Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Fast and slow integrated single-molecule dual dielectric switch based on crystal/flexible thin film

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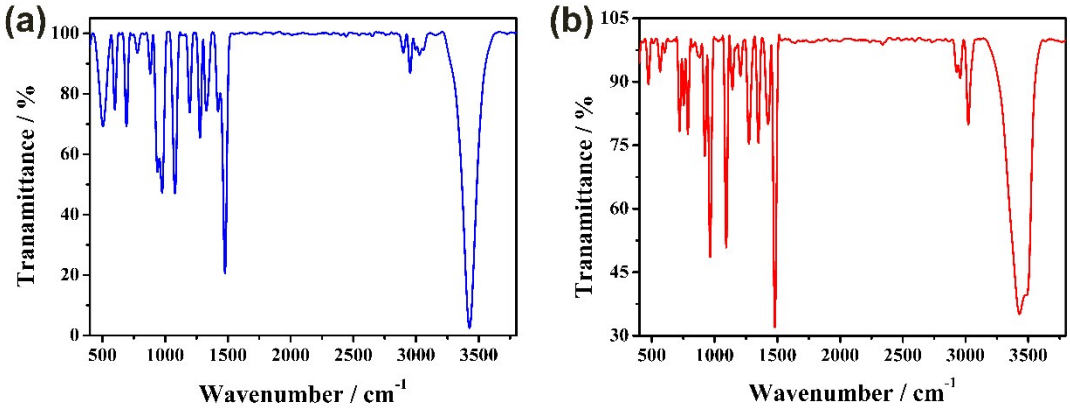

Fig. S1 Infrared spectrum of compound **1** (a) and **2** (b). Description: The IR spectrums of **1** and **2** definitely show the existence of typical strong stretching vibration peaks of C-N at 1000-1200 cm^{-1}, the C-Cl stretching vibration at 600-800 cm^{-1}, and the N-H/C-H stretching vibration at 2800-3200 cm^{-1}. In addition, the finger-print region of about 3200-3500 cm^{-1} may belong to the stretching vibration of O-H, which serves as indirect proof to the crystalline structure we have obtained.

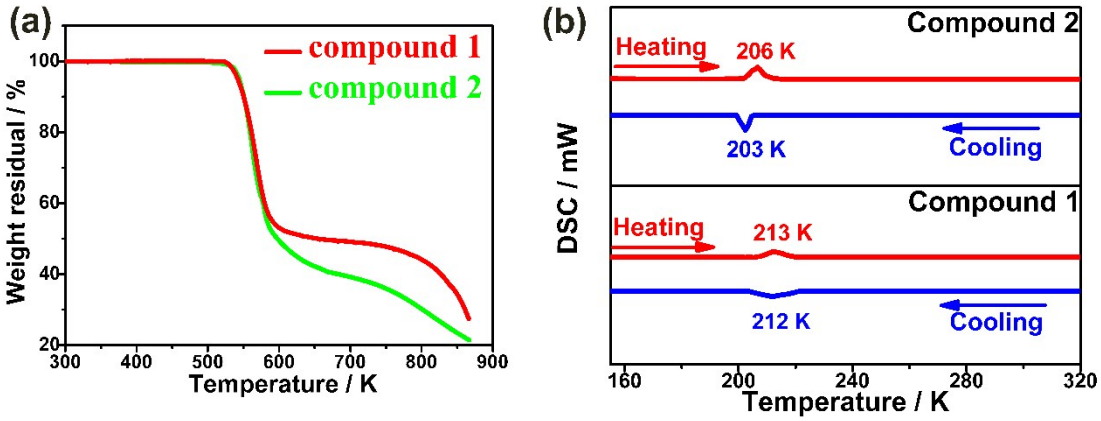

Fig. S2 (a) TGA curves for **1** (red) and **2** (green). (b) DSC curves of **1** and **2** obtained on a cooling-heating cycle from LTP to RTP.

