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Mixed halide hybrid halobismuthates and their *in situ* transformations

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Synthesis of compounds 1a–3a. CH_3I (27.8 g, 196 mmol) was added to a solution of the corresponding picoline (14.9 g, 160 mmol) in 96% ethanol (25 ml), and the mixture was kept for one day in a closed flask at room temperature. The resulting beige precipitate was filtered off *in vacuo* and dried in the air. The yields were for **1a**: 29.72 g (79.0%) and for **3a**: 28.82 g (76.6%). Product **2a** was a highly hygroscopic compound, which we failed to isolate in a dry form. The nature and purity of the obtained products were confirmed by ^{1}H NMR (300 MHz, D_2O, Figure S3(*a*–*c*)). ^{1}H NMR data for **1a**: 8.60 (d, 1H), 8.27 (t, 1H), 7.80 (m, 1H), 7.73 (m, 1H), 4.14 (s, 3H), 2.70 (s, 3H). ^{1}H NMR data for **2a**: 8.55 (s, 1H), 8.49 (d, 1H), 8.25 (d, 1H), 7.81 (t, 1H), 4.24 (s, 3H), 2.44 (s, 3H). ^{1}H NMR data for **3a**: 8.47 (d, 2H), 7.75 (d, 2H), 4.20 (s, 3H), 2.54 (s, 3H).

Synthesis of compounds 1b–3b. A solution of $Bi(NO_3)_3 \cdot 5H_2O$ (1.03 g, 2.1 mmol) and KBr (4.48 g, 37.6 mmol) in H_2O (10 ml) was added to an aqueous solution containing corresponding iodide **1a** or **3a** (0.50 g, 2.1 mmol), KBr (2.24 g, 18.8 mmol), and H_2O (10 ml). The yellowish-orange crystalline precipitate was formed and kept in the mother liquor at room temperature.

After two days, the resulting precipitate was filtered off *in vacuo* and dried in the air. The yields were for **1b**: 0.696 g (10.5%) and for **3b**: 0.766 g (23.1%). The reaction of **2a** was carried out in a similar way using 1 g of the wet compound instead of 0.5 g of the dry compound as was in the cases of **1a** and **3a**. Yield: 1.398 g.

Synthesis of compound 3c. A solution of $Bi(NO_3)_3 \cdot 5H_2O$ (1.03 g, 2.1 mmol) and KI (6.25 g, 37.7 mmol) in H_2O (10 ml) was added to an aqueous solution containing iodide **3a** (0.50 g, 2.1 mmol), KI (3.12 g, 18.8 mmol), and H_2O (10 ml), and the formed red fine-crystalline precipitate was kept in the mother liquor at room temperature. After two days, the precipitate was filtered off *in vacuo* and dried in the air. The yield was 1.33 g (76.8%).

Synthesis of compound 4a. CH_3I (22.7 g, 160 mmol) was added to a solution of 4-cyanopyridine (16.6 g, 160 mmol) in 96% ethanol (25 ml), and the mixture was kept for one day in a closed flask at room temperature. The resulting yellowish-orange precipitate of **4a** was filtered off *in vacuo* and dried in the air. The yield was 12.21 g (31.0%). The nature and purity of the product obtained were confirmed by ^1H NMR (300 MHz, D_2O, Figure S3(*d*)): 9.01 (d, 2H), 8.38 (d, 2H), 4.40 (s, 3H).

Synthesis of compound 4b. A solution of $Bi(NO_3)_3 \cdot 5H_2O$ (0.985 g, 2.0 mmol) and KBr (4.28 g, 36.0 mmol) in H_2O (10 ml) was added to an aqueous solution containing iodide **4a** (0.50 g, 2.0 mmol), KBr (2.14 g, 18.0 mmol), and H_2O (10 ml). The orange crystalline precipitate was formed and kept in the mother liquor at room temperature. After two days, orange crystals of **4b** were filtered off *in vacuo* and dried in the air. The yield was 0.625 g (17.3%).

Synthesis of compound 4f. A solution of $Bi(NO_3)_3 \cdot 5H2O$ (0.985 g, 2.0 mmol) and KI (6.00 g, 36.1 mmol) in H_2O (10 ml) was added to an aqueous solution containing iodide **4a** (0.50 g, 2.0 mmol), KI (3.00 g, 18.1 mmol), and H_2O (10 ml). The red precipitate was formed and kept in the mother liquor at room temperature. After two days, the resulting precipitate of **4f** was filtered off *in vacuo* and dried in the air. The yield was 1.138 g.

Table S1 Results of EDX analysis (at%) for compound **1b** normalized with respect to Bi.

Spectrum	Bi	Br	I	Br/Hal (%)[a]
Spectrum 1	1	3.31	1.28	72.1
Spectrum 2	1	3.28	1.33	71.1
Spectrum 3 (overview)	1	3.53	1.23	74.2

[a] The halogen ratio Br/Hal in initial solution (before precipitation) was 96.4%

Table S2 Results of EDX analysis (at%) for compound **2b** normalized with respect to Bi.

Spectrum	Bi	Br	I	Br/Hal (%)
Spectrum 1	1	3.20	1.34	70.5
Spectrum 2	1	3.15	1.31	70.6
Spectrum 3 (overview)	1	3.32	1.42	70.0

Table S3 Results of EDX analysis (at%) for compound **3b** normalized with respect to Bi.

Spectrum	Bi	Br	I	Br/Hal (%)[a]
Spectrum 1	1	3.46	1.03	77.1
Spectrum 2	1	3.07	1.33	69.8
Spectrum 3 (overview)	1	3.24	1.08	75.0

[a] The halogen ratio Br/Hal in initial solution (before precipitation) was 96.4%

Table S4 Results of EDX analysis (at%) for compound **4b** normalized with respect to Bi.

Spectrum	Bi	Br	I	Br/Hal (%)
Spectrum 1	1	3.65	1.39	72.4
Spectrum 2	1	4.09	1.06	79.4
Spectrum 3	1	3.91	1.14	77.4
Spectrum 4 (overview)	1	3.83	1.28	75.0

[a] The halogen ratio Br/Hal in initial solution (before precipitation) is 96.4%

Table S5 Results of EDX analysis (at%) for compound **4f** normalized with respect to Bi.

Spectrum	Bi	I	K
Spectrum 1	1	4.09	0.00
Spectrum 2	1	5.87	0.02
Spectrum 2	1	3.95	0.00
Spectrum 3 (overview)	1	4.64	0.06

Table S6 Crystal data and structure refinement parameters for compounds **1b–4e**.

Compound number[a]	**1b**	**2b**	**3b**	**4b_100K**	**4b_150K**
Empirical formula	$C_{42}H_{60}Bi_4Br_{12.86}I_{5.14}N_6$	$C_{21}H_{30}Bi_2Br_{6.26}I_{2.74}N_3$	$C_{21}H_{30}Bi_2Br_{6.60}I_{2.40}N_3$	$C_{28}H_{28}Bi_2Br_{7.42}I_{2.58}N_8$	$C_{28}H_{28}Bi_2Br_{7.52}I_{2.48}N_8$
Formula weight	3164.79	1590.38	1574.40	1814.88	1810.18
T/K	150(2)	150(2)	150(2)	100(2)	150(2)
λ/Å	0.67522	0.71073	0.67522	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_1/n$	*P*bca	*P*bca
a/Å	10.2477(3)	11.8243(4)	18.7476(7)	16.7680(5)	16.8149(6)
b/Å	16.8771(3)	11.8539(4)	11.7296(3)	9.8073(3)	9.8623(4)
c/Å	42.4017(9)	13.3778(4)	19.0123(7)	27.5212(7)	27.5955(10)
β/deg	90	95.8019(11)	118.158(5)	90	90
V/Å^3	7333.4(3)	1865.48(11)	3686.0(3)	4525.8(2)	4576.3(3)
Z	4	2	4	4	4
d_{calc}/mg m^{-3}	2.866	2.831	2.837	2.664	2.627
μ/mm^{-1}	16.382	18.408	16.335	16.107	15.949
F(000)	5634	1415	2805	3258	3251
Crystal size/mm	0.04 × 0.02 × 0.02	0.18 × 0.12 × 0.10	0.02 × 0.01 × 0.01	0.28 × 0.2 × 0.12	0.22 × 0.12 × 0.06
θ range/deg	1.465, 26.753	2.192, 30.052	1.994, 23.697	2.429, 28.315	2.422, 27.156
Index ranges	–10 <= h <= 10 –22 <= k <= 22 –56 <= l <= 56	–16 <= h <= 16 –16 <= k <= 16 –18 <= l <= 18	–22 <= h <= 22 –13 <= k <= 13 –22 <= l <= 22	–22 <= h <= 22 –13 <= k <= 13 –36 <= l <= 36	–21 <= h <= 21 –12 <= k <= 12 –35 <= l <= 35
Reflections collected	52603	64774	19649	53397	51753
Independent reflections, R_{int}	16331, 0.0412	10938, 0.0411	6245, 0.0344	5623, 0.0759	5076, 0.0782
Completeness to θ = 25.242°	94.2 %	99.9 %	95.9 %	100.0 %	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max., min. transmission	1, 0.73988	0.0232, 0.0026	1, 0.8548	0.2627, 0.0977	0.0943, 0.0258
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	Full-matrix least-squares on F^2
Data / restraints / parameters	16331 / 54 / 695	10938 / 1 / 367	6245 / 108 / 379	5623 / 0 / 226	5076 / 0 / 217
Goodness-of-fit	1.049	1.198	0.945	1.007	1.060
R_1, wR_2 [$I > 2\sigma(I)$]	0.0348, 0.0881	0.0450, 0.1108	0.0289, 0.0825	0.0353, 0.0788	0.0398, 0.0858
R_1, wR_2 (all data)	0.0384, 0.0897	0.0490, 0.1128	0.0327, 0.0848	0.0552, 0.0866	0.0644, 0.0953
Absolute structure parameter	0.011(3)	–0.027(2)			
Largest diff. peak and hole/e.Å^{-3}	2.026, –1.349	2.386, –1.198	1.266, –1.070	1.882, –1.386	1.399, –1.460

Compound number	**3c**	**4c**	**4d**
Empirical formula	$C_7H_{10}BiI_4N$	$C_{56}H_{56}Bi_3Br_{12}I_{15}N_{16}$	$C_{35}H_{35}Bi_2I_{12}KN_{10}$
Formula weight	824.74	4442.52	2575.59
T/K	100(2)	150(2)	150(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal	Monoclinic
Space group	$P2_1/c$	$I4/m$	$P2_1/n$
a/Å	14.4469(10)	14.7016(6)	9.8150(2)
b/Å	14.0102(10)	14.7016(6)	14.9572(3)
c/Å	7.7784(5)	24.3159(10)	20.8682(4)
β/deg	104.175(2)	90	92.0850(10)
V/Å^3	1526.44(18)	5255.6(5)	3061.53(11)
Z	4	2	2
d_{calc}/mg m^{-3}	3.589	2.807	2.794
μ/mm^{-1}	19.608	14.017	11.891
F(000)	1416	3936	2272
Crystal size/mm	0.28 × 0.12 × 0.1	0.22 × 0.12 × 0.06	0.2 × 0.16 × 0.1
θ range/deg	2.908, 26.373	2.578, 31.023	2.262, 31.552
Index ranges	–18 <= *h* <= 18	–21 <= *h* <= 20	–14 <= *h* <= 14
	–17 <= *k* <= 17	–20 <= *k* <= 20	–21 <= *k* <= 21
	–9 <= *l* <= 9	–34 <= *l* <= 34	–30 <= *l* <= 30
Reflections collected	15899	37819	72867
Independent reflections, R_{int}	3116, 0.0387	4258, 0.0553	10022, 0.0631
Completeness to θ = 25.242°	99.8 %	99.9 %	100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max,. min. transmission	0.0473, 0.0093	0.0518, 0.0136	0.1015, 0.0255
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on *F*2
Data / restraints / parameters	3116 / 0 / 121	4258 / 0 / 149	10022 / 20 / 313
Goodness-of-fit	1.326	1.010	0.925
R_1, wR_2 [$I > 2\sigma(I)$]	0.0284, 0.0614	0.0339, 0.0904	0.0309, 0.0743
R_1, wR_2 (all data)	0.0294, 0.0616	0.0549, 0.1003	0.0495, 0.0838
Largest diff. peak and hole/e.Å^{-3}	2.346, –1.167	1.665, –1.235	2.136, –0.982

[a] **1b** = $[1,2\text{-}Me_2Py]_6[Bi_2Br_6I_3][Bi_2Br_{6.85}I_{2.15}]$; **2b** = $[1,3\text{-}Me_2Py]_3[Bi_2Br_{6.26}I_{2.74}]$; **3b** = $[1,4\text{-}Me_2Py]_3[Bi_2Br_{6.60}I_{2.40}]$; **4b** = $[4\text{-CNMePy}]_4[Bi_2Br_{7.52}I_{2.48}]$; **3c** = $[1,4\text{-}Me_2Py][BiI_4]$; **4c** = $[4\text{-CNMePy}]_8[Bi_3Br_{12}I_4][I_7]\cdot 2(I_2)$; **4d** = $[4\text{-CNMePy}]_5[K(BiI_6)_2]$

Table S7 Bond lengths [Å] in compounds **1b–4d**.

