ChemComm



COMMUNICATION

Check for updates

Cite this: Chem. Commun., 2017, 53, 8767

Received 8th June 2017, Accepted 14th July 2017

DOI: 10.1039/c7cc04446a

rsc.li/chemcomm

From the combination of STM imaging and DFT calculations, we show that both alkali metal and halogens interact with different sites of the target molecules resulting in structural formation in a synergistic way. The elementary metal–organic motifs are connected by Cl in a variety of fashions demonstrating structural diversity.

The construction of supramolecular surface nanostructures via noncovalent interactions, for example, selective/directional hydrogen bonds, coordination bonds, dipole-dipole interactions together with electrostatic interactions and van der Waals forces, has been extensively studied owing to their promising applications in the field of surface structure related nanotechnology during the last few decades.^{1–7} With the rapid development of the on-surface molecular self-assembly field, more and more sophisticated structures with different functionalities are required and fabricated. For instance, in multicomponent systems, metal elements are always used to make the whole structures stable and endow them with exceptional electronic and magnetic properties. For this purpose, various transition metals have been applied to fabricate a variety of metal-organic coordination structures on surfaces.² Moreover, electrostatic interactions generated between molecules and alkali metals have also been utilized to construct well-organized nanostructures.⁸⁻¹⁰ In addition, direct introduction of metal halides onto surfaces provides a facile way to offer metal and non-metal elements simultaneously as reactants with organic molecules.^{11–16} In most of the cases, only metal atoms are found to participate in the formation of metalorganic structures. While, the halogens either penetrate to the bulk¹²⁻¹⁵ or form molecular halogens,¹⁶ which have little influence on the formation of surface structures. It is therefore of general interest to explore the role of halogens in affecting the surface nanostructures, which may extend the regulation strategies of on-surface self-assembly.



Structural diversity of metal-organic

Lei Xie, Chi Zhang, Yuanqi Ding, Wenlong E, Chunxue Yuan 💿 and Wei Xu 💿 *

self-assembly assisted by chlorine⁺

Scheme 1 Schematic illustration of the structural formation of metal–organic motifs mediated by the Cl ions.

In this study, we chose the 1-methylcytosine (shortened as 1mC, see Scheme 1) molecules and a typical kind of alkali halide NaCl to explore the feasibility of the construction of supramolecular nanostructures cooperated by both the cation and anion on the Au(111) surface. The cytosine moiety possesses both N and O binding sites to interact with metals, and it was shown that the formed metal-organic clusters (occupying both N and O sites) cannot bind together because there are no available binding sites anymore for potential hydrogen bonds or coordination bonds between the clusters.¹⁷ On the other hand, it was also shown that the hydrogen-rich positions can provide residence for halogen via electrostatic interactions.^{11,18,19} Herein, from the combination of high-resolution scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we show that the formation of various surface nanostructures, where elementary metal-organic motifs (i.e. 1mC₄Na₂) are connected by Cl in various manners thus demonstrating structural diversity, and one of the connection modes is shown in Scheme 1. In this study, both alkali metals and halogens interact with different sites of the 1mC molecules resulting in structural formation in a synergistic way. This study offers a method to modulate the metal-organic structural diversity by the assistance of halogens through weak electrostatic interactions.

Deposition of 1mC molecules on Au(111) at room temperature (RT) results in the formation of self-assembled chain structures as shown in Fig. 1. The large scale STM image (Fig. 1a) illustrates that the 1mC chains are separately distributed on the Au(111)

Interdisciplinary Materials Research Center, Tongji-Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering, Tongji University, Shanghai 201804, People's Republic of China. E-mail: xuwei@tongji.edu.cn

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cc04446a



Fig. 1 (a) A large-scale STM image of the self-assembled chain structures of 1mC molecules. (b) A close-up STM image with sub-molecular resolution showing the cytosine moiety (pointed by the blue arrow) and the methyl group (pointed by the white arrow). (c) High-resolution STM image superimposed with DFT-optimized gas-phase models. *L* and *R* indicate the molecular chiralities. Hydrogen bonds are depicted by blue dashed lines. H: white; C: gray; N: blue; O: red.

surface and the fuzzy parts show the tendency of molecular diffusion. The close-up STM image (Fig. 1b) shows that the chains are composed of dimers, and the sub-molecularly resolved image allows us to identify the individual molecular configuration in which the methyl group is imaged as a small bright dot (indicated by the white arrow) in connection with the cytosine moiety (the blue arrow). From the DFT calculated models superimposed on the high-resolution STM image (Fig. 1c), we identify that the chains consist of several fragments with different chiralities (as denoted by *R* and *L*), and each fragment is composed of homochiral 1mC dimers stabilized by double NH···N hydrogen bonds and such dimers are further linked with each other by NH···O hydrogen bonds.

