

Supporting information for

Bottom-up assembly of a surface-anchored supramolecular rotor enabled using a mixed self-assembled monolayer and pre-complexed components

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General Materials and Methods. Pyridin-4-yl-methanethiol **1** was prepared as described previously.[A.S. Wagman, H.E. Moser, Wagner, E.W. WO/2010/030810.], dodecanethiol **2** was purchased from Aldrich and was used as received, porphyrin **3** was prepared according to the published method.[Penon, O.; Marsico, F.; Santucci, D. Rodríguez, L.; Amabilino, D.B.; Pérez-García, L. J. Porphyrins Phthalocyanines 2012, 16, 1293] The gold surfaces were acquired from Georg Albert PVD-Coating.

Laser desorption ionization time-of-flight (LDI-TOF) mass spectrometry was performed on a LC/MSD-TOF mass spectrometer from Agilent Technologies. UV-Vis absorption spectra were recorded with a Varian Cary 5 UV-Vis-NIR Spectrophotometer, in a 1mm pathlength cell. In a typical experiment, a solution of **3** ($7 \cdot 10^{-5}$ M) in chloroform or toluene was measured and **1** (10^{-2} M in the same solvent) was sequentially added at different stoichiometric ratios and then reduced to the initial concentration of **3**.

STM characteristics and gold surface preparation. Scanning Tunnelling Microscopy (STM) studies were carried out using a 5100 SPM system from Agilent Technologies. All samples were prepared on gold films supported on mica with (111) preferred orientation (commercial provider Georg Albert PVD-Coating) and were measured at room temperature. Before sample preparation, the gold surfaces were cleaned and briefly flamed using a methane torch. A soft and rapid thermal treatment makes favourable the formation of Au (111) terraces, and hence, an extraordinary epitaxial alignment of molecules can be achieved on the surface. We employed constant current STM mode and Pt/Ir (80:20) STM tips in our experiments. The tips were mechanically cut in all measurements. To confirm the validity of the measurements, imaging performed on different surfaces using different tips in all sessions. The images are not corrected for noise or drift in any case.

Preparation of SAMs of **1 or **2**.** After the preparation the gold substrate film supported on mica by annealing using a methane flame, the Au(111) was immediately dipped into a toluene solution of the thiol ($1 \cdot 10^{-5}$ M). Typically, the gold substrate was left immersed in the solution for approximately 12 hours. After this time, the substrate was exhaustively rinsed with fresh toluene and dried with a flow of nitrogen gas.

Preparation of 1:1 mixed SAM. The synthesis was performed as described for the preparation of **1** SAM, however, in this case the toluene solution contained **1** and **2** molecules in a 1 to 1 molar ratio ($1 \cdot 10^{-5}$ M).

Preparation of 10:1 mixed SAM. The synthesis was similar to 1:1 mixed SAM preparation but the toluene solution where the Au(111) was immersed contained **1** and **2** molecules in a 10 to 1 molar ratio ($1 \cdot 10^{-5}$ M and $1 \cdot 10^{-6}$ M).

Coordination of 3 with a 10:1 mixed SAM. After formation of 10:1 mixed SAM, the sample was immersed in a toluene solution of **3** ($1 \cdot 10^{-4}$ M) for 12 hours. Again, a cleaning process with pure toluene and a drying step with nitrogen gas were necessary before STM measurement were performed.

Functionalisation of Au(111) with 3-1 in solution. A clean and thermally treated gold substrate was immersed 12 hours in a toluene solution containing the **3-1** complex (concentration of each component $1 \cdot 10^{-5}$ M and $1 \cdot 10^{-4}$ M, respectively). The gold substrate was then thoroughly cleaned with pure toluene and dried with nitrogen gas before STM measurements could be conducted.

Functionalisation of Au(111) with a mixed solution containing 1, 2, and 3. In this sample preparation, a clean annealed gold substrate was immersed for 12 hours in a toluene solution containing **1** ($1 \cdot 10^{-5}$ M), **2** ($1 \cdot 10^{-6}$ M), and **3** ($1 \cdot 10^{-4}$ M), and the sample was cleaned as for the other samples.

