Insights into the synthesis of a semiconducting nickel bis(dithiolene) coordination polymer

Chokchai Kaiyasuan,[a] *Govindasamy Sathiyan,*[a] *David J. Harding,*[b] *Daniel Crespy,*[a,] * *and*
Pichaya Pattanasattayavong[a,] *

[a] Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand

[b] School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

* Corresponding authors: daniel.crespy@vistec.ac.th, pichaya.p@vistec.ac.th

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ABSTRACT

Nickel bis(dithiolene) complexes are promising candidates for developing coordination polymer n-type semiconductors with a 1D ladder-type structure which are air-stable and highly conductive. A key issue related to these materials is that their synthesis often yields undesired products that greatly limit the degree of polymerization and purity, which then have detrimental effects on their electronic properties. Furthermore, there is still a lack of in-depth identification of these species and understanding of the reaction mechanism. This study explores the mechanism of a reaction forming the coordination polymer nickel-thieno[3,2-b]thiophenetetrathiolate (**Ni-TT**). We find that the **Unoxidized Ni-TT** intermediate contains negatively charged polymer chains with Ni^{2+} counter cations. Oxidation in the final synthetic step occurs primarily at the ligand, resulting in a more neutral **Ni-TT**. Our study also reveals that the ligand can form dimeric and trimeric species via disulfide bonds as byproducts. These insights provide pivotal knowledge to improve and optimize the synthesis of nickel bis(dithiolene)-based coordination polymers to achieve purity and quality required for electronic applications.

1. INTRODUCTION

Nickel bis(dithiolene)-based 1D ladder-type coordination polymers (CPs) have recently emerged as promising candidates for highly conductive n-type semiconductors. They are highly stable in atmospheric, aqueous, and acidic/basic conditions compared to conventional organic n-type semiconductors.[1,2] Coordination between the bis(dithiolene) ligand and the nickel(II) metal center results in a square planar geometry, which facilitates efficient long-range electron delocalization along the polymer backbone through π-d hybridization between the ligand and the metal center.[3–6] These unique properties have prompted significant research interest, leading to several studies exploring novel designs of bis(dithiolene)-based ligands and their electronic and electrical properties.[7–9] Early studies since 1977 reported transition metal complexes based on tetrathionaphthalene, tetrathiafulvalene tetrathiolate, and ethylene tetrathiolate as ligands, which showed relatively low conductivity.[10–12] In 1985, complexes with high electrical conductivities of up to 20 S cm^{-1} were achieved by Reynolds et al., using transition metals (Pd^{II}, Ni^{II}, Cu^{II}) with tetrathio-oxalate ligands.[13] Recently, highly conductive nickel thieno[3,2-b]thiophene (**Ni-TT**) CPs have been designed and prepared, exhibiting remarkably high n-type conductivity exceeding 200 S cm^{-1}, while being stable under atmospheric conditions.[1] Thienothiophene or TT unit is an important building block for organic semiconductors, enabling high-performance transistor devices.[14–16] However, despite several decades of research, applications of metal bis(dithiolene) CPs are mostly limited to thermoelectric generators.[8,9,17–22] The broader electronic and optoelectronic applications require processable materials with high purity to allow the deposition of high quality thin films suitable for device fabrication.

One of the critical issues lies in the complexity of their chemical states and structures, including the valence states of the metal centers and ligands, the bonding characteristics of the ligand, and the presence of radicals and counter ions.[23] Moreover, it has been found that the synthesized CPs often contain undesirable species, such as oxidized and unknown species, which may contribute to poor synthetic reproducibility.[8,9,24] These factors inevitably impact their electronic and electrical properties, yet their features have not been clearly elucidated. The complexities primarily arise from the redox-active nature of the thiolate-based ligands, which can exhibit multiple oxidation states due to *in-situ* oxidation/reduction reactions.[25] As such, determining the precise chemical structures and their oxidation state remains challenging.

The synthesis of nickel bis(dithiolene) CPs involves the deprotection of the ligands to generate thiolate-active species using an alkali methoxide, which subsequently enables metal-ligand coordination. Previous studies on nickel ethenetetrathiolate (Ni-ETT) have shown that, following this stage, Ni-ETT requires further oxidation with chemical oxidants such as iodine. It was observed that the unoxidized product could not be obtained due to spontaneous oxidation when exposed to air during the filtration process.[9] In contrast, Liu et al. reported that Ni-ETT and other synthesized CPs were obtained without chemical oxidation. The CPs exhibited a negatively charged polymer chain in the presence of radical species.[8] Several chemical structures for these complexes were proposed, reflecting their complexity and the need for further clarification. For **Ni-TT**, a novel CP with highly promising properties as mentioned above, a detailed investigation into the chemical structure and the oxidation state has not been reported. This lack of understanding hinders the progress of improving the quality of materials and developing new CP semiconductors.

Herein, we elucidate the chemical structures of the intermediate and final products for the synthesis of **Ni-TT** by investigating the chemical environments and oxidation states of the nickel and sulfur species. We find that ligand species in both forms are in mixed valence states, with Ni^{2+} ions primarily serving as counter cations of the intermediate. Additionally, byproducts commonly observed during the synthesis of nickel bis(dithiolene) complexes were structurally identified as disulfide-based compounds. These findings contribute to a deeper understanding of the reaction mechanisms involved in the synthesis of nickel bis(dithiolene) complexes.

