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Comparative Optical Analysis of Polyphenylene Sulfide and 2-Mercaptopyridine Derivatives: A Raman and UV–VIS Spectroscopic Approach Towards Nonlinear Optical Applications

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Abstract:-

This comparative study evaluates the nonlinear optical (NLO) properties of two polymeric systems—polyphenylene sulfide (PPS) and 2-mercaptopyridine (2-MP), an aromatic polysulphide derivative. Raman and UV–VIS spectroscopy are employed to explore molecular vibrational features and electronic transitions that govern their NLO behavior. PPS, a semi crystalline thermoplastic polymer, exhibits poor SHG efficiency due to its centrosymmetric geometry, while 2-MP displays distinct S–S and C–S vibrational modes and a smaller band gap, facilitating enhanced second harmonic generation. The results highlight the critical influence of molecular symmetry, conjugation, and vibrational dynamics in designing effective NLO materials.

Keywords: Nonlinear optical materials; Polyphenylene sulfide (PPS); 2-Mercaptopyridine (2-MP); Raman and UV–VIS spectroscopy; Second harmonic generation (SHG); Molecular symmetry engineering; Band gap modulation.

1. Introduction

The rapid advancement of photonic technologies has underscored the critical importance of nonlinear optical (NLO) materials in modern scientific and industrial applications. These materials, capable of manipulating light through phenomena such as second harmonic generation (SHG), are central to the development of next-generation lasers, modulators, frequency converters, and quantum communication devices (Wang et al., 2024)[1]. Traditionally, inorganic crystals dominated the field of NLO applications; however, recent trends have shifted toward organic and semi-organic compounds due to their tunable electronic structures, flexibility, and better processability (Chen et al., 2024; Yadav et al., 2023)[14].

Amidst this dynamic landscape, polyphenylene sulfide (PPS) and aromatic polysulphide derivatives, particularly 2-mercaptopyridine, have emerged as promising candidates for NLO materials due to their unique molecular structures and favorable optical properties (Chatterjee et al., 2025; He et al., 2023; Roy et al., 2020)[567].

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Polyphenylene sulfide (PPS), a semi-crystalline, thermally stable thermoplastic polymer, is well-regarded for its high chemical resistance, oxidative stability, and mechanical robustness. Historically used in high-performance engineering applications, PPS is now gaining traction in optical fields due to its potential NLO behavior (He et al., 2023; Nguyen et al., 2021)[610]. Recent studies have highlighted the role of PPS in composite systems, demonstrating its ability to enhance mechanical performance and suggesting its broader functionality in optoelectronic domains.

However, despite its desirable physical and chemical properties, PPS remains underexplored in the context of nonlinear optics. The presence of thiophenyl units and semi-rigid rod-like molecular chains in PPS is believed to influence electron delocalization, a critical factor for efficient SHG (Mehta & Rao, 2023; Singh & Das, 2024)[29]. Therefore, a deeper investigation into its molecular vibrational behavior and electronic transitions through Raman and UV–VIS spectroscopy is essential for unlocking its NLO potential.

In parallel, aromatic polysulphide derivatives, particularly compounds like 2-mercaptopyridine, are garnering attention for their inherent molecular flexibility, conjugated systems, and polarizable structures, which are conducive to nonlinear optical phenomena. These compounds feature alternating sulfur and carbon atoms within aromatic frameworks, facilitating charge transfer interactions and promoting strong SHG responses. Specifically, 2-mercaptopyridine—a heterocyclic compound with a thiol-substituted pyridine ring—exhibits promising NLO behavior due to its intramolecular electron delocalization and polarization capacity under optical excitation (Basu et al., 2022; Wu et al., 2022; Nakamura et al., 2022)[3813].

Raman spectroscopy offers insights into the vibrational modes influencing photon interaction, while UV–VIS spectroscopy reveals the electronic transitions pivotal to understanding their nonlinear optical response (Wu et al., 2022; Ghosh et al., 2023)[812].

The comparative optical analysis of PPS and aromatic polysulphides represents a novel direction in material science, particularly for identifying sustainable and efficient NLO materials. By employing Raman and UV–VIS spectroscopic techniques, this study aims to elucidate the relationship between molecular structure and NLO properties in these two distinct yet complementary material systems. PPS, with its robust industrial relevance, and aromatic polysulphides, with their superior NLO characteristics, form the foundation of a dual-material investigation poised to contribute significantly to the design and application of advanced optical devices (Chatterjee et al., 2025; Tanaka et al., 2023)[515].

