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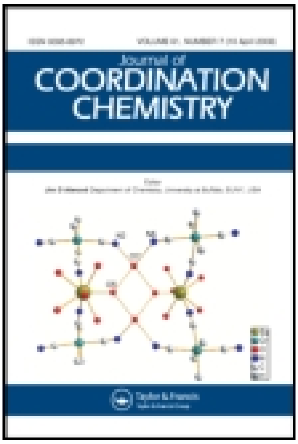

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Synthesis and characterization of a dysprosium complex with strong photoluminescence

Wentong Chen [a] & Zhongliang Yao [b]

[a] School of Chemistry and Chemical Engineering, Jiangxi Province Key Laboratory of Coordination Chemistry, Jinggangshan University , Ji'an, Jiangxi 343009, China

[b] Biology and Chemistry Engineering Department , Fuqing Branch of Fujian Normal University , Fuqing, Fujian 350300, China

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Synthesis and characterization of a dysprosium complex with strong photoluminescence

WENTONG CHEN*† and ZHONGLIANG YAO‡

†School of Chemistry and Chemical Engineering, Jiangxi Province Key Laboratory of Coordination Chemistry, Jinggangshan University, Ji'an, Jiangxi 343009, China
‡Biology and Chemistry Engineering Department, Fuqing Branch of Fujian Normal University, Fuqing, Fujian 350300, China

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A dysprosium complex [Dy(2-pyrazinecarboxylic acid)$_3$(H_2O)$_2$]$_n\cdot 6n$$H_2O$ (**1**) was prepared by hydrothermal reactions and structurally characterized by single-crystal X-ray diffraction. Complex **1** is an infinite 1-D structure with Dy^{3+} binding with six oxygens and three nitrogens to yield a distorted monocapped square antiprism. The [Dy(2-pyrazinecarboxylic acid)$_3$(H_2O)$_2$]$_n$ and lattice water interconnect *via* π–π and hydrogen-bonding interactions to form a 3-D supramolecular network. Photoluminescent investigations at room temperature reveal that **1** exhibits two intensive emissions that can be ascribed to $^4F_{9/2} \rightarrow {}^6H_J$ transitions ($J = 15/2$ and 13/2) of Dy^{3+} ions.

Keywords: Dysprosium; Lanthanide; Photoluminescence; 2-Pyrazinecarboxylic acid

1. Introduction

Lanthanide coordination complexes attract attention due to their photoluminescence, especially lanthanide coordination complexes with conjugated organic ligands because these complexes possess good properties for their applications in luminescent materials, probes, etc. [1]. Generally, lanthanide ions display intensive emission bands when f–f electronic transitions of the lanthanide ions occur. Unfortunately, lanthanide ions usually have poor absorption coefficients, which result in weak f–f electronic transitions. To improve the absorption coefficients of the lanthanide ions and achieve intensive emissions, organic ligands with conjugated structures, such as aromatic carboxylic acids and β-diketones, are employed because these organic ligands absorb ultraviolet light and then transfer the absorbed energy to the lanthanide ions called the "antenna effect" [2]. In particular, aromatic carboxylic acid lanthanide coordination complexes exhibit higher luminescent stability for practical applications than those possessing other organic ligands [3].

Among aromatic carboxylic acids, 2-pyrazinecarboxylic acid with a conjugated structure is a quite interesting synthon for constructing extended structures because it is

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*Corresponding author. Email: wtchen_2000@yahoo.cn

