Supporting information

Ultra high phase transition temperature in a metal-halide perovskite-type material containing unprecedented hydrogen bonding interactions

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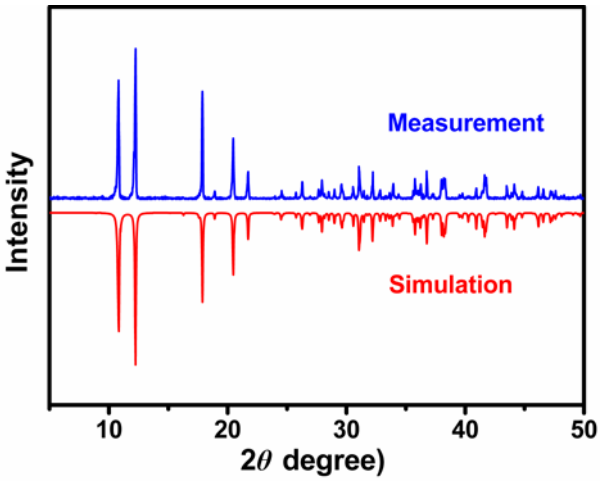

Fig. S1 PXRD patterns of **1** measured at 293 K matching very well with the simulated ones.

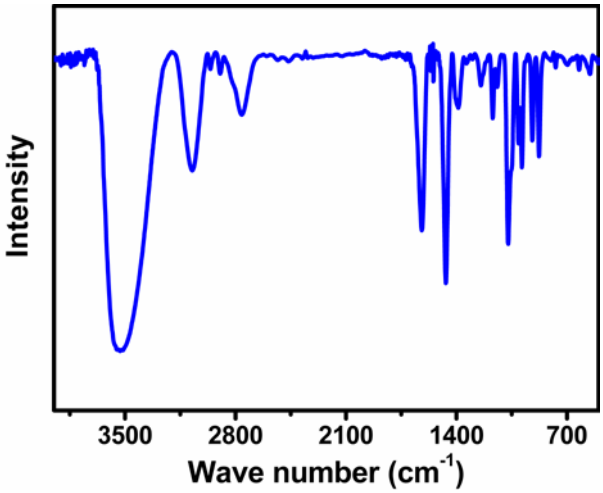

Fig. S2 Infrared (IR) spectra of solid compound **1** in KBr pellet was recorded on a Shimadzu model IR-60 spectrometer at room temperature.

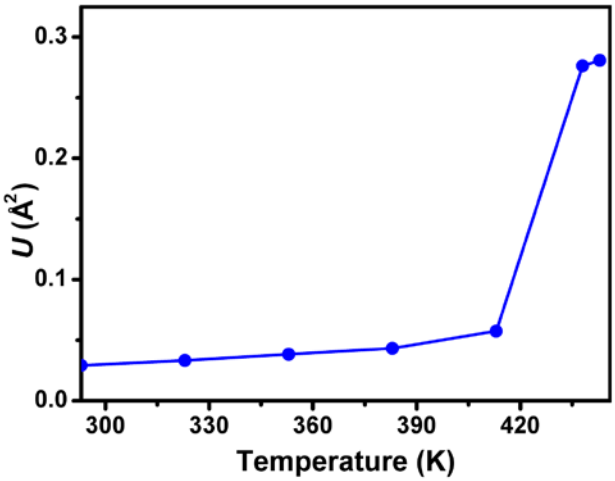

Fig. S3 Temperature-dependent plots of U values (in $Å^2$) of N atoms in DMEA cations.

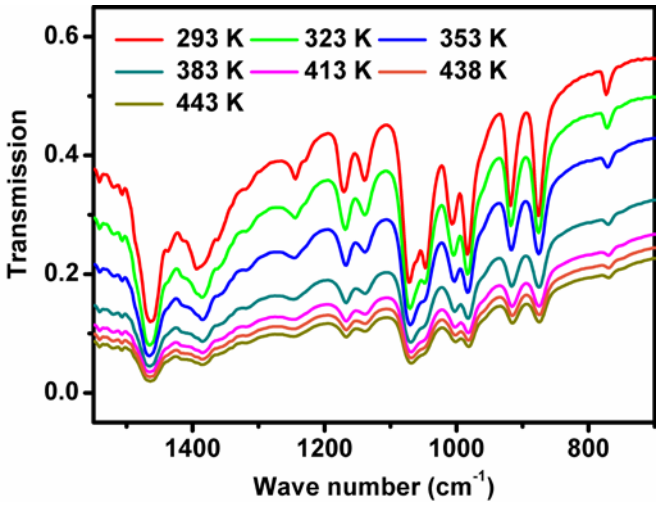

Fig. S4 Temperature dependence of the infrared spectrum of compound **1** in KBr pellet in the region 1550-700 cm^{-1}.

