Semiconductive Coordination Networks from 2,3,6,7,10,11-Hexakis(alkylthio)triphenylenes and Bismuth(III) Halides: Synthesis, Structure-Property Relations and Solution Processing

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Supporting Information

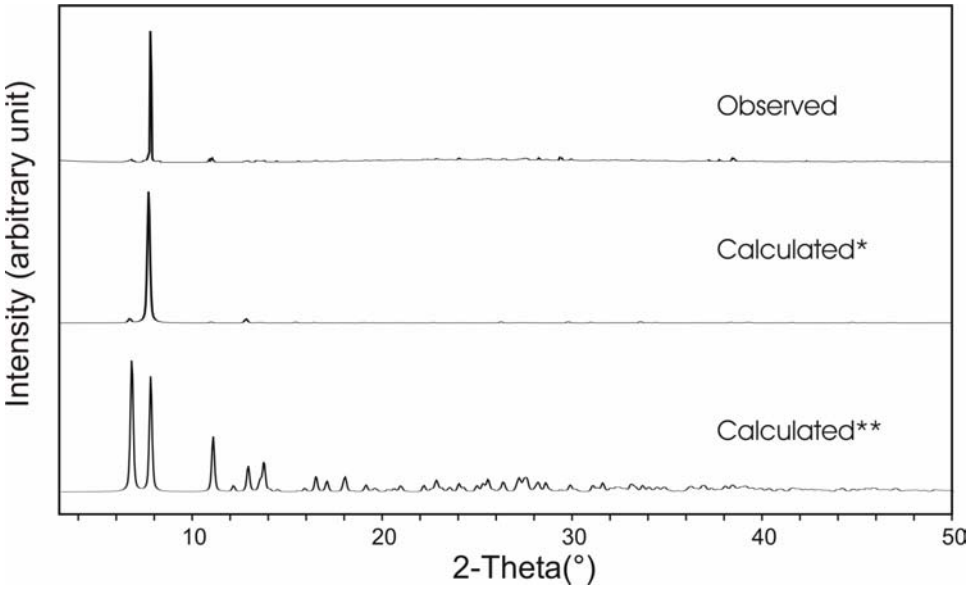

Figure S1. Room-temperature X-ray diffraction patterns (Cu Kα, λ = 1.5418 Å) for HMTT·$BiBr_3$ (**2**). Top: observed from a powder sample. Middle: (*) calculated pattern with orientation preference set at (0 -1 1) 0.4 and (1 0 0) 1.0. Bottom: (**) calculated pattern without orientation preference.

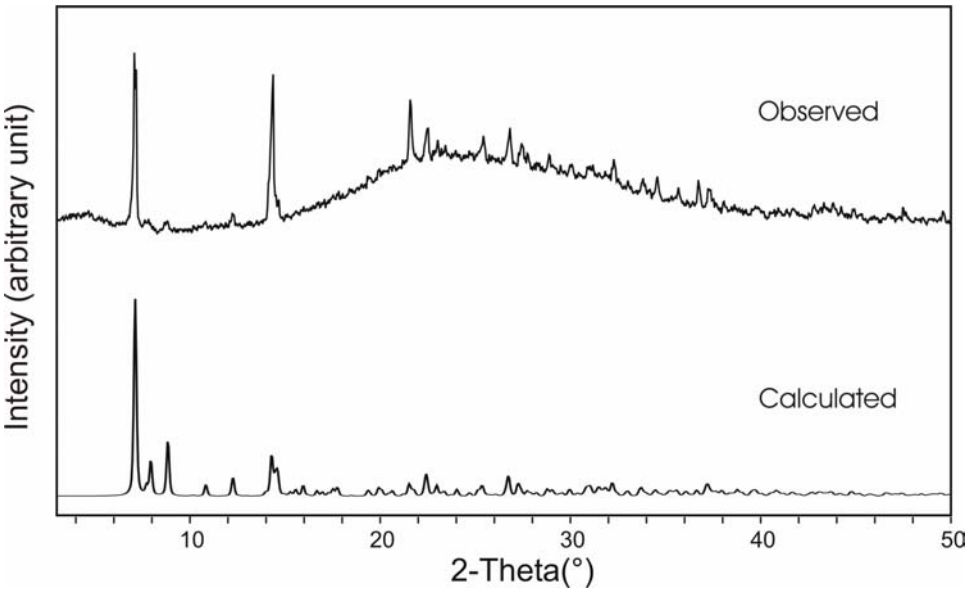

Figure S2. Room-temperature X-ray diffraction patterns (Cu Kα, λ = 1.5418 Å) for HMTT·2BiBr$_3$ (**3**). Top: observed from a powder sample. Bottom: calculated from the single crystal structure.

