Supplementary Information

Crystalline products of bromoantimonate(III) oxidation by Br2 in presence of different cations: diversity of structural types and patterns of halogen bond systems

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Table S1. SCXRD Experimental details

	1	**2**	**3**	**4**
Chemical formula	$C_{28}H_{36}Br_{15}N_4Sb_3$	$C_{14}H_{18}Br_9N_2Sb$	$C_{15}H_{20}Br_9N_2Sb$	$C_{16}H_{22}Br_9N_2Sb$
M_r	1992.51	1055.24	1069.27	1083.29
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Orthorhombic, $P2_12_12$	Triclinic, $P\bar{1}$
Temperature (K)	140	140	293	140
a, b, c (Å)	11.2062 (2), 15.7756 (3), 16.4774 (3)	7.4663 (5), 9.0838 (7), 10.3799 (9)	10.7933 (13), 15.7086 (12), 7.8096 (6)	7.1919 (2), 8.9352 (3), 12.0590 (4)
α, β, γ (°)	114.223 (2), 95.122 (2), 106.738 (2)	112.483 (7), 95.318 (6), 98.593 (6)	90, 90, 90	69.046 (3), 74.269 (3), 80.096 (3)
V (Å^3)	2471.12 (9)	634.47 (9)	1324.1 (2)	694.14 (4)
Z	2	1	2	1
μ (mm^{-1})	13.78	15.26	14.63	13.95
Crystal size (mm)	0.21 × 0.17 × 0.11	0.21 × 0.14 × 0.11	××	0.17 × 0.14 × 0.11
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.41.123a (Rigaku Oxford Diffraction, 2022) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.41.123a (Rigaku Oxford Diffraction, 2022) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.311, 1.000	0.257, 1.000	0.333, 1.000	0.295, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18516, 10746, 8817	4430, 2397, 2001	3825, 2350, 2089	5089, 2983, 2539
R_{int}	0.024	0.036	0.035	0.026
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.682	0.610	0.610	0.679
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.064, 1.01	0.041, 0.094, 0.99	0.040, 0.087, 1.03	0.033, 0.071, 1.01
No. of reflections	10746	2397	2350	2983
No. of parameters	454	121	124	130
No. of restraints	0	0	0	0
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.20, -1.35	1.56, -1.91	0.91, -0.93	1.08, -1.00
Absolute structure	–	–	Flack x determined using 700 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).	–
Absolute structure parameter	–	–	-0.01 (2)	–

	5	6
Chemical formula	$C_{17}H_{24}Br_9N_2Sb$	$C_{18}H_{26}Br_{12}N_2Sb_2$
M_r	1097.32	1472.83
Crystal system, space group	Triclinic, *P*1	Monoclinic, *C*2/*c*
Temperature (K)	130	130
a, *b*, *c* (Å)	7.7262 (2), 8.7072 (4), 11.2299 (4)	22.0906 (14), 7.8331 (5), 20.5614 (14)
α, β, γ (°)	75.662 (4), 82.363 (3), 82.661 (3)	90, 102.413 (7), 90
V (Å^3)	721.91 (5)	3474.7 (4)
Z	1	4
μ (mm^{-1})	13.42	15.37
Crystal size (mm)	0.19 × 0.14 × 0.07	0.21 × 0.16 × 0.10
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.41.123a (Rigaku Oxford Diffraction, 2022) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.424, 1.000	0.334, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5391, 4158, 3775	8051, 3916, 3314
R_{int}	0.026	0.025
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.683	0.684
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.034, 0.071, 0.98	0.025, 0.054, 1.00
No. of reflections	4158	3916
No. of parameters	263	156
No. of restraints	3	0
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.88, -1.02	1.09, -0.79
Absolute structure	Refined as an inversion twin.	–
Absolute structure parameter	0.151 (16)	–

Computer programs: *CrysAlis PRO* 1.171.41.123a (Rigaku OD, 2022), *CrysAlis PRO* 1.171.38.46 (Rigaku OD, 2015), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL2019*/2 (Sheldrick, 2019), *SHELXL2014*/7 (Sheldrick, 2014).

Powder X-ray Diffractometry. XRD analysis of polycrystals was performed on Shimadzu XRD-7000 diffractometer (CuK-alpha radiation, Ni – filter, linear One Sight detector, 0.0143° 2θ step, 2s per step). Plotting of PXRD patterns and data treatment was performed using X'Pert Plus software. In all cases red line is synthesized, blue is simulated.

