Supplementary Information

Halogen bonding-assisted assembly of bromoantimonate (V) and polybromide-bromoantimonate-based frameworks

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Preparations (optimized procedures)

In all cases, concentrated HBr was used.

1: 60 mg (0.2 mmol) of Sb_2O_3 were dissolved in 15 ml of HBr; then solution of Br_2 (1M, 5 ml) in HBr was added. Then, solution of 80 mg (0.4 mmol) of 1-n-PrPyBr in 12 ml of HBr was added. The mixture was kept at 6°C for 1 day, resulting in formation of cherry-red crystals of **1**. Yield 87%. For $C_8H_{12}Br_6NSb$ calcd, %: C, 13.4, H, 1.7; N, 2.0; found, %: C, 13.5, H, 1.9; N, 2.1.

2: 70 mg (0.24 mmol) of Sb_2O_3 were dissolved in 18 ml HBr; then solution of Br_2 (1M, 2 ml) in HBr was added. Then, solution of 103 mg (0.48 mmol) of 1-n-BuPyBr in 3 ml of HBr was added. The mixture was kept at 6°C for 1 day, resulting in formation of cherry-red crystals of **2**. Yield 85%. For $C_9H_{14}Br_6NSb$ calcd, %: C, 14.8; H, 1.9; N, 1.9; found, %: C, 14.8; H, 2.0; N, 2.1.

5: 62 mg (0.21 mmol) of Sb_2O_3 were dissolved in 10 ml HBr; then solution of Br_2 (1M, 4 ml) in HBr was added (solution 1). Separately, 100 mg (0.45 mmol) of 1,3-MePyI were dissolved in 7 ml of H_2O and equimolar amount of $AgNO_3$ was added, After 15 min stirring, AgI was filtered off and 5 ml of HBr were added to mother liquor. The mixture was added to solution 1 and the resulting mixture was kept at 6°C for 6 h, resulting in formation of dark crystals of **5**. Yield 88%. For $C_{14}H_{20}Br_9N_2Sb$ calcd, %: C, 16.0, H, 1.9, N, 2.7; found, %: C, 16.1, H, 2.1, N, 2.8.

7: 25 mg (0.09 mmol) of Sb_2O_3 were dissolved in 15 ml of HBr, then solution of Br_2 (1M, 4 ml) in HBr was added. Then, solution of 90 mg (0.35 mmol) in 15 ml of 1-Bz-2-MePyBr was added, resulting in formation of cherry-red crystals of **7** within 1 day. Yield 90%. For $C_{26}H_{28}Br_9N_2Sb$ calcd, %: C, 26.0; H, 2.4; N, 2.3; found, %: C, 25.9; H, 2.5; N, 2.5.

8: 35 mg (0.12 mmol) of Sb_2O_3 were dissolved in 7 ml of HBr, then solution of Br_2 (1M, 3 ml) in HBr was added (solution 1). Separately, 120 mg (0.48 mmol) of 1-Et-4-MePyI were dissolved in 6 ml of H_2O and equimolar amount of $AgNO_3$ was added, After 15 min stirring, AgI was filtered off and 4 ml of HBr were added to mother liquor. The mixture was added to solution 1 and the resulting mixture was kept at 6°C for 18 h, resulting in formation of dark crystals of **8**. Yield 82%. For $C_{16}H_{24}Br_9N_2Sb$ calcd, %: C, 17.9; H, 2.2; N, 2.6; found, %: C, 18.1; H, 2.4; N, 2.7.

9: 40 mg (0.14 mmol) of Sb_2O_3 were dissolved in 15 ml of HBr, then solution of Br_2 (1M, 4 ml) in HBr was added. Then, solution of 180 mg of 1-(4-BrBz)PyBr in 20 ml of HBr was added, resulting in formation of crystalline precipitate within several minutes. Yield 92%. For $C_{24}H_{22}Br_{11}N_2Sb$ calcd, %: C, 21.7, H, 1.7, N, 2.1; found, %: C, 21.7, H, 1.8, N, 2.2.

Thermogravimetric analyses (TGA) 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 20–600°C using the heating rate of 10°C min^{-1} the gas flow rate of 60 mL min^{-1} and open Al crucibles.

