Supporting Information

Rational design of periodic porous Titanium Nitride MXene as multifunctional catalystic membrane

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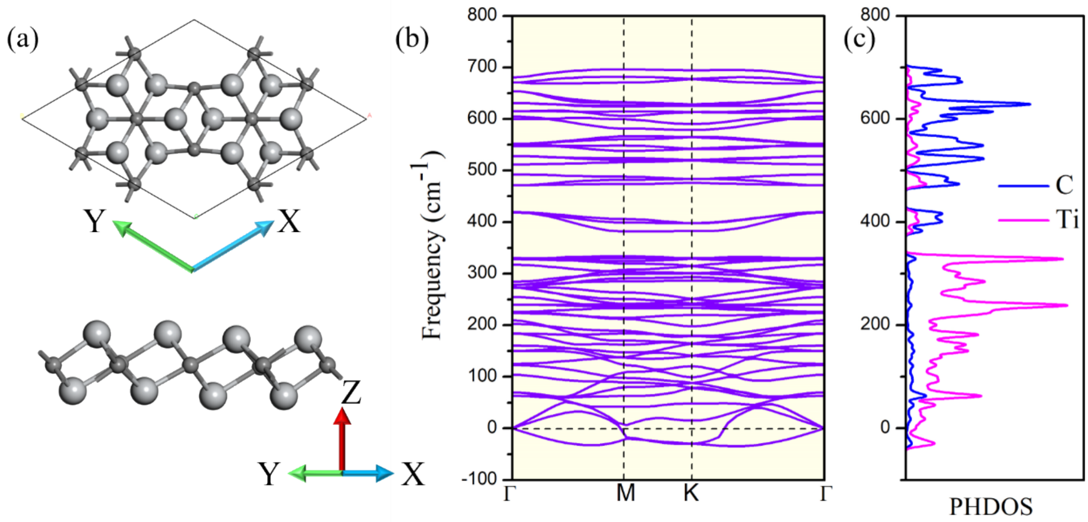

Fig. S1 Top and side view of optimized $Ti_{12}C_8$ (a), calculated phonon dispersion along the high symmetrical directions of the Brillouin zone (b) and the phonon PDOS (c). Little grey and big grey sphere represent carbon and titanium atom.

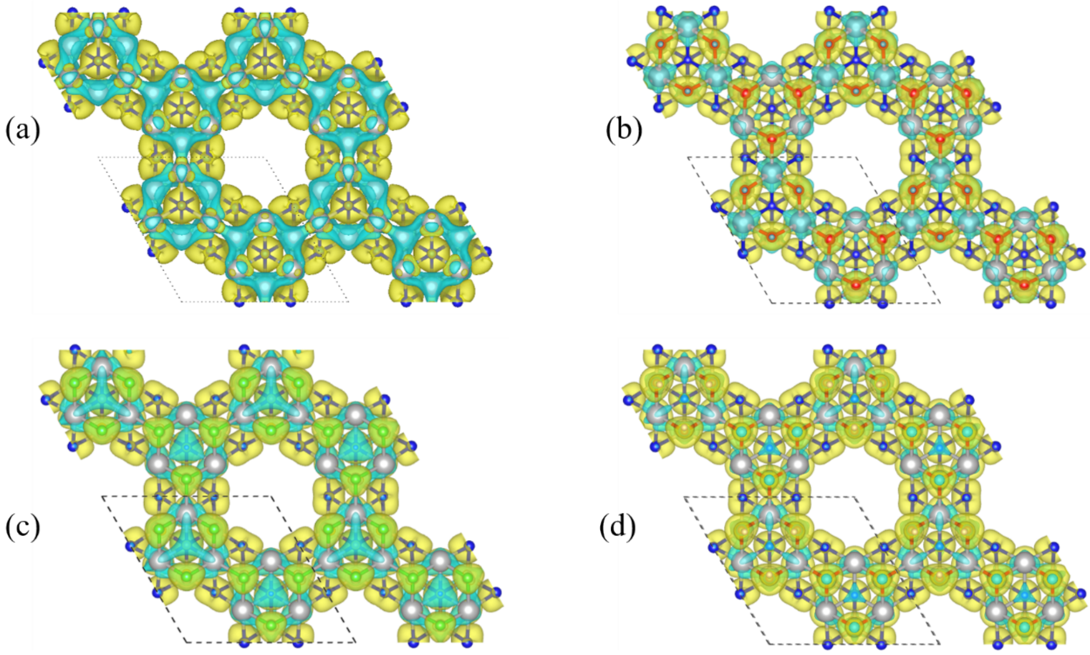

Fig. S2 Charge density difference of (a) $Ti_{12}N_8$, (b) $Ti_{12}N_8O_{12}$, (c) $Ti_{12}N_8F_{12}$ and (d)$Ti_{12}N_8(OH)_{12}$. Yellow zones represent electron accumulation and cyan zones are electron deficiency, isovalue =0.01 a.u.

