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Supplementary Information

Bi(III) polybromides: a new chapter in coordination chemistry of bismuth

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Details of the synthetic experiments

General remarks: All reagent, unless especially mentioned, were obtained from commercial sources and used as purchased. N-ethylpyridinium bromide was obtained by N-alkylation of pyridine by ethyl bromide and identified by ^{1}H NMR spectrum, 1,4-bis(pyridinium)butane was obtained by N-alkylation of pyridine (2 equivs) by 1,4-dibromobutane (See Chang et al., Polyhedron 2010, 29, 2976) and identified by ^{1}H NMR spectrum.

Synthesis of 1. 164 mg (0.54 mmol) of BiOBr were dissolved in 2 ml of 2M HBr. Then 4 ml of solution of Br_2 (1M) in 2M HBr were added. After that, solution of 4-methylpicolinium (52.5 mcl, 50 mg, 0.625 mmol) in 1 ml of 2M HBr was added. Within several minutes, deep orange crystalline precipitate of **1** starts to form; the process completes after 40-50 min. Yield 63%, based on Bi.

Synthesis of 2. 81 mg (0.265 mmol) of BiOBr were dissolved in 1 ml of 2M HBr. Then 4 ml of solution of Br_2 (1M) in 2M HBr were added. After that, solution of N-ethylpyridinium bromide (60 mg, 0.344 mmol) in 3 ml of 2M HBr was added. Within 1.5-2 hours, deep orange-red crystalline precipitate of **2** starts to form. Yield 42-46%, based on Bi.

Synthesis of 3. 81 mg (0.265 mmol) of BiOBr were dissolved in 1 ml of 2M HBr. Then 4 ml of solution of Br_2 (1M) in 2M HBr were added. After that, solution of bpe (50 mg, 0.271 mmol) in 4 ml of 2M HBr was added. Deep orange crystalline precipitate of **3** appears almost immediatey; the process completes within 30 minutes. Yield 82%.

Synthesis of 4. 41 mg (0.134 mmol) of BiOBr were 1 ml of 2M HBr. Then 5 ml of solution of Br_2 (1M) in 2M HBr were added. After that, solution of (BPB)Br_2 (50 mg, 0.133 mmol) in 5 ml

of 2M HBr was added. Deep red precipitate forms rapidly; the process completes within 30 minutes. Yield 68%, based on Bi.

X-ray crystallography. Diffraction data for single crystals of compounds **1–4** were obtained at 130 K on an automated Agilent Xcalibur diffractometer equipped with a CCD AtlasS2 detector (MoKα, graphite monochromator, ω-scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [S1]. The structures were solved by a direct method and refined by the full-matrix least squares technique in the anisotropic approximation (except hydrogen atoms) using the SHELX-2014 software package [S2]. Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinements are summarized in Table S1. Selected bond distances and angles are listed in Tables S2–S5. The CIF files are deposited at the Cambridge Crystallographic Data Center (CCDC 1450024-1450027).

[S1] CrysAlisPro 1.171.38.41. Rigaku Oxford Diffraction. 2015.
[S2] Sheldrick G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, A64, 112.

Table S1. Crystal data and structure refinement for **1–4**.

