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Dual Dielectric-responsive Hybrid Materials Accompanying With Fluorescent Properties

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Characterizations and Methods

Powder X-ray Diffraction

The powder X-ray diffraction experiment (PXRD) measurement was performed on a Rigaku Smartlab X-ray diffractometer. The diffraction pattern is recorded in the 2θ range of 5–50° with a step size of 0.02°. The powder X-ray diffraction measurement results are in good agreement with the crystal structure simulation results at room temperature, confirming the purity of the compound **1** and **2**.

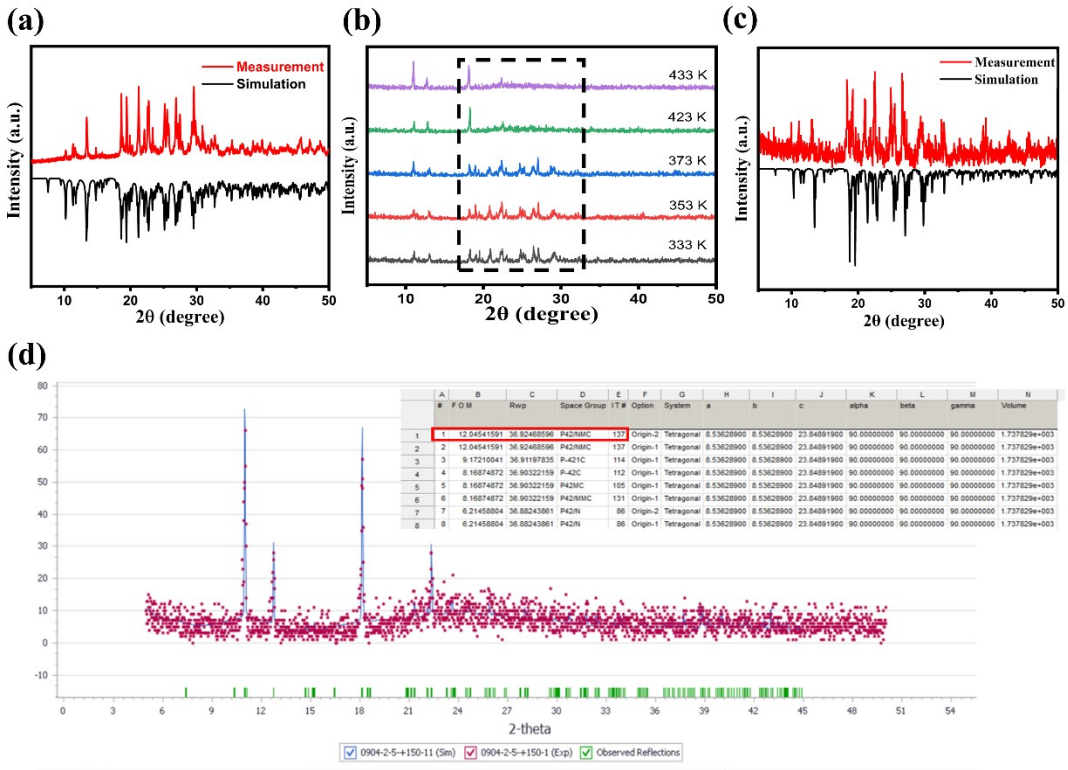

Fig. S1 (a)XRD of compound **1** at room temperature. (b)PXRD patterns of variable temperature for compound **1** in the temperature range from 333 K to 433 K. (c) XRD of compound **2** at room temperature. (d) The simulation result of the PXRD data of compound **1** at 423 K.

Thermogravimetric Tests

Thermogravimetric tests on NETZSCH TG 209F3 at a heating rate of 20 K min^{-1} over a temperature range of 310 K to 1073 K.

