Black Hybride Iodobismuthate Containing Linear Anionic Chains

Vitalii Yu. Kotov, Andrey B. Ilyukhin, Alexander A. Korlyukov, Alexander F. Smol'yakov and Sergey A. Kozyukhin

Electronic supplementary information

Synthesis of 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) bromides. A slightly heated mixture containing 5 ml of α,ω-dibromoalkane (Aldrich 97%) and 20 ml of 4-picoline (Aldrich 98%), was stirred with a magnetic stirrer for 24 h. The obtained PiC_nBr_2 precipitate was washed with acetonitrile (Component-Reaktiv dry) and ethanol (Component-Reaktiv 96%) and then dried in air. In the case of 1,5-dibromopentane, the thus-prepared product was hygroscopic. Therefore, after being washed with dry acetonitrile, it was immediately dissolved in water or concentrated HI (Sigma-Aldrich, 57 wt % in H_2O stabilized 99.95%) to obtain a 2M solution.

Synthesis of 1,1'-(1,2-ethanediyl)bis(4-methylpyridinium) iodobismuthate. The 3 ml of 2 M PiC_2Br_2 solution in concentrated HI was added to 15 ml of 0.1 M BiI_3 (Lankhit ultra dry 99.998%) solution in 15 ml of concentrated HI. A crystalline substance precipitated from red solutions in 1 hour. The red solid **1 (**1.427 g, 92.0%) was separated from the solution by decantation, washed three times with dry acetonitrile and ethanol, and then dried in air.

Synthesis of 1,1'-(1,5-pentanediyl)bis(4-methylpyridinium) iodobismuthates. The 3 ml of 2 M PiC_5Br_2 solution in concentrated HI was added to 15 ml of 0.1 M BiI_3 solution in 15 ml of concentrated HI. A crystalline solid precipitated from red solutions in 1 hour. The black solid **2 (**1.488 g, 90.2%) was separated from the solution by decantation, washed three times with dry acetonitrile and ethanol, and then dried in air.

The 3 ml of 2 M PiC_5Br_2 aqueous solution was added to 15 ml of 0.1 M BiI_3 solution in 15 ml of concentrated HI. A crystalline solid precipitated from red solutions in 1 hour. A mixture of black and red crystals was separated from the solution by decantation, washed three times with dry acetonitrile and ethanol, and then dried in air. Red crystals of **3** were mechanically separated from the black ones.

The 3 ml of 2 M PiC_5Br_2 aqueous solution was added to 15 ml of 0.1 M BiI_3 solution in 15 ml of saturated KI (Reakhim 99%) aqueous solution. A red non-crystalline solid precipitated from red solution in 1 hour. This red solid transformed to black one (**2a**) in several hours. Black

solid **2a** was separated from the solution by decantation, washed three times with water and ethanol, and then dried in air.

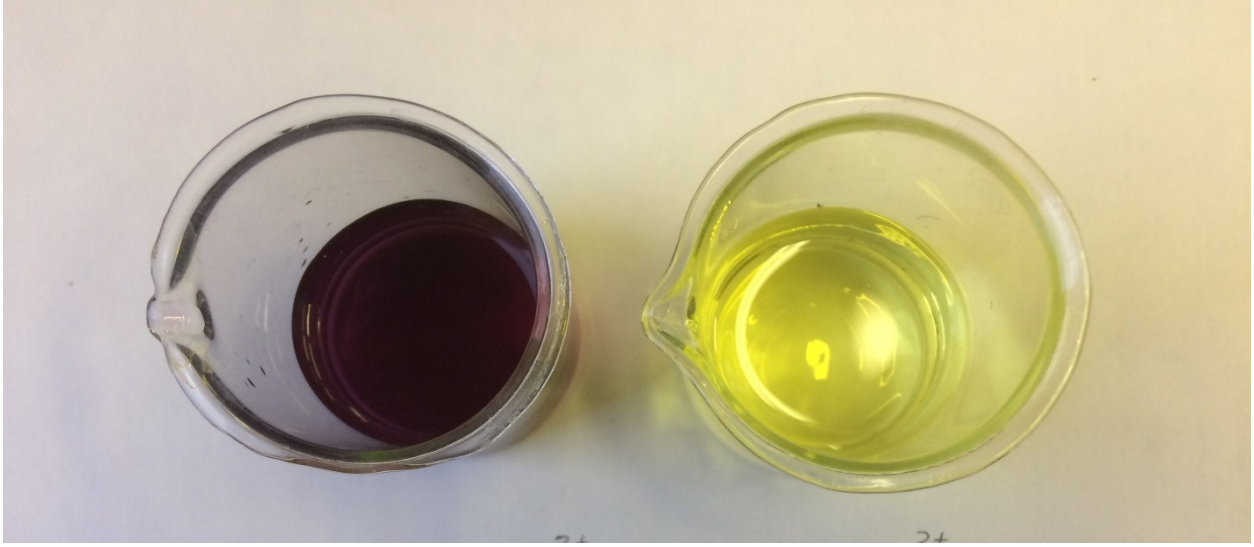
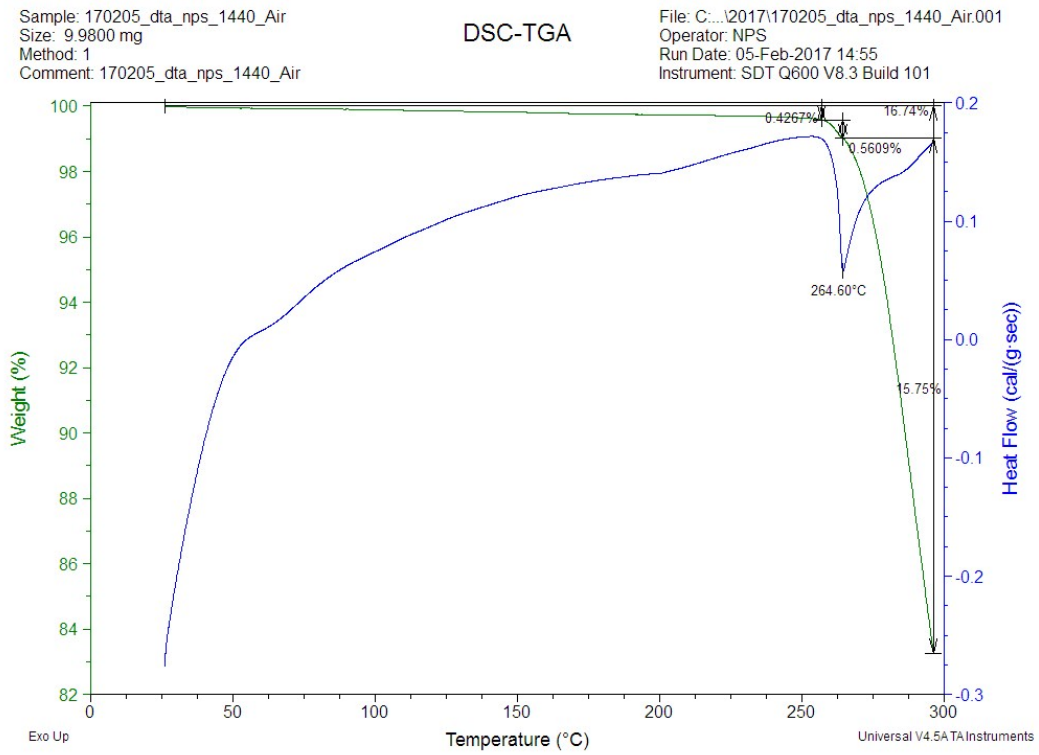
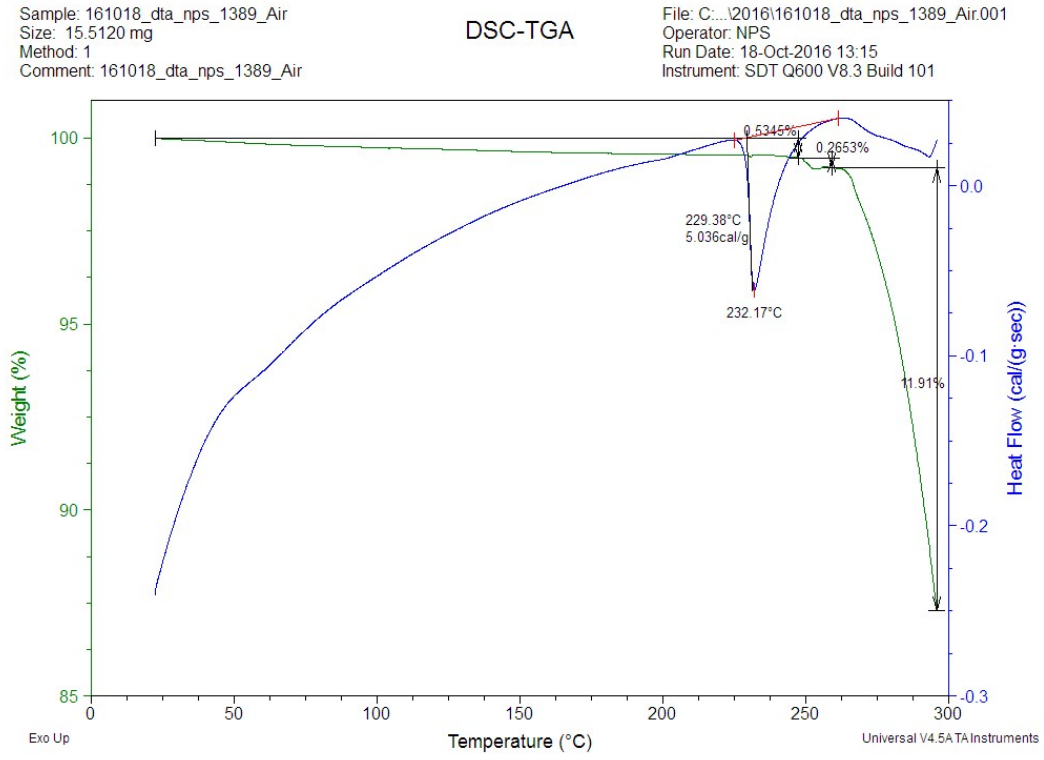


