One High-Nuclearity Cd(II)—Yb(III) Nanoring with Near-IR Luminescent Sensing to Antibiotics

Yanan Ma, Xiaoping Yang,* Dongliang Shi, Mengyu Niu, and Desmond Schipper

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ABSTRACT: One 12-metal Cd(II)–Yb(III) nanoring, $[Cd_8Yb_4L_8(OAc)_8]$ ·4OH (1), with a size of 1.2 × 2.8 × 2.8 nm was obtained from a designed flexible salen-type ligand that has eight coordination sites (O and N atoms). The near-IR emission of Yb(III) at 983 nm was detected upon the excitation of ligand-central absorption at 386 nm. This Cd(II)–Yb(III) nanoring exhibits high sensitivity to nitrofuran antibiotics (NFAs) even in the presence of other antibiotics. The quenching constants and limits of detection of NFAs are 2.5 × 10⁴–4.5 × 10⁴ M⁻¹ and 1.5–2.8 μ M, respectively.

uring recent years, the development of high-nuclearity metal nanorings has received much interest because of their beautiful geometrical configuration and special physical and chemical properties.^{1,2} Some large metallorings have been obtained from the assembly of d-block transition metals and lanthanides, e.g., $Mn_4Ln_4^{\ '3}$, $Mn_8Ln_8^{\ 4}$, $Fe_6Ln_3^{\ 5}$, $Co_{16}Ln_{24}^{\ 6}$, $Cu_{36}Ln_{24}^{\ 7}$, and $Cu_6(Zn_6)Ln_6^{\ 8}$. At present, growing attention has been devoted to fluorescence-based chemical sensors because of their fast response, high sensitivities, and convenient utilization.^{9,10} Among all kinds of detection objects, pharmaceutical antibiotics, which have been broadly used in many fields such as medical, aquaculture, and food processing, have been considered to be one of the most noticeable classes of environmental pollutants.^{11,12} For instance, nitrofuran antibiotics (NFAs) are a class of broad-spectrum antimicrobial compounds that have been proven to show potential carcinogenic and mutagenic effects. In recent years, some lanthanide complexes, including mononuclear complex and metal-organic frameworks, have been designed for the luminescence detection of antibiotics.^{13–15} As is known, some porphyrins and heterocyclic-based macrocycles, which have large ringlike structures, have been used as fluorescent sensors to detect small molecules and ions,¹⁶⁻¹⁸ while the construction of high-nuclearity d-4f nanorings as fluorescent probes for detection is still challenging.

For the synthesis of d–4f nanorings, much attention has been focused on the use of small bridging ligands, such as phosphonates,^{19,20} alkoxides,^{21,22} and carboxylates,^{5,7} for the purpose of obtaining single-molecule magnets (SMMs). In contrast, so far there are very few reported ringlike metal clusters with large organic ligands. Flexible long-chain Schiff base ligands can coordinate with metal ions by various modes in polynuclear d–4f complexes.^{23–25} We herein report a 12metal Cd(II)–Yb(III) nanoring, $[Cd_8Yb_4L_{10}(OAc)_8]$ ·4OH (1), with a new flexible salen-type Schiff base ligand, 6,6'-{(1*E*,1'*E*)-[[[butane-1,4-diylbis(oxy)]bis(2,1-phenylene)]bis-(azaneylylidene)]bis(methaneylylidene)}bis(2-methoxyphenol) (H₂L; Figure 1a), which has eight coordination sites (O and N atoms) to bind both d- and f-block metal ions. 1 exhibits interesting near-IR (NIR) emission sensing to antibiotics, particularly to NFAs at the parts per million level.

The salen-type ligand H₂L was synthesized with 2-nitrophenol, 1,4-dibromobutane, and 2-hydroxy-3-methoxybenzaldehyde as raw materials (Figure 1a), and its structure was confirmed by NMR, electrospray ionization mass spectrometry, and Fourier transform infrared (Figures S1 and S2). The product of 1 was formed as red crystals from the reaction of H_2L with $Yb(SO_3CF_3)_3$ and $Cd(OAc)_2$ in an ethanol (EtOH)/ methanol (MeOH) solution. Employment of a long salen-type ligand leads to the large size of 1 (about $1.2 \times 2.8 \times 2.8$ nm; Figure 1b). The centrosymmetric structure of 1 includes four equivalent Cd₂Yb moieties that are linked into a nanoscale ring by eight salen-type ligands. The diameter of the ring is about 1.6 nm. Eight O atoms from one OAc⁻ anion and four L²⁻ ligands bond to the Yb(III) ion, which exhibits a slightly distorted dodecahedral configuration.²⁶ The coordination numbers of Cd(II) ions are 6 and 7. In 1, the coordination modes of OAc⁻ and L²⁻ are $\mu_2(\eta^1:\eta^1 \text{ or } \eta^1:\eta^2)$ and $\mu_4(\eta^1:\eta^2:\eta^1:\eta^2:\eta^1)$, respectively. The distances between the adjacent Cd(II) and Yb(III) ions are from 3.693 to 3.736 Å. The Yb–O, Cd–N, and Cd–O bond lengths are 2.039–2.970, 2.190-2.460, and 1.907-2.529 Å, respectively. As shown in Figure 1c, the Cd/Yb molar ratio is found to be 2 by energydispersive X-ray spectroscopy (EDX) of 1, in agreement with its molecular formula. Thermogravimetric analysis (TGA) displays that 1 loses about 5% weight before 100 °C because of the escape of solvent molecules (e.g., MeOH, EtOH, and H_2O) uncoordinated in the structure, and then its weight hardly changes until it is heated to more than 200 °C (Figure S4). The thermodynamic stability of 1 is also investigated by