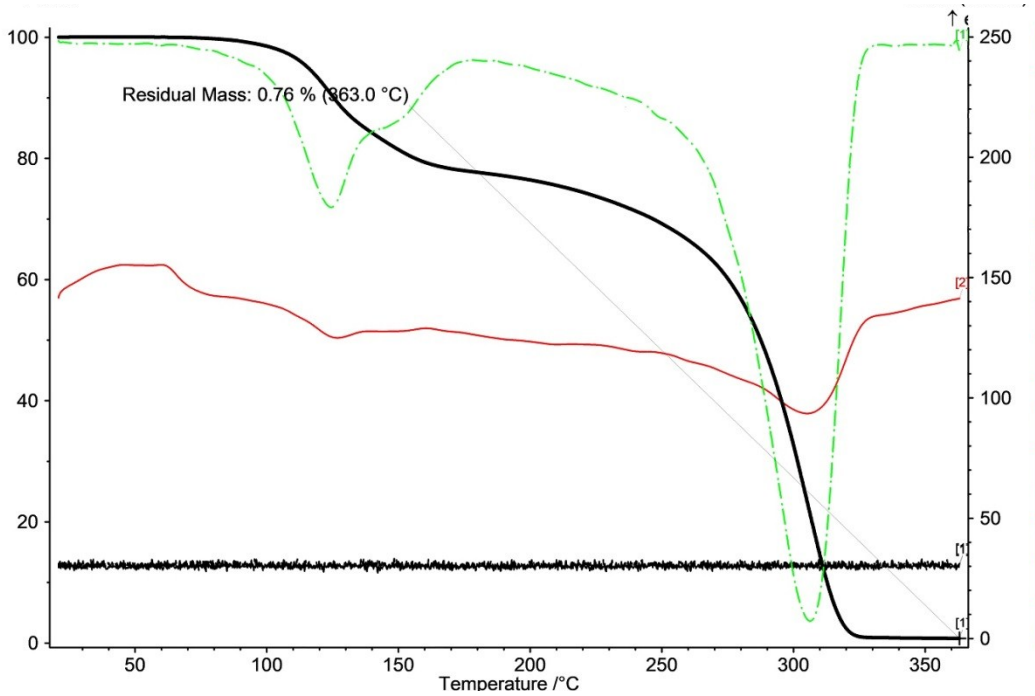

Figure 1S. TG, DTG and DSC curves for **1**

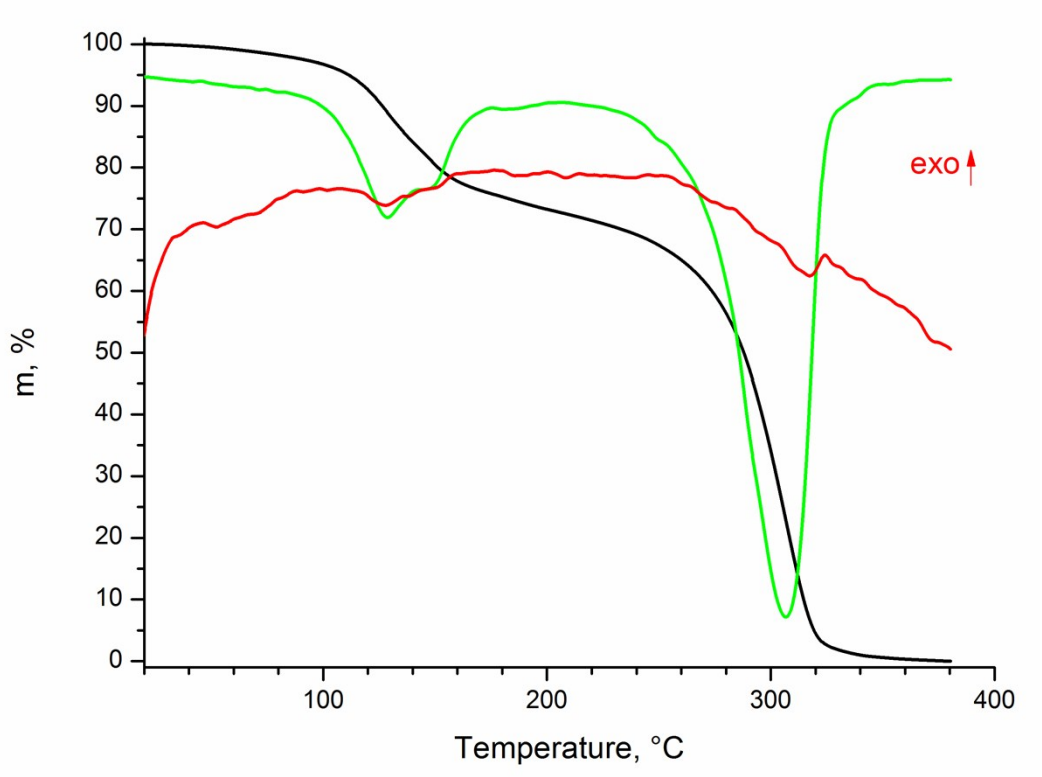

Figure 2S. TG, DTG and DSC curves for **2**

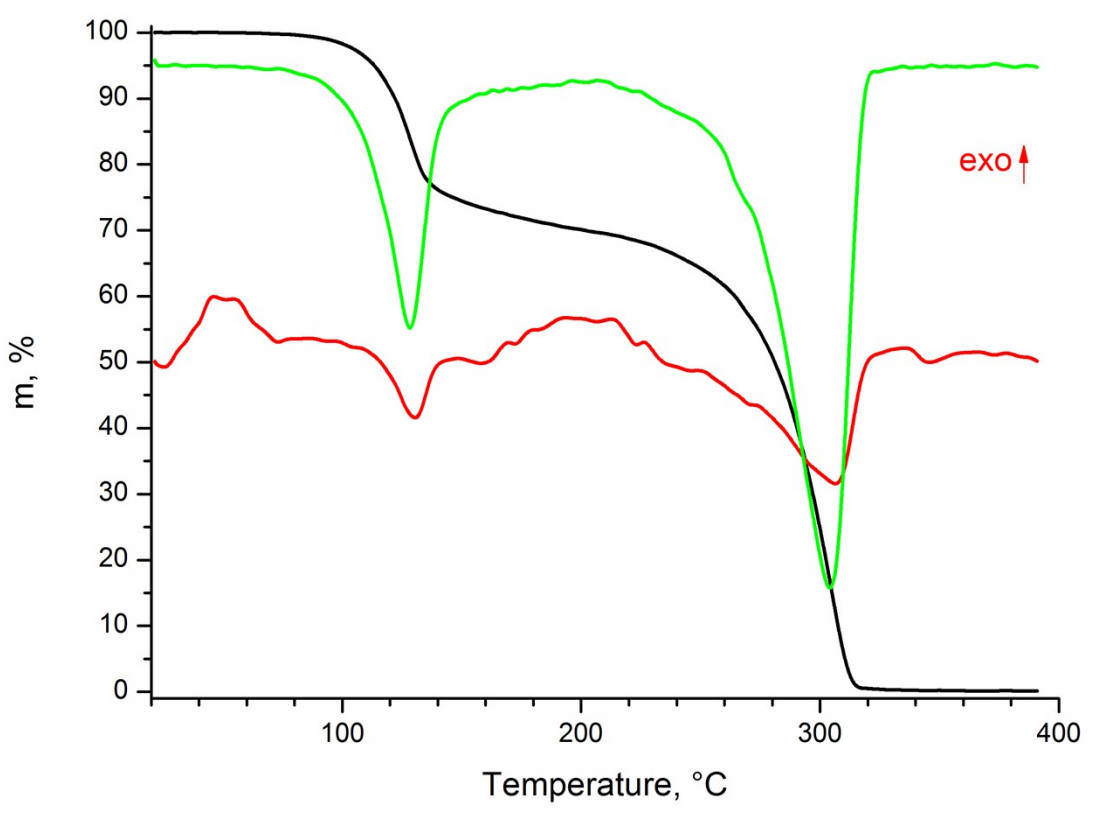

Figure 3S. TG, DTG and DSC curves for **5**

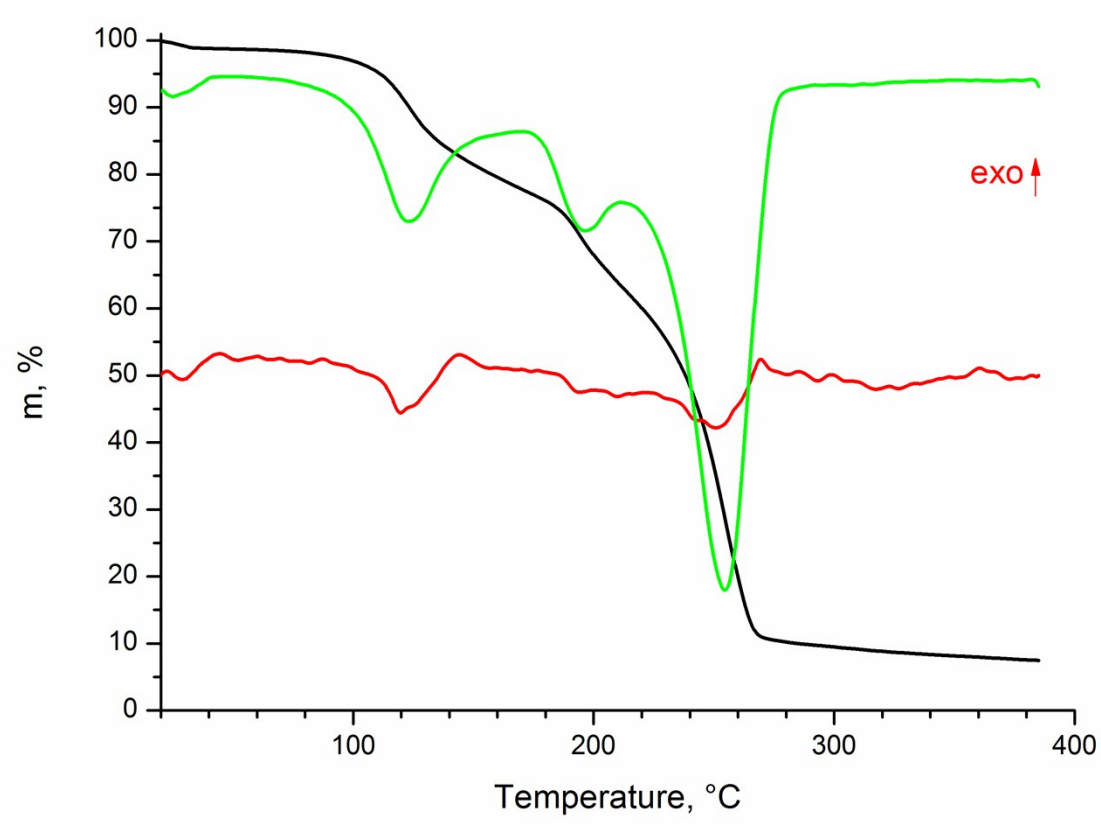

Figure 4S. TG, DTG and DSC curves for **7**

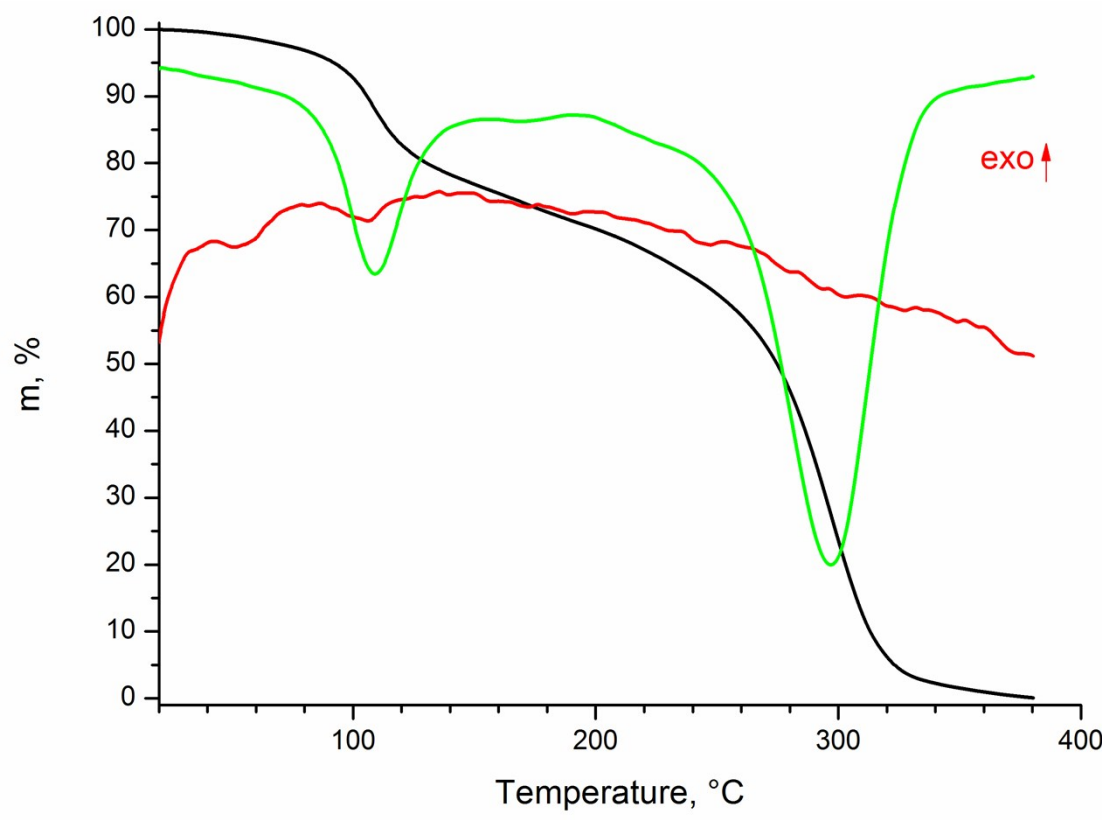

Figure 5S. TG, DTG and DSC curves for **8**

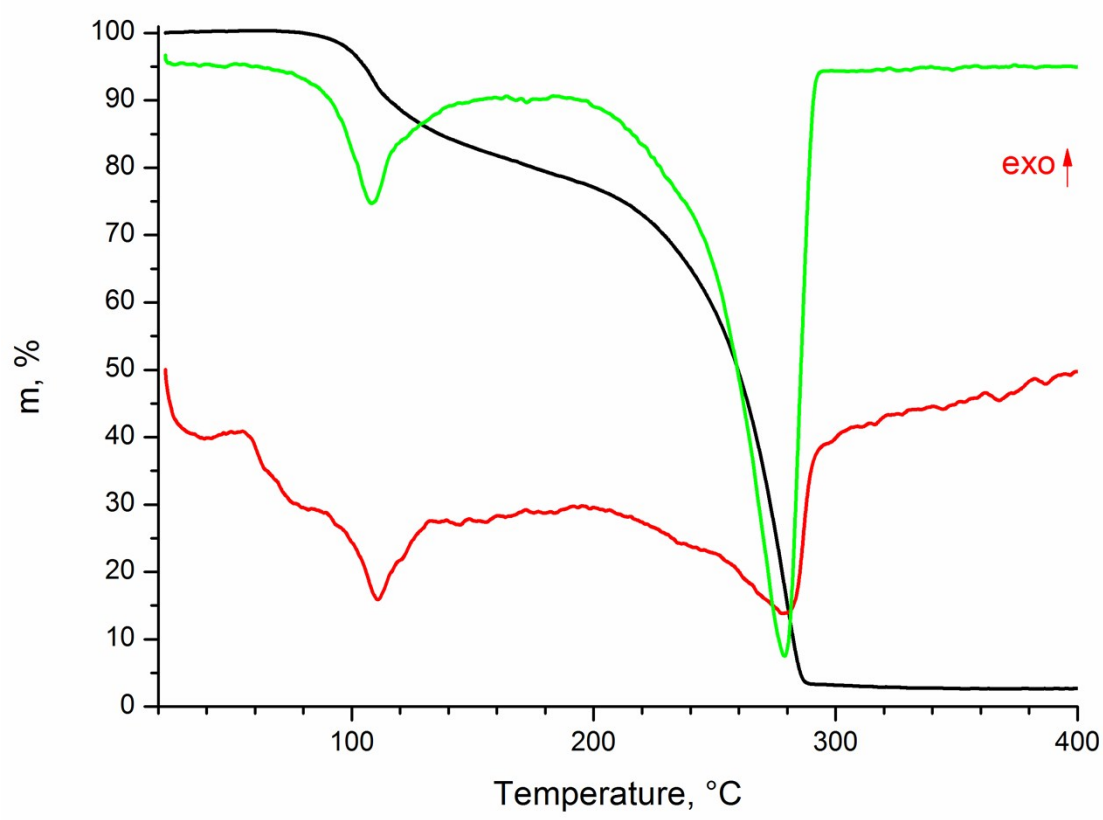

Figure 6S. TG, DTG and DSC curves for **9**

Computational details. The single point calculations based on the experimental X-ray geometries of **1–11** have been carried out at the DFT level of theory using the M06 functional with the help of Gaussian-09 [1] program package. The Douglas–Kroll–Hess 2nd order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using DZP-DKH basis sets for all atoms. The topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader [2] has been performed by using the Multiwfn program [3]. The Wiberg bond indices were computed by using the Natural Bond Orbital (NBO) partitioning scheme [4]. The Cartesian atomic coordinates for model supramolecular clusters **1–11** are presented in **Table S1**.

References:

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, C. J.;, D. J. Fox, in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, **2010**.
2. Bader, R. F. W. A quantum theory of molecular structure and its applications. *Chem. Rev.* **1991,** 91, (5) 893–928.
3. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, 33, (5), 580–592.
4. Glendening, E. D.; Landis, C. R.; Weinhold, F. Natural bond orbital methods. *WIREs Computational Molecular Science*, **2012,** 2, (1) 1–42.

Table S1. Cartesian atomic coordinates for model supramolecular clusters **1–11**.

Atom	X	Y	Z
1			

Br	0.748140	0.410941	8.293454
Br	4.334974	0.474518	8.881431
Br	2.884749	2.461037	6.245713
Sb	2.833190	0.000000	6.878538
Br	4.918241	-0.410941	5.463623
Br	1.331407	-0.474518	4.875645
Br	2.781632	-2.461037	7.511364
Br	4.953017	7.681558	8.188625
Br	2.524877	5.757134	6.379569
Br	4.229328	8.454359	4.757472
Sb	2.833190	8.235300	6.878538
Br	0.713363	8.789042	5.568452
Br	3.141503	10.713466	7.377507
Br	1.437052	8.016241	8.999604
Br	9.453751	8.646241	-1.414915
