Polymeric polyiodo-chlorotellurates(IV): new supramolecular hybrids within the halometalate chemistry

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Powder X-ray diffractometry (PXRD)

Analysis of polycrystals was performed on Bruker D8 Advance (CuK_α radiation, LYNXEYE XE-T linear detector, 4 – 50° 2θ range, 0.03° 2θ step, 0.5s per step). A polycrystalline sample was slightly ground with hexane in an agate mortar, and the resulting suspensions were deposited on the polished side of a standard quartz sample holder, and a smooth thin layer being formed after drying. The diffraction patterns of **1-3** were completely indexed by the results of the corresponding single crystal studies, and no extra lines were found, which indicated that the products were a single phase. Samples of **4** and **5** contain phases that were not identified.

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 **1-3** 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.

Diffuse reflectance spectra of **1-3** 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.

Computational details

The single point calculations based on the experimental X-ray geometries of **1**–**5** have been carried out at the DFT level of theory 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 has been performed by using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. Results are summarized in Table S7. The Cartesian atomic coordinates for model supramolecular associates are presented in Table S8.

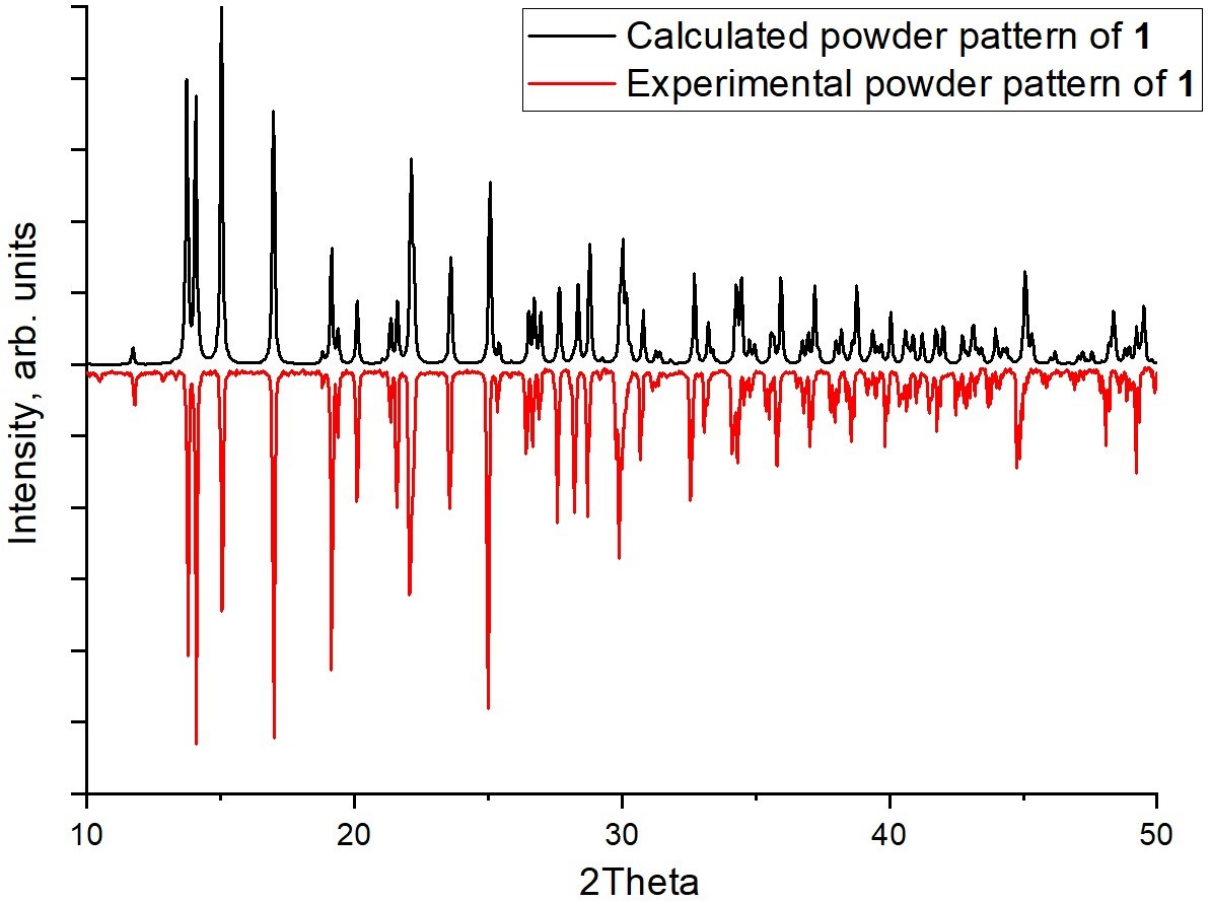

Figure S1. Experimental and calculated powder pattern of **1**.

