Supporting Information

[C$_5$H$_{12}$N]CdCl$_3$: An ABX$_3$ Perovskite–type Semiconducting Switchable Dielectric Phase Transition Material

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Calculation of '∆S' and 'N' For MPCC

Figure S1. Experimental and simulated PXRD Patterns of **MPCC**, verifying the phase purity.
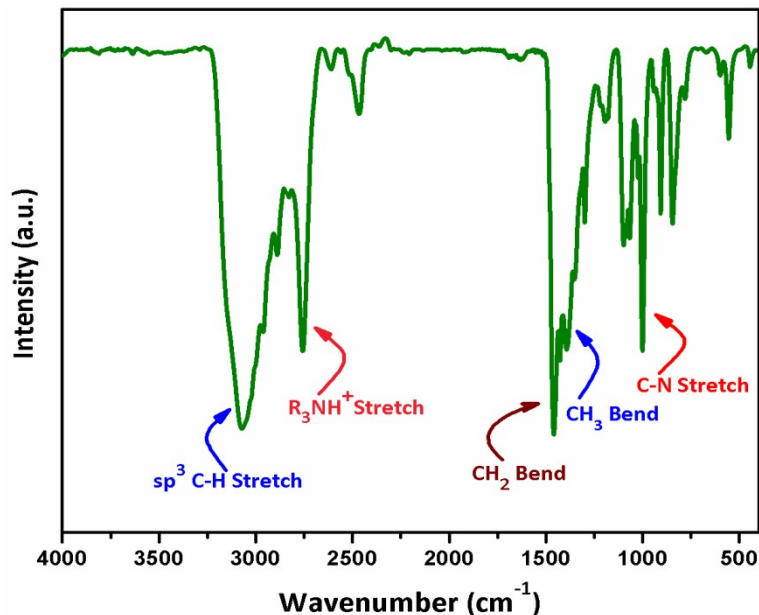
Figure S2. IR Spectrum of **MPCC**, verifying the phase purity.

Table S1. IR spectrum of **MPCC** displays characteristics peaks for stretching and bending vibrations

