



The synthesis of complexes using precursor complexes with ferrocenyl carboxylate units as building blocks

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ABSTRACT

Using ferrocenyl carboxylates as functional ligands, we synthesized a mononuclear complex $[\text{Zn}(\eta^2\text{-OOCCH}=\text{CHFc})(\text{CH}_3\text{OH})_2]$ (**1**) and a binuclear complex $[\text{Cd}(\text{bafca})_2(\text{H}_2\text{O})_2]$ (**2**) ($\text{bafca}^- = \alpha\text{-benzamido-}\beta\text{-ferrocenylacrylic carboxylate}$) as precursor complexes. Investigation on the substitution reaction of precursor complexes as building blocks in solution-state, four complexes $[\text{Zn}(\text{OOCCH}=\text{CHFc})(\text{bbbm})_n]$ (**1a**), $\{[\text{Zn}(\text{OOCCH}=\text{CHFc})(\text{ntb})(\text{CH}_3\text{OH})]\}$ (**1b**), $[\text{Cd}(\text{bafca})_2(2,2'\text{-bpy})_2 \cdot 9\text{H}_2\text{O}$ (**2a**) and $\{[\text{Cd}(\text{bafca})_2(\text{bbbm})(\text{CH}_3\text{OH})_2] \cdot 6\text{CH}_3\text{OH}\}_n$ (**2b**) were obtained ($\text{bbbm} = 1,1\text{-}(1,4\text{-Butanediyl})\text{bis-}1\text{H-benzimidazole}$, $\text{ntb} = \text{N,N-bis}(1\text{H-benzimidazol-}2\text{-ylmethyl})\text{-}1\text{H-Benzimidazole-}2\text{-methanamine}$ and $2,2'\text{-bpy} = 2,2'\text{-bipyridine}$). As anticipated, the structural integrity of precursor complexes can be maintained in these four complexes. It indicates that we can synthesize the desired complexes with the destination structures by using precursor complexes as building blocks and choosing appropriate auxiliary ligands. In addition, the electrochemical properties of all complexes were investigated, and it can be seen from the results that half-wave potentials of these complexes are slightly higher than that of the corresponding ligand.

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1. Introduction

The rational design and preparation of novel metal-organic complexes have attracted intense interest for their intriguing architectures and potential applications [1]. Considerable progress has been made on the theoretical forecast and practical approaches aiming at controlling the topology structure and geometry of the network. Over the past several years, some structures of metal-organic complexes could, to a certain extent, be predicted by exploiting organic linkers and elaborately choosing metal salts [2]. However, in some cases it is not easy to design and synthesize a desired metal-organic complex in a truly deliberate manner [3], the reason is that the self-assembly process of these complexes is influenced by many factors [4].

In recent years, utilizing precursor complexes as building blocks has become an important approach to construct metal-organic complexes [5]. Precursor complexes possess specific rigid geometries and potentially extend to form a multi-dimensional framework, so a feasible synthetic strategy for constructing metal-organic complexes is to assemble precursor complexes as building blocks into predetermined structures by decoration and expansion of the basic net topologies [6]. In other words, the precursor acts as a center and it has been utilized in the construction of a given structure [7]. Nevertheless, study on the designing of complexes

using precursor complexes as building blocks is still a challenge to chemists. Especially, the systematic study of ferrocene-containing precursor complexes is extremely rare comparing with large amounts of reports about aromatic carboxylate precursor complexes. As an extension to our previous work [8,9], our group aimed at exploring the products of complexes through the substitution reaction of ferrocenyl carboxylate precursor complexes containing facile leaving groups. Obviously, if the facile leaving groups could be replaced by appropriate auxiliary ligands, complexes with the destination topology structures would be designed.

As is well known, the carboxylate groups make the self-assembly of crystal engineering easily available due to their versatile coordination modes and strong coordinating capability [10]. Furthermore, the introduction of ferrocenyl carboxylate groups into metal-organic frameworks provides an effective way to prepare new functional materials with unique features. So ferrocenecarboxylate compounds have been extensively used as functional ligands [11]. Herein, we selected $\beta\text{-ferrocenylacrylic sodium}$ and $\alpha\text{-benzamido-}\beta\text{-ferrocenylacrylic sodium}$ as functional ligands to synthesize precursor complexes. In the present work, we synthesized a mononuclear precursor complex and a binuclear precursor complex, and there are two facile leaving groups in the central metal ion of each precursor complex. If the two facile leaving groups in the precursor complex could be replaced by bidentate bridging ligands, one-dimensional polymers or dimers can be designed by using the two precursor complexes as building blocks. If the two facile leaving groups could be replaced by chelate ligands, the

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complexes whose structures were similar to those of the precursor complexes could be obtained. As anticipated, four complexes without framework distortion were obtained by replacing the leaving groups with a bidentate bridging ligand, a bidentate chelate ligand and a multidentate chelate ligand. Hence, our findings demonstrate that the number of facile leaving groups in precursor complexes and the kind of auxiliary ligands can control the topology structures of the complexes. Additionally, high redox ability is one of the unique features of ferrocene and its derivatives, so the electrochemical properties of all complexes were investigated in solution.

2. Results and discussion

2.1. Design and synthesis of complexes

Mononuclear complex $[\text{Zn}(\eta^2\text{-OOCCH=CHFc})_2(\text{CH}_3\text{OH})_2]$ (**1**) and binuclear complex $[\text{Cd}(\text{bafca})_2(\text{H}_2\text{O})_2]_2$ (**2**) have been obtained by treatment of ferrocenyl carboxylate compounds with appropriate metal salts in some solvents. There are two coordinated methanol molecules and four coordinated water molecules in complexes **1** and **2**, respectively. We think that some coordinated solvent molecules are facile leaving groups in complexes. So we used these two complexes as precursor complexes, and the complexes with the destination structures could be designed and synthesized via the substitution reaction of precursor complexes.

