

Supporting Information

Self-assembly of *s*-indacene-tetrone on Cu(111): molecular trapping and patterning of Cu adatoms

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Isolated molecule

The adsorption of indacene-tetrone on Cu(111) was studied by DFT first in its isolated form. Metal surfaces, and in particular Cu(111), are usually reactive towards deprotonation reactions.¹⁻³ We have shown previously that deprotonation of the acidic terminal carbons occurs upon adsorption of INDO₄ on Ag(111),^{4,5} so we have considered only the deprotonated form of the molecule in the calculations. The adsorption site of the molecule corresponds to the center of the central ring above a surface bridge site with the four peripheral oxygen atoms near on-top positions of the underlying Cu atoms (Fig. S1). This was obtained by considering various initial orientations of the molecule as starting conformations before relaxation. The average distance between O-Cu is (2.11 ± 0.02) Å indicating a chemisorption state and one obtains a net charge transfer from the molecule to the surface of ~1.5 electron. As we will see below, this conformation is the basic seed composing the

different hydrogen-bonded self-assembled structures, but it is slightly disturbed when metallic adatoms in the self-assembled motifs are present.

References

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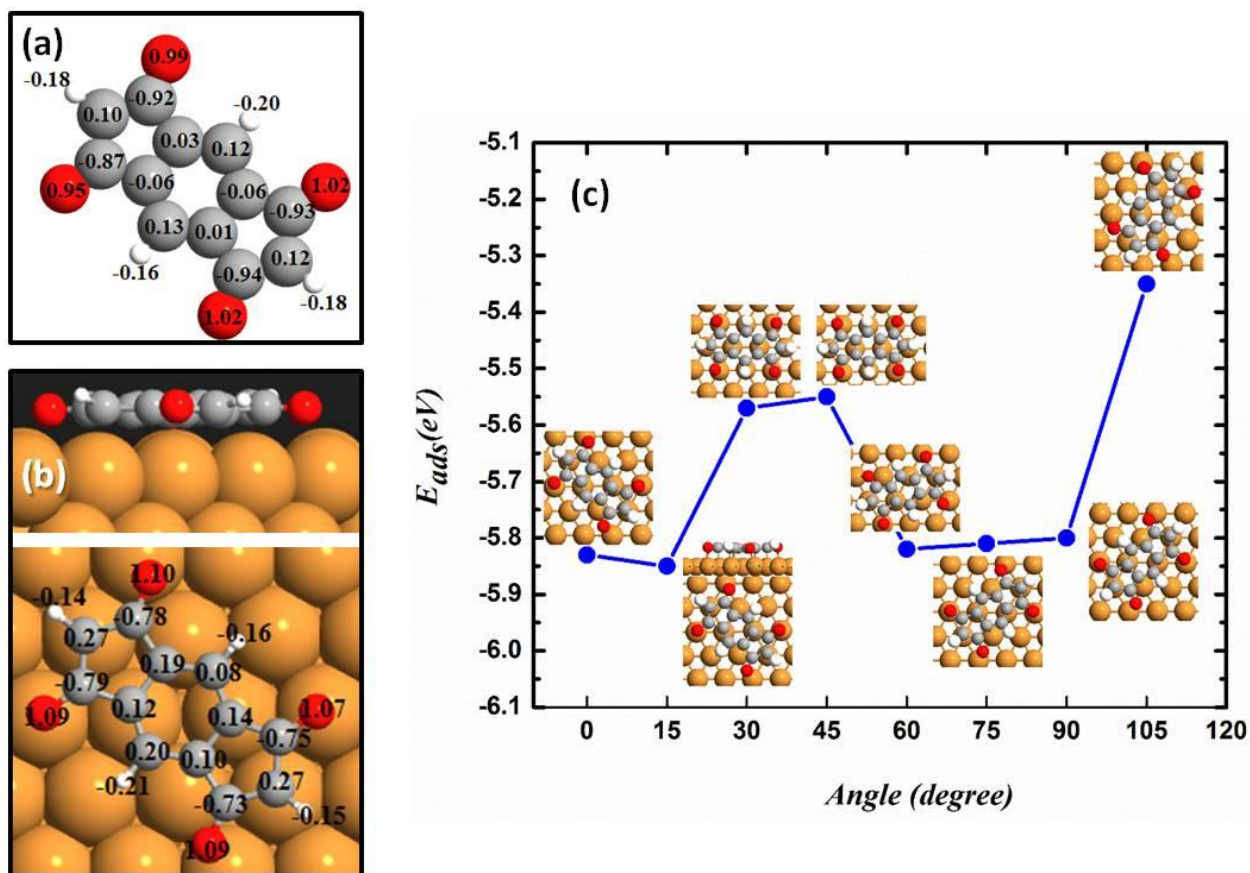


