

Assembly of Near-Infrared Luminescent Lanthanide Host(Guest) Complexes With a Metallacrown Sandwich Motif**

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Optical devices and biomedical imaging probes increasingly utilize the long lifetimes and narrow linewidths of luminescent lanthanide (Ln^{III}) ions.^[1] Near-infrared (NIR) emitting Ln^{III} ions draw particular interest because of the transparency of biological tissue in this spectral range and applications in telecommunications.^[2] Ln^{III} ions are typically sensitized through ligand absorptions by the antenna effect because the low extinction coefficients of the Laporte-forbidden f-f transitions preclude direct excitation. The major hindrance in realizing efficient Ln^{III} ion luminescence in the NIR region is non-radiative quenching by high energy X-H (X = C, N, O) vibrations in the ligand.^[3] Vibrational quenching has limited luminescence lifetimes to less than 6 μs in protic solvents.^[4] While careful ligand design can exclude N-H and O-H oscillators, C-H bonds are difficult to eliminate from organic substrates without relying on synthetically cumbersome deuterated or fluorinated ligands.^[5] Herein we present a self-assembly approach to realizing long-lived Ln^{III} luminescence in the NIR region by utilizing the unique metallacrown (MC) topology to eliminate high energy X-H oscillators from within 6.7 Å of the lanthanide ion. We report the synthesis, solution stability, and remarkable luminescence properties of a unique host(guest) complex in which a $\text{Ln}^{\text{III}}[12\text{-MC-4}]_2^{3+}$ sandwich complex is a guest encapsulated by a $[24\text{-MC-8}]$ host (Ln-1, Figure 1).

MCs^[6] are inorganic analogues of crown ethers.^[7] Much of the interest in MCs has focused on the exceptional solid-state architectures,^[8] magnetic properties,^[9] and molecular recognition capabilities^[10] that arise from their metal-rich topologies. Ln^{III} MCs^[11] have been prepared that display single-

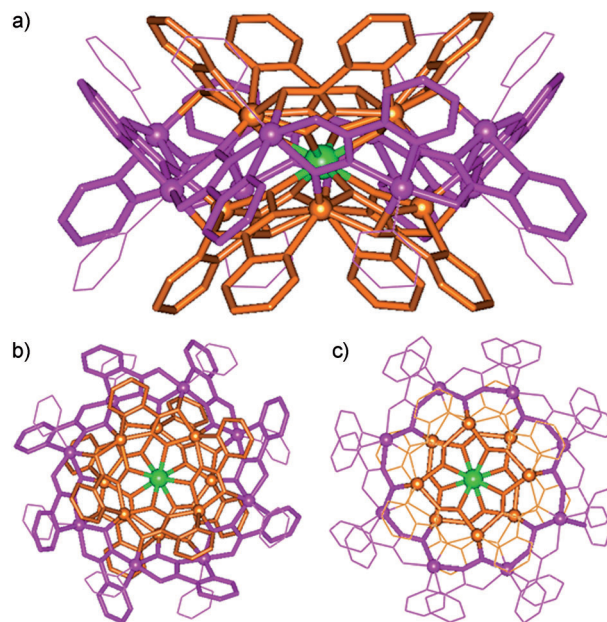


Figure 1. X-ray crystal structure of Tb-1 shown a) perpendicular to the C_4 axis, b) down the C_4 axis, and c) highlighting the MC macrocycle. Color scheme: bronze = $[12\text{-MC-4}]$, purple = $[24\text{-MC-8}]$, green = Tb^{III} . Pyridine ligands are displayed as thin purple lines.

molecule magnetism^[12] and selectively encapsulate anions in monomeric cavitands or dimeric compartments.^[13] Chiral $\text{Ln}^{\text{III}}[15\text{-MC-5}]$ complexes can serve as building blocks for mesoporous solids,^[14] resolved helices,^[15] and noncentrosymmetric solids that display second-harmonic generation.^[16] To date, Ln^{III} MCs have been prepared only with ring metals that contain partially filled d orbitals, which could provide a quenching pathway for luminescence. For this work, the Zn^{II} ion was judiciously chosen as the ring metal because its d^{10} electronic configuration precludes quenching through a d-d transition. To the best of our knowledge, no Ln^{III} MCs with Zn^{II} ring metals have been reported. Picoline hydroxamic acid (picHA) was selected as the ligand because it contains no N-H or O-H oscillators when bound in a Ln^{III} MC.^[17]