2. EXPERIMENTAL SECTION

2.1. Materials

All solvents used for the synthesis were of anhydrous grade, and all reactions were conducted under a nitrogen atmosphere. 2,3,5,6-Tetrabromothieno[3,2-b]thiophene (Br-TT, >98.0%, GC) and 3-bromopropanenitrile (>97.0%, GO) were purchased from TCI Chemicals. Tributyltin chloride (96.0%), tris(dibenzylideneacetone) dipalladium(0)-chloroform adduct [$Pd_2(dba)_3CHCl_3$], triphenylphosphine (PPh_3, 99.0%), thiourea (99.0%), sodium methoxide (NaOMe, 95.0%), nickel(II) acetate tetrahydrate ($NiOAc_2\cdot4H_2O$, ≥99.0%), 2-aminoethanol (≥99.0%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

2.2. Characterization techniques

^{1}H and ^{13}C NMR spectroscopy were conducted using a Bruker AVANCE III HD-600 MHz spectrometer. High-resolution mass spectrometric (HRMS) measurements were carried out using Bruker Compact in APCI Q-TOF mode. Fourier-transform infrared (FT-IR) spectra were collected using a PerkinElmer Frontier FTIR spectrometer in attenuated total reflectance (ATR) mode. Raman spectra were collected on a Bruker SENTERRA dispersive Raman spectrometer equipped with a 532 nm Nd:YAG laser, operating at an output power of 5 mW. Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 ADVANCE diffractometer with Cu K_α (λ = 1.5418 Å) operated at 40 kV and 40 mA. Data were collected over 2θ range of 5 to 50 deg with a step size of 0.01 deg and scanning rate of 0.8 deg min^{-1}. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) spectra were collected using a JEOL JSM-7610F electron microscope using a 15 kV accelerating voltage. The atomic compositions (S:Ni ratios) were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) with an Agilent Technologies 700 Series instrument, employing Ar gas as the plasma source. Thermogravimetric analysis (TGA) was performed using Rigaku TG8120 at a heating rate of 10 °C min^{-1} under nitrogen flow. X-ray photoelectron spectroscopy (XPS) data were obtained using a JEOL JPS-9010MC with a Mg K_α source (12 kV, 25 mA) under an ultra-high vacuum pressure (10^{-7} Pa). All binding energy values were referenced to the C 1s peak at 284.70 eV.

2.3. Materials syntheses

3,3',3'',3'''-(Thieno[3,2-b]thiophene-2,3,5,6-tetrayltetrakis(sulfanediyl))tetrapropanenitrile (TT-L). The ligand TT-L was synthesized according to a reported procedure.[1] First, 3-((tributylstannyl)thio)propanenitrile (Sn-TPN) was obtained via a two-step synthesis as described in the Supporting Information. Next, Br-TT (200 mg, 0.44 mmol), Sn-TPN (828 mg, 2.20 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (91 mg, 0.09 mmol), and PPh_3 (92 mg, 0.35 mmol) were dissolved in dry toluene (5.0 mL) under nitrogen atmosphere using standard Schlenk techniques, which was then stirred at 140 °C for 24 h. The product precipitated after cooling to room temperature, and was collected by filtration, washed with toluene and hexane to obtain TT-L (79 mg) as a slightly yellowish solid with 37% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.228-3.189 (m, 8H), 2.741 (t, J = 6.9 Hz, 4H), 2.622 (t, J = 6.9 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.89, 139.41, 127.44, 117.51, 117.41, 33.20, 30.26, 19.17, 18.54. HRMS APCI-QTOF *m/z* $[M]^+$ calcd. for $C_{18}H_{16}N_4S_6$ 479.9699; found 480.9734 $[M+H]^+$.

Unoxidized Ni-TT. A mixture of TT-L (24 mg, 0.05 mmol) and $NiOAc_2 \cdot 4H_2O$ (12.4 mg, 0.05 mmol) in dry dimethylformamide (DMF, 1.5 mL) was stirred at 60 °C under a nitrogen atmosphere. A solution of NaOMe (27 mg, 0.5 mmol) in methanol (0.2 mL) was then added to the mixture. The reaction mixture was stirred for 24 h before cooling to ambient temperature. Subsequently, a solution of glacial acetic acid (AcOH, 200 μL) and methanol (1.0 mL) was added. After stirring for 10 min, deionized water was added, and the mixture was placed in a refrigerator at approximately 4 °C for 3 days to facilitate precipitation. The resulting precipitates were collected by filtration, washed with water, methanol, and ether, yielding **Unoxidized Ni-TT** as black solid (13 mg).

Ni-TT. Following the synthesis of **Unoxidized Ni-TT**, a solution of iodine (I_2, 12.7 mg) in methanol (1.0 mL) was added to the reaction mixture after cooling to ambient temperature. The mixture was further stirred at room temperature for 2 h under a nitrogen atmosphere. Then, deionized water was added, and the mixture was placed in a refrigerator for 3 days to facilitate precipitation. The resulting Ni-TT precipitate was collected by filtration and washed with water, methanol, and ether, yielding **Ni-TT** as black powder (12 mg).

