Supplementary Information

Room-temperature magnetism in two-dimensional metal-organic frameworks enabled by electrostatic gating

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This file contains nine figures and four tables

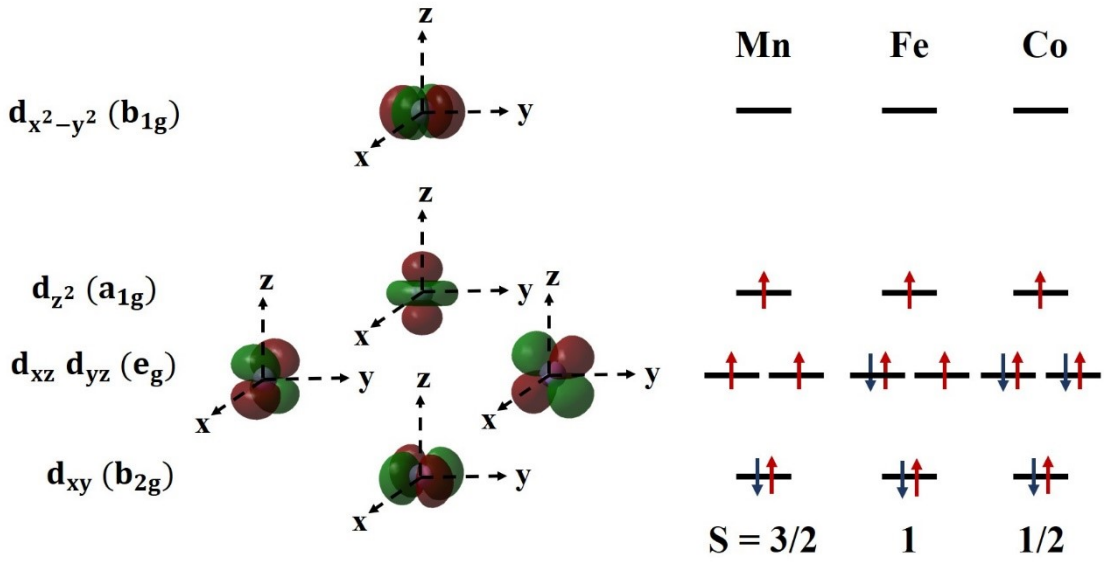

Figure S1. Schematics for the square-planar ligand field induced splitting of d-orbitals and filling of d-electrons of Mn, Fe and Co divalent ions.

