Supplementary materials

CrystEngComm

Thermal decomposition of DMSO or DMF solvates: an advanced method for obtaining new hybrid bismuth(III) halides

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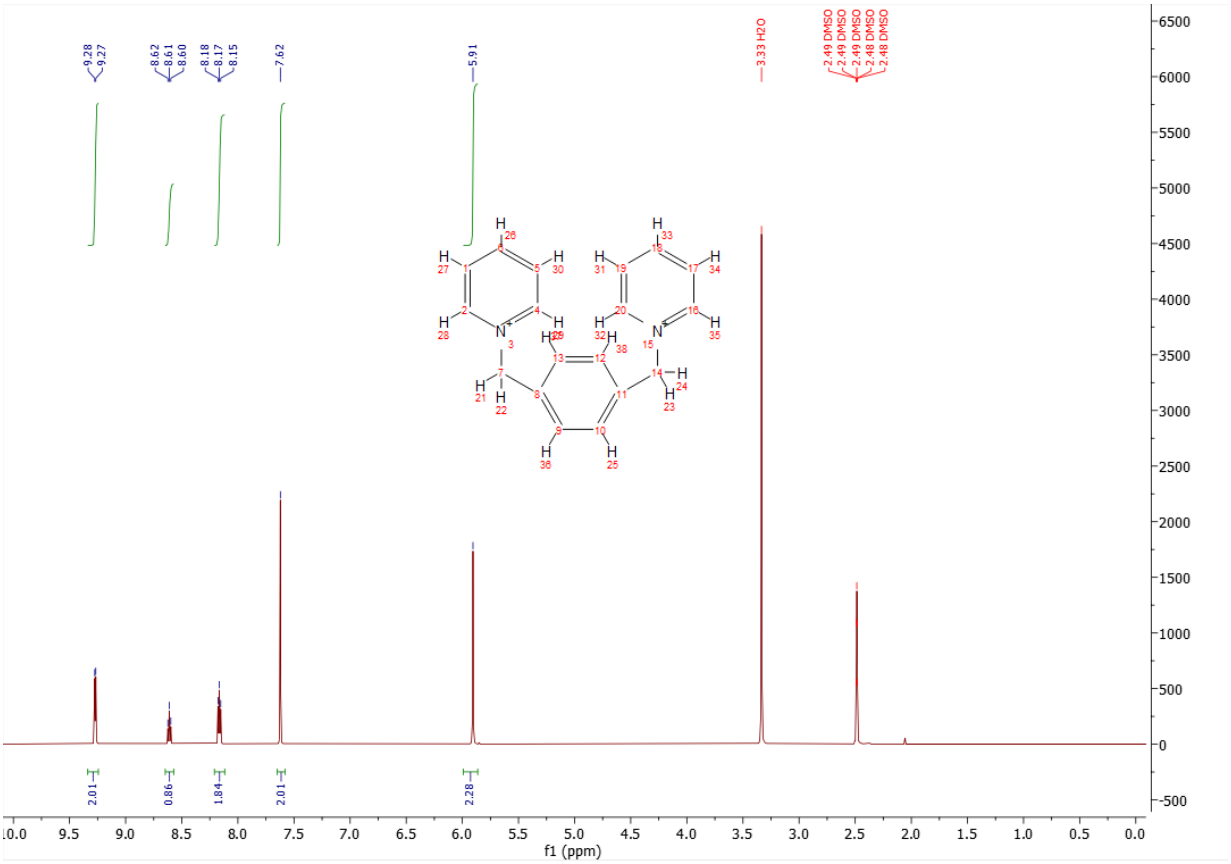
Table 1. Crystal data and structure refinement for bromide, iodide and **I-VIII**, **X**.

Identification code	$[Py_2(XK)]Br_2$	$[Py_2(XK)]I_2$	**I**	**II**	**III**
Empirical formula	$C_{20}H_{24}Br_2N_2O$	$C_{18}H_{18}I_2N_2$	$C_{42}H_{54}BiBr_7N_4O_3S_3$	$C_{42}H_{54}BiI_7N_4O_3S_3$	$C_{54}H_{54}Bi_2Br_{8.49}Cl_{3.51}N_6$
Formula weight	468.23	516.14	1527.42	1856.35	2007.85
Temperature/K	140	150(2)	100(2)	100(2)	140
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	Pbcm	$P2_1/c$	C2/m	C2/m	P-1
a/Å	12.7794(18)	6.8222(5)	16.5194(9)	16.9076(7)	12.790(3)
b/Å	8.1003(12)	11.0457(8)	14.5925(9)	15.1942(7)	14.769(4)
c/Å	19.956(3)	12.1817(9)	13.2748(7)	13.5491(6)	19.156(5)
α/°	90	90	90	90	67.593(5)
β/°	90	94.692(2)	125.2900(10)	125.4550(10)	73.276(5)
γ/°	90	90	90	90	80.529(7)
Volume/$Å^3$	2065.8(5)	914.89(12)	2612.0(3)	2835.3(2)	3197.5(13)
Z	4	2	2	2	2
$\rho_{calc}g/cm^3$	1.505	1.874	1.942	2.174	2.085
μ/mm^{-1}	3.934	3.436	8.889	7.068	10.987
F(000)	944	492	1468	1720	1886
Crystal size/mm^3	0.25 × 0.01 × 0.01	0.4 × 0.4 × 0.08	0.3 × 0.24 × 0.24	0.12 × 0.1 × 0.04	0.15 × 0.15 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.082 to 60.176	4.986 to 63.058	4.112 to 63.086	4.11 to 66.358	2.372 to 52.044
Index ranges	$-16 \le h \le 15$, $-6 \le k \le 11$, $-28 \le l \le 21$	$-10 \le h \le 10$, $-16 \le k \le 15$, $-17 \le l \le 17$	$-24 \le h \le 23$, $-21 \le k \le 21$, $-19 \le l \le 19$	$-26 \le h \le 25$, $-23 \le k \le 22$, $-20 \le l \le 20$	$-15 \le h \le 14$, $-18 \le k \le 18$, $-21 \le l \le 23$
Reflections collected	8538	14879	22807	25970	40876
Independent reflections	2992 [R_{int} = 0.0410, R_{sigma} = 0.0673]	3033 [R_{int} = 0.0386, R_{sigma} = 0.0291]	4494 [R_{int} = 0.0428, R_{sigma} = 0.0329]	5397 [R_{int} = 0.0262, R_{sigma} = 0.0215]	12597 [R_{int} = 0.0542, R_{sigma} = 0.0744]
Data/restraints/parameters	2992/0/123	3033/0/100	4494/18/162	5397/18/162	12597/5/718
Goodness-of-fit on F^2	1.04	1.115	0.993	0.971	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0806	R_1 = 0.0274, wR_2 = 0.0689	R_1 = 0.0259, wR_2 = 0.0579	R_1 = 0.0215, wR_2 = 0.0466	R_1 = 0.0487, wR_2 = 0.1086
Final R indexes [all data]	R_1 = 0.0610, wR_2 = 0.0846	R_1 = 0.0299, wR_2 = 0.0699	R_1 = 0.0315, wR_2 = 0.0601	R_1 = 0.0261, wR_2 = 0.0484	R_1 = 0.0721, wR_2 = 0.1182
Largest diff. peak/hole / e $Å^{-3}$	0.46/-0.52	1.16/-0.81	1.39/-1.65	0.79/-1.47	3.97/-2.59

Identification code	**IV**	**V**	**VI**	**VII**
Empirical formula	$C_{11}H_{15}BiBr_4NOS$	$C_{11}H_{15}BiI_4NOS$	$C_{30}H_{34}Bi_2I_9N_4O$	$C_{30}H_{34}BiI_6N_4O$
Formula weight	737.92	925.88	2026.67	1436.99
Temperature/K	140	140	100(2)	100.15
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1	P-1
a/Å	11.442(3)	11.7459(14)	10.4022(5)	11.0547(5)
b/Å	13.461(3)	14.2042(19)	12.5641(7)	13.7612(6)
c/Å	12.460(3)	12.5884(15)	19.9063(10)	13.8907(6)
α/°	90	90	94.466(2)	74.6500(10)
β/°	107.555(7)	106.018(4)	103.2530(10)	87.7940(10)
γ/°	90	90	112.5700(10)	72.9350(10)
Volume/Å^3	1829.8(8)	2018.7(4)	2298.2(2)	1946.28(15)
Z	4	4	2	2
ρ_{calc}g/cm^3	2.679	3.046	2.929	2.452
μ/mm^{-1}	18.476	14.948	13.719	9.316
F(000)	1340	1628	1786	1302
Crystal size/mm^3	0.12 × 0.07 × 0.05	0.08 × 0.07 × 0.01	0.2 × 0.16 × 0.12	0.22 × 0.14 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.24 to 52.03	4.2 to 52.034	4.384 to 63.19	4.232 to 63.112
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 16$, $-15 \le l \le 15$	$-14 \le h \le 14$, $-17 \le k \le 17$, $-15 \le l \le 15$	$-15 \le h \le 15$, $-18 \le k \le 18$, $-29 \le l \le 28$	$-16 \le h \le 16$, $-20 \le k \le 20$, $-20 \le l \le 20$
Reflections collected	18230	20088	53186	46406
Independent reflections	3599 [R_{int} = 0.0600, R_{sigma} = 0.0633]	3976 [R_{int} = 0.0668, R_{sigma} = 0.0581]	15231 [R_{int} = 0.0401, R_{sigma} = 0.0375]	12915 [R_{int} = 0.0282, R_{sigma} = 0.0261]
Data/restraints/parameters	3599/0/175	3976/0/175	15231/0/417	12915/0/396
Goodness-of-fit on F^2	1.034	1.026	1.089	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0323, wR_2 = 0.0752	R_1 = 0.0303, wR_2 = 0.0680	R_1 = 0.0258, wR_2 = 0.0576	R_1 = 0.0203, wR_2 = 0.0410
Final R indexes [all data]	R_1 = 0.0394, wR_2 = 0.0785	R_1 = 0.0401, wR_2 = 0.0714	R_1 = 0.0293, wR_2 = 0.0588	R_1 = 0.0229, wR_2 = 0.0417
Largest diff. peak/hole / e Å^{-3}	2.22/-0.90	1.02/-1.47	2.22/-1.86	1.46/-1.39

Identification code	**VIIa**	**VIII**	**X**
Empirical formula	$C_{120}H_{136}Bi_4I_{24}N_{16}O_4$	$C_{45}H_{57}BiI_7N_7O_3$	$C_{27}H_{28}BiBr_{4.11}Cl_{1.89}N_3$
Formula weight	5747.96	1841.25	998.93
Temperature/K	100.15	150(2)	100
Crystal system	orthorhombic	monoclinic	triclinic
Space group	$Pca2_1$	C2/m	P-1
a/Å	22.399(2)	17.3495(14)	9.4546(10)
b/Å	21.812(2)	14.7084(12)	13.2860(12)
c/Å	32.531(3)	13.8354(11)	13.9063(11)
α/°	90	90	81.087(3)
β/°	90	121.690(2)	76.125(4)
γ/°	90	90	69.233(4)
Volume/Å^3	15894(3)	3004.2(4)	1581.0(3)
Z	4	2	2
ρ_{calc}g/cm^3	2.402	2.035	2.098
μ/mm^{-1}	9.126	6.571	10.951
F(000)	10416	1708	940
Crystal size/mm^3	0.26 × 0.2 × 0.04	0.12 × 0.1 × 0.06	0.2 × 0.17 × 0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.892 to 52.044	4.73 to 54.202	3.288 to 61.194
Index ranges	-27 ≤ h ≤ 27, -26 ≤ k ≤ 26, -40 ≤ l ≤ 40	-22 ≤ h ≤ 22, -18 ≤ k ≤ 18, -17 ≤ l ≤ 17	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	216605	20006	62971
Independent reflections	31241 [R_{int} = 0.0624, R_{sigma} = 0.0438]	3441 [R_{int} = 0.0232, R_{sigma} = 0.0147]	9451 [R_{int} = 0.0816, R_{sigma} = 0.0653]
Data/restraints/parameters	31241/313/756	3441/18/142	9451/0/361
Goodness-of-fit on F^2	1.161	1.046	1.04
Final R indexes [I>=2σ (I)]	R_1 = 0.0751, wR_2 = 0.1617	R_1 = 0.0417, wR_2 = 0.1186	R_1 = 0.0384, wR_2 = 0.0546
Final R indexes [all data]	R_1 = 0.0934, wR_2 = 0.1753	R_1 = 0.0440, wR_2 = 0.1213	R_1 = 0.0698, wR_2 = 0.0633
Largest diff. peak/hole / e Å^{-3}	2.58/-5.85	1.43/-0.71	1.56/-1.00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8.61
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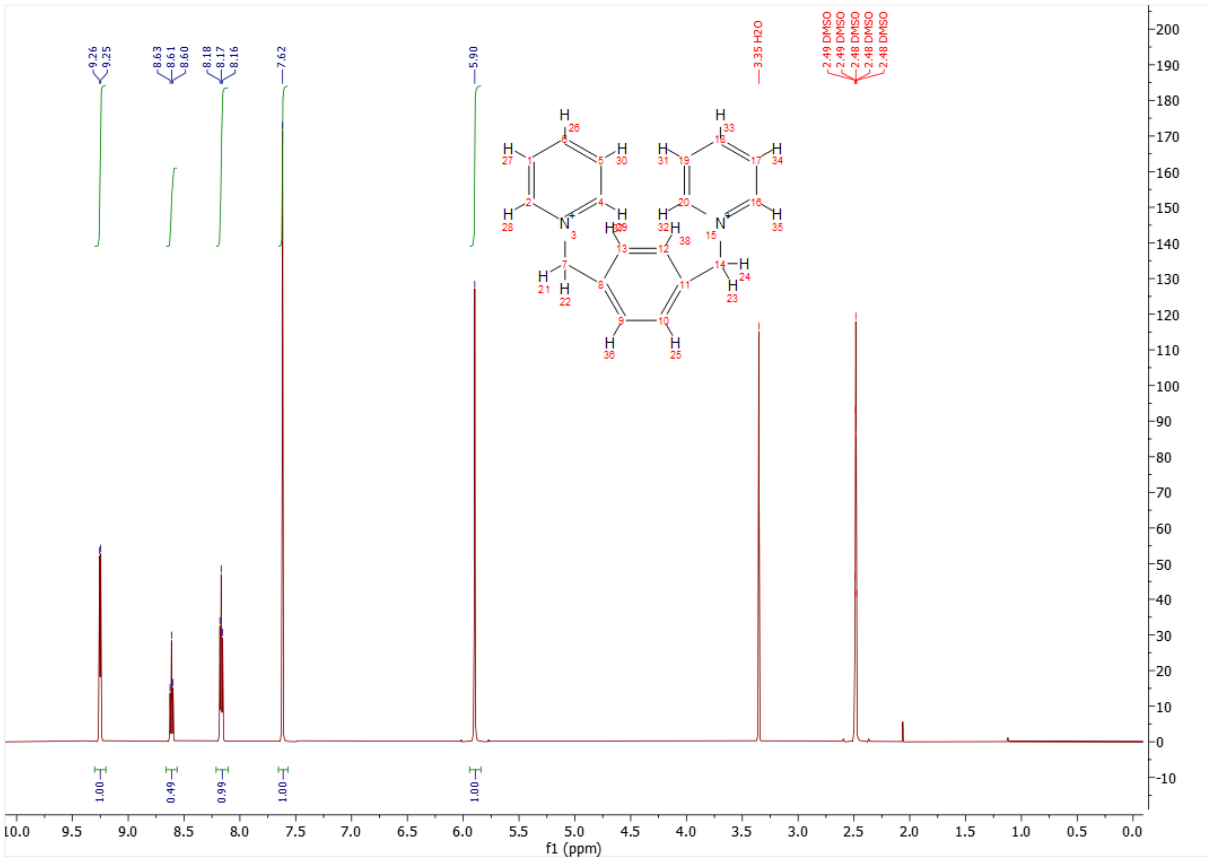
7.62
5.91
3.33 H2O
2.49 DMSO
2.49 DMSO
2.48 DMSO
2.48 DMSO
2.48 DMSO
2.01
0.86
1.84
2.01
2.28
f1 (ppm)