Br	5.866917	8.709818	-2.002893
Br	7.317142	10.696337	0.632826
Sb	7.368700	8.235300	0.000000
Br	5.283649	7.824359	1.414915
Br	8.870483	7.760782	2.002893
Br	7.420258	5.774263	-0.632826
2			
Br	4.171396	-1.986438	4.226853
Br	5.300407	0.546521	6.581012
Br	3.369205	1.478207	3.695080
Br	6.896619	2.299967	3.906045
Br	5.753496	-0.170117	1.536961
Br	7.664644	-1.184177	4.434297
Sb	5.524798	0.162487	4.063514
Br	6.970154	1.986438	-4.158097

Br	5.841143	-0.546521	-1.803938
Br	7.772345	-1.478207	-4.689870
Br	4.244931	-2.299967	-4.478905
Br	5.388054	0.170117	-6.847989
Br	3.476906	1.184177	-3.950653
Sb	5.616752	-0.162487	-4.321436
Br	3.256304	5.078212	4.158097
Br	2.127293	7.611171	1.803938
Br	4.058495	8.542857	4.689870
Br	0.531081	9.364617	4.478905
Br	1.674204	6.894533	6.847989
Br	-0.236944	5.880473	3.950653
Sb	1.902902	7.227137	4.321436
Br	10.684004	5.078212	4.158097
Br	9.554993	7.611171	1.803938
Br	11.486195	8.542857	4.689870
Br	7.958781	9.364617	4.478905
Br	9.101904	6.894533	6.847989
Br	7.190756	5.880473	3.950653
Sb	9.330602	7.227137	4.321436
3			
Br	4.946240	3.214380	-0.060391
Br	2.551108	5.781445	0.767942
Br	5.752295	5.663552	2.421935
Sb	4.973500	5.750850	0.000000
Br	5.000760	8.287320	0.060391
Br	7.395892	5.720255	-0.767942
Br	4.194705	5.838148	-2.421935
Br	9.987018	0.306060	2.539258
Br	8.281328	-1.913193	0.268772

Br	8.019935	1.638072	-0.168906
Sb	9.947000	0.000000	0.000000
Br	9.906982	-0.306060	-2.539258
Br	11.612672	1.913193	-0.268772
Br	11.874065	-1.638072	0.168906
Br	0.040018	0.306060	2.539258
Br	-1.665672	-1.913193	0.268772
Br	-1.927065	1.638072	-0.168906
Sb	0.000000	0.000000	0.000000
Br	-0.040018	-0.306060	-2.539258
Br	1.665672	1.913193	-0.268772
Br	1.927065	-1.638072	0.168906
Br	2.394269	6.056910	-10.402685
Br	4.099960	3.837657	-8.132199
Br	4.361353	7.388922	-7.694520
Sb	2.434288	5.750850	-7.863427
Br	2.474306	5.444790	-5.324169
Br	0.768615	7.664043	-7.594655
Br	0.507223	4.112778	-8.032333
4			
Br	0.284805	12.438128	4.511864
Br	-1.897250	10.429545	6.542834
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Sb	-1.672482	12.939400	6.066943
Br	-3.629769	13.440672	7.622022
Br	-1.447713	15.449255	5.591052
Br	-3.302088	12.695363	4.119454
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C	-4.430324	9.884408	14.507275

