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Construction of monomers and chains assembled by 3d/4f metals and 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine

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ABSTRACT

A series of transition metal and lanthanide complexes of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (HL, 1), namely $[M(L)_2]\cdot 5H_2O$ (M=Ni, 2; Co, 3), $[Zn(L)_2]_n\cdot 0.5nH_2O$ (4) and $[Ln(L)_3]_n$ (Ln=Nd, 5; Gd, 6; Er, 7) were hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Isomorphic compounds 2 and 3 are mononuclear molecules with two ligand chelating to the metal centers via tridentate terpyridyl, while compound 4 adopts 1D chain-like structure, in which five-coordinate zinc centers are surrounded by three ligands. Compounds 5–7 also display 1D chain-like structure, but the nine-coordinate lanthanide centers bonded by four ligands. Luminescent property indicates that compound 4 exhibits photoluminescence in the solid state at room temperature.

1. Introduction

The rational synthesis of metal-organic frameworks (MOFs) with specified structures and properties is an important aim for chemists [1–4]. We know that the resultant structure and physicochemical properties of MOFs largely depend on two key elements, center atoms and organic ligands [5,6]. Therefore, many target MOFs by judicious of metal atoms and tailored ligands have been successfully synthesized [7–10]. Terpyridine derivatives are important functional ligands for their tunable photophysical and electrochemical properties. In recent decades, the investigation on terpyridine derivatives, with the aim of exploring the potential utility ranging from catalysis to dye-sensitized solar cells, have been carried out widely [11–19]. Among these derivatives, terpyridine bearing carboxylate function, such as 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine [20–24], 2,2′:6′,2″-terpyridine-4′-carboxylate [25–27] and 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine [28–30], are perfect multidentate ligands to form novel complexes with intriguing architectures, and as well as a suitable anchorage on TiO_2 for electron injection. In our continuing investigation on MOFs of linear *N*-containing carboxylate ligand [31–35], we find 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (HL), showing structural similarity to the linear 4-(4-pyridyl)benzoate and featuring a tridentate terpyridyl and a carboxylate group set on opposite direction of benzene ring, are potential "expanded ligands" with typical scaffolds of $\{M(tyba)_2\}$ as bond to some six-coordination transition metals. Therefore, to further investigate the effect of substituted linear ligands on the structure and property of resultant coordination polymers, we reacted 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine to transition metal and lanthanide salts, and obtained a series of novel metal compounds: $[M(L)_2]\cdot 5H_2O$ (M=Ni, 2; Co, 3), $[Zn(L)_2]_n\cdot 0.5nH_2O$ (4) and $[Ln(L)_3]_n$ (Ln=Nd, 5; Gd, 6; Er, 7).

2. Experimental section

2.1. Materials and measurements

Aqueous solution of $Ln(NO_3)_3$ was made by dissolving Ln_2O_3 in an appropriate amount of nitric acid. All other reagents and solvents employed were commercially available and used without further purification. IR spectra were measured as KBr pellets on a NICOLET-Avatar 37 in the range 400–4000 cm^{-1}. Thermalgravimetric data were collected on a NETZSCH-STA409PC analyzer in flowing nitrogen at a heating rate of 10 °C/min. Luminescence spectrum was recorded by using a HitaChi-4500 spectrometer. The photoluminescence quantum yields were measured by Edingburgh Instruments FLS920.

2.2. Preparation

2.2.1. 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (1)

Powder sample of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine is synthesized according to the literature procedure [29,36], while its crystals were prepared by mixing the powder of HL (0.110 g,

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Table 1
Crystallographic data and structure refinement for compounds 1–7.

