

Electronic Supplementary Information

Organobismuth compounds with the pincer ligand 2,6-(Me₂NCH₂)₂C₆H₃: Monoorganobismuth(III) carbonate, sulfate, nitrate, and a diorganobismuthenium(III) salt

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[2,6-(Me₂NCH₂)₂C₆H₃]BiCO₃ (2**)**

- the crystal contains a 1:1 mixture of (*S*_{N1},*R*_{N2})-**2a** / (*R*_{N1},*S*_{N2})-**2a** and (*R*_{N3},*S*_{N4})-**2b** / (*S*_{N3},*R*_{N4})-**2b** isomers

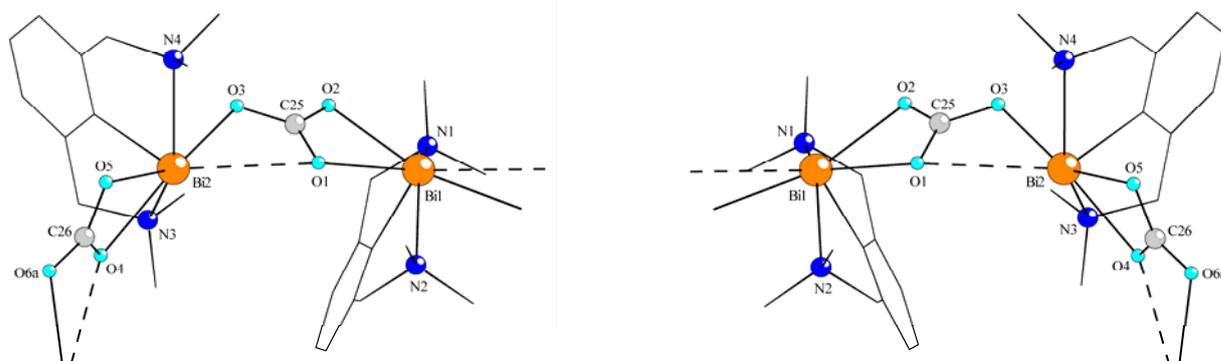


Figure S1. (a) (*S*_{N1},*R*_{N2})-**2a** / (*R*_{N3},*S*_{N4})-**2b** isomers (*left*) and (*R*_{N1},*S*_{N2})-**2a** / (*S*_{N3},*R*_{N4})-**2b** isomers (*right*) in the crystal of **2**.

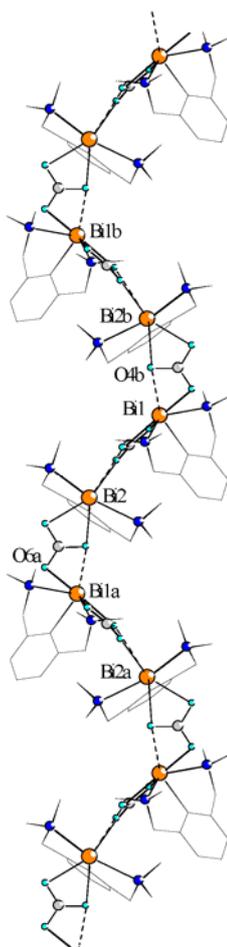


Figure S2. View along *c* axis of the chain polymer based on intermolecular bismuth-oxygen interactions between alternating (*S*_{N1},*R*_{N2})-**2a** and (*R*_{N3},*S*_{N4})-**2b** isomers in the crystal of **2** [symmetry equivalent atoms ($1-x, -0.5+y, 0.5-z$) and ($1-x, 0.5+y, 0.5-z$) are given by “a” and “b”, respectively]. Hydrogen atoms are omitted for clarity.