a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2.49 DMSO
2.49 DMSO
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2.48 DMSO
2.48 DMSO
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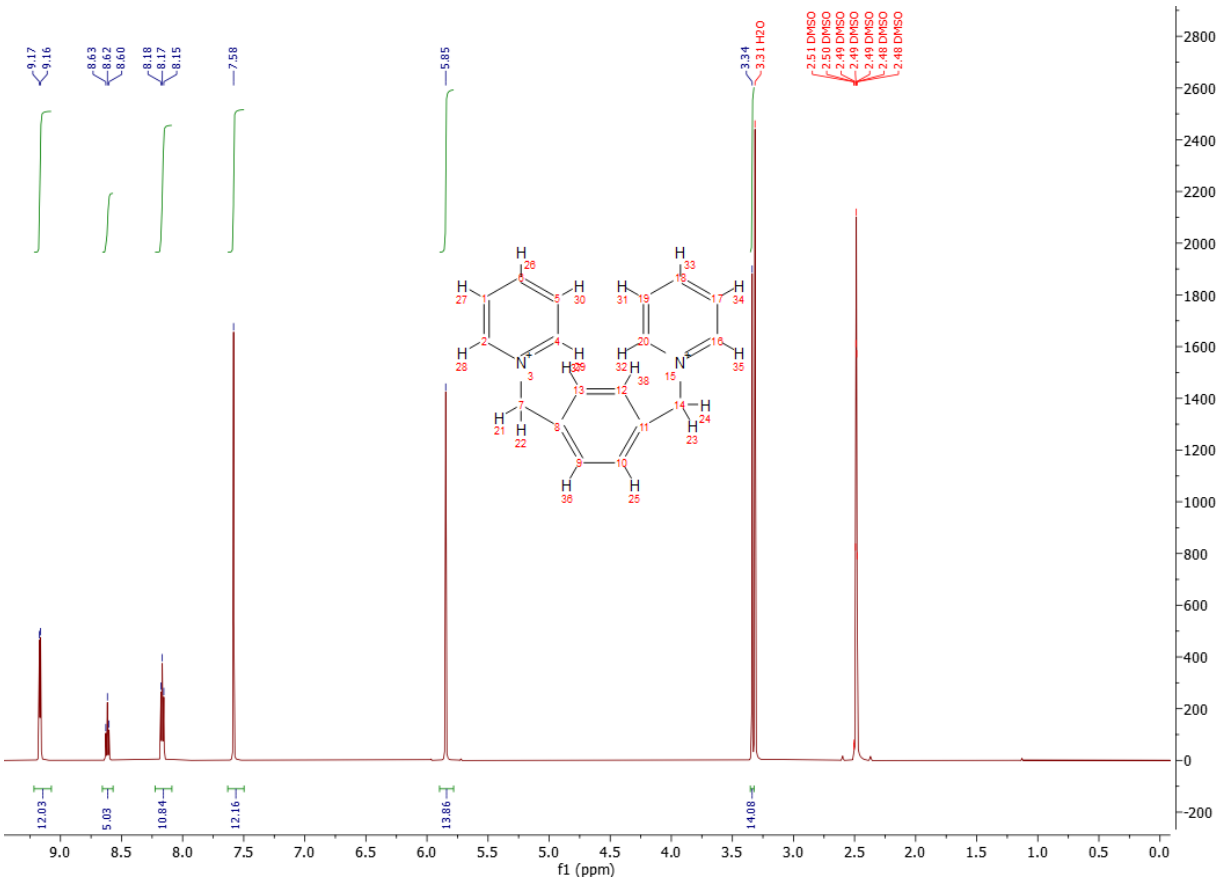
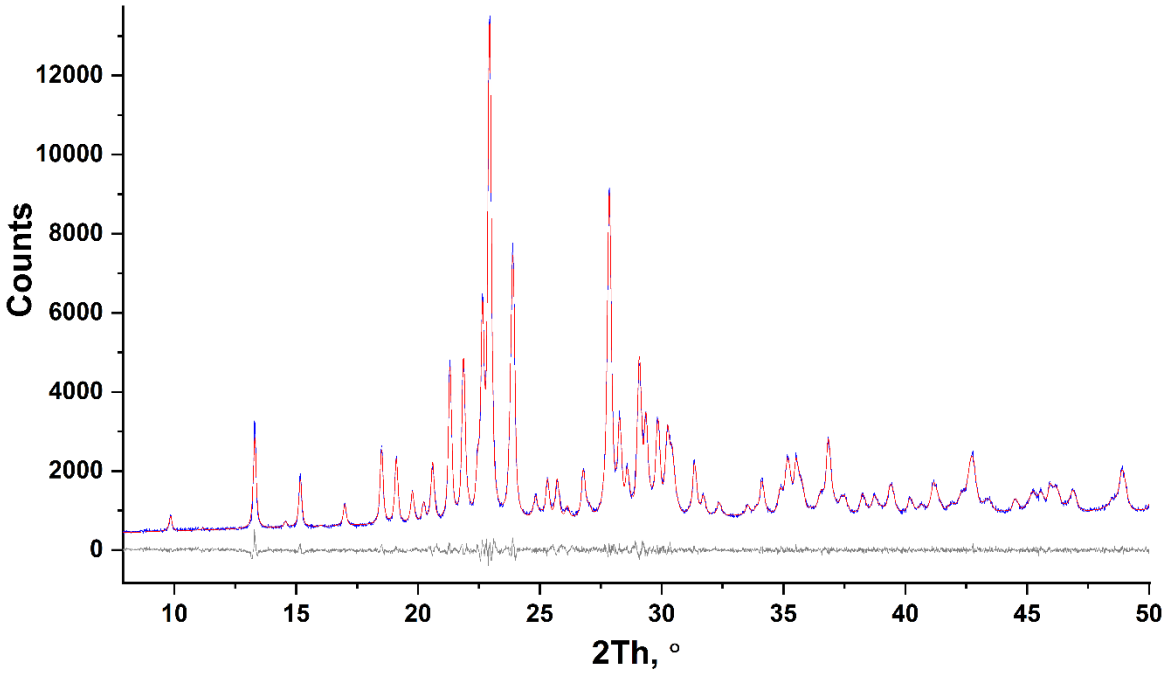
1.00
1.00
f1 (ppm)

b

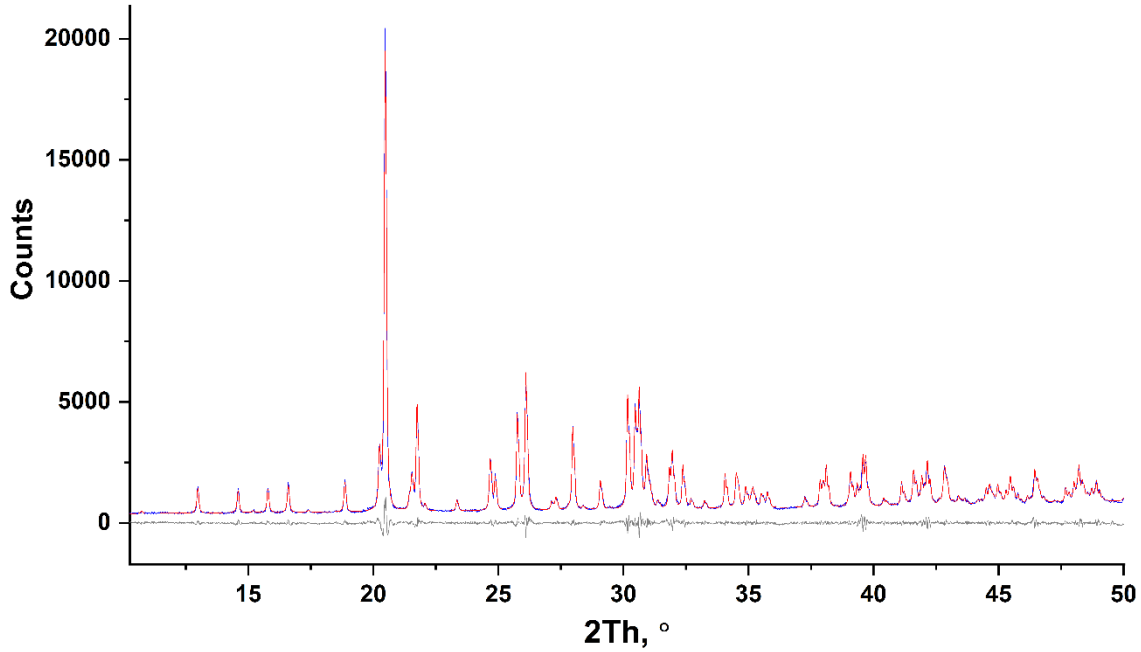


c

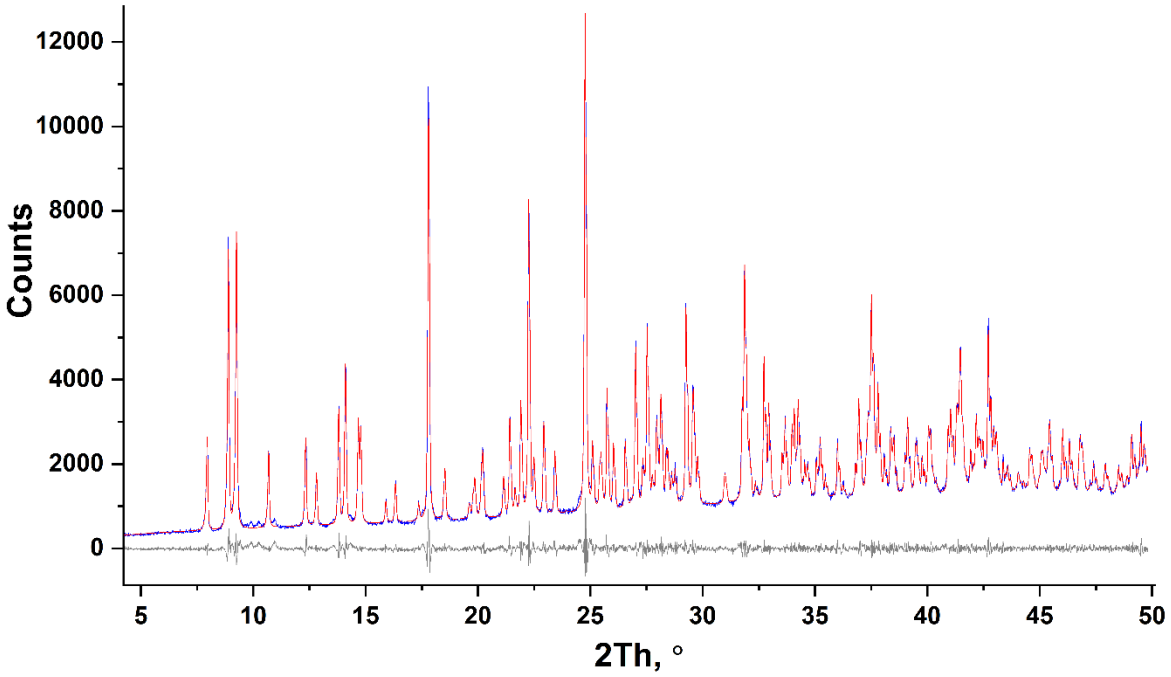
Fig. S1. ^{1}H NMR spectra of $[Py_2(XK)]Cl_2$ (a), $[Py_2(XK)]Br_2$ (b), $[Py_2(XK)]I_2$ (c).



