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Near-infrared lanthanide-based emission from fused bis[Ln(III)/Zn(II) 14-metallacrown-5] coordination compounds.

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Lanthanides, Near-infrared, Luminescence, Metallacrowns, Heterobimetallic Complexes, Single-crystal X-ray Diffraction

A set of $(\text{Ln}[14\text{-MC}_{\text{Zn}}^{(\text{II})}_{\text{N}(\text{quinHA})\text{-5}}])_2\text{Ln}_2\text{Zn}_2(\text{quinHA})_2(\text{ph})_2(\text{Hph})_4(\text{OH})_8(\text{H}_2\text{O})_4$ metallacrowns (**Ln-1**, Ln = Tb, Gd, or Yb; H₂quinHA = quinaldic hydroxamic acid, H₂ph = phthalic acid) have been synthesized via solution-state self-assembly. The MCs possess an uncommon topology within the metallacrown family where two rarely seen 14-metallacrown-5 moieties are fused by a Yb₂Zn₂(quinHA)₂ bridge. Moreover, **Yb-1** analyzed in the solid state exhibits a characteristic near-IR luminescence signal arising from Yb³⁺ ²F_{5/2}→²F_{7/2} transition despite the proximity of high energy O–H oscillators.

Compounds formed with trivalent lanthanide cations (Ln³⁺) possess unique magnetic and luminescence properties that are examined across a variety of fields.^{1,2} These properties result from 4f valence electrons that are shielded from their environment by filled 5s and 5p orbitals.³ From a magnetic perspective, Ln³⁺ have been studied as single-molecule magnets, thanks to unquenched spin-orbit coupling that enhances anisotropy, and as contrast agents for magnetic resonance imaging.⁴⁻⁹ From a luminescence point of view, Ln³⁺ are attractive because of their characteristic and narrow emission bands, as well as their long luminescence lifetimes.^{3,10-15} In addition, several Ln³⁺ ions emit photons in the near-IR spectroscopic range that are of special interest for deep tissue imaging and telecommunications.¹⁰ However, Ln³⁺ have low absorbance because most f–f

transitions are parity forbidden. To counteract this limitation organic chromophoric ligands with large molar absorption coefficients can be used to sensitize Ln^{3+} via energy transfer, leading to enhanced emission (antenna effect).^{16,17}

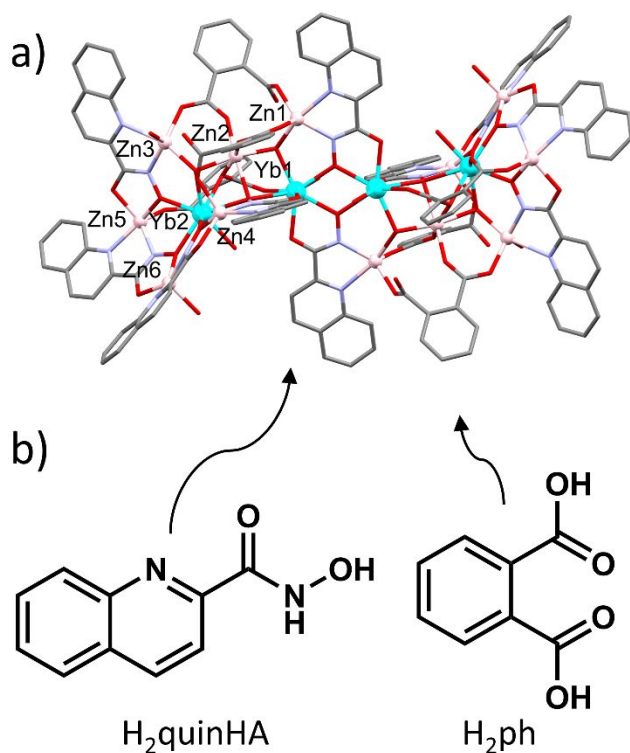


Figure 1. Representation of the molecular structure of **Yb-1** from single crystal diffraction data (a), and schematic representation of the two parent ligands: quinaldic hydroxamic acid (H₂quinHA) and phthalic acid (H₂ph) (b). Aqua = Yb, pink = Zn, light blue = N, red = O, grey = C. Solvent molecules and hydrogen atoms are omitted for clarity.

