Supplementary Information

Homo- and Heterosolvent Modifications of Hofmann-Type Flexible Two-Dimensional Layers for Colossal Interlayer Thermal Expansions

Ryo Ohtani,*[†] Junichi Yanagisawa,[‡] Hiromu Matsunari,[‡] Masaaki Ohba,[†] Leonard F. Lindoy,[§] Shinya Hayami*[‡¶]

[†]Department of Chemistry, Faculty of Science, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.
[‡]Department of Chemistry, Graduate School of Science and Technology and [¶]Institute of Pulsed Power Science, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555 Japan.
[§]School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia.

Corresponding authors:
R. Ohtani, ohtani@chem.kyushu-univ.jp
S. Hayami, hayami@kumamoto-u.ac.jp

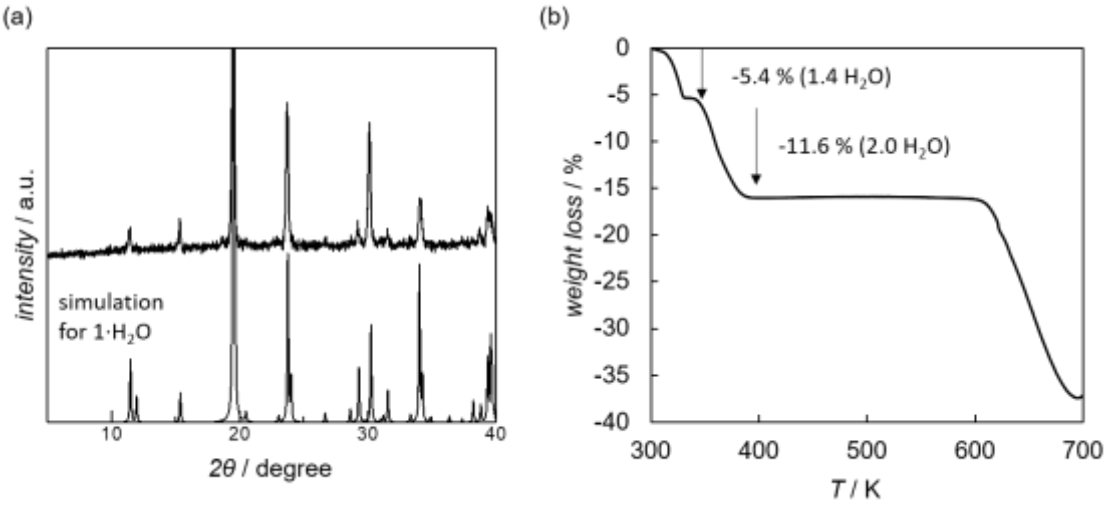


Figure S1. (a) PXRD results for powders of **1·4H₂O**. Partial dehydration from **1·4H₂O** occurred, giving rise to the pattern of **1·H₂O** phases. (b) A TGA result for powders of **1·4H₂O**.

Table S1. Crystallographic data for **1·4H₂O**

T / K	120	140	160	180
Formula	$C_4MnN_4O_6Pd$	$C_4MnN_4O_6Pd$	$C_4MnN_4O_6Pd$	$C_4MnN_4O_6Pd$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a / Å	12.1306(5)	12.1417(5)	12.1716(3)	12.1880(4)
b / Å	14.3780(5)	14.3736(4)	14.3839(4)	14.3980(5)
c / Å	7.5171(2)	7.5135(2)	7.5215(2)	7.5189(2)
V / Å^3	1311.09(8)	1311.26(7)	1316.83(6)	1319.44(7)
Z	4	4	4	4
R1	3.64	3.67	3.47	3.39
wR2	10.21	10.10	9.92	9.70
G.O.F	1.052	1.042	1.045	1.074

T / K	200	220	240	260
Formula	$C_4MnN_4O_6Pd$	$C_4MnN_4O_6Pd$	$C_4MnN_4O_6Pd$	$C_4MnN_4O_6Pd$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a / Å	12.2117(5)	12.2280(4)	12.2682(4)	12.2851(4)
b / Å	14.3939(5)	14.3988(5)	14.4167(4)	14.4234(5)
c / Å	7.5130(2)	7.5122(2)	7.5118(2)	7.5116(2)
V / Å^3	1320.59(8)	1322.66(7)	1328.59(7)	1331.00(7)
Z	4	4	4	4
R1	3.49	3.24	3.14	3.04
wR2	9.61	8.98	8.88	8.71
G.O.F	1.035	1.045	1.017	1.062

