Bull. Chem. Soc. Ethiop. **2020**, 34(3), 479-488. ISSN 1011-3924
© 2020 Chemical Society of Ethiopia and The Authors Printed in Ethiopia
DOI: https://dx.doi.org/10.4314/bcse.v34i3.5

PREPARATION AND CHARACTERIZATION OF A GADOLINIUM COMPOUND WITH HIGH THERMAL STABILITY

Wen-Tong Chen[1,2,3*]

[1]Institute of Applied Chemistry, School of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an, Jiangxi 343009, China
[2]Department of Ecological and Resources Engineering, Fujian Key laboratory of Eco-Industrial Green Technology, Wuyi University, Wuyishan, Fujian 354300, China
[3]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

(Received July 8, 2019; Revised December 14, 2020; Accepted December 15, 2020)

ABSTRACT. A new lanthanide compound [Gd(2,5-HPA)(2,5-PA)]$_n$ (**1**; 2,5-H_2PA = 2,5-pyridinedicarboxylic acid) was obtained through hydrothermal reactions and structurally characterized by single-crystal X-ray diffraction. It possesses a three-dimensional (3-D) framework structure. Solid-state photoluminescence experiment revealed that it shows dark blue emission band, which can be assigned to the characteristic emission of the 4*f* electron intrashell transition of $^6P_{7/2} \rightarrow {}^8S_{7/2}$ (Gd^{3+}). The energy transfer mechanism was explained by an energy level diagram of the gadolinium ion and 2,5-pyridinedicarboxylic acid ligand. It displayed remarkable CIE chromaticity coordinates of 0.1346 and 0.0678. The solid-state UV/Vis diffuse reflectance spectra unveiled that it possesses a wide optical band gap of 3.52 eV. Thermogravimetry (TG) measurements revealed that this compound is highly thermal stable up to around 500 °C.

KEY WORDS: CIE, Energy transfer, Lanthanide, Photoluminescence, Thermal stability

INTRODUCTION

In recent years lanthanide compounds are one of the research hotspots in material science and have gained more and more interest and, up to date, a large number of investigations have been carried out on the lanthanide compounds [1-9]. This is mainly because of the following reasons that lanthanide compounds show wide applications in many fields such as sensors, light-emitting materials, magnetic materials, cell imaging, electroluminescent devices, luminescence probes, catalysts and so forth [10-19]. The wide applications come from the various properties of the lanthanide compounds. Amongst the properties, photoluminescence is especially attractive. The photoluminescence of the lanthanide compounds is dominantly resulted from the lanthanide ions, because the lanthanide ions possess rich 4*f* electrons. If the 4*f* electrons can efficiently transfer, lanthanide compounds could usually emit ideal photoluminescence. As a matter of fact, however, the 4*f* electrons cannot efficiently transfer because the lanthanide ions generally possess low absorption coefficient. So, for the sake of promoting the transition of the 4*f* electrons of the lanthanide ions and increase the absorption coefficient, people adopt many kinds of organic molecules which possess conjugated structures as coordinating ligands to design and prepare new lanthanide compounds. Aromatic carboxylic acids and heterocyclic derivatives are just such organic molecules. It is believed that these organic molecules could absorb light, then transfer the light energy to the lanthanide ions and promote the transition of the 4*f* electrons, which is known as 'antenna effect' [20, 21]. In comparison with the great number of investigations on the photoluminescence performance, the studies on the

---

*Corresponding author. E-mail: cwtqq@aliyun.com semiconductor performance of lanthanide compounds are still rare and needed to be explored [22].

Being one of the aromatic carboxylic acids and heterocyclic derivatives, 2,5-pyridinedicarboxylic acid (2,5-H_2PA) is an important and useful building unit, because it is a linear molecule and has two carboxylic groups at both ends and one nitrogen atom at the heterocyclic ring. Therefore, 2,5-H_2PA possesses five coordinating atoms which enable it to bind to several metal ions to achieve different coordination geometries or extended structures. It is supposed that lanthanide compounds containing a 2,5-H_2PA ligand may have interesting extended structures and novel physicochemical behavior. We recently keep focusing on the crystal engineering of the lanthanide compounds with a 2,5-H_2PA ligand. In this work we report the hydrothermal synthesis, crystal structure, photoluminescence, energy transfer mechanism and solid-state UV/Vis diffuse reflectance of a novel lanthanide compound, $[Gd(2,5\text{-HPA})(2,5\text{-PA})]_n$ (**1**; 2,5-H_2PA = 2,5-pyridinedicarboxylic acid), which is characterized by a 3-D framework motif. It is noteworthy that this compound is highly thermal stable up to around 500 °C.

