Supplementary Information For:

Halogen Bond and Polymorphism in *trans*-Bis(2-Iodo-5-Halopyridine)dihalocopper(II) Complexes; Crystallographic, Theoretical and Magnetic studies.

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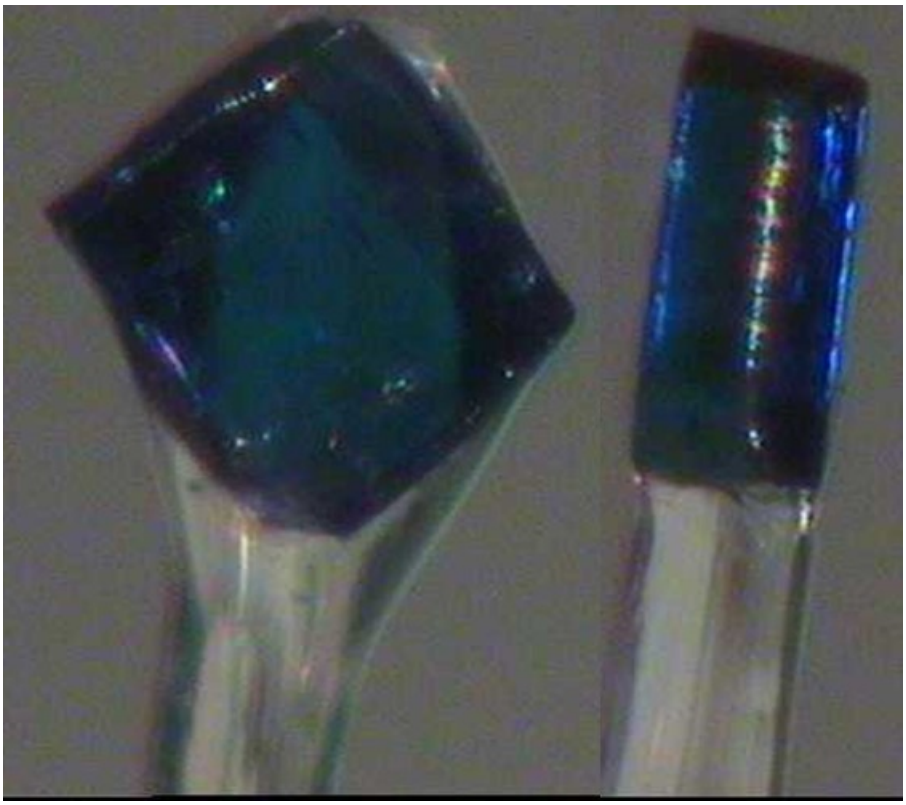


Figure S1. Optical images of the crystals *P*-1 phase (left) and the $P2_{1/n}$ phase (right) of 2I5Cl-Cl