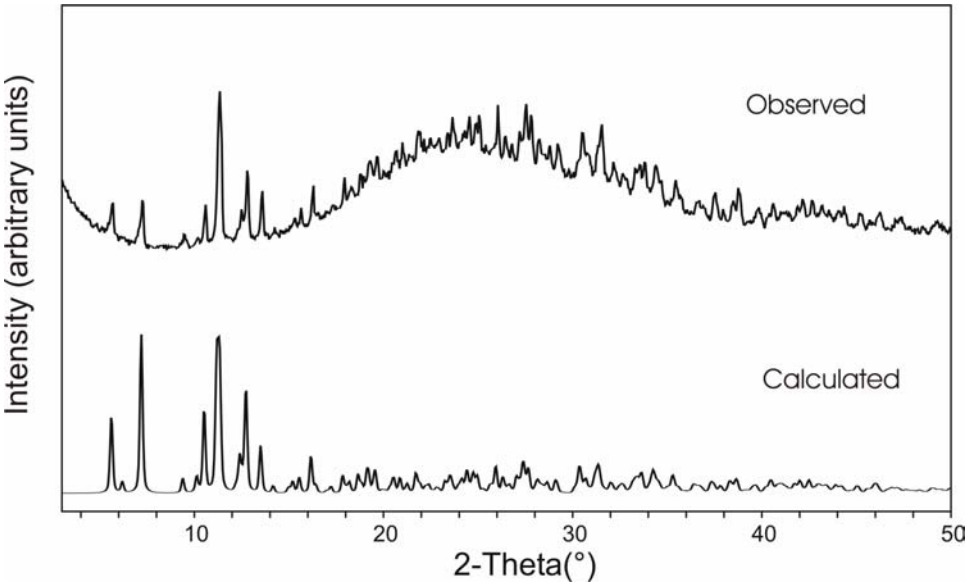

Figure S3. Room-temperature X-ray diffraction patterns (Cu Kα, λ = 1.5418 Å) for HETT·2BiBr$_3$ (**4**). Top: observed from a powder sample. Bottom: calculated from the single crystal structure.