EXPERIMENTAL

Materials and instrumentation

The chemicals $Gd(NO_3)_3 \cdot 6H_2O$ and 2,5-pyridinedicarboxylic acid used in this work were commercially obtained and used without further purification. Photoluminescence spectra were performed on a F97XP photoluminescence spectrometer. Phosphorescence spectrum was carried out on a FLS980 fluorescence spectrometer. Solid-state and solution UV/Vis spectra were conducted on a TU1901 UV/Vis spectrometer. Thermogravimetry (TG) measurement was carried out on a NETZSCH TG 209F3 analyzer in nitrogen atmosphere. A powder X-ray diffraction (PXRD) pattern was measured on an AL-Y3000 powder diffractometer.

*Synthesis of **1***

It was synthesized from the mixture of $Gd(NO_3)_3 \cdot 6H_2O$ (1 mmol, 452 mg), 2,5-pyridinedicarboxylic acid (2 mmol, 334 mg) and 10 mL distilled water in a 25 mL Teflon-lined autoclave under autogenous pressure at 413 K for ten days and then power off. After cooling down to room temperature, block-like crystals were obtained in a 38% yield (based on $Gd(NO_3)_3 \cdot 6H_2O$).

Crystal structure determination

The X-ray diffraction data set was obtained on a Super Nova CCD X-ray diffractometer with carefully selected single crystal. The X-ray source is graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). The data reduction and empirical absorption correction were performed by using Crystal Clear software. The crystal structure was solved through the direct method by using the Siemens SHELXTL^{TM} V5 software and refined with a full-matrix least-squares refinement on F^2. Non-hydrogen atoms were found on their difference Fourier sites and anisotropically refined, while hydrogen atoms were theoretically generated on the parent atoms and included in the structural factor calculations with an assigned isotropic thermal parameter. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths are listed in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1874319. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk).

Table 1. Crystal data and structure refinement details.

Formula	$C_{14}H_7GdN_2O_8$
Fw	488.47
Color	Colorless
Crystal size (mm)	0.17 × 0.15 × 0.12
Crystal system	Orthorhombic
Space group	*Pbcn*
a (Å)	9.8855(4)
b (Å)	8.6592(3)
c (Å)	15.7260(6)
V (Å^3)	1346.15(9)
Z	4
$2\theta_{max}$ (°)	50
Reflections collected	3898
Independent, observed reflections (R_{int})	1191, 1069 (0.0232)
$d_{calcd.}$ (g/cm^3)	2.410
μ (mm^{-1})	4.981
F (000)	932
T (*K*)	100
*R*1, *wR*2	0.0196, 0.0406
S	1.093
$\Delta\rho$ (max, min) (e/Å^3)	0.430, -0.621

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

Gd(1)-O(4)#1	2.334(2)	O(4)#1-Gd(1)-O(3)	145.97(8)
Gd(1)-O(4)#2	2.334(2)	O(4)#2-Gd(1)-O(3)	74.37(8)
Gd(1)-O(3)	2.373(2)	O(4)#2-Gd(1)-O(1)#5	76.47(8)
Gd(1)-O(3)#3	2.373(2)	O(3)-Gd(1)-O(1)#5	109.14(8)
Gd(1)-O(1)#4	2.393(2)	O(4)#2-Gd(1)-N(1)#3	122.94(8)
Gd(1)-O(1)#5	2.393(2)	O(3)#3-Gd(1)-N(1)#3	65.75(8)
Gd(1)-N(1)#3	2.566(3)	O(1)#4-Gd(1)-N(1)#3	155.75(8)
Gd(1)-N(1)	2.566(3)	N(1)#3-Gd(1)-N(1)	120.97(11)

Symmetry codes: #1 *x*+1/2, *y*+1/2, -*z*+3/2; #2 -*x*-1/2, *y*+1/2, *z*; #3 -*x*, *y*, -*z*+3/2; #4 -*x*, -*y*, -*z*+2; #5 *x*, -*y*, *z*-1/2.

