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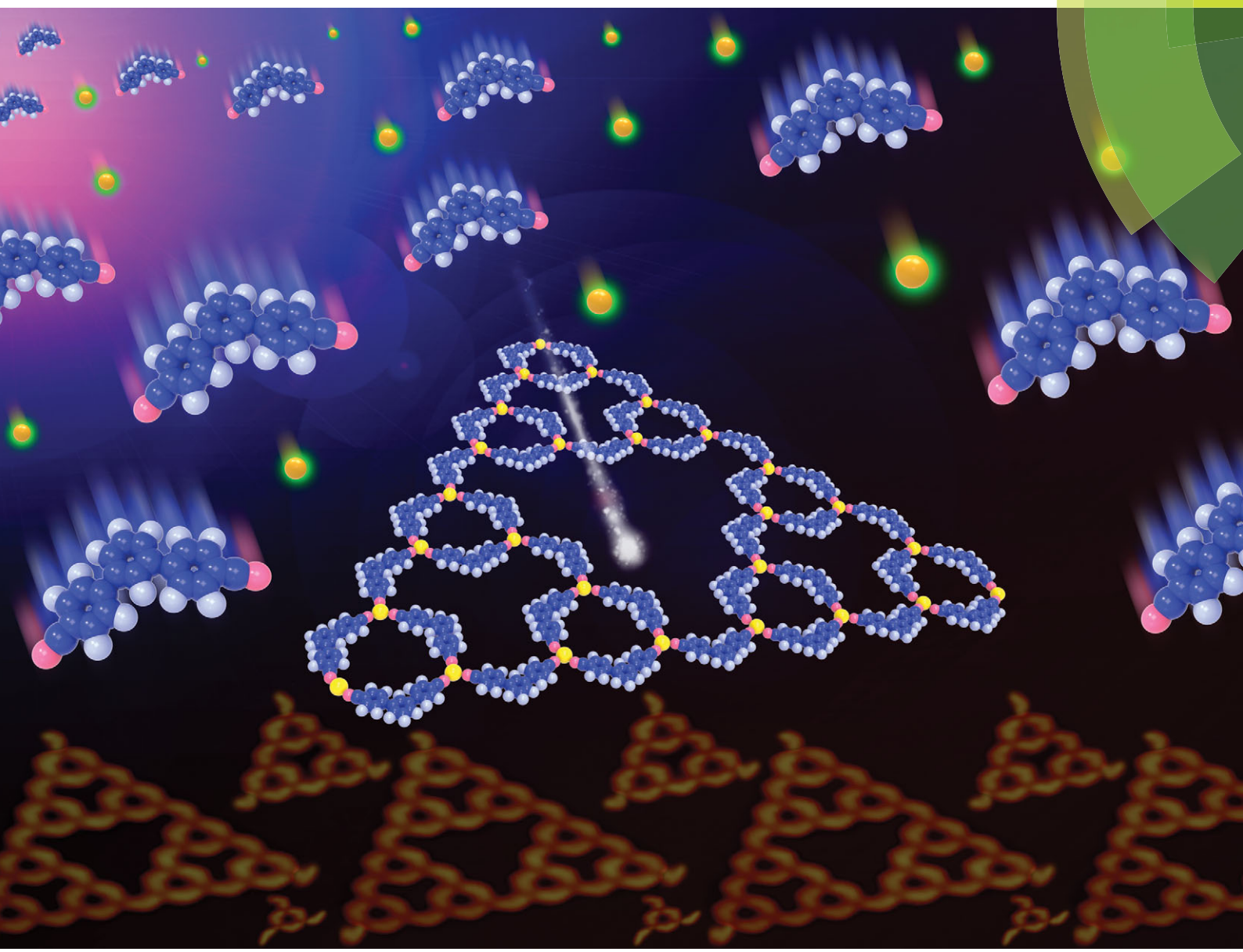

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On-surface construction of a metal–organic Sierpiński triangle†

