

Electronic Supplementary Information

**Structural Regularity and Diversity in Hybrids of Aromatic
Thioethers and BiBr₃: from Discrete Complexes to Layers
and 3D Nets**

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Synthesis of 3-bromo-4-iodomethylthiobenzene: In a nitrogen filled glove box, sodium thiomethoxide (95%, 0.35 g, 5.1 mmol) and a magnetic stirring bar were loaded into a 2-neck round bottom flask. The flask was then taken out of the glove box and connected to a nitrogen bubbler. DMEU (anhydrous, 15 mL) was transferred via a cannula into the flask and the stirring was started. 3-bromo-4-iodofluorobenzene (1.50 g, 5.0 mmol) dissolved in DMEU (anhydrous, 5 mL) was purged with nitrogen for 2 min and then transferred into the flask slowly at rt. After the solution was stirred at rt for 20 min, the mixture changed to a light-yellow solution. The reaction was complete after 5 h at rt. Then, the resultant light yellow solution was poured into water (100 mL) and the aqueous suspension was extracted with toluene (100 mL × 3). The organic layers were combined and washed with water (200 mL × 3) and brine (200 mL). After being dried over anhydrous sodium sulfate for 10 min, the solvent was removed on a rotary evaporator to afford a light yellow oil product. The crude product (1.64 g, 100% based on 3-bromo-4-iodofluorobenzene) was pure enough without any further chromatography. ¹H NMR (300 MHz, CDCl₃): δ 2.45 (s, 3 H), 6.84-6.87 (m, 1 H), 7.45 (d, 1 H), 7.68 (d, 1H).

Synthesis of 3-bromo-4-trimethylsilylethynyl-methylthiobenzene: A Schlenk tube (100 mL) was loaded with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (140.2 mg, 0.2 mmol),

triphenylphosphine (280.4 mg, 1.07 mmol), copper(I) iodide (70.1 mg, 0.24 mmol), and 3-Bromo-4-iodo-methylthiobenzene (1.64 g, 5.0 mmol). The Schlenk tube was then connected to a vacuum manifold, evacuated and back-filled with nitrogen gas. After the Schlenk was thus purged three times, a 1:1 triethylamine/ THF mixture (30.0 mL, pre-purged with nitrogen gas) was injected via cannula under nitrogen protection, followed by injection of trimethylsilylacetylene (TMSA, 98%, 0.49 g, 5.0 mmol). The Schlenk tube was then sealed with the plug and stirred at 70 °C overnight (15 h). After being cooled down to rt, the reaction mixture was poured into 200 mL of a 1:1 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo and the dark yellow oily residue was purified by flash chromatography (silica gel, flash column separation with hexanes as the eluent) to provide a light yellow oil product (1.0 g, 67% based on 3-Bromo-4-iodomethylthiobenzene). ¹H NMR (300 MHz, CDCl₃): δ 0.27 (s, 9 H), 2.46 (s, 3H), 7.04-7.08 (m, 1H), 7.34 (s, 1H), 7.38 (t, 1H).

Synthesis of 3-(4-methylthiophenylethynyl)-4-ethynyl-methylthiobenzene: A

Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (56.1 mg, 0.08 mmol), triphenylphosphine (104.8 mg, 0.40 mmol), copper(I) iodide (22.8 mg, 0.12 mmol), 3-Bromo-4-trimethylsilylethynyl-methylthiobenzene (1.0 g, 3.4 mmol) and

triethylamine (20 mL). The Schlenk tube was then bubbled with nitrogen gas for 5 min. 4-ethynyl-1-methylthiobenzene (0.55 g, 3.7 mmol) in 5.0 mL triethylamine (pre-flushed with nitrogen) was injected via cannula under nitrogen protection into the mixture. The Schlenk tube was then sealed with the plug and stirred while it was heated to 110 °C overnight. After being cooled down to rt, the reaction mixture was poured into 200 mL of a 1:2 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo to an orange oily residue. Tetrabutylammonium fluoride (TBAF, 1 M in THF, 3.0 mL) in 20 mL THF was added into the orange residue at rt. After stirring for 1 h, the orange color of the reactants became darker. The reaction mixture was then passed through a silica gel plug and washed with a mixture of 1:1 hexanes/dichloromethane. After the solvent was removed in vacuo on a rotary evaporator, the brownish residue was then purified by flash chromatography (silica gel, separation with a mixture of 2:1 hexanes/dichloromethane as the eluent) to give a yellow solid as the product (0.53 g, 53% based on 3-Bromo-4-trimethylsilylethynyl-methylthiobenzene). ¹H NMR (300 MHz, CDCl₃): δ 2.50 (s, 6H), 7.12 (m, 1H), 7.20 (d, 2H), 7.35 (d, 1H), 7.42 (d, 1H), 7.47 (d, 2H).

