Supplementary Information: Identification of Two-Dimensional Layered Dielectrics from First Principles

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Table S1. Four major categories of 2D layered Materials based on their chemical formula, space group (number) and Crystal Systems. Category 1 consists of three subcategories as appeared in a, b and c.

		Chemical Formula	Bulk Space Group (number)	Crystal System
Cat. 1	a	TlF	P4/nmm (129)	Tetragonal
	b	MOX (M = Lanthanide & X = Halogen): HoOI, LaOBr, LaOCl, LaOI, LuOBr, LuOI, NdOI, YOBr MXF (M = Semiconductor/Metal & X = Halogen): GeClF, PbClF, SrBrF MHX (M = Metal & X = I, Br): CaHBr, CaHI, SrHBr, SrHI		
	c	MOX (M = Metal & X = Halogen): AlOCl, BiOCl, InOCl, ScOBr	Pmmn (59)	Orthorhombic
Cat. 2		MX_2 (M = Metal & X = Halogen): CaI_2, $CdBr_2$, $CdCl_2$, $MgBr_2$, $MgCl_2$, MgI_2, PbI_2, $ZnBr_2$, $ZnCl_2$	$P\bar{3}m1$ (164): $Mg(Br_2, Cl_2, I_2)$, CaI_2 $R\bar{3}m$ (166): $Cd(Br_2, Cl_2)$, $Zn(Br_2, Cl_2)$	Trigonal
Cat. 3		MX_4 (M = Metal & X = Halogen): PbF_4, SnF_4	I4/mmm (139)	Tetragonal
Cat. 4		SrI_2	Pnma (62)	Orthorhombic

Table S2. The lattice constants of two-dimensional (2D) monolayer structures (a_{2d}), bulk interlayer distance (d_i), Monolayer thickness (t), cutoff energies, and Monolayer supercell thickness. Δ represents the percentage difference between the bulk interlayer distance and the monolayer thickness.

		Material	Bulk	Monolayer			Cutoff Energy (eV)	Monolayer Supercell Thickness (Å)
			d_i (Å)	a (Å)	t (Å)	Δ (%)		
Cat. 1	a	TlF	6.25	3.81	6.64	6.20	560	22.55
	b	CaHBr	8.06	3.83	8.14	0.91	700	25.63
		CaHI	8.79	4.01	8.83	0.47	520	26.50
		GeClF	7.56	3.76	7.70	1.82	560	25.95
		HoOI	9.22	3.90	9.26	0.41	520	25.99
		LaOBr	7.49	4.13	7.93	5.78	560	25.80
		LaOCl	6.91	4.10	7.08	2.52	560	25.72
		LaOI	9.19	4.14	9.25	0.65	520	26.51
		LuOBr	8.34	3.74	8.38	0.49	560	25.86
		LuOI	9.20	3.84	9.23	0.35	560	25.58
		NdOI	9.26	4.07	9.29	0.33	520	25.88
		PbClF	7.26	4.13	7.44	2.52	560	26.94
		SrBrF	7.42	4.22	7.75	4.39	560	25.47
		SrHBr	7.30	4.21	7.59	3.94	700	25.38
		SrHI	8.67	4.28	8.77	1.24	520	26.07
		YOBr	8.31	3.83	8.38	0.80	560	26.36
	c	AlOCl	7.89	3.16	7.94	0.52	520	25.71
		BiOCl	7.49	3.91	7.59	1.30	520	26.30
		InOCl	8.14	3.56	8.24	1.22	560	25.95
		ScOBr	8.72	3.56	8.76	0.45	560	26.20
Cat. 2		CaI_2	7.02	4.48	7.04	0.30	450	23.70
		$CdBr_2$	6.74	6.75	6.37	-5.54	450	23.10
		$CdCl_2$	6.25	6.26	5.92	-5.35	400	24.85
		$MgBr_2$	6.30	3.84	6.34	0.59	560	23.23
		$MgCl_2$	5.86	3.64	5.90	0.67	560	22.66
		MgI_2	6.92	4.16	6.94	0.31	560	23.20
		PbI_2	7.20	14.41	7.08	-1.68	450	24.37
		$ZnBr_2$	6.35	6.63	6.34	-1.18	360	22.94
		$ZnCl_2$	5.94	6.21	5.89	-0.85	360	23.05
Cat. 3		PbF_4	4.03	5.07	4.10	1.70	520	23.30
		SnF_4	4.52	4.97	4.11	-9.02	520	23.93
Cat. 4		SrI2	6.18	4.92	6.31	2.16	700	23.61