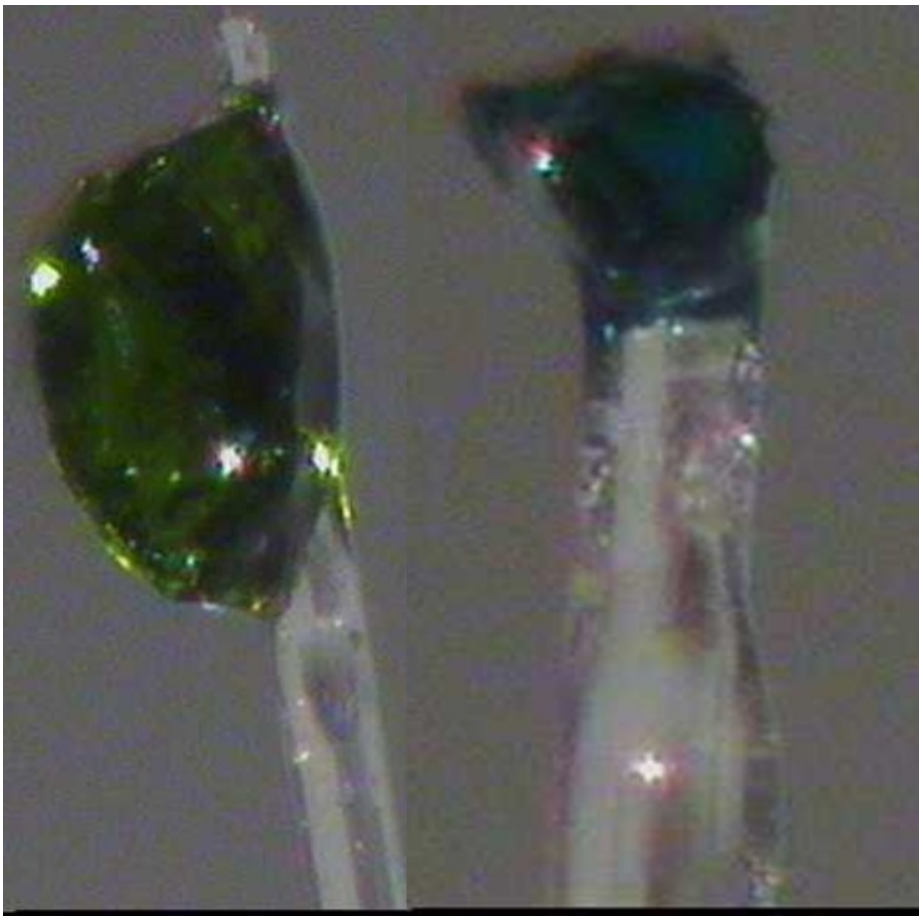


Figure S2. Optical images of the crystals of the syn-2I5Br-Cl conformer (left) and the anti-2I5Br-Cl (right).

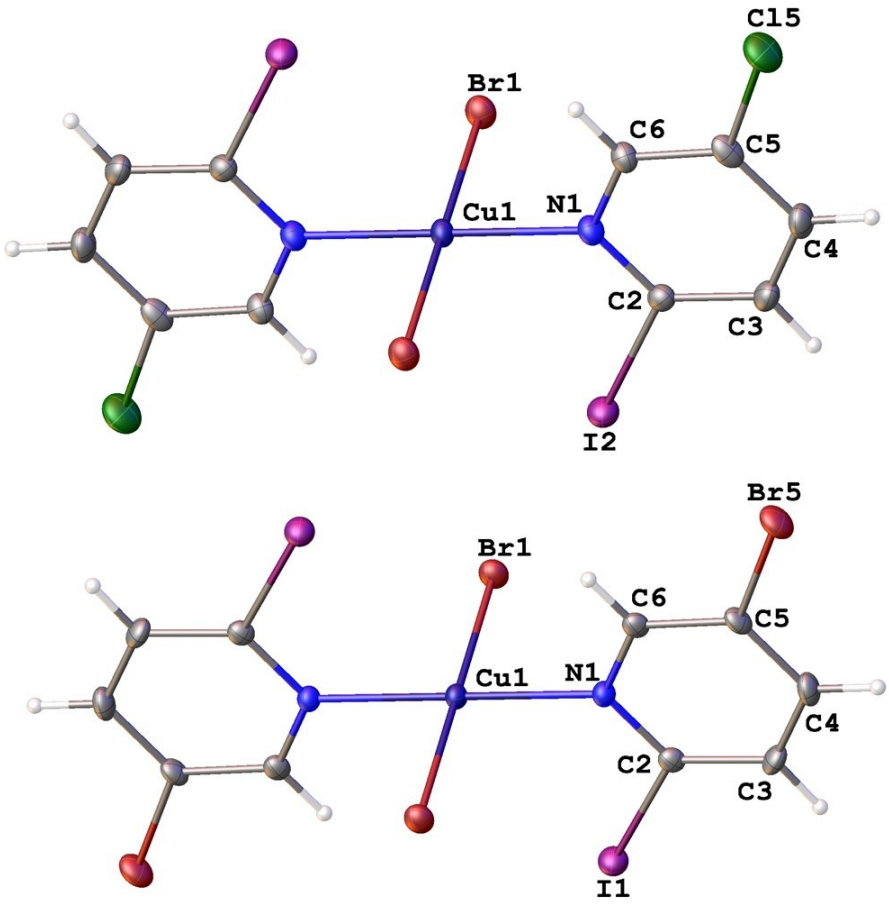


Figure S3. Thermal ellipsoid plot of structures of 2I5Cl-Br (top) and2I5Br-Br (bottom. Only Asymmetric unit is labeled. The equivalent atoms are generated by inversion center, the Symmetry transformations used to generate equivalent atoms are 1-x, 1-y, 1-x.

