

Figure 1S

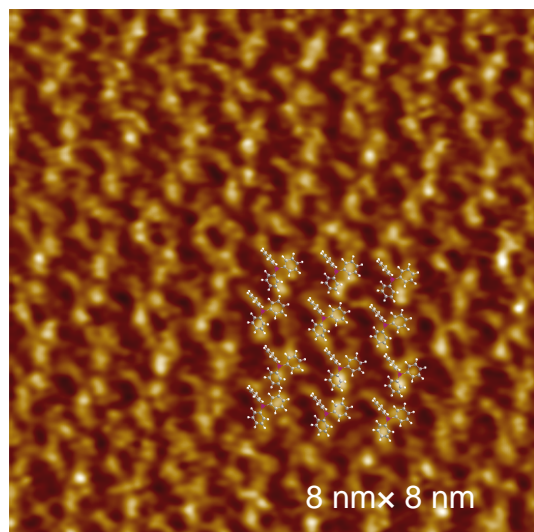


Fig. 1S STM image of SAM of the PPh₃ ligand molecules on Au(111) formed by dipping in an aqueous solution containing only the PPh₃ ligand molecules. The image was recorded in air.

Table 1S. XPS Binding Energies for Rh of various states.

Sample	Rh 3d _{5/2} (eV)	Rh valence	Reference
Rh metal	307.0	0	1
Rh film deposited on Au(111) from RhCl ₃	307.8	0	this work
RhCl(CO)(PPh ₃) ₂	308.2	+1	2
Surface-bound RhCl(CO)(PPh ₃) ₂ on Au(111)	308.4	+1	this work
Surface-bound RhCl(CO)(PPh ₃) ₂ on Au(111) after HER	307.8	0	this work

References

- (1) Contour, J. P.; Mouvier, G.; Hoogewys, M.; Leclere, C. *J. Catal.* **1977**, *48*, 217-228.
- (2) Gassman, P. G.; Macomber, D. W.; Willging, S. P. *J. Am. Chem. Soc.* **1985**, *107*, 2380-2388.