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On-Surface Fabrication of Bimetallic Metal–Organic Frameworks through the Synergy and Competition among Noncovalent Interactions

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(Cs)] and a transition metal [iron (Fe)] as model systems and successfully construct two kinds of bimetallic 2D-MOFs through the synergy and competition among noncovalent interactions, which is revealed by the high-resolution scanning tunneling



B ecause of their promising applications in catalysis, sensing, gas storage, and optoelectronics, metal–organic frameworks (MOFs) have attracted a great deal of attention in the past few decades.¹⁻⁷ In particular, two-dimensional MOFs (2D-MOFs) have attracted broad interest as a class of versatile 2D materials.^{8–14} In addition, theoretical studies also predicted that some 2D-MOFs can be treated as topological materials, which has inspired a new wave of studies of the atomically precise fabrication of various 2D-MOF structures.¹⁵ As is known, different noncovalent interactions such as intermolecular hydrogen bonds, electrostatic interactions,16-18 and coordination bonds between molecules and metals¹⁹⁻²¹ play crucial roles in the regulation of 2D-MOF structures. By using different metals, various 2D-MOF structures have been fabricated on surfaces in which only one kind of metal was introduced.^{22–27} Recently, transition metals (Cu and Fe) have been simultaneously introduced on the surface, while only one kind of metal (i.e., Fe) was engaged in the 2D-MOF structure also due to the selectivity of different coordination bonds.²⁸ Moreover, Barth et al. have successfully engineered a bimetallic network on the surface in which only one kind of noncovalent interaction (i.e., coordination bonds) was involved.²⁹ However, 2D-MOFs involving different kinds of noncovalent interactions and multiple metal components are more complex and less predictable, whose structures should be governed by the synergy and competition among the diverse noncovalent

interactions. Therefore, it is fundamentally important to construct a system involving different kinds of metal components (e.g., transition metals and alkali metals) to investigate the synergy and competition between coordination bonds and electrostatic ionic bonds together with intermolecular hydrogen bonds, which will advance our understanding of the fabrication of bimetallic 2D-MOFs with as-yet unprecedented functions and properties.

U₆Fe₂

In this work, we choose the RNA base uracil (U) molecule together with alkali metals [sodium (Na) and cesium (Cs)] and a transition metal [iron (Fe)] as the model system. The U molecule potentially contains both ionic and coordination bonding sites, which allows the introduction of ionic bonds and coordination bonds into the intrinsic hydrogen-bonded molecular networks. From the interplay of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we show that (i) upon introduction of Cs atoms into the prefabricated monometallic 2D-MOF composed of U_4Na_1 motifs on the Au(111) surface,

Received: March 23, 2021 Accepted: May 26, 2021 Published: May 28, 2021



Letter



Bimetallic

U₁₂Na₄Fe

we could fabricate a bimetallic 2D-MOF composed of $U_{10}Cs_2Na_1$ motifs through the synergy and competition between ionic bonds and intermolecular hydrogen bonds. (ii) Furthermore, upon sequential introduction of Fe and Na atoms into the monometallic U_4Na_1 2D-MOF, another more complicated bimetallic 2D-MOF composed of $U_{12}Na_4Fe_2$ motifs could be fabricated through the synergy and competition among intermolecular hydrogen bonds, ionic bonds, and coordination bonds (cf. Scheme 1).

