

Electronic Supplementary Information

Chiral and fractal: from simple design rules to complex supramolecular constructs

Damian Nieckarz^a and Paweł Szabelski^{b*}

^a*Supramolecular Chemistry Laboratory, University of Warsaw,*

Biological and Chemical Research Centre,

Ul. Żwirki i Wigury 101, 02-089 Warsaw, Poland

^b*Department of Theoretical Chemistry, Maria-Curie Skłodowska University,*

Pl. M.C. Skłodowskiej 3, 20-031 Lublin, Poland.

1. Details of the MC simulation

In the simulations we used the same MC algorithm as that described in our previous works.^{5,6,8,10} The calculations were performed on a 200 by 200 triangular lattice whose vertices were treated as equivalent adsorption sites. Periodic boundary conditions in both planar directions were used to eliminate edge effects. The molecules were treated as rigid planar structures composed of seven (**A**, **K**) and four (**s**) interconnected segments each of which was allowed to occupy one adsorption site. As the simulations were performed in the canonical ensemble, the number of molecules N , system size $L=200$ and temperature, T were fixed. The simulation started with N molecules of a given type (**A**, **K**, **s**) randomly distributed on the surface and having random in-plane orientation matching symmetry of the lattice. Next a molecule was picked up at random and its energy in the actual configuration, U_o was calculated by summing out segment-segment interactions between neighboring molecules. Such interaction was possible only when the active segments (red) of a pair of molecules occupied neighboring adsorption sites and, more importantly, the associated interaction directions were collinear (see the arrows in Fig.1). In this case the contribution to U_o was equal to ϵ ; in the remaining situations it was equal to zero. Next an attempt was made to move the molecule over the surface. To that end the molecule was randomly translated and rotated by a multiple of 60 degrees. The selected molecule was inserted in the new position only when the corresponding lattice sites therein were unoccupied. If it was the case, the energy of the molecule, U_n was calculated again using the same procedure as for U_o ; otherwise the trial ended and the molecule was left in the original position. According to the Metropolis

sampling scheme, to accept the new molecular configuration the associated probability $p = \min[1, \exp(-\Delta U / kT)]$ where $\Delta U = U_n - U_o$ was calculated and compared with uniformly distributed random number, r . If $r < p$ the new configuration was accepted; otherwise the molecule remained in the old position. The above sequence defines one MC step which is an elementary “time unit” in the simulations. To equilibrate the investigated systems we used typically $N \times 10^6$ MC steps of which last 10% were taken for averaging. To minimize the risk of trapping the adsorbed overlayer in metastable states we additionally slowly cooled it down starting from $T = 1.0$ down to $T = 0.01$ within 1000 intervals of equal length. The results presented in Fig. 3 are averages over ten system replicas.