Compound	1	2	3	4	5	6	7
CCDC code	871512	871517	871513	871518	871516	871515	871514
Formula	$C_{22}H_{15}N_3O_2$	$C_{44}H_{38}NiN_6O_9$	$C_{44}H_{38}CoN_6O_9$	$C_{44}H_{29}ZnN_6O_{4.5}$	$C_{66}H_{42}NdN_9O_6$	$C_{66}H_{42}GdN_9O_6$	$C_{66}H_4ErN_9O_6$
M_r	353.37	853.51	853.73	779.10	1201.33	1214.34	1224.35
T (K)	153(2)	153(2)	153(2)	293(2)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	P-1	P-1	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a (Å)	10.194(2)	8.7035(17)	8.7440(17)	33.088(7)	33.8052(6)	33.812(7)	33.794(4)
b (Å)	7.1491(14)	13.502(3)	14.494(3)	10.035(2)	13.9956(2)	13.872(3)	13.7643(16)
c (Å)	22.340(5)	16.591(3)	16.430(3)	24.697(5)	12.1766(2	12.253(3)	12.2604(14)
α (°)	90.00	93.16(3)	93.52(3)	90.00	90.00	90.00	90.00
β (°)	90.56(3)	97.45(3)	97.26(3)	119.12(3)	108.7210(10)	108.978(2)	109.2080(10)
γ (°)	90.00	91.07(3)	91.24(3)	90.00	90.00	90.00	90.00
V (Å^3)	1627.9(6)	1929.7(7)	2060.8(7)	7164(2)	5456.24(15)	5435(2)	5385.5(11)
Z	4	2	2	8	4	4	4
F (0 0 0)	736	888	886	3208	2436	2452	2468
D_c (g cm^{-3})	1.442	1.469	1.376	1.445	1.462	1.484	1.510
μ (mm^{-1})	0.095	0.571	0.480	0.742	1.016	1.285	1.623
GOF on F^2	1.036	1.082	0.955	1.069	1.039	1.003	1.030
R_1 $[I>2\sigma(I)]$[a]	0.0492	0.0495	0.0512	0.0473	0.0364	0.0191	0.0276
wR_2 $[I>2\sigma(I)]$[b]	0.1160	0.1211	0.1363	0.0994	0.0717	0.0501	0.0576

[a] $R_1=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$.
[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

0.3125 mmol) with silver nitrate (0.021 g, 0.125 mmol) in 5 mL distilled water and heating at 180 °C for 7 day. Yield: 42%, based on HL. Main IR absorption bands (cm^{-1}): 3448.29(w), 1703.88(s), 1588.24(v), 1471.92(s), 1264.96(sh), 857.67(w), 772.25(m), 733.72(w), 694.50(w).

2.2.2. Synthesis of $[Ni(L)_2]_n \cdot 5H_2O$ (2)

A mixture of $Ni(OAc)_2 \cdot 4H_2O$ (0.031 g, 0.125 mmol), HL (0.088 g, 0.25 mmol) in deionized water (5 mL) was adjusted to pH=11.0 with triethylamine, and sealed in a 28 mL Teflon-lined stainless steel vessel, which was heated at 180 °C for 7 day under autogenous pressure and thereafter cooled to room temperature. Brown block crystals of 2 were collected after washing with distilled water and dried in air (yield: 49%, based on Ni). Main IR absorption bands (KBr, cm^{-1}): 3437.42(b), 1605.07(s), 1552.90(s), 1367.78(s), 786.42(s).

2.2.3. Synthesis of $[Co(L)_2]_n \cdot 5H_2O$ (3)

Compound 3 was synthesized by a similar procedure to that of 2 except that $Ni(OAc)_2 \cdot 4H_2O$ was replaced by $Co(OAc)_2 \cdot 4H_2O$ (0.031 g, 0.125 mmol), a large quantity of black plate crystals were obtained (yield: 64%, based on Co). Main IR absorption bands (KBr, cm^{-1}): 3209.33(b), 1605.73(s), 1553.79(s), 1367.72(s), 787.33(s).

2.2.4. Synthesis of $[Zn(L)_2]_n \cdot 0.5nH_2O$ (4)

Compound 4 was synthesized by a similar procedure to that of 2 except that $Ni(OAc)_2 \cdot 4H_2O$ was replaced by $Zn(OAc)_2 \cdot 2H_2O$ (0.027 g, 0.125 mmol). Yellow prism crystals were obtained (yield: 52%, based on Zn). Main IR absorption bands (KBr, cm^{-1}): 3054.91(w), 1612.64(s), 1565.31(w), 1363.20(s), 785.09(s).