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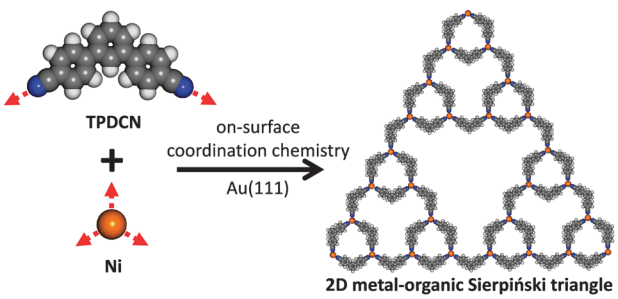
Through a careful design of the molecular precursor we have successfully constructed the metal–organic Sierpiński triangles on Au(111) *via* on-surface coordination chemistry, which is demonstrated by the interplay of high-resolution STM imaging and DFT calculations. The coordination Sierpiński triangles show high stabilities as evidenced by room temperature STM imaging, and could withstand a thermal treatment up to 450 K.

The formation of well organized patterns is ubiquitous and of utmost importance in pure art, mathematics, science and technology. In the last two decades, on-surface supramolecular chemistry has been rapidly developed and provided an efficient strategy for constructing a variety of low dimensional regular patterns.[1,2] For instance, molecular self-assembly protocols have been applied to achieve molecular chains,[3,4] polygon structures,[5–9] regular surface tessellations,[10–12] and Archimedean tessellation of the Kagome Lattice[13,14] and snub square tiling.[15] Fractals, which exhibit a self-similar nature at every scale, are one of the most fascinating patterns arousing the particular interest of artists and scientists. Fractals could be usually found in nature in the form of snowflakes, mountains, clouds, lightning, waterfall, leaves and trees, *etc.* Progress in the formation of molecular fractals has mainly been put forward in synthetic chemistry,[16–18] while construction of molecular fractals through the on-surface molecular self-assembly strategy is still challenging. Most recently, a molecular Sierpiński triangle fractal stabilized by synergistic halogen bonding and hydrogen bonding has been successfully fabricated on Ag(111).[19] However, a strict low-temperature window is mandatory for the formation and stabilization of the molecular fractal owing to the intrinsically weak intermolecular interactions and the relatively fragile C–Br bond characteristic on the surface. Thus, it would be of utmost importance to develop new strategies to construct more robust molecular fractals in a relatively facile manner.

Metal–organic interactions provide an alternative avenue for the formation of surface coordination nanostructures with selectivity, directionality and appreciably high bonding strengths.[20,21] As inspired by a recent literature,[22] we have synthesized a 120° ditopic organic molecule with carbonitrile endgroups capable of coordinating with transition metals.[12,23] The nickel atom and the Au(111) surface are chosen to fulfill the threefold coordination symmetry.[7,9,24] Here, from the interplay of high-resolution STM imaging and DFT calculations we demonstrate the formation of the metal–organic Sierpiński triangle on Au(111) as schematically shown in Scheme 1. The formed coordination Sierpiński triangle shows a high stability (compared with the self-assembled Sierpiński triangle[19]) as evidenced by room temperature (RT) STM imaging, and could withstand a thermal treatment up to 450 K. The successful construction of the metal–organic Sierpiński triangle shows the versatility of on-surface coordination chemistry in fabricating novel and complicated low-dimensional patterns.

As shown in Fig. 1a and b, deposition of TPDCN on Au(111) at RT results in the formation of chain-like structures, which are stabilized by the intermolecular hydrogen bonding between



Scheme 1 The space-filling models of the 120° ditopic carbonitrile linker (TPDCN), the nickel atom (Ni), and the coordination Sierpiński triangle. The red arrows indicate the directional metal–organic interactions. N: blue, C: gray, H: white and Ni: orange.