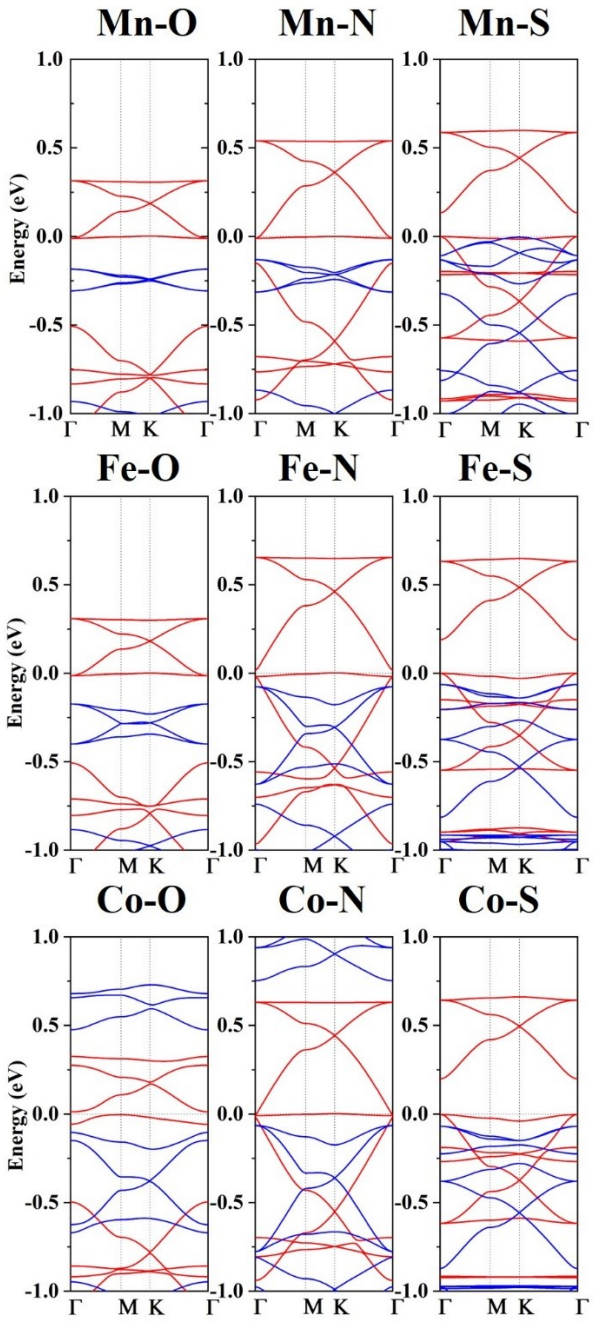

Figure S2. Spin-resolved band structures of monolayer M_3X_2 in its FM ground state, with M = Mn, Fe, and Co; X = HHTP, HITP, and HTTP in which the coordination atom is O, N, and S respectively. The red and blue lines represent two spin channels. The Fermi level has been shifted to 0.

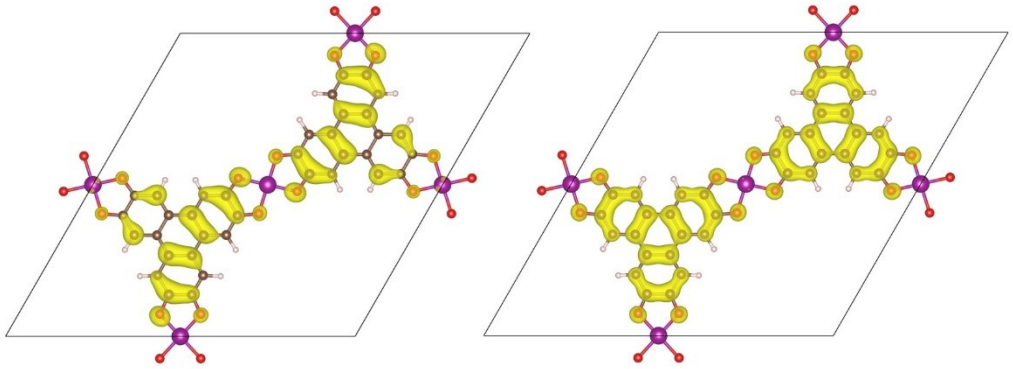

Figure S3. Partial charge density distributions of the bottom flat band coinciding with the Fermi level in monolayer $Mn_3(HHTP)_2$. The charge density distribution at the M and K points in the first Brillouin zone is shown on the left and right panels, respectively. The isovalue is 0.0005 e/Bohr^3.

