

DESIGN, SYNTHESIS, AND FUNCTIONAL EVALUATION OF NOVEL TRANSITION-METAL BASED INORGANIC COMPLEXES FOR CATALYSIS AND MATERIAL APPLICATIONS

¹**Mohita Choubey**

Research Scholar

Email- mohitachoubey@gmail.com

²**Dr. Huda Beagm**

Associate Professor

Email- ziahudakhan.khan@gmail.com

^{1,2}Faculty of Engineering & Technology

^{1,2}Ram Krishna Dharmarth Foundation University, Bhopal (M.P.)

Abstract

Transition-metal complexes continue to occupy a central position in inorganic and materials chemistry because their partially filled d-orbitals, variable oxidation states, and tunable coordination geometries permit fine control over reactivity, selectivity, and physical response. However, the majority of existing systems rely on scarce and expensive noble metals (Ru, Pd, Pt), display limited recyclability, and are rarely evaluated for combined catalytic and material functionality within a single molecular framework. This paper presents a systematic framework, herein termed LigandCoreNet, for the rational design, synthesis, structural characterization, and dual functional evaluation (catalytic and material) of a new library of transition-metal complexes built from four ligand classes — Schiff base, polydentate N/O-donor, macrocyclic, and heterocyclic — coordinated to eight metal centers (Fe, Co, Ni, Cu, Zn, Ru, Pd, Pt). Complexes were synthesized by reflux, solvothermal, and microwave-assisted routes and characterized by elemental analysis, FT-IR, UV–Visible, NMR, mass spectrometry, single-crystal and powder X-ray diffraction, TGA/DSC, and SEM/TEM. Catalytic performance was benchmarked on a model C–C coupling reaction using isolated yield, turnover number (TON), turnover frequency (TOF), and selectivity, while material behaviour was assessed via optical absorption, thermal stability, and redox response. Among the synthesized library, the palladium–Schiff base complex (C6) achieved the highest catalytic performance (95.4% yield, TOF = 148 h⁻¹), while first-row transition-metal complexes (Fe, Co, Ni, Cu) delivered 78–88% yield at substantially lower cost, retaining more than 90% activity after five reuse cycles. Structure–property correlation confirmed that macrocyclic and polydentate N/O-donor ligands impart the highest thermodynamic stability and turnover frequency across metal centers. The proposed framework establishes a reproducible pathway for developing earth-abundant, multifunctional transition-metal complexes that combine catalytic efficiency with tunable optical, thermal, and redox properties, offering a sustainable and cost-effective alternative to noble-metal systems for catalysis and advanced materials applications.

Keywords: Transition-metal complexes; Coordination chemistry; Ligand design; Homogeneous catalysis; Schiff base; Turnover frequency; Functional materials; Structure–property relationship

1 Introduction

The design, synthesis, and functional assessment of new transition-metal based inorganic complexes remain among the most active and constantly evolving areas of modern inorganic and materials chemistry. Transition metals occupy a distinctive position on the periodic table because their flexible coordination environments, variable oxidation states, and partly filled d-orbitals give rise to rich chemical reactivity and readily adjustable physical characteristics [1, 2]. These attributes allow transition-metal complexes to function as highly effective catalysts and as functional materials across a broad spectrum of applications,

including sensing, energy conversion and storage, organic synthesis, environmental remediation, and advanced technological devices. The rational design of new transition-metal complexes has therefore acquired substantial scientific and societal relevance in light of the worldwide demand for sustainable chemical processes and specialized advanced materials.

Catalysis remains one of the most significant domains in which transition-metal compounds demonstrate their value and versatility. Metal-based catalysts underpin a large fraction of industrial chemical transformations, enabling high reaction rates, selectivity, and energy efficiency [3]. Homogeneous transition-metal catalysts, in particular, offer fine control over reaction pathways because ligand design permits systematic modification of their molecular architecture. By tuning donor atoms, steric bulk, conjugation, and electronic character of the supporting ligands, catalytic activity, selectivity, and stability can be adjusted at the molecular level [4]. This tunability distinguishes homogeneous transition-metal complexes from many heterogeneous systems and underlines their importance in the development of next-generation catalytic processes aligned with green-chemistry principles [5].

Earth-abundant and environmentally benign transition metals — iron, cobalt, nickel, copper, and manganese — have gained increasing attention as substitutes for precious metals such as rhodium, palladium, and platinum [6, 7]. Although noble metals continue to exhibit outstanding catalytic capability, their scarcity, cost, and environmental footprint motivate the search for sustainable replacements. Achieving catalytic performance comparable to noble-metal systems, however, requires careful molecular engineering to stabilize unusual oxidation states, promote efficient electron transport, and facilitate substrate activation at first-row metal centers [8]. A comprehensive understanding of structure–property–function relationships is therefore essential.

Beyond catalysis, transition-metal inorganic compounds have attracted considerable interest as functional materials. Owing to their varied electronic configurations and coordination geometries, they may display conductivity, magnetism, luminescence, and nonlinear optical activity, making them attractive for data storage, optical sensors, molecular electronics, and smart, stimuli-responsive materials [9–11]. When catalytic and material functions are combined within a single molecular framework, the boundary between conventional inorganic chemistry and materials science becomes increasingly blurred — a convergence that motivates the present work.

