



## Construction of Cd(II)–ferrocenesuccinate coordination complexes via changing adjuvant ligands and anions

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### ABSTRACT

Seven Cd(II)–ferrocenesuccinate coordination complexes with the formulas  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{pbbbm})]_2$  (**1**),  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{pbbbm})\text{Cl}]_2$  (**2**),  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{pbbbm})]_2$  (**3**),  $\{[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{btx})_2]_2(\text{CH}_3\text{OH})_{0.5}\}$  (**4**),  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{bix})]_2(\text{H}_2\text{O})$  (**5**),  $\{[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{mbbbm})_{1.5}\text{Cl}] \cdot (\text{CH}_3\text{OH})_{0.5}\}_n$  (**6**), and  $\{[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{mbbbm})\text{Cl}] \cdot (\text{H}_2\text{O})_{2.75}\}_n$  (**7**) [ $\text{pbbbm} = 1,4\text{-Bis}(\text{benzimidazole-1-ylmethyl})\text{benzene}$ ,  $\text{btx} = 1,4\text{-bis}(\text{triazol-1-ylmethyl})\text{benzene}$ ,  $\text{mbbbm} = 1,3\text{-bis}(\text{benzimidazole-1-ylmethyl})\text{benzene}$ ,  $\text{bix} = 1,4\text{-bis}(\text{imidazol-1-ylmethyl})\text{benzene}$ ,  $\text{bbbm} = 1,1\text{-(1,4-Butanediyl)bis-1H-benzimidazole}$ ] have been synthesized and characterized. Single-crystal X-ray analysis reveals that complexes **1–5** are all dimers and bridged by pbbbm, btx and bix, respectively. But the five complexes present some differences in their dimeric conformations, which can be ascribed to the impacts of adjuvant ligands and counter anions. In contrast to complexes **1–5**, both **6** and **7** are of 1-D structures (with the same counter anions), and the former is double ladder-like structure only bridged by bbbm, while the latter is chain-like structure bridged by chlorine anions and adjuvant ligand mbbbm. Notably, various  $\pi\text{-}\pi$  interactions are found in complexes **1–7**, and they have significant contributions to molecular self-assembly processes. The electrochemical studies of complexes **1–7** in DMF solution display irreversible redox waves and indicate that the half-wave potentials of the ferrocenyl moieties in these complexes are all shifted to positive potential compared with that of ferrocenesuccinate.

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### 1. Introduction

In recent years, the rational design and synthesis of metal–organic complexes have been of increasing interest because of their intriguing architectures [1] and potential application to gas storage, ion change, catalysis, and so on [2]. Although a variety of metal coordination complexes with beautiful topologies and interesting properties have been synthesized to date, the prediction of coordination frameworks is still subjective and can not be generalized because the self-assembly process is highly influenced by several factors, such as the organic ligand, metal/ligand ratio, solvent system, templates, and counterions [3]. Among these factors, the organic ligand has a great influence on determining the type and topology of the products. Hence, from the viewpoint of crystal engineering, the appropriate choice of the well-designed organic ligands, containing modifiable backbones and connectivity information, is a reasonable and effective synthetic approach to build new coordination complexes with tailored-made architectures and specific chemical and physical properties [4].

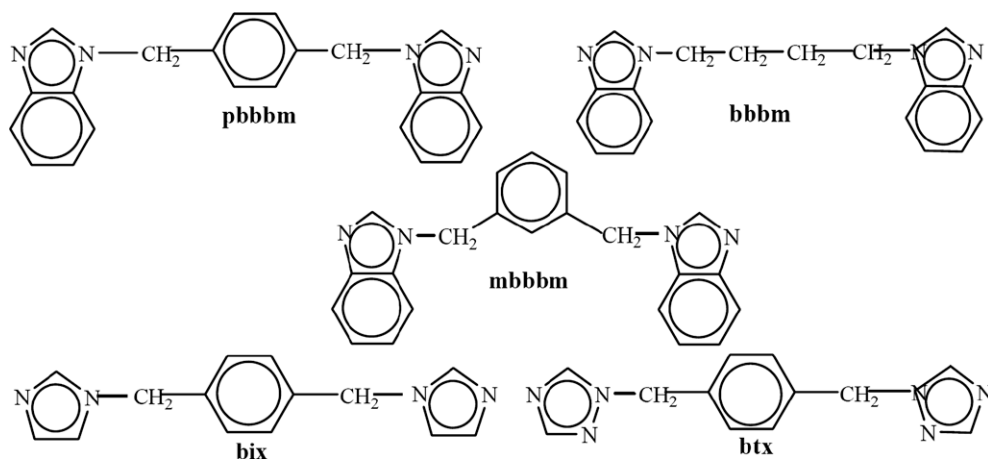
As we know, the derivatives of benzimidazole, imidazole and triazole are excellent adjuvant nitrogen-heterocyclic ligands and