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Figure 1. (a) Synthesis route of the salen-type ligand H_2L . (b) Ringlike crystal structure of 1 [Cd(II), green, Yb(III), blue]. (c) EDX. Inset: Field emission scanning electron microscopy image. (d) DLS analysis of 1 in CH₃CN.

melting point measurement, which indicates that it begins to decompose from 220 °C (see the Supporting Information, SI). The stability of the ringlike structure of 1 in solution is confirmed by dynamic light scattering (DLS) analysis, which displays a diameter distribution centered at 2.8 nm (Figure 1d), consistent with its crystal structure of 1.^{27–30}

In 1, the lanthanide ions are surrounded within the nanoring structure and separated from outside solvent molecules that may decrease the lanthanide emission.³¹ Meanwhile, no solvent molecules such as MeOH or H₂O bond to the Yb(III) ions. These factors are conducive to improvement of the luminescence properties of 1. The free H₂L ligand displays absorption bands at 280 and 338 nm (Figure S6) and exhibits a broad emission band at 554 nm (Figure S7a). Under excitation at 386 nm, the NIR emission of Yb(III) corresponding to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition was found at 983 nm (Figure S7b), with a lifetime (τ) of 7.48 μ s (Figure S8). The intrinsic quantum yield of Yb(III) ($\Phi_{Ln} = \tau/\tau_{0}$) is able to be estimated as 0.37%, with $\tau_{0} = 2000 \ \mu s.^{32}$ The quantum yield of the NIR emission of 1 (Φ_{em}) is measured as 0.09%. Consequently, the transfer energy efficiency ($\eta_{sens} = \Phi_{em}/\Phi_{Ln}$) of salen-type ligands is found to be 24.3%.³³ The energy gap between the excited triplet-state level (³LC) of the

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salen-type ligand and the ${}^{2}F_{5/2}$ level of Yb(III) in 1 plays a key role in the energy-transfer process.^{34,35} The ${}^{3}LC$ level of the salen-type ligand in 1 can be estimated from the visible emission of the Gd(III) analogue ([Cd₈Gd₄L₈(OAc)₈]·4OH; see the SI), in which energy transfer from the salen-type ligands to lanthanides does not occur. The ${}^{3}LC$ level of the salen-type ligand is determined to be 18200 cm⁻¹ (Figure S9). Hence, the energy gap between the ${}^{3}LC$ and ${}^{2}F_{5/2}$ levels [Yb(III): 10200 cm⁻¹] in 1 is calculated to be about 8000 cm⁻¹. This large energy gap suggests that the process of energy transfer in 1 may be decided by electron transfer or a phononassisted energy-transfer mechanism.^{36,37}

The sensing behavior of 1 to four types of classic antibiotics, i.e., nitrofurans (NFAs: NFZ, FZD, and NFT), nitroimidazoles (MDZ, RDZ and ODZ), sulfonamides (SMX, SDZ, and SMZ), and chloramphenicols (THI and CAP), and one commonly used antibiotics-pyrazinamide (PZA; Scheme S2) was studied in acetonitrile (CH₃CN). The addition of these antibiotics leads to various changes of the NIR emission of 1. Except SDZ and SMZ, the addition of other antibiotics decreases the emission of 1 (Figures 2 and S10). NFAs (NFZ,



Figure 2. Intensity changes of 1 ($c = 10 \ \mu$ M) at 983 nm caused by the addition of antibiotics at different concentrations. Inset: Quenching constants of antibiotics ($\lambda_{ex} = 386 \ nm$).

FZD, and NFT) decrease the lanthanide luminescence much faster than other antibiotics. For example, the addition of 100 μ M NFAs decreases the luminescence more than 70%, but less than 20% for the addition of other antibiotics with the same concentration (Figure S10).

The quenching constants (K_{SV}) of the antibiotics were calculated by the Stern–Volmer equation $(I_0/I = 1 + K_{SV}[A])$.³⁸ As shown in Figure 2, the K_{SV} values of NFZ, FZD, and NFT are 4.49 × 10⁴, 2.62 × 10⁴, and 2.51 × 10⁴ M⁻¹, respectively, which correspond to the highest numbers reported so far for NFA detection based on fluorescent metal complexes^{39–42} and higher than those obtained from fluorescent silica nanoparticles.⁴³ For 1, the limits of detection (LOD = $3\sigma/K_{SV}^{44}$) of these three NFAs are calculated to be 1.53, 2.63, and 2.74 μ M, respectively. This indicates that 1 has high luminescence sensitivity to NFAs at the parts per million level.