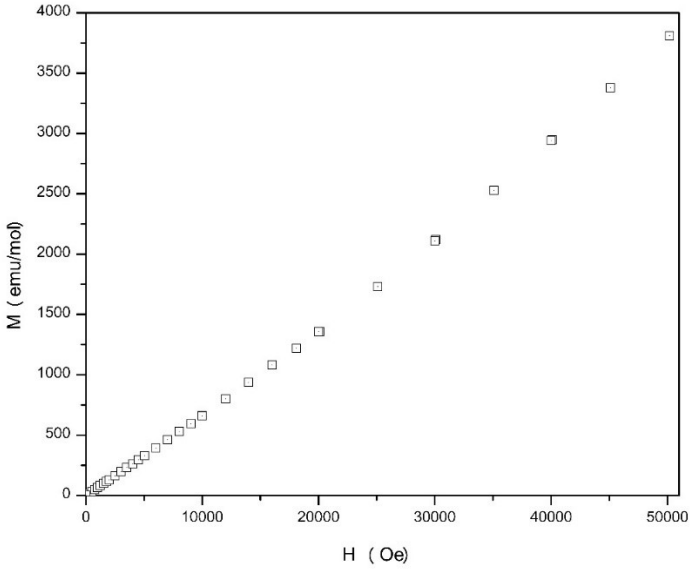


Figure S4. *M(H)* data for syn-2I5Br-Cl.

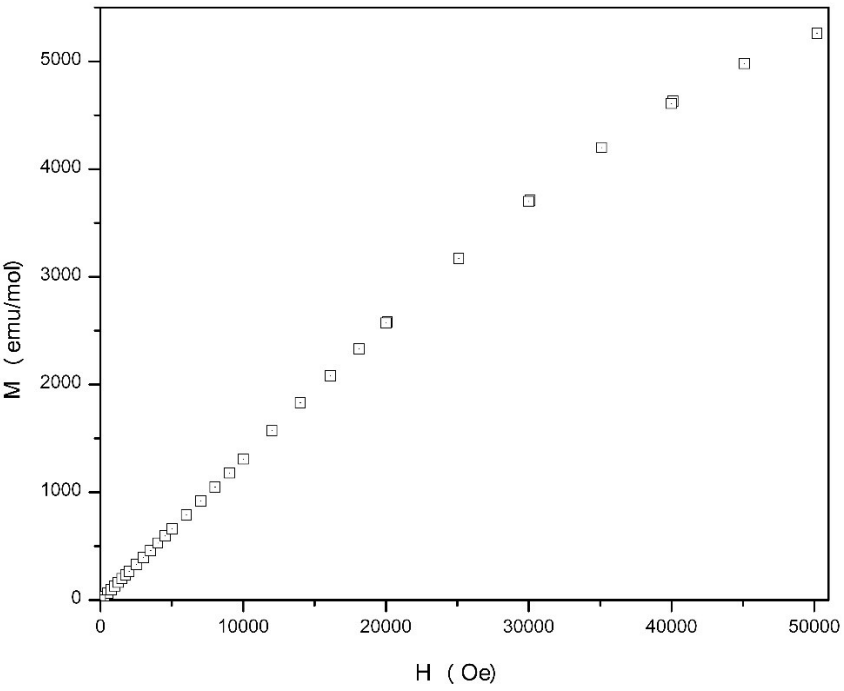


Figure S5. *M(H)* data for anti-2I5Br-Cl

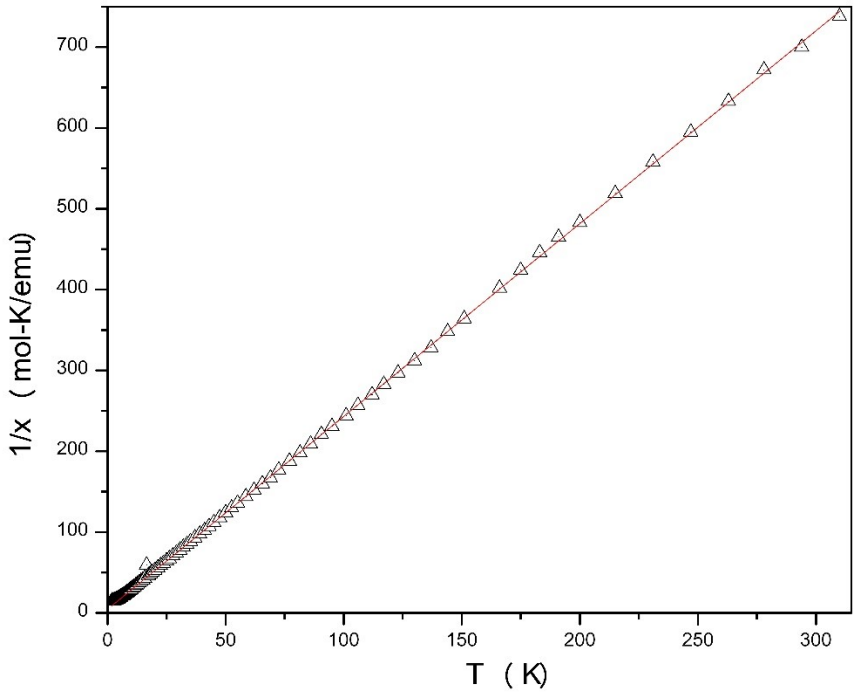


Figure S6. Curie-Weiss plot of the *χ(T)* data for syn-2I5Br-Cl.