often used to construct complexes with various configurations [5,6]. In particular, their aromatic rings attract our interest because of their importance in crystal engineering, which may form strong  $\pi\text{-}\pi$  stacking interactions, and may lead to variable  $\pi\text{-}\pi$  interactions modes and architectures. The synthesis of  $\pi\text{-}\pi$  stacked molecular architectures is of great importance to understand the electronic interactions between molecules since  $\pi\text{-}\pi$  interactions play an essential role in biology and in the functions of organic semiconducting materials [7]. Furthermore, from the viewpoint of constructing functional complexes, the introduction of ferrocenyl group into the metal–organic frameworks provides a good selection of preparing new functional materials with unique features [8]. Additionally, the coordinating capability of ferrocenyl carboxylate groups to metal ions is strong, and the coordination modes are also versatile [9]. Therefore, we choose ferrocenesuccinic acid as functional ligands to synthesize the complexes. The combinations of ferrocenesuccinic acid with adjuvant nitrogen-heterocyclic ligands as mentioned above may be expected to exhibit variable  $\pi\text{-}\pi$  interactions modes and interesting structures.

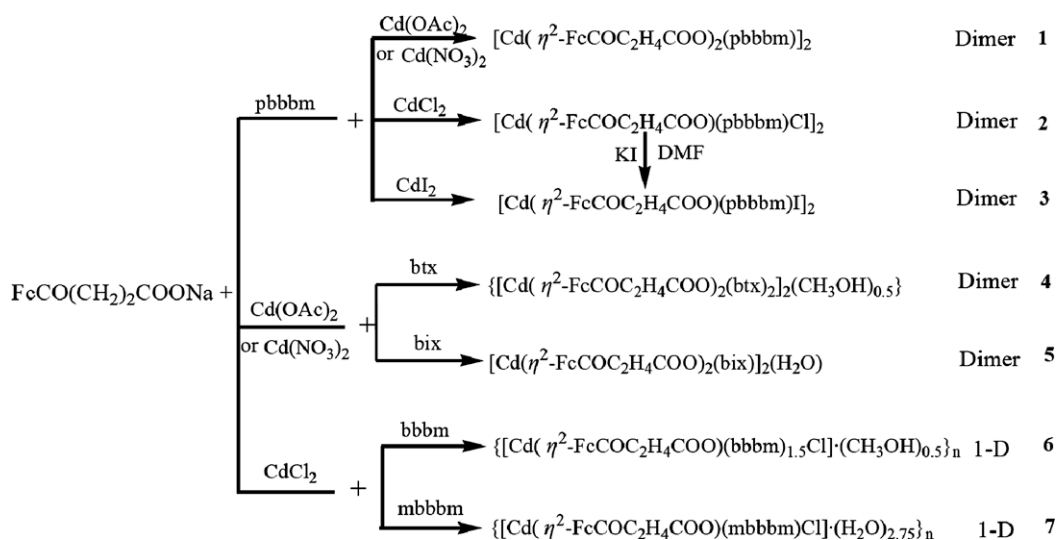
As a part of our ongoing efforts to design and synthesize metal–organic complexes based on above-mentioned reasons, a series of nitrogen-heterocyclic compounds as adjuvant ligands (Scheme 1) and ferrocenesuccinic acid were chosen to react with various Cd(II) salts. Herein, we report the preparations, crystal structures and

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Scheme 1. Organic nitrogen-heterocyclic ligands.



Scheme 2. Syntheses of complexes 1–7.

electrochemistry properties of seven new Cd(II)–ferrocenesuccinate coordination complexes (Scheme 2) self-assembled by  $\pi$ – $\pi$  stacking interactions and weak hydrogen bonds in combination with metal–ligand bonds. The influence of adjuvant ligands and anions ( $\text{Cl}^-$  and  $\text{I}^-$ ) on their structures and the  $\pi$ – $\pi$  stacking interactions involving the aromatic systems are discussed.