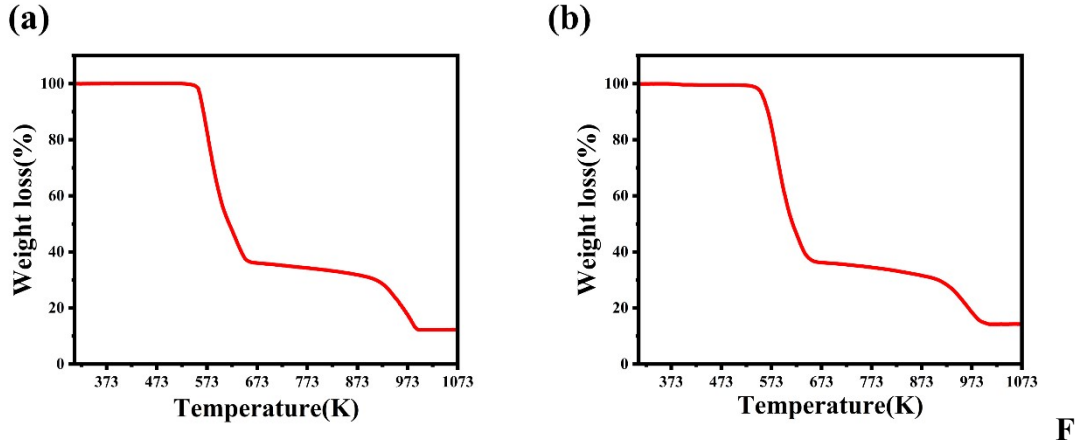

Fig. S2 TGA curves of compound **1** and **2** in the temperature range of 310 K-1073 K.

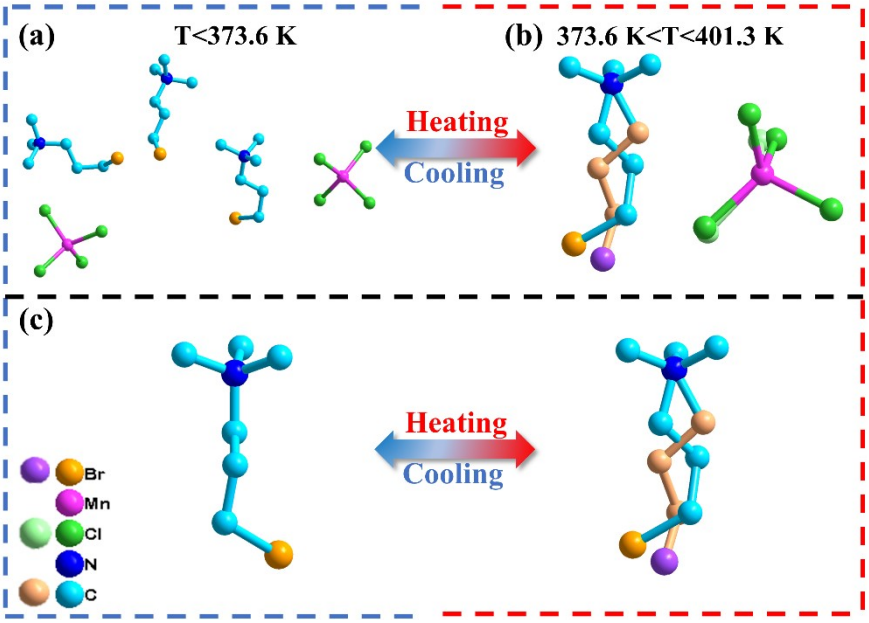

Fig. S3 The asymmetric units of compound **2** in (a) LTP (T<373.6 K) and (b) ITP (373.6 K<T<401.3 K). (c) Ordered and disordered movements of BTA cation.

