

无铅和稀土的大尺寸分子基绿光荧光晶体: $(C_5H_{13}ClN)_2[MnCl_4]$

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摘要: 通过氯化锰和 2-二甲氨基异丙基氯盐酸盐在溶液中的反应, 制备了一类绿光分子基晶态材料: $(C_5H_{13}ClN)_2[MnCl_4]$ (**1**)。该材料在紫外光激发后发出强烈的绿色荧光, 并且热分析测试表明其具有较好的热稳定性(分解温度大于 450 K)。结构和光谱分析表明其优异的光学性能归因于 $[MnX_4]^{2-}$ 四面体中 Mn^{2+} 的 ${}^4T_1(G) \rightarrow {}^6A_1$ 电子跃迁。

关键词: 有机-无机杂化; 晶体结构; 荧光性质

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Lead/Rare Earth-Free Green-Light-Emitting Crystal of Molecular-Based Hybrid Compound: $(C_5H_{13}ClN)_2[MnCl_4]$ with Large Crystal Size

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Abstract: Reaction of $MnCl_2$ and 2-dimethylaminoisopropyl chloride hydrochloride afforded one novel molecular-based material, $(C_5H_{13}ClN)_2[MnCl_4]$ (**1**). And it is interesting to note that **1** exhibits intense greenish fluorescent emission (520 nm) at room temperature and relatively high thermal stability (stable up to 450 K). Moreover, structure and spectra analyses reveal that its excellent optical property can be attributed to the ${}^4T_1(G) \rightarrow {}^6A_1$ electronic transition of Mn^{2+} in $[MnX_4]^{2-}$ tetrahedron. CCDC: 1570589.

Keywords: organic-inorganic hybrid; crystal structure; luminescence

0 Introduction

Luminescent materials recently are receiving increasing attention due to their promising applications in lighting, flat panel display, data storage and so on^[1-4]. However, the traditional luminescent materials were usually prepared by introducing rare-earth ions as dopants, which suffered from cumbersome preparation process and low light-emitting efficiency^[5-9]. With the flourishing development of $(CH_3NH_3)[PbI_3]$, the scientific research interest on luminescent materials

has been gradually shifted to organic-inorganic hybrid materials which possess richness of structural transformation and diversity of physical properties as well as potential practical applications^[10-20]. In particular, the organic-inorganic hybrid materials with chemical formula $(A)_2[MX_4]$ (A =organic cation, M =transition divalent metal ion and X =halide ion), possess various structures, modulated phases, magnetic properties and thermochromic behavior^[21-27]. Moreover, the organic-inorganic hybrid compounds, which overcome the drawbacks of traditional rare earth-doped luminescent

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materials and own facile synthesis and mechanical flexibility, would provide a new strategy for the fabrication of luminescent devices^[5].

From the viewpoint of the preservation of environment and the utilization of cheap natural resources, the research on luminescent materials on the basis of lead-free compounds has attracted growing attention. Mn^{2+} is well known to display interesting photophysical properties such as fluorescence and phosphorescence, and an essential feature of members of these groups is that they could emit either green (tetrahedrally coordinated Mn^{2+}) or red to pink (octahedrally coordinated Mn^{2+}) luminescence depending on their coordination environment^[28-30]. Especially, the tetrahedrally coordinated manganese(II) organic-inorganic hybrid complexes, constitute a special interest and might be promising phosphor materials due to their simple synthetic methods, interesting solid-state properties as well as enlarged applications in fluorescent tubes, radiation detectors, cathode-ray tubes, and X-ray imaging screens as well as in signs, toys, and so on^[28,31-38]. Besides, comparing with the green-emitting rare and rare-earth precious metal ions Tb, the inexpensive/abundant manganese would possess an increasingly predominant superiority in the preparation of luminescent materials. In the past few years, the optical properties of Mn-based compounds with various methylamine or pyridine and their derivative cations have been studied extensively both in experiment and theory. For instance, Xiong's group reported a series of organic-inorganic hybrid luminescent ferroelectrics on the basis of pyrrolidinium base^[5,36,39-42], which has inspired our research interest.

In search of new hybrids with interesting optical properties, we designed the luminescent organic-inorganic hybrid material, $(\text{C}_5\text{H}_{13}\text{ClN})_2[\text{MnCl}_4]$, which exhibits intense greenish fluorescent emission (520 nm) and high thermal stability. The synthesis and characterization of **1** were also disclosed through the X-ray single-crystal diffraction, powder X-ray diffraction, etc. Structure analysis, thermal analysis and optical analysis were used together to demonstrate the crystal structure as well as the PL emission

characteristics of **1**. It was hoped that this study would shed new light on the development of emitting materials based on organic-inorganic hybrid compounds and open new opportunities for probing novel emitting materials.