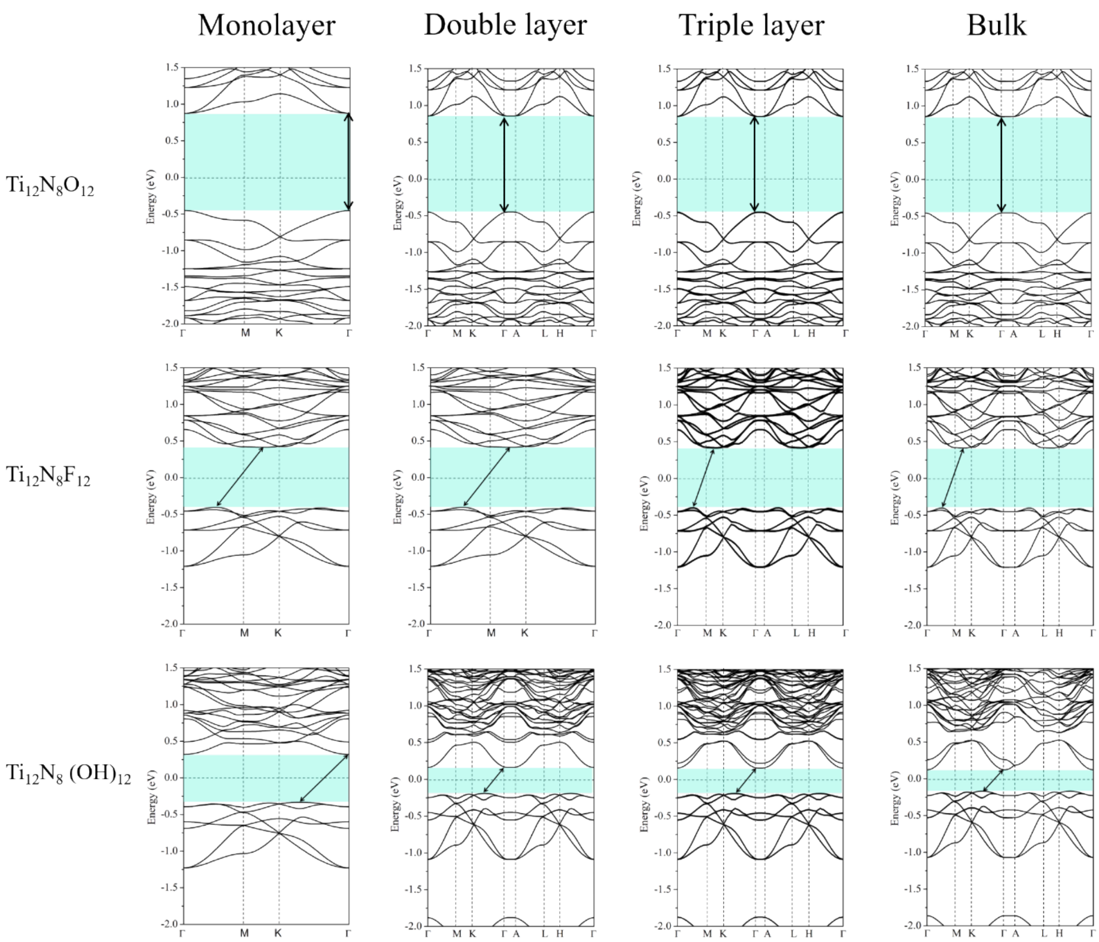

Fig. S3 Calculated band structure of the monolayer, bi-layer, triple layer and bulk of $Ti_{12}N_8O_{12}$, $Ti_{12}N_8F_{12}$ and $Ti_{12}N_8(OH)_{12}$ by GGA/PBE