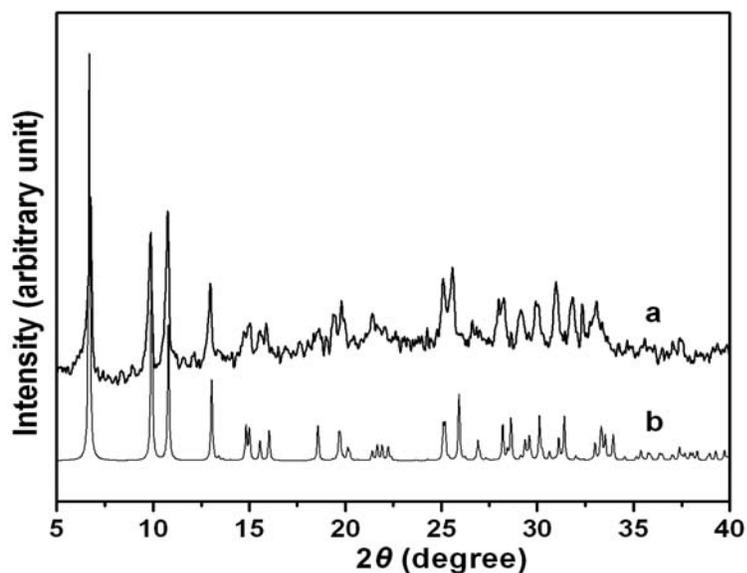


Fig. S1. X-ray diffraction patterns ($\text{Cu K}\alpha$, $\lambda = 1.5418 \text{ \AA}$) of **1** ($\text{L1}\cdot 2\text{BiBr}_3$). (a) Observed for a powder solid sample; (b) calculated pattern from the single crystal structure (single crystal data collected at 100 K).

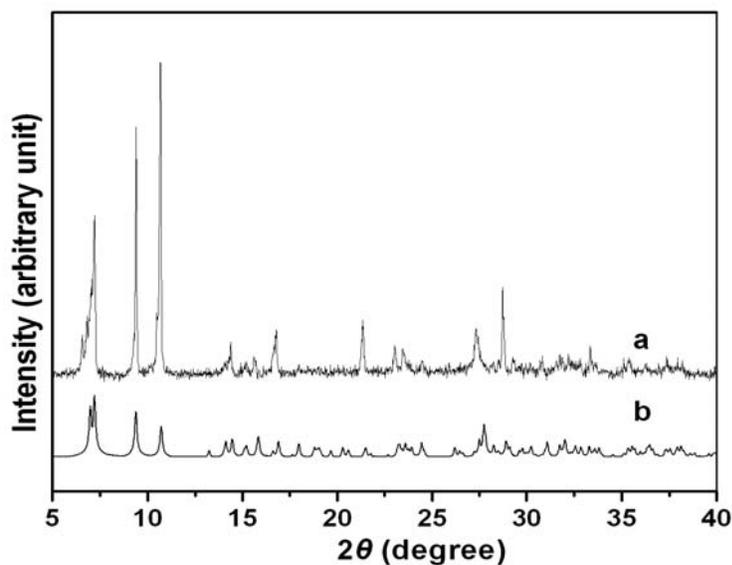


Fig. S2. X-ray diffraction patterns ($\text{Cu K}\alpha$, $\lambda = 1.5418 \text{ \AA}$) of **2** ($\text{L2}\cdot 2\text{BiBr}_3\cdot \text{C}_6\text{H}_6$). (a) Observed for a powder solid sample; (b) calculated pattern from the single crystal structure (single crystal data collected at 100 K).

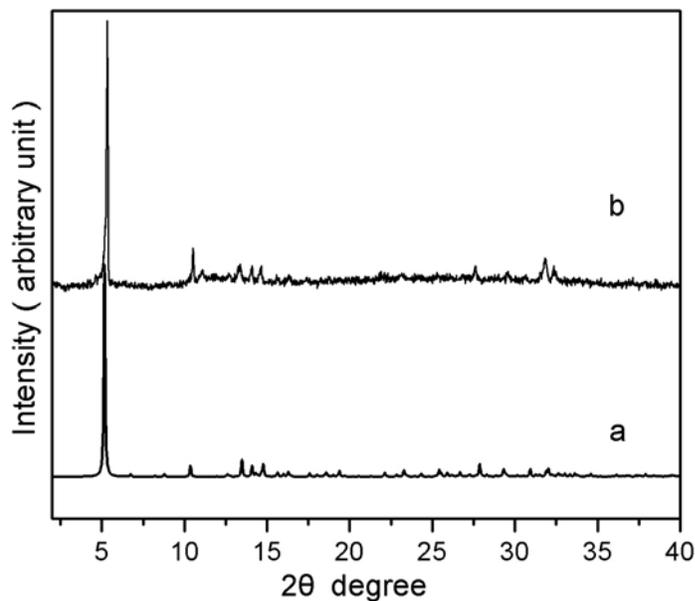


Fig. S3. X-ray diffraction patterns (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) of **3** ($\text{L3}\cdot 4\text{BiBr}_3\cdot \text{C}_6\text{H}_6$). a) Calculated pattern from the single crystal structure (single crystal data collected at 100 K); b) observed pattern at 298 K.