a ($[Py_2(XK)]Br_2$)



b ($[Py_2(XK)]I_2$)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35
40
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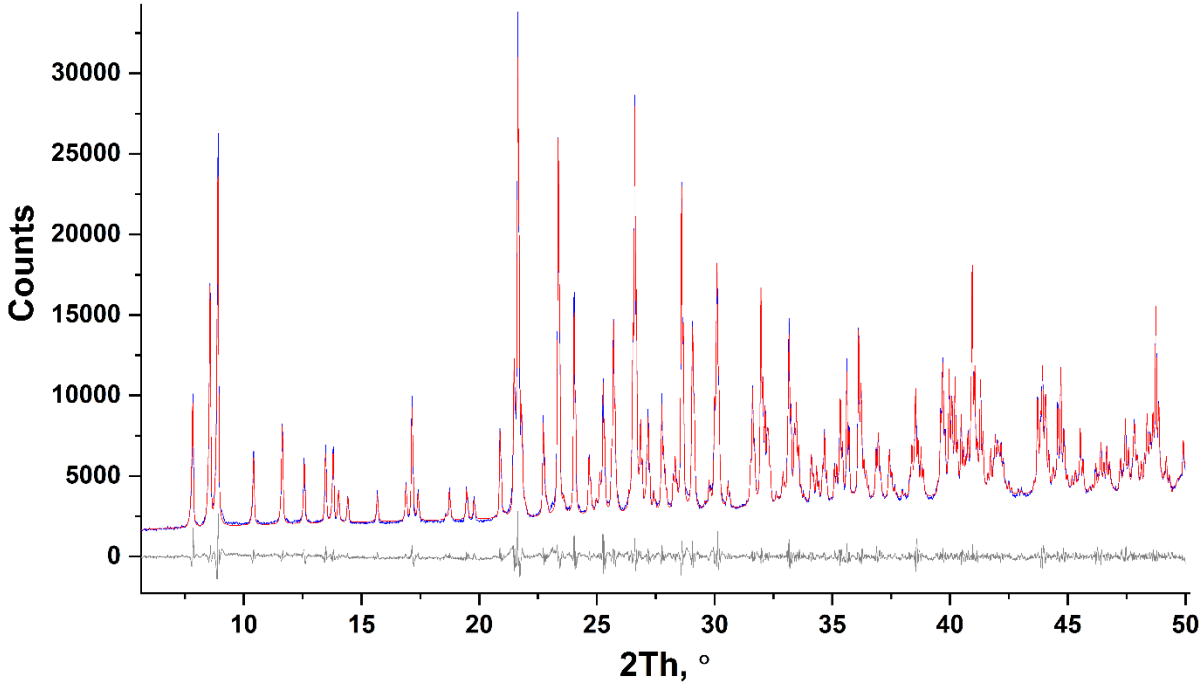
2Th, °

c (**I**)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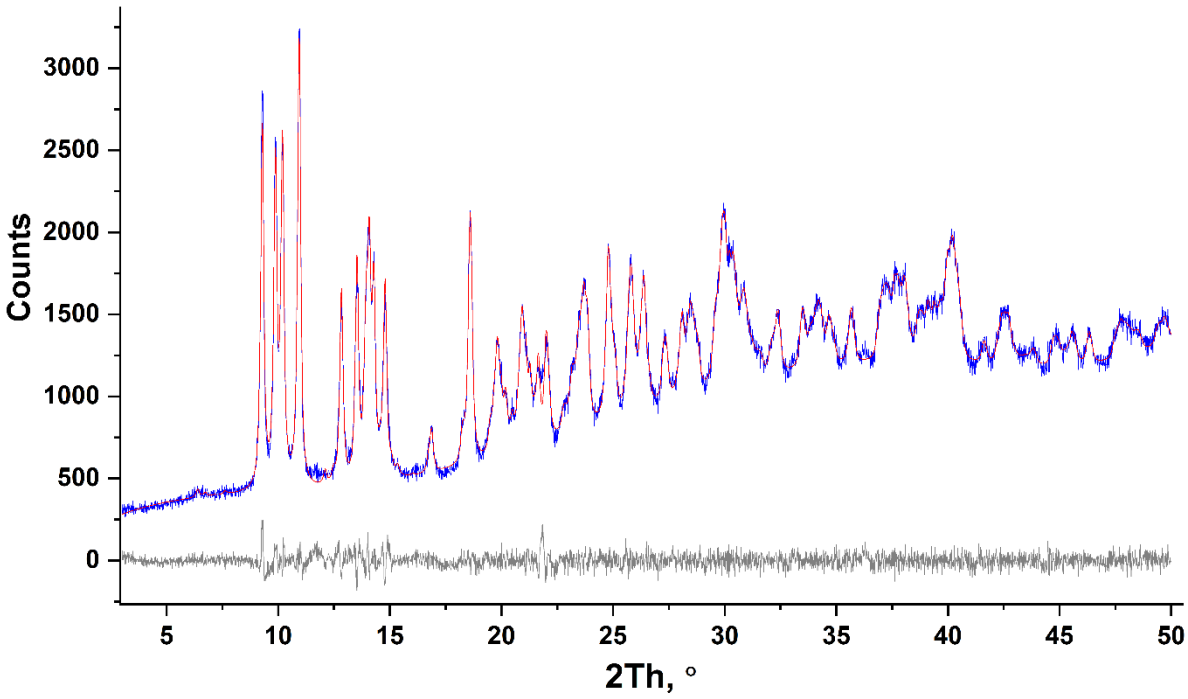
d (**II**)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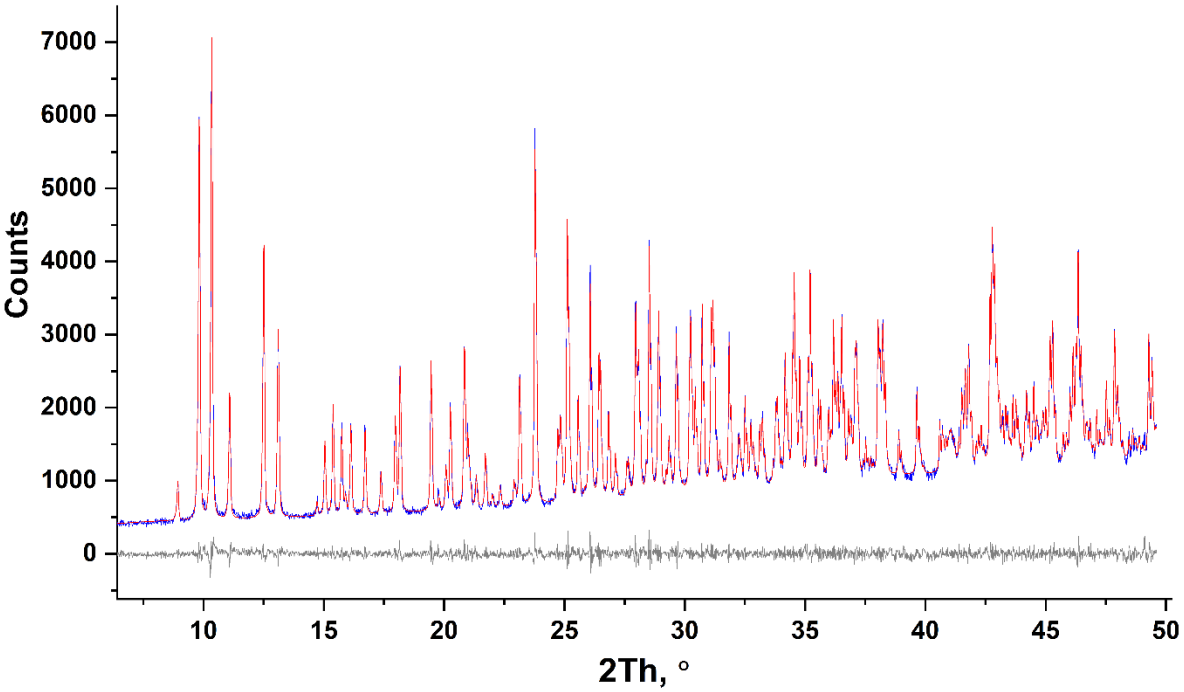
2Th, °

e (**III**)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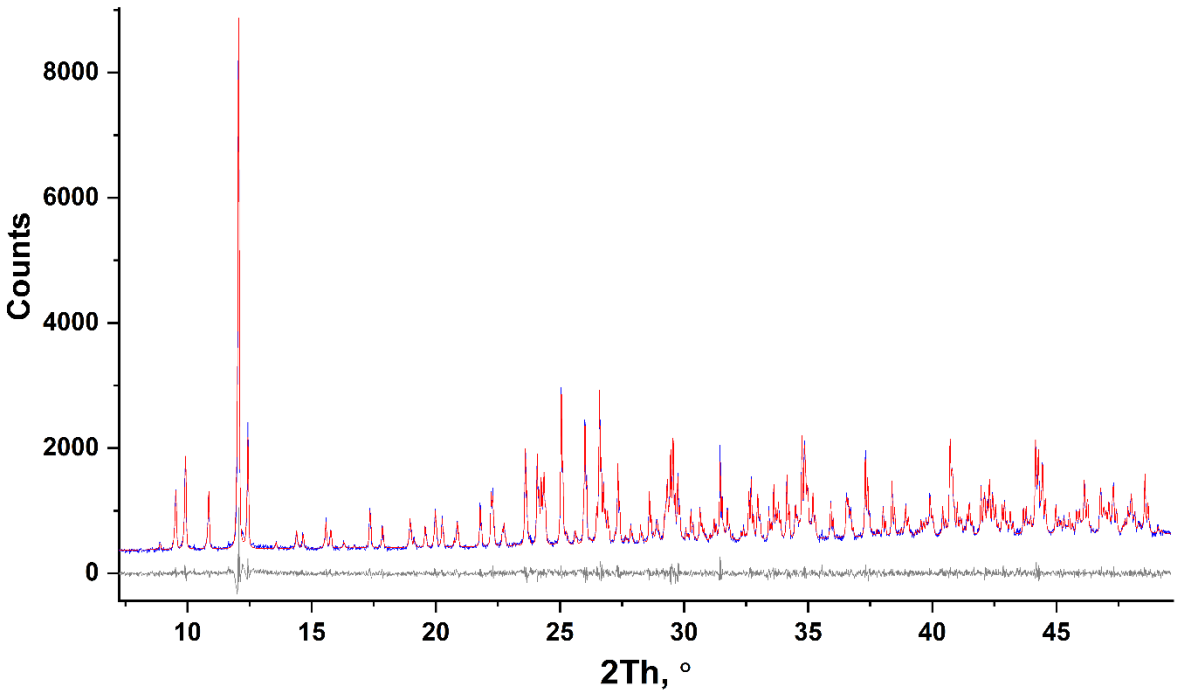
f (**IV**)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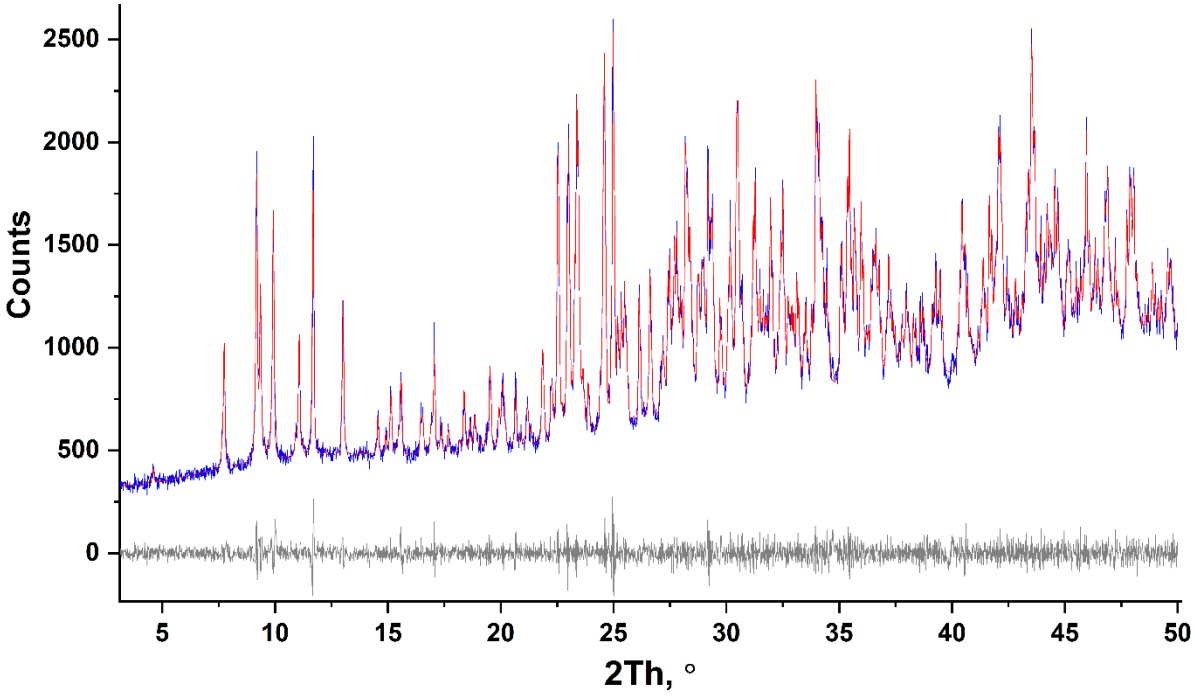
2Th, °

g (**V**)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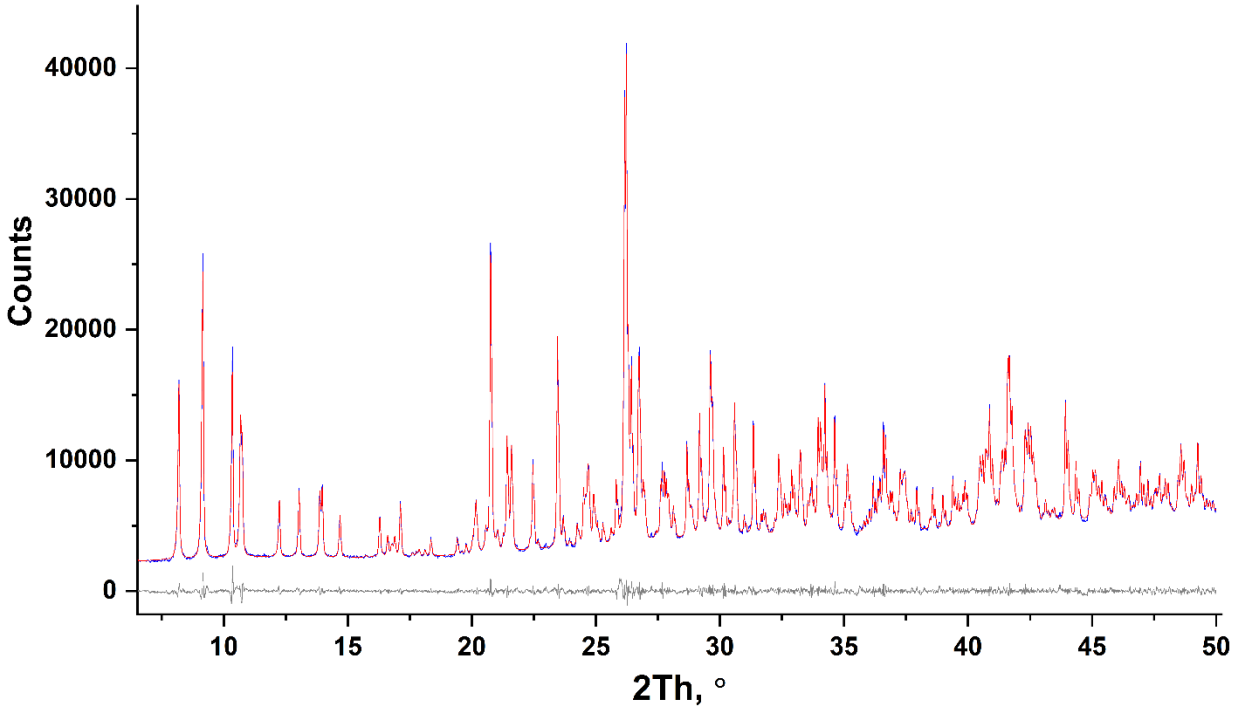
2Th, °

