Supporting Information: Out-of-plane Enhanced Magnetic Anisotropy Energy in Ni_3Bz_3 molecule

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Magnitudes of the quantum numbers

Tables S1 and S2 include the magnitudes of the angular moments L, S and J for Ni_3 and Ni_3Bz_3. It is noteworthy that the L values for Ni_3 in in-plane configurations are comparable to the S values. The addition of benzene molecules decreases the L value. For Ni_3Bz_3 and Ni_3, the largest local orbital magnetic moments are found for the most stable out-of-plane and in-plane configurations, respectively.

Non-spin-orbit electronic structure

Figure S1 displays the electronic levels for non-spin-orbit calculations of (a) Ni_3Bz_3 and (b) Ni_3 molecules. For the Ni_3Bz_3 molecule, the highest occupied molecular orbital (HOMO) for

Table S1: Values of the L, S and J angular moments in each of the atom spheres for the three different magnetic configurations found for the Ni_3 molecule.

	M_x			M_y			M_z		
	1	2	3	1	2	3	1	2	3
L	0.44	0.23	0.23	0.01	0.39	0.39	0.06	0.06	0.06
S	0.34	0.34	0.34	0.33	0.34	0.34	0.33	0.33	0.33
J	0.78	0.51	0.51	0.34	0.71	0.71	0.39	0.39	0.39

Table S2: Values of the L, S and J angular moments in each of the atom spheres for the three different magnetic configurations found for the Ni_3Bz_3 molecule.

	M_x			M_y			M_z		
	1	2	3	1	2	3	1	2	3
L	0.05	0.07	0.07	0.07	0.05	0.05	0.12	0.12	0.12
S	0.34	0.35	0.35	0.34	0.35	0.35	0.34	0.35	0.35
J	0.39	0.42	0.42	0.41	0.40	0.40	0.46	0.47	0.47

the minority spin is a doubly degenerated level occupied by an electron. The wave functions of these two levels, displayed nearby, show that they are mainly formed by a combination of d_{xz} and d_{yz} atomic orbitals in each Ni atom. The specific orbital composition of those levels is studied by the projected-density-of-states also shown in the Supplemental Material. In the case of Ni_3, there are two minority spin levels degenerated at the Fermi energy as for Ni_3Bz_3, however each level is totally filled with an electron. Their wave functions have d orbital contribution with strong z component, as for Ni_3Bz_3. These results agree with those of spin-orbit calculations.

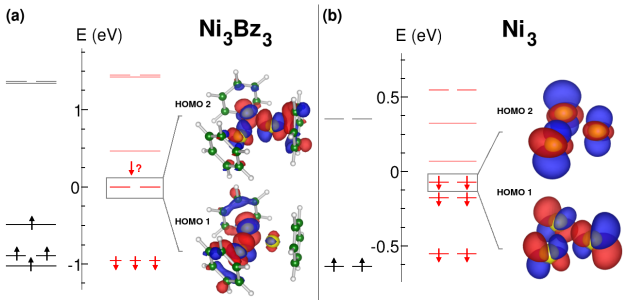

Figure S1: Electronic levels obtained with non spin-orbit calculations for the (a) Ni_3Bz_3 and (b) Ni_3 molecules. The wavefunctions of the down levels at the Fermi energy are displayed.

Projected density of states

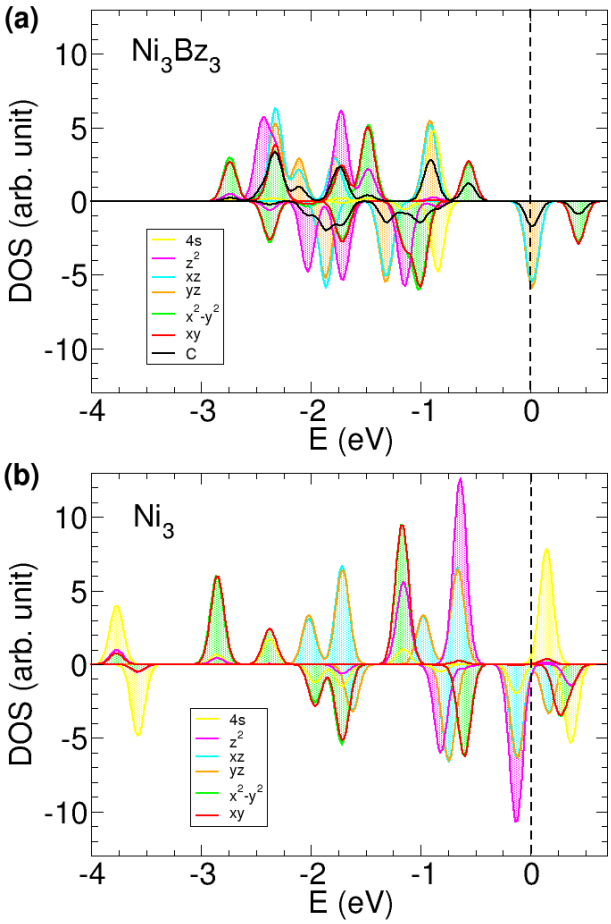

Figure S2: Projected density of states for (a) Ni_3Bz_3 and (b) Ni_3.

Figure S2 shows the projected density of states (PDOS) over C and Ni orbitals for (a) Ni_3Bz_3 and (b) Ni_3 molecules. The coordinate system is the same as used in the main article. We first comment the PDOS results of Ni_3Bz_3 in panel (a). The spin splitting for the d levels near the Fermi energy is estimated about 1 eV. Carbon contributions expand over almost all the energies, hybridizing with nickel orbitals. The Ni d orbital contributions are brought together into couples, such as $3d_{xz}$-$3d_{yz}$ and $3d_{xy}$-$3d_{x^2-y^2}$, because the hybridized molecular orbitals have contributions with similar weights at the same energies. The couple $3d_{xz}$-$3d_{yz}$ form molecular orbitals in the out-of-plane z-direction, and the second couple $3d_{xy}$-$3d_{x^2-y^2}$ forms orbitals in the Ni atom plane. Near the Fermi energy, there are two minority spin

levels composed of hybridizing $3d_{xz}$-$3d_{yz}$ Ni orbitals, which are occupied by one electron and are responsible for the magnetic anisotropy of Ni_3Bz_3.

Second we discuss the projected density of states for Ni_3 (see Fig. S2(b)). The scheme of hybridization between d orbitals is the same as for Ni_3Bz_3. However, the two occupied degenerated levels near the Fermi energy are totally filled, as shown in the level schemes in the main article. The contributions of 4s and $3d_{z^2}$ orbitals show differences between Ni_3 and Ni_3Bz_3 near the Fermi energy. The 4s orbital for Ni_3 is highly hybridized with the $3d_{xy}$-$3d_{x^2-y^2}$ couple and $3d_{z^2}$ orbital contributions. The addition of benzene molecules localize a molecular orbital composed of d_{z^2} Ni, that for the Ni_3Bz_3 molecule is being shifted towards deeper energies together with the 4s contribution. It is noteworthy that for Ni_3Bz_3 a level composed of 4s Ni appears about 1 eV below the Fermi energy.