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# A series of novel metal-ferrocenedicarboxylate coordination polymers: crystal structures, magnetic and luminescence properties

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## Abstract

Novel two-dimensional layered lanthanide(III)-ferrocenedicarboxylate coordination polymers $\{[M(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2]\cdot mH_2O\}_n$ (Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$, M = $Tb^{3+}$, $m = 2$, **1**; M = $Eu^{3+}$, $m = 2$, **2**; M = $Y^{3+}$, $m = 1$, **3**) with trapezium-shaped units and one-dimensional wave-shaped Cd(II)-ferrocenedicarboxylate polymer $\{[Cd(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(H_2O)_3]\cdot 4H_2O\}_n$ (**4**) have been prepared and structurally characterized by single crystal diffraction. In polymers **1**–**3**, each central metal ion (Tb(III), or Eu(III) or Y(III)) is located in a pseudo-capped-tetragonal prism coordination geometry, and ferrocenedicarboxylate anion ligands have two coordination modes (bidentate-chelating mode and tridentate-bridging mode). The magnetic behaviors for **1** and **2** are studied in the temperature range of 5.0–300 K. The results show that the paramagnetic behavior of **2** is mainly due to the effective spin–orbital coupling between the ground and excited states through the Zeeman perturbation, and the weak magnetic interaction between $Eu^{3+}$ centers can be observed. In addition, compared with sodium ferrocenedicarboxylate, the fluorescent intensities of the polymers **1**–**4** are enhanced in the solid state.

*Keywords:* Lanthanide metal; Sodium ferrocenedicarboxylate; Coordination polymer; Magnetic properties; Luminescence properties

## 1. Introduction

Along with the development of coordination chemistry, many ferrocenyl complexes have been prepared due to their varieties of molecular structures and unusual properties [1–8]; meanwhile, because of the size and the strong inductive effect of ferrocenyl-substituted carboxylate, this kind of compounds acting as ligands have also been utilized in the field [9]. Up date, researchers have reported many binuclear or polynuclear complexes with ferrocenyl-substituted carboxylate and explored their potential applications in catalysis, electrical and magnetic materials [10–21]. For instance, two groups have investigated the electrochemical behaviors of $\{[Ti](C{\equiv}C^tBu)_2\}CuO_2CFcCO_2Cu\{[Ti](C{\equiv}C^tBu)_2\}$ and $[Fc(CO_2)_2]_4[Ga_2\{CH(SiMe_3)_2\}]_4$, respectively [19,20]; Ros and coworkers have studied the catalytic activity of $[Ru(O_2C)(C_5H_4)Fe(C_5H_5)Cl(CO)(PPh_3)_2]$ in the procedure of ferrocencarboxylic acid to phenylethylenecanferrocenecarboxylic ester [21]; our group has reported the unusual magnetic properties of a novel ferrocenecarboxylato-bridged Gd(III) dimers [8].

On the other hand, although the design and syntheses of coordination polymers have been extensively explored since 1990s, the reported coordination polymers containing ferrocenyl-substituted carboxylate are limited. There are only several coordination polymers containing ferrocenyl groups such as one-dimensional polymers $[C_5H_5FeC_5H_4CO_2Sn(CH{=}CH_2)_3]_n$ [22], $\{[Pb_2(O_2CC_5H_4FeC_5H_5)_4(CH_3OH)]\cdot 1.5CH_3OH\cdot H_2O\}_n$ [23], $[Cd\{Fc(CO_2)_2\}(DMF)_2(H_2O)]_n$ [24], two-dimensional polymers $[Sm_2\{Fc(CO_2)_2\}_3(H_2O)_5]_n$, $[NaZn_3\{Fc(CO_2)_2\}_2(OH)_3(H_2O)]_n$, $[BaFc(CO_2)_2(H_2O)]_n$ [24,25] and the cluster polymer $[Na_2Mo_6Cl_8(O_2C_5H_4FeC_5H_5)_6\cdot CH_3OH]_n$ [26]. We only find that the electrochemical properties of the last two polymers have been investigated by differential pulse voltammetry or cyclic

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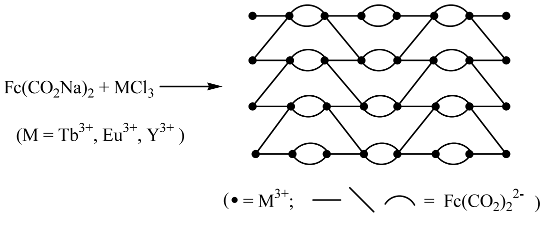
voltammetry methods. To the author's best knowledge the magnetic and fluorescent properties of these types of coordination polymers have not been reported in the literature.

Herein, we use sodium ferrocenedicarboxylate as ligand to react with $TbCl_3 \cdot 6H_2O$, or $EuCl_3 \cdot 6H_2O$, or $YCl_3 \cdot 6H_2O$ or $Cd(NO_3)_2 \cdot 6H_2O$, and obtain novel two-dimensional layered coordination polymers $\{[M(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2] \cdot mH_2O\}_n$ ($Fc = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$, $M = Tb^{3+}$, $m = 2$, **1**; $M = Eu^{3+}$, $m = 2$, **2**; $M = Y^{3+}$, $m = 1$, **3**), and one-dimensional wave-shaped Cd(II)-ferrocenedicarboxylate polymer $\{[Cd(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(H_2O)_3] \cdot 4H_2O\}_n$ (**4**). The magnetic properties of polymers **1** and **2** and the fluorescent properties of polymers **1**–**4** were investigated.

## 2. Results and discussion

### 2.1. Synthesis

Ferrocene derivatives containing electron-withdrawing substituent on the cyclopentadienyl ring may provide a greater photolability, and can undergo photolysis in some solvents to cause both ring-metal and ring-carbonyl cleavages [27–31]. So laying the mixture solution of $TbCl_3 \cdot 6H_2O$ (or $EuCl_3 \cdot 6H_2O$ or $YCl_3 \cdot 6H_2O$ or $Cd(NO_3)_2 \cdot 6H_2O$) with sodium ferrocenedicarboxylate in the dark is an effective route for preparation of ferrocenyl-containing complexes. If the mixture of metal ions and sodium ferrocenedicarboxylate ligand in methanol–water solution are under light, brown precipitate can produce from the mixture solution, and its composition cannot be identified, polymers **1**–**4** could not be obtained. So the procedures for single crystals of polymers **1**–**4** must be carried out in the dark. When an aqueous solution of $Fc(CO_2Na)_2$ was dropwise added into a methanol solution containing $Tb^{3+}$ or $Eu^{3+}$ or $Y^{3+}$ or $Cd^{2+}$, a clear orange solution was formed. Then the orange solution was put in the dark at room temperature. The colour of the solution is getting lighter and lighter, and red single crystals were formed as time goes on. After filtration, fine red X-ray quality single crystals for polymers **1**–**4** were obtained. The formations of polymers **1**–**3** are shown in Scheme 1.