X-ray diffraction analysis reveals that, in precursor complex **1**, the Zn(II) ion is six-coordinated by two oxygen atoms from two methanol molecules and four oxygen atoms arising from two FcCH=CHCOO^- units. The two methanol molecules are facile leaving groups. So a one-dimensional polymer or a dimer can be designed by substitution reaction of **1** with bidentate bridging ligand at moderate condition. As anticipated, one-dimensional polymer **1a** was gained through the reaction of **1** with bidentate bridging ligand *bbbm* at room temperature. At the same time, complex **1b** was obtained by substitution reaction with a multidentate chelate ligand *ntb*. Because of the spatial configuration and the strong coordinating capability of *ntb*, one ferrocene carboxylate group and two methanol molecules were also replaced by the ligand *ntb*. Thus, complex **1b** was a mononuclear complex (Scheme 1).

Complex **2** contains two Cd(II) centers bridged by two ferrocenecarboxylate anions [8], leading to a dimeric $[\text{Cd}_2(\text{bafca})_2]$ core. Each Cd(II) is seven-coordinated bonding to five oxygen atoms of three ferrocenecarboxylate units and two oxygen atoms from two coordinated water molecules, and two water molecules are facile leaving groups (Scheme 2). Accordingly, through substitution reaction of **2** with bidentate chelate ligands, new complexes with similar structures of **2** could be obtained. Meanwhile, a one-dimensional polymer could also be gained by substitution reaction with a bidentate bridging ligand. As a matter of fact, the dimer complex **2a** was obtained through the addition of bidentate chelate ligand *2,2'*-bpy into the solution of **2**, and the one-dimensional polymer **2b** was also obtained by using bidentate bridging ligand *bbbm* instead of *2,2'*-bpy (Scheme 2).

2.2. Description of crystal structures

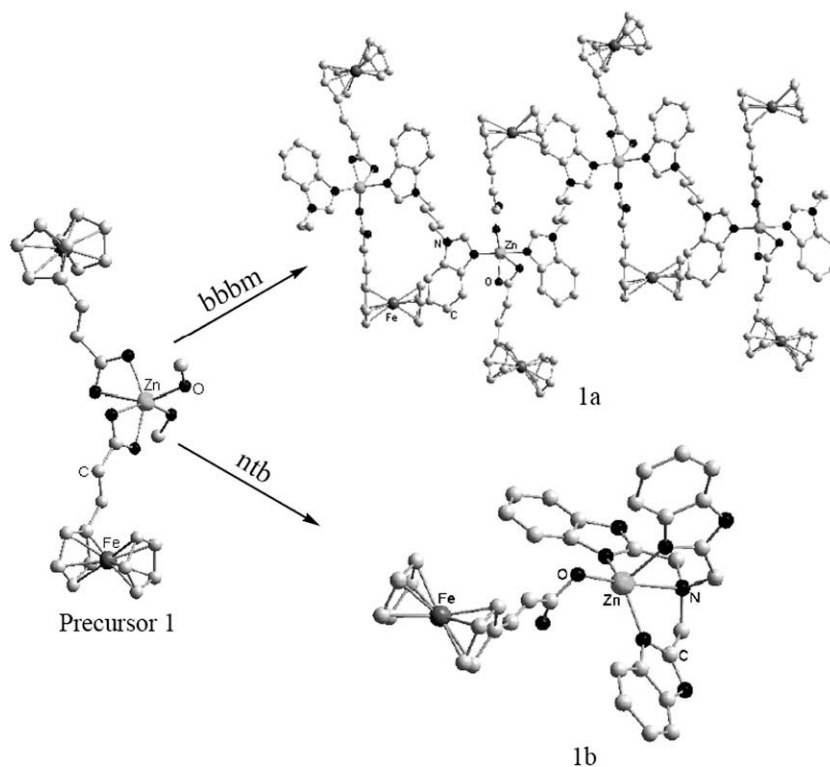
In complex **1** (Fig. 1), six-coordinated Zn(II) ion is in a distorted octahedral environment. The $\text{Zn1-O3}_{\text{methanol}}$ (2.027 Å) distance associated with $\text{Zn1-O2}_{\text{carboxyl}}$ (2.005 Å) distance, while the distance is shorter than $\text{Zn1-O1}_{\text{carboxyl}}$ (2.402 Å) distance. The hydrogen bonds between coordinated oxygen atoms of the OOCCH=CHFc^- groups and coordinated oxygen atoms of the methanol molecules in another **1** unit resulting in a 2-D infinite network.

Polymer **1a** exhibits one-dimensional zigzag chain (as shown in Fig. 2), each Zn(II) ion is four coordinated in a distorted tetrahedron geometry with two oxygen atoms from two terminal OOCCH=CHFc^- units, two nitrogen donors from two bridging ligands *bbbm*. The ligand *bbbm* connect Zn(II) ions leading to an infinite one-dimensional chain. Because of the spatial configuration and the steric effect of the ferrocene group and *bbbm* ligand, the distances of $\text{Zn}\cdots\text{O1}$ (2.910 Å) and $\text{Zn}\cdots\text{O4}$ (2.877 Å) are longer than $\text{Zn-O}_{\text{carboxyl}}$ in **1** (2.005 and 2.402 Å), and Zn1-O2 (1.914 Å) and Zn1-O3 (1.963 Å) distances are consistent with one of $\text{Zn-O}_{\text{carboxyl}}$ in **1** (2.005 Å). The Zn–N distances (from 2.010 to 2.031 Å) associated with the bridging ligand *bbbm* are comparable to those found in the literatures [12]. The bond angles around each Zn(II) ion range from 102.1 to 117.1°. Hence, average bond angle at Zn1 is 109.2°, which is slightly smaller than 109.5° for an ideal tetrahedron. In addition, the $\text{Zn}\cdots\text{Zn}$ distance in **1a** is 13.831 Å. Between adjacent zigzag chains, the benzimidazole rings are parallel with the average interplanar distance of 3.436 Å, which is in the range of common distances for π – π interactions between two aryl rings [13]. These π – π interactions among benzimidazole rings and hydrogen bonds resulting in a 3-D infinite network, as shown in Fig. 2. Although the π – π interactions are weak, they are important in the molecular assembly.

