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基于卤键的谢尔宾斯基三角分形自组装的模拟研究

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Simulation Studies of the Self-Assembly of Halogen-Bonded Sierpiński Triangle Fractals

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1.

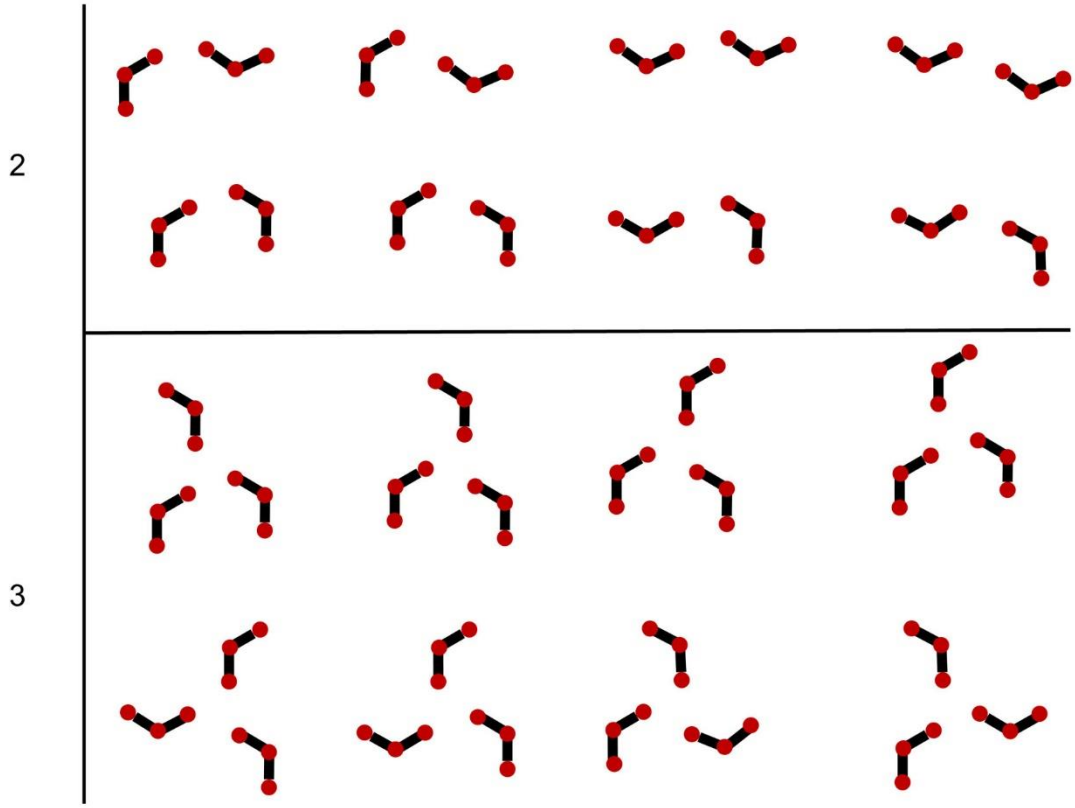

Fig.S1 Possible nodal motifs that can be formed in the adsorbed overlayer composed of molecule A in the simulation

The numbers 2 and 3 in the figure denote the nodal motifs composed of two molecules and three molecules, respectively.

