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# Metallacrowns: an ideal platform for accessing lanthanide luminescence

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Metallacrowns (MCs) are a distinctive class of metallamacrocycles that serve as inorganic counterparts to the well-known crown ethers, in which the characteristic  $-[C-O-O]-$  repeating units are replaced by  $-[M-N-O]-$  motifs. Much like their organic analogues, the donor oxygen atoms within the MC framework can capture cations in the central cavity. The modifiable nature of MCs provides remarkable structural diversity, as both ring-forming ligands and metal ions can be varied to tune and modify the chemical and physical properties of corresponding MC. In this minireview, we focus specifically on metallacrowns bearing gallium(III) as the ring metal, highlighting their structural versatility as well as the properties and applications of  $Ga^{III}-Ln^{III}$  heterometallic MCs. We begin by introducing the first  $Ga^{III}$ -based MC and trace the structural evolution of this family of MCs toward systems incorporating  $Ln^{III}$  ions with intriguing photophysical properties that open avenues for diverse functional and applied uses.

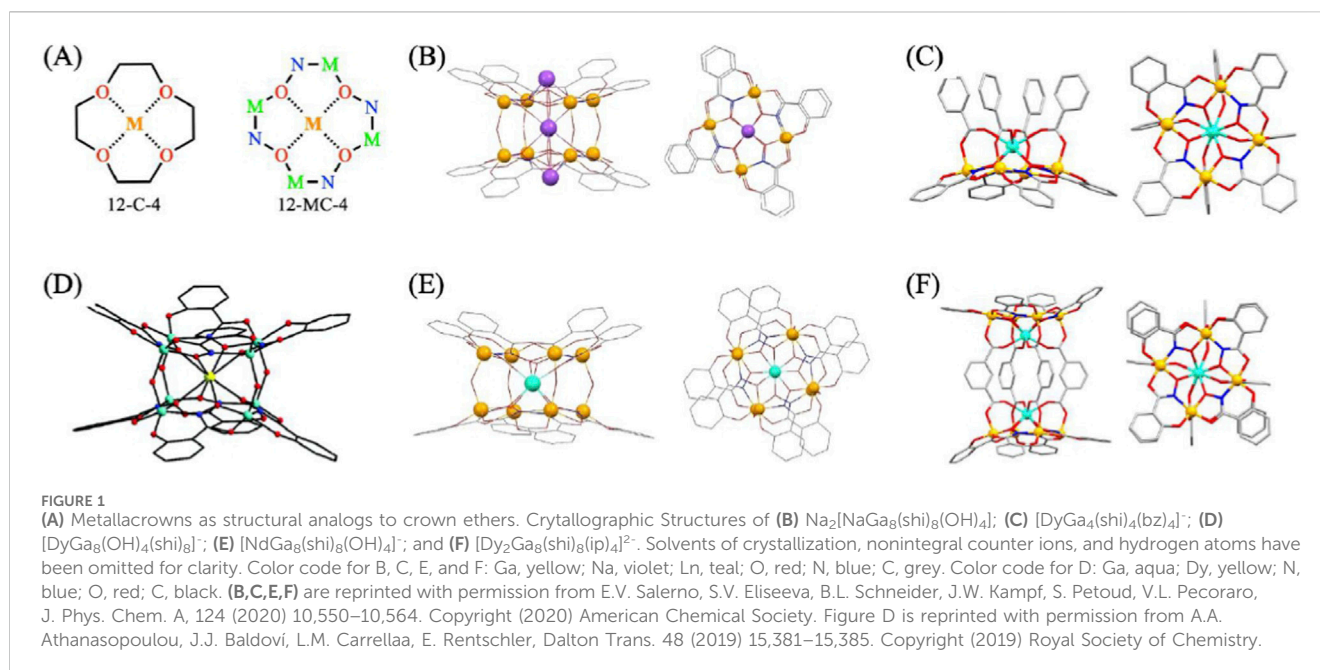
## KEYWORDS

metallacrowns, supramolecular, lanthanide luminescence, nanothermometry, white-light emission, biological imaging

## Introduction

Metallacrowns (MC) are metal-rich macrocyclic frameworks described by Pecoraro and coworkers in 1989 (Lah and Pecoraro, 1989; Lah and Pecoraro, 1990). Structurally similar to organic crown ethers, metallacrowns feature repeating  $-[M-N-O]-_n$  units in place of methylene groups in a cyclic arrangement, with oxygen donor atoms oriented inward capable of binding metal cations within the central cavity (Figure 1A). This family of metallamacrocycles is constructed using multidentate ligands capable of coordinating several metal ions, typically a hydroximate-based ligand whose N-O donor components bind two  $M^{n+}$  ions as part of a fused chelate ring. In addition to the ligand selection, (Ostrowska et al., 2019; Ostrowska et al., 2022), several other factors such as the choice of ring metal (Lutter et al., 2022; Jankolovits et al., 2013; Yang et al., 2020), counter-ion (Zhuang et al., 2022), solvent (Zaleski et al., 2007a; Jankolovits et al., 2014), and stoichiometry (Beccia et al., 2011) should also be considered in the synthesis of MCs. The broad selection of the ring metals and ligands has led to a diversity of MC structures with different size (e.g., 9-MC-3 to 60-MC-20), composition, and 3-dimensional topology (Johnson et al., 2003) described over more than 3 decades (Mezei et al., 2007).

