Supporting Information

Supramolecular diiodo-chlorometalates(III) of Group 15 elements with halogen-substituted pyridiniums: an interplay of cation···anion and I_2···halometalate halogen bonds

Raman spectra were collected using a LabRAM HR Evolution (Horiba) spectrometer with the excitation by the 633 nm line of the He-Ne laser. The spectra at room temperatures were obtained in the backscattering geometry with a Raman microscope. The laser beam was focused to a diameter of 2 μm using a LMPlan FL 50x/0.50 Olympus objective. The spectral resolution was 0.7 cm^{-1}. The laser power on the sample surface was about 0.03 mW.

Thermogravimetric analysis (TGA) of **1-2** was 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.

Diffuse reflectance spectra of **1-2** were measured on a setup which consists of a Kolibri-2 spectrometer (VMK Optoelektronica, Russia), fiber optic cable QR-400-7 (Ocean Optics, USA), and deuterium–tungsten lamp AvaLight-DHS (Avantes, Netherlands). The reference of 100% reflectance was $BaSO_4$ powder. The spectra were recorded five times in the wavelength interval of 300-1000 nm and then averaged to reduce the random error.

Table S1. Crystal data and structure refinement for **1** and **2**

Identification code	**1**	**2**
CCDC number	2493623	2493624
Empirical formula	$C_{10}H_{10}N_2Br_2SbCl_5I_2$	$C_{10}H_{10}N_2Br_2BiCl_5I_2$
M, g/mol	870.82	958.05
Temperature/K	150	150
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	14.9208 (3)	14.8900 (5)
b, Å	7.0913 (1)	7.1531 (2)
c, Å	20.9159 (4)	20.9598 (7)
α, deg.	90	90
β, deg.	97.395 (1)	98.109 (1)
γ, deg.	90	90
Volume, Å^3	2194.66 (7)	2210.10 (12)
Z	4	4
ρ_{calc}, g/cm^3	2.636	2.879
μ, mm^{-1}	8.32	14.99
F(000)	1584	1712
Crystal size, mm	0.09 × 0.07 × 0.02	0.2 × 0.03 × 0.02
Θ range for data collection, deg.	1.584 to 30.548	1.804 to 28.309
T_{min}, T_{max}	0.543, 0.746	0.420, 0.746
Range of h, k, l	$-21 \le h \le 21$, $-10 \le k \le 10$, $-29 \le l \le 29$	$-19 \le h \le 19$, $-8 \le k \le 9$, $-26 \le l \le 27$
$(sin\ \theta/\lambda)_{max}$ (Å^{-1})	0.715	0.667
R_{int}	0.046	0.048
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27773, 6700, 4944	24399, 5492, 4321
Data/restraints/parameters	6700/0/199	5492/0/199
Goodness-of-fit on F^2	1.025	1.035
Final R indexes [$I>=2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0598$	$R_1 = 0.0324$, $wR_2 = 0.0570$
Final R indexes [all data]	$R_1 = 0.0569$, $wR_2 = 0.0657$	$R_1 = 0.0487$, $wR_2 = 0.0606$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 1.1494P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 2.7791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.003
Largest diff. peak/hole, e/Å^3	0.81, −1.46	1.03, −1.50

Computer programs: SHELXT 2014/5 (Sheldrick, 2014), SHELXL 2017/1 (Sheldrick, 2015), Olex2 1.5 (Dolomanov et al., 2009).

Table S2. Crystal data and structure refinement for **3** and **4**.

Identification code	**3**	**4**
CCDC number	2493625	2493626
Empirical formula	$C_{10}H_{10}N_2Br_2SbCl_5I_2$	$C_{10}H_{10}N_2Br_2BiCl_5I_2$
M, g/mol	781.90	869.13
Temperature/K	150	150
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	14.5435 (3)	14.5781 (2)
b, Å	7.1608 (2)	7.2057 (1)
c, Å	20.8200 (4)	20.8721 (4)
α, deg.	90	90
β, deg.	96.131 (1)	97.312 (1)°
γ, deg.	90	90
Volume, Å^3	2155.86 (9)	2174.69 (6)
Z	4	4
ρ_{calc}, g/cm^3	2.409	2.655
μ, mm^{-1}	5.01	11.80
F(000)	1440	1568
Crystal size, mm	0.11 × 0.02 × 0.01	0.12 × 0.06 × 0.02
Θ range for data collection, deg.	1.629 to 30.569	1.967 to 31.539
T_{min}, T_{max}	0.580, 0.746	0.486, 0.746
Range of h, k, l	$-19 \le h \le 20$, $-10 \le k \le 10$, $-24 \le l \le 29$	$-21 \le h \le 19$, $-10 \le k \le 10$, $-30 \le l \le 30$
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.716	0.736
R_{int}	0.046	0.040
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27709, 6592, 5125	29267, 7246, 5933
Data/restraints/parameters	6592/0/199	7246/0/199
Goodness-of-fit on F^2	1.057	1.028
Final R indexes [$I>=2\sigma(I)$]	$R_1 = 0.0324$, $wR_2 = 0.0526$	$R_1 = 0.0274$, $wR_2 = 0.0512$
Final R indexes [all data]	$R_1 = 0.0466$, $wR_2 = 0.0579$	$R_1 = 0.0396$, $wR_2 = 0.0544$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0139P)^2 + 0.140P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0148P)^2 + 1.4093P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.002	0.002
Largest diff. peak/hole, e/Å^3	0.83, −1.01	0.76, −1.90

Computer programs: SHELXT 2014/5 (Sheldrick, 2014), SHELXL 2017/1 (Sheldrick, 2015), Olex2 1.5 (Dolomanov et al., 2009).

Table S3. Selected bond lengths and angles for **1**.

Bond length, Å			
Sb1—Cl2	2.4083 (9)	Sb1—Cl3	3.1523 (9)
Sb1—Cl4	2.4837 (9)	I1—I2	2.7293 (4)
Sb1—Cl5	2.4577 (9)	Br1—C2	1.8812 (4)
Sb1—Cl3	2.8231 (9)	Br2—C7	1.8834 (4)
Bond angle, (º)			
Cl2—Sb1—Cl4	89.21 (3)	Cl4—Sb1—Cl3	171.38 (3)
Cl2—Sb1—Cl5	91.66 (3)	Cl5—Sb1—Cl4	89.80 (3)
Cl2—Sb1—Cl3	82.19 (3)	Cl5—Sb1—Cl3	89.86 (3)
Cl3—Sb1—Cl3	140.93 (3)		

Table S4. Selected bond lengths and angles for **2**.

Bond lengths, Å			
Bi1—Cl5	2.5274 (12)	Bi1—Cl4	2.8402 (14)
Bi1—Cl1^{i}	3.0122 (12)	I1—I2	2.7093 (5)
Bi1—Cl1	2.8859 (13)	Br1—C2	1.8821 (5)
Bi1—Cl3	2.5703 (13)	Br2—C7	1.8886 (5)
Bi1—Cl2	2.5918 (13)		
Bond angles, (º)			
Cl5—Bi1—Cl1^{i}	162.91 (4)	Cl3—Bi1—Cl2	89.84 (4)
Cl5—Bi1—Cl1	81.83 (4)	Cl3—Bi1—Cl4	88.00 (4)
Cl5—Bi1—Cl3	90.06 (4)	Cl2—Bi1—Cl1	91.42 (4)
Cl5—Bi1—Cl2	92.03 (4)	Cl2—Bi1—Cl1^{i}	88.67 (4)
Cl5—Bi1—Cl4	90.17 (4)	Cl2—Bi1—Cl4	176.91 (4)
Cl1—Bi1—Cl1^{i}	81.086 (17)	Cl4—Bi1—Cl1	91.03 (4)
Cl3—Bi1—Cl1^{i}	107.02 (4)	Cl4—Bi1—Cl1^{i}	89.86 (4)
Cl3—Bi1—Cl1	171.83 (4)	Bi1—Cl1—Bi1^{ii}	140.58 (5)

Symmetry code(s): (i) −*x*+3/2, *y*−1/2, −*z*+3/2; (ii) −*x*+3/2, *y*+1/2, −*z*+3/2.

Table S5. Selected bond lengths and angles for **3**.

Bond length, Å			
Sb1—Cl4	2.4077 (7)	Sb1—Cl2	2.4760 (8)
Sb1—Cl5	2.4562 (8)	I1—I2	2.7319 (3)
Sb1—Cl3	2.8359 (9)	Cl7—C7	1.716 (3)
Sb1—Cl3	3.1599 (9)	Cl6—C2	1.727 (4)
Bond angle, (º)			
Cl4—Sb1—Cl5	90.96 (3)	Cl5—Sb1—Cl3	90.10 (3)
Cl4—Sb1—Cl3	82.22 (3)	Cl5—Sb1—Cl2	90.49 (3)
Cl4—Sb1—Cl2	89.77 (3)	Cl2—Sb1—Cl3	171.98 (3)
Cl3—Sb1—Cl3	142.98 (3)		

Table S6. Selected bond lengths and angles for **4**.

Bond length, Å			
Bi1—Cl4	2.5308 (8)	Bi1—Cl1	2.8249 (9)
Bi1—Cl3	2.8934 (8)	I1—I2	2.7095 (4)
Bi1—Cl3^{i}	3.0153 (8)	Cl6—C7	1.722 (4)
Bi1—Cl2	2.5672 (8)	Cl7—C2	1.718 (4)
Bi1—Cl5	2.5965 (8)		
Bond angle, (°)			
Cl4—Bi1—Cl3^{i}	162.79 (2)	Cl2—Bi1—Cl5	90.58 (3)
Cl4—Bi1—Cl3	81.75 (2)	Cl2—Bi1—Cl1	88.05 (3)
Cl4—Bi1—Cl2	90.37 (3)	Cl5—Bi1—Cl3^{i}	88.84 (2)
Cl4—Bi1—Cl5	91.39 (3)	Cl5—Bi1—Cl3	91.60 (3)
Cl4—Bi1—Cl1	90.06 (3)	Cl5—Bi1—Cl1	178.01 (3)
Cl3—Bi1—Cl3^{i}	81.042 (10)	Cl1—Bi1—Cl3	89.95 (2)
Cl2—Bi1—Cl3^{i}	106.84 (3)	Cl1—Bi1—Cl3^{i}	90.18 (2)
Cl2—Bi1—Cl3	171.87 (3)	Bi1—Cl3—Bi1^{ii}	142.36 (3)

Symmetry code(s): (i) −*x*+1/2, *y*+1/2, −*z*+1/2; (ii) −*x*+1/2, *y*−1/2, −*z*+1/2.

Table S7. Selected hydrogen bond parameters for **1**.

