ARTICLE

Trends of the Macroscopic Behaviors of Energetic Compounds: Insights from First-Principles Calculations

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Supplementary Material

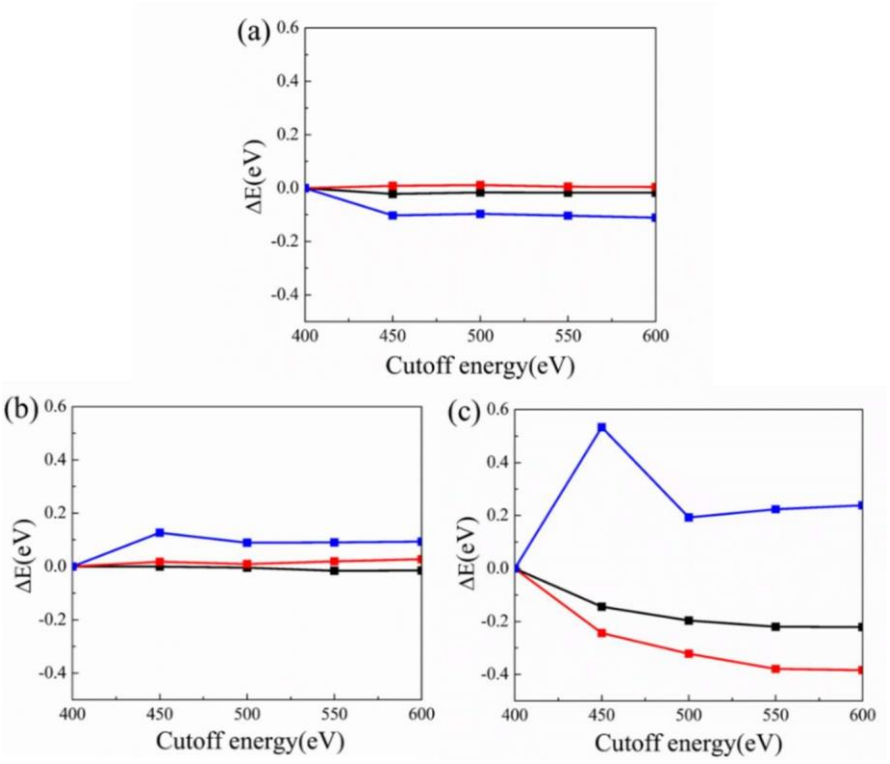

Figure 1S. Lattice energy convergence as a function of plane wave cutoff. (a) PBE. (b) DFT-D3. (c) optB88-vdW. Black for CHZ, red for CHZCP, and blue for CdCP. ΔE is the difference of lattice energy taking the value of 400 eV as reference.

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Electronic Supplementary Information (ESI) available: Supplementary material includes the test of cutoff energy, the total density of states and the integration, the partial density of states, lattice parameters and volumes of the eight TMCP molecular crystals with DFT-D3 correction, in addition to the study of magnetic moment and the band structures by using the PBE+U and SCANrVV10 methods. See DOI: 10.1039/x0xx00000x

Table 1S. Theoretical lattice constants and volumes of the eight molecular crystals by using the DFT-D3.

	a(Å)	b(Å)	c(Å)	α	β	γ	$V_{(theory)}$(Å^3)	$V_{(exp)}$(Å^3)	Error (%)
CHZ	9.021	4.219	10.533	90°	93.654°	90°	400.125	397.120	0.757
CHZCP	10.868	7.227	9.169	90°	109.400°	90°	679.355	662.940	2.476
MnCP	10.704	8.477	20.645	90°	97.731°	90°	1856.416	1842.600	0.750
FeCP	10.159	8.495	21.298	90°	99.567	90°	1812.393	1773.100	2.216
CoCP	10.145	8.443	21.481	90°	99.752°	90°	1813.261	1803.200	0.558
NiCP	10.141	8.498	21.924	90°	107.496°	90°	1801.918	1795.400	0.363
ZnCP	10.178	8.485	21.480	90°	100.641°	90°	1823.131	1756.641	3.785
CdCP	10.210	8.618	22.125	90°	107.556°	90°	1855.951	1860.400	-0.239

