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

Supporting Information

Unusual two-step sequential reversible phase transitions with coexistence switchable nonlinear optical and dielectric behaviors in $[(CH_3)_3NCH_2Cl]_2[ZnCl_4]$†

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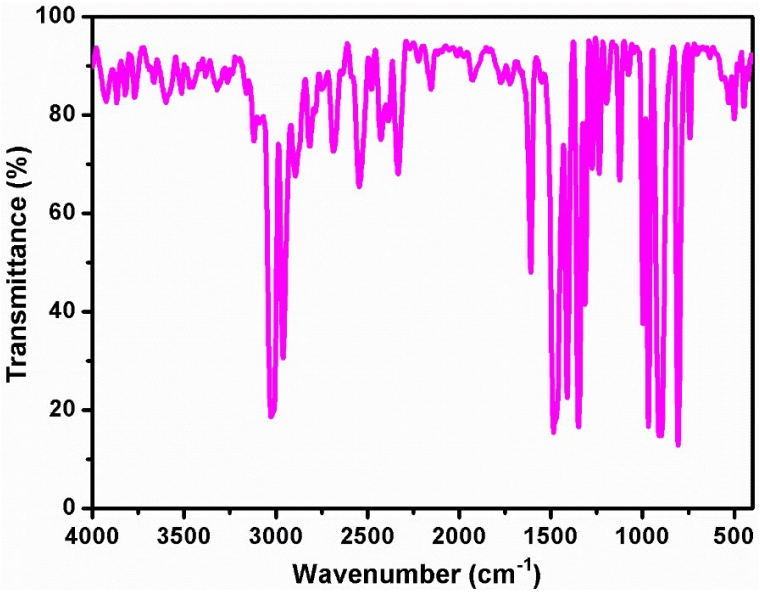

Fig. S1 The IR spectrum of $(TMCM)_2$-$ZnCl_4$ at room temperature.

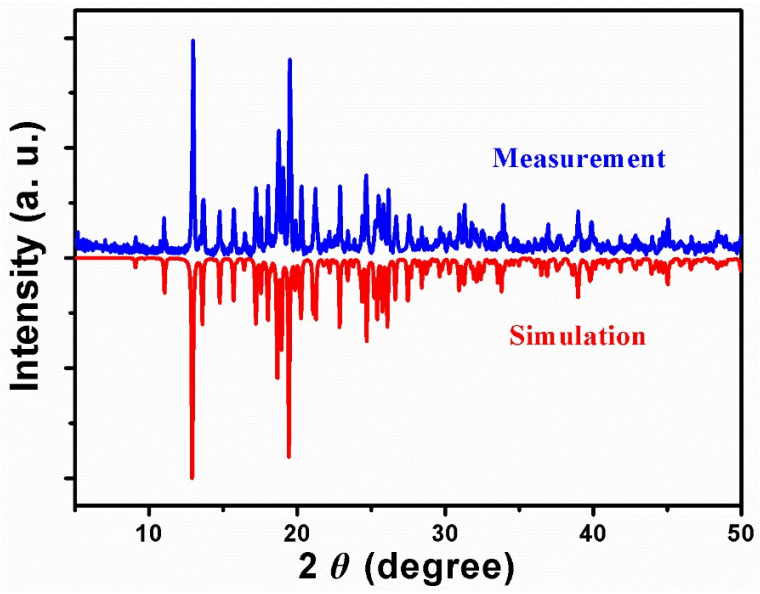

Fig. S2 The PXRD spectra of $(TMCM)_2$-$ZnCl_4$ based on the experiment data (blue line) and the simulation data (red line) at room temperature.

