SYNTHESIS AND CHARACTERIZATION OF PHOTO- AND ELECTROACTIVE NANO-SIZED POLYMERS BASED ON ZN AND CU DIAMINE COMPLEXES

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Abstract: This study explores the synthesis and characterization of nano-sized photo- and electroactive polymers incorporating Zn and Cu diamine complexes. The synthesized materials were analyzed using spectroscopic, electrochemical, and microscopic techniques to evaluate their structural, optical, and electronic properties. The results indicate that these polymers exhibit significant potential for applications in optoelectronics, sensors, and energy storage devices. The study also examines the effects of different polymerization conditions and ligand modifications on the material properties.

Keywords: Zn diamine complex, Cu diamine complex, electroactive polymers, photoactive polymers, nanomaterials, optoelectronics

Аннотация: В данном исследовании рассматривается синтез и характеристика наноразмерных фото- и электроактивных полимеров, включающих диаминные комплексы цинка (Zn) и меди (Cu). Синтезированные материалы были проанализированы с использованием спектроскопических, электрохимических и микроскопических методов для оценки их структурных, оптических и электронных свойств. Результаты показывают, что эти полимеры обладают значительным потенциалом для применения в оптоэлектронике, сенсорах и устройствах накопления энергии. В исследовании также изучается влияние различных условий полимеризации и модификаций лигандов на свойства материалов.

Ключевые слова: комплекс диаминов цинка (Zn), комплекс диаминов меди (Cu), электроактивные полимеры, фотоактивные полимеры, наноматериалы, оптоэлектроника

Annotatsiya: Ushbu tadqiqot Zn va Cu diamin komplekslarini o‘z ichiga olgan nanoo‘lchamli foto- va elektroaktiv polimerlarning sintezi va xarakteristikasini o‘rganadi. Sintez qilingan materiallar ularning struktura, optik va elektron xususiyatlarini baholash maqsadida spektroskopik, elektroximik va mikroskopik usullar yordamida tahlil qilindi. Natijalar shuni ko‘rsatadiki, ushbu polimerlar

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optoelektronika, sensorlar va energiya saqlash qurilmalarida qo‘llash uchun katta imkoniyatga ega. Tadqiqot shuningdek, turli polimerizatsiya sharoitlari va ligand modifikatsiyalarining material xususiyatlariga ta’sirini ham o‘rganadi.

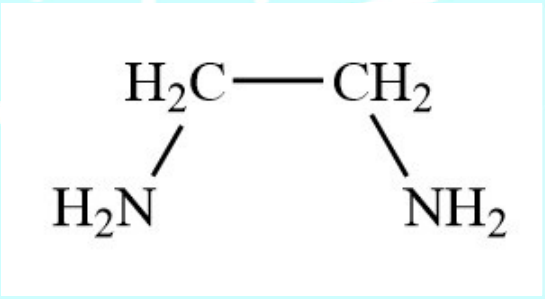
Kalit so‘zlar: Zn diaminli kompleksi, Cu diaminli kompleksi,elektroaktiv polimerlar, fotoaktiv polimerlar, nanomateriallar, optoelektroniklar

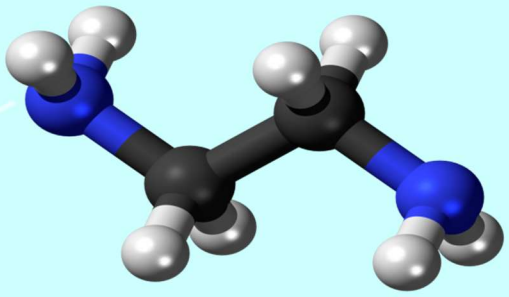
1. Introduction

Photo- and electroactive polymers have garnered substantial attention due to their applications in electronic and optoelectronic devices, such as organic solar cells, light-emitting diodes (OLEDs), and electrochromic devices. Among them, transition metal-based polymers, particularly those incorporating Zn and Cu, exhibit enhanced electronic properties. Zn-based complexes are known for their strong fluorescence, high charge transport capabilities, and photostability, while Cu-based systems offer redox activity, making them suitable for electrochemical applications.