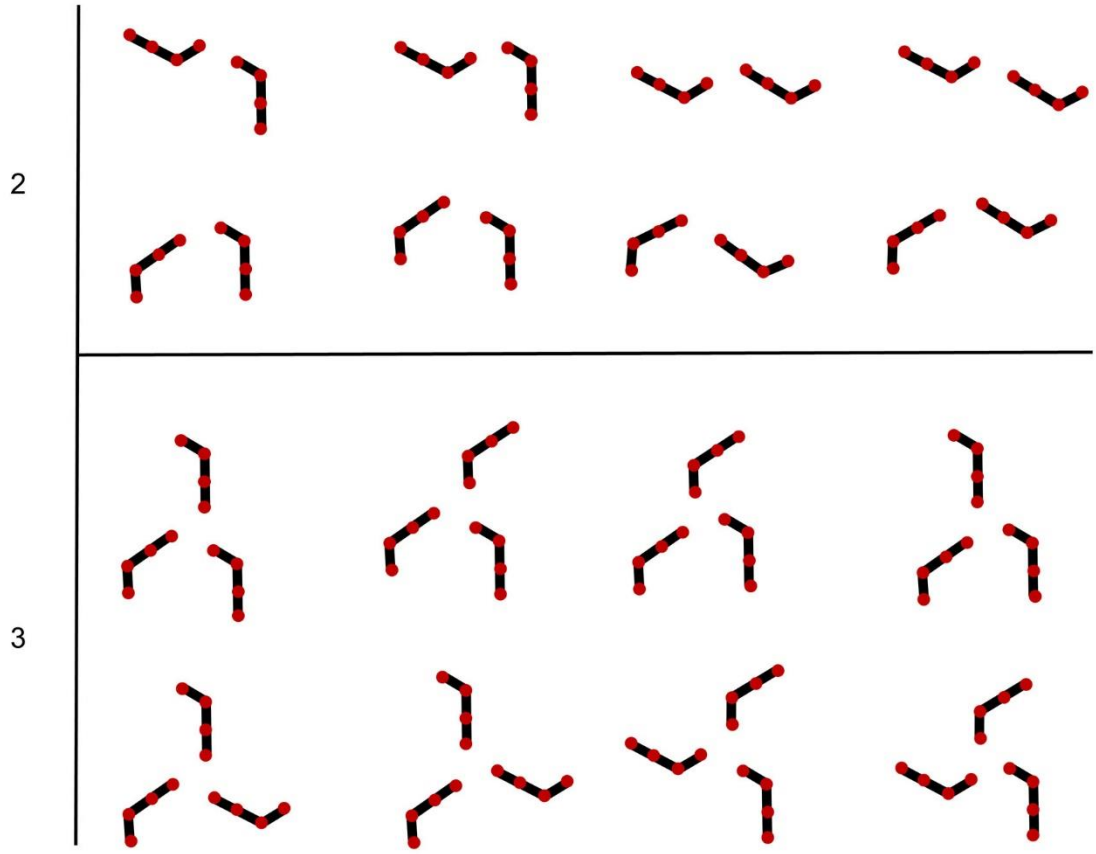

Fig.S2 Possible nodal motifs that can be formed in the adsorbed overlayer composed of molecule B_L in the simulation

The numbers 2 and 3 in the figure denote the nodal motifs composed of two molecules and three molecules, respectively.