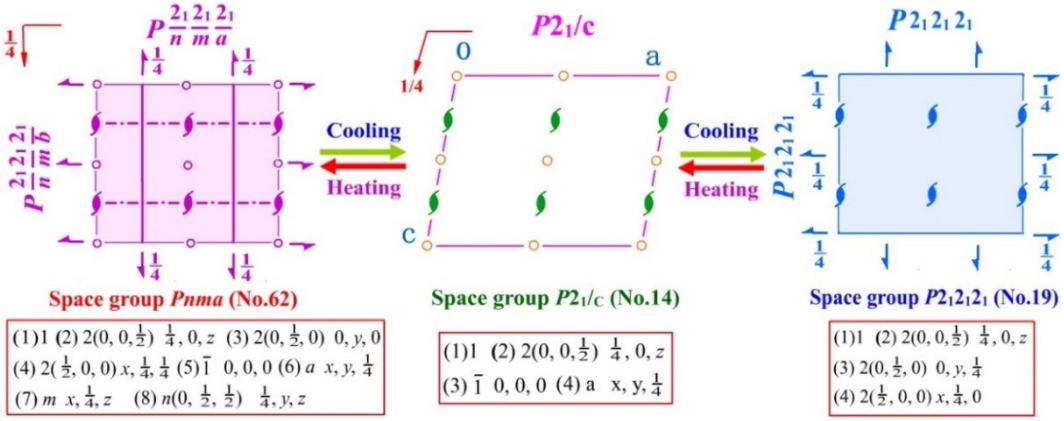

Fig. S3 Spatial symmetry operation change of $(TMCM)_2$-$ZnCl_4$ from the HTP (*P*nma) to the ITP (*P*21/c) the first phase transition and a symmetry breaking symmetry elements from E, C_2, $2C_2'$ (ITP) to E, C_2, σ_h, i (LTP) for the second phase transition.

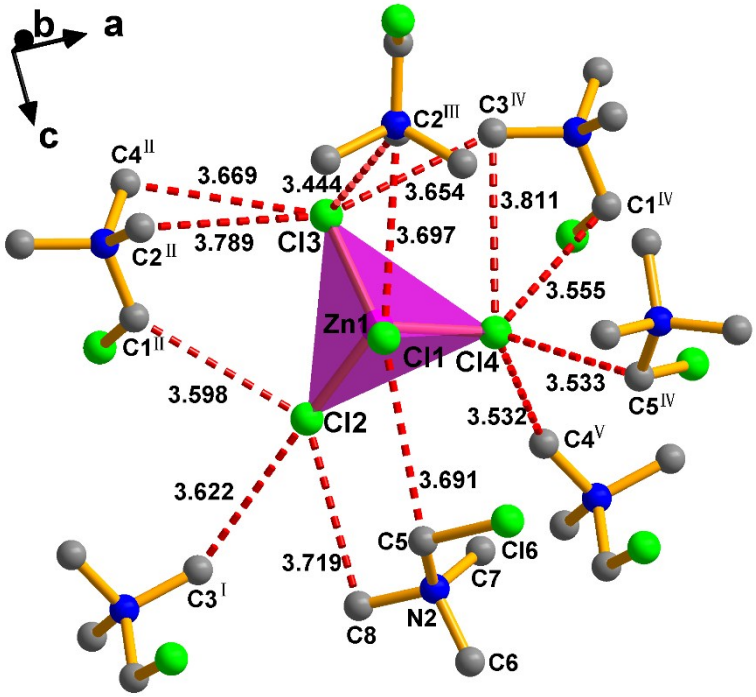

Fig. S4 The hydrogen bonds environment of anion at 223 K.

I -x, y-1/2, -z+1/2; II x-1/2, -y+1/2, -z+1; III x, y, z-1; IV x+1/2, -y+1/2, -z+1; V –x+1, y-1/2, -z+3/2.