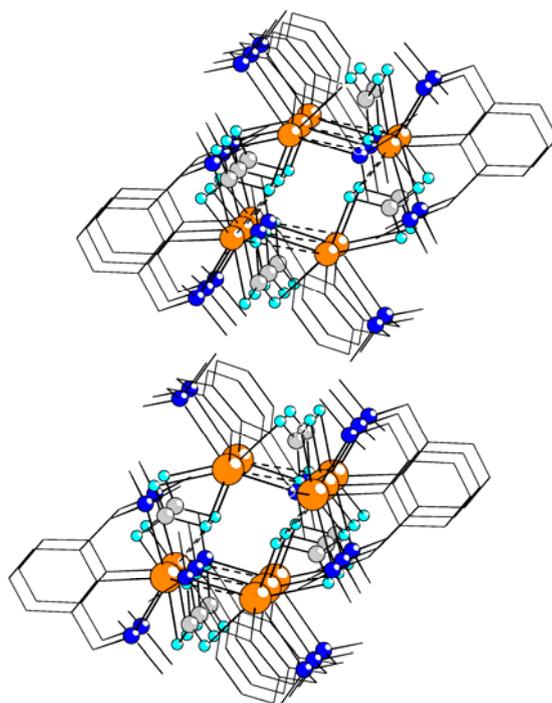


Figure S3. View along b axis of the M -helicoidal chain polymer from (S_{N1}, R_{N2}) -**2a** / (R_{N3}, S_{N4}) -**2b** isomers (*up*) and P -helicoidal chain polymer from (R_{N1}, S_{N2}) -**2a** / (S_{N3}, R_{N4}) -**2b** isomers in the crystal of **2**.

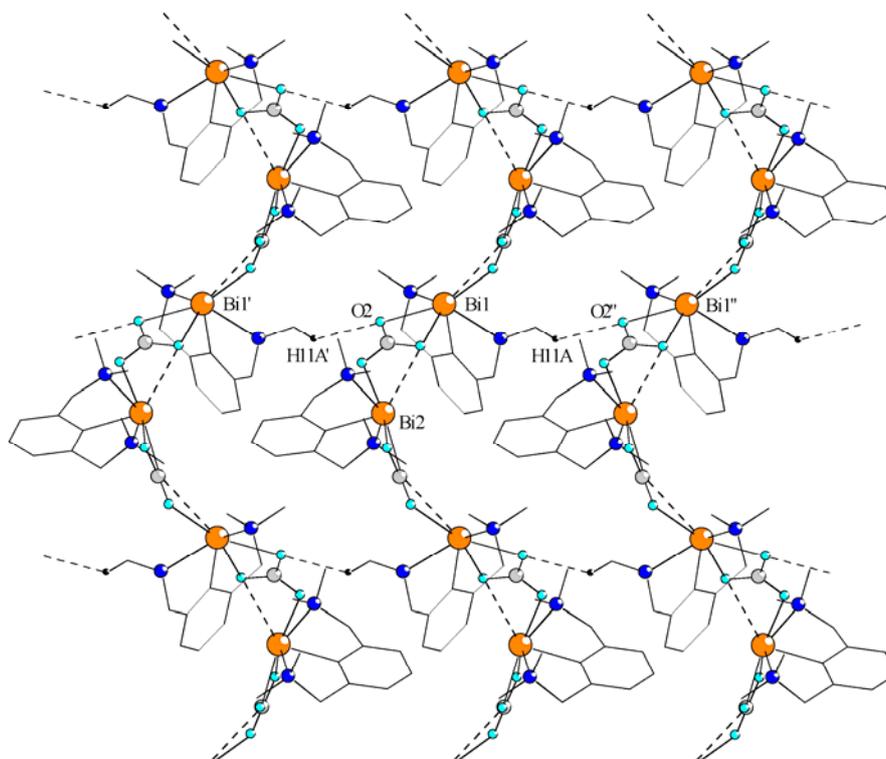


Figure S4. View along c axis of the layer formed by M -helicoidal chain polymers [(S_{N1}, R_{N2}) -**2a** / (R_{N3}, S_{N4}) -**2b** isomers] based on inter-chain oxygen-hydrogen contacts in the crystal of **2** [symmetry equivalent atoms $(-I+x, y, z)$ and $(I+x, y, z)$ are given by “prime” and “double prime”, respectively]. Only hydrogen atoms involved in inter-chain contacts are shown.