1b	
Bi(1)–Br(5)	2.7373(13)
Bi(1)–Br(4)	2.7463(14)
Bi(1)–I(6)	2.807(11)
Bi(1)–Br(6)	2.842(10)
Bi(1)–Br(1)	3.1003(13)
Bi(1)–Br(2)	3.1331(13)
Bi(1)–Br(3)	3.1847(11)
Bi(2)–Br(9)	2.686(12)
Bi(2)–Br(8)	2.742(9)
Bi(2)–Br(7)	2.7719(14)
Bi(2)–I(8)	2.809(16)
Bi(2)–I(9)	2.872(13)
Bi(2)–Br(1)	3.0979(14)
Bi(2)–Br(2)	3.1632(12)
Bi(2)–Br(3)	3.2300(12)
Bi(3)–Br(13)	2.7482(14)
Bi(3)–Br(15)	2.761(7)
Bi(3)–I(14)	2.796(12)
Bi(3)–Br(14)	2.824(7)
Bi(3)–Br(10)	2.9565(15)
Bi(3)–I(15)	3.01(2)
Bi(3)–Br(11)	3.056(4)
Bi(3)–Br(12)	3.062(10)
Bi(3)–I(11)	3.14(3)
Bi(3)–I(12)	3.155(14)
Bi(4)–Br(16)	2.7244(14)
Bi(4)–Br(18)	2.732(15)
Bi(4)–Br(17)	2.7677(15)
Bi(4)–I(18)	2.983(14)
Bi(4)–Br(10)	3.0150(15)
Bi(4)–I(11)	3.03(3)
Bi(4)–Br(11)	3.076(3)
Bi(4)–Br(12)	3.092(10)
Bi(4)–I(12)	3.288(13)
2b	
Bi(1)–Br(5)	2.771(3)

Bi(1)–I(4)	2.7930(15)
Bi(1)–Br(6)	2.834(19)
Bi(1)–I(5)	2.89(4)
Bi(1)–I(6)	2.931(14)
Bi(1)–I(1)	2.9904(15)
Bi(1)–Br(2)	3.117(14)
Bi(1)–I(2)	3.140(4)
Bi(1)–I(3)	3.1628(12)
Bi(2)–Br(9)	2.770(13)
Bi(2)–I(8)	2.7780(15)
Bi(2)–I(7)	2.78(2)
Bi(2)–Br(7)	2.811(9)
Bi(2)–I(9)	2.939(9)
Bi(2)–I(1)	3.0263(15)
Bi(2)–I(3)	3.1125(13)
Bi(2)–Br(2)	3.153(16)
Bi(2)–I(2)	3.242(6)

3b

Bi(1)–I(4)	2.7400(7)
Bi(1)–I(5)	2.746(18)
Bi(1)–Br(5)	2.754(9)
Bi(1)–I(6)	2.755(6)
Bi(1)–Br(6)	2.7576(14)
Bi(1)–I(2)	2.91(2)
Bi(1)–Br(2)	3.082(7)
Bi(1)–Br(3)	3.101(7)
Bi(1)–Br(1)	3.171(12)
Bi(1)–I(1)	3.191(5)
Bi(1)–I(3)	3.305(19)
Bi(2)–I(8)	2.698(17)
Bi(2)–Br(7)	2.749(5)
Bi(2)–I(9)	2.7644(8)
Bi(2)–I(7)	2.810(11)
Bi(2)–Br(8)	2.845(9)
Bi(2)–Br(3)	2.987(6)
Bi(2)–I(2)	3.00(3)
Bi(2)–Br(2)	3.059(9)
Bi(2)–Br(1)	3.158(11)

Bi(2)–I(3)	3.241(18)
Bi(2)–I(1)	3.321(5)

4b_100K

Bi(1)–Br(4)	2.725(12)
Bi(1)–I(3)	2.7863(7)
Bi(1)–I(1)	2.9116(7)
Bi(1)–I(4)	2.943(8)
Bi(1)–I(2)	2.9674(7)
Bi(1)–I(5)	3.0007(7)
Bi(1)–Br(5) (–x, –y+2, –z)	3.0074(7)

4b_150K

Bi(1)–I(3)	2.7935(8)
Bi(1)–I(4)	2.8653(8)
Bi(1)–I(1)	2.9205(8)
Bi(1)–I(2)	2.9791(8)
Bi(1)–I(5)	3.0045(9)
Bi(1)–Br(5) (–x, –y+2, –z)	3.0119(9)

3c

Bi(1)–I(3)	2.9212(6)
Bi(1)–I(4)	2.9311(6)
Bi(1)–I(1)	3.0299(5)
Bi(1)–I(2)	3.1666(5)
Bi(1)–I(1) (x, –y+3/2, z–1/2)	3.2782(5)
Bi(1)–I(2) (x, –y+3/2, z+1/2)	3.2834(5)

4c

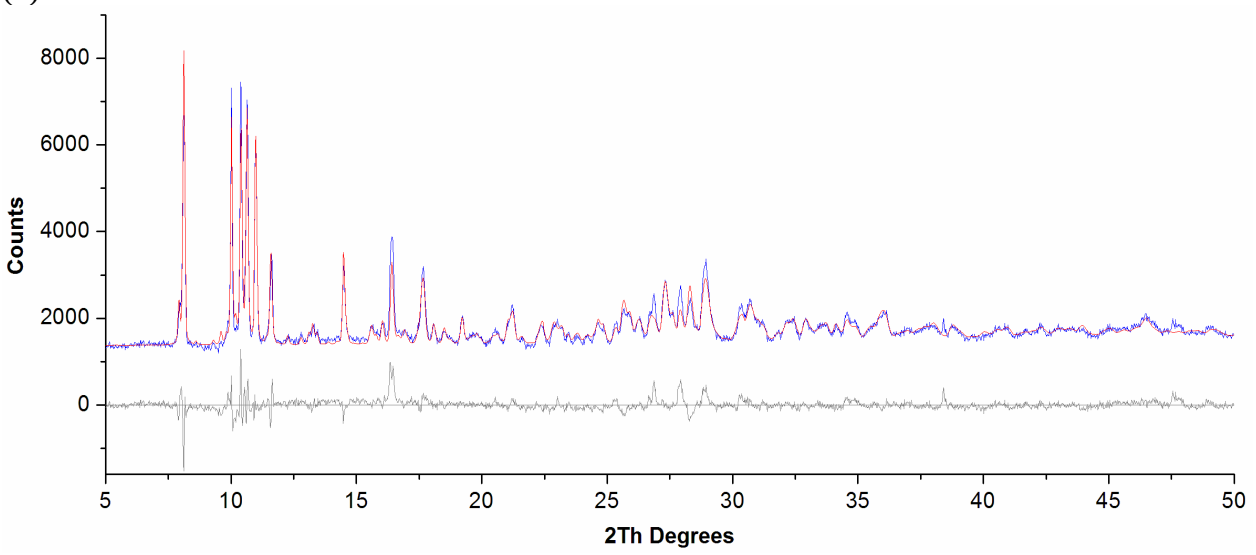
Bi(1)–I(12)	2.818(6)
Bi(1)–I(11)	2.847(3)
Bi(1)–I(13)	2.9721(5)
Bi(2)–Br(22)	2.8791(7)
Bi(2)–Br(21)	2.9077(9)

4d

Bi(1)–I(2)	3.0011(3)
Bi(1)–I(6)	3.0434(4)
Bi(1)–I(4)	3.0444(3)
Bi(1)–I(1)	3.1315(4)

Bi(1)–I(5)	3.1341(3)
Bi(1)–I(3)	3.1901(3)
Bi(1)–K(1)	4.30462(17)
I(1)–K(1)	3.4477(3)
I(3)–K(1)	3.4985(3)
I(5)–K(1)	3.5914(3)

