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Linear array of cesium atoms assisted by uracil molecules on Au(111)†

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Based on STM imaging and DFT calculations, we demonstrate that it is feasible to construct a series of metal–organic U + Cs structures composed of configuration-adjustable multiple-metal-center motifs, which is the consequence of the synergy and competition between hydrogen bonds and ionic bonds. Moreover, assisted by U molecules, the central Cs cations tend to form linear arrays.

Surface-assisted self-assembly is a promising method for bottomup fabrication of functionalized supramolecular nanostructures with atomic precision,^{1,2} in which the synergy and competition among various non-covalent interactions such as hydrogen bonds,^{3,4} coordination bonds,^{5,6} and electrostatic interactions^{7–9} are found to play an important role. In many self-assembled systems, the coexistence of a variety of non-covalent interactions is commonly encountered, and the delicate balance among them leads to the formation of various specific surface supramolecular nanostructures. By regulation of different parameters like substrate temperature,¹⁰ molecular coverage,^{11,12} and molecule/metal ratio,13-15 various metal-organic structures can be fabricated owing to the balance between hydrogen bonds and coordination bonds, and moreover, reversible conversions among these surface nanostructures were also achieved owing to the dynamic nature of non-covalent interactions.^{12,13,15} With respect to the formed metal-organic coordination motifs, in most of the cases, there were merely one or two metal centers within the elementary structural motif.¹⁶⁻¹⁹ It is interesting to note that by utilizing nucleobase molecules such as guanine (G), cytosine (C) and uracil (U) as precursors, the formation of three-metal-center structural motifs like G₃Fe₃,¹⁵ G₃Ni₃,¹⁴ C₃Ni₃²⁰ and U₃Ni₃²¹ has been achieved, in which the metals form specific triangular configurations binding with the molecules through coordination bonds. In comparison to the studies of metal-organic systems involving

Interdisciplinary Materials Research Center, College of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China. hydrogen bonds and coordination bonds, meanwhile, the synergy and competition between hydrogen bonds and electrostatic ionic bonds has been less discussed.^{22–28} Furthermore, in contrast to the directionality and saturability of coordination bonds, ionic bonds seem more flexible which may render the possibility to build up diverse multiple-metal-center structural motifs by balancing hydrogen bonds and ionic bonds within the whole structure.

It is well known that alkali metals are typical active metals that can form metal–organic structures involving ionic bonds.^{22,23,29} Among others, cesium (Cs) possesses the strongest metallicity which means the highest tendency to lose an electron and turn into a cation (Cs⁺). In this study, we then choose Cs to interact with one of the DNA base molecules, uracil (U), which contains two ionic bonding sites: O2 and O4 (see the chemical structure of U in Scheme 1), to introduce ionic bonds into hydrogen-bonded networks. From the interplay of high-resolution scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we present that: (i) by deposition of Cs atoms onto the U-precovered Au(111) surface step by step, we achieve the sequential formation of various surface nanostructures composed of U_5Cs_1 , U_6Cs_2 , and U_8Cs_3 metal–organic motifs, respectively (*cf.* Scheme 1).



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Fig. 1 STM images showing the structural transformations in response to the amount of Cs atoms. (a) Formation of the close-packed U island structure at RT. Structural transformations from the U island structure to metal–organic structures composed of (b) U_5Cs_1 motif, (c) U_6Cs_2 motif, and (d) U_8Cs_3 motif, respectively, by the stepwise dosage of Cs atoms on the U-precovered Au(111) surface and annealing at 370 K.

(ii) Interestingly, within the U_8Cs_3 motif, Cs cations are aligned into a linear array, which is different from the triangular configuration of metal clusters formed by transition metals like Fe and Ni.^{14,15,20,21} (iii) From the DFT relaxed structural models, we deduce that the formation of such a linear array of Cs cations is the consequence of the synergy and competition between hydrogen bonds and ionic bonds.

Deposition of U molecules on Au(111) at room temperature (RT) results in the formation of close-packed structures as shown in Fig. 1a (a high-resolution STM image is shown in Fig. S1, ESI†). After deposition of Cs atoms step by step in a controllable amount onto the U-precovered surface (~ 0.5 monolayer of U) followed by annealing at 370 K, it results in the formation of a series of 2D ordered metal–organic structures composed of various elementary structural motifs composed of U₅Cs₁ (Fig. 1b), U₆Cs₂ (Fig. 1c) and U₈Cs₃ (Fig. 1d), respectively.

