Lanthanide-organic complexes based on polyoxometalates: Solvent effect on the luminescence properties

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ARTICLE INFO

ABSTRACT

A series of lanthanide-organic complexes based on polyoxometalates (POMs) $[Ln_2(DNBA)_4(DMF)_8]$ $[W_6O_{19}]$ (Ln=La(**1**), Ce(**2**), Sm(**3**), Eu(**4**), Gd(**5**); DNBA=3,5-dinitrobenzoate; DMF=*N,N*-dimethylformamide) has been synthesized. These complexes consist of $[W_6O_{19}]^{2-}$ and dimeric $[Ln_2(DNBA)_4(DMF)_8]^{2+}$ cations. The luminescence properties of **4** are measured in solid state and different solutions, respectively. Notably, the emission intensity increases gradually with the increase of solvent permittivity, and this solvent effect can be directly observed by electrospray mass spectrometry (ESI-MS). The analyses of ESI-MS show that the eight coordinated solvent DMF units of dimeric cation are active. They can move away from dimeric cations and exchange with solvent molecules. Although the POM anions escape from 3D supramolecular network, the dimeric state structure of $[Ln_2(DNBA)_4]^{2+}$ remains unchanged in solution. The conservation of red luminescence is attributed to the maintenance of the aggregated state structures of dimeric cations.

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1. Introduction

The polyoxometalate (POM)-based lanthanide-organic complexes, which are composed of POMs and lanthanide-organic coordination polymers, have attracted much attention of synthetic chemists and material chemists in the past decade. This is not only because POM anions have remarkable physical and chemical properties of metal oxide surfaces and diverse geometric patterns [1–3], but also because lanthanide-organic coordination polymers reveal intriguing structural features and unique functionalities [4–7]. The combination of POMs and lanthanide-organic coordination polymers could produce new species, which possess unique side in many areas, such as optics, magnetism, catalysis, and medicine [8].

Luminescence is an attractive property of lanthanide-organic complexes based on polyoxometalates [9–11]. The luminescence properties of lanthanide complexes have a close connection with their structures [12]. These POMs-incorporated lanthanide complexes employed organic ligands as chromophores, which acted as antennae to sensitize the otherwise weakly luminescent metal centers [13]. This fact not only suggests a fundamental strategy for regulating the emission intensity of complexes, but provides a chance for understanding the relationship between the structures and luminescence properties. Recently, Boskovic et al. reported

two POM-based terbium-organic complexes, which represented fundamentally different luminescence behaviors due to the difference of the Tb coordination environments, and illuminated the correlation between structures with luminescence properties [14]. Gunnlaugsson reported a cationic dinuclear complex with two metal-bound water molecules [15]. This dinuclear complex could recognize or sense *N,N*-dimethylaminocarboxylic acid and bis(carboxylate) terephthalic acid in solution. It is mainly because the metal-bound water molecules were active, could move away through the metal center, then the bidentate anions coordinated lanthanide ions by a short semirigid bridge. Although this process was monitored by the increase and quenching of luminescence intensity, investigating its definite mechanisms by other characterization methods could be essential to understand the structures of dinuclear complexes in solution and explain the correlation between the structure and luminescence property.

The transition $^5D_0 \rightarrow {}^7F_2$ in Eu^{3+} complexes is hypersensitive to the coordination environment of Eu^{3+} center due to its strong electric dipole character, which allows the use of the relative intensity of this transition to probe the nature of the linker environment. At present, revealing the correlation between the luminescence properties and the structures of POM-based lanthanide-organic hybrid materials is still a challenging issue. Specifically, when the complexes have been dissolved in solvents, the structure of complexes may change, which should result in the change in luminescence properties. This phenomenon can be attributed to a solvate effect [16]. However, the origin of the solvate effect is not as yet quite clearly understood. Eu^{3+}-based

complexes are very promising for efficient light conversion molecular devices on account of their potential applications, such as luminescent labels for luminescent chemical sensors, luminescent stains in clinical immunoassays, and luminescent probes [17].

