Supporting Information

Two-Dimensional Multifunctional Metal-Organic Frameworks with simultaneous Ferri-/Ferromagnetism and Vertical Ferroelectricity

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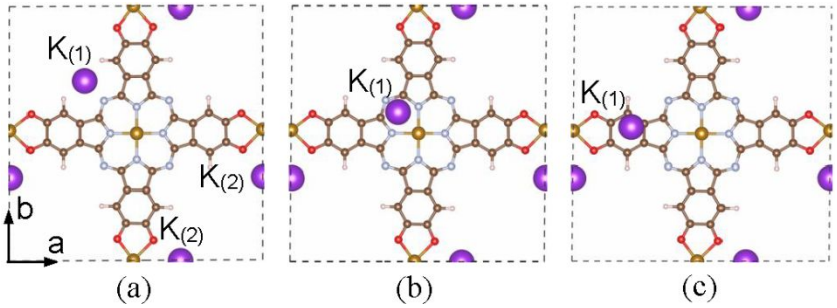

Figure S1. Top view of the optimized structures for three possible configurations of 2D $K_3Fe_2[PcMO_8]$ with the out-of-plane counter $K_{(1)}$ ions adsorbed at different sites. (a) is the structure used in the manuscript.

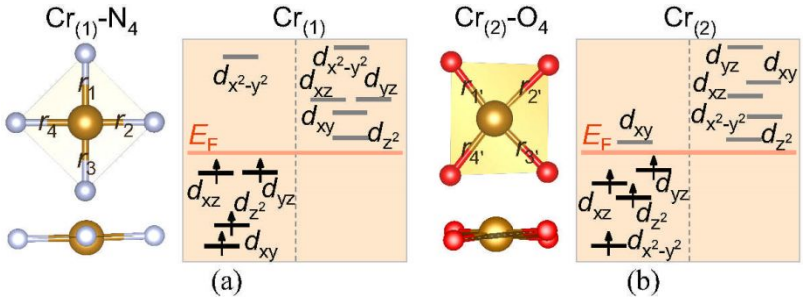

Figure S2. (a) Splitting diagrams of *d*-orbitals for $Cr_{(1)}$ atom in the square crystal field ($r_1=r_2=r_3=r_4$). (b) Splitting diagrams of *d*-orbitals for $Cr_{(2)}$ atom in a distorted square crystal field ($r_{1'}<r_{4'}<r_{3'}<r_{2'}$).

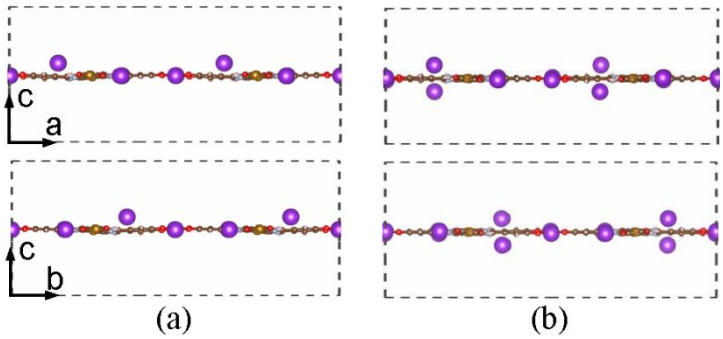

Figure S3. Side views along the **ac** and **bc** planes for 2D $K_3Fe_2[PcMO_8]$ in (a) ferroelectric and (b) antiferroelectric configurations.

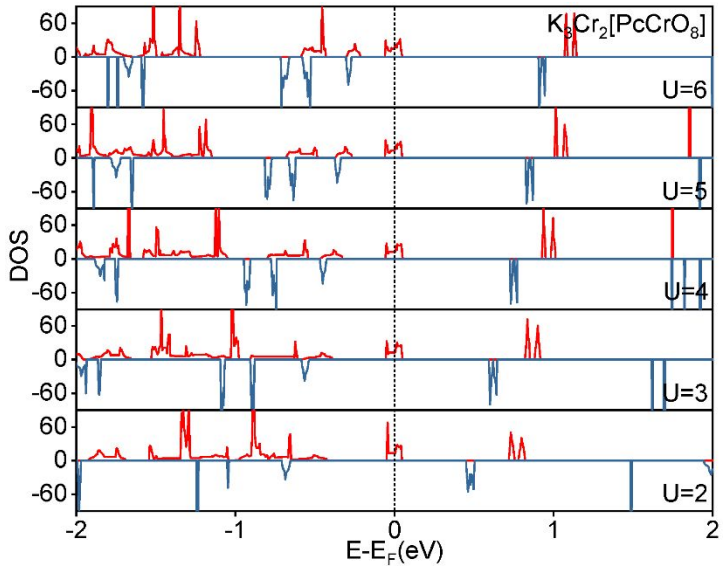

Figure S4. Calculated total density of states (DOS) for 2D metal organic framework (MOF) $K_3Cr_2[PcCrO_8]$ with different *U* values. Fermi levels (E_F) are all set to zero. Positive and negative values represent spin up and spin down, respectively.

