

Synthesis and Characterization of New Additive, 4-(3-bromophenyl)thiosemicarbazide for High-Conductivity Polymer Electrolyte

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Thiosemicarbazides are valued for their biological activities and versatile applications, with nitrogen and sulfur donor atoms offering new potential in polymer electrolyte studies. The main goal of this research is to synthesize and characterize 4-(3-bromophenyl)thiosemicarbazide and investigate its conductivity. 4-(3-bromophenyl)thiosemicarbazide was prepared by reacting 3-bromophenyl isothiocyanate with hydrazine hydrate and was successfully synthesized in 89% yield. CHNS analysis confirmed its high purity with <1% deviation from theoretical values. FTIR (cm⁻¹): 3275, 3146 [$\nu(\text{N-H})$]; 1632 [$\delta(\text{NH}_2) + \nu(\text{C}=\text{C})_{\text{ar}}$]; 1571 [$\nu(\text{C}=\text{C})_{\text{ar}}$]; 1524 [$\delta(\text{N-H})$]; 1211 [$\nu(\text{C}=\text{S})$]; 1076 [$\nu(\text{C-N})$]; 763 [$\gamma(\text{C-H})_{\text{ar}}$]; 696 [$\nu(\text{C-Br})$]. ¹³C NMR displayed signals at 180 ppm (C=S) and 121–141 ppm (aromatic carbons), confirming the proposed structure. UV-Vis spectra showed absorption at 270 and 212 nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions, respectively. Thermogravimetric analysis revealed a multi-step decomposition, indicating its thermal stability. Single-crystal XRD revealed a monoclinic crystal system (space group P2₁/n) with unit cell parameters $a = 6.2948(4) \text{ \AA}$, $\alpha = 90^\circ$; $b = 28.1751(18) \text{ \AA}$, $\beta = 99.168(2)^\circ$; $c = 10.8098(7) \text{ \AA}$, $\gamma = 90^\circ$, revealing intermolecular N–H $\cdots$ S and N–H $\cdots$ Br hydrogen bonds, and C–H $\cdots$ π and N–H $\cdots$ π interactions. The UV-Vis Tauc plot gave a band gap of 5.36 eV, while DFT calculated 4.92 eV, indicating a wide-band-gap electronic structure. EIS measurements indicated an ionic conductivity of $8.87 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature for the sample containing 10 wt% additive. Upon incorporation of 5 wt% 2,6-pyridinedicarboxylic acid, the conductivity increased by 8.3-fold to $7.32 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, reaching a maximum of $8.60 \times 10^{-4} \text{ S cm}^{-1}$ at 50 °C, beyond which thermal degradation effects reduce conductivity. Temperature-dependent studies revealed non-Arrhenius behavior, with conductivity peaking at 50°C ($8.60 \times 10^{-4} \text{ S cm}^{-1}$) and declining at higher temperatures, consistent with a negative apparent activation energy ($E_a = -2.21 \text{ kJ/mol}$) arising from thermal degradation effects that dominate above 50°C. Thus, the material shows great potential as a conductive additive for polymer electrolyte-based energy storage applications, with tunable ionic transport properties within its operational temperature window (<50°C).

Keywords: Thiosemicarbazide, HOMO-LUMO, crystal structure, polymer electrolyte, conductivity

Received: February 2026; Accepted: August 2026

Thiosemicarbazide and its derivatives have attracted increasing attention due to their versatile coordination chemistry and wide range of applications in catalysis, medicine, and materials science [1, 2]. Recent studies have combined spectroscopic, crystallographic, and computational methods to investigate their structural arrangements and conductivity properties.

These studies highlight how ligand geometry and the coordination environment around metal centers strongly influence electrical conductivity [3-5]. Thiosemicarbazide additives are particularly interesting because of their semiconducting nature and biological activity, with conductivity values often affected by temperature and by substituents on

the ligand framework [6, 7]. Despite this progress, the precise relationship between molecular structure and electrical conductivity in thiosemicarbazide derivatives remains unclear.

While it is well established that coordination through nitrogen and sulfur atoms plays a central role, the detailed charge-transfer pathways and the influence of intermolecular interactions such as hydrogen bonding and π - π stacking are still debated [8-10]. Conflicting studies exist regarding tautomerism and isomerization. Some evidence supports correlated barrier hopping as the main mechanism, whereas other research favors band gap modulation [3, 6]. This uncertainty hinders the rational design of thiosemicarbazide-based materials with predictable electrical conductivity [11, 12]. Ultimately, the interplay between molecular geometry, donor atom identity (N or S), and supramolecular organization dictates the electron or hole transfer pathways that determine macroscopic conductivity [13].

Building on this background, recent attention has turned to the incorporation of thiosemicarbazide derivatives into polymer electrolytes. Polymer-based electrolytes, particularly those using sustainable hosts such as carboxymethyl cellulose (CMC), have risen to prominence as a potential solution to the inherent drawbacks of conventional liquid electrolytes. This shift is driven by the need for safer, more stable, and environmentally friendly energy storage systems [14, 15]. Biopolymers like CMC offer biodegradability, flexibility, and film-forming ability, but their ionic conductivity is limited. Incorporating organosulfur additives such as thiosemicarbazides has been shown to improve ion transport, interfacial stability, and overall electrochemical performance [16, 17]. However, the exact chemical interactions and conduction pathways that arise when thiosemicarbazides are added to CMC-based matrices are not yet fully understood [18, 19].

In this research, we synthesize and characterize a new additive, 4-(3-bromophenyl)thiosemicarbazide, and investigate its role in enhancing the ionic conductivity of CMC-based polymer electrolytes. The thiosemicarbazide framework contains multiple nitrogen and sulfur donor atoms, including the thioamide (C=S) and amine (N-H) groups, which can coordinate with ions and facilitate charge transport within the polymer host. To further improve conductivity, 2,6-pyridinedicarboxylic acid was incorporated as a co-dopant into the optimized electrolyte system, where its carboxylic acid groups act as proton-donor sites and its pyridine nitrogen facilitates proton hopping through hydrogen-bonded networks *via* the Grotthuss mechanism. The 3-bromo substitution was selected to introduce a heavy atom

effect that may influence charge transport properties [20, 21] while maintaining synthetic accessibility [22, 23] and providing a handle for structural modification. By integrating this additive system into CMC-based polymer electrolytes, we aim to bridge the gap between high ionic mobility and structural stability, ensuring enhanced performance in electrochemical applications. A deeper understanding of these structure-property relationships is expected to advance the rational design of high-conductivity, sustainable electrolytes for next-generation energy storage devices.

EXPERIMENTAL

Chemicals and Materials

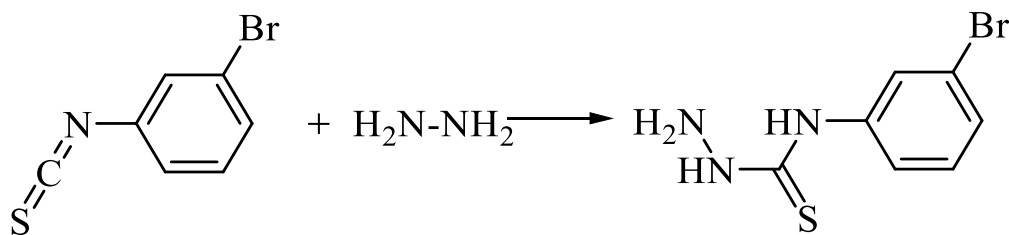
All chemicals and solvents were purchased from Sigma-Aldrich and used without further purification.

Instrumentation

A Flash Smart Elemental Analyzer was used to quantify the elemental content of C, H, N, and S. Vibrational spectra were recorded on a Perkin-Elmer FT-IR 100 instrument using the KBr pellet technique, spanning 400–4000 cm^{-1} . Solution-state ^{13}C NMR spectra (100 MHz) were acquired in DMSO- d_6 on a Bruker 400 MHz spectrometer. Optical absorption measurements were performed on a Shimadzu UV-1800 instrument using acetonitrile as solvent (concentration: 1×10^{-4} M) across 200–800 nm. Thermogravimetric profiles were generated on a Mettler-Toledo analyzer under flowing nitrogen, ramping from 25 to 500 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$. EIS-based conductivity measurements spanned 50 Hz to 1 MHz and were carried out with a HIOKI 3532-50 LCR Hi-Tester. Diffraction data for crystal structure determination were acquired on a Bruker SMART APEX II Duo system with Mo-K α radiation ($\lambda = 0.71073$ Å).