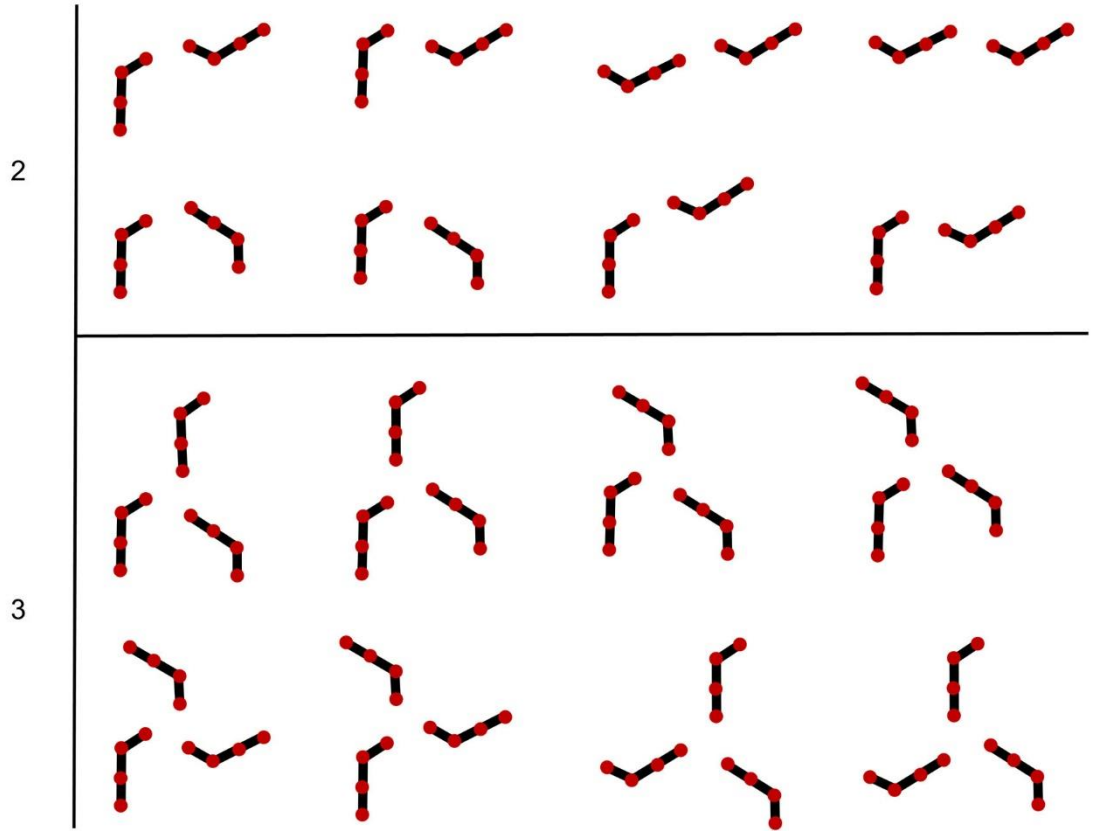

Fig.S3 Possible nodal motifs that can be formed in the adsorbed overlayer composed of molecule B_R in the simulation

The numbers 2 and 3 in the figure denote the nodal motifs composed of two molecules and three molecules, respectively.

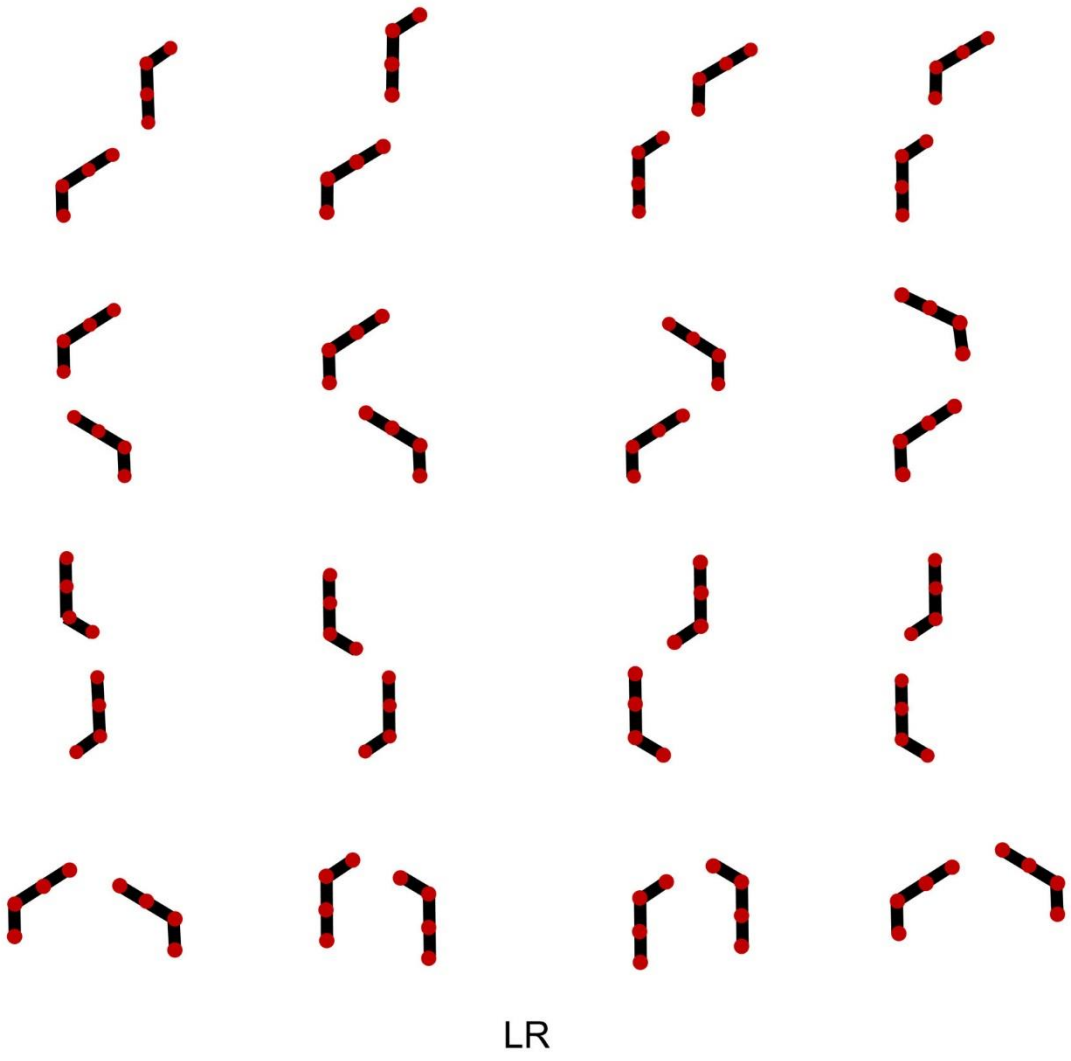

Fig.S4 Possible nodal motifs that can be formed in the adsorbed overlayer composed of molecules $\mathbf{B_L}$ and $\mathbf{B_R}$ in the simulation

Each nodal motif comprises both enantiomers of B.

