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Novel Pb(II), Zn(II), and Cd(II) Coordination Polymers Constructed from Ferrocenyl-Substituted Carboxylate and Bipyridine-Based Ligands

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Treatment of two kinds of ferrocenyl-substituted carboxylate ligands (3-ferrocenyl-2-crotonic acid, $HOOC{-}CH{=}(CH_3)CFc$ ($Fc{=}(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) or *O*-ferrocecarbonyl benzoic acid, *o*-$HOOCC_6H_4COFc$ with $Pb(OAc)_2{\cdot}3H_2O$, $Zn(OAc)_2{\cdot}2H_2O$, or $Cd(OAc)_2{\cdot}2H_2O$) resulted in four novel ferrocene-containing coordination polymers $\{[Pb(\mu_2\text{-}\eta^2\text{-}OOCCH{=}(CH_3)CFc)_2]{\cdot}MeOH\}_n$ (**1**), $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]{\cdot}2MeOH{\cdot}2H_2O\}_n$ (4,4′-bipy = 4,4′-bipyridine) (**2**), $\{[Cd(o\text{-}OOCC_6H_4COFc)_2(bpe)(MeOH)_2]{\cdot}2H_2O\}_n$ (bpe = 1,2-bis(4-pyridyl)ethene) (**3**), and $[Pb(o\text{-}OOCC_6H_4COFc)(\eta^2\text{-}o\text{-}OOCC_6H_4COFc)(bpe)]_n$ (**4**). Their crystal structures have been characterized by single X-ray determinations. In polymer **1**, Pb(II) ions are bridged by tridentate $FcC(CH_3){=}CHCOO^-$ anions, forming an infinite chain $[Pb(\mu_2\text{-}\eta^2\text{-}OOC{=}CH(CH_3)CFc)_2]_n$. In polymers **2**–**4**, there are three kinds of components, metal ions, *o*-$FcCOC_6H_4COO^-$ units, and organic bridging ligands. The bipyridine-based ligands connect metal ions leading to a one-dimensional chain with *o*-$FcCOC_6H_4COO^-$ units acting as monodentate or chelate ligands in the side chain. Such coordination polymers containing ferrocenyl-substituted carboxylate and bipyridine-based ligands are very rare. The solution-state differential pulse voltammetries of polymers **1**–**4** were determined. The results indicate that the half-wave potential of the ferrocenyl moieties is influenced by the Pb(II) ions in polymer **1** and strongly influenced by Zn(II), Cd(II), or Pb(II) ions in polymers **2**–**4**. The thermal properties of the four polymers were also investigated.

Introduction

It is well-known that the first publication about the synthesis of ferrocene by Kealy and Pauson[1] fifty years ago is considered a landmark event in organometallic chemistry. Due to the special chemical, stereochemical, and electrochemical properties of ferrocene,[2] there is great interest in ferrocene and its derivatives.[3−7] In the research field of coordination chemistry, people have exploited a large number of ferrocene-based ligands to produce multimetal-containing complexes. Many ferrocenyl complexes have some unusual properties, for example, as components in homogeneous catalysts,[2] and potential applications for material sciences such as molecular sensors[8] and molecular magnetic[6] and nonlinear optical materials.[5,9] Obviously, chemists are strongly interested in introducing the ferrocenyl group to the other molecular systems and hope to obtain new compounds with desired properties.

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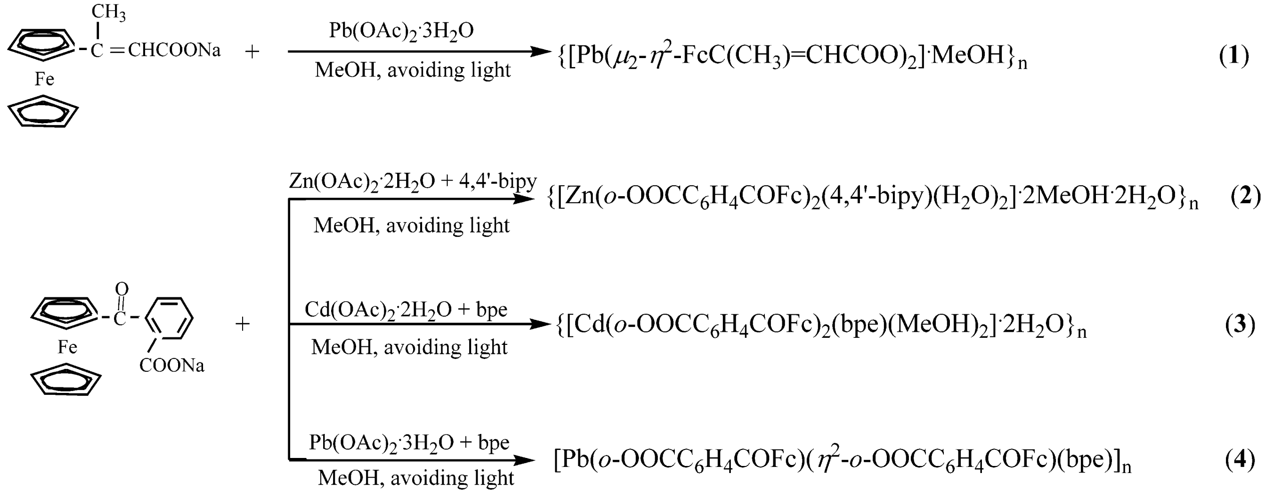
Scheme 1



On the other hand, the design and syntheses of coordination polymers, constructed from multifunctional ligands and transition metals, have been extensively explored over the past decades. A great number of coordination polymers have been published due to their fascinating structural diversity and potential applications, such as nonlinear optics,[10] catalysis,[11] molecular magnetic materials,[12] electrical conductivity,[13] molecular recognition[14] and so on.[15,16] But the reported coordination polymers containing ferrocenyl groups are limited.[17] It can be found that the preparation of the ferrocenyl coordination polymers usually uses two kinds of ferrocenyl derivatives as ligands, ferrocenyl-substituted carboxylate[17a−d,h] and pyridine-containing ferrocene.[17e−g] The known ferrocenyl-substituted carboxylate ligands in coordination polymers are only ferrocenecarboxylic acid[17a,b,h] and 1,1′-ferrocenedicarboxylic acid.[17c,d] In our recent paper,[17h] we described a series of unprecedented coordination polymers containing ferrocenecarboxylate components, $\{[Pb_2(OOCFc)(\eta^2\text{-}OOCFc)(\mu_2\text{-}\eta^2\text{-}OOCFc)(\mu_3\text{-}\eta^2\text{-}OOCFc)(MeOH)]\cdot 1.5MeOH\cdot H_2O\}_n$ (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) (**PbFC**), $[Pb(OOCFc)(\mu_2\text{-}OOCFc)(bpe)]_n$ (bpe = 1,2-bis(4-pyridyl)ethene), $\{[Zn(OOCFc)_2(bpt)]\cdot 2.5H_2O\}_n$ (bpt = *N*,*N*′-bis(3-pyridylmethyl)thiourea), and $[Zn(OOCFc)(\eta^2\text{-}OOCFc)(bbp)]_n$ (bbp = 4,4′-trimethylene-dipyridine). These results prompted us to prepare more coordination polymers containing ferrocenyl-substituted carboxylate and determine their crystal structures. Taking into account the diverse coordination mode of the carboxylate ligands, terminal monodentate, chelating to one metal center and bridging bidentate, we prepared ferrocenyl-substituted carboxylate ligands, *o*-$HOOCC_6H_4COFc$ and $HOOC{-}CH{=}(CH_3)CFc$, and tried to use them to form coordination polymers. It should be pointed out that the ligands used here are not only *o*-$HOOCC_6H_4COFc$ and $HOOC{-}CH{=}(CH_3)CFc$ but also bipyridine-based ligands. Consequently, a novel kind of coordination polymers, $\{[Pb(\mu_2\text{-}\eta^2\text{-}OOCCH{=}(CH_3)CFc)_2]\cdot MeOH\}_n$ (**1**), $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-}bipy)(H_2O)_2]\cdot 2MeOH\cdot 2H_2O\}_n$ (4,4′-bipy = 4,4′-bipyridine) (**2**), $\{[Cd(o\text{-}OOCC_6H_4COFc)_2(bpe)(MeOH)_2]\cdot 2H_2O\}_n$ (**3**), and $[Pb(o\text{-}OOCC_6H_4COFc)(\eta^2\text{-}o\text{-}OOCC_6H_4COFc)(bpe)]_n$ (**4**) were obtained (see Scheme 1), and their thermal and electrochemical properties were investigated.