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
N1—H1···Cl3^{i}	0.88	2.41	3.172 (3)	145.6
N2—H2···Cl3	0.88	2.43	3.185 (3)	143.5
C6—H6···Cl5^{i}	0.95	2.73	3.671 (4)	168.7
C9—H9···Cl1^{ii}	0.95	2.76	3.581 (4)	145.0
C5—H5···Cl1^{iii}	0.95	2.69	3.575 (4)	155.0

Symmetry code(s): (i) −*x*+3/2, *y*−1/2, −*z*+3/2; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*, *y*−1, *z*

Table S8. Selected hydrogen bond parameters for **2**.

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
N1—H1···Cl3^{i}	0.88	2.41	3.172 (3)	145.6
N2—H2···Cl3	0.88	2.43	3.185 (3)	143.5
C6—H6···Cl5^{i}	0.95	2.73	3.671 (4)	168.7
C9—H9···Cl1^{ii}	0.95	2.76	3.581 (4)	145.0
C5—H5···Cl1^{iii}	0.95	2.69	3.575 (4)	155.0

Symmetry code(s): (i) −*x*+3/2, *y*+1/2, −*z*+3/2; (ii) −*x*+1, −*y*+1, −*z*+1.

Table S9. Selected hydrogen bond parameters for **3**.

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
N1—H1···Cl3	0.88	2.42	3.181 (3)	145.7
N2—H2···Cl3^{i}	0.88	2.39	3.160 (3)	145.7
C4—H4···Cl1^{ii}	0.95	2.74	3.570 (3)	146.6
C10—H10···Cl1	0.95	2.68	3.533 (4)	149.9

Symmetry code(s): (i) −*x*+3/2, *y*−1/2, −*z*+3/2; (ii) −*x*+1, −*y*+1, −*z*+1.

Table S10. Selected hydrogen bond parameters for **4**.

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
N2—H2···Cl3	0.88	2.47	3.222 (3)	144.0
N1—H1···Cl3^{i}	0.88	2.50	3.242 (3)	142.2
C5—H5···Cl1	0.95	2.66	3.553 (4)	157.4

Symmetry code(s): (i) −*x*+1/2, *y*+1/2, −*z*+1/2.

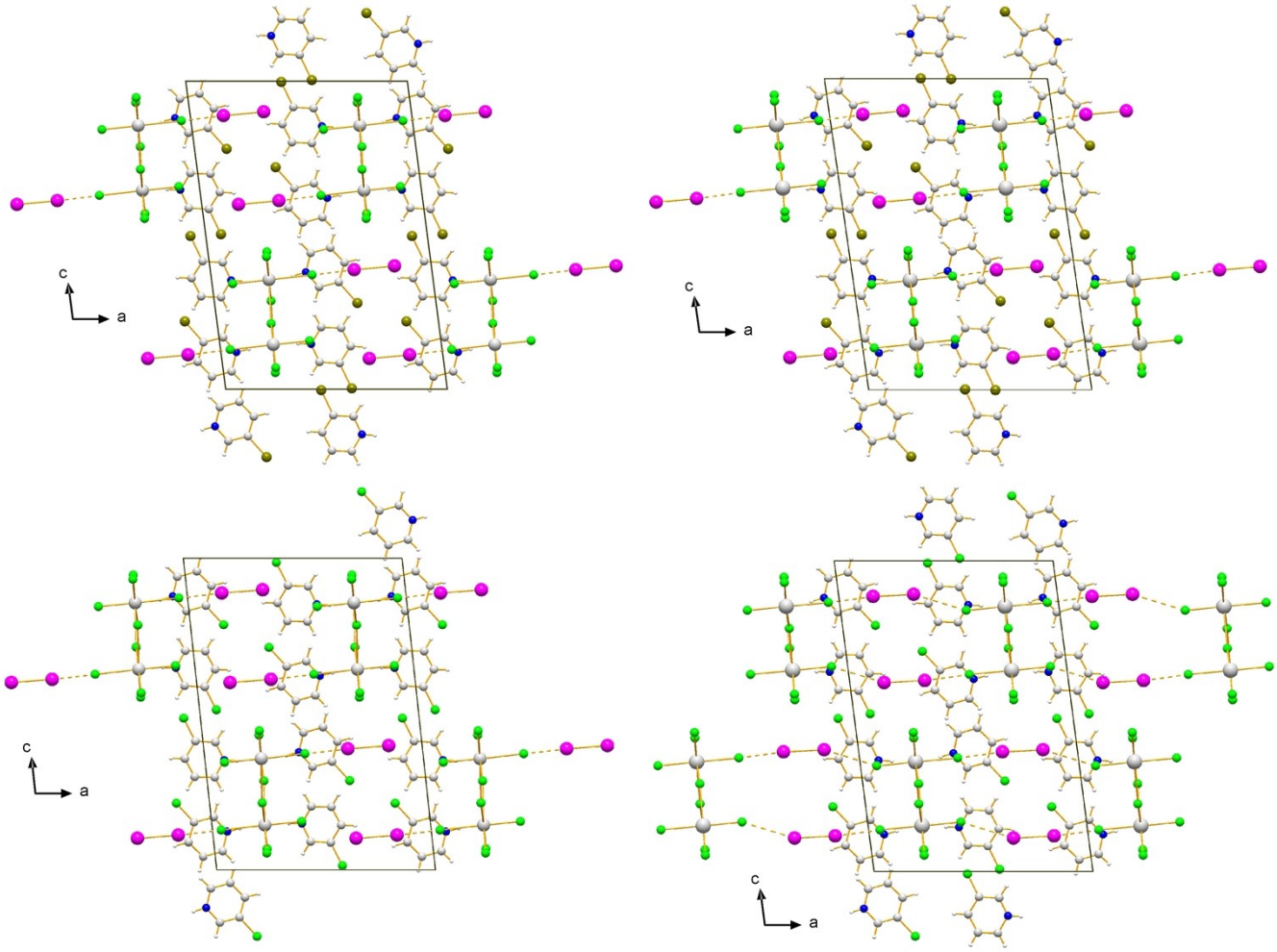

Figure S1. Crystal packing of **1**-**4** along *b* crystallographic axis.

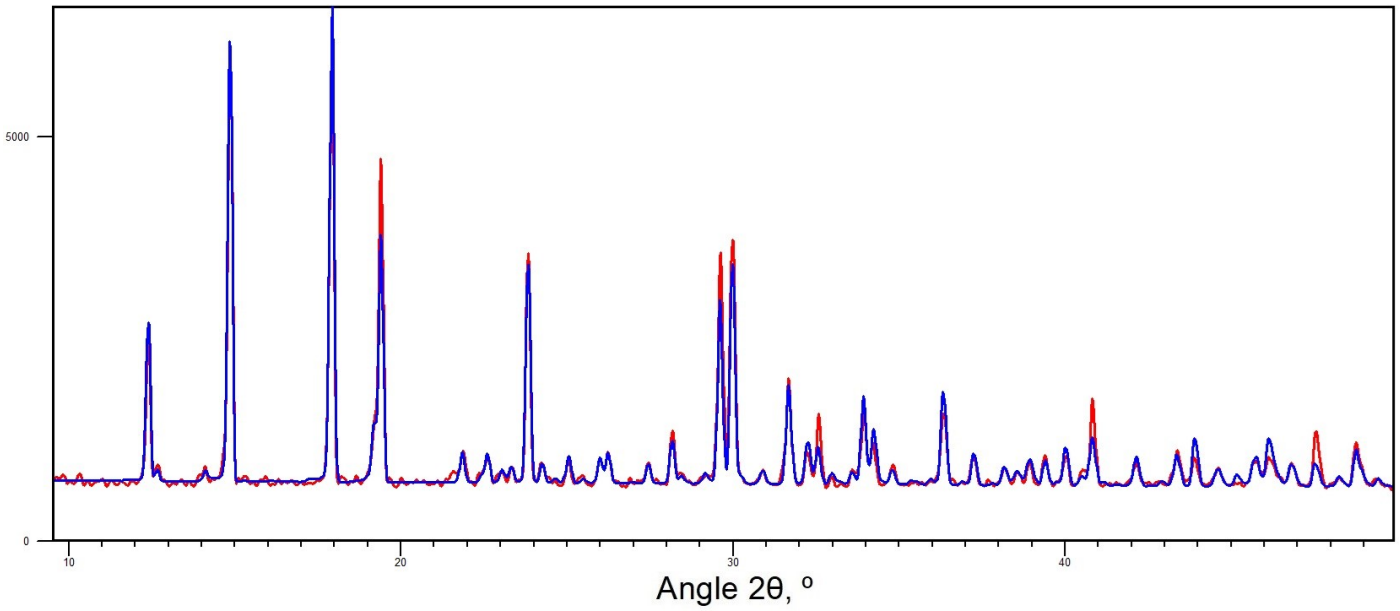

Figure S2. Experimental (red) and calculated from SCXRD data (blue) powder patterns comparison for **1**.

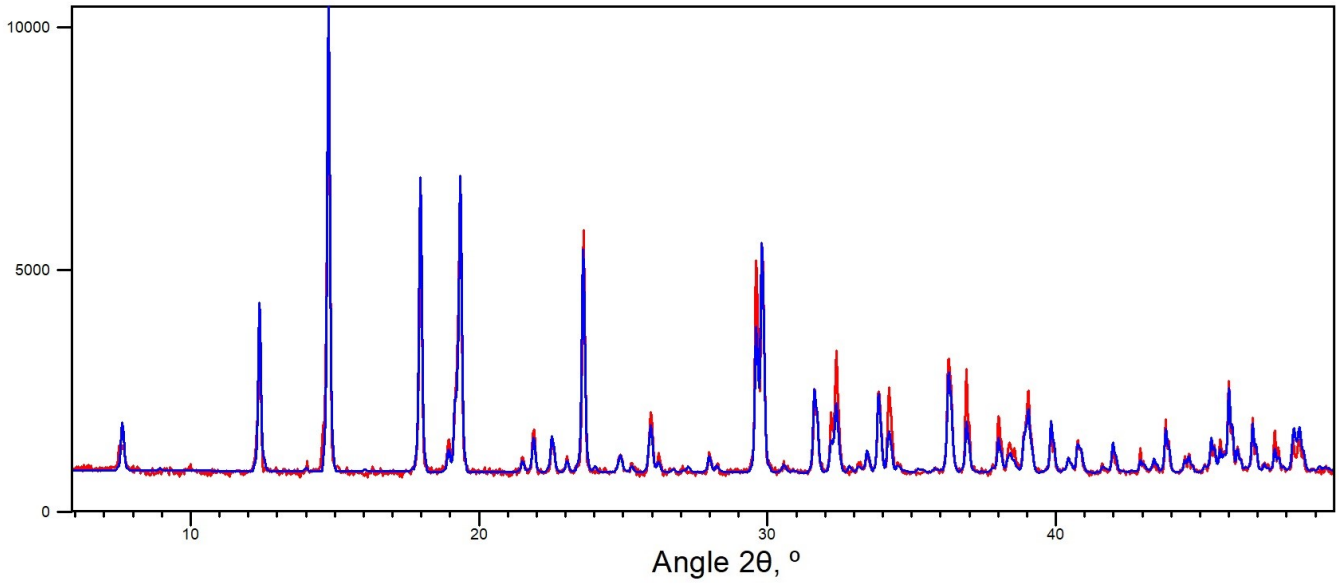

Figure S3. Experimental (red) and calculated from SCXRD data (blue) powder patterns comparison for **2**.