Scanning Tunnelling Microscopy of monolayers of **1** and **2**

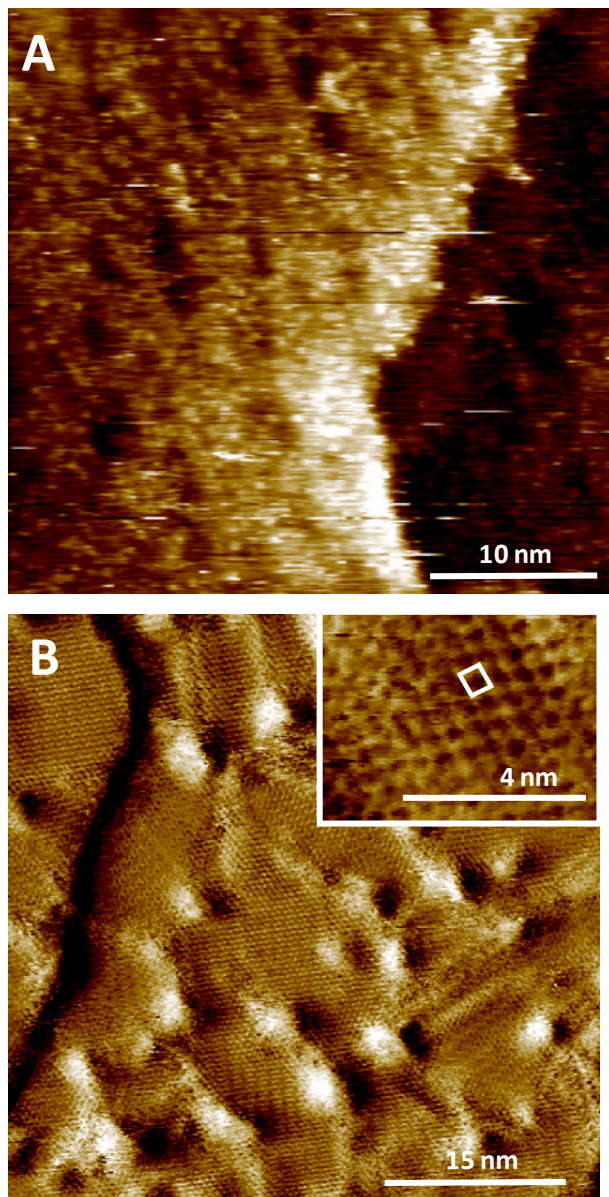
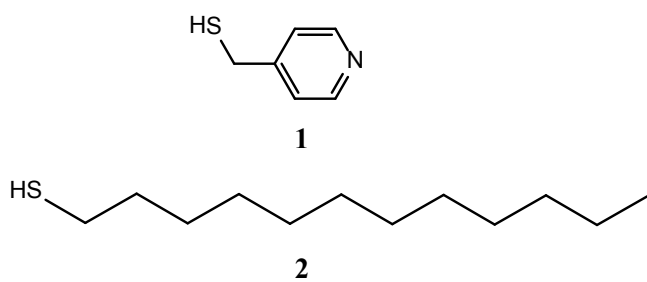


Figure S1. Chemical structures of compounds **1** and **2** and STM images of: (A) a SAM of **1** ($I_{\text{set}}=0.05\text{nA}$, $V_{\text{bias}}=-0.8\text{V}$) in topographic mode and (B) a SAM of **2** ($I_{\text{set}}=0.6\text{nA}$, $V_{\text{bias}}=0.85\text{V}$), both in current mode on Au(111). The inset in (B) shows the close-packed arrangement and the unit cell present in SAMs of **2**.

Scanning Tunnelling Microscopy of monolayers of mixed monolayer of 1 and 2 in 1:1 solution ratio

