Electronic Supplementary Material (ESI) for CrystEngComm.

Unraveling the Dual Character of Sulfur Atoms in a series of Hg(II) coordination polymers containing bis(4-pyridyl)disulfide

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Experimental Section

All starting materials, including 4,4'-Dithiodipyridine ligand, HgX_2 salts were purchased from Sigma-Aldrich and used as received. FT-IR and ATR-FT-IR spectra were recorded using Thermo Nicolet IR 100 FT-IR. Melting points were measured on an Electrothermal 9100 apparatus. Ultrasonic generator was carried out on a TECNO-GAZ, S.p.A., Tecna 6, input: 50–60 Hz/305. The samples were also characterized by field emission scanning electron microscope (FE-SEM) SIGMA ZEISS and TESCAN MIRA with gold coating. The thermal behavior was measured with a PL-STA 1500 apparatus with the rate of 10ºC.min^{-1} in a static atmosphere of argon. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu-Kα radiation.

Single-Crystal Diffraction

X-ray diffraction experiments were carried out at the MoKa wavelength at ambient temperature (except **3** at 173 K) using a Rigaku XtaLabPro diffractometer. A MicroMax-003 microfocus sealed tube generator coupled to a double-bounce confocal Max-Flux® multilayer optic was employed, and Bragg peak measurement was performed by an HPAD Pilatus 200K detector. The three structures were solved by phasing intrinsic methods (SHELXT),[1] and refined by full matrix least squares on F^2 using SHELXL-2014/7.0.[2] Anisotropic thermal parameters were used for all non-hydrogen atoms and aromatic H atoms, visible in residual maps, were refined with riding coordinates and with U_{eq} values set at $1.2U_{eq}$ (C atom). **2** turned out to be non-merohedral twinned as detected by the TwinRotMat macro in PLATON.[3] The two domains were rotated by only 0.4° around the ***c*** vector, giving fractional contributions of 0.82 and 0.18, which significantly improved the final R-factors.

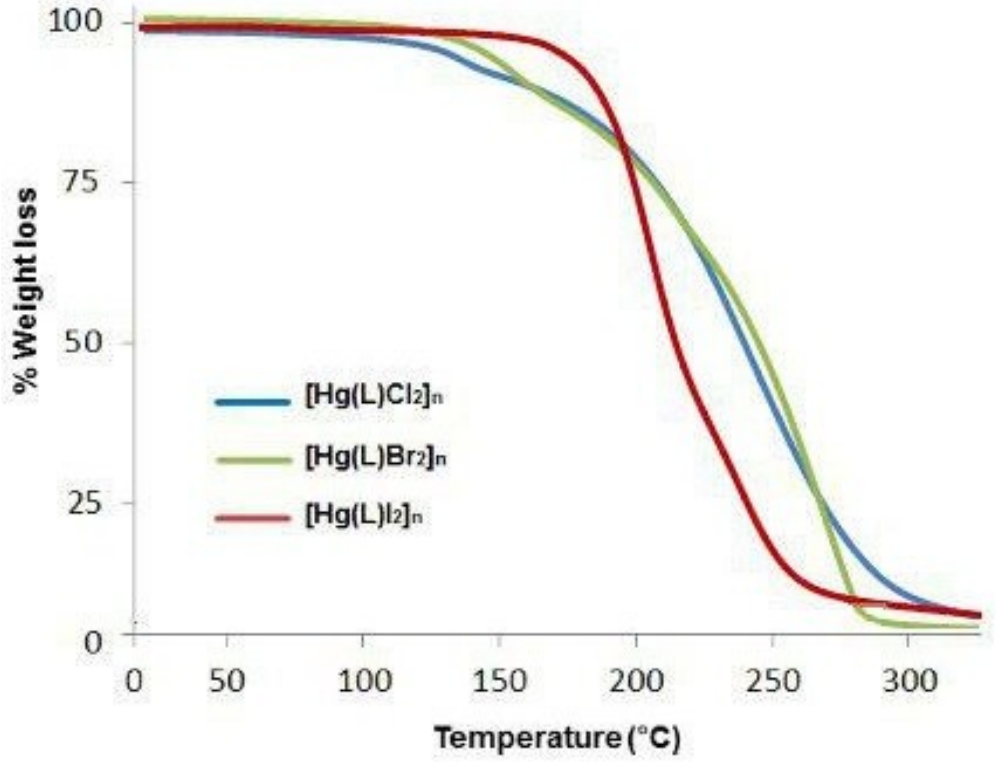


Figure S1. Stacked TG curves of compounds **1**, **2** and **3.**

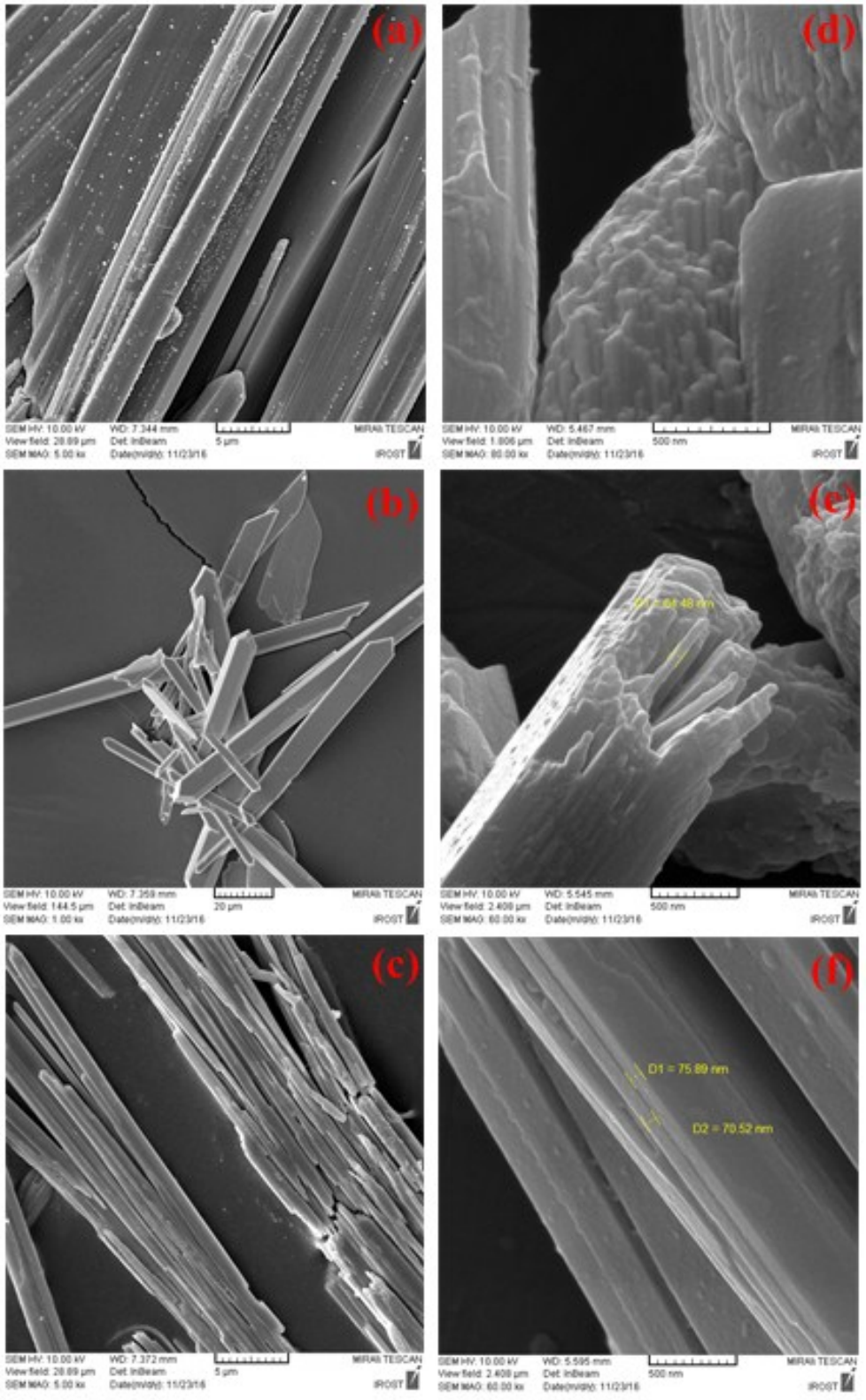
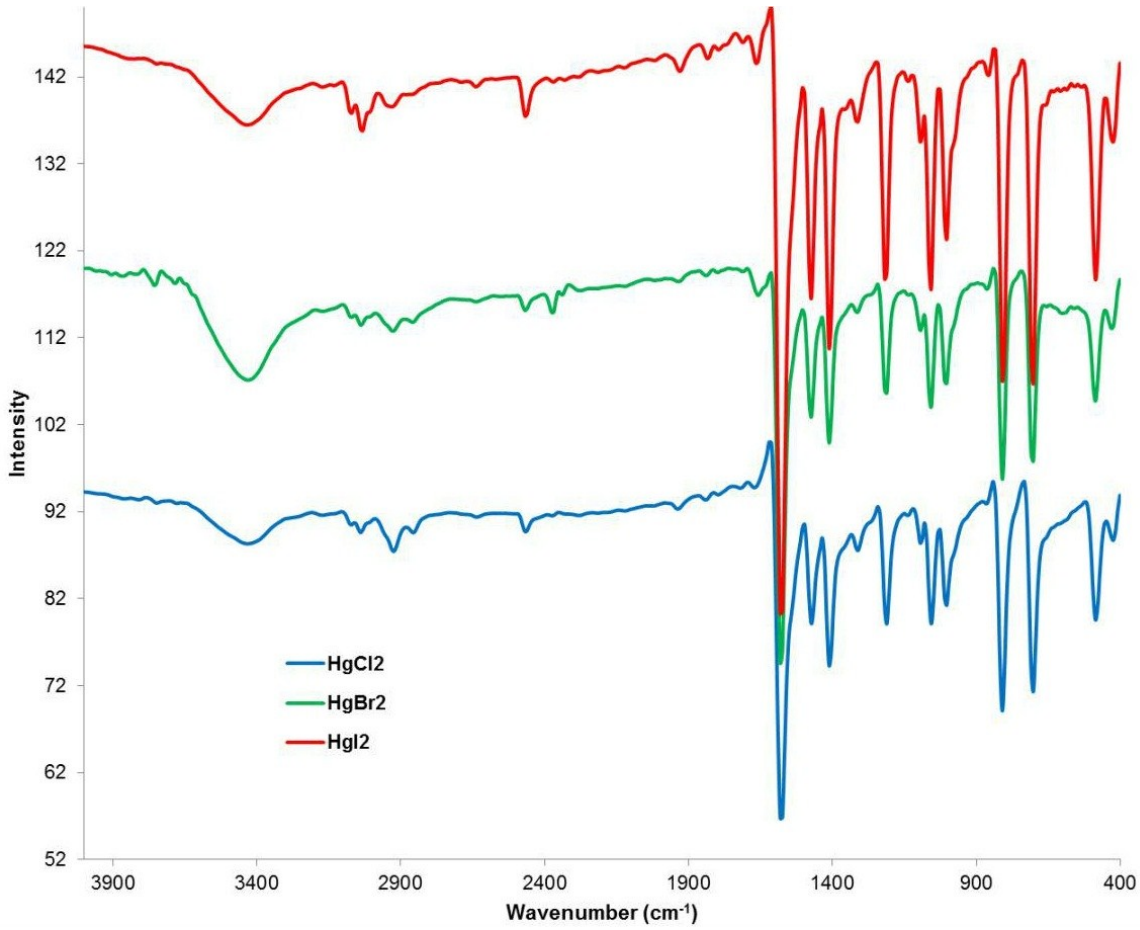
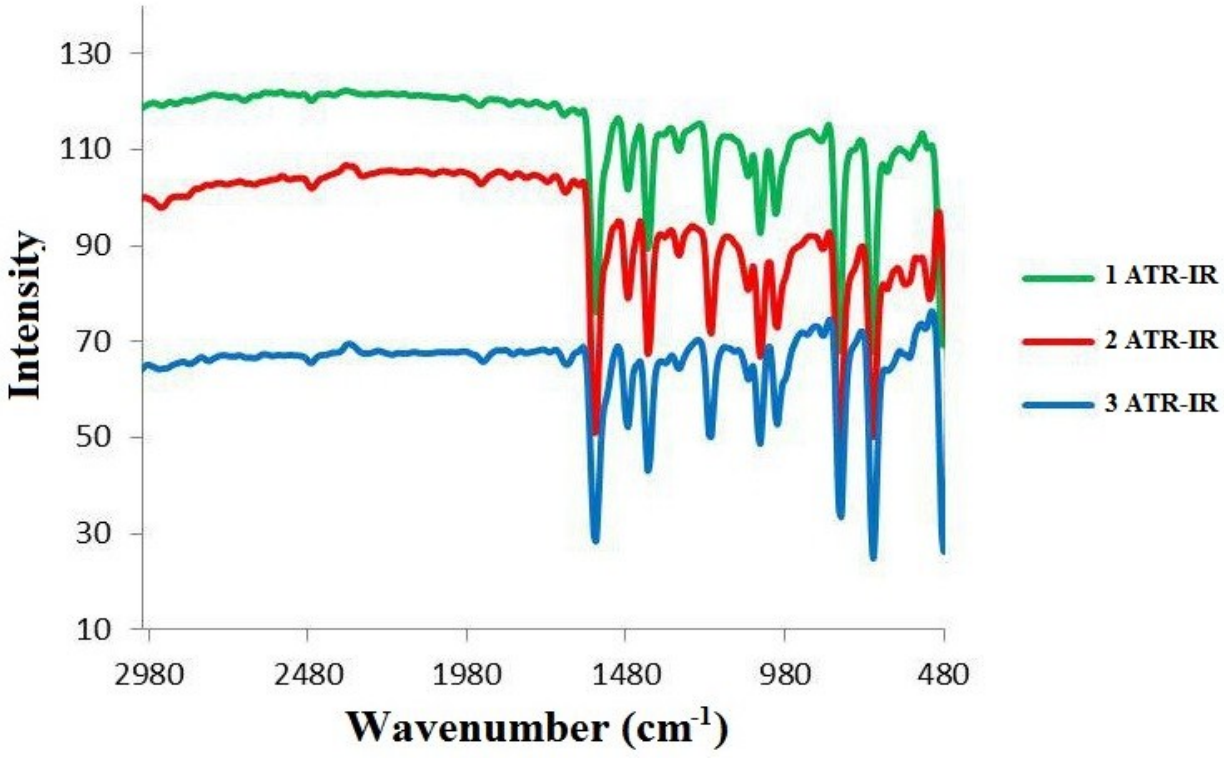