Group	Stretching Vibration (cm^{-1})
sp^3 C-H	3070
C-N	995
Tertiary amine salt (R_3NH^+)	2750
Group	**Bending Vibration (cm^{-1})**
Methyl (CH$_3$-)	1460
Methylene (-CH$_2$-)	1390
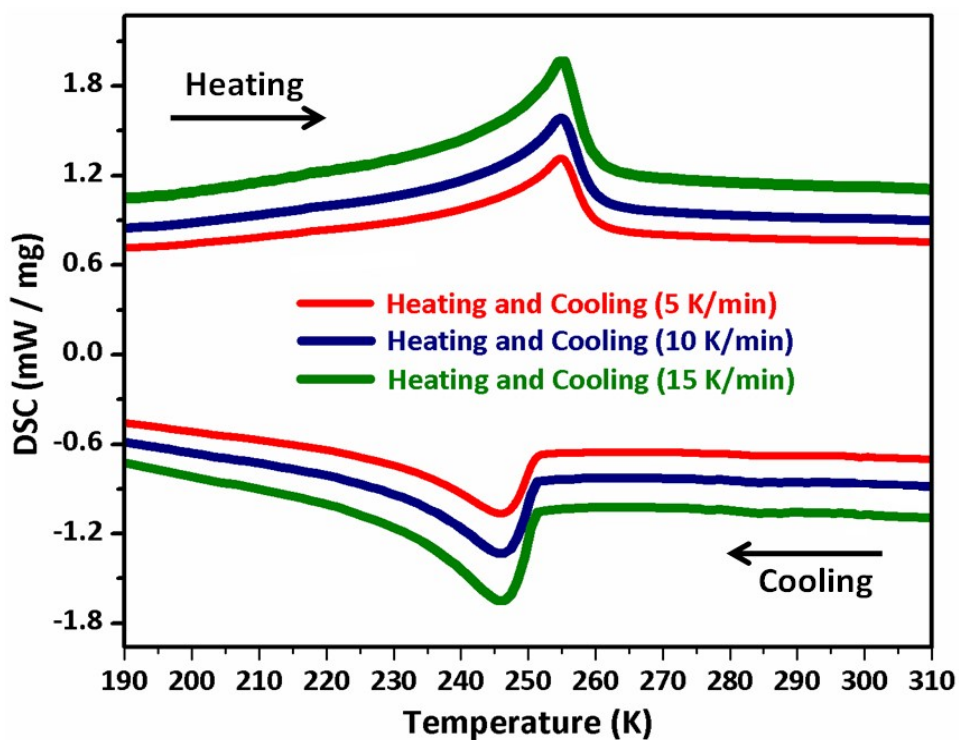
Figure S3. DSC curves of **MPCC** at different scanning rates (5 K/min, 10 K/min, and 15 K/min).
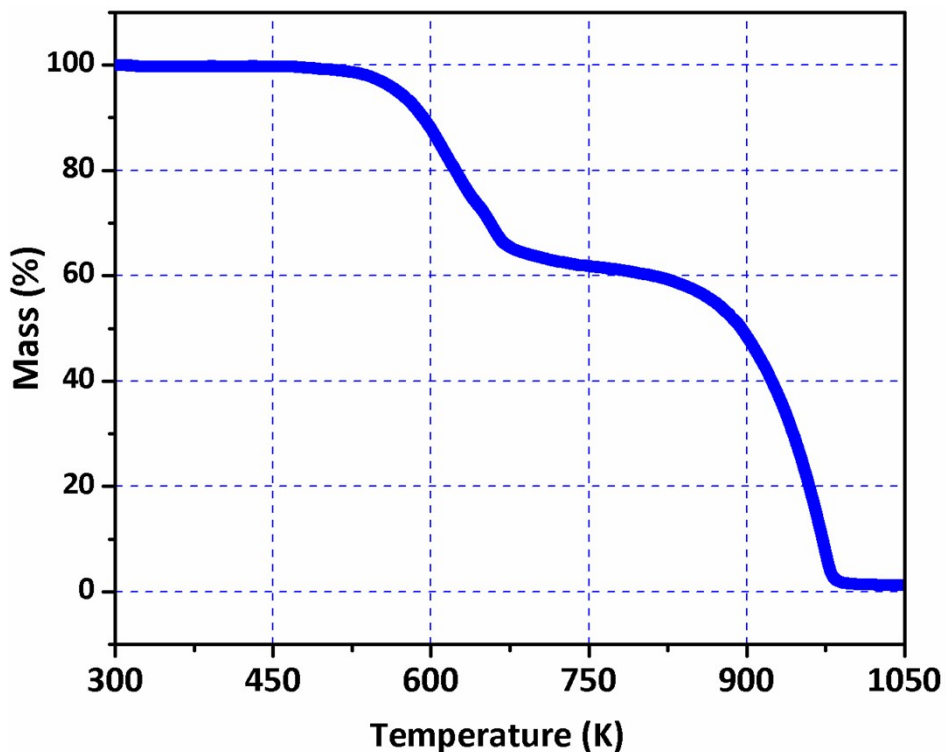