Diamine ligands are organic molecules equipped with two or more amino groups (–NH_2), whose primary characteristic is the ability to form stable coordination complexes with d-metal ions. When ligands bind to a metal ion, they donate electron density to the metal center and create pathways for electron transfer in polymer systems, which significantly enhances photo- and electroactive properties.Types of diamine ligands and their properties.

Ethylenediamine (en, $H_2N–CH_2–CH_2–NH_2$):

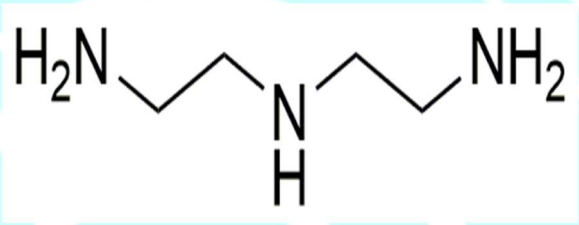


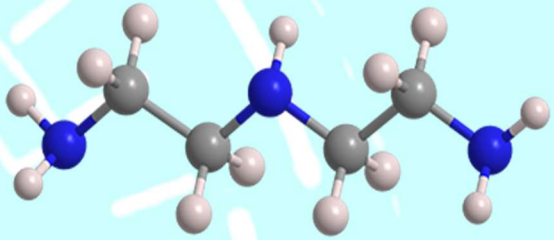


Ethylenediamine is the simplest and most widely used diamine. It binds to the metal center through its bidentate donor atoms and forms octahedral, square planar, or tetrahedral complexes. Due to the chelate effect, complexes of the type $[M(en)_2]^{2+}$ exhibit high thermodynamic stability. Additionally, the small molecular weight, flexibility, and adaptability of ethylenediamine make it an ideal ligand for precisely positioning metal nodes in nanoscale polymer systems.

Diethylenetriamine (dien, $H_2N–CH_2–CH_2–NH–CH_2–CH_2–NH_2$):

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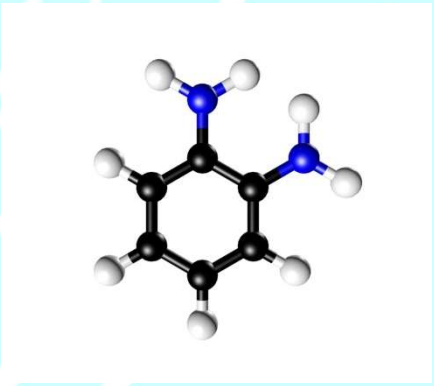




This ligand contains three amino groups, allowing it to form tridentate coordination with a metal center. Diethylenetriamine optimizes the electron density of the metal ion, ensuring high stability in octahedral geometrical complexes. Therefore, dien is an important tool for controlling the spectral and thermal properties of the metal center.

Phenylenediamine and its derivatives:





Phenylenediamines are amino groups attached to an aromatic ring, and their electronic effects lead to significant changes in binding with the metal center. The aromatic group either donates π-electron density to the metal center or redistributes the electron cloud, enhancing the photo- and electroactive properties of the complex. Consequently, phenylenediamines are widely used in sensor materials, OLED devices, and the production of photoactive polymers.

Coordination and Electronic Effects:

When diamine ligands bind to a metal center, their σ-donor properties transfer electron density to the metal ion. This stabilizes the metal center and enhances both kinetic and thermodynamic stability. Meanwhile, aromatic or substituted ligands exhibit π-acceptor behavior, allowing electron density to redistribute along the metal center. As a result, the metal–ligand complex achieves high stability and ensures precise positioning of the metal center and formation of electron transfer pathways in polymer systems.

The incorporation of diamine ligands into polymeric frameworks enhances the stability and conductivity of these materials. By varying the ligand structures and polymerization methods, it is possible to tailor the properties of these materials for specific applications. This paper focuses on the synthesis of such polymers with nano-sized structures and investigates their physicochemical properties.