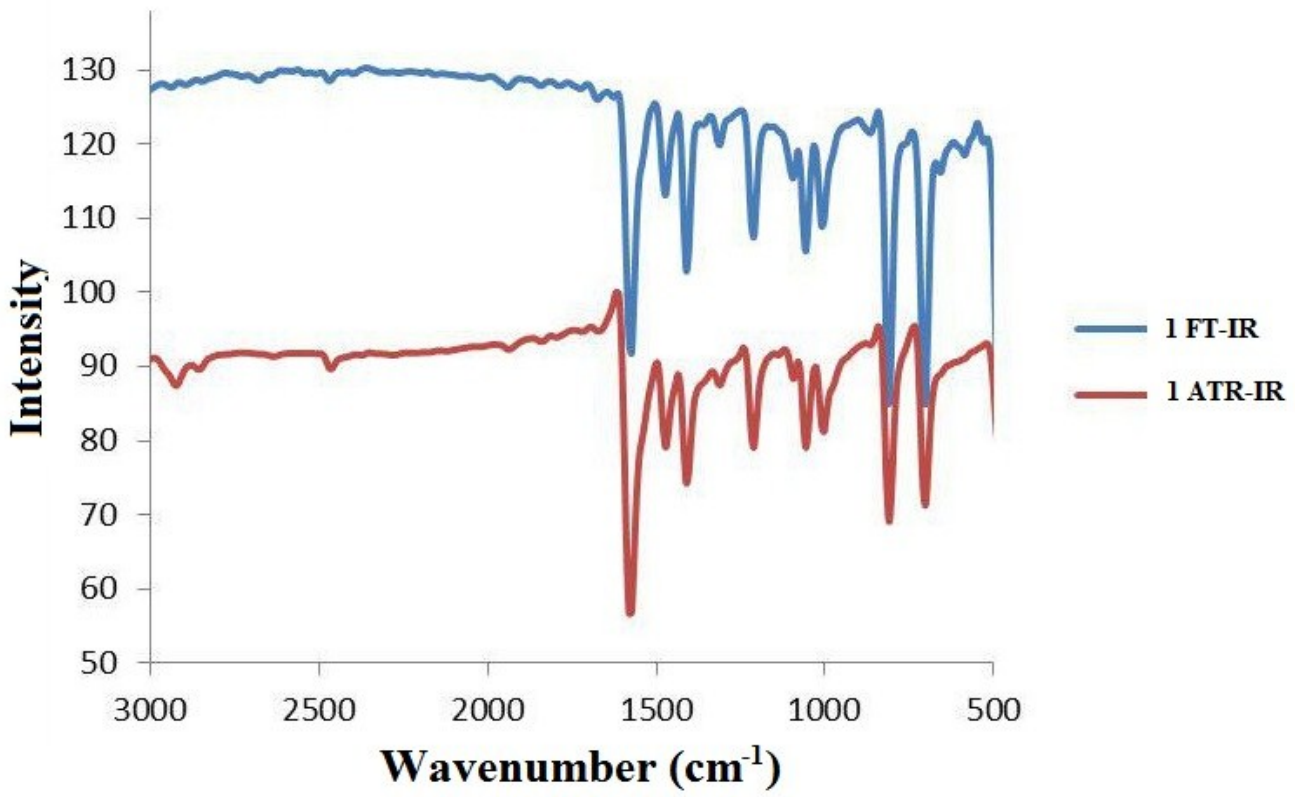
Figure S2. FE-SEM images of single crystals of compounds **1** (a), **2** (b) and **3** (c) prepared using layering technique and compounds **1** (d), **2** (e) and **3** (f) prepared using ultransonic irradiation


142
132
122
112
102
92
82
72
62
52
Intensity
3900
3400
2900
2400
1900
1400
900
400
Wavenumber (cm-1)
HgCl2
HgBr2
HgI2