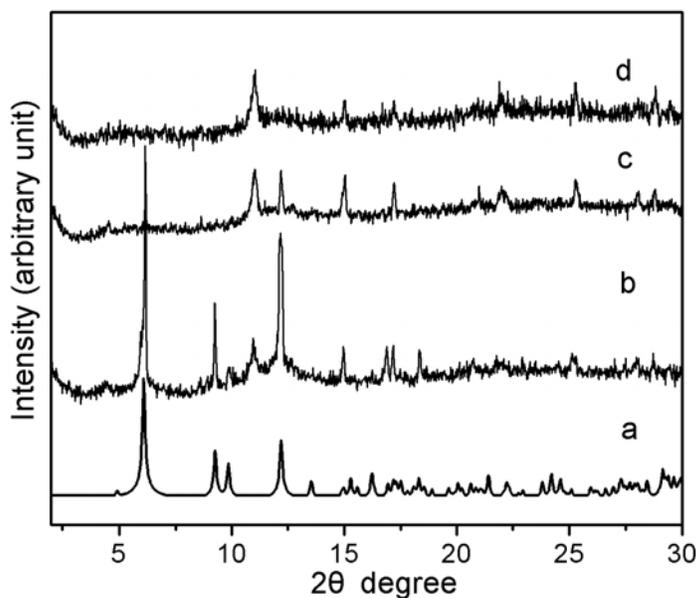


Fig. S4. X-ray diffraction patterns (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$). a) Calculated pattern from the single crystal structure (single crystal data collected at 100 K); b) observed pattern of fresh sample **4** at 298 K; c) observed pattern of the same sample of **4** after two hours in air at 298 K; d) observed pattern of the same sample of **4** after one day in air at 298 K.

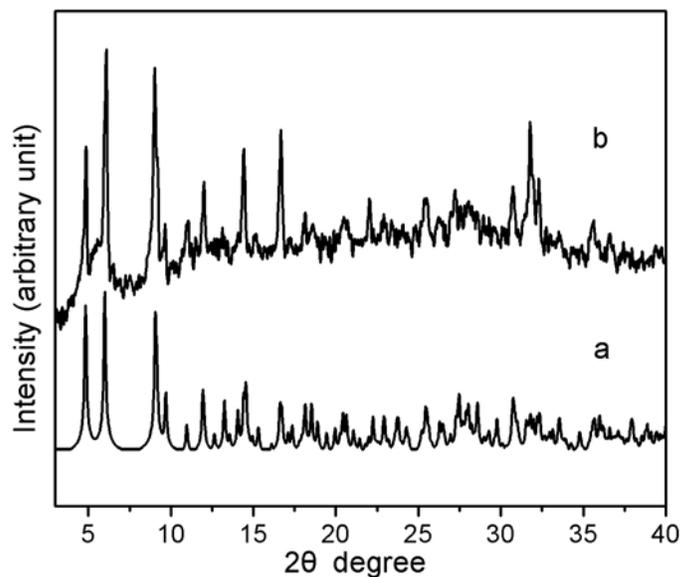


Fig. S5. X-ray diffraction patterns (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) of **5** ($\text{L5} \cdot 4.88\text{BiBr}_3 \cdot 0.5\text{C}_6\text{H}_6$). a) Calculated pattern from the single crystal structure (single crystal data collected at 100 K); b) observed pattern at 298 K.

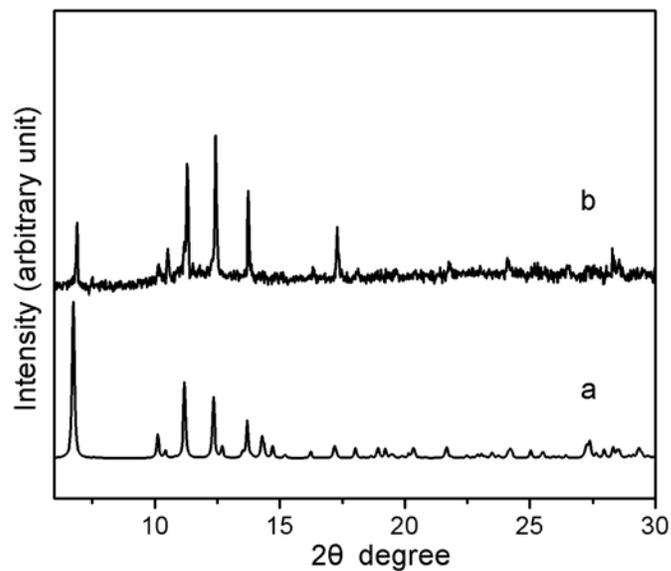


Fig. S6. X-ray diffraction patterns (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) of **6** ($\text{L6} \cdot 2\text{BiBr}_3$). a) Calculated pattern from the single crystal structure (single crystal data collected at 100 K); b) observed pattern at 298 K.

