Supporting Information
Supramolecular Chemistry Based on 4-Acetylbiphenyl on Au(111)

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LARGE COVERAGE OF SUPRAMOLECULES

At large density of ABP molecules, supramolecules assemble and can fill large extensions of the surface as shown in Fig. S1. In the figure the surface is covered by supramolecular tetramers approaching the monolayer limit. A few dimers, trimers and bigger conglomerates are also present.

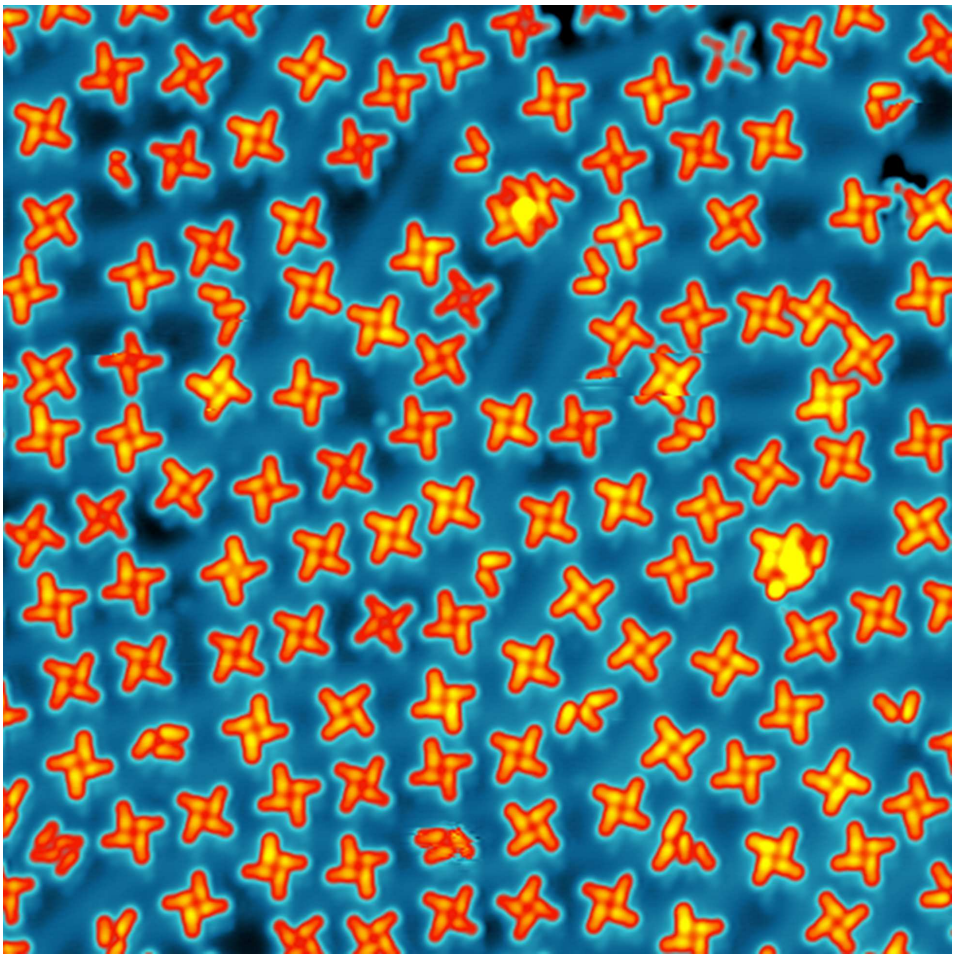

FIG. S1. STM image of an Au(111) terrace almost completely covered with ABP tetramer structures. Size: 40 nm x 40 nm; V = -0.58 V and I = 170 pA.

INTERACTION OF AU ADATOMS WITH TETRAMERS

Au adatoms do not form covalent bonds with the ABP molecules, but they rather induce a redistribution of charges leading to binding. This can be seen in the induced charge of the tetramer with one Au adatom (Fig. S2a) and in the study of the density of states, where the molecular orbital structure shifts to lower energies and broadens as the number of Au adatoms is increased (Fig. S2b).