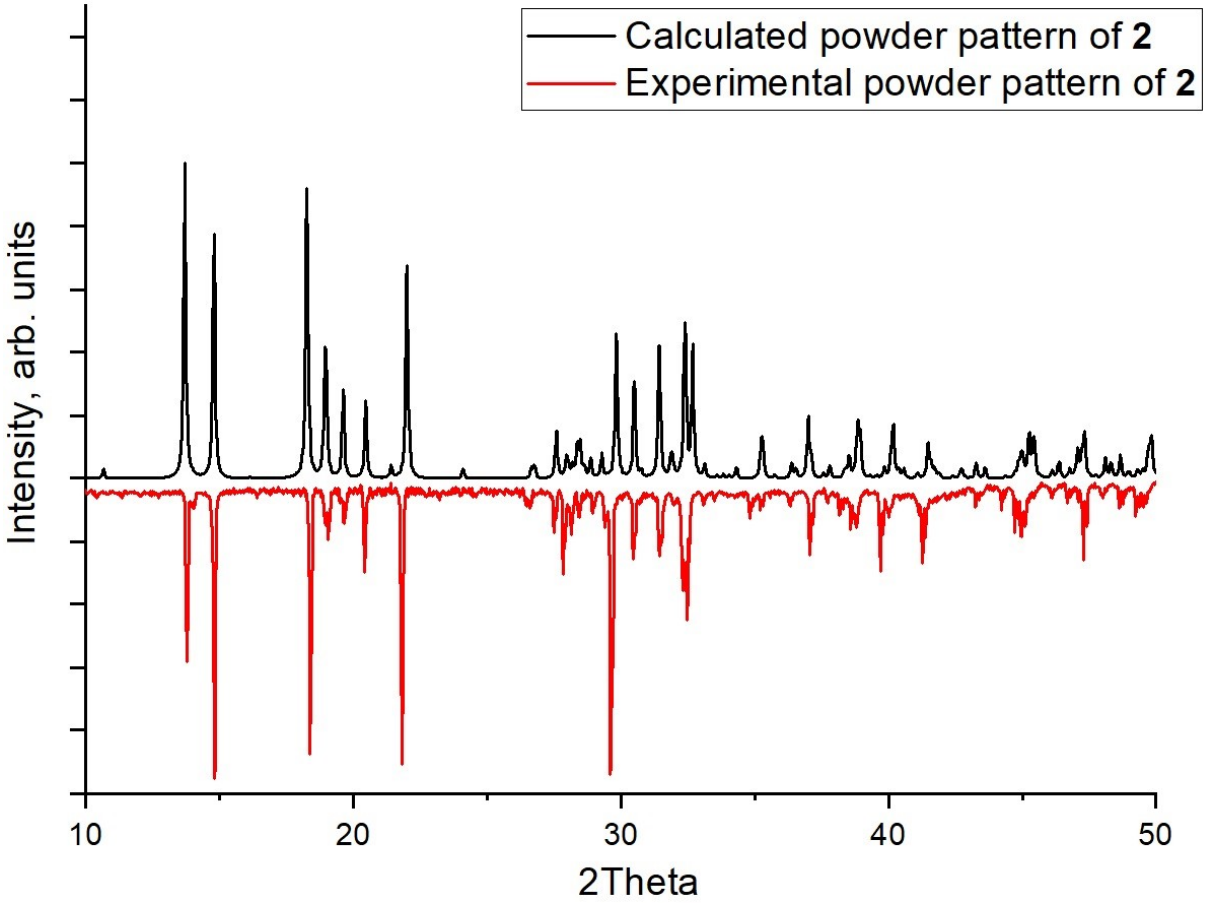

Figure S2. Experimental and calculated powder pattern of **2**.

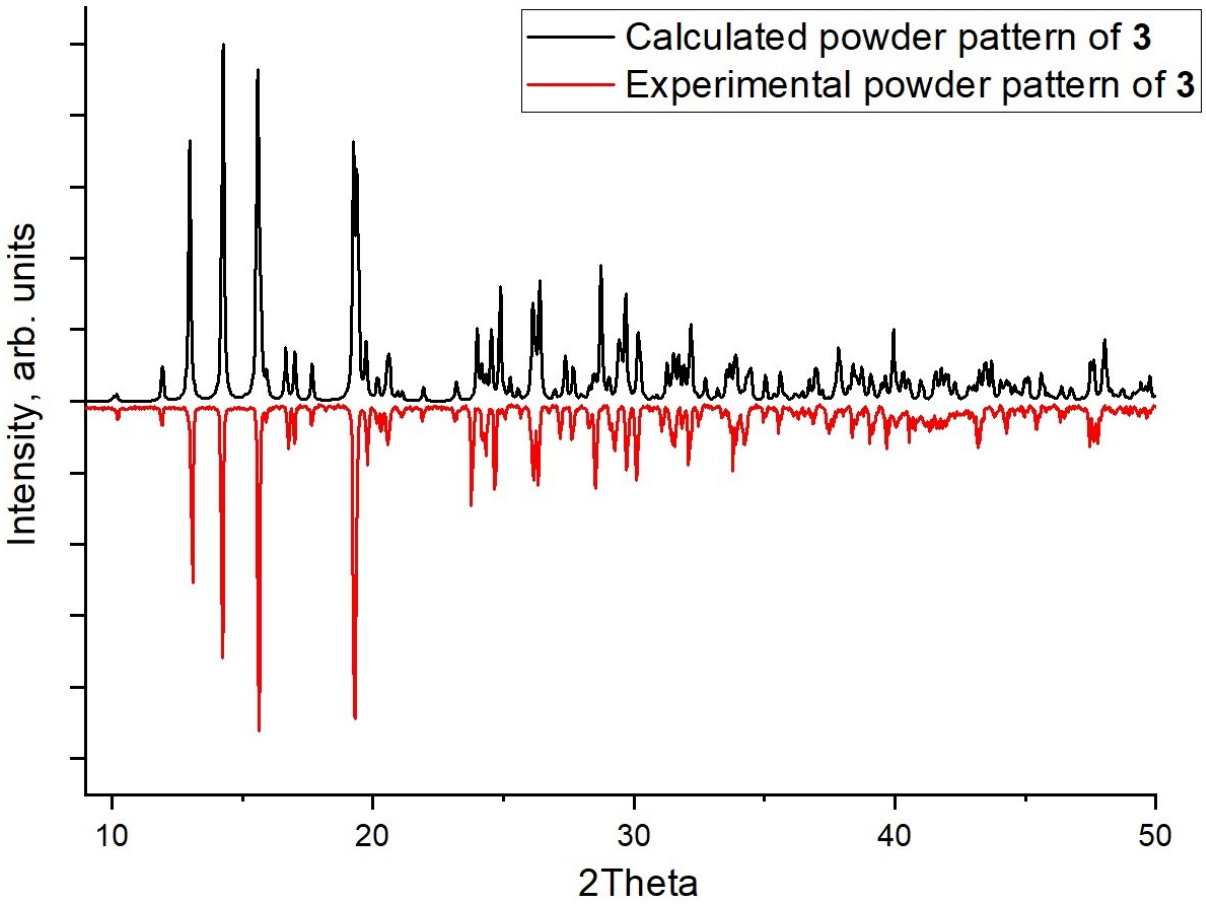

Figure S3. Experimental and calculated powder pattern of **3**.