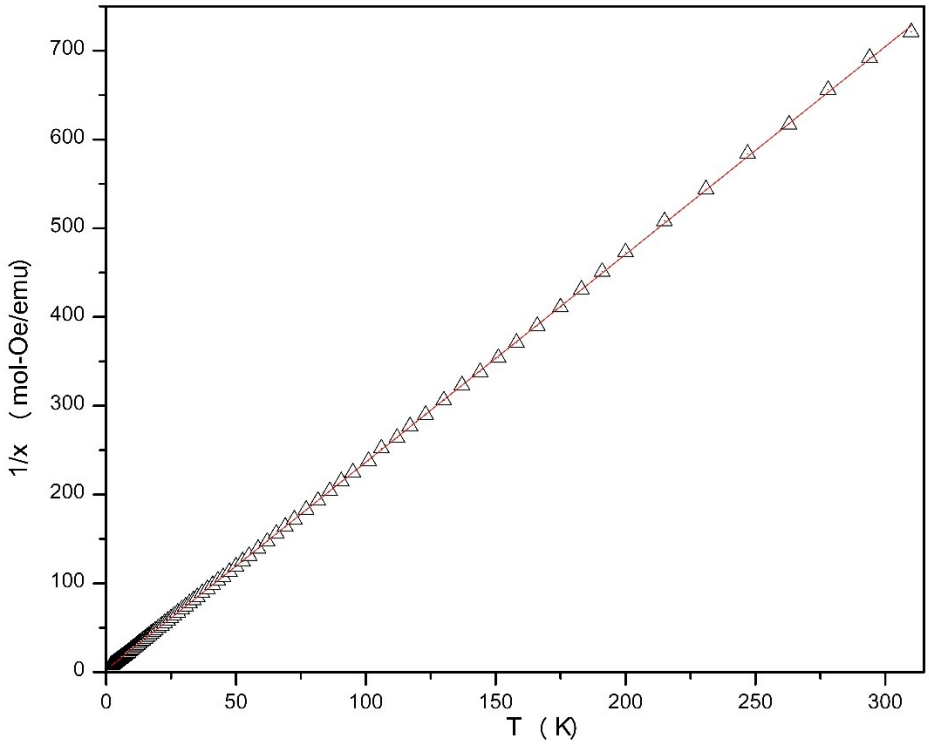
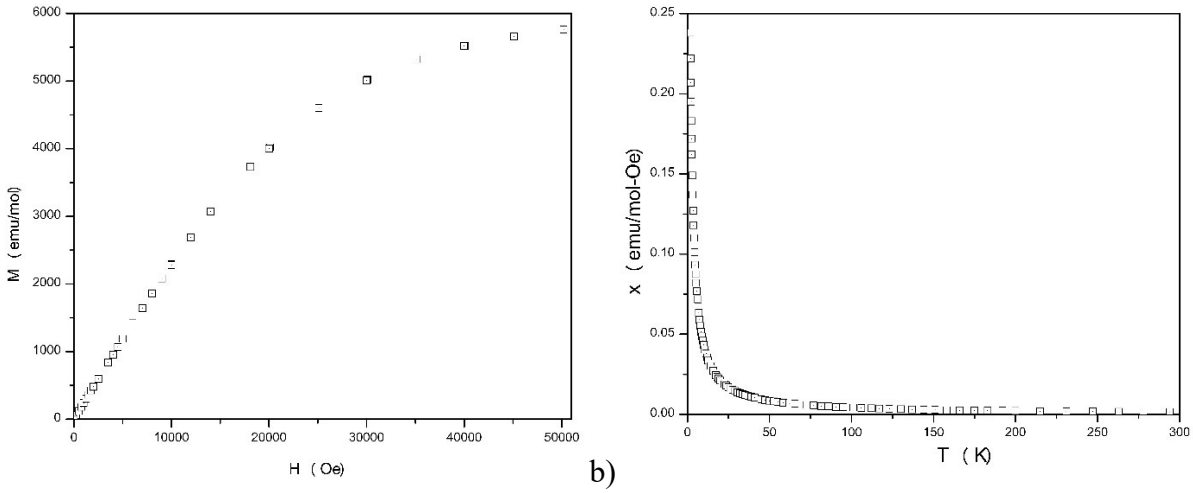
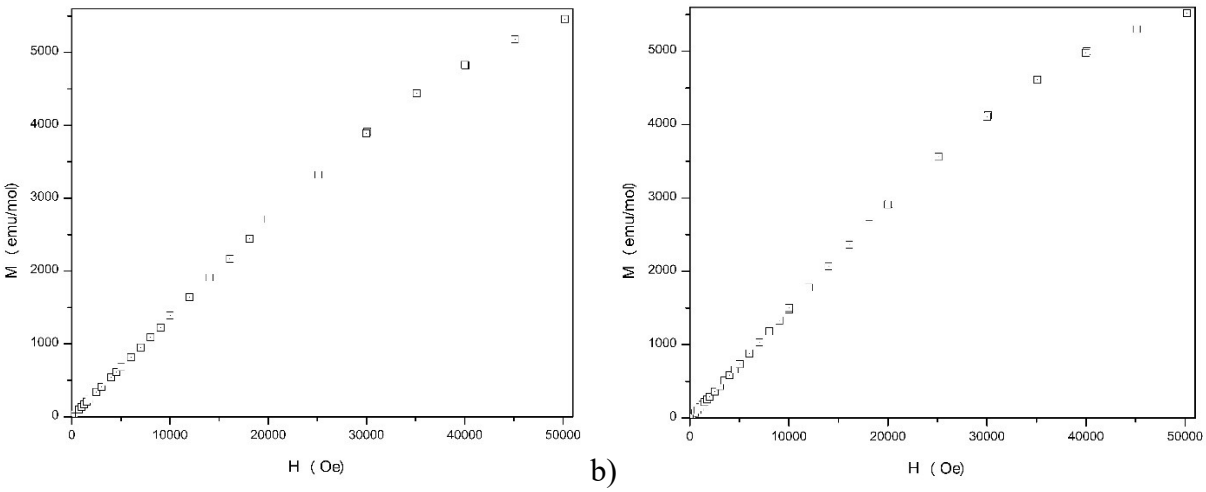