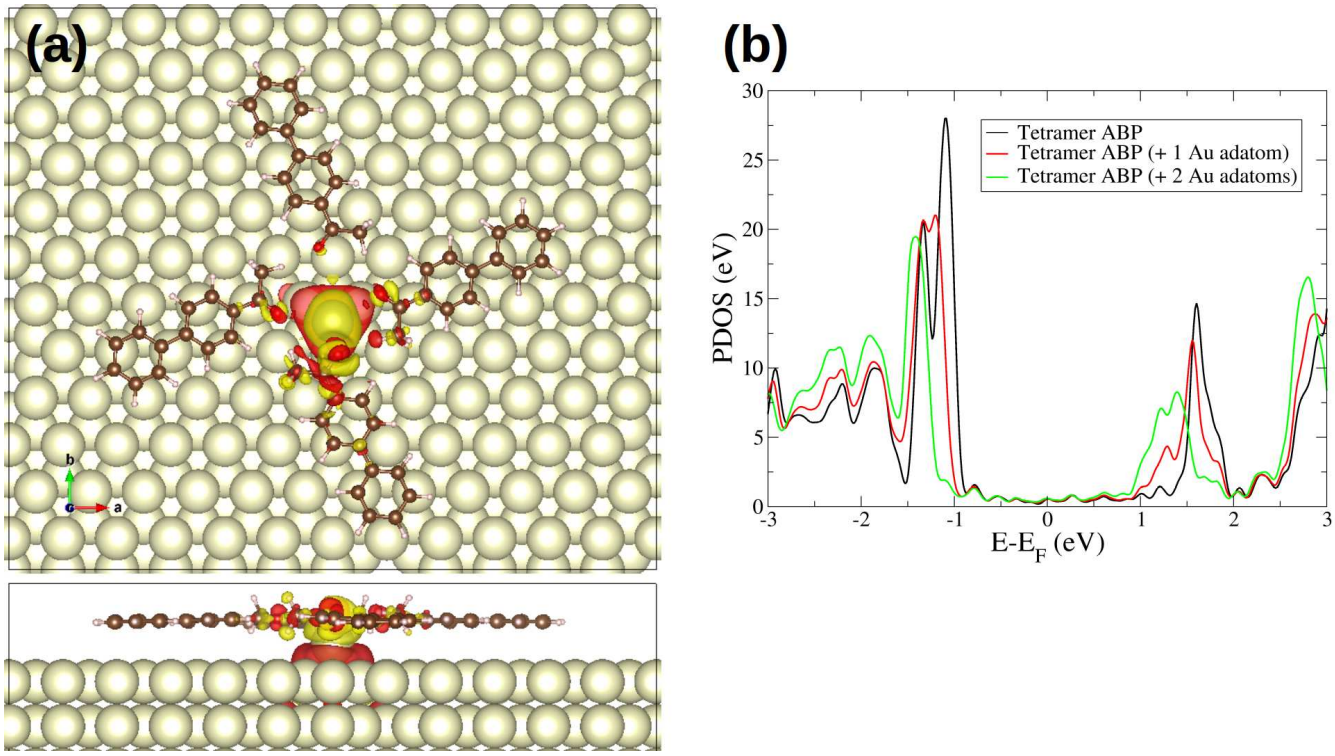

FIG. S2. (a) Induced charge density due to the presence of one Au adatom. Red (yellow) shows the accumulation (depletion) of electrons according to the expression: $\Delta\rho = \rho[(4ABP + Au)@Au111] - \rho[4ABP@Au111] - \rho[Au]$. (b) Projected density of states (PDOS) on the tetramer states with 0 (black), 1 (red) and 2 (green) gold adatoms.