Figure S4. Thermo-Gravimetric Analysis (TGA) spectrum of **MPCC**, shows its high thermal stability.
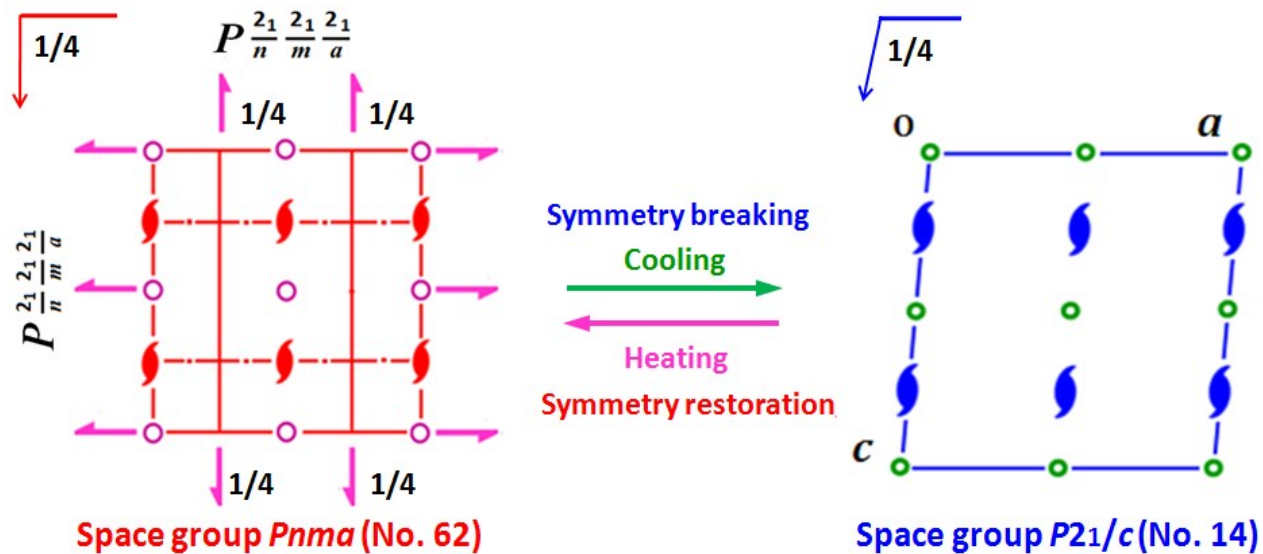
Figure S5. Symmetry breaking process in **MPCC** occurring from *Pnma* (HTP) to $P2_1/n$ (LTP).
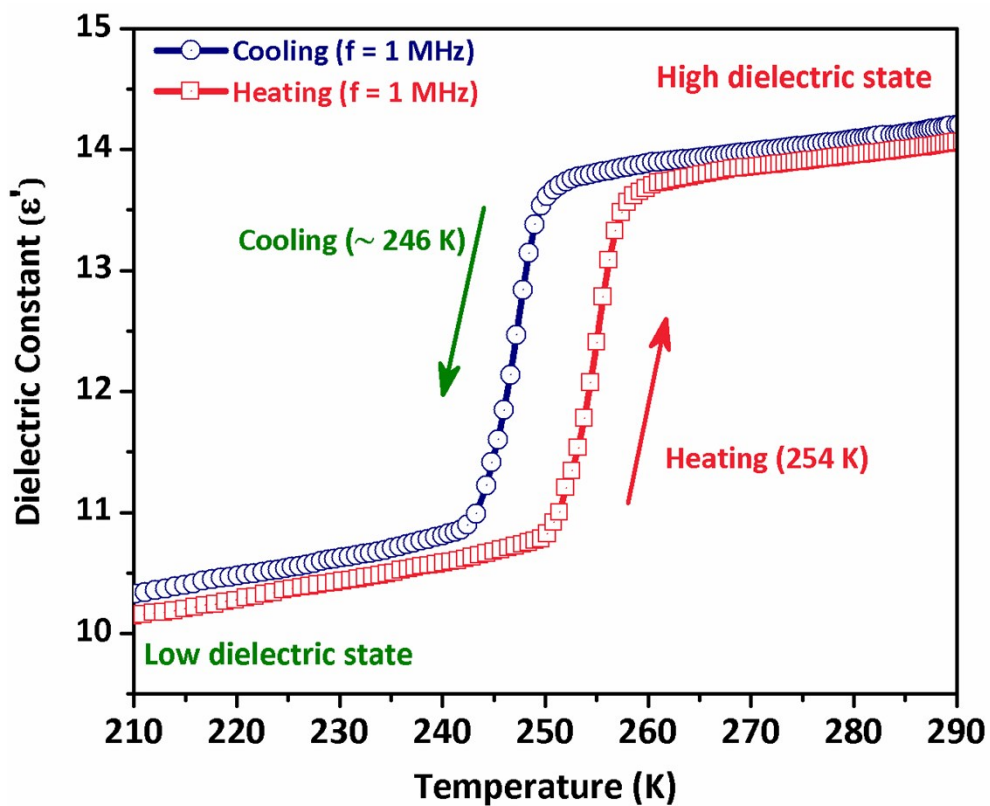
Figure S6. Temperature-dependent cycle of dielectric constant at 1 MHz for **MPCC**, displaying its switchable dielectric property.

