

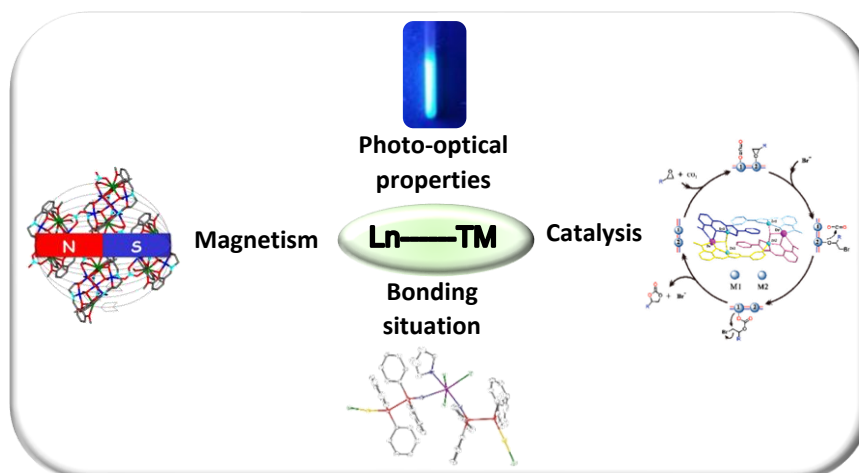


HETEROBIMETALLIC 3D-4F COMPLEXES: SYNTHESIS STRATEGIES AND MULTIFACETED APPLICATIONS

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The synthesis of heterobimetallic complexes, combining rare earth and transition metal ions, present inherent challenges, yet offers significantly enhanced utility compared to their monometallic counterparts. The developing field of these heterobimetallic complexes, highlights their high potential in catalysis, photoluminescence, and magnetism. In terms of catalysis, Ni–Lu complexes can efficiently lead to the catalytic hydrogenation of diphenylacetylene (DPA) to (*E*)-stilbene by tuning the Ni coordination sphere through the presence of highly Lewis acidic lanthanide ions in very close proximity.^[1] Hexanuclear 3d(Zn²⁺)-4f(Dy³⁺, Nd³⁺, Tb³⁺) complexes can also efficiently catalyse the conversion of CO₂ to cyclic carbonates,^[2] while Ni-RE(Sc³⁺, Y³⁺, La³⁺, Lu³⁺)-based bimetallic catalysts show tunable electronics and efficient catalytic activities towards alkyne semihydrogenation.^[3] Apart from hydrogenation, hetero bimetallic complexes also catalyze polymerization reactions, such as the ring-opening polymerization of lactones, where Y complexes with ferrocene-based ligands act as catalysts.^[4] In addition to their catalytic applications, TM–Ln bimetallic complexes exhibit large magnetic moments. The RE metals, renowned for their magnetic properties, when combined with transition metals (TM) and a suitable ligand, the single-molecule magnet (SMM) properties are enhanced by reducing quantum tunneling of magnetization (QTM). A notable example is [Cr₂Dy₂(OMe)₂(O₂CPh)₄(mdea)₂(NO₃)₂], which demonstrates strong 3d-4f exchange interactions, enhancing their effectiveness as SMMs.^[5] The TM-Ln complexes also show great luminescence properties. The TM antenna effect boosts RE luminescence, thereby rendering photo-optical properties to the complex.^[6] A carboxylic acid derivative served as the bridging ligand in a Ir³⁺–Eu³⁺ system where partial transfer of excited state energy from Ir³⁺ to Eu³⁺, resulted in white light emission.^[7] Overall, these studies show that RE/TM bimetallic complexes performs significantly well and sometimes seem to outperform their monometallic counterparts, making them promising candidates for advancements in catalysis, magnetism, and more.



Synthesis strategy of heterobimetallic complexes for diverse applications

Synthesizing heterobimetallic RE/TM complexes is challenging, since it often results in the formation of either TM- or RE-based complexes. The typical synthetic strategy involves two key steps^[8–11]: firstly choosing ligands based on HSAB theory,^[12] with two coordination sites—RE metals (hard acids) binding to O donors, and TM metals (soft acids) binding to N or P donors and secondly facilitating self-assembly by introducing suitable co-ligands. This multidentate ligand environment allows the combination of lanthanide ions with transition metal ions.