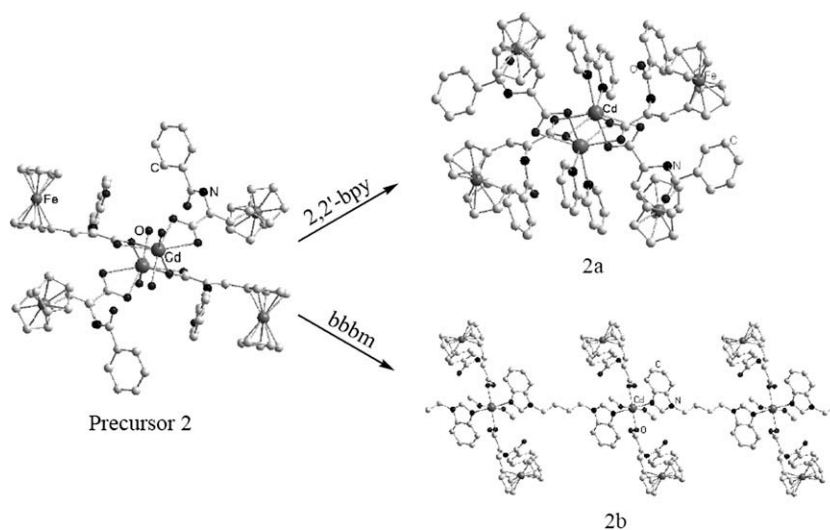
Mononuclear complex **1b** is depicted in Fig. 3, from which we can see that the Zn(II) ion is five-coordinated, with one oxygen atom from FcCH=CHCOO^- unit, four nitrogen donors from one *ntb* molecule. The equatorial position is occupied by N4, N6 and N2, and the distance of Zn1-N1 bond (2.517 Å) is longer than that of Zn1-O2 (1.983 Å). So the coordination environment around the Zn(II) ion is a distorted trigonal bipyramid. Moreover, the benzimidazole rings in adjacent **1b** molecules are also parallel with the average interplanar distance of 3.512 Å, which is similar to that of complex **1a**. The adjacent **1b** molecules are linked through π – π interactions and hydrogen bonds between uncoordinated oxygen atoms of the OOCCH=CHFc^- groups and *ntb* ligands, solvent CH_3OH molecules and *ntb* ligands resulting in a 2-D network.

The structure analysis by X-ray diffraction demonstrates that complex **2a** keeps the structural integrity of precursor complex **2**, and the four coordinated water molecules in **2** were replaced by two *2,2'*-bpy molecules through bidentate chelate coordination mode. In each **2a** unit, the two Cd(II) ions are equivalent, each Cd(II) ion adopts a distorted octahedral geometry with six donors, two nitrogen atoms from one chelate *2,2'*-bpy ligand and four oxygen atoms belonging to three *bafca*[−] groups; the two *2,2'*-bpy ligands are equivalent; the four *bafca*[−] ligands display two coordination modes, two *bafca*[−] groups acting as monodentate fashion bind to two Cd(II) ions, the other two *bafca*[−] as tridentate fashion bridge the two Cd(II) ions forming four-membered rings (as shown in Fig. 4). The bond lengths of Cd1–N are 2.305 and 2.349 Å, respectively; the bond lengths of Cd1–O are in the range of 2.269–2.437 Å. N4, O1, O2, O2A and Cd1 atoms are nearly coplanar (the mean deviation from plane is 0.0581 Å). Because of the spatial configuration and the steric effect of *2,2'*-bpy, the distance of $\text{Cd1}\cdots\text{O5}$ (2.707 Å) in **2a** is longer than those of $\text{Cd-O}_{\text{carboxyl}}$ in **2** (from 2.305 to 2.547 Å), so the coordination number of Cd(II) in **2a** is six. Additionally, the *2,2'*-bpy rings in adjacent **2a** molecules are also parallel with the average interplanar distance of 3.760 Å, thus π – π interactions between two *2,2'*-bpy rings are weak (Fig. 4).

The crystal structure of **2b** is significantly different from **2a**; it exhibits one-dimensional chain (as shown in Fig. 5), and this complex crystallizes in the space group *P1*. Each Cd(II) ion is six-coordinated with two oxygen atoms from two *bafca*[−] groups, two oxygen atoms from two methanol molecules, two nitrogen donors from two bridging ligands *bbbm*. Around Cd1, O1, O1A, O4, O4A are completely co-planar (the mean deviation from plane is 0.0000 Å),



Scheme 1. The design and conversion of precursor complex **1** to complexes **1a** and **1b**.



Scheme 2. The design and conversion of precursor complex **2** to complexes **2a** and **2b**.

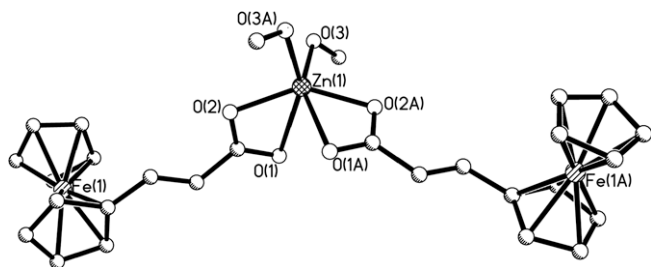


Fig. 1. The structure of the precursor complex $[\text{Zn}(\eta^2\text{-OOCCH}=\text{CHFc})_2(\text{CH}_3\text{OH})_2]$ (**1**) with heteroatom numbering. Hydrogen atoms are omitted for clarity in figure.

and they occupy the equatorial position, while N2, N2A are in axial positions, so the local coordination environment of Cd1 can be described as a distorted octahedral environment. Around the Cd(II) ion, the Cd1–O bond lengths are 2.259 and 2.363 Å, and the Cd1–N bond length is 2.305 Å. It is in conformity with those found in complexes $[\text{Cd}(\eta^2\text{-}o\text{-FcCOC}_6\text{H}_4\text{COO})(\mu_2\text{-}o\text{-FcCOC}_6\text{H}_4\text{COO})(\text{phen})_2 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}]$ (Cd–N: 2.317(2) and 2.353(2) Å) and $\{[\text{Cd}(o\text{-FcCOC}_6\text{H}_4\text{COO})_2(\text{bpe})(\text{CH}_3\text{OH})_2] \cdot 2\text{H}_2\text{O}\}_n$ (Cd–N: 2.300(5) and 2.360(5) Å) [14]. Moreover, in **2b** the ligand bbbm connect Cd(II) ions by replacing water molecules leading to an infinite one-dimensional chain, and the Cd···Cd distance in **2b** is 14.459 Å. The π – π interactions among benzimidazole rings result in a 2-D infinite network.