Figure S1: a) Bader charge distribution (in e^- , where $e^- = -|e| = -1.6 \times 10^{-19}$ C) on the atom centers for the deprotonated INDO₄ in gas phase. The oxygen atoms carry a negative charge of about $1e^-$ that is compensated for the neighboring carbon atoms with $\sim -1e^-$ on the four sites. b) Bader charge distribution for a molecule adsorbed on the Cu(111) surface: for O $1.09 \pm 0.01 e^-$, for C on the central ring $0.14 \pm 0.04 e^-$, for C connecting O $-0.76 \pm 0.02 e^-$, for C connecting H $+0.27 e^-$. Notice that each atomic site loses a fraction of charge compared to the gas phase, leading to a net charge transfer to the surface of $\sim 1.5 e^-$ for the deprotonated INDO₄. The average distance between O-Cu is $2.11 \text{ \AA} \pm 0.02 \text{ \AA}$ indicating a chemisorption state. (c) Geometrical structures and adsorption energy (in eV) with respect to the orientation of the molecule. The angle corresponds to the orientation of the molecule before the relaxation and the insets are the final conformations. One can observe that the position with the center of the ring above a bridge site is preferred. The accuracy of the calculations does allow to distinguish a clear and unique stable conformation.

Hydrogen-bonded trimer

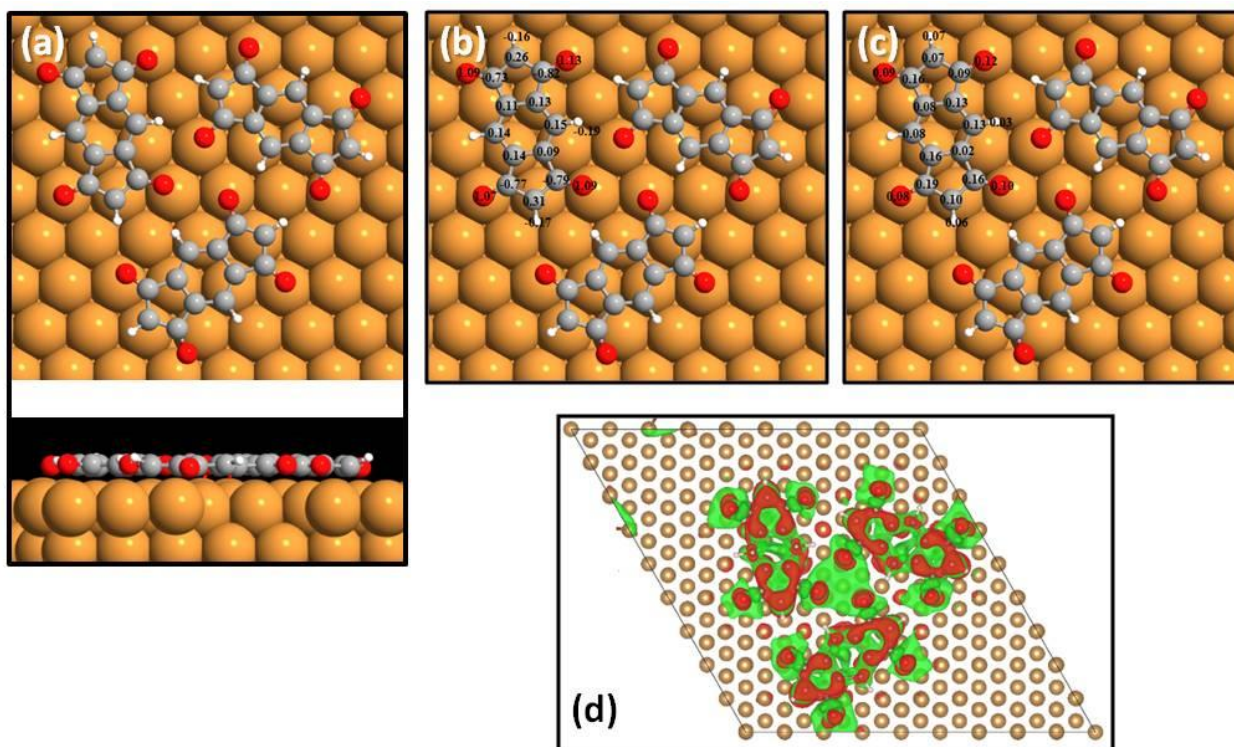