2.2.5. Synthesis of $[Nd(L)_3]_n$ (5)

Compound 5 is hydrothermally synthesized by mixing 0.1 M $Nd(NO_3)_3$ solution (0.125 mmol, 1.25 mL). HL (1 mmol, 374 mg), and deionized water (8 mL) in a 28 mL Teflon-lined stainless steel vessel and heated at 180 °C for 6 day and then cooled to room temperature. Light brown plate crystals of 5 were collected after washing with distilled water and dried in air (yield: 37%, based on Nd). Main IR absorption bands (cm^{-1}): 3427.40(w), 1583.92(s), 1547.68(s), 1406.72(s), 817.83(b), 783.85(s).

2.2.6. Synthesis of $[Gd(L)_3]_n$ (6)

Compound 6 was prepared by a similar procedure to that of 5 except that $Nd(NO_3)_3$ was replaced by $Gd(NO_3)_3$ (0.125 mmol, 1.25 mL). Light brown plate crystals of 6 were collected (yield: 40%, based on Gd). Main IR absorption bands (cm^{-1}): 3429.83(w), 1584.46(b), 1549.34(b), 1409.70(s), 819.18(b), 784.10(s).

2.2.7. Synthesis of $[Er(L)_3]_n$ (7)

Compound 7 was prepared by a similar procedure to that of 5 except that $Nd(NO_3)_3$ was replaced by $Er(NO_3)_3$ (0.125 mmol, 1.25 mL). Light brown plate crystals of 7 were collected (yield: 39%, based on Er). Main IR absorption bands (cm^{-1}): 2924.60(b), 1592.93(w), 1551.03(w), 1418.89(s), 819.08(b), 783.43(s).

2.3. X-ray crystallography

Suitable single crystals were selected and mounted on a glass fiber. The Data of 1–4 were collected on a Bruker *P*4 CCD, 5 on SADABS-2008/1-Bruker AXS and 6–7 on SMART APEX II area detectors with graphite-monochromated Mo K_α radiation (λ=0.71073 Å). All structures were solved by direct method and refined on F^2 by full-matrix least-squares methods using the SHEXTL 97 program package [37,38]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms on organic ligands were generated geometrically and allowed to ride on their parent atoms. While the hydrogen atoms associated with the lattice water molecules (O6, O7 and O8) were not located from the difference Fourier maps because they were disordered across two positions each. The crystallographic data are summarized in Table 1, and selected bond lengths are listed in Table S1 (see in Supporting materials). Crystallographic data (excluding structure factors) for compounds 1–7 in this paper have been deposited with Cambridge Crystallographic Data Center, CCDC reference number 871512–871518.

3. Results and discussion

3.1. Syntheses

Our original idea is to synthesize some novel 3d–4f heterometallic coordination polymers by using 4′-(4-carboxyphenyl)-2,2′:6′, 2″-terpyridine as ligand based on following consideration: (1) The linear γ-substituted pyridinecarboxylate, such as isonictonate [39,40] and 4-(4-pyridyl)benzoate [41], are perfect N,O-donating ligands to capture 3d and 4f ions simultaneously and to construct some heterometallic extend networks effectively. 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine, with a tridentate terpyridyl and a carboxylate group setting on opposite direction of benzene ring, maybe show some structure and coordination similarity to the linear γ-substitut ed pyridinecarboxylate. (2) The 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine prefers to bond transition metal ions through the terpyrdyl but leave carboxylate group uncoordination to form $\{M(L)_2\}$ scaffold, which can serve as potential expanded spacers as further assemble with lanthanide or other transition metal ions. (3) The compounds of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine are potential luminescent materials because the delocalized π-electron terpyridyl is a strongly absorbing chromophoric group. At first, we carried out the synthesis by mixing the first transition series of Zn, Ni, Co, Cu, and Fe with HL, and obtained title compounds of 2–4. Then, we further explored the assembly of HL with Ru and Cd salts, respectively, isomorphic compounds of $[Ru(L)_2]\cdot 5H_2O$ [27] and $[Cd(L)_2]_n\cdot nH_2O$ were obtained [22]. At the same time, we investigated the reaction between lanthanide ions and HL, crystal samples of 5–7 were appeared [24].

3.2. Description of the crystal structures

3.2.1. Structure of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (1)

In compound 1, the asymmetric unit contains one 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine molecule. The bond lengths and angles of four aromatic rings are in normal range, and the three pyridyl ring is coplanar with a *trans-trans-trans* configuration (Fig. S1, see in Supporting materials). Adjacent two molecules connect with each other via hydrogen bonds O(2)–H(2B)…N(3) to form the dimer expanding in [2 1 0] or [−2 1 0] direction (Fig. S2), then the dimers of same direction interact with each other and give rise to supermolecular chains via weak π–π stacking, and the perpendicular distance between the dimers is 3.4179 Å.