## 2. Experimental

### 2.1. General information and materials

Ferrocenesuccinic acid and its corresponding sodium salt were prepared according to literature methods [10]. 1,4-Bis(benzimidazole-1-ylmethyl)benzene (pbbbm), 1,3-bis(benzimidazole-1-ylmethyl)benzene (mbbbm), 1,4-bis(imidazol-1-ylmethyl)benzene (bix), 1,4-bis(triazol-1-ylmethyl)benzene (btx) and 1,1-(1,4-Butanediy)bis-1*H*-benzimidazole (bbbm) were prepared according to the literatures [11]. All other chemicals were obtained from commercial sources and used without further purification. Carbon, hydrogen and nitrogen analyses were carried out on a FLASH EA 1112 elemental analyzer. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400–4000  $\text{cm}^{-1}$  region. Cyclic voltammetric experiments were performed by

employing a CHI 660B electrochemical analyzer. A three-electrode system was used, which consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. The measurements were carried out in DMF solutions with tetrabutyl ammonium perchlorate ( $n\text{-Bu}_4\text{NClO}_4$ ) ( $0.1 \text{ mol dm}^{-3}$ ) as a supporting electrolyte. To prevent fouling, the working electrode was polished. Pure  $\text{N}_2$  gas was bubbled through the electrolytic solution to remove oxygen.

### 2.2. Preparation of $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{pbbbm})]_2$ (1)

The methanol solution (6 mL) of adjuvant ligand pbbbm (32.8 mg, 0.1 mmol) was added to a methanol solution (4 mL) of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (13.4 mg, 0.05 mmol) [or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (15.4 mg, 0.05 mmol)], and then methanol solution (6 mL) of  $\text{FcCOC}_2\text{H}_4\text{COONa}$  (30.8 mg, 0.10 mmol) was added to the above mixture. The resulting mixture was kept at room temperature in the dark. One week later, red crystals suitable for X-ray diffraction were obtained from the resultant orange solution. Yield: 55%. Anal. Calc. for  $\text{C}_{100}\text{H}_{88}\text{Cd}_2\text{Fe}_4\text{N}_8\text{O}_{12}$ : C, 58.77; H, 4.31; N, 5.48. Found: C, 58.90; H, 4.43; N, 5.31%. IR ( $\text{cm}^{-1}$ , KBr): 3446w, 3018w, 1663s, 1560s, 1509m, 1457s, 1385s, 1295m, 1260m, 1208m, 1086w, 1027w, 747s, 487w.

### 2.3. Preparation of $[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{pbbbm})\text{Cl}]_2$ (**2**)

The procedure was the same as that for **1**,  $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$  was used instead of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  [or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ]. Yield: 52%. Anal. Calc. for  $\text{C}_{36}\text{H}_{31}\text{CdClFeN}_4\text{O}_3$ : C, 56.01; H, 4.02; N, 7.26. Found: C, 55.94; H, 4.18; N, 7.31%. IR ( $\text{cm}^{-1}$ , KBr): 3446m, 3105m, 1663s, 1560m, 1457s, 1421s, 1260m, 1192m, 1006w, 748s, 487m.

### 2.4. Preparation of $[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{pbbbm})\text{I}]_2$ (**3**)

**Method A:** The procedure was the same as that for **1**,  $\text{CdI}_2 \cdot 5\text{H}_2\text{O}$  was used instead of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (13.4 mg, 0.05 mmol) [or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (15.4 mg, 0.05 mmol)]. Yield: 53%.

**Method B:** The crystals of complex **2** (7.71 mg, 0.01 mmol) were completely dissolved in DMF solution (5 mL). A methanol solution (5 mL) of KI (1.66 mg, 0.01 mmol) was added dropwise to the above solution. About one week later good quality red crystals were obtained from the resultant orange solution at room temperature in the dark. Yield: 43%.

Anal. Calc. for  $\text{C}_{36}\text{H}_{31}\text{CdIFeN}_4\text{O}_3$ : C, 50.07; H, 3.59; N, 6.49. Found: C, 50.14; H, 3.48; N, 6.31%. IR ( $\text{cm}^{-1}$ , KBr): 3446m, 3106m, 1661s, 1556s, 1509s, 1457s, 1386s, 1260m, 1193m, 1007w, 746s, 488m.

### 2.5. Preparation of $[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{btx})_2]_2 \cdot (\text{CH}_3\text{OH})_{0.5}$ (**4**)

The procedure was the same as that for **1**, **btx** was used instead of **pbbbm**. Yield: 56%. Anal. Calc. for  $\text{C}_{105}\text{H}_{103}\text{Cd}_2\text{Fe}_4\text{O}_{13}\text{N}_{24}$ : C, 53.45; H, 4.36; N, 14.25. Found: C, 53.76; H, 4.43; N, 13.98%. IR ( $\text{cm}^{-1}$ , KBr): 3420m, 3107m, 1655s, 1566s, 1518s, 1454s, 1414s, 1310s, 1277m, 1207m, 1131s, 1015m, 982m, 772m, 732m, 482m.