1 Experimental

1.1 Preparation of crystal

All reagents were purchased from Aladdin Co., Ltd. and used without further purification. $(\text{C}_5\text{H}_{13}\text{ClN})_2[\text{MnCl}_4]$ was prepared through the following process: a solution of 2-dimethylaminoisopropyl chloride hydrochloride (3.16 g, 0.02 mol) in methanol was slowly added to the methanol solution of anhydrous manganese chloride (1.26 g, 0.01 mol) under stirring. And slow evaporation of the mixed solution at 333 K yielded green crystals. Anal. Calcd. for $\text{C}_{10}\text{H}_{26}\text{Cl}_6\text{MnN}_2$ (%): C 27.17, H 5.93, N 6.34; Found(%): C 27.21, H 5.96, N 6.37.

1.2 Single crystal X-ray diffraction analysis

The X-ray diffraction data collection was carried out on a Rigaku Saturn 724 diffractometer equipped with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$) at 293 K. Data collection and cell refinement were performed using Crystalclear software package (Rigaku, 2005). The structure was solved by the direct method and full-matrix least-squares refinement based on F^2 was accomplished through SHELXL-97^[43]. All hydrogen atoms on carbon/nitrogen atoms were generated geometrically and refined using a "riding" model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$. The anisotropically refinements for non-hydrogen atoms were taken using all reflections with $I > 2\sigma(I)$. Details concerning crystal data and refinement could be found in Table 1. Selected bond lengths/angles and hydrogen bonds are available in Table S1.

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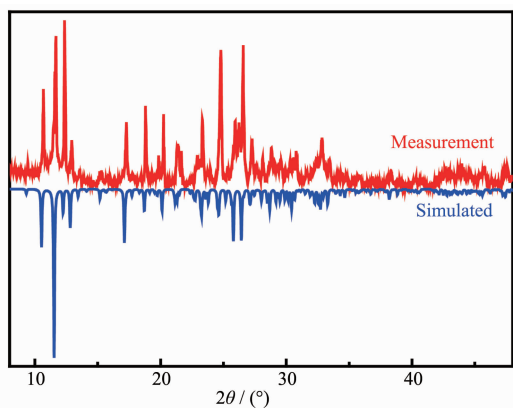
1.3 IR and powder X-ray diffraction measurements

IR spectrum was recorded on a Shimadzu model IR-60 spectrometer at room temperature, with the sample prepared into KBr diluted pellet (Fig.S1). The powder X-ray diffraction measurement of **1** was

Table 1 Crystal data and structure refinement for **1**

Empirical formula	C ₁₀ H ₂₆ Cl ₆ MnN ₂	Z	4
Formula weight	441.97	<i>D_c</i> / (g·cm ⁻³)	1.417
Crystal system	Monoclinic	<i>F</i> (000)	908
Space group	<i>P</i> 2 ₁ / <i>c</i>	Collected reflection	9 913
<i>a</i> / nm	1.142 4(2)	Unique reflection	3 601
<i>b</i> / nm	1.256 2(3)	<i>R</i> _{int}	0.095
<i>c</i> / nm	1.463 3(3)	Observed reflection	2 714
<i>β</i> / (°)	99.310(3)	Goodness-of-fit on <i>F</i> ²	1.116
Volume / nm ³	2.072 3(7)	<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.080, 0.307

carried out on a PANalytical X' Pert PRO X-ray diffractometer with Cu *Kα* radiation ($\lambda=0.154\ 18\ \text{nm}$) and a fixed power source (30.0 kV, 10.0 mA) at 293 K. The diffraction pattern was collected in the 2θ range of $5^\circ\sim 50^\circ$ with a step size of 0.02° . And the powder X-ray diffraction (PXRD) pattern of **1** matched pretty well with the pattern simulated from the single crystal structure, which indicated the phase purity (Fig.1).

Fig.1 Simulated and measured PXRD patterns of **1**

1.4 Luminescence measurements

Excitation and emission spectra measurements were carried out on Fluorolog 3-TCSPC spectrofluorometer (Horiba Jobin Yvon Inc). This kind of spectrofluorometer is equipped with a 450 W xenon lamp as an exciting source, and an emission monochromator, a double-excitation monochromator, and a photomultiplier as detection system. Measurements were performed at room temperature.

1.5 Thermogravimetric (TGA) analysis

Thermogravimetric analysis (TG) was performed on a TA type SDT-Q600 thermo-analyzer with a heating rate of $10\ \text{K}\cdot\text{min}^{-1}$ from 300 to 1 073 K, and

the sample was under nitrogen atmosphere in the process of measurement.