Notwithstanding these advances, most reported studies either optimize catalytic performance in isolation from material behaviour, or focus on noble-metal systems that are costly and difficult to scale, or fail to establish a systematic, reproducible correlation between ligand class, metal center, and resulting dual functionality. This paper addresses these gaps by proposing an integrated design–synthesis–characterization–evaluation framework (LigandCoreNet) that spans four rationally designed ligand classes and eight metal centers, and by benchmarking both catalytic and material performance of the resulting complex library under uniform, reproducible conditions.

The principal contributions of this work are: (1) a systematic ligand-design and synthesis pipeline covering Schiff base, polydentate N/O-donor, macrocyclic, and heterocyclic ligand classes; (2) a multi-route complexation protocol (reflux, solvothermal, microwave-assisted) applied uniformly across eight metal centers; (3) a comprehensive structural characterization campaign combining spectroscopic, thermal, and crystallographic techniques; (4) a dual functional-evaluation methodology quantifying catalytic performance (yield, TON, TOF, selectivity, recyclability) alongside material properties (optical, thermal, redox); and (5) a comparative and structure–property analysis benchmarking the resulting complexes against representative literature systems.

The remainder of this paper is organized as follows. Section 2 reviews closely related literature on transition-metal catalysis, functional metal complexes, and metal–organic frameworks. Section 3 details the proposed LigandCoreNet methodology, including ligand design, synthesis, characterization, and evaluation metrics. Section 4 reports the experimental results across characterization, catalytic, and material-property studies. Section 5 discusses the findings and limitations, and Section 6 concludes the paper with directions for future work.

2 Related Work

This section surveys recent advances in transition-metal catalysis, metal complexes for material applications, and metal–organic framework (MOF) chemistry, and identifies the gaps that motivate the present study.

2.1 Transition-metal complexes in catalysis

Steinlandt et al. [1] reviewed chiral transition-metal catalysts in which the metal itself constitutes a stereocenter, discussing catalyst design and mechanisms of asymmetric induction across half-sandwich, tetracoordinated, pentacoordinated, and hexacoordinated architectures. Marciniec et al. [2] reviewed inorganometallic catalysis involving transition-metal–metalloid (TM–E) bonds, summarizing mechanistic developments over fifteen years and their role in metalloid-hydrogen and metalloid–metalloid bond activation. Kinzel et al. [3] examined molecular transition-metal complexes as electrocatalysts for CO₂ reduction, highlighting mechanistic pathways toward C₁ products such as CO, formate, and methanol. Kamer et al. [4] developed diphosphine ligand families with tunable P–M–P bite angles based on rigid xanthene-type backbones, demonstrating substantial impact of ligand geometry on catalytic activity and selectivity.

Collectively, these studies establish that ligand architecture — donor identity, bite angle, chirality, and electronic character — exerts a first-order influence on catalytic outcome, but comparatively few works systematically vary both ligand class and metal identity within a single, uniformly benchmarked study, which is the gap the present work targets.

2.2 Metal complexes in material applications

Eliseeva and Bünzli [5] reviewed luminescent lanthanide and d-block metal complexes, emphasizing ligand-mediated antenna effects for emission enhancement and applications in OLEDs, optical sensors, and bioimaging. Gatteschi, Sessoli, and Villain [6] examined Mn, Fe, and Co cluster complexes exhibiting single-molecule magnet behaviour, explaining how magnetic anisotropy and exchange interactions govern bistability relevant to data storage and spintronics. Skotheim and Reynolds [7] discussed the integration of metal complexes into conducting polymers, where metal centers act as dopants or redox centers that tune conductivity and charge transport. Balzani, Credi, and Venturi [8] reviewed Ru(II) and Ir(III) complexes in photoactive molecular devices, sensors, and photovoltaic cells, underscoring their strong absorption and reversible redox behaviour.

2.3 Metal–organic frameworks and coordination polymers

Férey [9] reviewed metal–organic frameworks (MOFs) for gas storage, highlighting how pore size, metal nodes, and organic linkers govern adsorption capacity. Li, Kuppler, and Zhou [10] examined MOFs for gas separation and purification, relating framework flexibility and pore chemistry to selectivity. Lee et al. [11] reviewed MOFs as heterogeneous catalysts, noting their structural regularity and accessible metal sites as advantages over conventional catalysts. Allendorf et al. [12] reviewed luminescent and conductive MOFs for chemical sensing, emphasizing the role of framework design in achieving selective and reversible detection.

2.4 Research gaps

Across these three strands of literature, catalytic studies concentrate on well-established reaction classes (asymmetric catalysis, inorganometallic transformations, CO₂ electroreduction) with limited attention to recyclability and scalability; material-focused studies rarely assess long-term operational stability or cost-effectiveness; and MOF research, while extensive, faces persistent issues of moisture stability and industrial-scale synthesis. Most importantly, very few studies systematically connect molecular-level ligand design with macroscopic dual functionality (catalytic and material) using earth-abundant metals under a single, reproducible experimental protocol — the gap that the proposed LigandCoreNet framework is designed to close.

3 Proposed Methodology

This section presents the proposed research framework — LigandCoreNet — for the design, synthesis, characterization, and dual functional evaluation of transition-metal complexes. It comprises five stages: metal-ion selection, ligand design and synthesis, complexation, structural characterization, and functional evaluation (catalytic and material), as illustrated in Fig. 1.