### 2.6. Preparation of $[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{bix})_2]_2 \cdot (\text{H}_2\text{O})$ (**5**)

The procedure was the same as that for **1**, **bix** was used instead of **pbbbm**. Yield: 46%. Anal. Calc. for  $\text{C}_{84}\text{H}_{80}\text{Cd}_2\text{Fe}_4\text{N}_8\text{O}_{13}$ : C, 54.25; H, 4.31; N, 6.03. Found: C, 54.14; H, 4.48; N, 6.21%. IR ( $\text{cm}^{-1}$ , KBr): 3471m, 3118m, 1663s, 1568s, 1454m, 1417s, 1304m, 1257m, 1087m, 1008w, 826m, 743m, 484m.

### 2.7. Preparation of $\{[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{bbbm})_{1.5}\text{Cl}] \cdot (\text{CH}_3\text{OH})_{0.5}\}_n$ (**6**)

The methanol solution (4 mL) of **bbbm** (29 mg, 0.1 mmol) was added to a methanol solution (6 mL) of  $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$  (13.7 mg, 0.05 mmol), and then methanol solution (4 mL) of  $\text{FcCOC}_2\text{H}_4\text{COONa}$  (30.8 mg, 0.10 mmol) was slowly diffused into the above mixture. The resultant solution was kept at room temperature. Red crystals suitable for X-ray diffraction were formed three weeks later. Yield: 46%. Anal. Calc. for  $\text{C}_{41.25}\text{H}_{38}\text{CdFeClN}_6\text{O}_{3.25}$ : C, 56.67; H, 4.35; N, 9.62. Found: C, 56.54; H, 4.52; N, 9.65%. IR ( $\text{cm}^{-1}$ , KBr): 3444m, 3102m, 2938m, 1663s, 1558s, 1507m, 1457s, 1296s, 1199w, 1005w, 748s, 485s.

### 2.8. Preparation of $\{[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{mbbbm})\text{Cl}] \cdot (\text{H}_2\text{O})_{2.75}\}_n$ (**7**)

The procedure was the same as that for **6**, **mbbbm** was used instead of **bbbm**. Yield: 45%. Anal. Calc. for  $\text{C}_{36}\text{H}_{31}\text{CdClFeN}_4\text{O}_{4.75}$ : C, 54.04; H, 3.88; N, 7.01. Found: C, 54.14; H, 3.55; N, 7.13%. IR ( $\text{cm}^{-1}$ , KBr): 3450m, 3105m, 1708m, 1661s, 1564s, 1502s, 1457s, 1415s, 1260m, 1194m, 1089m, 1005w, 747s, 486m.

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

### 2.9. Crystal structure determination

A crystal suitable for X-ray determination was mounted on a glass fiber. The data of **1–7** were collected at room temperature on a Rigaku Saturn 724 CCD with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods and expanded with 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 with the SHELXL-97 crystallographic software package [12]. Table 1 showed crystallographic crystal data and processing parameters for all complexes, and Table 2 listed their selected bond lengths and bond angles.

## 3. Results and discussion

### 3.1. Crystal structures of $[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{pbbbm})]_2$ (**1**), $[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{pbbbm})\text{Cl}]_2$ (**2**) and $[Cd(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{pbbbm})\text{I}]_2$ (**3**)

Treatment of  $\text{FcCOC}_2\text{H}_4\text{COONa}$  with  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  [or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] in the presence of **pbbbm** yielded complex **1**. Crystallographic analysis reveals that **1** crystallizes in the monoclinic space group  $P2(1)/c$  and exhibits dimeric structure. Each Cd(II) ion is six-coordinated in a distorted octahedral environment with four oxygen atoms from two  $\eta^2\text{-FcCOC}_2\text{H}_4\text{COO}^-$  units, two nitrogen atoms from two adjuvant ligands **pbbbm** (Fig. 1). The Cd–N lengths are in the range of 2.265(4)–2.287(5) Å and Cd–O lengths are in the range of 2.293(4)–2.486(5) Å. The bond angles around Cd(II) ion vary from 54.14(13) to 136.43(13)°.