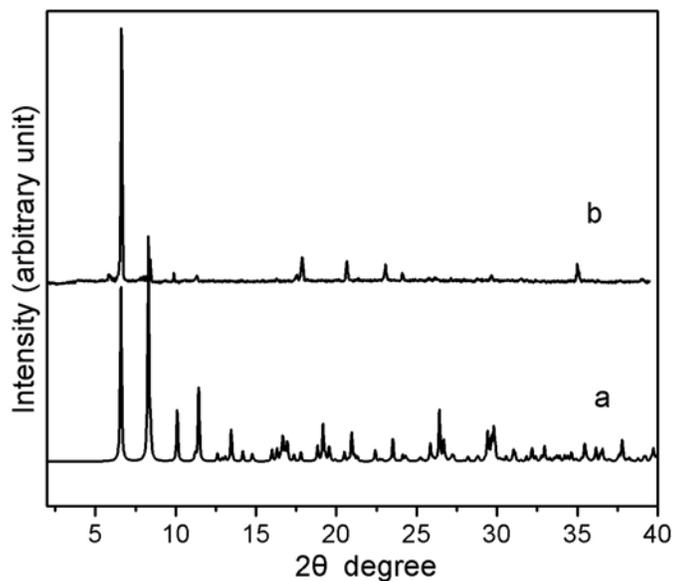


Fig. S7. X-ray diffraction patterns (Cu K α , $\lambda = 1.5418 \text{ \AA}$) of **7** ($\text{L7}\cdot 4\text{BiBr}_3\cdot 2\text{C}_6\text{H}_6$). a) Calculated pattern from the single crystal structure (single crystal data collected at 100 K); b) observed pattern at 298 K.

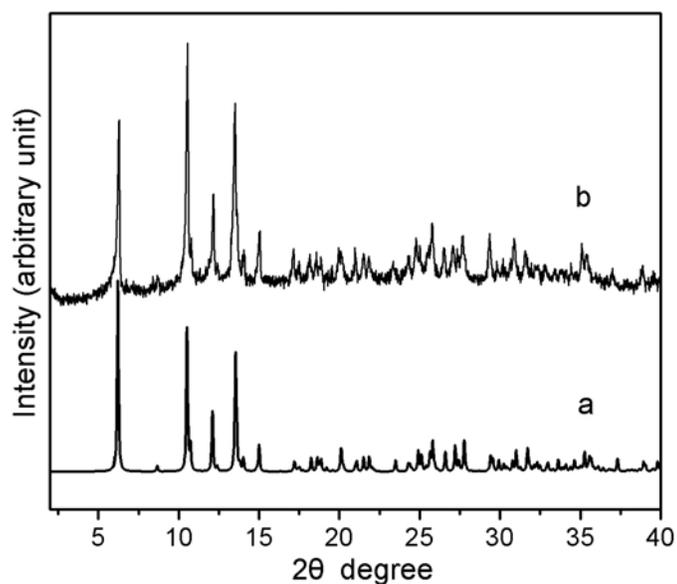


Fig. S8. X-ray diffraction patterns (Cu K α , $\lambda = 1.5418 \text{ \AA}$) of **8** ($\text{L8}\cdot 2\text{BiBr}_3$). a) Calculated pattern from the single crystal structure (single crystal data collected at 100 K); b) observed pattern at 298 K.

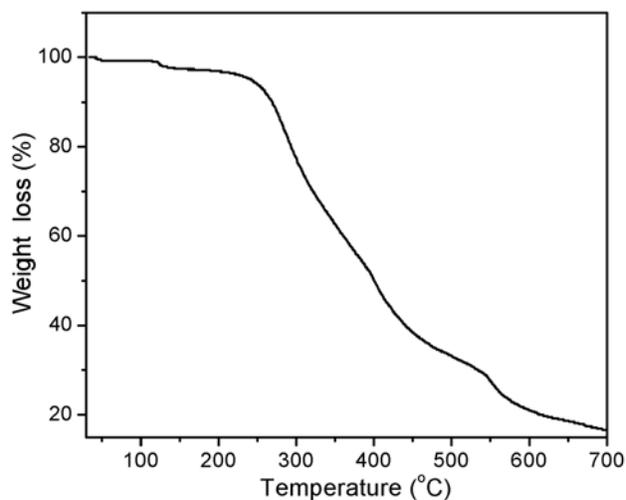


Fig. S9. Thermogravimetric analysis for a solid sample of **3** in He atmosphere. The weight loss at 141.7 °C (2.81%) is consistent with a formula of **L3**·4BiBr₃·C₆H₆ (calculated weight percentage for benzene: 3.17%). The observed weight losses are smaller than the calculated values. This is likely to be caused by the partial loss of the benzene guests prior to the TGA tests

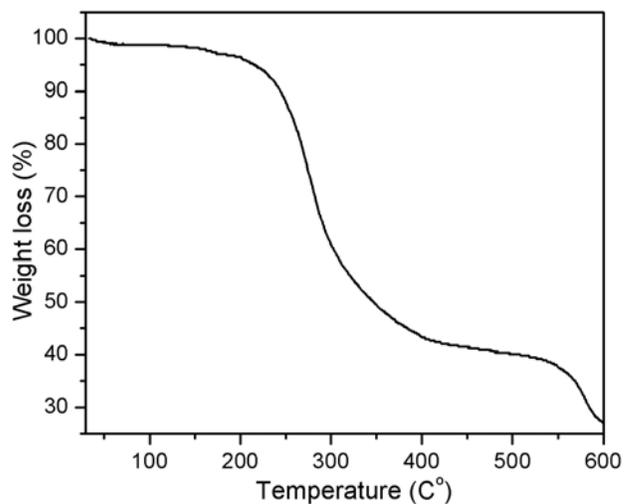


Fig. S10. Thermogravimetric analysis for a solid sample of **5** in He atmosphere.