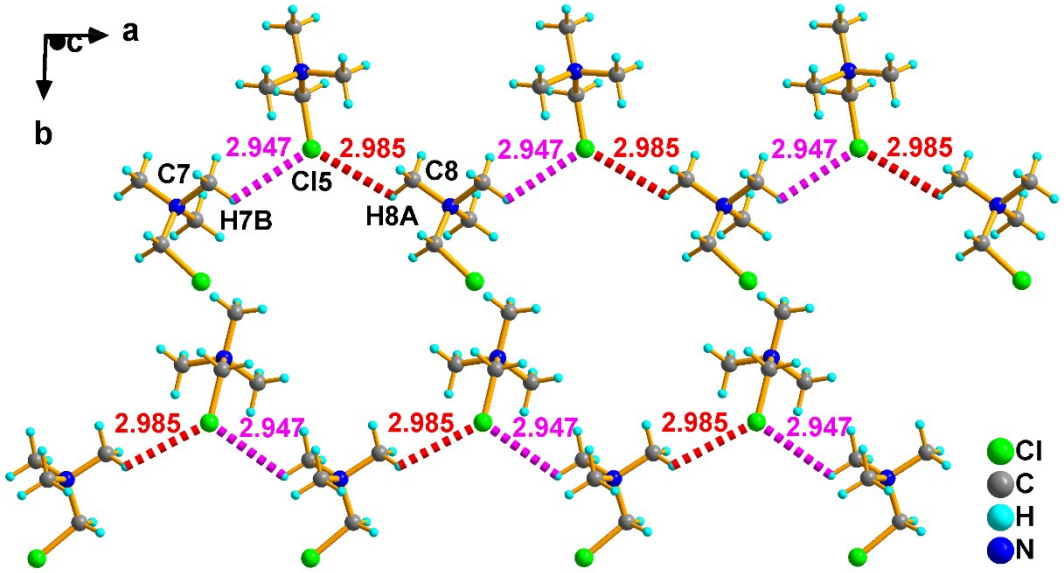

Fig. S5 The hydrogen bonds between cation A and B of $(TMCM)_2$-$ZnCl_4$ along c axis at 223 K.

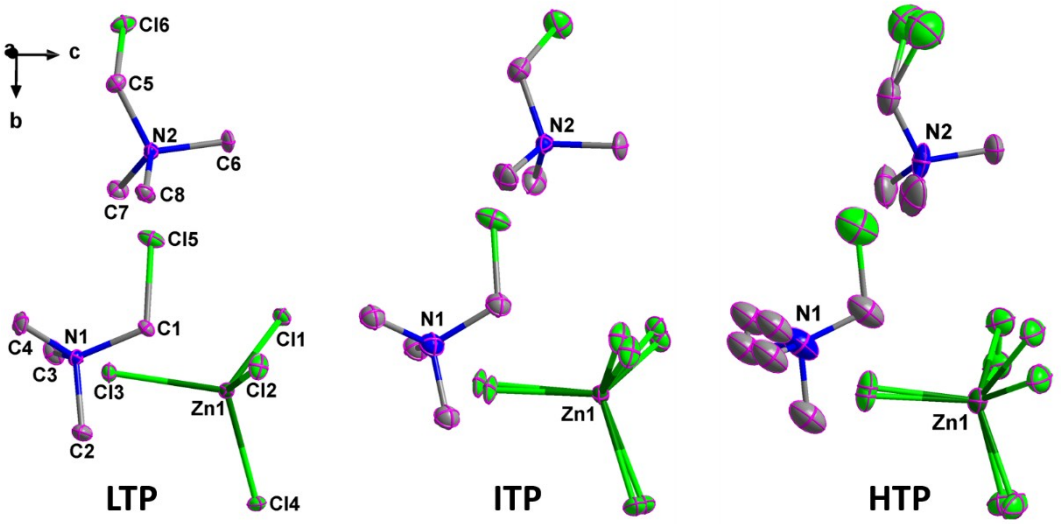

Fig. S6 View of the asymmetric units of $(TMCM)_2$-$ZnCl_4$ obtained at LTP, ITP, HTP showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 10% probability level. C and Cl atoms of cations are labeled to see more clearly.

