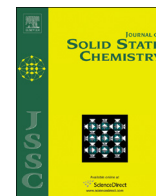




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Lanthanide coordination polymers: Synthesis, diverse structure and luminescence properties



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ABSTRACT

The new semirigid exo-bidentate ligand incorporating furfurysalicylamide terminal groups, namely, 1,4-bis-[(2'-furfurylaminoformyl)phenoxy]methyl]-2,5-bismethylbenzene (L) was synthesized and used as building blocks for constructing lanthanide coordination polymers with luminescent properties. The series of lanthanide nitrate complexes have been characterized by elemental analysis, IR spectroscopy, and X-ray diffraction analysis. The semirigid ligand L, as a bridging ligand, reacts with lanthanide nitrates forming three distinct structure types: chiral noninterpenetrated two-dimensional (2D) honeycomblike (6,3) (hcb, Schläfli symbol 6^3 , vertex symbol 6 6 6) topological network as type I, 1D zigzag chain as type II and 1D trapezoid ladder-like chain as type III. The structural diversities indicate that lanthanide contraction effect played significant roles in the structural self-assembled process. The luminescent properties of Eu^{III} , Tb^{III} and Dy^{III} complexes are discussed in detail. Due to the good match between the lowest triplet state of the ligand and the resonant energy level of the lanthanide ion, the lanthanide ions in Eu^{III} , Tb^{III} and Dy^{III} complexes can be efficiently sensitized by the ligand.

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1. Introduction

In recent years, the rational design and assembly of coordination polymers (CPs) has been of considerable interest because of their intriguing architectures and potential applications, such as gas storage, sensor, separation, catalysis, ion exchange, magnetism, luminescence, and other applications in materials science [1]. However, it is a great challenge to control structures with desired properties because many factors affect the result, such as the coordination geometry of the central metal ions, connection modes of organic ligands, reaction temperature, the ratio of reagents, solvents, pH value, anions, and so on [2]. The most effective and facile approach to overcome this problem is the appropriate choice of the well-designed organic bridging ligands containing modifiable backbones and connectivity information, together with the metal centers with various coordination preferences. Lanthanide centers with high coordination numbers and more variable nature of the coordination sphere have recently attracted intense attention in the field of lanthanide–organic frameworks (LnOFs) [3] owing to the magnetic and electronic properties of 4f ions which exhibit

unique molecular architectures and fascinating chemical/physical properties and have potential applications in catalysis [4], sensors [5], contrast agents [6], non-linear optics [7], displays [8], and electroluminescent devices [9].

Among various organic ligands used for constructing lanthanide coordination polymers [10–13], salicylamide ligands provide a fascinating prospect in preparing lanthanide-based CPs as a result of their interesting chemical ability to form a wide variety of frameworks with different dimensionalities and sensitize lanthanide luminescence successfully. To date, some lanthanide complexes with ligands incorporating salicylamide derivatives have been isolated [14], both the backbone and terminal groups can impact the structures as well as the luminescence properties effectively [15]. Led to this interesting and challenging field, we designed and synthesized the new semirigid exo-bidentate ligand incorporating furfurysalicylamide terminal groups, 1,4-bis-[(2'-furfurylaminoformyl)phenoxy]methyl]-2,5-bismethylbenzene (L). As a result, a series of novel lanthanide coordination polymers, namely, $[\text{Pr}_2(\text{NO}_3)_6\text{L}_3]_\infty$ (1), $\{[\text{Nd}(\text{NO}_3)_3\text{L}(\text{CH}_4\text{O})](\text{C}_3\text{H}_6\text{O})\}_\infty$ (2), $\{[\text{Eu}(\text{NO}_3)_3\text{L}(\text{CH}_4\text{O})](\text{C}_3\text{H}_6\text{O})\}_\infty$ (3), $[\text{Gd}_2(\text{NO}_3)_3\text{L}_3]_\infty$ (4), $[\text{Tb}(\text{NO}_3)_3\text{L}_3]_\infty$ (5) and $[\text{Dy}_2(\text{NO}_3)_3\text{L}_3]_\infty$ (6) were synthesized and characterized. The photoluminescent studies indicate that Eu^{III} , Tb^{III} and Dy^{III} complexes display metal-based emission properties.