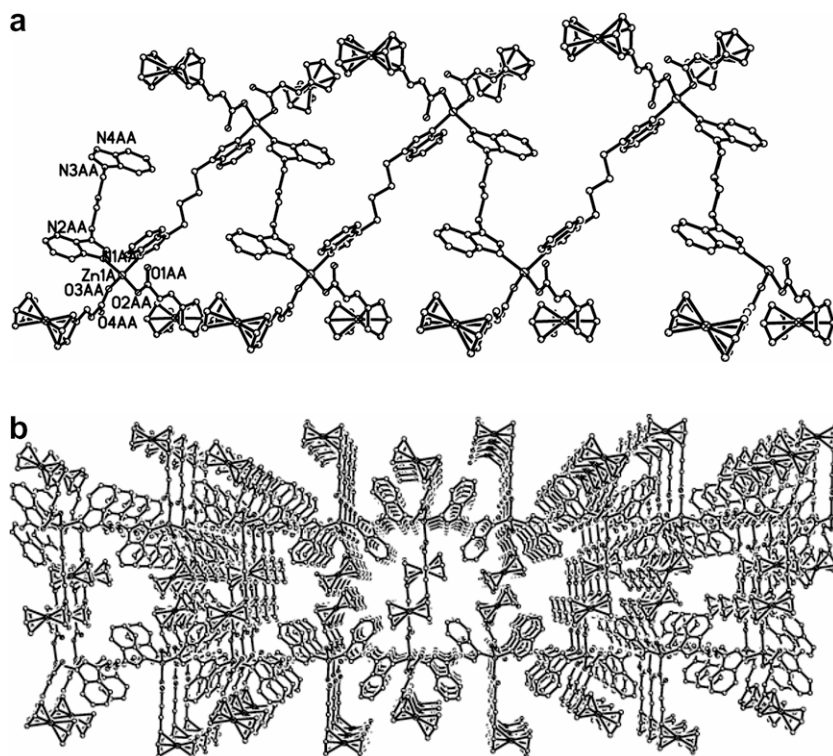


Fig. 2. (a) One-dimensional zigzag chain structure of complex $[Zn(OOCCH=CHFc)_2(bbbm)]_n$ (**1a**). (b) View of the infinite 3-D supramolecular structure of complex **1a**, generated through extensive hydrogen bonding and π - π interactions. Hydrogen atoms are omitted for clarity in figures (a) and (b).

2.3. Electrochemistry

We determined the molecular weights of polymers **1a** and **2b** in THF solution. The results show that the number-average molecular weights (M_n) are 2.687×10^4 for polymer **1a** and 3.567×10^4 for polymer **2b**. The weight-average molecular weights (M_w) are 4.342×10^4 and 5.122×10^4 for polymers **1a** and **2b**, respectively. Thus, we can confirm that the skeletons of polymers **1a** and **2b** are intact in solution [15], and the electrochemical properties in THF

solution of polymers **1a** and **2b** can represent the redox properties of polymers **1a** and **2b**.

The THF solution-state differential pulse voltammograms of **1-1b**, FcCH=CHCOOH and ferrocene are investigated (as shown in Fig. 6), and the differential pulse voltammograms of **2-2b**, bafcaNa and ferrocene are shown in Fig. 7. It can be seen from the figures that all these complexes show a single peak, which can be assigned to the electron-transfer process of the ferrocenyl moiety. Relative to ferrocene (0.544 V), the half-wave potentials ($E_{1/2}$) of the ferrocenyl carboxylate ligands FcCH=CHCOOH (0.632 V) and bafcaNa (0.612 V) are all shifted to higher potential. It is because that the electron-withdrawing ability of the carboxyl group and double bond serves to raise the potential above that of free ferrocene [16]. Furthermore, the half-wave potentials of **1** (0.668 V), **1a** (0.656 V) and **1b** (0.718 V) are slightly higher than that of FcCH=CHCOOH. Similarly, in contrast with bafcaNa, the half-wave potentials of **2** (0.624 V), **2a** (0.633 V) and **2b** (0.636 V) are also shifted to slightly higher potential. It is apparent that these shifts can be attributed to the influence of the central metal ions, and this is consistent with the previous results of transition metal-ferrocenyl systems [17]. The reason for this is that the conjugated π -electron systems between the two metal ions allow communication [18], and the electron-withdrawing nature of the coordinated metal centers makes the ferrocene unit harder to oxidize [19].

2.4. Conclusion

Using the precursor complexes **1** and **2** as building blocks are necessary to synthesize desired complexes. The structural integrity of precursor complexes was maintained in substitution reaction of precursor complexes with appropriate ligands in solution. It is noteworthy that the number of facile leaving groups in precursor complexes and the appropriate auxiliary ligands can control the topology structures of the complexes. In addition, all the crystals

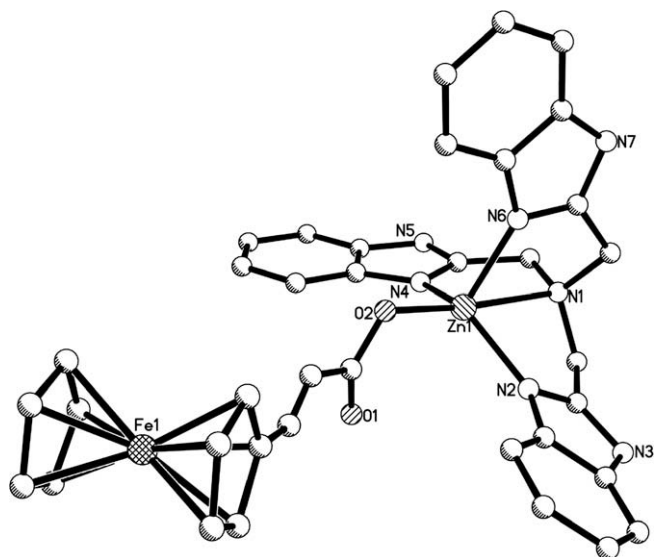


Fig. 3. The structure of the complex $\{[Zn(OOCCH=CHFc)(ntb)](CH_3OH)\}$ (**1b**) with heteroatom numbering. (Hydrogen atoms and solvent molecules are omitted for clarity.)