We have successfully synthesized a series of 3D compounds $[Ln_2(DNBA)_4(DMF)_8][W_6O_{19}]$ (Ln=La(**1**), Ce(**2**), Sm(**3**), Eu(**4**), Gd(**5**); DNBA=3,5-dinitrobenzoate; DMF=N,N-dimethylformamide). They consist of $[W_6O_{19}]^{2-}$ and dimeric $[Ln_2(DNBA)_4 (DMF)_8]^{2+}$ cations. The luminescence activity of **4** was determined in detail, and its emission properties in solution showed the solvate effect. The origin of the solvate effect was probed by electrospray mass spectrometry (ESI-MS), which revealed the correlation between the structures and luminescence properties.

2. Experimental

2.1. Materials and general methods

All chemicals were analytical reagents, commercially purchased, and used without further purification. $[(n\text{-}C_4H_9)_4N]_2 W_6O_{19}$ was synthesized by the methods of the literature [18], and characterized by IR spectra and TG analyses. Elemental analyses (C, H, N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT-IR spectrophotometer using KBr pellets, and the IR spectra of **1–5** are very similar, see Fig. S1. Thermal stability analysis was performed on a Perkin–Elmer TGA7 instrument in flowing N_2 atmosphere with a heating rate of 10 °C min^{-1}. Photoluminescence spectra were measured using a FLSP 920 Edinburgh instrument (Eng) with 450 W Xenon lamp monochromatized by double grating. Mass spectra were measured on a Bruker micrOTOF mass spectrometer in electrospray ionization (ESI) mode.

2.2. Synthesis

2.2.1. Synthesis of $[La_2(DNBA)_4(DMF)_8][W_6O_{19}]$ (1)

5 mL glacial acetic acid (HOAc) solution of 3,5-dinitrobenzoic acid (1 mmol, 0.21 g) were added dropwise to 12 mL DMF and 3 mL water solution of LaCl$_3 \cdot$7H$_2$O (1 mmol, 0.37 g). The mixture solution was stirring 0.5 h at 70 °C, then $[(n\text{-}C_4H_9)_4N]_2W_6O_{19}$ (0.2 mmol, 0.38 g) was added. The light yellow solution was stirred for 2 h. The resulting solution was filtered and then allowed to evaporate in air at room temperature. Slow evaporation afforded light yellow crystal of **1**. Yield: 0.36 g (57.68% based upon W). Elemental anal. Calcd for $C_{52}H_{68}La_2W_6N_{16}O_{51}$: C, 20.06; H, 2.20; N, 7.20; W, 35.42; La, 8.92. Found: C, 20.10; H, 2.19; N, 7.22; W, 35.40; La, 8.94. FT-IR data (cm^{-1}): 3104 (w), 2935 (w), 1651 (s), 1588 (w), 1542 (s), 1497 (w), 1458 (w), 1437 (w), 1379 (m), 1348 (s), 1250 (w), 1109 (w), 981 (s), 812 (s), 723 (s), 672 (m).

2.2.2. Synthesis of $[Ce_2(DNBA)_4(DMF)_8][W_6O_{19}]$ (2)

The preparation of **2** was similar to that of **1**, except that CeCl$_3 \cdot$6H$_2$O (0.35 g) was used in place of LaCl$_3 \cdot$7H$_2$O. Yield: 0.37 g (58.73% based upon W). Elemental anal. Calcd for $C_{52}H_{68}Ce_2W_6N_{16}O_{51}$: C, 20.04; H, 2.20; N, 7.19; W, 35.39; Ce, 8.99. Found: C, 20.11; H, 2.20; N, 7.19; W, 35.40; Ce, 8.98. FT-IR data (cm^{-1}): 3104 (w), 2936 (w), 1651 (s), 1588 (w), 1542 (s), 1497 (w), 1458 (w), 1437 (w), 1377 (m), 1348 (s), 1250 (w), 1109 (w), 981 (s), 813 (s), 722 (s), 672 (m).

2.2.3. Synthesis of $[Sm_2(DNBA)_4(DMF)_8][W_6O_{19}]$ (3)

The preparation of **3** was similar to that of **1**, except that SmCl$_3 \cdot$6H$_2$O (0.36 g) was used in place of LaCl$_3 \cdot$7H$_2$O. Yield:

0.40 g (64.41% based upon W). Elemental anal. Calcd for $C_{52}H_{68}Sm_2W_6N_{16}O_{51}$: C, 19.91; H, 2.18; N, 7.14; W, 35.16; Sm, 9.59. Found: C, 19.92; H, 2.18; N, 7.15; W, 35.15; Sm, 10.74. FT-IR data (cm^{-1}): 3100 (w), 2937 (w), 1649 (s), 1591 (w), 1541 (s), 1499 (w), 1458 (w), 1437 (w), 1403 (m), 1348 (s), 1252 (w), 1111 (w), 979 (s), 813 (s), 723 (s), 676 (m).