2. Additional results and schemes

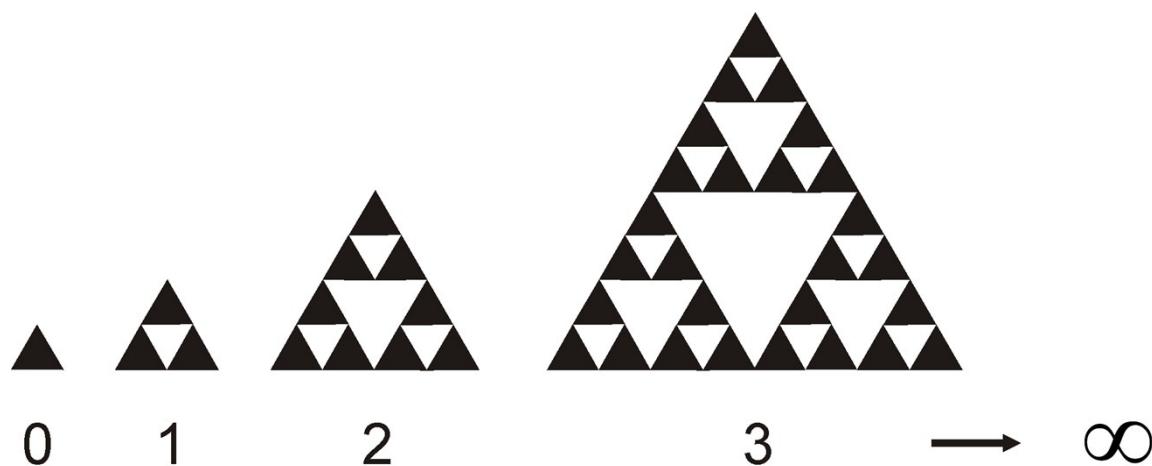


Figure S1. Construction of the Sierpiński triangle based on multiplication and assembly of composite elements. In the first step of the construction the input equilateral triangle (0) is triplicated and the resulting triangles are glued at vertices to form the larger triangle (1). In the next step the unit (1) is again triplicated and glued with its two copies to form (2). If the procedure is repeated infinitely many times one arrives at the Sierpiński triangle which is a self-similar deterministic fractal. A distinctive property of this geometric set is that any magnified fragment of the triangle is similar to the whole object.

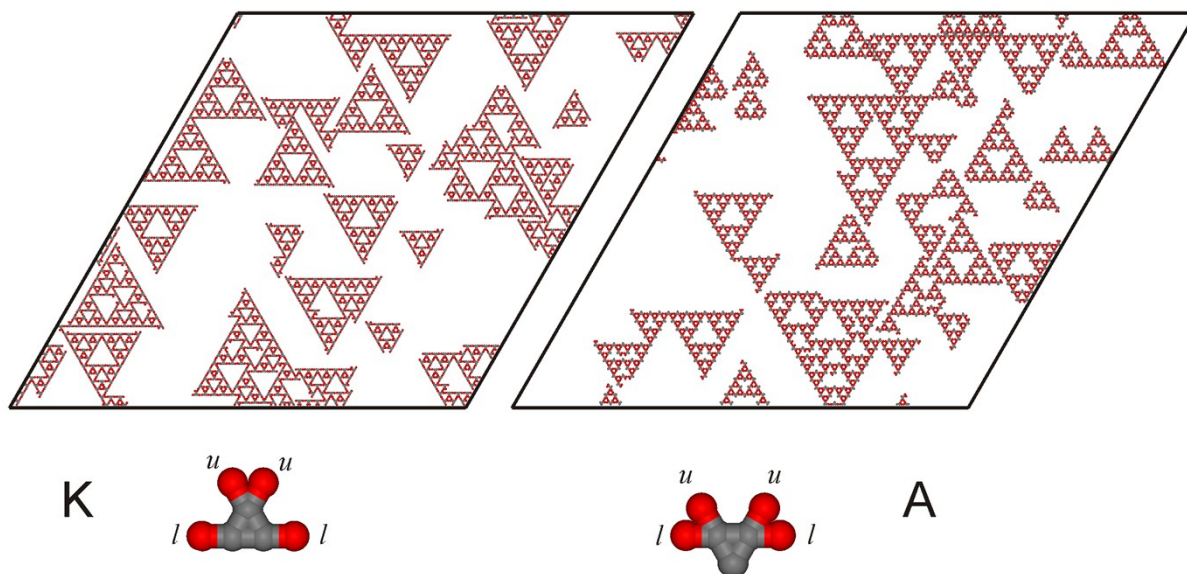


Figure S2. Snapshots of the adsorbed overlayers comprising 1000 molecules of **K** (left) and **A** (right) in which the formation of the nodes **b** and **b'** (**A**) and **d** and **d'** (**K**) was allowed (see Figs. 2 and 4); $T=0.1$. The letters *u* and *l* indicate upper and lower active segments of the molecules, respectively.