RESULTS AND DISCUSSION

Crystal structure

Single-crystal X-ray diffraction experiment unveiled that the title compound crystallizes in the space group of *Pbcn*. All the crystallographically independent atoms, except for Gd1, locate at general sites. As shown in Figure 1, the Gd^{3+} ion shows a slightly distorted square anti-prismatic geometry and bound by two nitrogen atoms and six oxygen atoms from six 2,5-pyridinedicarboxylic acid ligands. The Gd–O bond distance in **1** is in the span of 2.334(2) Å – 2.393(2) Å. The Gd–N bond distance in **1** is 2.566(3) Å. The O–Gd–O bond angles are in the range of 74.37(8)° – 145.97(8)°, while the O–Gd–N bond angles are in the range of 65.75(8)° – 155.75(8)°. The N–Gd–N bond angle is 120.97(11)°. The 2,5-pyridinedicarboxylic acid molecule acts as a μ_3-bridging ligand to link three Gd^{3+} ions. The shortest $Gd^{3+}\cdots Gd^{3+}$ distances are 6.5709(2) Å. Every Gd^{3+} ion is linked to six neighboring ones through six 2,5-pyridinedicarboxylic acid molecules to yield a 3-D framework structure, as presented in Figure 2.

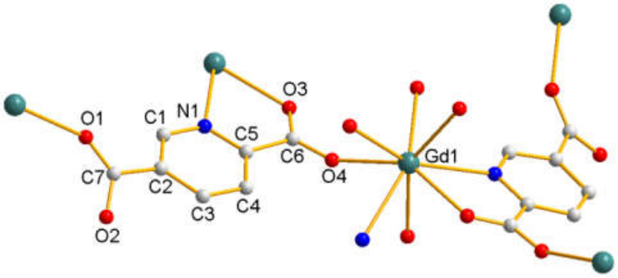

Figure. 1. The molecular structure of **1** with hydrogen atoms being omitted for clarity.

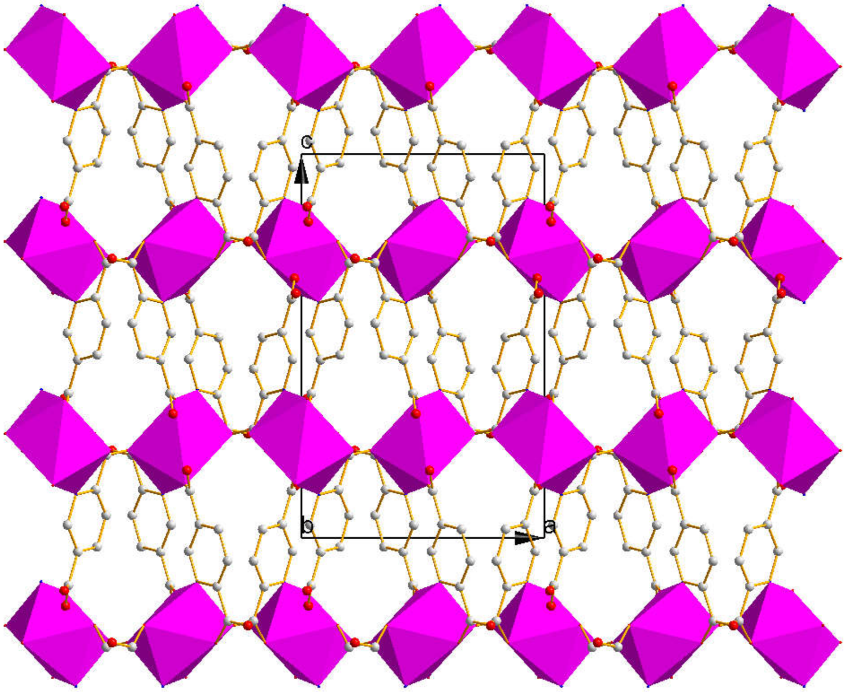

Figure 2. The 3-D structure of **1**.