Experimental Section

General Details. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. *O*-ferrocecarbonyl benzoic acid (*o*-$HOOCC_6H_4COFc$)[18]

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Table 1. Crystallographic Data for **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{29}H_{30}O_5Fe_2Pb$	$C_{24}H_{25}O_6NFeZn_{0.5}$	$C_{50}H_{48}O_{10}N_2Fe_2Cd$	$C_{48}H_{36}O_6N_2Fe_2Pb$
fw	777.42	511.99	1061.01	1055.68
crystal system	triclinic	monoclinic	monoclinic	triclinic
crystal size (mm^3)	0.26 × 0.20 × 0.16	0.25 × 0.20 × 0.18	0.28 × 0.20 × 0.18	0.28 × 0.25 × 0.20
space group	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$
a (Å)	10.820(2)	34.191(7)	24.716(5)	10.924(2)
b (Å)	16.645(3)	11.470(2)	14.047(3)	12.205(2)
c (Å)	7.7668(16)	12.100(3)	16.221(3)	16.393(3)
α (deg)	95.75(3)	90	90	90.82(3)
β (deg)	94.65(3)	104.57(3)	124.38(3)	107.16(3)
γ (deg)	73.42(3)	90	90	101.97(3)
V (Å^3)	1331.9(5)	4592.8(16)	4647.9(16)	2036.0(7)
D_c (mg m^{-3})	1.939	1.481	1.516	1.722
Z	2	8	4	2
μ (mm^{-1})	7.417	1.206	1.130	4.881
reflns collected/unique	4921/4921 R(int) = 0.0000	6400/4102 R(int) = 0.0867	5447/3239 R(int) = 0.0405	7440/7440 R(int) = 0.0000
data/restraints/parameters	4921/0/337	4102/0/314	3239/2/304	7440/0/540
R^a	0.0401	0.0733	0.0501	0.0468
$R_w{}^b$	0.1020	0.1289	0.1005	0.0952
GOF on F^2	1.117	1.022	1.041	1.075
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	−1.277 and 1.565	−0.556 and 0.644	−1.111 and 0.809	−1.138 and 1.237

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

and 3-ferrocenyl-2-crotonic acid (HOOC−CH═(CH$_3$)CFc)[19] were prepared according to literature methods. Their sodium salts were prepared by the reaction of them with sodium methoxide.

C, H, and N analyses were carried out on an MOD 1106 analyzer. IR data were recorded on a Bruker Tensor 27 spectrophotometer with KBr pellets in the 400−4000 cm^{-1} region. TGA-DTA measurements were performed by heating the sample from 20 °C to 1000 °C at a rate of 10 °C min^{-1} in air on a Perkin Elmer DTA-7 differential thermal analyzer. Differential pulse voltammetry studies were recorded with a CHI650 electrochemical analyzer utilizing the three-electrode configuration of a Pt working electrode, a Pt auxiliary electrode, and a commercially available saturated calomel electrode as the reference electrode with a pure N_2 gas inlet and outlet. The measurements were performed in DMF solution containing tetraethylammonium perchlorate (n-Bu_4NClO_4) (0.1 mol dm^{-3}) as supporting electrolyte, which has a 50 ms pulse width and a 20 ms sample width. The potential was scanned from +0.2 to +1.0 V at a scan rate of 20 mV s^{-1}.

Caution ! *Although no problems were encountered in this work, the salt perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.*

Preparation of {[Pb(μ_2-η^2-OOCCH═(CH$_3$)CFc)$_2$]·MeOH}$_n$ (1). NaOOCCH═(CH$_3$)CFc (29.2 mg; 0.10 mmol) in MeOH (4 mL) was added dropwise to a methanol solution (4 mL) of Pb(OAc)$_2$·3H$_2$O (19.0 mg; 0.05 mmol). The resulting pale orange solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after 1 week. Crystals of **1** are stable in the air. Yield: 63%. Anal. Calcd for $C_{29}H_{30}O_5Fe_2Pb$: C, 44.76; H, 3.86. Found: C, 44.42; H, 3.91. IR (cm^{-1}, KBr): 3425 m, 3098 m, 1618 s, 1521 s, 1403 s, 1328 m, 1250 s, 1104 m, 1026 m, 937 m, 819 m, 671 m, 501 m.

Preparation of {[Zn(o-OOCC$_6$H$_4$COFc)$_2$(4,4′-bipy)(H$_2$O)$_2$]·2MeOH·2H$_2$O}$_n$ (2). Zn(OAc)$_2$ × 2H$_2$O (11.0 mg; 0.05 mmol) and 4,4′-bipy (7.8 mg, 0.05 mmol) were dissolved in 5 mL of MeOH. o-NaOOCC$_6$H$_4$COFc (33.5 mg, 0.1 mmol) in 6 mL of MeOH was added dropwise to the former mixture. The resulting red solution was allowed to stand at room temperature in the dark. Good quality red crystals for **2** were obtained after 2 weeks. Yield: 58%. Anal. Calcd for $C_{48}H_{50}Fe_2N_2O_{12}Zn$: N, 2.73; C, 56.25; H, 4.88. Found: N, 2.50; C, 56.62; H, 4.70. IR (cm^{-1}, KBr): 3421 s, 3104 m, 1637 s, 1610 s, 1585 s, 1560 m, 1450 m, 1398 s, 1377 s, 1292 m, 816 m, 751 m, 510 m, 490 m.