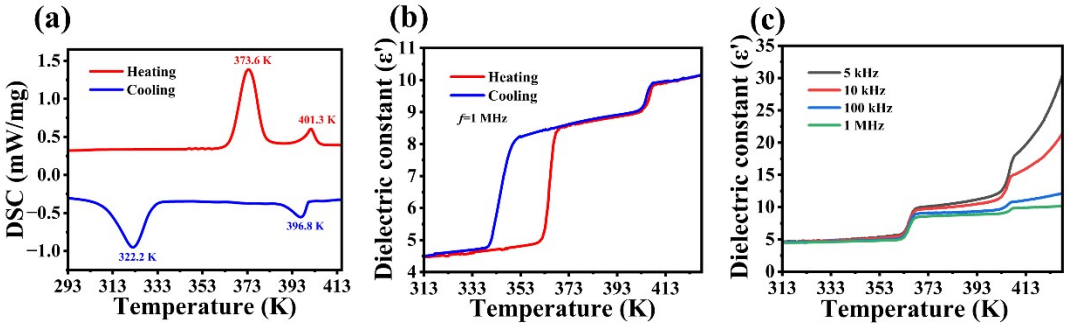

Fig. S4 (a) DSC curve of **2** during the heating and cooling processes. (b) Dielectric measurement of **2** at 1 MHz. (c) The dielectric measurement of **2** at different frequencies during the heating process.

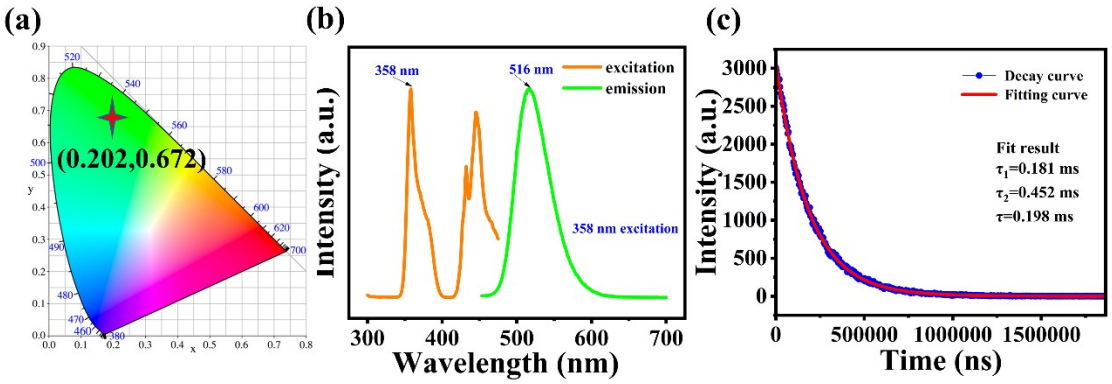

Fig. S5 (a) CIE coordinates of **2**. (b) Excitation (orange line) and emission (green line for λ_{ex}= 358 nm) spectra of **2**. (c) PL decay curve of **2**.

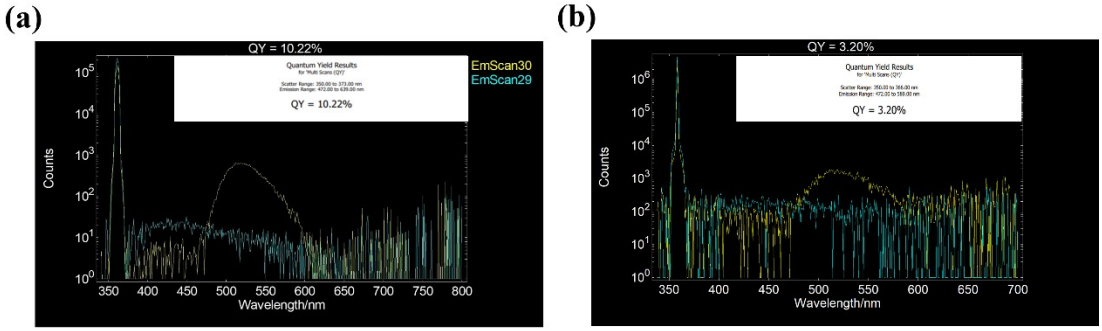

Fig.S6 Photoluminescence quantum yield measurement curves and results of compound **1** and **2**.

Table S1 Crystal data and structure refinement for $[(BTA)_2MnCl_{2.4}Br_{1.6}]$ at 282 K and 375 K.

