Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

Hypervalent organobismuth(III) carbonate, chalcogenides and halides with the pendant arm ligands 2-(Me_2NCH_2)C_6H_4 and 2,6-(Me_2NCH_2)$_2C_6H_3$

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Solid state structure

$[2\text{-}(Me_2NCH_2)C_6H_4]_2BiOH\cdot 2H_2O$ ($1\cdot 2H_2O$)

- the crystal contains a 1:1 mixture of (S_{N1},R_{N2}) and (R_{N1},S_{N2}) isomers

- the crystal contains polymeric chains built from (R_{N1},R_{N2}) or (S_{N1},S_{N2}) isomers connected through oxygen-hydrogen contacts.

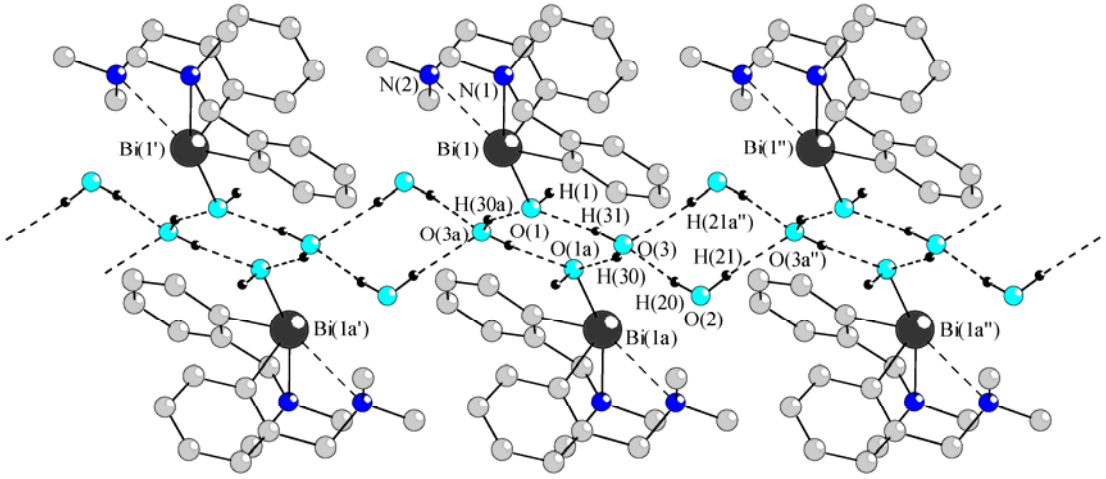

Figure S1. View along *a* axis of the ribbon-like polymer of (R_{N1},R_{N2})- and (S_{N1},S_{N2})-**1** isomers based on intermolecular oxygen-hydrogen contacts. Symmetry equivalent positions: H(30a) (-x, -y, 1-z); H(21a'') (-x, -y, -z). Intermolecular contacts within a chain: $O(1)\cdots H(30a)_{water}$ 2.04(9) Å; $O(1)\cdots H(31)_{water}$ 1.95(7) Å; $O(3)\cdots H(20)_{water}$ 2.08(11) Å; $O(3)\cdots H(21a'')_{water}$ 2.07(8) Å [c.f. $\sum r_{vdW}$(O,H) 2.60 Å]. No further inter-chain contacts.

[{2-(Me_2NCH_2)C_6H_4}$_2$Bi]$_2$S (4)

- the crystal contains a 1:1 mixture of (S_{N1},R_{N2}) and (R_{N1},S_{N2}) isomers