Figure S1. Solutions of 1,1'-(1,5-pentanediyl)bis(4-cyanopyridinium) bromide (left) and 1,1'-(1,5-pentanediyl)bis(4-methylpyridinium) bromide (right) after addition of potassium hexacyanoferrate solution. The difference in the color of solutions is due to the presence and absence of outer-sphere charge transfer bands in the visible region of spectra and indicates a greater electron affinity energy of the 1,1 '- (1,5-pentanediyl) bis (4-cyanopyridinium) cation compared to (1,5- pentanediyl) bis (4-methylpyridinium) cation [1].

1. S.I. Gorelsky, V.Yu. Kotov, and A.B.P. Lever. *Inorg. Chem.*, 1988, **37**, 4548

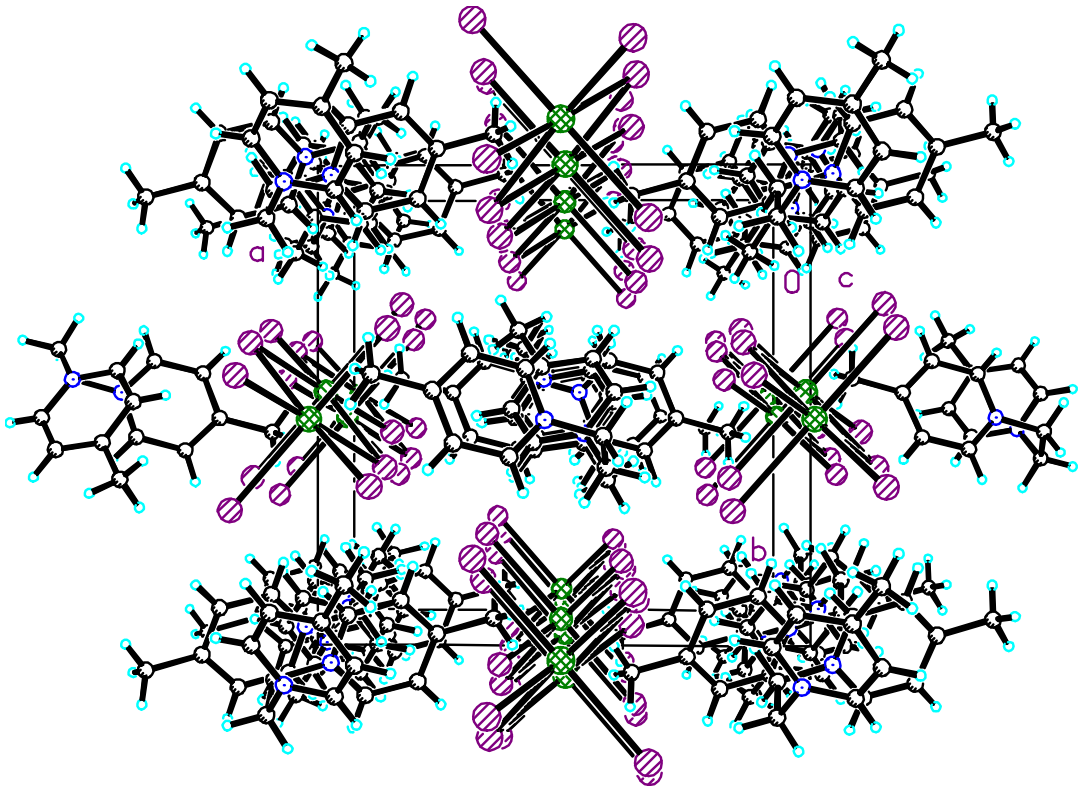


a

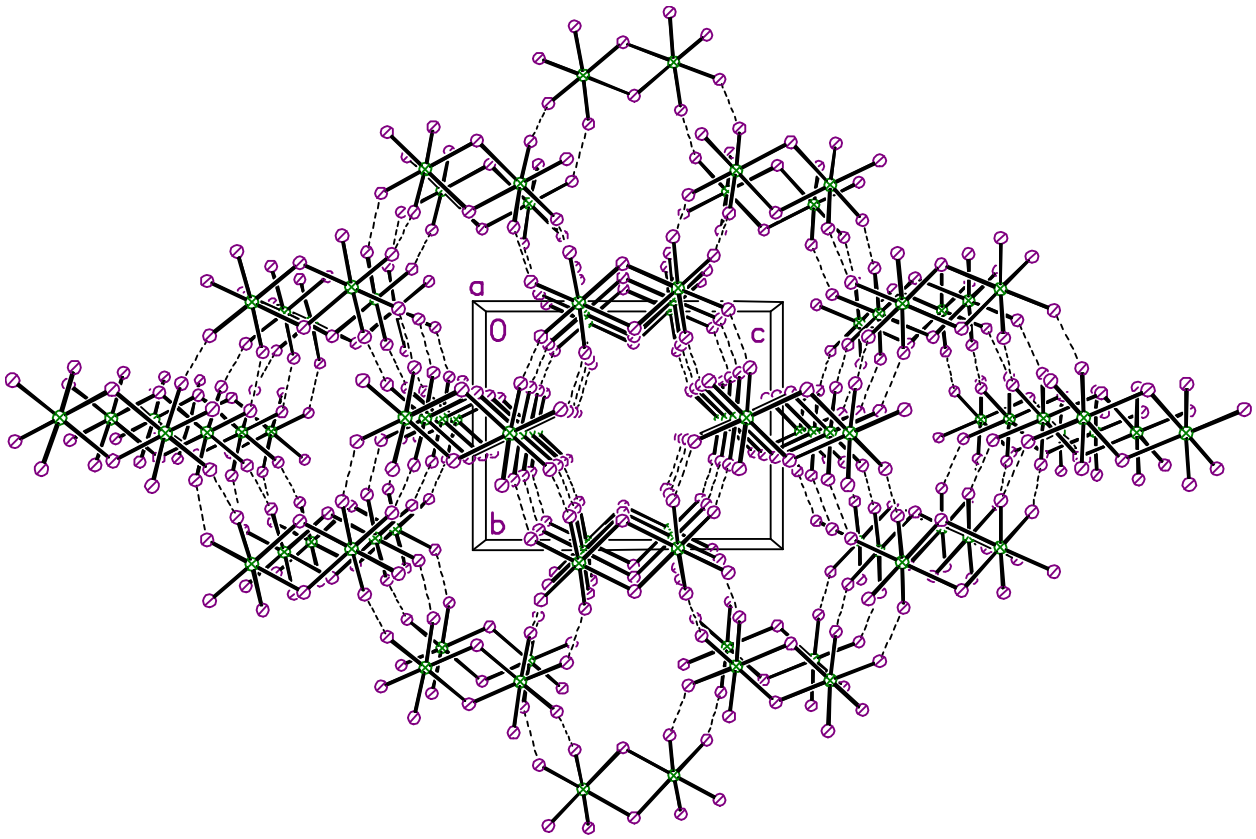


b

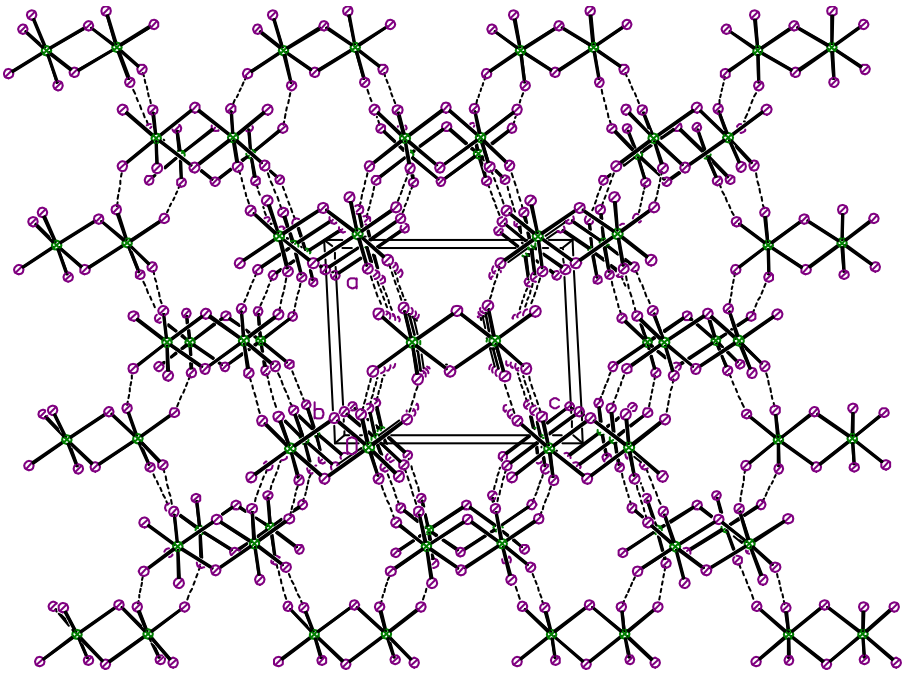
Figure S2. TG and DTA curves for **1** (a) and **2** (b).