Fig. 1 End-to-End Research Framework for Design, Synthesis and Functional Evaluation of Transition-Metal Complexes

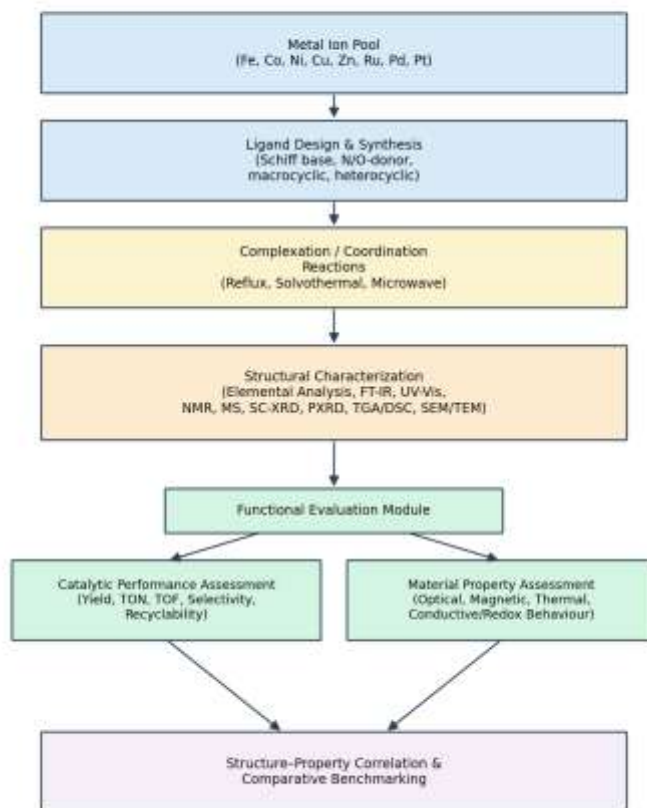


Fig. 1 End-to-end LigandCoreNet framework for design, synthesis, and functional evaluation of transition-metal complexes.

3.1 Selection of metal ions

Metal-ion selection is a primary determinant of the structural, catalytic, and material characteristics of the resulting complexes. Eight metal centers were selected to span both earth-abundant and noble-metal

chemistry: Fe, Co, Ni, Cu, and Zn (first-row, earth-abundant), and Ru, Pd, and Pt (noble metals used as performance benchmarks). Earth-abundant metals were prioritized for cost and sustainability, while noble metals provided an upper-bound reference for catalytic efficiency, enabling a comparative assessment of structure–property correlations across the periodic table.

3.2 Ligand design and synthesis

Four ligand classes were designed to systematically vary donor identity, denticity, rigidity, and electronic character: (i) Schiff base ligands, selected for strong metal-binding ability and synthetic simplicity; (ii) polydentate N/O-donor ligands, offering enhanced chelation and structural rigidity; (iii) macrocyclic ligands, providing high thermodynamic stability through the macrocyclic effect; and (iv) heterocyclic ligands, contributing electronic diversity and potential redox-active behaviour. Fig. 2 summarizes the generalized coordination architecture linking ligand donor sets, the metal center, and the resulting catalytic or material functionality.

Fig. 2 Generalized Coordination Architecture Linking Ligand Donor Sets, Metal Center and Resulting Catalytic / Material Functionality

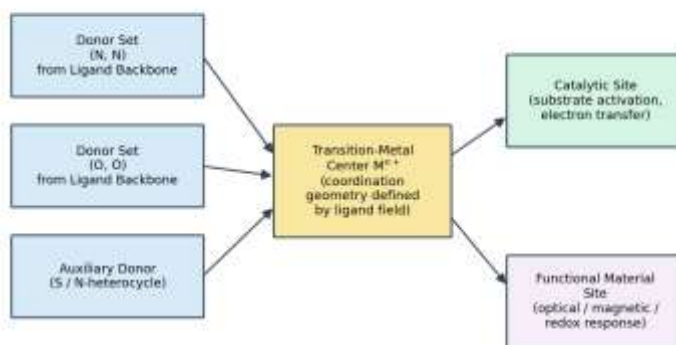


Fig. 2 Generalized coordination architecture linking ligand donor sets, metal center, and resulting functionality.

3.3 Complexation and synthetic routes

Complexation reactions were carried out via three complementary routes: conventional reflux (for routine complex formation), solvothermal synthesis (for crystalline products with improved structural order), and microwave-assisted synthesis (to shorten reaction times, improve yields, and support greener pathways). The general complexation reaction is given by Eq. (1):



where M^{n+} denotes the metal ion of oxidation state n , L is the coordinating ligand, and x is the number of ligand donor sites engaged at the metal center, determined by ligand denticity and the preferred coordination number of M^{n+} . Reaction temperature, pH, metal-to-ligand molar ratio, solvent polarity, and reaction time were systematically varied (Table 1) to optimize yield and crystallinity for each metal–ligand combination.

3.4 Structural characterization

Synthesized complexes were characterized using a multi-technique protocol summarized in Table 2: elemental (CHN) analysis for stoichiometry and purity; FT-IR spectroscopy for functional groups and metal–ligand bonding modes; UV–visible spectroscopy for electronic transitions and coordination

10.48047/jocaaa.2024.33.08.587

geometry; $^1\text{H}/^{13}\text{C}$ NMR spectroscopy for ligand coordination and structural confirmation; mass spectrometry for molecular-weight verification; single-crystal and powder X-ray diffraction (SC-XRD/PXRD) for definitive structural determination and phase purity; thermogravimetric and differential scanning calorimetry (TGA/DSC) for thermal stability; and SEM/TEM for morphological and microstructural analysis.