(*a*)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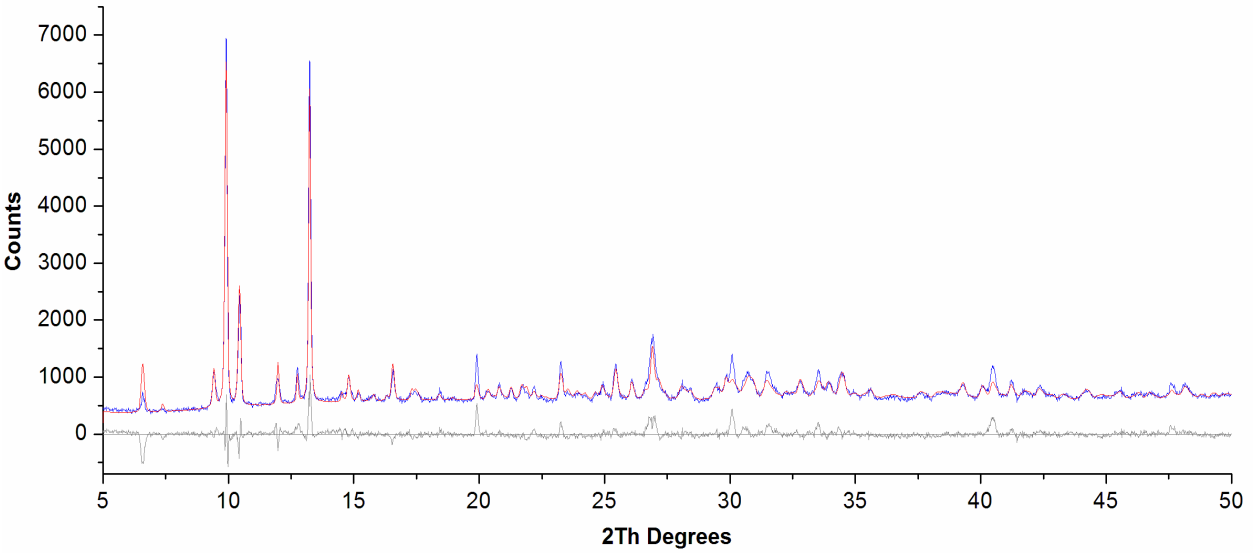
(*b*)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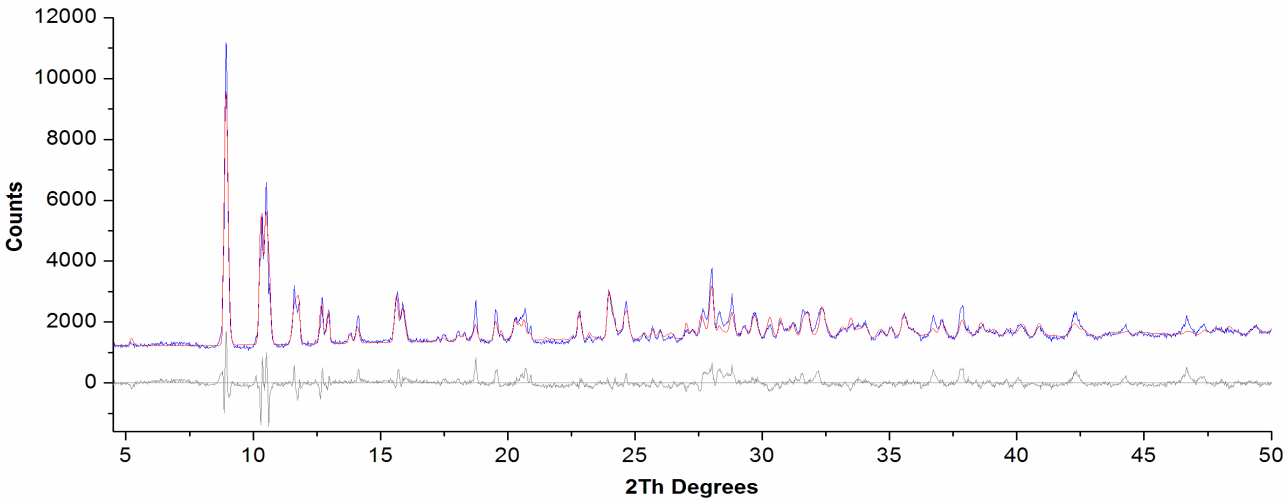
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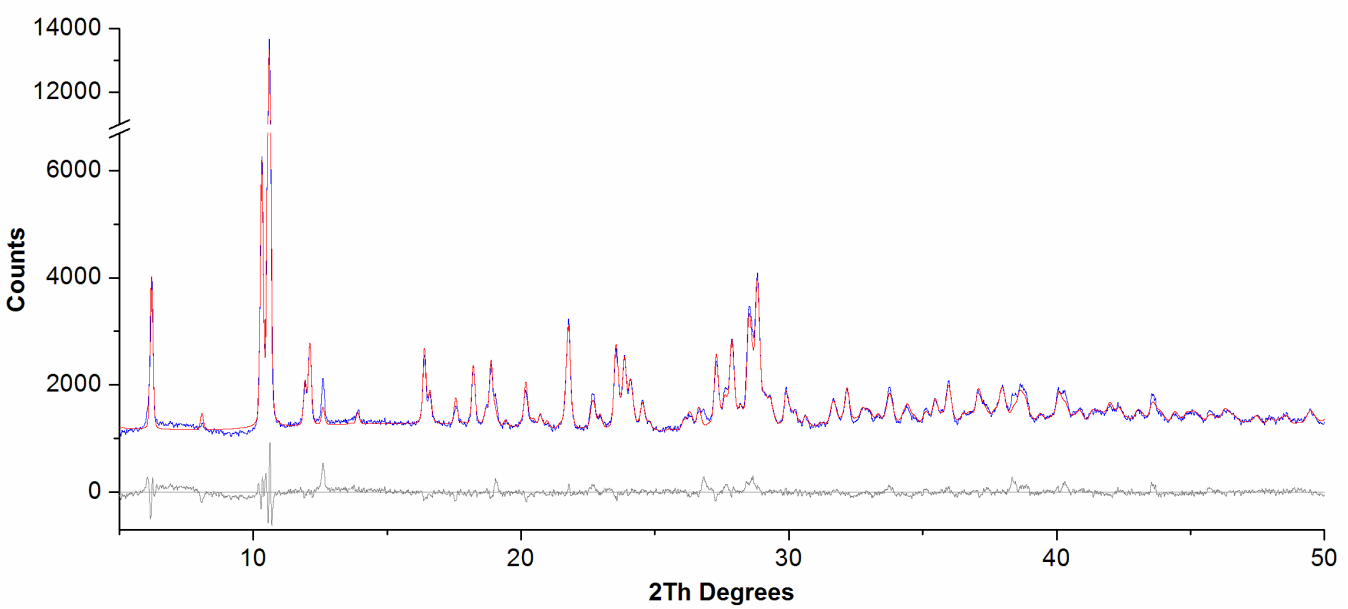


Figure S1 X-ray Rietveld refinement profiles for compounds (*a*) **1b**, (*b*) **2b**, (*c*) **3b**, and (*d*) **4b** recorded at RT. Red and blue lines correspond to the calculated profile and experimental pattern, respectively. The bottom trace shows the difference curve.

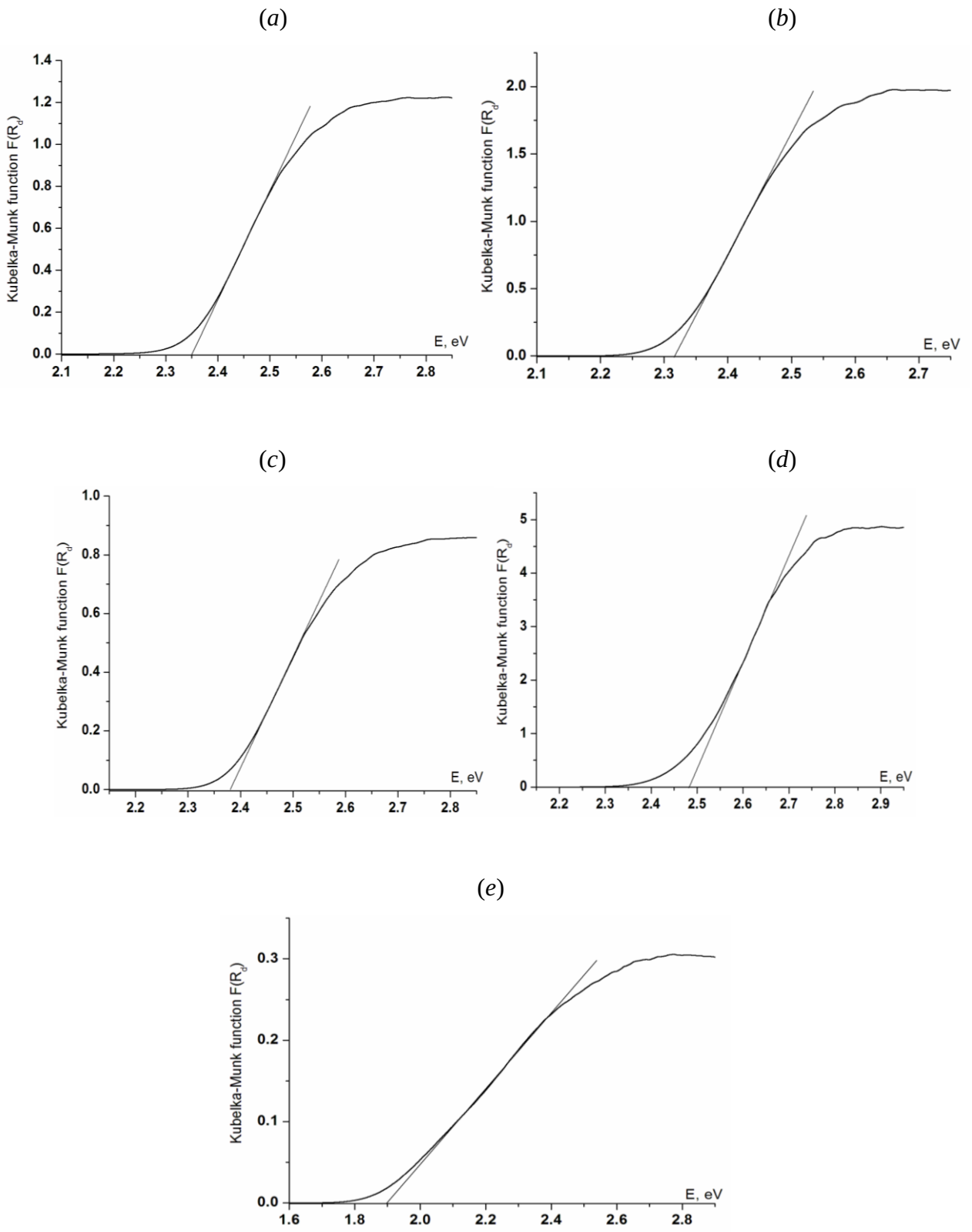
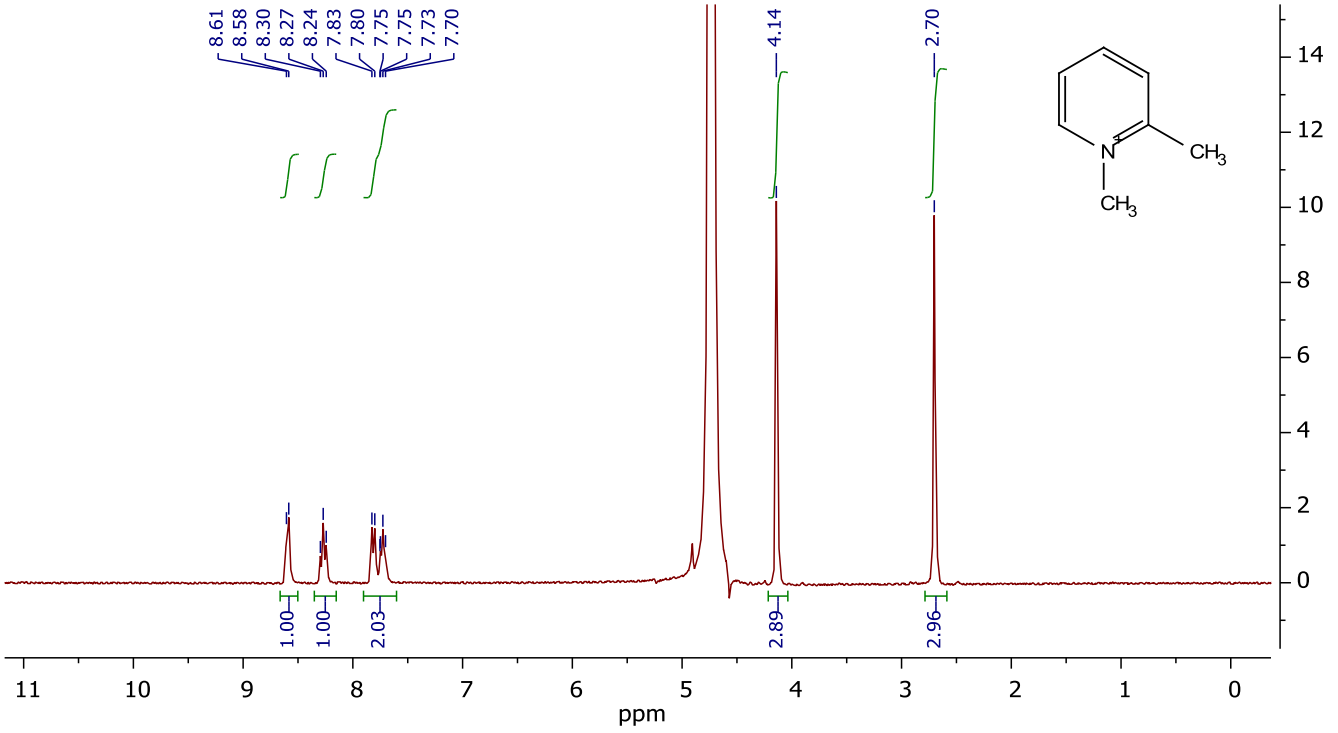


Figure S2 The reflectance spectra of compounds (*a*) **1b**, (*b*) **2b**, (*c*) **3b**, (*d*) **4b**, and (*e*) **4c**.