Solid-state photoluminescence

Lanthanide compounds are well-known photoluminescence materials, because most of the lanthanide elements have abundant 4*f* electrons. Up to date, a large number of lanthanide compounds possessing interesting photoluminescence behavior have been reported [23-25]. The title compound is expected to show photoluminescence performance, so, we measured the photoluminescence spectra using solid state sample and the result of the photoluminescence experiment is given in Figure 3. As for compound **1**, when it was excited by the wavelength of 290 nm, its photoluminescence emission spectrum exhibits one sharp emission band in the narrow range of 306–328 nm with the peak locating at 313 nm (Figure 3). This emission can be assigned to the characteristic emission of the 4*f* electron intrashell transition of $^6P_{7/2} \rightarrow {}^8S_{7/2}$ (Gd^{3+}) [26, 27]. The CIE system characterizes colors by two color coordinates x and y which specify the point on the chromaticity diagram. With regard to **1**, its CIE chromaticity coordinate is (x = 0.1346, y = 0.0678), as shown in Figure 4. Such a CIE chromaticity coordinate resides in the blue region, indicating that this compound is probably served as a blue emission material. To explore the energy adsorption status, solution UV/Vis spectra for **1** and 2,5-pyridinedicarboxylic acid were carried out in distilled water. As shown in Figure 5, both of them show two adsorption peaks at around 224 nm and 273 nm. This indicates that compound **1** indeed adsorbs light energy through the 2,5-pyridinedicarboxylic acid ligand.

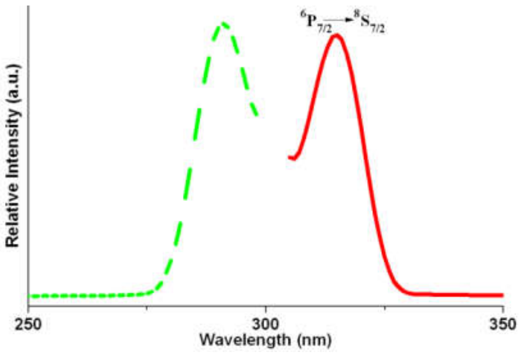

Figure 3. Solid-state photoluminescence spectra. Dashed: excitation; solid: emission.

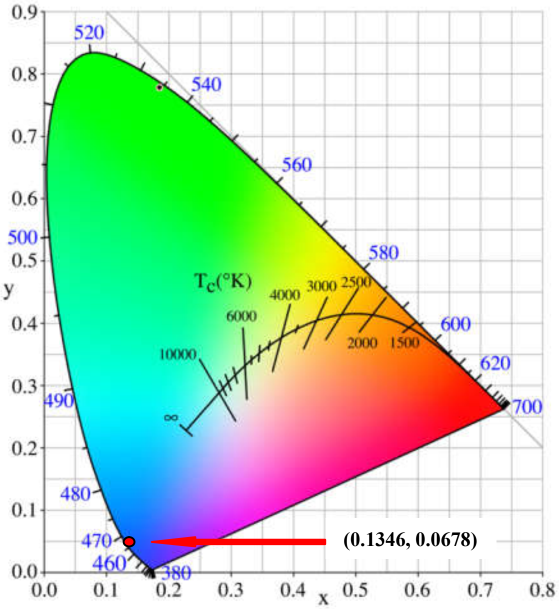

Figure 4. The CIE chromaticity diagrams and chromaticity coordinates of the photoluminescence emission spectra.

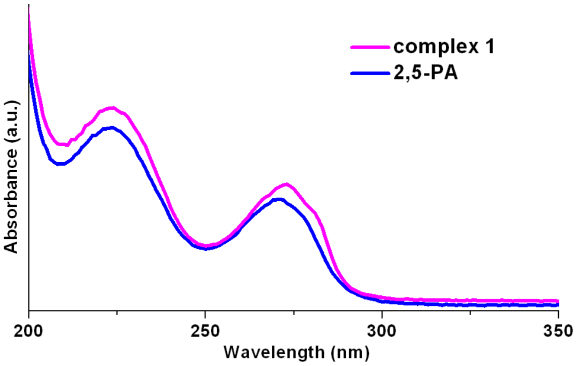

Figure 5. Solution UV/Vis spectra in distilled water.

Energy transfer mechanism

For the sake of revealing the nature of the photoluminescence emission of **1**, we measured the phosphorescence spectrum of 2,5-PA at 77 K, as shown in Figure 6. The inset of the phosphorescence emission spectrum of 2,5-PA is estimated to be 530 nm. So, the lowest triplet state energy of 2,5-PA could be 18868 cm^{-1}. The energy difference between the lowest triplet state of 2,5-PA and the resonant energy level of the Gd^{3+} ion ($^6P_{7/2}$, ~32000 cm^{-1}) is therefore about 13132 cm^{-1} for **1** (Figure 7). As mentioned above, compound **1** actually adsorbs light energy via the 2,5-pyridinedicarboxylic acid ligand. With regard to **1**, the 2,5-pyridinedicarboxylic acid ligand adsorbs the light energy and transfers the energy from the S$_1$ and T$_1$ states to the $^6P_{7/2}$ (Gd^{3+} ion) resonant energy level. Then, the energy is transferred from the $^6P_{7/2}$ (Gd^{3+} ion) resonant energy level to the $^8S_{7/2}$ (Gd^{3+} ion) ground state. Based on the fact that the 2,5-pyridinedicarboxylic acid ligand can adsorb the light energy and transfer the energy to the lanthanide ions, as well as **1** can exhibit well-shaped photoluminescence emission spectra, a conclusion can be made that the 2,5-pyridinedicarboxylic acid ligand is a suitable 'antenna' molecule for the title compound.

