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Prediction of huge magnetic anisotropy in organometallic molecules

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ABSTRACT

Using density functional theory, we systematically investigated the electronic configurations and magnetic properties of 5d $TMCOT_2$ molecules. The magnetic anisotropy energies (MAEs) were calculated using the torque method. We found that $TMCOT_2$ (TM = Ta, W, Re, Os and Ir) are magnetic, except for $WCOT_2$, which are nonmagnetic. The easy axis of the magnetization of $OsCOT_2$ molecule can be switched from in-plane to out-of-plane by means of charge injection. In particular, MAE of $OsCOT_2$ can be enhanced to 60 meV by injection of one hole, which makes it promising candidate for potential applications in spintronics and quantum computing devices.

1. Introduction

With the development of spintronics and quantum computing devices, research interests in the field of nanomagnetism are extremely vigorous in recent years [1–3]. For the use of magnetic units down to the nanometer scale, the key issue is how to stabilize the magnetic moments against thermal fluctuations by enhancing its blocking temperature (TB) to a practicable range. It is well known that TB mainly depends on the magnetic anisotropy energy (MAE), which measures the threshold energy barrier for flipping the spin moment between two degenerate orientations. For practical applications at room temperature, the MAEs of magnetic nanostructures need to be up to 30–50 meV. For this purpose, much attention has been paid to the magnetic properties of transition-metal (TM) small clusters and dimers [4–9]. Free transition-metal cluster with 3–7 atoms were predicted to show large value of MAE [8]. Especially, the MAEs of Ir_4 and Pt_4 are about 130 meV and 50 meV, respectively [9]. It was also reported that several isolated TM dimers might provide huge MAE up to the order of 100 meV [4]. Unfortunately, due to the strong chemical bonding, such fascinating MAE values cannot survive when the clusters and dimers are bound to some substrates. Thus, many efforts have been devoted to seek a suitable host [3,10–13].

Recently, with the significant advantages in the mechanical flexibility and the long spin lifetime, much interest in organometallic molecules has rapidly increased for novel spintronics [14–16]. Similarly, organic molecular magnets are very promising candidates as working units for magnetic data storage. Strikingly, Xiao et al. found that Co-dimer-benzene can exhibit huge MAE of the order of 100 meV [17]. Due to the hexagonal environment provided by the carbon ring, Co dimer can hold the electronic structure characteristics at utmost compared to the free dimer. They further enhanced the MAE up to 200 meV by placing heavy atoms atop [18]. More recent attention has been paid to organometallic sandwich-like molecule. Based on the density functional theory, Kenji et al. determined the MAE of metallocene (MCp_2) [19]. They found that the magnetization of the $CoCp_2$ energetically favors highly orienting along the perpendicular direction to the Cp plane, but, with a small MAE of 0.46 meV. Atodiresei et al. demonstrated the magnetization direction of $Eu_2(C_8H_8)_3$ (COT = cyclooctatetraene, C_8H_8) molecule can be easily manipulated by transferring electrons in or out of the molecule [20]. The MAE can be enhanced to 13.67 meV by adding one electron. Nevertheless, to achieve the greatest progress in spintronics and quantum computing devices, molecular magnets with large MAEs are highly desirable. To this end, one needs to find suitable molecules with large MAEs and, in particular, to find means that may lead to substantial enhancements of their MAEs.

In the present studies, based on the density functional theory (DFT), we systematically investigated the stability, the electronic configurations and magnetic properties of the $TMCOT_2$ (TM = Ta, W, Re, Os and Ir), to examine whether these systems are viable candidates for spintronics and quantum computing devices. We further proposed the strategy to manipulate the MAE of $OsCOT_2$

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through charge injection. In particular, MAE of $OsCOT_2$ can be enhanced to 60 meV by injection of one hole.