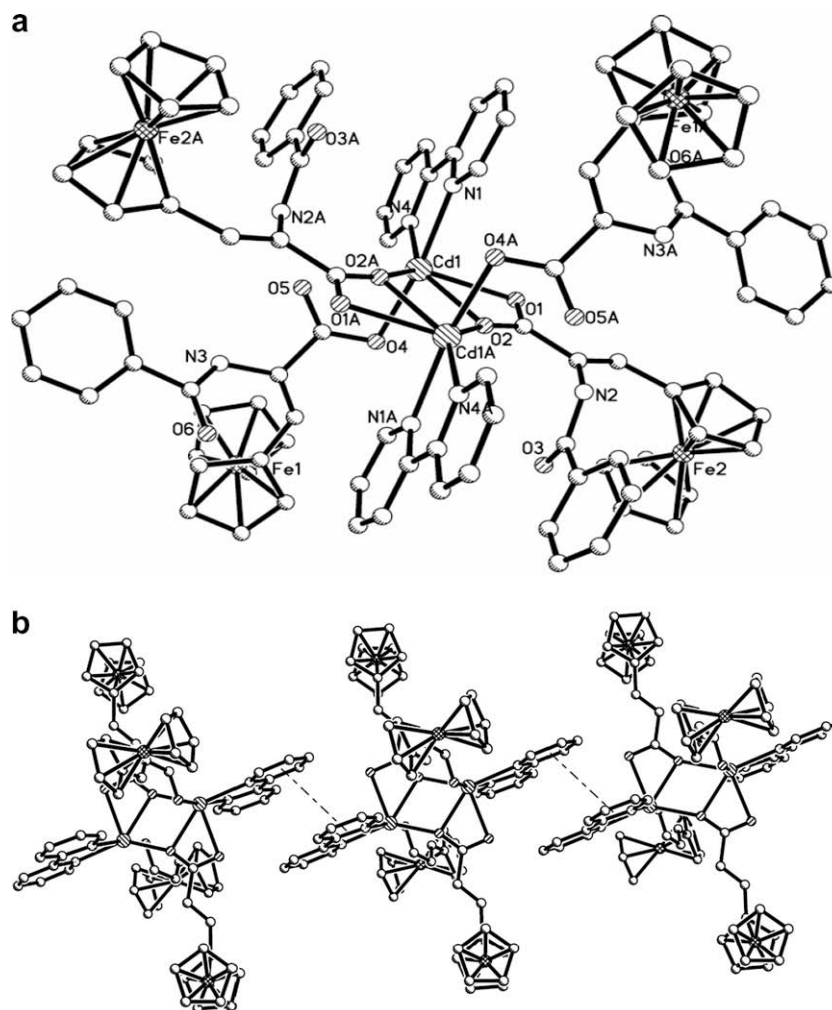


Fig. 4. (a) Perspective view of complex $[\text{Cd}(\text{bafca})_2(2,2'\text{-bpy})]_2 \cdot 9\text{H}_2\text{O}$ (**2a**) with partial atom-labeling scheme. (b) View of 1-D chain in complex **2a** showing the π - π interactions between the 2,2'-bpy rings. The hydrogen atoms and uncoordinated H_2O molecules are omitted for clarity in figures (a) and (b).

of complexes obtained from precursor complexes could not easily be obtained from one-pot reactions of ferrocenyl carboxylate ligands, metal salts and organic ligands.

3. Experimental

3.1. Materials and physical techniques

β -Ferrocenylacrylic acid and α -benzamido- β -ferrocenylacrylic acid and their corresponding sodium salts were prepared according to literature methods [20,21]. 1,1-(1,4-Butanediyl) bis-1H-benzimidazole (bbbm) and N,N-bis(1H-benzimidazol-2-ylmethyl)-1H-benzimidazole-2-methanamine (ntb) were prepared according to these literatures [22]. All other starting materials were of reagent-grade quality and were obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. Infrared spectra data were recorded on a Bruker TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region.

3.2. Synthesis of complexes **1–2b**

Synthesis of $[\text{Zn}(\eta^2\text{-OOCCH}=\text{CHFc})_2(\text{CH}_3\text{OH})_2]$ (**1**): $\text{FcCH}=\text{CHCOONa}$ (55.6 mg, 0.20 mmol) in methanol (8 mL) was added dropwise to the mixture of methanol (5 mL) and H_2O

(2 mL) of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (21.9 mg, 0.1 mmol). The resultant red solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained several days later. For **1**: Yield: 68%. Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{FeO}_3\text{Zn}_{0.5}$ (%): C, 52.70; H, 4.39. Found: C, 52.67; H, 4.38%. IR (cm^{-1} , KBr): 3427s, 2292m, 2366m, 1710s, 1638s, 1564m, 1408s, 1225m, 1107m, 822m, 450m.

Synthesis of $[\text{Zn}(\text{OOCCH}=\text{CHFc})_2(\text{bbbm})]_n$ (**1a**): The crystals of complex **1** (17.9 mg, 0.025 mmol) were dissolved in THF solution (3 mL). A methanol solution (6 mL) of bbbm (7.3 mg, 0.025 mmol) was added dropwise to the above solution. The resultant red solution was allowed to stand at room temperature in the dark. Good quality red crystals were obtained after several days. Yield: 62%. Anal. Calc. for $\text{C}_{22}\text{H}_{20.5}\text{FeN}_2\text{O}_3\text{Zn}_{0.5}$ (%): C, 60.91; H, 4.73; N, 6.46. Found: C, 60.95; H, 4.70; N, 6.48%. IR (cm^{-1} , KBr): 3419s, 3126s, 1708s, 1638s, 1580s, 1526m, 1369s, 1284m, 1240s, 1102s, 1029m, 976m, 827s, 749m, 686m, 657m, 623m, 494s.