h (**VI**)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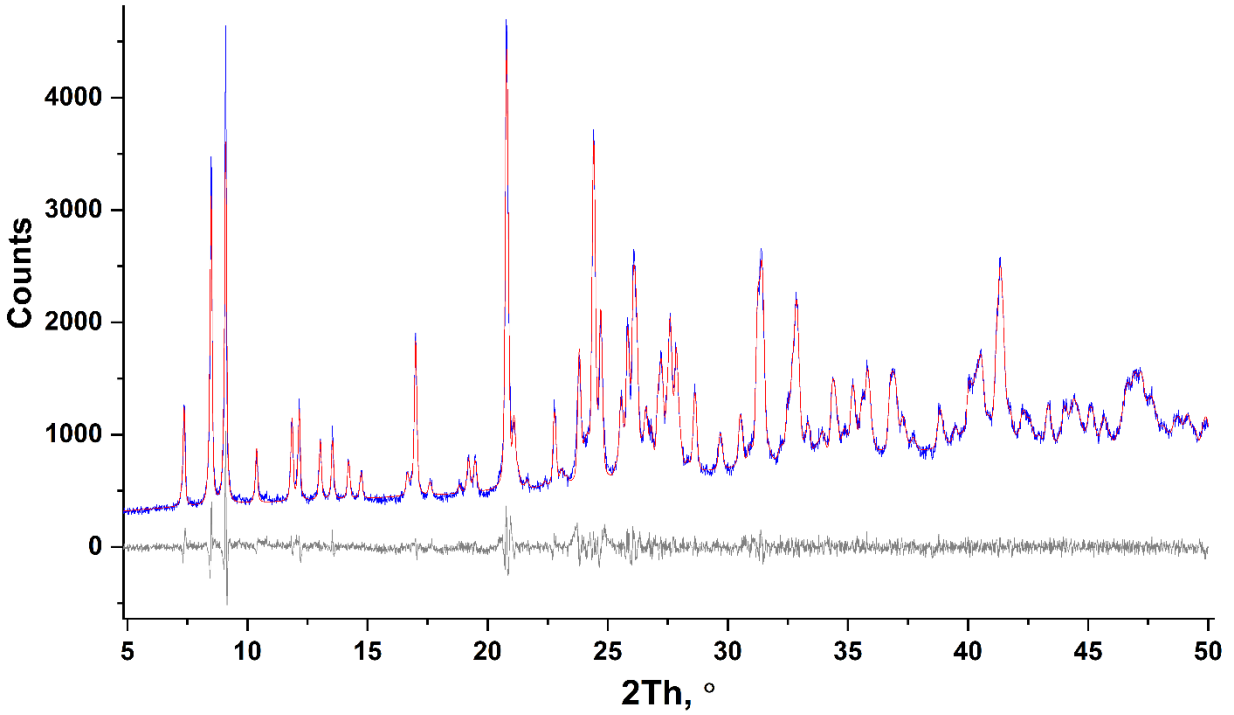
2Th, °

i **(VII)**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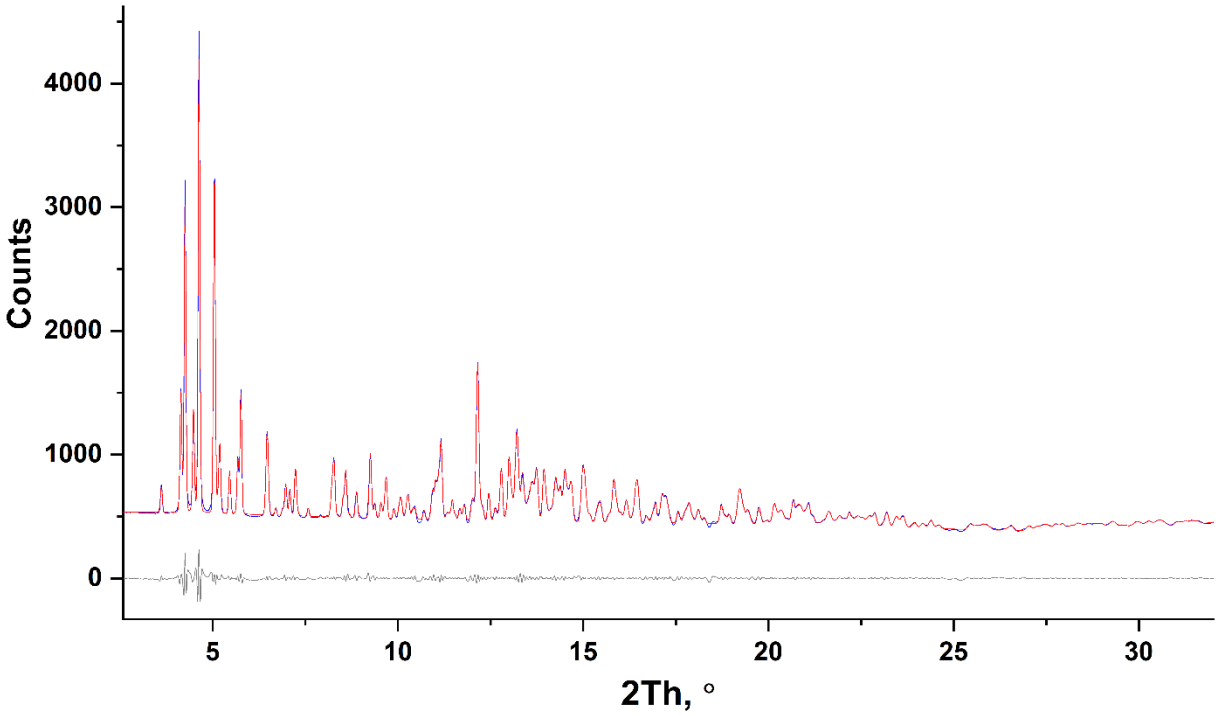
j **(VIII)**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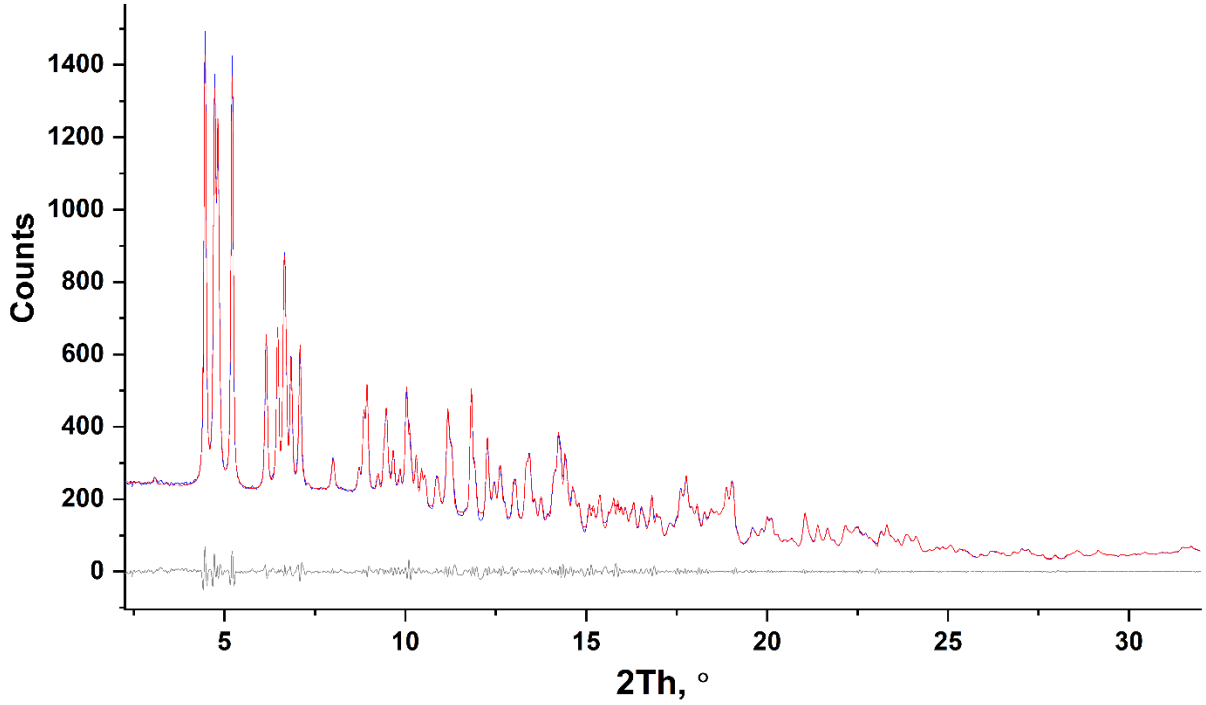
2Th, °

k (**IX**)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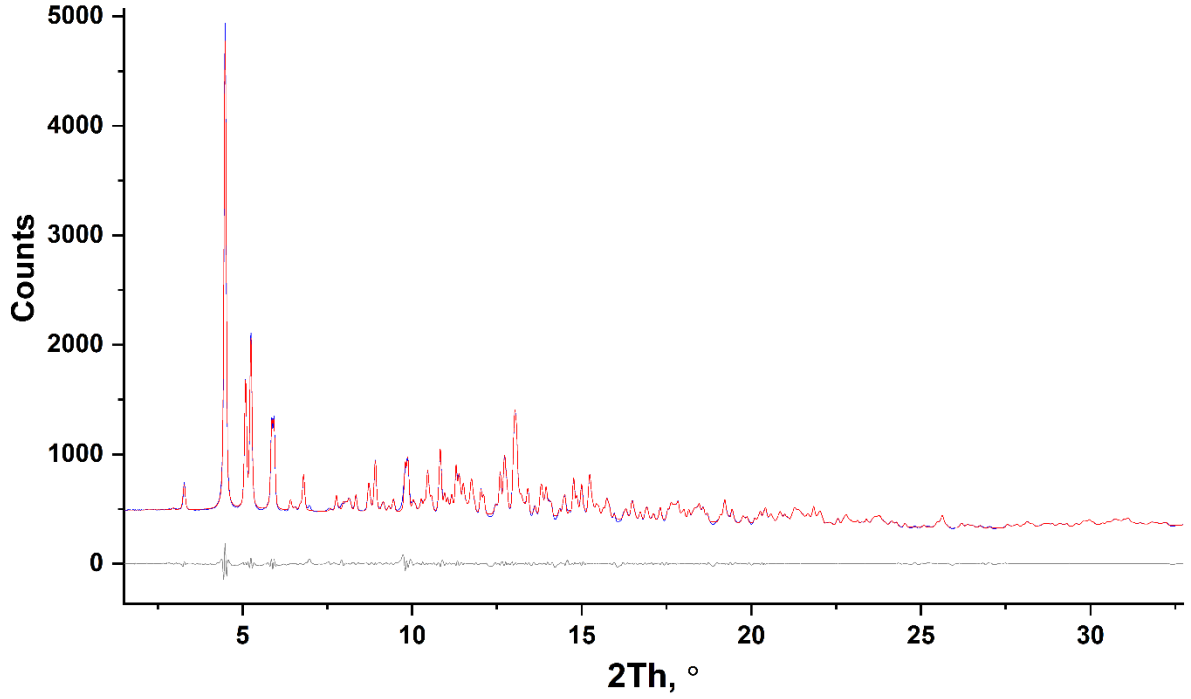
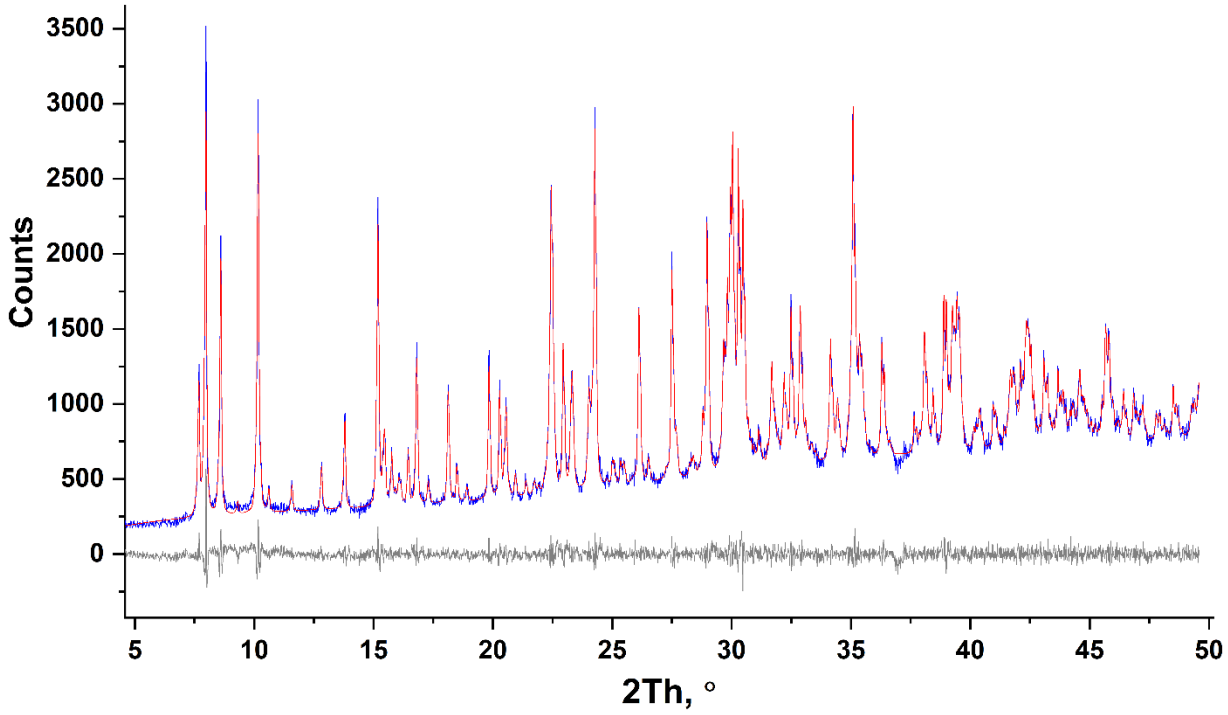
2Th, °