2. Method

The first-principles calculations were performed using projector augmented plane-wave (PAW) method within the framework of spin-polarized density function theory (DFT), as implemented in the Vienna Ab-initio Simulation Package (VASP) [21,22]. The exchange-correlation potential is treated in the Perdew-Burke-Eznerhof generalized-gradient approximation (PBE-GGA) [23]. The pseudopotentials were constructed by the projector augmented wave method. To mimic the appropriate environment for an isolated molecule, the molecules were placed into a large cubic box with an edge of 20 Å—this ensures that the separation between the periodically repeated images of the molecule is large enough to suppress any interactions. Only the Γ-point is used to sample the Brillouin zone. For geometry optimization, all the internal coordinates are fully relaxed until the Hellmann-Feynman forces are less than 0.01 eV/Å. The MAE is obtained by applying the torque approach which has been proved to be an effective method for the reliable determination of MAE [24,25]. In this method, the MAE is expressed as

$$MAE = \sum_{i \in occ} \left\langle \psi_i \left| \frac{\partial H_{SO}}{\partial \theta} \right| \psi_i \right\rangle_{\theta=45^\circ} \tag{1}$$

where θ is the polar angle away from the molecular axis for spin momentum, ψ_i is the relativistic eigenvector, and H_{SO} is the spin-orbit coupling Hamiltonian.

For the convenience of discussions, we recall that the contributions to MAE from the same spin, i.e. up-up or down-down within the second-order perturbation can be expressed as [26]:

$$MAE = (\xi)^2 \sum_{o,u} \frac{|\langle o|L_z|u\rangle|^2 - |\langle o|L_x|u\rangle|^2}{E_u - E_o} \tag{2}$$

where o and u denote occupied and unoccupied electronic states. E_o and E_u are their band energies, respectively. L_z and L_x are the angular momentum operators. ξ is the strength of SOC. Note that the corresponding contributions to the MAE from different spin, i.e. up-down or down-up can be expressed as:

$$MAE = (\xi)^2 \sum_{o,u} \frac{|\langle o|L_x|u\rangle|^2 - |\langle o|L_z|u\rangle|^2}{E_u - E_o} \tag{3}$$

Contributions from the d states, the nonzero matrix elements of the L_z and L_x operators are $\langle xz|L_z|yz\rangle = 1$, $\langle x^2 - y^2|L_z|xy\rangle = 2$, $\langle xy|L_x|xz\rangle = 1$, $\langle x^2 - y^2|L_x|yz\rangle = 1$ and $\langle z^2|L_x|xz,yz\rangle = \sqrt{3}$. It would be easy to find that the positive contribution to the MAE originates from two matrix elements of $\langle xz|L_z|yz\rangle$ and $\langle x^2 - y^2|L_z|xy\rangle$, while $\langle xy|L_x|xz\rangle$, $\langle x^2 - y^2|L_x|yz\rangle$ and $\langle z^2|L_x|xz,yz\rangle$ donate negative contribution, according to Eq. (1). However, contribution to MAE from the nonzero matrix elements of the L_z and L_x operators are opposite in sign for different spin coupling, described in Eq. (2).

3. Results and discussion

After full relaxation, the two COT rings are slightly bended due to the strong interaction between the carbon atoms and the metal atom, as shown in Fig. 1. The $d_{C\text{-}TM}$ denotes the distance between the TM atom and the N atom, which are in the range of 2.47 Å and 2.58 Å (Table 1). In order to determine the stability of those molecules, we calculated their formation energies E_{form}, which are obtained according to the following equation:

