Inorganic Chemistry

Construction of Chiral "Triple-Decker" Nd(III) Nanocluster with High NIR Luminescence Sensitivity toward Co(II)

Xia Liu, Yanan Ma, Xiaoping Yang,* Dongliang Shi, Desmond Schipper, and Richard A. Jones

ABSTRACT: One Nd(III) complex $[Nd_3L_3(OAc)_3]$ (1) was synthesized from a conjugate Schiff base ligand H₂L. It shows a chiral "triple-decker" structure (1.1 × 1.2 × 1.8 nm) with Nd(III) ions sandwiched between the Schiff base ligands. 1 exhibits NIR Nd(III) luminescence, and the LMET efficiency is calculated to be 13.8%. It displays high luminescence sensitivity and selectivity to Co(II). The K_{SV} value and LOD of 1 to Co(II) are 9.96 × 10⁴ M⁻¹ and 0.97 μ M, respectively.

Recently much attention has focused on the fluorescent response for selective detection of various analytes due to its potential application in environment, biology, and medicine.¹⁻⁶ Cobalt is one of the biological essential trace elements and plays a critical role in the metabolism of ions and formation of hemoglobin. However, an excessive level of cobalt in the body may cause adverse health effects such as blindness, deafness, and hypothyroidism.^{7,8} Cobalt has been classified by the International Agency for Research on Cancer (IARC) as a possible group (2B) human carcinogen. The toxic dose of cobalt is 500 mg, and the maximum tolerable limit in the diet is 10 mg/L.⁹ Owing to the versatile applications of cobalt in the industry, it has been found as a contaminant in the environment. Much effort has been devoted to the development of fluorescent sensors for the Co(II) detection, such as fluorescent organics,^{10–12} metal nanoparticles (NPs),^{13–15} and metal–organic frameworks (MOFs).^{16–18} In early research in this field, Govindaraju et al. developed some interesting fluorescent Schiff bases and chromogenic resorufin dyes for the detection of Co(II) in organisms.^{19–21} So far, many visible luminescent lanthanide complexes bearing Eu^{3+} and Tb^{3+} ions have been used as probes to detect various analytes;²²⁻²⁴ however, there are very few reports on the NIR luminescent lanthanide complexes in this field.^{25,26} NIR fluorescent probes may offer the advantage of lower levels of absorption and autofluorescence of biomolecules in this wavelength range.

For the past few years, the construction of chiral metal complexes has attracted much attention of researchers due to their potential application in pharmaceuticals, catalysis, and functional materials.^{27–29} We have previously reported the synthesis of one chiral complex $[Yb_3(L')_3]$ with Schiff base ligand N,N'-bis(5-bromo-3-methoxysalicylidene)phenylene-1,2-diamine (H₂L', Scheme S1). In the "triple-decker" structure of this complex, the back H₂L' ligand deflects in a clockwise (or anticlockwise) fashion to form a Δ (or Λ) designation.³⁰ It is found that some factors such as the types of metal salts and ligand structures may affect the construction of "multi-decker" lanthanide complexe.^{31–33} With this consideration, one lanthanide complex [Nd₃L₃(OAc)₃] (1) was synthesized by the use of a new conjugate Schiff base ligand

N,N'-bis(3-methoxysalicylidene)(4-methylphenylene)-1,2-diamine (H₂L, Scheme S1) that has one methyl group on the central benzene ring. I shows a chiral "triple-decker" structure (1.1 \times 1.2 \times 1.8 nm) with the Nd(III) ions sandwiched between the alternating layers of Schiff base ligands. Interestingly, luminescent sensing studies show that I displays high sensitivity and selectivity to Co(II). To the best of our knowledge, this is the first report on the NIR luminescent detection of Co(II) based on chiral lanthanide complex.

The Schiff-base ligand was synthesized from the reaction of 2-hydroxy-3-methoxybenzaldehyde and 4-methylbenzene-1,2diamine (yield, 82%).³⁴ The signal of an imino proton (-CH=N-) in the ¹H NMR spectrum of H₂L is found at 8.61 ppm (Figure S1). The reaction of H_2L with Nd(OAc)₃. 6H₂O in refluxing MeOH gave the complex, and the slow diffusion of diethyl ether into the reaction solution led to the formation of the crystalline product of 1. In the chiral "tripledecker" structure of 1 (Figure 1a), the backmost Schiff base ligand deflects counter clockwise, resulting in the " Λ " designation as found in $[Yb_3(L')_3]$.²⁸ The coordination number of all Nd(III) is eight. Nd(1) is surrounded by eight oxygen atoms from the front Schiff base ligand and three OAc⁻ anions. Nd(2) is bound to the N_2O_2 and O_2O_2 donor sets of two back L^{2-} ligands, while Nd(3) is coordinated with two N_2O_2 sets of the L²⁻ ligands. The coordination geometry about the Nd(III) ions is a slightly distorted dodecahedron. The Nd(III) ions in 1 are linked together by two L^{2-} ligands and one OAc⁻ anion, and the Nd(III)…Nd(III) distances are from 3.730 to 3.853 Å.

