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Semiconductive Coordination Networks from Bismuth(III) Bromide and 1,2-Bis(methylthio)phenylacetylene-Based Ligands

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This paper reports our initial efforts to integrate phenylacetylene-based conjugate π-electron systems into hybrid semiconductive coordination networks, as part of the larger scheme to fully synergize organic functionalities and electronic properties in crystalline solid-state materials. On the basis of a well-established Pd-catalyzed procedure, ligands of 3,3′,4,4′-tetrakis(methylthio)tolan (**L1**) and 1,3,5-tris{[3,4-bis(methylthio)phenyl]ethynyl}benzene (**L2**) were efficiently synthesized in relatively simple procedures. Molecule **L1** reacts with $BiBr_3$ to form a 2D semiconductive coordination network (**L1**·$2BiBr_3$), which consists of infinite chains of the $BiBr_3$ component cross-linked by **L1** through the chelation between the 1,2-bis(methylthio) groups and the Bi(III) centers. Molecule **L2** reacts with $BiBr_3$ to from a 1D semiconductive coordination network (**L2**·$2BiBr_3$), which features discrete tetrameric Bi_4Br_{12} units linked by the thioether groups from **L2** [only two of the three 1,2-bis(methylthio) groups from each **L2** molecule are bonded to the Bi(III) centers]. Diffuse reflectance spectra of both **L1**·$2BiBr_3$ and **L2**·$2BiBr_3$ feature strong optical absorptions at energy levels significantly lower than those of the corresponding molecular solids (**L1** and **L2)** and $BiBr_3$, indicating significant electronic interaction between the organic π-electron systems and the $BiBr_3$ components. Both **L1**·$2BiBr_3$ and **L2**·$2BiBr_3$ readily form in high yields and are stable to air, providing advantages for further studies as potentially applicable semiconductive materials.

Introduction

In the field of extended coordination frameworks,[1−5] it is of interest to access systems with tunable conducting/semiconducting properties,[1,6−10] as the rich chemical functionalities of such organics-containing systems provide attractive opportunities for structure modifications and for exploring future-generation crystalline electronic materials. Among the rapidly growing number of reported coordination networks, however, the organic ligands are usually of low electroactivity, and their electronic communications with the metal centers are quite weak. As a result, most of the reported coordination networks are insulators, while conductive or semiconductive systems are relatively rare.[1,6−10] To enhance the solid-state electroactivity, it is desirable to use electroactive organic ligands that can provide significant electronic interactions with metal centers. For example, redox-active molecules such as tetrathiafulvalene and its derivatives have been equipped with chelating sites such as the phosphine[11−14] and organylthio[8−10] groups, thus offering an avenue to

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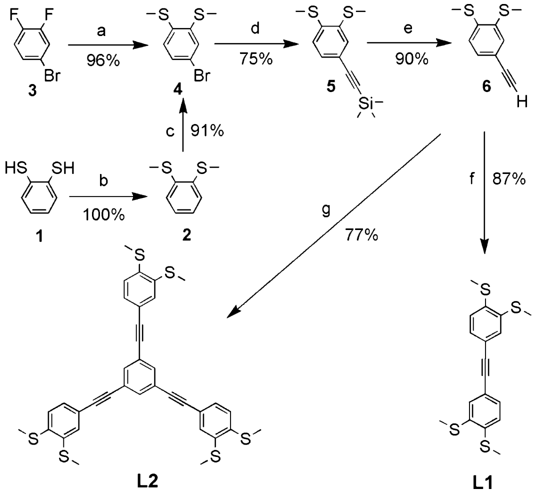
potentially stronger electronic interaction between the ligand and the metal center. Research in this direction has produced a series of metal−organic complexes consisting of isolated molecular species[10,11,13,15,16] or networks based on relatively "inert" ions such as Ag^+ or Cu^+.[8,17−19] Such pioneering exercises provide a stepping stone for achieving coordination networks with stronger electronic communication between the ligand and the metal center.