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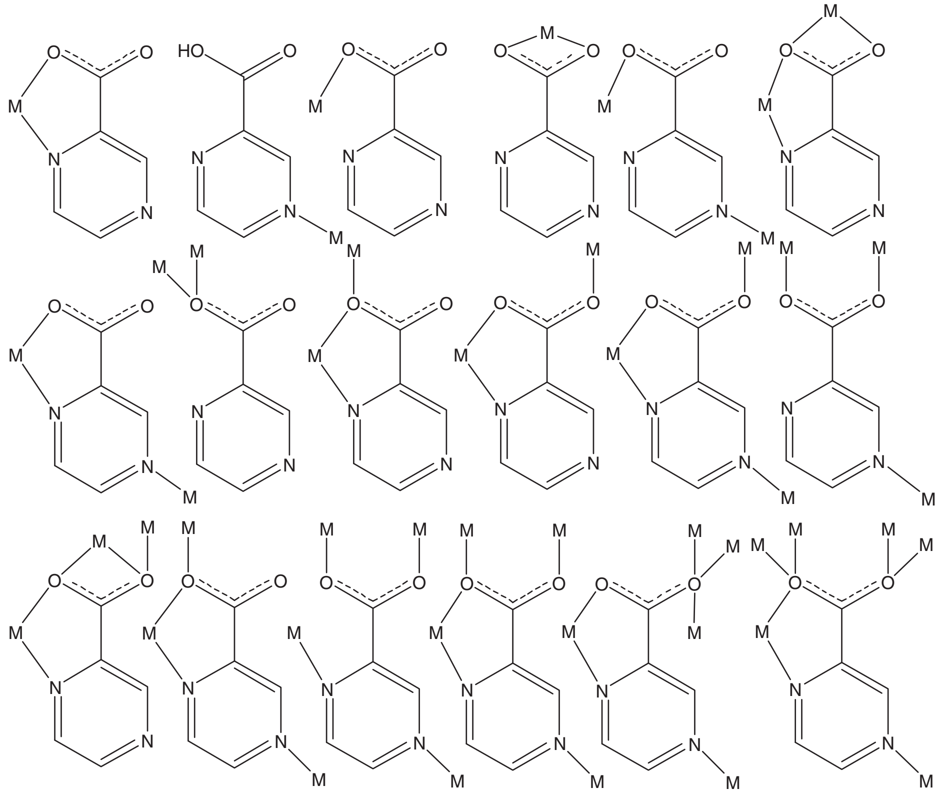


Scheme 1. Various coordination modes of 2-pyrazinecarboxylic acid with metal ions (M = metal ion).

an unsymmetrical ligand and can link several metal centers by coordinating to metal ions through nitrogen and carboxylate (scheme 1). Accordingly, we choose 2-pyrazinecarboxylic acid to synthesize lanthanide coordination complexes that may display strong luminescence. We herein report the synthesis, characterization, and photoluminescence of $[Dy(2\text{-pyrazinecarboxylic acid})_3(H_2O)_2]_n \cdot 6nH_2O$ (**1**) with an infinite 1-D chain-like structure. Complex **1** shows two strong luminescent emissions that can be ascribed to $^4F_{9/2} \rightarrow {}^6H_J$ transitions ($J = 15/2$ and $13/2$) of Dy^{3+} ions.

A number of pyridine carboxylates and benzene carboxylates have been documented [4]. However, among those complexes, only small amount of them have been investigated on their photoluminescent properties, especially studies are rare on photoluminescent properties of pyridine carboxylates or benzene carboxylates of lanthanides [4a,e,g,h].

2. Experimental

2.1. *Materials and instrumentation*

All reactants of A.R. grade were obtained commercially and used without purification. Carbon, hydrogen, and nitrogen elemental analyses were carried out with an Elementar

Vario EL III microanalyser. The fluorescence data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer.

2.2. *Synthesis of [Dy(2-pyrazinecarboxylic acid)$_3$(H$_2$O)$_2$]$_n$·6nH$_2$O (1)*

This complex was prepared by mixing Dy(Ac)$_3\cdot4H_2O$ (1 mmol, 412 mg), 2-pyrazinecarboxylic acid (3 mmol, 372 mg), and 10 mL distilled water in a 23 mL Teflon-lined stainless steel autoclave and heating at 180°C for 7 days. After being slowly cooled to room temperature at 6°C h^{-1}, colorless crystals suitable for X-ray analysis were obtained. The yield is 61%. Anal. Calcd for $C_{15}H_{25}DyN_6O_{14}$ (%): C, 26.63; H, 3.70; N, 12.43. Found (%): C, 26.78; H, 3.67; N, 12.25.

