Inorganic Chemistry

Dissolution of Sn, SnO, and SnS in a Thiol—Amine Solvent Mixture: Insights into the Identity of the Molecular Solutes for Solution-Processed SnS

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S Supporting Information

ABSTRACT: Binary solvent mixtures of alkanethiols and 1,2ethylenediamine have the ability to readily dissolve metals, metal chalcogenides, and metal oxides under ambient conditions to enable the facile solution processing of semiconductor inks; however, there is little information regarding the chemical identity of the resulting solutes. Herein, we examine the molecular solute formed after dissolution of Sn, SnO, and SnS in a binary solvent mixture comprised of 1,2ethanedithiol (EDT) and 1,2-ethylenediamine (en). Using a combination of solution ¹¹⁹Sn NMR and Raman spectroscopies, bis(1,2-ethanedithiolate)tin(II) was identified as the likely molecular solute present after the dissolution of Sn, SnO,



and SnS in EDT-en, despite the different bulk material compositions and oxidation states (Sn⁰ and Sn²⁺). All three semiconductor inks can be converted to phase-pure, orthorhombic SnS after a mild annealing step (\sim 350 °C). This highlights the ability of the EDT-en solvent mixture to dissolve and convert a variety of low-cost precursors to SnS semiconductor material.

INTRODUCTION

Solution processing of inorganic semiconductors for the fabrication of affordable and scalable electronic thin films is emerging as a commercially viable alternative to traditional high-vacuum deposition methods.¹ Using this approach, semiconductor thin films can be printed onto various substrates (e.g., plastics, glasses) at relatively low temperatures using existing high-throughput technologies, such as roll-to-roll manufacturing and spray coating.² Innovations in the area of molecular semiconductor inks have led to high-quality electronic thin films, which have shown promise in photo-voltaics,^{1,3} thermoelectrics,⁴ thin film transistors,⁵ and phase change memory materials.⁶

Molecular semiconductor inks are comprised of molecular solutes and are typically prepared using one of two methods: (i) a discrete inorganic coordination complex can be dissolved as a premade soluble precursor,^{7,8} or (ii) bulk materials having the desired elemental composition of the recovered semiconductor may be directly dissolved.^{9–13} Direct dissolution offers a number of advantages over other methods, that is, in a single step, cheap bulk materials can be used as elemental sources for high-quality semiconductors using a simple "dissolve and recover" process. Additionally, this approach offers the ability to tune semiconductor composition because

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the stoichiometry of the final product is often dependent on the nominal stoichiometry of the dissolved bulk material or combinations of materials. The challenge of this approach, however, lies in the fact that most bulk metals, metal oxides, and metal chalcogenides are insoluble in common solvents, as dissolution of these bulk materials involves breaking the strong bonds that make up these frameworks.

Hydrazine is one solvent capable of dissolving metal chalcogenide frameworks to yield soluble semiconductor inks. Mitzi and co-workers at IBM first employed hydrazine in the presence of elemental chalcogen as an effective solvent for the dissolution of bulk metal chalcogenides.^{9–11} This dissolution process is facilitated by nucleophilic attack by chalcogenides $(E^{2-} = S^{2-}, Se^{2-}, and Te^{2-})$ formed via the in situ reduction of elemental chalcogen in hydrazine. Reaction between the resulting E^{2-} and bulk metal chalcogenides yields soluble hydrazinium chalcogenidometallate species, which are soluble in hydrazine and other polar solvents, and can be easily solution deposited to form high-quality metal chalcogenide thin films upon annealing. A number of studies have investigated the nature of the molecular solutes, the solute/solvent interactions,

Received: February 2, 2016

and the molecular condensation reactions that occur upon annealing to recover the semiconductor.^{11,14–19} This knowledge has provided key insights into the phase formation mechanism of as-deposited films and has ultimately allowed for more control over the resulting crystalline phase, composition, band gap, and film morphology.