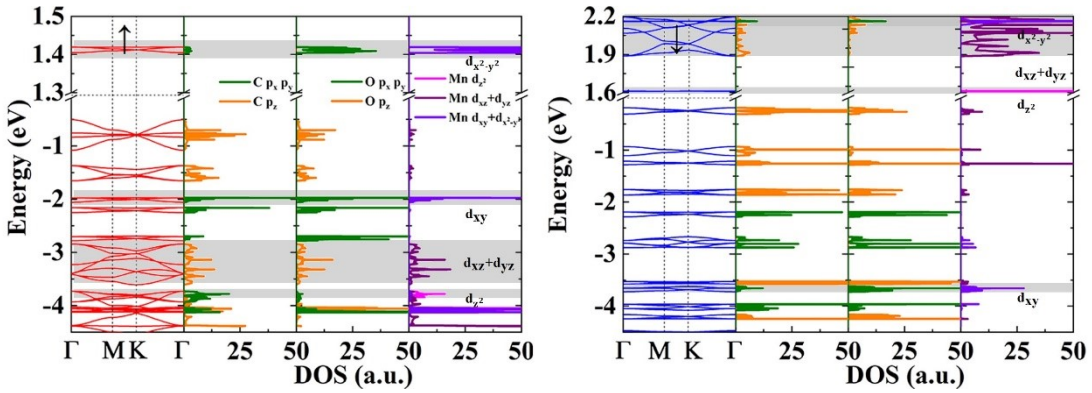

Figure S4. Spin-resolved band structure and partial density of states (pDOS) of monolayer $Mn_3(HHTP)_2$ in its FM ground state. The red and blue lines in the band structure represent majority (left panel) and minority (right panel) spin channels, respectively. The locations of both unoccupied and occupied d-bands of metal ions are shaded in grey.