AU ADATOMS AWAY FROM THE CENTER OF THE TETRAMER

Au adatoms can also be adsorbed underneath the tetramer but away from the center. In Fig. S4a one of such configurations is shown, where two Au adatoms at the center contribute to the supramolecular binding and an extra Au adatom is located under one of the ABP molecules. Fig. S4b shows a simulated constant current STM image, where the off-center adatom is clearly visible, in contrast to the adatoms at the center. This image is in good agreement with experimental images of adatoms pushed underneath a tetramer (ref. 10).

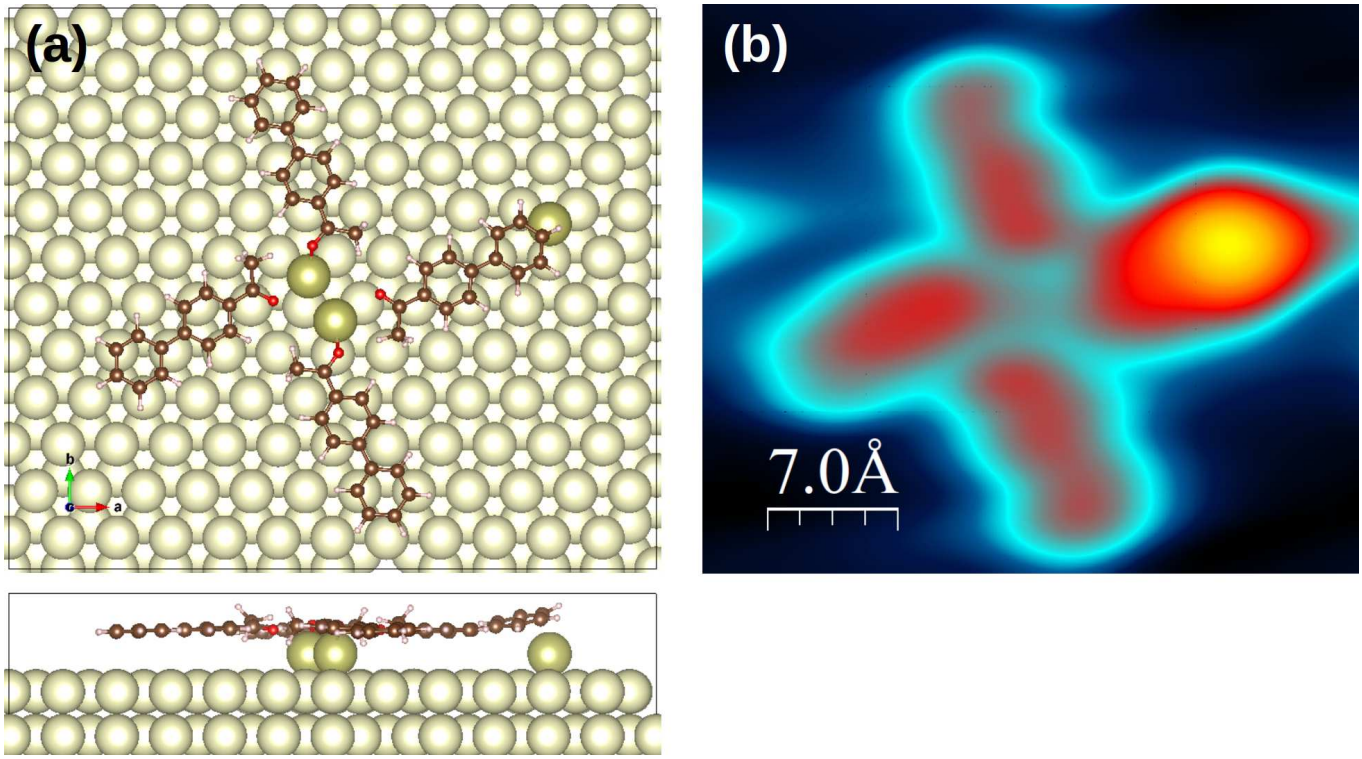

FIG. S3. (a) Relaxed structure of the tetramer with two Au adatoms at the center and one additional Au adatom off-center. (b) Corresponding simulated constant current STM image.