Synthesis of $\{[\text{Zn}(\text{OOCCH}=\text{CHFc})(\text{ntb})](\text{CH}_3\text{OH})\}_n$ (**1b**): A methanol solution (10 mL) of ntb (10.18 mg, 0.025 mmol) was added to THF (4 mL) solution of **1** (17.9 mg, 0.025 mmol) at room temperature. Allowing the mixture to set at room temperature in the dark for two weeks afforded the product as red crystals. Yield: 65%. Anal. Calc. for $\text{C}_{15.2}\text{H}_{13.2}\text{Fe}_{0.4}\text{N}_{2.8}\text{O}_{1.2}\text{Zn}_{0.4}$ (%): C, 60.24; H, 4.36; N, 12.95. Found: C, 60.20; H, 4.35; N, 12.98%. IR (cm^{-1} , KBr): 3420m, 2919m, 1705m, 1639s, 1558s, 1538s, 1470m, 1454s, 1401s, 1349m, 1275m, 1254m, 1041s, 1002m, 820m, 751s, 490m.

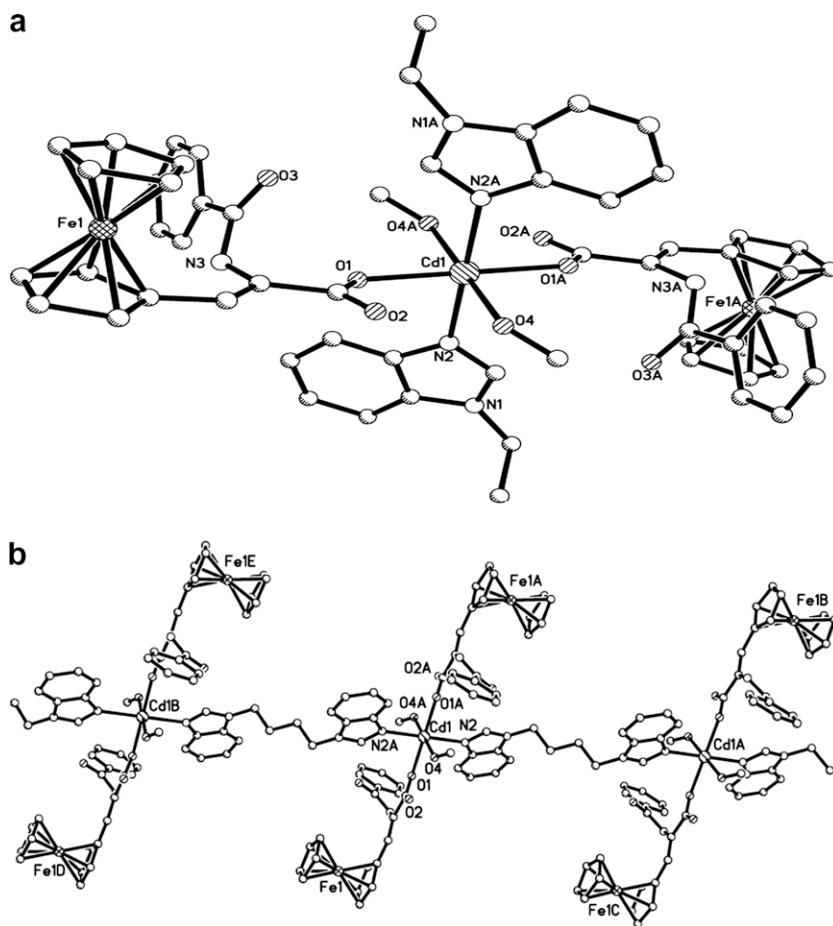


Fig. 5. (a) Perspective view of the repeating unit in complex $\{[\text{Cd}(\text{bafca})_2(\text{bbbm})(\text{CH}_3\text{OH})_2] \cdot 6\text{CH}_3\text{OH}\}_n$ (**2b**). (b) One-dimensional chain structure of complex $\{[\text{Cd}(\text{bafca})_2(\text{bbbm})(\text{CH}_3\text{OH})_2] \cdot 6\text{CH}_3\text{OH}\}_n$ (**2b**). Hydrogen atoms and solvent molecules are omitted for clarity in figures (a) and (b).

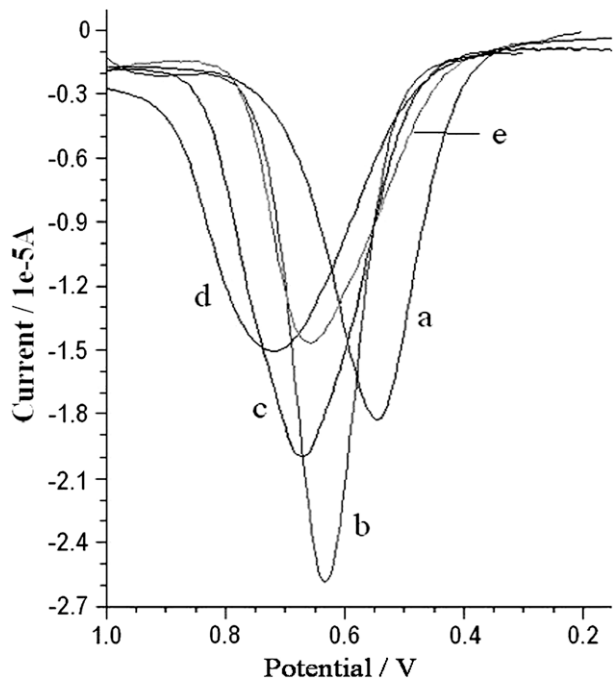


Fig. 6. Differential pulse voltammogram of (a) **Fc**, (b) **FcCH=CHCOOH**, (c) **1**, (d) **1b** and (e) **1a** in THF containing $n\text{-Bu}_4\text{NClO}_4$ (0.1 M) at a scan rate of 20 mV s^{-1} .

