Supporting information to article:

**Stereoselective formation of coordination polymers with 1,4-diaminonaphthalene on various Cu substrates**

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**Experimental method:**

All experiments were performed in UHV conditions using low-temperature STM system (Omicron GmbH). Samples (Cu single crystals) were cleaned using several cycles of Ar⁺ sputtering and annealing. 1,4-diaminonaphthalene (Sigma-Aldrich) was sublimated under UHV conditions at 328K using thermal evaporation source (Kentax) directly at the clean substrate at different temperatures. Temperature of the substrate was monitored using thermocouple attached to manipulator head and pyrometer (Optris). STM pictures were obtained at 78K.

**Structures determination:**

All proposed structures in this article were based on STM pictures and using the calculated Cu-Cu distance of a relaxed surface structure (0.249nm) and single mer DFT optimization in vacuum. On Cu (111) we observed that the distances of mers in the polymers measured from STM pictures (0.75 nm) are equal to the multiplicity of the Cu atom distances at surfaces (3 x 0.25 nm).
Additionally polymers were formed along the three main crystallographic directions of the Cu (111) which is in good agreement with proposed molecular system.

On the Cu (110) surface the polymers are formed along only one crystallographic direction with periodicity of the trans-cis-trans-cis structure 3 nm. The measured distances between Cu atoms in the polymer chain is 0.79 nm.

The polymers on Cu (110) can grow also in trans-trans configuration but only along one of the specific crystallographic direction (or it mirror direction) as depicted on Fig. 4 in the main article.
Also based on symmetry of the substrate we can determine the structure of the cyclic tetramer which occurs only in two different orientations at the surface mirrored in \(<1,0,1>\) axes.