In-Plane Mechanical Property of Terephthalate-based Two-Dimensional Metal-Organic Frameworks

Supporting Information

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Section I – Materials Synthesis and Characterization

All starting materials for synthesis were purchased commercially and were used without further purification. Zinc Nitrate Hexahydrate 98% and Manganese(II) Nitrate tetrahydrate were purchased from Sigma Aldrich. Terephthalic acid >99% was purchased from Tokyo Chemical Industry. Nitric Acid ACS reagent, Absolute Ethanol, and N,N Dimethyl Formamide were purchased from Thermo Fisher.

Powder X-ray diffraction patterns were measured using a Bruker D8 Advance Diffractometer with Lynxeye detector using CuKα radiation. X-ray source operated at 40kV/40mA and Ni filter was used to suppress Beta radiation. 2.5 deg primary and secondary Soller slits were used to suppress axial divergence. Diffraction patterns were recorded from 2 to 60 2θ in variable slits mode and with a knife edge installed. A typical scan rate was 1 sec/step with a step size of 0.02 deg.

Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a PHOTON III CMOS detector and a $Cu\,K\alpha$ INCOATEC ImuS micro-focus source (λ= 1.54178 Å). Data collection and processing were carried out using standard procedures. The crystal structures were solved and refined using full-matrix least-squares methods on F^2. The crystallographic data and refinement details of $(DMA)_2[Zn_3(BDC)_4\cdot 1.5H_2O]$ (BDC = 1,4-benzenedicarboxylate, DMA = dimethylammonium) and $Zn_3(BDC)_3(H_2O)_2\cdot 4(DMF)$ (DMF = N,N-Dimethylformamide) are summarized in in **Table S1** and **Table S5** and geometrical parameters in **Tables S2-S4** and **Tables S6-S9**.

Table S1. Crystal data and structure refinement of $(DMA)_2[Zn_3(BDC)_4 \cdot 1.5H_2O]$ at 298 K.

Item	Value
Identification code	$(DMA)_2[Zn_3(BDC)_4 \cdot 1.5H_2O]$
Empirical formula	$C_{36}H_{32}N_2O_{17.5}Zn_3$
Formula weight	968.74
Temperature / K	298
Crystal system	Monoclinic
Space group	*C*2/*c*
a / Å	33.243(2)
b / Å	9.7417(7)
c / Å	18.2880(10)
α / °	90
β / °	93.412(3)
γ / °	90
Volume / $Å^3$	5911.9(6)
Z	4
ρ_{calc} / $g \cdot cm^{-3}$	1.088
μ / mm^{-1}	1.880
F(000)	1968
Crystal size / mm^3	0.11 × 0.095 × 0.07
Radiation	Cu Kα (λ = 1.54178 Å)
2θ range for data collection / °	5.326–158.57
Index ranges	$-42 \le h \le 42$, $-12 \le k \le 12$, $-22 \le l \le 23$
Reflections collected	86762
Independent reflections	6369 (Rint = 0.0510, Rσ = 0.0251)
Data / restraints / parameters	6369 / 96 / 324
Goodness-of-fit on F^2	1.115
Final R indices [I > 2σ(I)]	R1 = 0.0577, wR2 = 0.1845
Final R indices [all data]	R1 = 0.0607, wR2 = 0.1884
Largest diff. peak / hole / $e \cdot Å^{-3}$	0.80 / −0.50

Table S2. Bond lengths [Å] for (DMA)2[$Zn_3(BDC)_4 \cdot 1.5H_2O$] at 298 K.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1_1	O3_1	1.965(2)	C6_1	C11_1	1.384(5)
Zn1_1	O14_1[1]	1.976(2)	C7_1	C8_1	1.375(5)
Zn1_1	O15_1	1.947(3)	C8_1	C9_1	1.386(5)
Zn1_1	O21_1	1.985(2)	C9_1	C10_1	1.384(4)
Zn2_1	O5_1[2]	2.047(2)	C9_1	C13_1	1.502(4)
Zn2_1	O5_1[3]	2.047(2)	C10_1	C11_1	1.378(5)
Zn2_1	O12_1[4]	2.037(2)	C16_1	C18_1	1.511(5)
Zn2_1	O12_1	2.037(2)	C18_1	C19_1	1.367(8)
Zn2_1	O21_1[3]	2.244(2)	C18_1	C20_1[5]	1.358(8)
Zn2_1	O21_1[2]	2.244(2)	C19_1	C20_1	1.377(7)
O3_1	C4_1	1.263(4)	C22_1	C24_1	1.495(4)
O5_1	C4_1	1.243(4)	C24_1	C25_1	1.386(5)
O12_1	C13_1	1.237(4)	C24_1	C26_1[6]	1.403(5)
O14_1	C13_1	1.257(4)	C25_1	C26_1	1.385(5)
O15_1	C16_1	1.241(6)	N1_2	C2_2	1.469(12)
O17_1	C16_1	1.229(6)	N1_2	C3_2	1.467(13)
O21_1	C22_1	1.305(4)	N1_3	C2_3	1.49(2)
O23_1	C22_1	1.215(5)	N1_3	C3_3	1.45(2)
C4_1	C6_1	1.501(4)	N1_4	C2_4	1.47(2)
C6_1	C7_1	1.383(4)	N1_4	C3_4	1.49(2)