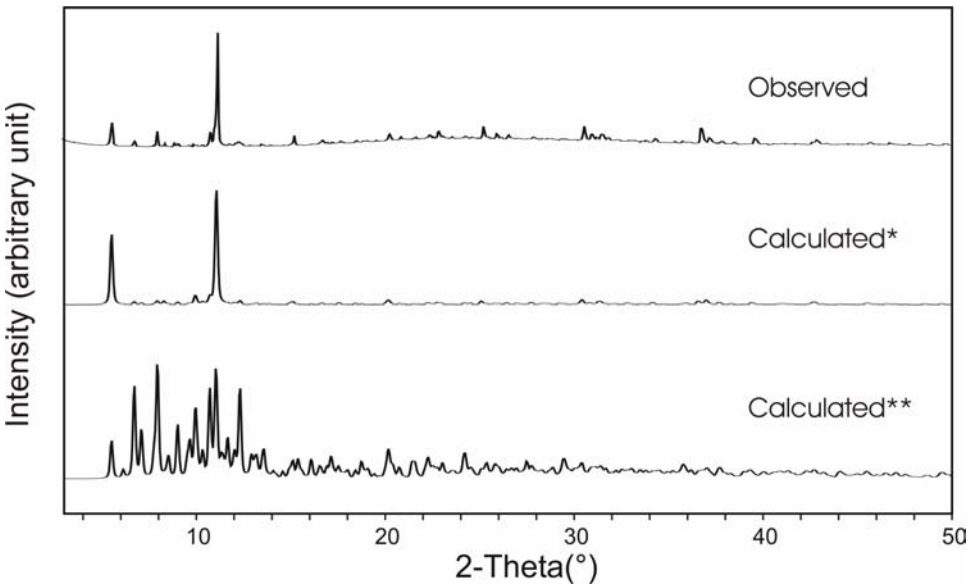

Figure S4. Room-temperature X-ray diffraction patterns (Cu Kα, λ = 1.5418 Å) for HiPTT·2BiBr$_3$·C$_7$H$_8$ (**5**). Top: observed from a powder sample. Middle: (*) calculated pattern with orientation preference set at (4 0 0) 0.5 and (0 1 1) 1.2. Bottom: (**) calculated pattern without orientation preference.

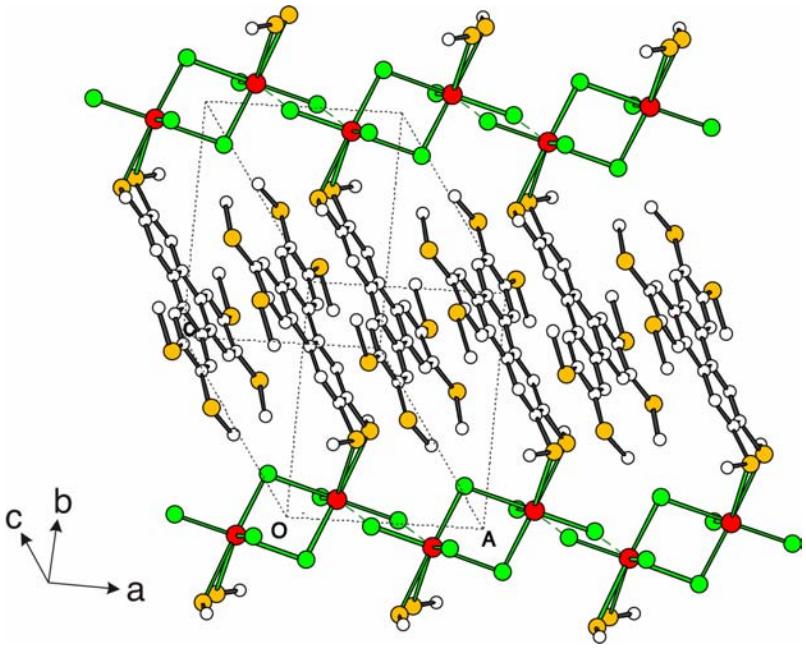

Figure S5. Interdigitation of the hybrid chains in the crystal structure of HMTT·BiCl$_3$ (**1**) along the [0 1 -1] plane. Large red sphere: Bi; medium green: Cl; medium yellow: S; small white: C.

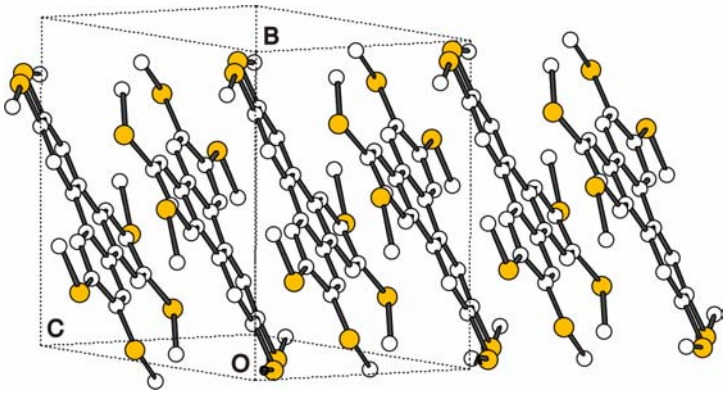

Figure S6. A column of HMTT molecules in the crystal structure of HMTT. Large yellow sphere: S; small white: C.