$[(BTA)_2MnCl_{2.4}Br_{1.6}]$	282 K	375 K
Empirical formula	$C_{36}H_{90}Br_{10.76}Cl_{7.24}Mn_3N_6$	$C_{36}H_{90}Br_{10.94}Cl_{7.06}Mn_3N_6$
Formula weight	1888.44	1896.45
Temperature/K	282(3)	374.98(10)
Crystal system	monoclinic	monoclinic
Space group	*P*2/*c*	*P*2/*c*
a/Å	23.5235(8)	23.6709(12)
b/Å	9.3471(3)	9.4002(4)
c/Å	15.7733(5)	15.9372(7)

α/°	90	90
β/°	91.648(3)	91.605(4)
γ/°	90	90
Volume/Å^3	3466.7(2)	3544.8(3)
Z	2	2
F(000)	1845.0	1852.0
GOF	1.028	1.025
R_1[I>=2σ (I)]	0.0410	0.0562
wR_2[I>=2σ (I)]	0.0979	0.1791

Table S2 Crystal data and structure refinement for $[(BTA)_2MnCl_4]$ at 284 K and 375 K.

$[(BTA)_2MnCl_4]$	284 K	375 K
Empirical formula	$C_{12}H_{30}Br_2Cl_4MnN_2$	$C_{12}H_{30}Br_2Cl_4MnN_2$
Formula weight	558.94	558.94
Temperature/K	284.15	374.99(10)
Crystal system	monoclinic	monoclinic
Space group	*P*2/*c*	*C*2/*c*
a/Å	23.3275(8)	16.385(3)
b/Å	9.2150(3)	9.5496(11)
c/Å	15.6388(5)	15.941(2)
α/°	90	90
β/°	91.636(3)	111.036(19)
γ/°	90	90

Volume/Å^3	3360.39(19)	2328.1(7)
Z	6	4
F(000)	1674.0	1116.0
GOF	1.043	1.217
R_1[I>=2σ (I)]	0.0561	0.1433
wR_2[I>=2σ (I)]	0.1012	0.2908

Table S3 The main bond length (Å) of the crystal structure of $[(BTA)_2MnCl_{2.4}Br_{1.6}]$ at 282 K

Bond lengths [Å]			
Br9-C18	1.938(4)	N3-C15	1.489(4)
Br8-C12	1.941(4)	N3-C13	1.486(5)
Mn1-Cl2	2.4320(8)	N3-C14	1.499(5)
Mn1-Cl2[1]	2.4321(8)	N1-C4	1.515(5)
Mn1-Cl1[1]	2.4006(8)	N1-C3	1.485(5)
Mn1-Cl1	2.4006(8)	N1-C2	1.495(5)
Mn1-Br2	2.4320(8)	N1-C1	1.494(5)
Mn1-Br1	2.4006(8)	N2-C10	1.504(5)
Mn2-Cl4	2.4265(8)	N2-C9	1.491(5)
Mn2-Cl5	2.4649(8)	N2-C7	1.499(5)
Mn2-Cl3	2.4284(8)	N2-C8	1.491(5)
Mn2-Cl6	2.4261(8)	C16-C17	1.493(5)
Mn2-Br3	2.4284(8)	C11-C10	1.500(5)
Mn2-Br4	2.4265(8)	C11-C12	1.495(5)
Mn2-Br5	2.4649(8)	C4-C5	1.515(6)
Mn2-Br6	2.4261(8)	C17-C18	1.512(6)
Br7-C6	1.921(5)	C5-C6	1.518(7)
N3-C16	1.528(5)		

[1]**1-X, +Y, 1/2-Z**

Table S4 The main bond angles (°) of the crystal structure of $[(BTA)_2MnCl_{2.4}Br_{1.6}]$ at 282 K