Preparation of {[Cd(o-OOCC$_6$H$_4$COFc)$_2$(bpe)(MeOH)$_2$]·2H$_2$O}$_n$ (3). Cd(OAc)$_2$·2H$_2$O (13.4 mg; 0.05 mmol) and bpe (9.1 mg, 0.05 mmol) were dissolved in 6 mL of MeOH. o-NaOOCC$_6$H$_4$COFc (33.5 mg, 0.1 mmol) in 6 mL of MeOH was added dropwise to the former mixture. The resulting red solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after 2 weeks. Yield: 61%. Anal. Calcd for $C_{50}H_{48}O_{10}N_2Fe_2Cd$: N, 2.64; C, 56.55; H, 4.52. Found: N, 2.59; C, 56.32; H, 4.41. IR (cm^{-1}, KBr): 3438 s, 3112 m, 1651 s, 1607 s, 1549 s, 1453 m, 1394 m, 1290 m, 1017 m, 830 m, 749 m, 535 m, 494 m.

Preparation of [Pb(o-OOCC$_6$H$_4$COFc)(η^2-o-OOCC$_6$H$_4$COFc)(bpe)]$_n$ (4). The complex **4** was prepared in a manner analogous to that used to prepare **3**, only Pb(OAc)$_2$·3H$_2$O instead of Cd(OAc)$_2$·2H$_2$O. Crystals of **4** are unstable in the air. Yield: 63.5%. Anal. Calcd for $C_{48}H_{36}O_6N_2Fe_2Pb$: N, 2.65; C, 54.56; H, 4.55. Found: N, 2.35; C, 54.21; H, 4.85. IR (cm^{-1}, KBr): 3437 s, 3107 m, 1654 s, 1608 s, 1549 s, 1450 m, 1383 s, 1287 m, 1105 m, 1041 m, 835 m, 759 m, 522 m, 495 m.

X-ray Crystallography. Crystal data and experimental details for compounds **1**−**4** are contained in Table 1. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Red prismatic single crystals of **1** (0.26 × 0.20 × 0.16 mm^3), of **2** (0.25 × 0.20 × 0.18 mm^3), of **3** (0.28 × 0.20 × 0.18 mm^3), and of **4** (0.28 × 0.25 × 0.20 mm) were selected and mounted on a glass fiber. All data were collected at a temperature of 291(2) K using the ω−2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The four structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**4**

1[a]			
Pb(1)−O(1)	2.730(5)	O(1)−C(13)	1.253(8)
Pb(1)−O(2)	2.425(5)	O(2)−C(13)	1.297(8)
Pb(1)−O(3)	2.429(5)	O(3)−C(27)	1.282(9)
Pb(1)−O(4)	2.469(5)	O(4)−C(27)	1.233(9)
Pb(1)−O(2)#1	2.602(5)	C(11)−C(12)	1.336(10)
Pb(1)−O(3)#2	2.720(5)	C(25)−C(26)	1.335(10)
O(2)−Pb(1)−O(3)	81.88(17)	O(4)−Pb(1)−O(2)#1	72.34(17)
O(2)−Pb(1)−O(4)	81.23(19)	O(2)−Pb(1)−O(3)#2	123.97(16)
O(3)−Pb(1)−O(4)	52.79(17)	O(3)−Pb(1)−O(3)#2	69.13(18)
O(2)−Pb(1)−O(2)#1	72.93(18)	O(4)−Pb(1)−O(3)#2	112.60(17)
O(3)−Pb(1)−O(2)#1	122.34(16)	O(2)#1−Pb(1)−O(3)#2	162.39(16)
2[b]			
Zn(1)−O(1)#1	2.079(4)	Zn(1)−O(4)	2.150(4)
Zn(1)−O(1)	2.079(4)	Zn(1)−O(4)#1	2.150(4)
Zn(1)−N(2)#2	2.142(7)	Zn(1)−N(1)	2.218(7)
O(1)−#1−Zn(1)−O(1)	178.6(2)	O(4)−Zn(1)−N(1)	90.16(14)
O(4)−Zn(1)−O(4)#1	179.7(3)	O(1)−Zn(1)−O(4)	87.98(19)
N(2)#2−Zn(1)−N(1)	180.00(3)	O(1)#1−Zn(1)−O(4)	92.02(19)
3[c]			
Cd(1)−O(1)#1	2.269(4)	Cd(1)−O(4)#1	2.344(4)
Cd(1)−O(1)	2.269(4)	Cd(1)−O(4)	2.344(4)
Cd(1)−N(1)	2.300(5)	Cd(1)−N(2)	2.360(5)
O(1)#1−Cd(1)−O(1)	175.11(18)	O(4)−Cd(1)−N(1)	88.32(9)
O(4)−Cd(1)−O(4)#1	176.64(19)	O(1)−Cd(1)−O(4)	90.32(17)
N(2)−Cd(1)−N(1)	180.00(1)	O(1)#1−Cd(1)−O(4)	89.82(17)
4			
Pb(1)−O(4)	2.316(5)	Pb(1)−N(1)	2.619(6)
Pb(1)−O(2)	2.559(7)	Pb(1)−N(2)	2.669(6)
Pb(1)−O(1)	2.574(6)		
N(1)−Pb(1)−N(2)	157.0(2)	O(2)−Pb(1)−O(1)	50.5(2)
O(1)−Pb(1)−N(2)	119.9(2)	O(4)−Pb(1)−N(1)	84.2(2)
O(2)−Pb(1)−N(1)	124.1(2)	O(1)−Pb(1)−N(1)	73.6(2)
O(4)−Pb(1)−O(2)	85.1(2)	O(4)−Pb(1)−N(2)	81.1(2)
O(4)−Pb(1)−O(1)	78.1(2)	O(2)−Pb(1)−N(2)	72.1(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x + 2, -y + 1, -z + 3$; #2 $-x + 2, -y + 1, -z + 2$. [b] Symmetry transformations used to generate equivalent atoms: #1, $x, y, -z + 7/2$; #2, $x, y + 1, z$. [c] Symmetry transformations used to generate equivalent atoms: #1, $x, y, -z + 1/2$.

but not refined. The final cycle of full-matrix least squares refinement was based on 4921 observed reflections and 337 variable parameters for **1**, 4102 observed reflections and 314 variable parameters for **2**, 3239 observed reflections and 304 variable parameters for **3**, and 7440 observed reflections and 540 variable parameters for **4**. All calculations were performed using the SHELX-97 crystallographic software package.[20] Selected bond lengths and bond angles are listed in Table 2.

Results and Discussion

Synthesis. It is worth emphasizing that the self-assembly reaction of ferrocenyl-substituted carboxylate ligands with metal ions in the dark is an effective route for preparation of a novel coordination polymer-containing ferrocene group. In our previous paper concerning the reaction of a lanthanide ion with a ferrocenecarboxylato ligand,[21] we have given detailed explanations why the reaction mixture should be placed avoiding light. Although *o*-ferrocecarbonyl benzoic acid and 3-ferrocenyl-2-crotonic acid were used here, they all contain a photoactive carbonyl group on the cyclopentadienyl ring. So they may undergo photolysis in methanol solution. If the mixture of NaOOCCH═(CH$_3$)CFc (or *o*-NaOOCC$_6$H$_4$COFc) and metal ions in methanol was put under light, it would rapidly yield brown precipitate, whose composition cannot be identified. So crystals suitable for X-ray crystallography for compounds **1**−**4** were grown by slow evaporation of their methanol solutions in the dark.