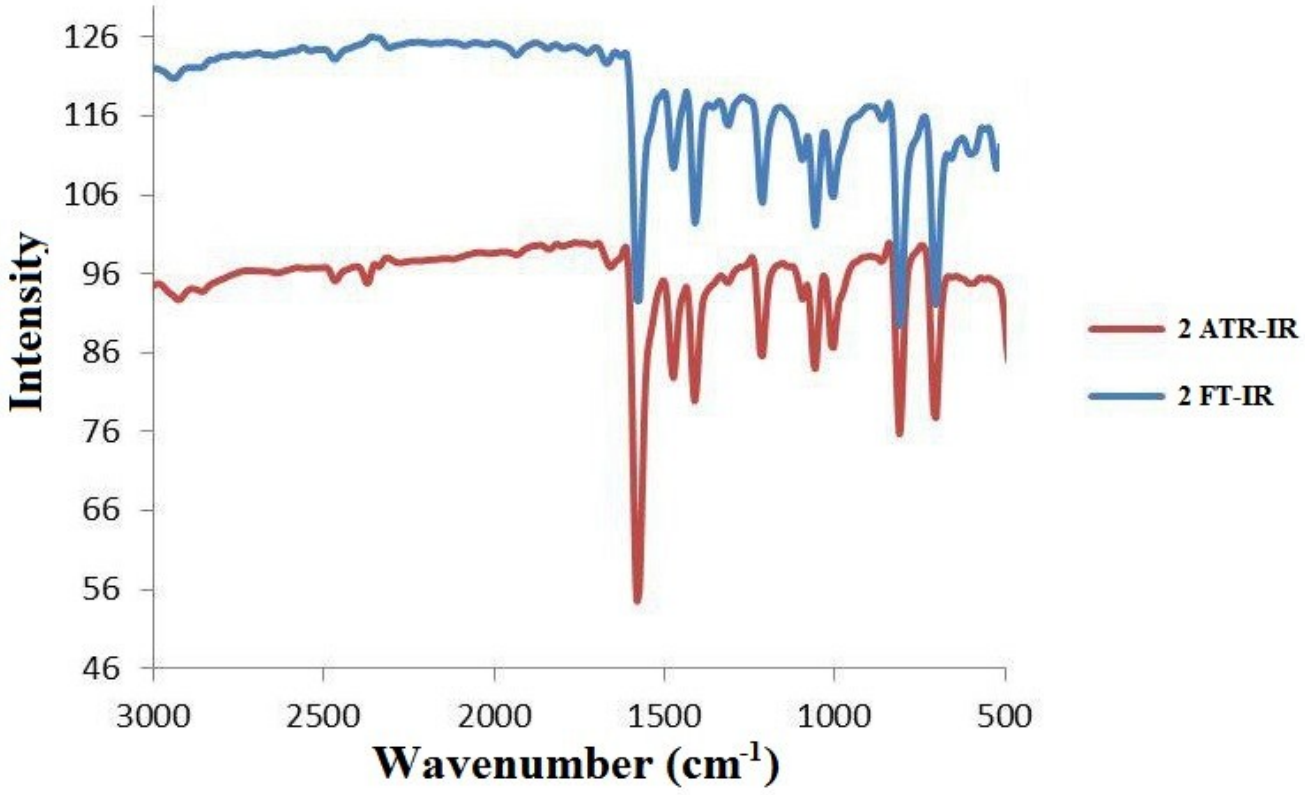
(a)


130
110
90
70
50
30
10
Intensity
2980
2480
1980
1480
980
480
Wavenumber (cm-1)
1 ATR-IR
2 ATR-IR
3 ATR-IR

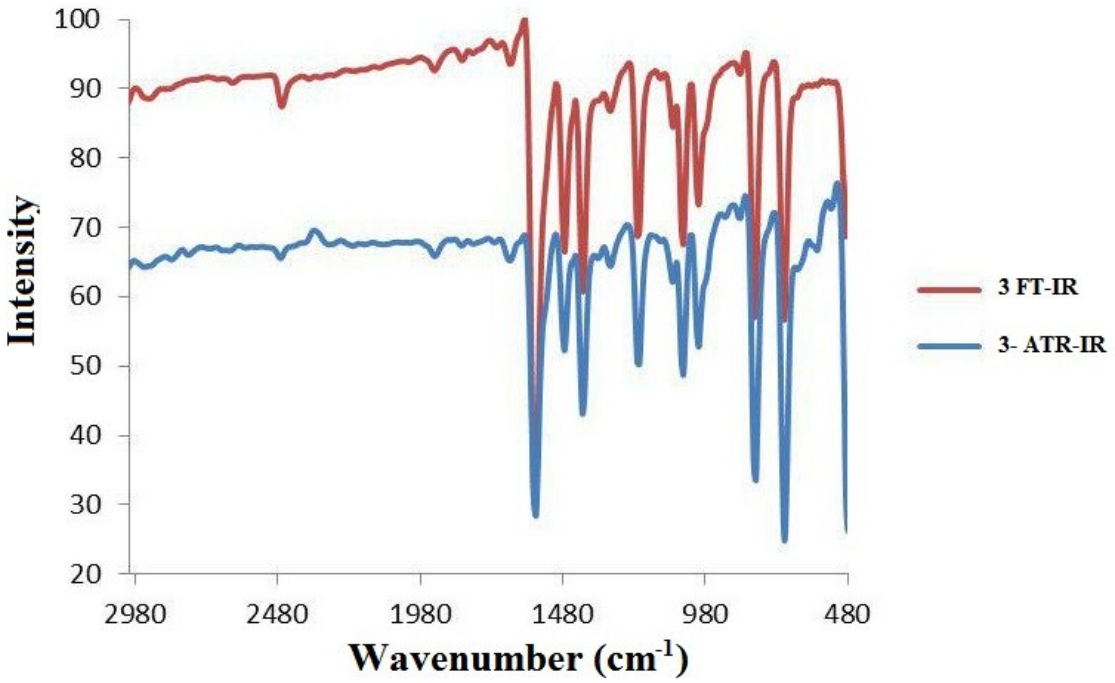
(b)


Intensity
130
120
110
100
90
80
70
60
50
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
1 FT-IR
1 ATR-IR

(c)

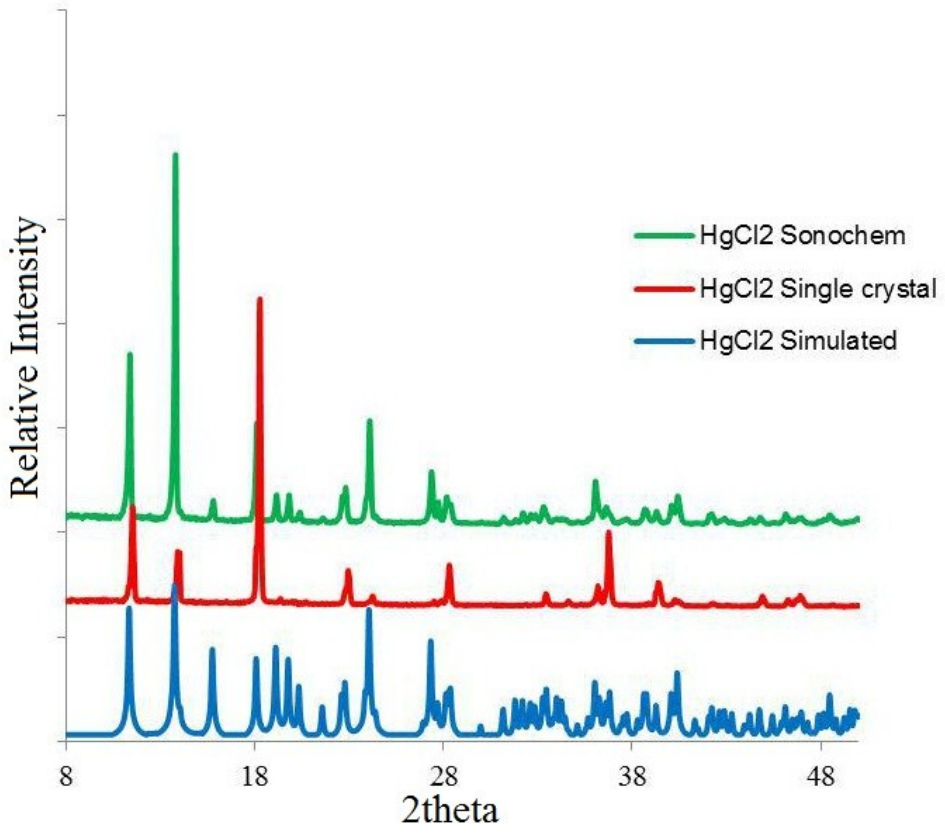

Intensity
126
116
106
96
86
76
66
56
46
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
2 ATR-IR
2 FT-IR

(d)

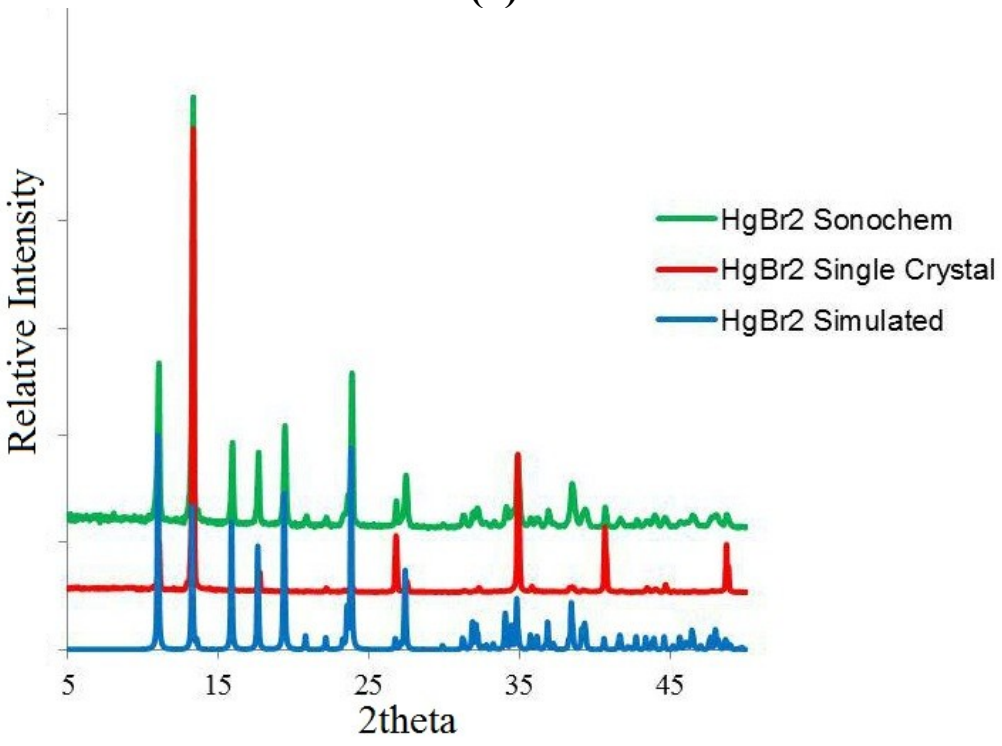


(e)