Scheme 1.

### 2.2. Crystal structures of $\{[M(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2] \cdot mH_2O\}_n$ ($Fc = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$, $M = Tb^{3+}$, $m = 2$, 1; $M = Eu^{3+}$, $m = 2$, 2; $M = Y^{3+}$, $m = 1$, 3)

bidentate-chelating ($\eta^2$-$O_2C$-Fc-) tridentate-bridging ($\mu_2$–$\eta^2$-$O_2C$-Fc-)

(1)

In polymer **1** two different types of coordination modes of ferrocenedicarboxylate anion ligands are presented: bidentate-chelating and tridentate-bridging modes (Chart 1). The local environment around the terbium atom was depicted in Fig. 1. Each central terbium atom is located in a pseudo-capped-tetragonal prism coordination geometry and coordinated by nine oxygen atoms, of which four from two $\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2$ units, three from two $\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2$ units and two from coordination water molecules. Tb1–O5 bond length (2.342(5) Å) is the shortest bond length and Tb1–O5B bond length (2.925 Å) is the longest one. As a result of the inversion center the Tb1(O5, O5B)Tb1B double bridging network is perfectly planner.

Fig. 2 gives the $[Tb_6(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)_4(\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_2]$ trapezium-shaped structural unit. Each trapezium unit consists of four $\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2$ groups, two $\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2$ groups, and six terbium atoms which are nearly co-planar and form a distorted trapezium. Among the six terbium atoms Tb1D, Tb1L, Tb1H, and Tb1B occupy the four corners of the trapezium. The top margin length of the trapezium (Tb1D···Tb1L distance) is 6.134 Å, and the bottom margin length (Tb1B···Tb1H distance) is 14.278 Å. Both the lengths (Tb1D···Tb1B and Tb1L···Tb1H distances) of the two edges, which are formed by $\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2$ units bridging two terbium atoms, are 11.714 Å. The two Fe2 atoms (Fe2A, Fe2E) in $\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2$ units are on the two edges, respectively, and gives the distance of 10.140 Å. Fe1E, Fe1M, Fe1D and Fe1L atoms are 3.8985 Å above or below the trapezium. The distance between Fe1E and Fe1M is 7.879 Å.

The 2-D trapezium-shaped structure can also be seen to the assembly of many linear chains ($\cdots Tb(O)_2Tb(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)_2Tb(O)_2Tb(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)_2Tb\cdots$) and the bridging $(\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)^{2-}$ units (Fig. 3). Along the linear chain, the Tb···Tb distance in $Tb(O)_2Tb$ unit is 4.277 Å and the two Tb atoms are bridged by two oxygen atoms from two $(\mu_2\text{-}\eta^2O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)^{2-}$ units; Tb···Tb distance in $Tb(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)_2Tb$ unit is 6.134 Å and the two

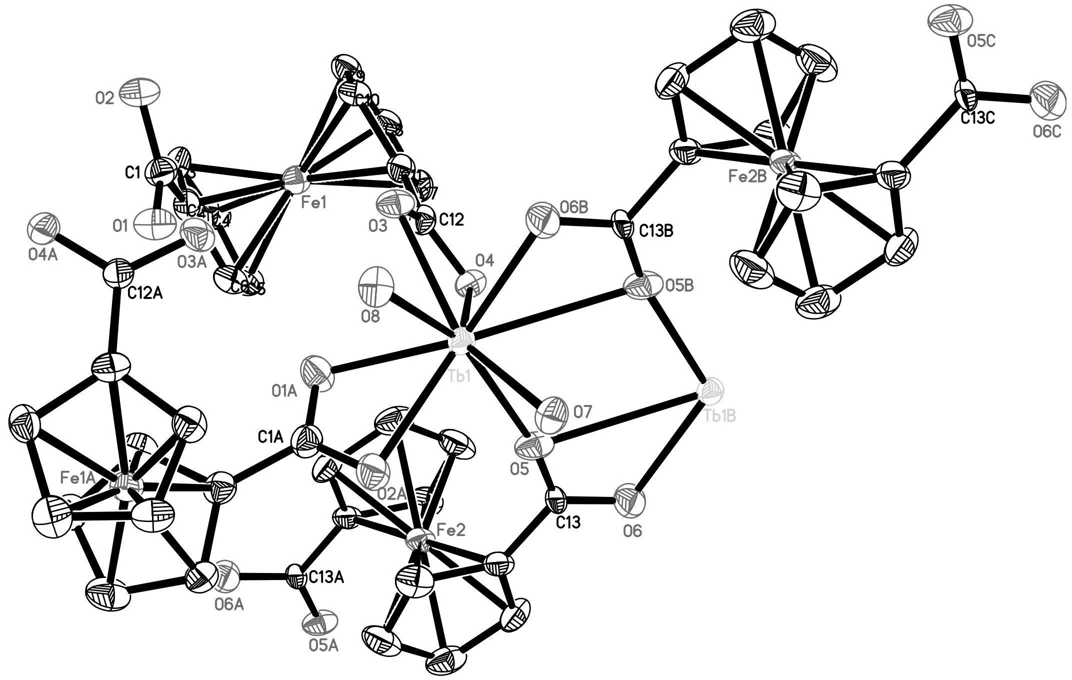


Fig. 1. The local environment around the Tb(III) ion in polymer $\{[Tb(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2]\cdot 2H_2O\}_n$ (**1**) with atom numberings, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Tb atoms are connected by two $(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)^{2-}$ units.

The Fe1–$C_{ring}$ and Fe2–$C_{ring}$ distances, and the intra C–C bond lengths of the cyclopentadienyl are close to those of free ferrocene. The dihedral angle between two cyclopentadienyl rings at Fe1 is 2.6°, and the two cyclopentadienyl rings at Fe2 are parallel to each other.