As is known, alkali halides are usually deposited to form insulating layers between metal surfaces and organic molecules to retain the pristine properties of target molecules.²⁰⁻²² In recent studies, alkali halides have also been introduced onto surfaces as reactants.^{12–16} We then deposit NaCl onto the 1mCprecovered surface at room temperature (Fig. S1, ESI⁺) where the chains are disrupted and decorated with small patches of the NaCl island and afterwards the sample is annealed at 370 K for 10 min. As shown in Fig. S2 (ESI[†]), when the salt is provided in a small dosage, we observe a patch of structural transition highlighted by the white rectangle, while the remaining chains are intact. When the salt is supplied sufficiently, the previous 1mC chain structures are totally transformed into different chains and network structures with great diversities coexisting on the surface as shown in Fig. 2 (see more examples of typical structures in Fig. S3 (ESI[†]) and large-scale STM images showing an overview of the sample in S4, ESI[†]). Fig. 2a and b show two kinds of chain structures composed of the elementary metalorganic motifs (highlighted by the white and blue ellipses) assigned to 1mC₄Na₂ (as detailed below). Fig. 2a shows that the linear chains are composed of 1mC₄Na₂ motifs with the same chirality (as indicated by the R and L notations) within a chain, and the zigzag chain structure composed of the 1mC₄Na₂ motifs with alternate chiralities is shown in Fig. 2b. Moreover, chain structures can be further linked together into various network structures with great diversities, and typical examples are shown in Fig. 2c and d, in which two selected chains are highlighted representing the binding modes within



Fig. 2 A variety of ordered structures formed by deposition of NaCl onto the 1mC-precovered Au(111) surface and annealing at 370 K for 10 min. (a) A type of linear chain structure composed of the metal–organic 1mC₄Na₂ motifs (highlighted by the white and blue ellipses) with the same chirality (as indicated by the *R* and *L* notations) within a chain. (b) A type of zigzag chain structure composed of the 1mC₄Na₂ motifs with alternate chiralities. (c and d) Various networks formed by different linked chains.

individual chains and the connections between them. It is notable that we try different annealing temperatures from 350 to 400 K, and those diverse structures are found to coexist on the surface, while it also shows the tendency that chains prevail at higher temperatures (see a large-scale example in Fig. S5, ESI[†]).

To reveal the atomic-scale structure of the elementary metalorganic motifs and their interconnections, we have further analyzed the STM images and performed extensive DFT calculations. From the close-up STM image (Fig. 3a) with a special tip state, we distinguish that each metal-organic motif is composed of four 1mC molecules and two additional dots (as highlighted by white circles). On the basis of previous literature,^{9,10,15,23,24} the two dots are attributed to Na ions, and the metal-organic motif is thus assigned to the 1mC₄Na₂ structure. The DFT relaxed gas-phase model is superimposed on a close-up STM image of the 1mC₄Na₂ motif as shown in Fig. 3b. From the most stable structural model (see the details of the structural confirmation process in Fig. S6, ESI[†]), we find out that the binding mode of 1mC₄Na₂ is similar to that of 9eG₄Fe₂,²³ in which two Na ions interact with O and N sites simultaneously. Within the motif, two additional NH···N hydrogen bonds are formed to stabilize the structure. Considering that only hydrogen atoms are available in the periphery of a 1mC₄Na₂ motif, which is similar to that of the previously reported C₃Ni₃ motif,¹⁷ such motifs cannot connect together by themselves because there are no potential binding sites. On the other hand, it was shown that the hydrogen-rich positions can provide residence for halogen via electrostatic interactions.^{11,18,19} We thus attribute the bigger dots (highlighted by green circles in Fig. 3c)



Fig. 3 (a) A close-up STM image with a special tip state showing two dots (as highlighted by white circles) within each $1mC_4Na_2$ motif (highlighted by white and blue ellipses). (b) A close-up STM image of the $1mC_4Na_2$ motif superimposed with a DFT-optimized gas-phase model. (c) The STM image showing the linkages among $1mC_4Na_2$ motifs through chlorine (as depicted by green circles). (d) STM images of linear and zigzag chains superimposed with the corresponding gas-phase models, respectively. Hydrogen bonds are depicted by blue dashed lines. H: white; C: gray; N: blue; O: red; Na: pink; Cl: green.

to Cl ions which serve as the linking points among $1\text{mC}_4\text{Na}_2$ motifs. The STM image with a special tip state illustrating both Na and Cl ions simultaneously is shown in Fig. S7 (ESI[†]). Normally, one Cl ion is needed between two adjacent motifs within a single chain, which is depicted by the DFT relaxed gas-phase models superimposed on the corresponding STM images of linear and zigzag chains (Fig. 3d). When two chains are laterally linked together, more Cl ions are employed to form additional weak hydrogen bonds to stabilize the whole structure. Two examples of the conjugations of linear and zigzag chains are shown in Fig. S8a and b (ESI[†]) with tentative models illustrating the typical binding sites, respectively. Owing to the relatively weak electrostatic interactions, the elementary motifs can be linked together into various network structures as shown above.