The reaction between picHA, sodium hydroxide, zinc(II) triflate, and terbium(III) nitrate in methanol provided the complex formulated as $\text{Tb}^{\text{III}}[12\text{-MC}_{\text{Zn}^{\text{II}}, \text{N}, \text{picHA}^-}4]_2[24\text{-MC}_{\text{Zn}^{\text{II}}, \text{N}, \text{picHA}^-}8](\text{pyridine})_8(\text{triflate})_3$ (Tb-1, Figure 1) upon crystallization from the reaction solution with added pyridine. Single crystal X-ray crystallographic analysis shows two concave $[12\text{-MC}_{\text{Zn}^{\text{II}}, \text{N}, \text{picHA}^-}4]$ units that sandwich an eight-coordinate Tb^{III} central metal. This sandwich complex (Figure 2A, B) is encapsulated in the cavity of a $[24\text{-MC}_{\text{Zn}^{\text{II}}, \text{N}, \text{picHA}^-}8]$ unit (Figure 2C). The $\text{Tb}^{\text{III}}[12\text{-MC-4}]_2[24\text{-MC-8}]^{3+}$ com-

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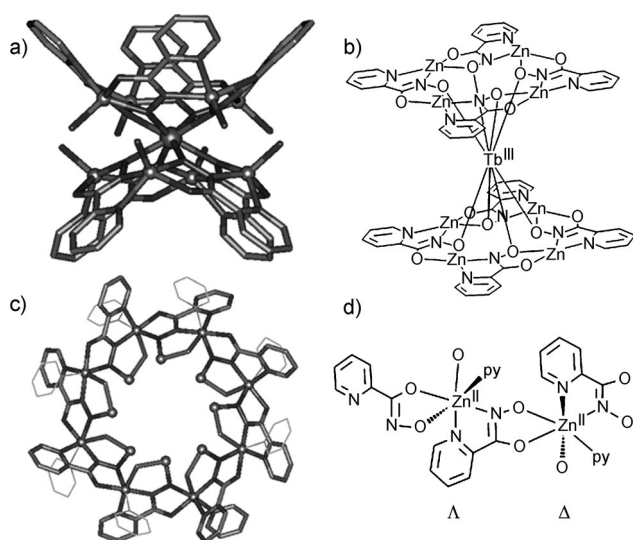


Figure 2. a) Tb-1 crystal structure displaying the $\text{Tb}^{\text{III}}[12\text{-MC-4}]_2$ motif, b) structural formula of $\text{Tb}^{\text{III}}[12\text{-MC-4}]_2$, c) Tb-1 crystal structure displaying the [24-MC-8] ring (central atoms are part of the [12-MC-4]), d) structural formula of the Λ and Δ Zn^{II} ions in [24-MC-8] (py = pyridine, O = ketone oxygen of [12-MC-4] picHA). Metal ions are depicted as spheres in (a) and (c).

plex (Tb-1) has overall S_8 symmetry. Charge balance is achieved with three unbound triflate counterions. The [24-MC-8] ring is assembled with octahedral Zn^{II} ions that possess alternating Λ and Δ absolute stereochemical configuration (Figure 2D), which is consistent with the coordination seen in other large MC rings.^[18] An unbound, isostructural $\text{La}^{\text{III}}[12\text{-MC-4}]_2^{3+}$ sandwich complex has been isolated and structurally characterized, demonstrating that this MC sandwich motif is stable independently. Thus, we may consider the $\text{Tb}^{\text{III}}[12\text{-MC-4}]_2^{3+}$ subunit as a host-guest complex and describe Tb-1 as a host(host-guest) complex.