3.2.2. Structure of $[M(L)_2]\cdot 5H_2O$ (M=Ni, 2; Co, 3)

Compounds 2 and 3 are isomorphic to ruthenium (II) complex of 4′-(4-carboxyphenyl)- 2,2′:6′,2″-terpyridine reported by Constable et al. (Fig. S3) [27]. The asymmetric unit of 2 comprises one Ni(II) atom, two L ligands, and five lattice water molecules (Fig. 1). Each Ni(II) center is six-coordinated by six nitrogen atoms from two ligands and leave carboxylate group uncoordination (Scheme 1a). Three pyridyl rings in *cis-cis-cis* terpyridyl are nearly coplanar. In the structures of 2 and 3, Ni–N distances vary from 1.9888(17) to 2.1149(19) Å, while the Co–N distances range from 1.877(2) to 2.163(2) Å. The monomeric molecules stretch along *c* axis forming a potential expand spacer.

3.2.3. Structure of $[Zn(L)_2]_n\cdot 0.5nH_2O$ (4)

As shown in Fig. 2, the asymmetric unit of compound 4 comprises one Zn(II) atom, and two L ligands. The Zn(II) center is five-coordinated by three nitrogen atoms and two oxygen atoms from three ligands. The Zn–O and Zn–N distances fall in the normal range [42,43]. In 4, the two crystallographically independent 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine present two types of coordination modes: μ_2-L-1κ^3N,N′,N″:2κ^1O links two Zn(II) ions through the tridentate chelating terpyridyl and monodentate carboxylate to form one-dimensional chain along *c* axis (Scheme 1b, Fig. 3a); and L-κ^2O,O′ just serves as terminal ligand to complete the coordination sphere of Zn(II) center *via* the bidentate chelating carboxylate group bonding to Zn(II) but leave the *trans-trans-trans* terpyridyl uncoordination (Scheme 1c). the terminal ligands on the chain stretch in two directions with an angle of about 90° but not the 180° as reported in $[Cd(tyba)_2]_n\cdot nH_2O$. In addition, It is worthwhile to mention that the chain structure of 4 is also different from double chain structure of $[Cd(tyba)_2]_n\cdot nH_2O$, in which the Cd(II) center is seven-coordinated and the bridging ligand adopts μ_2-L-1κ^3N,N′,N″:2κ^2O,O′ coordination mode. Finally, the chains pack with–ABAB-mode along *a* axis (Fig. 3b).

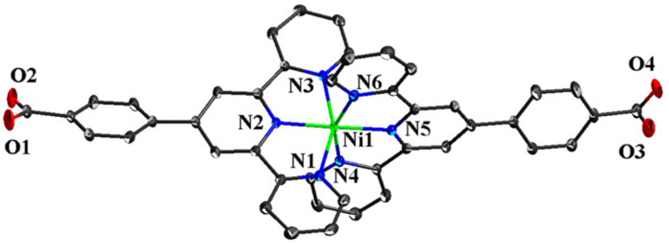
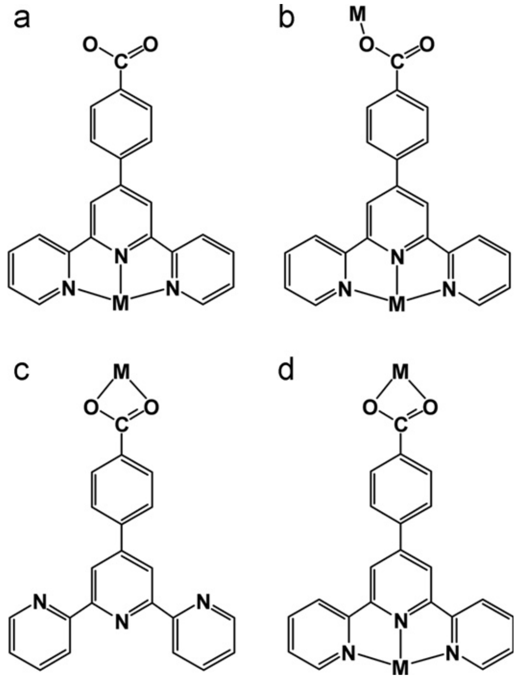


Fig. 1. ORTEP view of 2 with 50% thermal ellipsoids.