The ^{1}H NMR spectra were recorded using a Bruker AVANCE 300 instrument operating at 300 MHz frequency at 303 K.

The ^{1}H NMR spectra were recorded using a Bruker AVANCE 300 instrument operating at 300 MHz frequency at 303 K.

(*a*)



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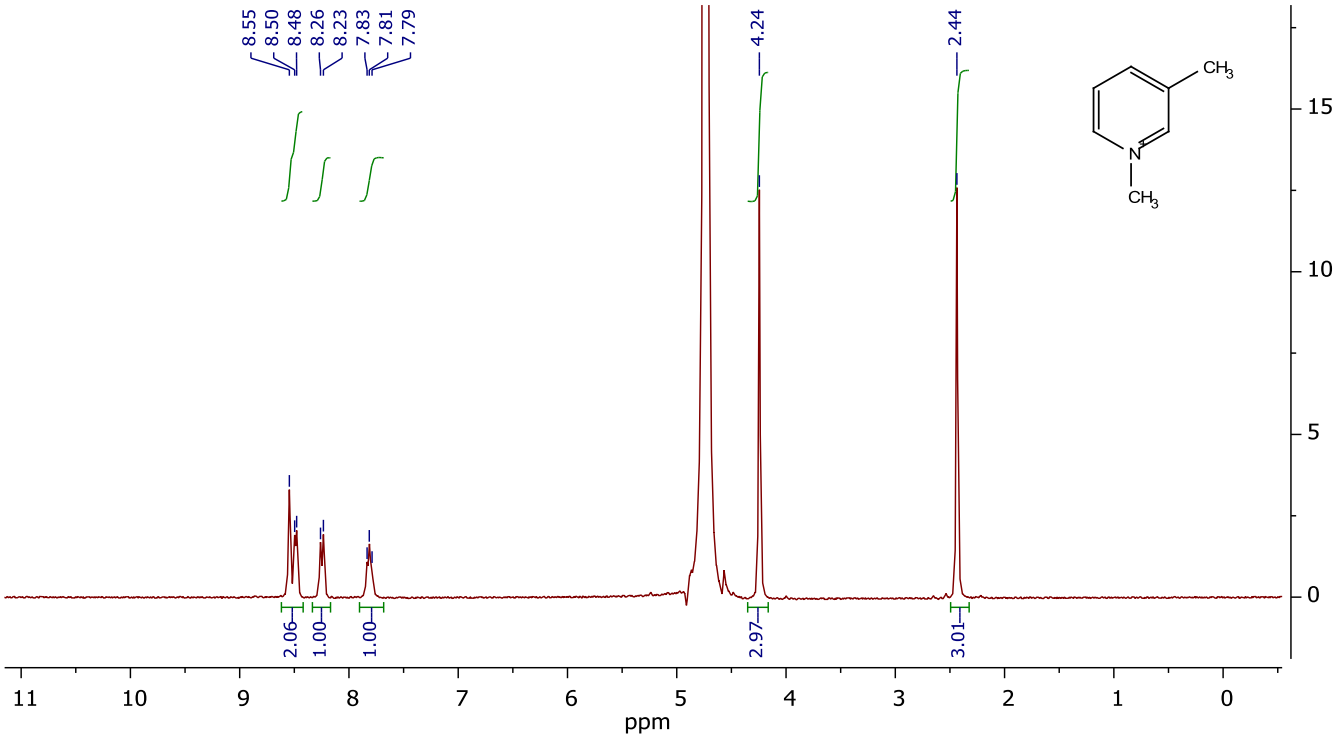

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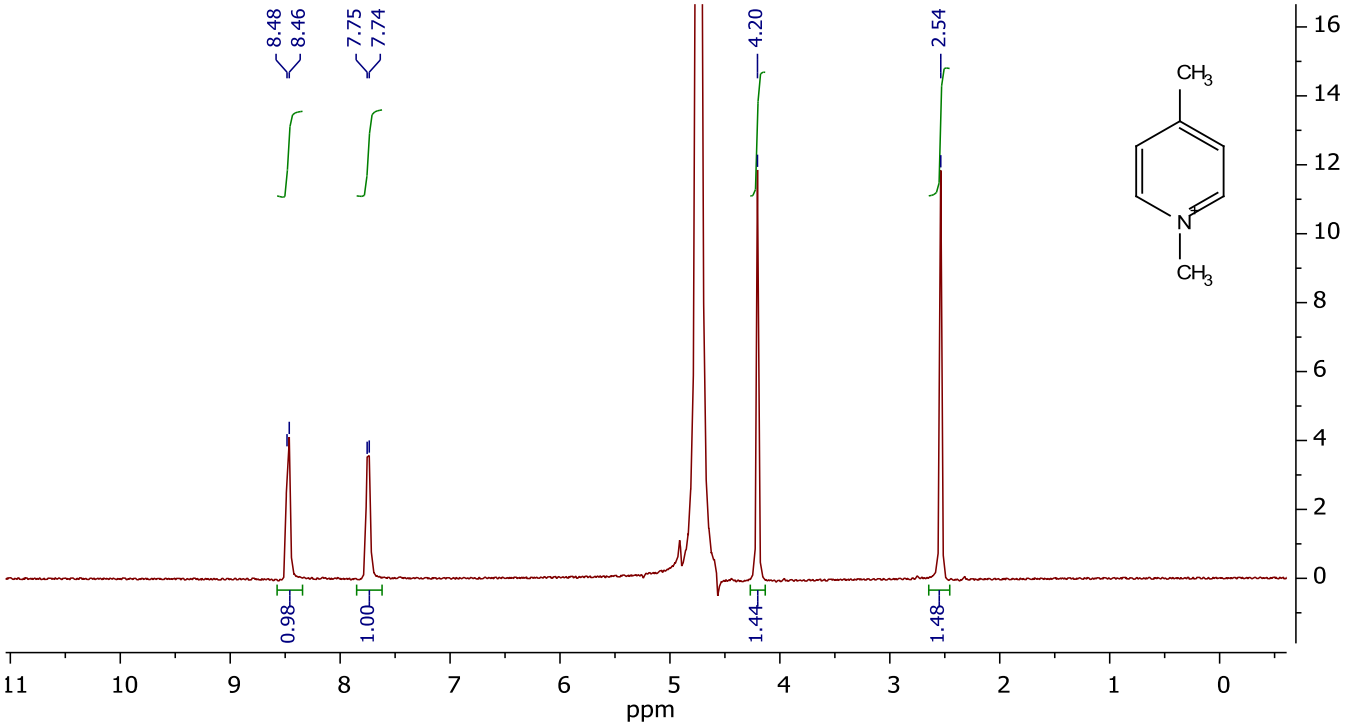


(*d*)

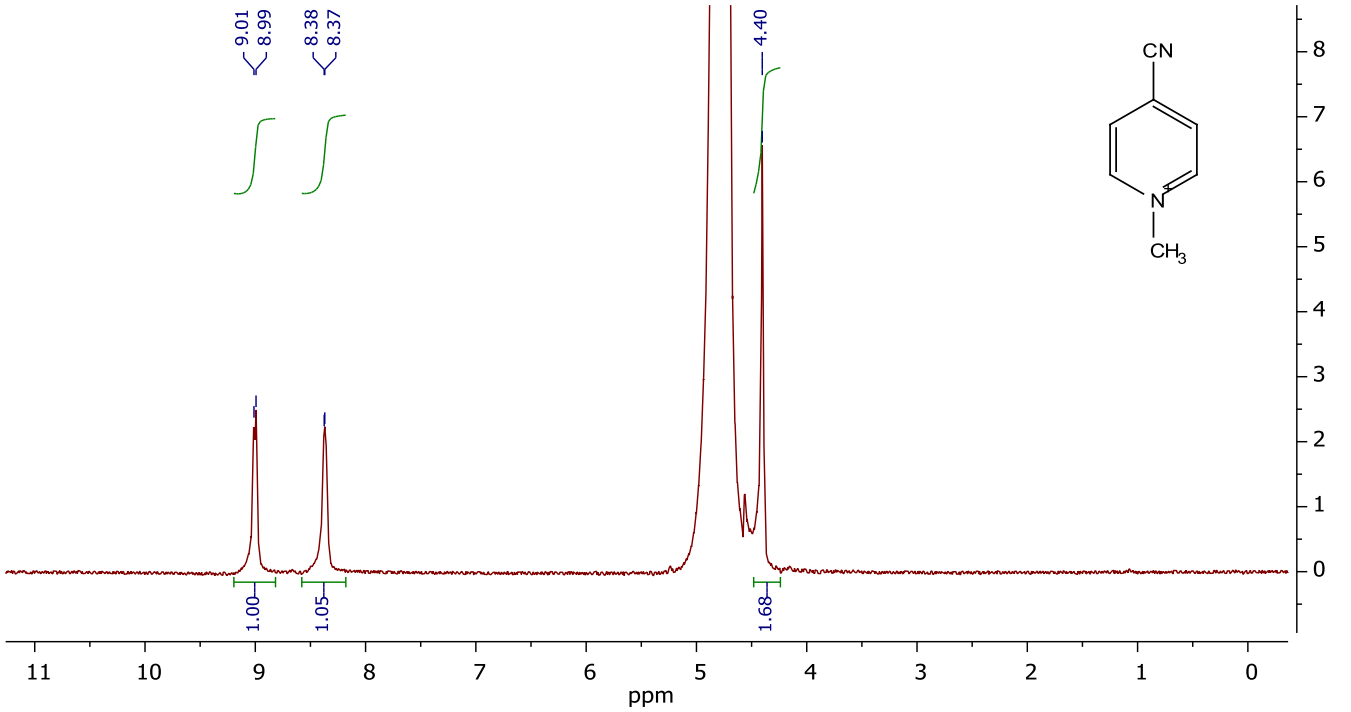
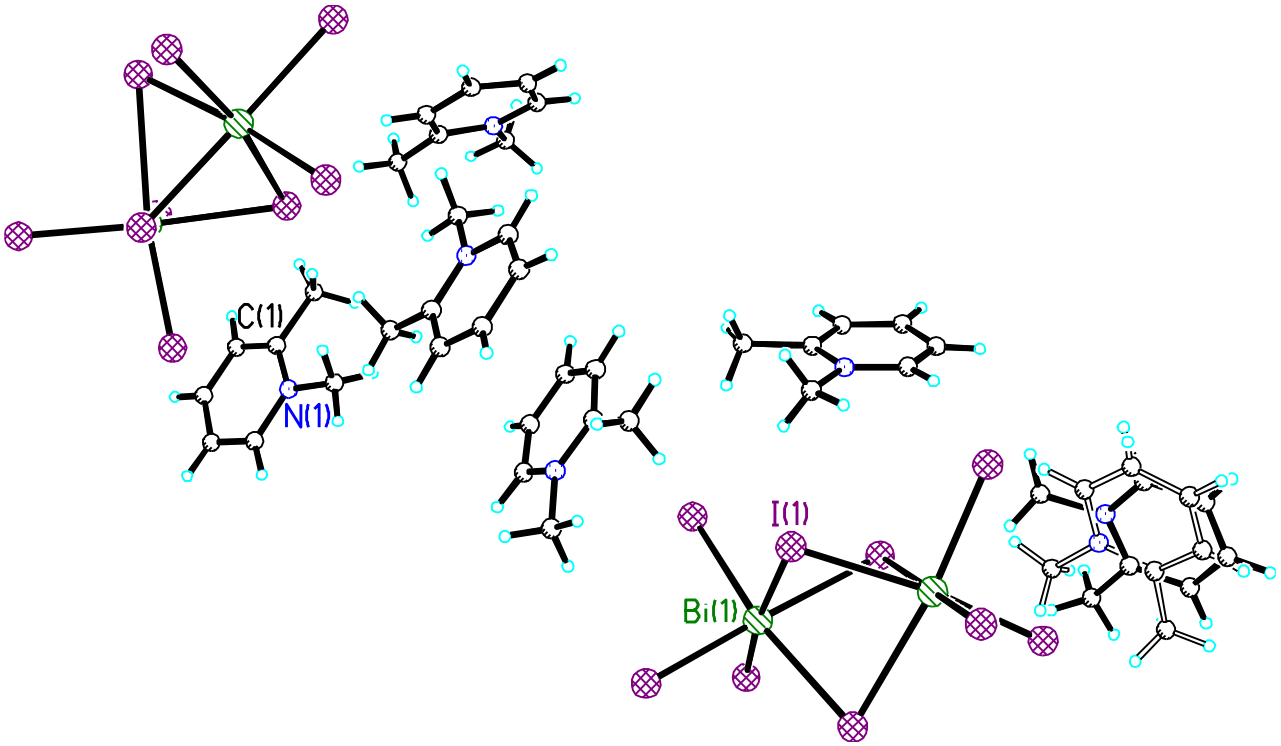


Figure S3 ^{1}H NMR spectra of compounds (*a*) **1a**, (*b*) **2a**, (*c*) **3a**, and (*d*) **4a**.