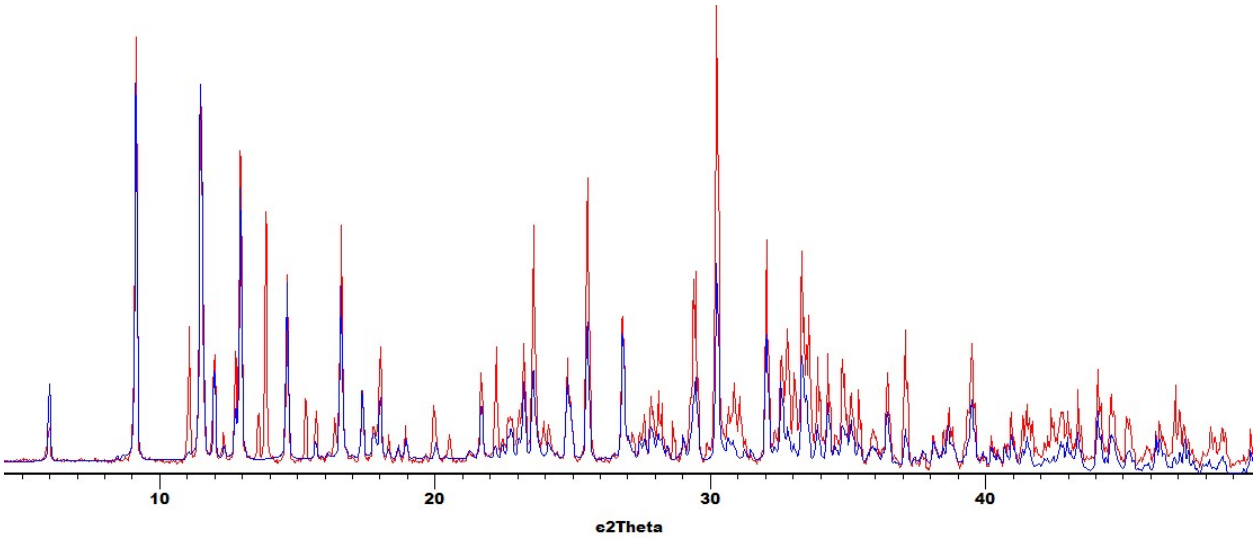

Figure 1S. PXRD data for **1**

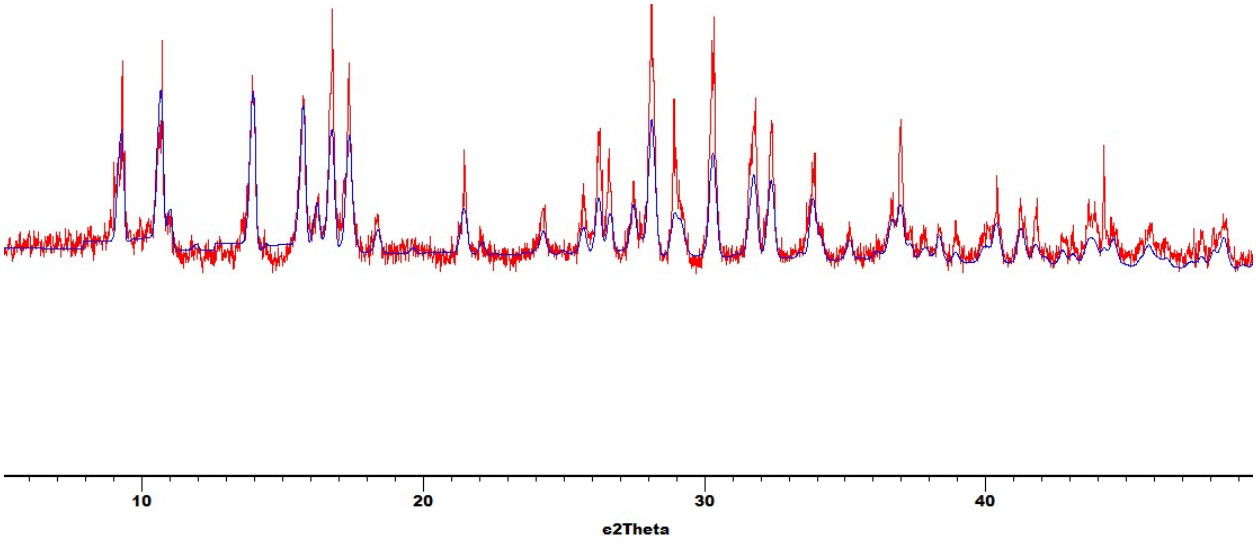

Figure 2S. PXRD data for **2**

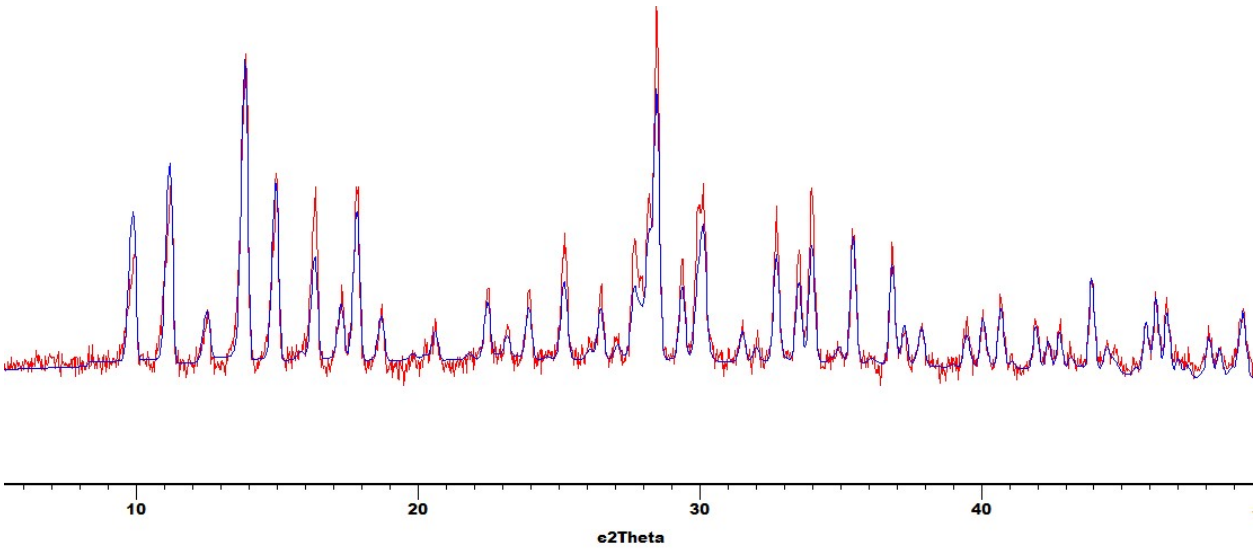

Figure 3S. PXRD data for **3**

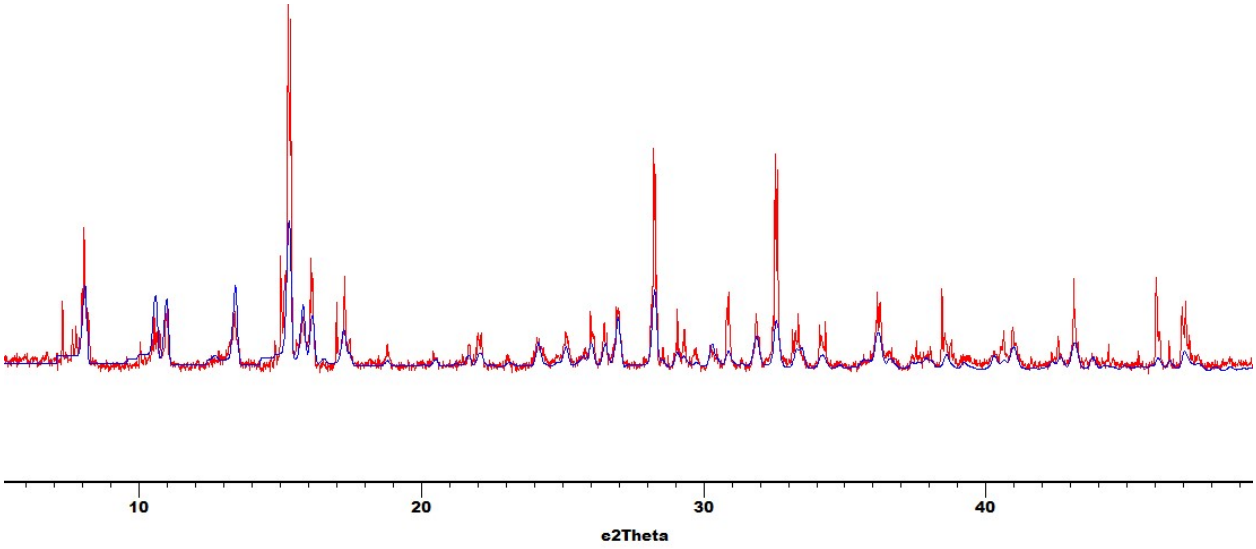

Figure 4S. PXRD data for **4**

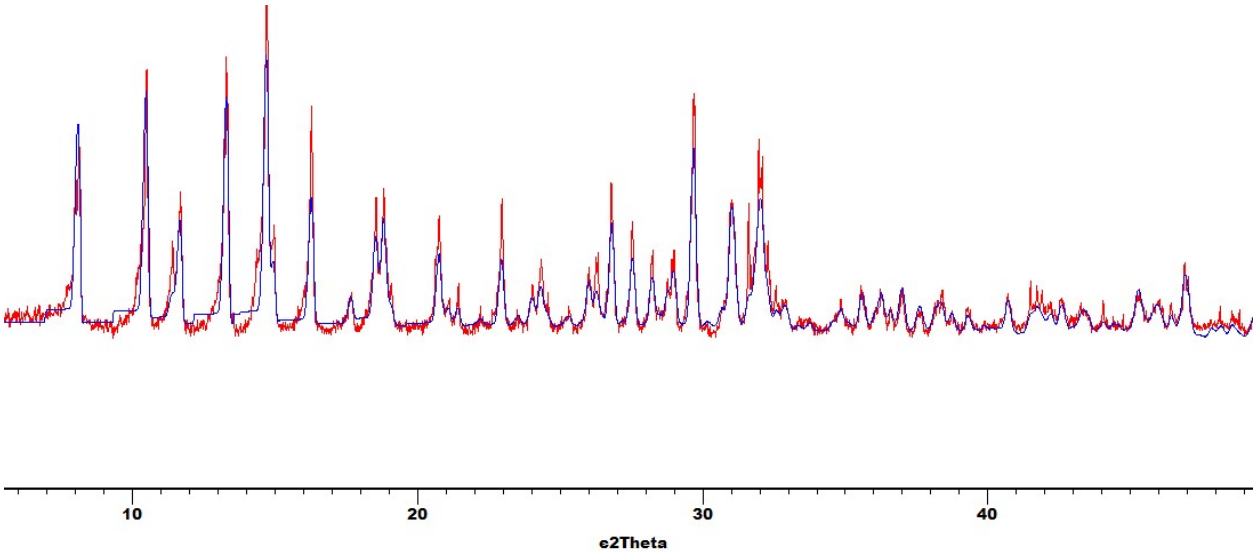

Figure 5S. PXRD data for **5**

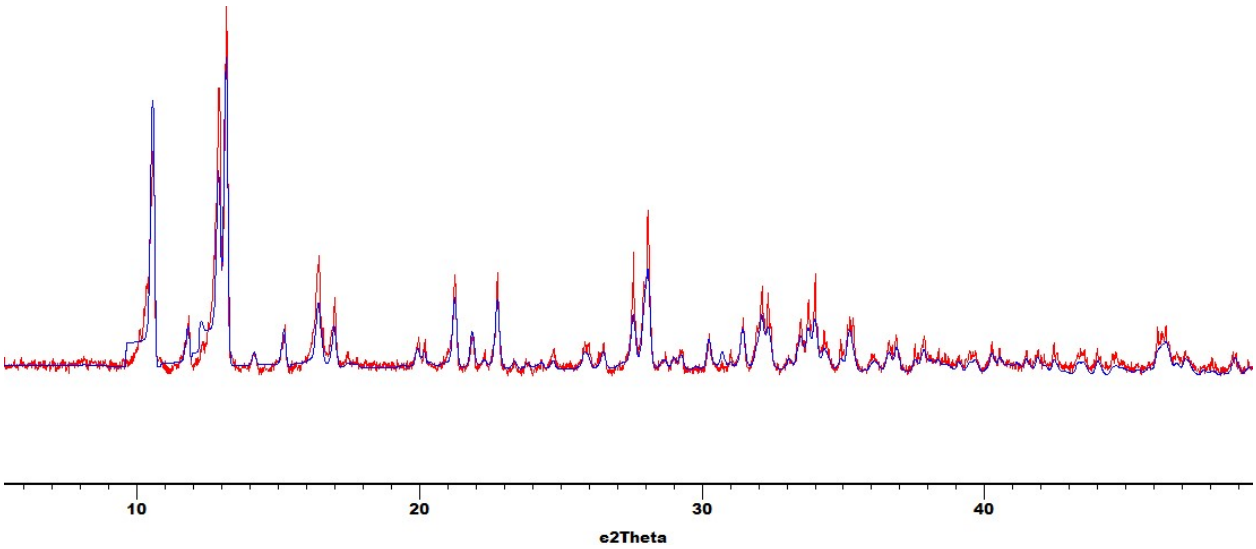

Figure 6S. PXRD data for **6**

Computational details

The DFT calculations based on the obtained experimental X-ray geometries of **1**–**6** have been carried out using the M06 functional with the help of Gaussian-09 [M. J. Frisch et al. Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets [Mol. Phys. 2010, 108, 1965. || J. Chem. Phys. 2009, 130, 064108. || Chem. Phys. Lett. 2013, 582, 158. || J. Mol. Struct. - Theochem 2010, 961, 107.] for all atoms. Note that this level of theory was also successfully used in our previous studies of such chemical systems (viz. Sb(III) and Sb(V) coordination compounds with halide ligands) [Chem. Eur. J. 2018, 24, 10165. || Chem. Eur. J. 2018, 24, 14707. || CrystEngComm 2019, 21, 850. || Z. Anorg. Allg. Chem. 2019, 645, 1141. || Inorg. Chim. Acta 2020, 502, 119278.]