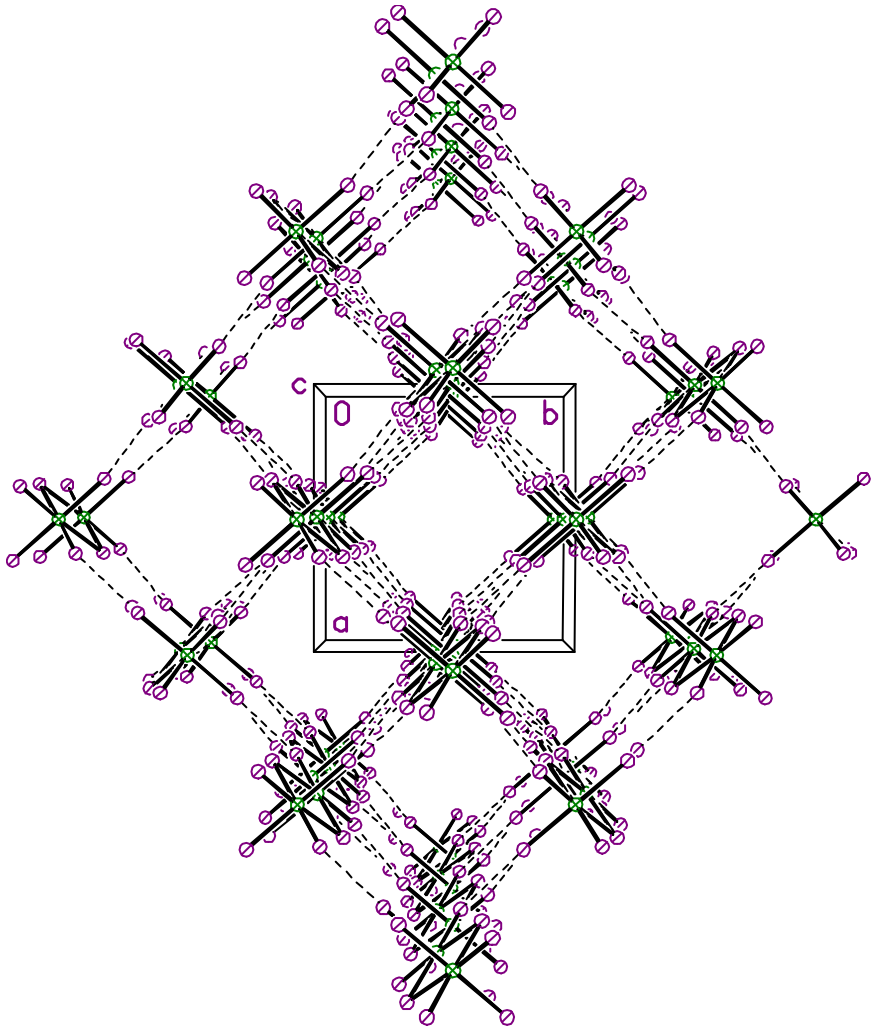
a



b

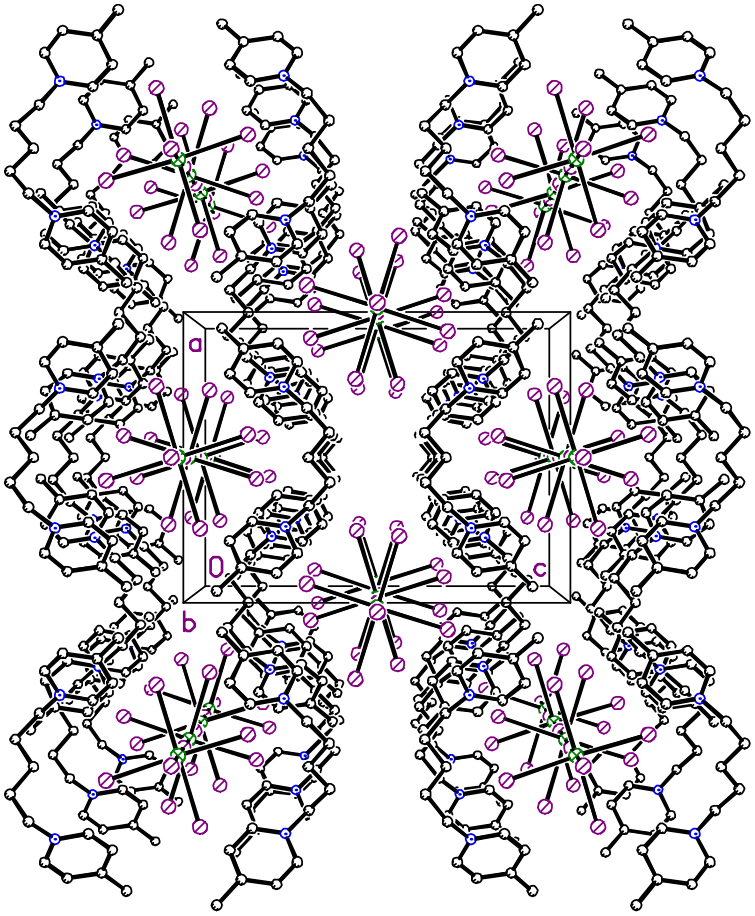


c

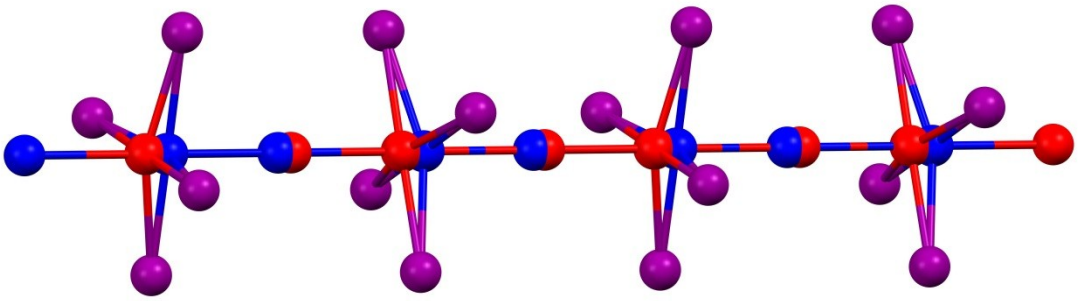


d

Figure S3. Projection of the structure of **1** along axis c (a). A schematic representation of short contacts I…I in the structure of **1** (b-d).



a



b

Figure S4. Projection of the structure of **2** along axis b (a). The structure of disordered 1D-chain $(BiI_5)_n^{2n-}$ in **2** (b). I(1,2) atoms identical for two orientations are violet, atoms of Bi and I different for two orientations are denoted by red and blue.

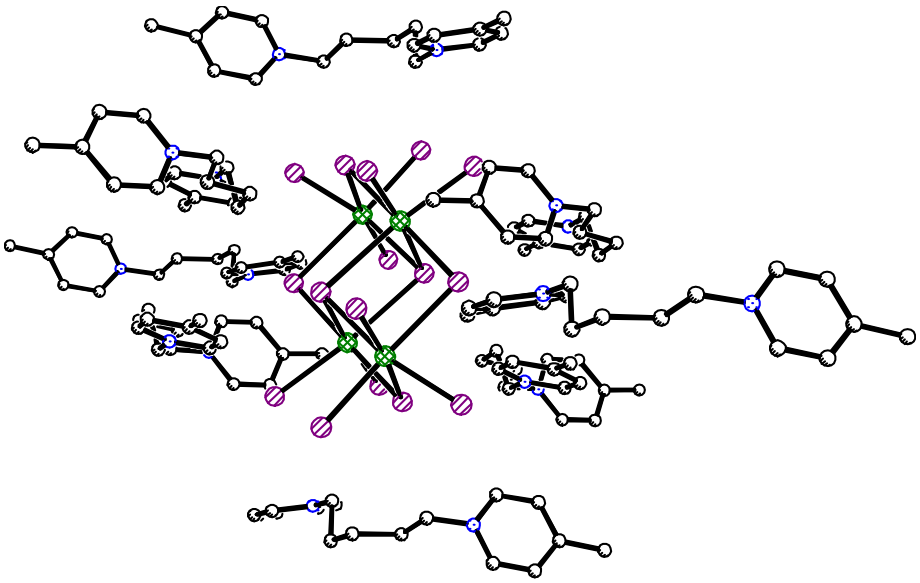


Figure S5. Immediate environment of the $Bi_4I_{16}^{4-}$ anion in **3**.