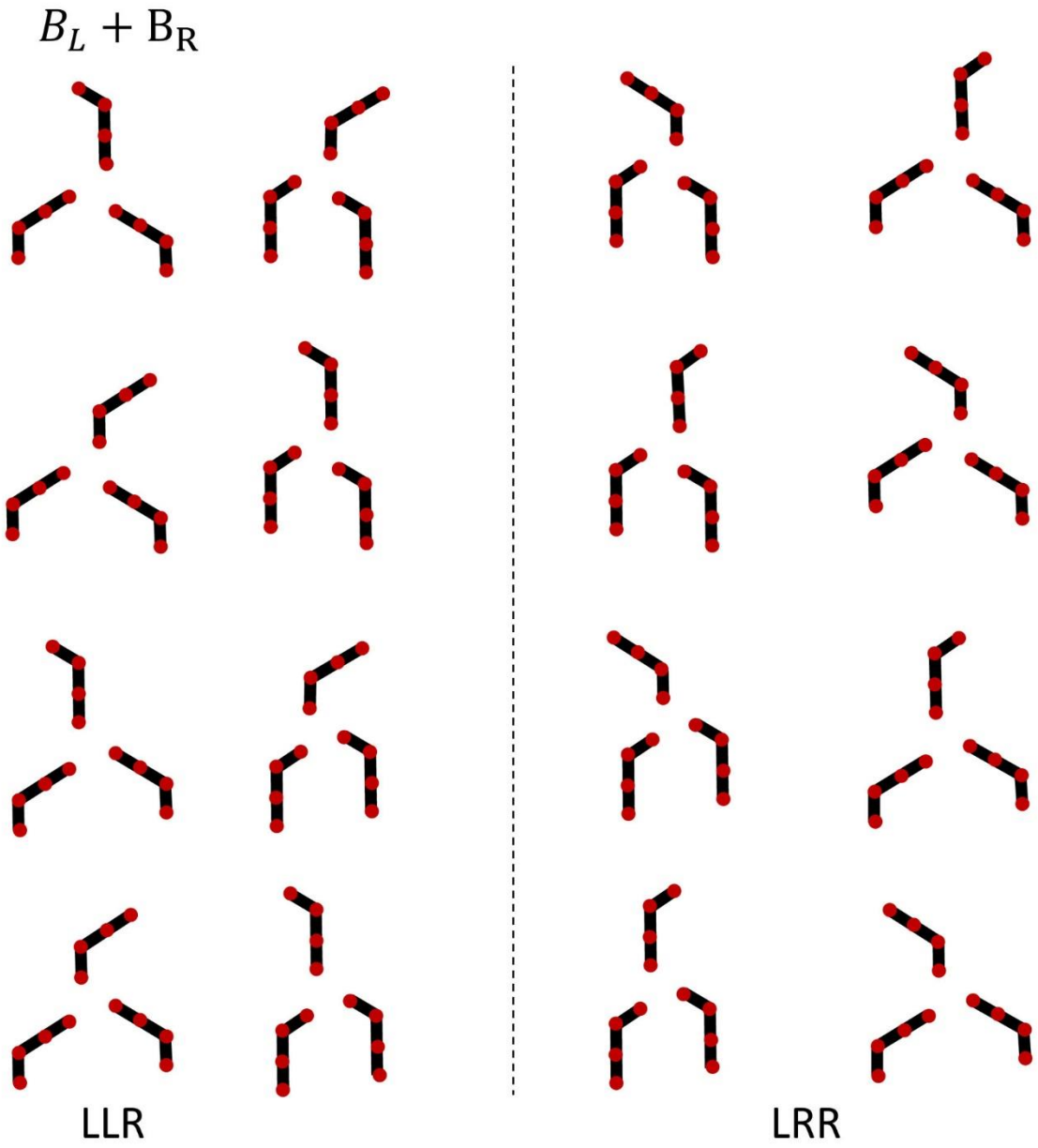

Fig.S5 Additional to Fig.S2, Fig.S3, and Fig.S4, possible nodal motifs that can be formed in the adsorbed overlayer composed of molecules $\mathbf{B_L}$ and $\mathbf{B_R}$ in the simulation

The dashed line represents the mirror plane.