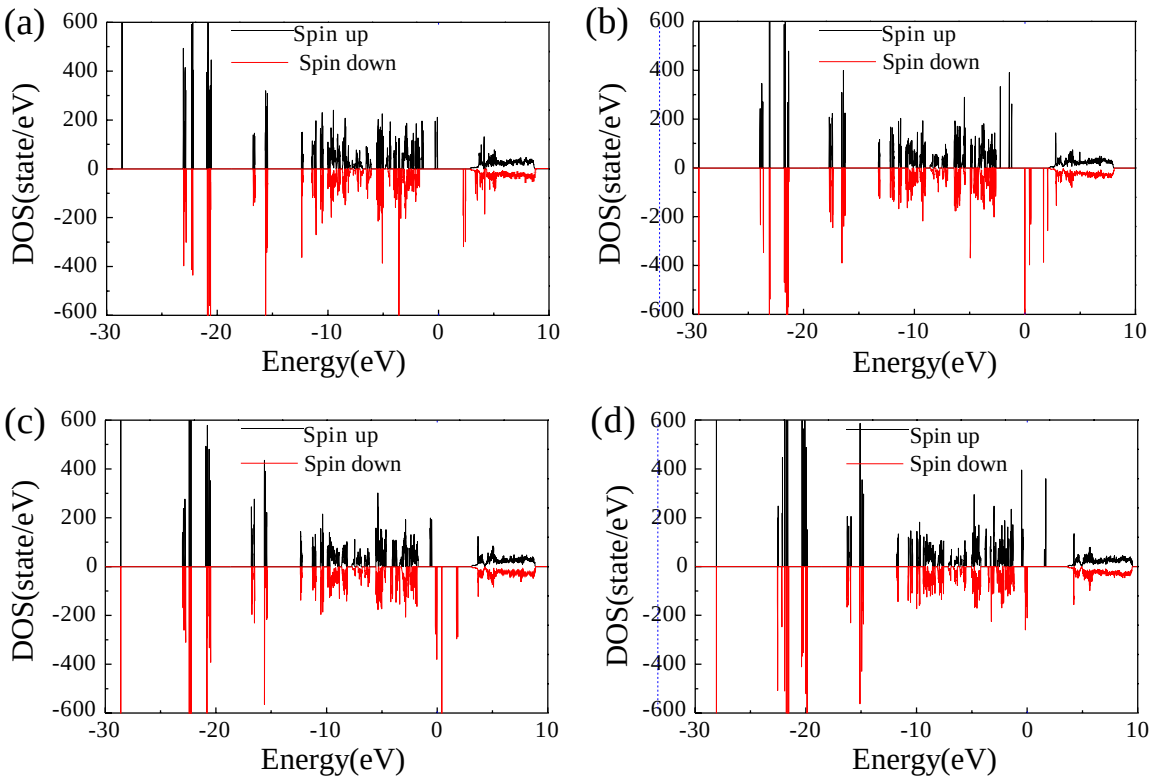

Figure 2S. The total density of states of four complexes. (a) MnCP. (b) FeCP. (c) CoCP. (d) NiCP.

Table 2S. The number of unpaired electrons from the integration of the TDOS of the four molecular crystals. Each complex contains four single molecules; each single molecule contains one metal ion.

	Unpaired electrons (crystal)	Unpaired electrons (single molecule)
MnCP	20	5
FeCP	16	4
CoCP	12.2	3.05
NiCP	8	2