In recent years, trivalent lanthanide ions ( $Ln^{III}$ ) have attracted considerable research interests owing to their luminescence and magnetic properties. The first example of a metallacrown incorporating an *f*-block metal ion was reported in 1996 based on efforts to design and develop agents capable of selectively binding rare earths over other hard metal ions such as  $Ca^{2+}$ . This planar 15-MC-5 structure, featuring  $Cu^{II}$  as the ring metal, was shown to bind the uranyl cation

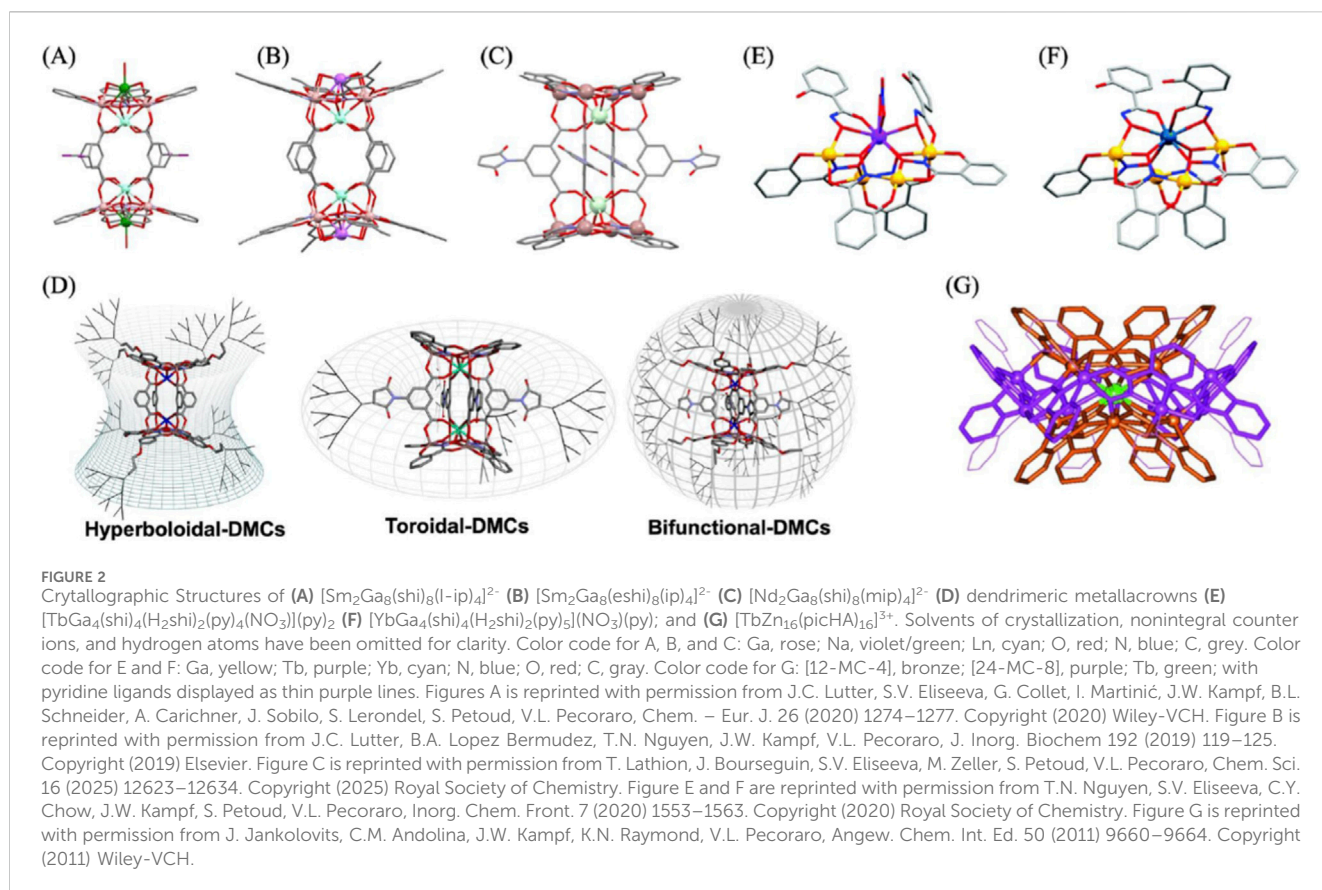


( $\text{UO}_2^{2+}$ ) preferentially over  $\text{Cu}^{\text{II}}$  and  $\text{Ca}^{2+}$  (Stemmler et al., 1996). In the following years, an alternative planar 12-MC-4 with  $\text{Mn}^{\text{III}}$  as ring metals and lanthanides as central guests (Azar et al., 2014), as well as more complex metallacrowns containing  $\text{Mn}^{\text{III}}$  in the ring positions and  $\text{Ln}^{\text{III}}$  in the central metal positions (Zaleski et al., 2004; Zaleski et al., 2007b; Boron et al., 2010), were also reported. These and related structures were instrumental for the development of numerous lanthanide-containing metallacrowns with various applications in magnetism and molecular recognition (Bodwin et al., 2001; Chow et al., 2015a; Zaleski, 2022; Lutter et al., 2018; Gil et al., 2022; Katkova et al., 2018; Pavlishchuk et al., 2018; Naseri et al., 2025). In fact, owing to their rigid and preorganized coordination environments that place multiple metal centers in close proximity, MCs have been exploited to stabilize high-anisotropy  $\text{Ln}^{\text{III}}$  ions. This has led to the development of several single-molecule magnets (SMMs) and single-ion magnets (SIMs) based on the MC platform (Happ et al., 2015; Li et al., 2015; Deb et al., 2014; Athanasopoulou et al., 2019; Wu et al., 2021; Pavlishchuk et al., 2024). As magnetism lies beyond the scope of this minireview, we direct interested readers to the cited literature for a more comprehensive discussions. Nevertheless, it was not until 2011 that the remarkable luminescence properties of lanthanide-containing metallacrowns were identified (Jankolovits et al., 2011). Lanthanide MCs have high thermodynamic stability and avoid typically limiting restrictions such as vibrational quenching from high energy oscillators and quenching solvent interactions (Bünzli and Piguet, 2005) by offering a highly encapsulated environment. The hydroxamic acid ligands also serve as a built-in antenna that are photostable, with high extinction coefficients. While cryptates (e.g.,  $[\text{Ln}(\text{cbpy})_2(\text{CO}_2\text{Et})_2]^{3+}$ ) (Vila-Nova et al., 2004) are well-known for their ability to surround the central lanthanide ion, expelling solvent molecules from the first coordination sphere, they often suffer from vibrational quenching. While offering high kinetic stability, their synthesis often requires multistep procedures, and their encapsulation is generally less rigid than that of MCs.  $\beta$ -diketonate complexes (e.g.,  $[\text{Eu}(\text{terpy})(\text{hfac})_3]$ ) (Xian et al., 2024) exhibit high quantum yields, but suffer from poor

