



Recent advances in computational studies of organometallic sheets: Magnetism, adsorption and catalysis



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ABSTRACT

The unique geometry and novel properties of graphene have tremendously motivated scientists to explore other monolayer materials, especially those with separately distributed and exposed metal ions for magnetism, hydrogen storage, CO₂ capture and catalysis. The recent successful synthesis of 2D organometallic sheets has opened a new pathway to design and fabricate such desirable 2D materials going beyond graphene and other inorganic sheets. This article briefly reviews the recent advances in computational studies of 2D organometallic sheets based on density functional theory, quantum chemistry modeling and Monte Carlo simulation focusing on stability, magnetic coupling, magnetism tuning, hydrogen storage, CO₂ capture and catalysis. Future research directions in this field are also discussed.

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1. Introduction

The discovery of graphene in 2004 has opened up a new epoch for two dimensional (2D) monolayer materials [1]. The hitherto reported monolayers, such as graphene, boron nitride (BN), silicene, and MoS₂ [1–4], exhibit various novel properties and have potential applications in lithium ion batteries, integrated circuits, transparent conducting electrodes, photoluminescence and valleytronics [5–10]. However, neither of these graphene-like inorganic monolayer materials are intrinsically magnetic in their pristine forms, nor of them show a distinctive property in gas adsorption and catalysis. It has been found that the metal adatom migration activation barriers for the lowest energy migration paths on pristine monolayer, bilayer, and trilayer graphene are smaller than or within an order of magnitude of $k_B T$ (0.026 eV) at room temperature, implying very high mobilities for the adatoms. For example, the binding energy of a Cr atom with graphene is about –0.5 eV and the migration energy barrier is only 0.02 eV [11]. This suggests that metal atoms on graphene quickly migrate across the lattice and bind together forming clusters. One possible way is to make graphene porous so that the edge state may prevent the introduced metal atom from clustering [12–14]. However, it is very

difficult to control the shape, size and distribution of defects precisely in experiment, and the induced magnetic properties depend sensitively on experimental conditions and structural morphologies [15]. While the problem for the intrinsically metal-containing sheets like MnO₂, MoS₂ is that in these monolayers, the metal ions are separately distributed but not well exposed [16,17], therefore they are not good for gas adsorption and catalysis.

The key challenge becomes how to synthesize a sheet with separately distributed and exposed metal ions? For design and synthesis, phthalocyanine (Pc) and porphyrin (Por) are widely used as ideal constituent units, where the pores endow the feasibility of embedding metal atoms or complexes. The successful synthesis of 2D FePc-based sheet paved the way for exploring 2D organometallic materials where the metal species could be replaced with other elements using STM tip, showing flexibility and diversity [18,19]. Furthermore, the diverse organic ligands with extended π -conjugation are interesting and appealing oligomers due to their versatile functional properties that show a wide range of applications [20]. The high thermal and chemical stabilities, facile synthesis and robust nature make the organometallic molecules attractive building blocks for the assembly of monolayer nanomaterials [21–23]. Based on the theoretical and experimental advances on diverse organometallic sheets, scientists have obtained high surface area materials with separately distributed and exposed metal ions for magnetism, adsorption and catalysis [24,25].

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This review briefly summarizes the recent advances made by Chinese research groups in computational studies of organometallic sheets focusing on tunable magnetism, hydrogen storage, CO₂ capture and catalysis.

2. Tunable magnetism

Previous studies have demonstrated that the magnetism of nanomaterials distinguishes from that of bulk materials in a fundamental way because both magnetic coupling and magnetic moments are strongly dependent on coordination number, symmetry, bond-length and dimensionality-related quantum confinements [26], which provide the variables for tuning the magnetism.

2.1. Phthalocyanine-based organometallic sheets

The experimental success in embedding transition metal (TM) atoms in 2D Pc sheets paves the way for achieving the longstanding dream of 2D atomic sheets with regularly and separately distributed TM atoms [18]. To better understand this kind of 2D sheets, first-principles calculations have been carried out to investigate the electronic and magnetic properties, as shown in Fig. 1 [27]. It has been found that among the 3d elements from Cr to Zn, only the 2D MnPc framework is ferromagnetic (FM), while 2D CrPc, FePc, CoPc, and CuPc are antiferromagnetic (AFM) and 2D NiPc and ZnPc are nonmagnetic. The difference in magnetic couplings for the studied systems is found to be related to the different orbital interactions. The calculated projected densities of states of the central metal ions evince that only MnPc displays metallic d_{xz} and d_{yz} orbitals that can hybridize with p electrons of Pc moiety, which mediates the long-range FM coupling (Fig. 1). Monte Carlo simulations based on the Ising model suggested that the

Curie temperature (T_C) of the 2D MnPc framework is ~ 150 K, which is comparable to the highest T_C achieved experimentally in Mn-doped GaAs. The 2D TMPc nanostructures exhibit very interesting magnetic properties in comparison with dilute magnetic semiconductors (DMSs) such as Mn-doped Si, GaN, or ZnO, where the doped TM atoms easily form clusters [28,29], thus resulting in nonintrinsic magnetism.

