Designing Artificial 2D Molecular Magnets on Surfaces

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Engineering a two-dimensional (2D) honeycomb network with magnetic atoms on a substrate surface can result in non-trivial topological magnetic structures. We have employed on-surface synthesis methods to realize such a system [1-3]. To date, we have investigated the creation of a 2D magnetic cobalt nanocluster array using 2D covalent organic frameworks (COFs) synthesized from 1,3,5-tris(4-bromophenyl)-benzene (TBB) precursors on a noble metal Cu(111) surface [1]. Additionally, crown ether molecules possess the functionality to trap adsorbed guest magnetic atoms, producing magnetic cobalt nanoclusters [2,3]. However, this system could not establish a 2D lattice comprising single isolated magnetic atoms.

Thus, in this study, we aimed to create 2D metal-organic frameworks (MOFs) on Cu(111). We discovered that a 2D honeycomb network could form on an atomically flat and clean Cu(111) surface at 300 K without the necessity for magnetic atom deposition. We analyzed the surface morphology and structures using a low-temperature (78 K) ultrahigh vacuum (UHV) scanning tunneling microscopy/spectroscopy (STM/STS) setup.

Initially, we employed 1,4-Di(4-pyridyl)benzene (DPB) molecules as a precursor but observed a disordered 1D network along with a self-assembled monolayer (SAM) array, indicating the absence of a clear honeycomb network. However, by utilizing quaterphenyl-4,4'-carbonitride (Ph₄DN) molecules and depositing approximately 0.15 nm on Cu(111) at 300 K, we achieved an ordered honeycomb network, resulting in sub-monolayer coverage on the surface. This indicates the formation of N-Cu-N bonds, with the possibility of Cu ions possessing a spin state.

When we further deposited Co atoms (0.3 monolayers) onto the 2D honeycomb network at 300 K, the anticipated 2D honeycomb network consisting of N-Co-N bonds did not form. Instead, all Co atoms likely remained within the nanopores.

References:

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