Figure S7. Curie-Weiss plot of the χ(T) data for anti-2I5Br-Cl.



a) b)

Figure S8. b) *M(H)* data for 2I5Br-Br. b) *χ(T)* data for 2I5Br-Br.



a) b)

Figure S9. a) *M(H)* data for *syn*-2I5I-Cl. b) M(H) data for *anti*-2I5I-Cl.

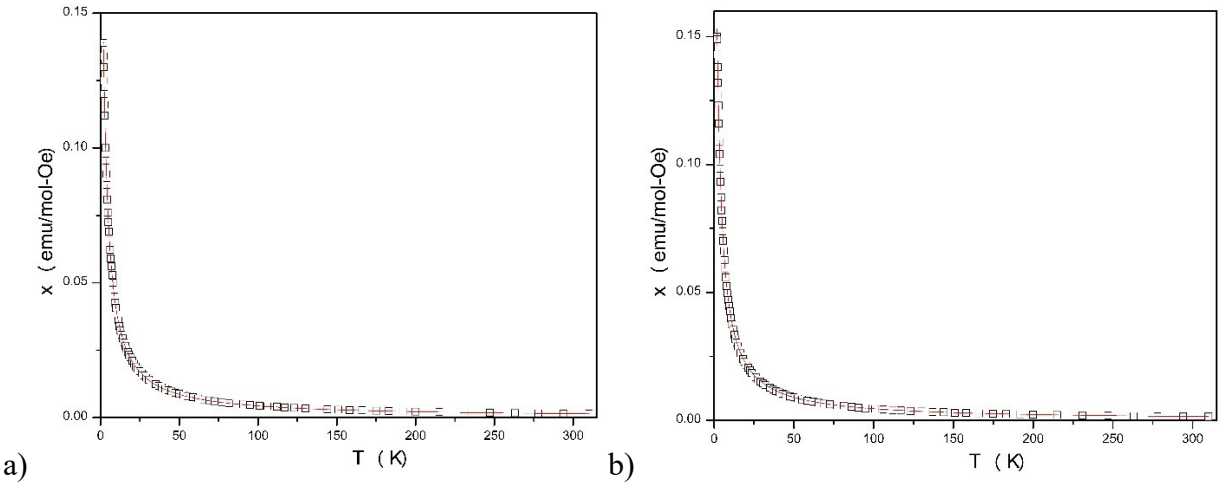


Figure S10. a) $\chi(T)$ data for syn-2I5I-Cl. b) $\chi(T)$ data for *anti*-2I5I-Cl. The solid line represents the fit to the uniform AFM chain model.