. The topological analysis of the electron density distribution has been performed by using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. The Cartesian atomic coordinates for model structures are presented in **Table S2**.

Table S2. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
1			
Br	-4.373956	0.190208	12.116199
Br	-3.734120	-2.471227	14.488584
Br	-1.258348	0.040606	13.984856
Sb	-3.742701	0.051606	14.596599
Br	-3.111446	-0.086995	17.076999
Br	-3.751283	2.574440	14.704614
Br	-6.227054	0.062607	15.208343
Br	1.006019	-7.483213	13.971281
Br	-1.485341	-4.984801	14.820511

Br	-0.847202	-7.729385	17.069263
Sb	-1.471049	-7.502001	14.596599
Br	-3.948116	-7.520789	15.221917
Br	-1.456756	-10.019202	14.372687
Br	-2.094896	-7.274617	12.123935
Br	1.577295	2.012796	8.798392
Br	-0.384125	-1.017015	8.269119
Br	2.715668	-3.450806	8.584260
Br	1.891116	-0.751909	11.359657
Br	2.468512	-0.298399	5.695447
Br	5.241993	0.123286	8.784087
Br	8.096487	0.333096	6.233624
Br	5.065780	2.491699	5.915418
Br	5.798252	0.229034	3.207165
Sb	5.554231	0.013064	5.831633
Sb	2.119326	-0.603846	8.735335
Br	13.683267	0.018788	-0.625318
Br	11.191907	2.517200	0.223912
Br	11.830047	-0.227384	2.472664
Sb	11.206200	0.000000	0.000000
Br	8.729133	-0.018788	0.625318
Br	11.220493	-2.517200	-0.223912
Br	10.582353	0.227384	-2.472664
Br	3.614552	5.592418	5.798207
Br	5.575971	8.622228	6.327480
Br	2.476178	11.056019	6.012339
Br	3.300731	8.357123	3.236942
Br	2.723335	7.903613	8.901152
Br	-0.050146	7.481928	5.812512
Br	-2.904641	7.272117	8.362975
Br	0.126066	5.113515	8.681181
Br	-0.606406	7.376180	11.389434
Sb	-0.362384	7.592149	8.764966
Sb	3.072521	8.209059	5.861264
Br	-9.628905	2.012796	8.798392
Br	-11.590325	-1.017015	8.269119
Br	-8.490532	-3.450806	8.584260
Br	-9.315084	-0.751909	11.359657
Br	-8.737688	-0.298399	5.695447
Br	-5.964207	0.123286	8.784087
Br	-3.109713	0.333096	6.233624
Br	-6.140420	2.491699	5.915418
Br	-5.407948	0.229034	3.207165
Sb	-5.651969	0.013064	5.831633
Sb	-9.086874	-0.603846	8.735335
Br	2.477067	0.018788	-0.625318
Br	-0.014293	2.517200	0.223912
Br	0.623847	-0.227384	2.472664