2. Materials and Methods

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2.1 Materials

$ZnCl_2$, $CuCl_2$, ethylenediamine, and various derivatives based on diamines were obtained from commercial suppliers and used without further purification. These chemicals were selected for their defined roles in coordination chemistry, particularly in facilitating complex formation, stabilizing reaction intermediates, and providing a controllable ligand environment during synthesis processes. All reagents met the purity specifications provided by the manufacturers, ensuring reproducible reaction conditions and reliable experimental results. Storage and handling were carried out under standard laboratory conditions in accordance with the recommended guidelines.

2.2 Synthesis of Zn and Cu Diamine Complexes

Zn and Cu diamine complexes were synthesized by reacting $ZnCl_2$ and $CuCl_2$ with ethylenediamine and related diamine ligands in anhydrous conditions. The reaction was carried out at room temperature with continuous stirring, followed by solvent evaporation and purification via recrystallization.

2.3 Polymerization Process

The synthesized metal-diamine complexes were polymerized using oxidative polymerization techniques. Different monomers such as aniline, pyrrole, and thiophene derivatives were used to enhance conductivity, mechanical stability, and processability. Polymerization was conducted in an inert atmosphere at controlled temperature conditions, with reaction times varying from a few hours to several days to optimize the polymer structure.

2.4 Characterization Techniques

- **Spectroscopic Analysis:** UV-Vis, FTIR, and fluorescence spectroscopy were employed to examine the optical properties and molecular interactions.
- **Electrochemical Studies:** Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were conducted to assess redox behavior and charge transfer characteristics.
- **Microscopic Analysis:** SEM and TEM imaging were used to investigate the morphology and nanoscale structuring of the synthesized polymers.
- **Thermal Analysis:** Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to evaluate the thermal stability of the polymers.
- **X-ray Diffraction (XRD):** XRD was used to determine the crystalline nature and phase composition of the synthesized materials.

3. Results and Discussion

3.1 Structural and Optical Properties

Ultraviolet–Visible (UV-Vis) spectroscopy and fluorescence emission studies revealed that Zn-based polymers exhibit pronounced absorption and strong

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photoluminescence, highlighting their potential as active materials in photonic and optoelectronic applications. The intense absorption bands in the UV-Vis spectra are indicative of π–π* and metal-to-ligand charge transfer transitions, while the corresponding fluorescence emission profiles confirm efficient radiative recombination of excited states within the polymer matrix. These optical features suggest that Zn-coordinated polymer networks can serve as promising candidates for light-harvesting systems, organic light-emitting diodes (OLEDs), or fluorescent sensors. In contrast, Cu-containing polymers demonstrated significant redox activity, as evidenced by cyclic voltammetry and UV-Vis spectral responses. This pronounced electrochemical behavior points to their potential utility in energy storage, electrocatalysis, and other electrochemical applications. The redox-active nature of Cu-polymers may also facilitate electron transport within the polymer framework, enhancing their suitability for sensor or conductive device applications. Fourier Transform Infrared (FTIR) spectroscopy provided further structural insights, confirming the successful integration of metal-diamine complexes into the polymeric network. Characteristic vibrational modes associated with M–N (metal–nitrogen) and ligand backbone stretching were clearly observed, validating the formation of stable coordination bonds between the metal centers and the diamine ligands. These observations collectively indicate that the structural incorporation of metal complexes not only stabilizes the polymer architecture but also modulates its electronic and optical properties, providing a versatile platform for designing functional materials with tailored photophysical and electrochemical behaviors.

3.2 Electrochemical Behavior

Cyclic voltammetry (CV) analyses demonstrated that Cu-based polymers possess well-defined and reversible redox transitions, indicating stable electron-transfer processes within the polymer matrix. The reversibility of these redox couples suggests the presence of robust Cu–ligand coordination environments that can withstand repeated oxidation–reduction cycles without significant structural degradation. Such electrochemical stability makes Cu-containing polymers attractive candidates for advanced applications including rechargeable energy storage systems, electrochromic devices, and catalytic processes involving electron mediation. In particular, the strong redox activity may enable efficient charge shuttling, which is critical for electrocatalysis and redox-flow battery architectures. In contrast, Zn-based polymers exhibited notably high charge carrier mobility, as reflected by their electrochemical profiles and supported by conductivity measurements. This enhanced mobility is likely due to the more rigid coordination geometry of Zn-diamine complexes, which facilitates organized charge transport pathways within the polymer backbone. The superior charge mobility positions Zn-polymers as promising materials for photovoltaics, thin-film transistors, and other