Figure S7. UV–vis diffuse reflectance spectroscopy result of **MPCC**.
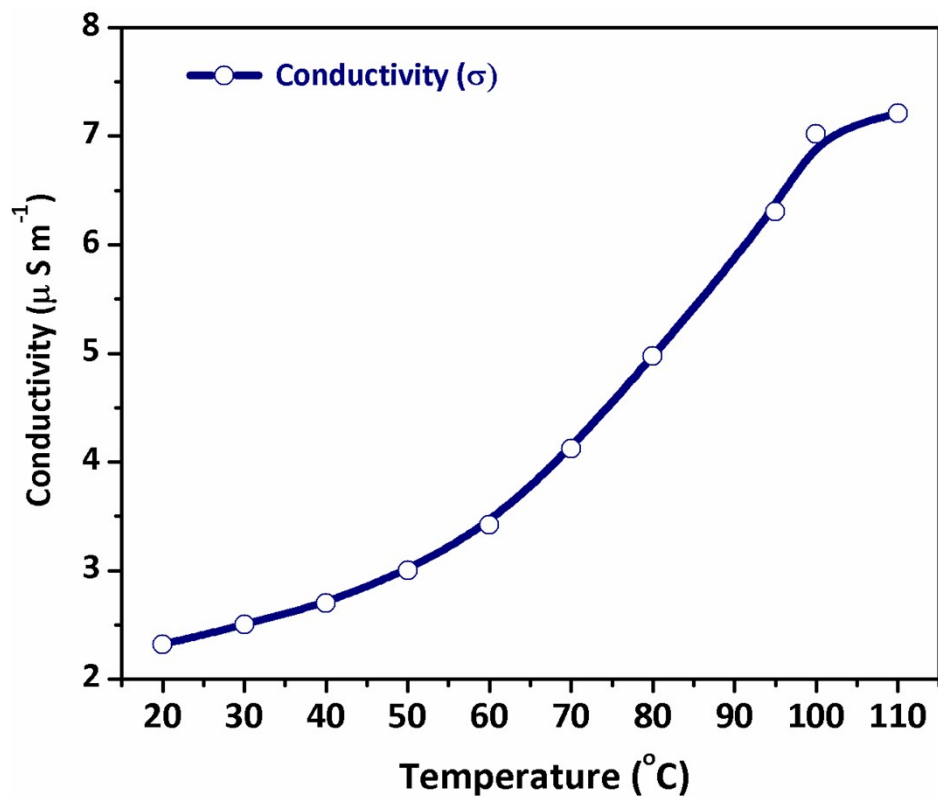
Figure S8. Temperature-dependent conductivity of **MPCC**, showing its semiconducting behaviour.

