

On-Surface Engineering of Porphyrin-Based Two-Dimensional Coordination Networks on Cu(111)

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Two-dimensional metal–organic coordination networks enables precise tuning of electronic and magnetic properties at the nanoscale.^{1,2} Porphyrin-based building blocks are particularly suited for this purpose due to their structural versatility and chemical tunability.³ Combined with on-surface synthesis, which enables atomic-scale control on metallic substrates,^{4,5} these systems provide a powerful platform for engineering functional low-dimensional materials. Here, we examine the coordination behavior of 5,10,15,20-tetrakis[4'-(4-pyridyl)phenyl]porphyrin on Cu(111). Using scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), we systematically probe the influence of thermal treatment on network formation. After room-temperature deposition, molecules are disordered and adopt an inverted adsorption geometry. Annealing at 400 K results in the coexistence of a square Cu-coordinated framework, in which the molecules adopt a saddle-shaped conformation, and one-dimensional chain-like structures. Further annealing at 450 K drives a transition toward one-dimensional chains, where molecules revert to the inverted configuration. These results demonstrate that network topology, molecular conformation, and dimensionality can be precisely tuned by controlling deposition and annealing parameters, thereby providing a pathway for the design of functional two-dimensional materials.

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