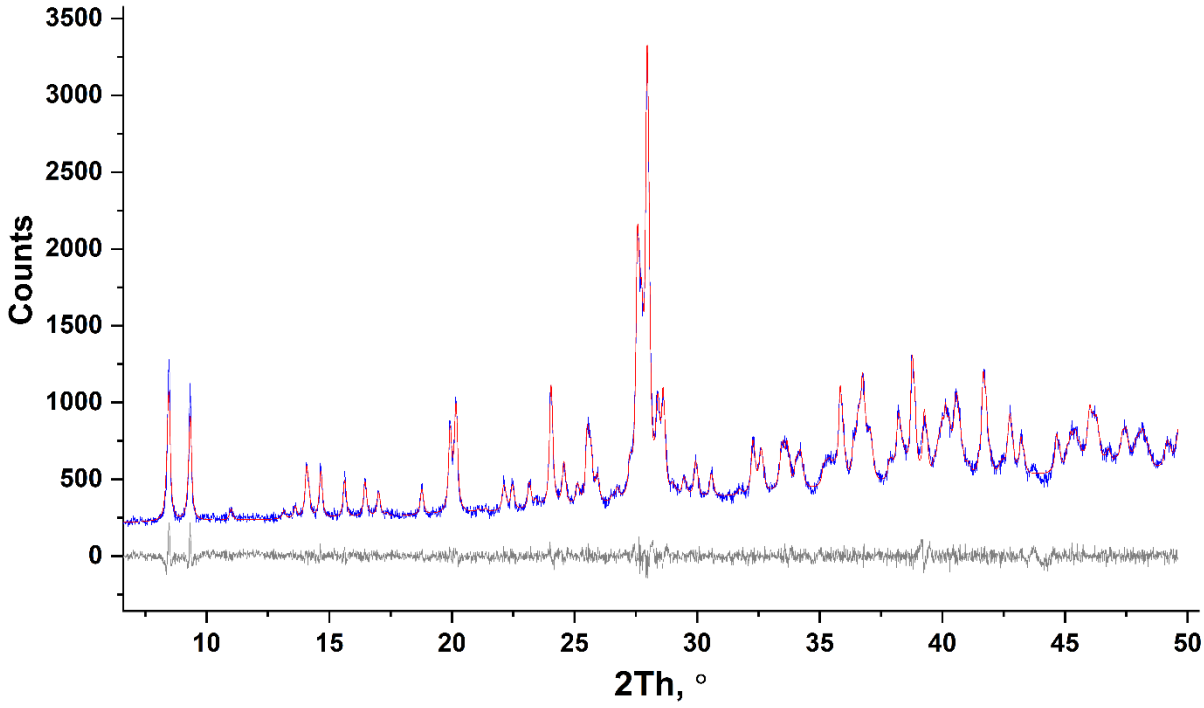
l (**X**)



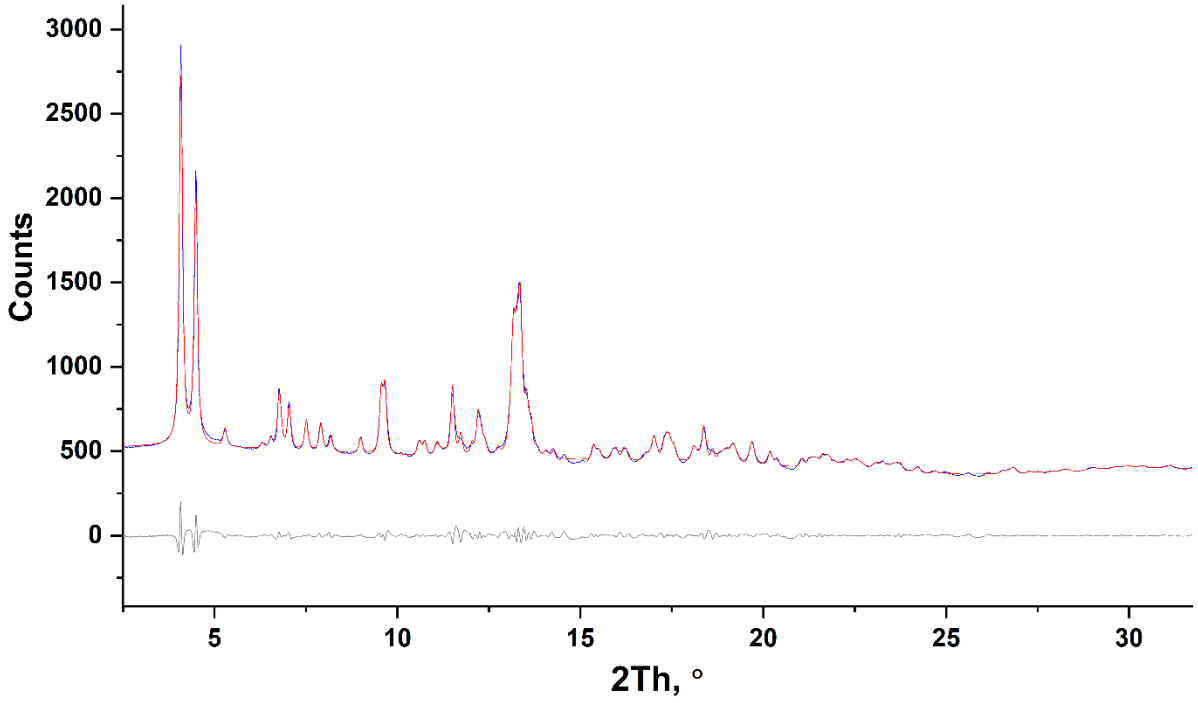
m (**XI**)



n (**XII**)

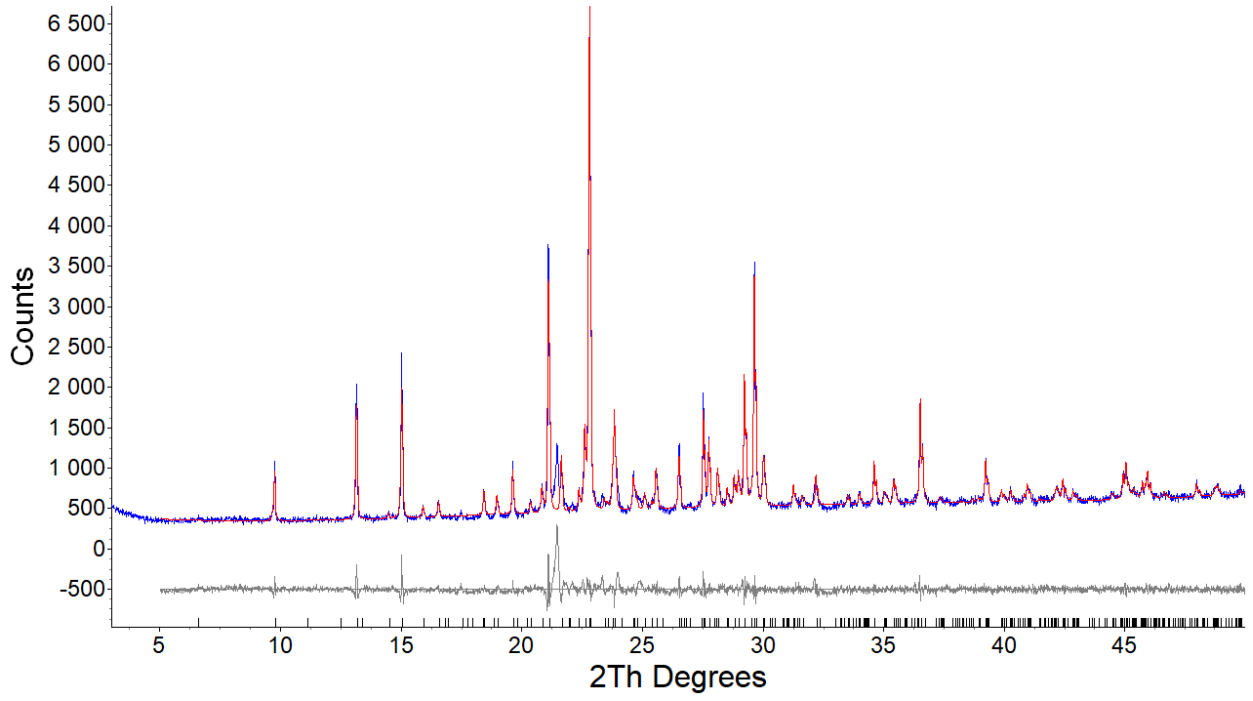


o (**XIII**, isolated from DMSO solution)

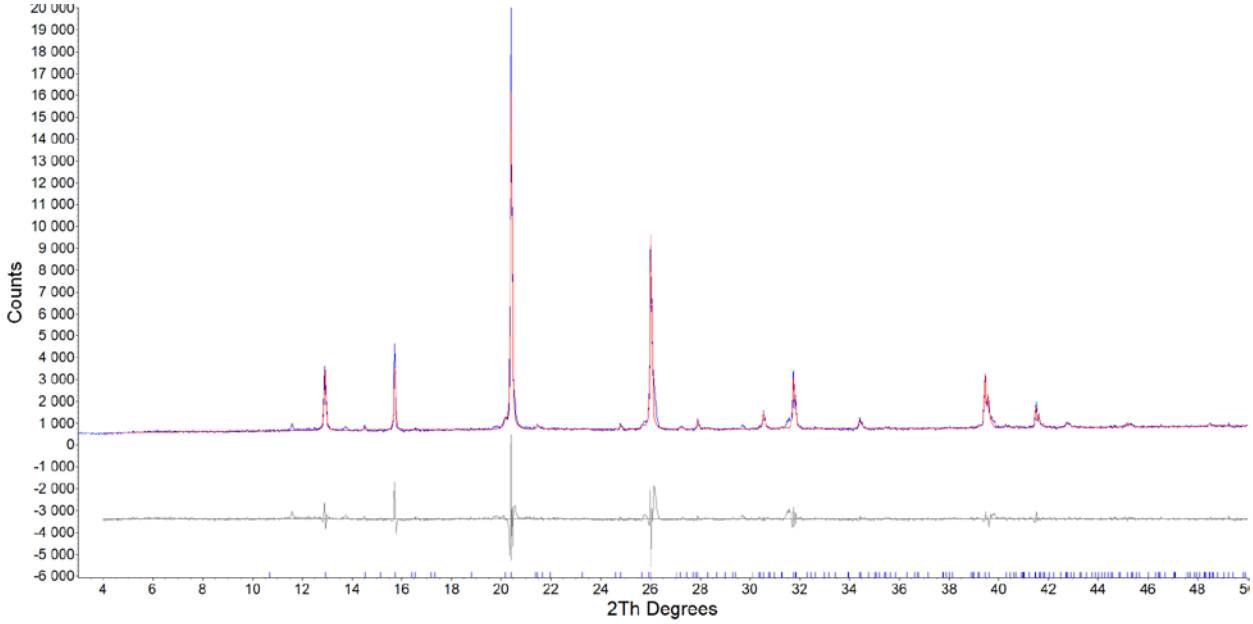


p (**XIII**, isolated from H_2O solution)

Fig. S2. Pawley refinement profiles for $[Py_2(XK)]Br_2$ (a), $[Py_2(XK)]I_2$ (b), **I-XIII** (c-p) recorded at RT. Red and blue lines correspond to the calculated profile and experimental pattern respectively. The bottom trace shows the difference curve.



a



b

Fig. S3. Pawley refinement profiles for extracted $[Py_2(XK)]Br_2$ from decomposed product of **I** (a) and extracted $[Py_2(XK)]I_2$ from decomposed product of **II** (b) recorded at RT. Red and blue lines correspond to the calculated profile and experimental pattern respectively. The bottom trace shows the difference curve.

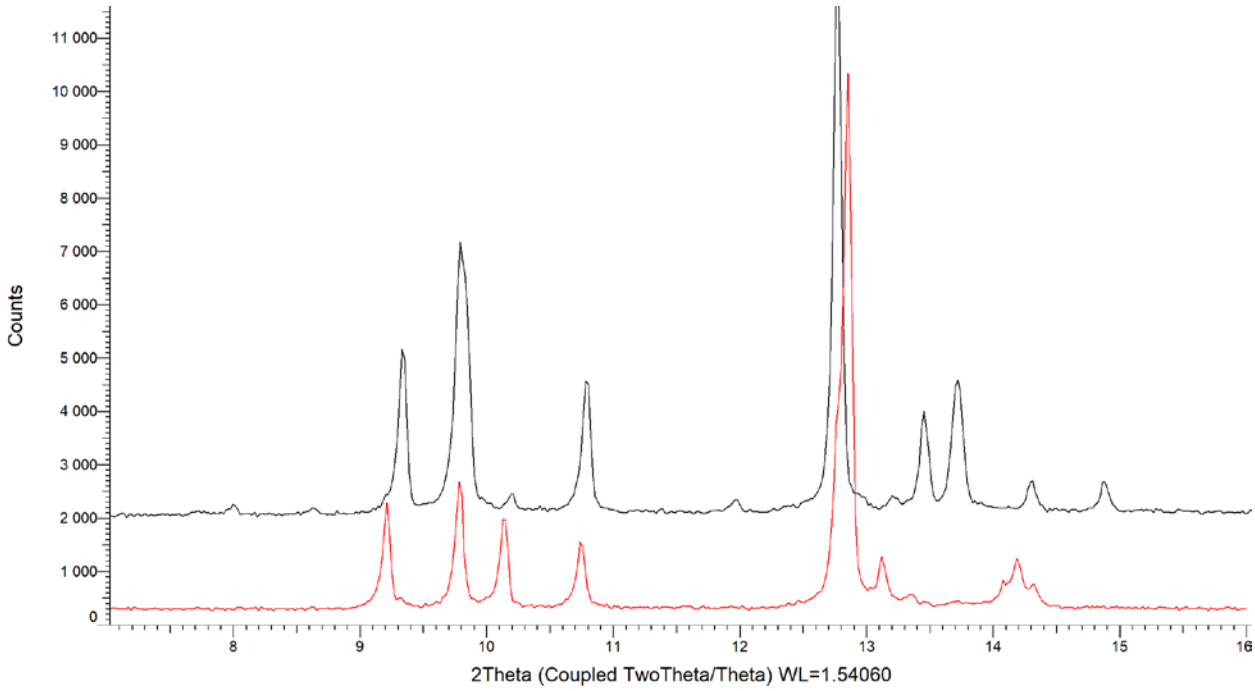
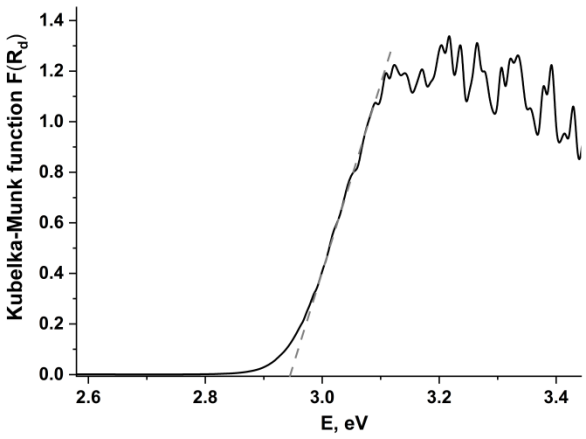
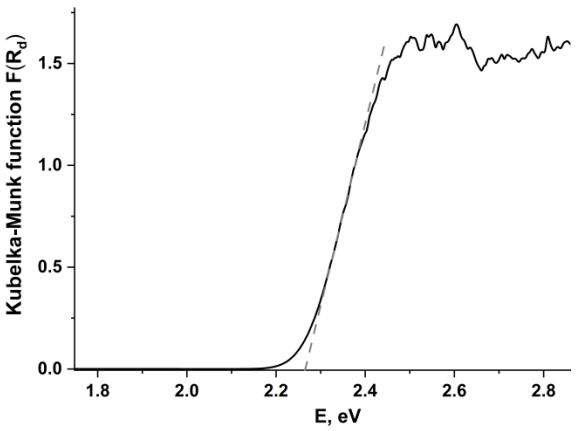


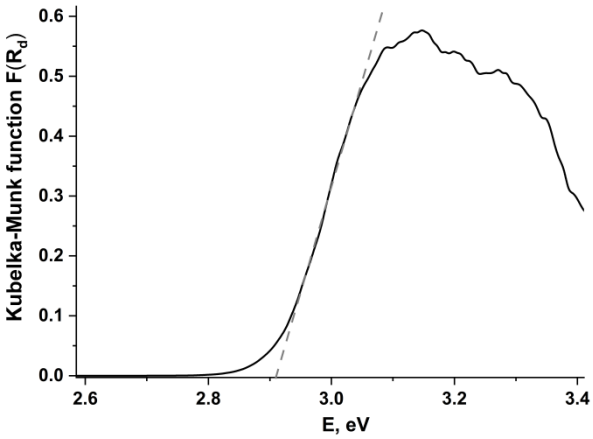
Fig. S4. PXRD profiles for compound $[Py_2(XK)]_3[BiBr_{6-x}Cl_x]_2$ (**III**) before (black line) and after (red line, **III** → **X**) UV irradiation.