[1]+X,2-Y,1/2+Z; [2]+X,2-Y,-1/2+Z; [3]3/2-X,1/2+Y,3/2-Z; [4]3/2-X,5/2-Y,1-Z; [5]1-X,1-Y,2-Z; [6]3/2-X,1/2-Y,2-Z

Table S3. Bond Angles [°] for $(DMA)_2[Zn_3(BDC)_4 \cdot 1.5H_2O]$ at 298 K.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3_1	Zn1_1	O14_1[1]	108.94(13)	C7_1	C6_1	C4_1	120.7(3)
O3_1	Zn1_1	O21_1	110.33(10)	C7_1	C6_1	C11_1	118.9(3)
O14_1[1]	Zn1_1	O21_1	99.78(11)	C11_1	C6_1	C4_1	120.4(3)
O15_1	Zn1_1	O3_1	97.75(13)	C8_1	C7_1	C6_1	121.0(3)
O15_1	Zn1_1	O14_1[1]	106.08(13)	C7_1	C8_1	C9_1	119.9(3)
O15_1	Zn1_1	O21_1	132.78(13)	C8_1	C9_1	C13_1	119.7(3)
O5_1[2]	Zn2_1	O5_1[3]	180.0	C10_1	C9_1	C8_1	119.3(3)
O5_1[2]	Zn2_1	O21_1[3]	89.33(9)	C10_1	C9_1	C13_1	120.9(3)
O5_1[3]	Zn2_1	O21_1[2]	89.33(9)	C11_1	C10_1	C9_1	120.4(3)
O5_1[3]	Zn2_1	O21_1[3]	90.67(9)	C10_1	C11_1	C6_1	120.4(3)
O5_1[2]	Zn2_1	O21_1[2]	90.67(9)	O12_1	C13_1	O14_1	125.5(3)
O12_1[4]	Zn2_1	O5_1[3]	85.72(10)	O12_1	C13_1	C9_1	118.0(3)
O12_1[4]	Zn2_1	O5_1[2]	94.28(10)	O14_1	C13_1	C9_1	116.5(3)
O12_1	Zn2_1	O5_1[2]	85.72(10)	O15_1	C16_1	C18_1	116.8(4)
O12_1	Zn2_1	O5_1[3]	94.28(10)	O17_1	C16_1	O15_1	122.6(4)
O12_1	Zn2_1	O12_1[4]	180.0	O17_1	C16_1	C18_1	120.7(5)
O12_1[4]	Zn2_1	O21_1[3]	89.34(8)	C19_1	C18_1	C16_1	120.5(5)
O12_1	Zn2_1	O21_1[3]	90.66(8)	C20_1[6]	C18_1	C16_1	121.1(5)
O12_1[4]	Zn2_1	O21_1[2]	90.66(8)	C20_1[6]	C18_1	C19_1	118.4(4)
O12_1	Zn2_1	O21_1[2]	89.34(8)	C18_1	C19_1	C20_1	120.6(6)
O21_1[3]	Zn2_1	O21_1[2]	180.00(12)	C18_1[6]	C20_1	C19_1	121.0(5)
C4_1	O3_1	Zn1_1	123.9(2)	O21_1	C22_1	C24_1	116.4(3)
C4_1	O5_1	Zn2_1[5]	135.7(2)	O23_1	C22_1	O21_1	122.0(3)
C13_1	O12_1	Zn2_1	136.7(2)	O23_1	C22_1	C24_1	121.6(3)
C13_1	O14_1	Zn1_1[3]	118.3(2)	C25_1	C24_1	C22_1	121.5(3)
C16_1	O15_1	Zn1_1	110.6(3)	C25_1	C24_1	C26_1[7]	119.5(3)
Zn1_1	O21_1	Zn2_1[5]	100.94(9)	C26_1[7]	C24_1	C22_1	119.0(3)
C22_1	O21_1	Zn1_1	107.5(2)	C26_1	C25_1	C24_1	120.8(3)
C22_1	O21_1	Zn2_1[5]	123.3(2)	C25_1	C26_1	C24_1[7]	119.8(3)
O3_1	C4_1	C6_1	116.5(3)	C3_2	N1_2	C2_2	108.2(11)
O5_1	C4_1	O3_1	126.9(3)	C3_3	N1_3	C2_3	115(3)
O5_1	C4_1	C6_1	116.7(3)	C2_4	N1_4	C3_4	114(3)