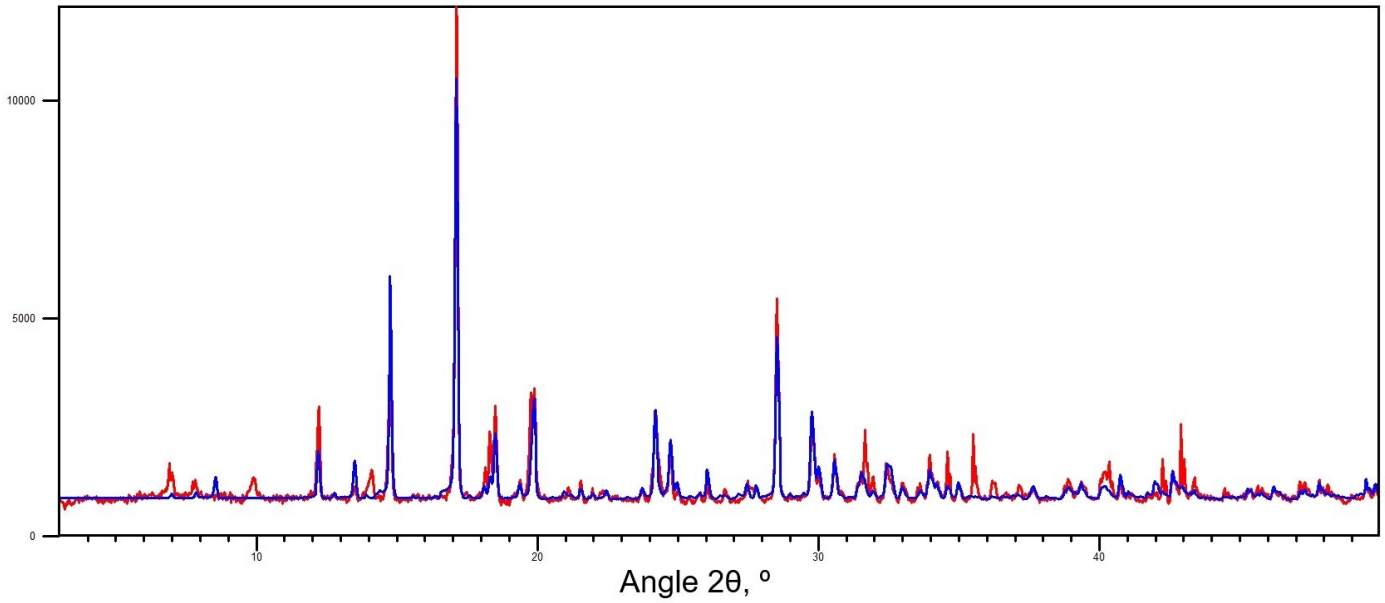

Figure S4. Experimental (red) and calculated from SCXRD data (blue) powder patterns comparison for **3**.

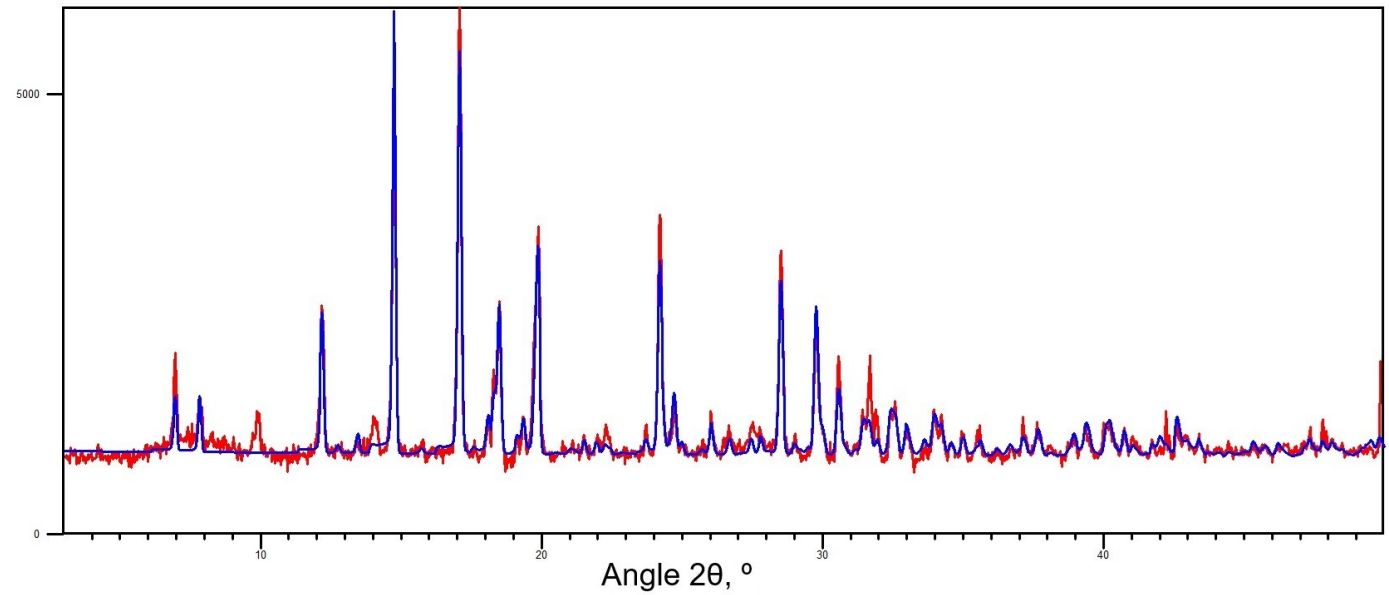

Figure S5. Experimental (red) and calculated from SCXRD data (blue) powder patterns comparison for **4**.

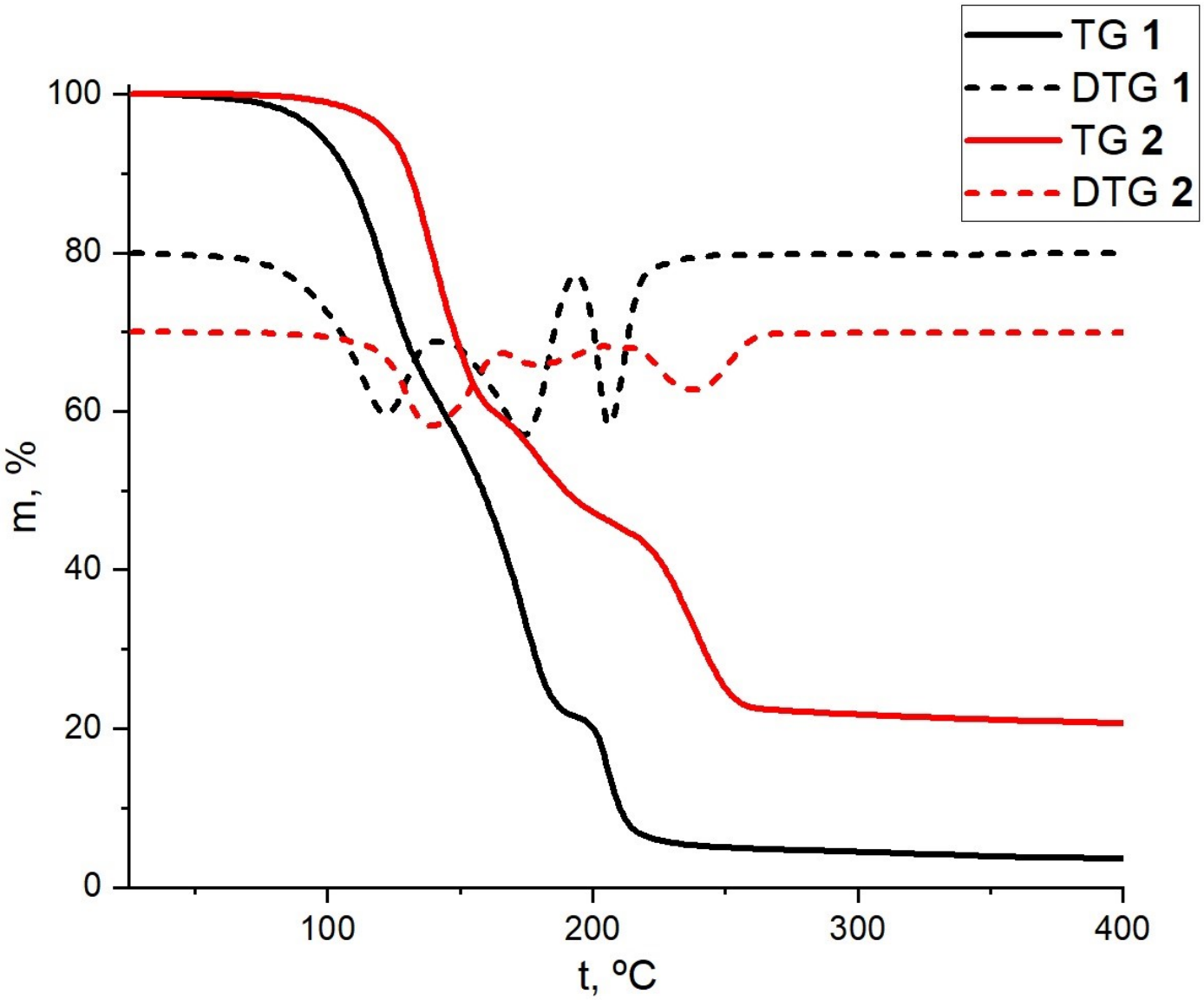

Figure S6. TG and DTG curves for **1** and **2**.