In our synthesis process, the same method to that used to prepare **1** was utilized to react *o*-NaOOCC$_6$H$_4$COFc with Pb(OAc)$_2$·3H$_2$O in methanol solution, but a polymer only with *o*-FcCOC$_6$H$_4$COO$^-$ units and Pb(II) ions could not be obtained. A reasonable explanation is due to the steric effects of the *o*-NaOOCC$_6$H$_4$COFc ligand. When *o*-FcCOC$_6$H$_4$COO$^-$ units coordinate to a Pb(II) ion, the bulky ferrocenyl and phenyl groups hold the oxygen atoms of the carboxylate groups to coordinate to more Pb(II) ions simultaneously. Only when bipyridine-based ligands (4,4′-bipy or bpe) were added, the *o*-FcCOC$_6$H$_4$COO$^-$ units could be introduced to form polymers **2**, **3**, or **4**. As for NaOOCCH═(CH$_3$)CFc, the long −C(CH$_3$)C═CH$^-$ chain reduces the steric effect of the ferrocenyl group. Thus, the carboxylate group of the FcC(CH$_3$)═CHCOO$^-$ anion acts as tridentate ligands bridging Pb(II) ions producing a one-dimensional chain polymer **1**.

Polymers **1**−**4** are not soluble in common organic solvents, such as MeOH, EtOH, MeCN, and THF, but just soluble in high-polar solvents DMSO or DMF.

Crystal Structure of {[Pb(μ_2-η^2-OOCCH═(CH$_3$)CFc)$_2$]·MeOH}$_n$ (1). The structure determination of **1** reveals that each FcC(CH$_3$)═CHCOO$^-$ anion acts in a tridentate fashion bridging the central Pb(II) ions forming a 1-D chain. This molecule crystallizes in the space group $P\bar{1}$. An ORTEP drawing of the chain structure with an atom labeling scheme is shown in Figure 1.

The geometry around each Pb(II) ion is described as a boat conformation. The four oxygen atoms (O1, O2, O3, O4) form the bottom of the boat, where the four O atoms are almost coplanar (the mean deviation from plane is 0.2237 Å) and atoms O1, O2 are from one FcC(CH$_3$)═CHCOO$^-$ unit and O3 and O4 are from another FcC(CH$_3$)═CHCOO$^-$ unit. The Pb atom is located within the inner portion of the boat. O2A and O3B from two distinct FcC(CH$_3$)═CHCOO$^-$ units occupy the bow and stern of the boat. It can be seen from Figure 1 that the Pb1−O2A−Pb1A−O2 ring is similar to that in the structures of the reported Pb-carboxylate polymers.[22,23] Pb−O bond distances are in the range of 2.425(5)−2.730(5) Å. The bond angles around Pb1 are between 50.41° and 162.39°. The dihedral angles between planes Pb1B−O3B−Pb1−O3 and Pb1A−O2A−Pb1−O2 and planes

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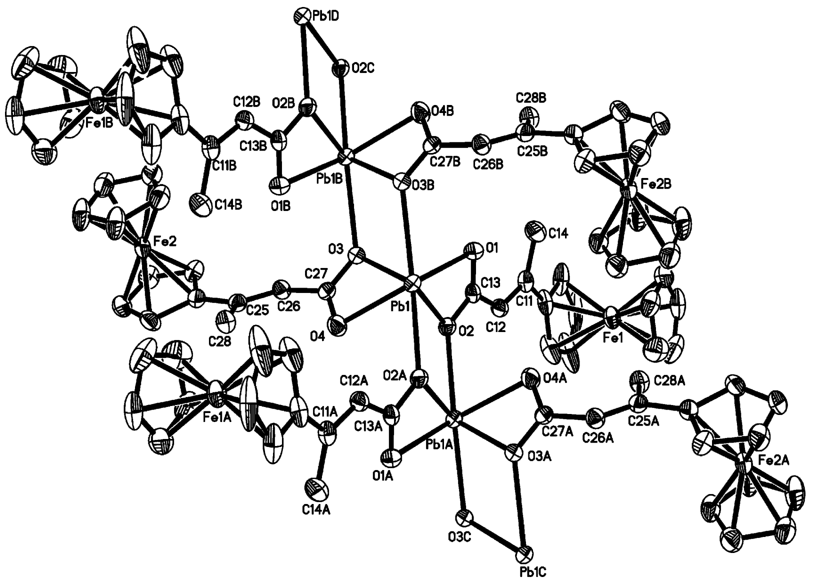

Figure 1. Perspective view of {[Pb(μ_2-η^2-OOCCH═(CH$_3$)CFc)$_2$]·MeOH}$_n$ (**1**) with atom labeling scheme (H atoms and solvent molecule omitted for clarity).

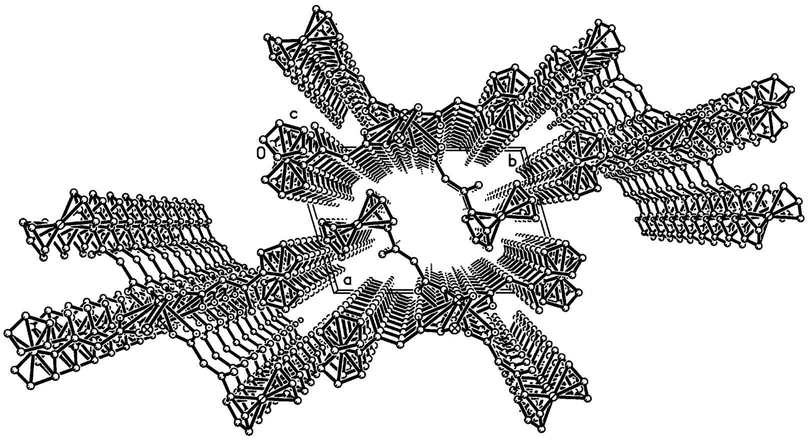

Figure 2. Crystal packing view from the *c*-axis of {[Pb(μ_2-η^2-OOCCH═(CH$_3$)CFc)$_2$]·MeOH}$_n$ (**1**).

C27−O4−Pb1−O3 (the mean deviation from the plane is 0.0287 Å) and C13−O1−Pb1−O2 (the mean deviation from the plane is 0.0090 Å) are 61.0° and 82.6°, respectively. The intrachain distances between metallic cations are 4.044 Å for Pb1...Pb1A and 4.243 Å for Pb1...Pb1B.

Within the ferrocene fragments, the C−C distances, Fe−C$_{\mathrm{ring}}$ distances, and C−C−C angles are all similar to those reported in the literature.[24] The cyclopentadienyl rings are planar and parallel with a dihedral angle of 0.6° at Fe1 or 0.2° at Fe2. Viewed along the *c*-axis, {[Pb(μ_2-η^2-OOCCH═(CH$_3$)CFc)$_2$]·MeOH}$_n$ chains pack each other by intermolecular interactions (Figure 2).