[1]+X,2-Y,1/2+Z; [2]3/2-X,1/2+Y,3/2-Z; [3]+X,2-Y,-1/2+Z; [4]3/2-X,5/2-Y,1-Z; [5]3/2-X,-1/2+Y,3/2-Z; [6]1-X,1-Y,2-Z; [7]3/2-X,1/2-Y,2-Z

Table S4. Torsion Angles [°] for $(DMA)_2[Zn_3(BDC)_4 \cdot 1.5H_2O]$ at 298 K.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Zn1_1	O3_1	C4_1	O5_1	-10.5(5)	O21_1	C22_1	C24_1	C26_1[4]	-175.3(3)
Zn1_1	O3_1	C4_1	C6_1	168.6(2)	O23_1	C22_1	C24_1	C25_1	-170.9(4)
Zn1_1[1]	O14_1	C13_1	O12_1	-5.8(5)	O23_1	C22_1	C24_1	C26_1[4]	7.4(5)
Zn1_1[1]	O14_1	C13_1	C9_1	174.4(2)	C4_1	C6_1	C7_1	C8_1	179.4(4)
Zn1_1	O15_1	C16_1	O17_1	-6.3(7)	C4_1	C6_1	C11_1	C10_1	-179.0(4)
Zn1_1	O15_1	C16_1	C18_1	174.9(4)	C6_1	C7_1	C8_1	C9_1	-0.2(7)
Zn1_1	O21_1	C22_1	O23_1	15.4(4)	C7_1	C6_1	C11_1	C10_1	0.0(7)
Zn1_1	O21_1	C22_1	C24_1	-161.9(2)	C7_1	C8_1	C9_1	C10_1	-0.4(6)
Zn2_1[2]	O5_1	C4_1	O3_1	-15.0(6)	C7_1	C8_1	C9_1	C13_1	179.1(4)
Zn2_1[2]	O5_1	C4_1	C6_1	165.9(2)	C8_1	C9_1	C10_1	C11_1	0.8(7)
Zn2_1	O12_1	C13_1	O14_1	45.7(5)	C8_1	C9_1	C13_1	O12_1	10.3(5)
Zn2_1	O12_1	C13_1	C9_1	-134.4(3)	C8_1	C9_1	C13_1	O14_1	-169.8(4)
Zn2_1[2]	O21_1	C22_1	O23_1	-101.0(4)	C9_1	C10_1	C11_1	C6_1	-0.7(8)
Zn2_1[2]	O21_1	C22_1	C24_1	81.7(3)	C10_1	C9_1	C13_1	O12_1	-170.1(4)
O3_1	C4_1	C6_1	C7_1	-171.3(4)	C10_1	C9_1	C13_1	O14_1	9.8(5)
O3_1	C4_1	C6_1	C11_1	7.8(5)	C11_1	C6_1	C7_1	C8_1	0.4(6)
O5_1	C4_1	C6_1	C7_1	7.9(5)	C13_1	C9_1	C10_1	C11_1	-178.7(4)
O5_1	C4_1	C6_1	C11_1	-173.0(4)	C16_1	C18_1	C19_1	C20_1	178.2(7)
O15_1	C16_1	C18_1	C19_1	178.5(6)	C18_1	C19_1	C20_1	C18_1[3]	0.4(14)
O15_1	C16_1	C18_1	C20_1[3]	-2.9(9)	C20_1[3]	C18_1	C19_1	C20_1	-0.4(14)
O17_1	C16_1	C18_1	C19_1	-0.4(10)	C22_1	C24_1	C25_1	C26_1	178.2(3)
O17_1	C16_1	C18_1	C20_1[3]	178.2(7)	C24_1	C25_1	C26_1	C24_1[4]	0.1(6)
O21_1	C22_1	C24_1	C25_1	6.5(5)	C26_1[4]	C24_1	C25_1	C26_1	-0.1(6)

[1]+X,2-Y,-1/2+Z; [2]3/2-X,-1/2+Y,3/2-Z; [3]1-X,1-Y,2-Z; [4]3/2-X,1/2-Y,2-Z

Table S5. Crystal data and structure refinement of $Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$ at 298 K.