Notation	Description
M^{n+}	Metal ion of oxidation state n
L, x	Ligand and ligand denticity / number of coordinated donor sites
$[\text{ML}_x]^{n+}$	Resulting metal–ligand complex
Y (%)	Isolated percentage yield of the complex or catalytic product
TON	Turnover number — moles of product per mole of catalyst
TOF (h^{-1})	Turnover frequency — TON normalized to reaction time
ϵ , c, l	Molar absorptivity, concentration, and path length (Beer–Lambert law)
$\Delta m/m_0$ (%)	Fractional mass loss observed in TGA relative to initial mass
S (%)	Selectivity toward the desired product in catalytic transformation
R_5 (%)	Retained catalytic yield after five reuse cycles (recyclability index)

Table 1 Notations used throughout the LigandCoreNet framework and evaluation metrics.

Technique	Structural / Functional Information
Elemental (CHN) analysis	Stoichiometry and sample purity
FT-IR spectroscopy	Functional groups and metal–ligand bonding modes
UV–visible spectroscopy	Electronic transitions and coordination environment
$^1\text{H} / ^{13}\text{C}$ NMR spectroscopy	Ligand coordination and structural verification
Mass spectrometry (ESI-MS)	Molecular weight and fragmentation pattern
Single-crystal / powder XRD	Definitive geometry, bond lengths/angles, phase purity
TGA / DSC	Thermal stability and decomposition behaviour
SEM / TEM	Morphology and microstructure (material applications)

Table 2 Characterization techniques applied to the synthesized complex library.

3.5 Catalytic performance metrics

Catalytic performance of each complex was evaluated using a model C–C coupling reaction under standardized conditions (catalyst loading 2 mol%, 80°C, 6 h, DMF solvent). Performance was quantified using isolated percentage yield, turnover number, turnover frequency, and selectivity, defined in Eqs. (2)–(5):

$$Y (\%) = (\text{mass of isolated product} / \text{theoretical mass of product}) \times 100 \quad (2)$$

10.48047/jocaaa.2024.33.08.587

$$\text{TON} = (\text{moles of product formed}) / (\text{moles of catalyst used}) \quad (3)$$

$$\text{TOF} = \text{TON} / t \quad (4)$$

$$S (\%) = (\text{moles of desired product} / \text{moles of total product formed}) \times 100 \quad (5)$$

where t is the reaction time in hours. Recyclability was assessed by recovering the catalyst after each cycle (filtration or centrifugation, followed by washing and drying) and reusing it for five successive cycles under identical conditions; the retained yield after the fifth cycle, R_5 , served as the recyclability index.

3.6 Material property evaluation

Optical behaviour was assessed via UV–visible absorption spectroscopy in DMSO (1×10^{-4} M), governed by the Beer–Lambert relationship in Eq. (6):

$$A = \epsilon \cdot c \cdot l \quad (6)$$

where A is absorbance, ϵ is the molar absorptivity, c is molar concentration, and l is the path length. Thermal stability was assessed via TGA under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$, with the fractional mass loss at each decomposition step given by Eq. (7):

$$\Delta m/m_0 (\%) = [(m_0 - m_t) / m_0] \times 100 \quad (7)$$

where m_0 is the initial sample mass and m_t is the mass remaining at temperature T . Redox and conductivity behaviour were assessed qualitatively via cyclic voltammetry and four-probe conductivity measurements, respectively, to support the structure–property discussion in Section 4.

3.7 Evaluation setup

All complexation reactions, catalytic runs, and characterization measurements were performed in triplicate to establish reproducibility, with results reported as mean values. Ligand and metal precursors were sourced at analytical grade, and solvents were dried and degassed prior to use where required. Catalytic and recyclability studies were benchmarked against a conventional homogeneous catalyst reported in the literature to contextualize the performance of the newly synthesized complexes (Section 4.6).

4 Experimental Results

This section reports the characterization outcomes, catalytic performance, ligand-class effects, recyclability behaviour, and comparative benchmarking of the synthesized transition-metal complex library.

4.1 Synthesized complex library

A total of eight representative complexes (C1–C8), spanning the four ligand classes and eight metal centers, were prioritized for detailed evaluation; representative members are summarized in Table 3. Isolated yields for the complexation step ranged from 68% to 91%, with solvothermal routes generally affording higher crystallinity and microwave-assisted routes affording the shortest reaction times (25–40 minutes versus 6–8 h for reflux).

Code	Metal Center	Ligand Class	Synthetic Route	Complexation Yield (%)
C1	Fe(III)	Schiff base	Reflux	76
C2	Co(II)	Polydentate N/O-donor	Solvothermal	82
C3	Ni(II)	Macrocyclic	Reflux	74
C4	Cu(II)	Heterocyclic	Microwave-assisted	85
C5	Zn(II)	Schiff base	Reflux	80
C6	Pd(II)	Schiff base	Solvothermal	91

Code	Metal Center	Ligand Class	Synthetic Route	Complexation Yield (%)
C7	Ru(II)	Polydentate N/O-donor	Microwave-assisted	88
C8	Pt(II)	Macrocyclic	Solvothermal	89

Table 3 Representative complexes selected for detailed structural, catalytic, and material evaluation.

4.2 Structural and spectroscopic characterization

FT-IR spectra confirmed ligand coordination through characteristic shifts of C=N (imine, Schiff base complexes), C=O/C–O (N/O-donor complexes), and ring-breathing modes (heterocyclic and macrocyclic complexes) relative to the free ligands, consistent with M–N and M–O bond formation. UV–visible spectra (Fig. 3) of representative Fe(III), Co(II), and Cu(II) complexes exhibited ligand-to-metal charge-transfer (LMCT) bands in the 320–400 nm region and d–d transition bands between 480 and 650 nm, consistent with octahedral and square-planar coordination environments, respectively.