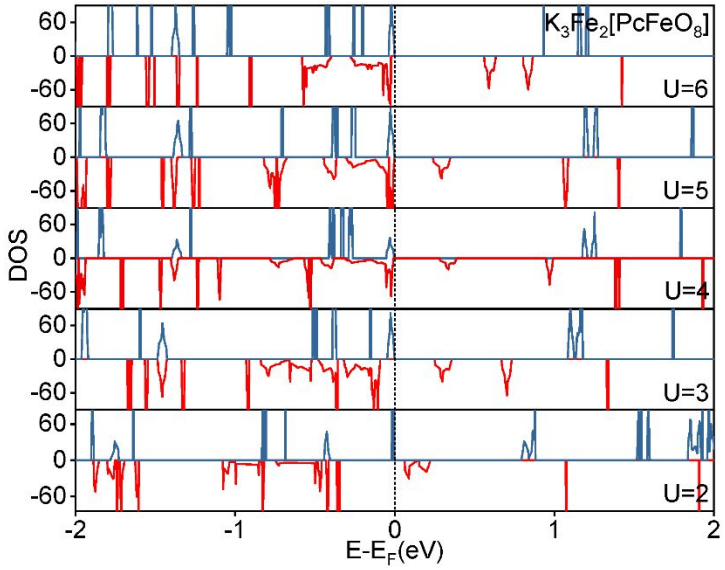

Figure S5. Calculated total DOS for 2D MOF $K_3Fe_2[PcFeO_8]$ with different *U* values. Fermi levels (E_F) are all set to zero. Positive and negative values represent spin up and spin down, respectively.

Table S1. Calculated adsorption energy (E_{ads}) of $K_{(1)}$ ion in 2D $K_3Fe_2[PcFeO_8]$ defined as $E_{ads} = E_{K3Fe2[PcFeO8]} - E_{K2Fe2[PcFeO8]} - E_{K(1)}$ for different configurations in Figure S1.

$K_3Fe_2[PcFeO_8]$	$E_{K3Fe2[PcFeO8]}$ (eV)	$E_{K2Fe2[PcFeO8]}$ (eV)	$E_{K(1)}$ (eV)	E_{ads} (eV)
Configure (a)	-465.631	-462.929	-0.177	-2.525
Configure (b)	-465.071			-1.965
Configure (c)	-465.391			-2.285

Table S2. Electron occupation numbers on the five *d* orbitals of $Cr_{(1)}$ and $Cr_{(2)}$ atoms in the $K_3Cr_2[PcCrO_8]$ framework. Here, $n_{occ} = n\uparrow + n\downarrow$ and $S_z = \frac{1}{2}(n\uparrow - n\downarrow)$, with $n\uparrow$ and $n\downarrow$ being the spin-up and spin-down occupation numbers, respectively.

$Cr_{(1)}$	d_{xy}	d_{yz}	d_{z^2}	d_{xz}	$d_{x^2-y^2}$	Total
$n\uparrow$	0.91	0.83	0.85	0.83	0.33	3.75
$n\downarrow$	0.01	0.03	0.04	0.03	0.24	0.34
n_{occ}	0.92	0.86	0.89	0.86	0.57	4.09
S_z	0.45	0.40	0.41	0.40	0.05	1.70
$Cr_{(2)}$	d_{xy}	d_{yz}	d_{z^2}	d_{xz}	$d_{x^2-y^2}$	Total
$n\uparrow$	0.26	0.91	0.84	0.81	0.93	3.75
$n\downarrow$	0.18	0.02	0.03	0.04	0.03	0.30
n_{occ}	0.44	0.93	0.87	0.85	0.96	4.05
S_z	0.04	0.45	0.40	0.38	0.45	1.73

Table S3. Calculated intensity of polarization and ferroelectric transition barrier for 2D metal-organic frameworks with different alkali metal counter ions.

	Polarization (pC/m)	Barrier (eV)
$Na_3Fe_2[PcFeO_8]$	107.2	0.13
$K_3Fe_2[PcFeO_8]$	143.2	0.38
$Rb_3Fe_2[PcFeO_8]$	178.1	0.44

Table S4. Calculated relative energies of ferrimagnetic (FiM) state to ferromagnetic (FM) state Δ*E* (meV per formula) for $K_3Cr_2[PcCrO_8]$ and $K_3Fe_2[PcFeO_8]$ at different values of onsite Coulomb interaction *U*.

$K_3M_2[PcMO_8]$	*U*=2	*U*=3	*U*=4	*U*=5	*U*=6
Δ*E*(M=Cr)	39.4	59.5	73.0	77.6	75.4
Δ*E*(M=Fe)	-83.4	-80.1	-68.1	-60.4	-30.9