Supporting Information

Challenge in Optoelectronic Duple Switches: A Red Emission Large-size Single Crystal and Unidirectional Flexible Thin Film in a Hybrid Multifunctional Material

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Table S1 Crystal data and structure refinement for compound **1** at 293K and 103K

	HTP(293K)	LTP(103K)
Empirical formula	$[N(NH_2CH_2CH_2)_3]_2Mn_2Cl_{12}$	$[N(NH_2CH_2CH_2)_3]_2Mn_2Cl_{12}$
Formula weight	1164.78	1164.78
Temperature(K)	293(2)	103(2)
Crystal system	trigonal	trigonal
Space group	*R*-3*c*	*R*-3*c*
a/ Å	10.0000(5)	9.6566(7)
b/ Å	10.0000(5)	9.6566(7)
c/ Å	73.0000(73)	72.509(2)
Volumn(Å3)	6322	5855.6
Z	6	6
Radiation type	Mo-Ka	Mo-Ka
Absorption correction	Semi-empirical	Semi-empirical
D_{calc} / g cm^{-3}	2.000	1.982
F(000)	3648	3166
Completeness to θ (%)	82.6	99
R1/wR2[I > 2σ(I)]	0.0894/0.2574	0.0973/0.3304
R1/wR2(all data)	0.0917/0.2587	0.1101/0.3433
GOF	1.373	3.924

Table S2 Selected structural data for **1** under 293 K

Selected bond lengths (Å)			
Mn2−Cl3^{i}	2.649(12)	N1−C2	1.578(7)
Mn2−Cl3^{ii}	2.649(12)	N1−C2^{x}	1.578(7)

Mn2−Cl3^{iii}	2.649(12)	C1−C2	1.552(7)
Mn2−Cl3^{iv}	2.649(12)	N3−C3^{xi}	1.608(7)
Mn2−Cl3	2.649(12)	N3−C3	1.608(7)
Mn2−Cl3^{v}	2.649(12)	N3−C3^{xii}	1.608(7)
Mn1−Cl2	2.468(12)	C3−C4	1.480(7)
Mn1−Cl2^{vi}	2.468(12)	C4−N4	1.611(7)
Mn1−Cl2^{vii}	2.468(12)	N3'−C3'^{xi}	1.717(8)
Mn1−Cl1^{viii}	2.700(3)	N3'−C3'	1.717(8)
Mn1−Cl1	2.700(3)	N3'−C3'^{xii}	1.717(8)
N2−C1	1.533(7)	C3'−C4'	1.455(13)
N1−C2^{ix}	1.533(7)	C4'−N4'	1.606(8)

Symmetry codes used to generate equivalent atoms: (i) *y*, −*x*+*y*+1, −*z*; (ii) *x*−*y*+1, *x*, −*z*; (iii) −*x*+2, −*y*+2, −*z*; (iv) −*y*+2, *x*−*y*+1, *z*; (v) −*x*+*y*+1, −*x*+2, *z*; (vi) −*y*, *x*−*y*+1, *z*; (vii) −*x*+*y*−1, −*x*, *z*; (viii) *y*−2/3, *x*+2/3, −*z*+1/6; (ix) −*x*+*y*−1, −*x*−1, *z*; (x) −*y*−1, *x*−*y*, *z*; (xi) −*y*+1, *x*−*y*, *z*; (xii) −*x*+*y*+1, −*x*+1, *z*.

Table S3 Hydrogen bonds under 293 K

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
N(4')−H(4'C)···N(3')#11	0.891	2.753	2.8257(13)	137.1
Cl(3)−H(4'E)···N(4')#12	2.092	0.924	2.7188(13)	125.3
N(4)−H(4C)···N(3)#11	0.916	2.251	2.7729(13)	110.6
Cl(3)−H(4B)···N(4)#11	2.558	1.188	3.2370(15)	128.4
N(1)−H(2C)···Cl(4)#15	0.913	2.541	3.2999(15)	141.7

Symmetry transformations used to generate equivalent atoms:

#1-x+2, -y+2, -z #2 y, -x+y+1, -z #3 -y+2, x-y+1, z

#4x-y+1, x, -z #5 -x+y+1, -x+2, z #6 -y+1, x-y, z

#7-x+y+1, -x+1, z #8 y+1/3, x-1/3,-z+1/6 #9 -x+y, -x+1, z

#10-y+1, x-y+1, z #11 -x+1, -y, -z #12 x-y, x, -z

#13-y, x-y, z #14 x-1, y, z #15 y-2/3, x-1/3, -z+1/6

Table S4 Selected structural data for **1** under 103 K

Selected bond lengths (Å)