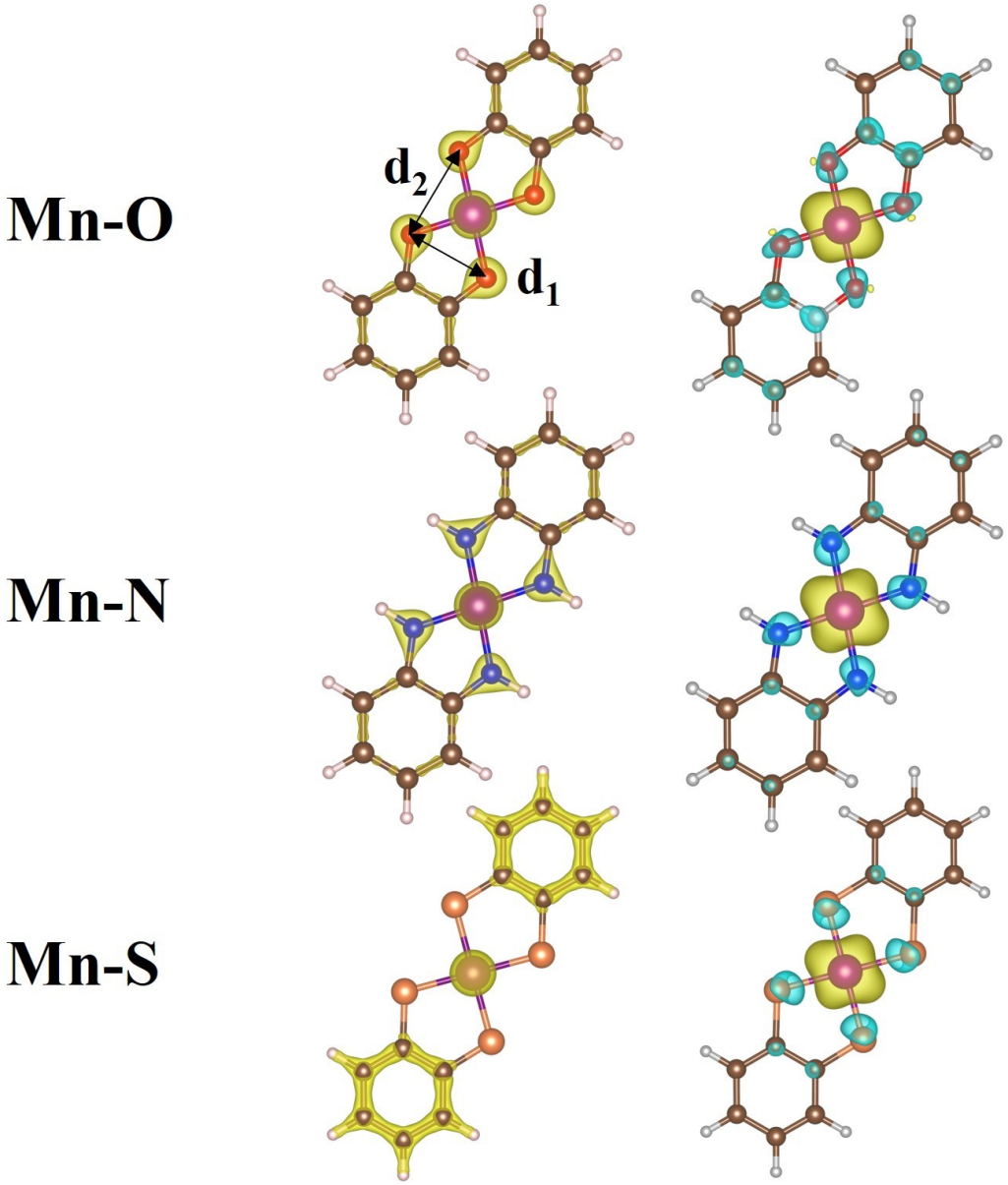

Figure S5. Total charge density distribution (left, isovalue is 0.3 e/Bohr^3) and spin density distribution (right, isovalue is 0.005 e/Bohr^3) in the secondary building units of $Mn_3(HHTP)_2$, $Mn_3(HITP)_2$, and $Mn_3(HTTP)_2$.

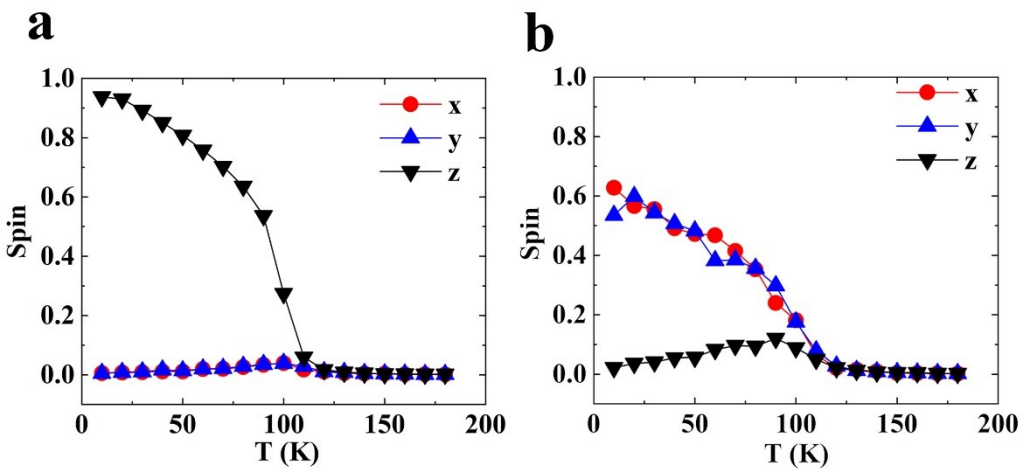

Figure S6. Three normalized spin components per magnetic site as a function of the temperature in a) $Mn_3(HHTP)_2$ and b) $Fe_3(HHTP)_2$ from the Monte Carlo simulation.