Synthesis of Additive

The additive was synthesized with slight modifications to previous studies. Dichloromethane (20 mL) was added to a round bottom flask followed by 3-bromophenyl isothiocyanate (2 mmol). Then, 80% hydrazine hydrate (2 mmol) was added slowly. The mixture was stirred for 5 hours in an ice salt bath to maintain consistent low temperature. The resulting white precipitate was filtered, dried and weighed. It was then recrystallized with ethanol by dissolving, filtering, reducing in solvent and drying in vacuum to increase its purity before further analysis. The chemical equation for the reaction is shown in Scheme 1.



Scheme 1. Synthesis of 4-(3-bromophenyl)thiosemicarbazide.

X-ray Crystallography

Block-shaped colorless crystals of dimensions $1.134 \times 0.561 \times 0.266 \text{ mm}^3$ were grown from ethanol through ambient-temperature slow evaporation. A Bruker SMART APEX II Duo CCD system with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used for data acquisition at room temperature. Integration of reflection intensities and empirical absorption correction were handled by SAINT and SADABS, respectively [24]. Structure solution proceeded *via* direct methods, with subsequent least-squares refinement against F^2 carried out in SHELXTL [25]. All atoms except hydrogen were modeled with anisotropic thermal parameters. PLATON was used for geometry checking, and SHELXP produced the molecular illustrations [24]. Final crystallographic figures of merit are summarized in Table 5.

Computational Methods

Molecular geometry optimization was executed at the DFT/B3LYP level with a 6-311G(d,p) basis set using Gaussian 16. Visual analysis and orbital mapping were performed *via* GaussView 6.0. The energies of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) were calculated from the optimized models and compared against experimental findings to validate the electronic transitions.

Polymer Electrolyte Film Preparation

Polymer electrolyte films were fabricated using the solution casting method. Carboxymethyl cellulose (CMC, 1 g) was dissolved in 20 mL of deionized water under continuous stirring. To optimize the additive concentration, 4-(3-bromophenyl)thiosemicarbazide was incorporated at loadings of 0, 5, 10, 15, 20, and 25 wt% alongside a fixed 8 wt% PEG (0.08 g) as plasticizer. For the optimized system, 5 wt% 2,6-pyridinedicarboxylic acid was further incorporated.

The mixture was stirred vigorously until a homogeneous dope was achieved, poured into a leveled Petri dish mold, and dried at 60°C to produce free-standing electrolyte films.

Electrochemical Impedance Spectroscopy (EIS)

The ionic conductivity of the polymer electrolyte films was assessed *via* Electrochemical Impedance Spectroscopy (EIS) at room temperature. The films were cut into $2 \times 2 \text{ cm}$ squares and placed in a spring-loaded stainless steel holder. For the temperature-dependent measurements, ionic conductivity was investigated over the range of $30\text{--}80^\circ\text{C}$. The conductivity values were derived from the bulk resistance (R_b) obtained from the high-frequency intercept of the Nyquist plots, utilizing the equation:

$$\sigma = t / (A \times R_b) \quad \text{Equation 1}$$

Here, t is the specimen thickness, A is the electrode-electrolyte contact area, and R_b is the bulk resistance derived from the intercept of the complex impedance (Cole-Cole) plot on the real axis (Z').

RESULTS AND DISCUSSION

Physical Properties

The synthesis of 4-(3-bromophenyl)thiosemicarbazide produced a white precipitate, confirming the successful formation of the desired additive. The reaction yielded 0.4512 g of product, with a theoretical yield of 0.5070 g, and the physical properties are summarized in Table 1. Elemental analysis (CHNS), as shown in the same table, showed that the experimental elemental composition matched the theoretical values for the molecular formula $\text{C}_7\text{H}_6\text{BrN}_3\text{S}$ with only minor deviations. This strong agreement confirms both the successful synthesis and the high purity of the additive.

Table 1. Physical properties of 4-(3-bromophenyl)thiosemicarbazide.

Melting point (°C)	Color	Yield (%)	Experimental (Theoretical) %			
			C	H	N	S
118	White	89%	34.28 (34.13)	3.30 (3.25)	17.08 (17.06)	13.13 (13.03)

Fourier-Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectrum of 4-(3-bromophenyl)thiosemicarbazide was recorded in the range 4000-500 cm^{-1} , as shown in Figure 1 and summarized in Table 2, to confirm the structure and identify the functional groups present, including the thiosemicarbazide moiety and bromophenyl substituent. The spectrum displays characteristic absorption peaks associated with various vibrational modes, such as bond stretching and bending [26, 27]. The N-H stretching vibrations are observed at 3275 and 3146 cm^{-1} , consistent with the typical range of 3450-3250 cm^{-1} for secondary and primary amines [28]. A strong absorption at 1632 cm^{-1} is attributed to NH_2 scissoring vibrations coupled with aromatic $\text{C}=\text{C}$ stretching, characteristic of hydrazine-containing compounds. The aromatic $\text{C}=\text{C}$ stretching vibrations are observed at 1571 cm^{-1} and contribute to the 1632 cm^{-1} band,

confirming the presence of the bromophenyl ring. The N-H in-plane bending vibration appears at 1524 cm^{-1} , close to the reported value of 1529 cm^{-1} [28]. The most diagnostic peak for thiosemicarbazides is the $\text{C}=\text{S}$ stretching vibration at 1211 cm^{-1} , which falls within the characteristic range of 1000-1250 cm^{-1} for thiocarbonyl groups [27]. This band, known as the thioamide IV band, confirms the presence of the $\text{C}=\text{S}$ functional group. The C-N stretching vibration is observed at 1076 cm^{-1} . The aromatic C-H out-of-plane bending vibration of the meta-disubstituted ring appears at 763 cm^{-1} , while the C-Br stretching vibration at 696 cm^{-1} confirms the presence of the bromophenyl substituent, consistent with typical C-Br absorptions in the 690-515 cm^{-1} region. These spectroscopic data fully support the proposed structure of 4-(3-bromophenyl)thiosemicarbazide.

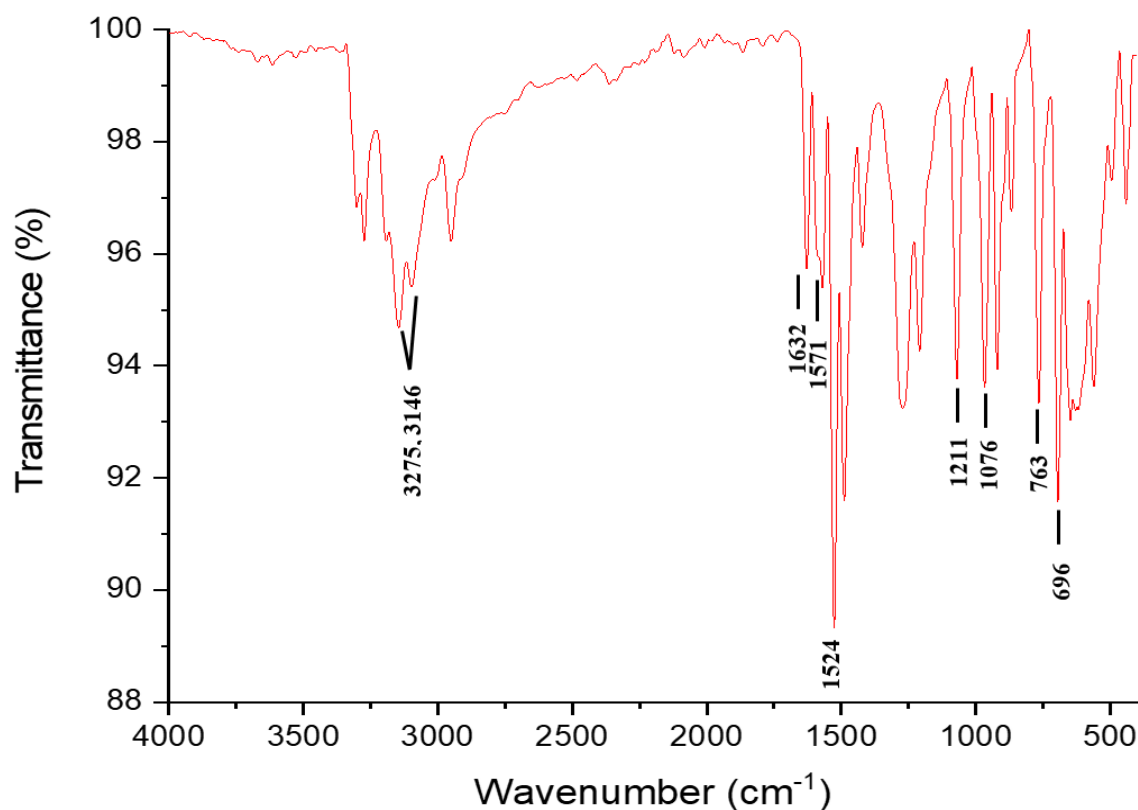


Figure 1. FT-IR spectrum of 4-(3-bromophenyl)thiosemicarbazide.