Compound	**1**	**2**	**3**	**4**
Empir. formula	$C_{21}H_{30}Bi_2Br_{13}N_3$	$C_{18}H_{24}Bi_2Br_{11}N_3$	$C_{12}H_{14}BiBr_7N_2$	$C_{28}H_{36}BiBr_{13}N_4$
M, g/mol	1781.27	1579.37	954.60	1676.42
Crystal system	*Monoclinic*	*Monoclinic*	*Orthorhombic*	*Orthorhombic*
Space group	*C*2/*c*	*P*2$_1$/*c*	*Cmcm*	*Pnma*
a, Å	11.91371(17)	9.5341(3)	14.1671(3)	16.0606(4)
b, Å	15.9042(2)	21.4727(6)	19.7299(4)	13.9864(3)
c, Å	21.6218(4)	35.0550(10)	7.74397(16)	19.4745(4)
β, deg.	91.0689(14)	97.093(3)		
V, Å^3	4096.14(11)	7121.6(4)	2164.56(8)	4374.56(17)
Z	4	8	4	4
$D_{calc.}$, g/cm^3	2.888	2.946	2.929	2.545
μ, mm^{-1}	21.280	22.229	21.064	15.931
F(000)	3192	5632	1712	3080
Crystal size, mm	0.46 × 0.34 × 0.03	0.20 × 0.14 × 0.10	0.31 × 0.19 × 0.01	0.07 × 0.07 × 0.06
θ range, deg.	3.42–25.68	3.34–25.68	3.34–26.37	3.28–29.10
Index ranges	$-14 \le h \le 14$, $-19 \le k \le 19$, $-26 \le l \le 26$	$-11 \le h \le 11$, $-20 \le k \le 26$, $-35 \le l \le 42$	$-17 \le h \le 17$, $-24 \le k \le 23$, $-9 \le l \le 7$	$-20 \le h \le 11$, $-18 \le k \le 14$, $-24 \le l \le 26$
Reflections collected / independent	29030 / 3878	30674 / 13202	8963 / 1235	19395 / 5359
R_{int}	0.0554	0.0399	0.0659	0.0268
Reflections with $I > 2\sigma(I)$	3434	9787	1139	4521
GooF	1.064	1.036	1.074	1.031
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0494$, $wR_2 = 0.1707$	$R_1 = 0.0496$, $wR_2 = 0.1039$	$R_1 = 0.0302$, $wR_2 = 0.0760$	$R_1 = 0.0227$, $wR_2 = 0.0339$
R indices (all data)	$R_1 = 0.0577$, $wR_2 = 0.1822$	$R_1 = 0.0761$, $wR_2 = 0.1185$	$R_1 = 0.0336$, $wR_2 = 0.0782$	$R_1 = 0.0346$, $wR_2 = 0.0362$
Largest diff. peak and hole, e/Å^3	4.071 / −3.245	2.464 / −3.986	1.530 / −1.112	1.049 / −0.882

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

Bond	*d*, Å	Bond	*d*, Å
Bi(1)–Br(1)	2.7080(14)	Bi(1)–Br(5)^{i}	3.0531(15)
Bi(1)–Br(2)	2.7831(13)	Br(4)–Bi(1)^{i}	3.0808(14)
Bi(1)–Br(3)	2.7057(15)	Br(5)–Bi(1)^{i}	3.0533(15)
Bi(1)–Br(4)	3.0808(14)	Br(7)–Br(7)^{i}	2.337(3)
Bi(1)–Br(5)	2.9332(13)	Br(6)–Br(6)#2	2.334(3)
Angle	ω, deg.	Angle	ω, deg.
Br(1)–Bi(1)–Br(2)	96.02(4)	Br(3)–Bi(1)–Br(4)	92.59(4)
Br(1)–Bi(1)–Br(4)	168.04(4)	Br(3)–Bi(1)–Br(5)	93.56(5)
Br(1)–Bi(1)–Br(5)	87.12(4)	Br(3)–Bi(1)–Br(5)^{i}	170.57(4)
Br(1)–Bi(1)–Br(5)^{i}	93.50(5)	Br(5)^{i}–Bi(1)–Br(4)	79.99(4)
Br(2)–Bi(1)–Br(4)	94.00(4)	Br(5)–Bi(1)–Br(4)	81.88(3)
Br(2)–Bi(1)–Br(5)^{i}	89.96(4)	Br(5)–Bi(1)–Br(5)^{i}	79.71(5)
Br(2)–Bi(1)–Br(5)	169.38(5)	Bi(1)–Br(4)–Bi(1)^{i}	81.54(5)
Br(3)–Bi(1)–Br(1)	92.75(5)	Bi(1)–Br(5)–Bi(1)^{i}	84.44(4)
Br(3)–Bi(1)–Br(2)	96.41(5)		

Symmetry transformations used to generate equivalent atoms:
i) $-x + 1, y, -z + ½$; ii) $-x + 1, -y + 1, -z + 1$.