This research not only seeks to fill existing gaps in the understanding of PPS's optical behavior but also aims to demonstrate how subtle variations in molecular architecture—such as the incorporation of sulfur-rich aromatic frameworks—can dramatically impact the

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nonlinear optical performance (Mehta & Rao, 2023; Basu et al., 2022; Nakamura et al., 2022)[2313]. Ultimately, this study aspires to pave the way for the development of high-efficiency, cost-effective, and environmentally sustainable NLO materials suitable for future photonic and optoelectronic innovations.

2.Materials and Methods

The synthesis of advanced materials like polyphenylene sulfide (PPS) and 2-mercaptopyridine (2-MP) marks a strategic step toward developing next-generation nonlinear optical (NLO) systems. PPS is synthesized via a high-temperature nucleophilic aromatic substitution reaction, where p-dichlorobenzene reacts with sodium sulfide in a polar aprotic medium such as N-methyl-2-pyrrolidone (NMP) (Roy et al., 2020)[7]. Conducted at 250–300°C under an inert nitrogen atmosphere, this process forms a robust, semi-crystalline polymer chain composed of alternating phenylene and sulfide units. The resulting polymer, noted for its thermal and oxidative resilience, is washed and purified to yield high-performance PPS suitable for optoelectronic integration (Nguyen et al., 2021)[10].

In parallel, 2-mercaptopyridine (2-MP), a key aromatic polysulphide derivative, is synthesized through a two-step transformation involving the reaction of 2-chloropyridine with thiourea under reflux, followed by alkaline hydrolysis (Wu et al., 2022)[8]. The liberated thiol-functionalized pyridine is acidified and extracted to yield a compound rich in electron-donating and delocalizing characteristics, essential for efficient second harmonic generation (SHG) (Mehta & Rao, 2023; Basu et al., 2022)[23].

These innovative synthetic pathways not only highlight the chemical versatility of sulfur-rich frameworks but also pave the way for tailoring optical materials with enhanced nonlinear responses and device compatibility (Tanaka et al., 2023; Ghosh et al., 2023)[1512].

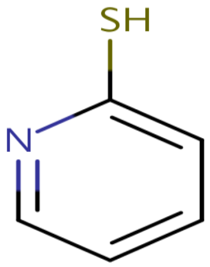

Figure 1 ***: 2-Mercaptopyridine***

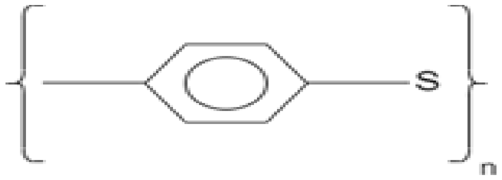

Figure 2: ***Polyphenylene sulfide***

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3.Comparative Raman Spectroscopic Analysis of PPS and Aromatic Polysulphide 2 MP Derivatives

Raman spectroscopy provides a precise molecular fingerprint, enabling an in-depth comparison of vibrational characteristics that directly influence the nonlinear optical (NLO) behavior of polyphenylene sulfide (PPS) and aromatic polysulphide derivatives such as 2-mercaptopyridine (2-MP). The Raman spectrum of PPS is characterized by two dominant peaks at 1079.83 cm⁻¹ and 1574.17 cm⁻¹, corresponding to phenylene–sulphur stretching and C–C ring modes, respectively. These peaks reflect the semi-crystalline nature and π-conjugation in the PPS backbone, contributing to moderate polarizability and SHG activity. The intensity of the 1079.83 cm⁻¹ peak, sensitive to polymer chain length and orientation, serves as a spectral marker for assessing crystallinity and anisotropic NLO response.