Figure S2: (a) Geometrical structure of a hydrogen-bonded trimer on Cu(111). (b) Bader charge distribution (in e^-), for O $+(1.09 \pm 0.02) e^-$, for C on the central ring $+(0.12 \pm 0.02) e^-$, for C connecting O $-(0.78 \pm 0.03) e^-$, and for C connecting H $+(0.28 \pm 0.03) e^-$. The mean distance between the three oxygen atoms in the center is $(3.14 \pm 0.1) \text{ \AA}$. Recall that the distance between two Cu atoms is 2.55 \AA . (c) Charge transfer (in e^-) between the molecules and the substrate, calculated by subtraction of Bader charge distributions per atom when the molecule is adsorbed and when it is alone in the gas phase. (d) Charge density difference ($\rho_{\text{complex}} - \rho_{\text{Cu(111)}} - \rho_{\text{molecule}}$) profiles with isovalue of 0.002 Bohr^{-3} for the trimer adsorbed on the Cu(111) surface.

Metal-organic trimer

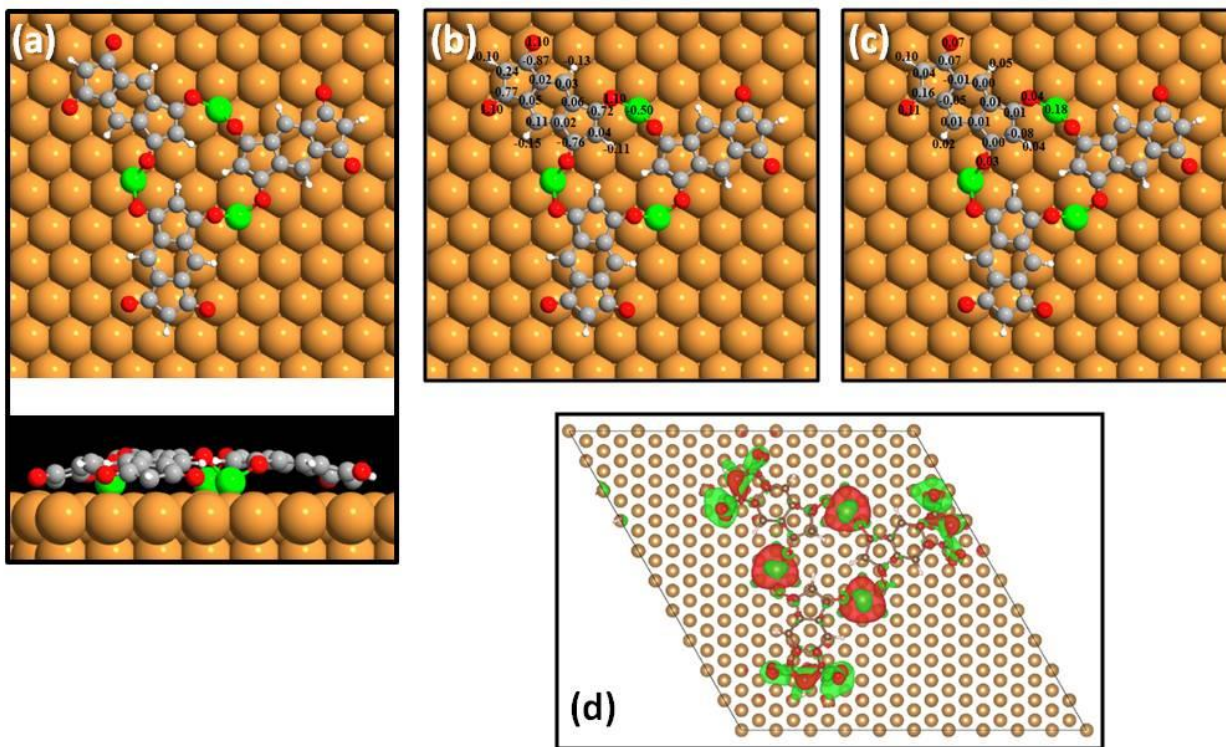


Figure S3: (a) Geometrical structure the metal-organic trimer consisting of three self-assembled molecules in presence of three metal adatoms (in green). Notice that the molecules are slightly bent due to the presence of the adatoms. (b) Charge density (in e^-) calculated using Bader charge analysis. The three adatoms are positively charged (around $-0.5 e^-$) due to the proximity of the oxygen atoms of the molecules. (c) Charge transfer (in e^-) between the molecules and the substrate. For the oxygen atoms close to a metal adatom, the charge transfer is around $0.04 e^-$ and for those far from an adatom, it is $0.08 e^-$ in average. (d) Charge density difference ($\rho_{\text{complex}} - \rho_{\text{Cu(111)}} - \rho_{\text{molecule}}$) profiles with isovalue of 0.002 Bohr^{-3} for the metal-organic trimer adsorbed on the Cu(111) surface.