Fig. 2a shows the formation of an ordered U₅Cs₁ network (the ordering is also indicated by the periodic bright dots in the fast Fourier transform (FFT) image in the inset). The unit cell of the network is measured to be $a_1 = 20.1 \pm 0.5$ Å, $b_1 = 19.6 \pm 0.5$ Å, and $\theta_1 = 100^{\circ} \pm 1^{\circ}$. On the basis of previous literature,^{30,31} the brighter protrusions are assigned to Cs cations and the dimmer protrusions are U molecules. The elementary structural motifs are depicted by white pentagons. Closer inspection allows us to identify that the structural motif is composed of five U molecules and one Cs cation resulting in a five-membered metal-organic motif (*i.e.*, U_5Cs_1) as shown in Fig. 2b. Note that by incorporation of Cs into hydrogen-bonded U structures, we thus introduce another non-covalent interaction, that is, electrostatic ionic bonds (e.g., between O and Cs) into hydrogen-bond networks, and by doing so, interestingly, we achieve the structural transformation from a close-packed structure (i.e., U self-assembled one) to an ordered network (*i.e.*, U₅Cs₁ structure). To further understand such a structural transformation, we have performed DFT calculations on periodic structures to build up atomicscale models. From the superimposed DFT-relaxed model in Fig. 2b, we identify that each U₅Cs₁ motif shares a U dimer with the adjacent ones on both sites to form one-dimensional chains, and the chains are linked together laterally by double NH···O hydrogen bonds between U molecules. Further analysis of the high-resolution STM image superimposed with the



Fig. 2 Formation of the 2D metal–organic structure composed of U_5Cs_1 motifs. (a) A large-scale STM image to distinguish U_5Cs_1 elementary motifs as depicted by white pentagons where the Cs cations are indicated by circles and the corresponding FFT inset of the U_5Cs_1 structure. The unit cell is indicated. (b) An STM image of the U_5Cs_1 network superimposed with the DFT-optimized model on Au(111) (the substrate is omitted for clear presentation). (c) An STM image of the U_5Cs_1 motif superimposed with the DFT-optimized model on Au(111). Hydrogen bonds are depicted by blue dashed lines. (d) Top and side views of the DFT-optimized structural model of the U_5Cs_1 motif on Au(111). H: white; C: gray; N: blue; O: red. Cs: orange.

structural model shown in Fig. 2c allows us to distinguish that within the U_5Cs_1 motif, the central Cs interacts with O sites of U molecules *via* ionic bonds, and the neighboring U molecules are linked with each other by NH···O single or double hydrogen bonds (depicted by blue dashed lines). The top and side views of the structural model of the motif including the Au(111) surface are shown in Fig. 2d. Based on the above analysis, the delicate balance between hydrogen bonds and ionic bonds results in the structural transformation from a hydrogen-bonded molecular structure to a metalorganic structure.

To use Cs/U ratio as a regulation parameter to vary the formation of 2D metal-organic structures, we then controllably deposit Cs atoms onto the U5Cs1-precovered surface in the same procedure followed by annealing at 370 K; interestingly, another ordered U + Cs network is achieved as indicated by the periodic bright dots in the FFT image as shown in Fig. 3a. The unit cell of the network is measured to be a_2 = 12.8 \pm 0.5 Å, b_2 = 17.2 \pm 0.5 Å, and $\theta_2 = 101^\circ \pm 1^\circ$. The elementary structural motifs are depicted by white contours in Fig. 3a, and closer inspection allows us to identify that the structural motif is composed of six U molecules and two Cs cations resulting in a six-membered metal-organic motif (*i.e.*, U_6Cs_2) as shown in Fig. 3b, in which the DFT-relaxed model on periodic structures is also superimposed. From the further observation of Fig. 3b, we identify that each U₆Cs₂ motif shares a U dimer with the adjacent ones on both sites to form one-dimensional chains, and the chains are linked together laterally via hydrogen bonds between U molecules. From the high-resolution STM image together with the structural model shown in Fig. 3c and the model including the Au(111) surface in Fig. 3d, we distinguish that within the six-membered ring, two Cs cations interact with O sites of six U molecules via ionic bonds, and in comparison with the U₅Cs₁ motif (in which all of the U molecules are linked by hydrogen bonds), it is noted that some neighboring U molecules are not linked by hydrogen bonds any more, which indicates that the increased amount of

Cs atoms induces the breakage of the original hydrogen bonds between U molecules and meanwhile introduces additional ionic bonds to keep the whole structure stable.

