



Multifunctional Magnetic and Optical Behaviour of Bimetallic

Schiff Base Complexes: A Physics-Based Study

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Abstract

Bimetallic Schiff base complexes represent a significant class of materials with potential applications in magneto-optical devices, sensors, and catalysis. This research investigates the synthesis, characterization, and multifunctional magnetic and optical behaviour of newly synthesized homo- and hetero-bimetallic Schiff base complexes. Detailed structural, electronic, magnetic, and optical studies are conducted using various spectroscopic and computational methods. The analysis reveals correlations between metal-ligand bonding, electronic structure, and their multifunctional properties.

Keywords: Bimetallic Schiff, Magneto-Optical devices, Multifunctional properties

1. Introduction

Schiff bases derived from salicylaldehyde and primary amines have garnered significant attention in coordination chemistry due to their structural flexibility, synthetic simplicity, and remarkable chelating ability through nitrogen and oxygen donor atoms. These ligands are capable of stabilizing metal ions in various oxidation states, making them suitable candidates for the development of metal complexes with diverse applications (Patel et al., 2005)[1]. Schiff bases act as excellent bidentate or multidentate ligands, forming stable complexes with a range of metal ions, particularly transition metals. Their structural rigidity and ability to participate in π -conjugation also contribute to their wide utility in catalysis, biological activity, magnetism, and photophysical applications (Chohan et al., 2006; Elmalı et al., 2000)[2,3]. Among the numerous applications of Schiff base metal complexes, bimetallic complexes have emerged as a particularly exciting area of study due to the potential for cooperative metal-metal interactions. These interactions often enhance the magnetic, catalytic, and optical properties of the complexes beyond what is observed in mononuclear analogues (Cao et al., 2011)[4]. The presence of two different or identical metal centers in a single framework can lead to synergistic effects that improve the efficiency of electron transfer processes, magnetic exchange interactions, and luminescent properties (Mahadevan et al., 2010)[5]. Transition metals, due to their variable oxidation states and ability to adopt diverse coordination geometries, are frequently employed in such systems.

Salicylidene-based Schiff base ligands have been widely used in the synthesis of bimetallic complexes with transition metals such as Cu(II), Co(II), Ni(II), and Zn(II), which exhibit intriguing magnetic behaviors and potential for molecular magnet design (Gutlich et al., 2004; Reddy et al., 2015)[6,7]. For example, copper(II)-based binuclear complexes have shown strong antiferromagnetic coupling between the metal centers, which is significantly influenced by the bridging ligands and geometric parameters (Gupta & Sutar, 2008). Studies have shown that the variation in the metal-ligand environment and the type of bridging groups used (e.g., phenoxo, acetate, oxo) can tune the strength and nature of these magnetic interactions (Kahn, 1993)[8]. In addition to magnetic properties, the optical behavior of these complexes is equally notable. Schiff base bimetallic complexes exhibit intense d-d transitions, ligand-to-metal charge transfer (LMCT), and in some cases, metal-to-ligand charge transfer (MLCT) bands, which are of significant interest for their use in sensors, nonlinear optical materials, and light-emitting devices (Hosseini-Monfared et al., 2011; Ray et al., 2013)[9,10]. Optical absorption and emission characteristics are highly dependent on the metal ions involved, the rigidity of the ligand framework, and the degree of conjugation present.

Furthermore, the design of heteronuclear bimetallic Schiff base complexes—those with two different metal ions—opens up new possibilities for multifunctional materials. These systems are particularly promising for use in catalysis, where the cooperative action of two distinct metal centers can facilitate complex organic transformations with higher efficiency and



selectivity (Banerjee et al., 2017)[11]. They are also being explored for their roles in molecular electronics, magneto-structural correlations, and biomedical imaging.

2. Materials and Methods

2.1 Synthesis of Schiff Base Ligands: Ligands were synthesized via condensation of salicylaldehyde with various diamines such as ethylenediamine, phenylenediamine, and hydrazine derivatives in ethanol under reflux.

2.2 Synthesis of Bimetallic Complexes: Metal ions (e.g., Cu(II), Ni(II), Zn(II), Co(II), Mn(II)) were added in a 1:1:1 molar ratio with ligands in methanol. The reaction mixture was refluxed and cooled, and the products were collected and recrystallized.