SIMULATION RESULTS FOR THE ABP TRIMER

Similarly to the results for the ABP tetramer shown in Fig. 3, we have performed simulations of STM topographic images an dI/dV maps for the ABP trimers shown in Fig. 1. The corresponding DFT optimized models have been already shown in Fig. 1. As for the tetramer, the inclusion of a Au adatom for the intersecting trimer stabilizes the supramolecule.

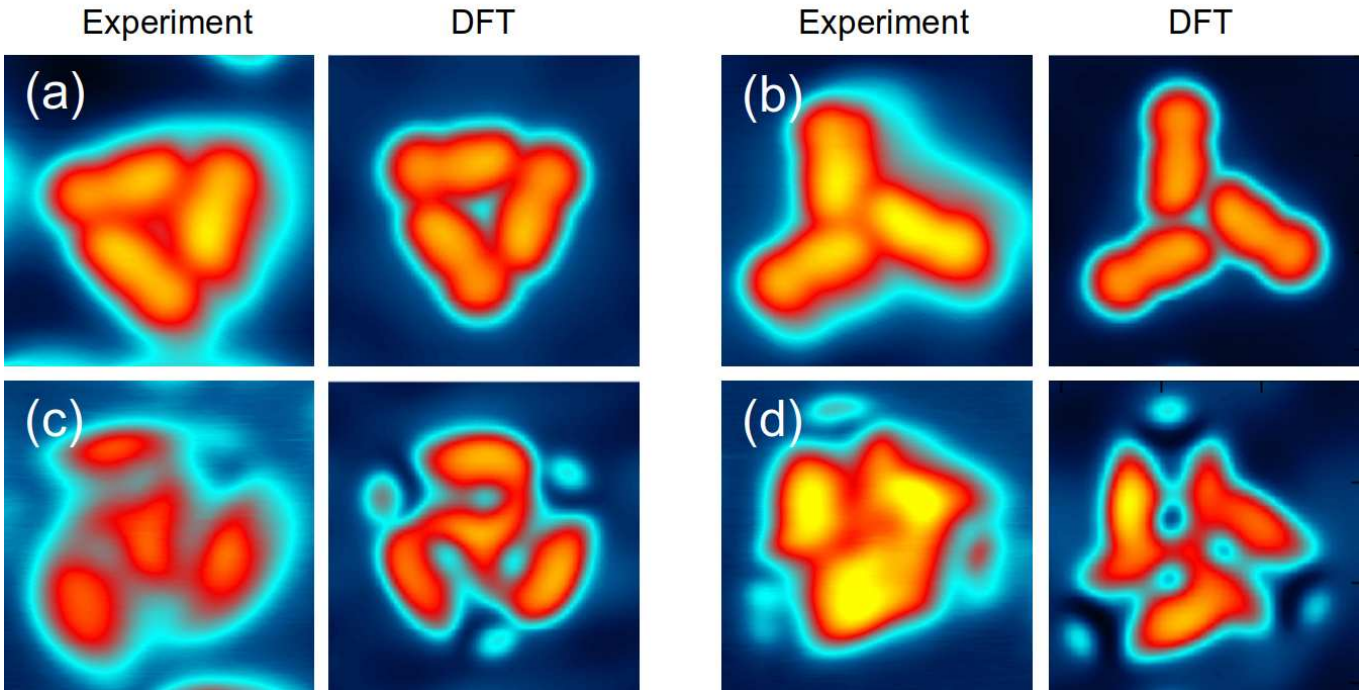

FIG. S4. Upper row: STM images for the trimer (a) and the intersecting trimer (b). The corresponding DFT optimized models are shown in Fig.1. Lower row: experimental dI/dV maps and the corresponding simulations. The experimental parameters are, for the topographic images, V = 0.1 V, I = 41 pA, and for the dI/dV maps, V = 2.15 V, I = 25 pA. The theoretical biases to obtain the dI/dV maps are 1.6 and 1.36 V, respectively.