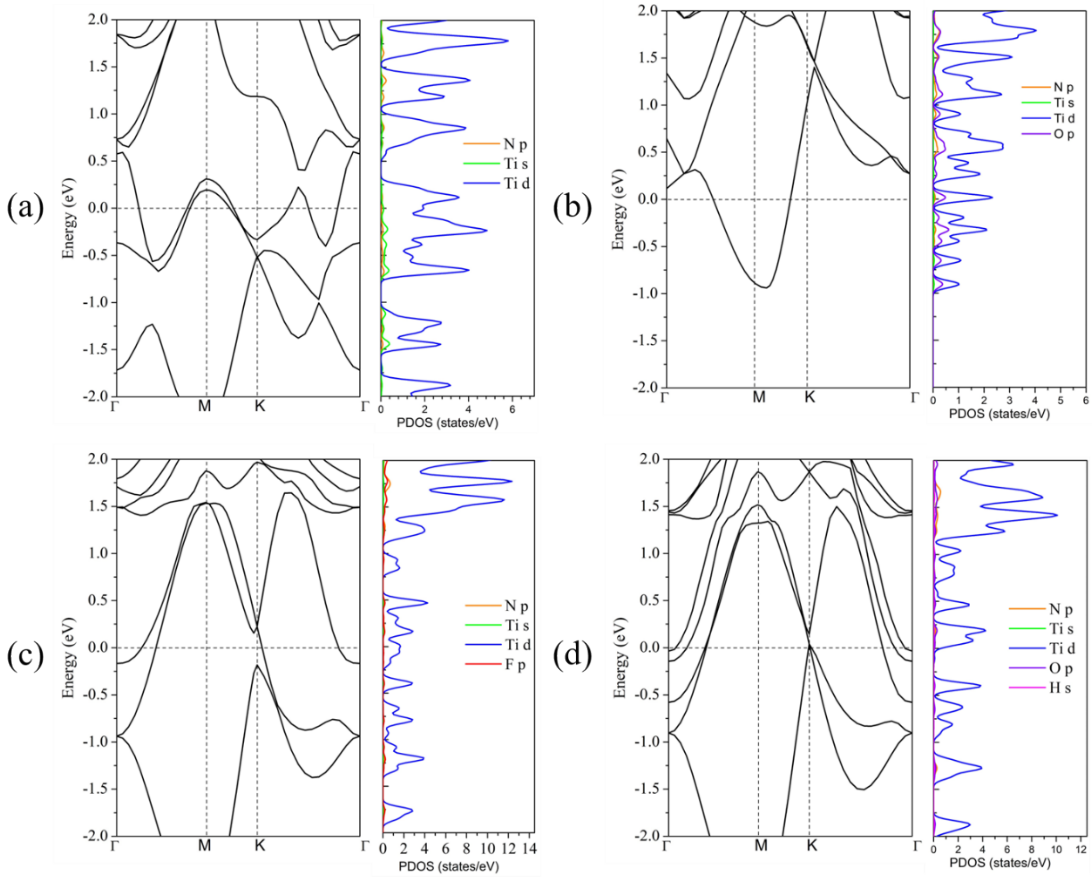

Fig. S4 Band structure (left) and density of states (right) of (a) Ti_2N, (b) Ti_2NO_2, (c) Ti_2NF_2 and (d) $Ti_2N(OH)_2$ under HSE06 theoretical level.