In the $\text{Tb}^{\text{III}}[12\text{-MC-4}]_2$ subunit of Tb-1, each Zn^{II} ion has a square pyramidal geometry, with the Zn^{II} ion extending out of the picHA equatorial plane by 0.63 or 0.70 Å. Based on the MC structural paradigm,^[19] the fused five-membered chelate rings on picHA are expected to promote a [15-MC-5] motif, as has been observed with Cu^{II} and Ni^{II} ring metals. However, the distorted square-pyramidal geometry of Zn^{II} generates the concave [12-MC-4]. Strain in the [12-MC-4] structure is apparent in the long $\text{Zn}^{\text{II}}\text{-N}_{\text{pyridyl}}$ bond lengths (av = 2.17 Å). The $\text{Zn}^{\text{II}}\text{-O}_{\text{hydroximate}}$ and $\text{Zn}^{\text{II}}\text{-N}_{\text{hydroximate}}$ distances fall within the expected range (2.00–2.07 Å). The $\text{Zn}^{\text{II}}\text{-O}_{\text{carbonyl}}$ distances are long (av = 2.14 Å), because the oxygen atom also coordinates to a [24-MC-8] Zn^{II} ion. Interestingly, $\text{Cu}^{\text{II}}[12\text{-MC-4}]$ and $\text{Ni}^{\text{II}}[12\text{-MC-4}]$ complexes are known intermediates in the assembly of $\text{Ln}^{\text{III}}[15\text{-MC-5}]$ complexes.^[20] A crystal structure of these complexes has not been reported. Based on DFT calculations, Tegoni et al. predicted the $\text{Cu}^{\text{II}}[12\text{-MC-4}]$ possessed a concave structure.^[21] The [12-MC-4] motif in Tb-1 strongly supports this prediction.

The [12-MC-4] units in Tb-1 bind an eight-coordinate Tb^{III} ion with average Tb–O bond lengths of 2.35 Å. The coordination geometry of the central metal is best described as a square antiprism based on shape analysis^[22] ($S(D_{4d}) = 3.34^\circ$).

The [12-MC-4] units have a 0.73 Å cavity radius. The eight-coordinate Tb^{III} ion has an ionic radius of 1.04 Å, making it too large for the [12-MC-4] cavity. Thus the metal ions lay 1.06 or 1.16 Å above the [12-MC-4] oxygen mean planes. The sandwich complex is the first of this type reported for Ln^{III} MCs, and complements a select number of other MC sandwich complexes.^[23] The analogous $\text{Ln}^{\text{III}}[12\text{-crown-4}]$ sandwich complexes are also known.^[24]

The [24-MC-8] binds the $\text{Tb}^{\text{III}}[12\text{-MC-4}]_2$ sandwich through coordination of its hydroximate oxygen atom to the axial position of each Zn^{II} ion on the [12-MC-4] units (av bond length = 1.98 Å). Additionally, each Zn^{II} ion on the [24-MC-8] coordinates to a picHA carbonyl oxygen atom on the [12-MC-4] unit (av bond length = 2.27 Å). The octahedral Zn^{II} ions on the [24-MC-8] also coordinate an *O,O*-picHA, *N,N*-picHA, and a pyridine molecule (Figure 2D). The [24-MC-8] and $\text{Tb}^{\text{III}}[12\text{-MC-4}]_2$ further associate through π -stacking interactions between the picHA rings.

Impressively, Ln-1 is stable in solution. ESI-MS spectra of Ln-1-triflate (Ln = Y^{III}, La^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Dy^{III}, Tb^{III}, Yb^{III}) dissolved in methanol primarily show an Ln-1³⁺ peak, thus suggesting that Ln-1 is the predominant species in solution (Figure 3). Based on ESI-MS, Eu-1 is also stable in acetonitrile, dimethylformamide, dimethylsulfoxide, and in methanol/pyridine mixtures. Additional evidence for solution stability is found in the ¹H NMR spectrum of the diamagnetic Y-1-triflate grown with [D₅]pyridine (Figure 4); six peaks are observed in the aromatic region of this spectrum. Based on the relative integrals, these peaks consist of five single proton

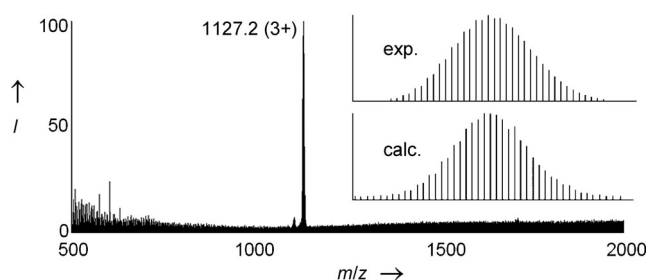


Figure 3. ESI-MS spectrum of Tb-1 in methanol. The peak at 1127.2 (3+) corresponds to Tb-1^{3+} . Inset: Experimental (top) and calculated (bottom) isotope distribution for the Tb-1^{3+} peak.