The crystal structures of polymers **2** and **3** are similar to that of polymer **1**. Each Eu(III) or Y(III) ion is coordinated by two oxygen atoms from two water molecules and seven oxygen atoms from four ferrocenedicarboxylate ligands. Ferrocenedicarboxylate ligands also show two kinds of coordination modes, bidentate-chelating mode $\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2$ and tridentate-bridging mode $\mu_2\text{-}\eta^2O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2$. The central metal ions are linked by two kinds of ferrocenedicarboxylate ligands leading to two-dimensional layers consisting of infinite trapezium-shaped units. Each trapezium-shaped unit consists of six metal ions and six ferrocenedicarboxylate ligands. The top margin lengths of the trapezium are 6.178 Å for polymer **2** and 6.110 Å for polymer **3**, the bottom margin lengths are 14.249 and 14.316 Å for polymers **2** and **3**, respectively, and the edge lengths are 11.719 and 11.712 Å for **2** and **3**, respectively.

The two-dimensional ferrocenedicarboxylate-containing coordination polymers $[Sm_2\{Fc(CO_2)_2\}_3(H_2O)_5]_n$, $[NaZn_3\{Fc(CO_2)_2\}_2(OH)_3(H_2O)]_n$ and $[BaFc(CO_2)_2(H_2O)]_n$ have been reported in two communications [24,25]. $[Sm_2\{Fc(CO_2)_2\}_3(H_2O)_5]_n$ shows a similar structure as polymer **1**; in $[NaZn_3\{Fc(CO_2)_2\}_2(OH)_3(H_2O)]_n$, zinc, sodium and oxygen atoms compose the two-dimensional inner layers in stoichiometry $NaZn_3O_{12}$ and ferrocene moieties slant up and down the layers; $[BaFc(CO_2)_2(H_2O)]_n$ consists a BaO inorganic inner polymer and ordered ferrocenyl outer layers.

### 2.3. *Crystal structure of $\{[Cd(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(H_2O)_3]\cdot 4H_2O\}_n$ (4)*

In the crystal structural unit of **4**, there is one Cd(II) atom, one bidentate-chelating ferrocenedicarboxylate ligand, and three lattice water molecules in each independent crystallographic unit (Fig. 4). Each Cd(II) atom is coordinated by seven oxygen atoms, of which four belong to two $(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)^{2-}$ ligands and the other three to three water molecules. Around the central Cd(II) atom, the bond lengths of Cd1–O are in the range of 2.310(2)–2.494(3) Å, the O6–Cd1–O7 bond angle (176.01(9)°) is close to 180°, O1, O2, O3A, O4A and O5 atoms are nearly co-planar (the mean deviation from plane is 0.1108 Å). So the local environment around the Cd(II) atom can be best described as a distorted pentagonal bipyramid.

Every Cd(II) atom is linked by two bidentate-chelating $(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)^{2-}$ ligands, and each $(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)^{2-}$ ligand bridges two Cd(II) atoms together via oxygen atoms to form a one-dimensional wave-shaped chain (Fig. 5), the Cd···Cd distance is 5.324 Å. All of the ferrocenyl moieties are equivalent. They are located in the wave crest and trough, respectively. The cyclopentadienyl rings in each ferrocenyl

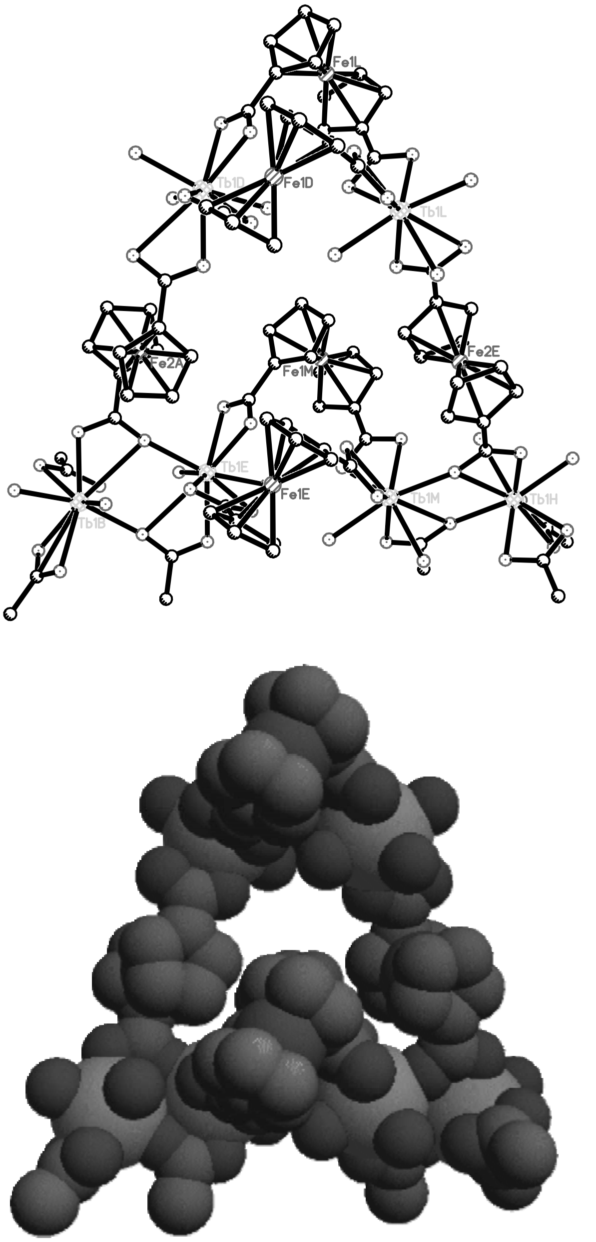


Fig. 2. $[Tb_6(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)_4(\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_2]$ trapezium-shaped structural unit with hydrogen atoms omitted for clarity.

fragment are planar and nearly parallel with a dihedral angle of 1.5°.

In the reported ferrocenedicarboxylate-containing metal complexes, the crystal structure of $[Fe(cyclam)][\{Fc(CO_2)_2\}_2H]$ consists of monomeric units of *trans*-$[Fe(cyclam)][\{Fc(CO_2)_2\}_2H]$ linked into a one-dimensional polymeric chain in which the symmetrical hydrogenbisdicarboxylate $[O_2CFcCO_2\cdots H\cdots O_2CFcCO_2]$ moiety is the bridging unit; carboxylate group of the $[O_2CFcCO_2]$ unit acts as monodentate ligand. $[Zn_2\{Fc(CO_2)_2\}_2$(1-methylimidazole)$_4]$ is a centrosymmetric cyclic dimer in which each Zn atom exhibits a slightly distorted tetrahedral geometry; the ferrocenedicarboxylic unit acts as a syn-bound O,O′-bridging ligand. $[Fc(CO_2)_2]_4[Ga_2\{CH(SiMe_3)_2\}]_4$ has a large macrocycle in its molecular center comprising four dialkyldigallium groups bridged by four ferrocene dicarboxylato ligands, which give a total number of 32 atoms in the heterocycle; Ga···Ga are bridged by two ($\eta^2$-$O_2C$–) units. The known one-dimensional ferrocenedicarboxylate-containing coordination polymers are $[Cd\{Fc(CO_2)_2\}(DMF)_2(H_2O)]_n$ which shows infinite zigzag chain formed by ($\eta^2$-$O_2CFcCO_2$-$\eta^2$) units bridging Cd ions. Polymer **4** possesses one-dimensional wave-shaped chain structure, in which ferrocenyl moieties are located in the wave crest and trough.