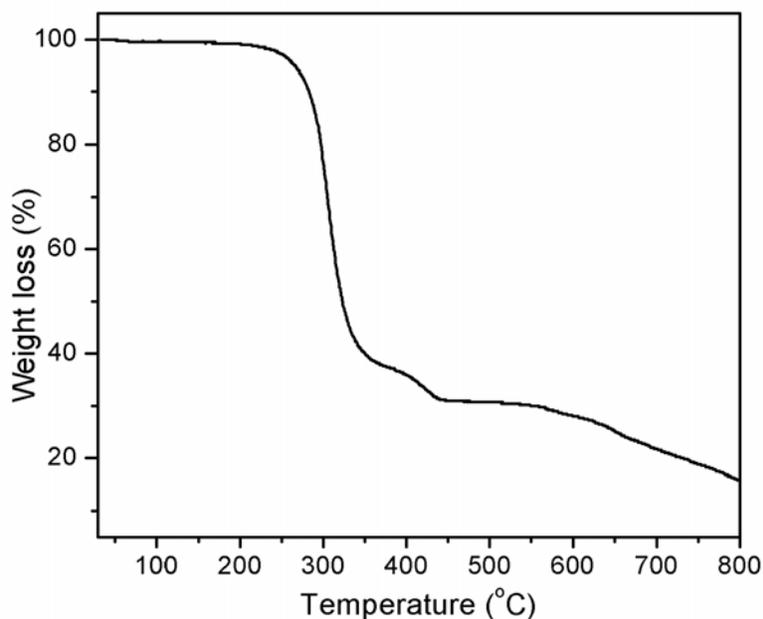


Fig. S11. Thermogravimetric analysis for a solid sample of **6** in He atmosphere.

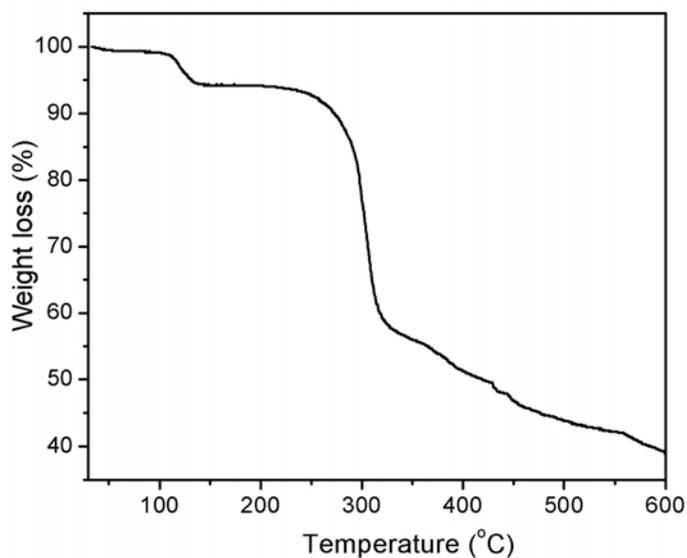


Fig. S12. Thermogravimetric analysis for a solid sample of **7** in He atmosphere. The weight loss at 144.1 °C (5.80%) is consistent with a formula of **L7**·4BiBr₃·2C₆H₆ (calculated weight percentage for benzene: 6.20%). The observed weight losses are smaller than the calculated values. This is likely to be caused by the partial loss of the benzene guests prior to the TGA tests

Table S1. Structural parameters and electronic properties of the hybrids and molecules.