Table 2. Functional groups and vibrational assignments of 4-(3-bromophenyl)thiosemicarbazide.

No.	Wavenumber (cm^{-1})	Assignment	Intensity
1.	3275, 3146	$\nu(\text{N-H})$	<i>m</i>
2.	1632	$\delta(\text{NH}_2) + \nu(\text{C}=\text{C})_{\text{ar}}$	<i>s</i>
3.	1571	$\nu(\text{C}=\text{C})_{\text{ar}}$	<i>m</i>
4.	1524	$\delta(\text{N-H}) + \nu(\text{C}=\text{C})_{\text{ar}}$	<i>m</i>
5.	1211	$\nu(\text{C}=\text{S})$	<i>s</i>
6.	1076	$\nu(\text{C-N})$	<i>m</i>
7.	763	$\gamma(\text{C-H})_{\text{ar}}$	<i>m</i>
8.	696	$\nu(\text{C-Br})$	<i>s</i>

ν = stretching, δ = bending, ar = aromatic, γ = out-of-plane bending

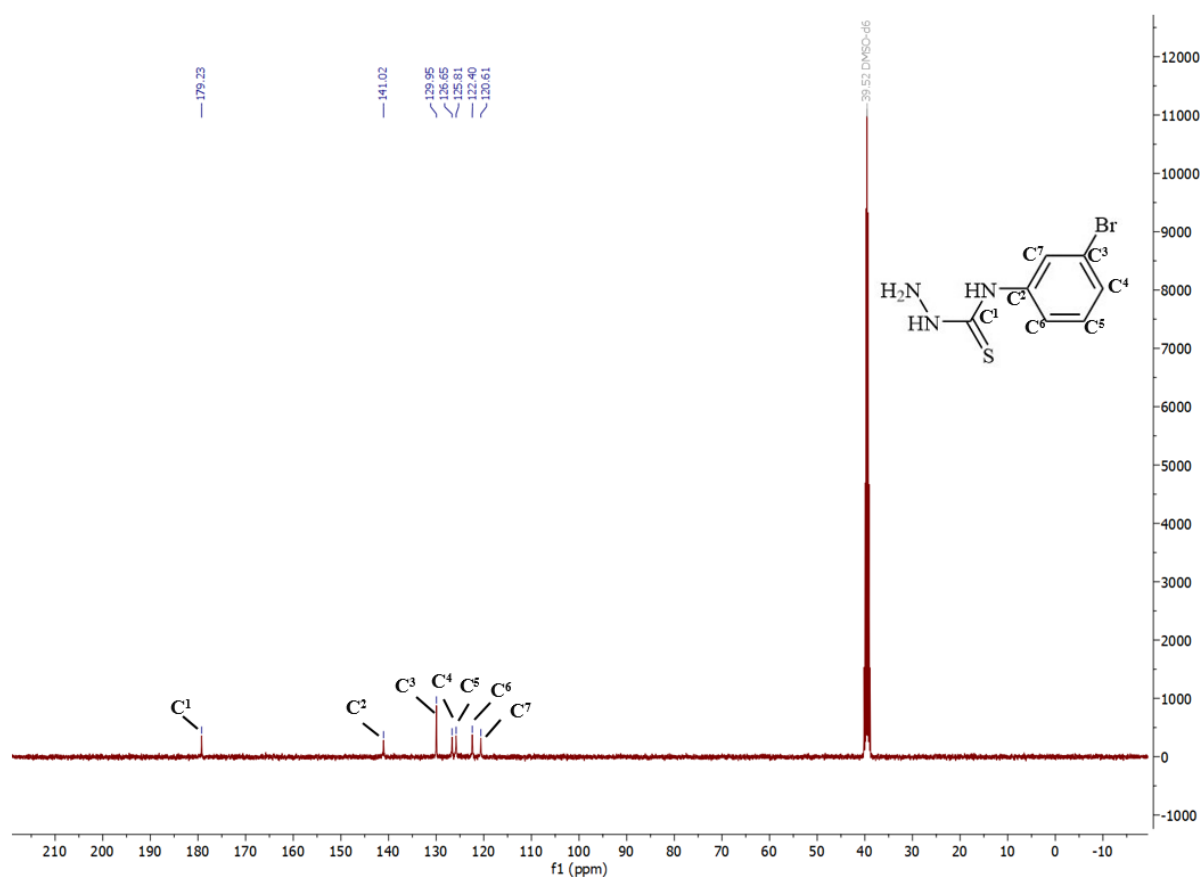


Figure 2. ^{13}C NMR spectrum of 4-(3-bromophenyl)thiosemicarbazide.

Table 3. ^{13}C NMR spectral data of 4-(3-bromophenyl)thiosemicarbazide in $\text{DMSO}-d_6$.

No.	Chemical shift, δ_c (ppm)	Assignment
1	179.23	$\text{C}=\text{S}$ (C^1)
2	141.02	$\text{C}-\text{N}$ (Ar, C^2)
3	129.95	$\text{C}-\text{Br}$ (Ar, C^3)
4	126.65	$\text{C}=\text{C}$ (Ar, C^4)
5	125.81	$\text{C}=\text{C}$ (Ar, C^5)
6	122.40	$\text{C}=\text{C}$ (Ar, C^6)
7	120.61	$\text{C}=\text{C}$ (Ar, C^7)

Ar = aromatic carbon

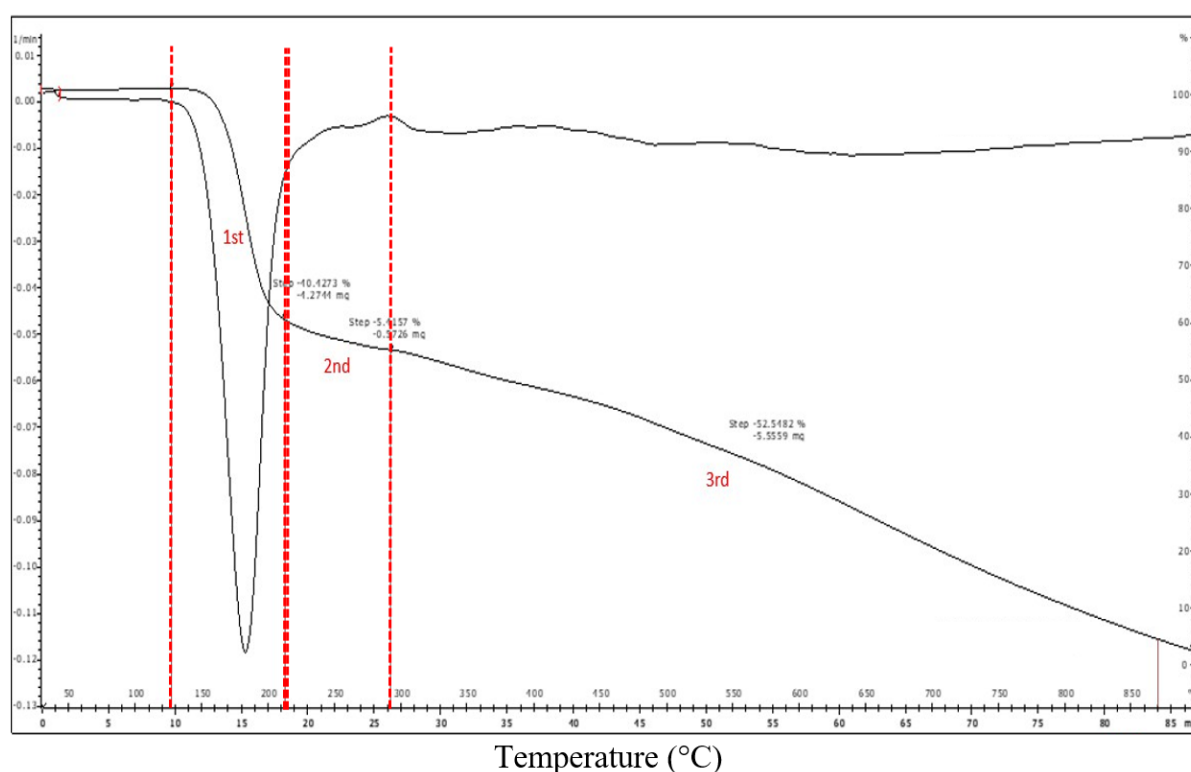


Figure 3. Thermogravimetric analysis (TGA) curve of 4-(3-bromophenyl)thiosemicarbazide.