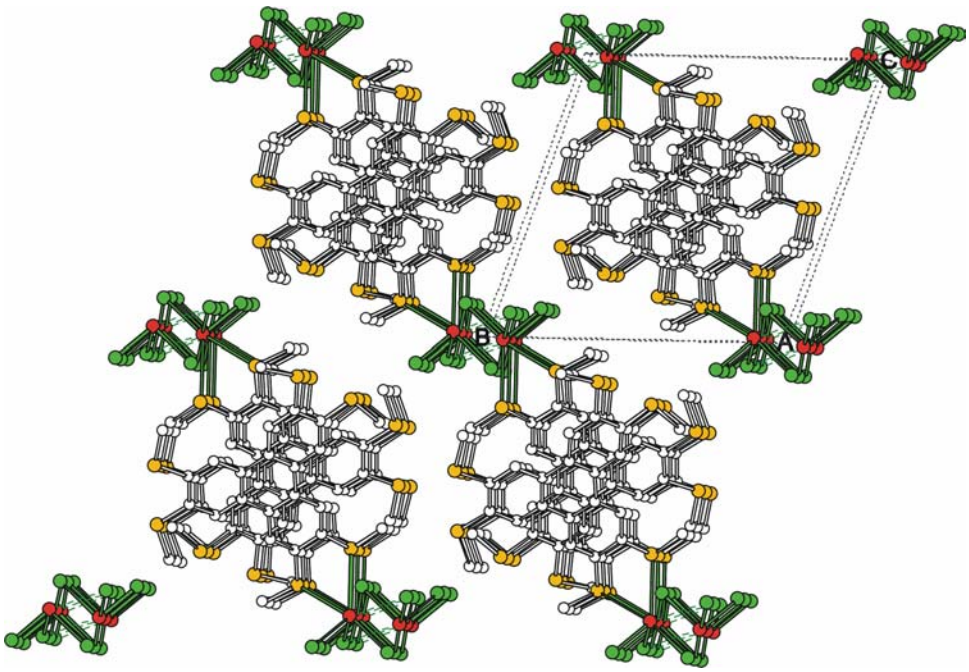

Figure S7. Overview of the crystal structure of HMTT·$BiCl_3$ (**1**) (along the *a* axis). Large red sphere: Bi; medium green: Cl; medium yellow: S; small white: C.

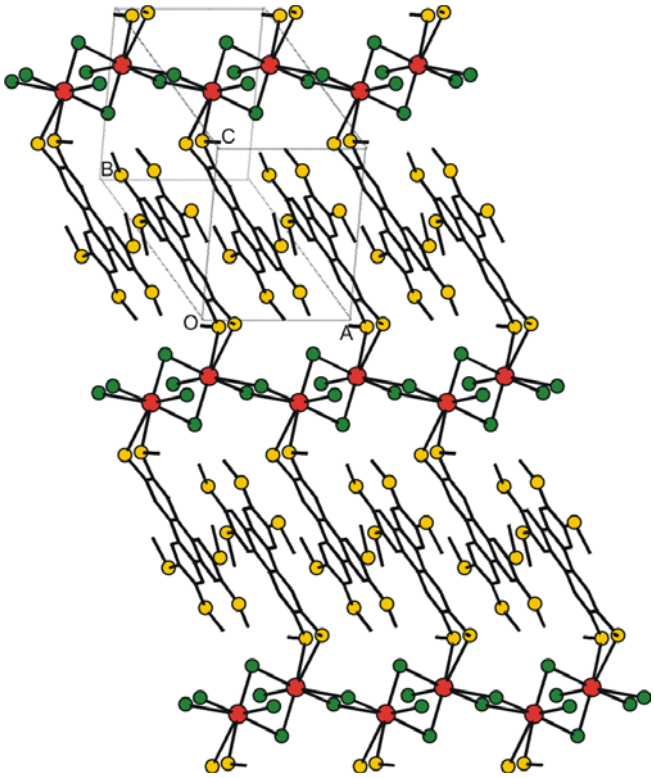

Figure S8. Interdigitated hybrid chains in HMTT·$BiBr_3$ (**2**) along the [0 1 -1] plane. Large red sphere: Bi; small green: Br; small yellow: S.