2.3. *X-ray structure determination*

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections [5]. The structure was solved by direct methods using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software [6]. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen positions were generated theoretically, except for those of lattice water molecules that were yielded by difference Fourier maps, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The summary of crystallographic data and structure analysis is given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

Complex **1** consists of infinite 1-D [Dy(2-pyrazinecarboxylic acid)$_3$(H$_2$O)$_2$]$_n$ chains and isolated water molecules. Dy^{3+} coordinates with three nitrogens of three 2-pyrazinecarboxylic acid ligands and six oxygens, of which four are from four 2-pyrazinecarboxylic acid ligands and two are from water, giving a distorted monocapped square antiprism with the top and bottom planes defined by O(1W), N(3), O(5), N(5) and O(1), O(2W), O(3), O(6) ($-1.5 - x$, $-0.5 + y$, z), respectively, and N(1) as the apex, as shown in figure 1. The Dy–O$_{\text{2-pyrazinecarboxylic acid}}$ bond lengths are in the range 2.326(2)–2.352(2) Å with an average value of 2.347(2) Å, shorter than Dy–O$_{\text{water}}$ bond lengths, 2.382(2) and 2.388(2) Å, indicating that 2-pyrazinecarboxylic acid exhibits stronger attraction to dysprosium than water. In **1**, there are three crystallographic independent 2-pyrazinecarboxylic acid ligands, one is tridentate while the other is bidentate. The Dy···Dy distance is 6.504 Å. Neighboring Dy^{3+} ions interlink through tridentate 2-pyrazinecarboxylic acid to yield an infinite 1-D zigzag chain parallel to the crystallographic *b*-axis, as shown in figure 2. A 2-D supramolecular

Table 1. Summary of crystallographic data and structure analysis.

Empirical formula	$C_{15}H_{25}DyN_6O_{14}$
Formula weight	675.91
Color	Colorless
Crystal size (mm^3)	$0.14 \times 0.11 \times 0.10$
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions (Å, °)	
a	19.394(3)
b	11.913(2)
c	19.845(3)
Volume (Å^3), *Z*	4585(1), 8
$2\theta_{\max}$ (°)	50
Index ranges	$-21 \le h \le 23$; $-13 \le k \le 14$; $-23 \le l \le 23$
Reflections collected	28,021
Independent, observed reflections (R_{int})	4022, 3822 (0.0332)
Calculated density (g cm^{-3})	1.958
Absorption coefficient, μ, (mm^{-1})	3.343
Temperature (*K*)	123.1500
F(000)	2680
R_1, wR_2	0.0197, 0.0471
S	1.032
Largest and mean Δ/σ	0.003, 0
$\Delta\rho$(max, min) (e Å^{-3})	1.292, −0.410

Table 2. Selected bond lengths (Å) and angles (°).

Dy(1)–O(1)	2.360(2)	O(1)–Dy(1)–O(1W)	140.72(6)
Dy(1)–O(3)	2.326(2)	O(2W)–Dy(1)–O(1W)	132.42(8)
Dy(1)–O(5)	2.352(2)	O(3)–Dy(1)–N(1)	71.20(6)
Dy(1)–O(6)#1	2.350(2)	O(6)#1–Dy(1)–N(1)	70.39(6)
Dy(1)–O(1W)	2.388(2)	O(5)–Dy(1)–N(1)	137.68(6)
Dy(1)–O(2W)	2.382(2)	O(1)–Dy(1)–N(1)	64.45(6)
Dy(1)–N(1)	2.585(2)	O(2W)–Dy(1)–N(1)	74.68(6)
Dy(1)–N(3)	2.631(2)	O(1W)–Dy(1)–N(1)	141.04(7)
Dy(1)–N(5)	2.672(2)	O(3)–Dy(1)–N(3)	63.98(6)
		O(6)#1–Dy(1)–N(3)	133.24(6)
O(3)–Dy(1)–O(6)#1	79.87(6)	O(5)–Dy(1)–N(3)	72.96(6)
O(3)–Dy(1)–O(5)	136.88(6)	O(1)–Dy(1)–N(3)	134.49(6)
O(6)#1–Dy(1)–O(5)	133.45(6)	O(2W)–Dy(1)–N(3)	65.60(7)
O(3)–Dy(1)–O(1)	135.00(6)	O(1W)–Dy(1)–N(3)	68.11(7)
O(6)#1–Dy(1)–O(1)	91.97(6)	N(1)–Dy(1)–N(3)	119.34(6)
O(5)–Dy(1)–O(1)	78.59(6)	O(3)–Dy(1)–N(5)	139.01(6)
O(3)–Dy(1)–O(2W)	88.31(7)	O(6)#1–Dy(1)–N(5)	69.18(6)
O(6)#1–Dy(1)–O(2W)	145.06(6)	O(5)–Dy(1)–N(5)	64.39(6)
O(5)–Dy(1)–O(2W)	75.67(6)	O(1)–Dy(1)–N(5)	73.84(6)
O(1)–Dy(1)–O(2W)	73.46(7)	O(2W)–Dy(1)–N(5)	132.20(6)
O(3)–Dy(1)–O(1W)	81.13(7)	O(1W)–Dy(1)–N(5)	67.10(7)
O(6)#1–Dy(1)–O(1W)	78.30(7)	N(1)–Dy(1)–N(5)	119.36(6)
O(5)–Dy(1)–O(1W)	81.06(7)	N(3)–Dy(1)–N(5)	121.29(6)

