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Self-assembling metal–organic coordinated fractal crystals



Fractals are essentially characterized by their self-similarity at different scales and non-integer Hausdorff dimensions [1], while crystals always show certain symmetries and discrete diffraction diagrams [2]. Thus, a fractal crystal by definition must be identical at all scales with a compatible symmetry with crystals. Although fractals, e.g. snowflakes, trees, coastlines and blood-vascular systems, are everywhere in nature, irregular molecular fractals that form through the diffusion-limited aggregation process [3] and exhibit quasi or statistical self-similarity are not fractal crystal. It remains a great challenge to synthesize perfect molecular fractal crystals that duplicate symmetric fractal patterns, such as the famous C_{3v} -symmetric Sierpiński triangle (ST) and C_{4v} -symmetric Sierpiński carpet [1]. Recently, Yongfeng Wang and coworkers reported the first success in constructing extended and defect-free fractal crystal resembling to ST via self-assembly of small molecular building blocks on a silver surface at cryogenic temperature [4]. As these STs were essentially stabilized by cyclic halogen bonds between the molecular building blocks, one may immediately raise a question: Is that possible to construct similar ST fractal crystals with other types of intermolecular coupling, such as hydrogen bonding, covalent bonding and metal–organic coordination? Now, as they report in Chinese Chemical Letters [5], Yongfeng Wang and collaborators give a positive answer: They have demonstrated the formation of perfect metal–organic coordinated ST fractal crystal by the spontaneous self-assembly of small molecular building blocks and iron atoms on a gold surface in ultrahigh vacuum at elevated temperature.

To fabricate such remarkable metal–organic coordinated ST fractal crystal, Wang and coworkers carefully choose desirable molecular building blocks with proper shape and functional groups based on the concept of crystal engineering. The experience of synthesizing halogen-bonded ST indicates that the molecular building blocks should have “V”-shaped backbones and form 3-fold nodes. Thus, the 120° tick-shaped 4,4'-dicyano-1,1':3,1'-terphenyl (C3PC) molecules are adopted, each having two cyano groups that favor the formation of 3-fold bonds with iron atoms [6]. The C_{3v} -symmetric Au(111) substrate coincides with the symmetry of ST. Co-deposition of the C3PC molecules and iron atoms on Au(111) surface with subsequent annealing in ultrahigh vacuum indeed results in the formation of perfect metal–organic coordinated ST fractal crystal with C_{3v} point group. State-of-the-art scanning tunneling microscopy measurements and density functional theory calculations reveal that each node of the ST fractal crystal consists of an iron atom and three surrounding molecules. The entire ST fractal crystal is stabilized by the 3-fold bonds formed between the molecular cyano groups and iron atoms. As the molecules are aligned with the $\langle 11\bar{2} \rangle$ directions of the substrate, the ST

fractal crystal exhibits a discrete diffraction pattern with the C_{3v} symmetry.

This amazing spontaneous assembly cannot be achieved without an efficient error-correction mechanism. Three C3PC molecules coordinated with an iron atom may be arranged in a heterotactic or homotactic fashion. As the probability for the heterotactic node formation is about three times larger than that for the homotactic node, any unwanted homotactic node occasionally cooperated in the ST will be eventually eliminated upon annealing. Interestingly, it seems that a delicate control of annealing temperature and cooling rate is not required for the formation of such metal–organic coordinated ST fractal crystal, distinct to previous work of halogen-bonded ST. This is probably due to the strong metal–organic coordination stabilizing the ST fractal crystal.

The synthesis of halogen-bonded and metal–organic coordinated ST fractal crystals with unprecedented complexity and hierarchy is an excellent demonstration of achievement in supramolecular chemistry and on-surface chemistry. Yet, various challenges remain in the design of molecular fractal crystals and their applications: Can we construct hydrogen- or covalent-bonded ST fractal crystals? What about molecular fractal crystals that display 4-fold symmetry, such as the Sierpiński carpet? What new physical and chemical properties may such novel fractal crystals exhibit? Can we functionalize the molecular fractal crystals for applications? The answer to these questions points to the achievement of spontaneous self-assembly in synthetic systems that approaches the elegance and complexity of self-assembled structures in nature and demonstrates its usage in our daily life.

References

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