photostability under UV light. Their open coordination environment leaves the lanthanide exposed to solvent, leading to solvent quenching and vibrational deactivation. Lanthanide-containing porous coordination polymers, such as lanthanide-based MOFs, offer high modularity and tunable luminescence properties due to the ability to host molecules within their network pores that can influence the lanthanide emission (Binnemans, 2009). However, these extended porous frameworks often introduce guest-molecule interactions that can enhance non-radiative deactivation of the  $\text{Ln}^{\text{III}}$  center luminescence, which limits their applications to Ln-based luminescent sensors and are of a sufficiently large size to fall outside the range for molecular applications (Zhao et al., 2018). One of the most important lanthanide-based luminescent materials, being used commercially, are known as Lumiphors, which are based on macrocyclic bifunctional chelators IAMs<sup>1</sup>, TAMs<sup>2</sup>, and HOPOs<sup>3</sup>. Their  $\text{Tb}^{\text{III}}$  complexes, with high quantum yields ( $\Phi_{\text{total}} \geq 50\%$ ) and large extinction coefficients ( $\geq 20,000 \text{ M}^{-1}\text{cm}^{-1}$ ), are among the brightest lanthanide luminescent materials (Supplementary Table S1) (Xu et al., 2011).

The first luminescent Ln-MC formed by self-assembly upon the reaction between picoline hydroxamic acid ( $\text{H}_2\text{picHA}$ ), sodium hydroxide, zinc(II) triflate, and lanthanide(III) nitrate in methanol ( $\text{Ln}^{\text{III}}\text{-Zn}^{\text{II}}$  metallacrowns, where  $\text{Ln}^{\text{III}} = \text{Y, La, Sm, Eu, Gd, Dy, Tb, and Yb}$ ) (Jankolovits et al., 2011). Single-crystal X-ray analysis of the resulting  $\text{LnZn}_{16}$  metallacrowns revealed a unique “encapsulated sandwich” architecture. In this structure, two concave  $[\text{12-MC}_{\text{Zn}}^{\text{II}}\text{N}(\text{picHA})\text{-4}]$  units sandwich an eight-coordinate  $\text{Ln}^{\text{III}}$  ion, and the entire assembly is further encapsulated within the cavity of

- 1 Hydroxyisophthalamides
- 2 Dihydroxyterephthalamides
- 3 Hydroxypyridinones



an outer  $[\text{24-MC}_{\text{Zn}^{\text{II}}\text{N}(\text{picHA})\text{-8}}$  ring (Figure 2G). This topology effectively excluded C-H oscillators from the proximity of the central lanthanide, with the nearest C-H bond located 6.7 Å away from the  $\text{Ln}^{\text{III}}$  ion, and no solvent molecules bound to the central lanthanide. Photophysical measurements on  $\text{Yb}^{\text{III}}$  and  $\text{Nd}^{\text{III}}$  analogues exhibited bright luminescence, demonstrating that the unique MC architecture can enable near-infrared emission by protecting the lanthanide center from high-energy oscillators (Jankolovits et al., 2011). Building on their promising luminescence properties, the library of encapsulated sandwich  $\text{LnZn}_{16}$  metallacrowns was expanded by including isostructural analogues with quinaldine- ( $\text{quinHA}^{2-}$ ) (Trivedi et al., 2014) and pyrazine- ( $\text{pyzHA}^{2-}$ ) (Martinić et al., 2017a) hydroximate ligands to either shift the excitation wavelengths or increase water solubilities, respectively. In recent years, several research groups worldwide have also explored lanthanide luminescence in MC frameworks using other diamagnetic metals, such as  $\text{Al}^{\text{III}}$  and  $\text{Cd}^{\text{II}}$ , whose optical inertness is crucial for exploiting the intrinsic properties of the central  $\text{Ln}^{\text{III}}$  ion (Eliseeva et al., 2022a; Li et al., 2025).

In this minireview, however, we focus on lanthanide-containing metallacrowns that use the closed-shell  $\text{Ga}^{\text{III}}$  ion as the ring metal and salicylhydroximate ( $\text{shi}^{3-}$ ) as the ring-forming ligand, which also initially served as the antenna. The colorless and diamagnetic nature of the  $\text{Ga}^{\text{III}}$  ion, together with its hard Lewis acid character that promotes exceptionally strong and kinetically stable bonds with the  $\text{shi}^{3-}$  ligand, provides an ideal platform for investigating lanthanide luminescence. Additionally, the compatibility between the +3 charge

of the ring metal and the deprotonation state of the ring ligand helps maintain charge balance within the MC framework.