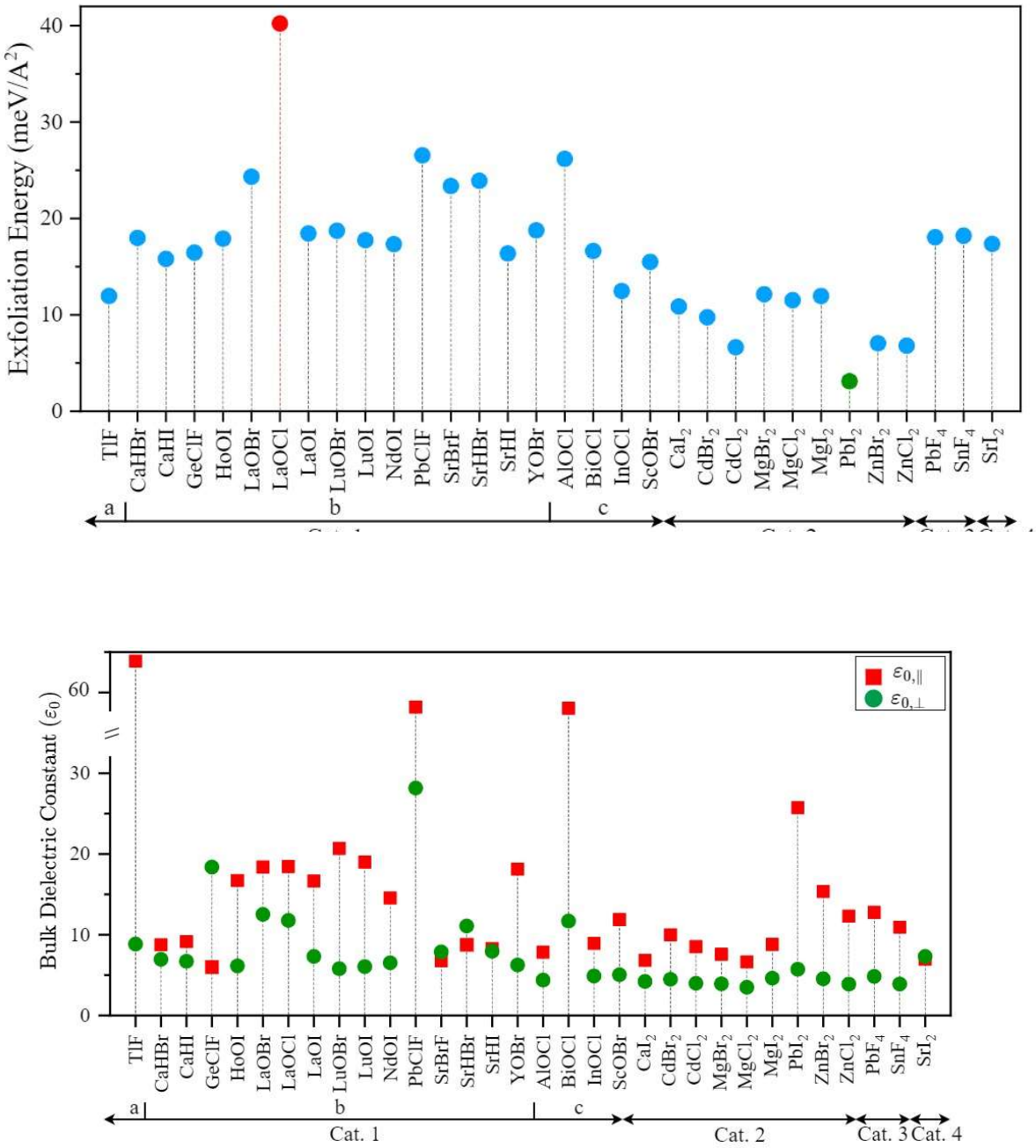

Figure S2. The static in-plane and out-of-plane dielectric constants of 32 layered vdW materials. The in-plane dielectric values ranges between 6.01 (GeClF) and 63.86 (TlF), and the out-of-plane dielectric values are located in the range of 3.49 ($MgCl_2$) and 28.15 (PbClF). The red squares and green dots respectively show the in-plane and the out-of-plane static dielectric constants.