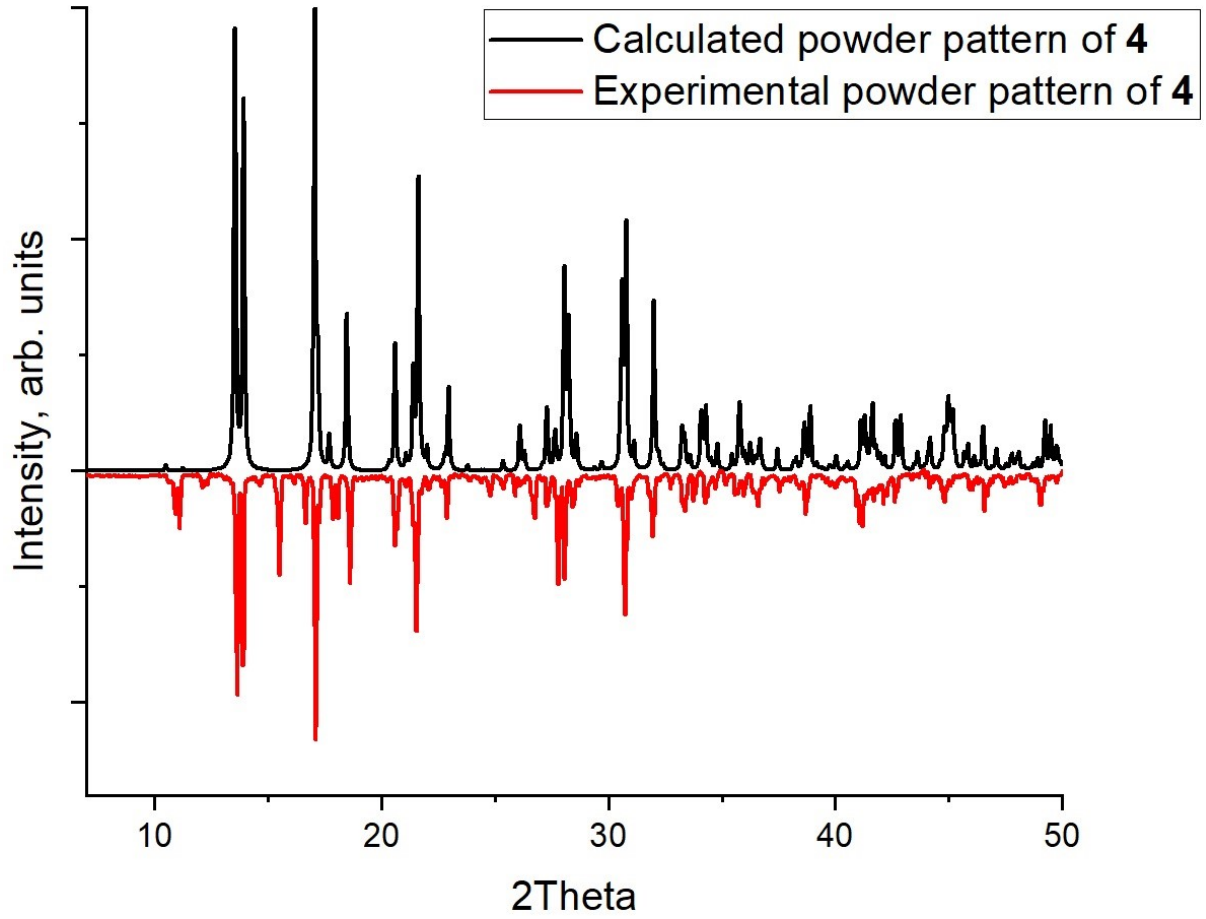

Figure S4. Experimental and calculated powder pattern of **4**.

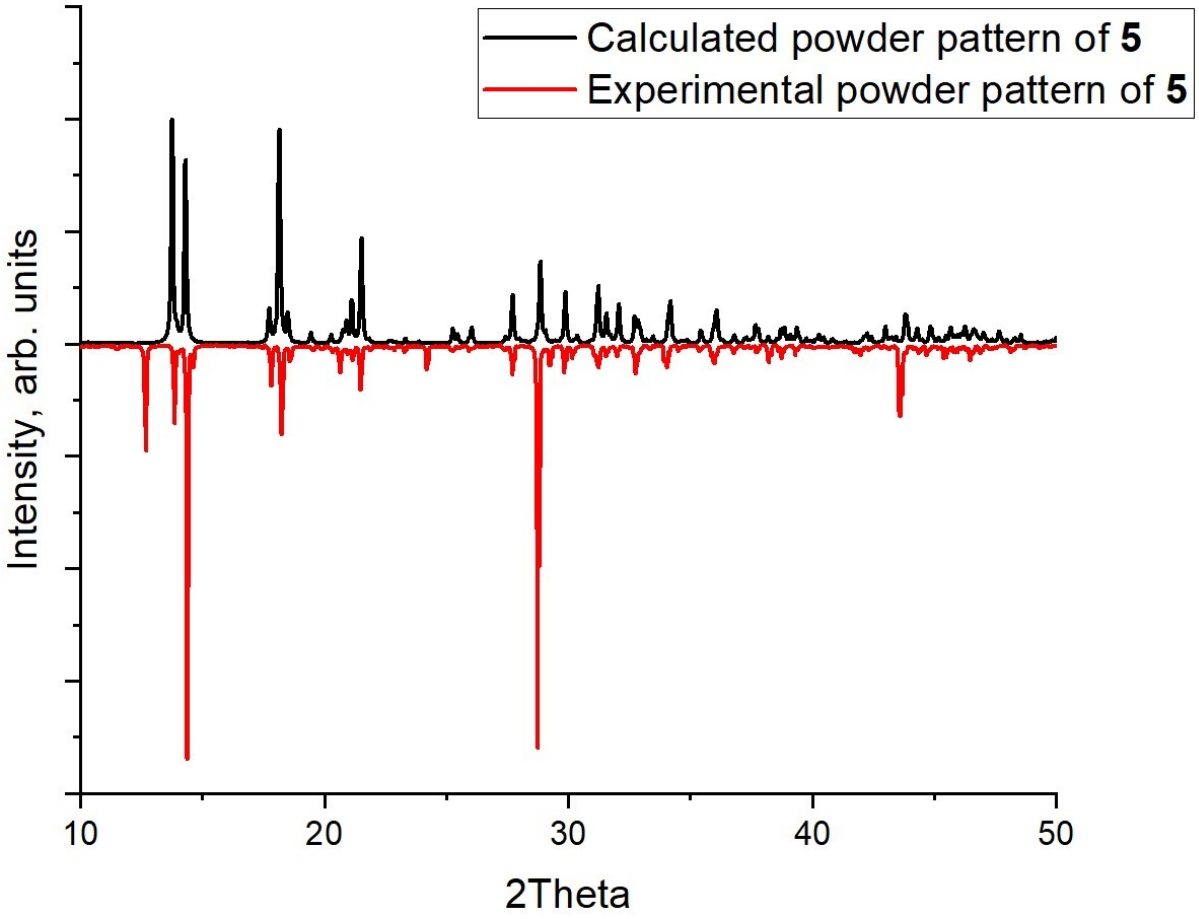

Figure S5. Experimental and calculated powder pattern of **5**.

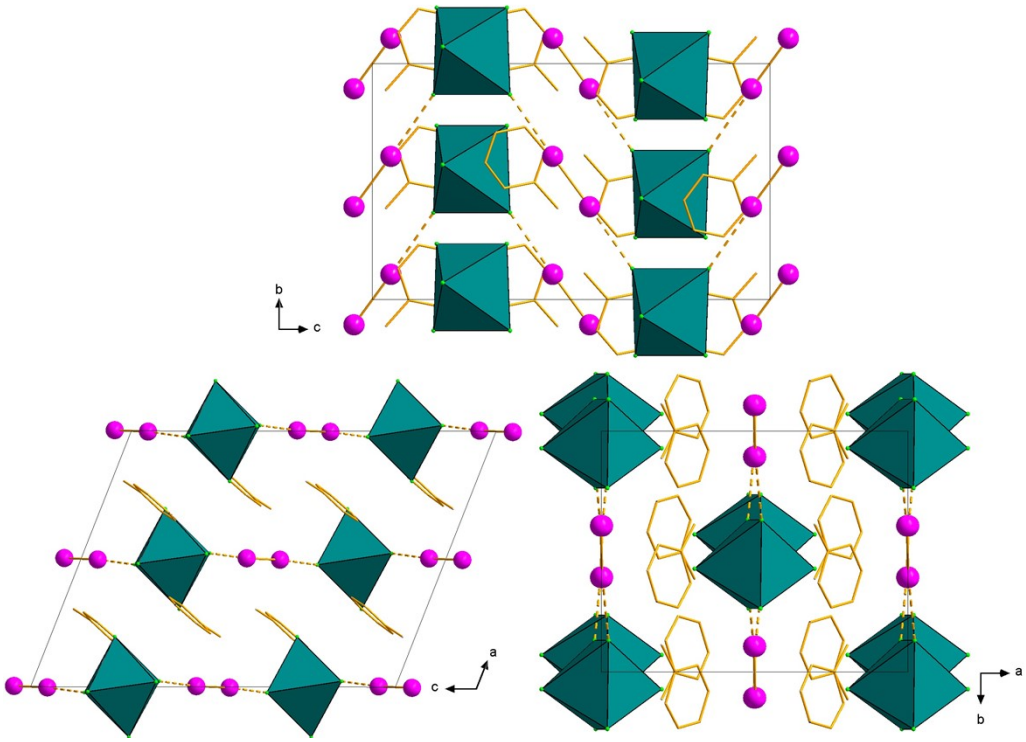

Figure S6. Crystal packing along *a* (top), *b* (bottom left) and *c* (bottom right) axes in **4**. Only one disordered part of cation with occupancy of 64% is shown.