Item	Value
Identification code	$Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$
Empirical formula	$C_{36}H_{44}N_4O_{18}Zn_3$
Formula weight	1016.86
Temperature / K	298
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	13.0506(6)
b / Å	9.6677(4)
c / Å	18.4447(8)
α / °	90
β / °	106.761(2)
γ / °	90
Volume / $Å^3$	2228.29(17)
Z	2
ρ_{calc} / $g \cdot cm^{-3}$	1.516
μ / mm^{-1}	2.540
F(000)	1044
Crystal size / mm^3	0.20 × 0.16 × 0.02
Radiation	Cu Kα (λ = 1.54178 Å)
θ range for data collection / °	3.537–70.186
Index ranges	$-15 \le h \le 15$, $0 \le k \le 11$, $0 \le l \le 22$
Reflections collected	4233
Independent reflections	4233 (Rint = 0.0664)
Completeness to θ = 67.679°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4233 / 3 / 288
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0398, wR2 = 0.1065
Final R indices [all data]	R1 = 0.0433, wR2 = 0.1101
Largest diff. peak/ hole/$e \cdot Å^{-3}$	0.574 / −0.589

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0655P)^2+1.6206P]$ where $P=(Fo^2+2Fc^2)/3$

Table S6. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$ at 298 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}*
Zn(1)	10000	10000	10000	1	32(1)
Zn(2)	7423(1)	4561(1)	4519(1)	1	33(1)
O(1A)	9157(2)	8639(2)	9210(2)	1	43(1)
O(2A)	7472(2)	9281(3)	8653(2)	1	47(1)
C(3A)	8327(2)	8666(3)	8662(2)	1	37(1)
O(4A)	7522(2)	5607(3)	5434(2)	1	47(1)
O(5A)	9310(2)	5620(3)	5828(2)	1	47(1)
C(6A)	8415(2)	5888(3)	5904(2)	1	39(1)
C(7A)	8340(2)	7911(3)	7955(2)	1	40(1)
C(8A)	7420(3)	7827(4)	7352(2)	1	50(1)
H(8A)	6784.7	8210.65	7392.42	1	59
C(9A)	7443(3)	7170(4)	6687(2)	1	49(1)
H(9A)	6823.68	7115.38	6283.02	1	59
C(10A)	8381(2)	6598(3)	6624(2)	1	41(1)
C(11A)	9303(3)	6665(4)	7233(2)	1	54(1)
H(11A)	9935.51	6271.43	7195.53	1	65
C(12A)	9277(3)	7317(4)	7893(2)	1	51(1)
H(12A)	9894.75	7358.42	8299.54	1	61
O(1B)	7793(2)	2212(3)	5173(2)	1	66(1)
O(2B)	8741(2)	3430(2)	4591(2)	1	40(1)
C(3B)	8569(2)	2309(3)	4927(2)	1	42(1)
C(4B)	9321(2)	1125(3)	4966(2)	1	39(1)
C(5B)	10042(3)	1122(3)	4547(2)	1	46(1)
H(5B)	10076.13	1879.29	4243.72	1	55
C(6B)	10715(3)	8(3)	4573(2)	1	46(1)
H(6B)	11192.54	12.66	4283.33	1	56
O(1C)	5970(2)	3885(3)	4094(2)	1	62(1)
H(1CA)	5690(40)	3360(50)	4360(20)	1	92
H(1CB)	5450(30)	4400(50)	3790(20)	1	92
O(1D)	4947(3)	2359(6)	4817(3)	1	127(2)
C(2D)	5341(5)	1655(6)	5357(4)	1	95(2)
H(2D)	6066.56	1453.28	5471.14	1	115
N(3D)	4786(4)	1134(5)	5812(3)	1	99(2)