Table S1. Data collection and refinement parameters of 2I5Y-X compounds.

compound	2I5Cl-Cl	2I5Cl-Cl	2I5Cl-Br	*Anti*-2I5Br-Cl	*Syn*-2I5Br-Cl	2I5Br-Br
CCDC #	2224781	2224782	2224783	2224785	2224784	2224786
Emp. formula	$C_{10}H_6N_2Cl_4CuI_2$	$C_{10}H_6N_2Cl_4CuI_2$	$C_{10}H_6N_2Cl_2CuBr_2I_2$	$C_{10}H_6N_2Cl_2CuBr_2I_2$	$C_{10}H_6N_2Cl_2CuBr_2I_2$	$C_{10}H_6N_2CuBr_4I_2$
Formula weight	613.31	613.31	702.23	702.23	702.23	791.15
Temperature/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$
a/Å	6.6375(11)	6.5889(19)	6.5931(3)	10.8035(8)	8.4631(4)	6.5988(12)
b/Å	8.1893(14)	8.4455(10)	8.5490(4)	14.9629(5)	13.1568(6)	8.5468(7)
c/Å	8.4260(13)	14.910(7)	15.1333(9)	6.6080(5)	14.6722(5)	15.443(12)
α/°	69.401(15)	90	90	90	90	90
β/°	88.117(13)	99.21(4)	98.729(5)	128.800(11)	91.403(4)	98.57(4)
γ/°	73.592(15)	90	90	90	90	90
Volume/Å^3	410.14(13)	819.0(4)	843.10(8)	832.48(14)	1633.22(12)	861.3(7)
Z	1	2	2	2	4	2
ρ_{calc} g/cm^3	2.483	2.487	2.766	2.801	2.856	3.051
μ/mm^{-1}	5.732	5.741	10.000	10.127	10.324	14.118
F(000)	283.0	566.0	638.0	638.0	1276.0	710.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Index ranges	$-8 \le h \le 8$, $-10 \le k \le 8$, $-11 \le l \le 7$	$-8 \le h \le 8$, $-10 \le k \le 11$, $-19 \le l \le 9$	$-6 \le h \le 8$, $-10 \le k \le 11$, $-20 \le l \le 12$	$-8 \le h \le 14$, $-18 \le k \le 17$, $-8 \le l \le 5$	$-11 \le h \le 8$, $-17 \le k \le 10$, $-19 \le l \le 13$	$-9 \le h \le 6$, $-10 \le k \le 10$, $-14 \le l \le 19$
Reflections collected	3186	4062	3694	3956	3653	4084
Independent reflections	1871	1930	1956	1933	1901	1996
R_{int}	0.0400	0.0269	0.0317	0.0330	0.0254	0.0256
Data/restraints/	1871/0/88	1930/0/88	1956/0/88	1933/0/88	1901/0/87	1996/0/89

parameters						
Goodness-of-fit on F^2	1.058	1.035	1.024	1.046	1.013	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0390 wR_2 = 0.0844	R_1 = 0.0324 wR_2 = 0.0557	R_1 = 0.0356 wR_2 = 0.0671	R_1 = 0.0384 wR_2 = 0.0721	R_1 = 0.0324 wR_2 = 0.0576	R_1 = 0.0338 wR_2 = 0.0583
Largest diff. peak/hole / e $Å^{-3}$	0.71/-0.98	0.76/-0.53	0.77/-0.67	0.63/-1.06	0.50/-0.86	0.94/-0.76

Table S2. Electron density (ρ), Laplacian(∇^2), electron potential energy density (V), electron kinetic energy density (G), and the total electron energy density (Hc) = (V+G) of optimized *anti*-conformers of 2I5Y-X. All units are in atomic units.

Compound	BCP #	ρ	∇^2	V	Hc	G	DI
2I5Br-Br	1	0.0475	0.1454	-0.0408	-0.0024	0.0384	0.569
	2	0.0687	0.4050	-0.0976	0.0018	0.0994	0.411
	3	0.1230	0.0048	-0.0995	-0.0658	0.0337	1.092
2I5Br-Cl	1	0.0630	0.2843	-0.0738	-0.0014	0.0724	0.590
	2	0.0637	0.3724	-0.0861	0.0035	0.0896	0.380
	3	0.1226	0.0034	-0.0989	-0.0654	0.0335	1.090
2I5Cl-Br	1	0.0475	0.1451	-0.0407	-0.0024	0.0383	0.568
	2	0.0687	0.4048	-0.0976	0.0018	0.0994	0.411
	3	0.1229	0.0040	-0.0994	-0.0658	0.0336	1.091
2I5Cl-Cl	1	0.0628	0.2837	-0.0736	-0.0013	0.0723	0.589
	2	0.0636	0.3722	-0.0860	0.0035	0.0895	0.381
	3	0.1226	0.0029	-0.0989	-0.0655	0.0334	1.089
2I5F-Cl	1	0.0626	0.2828	-0.0732	-0.0012	0.0720	0.537
	2	0.0639	0.3743	-0.0867	0.0034	0.0901	0.382
	3	0.1223	0.0020	-0.0984	-0.0652	0.0332	1.086
2I5F-Br	1	0.0474	0.1449	-0.0406	-0.0023	0.0383	0.567
	2	0.0690	0.4068	-0.0983	0.0017	0.1000	0.412
	3	0.1227	0.0035	-0.0990	-0.0656	0.0334	1.089

