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Electronic Supplementary Information (ESI): Large Piezoelectric Response in Ferroelectric/Multiferroelectric Metal Oxyhalide MOX_2 (M = Ti, V and X = F, Cl and Br) Monolayers

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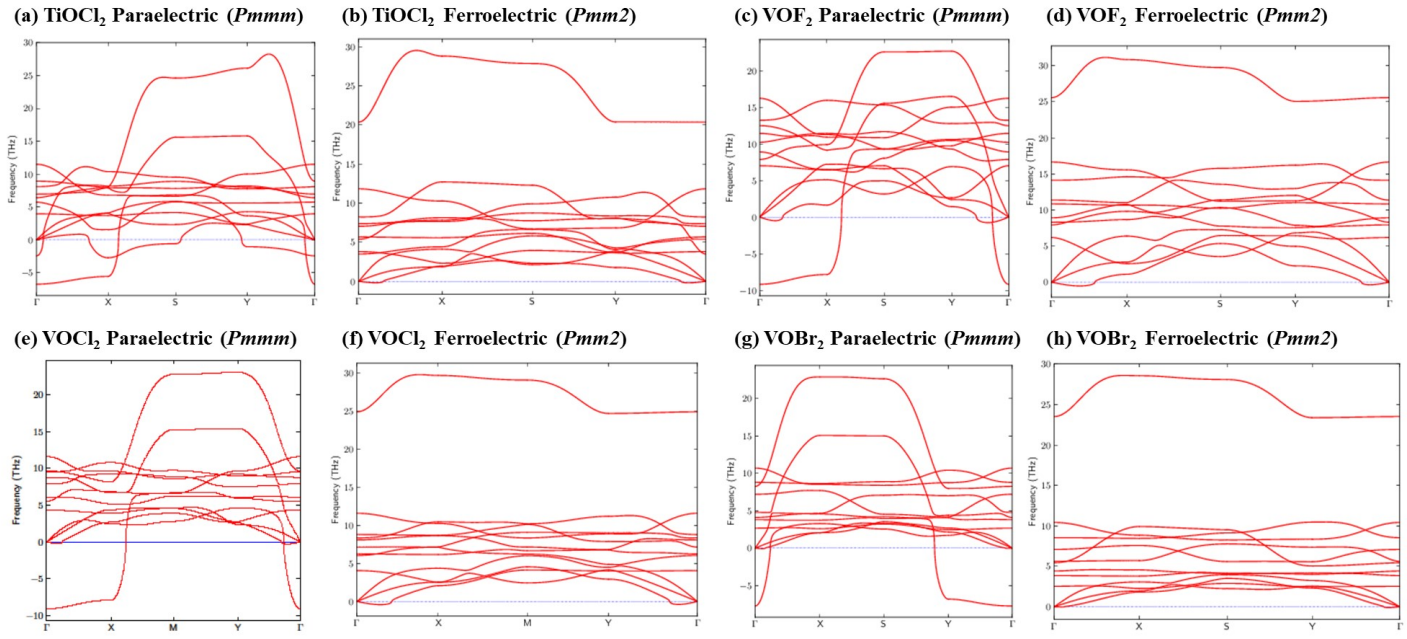

Fig. S1 Phonon band structure of the monolayers in (a) paraelectric (space group: Pmmm) and (b) ferroelectric (space group: Pmm2) phase. For paraelectric phase, we see an imaginary polar phonon (soft) mode at the Γ-point. Following this soft mode, we obtain ferroelectric phase.

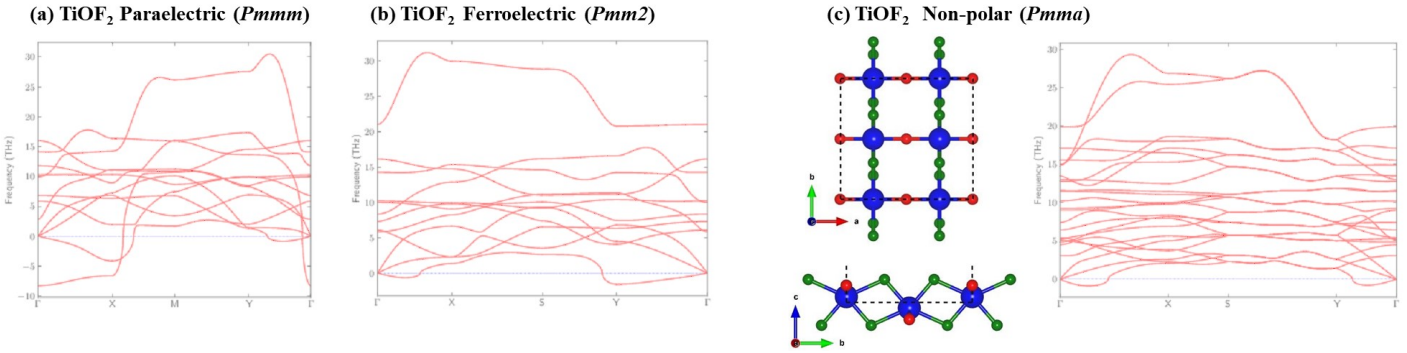

Fig. S2 Phonon band structure of $TiOF_2$ monolayer in (a) paraelectric (space group: *Pmmm*) and (b) ferroelectric (space group: *Pmm*2) phase are shown. For paraelectric phase, we see an imaginary polar phonon (soft) mode at the Γ-point. Following this soft mode, we obtain ferroelectric phase, however now there is an imaginary mode the Y-point, which leads to a new non-polar (space group: *Pmma*) phase (c). Blue, red, and green balls represent Ti, O, and F, respectively. The dashed lines represent the rectangle simulation cells. The "U-shape" soft mode around the Γ-point (c) for non-polar (space group: *Pmma*) phase is due to flexural acoustic mode of 2D materials.