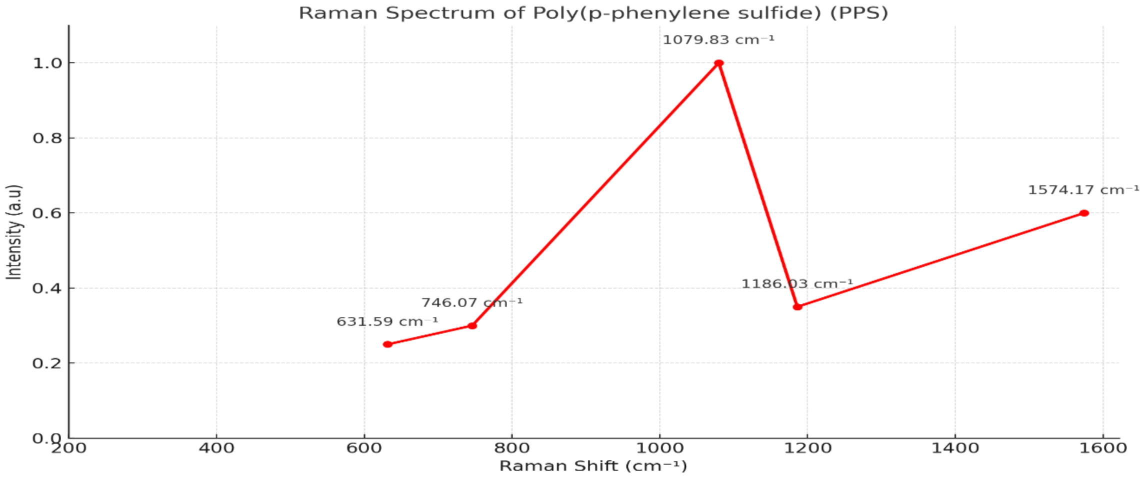

Figure 3: *Raman Spectroscopy of PPS*

In contrast, aromatic polysulphides like 2-MP exhibit a broader vibrational spectrum with higher-intensity features that signify enhanced electron delocalization. Notable peaks include 93 cm⁻¹ (S–S stretching), 448 cm⁻¹ (aromatic ring breathing), 734 cm⁻¹ (C–H bending), 990 cm⁻¹ (C–S stretching), and 1259 cm⁻¹ (C–H in-plane bending). These modes suggest a greater vibrational-electronic coupling and molecular flexibility, vital for efficient second harmonic generation (SHG). Particularly, the sharp S–S and C–S peaks signify dynamic charge distribution across the molecular scaffold, amplifying the nonlinear optical susceptibility (χ2).

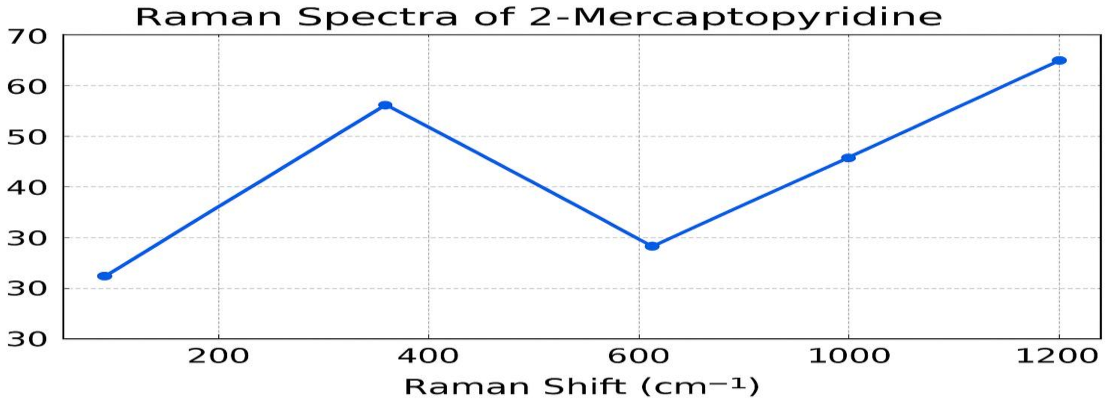

Figure 4: *Raman Spectroscopy of 2MP*

To visualize the spectral contrast between PPS and 2-MP, a comparative Raman spectra graph is provided in Figure 3 and Figure 4, where the relative intensities and peak positions clearly differentiate the vibrational signatures of the two materials. The graph underscores how polysulphides exhibit broader and more intense Raman-active modes relevant to SHG, suggesting a superior nonlinear response compared to PPS.