Symmetry code: #1 $-x-3/2$, $y-1/2$, z.

layer, extending along the *ab* plane, is constructed from zigzag chains interconnecting *via* π–π interactions (figure 3).

There are many π–π interactions and hydrogen bonds in **1**. All the 2-pyrazinecarboxylic acid ligands take part in π–π interactions and hydrogen-bonding

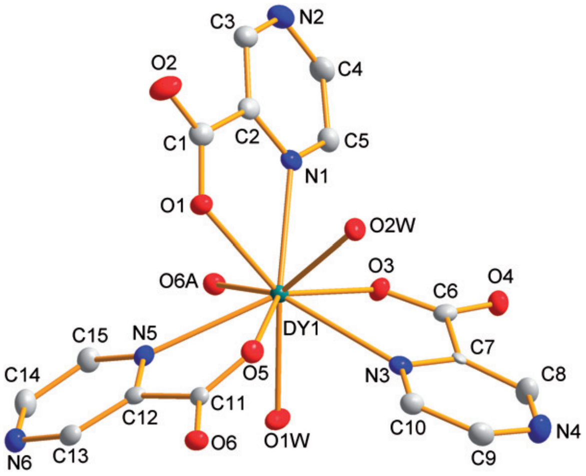


Figure 1. ORTEP view of **1** showing 50% thermal ellipsoids. Lattice water and hydrogens were omitted for clarity. Symmetry code: A $- 1.5 - x$, $-0.5 + y$, z.