Table S1 Crystal Data and Structure Refinement Details for **1.**

Empirical formula	$[C_4H_{12}NO]CdCl_3$			
T (K)	293 K	323 K	353K	383K
Formula	308.91	308.91	308.91	308.91
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	9.9590(3)	9.9729(5)	9.9895(3)	10.0135(3)
b/Å	14.4583(4)	14.4775(7)	14.5119(5)	14.5453(5)
c/Å	6.8309(2)	6.8340(3)	6.8343(2)	6.8362(2)
β (deg)	95.416(3)	95.483(4)	95.516(3)	95.509(3)
V/Å^3	917.19(5)	982.20(8)	986.16(5)	991.09(5)
Z	4	4	4	4
F(000)	600	600	600	600
Unique reflections	1716	1724	1733	1739
Parameters refined	95	95	94	94
GOF	1.058	1.052	1.121	1.094
R_1	0.0279	0.0489	0.0447	0.0346
wR_2	0.0690	0.1400	0.1291	0.0950
T (K)	413 K	438 K	443 K	
Formula	308.91	308.91	308.91	
Crystal system	monoclinic	monoclinic	orthorhombic	
Space group	$P2_1/c$	*Pnma*	*Pnma*	
a/Å	10.0482(5)	14.9224(15)	14.9615(14)	
b/Å	14.6113(7)	6.7659(6)	6.7750(4)	
c/Å	6.8335(3)	10.0562(11)	10.0904(9)	
β (deg)	95.511(4)	90	90	
V/Å^3	998.64(8)	1015.31(18)	1022.81(15)	
Z	4	4	4	
F(000)	600	600	600	
Unique reflections	1752	971	978	
Parameters refined	94	55	58	
GOF	1.076	1.101	1.072	
R_1	0.0414	0.0737	0.041	
wR_2	0.1248	0.2244	0.138	

Table S2 Selected bond lengths [Å] and angles [°] for compound **1** at 293 K.

293 K	Cd(1)-Cl(1)	2.6118(6)	Cd(1)-Cl(1)#1	2.6270(7)
	Cd(1)-Cl(2)#1	2.6336(7)	Cd(1)-Cl(2)	2.6478(7)
	Cd(1)-Cl(3)#1	2.6897(7)	Cd(1)-Cl(3)	2.6905(7)
	Cl(1)-Cd(1)#2	2.6270(7)	Cl(2)-Cd(1)#2	2.6336(7)
	Cl(3)-Cd(1)#2	2.6897(7)		
	Cl(1)-Cd(1)-Cl(1)#1	170.16(3)	Cl(1)-Cd(1)-Cl(2)#1	101.22(2)
	Cl(1)#1-Cd(1)-Cl(2)#1	85.09(2)	Cl(1)-Cd(1)-Cl(2)	85.10(2)
	Cl(1)#1-Cd(1)-Cl(2)	101.83(2)	Cl(2)#1-Cd(1)-Cl(2)	96.35(3)
	Cl(1)-Cd(1)-Cl(3)#1	91.82(2)	Cl(1)#1-Cd(1)-Cl(3)#1	81.51(2)
	Cl(2)#1-Cd(1)-Cl(3)#1	82.03(2)	Cl(2)-Cd(1)-Cl(3)#1	176.19(2)
	Cl(1)-Cd(1)-Cl(3)	81.77(2)	Cl(1)#1-Cd(1)-Cl(3)	92.24(2)
	Cl(2)#1-Cd(1)-Cl(3)	176.35(2)	Cl(2)-Cd(1)-Cl(3)	81.75(2)
	Cl(3)#1-Cd(1)-Cl(3)	100.06(3)		

Symmetry codes: #1 x, -y+1/2, z-1/2; #2 x, -y+1/2, z+1/2.

Table S3 Selected bond lengths [Å] and angles [°] for compound **1** at 443 K.

443K	Cd(1)-Cl(2)	2.6193(16)	Cd(1)-Cl(2)#2	2.6193(16)
	Cd(1)-Cl(1)	2.6448(15)	Cd(1)-Cl(1)#2	2.6448(15)
	Cd(1)-Cl(3)	2.6546(17)	Cd(1)-Cl(3)#2	2.6546(17)
	Cl(1)-Cd(1)#4	2.6448(15)	Cl(2)-Cd(1)#3	2.6193(16)
	Cl(3)-Cd(1)#4	2.6546(17)		
	Cl(2)-Cd(1)-Cl(2)#2	180.0	Cl(2)-Cd(1)-Cl(1)#2	83.80(6)
	Cl(2)#2-Cd(1)-Cl(1)#2	96.20(6)	Cl(2)-Cd(1)-Cl(1)	96.20(6)
	Cl(2)#2-Cd(1)-Cl(1)	83.80(6)	Cl(1)#2-Cd(1)-Cl(1)	180.0
	Cl(2)-Cd(1)-Cl(3)	97.16(6)	Cl(2)#2-Cd(1)-Cl(3)	82.84(6)
	Cl(1)#2-Cd(1)-Cl(3)	96.94(6)	Cl(1)-Cd(1)-Cl(3)	83.07(6)
	Cl(2)-Cd(1)-Cl(3)#2	82.84(6)	Cl(2)#2-Cd(1)-Cl(3)#2	97.16(6)
	Cl(1)#2-Cd(1)-Cl(3)#2	83.07(6)	Cl(1)-Cd(1)-Cl(3)#2	96.93(6)
	Cl(3)-Cd(1)-Cl(3)#2	180.0		

Symmetry codes: #1 x, -y+1/2, z; #2 -x+2, -y+1, -z+1; #3 -x+2, y+1/2, -z+1; #4 -x+2, y-1/2, -z+1.

Table S4 Hydrogen bond geometry (Å, degree) at 293 K and 443 K in compound **1**.

	D-H···A	H···A[Å]	D···A[Å]	D-H···A [°]
293 K	O(1)-H(1)...Cl(3)#2	2.30	3.101(3)	165.9
	N(1)-H(1E)...O(1)#2	2.08	2.884(3)	146.0
443 K	N(1)-H(1A)...Cl(3)#6	2.74	3.619(18)	166.1
	O(1)-H(1)...Cl(3)#7	2.81	3.49(2)	137.8

Symmetry codes: #2 x, -y+1/2, z+1/2 (293 K), #6 x-1/2, y, -z+1/2 (443 K), #7 -x+3/2, -y+1, z+1/2 (443 K).