When we utilized  $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$  instead of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  [or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] to react with  $\text{FcCOC}_2\text{H}_4\text{COONa}$  and **pbbbm** ligands, we obtained complex **2** (Fig. 2a). **2** crystallizes in the triclinic space group  $P-1$ . Different from complex **1**, the central Cd(II) ion in complex **2** is five-coordinated in an axially distorted, trigonal bipyramidal arrangement with one chlorine anion, two oxygen atoms from one  $\eta^2\text{-FcCOC}_2\text{H}_4\text{COO}^-$  ligand and two nitrogen atoms from two adjuvant **pbbbm** ligands. By making a comparison between the two complexes, one can see that the two bidentate coordinated  $\text{FcCOC}_2\text{H}_4\text{COO}^-$  units in complex **1** are replaced by two chlorine anions, respectively. This can be ascribed to the competition between the chlorine anions and the  $\text{FcCOC}_2\text{H}_4\text{COO}^-$  ligands in coordination with Cd(II) ions, and finally chlorine anions participate in coordination. As far as we know, it is rare to report such case that the chlorine anion can compete with ferrocenyl carboxylate ligand for the coordination with transition metal ions [13]. The Cd–O bond lengths are 2.231(3) and 2.561(3) Å, and the Cd–N bond lengths are 2.217(3) and 2.244(3) Å, respectively, all of which are different from those in **1**. The bond angles around Cd vary from 54.30(11) to 122.18(13)°.

Similarly, when we utilize  $\text{CdI}_2 \cdot 5\text{H}_2\text{O}$  instead of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  [or  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] to react with  $\text{FcCOC}_2\text{H}_4\text{COONa}$  and **pbbbm** ligands, complex **3** is obtained. It is worthy to note that the structure of **3** is similar to that of **2**, except that the two Cl anions are replaced by two I anions. Besides, the Cd··Cd distance in **3** [10.985(3) Å] is slightly shorter than that of **2** [10.997(3) Å] (see Fig. S1 of the Supporting information), and the Cd··Cd distance in **1** [11.414(2) Å] is distinctly longer than those of **2** and **3**. No hydrogen bonds exist in dimeric structures of **1**, **2** and **3**. The  $\pi$ – $\pi$  interactions play a crucial role in molecular self-assembly processes. Analysis of the crystal packing of **1** revealed that an infinite 2-D supramolecular network (see Fig. S2 of the Supporting information) was formed by the head-to-tail  $\pi$ – $\pi$  stacking interactions between two adjacent benzimidazole rings, with the inter-planar

**Table 1**  
Crystal data and structure refinement for complexes 1–7.

Complex	1	2	3	4	5	6	7
Formula	C <sub>100</sub> H <sub>88</sub> Cd <sub>2</sub> Fe <sub>4</sub> N <sub>8</sub> O <sub>12</sub>	C <sub>36</sub> H <sub>31</sub> CdClFeN <sub>4</sub> O <sub>3</sub>	C <sub>36</sub> H <sub>31</sub> CdIFeN <sub>4</sub> O <sub>3</sub>	C <sub>105</sub> H <sub>105</sub> Cd <sub>2</sub> Fe <sub>4</sub> O <sub>13</sub> N <sub>24</sub>	C <sub>84</sub> H <sub>80</sub> Cd <sub>2</sub> Fe <sub>4</sub> N <sub>8</sub> O <sub>13</sub>	C <sub>41.25</sub> H <sub>38</sub> CdFeClN <sub>6</sub> O <sub>2.25</sub>	C <sub>36</sub> H <sub>31</sub> CdClFeN <sub>4</sub> O <sub>4.75</sub>
fw	2041.98	771.35	862.80	2357.31	1857.78	873.48	799.35
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2) K	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P2(1)/c	P-1	P-1	P2(1)/c	P-1	P-1	P-1
a (Å)	13.455(3)	11.810(3)	11.972(2)	21.092(4)	13.130(3)	10.050(2)	11.364(2)
b (Å)	16.518(3)	12.498(3)	12.836(3)	10.342(2)	13.239(3)	14.603(3)	12.898(3)
c (Å)	20.645(4)	13.614(3)	13.555(3)	24.747(5)	14.456(3)	16.456(3)	15.094(3)
α (°)	90	63.05(3)	63.25(3)	90	73.10(3)	65.21(3)	66.94(3)
β (°)	99.86(3)	77.67(3)	76.77(3)	101.62(3)	65.49(3)	89.22(3)	80.08(3)
γ (°)	90	66.94(3)	65.25(3)	90	61.92(3)	70.72(3)	68.82(3)
V (Å <sup>3</sup> )	4520.7(16)	1646.4(6)	1687.3(6)	5287.7(18)	2003.0(8)	2047.4(7)	1896.7(7)
Z	2	2	2	2	1	2	2
D <sub>c</sub> (g cm <sup>-3</sup> )	1.500	1.556	1.698	1.481	1.540	1.428	1.400
F (000)	2080	780	852	2393	944	889	808
θ Range for data collection (°)	3.07–27.43	3.05–27.51	3.01–27.54	3.02–27.48	3.03–27.48	2.17–25.00	3.00–25.00
Reflections collected/unique	53430/10287	20263/7525	20513/7711	62498/12092	24408/9143	20747/7188	19218/6673
Data/restraints/params	10287/40/568	7525/0/415	7711/40/415	12092/40/677	9143/40/505	7188/78/496	6673/70/460
Goodness-of-fit on F <sup>2</sup>	1.188	1.085	1.120	1.093	1.120	1.136	1.115
Final R <sub>1</sub> <sup>a</sup> , wR <sub>2</sub> <sup>b</sup>	0.0710, 0.1482	0.0561, 0.1122	0.0715, 0.2004	0.0685, 0.1623	0.0536, 0.1302	0.0564, 0.1651	0.0711, 0.1876