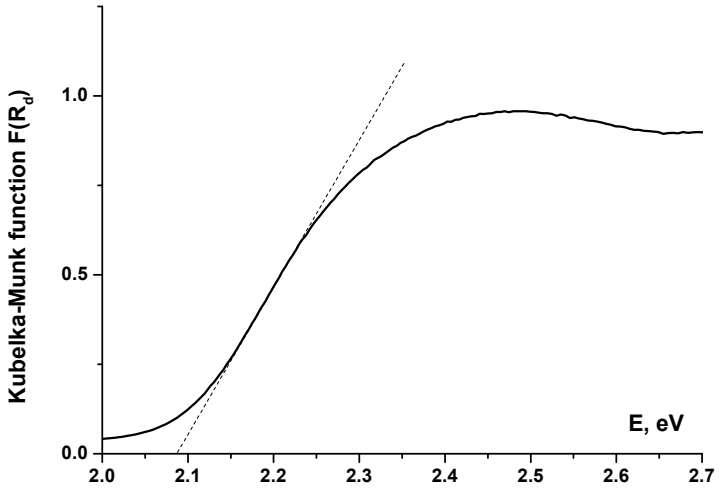


Figure S6. Reflectance spectra of **1** (E_g = 2.08 eV). The Kubelka-Munk function is defined as in [24]: $F(R_d) = \frac{(1-R_d)^2}{2R_d}$, where R_d is the absolute reflectance of the sample layer.

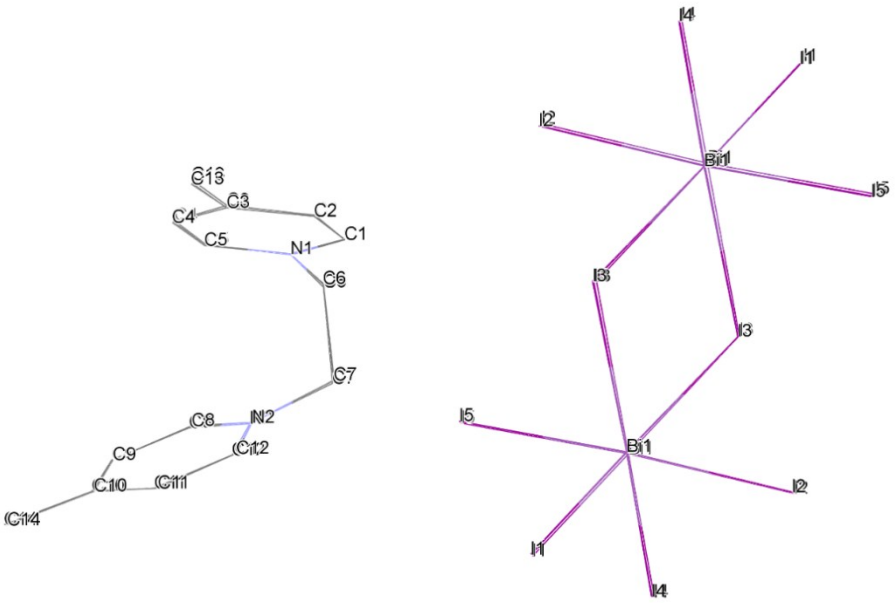
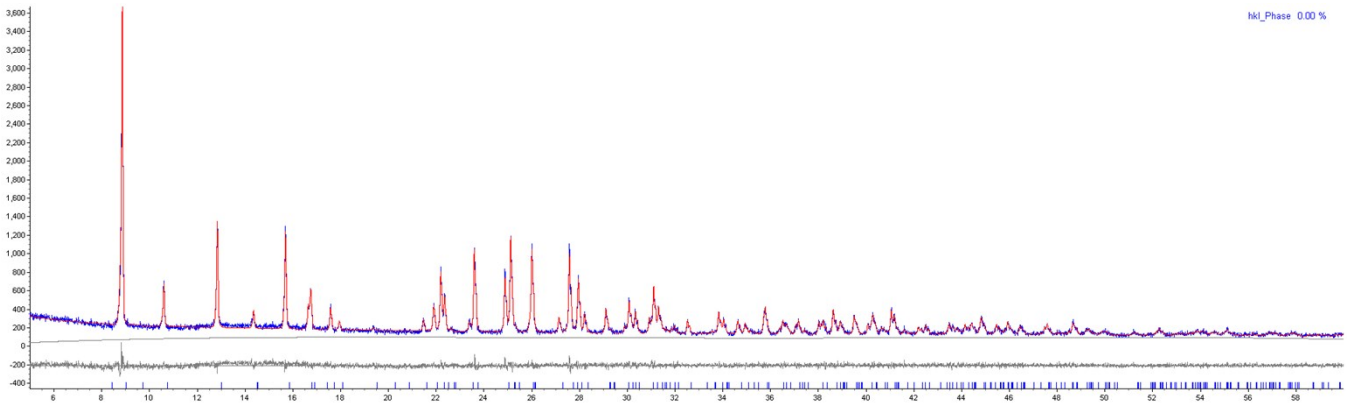
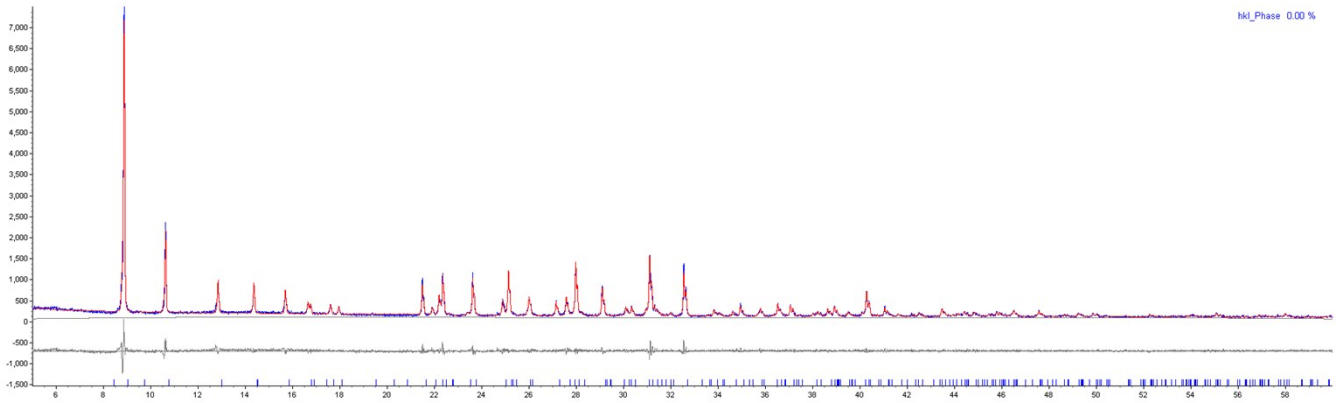


Figure S7. Superposition of structural fragments of **1**. The experiments were performed at 100, 150, and 298 K.

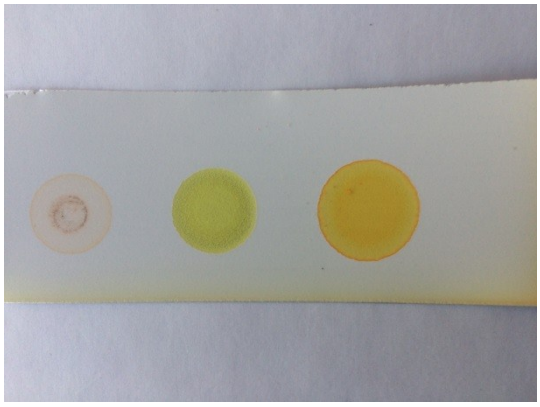


a

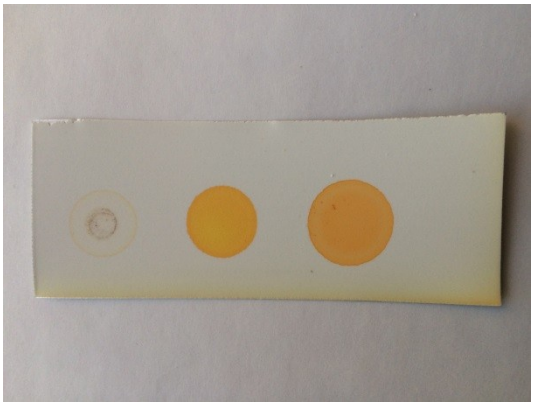


b

Figure S8. The results of refinements for **2** (a) and **2a**. (b)



a



b

c

d

e

f

Figure S9. Drops of solutions of **2** in acetonitrile, dimethylformamide and dimethylsulfoxide on SiO_2 substrate before heating (a) and after heating to 160°C (b). The dried solution of **2** in dimethylformamide before (c) and after (d-f) treatment with water vapor during 1 minute. Time after treatment is 1 minute (d), one hour (e), and one day (f).

Table S1. Geometric parameters [Å and deg.] of **1-3**.