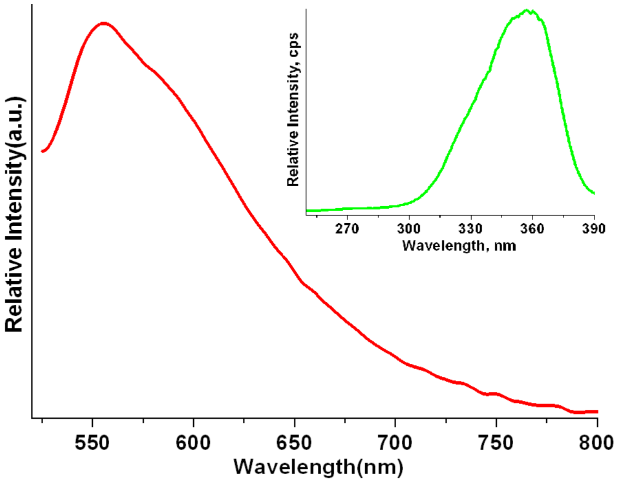

Figure 6. Phosphorescence spectrum of 2,5-PA measured at 77 K.

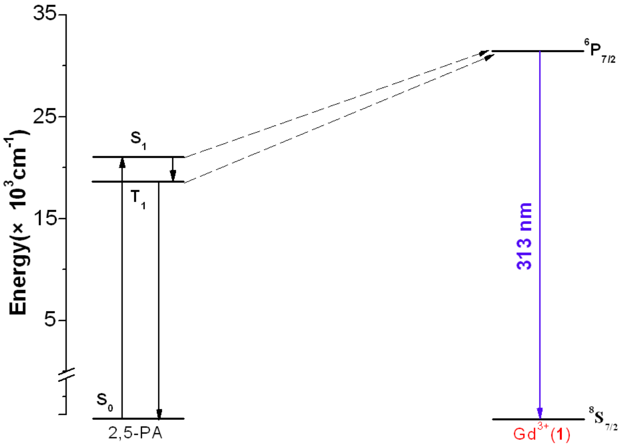

Figure 7. Schematic and partial energy level diagram of the main energy absorption transfer and phosphorescence processes in **1** and 2,5-PA.

Solid-state UV-Vis diffuse reflectance spectroscopy

In order to more broadly investigating the photophysical performance, the solid-state UV/Vis diffuse reflectance spectrum of **1** was measured with the use of powder sample at room temperature. The data of the solid-state diffuse reflectance spectra were treated by using the Kubelka-Munk function, namely, $\alpha/S = (1\text{-}R)^2/2R$. With regard to this function the parameter α is the absorption coefficient, S means the scattering coefficient, while R refers to the reflectance. The value of the optical band gap of **1** could be determined by extrapolating from the linear section of the absorption edge of the α/S vs energy curve. In this way the solid-state UV/Vis diffuse reflectance spectrum revealed that the title compound has a wide optical band gap of 3.52 eV, as depicted in Figure 8. Therefore, compound **1** may be a candidate for the wide band gap semiconductor materials and can be potentially used in the fields of color displays, optical storage, laser diodes, and so on. The slow slope of the optical absorption edge of **1** suggests that this compound should go through an indirect transition process [28].

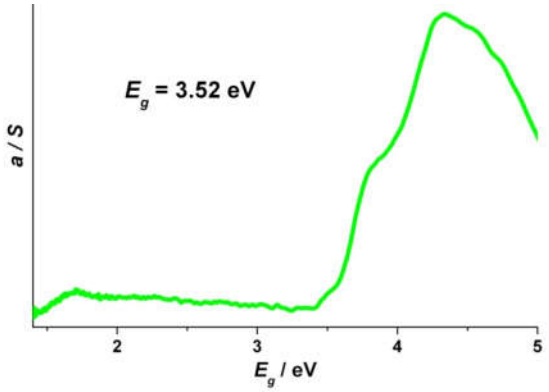

Figure 8. Solid-state UV/Vis diffuse reflectance spectrum for compound **1**.