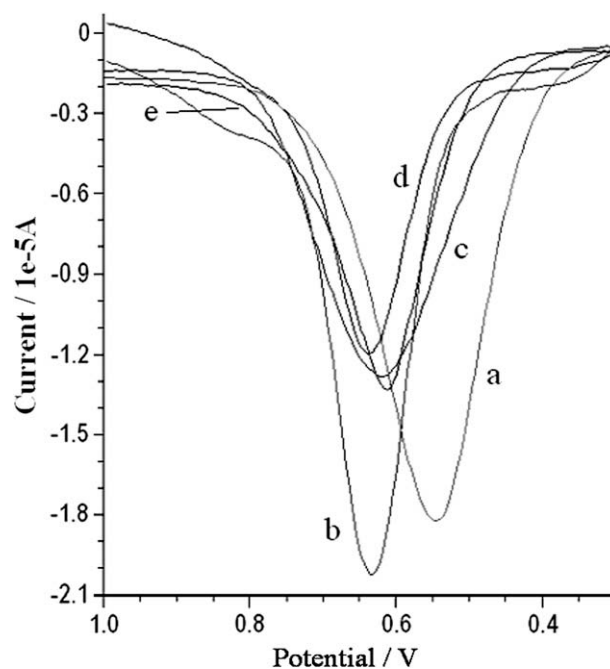


Fig. 7. Differential pulse voltammogram of (a) **Fc**, (b) **2a**, (c) **2**, (d) **2b** and (e) **bafcaNa** in THF containing $n\text{-Bu}_4\text{NClO}_4$ (0.1 M) at a scan rate of 20 mV s^{-1} .

Table 1
Crystal data and structure refinement for complexes **1–2b**.

Complex	1	1a	1b	2a	2b
Formula	C ₁₄ H ₁₄ FeO ₃ ZnO ₅	C ₂₂ H _{20.5} FeN ₂ O ₂ ZnO ₅	C _{15.2} H _{13.2} FeO ₄ N _{2.8} O _{1.2} ZnO ₄	C ₅₀ H ₄₂ Fe ₂ N ₄ O _{10.5} Cd	C ₆₆ H ₈₀ Fe ₂ N ₆ O ₁₄ Cd
Formula weight	318.79	433.44	302.77	1090.98	1405.46
Temperature (K)	291(2)	291(2)	293(2)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	<i>pbcn</i>	<i>P2(1)2(1)2(1)</i>	<i>P2(1)/c</i>	<i>P1</i>	<i>P1</i>
<i>a</i> (Å)	7.5435(15)	9.875(2)	12.700(3)	11.5673(10)	9.924(3)
<i>b</i> (Å)	10.591(2)	15.845(3)	19.630(4)	14.0736(12)	10.586(3)
<i>c</i> (Å)	34.010(7)	25.158(5)	14.781(3)	16.2488(14)	15.880(4)
α (°)	90	90	90	96.3300(10)	80.254(4)
β (°)	90	90	106.20(3)	98.6790(10)	83.254(4)
γ (°)	90	90	90	108.0320(10)	89.596(4)
<i>V</i> (Å ³)	2717.3(9)	3847.6(13)	3538.8(12)	2451.6(4)	1632.8(7)
<i>Z</i>	8	8	10	2	1
<i>D_c</i> (g cm ⁻³)	1.558	1.463	1.421	1.478	1.429
<i>F</i> (000)	1304	1788	1560	1108	730
θ range for data collection (°)	2.40–26.00	2.22–25.25	2.66–25.00	2.44–25.50	2.31–27.50
Reflections collected/unique	15 253/2626	26 470/6909	34 260/5977	13 242/8933	9935/7216
Data/restraints/parameters	2626/0/168	6909/0/496	5977/0/453	8933/0/610	7216/9/410
Goodness-of-fit (GOF) on <i>F</i> ²	1.000	0.933	1.116	1.062	1.029
Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b	0.0637, 0.1156	0.0754, 0.0602	0.0992, 0.1735	0.0485, 0.1356	0.04447, 0.1051

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$.^b $wR2 = [w(|F_o|^2 - |F_c|^2) / \sum (|F_o|^2)]^{1/2}$, $w = 1 / [\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2) / 3$.**Table 2**
Selected bond lengths (Å) and angles (°) for complexes **1–2b**.

Complex 1^a					
Zn1–O1	2.402(4)	Zn1–O2	2.005(3)	Zn1–O3	2.027(4)
Zn1–O1#1	2.402(4)	Zn1–O2#1	2.005(3)	Zn1–O3#1	2.027(4)
O(2)–Zn(1)–O(1)	58.78(13)	O(3)–Zn(1)–O(1)	95.33(17)	O(2)–Zn(1)–O(3)	109.63(18)
O(2)#1–Zn(1)–O(1)	94.20(15)	O(3)#1–Zn(1)–O(1)	152.42(14)	O(1)#1–Zn(1)–O(1)	85.1(2)
O(2)#1–Zn(1)–O(2)	144.8(2)	O(3)–Zn(1)–O(3)#1	96.7(3)	O(2)–Zn(1)–O(3)#1	93.75(16)
Complex 1a^b					
Zn(1)–O(2)	1.914(5)	Zn(1)–O(3)	1.963(5)	Zn(1)–N(1)	2.010(6)
Zn(1)–N(4)#1	2.031(6)	O(2)–Zn(1)–O(3)	111.7(2)	N(4)–Zn(1)#2	2.031(6)
O(2)–Zn(1)–N(1)	117.1(2)	O(3)–Zn(1)–N(1)	110.5(3)	O(2)–Zn(1)–N(4)#1	108.7(3)
O(3)–Zn(1)–N(4)#1	102.1(3)	N(1)–Zn(1)–N(4)#1	105.4(2)		
Complex 1b					
Zn(1)–N(1)	2.512(5)	Zn(1)–N(2)	2.013(5)	Zn(1)–N(4)	2.058(5)
Zn(1)–N(6)	2.060(5)	Zn(1)–O(2)	1.985(4)	O(2)–Zn(1)–N(2)	109.2(2)
O(2)–Zn(1)–N(4)	106.9(2)	N(2)–Zn(1)–N(4)	125.2(2)	O(2)–Zn(1)–N(6)	100.0(2)
N(2)–Zn(1)–N(6)	105.9(2)	N(4)–Zn(1)–N(6)	106.8(2)	O(2)–Zn(1)–N(1)	174.57(19)
N(2)–Zn(1)–N(1)	73.95(19)	N(4)–Zn(1)–N(1)	73.87(19)	N(6)–Zn(1)–N(1)	74.74(19)
Complex 2a^c					
Cd(1)–O(1)	2.437(3)	Cd(1)–O(2)	2.379(3)	Cd(1)–O(2)#1	2.395(3)
Cd(1)–O(4)	2.269(3)	Cd(1)–N(1)	2.305(3)	Cd(1)–N(4)	2.349(3)
O(4)–Cd(1)–N(1)	166.95(12)	O(4)–Cd(1)–N(4)	96.40(12)	N(1)–Cd(1)–N(4)	71.18(12)
O(4)–Cd(1)–O(2)	87.38(11)	N(1)–Cd(1)–O(2)	105.08(11)	N(4)–Cd(1)–O(2)	145.26(11)
O(4)–Cd(1)–O(2)#1	96.35(12)	N(1)–Cd(1)–O(2)#1	91.62(12)	N(4)–Cd(1)–O(2)#1	142.70(11)
O(2)–Cd(1)–O(2)#1	70.23(11)	O(4)–Cd(1)–O(1)	90.90(12)	N(1)–Cd(1)–O(1)	93.28(12)
N(4)–Cd(1)–O(1)	91.07(11)	O(2)–Cd(1)–O(1)	54.27(10)	O(2)#1–Cd(1)–O(1)	123.58(10)
Complex 2b^d					
Cd(1)–O(1)	2.259(2)	Cd(1)–O(1)#1	2.259(2)	Cd(1)–O(4)	2.363(3)
Cd(1)–O(4)#1	2.363(3)	Cd(1)–N(2)	2.305(3)	Cd(1)–N(2)#1	2.305(3)
O(1)#1–Cd(1)–O(1)	180.00(12)	O(1)#1–Cd(1)–N(2)#1	91.20(9)	O(1)–Cd(1)–N(2)#1	88.80(9)
O(1)#1–Cd(1)–N(2)	88.80(9)	O(1)–Cd(1)–N(2)	91.20(9)	N(2)#1–Cd(1)–N(2)	180.000(2)
O(1)#1–Cd(1)–O(4)#1	88.25(9)	O(1)–Cd(1)–O(4)#1	91.75(9)	N(2)#1–Cd(1)–O(4)#1	93.25(12)
N(2)–Cd(1)–O(4)#1	86.75(12)	O(1)#1–Cd(1)–O(4)	91.75(9)	O(1)–Cd(1)–O(4)	88.25(9)
N(2)#1–Cd(1)–O(4)	86.74(12)	N(2)–Cd(1)–O(4)	93.26(12)	O(4)#1–Cd(1)–O(4)	180.00(14)