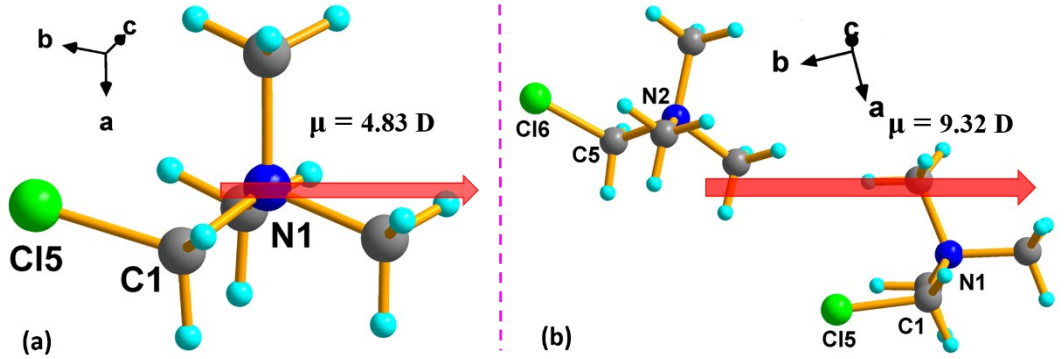

Fig. S7 The dipole moment direction and magnitude of cation A (a) and two cations (b) of $(TMCM)_2$-$ZnCl_4$ at LTP was calculated through GaussView 5.0.9 software.