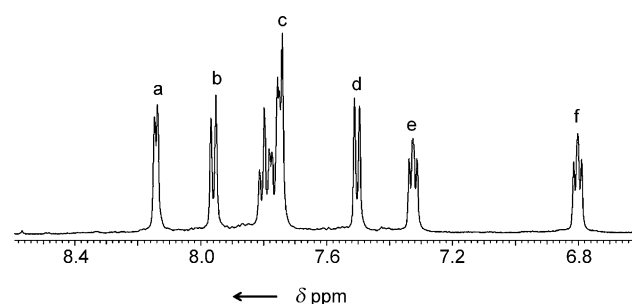


Figure 4. ¹H NMR spectrum of Y-1·([D₅]pyridine)₈ in [D₄]methanol at room temperature. Signal assignment (500 MHz, tetramethylsilane): a: $\delta = 8.14$ ppm (d, ³J(H,H) = 5 Hz, 1 H), b: $\delta = 7.96$ ppm (d, ³J(H,H) = 8 Hz, 1 H), c: $\delta = 7.77$ ppm (m, 3 H), d: $\delta = 7.50$ ppm (d, ³J(H,H) = 8 Hz, 1 H), e: $\delta = 7.32$ ppm (t, ³J(H,H) = 6 Hz, 1 H), f: $\delta = 6.80$ ppm (t, ³J(H,H) = 6 Hz, 1 H).

resonances (peaks a,b,d,e,f) and a peak with three overlapping proton resonances (peak c). This pattern is consistent with the expected spectrum for **Y-1**, which should contain eight proton resonances from the two chemically distinct picHA rings. The coupling in the spectrum matches the expected four doublets and four triplets. Two-dimensional ^1H COSY NMR (see the Supporting Information) demonstrates that two chemically distinct picHA ligands are present. Furthermore, ^1H stimulated pulsed gradient spin echo NMR was used to determine that the diffusion coefficient was $(3.48 \pm 0.01) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. By using the Stokes–Einstein equation, the hydrodynamic radius of the complex was found to be $(11.6 \pm 0.2) \text{ \AA}$, which reasonably matches the 10.7 \AA radius measured in the crystal structure of **Tb-1**.

To address whether **Ln-1** is stable or merely persistent in solution, lanthanide exchange was monitored by adding a tenfold excess of $\text{Ln}(\text{NO}_3)_3$ ($\text{Ln} = \text{La}^{\text{III}}, \text{Y}^{\text{III}}$) to **Eu-1**-triflate in methanol. The ESI-MS spectrum of the solutions showed no peaks for **La-1** or **Y-1** after two weeks at room temperature. Importantly, the absence of **La-1** or **Y-1** peaks suggests that the Ln^{III} ion in **Eu-1** is kinetically stable. Given its composition from 33 separate components and the geometric strain in the [12-MC-4] subunits, the self-assembly and stability of **Ln-1** is impressive. The stability can be rationalized by the strong ionic interactions between the acidic Ln^{III} ion and the negatively charged oxygen atoms on the [12-MC-4] units. Moreover, the complex contains 48 five-membered chelate rings. The solution stability of **Ln-1** contrasts other large MCs with 24-membered rings or greater, which tend to form upon crystallization but persist as lower-order aggregates in solution.