1

	100K	150K	298K
Bi(1)-I(4)	2.9141(2)	2.9140(3)	2.9176(4)
Bi(1)-I(1)	2.9460(2)	2.9467(3)	2.9516(5)
Bi(1)-I(5)	3.0344(2)	3.0342(3)	3.0371(4)
Bi(1)-I(2)	3.0543(2)	3.0553(3)	3.0645(4)
Bi(1)-I(3)#1	3.3071(2)	3.3088(3)	3.3252(5)
Bi(1)-I(3)	3.3134(2)	3.3144(3)	3.3241(4)

	100K	150K	298K
I(4)-Bi(1)-I(1)	92.169(7)	92.348(8)	93.001(15)
I(4)-Bi(1)-I(5)	87.400(7)	87.448(8)	87.311(14)
I(1)-Bi(1)-I(5)	87.866(7)	87.796(8)	87.772(14)
I(4)-Bi(1)-I(2)	90.914(7)	90.972(8)	91.337(14)
I(1)-Bi(1)-I(2)	89.711(7)	89.808(8)	89.855(13)
I(5)-Bi(1)-I(2)	176.993(7	177.073(9)	177.204(12)
I(4)-Bi(1)-I(3)#1	88.324(7)	88.424(8)	88.297(14)
I(1)-Bi(1)-I(3)#1	178.562(6)	178.481(8)	178.311(11)
I(5)-Bi(1)-I(3)#1	93.507(6)	93.547(8)	93.371(13)
I(2)-Bi(1)-I(3)#1	88.930(6)	88.871(7)	89.034(12)
I(4)-Bi(1)-I(3)	176.657(6)	176.525(8)	175.673(12)
I(1)-Bi(1)-I(3)	89.660(7)	89.817(8)	90.318(14)
I(5)-Bi(1)-I(3)	89.872(6)	89.921(8)	90.046(13)
I(2)-Bi(1)-I(3)	91.895(7)	91.753(8)	91.448(13)
I(3)#1-Bi(1)-I(3)	89.914(6)	89.475(7)	88.438(13)
Bi(1)#1-I(3)-Bi(1)	90.087(6)	90.524(7)	91.563(12)

	100K	150K	298K
C(5)-N(1)-C(1)-C(2)	-0.2(4)	-0.4(5)	-0.8(7)
C(6)-N(1)-C(1)-C(2)	176.5(3)	175.8(3)	175.7(5)
N(1)-C(1)-C(2)-C(3)	-0.3(4)	-0.4(6)	-0.2(8)
C(1)-C(2)-C(3)-C(4)	0.8(4)	1.2(6)	0.8(8)
C(1)-C(2)-C(3)-C(13)	-179.0(3)	-179.8(4)	-179.2(5)

C(2)-C(3)-C(4)-C(5)	-0.7(4)	-1.3(6)	-0.5(8)
C(13)-C(3)-C(4)-C(5)	179.1(3)	179.7(4)	179.5(6)
C(1)-N(1)-C(5)-C(4)	0.3(4)	0.4(5)	1.1(8)
C(6)-N(1)-C(5)-C(4)	-176.5(3)	-175.9(3)	-175.4(5)
C(3)-C(4)-C(5)-N(1)	0.2(5)	0.5(6)	-0.4(9)
C(1)-N(1)-C(6)-C(7)	-84.8(3)	-84.6(4)	-85.0(6)
C(5)-N(1)-C(6)-C(7)	91.9(3)	91.6(4)	91.4(6)
C(8)-N(2)-C(7)-C(6)	-75.7(3)	-76.6(4)	-76.8(6)
C(12)-N(2)-C(7)-C(6)	100.5(3)	100.6(4)	101.0(6)
N(1)-C(6)-C(7)-N(2)	-58.5(3)	-58.3(4)	-59.0(6)
C(12)-N(2)-C(8)-C(9)	-0.9(5)	-2.1(6)	-1.5(9)
C(7)-N(2)-C(8)-C(9)	175.2(3)	175.2(4)	176.3(6)
N(2)-C(8)-C(9)-C(10)	0.3(5)	1.0(6)	0.6(10)
C(8)-C(9)-C(10)-C(11)	0.5(5)	0.7(6)	0.1(10)
C(8)-C(9)-C(10)-C(14)	-177.4(3)	-178.2(4)	-177.6(6)
C(9)-C(10)-C(11)-C(12)	-0.9(5)	-1.4(6)	0.1(9)
C(14)-C(10)-C(11)-C(12)	177.0(3)	177.5(4)	177.8(6)
C(8)-N(2)-C(12)-C(11)	0.5(4)	1.4(6)	1.7(8)
C(7)-N(2)-C(12)-C(11)	-175.6(3)	-175.9(4)	-176.1(5)
C(10)-C(11)-C(12)-N(2)	0.4(5)	0.4(6)	-1.0(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

2

Bi(1)-I(3)#1	2.905(16)
Bi(1)-I(2)	3.0390(8)
Bi(1)-I(1)	3.0796(9)
Bi(1)-I(3)	3.188(16)
Bi(1)-I(4)	3.511(10)
Bi(1)-I(4)#3	3.845(11)
Bi(1B)-I(4)	2.929(11)
Bi(1B)-I(1)	3.0265(8)
Bi(1B)-I(2)	3.0921(9)
Bi(1B)-I(4)#3	3.263(10)

Bi(1B)-I(3)#1	3.487(16)
Bi(1B)-I(3)	3.771(16)
Bi(1)…Bi(1B)	0.5824(18)
I(3)…I(3)#1	0.28(3)
I(4)…I(4)#3	0.33(2)

C(5)-N(1)-C(1)-C(2)	-1(2)
C(6)-N(1)-C(1)-C(2)	-179.5(16)
N(1)-C(1)-C(2)-C(3)	2(3)
C(1)-C(2)-C(3)-C(4)	-2(3)
C(1)-C(2)-C(3)-C(9)	179.8(16)
C(2)-C(3)-C(4)-C(5)	1(3)
C(9)-C(3)-C(4)-C(5)	179.6(16)
C(1)-N(1)-C(5)-C(4)	0(2)
C(6)-N(1)-C(5)-C(4)	178.9(16)
C(3)-C(4)-C(5)-N(1)	-1(3)
C(5)-N(1)-C(6)-C(7)	107.9(16)
C(1)-N(1)-C(6)-C(7)	-73.7(17)
N(1)-C(6)-C(7)-C(8)	-60.9(16)
C(6)-C(7)-C(8)-C(7)#3	-176.9(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,z #2 -x,y,-z+1 #3 -x,-y,z

3

Bi(1)-I(7)	2.8834(5)
Bi(1)-I(6)	2.8939(5)
Bi(1)-I(4)	3.0379(5)
Bi(1)-I(5)	3.1294(5)
Bi(1)-I(3)#1	3.3318(5)
Bi(1)-I(3)	3.3508(5)
Bi(2)-I(8)	2.9155(5)
Bi(2)-I(10)	2.9200(5)
Bi(2)-I(9)	2.9264(5)
Bi(2)-I(5)#1	3.2654(5)

Bi(2)-I(4)	3.2723(5)
Bi(2)-I(3)	3.3618(5)

C(5)-N(1)-C(1)-C(2)	-0.9(10)
C(6)-N(1)-C(1)-C(2)	-174.7(7)
N(1)-C(1)-C(2)-C(3)	1.1(11)
C(1)-C(2)-C(3)-C(4)	-1.0(10)
C(1)-C(2)-C(3)-C(16)	177.8(7)
C(2)-C(3)-C(4)-C(5)	0.9(10)
C(16)-C(3)-C(4)-C(5)	-177.9(6)
C(1)-N(1)-C(5)-C(4)	0.9(10)
C(6)-N(1)-C(5)-C(4)	174.6(6)
C(3)-C(4)-C(5)-N(1)	-0.9(10)
C(1)-N(1)-C(6)-C(7)	88.3(7)
C(5)-N(1)-C(6)-C(7)	-85.4(7)
N(1)-C(6)-C(7)-C(8)	-173.7(6)
C(6)-C(7)-C(8)-C(9)	-167.5(6)
C(7)-C(8)-C(9)-C(10)	77.4(7)
C(11)-N(2)-C(10)-C(9)	-69.4(8)
C(15)-N(2)-C(10)-C(9)	111.9(8)
C(8)-C(9)-C(10)-N(2)	-178.8(6)
C(15)-N(2)-C(11)-C(12)	-1.0(11)
C(10)-N(2)-C(11)-C(12)	-179.6(7)
N(2)-C(11)-C(12)-C(13)	2.5(12)
C(11)-C(12)-C(13)-C(14)	-2.1(11)
C(11)-C(12)-C(13)-C(17)	177.0(7)
C(12)-C(13)-C(14)-C(15)	0.3(11)
C(17)-C(13)-C(14)-C(15)	-178.8(7)
C(11)-N(2)-C(15)-C(14)	-0.9(11)
C(10)-N(2)-C(15)-C(14)	177.7(7)
C(13)-C(14)-C(15)-N(2)	1.2(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

Table S2. Optimized atomic coordinates of structure **2** (copy of VASP CONTCAR file)