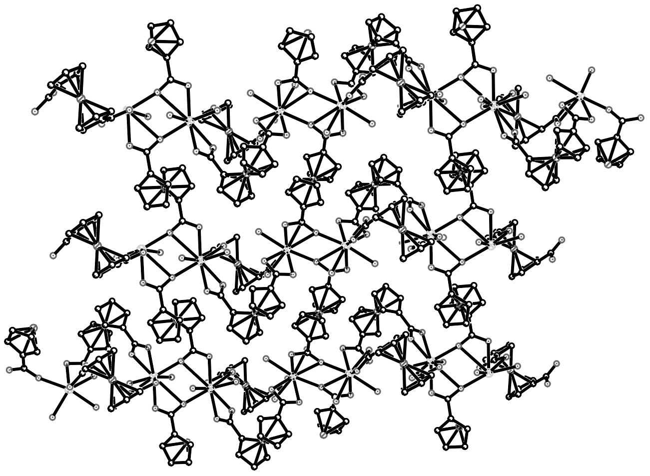


Fig. 3. Two-dimensional structure of $\{[Tb(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2]\cdot 2H_2O\}_n$ (**1**).

### 2.4. Magnetic properties of polymers 1 and 2

The magnetic properties of polymers **1** and **2** in the solid state have been investigated at 500 G over the temperature range 5–300 K.

For polymer **1**, the effective magnetic moment of the $Tb^{3+}$ ion is determined to be $8.77\mu_B$ at room temperature, which is lower than the theoretical value of $9.72\mu_B$ for the free $Tb^{3+}$ ion. The thermal evolution of $\chi_M^{-1}$ obeys Curie–Weiss law, $\chi_M = C/(T-\theta)$ with $C_M = 9.672$ cm$^3$ K mol$^{-1}$ and $\theta = -0.920$ K; at 300 K the value of $\chi_M T$ is equal to 9.611 cm$^3$ K mol$^{-1}$ and remains almost constant to ca. 60 K, then drops rapidly below 60 K to 7.367 cm$^3$ K mol$^{-1}$ at 5 K (Fig. 6(a)). At the same time, without appropriate equation to fit the magnetic susceptibility data of **1**, we could not give detail analysis of the magnetic behavior. We state that the feature of $\chi_M T$ is primarily due to the splitting of the ligand field of the $Tb^{3+}$ because of strong spin–orbital coupling, and partly contributed to by the possible antiferromagnetic interaction between the $Tb^{3+}$ ions for difficulty to determine the interactions between two

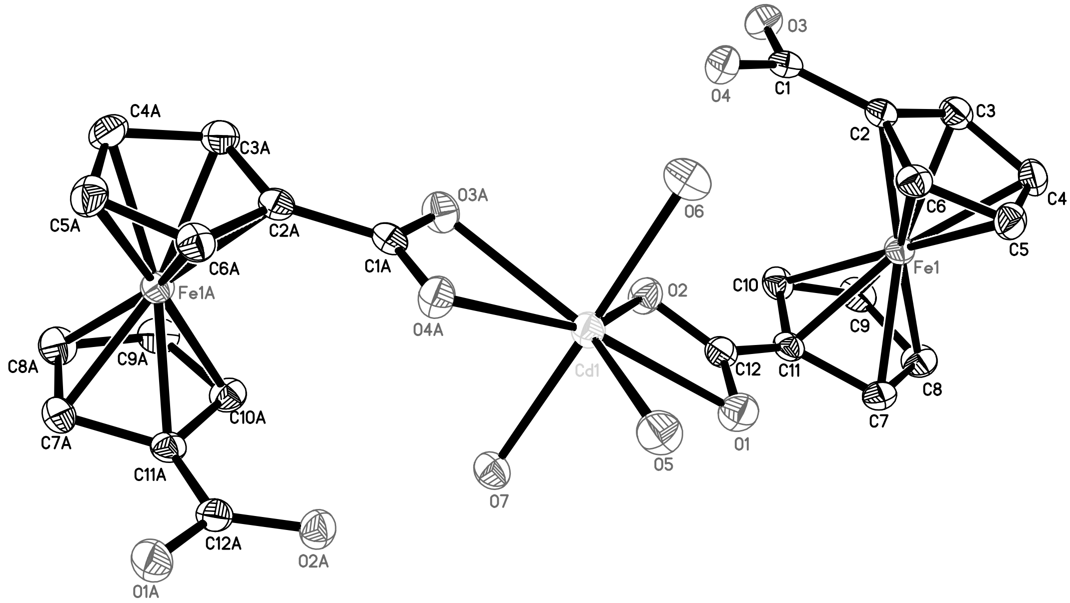


Fig. 4. The structural unit of $\{[Cd(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(H_2O)_3]\cdot 4H_2O\}_n$ (**4**) with atom numberings, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

neighboring Tb(III) ions only from the shape of the $\chi_M T$ versus $T$ curve.

For polymer **2**, as can be seen from the Fig. 6(b), at ca. 300 K, $\chi_M T$ is equal to 1.198 $cm^3$ K $mol^{-1}$; the $\chi_M T$ values decreases with temperature to 0.0343 $cm^3$ K $mol^{-1}$ at 4.99 K (Fig. 6(b)). It is noted in a polynuclear complex the thermal variation of $\chi_M T$ depends on the populations of the Stark levels and on the exchange coupling constant [32]. Obviously, these factors also cause the large deviation from normal Curie–Weiss law, $\chi_M = C/(T-\theta)$ over the whole temperature range.

