna ab initio simulation package (VASP).47,48 The projector-augmented wave method was used to describe the interaction between ions and electrons.^{49,50} The Perdew–Burke– Ernzerhof generalized gradient approximation exchange-correlation functional was employed,⁵¹ and van der Waals interactions were included using the dispersion-corrected DFT-D3 method of Grimme.⁵² The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were $\leq 0.03 \text{ eV/Å}$. Plane waves were used as a basis set with an energy cutoff of 400 eV. For the structural models, the Au(111) substrates were modeled by threelayered slabs separated by a 15 Å vacuum region, where the bottom layer was fixed. Reaction pathways were calculated by a combination of the climbing image-nudged elastic band (CI-NEB)⁵³ and dimer methods.⁵⁴ The CI-NEB method was used to find an initial guess of a transition state, which was then refined by the dimer method until the forces acting on the path typically converged to $\leq 0.03 \text{ eV/Å}$.

RESULTS AND DISCUSSION

After deposition of H₂TPP molecules (the leftmost panel of Figure 1a) and alkali metal Na onto Au(111) held at room temperature (RT, 300 K), the self-assembled H₂TPP structure (at a coverage of around 0.6-0.8 monolayer) was obtained without the involvement of Na in this structure (Figure 1b), due to the absence of intermolecular molecule-metal interactions. Accordingly, the ratio of Na/H2TPP cannot be estimated precisely, and the dosage of Na was mainly controlled by conventional resistance heating using the same current and different durations. Such a structure formation was independent of the deposition sequence of H₂TPP molecules and Na atoms. The single-molecule morphology of H₂TPP can be distinguished from the close-up STM image (Figure 1c), as depicted by the white rectangle. In addition, all the molecules have the same morphology with an empty feature at the molecular center, consistent with the reported morphology of intact H₂TPP.^{43,55} After annealing the above sample at 500 K for 10 min, $67.0 \pm 1.7\%$ of the total molecules showed different morphologies (Figure 1d), with obvious bright protrusions appearing at the molecular centers as depicted by the green rectangle in Figure 1e. Note that such bright molecular species can only be obtained by annealing the sample with the coexistence of H₂TPP and Na at high

temperatures, and their ratio is directly related to the dosage of Na, similar to the reported case of the metalation reaction of H_2TPyP and Na.³⁷ In addition, a rectangular single-molecule morphology with four protrusions of the phenyl groups located at the corners can be distinguished, indicating its nonplanar saddle-shaped conformation.⁴² Thus, the possibility of the formation of Au-TPP can be ruled out, since it has been reported that the self-metalation of H_2TPP molecules on Au(111) takes place after the cyclodehydrogenation reaction to form a planar Au-incorporated molecular structure.^{55,56} Moreover, the insertion of Na atoms and the release of the two central hydrogen atoms after annealing were further evidenced by XPS measurements (see Figure 2 and related discussions



Figure 2. XPS spectra of (a) the reversible metalation and demetalation reactions of the H_2 TPP and Na-TPP molecules and (b) the self-metalation of the H_2 TPP molecules on Au(111).

below). Accordingly, the formed bright species were attributed to the metalated Na-TPP molecules. To further figure out the atomic structure, DFT calculations were performed on various possible molecular structures with different numbers of central Na atoms (Figure S1). Consequently, only the Na₅TPP structure can well match the experimental morphology of the bright species, with a uniform bright feature at the molecular center.

Thereafter, to explore the feasibility of the reverse demetalation reaction, extrinsic hydrogen atoms were introduced into the system. After annealing the above sample at 480 K for 10 min while exposed to the atmosphere of atomic hydrogen at a pressure of 2.0×10^{-7} mbar (see Methods for more details), surprisingly, the proportion of the metalated Na-TPP molecules significantly decreased to 1.0%, as shown in Figure 1f, g. In addition, the dominant molecules shared the same empty central features as the intact ones and were thus attributed to the H₂TPP molecules via the demetalation of Na and the addition of hydrogen at the molecular centers (see detailed discussions below). Consequently, the on-surface demetalation of Na-TPP was successfully achieved with the supply of extrinsic atomic hydrogen.

Furthermore, to examine the repeatability of such a metalation and demetalation reaction, the above sample was



Figure 3. Reversible metalation and demetalation based on H_2 TPyP and Na in a repeatable manner. (a) Schematic illustration showing the reversible interconversion between the porous network composed of H_2 TPyP and Na and the more close-packed one composed of H_2 TPyP, Na-TPyP, and Na, where the porphyrin molecules are illustrated in the same number via interactions with surrounding Na atoms. (b) Large-scale and (c) close-up STM images showing the partially porous coassembled structures based on H_2 TPyP and Na after deposition on Au(111) held at RT. (d) and (e) STM images showing the formation of metalated Na-TPyP after annealing the above sample at 510 K, with the molecular assembly becoming more close-packed. (f) and (g) Reverse demetalation back to the partially porous assembled structure with a decreased proportion of Na-TPyP after annealing at 480 K while exposed to the atmosphere of atomic hydrogen at a pressure of 2.0×10^{-7} mbar. (h) and (i) Repeatable metalation obtained after further annealing at 510 K to reform the more close-packed structure involving more Na-TPyP. Scanning conditions: V = -1.2 to -1.5 V, and I = 0.5-1.0 nA.

annealed again at 500 K for 10 min. Interestingly, the H_2 TPP molecules were metalated again, with the proportion of Na-TPP molecules increasing to 45.0 ± 6.3% (Figure 1h,i). The variation of molecular proportions during the whole process is summarized in Table S1. Therefore, the reversible and repeatable interconversion between H_2 TPP and Na-TPP on Au(111) was successfully achieved by providing different atmospheres during annealing in the solvent-free UHV environment.