Hybrid	Network	BiBr ₃ aggregates	Band gap of hybrid (eV)	Band gap of ligand (eV)	Band gap shift (eV) ^a	Bi-S distances (Å)	Bi-Br distances (Å) ^b
6	2D	linear Bi ₄ Br ₁₂	1.75	3.31	1.56	2.908, 2.952, 3.018	(2.860, 3.149) (2.824, 3.123)
7	1D	cyclic Bi ₄ Br ₁₂	2.04	3.15	1.11	2.904, 2.938	(2.828, 3.132) (2.734, 3.206) (2.785, 3.032)
TMT·2BiBr ₃	2D	chain	2.11	3.07	0.96	3.016	(2.771, 3.081)
HMTT·2BiBr ₃	2D	chain	1.64	2.96	1.32	3.099, 3.117, 3.312	(2.642, 3.402) (2.716, 3.297) (2.717, 3.289)
HMTT·BiBr ₃	1D	chain	1.75	2.96	1.21	3.027, 3.298	(2.799, 3.069) (2.717, 3.479)
HETT·2BiBr ₃	Quasi-1D	linear tetramer	1.97	2.96	0.99	2.908, 3.043, 3.219, 3.318	(2.854, 3.105) (2.675, 3.760)
HiPTT·2BiBr ₃	0D	dimer and monomers	2.18	2.96	0.78	3.009, 3.124, 3.146 ^c	(2.688, 3.314) (2.756, 3.218)
5	2D	chain	1.77	2.74	0.97	3.014, 3.082	(2.702, 3.230) (2.705, 3.236) (2.754, 3.173) (2.729, 3.174) (2.617, 3.169) (2.538, 3.283) (2.757, 3.097)
MPEB·2BiBr ₃	1D	Cyclic Bi ₄ Br ₁₂	2.01	2.59	0.58	2.914	(2.748, 3.100) (2.692, 3.214)
1	2D	chain	1.89	2.60	0.71	3.004	(2.741, 3.183)
8	Quasi-3D	dimer Bi ₂ Br ₆	2.18	2.49	0.31	3.068, 3.256	(2.723, 3.292) (2.724, 3.207) (2.788, 3.060) (2.793, 3.046)
3	2D	chain	1.77	2.43	0.66	2.995, 3.044	(2.709, 3.215) (2.743, 3.101)
2	2D	chain	1.64	2.15	0.51	3.040	

^a Relative to the solid samples of the organic molecules. ^b For bridging Br atoms (the two Bi-Br lengths for each Br atom are grouped in parentheses); see the figure captions for the Bi-Br lengths of terminal Br atoms. ^c Selected data; see Fig. S20 for more Bi-S bond length.

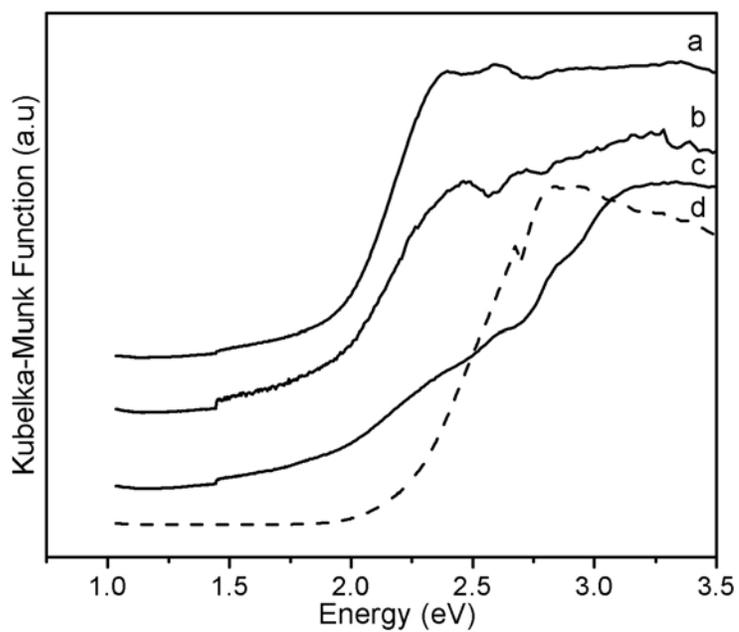


Fig. S13. Room-temperature solid-state absorption spectra. (a) Fresh solid sample of **4**; (b) the same solid sample of **4** after two hours; (c) the same solid sample of **4** after one day; (d) solid sample of **L4**.

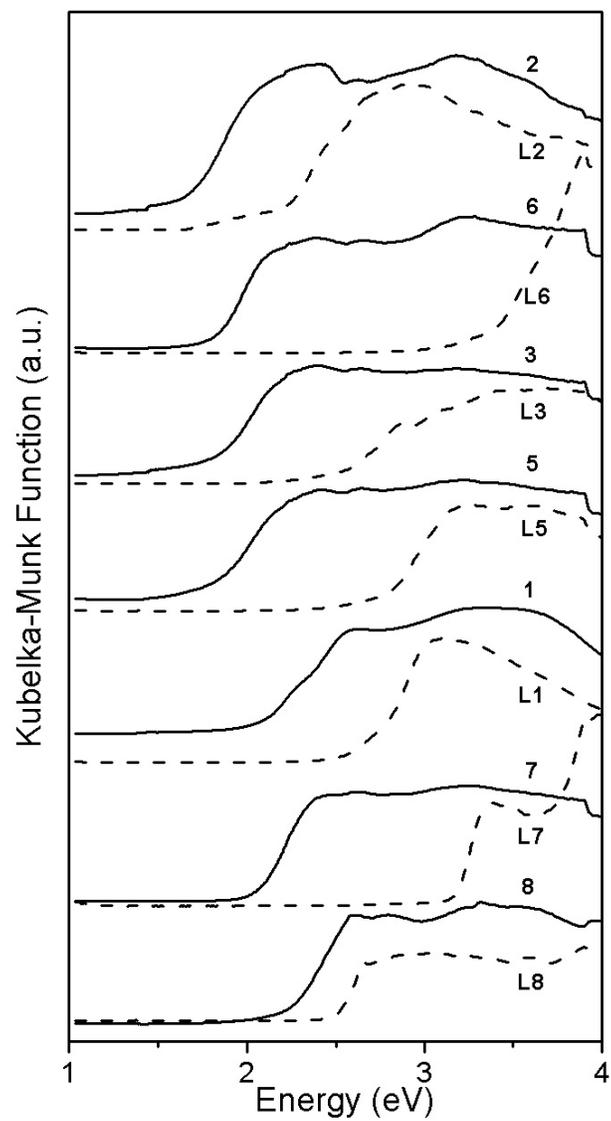


Fig. S14. Room temperature solid state absorption spectra for **1-8** (solid curves) and **L1-L8** (dashed)