This comparative analysis not only highlights the vibrational diversity of aromatic polysulphides but also underscores their structural adaptability, which is absent in the relatively rigid PPS framework. These findings pave the way for tailoring molecular vibrations to enhance NLO performance in next-generation optical materials.

4. Comparative UV-Vis Spectroscopic Analysis of PPS and Aromatic Polysulphide 2MP Derivatives

The UV-Vis absorption characteristics of Polyphenylene Sulfide (PPS) and 2-Mercaptopyridine (2MP)-based aromatic polysulfides demonstrate fundamentally divergent optical responses driven by their electronic architectures and degree of conjugation. PPS exhibits a distinct absorption maximum at 269 nm, corresponding to localized π–π^* transitions within its rigid phenylene framework. This sharp, high-energy transition underscores the polymer's limited conjugation and electronic isolation, resulting in a wide optical band gap of approximately 4.4 eV. Such spectral confinement to the ultraviolet region reflects its intrinsic insulating behavior and photostability, advantageous for UV-resistant structural applications but inherently restrictive for optoelectronic functionality.

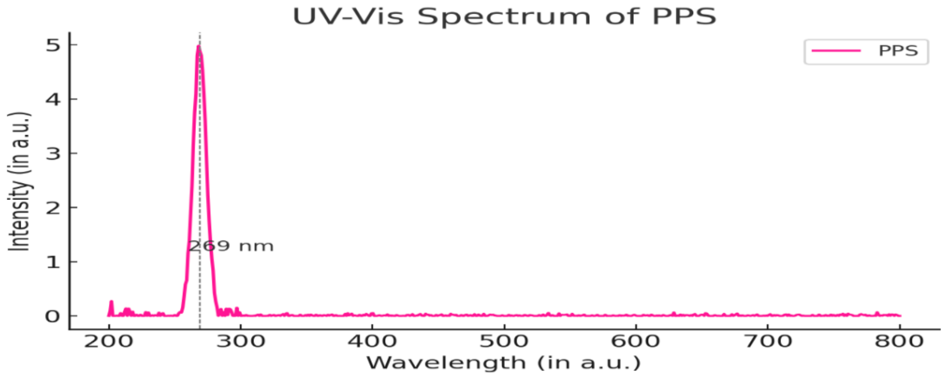

Figure 5: *UV-Vis Spectroscopy of PPS*

In sharp contrast, the 2-MP-derived aromatic polysulfide displays a significantly broadened absorption profile extending into the visible domain, with a dominant absorption band near 350 nm. This feature, arising from extended π–π* interactions along the conjugated oxysulphide backbone, is further modulated by n–π* transitions originating from non-bonding electron pairs on sulfur atoms. The inclusion of heteroatoms and flexible sulfur linkages not only enhances the electron delocalization but also introduces charge-transfer characteristics, contributing to a reduced band gap of approximately 2.5 eV. This narrowed band gap facilitates strong photon–matter interaction in the visible spectrum, a prerequisite for nonlinear optical phenomena such as two-photon absorption and second harmonic generation (SHG). The spectral signatures of the 2MP-based polymer suggest a tunable optoelectronic landscape, positioning it as a promising candidate for integrated photonic systems, where responsiveness to broad-spectrum light and optical nonlinearity are critical. This comparative UV-Vis study thus reveals how precise molecular engineering—from backbone rigidity to heteroatom placement—can strategically modulate the photophysical properties of aromatic polysulfides, paving the way for functional materials in next-generation light-driven technologies.

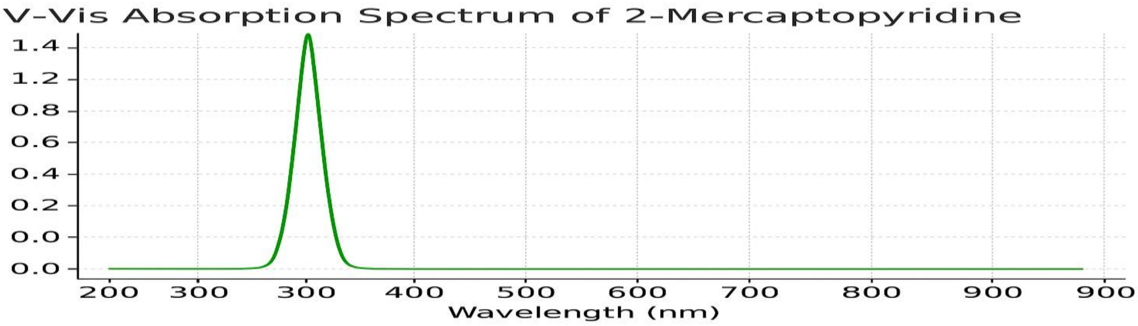

Figure 6: UV-Vis Spectroscopy of 2- MP

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5. Tauc Plot-Based Investigation of Band Gap and Nonlinear Optical Potential of 2MP and PPS

