



## Magnetism and spin transport in transition metal organometallic clusters

Ivan Stich

*Institute of Physics, Slovak Academy of Sciences, Slovakia*

*E-mail: [ivan.stich@savba.sk](mailto:ivan.stich@savba.sk)*

Transition metal organometallics has recently attracted much attention due to its potential for applications in catalysis, molecular recognition, high-density storage, quantum computing, and spintronics. Despite these applications, reliable theoretical and experimental knowledge of energetics, dissociation energy, spin multiplicity, spin gaps, etc. of these systems is still missing. Therefore, we have performed very accurate fixed-node quantum Monte Carlo (QMC) calculations with the quest to elucidate electronic, magnetic, and atomic structure of these systems in both neutral and charged states and thus to provide ultimate answers to the open questions. For half-sandwich systems (vanadium-benzene and cobalt-benzene) which are important model systems for magnetic adatoms on graphene, we find results qualitatively different from DFT predictions for both spin ground-states as well as for fragmentation energies. Perhaps surprisingly, we conclude that also some experimental results may be strongly biased. We have also studied full-sandwich vanadium-benzene multi-decker clusters,  $V_n Bzn+1$ ,  $n=1-3$  in both neutral and charged states. The most important prospective applications of these and related systems are in spintronics as spin filters. Use as spin filters requires them to be half-metal ferromagnets, in order to feature a metallic gap for the minority-spin electrons and semiconducting gap for the majority-spin electrons. We find that, while magnetic structure of these systems is consistent with ferromagnetic coupling, their electronic structure is not consistent with half-metallic behavior as previously assumed, but rather these systems are ferromagnetic insulators with large and broadly similar  $-\uparrow/-\downarrow$ -spin gaps, implying thus a limited potential of these and related materials for spintronics applications unless they are further modified or functionalized. Transition-metal atom/ $\pi$ -conjugated ring sandwich compounds are promising candidates for application in molecular spintronics. However, a great challenge that has significantly restrained the practical application of these sandwich compounds is their fabrication on a well-characterized solid-state substrate in a controllable manner. In this work, we suggested a two-step self-assemble way to fabricate the  $Eu-CnHn-2$  compounds on the hydrogen-terminated Si(100) surface and theoretically studied the geometric structure and electronic and magnetic properties. Theoretical results indicate that the silicon surface is an ideal substrate to support such kind of metal atom-encapsulated sandwich compounds as the lattice distance of silicon (100) surface is close to the inter-ring distances of freestanding gas-phase sandwich compounds. On the basis of the spin-polarized density functional theory calculations and ab initio molecular dynamics simulations, we find that the silicon surface-supported Si-[EuCh]N, Si-[EuCOT]N, and Si-[EuCnt]N sandwich compounds all possess a ferromagnetic ground state. Moreover, the cycloheptatrienyl (Ch) and cyclononatetraenyl (Cnt) Eu sandwich compounds show half-metallic properties. The calculation of electron/spin transport properties using the nonequilibrium Green's-function method confirms that the Ch Eu sandwich compounds are excellent spin filters, and the spin filter efficiency (SFE) is independent of the cluster size (N), whereas the SFE of Si-[EuCOT]N decreases rapidly with the increase of cluster size. The perfect half-metallic properties of these surface-supported sandwich compounds are promising for future application in spin devices. The present work suggests a way to fabricate the half-metallic sandwich compounds on a semiconductor silicon surface. Results on structural, energetic, electronic, and magnetic properties of linear sandwich  $V_n Bzn+1$  clusters obtained using high-accuracy density functional computations are presented and analyzed. Energetically close-lying configurations and states of different spin-multiplicities are identified. The computed characteristics are in good agreement with the available experimental data. The computations predict that the most stable forms of the clusters in the size range  $n \geq 4$  are chiral. This feature, combined with the magnetism of these systems, makes them of potential importance as building blocks of nanosystems with coupled optical and magnetic functionalities.

With the purpose of searching for new intriguing nanomaterial for spintronics, a series of novel metalloporphyrin nanowires (M-PPNW,  $M=Cr, Mn, Fe, Co, Ni, Cu$  and  $Zn$ ) and hybrid nanowires fabricated by metalloporphyrin and metal-phthalocyanine (M-PCNW) are systematically investigated by means of first-principles calculations. Our results indicate that the transition metal atoms (TMs) embedded in the frameworks distribute regularly and separately, without any trend to form clusters, thus leading to the ideally ordered spin distribution. Except for the cases embedded with Ni and Zn, the others are spin-polarized. Remarkably, the Mn-PPNW, Mn-PCNW, MnCu-PPNW, MnCr-PCNW and MnCu-PCNW frameworks all favor the long-ranged ferromagnetic spin ordering and display half-metallic nature, which are of greatest interest and importance for electronics and spintronics. The predicted Curie temperature for the Mn-PCNW is about 150 K. In addition, it is found that the discrepancy in magnetic coupling for these materials is related to the competition mechanisms of through-bond and through-space exchange interactions. In the present work, we propose not only two novel sets of 1D frameworks with appealing magnetic properties, but also a new strategy in obtaining the half-metallic materials by the combination of different neighboring TMs.

**Bottom Note:** This work is partly presented at 4th International Conference on Physical and Theoretical Chemistry September 18-19, 2017, Dublin, Ireland