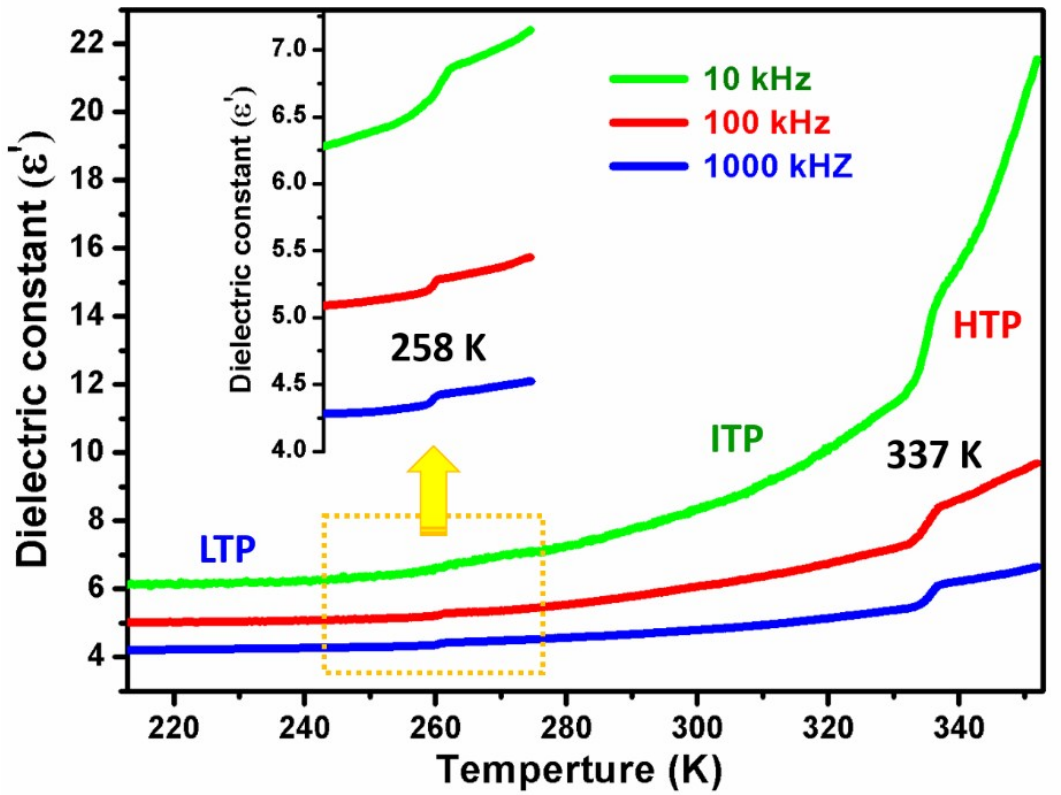

Fig. S8 The temperature-dependence of the real part (ε') of the polycrystalline sample of $(TMCM)_2$-$ZnCl_4$ at 10 kHz, 100 kHz and 1000 kHz.

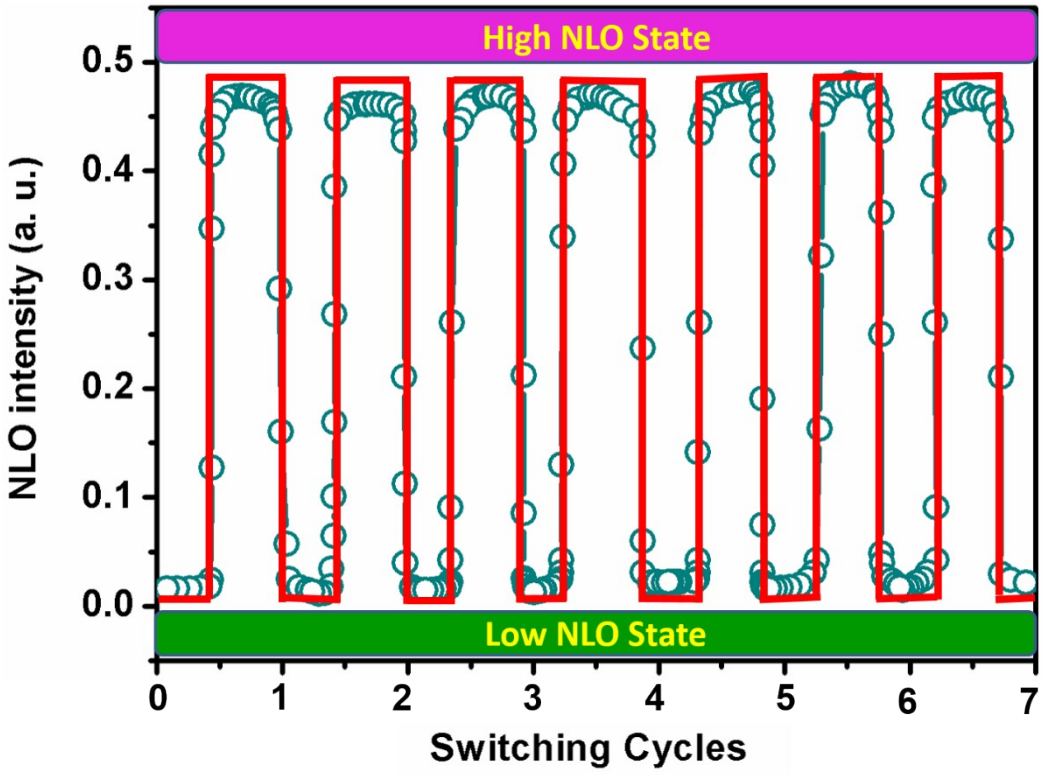

Fig. S9 Completely reversible switching cycles of NLO effects of $(TMCM)_2$-$ZnCl_4$.

Table S1 Crystal data and structure refinement for $(TMCM)_2$-$ZnCl_4$ at 223 K, 293 K, 348 K.