H	-4.765303	9.836700	15.395148
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H	-3.335112	8.138844	14.543713
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Br	2.380102	3.099449	8.910405
Sb	4.127019	4.316322	10.311537
Br	2.303853	5.423484	11.704316
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Sb	-3.134081	4.316322	10.311537
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Br	0.248234	2.158161	5.155768
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Br	3.937500	5.257528	6.396700
Sb	6.019251	6.315247	5.397239
Br	5.964572	8.136497	7.187503
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Br	8.101003	7.372966	4.397778
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Br	7.247200	0.000000	0.000000
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7			
Br	3.493931	4.609449	5.239127
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9			
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Br	-7.147206	7.511017	6.295215
Br	-9.612557	10.139083	6.447184
Sb	-9.679650	7.594250	6.595854
Br	-9.931156	7.432948	4.051174
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Sb	-0.070841	6.670350	5.123146
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H	6.742101	8.425973	9.594101
C	7.203973	10.197631	8.692400
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H	5.171463	11.568548	6.765254
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Br	7.793682	6.670350	2.640595
Br	8.330268	9.237367	5.123634
Sb	8.333259	6.670350	5.123146
Br	8.330268	4.103333	5.123634
C	8.840405	10.180288	9.561762
H	9.373256	10.948979	9.270879
H	9.316543	9.351350	9.344592
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11			
Br	-2.695761	3.726395	9.278698
Br	-0.914738	5.964174	11.484945
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Br	0.946525	7.238890	8.661108
Br	-0.844642	5.054017	6.438869

Br	0.867650	3.651375	9.327829
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Br	2.850562	10.333300	8.243336
Br	2.402474	10.235754	5.742802
Br	3.298650	10.430846	10.743869
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Br	-4.923026	10.235754	5.742802
Br	-4.026850	10.430846	10.743869
Br	-3.507949	6.606905	17.522034
Br	-1.726927	4.369126	19.728280
Br	-3.428019	3.032204	16.837178
Br	0.134337	3.094410	16.904443
Br	-1.656830	5.279283	14.682205
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Br	2.850562	0.000000	8.243336
Br	3.189264	-0.700598	5.816827
Br	2.511859	0.700598	10.669844

Table 2S. XRD Experimental details

Experiments were carried out at 130 K with Mo *K*a radiation using a New Xcalibur, AtlasS2. Absorption was corrected for by multi-scan methods, *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. H-atom parameters were constrained.

	1	**2**	**3**	**4**
Chemical formula	$C_8H_{12}Br_6NSb$	$C_9H_{14}Br_6NSb$	$C_9H_{14}Br_6NSb$	$C_{10}H_{10}Br_9I_2N_2Sb$
M_r	723.40	737.42	737.42	1252.94
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a, *b*, *c* (Å)	7.3687 (2), 16.4706 (4), 13.8620 (4)	7.4277 (5), 14.1293 (8), 16.7699 (7)	9.9470 (3), 11.5017 (3), 16.4632 (5)	8.1800 (5), 12.9394 (8), 12.5865 (7)
α, β, γ (°)	90, 97.054 (3),	90, 90, 90	90, 107.201 (3), 90	90, 105.412 (7), 90

	90			
V (Å^3)	1669.65 (8)	1759.97 (17)	1799.27 (9)	1284.30 (14)
Z	4	4	4	2
μ (mm^{-1})	15.99	15.17	14.84	17.48
Crystal size (mm)	0.26 × 0.26 × 0.12	0.32 × 0.30 × 0.15	0.12 × 0.10 × 0.05	0.50 × 0.40 × 0.40
T_{min}, T_{max}	0.465, 1.000	0.133, 1.000	0.271, 1.000	0.361, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8273, 3729, 3239	5772, 3561, 3001	13341, 4208, 3610	5485, 2811, 2293
R_{int}	0.025	0.047	0.022	0.037
θ values (°)	θ_{max} = 29.1, θ_{min} = 3.3	θ_{max} = 29.0, θ_{min} = 3.3	θ_{max} = 28.9, θ_{min} = 3.3	θ_{max} = 29.0, θ_{min} = 3.4
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.683	0.681	0.680	0.682
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.060, 1.17	0.066, 0.161, 1.02	0.022, 0.045, 1.02	0.041, 0.083, 1.02
No. of reflections, parameters, restraints	3729, 148, 0	3561, 155, 42	4208, 157, 0	2811, 112, 0
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0185P)^2 + 0.1107P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0956P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.028P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.76, -0.90	2.72, -2.13	0.68, -0.99	1.28, -1.58
Absolute structure	–	Refined as an inversion twin.	–	–
Absolute structure parameter	–	0.46 (4)	–	–

	5	**6**	**7**	**8**
Chemical formula	$C_{14}H_{20}Br_9N_2Sb$	$C_{16}H_{24}Br_9N_2Sb$	$C_{26}H_{28}Br_9N_2Sb$	$C_{16}H_{24}Br_9N_2Sb$
M_r	1057.26	1085.31	1209.44	1085.31
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
a, b, c (Å)	7.2611 (8), 9.0862 (10), 11.1895 (9)	7.2472 (3), 9.4088 (5), 11.5541 (5)	8.9834 (4), 10.2599 (5), 10.3601 (5)	8.4645 (4), 13.0802 (6), 13.1574 (6)
α, β, γ (°)	67.617 (9), 87.457 (8), 72.163 (10)	69.263 (4), 81.162 (4), 71.303 (4)	94.223 (4), 102.737 (4), 111.846 (4)	90, 105.702 (5), 90
V (Å^3)	647.61 (12)	697.20 (6)	851.62 (7)	1402.39 (12)
Z	1	1	1	2
μ (mm^{-1})	14.95	13.89	11.39	13.81
Crystal size (mm)	0.50 × 0.20 × 0.08	0.18 × 0.18 × 0.08	0.20 × 0.15 × 0.10	0.30 × 0.25 × 0.15
T_{min}, T_{max}	0.128, 1.000	0.408, 1.000	0.552, 1.000	0.516, 1.000
No. of measured, independent and	4812, 2792, 2244	5318, 3012, 2526	6184, 3645, 2988	6198, 3059, 2572

observed [$I > 2\sigma(I)$] reflections				
R_{int}	0.031	0.032	0.027	0.026
θ values (°)	θ_{max} = 28.9, θ_{min} = 3.4	θ_{max} = 28.9, θ_{min} = 3.5	θ_{max} = 28.9, θ_{min} = 3.5	θ_{max} = 28.9, θ_{min} = 3.5
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.680	0.680	0.679	0.679
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.137, 1.01	0.034, 0.066, 0.99	0.033, 0.059, 1.02	0.031, 0.055, 1.02
No. of reflections, parameters, restraints	2792, 121, 0	3012, 130, 0	3645, 175, 0	3059, 130, 0
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0781P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0139P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0164P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.87, -2.54	0.80, -1.10	0.66, -0.73	0.66, -0.87
Absolute structure	–	–	–	–
Absolute structure parameter	–	–	–	–

	9	**10**	**11**
Chemical formula	$C_{24}H_{22}Br_{11}N_2Sb$	$C_{12}H_{14}Br_{11}N_2Sb$	$C_{10}H_{10}Br_{11}N_2Sb$
M_r	1339.19	1187.01	1158.96
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, *Im*	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	8.6483 (4), 15.1885 (9), 13.3520 (5)	8.4041 (9), 13.3407 (16), 12.2371 (11)	7.3255 (4), 20.6666 (10), 16.5665 (7)
α, β, γ (°)	90, 98.887 (4), 90	90, 95.731 (9), 90	90, 95.627 (4), 90
V (Å^3)	1732.79 (15)	1365.1 (3)	2496.0 (2)
Z	2	2	4
μ (mm^{-1})	13.50	17.11	18.72
Crystal size (mm)	0.20 × 0.15 × 0.10	0.30 × 0.20 × 0.20	0.40 × 0.35 × 0.15
T_{min}, T_{max}	0.546, 1.000	0.303, 1.000	0.040, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8438, 3805, 3055	3259, 2096, 2025	10924, 5408, 3737
R_{int}	0.026	0.070	0.069
θ values (°)	θ_{max} = 28.9, θ_{min} = 3.3	θ_{max} = 28.7, θ_{min} = 4.2	θ_{max} = 28.9, θ_{min} = 3.4
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.680	0.675	0.679
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.060, 1.01	0.056, 0.154, 1.04	0.091, 0.266, 1.09
No. of reflections, parameters, restraints	3805, 175, 0	2096, 91, 2	5408, 220, 12
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1041P)^2 + 14.9071P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1469P)^2 + 10.1836P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.71, -0.94	2.70, -2.86	3.15, -3.52
Absolute structure	–	Refined as an inversion twin.	–
Absolute structure parameter	–	0.54 (4)	–