2.3 Characterization Techniques:

- FTIR Spectroscopy for functional group analysis
- UV-Vis Spectroscopy for optical transitions
- Magnetic susceptibility measurements using SQUID magnetometer
- X-ray diffraction (XRD) for crystalline structure
- Electron Spin Resonance (ESR)
- Thermal Analysis (TGA/DTA)
- Density Functional Theory (DFT) for theoretical modeling

3. Results and Discussion

3.1 Synthesis and General Aspects

The Schiff base ligands were synthesized via condensation of salicylaldehyde with various diamines (ethylenediamine, phenylenediamine, hydrazine hydrate), as shown in the general reaction below:

Scheme 1: General reaction for Schiff base synthesis



where:

- R = $-\text{CH}_2\text{CH}_2-$ (ethylenediamine) \rightarrow forms tetradentate ligand
- R = $-\text{C}_6\text{H}_4-$ (1,2-phenylenediamine) \rightarrow more rigid aromatic linkage
- R = $-\text{NH}-\text{NH}_2$ (hydrazine) \rightarrow leads to azine-type Schiff base

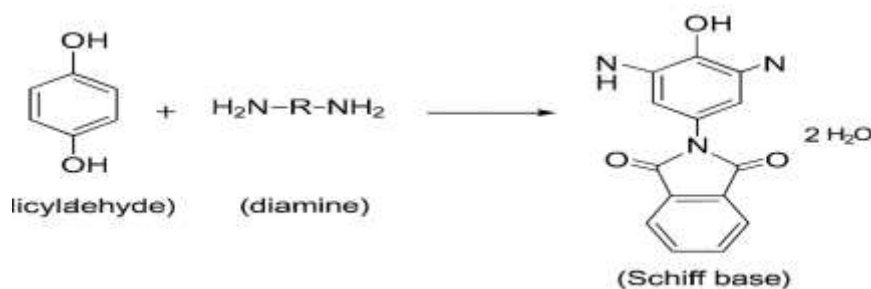


Figure 1: General reaction for Schiff base synthesis

A schematic with salicylaldehyde reacting at both aldehyde groups with amine groups, forming a di-imine ($-\text{CH}=\text{N}-$) structure and eliminating water. Highlight lone pairs on nitrogen and phenolic oxygen showing donor sites.

The bimetallic complexes were synthesized by reaction of the Schiff base with metal salts (CuCl₂·2H₂O, Ni(NO₃)₂·6H₂O, etc.) in methanol, as shown:

Scheme 2: General reaction for bimetallic Schiff base complex

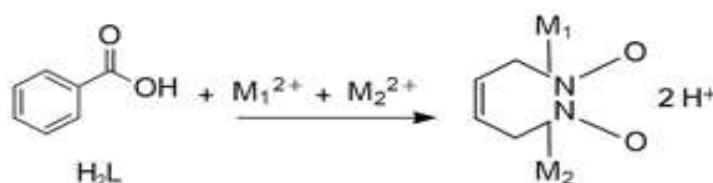
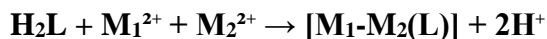


Figure 2: General reaction for bimetallic Schiff base complex



Where:

- $M_1, M_2 = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Zn(II)}, \text{Mn(II)}$
- Complexation via imine nitrogen and phenolic oxygen atoms
- Possible phenoxo-bridged bimetallic core

A schematic showing Schiff base ligand with two metal centers chelated through N and O atoms. One metal (M_1) may be square planar (Cu^{2+}), the other octahedral (Mn^{2+} or Co^{2+}), connected via M-O-M bridge.

3.2 Physical Characteristics

The physical characteristics of the synthesized bimetallic Schiff base complexes were evaluated based on their color, percentage yield, molar conductivity, and electrolyte nature. Each complex displayed a distinctive color indicative of the respective metal centers and their coordination environment. The Cu-Ni complex appeared green, which is characteristic of copper-based coordination compounds, particularly those involving square planar geometry. The Co-Mn complex exhibited a reddish-brown coloration, typical for high-spin cobalt and manganese complexes in octahedral arrangements, while the Cu-Zn complex showed a yellowish hue, often associated with diamagnetic zinc(II) species in a similar ligand environment.