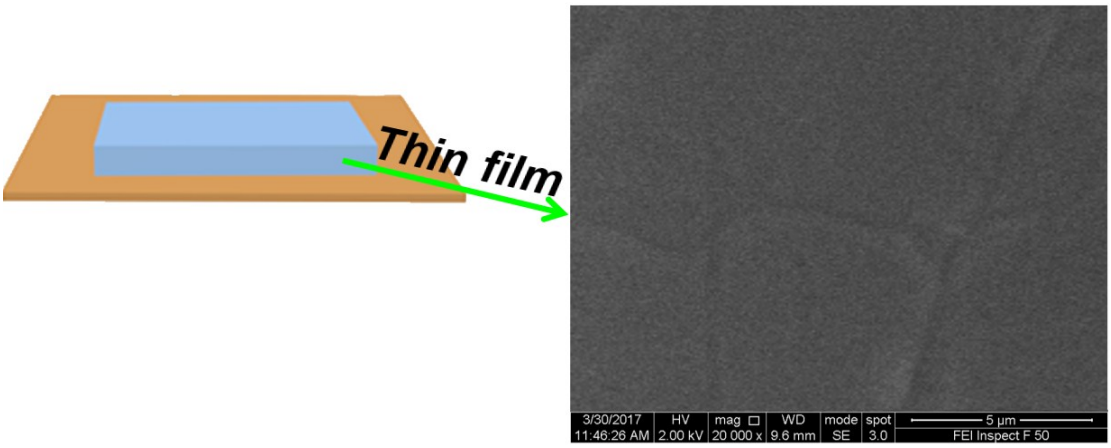

Fig. S3 The scanning electron microscopy (SEM) topography of compound **2**.

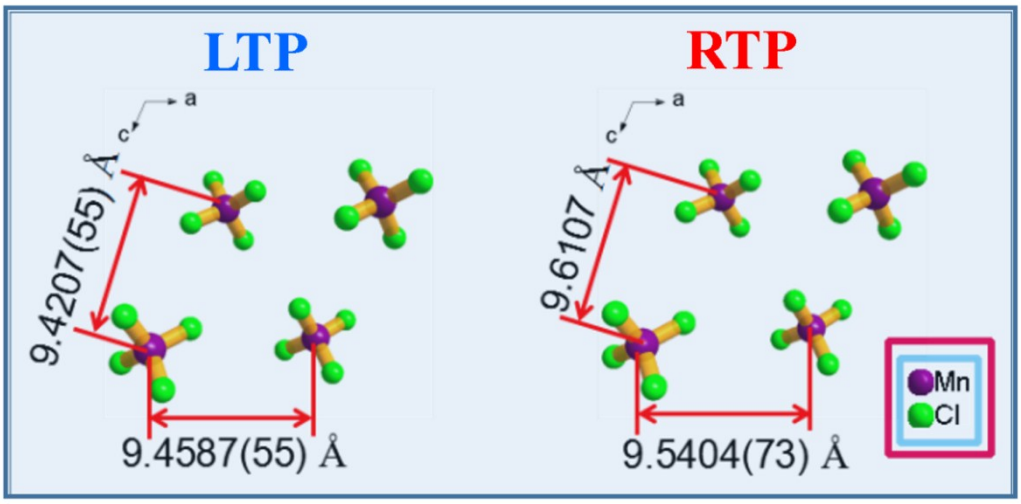

Fig. S4 Crystal-packing views of compound **2** at LTP (103 K) and RTP (293 K), while other atoms omitted for clarity.

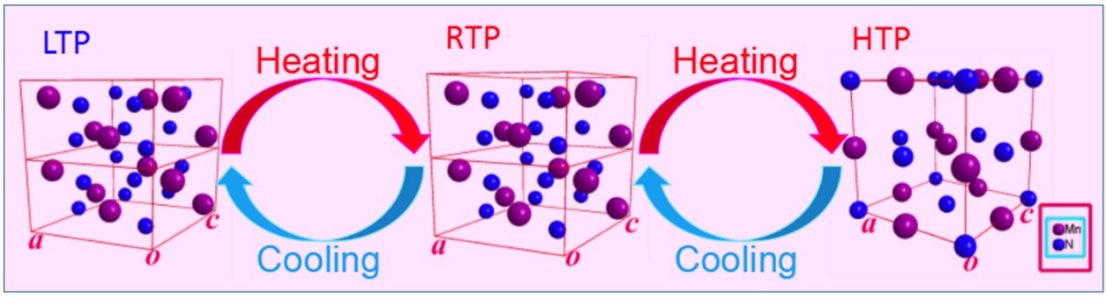

Fig. S5 Schematic presentations of the positions of N and Mn atoms in (a) LTP at 103 K, (b) RTP at 293 K, and (c) HTP, while other atoms omitted for clarity. The presentation of HTP is a hypothetical state based upon the space group.