2.

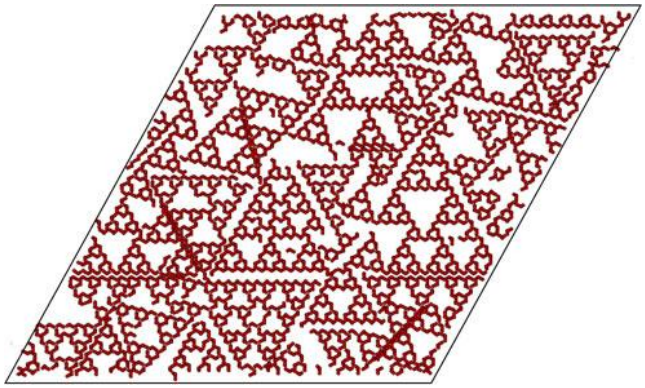

Fig.S6 Snapshot of the adsorbed overlayer composed of 1600 molecules of B_L on 300×300 grids with $T = 0.2$, $\varepsilon_a = -1$, $\varepsilon_r = 0.5$

3. The snapshots of the adsorbed overlayer under different temperature

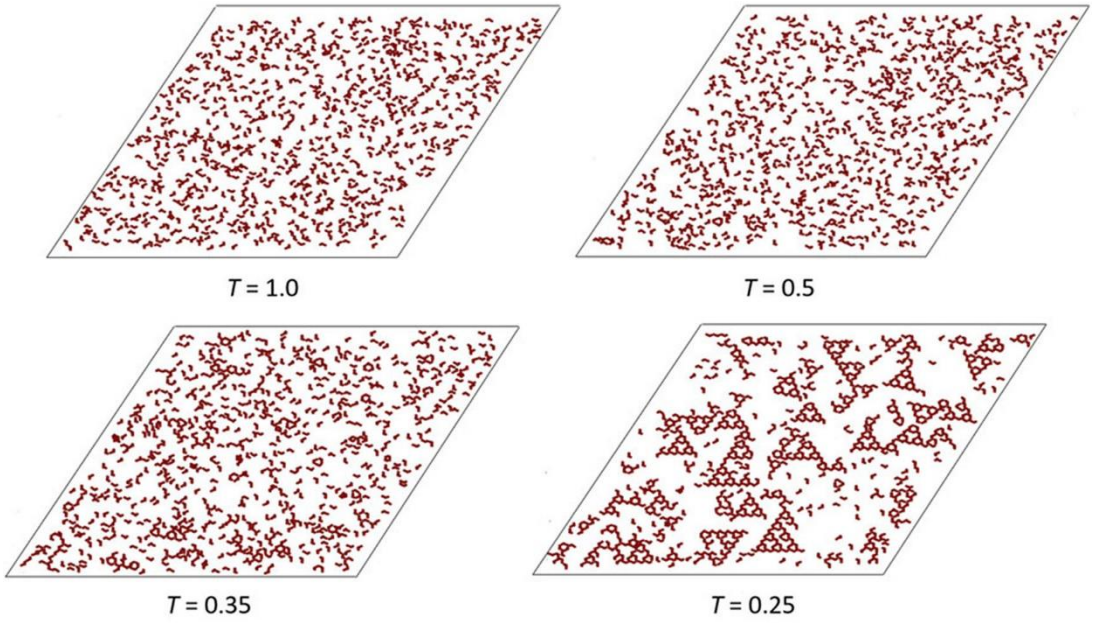

Fig.S7 Four snapshots of the adsorbed overlayer comprising 800 molecules of B_L on 300×300 grids under different temperatures, with the parameters $\varepsilon_a = -1, \varepsilon_r = 0.5$