Our approach to semiconductive networks bears certain resemblance to the above works with regard to ligand design but relies on metal halide fragments (instead of individual metal ions) to interconnect the organic ligands. Specifically, this method has recently resulted in a series of solution-processable semiconductive networks based on bismuth(III) bromide (or chloride) and the large aromatic ligands of 2,3,6,7,10,11-hexakis(alkylthio)triphenylene (alkyl: methyl, ethyl, and isopropyl).[20,21] Within these hybrid systems, the bismuth halide components formed chains or isolated units and were integrated into semiconductive networks through the chelating alkylthio groups from the triphenylene-based ligands. Besides the effective electronic interaction between the organic ligands and the metal centers, the bismuth halide component as interconnecting units also helps to maintain the reversibility of the crystallization process, as a result of the relative weakness of the bismuth−halogen bonds. In general, hybrid networks involving metal−halogen bonds[22−47] tend to be more soluble in organic solvents (compared with chalcogenides, for example) and have been widely studied for properties such as photoluminescence,[28,45] porosity,[29] magnetism,[32,33] and semiconductivity.[41−43,46,47]

Scheme 1. Synthesis of **L1** and **L2**.[a]



[a] Reagents and conditions: (a) MeSNa, MeI, DMEU, 70 °C; (b) NaOMe, MeI, DMEU, rt; (c) Br_2, CH_2Cl_2, rt; (d) TMSA, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, diisopropylamine, 100 °C; (e) K_2CO_3, methanol, rt; (f) **2**, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, diisopropylamine/THF, 80 °C; (g) 1,3,5-tribromobenzene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, diisopropylamine/THF, 80 °C.

To build on this recent discovery and to explore hybrid semiconductors with a wider range of organic functions, we have studied the interactions between $BiBr_3$ and two organic compounds that contain phenylacetylene-based backbones as the conjugate π-electron fragments, that is, molecules 3,3′,4,4′-tetrakis(methylthio)tolan (**L1**) and 1,3,5-tris{[3,4-bis(methylthio)phenyl]ethynyl}benzene (**L2**), as shown in Scheme 1. On the basis of the highly efficient Pd-mediated coupling reactions between terminal alkynes and aryl halides, aryl acetylene-based molecules of various geometries and functions have been synthesized and widely studied.[48−58] These types of molecules, with their highly modifiable

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Table 1. Selected Crystallographic Data for L1·$BiBr_3$ and L2·2$BiBr_3$

	L1·2$BiBr_3$	**L2**·2$BiBr_3$
chem formula	$C_{18}H_{18}S_4Bi_2Br_6$	$C_{36}H_{30}S_6Bi_2Br_6$
fw	1259.96	1552.38
space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.9159(2)	9.989(1)
b, Å	9.5429(3)	11.918(1)
c, Å	11.5226(4)	20.045(2)
α, deg	91.367(2)	92.579(2)
β, deg	95.337(2)	98.847(2)
γ, deg	109.358(2)	110.781(2)
V, Å^3	713.15(4)	2191.6(4)
Z	1	2
ρ_{calcd}, g/cm^3	2.934	2.352
wavelength, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
abs coeff (μ), cm^{-1}	21.026	13.801
R_1[a]	2.35% [I >2s(I)]	4.22% [I >2s(I)]
wR_2[b]	5.79% [I >2s(I)]	10.12% [I >2s(I)]

[a] $R_1 = \Sigma[(|F_o| - |F^c|)/\Sigma(|F_o|)]$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

conjugate π-electron systems, therefore, appear rather attractive as potential building blocks for assembling functional hybrid networks. We report here two hybrid networks based on **L1** and **L2**, as the initial attempts to conjoin the versatile synthesis of arylacetylene-based molecules with the abovementioned method of assembling hybrid semiconductive networks. Like the previously reported triphenylene-based systems, these phenylacetylene-based hybrids also exhibit substantial electronic interactions between the organic π-electron systems and the $BiBr_3$ components, pointing to potential generality of this method of making semiconductive coordination networks from organic conjugate ligands and metal halide components.