The MC topology effectively excludes C–H oscillators from the proximity of the central metal, with the nearest C–H bond in **Ln-1** located over 6.7 \AA from the Ln^{III} ion. Also, there is no solvent bound to the central Ln^{III} ion. These observations prompted investigations of the NIR luminescence of **Ln-1**. The electronic absorption spectrum of **Yb-1** in methanol (Figure 5a) shows picHA ligand absorptions between 200–400 nm with apparent maxima at 284 and 325 nm. Both Yb^{III} and Nd^{III} ions are readily sensitized by **Ln-1** in methanol and acetonitrile upon excitation of the picHA absorption bands. The characteristic $^5\text{F}_{5/2} \rightarrow ^5\text{F}_{7/2}$ transition is observed in the emission spectrum of **Yb-1** (Figure 5b), while **Nd-1** displays $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ transitions (see the Supporting

Information). By using $[\text{Yb}(\text{dipicolinate})_3]^{3-}$ as a reference ($\Phi = (0.015 \pm 0.02) \%$),^[25] a quantum yield of $(0.89 \pm 0.18) \%$ was measured in methanol (Table 1), which is quite large for Yb^{III} complexes in a protic solvent.^[2,4] The time-resolved photoluminescence lifetime of **Yb-1** is $14 \mu\text{s}$ in methanol at 25.0°C , and the lifetime is extended to $33 \mu\text{s}$ in acetonitrile, which is one of the longest lifetimes observed for a NIR-emitting complex.^[26] The photoluminescence lifetime of **Nd-1** is over $1 \mu\text{s}$ in acetonitrile and compares well with reported complexes.^[2,4] The number of methanol molecules bound in the inner-sphere of Yb^{III} and Nd^{III} ions, q , was estimated by comparing the luminescent lifetimes in methanol and deuterated methanol (CD_3OD).^[27] Values of 0.03 and 0.09 were determined for the Yb^{III} and Nd^{III} complexes, respectively, thus revealing that no methanol molecules are directly coordinated to the central Ln^{III} ions in solution. This observation is consistent with the crystal structure of **Tb-1**. The magnitude of the quantum yield of a lanthanide complex and the measured luminescence lifetimes depend on the proximity of the X–H oscillator groups that can non-radiatively deactivate the Ln^{III} excited state. **Yb-1** and **Nd-1** display strong luminescence, making them the first luminescent Ln^{III} MCs and demonstrating that the MC topology generates bright NIR-emitting Ln^{III} complexes by excluding C–H oscillators from the proximity of the lanthanide.

Table 1: Photophysical data for **Ln-1** at 25.0°C .

Ln	Solvent	$\Phi_{\text{H}} [\%]^{\text{[a]}}$	$\Phi_{\text{D}} [\%]^{\text{[a]}}$	$\tau_{\text{H}} [\mu\text{s}]^{\text{[b]}}$	$\tau_{\text{D}} [\mu\text{s}]^{\text{[b]}}$	$q^{\text{[c]}}$
$\text{Nd}^{\text{III}^{\text{[d]}}}$	$\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$	–	–	0.60	2.3	0.09
$\text{Nd}^{\text{III}^{\text{[e]}}}$	$\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$	–	–	1.4	2.6	–
$\text{Yb}^{\text{III}^{\text{[e]}}}$	$\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$	0.89	2.5	14	122	0.03
$\text{Yb}^{\text{III}^{\text{[e]}}}$	$\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$	1.2	2.2	33	59	–

[a] Quantum yield, estimated error is 20%. [b] Observed luminescent lifetimes, estimated error is 10%. [c] Number of methanol molecules bound to Yb^{III} . [d] $\lambda_{\text{excitation}} = 320 \text{ nm}$. [e] $\lambda_{\text{excitation}} = 325 \text{ nm}$.

In summary, a self-assembled Ln^{III} MC has been synthesized that is striking for its structure, solution stability, and luminescence properties. The $\text{Ln}^{\text{III}}[\text{12-MC-4}]_2$ sandwich motif complements the versatile sandwich complexes of organic macrocycles, and its inclusion in the [24-MC-8] ring to form a host(guest) complex is a remarkable example of self-assembly. Moreover, **Nd-1** and **Yb-1** exhibit excellent luminescence properties for NIR-emitting complexes, thus demonstrating that Ln^{III} MCs are an effective route to realizing bright NIR-emitting chromophores because the unique MC topology excludes high energy oscillators from the proximity of the lanthanide. Further investigations into the assembly, energy transfer mechanism, and luminescence of **Ln-1** and other Ln^{III} metallamacrocycles are underway.