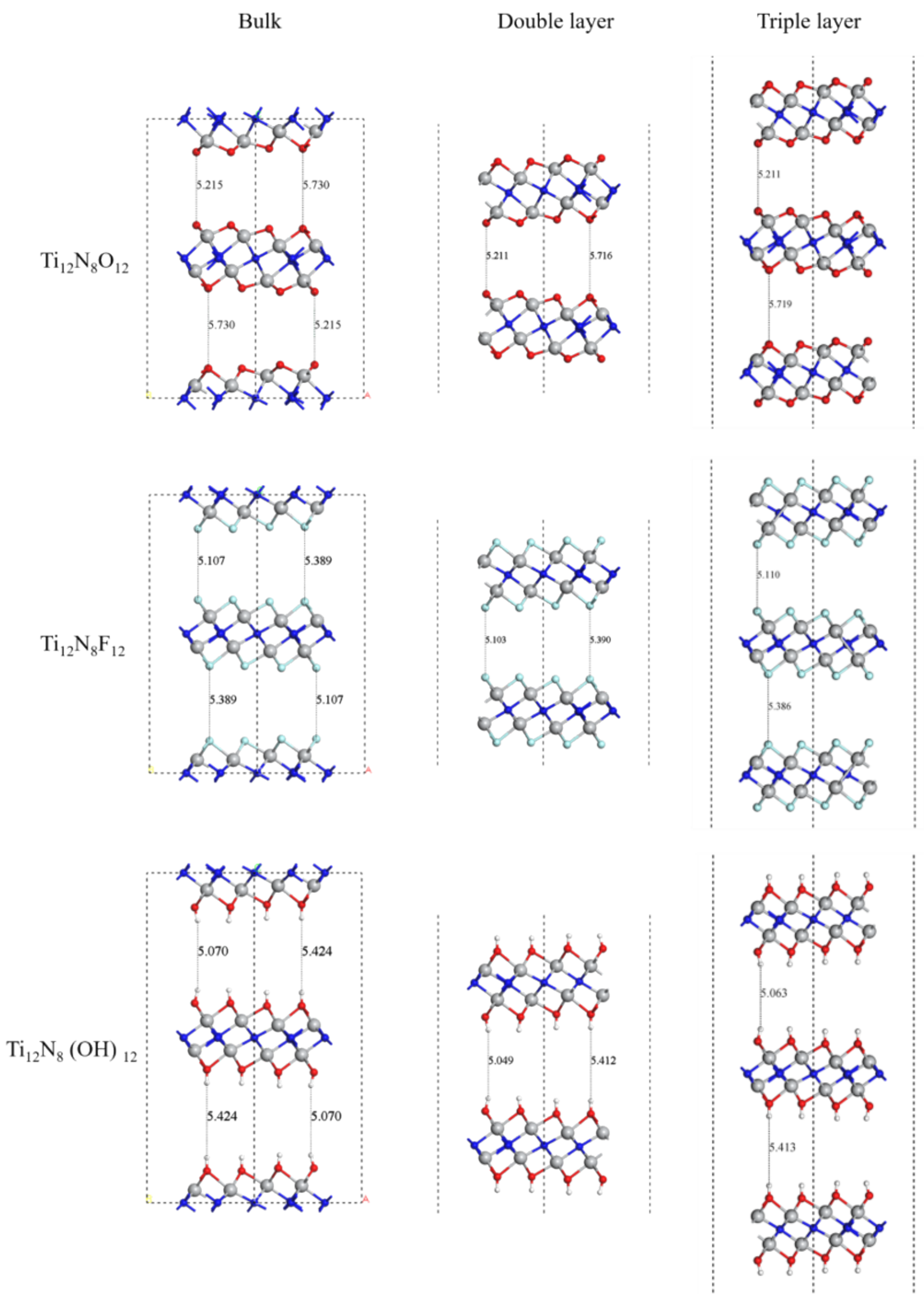

Fig. S5 Snapshoot of bulk, bi-layer and triple layered $Ti_{12}N_8O_{12}$, $Ti_{12}N_8F_{12}$ and $Ti_{12}N_8(OH)_{12}$.