ENERGY BARRIER CALCULATIONS

Nudged-elastic-band calculations yield diffusion barriers that are consistently higher for supramolecules containing Au adatoms. Indeed the barrier for diffusion along the $[11\bar{2}]$ direction of a tetramer without adatoms is 243 meV (Fig. S5), while with two adatoms the barrier becomes 347 meV (Fig. S6).

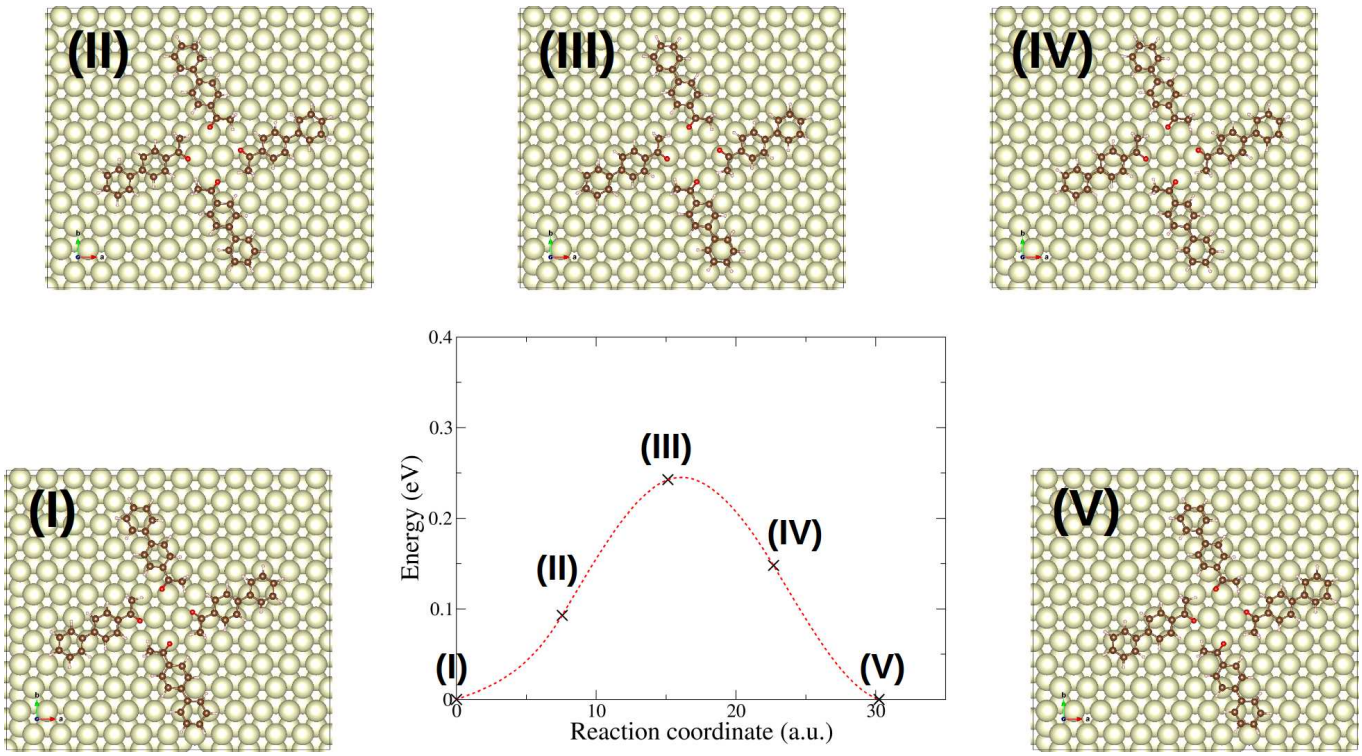

FIG. S5. Computed diffusion barrier for a supramolecular tetramer along the $[11\bar{2}]$ direction. The sequence of steps in the minimimum potential energy surface is represented by the reaction coordinate. The geometries of the steps are also shown in the figure.