Experimental Section

General Procedure. Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich and Fisher Scientific) and used without further purification. Syntheses of ligands **L1** and **L2** are outlined in Scheme 1. Melting points were measured on a Mel-temp II melting point apparatus and were uncorrected. Solution ^{1}H and ^{13}C NMR spectra were recorded on a 200 MHz Varian Mercury spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard.

X-ray data sets of the single-crystal samples were collected on a Bruker AXS SMART APEX CCD system using Mo Kα (λ = 0.710 73 Å) radiation at 100(2) K. The structures were solved and refined by full-matrix least-squares on F_o^2 using SHELXL 6.10. Selected crystallographic data are summarized in Table 1, with details of the X-ray diffraction studies on the single crystals provided in the Supporting Information. X-ray diffraction patterns for the bulk samples were collected at room temperature on a Rigaku Miniflex diffractometer (Cu Kα, λ = 1.5418 Å). The powder samples were spread onto a quartz substrate for data collection. A 2θ range of 3−30° was collected. The program JADE (Materials Data, Inc.) was used in the calculation of powder patterns from single-crystal structures.

Optical diffuse reflectance measurements were performed at room temperature with a JASCO V-570 double-beam, single-monochromator spectrophotometer in the 250−1200 nm region. The instrument was equipped with an integrating sphere. $BaSO_4$ powder was used as a reference (100% reflectance). Absorption data α/*S* (α, absorption coefficient; *S*, scattering factor) were calculated from the reflectance data using the Kubelka−Munk function. The band gap was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the sharp absorption edge in the α/*S* versus *E* (eV) plot. The solid sample was finely ground and pressed between two Mylar tapes (sample thickness is ~1 mm and much greater than the particle size, and therefore, an ideal diffuse reflection can be assumed). The sample was held against a white background for data collection.

Synthesis of 1,2-Bis(methylthio)benzene (2). Under nitrogen protection, a stock solution of 1,2-benzenedithiol (**1**) in anhydrous DMEU (*N*,*N*-dimethylimidazolidinone) was first prepared (concentration: 0.26 g/mL); 8.4 mL of this solution (equivalent to 15.3 mmol of **1**) was then transferred via cannula into a two-neck round-bottom flask containing sodium methoxide (1.74 g, 98%, 31.6 mmol), DMEU (30 mL), and a magnetic stirring bar. The resultant mixture was stirred at room temperature (rt) for 90 min, heated to 70 °C for 30 min, and then cooled back to rt. Methyl iodide (2.1 mL, 33.7 mmol) was then injected, and the reaction mixture was stirred for another 10 min, after which it was poured into water (150 mL) and extracted with hexanes (50 mL × 3). The combined hexane solution was washed with water, dried over sodium sulfate, and then evaporated in vacuo to yield the product as a colorless oil (2.60 g, 100% based on **1**). 1,2-Bis(methylthio)benzene (**2**) thus prepared was used for the next step without further purification. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.48 (s, 6 H), 7.13−7.25 (m, 4 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 16.27, 125.87, 126.69, 137.40.

Synthesis of 1,2-Bis(methylthio)-4-bromobenzene (4). 1,2-Bis(methylthio)-4-bromobenzene (**4**) was synthesized either by a reported method of direct bromination using bis(methylthio)benzene[59] or by the following procedure using 1-bromo-3,4-difluorobenzene (**3**) and sodium thiomethoxide. Into a 100 mL two-neck round-bottom flask (under nitrogen protection and chilled in an ice/water bath) containing sodium thiomethoxide (95%, 1.77 g, 24.0 mmol) dissolved in DMEU (anhydrous, 50 mL) was injected 1-bromo-3,4-difluorobenzene (**3**, 98%, 1.35 mL, 11.7 mmol) dropwise with stirring. The ice/water bath was then removed, and the mixture was stirred at rt for another 4 h. Methyl iodide (99%, 1.8 mL, 28.6 mmol) was then injected, and the reaction mixture was stirred for another 10 min, after which it was poured into 150 mL of water and extracted with hexanes (100 mL × 2). The hexane solution was washed with water (200 mL), dried over sodium sulfate, and evaporated in vacuo to yield a slightly yellow oily product (2.79 g, 96% based on **3**). The product of **4** thus prepared was found to be sufficiently pure (by NMR) and was used for the subsequent reaction without further purification. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.45 (s, 3 H), 2.46 (s, 3 H), 7.06 (d, 1 H, J = 8.8 Hz), 7.22−7.26 (m, 2 H). ^{13}C NMR (acetone-d_6, 50 MHz): δ 19.36, 19.61, 123.48, 132.12, 132.39, 132.73, 140.82, 144.63.