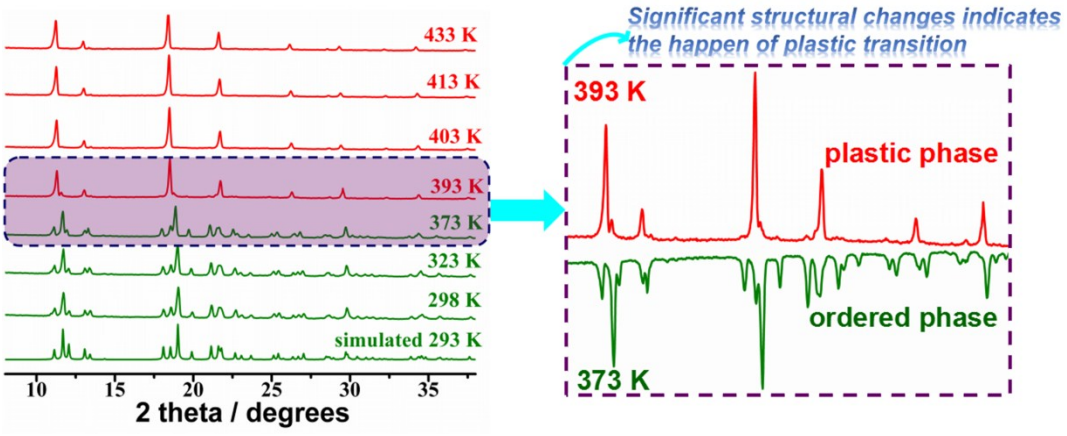

Fig. S6 Variable-temperature PXRD patterns of **1**, the right picture showed the contrast of plastic phase and ordered phase.

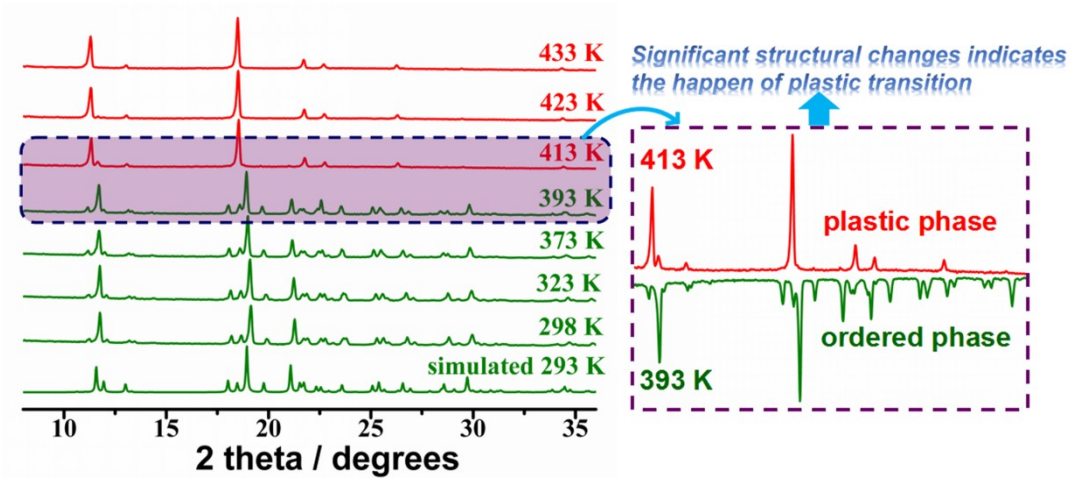

Fig. S7 Variable-temperature PXRD patterns of **2**, the right picture showed the contrast of plastic phase and ordered phase.

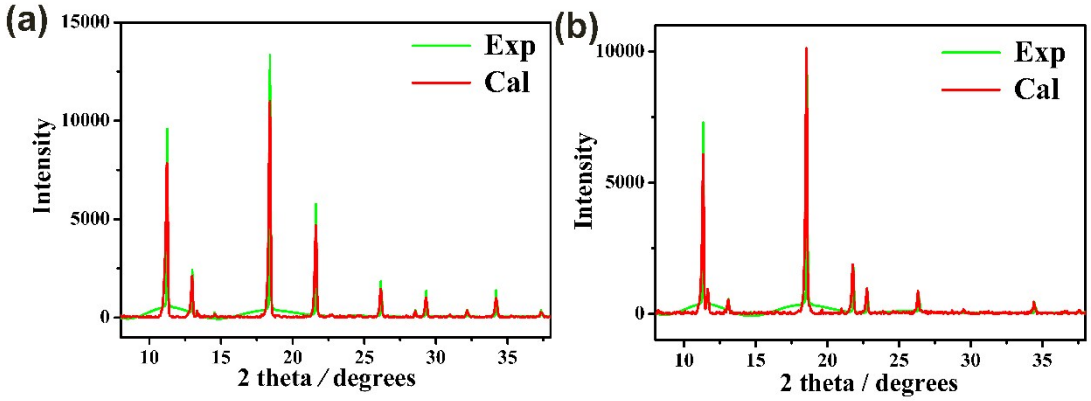

Fig. S8 Pawley refinement on the PXRD patterns of compound **1** and **2** at 413 K. Experimental pattern (green line), calculated pattern (red line), the appointed unit-cell parameters and space group are got through the calculated peak positions.