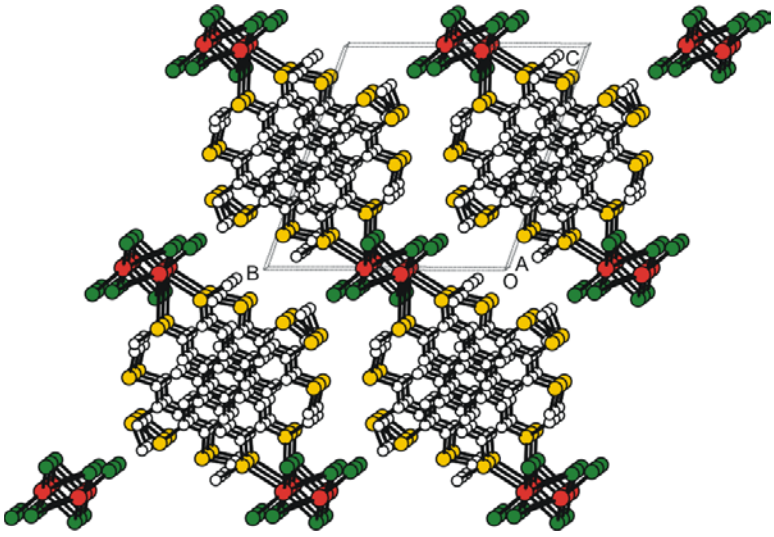

Figure S9. Overview of the crystal structure of HMTT·$BiBr_3$ (**2**) along the *a* axis. Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C.

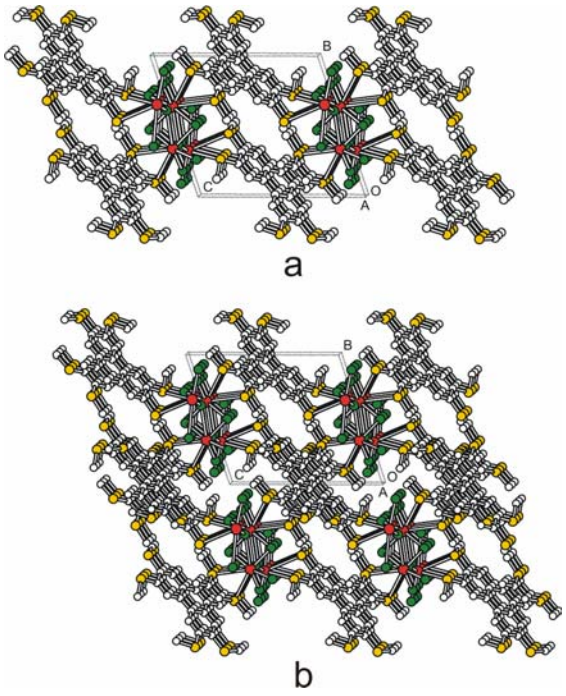

Figure S10. View of 2D network in HMTT·2BiBr$_3$ (**3**) along the *a* axis. a) A single 2-D network. b) Two networks interacting through π-π stacking of the HMTT molecules. Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C.

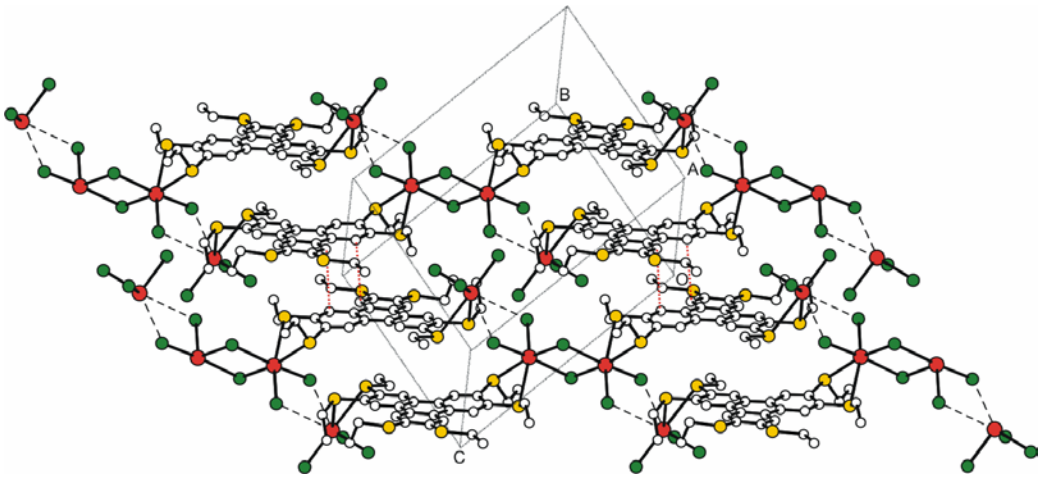

Figure S11. Two neighboring coordination networks in the crystal structure of HETT·2BiBr$_3$ (**4**). Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C. The red dotted lines delineate the closest intermolecular C···C contacts (3.82 Å).