Synthesis of 4-Trimethylsilylethynyl-1,2-bis(methylthio)benzene (5). A Schlenk tube (Chemglass Airfree, 100 mL) was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (84.1 mg, 0.12 mmol), triphenylphosphine (157.2 mg, 0.60 mmol), copper(I) iodide (34.3 mg, 0.18 mmol), and **4** (1.50 g, 6.0 mmol). The Schlenk tube was then connected to a vacuum manifold to be evacuated and back-filled with nitrogen gas. With the Schlenk tube having been thus purged three times, diisopropylamine (50 mL, preflushed with nitrogen) was injected via cannula under nitrogen protection, followed by the injection of trimethylsilylacetylene (TMSA, 98%, 1.3 mL, 9.0 mmol). The Schlenk tube was then sealed with the plug and heated with stirring to 100 °C overnight (15 h). After being cooled to rt, the reaction mixture was

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poured into 200 mL of a 2:1 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo, and the orange oily residue was purified by flash chromatography to provide a light yellow oily product (silica gel, 3:1 hexanes/dichloromethane; yield, 1.22 g; 75% based on **4**). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.10 (s, 9 H), 2.30 (s, 3 H), 2.32 (s, 3 H), 6.91 (d, 1 H, $J = 7.8$ Hz), 7.05−7.11 (m, 2 H). ^{13}C NMR (CD$_2$Cl$_2$, 50 MHz): δ 0.21, 16.09, 16.44, 95.01, 105.02, 120.56, 125.49, 129.63, 129.75, 137.31, 139.25.

Synthesis of 4-Ethynyl-1,2-bis(methylthio)benzene (6). Under nitrogen protection, a reaction mixture of 4-trimethylsilylethynyl-1,2-bis(methylthio)benzene (**5**, 1.10 g, 4.1 mmol) and potassium carbonate (99%, 1.71 g, 12.4 mmol) in methanol (30 mL, prepurged with nitrogen) was stirred at rt overnight. The solvent was then removed on a rotary evaporator. The white residue was then extracted with dichloromethane (50 mL × 2), and the combined dichloromethane solution was then washed with water (100 mL) and brine (saturated, 100 mL), dried over sodium sulfate, and evaporated in vacuo to yield an off-white solid (0.72 g, 90% based on **5**, mp 43−45 °C). The product thus obtained was proved sufficiently pure by NMR and was used without further purification. ^{1}H NMR (acetone-d_6, 200 MHz): δ 2.50 (s, 6 H), 3.65 (s, 1 H), 7.19−7.31 (m, 3 H). ^{13}C NMR (acetone-d_6, 50 MHz): δ 19.13, 19.41, 82.95, 87.45, 123.35, 129.27, 133.02, 133.35, 141.26, 143.28.

