SUPPLEMENTARY INFORMATION:

Transition-Metal Nitride Halide Dielectrics for Transition-Metal Dichalcogenide Transistors

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Table S1. Structural characterization of the materials under study. The TMNH dielectric materials are categorized under α-form and β-form, with orthorhombic and trigonal crystal systems, respectively. The space group of the bulk is also listed for each material.

Materials	Type	Bulk Space Group	Crystal System
ZrNCl	β - form	R-3m	Trigonal
HfNCl	β - form	R-3m	Trigonal
TiNCl	α - form	Pmmn	Orthorhombic
ZrNBr	β - form	R-3m	Trigonal
HfNBr	β - form	R-3m	Trigonal
TiNBr	α - form	Pmmn	Orthorhombic

Table S2. Structural parameters of TMNH materials in this study. Exfoliation energy for each material is reported.

Material	Bulk	Monolayer			Monolayer Supercell Thickness (Å)	Exfoliation Energy (meV/Å^2)
	d_i (Å)	a (Å)	t (Å)	Δ (%)		
ZrNCl	9.26	3.61	9.27	0.07	26.49	16.96
HfNCl	9.24	3.59	9.26	0.21	26.43	17.85
TiNCl	7.77	3.26	7.88	1.36	25.69	15.55
ZrNBr	9.80	3.65	9.82	0.18	26.83	18.81
HfNBr	9.80	3.61	9.82	0.18	26.77	18.95
TiNBr	8.38	3.36	8.40	0.31	24.96	18.00

Table S3. Monolayer phonon energy for TMNHs.

Material	Phonon Energy (meV)					
ZrNCl	79.28	72.93	72.93	70.98	62.57	62.57
	8.94	3.62	1.82	21.51	21.51	19.17
	19.17	14.68	14.68	0.01i	0.05i	0.05i
HfNCl	79.35	77.51	77.51	74.29	67.36	67.36
	33.84	32.25	18.92	17.92	17.92	17.57
	17.57	12.90	12.90	0.01i	0.02i	0.02i
TiNCl	79.63	74.12	73.58	56.76	49.98	49.80
	42.17	35.81	26.71	25.94	24.76	17.44
	15.80	14.28	13.45	0.02i	0.08i	0.09i
ZrNBr	78.83	70.08	69.95	69.95	59.51	59.51
	35.25	25.15	20.34	20.34	15.90	14.30
	14.30	9.90	9.90	0.00i	0.00i	0.02i
HfNBr	79.07	74.11	74.11	73.55	63.79	63.79
	27.42	23.03	15.47	15.47	15.43	12.62
	12.62	9.67	9.67	0.00i	0.01i	0.01i
TiNBr	78.93	74.07	73.91	53.63	49.22	42.76
	33.84	32.51	27.68	25.63	17.03	13.30
	10.89	10.02	7.39	0.01i	0.08i	0.11i

Table S4. Bulk phonon energy for TMNHs.

Material	Phonon Energy (meV)					
ZrNCl	80.02	80.00	75.27	73.00	73.00	72.63
	72.63	72.62	72.62	71.15	71.09	71.09
	62.57	62.51	62.19	62.14	62.13	62.09
	39.51	39.43	39.40	35.15	35.12	32.10
	23.48	22.62	22.57	22.28	22.19	22.15
	22.15	22.06	22.00	21.04	20.97	20.93
	20.86	20.47	20.36	16.31	16.16	16.09
	15.97	15.82	15.75	3.28	3.09	2.69
	1.65	0.46	0.66	1.03i	2.31i	2.96i
HfNCl	80.12	80.12	77.56	77.56	77.56	77.56
	77.56	77.56	75.24	74.46	74.46	74.45
	67.40	67.40	67.39	67.39	67.39	67.39
	34.83	34.42	34.42	33.35	33.35	30.30
	19.75	19.21	19.21	18.60	18.60	18.46
	18.46	18.46	18.46	18.13	18.13	18.13
	18.13	17.93	17.93	13.16	13.16	13.03
	13.03	13.03	13.03	3.14	3.14	1.23
	1.23	1.23	1.23	0.02i	0.02i	0.02i
TiNCl	79.82	76.95	74.20	56.57	49.82	49.28
	43.10	35.81	26.30	24.51	24.21	15.78
	15.27	14.31	11.77	0.02i	0.10i	0.16i
ZrNBr	79.91	79.91	74.86	70.75	70.75	70.75
	70.67	70.67	70.66	70.66	70.66	70.66
	60.22	60.22	60.22	60.22	60.02	60.02
	35.43	35.43	35.33	26.95	26.95	25.50
	20.39	20.39	20.36	20.36	20.36	20.36
	19.53	18.91	18.91	16.90	16.90	16.90
	16.90	16.73	16.73	14.24	14.24	14.11
	14.11	14.11	14.11	6.81	6.81	5.56
	5.56	5.56	5.56	1.33i	1.93i	1.93i

Table S4 (Cont.). Bulk phonon energy for TMNHs.

