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Synthesis, structure and properties of a tetranuclear europium(III) complex based on 9,9-dimethylfluorene-2,7-diphosphonic acid

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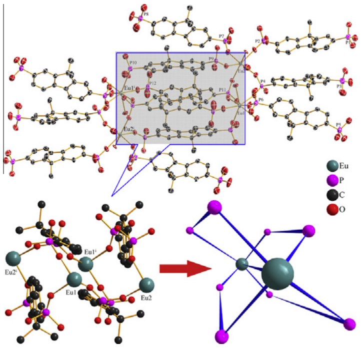
HIGHLIGHTS

- An europium(III) phosphonate (**EuMFDP**) has been synthesized.
- The ligand is 9,9-dimethylfluorene-2,7-diphosphonic acid (H_4MFDP).
- **EuMFDP** features a strip-like tetranuclear structure.
- **EuMFDP** exhibits very weak red emission.
- IR spectrum and TGA have also been discussed.

GRAPHICAL ABSTRACT

One tetranuclear europium(III) complex (**EuMFDP**) constructed from 9,9-dimethylfluorene-2,7-diphosphonic acid (H_4MFDP) has been synthesized. **EuMFDP** features a strip-like tetranuclear structure with the core composed of four paddle-like arranged ligands and four Eu(III) ions. **EuMFDP** shows only very weak characteristic emission of Eu(III) ions, probably due to the strong quenching effect of OH vibration.



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ABSTRACT

One tetranuclear europium(III) phosphonate complex $[Eu_2(H_4MFDP)(H_3MFDP)_4(H_2MFDP)(H_2O)_4]\cdot 13.5H_2O$ (**EuMFDP**), has been prepared by reactions of the new ligand 9,9-dimethylfluorene-2,7-diphosphonic acid (H_4MFDP) with europium(III) nitrates. The crystal structure of complex **EuMFDP** has been determined using single-crystal X-ray diffraction. It features a strip-like tetranuclear structure, in which four ligands and four Eu(III) ions constitute the core. Interestingly, the four ligands in the core possess paddle-like arrangement. Although the free ligand H_4MFDP exhibits the emission centered at 333 nm and 438 nm upon excitation at 310 nm, complex **EuMFDP** shows only very weak characteristic emission of Eu(III) ions, probably due to the strong quenching effect of OH vibration. The thermal property of **EuMFDP** has also been studied.

Introduction

Lanthanide complexes possess not only the diverse structures but also the outstanding optical, electrical and magnetic properties, so they have received much attentions and have been

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intensively studied in the fields of single molecular magnets (SMMs) or single ion magnets (SIMs) [1–4], fluorescent chemical sensors [5–10], catalysts [11–13] and solar energy conversion [14–16]. Depending on the different topics of the researches, large amounts of different ligands such as aromatic carboxylic acids [17], imide-based ligands [18], organophosphonic acids [19–20], porphyrins [21] and polyaminocarboxylic acids [22] have been designed and synthesized and employed in the preparations of the novel multi-functional lanthanide complexes. Meanwhile, metal phosphonates are a class of important coordination complexes in which structures may be designed for specific physical and chemical properties [23]. Much effort has been devoted to develop new kinds of phosphonates in the past decade. Zheng and coworkers successfully developed homochiral zinc [24] and lanthanide [25] phosphonates using enantiopure organophosphonic acid and constructed layered nickel [26] phosphonate showing ferromagnetic behavior. Recently, Sen and coworkers successfully developed a phosphonate-based MOF which is a highly efficient epoxidation catalyst, and remain high selectivity and activity after several cycles [27]. Considering that lanthanide phosphonates based organophosphonic acids show high thermostability and outstanding luminescent and magnetic properties [19,28–30], it is interesting to rationally design and synthesis new lanthanide phosphonates. However, compared with the intensively studied phosphonates of the d-block transition metals, reports on lanthanide phosphonates are still limited.

The fluorene molecule is well known for their unique role in photoluminescent and electroluminescent materials and is easily modified at its 2-, 7- and 9-positions by functional groups [31–36]. Due to its chemical, structural and optical properties, it was considered a good chromophore for developing lanthanide complexes. Indeed, the previous work by our group indicate that the ligand 9,9-dimethylfluorene-2,7-dicarboxylic acid is an effective sensitizer for Eu(III) [37,38]. In order to extend the research field, hence we prepared 9,9-dimethylfluorene-2,7-diphosphonic acid (H_4MFDP) by the reactions of 9,9-dimethyl-2,7-dibromofluorene and diethyl phosphite (Scheme 1). Moreover, assembly of H_4MFDP with europium(III) nitrates afforded one europium phosphonate, $[Eu_2(H_4MFDP)(H_3MFDP)_4(H_2MFDP)(H_2O)_4]\cdot 13.5H_2O$ (**EuMFDP**). Herein, we reported synthesis, crystal structure and properties of **EuMFDP**.