Since Eu(III) has an effective magnetic moment of zero due to the mutual cancellation of the spin and orbital angular momentum (assuming the $^7F_0$ ground state), people used to focus their attention on luminescent properties of Eu(III) compounds. There are few reports about magnetic data concerning the Eu(III) system [33–36]. On the other hand, the understanding of the magnetic interactions involving rare-earth ions is still far from being satisfactory [37]. Lu and coworkers have demonstrated that the free-ion approximation is also appropriate for the interpretation of the magnetic properties of polynuclear rare earth metal species, while the contribution from the overlap of the magnetic orbitals can be almost ignored [33]. The magnetic susceptibility data of **2** were quantitatively analyzed based on the equation from Ref. [45]. The least-squares fit is given as a solid line in Fig. 6(b). The best-fit parameters are $\lambda = 403.5$ $cm^{-1}$, the $\theta = 0.925$. Here, $\lambda$ is the spin–orbit coupling parameter between ground and excited states through the Zeeman perturbation, while $\theta$ is the Curie–Weiss temperature. The discrepancy factor $\sigma = [\Sigma(\chi_{obs}-\chi_{calc})^2/\Sigma\, \chi_{obs}]^{1/2}$ in the least-squares fits is $1.6\times 10^{-4}$. The $\lambda$ and $\theta$ values are slightly larger than these in polymer $\{[Eu_2(btc)(H_2btc)(H_2O)]\cdot 4H_2O\}_n$ ($\lambda =$ 393.99 $cm^{-1}$ and $\theta = 0.897$ K). These results demonstrate that the paramagnetic behavior is mainly depends on the spin–orbital coupling, and on the weak ferromagnetic interactions between $Eu^{3+}$ centers through oxygen atoms and the ferrocenyl ligands. Our group have investigated the magnetic behaviors of ferrocenecarboxylato-bridged Gd(III) and Nd(III) dimers [8]. The results show unexpected ferromagnetic coupling between the Gd(III) ions; the best fittings to the experi-

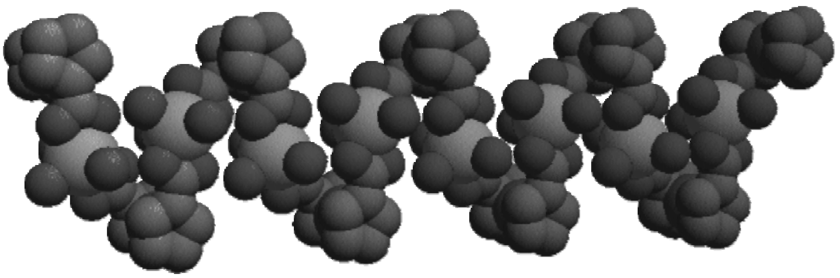


Fig. 5. One-dimensional wave-shaped chain of polymer $\{[Cd(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(H_2O)_3]\cdot 4H_2O\}_n$ (**4**).

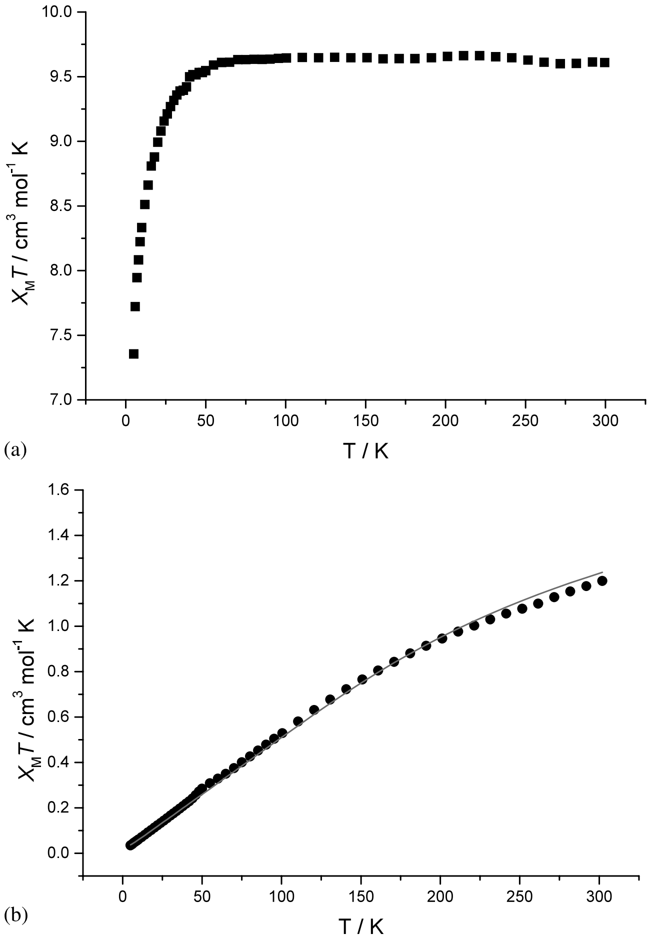


Fig. 6. Plots of $\chi_M T$ vs. $T$ for **1** (a) and **2** (b).

mental magnetic susceptibilities gave $J = 0.006$ cm$^{-1}$, $g = 2.0$. In Nd(III) dimer, there are crystal field effect and possible antiferromagnetic interaction between Nd(III) ions.

### 2.5. *Fluorescent properties of polymers **1**–**4***

Polymers **1**–**4** exhibit intense luminescence in the solid state. Excitation at 240 nm leads to intense wide emission band at 393 nm. Compared with the free ligand sodium ferrocenedicarboxylate, the fluorescent intensities of the polymers are enhanced. The fluorescence emissions of sodium ferrocenedicarboxylate and polymers **1**–**4** are illustrated in Fig. 7. The emissions of polymers **1**–**4** ($\lambda_{max} = 393$ nm) are neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature, and can mainly be assigned to the intraligand fluorescent emissions since a similar emission ($\lambda_{max} = 393$ nm) is also observed for the sodium ferrocenedicarboxylate ligand. Among the four polymers, polymer **4** possesses the weakest luminescence emission, and this can probably be attributed to the loss of energy causing by the high frequency O–H vibration of coordination water molecules. Owing to the violet fluorescence emissions of compounds **1**–**4**, they may be used as advanced materials for violet-light emitting diode devices. The fluorescence properties of some ferrocene compounds have been studied, for example, 6-(*N*-ferrocenylmethylidene-hydrazino)-2-butyl-benzo[de]isoquinoline-1,3-diones shows excitation at 328 nm and emission at 554 nm [38], [Ru(tpy)(Fctpy)](PF$_6$)$_2$ (tpy = terpyridines, Fctpy = 4′-(ferrocenyl)2,2′:6′,2″-terpyridine) gives the emission at bands of 601 and 646 nm, respectively [39].

## 3. Experimental

### 3.1. *General information and materials*

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Carbon, hydrogen and nitrogen analyses were carried out on a Carlo-Erba 1106 elemental analyzer. IR data were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer with KBr pellets in the 400–4000 cm$^{-1}$ region. Variable-temperature magnetic susceptibility data were obtained on a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range 5–300 K with an applied field of 500 G. All data have been corrected for diamagnetism by using Pascal's constants [40].