In conclusion, by a combination of sub-molecularly resolved STM imaging and DFT calculations, we have demonstrated a method to fabricate the surface nanostructures by introducing alkali halide NaCl onto the surface, in which both alkali metals and halogens interact with different sites of target molecules resulting in structural formation in a synergistic way. Owing to the intrinsic properties of the electrostatic interaction, the formed metal–organic motifs can be linked by halogens in a variety of fashions thus demonstrating structural diversity. More importantly, such a method may be extended to other more general cases to study the fundamental physical properties like those of alkali/halogen doped polyacetylene.

There are no conflicts of interest to declare.

The authors acknowledge financial support from the National Natural Science Foundation of China (21473123, 21622307, 51403157).

Notes and references

- 1 Y. Yang and C. Wang, Chem. Soc. Rev., 2009, 38, 2576.
- 2 N. Lin, S. Stepanow, M. Ruben and J. V. Barth, Top. Curr. Chem., 2008, 287, 1.
- 3 Y. Zhang, Y. Luo, Y. Zhang, Y. J. Yu, Y. M. Kuang, L. Zhang, Q. S. Meng, Y. Luo, J. L. Yang, Z. C. Dong and J. G. Hou, *Nature*, 2016, **531**, 623.
- 4 J. I. Urgel, D. Écija, G. Lyu, R. Zhang, C. A. Palma, W. Auwärter, N. Lin and J. V. Barth, *Nat. Chem.*, 2016, **8**, 657.
- 5 L. Cai, Q. Sun, M. Bao, H. Ma, C. Yuan and W. Xu, *ACS Nano*, 2017, 11, 3727.
- 6 Y. Yu, Y. Zheng and S. Lei, J. Phys. Chem. C, 2017, 121, 593.
- 7 L. Cao, L. Xu, D. Zhao, K. Tahara, Y. Tobe, S. De Feyter and S. Lei, *Chem. Commun.*, 2014, **50**, 11946.
- 8 S. Stepanow, R. Ohmann, F. Leroy, N. Lin, T. Strunskus, C. Woll and K. Kern, *ACS Nano*, 2010, 4, 1813.
- 9 W. Xu, J. G. Wang, M. Yu, E. Lægsgaard, I. Stensgaard, T. R. Linderoth, B. Hammer, C. Wang and F. Besenbacher, J. Am. Chem. Soc., 2010, 132, 15927.
- 10 W. Xu, Q. Tan, M. Yu, Q. Sun, H. Kong, E. Lægsgaard, I. Stensgaard, J. Kjems, J. G. Wang, C. Wang and F. Besenbacher, *Chem. Commun.*, 2013, **49**, 7210.
- 11 L. Xie, C. Zhang, Y. Ding and W. Xu, Angew. Chem., Int. Ed., 2017, 56, 5077.
- 12 D. Skomski, S. Abb and S. L. Tait, J. Am. Chem. Soc., 2012, 134, 14165.
- 13 D. Skomski and S. L. Tait, J. Phys. Chem. C, 2013, 117, 2959.
- 14 T. K. Shimizu, J. Jung, H. Imada and Y. Kim, *Angew. Chem.*, 2014, **126**, 13949.
- 15 C. Zhang, L. Wang, L. Xie, H. Kong, Q. Tan, L. Cai, Q. Sun and W. Xu, *ChemPhysChem*, 2015, **16**, 2099.
- 16 C. Wäckerlin, C. Iacovita, D. Chylarecka, P. Fesser, T. A. Jung and N. Ballav, *Chem. Commun.*, 2011, 47, 9146.
- 17 H. Kong, L. Wang, Q. Tan, C. Zhang, Q. Sun and W. Xu, Chem. Commun., 2014, 50, 3242.
- 18 B. E. Hirsch, K. P. McDonald, B. Qiao, A. H. Flood and S. L. Tait, ACS Nano, 2014, 8, 10858.
- 19 J. Lu, D. L. Bao, H. Dong, K. Qian, S. Zhang, J. Liu, Y. Zhang, X. Lin, S. Du, W. Hu and H. J. Gao, *J. Phys. Chem. Lett.*, 2016, 8, 326.
- 20 J. Repp, G. Meyer, S. M. Stojković, A. Gourdon and C. Joachim, *Phys. Rev. Lett.*, 2005, **94**, 026803.
- 21 B. Such, G. Goryl, S. Godlewski, J. J. Kolodziej and M. Szymonski, Nanotechnology, 2008, 19, 475705.
- 22 P. Liljeroth, J. Repp and G. Meyer, Science, 2007, 317, 1203.
- 23 C. Zhang, L. Wang, L. Xie, Y. Ding and W. Xu, Chem. Eur. J., 2016,
- 23, 2356.
 24 C. Zhang, L. Xie, L. Wang, H. Kong, Q. Tan and W. Xu, J. Am. Chem. Soc., 2015, 137, 11795.