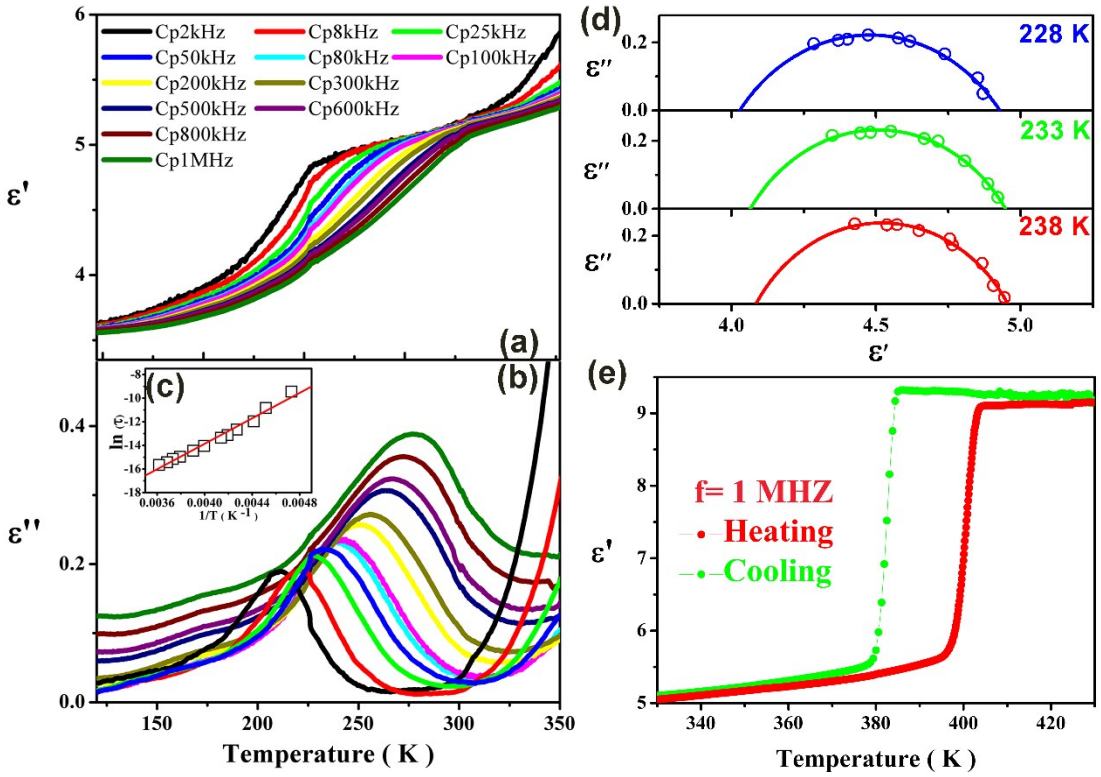

Fig. S9 (a) Real part (ε') of the dielectric permittivity of Compound **2** as a function of temperature at various frequencies on cooling process for the polycrystalline sample; (b) imaginary part (ε'') of the dielectric permittivity measured at different frequencies on cooling course for the polycrystalline sample; (c) Arrhenius plots for the dielectric relaxation on cooling. (d) Cole-Cole diagrams of ε'' versus ε' for the polycrystalline sample of **2** at three selected temperatures, which shows the relaxation nature of the dielectric dispersion in compound **2**. (e) Temperature-dependence of the real part (ε') of the polycrystalline samples of **2** at 1 MHz upon heating and cooling.