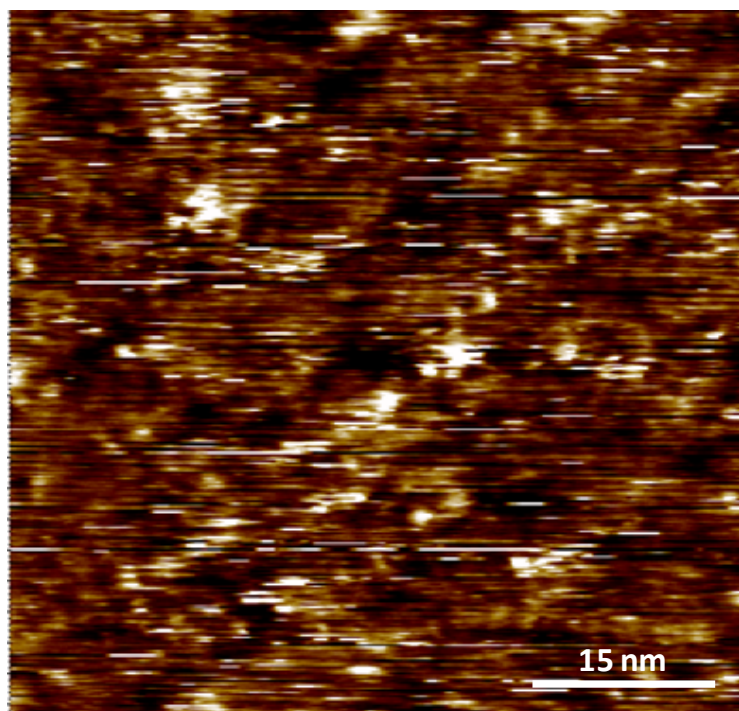


Figure S2. STM image of mixed SAM comprising **1** and **2** at 1:1 solution deposition ratio ($I_{\text{set}}=0.04\text{nA}$, $V_{\text{bias}}=-0.8\text{V}$).

Supporting spectroscopic evidence for formation of complexes between axle and rotor follow:

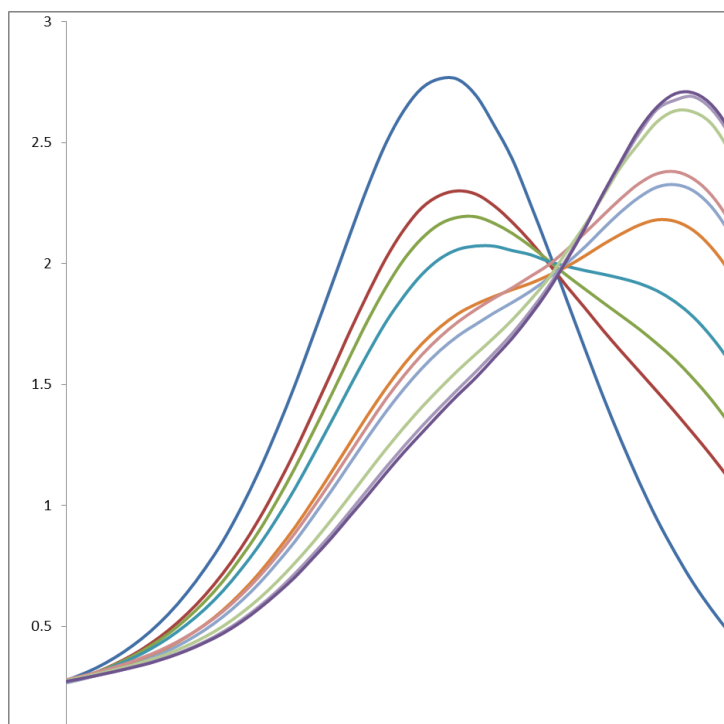


Figure S3. UV-Visible absorption spectra of **3** (blue line) and the **3-1** complex formation in chloroform.