KOTOV27-MODEL1 CRYSTAL
1.00000000000000
12.2018000000000004 0.0000000000000000 0.0000000000000000
0.0000000000000000 13.4498999999999995 0.0000000000000000
0.0000000000000000 0.0000000000000000 16.2572000000000010
Bi I N C H
4 20 8 68 96
Direct
0.5000063935729531 0.2272074272775614 -0.0000153605535187
0.0000104708819096 0.7272326107032810 0.4999789519679056
0.4999052946488904 0.7281431415680338 -0.0000356379248280
0.0000002639026724 0.2273285238639269 0.5000301158152481
0.5749085779863283 0.2707918353070367 0.1775370127679931
0.5000084045514448 0.5071870589617181 0.0000185969642260
0.4252210448164261 0.2708305496978619 0.8224528858820083
0.2567876188089501 0.2248309658134649 0.0563023014264346
0.7432508159367721 0.2247954514966573 0.9436844415538613
0.5001148513509922 0.0060274427760025 0.0000010601415572
0.9252181396984981 0.7708346391242812 0.3224506702840736
0.0749088599485169 0.7707882095677450 0.6775393839379271
0.2433145355269191 0.7245631596895258 0.4436207789492610
0.7567967036037483 0.7250210386367651 0.5561684390810012
-0.0010597738736570 0.5062744456687683 0.4999987548751698
0.9210392060960912 0.2292157178958971 0.6794284032635830
0.0789433850208649 0.2292061578952393 0.3205822350902415
0.2377660193013962 0.2724157738258522 0.5559666639552100
0.7619291258100053 0.2721728191708347 0.4445526599456991
0.0001571547432878 0.0064505502010944 0.5006546065507952
0.4214172481685296 0.7292239130364935 0.1793856267545020
0.5789280958352745 0.7292536773535696 0.8205559872764515
0.2613049137927317 0.7719225272300128 0.9447704984418261
0.7380925968589034 0.7722264516923959 0.0553835455128986
0.7727563690967448 0.9421566473802331 0.7755841287049473

0.2274587801028577 0.0577711808701152 0.7762186363700309
0.7726980828919929 0.0578216207460476 0.2238288374922640
0.2272805011565251 0.9421236585431139 0.2244056353664010
0.2727038275693264 0.4421372531197852 0.2756464214494818
0.7273665262028055 0.5577439660727932 0.2761379531983966
0.7272227870611736 0.4421800287714281 0.7244130972130934
0.2725527725064963 0.5578933831068318 0.7237396577441160
0.3099375081133811 0.0025691306716448 0.8079763841755858
0.1898211528909383 0.4970057459240780 0.3071914340703775
0.2943476255715785 0.4442371002045337 0.1940021255509541
0.8098897688283154 0.5025725056838346 0.3078547063388647
0.1259566852117451 0.5560115146561827 0.2569895645417518
0.8736789868078501 0.4432706842210933 0.2578224672724682
0.8543870675256533 0.4395715417041655 0.1728812391988801
0.1453525931040042 0.5596470528380875 0.1720911306342481
0.2319421489753164 0.5019212503436580 0.1416571466987036
0.7677680046702726 0.4971848505346824 0.1423373129301654
0.7055927180741604 0.5552313457192700 0.1945459012616593
0.6606457798185423 0.6202174790461547 0.3320936388188081
0.3738897590060727 0.0561451126852811 0.2430789975847525
0.2681260526187063 0.0017513722578210 0.3584247495529774
-0.0001755977334786 0.0000465371543582 0.1673780556743620
0.4223244147168024 0.1231344990653895 0.3838017925076747
0.6263151733323221 0.9434268028365680 0.2421130291284526
0.3545825485014767 0.0596393439822713 0.3279929498768433
0.7323549561438698 0.9971237851693915 0.3576013127820155
0.2057361733902192 0.9440724276239412 0.3060648341710687
0.7945230667046216 0.0552031495117526 0.3054129110114684
0.8394626720003704 0.1202794148345934 0.1678926343194765
0.1605185560993696 0.8801654283944226 0.1680760833716890
0.9178067779497810 0.0584331643200881 0.1157739599509230
0.0826251254796932 0.9424286236063983 0.1159015497211824
0.5776723640965856 0.8763151429225614 0.3828194151349287
0.6899880089310094 -0.0028389946414885 0.8071306465593449
0.1455131880079049 0.4396244862926033 0.8269043787941028

0.8545762292219301 0.5596516724352776 0.8279943023345374
0.2321387175586350 0.4971956113229382 0.8574923089812747
0.7681218220962915 0.5017637052858759 0.8584321641368360
0.2943166147919906 0.5553011783283407 0.8053346880787196
0.7057072404363348 0.4441006416099714 0.8060756903461925
0.3393770675858548 0.6203427577822099 0.6678392825508824
0.6604719466220216 0.3802381741386027 0.6680679627948156
0.4177713446085431 0.5585011651710411 0.6157634073684310
0.5825783933476774 0.4425200448926617 0.6159133734895912
0.4997407738549541 0.5000882272979678 0.6673899234082299
0.9223438632923584 0.6231356214789525 0.8837868992025815
0.0775353950098729 0.3763195075919152 0.8826847913659530
0.3737375559710246 0.9432484891755477 0.7579638579298883
0.6261395942600942 0.0561682949834847 0.7569196082936848
0.7318910948854358 0.0017798902474456 0.6415689408853893
0.2679779659419846 0.9972464976335667 0.6424299913525772
0.7942908349934091 0.9441014111445298 0.6939249108356810
0.8395232948887569 0.8802139776256733 0.8319189003419202
0.1606737021631398 0.1202509265739083 0.8321257047110742
0.0822478642905427 0.0584543276647403 0.8842131259307446
0.9174216586897503 0.9424891044965561 0.8840765856072821
0.0002446598791015 0.0000685558438396 0.8325956392324617
0.5777045804116705 0.1231901186858161 0.6162184996945904
0.4224791848231874 0.8762789222747965 0.6172151643752324
0.3100453210086186 -0.0028654839111322 0.1928628877933972
0.6901058307781631 0.0027466209465947 0.1920955929153814
0.3394971299217792 0.3801858233431618 0.3319593250697703
0.4174063524923248 0.4424548861868955 0.3841126447335543
0.5822633793192580 0.5584134435660908 0.3842158349555900
0.5001967464816028 0.5000662124438605 0.3326228399350974
0.0775422816966038 0.6231282177570671 0.1163292484851454
0.9223627371055335 0.3763064022854464 0.1170726748052760
0.8099666856133685 0.4972094942346890 0.6928648057173231
0.1899962659240960 0.5027944671151692 0.6919762894848862
0.8738413849207609 0.5561908638074091 0.7430749715942493

0.1262063193673579 0.4434366851036676 0.7419701266183818
0.6454385129746284 0.0596674292325485 0.6720058005574999
0.3545189879085333 0.9395728282380502 0.6730116640344722
0.6456687308877236 0.9396033429010063 0.3270417079675044
0.2057689963124128 0.0552937668025712 0.6946137540956253
0.3229441741581472 0.0079121890351991 0.8740748310753005
0.1765640163600733 0.4916515448749347 0.3732515085049812
0.3626656828319492 0.3987386564377457 0.1729481244717694
0.8229667368160454 0.5079430860625505 0.3739432796333787
0.0609348891051006 0.6003179872445742 0.2847996956209301
0.9384943750628298 0.3988489082200906 0.2858228115603826
0.2532060520247895 0.5019450670376444 0.0766150055663671
0.7464217385683876 0.4969094451922249 0.0773063377220741
0.6372912880349290 0.6007127335738147 0.1734956864250714
0.6156193610764542 0.6727583335566665 0.2930228819263500
0.7181027764416902 0.6622298826675416 0.3707776537711032
0.4388200030826971 0.1005596927903203 0.2152660813029013
0.2469463698945826 0.0016421805525147 0.4234819159555275
0.0430572470829981 0.0521572825181459 0.2084582227037370
0.4857453645861254 0.1642014460572475 0.3501903602598713
0.3697624194836334 0.1758216825459490 0.4175203596957700
0.4627921260801084 0.0775329984430807 0.4310396415254314
0.5614416084642920 0.8990822425592231 0.2141096313790684
0.7537428591297378 0.9967414512278941 0.4226254649147796
0.1375088996230009 0.8984594139174199 0.3271165187989984
0.8628598265156451 0.1006384134018861 0.3264624736695148
0.8845143786466642 0.1727916294589182 0.2069733007032318
0.7820337982754072 0.1623251483819584 0.1292105567049143
0.1152092258461367 0.8274928516766608 0.2068306674016716
0.2180812062158215 0.8382269676062528 0.1294233258309487
0.8706436757589253 0.0080866714543535 0.0756303261067266
0.9606569920251885 0.1107666926543222 0.0747184520233450
0.1300843998629786 0.9934923050206590 0.0765778056642655
0.0404673994320111 0.8904633375149427 0.0741158090859799
0.5151065863335207 0.8343794261591686 0.3490469214706853

