Short communication

Synthesis and Characterization of (4,4'-H_2bipy)[CdI_4] · H_2O with Strong Fluorescence

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Abstract

(4,4'-H_2bipy)[CdI_4]·H_2O (**1**) has been synthesized via hydrothermal reaction and characterized by single crystal X-ray diffraction. The crystal belongs to monoclinic, space group $P2_1/c$ with a = 8.3935(6), b = 24.304(2), c = 9.9388(7) Å, β = 106.230(1)°, $C_{10}H_{12}CdI_4N_2O$, M_r = 796.22, V = 1946.6(2) Å^3, Z = 4, D_c = 2.717 g/cm^3, S = 1.080, μ(Mo$K\alpha$) = 7.458 mm^{-1}, F(000) = 1416, R = 0.0439 and wR = 0.1455. The crystal structure analysis of **1** reveals that the title compound features an isolated structure, based on discrete 4,4'-H_2bipy moieties, lattice water molecules and tetrahedral cadmium atoms terminally coordinated by four iodine atoms. The 4,4'-H_2bipy moieties and lattice water molecules are linked via hydrogen bonds. Luminescent investigation reveals a strong emission in blue region, which may be originating from $\pi \rightarrow \pi^*$ charge-transfer interaction of the 4,4-H_2bipy.

Keywords: Cadmium, crystal structure, bipy, photoluminescence

1. Introduction

Fluorescent materials, particularly blue fluorescent materials have gained strong interest because blue fluorescence is one of the key color components required for full-color EL displays and blue fluorescent materials are still rare up to date.[1] Recently, 4,4'-bipyridine (bipy) with delocalized π-electrons of the pyridyl rings obtains increasing attention in preparing light emitting compounds in different technical applications, such as emitting materials for organic light emitting diodes,[2] sensitizers in solar energy conversion,[3] chemical sensors[4] and so forth. Group 12 (IIB) metal halide-bipy materials are relatively rare, although many structures of metal halide-bipy materials were reported nowadays.[5] Moreover, among which, IIB-halide-bipy materials with strong blue fluorescence are more rare. To obtain a novel material that may possess good photoluminescent property, our recent efforts in synthesizing novel IIB-based compounds are focused largely on the systems containing 4,4'-H_2bipy. Herein we describe the synthesis and characterization of (4,4'-H_2bipy)[CdI_4] · H_2O (**1**).

2. Experimental

The fluorescent study was conducted at room temperature on a JY Fluorolog-322 fluorescence spectroscopy instrument. The starting materials were commercially available and used without further purification. CdI_2 (0.3 mmol, 110 mg), 4,4'-bipy (0.2 mmol, 31 mg), HI acid (1 mL) and distilled water (3 mL) were loaded into a Teflon-lined stainless steel autoclave (25 mL) and kept at 373 K for 3 days. After being slowly cooled to room temperature at a rate of 6 K/h, yellow crystals suitable for X-ray analysis were obtained. Yield: 63% (based on cadmium).

The intensity data set was collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) by using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections.[6] The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software.[7] The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The hydrogen atom positions were generated theoretically, except for those on the lattice water molecules that were

yielded by the 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 structures were refined using a full-matrix least-squares refinement on F^2. All atoms except for hydrogen atoms were refined anisotropically. A summary of crystallographic data and structure analysis is listed in Table 1, and selected bond distances and bond angles are given in Table 2.

Table 1. Summary of Crystallographic Data and Structure Analysis for **1**.

Formula	$C_{10}H_{12}CdI_4N_2O$
Fw	796.22
color	yellow block
Crystal size/mm^3	0.35 0.19 0.12
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	8.3935(6)
b (Å)	24.304(2)
c (Å)	9.9388(7)
β (°)	106.230(1)
V (Å^3)	1946.6(2)
Z	4
$2\theta_{max}$ (°)	50
Reflections collected	11494
Independent, observed reflections (R_{int})	3386, 2581 (0.0314)
Absorption correction	multi-scan
T_{max}	0.411
T_{min}	0.198
$d_{calcd.}$ (g/cm^3)	2.717
?(mm^{-1})	7.458
T (K)	293(2)
F(000)	1416
R1, *w*R2	0.0439, 0.1455
S	1.080
Largest and Mean Δ/σ	0.002, 0
$\Delta\rho$ (max/min) (e/Å3)	1.180/–0.906