Table S2. The SCXRD data and structure refinement details of **MPCC** at 280 K and 230 K.

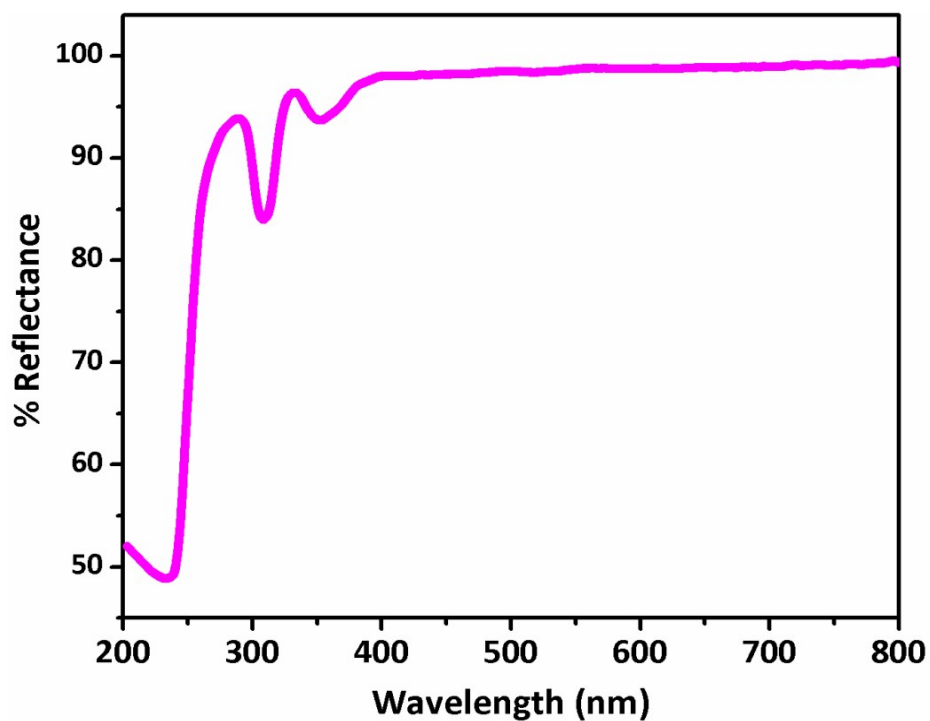|		
Temperature (K)	280 K, Mo-$K\alpha$	230 K, Cu-$K\alpha$
Sum formula	$C_5 H_{12} Cd Cl_3 N_1$	$C_5 H_{12} Cd Cl_3 N_1$
Moiety formula	$C_5 H_{12} N$, $Cd Cl_3$	$C_5 H_{12} N$, $Cd Cl_3$
Formula Weight	304.91	304.91
Crystal system	Orthorhombic	Monoclinic
	Pnma	*P 2$_1$/c*
Cell parameters	a= 14.8934 (10) Å	a= 6.6875 (4) Å
	b= 6.7188 (3) Å	b= 10.0809 (5) Å
	c= 9.9423 (5) Å	c= 14.5347 (10) Å
	α= 90°	α= 90°
	β= 90°	β= 92.298(5)°
	γ= 90°	γ= 90°
Volume (Å^3)	994.88(9)	979.08(10)
Z	4	4
ρcal. (g/cm^3)	2.036	2.069
F(000)	592.0	592.0
Theta range (°)	3.9110-28.3620	5.3250 - 72.5490
Limiting indices	-13<=h<=18,	-7<=h<=7,
	-8<=k<=8,	-12<=k<=12,
	-12<=l<=12	-17<=l<=17
Completeness	99.8%	98.8%
GOF	1.043	1.177
R_1 [on $F_\circ^2$ $I > 2\sigma(I)$]	0.0320 (849)	0.0961 (1417)
wR_2 [on $F_\circ^2$ $I > 2\sigma(I)$]	0.0777 (1106)	0.2680 (1699)

$\alpha R_1 = \Sigma\ [(F_o) - (F_c)]\ /\ \Sigma\ [F_o]$, w$R_2 = [\Sigma\ (|F_o|^2 - |F_c|^2)\ /\ \Sigma|F_o|^2]^{1/2}$