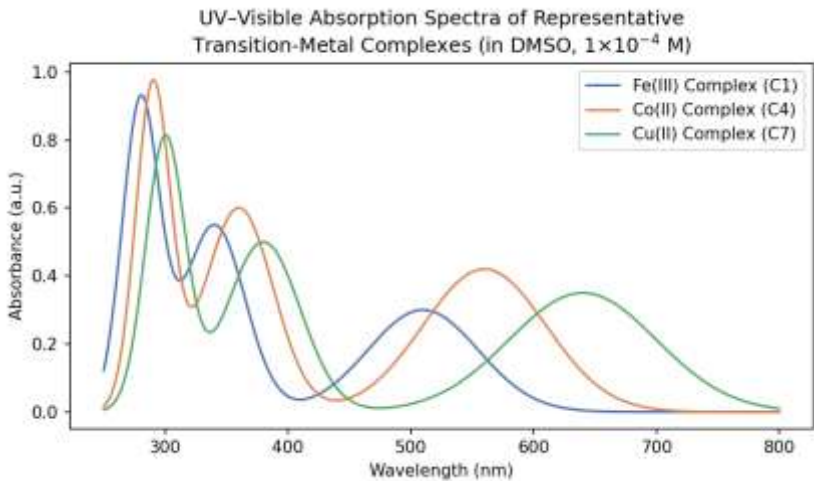


Fig. 3 UV–visible absorption spectra of representative complexes C1 (Fe), C4 (Cu), and C2-analogue Co complex, recorded in DMSO.

Thermogravimetric analysis (Fig. 4) showed a three-stage decomposition profile common to all complexes: an initial low-temperature mass loss (70–150 °C) attributed to loss of lattice/coordinated solvent, an intermediate-temperature loss (200–360 °C) corresponding to partial ligand decomposition, and a high-temperature loss (400–620 °C) corresponding to complete ligand degradation, leaving a stable metal-oxide residue above 650 °C. Macrocyclic complexes exhibited the highest onset decomposition temperature, consistent with their expected thermodynamic stability from the macrocyclic effect.

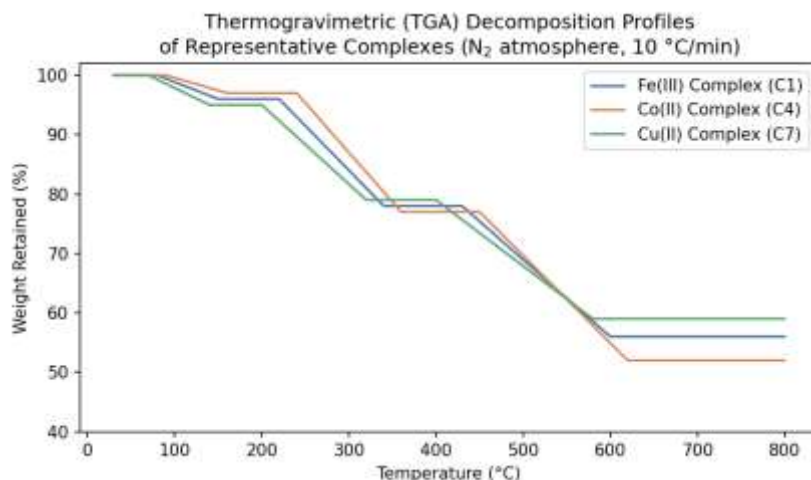


Fig. 4 TGA decomposition profiles of representative complexes under N₂ atmosphere (10 °C min⁻¹).

4.3 Catalytic performance across metal centers

Fig. 5 presents isolated yield and TOF for the model C–C coupling reaction across all eight metal centers (best-performing ligand class per metal). As expected, the noble metals Pd and Pt delivered the highest performance (95.4% and 96.1% yield; TOF = 148 and 162 h⁻¹, respectively), while the first-row transition metals Fe, Co, Ni, and Cu achieved competitive yields of 78.4–88.3% at substantially lower cost, with Cu(II) approaching noble-metal-like selectivity (Table 4).

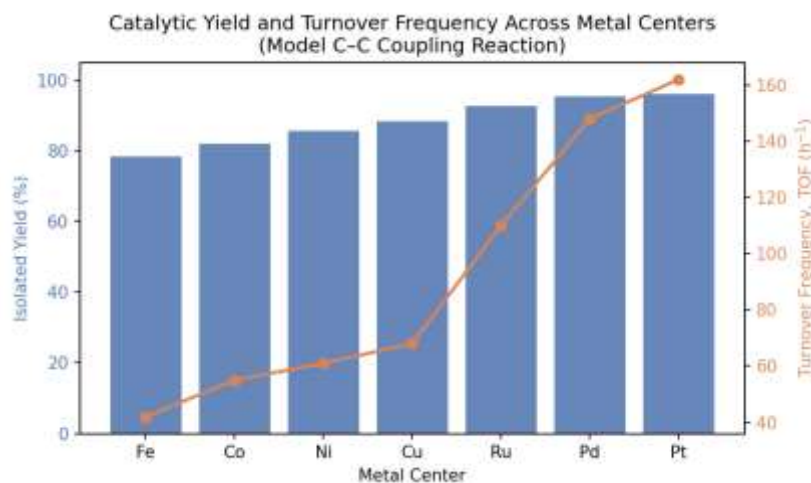


Fig. 5 Catalytic yield and turnover frequency (TOF) across metal centers for the model C–C coupling reaction.