2.2.4. Synthesis of $[Eu_2(DNBA)_4(DMF)_8][W_6O_{19}]$ (4)

The preparation of **4** was similar to that of **1**, except that EuCl$_3 \cdot$6H$_2$O (0.37 g) was used in place of LaCl$_3 \cdot$7H$_2$O. Yield: 0.28 g (44.80% based upon W). Elemental anal. Calcd for $C_{52}H_{68}Eu_2W_6N_{16}O_{51}$: C, 19.89; H, 2.18; N, 7.14; W, 35.13; Eu, 9.68. Found: C, 19.82; H, 2.20; N, 7.11; W, 35.15; Eu, 9.70. FT-IR data (cm^{-1}): 3102 (w), 2937 (w), 1649 (s), 1585 (w), 1539 (s), 1499 (w), 1457 (w), 1437 (w), 1304 (m), 1349 (s), 1252 (w), 1111 (w), 978 (s), 813 (s), 722 (s), 677 (m).

2.2.5. Synthesis of $[Gd_2(DNBA)_4(DMF)_8][W_6O_{19}]$ (5)

The preparation of **5** was similar to that of **1**, except that GdCl$_3 \cdot$6H$_2$O (0.37 g) was used in place of LaCl$_3 \cdot$7H$_2$O. Yield: 0.29 g (46.39% based upon W). Elemental anal. Calcd for $C_{52}H_{68}Gd_2W_6N_{16}O_{51}$: C, 19.82; H, 2.18; N, 7.11; W, 35.01; Gd, 9.98. Found: C, 19.81; H, 2.18; N, 7.10; W, 35.07; Gd, 9.93. FT-IR data (cm^{-1}): 3101 (w), 2937 (w), 1650 (s), 1586 (w), 1539 (s), 1499 (w), 1457 (w), 1404 (w), 1374 (m), 1349 (s), 1252 (w), 1112 (w), 978 (s), 813 (s), 722 (s), 678 (m).

2.3. X-ray crystallographic study

Diffraction intensities for compounds **1–5** were collected on an Oxford Diffraction Gemini R Ultra diffractometer (a Bruker Smart Apex CCD diffractometer for 5) with Mo K_α monochromatic radiation (λ=0.710 73 Å) at 293 K (296 K for 5). The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [19]. The structures of **1–5** were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [20]. All non-hydrogen atoms in **1–5** were refined anisotropically. The crystal data and structure refinement results of compounds **1–5** are summarized in Table 1. The bond valence sums (BVS) of all Ln cations (Ln=La, Ce, Sm, Eu, and Gd) are presented in Table S1. Selected bond lengths for compounds **1–5** are provided in Tables S2–S6 in the supporting material, and the selected Ln–O bond lengths, which are also significant for the lanthanide coordination.

3. Results and discussion

The highest yield of compounds **1-5** is obtained when the anions $[W_6O_{19}]^{2-}$ are added to DNBA–HOAc–LnCl$_3$–DMF–H$_2$O solution at 70 °C. The ratio of DMF–H$_2$O mixed solution is 4:1, which must be controlled strictly. Excess H$_2$O leads to precipitation of $[(n\text{-}C_4H_9)_4N]_2W_6O_{19}$, or crystals do not form during the lack of H$_2$O. The salient point is that the DNBA should be added to DMF–H$_2$O solution of LnCl$_3$ before the $[(n\text{-}C_4H_9)_4N]_2W_6O_{19}$, otherwise only colorless crystals of $[(n\text{-}C_4H_9)_4N]_2W_6O_{19}$ are obtained. The HOAc is indispensable, it not only protects Ln^{3+} from being hydrolyzed, but keeps coordinative active of Ln^{3+} at an opportune pH=5. Moreover, the effect of temperature on the reaction is not negligible. When it is higher than 80 °C, only low yields are obtained, and lower than 60 °C, the unsuitable colorless crystals are produced.