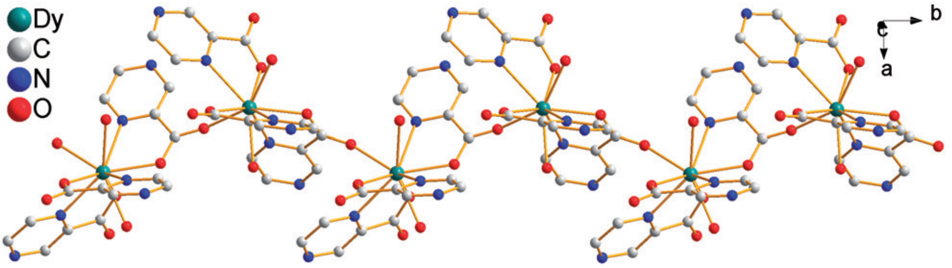
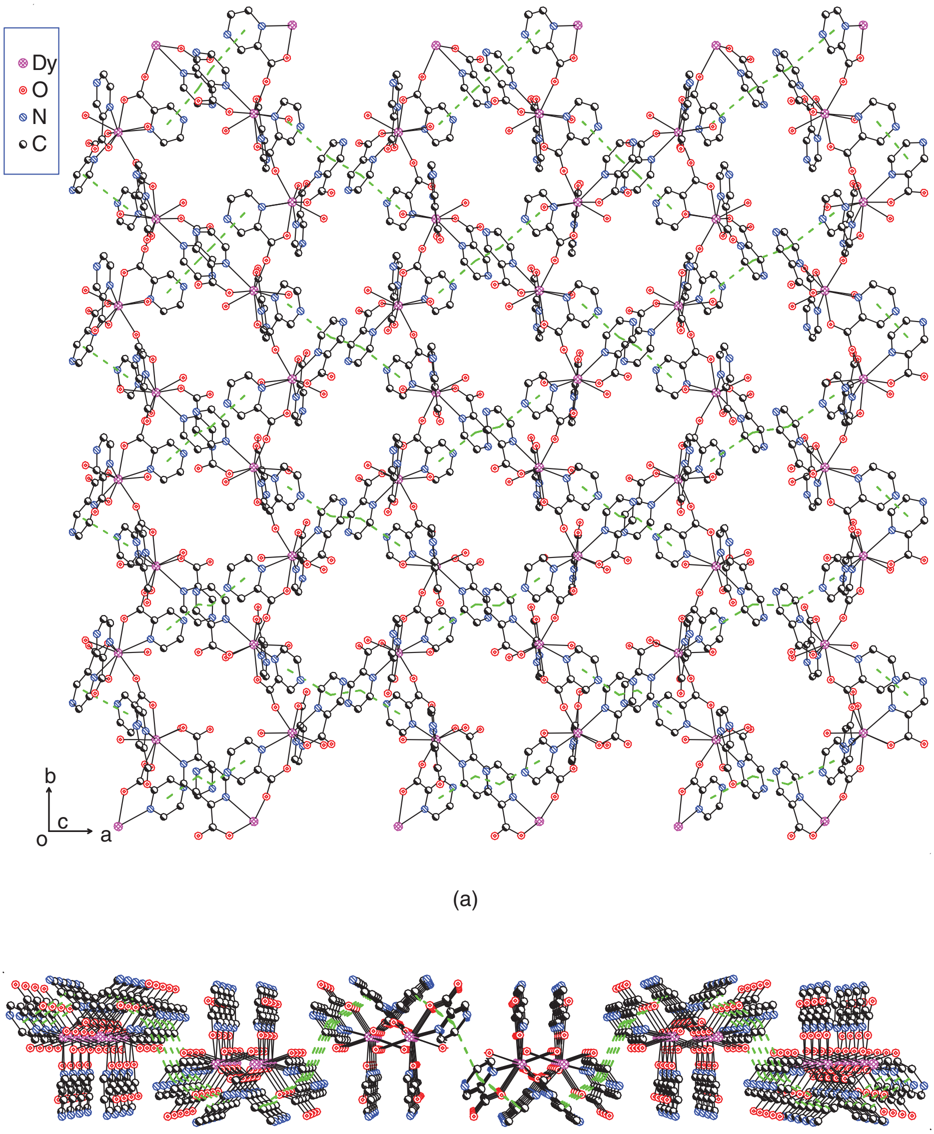


Figure 2. The chain-like structure.

interactions. In **1**, there are six types of hydrogen-bonding interactions, O $\cdots$ O, O $\cdots$ N, C $\cdots$ O, C $\cdots$ N, C–H $\cdots$ π, and O–H$\cdots\pi$. Lattice water and the 2-D supramolecular layers interconnect through hydrogen bonds and π–π stacking interactions to complete a 3-D supramolecular framework, as shown in figure 4. Bond valence calculations reveal that dysprosium is +3 (Dy1: 3.3) [7]. Although dozens of 2-pyrazinecarboxylic acid-containing complexes have been documented, it is rare that a complex contains both bidentate and tridentate 2-pyrazinecarboxylic acid ligands [8].

Considering the excellent photoluminescent properties of Dy^{3+} complexes, we investigated the photoluminescent spectra of **1** at room temperature (figure 5). The emission spectra of **1** display good photoluminescence with narrow, sharp, and well-separated emission bands. The excitation spectra of **1** reveal that the effective energy absorption occurs in the ultraviolet at 280–350 nm. The emission spectra exhibit two intense emission bands under excitation of 321 nm: 479 and 573 nm, with a broad but weak band at 388 nm. Dy^{3+} ions usually show several emission bands around 480 and 571 nm, which originated from ${}^4F_{9/2} \rightarrow {}^6H_J$ transitions ($J = 15/2$ and $13/2$) of Dy^{3+}



(a)

(b)

Figure 3. A 2-D layer: (a) viewed along the *c*-axis. (b) viewed along the *b*-axis. The dashed green lines represent π–π interactions (Å, °): $C_g(1)\cdots C_g(1)$ 3.957(2), 0.02; $C_g(1)\cdots C_g(2)$ 3.784(2), 28.75 [$C_g(1)$ and $C_g(2)$ represent the centers of gravity of the rings N1(C2–C5, N2) and N5(C12–C15, N6), respectively].

ions [9]. Therefore, for **1**, the two intense emission bands at 479 and 573 nm should be attributed to $^4F_{9/2} \rightarrow {}^6H_J$ transitions ($J = 15/2$ and $13/2$) of Dy^{3+}. This implies that effective energy transfer occurs and that conjugated systems are formed between the 2-pyrazinecarboxylic acid ligands and Dy^{3+} in **1**.