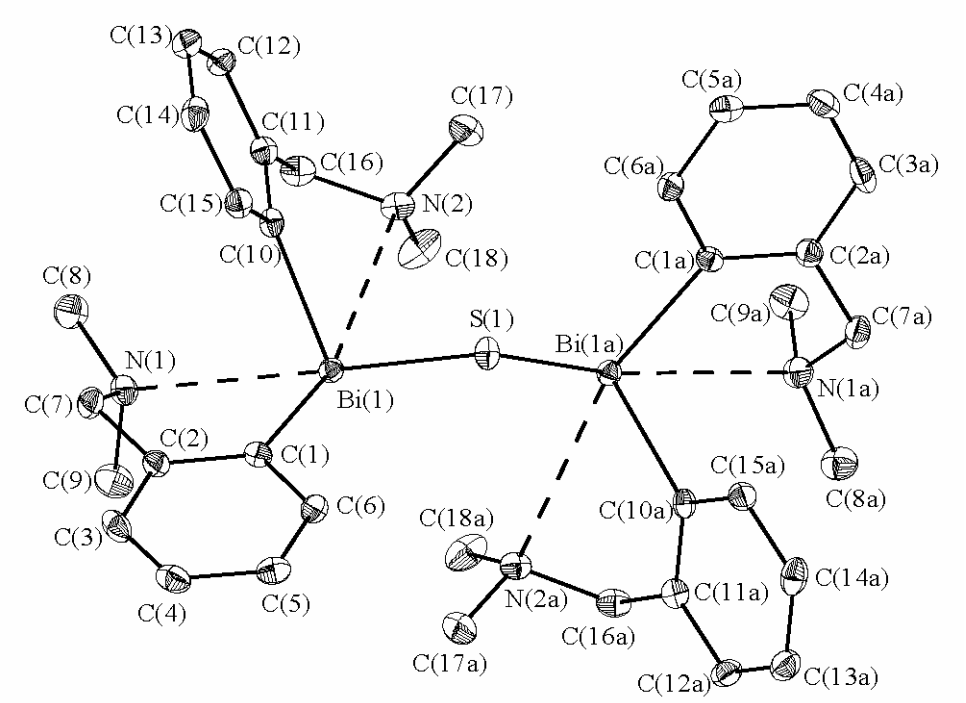

Figure S2. ORTEP representation at 30% probability and atom numbering scheme for (S_{N1},R_{N2})-**4** isomer [symmetry equivalent atoms (1 −x, y, 0.5 − z) are given by "a"]. Hydrogen atoms are omitted.

[2-(Me_2NCH_2)C_6H_4]$_2$BiBr (5)

- the crystal contains a 1:1 mixture of (S_{N1},R_{N2}) and (R_{N1},S_{N2}) isomers

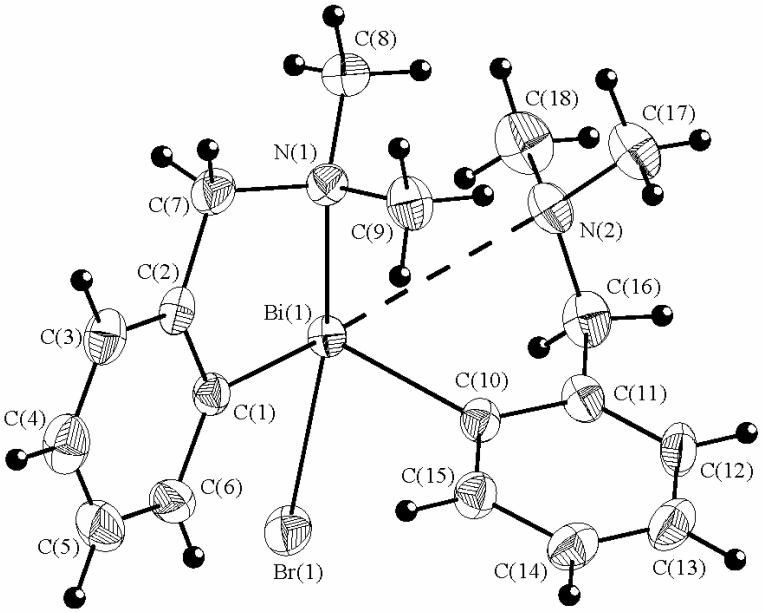

Figure S3. ORTEP representation at 30% probability and atom numbering scheme for (S_{N1},R_{N2})-**5** isomer.