In addition to hydrazine, an alternative binary solvent system comprised of alkanethiols and 1,2-ethylenediamine (en) has been developed by our group for the facile dissolution of a wide array of metals, metal oxides, and metal chalcogenides. The dissolved materials can be directly recovered as phase-pure binary metal chalcogenides at relatively low temper-atures.^{12,13,20,21} The solvent system can also be used to dissolve multiple bulk components in order to controllably deposition more compositionally complex semiconductors (e.g., CuIn (S_x Se_{1-x})₂, Cu₂ZnSnS_{4-x}Se_x or CZTSSe, and Cu₂SnSe₃).^{22–26} For example, alkanethiol–en-processed CZTSSe photovoltaic devices have been reported with power conversion efficiencies > 7%.²⁷

Recently, the EDT-en solvent system has been applied to the solution processing of SnS semiconductor thin films.^{20,21,24} SnS is an indirect narrow band gap semiconductor ($E_g = 1.08$ eV) comprised of earth-abundant elements that has been receiving increasing attention as an absorber material for singlejunction solar cells,²⁸ with devices currently achieving power conversion efficiencies > 4% where the absorber layer was deposited by atomic layer deposition.²⁹ The solution deposition of SnS may ultimately allow for the low-cost fabrication of large area devices. Bulk SnO and SnS have been previously dissolved using the alkanethiol-en solvent system for the recovery of phase-pure SnS,^{20,21,24} and herein, we report the dissolution of elemental Sn toward the solution processing of SnS for the first time; however, nothing has heretofore been reported on the nature of the dissolved species. Toward this end, here we explore the solute identity of three bulk tin-containing materials (i.e., Sn, SnO, and SnS) dissolved in a 1,2-ethanedithiol (EDT)-en solvent system to give semiconductor inks to SnS.

EXPERIMENTAL SECTION

Materials and Methods. 1,2-Ethylenediamine (en, ≥99%), tin(II) sulfide (SnS, 99.99%), and tin(IV) chloride pentahydrate (SnCl₄: 5H₂O, 98%) were purchased from Sigma-Aldrich. 1,2-Ethanedithiol (EDT, 98+%), elemental tin (Sn, 99.85%), and tin(II) oxide (SnO, 99%) were purchased from Alfa Aesar. Tin(II) chloride dihydrate (SnCl₂·2H₂O, 98%) was purchased from Strem Chemicals. 1,2-Ethylenediamine and 1,2-ethanedithiol were purged using nitrogen gas for a minimum of 10 min before use in the dissolution experiments; all other reagents and solvents were used as received without further purification.

Preparation of lnks. The dissolved inks were prepared by mixing the appropriate bulk material (50 mg) with en (1.00 mL) and EDT (0.1 mL) at room temperature under a nitrogen atmosphere. The solutions were stirred for ca. 5 days to yield transparent light-yellow solutions. Complete dissolution was observed for bulk SnS and SnO. While elemental Sn did not fully dissolve, excess Sn was easily removed by filtration through a 450 nm PTFE membrane.

Synthesis of (EDT)₂**Sn(IV)** (1). 1 was synthesized by following a literature procedure³⁰ where an aqueous mixture of 1,2-ethanedithiol and potassium hydroxide was added to a solution of SnCl₄·SH₂O; the resulting white precipitate was recrystallized from DCM to yield colorless crystals. Anal. Calcd for C₄H₈S₄Sn: C, 15.85; H, 2.66; S, 42.32. Found: C, 15.96; H, 2.73; S, 43.38. ¹H NMR (CDCl₃, 25 °C, 500 MHz): δ 3.22 ppm. ¹³C{¹H} NMR (CDCl₃, 25 °C, 125 MHz): δ 35.9 ppm. ¹¹⁹Sn NMR (CDCl₃, 25 °C, 186.5 MHz): δ 281 ppm. Mp: 186 °C.

Thermal Recovery of SnS. Solvent removal entailed heating the drop-cast inks on a temperature-controlled hot plate to 100 $^{\circ}$ C under flowing nitrogen followed by heating to 107 $^{\circ}$ C under vacuum (24 h). The deposited inks were then annealed on a temperature-controlled hot plate to 350 $^{\circ}$ C under flowing nitrogen followed by a slow cool down to room temperature.