	223 K	293 K	348 K
Empirical formula	$C_8H_{22}Cl_6N_2Zn$	$C_8H_{22}Cl_6N_2Zn$	$C_8H_{22}Cl_6N_2Zn$
Formula weight	424.37	424.37	424.37
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$Pmcn$
a (Å)	8.940(7)	9.140(6)	9.160(11)
b (Å)	16.574(14)	16.708(11)	16.94(2)
c (Å)	12.013(10)	12.008(8)	12.125(14)
α (deg)	90	90	90
β (deg)	90	93.347(12)	90
γ (deg)	90	90	90
Volume (Å^3), Z	1780(3), 4	1831(2), 4	1881(4), 4
D_{calcd} / g cm^{-3}	1.584	1.539	1.499
μ (mm^{-1})	2.264	2.201	2.142
F(000)	864	864	864
Flack parameter	0.44(3)		
Goodness-of-fit on F^2	0.960	1.009	1.020
Tmin/Tmax	0.636 / 0.472	0.644 / 0.482	0.652/0.942
R_1 [a] (> 2σ)	0.0455	0.0786	0.2805
wR_2 [b] (> 2σ)	0.0707	0.2226	0.5218

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2) / \Sigma|F_o|^2]^{1/2}$

Table S2 Hydrogen bonds parameters of $(TMCM)_2$-$ZnCl_4$ at 223 K, 293 K, 348 K.

D-H···A	D-H	H···A	D···A	∠D-H···A
223 K				
C1-H1A...Cl2_#1	0.96	2.84	3.598(8)	136.2
C1-H1B...Cl4_#2	0.96	2.68	3.556(8)	151.9
C2-H2A...Cl3_#1	0.96	2.92	3.790(10)	151.8
C2-H2B...Cl1_#3	0.96	2.79	3.697(9)	158.8
C2-H2B...Cl3_#3	0.96	2.91	3.443(8)	116.0
C3-H3A...Cl3_#2	0.96	2.98	3.654(9)	128.0
C3-H3A...Cl4_#2	0.96	2.98	3.811(10)	145.8
C3-H3C...Cl2_#4	0.96	2.93	3.622(9)	129.7
C4-H4A...Cl3_#1	0.96	2.76	3.669(10)	157.4
C4-H4B...Cl4_#5	0.96	2.86	3.532(8)	128.0
C5-H5A...Cl1	0.96	2.83	3.691(8)	149.1
C5-H5B...Cl4_#2	0.96	2.72	3.534(9)	142.6
C7-H7B...Cl5_#6	0.96	2.95	3.426(9)	112.1
C8-H8A...Cl5_#7	0.96	2.99	3.480(9)	113.4
C8-H8B...Cl2	0.96	2.79	3.720(10)	162.7
293 K				
C(1)-H(1A)...Cl(3')#1	0.97	3.18	3.96(4)	138.9
C(1)-H(1B)...Cl(2)#2	0.97	2.63	3.59(5)	169.1
C(1)-H(1B)...Cl(2')#2	0.97	2.80	3.75(5)	165.5
C(2)-H(2C)...Cl(2')#1	0.96	2.88	3.80(3)	158.8
C(4)-H(4C)...Cl(1)#2	0.96	2.88	3.79(5)	157.2
C(4)-H(4C)...Cl(1')#2	0.96	2.74	3.66(5)	161.9