<sup>a</sup> R<sub>1</sub> = |F<sub>o</sub> - F<sub>c</sub>|/F<sub>o</sub>.

<sup>b</sup> wR<sub>2</sub> = [w(|F<sub>o</sub> - F<sub>c</sub>|) / (|F<sub>o</sub>| + |F<sub>c</sub>|)]<sup>2</sup> / [w(F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)]<sup>1/2</sup>, where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3.

separation of 3.477 Å (center-to-center separation: 3.863 Å) [14]. Similarly, in **2** or **3**, the dimers are further stacked by the same π-π stacking interactions as that of **1** with the inter-planar separations of 3.472 Å (**2**) and 3.494 Å (**3**) [center-to-center separations: 3.793 Å (**2**) and 3.902 Å (**3**)], which form an infinite 2-D supramolecular network (Fig. 2b).

In addition, when KI was introduced into the DMF/methanol mixture solution of **2** (completely dissolving in the DMF/methanol mixture solution) at room temperature, **2** may serve as a precursor complex for **3** and the substitution reaction of **2** with KI yields **3**. Similarly, for the degree of ion polarization of iodine anion is bigger than that of chlorine anion, the solubility of AgI is smaller than that of AgCl and the transformation from AgCl to AgI can take place. Hence, the same phenomenon occurs between **2** and **3**.

### 3.2. Crystal structures of [Cd(η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO)<sub>2</sub>(btx)<sub>2</sub>]<sub>2</sub> · (CH<sub>3</sub>OH)<sub>0.5</sub> (**4**) and [Cd(η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO)<sub>2</sub>(bix)<sub>2</sub> · (H<sub>2</sub>O) (**5**)

Complex **4** is a neutral binuclear molecule which is composed of two Cd(II) cations, four btx ligands, two η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO<sup>-</sup> units (Fig. 3). This molecule crystallizes in the monoclinic space group P2(1)/c. The central Cd(II) ion is seven-coordinated in a distorted penta bipyramid with four oxygen atoms from two η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO<sup>-</sup> unit, three nitrogen atoms from three adjuvant btx ligands. The bond angles around Cd(II) ion vary from 54.34(13) to 176.03(13)°. The Cd-N lengths are in the range of 2.320(4)–2.379(4) Å and Cd-O lengths range from 2.343(3) to 2.538(5) Å. In the dimeric structure, two of four btx ligands (Fig. 3) act as adjuvant ligands, bonding to separate Cd(II) centers. The other two btx ligands bind to two separate Cd(II) centers, respectively. However, the N4 and N4A atoms of the residuary two btx ligands don't participate in coordination (Fig. 3) and the non-bonding distances of adjacent Cd···N are 4.971(5) Å. Due to the effect of space hinderance, the central Cd(II) ion can not hold more btx ligands.