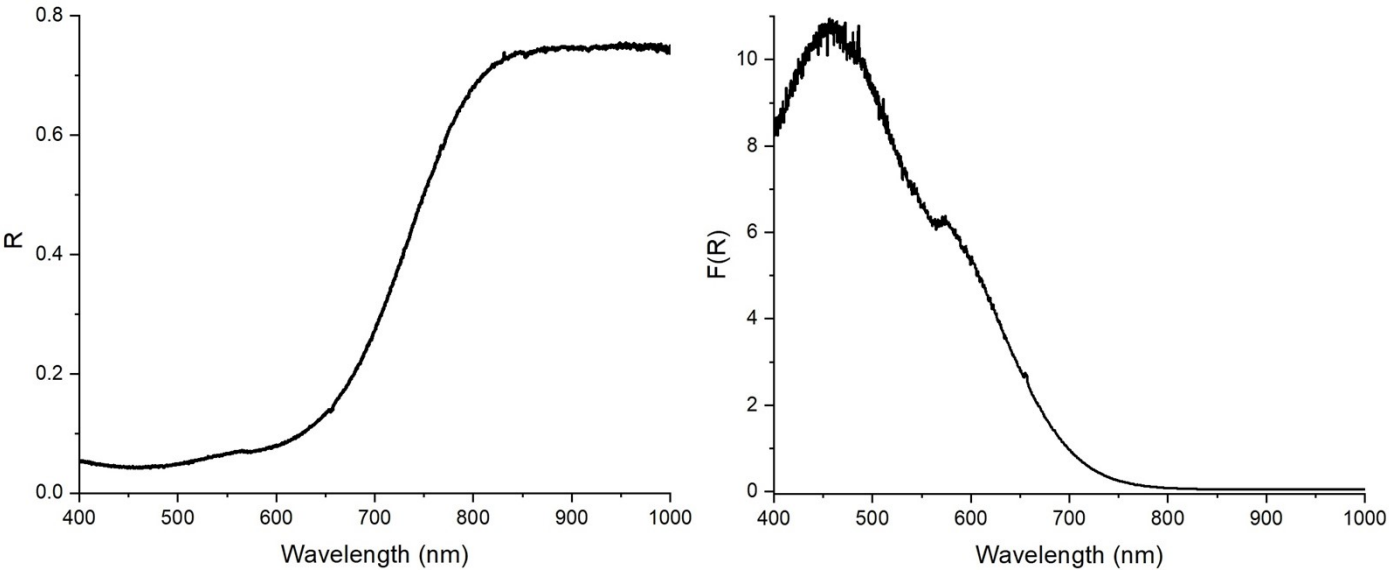

Figure S7. Diffuse reflectance spectrum (*left*) and Cubelka-Munk function (*right*) for **1**.

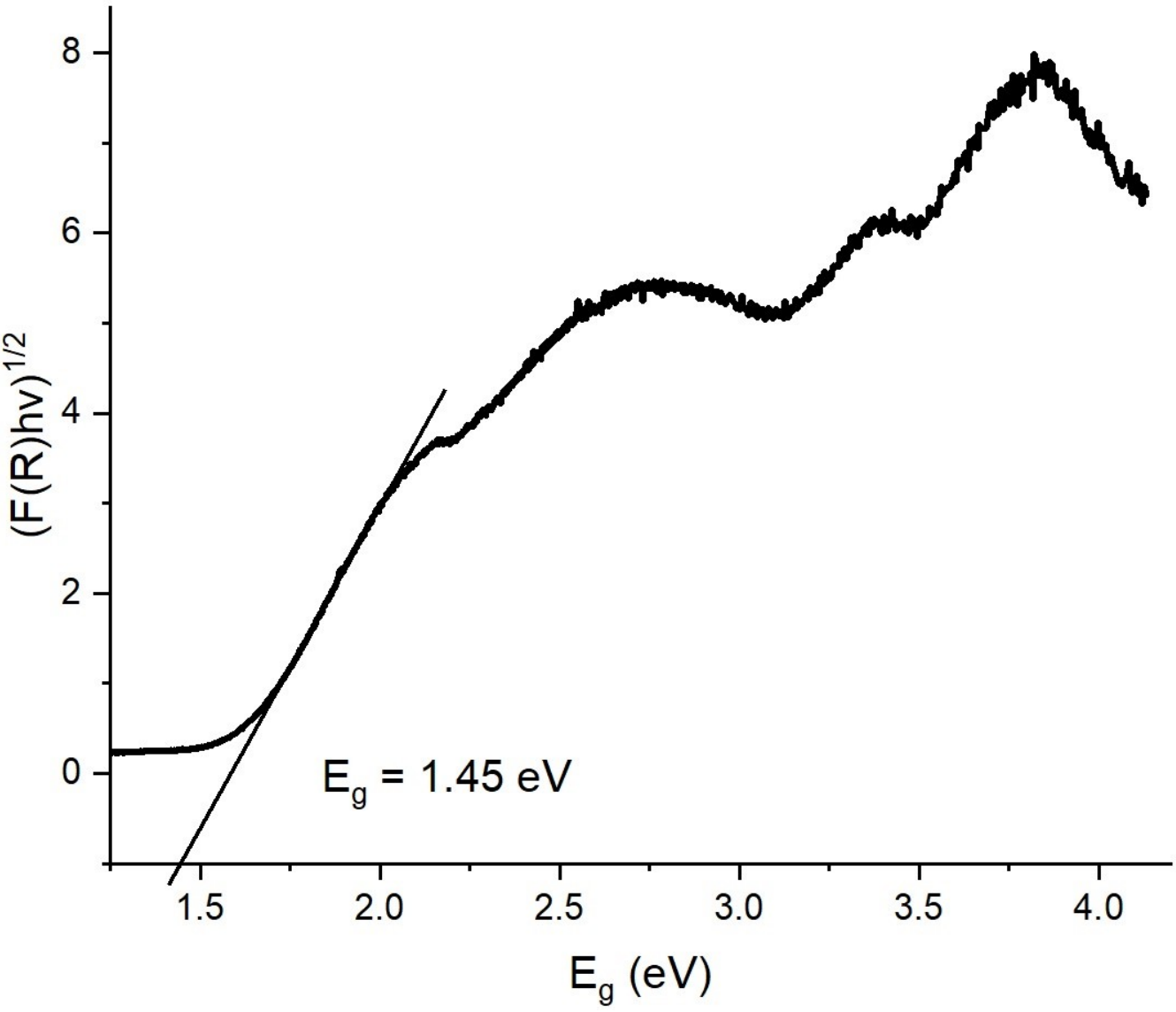

Figure S8. Band gap determination for **1**.

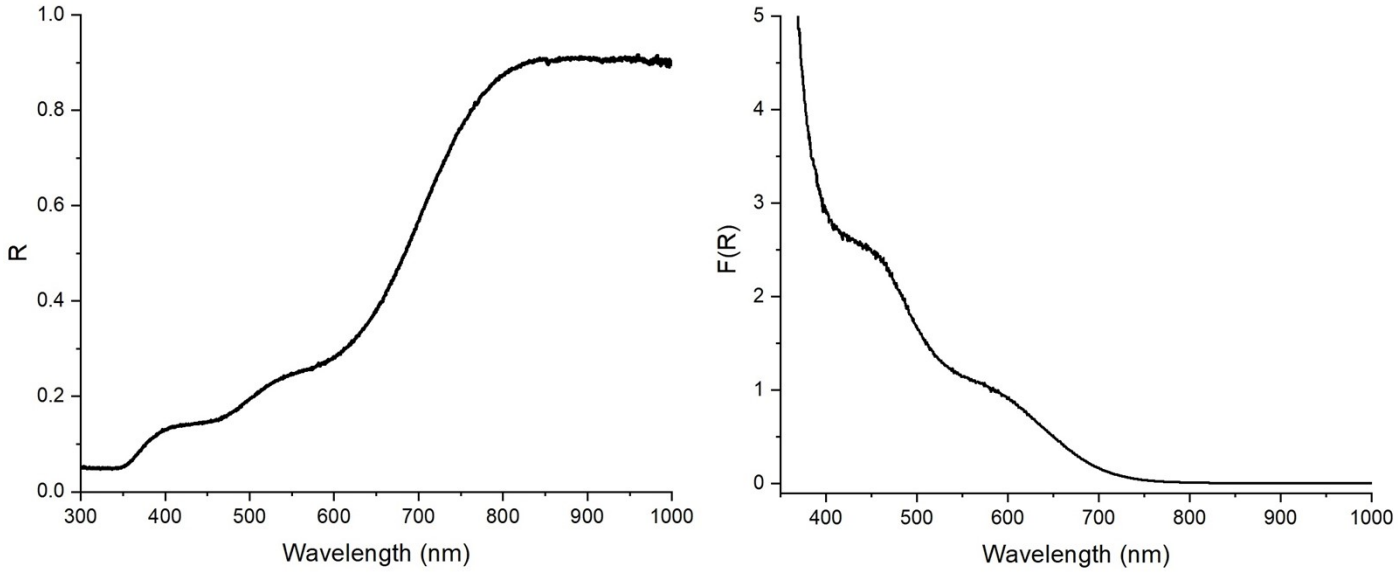

Figure S9. Diffuse reflectance spectrum (*left*) and Cubelka-Munk function (*right*) for **2**.

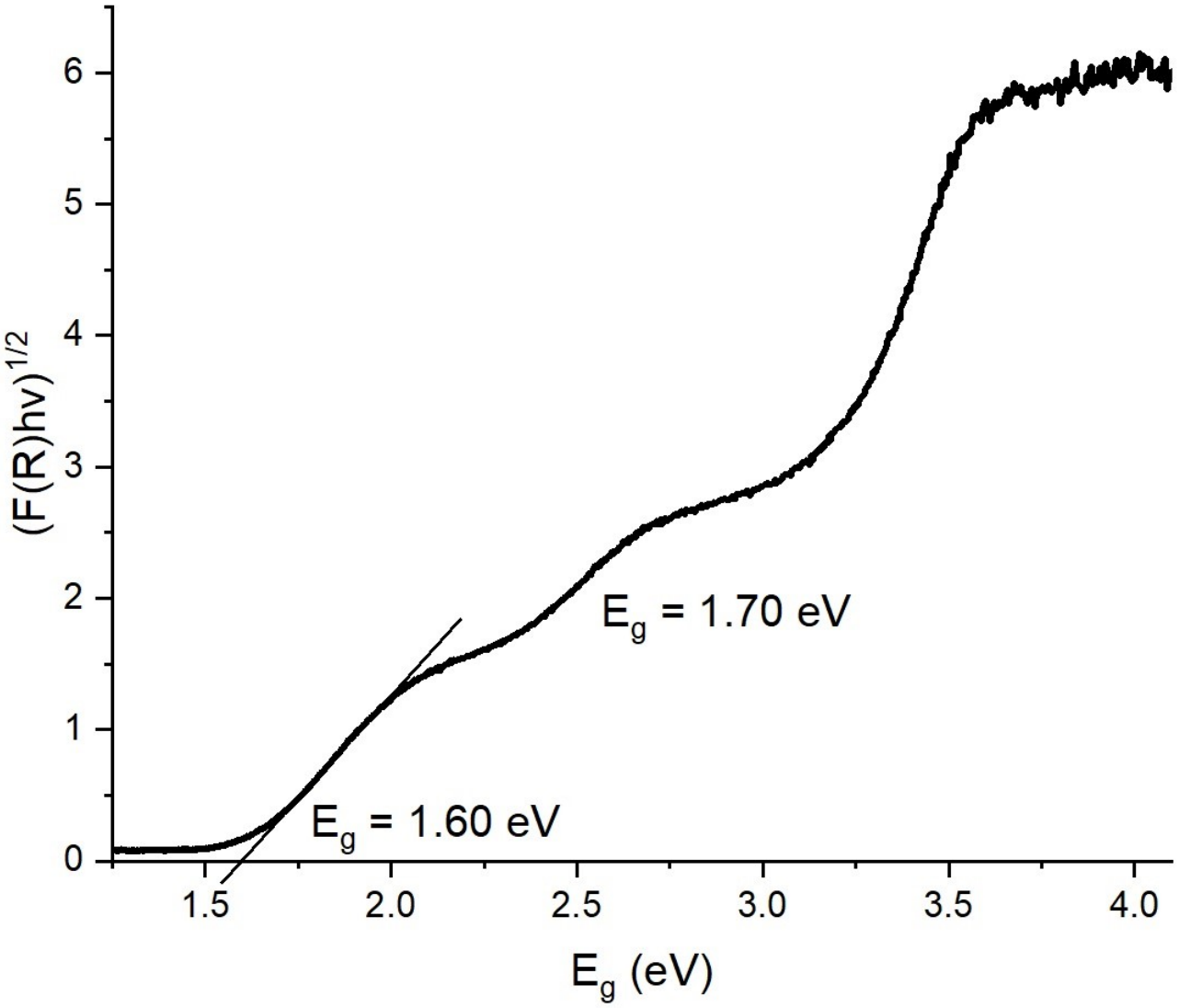

Figure S10. Band gap determination for **2**.