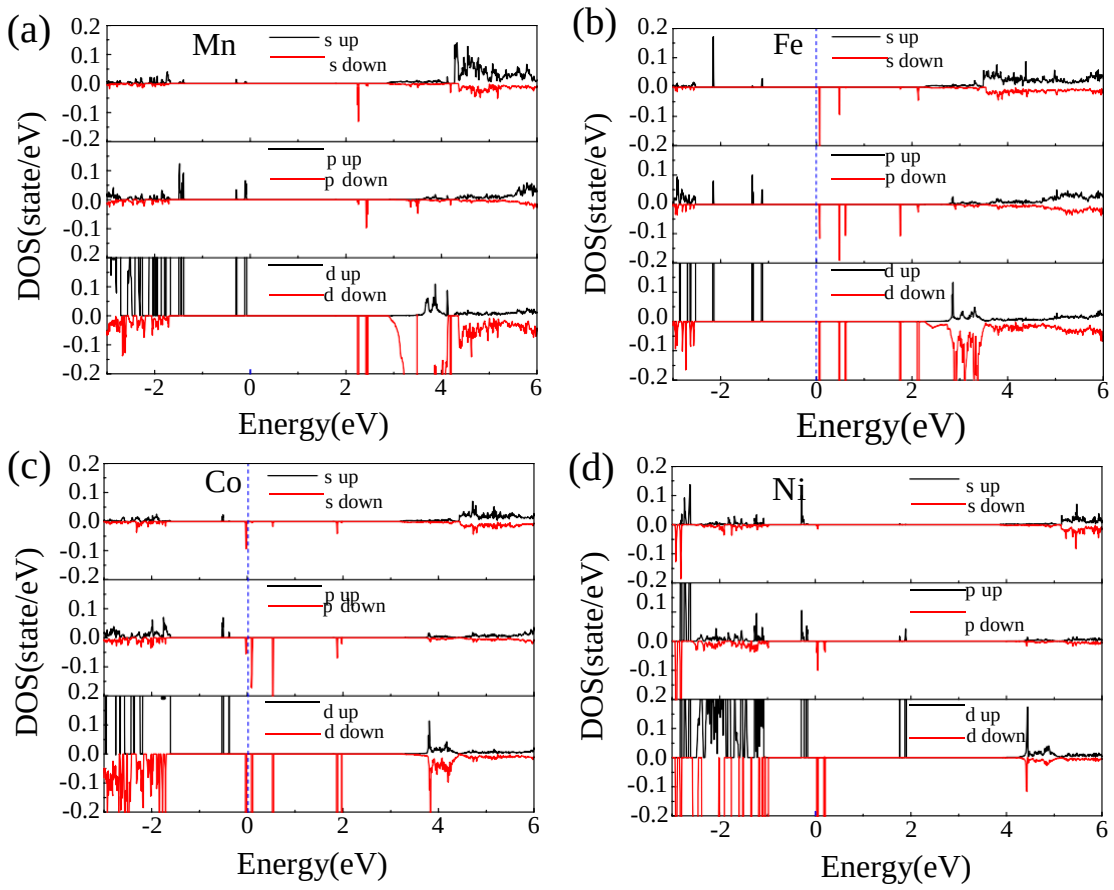

Figure 3S. Partial density of states of metal atoms in the molecular crystals. (a) MnCP. (b) FeCP. (c) CoCP. (d) NiCP.

First, starting from the equilibrium lattice volume and shape, we change the volume by fixing the shape of the lattice. Then, for the same volume, we set different initial magnetic moments of the metal ions. Finally, structural optimization is performed to obtain the final magnetic moments of those systems at certain volume. Through the analysis of the results (Table 3S and Table 4S), we find that for the FeCP crystals under non-equilibrium volumes, no matter what initial magnetic moments are given to the Fe ions, the final systems are not magnetic; and for the FeCP crystal under the equilibrium volume, when the initial magnetic moments of the four Fe ions are set to 4 4 4 4μB and -4 -4 -4 -4μB, after relaxation, the final magnetic moments of the crystals are 16μB and -16μB, respectively.

Table 3S. The magnetic results of FeCP crystals at different volumes and initial magnetic moments.

Final magnetic moment (μ_B) / V (Å^3) / Initial magnetic moment (μ_B)	1606.622	1707.441	1812.393	1921.559	2035.024
4 4 4 4	0	0	16	0	0
-4 -4 4 4	0	0	0	0	0
-4 -4 -4 -4	0	0	-16	0	0
-4 4 -4 4	0	0	0	0	0
-4 4 4 -4	0	0	0	0	0
4 -4 -4 4	0	0	0	0	0
4 -4 4 -4	0	0	0	0	0
4 4 -4 -4	0	0	0	0	0

Table 4S. The magnetic results of MnCP crystals at different volumes and initial magnetic moments.