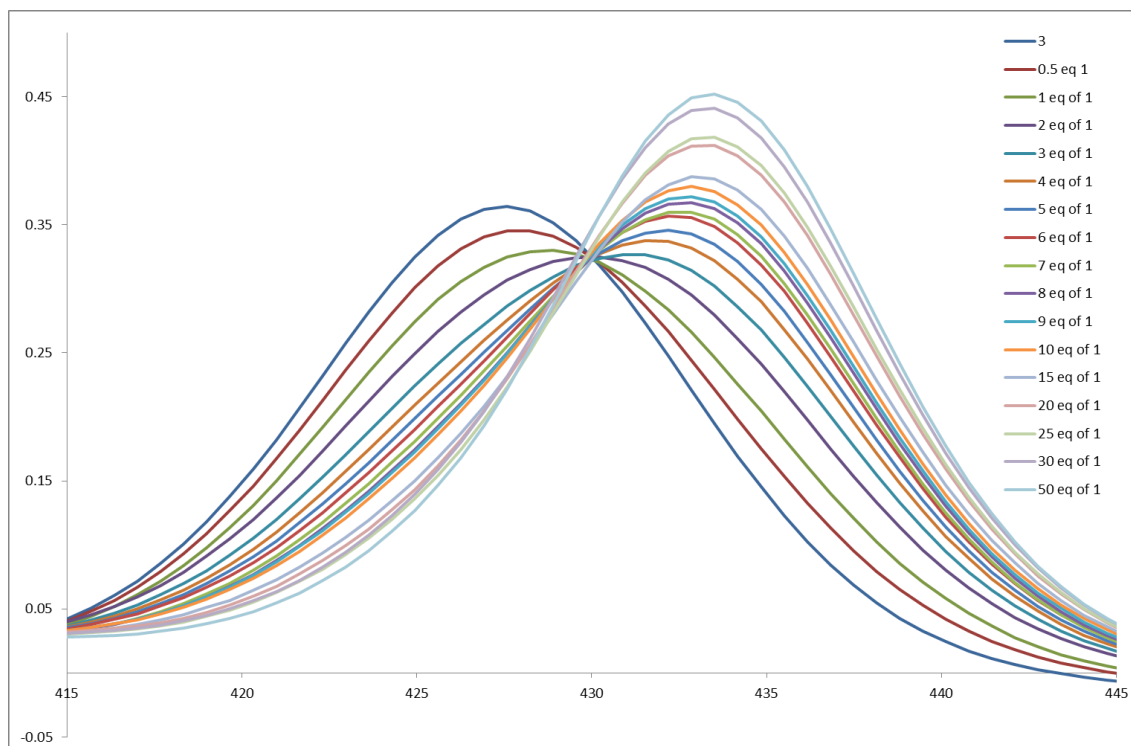


Figure S4. UV-Visible absorption spectra of **1** (blue line) and the formation of the **3-1** complex in toluene.

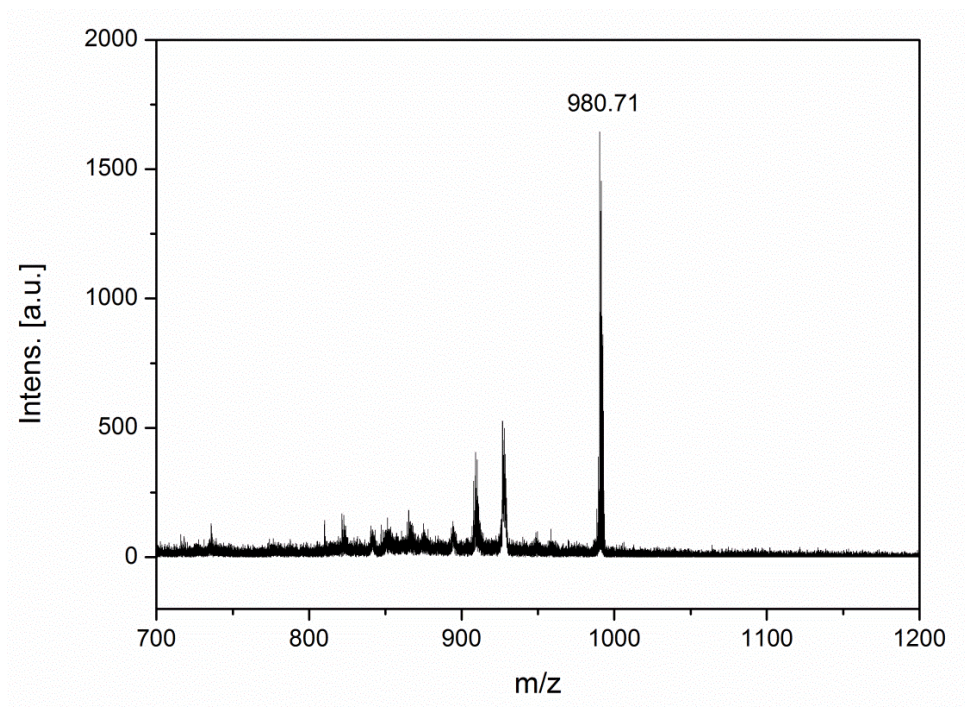


Figure S5. LDI-TOF mass spectra of **3-1** complex on a **10:1** mixed SAM of **1** and **2** on gold(111).