Energetics of the different adsorption states

We have assessed the adsorption of the molecules with and without adatoms on the copper surface, considering the adsorption geometries in Fig. S4. The adsorption energies in Table S1 were calculated by subtracting the energy of the combined system (surface + molecules + adatoms) from the energy of the adatoms on surface and the energy of the molecules alone divided by the number of the molecules (n).

$$E_{ads} = \frac{E_{\text{complex}} - E_{\text{Cu}_n/\text{Cu(111)}} - nE_{\text{molecule}}}{n}$$

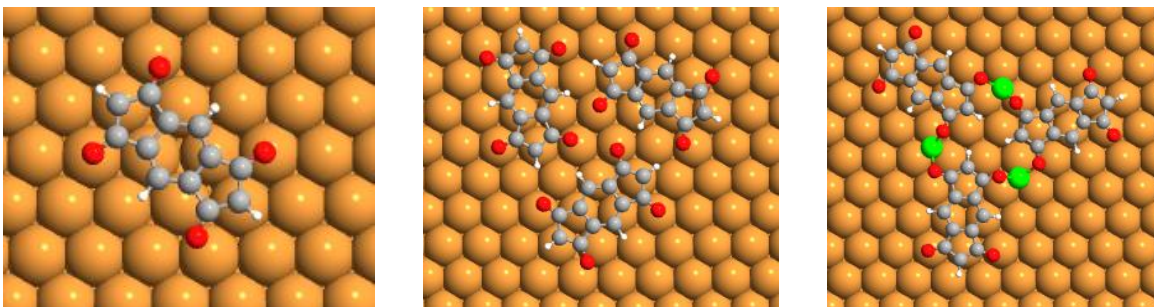


Figure S4: Geometrical structure for an isolated molecule, a hydrogen-bonded trimer, and a metal-organic trimer adsorbed on the Cu(111) surface.

Per molecule	<i>Isolated molecule</i>	<i>H-bonded Trimer</i>	<i>Metal-organic trimer</i>
d_{O-Cu}	----	----	1.98
$d_{Cu-Cu(111)}$	----	----	1.87
<i>Charge Transfer</i> (e^-)	2	$\frac{5.77}{3} = 1.92$	$\frac{2.66}{3} = 0.89$
E_{ads} (eV)	-5.85	$\frac{-15.23}{3} = -5.08$	$\frac{-16.55}{3} = -5.52$

Table S1: Distance between the O atoms and the Cu atoms (d_{O-Cu} in Å), vertical distance between the Cu adatoms and the Cu(111) surface ($d_{Cu-Cu(111)}$ in Å), charge transfer (in e^-) between the substrate and the molecules, and adsorption energies (E_{ads} in eV) for the three different configurations presented in Fig. S4.