Final magnetic moment (μ_B) / V (Å^3) / Initial magnetic moment (μ_B)	1655.983	1754.292	1856.416	1962.429	2072.404
5 5 5 5	20	20	20	20	20
-5 -5 5 5	0	0	0	0	0
-5 -5 -5 -5	-20	-20	-20	-20	-20
-5 5 -5 5	0	0	0	0	0
-5 5 5 -5	0	0	0	0	0
5 -5 -5 5	0	0	0	0	0
5 -5 5 -5	0	0	0	0	0
5 5 -5 -5	0	0	0	0	0

Table 5S. Magnetic moments of MnCP, FeCP and CoCP crystals under different volumes.

Complexes	MnCP		FeCP		CoCP	
V(Å^3)	1530.999	1856.416	1730.138	1812.393	1659.386	1813.261
Magnetic moment (μ_B)	4	20	0	16	4	12

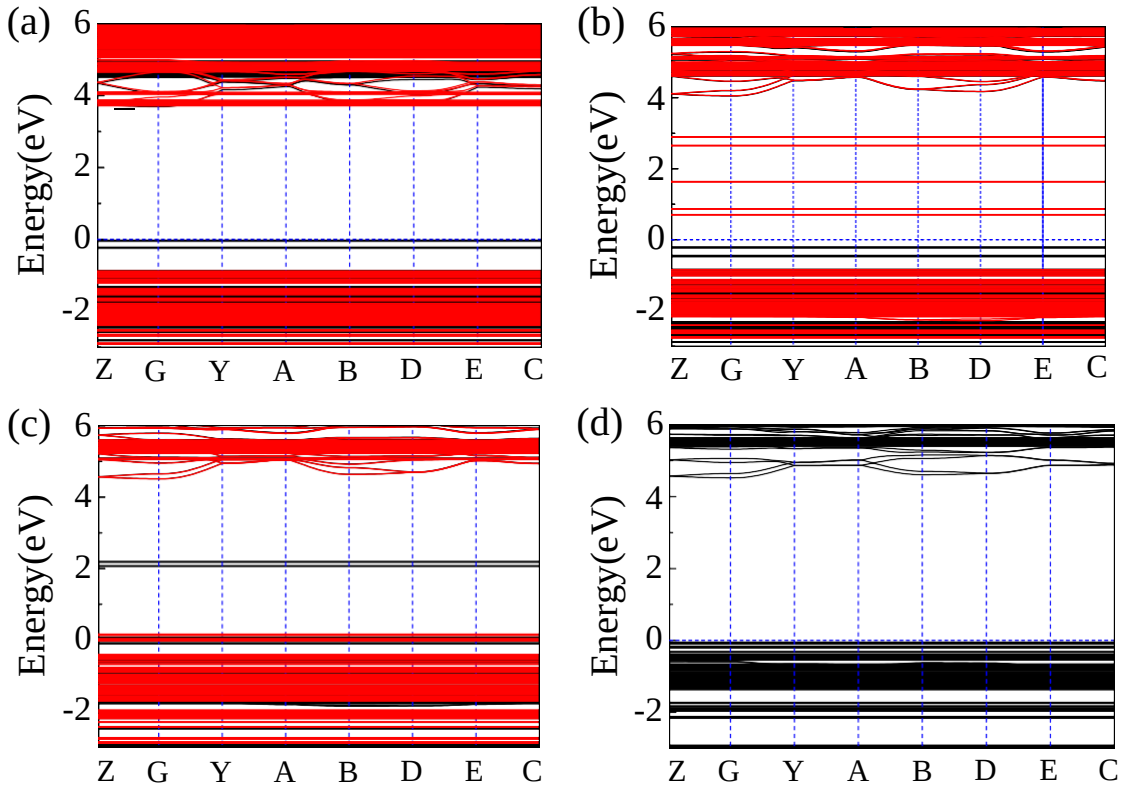

Figure 4S. The band structures of molecular crystals using the PBE+U. (a) MnCP. (b) CoCP. (c) NiCP. (d) CdCP. When the system is magnetic, black solid line represents spin up, red solid line represents spin down.