Table S2. Crystallographic data for **1·H_2O**

T / K	120	140	160	180
Formula	$C_4MnN_4O_3Pd$	$C_4MnN_4O_3Pd$	$C_4MnN_4O_3Pd$	$C_4MnN_4O_3Pd$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Imma*	*Imma*	*Imma*	*Imma*
a / Å	14.693(7)	14.7046(19)	14.7375(8)	14.7535(10)
b / Å	7.496(3)	7.5011(10)	7.4932(4)	7.4852(4)
c / Å	8.976(8)	8.975(2)	8.9788(9)	9.0012(10)
V / Å^3	988.6(11)	989.9(3)	991.54(12)	994.03(14)
Z	4	4	4	4
R1	6.91	6.39	5.20	4.54
wR2	18.19	17.71	13.81	12.12
G.O.F	1.074	1.138	1.180	1.266

T / K	200	220	240	260
Formula	$C_4MnN_4O_3Pd$	$C_4MnN_4O_3Pd$	$C_4MnN_4O_3Pd$	$C_4MnN_4O_3Pd$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Imma*	*Imma*	*Imma*	*Imma*
a / Å	14.7711(11)	14.7817(10)	14.8040(10)	14.8343(10)
b / Å	7.4870(4)	7.4817(4)	7.4800(4)	7.4884(6)
c / Å	9.0109(12)	9.0163(10)	9.0327(11)	9.0527(15)
V / Å^3	996.53(16)	997.13(14)	1000.23(15)	1005.6(2)
Z	4	4	4	4
R1	4.44	4.42	4.28	4.40
wR2	11.15	11.51	11.31	11.11
G.O.F	1.113	1.186	1.186	1.217

T / K	280	300
Formula	$C_4MnN_4O_3Pd$	$C_4MnN_4O_3Pd$
Crystal system	orthorhombic	orthorhombic
Space group	*Imma*	*Imma*
a / Å	14.8462(11)	14.8755(11)
b / Å	7.4873(4)	7.4867(4)
c / Å	9.0664(12)	9.0816(12)
V / Å^3	1007.80(16)	1011.40(16)
Z	4	4
R1	3.97	3.55
wR2	10.58	9.50
G.O.F	1.187	1.168

Table S3. Crystallographic data for **1**

T / K	320
Formula	$C_4MnN_4O_2Pd$
Crystal system	orthorhombic
Space group	*Cmmm*
a / Å	7.4409(4)
b / Å	8.5949(10)
c / Å	7.6410(6)
V / Å^3	488.67(7)
Z	2
R1	3.94
wR2	11.36
G.O.F	1.062

Table S4. Crystallographic data for **2·2MeOH**

T / K	140	160	180	200
Formula	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	7.6358(2)	7.6372(3)	7.6405(2)	7.6182(3)
b / Å	7.4845(2)	7.4908(3)	7.4980(2)	7.4960(3)
c / Å	24.1619(7)	24.2548(10)	24.3554(10)	24.5688(13)
β / °	94.397(2)	94.280(3)	94.038(3)	92.042(4)
V / Å^3	1376.79(7)	1383.72(10)	1391.82(8)	1402.14(11)
Z	4	4	4	4
R1	4.71	5.08	5.84	5.68
wR2	11.40	12.63	14.50	13.59
G.O.F	1.079	1.103	1.101	1.069

T / K	220	240	260	280
Formula	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	7.6158(2)	7.6154(2)	7.6163(2)	7.6106(4)
b / Å	7.5106(2)	7.5128(2)	7.5168(2)	7.5244(5)
c / Å	24.6864(10)	24.7495(11)	24.8393(11)	24.893(2)
β / °	91.830(3)	91.597(3)	91.326(4)	91.015(6)
V / Å^3	1411.32(8)	1415.44(9)	1421.67(8)	1425.26(17)
Z	4	4	4	4
R1	5.64	5.28	6.07	8.60
wR2	13.52	13.20	14.87	21.58
G.O.F	1.112	1.042	1.068	1.167

Table S5. Crystallographic data for **3·MeOH**

T / K	100	120	140	160
Formula	$C_7MnN_4O_3Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a / Å	14.6768(6)	14.7061(7)	14.7173(6)	14.7188(8)
b / Å	7.5621(3)	7.5631(3)	7.5668(3)	7.5681(4)
c / Å	11.8241(7)	11.8735(7)	11.9140(8)	11.9563(9)
V / Å^3	1312.33(11)	1320.61(11)	1326.78(12)	1331.85(14)
Z	4	4	4	4
R1	5.93	5.60	5.65	5.78
wR2	14.05	13.27	13.10	13.14
G.O.F	1.206	1.186	1.170	1.187