We also measured the photoluminescent spectra of pure 2-pyrazinecarboxylic acid at room temperature showing one strong and broad emission band at 350–600 nm with

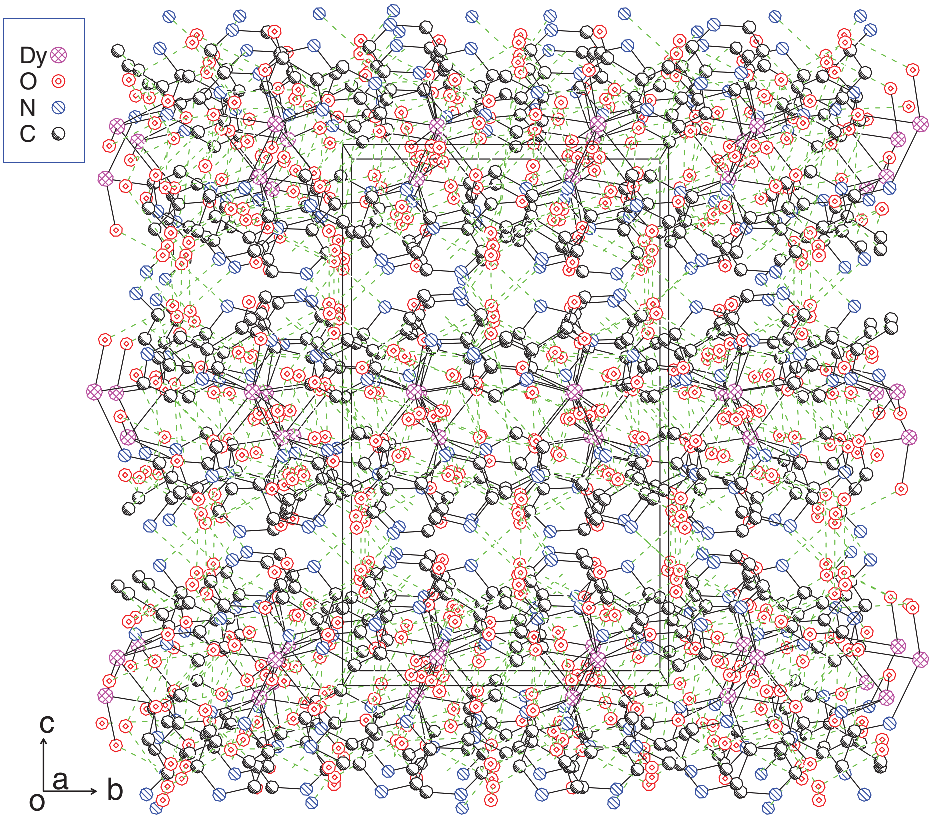


Figure 4. Crystal packing diagram with the dashed lines representing the hydrogen-bonding and π–π interactions (Å, °): O1W–H1WB$\cdots$O4W 2.705(3), 170(4); O1W–H1WA$\cdots$O8W 2.779(3), 177(3); O2W–H2WA$\cdots$O3W 2.706(3), 171(3); O2W–H2WB$\cdots$O6W 2.819(3), 172(4); O3W–H3WA$\cdots$O7W 2.713(3), 173(3); O3W–H3WB$\cdots$O8W 2.787(3), 162(4); O4W–H4WA$\cdots$O3W 2.885(3), 146(4); O4W–H4WB$\cdots$O4 2.840(3), 176(2); O5W–H5WB$\cdots$O1 2.827(3), 171(3); O5W–H5WA$\cdots$O4 2.851(3), 176.3(18); O6W–H6WA$\cdots$N2 2.938(3), 142(3); O6W–H6WB$\cdots$O7W 2.700(3), 155(3); O7W–H7WB$\cdots$O5W 2.791(3), 167(3); O7W–H7WA$\cdots$N6 2.859(3), 174(3); O8W–H8WB$\cdots$O5 2.883(3), 165(4); O8W–H8WA$\cdots$O6W 2.859(3), 163(3); C5–H5A$\cdots$O3 2.896(3), 120; C10–H10A$\cdots$O5 3.014(3), 121; C13–H13A$\cdots$N4 3.078(3), 124; C15–H15A$\cdots$O6 2.949(3), 116; C13–H13A$\cdots C_g(1)$ 3.150(3), 89.45; O4W–H4WB$\cdots C_g(2)$ 3.234(2), 86(3); O6W–H6WA$\cdots C_g(2)$ 3.275(2), 79(3); O6W–H6WB$\cdots C_g(2)$ 3.275(2), 94(2); $C_g(1)\cdots C_g(1)$ 3.957(2), 0.02; $C_g(1)\cdots C_g(3)$ 3.784(2), 28.75 [$C_g(1)$, $C_g(2)$, and $C_g(3)$ represent the centers of gravity of the rings N1(C2–C5, N2), N3(C7–C10, N4), and N5(C12–C15, N6), respectively].

