Supporting Information

PyPP1 molecules were synthesized as described elsewhere.[1] All other chemicals were commercially available and in reagent grade. SAMs were prepared by immersing Au substrates into 20 μM ethanolic PyPP1 solution typically for 12 h. Au(111) substrates were prepared by depositing 150 nm au film on freshly-cleaved mica sheets at 450°C by physical vapor deposition. Prior to the SAMs deposition, these Au/mica substrates were annealed within a hydrogen flame as described elsewhere.[2]

The open circuit potential (OCP) measurements were performed using a conventional three-electrode cell, in which a Pt foil and an Ag/AgCl (3 M KCl) electrode were used as counter and reference electrodes, respectively. In the article, all potentials were converted and given w.r.t. standard hydrogen electrode (SHE) for convenience. The cell was filled with 100 ml electrolyte solution (either 1 M H_2SO_4 or 5 μM $PdSO_4$ + 1 M H_2SO_4). The total volume of the cell was 300 ml. A constant gas flow with a rate of 15 l/h was maintained through the electrolyte solution both for N_2 and H_2:N_2 (1:99). The potentials were measured using an Ivium Compactstat (Ivium Technologies) potentiostat.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI Quantum 2000 ESCA using a monochromatized Al Kα radiation source ($h\upsilon$ = 1486.6 eV) operated at 15 kV and 25 W. Detection angle of the photoelectrons was fixed to 45°. The displayed data were normalized with regard to the Au $4d_{3/2}$ peaks for a better analysis of the layer sequence on the sample.

Scanning tunneling microscopy (STM) measurements were performed in ambient using a Nanoscope IIIa instrument. Scanning tunneling spectroscopy (STS) measurements in UHV were carried out using a Jeol JSPM-4500s instrument. The presented I/V curves are averaged over 30 I/V curves obtained on top of NPs and PyPP1-SAM. Images were recorded with a tunnel current (I_{tunnel}) of typically ~50-60 pA and a bias voltage (V_{sample}) of ~1 V. All STM data were acquired at room temperature and processed by using SPIP™ software.

References

1 B. Schupbach, A. Terfort, *Org. Biomol. Chem.*, 2010, **8**, 3552.
2 M. I. Muglali, A. Bashir, M. Rohwerder,; *Phys. Status Solidi A*, 2010, **207**, 793.