Table S1. Crystal data and structure refinement for **1**–**5**.

Identification code	**1**	**2**	**3**	**4**	**5**
CCDC number	2310058	2310059	2310060	2310061	2310062
Empirical formula	$C_{12}H_{16}N_2TeCl_6I_2$	$C_{10}H_{12}N_2TeCl_6I_2$	$C_{12}H_{16}N_2TeCl_6I_2$	$C_{12}H_{16}N_2TeCl_6I_2$	$C_6H_{20}N_2TeCl_6I_2$
M, g/mol	782.37	754.32	782.37	782.37	714.34
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	*Tetragonal*	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Monoclinic*
Space group	$P4_12_12$	*C2/c*	*P2/c*	*C2/c*	$P2_1/c$
a, Å	9.4279(2)	16.9466(9)	17.8598(11)	13.6493(11)	12.6722(2)
b, Å	9.4279(2)	9.6814(5)	7.4112(5)	10.0133(6)	9.9937(2)
c, Å	25.1636(7)	13.3524(7)	17.6492(11)	18.0921(14)	17.2207(3)
α, deg.	90	90	90	90	90
β, deg.	90	108.691(2)	100.334(2)	111.399(4)	102.588(1)
γ, deg.	90	90	90	90	90
Volume, Å^3	2236.67(11)	2075.15(19)	2298.2(3)	2302.3(3)	2128.44(7)
Z	4	4	4	4	4
ρ_{calc}, g/cm^3	2.323	2.414	2.261	2.257	2.229
μ, mm^{-1}	4.81	5.18	4.68	4.67	5.04
F(000)	1448	1384	1448	1448	1320
Crystal size, mm	0.06 × 0.04 × 0.04	0.17 × 0.10 × 0.02	0.18 × 0.06 × 0.02	0.07 × 0.05 × 0.03	0.09 × 0.07 × 0.05
Θ range for data collection, deg.	2.307 to 31.516	2.457 to 30.538	2.318 to 31.581	2.418 to 30.552	1.647 to 33.153
Tmin, Tmax	0.640; 0.746	0.551; 0.746	0.551; 0.746	0.658; 0.747	0.609; 0.746
Index ranges	$-13 \le h \le 11$, $-13 \le k \le 9$, $-28 \le l \le 37$	$-21 \le h \le 24$, $-13 \le k \le 13$, $-18 \le l \le 19$	$-26 \le h \le 26$, $-10 \le k \le 10$, $-25 \le l \le 21$	$19 \le h \le 19$, $-14 \le k \le 14$, $-25 \le l \le 21$	$-19 \le h \le 19$, $-15 \le k \le 15$, $-26 \le l \le 26$
R_{int}	0.040	0.048	0.037	0.046	0.032
Reflections collected/independent	20945/3730	20758/3163	29958/7664	14647/3531	30325/8123
Reflections with I > 2σ(I)	3422	2627	5821	2923	6710
Data/restraints/parameters	3730/0/107	3163/72/151	7664/0/216	3531/69/171	8123/78/238
Goodness-of-fit on F^2	1.048	1.044	1.040	1.029	1.038
Final R indexes [I>=2σ (I)]	$R_1 = 0.0226$, $wR_2 = 0.0378$	$R_1 = 0.0249$, $wR_2 = 0.0431$	$R_1 = 0.0313$, $wR_2 = 0.0498$	$R_1 = 0.0303$, $wR_2 = 0.0546$	$R_1 = 0.0280$, $wR_2 = 0.0549$
Final R indexes [all data]	$R_1 = 0.0274$, $wR_2 = 0.0390$	$R_1 = 0.0376$, $wR_2 = 0.0454$	$R_1 = 0.0526$, $wR_2 = 0.0550$	$R_1 = 0.0418$, $wR_2 = 0.0578$	$R_1 = 0.0398$, $wR_2 = 0.0586$
Largest diff. peak/hole, e/Å^3	0.47/-0.77	0.50/-0.62	1.37/-1.13	0.64/-0.96	0.83/-1.60

Table S2. Selected bond lengths and angles for **1**.

Bond length, Å			
I1—I1^{i}	2.6917 (5)	Te1—Cl2	2.4900 (13)
Te1—Cl1^{i}	2.5486 (9)	Te1—Cl3^{i}	2.5310 (8)
Te1—Cl1	2.5486 (9)	Te1—Cl3	2.5309 (8)
Bond angle, (º)			
Cl1—Te1—Cl1^{i}	179.59 (5)	Cl3—Te1—Cl1^{i}	88.55 (3)
Cl1^{i}—Te1—Cl4	90.21 (2)	Cl3^{i}—Te1—Cl1	88.55 (3)
Cl1—Te1—Cl4	90.21 (2)	Cl3^{i}—Te1—Cl1^{i}	91.46 (3)
Cl2—Te1—Cl1	89.79 (2)	Cl3—Te1—Cl1	91.46 (3)
Cl2—Te1—Cl1^{i}	89.79 (2)	Cl3—Te1—Cl3^{i}	178.29 (5)
Cl2—Te1—Cl3^{i}	90.85 (2)	Cl3—Te1—Cl4	89.15 (2)
Cl2—Te1—Cl3	90.85 (2)	Cl3^{i}—Te1—Cl4	89.15 (2)
Cl2—Te1—Cl4	180.000 (14)		

Symmetry code(s): (i) y, x, −z+1.

Table S3. Selected bond lengths and angles for **2**.

Bond length, Å			
Te1—Cl1	2.4601 (7)	Te1—Cl3	2.6165 (7)
Te1—Cl1^{i}	2.4601 (7)	Te1—Cl3^{i}	2.6165 (7)
Te1—Cl2^{i}	2.5334 (7)	I1—I1^{ii}	2.6947 (3)
Te1—Cl2	2.5334 (7)		
Bond angle, (º)			
Cl1—Te1—Cl1^{i}	89.72 (4)	Cl1—Te1—Cl3	179.03 (3)
Cl1—Te1—Cl2^{i}	89.19 (3)	Cl2—Te1—Cl2^{i}	177.84 (4)
Cl1—Te1—Cl2	89.28 (3)	Cl2—Te1—Cl3^{i}	89.96 (3)
Cl1^{i}—Te1—Cl2^{i}	89.28 (3)	Cl2^{i}—Te1—Cl3^{i}	91.56 (3)
Cl1^{i}—Te1—Cl2	89.19 (3)	Cl2—Te1—Cl3	91.55 (3)
Cl1^{i}—Te1—Cl3	89.80 (3)	Cl2^{i}—Te1—Cl3	89.96 (3)
Cl1^{i}—Te1—Cl3^{i}	179.03 (3)	Cl3—Te1—Cl3^{i}	90.70 (4)
Cl1—Te1—Cl3^{i}	89.80 (3)		

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

Table S4. Selected bond lengths and angles for **3**.