- the crystal contains dimer associations built from (R_{N1},S_{N2}) and (S_{N1},R_{N2}) isomers connected through halogen-hydrogen and arene···Bi contacts.

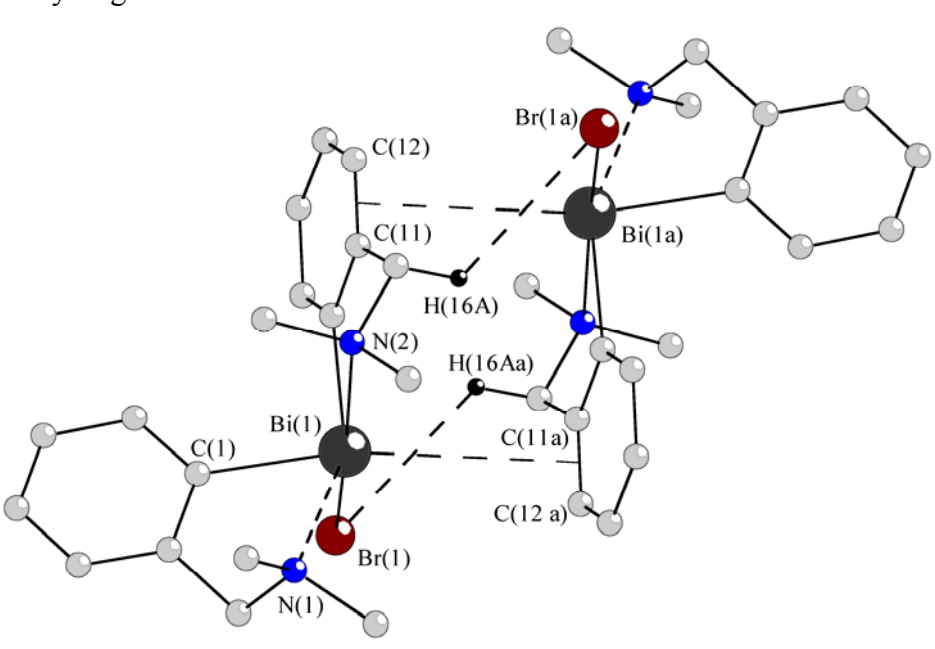

Figure S4. View of dimer association of (R_{N1},S_{N2}) and (S_{N1},R_{N2})-**5** isomers based on intermolecular Br···H (only hydrogens involved in intermolecular interactions are shown) and η^2-arene···Bi contacts in the crystal of **5**. Symmetry equivalent positions: Bi(1a) (-x, -y, 1-z). Intermolecular contacts within a dimer unit: Br(1)···H(16Aa)$_{methylene}$ 3.10(1) Å [c.f. $\sum r_{vdW}$(Br,H) 3.15 Å]; η^2-Ph···Bi(1) 3.705(3) Å; Bi(1)···C(11a) 3.785(6), Bi(1)···C(12a) 3.751(7) Å; the rest of the Bi(1)···C distances are in the range 4.144-4.548 Å; c.f. sums of the corresponding van der Waals radii, Σr_{vdW}(Bi,C) 4.25 Å]. No further inter-dimer contacts.

$[2\text{-}(Me_2NCH_2)C_6H_4]_2BiI$ (6)

- the crystal contains dimer associations built from (R_{N1},S_{N2}) and (S_{N1},R_{N2}) isomers connected through halogen-hydrogen and arene···Bi contacts.

