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Alkali-Metal-Induced Modulation of Intermolecular Interactions and Structural Transformations of Metal–Organic Nanostructures

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ABSTRACT: Metal-organic nanostructures are of fundamental interest in the field of surface science due to their high structural and property tunability. Alkali-based metal-organic nanostructures, characterized by greater flexibility in geometries, have been constructed on surfaces and tuned by different types and dosage of alkali metals, as well as coverage of organic molecules, which directly determine the metal-organic and molecule-molecule interactions, respectively. However, the diversity of intermolecular interactions induced by the introduction of alkali metals in the construction of metal-organic nanostructures has received less attention, which would provide fundamental insights into the subtle interplay of metal-organic interactions and molecule-molecule interactions. In this study, on the basis of scanning tunneling microscopy imaging and density functional theory calculations, structural transformations and diversity of intermolecular interactions induced by alkali metals (Na, K, and Cs) have been visualized in a stepwise manner on Au(111). With the increasing dosage of alkali atoms, the evolving synergy of metal-organic interactions and molecule-molecule interactions induced by alkali metals (Na, K, and Cs) have been visualized in a stepwise manner on Au(111). With the increasing dosage of alkali



has also been revealed, which would inspire the precise construction and regulation of metal-organic nanostructures.

1. INTRODUCTION

Molecular assembly on solid surfaces, with molecular building blocks organized in a predetermined pattern,¹⁻⁶ has long been a promising strategy for the preparation of molecular nanostructures as well as surface functionalization. This process is dominantly governed by noncovalent intermolecular interactions, including hydrogen bonds,^{7,8} coordination bonds,^{9,10} electrostatic interactions,¹¹⁻¹³ etc. Metal–organic nanostructures,¹⁴⁻¹⁸ as a representative class of assembled molecular structures with the integration of metal atoms, exhibit a high degree of structural and property tunability,¹⁹⁻²¹ where the embedded metals mainly vary from d-block transition metals^{22,23} to f-block lanthanides.^{24,25} In recent years, the integration of alkali metals has attracted increasing attention, as the corresponding metal-organic nanostructures are featured by greater tunability and flexibility in geometries when alkali metals electrostatically attract ligand molecules.^{11,12,14,26} These alkali-metal-based nanostructures have been generally tuned based on either the alkali metals or the organic molecules involved. Different types of alkali metals, such as Li, Na, K, and Cs, have been introduced to interact with molecules to form various metal-organic motifs with different molecular aggregation numbers due to their sizes.^{27,28} Moreover, the increasing dosage of alkali metal elements usually leads to structural transformations of metal-organic nanostructures with varied metal-organic interactions.^{14,28} Apart from the metal-organic interactions between alkali metals and molecules, molecule-molecule interactions themselves (e.g., hydrogen bonds and halogen bonds) also play a vital role in the construction of metal-organic nanostructures,

which are mainly regulated by molecule coverage^{29–31} and annealing temperature.^{32–34} However, the diversity of intermolecular interactions induced by the introduction of alkali metals in the construction of metal–organic nanostructures has received less attention. Therefore, exploring the role of alkali metals in modulating intermolecular interactions and structural transformations is essential for understanding the subtle interplay between metal–organic interactions and molecule–molecule interactions.

In this study, 4,4'-dibromo-2,2'-bipyridine (DBBPy, see Scheme 1a) was selected as the target molecule, which is composed of a bipyridyl moiety to potentially interact with alkali metals via electrostatic interactions^{26,35} (along with *trans*-to-*cis* isomerization) and two Br substitutes to potentially form halogen bonds. The calculated electrostatic potential (ESP) map of a *cis*-DBBPy molecule (Scheme 1b) illustrates that N sites on the bipyridyl moiety display negative potentials (red), while Br atoms have both negative (red) and positive potentials (blue) regions, corresponding to electron-rich belt and electron-depleted cap, respectively. It thus provides the possibility to construct and regulate the metal–organic nanostructures based on the introduction of alkali metals,