Bond length, Å			
I1—I1^{i}	2.6991 (4)	Te1—Cl3	2.4525 (7)
I2—I2^{ii}	2.7018 (5)	Te1—Cl4	2.5145 (8)
Te1—Cl1	2.6282 (8)	Te1—Cl5	2.5381 (8)
Te1—Cl2	2.4250 (9)		
Bond angle, (º)			
Cl1—Te1—Cl6	88.26 (3)	Cl3—Te1—Cl4	88.66 (3)
Cl2—Te1—Cl1	92.47 (3)	Cl3—Te1—Cl5	90.01 (3)
Cl2—Te1—Cl3	92.21 (3)	Cl3—Te1—Cl6	87.36 (3)
Cl2—Te1—Cl4	90.60 (3)	Cl4—Te1—Cl1	88.54 (3)
Cl2—Te1—Cl5	87.54 (3)	Cl4—Te1—Cl5	177.68 (3)
Cl2—Te1—Cl6	174.23 (3)	Cl4—Te1—Cl6	95.14 (3)
Cl3—Te1—Cl1	174.57 (3)	Cl5—Te1—Cl1	92.94 (3)

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

Table S5. Selected bond lengths and angles for **4**.

Bond length, Å			
Te1—Cl1^{i}	2.5168 (8)	Te1—Cl3	2.7347 (8)
Te1—Cl1	2.5168 (8)	Te1—Cl3^{i}	2.7347 (8)
Te1—Cl2	2.4086 (8)	I2—I2^{ii}	2.7043 (4)
Te1—Cl2^{i}	2.4086 (8)		
Bond angle, (º)			
Cl1—Te1—Cl1^{i}	178.13 (4)	Cl2^{i}—Te1—Cl1	89.42 (3)
Cl1^{i}—Te1—Cl3^{i}	91.18 (3)	Cl2^{i}—Te1—Cl2	90.48 (4)
Cl1—Te1—Cl3^{i}	90.19 (3)	Cl2^{i}—Te1—Cl3	91.46 (3)
Cl1^{i}—Te1—Cl3	90.19 (3)	Cl2—Te1—Cl3	178.01 (3)
Cl1—Te1—Cl3	91.18 (3)	Cl2^{i}—Te1—Cl3^{i}	178.01 (3)
Cl2—Te1—Cl1	89.26 (3)	Cl2—Te1—Cl3^{i}	91.46 (3)
Cl2—Te1—Cl1^{i}	89.42 (3)	Cl3^{i}—Te1—Cl3	86.59 (4)
Cl2^{i}—Te1—Cl1^{i}	89.27 (3)		

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

Table S6. Selected bond lengths and angles for **5**.

Bond length, Å			
I1—I2	2.6939 (2)	Te1—Cl4	2.4455 (6)
Te1—Cl1	2.5153 (7)	Te1—Cl5	2.4076 (7)
Te1—Cl2	2.5155 (7)	Te1—Cl6	2.6494 (7)
Te1—Cl3	2.6772 (7)		
Bond angle, (º)			
Cl1—Te1—Cl2	179.56 (3)	Cl4—Te1—Cl6	179.52 (2)
Cl1—Te1—Cl3	93.43 (3)	Cl5—Te1—Cl1	89.93 (3)
Cl1—Te1—Cl6	88.55 (3)	Cl5—Te1—Cl2	89.69 (3)
Cl2—Te1—Cl3	86.95 (3)	Cl5—Te1—Cl3	176.27 (3)
Cl2—Te1—Cl6	91.22 (2)	Cl5—Te1—Cl4	91.49 (3)
Cl4—Te1—Cl1	91.08 (3)	Cl5—Te1—Cl6	88.81 (3)
Cl4—Te1—Cl2	89.15 (2)	Cl6—Te1—Cl3	92.89 (3)
Cl4—Te1—Cl3	86.84 (3)		

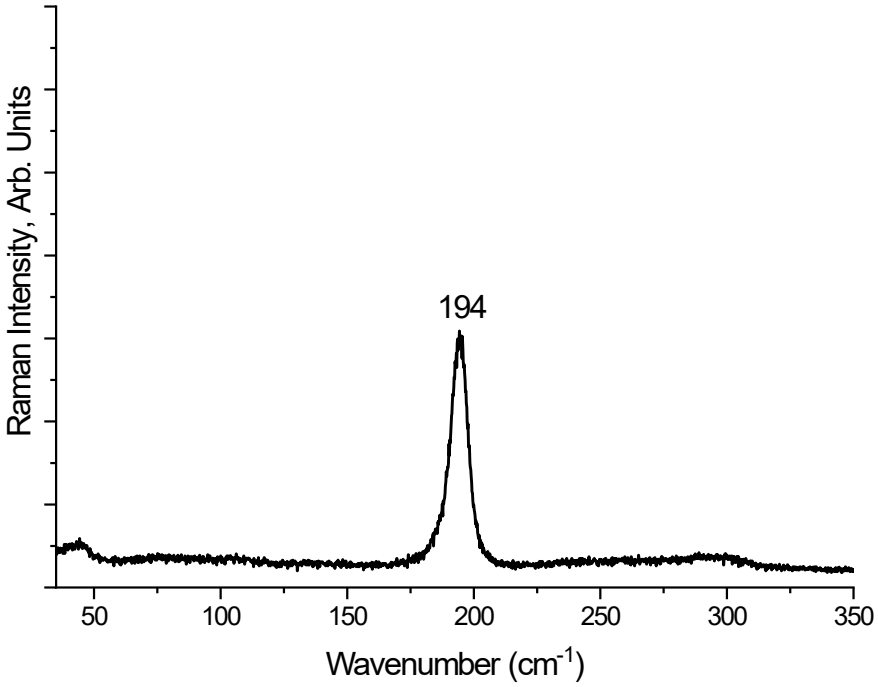

Figure S7. Raman spectrum of **2**.

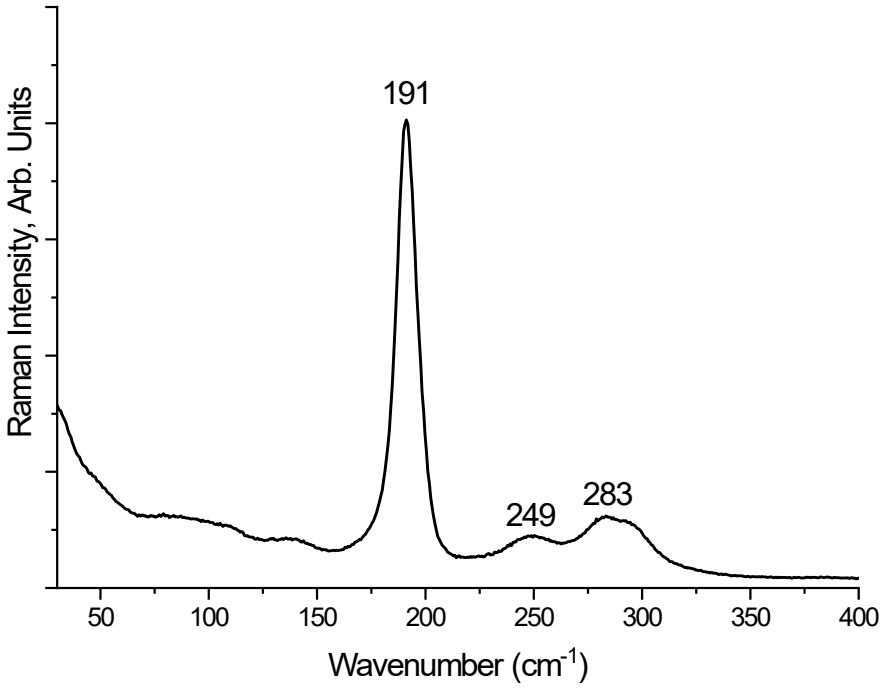

Figure S8. Raman spectrum of **3**.