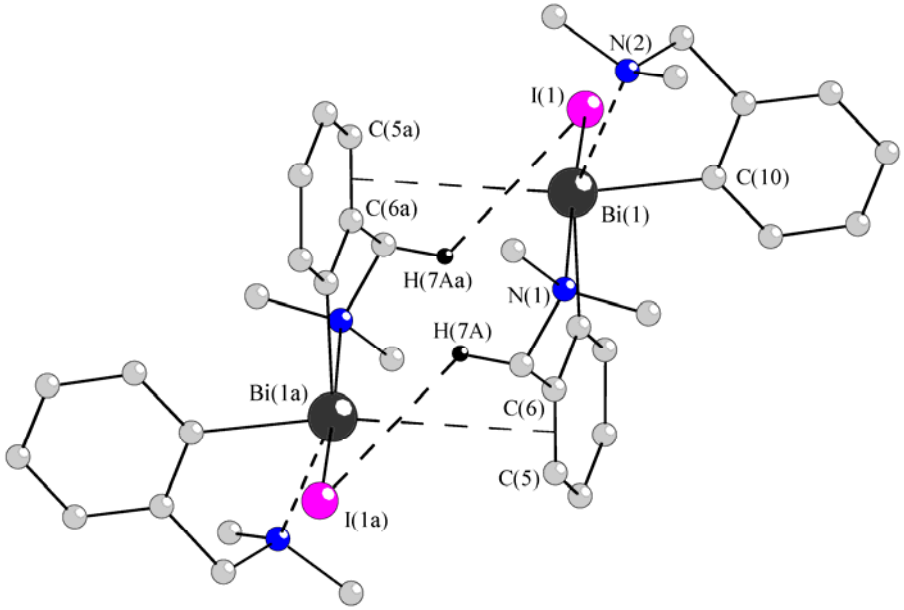

Figure S5. View of dimer association of (R_{N1},S_{N2}) and (S_{N1},R_{N2})-**6** isomers based on intermolecular I···H (only hydrogens involved in intermolecular interactions are shown) and η^2-arene···Bi contacts in the crystal of **6**. Symmetry equivalent positions: Bi(1a) (1-x, 1-y, 1-z). Intermolecular contacts within a dimer unit: I(1)···H(7Aa)$_{methylene}$ 3.22(1) Å [c.f. $\sum r_{vdW}$(I,H) 3.35 Å]; η^2-Ph···Bi(1) 3.718(1) Å; Bi(1)···C(5a) 3.770(5), Bi(1)···C(6a) 3.794(5) Å; the rest of the Bi(1)···C distances are in the range 4.127-4.513 Å; c.f. sums of the corresponding van der Waals radii, Σr_{vdW}(Bi,C) 4.25 Å].

