Atomically-defined, air-stable 2D metal-organic frameworks on graphene: how the support defines the system properties

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The functionality of 2D metal-organic frameworks (MOFs) crucially depends on the local environment of the embedded metal atoms, and such details are best ascertained on 2D MOFs supported on atomically flat surfaces. Here, we present three systems which are well-defined at the atomic-scale, decoupled from the metal support and stable both in ultrahigh vacuum and in ambient conditions: M-TCNQ (M = Ni, Fe, Mn) supported on epitaxial graphene/Ir(111). We show that these systems are monophase with $M_1(TCNQ)_1$ stoichiometry, and we demonstrate their remarkable chemical and thermal stability [1]. Furthermore, by a combined experimental and computational approach we study the differences between MOF systems supported on graphene and on Au(111), the prototypical surface for on-surface synthesis. We show that the Fe-TCNQ on graphene is non-planar with iron in quasi-tetrahedral sites, but on Au(111) it is planarized by stronger van-der-Waals interaction [2]. Combined with the distinct energy level alignment with the supports, this results in significant differences in the 2D MOF properties on these two surfaces. Our results outline the limitations of common on-surface approaches using metal supports and show that the intrinsic 2D MOF properties can be partially retained on graphene. The modular M-TCNQ/graphene system combines the atomic-scale definition required for fundamental studies with the robustness and stability needed for applications, thus we consider it an ideal model for research in single atom catalysis, spintronics or high-density storage media.

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