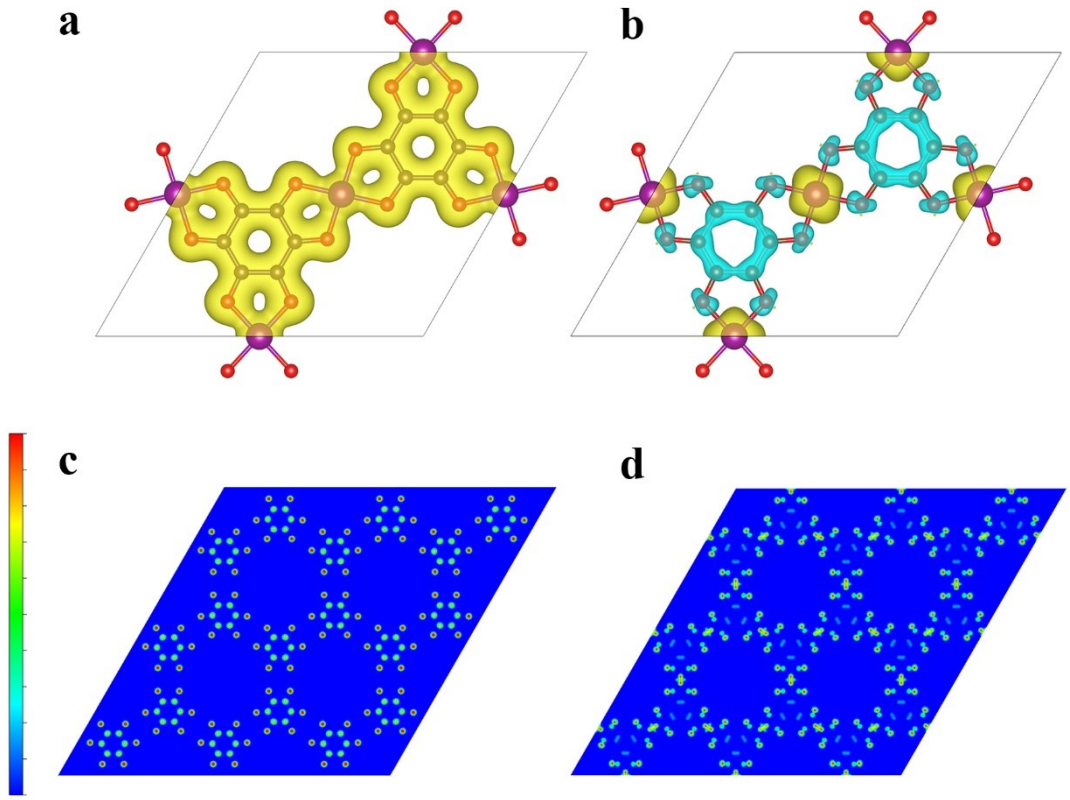

Figure S7. a) Charge density and b) spin density distribution of monolayer $Mn_3(THQ)_2$ in its FM ground state. The isovalue is 0.005 e/Bohr^3. Simulated STM topographies with bias of c) 0 eV and d) -2.21 eV corresponding to the honeycomb itinerant band and kagome d-band, respectively.