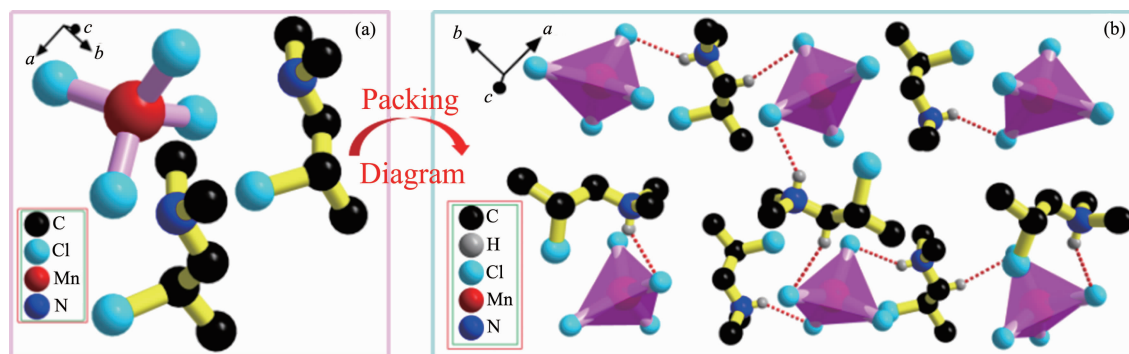
2 Results and discussion

2.1 Crystal structure of **1**

To understand the mechanism of emitting better, a precise single-crystal structure measurement for **1** was performed at room temperature. Compound **1** crystallizes in the monoclinic crystal system with the centrosymmetric space group *P*2₁/*c* and point group 2/*m*. As shown in Fig.2a, the asymmetric unit of **1** consists of two (C₅H₁₂ClN)⁺ cations and one isolated [MnCl₄]²⁻ anion, where the environment around Mn could be described as a distorted tetrahedral. Under room temperature, the Mn-Cl bond lengths varied from 0.236(2) to 0.238(2) nm, giving the mean value of 0.237(2) nm (Tables S1), which were within normal range and in accordance with other structurally similar compounds. The Cl-Mn-Cl angles were in the range from 102.82(8)° to 115.79(8)°, distorted from the ideal tetrahedral geometry of 109.471°. Moreover, the packing diagram of **1** was presented in Fig.2b. As shown in Fig.2b, one layer of cations was embedded in the free space between two neighboring inorganic [MnCl₄]²⁻ layer, forming an alternating well-known organic-inorganic hybrid structure. Moreover, as presented in Fig.2b, the packing was stabilized by N-H⋯Cl hydrogen bonds and each anion forms two N-H⋯Cl hydrogen bonds with two nearest cations, and the distances of H1D⋯Cl2 and H2D⋯Cl4ⁱ were 0.247 and 0.243 nm, respectively.

2.2 Thermal property of **1**

For characterizing the thermal stability of



Partial hydrogen-bonding interactions between organic and inorganic components were shown in red dashed lines

Fig.2 (a) Asymmetric unit of **1** with all H atoms omitted for clarity; (b) Packing diagram of **1** with partial cations and H atoms omitted for clarity

