Organisation and ordering of 1D porphyrin polymers synthesised by on-surface Glaser coupling

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Electronic Supplementary Information

Contents

Experimental Methods

Scanning probe microscopy (SPM) experiments were performed under ultrahigh vacuum (UHV) conditions within two separate systems: (1) Room Temperature (RT) system (base pressure 10^{-10} mbar), with a separate chamber (base pressure 10^{-10} mbar) used for the preparation of the sample. STM (Scanning Tunneling Microscopy) images were acquired with an Omicron STM-1 system operated in constant current mode; electrochemically etched tungsten tips were used, covered with silver from routine contact with a Ag(111) surface for tip optimization. (2) Low Temperature (LT) system (base pressure 10^{-11} mbar). STM and ncAFM (non-contact atomic force microscopy) images were acquired with an Omicron combined STM/AFM LT system operating at cryogenic temperatures (liquid nitrogen, ~78K). The STM images were acquired in constant current mode. AFM images were acquired in constant height mode. Lateral displacement of the tip (drift and creep) during the constant height AFM images was minimized by implementing an Atom tracking procedure.[1] A home-built custom quartz qPlus sensor,[2] incorporating a cantilever, with an electrochemically etched tungsten wire tips and separate tunnel current wire was used, covered with silver from routine indentation with the Ag(111) sample for tip optimization: Resonant frequency 22.736 KHz, oscillation amplitude 75 pm.

An Ag(111)/mica sample (Georg Albert PVD – Beschichtungen) was cleaned by argon ion sputtering (0.75 keV, I_{sample} = ~1.1 μA, P_{Ar} = ~2.5×10^{-5} mbar, 60 min) and subsequent annealing at ~400 ºC for 30 minutes. The **1D-Porph** molecule was deposited in vacuum using a rapid heating technique. A solution of **1D-Porph** in toluene (1 mg per ml) was drop-cast onto a Si wafer and introduced to the vacuum system. Rapid heating of the Si wafer (~500^{o}C) resulted in transfer of the molecule to the Ag(111) substrate, with the Ag(111) sample held at room temperature.

Transfer between the RT and LT systems was performed using a 'vacuum suitcase' – a small UHV assembly containing a sample storage stage on a linear transfer arm compatible with the Omicron 'spade' sample plates.

Additional Experimental Information

STM images acquired after deposition show small 2D islands (Fig. S1) where the period along the polymer chain is measured to be 1.31±0.07 nm; as expected for covalently coupled porphyrins and in good agreement with crystallographic data (1.353 nm)[3] and studies of similarly covalently bonded porphyrin polymer chains (1.33±0.07 nm).[4] This indicates that the observed coupling at RT is facilitated by activation (dehydrogenation) of a fraction of the molecules during deposition (as previously reported[5]). The average length of the islands after deposition is measured to be 14±4 nm, equivalent to ≈10 porphyrin units. Annealing the sample at 120 ^{o}C results in the formation of larger, more ordered, close-packed islands consisting of 1D polymer chains (Fig. 1c). The average island length after annealing the sample (28±10 nm, ≈21 porphyrin units) is approximately twice that observed prior to annealing, indicating that unreacted diffusing species are present at RT and that the reaction is driven to completion by supplying additional thermal energy.

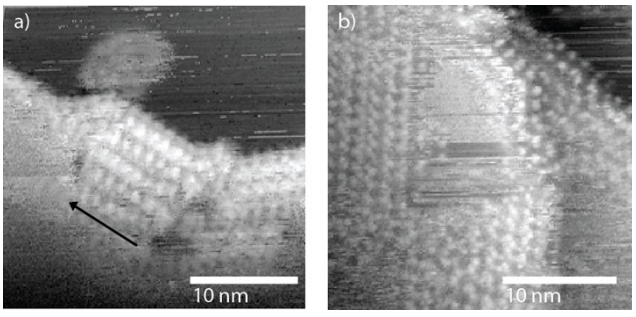

Fig. S1 Polymer chains on Ag(111) after deposition. (a) STM image of small islands of close-packed 1D polymer islands after deposition (black arrow indicates row direction). (b) STM image showing close-packed islands of the 1D polymer chains, with several chains seen to run along the step-edges. Image parameters: tunnel current, I = 40 pA, sample voltage, V = -3.00 V.