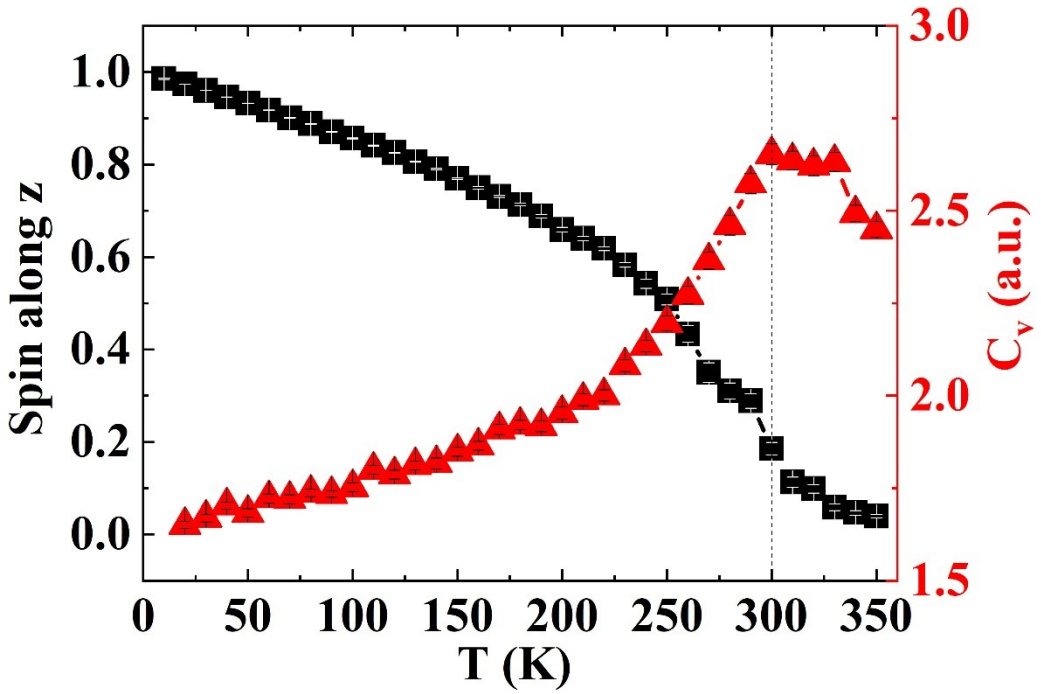

Figure S8. Normalized spin per Mn ion and heat capacity changing with the temperature in monolayer $Mn_3(THQ)_2$ with 1.5 e/f.u. hole doping from the Monte Carlo simulation.