(*a*)



(*b*)

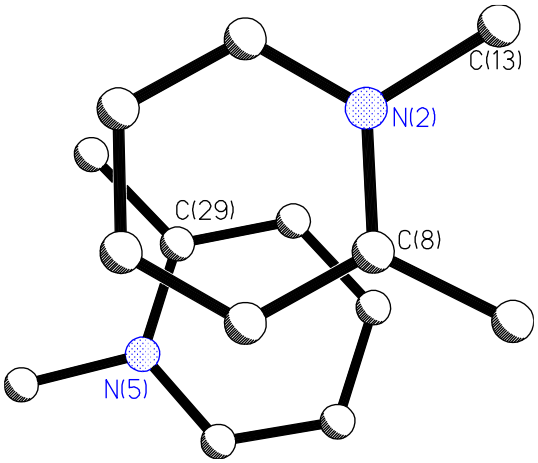
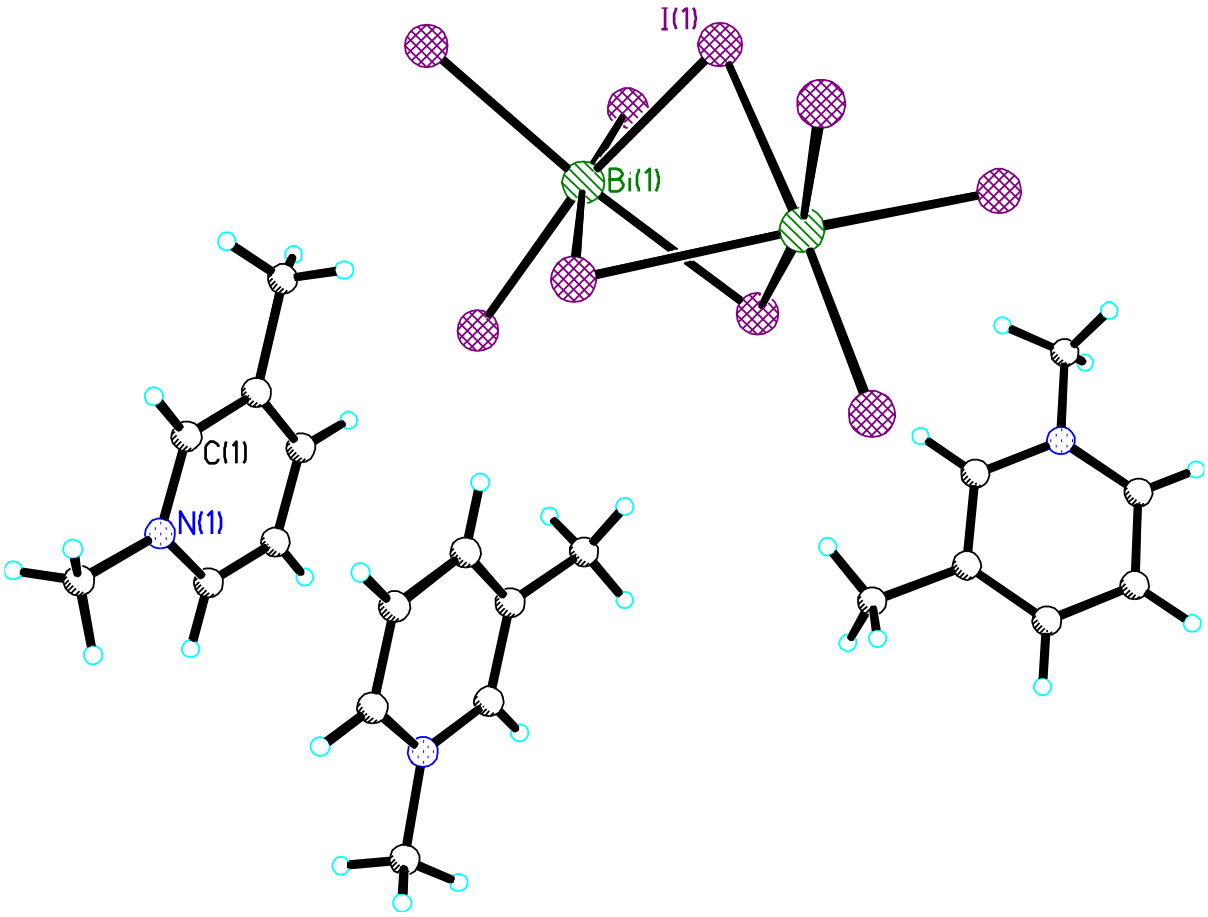


Figure S4 (*a*) A fragment of structure of $[1,2\text{-}Me_2Py]_6[Bi_2Br_6I_3][Bi_2Br_{6.85}I_{2.15}]$ (**1b**), where the Br atoms are omitted for clarity; and (*b*) stacking interaction between two cations.

(*a*)



(*b*) (*c*)

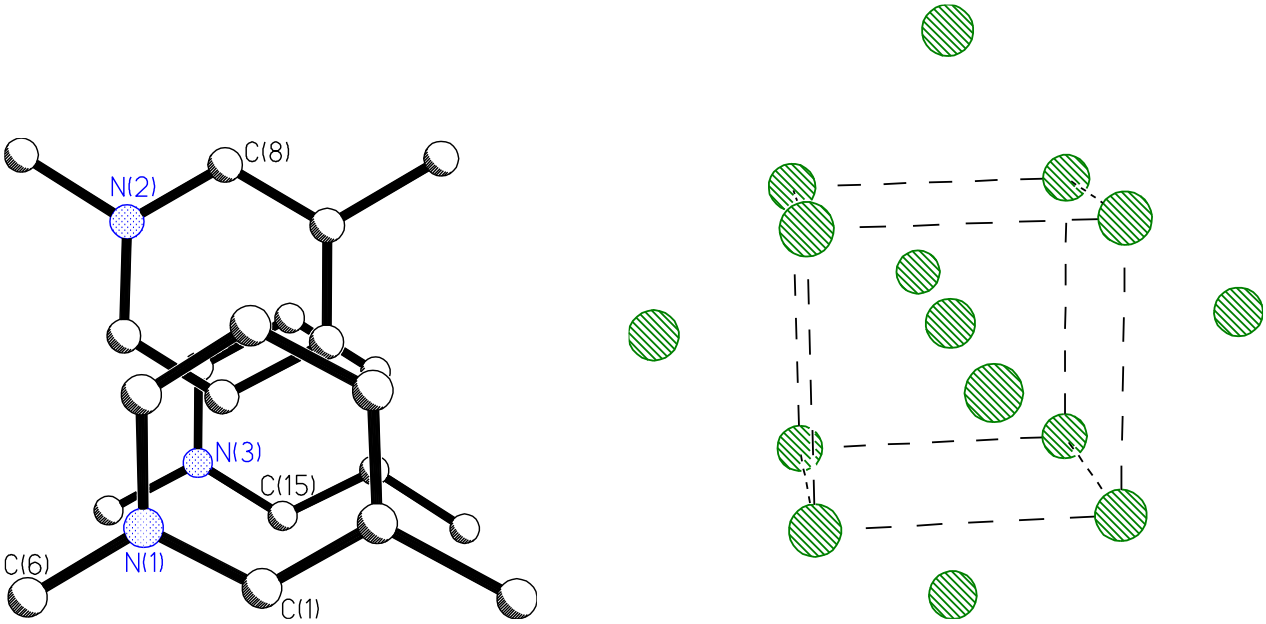
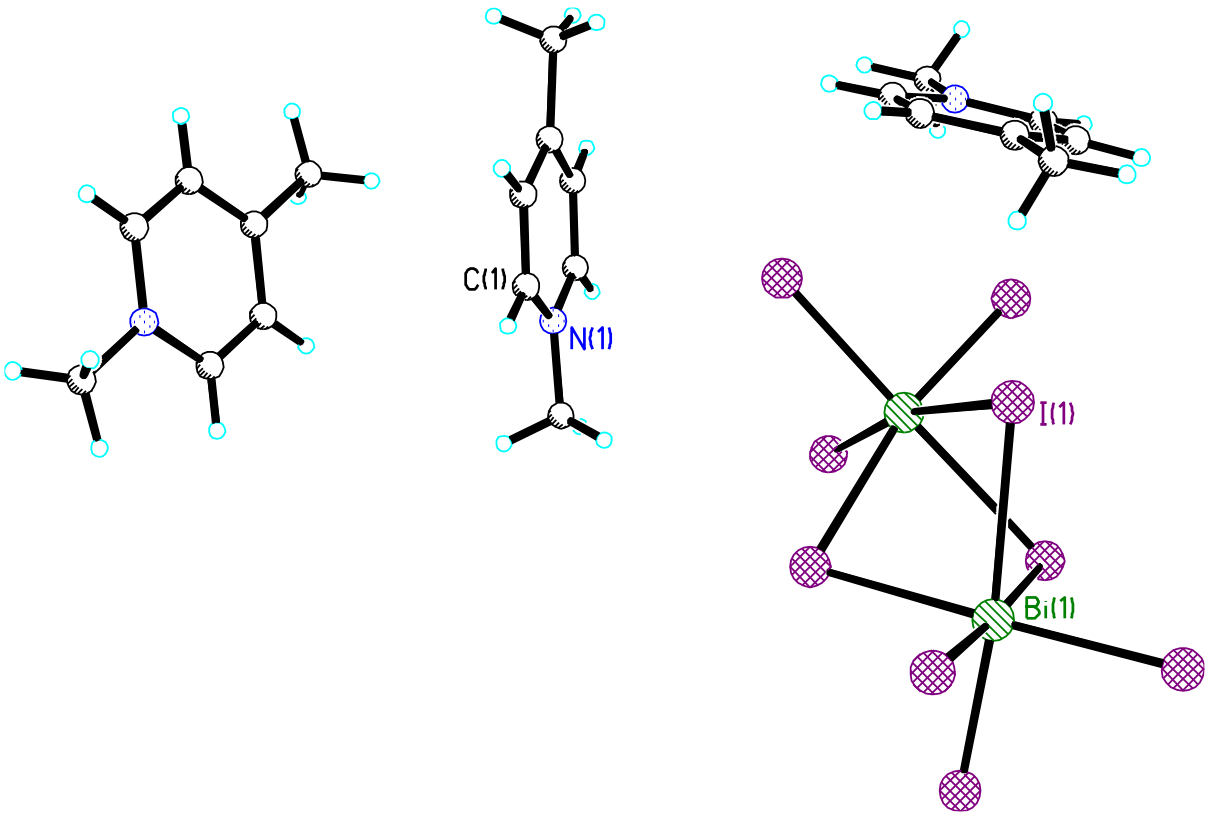


Figure S5 (*a*) A fragment of structure of [1,3-Me_2Py]$_3$[$Bi_2Br_{6.26}I_{2.74}$] (**2b**), where the Br atoms are omitted for clarity; (*b*) the stacking interaction between cations and mutual arrangement of anions; and (*c*) the Bi–Bi segment centers in one anion.