## $\text{Ln}(\text{III})/\text{Ga}(\text{III})$

The first example of a main group metal-based MC was reported in 1993, describing a dimeric gallium-based 12-MC-4 that captured one sodium ion between two  $12\text{-MC}_{\text{Ga}^{\text{III}}\text{N}(\text{shi})\text{-4}}$  metallamacrocycles and linked via four hydroxide bridges between  $\text{Ga}^{\text{III}}$  with two additional sodium ions bound to the outer faces (Figure 1B) (Lah et al., 1993). Despite this early report, main group MCs had remained relatively unexplored until the mid-2010s. The major breakthrough occurred in 2016 with the synthesis, structural characterization, and photophysical investigation of a new family of  $\text{Ln}^{\text{III}}\text{-Ga}^{\text{III}}$  metallacrowns. The resulting systems adopted the archetypical  $\text{Ln}^{\text{III}}[\text{12-MC}_{\text{Ga}^{\text{III}}\text{N}(\text{shi})\text{-4}}](\text{bz})_4$  framework ( $\text{Ln}^{\text{III}} = \text{Sm}\text{-Yb}$ ) and exhibited photophysical properties, with the ability to sensitize emission from many trivalent lanthanide ions including Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb. Notably, the  $\text{Dy}^{\text{III}}$  and  $\text{Sm}^{\text{III}}$  analogues emit in both the visible and near-infrared (NIR) regions, while the  $\text{YbGa}_4$  MC possesses rather a strong emission in the NIR with an observed quantum yield of 5.88% in the solid state (Chow et al., 2016). Single-crystal structural analysis of the  $\text{Dy}^{\text{III}}$  analogue revealed a pseudo-fourfold symmetry for the 12-MC-4 unit, composed of four crystallographically inequivalent  $\text{Ga}^{\text{III}}$  ions bridged by four  $\text{shi}^{3-}$  ligands in a nearly planar geometry

(Figure 1C). In addition, the central Dy<sup>III</sup> ion is tethered to the MC ring by four benzoate (bz) ligands and adopts an eight-coordinate square antiprism geometry.

Interestingly, the size and flat shape of these Ln[12-MC<sub>Ga</sub><sup>III</sup>-4](bz)<sub>4</sub> molecules closely resemble that of G-tetrads that stabilize telomeric DNA. The poly G-rich regions at the end of chromosomes are stabilized by K<sup>+</sup>. Given the shape similarity, it was hypothesized that Sm<sup>III</sup>Ga<sub>4</sub> or Tb<sup>III</sup>Ga<sub>4</sub> might form adducts to these nucleic acid structures. This was demonstrated in buffered aqueous solution in which Stern–Volmer plots gave ~10 μM affinities for GT-MC affinities. It was also shown that Sm<sup>III</sup>Ga<sub>4</sub> caused destabilization of the G-tetrad indicating a shape and size recognition between these molecules (Rajczak et al., 2017). This result indicated that MCs could serve as a probe for these important regulators of gene expression.

In 2019, upon reacting Ga(NO<sub>3</sub>)<sub>3</sub>, Dy(O<sub>2</sub>CMe)<sub>3</sub>, H<sub>3</sub>shi, Bu<sub>4</sub>NClO<sub>4</sub>, and piperidine in an 8:1:8:3:8 ratio in MeOH, Rentschler et al. reported a lanthanide containing complex that resembled the first gallium 12-MC-4 dimer reported in 1993 (Lah et al., 1993). An X-ray structure of this dimeric MC revealed that one Dy<sup>III</sup> ion was encapsulated between two 12-MC<sub>Ga</sub><sup>III</sup><sub>N(shi)</sub>-4 frameworks (Athanasopoulou et al., 2019). This structure formed a sandwich-like topology in which two 12-MC-4 units are connected to the central Dy<sup>III</sup> ion via the oxime oxygens of the shi<sup>3-</sup> ligands (Figure 1D). The authors focused their investigations on the magnetic properties of this compound and characterized it as a single-ion magnet (SIM) with an effective barrier (U<sub>eff</sub>) of 39.00 K (Athanasopoulou et al., 2019).

In the same year, the entire series of [LnGa<sub>8</sub>(shi)<sub>8</sub>(OH)<sub>4</sub>]Na (Ln<sup>III</sup> = Pr, Nd, Sm–Yb, and Y), was synthesized in order to examine the luminescent properties of this molecular class (Salerno et al., 2020a). X-ray single-crystal structural analysis of the NdGa<sub>8</sub> analogue exhibited that each molecule consists of two [12-MC<sub>Ga</sub><sup>III</sup><sub>N(shi)</sub>-4] units, with a composition identical to the previously presented MCs (Figure 1E) (Lah et al., 1993; Chow et al., 2016; Nguyen et al., 2018). Photophysical studies revealed that these dimeric MCs are among the few molecular complexes capable of sensitizing *f-f* transitions of ten out of fifteen trivalent lanthanide ions, excluding La<sup>III</sup> (4<sup>f</sup>), Ce<sup>III</sup> (impeded by 4<sup>f</sup>-5<sup>d</sup> transitions), Pm<sup>III</sup> (radioactive), Gd<sup>III</sup> (4<sup>f</sup>), and Lu<sup>III</sup> (4<sup>f</sup><sup>14</sup>). Notably, they can also sensitize the emissions of six Ln<sup>III</sup> ions across both the visible and NIR regions (Pr<sup>III</sup>, Sm<sup>III</sup>, Dy<sup>III</sup>, Ho<sup>III</sup>, Er<sup>III</sup>, and Tm<sup>III</sup>) (Supplementary Table S1) (Salerno et al., 2020a).

Another class of 12-MC<sub>Ga</sub><sup>III</sup><sub>N(shi)</sub>-4 dimers was reported when David Chow reasoned that stable, self-assembled dimers derived from the corresponding Ln<sup>III</sup> [12-MC<sub>Ga</sub><sup>III</sup><sub>N(shi)</sub>-4](bz)<sub>4</sub> complexes (Ln<sup>III</sup> = Pr–Yb, excluding Pm) could be formed by substituting the benzoate anions with meta-directed dicarboxylate ligands. It was demonstrated that the introduction of a second MC unit using isophthalate “bridging” ligands (ip<sup>2-</sup>) enhanced solution stability while maintaining the photophysical properties of the parent monomeric MCs (Nguyen et al., 2018). These dimeric and dianionic MCs exhibited large molar absorptivities, high quantum yields, and long luminescence lifetimes, particularly for the visible-emitting (TbGa<sub>4</sub>)<sub>2</sub>(ip<sup>2-</sup>)<sub>4</sub> complex and the NIR-emitting (YbGa<sub>4</sub>)<sub>2</sub>(ip<sup>2-</sup>)<sub>4</sub> in the solid state. The dimeric structure of (DyGa<sub>4</sub>)<sub>2</sub>(ip<sup>2-</sup>)<sub>4</sub> is shown as Figure 1F. Notably, the four rigid ip<sup>2-</sup> ligands lock the two Dy<sup>III</sup> cations at a fixed distance of 7.224 (1) Å. This report laid the cornerstone for future discoveries, leading to the introduction of several variations of this structure type.