Table S3. The PBE band gaps of Bulk and Monolayers, as well as HSE band gap and electron affinity of Monolayers. The HSE band gap of monolayers explicitly shows that the highest and the lowest band gaps belong to AlOCl (7.38 eV) and PbI_2 (3.32 eV).

		Material	PBE Band Gap (eV)		HSE Band Gap (eV)	Electron Affinity (eV)
			Bulk	Monolayer	Monolayer	Monolayer
Cat. 1	a	TlF	3.00	3.67	4.75	1.70
	b	CaHBr	4.00	4.18	5.44	2.11
		CaHI	3.17	3.82	4.87	2.30
		GeClF	2.56	2.91	3.96	4.17
		HoOI	3.44	3.55	4.52	2.36
		LaOBr	3.68	4.05	5.68	2.37
		LaOCl	4.05	4.24	5.83	2.31
		LaOI	3.24	3.40	4.81	2.48
		LuOBr	4.28	4.48	5.79	2.35
		LuOI	3.25	3.27	4.24	2.60
		NdOI	3.62	3.74	4.72	2.46
		PbClF	3.51	3.52	4.60	3.52
		SrBrF	5.15	5.32	6.57	1.86
		SrHBr	3.72	4.29	5.42	2.01
		SrHI	3.26	3.97	5.03	2.23
		YOBr	4.42	4.68	6.00	2.15
	c	AlOCl	5.72	5.86	7.38	1.51
		BiOCl	4.00	2.75	3.74	4.54
		InOCl	2.35	2.62	4.05	4.66
		ScOBr	3.29	3.27	4.82	3.30
Cat. 2		CaI_2	3.50	3.83	4.61	2.03
		$CdBr_2$	2.73	3.25	4.47	3.63
		$CdCl_2$	3.40	3.91	5.32	3.68
		$MgBr_2$	4.30	4.79	6.01	2.21
		$MgCl_2$	5.46	6.01	7.12	2.09
		MgI_2	3.52	3.62	4.61	2.48
		PbI_2	2.25	2.58	3.32	3.67
		$ZnBr_2$	3.10	3.45	4.77	3.12
		$ZnCl_2$	4.15	4.49	6.04	2.82
Cat. 3		PbF_4	1.86	2.49	4.24	7.81
		SnF_4	3.08	3.86	6.05	6.38
Cat. 4		SrI2	3.76	3.99	5.01	2.20

Table S4. The leakage current density for *n*-MOS applications through a monolayer (1L), bilayer (2L) and three-layer (3L) of each vdW material and the Equivalent Oxide Thickness (EOT) of a monolayer. The asterisks indicate materials with a negative band-offset that are not viable as insulators for *n*-MOS applications.

