

A new type of multifunctional single ionic dysprosium complex based on chiral salen-type Schiff base ligand



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ABSTRACT

A new type of multifunctional single ionic chiral dysprosium complex (**DyL**) was obtained by the reaction of Dy(NO₃)₃ and salen-type Schiff base ligand N,N'-bis(3,5-dichlorosalicylidene)-(1*R*,2*R*)-1,2-cyclohexylenediamine. In the synthesis reaction, Dy(III) was found not only to be the central metal to coordinate with two Schiff base ligands, but also the Lewis acid catalyst to promote the partial decomposition of salen-type Schiff base ligand. Complex **DyL** crystallizes in a chiral and polar space group *P*₂₁. The central metal Dy(III) adopts eight-coordinated square antiprism geometry with Δ absolute configuration. Complex **DyL** exhibits good SHG and ferroelectric properties. The single-crystal sample of **DyL** displays an obvious ferroelectric behavior with a remnant polarization (*P*_r) of ca. 4.51 $\mu\text{C cm}^{-2}$ and *E*_c of ca. 28.11 kV cm⁻¹. The solid luminescent spectrum of **DyL** presents characteristic emission ⁴F_{9/2} → ⁶H_{15/2} and ⁴F_{9/2} → ⁶H_{13/2} transitions of Dy(III).

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1. Introduction

For the past few decades, significant attention has been paid to the design and synthesis of various noncentrosymmetric ferroelectric compounds [1–5], for their potential applications in ferroelectric random-access memories (FeRAM), switchable nonlinear optical devices, electro-optical devices, and light modulators [6–9]. Recently, the design and construction of molecule-based metal–organic coordination compounds with hybridized physical properties, such as magnetic, second-order nonlinear optical (NLO), ferroelectric, photoluminescent, catalytic properties and gas adsorption is a challenging topic for synthetic chemists [10–14]. To date, studies on the multifunctional material with ferroelectric and luminescent properties have mainly focused on inorganic compounds, and there are few reports on the molecular compounds [15–19].

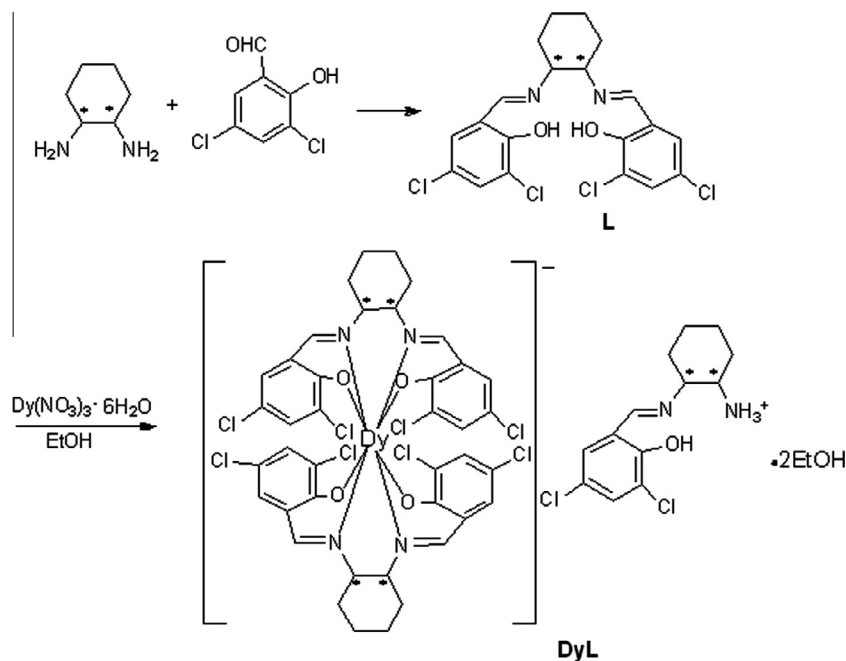
In recent years, a great number of multifunctional lanthanide complexes have been prepared utilizing various multidentate ligands [20–23]. ‘H₂salen’ (N,N'-ethylenbis(salicylideneimine) and its variations have been widely used as multidentate ligands to incorporate both f- and d-block transition metals, some of which exhibit interesting magnetic and luminescent properties [24–29]. But in the absence of d-block transition metals, only a few lanthanide complexes with salen-type Schiff base ligands have been docu-

mented, having polynuclear cluster or coordination polymer structures [30–33], and single ionic rare earth complex are very rare. Comparing with neutral metal–organic framework, the ionic metal–organic coordination compounds will be more effective in enlarging the polarity and ferroelectricity due to the existence of the separated positive and negative charge [34–37]. In addition, the imine N atoms have seldom been used to connect lanthanide ions owing to their poor affinity for hard Lewis acid metal ions [38]. If a strong electron-withdrawing group is introduced, it will facilitate the coordination of lanthanide ions to N-donor ligands [39–41].

