Supplementary materials

New Journal of Chemistry

Unusual isostructural Br/I substitution effect on the crystal structure and optical properties of hybrid halobismuthates

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Table of content

Table S1. Crystal data and structure refinement for **2-5**.

Identification code	**2**	**3**	**4**	**5**
Empirical formula	$C_{14}H_{18}BiBr_{4.39}I_{0.61}N_2$	$C_{14}H_{18}BiBr_{4.06}I_{0.94}N_2$	$C_{14}H_{18}BiBr_{3.78}I_{1.22}N_2$	$C_{14}H_{18}BiBr_{3.41}I_{1.59}N_2$
Formula weight	851.61	867.12	880.04	897.43
Temperature, K	100	100	140	100
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	12.0767(8)	12.1086(4)	12.168(3)	12.1996(7)
b, Å	11.5480(9)	11.5295(4)	11.602(3)	11.5845(8)
c, Å	14.9324(10)	15.0033(6)	15.055(4)	15.0730(11)
α, °	90	90	90	90
β, °	92.349(3)	92.440(2)	92.439(6)	92.533(5)
γ, °	90	90	90	90
Volume, $Å^3$	2080.7(3)	2092.65(13)	2123.5(9)	2128.1(2)
Z	4	4	4	4
D (calc), mg/m^3	2.719	2.752	2.753	2.801
μ, mm^{-1}	17.805	17.561	17.188	16.993
F(000)	1540	1564	1584	1610
Crystal size, mm	0.002 × 0.01 × 0.05	0.004 x 0.015 x 0.09	0.01 x 0.02 x 0.12	0.004 x 0.015 x 0.10
θ range, °	2.127, 26.012	2.118, 27.102	2.109, 26.068	2.103, 26.022
Index ranges	$-14 \le h \le 14$ $-12 \le k \le 14$ $-18 \le l \le 18$	$-15 \le h \le 15$ $-14 \le k \le 14$ $-11 \le l \le 19$	$-13 \le h \le 15$ $-14 \le k \le 14$ $-18 \le l \le 18$	$-15 \le h \le 15$ $-13 \le k \le 14$ $-13 \le l \le 18$
Reflections collected	14073	16052	12550	15210
Independent reflections, R_{int}	4091, 0.0590	4621, 0.0588	4189, 0.0962	4193, 0.0733
Completeness to θ = 25.242°	99.8 %	100 %	99.9 %	100 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	0.0955, 0.0575	0.0473, 0.0196	0.0192, 0.0037	0.0210, 0.0043
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4091 / 8 / 217	4621 / 2 / 213	4189 / 1 / 214	4193 / 8 / 213
Goodness-of-fit	1.092	1.025	0.914	1.007
R1, wR2 [I>2sigma(I)]	0.0386, 0.0574	0.0386, 0.0780	0.0472, 0.0892	0.0564, 0.1334
R1, wR2 (all data)	0.0543, 0.0609	0.0608, 0.0852	0.1076, 0.1061	0.0853, 0.1487
Largest diff. peak and hole, $e.Å^{-3}$	1.177, -1.193	1.757, -1.176	1.129, -1.284	2.439, -1.623

Table S2. Details of Powley refinement of PXRD profiles of 1-10 solid solutions.

Compound	a, Å	b, Å	c, Å	β, °	V, Å3	R-Bragg, %	R_{exp}, %	R_{wp}, %	R_p, %	GOF, %
1	12.0626(1)	11.6717(2)	14.9214(1)	92.0631(6)	2099.42(4)	0.133	2.65	3.56	2.52	1.35
2	12.1262(3)	11.6614(3)	15.0264(3)	92.1605(15)	2123.35(9)	0.203	2.65	4.08	2.96	1.54
3	12.1803(17)	11.6713(16)	15.1184(15)	92.261(6)	2147.6(5)	0.369	2.22	4.59	3.26	2.07
4	12.2390(19)	11.6992(18)	15.2016(18)	92.291(6)	2174.9(5)	0.228	2.26	4.07	3.03	1.80
5	12.2913(18)	11.7415(17)	15.2611(17)	92.274(6)	2200.7(5)	0.129	2.38	3.45	2.65	1.45
6	12.2875(5)	11.7337(5)	15.2639(5)	92.286(2)	2198.97(15)	0.140	2.78	3.74	2.95	1.34
7	12.3515(5)	11.7946(6)	15.3236(7)	92.283(3)	2230.59(17)	0.157	2.84	4.26	3.30	1.50
8	12.3766(6)	11.8336(7)	15.3452(8)	92.275(4)	2245.7(2)	0.169	2.98	4.44	3.44	1.49
9	12.4009(5)	11.8825(6)	15.3489(6)	92.317(3)	2259.86(17)	0.162	2.92	4.11	3.01	1.41
10	12.6440(3)	12.3105(3)	15.3812(3)	92.6824(12)	2391.52(9)	0.146	3.59	3.99	3.02	1.11

Table S3. The occupancy of different type halogen positions in the crystal structures of mixed hybrid bromo/iodobismuthates.

Refcode	Anion	Iodine content		
		bridge	term/bridge	term/term
CEHSIT	BiX_5	1	-	0.50
COXZEX	BiX_4	0.91	0.71	-
JAJFAC	BiX_5	0.00	0.71	0.14
EGEGUV	Bi_2X_9	0.48	0.40	-
TOVFAO	Bi_2X_9	0.44	0.28	-
	Bi_2X_9	0.19	0.27	-
TOVFES	Bi_2X_9	0.34	0.29	-
TOVFIW	Bi_2X_9	0.31	0.24	-
TOVFOC	Bi_2X_{10}	0.13	0.32	0.27

Table S4. CHN elemental analysis of 1-10. The molar fraction of iodine ($I_{CHN} = \frac{I,\%}{I,\% + Br,\%}$) was calculated on CHN carbon atoms concentration.

Solid solution	Molecular mass	Calculated			Experimental			I_{CHN}, %	I_{EDX}, %
		C	N	H	C	N	H		
1	1648.43	0.2040	0.0340	0.0220	0.2035	0.0339	0.0228	1.3	0.6
2	1690.73	0.1989	0.0331	0.0215	0.1990	0.0326	0.0212	9.2	9.6
3	1740.55	0.1932	0.0322	0.0208	0.1936	0.0316	0.0216	19.3	20.2
4	1772.51	0.1897	0.0316	0.0205	0.1893	0.0313	0.0219	27.7	27.0
5	1844.43	0.1823	0.0304	0.0197	0.1825	0.0304	0.0196	41.7	42.3
6	1824.22	0.1844	0.0307	0.0199	0.1843	0.0310	0.0191	37.9	38.0
7	1881.56	0.1787	0.0298	0.0193	0.1774	0.0301	0.0193	53.0	50.2
8	1906.94	0.1764	0.0294	0.0190	0.1734	0.0298	0.0189	62.3	55.6
9	1926.68	0.1745	0.0291	0.0188	0.1677	0.0283	0.0167	76.3	59.8
10	2110.45	0.1593	0.0265	0.0172	0.1608	0.0261	0.0166	94.7	98.9

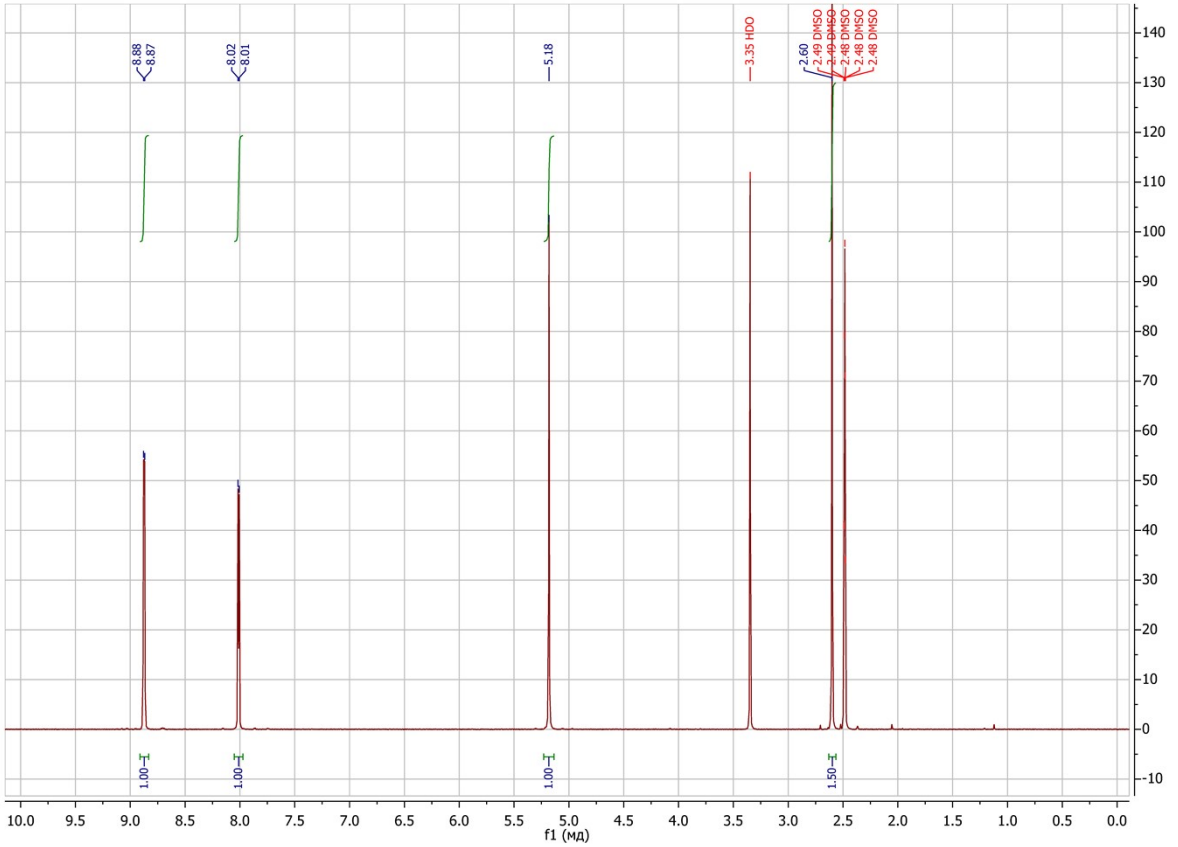


Fig. S1. ^{1}H NMR spectra of [4-Pi_2C_2]Br_2.

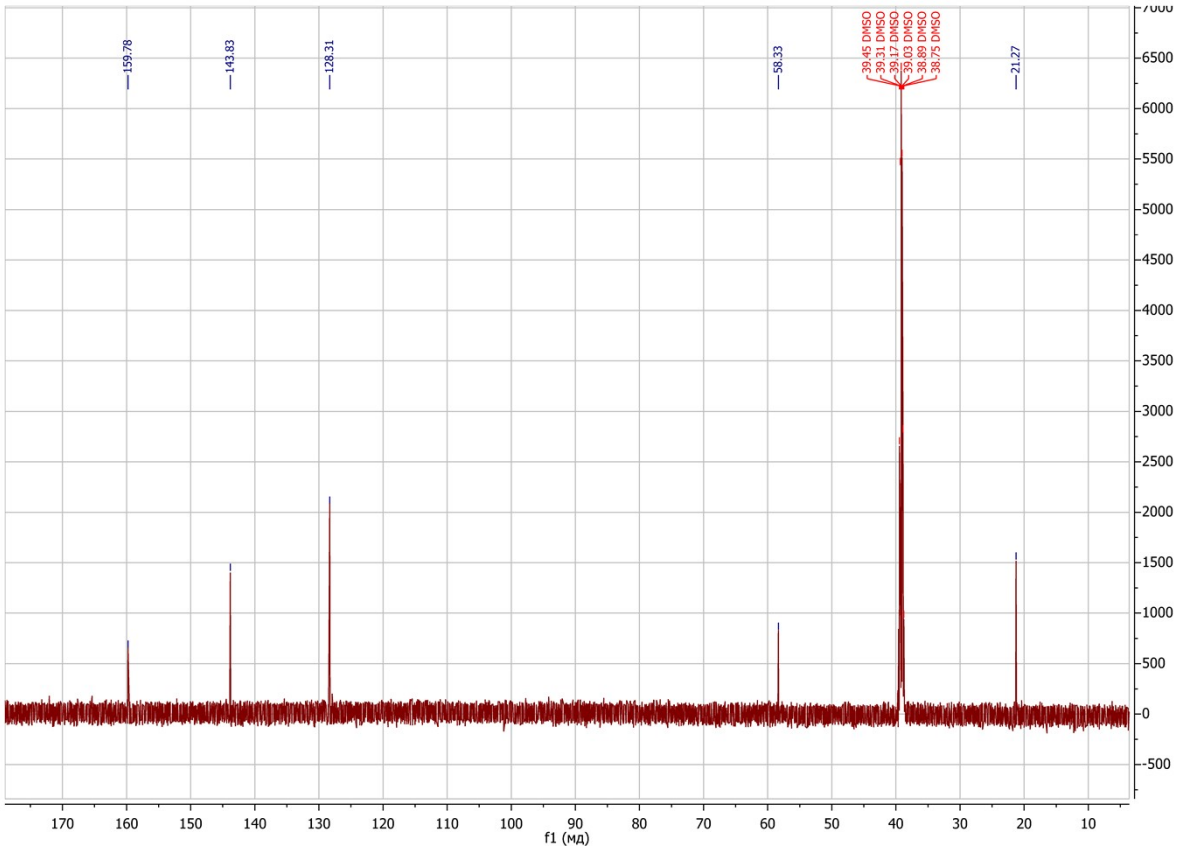
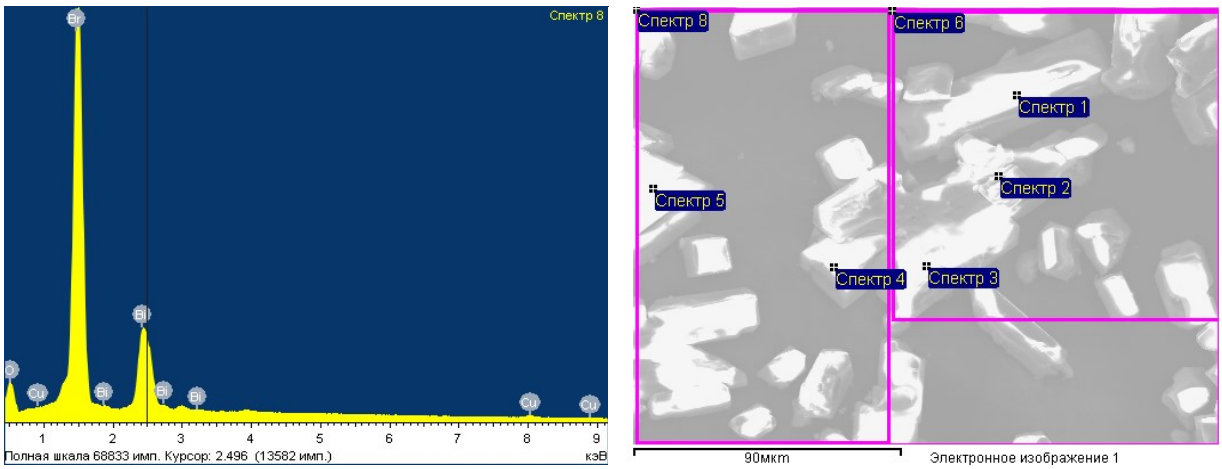
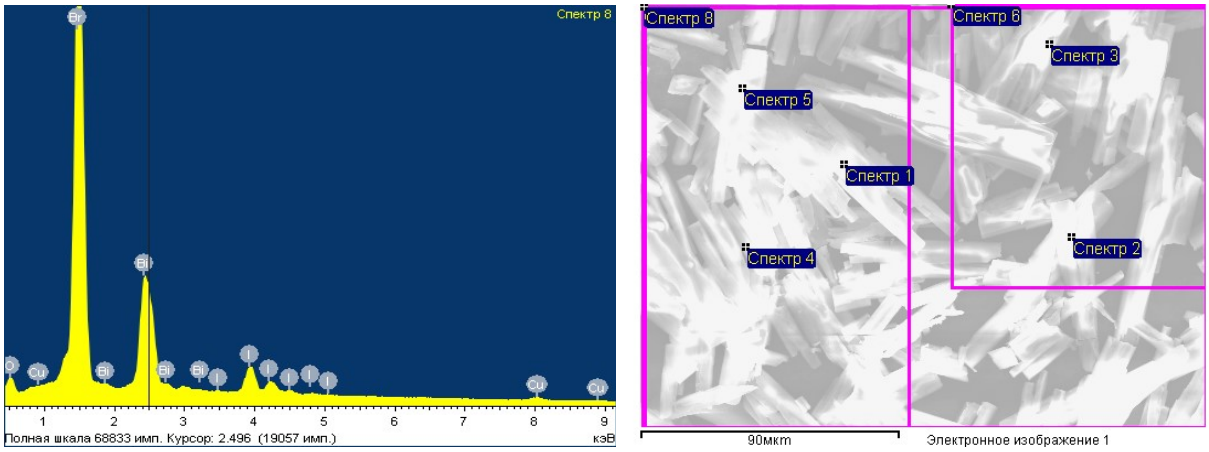