T / K	180	200	220	240
Formula	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a / Å	14.7108(7)	14.7386(7)	14.7553(7)	14.7650(8)
b / Å	7.5482(3)	7.5541(3)	7.5537(4)	7.5512(3)
c / Å	11.9724(7)	12.0156(9)	12.0600(8)	12.1204(10)
V / Å^3	1329.42(11)	1337.78(13)	1344.17(13)	1351.35(14)
Z	4	4	4	4
R1	5.81	6.33	5.64	6.83
wR2	13.13	13.62	13.06	15.54
G.O.F	1.150	1.183	1.190	1.166

T / K	260	280	300
Formula	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$	$C_7MnN_4O_4Pd$
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
a / Å	14.8017(9)	14.7901(8)	14.824(2)
b / Å	7.5711(5)	7.5456(4)	7.5472(9)
c / Å	12.1669(11)	12.2231(11)	12.336(3)
V / Å^3	1363.49(17)	1364.10(16)	1380.2(4)
Z	4	4	4
R1	6.20	7.20	6.90
wR2	14.13	14.43	18.05
G.O.F	1.125	1.177	1.131

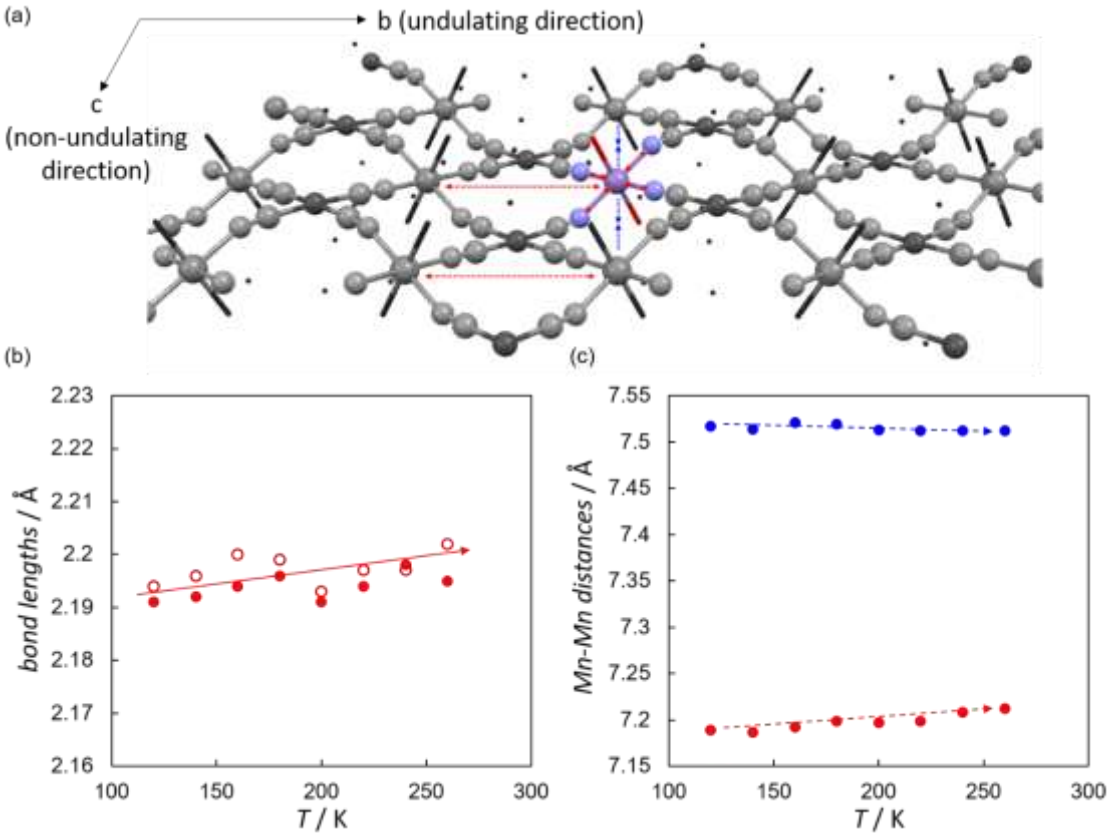


Figure S2. (a) Schematic image for the structural transformation manner associated with anisotropic TE behavior of $1 \cdot 4H_2O$. (b) The thermal variation of the bond lengths of Mn-N around the Mn^{2+} centers. (c) The thermal variation of Mn-Mn separations in the layers, indicated by the dashed arrows in (a).