In previous paper, we have reported one couple of ion ferroelectric based on chiral Schiff base nickel complexes with a polarization value higher than KDP [42]. As our continuous interest in molecular ferroelectric materials, a new type of single ionic rare earth complex was designed and synthesized utilizing the charge difference between ligand and central metal. Meanwhile the electron-withdrawing group (–Cl) was introduced to fulfill the coordination of the imine N atoms with lanthanide ions. To the best of our knowledge, it is the first time that single ionic rare earth complex coordinating with all N and O atoms of salen-type Schiff-base ligands is obtained. Lanthanide ion is firstly found to catalyze the partial decomposition of salen-type Schiff base. Complex **DyL** was obtained by the reaction of dysprosium nitrate and salen-type Schiff base ligand N,N'-bis(3,5-dichlorosalicylidene)-(1*R*,2*R*)-1,2-cyclohexylenediamine (Scheme 1). The structure, ferroelectric and luminescent properties were reported in this paper.

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Scheme 1. Synthesis routine of complex **DyL**.

2. Experimental

2.1. General materials and methods

(1*R*,2*R*)-(–)-1,2-cyclohexanediamine and 3,5-dichlorosalicylaldehyde were obtained from Aldrich company. All other reagents and solvents were purchased from commercial sources and used as received. The IR spectrum was performed on a Bruker Vector 22 FT-IR spectrometer with KBr discs in the 4000–400 cm^{-1} range. The electric hysteresis loops were recorded on a Ferroelectric Tester Multiferroic made by Radiant Technologies, Inc. Complex dielectric permittivity was performed using automatic impedance TongHui 2828 Analyzer. The measuring AC voltage was 1 V. Fluorescence measurement was conducted on Perkin Elmer LS-55 spectrofluorometer with both excitation and emission slits set at 5 nm.

2.2. Synthesis of Schiff base ligand

A mixture of (1*R*,2*R*)-(–)-1,2-cyclohexanediamine (0.1140 g, 1 mmol) and 3,5-dichlorosalicylaldehyde (0.3820 g, 2 mmol) in 50 mL ethanol was heated at 60 °C for 1.5 h, and then cooled to room temperature. The precipitate was collected, re-crystallized in ethanol solution and dried under vacuum. FT-IR (KBr, cm^{-1}): 3015(s), 2928(m), 1642(s), 1606(m), 1574(m), 1482(s).

2.3. Synthesis of complex **DyL**

The obtained Schiff base ligand (0.1840 g, 0.4 mmol) was dissolved in 30 mL of ethanol, and then $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.1864 g, 0.4 mmol) was added and refluxed for about 4 h. The mixed solution was cooled to r.t. and left to stand undisturbed. Upon slow evaporation at r.t. for several days, single crystals suitable for X-ray analysis were collected. FT-IR (KBr, cm^{-1}): 3329(s), 3010(s), 2942(m), 1658(s), 1640(s), 1600(m), 1571(m), 1457(s).

2.4. X-ray crystallography

Diffraction intensities for **DyL** were collected at 293(2) K on a Bruker Apex II CCD diffractometer with graphite-monochromated

Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption correction was applied using SADABS [43]. The structure was solved by direct methods and refined with the full-matrix least-squares technique using SHELXS-97 and SHELXTL-97 programs, respectively [44]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The H atoms were positioned geometrically and treated as riding on their parent atoms, with C–H distances of 0.97 Å (methylene) and 0.96 Å (methyl). Crystal data as well as details of data collection and refinement for the compounds are summarized in Table 1.

3. Results and discussion

3.1. Crystal structural descriptions

Complex **DyL** crystallizes in a chiral and polar space group $P2_1$. Its crystal structure is shown in Fig. 1. Selected bond lengths and

Table 1
Crystal data and structure refinements for **DyL**.

Compound	DyL
Empirical formula	$\text{C}_{57}\text{H}_{61}\text{Cl}_{10}\text{DyN}_6\text{O}_7$
Formula weight	1459.12
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	11.4982 (10)
b (Å)	21.5339 (19)
c (Å)	12.9149 (11)
β (°)	98.335 (1)
V (Å ³)	3164.0 (5)
Z	2
D_{calc} (Mg m^{-3})	1.532
θ range (°)	2.4–27.8
Collected reflections	18879
Unique reflections	9884
Parameters	734
T (K)	293 (2)
R_1 [$I > 2\sigma(I)$], wR_2 (all data) ^a	0.022, 0.057
Goodness-of-fit (GOF)	0.92
Flack parameter	–0.001 (5)
$\Delta\rho_{\text{max}}$ (e \AA^{-3})	0.51
$\Delta\rho_{\text{min}}$ (e \AA^{-3})	–0.36

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)|^2 / \sum w|F_o|^2]^2$.

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