Material	Phonon Energy (meV)					
HfNBr	79.84	79.84	74.61	74.23	74.23	74.22
	74.22	74.22	74.22	73.77	73.76	73.76
	63.89	63.89	63.89	63.89	63.88	63.88
	27.66	27.58	27.58	23.67	23.67	21.95
	16.34	15.72	15.72	15.56	15.56	15.55
	15.55	15.55	15.55	12.86	12.86	12.86
	12.86	12.78	12.78	9.96	9.96	9.81
	9.81	9.81	9.81	3.04	3.04	1.14
	1.14	1.14	1.14	0.01i	0.01i	0.01i
TiNBr	78.88	73.87	71.16	53.67	49.52	42.84
	33.64	32.05	27.91	25.90	17.99	13.52
	10.86	10.84	8.32	0.00i	0.03i	0.14i

Table S5. In-plane dielectric constant components (*x* and *y*). Among six TMNH dielectrics materials, only TiNCl and TiNBr are anisotropic since the *x* and *y* components are considerably different.

Material	Monolayer (ε_∞)		Monolayer (ε_0)		Bulk (ε_∞)		Bulk (ε_0)	
	x	y	x	y	x	y	x	y
ZrNCl	6.23	6.23	15.85	15.85	6.24	6.24	15.64	15.72
HfNCl	5.65	5.65	13.69	13.69	5.67	5.67	13.61	13.61
TiNCl	15.54	9.89	157.26	35.31	16.13	10.10	159.31	36.00
ZrNBr	6.69	6.69	15.30	15.30	6.72	6.72	14.87	14.88
HfNBr	6.10	6.10	13.18	13.18	6.12	6.12	13.16	13.16
TiNBr	16.70	10.27	128.04	35.07	17.16	10.42	132.22	35.20

Table S6. Bandgap and electron affinity values for TMNH materials in this study. Bandgap values are calculated by two methods: Perdew-Burke-Ernzerof (PBE) and Heyd–Scuseria–Ernzerhof (HSE). Electron affinity values are also calculated by HSE method.

Material	PBE Band Gap (eV)		HSE Band Gap (eV)	Electron Affinity (eV)
	Bulk	Monolayer	Monolayer	Monolayer
ZrNCl	1.77	1.91	2.89	4.53
HfNCl	2.19	2.37	3.36	4.07
TiNCl	0.56	0.57	1.55	5.60
ZrNBr	1.45	1.65	2.59	4.45
HfNBr	1.83	2.03	2.99	4.01
TiNBr	0.56	0.57	1.53	5.43

Table S7. Bandgap and electron affinity values for TMDs. Bandgap values are calculated using Heyd–Scuseria–Ernzerhof (HSE). Electron affinity values are also calculated by HSE method.

Material	HSE Band Gap (eV)	Electron Affinity (eV)
	Monolayer	Monolayer
WSe_2	1.60	3.55
WS_2	1.91	3.91
$MoSe_2$	1.63	3.96
MoS_2	1.97	4.30
$MoTe_2$	1.19	3.80

Table S8. Leakage current values of TMNH dielectrics under study in combination with five TMDs for *p*-MOS applications. We listed hBN for the porous of comparison. TiNCl and TiNBr cannot insulate the current when they are combined with WSe_2 and WS_2 channel materials (shown by stars) due to their band alignment.

