Assembling molecular Sierpiński triangle fractals

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1. Introduction

1.1. Fractals

- A fractal is "exactly the same at every scale or nearly the same at different scales", as described by French mathematician Benoit B. Mandelbrot.[1]
- Fractal patterns are very complicated and yet fascinating because of their importance in aesthetics, mathematics, science and engineering.

1.2. Building Molecular Fractals

- Only scattered, fragmented untunable molecular fractals was obtained, with strong intermolecular interactions (e.g. covalent or coordination bonds, *Figure 1*).[2,3]
- Extended molecular fractals formed by the self-assembly of small-molecule components were not achieved.

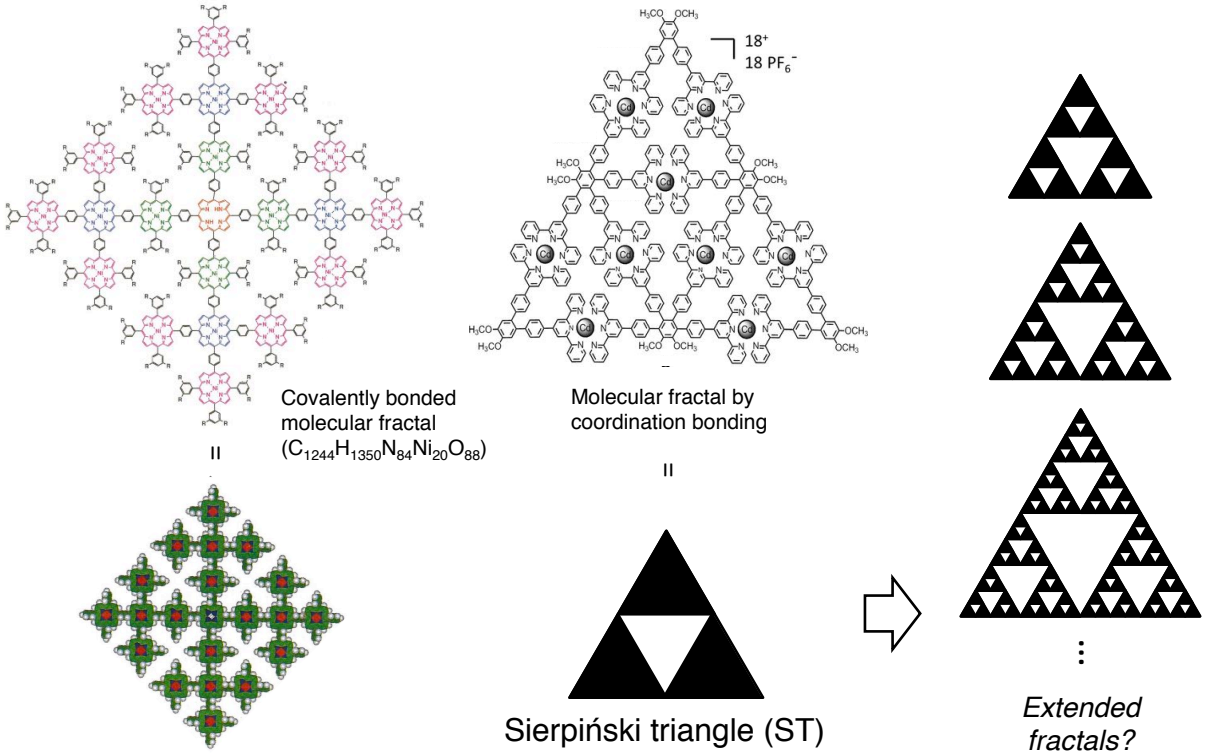

Figure 1. The reported molecular fractals with strong intermolecular interactions.

1.3. This Work

- Preparation of extended planar molecular Sierpiński triangles (STs) on Ag(111) surface was successful.
- Several guidelines for detect-free ST constructions were revealed.

2. Results and Discussion

2.1. Molecular Design

- Previously, the self-assembly of 4,4”-dibromo-*p*-terphenyl into planar porous network was reported through weak halogen bonding (*Figure 2*).[4]
- However, from the previous simulation, it was suggested that V-shaped or star-shaped precursor is required for the fractal formation.[5]
- In this work, **B3PB**, **B4PB** with 120º backbone and bromine atoms were used for molecular ST formation (*Figure 3*).