Complex **5** has a similar crystal structure and different space group P-1 as that of dimer **1**. **5** is also a neutral binuclear molecule which is composed of two Cd(II) cations, two bix ligands, two η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO<sup>-</sup> units (Fig. 4). Each Cd(II) ion is six-coordinated in a distorted octahedral environment with four oxygen atoms from two η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO<sup>-</sup> units, two nitrogen atoms from two adjuvant ligands bix. In the dimeric structure, two bix ligands act as adjuvant ligands, bonding the separate Cd(II) centers through nitrogen atoms from imidazole groups. Due to the difference between adjuvant ligands btx and bix, one Cd(II) ion can contain two imidazole groups in **5**, while in **4**, one Cd(II) ion can hold three triazole groups. In addition, in **4** and **5**, there are π-π stacking interactions between the inter-molecular triazole (or imidazole) rings with the inter-planar separations of 3.612 Å (**4**) and 3.338 Å (**5**) [center-to-center separation: 3.856 Å (**4**) and 3.651 Å (**5**)].

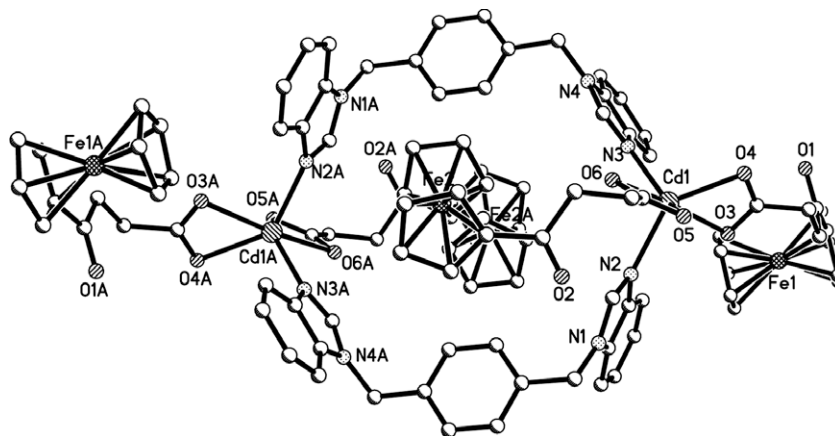
### 3.3. Crystal structures of {[Cd(η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO)(bbbm)<sub>1.5</sub>Cl] · (CH<sub>3</sub>OH)<sub>0.5</sub>]<sub>n</sub> (**6**) and {[Cd(η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO)(mbbbm)Cl] · (H<sub>2</sub>O)<sub>2.75</sub>]<sub>n</sub> (**7**)

Complex **6** features a 1-D double ladder-like chain structure. Each six-coordinated Cd(II) ion is in a distorted octahedral environment with two oxygen atoms from one η<sup>2</sup>-FcCOC<sub>2</sub>H<sub>4</sub>COO<sup>-</sup> unit, three nitrogen atoms from three adjuvant ligands bbbm and a chlorine anion (Fig. 5a). The bond angles around Cd(II) ion vary from 54.02(15)° to 162.23(16)°. The Cd-N lengths are in the range of 2.326(4)–2.418(4) Å and Cd-O lengths range from 2.346(3) to 2.467(4) Å. The chlorine anion competes with FcCOC<sub>2</sub>H<sub>4</sub>COO<sup>-</sup> ligand and participates in coordination. The Cd-Cl length is 2.523(2) Å. The adjuvant ligands bbbm link Cd(II) ions into an infinite 1-D double ladder-like chain (Fig. 5b). In the double ladder-