[2,6-(Me₂NCH₂)₂C₆H₃]BiSO₄ (3**)**

- the crystal contains a 1:1 mixture of (*R*_{N1},*R*_{N2}) and (*S*_{N1},*S*_{N2}) isomers

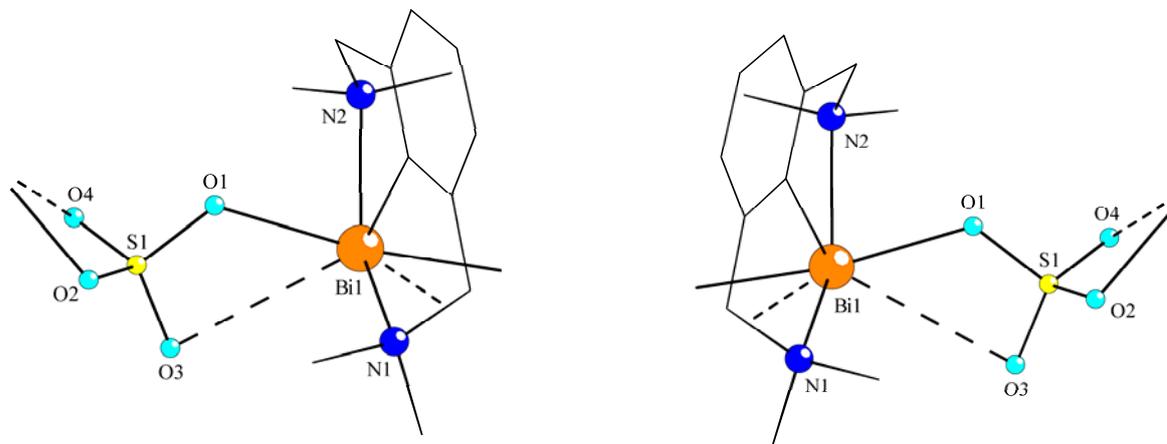


Figure S5. Molecular unit of (a) (*R*_{N1},*R*_{N2})-**3** isomer (*left*) and (*S*_{N1},*S*_{N2})-**3** isomer (*right*) in the crystal of **3**.

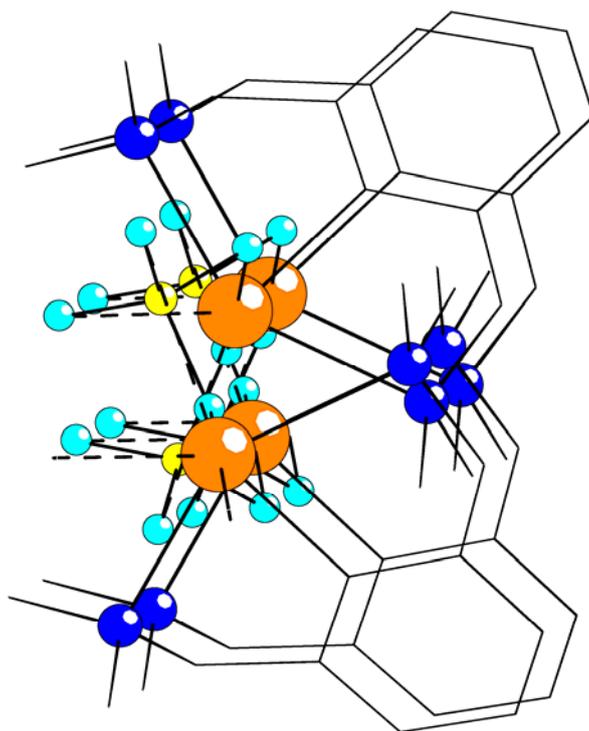


Figure S6. View along *c* axis of the chain polymer based on intermolecular bismuth-oxygen interactions between alternating (*R*_{N1},*R*_{N2})-**3** and (*S*_{N1},*S*_{N2})-**3** isomers in the crystal of **3**. Hydrogen atoms are omitted for clarity.

