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DOI: 10.1038/s42005-018-0078-4

OPEN

Large magnetic anisotropy in chemically engineered iridium dimer

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Exploring giant magnetic anisotropy in small magnetic nanostructures is of technological merit for information storage. Large magnetic anisotropy energy (MAE) over 50 meV in magnetic nanostructure is desired for practical applications. Here we show the possibility to boost the magnetic anisotropy of the smallest magnetic nanostructure—transition metal dimer. Through systematic first-principles calculations, we proposed an effective way to enhance the MAE of an iridium dimer from 77 meV to 223–294 meV by simply attaching a halogen atom at one end of the Ir–Ir bond. The underlying mechanism for the enormous MAE is attributed to the rearrangement of the molecular orbitals which alters the spin-orbit coupling Hamiltonian and hence the magnetic anisotropy. Our strategy can be generalized to design other magnetic molecules or clusters to obtain giant magnetic anisotropy.

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The continuous miniaturization of spintronics devices for modern technologies such as magnetic data storage will eventually reach the ultimate length scale (i.e., one to a few atoms)^{1–6}. Recently, reading and writing quantum magnetic states in magnetic nanostructures with only a few transition-metal (TM) or rare-earth (RE) atoms were achieved by several experimental groups^{1–7}. These investigations demonstrate the fascinating possibility to utilize magnetic nanostructures and even single atoms in nanometer-scale spintronics devices. In this realm, the magnetic anisotropy of a magnetic nanostructure is a critical factor because it prevents the random spin reorientation induced by thermal fluctuations. Therefore, large magnetic anisotropic energy (MAE) is desired in magnetic nanostructures that serve as the building blocks of spintronics devices. Except for Co adatoms on Ag(001)⁸, most magnetic nanostructures based on 3d TM atoms have MAEs of only a few meV which corresponds to a blocking temperature (T_B) under 50 K, implying that their magnetic states are stable only at very low temperature^{2,9}. For practical applications of magnetic nanostructures at room temperature, large MAEs of 30–50 meV are necessary.

The magnetic anisotropy of a magnetic nanostructure originates from the spin-orbit coupling (SOC) effect. By analysis of the SOC Hamiltonian with the second-order perturbation theory, Wang et al. expressed the MAE as a competition between the angular momentum components along z -axis (L_z) and x -axis (L_x)^{10,11}:

$$\text{MAE} \approx \xi^2 \sum_{u\alpha, o\beta} (2\delta_{\alpha\beta} - 1) \left[\frac{\langle u\alpha | L_z | o\beta \rangle^2}{E_{u\alpha} - E_{o\beta}} - \frac{\langle u\alpha | L_x | o\beta \rangle^2}{E_{u\alpha} - E_{o\beta}} \right] \quad (1)$$

Here ξ is the SOC constant; $E_{u\alpha}$ and $E_{o\beta}$ are the energy levels of an unoccupied state with spin α ($|u\alpha\rangle$) and an occupied state with spin β ($|o\beta\rangle$), respectively. Therefore, there are two keys to achieve a large MAE: (i) large SOC constant ξ which exists in heavy atoms such as 5d TM atoms; (ii) specific energy diagram to reduce the denominator in Eq. (1) that can be realized by appropriate ligand field. For example, a large MAE of 9 meV in a single Co atom was induced by placing it on Pt(111) substrate¹², while the MAE in bulk Co metal is only 0.045 meV per Co atom¹³. On the other hand, a giant zero field splitting (ZFS) of 58 meV for a Co adatom on a MgO(001) surface was observed in a recent experiment⁴, and such a giant ZFS was attributed to the special ligand field of the substrate. Roughly speaking, a large ZFS value usually implies a large MAE¹⁴. However, the ZFS cannot be obtained directly by regular density functional theory (DFT) calculations due to the single-electron approximation¹⁵. Alternatively, DFT calculations were performed to determine MAE of a TM adatom under various coordination environments^{8,15–18}. Interestingly, combining the effects of the ligand field, orbital multiplet, and large SOC constants, a larger MAE of 208 meV for an Os adatom on a MgO(001) surface were predicted by DFT calculations¹⁹. Recently, attempts to investigate the magnetic anisotropy of a single RE adatom such as Dy, Ho, and Er on different substrates were made^{20–22}. Despite the large SOC

constants in these RE atoms, the resulting ZFSs are relatively small, i.e., 21.4 meV for a Dy adatom on graphene, 5.3 meV and 3.9 meV for Er and Ho adatoms on Pt(111), respectively. Meanwhile an appreciable MAE of about 10 meV/atom for a Er adatom on Cu(111) was reported by Singha et al.²³. Nevertheless, the RE adatoms have longer magnetic lifetime than the 3d TM adatoms such as Co.