Fig. S2. ^{13}C NMR spectra of [4-Pi_2C_2]Br_2.



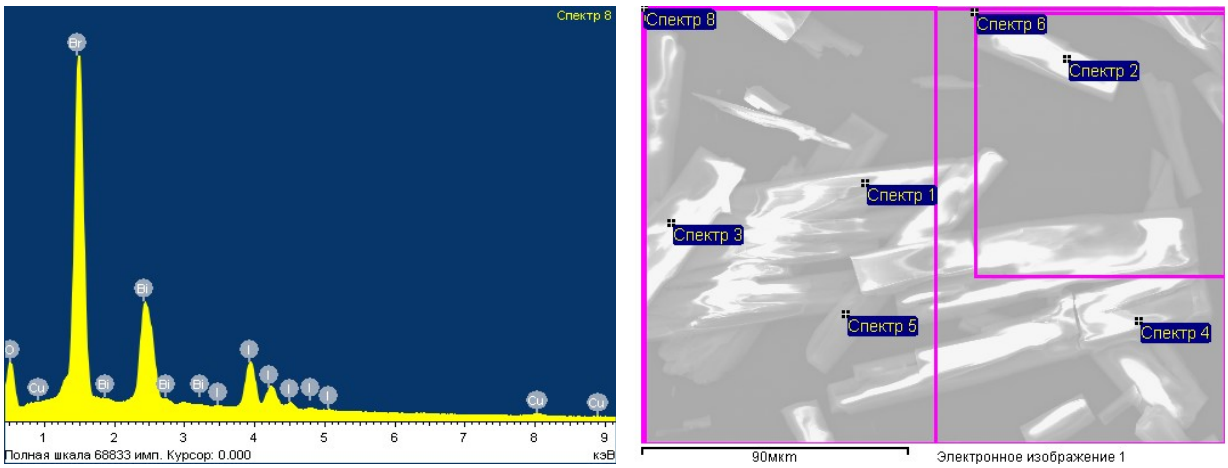
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	79.52	16.87	0.12	3.49
Spectrum 2	81.15	15.65	0.10	3.11
Spectrum 3	78.50	17.92	0.11	3.48
Spectrum 4	78.03	18.04	0.13	3.80
Spectrum 5	78.64	17.57	0.12	3.67
Spectrum 6	94.92	4.31	0.02	0.75
Spectrum 7	96.77	2.75	0.02	0.46
Spectrum 8	**96.07**	**3.34**	**0.02**	**0.57**

Fig. S3. EDX spectra of solid solution **1**.



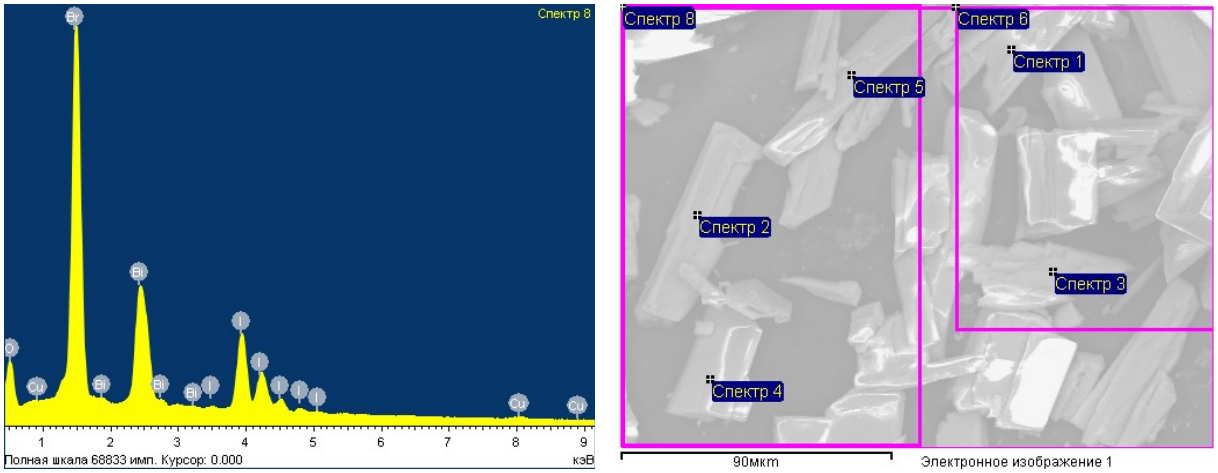
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	89.33	8.02	0.93	1.72
Spectrum 2	75.22	18.06	2.52	4.21
Spectrum 3	74.92	18.15	2.65	4.29
Spectrum 4	64.48	26.85	2.80	5.86
Spectrum 5	78.98	16.08	1.47	3.47
Spectrum 6	92.66	5.59	0.61	1.14
Spectrum 7	91.71	6.32	0.67	1.29
Spectrum 8	**93.23**	**5.16**	**0.55**	**1.05**

Fig. S4. EDX spectra of solid solution **2**.



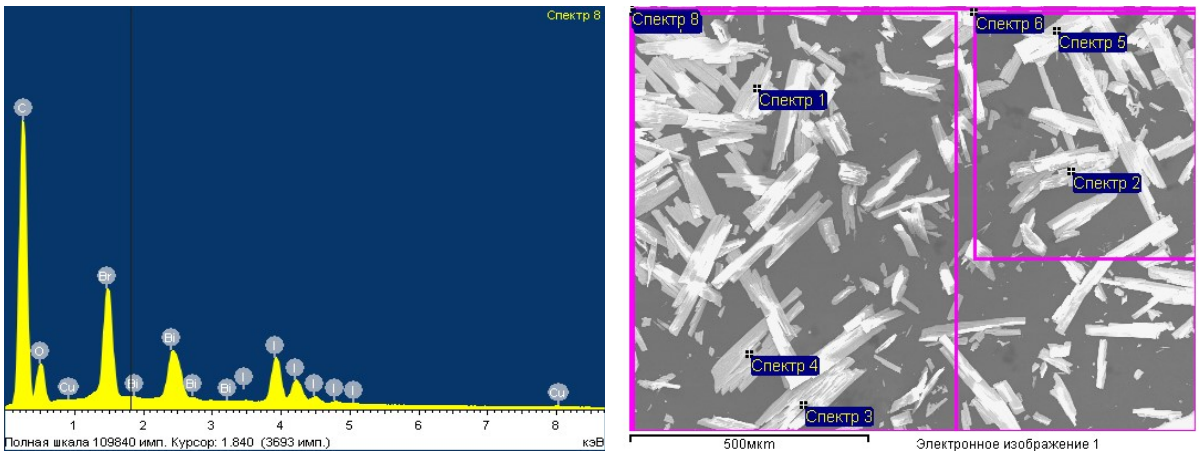
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	78.24	14.89	3.12	3.75
Spectrum 2	84.53	10.08	2.64	2.75
Spectrum 3	81.13	12.93	2.67	3.27
Spectrum 4	79.90	14.02	2.57	3.51
Spectrum 5	76.32	16.07	3.49	4.13
Spectrum 6	96.80	2.15	0.56	0.49
Spectrum 7	96.05	2.71	0.64	0.61
Spectrum 8	**96.21**	**2.56**	**0.65**	**0.58**

Fig. S5. EDX spectra of solid solution **3**.



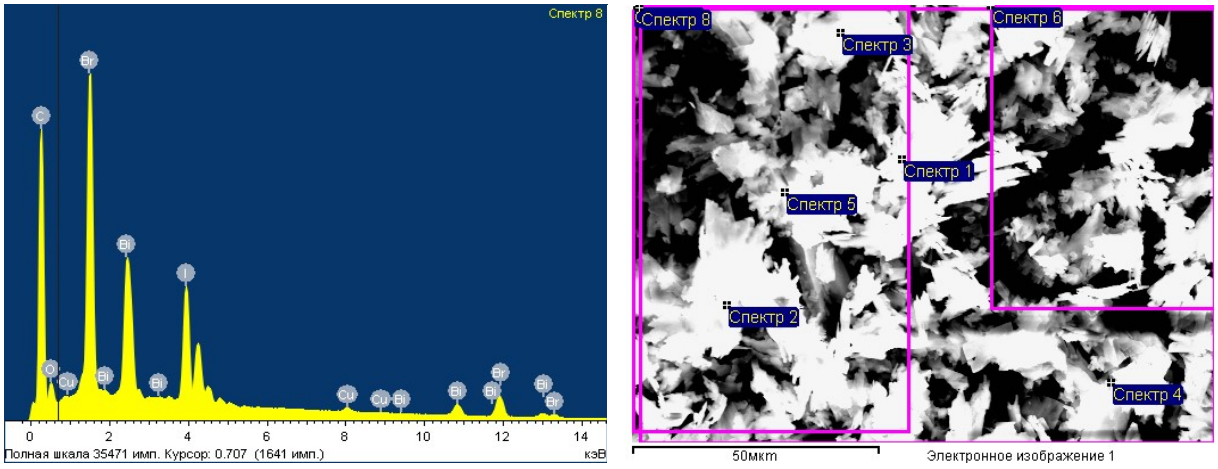
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	86.82	8.06	2.93	2.19
Spectrum 2	80.05	12.62	3.99	3.34
Spectrum 3	79.02	12.86	4.48	3.64
Spectrum 4	81.35	10.67	4.79	3.20
Spectrum 5	81.56	11.62	3.96	2.87
Spectrum 6	91.94	5.02	1.81	1.23
Spectrum 7	96.31	2.28	0.88	0.53
Spectrum 8	**94.81**	**3.22**	**1.19**	**0.78**

Fig. S6. EDX spectra of solid solution **4**.



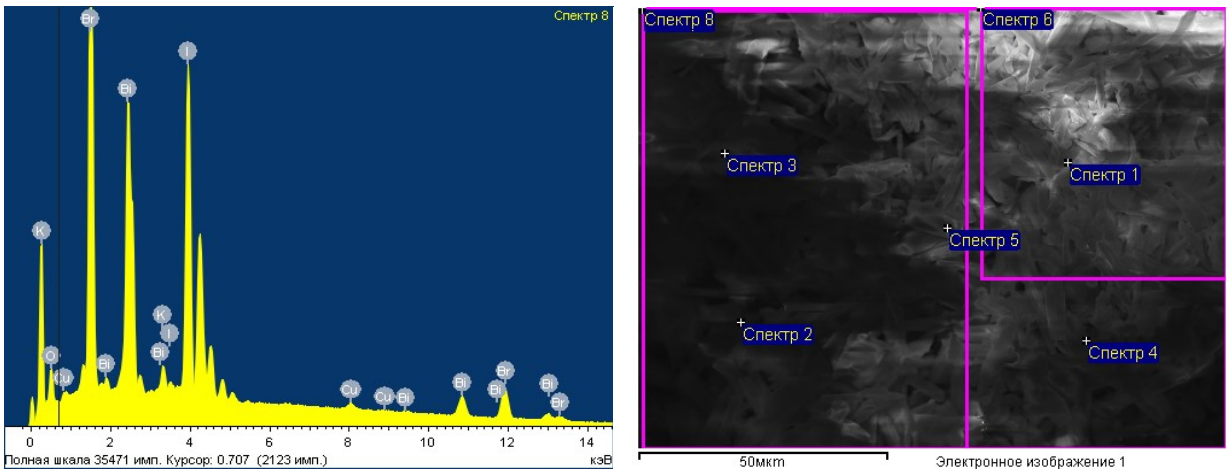
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	78.52	12.82	4.99	3.67
Spectrum 2	70.72	14.22	9.99	5.08
Spectrum 3	83.34	9.21	4.34	3.11
Spectrum 4	72.85	14.02	8.24	4.88
Spectrum 5	79.80	10.73	5.94	3.52
Spectrum 6	96.38	1.77	1.27	0.57
Spectrum 7	96.13	1.87	1.38	0.62
Spectrum 8	**96.43**	**1.73**	**1.27**	**0.57**

Fig. S7. EDX spectra of solid solution **5**.