Synthesis of 1,3,5-Tris{[3,4-bis(methylthio)phenyl]ethynyl}-benzene (L2). A Schlenk tube (Chemglass Airfree, 100 mL) was loaded with a magnetic stirring bar, bis(triphenylphosphine)-palladium(II) chloride (9.0 mg, 12.8 μmol), triphenylphosphine (16.5 mg, 62.9 μmol), copper(I) iodide (3.6 mg, 18.9 μmol), **6** (0.40 g, 2.1 mmol), and 1,3,5-tribromobenzene (98%, 0.20 g, 0.64 mmol). The Schlenk tube was then connected to a vacuum manifold to be evacuated and back-filled with nitrogen gas. With the Schlenk tube having been thus purged three times, a 1:1 diisopropylamine/tetrahydrofuran (THF) mixture (30 mL, prepurged with nitrogen gas) was injected via cannula under nitrogen protection. The Schlenk tube was then sealed with the plug and heated with stirring to 80 °C for 20 h. After cooling to rt, the reaction mixture was worked up by the same procedure as was used for 4-trimethylsilylethynyl-1,2-bis(methylthio)benzene. The crude product was then purified by flash chromatography (silica gel, 4:1 hexanes/dichloromethane) to provide a light yellow solid (0.32 g, 77% based on 1,3,5-tribromobenzene, mp 167−169 °C). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ 2.55 (s, 9 H), 2.56 (s, 9 H), 7.21 (d, 3 H, $J = 8.2$ Hz), 7.36−7.41 (m, 6 H), 7.69 (s, 3 H). ^{13}C NMR (CD$_2$Cl$_2$, 50 MHz): δ 16.01, 16.35, 88.35, 90.61, 119.94, 124.53, 125.53, 129.20, 129.24, 134.19, 137.43, 139.44.

Synthesis of 3,3′,4,4′-Tetrakis(methylthio)tolan (L1). In a procedure similar to that used for **L2**, **L1** was obtained from **6** (0.901 g, 4.6 mmol) and **4** (0.962 g, 3.9 mmol) as a slightly yellow solid (1.21 g, 87% based on **4**, mp 140−141 °C). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ 2.50 (s, 6 H), 2.51 (s, 6 H), 7.16 (d, 2 H, $J = 8.8$ Hz), 7.14−7.34 (m, 4H). ^{13}C NMR (CD$_2$Cl$_2$, 50 MHz): δ 16.05, 16.33, 89.62, 120.49, 125.66, 129.00, 129.03, 137.46, 138.78.

Crystallization of L2·2BiBr$_3$. In an argon-filled glovebox, **L2** (6.1 mg, 9.2 μmol) and BiBr$_3$ (12.3 mg, 27.4 μmol) were loaded into a heavy-wall borosilicate glass tube (Kimax, $^{3}/_{8}$ in. o. d.), and anisole (0.6 mL, anhydrous) was added. The tube was then sealed under a vacuum (with the reagents being frozen in liquid nitrogen) and heated at 80 °C in an oil bath for 24 h, followed by natural cooling to rt, during which orange-red blocklike single crystals suitable for single-crystal X-ray diffraction were formed. The pure phase bulk sample was prepared as follows. Under nitrogen protection, anisole (1.5 mL), **L2** (30.6 mg, 46.0 μmol), and BiBr$_3$ (47.5 mg, 105.8 μmol) were charged into a Schlenk tube (Chemglass Airfree, 5 mL) containing a magnetic stirring bar. The Schlenk tube was then sealed tightly and heated at 50 °C in an oil bath with stirring for 48 h. After the oil bath was cooled to rt, the orange-red solid thus formed was collected by suction filtration and rinsed with anisole (e.g., 1 mL × 3) and hexanes (e.g., 2 mL × 3) to provide the final product (64.2 mg, 90% yield based on **L2**). An X-ray powder diffraction study indicated a single phase consistent with the single-crystal structure of **L2**·2BiBr$_3$ (see Figure S1 in the Supporting Information). Chemical analysis of the product C$_{36}$H$_{30}$S$_6$Bi$_2$Br$_6$ yields the following: Anal. Calcd [C (27.85%), H (1.95%), S (12.39%), Br (30.88%)]. Found [C (28.61%), H (2.03%), S (12.30%), Br (29.37%)].