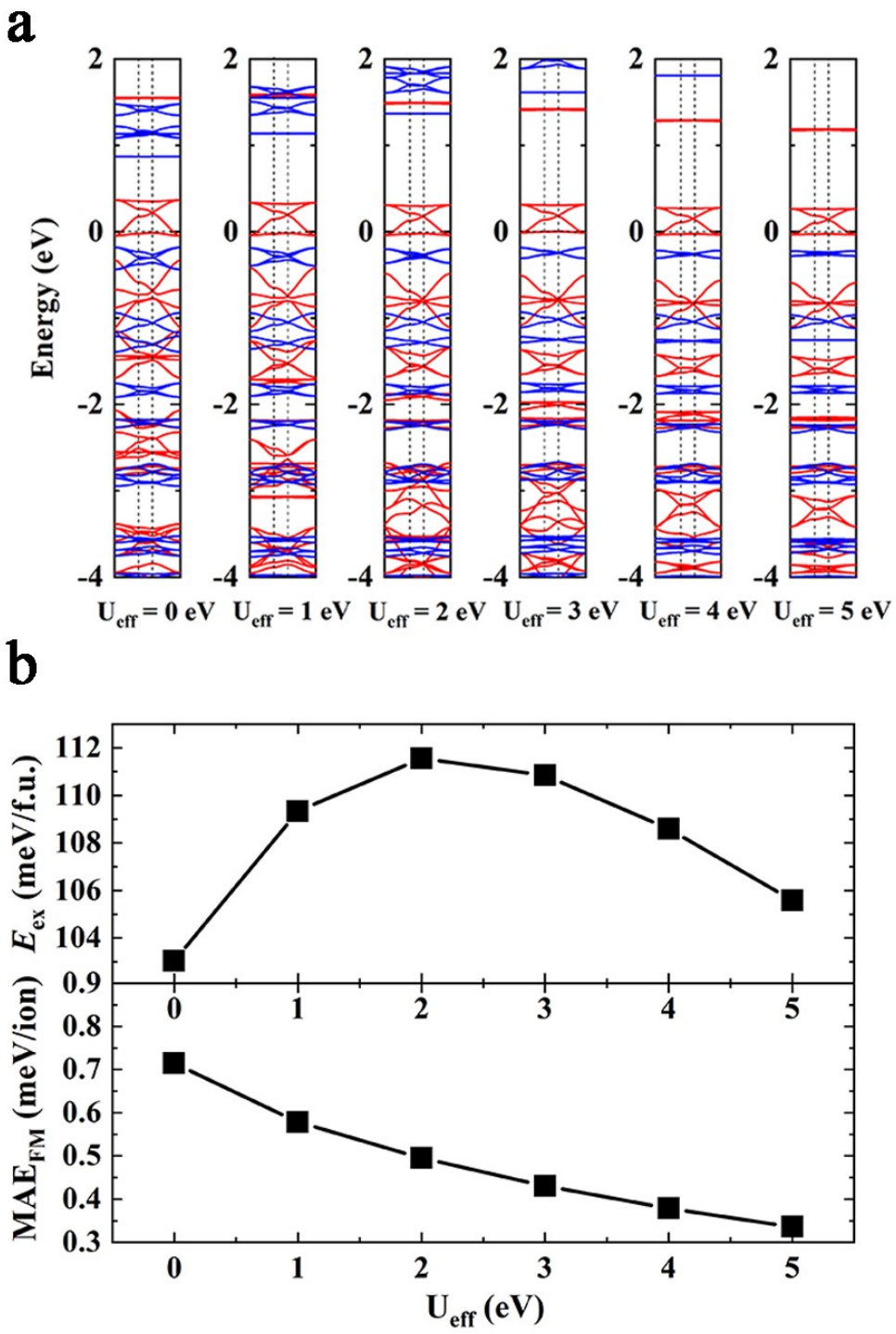

Figure S9. a) Spin-resolved band structures of monolayer $Mn_3(HHTP)_2$ in its FM ground state calculated by the PBE+U method with different on-site Coulomb repulsion energy $U_{eff} = U - J$. It shows that the four-bands of organic ligands on the honeycomb lattice sitting right above the Fermi level are barely influenced by U_{eff}. b) Exchange energy E_{ex} and magnetic anisotropy energy of the FM configuration MAE_{FM} calculated with different U_{eff}.

Table S1. Optimized lattice parameters of monolayer M_3X_2 (M = Mn, Fe, and Co; X = HHTP, HITP, and HTTP). All these MOFs share the same honeycomb-kagome lattice symmetry with $a = b$, $\alpha = \beta = 90°$, $\gamma = 60°$.

a (Å)	Mn	Fe	Co
HHTP	21.726	21.537	21.514
HITP	22.273	21.967	21.933
HTTP	23.451	23.288	23.212

Table S2. Geometric parameters of the square-planar coordination environment in Mn MOFs. The $d_1(d_2)$ denotes the distance between two nearest-neighbor coordination atoms from the same(different) organic ligand, as illustrated in Figure S5. The values in the parentheses are those calculated for the secondary building units.

Donor atom	Coordination bond length (Å)	d_1 (Å)	d_2 (Å)
O	1.874	2.544	2.754
	(1.833)	(2.463)	(2.716)
N	1.936	2.529	2.932
	(1.906)	(2.494)	(2.886)
S	2.206	3.141	3.099
	(2.175)	(3.071)	(3.079)

Table S3. Relative energies (meV) of each 2D MOF with different magnetic configurations.

E	Mn-O	Mn-N	Mn-S	Fe-O	Fe-N	Fe-S	Co-O	Co-N	Co-S
$E_{FM}^{\perp}$	0	0	0	0.303	0	0	1.231	0.834	0.901
$E_{FM}^{\parallel}$	1.291	1.225	1.145	0	0.925	0.814	0	0	0
$E_{FIM}^{\perp}$	111.366	46.463	3.750	120.422	28.311	12.004	100.022	27.672	N.A.
$E_{FIM}^{\parallel}$	112.664	47.692	4.900	120.120	29.082	12.829	98.909	26.996	N.A.

Table S4. Parameters in the generalized Hamiltonian model and Curie temperature of monolayer M_3X_2 (M = Mn, Fe, and Co; X = THQ, HHTP, HITP, and HTTP). The coordination atom is O for THQ and HHTP, N for HITP, and S for HTTP.

Metal	Donor atom	J (meV)	A (meV)	B (meV)	T_c (K)
Mn	O (THQ)	16.374	0.188	2.8×10^{-4}	250
	O (HHTP)	6.187	0.192	-3.9×10^{-4}	100
	N	2.581	0.182	-2.1×10^{-4}	45
	S	0.209	0.170	-2.9×10^{-4}	5
Fe	O	15.015	-0.104	0.001	110
	N	3.520	0.270	0.019	30
	S	1.502	0.274	-0.001	15
Co	O	49.454	-1.524	-0.059	90
	N	13.498	-0.954	-0.079	25
	S	N.A.[1]	N.A.	N.A.	N.A.

[1]The FIM configuration is not stable, which always relaxes to the FM one.