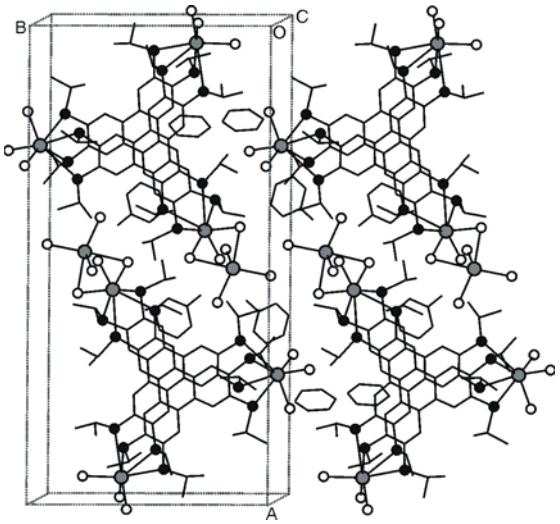

Figure S12. Packing of the isolated (0D) coordination units (each containing two HiPTT molecules, two $BiBr_3$ and one Bi_2Br_6 fragments) along the [0 0 1] plane in $HiPTT{\cdot}2BiBr_3{\cdot}C_7H_8$ (**5**). Large gray spheres: Bi; small white: Br; small black: S; isolated hexagons: crystallographically located atoms from the toluene molecules.

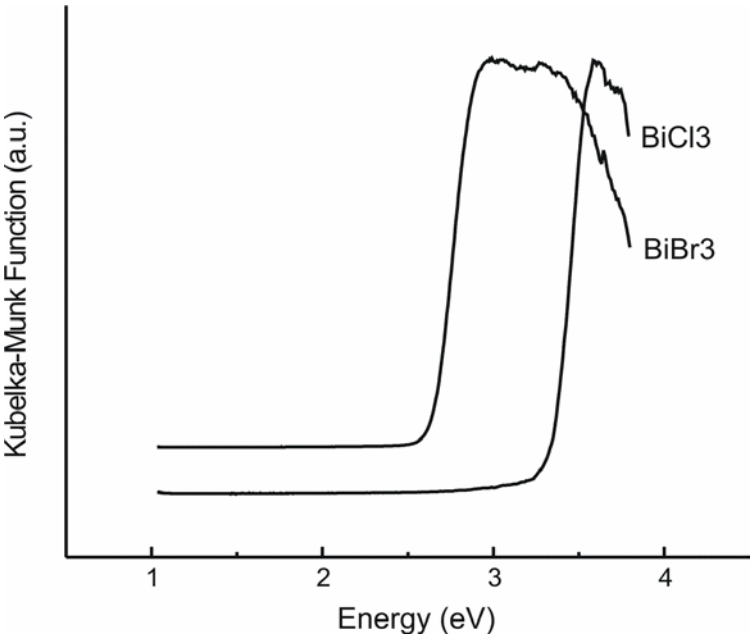

Figure S13. Room-temperature optical absorption spectra for solid samples of $BiCl_3$ (band gap: 3.366 eV) and $BiBr_3$ (band gaps: 2.662 eV).

