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Series of chiral interpenetrating 3d–4f heterometallic MOFs: Luminescent sensors and magnetic properties

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ABSTRACT

Series of chiral 3d-4f heterometallic MOFs based on a multidentate terpyridyl carboxylic acid ligand have been synthesized under the solvothermal conditions, namely, $[LnZnL(CO_3)_2(H_2O)]_n$ (Ln = Eu (**1**), Gd (**2**), Dy (**3**), Ho (**4**), Er (**5**), Tm (**6**), Yb (**7**), Lu (**8**)) (HL = 4′-(4-carboxyphenyl)−2,2′:6′,2″-terpyridine). Compounds **1**–**8** were structurally characterized by the elemental analyses, infrared spectra, and single crystal X-ray diffractions. Compounds **1**–**8** exhibit the chiral interpenetrating 3D frameworks. Interestingly, **1** can serve as the luminescent sensor to detect nitrobenzene molecules with high sensitivity. The investigations on CD spectra of single crystals clearly assigned the Cotton effect, indicating that there exist two chiral enantiomers of **1**–**8** in the course of crystallization. The magnetic properties of **2** and **7** were exploited, respectively.

1. Introduction

The rational design and fabrication of heterometal–organic frameworks (HMOFs) comprised of d and f block metal ions have currently been attracted the great attentions, not only because their fascinating topological structures but also for their versatile applications in the field of adsorption, separation, molecular magnetism, catalysis, and luminescent probes [1–10]. In addition, the chemosensor research based on HMOFs has been a frontier due to the intriguing photophysical properties of heterometallic ions in frameworks. The luminescent ions are introduced to make the abundant structures and more controllable energy levels of HMOFs, which are sensitive to certain metal ions and organic molecules through enhancing or quenching the luminescent intensities of HMOF [11]. Therefore, the construction and synthesis of HMOFs, which can recognize the metal ions and organic molecules by the specific functional sites in structures and then might exhibit the selective luminescent properties, have been drawn the tremendous interests in the area of HMOFs.

Chemists have also made the great efforts to construct chiral MOFs because chirality plays a crucial role in many fields of nature. Some chiral MOFs in the field of luminescence, catalysis, magnetism, and enantiomeric separation have been reported [12–20], however, only few chiral d–f HMOFs were investigated [11,21–24].

According to the soft–hard theory, d and f metal ions have the different affinities for N and O donors, respectively, hence we select the 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine ligand (HL) to imbed both 3d and 4f metal ions into HMOFs in this contribution. As a polydentate N and O donor bridging ligand, HL can link the adjacent metal centers through the coordination bonding interactions, the terpyridyl groups can serve as the chelating groups with d block elements and the carboxylate group may act as the bridging group with f block ones, which might extend the structure into high dimensional HMOFs. Simultaneously, HL ligand with the large conjugated π electronic system may function as an ideal luminescent chromophore, which can transfer the energy to luminescent centers effectively. As expected, $[LnZnL(CO_3)_2(H_2O)]_n$ (Ln = Eu (**1**), Gd (**2**), Dy (**3**), Ho (**4**), Er (**5**), Tm (**6**), Yb (**7**), Lu (**8**)) with the 2-fold interpenetrating chiral structures have been synthesized. Complex **1** can be purposed as a luminescent sensor with high sensitivity to detect nitrobenzene molecule. The CD spectra of several single crystals were explored to clearly confirm the Cotton effect of two enantiomers.

2. Experimental

2.1. Materials and general methods

The chemical reagents and metal salts were commercially available and used without further purification. Elemental analyses (C, H and N) were determined on Perkin-Elmer 2400 analyzer. The IR spectra were recorded as KBr pellets on a Nicolet Avatar-360 spectrometer in the 400–4000 cm^{-1} region. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 25 to 900 °C

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Table 1
Crystal data of **1–8**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{24}H_{16}EuN_3O_9Zn$	$C_{24}H_{16}GdN_3O_9Zn$	$C_{24}H_{16}DyN_3O_9Zn$	$C_{24}H_{16}HoN_3O_9Zn$
Formula weight	707.76	713.02	718.29	720.70
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_3$	$P4_1$	$P4_1$	$P4_3$
a(Å)	12.2456(6)	12.2428(4)	12.2203(5)	12.2220(10)
b(Å)	12.2456(6)	12.2428(4)	12.2203(5)	12.2220(10)
c(Å)	15.2080(11)	15.1663(11)	15.0611(10)	15.0661(18)
α(°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	90.00	90.00
γ(°)	90.00	90.00	90.00	90.00
V(Å^3)	2280.5(2)	2273.2(2)	2249.2(2)	2250.5(4)
Z	4	4	4	4
D_{calc}(g cm$^{-3)}$	2.061	2.083	2.121	2.127
μ (mm^{-1})	21.348	20.537	19.458	8.249
F(000)	1384	1388	1396	1400
Flack parameter	−0.026(7)	0.009(5)	−0.008(11)	0.000
Rint	0.0928	0.0866	0.0466	0.0624
GOF	1.027	1.020	1.030	1.038
R_1[a] [$I > 2\sigma(I)$]	0.0695	0.0502	0.0710	0.1094
ωR_2[b] [$I > 2\sigma(I)$]	0.1658	0.1062	0.1679	0.2668
R_1 (all data)	0.0912	0.0676	0.0929	0.1530
wR_2 (all data)	0.1784	0.1155	0.1868	0.3137
Compound	**5**	**6**	**7**	**8**
Formula	$C_{24}H_{16}ErN_3O_9Zn$	$C_{24}H_{16}TmN_3O_9Zn$	$C_{24}H_{16}$ Yb N_3O_9Zn	$C_{24}H_{16}LuN_3O_9Zn$
Formula weight	723.03	724.72	728.81	730.76
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$P4_3$	$P4_3$	$P4_1$	$P4_1$
a(Å)	12.1929(4)	12.2125(4)	12.1961(6)	12.2070(6)
b(Å)	12.1929(4)	12.2125(4)	12.1961(6)	12.2070(6)
c(Å)	15.0143(7)	15.1593(6)	14.9534(9)	15.0352(9)
α(°)	90.00	90.00	90.00	90.00
β (°)	90.00	90.00	90.00	90.00
γ(°)	90.00	90.00	90.00	90.00
V(Å^3)	2232.14(14)	2246.03(14)	2224.2(2)	2240.4(2)
Z	4	4	4	4
D_{calc}(g cm$^{-3)}$	2.152	2.149	2.176	2.172
μ (mm^{-1})	8.676	9.085	9.480	10.155
F(000)	1404	1408	1412	1416
Flack parameter	−0.030(3)	0.000	−0.050(3)	0.000
Rint	0.0800	0.0812	0.1109	0.0567
GOF	1.087	1.076	1.088	1.065
R_1[a] [$I > 2\sigma(I)$]	0.0824	0.0887	0.0779	0.1051
ωR_2[b] [$I > 2\sigma(I)$]	0.1733	0.2262	0.1819	0.2588
R_1 (all data)	0.1056	0.1007	0.1116	0.1238
wR_2 (all data)	0.187	0.2376	0.2054	0.2832