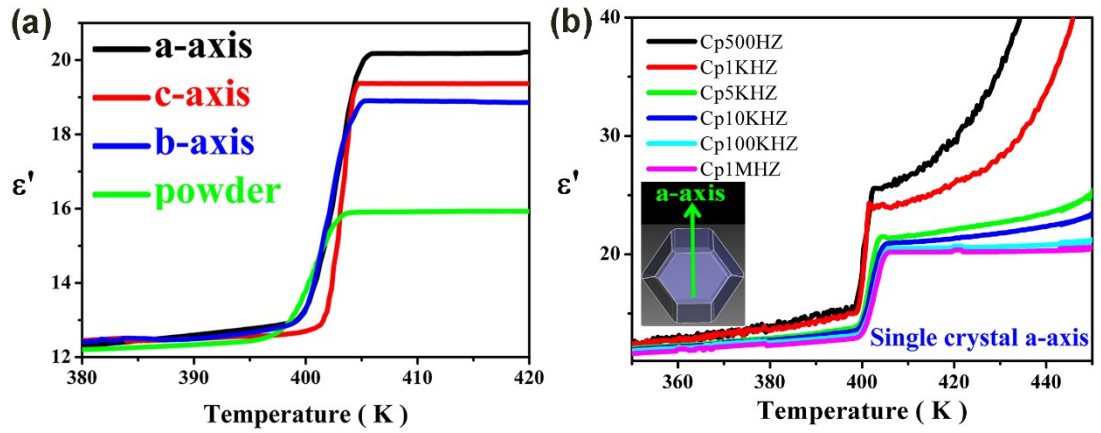

Fig. S10 (a) Anisotropic dielectric permittivity (ε') of **2** along the a, b, and c axes at 1000 KHz upon heating. (b) Temperature-dependent real part (ε') of the dielectric constant of compound **2**, measured along the a-axis in the frequency range 0.5-1000 KHz upon heating.

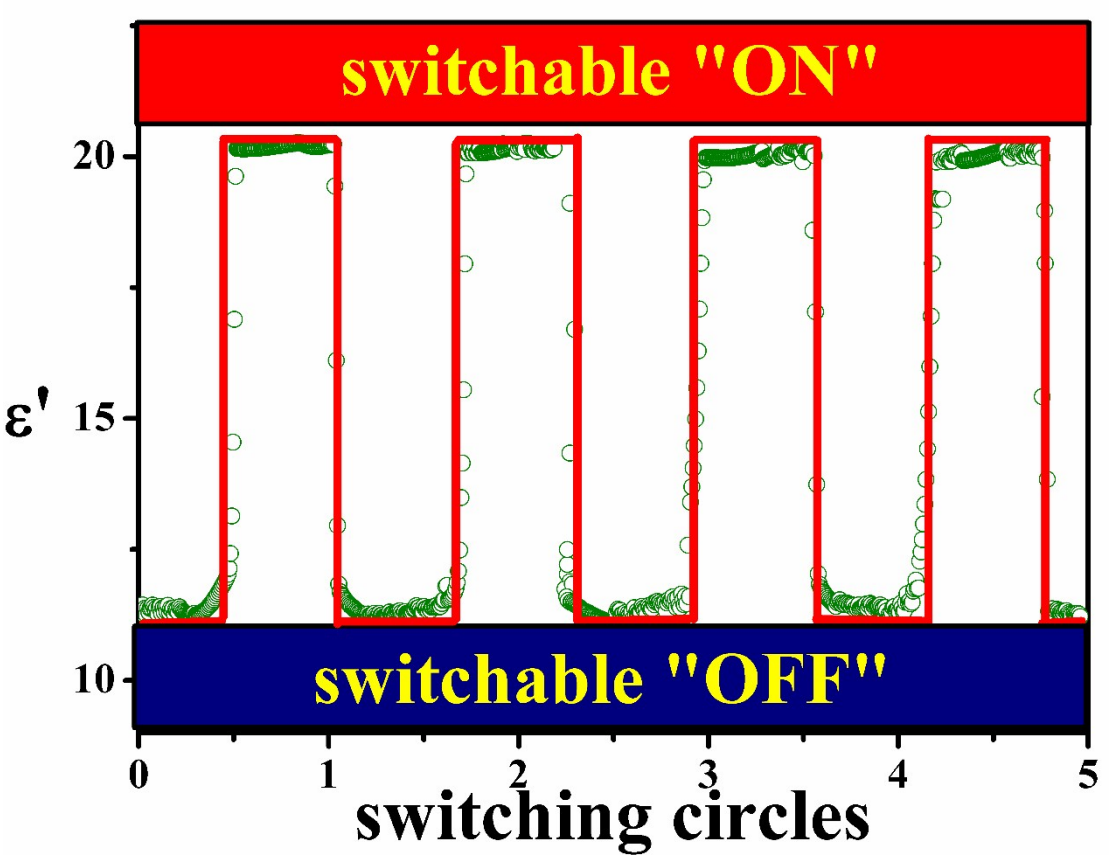

Fig. S11 ε'-switching of crystal **2** is completely reversible without wastage after at least four "on"/"off" cycles along a-axis at frequencies of 1 MHz.