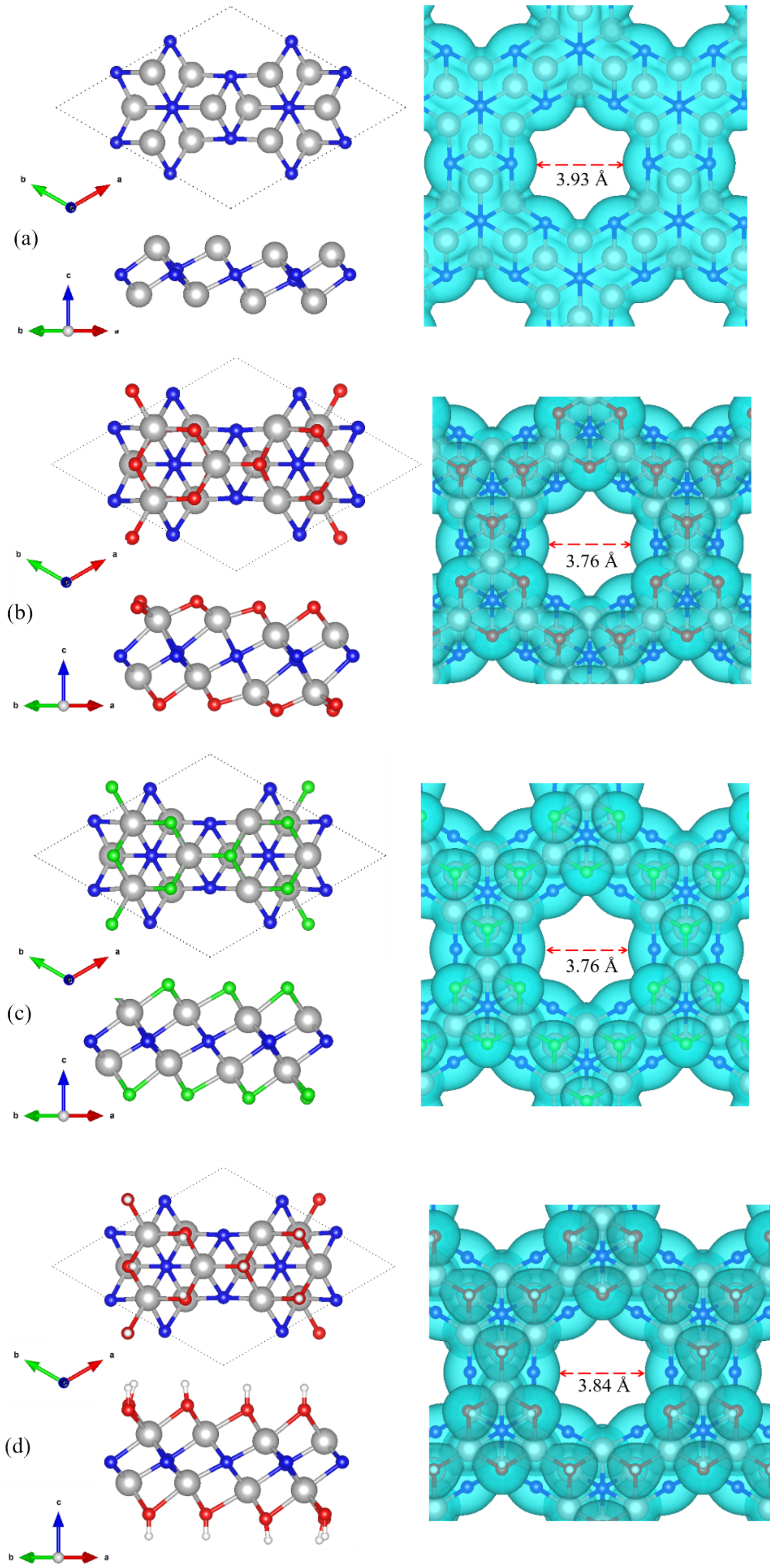

Fig.S6 Structure and electron density of (a) $Ti_{12}N_8$, (b) $Ti_{12}N_8O_{12}$, (c) $Ti_{12}N_8F_{12}$ and (d) $Ti_{12}N_8(OH)_{12}$

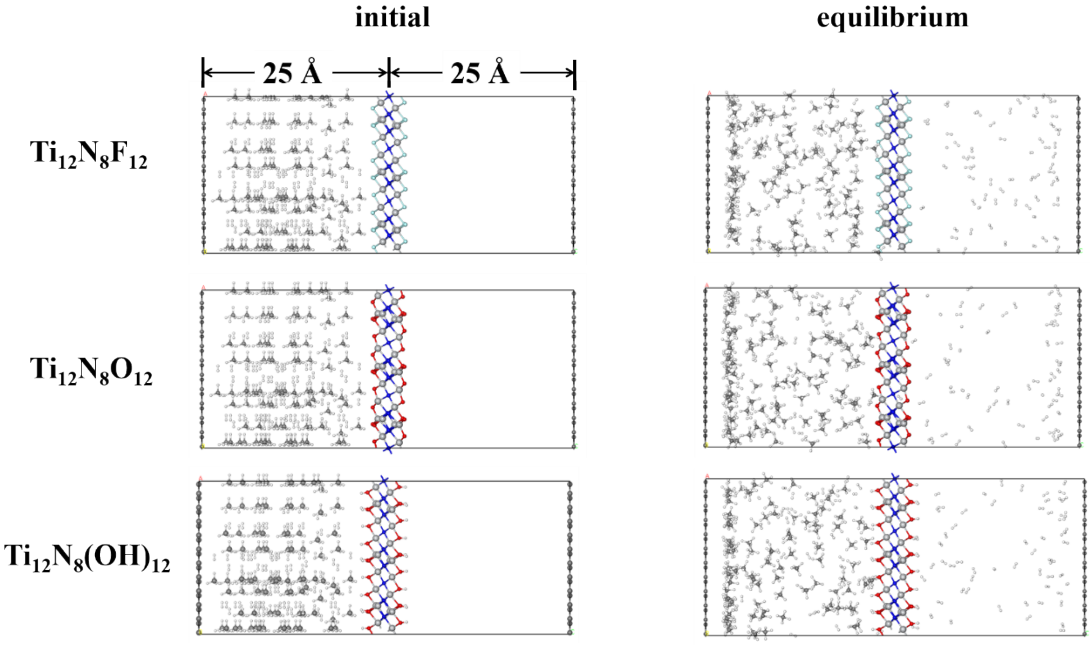

Fig. S7 Snapshots of the equimolar H_2/CH_4 mixed gases penmeating $Ti_{12}N_8T_{12}$ before and after 20 ns MD simulations (C, gray; O red; H, white; N blue; F, cyan)