➤ Catalytic Activity

Heterobimetallic complexes of Ni(0) with trivalent rare-earth ions (Sc, Y, La, Lu) or Ga³⁺ and ligand (L=[ⁱPr₂PCH₂NPh]⁻) were characterized as catalysts for the hydrogenation of diphenylacetylene (DPA) to (*E*)-stilbene. Each complex features a short Ni–RE/Ga bond (2.3 Å to 2.5 Å) and anodic peak potentials (–0.48 V to –1.23 V) inversely linked to RE(III) Lewis acidity. The Lewis acidity and ionic size of the RE ions in the complexes had a huge impact towards the catalytic activity. Weak Lewis acidity and large ionic size of rare-earth supports, such as in Ni–Y, Ni–Lu, and Ni–La, promote strong Ni–alkyne binding due to enhanced π -back-bonding into the alkyne unit and providing an open coordination site for phosphine ligand hemilability. Ni–Y/Lu/Ga exhibited high DPA conversion, with NiYL₃ most selective for (*E*)-stilbene. Ni–Ga showed fastest rates in both DPA hydrogenation and (*Z*)-stilbene isomerization, followed by Ni–Sc.^[13]

➤ Magnetic Properties

Designing 3d-4f Single-Molecule Magnets (SMMs) with significant anisotropic barriers and blocking temperatures is a challenging research area in physics and chemistry. The coordination environment around the 3d or 4f metal ions and the ligand field are crucial for the system's magnetic anisotropy. Recent reviews have outlined key synthetic requirements:^[14]

(a) Ligands should bind strongly to oblate 4f ions (Ce^{3+} , Pr^{3+} , Nd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+}) in the axial positions and to prolate 4f ions (Pm^{3+} , Sm^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+}) in the equatorial positions to minimize charge contact with the axial f element electron density.

(b) Multidentate ligands are preferred for combining 3d and 4f ions.

(c) Ligands should promote magnetic interaction between 3d and 4f ions by establishing maximum oxygen bridges.

(d) Intermolecular interactions should be as weak as possible.

Although no definitive ligands are established for creating strong 3d-4f SMMs, polyalkoxo ligands and Schiff bases of salicylaldehyde are commonly used.

Sixteen new binuclear $[\text{ZnLn}]$, $[\text{NiLn}]$, and $[\text{CuLn}]$ complexes were synthesized using ligands derived from o-vanillin with either 2-aminomethylpyridine or 2-(2-aminoethyl)pyridine. Subtle structural differences among the complexes were attributed to the stereochemical preferences of the 3d metal ions. Ferromagnetic exchange interactions were found in Cu^{2+} – Gd^{3+} , Ni^{2+} – Gd^{3+} , and Ni^{2+} – Ho^{3+} complexes, highlighting the potential of these complexes in magnetic applications.^[8]

➤ Photo-optical properties

Despite the extensive use of rare earths in analytical sensors, immunoassays, imaging techniques,^[15–17] organic light-emitting diodes, and optical communication^[18] for their luminescent properties, direct population of the f–f energy levels of lanthanide ions is hindered. This limitation arises from their very low absorption coefficients due to the formally forbidden f→f transitions under the Laporte rule. Complexation with transition metals enhanced the photoluminescence properties observed in these systems due to the antenna effect.

A carboxylic acid derivative of 2-(5-phenyl-4H-[1,2,4]triazol-3-yl)-pyridine served as the bridging ligand in a Ir^{3+} – Eu^{3+} system.^[7] It coordinated to Ir^{3+} at (N^N) sites, while its carboxyl group coordinated to Eu^{3+} . This arrangement facilitated partial transfer of excited state energy from Ir^{3+} to Eu^{3+} , resulting in white light emission. Many d-block metals can effectively sensitize NIR-emitting lanthanides due to their appropriate energy levels. Notably, Cr^{3+} enhances the excited state lifetimes of Nd^{3+} , Yb^{3+} , and Er^{3+} . Complexes containing Pt^{2+} and Ir^{3+} have tuneable excited state energy levels, making them ideal antennae for visible-light-sensitized Eu^{3+} emission. From the X-ray diffraction data it was found that the nonbonding distances between the two hetero metals in the Ir^{3+} – Eu^{3+} bimetallic complex was around 6 Å. Photophysical studies revealed efficient red luminescence from Eu^{3+} sensitized by Ir^{3+} 's MLCT energy.^[6]

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