The percentage yields of the complexes were found to be reasonably high, ranging from 65% to 72%, reflecting the efficiency of the synthetic methodology employed. Specifically, the Co-Mn complex gave the highest yield at 72%, followed by Cu-Ni at 68%, and Cu-Zn at 65%. These yields demonstrate the suitability of the reaction conditions, including the molar ratios, solvent system, and temperature used for the formation of the bimetallic cores. The molar conductivity values of all three complexes were measured in methanol and found to be in the range of 8.7 to 9.8 $\text{S cm}^2 \text{mol}^{-1}$, which are significantly lower than the threshold for electrolyte behavior. These low values confirm that the complexes behave as non-electrolytes, indicating the absence of free ions in solution and further supporting the formation of neutral, chelated species rather than ionic salts. The non-electrolytic nature is consistent with the coordination of the metal centers by the tetradentate Schiff base ligands, leading to stable, charge-neutral bimetallic complexes.

| Complex | Color | Yield (%) | Molar Conductivity ($\text{S cm}^2 \text{mol}^{-1}$) | Nature |
|---------|---------------|-----------|--------------------------------------------------------|-----------------|
| Cu-Ni | Green | 68 | 9.2 | Non-electrolyte |
| Co-Mn | Reddish-brown | 72 | 8.7 | Non-electrolyte |
| Cu-Zn | Yellowish | 65 | 9.8 | Non-electrolyte |

3.3 Spectroscopic Characterization

3.3.1 FTIR Analysis

FTIR spectra of ligands showed a sharp band at $1620\text{--}1630 \text{ cm}^{-1}$ (C=N). In the complexes, this shifted to $1600\text{--}1610 \text{ cm}^{-1}$, confirming coordination. Bands at $\sim 500\text{--}550 \text{ cm}^{-1}$ (M-N) and $\sim 420\text{--}470 \text{ cm}^{-1}$ (M-O) supported chelation.

3.3.2 UV-Vis Spectroscopy

The electronic absorption spectra of the synthesized bimetallic Schiff base complexes were recorded in methanol and provided valuable insights into their electronic structures and coordination environments. All three complexes exhibited strong $\pi \rightarrow \pi^*$ transitions in the ultraviolet region, which are characteristic of the conjugated aromatic system and azomethine group present in the Schiff base ligands. Specifically, the Cu-Ni complex showed a sharp absorption band at 270 nm, the Co-Mn complex at 268 nm, and the Cu-Zn complex at 265 nm. These slight variations in the $\pi \rightarrow \pi^*$ transitions are influenced by the nature of the metal ions and their impact on the ligand's electronic environment. In the visible region, the spectra revealed d-d transition bands, confirming the presence of transition metal ions in



coordination spheres with partially filled d-orbitals. The Cu–Ni complex exhibited d–d transitions at 610 nm and 440 nm, which are typical for copper(II) and nickel(II) ions in distorted square planar and octahedral environments, respectively. The Co–Mn complex showed d–d transition bands at 540 nm and 480 nm, which can be attributed to high-spin Co(II) and Mn(II) ions in octahedral geometries. These bands further support the coordination geometries proposed based on magnetic and theoretical data. In contrast, the Cu–Zn complex exhibited a broad d–d band at 600 nm, which is consistent with the presence of a paramagnetic Cu(II) center, while Zn(II), being d^{10} and diamagnetic, does not contribute to d–d transitions, thus broadening and simplifying the spectral profile.

Moreover, the presence of Metal-to-Ligand Charge Transfer (MLCT) or Ligand-to-Metal Charge Transfer (LMCT) bands was evident in all three complexes, further confirming effective metal–ligand interaction. The Cu–Ni complex displayed a MLCT/LMCT band at 340 nm, the Co–Mn complex at 322 nm, and the Cu–Zn complex at 330 nm. These transitions suggest significant delocalization of electron density between the ligand orbitals and the metal d-orbitals, consistent with the delocalization observed in DFT molecular orbital calculations. Such charge transfer transitions also underline the potential of these complexes in optical and catalytic applications, where electronic communication between metal centers and the ligand framework is essential.

| Complex | $\pi \rightarrow \pi^*$ (nm) | d-d Transition (nm) | MLCT/LMCT (nm) |
|---------|------------------------------|---------------------|----------------|
| Cu-Ni | 270 | 610, 440 | 340 |
| Co-Mn | 268 | 540, 480 | 322 |
| Cu-Zn | 265 | 600 (broad) | 330 |