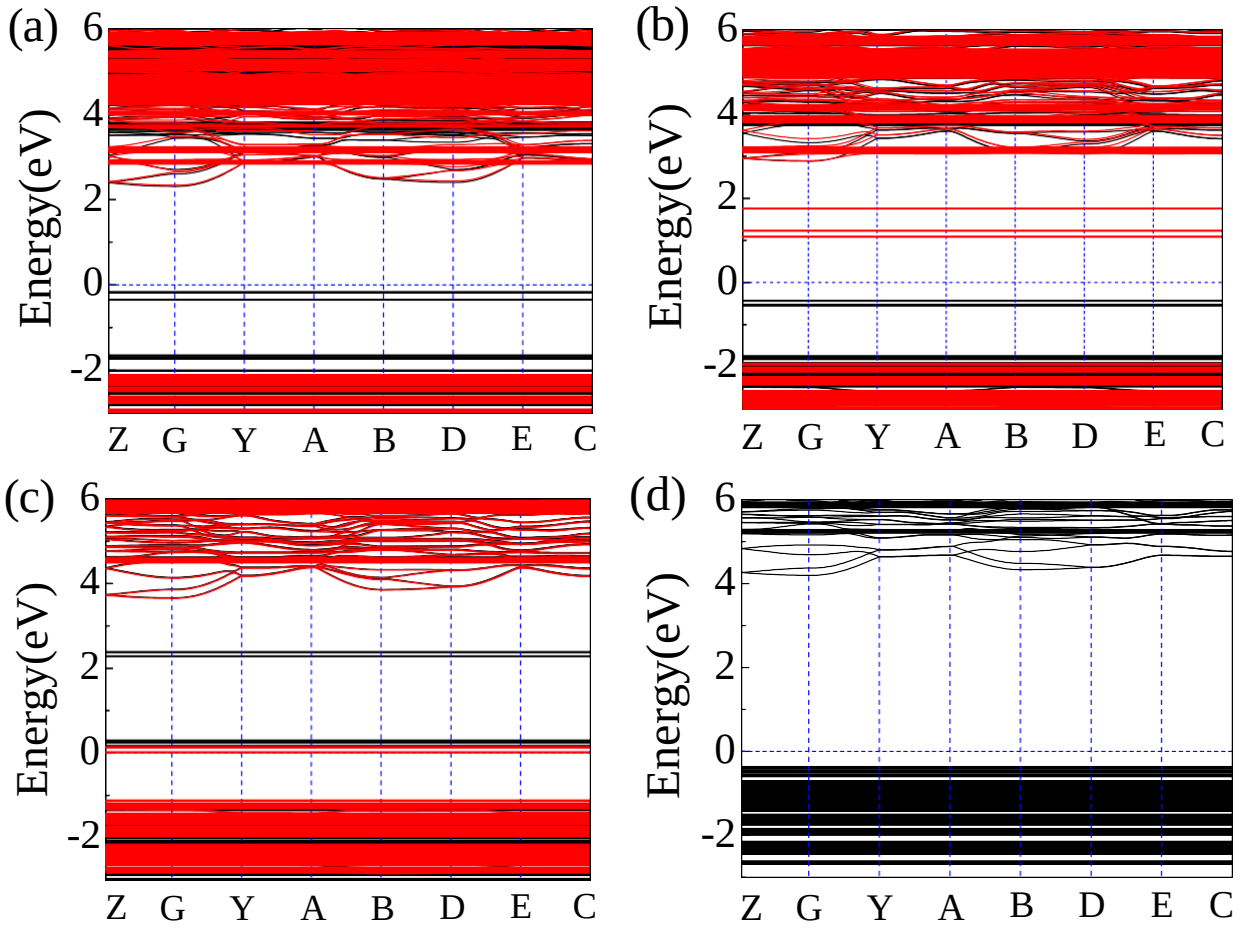

Figure 5S. The band structures of molecular crystals using the SCANrVV10. (a) MnCP. (b) CoCP. (c) NiCP. (d) CdCP. When the system is magnetic, black solid line represents spin up, red solid line represents spin down.