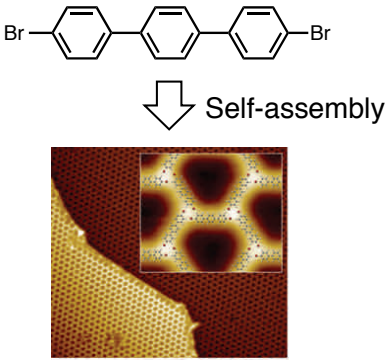

Figure 2. Self-assembly of 4,4”-dibromo-*p*-terphenyl into planar porous network.

2.2. Formation of molecular STs on Ag(111) surface

- After the thermal deposition of **B3PB** or **B4PB** and subsequent cooling down to < 80 K, the Ag(111) surface was covered with the series of triangular structures (*Figure 3*).
- The triangular structures were observed by scanning tunneling microscope (STM).
- The individual molecular STs could be observed.

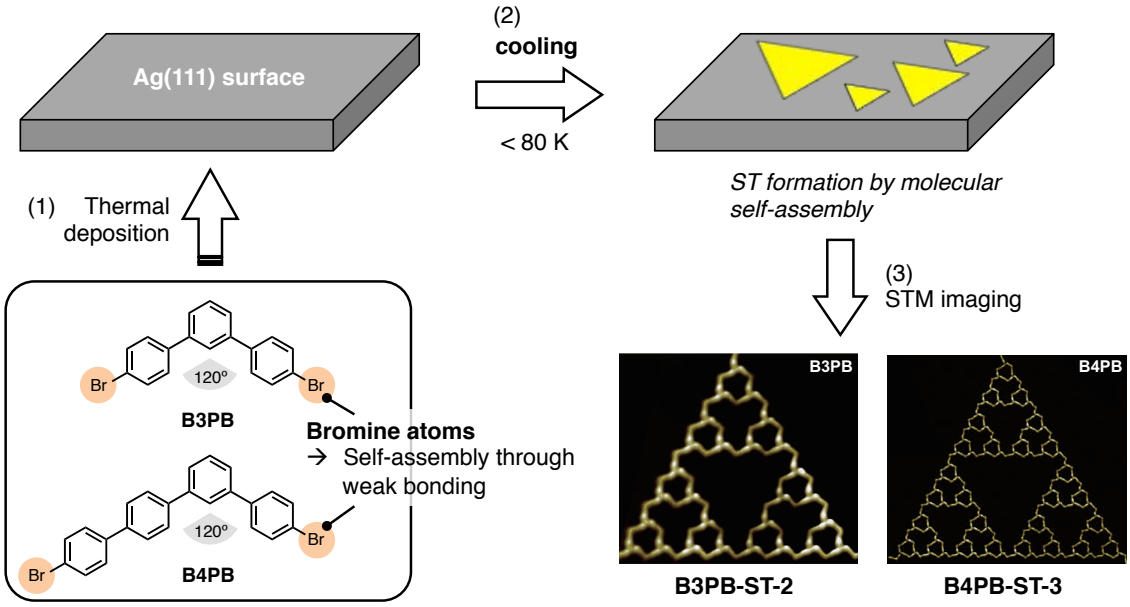

Figure 3. The molecules investigated in this work, and the ST formation through thermal deposition of the molecules on Ag(111) surface.

- Several size of the triangular structures consists of **B4PB** (B4PB-ST-*n*) were observed (*Figure 4*).
- Only imperfect structure was obtained for B4PB-ST-4.
- B4PB-ST-4 is the largest ST achieved in experiments.