Thermal stability

As a material that can be practically applied, its thermal stability should usually be under consideration. So, the thermal stability experiment of **1** was carried out in nitrogen atmosphere, as shown in Figure 9. With regard to **1**, the onset temperature of decomposition is 503.3 °C. At that temperature the 3-D framework starts to decompose. The 3-D framework totally collapsed at 563 °C. The total mass loss at 800 °C is 62.22%; this is because of the loss of all the 2,5-pyridinedicarboxylic acid molecules (calculated 67.80%). The XRD pattern after hating at 500 °C to ensure the thermal stability is shown in Figure 10. The result confirms that the compound is thermally stable up to 500 °C.

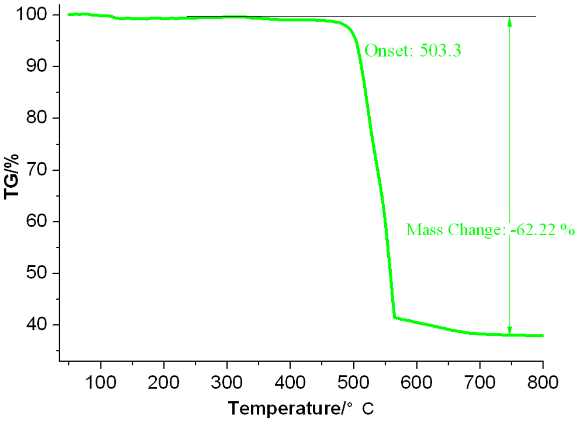

Figure 9. TG curve of **1**.

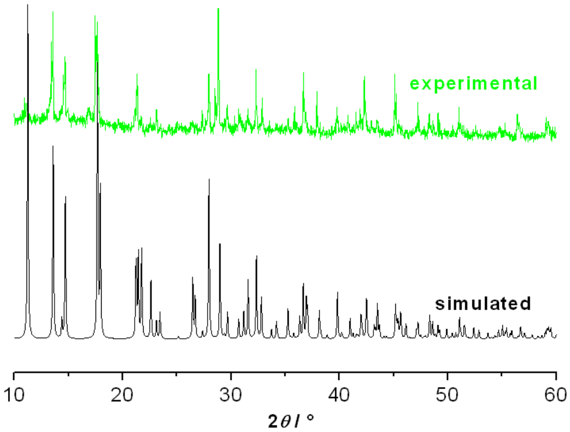

Figure 10. The PXRD patterns of **1**.

CONCLUSIONS

In brief, a novel lanthanide compound was prepared through hydrothermal reactions and characterized by single-crystal X-ray diffraction. It possesses a 3-D framework structure with the Gd^{3+} ion possessing a slightly distorted square anti-prismatic geometry. Solid-state photoluminescence experiments revealed that it can show well-shaped dark blue photoluminescence emissions, which can be assigned to the characteristic emission of the 4*f* electron intrashell transition of $^6P_{7/2} \rightarrow {}^8S_{7/2}$ (Gd^{3+}). Energy transfer mechanism was explained by the energy level diagram of the Gd^{3+} ion and 2,5-pyridinedicarboxylic acid ligand. The solution UV/Vis spectra for the title compound and 2,5-pyridinedicarboxylic acid revealed that this compound indeed adsorb light energy through the 2,5-pyridinedicarboxylic acid ligand. So, the 2,5-pyridinedicarboxylic acid ligand is a suitable 'antenna' molecule for this compound. The title compound shows remarkable CIE chromaticity coordinates of (0.1346, 0.0678). Solid-state UV/Vis diffuse reflectance spectrum revealed that it has wide optical band gaps of 3.52 eV. This compound is highly thermal stable up to around 500 °C. Therefore, the title compound is a potential photoluminescence material and wide band gap semiconductor.

ACKNOWLEDGMENTS

This work was supported by the NSF of China (21361013), the NSF of Jiangxi (20202BAB204003), the open foundation of the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (20180008).