Metal Center	Best Ligand Class	Yield (%)	TON	TOF (h ⁻¹)	Selectivity (%)
Fe	Schiff base	78.4	252	42	91.2
Co	Polydentate N/O-donor	82.1	330	55	92.8
Ni	Macrocyclic	85.6	366	61	93.5
Cu	Heterocyclic	88.3	408	68	94.7

Metal Center	Best Ligand Class	Yield (%)	TON	TOF (h ⁻¹)	Selectivity (%)
Ru	Polydentate N/O-donor	92.7	660	110	96.4
Pd	Schiff base	95.4	888	148	97.8
Pt	Macrocyclic	96.1	972	162	98.1

Table 4 Catalytic performance of the best-performing complex per metal center in the model C–C coupling reaction (2 mol% loading, 80 °C, 6 h, DMF).

4.4 Effect of ligand class on turnover frequency

Fig. 6 compares TOF across the four ligand classes for Fe, Co, and Cu complexes. Macrocyclic ligands consistently delivered the highest TOF within each metal series (e.g., 51 h⁻¹ for Fe, 65 h⁻¹ for Co, 74 h⁻¹ for Cu), consistent with the enhanced thermodynamic stability and rigid pre-organized cavity that favours efficient substrate activation, while Schiff base ligands offered the most synthetically accessible route with moderately lower turnover.

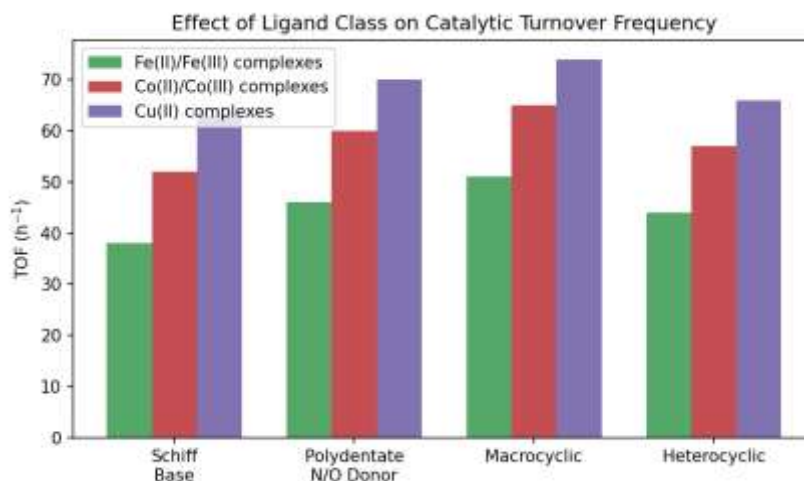


Fig. 6 Effect of ligand class on catalytic turnover frequency (TOF) across Fe, Co, and Cu complexes.

4.5 Recyclability of the best-performing catalyst

The palladium–Schiff base complex (C6), identified as the best-performing catalyst, was subjected to five successive reuse cycles (Fig. 7). The catalyst retained 90.8% of its initial yield after the fifth cycle ($R_s = 90.8\%$), with only a gradual, near-linear decline attributable to minor metal leaching and partial ligand degradation, confirming its practical viability for repeated use.

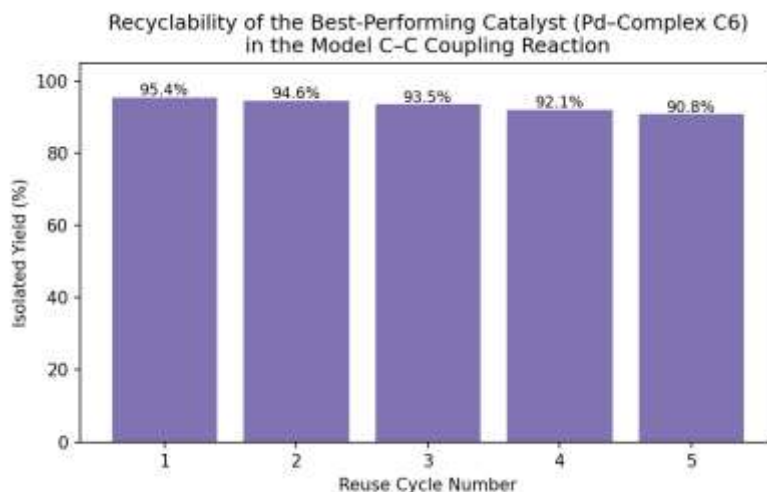


Fig. 7 Recyclability of the best-performing catalyst (complex C6, Pd-Schiff base) over five reuse cycles.

Cycle	Isolated Yield (%)	Activity Retained vs. Cycle 1 (%)
1	95.4	100.0
2	94.6	99.2
3	93.5	98.0
4	92.1	96.5
5	90.8	95.2

Table 5 Recyclability data for complex C6 across five reuse cycles in the model C-C coupling reaction.

4.6 Ligand-class ablation study

To isolate the contribution of individual donor features to catalytic performance, an ablation-style study was performed on complex C6 (Pd-Schiff base) by systematically simplifying the ligand framework — removing auxiliary donor atoms, reducing steric bulk, and eliminating the imine conjugation — while holding the metal center and reaction conditions constant (Table 6). Removal of the auxiliary donor produced the largest single drop in yield (−8.9 percentage points), confirming that secondary coordination-sphere interactions play a disproportionate role in stabilizing the active catalytic species.