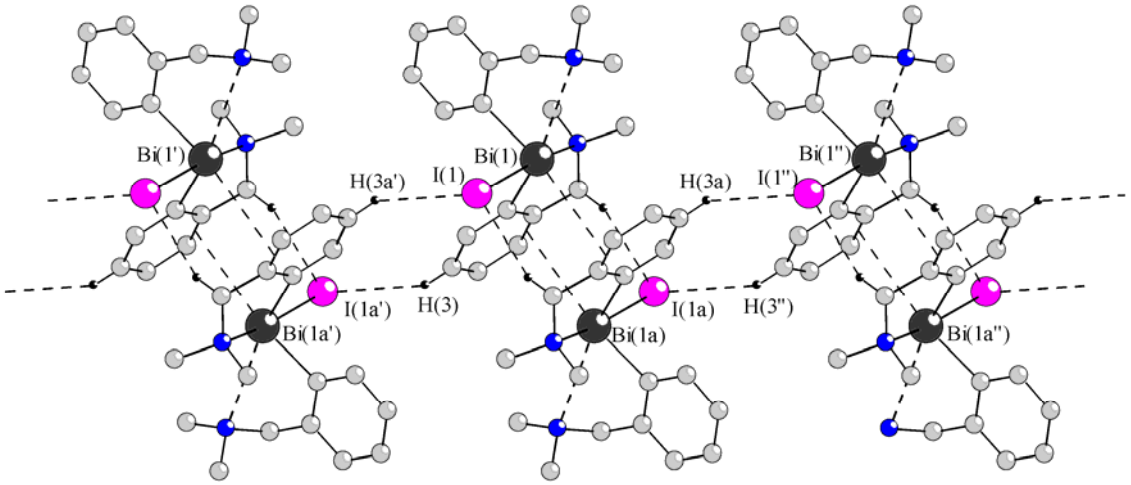

Figure S6. View along *c* axis of the ribbon-like polymer built from (R_{N1},S_{N2})/(S_{N1},R_{N2}) dimers through inter-dimer I···H contacts (only hydrogens involved in intermolecular interactions are shown) in the crystal of **6**. Symmetry equivalent positions: H(3a') (-x, 1-y, 1-z); H(3a'') (1+x, y, z). Inter-dimer contacts within the polymer: I(1)···H(3a')$_{aryl}$ 3.318(1) Å [c.f. $\sum r_{vdW}$(I,H) 3.35 Å].

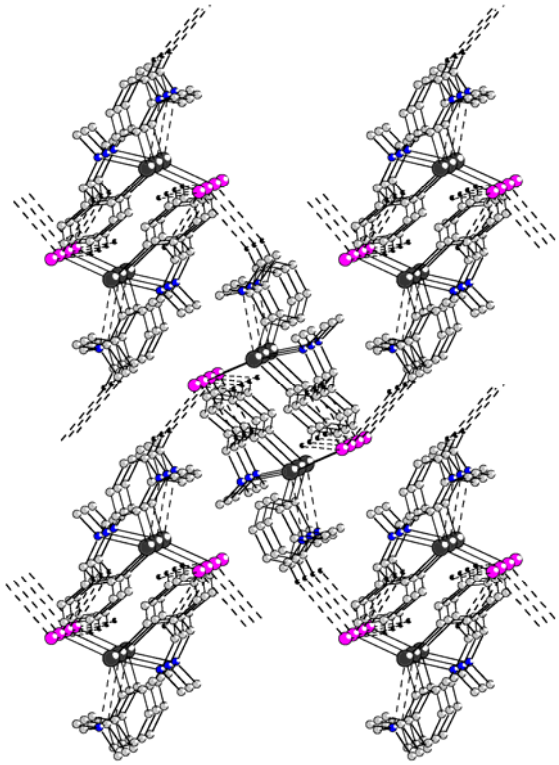

Figure S7. View along *a* axis of 3D supramolecular arhitecture built through I···H contacts (only hydrogens involved in intermolecular interactions are shown) between parallel ribbon-like polymers in the crystal of **6**. Symmetry equivalent positions: H(14b) (0.5-x, -0.5+y, 1.5-z). Inter-polymer contacts: I(1)···H(14b)$_{aryl}$ 3.261(6) Å [c.f. $\sum r_{vdW}$(I,H) 3.35 Å].

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiCl$_2$ (7)