Experimental Section

Picoline hydroxamic acid synthesis, additional experimental details, complex characterization, and crystallographic data are provided in the Supporting Information.

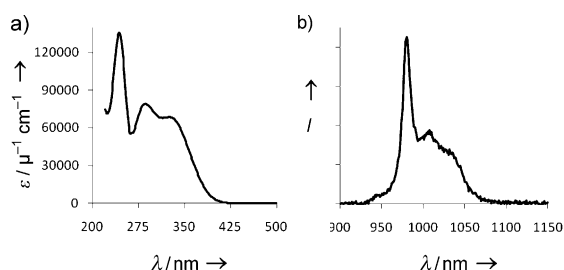


Figure 5. a) Absorption and b) emission spectra for **Yb-1** in methanol at 25.0°C . The emission spectrum was collected by excitation at 280 nm (14.5 nm bandpass) in 1 nm increments with a 4.0 nm bandpass.

Synthesis of Ln-1: A general strategy for the synthesis of Ln-1 complexes is described here for Tb-1. An alternate procedure was employed for Yb-1 (see the Supporting Information). PicHA (150 mg, 1.09 mmol) and sodium hydroxide (86.9 mg, 2.17 mmol) were stirred in methanol (20 mL). Once a homogeneous solution had formed, zinc trifluoromethanesulfonate (395 mg, 1.09 mmol) was added, and the solution turned cloudy. Terbium nitrate (29.5 mg, 0.068 mmol) was then added and the solution gradually clarified. After 20 min, pyridine (5 mL) was added. After stirring overnight, the solution was filtered by gravity and left to slowly evaporate. Yellow crystals were produced within two weeks. Occasionally a second filtration was required after about two days to remove a white precipitate. Yield = 115.2 mg, 36%. ESI-MS (methanol): 1127.2⁺ (1127.4⁺ calcd for [TbZn₁₆(C₆H₄N₂O₂)₁₆]³⁺); elemental analysis calcd (%) for TbZn₁₆(C₆H₄N₂O₂)₁₆(C₅H₅N)₈(CF₃SO₃)₃(H₂O)₁₂(CH₄O): C 35.69, H 2.82, N 11.89; found: C 35.22, H 2.38, N: 11.57.

Crystal data for 1: A yellow needle of dimensions 0.23 × 0.20 × 0.13 mm was mounted on a Rigaku AFC10K Saturn 944 + CCD-based X-ray diffractometer with a Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187 \text{ \AA}$) operated at 0.20 kW power (20 kV, 10 mA), $\mu = 4.510 \text{ mm}^{-1}$. A total of 1956 images were collected at 85(2) K with an oscillation width of 1.0° in ω . The exposure time was 10 s for the low angle images, 30 s for the high angle. The integration of the data yielded a total of 281 538 reflections to a maximum 2θ value of 136.52° of which 9625 were independent and 9181 were greater than $2\theta(I)$. Tetragonal cell constants of $a, b = 27.3594(4), c = 28.025(2), \alpha, \beta, \gamma = 90^\circ, V = 20977.6(16) \text{ \AA}^3$ were based on the xyz centroids of 229 034 reflections above $10\sigma(I)$. The data showed negligible decay during collection; the data were processed with CrystalClear 2.0^[28] and corrected for absorption. The structure was solved and refined with the SHELXTL (version 2008/4) software package^[29] using the space group $P4/nnc$ with $Z = 4$ for the formula TbZn₁₆(C₆H₄N₂O₂)₁₆(C₅H₅N)₈(CF₃SO₃)₃(OH)(H₂O)₂₃, $\rho_{\text{calcd}} = 1.502 \text{ mg m}^{-3}$. Triflate and numerous water molecules are disordered, and the third triflate counterion was assigned based on elemental analysis data and the presence of large voids. Full matrix least-squares refinement based on F^2 converged at $R_1 = 0.0535$ and $wR^2 = 0.1729$ [based on $I > 2\sigma(I)$], $R_1 = 0.0550$ and $wR^2 = 0.1744$ for all data. CCDC 816508 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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