As a step further, to simplify the experimental conditions for XPS measurements, the feasibility of using a convenient Na source,³⁷ i.e., NaCl, to accomplish such reversible reactions was investigated. As shown in Figure S2, the metalation and demetalation reactions can also take place reversibly based on the system of H_2 TPP and NaCl, consistent with the case using H_2 TPP and pure Na source.

Moreover, to gain more chemical insight into the above metalation and demetalation reactions, XPS measurements based on H₂TPP and NaCl were further conducted, as shown in Figure 2a. After deposition of H₂TPP molecules onto Au(111) held at RT, the N 1s spectrum showed asymmetric features. According to the previous work,⁴³ it can be divided into four specific peaks, including the iminic groups (-N=) and pyrrolic groups (-NH-) with and without the interaction with Au adatoms, respectively. For the intact H₂TPP molecule, the binding energies of the two N 1s peaks are typically located at 398.0 and 400.0 eV,³⁵ as depicted by the red and yellow

lines, respectively. In addition, some H₂TPP molecules interact with Au adatoms, and N 1s peaks can be further shifted to higher binding energies. Thereafter, the deposition of NaCl onto the sample held at RT was found to have less influence on the shape of the N 1s spectrum, indicating that the molecules were still unreacted, consistent with the STM observation of the self-assembled H₂TPP structure in Figure 1b,c. After annealing the sample at 490 K, the N 1s spectrum changed to a single sharp peak at the binding energy of 398.9 eV, with the disappearance of the intensities at the binding energies of 398.0 and 400.0 eV. This verifies the occurrence of the metalation reaction with the insertion of Na atoms and the release of the two central hydrogen atoms, in line with the formation of metalated Na-TPP molecules with bright centers as shown in Figure S2a, as well as the case shown in Figure 1d,e. Note that the above metalated products cannot be the Au-TPP from the self-metalation of H_2 TPP on Au(111) (Figure 2b), in terms of both the reaction temperature and the binding energy. Therefore, the metalated products formed in this case are attributed to the Na-TPP molecules. After further annealing the sample of Na-TPP at 400 K while exposed to the atmosphere of atomic hydrogen, the intensities at the binding energies of 398.0 and 400.0 eV were found to increase again, indicating the occurrence of the demetalation reaction from Na-TPP to H₂TPP molecules, in line with the STM observations of the decreased proportion of the bright molecules after annealing in the H atmosphere. Therefore,



Figure 4. Unidirectional metalation based on H₂TPP and Co to form CoTPP. (a) Large-scale and (b) close-up STM images showing the coexistence of H₂TPP and CoTPP after deposition of CoTPP onto Au(111) held at RT. The chemical structure of CoTPP is displayed in the inset of (b). (c) and (d) Further metalation to form more CoTPP molecules after annealing at 540 K. (e) Large-scale and (f) close-up STM images obtained after annealing the above sample at 480 K while exposed to the atmosphere of atomic hydrogen at a pressure of 2.0×10^{-7} mbar. The proportion of CoTPP molecules in the total molecules of each sample was displayed in (a, c, e), respectively. Scanning conditions: V = -1.2 V, and I = 0.7-0.8 nA.

the XPS measurements also support the scenario of the reversible metalation and demetalation reactions.

In an attempt to reveal the translocation of Na atoms during the reversible metalation and demetalation reactions, another precursor, H₂TPyP (the leftmost panel of Figure 3a), with the substitution of the phenyl rings by pyridyl rings, was selected to provide potential intermolecular interaction sites with Na. After deposition of H_2 TPyP (at a coverage of around 0.6–0.8 monolayer) and Na onto Au(111) at RT (regardless of the deposition sequence) with a stoichiometric ratio of Na/ H_2 TPyP greater than 1 (see Figure S3 and detailed discussions in the Supporting Information), a partially porous coassembled structure of H₂TPyP and Na was formed (Figure 3b), as also reported in our recent work.57 The close-up STM image (Figure 3c) clearly showed the molecular arrangement involved, with a regular porous region highlighted by a white dotted rectangle corresponding to the structural model shown in the leftmost panel of Figure 3a. In this case, all the molecules had the same morphology with an empty feature at the molecular center^{\$7,58} and were assigned to the intact H₂TPyP molecules. They were gathered by Na at the nodes of the assembled structures via electrostatic interactions between the pyridyl groups and Na atoms,⁵⁷ forming porous or semiporous structures according to the different local Na/H2TPyP ratios due to the limited diffusion space and ability. After annealing the above sample at 510 K for 10 min, the metalation of H₂TPyP took place, forming the Na-TPyP molecules (i.e., Na_2TPyP and Na_5TPyP)³⁷ with obvious bright features at the molecular centers (Figure 3d,e), which accounted for $52.0 \pm$ 0.8% of the total molecules. Simultaneously, the assembled structure transformed to a more close-packed one after metalation (see the typical structural model in the second panel of Figure 3a), indicating a decreased total number of Na atoms located at the nodes, which was also consistent with the integration of Na atoms at the center of Na-TPyP molecules.