### 3.2. *Preparation of ligand*

Sodium ferrocenedicarboxylate was prepared according to the literature method [41,42]. Anal. Calc. for $C_{12}H_8FeNa_2O_4$: C, 45.32; H, 2.54. Found: C, 45.01; H, 2.56%. IR (KBr) (cm$^{-1}$): 3423 m, 1529 s, 1480 s, 1389 s, 1355 s, 1187 m, 1031 m, 813 m, 799 m, 514 m.

### 3.3. *Preparation of* $\{[Tb(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2]\cdot 2H_2O\}_n$ (**1**)

The 4 ml aqueous solution of Fc(CO$_2$Na)$_2$ (0.1 mmol) was dropped slowly into the 5 ml CH$_3$OH solution of TbCl$_3$·6H$_2$O (0.05 mmol), the mixture was stirred and then was put in the dark. About 10 days later, the fine red X-ray quality single crystals were obtained. Crystals of **1** are stable in the air. Yield: 45%. Anal. Calc. for $C_{18}H_{20}Fe_{1.5}O_{10}Tb$: C, 33.83; H, 3.15. Found: C, 34.01; H, 3.28%. IR (KBr) (cm$^{-1}$): 3356 m, 1529 m, 1485 s, 1396 s, 1355 s, 1192 m, 1024 m, 798 m, 503 s.

### 3.4. *Preparation of* $\{[Eu(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2]\cdot 2H_2O\}_n$ (**2**)

The procedure was the same as that for **1**, yield: 54%. Anal. Calc. for $C_{18}H_{20}EuFe_{1.5}O_{10}$: C, 34.20; H, 3.19%. Found: C, 34.01; H, 3.28. IR (KBr) (cm$^{-1}$): 3377 m,

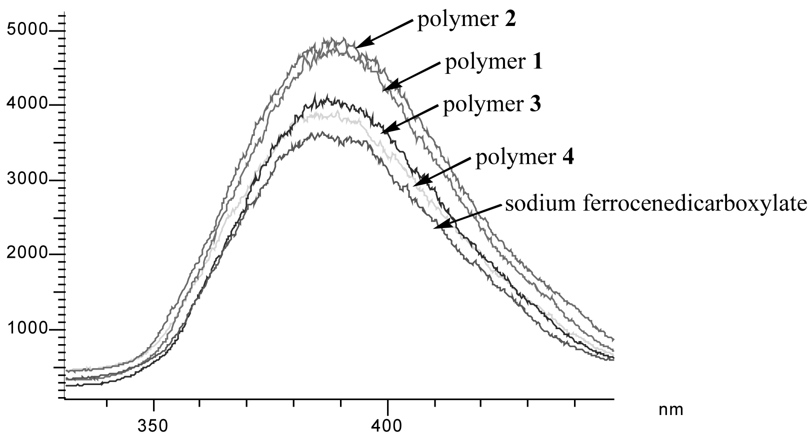


Fig. 7. Emission spectra of sodium ferrocenedicarboxylate and polymers **1**–**4** in solid state.

1530 s, 1485 s, 1395 s, 1355 s, 1191 m, 1026 m, 798 s, 501 s.

### 3.5. *Preparation of* $\{[Y(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(\mu_2\text{-}\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2\text{-}\mu_2)_{0.5}(H_2O)_2]\cdot H_2O\}_n$ (**3**)

The synthesis of polymer **3** was the same as that of **1**, yield: 49%. Anal. Calc. for $C_{18}H_{18}Fe_{1.5}O_9Y$: C, 37.24; H, 3.29%. Found: C, 37.16; H, 3.32. IR (KBr) (cm$^{-1}$): 3354 m, 1526 s, 1488 s, 1396 s, 1356 s, 1192 m, 1019 m, 792 s, 504 s.

### 3.6. *Preparation of* $\{[Cd(\eta^2\text{-}O_2CFcCO_2\text{-}\eta^2)(H_2O)_3]\cdot 4H_2O\}_n$ (**4**)

Five millilitre $CH_3OH$ solution of $Cd(NO_3)_2\cdot 6H_2O$ (0.05 mmol) was added drop-wise to an aq. solution of $Fc(CO_2Na)_2$ (0.1 mmol, 2 ml). The mixture solution was stirred at room temperature (r.t.), and then it was put in

Table 1
Crystal data and structure refinement for polymers **1**–**4**

| Polymers | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Formula | $C_{18}H_{20}Fe_{1.5}O_{10}Tb$ | $C_{18}H_{20}EuFe_{1.5}O_{10}$ | $C_{18}H_{18}Fe_{1.5}O_9Y$ | $C_{12}H_{22}CdFeO_{11}$ |
| Formula weight | 639.04 | 632.08 | 551.01 | 510.55 |
| Temperature (K) | 291(2) | 291(2) | 291(2) | 291(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Color | red | red | red | red |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | *P*2/*n* | *P*2/*n* | *P*2/*n* | P2$_1$/c |
| *a* (Å) | 11.302(2) | 11.286(2) | 11.265(2) | 6.6697(13) |
| *b* (Å) | 10.320(2) | 10.356(2) | 10.302(2) | 27.757(6) |
| *c* (Å) | 17.133(3) | 17.113(3) | 17.168(3) | 10.191(2) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 91.48(3) | 91.21(3) | 91.47(3) | 107.45(3) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 |
| *V* (Å$^3$) | 1997.7(7) | 1999.6(7) | 1991.8(7) | 1799.9(6) |
| *Z* | 4 | 4 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 2.155 | 2.129 | 1.928 | 1.855 |
| Absorption coefficient (mm$^{-1}$) | 4.641 | 4.237 | 4.029 | 2.040 |
| *F*(000) | 1248 | 1240 | 1124 | 1024 |
| Crystal sizes (mm) | 0.25 × 0.20 × 0.20 | 0.24 × 0.20 × 0.18 | 0.24 × 0.20 × 0.20 | 0.25 × 0.20 × 0.20 |
| Theta range for data collection (°) | 1.97–27.52 | 1.97–27.53 | 2.14–27.52 | 1.47–27.56 |
| Index ranges | $0 \le h \le 14$,<br>$-13 \le k \le 13$,<br>$-22 \le l \le 21$ | $-14 \le h \le 0$,<br>$-13 \le k \le 13$,<br>$-20 \le l \le 20$ | $0 \le h \le 13$,<br>$-12 \le k \le 12$,<br>$-20 \le l \le 20$ | $-8 \le h \le 8$,<br>$-36 \le k \le 36$,<br>$-12 \le l \le 0$ |
| Reflections collected/unique | 7079/4098 | 6948/3984 | 5172/2997 | 6892/3819 |
| Data/restraints/parameters | 4098/0/288 | 3984/0/293 | 2997/0/271 | 3819/0/243 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0603$, $wR_2 = 0.1539$ | $R_1 = 0.0541$, $wR_2 = 0.1178$ | $R_1 = 0.1117$, $wR_2 = 0.2939$ | $R_1 = 0.0482$, $wR_2 = 0.1252$ |
| *R* indices (all data) | $R_1 = 0.0855$, $wR_2 = 0.1680$ | $R_1 = 0.0852$, $wR_2 = 0.1272$ | $R_1 = 0.1474$, $wR_2 = 0.3211$ | $R_1 = 0.0592$, $wR_2 = 0.1300$ |
| Goodness-of-fit on $F^2$ | 1.128 | 1.129 | 1.103 | 1.101 |

