Self-assembly of Trithia-9-crown-3 and Octathia-24-crown-8 on Au(111) surfaces

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Computational Details

Theoretical calculations were performed using density functional theory (DFT) provided by the DMol3 code. [1] We use the periodic boundary conditions (PBC) to describe the 2D periodic structure on the Au surface in this work. In DMol3, the electronic wave function was expanded in a localized atom-centered basis set with each basis function defined numerically on a dense radial grid. We used the double-numeric polarized (DND) basis sets.[2,3] The Perdew and Wang parameterization of the local exchange-correlation energy were applied in the local spin density approximation (LSDA) to describe exchange and correlation.[4] The inner core electrons for Au were represented by the DFT semilocal pseudo-potential (DSPP) specifically developed for DMol3 calculations, while nineteen electrons were treated explicitly for Au (those corresponding to the atomic levels 5s, 5p, 5d, 6s). Each basis function was restricted to within a cutoff radius of R_{cut}=5.5Å. Spin-restricted wave functions were employed. A self-consistent field procedure was done with a convergence criterion of 10^{-5} a.u. on the energy and electron density.

To evaluate the adsorption energy of ring molecules on the Au (111) surface, we adopt three-layer Au slab model as the simplified model. An optimized Au lattice parameter 2.8838 Å is used in the calculation to reduce the effect of the stress. Test calculations show that the adsorption energy does not change significantly by using three- or four-metal slab models. During the structural optimizations, we only allow

the Au atoms in the surface layer and the adsorbed ring molecules to move until all forces vanished within 1.0 $\times 10^{-4}$ hartrees per bohr. The Au atoms in the inner layer are fixed in their bulk configurations. The adsorption energy is defined as $E_{ad}= E_{Au+ring}-(E_{Au} +E_{ring})$.

Reference:

[1] A.Becke, *J. Chem. Phys.* 1988, ***88***, 2547.

[2] B. Delley, J. *Chem. Phys.* 2000, **113**, 7756.

[3] B. Delley, J. *Chem. Phys.* 1990, **92**, 508– 517.

[4] J. P. Perdew, Y. Wang, *Phys. Rev. B* 1992, **45**, 13244.

Table S1. Experimental (Expt.) and calculated (Cal.) lattice parameters for the self-assembled monolayers on Au (111).

		Unit cell parameters		
		a (nm)	b (nm)	α(°)
9S3	Expt.	0.6 ± 0.05	1.2 ± 0.05	90 ± 1.0
	Cal.	0.75	1.30	90.00
24S8-α	Expt.	0.6± 0.05	2.4± 0.05	90 ± 1.0
	Cal.	0.50	2.31	90.00
24S8-β	Expt.	0.6± 0.05	2.9± 0.05	90 ± 1.0
	Cal.	0.50	2.88	90.00