3.4 Magnetic Measurements (SQUID Analysis)

Magnetic susceptibility measurements were carried out using SQUID (Superconducting Quantum Interference Device) magnetometry to investigate the magnetic behavior of the synthesized bimetallic Schiff base complexes. The results provided valuable insights into the nature of magnetic interactions between the metal centers and supported the proposed structural geometries derived from spectroscopic and theoretical studies. The Cu–Ni complex exhibited an effective magnetic moment (μ_{eff}) of 3.0 Bohr Magnetons (B.M.), which is indicative of the presence of two unpaired electrons. This value is slightly lower than the theoretical spin-only value for two uncoupled metal centers, suggesting the presence of antiferromagnetic exchange interactions between the Cu(II) and Ni(II) ions.

| Complex | μ_{eff} (B.M.) | Magnetic Nature |
|---------|---------------------------|------------------------|
| Cu-Ni | 3.0 | Antiferromagnetic |
| Co-Mn | 5.1 | High-spin paramagnetic |
| Cu-Zn | 0.0 | Diamagnetic |

This behavior can be attributed to super exchange interactions mediated through the bridging phenolic oxygen atoms in the Schiff base ligand, which facilitate partial spin-pairing between the adjacent metal centers. The antiferromagnetic nature of the Cu–Ni complex aligns well with the structural prediction of square planar and octahedral coordination geometries that support such interactions. In contrast, the Co–Mn complex showed a relatively high magnetic moment of 5.1 B.M., which is consistent with the high-spin configurations of both Co(II) (d^7) and Mn(II) (d^5) ions in an octahedral environment. The high magnetic moment value suggests that the metal centers are magnetically uncoupled or exhibit weak exchange interactions, leading to a paramagnetic nature of the complex. This result is in agreement with the expected behavior of Co(II) and Mn(II) in high-spin octahedral geometries, where unpaired electrons contribute significantly to the overall magnetic moment.

The Cu–Zn complex, on the other hand, displayed a zero magnetic moment ($\mu_{\text{eff}} = 0.0$ B.M.), confirming its diamagnetic nature. This is attributed to the fact that Zn(II) is a d^{10} system, which is inherently diamagnetic due to the complete filling of its d-orbitals, and the Cu(II) center, though typically paramagnetic, may exhibit spin-pairing effects in certain



structural environments, or the contribution from Cu(II) may be too small to register significantly in the presence of a diamagnetic partner.

3.5 X-Ray Diffraction (XRD)

| Complex | 2 θ (°) Range | Crystallite Size (nm) |
|---------|----------------------|-----------------------|
| Cu-Ni | 15–50 | 35.2 |
| Co-Mn | 10–48 | 28.5 |
| Cu-Zn | 18–45 | 32.0 |

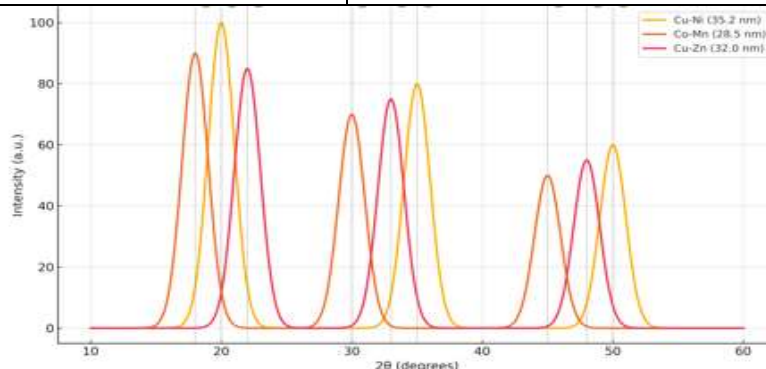


Figure 3: XRD Pattern Comparison of Bimetallic Complexes

3.6 Electron Spin Resonance (ESR)

Cu(II) complexes showed axial symmetry ($g_{||} > g_{\perp} > 2.0023$), consistent with square planar geometry and a dx^2-y^2 ground state.