The origin of emission quenching of **1** caused by antibiotics can be due to an "inner filter effect", ^{39,40} in which the added antibiotics also absorb light energy at the excitation wavelength (386 nm), resulting in a decrease in energy absorption of **1**. As

shown in Figure 3, NFAs exhibit strong absorption at 386 nm; however, other antibiotics have very little absorption. For



Figure 3. UV–vis absorption spectra of tested antibiotics ($c = 10 \ \mu M$) in CH₃CN.

instance, the absorption coefficients of NFT and NFZ at λ_{ex} are 7.27 × 10⁴ and 7.73 × 10⁴ M⁻¹ cm⁻¹, respectively, which are larger than that of 1 (6.47 × 10⁴ M⁻¹ cm⁻¹). Therefore, the added NFAs can effectively compete with the salen-type ligands of 1 to absorb light energy. In addition, another mechanism that may be involved is the photoinduced electron-transfer (PET) process, where emission quenching of 1 is due to excited electron transfer from the salen-type ligand to the LUMO of antibiotics.^{17,41} According to the literature,⁴⁵ the approximate LUMO energy level of the salen-type ligand in 1 is at about –1 eV, which is higher than those of NFAs. Thus, antibiotics with lower LUMO energy levels have a stronger ability to accept an electron from the ligand. As shown in Scheme 1, although the LUMO energy levels of NFAs are

Scheme 1. HOMO and LUMO Energy Levels of the Antibiotics



generally lower than those of other antibiotics, the changing trends of the K_{SV} values of all antibiotics and their LUMO energy levels are not the same. For instance, the LUMO energy levels of MDZ, RDZ, ODZ, THI, and CAP are much lower than those of SMX, PZA, SDZ, and SMZ; however, these nine antibiotics have similar K_{SV} values. These results suggest that the PET mechanism may not play a key role in emission quenching caused by antibiotics, while the "inner filter effect" dominates the quenching process of **1** to NFAs.

In the presence of other antibiotics, the sensing behavior of 1 to NFAs was studied in CH_3CN . It was found that the

existence of other antibiotics with 10 times concentration does not change the emission quenching of 1 caused by NFZ (Figure 4a). In addition, the stepwise addition of antibiotics



Figure 4. NIR emission sensing of **1** ($c = 10 \ \mu$ M) to NFZ in the presence of other antibiotics in CH₃CN: (a) percentages of emission quenching before and after the addition of NFZ ($c = 100 \ \mu$ M) with the existence of other antibiotics ($c = 1000 \ \mu$ M); (b) decrease of the luminescence intensities with the stepwise addition of other antibiotics and NFZ (15 μ M each time).

also confirms the selectivity of **1** to NFAs (Figure 4b). For instance, emission quenching is not very obvious with the addition of MDZ twice first. However, the continued addition of NFZ gives a rapid decrease of the lanthanide emission. In the following addition cycles, this changing trend of the luminescence intensities repeats again, which indicates that **1** exhibits high selectivity to NFZ even in the presence of other antibiotics.

In order to evaluate the practicality of the Yb(III) nanoring on real samples, the luminescent response of 1 to antibiotic drugs sold in pharmacies was investigated. For example, the addition of 60 mg L⁻¹ nitrofurazone (containing NFZ) and furazolidone (containing FZD) reduces the luminescence intensities by 95% and 73%, respectively (Figure S11). These results show that 1 displays high sensitivity to real antibiotic drugs containing NFAs.

In brief, one 12-metal Cd(II)–Yb(III) nanoring, 1, was constructed by the use of a new flexible salen-type ligand that shows a $\mu_4(\eta^1:\eta^2:\eta^1:\eta^2:\eta^1)$ coordination mode. The molecular size of the metal nanoring is about 1.2 × 2.8 × 2.8 nm. 1 exhibits NIR emission sensing to NFAs at the ppm level. The quenching constants and LODs of NFAs are 2.5 × 10⁴-4.5 × 10⁴ M⁻¹ and 1.5-2.8 μ M, respectively. The presence of other antibiotics does not affect the high sensitivity and selectivity of 1 to NFAs. The practicality of 1 was investigated by its luminescent response to real antibiotic drugs

such as nitrofurazone and furazolidone. Further studies in the design of luminescent d-4f nanorings with sensing properties to more antibiotics 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.0c02567.

Synthesis process of H_2L and 1, IR, NMR, PXRD, and UV–vis spectra, TGA, luminescence properties, and X-ray crystallography (PDF)

Accession Codes

CCDC 2025645 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

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

Mengyu Niu – College of Chemistry and Materials

Engineering, Wenzhou University, Wenzhou 325035, China Desmond Schipper – Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c02567

Notes

The authors declare no competing financial interest.

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