Sb	0.000000	0.000000	0.000000
Br	-2.477067	-0.018788	0.625318
Br	0.014293	-2.517200	-0.223912
Br	-0.623847	0.227384	-2.472664
2			
Sb	1.894876	6.901927	4.730560
Br	1.865746	4.787228	3.287739
Br	3.542293	5.792136	6.285968
Br	3.838376	7.800250	3.321704
Br	1.924006	9.016625	6.173381
Br	0.247459	8.011718	3.175152
Br	-0.048624	6.003604	6.139415
Br	0.000000	0.000000	0.000000
Br	0.581121	2.049289	1.388325
Br	-0.581121	-2.049289	-1.388325
Sb	-5.571424	6.901927	4.730560
Br	-5.600554	4.787228	3.287739
Br	-3.924007	5.792136	6.285968
Br	-3.627924	7.800250	3.321704
Br	-5.542294	9.016625	6.173381
Br	-7.218841	8.011718	3.175152
Br	-7.514924	6.003604	6.139415
Br	-1.357252	8.981831	0.000000
Br	-0.776131	11.031121	1.388325
Br	-1.938373	6.932542	-1.388325
3			
Sb	5.396650	0.000000	1.295144
Br	7.155310	0.423975	3.103145
Br	4.810574	2.479917	1.335364
Br	3.646948	-0.424603	-0.525742
Br	3.637990	-0.423975	3.103145
Br	5.982726	-2.479917	1.335364
Br	7.146352	0.424603	-0.525742
Br	4.301238	5.576710	2.704386
Br	5.396650	7.854300	2.720865
Br	6.492062	10.131890	2.704386
Br	11.888712	-2.277590	5.105214
Br	10.793300	0.000000	5.088735
Br	9.697888	2.277590	5.105214
Br	11.888712	-2.277590	-2.704386
Br	10.793300	-0.000000	-2.720865
Br	9.697888	2.277590	-2.704386
Br	1.095412	-2.277590	5.105214
Br	0.000000	0.000000	5.088735
Br	-1.095412	2.277590	5.105214
Br	1.095412	-2.277590	-2.704386
Br	-0.000000	-0.000000	-2.720865
Br	-1.095412	2.277590	-2.704386

4			
Br	8.179661	5.366467	6.434213
Br	5.978892	4.483575	3.686311
Br	7.309041	7.833372	3.914499
Sb	5.999093	6.304478	5.482645
Br	3.818526	7.242488	4.531077
Br	6.019295	8.125380	7.278979
Br	4.689146	4.775583	7.050791
Br	6.693414	1.788050	1.734161
Br	7.191900	0.000000	0.000000
Br	7.690386	-1.788050	-1.734161
Br	8.230249	10.590092	1.734161
Br	8.728735	8.802042	0.000000
Br	9.227221	7.013991	-1.734161
Br	15.371561	5.366467	6.434213
Br	13.170792	4.483575	3.686311
Br	14.500941	7.833372	3.914499
Sb	13.190993	6.304478	5.482645
Br	11.010426	7.242488	4.531077
Br	13.211195	8.125380	7.278979
Br	11.881046	4.775583	7.050791
5			
Br	-0.205978	1.757720	9.965108
Br	1.329627	-0.746017	7.845671
Br	-0.332553	2.073373	6.324662
Br	1.649826	4.381919	8.229007
Br	3.336292	1.560052	9.830621
Sb	1.486474	1.823198	8.086622
Br	3.264665	1.874430	6.245355
Br	3.893534	-1.145432	1.996743
Br	4.568874	1.204587	2.691249
Br	5.363814	3.493354	3.471878
Br	5.385948	1.466315	12.816269
Br	6.061288	3.816333	13.510774
Br	6.856228	6.105100	14.291403
Br	0.906277	10.393588	9.965108
Br	2.441882	7.889851	7.845671
Br	0.779703	10.709241	6.324662
Br	2.762082	13.017788	8.229007
Br	4.448547	10.195920	9.830621
Sb	2.598729	10.459066	8.086622
Br	4.376920	10.510298	6.245355
Br	-2.340252	1.466315	12.816269
Br	-1.664912	3.816333	13.510774
Br	-0.869972	6.105100	14.291403
Br	-3.832666	-1.145432	1.996743
Br	-3.157326	1.204587	2.691249
Br	-2.362386	3.493354	3.471878

6			
Sb	3.312742	-1.958275	10.040374
Br	4.827004	-0.731455	11.668521
Br	2.553172	0.278232	9.082321
Br	5.209453	-2.028616	8.333108
Br	1.798481	-3.185095	8.412227
Br	4.072313	-4.194782	10.998426
Br	1.416032	-1.887934	11.747639
Sb	7.730439	-4.762446	15.060560
Br	8.496845	-2.998746	16.693125
Br	5.431511	-4.856209	16.140302
Br	6.944328	-6.575809	13.419160
Br	6.964033	-2.998746	13.427996
Br	10.029366	-4.856209	13.980819
Br	8.516549	-6.575809	16.701961
Sb	-1.104954	-6.987204	5.020187
Br	-1.871360	-8.750904	3.387622
Br	1.193974	-6.893441	3.940445
Br	-0.318844	-5.173841	6.661587
Br	-0.338548	-8.750904	6.652752
Br	-3.403881	-6.893441	6.099929
Br	-1.891064	-5.173841	3.378787
Sb	-3.314861	-0.845896	15.060560
Br	-2.548455	0.917804	16.693125
Br	-5.613789	-0.939659	16.140302
Br	-4.100972	-2.659259	13.419160
Br	-4.081267	0.917804	13.427996
Br	-1.015934	-0.939659	13.980819
Br	-2.528751	-2.659259	16.701961

Table S3. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate λ_2 eigenvalues, energy density – H_b, potential energy density – $V(\mathbf{r})$, Lagrangian kinetic energy – $G(\mathbf{r})$, and electron localization function – ELF (a.u.) at the bond critical points (3, –1), corresponding to noncovalent interactions Br···Br in the X-ray structures **1**-**6**, and estimated strength for these interactions E_{int} (kcal/mol).