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

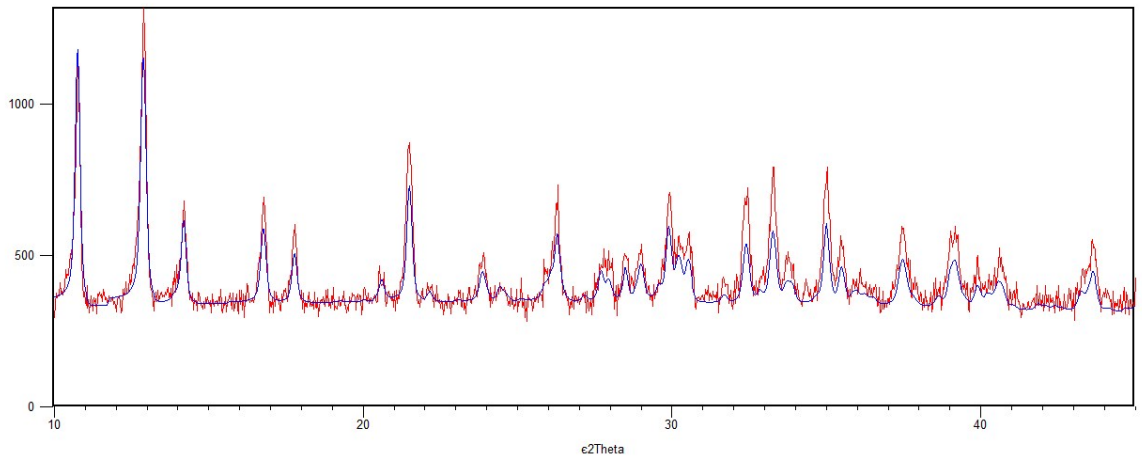

Figure 7S. Simulated and experimental PXRD patterns for **1**

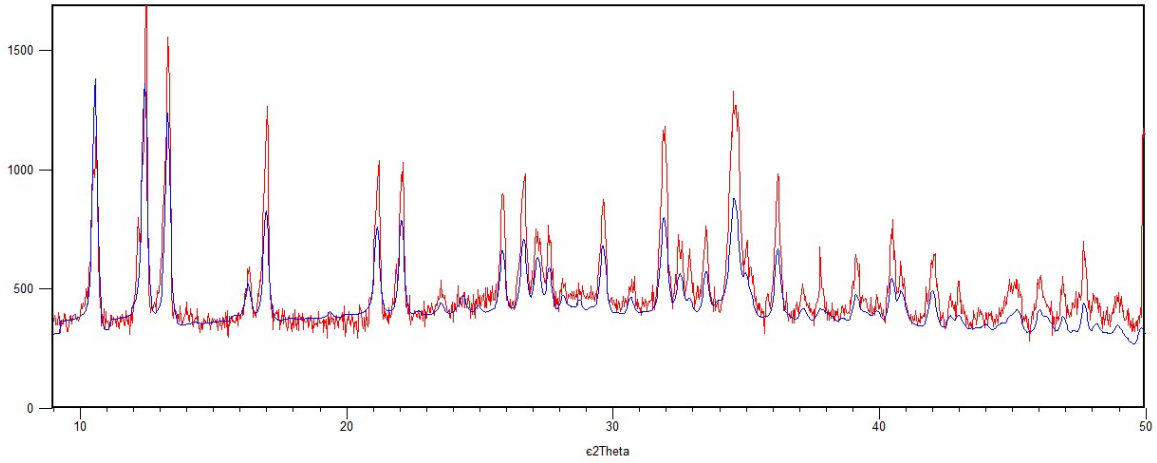

Figure 8S. Simulated and experimental PXRD patterns for **2**

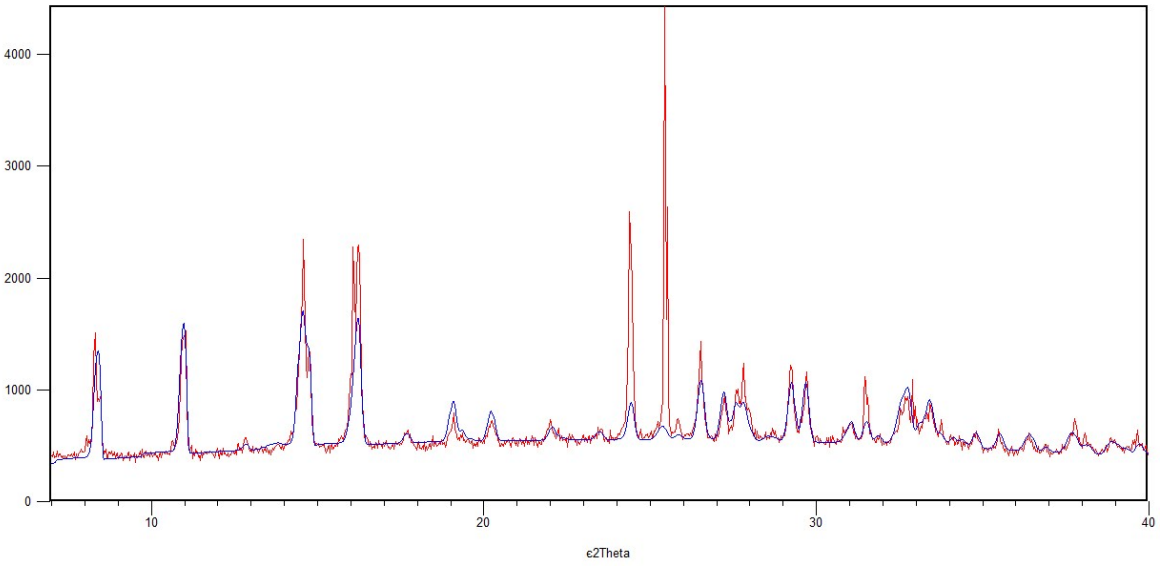

Figure 9S. Simulated and experimental PXRD patterns for **5**