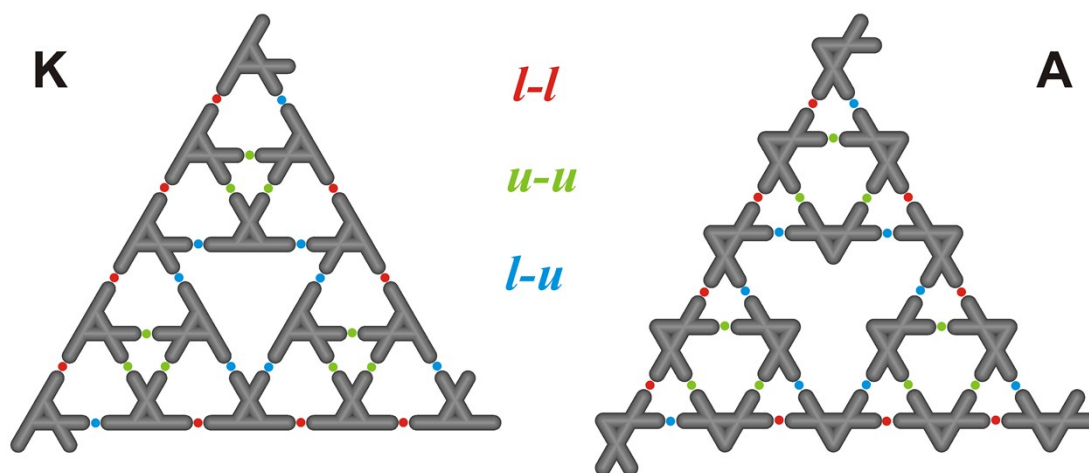


Figure S3. Distribution of bonds of different types (*l-l*, *u-u*, *l-u*) within the STs formed by the molecules **K**(left) and **A**(right). In every generation of these STs the numbers of bonds *l-l*, *u-u*, *l-u* are equal to each other. In the example shown here there are nine bonds of each type.

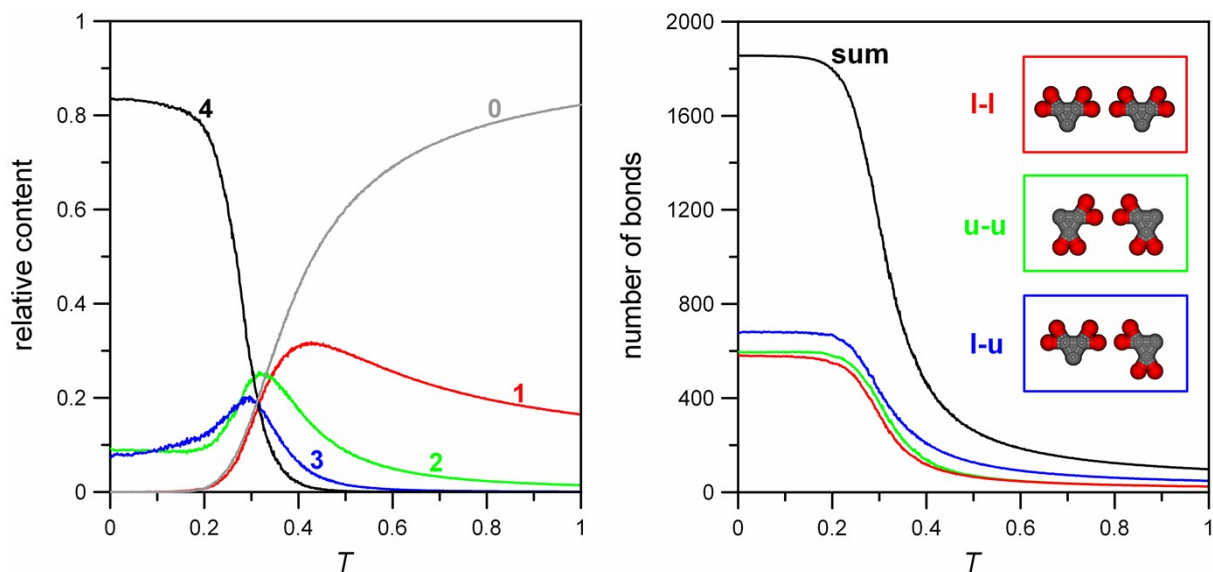


Figure S4. Effect of temperature on the relative content of molecules **A** with n bonds (n shown in the corresponding color). (right) Associated changes in the number of bimolecular bonds in which molecular arms of different types (l,u) are engaged (examples are encircled in the corresponding color).