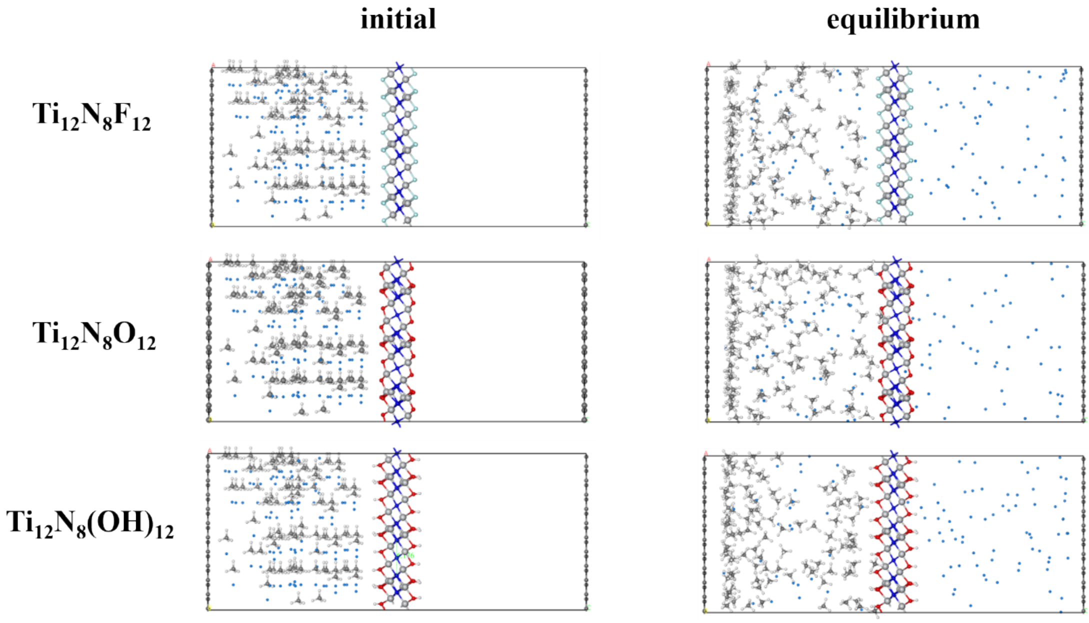

Fig. S8 Snapshots of the equimolar He/CH_4 mixed gases penmeating $Ti_{12}N_8T_{12}$ before and after 20 ns MD simulations (C, gray; O red; H, white; N blue; F, cyan; He, light blue)

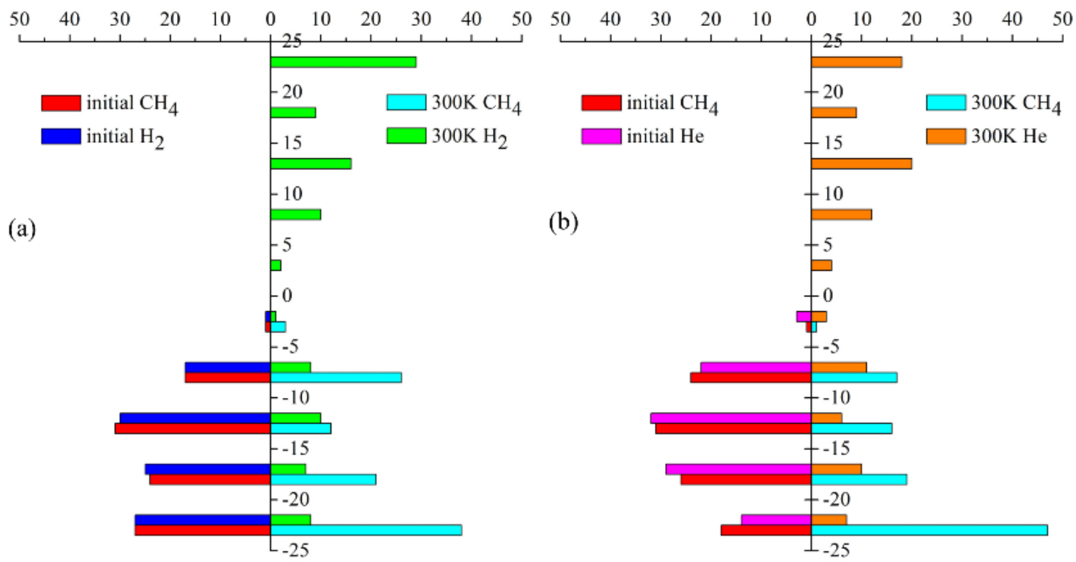

Fig. S9 Distribution of gas molecules after 20 ns MD simulations upon $Ti_{12}N_8F_{12}$

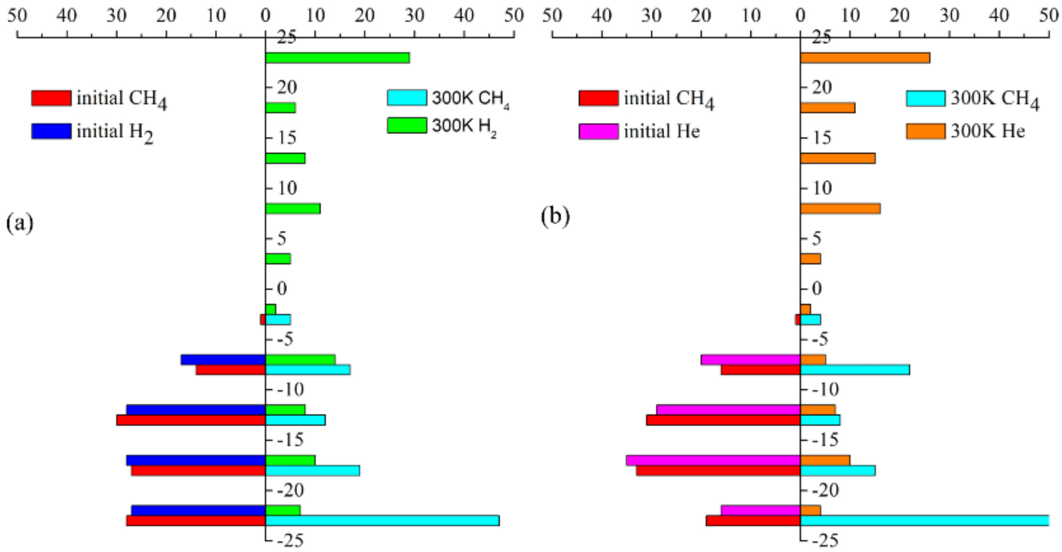

Fig. S10 Distribution of gas molecules after 20 ns MD simulations upon $Ti_{12}N_8(OH)_{12}$