TMD	TMNH	Leakage Current Density (A/cm^2)			
		Thermionic	Tunneling (VB)	Tunneling (CB)	Total
WSe_2	ZrNCl	3.04×10^{-26}	2.63×10^{-20}	5.84×10^{3}	5.84×10^{3}
	HfNCl	2.11×10^{-26}	2.05×10^{-20}	3.63×10^{-2}	3.63×10^{-2}
	TiNCl	2.74×10^{-21}	3.06×10^{-12}	*	*
	ZrNBr	1.85×10^{-20}	4.49×10^{-15}	4.10×10^{2}	4.10×10^{2}
	HfNBr	7.73×10^{-20}	1.76×10^{-14}	1.84×10^{-3}	1.84×10^{-3}
	TiNBr	1.08×10^{-18}	9.02×10^{-11}	*	*
	hBN	3.44×10^{-16}	4.62×10^{2}	7.53×10^{-8}	4.62×10^{2}
WS_2	ZrNCl	5.34×10^{-15}	2.64×10^{-9}	7.16×10^{-5}	7.16×10^{-5}
	HfNCl	5.72×10^{-15}	2.12×10^{-9}	1.19×10^{-11}	2.14×10^{-9}
	TiNCl	4.82×10^{-10}	1.66×10^{-3}	3.02×10^{7}	3.2×10^{7}
	ZrNBr	3.26×10^{-9}	1.38×10^{-4}	8.50×10^{-7}	1.39×10^{-4}
	HfNBr	1.36×10^{-8}	4.20×10^{-4}	1.10×10^{-13}	4.20×10^{-4}
	TiNBr	1.90×10^{-7}	5.64×10^{-2}	1.46×10^{6}	1.46×10^{-6}
	hBN	6.06×10^{-5}	1.68×10^{5}	9.53×10^{-12}	1.68×10^{5}
$MoSe_2$	ZrNCl	7.37×10^{-19}	7.13×10^{-13}	7.01×10^{-2}	7.01×10^{-2}
	HfNCl	5.13×10^{-19}	5.67×10^{-13}	3.68×10^{-8}	3.68×10^{-8}
	TiNCl	6.65×10^{-14}	2.56×10^{-6}	*	*
	ZrNBr	4.50×10^{-13}	6.09×10^{-8}	1.56×10^{-3}	1.56×10^{-3}
	HfNBr	1.88×10^{-12}	2.03×10^{-7}	6.28×10^{-10}	2.04×10^{-7}
	TiNBr	2.61×10^{-11}	8.80×10^{-5}	6.53×10^{7}	6.53×10^{7}
	hBN	4.19×10^{-4}	2.51×10^{5}	2.23×10^{-10}	2.51×10^{5}
MoS_2	ZrNCl	1.91×10^{-7}	5.13×10^{-3}	1.88×10^{-11}	5.13×10^{-3}
	HfNCl	1.33×10^{-7}	4.23×10^{-3}	4.03×10^{-19}	4.23×10^{-3}
	TiNCl	1.72×10^{-2}	1.21×10^{2}	1.14×10^{4}	1.15×10^{4}
	ZrNBr	1.17×10^{-1}	7.42×10^{1}	6.10×10^{-14}	7.43×10^{1}
	HfNBr	4.86×10^{-1}	1.83×10^{2}	1.06×10^{-21}	1.83×10^{2}
	TiNBr	4.77	3.30×10^{3}	1.36×10^{2}	3.44×10^{3}
	hBN	2.17×10^{3}	5.16×10^{6}	1.61×10^{-14}	5.16×10^{6}
$MoTe_2$	ZrNCl	7.74×10^{-16}	4.63×10^{-10}	1.84×10^{5}	1.84×10^{5}
	HfNCl	5.39×10^{-16}	3.71×10^{-10}	3.14	3.14
	TiNCl	4.98×10^{-11}	4.23×10^{-4}	*	*
	ZrNBr	4.72×10^{-10}	2.72×10^{-5}	1.92×10^{4}	1.92×10^{4}
	HfNBr	1.97×10^{-9}	8.42×10^{-5}	2.31×10^{-1}	2.31×10^{-1}
	TiNBr	2.74×10^{-8}	1.45×10^{-2}	*	*
	hBN	7.10×10^{-19}	9.87×10^{1}	5.82×10^{-7}	9.87×10^{1}

Table S9. Comparison of bandgaps, electron affinities, and polarizability between values calculated in this study and extracted from Ref. [35]. We also added the values calculated in several other studies for the purpose of comparison.

Material	HSE Band Gap (eV)			Electron Affinity (eV)		Polarizability (Å)	
	Our Study	C2DB	Others	Our Study	C2DB	Our Study	C2DB
ZrNCl	2.89	3.08	2.87 [1], 2.93 [2], 2.70 [3]	4.53	4.35	0.59	0.59
HfNCl	3.36	3.45	3.37 [2]	4.07	3.99	0.59	0.51
TiNCl	1.55	2.09	1.41 [4], 1.41 [5]	5.60	4.89	0.50	0.50
ZrNBr	2.59	2.76	2.60 [1], 2.52 [3]	4.45	4.21	0.65	0.59
HfNBr	2.99	3.05	-	4.01	3.88	0.65	0.57
TiNBr	1.53	2.08	1.39 [4], 1.39 [5]	5.43	4.68	0.55	0.54

Table S10. Lattice mismatch between five TMDs used in this study and six TMNHs.

TMD	TMNH	Lattice Mismatch (%)
WSe_2	ZrNCl	8.78
	HfNCl	7.81
	TiNCl	1.04
	ZrNBr	9.80
	HfNBr	8.80
	TiNBr	2.00
WS_2	ZrNCl	12.39
	HfNCl	11.45
	TiNCl	2.96
	ZrNBr	13.37
	HfNBr	12.40
	TiNBr	5.87
$MoSe_2$	ZrNCl	12.66
	HfNCl	11.73
	TiNCl	3.26
	ZrNBr	13.64
	HfNBr	12.68
	TiNBr	6.17
MoS_2	ZrNCl	8.23
	HfNCl	7.25
	TiNCl	1.65
	ZrNBr	9.25
	HfNBr	8.25
	TiNBr	1.40
$MoTe_2$	ZrNCl	1.29
	HfNCl	0.24
	TiNCl	9.33
	ZrNBr	2.40
	HfNBr	1.32
	TiNBr	6.04

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