Metallacrowns (MCs) were first introduced by Pecoraro and Lah in 1989 as inorganic analogues to crown ethers, where the $[-C-C-O-]_n$ repeating unit is replaced by a $[-M-N-O-]_n$ unit to form a rigid macrocycle.^{18,19} M is typically a third-row metal ion, and the N–O binding unit is usually provided by hydroximates.^{20–22} Since 2011, MCs have been studied as antenna for Ln^{3+} ,²³ typically including optically silent metals such as Zn^{2+} and Ga^{3+} to form the metallamacrocycle structure. Such Ln^{3+} -based MCs have shown promises for optical imaging, orthogonal functionalization, nanothermometry, and white-light emission.^{24–33} Here, we present a series of Ln^{3+}/Zn^{2+} MCs ($Ln[14-MC_{Zn}^{II}N(quinHA)-5]_2Ln_2Zn_2(quinHA)_2(ph)_2(Hph)_4(OH)_8(H_2O)_4$ (**Ln-1**, Ln = Tb, Gd, or Yb; $H_2quinHA$ = quinaldic hydroxamic acid, H_2ph = phthalic acid, **Figure 1**) possessing a different structure that hasn't been reported so far. They contain two fused [14-MC-5] motifs and are able to sensitize Yb^{3+} luminescence in the near-IR range.


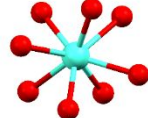


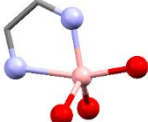
The self-assembly synthesis of **Ln-1** compounds was achieved via a stoichiometric addition of the appropriate components in *N,N*-dimethylformamide. A diffusion of water into *N,N*-dimethylformamide solutions of **Ln-1** formed single crystals. X-ray diffraction confirmed the same unit cell parameters for each of the series of **Ln-1**. Detailed analysis was performed on **Yb-1** that is comprised of four Yb^{3+} , twelve Zn^{2+} , ten $quinHA^{2-}$, four Hph^- , two ph^{2-} , eight OH^- , and four



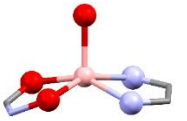
H₂O. This structure contains two [14-MC-5] motifs that are spanned by a central Yb₂Zn₂(quinHA)₂ moiety (**Figures S1 and S2**, Supporting Information). The solid-state packing of **Yb-1** molecules is stabilized by through-solvent intermolecular interactions (including hydrogen bonding and van der Waals interactions) and π - π stacking of adjacent quinHA²⁻ located on neighboring molecules. Each metal ion was analyzed for its coordination geometry. In particular, coordination number (CN), shape, crystal shape measure parameter (CShM), average bond length (d_{av}), and bond-valence sums (BVS) were determined (**Table 1**). Representations generated from the crystallographic data of each ligand field may be observed in **Table 1** and **Figure S3** (Supporting Information).

Two unique Yb³⁺ cation sites can be distinguished, yet analysis with SHAPE v2.1 software on both Yb1 and Yb2 confirm eight-coordinate trigonal dodecahedral environments comprised of eight oxygens.³⁴ Bond-valence sums confirmed the +3 oxidation state for each of the two Yb³⁺ cations. Yb1 is a part of the spanning moiety while Yb2 is a part of the [14-MC-5] motif. There are six Zn²⁺ in the asymmetric unit, and all but Zn2 adopt a coordination number of five. Zn2 is in a six-coordinate octahedral coordination environment comprised of oxygen atoms. Zn1 and Zn3–Zn6 are all in five-coordinate coordination environments comprised of three oxygen and two

nitrogen donor atoms. Analysis with SHAPE v2.1 suggests that the best coordination geometry to describe Zn1 and Zn4–Zn6 is square pyramidal while Zn3 is best described as a trigonal bipyramidal geometry.³⁴ Bond-valence sums confirm the +2 oxidation state for each Zn²⁺ cation. Zn1 is the only Zn²⁺ cation that is a part of the spanning moiety, whereas the other five Zn²⁺ cations are a part of the [14-MC-5] motif.

Table 1. Geometric information for metal cations in **Yb-1**.