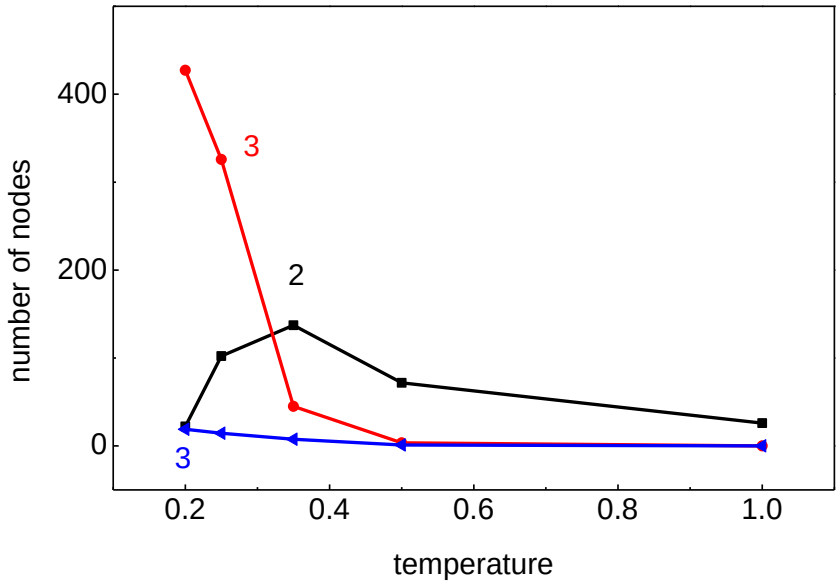

Fig.S8 Number of n-fold nodes (n is 2 or 3, shown in the corresponding color) for molecule $\mathbf{B_L}$ as a function of temperature

The results are averages over 10 independent MC runs. The number of nodes for the two-fold are plotted using black square, the heterotactic three-fold nodes using red dot, and the windmill-like three-fold nodes using blue triangular.

4. Density functional theory

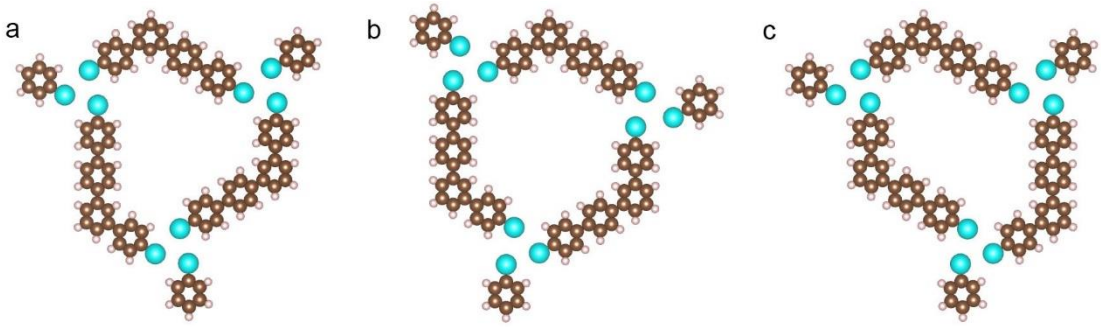

Fig.S9 The interaction energy of three molecular models was calculated by density functional theory (DFT), where $\Delta E_{ba} = 2.5\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta E_{ca} = 1.3\ \mathrm{kJ \cdot mol^{-1}}$

5.

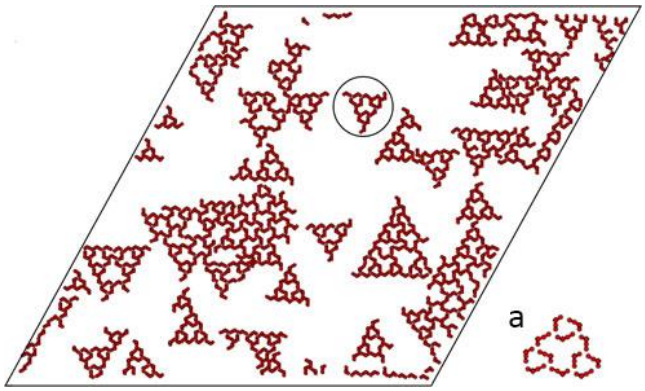

Fig.S10 A snapshot of the system composing 800 molecules of B_L and B_R with the ration of 1:1

The magnified fragment shows the fractal structure with one type of handedness with the ratio of B_L and B_R as 1:3.