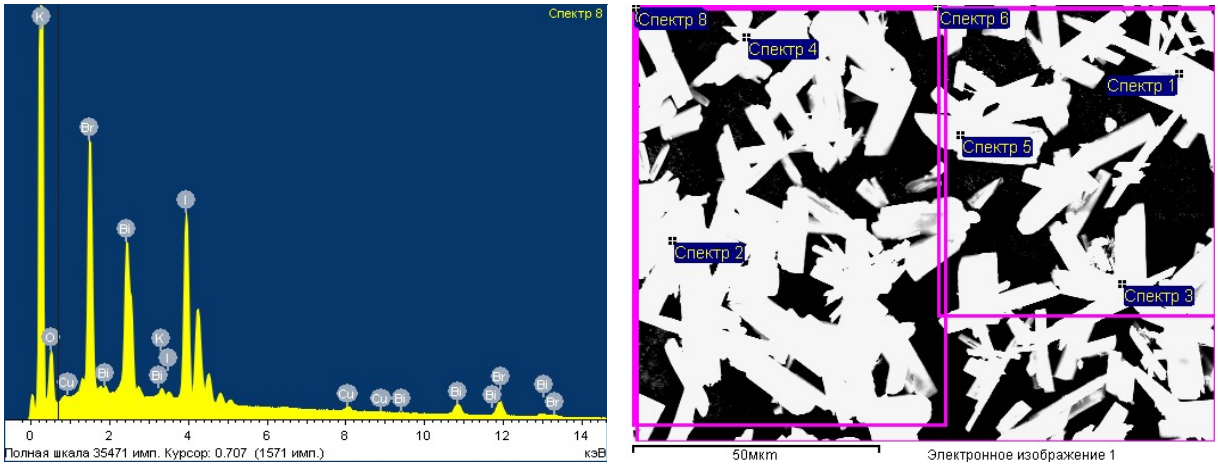
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	88.59	6.22	3.32	1.86
Spectrum 2	88.40	6.01	3.64	1.95
Spectrum 3	93.10	4.00	1.85	1.05
Spectrum 4	89.78	5.46	3.07	1.69
Spectrum 5	83.12	9.64	4.10	3.14
Spectrum 6	94.24	2.87	1.97	0.91
Spectrum 7	93.38	3.51	2.05	1.06
Spectrum 8	**92.76**	**3.77**	**2.31**	**1.16**

Fig. S8. EDX spectra of solid solution **6**.



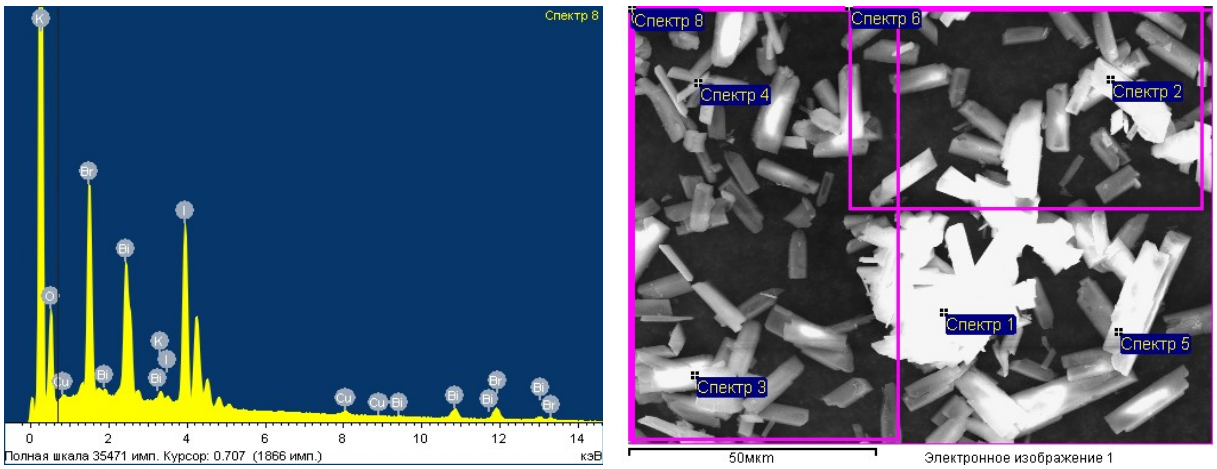
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	71.95	11.44	11.96	4.66
Spectrum 2	38.00	20.03	31.52	10.45
Spectrum 3	54.54	13.76	24.22	7.47
Spectrum 4	13.38	10.29	65.32	11.00
Spectrum 5	32.91	15.75	41.19	10.15
Spectrum 6	75.86	9.66	10.42	4.05
Spectrum 7	75.39	10.46	10.08	4.07
Spectrum 8	**75.31**	**10.25**	**10.32**	**4.12**

Fig. S9. EDX spectra of solid solution **7**.



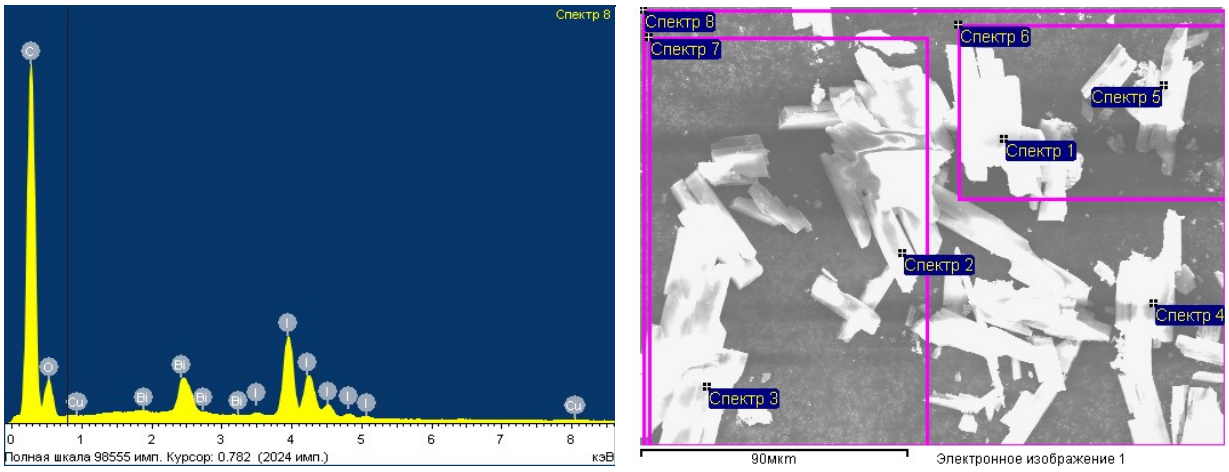
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	96.25	2.20	1.02	0.53
Spectrum 2	92.04	2.58	4.19	1.20
Spectrum 3	92.32	2.20	4.23	1.24
Spectrum 4	92.24	2.89	3.49	1.37
Spectrum 5	83.87	6.14	7.21	2.78
Spectrum 6	95.05	1.87	2.29	0.79
Spectrum 7	92.50	2.75	3.55	1.21
Spectrum 8	**94.06**	**2.21**	**2.77**	**0.95**

Fig. S10. EDX spectra of solid solution **8**.



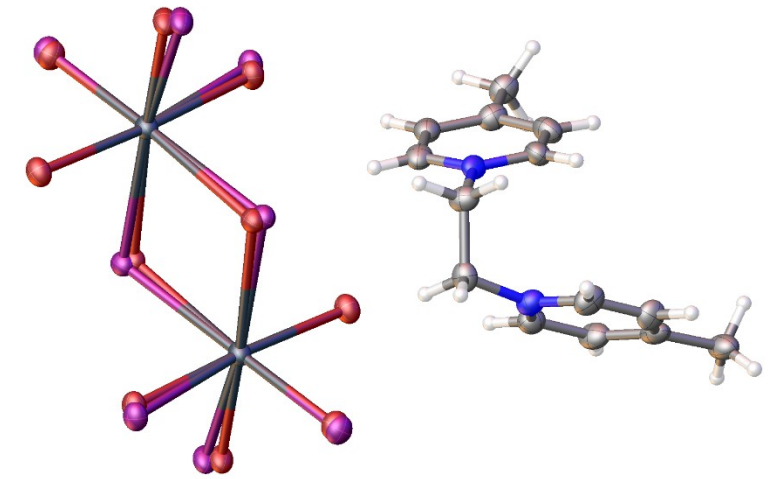
Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	89.07	3.09	6.08	1.76
Spectrum 2	84.39	4.64	7.85	3.12
Spectrum 3	82.36	6.60	8.14	2.89
Spectrum 4	92.98	2.74	3.09	1.19
Spectrum 5	83.21	6.25	7.54	3.00
Spectrum 6	96.83	1.05	1.63	0.49
Spectrum 7	96.45	1.27	1.73	0.55
Spectrum 8	**95.95**	**1.37**	**2.04**	**0.64**

Fig. S11. EDX spectra of solid solution **9**.

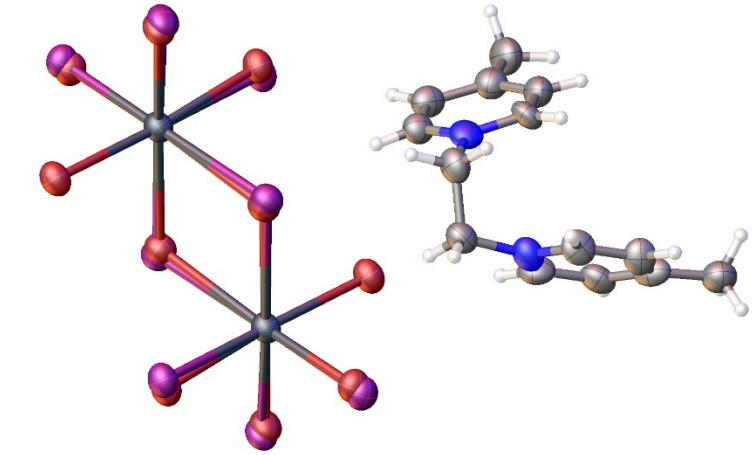


Spectra	C, at%	Br, at%	I, at%	Bi, at%
Spectrum 1	99.87	0.01	0.10	0.02
Spectrum 2	98.78	0.02	1.00	0.19
Spectrum 3	83.38	0.15	13.51	2.97
Spectrum 4	88.59	0.09	9.73	1.58
Spectrum 5	84.60	0.12	12.38	2.89
Spectrum 6	98.14	0.02	1.56	0.29
Spectrum 7	95.95	0.03	3.40	0.62
Spectrum 8	**96.70**	**0.03**	**2.78**	**0.49**

Fig. S12. EDX spectra of solid solution **10**.



a



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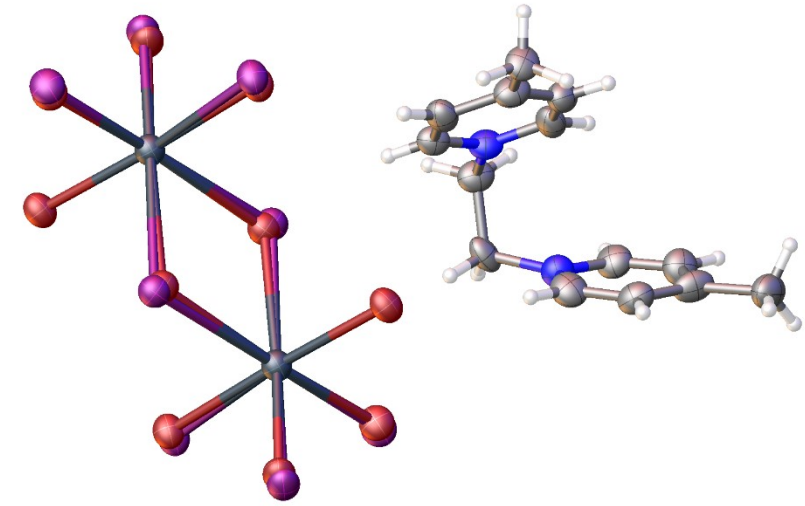


c

Fig. S13. Fragments of crystal structures **3** (a), **4** (b) and **5** (c).