Table S3. Selected Bond Angles [°] for **MPCC** at 280 K and 230 K

T (K)	Atom- Atom- Atom	Angles [°]	Atom- Atom- Atom	Angles [°]
280 K	Cl4—Cd1—Cl2^{iii}	83.15(4)	Cl3—Cd1—Cl2^{iii}	96.68(4)
	Cl4^{iii} —Cd1—Cl2	83.15(4)	Cl3^{iii}—Cd1—Cl2	96.68(4)
	Cl4^{iii} —Cd1—Cl3	84.92(4)	Cl4—Cd1—Cl3	95.08(5)
	Cl4—Cd1— Cl3^{iii}	84.92(4)	Cl4^{iii}—Cd1—Cl3^{iii}	95.08(4)
	Cl3—Cd1—Cl2	83.31(4)	Cl4^{iii}—Cd1—Cl2^{iii}	96.85(4)
	Cl3^{iii}—Cd1—Cl2^{iii}	83.32(4)	Cl4—Cd1—Cl2	96.85(4)
	Cd1 ‑ Cl2 ‑ Cd1^{i}	78.58(4)	Cl2—Cd1—Cl2^{iii}	180.0
	Cd1^{i} − Cl3 ‑ Cd1	78.82(4)	Cl3—Cd1—Cl3^{iii}	180.0
	Cd1 ‑ Cl4 ‑ Cd1^{ii}	79.83(5)	Cl4^{iii}—Cd1—Cl4	180.0
	Cd1^{i}—Cd1—Cd1^{ii}	180.0		

Symmetry codes:
    i)   1-X, 1/2+Y, 2-Z;
    ii)   1-X, -1/2+Y, 2-Z;
    iii)   1-X, 1-Y, 2-Z;
    iv)   X, 3/2-Y, +Z

T (K)	Atom- Atom- Atom	Angles [°]	Atom- Atom- Atom	Angles [°]
230 K	Cl3—Cd1—Cl4^{ii}	84.19(9)	Cl3—Cd1—Cl4	95.81(9)
	Cl3^{ii}—Cd1—Cl4	84.19(9)	Cl3^{ii}—Cd1—Cl4^{ii}	95.81(9)
	Cl3—Cd1—Cl5	85.23(10)	Cl3—Cd1—Cl5^{ii}	94.77(10)
	Cl3^{ii}—Cd1—Cl5^{ii}	85.23(10)	Cl3^{ii}—Cd1—Cl5	94.77(10)
	Cl4—Cd1—Cl5^{ii}	83.28(9)	Cl4—Cd1—Cl5	96.72(9)
	Cl4^{ii}—Cd1—Cl5	83.28(9)	Cl4^{ii}—Cd1—Cl5^{ii}	96.72(9)
	Cl3^{ii}—Cd2—Cl5^{ii}	84.86(10)	Cl3^{ii}—Cd2—Cl5^{iii}	95.14(10)
	Cl3^{iii}-Cd2-Cl5^{iii}	84.86(10)	Cl3^{iii}—Cd2—Cl5^{ii}	95.14(10)
	Cl4-Cd2-Cl3^{ii}	83.86(9)	Cl4—Cd2—Cl3^{iii}	96.14(9)
	Cl4^{iv}—Cd2—Cl3^{iii}	83.86(9)	Cl4^{iv}—Cd2—Cl3^{ii}	96.14(9)
	Cl4—Cd2—Cl5^{ii}	83.40(9)	Cl4—Cd2—Cl5^{iii}	96.60(9)
	Cl4^{iv}—Cd2—Cl5^{iii}	83.40(9)	Cl4^{iv}—Cd2—Cl5^{ii}	96.60(9)
	Cd2—Cd1—Cd2^{i}	180.0	Cd1^{iii}—Cd2—Cd1	180.0
	Cl3^{ii}—Cd1—Cl3	180.0	Cl3^{ii}—Cd2—Cl3^{iii}	180.0(1)
	Cl4^{ii}—Cd1—Cl4	180.0	Cl4—Cd2—Cl4^{iv}	180.0(8)
	Cl5—Cd1—Cl5^{ii}	180.0	Cl5^{ii}—Cd2—Cl5^{iii}	180.0

Symmetry codes:
    i).   X, Y, Z;
    ii).   1-X,-Y,1-Z;
    iii).   -1+X, Y, Z;
    iv).   -X, -Y, 1-Z

