

Electronic Supplementary Information

Halogen-dependent photoinduced electron transfer and chromism of three protonated nicotinohydrazide halozincates

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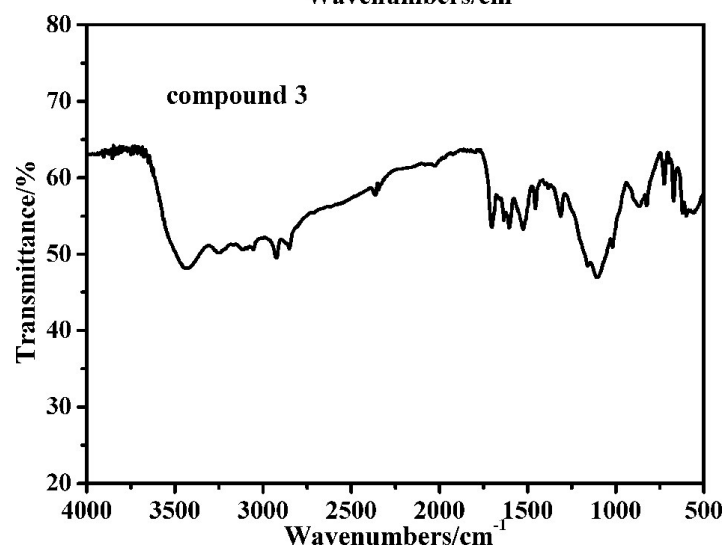
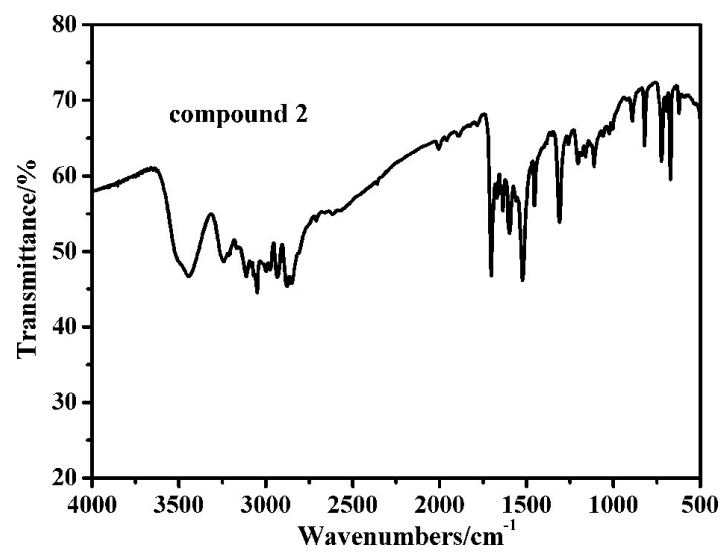
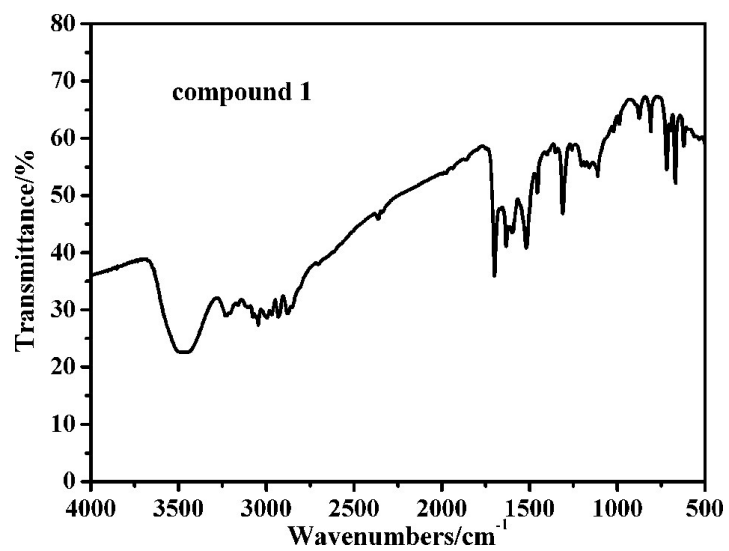
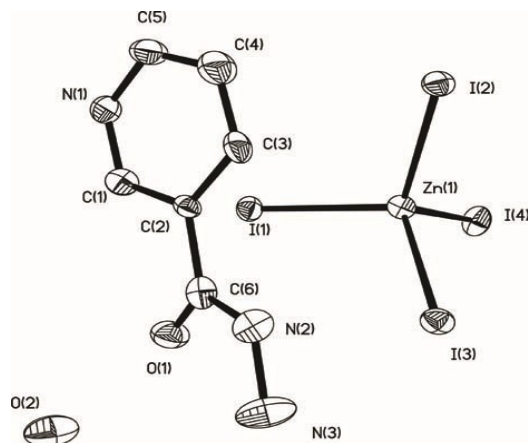
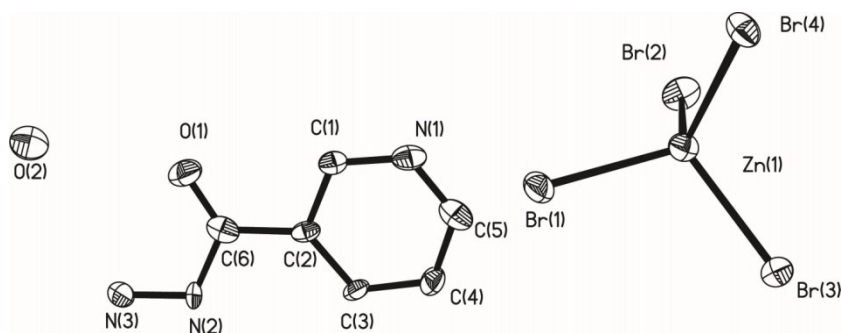