^{13}C Nuclear Magnetic Resonance (NMR)

The ^{13}C NMR spectrum of 4-(3-bromophenyl)thiosemicarbazide was recorded in $\text{DMSO}-d_6$ at 100 MHz as shown in Figure 2 and Table 3. Seven distinct carbon signals were observed, consistent with the proposed structure. The most deshielded signal at $\delta_c = 179.23$ ppm is assigned to the thiocarbonyl carbon ($\text{C}=\text{S}$, C^1), characteristic of thiosemicarbazide derivatives [29]. The aromatic signals at $\delta_c = 141.02$ ppm and 129.95 ppm correspond to the quaternary carbons bearing nitrogen (C^2) and bromine (C^3) substituents, respectively. The remaining aromatic carbons (C^4 – C^7) resonate between $\delta_c = 126.65$ –

120.61 ppm, with chemical shifts influenced by the electronic effects of the bromine and thiosemicarbazide substituents. The well-resolved signals confirm the successful synthesis and structural integrity of the additive.

Thermogravimetric Analysis (TGA)

The thermal stability of 4-(3-bromophenyl)thiosemicarbazide was characterized by thermogravimetric analysis (TGA), where Figure 3 shows the TGA and DTG curves. Table 4 lists the decomposition temperatures and weight loss. The analysis revealed a multi-step decomposition profile

consisting of two distinct stages and one broad continuous degradation zone. The first major decomposition stage occurs between 130 and 210°C with a mass loss of 10.4%, attributed to loss of the hydrazine moiety and fragmentation of the bromophenyl substituent. A second, minor decomposition step is observed between 210 and 290°C with a 5.4% mass loss, corresponding to further decomposition of the thiosemicarbazide backbone. Beyond 290°C, a broad and continuous mass loss of 52.5% extends to 500°C, associated with complete degradation of the remaining organic framework and formation of carbonaceous residues. This gradual profile is characteristic of aromatic

framework breakdown rather than a discrete decomposition event. A final residue of 9.2% remains above 500°C. The compound exhibits thermal stability up to approximately 130°C, well above the <50°C operational window established by the conductivity studies, indicating additive decomposition is not a limiting factor within this range. Similar thermal degradation patterns have been documented for thiosemicarbazides [30] and substituted thiosemicarbazides such as 1-(4'-nitrobenzoyl)-3-thiosemicarbazide [31], which exhibit well-defined stability regions and successive degradation events.

Table 4. Thermal decomposition stages of 4-(3-bromophenyl)thiosemicarbazide from TGA analysis.

Stage	T _{onset} (°C)	T _{endset} (°C)	Mass loss (%)	Assignment
1st	130	210	10.4	Hydrazine moiety loss and fragmentation occurred.
2nd	210	290	5.4	Thiosemicarbazide backbone decomposition took place.
3rd	290	500	52.5	Complete organic framework degradation was observed.
Residue	>500	-	9.2	Final residue remained.

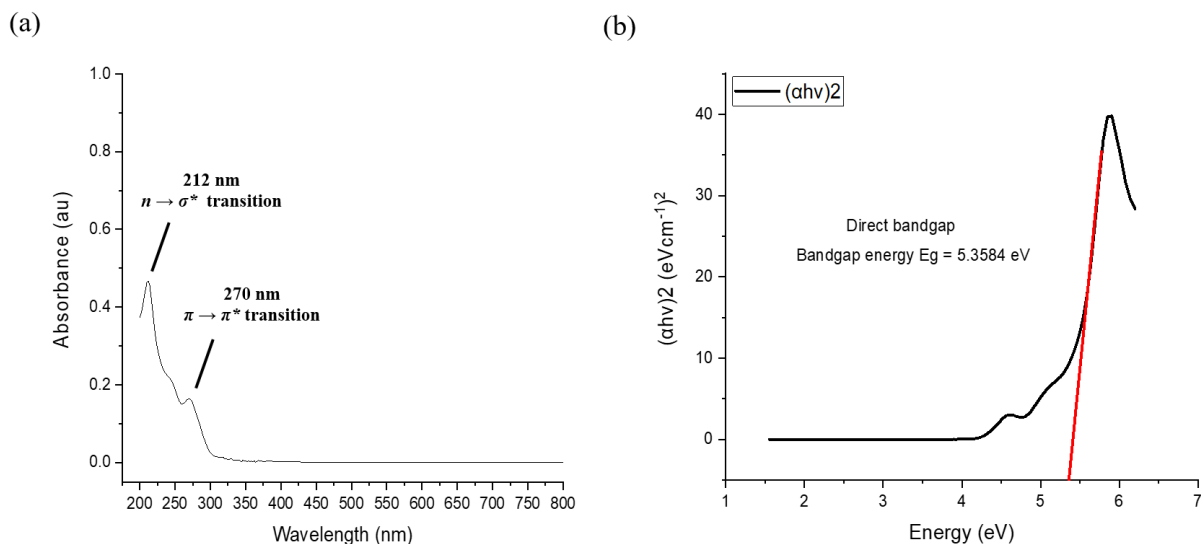


Figure 4. 4-(3-bromophenyl)thiosemicarbazide: (a) UV-Vis spectrum; (b) Tauc plot.

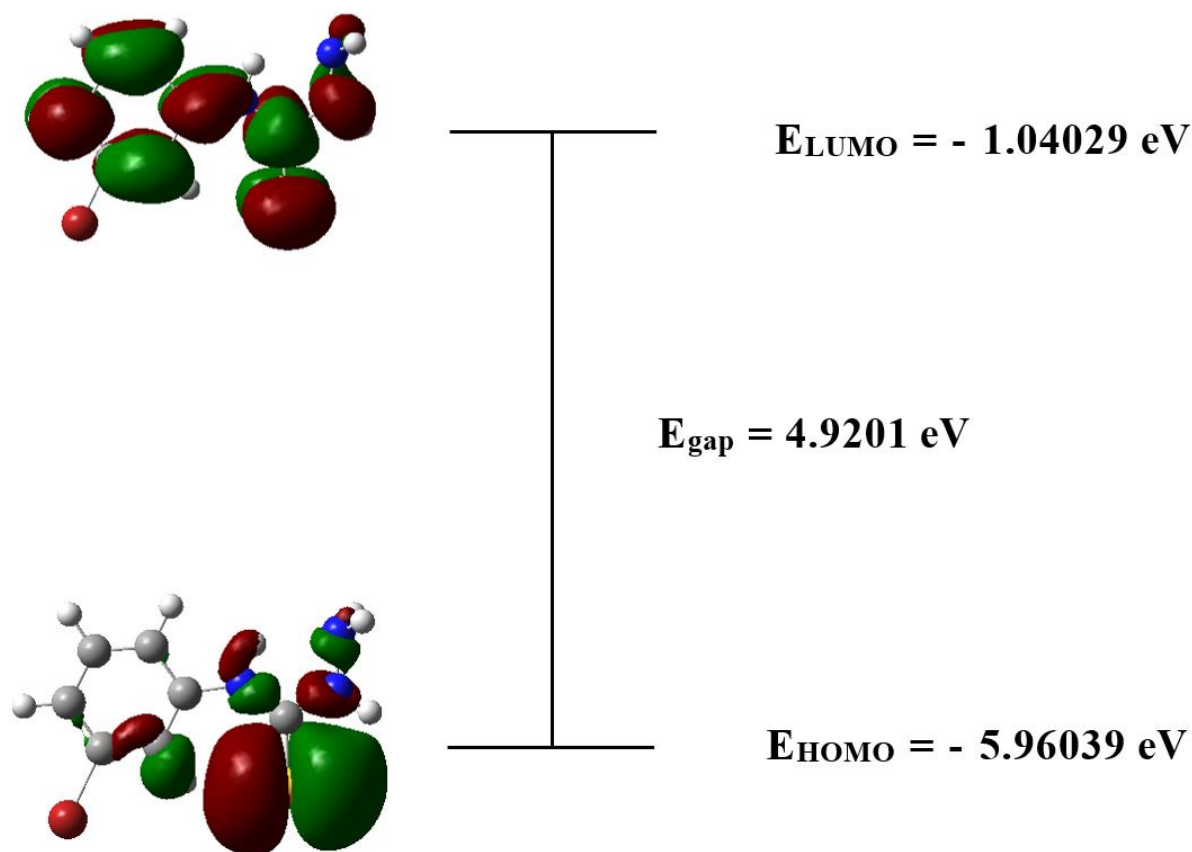


Figure 5. HOMO-LUMO energy diagram of 4-(3-bromophenyl)thiosemicarbazide calculated at B3LYP/6-311G(d,p) level.