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

Cd(1)-I(1)	2.7751(5)	Cd(1)-I(3)	2.7812(4)
Cd(1)-I(2)	2.7604(5)	Cd(1)-I(4)	2.7934(4)
I(1)-Cd(1)-I(2)	114.839(14)	I(2)-Cd(1)-I(3)	107.099(14)
I(1)-Cd(1)-I(3)	109.142(15)	I(2)-Cd(1)-I(4)	110.784(15)
I(1)-Cd(1)-I(4)	104.961(14)	I(3)-Cd(1)-I(4)	109.990(13)

3. Results and Discussion

Single crystal X-ray diffraction analysis reveals that the structure of the title compound is characterized by an isolated structure, consisting of 4,4'-H_2bipy cations, lattice water molecules and $[CdI_4]^{2-}$ anions, as shown in Fig. 1. The cadmium atom is bound by four terminal iodine atoms to form a tetrahedron with the bond lengths ranging from 2.7604(5) to 2.7934(4) Å, comparable with those previously reported in the literature.[8] The bond angles of I-Cd-I are in the wide range of 104.96(1)–114.84(1)°, which are close to those in a regular tetrahedron. The two pyridyl rings of the 4,4'-H_2bipy moiety are slightly twisted with a small dihedral angle of *ca*. 3.96°, which is comparable with that previously documented.[9] For the title compound, no π…π stacking interactions were found between the 4,4'-H_2bipy moieties. The 4,4'-H_2bipy moieties and the lattice water molecules are linked via N…O hydrogen bonds with a distance of 2.539(8) Å, as shown in Fig. 2. The hydrogen bonds and electrostatic interactions among the $(4,4'\text{-}H_2bipy)^{2+}$ cations, the lattice water molecules and the $[CdI_4]^{2-}$ anions contribute to the stabilization of the crystal packing of the title compound (Fig. 2). Results of the bond valence calculations indicate that the cadmium atom is in +2 oxidation state (Cd1: 2.28).[10] Due to all the iodine atoms are in –1 oxidation state, for the requirement of charge balance, the nitrogen atoms of the 4,4'-bipy moiety must be protonated, as the cases found in many other compounds.[11]

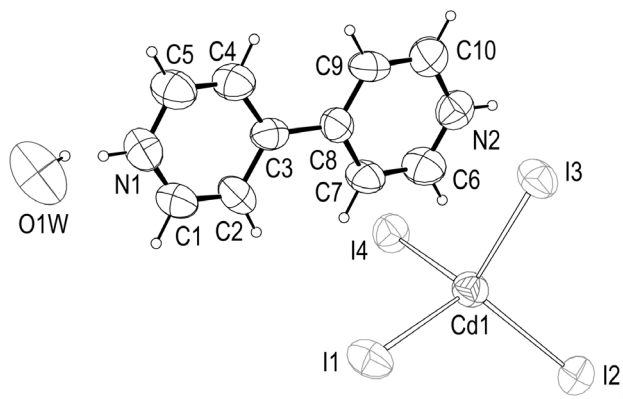

Fig. 1. ORTEP drawing of **1** with 35% thermal ellipsoids and hydrogen atoms are shown as small spheres.

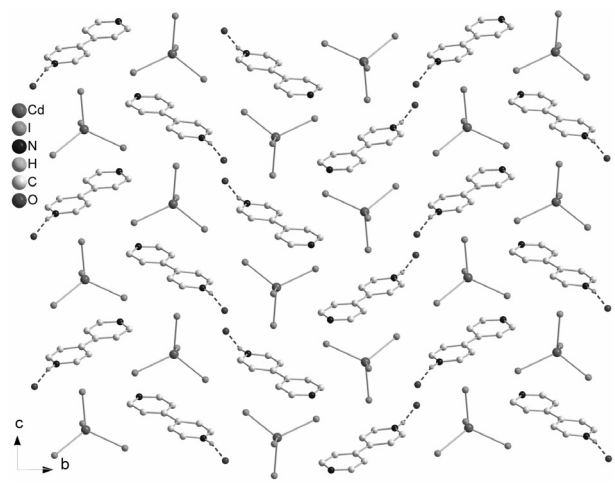

Fig. 2. Packing diagram of **1** with the dashed lines representing hydrogen bond. Hydrogen bond (Å): N1...O1W 2.539(8).