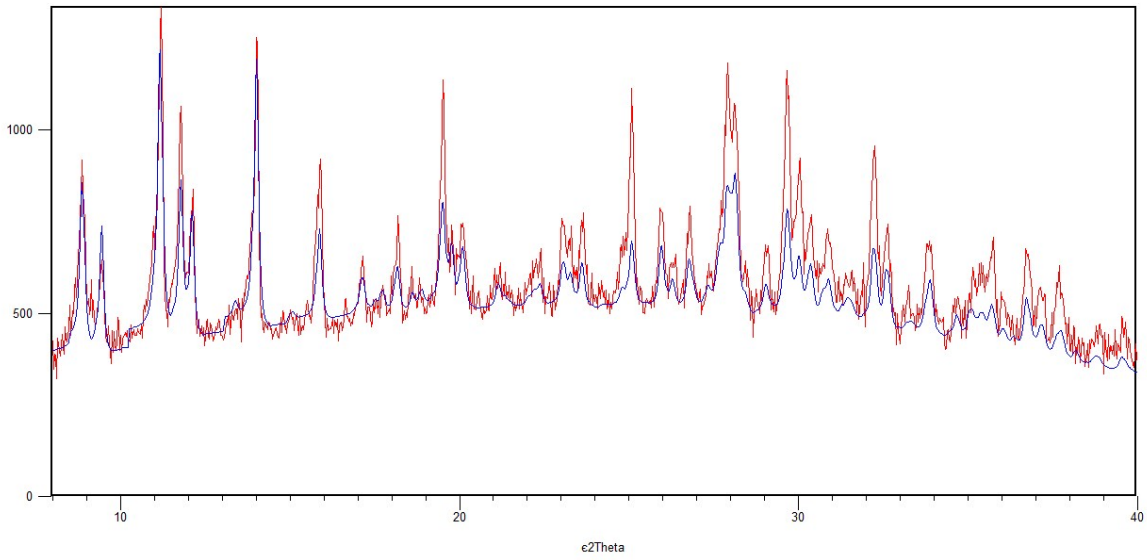

Figure 10S. Simulated and experimental PXRD patterns for**7**

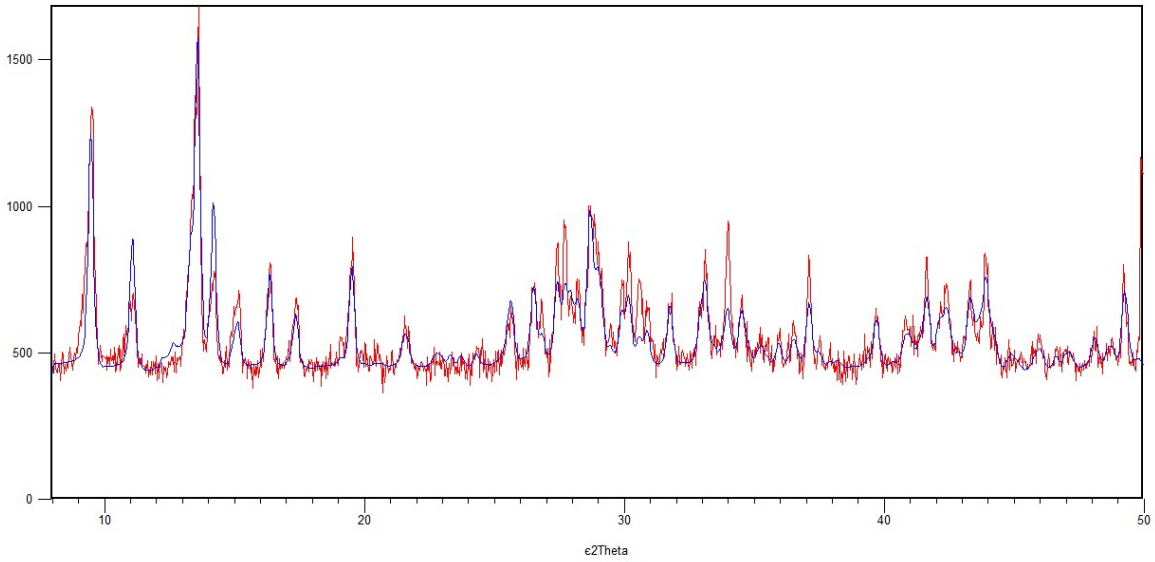

Figure 11S. Simulated and experimental PXRD patterns for **8**

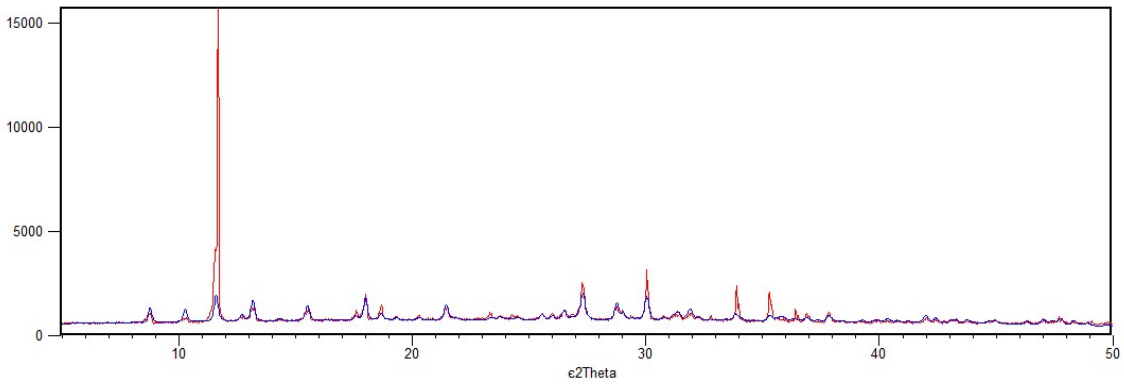

Figure 12S. Simulated and experimental PXRD patterns for **9**