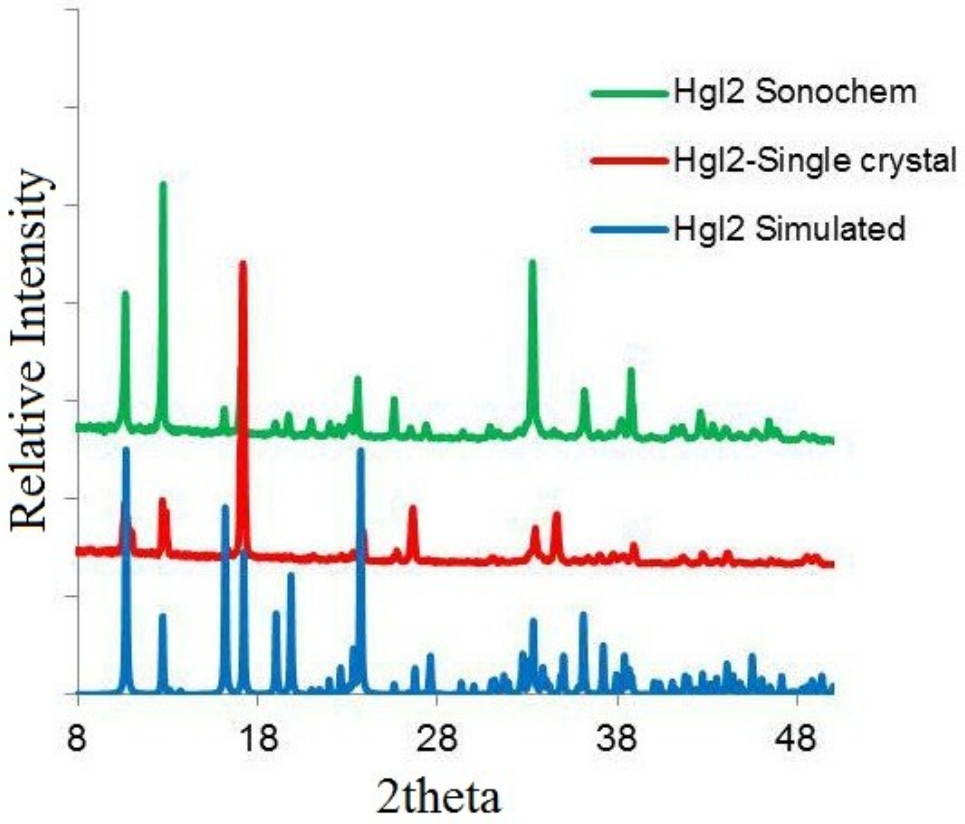
Figure S3. FT-IR spectra (a) ATR-IR spectra (b) and comparison of FT-IR and ATR-IR spectra of compounds **1**-**3** prepared by ultrasonic irradiation. The FT-IR spectra of the compounds generated by the sonochemical method and of the layering technique are indistinguishable.


Relative Intensity
HgCl2 Sonochem
HgCl2 Single crystal
HgCl2 Simulated
8
18
28
38
48
2theta

(a)


Relative Intensity
HgBr2 Sonochem
HgBr2 Single Crystal
HgBr2 Simulated
5
15
25
35
45
2theta

(b)



(c)

Figure S4. Simulated and experimental PXRD patterns of compounds **1** (a), **2** (b) and **3** (c) prepared by layering technique and ultrasonic irradiation

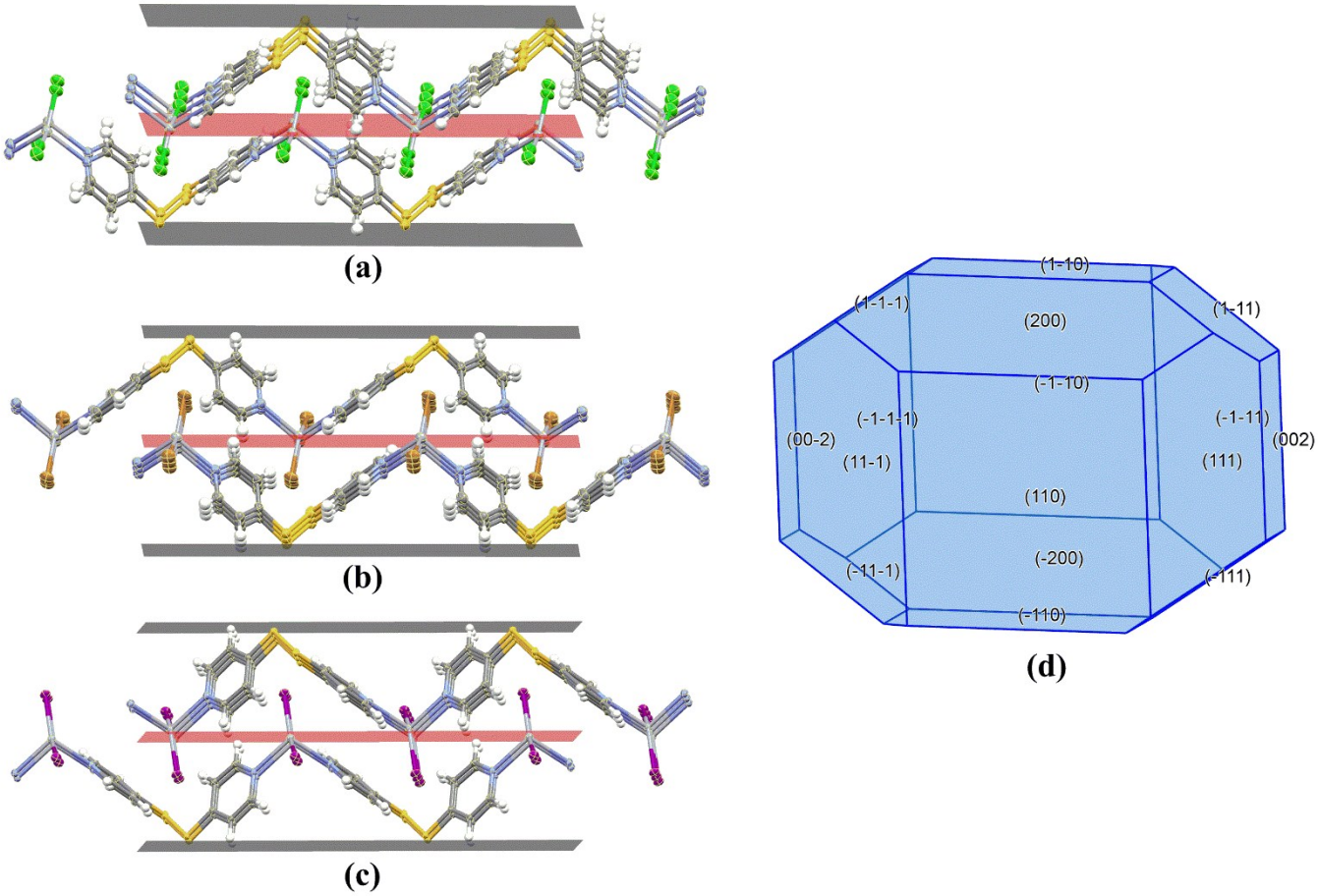


Figure **S5**. Predicted crystal morphologies of complexes **1** (a), **2** (b) and **3** (c) and their packing along the [110] plane.

Table **S1**. Face lists generated according to the BFDH law using materials studio package.[4]

Compound 1					
hkl	**multiplicity**	**dhkl**	**distance**	**Total facet area**	**% total facet area**
{ 1 1 0}	4	7.80568861	12.81116952	1.385686e+003	37.27103829
{ 1 1 -1}	4	6.52375803	15.32858815	891.10355014	23.96816321
{ 2 0 0}	2	6.43981829	15.52838846	388.43183201	10.44771682
{ 1 1 1}	4	6.30838364	15.85192114	685.63380039	18.44160853
{ 0 0 2}	2	5.62549487	17.77621387	367.00788011	9.87147315
{ 0 2 0}	2	4.90660000	20.38071169		
{ 1 1 -2}	4	4.64337401	21.53606404		
{ 0 2 1}	4	4.49752029	22.23447445		
{ 1 1 2}	4	4.48815298	22.28088044		
{ 2 0 -2}	2	4.36648314	22.90172590		