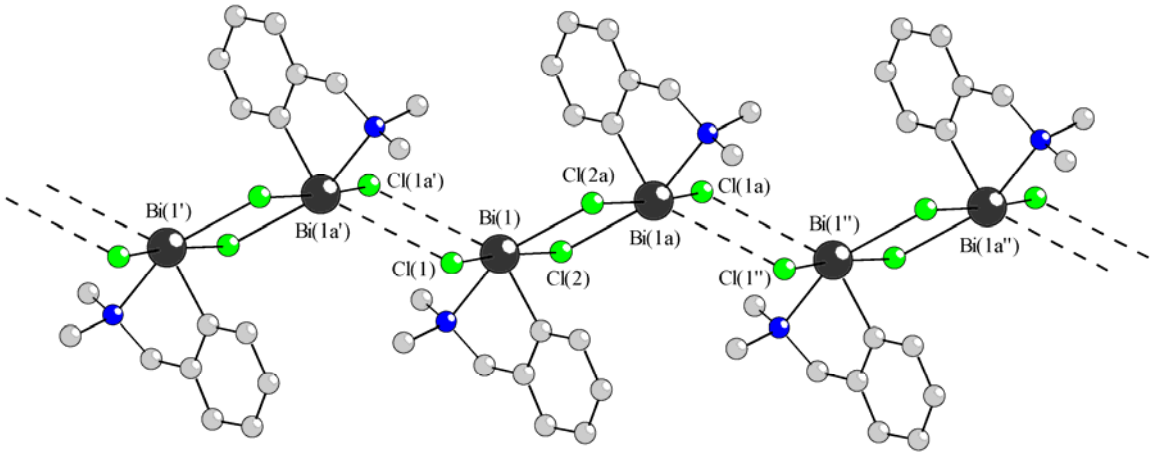

Figure S8. View of the ribbon-like polymer built from (*R*,*S*) dimers through inter-dimer Bi···Cl interactions in the crystal of **7**. Symmetry equivalent positions: Bi(1a) (1-x, -y, 1-z); Bi(1a') (-x, -y, 1-z); Bi(1'') (1+x, y, z). Inter-dimer interactions within the polymer: Bi(1)···Cl(1a') 3.690(2) Å [c.f. $\sum r_{vdW}$(Bi,Cl) 4.20 Å].

- these ribbon-like polymers are associated into a 3D architecture through halogen-hydrogen contacts.