Material Characterization. Solution ¹¹⁹Sn NMR spectra were recorded on a Varian 500 MHz spectrometer at 186.5 MHz. Spectra were obtained at room temperature without deuterium locking of the main magnetic field. Each experiment used a 10 μ s pulse width and a 0.5 s relaxation delay and collected 1024 scans. A spectral window from -1000 to +1500 ppm was used to search for the signals in 500 ppm increments. $\delta_{119\text{Sn}}$ were referenced to the internal standard of the probe. The NMR samples were prepared in 5 mm J-Young tubes under nitrogen. Electrospray ionization mass spectrometry (ESI-MS) was performed using a Waters LCT Premier operated using electrospray ionization with negative ion detection. The carbon, hydrogen, nitrogen, and sulfur chemical composition of the dried solutions was analyzed using a Flash 2000 CHNS Elemental Analyzer. Samples (3 mg) were prepared for elemental analysis by drying under vacuum at 107 °C for 24 h. Raman spectra of the solutions were recorded under ambient conditions using a Horiba Jobin Yvon spectrometer, equipped with a liquid sample holder. An excitation source of 785 nm from a diode laser was employed at a power level of 50 mW. UV-vis absorption spectra were taken in a nitrogen atmosphere using a PerkinElmer Lambda 950 spectrophotometer. SnO and SnS solutions were prepared as described above. A 1:10 vol/ vol mixture of EDT-en was used for the blank, and each solution was diluted with this same solvent mixture prior to data collection to reach the reported concentrations. The spectrum of the EDT-en solvent mixture was measured against an empty cuvette. FT-IR spectra were recorded on a Bruker Vertex 80 spectrometer. All samples were drop cast onto ZnSe windows and either dried at 107 °C under vacuum for 24 h or annealed to 350 °C and then immediately cooled. The resulting spectra were then baseline corrected using a rubber band mode with 5 iterations and normalized to the largest peak. Thermal analysis measurements were made on a Netzsch DSC/TGA-MS/IR STA449 F1 using sample sizes of ~20 mg. Argon was used as a protective and flow gas. Mass flow controllers were set to 40 mL min⁻¹ for the protective gas and 10 mL min⁻¹ for the purge gas. The thermal range examined was 50-500 °C with a heating rate of 10 °C min⁻¹. Powder X-ray diffraction (XRD) data was collected with a Rigaku Ultima IV diffractometer in parallel beam geometry (2 mm beam width) using Cu K α radiation ($\lambda = 1.54$ Å). Scanning electron microscope-energy-dispersive X-ray spectroscopy (SEM-EDX) was used for elemental analysis on a JEOL JSM-6610 scanning-electron microscope. Diffuse reflectance UV-vis-NIR spectroscopy was performed using the reflectivity mode in a PerkinElmer Lambda 950 that was equipped with a 150 mm integrating sphere. The samples were prepared by thoroughly grinding 9 mg of material with 290 mg of MgO using a powder sample holder at the end of the integrating sphere.

RESULTS AND DISCUSSION

Dissolution of Sn, SnO, and SnS. Inks were prepared by the dissolution of bulk Sn, SnO, and SnS in a 1:10 vol/vol mixture of EDT–en according to previous reports.¹² The solubilities, expressed as wt % solute in the saturated solution of EDT–en at room temperature and ambient pressure, of both SnO and SnS have been previously determined.^{20,21} SnO when dissolved at room temperature for a period of 15 h was soluble up to 15 wt % in a 1:4 vol/vol ratio of EDT–en, while SnS was soluble up to 12 wt % in an a 1:11 vol/vol ratio of EDT–en after mild heating (50 °C, 12 h). Here, a lower concentration of 4.5 wt % in a 1:10 vol/vol mixture of EDT–en was used for all three materials due to the lower solubility limit of elemental Sn in the solvent system. At this concentration, both SnO and SnS were fully soluble after stirring for 24 h. Longer dissolution times were required for elemental Sn; even after 5 days a small amount of Sn remained undissolved. Despite the relatively reduced solubility of elemental Sn, all three materials gave lightyellow, optically transparent solutions that were free of visible scattering and stable for a period of months at a concentration of 4.5 wt % (Figure 1a).



400 350 300 250 200 150 100 50 0 ¹¹⁹Sn δ(ppm)

Figure 1. (a) Photograph of bulk elemental Sn, SnO, and SnS dissolved in a 1:10 vol/vol EDT–en solvent mixture at 4.5 wt %. (b) Solution ¹¹⁹Sn NMR spectra of Sn, SnO, and SnS dissolved in EDT– en giving a single resonance at $\delta_{119Sn} = 217$ ppm.