C(4D)	5352(8)	300(9)	6436(5)	1	146(3)
H(4DA)	5191.1	605.6	6886.3	1	218
H(4DB)	6107.06	381.13	6504.47	1	218
H(4DC)	5138.83	-648.28	6337.86	1	218
C(5D)	3712(6)	1402(10)	5674(6)	1	161(4)
H(5DA)	3594.78	1881.33	6098.52	1	242
H(5DB)	3322.19	545.86	5597.58	1	242
H(5DC)	3468.58	1964.9	5228.28	1	242
O(1E)	4533(3)	5376(5)	3104(2)	1	102(2)
C(2E)	3765(4)	5872(5)	3263(3)	1	73(2)
H(2E)	3739.43	5775.04	3759.41	1	88
N(3E)	2976(3)	6527(5)	2789(2)	1	85(2)
C(4E)	2073(5)	7043(7)	2992(4)	1	111(2)
H(4EA)	1439.82	6566.14	2706.17	1	167
H(4EB)	1994.7	8015.36	2883.16	1	167
H(4EC)	2175.18	6896.18	3522.74	1	167
C(5E)	2973(8)	6710(13)	2022(4)	1	200(6)
H(5EA)	3653.65	7064.61	2008.19	1	301
H(5EB)	2419.33	7351.51	1777.92	1	301
H(5EC)	2842.32	5836.92	1764.05	1	301

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S7. Anisotropic displacement parameters ($Å^2x10^3$) for $Zn_3(BDC)_3(H_2O)_2·4(DMF)$ at 298 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	39(1)	30(1)	27(1)	-6(1)	11(1)	-2(1)
Zn(2)	40(1)	30(1)	30(1)	2(1)	11(1)	1(1)
O(1A)	52(2)	36(2)	37(2)	-3(1)	6(1)	-10(1)
O(2A)	48(2)	54(2)	40(2)	-1(1)	14(1)	-19(1)
C(3A)	46(2)	32(2)	32(2)	-8(2)	13(2)	-6(2)
O(4A)	50(2)	53(2)	37(2)	4(1)	13(1)	-14(1)
O(5A)	54(2)	55(2)	37(2)	3(1)	20(1)	-9(1)
C(6A)	51(2)	36(2)	34(2)	4(2)	16(2)	1(2)
C(7A)	46(2)	40(2)	33(2)	-2(2)	13(2)	-7(2)
C(8A)	46(2)	62(2)	41(2)	5(2)	12(2)	-16(2)
C(9A)	48(2)	61(2)	36(2)	6(2)	8(2)	-14(2)
C(10A)	49(2)	42(2)	34(2)	-1(2)	14(2)	-7(2)
C(11A)	46(2)	70(2)	47(2)	7(2)	15(2)	-14(2)
C(12A)	46(2)	65(2)	38(2)	3(2)	7(2)	-16(2)
O(1B)	63(2)	45(2)	103(2)	13(2)	44(2)	12(2)
O(2B)	49(2)	26(1)	43(2)	5(1)	8(1)	0(1)
C(3B)	47(2)	31(2)	47(2)	2(2)	11(2)	-2(2)
C(4B)	45(2)	25(2)	47(2)	2(1)	11(2)	-1(2)
C(5B)	59(2)	28(2)	56(2)	4(2)	23(2)	5(2)
C(6B)	59(2)	33(2)	55(2)	5(2)	29(2)	2(2)
O(1C)	46(2)	63(2)	69(2)	-10(2)	6(2)	15(2)
O(1D)	89(3)	143(4)	146(4)	-18(3)	26(3)	71(3)
C(2D)	88(3)	94(4)	105(4)	-6(3)	31(3)	14(4)
N(3D)	121(4)	81(3)	110(4)	19(3)	55(3)	30(3)
C(4D)	182(9)	128(6)	118(6)	17(6)	28(6)	46(5)
C(5D)	145(6)	153(7)	222(10)	53(6)	109(7)	73(8)
O(1E)	69(2)	129(3)	102(3)	27(2)	18(2)	39(3)
C(2E)	70(3)	77(3)	68(3)	-1(2)	12(2)	17(2)
N(3E)	76(2)	109(3)	70(2)	29(2)	23(2)	28(2)
C(4E)	103(4)	110(5)	131(5)	35(4)	49(4)	24(4)
C(5E)	184(8)	343(16)	87(5)	151(10)	61(5)	99(7)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S8. Bond lengths [Å] for $Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$ at 298 K with estimated standard deviations in parentheses.