Contact Br···Br*	% vdW radii sum	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	ELF	E_{int}**
1									
3.389 Å	93	0.014	0.036	-0.014	0.001	-0.008	0.009	0.063	2.9
3.426 Å	94	0.011	0.028	-0.011	0.001	-0.006	0.007	0.053	2.2
3.660 Å	100	0.008	0.019	-0.008	0.000	-0.004	0.004	0.041	1.5
3.693 Å	101	0.008	0.019	-0.008	0.001	-0.004	0.005	0.040	1.5
3.714 Å	101	0.007	0.015	-0.007	0.001	-0.003	0.004	0.045	1.1
3.914 Å	107	0.005	0.013	-0.005	0.000	-0.003	0.003	0.023	1.1
2									
3.571 Å	98	0.009	0.021	-0.009	0.000	-0.005	0.005	0.044	1.8
3.655 Å	100	0.009	0.021	-0.009	0.000	-0.005	0.005	0.041	1.8
3.688 Å	101	0.008	0.020	-0.008	0.001	-0.004	0.005	0.032	1.5
3.884 Å	106	0.006	0.014	-0.006	0.000	-0.003	0.003	0.024	1.1
3									
3.424 Å	94	0.012	0.030	-0.012	0.000	-0.007	0.007	0.059	2.5
3.729 Å	102	0.008	0.019	-0.008	0.000	-0.004	0.004	0.035	1.5
3.833 Å	105	0.006	0.016	-0.006	0.000	-0.004	0.004	0.027	1.5
4									
3.404 Å	93	0.011	0.028	-0.011	0.001	-0.006	0.007	0.059	2.2
3.633 Å	99	0.009	0.021	-0.009	0.000	-0.005	0.005	0.048	1.8
3.799 Å	104	0.007	0.016	-0.007	0.000	-0.004	0.004	0.029	1.5
5									
3.573 Å	98	0.010	0.024	-0.010	0.001	-0.005	0.006	0.048	1.8
3.617 Å	99	0.008	0.018	-0.008	0.000	-0.004	0.004	0.046	1.5
3.623 Å	99	0.009	0.022	-0.009	0.000	-0.005	0.005	0.045	1.8
3.778 Å	103	0.007	0.017	-0.007	0.000	-0.004	0.004	0.031	1.5
3.837 Å	105	0.006	0.016	-0.006	0.000	-0.003	0.004	0.025	1.1
3.845 Å	105	0.006	0.016	-0.006	0.001	-0.003	0.004	0.023	1.1
6									
3.392 Å	93	0.011	0.029	-0.011	0.001	-0.006	0.007	0.056	2.2
3.435 Å	94	0.011	0.027	-0.011	0.000	-0.006	0.006	0.053	2.2
3.578 Å	98	0.009	0.023	-0.009	0.000	-0.005	0.005	0.048	1.8

* The Bondi's van der Waals (vdW) radius for bromine atom is 1.83 Å.

** $E_{int} = 0.58(-V(\mathbf{r}))$ (this empirical correlation between the interaction energy and the potential energy density of electrons at the bond critical points (3, –1) was specifically developed for noncovalent interactions involving bromine atoms).

Thermogravimetric analyses were carried out on a TG 209 F1 Iris thermobalance (NETZSCH, Germany). The measurements were made in a helium flow in the temperature range of 30–450°C using the heating rate of 10°C/min the gas flow rate of 60 mL/min and open Al crucibles.