Ultraviolet-Visible Spectroscopy (UV-Vis)

Absorption spectra of 4-(3-bromophenyl)thiosemicarbazide were measured across 200–800 nm and are presented in Figure 4a. Two distinct bands are observed: a more intense band at 270 nm assignable to $\pi \rightarrow \pi^*$ transitions delocalized over the conjugated bromophenyl ring, and a shorter-wavelength band at 212 nm arising from $n \rightarrow \sigma^*$ excitations of the nitrogen and sulfur lone pairs within the thiosemicarbazide fragment. Both features are in good agreement with previously reported spectra of halogen-substituted thiosemicarbazide derivatives [32]. The electron-withdrawing character of the bromine atom perturbs the aromatic electronic density, shifting the absorption maxima relative to unsubstituted analogues. The optical band gap was evaluated using the Tauc approach, whereby the absorption coefficient (α) was derived from the UV-Vis data and $(\alpha h\nu)^2$ was plotted against photon energy ($h\nu$) as shown in Figure 4b [33]. Linear extrapolation of the absorption edge to $(\alpha h\nu)^2 = 0$ yielded a direct band gap of 5.36 eV [34, 35], placing the compound firmly in the insulator regime and

suggesting utility in UV-absorbing and optoelectronic applications.

Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO)

Frontier molecular orbitals govern charge transfer behavior and electronic reactivity [36, 37]. Figure 5 presents the computed HOMO and LUMO surfaces alongside the energy gap (E_{gap}) for 4-(3-bromophenyl)thiosemicarbazide. Electron density in the HOMO is concentrated primarily on the thiosemicarbazide fragment, with negligible contribution from the bromine-substituted phenyl ring. Upon excitation, the LUMO distributes electron density more broadly across the entire molecule, reflecting greater delocalization and implying favorable intramolecular charge transfer. The computed E_{gap} of 4.92 eV aligns reasonably well with the experimentally derived optical band gap of 5.36 eV, with the 0.44 eV offset attributable to excitonic contributions absent from ground-state DFT calculations [37, 38].

Table 5. Crystal data and structure refinement parameters for 4-(3-bromophenyl)thiosemicarbazide.

CCDC num.	2480242
Empirical formula	C ₇ H ₈ BrN ₃ S
Formula weight	246.13
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 6.2948(4) Å α = 90°. b = 28.1751(18) Å β = 99.168(2)°. c = 10.8098(7) Å γ = 90°.
Volume	1892.7(2) Å ³
Z	8
Density (calculated)	1.728 Mg/m ³
Absorption coefficient	4.513 mm ⁻¹
F(000)	976
Crystal size	1.134 x 0.561 x 0.266 mm ³
Theta range for data collection	1.445 to 27.497°.
Index ranges	-8 ≤ h ≤ 8, -36 ≤ k ≤ 36, -14 ≤ l ≤ 14
Reflections collected	59863
Independent reflections	4336 [R(int) = 0.1583]
Completeness to theta = 25.242°	100.00%
Refinement method	Full-matrix least-squares on F ₂
Data / restraints / parameters	4336 / 0 / 249
Goodness-of-fit on F ₂	1.068
Final R indices [I > 2σ(I)]	R ₁ = 0.0627, wR ₂ = 0.1555
R indices (all data)	R ₁ = 0.1206, wR ₂ = 0.1827
Extinction coefficient	n/a
Largest diff. peak and hole	0.790 and -1.590 e.Å ⁻³

Contextualizing these values against related compounds, HnbphTSC and ChtcTSC exhibit considerably narrower gaps of 3.16 eV and 2.87 eV, respectively [39, 40], while the structurally analogous 3-bromophenylacetic acid shows a wider E_{gap} of 4.44 eV [41]. The comparatively broad gap of the present compound confirms that the thiosemicarbazide scaffold meaningfully modulates electronic structure. Although intrinsic electronic conductivity is therefore limited, the substantial conductivity gains observed in the CMC-based electrolyte films establish that charge transport in this system proceeds *via* ionic rather than electronic pathways.

Structure Description

X-ray crystallographic data collection for 4-(3-bromophenyl)thiosemicarbazide, including its atomic bond lengths and angles, are summarized in Table 5. An ORTEP representation of the two crystallographically independent molecules in the asymmetric unit is presented in Figure 6. The

relatively high R(int) value of 0.1583 is attributed to the large crystal size (1.134 × 0.561 × 0.266 mm³), which introduces significant absorption effects despite multi-scan correction using SADABS. The presence of the heavy bromine atom further contributes to absorption errors. Nevertheless, the final R₁ = 0.0627 for observed reflections and a goodness-of-fit of 1.068 confirm that the refined structure is reliable and the geometric parameters are well-determined. The overall structural reliability regarding bond lengths, angles, and intermolecular interactions remain valid.

The molecule crystallizes as colorless blocks with molecular formula C₇H₈BrN₃S (M = 246.13 g mol⁻¹) in the monoclinic space group P2₁/n. Both molecules adopt a *cis* conformation about the N2–C7 bond with respect to the N1–C7 and N2–N3 bonds, while maintaining a *trans* arrangement between the N3–N2 and C7–S1 bonds. The thiosemicarbazide framework (defined by S1A/C7A/N2A/N3A/N1A) and aromatic ring fragment (C1A–C6A) in the first molecule is essentially planar, with a maximum

deviation of 0.023(4) Å and 0.009(5) Å for atom N1A and C5A, respectively. The dihedral angle between these two mean planes is 52.6(2)°. In the second molecule, atoms S1B/C7B/N2B/N3B/N1B are coplanar, with a maximum deviation of 0.037(4) Å from their least-squares plane (at N1B). The attached phenyl ring (C1B–C6B) is planar within 0.009(6) Å (maximum deviation at C1B).

The C6A–N1A and C6B–N1B bond lengths of 1.416(6) and 1.431(6) Å, respectively, are marginally longer than the C–N bond length of 1.341(3) Å

reported for the biphenyl thiosemicarbazide analogue [42], confirming the absence of imine character at this position in the present structure. The C7A–N2A–N3A and C7B–N2B–N3B bond angles of 119.7(5)° and 120.5(4)°, respectively, are comparable to the value of 118.4(2)° observed in the biphenyl-substituted analogue [42]. Other geometric parameters fall within the expected ranges. These data indicate that substitution of the bromophenyl group at the meta position does not significantly influence the bond lengths and angles of the C–N–N hydrazone unit.

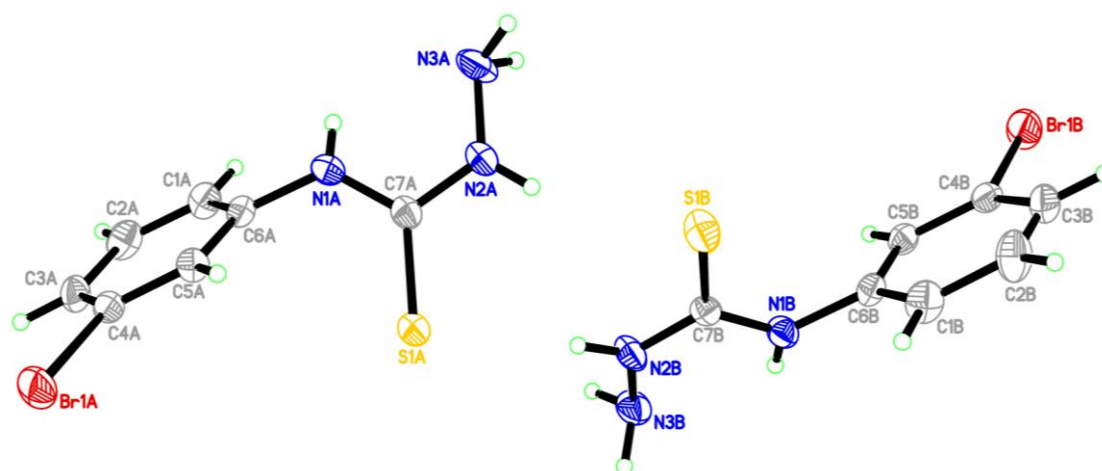


Figure 6. ORTEP structure of two crystallographically independent molecules in the asymmetric unit for 4-(3-bromophenyl)thiosemicarbazide, showing 50% probability ellipsoids.