Metal	d_{av}	CN	Crystallographic Representation	Shape	CShM ^a	BVS ^{35,36}	Addison Tau ³⁷
Yb1	2.321	8 [5 O _{quinHA} , 1 O _{ph} , 1 O _{OH} , 1 O _{water}]		Trigonal Dodecahedron	1.01186	3.036	-----
Yb2	2.337	8 [4 O _{quinHA} , 2 O _{ph} , 1 O _{OH} , 1 O _{water}]		Trigonal Dodecahedron	0.60167	2.950	-----
Zn1	2.066	5 [2 N _{quinHA} , 2 O _{ph} , 1 O _{OH}]		Square Pyramid	2.06806	1.988	0.446
Zn2	2.098	6 [1 O _{quinHA} , 3 O _{ph} , 1 O _{OH}]		Octa- hedron	1.17399	2.050	-----
Zn3	2.074	5 [2 N _{quinHA} , 1 O _{ph} , 2 O _{OH}]		Trigonal Bipyramid	2.20789	1.995	0.583

Zn4	2.052	5 [2 N _{quinHA} , 2 O _{quinHA} , 1 O _{ph}]		Square Pyramid	0.59023	2.022	0.110
Zn5	2.035	5 [2 N _{quinHA} , 2 O _{quinHA} , 1 O _{ph}]		Square Pyramid	0.88679	2.113	0.169
Zn6	2.048	5 [[2 N _{quinHA} , 2 O _{quinHA} , 1 O _{OH}]]		Square Pyramid	1.28931	2.038	0.103

^a Smallest CShM out of all ideal geometries from SHAPE v2.1 analysis.³⁴

There are other examples of MCs formed with Zn²⁺, including [12-MC-4]s, [15-MC-5]s, and a bis[12-MC-4][12-MC-8] “encapsulated sandwich” compounds.^{24,38–45} The structure reported here stands out among these examples since examples of [14-MC-5]s are rare and **Ln-1** series is only the second example reported. The first example of a [14-MC-5] was comprised of Mn³⁺ and salicylhydroximate ligands that encapsulate a single Ln³⁺ in their cavity, plus another Ln³⁺ as a part of the MC ring.⁴⁸ Even though both compounds are [14-MC-5]s, there are significant differences in their structural compositions (**Figure 2**). Both [14-MC-5] compounds have a M–O–M “stutter” using a μ₃-OH⁻ or μ₃-O²⁻ rather than a hydroximate group that induces the removal of a nitrogen atom from the standard M–N–O–M motif. Another difference that can be observed

between the two structures is the presence of a mirror plane that bisects the molecule in $\text{Mn}^{3+}/\text{Ln}^{3+}$ [14-MC-5] MC. Conversely, **Yb-1** does not possess a mirror plane and maintains the M–N–O sequence for each of the four subunits. In addition, the $\text{Mn}^{3+}/\text{Ln}^{3+}$ MC has a Ln^{3+} in the [14-MC-5] MC ring, while that in the **Ln-1** consists only of Zn^{2+} ring metal ions. Lastly, the [14-MC-5] ring in Mn^{3+} is planar since each Mn^{3+} is located in an octahedral coordination environment with the 5,6-fused chelate motif of the salicylhydroximate ligand. In the case of **Ln-1**, both the square pyramidal Zn^{2+} centers and the 5,5-fused chelate motif requires some bowling to complete the cycle with reasonable bond lengths.