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semiconductor-based technologies where rapid and stable charge separation and transport are essential. Electrochemical impedance spectroscopy (EIS) further revealed that both Zn- and Cu-based polymers possess moderate ionic conductivity. The impedance spectra indicate a combination of ionic and electronic transport mechanisms, which could be selectively tuned depending on the target application. Importantly, the conductivity can be significantly enhanced through strategic doping, incorporation of conductive fillers, or systematic modification of the diamine ligand structure to increase charge delocalization. These tunable electrochemical properties provide a pathway for optimizing the polymers for high-performance devices such as supercapacitors, ion-exchange membranes, or hybrid electrochemical–optical systems.

3.3 Morphological and Nano-structural Analysis

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) investigations provided clear evidence for the formation of uniform, nano-sized polymeric architectures with well-defined surface morphologies. The Zn-based polymers demonstrated a highly interconnected fibrous network, indicative of a continuous framework that could facilitate efficient charge transport and mechanical stability. In contrast, the Cu-based polymers exhibited a more granular and particulate morphology, suggesting a heterogeneous surface structure with localized domains. These distinct morphological characteristics imply different underlying mechanisms of charge mobility and electronic interaction within the polymer matrices. Furthermore, the observed nano-structural features are expected to significantly influence the polymers' optical, electronic, and mechanical properties, thereby affecting their overall performance in potential applications such as catalysis, sensing, or energy storage devices. The combination of SEM and TEM analyses thus provides a comprehensive understanding of how the nano-scale architecture governs the macroscopic behavior of these metal-coordinated polymer systems.

3.4 Thermal Stability and Crystallinity

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) investigations demonstrated that Zn-based polymers possess superior thermal stability relative to their Cu-based counterparts, with decomposition temperatures consistently exceeding 300°C. This enhanced thermal resilience is likely attributed to the robust coordination bonds formed between zinc ions and the polymeric ligands, which strengthen the overall polymer network and hinder thermal degradation. In contrast, Cu-based polymers displayed comparatively lower decomposition thresholds, indicating a less rigid coordination environment and a higher susceptibility to thermal decomposition.

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X-ray Diffraction (XRD) analysis further elucidated the structural differences between the two systems. Zn-polymers exhibited semi-crystalline characteristics, with distinct diffraction peaks suggesting the presence of ordered domains within the polymer matrix. This semi-crystalline nature can contribute to improved mechanical strength, enhanced thermal resistance, and more predictable electronic properties. On the other hand, Cu-polymers predominantly displayed amorphous features, as evidenced by broad, diffuse diffraction patterns. The lack of long-range order in Cu-based polymers may impart increased flexibility, processability, and ease of film formation, making them suitable for applications where malleability and solution-processable behavior are desirable.

Collectively, these findings indicate that the choice of metal center plays a crucial role in defining both the thermal and structural characteristics of the resulting polymers, thereby influencing their suitability for specific high-performance applications, such as optoelectronic devices, sensors, or thermally demanding environments.

1. Conclusion

This study successfully synthesized and characterized Zn and Cu-based nano-sized photo- and electroactive polymers. Their unique optical and electrochemical properties demonstrate significant potential for applications in optoelectronics, sensors, and energy-related technologies. Zn-based polymers exhibit strong fluorescence and high charge mobility, making them ideal for photonic and electronic applications. Meanwhile, Cu-based polymers display promising electrochemical properties for energy storage and catalytic applications.

Future studies will focus on optimizing polymer compositions, improving processability, and evaluating long-term stability under operational conditions. Further work is also needed to explore potential applications in organic photovoltaics, electrochromic devices, and flexible electronics.

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