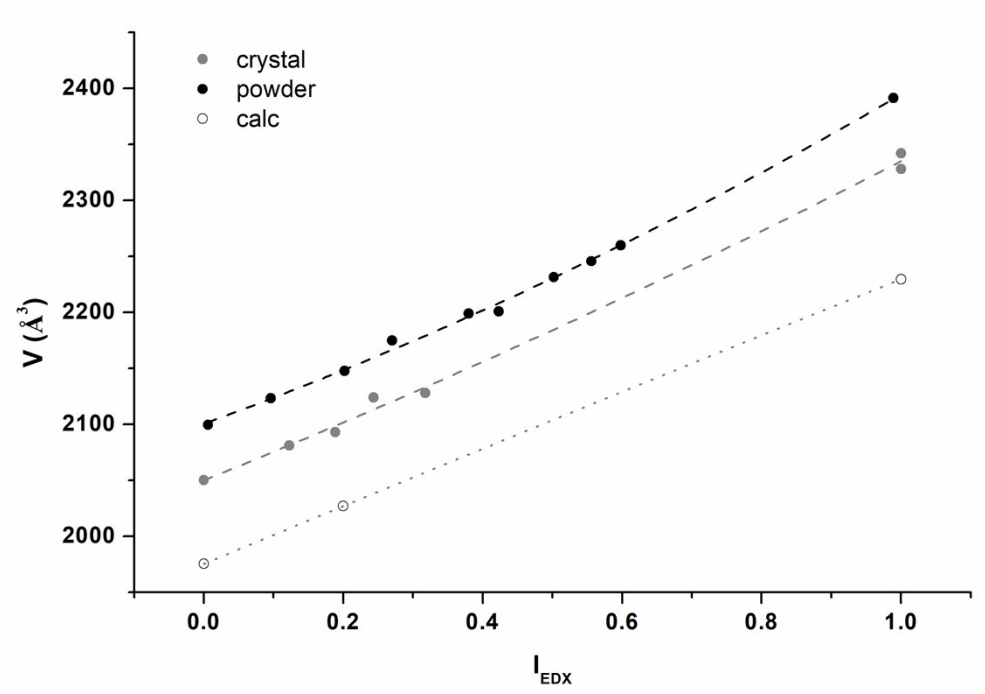
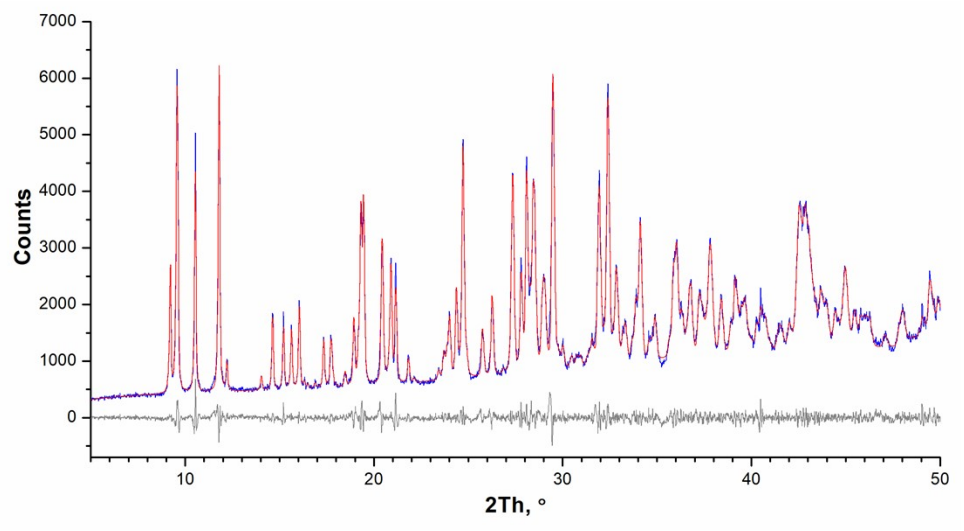


Fig. S14. Dependence of crystal unit cell volume on the composition of the $[4\text{-}Pi_2C_2]_2[Bi_2Br_{10-x}I_x]$ solid solutions. The difference in the volume values for different methods is due to the different temperature of the experiments (PXRD (powder) – RT, XRD (crystal) – 100-140K, calculation – 0K). Fitting curves are shown for visual convenience and have no physical sense.



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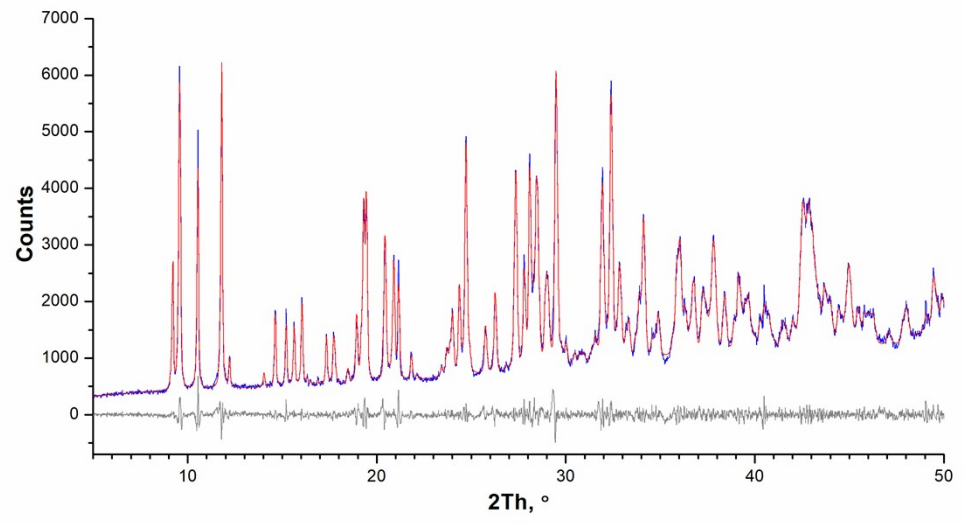

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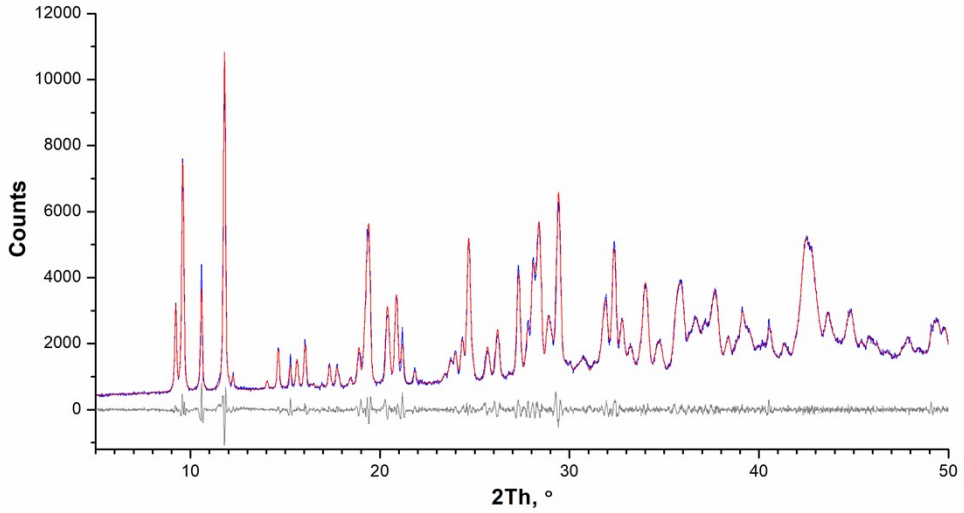

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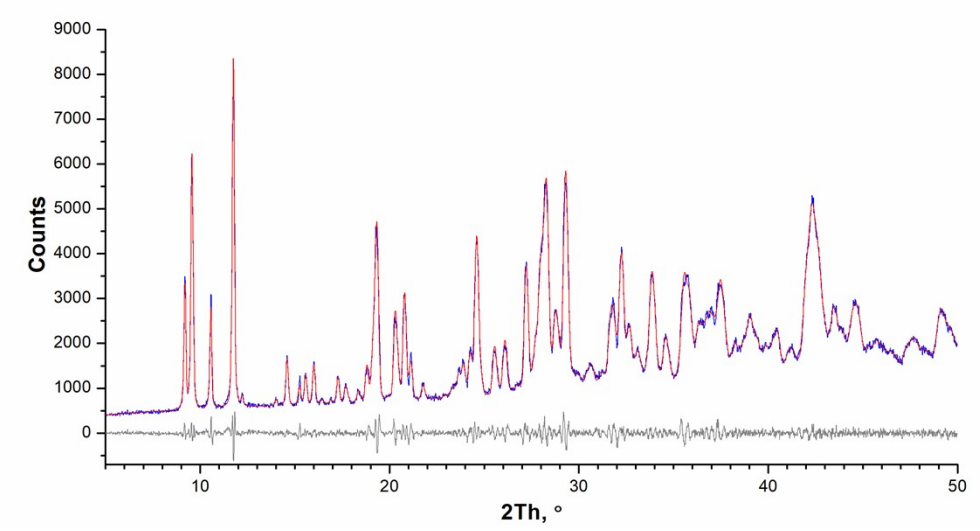
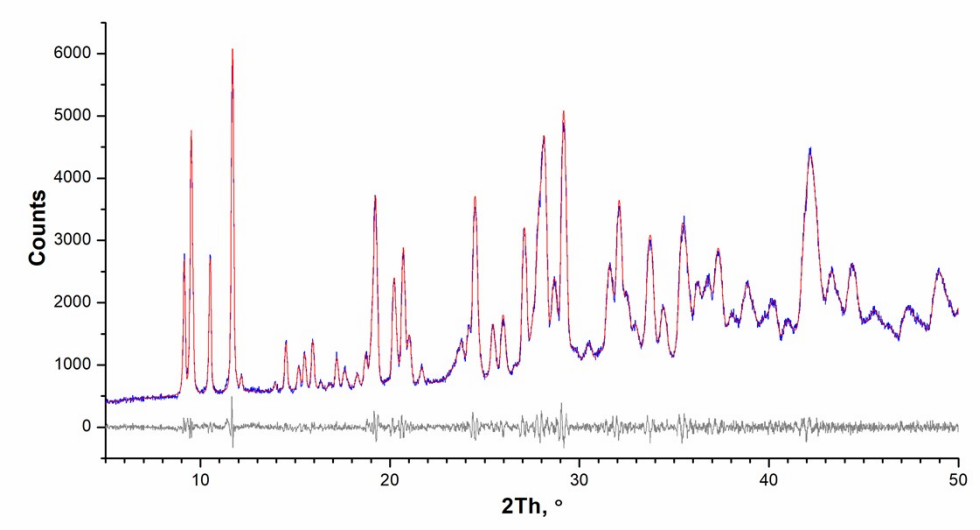
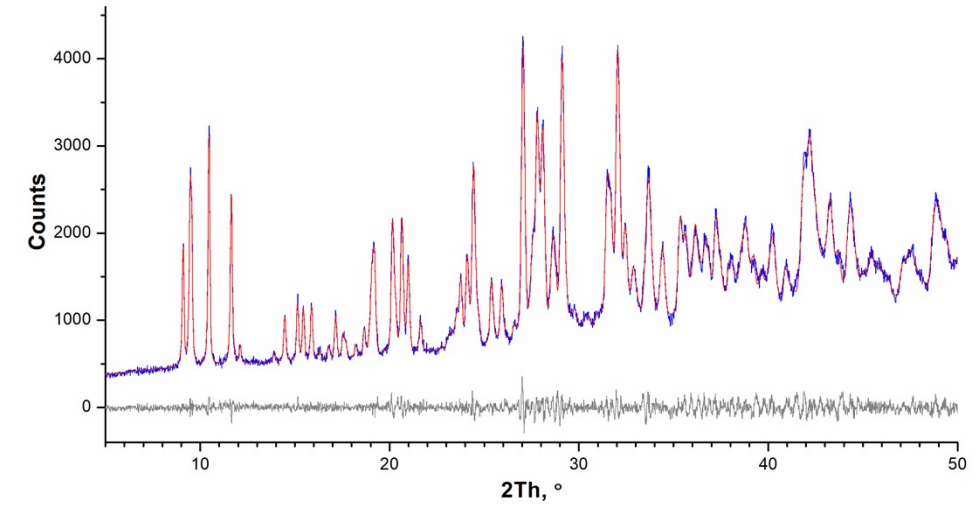


