## **SUPPORTING INFORMATION**

# An optimized alkyl chain-based binding motif for 2D self-assembly: a comprehensive crystallographic approach

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#### Supporting Information

#### **Chemical synthesis**

Compound **1** was synthesized by McMurry reaction starting from the corresponding aldehyde as depicted below.



A suspension of Zn powder (600 mg) in THF (5 mL) was slowly added to a mixture of  $3^1$  (300 mg, 0.72 mmol) and TiCl<sub>4</sub> (0.5 mL) in THF (5 mL) at -10°C under argon. The reaction mixture was then heated under reflux for 12 h, quenched with 1M NaHCO<sub>3</sub>, extracted with Et<sub>2</sub>O. The organic phases were dried over MgSO<sub>4</sub> and evaporated under reduced pressure. Purification by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes 4:6) gave **1** as a white solid (486 mg, 84%). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>) :  $\delta$  0.87 (t, J = 6.7 Hz, 12H), 1.28 (m, 56H), 1.75 (m, 8H), 3.94 (t, J = 6.7 Hz, 8H), 6.35 (t, J = 2.1 Hz, 2H), 6.61 (d, J = 2.4 Hz, 4H), 6.98 (s, 2H).

### **STM measurements**

STM images were acquired at room temperature with a homemade digital system. The fast scan axis was kept perpendicular to the sample slope. Images acquired simultaneously in both fast scan directions are systematically recorded and compared. The solvent was phenyloctane (Aldrich, 98%), which avoids the coadsorption often observed with linear alkanes. The substrate were HOPG (Goodfellow) and Au(111), and the tips were mechanically formed from a 250 mm Pt–Ir wire (Pt80/Ir20, Goodfellow). The monolayers were formed by immersing the STM junction in a droplet (ca. 10 mL) of solution immediately after cleaving the substrate and approaching the STM tip. The concentrations of the solutions were around  $10^{-4}$ M.

A software drift correction is systematically applied. The program exploits the comparison between the images acquired during two successive upward and downward frame scans to evaluate the X-Y components of the drift. The images are then corrected accordingly. The acquisition also accounts for

<sup>&</sup>lt;sup>1</sup> Compound **3** was prepared following the procedure by D. Pez et al., Bioorg. Med. Chem. 2003, **11**, 4693.

possible 4-quadrant piezoelectric tube anisotropy. Altogether, the angle measurement accuracy is better than 1°.

The calibration of length measurements is achieved based on atomic-resolution images of HOPG after above-described drift and anisotropy corrections. The remaining error is to be attributed mainly to the tip-to-tip variations of tip-length sizes. The corresponding accuracy is thus estimated to 4%, a value confirmed by the dispersion of HOPG period measurements obtained with various tips. This error affects mostly the overall scaling factor. This explains why the accuracy of angle measurements is significantly better than that of length measurements.



Figure S1. STM image of 1 on Au(111) showing simultaneously the molecular network and the chevrons of gold surface reconstruction. Imaging parameters:  $I_t = 4 \text{ pA}$  and  $V_{\text{bias}} = -1300 \text{ mV}$ ,  $87 \times 54 \text{ nm}^2$ .



Figure S2. STM images of 1 at room temperature on a) HOPG and b) Au(111) after rinsing the surfaces twice with pure phenyloctane. Imaging parameters: a)  $I_t = 100 \text{ pA}$  and  $V_{\text{bias}} = -1255 \text{ mV}$ ,  $98 \times 58 \text{ nm}^2$  and b)  $I_t = 50 \text{ pA}$  and  $V_{\text{bias}} = -550 \text{ mV}$ ,  $70 \times 32 \text{ nm}^2$ .