Table S4. Selected Bond Lengths [Å] for **MPCC** at 280 K and 230 K

T (K)	Atom-Atom	Bond length (Å)	Atom-Atom	Bond length (Å)
280 K	Cd1—Cd1^i Cd1—Cd1^{ii} Cd1—Cl2 Cd1—Cl2^{iii} Cd1—Cl3^{iii} Cd1—Cl3 Cd1—Cl4^{iii} Cd1—Cl4	3.35940(15) 3.35940(15) 2.6525(12) 2.6525(12) 2.6458(12) 2.6458(12) 2.6178(13) 2.6178(13)	Cl2—Cd1^{ii} Cl3—Cd1^{ii}	2.6525(12) 2.6458 (12)

	Symmetry codes:
	    i. 1-X, -1/2+Y, 2-Z;
	    ii. 1-X, 1/2+Y, 2-Z;
	    iii. 1-X, 1-Y, 2-Z;
	    iv. X, 3/2-Y, +Z			

T (K)	Atom-Atom	Bond length (Å)	Atom-Atom	Bond length (Å)
230 K	Cd1—Cl3^{ii} Cd1—Cl3 Cd1—Cl4 Cd1—Cl4^{ii} Cd1—Cl5^{ii} Cd1—Cl5 Cd1—Cd2 Cd1—Cd2^i	2.616(3) 2.616(3) 2.628(3) 2.628(3) 2.666(3) 2.666(3) 3.3438(2) 3.3438(2)	Cd2—Cl3^{ii} Cd2—Cl3^{iii} Cd2—Cl4 Cd2—Cl4^{iv} Cd2—Cl5^{ii} Cd2—Cl5^{iii} Cl3—Cd2^i Cl5—Cd2^i Cd2—Cd1^{iii}	2.637(3) 2.637(3) 2.624(3) 2.624(3) 2.663(3) 2.663(3) 2.637(3) 2.663(3) 3.3437(2)

	Symmetry codes:
	    i. X, Y, Z;
	    ii. 1-X, -Y, 1-Z;
	    iii. -1+X, Y, Z;
	    iv. -X, -Y, 1-Z			

Table S5. Hydrogen-Bond Geometry (Å, degree) for the N–H⋯Cl at 280 K and 230 K in **MPCC**

	D–H⋯A	H⋯A [Å]	D⋯A [Å]	D–H⋯A [°]
280 K	N1–H1⋯Cl2	2.275	3.176	170.46
	N2–H2⋯Cl3	2.496	3.397	170.21
230 K	N3–H3⋯Cl5	2.475	3.357	158.4

Calculation of 'ΔS' and 'N' For MPCC:

According to Boltzmann equation:

$\Delta S = nR\ln N$

Where;

ΔS = entropy change, extracted from the C_P data,

R = the universal gas constant,

n = the number of guest particles per mole (n =1, here), and

N = the number of possible orientations for the disordered system.

The ΔS and N values on the heating process of **MPCC** are calculated as follows: [S1]

$$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} \, dT$$

$$\Delta S \cong \frac{\Delta H}{T_c}$$

$$\Delta S = \frac{3.4406 \, J \, g^{-1} \times 304.91 \, g \, mol^{-1}}{255.5 \, K} \quad ; \text{where 304.91 g mol}^{-1} \text{ is a formula weight of } \textbf{MPCC}.$$

$$\Delta S = \frac{1049.07 \, J \, mol^{-1}}{255.5 \, K}$$

$$\Delta S = \textbf{4.114 J} \, mol^{-1}K^{-1}$$

$$\Delta S = R\ln N$$

$$N = e^{(\frac{\Delta S}{R})}$$

$$N = e^{(\frac{4.114 \, J \, mol^{-1}K^{-1}}{8.314 \, J \, mol^{-1}K^{-1}})}$$

$$N = 1.64$$

Reference:

S1. Y.-Z. Tang, Z.-F. Gu, J.-B. Xiong, J.-X. Gao, Y. Liu, B. Wang, Y.-H. Tan and Q. Xu, *Chem. Mater*., 2016*, ***28**, 4476–4482.