In the solid state, 1 reveals an open 3D channel structure (Figure 1b). Intermolecular (OAc⁻)H···O(OAc⁻) hydrogen bonding (i.e., 2.461 Å–2.666 Å), $\pi \cdots \pi$ (i.e., 3.625–3.990 Å),

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Figure 1. (a) Chiral "tri-decker" structure of **1**. (The aromatic methyl groups are drawn in black to show the anticlockwise deflection of the back Schiff base ligand.) (b) Open 3D channel structure along the *a* axis. (c) SEM image. (d) EDX spectroscopy.

and (OAc⁻)-H… π interactions (i.e., 2.811 Å-3.102 Å)^{35,36} are formed among neighbor molecules in the crystal packing structure of 1. The empty volume calculated by the PLATON program is 16.9% of the total crystal volume. The scanning electron microscopy (SEM) image of 1 is displayed in Figure 1c. The energy dispersive X-ray (EDX) spectroscopy exhibits that the weight content of Nd(III) in 1 is about 23% (Figure 1d), which is also confirmed by inductively coupled plasmaatomic emission spectrometry (ICP-AES, Figure S3A). These results as well as the elemental analysis of 1 (see ESI) indicate that the crystalline product of the complex is pure. Due to the escaping of solvent molecules in the 3D channel structure, the crystal packing structure of 1 collapses rapidly after the crystalline product is separated from the mother solution. A large background is found in the powder XRD spectrum of 1, indicating the amorphous nature of the complex in the solid state (Figure S4). Both thermogravimetric analysis (Figure S5) and melting point measurement (see ESI) exhibit that 1 is stable in the solid state until heated to 206 °C. The stability of 1 in solution is confirmed by a molar conductivity study. The complex is neutral in CH₃CN, in agreement with its crystal structure.

The free Schiff base ligand and the complex show a broad absorption band at about 300 nm (Figure S6). The photoluminescence spectrum of free H₂L exhibits an emission band with $\lambda_{max} = 482$ nm (Figure S7a). The emission spectrum of 1 in either solution or the solid state displays the NIR luminescence of Nd(III) (Figure S7b). The excitation spectrum of 1 exhibits the strongest peak at about 300 nm, which is similar to the absorption of free H₂L. This indicates that the lanthanide emission is sensitized by the Schiff base ligand through the ligand-to-metal energy transfer (LMET) process. The NIR emission lifetime (τ) and quantum yield (Φ_{em}) of 1 are measured to be 4.0 μ s and 0.22%, respectively (Figure S7b). Thus, the intrinsic quantum yields (Φ_{Ln}) of Nd(III) and LMET efficiency (η_{sens}) in 1 are calculated to be 1.6% and 13.8%, respectively, using equations $\Phi_{Ln} = \tau/\tau_0^{37}$ ($\tau_0 = 250 \ \mu s$, the natural lifetime of Nd(III)) and $\eta_{sens} = \Phi_{em}/\Phi_{Ln}^{38}$.

In the structure of the complex, there are 18 electronegative O atoms (from L^{2-} ligands and OAc⁻ anions), which may help to attract the metal cations in solution. Since the solubility of **1** in water is poor, the luminescent sensing of **1** to metal cations was investigated in CH₃CN. Interestingly, the addition of Co(II), Cu(II), Pd(II), Mg(II), Cr(III), Ag(I), and Mn(II) decreases the luminescence intensity of **1**, while the addition of Cd(II), Al(III), and Hg(II) slightly increases the luminescence (Figures 2 and S8). It is noticeable that the addition of Co(II)



Figure 2. Lanthanide luminescent response of 1 (10 μ M) to the addition of Co(II) in CH₃CN (λ_{ex} = 296 nm).