n-MOS		Material	Leakage Current Density (pA/μm)			EOT (nm)
			1L	2L	3L	1L
Cat. 1	a	TlF	3.11×10^{-11}	7.07×10^{-27}	1.33×10^{-27}	0.37
	b	CaHBr	8.71×10^{-10}	1.12×10^{-19}	1.77×10^{-20}	0.69
		CaHI	1.56×10^{-8}	6.75×10^{-18}	1.92×10^{-18}	0.37
		GeClF	(*)	(*)	(*)	0.27
		HoOI	2.24×10^{-8}	1.91×10^{-16}	4.71×10^{-17}	0.51
		LaOBr	1.10×10^{-5}	5.36×10^{-17}	1.77×10^{-17}	0.23
		LaOCl	9.41×10^{-5}	8.32×10^{-19}	1.57×10^{-19}	0.05
		LaOI	1.18×10^{-6}	1.47×10^{-14}	3.63×10^{-15}	0.51
		LuOBr	8.28×10^{-7}	4.80×10^{-16}	9.34×10^{-17}	0.57
		LuOI	7.94×10^{-5}	2.71×10^{-12}	6.14×10^{-13}	0.57
		NdOI	5.24×10^{-7}	8.98×10^{-15}	2.12×10^{-15}	0.55
		PbClF	4.98×10^{7}	5.28×10^{4}	4.32×10^{2}	0.19
		SrBrF	1.94×10^{-12}	6.43×10^{-25}	1.56×10^{-25}	0.37
		SrHBr	7.91×10^{-10}	1.90×10^{-22}	4.80×10^{-23}	0.33
		SrHI	2.25×10^{-9}	3.27×10^{-19}	1.03×10^{-19}	0.31
		YOBr	1.02×10^{-9}	1.76×10^{-19}	3.46×10^{-20}	0.56
	c	AlOCl	2.26×10^{-18}	1.21×10^{-29}	1.85×10^{-30}	0.68
		BiOCl	(*)	(*)	(*)	0.29
		InOCl	(*)	(*)	(*)	0.66
		ScOBr	1.10×10^{5}	6.12	1.04	0.66
Cat. 2		CaI_2	3.71×10^{-8}	1.48×10^{-20}	1.96×10^{-21}	0.62
		$CdBr_2$	2.72×10^{9}	2.34×10^{7}	2.18×10^{6}	0.55
		$CdCl_2$	9.81×10^{9}	1.17×10^{8}	1.16×10^{7}	0.44
		$MgBr_2$	2.34×10^{-4}	4.92×10^{-17}	4.96×10^{-18}	0.61
		$MgCl_2$	1.34×10^{-4}	2.60×10^{-18}	1.46×10^{-19}	0.65
		MgI_2	1.72×10^{-2}	4.27×10^{-13}	5.84×10^{-14}	0.56
		PbI_2	1.23×10^{9}	1.75×10^{7}	1.91×10^{6}	0.45
		$ZnBr_2$	1.71×10^{5}	8.36×10^{-1}	6.67×10^{-3}	0.54
		$ZnCl_2$	1.45×10^{3}	6.54×10^{-5}	1.33×10^{-7}	0.57
Cat. 3		PbF_4	(*)	(*)	(*)	0.18
		SnF_4	(*)	(*)	(*)	0.29
Cat. 4		SrI2	2.45×10^{-4}	4.20×10^{-18}	2.17×10^{-19}	0.30

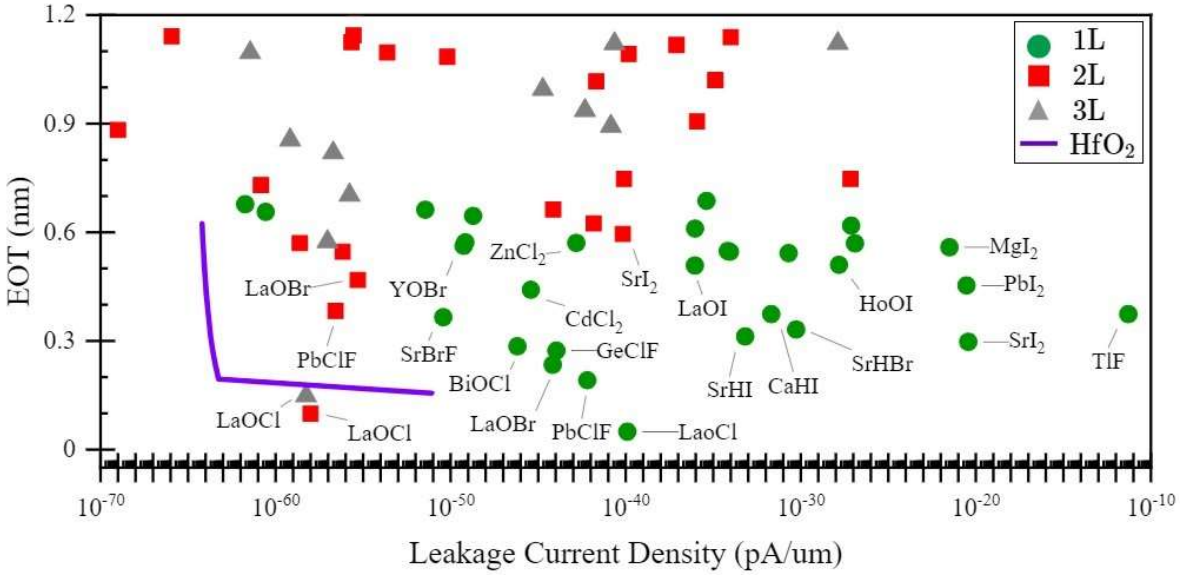

Figure S3. The Leakage current density and (Equivalent Oxide Thickness) EOT for monolayers (green circles), bilayers (red squares), and trilayers (grey triangles) in *p*-MOS applications. Reference dielectrics are also shown: The dark purple line shows the EOT corresponding to the different thicknesses of HfO_2 (between 1-4 nm).