Scheme 1. Coordination modes of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine in 2–7.

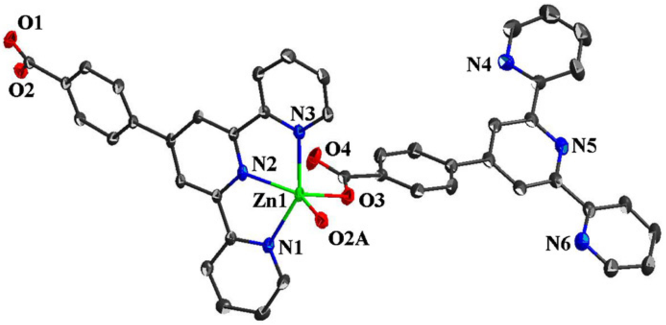


Fig. 2. ORTEP view of 4 with 50% thermal ellipsoids.

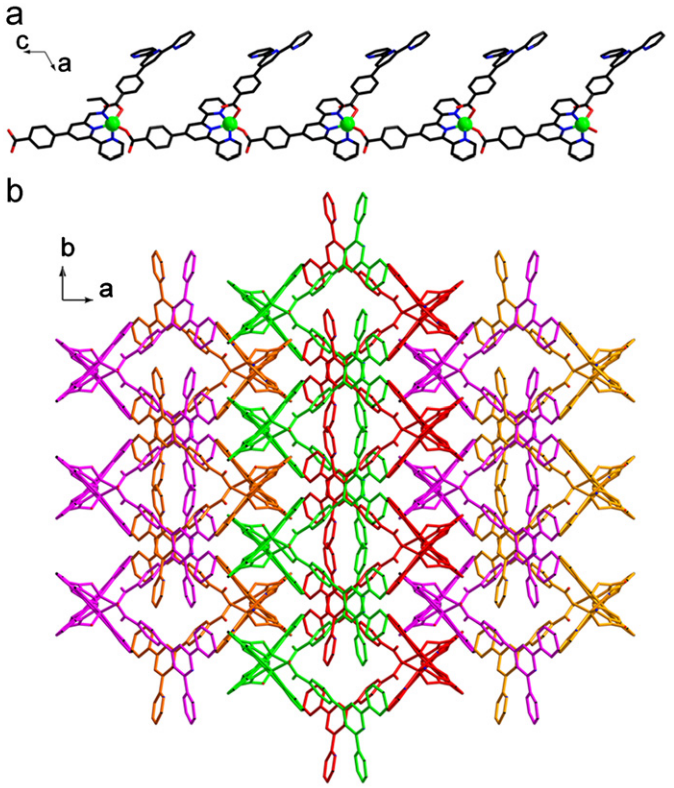


Fig. 3. View of (a) the chain structure along *b axis* and (b) the chains stacking mode in 4.

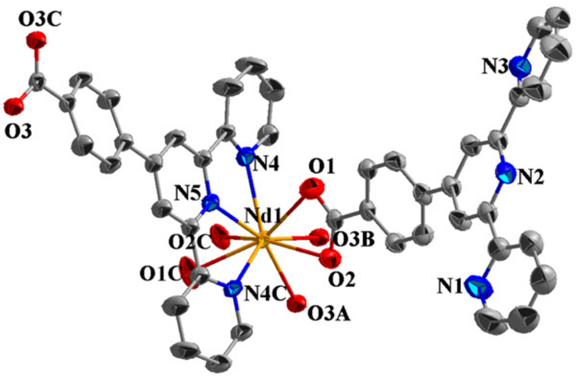


Fig. 4. ORTEP view of 5 with 50% thermal ellipsoids.