Scheme 1. Illustration of the Formation of Different 2D-MOFs, Including Two Bimetallic MOF Structures



Deposition of U molecules and Na atoms on the Au(111)surface followed by annealing at 350 K leads to the formation of a 2D-MOF as shown in Figure 1a. From the high-resolution STM image superimposed with the structural model (Figure 1d), and also a previous study,³⁰ the elementary structural motif (depicted by the blue contour) is attributed to a U_4Na_1 motif, in which U molecules interact with the central Na via electrostatic ionic bonds and the neighboring U molecules interact with each other by intermolecular hydrogen bonds that are depicted by blue dashed lines. The corresponding simulated STM image shown in Figure S1e is in good agreement with the experimental one. The U₄Na₁ motifs are then linked together by hydrogen bonds to form an extended 2D-MOF, as shown in Figure 1g. To investigate the synergy and competition between different ionic bonds, and the formation of bimetallic structures, we then introduce another alkali metal Cs onto the U4Na1-precovered surface, after annealing at 370 K; interestingly, a different sort of 2D-MOF is achieved as shown in Figure 1b. The closer inspection (Figure 1e) allows us to identify that the 2D-MOF is composed of 10membered motifs depicted by blue contours. From the previous studies,¹⁸ we propose that the 10-membered motif contains two U₅Cs₁ pentamers linked by one Na cation; from the DFT-calculated model superimposed on the STM image (Figure 1e), we identify that two kinds of ionic bonds (i.e., U-Na and U-Cs) are involved, and the $U_{10}Cs_2Na_1$ motifs are then linked together by NH…O hydrogen bonds to form an extended bimetallic 2D-MOF as shown in Figure 1h. Unexpectedly, after further deposition of Na atoms on the U₁₀Cs₂Na₁-precovered surface followed by annealing at 430 K, we gain another kind of 2D-MOF with some bright protrusions sporadically located in the cavities as shown in Figure 1c. We propose this 10-membered motif is composed of U₁₀Na₄ as depicted by the blue contour in Figure 1f, and the four dim central spots corresponding to Na are visible in a special tip state (Figure S2). The control experiment shows that directly annealing U molecules and Na atoms on the surface at 430 K results in the same U₁₀Na₄ structure just without the bright



Figure 1. STM images and DFT calculations showing the formation of U_4Na_1 , $U_{10}Cs_2Na_1$, and $U_{10}Na_4$ 2D-MOFs. (a–c) Large-scale STM images showing the structural transformations from U_4Na_1 via $U_{10}Cs_2Na_1$ to $U_{10}Na_4$ MOFs on the Au(111) surface. (d–f) Closeup STM images allow us to distinguish the elementary structural motifs, e.g., U_4Na_1 , $U_{10}Cs_2Na_1$, and $U_{10}Na_4$, respectively, as depicted by blue contours, which are superimposed with DFT-optimized models. (g–i) DFT-optimized structural models of the network structures composed of U_4Na_1 , $U_{10}Cs_2Na_1$, and $U_{10}Na_4$, respectively, on Au(111) (the surface is removed for clear presentation) to demonstrate the intermolecular hydrogen bonds and ionic bonds between the motifs. Hydrogen bonds are depicted as blue dashed lines. H, white; C, gray; N, blue; O, red; Na, pink; Cs, modena.

protrusion in the cavity. Further depositing Cs atoms on the pure U₁₀Na₄ network leads to the appearance of bright protrusions in the cavities as shown in Figure S3b. On this basis, and on the basis of the literature, 31,32 the bright protrusions in cavities are assigned to Cs cations as labeled in Figure 1c. From the superimposed optimized structural models shown in Figure 1f, we found that U molecules interact with the central Na cations via electrostatic ionic bonds, and the U molecules interact with each other by intermolecular hydrogen bonds that are depicted by blue dashed lines. The U₁₀Na₄ motifs are then linked together by ionic bonds between U molecules and Na cations to form the extended 2D-MOF, as shown in Figure 1i. The findings presented above show that by the synergy and competition between U-Na and U-Cs ionic bonds together with intermolecular hydrogen bonds different 2D-MOFs could be formed and transformed on the surface, a kind of bimetallic 2D-MOF involving two different ionic bonds.