In addition to single TM and RE adatoms on certain substrates, TM and RE dimers are of particular interest^{23–28} due to their special symmetry and molecular orbitals. A homo-nuclear TM dimer is rotationally invariant around the molecular axis. Consequently, its magnetic anisotropy will arise at the first-order perturbation treatment of SOC interaction and therefore can be anomalously large compared to most other magnetic nanostructures²⁴. In fact, appreciable MAEs of 30–70 meV were predicted theoretically for some free-standing TM dimers^{27,29,30} (positive MAE means easy axis parallel to the dimer axis).

Intuitively, the energy diagram of a given TM dimer can be modified effectively by chemical functionalization, which can in turn affect the magnetic anisotropy as clearly expressed in Eq. (1). Therefore, it is tempting to explore feasible ways to enhance the magnetic anisotropy of TM dimers. Besides placing a TM dimer on substrates, one possible tactic is to attach a light nonmetal atom which can form a strong chemical bond(s) with the TM atom(s) (thus affect the energy diagram) yet still retain the spin moment of the entire cluster.

Here, we show the possibility to engineer the magnetic anisotropy of a TM dimer by halogen functionalization. We choose the iridium dimer (Ir_2) as a prototype since Ir_2 possesses the largest MAE (70 meV) among free-standing homonuclear TM dimers²⁷. Our first-principles calculations demonstrate that a MAE up to 294 meV can be achieved in Ir_2 functionalized with a halogen atom (F, Cl, Br, I) and is of great potential for application in molecular spintronics devices.

Results

Magnetic anisotropy of Ir_2 . First, we calculate the structural and magnetic properties of Ir_2 as given in Table 1. The equilibrium Ir–Ir bond length is 2.24 Å, slightly shorter than the experimental value (2.27 Å)³¹ but close to a previously computed value (2.22 Å) based on the DFT/PW91 method²⁷. The calculated binding energy is 5.4 eV, significantly larger than the experimentally estimated upper limit (4.66 ± 0.21 eV)^{31,32} but in good agreement with previous calculation using the LDA method and LanL2DZ-BSSSE basis set correction (5.5 eV)³³. It is known that LDA tends to overbind metal clusters^{33–35} and the difference between the computational and experimental values originates from the approximation of LDA itself, as well as the zero-temperature nature of DFT static calculations (while there are temperature effects in experiments). Qualitatively, the large binding energy reflects a strong interaction between the two Ir atoms. The spin moment (M_S) is $4 \mu_B$ without considering the SOC effect. After including the SOC effect, M_S reduces slightly to $3.86 \mu_B$ while a large orbital moment (M_L) of $2.06 \mu_B$ is induced, in line with

Table 1 Summary of basic properties of Ir_2 and Ir_2X						
	Geometry	d (Å)	E_b (eV)	M_S (μ_B)	M_L (μ_B)	MAE (meV)
Ir_2		2.24	5.4	3.86	2.06	77
Ir_2F		2.23 (1.87)	10.7	3.02	0.98	232
Ir_2Cl		2.24 (2.19)	9.5	3.04	0.98	223
Ir_2Br		2.24 (2.31)	9.3	3.03	0.98	294
Ir_2I		2.24 (2.49)	8.8	3.01	0.99	228

Fig. 1 Molecular orbitals of an iridium dimer (Ir_2). **a** Energy diagram of the molecular orbitals of Ir_2 without and with the spin-orbit coupling (SOC) effect (separated by a vertical dashed line). Black and red colors refer to energy levels in the majority (up) and minority (down) channels, respectively. Both magnetizations perpendicular ($\perp$, hard axis) and parallel ($\parallel$, easy axis) to the Ir-Ir bond are presented. The dashed lines connect the energy levels of each molecular orbital between the two magnetizations. **b** Radial wave functions of the molecular orbitals without the SOC effect. The paratactic orbitals are energetically degenerate. Yellow and blue colors stand for positive and negative wave functions, respectively, with a cutoff radius of ± 0.02 a.u.