Compound 2					
hkl	**multiplicity**	**dhkl**	**distance**	**Total facet area**	**% total facet area**
{ 1 1 0}	4	8.04756025	12.42612629	1.337497e+003	37.70682392
{ 2 0 0}	2	6.69138612	14.94458671	390.15896587	10.99939470
{ 1 1 -1}	4	6.54596899	15.27657711	771.82761197	21.75942958
{ 1 1 1}	4	6.51990161	15.33765478	748.28277813	21.09565162
{ 0 0 2}	2	5.59366300	17.87737302	299.32870168	8.43870018
{ 0 2 0}	2	5.03605000	19.85683224		
{ 1 1 -2}	4	4.60219434	21.72876515		
{ 0 2 1}	4	4.59221293	21.77599373		
{ 1 1 2}	4	4.58407552	21.81464936		
{ 2 0 -2}	2	4.30650024	23.22071158		
Compound 3					
hkl	**multiplicity**	**dhkl**	**distance**	**Total facet area**	**% total facet area**
{ 1 1 0}	4	8.27166667	12.08946201	1.304476e+003	38.19842641
{ 2 0 0}	2	6.95536646	14.37738767	405.83116201	11.88378280
{ 1 1 -1}	4	6.74792687	14.81936629	860.47296390	25.19686698
{ 1 1 1}	4	6.45502559	15.49180535	619.88921320	18.15195445
{ 0 0 2}	2	5.46685712	18.29204564	224.33029253	6.56896937
{ 0 2 0}	2	5.14405000	19.43993546		
{ 1 1 -2}	4	4.66064188	21.45627203		
{ 0 2 1}	4	4.65463392	21.48396667		
{ 2 0 -2}	2	4.46970787	22.37282677		
{ 1 1 2}	4	4.46706228	22.38607695		

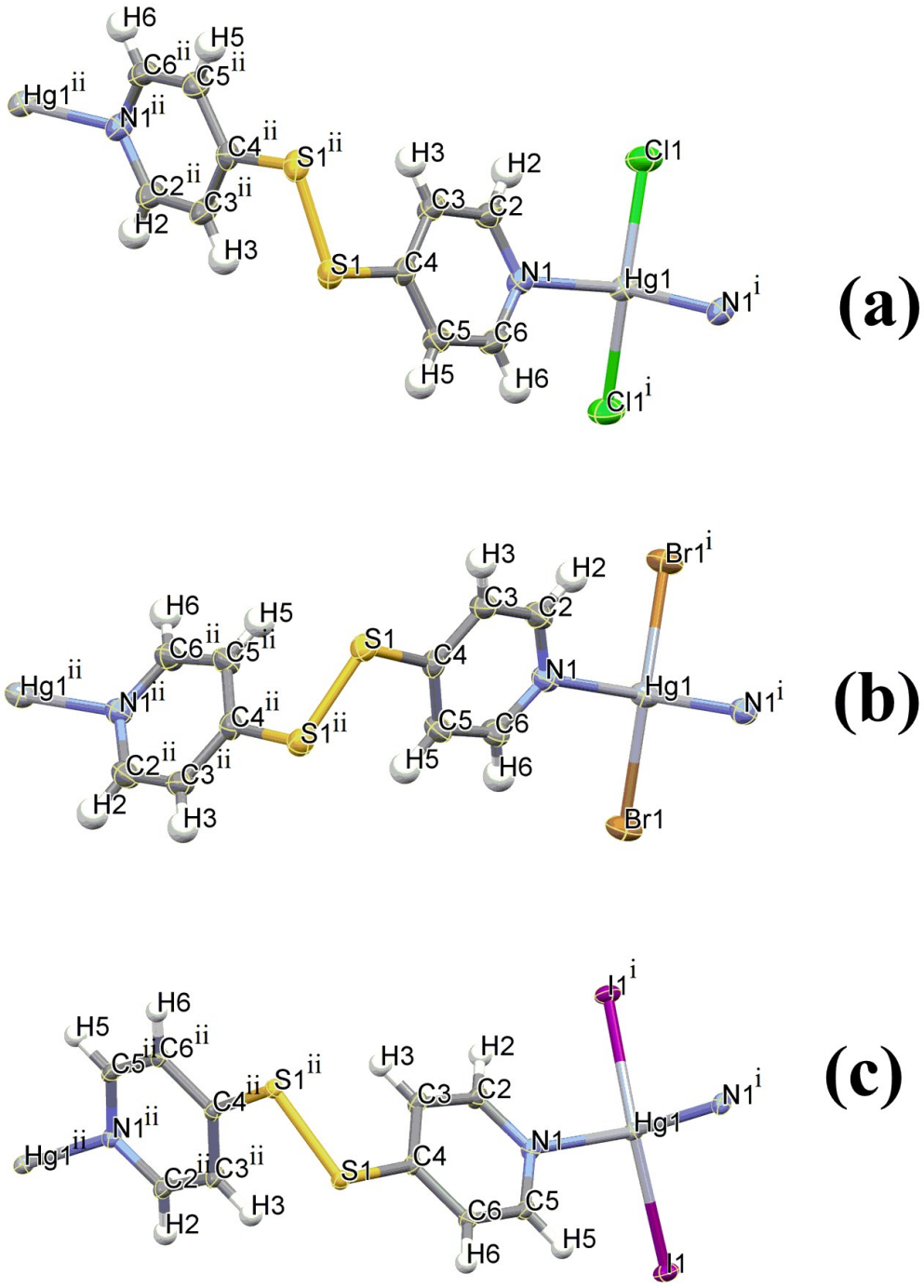


Figure S6. Portion of the structure of the coordination compounds **1** (a), **2** (b) and **3** (c) showing the coordination geometry around the Hg(II). Symmetry codes: (a) i at 1-x, y, 1.5-z; ii at 1-x, y, ½-z (b) i at 1-x, y, 1.5-z; ii at 1-x, y, ½-z (c) i at 1-x, y, ½-z; ii at 1-x, y, 1.5-z. ORTEP diagrams were drawn by 30% probability.

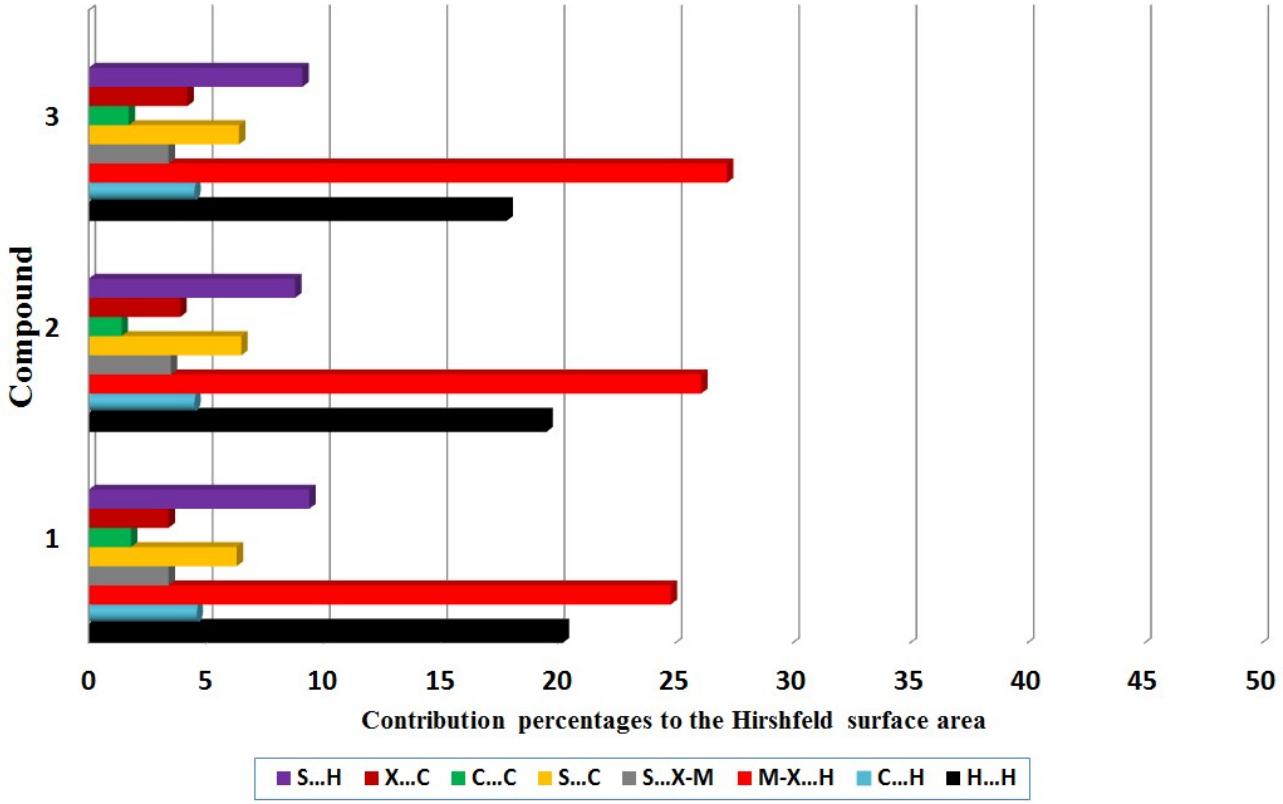


Figure S7. Relative contributions of various non-covalent contacts to the Hirshfeld surface area in compounds **1-3**.