N1−C1	1.465(6)	Mn1−Cl2^{viii}	2.3756(17)
N2−C2^{i}	1.507(5)	Mn1−Cl2^{ix}	2.3756(17)
N2−C2	1.507(5)	Mn1−Cl2	2.3756(17)
N2−C2^{ii}	1.507(5)	Mn1−Cl1^{x}	2.671(3)
C1−C2	1.518(6)	Mn1−Cl1	2.672(3)
Mn2−Cl3^{iii}	2.5605(11)	C4−C3	1.414(12)
Mn2−Cl3	2.5605(11)	C4−N4	1.495(14)
Mn2−Cl3^{iv}	2.5605(11)	N3−C3^{viii}	1.181(12)
Mn2−Cl3^{v}	2.5605(11)	N3−C3	1.181(12)
Mn2−Cl3^{vi}	2.5605(11)	N3−C3^{ix}	1.181(12)
Mn2−Cl3^{vii}	2.5605(11)		

Table S5 Hydrogen bonds under 103 K

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
N4−H4*C*···Cl3^{viii}	0.91	1.80	2.55 (2)	139
N1−H1*C*···Cl1^{xi}	0.91	2.37	3.273 (5)	171
N1−H1*A*· ·Cl4	0.91	2.43	3.194 (5)	141

Symmetry codes: (vi) −*y*, *x*−*y*, *z*; (viii) −*y*+1, *x*−*y*, *z*; (xi) *x*−1, *y*, *z*; (xii) *x*, *y*−1, *z*.