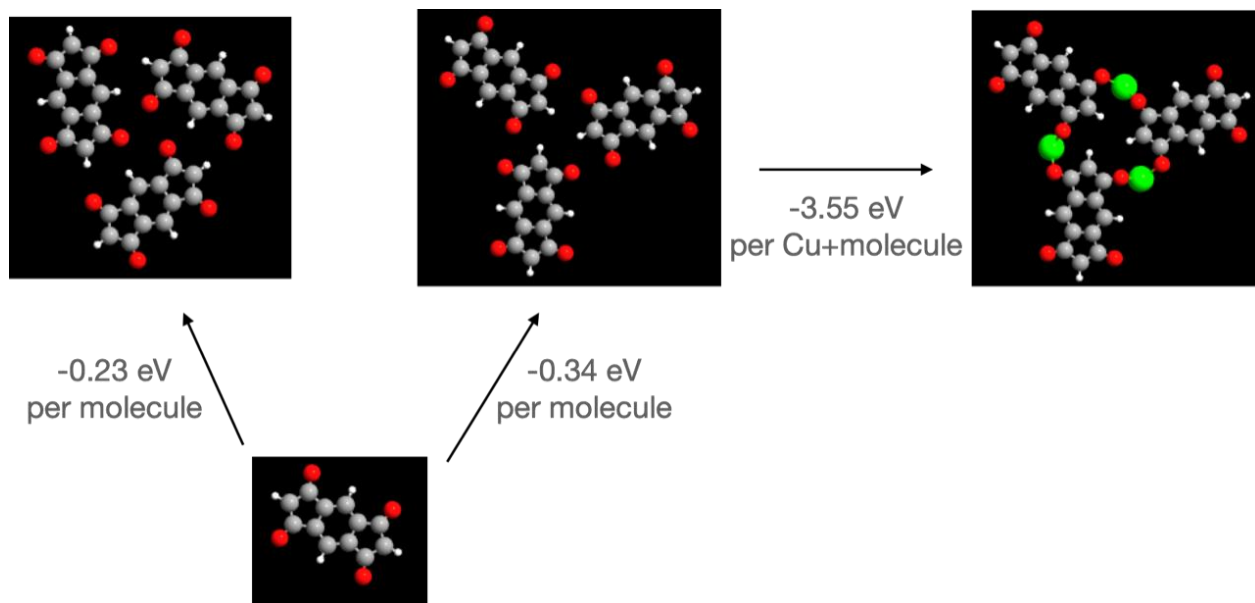


Figure S5: Comparison between the hydrogen bond interaction energy for two different trimers and the interaction energy for the metal-organic trimer of Fig. S3 (in free-standing configurations).

P5 phase

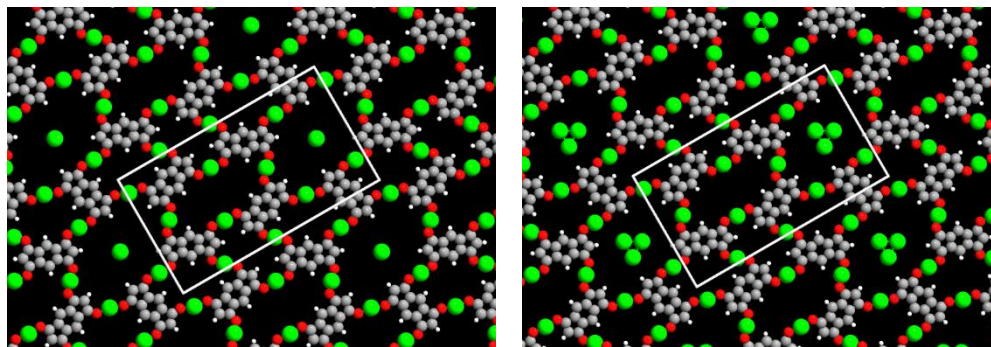
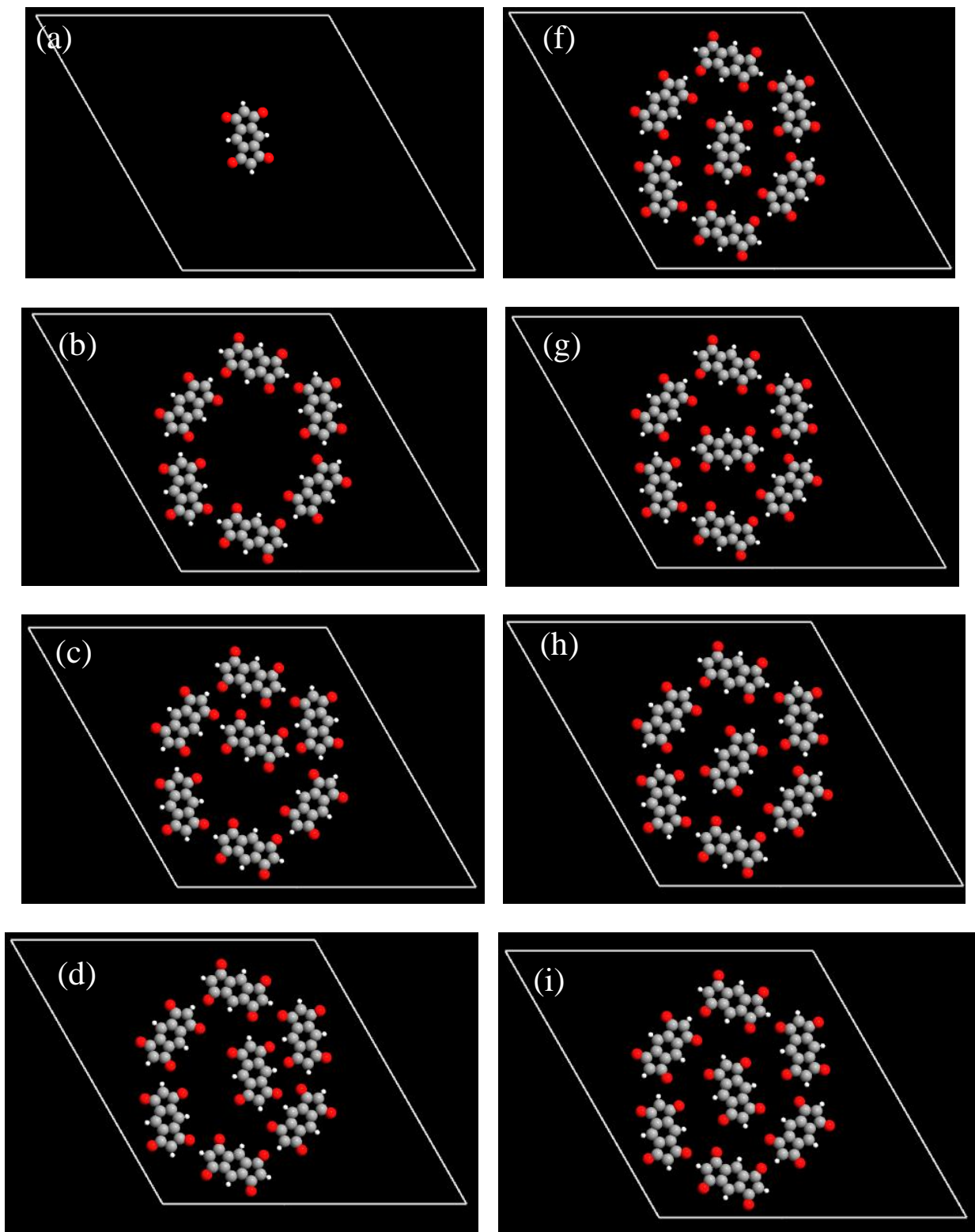