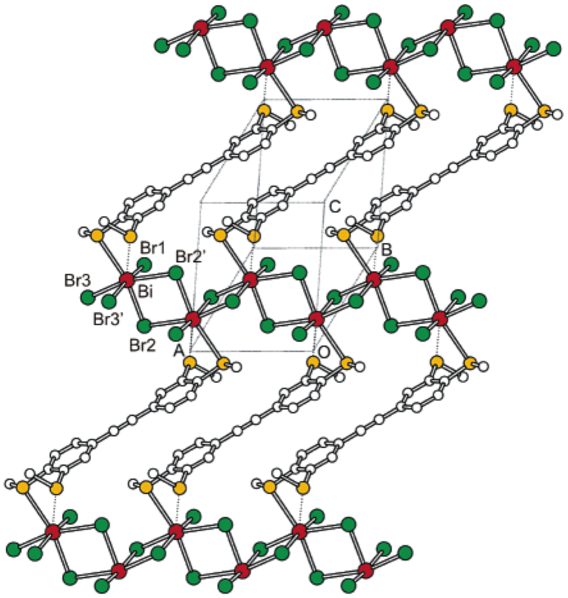

Figure 1. 2D coordination network in **L1**·2BiBr$_3$. Large red sphere, Bi; medium green, Br; medium yellow, S; small white, C. Dotted lines show the longer Bi−S distance (3.486 Å).

Crystallization of L1·2BiBr$_3$. The orange-red crystals of **L1**·2BiBr$_3$ suitable for single-crystal X-ray diffraction study were obtained by a procedure similar to that given above; so was the single phase bulk sample (see Figure S2 in the Supporting Information for the X-ray powder pattern). The yields are also comparable. Chemical analysis of the product C$_{18}$H$_{18}$S$_4$Bi$_2$Br$_6$ yields the following: Anal. Calcd [C (17.16%), H (1.44%), S (10.18%), Br (38.05%)]. Found [C (17.43%), H (1.40%), S (9.97%), Br (37.68%)].

Results and Discussion

Single-Crystal Structure of L1·2BiBr$_3$. The structure exhibits the space group $P\bar{1}$, with one BiBr$_3$ unit and half of an **L1** molecule in the asymmetric portion of the unit cell. The structure features one-dimensional (BiBr$_3$)$_n$ chains, to which ligands of **L1** are periodically attached through the chelations between the Bi(III) centers and the sulfur atoms (see Figure 1). Because of the multitopic nature of ligand **L1**, a 2D coordination network (i.e., based on the Bi−Br and Bi−S interactions) is thus resulted. The connectivity of the BiBr$_3$ chains is similar to those of HMTTBiBr$_3$ and HMTTBiCl$_3$ previously reported by this group.[21] The Bi atom is surrounded by five Br atoms (e.g., Br1, Br2, Br3, Br2′, Br3′) and a pair of sulfur atoms from an **L1** molecule. The

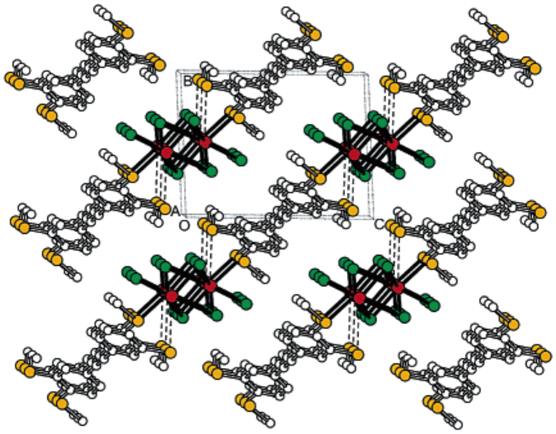

Figure 2. Overview of the crystal structure of **L1**·2BiBr$_3$ (along the *a* axis). Large red sphere, Bi; medium green, Br; medium yellow, S; small white, C.

coordination geometry around the Bi atom can be deconstructed into three portions. First, the Bi atom forms a trigonal pyramid with three Br atoms (Br1, Br2, and Br3) at rather short distances (Bi−Br1, 2.656 Å; Bi−Br2, 2.771 Å; Bi−Br3, 2.718 Å) and with bond angles around 90° (Br1−Bi−Br2, 94.73°; Br1−Bi−Br3, 90.50°; Br2−Bi−Br3, 83.93°). Second, the Br2′ and Br3′ atoms form distinctly longer bonds (distances: Bi−Br2′, 3.081 Å; Bi−Br3′, 3.161 Å; Bi···Br van der Waals distance > 3.8[60]) to constitute a distorted square pyramid around the Bi^{3+} center, with Br2 at the apex and the other four Br atoms at the basal plane. Third, the open space opposite (i.e., trans to) the Br2 apex is occupied by two sulfur atoms from **L1** (Bi−S distances: 3.016 and 3.486 Å), furnishing a 7-fold coordination geometry resembling a monocapped trigonal antiprism. The BiBr$_3$ chains are based on edge sharing between the individual coordination units (i.e., two edges are shared from each Bi unit: one is that of Br2 and Br2′ and the other is that of Br3 and Br3′, see Figure 1).