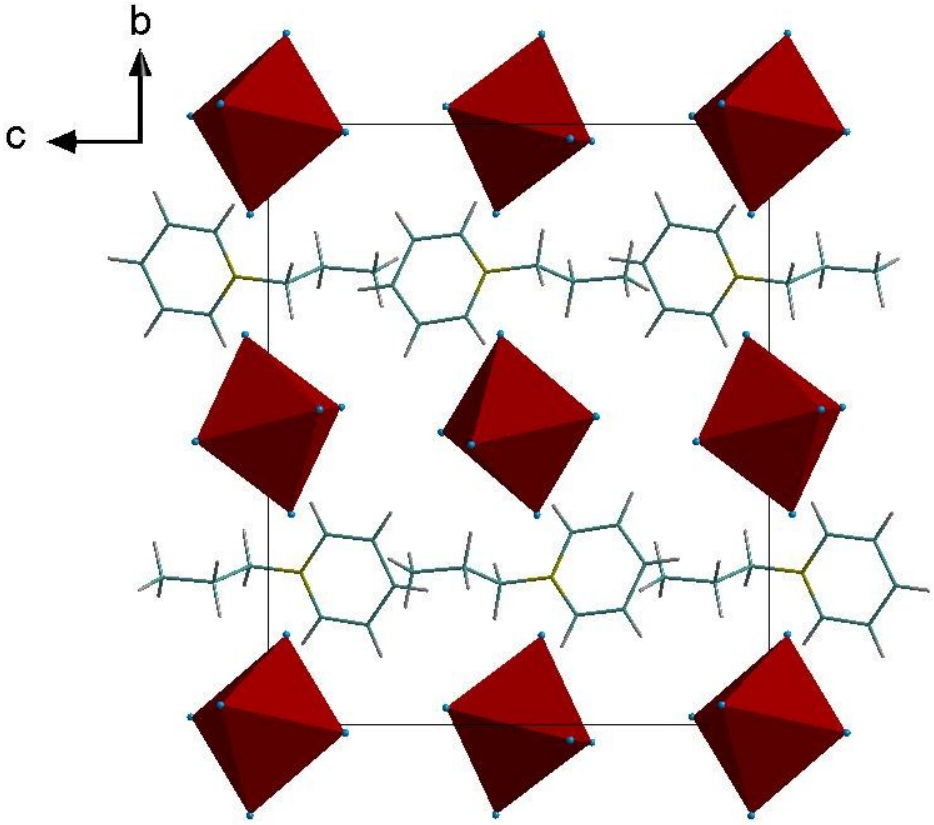

Figure 13S. Crystal packing in **1**

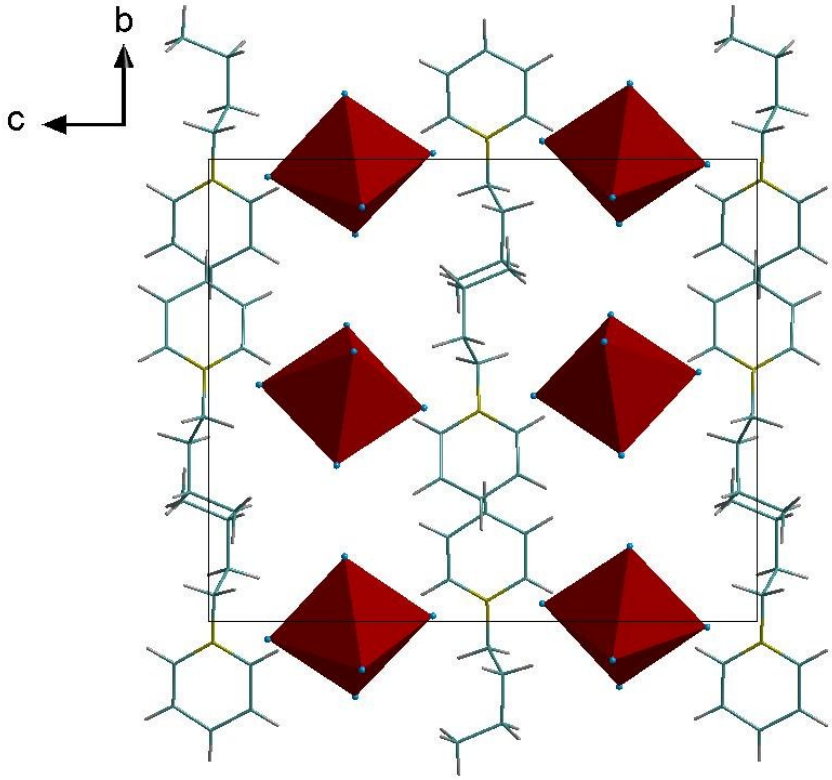

Figure 14S. Crystal packing in **2**

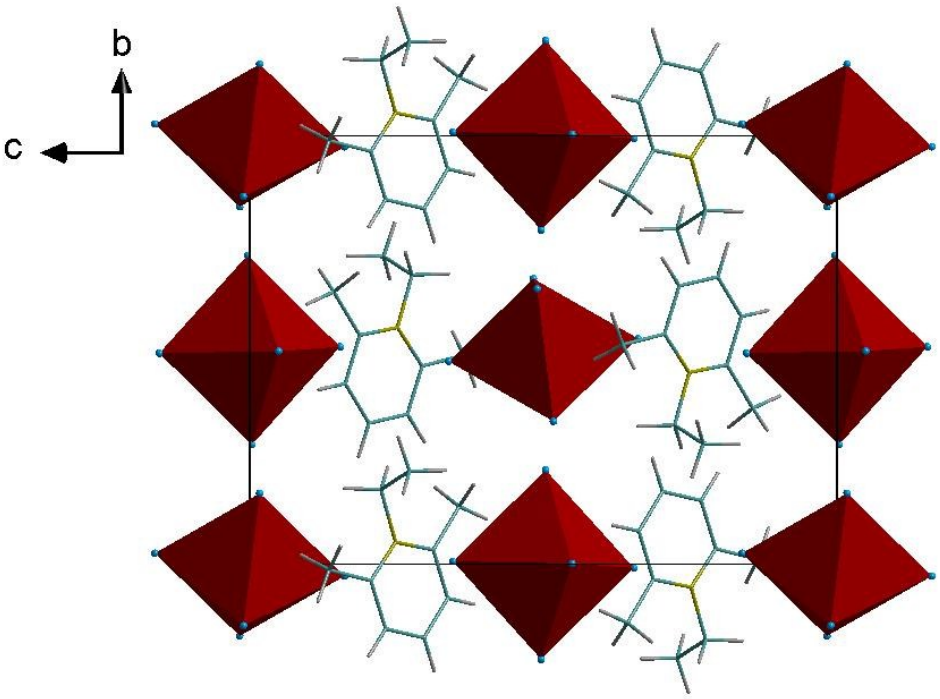

Figure 15S. Crystal packing in **3**

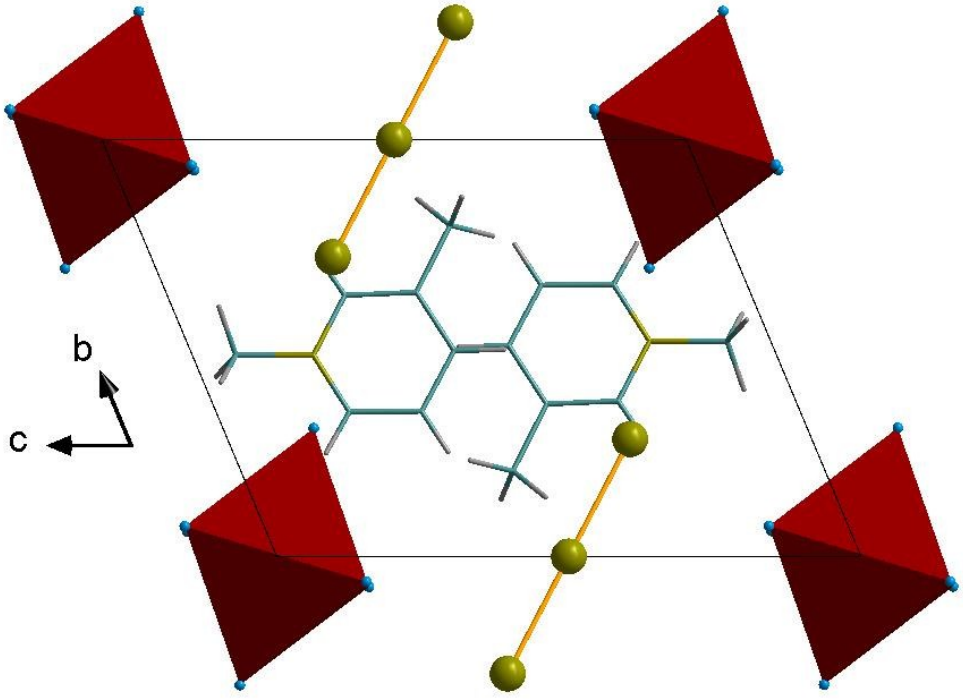

Figure 16S. Crystal packing in **5**

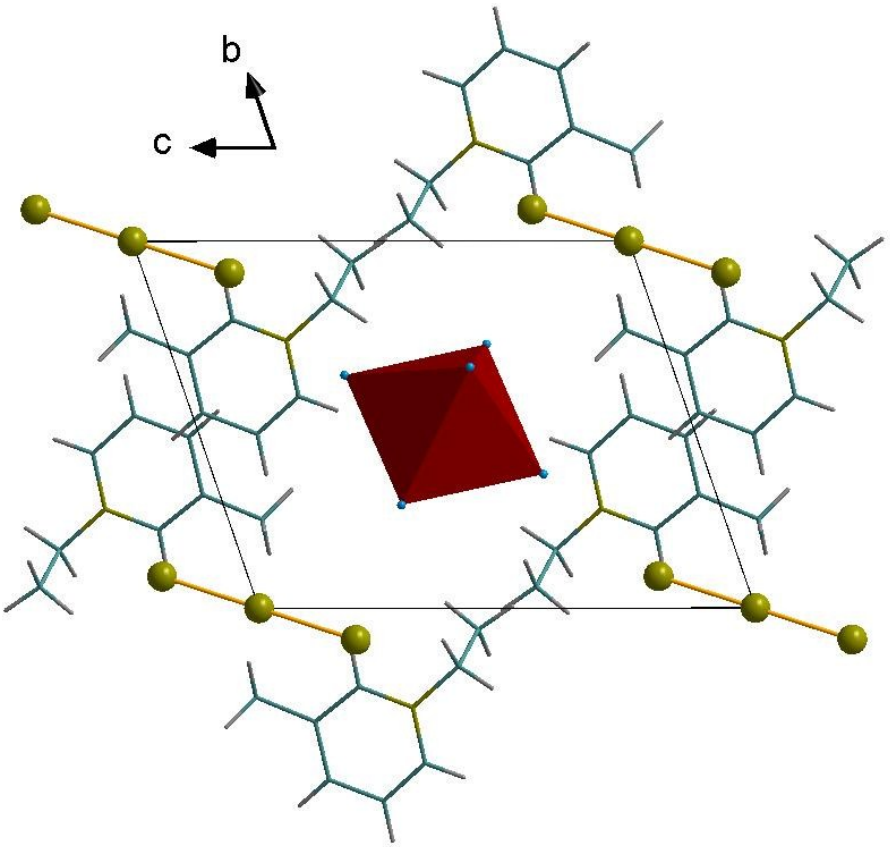