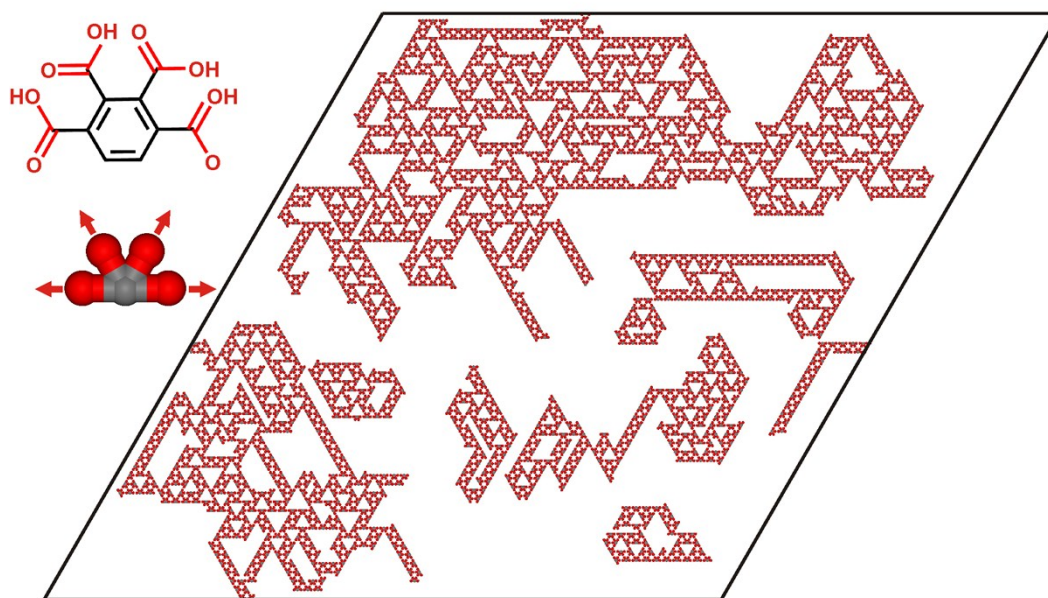


Figure S5. Snapshot of the adsorbed overlayer comprising 2000 molecules of **s** for which the formation of the homotactic nodes (**f** and **f'**, see FigS4) was allowed, $T=0.1$. Contrary to **A** and **K**, elimination of these nodes does not improve the formation of the STs (compare with Fig. 5). The inset in the left upper corner presents benzene-1,2,3,4-tetracarboxylic acid which can correspond to the model tecton **s** with indicated interaction directions (red arrows).

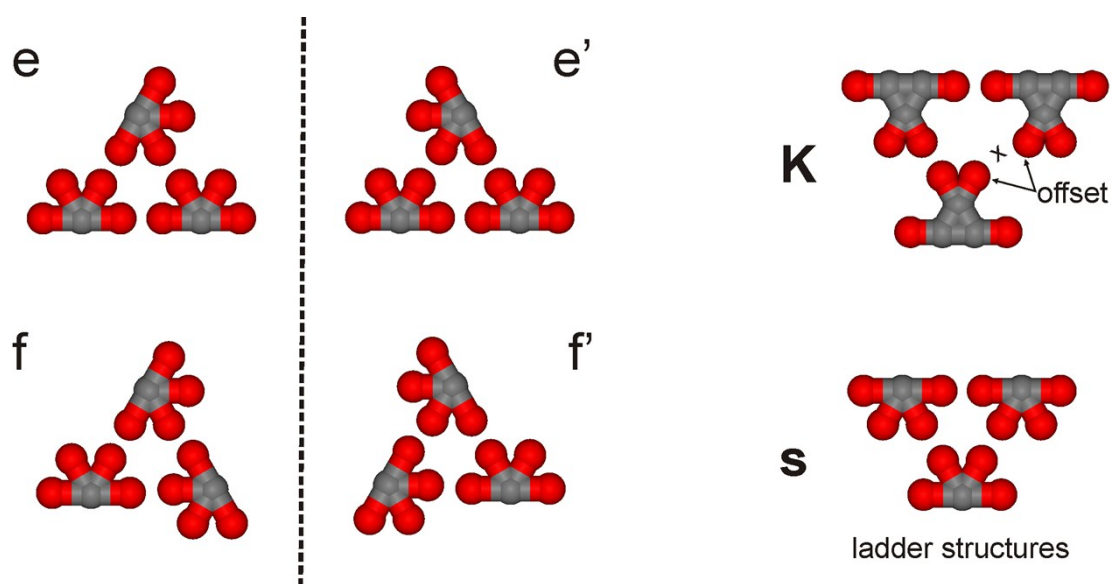


Figure S6. (left) Heterotactic (**e** and **e'**) and homotactic (**f** and **f'**) nodes formed by the molecules of **s**. (right) Illustration of the offset effect preventing the formation of the ladder structures comprising molecules **K** (and also **A**, not shown). In the case of the molecule **s**, the offset (**x**) does not occur, so that the ladders can grow and reduce the creation of STs.