Deprotected TT-L. TT-L (24 mg, 0.05 mmol) was dissolved in dry DMF (1.5 mL) by stirring at 60 °C under a nitrogen atmosphere. A solution of NaOMe (27 mg, 0.5 mmol) in methanol (0.2 mL) was then added to the mixture. The reaction mixture was stirred for 24 h before cooling to ambient temperature. Subsequently, a solution of glacial acetic acid (200 μL) in methanol (1.0 mL) was added. After stirring for 10 min, a liquid portion was partially isolated, which was then dried at 60 °C under a nitrogen atmosphere to obtain **Deprotected TT-L**. Another portion of the **Deprotected TT-L** was further treated with I_2 solution. The solid suspension was collected by filtration to obtain **Deprotected TT-L (+I_2)**.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization

The synthesis of **Ni-TT** has been recently reported in the literature.[1] To gain deeper insight into the synthesis mechanism, the overall synthetic procedure has been slightly optimized (**Figure 1**) in order to obtain the intermediate of the reaction. As described in **Section 2**, TT-L which is the thienothiophenetetrathiolate ligand fully protected by cyanoethyl was prepared via a Stille C-S cross-coupling reaction between commercially available Br-TT and a synthesized organotin compound Sn-TPN (described in the Supporting Information). The reaction was catalyzed by the Pd(0) catalyst complex in dry toluene at 140 °C under a nitrogen atmosphere, affording TT-L in 37% yield. **Ni-TT** was subsequently synthesized by reacting TT-L with $Ni(OAc)_2 \cdot 4H_2O$ in anhydrous DMF under a nitrogen atmosphere at 60 °C. Upon the addition of excess NaOMe, the reaction mixture turned brown and then black, implying the decyanoethylation of TT-L and the subsequent formation of Ni-S bonds in the coordination polymer. The instantaneous change in the color of the mixture indicates the reactive nature of the deprotected ligand. After completion of the reaction, the mixture was neutralized with acetic acid at ambient temperature. We noticed that the mixture appeared as a fine suspension, making it difficult to collect using standard methods such as filtration and centrifugation. To efficiently collect the product, the mixture was allowed to settle in a refrigerator for 3 days to obtain a precipitate of **Unoxidized Ni-TT**, which was then retrieved by filtration.

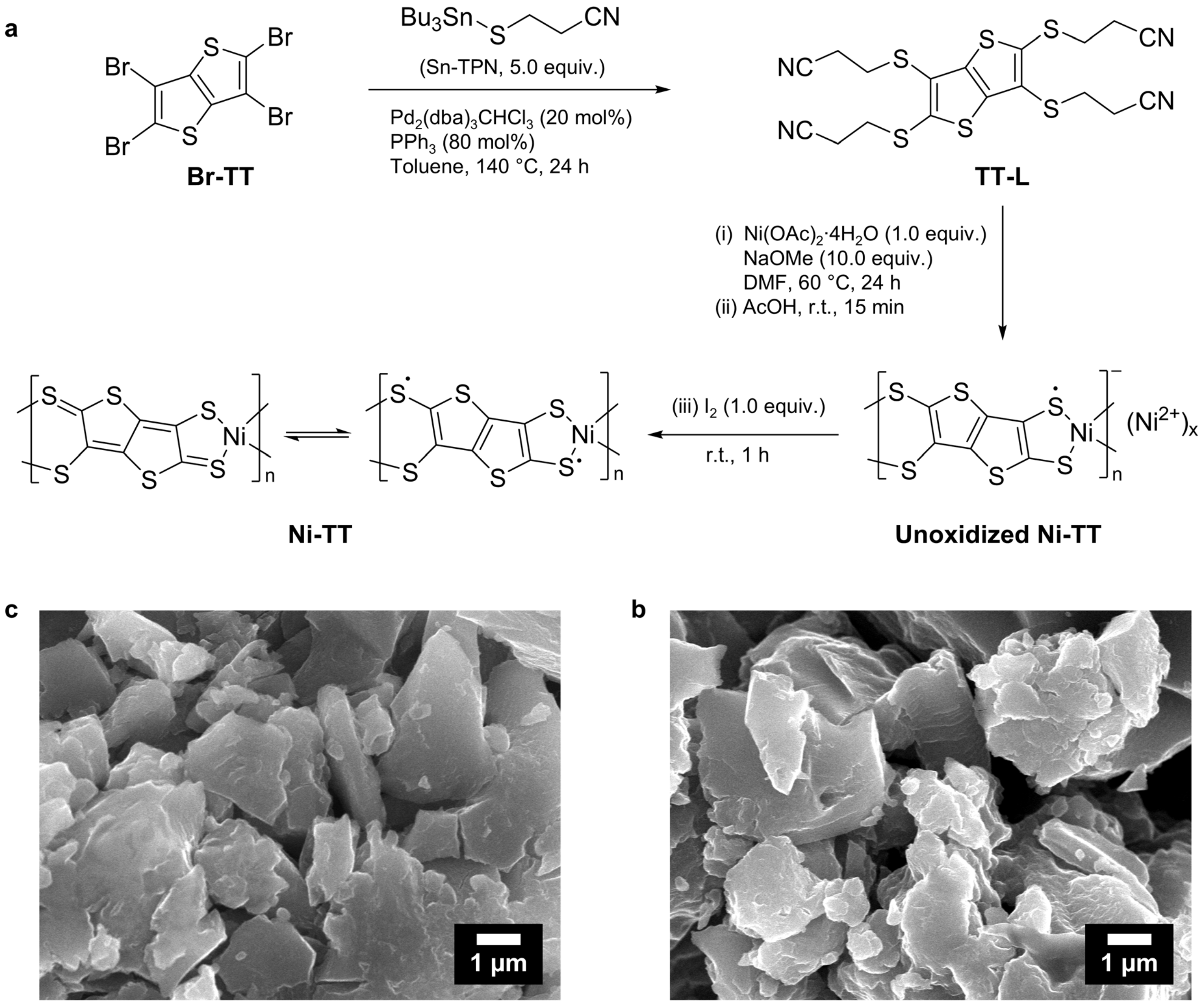

Figure 1. (a) Schematic synthesis and proposed chemical structures of **Unoxidized Ni-TT** and **Ni-TT**, along with their SEM images (b-c).