Figure S6: Geometrical structure of the P5 phase. Cu adatoms are in green. The unit cell comprises eleven or thirteen adatoms and five indacene molecules.

Molecular trapping



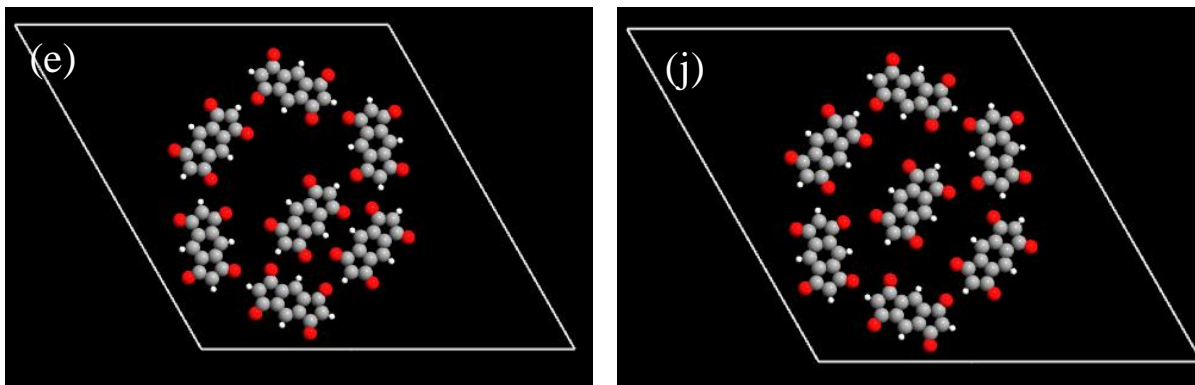


Figure S7: Geometrical structures of ring-shaped configurations in the KG2 phase. (c-j) An additional molecule is included inside the pore composed of six molecules. The corresponding energies are in Tab. S2.

	Fig.7c	Fig.7d	Fig.7e	Fig.7f	Fig.7g	Fig.7h	Fig.7i	Fig.7j
$E_{cohesive}$ (eV)	-0.46	-0.48	-0.51	-0.263	-0.110	-0.003	-0.16	-0.00

Table S2: Cohesive energies (eV) [$E_{cohesive} = E_{seven\ molecules\ (c-j)} - E_{six\ molecules\ (b)} - E_{one\ molecule\ (a)}$] for a molecule placed inside a pore of six surrounding molecules (see Fig. S7). One remarks that the most preferable configurations (c-e) are with the inside molecule located in lateral position closer to the molecules of the ring (~ -0.5 eV), indicating stronger attractive intermolecular interactions by hydrogen bonding.