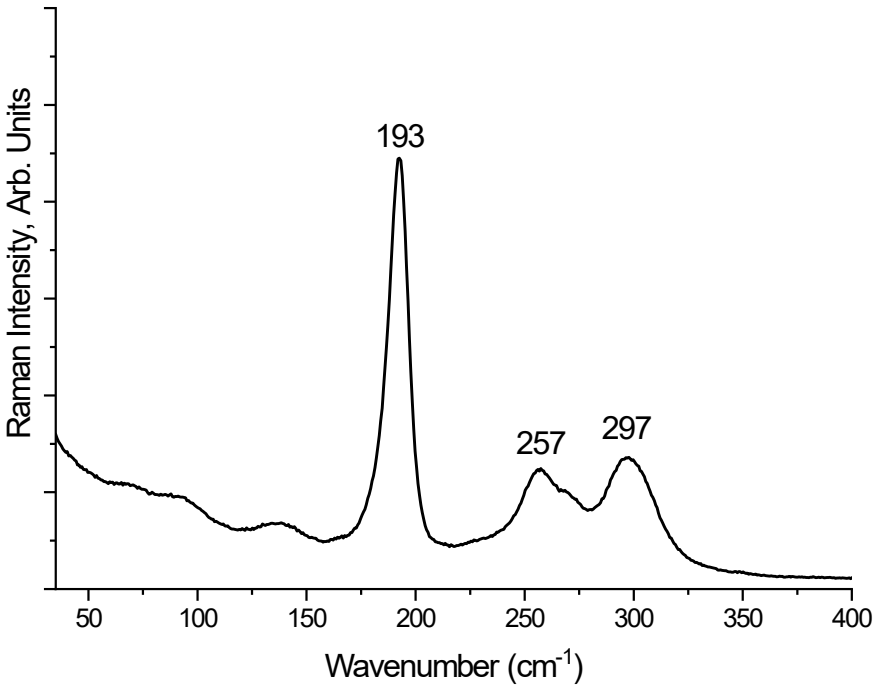

Figure S9. Raman spectrum of **4**.

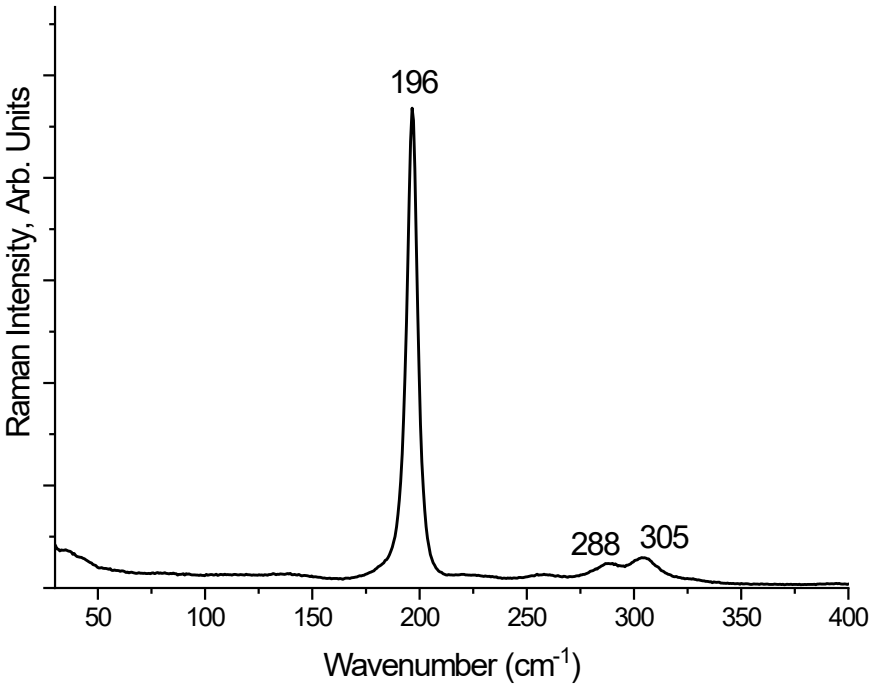

Figure S10. Raman spectrum of **5**.