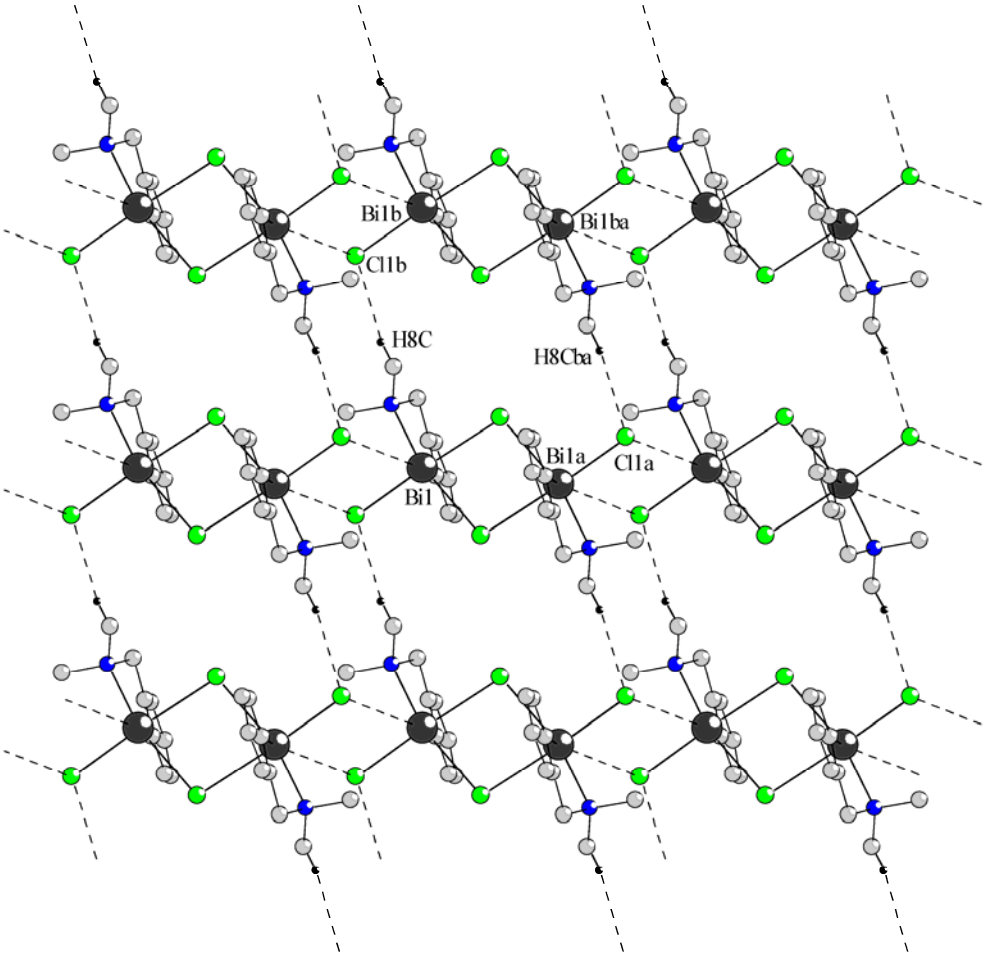

Figure S9. View along *c* axis of layer built from ribbon-like polymers through inter-polymer Cl···H contacts (only hydrogens involved in inter-polymer interactions within a layer are shown) in the crystal of **7**. Symmetry equivalent positions: Cl(1b) (x, 1+y, z); H(8Cba) (1-x, 1-y, 1-z). Inter-polymer interactions within the layer: Cl(1a)···H(8Cba)$_{methyl}$ 2.840(2) Å [c.f. $\sum r_{vdW}$(Cl,H) 3.0 Å].

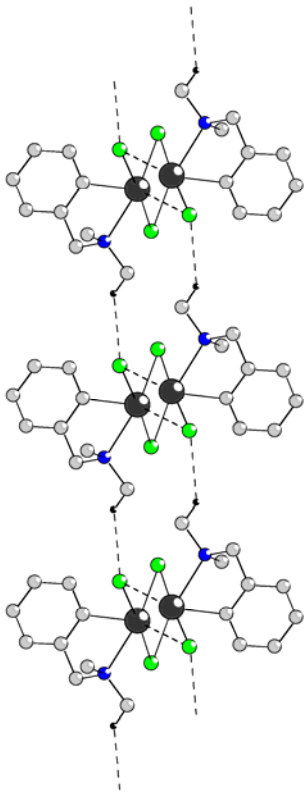

Figure S10. View along *a* axis of layer built from ribbon-like polymers through inter-polymer Cl···H contacts in the crystal of **7**.