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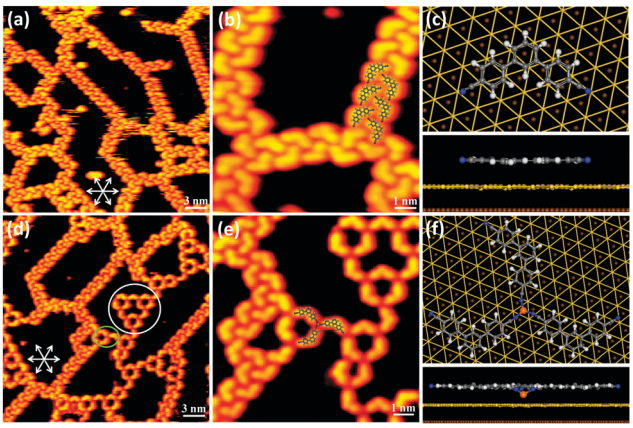

Fig. 1 (a) and (b) STM images of the self-assembled chain structures formed by the TPDCN molecules on Au(111). The scaled gas-phase model showing the hydrogen bonding configuration (CH···N) is superimposed on the close-up STM image in (b). (c) Top and side views of the DFT optimized model of the TPDCN molecule adsorbed on Au(111). (d) and (e) STM images show the appearance of the coordination structures after depositing a small amount of Ni atoms on the TPDCN covered surface. The elementary coordination motif (a heterotactic fan blade structure) is indicated by a green circle, and a first generation Sierpiński triangle is indicated by a white circle in (d). The scaled calculated model of the elementary motif is superimposed on the close-up STM image in (e). (f) Top and side views of the DFT optimized model of the elementary motif $(TPDCN)_3Ni_1$ in heterotactic form on Au(111). The close-packed directions of Au(111) are indicated by the white arrows in (a) and (d).

the carbonitrile groups and the phenyl groups (CH···N) as also commonly observed in other surface self-assemblies.[25–27] The DFT-optimized gas-phase model of the chain structure is overlapped on the STM image (Fig. 1b) to demonstrate the molecular arrangements and the hydrogen bonding scheme. By relaxing a single TPDCN on Au(111) as shown in Fig. 1c we identify that the molecule adopts a flat-lying geometry on the surface. Interestingly, as shown in Fig. 1d and e, after deposition of a small amount of Ni atoms on the TPDCN pre-covered surface, a portion of chain structures evolves into metal–organic coordination structures where the elementary motif (indicated by the green circle) is identified as a threefold structure, and more excitingly, such a motif is just the node of the expected metal–organic Sierpiński triangle,[22] and the first generation Sierpiński triangle has been already presented on the surface (indicated by the white circle). Note that the herringbone reconstruction of Au(111) remains unchanged following adsorption of the molecular and/or metallic species.

A closer inspection of the elementary coordination motifs allows us to distinguish that most of them are in the form of heterotactic fan blade structure (the difference between the homotactic and heterotactic arrangements is shown in Fig. S1, ESI†). To get further insight into the elementary motifs, DFT calculations have been performed on both heterotactic and homotactic forms on Au(111) (Fig. 1f and Fig. S1, ESI†). In both motifs, the Ni atoms are located below the molecular plane and with a height of ~1.84 Å above the surface plane. The nitrogen atoms are tilted downwards when coordinating with the Ni atom, and the bond lengths of N···Ni are ~1.93 Å. Moreover, the heterotactic and homotactic motifs are almost equally stable on Au(111). Thus, we speculate that the preferential formation of heterotactic motifs possibly originates from the entropic effect as also proposed in the literature,[22,28] which should be the key to the development of the Sierpiński triangle subsequently. Note that the Sierpiński triangles are achiral due to the almost achiral nodes within the triangles.