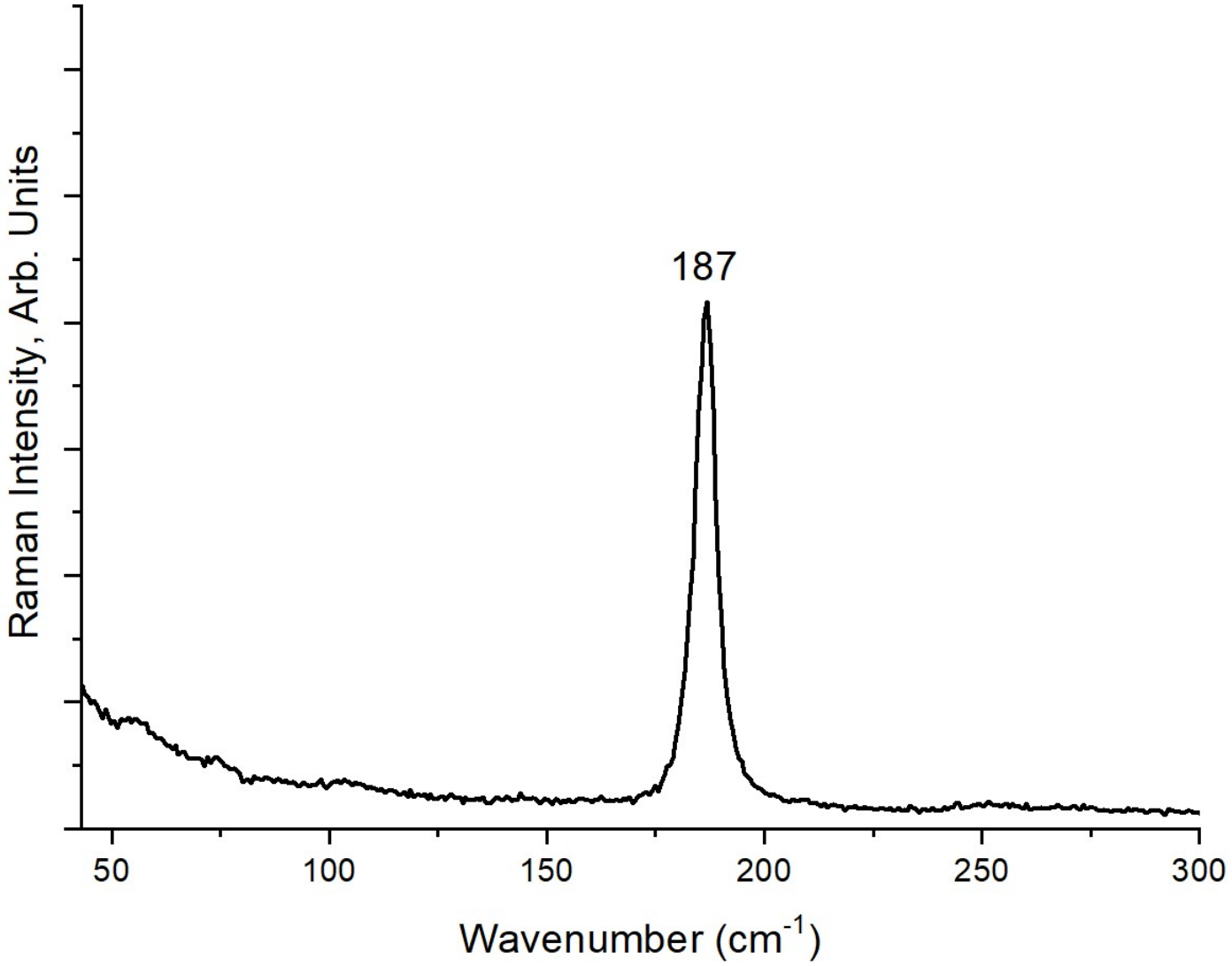

Figure S11. Raman spectrum of **1**.

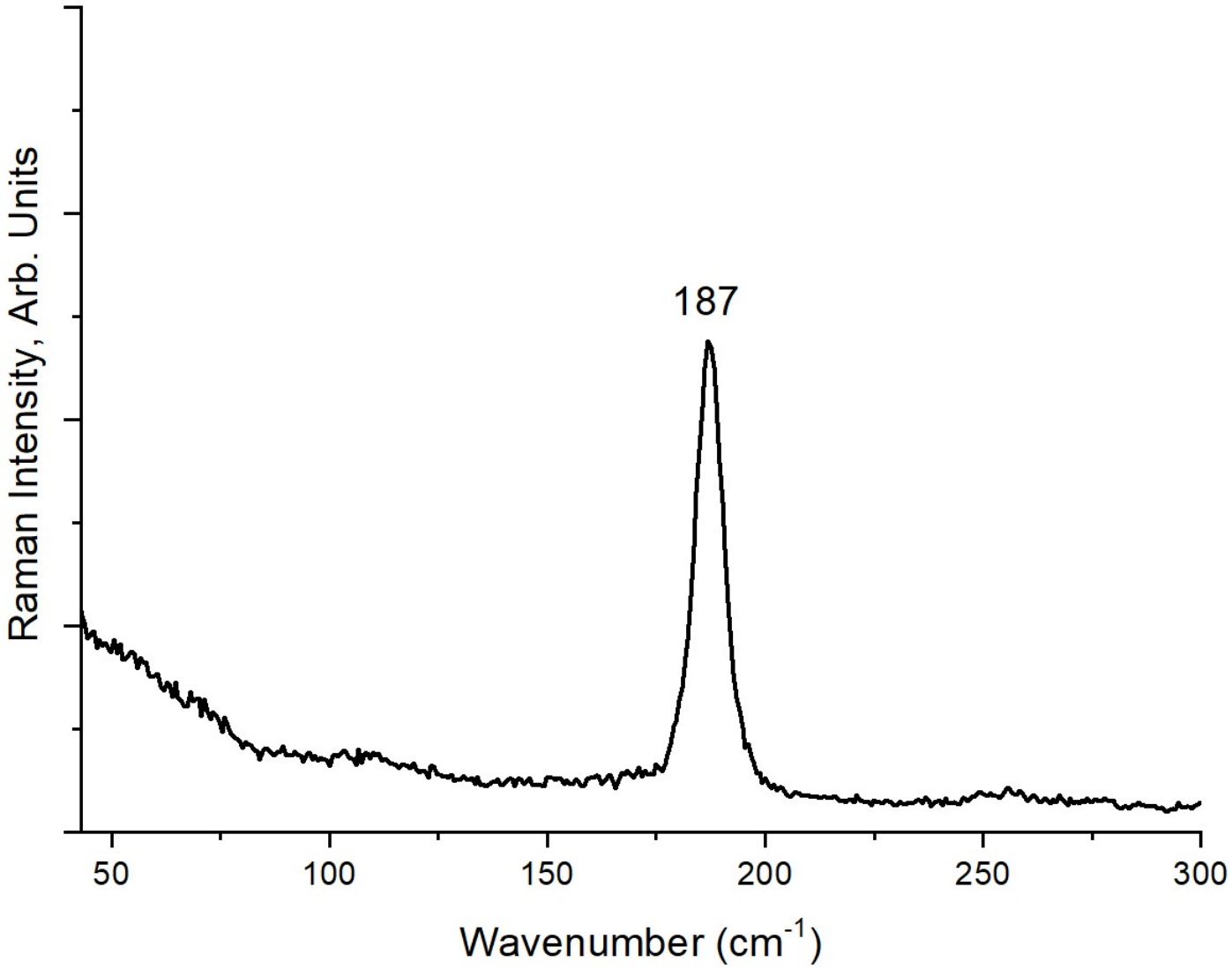

Figure S12. Raman spectrum of **3**.