Fig. 2 Projected density of states (PDOS) and orbital resolved magnetic anisotropy energy (MAE) of an iridium dimer (Ir_2). **a** PDOS of the s and d orbitals of Ir_2 . The vertical dashed line marks the Fermi level (E_F). **b** Nonzero contribution from each pair of molecular orbitals in the minority spin channel (E_{dd}) and in the opposite spin channels (E_{ud}). The horizontal dashed line shows the position of E_F . The thickness of each vertical line scales with the magnitude of the corresponding contribution to MAE distinguished by different colors.

previous calculation²⁷. The MAE is 77 meV with easy axis parallel to the molecular axis, and it is slightly larger than that reported previously (70 meV)²⁷, probably due to different choice of DFT methods (e.g., exchange-correlation functional and basis set).

This table lists geometry, interatomic distance (d), binding energy (E_b), spin moment (M_S), orbital moment (M_L), and magnetic anisotropy energy (MAE). The interatomic distances are shown as Ir-Ir (Ir-X) bond lengths for Ir_2X . A positive MAE indicates the easy axis parallel to the molecular axis.

To understand the origin of the novel magnetic characteristic of Ir_2 , the energy diagram of its molecular orbitals is plotted in Fig. 1a. Due to the rotational symmetry of Ir_2 , the Ir-5d orbitals split into three groups: d_{xy/x^2-y^2} , $d_{xz/yz}$ and d_{z^2} . The basal plane of d_{xy/x^2-y^2} is perpendicular to the Ir-Ir bond, and those of $d_{xz/yz}$ and d_{z^2} cross the Ir-Ir bond. Consequently, the interaction between the two Ir atoms results in three types of hybridizations: $d_{xy/x^2-y^2} - d_{xy/x^2-y^2}$, $d_{xz/yz} - d_{xz/yz}$, and $d_{z^2} - d_{z^2}$. The corresponding bonding and antibonding states (i.e., six molecular orbitals in each spin channel) can be thus notated as δ_d/δ_d^* , π_d/π_d^*

and σ_d/σ_d^* . Based on the radial wave functions in Fig. 1b and the spin-polarized projected density of states (PDOS) in Fig. 2a of these molecular orbitals, we identified the orbital characters of all energy levels and marked them in Fig. 1a. Clearly, the hybridization $d_{z^2} - d_{z^2}$ is much stronger than the others, which leads to large energy separation between σ_d and σ_d^* . The interaction between the two d_{xy/x^2-y^2} orbitals is weakest, thus the corresponding energy separation is smallest. It can be seen that all these molecular orbitals are occupied in the majority spin channel. While in the minority spin channel, the doubly degenerate δ_d^* is half occupied, and π_d^* and σ_d^* are unoccupied. Therefore, the electronic configuration of these molecular orbitals is $(\sigma_d)^2(\pi_d)^4(\delta_d)^4(\delta_d^*)^3(\pi_d^*)^2(\sigma_d^*)^1$. On the other hand, the interaction between the Ir-6s orbitals is also strong, and the antibonding-state molecular orbitals (σ_s^*) in both spin channels are unoccupied, resulting in an electronic configuration $(\sigma_s)^2(\sigma_s^*)^0$. In addition, there is moderate hybridization between d_{z^2} and s orbitals, as shown in Fig. 2a. Note that the electronic configuration of an isolated Ir atom is $(5d)^7(6s)^2$. Accordingly, we can

