Electronic Supplementary Information

Self-assembly of conformationaly flexible molecules under 2D confinement: structural analysis from computer simulations

Damian Nieckarz and Paweł Szabelski

Department of Theoretical Chemistry, Maria-Curie Skłodowska University,

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

1. Details of the model and MC simulation

The molecules of *m*TBPB were modeled as rigid planar structures comprising four segments (core plus three arms) each of which corresponded to one phenyl ring of *m*TBPB and which was allowed to occupy one vertex of a triangular lattice (adsorption site). Silver atoms were represented by single segments. The interaction between *m*TBPB and metal atoms was assumed to be highly directional and its range was limited to nearest neighbors on the lattice. To account for the directional character of the metal-organic interactions the arm segments of *m*TBPB were assigned unique interaction directions according to the *meta* positions of the halogen atoms in the outer phenyl rings. Specifically, these directions were rotated by ± 60 degrees with respect to the arms, to obtain the possible planar conformers of *m*TBPB shown in Fig. 1. Similarly, two-coordinate Ag atoms were equipped with a pair of collinear interaction directions. The interaction between *m*TBPB and a metal atom was possible when the corresponding segments occupied neighboring lattice sites and the associated interaction directions were collinear ($\rightarrow\leftarrow$). In this case the interaction energy was

equal to ε. The remaining types of interactions, including molecule-molecule and metal-metal interactions were neglected. The same refers to the molecule-substrate and metal-substrate interactions whose energy was set equal to zero.

The simulations were performed on a 100 by 100 triangular lattice of equivalent adsorption sites representing the Cu(111) surface. Larger lattices (200 by 200) were used to collect representative snapshots shown in Figs. 2-4. To minimize edge effects periodic boundary conditions in both planar directions were imposed. The calculations were carried out using the standard canonical Monte Carlo simulation method with Metropolis sampling. Accordingly, the system size, total number of adsorbed species and temperature were held constant. Specifically, the simulation algorithm can be outlined as follow. First a pre-selected total number of *m*TBPB molecules (including different conformers and their mixtures) and metal atoms were randomly distributed on the surface and the temperature, *T* was fixed. Next a series of trial MC moves (steps) was performed to equilibrate the adsorbed phase. To that purpose each MC step involved translation of a randomly selected species to a new position on the lattice. In this procedure, the total interaction energy of the selected species (*m*TBPB molecule or metal atom) in the old position, E_{old} was calculated by counting the number of collinear interactions ($\rightarrow\leftarrow$)with neighboring species of the opposite type (metal or *m*TBPB molecule). If this directional interaction occurred, it contributed to E_{old} with ε. A similar procedure was used to calculate the total interaction energy of the selected species in the new position, E_{new}. In this case the selected *m*TBPB molecule or metal atom was randomly moved over the surface to a new position and inserted if a sufficient number of empty adsorption sites was found there; otherwise the attempt ended. For the *m*TBPB molecule the translation was additionally combined with random in-plane rotation by a multiple of 60 degrees. The total interaction energy in the new position was determined in the same manner as for E_{old}.

To accept the new molecular configuration the associated acceptance probability was calculated: $p = \min[1, \exp(-\Delta U / kT)]$, where $\Delta U = E_{new} - E_{old}$ and k is the Boltzmann constant and compared with a randomly chosen number $r \in (0,1)$. If $r < p$ the new configuration was accepted. In the opposite case the molecule was left in the original (old) position. The above sequence was repeated several times, typically 10^{10} to equilibrate the adsorbed overlayer. To minimize the risk of trapping the modeled structures in metastable states we applied the cooling procedure in which the temperature was gradually decreased from 1 to 0.01 using 1000 equal decrements. The energies and temperatures in our model are reduced quantities expressed in units of ε and $|\varepsilon| / k$, respectively.