Additional STM images

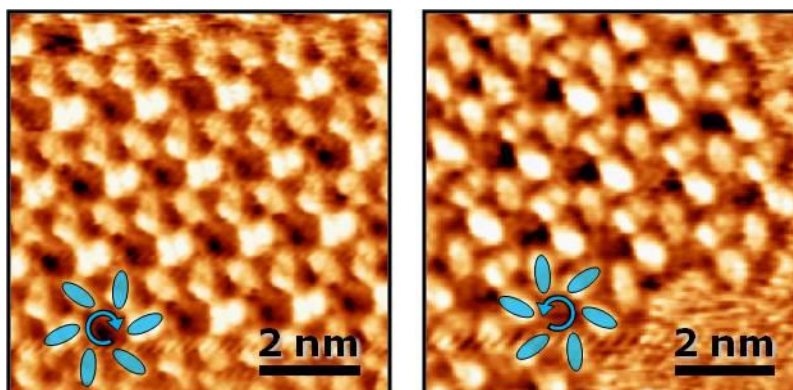


Figure S8. STM images showing two different domains of KG1 phase with opposite chirality.

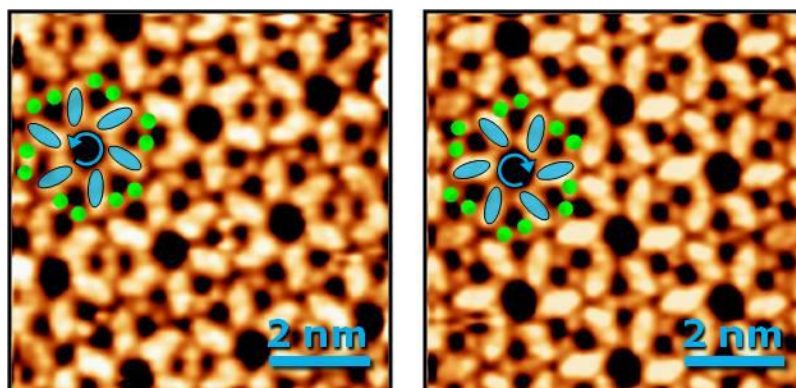


Figure S9. STM images showing two different domains of P3 phase with opposite chirality.