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Scheme 1. Schematic Illustration of Two Synergistic Interactions, Namely, Electrostatic Interaction and Halogen Bonding, in the Metal–Organic Structures^a



^a1 (a) Isomerization of the DBBPy molecule. (b) Electrostatic potential (ESP) map of a *cis*-DBBPy molecule. (c) Charge-density difference maps of a metal–organic dimer (left) and a molecular trimer (right) in 2D slice, showing electrostatic interaction and halogen bonding with obvious charge transfer, respectively. Red and blue isosurfaces correspond to charge accumulation and depletion, respectively. Na: pink; N: blue; C: gray; H: white; Br: brown



Figure 1. Initial structural transformation induced by introducing Na atoms to the *trans*-DBBPy structure on Au(111). (a) Large-scale and (b) high-resolution STM images of close-packed *trans*-DBBPy structure after deposition at RT, with superimposed molecular models. (c) Large-scale and (d) magnified STM images obtained after the addition of Na to the above sample at RT, where the Na-embedded dimers are highlighted by white rectangles and molecular models are also overlaid. (e) DFT-optimized structural model of a *cis*-DBBPy dimer anchored by one Na on Au(111). (f) Charge-density-difference map in 2D slice illustrating the electron distribution in the Na-embedded dimer. (g) Corresponding simulated STM image. Scanning parameters: V = 1.2 V, I = 0.5-0.7 nA. The close-packed directions of the Au(111) substrate are indicated by the black arrows. Au substrate: light yellow; Na: pink; N: blue; C: gray; H: white; Br: brown.

along with the formation of metal-organic dimers (via Na…N electrostatic interaction) and molecular motifs (via halogen bonds), as typically shown in Scheme 1c. Based on the combination of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT)

calculations, the structural transformations induced by the introduction of the alkali metals Na, K, and Cs have been visualized in a stepwise manner during the construction of metal–organic nanostructures on Au(111), and the alkalimetal-induced diversity of intermolecular interactions has been



Figure 2. Structural transformations obtained after further dosing Na on Au(111). (a, e) Large-scale and (b, f) high-resolution STM images of metal-organic nanostructures in response to the increasing Na dosage, overlaid with the corresponding DFT-optimized structural models. (c, g) DFT-optimized structural models. (d, h) Charge-density-difference maps in 2D slice of two structural motifs highlighted in (c, g), showing charge transfer within the 4-fold and 3-fold halogen-bonding configurations, respectively. The red and blue isosurfaces indicate charge accumulation and depletion, respectively. Scanning parameters: V = 1.2 V, I = 0.5-0.7 nA. Na: pink; N: blue; C: gray; H: white; Br: brown.

demonstrated. With the increasing dosage of Na atoms, the isomerization of *trans*-DBBPy molecules was facilitated with the formation of metal–organic dimers composed of *cis*-DBBPy, leading to the variation of intermolecular interactions and the formation of various metal–organic nanostructures. Moreover, the generality of this alkali-metal-induced mod-ification of intermolecular interactions and structural transformations was verified by introducing K or Cs into the *trans*-DBBPy precovered Au(111) sample, showing the influence of alkali metal size. Our study displays the role of alkali metals in modulating intermolecular interactions and constructing metal–organic nanostructures and reveals the synergy of metal–organic interactions and molecule–molecule interactions, which will inspire the precise construction and regulation of metal–organic nanostructures.

2. METHODS

The STM experiments were performed in an ultrahigh-vacuum (UHV) chamber equipped with a variable-temperature "Aarhus-type" STM from SPECS.^{36,37} The Au(111) substrate was cleaned by Ar^+ -ion sputtering and annealing at ~ 800 K for repeated cycles. A standard molecular evaporator (purchased from CASAcme Technology) was used for sample preparation. After thoroughly degassing, the DBBPy molecules (purchased from Bidepharm, with purity greater than 98%) were deposited by thermal sublimation at ~295 K onto a clean Au(111) substrate. The pure sodium (Na, from SAES Getters) was evaporated through conventional resistance heating of a wire-type Na dispenser after fully degassing. The sample was thereafter transferred within the UHV chamber to the STM head for scanning. All of the STM images were recorded in a typical temperature range of 100–150 K and were further smoothed to eliminate noises.