Next, to trigger its demetalation, the above sample was further annealed at 480 K for 10 min in the atmosphere of atomic hydrogen. As expected, the majority of the bright Na-TPyP molecules transformed back to the H₂TPyP with an empty central feature (Figure 3f, g), with only $15.0 \pm 1.5\%$ Na-TPyP molecules present. At the same time, the assembled structure transformed back to the partially porous one, indicating the translocation of Na atoms from the molecular centers to the structural nodes again. Accordingly, the demetalation from Na-TPyP to H₂TPyP was also achieved. Moreover, further annealing of the above sample to 510 K resulted in the remetalation (Figure 3h, i), identical to the case shown in Figures 3d and e. By applying this strategy, such demetalation and metalation with more repeatable cycles can also be achieved (Figure S3 and Table S2), indicating its high repeatability. Note that throughout the processes, the proportions of Na-TPyP molecules on the metalated samples were at a similar level, indicating the nice recycling of intermolecular and intramolecular Na atoms. Therefore, the reversible on-surface metalation and demetalation of two types of porphyrins with different molecular backbones were evidenced on Au(111) in a global and repeatable manner by annealing under UHV conditions and by annealing in the atmosphere of atomic hydrogen, respectively, verifying the universality of such a strategy.

Thereafter, an interesting question arises: is it possible to extend such a strategy of providing different atmospheres during annealing to the on-surface metalation and demetalation reactions of other porphyrins? In general, it is easy for porphyrins embedded with alkali metals to demetal in acidic solutions, while porphyrins with transition metals are more stable and thus resistant against demetalation.^{59,60} To explore the feasibility in the case of transition metals, CoTPP, a well-established on-surface metalation system based on H₂TPP and Co in extensive studies,^{61–63} was selected herein. Deposition of the commercially available CoTPP molecules onto Au(111)



Figure 5. DFT-calculated total energies of (a) Na_2TPyP and (b) CoTPP on Au(111) with the involvement of one or two additional H atoms, respectively. Graphs showing the variation of total energies when one and two additional H atoms were adsorbed at different sites, as depicted by the black lines, with respect to those of the corresponding "H on sub" and "both H on sub" cases (indicated by the gray dotted lines and set to zero for reference). The labels "H on sub", "H on N", and "H on Na/Co" indicate the sites where the additional H atom adsorbed on the Au(111) substrate, the N atom of the pyrrole, and the corresponding metal center, respectively. The label "forming H_2 " indicates the situation that the two additional H atoms form a H_2 molecule. The corresponding demetalated structures of one 2H-porphyrin molecule with free metal atoms on the substrate are also included for comparison, with their energies highlighted by red lines. More details on the corresponding structural models and the total energies are shown in Tables S3–S6 in the Supporting Information.

held at RT led to the coexistence of CoTPP and H₂TPP (Figure 4a,b), with bright and empty features at the molecular centers, respectively, where the proportion of CoTPP in the total molecules as deposited was counted to be $60.0 \pm 0.4\%$, similar to the previously reported results⁴² using commercial CoTPP (see Figure 4 and detailed discussion in the Supporting Information). After annealing the above sample at 540 K for 10 min, almost all the molecules (91.0 \pm 0.6%) turned bright (Figure 4c). From the magnified STM image (Figure 4d), the saddle-shaped conformation can be inferred as in the case of Na-TPP, which also excludes the possibility of Au-TPP.^{55,56} Moreover, the metalation between 2H-porphyrin molecules and Co to form Co-porphyrins has been reported on $Ag(111)^{62}$ and $BN/Cu(111)^{64}$ (as an insulating film for decoupling), and the metalation between pyrphyrin (as an analogue of porphyrin) and Co has been achieved on Au(111).⁶⁵ It has also been reported that other metal elements with similar metalation capabilities,⁵⁹ e.g., Fe and Ni, can metalate porphyrins on Au(111).^{66,67} Accordingly, the metalation of porphyrin and Co should also be available on Au(111). Furthermore, all the bright molecules shared the same morphology in our case (Figure 4c,d), and thus, it is reasonable to attribute them to CoTPP, which also indicates the presence of free Co atoms on the sample after the deposition at RT. Then, similar attempts were made to induce the reverse demetalation reaction of CoTPP by annealing the above sample at 480 K for 10 min in an atmosphere of atomic hydrogen. Nevertheless, no transformation was observed (Figure 4e,f), with CoTPP still accounting for 90.0 \pm 0.6%. Further treatment of the sample at higher annealing temperatures with exposure to atomic hydrogen made no difference, suggesting the same situation as in solution, where the integration of transition metals (with partially filled d-orbitals) into porphyrin molecules makes them more stable.^{59,60} Thus, porphyrin molecules and the transition metal Co can only undergo unidirectional metalation, but not the reverse demetalation.