leads to a rapid decrease of the luminescence. For example, the emission intensity at 1066 nm is decreased more than 50% when the concentration of added Co(II) is 25 μ M. However, for other metal cations, the concentrations needed to decrease the intensity by half are much higher than 25 μ M (Figures 2 and S7). The linear relationship between luminescence intensity decreases and the concentrations of added metal cations can be fitted into the Stern–Volmer (S–V) equation,³⁹ which gives the quenching constants (K_{SV}) of 1 to metal cations. The K_{SV} value of 1 to Co(II) is 9.96 × 10⁴ M⁻¹, which is among the highest values reported so far for the fluorescent sensing of Co(II).^{10–18} As shown in Figure 3, this value is much larger than those of 1 to other metal cations (<0.4 × 10⁴ M⁻¹). The limit of detection (LOD) of 1 to Co(II) can be calculated by $3\sigma/K_{SV}$, where σ is the standard deviation



Figure 3. Lanthanide luminescence quenching constants (K_{SV}) of **1** to metal cations.

calculated from 21 blank measurements of 1.⁴⁰ The LOD of 1 to Co(II) is 0.97 μ M, which is smaller than the maximum permitted level of 1.7 μ M of groundwater quality criterion defined by the Department of Environmental Protection of New Jersey.^{7,8} In addition, 1 is recyclable for the detection of Co(II). The NIR luminescent response behavior of the recycled sample of 1 after treatment with Co(II) is similar to that before treatment with Co(II) (Figure S9). ICP-AES analysis shows that the weight content of Nd(III) in the recycled sample of 1 has not changed (Figure S3B). These results indicate that 1 meets the basic requirements of application for Co(II) chemosensors.^{16,41}

Chelation enhancement of the quenching emission (CHEQ) and chelation-enhanced fluorescence (CHEF) effects have been used to explain the influence of added metal cations on the lanthanide luminescence.⁴² For example, Co(II), Cu(II), Pd(II), Cr(III), and Mn(II) have d-d transitions, which may quench the luminescence of 1 by energy transfers from Nd(III) to these d-block metal cations.^{43,44} In addition, the added metal cations may affect the LMET process in 1, resulting in the luminescence intensity changes. It is found that the LMET efficiency (η_{sens}) in 1 is decreased to 9.8% after the addition of 25 μ M Co(II) (in this case, the luminescence lifetime (τ) and quantum yield (Φ_{em}) of 1 are measured to be 2.3 μ s and 0.09%, respectively (Figure S10)).^{37,38} Meanwhile, the luminescence intensity is also dependent on the ability of the complex to absorb light energy at the excitation wavelength (λ_{ex}) . UV-vis titration of 1 indicates that the addition of Co(II) (e.g., 67.9 μ M) decreases the absorption of the complex at $\lambda_{ex} = 296$ nm (Figure S11),⁴⁵ which is unfavorable to the sensitization effect of the Schiff base ligand to the lanthanide luminescence.⁴

The selectivity of 1 to Co(II) in the presence of other competitive metal cations was investigated. As shown in Figure 4, the existence of another metal cation with the same concentration does not affect the high quenching percentage of 1 to Co(II).



Figure 4. Luminescence quenching percentages of 1 (10 μ M) before and after the addition of Co(II) (50 μ M) in the presence of another competitive metal cation (50 μ M) in CH₃CN.

In brief, a new conjugate Schiff base ligand was used to synthesize the trinuclear Nd(III) complex **1**. It shows a chiral "tri-decker" structure with lanthanide ions sandwiched between the Schiff base ligands. **1** displays the NIR luminescence of Nd(III), and the LMET efficiency is calculated to be 13.8%. It shows high luminescence sensitivity to Co(II) even in the presence of other metal cations. The K_{SV}

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value and LOD of 1 to Co(II) are $9.96 \times 10^4 \text{ M}^{-1}$ and 0.97μ M, respectively. To the best of our knowledge, 1 represents the first report of a chiral lanthanide complex for NIR luminescent detection of Co(II). Further studies focused on the improvement of the solubility of 1 in H₂O by the introduction of some water-soluble groups such as carboxylic and sulfonic groups into the Schiff base ligand are in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01146.

Detailed synthesis of ligand H₂L and complex 1, ¹H NMR, IR, TGA, PXRD and UV–vis spectra, luminescence properties, and X-ray crystallography (PDF)

Accession Codes

CCDC 1988628 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Xiaoping Yang – College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China; orcid.org/0000-0002-4370-517X; Email: xpyang@ wzu.edu.cn

Authors

- Xia Liu College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China
- **Yanan Ma** College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China
- **Dongliang Shi** College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China
- **Desmond Schipper** The University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, Texas 78712, United States
- Richard A. Jones The University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, Texas 78712, United States; orcid.org/0000-0003-4174-6530

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c01146

Notes

The authors declare no competing financial interest.

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