a maximum wavelength of 436 nm upon photo-excitation at 326 nm, as shown in the inset of figure 5. Therefore, it is proposed that the weak band at 388 nm in **1** is caused by 2-pyrazinecarboxylic acid. In **1**, the weak ligand-based emission and the intense emission bands of Dy^{3+} suggest that energy transfer from the 2-pyrazinecarboxylic acid ligand to the lanthanide is very effective.

Thus, 2-pyrazinecarboxylic acid is perfect for sensitization of Dy^{3+} in **1**, a highly effective antenna for the photoluminescence of Dy^{3+}.

As reported by Eliseeva *et al.* [4a], the lowest triplet state energy of 2-pyrazinecarboxylic acid can be determined as around 24,000 cm^{-1} (scheme 2). The energy difference between the lowest triplet state of 2-pyrazinecarboxylic acid and the

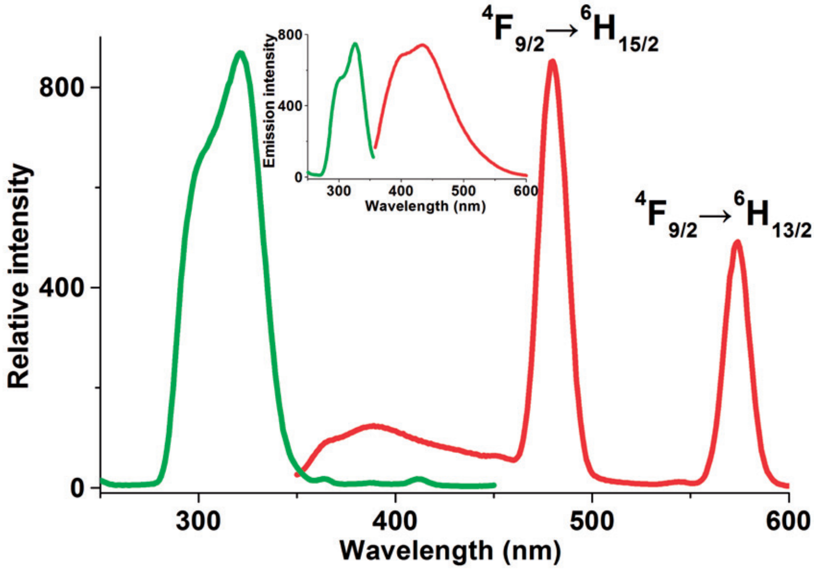
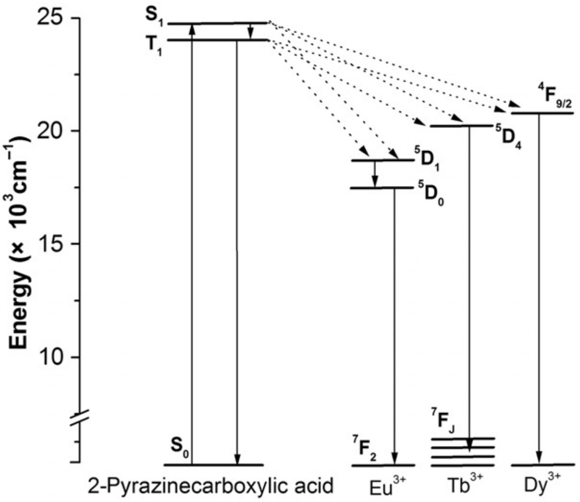


Figure 5. Emission spectra of **1** at room temperature (inset: the luminescent spectra of pure 2-pyrazinecarboxylic acid). Green: excitation spectra; red: emission spectra.