To elucidate the underlying mechanisms of the different demetalation behaviors of Na- and Co-porphyrins, DFT calculations were performed based on the Na_2TPyP (to simplify the system) and CoTPP on Au(111). The first fundamental question is why the demetalation with extrinsic H

is only valid for Na-porphyrins but not for Co-porphyrin. Figure 5 illustrates the DFT-calculated total energies of the molecular systems containing one Na₂TPyP or CoTPP molecule and one or two additional H atoms on Au(111). After introducing additional H atoms into the system, three adsorption sites were considered, i.e., adsorption on the substrate (labeled "H on sub"), on the N atom of the pyrrole ("H on N"), and on the metal center ("H on Na/Co"). The total energies are given with respect to those of the corresponding "H on sub" and "both H on sub" cases, as indicated by the gray dotted lines and set to zero for reference.

In the case of Na₂TPyP with an additional H atom, as shown in the upper panel of Figure 5a, "H on N" is the energetically most favorable structure (-0.51 eV), while "H on Na" is the most unstable (2.58 eV). The corresponding structural models are shown in Table S3 in the Supporting Information. On the contrary, when an additional H atom is introduced into the CoTPP system, as shown in the upper panel of Figure 5b, "H on N" is the energetically most unfavorable structure (0.05 eV), and instead, the H atom prefers to adsorb on the Co atom (with a total energy of -0.1 eV). The corresponding structural models are shown in Table S4. A similar trend also occurs when two H atoms are introduced into the corresponding systems. For a direct comparison between the adsorption of H atoms in the metalloporphyrin systems and the demetalated structures, the total energies of the 2H-porphyrin molecule with free metal atoms on the substrate (represented by the red lines) have also been included in the graphs as shown in the lower panels of Figure 5a,b, respectively. In the case of Na2TPyP with two additional H atoms, the demetalated structure "H₂TPyP + 2Na" with both Na atoms adsorbed on the substrate is calculated to be the most stable, in good agreement with the experimental observations of the demetalation of Na-TPyP. In contrast, in the case of CoTPP with two additional H atoms, the proposed demetalated structure " $H_2TPP + Co$ " with Co adsorbed on the substrate is the most unstable one, while the situation of "forming H₂" is strongly favored. The corresponding structural models and detailed total energies are shown in Tables S5 and S6. It thus suggests that extrinsic H atoms tend to form H₂ rather than participate in the CoTPP system (to facilitate the demetalaTherefore, the different demetalation behaviors can be rationalized by the variation of the total energies of different binding structures involving H atoms, metal atoms (Na or Co), and porphyrin molecules on Au(111). Specifically, in the case of Na₂TPyP, the weak interaction between Na and H makes the H atom preferentially adsorb on the N atom, which may provide an opportunity for the Na atoms to escape. The existence of "H₂TPyP + 2Na" as the energetically most favorable structure, among others, further supports this demetalation behavior. Conversely, as for CoTPP, the demetalation is prevented both by the preferential adsorption of a H atom on the Co atom and by the desorption of two H atoms as H₂, which is also consistent with the highly unfavorable situation of "H₂TPP + Co".

Moreover, another critical question is how the demetalation reaction of Na-TPyP molecules occurs with the supply of extrinsic hydrogen. Generally, there are two kinds of mechanisms for reactions that occur at the gas-solid interface, i.e., Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) processes. The LH process indicates that all the reactants first adsorb on the substrate (i.e., the case of "both H on sub"), and then they react with each other, while in the ER process, the gas molecules react with the adsorbed molecules directly via the gas-surface collision, i.e., the case of "both H on N". Given that the demetalation reaction takes place at high temperatures with the continuous supply of an atomic H atmosphere, both mechanisms should be possible. To simplify the calculations, the structure of "both H on N" was selected as the starting phase. Further DFT calculations were performed on the reaction pathways of Na₂TPyP in the absence and presence of additional H atoms, and the sequential demetalation pathways are shown in Figure S4. Due to the double-layered structure of Na atoms in the Na-TPyP,³⁷ a sequential demetalation process was considered, and the simplified Na₂TPyP structure was applied. In the first step, in the absence of H atoms, the Na₂TPyP molecule transforms to the NaTPyP structure with the release of the bottom-layer Na atom, and the top-layer Na atom simultaneously moves downward. The whole process is highly endothermic with an energy barrier of 1.29 eV, as shown in Figure S4a. Significantly, the energy barrier can be reduced to 0.23 eV with the assistance of two additional H atoms, and the whole process becomes exothermic. Subsequently, in the second-step demetalation, the transformation from NaTPyP to TPyP was calculated to have an energy barrier of 2.38 eV in the absence of H atoms, which could be further lowered to 0.76 eV with the formation of H₂TPyP instead in the atmosphere of H atoms (Figure S4b). Thus, the entire demetalation reaction of Na2TPyP under UHV conditions suffers from a high reaction barrier of 2.38 eV, as well as the highly endothermic processes for both steps, leaving the metalated Na₂TPyP structure energetically more favorable. In contrast, by the introduction of extrinsic H atoms into the Na₂TPyP system, the reaction barrier of the whole demetalation process can be further reduced to 0.76 eV, verifying the crucial role of H atoms. Moreover, due to the highest stability of "H2TPP + 2Na" compared to other structures (cf. Figure 5 and Table S5), the entire demetalation becomes exothermic instead. Thus, these reaction pathways provide a simplified prototype demonstrating that the H atmosphere is the key in the demetalation processes of Naporphyrins, while the real situation should be more