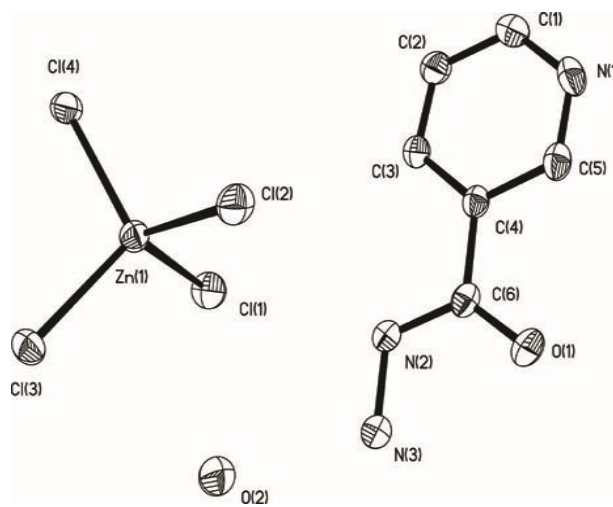
Fig. S1. IR spectra of 1-3.



(a)



(b)



(c)

Fig. S2. The asymmetric unit diagrams of **1** (a), **2** (b) and **3** (c).

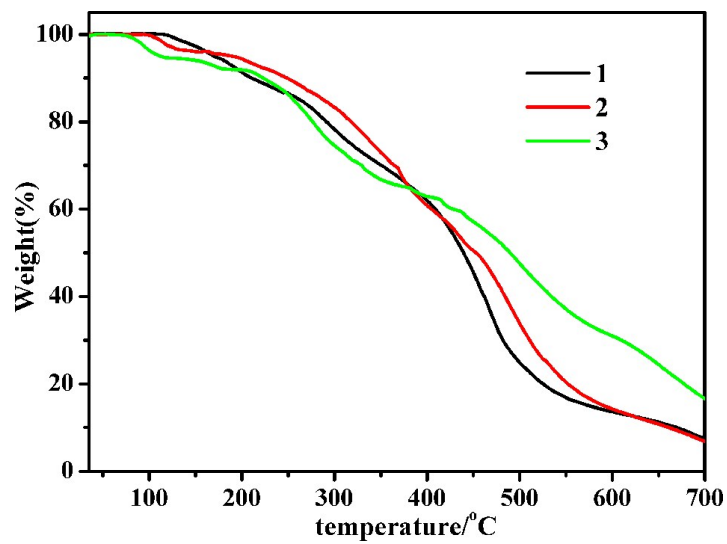


Figure S3. The TGA curves of **1-3**

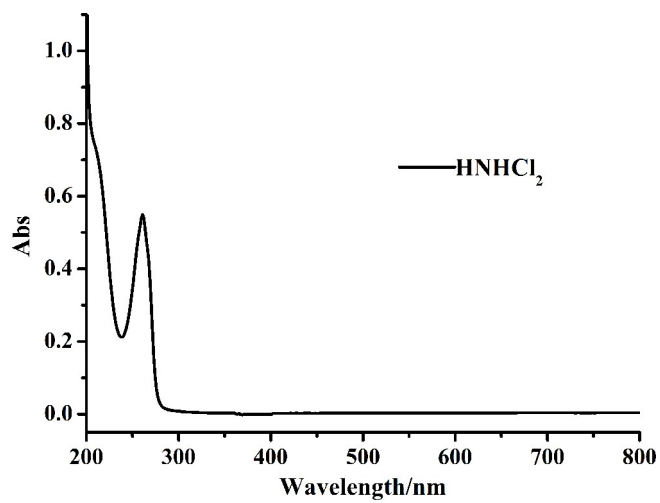


Fig. S4. The UV-vis absorption spectrum of HNHCl₂.