To our surprise, with the increase of the Cs dosage, the Cs cations tend to form a linear array with the number of Cs from two to three by forming a third kind of U + Cs network composed of U₈Cs₃ motifs as shown in Fig. 4a. The unit cell of the network is measured to be $a_3 = 21.3 \pm 0.5$ Å, $b_3 = 21.7 \pm 0.5$ Å, and $\theta_3 = 84^{\circ} \pm 1^{\circ}$. The elementary structural motifs are depicted by white rectangles, and closer inspection allows us to identify that the structural motif is composed of eight U molecules and three Cs cations which are aligned into a linear array resulting in an eight-membered metal-organic motif (*i.e.*, U_8Cs_3) as shown in Fig. 4b, in which the DFT-relaxed model on periodic structures is also superimposed. It is noted that in this U₈Cs₃ motif, three Cs cations are aligned into a linear array enclosed by eight U molecules in the periphery, which is dramatically different from our previous studies on the formation of the U₃Ni₃ metal-organic coordination motif, in which three Ni atoms form a triangular configuration.²¹ From the high-resolution STM image together with the structural model shown in Fig. 4c and the model including the Au(111) surface in Fig. 4d, we distinguish that within the motif three Cs cations interact with O sites of eight U molecules via ionic bonds, and the neighboring U molecules are divided into four hydrogen bonded dimers. Also note that, within



Fig. 3 Formation of the 2D metal–organic structure composed of U_6Cs_2 motifs. (a) A large-scale STM image to distinguish U_6Cs_2 elementary motifs as depicted by white contours where the Cs cations are indicated by circles and the corresponding FFT inset of the U_6Cs_2 structure. The unit cell is indicated. (b) An STM image of the U_6Cs_2 network superimposed with the DFT-optimized model on Au(111). (c) An STM image of the U_6Cs_2 motif superimposed with the DFT-optimized model on Au(111). Hydrogen bonds are depicted by blue dashed lines. (d) Top and side views of the DFT-optimized structural model of the U_6Cs_2 motif on Au(111). H: white; C: gray; N: blue; O: red. Cs: orange.



Fig. 4 Formation of the 2D metal–organic structure composed of U_8Cs_3 motifs. (a) A large-scale STM image to distinguish U_8Cs_3 elementary motifs as depicted by white rectangles where the Cs cations are indicated by circles and the corresponding FFT inset of the U_8Cs_3 structure. The unit cell is indicated. (b) An STM image of the U_8Cs_3 network superimposed with the DFT-optimized model on Au(111). (c) An STM image of the U_8Cs_3 motif superimposed with the DFT-optimized model on Au(111). (d) Top and side views of the DFT-optimized structural model of the U_8Cs_3 motif on Au(111). H: white; C: gray; N: blue; O: red. Cs: orange.



Fig. 5 Formation of the 2D ordered structure composed of U_8Cs_4 motifs. (a) An STM image of the U_8Cs_4 structure. The unit cell is indicated. (b) The STM image superimposed with the DFT-relaxed structural model on Au(111). (c) A close-up STM image of the U_8Cs_4 motif superimposed with the DFT-relaxed structural model on Au(111). Hydrogen bonds are depicted by blue dashed lines. H: white; C: gray; N: blue; O: red. Cs: orange.

this U_8Cs_3 motif, the contribution of hydrogen bonds is further weakened by ionic bonds. To further elaborate the charge state, we have also calculated the Bader charge for each motif as shown in Fig. S2 (ESI†). It is seen that the Cs almost loses ~0.9 e^- in each motif, and each O around Cs gets ~1.2 e^- indicating the electrostatic interactions between Cs and O within the metal–organic motifs. The Au substrate gets less than 0.1 e^- . In the observed U_5Cs_1 , U_6Cs_2 and U_8Cs_3 structures, all of the U molecules are linked by ionic bonds with the Cs cations within the motifs, and hydrogen bonds also exist between some U molecules. The synergy and competition between molecule–molecule, molecule–metal, and metal–metal interactions on the substrate lead to the stability of the observed periodic close-packed structures.

Depositing more Cs atoms onto the U₈Cs₃-precovered surface in the same procedure followed by annealing at 370 K results in a more intricate ordered U + Cs structure in which four Cs cations are similarly aligned in a linear array as shown in Fig. 5. The unit cell of the network is measured to be $a_4 = 19.4 \pm 0.5$ Å, $b_4 = 27.3 \pm 0.5$ Å, and $\theta_4 = 90^{\circ} \pm 1^{\circ}$. The DFT-relaxed model of the periodic structure is superimposed on the STM image (Fig. 5b). From the zoomed-in STM image together with the structural model shown in Fig. 5c, it is noticed that the electrostatic interactions play the main role in stabilizing such a metalorganic motif. Moreover, with further increase of the Cs dosage, we achieve the formation of metallic linear arrays involving even more than four Cs cations within the metal–organic motifs as shown in the supporting information (*cf.* Fig. S3, ESI[†]).

In conclusion, by a combination of STM imaging and DFT calculations, we have successfully achieved the on-surface formation of metal-organic structures composed of configurationadjustable multiple-metal-center motifs, in which the synergy and competition between hydrogen bonds and ionic bonds are found to be the key. These findings demonstrate the feasibility of using the versatile ionic bonds to regulate various metal-organic structural motifs; in particular, owing to the non-directionality and non-saturability of ionic bonds, fabrication of more and more complicated metal-organic structures can be foreseen.

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Conflicts of interest

There are no conflicts to declare.

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