Energetic and electronic properties of doped Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are crystalline porous solids with large surface areas formed by coordination bonding between organic ligands and metal centers (ions or clusters), which can be synthetized in different structures (1D, 2D, and 3D crystals). Owing to their structural diversity and functional adjustability, these nanoporous materials have been extensively investigated in physics, chemistry, and material science for applications in spin-crossover centers, single-atom catalysis, gas storage, and sensors for the detection of hazardous chemicals like volatile organic compounds and toxic gases.[1] Thousands unique structures have since been synthesized and rapidly transformed in a new class of crystalline materials with dynamic response to external stimuli.[2] However, despite the enormous amount of information on synthesis and applications of MOF delivered in recent reviews, only a few works on fundamental electronic structure and transport properties have been published.[3]

In this work we study the structural and electronic properties of the metal-organic framework of composition $Zn_4O(BDC)_3$ (BDC=benzene-1,4-dicarboxylate), known as IRMOF-1 [4], which is an insulator with experimental bandgap of 4.7 eV. We explore formation energy, transition levels, and charge carrier properties by atomistic DFT calculations using the hybrid HSE functional. This methodology gives us a good description of the electronic properties, providing a theoretical bandgap of 4.8 eV. We focus on the stability and electronic structure of doped MOF with Cu, Al, and Ti substitutional impurities at Zn sites. Our results show that doped IRMOF-1 behaves as wide-bandgap semiconductors where the addition of donor (Al_{Zn}) and acceptor (Cu_{Zn}) impurities render the material n-type and p-type characteristics, respectively, while Ti_{Zn} introduces deep levels in the bandgap. Formation energy calculations indicate that substitutional impurities under consideration are likely to be incorporated, suggesting that doping could play a crucial role in designing semiconductor properties of MOF materials for engineering applications.

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References:

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