Furthermore, the efficiency of ligand deprotection was elucidated by investigating the reaction residue obtained after filtration. FT-IR showed no presence of the 2-cyanoethylene-protected ligand, indicating that the thiolate moieties were fully deprotected (**Figure S1**). In order to obtain the final **Ni-TT** product, **Unoxidized Ni-TT** intermediate was treated with I_2 at ambient temperature under a nitrogen atmosphere for 2 h. Both as-synthesized complexes appeared as black, plate-like solids. SEM images (**Figure S2**) of the synthesized complexes without grinding revealed a stacked, sheet-like structure, suggesting a planar morphology and consistent with previous reports.[1,2] After gentle grinding, we observed their internal structure, revealing a 2D flake morphology in both the unoxidized (**Figure 1b**) and oxidized forms (**Figure 1c**). The resulting morphological features could be related to their π-stacking nature, as evidenced by grazing-incidence wide-angle X-ray diffraction (GIWAXD) analysis in the literature.[1]

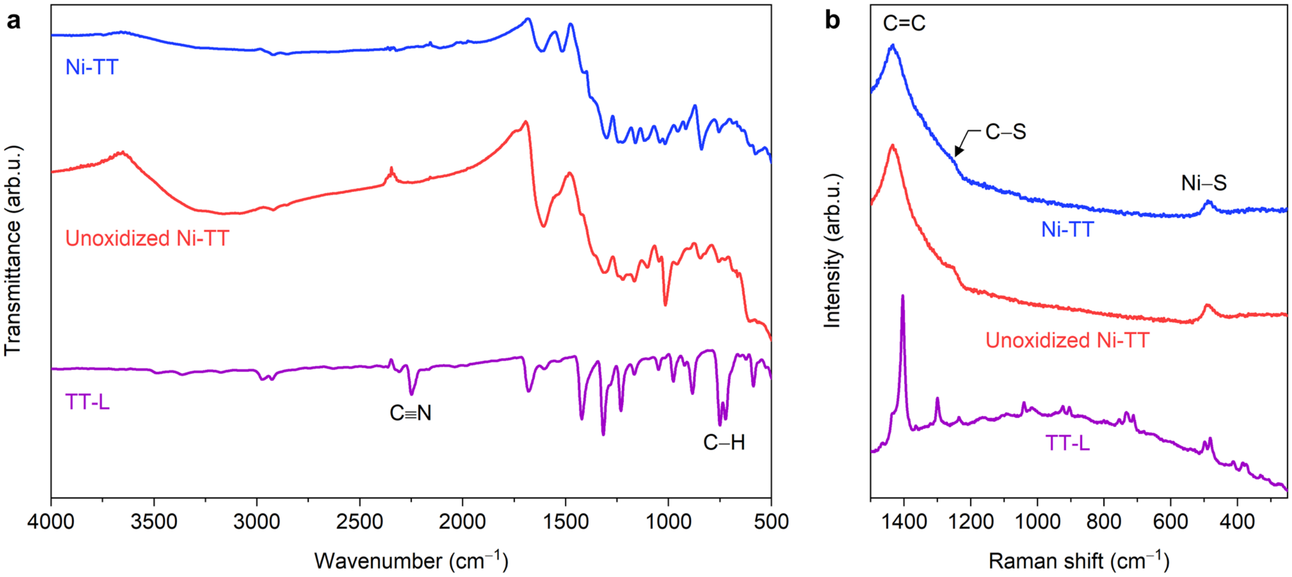

Figure 1. (a) FT-IR and (b) Raman spectra of **Unoxidized Ni-TT** and **Ni-TT**. Data of **TT-L** are also shown for reference.

The formation of synthesized CPs was confirmed by FT-IR and Raman spectroscopy. As shown in **Figure 2a**, the bands at 2250 and 733 cm^{-1}, while present in **TT-L**, disappeared in the spectra of **Unoxidized Ni-TT** and **Ni-TT**. The loss of these bands, which were associated with the

C≡N and C-H vibrational modes,[26] respectively, suggested the complete removal of the 2-cyanoethyl groups. The presence of Raman signals at 490, 1256, and 1435 cm^{-1}, which could be attributed to Ni-S, C-S, and C=C bonds, respectively, confirmed the coordination between the Ni metal and the thiolate-based ligand in both unoxidized and oxidized forms (**Figure 2b**), consistent with previous literature.[2] The unchanged Raman signals between both forms of the synthesized CPs implied that oxidation did not affect the bonding in the CPs. As shown in **Figure S3a**, PXRD patterns revealed broad features of both unoxidized and oxidized **Ni-TT**, indicating their low crystallinity nature. The domain sizes were calculated using the peak around 25° to be approximately 1 nm according to the Scherrer equation,[27] similar to previously reported size in nickel bis(dithiolene) polymers.[2] In addition, the thermal properties of the CPs were characterized by TGA under a nitrogen atmosphere (**Figure S3b**). The TGA profile revealed that both forms of the synthesized CPs were stable up to 200 °C with an initial mass loss below 200 °C attributed to the loss of moisture and trapped solvent, particularly DMF, used in the synthesis.