	Y_x	Y_y	ν_x	ν_y
VOF_2(FM)	65.652	93.454	0.156	0.222
$VOCl_2$(FM)	52.458	56.844	0.150	0.162
$VOCl_2$(AFM1)	49.693	41.527	0.162	0.136
$VOBr_2$(FM)	53.566	49.204	0.150	0.138
$VOBr_2$(AFM1)	52.050	39.761	0.153	0.117
$TiOCl_2$	77.040	55.652	0.147	0.106
$TiOBr_2$	75.953	47.247	0.144	0.089

Table S1 Young's modulus along *a*-direction ($Y_x = (C_{11}C_{22} - C_{12}^2)/C_{22}$) and *b*-direction ($Y_y = (C_{11}C_{22} - C_{12}^2)/C_{11}$) in 2D unit of N/m and Poisson's ratio along *a*-direction ($\nu_x = C_{12}/C_{22}$) and *b*-direction ($\nu_y = C_{12}/C_{11}$) obtained from elastic constants[1,2]. Compared to graphene (Y = 342.2 N/m) or *h*-BN monolayer (Y = 275.8 N/m)[2], MOX_2 monolayers have quite low Young's modulus, indicating their flexibility. Note that anisotropic Y and ν of MOX_2 monolayers are quite comparable with those of piezoelectric Janus monolayers like $TiSe_2S$[1].

	e_{11}^{elc}	e_{11}^{ion}	e_{11}	e_{12}^{elc}	e_{12}^{ion}	e_{12}	C_{11}	C_{22}	C_{12}	C_{66}	d_{11}	d_{12}
U_{eff}=0	4.217	11.937	16.153	2.974	-0.824	2.150	54.694	50.240	7.528	17.176	29.555	-0.149
U_{eff}=1	4.153	14.335	18.488	2.894	-0.801	2.094	61.061	49.736	7.942	17.201	30.362	-0.639
U_{eff}=2	4.084	17.011	21.095	2.767	-1.695	1.072	66.124	49.097	7.976	17.255	32.271	-3.059
U_{eff}=3	4.033	22.373	26.406	2.609	-1.403	1.206	71.882	48.413	8.103	17.342	37.155	-3.728

Table S2 The electronic (e_{11}^{elc} and e_{12}^{elc}) and ionic (e_{11}^{ion} and e_{12}^{ion}) part of the total piezoelectric stress constant $e_{11}$and e_{12} in 2D piezoelectric unit of 10^{-10} C/m, elastic constants (C_{11} , C_{22} , C_{12} , and C_{66}) in 2D unit of N/m, and piezoelectric strain coefficients (d_{11} and d_{12}) in pm/V of $VOBr_2$(FM) monolayers obtained using different value of U_{eff} ranging from 1 eV to 3 eV in GGA+U_{eff} calculations[3].

	a (Å)	b (Å)	M-O (Å)	M-X (Å)	Z_{11} (M)	Z_{11} (O)	Z_{11} (X)	P_1	$\triangle E$	$i\omega_\Gamma$
$VOCl_2$	3.783(3.609)	3.368(3.411)	1.650(1.804)	2.382(2.394)	4.788(15.308)	-4.138(-12.955)	-0.325(-1.176)	313.251	131.204	402.812
$VOBr_2$	3.771(3.619)	3.579(3.616)	1.661(1.810)	2.542(2.554)	4.951(15.056)	-4.497(-13.122)	-0.227(-0.967)	273.428	91.349	315.617

Table S3 Structural information of $VOCl_2$(AFM3) and $VOBr_2$(AFM3) monolayers: optimized lattice parameters (a and b are normalized to unit cell; see the rectangular 2x2x1 supercell for AFM3 in Fig. 1 (c)). M-O (M-X) represents the bond length between metal (M) and oxygen (halogen; X) atoms. Z_{11} is the Born effective charge in $|e|$ unit. The values in the parentheses are for paraelectric phases. P_1 (10^{-12} C/m) and $\triangle E$ (meV/fu) are the in-plane electric polarization and energy difference between ferroelectric and paraelectric phase (positive $\triangle E$ value suggests FE phase is lower in energy compared to PE). $i\omega_\Gamma$(cm^{-1}) stands for the lowest imaginary frequency of PE phase at the Γ-point.

	e_{11}^{elc}	e_{11}^{ion}	e_{11}	e_{12}^{elc}	e_{12}^{ion}	e_{12}	C_{11}	C_{22}	C_{12}	C_{66}	d_{11}	d_{12}
$VOCl_2$ (AFM3)	4.725	11.288	16.013	3.319	-0.609	2.710	51.377	42.763	6.990	18.688	30.994	1.271
$VOBr_2$ (AFM3)	4.388	11.956	16.344	2.960	-0.585	2.375	53.918	40.737	6.328	17.129	30.180	1.142

Table S4 Piezoelectric constants of $VOCl_2$(AFM3) and $VOBr_2$(AFM3) monolayers: the electronic (e_{11}^{elc} and e_{12}^{elc}) and ionic (e_{11}^{ion} and e_{12}^{ion}) part of the total piezoelectric stress constant $e_{11}$and e_{12} in 2D piezoelectric unit of 10^{-10} C/m, elastic constants (C_{11} , C_{22} , C_{12} , and C_{66}) in 2D unit of N/m, and piezoelectric strain coefficients (d_{11} and d_{12}) in pm/V.