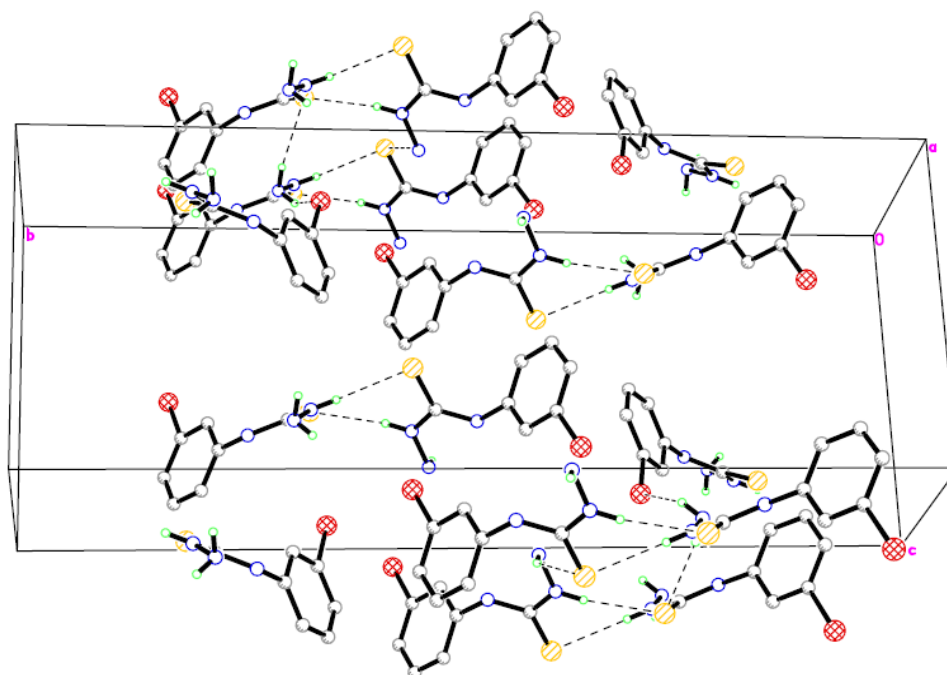


Figure 7. Crystal packing of structure 4-(3-bromophenyl)thiosemicarbazide, showing molecules connected by intermolecular hydrogen bonds (dashed lines).

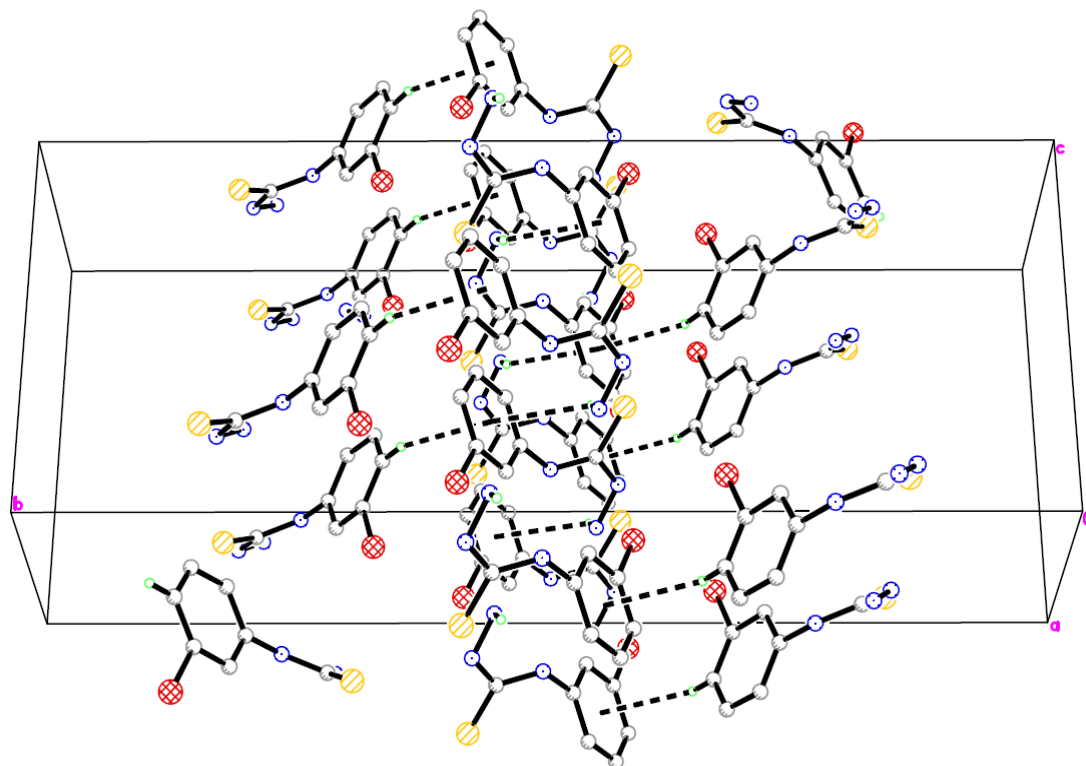


Figure 8. C-H $\cdots\pi$ and N-H $\cdots\pi$ interactions in 4-(3-bromophenyl)thiosemicarbazide.

In the crystal structure, adjacent molecules are linked *via* a complex network of intermolecular hydrogen bonds [N2A–H2A $\cdots$ S1B, N2B–H2B $\cdots$ S1A, N3A–H3A $\cdots$ Br1A, N3A–H4A $\cdots$ S1A, and N3B–H4B $\cdots$ S1B; symmetry codes in Table 6], generating a one-dimensional chain propagating parallel to the c-axis (Figure 7). The crystal packing is further stabilized by C–H $\cdots\pi$ and N–H $\cdots\pi$ intermolecular interactions propagating along the c-axis (Figure 8). Specifically, the C3A–H3AA donor group forms a C–H $\cdots\pi$ contact with the C1B–C6B phenyl ring [H $\cdots$ Cg = 2.75 Å, C–H $\cdots$ Cg = 151°, symmetry code: 3/2–x, –1/2+y, 1/2–z], while the N3B–H4B moiety establishes

an N–H $\cdots\pi$ interaction with the same aromatic ring [H $\cdots$ Cg = 2.88(6) Å, N–H $\cdots$ Cg = 121(5), symmetry code: 1+x, y, z]. These non-covalent interactions contribute to the three-dimensional supramolecular architecture and influence the solid-state packing arrangement. The geometric parameters for all hydrogen-bond interactions are summarized in Table 6, while selected bond lengths and angles are listed in Table 7. The observed intermolecular interactions provide valuable insight into the structure–property relationship of this compound and warrant further investigation of its solid-state behavior and potential functional properties.

Table 6. Hydrogen-bond geometry (Å, °).

D–H $\cdots$ A	D–H (Å)	H $\cdots$ A (Å)	D $\cdots$ A (Å)	D–H $\cdots$ A (°)	Symmetry code
N2A–H2A $\cdots$ S1B	0.84(5)	2.53(5)	3.344(5)	166(5)	x, y, z
N2B–H2B $\cdots$ S1A	0.87(4)	2.53(5)	3.344(5)	166(5)	x, y, z
N3A–H3A $\cdots$ Br1A	0.80(6)	2.93(7)	3.527(6)	133(6)	–3/2+x, 1/2–y, –1/2+z
N3A–H4A $\cdots$ S1A	0.94(7)	2.62(7)	3.540(6)	166(4)	–1+x, y, z
N3B–H4B $\cdots$ S1B	0.91(8)	2.672(7)	3.516(6)	146(5)	1+x, y, z
C3A–H3AA $\cdots$ Cg2	–	2.75	3.591(6)	151	3/2–x, –1/2+y, 1/2–z
N3B–H4B $\cdots$ Cg2	–	2.88(6)	3.438(5)	121(5)	1+x, y, z

Cg2: C1B–C6B

Table 7. Selected bond lengths [Å] and angles [°] for 4-(3-bromophenyl)thiosemicarbazide.

Bond	Bond length, Å	Bond	Bond angle, °
Br1A - C4A	1.894(5)	C6A - N1A - C7A	127.0(4)
S1A - C7A	1.691(5)	N3A - N2A - C7A	119.7(5)
N1A - C6A	1.416(6)	Br1A - C4A - C3A	120.5(4)
N1A - C7A	1.339(6)	S1A - C7A - N1A	124.4(4)
N2A - N3A	1.413(6)	N1A - C7A - N2A	115.8(5)
N2A - C7A	1.324(6)	C6B - N1B - C7B	125.3(5)
Br1B - C4B	1.892(5)	N3B - N2B - C7B	120.5(4)
S1B - C7B	1.690(5)	Br1B - C4B - C3B	119.0(4)
N1B - C6B	1.431(6)	S1B - C7B - N1B	123.4(4)
N1B - C7B	1.338(6)	N1B - C7B - N2B	116.5(4)
N2B - N3B	1.414(6)		
N2B - C7B	1.317(6)		

Table 8. Effect of additive loading on ionic conductivity of CMC + 8 wt% PEG polymer electrolytes.