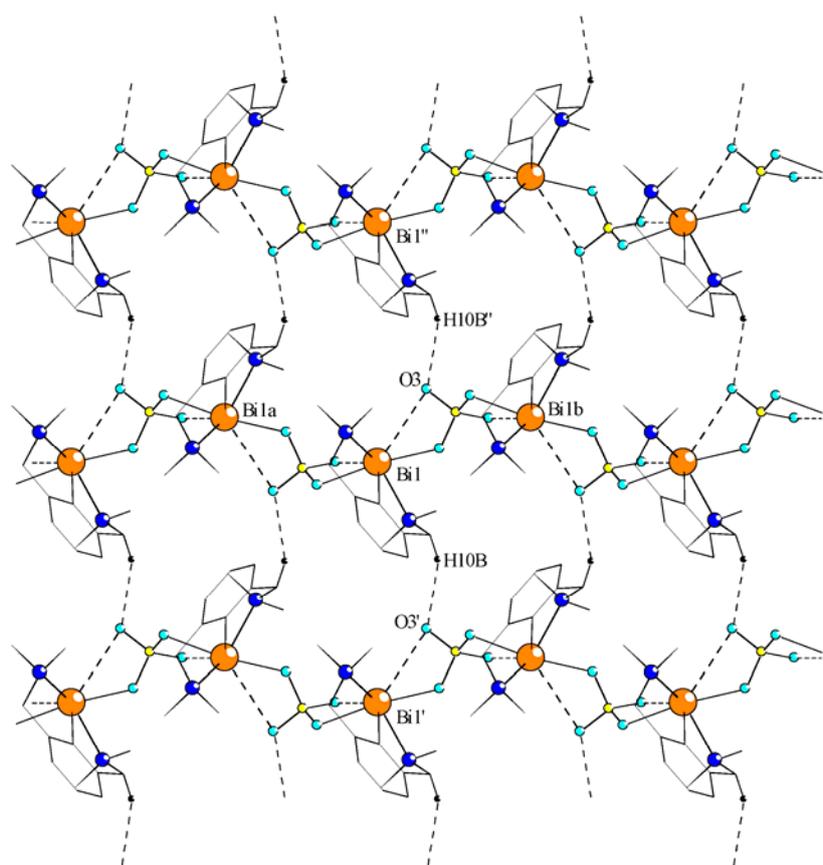


Figure S7. View along a axis of the layer association of parallel $(R_{N1}, R_{N2})\text{-}\mathbf{3}$ / $(S_{N1}, S_{N2})\text{-}\mathbf{3}$ chain polymers based on inter-chain oxygen-hydrogen contacts in the crystal of $\mathbf{3}$ [symmetry equivalent atoms $(x, 2-y, 0.5+z)$, $(x, 2-y, -0.5+z)$, $(x, -1+y, z)$ and $(x, 1+y, z)$ are given by “a”, “b”, “prime” and “double prime”, respectively]. Only hydrogen atoms involved in inter-chain contacts are shown.

[2,6-(Me₂NCH₂)₂C₆H₃]Bi(NO₃)₂ (4**)**

- the crystal contains a 1:1 mixture of (*R*_{N1},*R*_{N2}) and (*S*_{N1},*S*_{N2}) isomers