complicated beyond the calculations. Accordingly, by providing different atmospheres during annealing, the reversible and repeatable interconversion between H_2 TPyP and Na-TPyP on Au(111) was successfully achieved in experiments.

CONCLUSIONS

pubs.acs.org/cm

In summary, based on STM imaging, XPS measurements, and DFT calculations, the reversible metalation and demetalation of porphyrin molecules were achieved on Au(111) both controllably and globally in a solvent-free UHV environment. In the case of the alkali metal Na, the porphyrins and metalloporphyrins can interconvert reversibly by providing different atmospheres during annealing, independent of the molecular backbones. In contrast, in the case of the transition metal Co, the on-surface metalation was found to be unidirectional. DFT calculations revealed that such different demetalation behaviors were driven by the different energy preferences of the binding structures of H atoms and metal atoms (Na and Co) on porphyrin molecules on Au(111). Moreover, the critical role of extrinsic H atoms in the demetalation pathways of Na-porphyrins was also demonstrated. Our results provide an effective strategy to steer the reversible on-surface metalation and demetalation reactions, which should provide fundamental insights into the reversible control of molecular interconversions.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.4c03420.

Supplementary STM images and DFT calculations (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Chi Zhang Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China; orcid.org/0000-0002-2335-4579; Email: zhangchi11@ tongji.edu.cn
- Wei Xu Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China; orcid.org/ 0000-0003-0216-794X; Email: xuwei@tongji.edu.cn

Authors

- Zewei Yi Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China
- Zhaoyu Zhang Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China
- Rujia Hou Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China
- Yuhong Gao Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China
- Yuan Guo Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China

- Yuanqi Ding Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China
- Lei Xie Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201204, People's Republic of China
- Fei Song Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201204, People's Republic of China;
 orcid.org/0000-0002-6408-7796

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.4c03420

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research is supported by the National Natural Science Foundation of China (Grants Nos. 22202153, 22125203, and 22102117) and the Fundamental Research Funds for the Central Universities. This work also used computational resources of the Supercomputer HOKUSAI BigWaterfull 2 provided by RIKEN through the HPCI System Research Project (Project ID: hp240096).

REFERENCES

(1) Murahashi, T.; Shirato, K.; Fukushima, A.; Takase, K.; Suenobu, T.; Fukuzumi, S.; Ogoshi, S.; Kurosawa, H. Redox-Induced Reversible Metal Assembly Through Translocation and Reversible Ligand Coupling in Tetranuclear Metal Sandwich Frameworks. *Nat. Chem.* **2012**, *4*, 52–58.

(2) Amendola, V.; Fabbrizzi, L.; Mangano, C.; Pallavicini, P. Molecular Machines Based on Metal Ion Translocation. *Acc. Chem. Res.* **2001**, *34*, 488–493.

(3) Najjari, B.; Le Gac, S.; Roisnel, T.; Dorcet, V.; Boitrel, B. Metal Migration Processes in Homo- and Heterobimetallic Bismuth(III)– Lead(II) Porphyrin Complexes: Emergence of Allosteric Newton's Cradle-like Devices. J. Am. Chem. Soc. **2012**, *134*, 16017–16032.

(4) Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. Using the Dynamic Bond to Access Macroscopically Responsive Structurally Dynamic Polymers. *Nat. Mater.* **2011**, *10*, 14–27.

(5) Fabbrizzi, L.; Foti, F.; Patroni, S.; Pallavicini, P.; Taglietti, A. A Sleeping Host Awoken by Its Guest: Recognition and Sensing of Imidazole-Containing Molecules Based on Double Cu²⁺ Translocation inside a Polyaza Macrocycle. *Angew. Chem., Int. Ed.* **2004**, 43, 5073–5077.

(6) Lin, Q.; Lu, J.; Yang, Z.; Zeng, X. C.; Zhang, J. Porphyrinic Porous Organic Frameworks: Preparation and Post-Synthetic Modification via Demetallation–Remetallation. *J. Mater. Chem. A* **2014**, *2*, 14876–14882.

(7) Zhang, K.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. Complete Double Epoxidation of Divinylbenzene Using Mn(porphyrin)-Based Porous Organic Polymers. *ACS Catal.* **2015**, *5*, 4859–4866.

(8) Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. Gas Phase Chemical Equilibrium in Dinitrogen Trioxide and Dinitrogen Tetroxide. *Thermochim. Acta* **1974**, *10*, 359–371.