In known Pb(II) carboxylates,[25] the coordination number around the Pb(II) center is usually 7,[26,23a] 9,[27] and 10,[28] but 6 limited. It has been reported that the solid-state structure of a Pb-carboxylate compound depends strongly on the size of the carboxylate substituent; as the substituent becomes progressively bulkier, the structure changes from a polymeric one, to a sheet structure, and then to a chain structure.[22,26] The chain structure of **1** is consistent with the above conclusion.

Interestingly, comparison of the structure of **1** with that of the reported Pb(II)-ferrocenecarboxylate polymer {[Pb$_2$-(OOCFc)(η^2-OOCFc)(μ_2-η^2-OOCFc)(μ_3-η^2-OOCFc) (MeOH)]·1.5MeOH·H$_2$O}$_n$ (**PbFC**)[17h] indicates some differences. First, the coordinate modes of the carboxylate groups in polymer **1** have only one kind, tridentate (μ_2-η^2-OOCCH═(CH$_3$)CFc) ligands, but there are four kinds of carboxylate groups in the reported polymer **PbFC**, mono- (FcCOO$^-$) and bi-(η^2-FcCOO$^-$), tri-(μ_2-η^2-FcCOO$^-$), and tetradentate (μ_3-η^2-FcCOO$^-$) ligands. Consequently, in **1** there is one kind of Pb(II) ion, but in **PbFC** there are two kinds of Pb(II) ions, which form a ···Pb1Pb1Pb2Pb2Pb1Pb1··· chain. Obviously, these structural differences are mainly due to the different carbochain distances between the carboxylate and ferrocenyl group. The long −C(CH$_3$)C═CH− chain in **1** can benefit

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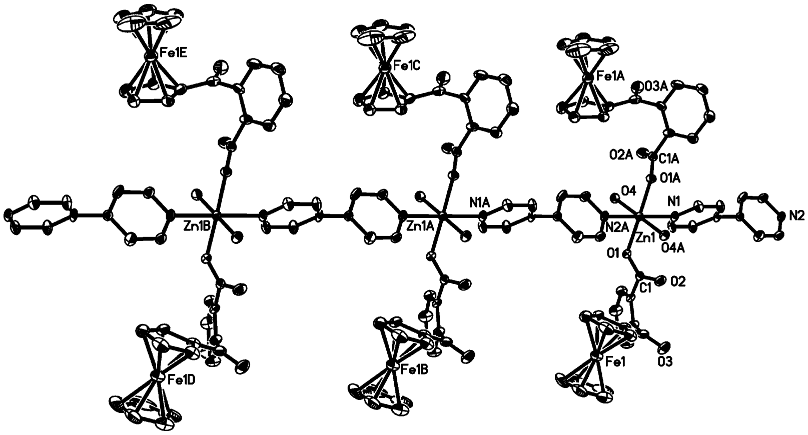

Figure 3. One-dimensional chain structure of $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]\cdot 2MeOH\cdot 2H_2O\}_n$ (**2**) (H atoms and solvent molecule omitted for clarity).

its carboxylate acting in a tridentate fashion. The steric effects of the ferrocenyl group in the compound **PbFC** make the carboxylate show various coordination modes.

Crystal Structure of $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]\cdot 2MeOH\cdot 2H_2O\}_n$ (2). X-ray diffraction analysis of compound **2** shows that it crystallizes in the space group *C*2/*c*. The structure consists of a polymeric chain in which adjacent $[[Zn(o\text{-}OOCC_6H_4COFc)_2(H_2O)_2]$ units are linked by 4,4′-bipy ligands. A view of the chain structure of **2** is depicted in Figure 3.

Each Zn(II) ion is at a six-coordinated geometry in which four oxygen atoms come from two $o\text{-}FcCOC_6H_4COO^-$ units, two coordinated water molecules occupying the equatorial plane, and two nitrogen atoms from the bridging 4,4′-bipy ligands occupying the axial positions. Deviation of Zn atoms from the mean plane formed by the four equatorial atoms is about 0.0161 Å, and the maximum deviation of any equatorial atom from the mean plane is 0.0101 Å. The Zn−O bond lengths range from 2.079(4) Å to 2.150(4) Å, while the axial Zn1−N1 and Zn1−N2A bond distances are 2.142(7) Å and 2.218(7) Å, respectively, giving rise to a slightly distorted octahedral coordination sphere. The Zn−N distances can be compared to those found in several Zn-4,4′-bipy coordination polymers, for example, in [Zn(tp)(4,4′-bipy)] (tp = terephthalate) (Zn−N, 2.007(2)−2.154(2) Å),[29a] $[Zn(4,4'\text{-bipy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bipy})_{1.5}\cdot H_2O$ (Zn−N, 2.104(2)−2.117(2) Å),[29b] and $[Zn(4,4'\text{-bipy})(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bipy})_2\cdot H_2O$ (Zn−N, 2.129(3)−2.196(3) Å).[29c] The bond angles around each Zn(II) ion vary from 87.98(19)° to 180.00(3)°. The intrachain distance between metallic cations Zn1...Zn1A is 11.470 Å, which is slightly longer than that in the reported polymer $[Zn(4,4'\text{-bipy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bipy})_{1.5}\cdot H_2O$ (11.299(2) Å).[29b] The dihedral angle between the pyridyl rings is 83.1°, which is larger than that of the polymer $[Zn(4,4'\text{-bipy})(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bipy})_2\cdot H_2O$ (49.5°).[29c]

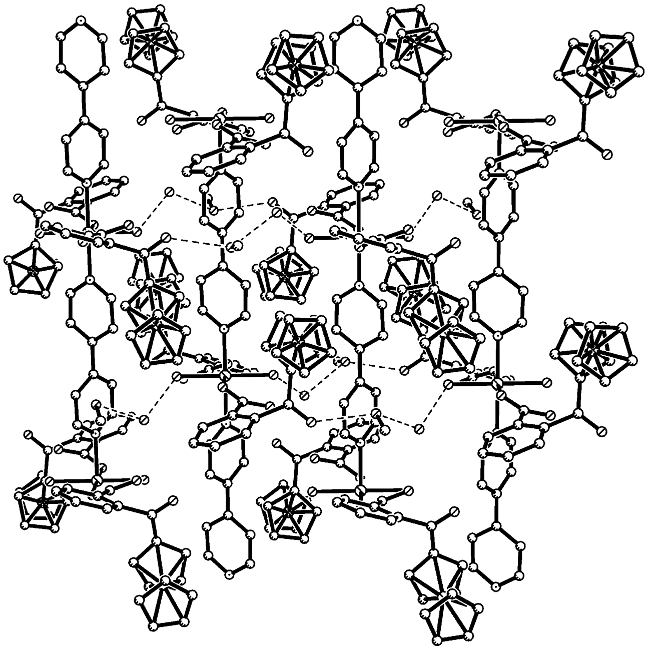

Figure 4. Two-dimensional sheet supported by hydrogen bonding of $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]\cdot 2MeOH\cdot 2H_2O\}_n$ (**2**).