The calculations were performed in the framework of DFT by using the Vienna *ab initio* simulation package (VASP).^{38,39} The projector-augmented wave method was used to describe the interaction between ions and electrons.^{40,41} The Perdew–Burke–Ernzerhof generalized gradient approximation ex-

change-correlation functional was employed,⁴² and van der Waals interactions were included using the dispersioncorrected DFT-D3 method of Grimme.⁴³ 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. The Au(111) substrates were modeled by three-layered slabs separated by a ~15 Å vacuum region for the structural models, where the bottom layer was fixed. The simulated STM images were obtained by using the Tersoff–Hamann method,⁴⁴ in which the local density of states is used to approximate the tunneling current.

3. RESULTS AND DISCUSSION

After deposition of DBBPy molecules on Au(111) held at room temperature (RT, ~300 K), a close-packed selfassembled structure was obtained (Figure 1a). The zoomedin STM image (Figure 1b) shows that each individual molecule appears as a zigzag shape with two bright end points and a darker central region and is attributed to the transconformation (as shown in the inset of Figure 1a). The trans-DBBPy molecules are aligned in an alternating head-to-head way to form the self-assembled structure, as illustrated by the superimposed models in Figure 1b. Notably, the structure was constructed exclusively by trans-DBBPy molecules owing to their higher stability compared to cis-DBBPy on the surface. In order to explore the influence of alkali metal on the intermolecular interactions and structural transformations, we dosed the alkali metal Na onto the trans-DBBPy-precovered Au(111) surface at RT in a stepwise manner (Figure S1). Interestingly, a porous aperiodic structure was formed, as shown in Figure 1c. More details can be observed from the magnified high-resolution STM image (Figure 1d) that the structure is composed of a mixture of zigzag trans-DBBPy and arch-like cis-DBBPy molecules. Meanwhile, two adjacent cis-DBBPy molecules interact with each other in a back-to-back manner forming dimers with a slit between them, and are



Figure 3. Cs-induced stepwise structural transformation on Au(111). (a–c) Large-scale STM images showing the sequential transformation from *trans*-DBBPy islands to the metal—organic structures induced by dosing Cs. (d) Top and side views of the optimized structural model of the dimer formed by one Cs and two *cis*-DBBPy molecules. (e) Charge-density-difference map of the dimer in 2D slice, showing the electrostatic interactions between Cs and *cis*-DBBPy molecules with obvious charge transfer. (f) Simulated STM images based on the dimer model. (g, j) Magnified high-resolution STM images of the two Cs-embedded porous network structures. (h, i, k) Charge-density-difference maps of elementary motifs involved in (g, j), respectively. Scanning parameters: V = 1.2 V, I = 0.5-0.7 nA. Cs: purple; N: blue; C: gray; H: white; Br: brown.

depicted by white dashed rectangles. According to previous studies,^{11,27,45} Na usually loses its valence electrons upon adsorption on Au(111) and has low electron density and low apparent height compared to the molecular plane, resulting in its weak contrast, which is difficult to identify in STM images under normal scanning conditions. Thus, this dark slit is tentatively attributed to Na. Accordingly, DFT calculations were conducted on the dimer structure adsorbed on Au(111) and the most energetically favorable structure is illustrated in Figure 1e, where a Na atom is located at the center of two pairs of bipyridyl moieties. From the charge-density-difference map in 2D slice (Figure 1f), obvious charge transfer can be seen between the central Na atom and four neighboring N sites, proving their electrostatic interaction, which contributes to the formation of the stable metal-organic dimer. Furthermore, the simulated STM image of the dimer (Figure 1g) also exhibits high agreement with the experimental one, in which the central Na atom is invisible, confirming the assignment of the structure. In particular, the electrostatic interaction between Na atoms and the N sites on the bipyridyl moieties leads to the trans-to-cis isomerization of DBBPy molecules as also demonstrated in our recent work.³⁵ Two cis-DBBPy molecules are then anchored through one Na atom to form the metalorganic dimer. Due to the insufficient dosage of Na, such

metal—organic dimers are surrounded by a number of *trans*-DBBPy molecules, as indicated by the superimposed structural models (Figure 1d).