Armed with these solution-stable and highly luminescent dimeric compounds, which efficiently sensitized the emission of up to 10 different lanthanide ions, the next objective was to develop versatile functionalization strategies for these MCs. Fortunately, there are many examples of modified shi<sup>3-</sup> and ip<sup>2-</sup> ligands that can serve as precursors for these compounds. Both shi<sup>3-</sup> and ip<sup>2-</sup> were substituted with iodo groups (meta-iodo-shi (I-shi) and 5-iodoisophthalate (I-ip)) allowing the preparation of [Ln<sub>2</sub>Ga<sub>8</sub>(shi)<sub>8</sub>(I-ip)<sub>4</sub>]<sup>2-</sup>, [Ln<sub>2</sub>Ga<sub>8</sub>(I-shi)<sub>8</sub>(ip)<sub>4</sub>]<sup>2-</sup>, and [Ln<sub>2</sub>Ga<sub>8</sub>(I-shi)<sub>8</sub>(I-ip)<sub>4</sub>]<sup>2-</sup>. The Sm<sub>2</sub>Ga<sub>8</sub>(shi)<sub>8</sub>(I-ip)<sub>4</sub> is shown as Figure 2A (Lutter et al., 2020). The goal was to prepare bimodal near-infrared and X-ray computed tomography (XCT) imaging agents. These variations enabled systematic control over iodine content and location, allowing the authors to assess the impact of each modification on X-ray attenuation and NIR luminescence. The conclusion was that iodination did not diminish the emission intensity of the metallacrowns. There was a linear dependence on X-ray attenuation based on the degree of iodination, with [Ln<sub>2</sub>Ga<sub>8</sub>(I-shi)<sub>8</sub>(I-ip)<sub>4</sub>]<sup>2-</sup> showing a nearly 50-fold enhancement compared to the clinically administered iobitridol. Surprisingly, even [Ln<sub>2</sub>Ga<sub>8</sub>(shi)<sub>8</sub>(ip)<sub>4</sub>]<sup>2-</sup> was superior to this clinical agent because the X-ray cross section of the two lanthanide ions is much greater than iodine.

Because there are so many commercially available functionalized H<sub>3</sub>shi and H<sub>2</sub>ip molecules, both the ring and bridging positions can be modified using highly effective synthetic processes. For example, by exploiting the versatility of “click” chemistry, the dimeric MCs can be functionalized via the copper-catalyzed alkyne azide [3 + 2] cycloaddition (CuAAC) (Huisgen, 1961) and the thiol-maleimido coupling via Michael addition (Northrop et al., 2015). An alkyne substituent was installed on the shi<sup>3-</sup> (eshi<sup>3-</sup>) for the CuAAC reaction and photocatalytic radical couplings, while a maleimide group was added on the back of isophthalate (mip<sup>2-</sup>) for thiol couplings (Lutter et al., 2019). Structural analysis of the [Sm<sub>2</sub>Ga<sub>8</sub>(eshi)<sub>8</sub>(ip)<sub>4</sub>]<sup>2-</sup> and [Nd<sub>2</sub>Ga<sub>8</sub>(shi)<sub>8</sub>(mip)<sub>4</sub>]<sup>2-</sup> analogues (Figures 2B,C) closely resemble that of the previously reported {Dy[12-MC<sub>Ga</sub><sup>III</sup><sub>N(shi)</sub>-4]<sub>2</sub>(ip)<sub>4</sub>} metallacrown (Figure 1F), indicating that adorning the periphery of the MCs does not perturb the basic structure of the dimer.

The preparation of dendrimeric MCs (DMCs) provides an instructive example of the power of having orthogonal coupling groups to attach side chains for functionalization (Pecoraro et al., 2021). By starting with cysteamine, one can alternately couple methyl acrylate and ethylene diamine to make dendrons of successively higher molecular weight and complexity. By the time one prepares generation 2 dendrons (G-2), symmetric subunits of significant molar mass are realized and these may be coupled to either the maleimide group, to provide substitution only at the mip<sup>2-</sup> bridges, to use photochemistry to induce radical coupling to eshi<sup>3-</sup> or, by subsequent coupling steps, first functionalize the eshi ligand followed by clicking a different generation of type of functional group to the mip ligand. These different approaches can lead to a wide variety of dendrimeric metallacrowns as shown schematically in Figure 2D. All of these structures yield dendrimeric metallacrowns that are highly luminescent, water soluble, and biocompatible.