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

Bond	*d*, Å	Bond	*d*, Å
Bi(1)–Br(11)	2.6799(13)	Bi(3)–Br(23)	2.7565(11)
Bi(1)–Br(12)	2.7709(14)	Bi(3)–Br(24)	2.9697(12)
Bi(1)–Br(13)	2.7133(12)	Bi(3)–Br(25)	2.9988(15)
Bi(1)–Br(14)	3.0215(11)	Bi(3)–Br(26)	2.9965(12)
Bi(1)–Br(15)	3.0545(15)	Bi(4)–Br(24)	3.0489(12)
Bi(1)–Br(16)	3.0909(14)	Bi(4)–Br(25)	3.0570(15)
Bi(2)–Br(14)	3.0369(12)	Bi(4)–Br(26)	3.0702(13)
Bi(2)–Br(15)	3.0818(16)	Bi(4)–Br(27)	2.7167(13)
Bi(2)–Br(16)	2.9475(13)	Bi(4)–Br(28)	2.7429(13)
Bi(2)–Br(17)	2.7547(13)	Bi(4)–Br(29)	2.7034(12)
Bi(2)–Br(18)	2.7350(15)	Br(1)–Br(2)	2.3227(17)
Bi(2)–Br(19)	2.7088(13)	Br(3)–Br(3)^{i}	2.318(3)
Bi(3)–Br(21)	2.7411(12)	Br(4)–Br(4)^{ii}	2.317(4)
Bi(3)–Br(22)	2.7546(13)	Br(5)–Br(5)^{ii}	2.324(5)
Angle	ω, deg.	Angle	ω, deg.
Br(11)–Bi(1)–Br(12)	95.01(4)	Br(21)–Bi(3)–Br(22)	92.76(4)
Br(11)–Bi(1)–Br(13)	91.57(4)	Br(21)–Bi(3)–Br(23)	89.96(4)
Br(11)–Bi(1)–Br(14)	93.04(4)	Br(21)–Bi(3)–Br(24)	88.92(4)
Br(11)–Bi(1)–Br(15)	95.95(4)	Br(21)–Bi(3)–Br(25)	93.66(5)
Br(11)–Bi(1)–Br(16)	174.47(4)	Br(21)–Bi(3)–Br(26)	172.60(4)
Br(12)–Bi(1)–Br(14)	88.01(4)	Br(22)–Bi(3)–Br(23)	92.44(4)
Br(12)–Bi(1)–Br(15)	165.41(4)	Br(22)–Bi(3)–Br(24)	95.92(4)
Br(12)–Bi(1)–Br(16)	88.21(4)	Br(22)–Bi(3)–Br(25)	173.48(5)
Br(13)–Bi(1)–Br(12)	92.74(4)	Br(22)–Bi(3)–Br(26)	91.72(4)
Br(13)–Bi(1)–Br(14)	175.25(4)	Br(23)–Bi(3)–Br(24)	171.61(4)
Br(13)–Bi(1)–Br(15)	96.56(4)	Br(23)–Bi(3)–Br(25)	88.71(4)
Br(13)–Bi(1)–Br(16)	92.77(4)	Br(23)–Bi(3)–Br(26)	95.73(4)
Br(14)–Bi(1)–Br(15)	81.82(3)	Br(24)–Bi(3)–Br(25)	83.06(4)
Br(14)–Bi(1)–Br(16)	82.56(3)	Br(24)–Bi(3)–Br(26)	84.76(3)
Br(15)–Bi(1)–Br(16)	80.15(4)	Br(26)–Bi(3)–Br(25)	81.77(5)
Br(14)–Bi(2)–Br(15)	81.13(4)	Br(24)–Bi(4)–Br(25)	80.80(4)