^a Symmetry transformations used to generate equivalent atoms in complex **1**: #1 $-x, y, -z + 1/2$.^b Symmetry transformations used to generate equivalent atoms in complex **1a**: #1 $-x + 2, y + 1/2, -z + 3/2$; #2 $-x + 2, y - 1/2, -z + 3/2$.^c Symmetry transformations used to generate equivalent atoms in complex **2a**: #1 $-x + 1, -y + 2, -z$.^d Symmetry transformations used to generate equivalent atoms in complex **2b**: #1 $-x + 2, -y + 1, -z + 1$; #2 $-x + 3, -y, -z + 1$.

Synthesis of [Cd(bafca)₂(2,2'-bpy)]₂ · 9H₂O (**2a**): A solution of 2,2'-bpy (15.6 mg 0.1 mmol) in the methanol (10 mL) was added to the solution of **2** (179.4 mg 0.1 mmol) in H₂O (10 mL) to give a clear solution. The solution was kept at room temperature in the

dark. A few days later, red crystals of **2a** were obtained. Yield: 68%. Anal. Calc. for C₅₀H₄₂CdFe₂N₄O_{10.5} (%): C, 54.99; H, 3.85; N, 5.13. Found: C, 54.96; H, 3.81; N, 5.17%. IR (cm⁻¹, KBr): 3423m, 2938m, 2786s, 1568s, 1397m, 826m, 748s.

Synthesis of $\{[\text{Cd}(\text{bafca})_2(\text{bbbm})(\text{CH}_3\text{OH})_2] \cdot 6\text{CH}_3\text{OH}\}_n$ (**2b**): A solution of **bbbm** (29.2 mg 0.1 mmol) in the methanol (10 mL) was added to the solution of **2** (179.4 mg 0.1 mmol) in H_2O (10 mL) to give a clear solution. The solution was kept at room temperature in the dark. About three weeks later, red crystals of **2b** were obtained. Yield: 59%. Anal. Calc. for $\text{C}_{66}\text{H}_{80}\text{CdFe}_2\text{N}_6\text{O}_{14}$ (%): C, 56.35; H, 5.69; N, 5.98. Found: C, 56.39; H, 5.71; N, 5.95%. IR (cm^{-1} , KBr): 3426m, 2879m, 2368s, 1576s, 1324m, 856m, 738s.

3.3. Crystallographic studies

Single crystals of **1**, **1a** and **1b** were selected for indexing and intensity data collection on a Rigaku Saturn 724 CCD diffractometer using graphite-monochromated $\text{Mo K}\alpha$ X-radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. For **2a** and **2b**, Single crystal X-ray diffraction was performed by using a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$) at room temperature. A single crystal suitable for X-ray diffraction was mounted on a glass fiber. The data were integrated using the Siemens SAINT program [23]. Absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL [24]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic and refinement details are listed in Table 1, with selected bond lengths and angles in Table 2.

3.4. Differential pulse voltammetry measurements

Differential pulse voltammetry studies were recorded with a CHI 660B electrochemical analyzer. A three-electrode system was used, which consists of a platinum working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. The measurements were performed in THF containing tetrabutyl ammonium perchlorate ($n\text{-Bu}_4\text{NClO}_4$) (0.1 mol dm^{-3}) as supporting electrolyte, which has a 50 ms pulse width and a 16.7 ms sample width. The potential was scanned from 0.0 to +1.0 V at a scan rate of 20 mV s^{-1} .

3.5. Molecular weight measurements

The molecular weight and molecular weight distribution of the polymers were determined at $40 \text{ }^\circ\text{C}$ with gel permeation chromatography (Waters Associates model HPLC/GPC 515 liquid chromatography, equipped with a refractive index detector and calibrated with standard polystyrene), using THF as eluent and a flow rate of 1.0 mL min^{-1} .

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.008.

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