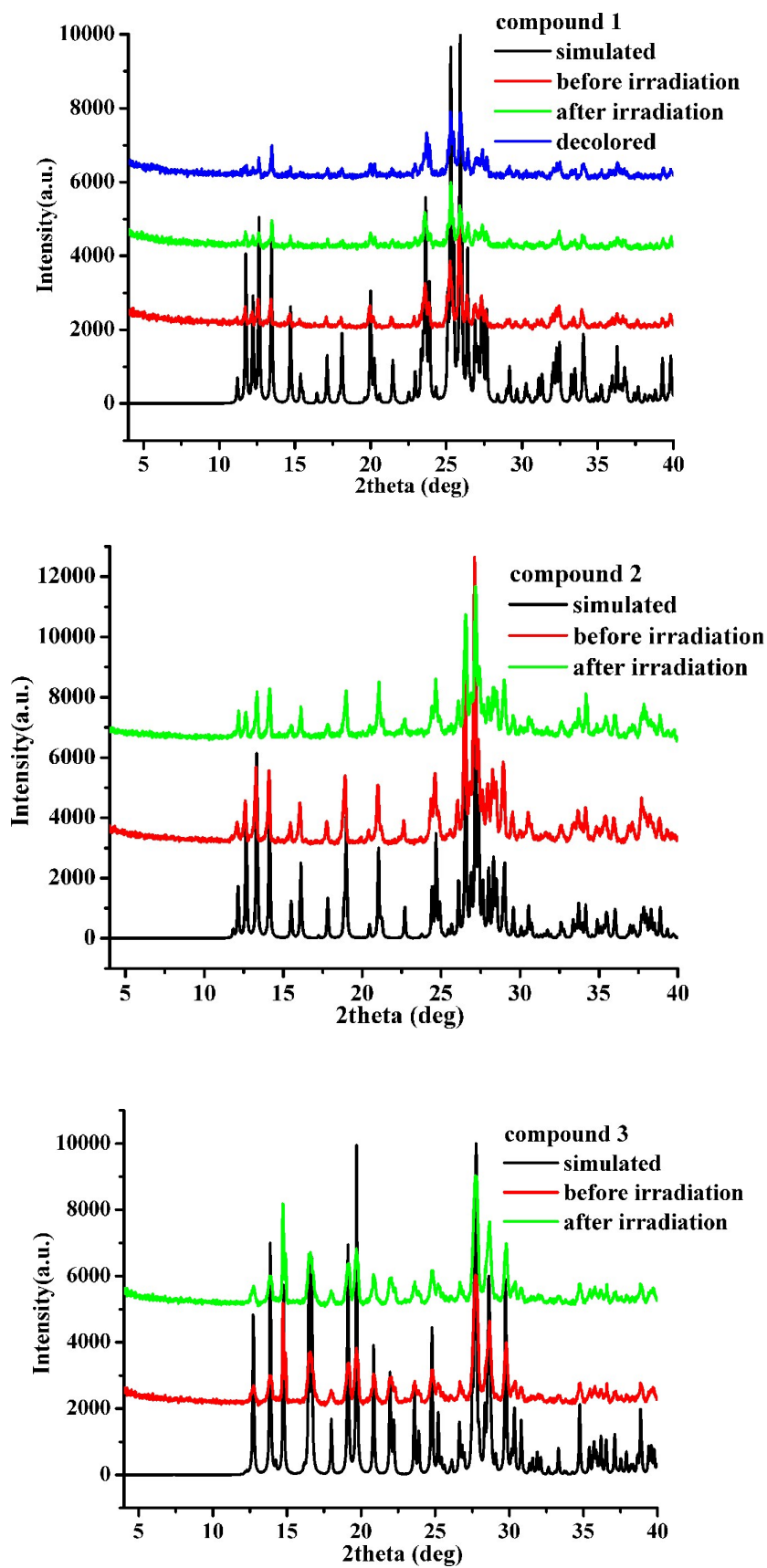


Fig. S5. Powder X-ray diffraction (PXRD) patterns of 1-3.

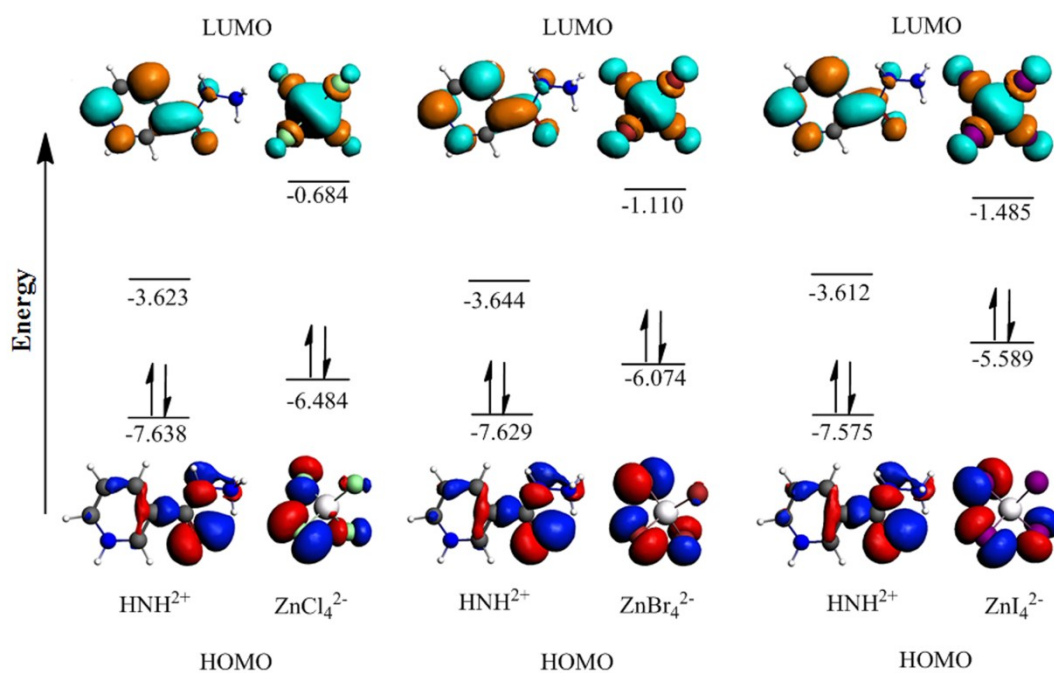


Fig. S6. HOMO and LUMO energy levels of organic HNH²⁺ dication and inorganic ZnX₄²⁻ anions.

Molecular orbital calculations

All the calculations were carried out with ADF2016 suite of programs.¹ The exchange and correlation energies were calculated using the PBE density functional. The basis functions were triple- ξ plus polarization Slater basis sets (TZP), in combination with the zero-order regular approximation (ZORA)² to account for the scalar relativistic effect. Full geometry optimizations were carried out in the presence of conductor-like screening solvent model (COSMO, acetonitrile).³ The ionic radii used in the COSMO are 1.350, 1.517, 1.700, 1.608, 1.725, 1.85, 1.967, 1.908 Å for H, O, C, N, Cl, Br, I, Zn, respectively. The other parameters are set to default values. The inclusion of COSMO is aimed to improve theoretical data.

The model structure of each compound is extracted from the crystallographic data in CIF format and includes one organic HNH²⁺ dication and one adjacent inorganic ZnX₄²⁻ anion. Then the model is optimized without constraints at the level of PBE/TZP. The molecular orbitals shown in Fig. S6 are based on the optimized model structure.