0.5359669702523212 0.9223347463961745 0.4291765652262522
0.6301103413083129 0.8245287246867696 0.4175830614082315
0.6768125345019781 0.9919206857339922 0.8732054813544748
0.2534784158636172 0.4968379337601769 0.9225248437243880
0.7469564620567082 0.5016551347494439 0.9234907630378113
0.3626228413542303 0.6007523053512316 0.8264183903086317
0.6374796182456769 0.3984917918454556 0.8271308765300632
0.3843930293651109 0.6728522342813641 0.7069452762615959
0.2819951140702006 0.6623902851297850 0.6291205241430400
0.6151785219763866 0.3275291819836660 0.7067991822232520
0.7180467157588365 0.3383346484440042 0.6293995353129399
0.3706452270538029 0.5081704104877697 0.5755816836061528
0.4606727053630530 0.6108402377773972 0.5747410147687554
0.6300400336473398 0.4936263871969765 0.5766287848724115
0.5404461633500960 0.3905812947433550 0.5740892157918448
0.4558857166092692 0.4473971636173287 0.7075908113784493
0.5429461558129670 0.5521740850929264 0.7085088600546747
0.9857683912018570 0.6641876399909783 0.8501675128383029
0.9627995796780965 0.5775485973417408 0.9310395098066115
0.8697895291974199 0.6758363465485444 0.9174995633935505
0.0150103253492614 0.3343365749137119 0.8489104064568618
0.0357860020240111 0.4223418199901766 0.9290174346430492
0.1299913012231775 0.3245698427374071 0.9174698224783493
0.4385182255437893 0.8987985320596966 0.7859816512452589
0.7530693559894086 0.0016803335772713 0.5765126697789972
0.8848186445743892 0.8275174230208504 0.7931765242616772
0.7819573307599953 0.8382991132614768 0.8705865831303704
0.1156835183329881 0.1727790903246119 0.7930200550893980
0.2180844555032330 0.1622772032453037 0.8708384432389743
0.1293427880811887 0.0081055853895457 0.9243993784697693
0.0393752986118554 0.1108222389770972 0.9252279839014546
0.8699606235538334 0.9935823951646002 0.9233731919095076
0.9595626957719340 0.8905397188478450 0.9258865623951223
0.5143212388812032 0.1642863126797425 0.6498446611216271
0.5372027977930417 0.0776154899896973 0.5689807473613762

0.6302872296786908 0.1758530524448663 0.5824899314674702
0.4849907942482063 0.8342682079932461 0.6509792579531714
0.4642415432470893 0.9223056480585698 0.5708919821517425
0.3700008588316688 0.8245563114976528 0.5824195031123760
0.3232290811147677 0.9918961539366182 0.1267876738858607
0.6769948258582781 0.0081893799233764 0.1260138341489224
0.3847922082026185 0.3275095130660602 0.2931964325997534
0.2819508632470528 0.3382489400957159 0.3706255023336222
0.3699510762450603 0.4935275789455277 0.4234308867083871
0.4595786260876927 0.3904986696227719 0.4258991110040891
0.6293921864095580 0.5080486228752984 0.4243663206295748
0.5394415567723329 0.6107740163779944 0.4252657730966757
0.5439873225548805 0.4474050660812500 0.2923563263756749
0.4569541211548540 0.5522028784753530 0.2915719335528318
0.0369864031875729 0.5775201723469264 0.0691380845425158
0.0141835561366537 0.6642139260083534 0.1499900237599609
0.1300616733792595 0.6757835564329884 0.0825398377056340
0.9849370814675221 0.3343558072584288 0.1508234649142228
0.9640491611407815 0.4223439340545794 0.0707188116003342
0.8231222810175139 0.4919963032082888 0.6267851726366784
0.1769211488301004 0.5082338458045130 0.6258886444094232
0.9387623929045330 0.6006105840567816 0.7152552113492480
0.0613768907814086 0.3990582814701094 0.7139416971462673
0.1375045017993159 0.1008018982152823 0.6735411934364834
0.0440760955547291 0.9473804365479471 0.7923789429549295
0.9570314586556828 0.0521695711940952 0.7914945300284199
0.9559914529520065 0.9473791514378422 0.2076131728323621
0.5612221133177114 0.1005913844418586 0.7847365452922569
0.8699108299599229 0.3245314209306603 0.0823086682327269
0.2467097289858326 0.9969960375880490 0.5773845517754277
0.8625268560454632 0.8985023240605355 0.6728705222209395

Energy = -1108.38709784 eV

Table S3. Optimized atomic coordinates of structure **3** (copy of VASP CONTCAR file)

kotov28 crystal

1.00000000000000

16.0487159999999989 0.0000000000000000 -4.9967750000000004

0.0000000000000000 12.0002999999999993 0.0000000000000000

0.0000000000000000 0.0000000000000000 17.7036000000000016

Bi I N C H

8 32 8 68 96

Direct

0.0787499793438312 0.4897579118251099 0.1371096284054582

0.4212500206561691 0.9897579118251103 0.3628903715945422

0.9212500206561680 0.5102420881748897 0.8628903715945410

0.5787499793438320 0.0102420881748899 0.6371096284054590

0.7835001566603729 0.5534472987727637 0.0651364553435943

0.7164998433396271 0.0534472987727644 0.4348635446564058

0.2164998433396264 0.4465527012272354 0.9348635446564049

0.2835001566603733 0.9465527012272363 0.5651364553435951

0.6640753895958376 0.3974633566198862 0.1024248041047302

0.8359246104041624 0.8974633566198853 0.3975751958952699

0.3359246104041626 0.6025366433801147 0.8975751958952700

0.1640753895958375 0.1025366433801133 0.6024248041047300

0.9475152666009902 0.6723606349643291 0.0229692397594143

0.5524847333990098 0.1723606349643289 0.4770307602405858

0.0524847333990102 0.3276393650356711 0.9770307602405854

0.4475152666009898 0.8276393650356709 0.5229692397594146

0.9237167609230837 0.3781775344228991 0.1629332440236115

0.5762832390769163 0.8781775344228986 0.3370667559763891

0.0762832390769157 0.6218224655771014 0.8370667559763882

0.4237167609230842 0.1218224655771012 0.6629332440236118

0.2338326851958288 0.5882195235831842 0.0968758906979459

0.2661673148041714 0.0882195235831840 0.4031241093020541

0.7661673148041711 0.4117804764168161 0.9031241093020542

0.7338326851958289 0.9117804764168158 0.5968758906979458

0.1799017415724770 0.3145810735859856 0.2373073019803944

0.3200982584275224 0.8145810735859856 0.2626926980196058

0.8200982584275229 0.6854189264140144 0.7626926980196052

0.6799017415724771 0.1854189264140138 0.7373073019803948
0.1072928154781966 0.6488097112997595 0.2672685949484780
0.3927071845218033 0.1488097112997589 0.2327314050515224
0.8927071845218048 0.3511902887002411 0.7327314050515233
0.6072928154781952 0.8511902887002405 0.7672685949484767
0.6505289441808330 0.6965864206448913 0.9627049001069966
0.8494710558191670 0.1965864206448907 0.5372950998930034
0.3494710558191669 0.3034135793551092 0.0372950998930035
0.1505289441808327 0.8034135793551087 0.4627049001069964
0.8088355440278292 0.7062036464382522 0.2023249251874578
0.6911644559721708 0.2062036464382523 0.2976750748125420
0.1911644559721704 0.2937963535617477 0.7976750748125434
0.3088355440278296 0.7937963535617478 0.7023249251874566
0.0033087793582797 0.2340269461668776 0.3844075383565201
0.4966912206417204 0.7340269461668779 0.1155924616434800
0.9966912206417203 0.7659730538331221 0.6155924616434796
0.5033087793582797 0.2659730538331225 0.8844075383565204
0.1406016863800522 0.9745329437463246 0.1119072008632984
0.3593983136199481 0.4745329437463239 0.3880927991367014
0.8593983136199478 0.0254670562536760 0.8880927991367016
0.6406016863800522 0.5254670562536754 0.6119072008632984
0.9255034836195315 0.2748068205065674 0.3719801590293571
0.5744965163804685 0.7748068205065668 0.1280198409706426
0.0744965163804683 0.7251931794934332 0.6280198409706423
0.4255034836195313 0.2251931794934325 0.8719801590293577
0.1204510290587614 0.9832331417139288 0.1877409711412486
0.3795489709412379 0.4832331417139286 0.3122590288587509
0.8795489709412391 0.0167668582860713 0.8122590288587515
0.6204510290587609 0.5167668582860712 0.6877409711412485
0.1346917067826593 0.8740216649868426 0.0757598753150533
0.3653082932173403 0.3740216649868422 0.4242401246849475
0.8653082932173403 0.1259783350131576 0.9242401246849463
0.6346917067826597 0.6259783350131574 0.5757598753150537
0.1535624717973857 0.8622218398735909 0.0054613576827056
0.3464375282026141 0.3622218398735915 0.4945386423172942