Table S3. Electron density (ρ), Laplacian(∇^2), electron potential energy density (V), electron kinetic energy density (G), the total electron energy density (Hc) = (V+G), and *Eint* (bonding energy, $kJmol^{-1}$) of optimized *syn*-conformers of 2I5Y-X. All units are in atomic units.

	BCP	ρ	∇^2	V	Hc	G	$Eint$ [Ha]	E_{int} [Hb]	DI
2I5Br-Br	1	0.0471	0.1474	-0.0408	-0.0021	0.0387	N/A	N/A	0.581
	2	0.0637	0.3703	-0.0857	0.0034	0.0891	N/A	N/A	0.401
	3	0.1229	0.0047	-0.0995	-0.0658	0.0337	N/A	N/A	1.090
	5	0.0097	0.0323	-0.0054	0.0013	0.0067	7.09	7.55	0.050
	4	0.0046	0.0107	-0.0016	0.0005	0.0021	N/A	N/A	0.065
2I5Br-Cl	1	0.0616	0.2846	-0.0723	-0.0006	0.0717	N/A	N/A	0.596
	2	0.0604	0.3502	-0.0788	0.0044	0.0832	N/A	N/A	0.380
	3	0.1224	0.0041	-0.0988	-0.0653	0.0335	N/A	N/A	1.092
	5	0.0118	0.0399	-0.0071	0.0014	0.0085	9.32	9.57	0.056
	4	0.0039	0.0087	-0.0013	0.0004	0.0017	N/A	N/A	0.055
2I5Cl-Br	1	0.0471	0.1468	-0.0406	-0.0021	0.0385	N/A	N/A	0.578
	2	0.0642	0.3733	-0.0868	0.0032	0.0900	N/A	N/A	0.402
	3	0.1230	0.0044	-0.0996	-0.0659	0.0337	N/A	N/A	1.094
	5	0.0090	0.0315	-0.0050	0.0015	0.0065	6.56	7.32	0.045
	4	0.0046	0.0106	-0.0016	0.0005	0.0021	N/A	N/A	0.065
2I5Cl-Cl	1	0.0616	0.2849	-0.0723	-0.0005	0.0718	N/A	N/A	0.597
	2	0.0602	0.3484	-0.0782	0.0044	0.0826	N/A	N/A	0.380
	3	0.1223	0.0037	-0.0987	-0.0652	0.0335	N/A	N/A	1.092
	5	0.0119	0.0399	-0.0072	0.0014	0.0086	9.45	9.69	0.057
	4	0.0040	0.0089	-0.0013	0.0005	0.0018	N/A	N/A	0.056

[Ha] *Eint* (kJ/mol) = - 1 /2 V (r_b) * 2625.5 [1, 2]

[Hb] *Eint* (kJ/mol) = 0.429 G (r_b) * 2625.5[1, 2]

Table S4. Electron density (ρ), Laplacian(∇^2), electron potential energy density (V), electron kinetic energy density (G), the total electron energy density (Hc) = (V+G), delocalization index (DI) and *Eint* (bonding energy, kJmol^{-1}) of 2I5Y-X conformers, coordinates were extracted from X-ray crystal structure.

Compound	BCP	ρ	∇^2	V	Hc	G	DI	$Eint$ [Ha]	E_{int} [Hb]
2I5Br-Br	1	0.0542	0.1795	-0.0520	-0.0038	0.0482	0.575	N/A	N/A
	2	0.0859	0.5121	-0.1415	-0.0067	0.1347	0.453	N/A	N/A
	3	0.1283	0.0053	-0.1066	-0.0713	0.0353	1.098	N/A	N/A