Label	Distances
Zn(1)-O(1A)#1	2.035(2)
Zn(1)-O(1A)	2.035(2)
Zn(1)-O(5A)#2	2.072(2)
Zn(1)-O(5A)#3	2.072(2)
Zn(1)-O(2B)#2	2.204(2)
Zn(1)-O(2B)#3	2.204(2)
Zn(2)-O(2A)#4	1.967(2)
Zn(2)-O(4A)	1.940(2)
Zn(2)-O(2B)	2.009(2)
Zn(2)-O(1C)	1.944(2)
O(1A)-C(3A)	1.250(4)
O(2A)-C(3A)	1.261(4)
C(3A)-C(7A)	1.499(4)
O(4A)-C(6A)	1.265(4)
O(5A)-C(6A)	1.243(4)
C(6A)-C(10A)	1.507(4)
C(7A)-C(8A)	1.383(4)
C(7A)-C(12A)	1.386(4)
C(8A)-H(8A)	0.9300
C(8A)-C(9A)	1.390(4)
C(9A)-H(9A)	0.9300
C(9A)-C(10A)	1.378(4)
C(10A)-C(11A)	1.391(4)
C(11A)-H(11A)	0.9300
C(11A)-C(12A)	1.379(5)
C(12A)-H(12A)	0.9300
O(1B)-C(3B)	1.226(4)
O(2B)-C(3B)	1.299(4)
C(3B)-C(4B)	1.497(4)
C(4B)-C(5B)	1.379(5)
C(4B)-C(6B)#5	1.395(4)
C(5B)-H(5B)	0.9300
C(5B)-C(6B)	1.382(4)
C(6B)-H(6B)	0.9300

O(1C)-H(1CA)	0.861(19)
O(1C)-H(1CB)	0.899(19)
O(1D)-C(2D)	1.193(7)
C(2D)-H(2D)	0.9300
C(2D)-N(3D)	1.354(7)
N(3D)-C(4D)	1.425(8)
N(3D)-C(5D)	1.375(8)
C(4D)-H(4DA)	0.9600
C(4D)-H(4DB)	0.9600
C(4D)-H(4DC)	0.9600
C(5D)-H(5DA)	0.9600

Symmetry transformations used to generate equivalent atoms:
(1) -x+2,-y+2,-z+2 (2) x,-y+3/2,z+1/2 (3) -x+2,y+1/2,-z+3/2 (4) x,-y+3/2,z-1/2 (5) -x+2,-y,-z+1 (6) -x+2,y-1/2,-z+3/2

Table S9. Bond angles [°] for $Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$ at 298 K with estimated standard deviations in parentheses.

Label	Angles
O(1A)#1-Zn(1)-O(1A)	180.0
O(1A)-Zn(1)-O(5A)#2	94.63(10)
O(1A)-Zn(1)-O(5A)#3	85.37(10)
O(1A)#1-Zn(1)-O(5A)#2	85.37(10)
O(1A)#1-Zn(1)-O(5A)#3	94.63(10)
O(1A)#1-Zn(1)-O(2B)#2	89.75(8)
O(1A)#1-Zn(1)-O(2B)#3	90.25(8)
O(1A)-Zn(1)-O(2B)#2	90.25(8)
O(1A)-Zn(1)-O(2B)#3	89.75(8)
O(5A)#2-Zn(1)-O(5A)#3	180.0
O(5A)#2-Zn(1)-O(2B)#2	90.67(9)
O(5A)#3-Zn(1)-O(2B)#2	89.33(9)
O(5A)#2-Zn(1)-O(2B)#3	89.33(9)
O(5A)#3-Zn(1)-O(2B)#3	90.67(9)
O(2B)#2-Zn(1)-O(2B)#3	180.0
O(2A)#4-Zn(2)-O(2B)	97.79(9)
O(4A)-Zn(2)-O(2A)#4	113.59(10)
O(4A)-Zn(2)-O(2B)	112.65(9)
O(4A)-Zn(2)-O(1C)	109.79(12)
O(1C)-Zn(2)-O(2A)#4	96.91(11)
O(1C)-Zn(2)-O(2B)	124.08(11)
C(3A)-O(1A)-Zn(1)	136.8(2)
C(3A)-O(2A)-Zn(2)#2	119.62(19)
O(1A)-C(3A)-O(2A)	125.3(3)
O(1A)-C(3A)-C(7A)	118.0(3)
O(2A)-C(3A)-C(7A)	116.8(3)
C(6A)-O(4A)-Zn(2)	121.6(2)
C(6A)-O(5A)-Zn(1)#6	139.9(2)
O(4A)-C(6A)-C(10A)	116.4(3)
O(5A)-C(6A)-O(4A)	126.0(3)
O(5A)-C(6A)-C(10A)	117.5(3)
C(8A)-C(7A)-C(3A)	120.2(3)
C(8A)-C(7A)-C(12A)	119.5(3)
C(12A)-C(7A)-C(3A)	120.3(3)