2. Additional snapshots and statistics

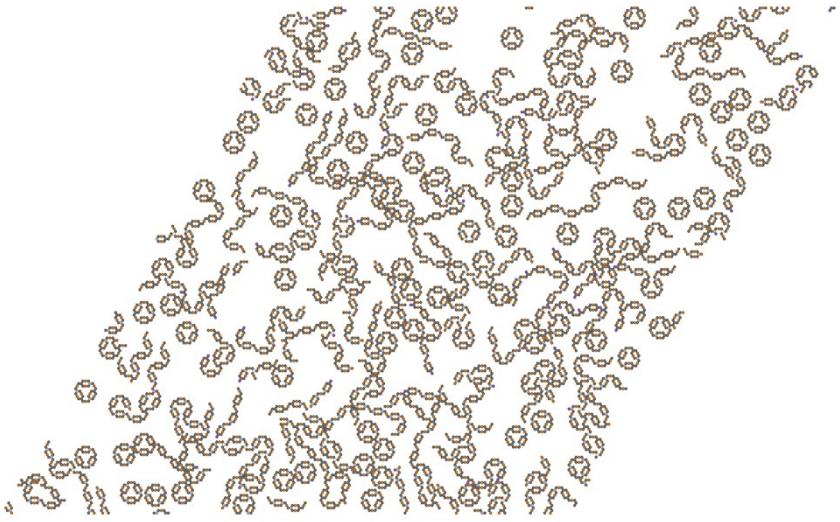

Figure S1. Snapshot of the adsorbed overlayer comprising 2400 metal atoms and 1600 molecules of mTBPB with 5% content of the windmill conformers **A** and **A***, corresponding to the experimental data (Ref. 13).