Before expanding on the applications of the monomeric and dimeric metallacrowns discussed thus far, we will introduce a few

more structures that have been prepared using gallium and lanthanides. The isostructural complexes  $[\text{Ga}_4\text{Ln}_2(\text{shi})_4(\text{Hshi})_2(\text{H}_2\text{shi})_2]^{4+}$  (where  $\text{Ln}^{\text{III}} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}, \text{and } \text{Y}$ ) were prepared to examine their magnetic properties (Chow et al., 2015b). All complexes (except Er) exhibit antiferromagnetic exchange coupling with a diamagnetic ground state. The  $\text{Dy}^{\text{III}}$  complex acted as a single-molecule magnet (SMM), exhibiting relaxation processes that are due to the excited ferromagnetic state and the uncoupled  $\text{Dy}^{\text{III}}$  centers. The observed antiferromagnetic coupling in the  $\text{Dy}^{\text{III}}$  complex was shown to be mainly due to an exchange mechanism, not dipolar interactions. These studies suggest that the two closely separated states could be considered an entry point for the formation of qubits using metallocrowns. Another interesting family of  $\text{Ga}^{\text{III}}\text{-Ln}^{\text{III}}$  metallocrowns was made upon direct reaction of salicylhydroxamic acid ( $\text{H}_3\text{shi}$ ) with  $\text{Ga}^{\text{III}}$  and  $\text{Ln}^{\text{III}}$  nitrates in a  $\text{CH}_3\text{OH}/\text{pyridine}$  mixture (Nguyen et al., 2020). Single-crystal X-ray diffraction analysis revealed two distinct types of structures,  $[\text{LnGa}_4(\text{shi})_4(\text{H}_2\text{shi})_2(\text{py})_4(\text{NO}_3)](\text{py})_2$  ( $\text{Ln}^{\text{III}} = \text{Gd}, \text{Tb}, \text{Dy}, \text{and } \text{Ho}$ ) and  $[\text{LnGa}_4(\text{shi})_4(\text{H}_2\text{shi})_2(\text{py})_5](\text{NO}_3)(\text{py})$  ( $\text{Ln}^{\text{III}} = \text{Er}, \text{Tm}, \text{and } \text{Yb}$ ), depending on whether the nitrate counterion bounds to the central  $\text{Ln}^{\text{III}}$  ion or not. While with early  $\text{Ln}^{\text{III}}$  ions (Nd, Sm, and Eu) no pure MC products were obtained, the mid-series ions (Gd, Tb, Dy, and Ho) formed complexes in which the  $\text{Ln}^{\text{III}}$  center is nine-coordinated (Figure 2E). Meanwhile, the complexes formed with the smallest  $\text{Ln}^{\text{III}}$  ions of the series (Er, Tm, and Yb) yielded eight-coordinated lanthanides (Figure 2F). This family of MCs demonstrated that planar  $\text{Ga}^{\text{III}}$ -based MCs are not a requirement for lanthanide luminescence and that the presence of protonated  $\text{H}_2\text{shi}$  does not lead to significant vibrational quenching.

## Applications of luminescent lanthanides

The unique electronic configurations of  $\text{Ln}^{\text{III}}$  ions give rise to narrow emission bands, long luminescence lifetimes, and strong resistance to photobleaching. These properties make  $\text{Ln}^{\text{III}}$ -based luminescence highly valuable for practical applications in biomedical imaging (Lengacher et al., 2023; Bao et al., 2021; Alexander et al., 2025), solar energy conversion (Golesorkhi et al., 2021; Haseg et al., 2024; Bünzli et al., 2014), light-emitting diodes (Salerno et al., 2024; Utochnikova et al., 2021; Monteiro et al., 2018), and telecommunications (Tessitore et al., 2023; Bünzli and Eliseeva, 2010). Furthermore, NIR-emitting  $\text{Ln}^{\text{III}}$  ions draw particular interest because of the transparency of biological tissue in this spectral range.

However, due to the symmetry forbidden nature of  $f\text{-}f$  transitions, most lanthanide(III) ions exhibit extremely low molar absorption coefficients, which in turn limits both the number of emitted photons and the overall detection sensitivity. As a result, direct population of excited states generally requires high-power laser excitation sources, a condition that is particularly unfavorable for biological imaging applications. To overcome this intrinsic limitation, organic chromophoric frameworks are commonly employed for the complexation and sensitization of lanthanide(III) ions via the so-called “antenna effect”, in which the lanthanide center is embedded into an environment with good light-harvesting and energy transfer properties. In this way, extremely large pseudo-Stokes shifts (the difference in energy

where the antenna absorbs and the lanthanide emits) can be thousands of wavenumbers. Therefore, quantification of the emission is unlikely to be complicated by overlap with a broad excitation band. Another critical consideration in designing luminescent lanthanide materials is the presence of nearby C–H, O–H, or N–H bonds, whose high-energy vibrational overtones can easily couple with the small energy gaps between the emitting and first levels of the ground multiplet in NIR-emitting lanthanides and quench emission through non-radiative pathways. Such vibrations are commonly found in organic antennae, which limits their efficiency in sensitizing NIR-emitting lanthanides. This limitation is evident when comparing the highest reported overall quantum yields of lanthanide complexes containing C–H bonds, with NIR-emitting lanthanide complexes exhibiting relatively low yields of 3.8% for  $\text{Yb}^{\text{III}}$ , 0.42% for  $\text{Nd}^{\text{III}}$ , and 0.033% for  $\text{Er}^{\text{III}}$  (Bünzli and Piguet, 2005; Bünzli and Eliseeva, 2010; Eliseeva and Bünzli, 2010), whereas visible-emitting lanthanide complexes such as those of  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  can achieve quantum yields exceeding 80% (Botelho et al., 2013; Zhou et al., 2019; Zhao et al., 2020). Not only is it essential to isolate the  $\text{Ln}^{\text{III}}$  ion from C–H, O–H, or N–H bonds, but it also necessary to ensure that paramagnetic ring metal ions, which have detrimental effect on radiative process and quench luminescence, are not present.