3.2.4. *Structure of [Ln(L)$_3$]$_n$ (Ln=Nd, 5; Gd, 6; Er, 7)*

X-ray analysis reveals that 5–7 are isomorphous compounds crystallizing in the monoclinic space group *C*2/*c*. The asymmetric unit of 5 contains half Nd(III) ion and one and a half L anions. Nd(III) center is nine-coordinated by three nitrogen atoms of terpyridyl and six oxygen atoms from three ligands (Fig. 4). The average bond length of Nd–N 2.5826 Å is longer than that of Nd–O 2.4951 Å. In 5, 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine displays two types of coordination mode, μ_2-L-1κ^3N,N′,N″:2κ^2O,O′ and L-1κ^2O,O′, with all the bond lengths of four aromatic rings are in normal range (Schemes 1c and d). the *cis-cis-cis* terpyridyl of μ_2-L-1κ^3N,N′,N″:2κ^2O,O′ are noncoplanar with a dihedral angle about 25.13° between two side pyridine ring (C1–C5, N1) and (C11–C15, N3), and the dihedral angle of the *trans-trans-tans* terpyridyl of L-1κ^2O,O′ is about 17.67° between the ring of (C23–C27, N4) and its symmetrical generated ring of (C23A–C27A, N4A). The μ_2-L-1κ^3N,N′,N″:2κ^2O,O′ connects two Nd(III) centers via bidentate chelating carboxylate and tridentate terpyridyl of *cis-cis-cis* configuration to form a 1D chain along *b* axis, while the L-1κ^2O,O′ coordinate to the Nd(III) center through bidentate chelating carboxylate and set on the opposite sides of the chain (Fig. 5). Then, adjacent chains connect each other via two types of π–π stacking interactions, π(C1–C5, N1)$\cdots\pi$(C6D–C7D, N2D) ($D=x$, $2-y$, $1/2+z$), centroid–centroid distance=4.2212 Å, face distance=3.6235 Å, dihedral angle=24.756° and π(C6–C10, N2) $\cdots\pi$(C6E–C10E, N2E) ($E=1/2-x$, $1/2-y$, z), centroid–centroid distance=3.6552, to form the 3-D supramolecular network (Fig. S4). Isomorphic compounds 6 and 7 exhibit similar structural features to that of 4 (Fig. S5).

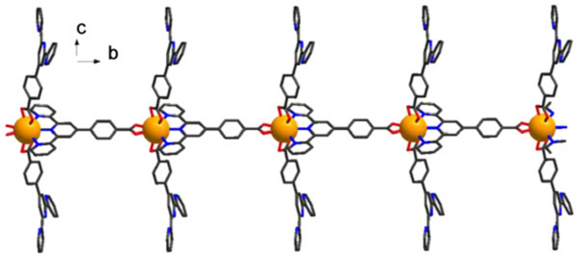
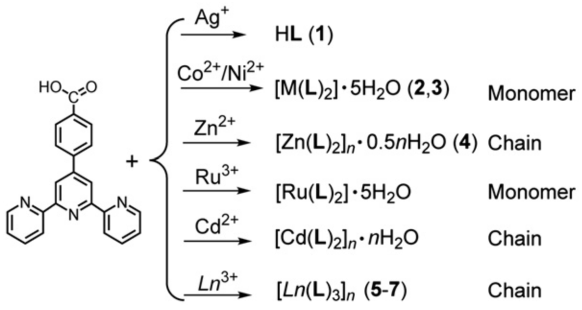


Fig. 5. View of 1D chain structure of compound 5.



Scheme 2. Synthetic pathway of the compounds 1–7.

From above discussion, we can find that the radius of metal centers and electron configuration play key role in the structure of title compounds: for 2 or 3, the six-coordinated Ni(II) or the Co(II) ion has larger radius than Zn(II), and exists in the octahedral geometrical environment; for 4, the smaller radius of Zn(II) ion will produce greater tension for the coordination of terpyridyl (the angle of N1–Zn1–N3 is 150.75°, that of N1–Ni–N3 is 155.97°), which force other ligands to abandon same coordination behavior as bonding to the metal; for 5, the larger radii of lanthanide ions permit more 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine to appear in the coordination space, which further effect the linkage of resultant framework (Scheme 2).

3.3. *IR spectroscopy and thermal stability analysis*

In compounds 2–7, the characteristic features of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine dominate the IR spectrum, in which the absence of any strong bands around 1700 cm^{-1} indicates that 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine are deprotonated. The medium intensity peaks around 1600 cm^{-1} can be attributed to the characteristic stretching vibration of pyridine and benzene rings, while those appearing at about 1550 and 1450 cm^{-1} are asymmetric and symmetric stretching vibrations of –COO$^-$. As for compound 1, the sharp peak at 1703 cm^{-1} shows the stretching vibration of protonated –COOH (Fig. S6).