Br(16)–Bi(2)–Br(14)	84.72(4)	Br(24)–Bi(4)–Br(26)	82.17(3)
Br(16)–Bi(2)–Br(15)	81.99(4)	Br(25)–Bi(4)–Br(26)	79.65(4)
Br(17)–Bi(2)–Br(14)	89.18(3)	Br(27)–Bi(4)–Br(24)	95.18(4)
Br(17)–Bi(2)–Br(15)	92.84(4)	Br(27)–Bi(4)–Br(25)	95.61(5)
Br(17)–Bi(2)–Br(16)	172.54(4)	Br(27)–Bi(4)–Br(26)	174.87(4)
Br(18)–Bi(2)–Br(14)	87.46(4)	Br(27)–Bi(4)–Br(28)	91.19(4)
Br(18)–Bi(2)–Br(15)	166.77(4)	Br(28)–Bi(4)–Br(24)	88.32(3)
Br(18)–Bi(2)–Br(16)	90.35(4)	Br(28)–Bi(4)–Br(25)	167.63(4)
Br(18)–Bi(2)–Br(17)	93.68(4)	Br(28)–Bi(4)–Br(26)	93.12(4)
Br(19)–Bi(2)–Br(14)	177.23(4)	Br(29)–Bi(4)–Br(24)	172.69(4)
Br(19)–Bi(2)–Br(15)	98.25(5)	Br(29)–Bi(4)–Br(25)	96.18(5)
Br(19)–Bi(2)–Br(16)	92.52(4)	Br(29)–Bi(4)–Br(26)	90.75(4)
Br(19)–Bi(2)–Br(17)	93.55(4)	Br(29)–Bi(4)–Br(27)	91.73(4)
Br(19)–Bi(2)–Br(18)	92.83(5)	Br(29)–Bi(4)–Br(28)	93.92(4)
Bi(1)–Br(14)–Bi(2)	81.71(3)	Bi(3)–Br(24)–Bi(4)	81.89(3)
Bi(1)–Br(15)–Bi(2)	80.45(4)	Bi(3)–Br(25)–Bi(4)	81.29(4)
Bi(2)–Br(16)–Bi(1)	82.00(3)	Bi(3)–Br(26)–Bi(4)	81.10(3)

Symmetry transformations used to generate equivalent atoms:
i) $-x + 1, -y, -z + ½$; ii) $-x + 1, -y + 1, -z + 1$.

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

Bond	*d*, Å	Bond	*d*, Å
Bi(1)–Br(11)	2.7220(8)	Bi(1)–Br(13)^{iii}	3.030(5)
Bi(1)–Br(12)	2.8400(8)	Br(1)–Br(1)^{vi}	2.3548(19)
Bi(1)–Br(13)	2.992(5)		
Angle	ω, deg.	Angle	ω, deg.
Br(11)^{i}–Bi(1)–Br(11)	97.01(4)	Br(12)–Bi(1)–Br(12)^{ii}	175.49(4)
Br(11)–Bi(1)–Br(12)	88.505(13)	Br(12)–Bi(1)–Br(13)	91.577(14)
Br(11)–Bi(1)–Br(13)^{i}	85.82(5)	Br(12)–Bi(1)–Br(13)^{iii}	91.852(16)
Br(11)–Bi(1)–Br(13)^{iii}	96.64(5)	Br(13)–Bi(1)–Br(13)^{iii}	80.53(2)
Br(11)–Bi(1)–Br(13)^{iv}	166.34(5)	Br(13)–Bi(1)–Br(13)^{i}	91.35(9)
Br(11)–Bi(1)–Br(13)	177.17(5)	Bi(1)–Br(13)–Bi(1)^{v}	169.17(9)

Symmetry transformations used to generate equivalent atoms:
i) $x, y, -z + 3/2$; ii) $-x + 1, y, -z + 3/2$; iii) $-x + 1, -y + 1, z - ½$;
iv) $x, -y + 1, -z + 2$; v) $-x + 1, -y + 1, -z + 2$; vi) $-x, y, -z + 3/2$.