A search from the Cambridge Crystallographic Data Centre (CCDC) shows that there are dozens of compounds containing isolated $[CdI_4]^{2-}$ anions.[8,12] However, in these compounds the counterpart cations are various but none of them is bipy. Therefore, compound **1** is the first example of $[CdI_4]^{2-}$-containing compounds with bipy as a moiety. Usually, bipy moiety favors to link metal atoms into an extended structure, while discrete structures containing bipy moieties are relatively rare in IIB metal halides, to our knowledge, only several examples have been reported thus far, i. e. (4,4'-H_2bipy)[$ZnCl_4$], (4,4'-H_2 bipy)[$ZnBr_4$], (4,4'-H_2bipy)[$HgCl_4$], (4,4'-H_2bipy) [$HgBr_4$] · H_2O and (4,4'-H_2bipy)[$CdBr_4$].[9,13] It is noteworthy that none of the above-mentioned five compounds is iodine-containing compounds; therefore, compound **1** is the only example of iodine-containing compounds in this system.

The solid-state emission spectra of the title compound are investigated at room temperature. The emission spectrum of the title compound is given in Fig. 3. The fluorescent spectrum study shows that the title compound exhibits a broad and strong blue-light emission band with a maximum wavelength of 412 nm upon photo-excitation at 340 nm. To understand the nature of the luminescence of **1**, the luminescent spectra of pure bipy were also measured under the same condition. For pure bipy, the emission spectra show one intense emission band in blue region with the maximum wavelength of 438 nm upon photo-excitation at 357 nm (inner plot of Fig. 3). The similarity of the luminescent spectra of **1** and pure bipy suggests that the emission spectra of **1** should be assigned as a $\pi \rightarrow \pi^*$ transition of 4,4'-H_2bipy moiety. Thus, this compound may be a candidate in blue-light luminescent materials.

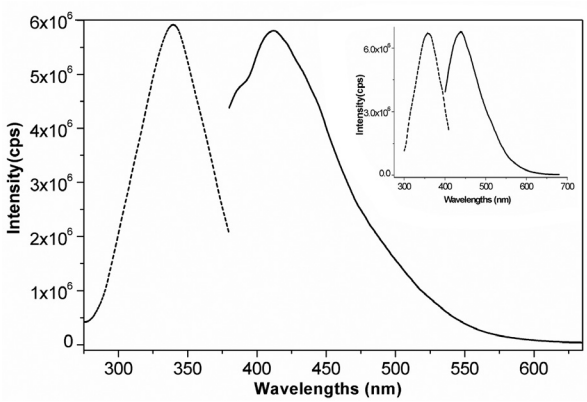

Fig. 3. Solid-state emission and excitation spectra of **1** at room temperature (Inner plot: pure bipy moiety). Solid line: emission spectrum; dashed line: excitation spectrum.

4. Conclusions

In summary, a new bipy-IIB metal halide, (4,4'-H_2 bipy)[CdI_4] · H_2O (**1**), has been synthesized via hydrothermal reaction. This compound exhibits a broad and strong fluorescent emission band, and it may be used as a blue-light material. Further investigations on this field are in progress in our laboratory.

5. Acknowledgements

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6. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 686347. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Povzetek

Spojino (4,4'-H_2bipy)[CdI_4]·H_2O (**1**) smo pripravili s hidrotermalno reakcijo in ji določili strukturo z rentgensko strukturno analzo. Spojina kristalizira v monoklinski prostorski skupini $P2_1/c$, a = 8.3935(6), b = 24.304(2), c = 9.9388(7) Å, β = 106.230(1)°, $C_{10}H_{12}CdI_4N_2O$, M_r = 796.22, V = 1946.6(2) Å^3, Z = 4, D_c = 2.717 g/cm^3, S = 1.080, μ(Mo$K\alpha$) = 7.458 mm^{-1}, F(000) = 1416, R = 0.0439 and wR = 0.1455. Struktura vsebuje 4,4'-H_2bipy katione, molekule mrežne vode in tetraedrične anione. Kationi in molekule vode so povezani z vodikovimi vezmi. Meritve luminescence kažejo intenzivno emisijo v modrem, ki je verjetno zaradi $\pi \rightarrow \pi^*$ prenosa naboja v 4,4-H_2bipy.