conclude that each Ir-6s orbital donates one electron to the Ir-5d orbitals. As a consequence, the total M_s of Ir_2 is $4\mu_B$, contributed by δ_d^* ($1\mu_B$), π_d^* ($2\mu_B$), and σ_d^* ($1\mu_B$), respectively. With the SOC effect, the energy diagram does not change much if the magnetization is along the hard axis. On the contrary, most orbitals split significantly when the magnetization is along the easy axis (i.e., Ir–Ir bond). In particular, the splitting of the energy level of δ_d^* is as large as ~ 0.9 eV, so that the half occupancy in the minority spin channel is eliminated. Such different SOC effect according to the magnetization directions leads to large anisotropies for both spin and orbital moments. As seen in Supplementary Table 1, the spin moments along the easy and hard axes are 3.86 and $3.28\mu_B$, while the corresponding orbital moments are 2.06 and $1.16\mu_B$, respectively. Intuitively, the SOC splitting of the energy levels and the anisotropies of the spin and orbital moments are responsible for the large MAE of Ir_2 ²⁴.

To further elucidate the underlying mechanism of the large MAE of Ir_2 , we applied Eq. (1) to distinguish respective contribution from each pair of orbitals to the MAE. For convenience, we divide total MAE into three parts: $\text{MAE} = \text{MAE}_{uu} + \text{MAE}_{dd} + \text{MAE}_{ud}$, respectively from coupling between majority spin states (uu), minority spin states (dd), and cross-spin states (ud). Since the s orbital is not involved in SOC, the MAE of Ir_2 is determined by the Ir-5d related molecular orbitals. From the energy diagram in Fig. 1a and the PDOS in Fig. 2a, the Ir-5d related molecular orbitals in the majority spin channel are occupied completely, thus MAE_{uu} is negligible. For MAE_{dd} and MAE_{ud} , the nonzero contributions from the angular momentum components in Eq. (1) are plotted in Fig. 2b. Clearly, for MAE_{dd} , the contribution from L_z is much larger than that from L_x , resulting in a positive MAE_{dd} ($\sim 10\xi^2$). For cross-spin coupling, L_z still contributes more to MAE_{ud} than L_x , but this leads to a negative MAE_{ud} ($\sim -3\xi^2$) due to the negative sign in Eq. (1). Nevertheless, the absolute magnitude of MAE_{dd} is larger than that of MAE_{ud} , resulting in a positive total MAE (about $7\xi^2$) for Ir_2 .

Furthermore, it can be seen from Fig. 2b that both the sign and magnitude of MAE_{dd} and MAE_{ud} are dominated by L_z that are related to the δ_d and δ_d^* orbitals: $\delta_d, \downarrow |L_z|\delta_d^*, \downarrow$ ($\sim 17\xi^2$), $\delta_d, \uparrow |L_z|\delta_d^*, \downarrow$ ($\sim 8\xi^2$) and $\delta_d^*, \uparrow |L_z|\delta_d^*, \downarrow$ ($\sim 16\xi^2$). Therefore, the MAE of Ir_2 is mainly attributed to the SOC effect associated with the d_{xy}/x^2-y^2 orbitals through the angular momentum component L_z .

Magnetic anisotropy of functionalized Ir_2 . According to the discussions above and Eq. (1), if there is an effective way to modify the energy diagram of Ir_2 , the contribution from each pair of the molecular orbitals will be revised, which alters the total MAE. One possible tactic is to attach an additional nonmetal atom to Ir_2 to tailor the interaction between the two Ir atoms and thus the magnetic property of Ir_2 . To this end, we examined a series of nonmetal atoms (X), including C, Si, N, P, O, S, and halogen atoms, to construct Ir_2X trimers. As shown in Supplementary Tables 2 and 3, there are three types of possible equilibrium structures: (i) linear chain with an X atom at one end of the Ir–Ir bond; (ii) isosceles triangle with an X atom over the middle point of the Ir–Ir bond; (iii) linear chain with an X atom at the middle point. We obtained ground-state structures and MAEs for all Ir_2X clusters and found that only the halogen atoms can result in huge MAEs. Hereafter, we only take the halogen as a prototype to discuss the strategy to engineer the magnetic anisotropy of TM dimers.