REFERENCES

1. Liu, S.-J.; Cao, C.; Xie, C.-C.; Zheng, T.-F.; Tong, X.-L.; Liao, J.-S.; Chen, J.-L.; Wen, H.-R.; Chang, Z.; Bu, X.-H. Tricarboxylate-based Gd(III) coordination polymers exhibiting large magnetocaloric effects. *Dalton Trans*. **2016**, 45, 9209-9215.
2. Yuasa, J.; Nakagawa, T.; Kita, Y.; Kaito, A.; Kawai, T. Photoactivatable europium luminescence turn-on by photo-oxygenation of β-diketone having pyrrole rings. *Chem. Commun*. **2017**, 53, 6748-6751.
3. Wang, Z.; Zhou, L.P.; Zhao, T.H.; Cai, L.X.; Guo, X.Q.; Duan, P.F.; Sun, Q.F. Hierarchical self-assembly and chiroptical studies of luminescent 4d-4f cages. *Inorg. Chem*. **2018**, 57, 7982-7992.
4. Zheng, T.-F.; Yao, S.-L.; Cao, C.; Liu, S.-J.; Hu, H.-K.; Zhang, T.; Huang, H.-P.; Liao, J.-S.; Chen, J.-L.; Wen, H.-R. Large magnetic entropy changes in three Gd^{III} coordination polymers containing Gd^{III} chains. *New J. Chem*. **2017**, 41, 8598-8603.
5. Yang, X.; Wang, S.; Zhang, Y.; Liang, G.; Zhu, T.; Zhang, L.; Huang, S.; Schipper, D.; Jones, R. A self-assembling luminescent lanthanide molecular nanoparticle with potential for live cell imaging. *Chem. Sci.* **2018**, 9, 4630-4637.
6. Yao, S.-L.; Cao, C.; Tian, X.-M.; Zheng, T.-F.; Liu, S.-J.; Tong, X.-L.; Liao, J.-S.; Chen, J.-L.; Li, Y.-W.; Wen, H.-R. Three Gd-based metal-organic frameworks constructed from similar dicarboxylate ligands with large magnetic entropy changes. *ChemistrySelect* **2017**, 2, 10673-10677.
7. Han, S.-D.; Liu, S.-J.; Wang, Q.-L.; Miao, X.-H.; Hu, T.-L.; Bu, X.-H. Synthesis and magnetic properties of a series of octanuclear [Fe_6Ln_2] nanoclusters. *Cryst. Growth Des*. **2015**, 15, 2253-2259.
8. Wang, C.; Yang, X.; Wang, S.; Zhu, T.; Bo, L.; Zhang, L.; Chen, H.; Jiang, D.; Dong, X.; Huang, S. Anion dependent self-assembly of drum-like 30- and 32-metal Cd-Ln nanoclusters: visible and NIR luminescent sensing of metal cations. *J. Mater. Chem. C* **2018**, 6, 865-874.
9. Liu, S.-J.; Cao, H.; Yao, S.-L.; Zheng, T.-F.; Wang, Z.-X.; Liu, C.; Liao, J.-S.; Chen, J.-L.; Li, Y.-W.; Wen, H.-R. Temperature- and vapor-induced reversible single-crystal-to-single-crystal transformations of three 2D/3D Gd^{III}-organic frameworks exhibiting significant magnetocaloric effects. *Dalton Trans*. **2017**, 46, 64-70.
10. Hewitt, S.H.; Butler, S.J. Application of lanthanide luminescence in probing enzyme activity. *Chem. Commun*. **2018**, 54, 6635-6647.
11. Zhu, Z.; Tian, D.; Shu, X. Auto-phase-locked time-gated luminescence detection for

background-free upconversion spectra measurement and true-color biological imaging. *Sensor. Actuat. B-Chem*. **2018**, 260, 289-294.