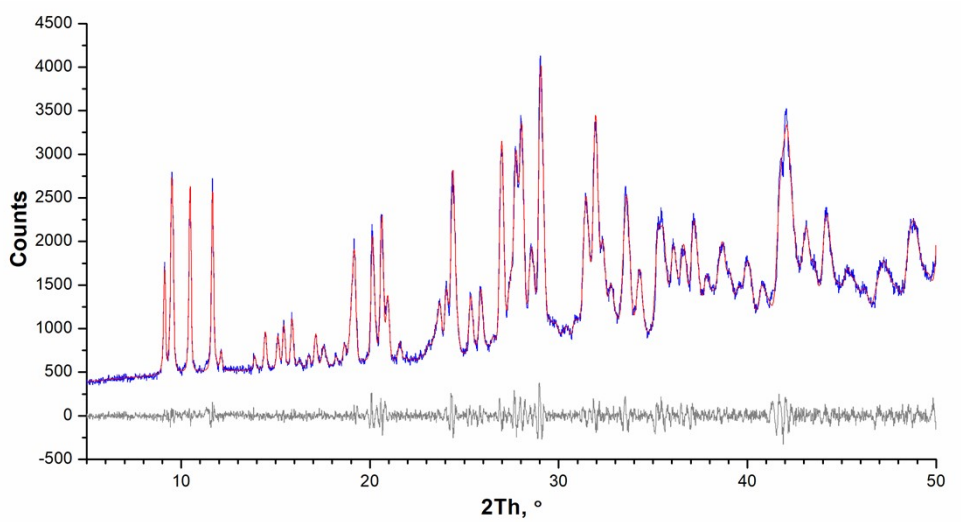
d



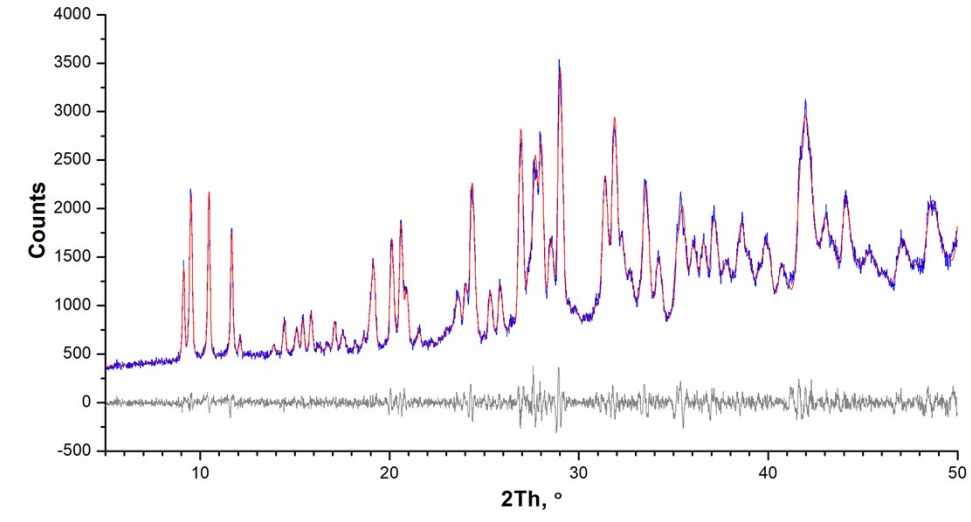
e



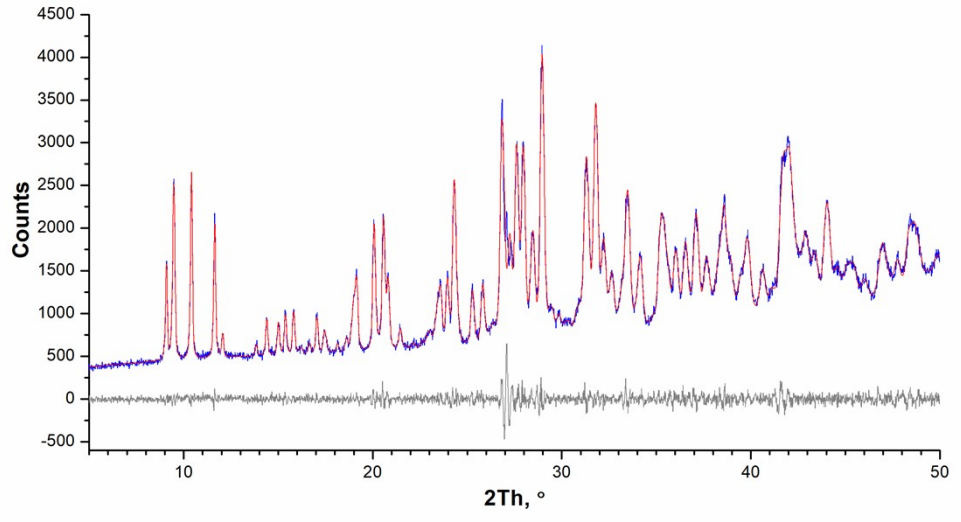
f



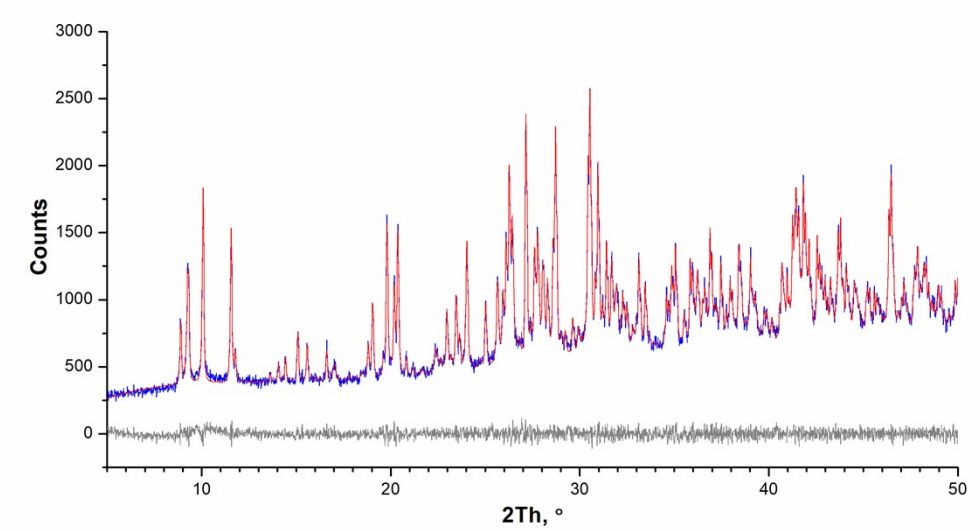
g



h

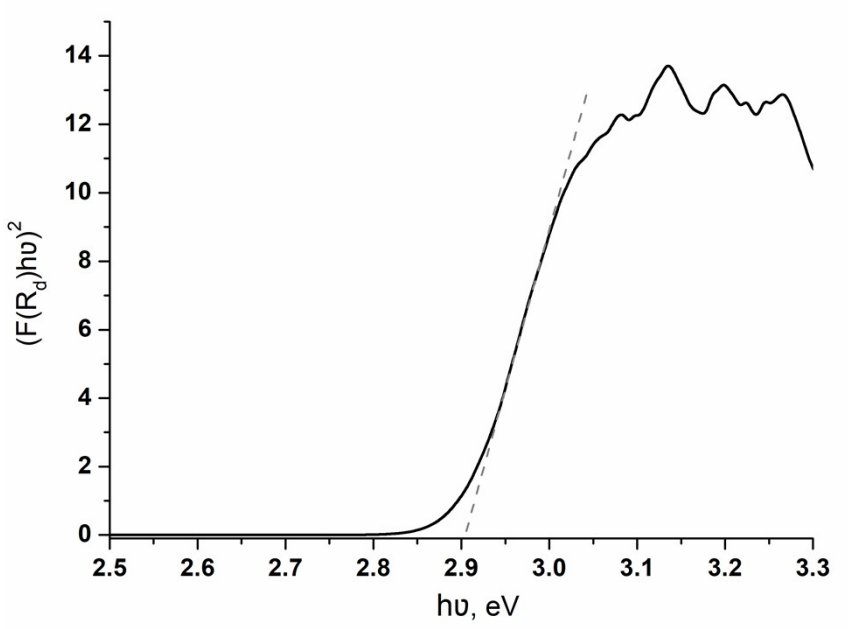


i

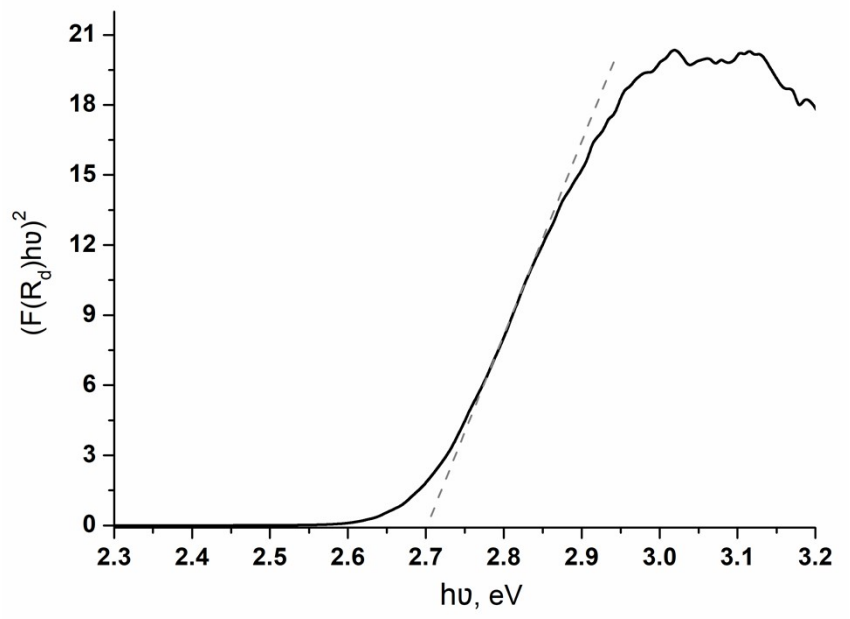


j

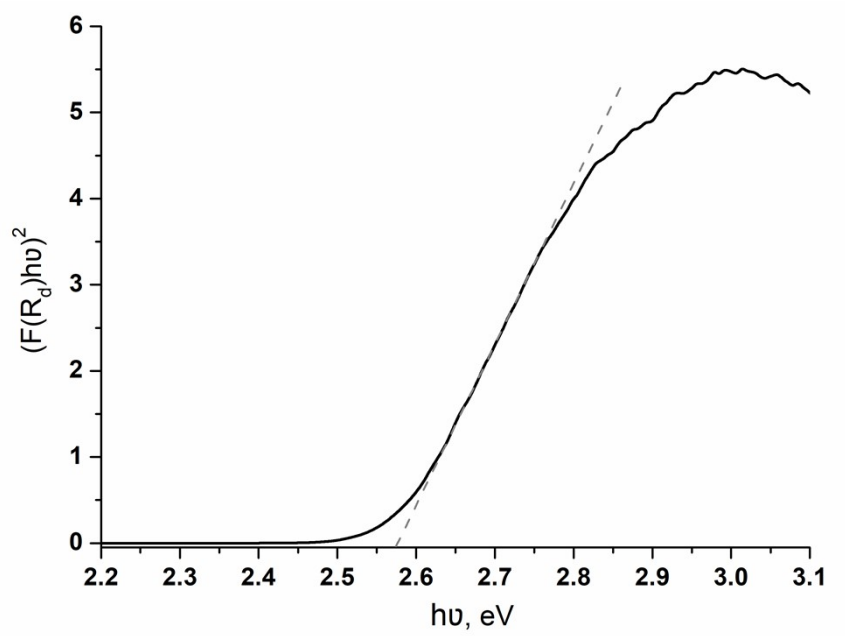
Fig. S15. Pawley refinement profiles for **1-10** solid solutions (a-j) obtained from aqueous solutions. All profiles were recorded at RT. Red and blue lines correspond to the calculated profile and experimental pattern respectively. The bottom trace shows the difference curve.



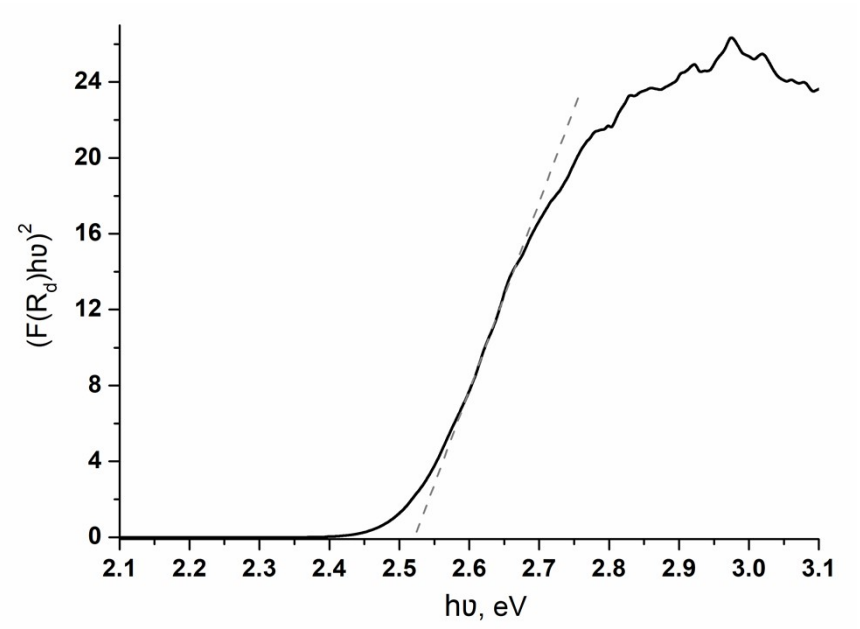
a (1, I_{EDX} = 0.6%, E_g = 2.90 eV)



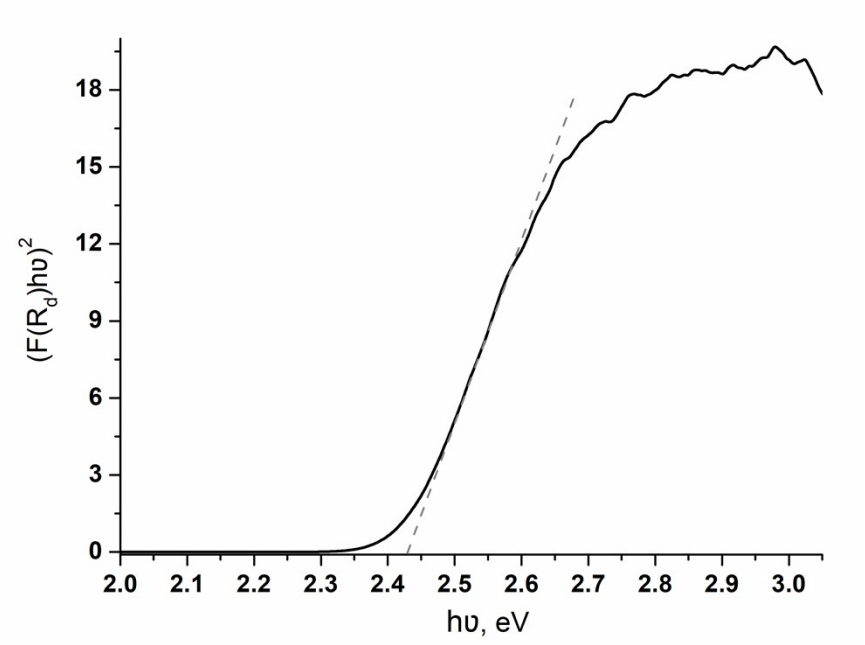
b (**2**, I_{EDX} = 9.6%, E_g = 2.70 eV)



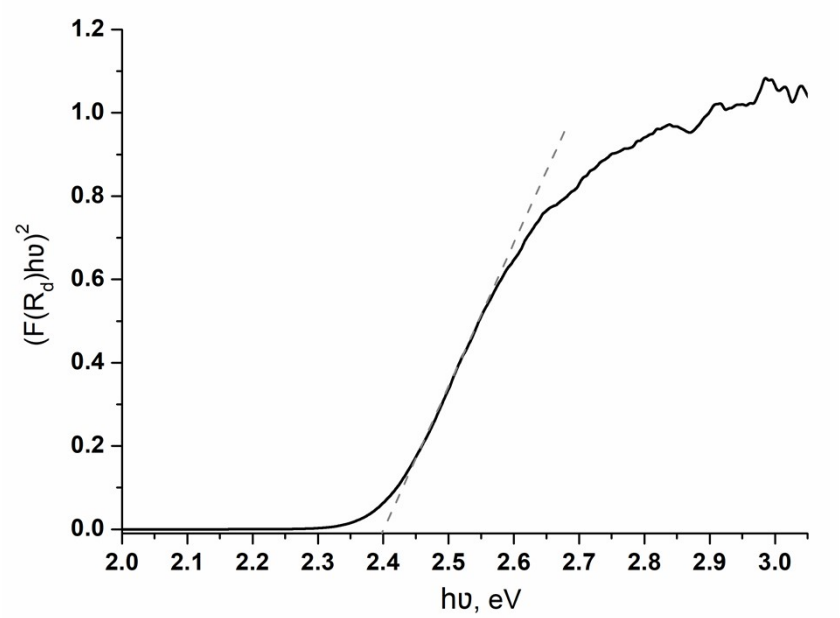
c (**3**, I_{EDX} = 20.2%, E_g = 2.58 eV)