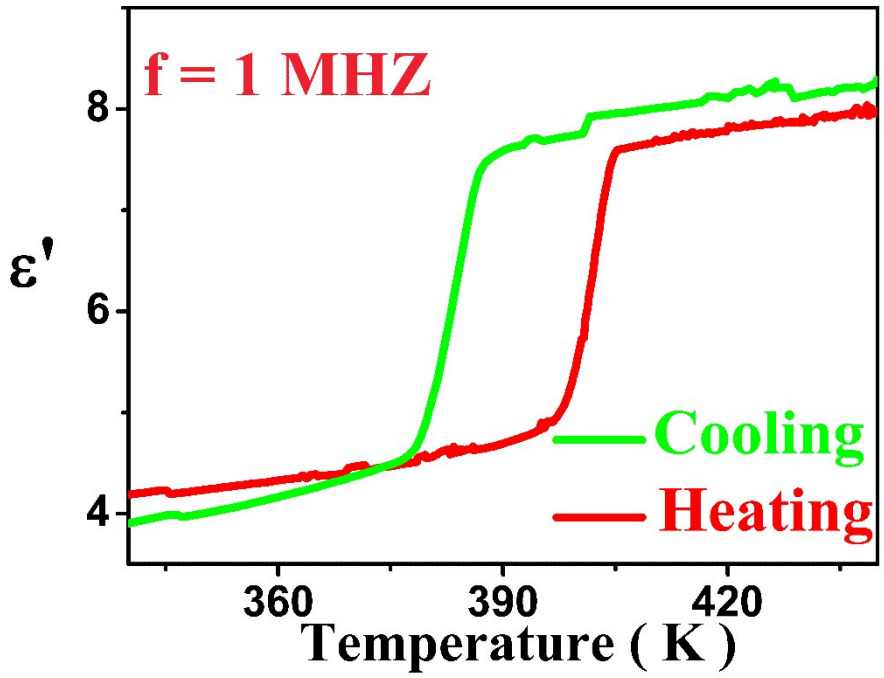

Fig. S13 Temperature-dependence of the real part (ε') of the flexibility thin films samples of **2** at 1 MHz upon heating and cooling.

Table S1 Summary of crystallographic data for compounds 1 and 2

	$[C_3H_9Cl_2NO]_2[CdCl_4]$ (**1**)		$[C_3H_9Cl_2NO]_2[MnCl_4]$ (**2**)	
Temperature(K)	RTP(293K)	LTP(103K)	RTP(293K)	LTP(103K)
Empirical formula	$C_{12}H_{30}Cl_6CdN_2O_2$	$C_{12}H_{30}Cl_6CdN_2O_2$	$C_{12}H_{30}Cl_6MnN_2O_2$	$C_{12}H_{30}Cl_6MnN_2O_2$
Formula weight	558.47	558.47	502.02	502.02
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	16.440 (3)	16.407 (14)	16.394 (16)	16.287 (12)
b (Å)	9.787 (2)	9.691 (7)	9.763 (9)	9.623 (7)
c (Å)	15.935 (3)	15.708 (13)	15.901 (15)	15.636 (12)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	113.23 (3)	113.897 (13)	112.971 (14)	113.41 (4)
γ (deg)	90.00	90.00	90.00	90.00
Volume (Å^3)	2356.1 (8)	2283 (3)	2343 (4)	2249 (3)
Radiation type	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Z, Calculated density	4, 1.577 Mg m^{-3}	4, 1.624 Mg m^{-3}	4, 1.423 Mg m^{-3}	4, 1.483 Mg m^{-3}
F(000)	1128	1124	1036	1036
$T_{min/max}$	0.964/0.970	0.9/1.0	0.964/0.970	0.9/1.0
Goodness-of-fit on F^2	1.052	1.059	1.122	1.131
R_1 [$I > 2s(I)$]	0.076	0.076	0.092	0.079
wR_2 [$I > 2s(I)$]	0.215	0.237	0.346	0.295