Within each hybrid layer, the BiBr$_3$ chains run along the crystallographic *a* axis and alternate with rows of **L1** molecules that are stacked in a face-to-face fashion (shortest intermolecular C···C distance: 3.35 Å), as shown in Figure 2. The layers are packed along the [0−11] direction to furnish the complete crystal structure, which is, on a global scale, reminiscent of distinct columnar domains of the BiBr$_3$ component imbedded in a matrix of the organic molecules (Figure 2).[61]

Single-Crystal Structure of L2·2BiBr$_3$. This structure exhibits the space group $P\bar{1}$, and the asymmetric portion of the unit cell consists of one molecule of **L2** and two BiBr$_3$ fragments. Unlike the infinite chain of BiBr$_3$ in **L1**·2BiBr$_3$, the BiBr$_3$ component in this structure forms isolated tetrameric units (Figure 3; the crystallographic data located two sets of positions for Br5 and Br6, i.e., Br5A and Br5B, Br6A and Br6B; for brevity, only Br5A and Br6A are presented here, with more structural details given in the Supporting Information). The tetrameric unit is centrosymmetric and features an eight-membered ring of Bi$_4$Br$_4$ with an alternating arrangement of the Bi and Br atoms. Across this eight-membered ring, the two centrosymmetrically related Bi2 atoms are further connected by two crystallographically equivalent Br atoms (e.g., Br5A). The remaining Br atoms are all terminal, each being bonded exclusively to one Bi atom (i.e., Br1 and Br2 to Bi1, Br4 to Bi2). In total, Bi1 is bonded to four Br atoms in a sawhorse geometry, with the equatorial positions further taken up by a pair of chelating S atoms (Bi−S distances: 3.013 and 3.098 Å) from ligand **L2** to complete a distorted octahedral coordination geometry; Bi2 is bonded to four Br atoms in a square-pyramidal geometry, with open space opposite (i.e., trans to) the apex (i.e., Br5A) further occupied by a pair of S atoms (Bi−S distances: 2.914 and 3.555 Å) to furnish the complete coordination geometry.

The interaction between the tetrameric Bi$_4$Br$_{12}$ unit and the organic ligand (**L2**) results in a 1D coordination network (Figure 3). While all the Bi sites are bonded to the sulfur atoms, only two pairs of sulfur atoms from each organic ligand are coordinated to Bi centers (the other pair of S atoms remain unbonded). As a result, the neighboring tetramers of Bi$_4$Br$_{12}$ within the 1D coordination network are connected by two ligands of **L2**, with a substantial portion of the their π-electron systems overlapping in a face-to-face fashion (short intermolecular C···C distances < 3.50 Å). The composite chains run along the [101] direction, and they stack to form layers that are perpendicular to the [010] direction (see Figure S3 in the Supporting Information for more views of the crystal structure). Extensive aggregation of the hydrocarbon components occurs across the individual chains and layers, effectively separating the individual Bi$_4$Br$_{12}$ units into distinct isolated domains.[61]

Electronic Property Studies. In contrast to the almost colorless crystals of the organic compounds (**L1** and **L2**) and light yellowish bismuth tribromide, the hybrid compounds of both **L1**·2BiBr$_3$ and **L2**·2BiBr$_3$ are bright red. Optical absorption measurements (see Experimental Section for more detail) provide a more quantitative assessment of the electronic band gaps of the hybrid semiconductors. As shown in Figure 4, the electronic band gaps of **L1**·2BiBr$_3$ (2.11 eV) and **L2**·2BiBr$_3$ (2.01 eV) are very similar, both being significantly smaller than those of the molecular solids of **L1** and **L2** (band gaps > 2.5 eV; see Figure S4 in the Supporting Information). For further comparison, similar diffuse reflectance measurements indicated the band gap of BiBr$_3$ to be 2.66 eV.[21] The significantly smaller band gaps (and, thus, the darker coloring) of the hybrid systems, thus, point to substantial electronic interaction between the bismuth(III) bromide components and the organic π-electron systems. Presumably, such interaction is effectively mediated by the thioether sulfur atoms that are simultaneously bonded to the organic π systems and the Bi(III) centers, although electronic structure calculations would certainly be helpful in further delineating the origin of the electroactivity of these hybrid networks.