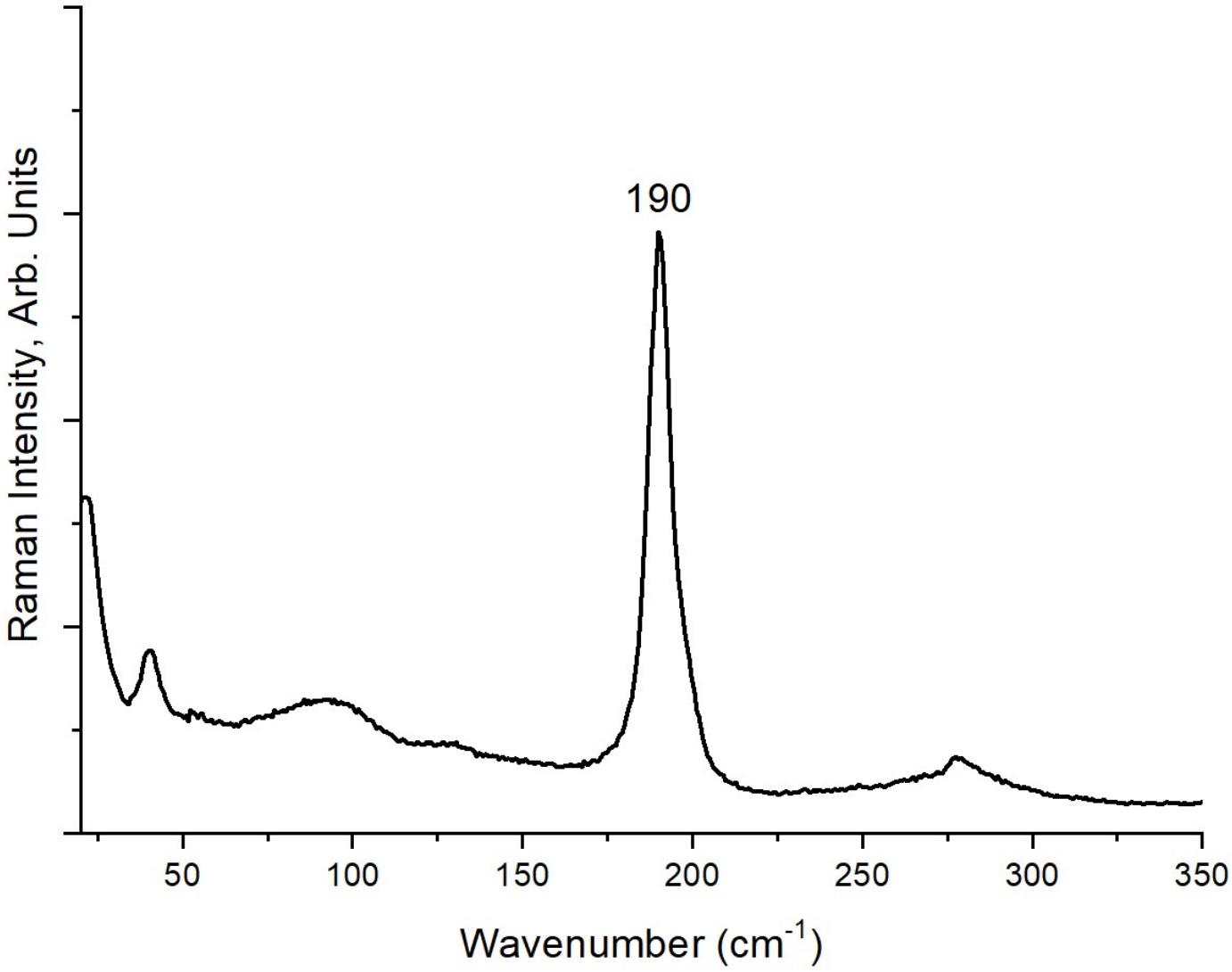

Figure S13. Raman spectrum of **4**.

Table S11. Raman spectra data for polyiodo-chlorometallates reported so far.

Compound	I-I distance, Å	Raman active band, cm^{-1}	Source
$(3\text{-BrPyH})_2\{[SbCl_5](I_2)\}$, **1**	2.7292(4)	187	This work
$(3\text{-BrPyH})_2\{[BiCl_5](I_2)\}$, **2**	2.7094(5)	195	This work
$(3\text{-ClPyH})_2\{[SbCl_5](I_2)\}$, **3**	2.7318(4)	187	This work
$(3\text{-ClPyH})_2\{[BiCl_5](I_2)\}$, **4**	2.7095(4)	190	This work
$(1\text{-MePy})_2\{[TeCl_6](I_2)\}$	2.6918(4)	196	[10.1039/D4CE00088A]
$(PyH)_2\{[TeCl_6](I_2)\}$	2.6947(3)	194	[10.1039/D4CE00088A]
$(2\text{-MePyH})_2\{[TeCl_6](I_2)\}$	2.6991(5), 2.7019(6)	191	[10.1039/D4CE00088A]
$(4\text{-MePyH})_2\{[TeCl_6](I_2)\}$	2.7043(4)	193	[10.1039/D4CE00088A]
$(Me_3NH)_2\{[TeCl_6](I_2)\}$	2.6940(4)	196	[10.1039/D4CE00088A]
$(Py(CH_2)_2Py)\{[BiCl_5](I_2)\}$	2.7143(4)	194.5	[10.1021/acs.inorgchem.4c02593]
$(Py(CH_2)_3Py)\{[BiCl_5](I_2)_{0.5}\}$	2.7166(3)	190	[10.1021/acs.inorgchem.4c02593]
$(H_2bpe)\{[SbCl_5](I_2)\}$	2.7454(5)	184	[10.1039/D5DT00697J]
$(H_2bpe)\{[BiCl_5](I_2)\}$	2.7108(4)	192	[10.1039/D5DT00697J]
$(H_2bpp)\{[SbCl_5](I_2)\}$	2.7156(4)	191	[10.1039/D5DT00697J]
$(H_2bpp)\{[BiCl_5](I_2)\}$	2.7170(4)	196	[10.1039/D5DT00697J]

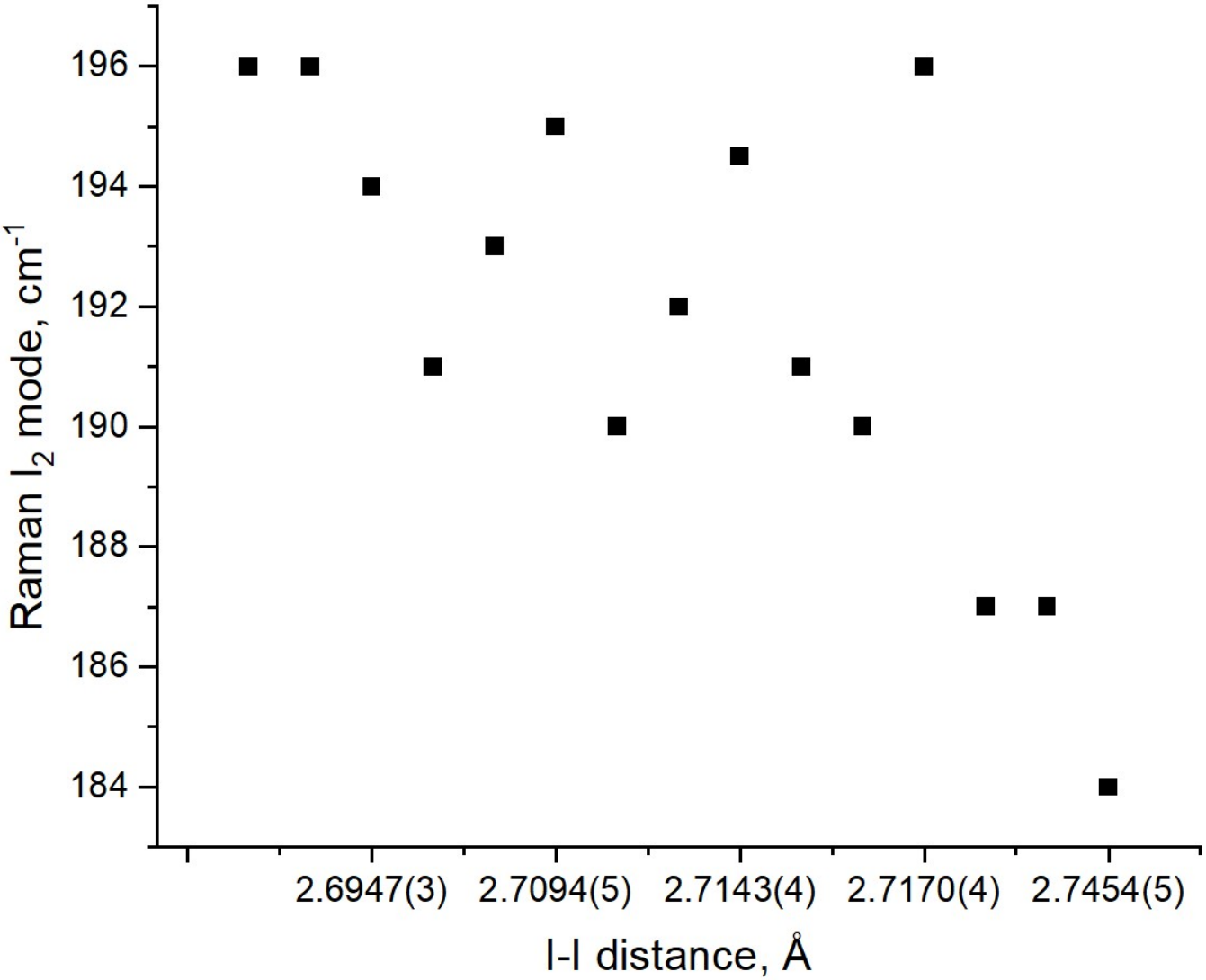

Figure S14. Scatterplot built of data from Table S11.

Computational details

The DFT calculations based on the experimental X-ray geometries of **1**-**4** have been carried out using the dispersion-corrected hybrid functional ωB97XD [Phys. Chem. Chem. Phys. 2008, 10, 6615.] 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. The topological analysis of the electron density distribution (QTAIM), electron localization function (ELF), and reduced density gradient (RDG) analyses have been performed by using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. The Cartesian atomic coordinates for model supramolecular associates presented in **Tables S14-S15**, Supporting Information. The calculations of electrostatic surface potential distribution on $\{SbCl_5\}^{2-}$ and $\{BiCl_5\}^{2-}$ units in the X-ray structures **1**-**4** were carried out in Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.], and VMD program [J. Molec. Graphics 1996, 14.1, 33.] was used for the visualization.

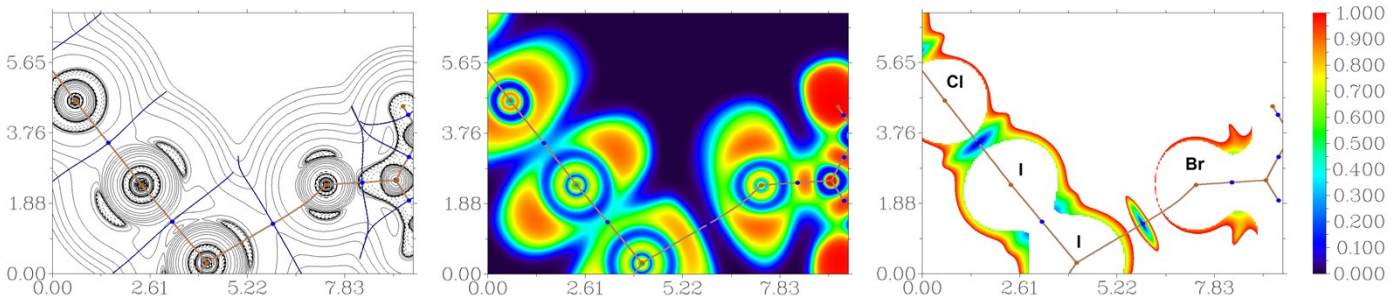

Figure S15. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (left panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, right panel) analyses for intermolecular interactions Br···I and I···Cl in **1**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