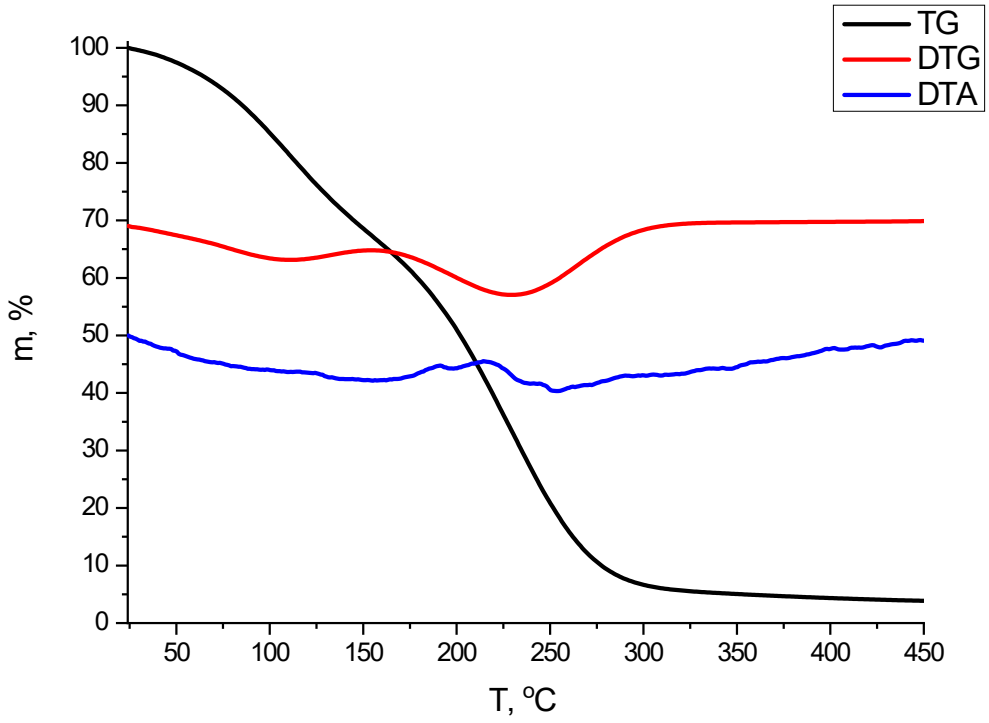

Figure S11. TG, DTG and DTA data for **2.**

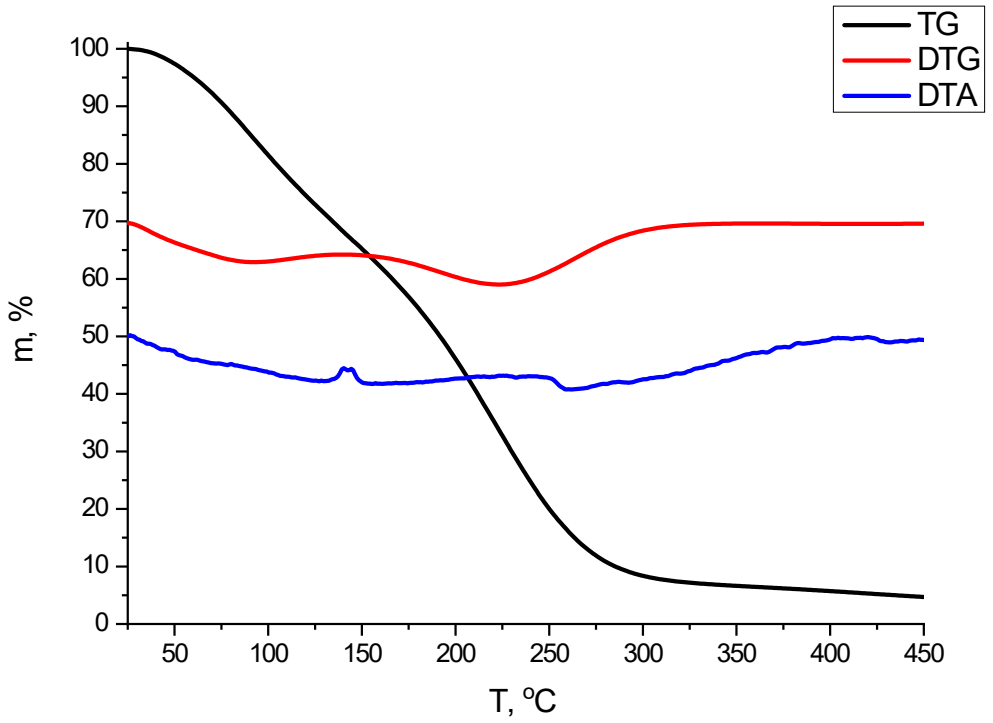

Figure S12. TG, DTG and DTA data for **3**.

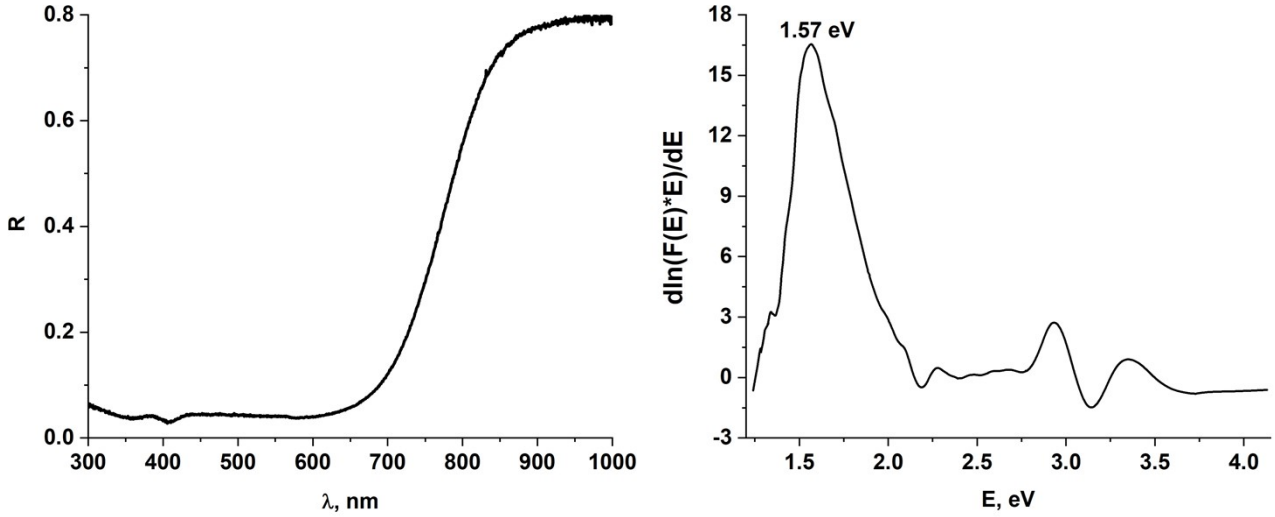

Figure S13. Diffuse reflectance spectra and optical band gap determination for **1**.

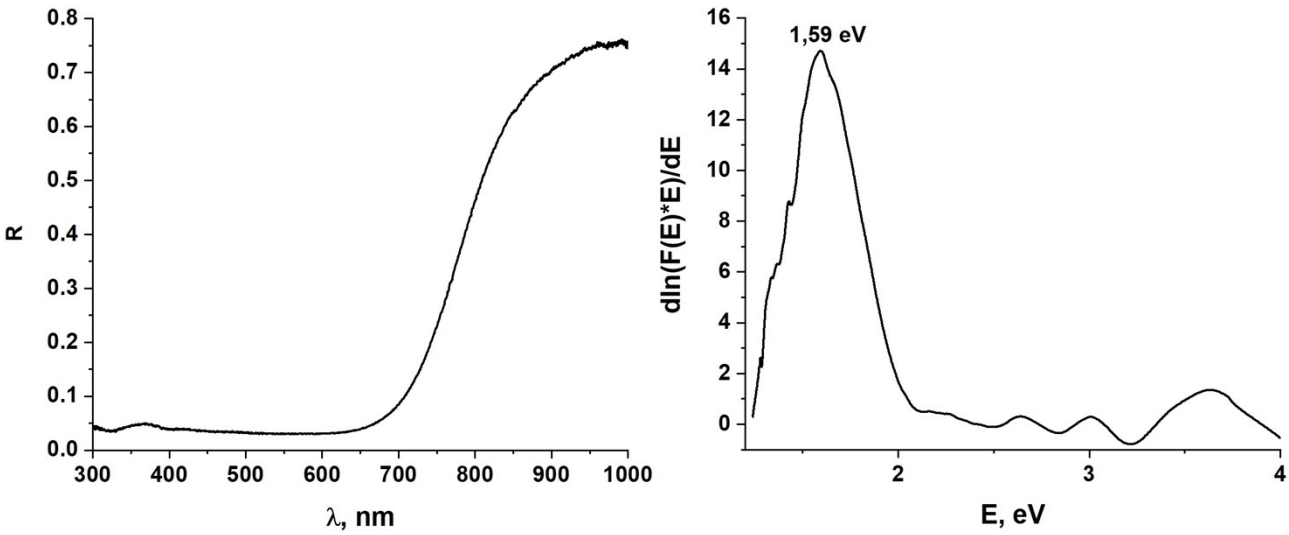

Figure S14. Diffuse reflectance spectra and optical band gap determination for **2**.