Astonishingly, by delicately regulating the dosage of Ni atoms we have succeeded in constructing different generations of metal–organic Sierpiński triangles on Au(111) as indicated in Fig. 2. Two kinds of typical molecular Sierpiński triangles, *i.e.* first generation and second generation (highlighted by green and blue triangles in Fig. 2a, respectively), are experimentally observed. The first generation consists of 15 TPDCN monomers and 9 Ni atoms and the second generation consists of 42 TPDCN monomers and 27 Ni atoms, as shown in Fig. 2c and d, respectively. Moreover, the zero generation is also highlighted by a red triangle in Fig. 2a and illustrated in Fig. 2b. It is noticeable that the metal–organic Sierpiński triangles could withstand a thermal treatment up to ~450 K, which thus shows a much higher stability than the halogen bonded molecular Sierpiński triangle.[19] Several experimental parameters including the molecular coverage (Fig. S2, ESI†), annealing temperature and duration, and cooling rate have been tried with the aim of growing even higher generation fractals, however, due to the strict structural requirements of the Sierpiński triangle, only the incomplete third generation was obtained (Fig. S3, ESI†).

To test the stability of the metal–organic fractals we have scanned the sample at RT. As indicated in Fig. 3, during scanning the first and second generation Sierpiński triangles remain intact. Moreover, the fast-scanning characteristic of

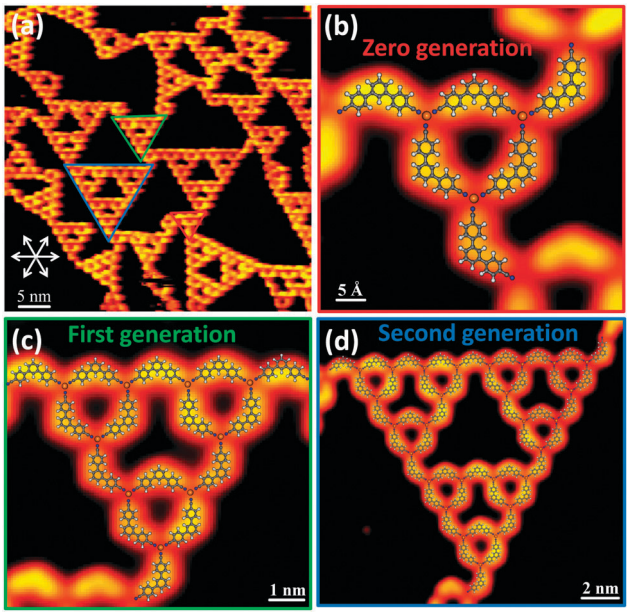

Fig. 2 (a) STM images showing the formation of the metal–organic Sierpiński triangles after codeposition of TPDCN molecules and Ni atoms on Au(111). (b)–(d) High-resolution STM images of zero, first, and second generation Sierpiński triangles with the theoretically proposed models.

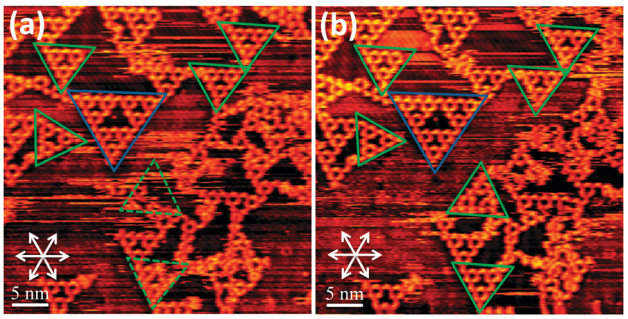

Fig. 3 (a) and (b) Two successive STM images scanned in the same region at a time interval of 10 seconds at 300 K, which shows the high stability of the first and second generation Sierpiński triangles (indicated by green and blue solid triangles), and the spontaneous formation of the first generation Sierpiński triangles (indicated by green dashed triangles in (a) and the corresponding solid triangles in (b)).

''Aarhus STM'' allows us to catch the surface dynamic processes where the spontaneous formation of the first generation Sierpiński triangles is observed, and there are no further changes thereafter.

In conclusion, by a careful design of the molecular precursor we have successfully constructed the robust metal–organic Sierpiński triangles *via* on-surface coordination chemistry. The high stability and the incorporation of metal atoms in such a fascinating fractal structure could be useful in related areas such as redox, photochemistry, and magnetics. Further work on designing other molecular precursors and regulating the interplay with different metal atoms with the aim of fabricating higher generations of Sierpiński triangles and other kinds of molecular fractals is underway.

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