2I5C-Cl ($P2_1$/n phase)	1	0.0644	0.2949	-0.0776	-0.0019	0.0757	0.570	N/A	N/A
	2	0.0845	0.5079	-0.1386	-0.0058	0.1328	0.437	N/A	N/A
	3	0.1291	0.0057	-0.1076	-0.0721	0.0355	1.102	N/A	N/A
2I5C-Cl (*P*-1 phase)	1	0.0653	0.2996	-0.0794	-0.0023	0.0772	0.576	N/A	N/A
	2	0.0818	0.4914	-0.1313	-0.0042	0.1271	0.430	N/A	N/A
	3	0.1301	0.0074	-0.1090	-0.0731	0.0360	1.104	N/A	N/A
2I5C-Br	1	0.0548	0.1820	-0.0530	-0.0040	0.0490	0.577	N/A	N/A
	2	0.0875	0.5229	-0.1461	-0.0077	0.1384	0.456	N/A	N/A
	3	0.1278	0.0042	-0.1060	-0.0708	0.0351	1.095	N/A	N/A
2I5Br-Cl ($P2_1$/n phase)	1	0.0650	0.2978	-0.0788	-0.0022	0.0766	0.575	N/A	N/A
	2	0.0814	0.4886	-0.1302	-0.0040	0.1262	0.427	N/A	N/A
	3	0.1275	0.0018	-0.1054	-0.0705	0.0349	1.090	N/A	N/A
2I5Br-Cl (*C*2/c phase)	1	0.0658	0.3169	-0.0828	-0.0018	0.0810	0.602	N/A	N/A
	2	0.0760	0.4599	-0.1170	-0.0010	0.1160	0.426	N/A	N/A
	3	0.1291	0.0035	-0.1078	-0.0722	0.0356	1.104	N/A	N/A
	5	0.0102	0.0406	-0.0064	0.0019	0.0083	0.0446	8.40	9.35
	4	0.0087	0.0237	-0.0038	0.0010	0.0048	0.1146	N/A	N/A

Table S5. Electron density (ρ), Laplacian(∇^2), electron potential energy density (V), electron kinetic energy density (G), delocalization index (DI), and $Eint$ (bonding energy, kJmol^{-1}) of dimers fromed based on C5-Y···X halogen bonding interactions,[3] coordinates were extracted from X-ray crystal structure.

compound	ρ	∇^2	V	G	DI	[a]$Eint$	[b]$Eint$	[c]$Eint$	[d]$Eint$
anti-2I5Br-Cl	0.0073	0.0234	-0.0037	0.0048	0.0857	5.63	7.18		
anti-2I5Br-Br	0.0084	0.0244	-0.0041	0.0051	0.1087	6.24	7.63		
anti-2I5Cl-Cl	0.0048	0.0141	-0.0023	0.0029	0.0523			2.96	3.58
anti-2I5Cl-Cl	0.0053	0.0156	-0.0026	0.0032	0.0578			3.34	3.95
anti-2I5Cl-Br	0.0063	0.0181	-0.003	0.0038	0.0771			3.86	4.69
anti-2I5Br-Cl	0.0072	0.0232	-0.0037	0.0047	0.0851	5.63	7.03		
syn-2I5Br-Cl	0.0079	0.0246	-0.004	0.0051	0.096	6.09	7.63		

[a]$Eint = -0.58 \times V$ (for interactions with Br atom as electron acceptor)

[b]$Eint = 0.57 \times G$ (for interactions with Br atom as electron acceptor)

[c]$Eint = -0.49 \times V$ (for interactions with Cl atom as electron acceptor)

[d]$Eint = 0.47 \times G$ (for interactions with Cl atom as electron acceptor)

<u>The used formula to fit the magnetic data[4]</u>

Uniform 1-D QHAF

Single J format, positive J is antiferromagnetic. 1: CC, the Curie Constant. Parameter 2: Jk, the exchange strength expressed as a temperature . Parameter 3: PARA, the percentage of paramagnetic contribution Chi = (1-0.01* PARA)*(CC/T)*(1.+(-0.053837836)*(Jk/T) +0.097401365*(Jk/T)^2 +0.0144 67437*(Jk/T)^3 +0.0013925193*(Jk/T)^4 +0.00011393434*(Jk/T)^5)/ (1. +0.44616216*(Jk/T) +0.32048245*(Jk/T)^2 +0.13304199*(Jk/T)^3 +0.0"

References.

1. E. V. Bartashevich and V. G. e. Tsirelson, *Russian Chemical Reviews*, 2014, **83**, 1181.
2. E. Espinosa, E. Molins and C. Lecomte, *Chemical physics letters*, 1998, **285**, 170-173.
3. E. V. Bartashevich and V. G. Tsirelson, *Russian Chemical Reviews*, 2014, **83**, 1181.
4. C. P. Landee and M. M. Turnbull, *Journal of Coordination Chemistry*, 2014, **67**, 375-439.