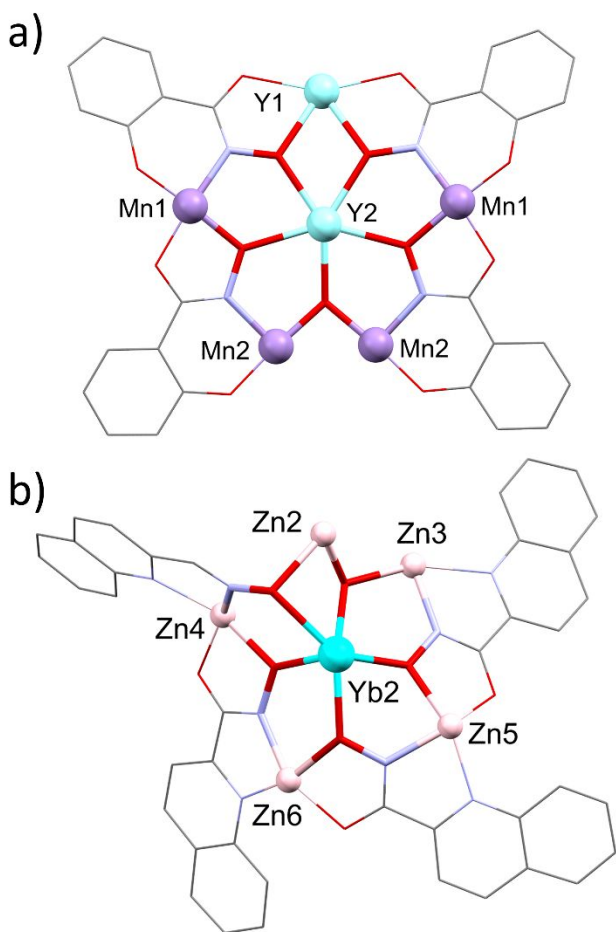


Figure 2. Molecular representation of [14-MC-5] motifs established from crystallographic data for the $\text{Mn}^{3+}/\text{Y}^{3+}$ (a) and **Yb-1** (b) MCs. The MC ring and encapsulated Ln^{3+} are highlighted. Teal = Y, aqua = Yb, indigo = Mn, pink = Zn, light blue = N, red = O, grey = C.

Absorption spectra were collected for each **Ln-1** and the parent ligands in *N,N*-dimethylformamide solution at ambient temperature (**Figure S4**, Supporting Information). Compared to the H_2quinHA and H_2ph that possess absorption bands in the UV range up to 350

and 300 nm, respectively, absorption spectra of **Ln-1** are significantly red-shifted and extend up to 475 nm. The broad lower energy absorption band with a maximum at 380 nm ($\epsilon_{380} = 2.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) could be assigned to intra- and/or inter-ligand charge transfer (ILCT) transitions considering that Zn^{2+} usually does not participate in metal-to-ligand or ligand-to-metal charge transfer transitions and that the absorption spectra of **Ln-1** are independent of Ln^{3+} identity. Similar ILCT absorption bands were observed for $\text{Zn}^{2+}/\text{Ln}^{3+}$ MCs with an ‘encapsulated sandwich’ structure assembled using quin HA^{2-} ligands.²⁴ Diffuse reflectance spectra of **Ln-1** formed with the different Ln^{3+} are similar to each other and exhibit broad bands in the UV and visible range up to 550 nm (**Figure S5**, Supporting Information).

Luminescent properties of **Ln-1** were analyzed in the solid state. Energy positions of the ligand-centered levels, in particular triplet states, employ Gd^{3+} since the emissive state ($32\,200 \text{ cm}^{-1}$)⁴⁹ is too high in energy for many organic sensitizers. However, no phosphorescence could be detected upon excitation of **Gd-1** in the range of 280–340 nm at 77 K in time resolved mode. On the other hand, **Gd-1** exhibited broad-band emission in the range 450–750 nm arising from the ILCT in steady-state mode (**Figure S6**, Supporting Information). The energy position of the ILCT state was determined to be $21\,410 \text{ cm}^{-1}$ (467 nm) from the onset of the emission band of **Gd-1**, a value

similar to the $\text{Zn}^{2+}/\text{Ln}^{3+}$ ‘encapsulated sandwich’ MCs ($21\,560\text{ cm}^{-1}$).²⁴ Upon excitation into ILCT band at 400 nm, **Tb-1** exhibited only a broad-band emission in the range 450–750 nm (**Figure S6**, Supporting Information). The latter could be explained by a high probability of back energy transfer because of the energy match between the ILCT ($21\,410\text{ cm}^{-1}$) and the $\text{Tb}^{3+}\ ^5\text{D}_4$ emitting level ($20\,500\text{ cm}^{-1}$) in **Tb-1**. On the other hand, **Yb-1** upon excitation at 400 nm displays Yb^{3+} -centered luminescence in the near-infrared range due to the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition (**Figure 3**). Excitation spectrum of **Yb-1** upon monitoring emission at 980 nm resembles the diffuse reflectance one (**Figure 3**, solid vs. dashed black traces) and exhibits broad bands in the UV and visible ranges up to 550 nm pointing towards a sensitization of Yb^{3+} through the MC scaffold.¹⁷ It should be noted that Yb^{3+} near-infrared emission in **Yb-1** could be observed despite the presence of water molecules in the first coordination sphere of Yb^{3+} that often quench near-IR emitting Ln^{3+} .³ The Yb^{3+} -centered absolute quantum yield (Q_{Yb}^{L}) of **Yb-1** upon excitation at 400 nm is 0.051(1)%. Luminescence decays of **Yb-1** were best fitted by a monoexponential function (**Figure S7**) where the luminescence lifetime is 714(8) nanoseconds. Both values of Q_{Yb}^{L} and τ_{obs} of **Yb-1** are smaller than the ones reported for the $\text{Zn}^{2+}/\text{Yb}^{3+}$ ‘encapsulated sandwich’ MC ($Q_{\text{Yb}}^{\text{L}} = 2.44(4)\%$; $\tau = 47.8(4)$

ms),²⁴ due to the presence of water molecules directly bound to the lanthanide cation as well as self-quenching induced by proximal Yb³⁺.