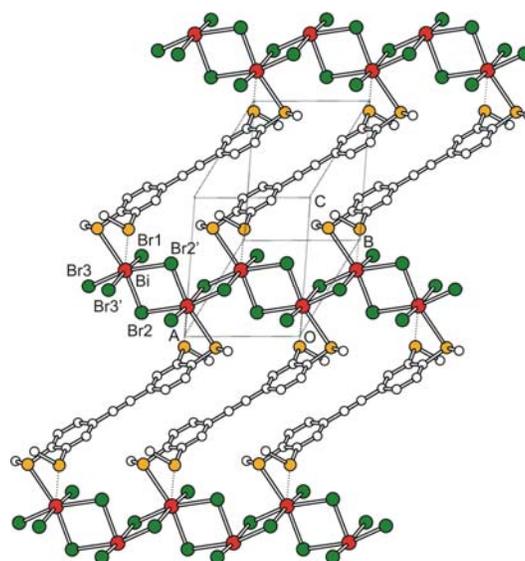


Fig. S15 A 2D coordination network in TMT·2BiBr₃. Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C. Dotted lines show the longer Bi-S distance (3.486 Å). Reprinted with permission from ref.[14]. Copyright 2005 American Chemical Society.

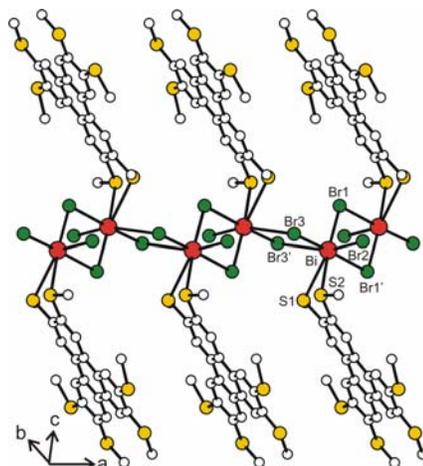


Fig. S16. A hybrid chain in HMTT·BiBr₃. Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C. Selected bond lengths: Bi-Br1, 2.7992(6) Å; Bi-Br1', 3.0688(6) Å; Bi-Br2, 2.6185(7) Å; Bi-Br3, 2.7168(6) Å; Bi-Br3', 3.4788(7) Å; Bi-S1, 3.298(1) Å; Bi-S2, 3.027(1) Å. Reprinted with permission from ref.[15]. Copyright 2005 American Chemical Society.

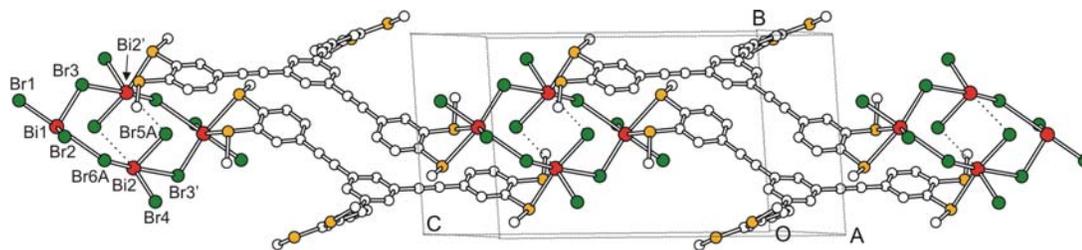


Fig. S17 The 1D coordination network in the crystal structure of MPEB·2BiBr₃. Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C. Elongated Bi-Br bonds are shown in dotted lines. Selected bond lengths: Bi1-Br1, 2.6212(7) Å; Bi1-Br2, 2.6784(8) Å; Bi1-Br3, 2.7575(9) Å; Bi1-Br6A, 3.283(2) Å; Bi2-Br6A, 2.538(2) Å; Bi2-Br4, 2.6207(7) Å; Bi2-Br3', 3.097(1) Å; Bi2-Br5A, 2.784(2) Å; Bi2'-Br5A, 3.301(2) Å (disordering of Br5A and Br6A are not shown). Reprinted with permission from ref.[14]. Copyright 2005 American Chemical Society.