Scheme 2. A schematic and partial energy level diagram of the main energy absorption, transfer, and luminescence processes in lanthanides and 2-pyrazinecarboxylic acid.

energy levels of Eu^{3+} ($^5D_1$, 18,674 cm^{-1}), Tb^{3+} ($^5D_4$, 20,500 cm^{-1}), and Dy^{3+} ($^4F_{9/2}$, 20,875 cm^{-1}) are calculated and the results are listed in table 3.

Based on the intramolecular energy transfer mechanism documented by Dexter *et al.* [10], intramolecular energy migration efficiency depends mainly on two energy transfer processes, i.e. (a) the energy transfer from the lowest triplet energy level of the ligand to the resonant energy level of the lanthanide by Dexter's resonant exchange interaction and (b) the inverse energy transfer from Ln^{3+} to organic ligand by a thermal

Table 3. The energy difference between the lowest triplet energy of 2-pyrazinecarboxylic acid and the resonant energy level of the Ln^{3+} ions, Eu^{3+} ($^5D_1$, 18,674 cm^{-1}), Tb^{3+} ($^5D_4$, 20,500 cm^{-1}), and Dy^{3+} ($^4F_{9/2}$, 20,875 cm^{-1}).

Ln^{3+}	Lowest triplet state energy of 2-pyrazinecarboxylic acid (Tr) (cm^{-1})	ΔE(Tr–Ln^{3+}) (cm^{-1})
Eu	24,000	5326
Tb	24,000	3500
Dy	24,000	3125

deactivation mechanism. If the energy difference is too small, the inverse energy transfer will take place much easier. Both energy transfer processes depend on the energy gap between the lowest triplet energy level of the organic ligand and the resonant energy level of the lanthanide. Obviously, there is an opposite influence between the two energy transfer processes. Based on the intramolecular energy transfer mechanism, an optimal value of the energy gap is around $3000 \pm 500\,cm^{-1}$ [11]. Larger or smaller energy difference may result in a decrease in the photoluminescent intensities of the lanthanide-containing complexes.

As shown in table 3, the energy difference for Dy^{3+} is 3125 cm^{-1}, which is close to the optimal value of the energy gap ($3000 \pm 500\,cm^{-1}$), indicating that 2-pyrazinecarboxylic acid is suitable for excitation of Dy^{3+}, in good agreement with the photoluminescence of **1**. Similarly, 2-pyrazinecarboxylic acid should be suitable for excitation of Tb^{3+}, in good agreement with the results in $[Tb(2\text{-pyrazinecarboxylic acid})_3(H_2O)_2]_n \cdot 6nH_2O$ reported by Eliseeva *et al.* [4a]. Comparing Dy^{3+} and Tb^{3+}, the energy difference of Eu^{3+} ion is larger (5326 cm^{-1}), deviating from the optimal value, suggesting that 2-pyrazinecarboxylic acid should not be suitable for the excitation of Eu^{3+} ions. However, this prediction conflicts with the result for $[Eu(2\text{-pyrazinecarboxylic acid})_3(H_2O)_2]_n \cdot 6nH_2O$ reported by Eliseeva *et al.* [4a]. This discrepancy may be caused by an inaccurate optimal value estimated, because factors like oscillation of coordinated water that can affect photoluminescent properties are not included in the estimation.

We have prepared and characterized $[Dy(2\text{-pyrazinecarboxylic acid})_3(H_2O)_2]_n \cdot 6nH_2O$ with an infinite 1-D chain-like structure. Complex **1** displays two strong photoluminescent emissions ascribed to characteristic emissions of $^4F_{9/2} \rightarrow {}^6H_J$ transitions ($J = 15/2$ and 13/2) of Dy^{3+}. The photoluminescence suggests that 2-pyrazinecarboxylic acid is an excellent antenna for Dy^{3+}.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 737792. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CBZ 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgment

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