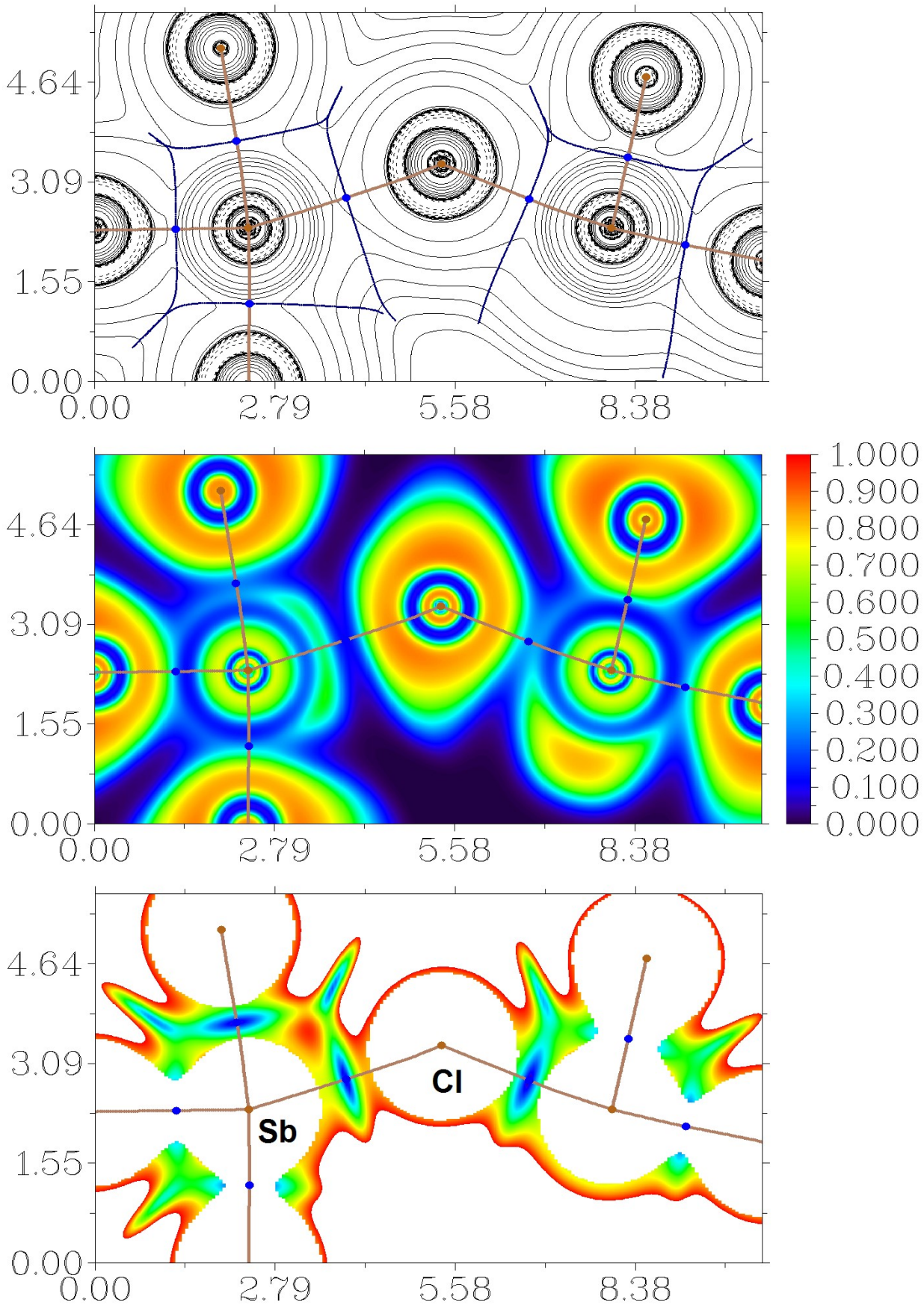

Figure S16. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for intermolecular interactions Sb···Cl in **1**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

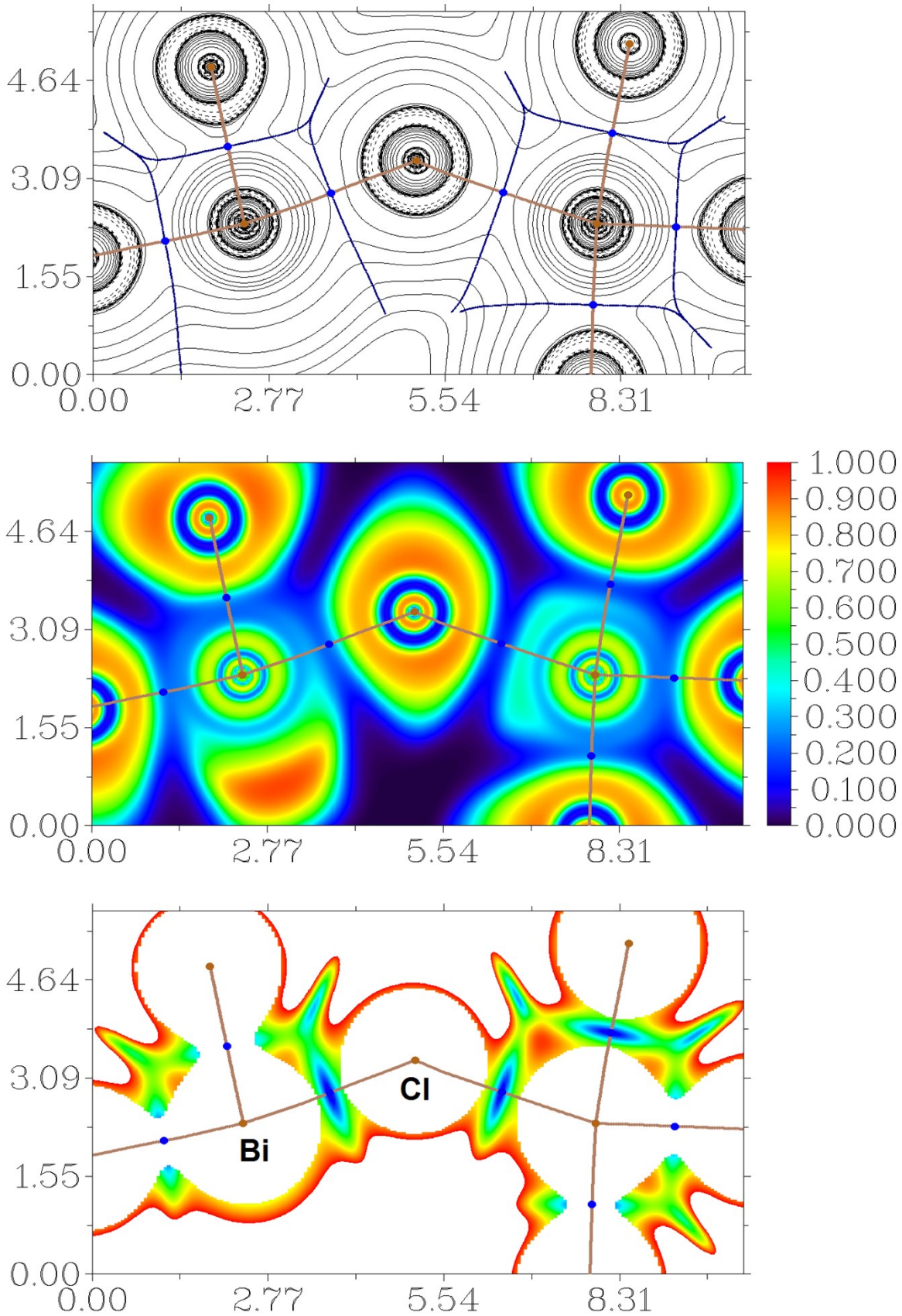

Figure S17. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top panel), visualization of electron localization function (ELF, center panel) and reduced density gradient (RDG, bottom panel) analyses for intermolecular interactions Bi···Cl in **2**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

Table S12. 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 intermolecular halogen···halogen interactions in the X-ray structures **1**-**4**, and estimated strength for these contacts E_{int} (kcal/mol).

Contact*	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	ELF	E_{int}**
1								
Br···I 3.821 Å	0.007	0.022	-0.007	0.001	-0.003	0.004	0.029	0.9
I···Br 3.888 Å	0.007	0.022	-0.007	0.001	-0.004	0.005	0.027	1.3
I···Cl 2.860 Å	0.036	0.055	-0.036	-0.004	-0.022	0.018	0.284	6.9
Br···Cl 3.424 Å	0.009	0.028	-0.009	0.001	-0.005	0.006	0.035	1.6
Br···Cl 3.704 Å	0.006	0.018	-0.006	0.001	-0.003	0.004	0.026	0.9
Br···Cl 3.833 Å	0.005	0.014	-0.005	0.001	-0.002	0.003	0.020	0.6
2								
Br···I 3.855 Å	0.007	0.022	-0.007	0.001	-0.004	0.005	0.025	1.3
I···Br 3.845 Å	0.007	0.022	-0.007	0.001	-0.004	0.005	0.026	1.3
I···Cl 2.959 Å	0.026	0.062	-0.026	-0.001	-0.018	0.017	0.128	5.6
Br···Cl 3.392 Å	0.009	0.030	-0.009	0.001	-0.005	0.006	0.034	1.6
Br···Cl 3.713 Å	0.006	0.018	-0.006	0.001	-0.003	0.004	0.026	0.9
Br···Cl 3.883 Å	0.005	0.013	-0.005	0.001	-0.002	0.003	0.017	0.6
3								
I···Cl 2.885 Å	0.032	0.064	-0.032	-0.003	-0.022	0.019	0.197	6.9
I···Cl 3.814 Å	0.006	0.017	-0.006	0.001	-0.002	0.003	0.024	0.6
I···Cl 3.961 Å	0.004	0.016	-0.004	0.001	-0.002	0.003	0.013	0.6
Cl···I 3.857 Å	0.006	0.020	-0.006	0.001	-0.003	0.004	0.022	0.9
Cl···Cl 3.547 Å	0.006	0.020	-0.006	0.001	-0.003	0.004	0.021	0.9
Cl···Cl 3.657 Å	0.005	0.017	-0.005	0.001	-0.002	0.003	0.019	0.6
Cl···Cl 3.668 Å	0.005	0.017	-0.005	0.001	-0.002	0.003	0.020	0.6
4								
I···Cl 3.009 Å	0.026	0.055	-0.026	-0.001	-0.016	0.015	0.156	5.0
I···Cl 3.672 Å	0.009	0.022	-0.009	0.000	-0.004	0.004	0.056	1.3
I···Cl 3.924 Å	0.005	0.017	-0.005	0.001	-0.002	0.003	0.016	0.6
Cl···I 3.846 Å	0.005	0.020	-0.005	0.001	-0.003	0.004	0.015	0.9
Cl···Cl 3.501 Å	0.007	0.023	-0.007	0.002	-0.003	0.005	0.022	0.9
Cl···Cl 3.663 Å	0.006	0.018	-0.006	0.000	-0.003	0.003	0.020	0.9
Cl···Cl 3.730 Å	0.005	0.015	-0.005	0.001	-0.002	0.003	0.017	0.6

* The Alvarez's van der Waals radii for Cl, Br, and I atoms are 1.82, 1.86, and 2.04 Å, respectively [Dalton Trans., 2013, 42, 8617.].