It is noteworthy that $o\text{-}FcCOC_6H_4COO^-$ units as a terminal monodentate coordinate to the central metal ion and hang at the main chain, $[Zn(4,4'\text{-bipy})]_n$. The distance between the two neighboring phenyl rings on the same side is 10.855 Å, and the phenyl rings are parallel. The cyclopentadienyl rings in each ferrocenyl fragment are planar and nearly parallel with a dihedral angle of 3.0° at Fe1. $Fe-C_{ring}$ distances range from 2.017(10) to 2.062(8) Å (average 2.039 Å), intracyclopentadienyl C−C bond lengths lie in the range 1.330(14)−1.444(19) Å (average 1.405 Å), and C−C−C angles vary from 104.5(9) to 109.1(10)° (average 108.0°), which are all similar to those reported in the literature.[24]

In the solid-state structure of **2**, linear $[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]_n$ chains are linked by intermolecular hydrogen bonds forming a two-dimensional sheet. It can be seen from Figure 4, the coordinated water, crystallized water, and methanol molecules are involved in the hydrogen bonds between the neighboring $[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-}$

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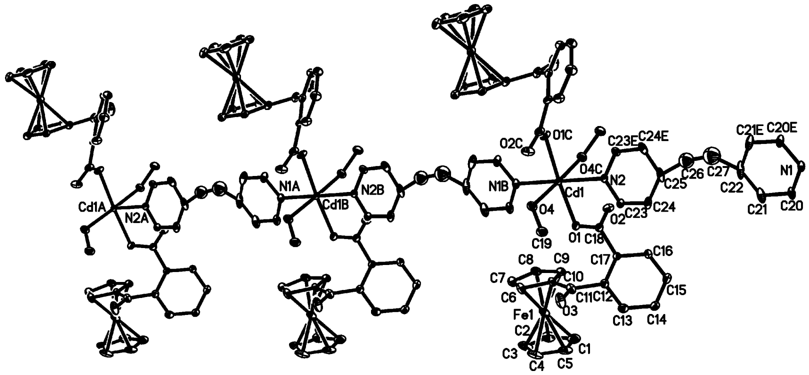

Figure 5. Perspective view of $\{[Cd(o\text{-}OOCC_6H_4COFc)_2(bpe)(MeOH)_2]\cdot 2H_2O\}_n$ (**3**) with atom labeling scheme (H atoms and solvent molecule omitted for clarity).

bipy)$(H_2O)_2]_n$ chains. There are three kinds of hydrogen bonds. One is between the O unit of the coordinated water from one $[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]$ group and an OH of one crystallization water molecule. The other is arising from the interaction of an OH of the crystallization water molecule with an O of one crystallization methanol molecule. The third originates from an OH of the crystallization methanol molecule with an O from the carbonyl group of a neighboring $[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]$ unit. Thus, the hydrogen bonding chain ($O_{\text{coordinated water}}...H-O-H_{\text{crystallized water}}...O-H_{\text{crystallized methanol}}...O_{\text{carbonyl group}}$) is formed.

To our best knowledge, the coordination polymers with ferrocene units in the side chain were only found in our recent publication,[17h] in which two Zn coordination polymers $\{[Zn(OOCFc)_2(bpt)]\cdot 2.5H_2O\}_n$ and $[Zn(OOCFc)(\eta^2\text{-}OOCFc)(bbp)]_n$, and one Pb polymer $[Pb(FcCOO)(\mu_2\text{-}FcCOO)(bpe)]_n$ were described. The two Zn polymers show ladder and zigzag chain structures, respectively. However, compound **2** exhibits linear chain structure. These structural differences may be mainly due to the different influences of the bipyridine-base ligands; the bridging ligands in polymers $\{[Zn(OOCFc)_2(bpt)]\cdot 2.5H_2O\}_n$ and $[Zn(OOCFc)(\eta^2\text{-}OOCFc)(bbp)]_n$ are flexible a bpt or bbp ligand and a rigid 4,4′-bipy ligand in **2**.

Crystal Structure of $\{[Cd(o\text{-}OOCC_6H_4COFc)_2(bpe)(MeOH)_2]\cdot 2H_2O\}_n$ (3). The crystal structure of polymer **3** comprises $[Cd(o\text{-}OOCC_6H_4COFc)_2(bpe)(MeOH)_2]_n$ polymeric chains. It crystallizes in the space group *C*2/*c* as polymer **2**.

As shown in Figure 5, each Cd(II) ion is six-coordinated in a slightly distorted octahedral environment with four oxygen atoms from two $o\text{-}FcCOC_6H_4COO^-$ units and two coordinated methanol molecules and two nitrogen atoms from two bridging bpe ligands. The bridging bpe ligands occupy the axial positions, while in the equatorial ones two $o\text{-}FcCOC_6H_4COO^-$ units and methanol are located. The $Cd-O_{FcCOC6H4COO}$ distance (2.269(4) Å) is slightly shorter than the $Cd-O_{\text{methanol}}$ distance (2.344(4) Å). The two Cd−N distances (Cd1−N1 = 2.300(5) Å and Cd1−N2 = 2.360(5) Å) have typical bond lengths (2.32−2.39 Å).[30] The bond angles around the central Cd(II) ion vary from 87.56(9)° to 180.00(1)°, which are very close to the ideal ones. The Cd...Cd distance through the bpe bridge being 14.047 Å is significantly longer than the Zn...Zn distance (through the 4,4′-bipy bridge) in polymer **2** and close to the reported Cd polymer, $\{[Cd(NO_3)_2(bpe)_{1.5}]\}_n$.[31a] The dihedral angle between the two pyridyl rings is 15.6° indicating a slight twist. The bond lengths and angles within the ferrocenyl group are unexceptional and close to those reported in the literature.[24] It is noteworthy the dihedral angle between the phenyl ring plane and the cyclopentadienyl ring plane to which it is linked is a relatively large value, 60.4°, which may be due to the steric effects.

Crystal Structure of $[Pb(o\text{-}OOCC_6H_4COFc)(\eta^2\text{-}o\text{-}OOCC_6H_4COFc)(bpe)]_n$ (4). X-ray diffraction analysis of compound **4** shows that it crystallizes in the space group $P\bar{1}$ as polymer **1**. The structure of **4** is made up of a one-dimensional array of $[Pb(o\text{-}OOCC_6H_4COFc)(\eta^2\text{-}o\text{-}OOCC_6H_4COFc)]$ units bridged by bpe ligands. The ORTEP plot showing the structural unit of **4** is illustrated in Figure 6.

As seen in Figure 6, the central Pb(II) ion is five-coordinated with three oxygen atoms from two $o\text{-}FcCOC_6H_4COO^-$ units and two nitrogen atoms from bridging bpe ligands. One of the two $o\text{-}FcCOC_6H_4COO^-$ units acts as a terminal monodentate ligand, and the other, as a bidentate ligand. The Pb−O distances are in the range 2.316(5)−2.574(6) Å (average 2.483 Å), which can be comparable to those of the compound **1**. Two Pb−N distances are not equal (Pb1−N = 2.619(6) Å, Pb1−N2 = 2.669(6) Å). The average Pb−N distance is 2.644 Å, which is close to that of a related Pb polymer $[Pb(NCS)(bpa)]_n$ (bpa = 1,2-bis(4-pyridyl)ethane) (2.642 Å). [32] The angles around the Pb(II) ion are between 85.1(2)° and 157.0(2)°. Obviously, the Pb(II) ion is in a significantly distorted trigonal biyramid geometry.