For all halogen elements X ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$), the Ir_2X trimers prefer type-I configuration (see Supplementary Table 3). As seen from Table 1, the Ir–Ir bond length in Ir_2X changes slightly, while the Ir–X bond length increases monotonically with X from F to I due to the increasing atomic radius. Moreover, the binding energies of Ir_2X are about twice of that of Ir_2 , indicating strong binding between the Ir and X atoms and high structural stability of Ir_2X . Consequently, the Ir–Ir bond is significantly weakened, which leads to remarkable change of the energy levels of Ir-5d orbitals as manifested by the PDOS in Fig. 3a. Clearly, the F-2p

Fig. 3 Projected density of states (PDOS) and orbital resolved magnetic anisotropy energy (MAE) of Ir_2F . **a** PDOS of the F atom and two Ir atoms. Ir1 and Ir2 denote the Ir atom close to the F atom and at the other end of the trimer, respectively. The vertical dashed line indicates the Fermi level (E_F). **b, c** Nonzero contribution from each pair of molecular orbitals in the minority spin channel (E_{dd}) and in the opposite spin channels (E_{ud}). The horizontal dashed line shows the position of E_F for each case. The width of each vertical line scales with the magnitude of the corresponding contribution to MAE distinguished by different colors

orbitals hybridize strongly with the $d_{xz/yz}$ and d_{z^2} orbitals of Ir1 (the Ir atom bonding with X). Compared to Ir₂, the energy levels of the bonding states of both $d_{xz/yz}$ and d_{z^2} orbitals of Ir1 shift downward by about 0.3 eV in the majority spin channel and 0.6 eV in the minority spin channel, while those of the corresponding antibonding states shift upward by about 0.7 eV and 0.3 eV, respectively. As a result, the hybridization between the two Ir atoms through the $d_{xz/yz}$ and d_{z^2} orbitals is markedly weakened. For Ir₂ (the Ir atom at the other end of Ir₂X), the energy levels of the $d_{xz/yz}$ and d_{z^2} orbitals shift upwards, and the energy separations between the corresponding bonding and antibonding states become narrower. Meanwhile, some electrons are transferred from the $d_{xz/yz}$ and d_{z^2} orbitals in Ir1, as shown in Supplementary Fig. 1. On the other hand, the d_{xy/x^2-y^2} orbitals do not change much because these orbitals do not hybridize with the F-2p orbitals and the Ir–Ir bond length changes little. Therefore, the δ_d and δ_d^* are similar to those of Ir₂, but their energy separation is narrowed by about 0.24 eV and the exchange splitting increases by about 0.52 eV [see Figs. 2a and 3a].

The magnetic moments are also significantly modified by attaching an X atom to Ir₂. Without considering the SOC effect, the total spin moments of these Ir₂X trimers are all 5 μ_B as listed in Supplementary Table 3, increasing by 1 μ_B compared to Ir₂. According to the Milliken population analysis, Ir₂ donates the electron on $\delta_d^*(\downarrow)$ to the halogen atom X, so that the Fermi level (E_F) is pinned between the energy levels of $\pi_d^*(\uparrow)$ and $\delta_d^*(\downarrow)$. Thus, the spin moment of Ir₂X is contributed by $\delta_d^*(2\mu_B)$, $\pi_d^*(2\mu_B)$, and $\sigma_d^*(1\mu_B)$. However, the SOC effect notably reduces M_s of Ir₂X to 3 μ_B (see Table 1), which is even smaller than that of Ir₂ by 1 μ_B . On the contrary, M_s of Ir₂ is only altered slightly by the SOC effect. From the PDOS without SOC (Fig. 3a), we can see that the Fermi level (E_F) is pinned within the small gap (61 meV) between $\pi_d^*(\uparrow)$ and $\delta_d^*(\downarrow)$. In other words, $\pi_d^*(\uparrow)$ is fully occupied with two electrons and $\delta_d^*(\downarrow)$ is empty. After including the SOC effect with easy-axis magnetization, the degenerate energy levels of both $\pi_d^*(\uparrow)$ and $\delta_d^*(\downarrow)$ split by 498 meV and 896 meV, respectively (see Supplementary Fig. 2). Consequently, the higher energy level stemmed from $\pi_d^*(\uparrow)$ shifts upward and locates above E_F , while the lower energy level stemmed from $\delta_d^*(\downarrow)$ shifts downward and locates below E_F . Therefore, both $\pi_d^*(\uparrow)$ and $\delta_d^*(\downarrow)$ are occupied by one electron. Obviously, one electron on $\pi_d^*(\uparrow)$ transfers to $\delta_d^*(\downarrow)$, resulting in the reduction of M_s by 1 μ_B . Accordingly, the spin configuration becomes $\delta_d^*(1\mu_B)$, $\pi_d^*(1\mu_B)$, and $\sigma_d^*(1\mu_B)$. In addition, the orbital moments of Ir₂X are about 1 μ_B , which is about half of that of Ir₂. As shown in Supplementary Table 1, both the local spin moment and orbital moment on Ir1 are smaller than those on Ir₂, which is caused by the hybridization between Ir1 and X. It is noteworthy that the orbital moment of Ir₂X show little anisotropy between the easy and hard axes, despite of the enhanced anisotropy of the spin moment with respect to Ir₂.