Subsequently, the dosage of Na was gradually increased (Figure 2). The addition of Na resulted in the transformation of the porous aperiodic structures into a well-ordered network structure (Figure 2a). Close inspection of the structure (Figure 2b) shows that more *cis*-dimers appeared and were aligned in parallel, surrounded by a line of trans-DBBPy molecules. Based on the high-resolution STM image, DFT calculations were performed on the network structure as shown in Figure 2c, clearly displaying the molecular alignment. In this metalorganic network, cis-dimers are formed by the 4-fold electrostatic interaction between Na and N sites and simultaneously bind with remaining trans-DBBPy molecules. Moreover, the charge-density-difference map of the elementary motif highlighted in yellow in Figure 2c shows obvious charge transfer among four adjacent molecules via Br…Br halogen bonds (Figure 2d), consistent with the reported cases.^{29,46,47} In addition, the DFT-optimized structural model was further superimposed on Figure 2b with a good agreement, verifying the formation of Na-based metal-organic network with the synergy of electrostatic interaction between Na and N and 4fold halogen bonds.

To further explore the influence of Na atoms on the intermolecular interactions and corresponding structures, additional Na atoms were dosed to the above sample at RT. As a result, a helical molecular structure appeared, as shown in Figure 2e, which is distinct from the porous phase obtained above in the molecular arrangement. The magnified STM image (Figure 2f) displays that the structure is entirely composed of Na-embedded cis-dimers with all cis-DBPPy molecules involved, while three adjacent cis-DBPPy molecules gather together via the Br substituents. The corresponding DFT calculated model (Figure 2g) corroborates that the helical structure consists of cis-DBPPy molecules with Na located at the center of dimers and Br substitutes aligned in a triangular pattern (as highlighted in yellow). Accordingly, the charge-density-difference map (Figure 2h) of such three cis-DBBPy molecules as a motif exhibits charge transfer among three Br atoms, i.e., 3-fold halogen bonds. The DFT-optimized structure model was then superimposed on the STM image with high consistency (Figure 2f). It is worth noting that the binding energy of the helical structure (Figure 2g) was calculated to be 1.76 eV per molecule, much higher than that of the porous one (Figure 2c) by 0.5 eV per molecule, indicating the synergy of electrostatic interactions and halogen bonds involved in these structures. Such an energy difference also rationalizes the Na-induced structural transformation from the standpoint of thermodynamics. Therefore, the introduction of Na atoms into the molecular structures successfully induced the transformation from an aperiodic structure through a regular porous metal-organic network to the helical metalorganic structure with modulations on the intermolecular interactions.

In addition, similar experiments involving DBBPy molecules and K atoms have also been conducted. Figure S2 exhibits the gradual structural transformation of DBBPy-based nanostructures in response to the increasing dosage of K on Au(111), including a porous aperiodic structure, a well-ordered network structure, and eventually, a helical molecular structure consisting entirely of K-embedded *cis*-dimers. These Kembedded molecular structures exhibit morphological congruence with those in the case of Na, which may be attributed to the similar atomic radius of Na and K.