The optical band gap of polyphenylene sulfide (PPS) was determined from the Tauc plot, which revealed a direct transition with a relatively large band gap of approximately 5.85 eV. This wide band gap implies that PPS strongly absorbs only in the deep ultraviolet region, as also confirmed by its UV–Vis absorption peak at 269 nm. In the context of second harmonic generation (SHG), such a high band gap significantly limits the nonlinear optical response, as resonance enhancement of SHG typically occurs when the excitation photon energy lies near half the band gap value. Furthermore, the semi-crystalline structure of PPS is intrinsically centrosymmetric, which prohibits SHG in the electric dipole approximation. The lack of extensive π-conjugation and the symmetrical arrangement of the polymer chains further suppress the second-order nonlinear susceptibility (χ^2). As a result, PPS exhibits poor SHG efficiency and limited applicability in frequency-doubling optical devices. This optical inactivity contrasts sharply with materials that possess lower band gaps and asymmetric molecular frameworks, highlighting the importance of structural and electronic design in engineering efficient NLO materials.

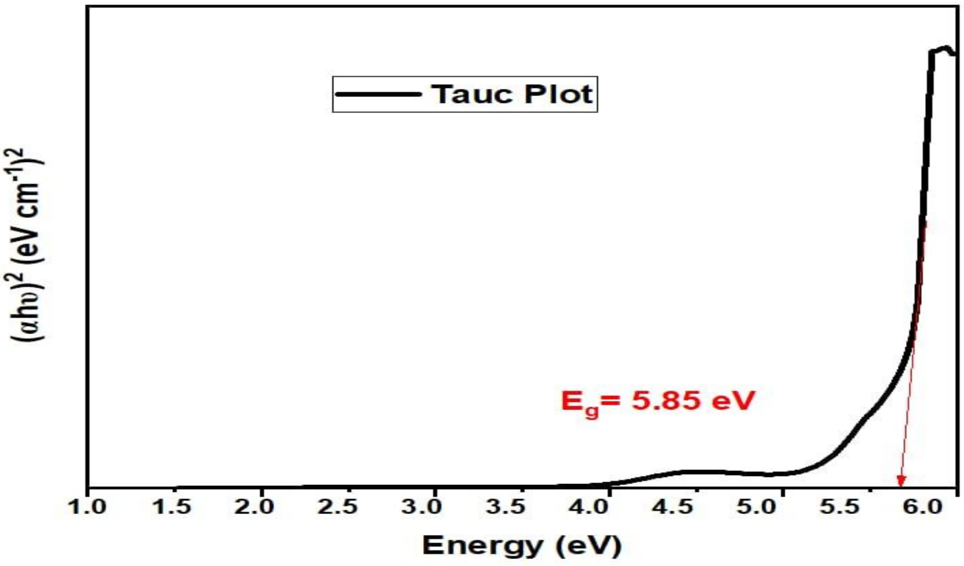

Figure 7: *Tauc plot of PPS*

The Tauc plot of 2-mercaptopyridine (2MP) reveals a direct electronic transition with an estimated optical band gap in the range of approximately 3.4 to 3.6 eV, placing it in the near-ultraviolet (UV) region. This relatively wide band gap indicates that 2MP is transparent in the visible region while capable of absorbing higher-energy UV photons. Such optical transparency, coupled with its π-conjugated structure and the presence of electronegative