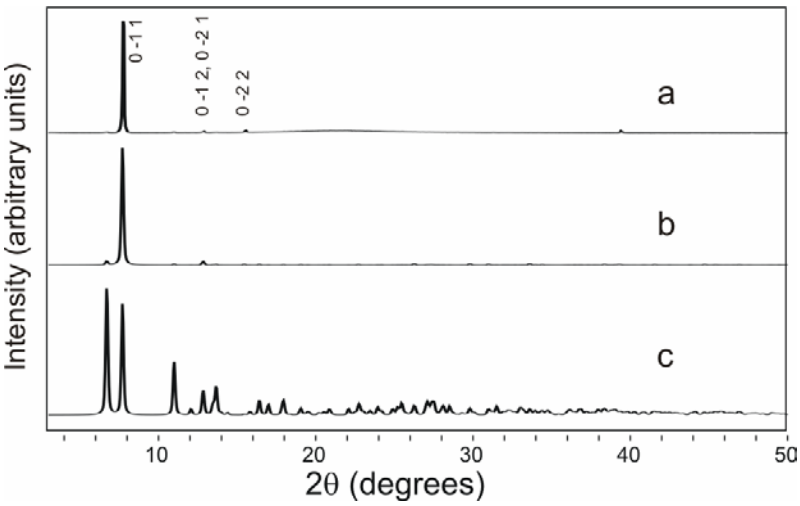

Figure S14. X-ray diffraction patterns (Cu Kα, λ= 1.5418 Å) of *p*-HMTT·$BiBr_3$ (**2**): (a) observed (at room temperature) for a solution-deposited sample; (b) calculated from the single crystal structure with an orientation preference of 0.4 for [0 -1 1]: meaning 60% more crystallites are oriented along [0 -1 1] when compared to the randomly oriented state(JADE, Materials Data, Inc); (c) calculated from the single crystal structure with random orientation of crystallites.

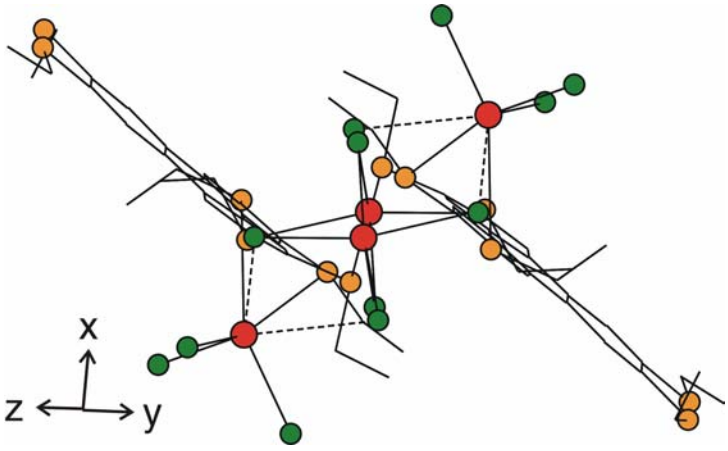

Figure S15. View of the quasi-1D coordination chain in the crystal structure of HETT·$2BiBr_3$ (**4**) (along the chain direction). Large red sphere: Bi; small green: Br; small orange: S.

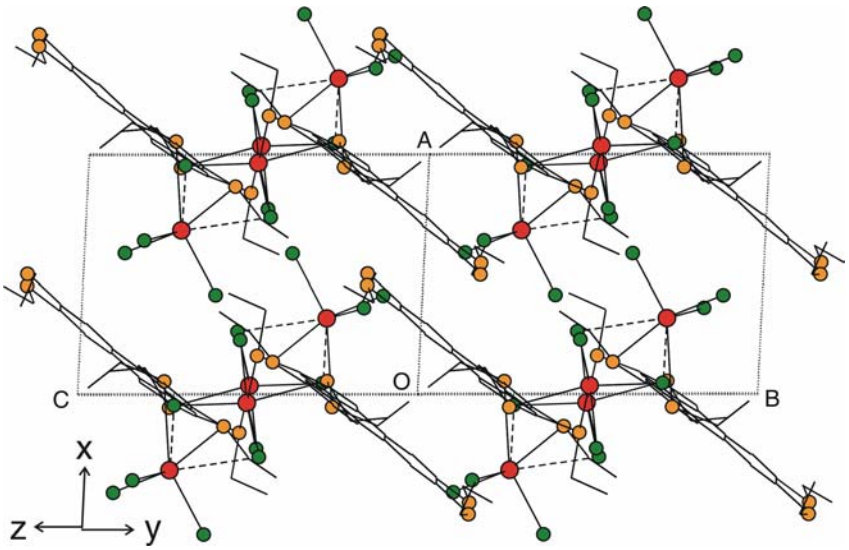

Figure S16. Packing of the quasi-1D coordination chains in the crystal structure of HETT·2$BiBr_3$ (**4**) (along the chain direction). Large red sphere: Bi; small green: Br; small orange: S.