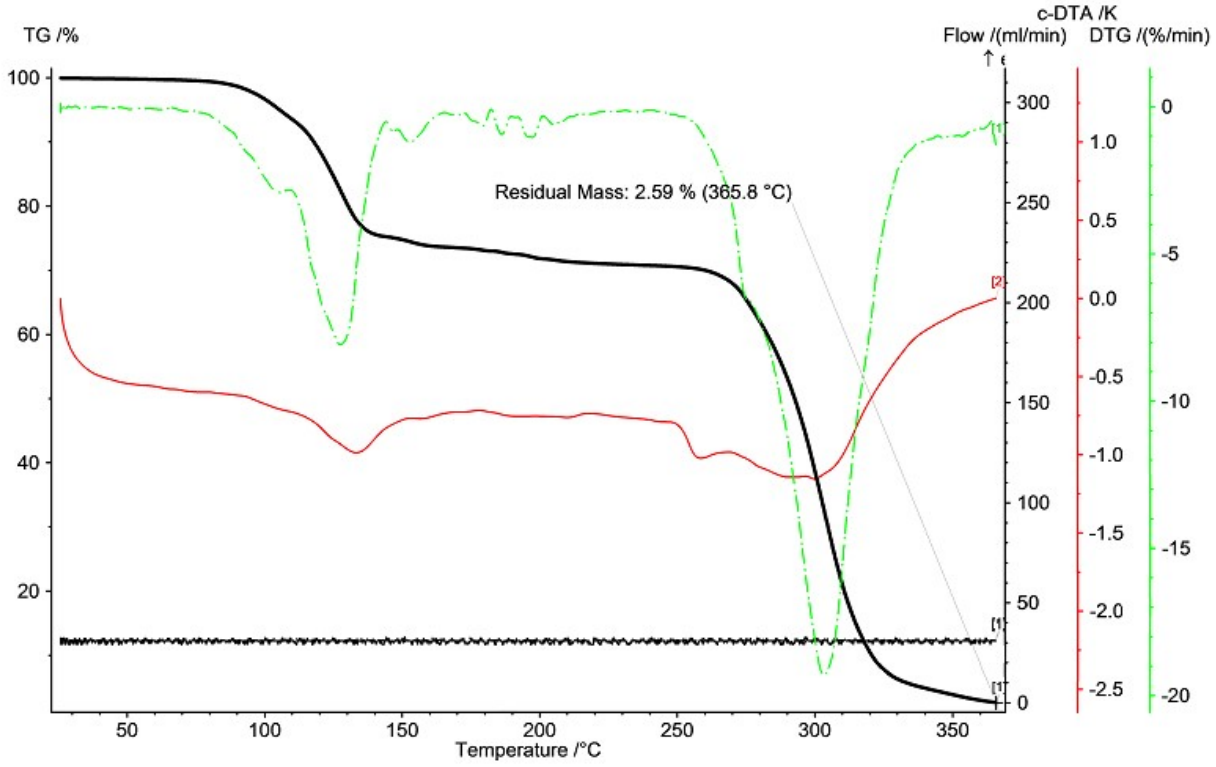

Figure 7S. TGA experiment for **2**

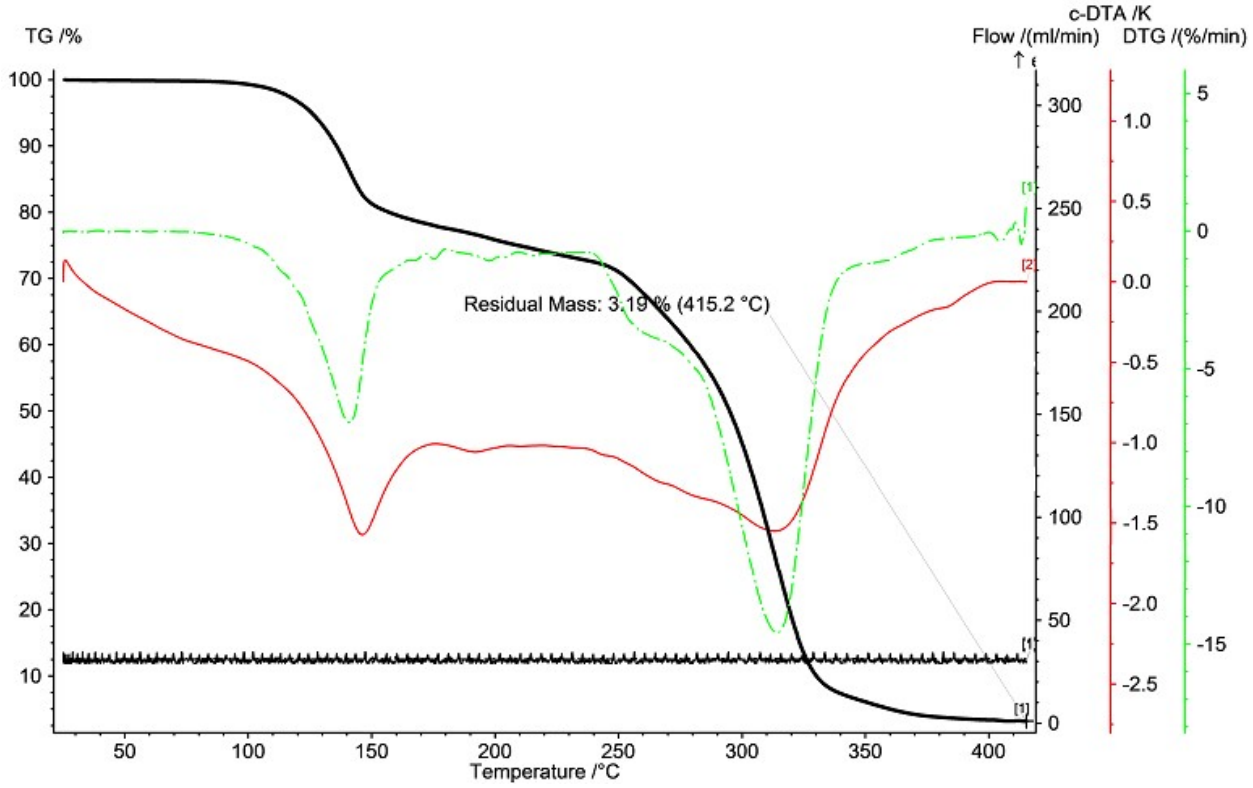

Figure 8S. TGA experiment for **3**