Table S2 Selected structural data for 1 under 103K

Bond lengths / Å and bond angles / °			
Cd(1)-Cl(1)	2.459(4)	Cd(1)-Cl(1)#1	2.459(4)
Cd(1)-Cl(2)	2.447(3)	Cd(1)-Cl(2)#1	2.447(3)
Cl(3)-C(1)	1.727(14)	C(1)-C(2)	1.496(17)
C(3)-C(2)	1.42(2)	N(1)-C(3)	1.483(14)
N(1)-C(4)	1.480(18)	N(1)-C(5)	1.493(18)
N(1)-C(6)	1.426(18)	C(2)-O(1)	1.57(2)
Cl(1)-Cd(1)-Cl(1)#1	110.6(2)	Cl(1)#1-Cd(1)-Cl(2)	107.91(14)
Cl(1)#1-Cd(1)-Cl(2)#1	110.89(17)	Cl(1)-Cd(1)-Cl(2)	110.89(17)
Cl(1)-Cd(1)-Cl(2)#1	107.91(14)	Cl(2)#1-Cd(1)-Cl(2)	108.63(18)
C(3)-N(1)-C(5)	113.1(11)	C(3)-N(1)-C(4)	110.9(13)
C(3)-N(1)-C(6)	107.0(12)	C(5)-N(1)-C(4)	107.9(12)
C(4)-N(1)-C(6)	108.9(11)	C(5)-N(1)-C(6)	109.0(13)
C(2)-C(1)-Cl(3)	113.7(11)	O(1)-C(2)-C(1)	102.8(14)
N(1)-C(3)-C(2)	119.4(14)	C(3)-C(2)-O(1)	102.7(14)
C(3)-C(2)-C(1)	114.0(14)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+1/2.

Table S3 Selected structural data for 1 under 293K

Bond lengths / Å and bond angles / °			
Cd(1)-Cl(1)	2.4481 (12)	Cd(1)-Cl(1)#1	2.4481(12)
Cd(1)-Cl(2)	2.4336 (11)	Cd(1)-Cl(2)#1	2.4336(11)
Cl(3)-C(1)	1.769(2)	Cl(3A)-C(1A)	1.772(3)
C(1)-C(2)	1.523(3)	C(1A)-C(2A)	1.515(3)
C(3)-C(2)	1.502(4)	C(3A)-C(2A)	1.479(5)
N(1)-C(3)	1.504(3)	N(1A)-C(3A)	1.502(4)
N(1)-C(4)	1.500(4)	N(1A)-C(4A)	1.502(4)
N(1)-C(5)	1.508(5)	N(1A)-C(5A)	1.505(6)
N(1)-C(6)	1.493(5)	N(1A)-C(6A)	1.493(5)
C(2)-O(1)	1.507(4)	C(2A)-O(1A)	1.496(5)
Cl(1)-Cd(1)-Cl(1)#1	111.16(6)	Cl(1)#1-Cd(1)-Cl(2)	107.15(4)
Cl(1)#1-Cd(1)-Cl(2)#1	111.25(4)	Cl(1)-Cd(1)-Cl(2)	111.25(4)
Cl(1)-Cd(1)-Cl(2)#1	107.15(4)	Cl(2)#1-Cd(1)-Cl(2)	108.90(5)

C(3)-N(1)-C(5)	110.9(3)	C(5A)-N(1A)-C(3A)	95.5(3)
C(3)-N(1)-C(4)	115.6(4)	C(4A)-N(1A)-C(3A)	146.4(5)
C(3)-N(1)-C(6)	92.4(3)	C(6A)-N(1A)-C(3A)	105.8(3)
C(5)-N(1)-C(4)	105.0(3)	C(4A)-N(1A)-C(5A)	102.6(5)
C(4)-N(1)-C(6)	123.9(3)	C(4A)-N(1A)-C(6A)	91.2(5)
C(5)-N(1)-C(6)	108.6(4)	C(5A)-N(1A)-C(6A)	116.4(4)
C(2)-C(1)-Cl(3)	113.41(18)	C(2A)-C(1A)-Cl(3A)	114.6(2)
O(1)-C(2)-C(1)	108.3(3)	O(1A)-C(2A)-C(1A)	108.5(3)
N(1)-C(3)-C(2)	115.2(2)	C(2A)-C(3A)-N(1A)	91.2(2)
C(3)-C(2)-O(1)	107.2(2)	C(3A)-C(2A)-O(1A)	111.5(4)
C(3)-C(2)-C(1)	108.7(2)	C(3A)-C(2A)-C(1A)	110.6(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y, -z+1/2.