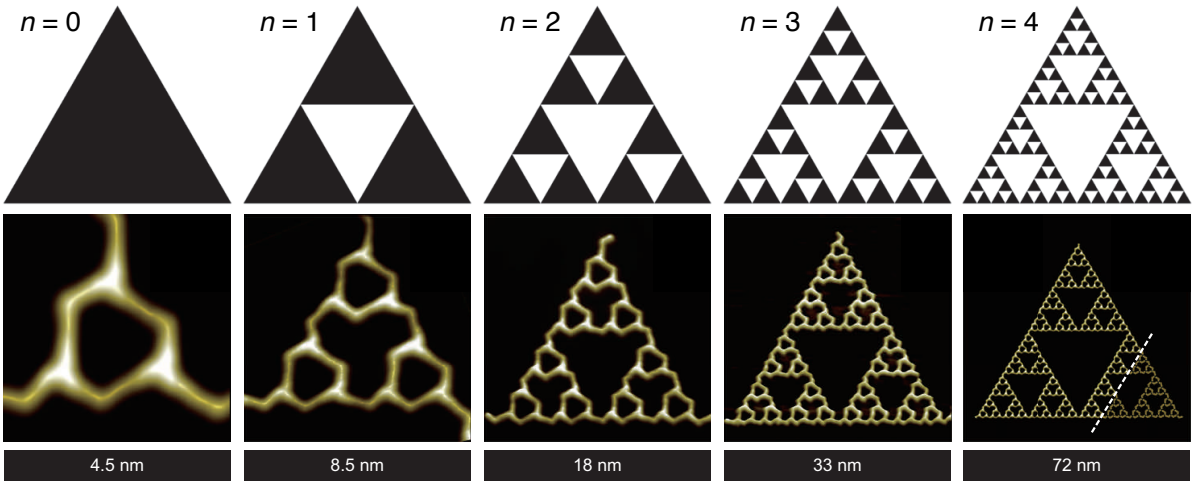

Figure 4. The whole family of the observed B4PB molecular STs. Upper row: models of the STs and the lower row: corresponding STM images of B4PB-ST-*n*. To the missing bottom-right corner of B4PB-ST-4 (separated by the dashed line), the modeled molecules were artificially added for clear illustration.

2.3. Cyclic Halogen Bonding for the Chiral ST Formation

- Chirality was observed in the molecular STs (*Figure 5a*).
- At each node, three **B4PB** molecules cluster with their Br terminals in a cyclic way (*Figure 5b,5c*).
- This cyclic weak halogen and hydrogen bonding was responsible for the formation of the molecular STs.
- This chirality directly relates to the ST orientation with respect to the Ag(111) lattice (*Figure 5d*).

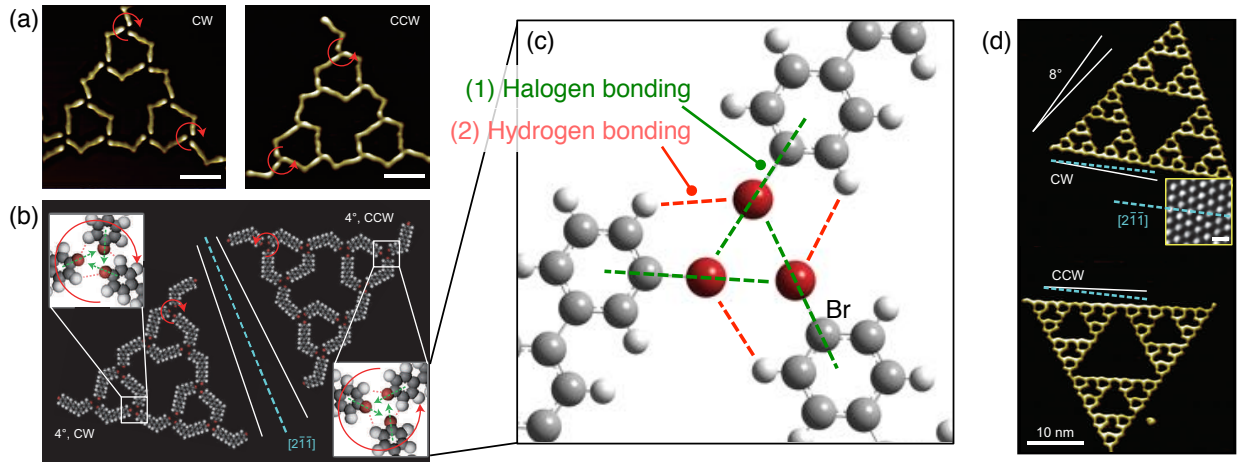

Figure 5. (a) High-resolution STM images of the B4PB-ST-1 enantiomers (CW: clockwise, CCW: counterclockwise). (b) Molecular models for the STM images in (a). (c) Enlarged view of the cyclic halogen bonding node. (d) STM image of a pair of B4PB-ST-3 enantiomers.

2.4. Kinetic Optimization for Large STs

- The cooling rate had great importance for the larger STs (*Figure 6*).
- The slower cooling rate resulted in higher yield of B4PB-ST-3 (highlighted by the yellow triangles).
- The 0.02 K/min cooling rate not only gave 55% B4PB-ST-3 but also induced the formation of incomplete B4PB-ST-4 structures.