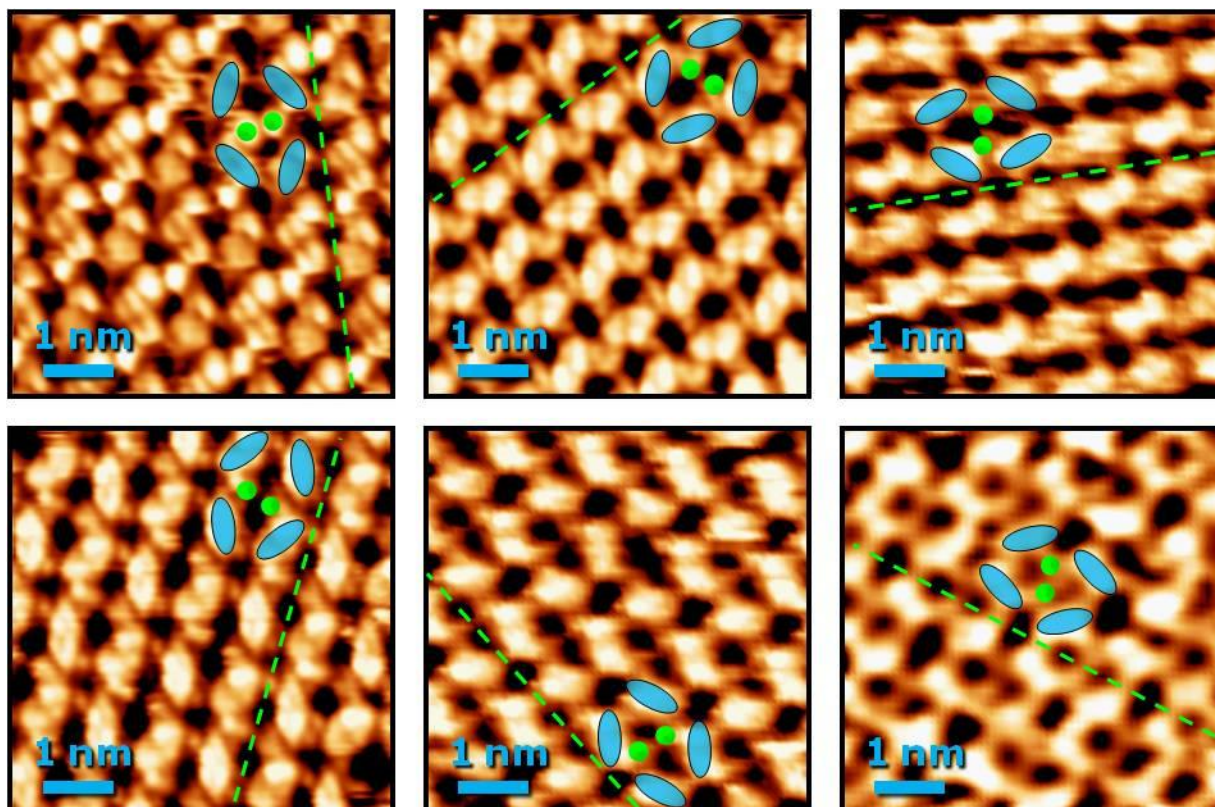


Figure S10. STM images showing the six different symmetry domains obtained for P4 phase.

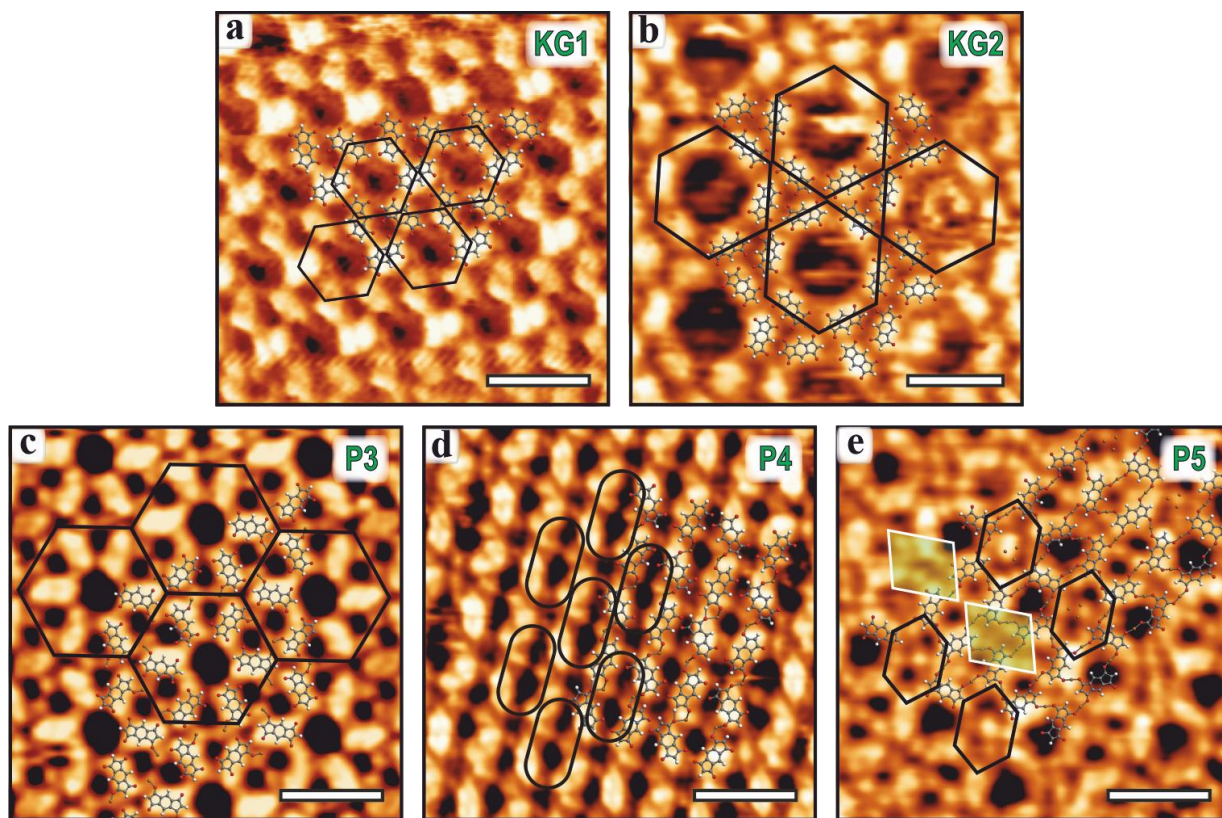


Figure S11. STM images of all supramolecular phases with superimposed models. Scale bars: 2 nm.