Table S1. Selected bond lengths [Å] and angles [°] for **1** and **1P**

	1		1P	change upon UV irradiation ^a
Zn(1)-I(1)	2.6327(11)	Zn(1)-I(1)	2.7935(10)	+0.1608
Zn(1)-I(2)	2.6142(11)	Zn(1)-I(2)	2.7758(10)	+0.1616
Zn(1)-I(3)	2.6158(13)	Zn(1)-I(3)	2.7752(10)	+0.1594
Zn(1)-I(4)	2.6042(14)	Zn(1)-I(4)	2.7645(10)	+0.1603
C(1)-N(1)	1.298(13)	C(1)-N(1)	1.299(14)	+0.001
C(1)-C(2)	1.366(13)	C(1)-C(2)	1.366(13)	0
C(2)-C(3)	1.396(13)	C(2)-C(3)	1.405(14)	+0.009
C(2)-C(6)	1.475(14)	C(2)-C(6)	1.454(14)	-0.021
C(3)-C(4)	1.361(17)	C(3)-C(4)	1.375(17)	+0.014
C(4)-C(5)	1.344(14)	C(4)-C(5)	1.380(17)	+0.036
C(5)-N(1)	1.317(14)	C(5)-N(1)	1.372(15)	+0.055
C(6)-O(1)	1.210(11)	C(6)-O(1)	1.239(12)	+0.029
C(6)-N(2)	1.350(12)	C(6)-N(2)	1.352(13)	+0.002
N(2)-N(3)	1.407(13)	N(2)-N(3)	1.344(14)	-0.063
I(2)-Zn(1)-I(1)	105.12(4)	I(2)-Zn(1)-I(1)	102.55(3)	-2.57
I(2)-Zn(1)-I(3)	108.15(5)	I(2)-Zn(1)-I(3)	106.78(3)	-1.37
I(3)-Zn(1)-I(1)	110.36(4)	I(3)-Zn(1)-I(1)	110.16(3)	-0.20
I(4)-Zn(1)-I(1)	110.13(5)	I(4)-Zn(1)-I(1)	110.71(3)	+0.58
I(4)-Zn(1)-I(2)	112.77(5)	I(4)-Zn(1)-I(2)	116.06(3)	+4.71
I(4)-Zn(1)-I(3)	110.18(4)	I(4)-Zn(1)-I(3)	110.24(3)	+0.06
C(1)-C(2)-C(3)	116.8(10)	C(1)-C(2)-C(3)	116.8(9)	0
C(1)-C(2)-C(6)	117.5(8)	C(1)-C(2)-C(6)	117.9(8)	+0.4
C(3)-C(2)-C(6)	125.6(9)	C(3)-C(2)-C(6)	125.2(9)	-0.4
C(4)-C(3)-C(2)	120.2(10)	C(4)-C(3)-C(2)	121.0(10)	+0.8
C(5)-C(4)-C(3)	119.4(11)	C(5)-C(4)-C(3)	118.7(11)	-0.7
N(1)-C(1)-C(2)	120.5(9)	N(1)-C(1)-C(2)	122.4(9)	+1.9
N(1)-C(5)-C(4)	119.3(12)	N(1)-C(5)-C(4)	118.6(10)	-0.7
N(2)-C(6)-C(2)	119.0(9)	N(2)-C(6)-C(2)	118.1(8)	-0.9
O(1)-C(6)-N(2)	119.8(11)	O(1)-C(6)-N(2)	119.8(10)	0
O(1)-C(6)-C(2)	121.2(9)	O(1)-C(6)-C(2)	121.9(9)	+0.7
C(1)-N(1)-C(5)	123.7(9)	C(1)-N(1)-C(5)	122.3(9)	-1.4
C(6)-N(2)-N(3)	117.7(9)	C(6)-N(2)-N(3)	119.1(10)	+1.4

^a(+) and (-) denote an expansion and a contraction in the bond lengths and angles upon UV irradiation, respectively.

As shown in Table S2, compound **1** can retain structural integrity after light irradiation. The slight increase of bond lengths of Zn–I can be attributed to the photoinduced electron transfer from ZnI_4^{2-} anion to HNH^{2+} dication⁴ and consequent weakening of bond energy of Zn–I.