6. The schematic diagram of porous network

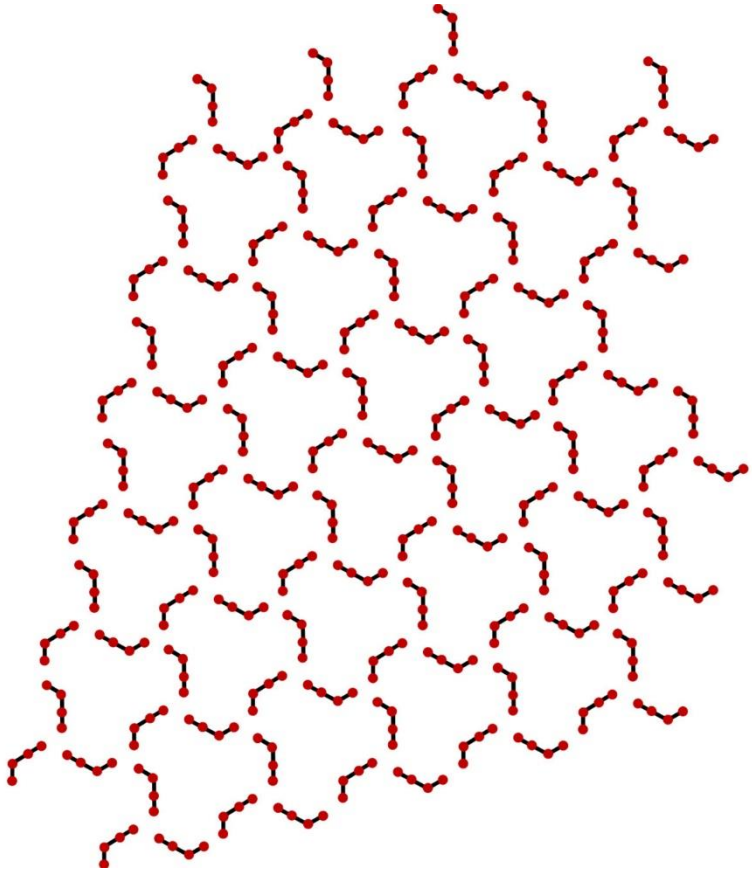

Fig.S11 The schematic diagram of porous network comprising of 100 molecules B_L

7. Estimation of the free energies of the porous network (Fig.7(a)) and the fractal

structure (Fig.7(b)).

We compare the relative stability of the two states. We calculated their free energies by $F = -k_b T ln Z$, where k_b is Boltzmann constant, *T* is the temperature, Z is the partition function. The free energy difference is $\Delta F = -k_b T ln Z_A - (-k_b T ln Z_B)$, where $Z_A = \sum_{i=1}^{m} e^{-\beta E_i}$ and $Z_B = \sum_{i=1}^{n} e^{-\beta E_i}$ are partition function of state A and state B, respectively, m and n are the number of microscopic configurations of the same energy for each state, respectively. Therefore,

$$\Delta F = F_A - F_B$$

$$= -k_b T ln\left(\sum_{i=1}^{m} e^{-\beta E_i}\right) - \left(-k_b T ln\left(\sum_{i=1}^{n} e^{-\beta E_i}\right)\right)$$

$$= -k_b T ln\left(m e^{-\beta E_A}\right) - \left(-k_b T ln\left(n e^{-\beta E_B}\right)\right)$$

$$= E_A - k_b T ln(m) - (E_B - k_b T ln(n)),$$

where E_A, E_B denote the energy of state A , state B, respectively.

For the porous network (state A), six molecules form a cycle pattern in which every two neighbouring molecules form a two-fold node (Fig. 7(a)). Thus, the number of the two-fold node formed by six molecules is six. When another molecule attached to one of the six accessible points, due to the asymmetric feature of molecule B there are two possibilities. So if six molecules attached to the six accessible points, the number of the configurations is 2^6. Due to the three fold of the cycle, we need to exclude repeating configurations and fractal-like configurations.

The clockwise pattern should be taken into consideration, when we calculate the number of configuration formed by 12 molecules B_L .The total number of configurations is $\Omega = 22$. The interaction energy of the system is $E = -18$. Thus the free energy of the porous network is ~-18.62 with the temperature $T = 0.2$.

For the fractal structure (state B), the total number of configurations is $\Omega = 2$, the interaction energy of the system is $E = -21$. The value of the free energy is

about ~-21.14.

The free energy difference is $\Delta F = F_{\mathrm{A}} - F_{\mathrm{B}} \sim 2.52$. It shows that the building blocks of the fractal structure are indeed thermodynamically more stable.