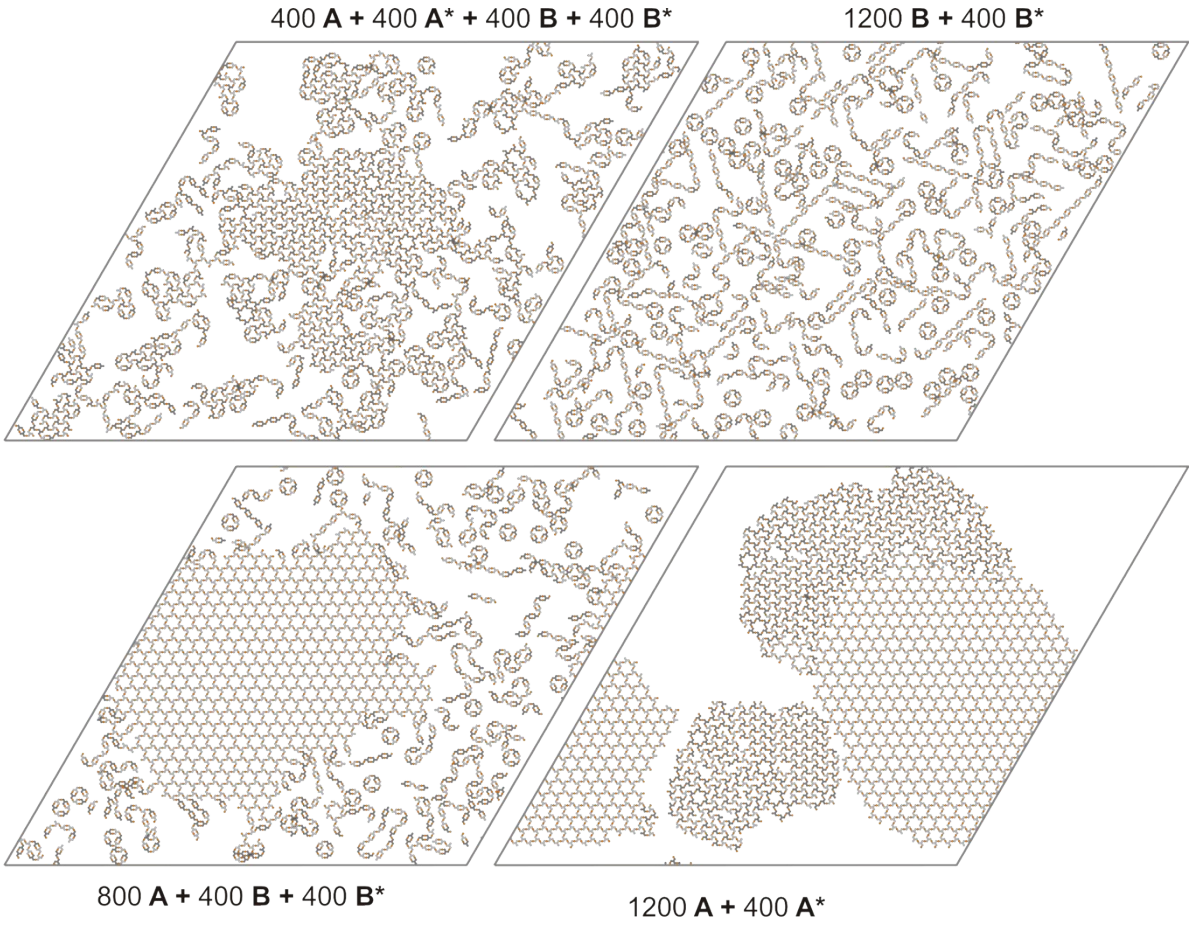

Figure S2. Snapshot of the adsorbed overlayers comprising 2400 metal atoms and 1600 molecules of mTBPB mixed at the various proportions shown in each panel.