Table S1 Bond lengths of porous MXene $Ti_{12}N_8$ and $Ti_{12}N_8T_{12}$ (T = O, F, OH)

	Bond length (Å)						
	N_1-Ti_1	N_1-Ti_3	N_2-Ti_1	N_2-Ti_3	T_1-Ti_1	T_2-Ti_2	T_2-Ti_1
Ti_2N		2.070				/	
Ti_2NO_2		2.148				1.980	
Ti_2NF_2		2.059				2.145	
$Ti_2N(OH)_2$		2.084				2.166	
$Ti_{12}N_8$	2.050	2.045	2.008	1.974	/	/	/
$Ti_{12}N_8O_{12}$	2.256	2.029	2.282	1.930	1.874	2.070	1.865
$Ti_{12}N_8F_{12}$	2.022	2.005	2.104	1.956	2.050	2.188	2.117
$Ti_{12}N_8(OH)_{12}$	2.028	2.012	2.104	1.968	2.129	2.208	2.129

Table S2 Bond angle of porous MXene $Ti_{12}N_8$ and $Ti_{12}N_8T_{12}$ (T = O, F, OH)

Bond angles (°)	$Ti_{12}N_8$	$Ti_{12}N_8O_{12}$	$Ti_{12}N_8F_{12}$	$Ti_{12}N_8(OH)_{12}$
Ti_1-N_1-Ti_1	100.5	84.2	89.6	91.3
Ti_1-N_1-Ti_3	83.4	90.0	86.6	86.0
N_1-Ti_1-N_2	94.6	80.7	91.0	89.6
N_1-Ti_3-N_2	95.2	95.8	96.0	91.8
Ti_1-N_2-Ti_2	96.8	91.5	97.7	98.1
Ti_1-N_2-Ti_4	91.6	103.7	95.5	95.0
N_2-Ti_1-N_2	88.4	76.3	84.5	85.0
N_2-Ti_2-N_2	105.2	102.6	102.6	103.4
T_1-Ti_1-T_1	/	99.4	90.2	89.6
Ti_1-T_1-Ti_1	/	99.4	87.9	85.9
T_1-Ti_1-T_2	/	111.1	92.8	91.5
Ti_2-T_2-Ti_2	/	92.8	86.8	85.7
T_2-Ti_2-T_2	/	84.1	83.2	83.1
N_1-Ti_1-T_1	/	84.0	91.2	91.4
N_2-Ti_1-T_1	/	89.9	92.6	92.6
N_2-Ti_2-T_2	/	85.7	86.9	86.5
N_3-Ti_2-T_2	/	85.7	87.7	88.5

Table S3 The permeation barrier of $Ti_{12}N_8T_{12}$ (T = F, O, OH)

	H_2(meV)	He(meV)	CH_4(meV)
$Ti_{12}N_8F_{12}$	138	48	940
$Ti_{12}N_8O_{12}$	142	54	1116
$Ti_{12}N_8(OH)_{12}$	143	43	850

POSCAR of $Ti_{12}N_8O_{12}$

```
Ti12N8O12
1.0
        8.9134998322         0.0000000000         0.0000000000
       -4.4567499161         7.7193172913         0.0000000000
        0.0000000000         0.0000000000        24.4171009064
   Ti    O    N
   12   12    8
Direct
     0.553539986         0.446460020         0.434779992
     0.446460039         0.553540030         0.565220008
     0.553539994         0.107079987         0.434779992
     0.446460020         0.892920039         0.565220008
     0.892920060         0.446460020         0.434779992
     0.107080005         0.553540030         0.565220008
     0.778789994         0.557590045         0.536650009
     0.221210004         0.442410004         0.463349991
     0.442409979         0.221199999         0.536650009
     0.557590012         0.778800036         0.463349991
     0.778800052         0.221210006         0.536650009
     0.221200019         0.778790028         0.463349991
     0.562950005         0.437050023         0.586749985
     0.437049978         0.562949996         0.413250015
     0.562950002         0.125900004         0.586749985
     0.437050019         0.874099984         0.413250015
     0.874099949         0.437049992         0.586749985
     0.125900005         0.562949996         0.413250015
     0.773030028         0.546049998         0.403049995
     0.226970020         0.453949990         0.596950005
     0.453950009         0.226979968         0.403049995
     0.546049992         0.773020036         0.596950005
     0.773020064         0.226970022         0.403049995
     0.226979964         0.773029981         0.596950005
     0.341970009         0.341970013         0.500000000
     0.658030042         0.658030036         0.500000000
     0.658030048         0.000000000         0.500000000
     0.341970005         0.000000000         0.500000000
    -0.000000006         0.658030036         0.500000000
     0.000000004         0.341970013         0.500000000
     0.666666670         0.333333340         0.493279977
     0.333333309         0.666666617         0.506720023
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POSCAR of $Ti_{12}N_8F_{12}$