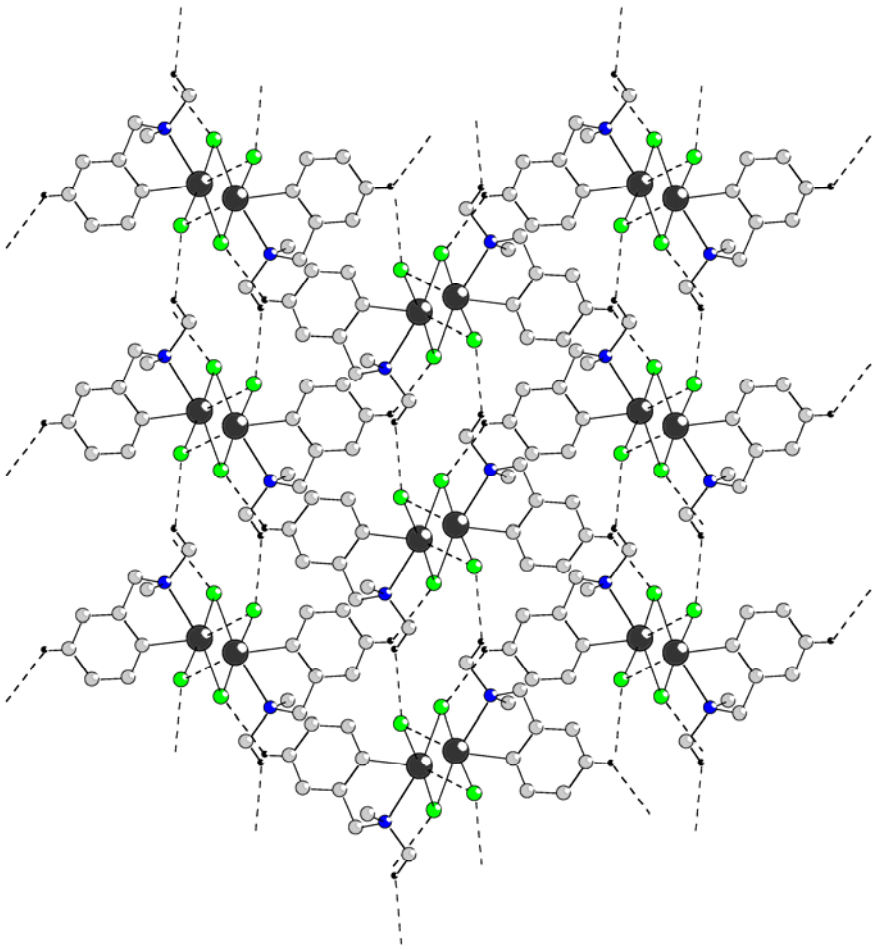

Figure S11. View along *a* axis of the 3D architecture built from polymer layers through inter-layer Cl···H contacts (only hydrogens involved in inter-polymer interactions are shown) in the crystal of **7**. Symmetry equivalent positions: H(4^{i}) (1-x, 0.5+y, 0.5-z);. Inter-layer interactions: Cl(2)···H$(4^{i})_{phenyl}$ 2.840(2) Å.

[{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}BiS]$_2$ (9)

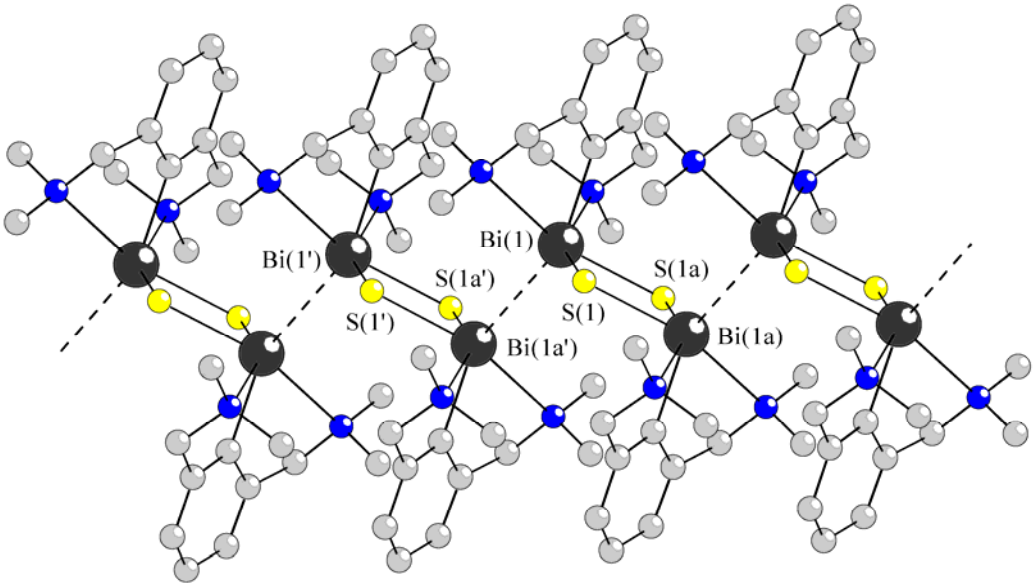

Figure S12. View of polymer built in the crystal of **9** through Bi···Bi interactions. Symmetry equivalent positions: Bi(1a') (-x, 1-y, -z). Bi(1)···Bi(1a') 3.917(1) Å [c.f. Σ_{vdW}(Bi,Bi) 4.80 Å].