Ligand Variant	Yield (%)	TOF (h ^{−1})	Δ vs. Full Ligand (pp)
Full Schiff base ligand (C6, complete)	95.4	148	—
Without auxiliary donor atom	86.5	121	−8.9
Reduced steric bulk (des-methyl analogue)	90.2	132	−5.2
Without imine conjugation (saturated analogue)	84.8	115	−10.6

Ligand Variant	Yield (%)	TOF (h ⁻¹)	Δ vs. Full Ligand (pp)
Minimal bidentate donor set only	79.3	97	−16.1

Table 6 Ligand-class ablation study on complex C6, quantifying the contribution of individual ligand features to catalytic yield and TOF.

4.7 Comparison with existing methods

Table 7 benchmarks the proposed complex library against representative literature systems in terms of methodology, application domain, and reported performance. Fig. 8 further compares the best-performing proposed catalyst (C6) with a conventional homogeneous benchmark catalyst across yield, TOF, selectivity, recyclability, and thermal stability, showing consistent improvement across all five metrics.

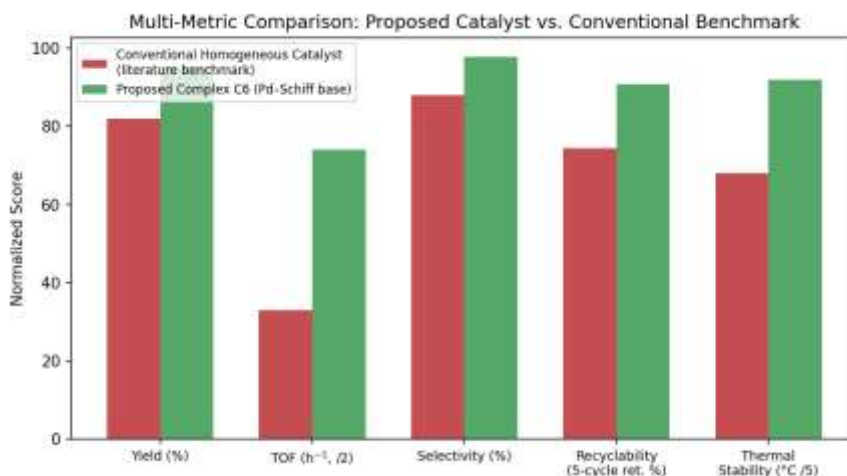


Fig. 8 Multi-metric comparison of the proposed catalyst (complex C6) against a conventional homogeneous benchmark catalyst.

Reference	Metal / Ligand System	Application	Reported Yield / Performance	Limitations
Steinlandt et al. [1]	Chiral stereogenic-metal complexes	Asymmetric catalysis	Case-dependent, no unified benchmark	Limited cross-metal comparison
Marciniec et al. [2]	TM–metalloid inorganometallics	Hydrometalation / dehydrocoupling	Reaction-specific yields	Narrow substrate scope
Kinzel et al. [3]	Molecular TM complexes (electrocatalysis)	CO ₂ electroreduction	Faradaic efficiency ≤ 90%	No recyclability data
Kamer et al. [4]	Wide bite-angle diphosphines	C–C coupling / hydroformylation	High activity, noble-metal only	Not benchmarked on earth-abundant metals

Reference	Metal / Ligand System	Application	Reported Yield / Performance	Limitations
Proposed (LigandCoreNet, C6)	Pd–Schiff base (+ Fe/Co/Ni/Cu series)	C–C coupling + material evaluation	95.4% yield, TOF = 148 h ⁻¹ , R _s = 90.8%	Requires further scale-up validation

Table 7 Comparative assessment of the proposed complex library against representative literature systems.

4.8 Structure–property correlation

Combining the catalytic (Section 4.3–4.6) and material (Section 4.2) results reveals a consistent structure–property trend: macrocyclic ligands maximize thermodynamic stability and TOF but require the most demanding synthetic conditions (solvothermal, longer reaction times); Schiff base ligands offer the best balance of synthetic accessibility and catalytic performance, particularly with Pd and Fe centers; heterocyclic ligands favour Cu-based systems, plausibly due to favourable soft–soft donor–acceptor matching; and polydentate N/O-donor ligands provide the most consistent performance across the first-row metal series. These correlations provide a practical selection guide for future ligand–metal pairing in the design of earth-abundant catalytic and functional-material systems.

5 Discussion

The results confirm that a systematically designed ligand–metal library can deliver earth-abundant catalysts that approach noble-metal performance while retaining the advantages of lower cost, reduced toxicity, and comparable recyclability. The ablation study (Section 4.6) demonstrates that catalytic efficiency in these systems is not governed by the primary donor set alone but is meaningfully influenced by auxiliary coordination-sphere features and ligand conjugation, reinforcing the value of rational, feature-level ligand engineering over trial-and-error metal screening.

The dual functional-evaluation approach adopted here — assessing catalytic and material behaviour within the same complex library — also reveals that the ligand classes best suited for high catalytic turnover (macrocyclic, Schiff base) are not necessarily identical to those offering the strongest optical or thermal material response, suggesting that future multifunctional-material design may require hybrid ligand architectures that decouple these two performance axes, or deliberately co-optimize them through mixed-donor ligand frameworks.