12. Zheng, T.-F.; Tian, X.-M.; Yao, S.-L.; Cao, C.; Cai, J.-B.; Liu, S.-J. Two chain-based Tb^{III} /Dy^{III} complexes derived from m-nitrobenzoic acid with totally different structures and magnetic properties. *J. Mol. Struct.* **2018**, 1165, 326-331.
13. Liu, S.-J.; Xie, X.-R.; Zheng, T.-F.; Bao, J.; Liao, J.-S.; Chen, J.-L.; Wen, H.-R. Three-dimensional two-fold interpenetrated Cr^{III}-Gd^{III} heterometallic framework as an attractive cryogenic magnetorefrigerant. *CrystEngComm* **2015**, 17, 7270-7275.
14. Nakajima, A.; Nakanishi, T.; Kitagawa, Y.; Fushimi, K.; Hasegawa, Y. Thermosensitive luminescent lanthanide complex with two photosensitized ligands. *Sensor. Mater*. **2016**, 28, 845-850.
15. Petrochenkova, N.V.; Mirochnik, A.G.; Emelina, T.B.; Sergeev, A.A.; Leonov, A.A.; Voznesenskii, S.S. Luminescent amine sensor based on europium(III) chelate. *Spectrochim. Acta A* **2018**, 200, 70-75.
16. Zheng, T.-F.; Cao, C.; Dong, P.-P.; Liu, S.-J.; Wang, F.-F.; Tong, X.-L.; Liao, J.-S.; Chen, J.-L.; Wen, H.-R. Synthesis, structures and magnetocaloric properties of two dinuclear Gd^{III} clusters derived from monocarboxylate ligands. *Polyhedron* **2016**, 113, 96-101.
17. Buenzli, J.-C.G. Rising stars in science and technology: Luminescent lanthanide materials. *Eur. J. Inorg. Chem*. **2017**, 2017, 5058-5063.
18. Singha, S.; Ahn, K.H. Detection of ciprofloxacin in urine through sensitized lanthanide luminescence. *Sensors* **2016**, 16, 2065/1-2065/10.
19. Li, R.-P.; Liu, Q.-Y.; Wang, Y.-L.; Liu, C.-M.; Liu, S.-J. Evolution from linear tetranuclear clusters into one-dimensional chains of Dy(III) single-molecule magnets with an enhanced energy barrier. *Inorg. Chem. Front.* **2017**, 4, 1149-1156.
20. Coban, M.B.; Amjad, A.; Aygun, M.; Kara, H. Sensitization of Ho^{III} and Sm^{III} luminescence by efficient energy transfer from antenna ligands: Magnetic, visible and NIR photoluminescence properties of Gd^{III}, Ho^{III} and Sm^{III} coordination polymers. *Inorg. Chim. Acta* **2017**, 455, 25-33.
21. Rong, J.W.; Zhang, W.W.; Bai, J.F. Synthesis and structure of color tunable and white-light emitting lanthanide metal-organic framework materials constructed from conjugated 1,1'-butadiynebenzene-3,3',5,5'-tetracarboxylate ligand. *RSC Adv.* **2016**, 6, 103714-103723.
22. Wang, W.; Peng, D.F.; Zhang, H.L.; Yang, X.H.; Pan, C.F. Mechanically induced strong red emission in samarium ions doped piezoelectric semiconductor CaZnOS for dynamic pressure sensing and imaging. *Opt. Commun*. **2017**, 395, 24-28.
23. Jiang, D.; Yang, X.; Zheng, X.; Bo, L.; Zhu, T.; Chen, H.; Zhang, L.; Huang, S. Self-assembly of luminescent 12-metal Zn-Ln planar nanoclusters with sensing properties towards nitro explosives. *J. Mater. Chem. C* **2018**, 6, 8513-8521.
24. Swabeck, J. K.; Fischer, S.; Bronstein, N. D.; Alivisatos, A. P. Broadband sensitization of lanthanide emission with indium phosphide quantum dots for visible to near-infrared downshifting. *J. Am. Chem. Soc*. **2018**, 140, 9120-9126.
25. Kovacs, D.; Phipps, D.; Orthaber, A.; Borbas, K.E. Highly luminescent lanthanide complexes sensitised by tertiary amide-linked carbostyril antennae. *Dalton Trans.* **2018**, 47, 10702-10714.
26. Singh, V.; Sivaramaiah, G.; Singh, N.; Rao, J.L.; Singh, P.K.; Pathak, M.S.; Hakeem, D.A. EPR and PL studies on UVB-emitting gadolinium-doped $SrAl_{12}O_{19}$ phosphors. *Optik* **2018**, 158, 1227-1233.
27. Galleani, G.; Santagneli, S.H.; Ledemi, Y.; Messaddeq, Y.; Janka, O.; Pottgen, R.; Eckert, H. Ultraviolet upconversion luminescence in a highly transparent triply-doped Gd^{3+}-Tm^{3+}-Yb^{3+} fluoride-phosphate glasses. *J. Phys. Chem. C* **2018**, 122, 2275-2284.
28. Huang, F.Q.; Mitchell, K.; Ibers, J.A. New layered materials: Syntheses, structures, and optical and magnetic properties of $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$. *Inorg. Chem*. **2001**, 40, 5123-5126.