** $E_{int} = -V(\mathbf{r})/2$

Table S13. 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 intermolecular pnictogen bonding Sb···Cl and Bi···Cl in the X-ray structures **1**-**4**, and estimated strength for these contacts E_{int} (kcal/mol).

Contact*	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	ELF	E_{int}**
1								
Sb···Cl 3.152 Å	0.019	0.044	-0.019	0.000	-0.011	0.011	0.112	3.5
2								
Bi···Cl 3.012 Å	0.028	0.069	-0.028	0.001	-0.018	0.017	0.145	5.6
3								
Sb···Cl 3.160 Å	0.019	0.044	-0.019	0.000	-0.011	0.011	0.111	3.5
4								
Bi···Cl 3.015 Å	0.027	0.068	-0.027	0.001	-0.018	0.017	0.145	5.6

* The Alvarez's van der Waals radii for Cl, Sb, and Bi atoms are 1.82, 2.47, and 2.54 Å, respectively [Dalton Trans., 2013, 42, 8617.].

** $E_{int} = -V(\mathbf{r})/2$

Table S14. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
1			
Sb	9.316181	5.246995	13.372944
Cl	9.456794	3.758885	11.484807
Cl	9.486551	7.177885	11.819996
Cl	11.759417	5.256072	13.638856
Cl	9.177635	2.811133	14.793352
Cl	6.413565	5.295286	13.043563
I	3.578764	5.148355	12.694061
I	0.862176	5.088504	12.438521
Br	12.546814	5.431439	10.311643
N	15.285654	5.250399	7.328539
H	16.155903	5.131520	7.279152
C	13.362325	5.439736	8.616405
C	14.718384	5.268127	8.537793
H	15.242671	5.164651	9.323103
C	14.606351	5.403571	6.193540
H	15.058468	5.397720	5.358097
C	12.622898	5.585108	7.473317
H	11.681406	5.697725	7.523015
C	13.262987	5.567380	6.243321
H	12.762675	5.669650	5.442745
Br	-2.373986	5.431439	10.311643
N	0.364854	5.250399	7.328539
H	1.235103	5.131520	7.279152
C	-1.558475	5.439736	8.616405
C	-0.202416	5.268127	8.537793
H	0.321871	5.164651	9.323103
C	-0.314449	5.403571	6.193540
H	0.137668	5.397720	5.358097
C	-2.297902	5.585108	7.473317
H	-3.239394	5.697725	7.523015
C	-1.657813	5.567380	6.243321
H	-2.158125	5.669650	5.442745
Br	0.059740	5.097085	16.174764
N	-3.412101	5.380878	18.242320
H	-4.259187	5.487028	18.031271
C	-1.193826	5.158921	17.578993
C	-2.515107	5.322021	17.251685
H	-2.787131	5.392260	16.344081
C	-0.803039	5.075243	18.902121
H	0.114480	4.979263	19.128063
C	-1.768857	5.133392	19.894207
H	-1.520082	5.067159	20.808843
C	-3.087042	5.286564	19.543046
H	-3.761119	5.325843	20.210750
2			

Bi	9.162130	1.934914	13.449679
Cl	9.313647	3.487923	11.461392
Cl	8.987095	4.440001	14.871485
Cl	9.297610	-0.094564	11.878056
Cl	11.738771	1.885200	13.723997
Cl	6.337415	1.837631	13.169136
Cl	8.913123	0.863451	16.253866
I	3.408840	1.923826	12.757451
I	0.709931	1.937346	12.519861
Br	-2.490903	1.715027	10.401055
N	0.229518	1.803297	7.397458
H	1.106662	1.857896	7.337552
C	-0.320451	1.799005	8.613422
H	0.216027	1.859119	9.396017
C	-1.693223	1.703868	8.696423
C	-2.445758	1.616601	7.551010
H	-3.391893	1.550420	7.599151
C	-0.472971	1.730335	6.266571
H	-0.031150	1.750564	5.425377
C	-1.807949	1.627330	6.324671
H	-2.314947	1.561014	5.524750
Br	-0.123796	1.950078	16.283331
N	-3.644302	1.759663	18.293406
H	-4.492706	1.694391	18.070403
C	-3.325803	1.831909	19.590296
H	-4.009503	1.807152	20.249697
C	-2.720938	1.782553	17.320220
H	-2.974143	1.716222	16.407791
C	-1.397443	1.904155	17.677124
C	-2.007345	1.943497	19.972100
H	-1.773254	1.990765	20.891501
C	-1.031866	1.984270	18.998914
H	-0.116268	2.066695	19.240550
I	8.524639	5.229274	7.992783
I	11.223548	5.215754	8.230373
Br	12.399097	1.715027	10.401055
N	15.119518	1.803297	7.397458
H	15.996662	1.857896	7.337552
C	14.569549	1.799005	8.613422
H	15.106027	1.859119	9.396017
C	13.196777	1.703868	8.696423
C	12.444242	1.616601	7.551010
H	11.498107	1.550420	7.599151
C	14.417029	1.730335	6.266571
H	14.858850	1.750564	5.425377
C	13.082051	1.627330	6.324671
H	12.575053	1.561014	5.524750
3			
Sb	9.360344	1.786190	13.320004

Cl	9.488964	3.311942	11.461890
Cl	11.804351	1.810895	13.562619
Cl	9.184504	4.202172	14.794531
Cl	9.514250	-0.122593	11.750461
Cl	6.457767	1.758191	12.990860
I	3.603841	2.011326	12.656954
I	0.886918	2.203163	12.446219
Sb	2.959537	5.374610	7.380912
Cl	2.830918	3.848858	9.239026
Cl	0.515530	5.349905	7.138297
Cl	3.135378	2.958628	5.906385
Cl	2.805631	7.283393	8.950455
Cl	5.862114	5.402609	7.710056
Cl	0.457896	2.089879	16.277751
N	-2.924408	1.657009	18.167124
H	-3.761859	1.501634	17.945148
C	-0.348375	2.090954	18.867643
H	0.558133	2.236719	19.109347
C	-1.321141	1.994283	19.827130
H	-1.091998	2.079303	20.745278
C	-2.615889	1.775878	19.465071
H	-3.293141	1.708481	20.127190
C	-0.714730	1.971368	17.539472
C	-2.014544	1.763705	17.197493
H	-2.269496	1.696272	16.284852
I	18.147341	2.011326	12.656954
I	15.430418	2.203163	12.446219
Cl	12.344110	1.474982	10.073066
N	15.040637	1.900476	7.286515
H	15.897019	2.099776	7.255216
C	13.122385	1.535992	8.545338
C	14.457411	1.834597	8.478267
H	14.957041	1.991719	9.270429
C	14.409982	1.683504	6.144239
H	14.874356	1.740884	5.317527
C	12.427099	1.301117	7.381947
H	11.501354	1.089602	7.413702
C	13.077549	1.374874	6.173634
H	12.604990	1.212775	5.365305
4			
Bi	2.763193	1.729512	7.303587
Cl	2.619982	0.139502	9.267206
Cl	2.974739	-0.757607	5.840137
Cl	2.642749	3.737164	8.898911
Cl	0.179417	1.745004	7.046464
Cl	5.574292	1.809639	7.569405
Cl	2.986090	2.845243	4.511045
I	8.549448	1.609897	7.974551
I	11.253235	1.503830	8.115534

Cl	-2.743935	1.557152	4.314166
N	0.677260	1.903025	2.470206
H	1.516867	2.030047	2.703480
C	-0.251427	1.821601	3.436385
H	-0.008333	1.890920	4.352279
C	0.385459	1.799263	1.165543
H	1.072955	1.854164	0.512673
C	-0.917159	1.612636	0.785448
H	-1.138367	1.536572	-0.135145
C	-1.559773	1.636414	3.066848
C	-1.902804	1.535535	1.741069
H	-2.809881	1.413657	1.487134
I	-6.028652	1.609897	7.974551
I	-3.324865	1.503830	8.115534
Cl	-0.259876	2.033304	10.507485
N	-2.957564	1.720721	13.301269
H	-3.824866	1.576931	13.337105
C	-1.030618	1.988773	12.042358
C	-2.372829	1.771161	12.107157
H	-2.882530	1.658039	11.313863
C	-2.290081	1.878526	14.450250
H	-2.748977	1.837879	15.280229
C	-0.304454	2.147299	13.199827
H	0.633800	2.290418	13.163184
C	-0.957500	2.095418	14.415056
H	-0.471394	2.211321	15.223856

Table S15. Cartesian atomic coordinates for model supramolecular associates with pnictogen bonding.

Atom	X	Y	Z
1 (pnictogen bonding)			
Sb	9.316181	5.246995	13.372944
Cl	9.456794	3.758885	11.484807
Cl	9.486551	7.177885	11.819996
Cl	11.759417	5.256072	13.638856
Cl	9.177635	2.811133	14.793352
Cl	6.413565	5.295286	13.043563
Sb	9.026920	8.792645	17.739950
Cl	8.886307	7.304535	19.628088
Cl	8.856550	10.723535	19.292899
Cl	6.583685	8.801722	17.474039
Cl	9.165466	6.356783	16.319543
Cl	11.929536	8.840936	18.069332
2 (pnictogen bonding)			
Bi	9.162130	1.934914	13.449679
Cl	9.313647	3.487923	11.461392
Cl	8.987095	4.440001	14.871485
Cl	9.297610	-0.094564	11.878056
Cl	11.738771	1.885200	13.723997
Cl	6.337415	1.837631	13.169136
Bi	8.738089	5.511464	17.675672
Cl	8.913123	8.016551	16.253866
Cl	8.586571	7.064473	19.663959
Cl	8.602609	3.481986	19.247294
Cl	6.161448	5.461750	17.401353
Cl	11.562804	5.414181	17.956215
3 (pnictogen bonding)			
Sb	9.360344	1.786190	13.320004
Cl	9.488964	3.311942	11.461890
Cl	11.804351	1.810895	13.562619
Cl	9.184504	4.202172	14.794531
Cl	9.514250	-0.122593	11.750461
Cl	6.457767	1.758191	12.990860
Sb	9.119478	-1.794210	17.731370
Cl	8.990858	-0.268458	19.589484
Cl	6.675471	-1.769505	17.488755
Cl	9.295319	0.621772	16.256843
Cl	8.965572	-3.702993	19.300913
Cl	12.022055	-1.822209	18.060514
4 (pnictogen bonding)			
Bi	2.763193	8.935212	7.303587
Cl	2.619982	7.345202	9.267206
Cl	2.974739	6.448093	5.840137
Cl	2.642749	10.942864	8.898911
Cl	0.179417	8.950704	7.046464
Cl	5.574292	9.015339	7.569405

Bi	3.197636	5.332362	3.047595
Cl	2.986090	2.845243	4.511045
Cl	3.340847	3.742352	1.083976
Cl	3.318080	7.340014	1.452271
Cl	5.781412	5.347854	3.304718
Cl	0.386537	5.412489	2.781777