Figure 17S. Crystal packing in **6**

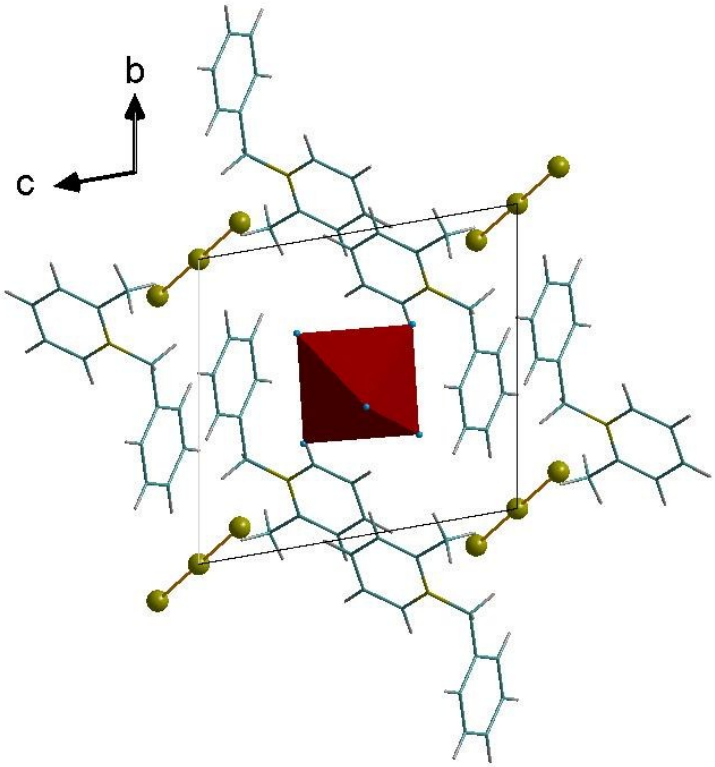

Figure 18S. Crystal packing in **7**

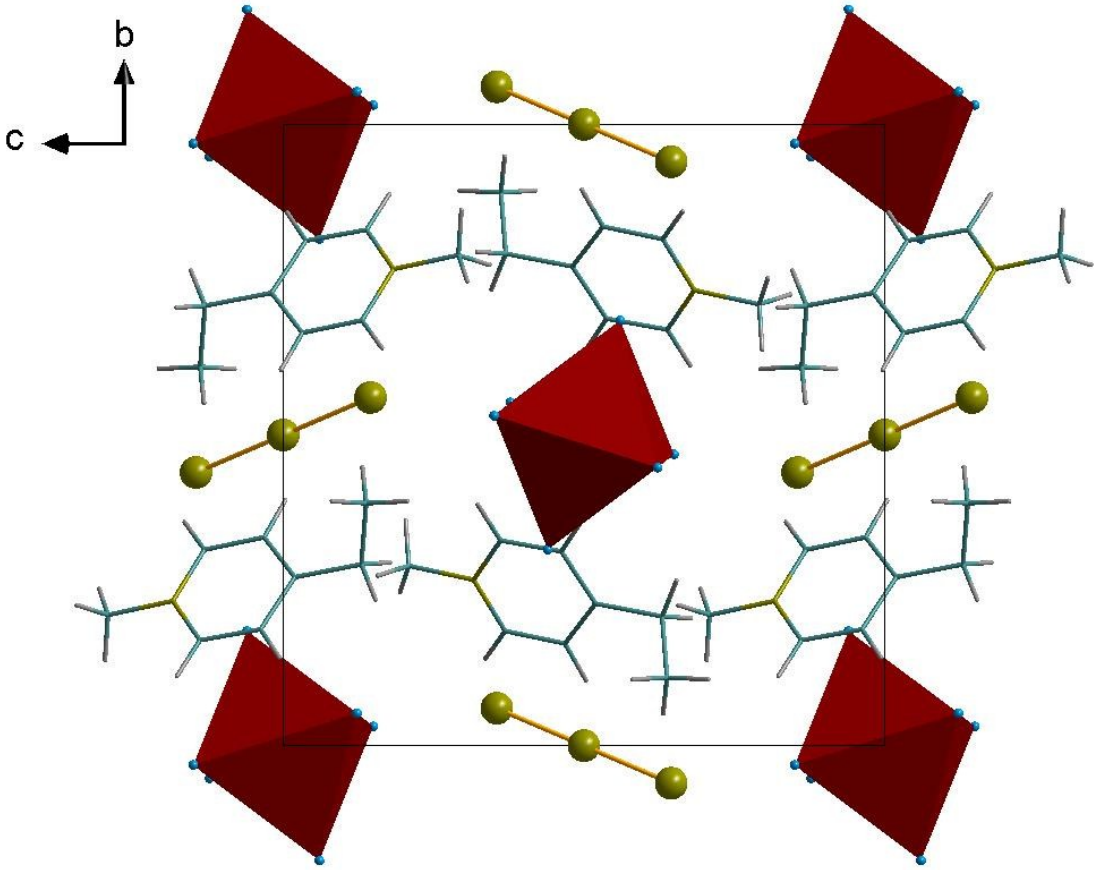

Figure 19S. Crystal packing in **8**

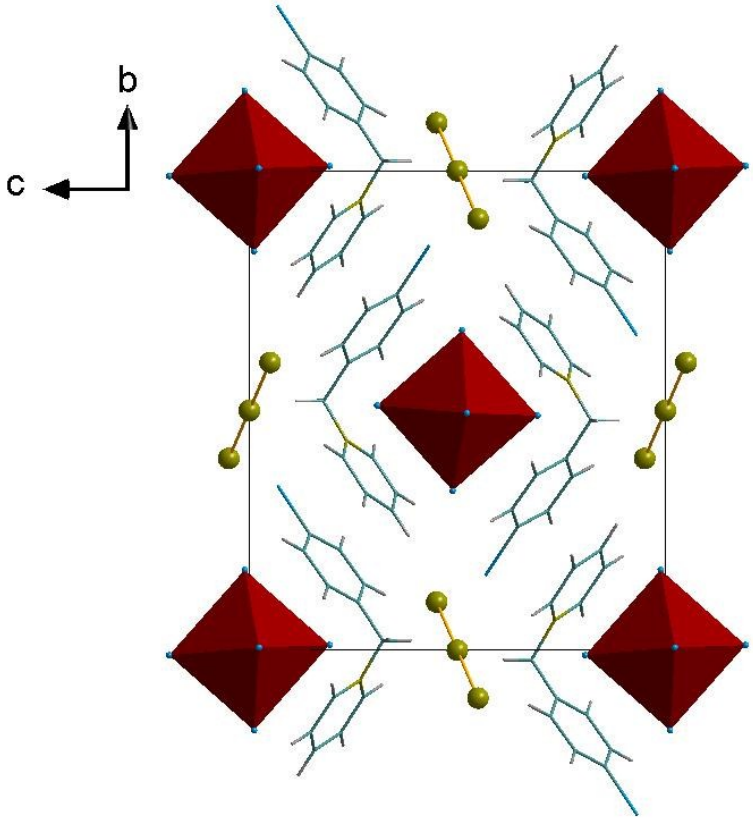

Figure 20S. Crystal packing in **9**

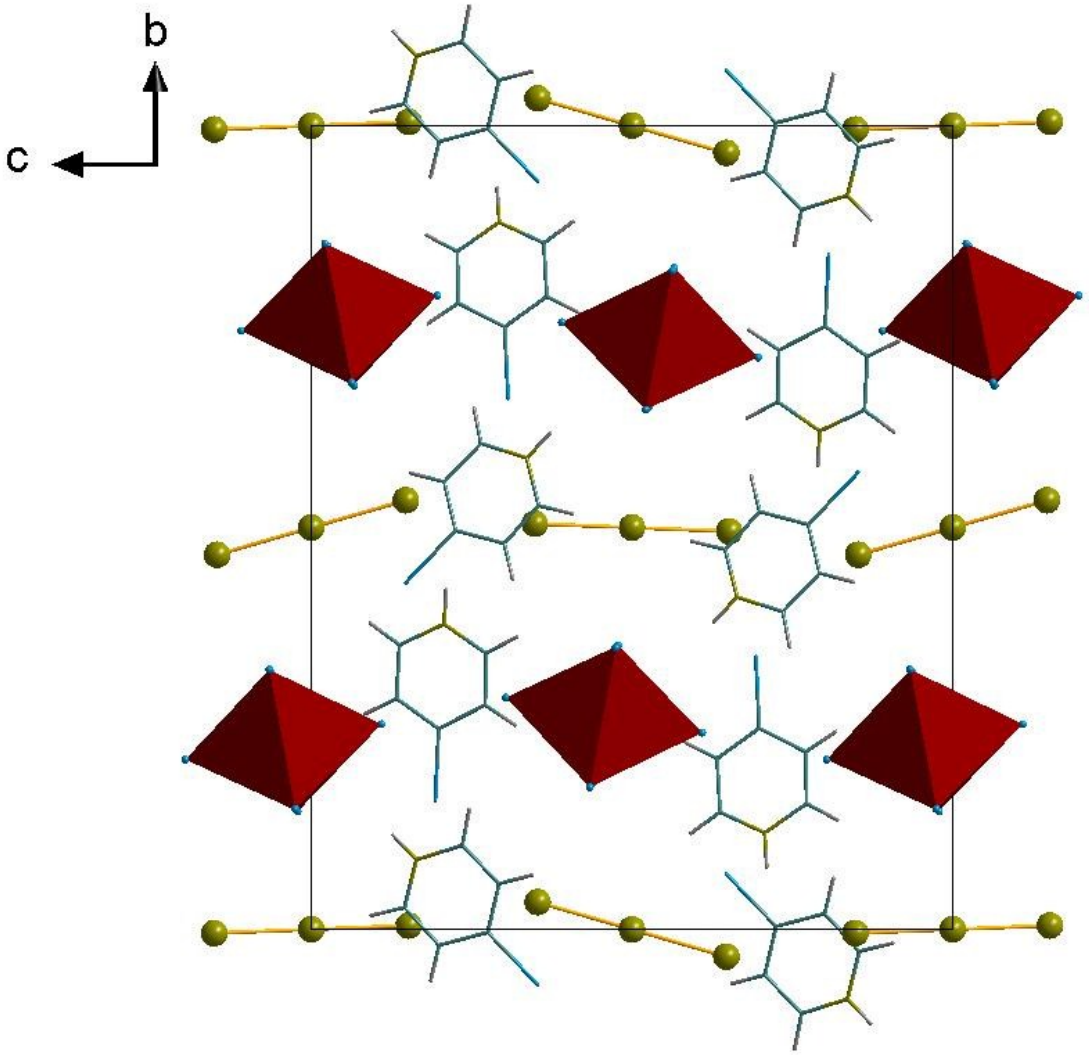

Figure 201S. Crystal packing in **11**