Bond angles [°]			
Cl2-Mn1-Cl2[1]	106.91(4)	C13-N3-C14	108.4(3)
Cl1[1]-Mn1-Cl2[1]	102.95(3)	C14-N3-C16	106.6(3)
Cl1-Mn1-Cl2	102.95(3)	C3-N1-C4	111.7(3)
Cl1-Mn1-Cl2[1]	109.93(3)	C3-N1-C2	109.8(3)
Cl1[1]-Mn1-Cl2	109.93(3)	C3-N1-C1	108.4(3)
Cl1[1]-Mn1-Cl1	123.35(5)	C2-N1-C4	110.8(3)
Br1-Mn1-Br2	102.95(3)	C1-N1-C4	107.1(3)
Cl4-Mn2-Cl5	106.12(3)	C1-N1-C2	109.1(3)
Cl4-Mn2-Cl3	115.58(3)	C9-N2-C10	111.1(3)
Cl3-Mn2-Cl5	107.38(3)	C9-N2-C7	107.9(3)
Cl6-Mn2-Cl4	110.31(3)	C7-N2-C10	107.5(3)
Cl6-Mn2-Cl5	106.59(3)	C8-N2-C10	110.8(3)
Cl6-Mn2-Cl3	110.34(3)	C8-N2-C9	110.4(4)
Br3-Mn2-Br5	107.38(3)	C8-N2-C7	109.0(4)
Br4-Mn2-Br3	115.58(3)	C17-C16-N3	114.5(3)
Br4-Mn2-Br5	106.12(3)	C12-C11-C10	108.5(3)
Br6-Mn2-Br3	110.34(3)	C11-C10-N2	115.9(3)
Br6-Mn2-Br4	110.31(3)	C5-C4-N1	114.1(3)
Br6-Mn2-Br5	106.59(3)	C11-C12-Br8	112.5(3)
C15-N3-C16	110.9(3)	C16-C17-C18	112.0(3)
C15-N3-C14	108.9(3)	C17-C18-Br9	113.1(3)
C13-N3-C16	112.1(3)	C4-C5-C6	112.1(4)
C13-N3-C15	109.9(3)	C5-C6-Br7	112.5(3)

[1]**1-X, +Y, 1/2-Z**

Table S5 The main bond length (Å) of the crystal structure of $[(BTA)_2MnCl_{2.4}Br_{1.6}]$ at 375 K

Bond lengths [Å]			
Mn1-Cl2	2.4217(12)	N1-C2	1.504(9)

Mn1-Cl2[1]	2.4217(12)	N1-C1	1.483(6)
Mn1-Cl1[1]	2.3989(12)	N1-C3	1.530(12)
Mn1-Cl1	2.3989(12)	N1-C4	1.532(15)
Mn1-Br2	2.4217(12)	N4-C15	1.500(8)
Mn1-Br1	2.3989(12)	N4-C21	1.505(8)
Br7-C13	1.899(7)	N4-C19	1.504(8)
Mn2-Cl4	2.4674(13)	N4-C17	1.506(8)
Mn2-Cl3	2.4242(12)	C5-C6	1.495(9)
Mn2-Cl5	2.4305(13)	C11-C12	1.483(9)
Mn2-Cl6	2.4259(14)	C6-C7	1.487(9)
Mn2-Br5	2.4305(13)	C12-C13	1.522(9)
Mn2-Br3	2.4242(12)	C21-C23	1.545(8)
Mn2-Br4	2.4674(13)	C23-C24	1.546(8)
Mn2-Br6	2.4259(14)	C14-N3	1.496(8)
Br9-C7	1.902(7)	Br8-C25	1.751(9)
Br10-C24	1.818(8)	C25-C22	1.579(11)
N2-C9	1.491(7)	C22-C20	1.539(9)
N2-C8	1.486(7)	C20-N3	1.535(9)
N2-C11	1.533(8)	N3-C18	1.504(8)
N2-C10	1.504(8)	N3-C16	1.520(9)
N1-C5	1.508(8)		

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

Table S6 The main bond angles (°) of the crystal structure of $[(BTA)_2MnCl_{2.4}Br_{1.6}]$ at 375 K