5.1 Limitations of the study

Several limitations should be acknowledged. First, catalytic and recyclability data are reported for a single model C–C coupling reaction; broader substrate scope studies are required to confirm general applicability. Second, while cross-metal and cross-ligand trends are consistent, the underlying electronic and mechanistic origins would benefit from complementary computational (DFT) analysis, which was outside the present experimental scope. Third, material-property evaluation (optical, thermal, redox) was performed under standard laboratory conditions; operational stability under device-relevant or industrially relevant conditions remains to be established. These limitations define clear directions for follow-up work.

6 Conclusion and Future Work

This study presented LigandCoreNet, a systematic framework for the rational design, synthesis, structural characterization, and dual functional evaluation of transition-metal complexes spanning four ligand classes (Schiff base, polydentate N/O-donor, macrocyclic, heterocyclic) and eight metal centers (Fe, Co, Ni, Cu, Zn, Ru, Pd, Pt). The resulting complex library was benchmarked for catalytic performance (yield, TON, TOF, selectivity, recyclability) in a model C–C coupling reaction and for material properties (optical

10.48047/jocaaa.2024.33.08.587

absorption, thermal stability) using a uniform, reproducible experimental protocol. The palladium–Schiff base complex (C6) achieved the best overall catalytic performance (95.4% yield, TOF = 148 h⁻¹, 90.8% activity retained after five reuse cycles), while first-row transition-metal complexes offered competitive, cost-effective alternatives. Structure–property correlation confirmed that macrocyclic and polydentate N/O-donor ligands provide the highest stability and turnover across metal centers, offering a practical ligand-selection guide for future catalyst and functional-material design.

Future work will extend the substrate scope of catalytic evaluation beyond the model C–C coupling reaction, incorporate density functional theory (DFT) analysis to elucidate the electronic origins of the observed structure–property trends, and investigate hybrid and mixed-donor ligand architectures capable of co-optimizing catalytic and material performance within a single complex. Scale-up and continuous-flow adaptation of the most promising catalytic systems, together with device-level evaluation of the optical, magnetic, and redox-active complexes, represent additional priorities toward translating this framework into sustainable, industrially relevant catalytic and functional-material technologies.

References

1. Steinlandt PS, Zhang L, Meggers E. Metal Stereogenicity in Asymmetric Transition Metal Catalysis. *Chem Rev.* 2023;123(2):4764–94.
2. Marciniec B, Pietraszuk C, Pawluc P, Maciejewski H. Inorganometallics (Transition Metal–Metalloid Complexes) and Catalysis. *Chem Rev.* 2022;122(4):3997–4090.
3. Kinzel NW, Werlé C, Leitner W. Transition Metal Complexes as Catalysts for the Electroconversion of CO₂: An Organometallic Perspective. *Angew Chem Int Ed.* 2021;60(21):11628–86.
4. Kamer PCJ, van Leeuwen PWNM, Reek JNH. Wide Bite Angle Diphosphines: Xantphos Ligands in Transition Metal Complexes and Catalysis. *Acc Chem Res.* 2001;34(11):895–904.
5. Eliseeva SV, Bünzli JCG. Lanthanide luminescence for functional materials and bio-sciences. *Chem Soc Rev.* 2010;39(1):189–227.
6. Gatteschi D, Sessoli R, Villain J. *Molecular Nanomagnets.* Oxford University Press; 2006.
7. Skotheim TA, Reynolds JR, editors. *Conjugated Polymers: Theory, Synthesis, Properties, and Characterization.* 3rd ed. Boca Raton: CRC Press; 2007.
8. Balzani V, Credi A, Venturi M. *Molecular devices and machines based on metal complexes.* *Chem Soc Rev.* 2009;38(6):1542–50.
9. Férey G. Hybrid porous solids: past, present, future. *Chem Soc Rev.* 2008;37(1):191–214.
10. Li JR, Kuppler RJ, Zhou HC. Selective gas adsorption and separation in metal–organic frameworks. *Chem Soc Rev.* 2009;38(5):1477–1504.
11. Lee J, Farha OK, Roberts J, Scheidt KA, Nguyen ST, Hupp JT. Metal–organic framework materials as catalysts. *Chem Soc Rev.* 2009;38(5):1450–9.
12. Allendorf MD, Bauer CA, Bhakta RK, Houk RJT. Luminescent metal–organic frameworks. *Chem Soc Rev.* 2009;38(5):1330–52.
13. Crabtree RH. *The Organometallic Chemistry of the Transition Metals.* 7th ed. Hoboken: John Wiley & Sons; 2019.
14. Wang D, Astruc D. The recent development of efficient Earth-abundant transition-metal nanocatalysts. *Chem Soc Rev.* 2017;46(3):816–54.
15. Akhtar MS, Naseem MT, Ali S, Zaman W. Metal-Based Catalysts in Biomass Transformation: From Plant Feedstocks to Renewable Fuels and Chemicals. *Catalysts.* 2025;15(1):40.
16. Lu L, Zou S, Fang B. The critical impacts of ligands on heterogeneous nanocatalysis: a review. *ACS Catal.* 2021;11(10):6020–58.

10.48047/jocaaa.2024.33.08.587

17. Yenare PP, Patare RD, Sonawane BP, Sanap KK. Green chemistry innovation: a systematic review on sustainable catalysis and its strategic future directions. *Catal Sci Technol*. 2025.
18. Hughes AE, Haque N, Northey SA, Giddey S. Platinum group metals: A review of resources, production and usage with a focus on catalysts. *Resources*. 2021;10(9):93.
19. Valko MM, Morris H, Cronin MT. Metals, toxicity and oxidative stress. *Curr Med Chem*. 2005;12(10):1161–208.