C(5)-H(5B)...Cl(1)#3	0.97	2.67	3.57(5)	154.6
C(5)-H(5B)...Cl(1')#3	0.97	2.64	3.53(5)	152.6
C(6)-H(6A)...Cl(2')#4	0.96	2.88	3.78(4)	155.9
C(6)-H(6C)...Cl(3)#2	0.96	2.91	3.85(4)	167.6
C(7)-H(7B)...Cl(4')#3	0.96	2.82	3.69(3)	150.9
C(7)-H(7C)...Cl(2)#4	0.96	3.14	4.00(4)	149.9
C(8)-H(8C)...Cl(4)#4	0.96	2.92	3.45(5)	116.0
348K				
C(6)-H(6A)...Cl(3)#3	0.96	2.82	3.72(4)	155.5
C(6)-H(6A)...Cl(3)#4	0.96	2.82	3.72(4)	155.5
C(6)-H(6A)...Cl(1')#4	0.96	3.04	3.56(3)	115.3
C(6)-H(6A)...Cl(1)#4	0.96	2.54	3.08(3)	115.5
C(5')-H(5C)...Cl(1')#5	0.76	3.00	3.61(4)	139.3
C(5')-H(5'C)...Cl(1)#5	0.96	2.76	3.69(4)	163.8
C(5)-H(5C)...Cl(1')#5	0.96	3.00	3.93(5)	163.6
C(5)-H(5C)...Cl(1)#5	0.96	3.14	4.07(5)	163.8
C(5')-H(5'B)...Cl(6)	0.96	2.87	3.36(5)	113.1
C(5)-H(5'B)...Cl(6)	0.46	2.87	2.98(5)	99.4
C(5')-H(5'A)...Cl(3)#3	0.96	2.57	3.49(5)	159.1
C(5')-H(5'A)...Cl(3)#4	0.96	3.00	3.81(6)	143.8
C(5)-H(5A)...Cl(3)#3	0.96	2.88	3.77(5)	153.8
C(5)-H(5A)...Cl(3)#4	0.96	3.19	4.01(5)	144.5
C(5')-H(5C)...Cl(1')#5	0.76	3.00	3.61(4)	139.3
C(5')-H(5'C)...Cl(1)#5	0.96	2.76	3.69(4)	163.8
C(5)-H(5C)...Cl(1')#5	0.96	3.00	3.93(5)	163.6
C(5)-H(5C)...Cl(1)#5	0.96	3.14	4.07(5)	163.8
C(5')-H(5'B)...Cl(2')#6	0.96	3.23	4.06(4)	145.9
C(5')-H(5'B)...Cl(2)#6	0.96	3.00	3.67(4)	128.2
C(5)-H(5'B)...Cl(2')#6	0.46	3.23	3.65(3)	157.9
C(5)-H(5'B)...Cl(2)#6	0.46	3.00	3.40(3)	148.6
C(4)-H(4B)...Cl(2')#2	0.96	2.39	3.34(3)	168.4
C(4)-H(4B)...Cl(2)#2	0.96	2.82	3.73(3)	159.2
C(4)-H(4A)...Cl(2')	0.96	2.39	3.34(3)	168.4
C(4)-H(4A)...Cl(2)	0.96	2.82	3.73(3)	159.2
C(2)-H(2C)...Cl(2)	0.96	2.71	3.63(3)	160.5
C(2)-H(2A)...Cl(2')#7	0.96	2.90	3.80(3)	155.4
C(2)-H(2A)...Cl(2)#7	0.96	2.80	3.75(3)	171.2
C(1)-H(1A)...Cl(3)#8	0.96	3.05	3.70(4)	126.3
C(1)-H(1A)...Cl(3)#7	0.96	2.91	3.70(4)	140.4

Symmetry transformations used to generate equivalent atoms **for 223 K**: #1 x+1/2, -y+1/2, -z+1; #2 x-1/2, -y+1/2, -z+1; #3 x, y, z+1; #4 -x, y+1/2, -z+3/2; #5 -x+1, y+1/2, -z+3/2; #6 -x+1, y-1/2, -z+3/2; #7 -x, y-1/2, -z+3/2; **for 293 K**: #1 -x+1,y-1/2,-z+1/2; #2 x,-y+1/2,z-1/2; #3 x+1,y,z; #4 -x+1,-y+1,-z; **for 348 K**: #1 -x+3/2,y,z; #2 -x+1/2,y,z; #3 x-1/2,-y+2,-z+1; #4 -x+1,-y+2,-z+1; #5 x-1,y,z; #6 -x+1/2,-y+3/2,z-1/2; #7 x,-y+3/2,z-1/2; #8 -x+3/2,-y+3/2,z-1/2.