$$E_{form} = E(TM) + 2E(COT) - E(TMCOT_2) \tag{4}$$

where E(TM), E(COT), and $E(TMCOT_2)$ refer to the total energy of TM atom, COT ring and $TMCOT_2$ molecule, respectively. The formation energies of these molecules are listed in Table 1. As Table 1 illustrates, the value for the formation energy gradually decreases with the increasing of atomic number of the TM atoms. The corresponding calculated formation energies for $TaCOT_2$, $WCOT_2$, $ReCOT_2$, $OsCOT_2$ and $IrCOT_2$ are 9.58, 7.49, 4.35, 3.86 and 2.56 eV, respectively. It is clear that the all molecules can exist stably. Moreover, we found that except for W, which is spin singlet, the other molecules favor spin-polarized ground states: the calculated magnetic moments of $TaCOT_2$, $WCOT_2$, $ReCOT_2$, $OsCOT_2$ and $IrCOT_2$ are 1.0, 0.0, 1.0, 2.0 and 1.0 μB, respectively. The spin configuration of a specific $TMCOT_2$ molecule is completely determined by the occupation of the central metal 5d atomic orbitals.

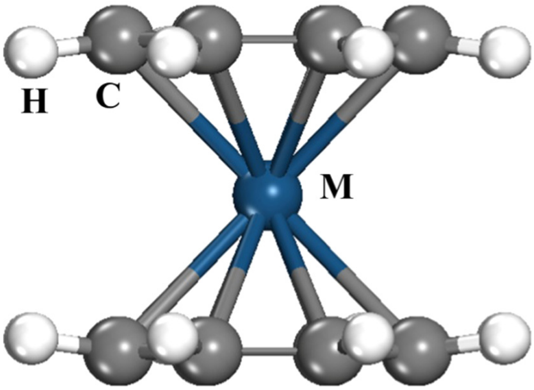

Fig. 1. Optimized structures of $MCOT_2$ molecules.

To illustrate their magnetic states, we present the projected density of states (PDOS) of different d orbitals of $TMCOT_2$ (TM = Ta, W, Re, Os and Ir). By the crystal field, the five 5d-orbitals of metal atoms split into three groups, namely, the d_{z^2}, d_{xy/x^2-y^2} and $d_{xz/yz}$. For the $TaCOT_2$, as shown in Fig. 3(a), the d_{xy/x^2-y^2} states are fully occupied while the d_{z^2} states are half occupied, resulting in the magnetic moment being 1.0 μB. From the energy diagram, the spin density of $TaCOT_2$ is expected to show the d_{z^2} character feature. The calculated spin density of $TaCOT_2$ is given in Fig. 2 as an example. One can clearly observe the d_{z^2} character feature. When passing Ta to W, one additional electron occupies the minority d_{z^2} states, the d_{z^2} and d_{xy/x^2-y^2} states are fully filled by six spin electrons, rendering $WCOT_2$ nonmagnetic. For the Re, where the number of electrons is two more than that of the Ta, only one electron occupies the majority $d_{xz/yz}$ states, thus the magnetic moment is 1.0 μB for $ReCOT_2$. For the $OsCOT_2$, as shown in Fig. 3(d), the d_{z^2} and d_{xy/x^2-y^2} states are fully filled as well as the majority $d_{xz/yz}$ states, while the minority $d_{xz/yz}$ states locate above the Fermi level, indicating $OsCOT_2$ possess a magnetic moment of 2.0 μB. Compared to $OsCOT_2$, $IrCOT_2$ has one additional electron to occupy the minority $d_{xz/yz}$ states, thus the magnetic moment is 1.0 μB for $IrCOT_2$.

Now, we turn our attention to see if giant MAEs may exist in these systems for the use in high density magnetic data storage. The calculated MAEs are listed in Table 1. The magnetization of the $TaCOT_2$ energetically favors to lie along the parallel direction the COT plane with MAE −0.68 meV. In particular, the MAE for $ReCOT_2$ and $IrCOT_2$ are 8.6 and 9.3 meV, with an easy axis perpendicular to the plane of COT ring. $OsCOT_2$ possesses the largest MAE = −22.1 meV, while the easy axis is in the plane of COT ring. According to Eq. (1), the driving factor of the MAE can be revealed, and then obtain more hints to manipulate the MAE. For $TaCOT_2$, the negative MAE is mainly produced by the coupling between