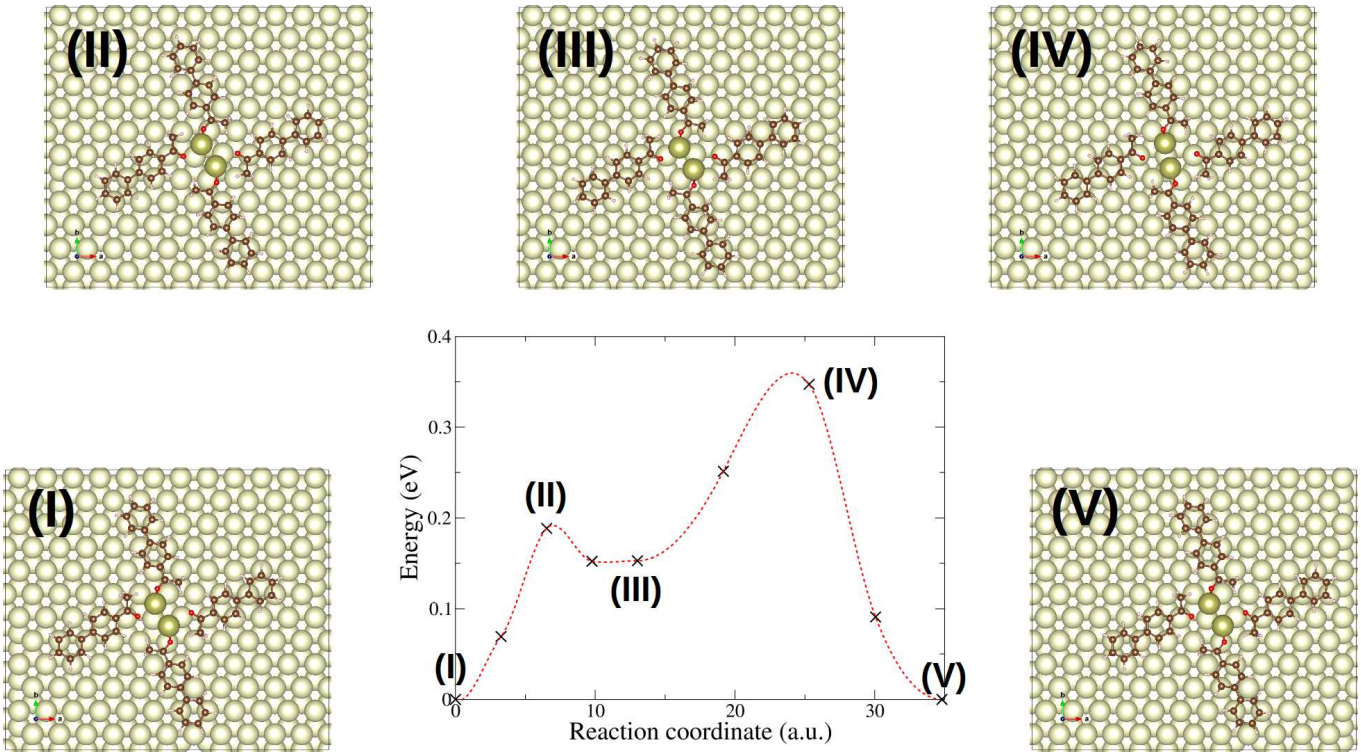

FIG. S6. Computed diffusion barrier for a supramolecular tetramer including two Au adatoms along the $[11\bar{2}]$ direction. The sequence of steps in the minimimum potential energy surface is represented by the reaction coordinate. Five images of these steps are also shown in the figure. Initial and final configurations (I and V) correspond to the two adatoms occupying FCC hollow positions. The local minimum in the middle (III) corresponds to the adatoms at HCP hollow positions.