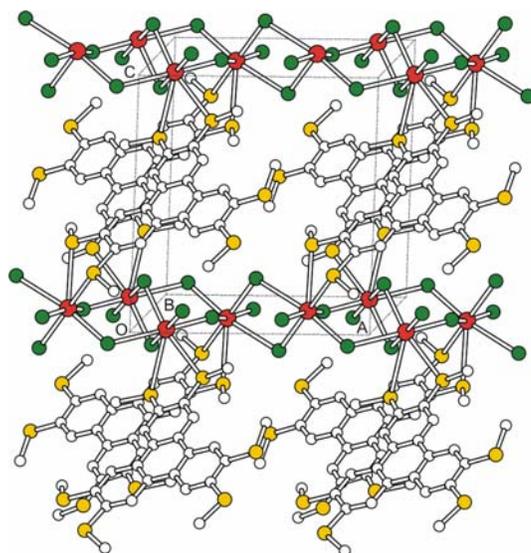


Fig. S18. A hybrid 2D network in the crystal structure of HMTT·2BiBr₃. Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C. Reprinted with permission from ref.[15]. Copyright 2005 American Chemical Society.

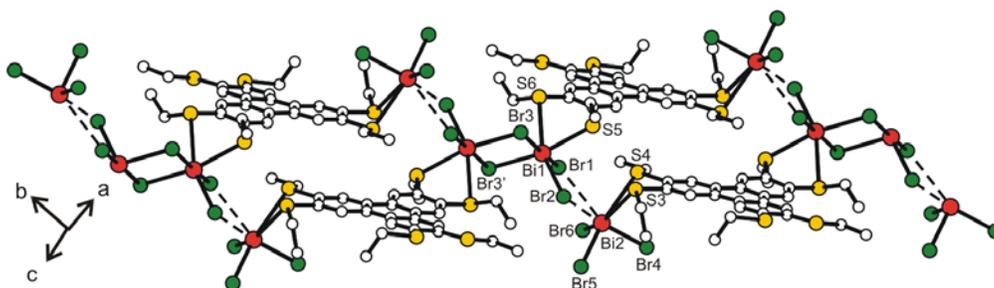


Fig. S19. The quasi-1D coordination network in the crystal structure of HETT·2BiBr₃. Large red sphere: Bi; medium green: Br; medium yellow: S; small white: C. Elongated Bi-Br bonds are shown in dashed lines. Selected bond lengths: Bi1-Br1, 2.671(2) Å; Bi1-Br2, 2.675(2) Å; Bi1-Br3, 3.105(1) Å; Bi1-Br3', 2.854(1) Å; Bi2-Br1, 3.636(1) Å; Bi2-Br2, 3.760(2) Å; Bi2-Br4, 2.619(1) Å; Bi2-Br5, 2.652(1) Å; Bi2-Br6, 2.659(1) Å; Bi1-S5, 2.908(2) Å; Bi1-S6, 3.043(3) Å; Bi2-S3, 3.318(2) Å; Bi2-S4, 3.219(2) Å. Reprinted with permission from ref.[15]. Copyright 2005 American Chemical Society.

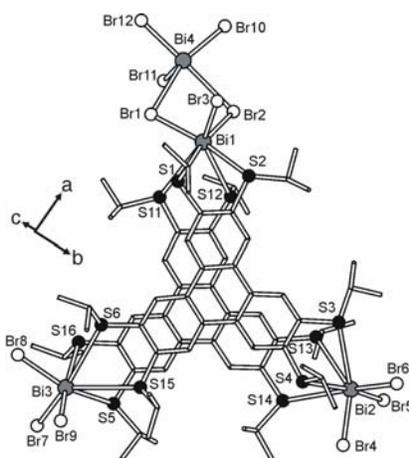


Fig. S20. An isolated (0D) coordination unit (containing two HiPTT molecules, two BiBr₃ and one Bi₂Br₆ fragments) in HiPTT·2BiBr₃. Large gray spheres: Bi; small white: Br; small black: S. Selected bond lengths: Bi1-Br1, 2.688(2) Å; Bi1-Br2, 2.756(2) Å; Bi1-Br3, 2.621(2) Å; Bi2-Br4, 2.609(2) Å; Bi2-Br5, 2.665(2) Å; Bi2-Br6, 2.608(2) Å; Bi3-Br7, 2.627(2) Å; Bi3-Br8, 2.625(3) Å; Bi3-Br9, 2.661(3) Å; Bi4-Br1, 3.314(2) Å; Bi4-Br2, 3.218(2) Å; Bi4-Br10, 2.646(2) Å; Bi4-Br11, 2.580(3) Å; Bi4-Br12, 2.610(2) Å; Bi1-S1, 3.009(4) Å; Bi1-S2, 3.124(4) Å; Bi1-S11, 3.495(4) Å; Bi1-S12, 3.291(4) Å; Bi2-S3, 3.476(4) Å; Bi2-S4, 3.150(4) Å; Bi2-S13, 3.355(4) Å; Bi2-S14, 3.451(4) Å; Bi3-S5, 3.248(4) Å; Bi3-S6, 3.382(4) Å; Bi3-S15, 3.534(4) Å; Bi3-S16, 3.146(4) Å. Reprinted with permission from ref.[15]. Copyright 2005 American Chemical Society.