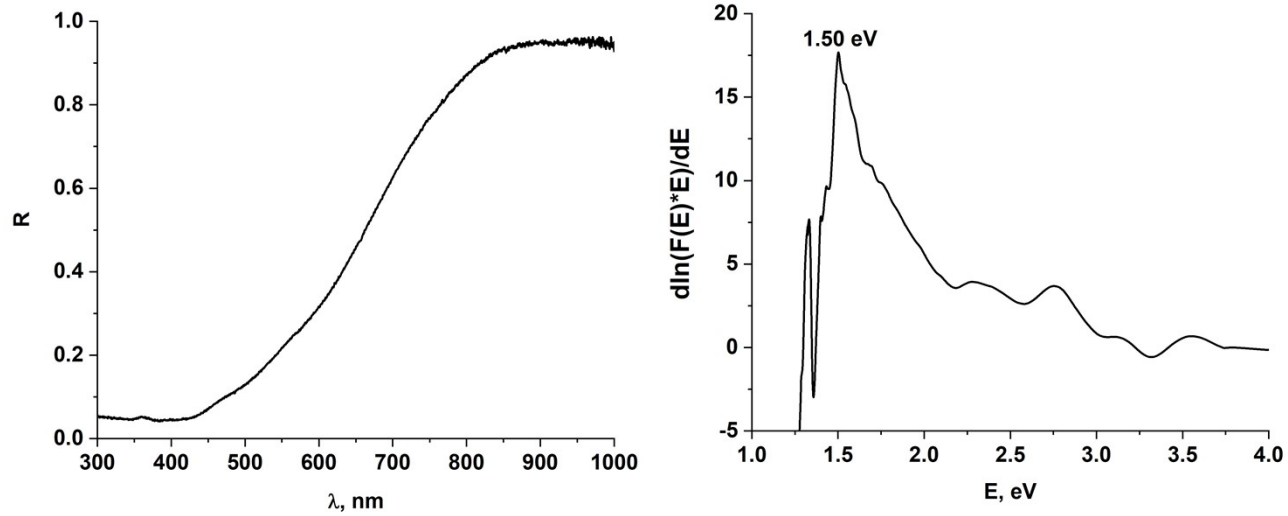

Figure S15. Diffuse reflectance spectra and optical band gap determination for **3**.

Table S7. 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 – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1), corresponding to various intermolecular interactions I···Cl in the X-ray structures **1**–**5**, and estimated strength for these interactions E_{int} (kcal/mol).

Contact*	$\%_{vdw\ sum}$	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}**
1								
I10···Cl6 3.823 Å (type I)	102	0.006	0.022	-0.006	0.001	-0.003	0.004	1.3
I1···Cl7 3.976 Å (type I)	107	0.005	0.017	-0.005	0.001	-0.002	0.003	0.9
I2···Cl7 3.976 Å (type I)	107	0.005	0.017	-0.005	0.001	-0.002	0.003	0.9
I12···Cl4 3.127 Å (type II)	84	0.021	0.049	-0.021	0.000	-0.012	0.012	5.1
2								
I2···Cl8 3.882 Å (type I)	104	0.006	0.020	-0.006	0.001	-0.003	0.004	1.3
I1···Cl8 3.961 Å (type I)	106	0.005	0.017	-0.005	0.001	-0.002	0.003	0.9
I11···Cl6 3.926 Å (type I)	105	0.005	0.019	-0.005	0.001	-0.003	0.004	1.3
I10···Cl6 4.024 Å (type I)	108	0.004	0.016	-0.004	0.001	-0.002	0.003	0.9
I12···Cl4 3.117 Å (type II)	84	0.019	0.044	-0.019	0.000	-0.011	0.011	4.7
3								
I1···Cl11 3.188 Å (type II)	85	0.019	0.045	-0.019	0.000	-0.011	0.011	4.7
I3···Cl6 3.190 Å (type II)	86	0.018	0.044	-0.018	0.000	-0.011	0.011	4.7
4								
I10···Cl5 3.937 Å (type I)	106	0.005	0.018	-0.005	0.001	-0.003	0.004	1.3

I8···Cl7 3.213 Å (type II)	86	0.018	0.041	-0.018	0.000	-0.010	0.010	4.3
5								
I10···Cl5 3.741 Å (type I)	100	0.008	0.027	-0.008	0.001	-0.004	0.005	1.7
I17···Cl4 3.913 Å (type I)	105	0.005	0.019	-0.005	0.001	-0.003	0.004	1.3
I16···Cl4 4.193 Å (type I)	112	0.003	0.011	-0.003	0.001	-0.001	0.002	0.4
I1···Cl8 3.723 Å (type I)	100	0.008	0.027	-0.008	0.001	-0.004	0.005	1.7
I19···Cl7 3.825 Å (type I)	103	0.006	0.022	-0.006	0.001	-0.003	0.004	1.3
I12···Cl6 3.004 Å (type II)	81	0.026	0.056	-0.026	0.000	-0.017	0.017	7.3
I15···Cl9 3.126 Å (type II)	84	0.021	0.048	-0.021	0.000	-0.012	0.012	5.1

* Two types of short contacts involving halogen atoms usually discussed in the literature. Type I is believed to depend on the effects of crystal packing, while type II is due to a classic halogen bonding, see [Chem. Rev. 2016, 116, 2478.] for details. The Bondi's (shortest) van der Waals radii for iodine and chlorine atoms are 1.98 and 1.75 Å, respectively [J. Phys. Chem. 1966, 70, 3006.]. The numeration of atoms corresponds to their ordering in attached xyz-files for model supramolecular associates.

** $E_{int} = 0.68(-V(\mathbf{r}))$ (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 iodine atoms) [Russ. Chem. Rev. 2014, 83, 1181.]

Table S8. Cartesian atomic coordinates for model supramolecular associates.

Atom	X	Y	Z
1			
I	2.497451	0.676169	12.190758
I	0.676169	2.497451	12.972842
Te	6.043284	6.043284	12.581800
Cl	4.398021	7.701463	11.562423
Cl	7.803944	7.803944	12.581800
Cl	5.342697	6.690509	14.926041
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Cl	7.701463	4.398021	13.601177
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I	11.163206	3.457131	6.947911
Te	7.403558	6.595551	3.162051
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I	-1.574635	2.998127	3.241655
I	7.101740	5.220449	5.206963
I	9.175050	5.220449	3.474492
Te	2.823996	5.771843	9.070730
Cl	4.724081	5.791482	7.254918
Cl	3.775162	7.672964	10.237518
Cl	0.909794	5.669716	10.600576
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Cl	4.155657	4.283155	10.636691
Cl	1.891511	3.495122	7.951344
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Te	5.174377	5.679744	4.211218
Cl	2.983211	5.720899	2.973793
Cl	4.330596	7.375697	5.698788
Cl	6.117185	3.689400	2.590067
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Cl	6.018157	7.375697	2.723647
Cl	4.231569	3.689400	5.832368
I	3.793250	1.069020	7.639486
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I	10.079607	3.937630	9.205385
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I	0.542485	6.294432	11.192459
I	0.958458	8.489948	9.687750
Te	1.869525	3.015299	6.300181
Cl	4.367128	2.960434	6.593963
Cl	-0.630126	3.074162	6.025222
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Cl	1.701235	4.649169	8.060520

Cl	1.680206	1.107202	8.128588
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I	2.419015	-1.297582	2.789081
I	2.834988	-3.493098	1.284372
I	0.542485	-3.699268	11.192459
I	0.958458	-1.503752	9.687750
I	8.376656	3.699268	5.614297
I	7.960683	1.503752	7.119006
I	2.419015	8.696118	2.789081
I	2.834988	6.500602	1.284372