Solution ¹¹⁹Sn NMR Spectroscopy. Solution ¹¹⁹Sn NMR spectroscopy was used to probe the identity of the dissolved Sn. SnO, and SnS in EDT-en. The ¹¹⁹Sn isotope is useful in this regard because it yields narrow signals over a very wide chemical shift (δ_{Sn119}) range of ca. 6500 ppm for organotin and inorganic tin compounds, making the chemical shift sensitive to even small structural changes.³¹⁻³³ For example, a correlation exists between the chemical shift range and the tin coordination number, whereby irrespective of the formal oxidation state, the coordination number can be inferred from ¹¹⁹Sn chemical shift.^{32,33} The ¹¹⁹Sn NMR spectra, obtained directly after dissolution of the bulk Sn, SnO, and SnS materials in the EDT-en solvent system, reveal an identical, single sharp resonance at $\delta_{\text{Sn119}} = 217$ ppm for all three materials (Figure 1b). Thus, even though the three systems have different bulk material compositions (Sn, SnO, and SnS) and oxidation states $(Sn^0 \text{ and } Sn^{2+})$, they all yield an equivalent solute on the NMR time scale upon dissolution in EDT-en. The lack of J_{Sn-Sn} coupling in the ¹¹⁹Sn NMR spectra suggests that the solutes are mononuclear. The observed resonance at $\delta_{\text{Sn119}} = 217$ ppm is consistent with those chemical shifts reported for mononuclear tin tetrathiolate compounds in the relatively narrow chemical shift window of ca. 20-300 pm; the chemical shifts of tin tetrathiolates are in the range from 138 to 26 ppm for $(EtS)_4Sn(IV)$ and $({}^tBuS)_4Sn(IV)$, respectively.^{34,3} This chemical shift range is extended further downfield when tin is coordinated by a chelating dithiolate, such as EDT. For example, $(EDT)_2Sn(IV)$ gives a chemical shift of $\delta_{Sn119} = 277$ ppm.³¹ From these initial ¹¹⁹Sn NMR spectra it can be inferred that regardless of the bulk material that was dissolved, a single four-coordinate tin thiolate compound was formed in the EDT-en solvent system.

Given the indication by ¹¹⁹Sn NMR data that the molecular solute was a four-coordinate tin thiolate compound, it was hypothesized that the dissolved species could be similar in nature to the known compound $(EDT)_2Sn(IV)$ (1). To test this hypothesis, 1 was synthesized following a literature procedure whereby an aqueous mixture of EDT and KOH was added to a solution of $SnCl_4$ ·SH₂O in water.³⁰ The

resulting white precipitate was recrystallized from dichloromethane to yield colorless crystals that were confirmed to be **1** by NMR spectroscopy, melting point determination, and combustion analysis (vide supra). Compound **1** has been previously characterized using NMR with a reported $\delta_{119Sn} =$ 277 ppm in thioformaldehyde.³¹ While this value does not match the $\delta_{119Sn} = 217$ ppm for the dissolved Sn, SnO, and SnS species, it was plausible that the EDT–en solvent system could cause differences in chemical shift. To test this hypothesis, **1** was characterized in several solvents using ¹¹⁹Sn NMR (Figure 2). The δ_{119Sn} of **1** varied quite drastically between +280 and



Figure 2. ¹¹⁹Sn NMR spectra of **1** in various solvents showing the dependence of δ_{119Sn} on solvent and tin coordination number. Red and blue shaded areas indicate the general δ_{119Sn} ranges for four- and six-coordinate tin compounds, respectively.