Table 2
Selected bond lengths (Å) and angles (°) for polymers **1**–**4**

| | | | |
|---|---|---|---|
| Polymer **1** [a] | | | |
| *Bond lengths* | | | |
| Tb(1)–O(5) | 2.342(5) | Tb(1)–O(6)#1 | 2.359(5) |
| Tb(1)–O(8) | 2.399(5) | Tb(1)–O(1)#2 | 2.409(5) |
| Tb(1)–O(4) | 2.428(4) | Tb(1)–O(7) | 2.437(5) |
| Tb(1)–O(2)#2 | 2.458(5) | Tb(1)–O(3) | 2.496(5) |
| Tb(1)–O(5)#2 | 2.925 | | |
| *Bond angles* | | | |
| O(5)–Tb(1)–O(6)#1 | 119.37(17) | O(5)–Tb(1)–O(8) | 152.65(18) |
| O(6)#1–Tb(1)–O(8) | 72.36(18) | O(5)–Tb(1)–O(1)#2 | 97.78(17) |
| O(6)#1–Tb(1)–O(1)#2 | 139.89(17) | O(8)–Tb(1)–O(1)#2 | 81.41(18) |
| O(5)–Tb(1)–O(4) | 75.98(15) | O(6)#1–Tb(1)–O(4) | 93.31(18) |
| O(8)–Tb(1)–O(4) | 130.19(16) | O(1)#2–Tb(1)–O(4) | 80.81(16) |
| O(5)–Tb(1)–O(7) | 77.97(16) | O(6)#1–Tb(1)–O(7) | 76.85(18) |
| O(8)–Tb(1)–O(7) | 81.47(16) | O(1)#2–Tb(1)–O(7) | 129.11(16) |
| O(4)–Tb(1)–O(7) | 142.73(14) | O(5)–Tb(1)–O(2)#2 | 80.84(17) |
| O(6)#1–Tb(1)–O(2)#2 | 140.27(18) | O(8)–Tb(1)–O(2)#2 | 76.45(18) |
| O(1)#2–Tb(1)–O(2)#2 | 54.75(16) | O(4)–Tb(1)–O(2)#2 | 125.88(17) |
| O(7)–Tb(1)–O(2)#2 | 74.72(16) | O(5)–Tb(1)–O(3) | 128.60(16) |
| O(6)#1–Tb(1)–O(3) | 72.78(17) | O(8)–Tb(1)–O(3) | 77.46(17) |
| O(1)#2–Tb(1)–O(3) | 72.26(17) | O(4)–Tb(1)–O(3) | 52.82(15) |
| O(7)–Tb(1)–O(3) | 147.04(16) | O(2)#2–Tb(1)–O(3) | 123.36(16) |
| Polymer **2** [b] | | | |
| *Bond lengths* | | | |
| Eu(1)–O(5)#1 | 2.391(4) | Eu(1)–O(6) | 2.405(5) |
| Eu(1)–O(8) | 2.427(4) | Eu(1)–O(1)#2 | 2.429(5) |
| Eu(1)–O(4) | 2.447(4) | Eu(1)–O(7) | 2.462(5) |
| Eu(1)–O(2)#2 | 2.479(4) | Eu(1)–O(3) | 2.516(4) |
| Eu(1)–O(5) | 2.825(4) | | |
| *Bond angles* | | | |
| O(5)#1–Eu(1)–O(6) | 119.95(14) | O(5)#1–Eu(1)–O(8) | 152.80(15) |
| O(6)–Eu(1)–O(8) | 71.39(15) | O(5)#1–Eu(1)–O(1)#2 | 98.63(15) |
| O(6)–Eu(1)–O(1)#2 | 139.15(15) | O(8)–Eu(1)–O(1)#2 | 80.31(15) |
| O(5)#1–Eu(1)–O(4) | 75.50(13) | O(6)–Eu(1)–O(4) | 95.97(15) |
| O(8)–Eu(1)–O(4) | 130.23(14) | O(1)#2–Eu(1)–O(4) | 80.20(14) |
| O(5)#1–Eu(1)–O(7) | 77.74(15) | O(6)–Eu(1)–O(7) | 76.92(16) |
| O(8)–Eu(1)–O(7) | 81.62(15) | O(1)#2–Eu(1)–O(7) | 127.90(14) |
| O(4)–Eu(1)–O(7) | 143.85(12) | O(5)#1–Eu(1)–O(2)#2 | 81.83(14) |
| O(6)–Eu(1)–O(2)#2 | 139.05(16) | O(8)–Eu(1)–O(2)#2 | 75.75(15) |
| O(1)#2–Eu(1)–O(2)#2 | 53.56(14) | O(4)–Eu(1)–O(2)#2 | 124.14(15) |
| O(7)–Eu(1)–O(2)#2 | 74.71(15) | O(5)#1–Eu(1)–O(3) | 128.24(14) |
| O(6)–Eu(1)–O(3) | 73.30(15) | O(8)–Eu(1)–O(3) | 77.67(14) |
| O(1)#2–Eu(1)–O(3) | 72.29(14) | O(4)–Eu(1)–O(3) | 52.82(12) |
| O(7)–Eu(1)–O(3) | 147.84(15) | O(2)#2–Eu(1)–O(3) | 122.47(14) |
| O(5)#1–Eu(1)–O(5) | 71.74(16) | O(6)–Eu(1)–O(5) | 48.92(13) |
| O(8)–Eu(1)–O(5) | 118.43(14) | O(1)#2–Eu(1)–O(5) | 156.00(14) |
| O(4)–Eu(1)–O(5) | 76.13(12) | O(7)–Eu(1)–O(5) | 72.68(13) |
| O(2)#2–Eu(1)–O(5) | 141.47(13) | O(3)–Eu(1)–O(5) | 96.02(13) |
| Polymer **3** [c] | | | |
| *Bond lengths* | | | |
| Y(1)–O(5)#1 | 2.320(16) | Y(1)–O(6) | 2.370(16) |
| Y(1)–O(3) | 2.396(16) | Y(1)–O(2)#2 | 2.401(14) |
| Y(1)–O(8) | 2.418(16) | Y(1)–O(7) | 2.432(14) |
| Y(1)–O(4) | 2.468(15) | Y(1)–O(1)#2 | 2.497(13) |
| Y(1)–O(5) | 2.993 | | |
| *Bond angles* | | | |
| O(5)#1–Y(1)–O(6) | 118.2(6) | O(5)#1–Y(1)–O(3) | 98.3(6) |
| Polymer **1** [a] | | | |
| O(6)–Y(1)–O(3) | 140.1(6) | O(5)#1–Y(1)–O(2)#2 | 76.7(5) |
| O(6)–Y(1)–O(2)#2 | 91.9(6) | O(3)–Y(1)–O(2)#2 | 80.7(5) |
| O(5)#1–Y(1)–O(8) | 152.0(6) | O(6)–Y(1)–O(8) | 73.3(7) |
| O(3)–Y(1)–O(8) | 82.0(6) | O(2)#2–Y(1)–O(8) | 130.3(5) |
| O(5)#1–Y(1)–O(7) | 77.4(5) | O(6)–Y(1)–O(7) | 76.5(6) |
| O(3)–Y(1)–O(7) | 130.5(5) | O(2)#2–Y(1)–O(7) | 141.9(5) |
| O(8)–Y(1)–O(7) | 81.3(5) | O(5)#1–Y(1)–O(4) | 81.2(6) |
| O(6)–Y(1)–O(4) | 140.9(7) | O(3)–Y(1)–O(4) | 55.5(5) |
| O(2)#2–Y(1)–O(4) | 126.8(5) | O(8)–Y(1)–O(4) | 76.0(6) |
| O(7)–Y(1)–O(4) | 75.4(5) | O(5)#1–Y(1)–O(1)#2 | 128.6(5) |
| O(6)–Y(1)–O(1)#2 | 72.9(6) | O(3)–Y(1)–O(1)#2 | 71.6(5) |
| O(2)#2–Y(1)–O(1)#2 | 52.1(5) | O(8)–Y(1)–O(1)#2 | 78.3(5) |
| O(7)–Y(1)–O(1)#2 | 147.0(5) | O(4)–Y(1)–O(1)#2 | 123.4(5) |
| Polymer **4** [d] | | | |
| *Bond lengths* | | | |
| Cd(1)–O(2) | 2.310(2) | Cd(1)–O(5) | 2.319(3) |
| Cd(1)–O(6) | 2.327(3) | Cd(1)–O(7) | 2.348(3) |
| Cd(1)–O(4)#1 | 2.351(3) | Cd(1)–O(3)#1 | 2.466(3) |
| Cd(1)–O(1) | 2.494(3) | | |
| *Bond angles* | | | |
| O(2)–Cd(1)–O(5) | 133.85(10) | O(2)–Cd(1)–O(6) | 85.81(10) |
| O(5)–Cd(1)–O(6) | 90.67(11) | O(2)–Cd(1)–O(7) | 90.58(10) |
| O(5)–Cd(1)–O(7) | 93.06(10) | O(6)–Cd(1)–O(7) | 176.01(9) |
| O(2)–Cd(1)–O(4)#1 | 141.50(9) | O(5)–Cd(1)–O(4)#1 | 84.65(10) |
| O(6)–Cd(1)–O(4)#1 | 95.82(10) | O(7)–Cd(1)–O(4)#1 | 85.95(10) |
| O(2)–Cd(1)–O(3)#1 | 87.45(9) | O(5)–Cd(1)–O(3)#1 | 138.47(9) |
| O(6)–Cd(1)–O(3)#1 | 88.08(10) | O(7)–Cd(1)–O(3)#1 | 90.06(10) |
| O(4)#1–Cd(1)–O(3)#1 | 54.27(8) | O(2)–Cd(1)–O(1) | 53.98(8) |
| O(5)–Cd(1)–O(1) | 80.43(10) | O(6)–Cd(1)–O(1) | 93.42(11) |
| O(7)–Cd(1)–O(1) | 85.81(10) | O(4)#1–Cd(1)–O(1) | 162.52(9) |
| O(3)#1–Cd(1)–O(1) | 141.09(8) | | |