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2. Experimental

2.1. Materials and instrumentation

Furfuryllamine and 1,4-xylene was obtained from Alfa Aesar Co. Other commercially available chemicals were of analytical grade and were used without further purification. The lanthanide nitrates [16] were prepared according to the literature method.

Carbon, nitrogen and hydrogen analyses were performed using an EL elemental analyzer. Melting points were determined on a Kofler apparatus. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were obtained with KBr discs on a Thermo Mattson FTIR spectrometer. Powder X-ray diffraction patterns (PXRD) were determined on a Rigaku-D/Max-II X-ray diffractometer with graphite-monochromatized Cu-K α radiation. ^1H NMR spectra were recorded in CDCl_3 solution at room temperature on a Bruker 400 instrument operating at a frequency of 400 MHz and referenced to tetramethylsilane (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as s=singlet, d=doublet, t=triplet and m=multiplet. Fluorescence measurements of the well grinded thick solid samples were made on FLS920 of Edinburgh Instrument. The 77 K solution-state phosphorescence spectra of the Gd^{III} complex was recorded with solution samples (a 1:1 ethyl acetate-MeOH (v/v) mixture) loaded in a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen in the phosphorescence mode on a Hitachi F-7000 spectro photometer and equipped with a xenon lamp as the excitation source (front-face mode) [17]. Samples were placed between two quartz cover slips and the excitation and emission slit of 1.0 nm or 2.5 nm were used. Quantum yields were determined by an absolute method [18] using an integrating sphere on FLS920 of Edinburgh Instrument. The luminescence decays were recorded using a pumped dye laser (Lambda Physics model FL2002) as the excitation source. The nominal pulse width and the line width of the dye-laser output were 10 ns and 0.18 cm^{-1} , respectively. The emission of the sample was collected by two lenses in a monochromator (WDG30), detected by a photomultiplier and processed by a Boxcar Average (EGG model 162) in line with a microcomputer. Reported quantum yields and luminescence lifetimes are averages of at least three independent determinations. The estimated errors for quantum yields and luminescence lifetimes are 10%.

2.2. Synthesis of the ligand

The synthetic route for the ligand (L) is shown in Scheme 1. 2-Furfurylsalicylamide [19] and 1,4-bis(bromomethyl)-2,5-dimethylbenzene [20] was prepared according to the literature procedure.

To a solution of 2-furfurylsalicylamide (2.28 g, 10.5 mmol) in dry acetone was added 1.52 g (11 mmol) dried K_2CO_3 , and the mixture was stirred for 30 min at room temperature, 1.45 g (5 mmol) 1,4-bis(bromomethyl)-2,5-dimethylbenzene in 20 ml of dry acetone was

added dropwise in 30 min and the resulting solution stirred and heated to reflux for 12 h. After cooling down, inorganic salts were separated by filtration and the solvent removed from the filtrate under reduced pressure. The pure product was obtained using chromatography on silica gel. Chromatography (10–60% ethyl acetate in petroleum ether gradient). Yield: 87%. Mp: 158–159 °C. Analytical data for $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_6$, Calcd: C, 72.32; H, 5.71; N, 4.86; Found: C, 72.68; H, 5.69; N, 4.85. IR (KBr, ν , cm^{-1}): 3386 (s), 2923 (m), 1648 (vs), 1597 (s), 1537 (vs), 1480 (m), 1446 (m), 1293 (m), 1221 (s), 1004 (m), 960 (w), 750 (s) (br, broad; w, weak; m, medium; s, strong; vs, very strong) ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 2.24 (s, 6H, $-\text{CH}_3$), 4.42 (t, 4H, $-\text{CH}_2-$), 5.25 (s, 4H, $-\text{CH}_2-$), 5.80 (d, 2H, Ar-H), 6.13 (t, 2H, Ar-H), 7.09–7.54 (m, 8H, ArH), 7.53 (t, 2H), 8.11 (s, 2H, $-\text{NH}$), 8.31 (d, 2H, ArH). ESI-MS: m/z 547.7 ($\text{M}+\text{H}^+$).