Table S5. The leakage current density for *p*-MOS applications through a monolayer (1L), bilayer (2L) and three-layer (3L) of each vdW material and the Equivalent Oxide Thickness (EOT) of a monolayer. The asterisks indicate materials with a negative band-offset that are not viable as insulators for *p*-MOS applications.

p-MOS		Material	Leakage Current Density (pA/μm)			EOT (nm)
			1L	2L	3L	1L
Cat. 1	a	TlF	5.15×10^{-12}	7.00×10^{-28}	1.31×10^{-28}	0.37
	b	CaHBr	4.14×10^{-36}	1.11×10^{-45}	1.75×10^{-46}	0.69
		CaHI	2.07×10^{-32}	8.06×10^{-41}	2.29×10^{-41}	0.37
		GeClF	1.09×10^{-44}	6.75×10^{-57}	1.97×10^{-57}	0.27
		HoOI	1.52×10^{-28}	1.31×10^{-35}	3.24×10^{-36}	0.51
		LaOBr	6.74×10^{-45}	5.03×10^{-56}	1.66×10^{-56}	0.23
		LaOCl	1.25×10^{-40}	9.90×10^{-59}	5.59×10^{-59}	0.05
		LaOI	9.00×10^{-37}	2.09×10^{-49}	5.18×10^{-43}	0.51
		LuOBr	6.86×10^{-50}	2.89×10^{-56}	5.62×10^{-57}	0.57
		LuOI	1.26×10^{-27}	1.00×10^{-34}	2.27×10^{-35}	0.57
		NdOI	8.89×10^{-35}	1.48×10^{-40}	3.51×10^{-41}	0.55
		PbClF	6.48×10^{-43}	2.68×10^{-57}	9.25×10^{-58}	0.19
		SrBrF	3.77×10^{-51}	1.47×10^{-61}	3.57×10^{-62}	0.37
		SrHBr	5.47×10^{-31}	7.27×10^{-45}	1.83×10^{-45}	0.33
		SrHI	6.76×10^{-34}	1.47×10^{-42}	4.64×10^{-43}	0.31
		YOBr	5.55×10^{-50}	2.14×10^{-56}	4.22×10^{-57}	0.56
	c	AlOCl	1.84×10^{-62}	3.97×10^{-68}	6.06×10^{-69}	0.68
		BiOCl	6.53×10^{-47}	2.44×10^{-59}	6.81×10^{-60}	0.29
		InOCl	2.72×10^{-61}	1.75×10^{-65}	2.94×10^{-66}	0.66
		ScOBr	3.58×10^{-52}	7.58×10^{-56}	1.40×10^{-56}	0.66
Cat. 2		CaI_2	7.67×10^{-28}	4.43×10^{-43}	5.85×10^{-44}	0.62
		$CdBr_2$	6.76×10^{-35}	2.40×10^{-54}	2.91×10^{-55}	0.55
		$CdCl_2$	3.87×10^{-46}	9.92×10^{-70}	1.29×10^{-70}	0.44
		$MgBr_2$	9.28×10^{-37}	3.62×10^{-56}	3.88×10^{-56}	0.61
		$MgCl_2$	1.95×10^{-49}	3.50×10^{-72}	2.96×10^{-73}	0.65
		MgI_2	3.14×10^{-22}	7.96×10^{-38}	1.13×10^{-38}	0.56
		PbI_2	2.94×10^{-21}	1.19×10^{-36}	2.13×10^{-37}	0.45
		$ZnBr_2$	2.02×10^{-31}	6.41×10^{-51}	7.80×10^{-52}	0.54
		$ZnCl_2$	1.50×10^{-43}	1.17×10^{-66}	1.14×10^{-67}	0.57
Cat. 3		PbF_4	(*)	(*)	(*)	0.18
		SnF_4	(*)	(*)	(*)	0.29
Cat. 4		SrI2	3.76×10^{-21}	6.90×10^{-41}	1.44×10^{-41}	0.30