-350 ppm depending on the solvent used; recall that the chemical shifts are very characteristic of tin coordination environments where δ_{119Sn} of 20–300 ppm are indicative of four-coordinate tin thiolates, while upfield chemical shifts ranging from $\delta_{119\text{Sn}}$ of ca. -125 to -515 ppm are indicative of six-coordinate tin compounds.³⁶ In CDCl₃, compound 1 gives a single peak in the ¹¹⁹Sn NMR with a $\delta_{119\text{Sn}}$ of 281 ppm, consistent with a four-coordinate tin thiolate and in good agreement with literature values.³¹ In pure EDT, the δ_{1195n} shifted slightly upfield to 269 ppm and was significantly broadened, implying dynamic exchange between the ethanedithiolate ligands and EDT on the NMR time scale. Addition of deprotonated EDT^{2-} to 1 in D_2O resulted in the binding of an additional ethanedithiolate ligand to 1 rather than exchange with the existing ligands, as evidenced by the large upfield shift to -352 ppm, a region characteristic of six-coordinate tin compounds.^{37,38} Similarly, when en was used as a solvent it appeared to coordinate to 1, yielding an apparent six-coordinate compound having a $\delta_{119\text{Sn}}$ at -263 ppm. The negative ion ESI-MS spectrum of 1 in the presence of en reveals that 1 is readily chelated by en, as evidenced by the main ion cluster observed at m/z = 362.9 that corresponds to a formula of [Sn- $(EDT)_2(en)$ ⁻ (see Supporting Information, Figure S2). Finally, when 1 was dissolved in the binary EDT-en solvent system, the resulting δ_{119Sn} of -346 ppm was significantly broadened and located in a chemical shift range also consistent with a six-coordinate tin compound.

These results collectively suggest that the molecular solute of Sn, SnO, and SnS dissolved in EDT-en was not 1, since the Sn(IV) compound appears to be easily chelated by EDT^{2-} or en in the solvent system to form six-coordinate compounds. In contrast, the dissolved Sn, SnO, and SnS all give a molecular solute that remains four coordinate in the EDT-en solvent system. Four-coordinate Sn(IV) compounds have the propensity to go six coordinate in the presence of donor solvents, whereas the analogous four-coordinate Sn(II) compounds do not.³⁹ On the basis of the apparent coordination number of four in EDT-en by ¹¹⁹Sn NMR for the molecular solutes of the dissolved Sn, SnO, and SnS, it appears that the dissolved species are in the Sn²⁺ oxidation state. The influence of tin oxidation state (Sn²⁺ vs Sn⁴⁺) on δ_{119Sn} is rarely reported in the literature; thus, further control experiments were performed to help identify the dissolved tin species. As a simple test, Sn²⁺ and Sn^{4+} in the form of $SnCl_2 \cdot 2H_2O$ and $SnCl_4 \cdot 5H_2O$, respectively, were dissolved in EDT-en and characterized using ¹¹⁹Sn NMR (see Supporting Information, Figure S3). Dissolution of SnCl₄. $5H_2O$ yielded a single resonance at $\delta_{119Sn} = -347$ ppm, consistent with our previous experiment showing 1 forms a sixcoordinate compound when dissolved in EDT-en. Dissolution of SnCl₂·2H₂O in EDT-en, on the other hand, gives a single resonance by ¹¹⁹Sn NMR that is nearly identical to that of the dissolved Sn, SnO, or SnS at δ_{119Sn} = 210 ppm. It is likely that this species represents the same compound as that formed from the dissolution of Sn, SnO, and SnS, as a 1:1 wt/wt mixture of SnCl₂·2H₂O and SnO dissolved in EDT-en yields a single resonance at δ_{119Sn} = 216 ppm. This further supports the hypothesis that the dissolved Sn, SnO, and SnS species are in the 2+ oxidation state and remain four coordinate in the EDTen solvent system, with en acting as a noncoordinating solvent and possible countercation (in the form of enH^+/enH_2^{2+}).

To further validate this hypothesis, a DFT calculation was carried out to model the gas-phase ¹¹⁹Sn NMR chemical shift of bis(1,2-ethanedithiolate)tin(II). The calculation was performed using Gaussian 09 at the B3PW91/TZP level of theory. Vibrational frequencies were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0). The δ_{119Sn} was calculated using direct implementation of the gauge including atomic orbitals (GIAO) method on the gasphase-optimized geometry of B3PW91/TZP (see Supporting Information, Figure S4), with the δ_{119Sn} being referenced to Me₄Sn (calculated absolute shift $\sigma_{Sn} = 2751$). The B3PW91 functional has been previously found to give reliable trends for tin compounds.⁴⁰ The calculated δ_{119Sn} of bis(1,2ethanedithiolate)tin(II) (with $\sigma_{sn} = 2443$) was found to be 308 ppm, which is within the experimentally determined ¹¹⁹Sn NMR window of four-coordinate tin thiolate compounds and lies within the range previously reported between experimental and gas-phase calculated δ_{119Sn} for a variety of Sn(II) compounds.⁴¹