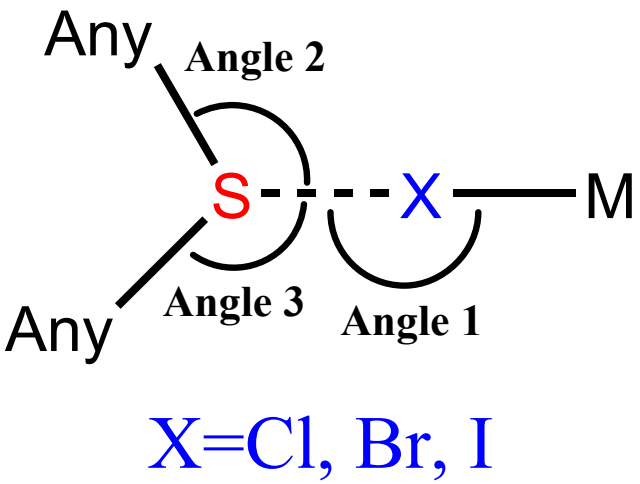
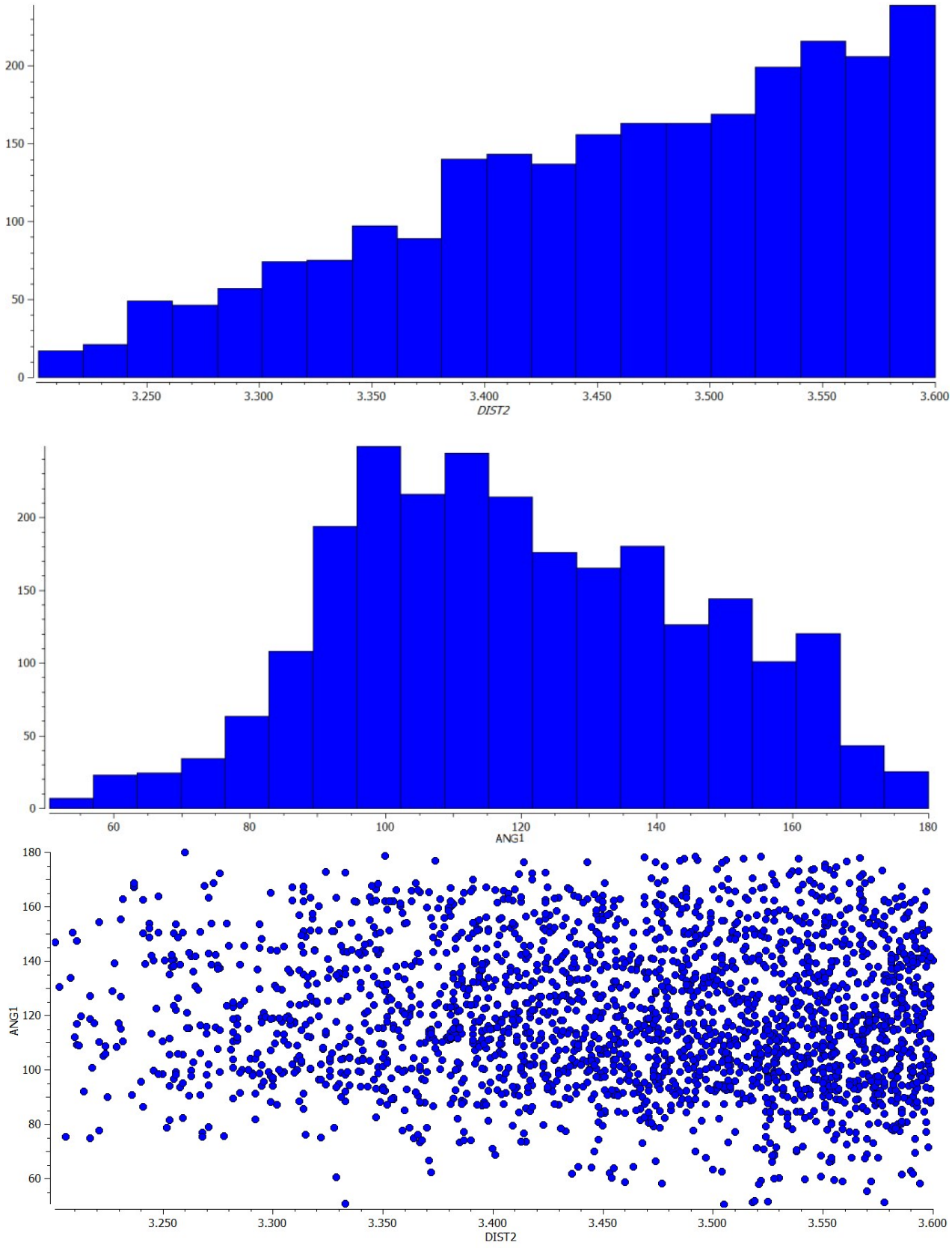
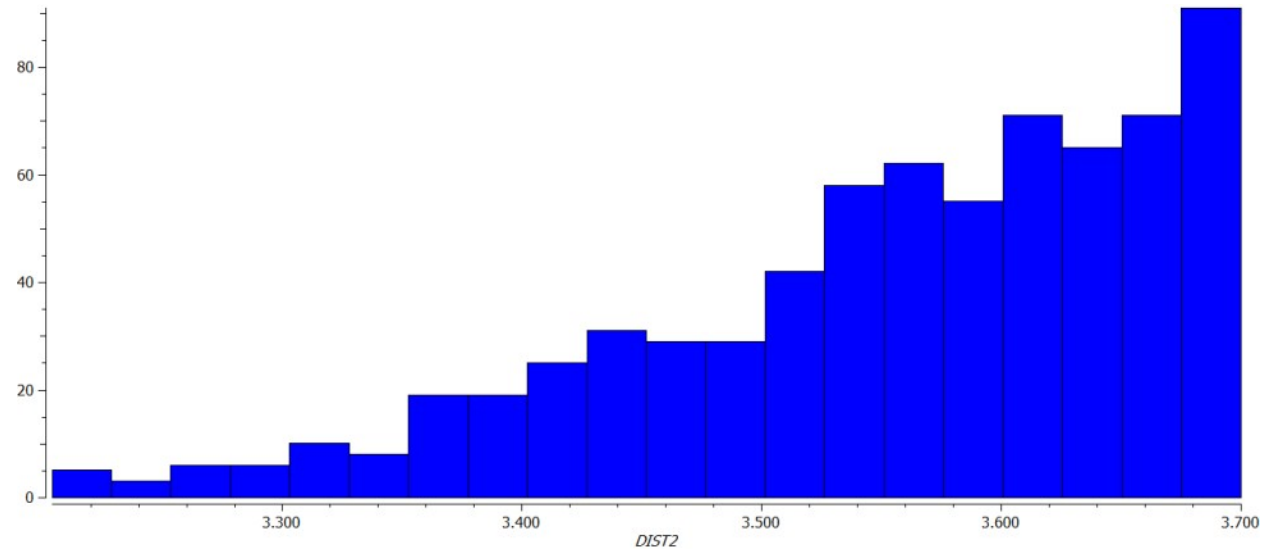
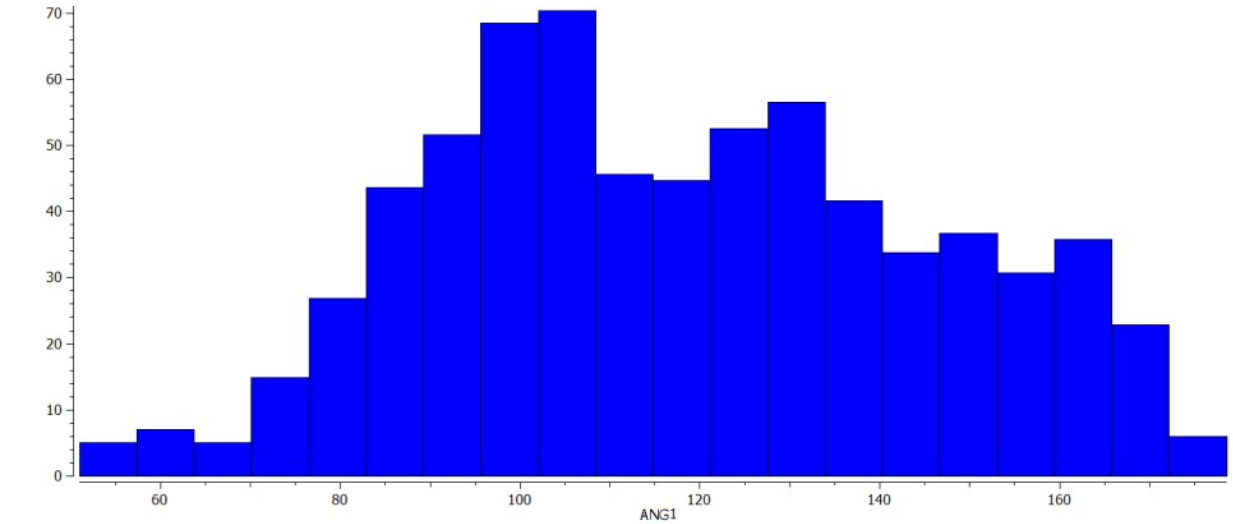


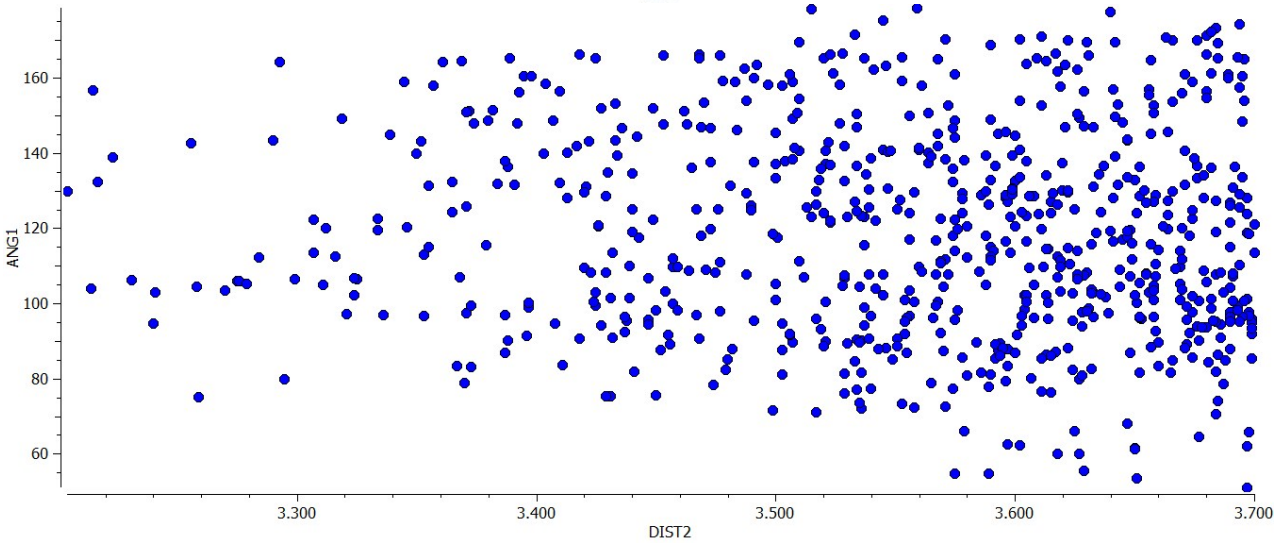
Figure S8. CSD searching query for analyzing S···X-M interaction (search criteria: M: any metals; Any: any atoms; Angle 1-3 in the range of 50-180˚ and S···X interaction distances of 3.2-3.6, 3.3-3.7 and 3.3-3.85 for Cl, Br and I, respectively). S···Cl-M (1147 hits), S···Br-M (307 hits) and S···I-M (212 hits) found. The CSD searches have been done using Cambridge Structural Database, version 5.37 (Last update may 2016); CCDC: Cambridge, U.K.