3.2. Proposed chemical structures and oxidation states

The proposed chemical structures of both synthesized **Ni-TT** were inspired by other previously reported nickel bis(dithiolene) complexes,[1,6,28] where nickel centers coordinate with 4 sulfur atoms (NiS_4) forming a square planar geometry. The alternating coordination between the bis(dithiolene) ligand with a square planar metal center results in a planar 1D ladder structure. Accordingly, Ni-TT with a large number of repeating units would exhibit a S:Ni ratio of approximately 6, assuming the polymer chain is neutral and terminated by thiol groups (-SH) (see **Figure S4**). Elemental analysis, including ICP-OES (**Table S1**) and EDS (**Figure S5** and **S6**), revealed the following average S:Ni ratios: for **Unoxidized Ni-TT**, 6.3 (ICP-OES) and 4.9 (EDS); and for **Ni-TT**, 9.8 (ICP-OES) and 7.2 (EDS). Notably, a significantly higher Ni content was observed in **Unoxidized**

Ni-TT compared to **Ni-TT**, while Na ions were detected in trace amounts in the unoxidized form (Ni:Na ratio of approximately 28 on average based on EDS). Interestingly, this suggested that Ni^{2+} ions themselves likely acted as counter cations to the negatively charged polymer chains of **Unoxidized Ni-TT**. The subsequent decrease in Ni content in the oxidized form implied a reduction in the negatively charged polymer chains due to oxidation. However, the amount of detected Na^+ ions was higher relative to Ni^{2+} in **Ni-TT** (Ni:Na ratio of approximately 7 on average based on EDS). This suggests that the oxidized form was almost neutral with some remaining negative charges balanced by Na^+ counter ions, similar to what was observed for the oxidized form in the literature.[1,9] Furthermore, it is noticeable that **Unoxidized Ni-TT** exhibited a significant vibronic feature at 1015 cm^{-1}, which diminished in **Ni-TT**, as shown in the FT-IR spectra (**Figure 3a**). This band can be attributed to a C-S radical species ($C\text{-}S^{\bullet}$) which has also been observed in metal bis(dithiolene) complexes with mono-radical character.[5,29] This evidence suggests that mono-radical species of the thiolate ligand could have a significant contribution to the chemical structure of **Unoxidized Ni-TT**. In contrast, the much weaker presence of this band in **Ni-TT** implied a small amount of $C\text{-}S^{\bullet}$ remaining.

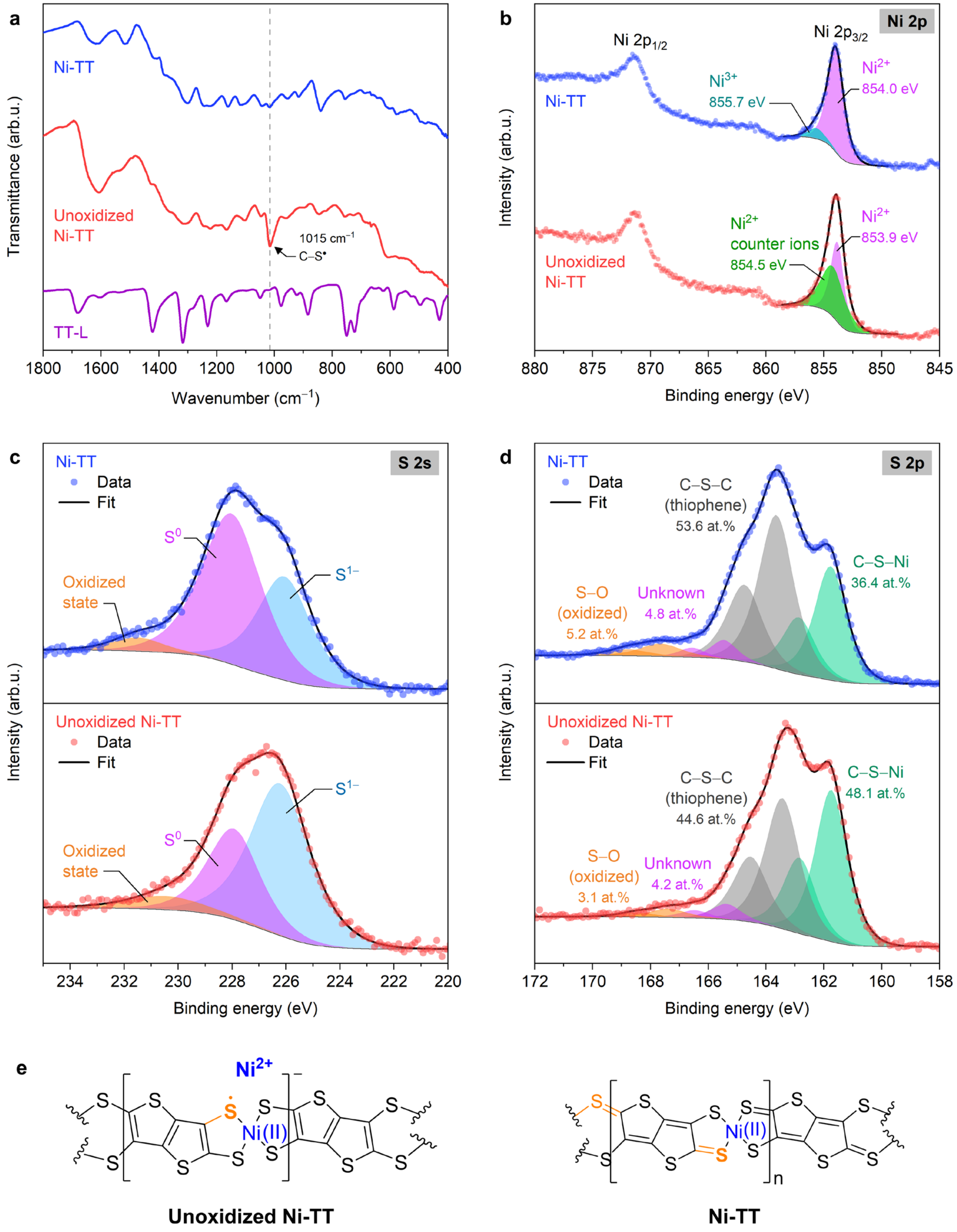

Figure 3. (a) Closed-up FTIR spectra showing the radical character. High-resolution XPS spectra of (b) Ni 2p, (c) S 2s, and (d) S 2p. (e) Proposed chemical structures of **Unoxidized Ni-TT** and **Ni-TT**.