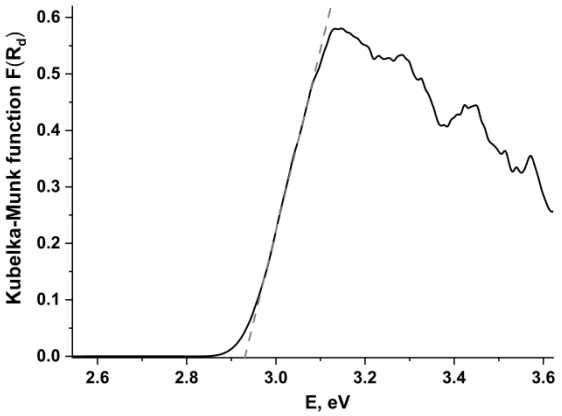
a (**I**)



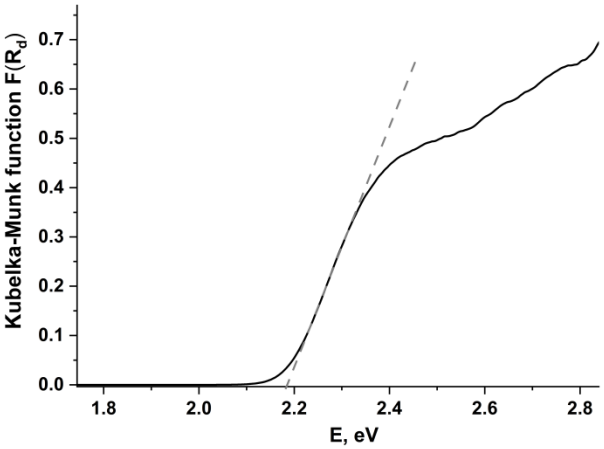
b (**II**)



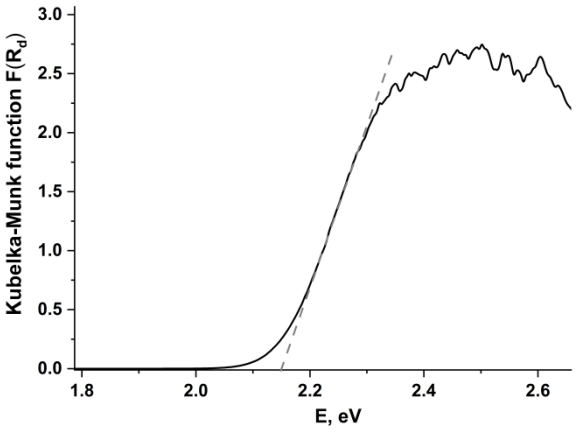
c (**III**)



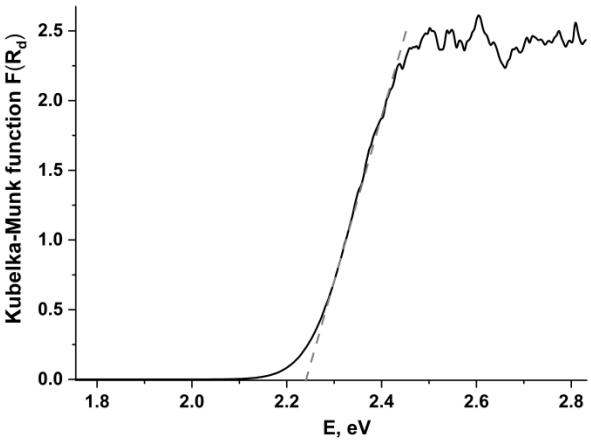
d (**IV**)



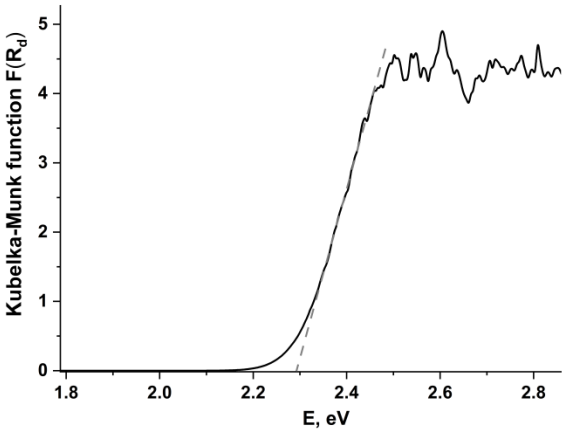
e (**V**)



f (**VI**)



g (**VII**)



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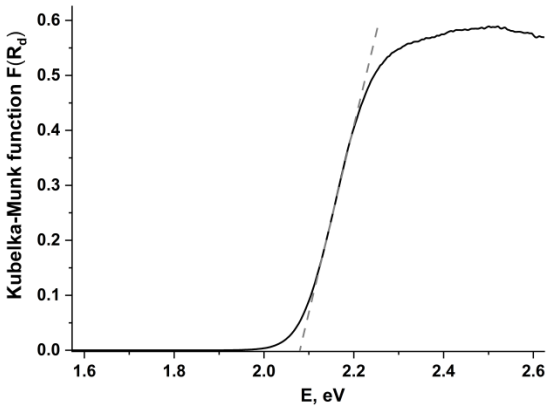
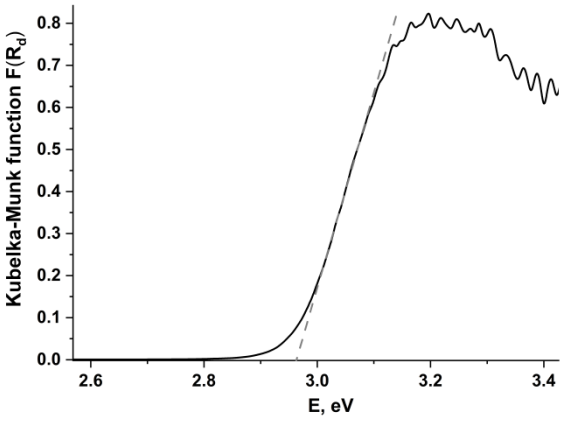
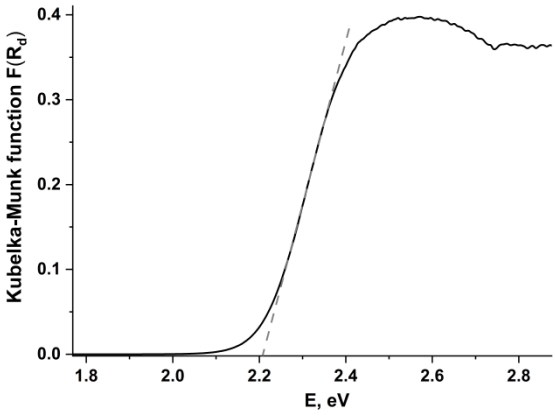


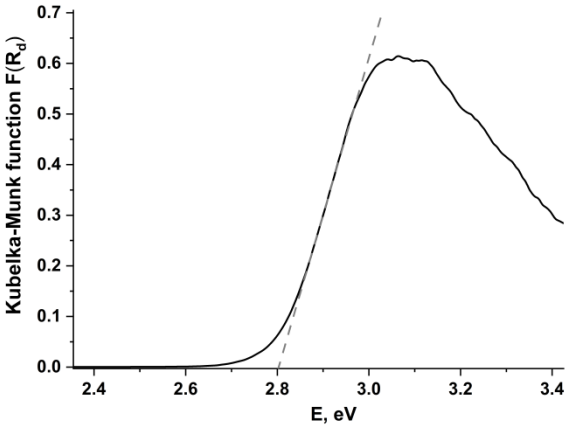
i (**IX**)



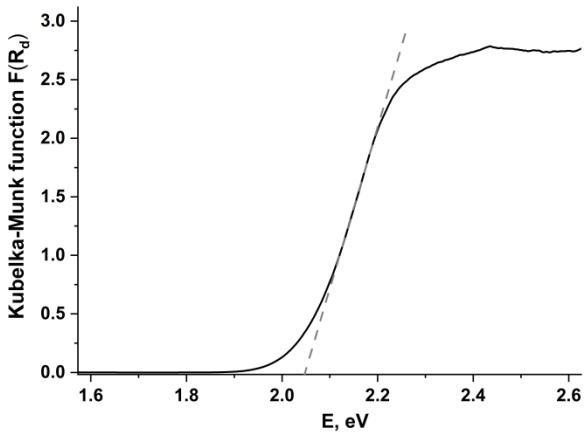
j (**X**)



k (**XI**)

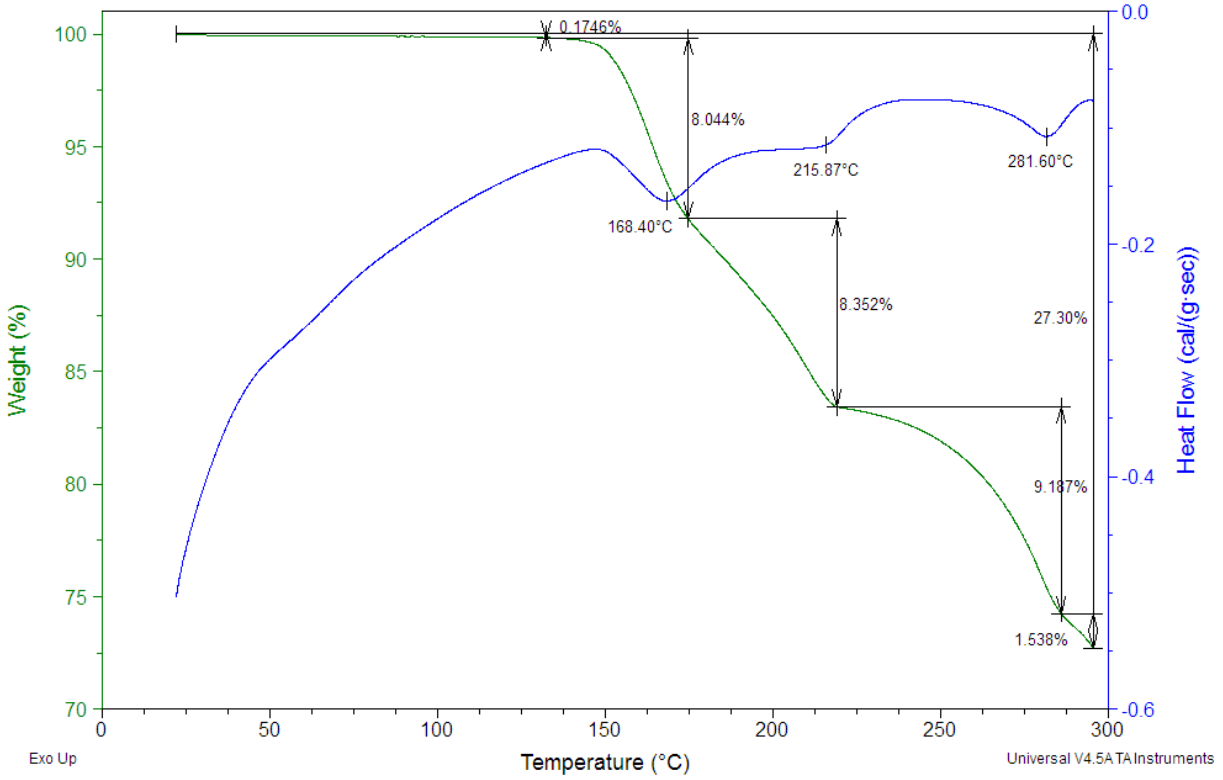


l (**XII**)

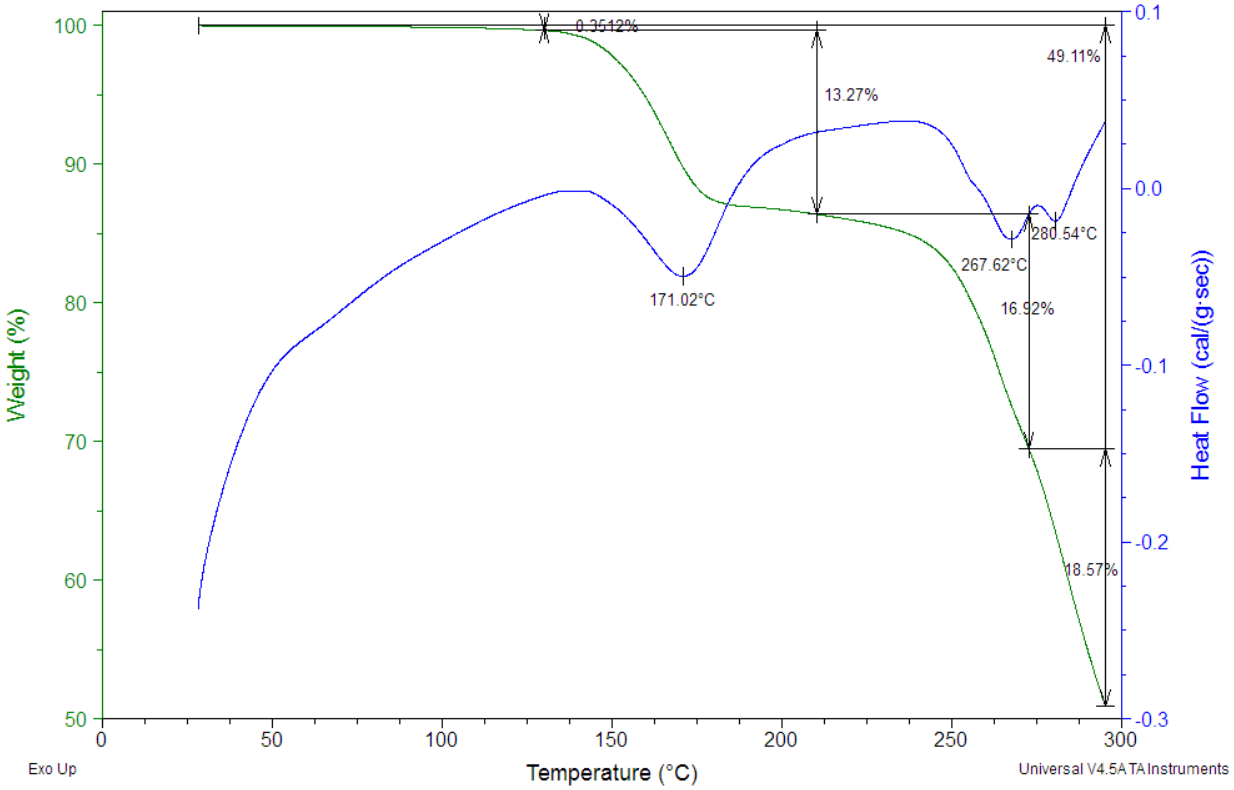


m (**XIII**)