Bond angles [°]			
Cl2-Mn1-Cl2[1]	107.39(7)	C2-N1-C4	92.0(17)
Cl1-Mn1-Cl2	109.49(4)	C1-N1-C5	107.2(5)
Cl1[1]-Mn1-Cl2[1]	109.49(4)	C1-N1-C2	107.4(5)
Cl1-Mn1-Cl2[1]	103.45(4)	C1-N1-C3	102.9(10)
Cl1[1]-Mn1-Cl2	103.45(4)	C1-N1-C4	118.5(13)
Cl1[1]-Mn1-Cl1	122.87(8)	C15-N4-C21	115(3)
Br1-Mn1-Br2	109.49(4)	C15-N4-C19	89(3)
Cl3-Mn2-Cl4	106.08(5)	C15-N4-C17	115.3(15)

Cl3-Mn2-Cl5	116.20(5)	C21-N4-C17	111.5(14)
Cl3-Mn2-Cl6	110.07(5)	C19-N4-C21	110.4(14)
Cl5-Mn2-Cl4	107.20(5)	C19-N4-C17	114.0(15)
Cl6-Mn2-Cl4	107.45(5)	C6-C5-N1	116.0(5)
Cl6-Mn2-Cl5	109.42(5)	C12-C11-N2	114.7(5)
Br5-Mn2-Br4	107.20(5)	C7-C6-C5	109.5(6)
Br3-Mn2-Br5	116.20(5)	C11-C12-C13	111.7(6)
Br3-Mn2-Br4	106.08(5)	C12-C13-Br7	114.6(5)
Br3-Mn2-Br6	110.07(5)	C6-C7-Br9	113.0(5)
Br6-Mn2-Br5	109.42(5)	N4-C21-C23	118(3)
Br6-Mn2-Br4	107.45(5)	C21-C23-C24	107(4)
C9-N2-C11	111.4(5)	C23-C24-Br10	106(3)
C9-N2-C10	107.6(5)	C22-C25-Br8	118.7(8)
C8-N2-C9	109.7(5)	C20-C22-C25	106.2(8)
C8-N2-C11	114.2(5)	N3-C20-C22	110.2(7)
C8-N2-C10	108.0(5)	C14-N3-C20	110.7(7)
C10-N2-C11	105.6(5)	C14-N3-C18	112.8(7)
C5-N1-C3	106.5(9)	C14-N3-C16	108.0(7)
C5-N1-C4	119.6(12)	C18-N3-C20	112.1(7)
C2-N1-C5	110.4(5)	C18-N3-C16	106.5(7)
C2-N1-C3	121.5(12)	C16-N3-C20	106.3(7)

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

Table S7 The main bond length (Å) of the crystal structure of $[(BTA)_2MnCl_4]$ at 284 K

Bond lengths [Å]			
Br1-C6	1.946(4)	N3-C16	1.510(5)
Br2-C12	1.943(4)	N3-C15	1.490(5)
Mn1-Cl2	2.3610(10)	N3-C13	1.493(5)
Mn1-Cl2[1]	2.3611(10)	N3-C14	1.498(5)
Mn1-Cl1[1]	2.3825(11)	N2-C10	1.505(5)
Mn1-Cl1	2.3825(11)	N2-C8	1.496(5)
Mn2-Cl6	2.3857(11)	N2-C7	1.493(5)
Mn2-Cl4	2.3781(11)	N2-C9	1.485(5)
Mn2-Cl3	2.3541(11)	C4-C5	1.512(5)
Mn2-Cl5	2.3560(12)	C10-C11	1.509(6)
Br3-C18	1.933(5)	C16-C17	1.512(6)
N1-C4	1.519(5)	C11-C12	1.501(5)
N1-C1	1.490(5)	C6-C5	1.507(5)
N1-C2	1.497(5)	C17-C18	1.516(6)
N1-C3	1.493(5)		

[1]**2-X, +Y, 1/2-Z**

Table S8 The main bond angles (°) of the crystal structure of $[(BTA)_2MnCl_4]$ at 284 K