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

Bond	*d*, Å	Bond	*d*, Å
Bi(1)–Br(1)	2.8653(2)	Br(4)–Br(6)	2.7489(6)
Bi(1)–Br(2)	2.7510(4)	Br(6)–Br(7)	2.4192(6)
Bi(1)–Br(3)	2.8469(5)	Br(8)–Br(9)	2.3603(8)
Bi(1)–Br(4)	3.0224(4)	Br(10)–Br(11)	2.6181(7)
Bi(1)–Br(5)	2.8087(5)	Br(11)–Br(12)	2.4861(7)
Angle	ω, deg.	Angle	ω, deg.
$Br(1)^{i}$–Bi(1)–Br(1)	177.427(12)	Br(3)–Bi(1)–Br(4)	86.806(14)
Br(1)–Bi(1)–Br(4)	90.991(6)	Br(5)–Bi(1)–Br(1)	90.828(7)
Br(2)–Bi(1)–Br(1)	88.989(6)	Br(5)–Bi(1)–Br(3)	176.333(13)
Br(2)–Bi(1)–Br(3)	91.800(14)	Br(5)–Bi(1)–Br(4)	89.527(13)
Br(2)–Bi(1)–Br(4)	178.606(15)	Br(6)–Br(4)–Bi(1)	152.09(2)
Br(2)–Bi(1)–Br(5)	91.867(14)	Br(7)–Br(6)–Br(4)	179.05(3)
Br(3)–Bi(1)–Br(1)	89.236(7)	Br(12)–Br(11)–Br(10)	178.36(3)

Symmetry transformations used to generate equivalent atoms: i) x, $-y + 3/2$, z.

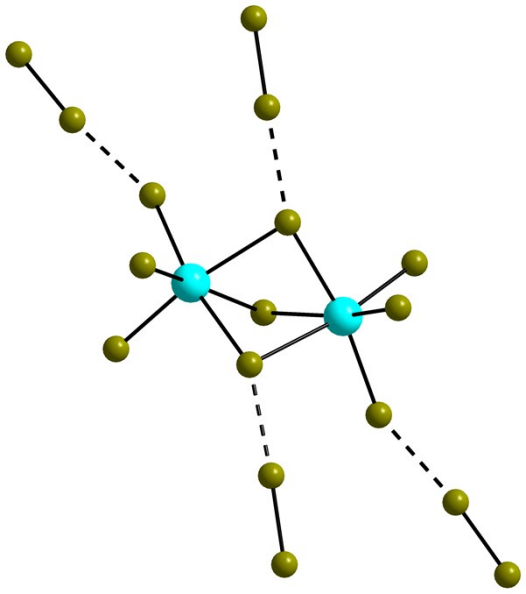

Fig. S1. Specific Br…Br contacts between $[Bi_2(\mu\text{-}Br)_3Br_6]^{3+}$ cation and Br_2 molecules in the structure **1**.