Remarkably, the MAEs of all Ir₂X trimers are largely enlarged (see Table 1). Among them, Ir₂Cl possesses the least MAE yet it is still as large as 223 meV; Ir₂Br has the largest MAE of 294 meV; and the MAEs of the other two trimers are about 230 meV. All these MAE values are comparable to the highest theoretical values reported in literature, i.e., the lower and upper estimates of the MAE for the heteronuclear dimer CoIr decorated by benzene are 248 meV and 289 meV, respectively³⁶.

To confirm our view of the underlying mechanism for the extraordinary enhancement of MAE due to halogen functionalization, we extracted the energy levels from the PDOS in Fig. 3a and estimated the orbital resolved MAEs of Ir₂F using Eq. (1), as plotted in Fig. 3b,c. It can be seen that the main contributions to the total MAE stem from the matrix elements of L_z

($\langle\delta_d, \downarrow|L_z|\delta_d^*, \downarrow\rangle$, $\langle\delta_d, \uparrow|L_z|\delta_d^*, \downarrow\rangle$, $\langle\delta_d^*, \uparrow|L_z|\delta_d^*, \downarrow\rangle$) and L_x ($\langle\pi_d^*, \uparrow|L_x|\delta_d^*, \downarrow\rangle$) of both Ir atoms. Compared to Ir₂ (see Supplementary Table 4), the positive contribution from $\langle\delta_d, \downarrow|L_z|\delta_d^*, \downarrow\rangle$ increases lightly and the negative contributions from $\langle\delta_d, \uparrow|L_z|\delta_d^*, \downarrow\rangle$ and $\langle\delta_d^*, \uparrow|L_z|\delta_d^*, \downarrow\rangle$ are slightly reduced. Interestingly, the contribution from $\langle\pi_d^*, \uparrow|L_x|\delta_d^*, \downarrow\rangle$ is minor in Ir₂ due to the relatively large energy separation between the corresponding orbitals. However, the energy levels of $\pi_d^*(\uparrow)$ and $\delta_d^*(\downarrow)$ become very close (e.g., ~61 meV for Ir₂F as shown in Fig. 3a), which results in huge contribution to MAE from $\langle\pi_d^*, \uparrow|L_x|\delta_d^*, \downarrow\rangle$. The final estimated MAE_{dd} and MAE_{ud} are $13\xi^2$ and $44\xi^2$ respectively, both being larger than the corresponding values in Ir₂ ($10\xi^2$ and $-3\xi^2$). Consequently, the total MAE of Ir₂F increases dramatically to 232 meV, about three times as in Ir₂ (77 meV). In fact, for all Ir₂X trimers considered here, the term $\langle\pi_d^*, \uparrow|L_x|\delta_d^*, \downarrow\rangle$ dominates the MAE (see Supplementary Table 4) because they all have similar energy diagrams (see Supplementary Fig. 3).