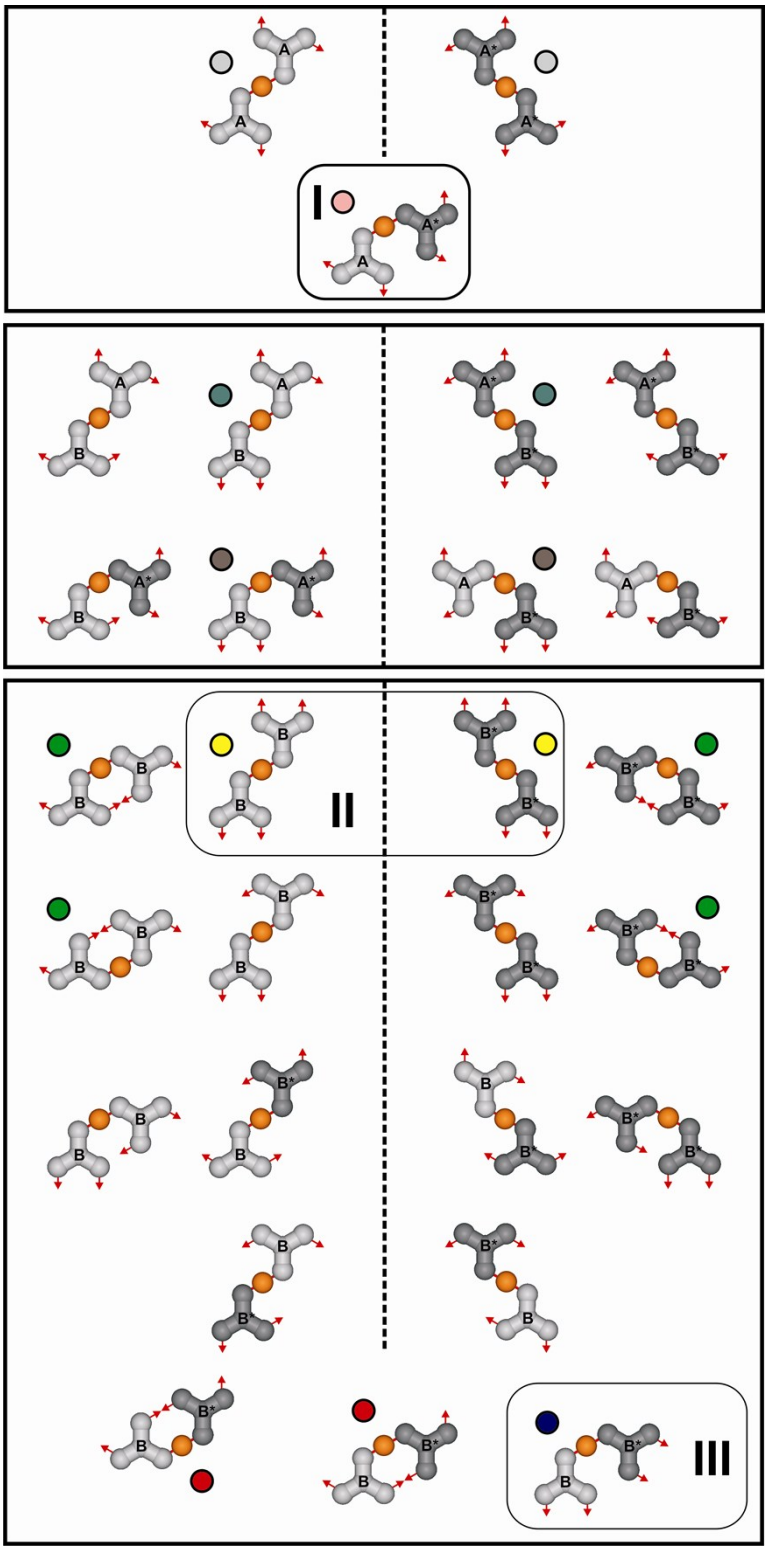

Figure S3. Survey of the metal-organic coordination nodes formed by the four conformers of mTBPB. The most abundant nodes were marked with different colors and used for the statistics shown in the next figure. The nodes I, II and III (encircled) are these discussed in the main text.

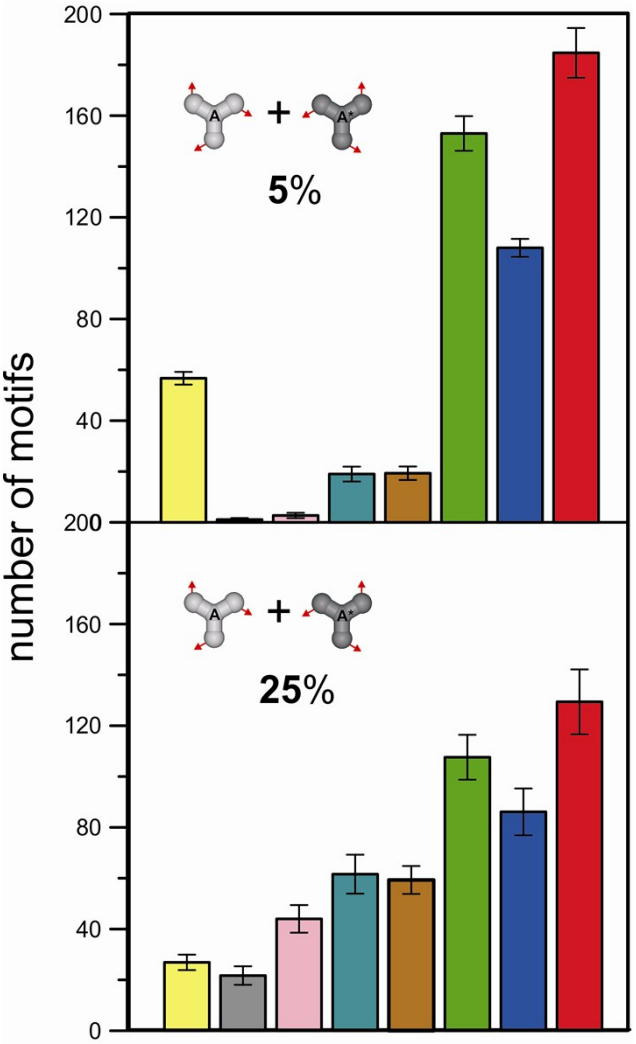

Figure S4. Statistics of the coordination motifs occurring in the overlayers with the biased (5%) and natural (25%) distribution of the windmill conformers **A** and **A***. The color scheme used in the figure is consistent with the preceding Fig. S3.