In a step forward, to increase the complexity of the system, we try to introduce a transition metal (Fe) into the U_4Na_1 structure to investigate the synergy and competition between coordination bonds and electrostatic ionic bonds. After Fe atoms have been deposited onto the U_4Na_1 -precovered surface followed by annealing at 800 K, interestingly, a porous network structure is achieved as shown in Figure 2b. Closer inspection (Figure 2e) allows us to identify that the network is composed of six-membered motifs depicted by blue contours. From the



Figure 2. STM images and DFT calculations showing the formation of U₄Na₁, U₆Fe₂, and U₁₂Na₄Fe₂ 2D-MOFs. (a–c) Large-scale STM images showing the structural transformations from U₄Na₁ via U₆Fe₂ to U₁₂Na₄Fe₂ MOFs on the Au(111) surface. (d–f) Close-up STM images allow us to distinguish the elementary structural motifs, e.g., U₄Na₁, U₆Fe₂, and U₁₂Na₄Fe₂, respectively, as depicted by blue contours that are superimposed by DFT-optimized models. (g–i) DFT-optimized structural models of the network structures composed of U₄Na₁, U₆Fe₂, and U₁₂Na₄Fe₂, respectively, on Au(111) (the surface has been removed for the sake of clarity) to demonstrate the intermolecular hydrogen bonds and coordination bonds between the motifs. Hydrogen bonds are depicted as blue dashed lines. H, white; C, gray; N, blue; O, red; Na, pink; Fe, light purple.

DFT-calculated model superimposed on the STM image, we propose that this six-membered motif is composed of U_6Fe_2 as depicted by the blue contour in Figure 2e, in which the central Fe atoms interact with U molecules via coordination bonds, and the neighboring U molecules interact with each other by intermolecular hydrogen bonds. The U₆Fe₂ motifs are then linked together by intermolecular hydrogen bonds to form the extended 2D-MOF, as shown in Figure 2h. The control experiment shows that directly annealing U molecules and Fe atoms on the surface at 800 K results in the same U₆Fe₂ structure (Figure S4b). More interestingly, after further deposition of Na atoms on the U₆Fe₂-precovered surface followed by annealing at 430 K, we also gain another kind of network structure as shown in Figure 2c. Closer inspection (Figure 2f) allows us to identify that the structure is composed of 12-membered motifs. From the DFT-calculated model superimposed on the STM image, we propose that the 12membered motif $(U_{12}Na_4Fe_2)$ contains two U_6Na_2 hexamers linked by two Fe atoms, in which two kinds of noncovalent interactions (i.e., U-Na ionic bonds and U-Fe coordination bonds) are involved, and the U₁₂Na₄Fe₂ motifs are then linked together by U-Fe coordination bonds to form an extended bimetallic 2D-MOF as shown in Figure 2i. The findings presented above show that by the synergy and competition between U-Na ionic bonds and U-Fe coordination bonds together with intermolecular hydrogen bonds different 2D-MOFs could be formed and transformed on the surface.

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For systematically investigating the synergy and competition among noncovalent interactions, further comparative experiments to introduce an alkali metal (Na) and a transition metal (Fe) into a U_5Cs_1 -precovered surface are performed. Upon deposition of U molecules and Cs atoms on the Au(111) surface followed by annealing at 370 K, a network structure is formed as shown in panels b and e of Figure 3, which was



Figure 3. (a) Schematic illustration on the formation of different 2D-MOFs, including one bimetallic MOF structure. (b–d) Close-up STM images showing the structural transformations from U_5Cs_1 via $U_{10}Cs_2Na_1$ to U_8Cs_2 MOFs on the Au(111) surface allowing us to distinguish the elementary structural motifs, e.g., U_5Cs_1 , $U_{10}Cs_2Na_1$, and U_8Cs_2 , respectively, as depicted in blue, which are superimposed with DFT-optimized models. (e–g) DFT-optimized structural models of the network structures composed of U_5Cs_1 , $U_{10}Cs_2Na_1$, and U_8Cs_2 , respectively, on Au(111) (the surface has been removed for the sake of clarity) to demonstrate the intermolecular hydrogen bonds and ionic bonds between the motifs. Hydrogen bonds are depicted as blue dashed lines. H, white; C, gray; N, blue; O, red; Na, pink; Cs, modena.