200
150
100
50
0
3.250
3.300
3.350
3.400
3.450
3.500
3.550
3.600
DIST2
200
150
100
50
0
60
80
100
120
140
160
180
ANG1
180
160
140
120
100
80
60
ANG1
3.250
3.300
3.350
3.400
3.450
3.500
3.550
3.600
DIST2

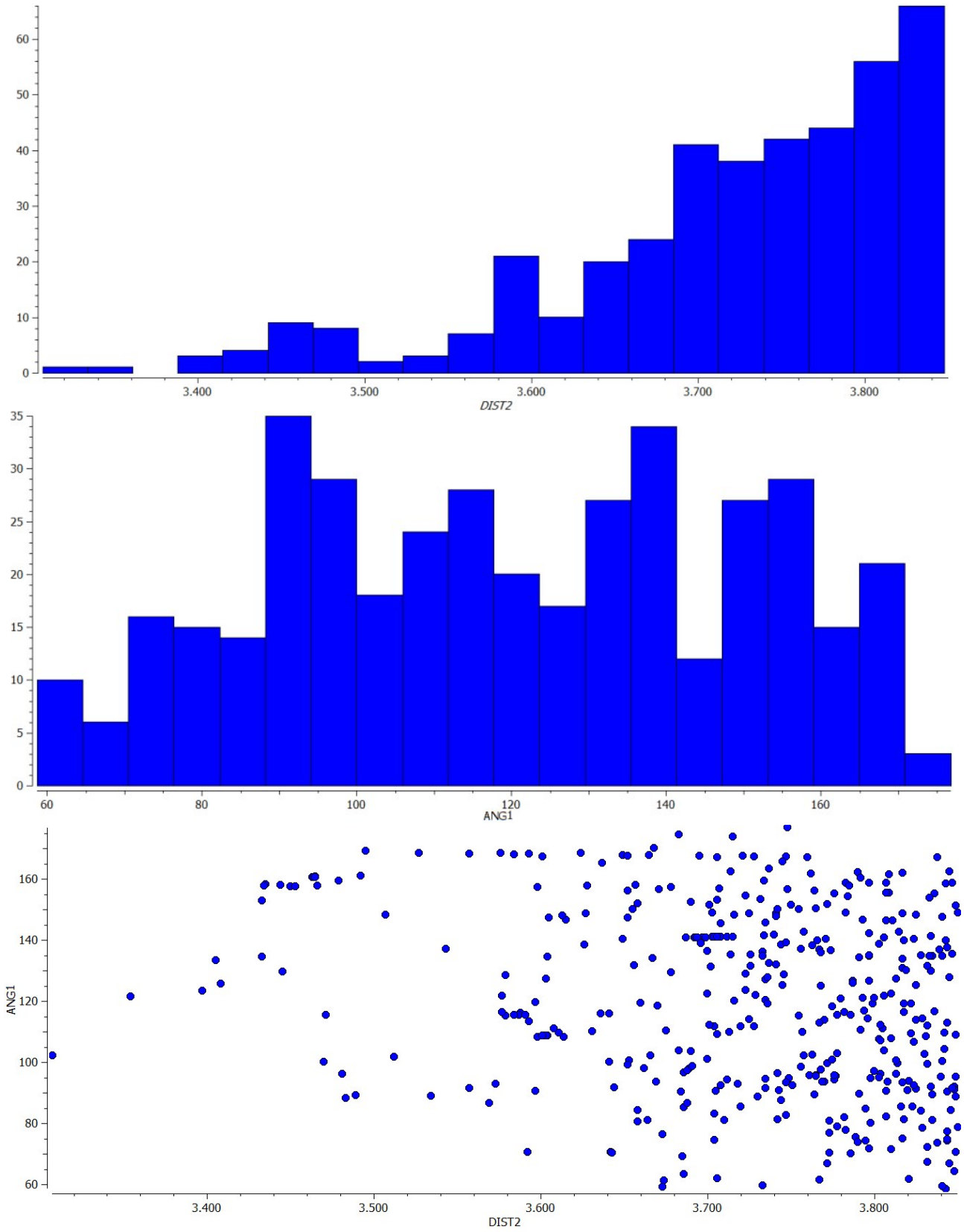
(a)


80
60
40
20
0
3.300
3.400
3.500
3.600
3.700
DIST2


70
60
50
40
30
20
10
0
60
80
100
120
140
160
ANG1

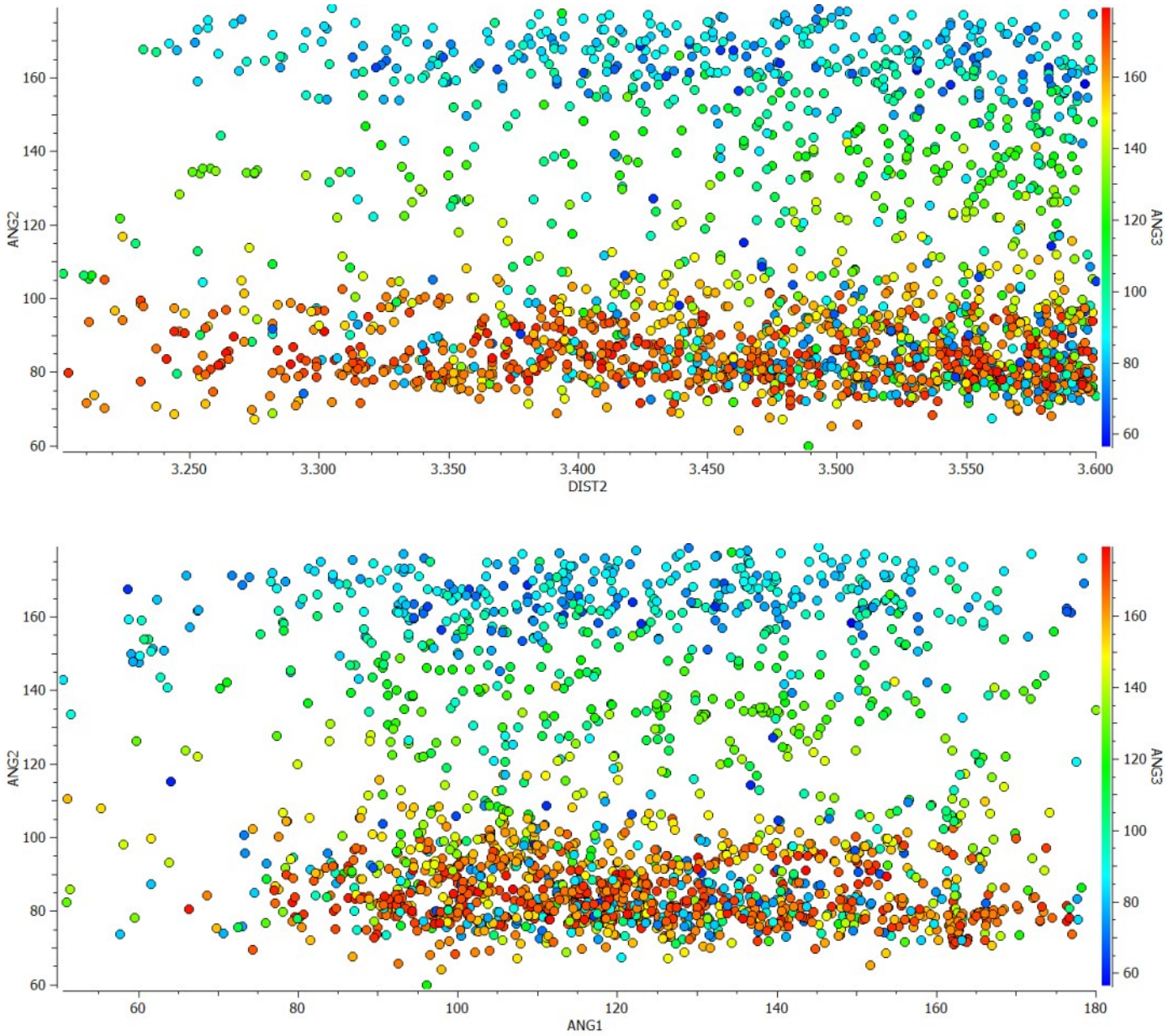

160
140
120
100
80
60
ANG1
3.300
3.400
3.500
3.600
3.700
DIST2

(b)