No.	Additive Loading (wt% relative to CMC)	Ionic Conductivity (S cm ⁻¹)
1	0 (blank)	3.73×10^{-9}
2	5	8.09×10^{-5}
3	10	8.87×10^{-5}
4	15	8.44×10^{-5}
5	20	8.35×10^{-5}
6	25	8.11×10^{-5}

Conductivity Analysis

Ionic conductivity exhibited an additive loading-dependent behavior, as summarized in Table 8, with 4-(3-bromophenyl)thiosemicarbazide incorporated at loadings ranging from 5 to 25 wt% to determine the optimal additive concentration. Conductivity initially increased from 5 wt%, reaching a maximum of 8.87×10^{-5} S cm⁻¹ at 10 wt% loading. This enhancement is attributable to the increased segmental mobility of the polymer matrix, which facilitates ion transport through the creation of continuous ionic pathways and accessible sites for ionic hopping [43]. The multiple nitrogen and sulfur donor atoms in the thiosemicarbazide structure provide coordination sites for ions, creating additional conduction pathways within the polymer host and facilitating charge carrier mobility during electrochemical measurements. A decline in conductivity beyond 10 wt% loading is attributed to excess additive aggregation, which results in the formation of a thick film that impedes ion transport pathways [44, 45].

The Cole-Cole plots for the systems with and without 5 wt% 2,6-pyridinedicarboxylic acid are presented in Figures 9 and 10, respectively. As shown in Table 9, the incorporation of 5 wt% 2,6-pyridinedicarboxylic acid as a co-dopant into the optimized system (1 g CMC, 8 wt% PEG, and 10 wt% additive) resulted in a substantial conductivity

enhancement to 7.32×10^{-4} S cm⁻¹, representing an approximately 8.3-fold enhancement compared to the system without acid (Table 9). This enhancement reflects a marked improvement in charge transport approaching conductivity values characteristic of ion-conducting polymer electrolytes. Notably, the thiosemicarbazide additive alone already elevated conductivity from 3.73×10^{-9} S cm⁻¹ (blank) to 8.87×10^{-5} S cm⁻¹ (Table 8), confirming its primary role in ionic transport, while the dicarboxylic acid further amplifies this through the pre-established hydrogen-bonded network *via* its carboxylic groups as proton donors and pyridine nitrogen as a weakly basic site [46, 47].

Proton transport occurs primarily *via* the Grotthuss mechanism, which involves rapid hydrogen bond rearrangement and proton transfer along hydrogen-bonded chains, a process well-established in proton exchange membrane systems [48]. The formation of hydrogen-bonded complexes between the acid and the thiosemicarbazide additive creates additional proton transport pathways, resulting in enhanced ionic mobility and improved diffusion coefficients [49]. These synergistic effects demonstrate that the combination of polymer segmental mobility enhancement and acid-facilitated proton conduction establishes an efficient ionic transport network that substantially improves the overall conductivity of the polymer electrolyte system.

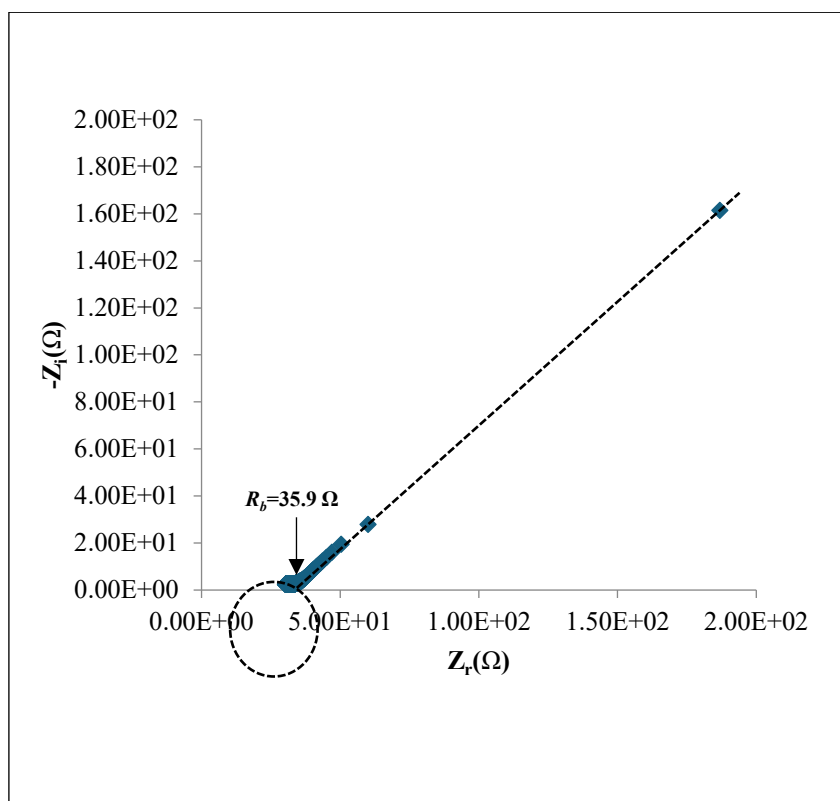


Figure 9. Cole-Cole plot for CMC + 8 wt% PEG + 10 wt% additive at room temperature.

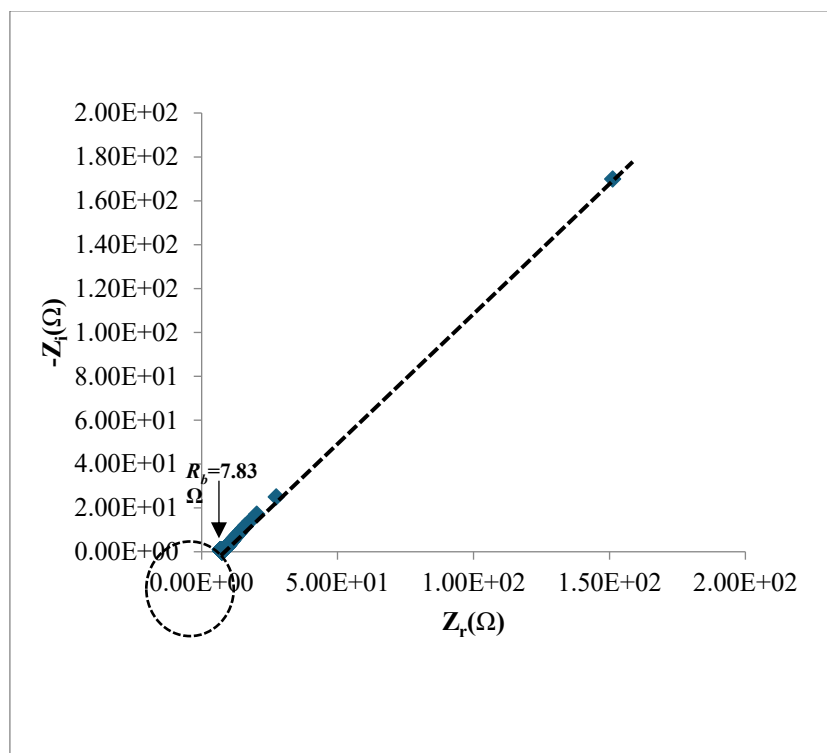


Figure 10. Cole-Cole plot for CMC + 8 wt% PEG + 10 wt% additive + 5 wt% 2,6-pyridinedicarboxylic acid at room temperature.

Table 9. Bulk resistance and ionic conductivity of polymer electrolyte films at room temperature.

Polymer Electrolyte Film	Thickness, t (cm)	Bulk Resistance, R_b (Ω)	Conductivity, σ (Scm^{-1})
CMC + PEG + 10% additive	0.010	35.9	8.87×10^{-5}
CMC + PEG + 10% additive + 5 wt% 2,6-pyridinedicarboxylic acid	0.018	7.83	7.32×10^{-4}