(*a*)



(*b*)

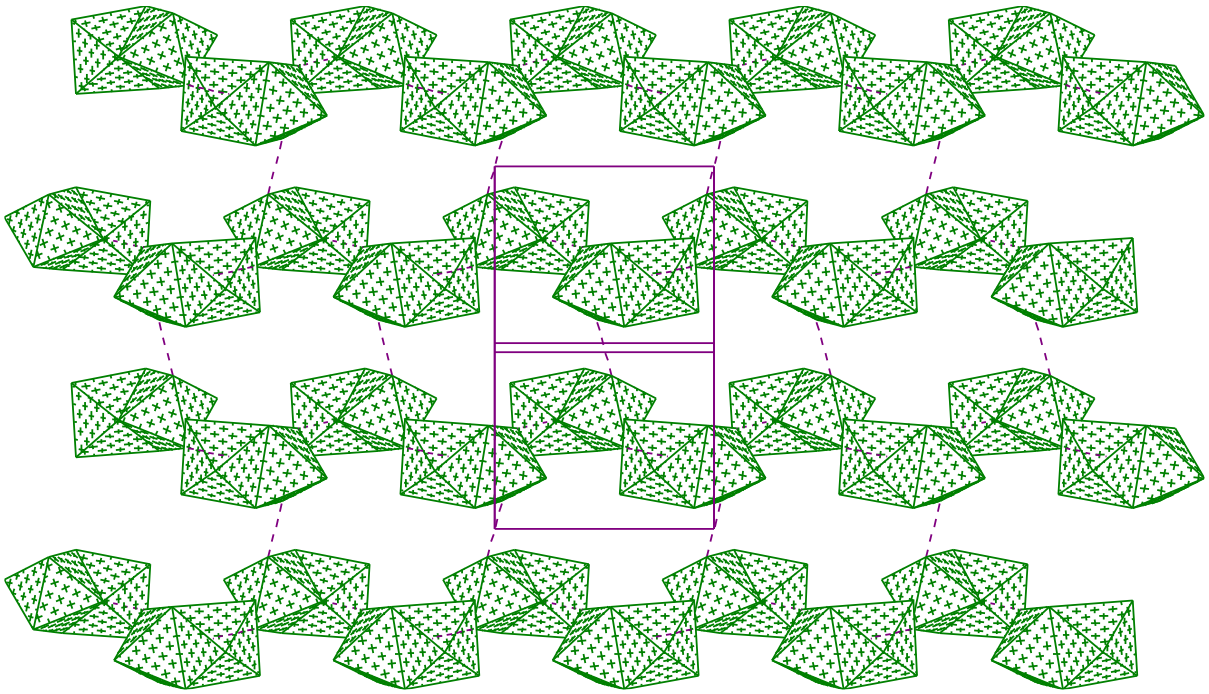
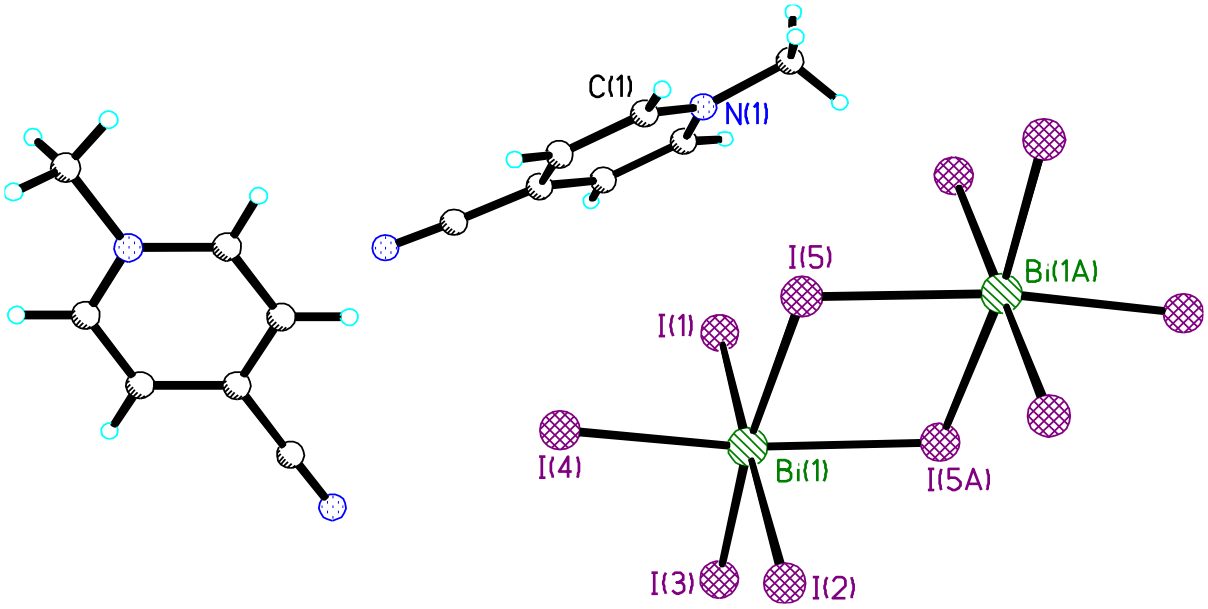


Figure S6 (*a*) A fragment of the structure of [1,4-Me_2Py]$_3$[$Bi_2Br_{6.60}I_{2.40}$] (**3b**), where the Br atoms are omitted for clarity; and (*b*) the structure of anion layer.

(*a*)



(*b*)

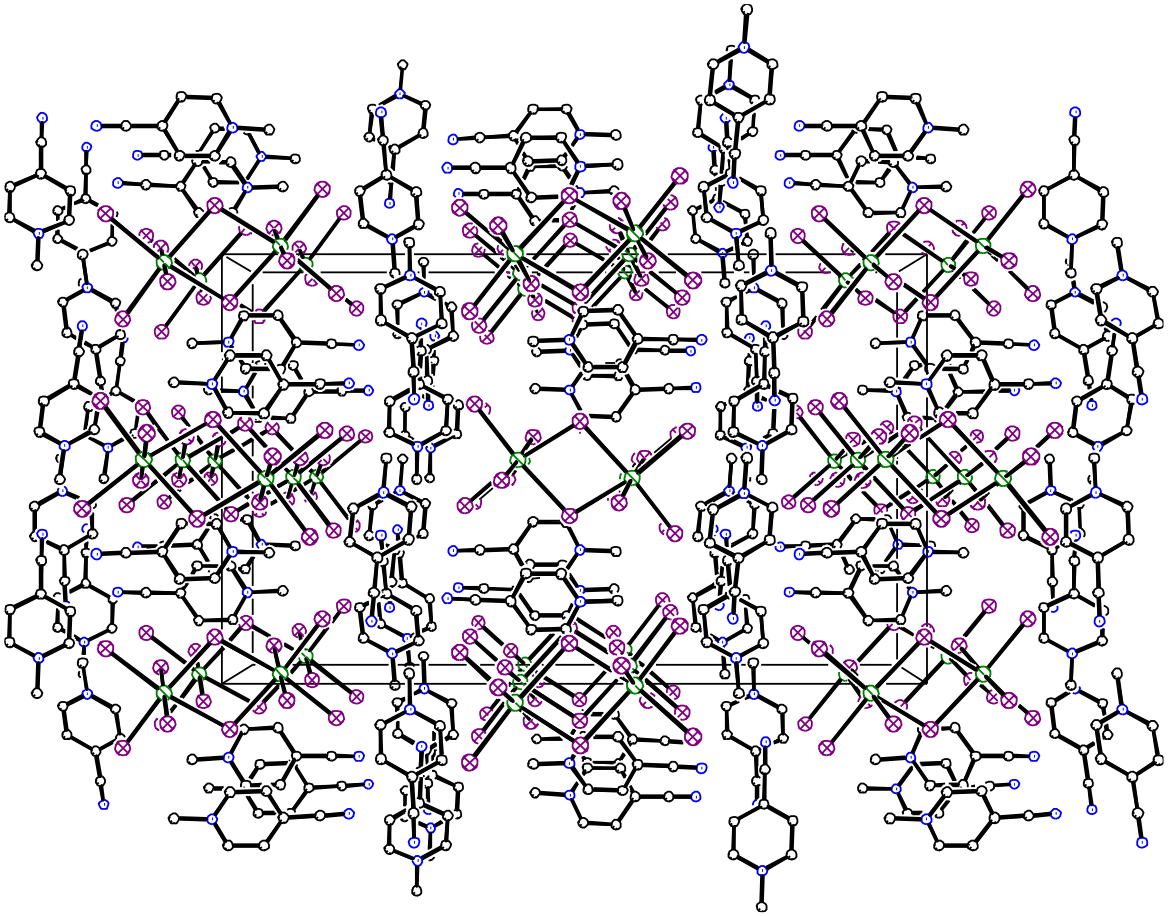
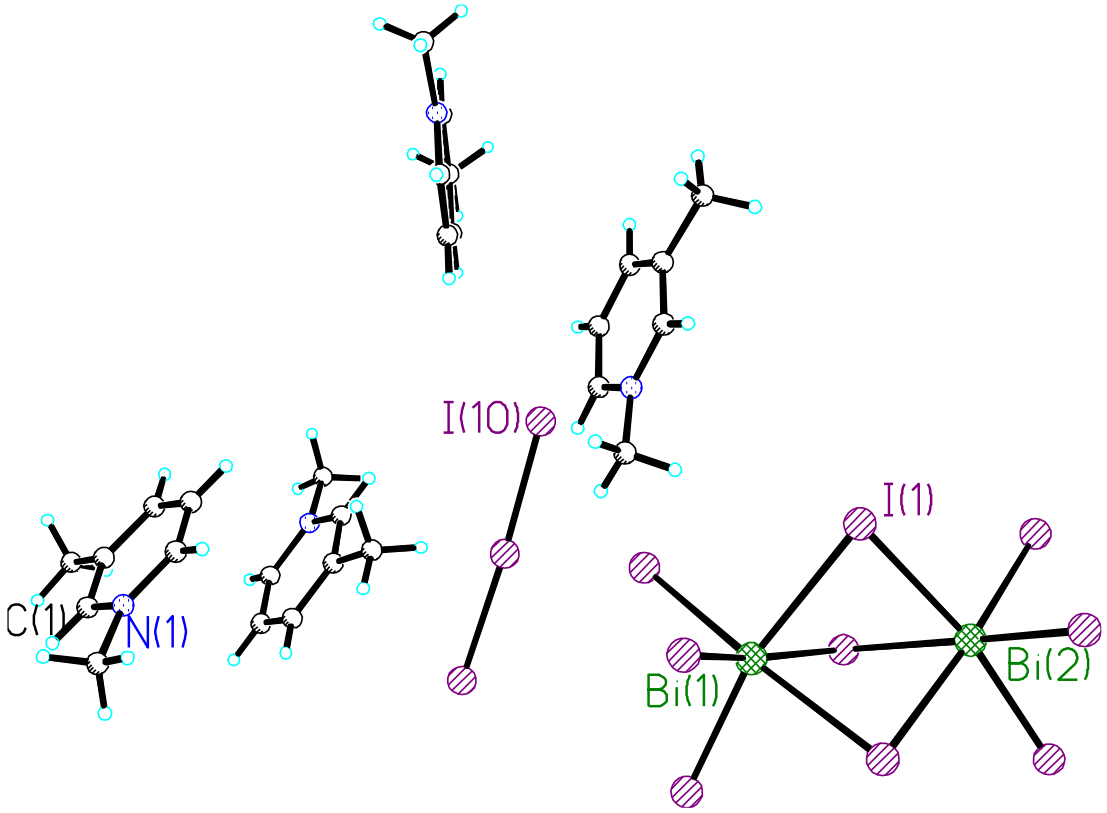


Figure S7 (*a*) A fragment of the structure of [4-CNMePy]$_4$[$Bi_2Br_{7.42}I_{2.58}$] (**4b_100K**), where the Br atoms are omitted for clarity; and (*b*) the projection along axis *y*.