(9) Bian, K.; Gerber, C.; Heinrich, A. J.; Müller, D. J.; Scheuring, S.; Jiang, Y. Scanning Probe Microscopy. *Nat. Rev. Methods Primers* **2021**, *1*, 36.

(10) Zhang, C.; Xu, W. Interactions Between Water and Organic Molecules or Inorganic Salts on Surfaces. *Aggregate* **2022**, *3*, No. e175. (11) Xie, L.; Ding, Y.; Li, D.; Zhang, C.; Wu, Y.; Sun, L.; Liu, M.; Qiu, X.; Xu, W. Local Chiral Inversion of Thymine Dimers by Manipulating Single Water Molecules. *J. Am. Chem. Soc.* **2022**, *144*, 5023–5028.

(12) Pavliček, N.; Gross, L. Generation, Manipulation and Characterization of Molecules by Atomic Force Microscopy. *Nat. Rev. Chem.* **2017**, *1*, No. 0005.

(13) Zhong, Q.; Li, X.; Zhang, H.; Chi, L. Noncontact Atomic Force Microscopy: Bond Imaging and Beyond. *Surf. Sci. Rep.* **2020**, *75*, No. 100509.

(14) Zhang, C.; Yi, Z.; Xu, W. Scanning Probe Microscopy in Probing Low-Dimensional Carbon-Based Nanostructures and Nanomaterials. *Mater. Futures* **2022**, *1*, No. 032301.

(15) Zhang, C.; Jaculbia, R. B.; Tanaka, Y.; Kazuma, E.; Imada, H.; Hayazawa, N.; Muranaka, A.; Uchiyama, M.; Kim, Y. Chemical Identification and Bond Control of π -Skeletons in a Coupling Reaction. J. Am. Chem. Soc. **2021**, 143, 9461–9467.

(16) Hou, R.; Gao, Y.; Guo, Y.; Zhang, C.; Xu, W. Directing Organometallic Ring-Chain Equilibrium by Electrostatic Interactions. *ACS Nano* **2024**, *18*, 31478-31484.

(17) Dong, L.; Gao, Z. A.; Lin, N. Self-Assembly of Metal–Organic Coordination Structures on Surfaces. *Prog. Surf. Sci.* **2016**, *91*, 101–135.

(18) Zhang, C.; Wang, L.; Xie, L.; Ding, Y.; Xu, W. On-Surface Dual-Response Structural Transformations of Guanine Molecules and Fe Atoms. *Chem.—Eur. J.* 2017, 23, 2356–2362.

(19) Seufert, K.; Bocquet, M. L.; Auwärter, W.; Weber-Bargioni, A.; Reichert, J.; Lorente, N.; Barth, J. V. Cis-Dicarbonyl Binding at Cobalt and Iron Porphyrins with Saddle-Shape Conformation. *Nat. Chem.* **2011**, 3, 114–119.

(20) Stróżecka, A.; Soriano, M.; Pascual, J. I.; Palacios, J. J. Reversible Change of the Spin State in a Manganese Phthalocyanine by Coordination of CO Molecule. *Phys. Rev. Lett.* **2012**, *109*, No. 147202.

(21) Liu, L.; Yang, K.; Jiang, Y.; Song, B.; Xiao, W.; Li, L.; Zhou, H.; Wang, Y.; Du, S.; Ouyang, M.; et al. Reversible Single Spin Control of Individual Magnetic Molecule by Hydrogen Atom Adsorption. *Sci. Rep.* **2013**, *3*, 1210.

(22) Zhang, J. L.; Wang, Z.; Zhong, J. Q.; Yuan, K. D.; Shen, Q.; Xu, L. L.; Niu, T. C.; Gu, C. D.; Wright, C. A.; Tadich, A.; et al. Single-Molecule Imaging of Activated Nitrogen Adsorption on Individual Manganese Phthalocyanine. *Nano Lett.* **2015**, *15*, 3181–3188.

(23) Liljeroth, P.; Repp, J.; Meyer, G. Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules. *Science* **200**7, *317*, 1203–1206.

(24) Auwärter, W.; Seufert, K.; Bischoff, F.; Ecija, D.; Vijayaraghavan, S.; Joshi, S.; Klappenberger, F.; Samudrala, N.; Barth, J. V. A Surface-Anchored Molecular Four-Level Conductance Switch Based on Single Proton Transfer. *Nat. Nanotechnol.* **2012**, *7*, 41–46.

(25) Kumagai, T.; Hanke, F.; Gawinkowski, S.; Sharp, J.; Kotsis, K.; Waluk, J.; Persson, M.; Grill, L. Controlling Intramolecular Hydrogen Transfer in a Porphycene Molecule with Single Atoms or Molecules Located Nearby. *Nat. Chem.* **2014**, *6*, 41–46.

(26) Schuler, B.; Fatayer, S.; Mohn, F.; Moll, N.; Pavliček, N.; Meyer, G.; Peña, D.; Gross, L. Reversible Bergman Cyclization by Atomic Manipulation. *Nat. Chem.* **2016**, *8*, 220–224.

(27) Albrecht, F.; Fatayer, S.; Pozo, I.; Tavernelli, I.; Repp, J.; Peña, D.; Gross, L. Selectivity in Single-Molecule Reactions by Tip-Induced Redox Chemistry. *Science* **2022**, *377*, 298–301.