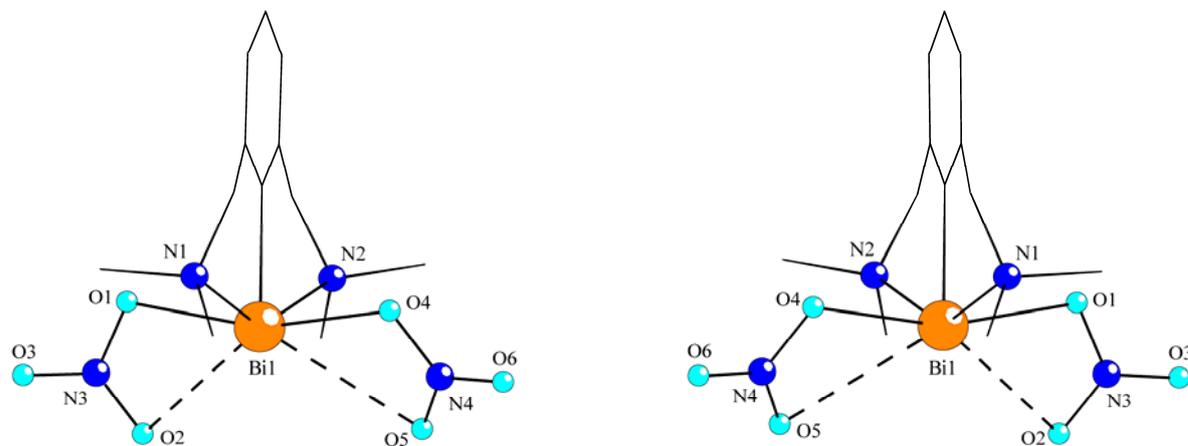


Figure S8. Molecular unit of (a) (*R*_{N1},*R*_{N2})-**4** isomer (*left*) and (*S*_{N1},*S*_{N2})-**4** isomer (*right*) in the crystal of **4**.

[[2,6-(Me₂NCH₂)₂C₆H₃]₂Bi][W(CO)₅Cl] (6**)**

- the crystal contains a 1:1 mixture of (*R*_{N1},*R*_{N2}) and (*S*_{N1},*S*_{N2}) isomers

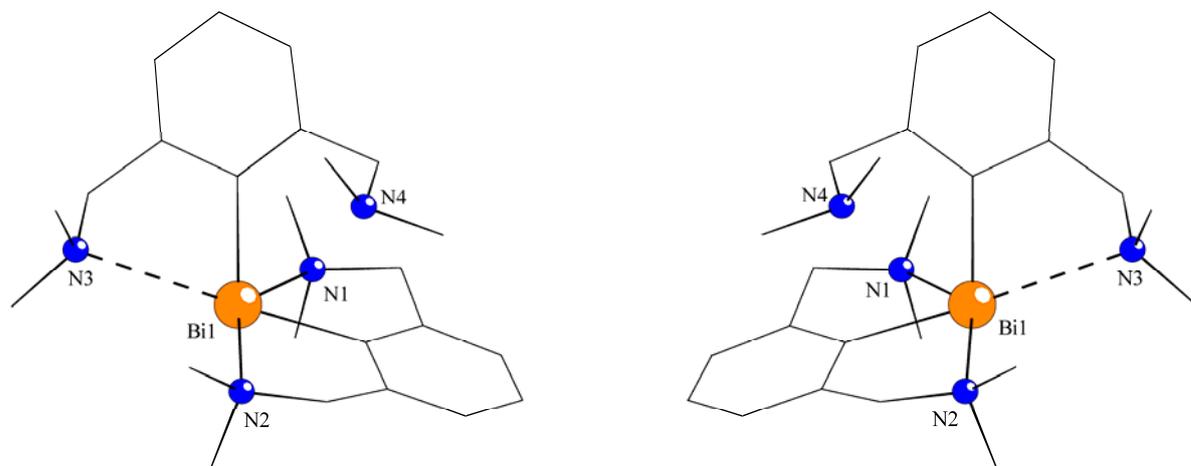


Figure S9. (a) (*R*_{N1},*S*_{N2})(*S*_{N3})-**6** cation (*left*) and (*S*_{N1},*R*_{N2})(*R*_{N3})-**6** cation (*right*) in the crystal of **6**.