

Synthesis, crystal structure and luminescent properties of a new samarium-fluorescein metal-organic framework



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ABSTRACT

A new metal-organic framework with empirical formula $C_{43}H_{30}NO_{12}Sm$ was solvothermally synthesized using $SmCl_3$, fluorescein and N, N-Dimethyl formamide (DMF) and characterized by single crystal X-ray diffraction, powder X-ray diffraction, infrared spectroscopy, UV–Visible spectroscopy, scanning electron microscopy, optical microscopy, photoluminescence spectroscopy, CHN elemental analysis and thermogravimetric analysis. Single crystal X-ray diffraction revealed that the crystal structure belongs to the triclinic system, $P-1$ space group with $a = 12.113(6)$ Å, $b = 12.1734(7)$ Å, $c = 13.2760(8)$ Å, $\alpha = 67.930(3)^\circ$, $\beta = 87.779(3)^\circ$, $\gamma = 77.603(3)^\circ$ and $V = 1769.71(17)$ Å³. The photoluminescence spectrum showed emission peaks at 550 nm, 600 nm and 647 nm due to the characteristic transitions $^4G_{5/2}$ to $^6H_{5/2}$, $^4G_{5/2}$ to $^6H_{7/2}$ and $^4G_{5/2}$ to $^6H_{9/2}$ respectively, when excited at 398 nm.

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1. Introduction

The design and synthesis of metal-organic frameworks (MOFs) containing lanthanide ions attracted much attention due to their versatile architecture and potential applications in catalysis, gas storage, magnetism, luminescence, sensors etc. [1–4]. The direct excitation of the 4f–4f transitions are parity forbidden and they consist mainly of magnetic dipole and electric dipole transitions. As a consequence of the forbidden nature, these transitions have relatively long excited state lifetime. This together with high colorimetric purity of the emitted light leads lanthanides as luminescent. In MOFs, the organic sensitizer (ligand) absorbs incident radiation and directly populates the f-excited state of lanthanides through energy transfer (antenna effect) and as a result they show high luminescence property [5]. The lanthanide centers have high and variable coordination numbers and flexible coordination environment. Hence it is possible to construct unusual topological frameworks and based on the selection of organic ligand, a variety of lanthanide complexes with various structures and properties can be obtained [6]. Also these complexes have excellent luminescent properties and give sharp and intense emission lines.

Due to the high affinity of lanthanide ions to hard donor atoms,

ligands containing oxygen atoms have been extensively used in the synthesis of lanthanide complexes [7]. Fluorescein is an important ligand with oxygen atoms and shows high quantum yield of fluorescence and large absorption in visible region. It can give varied absorption spectra, fluorescence spectra, quantum yield and lifetime in different media as it exists in different structural forms [8]. Even though the synthesis and structural characterization of various fluorescein–metal complexes are reported [9], a metal-organic framework with samarium and fluorescein has not been explored to date. Here, we report the solvothermal synthesis, characterizations and luminescent property of a novel metal-organic framework with samarium and fluorescein.

2. Experimental section

2.1. Materials

Fluorescein, N, N-Dimethyl formamide, and samarium chloride were purchased from M/S Merck Chemicals. All organic solvents were used without further purification. Distilled water was used throughout the experiment.

2.2. Synthesis of the compound

0.0664 g of fluorescein was dissolved in 6.0 mL of DMF/H₂O (2:1) mixture. To this 0.4 mL of 0.5M aqueous $SmCl_3$ solution was

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added with stirring. After adjusting the pH to 7.0, the mixture was stirred for 1 h and transferred in to a stainless steel teflon lined autoclave. The solvothermal reaction was proceeded at 393 K for 48 h and then cooled to room temperature to get red needle shaped crystals arranged in a flower like manner. The crystals were filtered, washed with water and dried. The proposed reaction mechanism is given in Scheme 1. Elemental analyzes (%): calcd for $C_{43}H_{30}NO_{12}Sm$ (903.03): C 57.18, H 3.34, N 1.55. Found: C 57.13, H 3.33, N 1.54.

2.3. Measurements

The single crystal X-Ray data collection for the crystal was performed using Bruker X8 KAPPA APEX II and powder X-ray diffraction patterns were obtained from Bruker D8 advanced diffractometer. Elemental analyses were carried out on Elementar Vario EL III instrument. FTIR spectra were taken within 400–4000 cm^{-1} region on Perkin–Elmer Spectrum 400FTIR/FTFIR spectrophotometer. Scanning electron microscopic image (SEM) was obtained from a JEOM JSM-6700 field-emission scanning electron microscope and optical microscopic image was taken by using Grandtec optical microscope. UV–visible absorption spectra were recorded from a UV-2400PC series spectrophotometer and fluorescence excitation and emission spectra were obtained on a SL174 spectrofluorometer using 150 W Xenon lamp as excitation source. Fluorescence lifetimes were measured using an IBH Pico-second single photon counting system. Shimadzu DTG-60 equipment was used for recording the thermogram of the synthesized crystals.