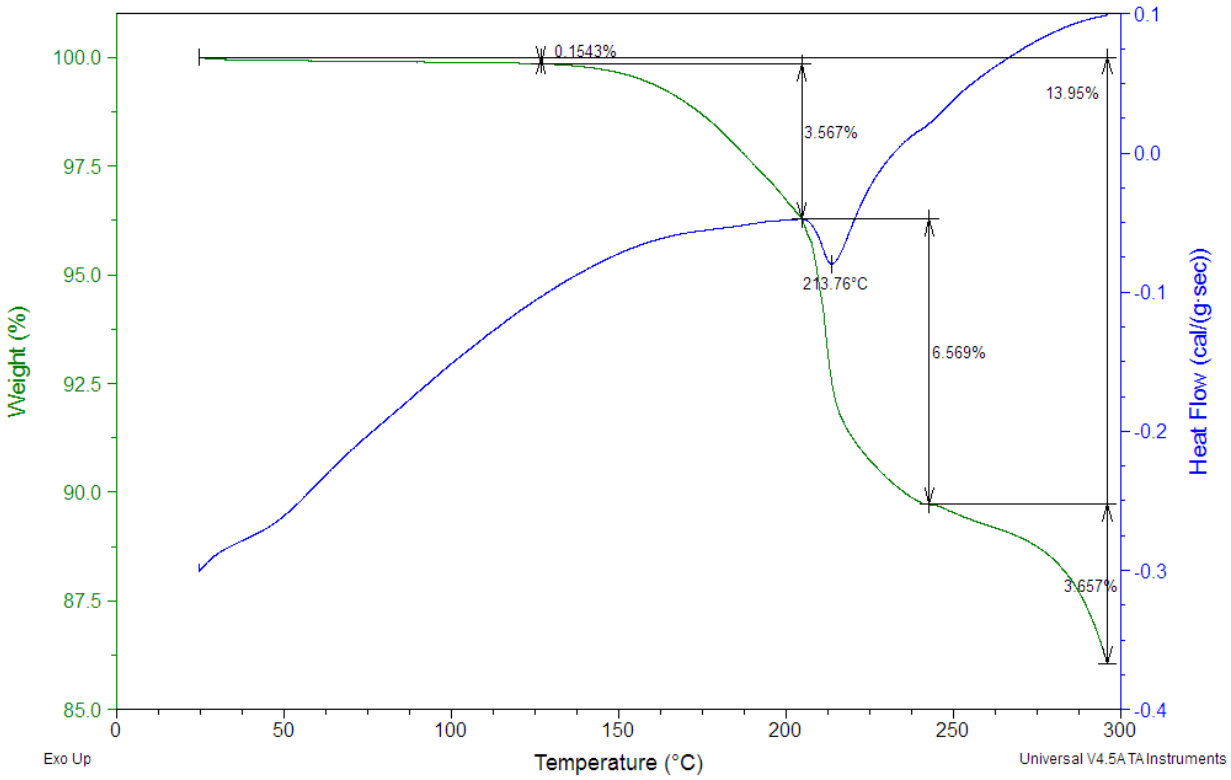
Fig. S5. The reflectance spectra of **I-XIII** (a-m). The linear part of the plot is extrapolated to the x-axis to determine E_g values.


0.1746%
8.044%
215.87°C
281.60°C
168.40°C
8.352%
27.30%
9.187%
1.538%
Weight (%)
Heat Flow (cal/(g·sec))
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

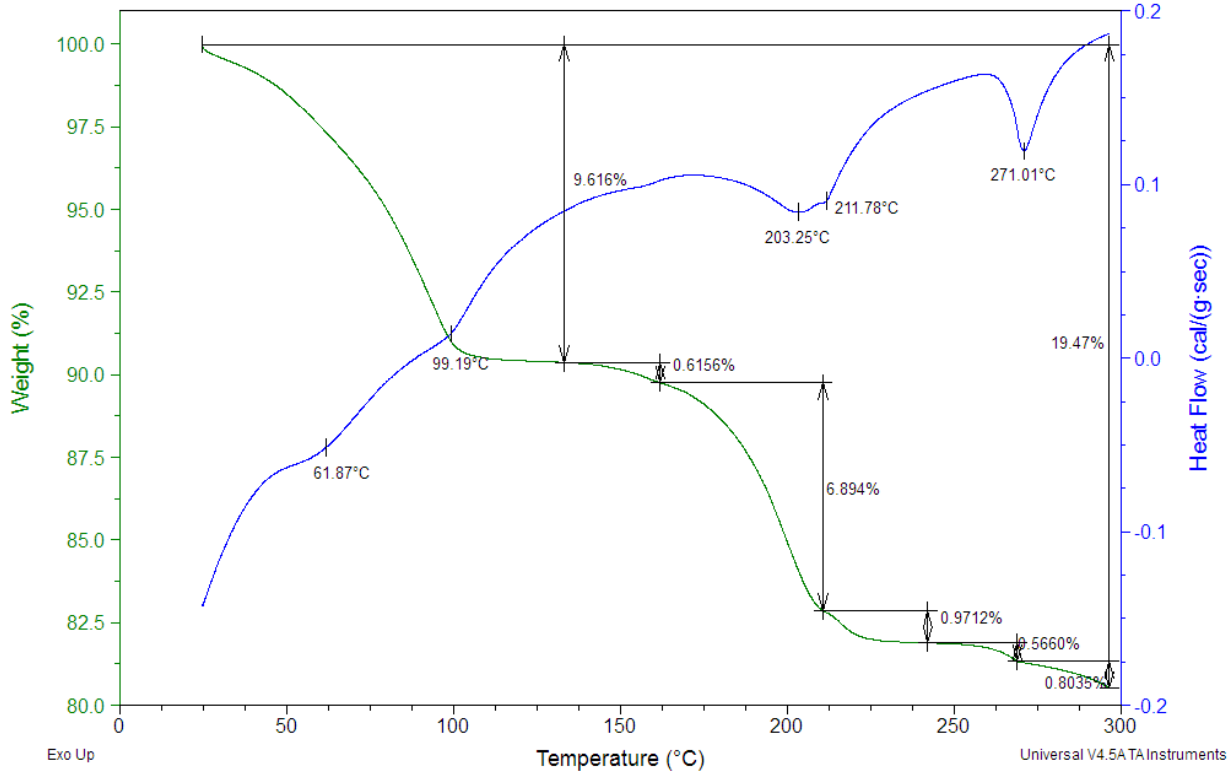
a (**I**)


0.3512%
49.11%
13.27%
280.54°C
267.62°C
171.02°C
16.92%
18.57%
Weight (%)
Heat Flow (cal/(g·sec))
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

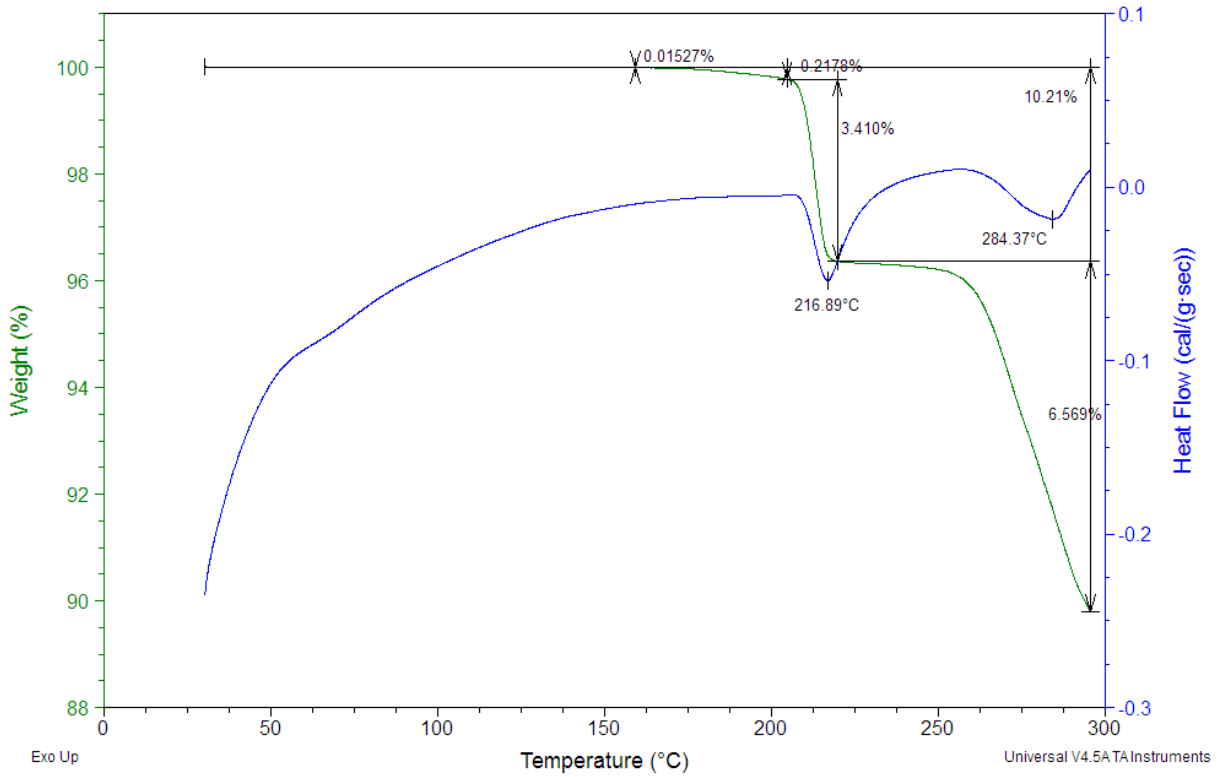
b (**II**)


0.1543%
3.567%
13.95%
213.76°C
6.569%
3.657%
Weight (%)
Heat Flow (cal/(g·sec))
Temperature (°C)
Exo Up
Universal V4.5A TA Instrumets

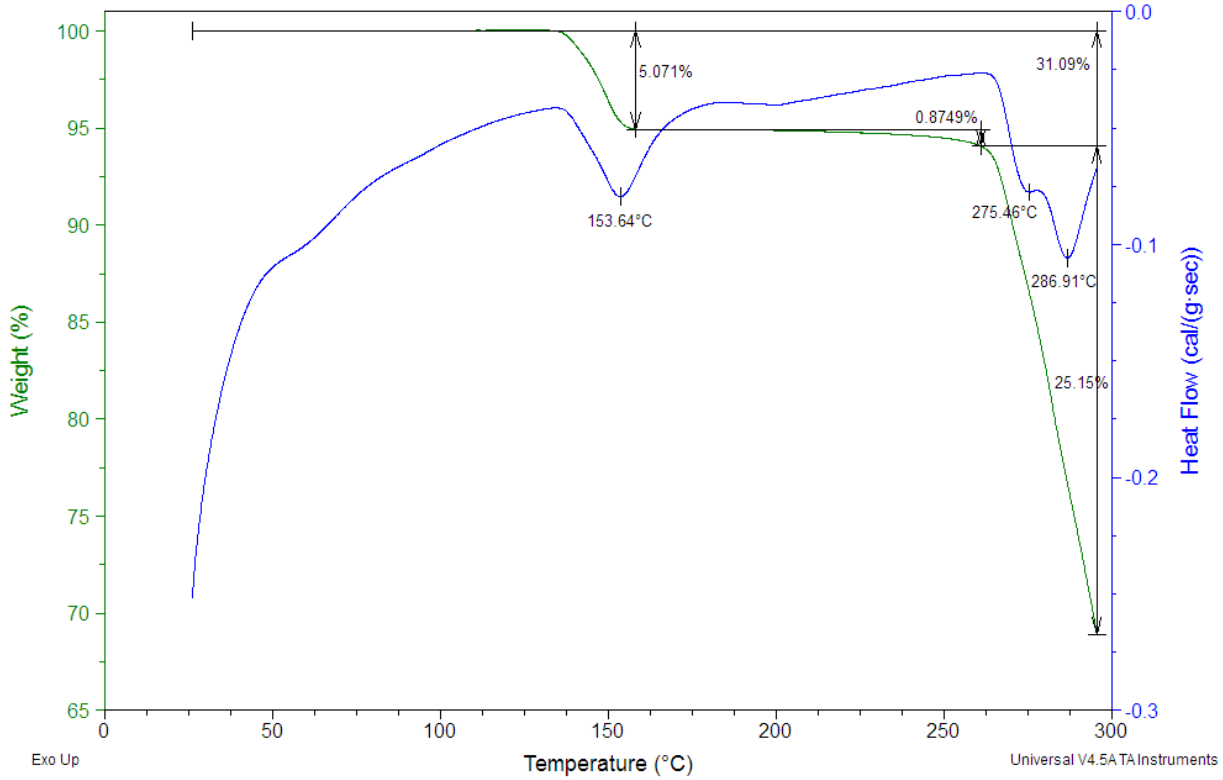
c (**IV**)


9.616%
271.01°C
211.78°C
203.25°C
99.19°C
0.6156%
19.47%
61.87°C
6.894%
0.9712%
0.5660%
0.8035%
Weight (%)
Heat Flow (cal/(g·sec))
Temperature (°C)
Exo Up
Universal V4.5A TA Instrumets