To further explore the generality of the modulation of intermolecular interactions by alkali metals, another alkali metal Cs was gradually dosed to the trans-DBBPy-precovered Au(111) (Figure 3a) at RT. Similarly, Cs-based metal–organic nanostructures were obtained in response to the dosage of Cs atoms (Figure 3b,c), with some differences in the detailed arrangements. Upon the initial deposition of Cs, a regular network structure with staggered tetragonal cavities was formed (Figure 3b). The magnified STM image (Figure 3g) shows that both cis- and trans-DBBPy molecules coexist in the structure due to insufficient Cs dosage, which is similar to the situations of the Na-induced intermediate phases. Notably, each Cs appears as a bright protrusion and can be easily distinguished in the STM images with larger atomic radius, in good agreement with previous studies.^{28,48} Interestingly, an individual Cs interacts with two neighboring cis-DBBPy molecules forming a dimer, while the position of the Cs atom is slightly off-center compared to that of the analogous Na-induced dimer structure. Simultaneously, an adjacent trans-DBBPy points to the dimer at one end as shown in Figure 3h and interacts with two cis-DBBPy molecules via a 3-fold Br…Br interaction (Figure 3i). The charge-density-difference map of the Cs-embedded motif in 2D slice (Figure 3h) shows that the predominant charge transfer occurs between Cs and four N sites, confirming that it is the electrostatic interaction that stabilizes this motif. At the same time, the minor halogen bonds among a *trans*-DBBPy and two *cis*-DBBPy molecules were also formed, as induced by the introduction of Cs (Figure 3i). Moreover, DFT-optimized structural models were overlaid on the STM image, in nice accordance with the arrangement of the metal–organic network (Figure 3g). In this way, a Cs-less metal–organic network was constructed, with the synergy of electrostatic interactions between Cs and N sites and other weaker intermolecular interactions.

As the dosage of Cs was further increased, the Cs-induced structural transformation also occurred, forming a more homogeneous network structure (Figure 3c). More details are observable in Figure 3j, where a complete trans-to-cis isomerization of DBBPy molecules took place, with Cs atoms staying at the center of the two pairs of parallel bipyridyl moieties. The DFT-optimized structural model of an individual Cs-involved cis-dimer on Au(111) is shown in Figure 3d, which exhibits similarity to the Na-involved cis-dimer in both the structure and the predominant electrostatic interaction (from the obvious charge transfer between Cs and N sites shown in Figure 3e). Based on the DFT-optimized model, the STM simulation (Figure 3f) was carried out, where Cs appears as bright dots, nicely reproducing the experimental morphology. In addition, these cis-dimers connect with each other via 4-fold halogen bonds (as shown in Figure 3k), extending to form the metal-organic network (cf. the overlaid DFT model in Figure 3j). Thus, such a Cs-involved metal–organic network is formed by the synergy of Cs…N electrostatic interaction and minor 4-fold halogen bonds.

It is noteworthy that Na-dimer and Cs-dimer are quite similar, while the eventual metal-organic networks are a bit different in the assembled patterns. In the case of Na, the synergistic interaction in the helical structure shown in Figure 2f,g is calculated to have a binding energy of 1.76 eV per molecule, which is energetically more favorable than the proposed pattern by adopting the Cs-involved alignment (1.72 eV per molecule), as shown in Figure S3. In contrast, in the case of Cs, the binding energy is calculated to be 1.48 eV per molecule for the experimental alignment as shown in Figure 3j,k, while the proposed structure based on the Na-involved alignment has a slightly lower binding energy of 1.47 eV per molecule (Figure S4). Consequently, the construction of the corresponding metal-organic nanostructures is thermodynamically driven, which may be related to the size of alkali metals involved.²⁷ The two series of structural transformations induced by the introduction of alkali metals also indicate the subtle interplay of the intermolecular interactions.

4. CONCLUSIONS

In conclusion, by combining STM imaging and DFT calculations, the construction and structural transformation of metal–organic nanostructures have been achieved based on the introduction of alkali metals (Na, K, and Cs, separately), along with the formation of diverse intermolecular interactions. In addition, the synergy of electrostatic interactions between Na/Cs and organic molecules and intermolecular halogen bonds has been displayed during the structural transformations, accompanied by the alkali-metal-facilitated *trans*-to-*cis* isomerization. Our results exhibit the role of alkali metals in the modulation of intermolecular interactions and the

formation of various metal—organic nanostructures, which would provide fundamental insights into the precise fabrication of alkali-based metal—organic nanostructures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.5c00908.

STM images of gradual structural evolution processes and DFT-optimized structural models with their binding energies (PDF)

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Notes

The authors declare no competing financial interest.

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