From above one can see that a freestanding poly-MnPc sheet has stable FM order, while most of the other poly-TMPc sheets exhibit weak AFM order and are not directly suitable for device applications [27]. One question is how to tune the magnetism in these organometallic sheets. Recall that in some DMSs, multi-decker nanowires, and graphene nanoribbons, carriers play an important role in tuning the magnetic coupling between magnetic atoms [30–33]. Following this idea, Zhou and Sun [34] carried out detailed studies showing that the magnetic couplings in poly-CrPc and poly-FePc sheets will be changed from AFM to FM with high exchange energies under electron doping. When electrons are injected to the poly-TMPc sheets, the magnetic coupling can be changed from AFM to FM with large exchange energies. Based on Monte-Carlo simulations, it was found that electron doping can induce stable FM states with T_C of 130–140 K, while hole doping will enhance the stability of the AFM states. Such changes in magnetic couplings depend on the balance of AFM superexchange and FM p–d exchange.

Since the interatomic separation between the TM atoms often determines their magnetic moment and coupling, one would wonder whether the magnetic properties of these systems can be further tuned by external strain. In 2012, Zhou *et al.* have studied strain-induced spin crossover in poly-TMPc (TM = Mn, Fe, Co, and Ni) systems [35]. It was found that the magnetic moment of the central TM atoms could be increased by $2 \mu_B$ when a strain was applied. These poly-TMPc systems, however, show different

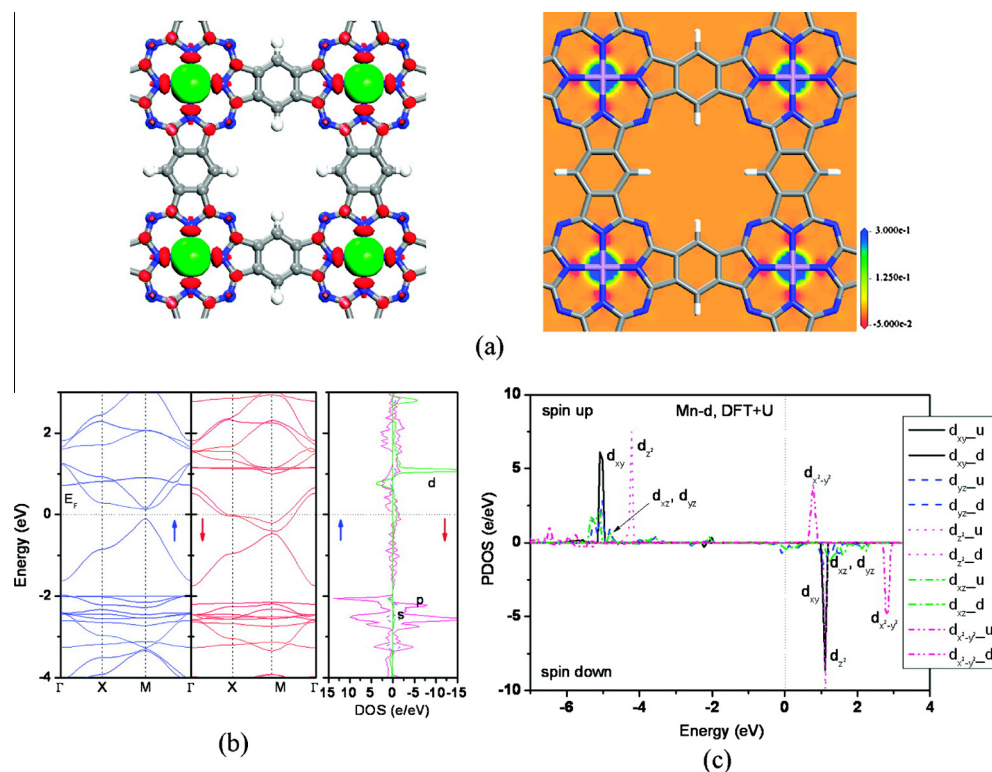


Fig. 1. (a) (left) Isosurface at a value of $0.01 \text{ e}/\text{\AA}^3$ and (right) 2D slice of the spin density ($\rho_{\uparrow} - \rho_{\downarrow}$) for FM 2D MnPc. (b) Band structure and corresponding DOS of FM 2D MnPc. (c) Projected DOS of the d orbitals on the Mn atom. Symbols: solid for d_{xy} ; dash for d_{yz} ; dot for d_z^2 ; dash-dot for d_{xz} ; dash-dot-dot for $d_{x^2-y^2}$. [Reproduced with permission from Ref. [27]. Copyright (2011) American Chemical Society].

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