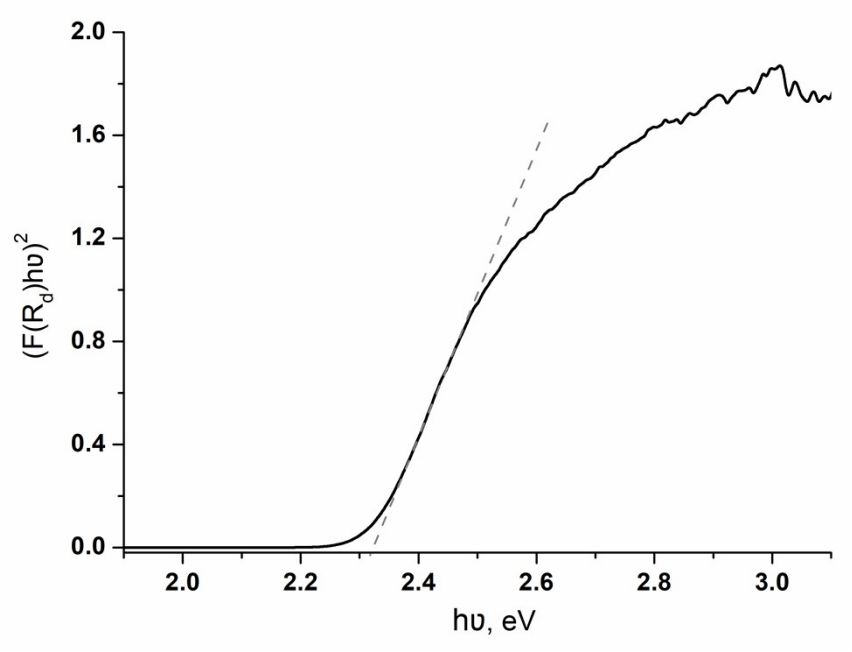
d (**4**, I_{EDX} = 27.0%, E_g = 2.52 eV)



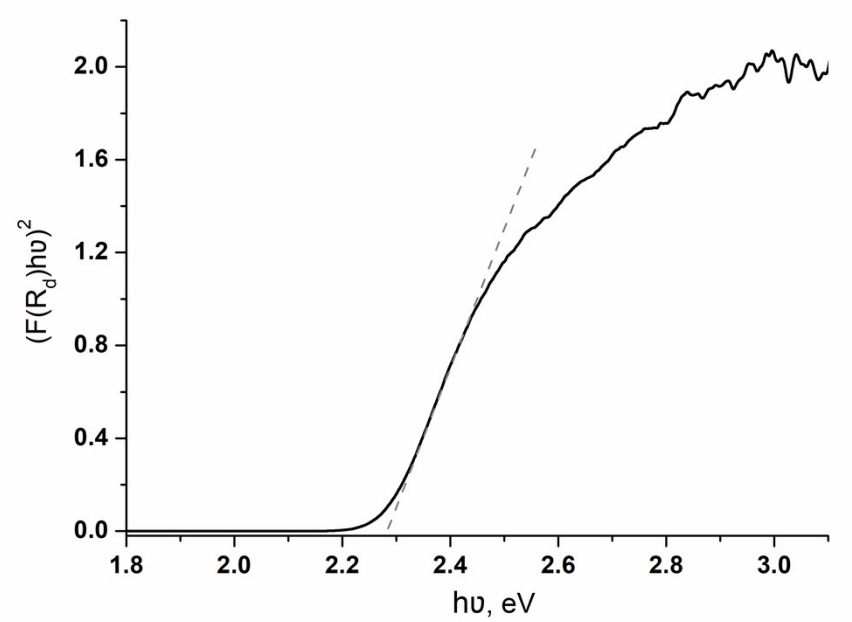
e (**5**, I_{EDX} = 42.0%, E_g = 2.43 eV)



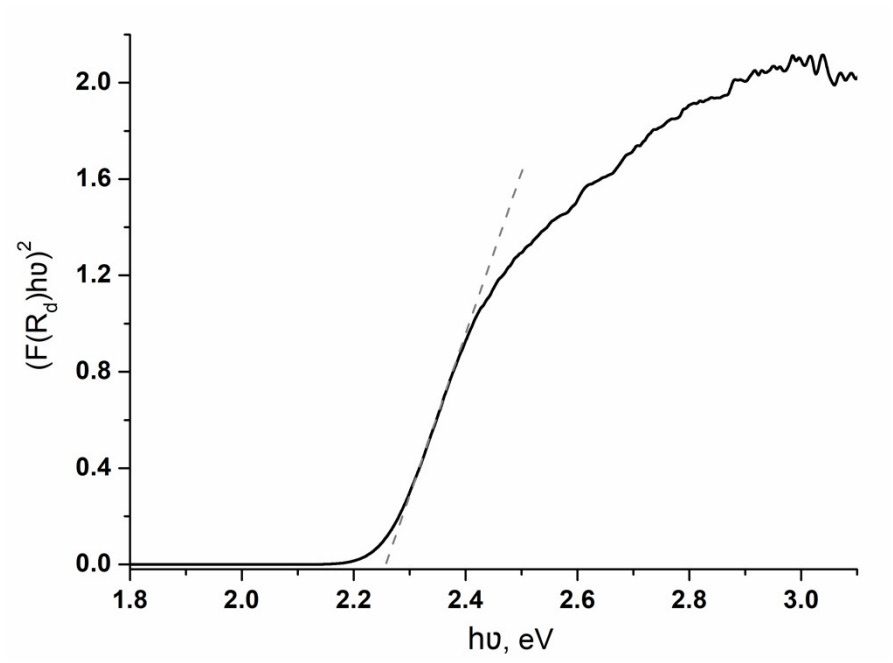
f (6, I_{EDX} = 38.0%, E_g = 2.40 eV)



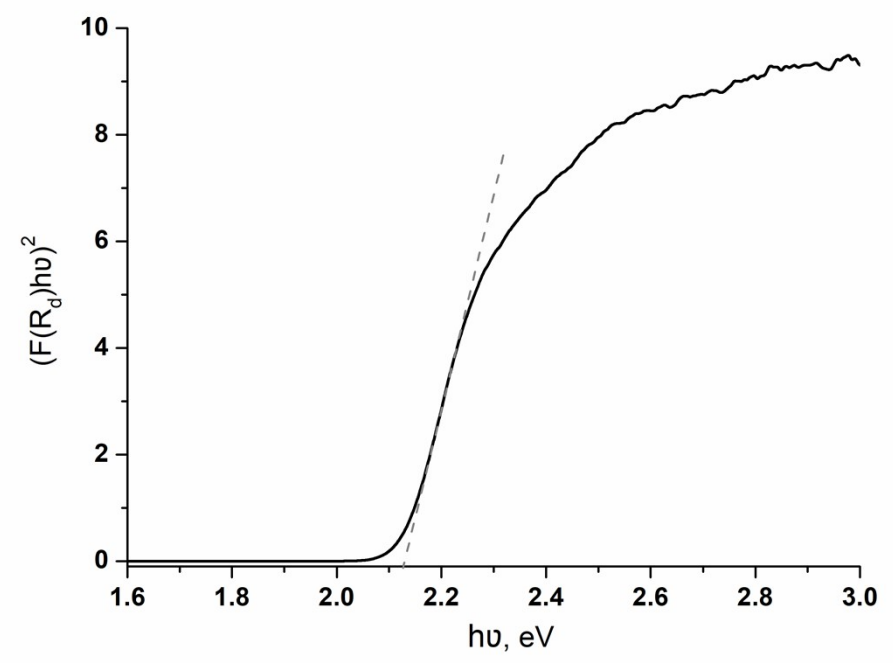
g (7, I_{EDX} = 50.2%, E_g = 2.32 eV)



h (8, I_{EDX} = 55.6%, E_g = 2.28 eV)

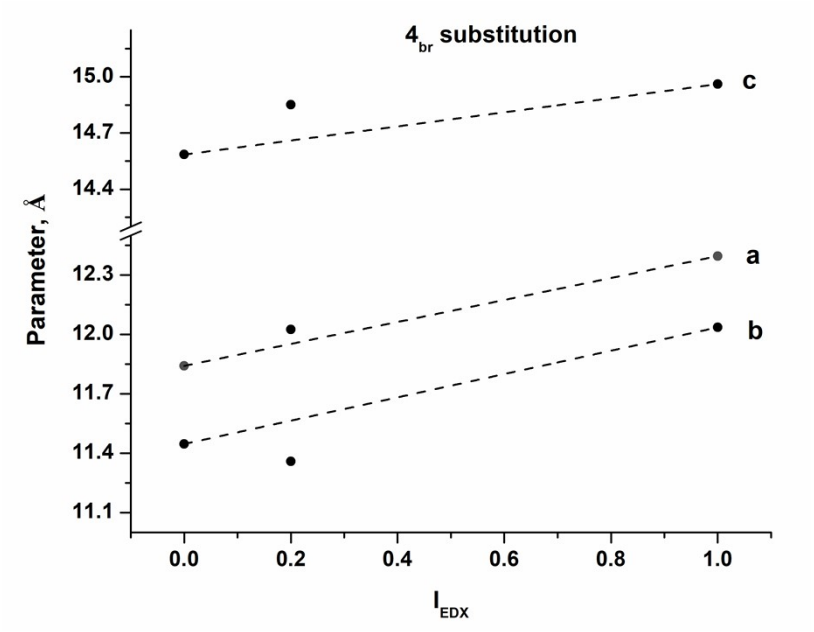


i (9, I_{EDX} = 59.8%, E_g = 2.16 eV)

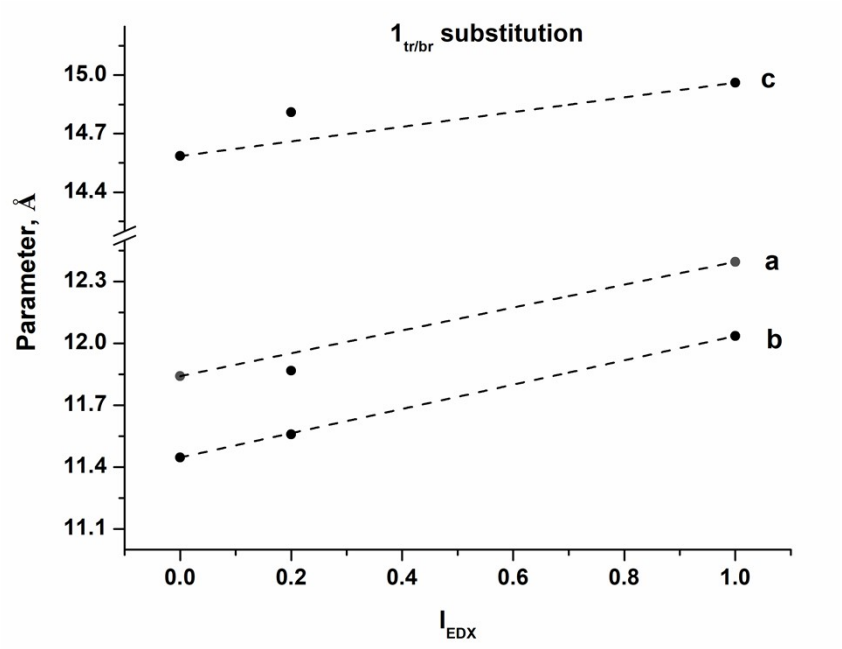


j (10, I_{EDX} = 98.9%, E_g = 2.13 eV)

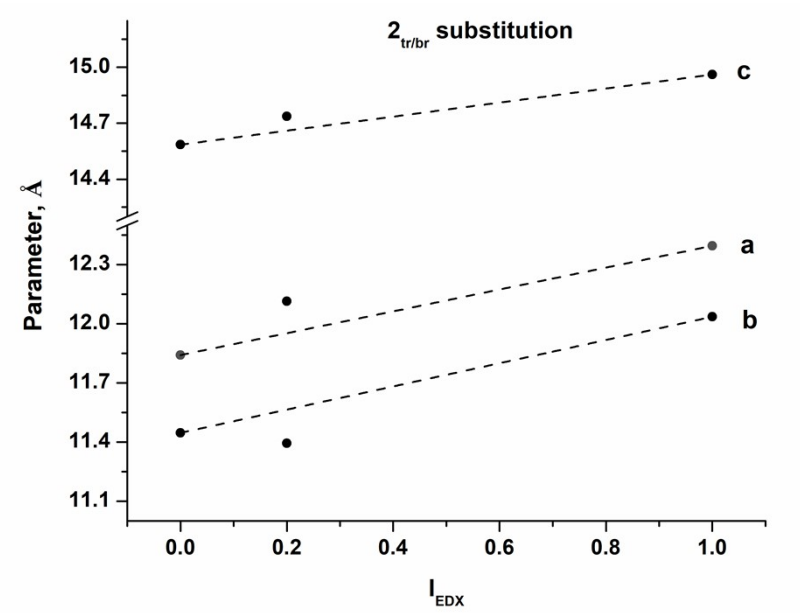
Fig. S16. Tauc plots of $[Py_2(XK)]_2[Bi_2Br_{10-x}I_x]$ solid solutions 1-10 (a-j). The linear part of the plot is extrapolated to the x-axis to determine E_g values.