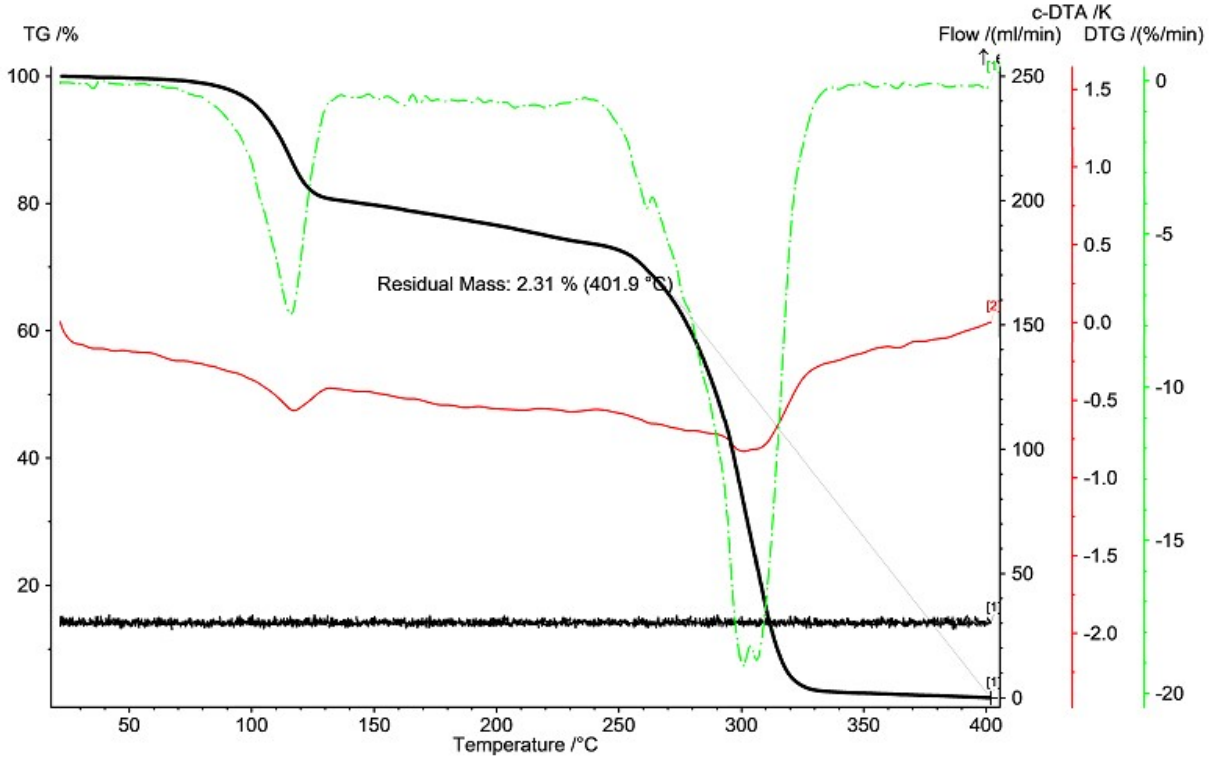

Figure 9S. TGA experiment for **4**

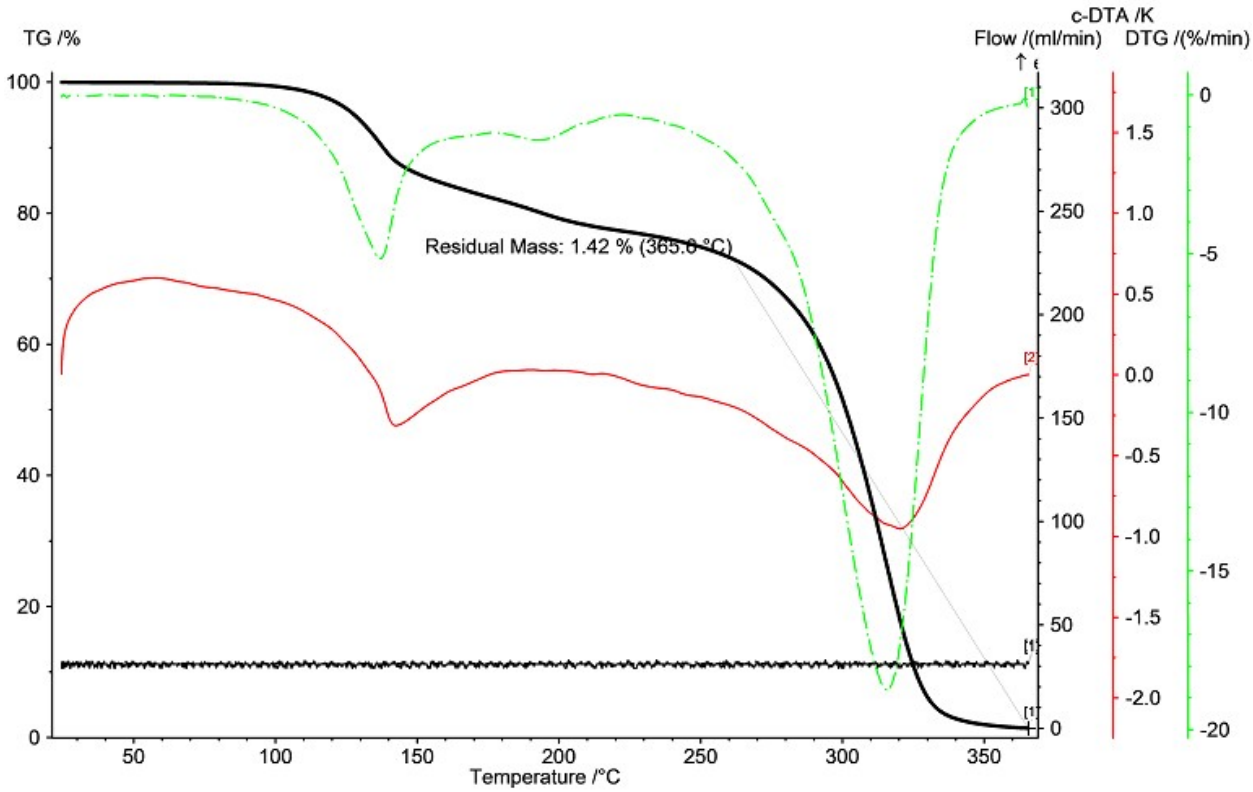

Figure 10S. TGA experiment for **6**