previously attributed to a U_5Cs_1 structure.¹⁸ We then introduce another alkali metal, Na, onto the U₅Cs₁-precovered surface; after annealing at 430 K, a bimetallic network structure $(U_{10}Cs_2Na_1)$ is achieved, which is the same as that in Figure 1b. Interestingly, after further deposition of Cs atoms on the $U_{10}Cs_2Na_1$ -precovered surface followed by annealing at 370 K, we gain the secondary structure of U-Cs composed of U₈Cs₂ motifs as shown in Figure 3d. From the optimized structural model shown in Figure 3g, the U₈Cs₂ motifs are then linked together by ionic bonds between U-Cs to form onedimensional chains and the chains are linked together laterally by NH…O hydrogen bonds. The findings presented above show that the formation of a bimetallic $U_{10}Cs_2Na_1$ structure is independent of the order of deposition of Na and Cs. Similarly, we also try to deposit Fe atoms on a U₅Cs₁-precovered surface followed by annealing at 800 K, the U₆Fe₂ structure decorated with Cs (depicted as blue circles) at the periphery of the network is achieved as shown in Figure S5c, and further deposition of Cs atoms on this structure does not change the U₆Fe₂ structural motifs.

In conclusion, we have successfully fabricated two complicated bimetallic 2D-MOFs by the synergy and

competition among diverse noncovalent interactions. Furthermore, the alkali metals could be displaced by either another alkali metal or a transition metal from the preformed MOF structures as a result of competition among ionic bonds and coordination bonds. Such a systematic study may help to improve our fundamental understanding of the interaction mechanism of noncovalent bonds, and moreover, such a bottom-up strategy for the fabrication of bimetallic 2D-MOFs will pave the way for further investigation of the unprecedented functions and properties of surface-supported MOF structures.

EXPERIMENTAL METHODS

A variable-temperature, fast-scanning "Aarhus-type" STM instrument was used to perform all STM experiments in a UHV chamber (2×10^{-10} mbar). The etched W tip purchased from SPECS^{33,34} was used. An e-beam evaporator and a molecular evaporator were used for sample preparation. Single-crystal Au(111) was prepared by Ar⁺ ion sputtering for several cycles and annealing to 800 K for 15 min. The U molecules (>98% pure, purchased from Sigma-Aldrich) were deposited on a clean Au(111) surface by thermal sublimation. The e-beam evaporator was used to evaporate the Fe atoms at an emission current of ~1.5 mA. By conventional resistance heating, the alkali metals (Na and Cs) were evaporated from Alvasource. All of the measurements were performed at ~150 K. Scanning conditions: $I_t = 0.5-0.9$ nA, and $V_t = -1300$ mV.

The Vienna ab initio simulation package $(VASP)^{35,36}$ was employed to perform DFT calculations by using the generalized gradient approximation of the Perdew–Burke– Ernzerhof^{37,38} and projector-augmented wave potentials.³⁹ The dispersion-corrected DFT-D3 method of Grimme⁴⁰ was used to consider the van der Waals interactions. The structures were relaxed using a conjugate gradient method until the forces on the unconstrained atoms were $\leq 0.03 \text{ eV/Å}$. On the basis of the Tersoff–Hamann method,^{41,42} the simulated STM images were obtained using the Hive program.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00942.

Simulated STM images, STM image of the $U_{10}Na_4$ MOF with a special tip state, STM image of Cs cations in cavities of $U_{10}Na_4MOF$, formation of U_6Fe_2MOF , and structural transformation upon introduction of Fe atoms on a U_5Cs_1 -precovered surface (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the National Natural Science Foundation of China (Project 21790351). Aidi Zhao is acknowledged for providing the Na and Cs sources.

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