(28) Katano, S.; Kim, Y.; Hori, M.; Trenary, M.; Kawai, M. Reversible Control of Hydrogenation of a Single Molecule. *Science* **2007**, *316*, 1883–1886.

(29) Yang, K.; Liu, L.; Zhang, L.; Xiao, W.; Fei, X.; Chen, H.; Du, S.; Ernst, K. H.; Gao, H. J. Reversible Achiral-to-Chiral Switching of Single Mn–Phthalocyanine Molecules by Thermal Hydrogenation and Inelastic Electron Tunneling Dehydrogenation. *ACS Nano* **2014**, *8*, 2246–2251.

(30) Sperl, A.; Kröger, J.; Berndt, R. Controlled Metalation of a Single Adsorbed Phthalocyanine. *Angew. Chem., Int. Ed.* **2011**, *50*, 5294–5297.

(31) Sperl, A.; Kröger, J.; Berndt, R. Demetalation of a Single Organometallic Complex. J. Am. Chem. Soc. 2011, 133, 11007–11009.

(32) Franke, M.; Marchini, F.; Steinrück, H. P.; Lytken, O.; Williams, F. J. Surface Porphyrins Metalate with Zn Ions from Solution. J. Phys. Chem. Lett. 2015, 6, 4845–4849.

(33) Fernández, C. C.; Franke, M.; Steinrück, H. P.; Lytken, O.; Williams, F. J. Demetalation of Surface Porphyrins at the Solid–Liquid Interface. *Langmuir* **2021**, *37*, 852–857.

(34) Auwärter, W.; Écija, D.; Klappenberger, F.; Barth, J. V. Porphyrins at Interfaces. *Nat. Chem.* **2015**, *7*, 105–120.

(35) Diller, K.; Papageorgiou, A. C.; Klappenberger, F.; Allegretti, F.; Barth, J. V.; Auwärter, W. In Vacuo Interfacial Tetrapyrrole Metallation. *Chem. Soc. Rev.* **2016**, 45, 1629–1656.

(36) Gottfried, J. M. Surface Chemistry of Porphyrins and Phthalocyanines. *Surf. Sci. Rep.* **2015**, *70*, 259–379.

(37) Yi, Z.; Zhang, C.; Zhang, Z.; Hou, R.; Guo, Y.; Xu, W. On-Surface Synthesis of Na-Porphyrins Using NaCl as a Convenient Na Source. *Precis. Chem.* **2023**, *1*, 226–232.

(38) Rieger, A.; Schnidrig, S.; Probst, B.; Ernst, K. H.; Wäckerlin, C. Ranking the Stability of Transition-Metal Complexes by On-Surface Atom Exchange. *J. Phys. Chem. Lett.* **2017**, *8*, 6193–6198.

(39) Herritsch, J.; Kachel, S. R.; Fan, Q.; Hutter, M.; Heuplick, L. J.; Münster, F.; Gottfried, J. M. On-Surface Porphyrin Transmetalation with Pb/Cu Redox Exchange. *Nanoscale* **2021**, *13*, 13241–13248.

(40) Besenbacher, F. Scanning Tunnelling Microscopy Studies of Metal Surfaces. *Rep. Prog. Phys.* **1996**, *59*, 1737–1802.

(41) Laegsgaard, E.; Österlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. A High-Pressure Scanning Tunneling Microscope. *Rev. Sci. Instrum.* **2001**, *72*, 3537–3542.

(42) Auwärter, W.; Seufert, K.; Klappenberger, F.; Reichert, J.; Weber-Bargioni, A.; Verdini, A.; Cvetko, D.; Dell'Angela, M.; Floreano, L.; Cossaro, A.; et al. Site-Specific Electronic and Geometric Interface Structure of Co-Tetraphenyl-Porphyrin Layers on Ag(111). *Phys. Rev. B* **2010**, *81*, No. 245403.

(43) Edmondson, M.; Frampton, E. S.; Judd, C. J.; Champness, N. R.; Jones, R. G.; Saywell, A. Order, Disorder, and Metalation of Tetraphenylporphyrin (2H-TPP) on Au(111). *Chem. Commun.* **2022**, 58, 6247–6250.

(44) Zuzak, R.; Jančařík, A.; Gourdon, A.; Szymonski, M.; Godlewski, S. On-Surface Synthesis with Atomic Hydrogen. *ACS Nano* **2020**, *14*, 13316–13323.

(45) Zhong, J. Q.; Wang, Z.; Zhang, J. L.; Wright, C. A.; Yuan, K.; Gu, C.; Tadich, A.; Qi, D.; Li, H. X.; Lai, M.; et al. Reversible Tuning of Interfacial and Intramolecular Charge Transfer in Individual MnPc Molecules. *Nano Lett.* **2015**, *15*, 8091–8098.

