Boron-based molecular magnets studied by first-principles calculations

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Successful incorporation of transition metals (M) into the core of planar boron clusters B_n, yields a fascinating class of borometallic molecules [1]. These novel compounds exhibit variable ring sizes, namely MB_n and MB_n^- with n = 8–10, and have been characterized through size-selected anion photoelectron spectroscopy [2]. In these molecular wheels, each B atom in the circumference contributes two electrons to the B–B peripheral covalent bonds and one electron to the delocalized bonds. So an atom with the appropriate number of valence electrons can fit into the center of the boron wheel to make the MB_n clusters. Delocalized bonding between the metal atom and the boron ring and localized bonding at the periphery of MB_n made transition metals promising candidates for the central position of the ring clusters to make an electronically stable borometallic cluster compound.

Following our previous experience with modeling of nanomaterials [3], here we perform first-principles calculations to study the electronic and magnetic properties of boron rings with a transition metal in the center, MB_{8-10} (M = Ti, Cr, Mn, Fe, Co, Nb, Mo), and boron double-rings sandwiching the metal atom, M–$2B_{8-10}$. Our study reveals that the overall magnetic moment of the clusters is a combination of the magnetic moment of the central metal ion and the induced magnetic moment of the peripheral boron atoms. These molecular-based magnets offer a platform to study magnetism in the zero-dimensional limit. Moreover, the M–$2B_{8-10}$ clusters can serve as building blocks of one-dimensional tubular forms.

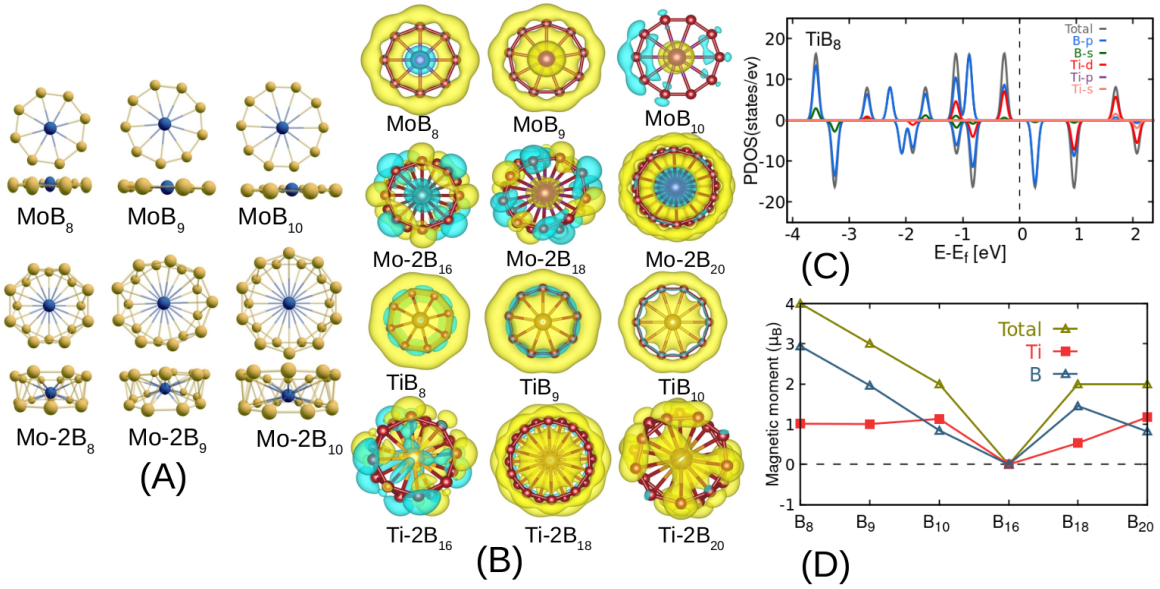

Figure 1: (A) Geometries of MB_{8-10} and M–$2B_{8-10}$ clusters where the metals are in the center and the outer wheels are made up of boron. (B) Electron density difference, $\Delta\rho(r) = \rho_\uparrow(r) - \rho_\downarrow(r)$, where spins up (down) are in yellow (blue). The projected density of states for TiB_8 and magnetic moment components for TiB_n (and Ti–$2B_n$) are shown in (C) and (D), respectively.

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[1] C. Romanescu et al., Angewandte Chemie International Edition **50**, 9334 (2011).

[2] C. Romanescu et al., Accounts of Chemical Research **46**, 350 (2012).

[3] S. Perveen et al., Computational Condensed Matter **37**, e00851 (2023).