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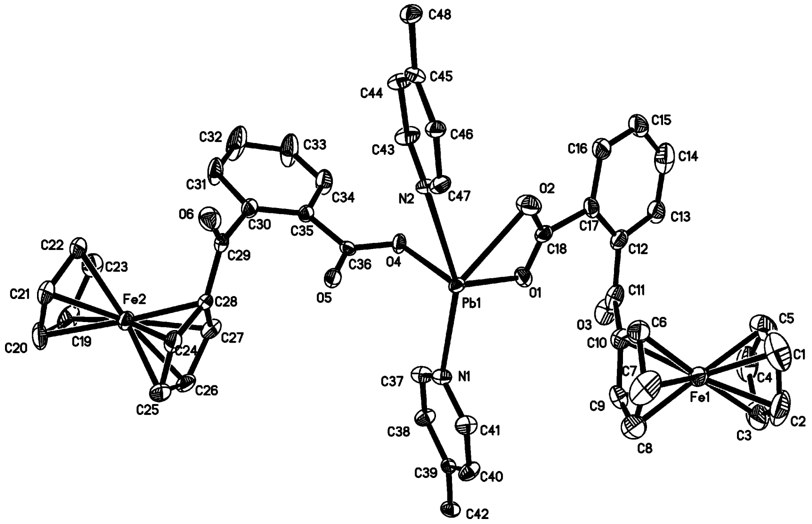

Figure 6. ORTEP plot showing the structure unit of [Pb(*o*-$OOCC_6H_4COFc$)(η^2-*o*-$OOCC_6H_4COFc$)(bpe)]$_n$ (**4**). The hydrogen atoms are omitted for clarity (H atoms omitted for clarity).

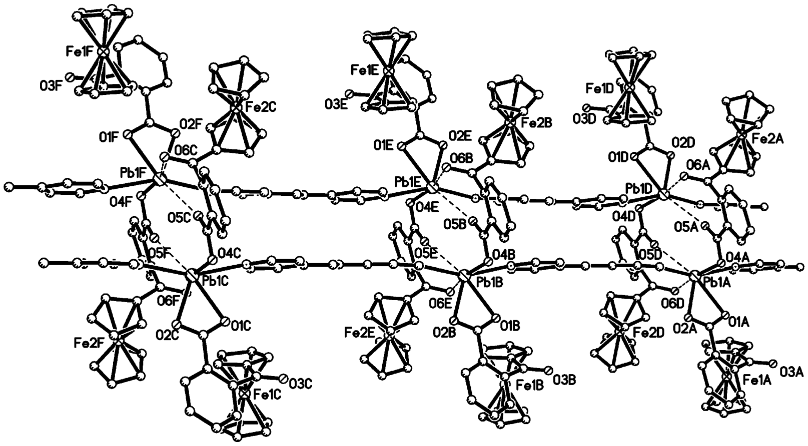

Figure 7. One-dimensional infinite ladderlike structure of [Pb(*o*-$OOCC_6H_4COFc$)(η^2-*o*-$OOCC_6H_4COFc$)(bpe)]$_n$ (**4**) (H atoms and solvent molecule omitted for clarity).

Interestingly, the linear chain [Pb(*o*-$OOCC_6H_4COFc$)(η^2-*o*-$OOCC_6H_4COFc$)(bpe)]$_n$ interacts with the neighboring [Pb(*o*-$OOCC_6H_4COFc$)(η^2-*o*-$OOCC_6H_4COFc$)(bpe)]$_n$ chain forming a one-dimensional ladderlike structure (Figure 7). It can be seen from Figure 7 that the distances between O5I and Pb1C and O6I and Pb1C are 3.150 Å and 3.527 Å, respectively, indicating the existence of weak interactions. At the same time, the pyridyl rings of neighboring [Pb(*o*-$OOCC_6H_4COFc$)(η^2-*o*-$OOCC_6H_4COFc$)(bpe)]$_n$ chains are nearly parallel with a dihedral angle of 8.1°, while the distance between the two rings is 3.334 Å showing the existence of $\pi-\pi$ interaction.

The intrachain distance between metallic cations Pb1E...Pb1D is 14.593 Å, which is slightly longer than the Cd...Cd distance in polymer **3** but close to that of the reported ferrocenecarboxylate polymer [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$ (14.526 Å),[17h] while the interchain distance between the nearest Pb cations Pb1E...Pb1B is 4.619 Å also consistent with that of the polymer [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$ (4.564 Å).[17h] The two pyridyl rings of one bridge bpe show a dihedral angle of 8.1°, which is smaller than that of the polymer **3**. The dihedral angle of the phenyl ring plane and cyclopentadienyl ring plane of the terminal monodentate *o*-$FcCOC_6H_4COO^-$ ligand is 83.1°, which is larger than that of the bidentate η^2-*o*-$FcCOC_6H_4COO^-$ ligand (57.5°). The bond lengths and angles within the ferrocenyl group are unexceptional and close to those reported in the literature.[24] In the solid-state structure, the ladderlike chains pack each other through the van der Waals interactions. Figure 8 gives the crystal packing structure of polymer **4**.

Although the reported ferrocenecarboxylate-containing polymers {[Zn(OOCFc)$_2$(bpt)]·2.5H_2O}$_n$, [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$,[17h] and **4** all indicate ladder structures, the interactions inside the double chain of the ladder are different. In {[Zn(OOCFc)$_2$(bpt)]·2.5H_2O}$_n$, the ladder was formed by interchain hydrogen bonds (N$-$H$_{\text{bpt}}$...O$_{\text{carbonyl group}}$) and $\pi-\pi$ interactions. In [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$, the strong Pb$-$O interactions of neighboring [Pb(FcCOO)(μ_2-FcCOO)(bpe)]$_n$ chains mainly give contribution to the construction of the ladder. In polymer **4**, the synergistic interactions of weak Pb...O interactions and $\pi-\pi$ stacking interactions make the neighboring [Pb(*o*-$OOCC_6H_4COFc$)(η^2-*o*-$OOCC_6H_4COFc$)(bpe)]$_n$ chains form a infinite ladder structure.

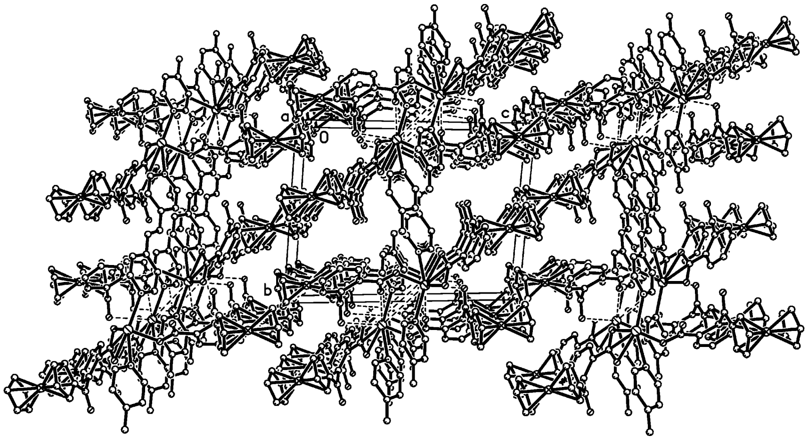

Figure 8. Crystal packing of [Pb(o-OOCC$_6$H$_4$COFc)(η^2-o-OOCC$_6$H$_4$COFc)(bpe)]$_n$ (**4**) in the solid state.