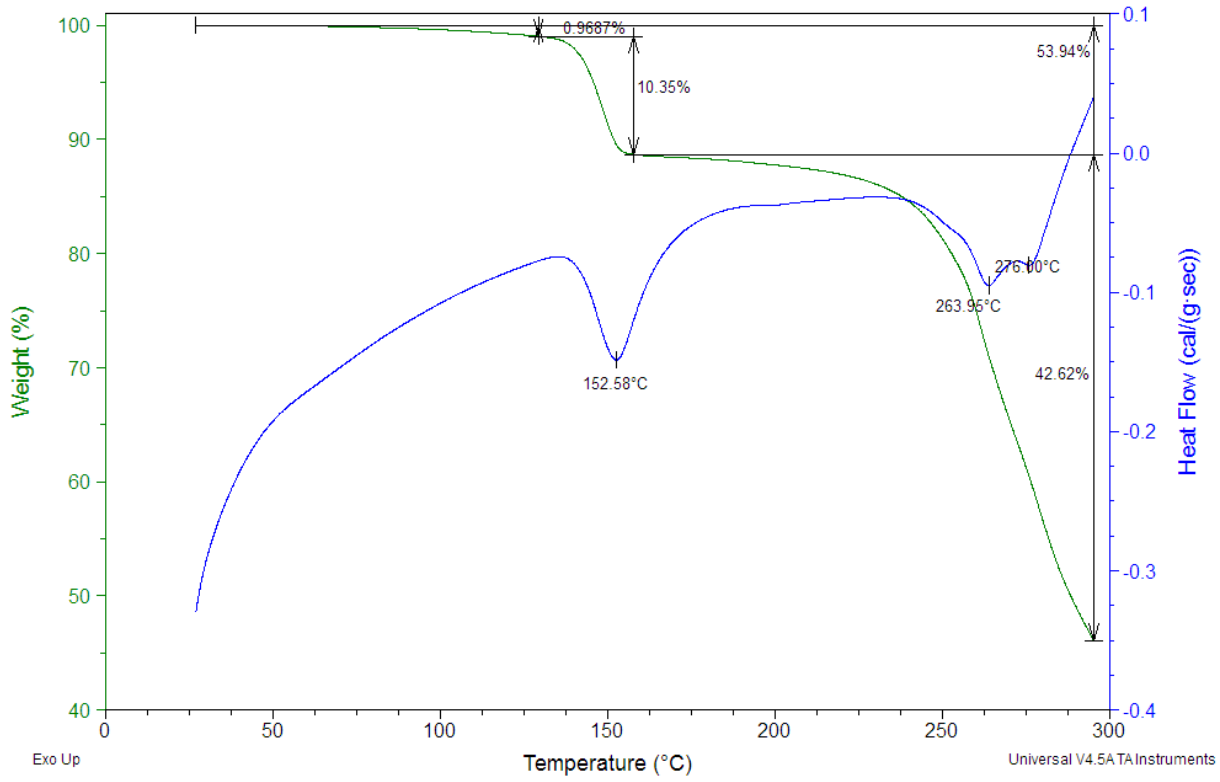
d (**V**)


0.01527%
0.2178%
10.21%
3.410%
284.37°C
216.89°C
6.569%
Weight (%)
Heat Flow (cal/(g·sec))
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

e (**VI**)


5.071%
31.09%
0.8749%
153.64°C
275.46°C
286.91°C
25.15%
Weight (%)
Heat Flow (cal/(g·sec))
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

f (**VII**)



g (**VIII**)

Fig. S6. TG (green) and DTA (blue) curves on heating compounds **I** (a), **II** (b), **IV-XIII** (c-g) under a flow of artificial air.

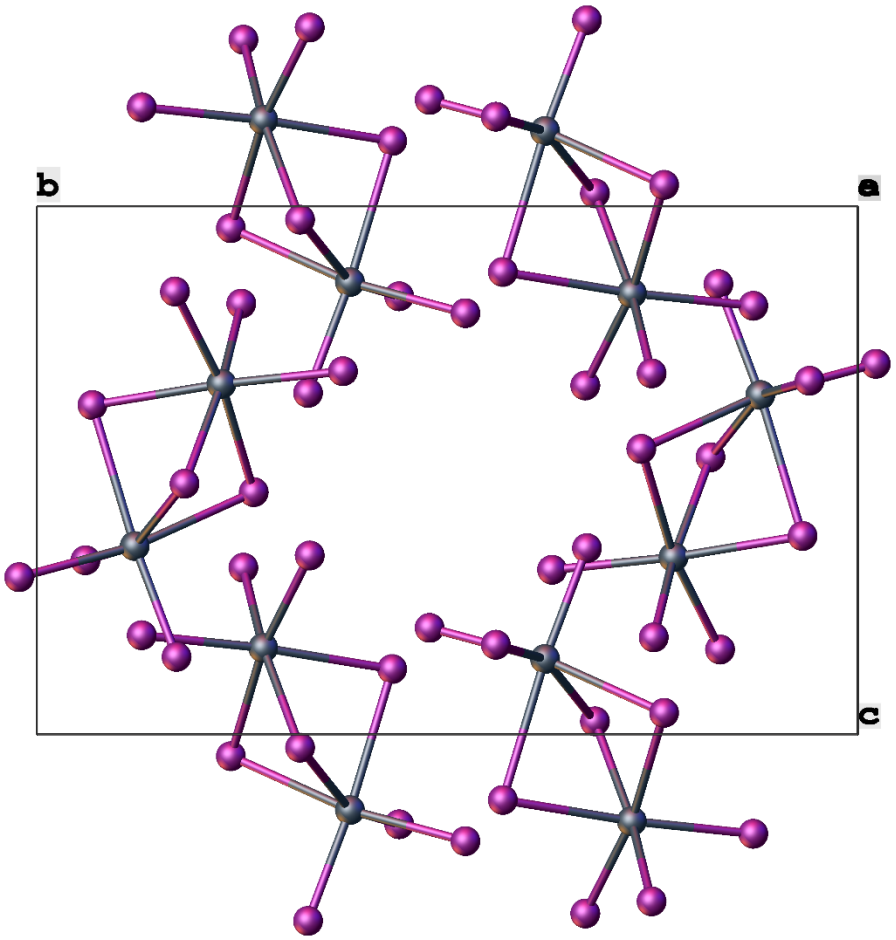


Fig. S7. Crystal packing of $[Bi_2I_9]^{3-}$ anions in **IX**.

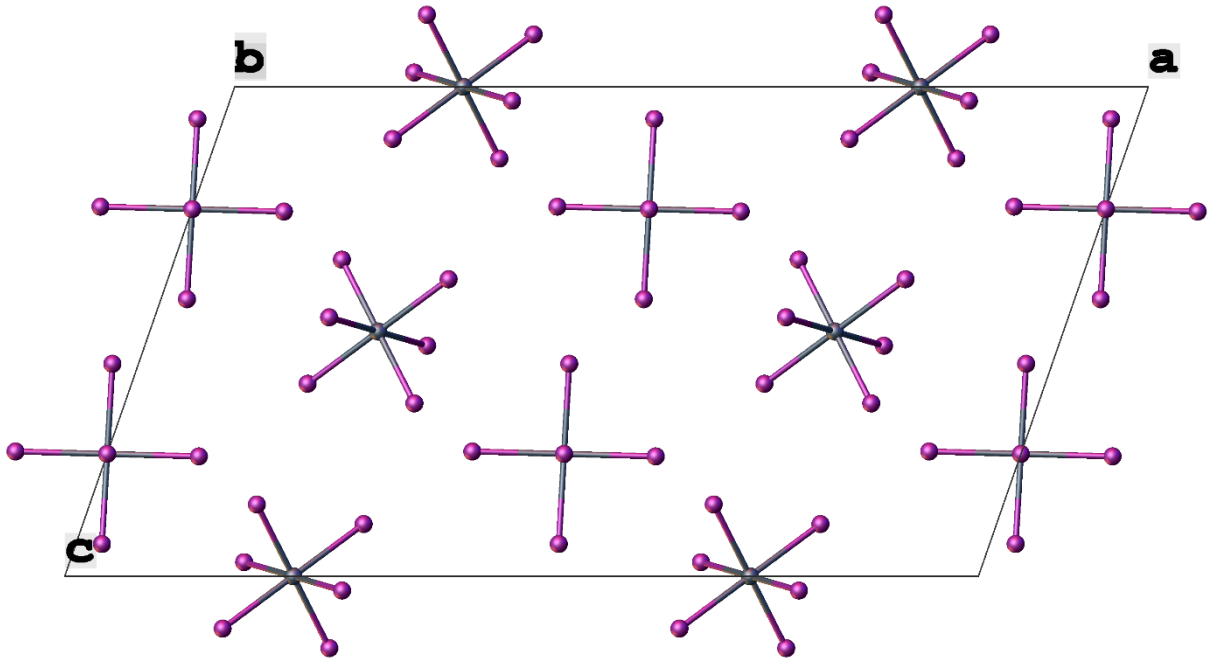


Fig. S8. Crystal packing of $[BiI_6]^{3-}$ anions in **XI**.

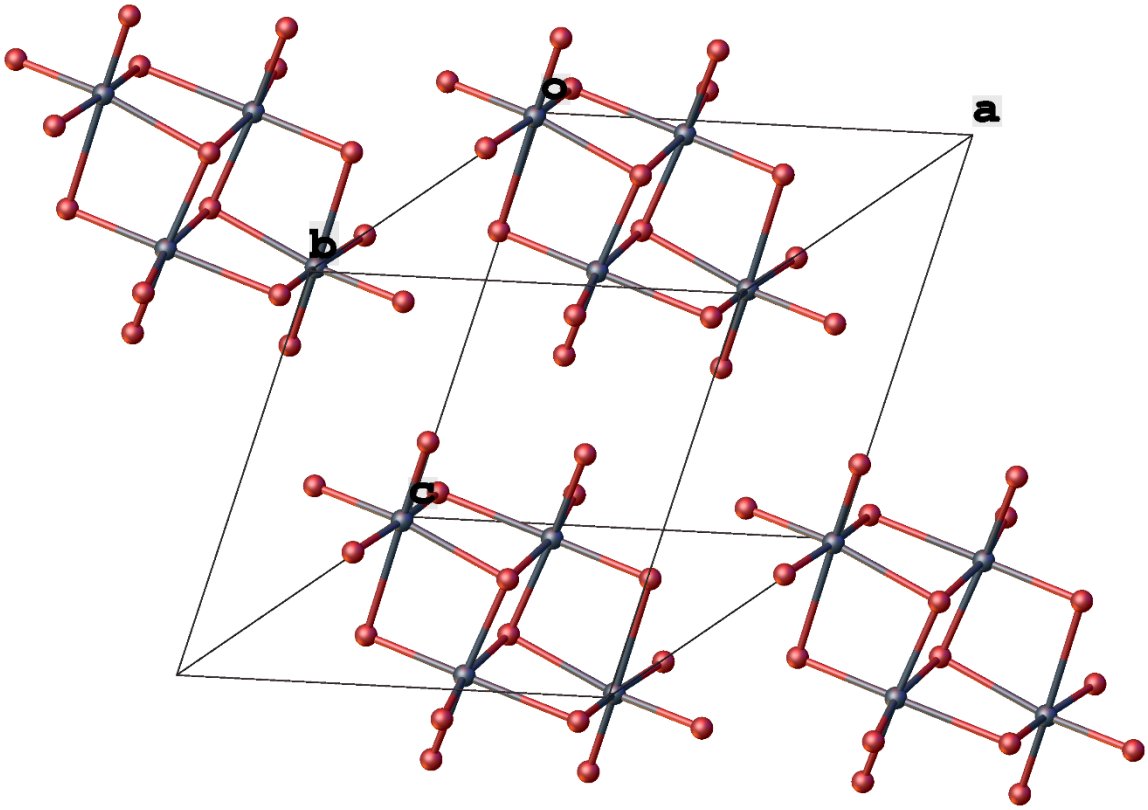


Fig. S9. Crystal packing of $[Bi_4Br_{16}]^{4-}$ anions in **XII**.

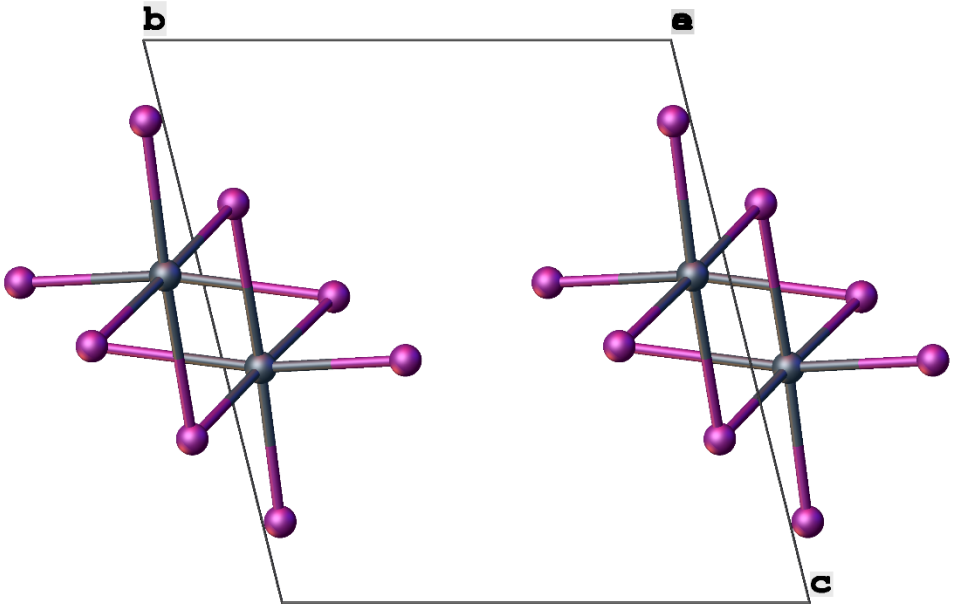


Fig. S10. Crystal packing of $[BiI_4]_n^{n-}$ anions in **XIII**.

Resulting CONTCAR files for compounds III and X (VASP program optimization result)

III

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-0.0000000000000000 0.5000000599999979 0.0000000000000000
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0.1636679352940279 0.3839162010152757 0.3605964582399419
0.8363320797059701 0.6160838289847199 0.6394035417600585

FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)
---
free energy TOTEN = -1570.72554557 eV
energy without entropy= -1570.72554557 energy(sigma->0) = -1570.72554557

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4.7107965786000001 12.4228095971000005 0.0000000000000000
3.3347927288000001 1.0397038526000000 13.4604361620000006
Bi Br N C H
2 12 6 54 56
Direct
-0.0000000000000000 0.0000000000000000 0.5000000599999979
0.4999999400000021 0.5000000599999979 0.0000000000000000
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FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)

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free energy TOTEN = -792.02383179 eV

energy without entropy= -792.02383179 energy(sigma->0) = -792.02383179