To gain deeper insight into their chemical structures and oxidation states, the synthesized complexes were characterized by XPS. The survey scans indicated the presence of Ni, S, C, N, O, Na elements as expected (**Figure S7**). The C 1s (BE = 284.7 eV) was used as internal standard for charge correction. The Ni 2p XPS spectra of both unoxidized and oxidized **Ni-TT** exhibited distinctive peaks at binding energies around 854 eV and 871 eV (**Figure 3b**), corresponding to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ spin-orbit splitting, respectively. Additionally, the satellite peak around 860 eV displayed a very weak intensity, indicating that the Ni centers in both forms of the synthesized CPs were in a low-spin state with square planar geometry.[30] The deconvoluted Ni $2p_{3/2}$ XPS spectra revealed the presence of Ni^{2+} species at 853.9 and 854.0 eV for **Unoxidized Ni-TT** and **Ni-TT**, respectively.[31,32] This data emphasized that the oxidation state of the metal centers of both synthesized CPs was mainly Ni(II). Noticeably, a peak at 854.5 eV was observed in the spectrum of **Unoxidized Ni-TT** but not detected in **Ni-TT**. This signal was still associated with Ni^{2+},[33] which could be attributed to the presence of Ni^{2+} counter cations in the unoxidized form, corroborating our abovementioned discussion based on the elemental analysis. In the oxidized form, only a small amount of Ni^{3+} was observed at 855.7 eV,[31,32] and the large majority of the metal centers remained in the Ni^{2+} state. The XPS results implied that the addition of I_2 did not significantly affect the metal centers. Instead, the oxidation mostly occurred at the ligands, as shown next.

The oxidation states of the thiolate ligand were also investigated with XPS. In both the unoxidized and oxidized forms, two primary S 2s species were identified at binding energies of 226.2 and 228.1 eV (**Figure 3c**). These peaks corresponded to sulfur in the reduced -1 (S^{1-}) and neutral (S^0) valence states, respectively, consistent with previous studies on π-conjugated nickel bis(dithiolene) complexes.[29,34] **Unoxidized Ni-TT** exhibited a higher proportion of the reduced state (S^0:S^{1-} ratio of 0.6) whereas **Ni-TT** featured a higher proportion of the neutral state (S^0:S^{1-}

ratio of 1.6). It is important to note that sulfur atoms at the thiophene position and in radical species display a neutral formal charge (0), while those at the thiolate position display a formal charge of -1 (**Figure S8**). The experimental S^0:S^{1-} ratios suggested that **Unoxidized Ni-TT** consisted of a mixture of TT^{4-} (S^0:S^{1-} = 0.5) and TT^{3-} (S^0:S^{1-} = 1.0) ligand states and that **Ni-TT** contained a mixture of TT^{3-} (S^0:S^{1-} = 1.0) and TT^{2-} (S^0:S^{1-} = 2.0) states (see also **Figure S8**). This evidence aligns well with the observed $C\text{-}S^{\bullet}$ species in the FT-IR spectra of both synthesized CPs. The moderate intensity of the $C\text{-}S^{\bullet}$ band in **Unoxidized Ni-TT** can be attributed to the presence of some TT^{3-}. Conversely, the $C\text{-}S^{\bullet}$ band almost disappeared in **Ni-TT**, due to a higher ratio of the TT^{2-} species. Although the tetrathiolate TT^{2-} species exhibits a diradical character, its more stable dithiolene-dithiolate resonance structure does not feature radicals (**Figure S8**), leading to the low intensity of the $C\text{-}S^{\bullet}$ band as observed. This is consistent with previously reported density functional theory (DFT) calculations, which suggested a low value for the open-shell singlet diradical character index for the TT ligand.[1]

Additionally, a broad peak with weak intensity at higher binding energy (~231 eV) was observed in the XPS spectra for both synthesized samples (**Figure 3c**). While previous studies attributed a similar S 2s peak[29,34] to a shake-up process associated with a strongly charge-delocalized nickel bis(dithiolene) complex, it is important to clarify that those reports based their discussion on reference XPS data of a different chemical state, S 2p.[35,36] In contrast, our analysis as shown below suggests that the peak at 231 eV in the S 2s XPS spectra could be more accurately attributed to oxidized thiolate species. This interpretation is strongly supported by relevant literature focusing on the oxidation of the sulfur chemical state.[37,38]

Our S 2p XPS spectra of both unoxidized and oxidized forms are shown in **Figure 3d**. The data could be deconvoluted into four sets of S $2p_{1/2}$ – S $2p_{3/2}$ spin-orbit splitting peaks (with a binding energy difference of 1.1 eV), indicating the presence of four distinct species. The dominant S $2p_{3/2}$ peak at 163.4 eV was assigned to C-S-C (thiophene),[39–41] which also corresponded to a similar peak observed in the TT-L ligand (**Figure S7b**). The chemical state at a lower binding energy of 161.7 eV was attributed to C-S-Ni, related to the presence of the metal-ligand coordination bond. Notably, the relative intensity of the S-Ni peak was lower in **Ni-TT** than in **Unoxidized Ni-TT**. We attributed the excess S-Ni signal in the latter to the additional bonds with the Ni^{2+} counter cations. This observation aligns with our previous discussion, where the decrease in the negatively charged C-S state (thiolate) was correlated with a reduced need for counter ions in the oxidized form. Based on our experimental evidence and discussion, we propose the structures of Unoxidized Ni-TT and Ni-TT as shown in **Figure 3e**.