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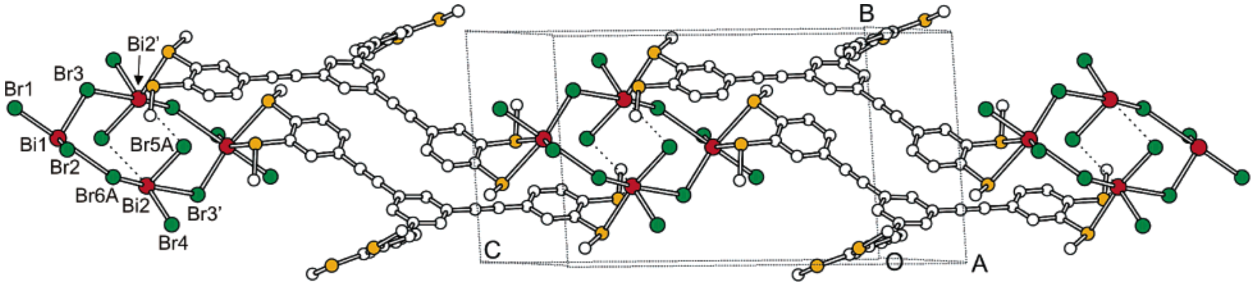

Figure 3. 1D coordination network in the crystal structure of **L2**·2BiBr$_3$. Large red sphere, Bi; medium green, Br; medium yellow, S; small white, C. Elongated Bi−Br bonds are shown in dotted lines. Selected bond lengths: Bi1−Br1, 2.6212(7) Å; Bi1−Br2, 2.6784(8) Å; Bi1−Br3, 2.7575(9) Å; Bi1−Br6A, 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).

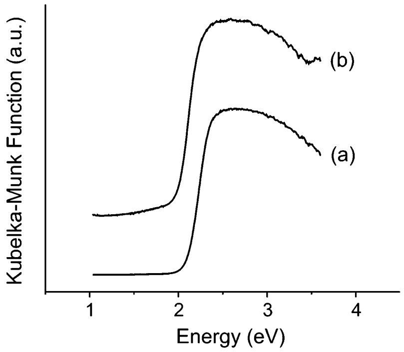

Figure 4. Room-temperature optical absorption spectra for solid samples of (a) **L1**·2BiBr$_3$ and (b) **L2**·2BiBr$_3$.

Conclusions

In this paper, chelating methylthio groups were directly attached to phenyl acetylene-based conjugate systems to provide molecular building blocks that readily interact with BiBr$_3$ to form air-stable semiconductive coordination networks in high yields. The substantially enhanced electroactivity of the solid-state products (as indicated by optical studies) appears to stem from the effective electronic interaction between the organic conjugate units and the inorganic components of BiBr$_3$ in the crystalline framework. Because of the general synthetic ease and flexibility of the phenylacetylene-based conjugate molecules, these preliminary results provide a basis to further explore hybrid semiconductive networks that incorporate richer organic functionalities for systematic structure−property studies within these fully integrated organic−inorganic systems.

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Supporting Information Available: Full crystallographic data in full tables and CIF format for compounds **L1**·2BiBr$_3$ and **L2**·2BiBr$_3$. Additional figures of the crystal structure of **L1**·2BiBr$_3$ and **L2**·2BiBr$_3$. X-ray powder diffraction patterns for bulk samples of **L1**·2BiBr$_3$ and **L2**·2BiBr$_3$. Diffuse reflectance spectra of compounds **L1**, **L2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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