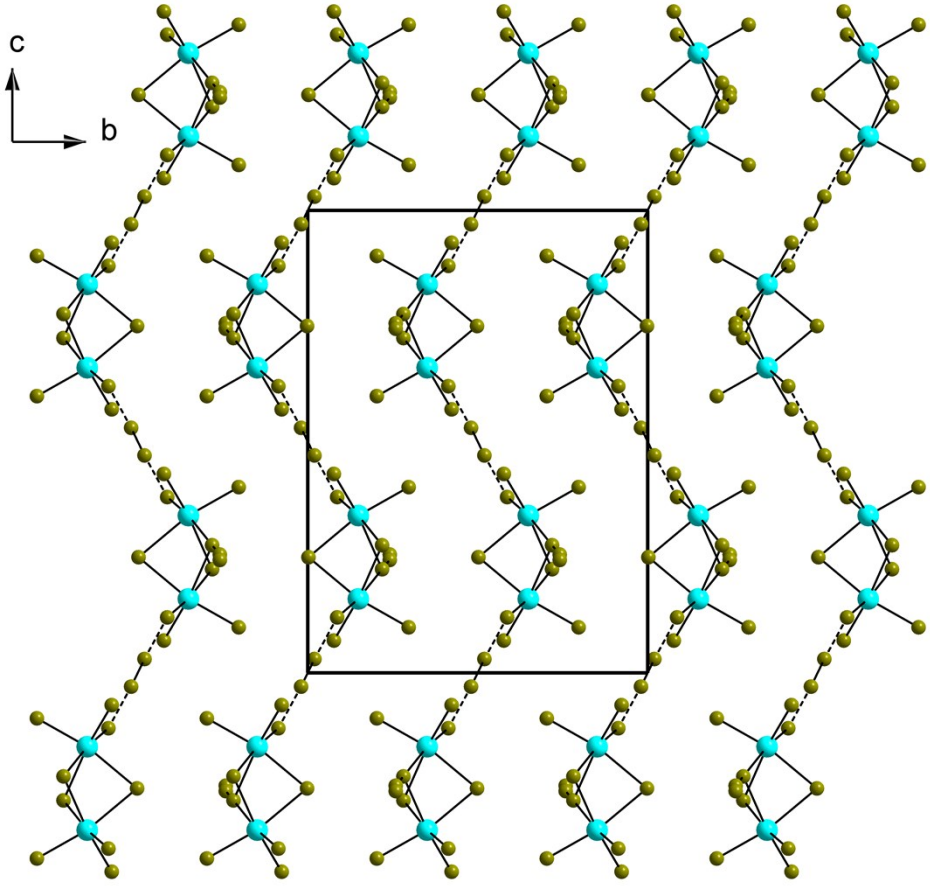

Fig. S2. Packing of supramolecular layers in the structure **1** (organic cations are omitted).

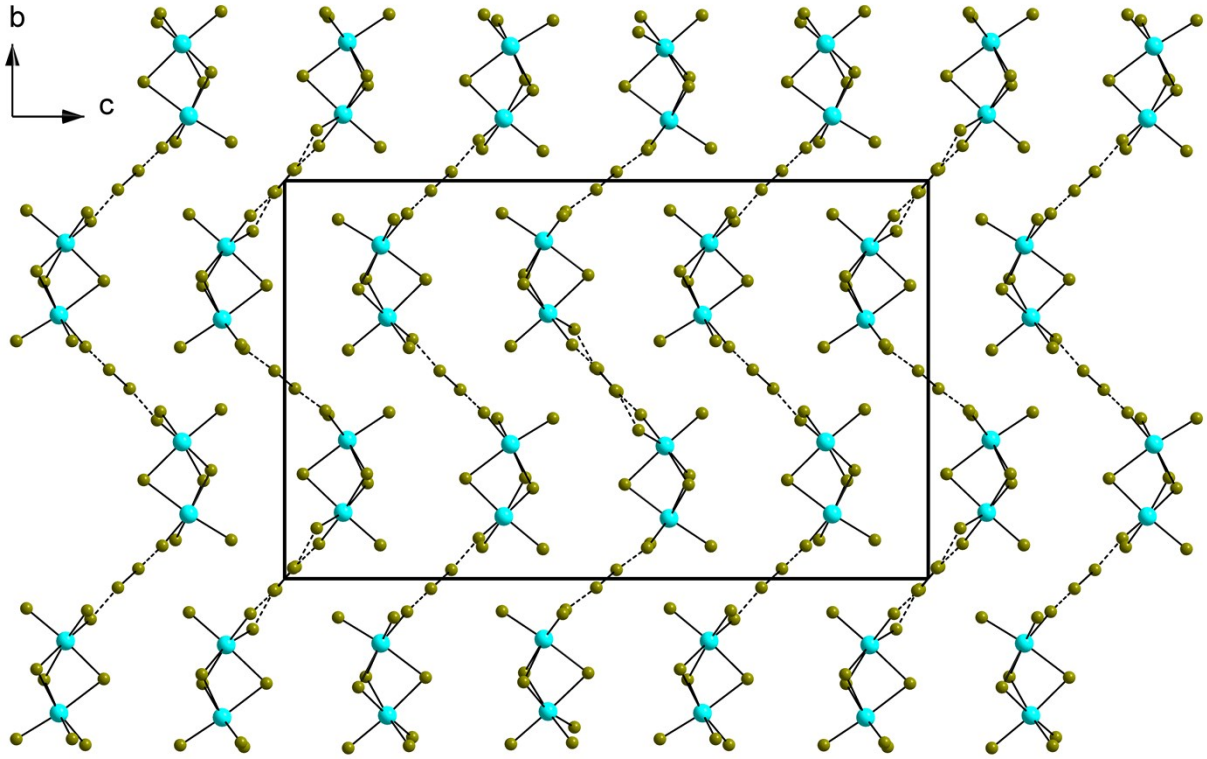

Fig. S3. Packing of layers in the structure **2** (organic cations are omitted).