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$.
[b] $\omega R_2 = [\Sigma[\omega(F_o^2-F_c^2)^2]/ \Sigma\omega(F_o^2)^2]^{1/2}$.

under nitrogen atmosphere. Powder X-ray power diffraction (PXRD) was performed on a X′Pert PRO (PW3071/xx Bracket) diffractometer with Cu *Ka* radiation (λ = 1.5406 Å). The fluorescent spectra were measured on a FLS920 spectrophotometer. The circular dichroism spectra were recorded on a JASCO J-1500 spectropolarimeter with KBr pellets. The variable-temperature magnetic susceptibility was measured on a Quantum Design SQUID MPMS XL-7 magnetometer. Diamagnetic corrections were estimated from Pascal's constants.

2.2. Synthesis of 1–8

A mixture of HL (0.2 mmol, 70.2 mg), $Ln(NO_3)_2 \cdot 6H_2O$ (Ln = Eu (**1**), Gd (**2**), Dy (**3**), Ho (**4**), Er (**5**), Tm (**6**), Yb (**7**), Lu (**8**)) (0.1 mmol), $Zn(CH_3COO)_2$ (0.2 mmol, 44.2 mg), and 8 mL of DMF/water (6:2) solutions were stirred for 30 mins at room temperature and were sealed in a 23 mL Teflon-lined stainless steel vessel, which was heated at 160 °C for 4 days and then slowly cooled to room temperature at a rate of 2 °C h^{-1}. The yellow needle shaped crystal was isolated by filtration and washed with H_2O several times, yield 50–60%. For **1**: IR (KBr pellet, cm^{-1}): 3517.04(s), 1633.98(s), 1584.08(m), 1448.49(m), 1321.62(s), 1259.93(m), 1215.89(s), 1128.95(w), 994.35(m), 829.00(m), 766.92(s); Anal. Calc. for $C_{24}H_{16}EuN_3O_9Zn$: C, 40.69; H, 2.26; O, 20.22; N, 5.93%. Found: C, 40.70 H, 2.25; O, 20.20; N, 5.94%. For **2**: IR (KBr pellet, cm^{-1}): 3644.02(s), 1636.89(s), 1585.29(m), 1439.26(m), 1316.39(s), 1258.73(m), 1223.49(s), 1128.93(w), 1001.28(m), 846.43(m), 792.11(s); Anal. Calc. for $C_{24}H_{16}GdN_3O_9Zn$: C, 40.39; H, 2.24; O, 20.20; N, 5.89%. Found: C, 40.40; H, 2.23; O, 20.19; N, 5.88%. For **3**: IR (KBr pellet, cm^{-1}): 3621.72(s), 1630.64(s), 1585.54(m), 1439.59(m), 1317.59(s), 1258.85(m), 1221.73(s), 1125.41(w), 992.86(m), 846.67(m), 794.26(s); Anal. Calc. for $C_{24}H_{16}DyN_3O_9Zn$: C, 40.10; H, 2.23; O, 20.05; N, 5.85%. Found: C, 40.11; H, 2.24; O, 20.06; N, 5.86%. For **4**: IR (KBr pellet, cm^{-1}): 3631.32(s), 1625.46(s), 1581.23(m), 1432.59(m), 1327.59(s), 1253.65(m), 1227.33(s), 1121.91(w), 989.76(m), 842.45(m), 786.34(s); Anal. Calc. for $C_{24}H_{16}HoN_3O_9Zn$: C, 39.96; H, 2.22; O, 19.98; N, 5.83%. Found: C, 39.97; H, 2.21; O, 19.99; N, 5.82%. For **5**: IR (KBr pellet, cm^{-1}): 3633.23(s), 1629.24(s), 1581.54(m), 1436.49(m), 1315.38(s), 1256.35(m), 1223.34(s), 1128.34(w),