Discussion

Generally speaking, the halogen functionalization causes charge transfer and energy shifts in the Ir₂ dimer delicately, thus resulting in enormous MAEs. This strategy to tune the MAE of a TM dimer should be universal. Our preliminary results indicate that the MAE of an Os₂ dimer functionalized by O (F) atom can reach 290 (240) meV, with easy axis perpendicular to the Os–Os bond. It should also be noted that only maximizing the MAE is not enough to obtain stable nanomagnets. Other physical factors including the quantum number of the ground state and crystal field symmetry also play important roles in the dynamics of magnetization, especially the magnetic lifetime. For practical device applications, the magnetic molecule should be placed on certain substrates which may destroy the magnetic anisotropy. Our preliminary calculations reveal that an Ir₂Br molecule supported by fully fluorinated graphene (GF) can retain its linear configuration, as well as large MAE of 238 meV. However, the binding energy between the Ir₂Br trimer and the GF substrate is only about 0.1 eV, which is insufficient to withstand thermal perturbation and migration for applications in spintronics devices at room temperature. Therefore, more efforts are needed to search for suitable substrates that can not only hold Ir₂X trimers but also retain their large MAEs. This is a challenging issue that deserves further exploration and the future results will be published elsewhere.

Our first-principles calculations have demonstrated that the MAE of an Ir₂ dimer can be significantly boosted up to 294 meV by attaching a Br atom at one end of the Ir–Ir bond. Analyses of the energy diagrams and the matrix elements of the SOC Hamiltonian show that the d_{xy/x^2-y^2} and $d_{xz/yz}$ orbitals are responsible for the colossal MAE. More specifically, the halogen atoms which have strong electronegativity lead to stable linear configuration for the Ir₂X trimers and modify the energy levels of the 5d orbitals of the Ir atoms. The strategy of chemical functionalization introduces a new synthetic approach to chemically engineering the magnetic anisotropy of small magnetic nanostructures towards future-generation magnetic information storages using one to a few atoms per bit.

Methods

The structural relaxations and electronic structure calculations were carried out with the OpenMX package³⁷ based on the density functional theory (DFT)^{38,39} (see details in Supplementary Note 1 including Supplementary Table 5 and Supplementary Fig. 4). We employed the spin-polarized local density approximation (LDA) in the Ceperley–Alder scheme^{40,41}, norm-conserving pseudopotentials^{42–46}, and pseudo-atomic localized basis functions^{47,48}. The cutoff radii of the radial wave function were 9.0, 7.0, 9.0, 9.0, and 11.0 a.u. and the valence orbitals were $s^2p^2d^2f^1$, $s^3p^3d^2$, $s^3p^3d^2$, $s^4p^4d^3f^1$, and $s^3p^3d^3f^2$ for Ir, F, Cl, Br and I, respectively. The fully relativistic pseudopotentials⁴⁶ were used, and the cutoff energy was set to 300 Ry.

The criteria for energy and force convergence were 10^{-7} Hartree and 10^{-4} Hartree per Bohr, respectively. To determine MAE and orbital magnetic moments, self-consistent calculations including the SOC effect were performed with fully unconstrained non-collinear DFT method^{49–52}. The MAEs of the linear molecules Ir_2 dimer and Ir_2X trimers are defined as the difference between the total energies with magnetizations parallel $[\text{E}(\parallel)]$ and perpendicular $[\text{E}(\perp)]$ to the Ir–Ir bond: $\text{MAE} = \text{E}(\parallel) - \text{E}(\perp)$.

Data availability

The data that support the findings of this study are available from the corresponding author on request.

Received: 20 April 2018 Accepted: 8 October 2018

Published online: 05 November 2018

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Acknowledgements

This work was supported by the National Natural Science Foundation of China (11574040, 11574223), the Natural Science Foundation of Jiangsu Province (BK20150303), the Fundamental Research Funds for the Central Universities of China (DUT17LAB19), and the Supercomputing Center of Dalian University of Technology. J. H. thanks the Jiangsu Specially-Appointed Professor Program of Jiangsu Province. X.C.Z. was supported by a State Key R&D Fund of China (2016YFA0200604) to USTC and University of Nebraska Holland Computing Center.

Author contributions

J.Z. and J.H. initiated and conducted the project. X.L. and X.W. performed simulations. All authors discussed the results. X.L. wrote the manuscript and X.C. Z supervised the project.

Additional information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s42005-018-0078-4>.

Competing interests: The authors declare no competing interests.

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