C(7A)-C(8A)-H(8A)	120.0
C(7A)-C(8A)-C(9A)	120.0(3)
C(9A)-C(8A)-H(8A)	120.0
C(8A)-C(9A)-H(9A)	119.8
C(10A)-C(9A)-C(8A)	120.3(3)
C(10A)-C(9A)-H(9A)	119.8
C(9A)-C(10A)-C(6A)	120.7(3)
C(9A)-C(10A)-C(11A)	119.6(3)
C(11A)-C(10A)-C(6A)	119.7(3)
C(10A)-C(11A)-H(11A)	120.0
C(12A)-C(11A)-C(10A)	120.0(3)
C(12A)-C(11A)-H(11A)	120.0
C(7A)-C(12A)-H(12A)	119.7
C(11A)-C(12A)-C(7A)	120.6(3)
C(11A)-C(12A)-H(12A)	119.7
Zn(2)-O(2B)-Zn(1)#6	100.82(8)
C(3B)-O(2B)-Zn(1)#6	128.72(19)
C(3B)-O(2B)-Zn(2)	102.90(18)
O(1B)-C(3B)-O(2B)	121.0(3)
O(1B)-C(3B)-C(4B)	121.6(3)
O(2B)-C(3B)-C(4B)	117.4(3)
C(5B)-C(4B)-C(3B)	121.2(3)
C(5B)-C(4B)-C(6B)#5	119.3(3)
C(6B)#5-C(4B)-C(3B)	119.5(3)
C(4B)-C(5B)-H(5B)	119.6
C(4B)-C(5B)-C(6B)	120.8(3)
C(6B)-C(5B)-H(5B)	119.6
C(4B)#5-C(6B)-H(6B)	120.0
C(5B)-C(6B)-C(4B)#5	120.0(3)
C(5B)-C(6B)-H(6B)	120.0
Zn(2)-O(1C)-H(1CA)	120(3)
Zn(2)-O(1C)-H(1CB)	123(3)
H(1CA)-O(1C)-H(1CB)	108(4)

Symmetry transformations used to generate equivalent atoms:
(1) -x+2,-y+2,-z+2 (2) x,-y+3/2,z+1/2 (3) -x+2,y+1/2,-z+3/2 (4) x,-y+3/2,z-1/2 (5) -x+2,-y,-z+1 (6) -x+2,y-1/2,-z+3/2

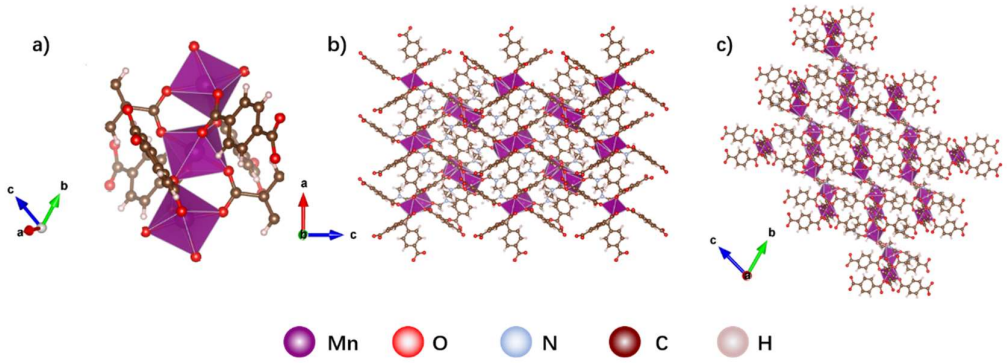

Figure S1. Crystal structures of 2D-Mn-MOFs tested in this study: (A) The inorganic part of the material and projection of the crystal structure along **(B)** b-axis and **(C)** a-axis.