Table S2. Selected bond lengths [\AA] and angles [$^\circ$] for **2** and **3**

Compound 2		Compound 3	
Zn(1)-Br(1)	2.4070(9)	Zn(1)-Cl(1)	2.2544(8)
Zn(1)-Br(2)	2.4114(9)	Zn(1)-Cl(2)	2.2792(8)
Zn(1)-Br(3)	2.4128(8)	Zn(1)-Cl(3)	2.2716(8)
Zn(1)-Br(4)	2.4058(9)	Zn(1)-Cl(4)	2.2714(7)
Br(1)-Zn(1)-Br(2)	106.48(3)	Cl(1)-Zn(1)-Cl(2)	107.02(4)
Br(1)-Zn(1)-Br(3)	110.79(3)	Cl(1)-Zn(1)-Cl(3)	111.71(3)
Br(2)-Zn(1)-Br(3)	108.53(3)	Cl(1)-Zn(1)-Cl(4)	110.54(3)
Br(4)-Zn(1)-Br(1)	110.20(3)	Cl(3)-Zn(1)-Cl(2)	108.25(3)
Br(4)-Zn(1)-Br(2)	110.98(3)	Cl(4)-Zn(1)-Cl(2)	110.22(3)
Br(4)-Zn(1)-Br(3)	109.80(3)	Cl(4)-Zn(1)-Cl(3)	109.06(3)

Table S3 Hydrogen bonds for 1-3 (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Compound 1				
N1-H1... I4#1	0.86	2.62	3.467(7)	169.3
N2-H2... I1#3	0.86	3.17	3.712(8)	123.5
N2-H2... I2#3	0.86	2.99	3.708(9)	142.9
N3-H3A... O2#4	0.89	2.41	3.093(14)	134.2
N3-H3B... O2#3	0.89	1.96	2.752(11)	148.2
N3-H3C ... O1#4	0.89	2.19	2.881(12)	133.8
N3-H3C... I3	0.89	3.27	3.911(10)	130.9
O2-H6... I3	0.99	2.70	3.654(7)	161.1
O2-H7... I1#5	0.99	3.03	3.782(7)	134.0
O2-H7... I2#6	0.99	2.94	3.629(8)	128.0
Compound 2				
N1-H1 ... Br4	0.86	2.38	3.225(5)	167.8
N2-H2... Br1#4	0.86	3.07	3.527(5)	115.8
N2-H2... Br2#4	0.86	2.74	3.497(5)	147.0
N3-H3A ... Br3#2	0.89	2.84	3.556(7)	138.1
N3-H3A... Br3#3	0.89	2.84	3.516(7)	133.9
N3-H3B... O2#4	0.89	1.82	2.705(7)	176.5
N3-H3C... O1 #3	0.89	2.36	2.872(7)	116.5
N3-H3C... Br1 #5	0.89	3.10	3.655(6)	122.1
O2-H6... Br2 #6	0.73	2.79	3.476(5)	155.5
O2-H7... Br3	0.74	2.75	3.450(5)	159.3
Compound 3				
N1-H1... Cl4#1	0.86	2.26	3.094(3)	162.7
N2-H2...Cl2#3	0.86	2.55	3.332(3)	151.0
N3-H3A... Cl3#5	0.89	2.68	3.322(3)	130.1
N3-H3A... Cl3#4	0.89	2.58	3.331(3)	142.0
N3-H3B... O2#5	0.89	1.80	2.688(4)	176.1
N3-H3C... O1#6	0.89	2.27	2.847(4)	122.0

N3-H3C... C11#7	0.89	2.86	3.464(3)	126.9
O2-H6... Cl2	0.97	2.36	3.321(3)	171.8
O2-H7... Cl3#7	0.97	2.38	3.342(3)	170.8

Symmetry code: for **1**: #1 x-1, y, z; #2 x, -y+1/2, z-1/2; #3 x, y, z-1; #4 -x+1, -y+1, -z+1; #5 -x+1, -y+1, -z+2; #6 -x+2, -y+1, -z+2. for **2**: #1 x+1, -y+3/2, z-1/2; #2 x+1, y, z; #3 -x+2, -y+1, -z+1; #4 x+1, y, z-1; #5 -x+1, -y+1, -z+1; #6 -x+1, -y+1, -z+2. for **3**: #1 x, y, z+1; #2 x+1, -y+3/2, z+1/2; #3 x+1, y, z; #4 x+1, y, z+1; #5 -x+2, -y+1, -z+1; #6 -x+2, -y+1, -z+2; #7 -x+1, -y+1, -z+1.

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