(*a*)



(*b*)

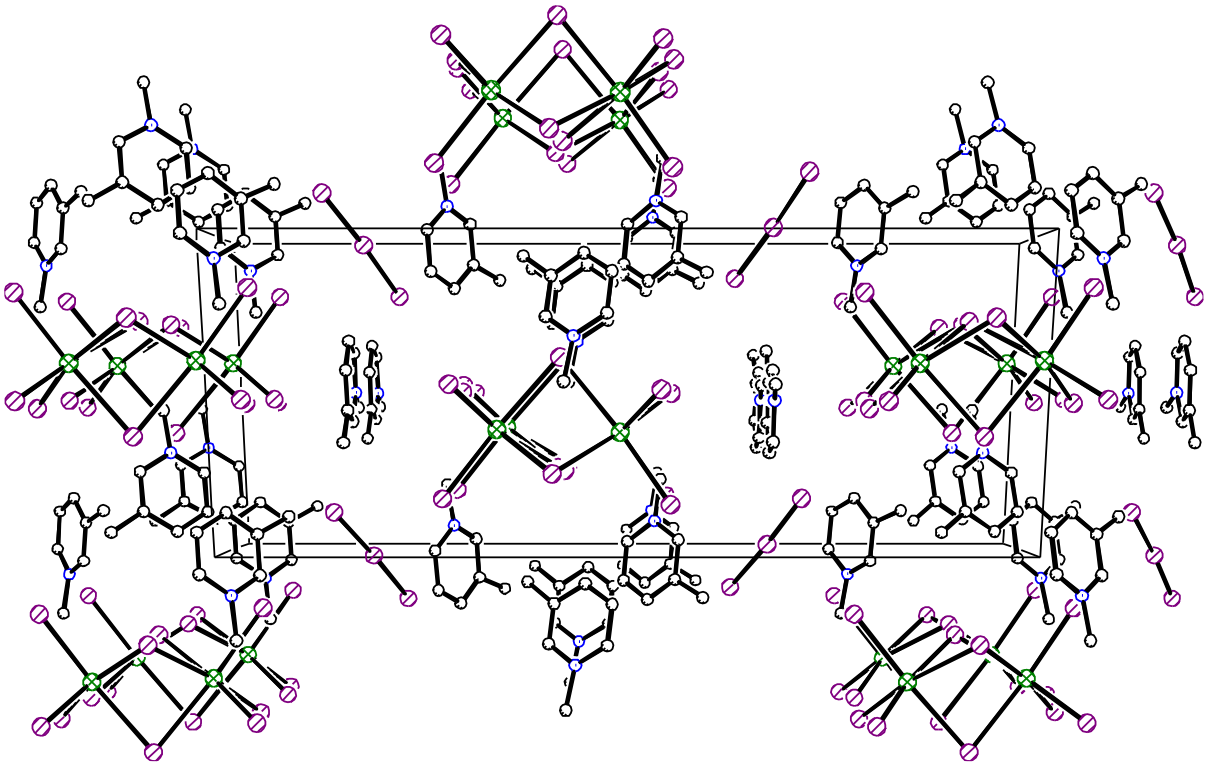
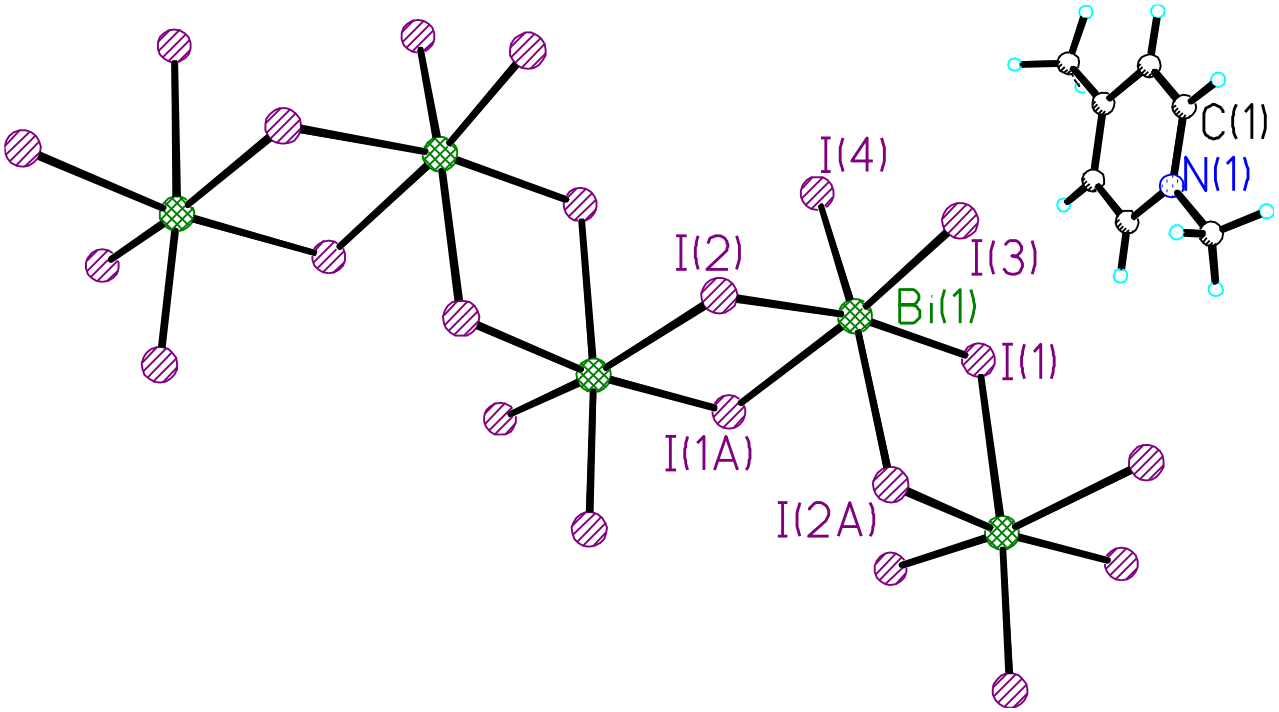


Figure S8 (*a*) A fragment of the structure of $[1,3\text{-}Me_2Py]_4[Bi_2I_9]I_3$ (**2c**) and (*b*) the projection along axis *x*.

(*a*)



(*b*)

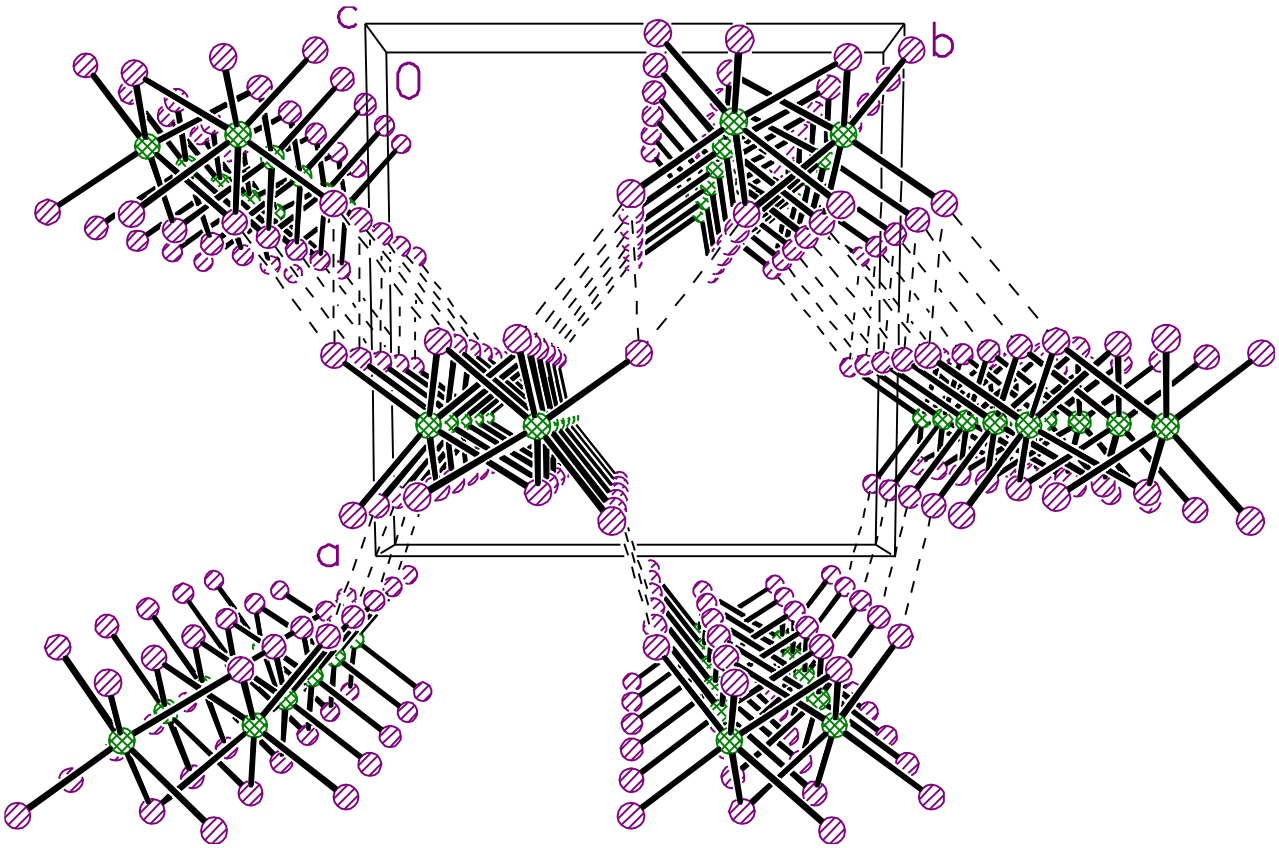
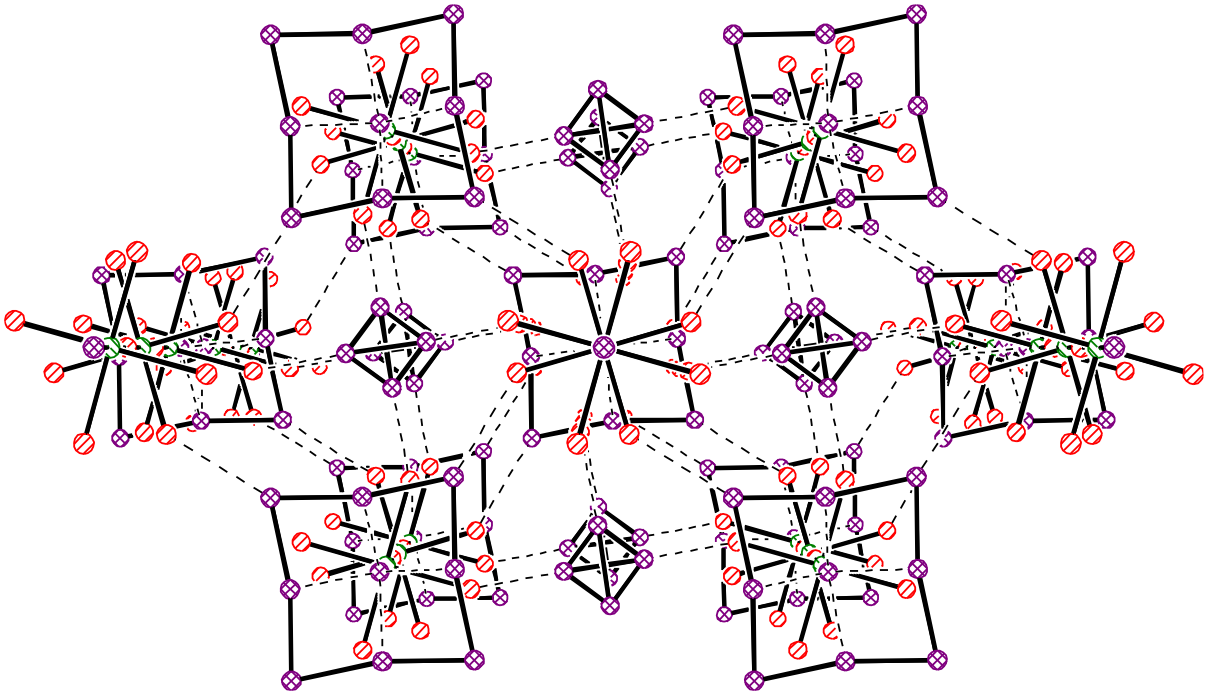