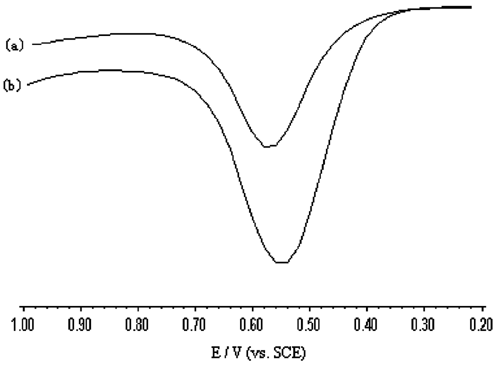

Figure 9. Differential pulse voltammogram of polymer **1** (a) and the corresponding ferrocenyl ligand NaOOCCH=(CH$_3$)CFc (b) (~1.0 × 10^{-3} M) in DMF containing n-Bu$_4$NClO$_4$ (0.1 M) at a scanning rate of 20 mV s^{-1} (vs SCE).

IR Spectroscopy. According to the references,[24,33] the characteristic IR bands of the ferrocenyl group at 3097 and 489 cm^{-1} are due to ν(C−H) and ν(Fe−Cp) vibrations, respectively, which can be found in the four compounds (3098 and 501 cm^{-1} for **1**; 3104 and 490 cm^{-1} for **2**; 3112 and 494 cm^{-1} for **3**; 3107 and 495 cm^{-1} for **4**). For compound **1**, the strong absorption bands at 1618 and 1521 cm^{-1} are assigned to ν_{as}(COO$^-$) and ν_s(COO$^-$) vibrations, respectively, and the vibrational bands around 1328 and 1026 cm^{-1} can be attributed to the δ(CH$_3$) and ρ(CH$_3$), respectively.[34] For compounds **2**−**4**, the characteristic IR bands indicate the existence of a phenyl ring (1610, 1560, and 1460 cm^{-1} for **2**; 1607, 1549, and 1453 cm^{-1} for **3**; 1608, 1549, and 1450 cm^{-1} for **4**). In the middle energy range, the strong absorption band around 1640 cm^{-1} can be assigned to the ν(C=O) vibration. In conclusion, these IR data are consistent with the crystal data of the four compounds.

Thermogravimetric Analysis (TGA). The TG-DTA measurements of polymers **1**−**4** were determined in the range of 20−1000 °C in air. TG data shows that polymer **1** is stable up to 81.8 °C, then loses weight from 81.8 to 193.8 °C corresponding to losses of solvent molecule, and keeps losing weight from 193.8 to 531.4 °C corresponding to the decomposition of the organic units of FcC(CH$_3$)=CHCOO$^-$ anions. Finally, a plateau region is observed from 531.4 to 1000 °C. A brown amorphous residue of PbO + 2FeO (observed 47.48%, calculated 47.22%) remained. There is one very strong exothermic peak at 431 °C on the DTA curve of **1**. There are two exothermic peaks at 290 and 389 °C on the DTA curve of polymer **2**; it first loses the crystallized and coordinated solvent molecules from 34 to 217 °C and secondly goes through complicated multiple weight loss steps in the temperature range of 227−917 °C corresponding to the decomposition of 4,4′-bipy and the organic units of o-OOCC$_6$H$_4$COFc anions. One very strong exothermic peak at 332 °C can be observed on the DTA curve of polymer **3**; it first loses the coordinated and crystallized solvent molecules in the temperature range of 52−210 °C, second, loses weight from 229 to 395.5 °C, and then shows a plateau region from 398 to 1000 °C. Polymer **4** is stable up to 162 °C, then loses weight from 164.5 to 234 °C corresponding to the decomposition of bpe, and goes on losing weight from 234 to 950 °C which is assigned to decomposition of the organic units of o-OOCC$_6$H$_4$COFc anions. One strong exothermic peak 399 °C on the DTA curve of **4** can be observed.

Redox Properties of Polymers 1−4. The solution-state differential pulse voltammetries of polymer **1**−**4** and their individual ferrocene-substitued carboxylate ligands are shown in Figures 9 and 10. It can be seen from Figures 9 and 10 these compounds all show single peaks with a half-wave potential at 0.58 V for **1**, 0.56 V for NaOOCCH=(CH$_3$)CFc, 0.66 V for **2**, 0.62 V for **3**, 0.61 V for **4**, and 0.55 V for o-NaOOCC$_6$H$_4$COFc, respectively. Obviously, these observed redox peaks correspond to the redox processes of the ferrocenyl moieties. The half-wave potential of the ferrocenyl moieties seems to be influenced by the Pb(II) ions in polymer **1**. The half-wave potential of polymers **2**−**4** are in the range of 0.61−0.66 V, which are shifted to higher potentials, compared with that of the free NaOOCCH=(CH$_3$)CFc (0.55 V). It is apparent that these metal ions, Zn(II), Cd(II), or Pb(II), have a large influence on the half-wave potential of the ferrocenyl moieties in **2**−**4**’s polymeric

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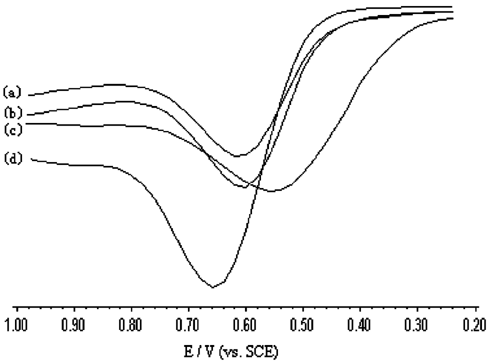

Figure 10. Differential pulse voltammogram of polymers **2** (d), **3** (a), **4** (b), and the corresponding ferrocenyl ligand *o*-$NaOOCC_6H_4COFc$ (c) (~1.0 × 10^{-3} M) in DMF containing *n*-Bu_4NClO_4 (0.1 M) at a scanning rate of 20 mV s^{-1} (vs SCE).

systems, which is consistent with the previous results of transition metal−ferrocenyl systems.[17g,35]

Conclusion

By reaction of ferrocenyl-substituted carboxylate and bipyridine-based ligands with metal ions by "avoiding light" and under mild conditions, four crystal products have been successfully prepared. The X-ray determinations show that they are novel ferrocene-containing coordination polymers. Our studies reveal that the utilization of bipyridine-based ligands benefits the attachment of ferrocenyl-substituted carboxylate units to polymer chains. The elemental analyses, IR data, and thermal data are consistent with the X-ray analysis results. The electrochemical studies show that Zn(II), Cd(II), and Pb(II) have some influence on the half-wave potential of the ferrocenyl moieties.

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Supporting Information Available: Crystallographic data in CIF and pdf formats. This material is available free of charge via the Internet at http://pubs.acs.org.

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