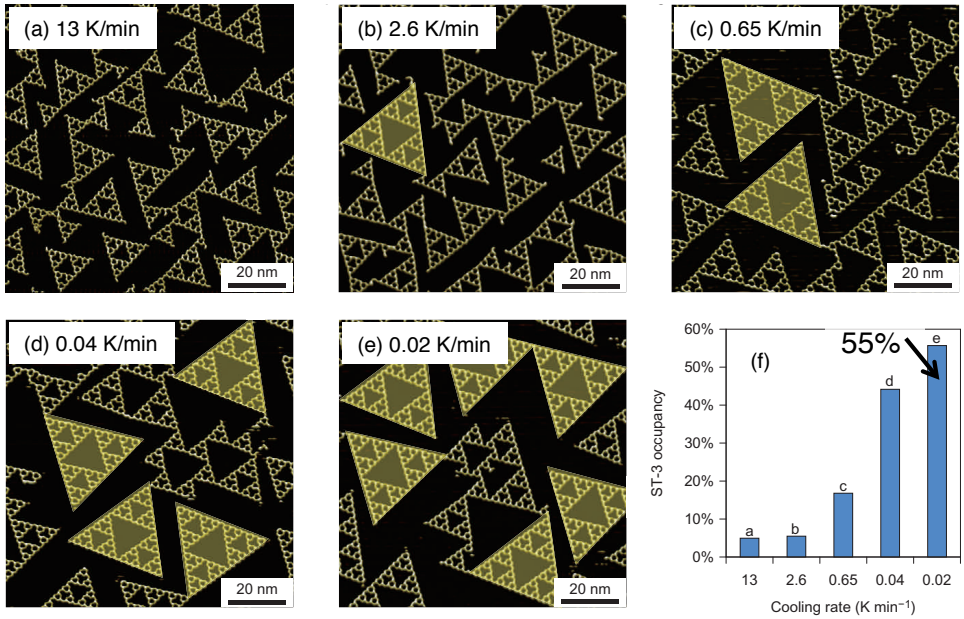

Figure 6. (a-e) Representative STM images of the fractal assemblies prepared at several cooling rate. (f) The histogram of the B4PB-ST-3 occupancy (defined as the percentage of the **B4PB** molecules that form the B4PB-ST-3 structures in total molecules deposited on the substrate).

2.5. Guidelines for the Construction of the Defect-Free ST Fractals

- Several other crucial guidelines were revealed (*Figure 7*).

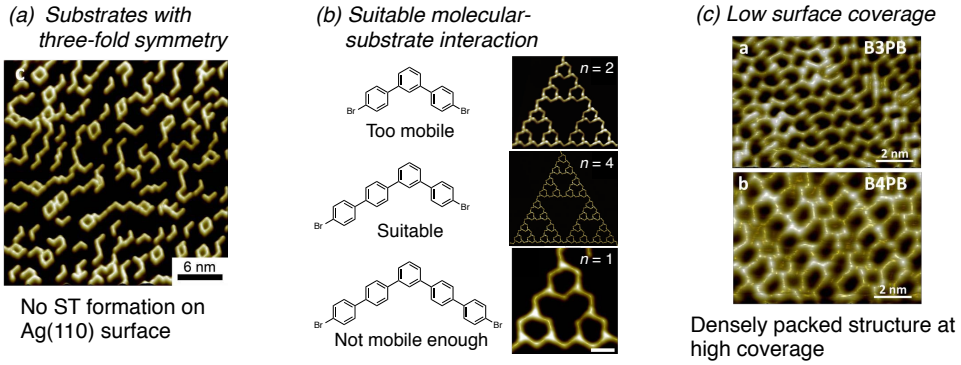

Figure 7. (a) No ST formation on Ag(110) substrate because of the symmetry mismatch. (b) Suitable molecular-substrate interaction for good mobility to form larger STs. (c) Formation of the densely packed structure by high coverage.

3. Conclusion

- The molecularly assembled defect-free STs were successfully fabricated.
- Crucial guidelines to construct detect-free STs and search for new series of ST fractals were obtained.

4. References

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3) Sarkar, R.; Guo, K.; Moorefield, C. N.; Saunders, M. J.; Wesdemiotis, C.; Newkome, G. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 12182.
4) Wang, W.; Shi, X.; Wang, S.; Van Hove, M. A.; Lin, N. *J. Am. Chem. Soc.* **2011**, *133*, 13264.
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