4br substitution
15.0
14.7
14.4
12.3
12.0
11.7
11.4
11.1
Parameter, Å
c
a
b
0.0
0.2
0.4
0.6
0.8
1.0
IEDX

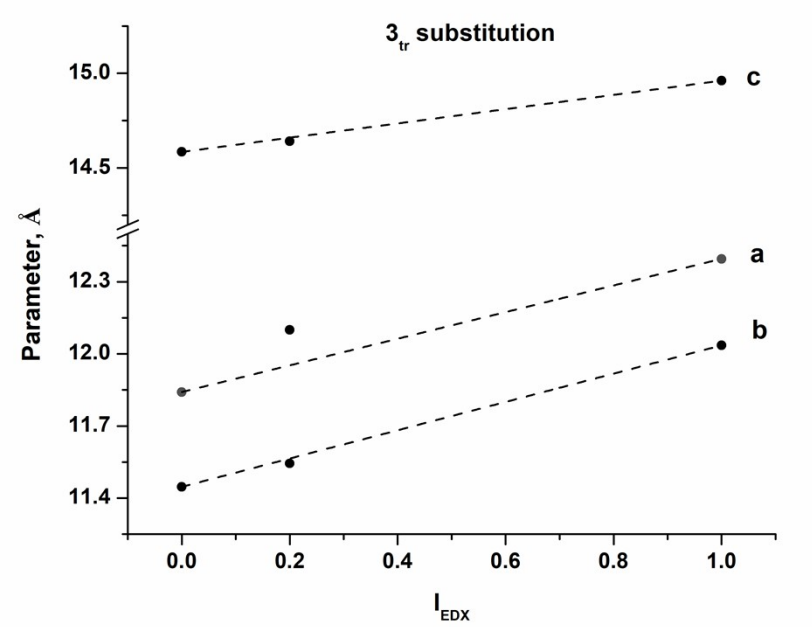
a


1tr/br substitution
15.0
14.7
14.4
12.3
12.0
11.7
11.4
11.1
Parameter, Å
c
a
b
0.0
0.2
0.4
0.6
0.8
1.0
IEDX

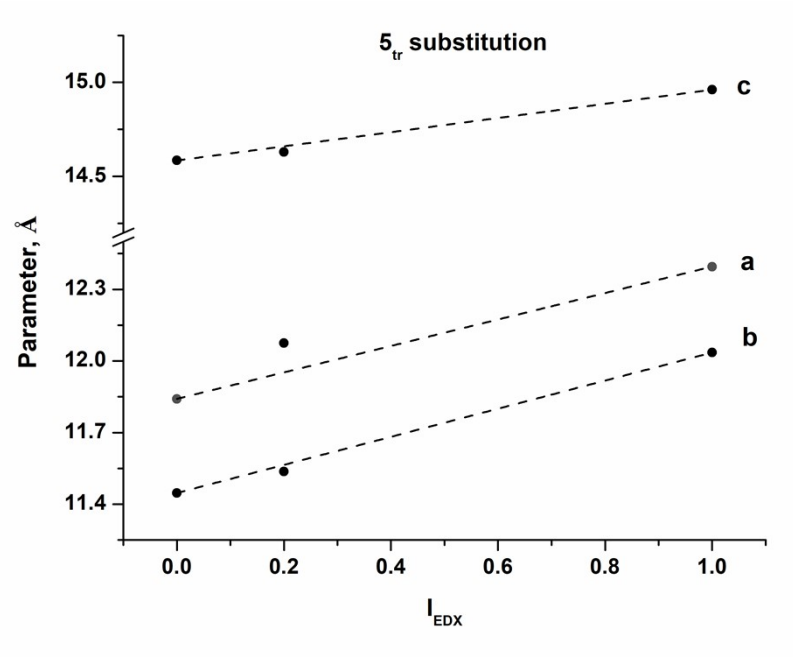
b


2tr/br substitution
15.0
14.7
14.4
12.3
12.0
11.7
11.4
11.1
Parameter, Å
0.0
0.2
0.4
0.6
0.8
1.0
IEDX
c
a
b

c

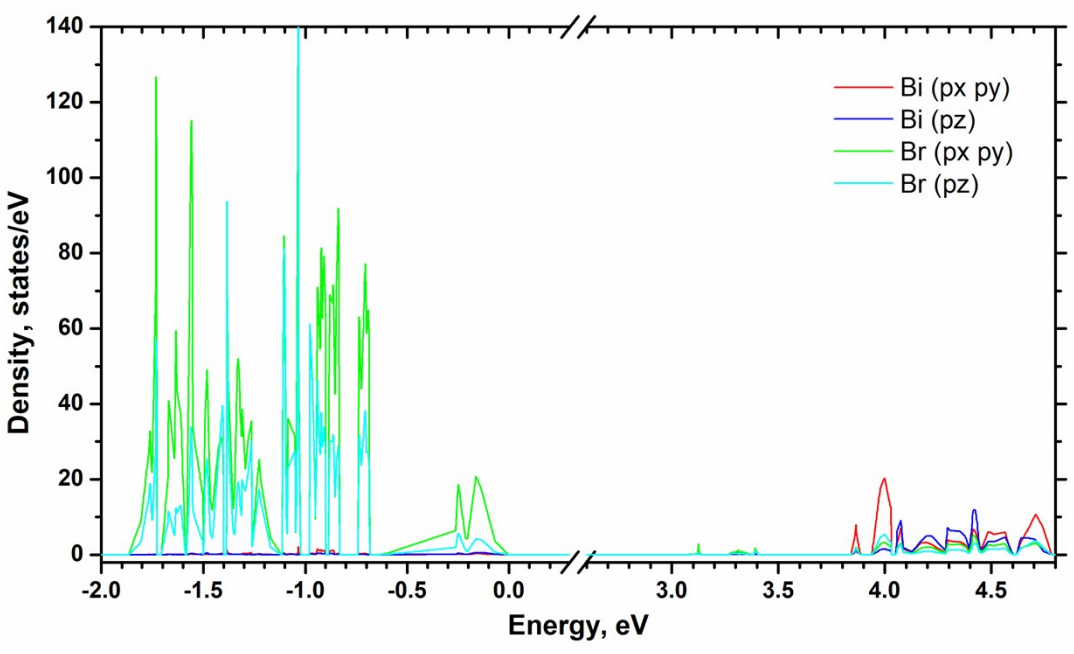

3tr substitution
15.0
14.5
12.3
12.0
11.7
11.4
Parameter, Å
0.0
0.2
0.4
0.6
0.8
1.0
IEDX
c
a
b

d

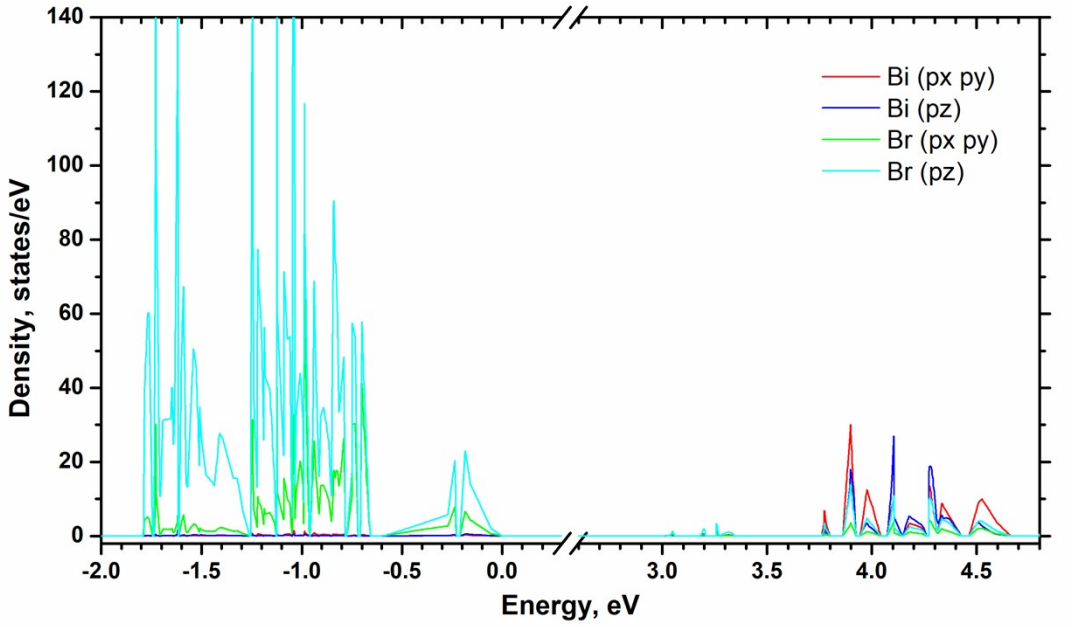


e

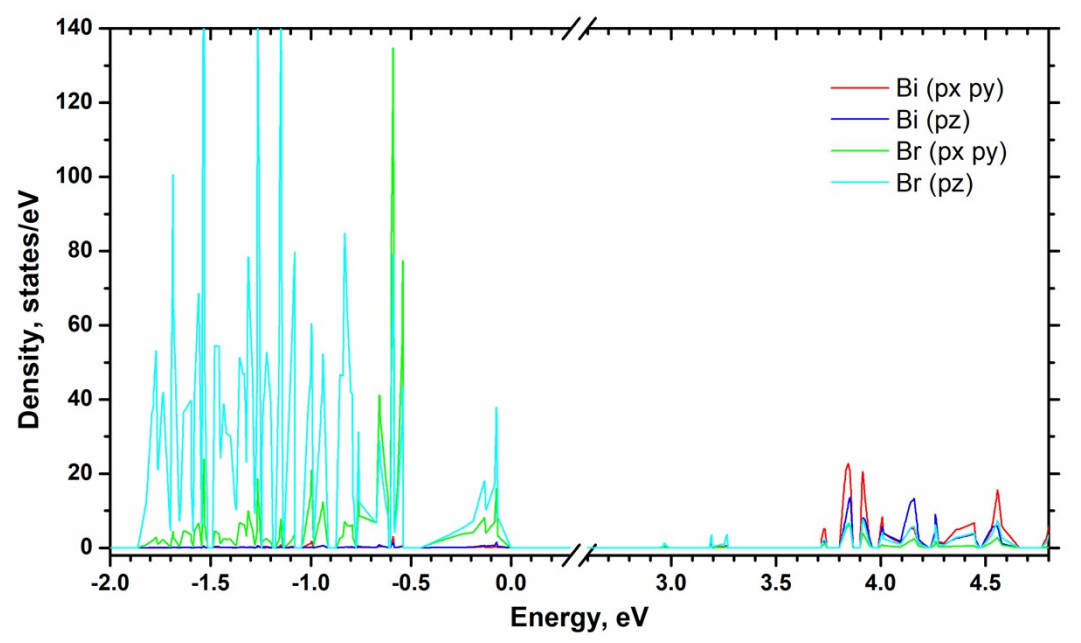
Fig. S17. Dependence of crystal lattice parameters on the composition of model compounds [4-$Pi_2C_2]_2[Bi_2Br_8I_2]$, where iodine atoms occupy the 4_{br} bridge (a), $1_{tr/br}$ (b) and $2_{tr/br}$ (c) term/bridge and 3_{tr} (d) and 5_{tr} (e) term/term positions. Fitting curves are shown for visual convenience and have no physical sense.


Density, states/eV
Energy, eV
Bi (px py)
Bi (pz)
Br (px py)
Br (pz)

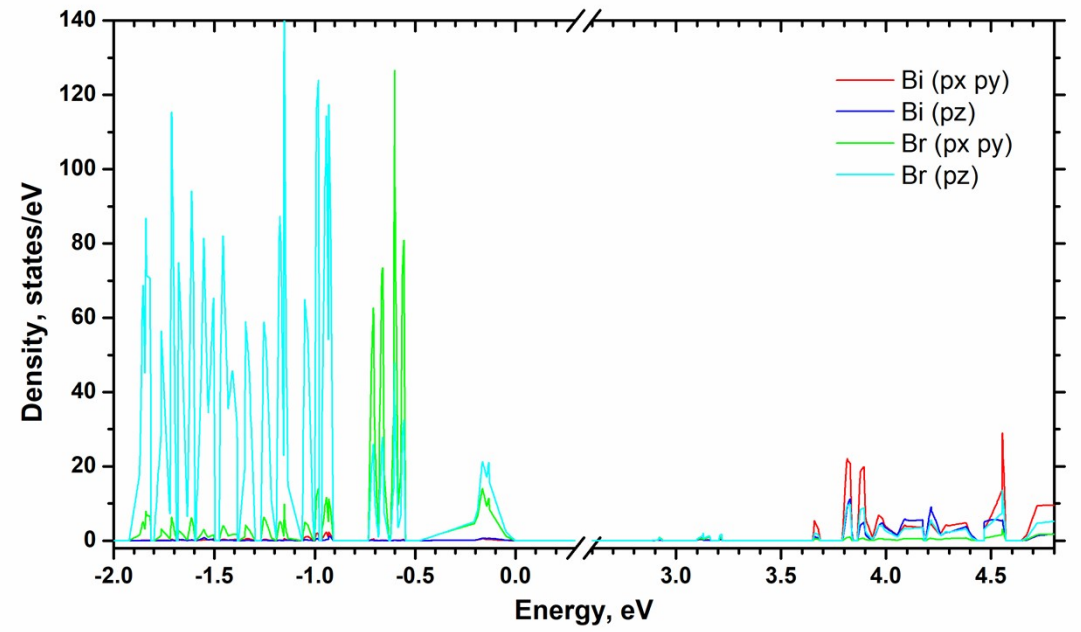
a


Density, states/eV
Energy, eV
Bi (px py)
Bi (pz)
Br (px py)
Br (pz)