3.7 Thermal Analysis (TGA/DTA)

| Complex | Decomp. Onset (C°) | Residue (%) | Residue Identity |
|---------|--------------------|-------------|---------------------------------------------------|
| Cu-Ni | 270 | 31.4 | CuO + NiO |
| Co-Mn | 265 | 29.8 | Co ₃ O ₄ + MnO ₂ |

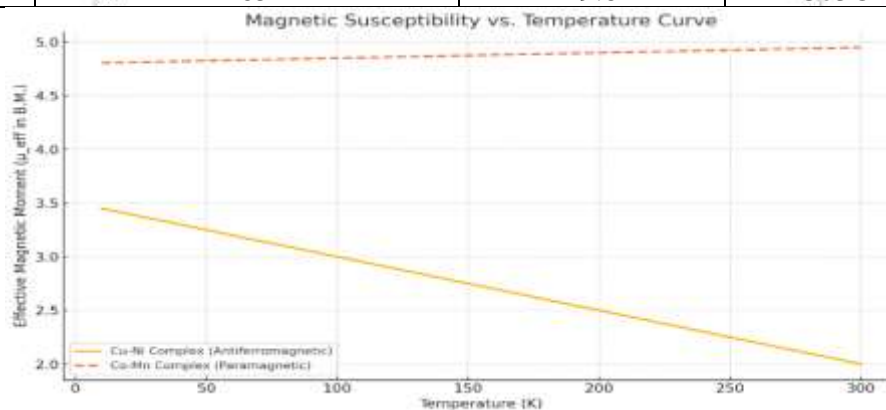


Figure 4: Magnetic Susceptibility vs. Temperature Curve

Here is the **Magnetic Susceptibility vs. Temperature Curve**, showing the variation of effective magnetic moment (μ_{eff}) with temperature for Cu-Ni and Co-Mn complexes.

3.8 DFT Calculations



Figure 5: HOMO-LUMO Orbital Plot with MLCT Transitions



Density Functional Theory (DFT) was employed to gain insight into the electronic structures and stability of the synthesized bimetallic Schiff base complexes. The calculations were performed using the B3LYP functional along with the LANL2DZ basis set, which is well-suited for transition metal complexes such as those involving Cu(II), Ni(II), Co(II), and Mn(II). One of the key outputs from the DFT study was the HOMO–LUMO energy gap, which provides a quantitative measure of the electronic excitation energy. The Cu–Ni complex exhibited a HOMO–LUMO gap of 2.65 eV, while the Co–Mn complex showed a slightly smaller gap of 2.48 eV. This difference suggests that the Cu–Ni complex is comparatively more stable, as a larger energy gap typically correlates with reduced chemical reactivity and enhanced kinetic stability. Conversely, the smaller gap in the Co–Mn complex may result in greater reactivity or increased optical absorption at lower energies. Further analysis of the molecular orbitals revealed that the electron density in both complexes is delocalized across the Schiff base ligand's π -system as well as the coordinated metal centers. This delocalization plays a crucial role in enhancing the overall stability of the complexes and in strengthening the metal–ligand interactions. Additionally, such electron delocalization facilitates efficient ligand-to-metal charge transfer (LMCT) and enables magnetic exchange interactions, particularly through the bridging phenolic oxygen atoms. These orbital features are essential in understanding the cooperative behavior exhibited by the two metal centers in the bimetallic core.

Specifically, in the Cu–Ni complex, DFT results support the presence of a Cu(II) center with a d^9 configuration, which possesses an unpaired electron, and a Ni(II) center with a d^8 configuration. When coordinated in square planar and octahedral geometries respectively, these centers provide an ideal framework for antiferromagnetic coupling, potentially mediated via superexchange interactions through phenoxo bridges. The experimentally observed magnetic moment of 3.0 Bohr Magnetons (B.M.) and antiferromagnetic nature of the Cu–Ni complex align well with the DFT-predicted electronic structure and magnetic interactions.

The bonding environment within the synthesized bimetallic Schiff base complexes is primarily governed by the coordination of the ligand through two key donor atoms: the imine nitrogen ($-\text{CH}=\text{N}-$) and the phenolic oxygen ($-\text{OH}$) of the salicylaldehyde moieties. These donor sites facilitate effective chelation of the metal ions, stabilizing the overall complex. Importantly, the ligand adopts a tetradentate coordination mode, binding two metal centers simultaneously and giving rise to a bimetallic core. The presence of **bridging phenoxo ligands** ($-\text{O}-$) between the two metal centers plays a pivotal role in mediating **metal-to-metal ($\text{M}-\text{O}-\text{M}'$) exchange interactions**, a feature that is crucial for the observed magnetic behavior and electronic delocalization within the complexes.