0.8464375282026142 0.1377781601264089 0.9945386423172952
0.6535624717973858 0.6377781601264091 0.5054613576827048
0.1810506435175487 0.9540162946252242 0.9708656982965986
0.3189493564824509 0.4540162946252239 0.5291343017034014
0.8189493564824495 0.0459837053747761 0.0291343017034021
0.6810506435175505 0.5459837053747758 0.4708656982965980
0.1873006947000893 0.0564317726502148 0.0102530625282393
0.3126993052999108 0.5564317726502149 0.4897469374717607
0.8126993052999109 0.9435682273497851 0.9897469374717601
0.6873006947000891 0.4435682273497855 0.5102530625282399
0.1669667061013601 0.0648785859592057 0.0802345291075334
0.3330332938986402 0.5648785859592054 0.4197654708924669
0.8330332938986408 0.9351214140407946 0.9197654708924677
0.6669667061013592 0.4351214140407947 0.5802345291075323
0.9654106276755323 0.5848341217070965 0.3980302475901204
0.5345893723244677 0.0848341217070966 0.1019697524098798
0.0345893723244675 0.4151658782929038 0.6019697524098797
0.4654106276755320 0.9151658782929035 0.8980302475901203
0.2043311397415715 0.9416711133989422 0.8960256310168037
0.2956688602584283 0.4416711133989421 0.6039743689831963
0.7956688602584269 0.0583288866010578 0.1039743689831966
0.7043311397415731 0.5583288866010578 0.3960256310168035
0.9121389619797985 0.3876249602433303 0.3772432452719705
0.5878610380202015 0.8876249602433310 0.1227567547280300
0.0878610380202006 0.6123750397566690 0.6227567547280299
0.4121389619797990 0.1123750397566694 0.8772432452719701
0.9790359269867036 0.4624979071306153 0.3952824524636152
0.5209640730132964 0.9624979071306144 0.1047175475363856
0.0209640730132970 0.5375020928693856 0.6047175475363863
0.4790359269867026 0.0375020928693851 0.8952824524636137
0.0591273578306680 0.4171977655248681 0.4080340464474850
0.4408726421693321 0.9171977655248681 0.0919659535525148
0.9408726421693335 0.5828022344751319 0.5919659535525159
0.5591273578306665 0.0828022344751318 0.9080340464474841
0.0698323951897538 0.3037723779518206 0.4023220412505877

0.4301676048102460 0.8037723779518203 0.0976779587494120
0.9301676048102460 0.6962276220481797 0.5976779587494119
0.5698323951897540 0.1962276220481794 0.9023220412505881
0.0140279871243660 0.1140109679707094 0.3700695577081711
0.4859720128756341 0.6140109679707094 0.1299304422918291
0.9859720128756340 0.8859890320292906 0.6299304422918288
0.5140279871243660 0.3859890320292914 0.8700695577081712
0.0107393216855960 0.0975347438266004 0.2837064332570444
0.4892606783144039 0.5975347438266017 0.2162935667429557
0.9892606783144036 0.9024652561733983 0.7162935667429567
0.5107393216855964 0.4024652561734002 0.7837064332570433
0.0125077750406617 0.9753295574860571 0.2599127348973241
0.4874922249593381 0.4753295574860577 0.2400872651026761
0.9874922249593383 0.0246704425139421 0.7400872651026754
0.5125077750406617 0.5246704425139429 0.7599127348973246
0.0285536862500007 0.9626304582561905 0.1793598861843056
0.4714463137499992 0.4626304582561907 0.3206401138156948
0.9714463137499996 0.0373695417438093 0.8206401138156956
0.5285536862500004 0.5373695417438095 0.6793598861843044
0.1407142715842334 0.0663484238906626 0.2114464407562771
0.3592857284157672 0.5663484238906620 0.2885535592437232
0.8592857284157662 0.9336515761093380 0.7885535592437224
0.6407142715842338 0.4336515761093370 0.7114464407562776
0.1596278497730476 0.9217716692136463 0.2281210687742980
0.3403721502269520 0.4217716692136463 0.2718789312257021
0.8403721502269519 0.0782283307863537 0.7718789312257018
0.6596278497730481 0.5782283307863537 0.7281210687742982
0.1150994014712105 0.8044350830460478 0.1054758709644463
0.3849005985287899 0.3044350830460466 0.3945241290355537
0.8849005985287892 0.1955649169539538 0.8945241290355528
0.6150994014712108 0.6955649169539522 0.6054758709644472
0.1472083850286380 0.7800697181491646 0.9780292652843984
0.3527916149713614 0.2800697181491640 0.5219707347156016
0.8527916149713619 0.2199302818508362 0.0219707347156009
0.6472083850286381 0.7199302818508354 0.4780292652843991

0.2086828173811888 0.1311383112233165 0.9871075473215183
0.2913171826188112 0.6311383112233153 0.5128924526784817
0.7913171826188115 0.8688616887766847 0.0128924526784837
0.7086828173811885 0.3688616887766837 0.4871075473215163
0.1714781664064110 0.1427732366171506 0.1129600719552380
0.3285218335935891 0.6427732366171508 0.3870399280447622
0.8285218335935871 0.8572267633828492 0.8870399280447615
0.6714781664064129 0.3572267633828494 0.6129600719552385
0.0186746794330767 0.6272803034003001 0.4391152695657405
0.4813253205669233 0.1272803034002998 0.0608847304342592
0.9813253205669232 0.3727196965996997 0.5608847304342591
0.5186746794330768 0.8727196965996999 0.9391152695657409
0.9086110321479910 0.6044690516087459 0.4137129321433273
0.5913889678520090 0.1044690516087455 0.0862870678566725
0.0913889678520076 0.3955309483912547 0.5862870678566732
0.4086110321479924 0.8955309483912541 0.9137129321433268
0.9577483521451879 0.6204661407010149 0.3388568933017874
0.5422516478548121 0.1204661407010157 0.1611431066982124
0.0422516478548122 0.3795338592989842 0.6611431066982102
0.4577483521451876 0.8795338592989851 0.8388568933017898
0.2021895051644757 0.0216351866334747 0.8653727239398387
0.2978104948355243 0.5216351866334744 0.6346272760601613
0.7978104948355249 0.9783648133665256 0.1346272760601618
0.7021895051644751 0.4783648133665251 0.3653727239398388
0.1639401195778812 0.8811235406253911 0.8560044733680773
0.3360598804221187 0.3811235406253914 0.6439955266319227
0.8360598804221187 0.1188764593746089 0.1439955266319227
0.6639401195778813 0.6188764593746090 0.3560044733680781
0.2679219591921066 0.9077373735488331 0.9092046758610072
0.2320780408078928 0.4077373735488333 0.5907953241389928
0.7320780408078934 0.0922626264511665 0.0907953241389930
0.7679219591921066 0.5922626264511669 0.4092046758610062
0.8745243796138753 0.2148859904090754 0.3567563076896114
0.6254756203861247 0.7148859904090756 0.1432436923103952
0.1254756203861250 0.7851140095909244 0.6432436923103886

0.3745243796138751 0.2851140095909244 0.8567563076896114
0.8482029590446482 0.4162391949660333 0.3660983488559955
0.6517970409553518 0.9162391949660322 0.1339016511440040
0.1517970409553525 0.5837608050339678 0.6339016511440035
0.3482029590446475 0.0837608050339672 0.8660983488559965
0.1135967777320198 0.4713098878998863 0.4212203214209474
0.3864032222679798 0.9713098878998860 0.0787796785790523
0.8864032222679807 0.5286901121001140 0.5787796785790532
0.6135967777320193 0.0286901121001139 0.9212203214209468
0.1304260715756454 0.2648386773753934 0.4109494324402629
0.3695739284243544 0.7648386773753938 0.0890505675597369
0.8695739284243550 0.7351613226246062 0.5890505675597369
0.6304260715756450 0.2351613226246069 0.9109494324402631
0.9641863619713814 0.0685633244995757 0.3853376942339609
0.5358136380286186 0.5685633244995754 0.1146623057660398
0.0358136380286190 0.9314366755004246 0.6146623057660400
0.4641863619713809 0.4314366755004245 0.8853376942339600
0.0738570167085857 0.0870681319662079 0.4109079346684374
0.4261429832914143 0.5870681319662083 0.0890920653315624
0.9261429832914152 0.9129318680337917 0.5890920653315622
0.5738570167085848 0.4129318680337923 0.9109079346684378
0.0631311943334817 0.1438521132372244 0.2734252846367796
0.4368688056665180 0.6438521132372249 0.2265747153632201
0.9368688056665179 0.8561478867627751 0.7265747153632207
0.5631311943334821 0.3561478867627749 0.7734252846367793
0.9539558136895229 0.1376688952360041 0.2457108378932178
0.5460441863104771 0.6376688952360033 0.2542891621067823
0.0460441863104780 0.8623311047639967 0.7542891621067829
0.4539558136895220 0.3623311047639959 0.7457108378932171
0.0608619848698108 0.9295898019725508 0.3050811343382967
0.4391380151301896 0.4295898019725504 0.1949188656617030
0.9391380151301886 0.0704101980274499 0.6949188656617025
0.5608619848698114 0.5704101980274492 0.8050811343382975
0.9530729580472984 0.9349689127408973 0.2577356387138977
0.5469270419527016 0.4349689127408972 0.2422643612861022

0.0469270419527019 0.0650310872591025 0.7422643612861015

0.4530729580472982 0.5650310872591027 0.7577356387138985

0.0110809418052868 0.8779329187879051 0.1565882950711209

0.4889190581947130 0.3779329187879049 0.3434117049288794

0.9889190581947125 0.1220670812120947 0.8434117049288806

0.5110809418052875 0.6220670812120949 0.6565882950711194

0.9895960554251089 0.0213540198539986 0.1360152314016723

0.5104039445748911 0.5213540198539978 0.3639847685983277

0.0104039445748911 0.9786459801460022 0.8639847685983263

0.4895960554251086 0.4786459801460012 0.6360152314016737

Energy = -1153.69658729 eV