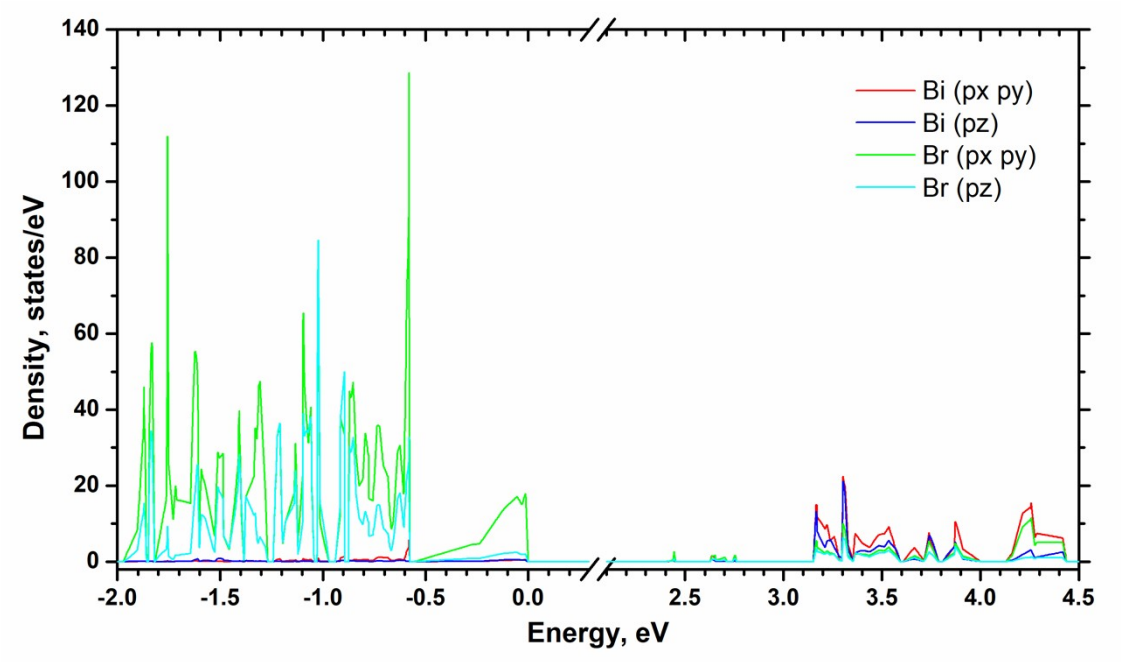
b


Density, states/eV
Energy, eV
Bi (px py)
Bi (pz)
Br (px py)
Br (pz)

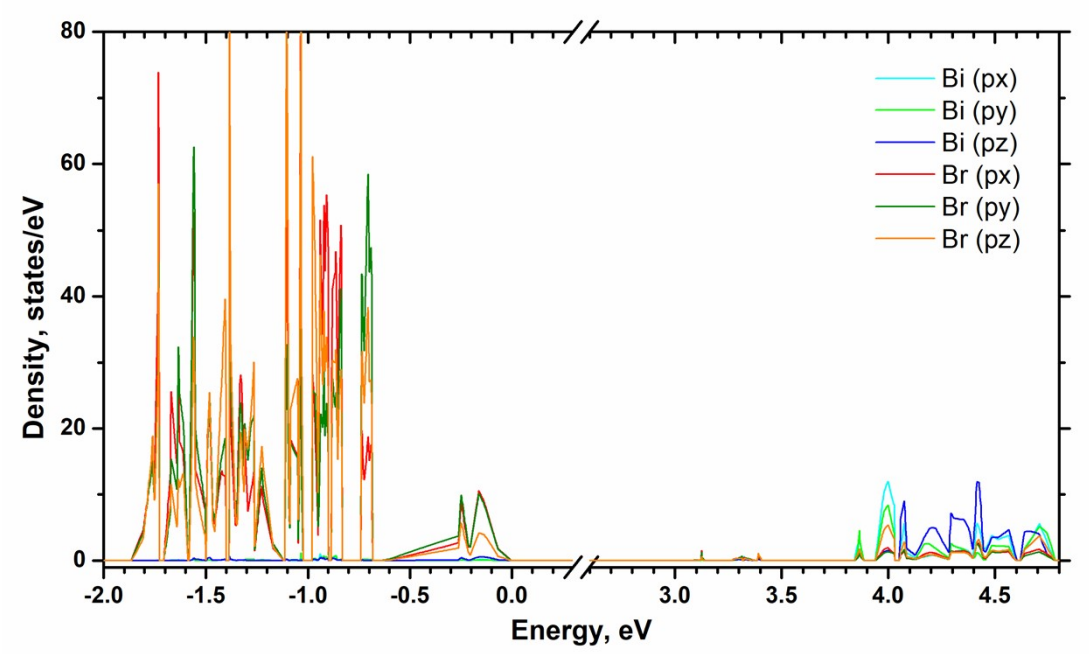
c


Density, states/eV
Energy, eV
Bi (px py)
Bi (pz)
Br (px py)
Br (pz)

d

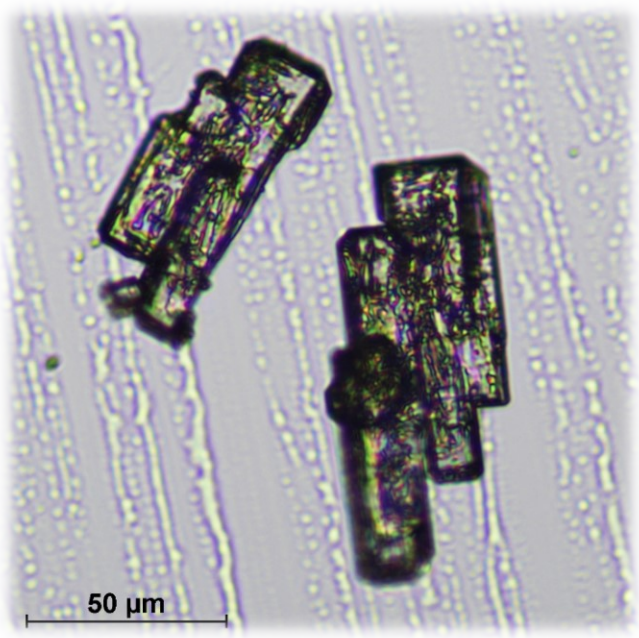


e

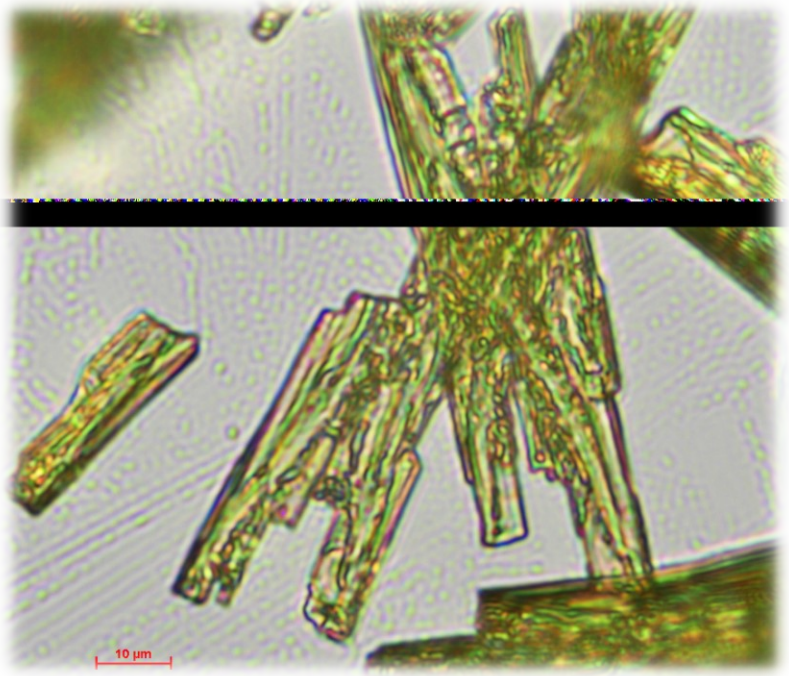


f

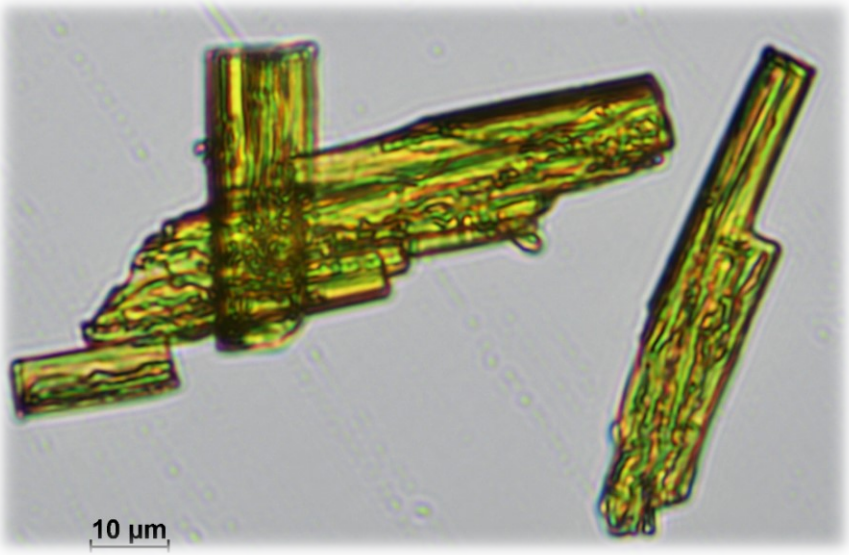
Fig. S18.Density of states of 1 (a, f), 4_{br} (b), $1_{tr/br}$ (c), 3_{tr} (d) and 10 (e).



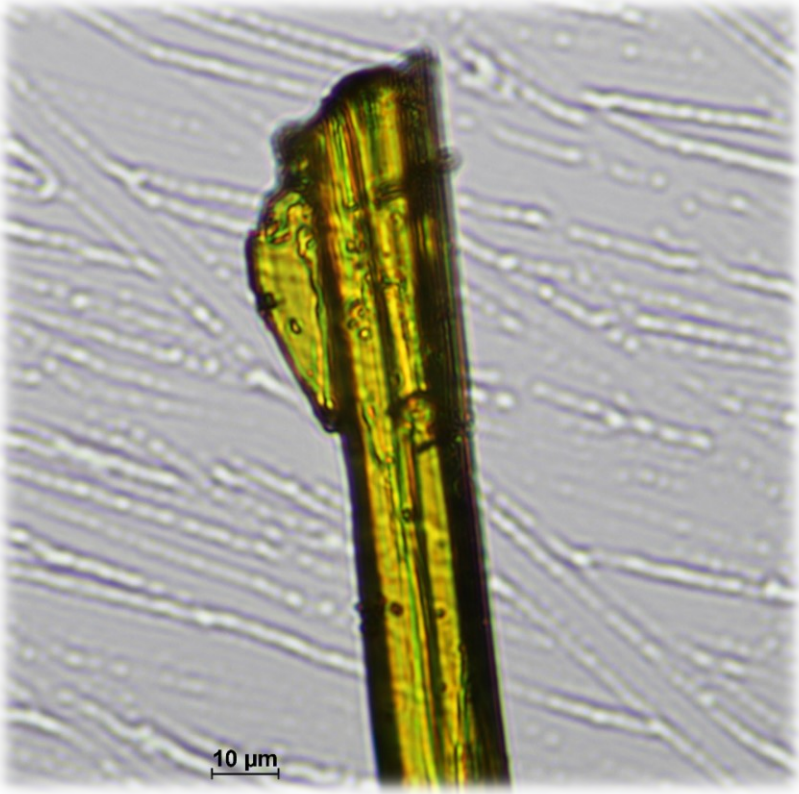
a



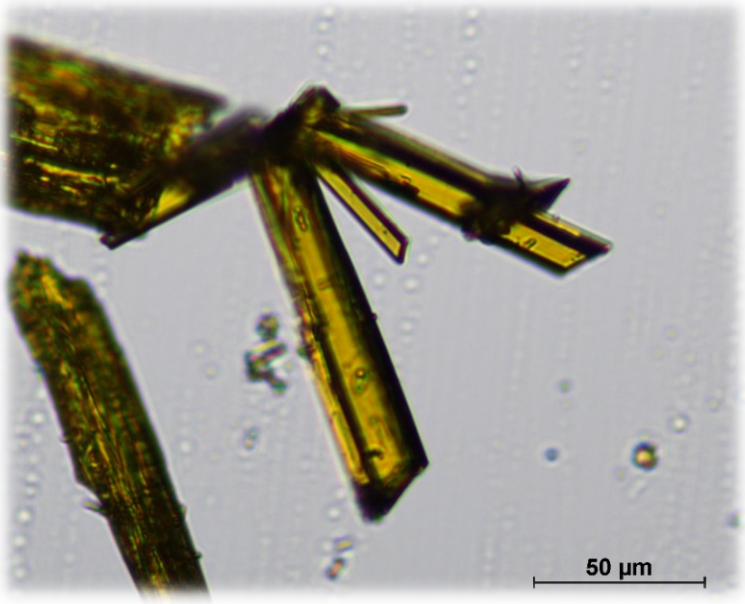
b



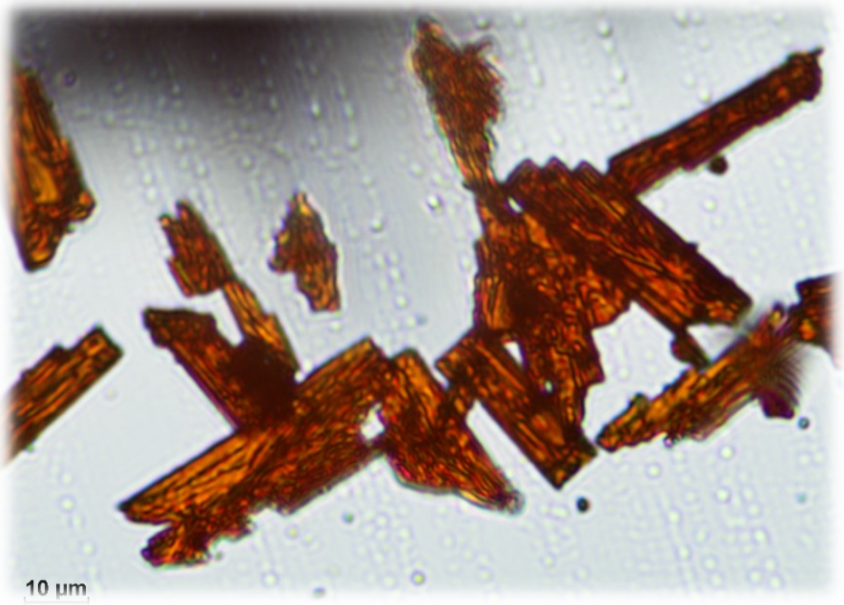
c



d



e



f

Fig. S19. Crystals of solid solutions 1-**5** (a-e) and 10 (f).