Experimental section

General

The chemicals used in this work are of analytical grade and available commercially and were used without further purification except solvents. Toluene, triethylamine and methylene chloride were dewatered by CaH_2 before use.

The FT-IR spectrum was measured with KBr pellets in the range of 4000–400 cm^{-1} on a SHIMADZU IR Prestige-21 fourier transform infrared spectrophotometer. Elemental analyses for C and H were performed on a Perkin–Elmer 240C analyzer. Thermogravimetric Analysis (TGA) was performed in a SHIMADZU DTG-60 simultaneous DTA-TG apparatus instrument, under dynamic N_2 atmosphere (20 mL/min) and heating rate of 10 °C/min from room temperature to 750 °C. ^1H NMR spectra of samples, in $CDCl_3$ or d^6-DMSO, were recorded at room temperature on a Bruker 400 M NMR spectrometer. Tetramethylsilane (TMS) was used as internal standard. Powder X-ray diffraction investigation on polycrystalline **EuMFDP** was carried out with a Bruker D8 advanced diffractometer equipped with a diffracted-beamed monochromator set for Cu Kα ($\lambda = 1.5418$ Å) radiation. The data was collected using a Ni-filtered Cu-target tube at room temperature in the 2θ range from 5° to 50° at an angular rate of 0.1 s/step, with a scan step width of 0.02°. Photoluminescent spectra were measured using a RF-5301PC spectrofluorophotometer.

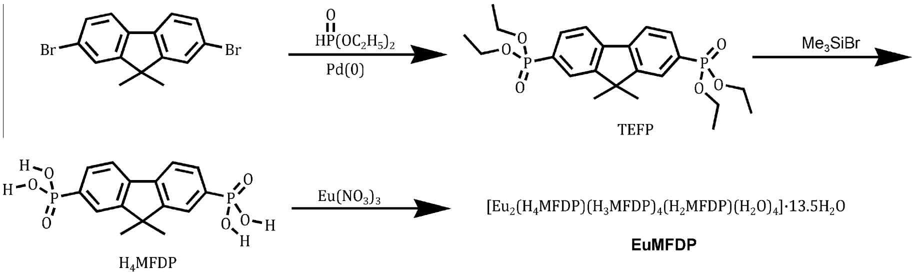
Synthesis of H_4MFDP

A mixture of 9,9-dimethyl-2,7-dibromofluorene (20 mmol) and diethyl phosphite (50 mmol) in 80 mL anhydrous toluene and 80 mL anhydrous triethylamine was refluxed under nitrogen in the presence of 3% $[Pd(PPh_3)_4]$ and 12% PPh_3 for 72 h. Solvents were removed under reduced pressure, and the residue dissolved in 200 mL ethyl acetate and washed twice with 100 mL water. The organic layer was dried over $MgSO_4$ and evaporated to dryness. Chromatography (1:1 v/v PE:EA) gave the pure tetraethyl 9,9-dimethylfluorene-2,7-diphosphonate (TEFP) as a mile white solid (16.14 mmol, 80.7% yield). ^1H NMR ($CDCl_3$) δ 7.93 (d, J = 13.3 Hz, 2H), 7.83 (m, 4H), 4.15 (m, 8H), 1.53 (s, 6H), 1.35 (t, J = 7.0 Hz, 12H).

A mixture of TEFP (20 mmol) and trimethylsilyl bromide (80 mmol) in 100 mL of anhydrous methylene chloride was stirred under nitrogen ar room temperature. After 24 h, the volatiles were removed under reduced pressure and the residue was dissolved in 50 mL of MeOH and stirred at room temperature for 1 h. After purification with activated carbon, the solvent was removed under reduced pressure and a pure product of 9,9-dimethylfluorene-2,7-diphosphonic acid (H_4MFDP, 90% yield) was obtained. ^1H NMR (^{6}d DMSO) δ 7.95 (q, $J1$ = 7.6 Hz, $J2$ = 2.8 Hz, 2H), 7.85 (d, $J1$ = 12.8 Hz, 2H), 7.68 (q, $J1$ = 12.8 Hz, $J2$ = 7.6 Hz, 2H), 1.46 (s, 6H).

*Synthesis of **EuMFDP***

H_4MFDP (88 mg, 0.25 mmol) and $Eu(NO_3)_3\cdot 6H_2O$ (37 mg, 0.083 mmol) were dissolved in 12.5 mL of MeOH. A white deposit precipitated immediately. The deposit was redissolved by adding 3.5 mL of 1:5 (v/v) hydrochloric acid. The solution was sealed with plastic wrap with a beaker and allowed to stand undisturbedly at room temperature. After 7 days, colorless piece-like crystals of **EuMFDP** were obtained, then collected and washed with deionized water and ethanol (yield 68%). Elemental analysis (%) calcd for



Scheme 1. Synthetic strategy used for the preparation of H_4MFDP and **EuMFDP**.