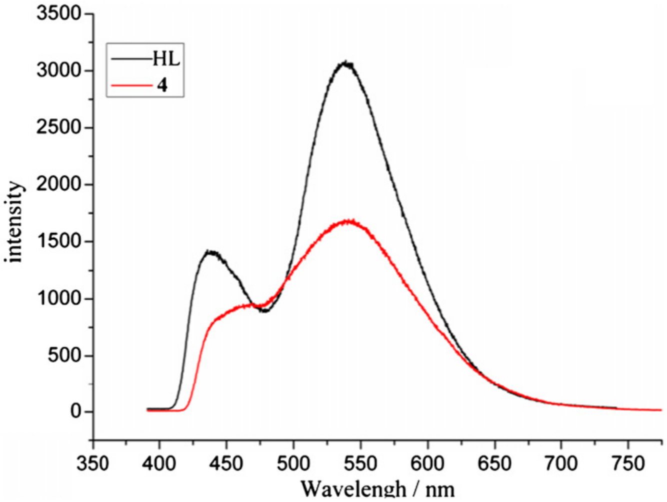


Fig. 6. The emission spectra of HL and compound 4.

The thermal stabilities of compounds 2–4 were examined through TG analyses in dry nitrogen atmosphere from 25 to 800 °C (Fig. S7). In the TGA curve of complex 2, the first weight loss of 11.13% from 25 to 343 °C corresponds to the loss of five lattice water molecules, which is in good agreement with the calculated value (10.54%). The second weight loss from 343 to 799 °C corresponds to the decomposition of two 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (obsd. 42.85% calcd. 41.28%). Complex 4 undergoes three main steps of weight losses. The first loss of 2.40% from 25 to 391 °C corresponds to the lattice water molecule (calcd. 1.16%). On further heating from 391 to 479 °C, the framework begins to break gradually with a weight loss of 45.07%, which corresponds to the decomposition of one 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine ligand (45.28%). The final step corresponds to that of the second ligand. By comparison, we see that the polymeric 4 is more stable than monomeric 2. The reason can be illustrate by the different coordination modes of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine: the L-1κ^3N,N′,N″ in 2 only bond to metal centers via terpyridyl but without the coordination of carboxylate, while μ_2-L-1κ^3N,N′,N″:2κ^1O in 4 coordinate to metal centers through both terpyridyl and carboxylate group. Because 5–7 are isomorphic to the reported examples, the thermal stability analyses have not been carried out repeatedly.

3.4. Fluorescence properties

Metal-organic frameworks assembled by d^{10} metal centers and delocalized π-electron ligands have been investigated widely for their fluorescent properties and potential applications. Therefore, the luminescence properties of free ligand and compound 4 were measured in the solid state at room temperature (Fig. 6, Fig. S8). The ligand shows two intense emission peaks at 445 and 550 nm (λ_{ex}=380 nm), which is assigned to the $\pi*\rightarrow\pi$ electronic transitions. For compound 4, the spectra profile is very similar to that of the free ligand, and also shows two emission peaks at 462 and 539 nm (λ_{ex}=371 nm). The external quantum yield (470–730 nm) of HL is 7.62% (λ_{ex}=375 nm), and the compound 4 is 5.94% (λ_{ex}=375 nm). The similarity between them reveals that the luminescence of 4 can be assigned mainly to intraligand transitions, and the small shift and weaken intension may be attributed to the deprotonation of the ligands in 4 and the existence of lattice water molecules [44,45].

4. Conclusions

In conclusion, we have prepared a series of monomers and chains constructed by 3d or 4f metals with 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine. The assembly of Ni(II), Co(II) or Zn(II) ions with the ligand gives rise to discrete monomers for Ni(II) and Co(II), and chain-like polymer for Zn(II). The structural variability between them results from the differences of ionic radii and electron configuration of metal centers. For the same reason, lanthanide compounds present other chain structure with the metal centers surrounded by four 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine. The monomeric molecules of 2 and 3 are potential expand spacer to construct some extend polymers as the uncoordination carboxylate further bond to other metal centers, such as lanthanide ions.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2012.07.002.

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