Molecular adaptation in supramolecular self-assembly: brickwall-type phases of indacene-tetrone on silver surfaces

Nataliya Kalashnyk[1,*], Frédéric Dumur[2], Didier Gigmes[2], Sylvain Clair[1,*]

[1] Aix Marseille Univ, Univ Toulon, CNRS, IM2NP, Marseille, France

[2] Aix Marseille Univ, CNRS, ICR, Marseille, France

* Corresponding authors: N. Kalashnyk (n.kalashnyk@yahoo.com), S. Clair (sylvain.clair@univ-amu.fr)

Supplementary Information

Methods

The experiments were performed in ultra-high vacuum (UHV, base pressure in the low 10^{-10} mbar range). The single-crystal Ag(111), Ag(100) and Ag(110) surfaces were cleaned by several cycles of Ar^+ bombardment followed by annealing. $INDO_4$ molecules were provided by Sigma-Aldrich as *rare and unique chemical*. The precursors were thoroughly degassed prior to deposition onto the atomically clean substrate held at room temperature (RT). The molecular powder was thermally sublimated from an evaporator heated to 150 °C for typical dosing time of 30 min. STM measurements were performed with a commercial Omicron VT-STM system operated at room temperature. The STM images were acquired in constant current mode with typical tunneling current $I_T \approx 0.3$ nA and sample bias $V_T \approx$ -(1–1.5) V. All images were subsequently calibrated using atomically resolved images of the pristine surfaces. Images were partly treated with the free software WSxM.[1]

The molecular models of Figures 1, 2 and S1 were obtained by manual overlap with the STM images and by seeking adsorption sites with all oxygen atoms as close as possible to on-top sites for A-type molecules. This arbitrary assignment is based on previous theoretical and experimental work for similar molecules where it was shown that the oxygen atoms tend to form chemical bonds to the silver surface atoms from on-top positions on all Ag(110) [2-5], Ag(100) [4] and Ag(111) [3-8] surfaces.

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	Phase	**a** [nm]	**b** [nm]	**gamma** [°]	Lateral hydrogen bonds length [Å]
Ag(100)	BW1	1.04	1.69	87	5.6
Ag(100)	BW2	0.82	1.04	79	2.8
Ag(110)	BW3	0.71	1.00	90	1.9
Ag(111)	BW4	1.26	1.32	86	3.2

Table S1: Summary of the unit cell parameters for all four brickwall (BW) phases of $INDO_4$. An estimation of the lengths of the lateral H-bonds (blue solid and dashed lines in Figs.1 and 2) is also given.

	Phase	Number of molecules in unit cell	Density [molecule/nm^2]	Molecular size [nm^2]
Ag(100)	BW1	2	1.14	0.88
Ag(100)	BW2	1	1.20	0.84
Ag(110)	BW3	1	1.41	0.71
Ag(111)	BW4	2	1.20	0.83

Table S2: Densities and molecular sizes (i.e. the inverse values) for all four BW phases of $INDO_4$.

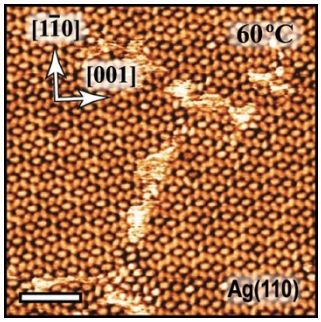

Figure S1: STM image of the extended phase obtained on Ag(110) after annealing at 60°C. Scale bar: 6 nm. Tunneling parameters: 250pA, -1310mV.

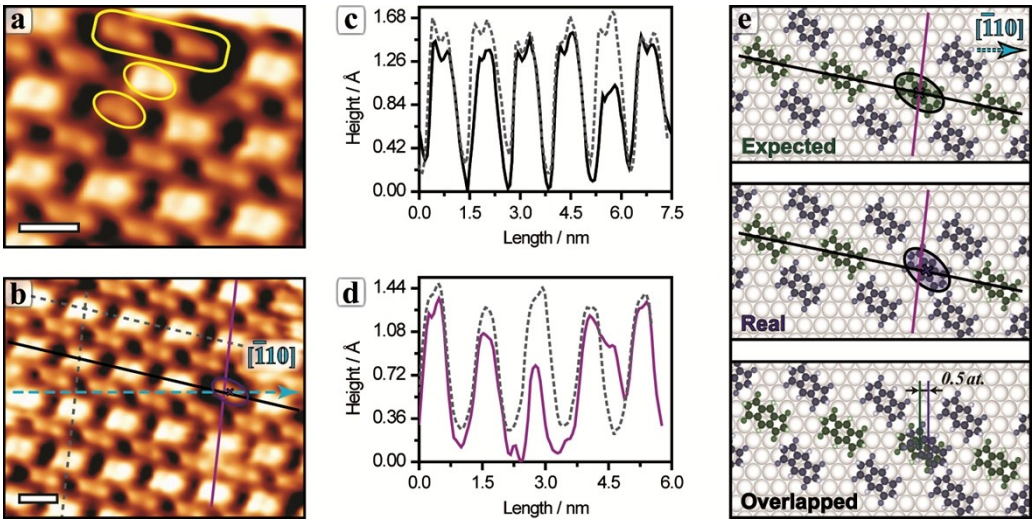

Figure S2: Defects in BW4 phase on Ag(111). (a,b) STM images of point defects corresponding to molecules at expected bright positions but imaged as dim, or vice-versa (yellow ovals in (a)). (c,d) Lines profiles along the lines marked in (b) showing a lowering of the apparent height of the molecule at the defect site and a shift of its position along the [-110] direction (along the blue dashed arrow). (e) Suggested adsorption models for the defective molecule. Scale bars: 1 nm. Tunneling parameters (a,b): 230pA, -1450mV.

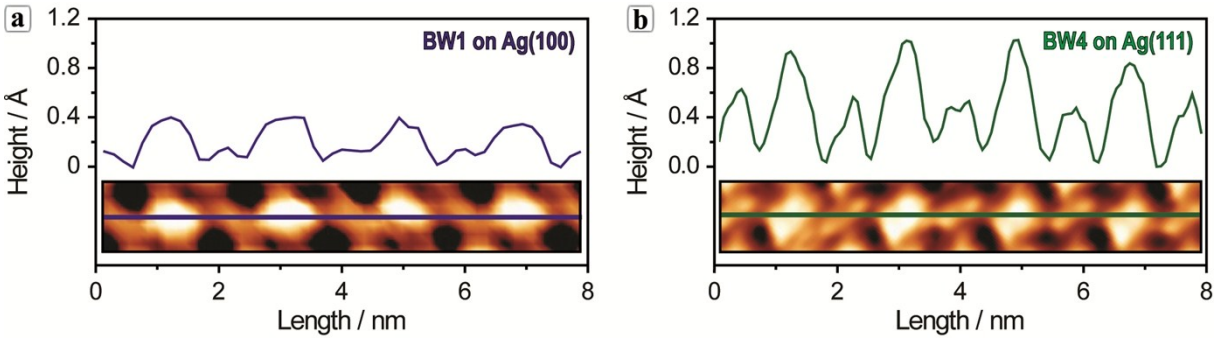

Figure S3: Line profiles along molecular rows with alternating bright and dim contrast for BW1 (a) and BW4 (b). Tunneling parameters: 230pA, -1480mV (a); 230pA, -1450mV (b).