[a] Symmetry transformations used to generate equivalent atoms in polymer **1**: #1 $-x+1$, $-y+1$, $-z+1$; #2 $-x+3/2$, $y$, $-z+3/2$; #3 $-x+1$, $-y+2$, $-z+1$.

[b] Symmetry transformations used to generate equivalent atoms in polymer **2**: #1 $-x+1$, $-y+1$, $-z+1$; #2 $-x+3/2$, $y$, $-z+3/2$; #3 $-x+1$, $-y$, $-z+1$.

[c] Symmetry transformations used to generate equivalent atoms in polymer **3**: #1 $-x$, $-y$, $-z$; #2 $-x+1/2$, $y$, $-z+1/2$; #3 $-x$, $-y-1$, $-z$.

[d] Symmetry transformations used to generate equivalent atoms in polymer **4**: #1 $x$, $-y+3/2$, $z-1/2$; #2 $x$, $-y+3/2$, $z+1/2$.

the dark. The reaction system gave some red crystals suitable for structure determination about 3 weeks later. Yield: 52%. Anal. Calc. for $C_{12}H_{22}CdFeO_{11}$: C, 28.23; H, 4.34%. Found: C, 28.15; H, 4.29. IR (KBr) (cm$^{-1}$): 3423 m, 1529 s, 1480 s, 1390 s, 1355 s, 1188 m, 1031 m, 798 m, 504 m.

### 3.7. Crystal structure determination

A red single crystal suitable for X-ray determination was mounted on a glass fiber. All data were collected at r.t. on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda =$

0.71073 Å). The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using SHELXL-97 crystallographic software package [43]. Table 1 shows crystallographic crystal data and processing parameters of polymers **1**–**4**. Selected bond lengths and bond angles are listed in Table 2.

### *3.8. Determination of fluorescent properties*

The luminescent spectra were measured on powder samples at r.t. using a model F-4500 HITACHI Fluorescence Spectrophotometer. The excitation slit was 5 nm and the emission slit was 5 nm too, the response time was 2 s.

## 4. Supplementary materials

The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers: CCDC 187421, 187420, 200181 and 200182 for polymers **1**–**4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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