Figure S9 (*a*) A fragment of the structure of [1,4-Me_2Py][BiI_4] (**3c**) and (*b*) a projection of the anion sublattice along axis *z*.

(*a*)



(*b*)

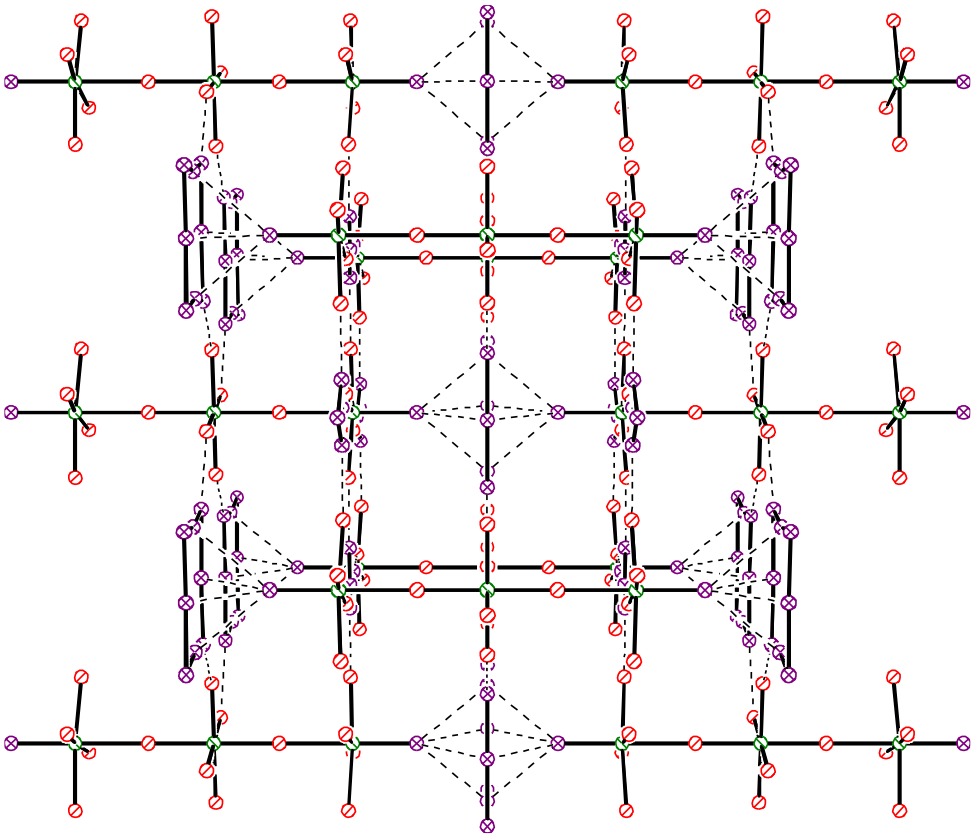


Figure S10 Projection of the anion sublattice (+ I_2 molecules) in the structure of [4-CNMePy]$_8$[$Bi_3Br_{12}I_4$]I_7·2(I_2) (**4c**) along axes (*a*) *z* and (*b*) *x*. The I_2 molecule is shown as a small square with diagonals, while the I_7^- anion is shown as a large square.

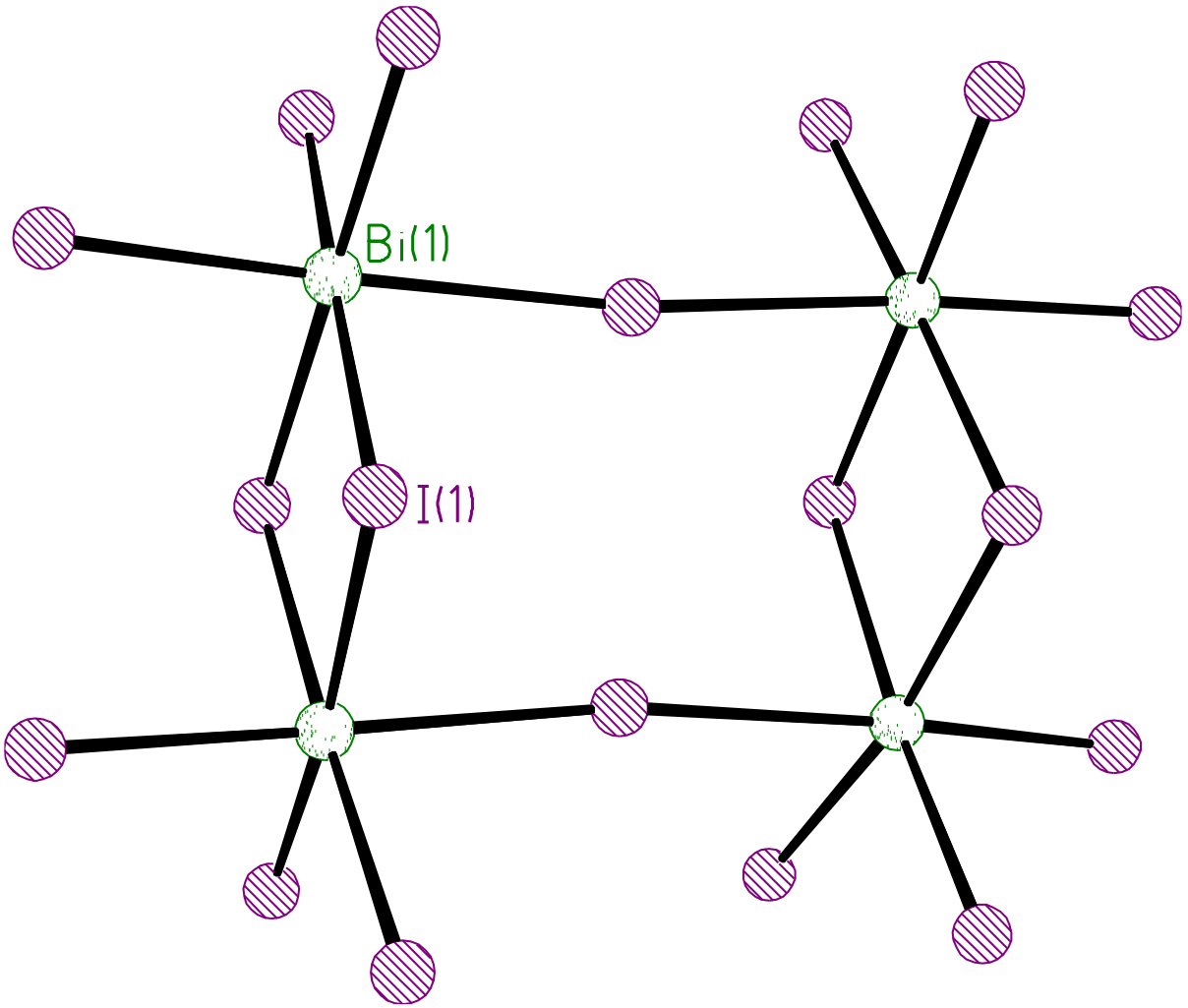


Figure S11 The structure of tetranuclear anion $[Bi_4I_{18}]^{6-}$ in the structure of $K_{5.64}(H_3O)_{4.36}[4\text{-}CNMePy]_8[Bi_4I_{18}]_3 \cdot 4.13H_2O$ (**4e**).

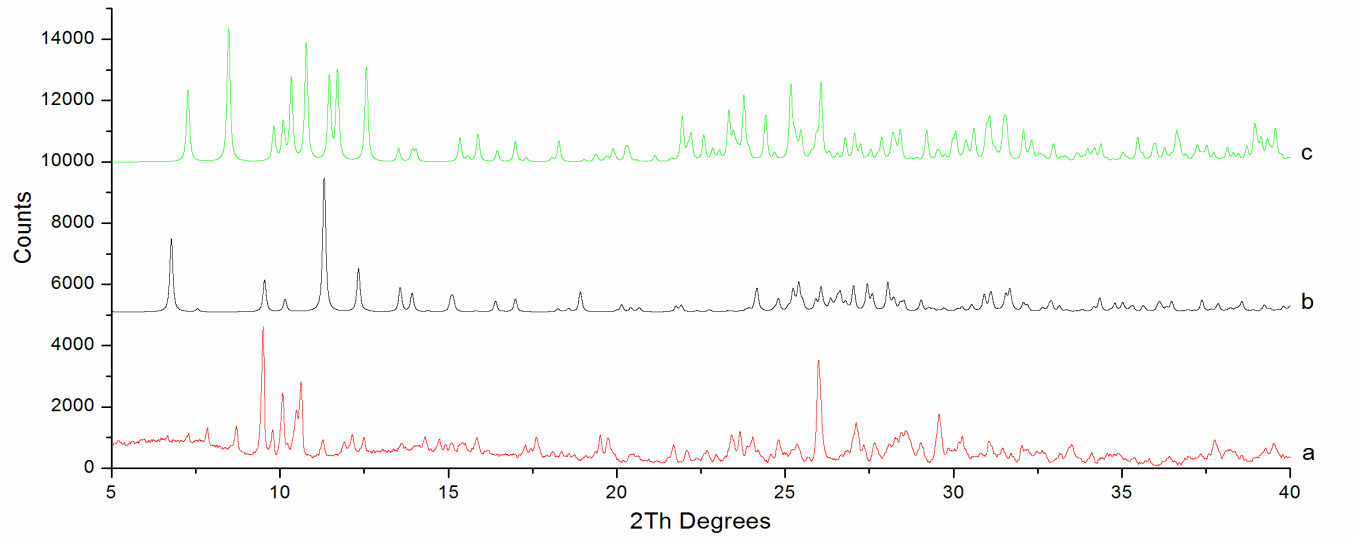


Figure S12 XRD patterns of (*a*) **4f** (experimental pattern), (*b*) **4e** (calculated profile), and (*c*) **4d** (calculated profile).