2.3. Synthesis of the complexes

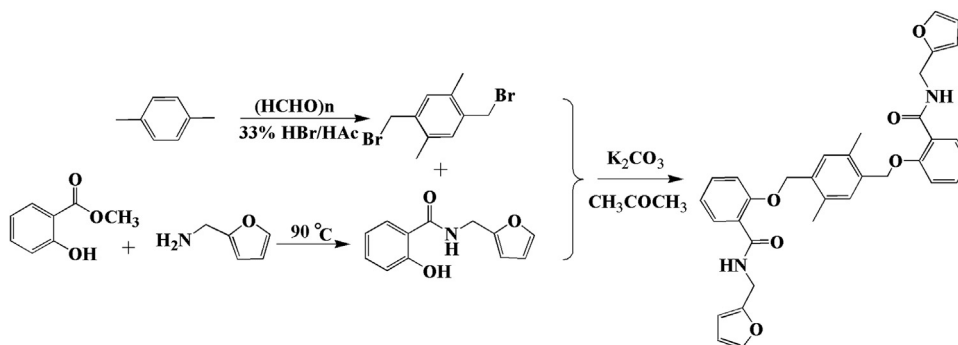
$[\text{Pr}_2(\text{NO}_3)_6\text{L}_3]_\infty$ (1). 56.4 mg (0.1 mmol) L and 43.5 mg (0.1 mmol) $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in a hot ethyl acetate+methanol+acetone (v: v=10:1:1) solution to make a concentrated solution. Then the flask was cooled, and the mixture was filtered into a sealed 10–20 ml glass vial for crystallization at room temperature. After about two weeks, pale green single crystals of 1 suitable for crystal analysis were obtained (yield: 78.7 mg, 67% based on $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Analytical data (%), Calcd: C, 52.18; H, 4.12; N, 7.16; Found: C, 51.98; H, 4.09; N, 7.12. IR (KBr, ν , cm^{-1}): 3342 (m), 2925 (m), 1611 (s), 1560 (m), 1484 (s), 1295 (s), 1223 (m), 1029 (m), 985 (m), 814 (w), 754 (m).

$[\{\text{Nd}(\text{NO}_3)_3\text{L}(\text{CH}_4\text{O})\}(\text{C}_3\text{H}_6\text{O})]_\infty$ (2). The procedure was the same as that for 1 using $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ instead. Pale purple single crystals of 2 were formed after three weeks (yield: 63.2 mg, 65% based on $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Analytical data (%), Calcd: C, 45.67; H, 4.35; N, 7.20; Found: C, 45.78; H, 4.38; N, 7.16. IR (KBr, ν , cm^{-1}): 3336 (m), 2925 (m), 1611 (s), 1561 (m), 1486 (s), 1303 (s), 1223 (m), 1031 (m), 988 (m), 815 (w), 754 (m).

$[\{\text{Eu}(\text{NO}_3)_3\text{L}(\text{CH}_4\text{O})\}(\text{C}_3\text{H}_6\text{O})]_\infty$ (3). The procedure was the same as that for 1 using $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ instead. Colorless single crystals of 3 were formed after three weeks (yield: 58.8 mg, 60% based on $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Analytical data (%), Calcd: C, 45.31; H, 4.32; N, 7.14; Found: C, 45.48; H, 4.29; N, 7.16. IR (KBr, ν , cm^{-1}): 3350 (m), 2924 (m), 1616 (s), 1557 (m), 1490 (s), 1291 (s), 1227 (m), 1030 (m), 985 (m), 815 (w), 758 (m).

$[\text{Gd}_2(\text{NO}_3)_6\text{L}_3]_\infty$ (4). The procedure was the same as that for 1 using $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ instead. Colorless micro crystals of 4 were formed after two weeks (yield: 73.7 mg, 62% based on $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Analytical data (%), Calcd: C, 51.47; H, 4.06; N, 7.06; Found: C, 51.48; H, 4.07; N, 7.05. IR (KBr, ν , cm^{-1}): 3334 (m), 2926 (m), 1611 (s), 1564 (m), 1503 (s), 1308 (s), 1223 (m), 1034 (m), 985 (m), 815 (w), 754 (m).

$[\text{Tb}_2(\text{NO}_3)_6\text{L}_3]_\infty$ (5). The procedure was the same as that for 1 using $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ instead. Colorless micro crystals of 5 were formed after two weeks (yield: 77.4 mg, 65% based on $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Analytical data (%), Calcd: C, 51.39; H, 4.06; N, 7.05; Found: C, 51.34;



Scheme 1. The synthetic route of the ligand L.

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