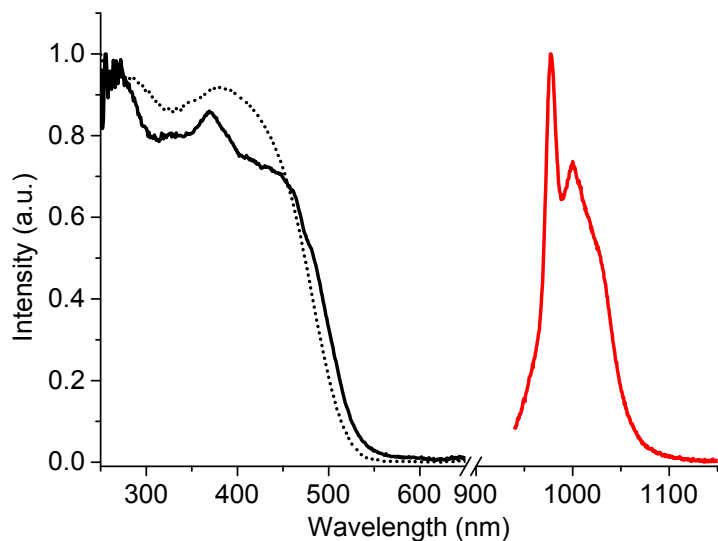


Figure 3. Normalized steady-state luminescence spectra of **Yb-1**. Excitation spectra (black traces) were recorded with $\lambda_{em} = 980$ nm. Emission spectra (red traces) were acquired with $\lambda_{ex} = 400$ nm. The diffuse reflectance spectrum of **Yb-1** is superimposed for comparison (dashed black trace).

The new **Ln-1** MCs we report here represent a significant addition to the library of metallacrown structures not only as an example of a 14-MC-5 system, but also for the ability to sensitize near-IR emission from Yb³⁺. The compound is a fused bis[14-MC-5] that contains both quinHA²⁻ and ph²⁻. Absorption spectra of **Ln-1** display broad bands at lower energy due to intra-/inter-ligand

charge transfer transitions. **Yb-1** in the solid-state displays characteristic Yb^{3+} emission in the near-IR range despite the presence of water molecules directly bound to the metal ion. Given the novelty of the structure and composition as well as the potential application of near-IR luminescence, **Ln-1** is a notable MC compound.

ASSOCIATED CONTENT

The following files are available free of charge.

Electronic Supplementary Information (ESI) available containing experimental details, additional spectroscopic information, and crystallographic parameters in word document format.

Single crystal diffraction data are available for **Yb-1** in CIF format free of charge from www.ccdc.cam.ac.uk using deposition number 2125941.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors have no conflicts of interest to declare.

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SUPPORTING INFORMATION

The Supporting Information available:

Experimental details, additional spectroscopic information and crystallographic parameters (in PDF format).

Single crystal diffraction data are available for **Yb-1** in CIF format free of charge from www.ccdc.cam.ac.uk using deposition number 2125941.

ABBREVIATIONS

MC, metallocrown; Ln³⁺, lanthanide; H₂quinHA, quinaldic hydroxamic acid; H₂ph, phthalic acid.

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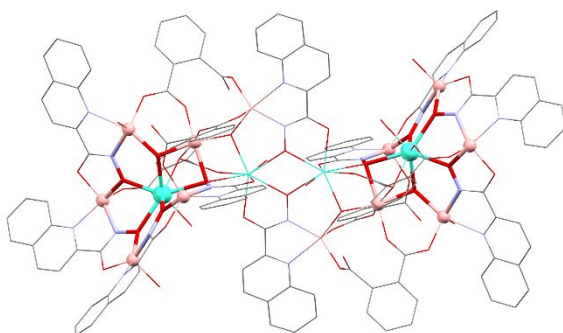
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Table of Contents Synopsis



A fused set of rarely observed 14-metallacrown-5 moieties is described using single-crystal X-ray diffraction data, and near-infrared emission from Yb^{3+} is observed in the solid state.