Moreover, both synthesized CPs presented two extra species at high binding energies (**Figure 3d**), with the one at 167.4 eV (S $2p_{3/2}$) possibly assignable to oxidized sulfur species such as S-O, as described in the literature.[42] In a previous study, the additional peak observed at 165.3 eV (S $2p_{3/2}$, denoted as 'Unknown' in **Figure 3d**) was assigned to a C-S species, potentially at the thiophene position.[1] However, the observed binding energy is substantially higher than what has been reported for most thiophene species,[39,41] making the precise identification of this peak unclear. We show below that this chemical state was likely due to ligand self-coupling.

3.3. Identification of unknown sulfur species

To elucidate the chemical species of the unknown by-product, an additional reaction was performed as shown in **Figure 4a**. We hypothesized that the synthesis of CPs involved several possible reactions, including metal-ligand coordination, ligand self-coupling, and oxidation. To simplify the identification and analysis, a similar reaction was conducted but without adding the metal precursor. Under these conditions, TT-L was deprotected with the addition of a base. The resulting product, partially isolated as a liquid, was dried at 60 °C under a nitrogen atmosphere to yield **Deprotected TT-L**. A portion of the **Deprotected TT-L** was then treated with I_2 solution, similar to the synthesis of **Ni-TT**, resulting in a precipitate that was collected by filtration, designated as **Deprotected TT-L (+I_2)**. As shown in **Figure 4b**, the mass spectra of **Deprotected TT-L** revealed the presence of dimeric and trimeric species of the ligand as main components, with mass-to-charge ratios (*m/z*) of 554 and 862, respectively. We propose that these species were self-coupled ligands formed through disulfide bonds with structures shown in **Figure 4c**. Note that the masses of these proposed species are very close to those found from mass spectrometry. Trimeric species were not present in **Deprotected TT-L (+I_2)**, suggesting that the iodide ion formed during I_2 addition potentially reduced the disulfide bonds of the trimeric species.