Metallocrowns provided an entry into the field of luminescent lanthanide complexes by avoiding all of the restrictions described above. The first example was the host(host-guest) self-assembled  $\text{Ln}^{\text{III}}\text{-Zn}^{\text{II}}$  metallocrowns ( $\text{Ln}^{\text{III}} = \text{Y}, \text{La}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Tb}, \text{and } \text{Yb}$ ) introduced in 2011 (vide supra) (Figure 2G). Subsequently, this synthetic strategy was expanded using different hydroxamate ligands in order to change excitation wavelengths and solubility (Lutter et al., 2020; Trivedi et al., 2014; Eliseeva et al., 2022b; Nguyen et al., 2023). Through these alterations, excellent human cell images could be obtained that distinguished necrotically vs apoptotically killed cells (Martinić et al., 2017a) and that could be used to simultaneously fix and image cells (Martinić et al., 2017b). The  $\text{Zn}_{16}$  metallocrown scaffold perfectly addressed this quenching concern as the central Ln was shielded from vibrational quenching, since the closest C–H oscillator was  $>7 \text{ \AA}$  from the captured Ln atom. Similarly, the  $\text{Zn}^{\text{II}}$  diamagnetic  $d^{10}$  electronic configuration removed concern of paramagnetic quenching. However, while these  $\text{LnZn}_{16}$  based metallocrowns exhibited large pseudo-Stokes shifts and were highly emissive in the Near IR, because their mechanism of Ln sensitization was achieved by intraligand charge transfer (ILCT), other lanthanides such as  $\text{Tb}^{\text{III}}$  and  $\text{Sm}^{\text{III}}$  did not emit in the visible region. Furthermore, selective functionalization of the molecule for targeting applications proved difficult, therefore, a different metallocrown scaffold was sought in an effort to broaden the utility of metallocrowns in luminescent applications. As described above, the  $\text{Ga}^{\text{III}}$  based 12-MC-4 scaffold resolved the limitations of  $\text{LnZn}_{16}$ .

Modern Light Emitting Diodes (LEDs) are constructed with multiple glass or polymer layers that each contain different chromophores that in coherent emission yield what our eyes see as white light (WLEs). These white light LEDs may be dichroic (blue/yellow), trichroic (red/green/blue) or tetrachroic (red/green/blue/cyan), with the latter being the most expensive to

make but yielding the highest quality light. Efforts to prepare single molecules that are tri- or tetrachoric are heavily studied since using such materials would markedly decrease fabrication costs while ensuring that the white light integrity would not change (to more blue or yellow) due to differential photobleaching of the emitters. Lanthanides are promising for this application as they have multiple emissive lines that do not photobleach. Notably, Dy<sup>III</sup> is of particular interest since it possesses three main sharp emission bands  ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$  (blue),  ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$  (yellow), and  ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$  (red) in the visible region that allows for the development of single-component WLEs. While crystal field perturbations of lanthanide orbital energies are often neglected, it has been shown that small variations in molecular symmetry around Dy<sup>III</sup> can alter the relative emission intensities of these transitions yielding different shades of white light. Optical analysis of the Dy<sup>III</sup>-Ga<sup>III</sup> metallacrowns demonstrated that the relative intensities of these emissions could be controlled through structural variation imparted by different MCs on the Dy<sup>III</sup> environment. Workers in this field use the Commission Internationale de l'Éclairage (CIE 1931) chromaticity standards to assess the quality of the WLE with coordinates  $x = 0.33$  and  $y = 0.33$  corresponding to pure white light. The “D<sub>4</sub>” symmetric [DyGa<sub>8</sub>(shi)<sub>8</sub>(OH)<sub>4</sub>]Na ( $x = 0.309$  and  $y = 0.334$ ) was within the acceptable range for WLE, whereas the “C<sub>1</sub>” symmetric [DyGa<sub>4</sub>(shi)<sub>4</sub>(H<sub>2</sub>shi)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] ( $x = 0.398$  and  $y = 0.430$ ) appeared pale yellow and intermediate coordinates were acquired for any of the “C<sub>4</sub>” symmetric monomeric [DyGa<sub>4</sub>(shi)<sub>4</sub>] ( $x = 0.352$  and  $y = 0.393$ ) or dimeric [DyGa<sub>8</sub>(shi)<sub>8</sub>] ( $x = 0.352$  and  $y = 0.393$ ) MCs containing benzoate or isophthalate, respectively (Eliseeva et al., 2020). Hence these molecules represented trichroic systems. Further tuning of the white light emission—from warm to neutral to cold white—to obtain tetrachoric emitters was achieved by varying the chromophoric building blocks. The strategy exploited controlling back energy transfer rates to introduce ligand-centered fluorescence in the blue spectral region while preserving the coordination geometry of Dy<sup>III</sup> (Salerno et al., 2024). New Dy<sup>III</sup>-Ga<sup>III</sup> MCs based on the [DyGa<sub>4</sub>(shi)<sub>4</sub>] or dimeric [DyGa<sub>8</sub>(shi)<sub>8</sub>] frameworks with various combinations of building blocks derived from substituted salicylhydroxamic (H<sub>3</sub>L') (Cl, Br, I, OMe, Me) were prepared (Salerno et al., 2024) and in some cases contained a ligand based fluorescent emission in the 370–420 nm region that could modify the CIE coordinates of the compounds. Thus, the new tetrachroic emitter shifted the [DyGa<sub>4</sub>(shi)<sub>4</sub>(bz)<sub>4</sub>] ( $x = 0.352$  and  $y = 0.393$ ) to [DyGa<sub>4</sub>(Cl-shi)<sub>4</sub>(bz)<sub>4</sub>] ( $x = 0.32$  and  $y = 0.33$ ) a near perfect WLE.