In addition to the close-packed islands, non-linear, curved, sections of 1D polymers are observed (see Fig. S2a). These structures are similar in form to those observed for analogous solution-synthesized polymers previously deposited via an electrospray technique.[4] The motion of single polymer chains may be observed at room temperature in instances where the polymer is pined at one end, with the non-pined end able to diffuse. Where diffusion occurs on a timescale faster than the STM acquisition rate (as in this case) such motion results in characteristic features, sometimes called 'Christmas tree' structures,[6] an example of which is shown in Fig. S3b. These features indicate a strong directional interaction between neighboring porphyrin units and is therefore in agreement with our assignment of covalent bonding between the porphyrin units.

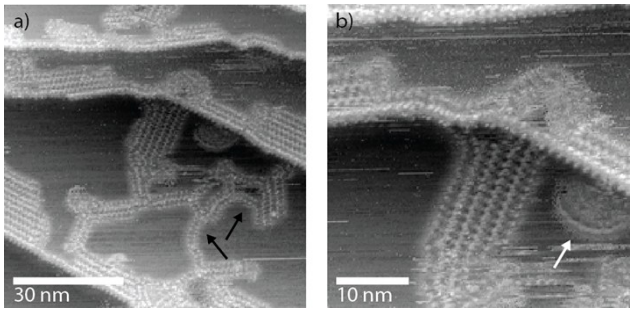

Fig. S2 Polymer chains on Ag(111) after annealing the sample at 120 °C. (a) STM image of structures formed from the 1D polymers. In addition to the close-packed islands non-linear single polymer chains are observed (black arrows indicate non-linear chains). (b) STM image showing close-packed island and a mobile polymer chain (indicated by white arrow). Image parameters: tunnel current, I = 30 pA, sample voltage, V = -1.80 V.

AFM imaging in constant height was observed to induce manipulation of the polymer chains as the tip-sample separation was decreased. Figure S3 shows a sequence of images where: (a) an STM image of a curved polymer chain was acquired, (b) the imaging mode was switched to constant height AFM and an image of the same region was obtained, (c) the tip-sample separation was reduced by 0.05nm resulting in an interaction between the tip and polymer

(black arrow), with further decreases in tip-sample separation resulting in manipulation of the chain – resultant structure shown in STM image (d).

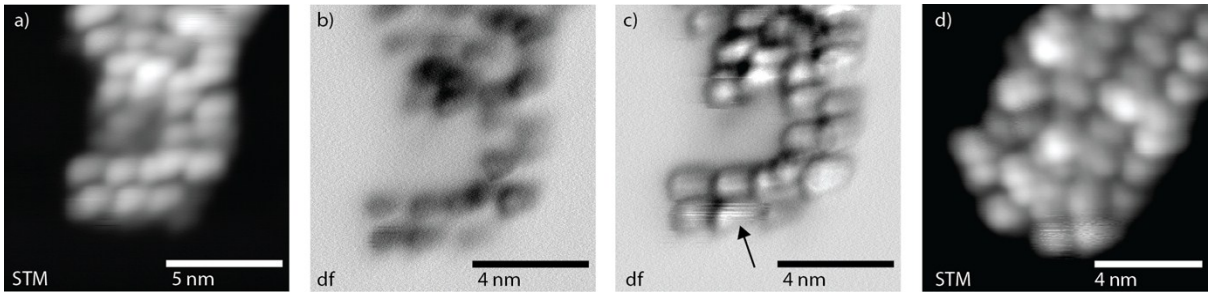

Fig. S3 Tip-induced manipulation of curved chains by AFM. (a) STM image of a curved chain. (b-c) AFM images of a curved chain; the tip-sample separation is decreased by 0.05 nm from (b) to (c). Further decrease in tip-sample separation results in manipulation of the chain. (d) STM image of the same chain in (a) after manipulation. Image parameters: (a,d) STM - tunnel current, I = 10 pA, sample voltage, V = -1.8 V, (b,c) AFM – constant height, sample voltage, V = +0.01 V.

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