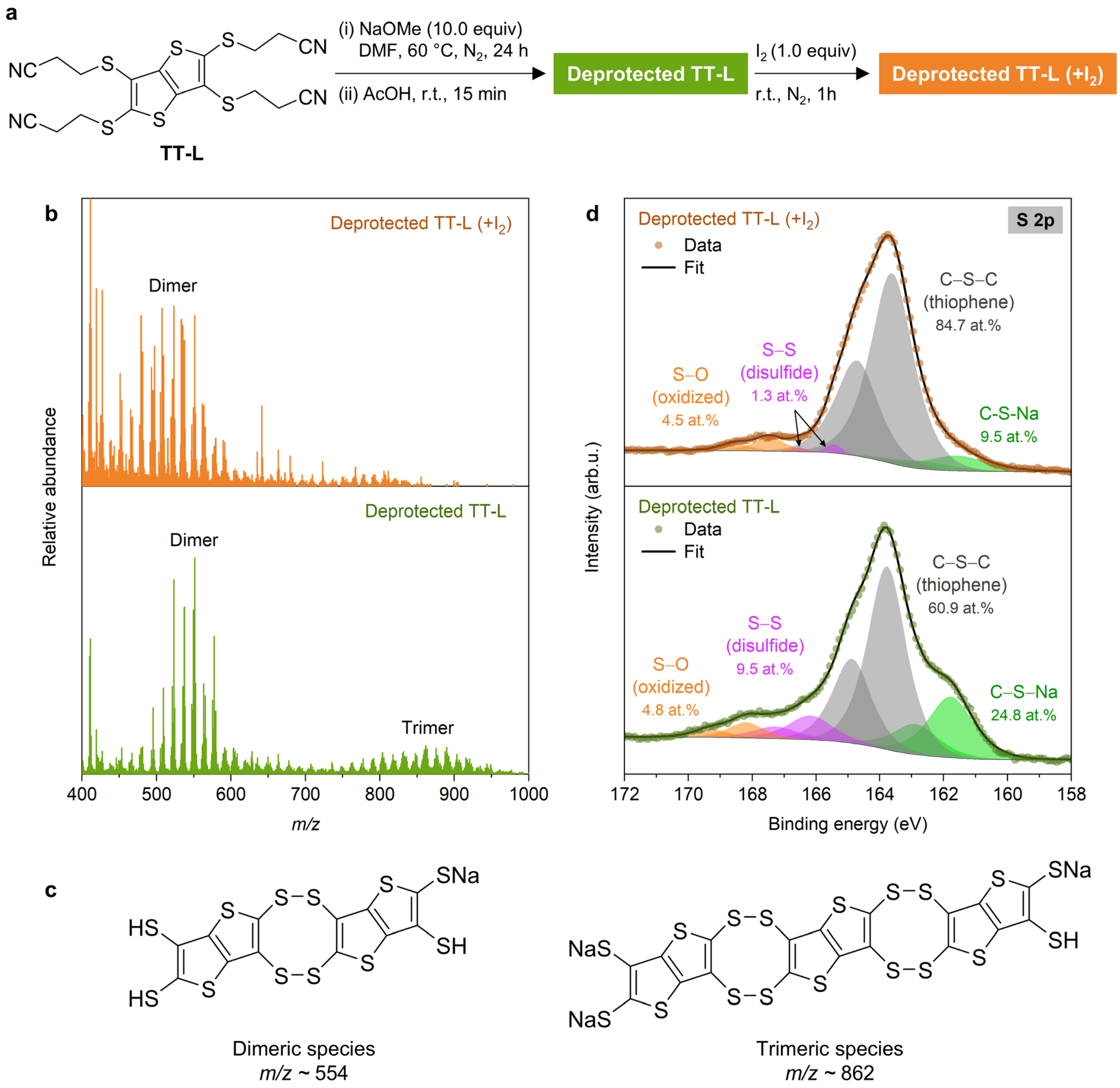

Figure 4. (a) Schematic synthesis of **Deprotected TT-L** with and without the addition of I_2. (b) Full scan APCI mass spectra. (c) Proposed chemical structures of the by-products. (d) High-resolution S 2p XPS spectra of the deprotected ligand samples.

In order to correlate these results with the synthesized complexes, the S 2p XPS spectra of the deprotected ligands were analyzed (see **Figure 4d**). The peak of the main chemical species at 163.7 eV (S $2p_{2/3}$) clearly corresponded to the C-S-C (thiophene) and was similar to that observed in the synthesized CPs. The presence of a peak at a lower binding energy at 161.8 eV (S $2p_{3/2}$) can be attributed to C-S-Na species, consistent with the observed species in the mass spectra. Importantly, the presence of a chemical species at binding energies around 165-166 eV, matching the species observed in the synthesized CPs, suggests that this peak could be attributed to disulfide bonds. This assignment is consistent with observations reported in the literature, where similar binding energies have been associated with disulfide linkages.[17,43,44] Notably, a decrease in the atomic percentage (at%) of this species was observed in **Deprotected TT-L (+I_2)**, which supports our earlier discussion that iodide ions may reduce disulfide bonds. We also attempted to quantify the amount of disulfide bonds present in the CPs. However, due to the polymers' insoluble nature, obtaining an accurate measurement of disulfide bonds proved challenging. Despite this, we estimated the atomic percentages based on the peak areas of the S 2p XPS spectra. The results indicate a low disulfide concentration, approximately 4-5 at%, in both synthesized CPs. This finding underscores that disulfide formation among the ligands is likely an impurity in the synthesis of nickel bis(dithiolene) complexes.

4. CONCLUSIONS

In summary, we have elucidated the chemical structures and oxidation states of both the intermediate (**Unoxidized Ni-TT**) and the final product (**Ni-TT**) from the reaction between thienothiophenetetrathiolate ligand and nickel. Combining elemental analysis with extensive XPS analysis, we reveal that **Unoxidized Ni-TT** was composed of ligand species in a mixed valence state between TT^{4-} and TT^{3-}, coordinating with Ni^{2+} ions and resulting in the presence of radical species. The negatively charged polymer chains were balanced by Ni^{2+} counter cations. Upon oxidation, the ligand was primarily oxidized, resulting in the **Ni-TT** final product containing TT^{3-} and TT^{2-} ligand species, with slightly remaining negative charges balanced by Na^{+} counter cations. Furthermore, the observed unknown sulfur species were structurally identified as dimeric and trimeric species formed through self-coupling of the ligand via disulfide bonds. These findings provide crucial insights into the reaction mechanisms involved in the synthesis of nickel bis(dithiolene) complexes, paving the way for further improvements and optimization in their synthesis.

ASSOCIATED CONTENT

Supporting Information

Synthetic method of organotin compound, supplementary table for S:Ni ratios from ICP-OES and EDS, additional FTIR spectra, SEM images, PXRD results, TGA results, schematic showing the variation of S:Ni ratio on the degree of polymerization, EDS spectra, wide scan XPS spectra, additional S 2p XPS spectrum, schematic showing chemical structures and oxidation states of the thienothiophenetetrathiolate ligand, ^{1}H NMR spectra, ^{13}C NMR spectra, and high-resolution mass spectrum.

AUTHOR INFORMATION

Corresponding Authors

Pichaya Pattanasattayavong – Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand; https://orcid.org/0000-0001-6374-1840; Email: pichaya.p@vistec.ac.th

Daniel Crespy – Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand; https://orcid.org/0000-0002-6023-703X; Email: daniel.crespy@vistec.ac.th

Authors

Chokchai Kaiyasuan – Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand; https://orcid.org/0000-0003-3038-3180

Govindasamy Sathiyan – Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand; https://orcid.org/0000-0002-7270-9268

David J. Harding – School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand; https://orcid.org/0000-0001-8866-2401

Present Address

Govindasamy Sathiyan – Department of Chemistry, PSG Institute of Advanced Studies, Coimbatore, Tamil Nadu 641004, India

Author Contributions

Chokchai Kaiyasuan: Methodology, Investigation, Formal analysis, Data curation, Visualization, and Writing – original draft. **Govindasamy Sathiyan:** Methodology and Investigation. **David J. Harding:** Conceptualization, Validation, Supervision, and Writing – review & editing. **Daniel Crespy:** Conceptualization, Validation, Supervision, Resources, and Writing – review & editing. **Pichaya Pattanasattayavong:** Conceptualization, Visualization, Validation, Supervision, Resources, Funding acquisition, Project administration, and Writing – review & editing. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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