```
Ti12N8F12
1.0
        8.9323997498         0.0000000000         0.0000000000
       -4.4661998749         7.7356851000         0.0000000000
        0.0000000000         0.0000000000        23.8318996429
    N    Ti     F
    8    12    12
Direct
     0.658510021         0.658510012         0.500000000
     0.341489964         0.341489958         0.500000000
     0.341489969        -0.000000000         0.500000000
     0.658510031        -0.000000000         0.500000000
    -0.000000005         0.341489958         0.500000000
    -0.000000009         0.658510012         0.500000000
     0.333333344         0.666666688         0.502960036
     0.666666603         0.333333313         0.497039964
     0.221369960         0.778629972         0.460660008
     0.778630018         0.221369983         0.539340032
     0.221369983         0.442739966         0.460660008
     0.778630018         0.557260036         0.539340032
     0.557259986         0.778629972         0.460660008
     0.442739965         0.221369983         0.539340032
     0.439590008         0.879189998         0.552279996
     0.560410004         0.120809972         0.447720004
     0.120809969         0.560399978         0.552279996
     0.879190005         0.439600023         0.447720004
     0.439600025         0.560410026         0.552279996
     0.560399991         0.439590006         0.447720004
     0.224930026         0.775070006         0.602779969
     0.775069967         0.224929980         0.397220031
     0.224929980         0.449859959         0.602779969
     0.775069990         0.550139980         0.397220031
     0.550140034         0.775070006         0.602779969
     0.449859967         0.224929995         0.397220031
     0.441549983         0.883109949         0.403400012
     0.558449971         0.116890014         0.596599988
     0.116889997         0.558439972         0.403400012
     0.883109948         0.441559998         0.596599988
     0.441559999         0.558449958         0.403400012
     0.558439971         0.441549982         0.596599988
```

POSCAR of $Ti_{12}N_8(OH)_{12}$

```
Ti12N8O12H12
1.0
        9.0165004730         0.0000000000         0.0000000000
       -4.5082502365         7.8085184629         0.0000000000
        0.0000000000         0.0000000000        26.5926990509
    N    Ti    O    H
    8    12    12    12
Direct
     0.657589953         0.657589954         0.500000000
     0.342410030         0.342410039         0.500000000
     0.342410021         0.000000000         0.500000000
     0.657589953         0.000000000         0.500000000
     0.000000009         0.342410039         0.500000000
     0.000000001         0.657589954         0.500000000
     0.333333331         0.666666662         0.503700017
     0.666666650         0.333333301         0.496299983
     0.222299986         0.777699994         0.465349991
     0.777700037         0.222299999         0.534649973
     0.222299999         0.444599998         0.465349991
     0.777699998         0.555399996         0.534649973
     0.555399982         0.777699994         0.465349991
     0.444600015         0.222299999         0.534649973
     0.440519976         0.881039953         0.546740002
     0.559480013         0.118960025         0.453259998
     0.118960023         0.559480017         0.546740002
     0.881039961         0.440519976         0.453259998
     0.440519981         0.559480017         0.546740002
     0.559480016         0.440519976         0.453259998
     0.222409993         0.777589953         0.594690033
     0.777590049         0.222410025         0.405309967
     0.222410025         0.444820050         0.594690033
     0.777589987         0.555179974         0.405309967
     0.555179938         0.777590014         0.594690033
     0.444820066         0.222409994         0.405309967
     0.441669997         0.883329999         0.412939986
     0.558329981         0.116670009         0.587059978
     0.116670013         0.558340032         0.412939986
     0.883329999         0.441659992         0.587059978
     0.441660013         0.558330017         0.412939986
     0.558340025         0.441670007         0.587059978
     0.236540009         0.763459949         0.630249975
     0.763459973         0.236540014         0.369750025
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0.236540014	0.473080027	0.630249975
0.763459983	0.526919966	0.369750025
0.526919967	0.763459949	0.630249975
0.473080033	0.236539998	0.369750025
0.441839995	0.883689985	0.376490014
0.558160024	0.116310001	0.623510022
0.116309988	0.558149993	0.376490014
0.883689956	0.441850000	0.623510022
0.441850011	0.558160008	0.376490014
0.558150012	0.441839985	0.623510022