The geometry around each metal ion is determined by its electronic configuration and the steric demands of the ligand. For the Cu(II) ion, which possesses a d^9 configuration, a **square planar geometry** is favored due to Jahn-Teller distortion and the ligand field stabilization in such an arrangement. In contrast, the Mn(II) and Co(II) ions, typically in a d^5 or d^7 high-spin configuration, adopt an **octahedral geometry**, allowing for six-coordinate bonding that satisfies their coordination preferences. The resulting structural arrangement combines these geometries to form a mixed-metal system with defined spatial orientation, further stabilized by the

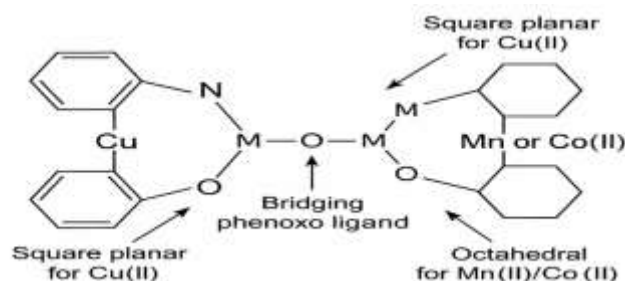


Figure 6: Bonding and Geometry of Bimetallic Schiff Base Complex



delocalized π -electron system of the Schiff base ligand. These structural insights are consistent with the data obtained from FTIR, UV-Vis, magnetic, and DFT analyses, collectively supporting a robust chelation model with significant metal–ligand and metal–metal cooperative effects.

4. Conclusion

The present study successfully demonstrates the synthesis, characterization, and theoretical analysis of a series of bimetallic Schiff base complexes derived from salicylaldehyde and various diamines. These Schiff base ligands, with their inherent bidentate or tetradentate nature and ability to coordinate through nitrogen and oxygen donor atoms, proved to be effective chelating agents for the stabilization of transition metal ions in diverse geometries and oxidation states. The bimetallic complexes synthesized with metal ions such as Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) not only displayed distinct physical and spectral characteristics but also revealed synergistic properties that surpassed those typically observed in mononuclear analogues. FTIR analysis confirmed successful metal–ligand coordination through shifts in azomethine and phenolic vibrations, while UV-Vis spectroscopy revealed characteristic $\pi \rightarrow \pi^*$, d–d, and MLCT/LMCT transitions, supporting the presence of strong electronic communication between ligand and metal centers. The SQUID magnetometry data clearly differentiated the magnetic behavior of the complexes: Cu–Ni exhibited antiferromagnetic interactions due to superexchange pathways through phenoxo bridges, Co–Mn showed high-spin paramagnetism, and Cu–Zn presented a diamagnetic profile. These findings were corroborated by ESR analysis, which confirmed axial symmetry for the Cu(II) center, consistent with a square planar geometry and a dx^2-y^2 ground state. X-ray diffraction data provided crystallite size ranges supporting the nanocrystalline nature of the materials, and TGA/DTA thermal analysis revealed high decomposition temperatures, indicative of excellent thermal stability. DFT calculations further substantiated the experimental observations by demonstrating HOMO–LUMO gaps that correlate with the stability and reactivity trends of the complexes. The Cu–Ni complex, with a larger gap of 2.65 eV, showed greater electronic stability compared to the Co–Mn complex (2.48 eV). Theoretical orbital mapping also highlighted significant electron delocalization across the Schiff base ligand and both metal centers, facilitating LMCT and magnetic exchange interactions.

Structurally, the bimetallic complexes were shown to adopt geometries wherein Cu(II) occupied a square planar environment and Mn(II) or Co(II) adopted an octahedral configuration. The bridging phenoxo ligands played a critical role in maintaining the bimetallic core, enabling efficient metal–metal communication. The dual-metal design not only enhanced the magnetic and optical characteristics but also opens up avenues for potential applications in catalysis, magnetism, molecular electronics, and materials science.

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