(46) Enderson, Z. A.; Murali, H.; Dasari, R. R.; Dai, Q.; Li, H.; Parker, T. C.; Brédas, J. L.; Marder, S. R.; First, P. N. Tailoring On-Surface Molecular Reactions and Assembly through Hydrogen-Modified Synthesis: From Triarylamine Monomer to 2D Covalent Organic Framework. *ACS Nano* **2023**, *17*, 7366–7376.

(47) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Open-Shell Transition Metals. *Phys. Rev. B* **1993**, *48*, 13115–13118.

(48) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(49) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* 1994, 50, 17953–17979.

(50) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(51) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(52) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* 2010, 132, 154104.

(53) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. J. Chem. Phys. **2000**, 113, 9901–9904. (54) Kästner, J.; Sherwood, P. Superlinearly Converging Dimer Method for Transition State Search. J. Chem. Phys. 2008, 128, No. 014106.

pubs.acs.org/cm

(55) Lu, J.; Da, B.; Xiong, W.; Du, R.; Hao, Z.; Ruan, Z.; Zhang, Y.; Sun, S.; Gao, L.; Cai, J. Identification and Electronic Characterization of Four Cyclodehydrogenation Products of H_2 TPP Molecules on Au(111). *Phys. Chem. Chem. Phys.* **2021**, *23*, 11784–11788.

(56) Cirera, B.; de la Torre, B.; Moreno, D.; Ondráček, M.; Zbořil, R.; Miranda, R.; Jelínek, P.; Écija, D. On-Surface Synthesis of Gold Porphyrin Derivatives via a Cascade of Chemical Interactions: Planarization, Self-Metalation, and Intermolecular Coupling. *Chem. Mater.* **2019**, *31*, 3248–3256.

(57) Hou, R.; Guo, Y.; Yi, Z.; Zhang, Z.; Zhang, C.; Xu, W. Construction and Structural Transformation of Metal–Organic Nanostructures Induced by Alkali Metals and Alkali Metal Salts. *J. Phys. Chem. Lett.* **2023**, *14*, 3636–3642.

(58) Yi, Z.; Guo, Y.; Hou, R.; Zhang, Z.; Gao, Y.; Zhang, C.; Xu, W. Revealing the Orientation Selectivity of Tetrapyridyl-Substituted Porphyrins Constrained in Molecular "Klotski Puzzles". J. Am. Chem. Soc. **2023**, 145, 22366–22373.

(59) Boucher, L. J.; Katz, J. J. The Infared Spectra of Metalloporphyrins (4000–160 Cm^{-1}). J. Am. Chem. Soc. **1967**, 89, 1340–1345.

(60) Lavallee, D. K. Complexation and Demetalation Reactions of Porphyrins. *Comments Inorg. Chem.* **1986**, *5*, 155–174.

(61) Shubina, T. E.; Marbach, H.; Flechtner, K.; Kretschmann, A.; Jux, N.; Buchner, F.; Steinrück, H. P.; Clark, T.; Gottfried, J. M. Principle and Mechanism of Direct Porphyrin Metalation: Joint Experimental and Theoretical Investigation. J. Am. Chem. Soc. 2007, 129, 9476–9483.

(62) Schouteden, K.; Ivanova, T.; Li, Z.; Iancu, V.; Janssens, E.; Van Haesendonck, C. Probing Magnetism in 2D Molecular Networks after in Situ Metalation by Transition Metal Atoms. *J. Phys. Chem. Lett.* **2015**, *6*, 1048–1052.

(63) Inami, E.; Yamaguchi, M.; Nemoto, R.; Yorimitsu, H.; Krüger, P.; Yamada, T. K. Direct Imaging of Precursor Adcomplex States during Cryogenic-Temperature On-Surface Metalation: Scanning Tunneling Microscopy Study on Porphyrin Array with Fe Adsorption at 78.5 K. J. Phys. Chem. C **2020**, *124*, 3621–3631.

(64) Urgel, J. I.; Schwarz, M.; Garnica, M.; Stassen, D.; Bonifazi, D.; Ecija, D.; Barth, J. V.; Auwärter, W. Controlling Coordination Reactions and Assembly on a Cu(111) Supported Boron Nitride Monolayer. J. Am. Chem. Soc. **2015**, 137, 2420–2423.

(65) Mette, G.; Sutter, D.; Gurdal, Y.; Schnidrig, S.; Probst, B.; Iannuzzi, M.; Hutter, J.; Alberto, R.; Osterwalder, J. From Porphyrins to Pyrphyrins: Adsorption Study and Metalation of a Molecular Catalyst on Au(111). *Nanoscale* **2016**, *8*, 7958–7968.

(66) Lin, T.; Kuang, G.; Wang, W.; Lin, N. Two-Dimensional Lattice of Out-of-Plane Dinuclear Iron Centers Exhibiting Kondo Resonance. *ACS Nano* **2014**, *8*, 8310–8316.

(67) Chen, M.; Feng, X.; Zhang, L.; Ju, H.; Xu, Q.; Zhu, J.; Gottfried, J. M.; Ibrahim, K.; Qian, H.; Wang, J. Direct Synthesis of Nickel(II) Tetraphenylporphyrin and Its Interaction with a Au(111) Surface: A Comprehensive Study. *J. Phys. Chem. C* **2010**, *114*, 9908– 9916.