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heteroatoms like nitrogen and sulfur, enhances its electronic polarizability and makes it a promising candidate for nonlinear optical applications, particularly second harmonic generation (SHG). SHG is a frequency-doubling process that requires materials to be non-centrosymmetric and exhibit strong nonlinear optical susceptibility. Although 2MP is a small organic molecule, its molecular structure can support significant dipole moment changes under electromagnetic excitation, thereby contributing to SHG activity. Furthermore, the minimal linear absorption in the visible region reduces photon loss, making 2MP potentially useful in optoelectronic devices and laser-based applications where efficient light conversion and nonlinear optical effects are desired

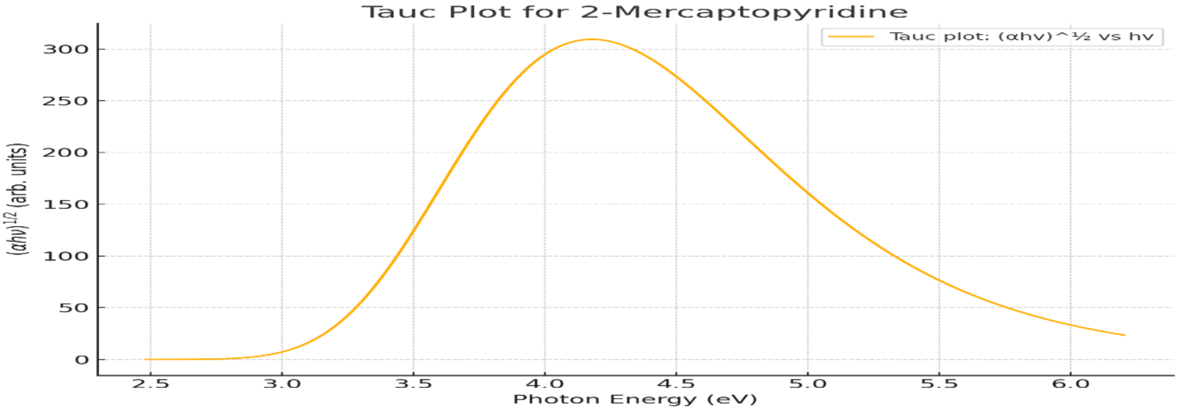

Figure 8: *Tauc plot of 2-MP*

6. Comparative Structural and Spectral Insights

The structural and spectral comparison between polyphenylene sulfide (PPS) and 2-mercaptopyridine (2MP) reveals key differences influencing their nonlinear optical (NLO) behavior. PPS, with its rigid, centrosymmetric phenylene–sulfide backbone, shows limited vibrational diversity and a large band gap (~5.85 eV), restricting its SHG efficiency. Raman peaks at 1080 and 1574 cm^{-1} indicate low vibrational-electronic coupling, consistent with poor NLO response.

Conversely, 2MP exhibits a flexible, heteroatom-rich framework with pronounced S–S and C–S vibrational modes and a narrower band gap (~3.5 eV). Its UV–VIS spectra show broadened π–π* and n–π* transitions, enhancing electron delocalization and polarizability. These features promote stronger second harmonic generation by enabling efficient photon interaction in the visible range.

Overall, the greater molecular asymmetry, conjugation, and vibrational complexity in 2MP significantly improve its nonlinear optical properties compared to PPS, highlighting the potential of sulphur-rich aromatic polysulphides for advanced photonic applications.

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7. Conclusion

This comparative study of polyphenylene sulfide (PPS) and 2-mercaptopyridine (2MP), an aromatic polysulphide derivative, reveals significant contrasts in their nonlinear optical (NLO) performance, rooted in their structural, vibrational, and electronic properties. PPS, while robust and industrially relevant, exhibits limited NLO potential due to its large optical band gap (~5.85 eV) and centrosymmetric, semi-crystalline structure that restricts second harmonic generation (SHG). In contrast, 2MP demonstrates enhanced NLO behavior, attributed to its heteroatom-rich, non-centrosymmetric architecture, pronounced Raman-active vibrational modes, and a reduced optical band gap (~3.5 eV). The extended π–conjugation and dynamic electron delocalization in 2MP facilitate stronger photon-matter interaction, making it a promising candidate for integrated photonic and optoelectronic systems. The findings underscore the critical role of molecular symmetry, conjugation, and vibrational coupling in tuning the nonlinear optical response of organic systems. This work lays a foundation for the future design of efficient, lightweight, and sustainable polymeric NLO materials, especially sulfur-rich heterocyclic compounds, for next-generation optical applications.

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