Bond angles [°]			
Cl2-Mn1-Cl2[1]	124.19(6)	C15-N3-C14	108.0(3)
Cl2-Mn1-Cl1	103.42(4)	C13-N3-C16	111.0(3)
Cl21-Mn1-Cl1[1]	103.42(4)	C13-N3-C14	109.1(3)
Cl21-Mn1-Cl1	109.21(4)	C14-N3-C16	107.9(3)
Cl2-Mn1-Cl1[1]	109.21(4)	C8-N2-C10	107.6(3)
Cl11-Mn1-Cl1	106.34(6)	C7-N2-C10	110.8(3)
Cl4-Mn2-Cl6	105.94(4)	C7-N2-C8	108.1(3)
Cl3-Mn2-Cl6	107.32(4)	C9-N2-C10	111.1(3)
Cl3-Mn2-Cl4	110.45(4)	C9-N2-C8	108.7(4)
Cl3-Mn2-Cl5	115.80(5)	C9-N2-C7	110.3(4)
Cl5-Mn2-Cl6	106.01(5)	C5-C4-N1	114.6(3)
Cl5-Mn2-Cl4	110.70(5)	N2-C10-C11	115.6(3)
C1-N1-C4	111.1(3)	N3-C16-C17	114.3(3)
C1-N1-C2	109.2(3)	C12-C11-C10	107.8(3)
C1-N1-C3	109.5(3)	C11-C12-Br2	112.3(3)
C2-N1-C4	106.9(3)	C5-C6-Br1	112.9(3)
C3-N1-C4	111.8(3)	C6-C5-C4	111.9(3)
C3-N1-C2	108.4(3)	C16-C17-C18	112.0(4)
C15-N3-C16	111.2(3)	C17-C18-Br3	112.2(3)
C15-N3-C13	109.5(3)		

[1]**2-X, +Y, 1/2-Z**

Table S9 The main bond length (Å) of the crystal structure of $[(BTA)_2MnCl_4]$ at 375 K

Bond lengths [Å]			
Mn1-Cl1[1]	2.366(3)	N1-C2	1.469(9)
Mn1-Cl1	2.366(3)	N1-C7	1.529(8)
Mn1-Cl2[1]	2.348(9)	N1-C4	1.630(16)
Mn1-Cl2	2.348(9)	C7-C8	1.561(8)
Mn1-Cl3	2.356(12)	C6-C5	1.646(16)
Mn1-Cl3[1]	2.356(12)	C8-C9	1.641(17)
Br2-C6	1.852(8)	C5-C4	1.625(16)
N1-C1	1.467(9)	Br1-C9	1.643(17)
N1-C3	1.475(9)		

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

Table S10 The main bond angles (°) of the crystal structure of $[(BTA)_2MnCl_4]$ at 375 K

Bond angles [°]			
Cl1-Mn1-Cl1[1]	107.5(2)	C1-N1-C4	87.3(15)
Cl2[1]-Mn1-Cl1	106.4(6)	C3-N1-C7	92.9(11)
Cl2-Mn1-Cl1	106.3(9)	C3-N1-C4	132.5(17)
Cl2-Mn1-Cl3[1]	113.5(19)	C2-N1-C3	109.5(11)
Cl2[1]-Mn1-Cl3[1]	11.3(10)	C2-N1-C7	115.8(12)
Cl3-Mn1-Cl1[1]	106.3(7)	C2-N1-C4	106.2(18)
Cl3[1]-Mn1-Cl1	106.3(7)	N1-C7-C8	108.6(14)
Cl3-Mn1-Cl1	116.4(14)	C5-C6-Br2	84.5(13)
Cl3[1]-Mn1-Cl1[1]	116.4(14)	C7-C8-C9	119(5)
Cl3-Mn1-Cl3[1]	104(2)	C4-C5-C6	96.9(18)
C1-N1-C3	107.9(11)	C5-C4-N1	102.1(18)
C1-N1-C2	110.5(11)	C8-C9-Br1	129(3)
C1-N1-C7	118.3(14)		

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