3. Results and discussion

3.1. Infrared spectra

IR spectra of fluorescein and the MOF are shown in Fig. 1. The peak due to C=O stretching vibration ($\nu_{C=O}$) at 1715 cm^{-1} in fluorescein disappears in the IR spectrum of MOF [10]. Also the difference between asymmetric (1589 cm^{-1}) and symmetric (1457 cm^{-1} and 1385 cm^{-1}) stretching of carboxylate group in the IR spectrum of fluorescein ($\nu_{as} - \nu_s = 132$ and 204 cm^{-1}) is decreased ($\nu_{as} - \nu_s = 112$ and 184 cm^{-1}) in the IR spectrum of complex indicating that the carboxylate groups are coordinated to the samarium ion in the complex [11]. Further the peak at 3068 cm^{-1} in

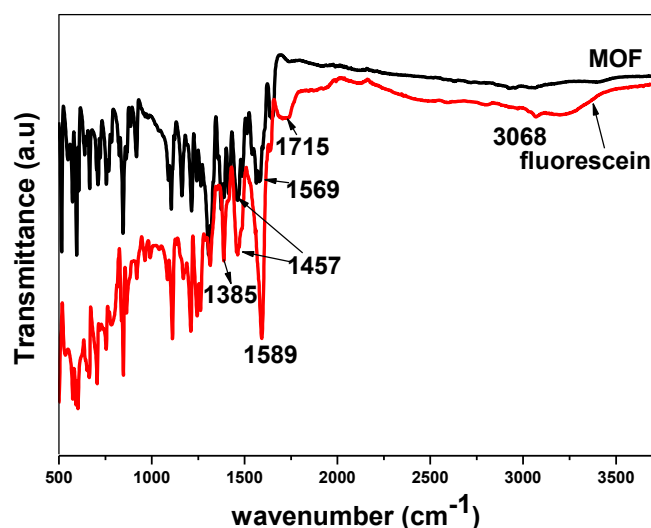
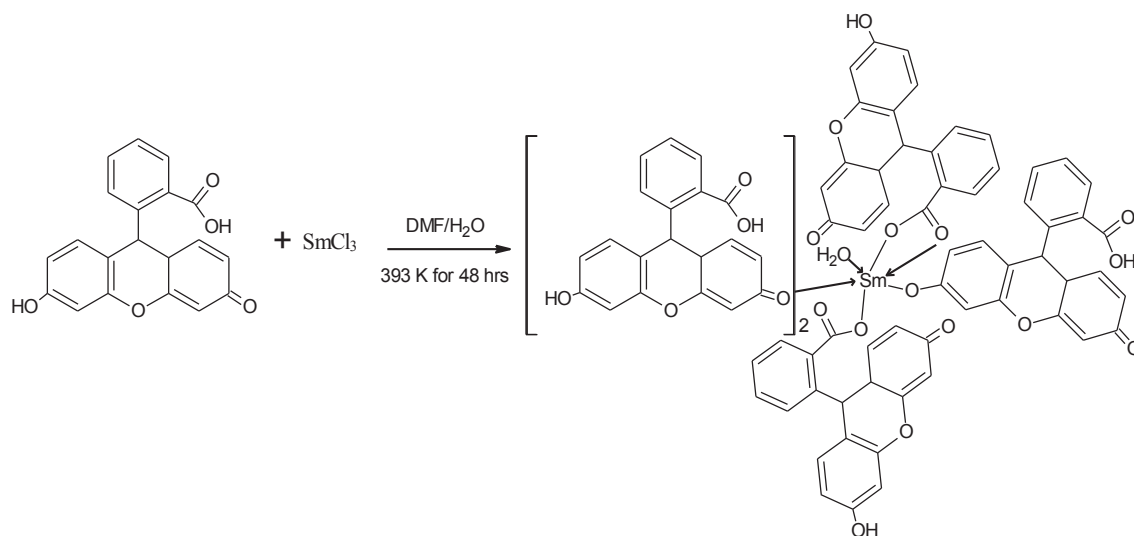


Fig. 1. Solid state Infrared spectra of fluorescein and synthesized MOF.

fluorescein due to the O–H stretching is absent in the IR spectrum of MOF, which reveals the involvement of O–H group in bond formation [12].

3.2. Crystal structure

The structure of the synthesized crystal was characterized by single crystal X-ray diffraction analysis and the details of crystal data and data collection parameters are shown in Table 1. The compound crystallizes in the triclinic system, space group P-1 with $a = 12.113(6)$ Å, $b = 12.1734(7)$ Å, $c = 13.2760(8)$ Å, $\alpha = 67.930^\circ$, $\beta = 87.779^\circ$, $\gamma = 77.603^\circ$. The analysis reveals that the compound has the empirical formula $C_{43}H_{30}NO_{12}Sm$ with formula weight 903.03. The compound shows a network structure in which the Sm^{3+} ion at the centre is coordinated to five different fluorescein molecules and a water molecule, giving distorted pentagonal bipyramidal geometry. The asymmetric unit of the MOF is shown in Fig. 2 and the coordination environment of the central Sm^{3+} ion is given in Fig. 3. One fluorescein molecule is coordinated to the Sm^{3+} ion through the oxygen atoms of the carboxylate group. Second and



Scheme 1. Proposed reaction mechanism.

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