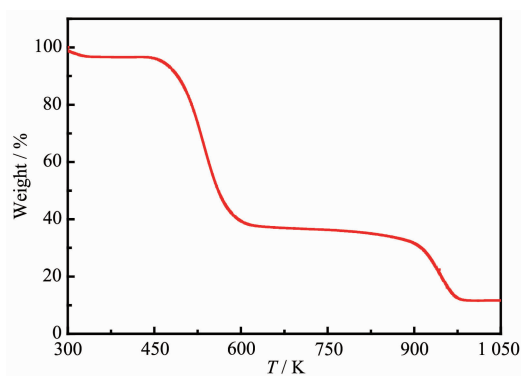
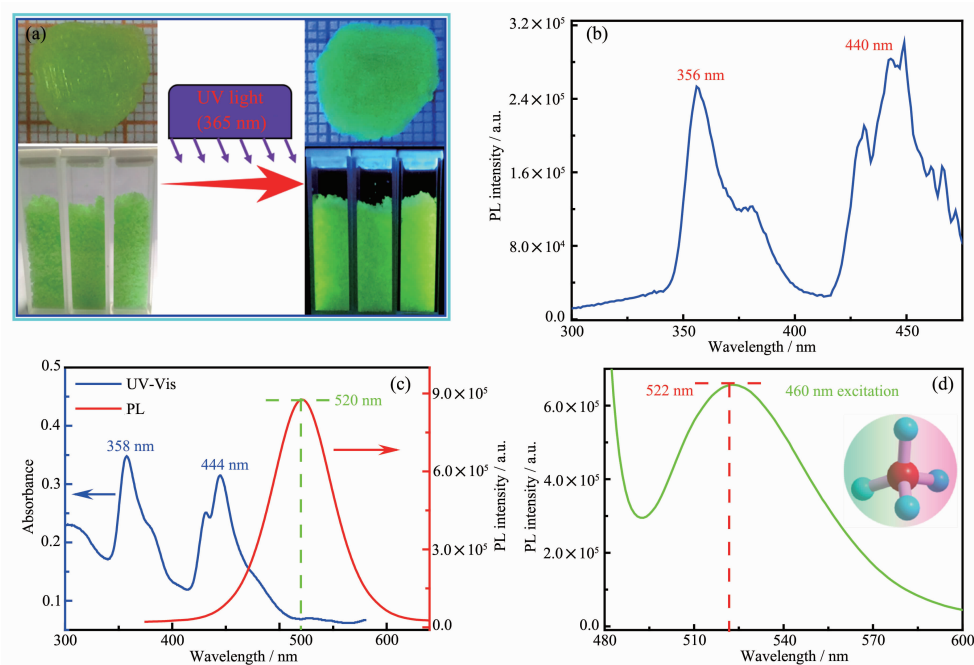


Fig.3 TGA curve of **1**

compound **1**, TGA measurement was performed from 300 to 1 073 K. As shown in Fig.3, the sample has a perfect thermal stability up to $T=473$ K. Besides, the decomposition process of **1** could be divided into the following stages. Firstly (473~614 K), **1** decomposed into metal(II) chloride and carbon^[21,44-50]. Secondly (910~1 027 K), the mixture of metal (II) chloride and elemental carbon decomposed continuously^[21].

2.3 Optical property of **1**

As shown in Fig.4a, the yellow green crystal and



Emission spectrum in (c) was obtained by excited the powder sample under 360 nm excitation wavelength; strong green-emission at around 520 nm was associated with the electronic transition of Mn^{2+} in $[\text{MnCl}_4]^{2-}$ tetrahedron in (c) and (d)

Fig.4 (a) Yellow green crystal and powder of **1** under sunlight and UV light (365 nm), and the size of crystal **1** was about 1 cm×1 cm×0.3 cm; (b) Excitation spectrum of **1** at room temperature; (c) Absorption (blue line) and emission (red line) spectra of **1** at room temperature; (d) Emission spectrum of **1** at room temperature under 460 nm excitation wavelength

powder of (C₅H₁₃ClN)₂[MnCl₄] emitted strong green light while illuminated by UV lamp (365 nm). And in order to better characterize the luminescence property of **1**, the absorption, excitation as well as emission spectra analyses were depicted as follows. The absorption spectrum of the powder sample includes two strong absorption peaks (358 and 444 nm) in the ultraviolet region, which are related to the ⁶A₁→⁴T₁ electronic transition of Mn²⁺. The excitation spectrum was recorded under room temperature and exhibited two dominant absorption peaks at around 357 and 450 nm (Fig.4b), which coincided with the UV results. These excitation peaks were also related to the electronic transition of Mn²⁺ from the ⁶A₁ ground state to different excited spin-quartet states, which can be attributed to tetrahedral crystal-field transition based on the related irreps in Td-symmetry notation^[5,37,51-52]. And the photoluminescence (PL) emission spectra were recorded by exciting the crystal using 360 and 460 nm excitation wavelength (Fig.4c and 4d). Interestingly, under the selected two excitation wavelength, a strong emission peak centered at around 521 nm could be observed, confirming the special emission property of compound **1**. The emission lifetime of **1** was as long as 83 μs. Besides, we also estimated the luminescence quantum yield of compound **1**, and a relatively high QE of 15% was obtained.

3 Conclusions

In summary, through deliberate selection to the organic cations, we successfully synthesized an organic-inorganic hybrid compound (C₅H₁₃ClN)₂[MnCl₄], which exhibits unusual thermal stability and excellent green light emission under external stimulus. Moreover, **1** was prepared through the simple and convenient solution method and its crystal structure and fluorescence property had been discussed in this paper. These perfect characteristics together with economic and environment friendly preparation process enable **1** to show potential applications as an emitting material. It is not only useful for the fabrication of low-cost emitting devices, but also advantageous to promote the development of emitting

materials in display and sensing fields.

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Supporting information is available at <http://www.wjhxsb.cn>

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