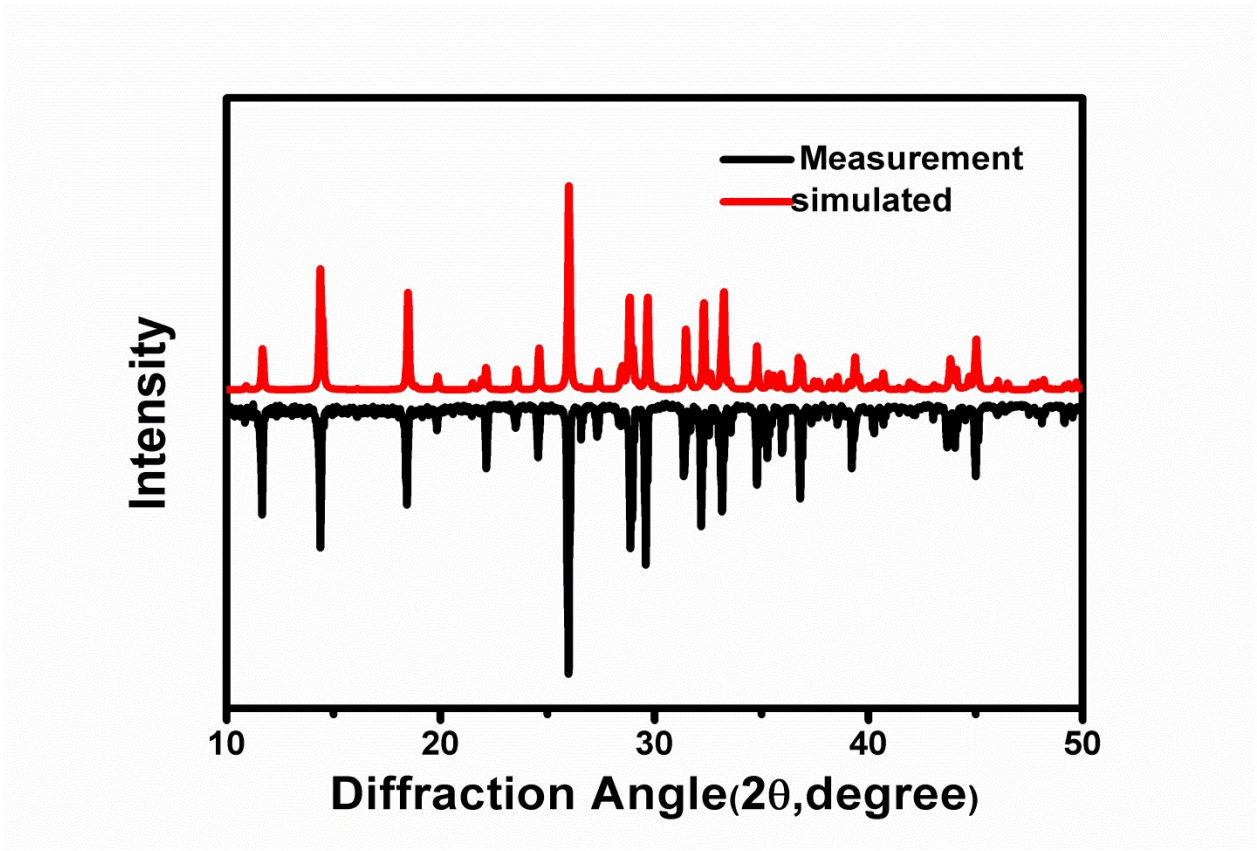

Figure S1 The powder X-ray diffraction (PXRD) pattern for compound **1**

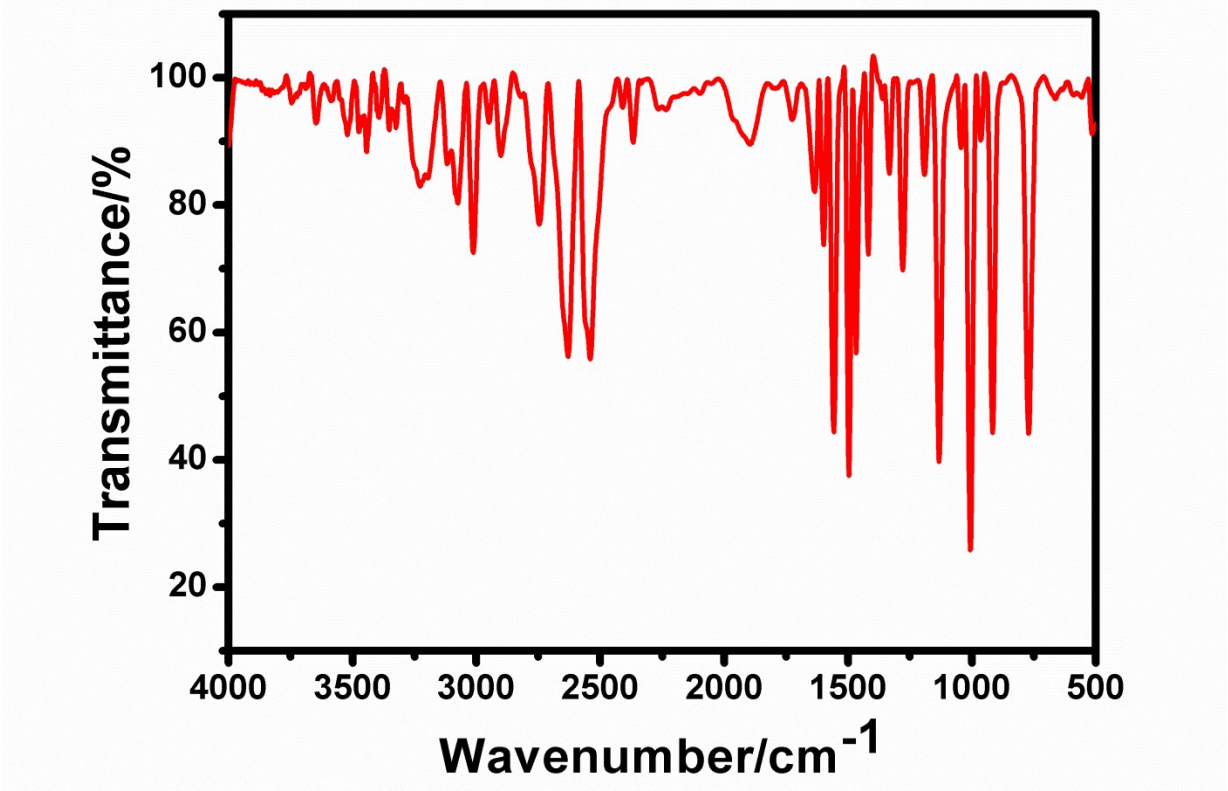

Figure S2 The IR spectrum for compound **1**

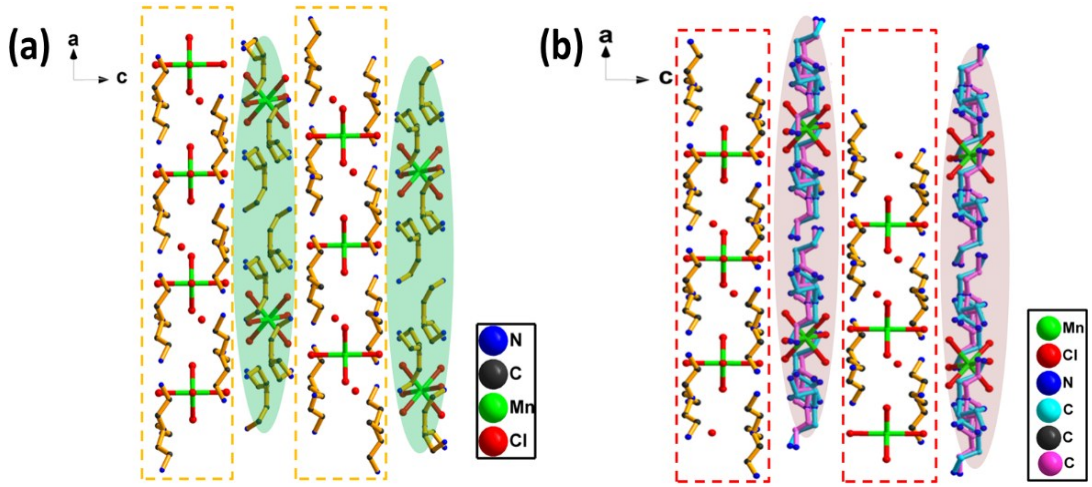

Figure S3. Packing diagram of compound **1** viewed along the b axis at LTP (a) and at HTP (b). The compound **1** has two different layer structures. All hydrogen atoms are omitted for clarity.

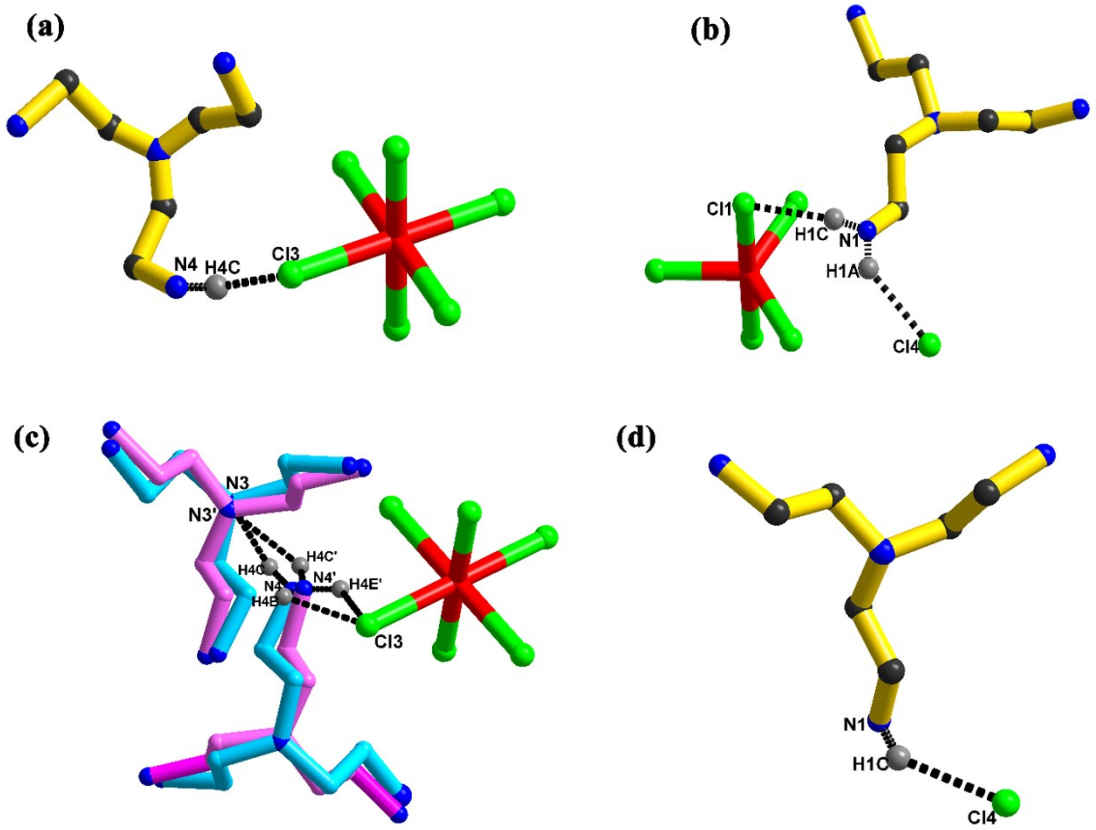

Figure S4. The views of the hydrogen bonding interactions between anion and amine shown at LTP (a)(b) and HTP (c)(d). At the LTP, the TAEA cations established N1−H···Cl1 hydrogen bond and N1−H···Cl4 hydrogen bond to the $[MnCl_5]^{3-}$. And the TAEA cations formed N4−H-Cl3 hydrogen bond to the $[MnCl_6]^{4-}$. But in the HTP, the amine group of the TAEA cations only formed N1−H···Cl4 hydrogen bond to the $[MnCl_5]^{3-}$ and formed Cl3···H−N4 and Cl3···H'−N4' hydrogen bonds to the

$[MnCl_6]^{4-}$, N4−H···N3 and N4'−H···N3' to the neighbouring TAEA cations.