Section II – Additional AFM Data and Analysis

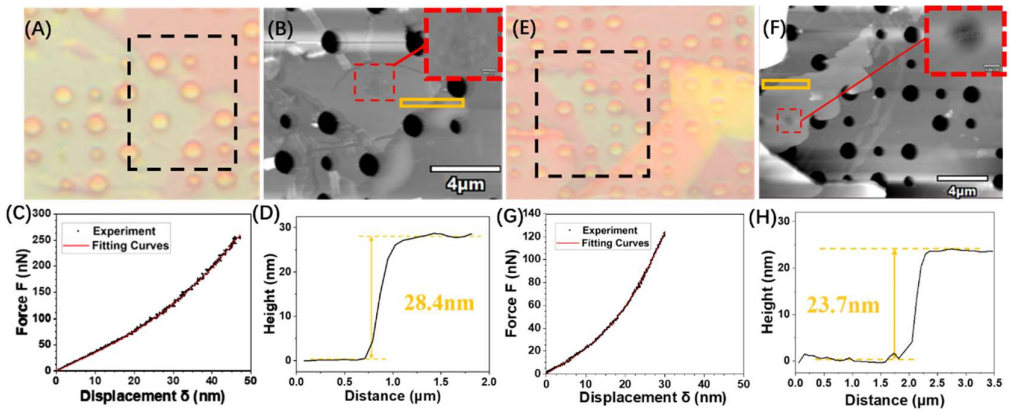

Figure S2. Representative Optical microscopy and AFM characterization of suspended 2D $Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$ (A-D) and 3D $(DMA)_2[Zn_3(BDC)_4 \cdot 1.5H_2O]$ (E-H) MOF membranes. (A, E) Optical images of the suspended regions; **(B, F)** corresponding AFM topography showing suspended membranes across micropores. **(C, G)** Representative force–displacement curves (black dots) and fitting results (red lines). **(D, H)** Height profiles of the nanosheets measured along the yellow lines in **(B, F)**.

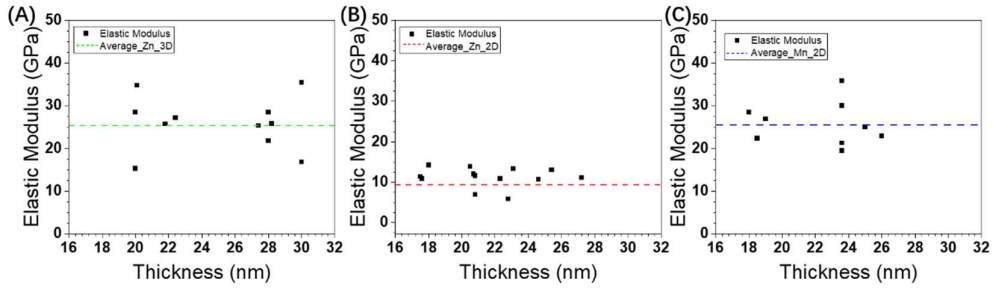

Figure S3. Thickness-independent in-plane elastic modulus $E_{\parallel}$ of Zn- and Mn-based MOFs. (A) 3D $(DMA)_2[Zn_3(BDC)_4 \cdot 1.5H_2O]$, **(B)** 2D $Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$, and **(C)** 2D $Mn_3(BDC)_3 \cdot 4(DMF)$. The dashed lines indicate the mean values of $E_{\parallel}$ for each MOF material, showing no significant dependence on the membrane thickness.

Table S10. Data for Figure 6 in the main text.

Chemical	$E_{\parallel}$(GPa)	Density	Category
$COF_{TAPB\text{-}DHTA}$	10.38 ± 3.42[1]	0.393[1]	2D COFs
$COF_{TTA\text{-}DHTA}$	25.9 ± 0.6[2]	0.5[2]	
COF-1	33[3]	0.41[3]	
$COF_{TAPB\text{-}PDA}$	42.98 ± 3.03[4]	0.38[4]	
$COF_{TAPB\text{-}DMTP}$	47.1 ± 2.3[4]	0.47[4]	
(2D) NUS-8	1[5]	1.028[5]	2D MOFs
Cu_{pym2S2}	5[6]	1.84[6]	
$Cu_{2\ NiTCPP}$	1.9[7]	1.239[7]	
$Cu_{\ PdTCPP}$	12[8]	1.1[8]	
$Zn_3(BDC)_3(H_2O)_2 \cdot 4(DMF)$ (2D-Zn-MOF in this work)	11.22 ± 2.45	1.516	
$Mn_3(BDC)_3 \cdot 4(DMF)$ (2D-Mn-MOF in this work)	25.53 ± 4.89	1.549	
$(DMA)_2[Zn_3(BDC)_4 \cdot 1.5H_2O]$ (3D-Zn-MOF in this work)	25.92 ± 6.3	1.088	3D MOF
Carbon Nanosheet (Unannealed)	12[9]	1.3[9]	Carbon Nanosheet
Carbon Nanosheet (Annealed)	48[9]	1.6[9]	
$Cu_3(C_6S_6)$	16±2[10]	2[10]	2D organo-metallic sheet
C4n3PbI	5.6±0.9[11]	3.4[11]	2D HOIPs
C12n1PbI	1.3[12]	2.054[12]	
C4n1PbCl	10.6[12]	1.88[12]	
Black Phosphorous (BP)	89.7 ±26.4[13]	2.619[13]	Other Typical 2D Inorganic Materials
Mica	202±22[14]	2.883[14]	
MoS_2	330±70[15]	5.06[15]	
MXene	330±30[16]	3.2[16]	

graphene	942±3[17]	2.27[17]	
hBN	856±3[17]	2.1[17]	

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