Raman and UV–vis Spectroscopy. Raman spectra collected for Sn, SnO, and SnS dissolved in EDT–en support the conclusion that identical solutes exist in solution. Figure 3 gives the Raman spectra of Sn, SnO, and SnS dissolved in the EDT–en system. Vibrational modes observed after dissolution of Sn, SnO, and SnS are attributed to the molecular solute, assuming that the Raman bands from the EDT–en solvent mixture remain constant (see Supporting Information, Figure S5). The Raman spectra obtained after dissolution of Sn, SnO, in EDT–en are nearly identical to one another in peak position, with each possessing major bands at ~197, 264,



Figure 3. Solution Raman spectra of Sn, SnO, and SnS dissolved in EDT-en at 4.5 wt %.

and 322 (\pm 3) cm⁻¹. It should be further noted that there are no significant bands in these spectra associated with the ν (Sn–N) symmetric stretch at ~178 cm⁻¹, which is readily observed with coordination of amines to 1 (see Supporting Information, Figure S6).^{42,43} On this basis, it is unlikely that en in the solvent mixture is coordinating to tin, leaving the molecular solute solely ligated by two dithiolate ligands (vide supra).

UV-vis spectroscopy was used to probe the possibility of polysulfide formation from the sulfur as a result of SnS dissolution. The EDT-en solvent system has a strong absorption onset in the UV at ca. 320 nm with a smaller absorption band at λ_{max} = 365 nm. To test for polysulfide anion formation, solutions of dissolved SnO (having no sulfur) were compared against dissolved SnS. Solutions of dissolved SnO and SnS both show strong, red-shifted absorption onsets with no other distinguishable absorption features at lower energies (see Supporting Information, Figure S7). The dissolved SnO and SnS also both show a similar slight red shift in absorption onset with an increase in concentration and no other absorption bands at lower energies. While UV-vis spectroscopy has been show to have limitations for detecting individual polysulfide species in nonaqueous solvents due to concentration-dependent disproportionation equilibria, it has been established that higher order polysulfides anions have absorption maxima at wavelengths > 330 nm, while sulfides and disulfides (such as $S_2^{2^-}$ and S^{2^-}) absorb at shorter wavelengths < 280 nm.^{44,45} As a result of the lack of absorption features at lower energies, higher order polysulfide anions may be ruled out as the fate of the sulfur when dissolving SnS at these concentrations; however, smaller sulfides or disulfides (supported by enH⁺ or enH₂²⁺ cations) may be present with absorption features at wavelengths that are masked by the strong absorption onset of the solutes at 375-400 nm.

Conversion to SnS upon Annealing. Coupled thermogravimetric analysis/differential scanning calorimetry-mass spectrometry (TGA/DSC-MS) was used to study the decomposition of the dried inks. TGA traces for the dried inks of dissolved Sn, SnO, and SnS all display the same thermal decomposition characteristics from 100 to 500 °C, with a single-step mass loss event ranging from 42% to 46% occurring at ca. 300 °C (Figure 4a). The similarities in decomposition behavior are again consistent with all three inks containing identical molecular solutes upon the dissolution of Sn, SnO, and SnS in EDT–en. By DSC, the dried inks display exotherms at ~275 °C and endotherms at ~315 °C, associated with ~15% and ~30% mass losses during decomposition, respectively. The major volatile decomposition products observed in the mass spectra at ~275 and ~315 °C are consistent with EDT



Figure 4. (a) TGA/DSC traces comparing the decomposition of dried inks of Sn, SnO, and SnS dissolved in EDT–en. (b) FT-IR spectra of the dried ink corresponding to SnO dissolved in EDT–en before and after annealing to 350 °C. (c) Powder XRD patterns of orthorhombic *Pnma* SnS obtained after annealing the dried inks to 350 °C under flowing nitrogen. (d) Tauc plots derived from UV–vis–NIR spectra showing the indirect optical band gaps of the recovered SnS.

pyrolysis from 1, with the molecular ion peak at m/z = 120 corresponding to $[C_4H_8S_2]^+$ from EDT decomposition (see Supporting Information, Figure S8), with no further signals from en being observed. Therefore, it is reasonable to infer that the dry inks contain coordinated EDT similar to 1, with en being completely expelled during the drying stage of the sample preparation (~105 °C under vacuum, 24 h).