Back energy transfer rates can also be exploited in the field of molecular nanothermometry. The Ga<sub>8</sub>Ln<sub>2</sub>(shi)<sub>8</sub>(ip)<sub>4</sub> MCs can be used as ratiometric luminescent molecular nanothermometers in the physiological temperature range. Using a 1:1 mixture of visible-emitting Tb<sub>2</sub>Ga<sub>8</sub> and Sm<sub>2</sub>Ga<sub>8</sub> molecules, they observed a luminescent molecular thermometer with interesting thermal sensitivity. At 328 K, the system exhibited a relative thermal sensitivity (S<sub>r</sub>) of 1.9% K<sup>-1</sup> and a minimal temperature uncertainty (dT) of less than 0.045 K, in an aqueous suspension of polystyrene nanobeads loaded with the corresponding MCs (Salerno et al., 2020b). The performance was further improved by preparing a new series of dimeric Ln<sub>2</sub>Ga<sub>8</sub>L<sub>8</sub>(ip)<sub>4</sub> metallacrowns (Ln<sup>III</sup> = Tb or Sm; L = salicylhydroxamic acid (H<sub>3</sub>shi), 5-methylsalicylhydroxamic acid

(H<sub>3</sub>mshi), 5-methoxysalicylhydroxamic acid (H<sub>3</sub>moshi), and 3-hydroxy-2-naphthohydroxamic acid (H<sub>3</sub>nha)) and investigating the effect of ligand energy levels on the thermal dependence of lanthanide emission (Salerno et al., 2022). Optical measurements on the MC series demonstrated that the energy gap ( $\Delta E$ ) between the Ln<sup>III</sup> excited state and the ligand excited (T<sub>1</sub>) state is the primary factor controlling the thermal dependence of emission intensity via the back energy transfer mechanism, where a smaller  $\Delta E$  leads to a greater decrease in emission intensity. However, when the energy difference between the ligand-centered singlet state (S<sub>1</sub>) and triplet state is small (below 3,760 cm<sup>-1</sup>), intersystem crossing between S<sub>1</sub> and T<sub>1</sub> (both S<sub>1</sub>→T<sub>1</sub> and the reverse S<sub>1</sub>←T<sub>1</sub>) also contributes to the thermal behavior of metallacrowns. Eventually, both mechanisms affect Ln<sup>III</sup>-centered room-temperature quantum yields with values ranging from 2.07(6)% to 31.2(2)% for Tb<sub>2</sub>Ga<sub>8</sub>L<sub>8</sub> and from 0.0267 (7)% to 2.27(5)% for Sm<sub>2</sub>Ga<sub>8</sub>L<sub>8</sub> (Salerno et al., 2022). Functional molecular thermometers could serve the temperature range 100–375 K.

Finally, *in vivo* imaging is best achieved using molecules that can both be sensitized and emit at wavelengths that exceed 620 nm (~16,000 cm<sup>-1</sup>) because these low energy photons can penetrate deeply into tissue. These requirements suggest that Ln<sup>III</sup> = Yb, Nd, and Er (NIR-II, 1000–1700 nm) would be ideal emitters; however, the H<sub>3</sub>shi ligands require excitation at much too high energies (>23,000 cm<sup>-1</sup>) to be practical. Hence, the next generation of luminescent MCs are appending organic or inorganic antenna to the back of the bridging isophthalic acid ligands, enabling absorption at longer wavelengths than the MC forming ligands.

An example of a metal-based antenna linked to the dimeric Ln<sup>III</sup>-Ga<sup>III</sup> metallacrowns uses Ru<sup>II</sup>-centered metal-to-ligand charge transfer (MLCT) states of Ru<sup>II</sup> polypyridyl complexes to sensitize the Ln<sup>III</sup> centers (Bădescu-Singureanu et al., 2024). The [Ln<sub>2</sub>Ga<sub>8</sub>(shi)<sub>8</sub>(bpy<sub>2</sub>RuPhenMip)<sub>4</sub>](PF<sub>6</sub>)<sub>6</sub> complexes (Ln<sup>III</sup> = Yb, Er, Nd, and Y) are the first examples of dimeric Ln<sup>III</sup>-Ga<sup>III</sup> MCs functionalized with appended transition metal complexes. Excitation of these molecules at ~450 nm (22,000 cm<sup>-1</sup>) yielded NIR-II emission in DMSO/H<sub>2</sub>O mixtures (Supplementary Table S1). A very recent report has exploited the well-studied coumarin group of antenna (Lathion et al., 2025). Again, these chromophores have excitation energies >20,000 cm<sup>-1</sup>; however, they provide proof of principle that organic fluorophores can sensitize NIR-II emission in this molecular class. The diethylcoumarin derivative was once again attached to the Ln<sub>2</sub>Ga<sub>8</sub>shi<sub>8</sub>(mip)<sub>4</sub> (Figure 2C) via thiol Click chemistry to the mip bridge. When excited at 420 nm, Yb<sup>III</sup>, Nd<sup>III</sup>, and Er<sup>III</sup> could all be sensitized, although the relative efficiency was not as effective for Yb<sup>III</sup>. Despite this observation, the Nd derivative was very bright and, most important, was taken up by living HeLa cells and provided excellent images without showing toxicity. To evaluate the biocompatibility of the MCs, live HeLa cells were incubated with varying concentration of [Ln<sub>2</sub>Ga<sub>8</sub>shi<sub>8</sub>(C-mip)<sub>4</sub>]<sup>2-</sup> for 24 h. Cell viability remained above 0.95 across all tested concentration until 100 μg·mL<sup>-1</sup>, at which point the MC began to show cytotoxicity and viability dropped to 0.86 (2) (Lathion et al., 2025; Lathion et al., 2025). While both of these examples provide the opportunity for longer wavelength excitation, future studies with additional, even lower energy absorbing, antenna are currently underway.

We hope that this brief review of metallacrowns has provided insight into a technologically useful and intellectually interesting

class of metallamacrocycles. We expect new structural and compositional modifications of this fascinating molecular class will not disappoint researchers that work in this field.

## Author contributions

SN: Writing – original draft, Writing – review and editing. VP: Supervision, Conceptualization, Writing – review and editing, Writing – original draft, Funding acquisition.

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## Conflict of interest

Author VP discloses that he is one of the founders of VieWaves, a company that uses some of the technology described herein.

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## Supplementary material

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