Table S4 Selected structural data for 1 under 103K

Bond lengths / Å and bond angles / °

Mn(1)-Cl(1)	2.351(2)	Mn(1)-Cl(1)#1	2.351(2)
Mn(1)-Cl(2)	2.367(2)	Mn(1)-Cl(2)#1	2.367(2)
Cl(3)-C(1)	1.726(8)	C(1)-C(2)	1.571(11)
C(3)-C(2)	1.423(15)	N(1)-C(3)	1.537(11)
N(1)-C(4)	1.545(10)	N(1)-C(5)	1.452(13)
N(1)-C(6)	1.476(10)	C(2)-O(1)	1.419(13)
Cl(1)-Mn(1)-Cl(1)#1	109.58(12)	Cl(1)#1-Mn(1)-Cl(2)	109.83(10)
Cl(1)#1-Mn(1)-Cl(2)#1	108.53(9)	Cl(1)-Mn(1)-Cl(2)	108.53(9)
Cl(1)-Mn(1)-Cl(2)#1	109.83(10)	Cl(2)#1-Mn(1)-Cl(2)	110.55(14)
C(3)-N(1)-C(5)	106.2(8)	C(3)-N(1)-C(4)	113.2(7)
C(3)-N(1)-C(6)	113.3(6)	C(5)-N(1)-C(4)	109.0(6)
C(4)-N(1)-C(6)	105.4(7)	C(5)-N(1)-C(6)	109.8(8)
C(2)-C(1)-Cl(3)	106.6(6)	O(1)-C(2)-C(1)	110.5(8)
N(1)-C(3)-C(2)	118.0(9)	C(3)-C(2)-O(1)	110.5(8)
C(3)-C(2)-C(1)	106.3(8)		

Symmetry transformations used to generate equivalent atoms: #1 -x, y, -z+1/2.

Table S5 Selected structural data for 2 under 293K

Bond lengths / Å and bond angles / °

Mn(1)-Cl(1)	2.3591 (17)	Mn(1)-Cl(1)#1	2.3591(17)
Mn(1)-Cl(2)	2.3756 (19)	Mn(1)-Cl(2)#1	2.3756(19)

Cl(3)-C(1)	1.766 (4)	Cl(3A)-C(1A)	1.7458(4)
C(1)-C(2)	1.519 (4)	C(1A)-C(2A)	1.551(4)
C(3)-C(2)	1.489 (5)	C(3A)-C(2A)	1.469(5)
N(1)-C(3)	1.488 (4)	N(1A)-C(3A)	1.521(4)
N(1)-C(4)	1.496 (6)	N(1A)-C(4A)	1.493(5)
N(1)-C(5)	1.494 (6)	N(1A)-C(5A)	1.496(6)
N(1)-C(6)	1.501 (6)	N(1A)-C(6A)	1.508(6)
C(2)-O(1)	1.499 (5)	C(2A)-O(1A)	1.487(5)
Cl(1)-Mn(1)-Cl(1)#1	109.15 (8)	Cl(1)#1-Mn(1)-Cl(2)	110.78(8)
Cl(1)#1-Mn(1)-Cl(2)#1	107.99 (8)	Cl(1)-Mn(1)-Cl(2)	107.99(8)
Cl(1)-Mn(1)-Cl(2)#1	110.78 (8)	Cl(2)#1-Mn(1)-Cl(2)	110.16(9)
C(3)-N(1)-C(5)	102.6 (4)	C(5A)-N(1A)-C(3A)	98.8(4)
C(3)-N(1)-C(4)	126.8 (4)	C(4A)-N(1A)-C(3A)	101.4(4)
C(3)-N(1)-C(6)	115.3 (4)	C(6A)-N(1A)-C(3A)	111.6(3)
C(5)-N(1)-C(4)	117.4 (4)	C(4A)-N(1A)-C(5A)	97.7(6)
C(4)-N(1)-C(6)	82.2 (5)	C(4A)-N(1A)-C(6A)	126.3(5)
C(5)-N(1)-C(6)	111.4 (5)	C(5A)-N(1A)-C(6A)	116.7(6)
C(2)-C(1)-Cl(3)	114.7 (3)	C(2A)-C(1A)-Cl(3A)	112.04(18)
O(1)-C(2)-C(1)	109.3 (4)	O(1A)-C(2A)-C(1A)	106.4(3)
N(1)-C(3)-C(2)	115.2 (3)	C(2A)-C(3A)-N(1A)	109.8(3)
C(3)-C(2)-O(1)	111.0 (3)	C(3A)-C(2A)-O(1A)	111.9(4)
C(3)-C(2)-C(1)	108.0 (3)	C(3A)-C(2A)-C(1A)	110.9(3)

Symmetry transformations used to generate equivalent atoms: #1 -x, y, -z+1/2.