Conversion of the light-yellow inks to the corresponding black SnS material was achieved using a mild annealing step under flowing nitrogen. The minimum annealing temperature required for conversion to SnS was determined by TGA, which showed that thermal decomposition events were completed by 350 °C. FT-IR spectra of the annealed SnS lacked any features attributable to organic species, confirming that 350 °C is an appropriate annealing temperature for the recovery of organicfree material (Figure 4b). Powder X-ray diffraction (XRD) established that the material obtained after annealing the dried inks to 350 °C was crystalline and phase-pure orthorhombic (Pnma) SnS. Figure 4c gives the diffraction patterns of the materials resulting from the inks for dissolved Sn, SnO, and SnS. The diffraction patterns are all identical, possessing a 100% intensity peak ($2\theta = 31.9^{\circ}$) indexed to the (111) reflection of orthorhombic Pnma SnS structure (JCPDS no. 01-073-1859). No crystalline Sn, SnO_x, or other sulfide (SnS₂, Sn₂S₃, Sn₃S₄, etc.) impurities were observed by XRD for any of the samples, further indicating their phase purity. Elemental analysis of five randomly selected large areas of powdered samples by scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDX) gave an average composition of 53 atom % Sn to 47 atom % S for SnS recovered from the ink with dissolved Sn, 57 atom % Sn to 43 atom % S for SnS recovered from the ink with dissolved SnO, and 56 atom % Sn to 44 atom % S for SnS recovered from the ink with dissolved SnS. These atomic percentages closely match those obtained for SnS recovered from EDT-en in previous studies²⁰ and also for a commercial SnS standard. Moreover, the optical properties of SnS obtained

after annealing the dried inks to 350 °C were investigated by diffuse reflectance UV–vis–NIR spectroscopy using an integrating sphere (see Supporting Information, Figure S9). Figure 4d shows the indirect optical band gap approximations obtained from Tauc plots of the UV–vis–NIR diffuse reflectance spectra. The SnS material derived from all three inks possess the same approximate indirect band gap transitions ($E_{e,ind} = 1.1 \text{ eV}$), which agree well with literature values.^{20,29}

CONCLUSION

We investigated the nature of the solutes produced after dissolution of three different bulk materials (i.e., Sn, SnO, and SnS) in the binary EDT-en solvent system. Our findings reveal that upon dissolution of these three bulk materials a single and identical molecular solute is produced, as evidenced by ¹¹⁹Sn NMR, Raman spectroscopy, and TGA/DSC. These data suggest that the likely identity of the molecular solute is bis(1,2-ethanedithiolate)tin(II). While this compound has not been previously reported as an isolated compound in the literature, it is likely forming from the dissolution of these tincontaining species in EDT-en. In all cases, mild annealing of the resulting semiconductor inks yields crystalline and phasepure orthorhombic SnS with an indirect optical band gap of 1.1 eV. Therefore, since all of the bulk materials converge to an identical molecular solute in the alkahest solution, which upon annealing the semiconductor inks give phase-pure material, the most inexpensive sources of tin (such as elemental Sn) can be readily used for the facile deposition of SnS.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00243.

NMR spectra of 1; ESI-MS of 1 in en; ¹¹⁹Sn NMR spectra of $SnCl_2$ and $SnCl_4$ dissolved in EDT–en; gasphase-optimized geometry of bis(1,2-ethanedithiolate)tin(II) by DFT; Raman spectra of the EDT–en solvent mixture and of 1 dissolved in EDT–en; UV–vis spectra of dissolved SnO and SnS; mass spectra of the volatiles produced by TGA/DSC upon decomposition of the semiconductor inks; diffuse reflectance UV–vis-NIR spectra of the recovered SnS (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under DMR-1506189. J.J.B. acknowledges the National Science Foundation for a Graduate Research Fellowship. J.D.P.-A. thanks ISU AGEP for a Postdoctoral Fellowship. Acknowledgement is also made to Dr. J. Greaves for performing ESI-MS measurements and providing assistance and access to the Mass Spectrometry facilities at UC Irvine.

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