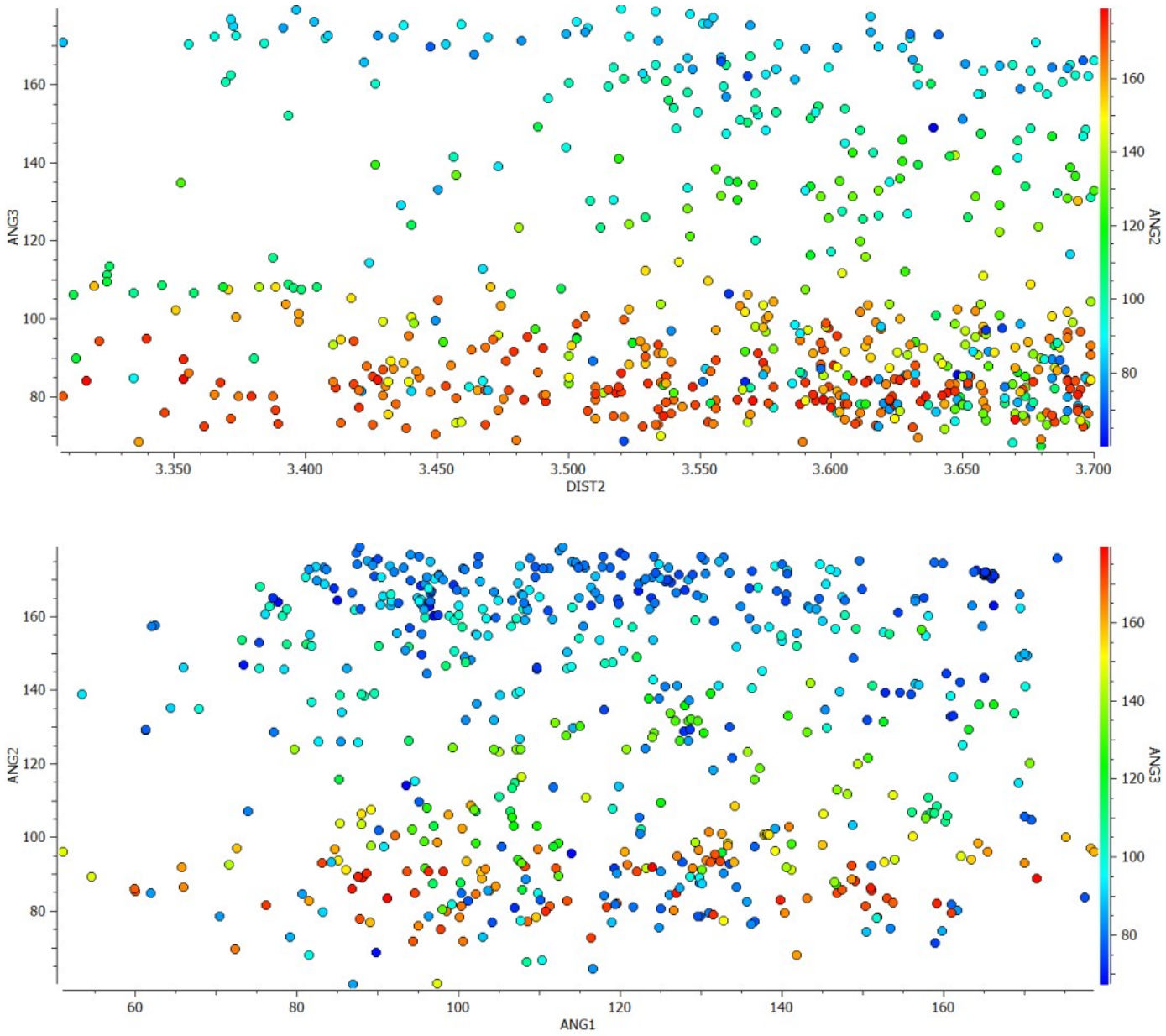


(c)

Figure S9. Histogram of the S···X-M chalcogen bond distance, histogram of the S···X-M chalcogen bond angle and scatter-plot of chalcogen bond distance versus the S···X-M angle, where X is Cl (a), Br (b) and I (c), respectively. Reported data were obtained from CSD, version 2015.

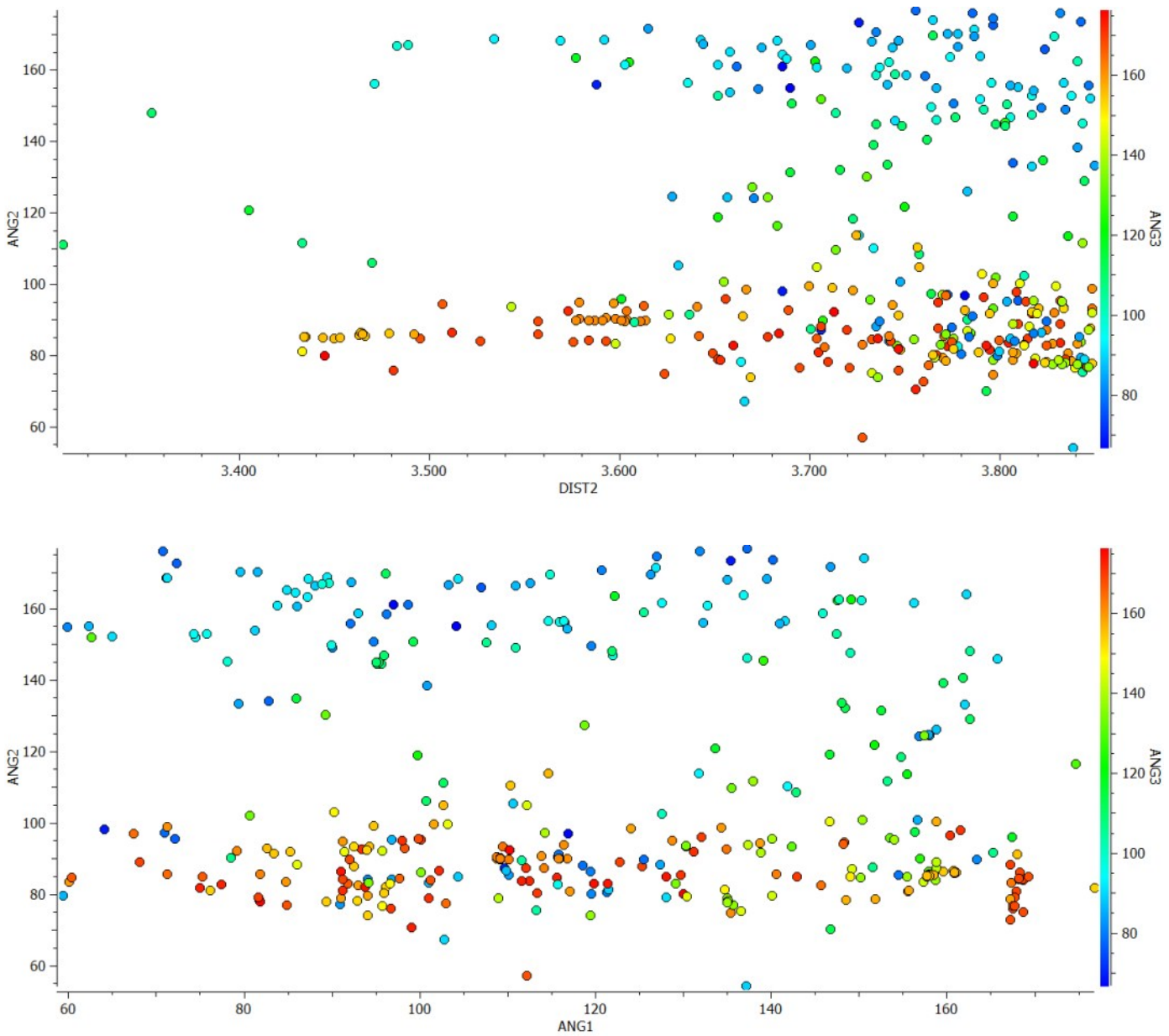


(a)


ANG3
160
140
120
100
80
3.350
3.400
3.450
3.500
3.550
3.600
3.650
3.700
DIST2
ANG2
160
140
120
100
80

ANG2
160
140
120
100
80
60
80
100
120
140
160
ANG1
ANG3
160
140
120
100
80

(b)



(c)

Figure S10. Scatter-plot of the S···X-M chalcogen bond distance and angle 1, 2 and 3 (defined in Figure S5), where X is Cl (a), Br (b) and I (c), respectively. Reported data were obtained from CSD, version 2015.

Table S2. Selected intra and intermolecular hydrogen bond geometries for coordination compounds **1-3**.

Compound	D-H…A	d(D-H)/Å	d(H…A)/Å	d(D…A)/Å	<D-H…A/°	Sym. Code
1	C5-H5…Cl1	0.930	2.9573(9)	3.588(3)	126.39(14)	*1.5x*, *-1/2+y*, 1.5-*z*
	C3-H3…S1	0.930	2.7117(7)	3.200(3)	113.67(13)	*x*, *y*, *z*
2	C2-H2…Br1	0.930	3.2436(8)	3.870(7)	126.5(4)	-1/2+x, -1/2+y, z
	C5-H5…S1	0.930	2.6991(1)	3.190(7)	113.8(4)	*x*, *y*, *z*
3	C3-H3…I1	0.930	3.3934(3)	3.949(3)	119.09(19)	1-x, 1-y, 1-z
	C3-H3…S1	0.930	2.6587(8)	3.168(3)	114.11(18)	*x*, *y*, *z*

References

1 Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3-8.

2 Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3-8.

3 Spek, A. L. (2009). *Acta Cryst.* D**65**, 148-155.

4 Yao, W.; Yan, Y. L.; Xue, L.; Zhang, C.; Li, G. P.; Zheng, Q. D.; Zhao, Y. S. Jiang, H.; Yao, J. N. *Angew. Chem., Int. Ed*., 2013, 52, 8713.