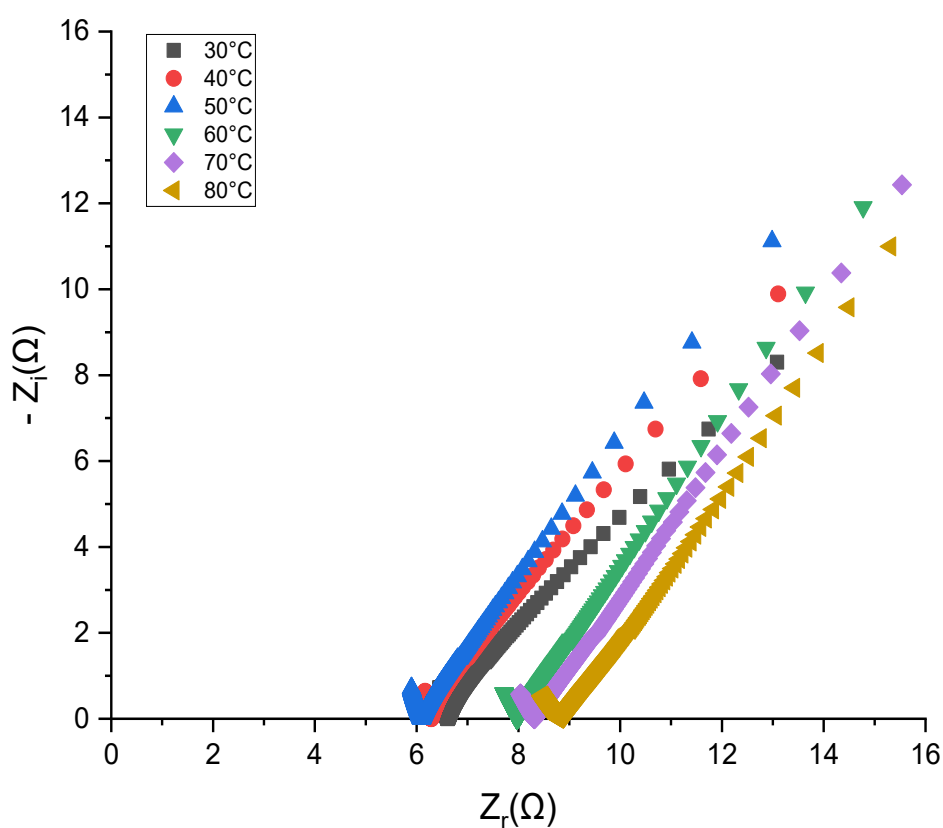


Figure 11. Cole-Cole plots (Nyquist plots) for CMC + 8 wt% PEG + 10 wt% additive + 5 wt% 2,6-pyridinedicarboxylic acid at temperatures ranging from 30–80°C.

Figure 11 presents the Cole-Cole plots at various temperatures, with the corresponding bulk resistance (R_b) and ionic conductivity (σ) values summarized in Table 10. The results reveal non-monotonic temperature dependence, with conductivity initially increasing from $7.95 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C to a maximum of $8.60 \times 10^{-4} \text{ S cm}^{-1}$ at 50°C, representing an 8% enhancement. This initial increase is attributed to enhanced segmental motion of the polymer chains and increased ion mobility within

the polymer matrix. Elevated temperatures provide sufficient thermal energy to promote polymer chain flexibility and reduce intermolecular interactions, thereby facilitating ion migration by lowering the energy barriers for ionic hopping between coordination sites [50]. Moderate temperature increases also facilitate ion dissociation and promote ion conduction through the amorphous regions of the polymer matrix, further contributing to the observed conductivity enhancement [51].

However, beyond 50°C, the conductivity progressively declined to $6.59 \times 10^{-4} \text{ S cm}^{-1}$ at 60°C, $6.33 \times 10^{-4} \text{ S cm}^{-1}$ at 70°C, and $5.96 \times 10^{-4} \text{ S cm}^{-1}$ at 80°C. This substantial decrease at elevated temperatures indicates that detrimental structural changes dominate over the beneficial effects of enhanced thermal mobility. Several mechanisms may account for the conductivity decline at elevated temperatures. Thermal degradation of the organic additives (4-(3-bromophenyl)thiosemicarbazide and 2,6-pyridinedicarboxylic acid) may reduce their functional contributions to ion transport. Structural rearrangements can disrupt optimized ionic conduction pathways [52], while increased crystallization of the polymer matrix may restrict ion mobility in amorphous regions [53, 54]. Additionally, partial evaporation or phase separation of the PEG plasticizer at higher temperatures may further impede ionic motion [55-57]. Similar non-linear behavior has been reported in other polymer electrolyte systems, often indicating thermal instability or upper operational temperature limits [58, 59]. These results indicate that 50°C represents the optimal operating temperature for this polymer electrolyte system, balancing thermal mobility enhancement against structural and compositional deterioration at higher temperatures.

The temperature dependence of ionic conductivity within the ascending regime (30-50 °C) was analyzed using the Arrhenius equation to determine the activation energy (E_a) for ion transport. The Arrhenius plot ($\ln \sigma$ vs $1000/T$) for this range exhibited good linear correlation ($R^2 = 0.9920$), yielding an activation energy of $E_a = 3.21 \text{ kJ/mol}$. This low positive activation energy is consistent with a highly mobile ion transport system, indicating that relatively little thermal energy is required to facilitate ionic hopping between coordination sites, characteristic of proton-conducting polymer electrolytes assisted by

hydrogen-bonded networks [60, 61]. However, above 50°C, conductivity declines systematically, and applying the Arrhenius equation across the full temperature range (30–80°C) yields a poor linear fit ($R^2 = 0.7232$) with an apparent negative activation energy of $E_a = -2.21 \text{ kJ/mol}$, confirming that a single thermally-activated hopping mechanism cannot describe ion transport across this range. This significant deviation from simple Arrhenius behavior reveals multiple competing temperature-dependent processes: structural changes in the polymer matrix [62], dynamic variations in ion association/dissociation equilibria [63, 64], and the interplay between amorphous and crystalline regions affecting conduction pathways [65].

In typical polymer electrolytes, ionic transport is coupled with polymer segmental dynamics and often follows Vogel-Tammann-Fulcher (VTF) behavior rather than simple thermally-activated Arrhenius hopping [66-69]. However, the negative activation energy observed here is exceptional and indicates that destructive processes (likely thermal degradation of the organic additives or polymer chain scission) outweigh the normal temperature enhancement of ionic mobility above 50°C. These findings indicate that while the incorporation of 4-(3-bromophenyl)thiosemicarbazide and 2,6-pyridinedicarboxylic acid produces a polymer electrolyte with satisfactory conductivity in the moderate temperature range (30–50°C), practical applications must be strictly constrained to temperatures below 50°C to maintain optimal ionic conductivity and prevent irreversible degradation. Future efforts will prioritize mapping the thermal degradation mechanisms using TGA and DSC, and explore stabilization strategies including antioxidant additives or alternative organic modifiers to extend the operational temperature range of this material system.

Table 10. Temperature-dependent bulk resistance and ionic conductivity of CMC + 8 wt% PEG + 10 wt% additive + 5 wt% 2,6-pyridinedicarboxylic acid.

Temperature (°C)	Thickness, t (cm)	Bulk Resistance, R_b (Ω)	Conductivity, σ (S cm^{-1})
30	0.018	6.64	7.95×10^{-4}
40	0.018	6.33	8.33×10^{-4}
50	0.018	6.13	8.60×10^{-4}
60	0.018	8.01	6.59×10^{-4}
70	0.018	8.34	6.33×10^{-4}
80	0.018	8.86	5.96×10^{-4}

CONCLUSION

4-(3-bromophenyl)thiosemicarbazide was successfully synthesized in 89% yield. CHNS, FTIR, ^{13}C NMR, UV-Vis, and TGA confirmed the composition and

functional properties of the compound, with single-crystal XRD unambiguously confirming the crystal structure, revealing a monoclinic $P2_1/n$ system stabilized by $N-H\cdots S$ and $N-H\cdots Br$ hydrogen bonds and $C-H\cdots\pi$ and $N-H\cdots\pi$ interactions. The optical band gap (5.36 eV) and DFT-calculated gap (4.92 eV) classify the compound as an insulator, with conductivity arising from ionic rather than electronic transport. Incorporation into CMC/PEG polymer electrolytes at 10 wt% loading gave $8.87 \times 10^{-5} \text{ S cm}^{-1}$, enhanced approximately 8.3-fold to $7.32 \times 10^{-4} \text{ S cm}^{-1}$ upon addition of 5 wt% 2,6-pyridinedicarboxylic acid, with a maximum of $8.60 \times 10^{-4} \text{ S cm}^{-1}$ at 50°C. Enhancement is driven by polymer chain mobility, hydrogen-bonded networks, and Grotthuss proton transport. Temperature studies showed low positive $E_a = 3.21 \text{ kJ/mol}$ (30–50°C), confirming facile ion hopping, but conductivity declined above 50°C with anomalous $E_a = -2.21 \text{ kJ/mol}$, limiting practical use to below 50°C. Future work should address thermal stability and long-term battery performance.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Higher Education, Malaysia (MOHE), for the financial support in the form of the grant scheme, Fundamental Research Grant Scheme (Ref. FRGS/1/2023/STG05/UMT/ 02/ 2) (FRGS-59732). The authors also thank the Faculty of Science and Marine Environment, Universiti Malaysia Terengganu (UMT), for research facilities. The authors also gratefully acknowledge the Universiti Sains Malaysia (USM) for the technical support.

SUPPLEMENTARY MATERIALS

PrintCIF file of 4-(3-bromophenyl)thiosemicarbazide described in this article is included as Supplementary data. CCDC no. 2480242 contains supplementary crystallographic data for 4-(3-bromophenyl)thiosemicarbazide dopant and this data can be obtained free of charge *via* or the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail through deposit@ccdc.cam.ac.uk. (Supplementary Materials)

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