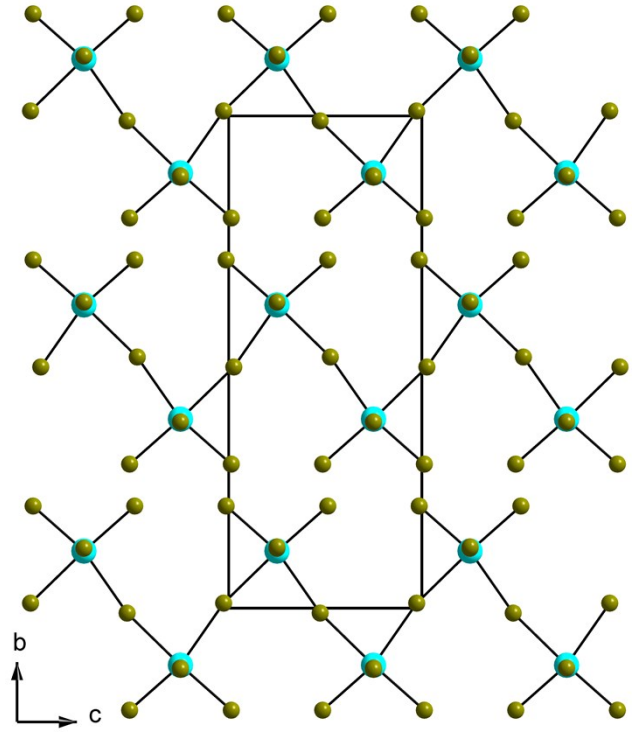

Fig. S4. Packing of layers in the structure **3** (organic cations are omitted).

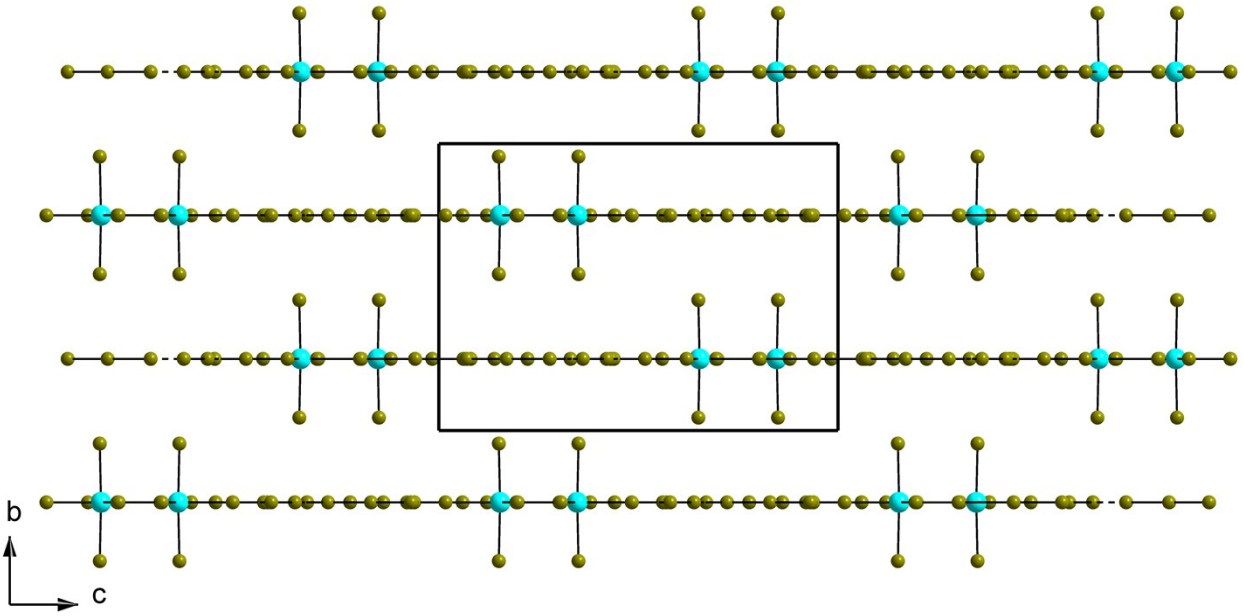

Fig. S5. Packing of layers in the structure **4** (organic cations are omitted).