**Table 2**  
Selected bond lengths (Å) and angles (°) for complexes 1–7.

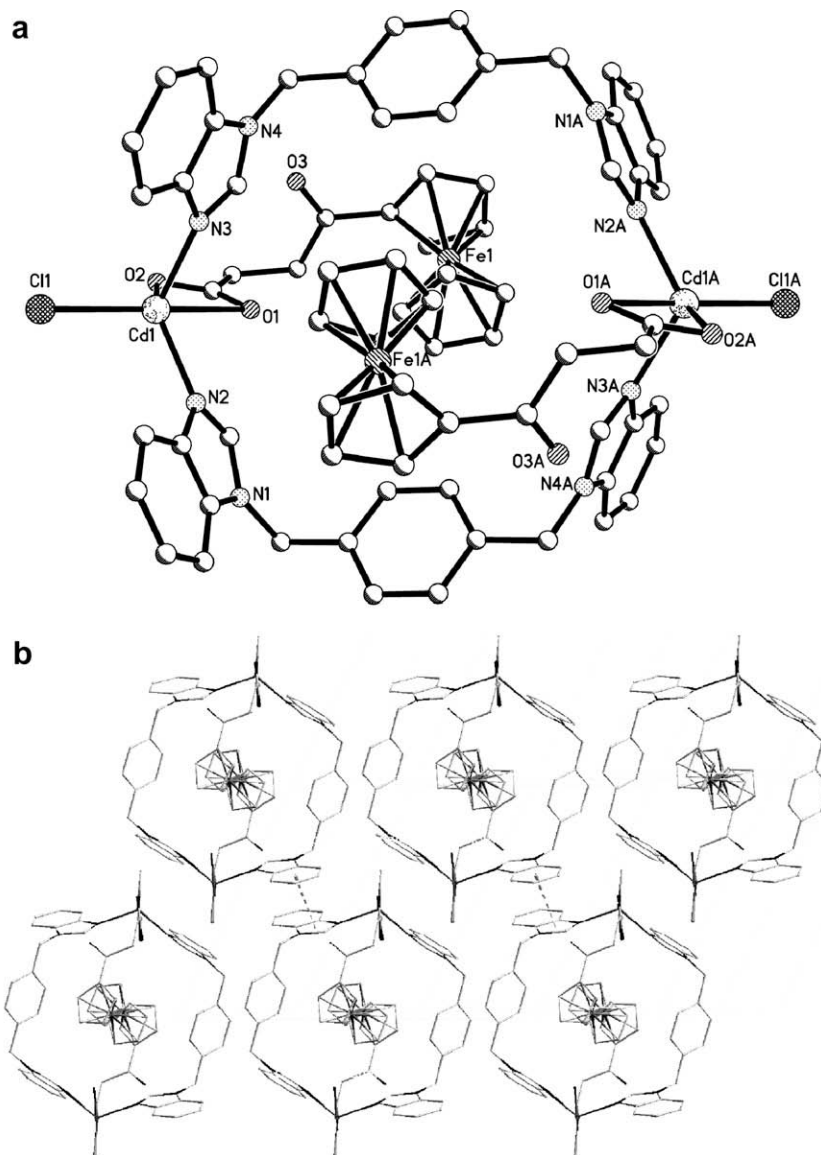
<b>Complex 1<sup>a</sup></b>					
Cd(1)–N(3)	2.265(4)	Cd(1)–N(2)	2.287(4)	Cd(1)–O(4)	2.293(4)
Cd(1)–O(5)	2.335(4)	Cd(1)–O(3)	2.481(4)	N(3)–Cd(1)–N(2)	110.44(14)
N(3)–Cd(1)–O(4)	99.48(15)	N(2)–Cd(1)–O(4)	136.43(13)	N(2)–Cd(1)–O(5)	91.48(14)
<b>Complex 2<sup>b</sup></b>					
Cd(1)–N(2)	2.217(3)	Cd(1)–O(2)	2.231(3)	Cd(1)–N(3)	2.244(3)
Cd(1)–O(1)	2.561(3)	Cd(1)–Cl(1)	2.4615(16)	N(3)–Cd(1)–O(1)	87.27(11)
N(2)–Cd(1)–N(3)	115.20(13)	O(2)–Cd(1)–N(3)	101.79(13)	Cl(1)–Cd(1)–O(1)	160.31(8)
<b>Complex 3<sup>c</sup></b>					
Cd(1)–N(3)	2.225(6)	Cd(1)–N(2)	2.262(6)	Cd(1)–O(1)	2.262(6)
Cd(1)–I(1)	2.7626(13)	Cd(1)–O(2)	2.527(6)	N(3)–Cd(1)–O(2)	83.8(2)
N(2)–Cd(1)–O(2)	87.2(2)	O(1)–Cd(1)–O(2)	54.2(2)	N(3)–Cd(1)–I(1)	104.04(16)
<b>Complex 4<sup>d</sup></b>					
Cd(1)–N(10)	2.320(4)	Cd(1)–O(1)	2.343(3)	Cd(1)–N(1)	2.371(4)
Cd(1)–N(7)	2.379(4)	Cd(1)–O(3)	2.384(4)	O(1)–Cd(1)–N(7)	90.53(14)
N(10)–Cd(1)–N(1)	86.34(16)	O(1)–Cd(1)–N(1)	85.88(14)	N(10)–Cd(1)–N(7)	97.36(16)
<b>Complex 5<sup>e</sup></b>					
Cd(1)–N(1)	2.226(3)	Cd(1)–O(3)	2.260(3)	Cd(1)–O(4)	2.329(3)
Cd(1)–O(2)	2.529(3)	Cd(1)–O(5)	2.579(3)	N(1)–Cd(1)–O(3)	103.17(12)
N(1)–Cd(1)–O(4)	95.34(12)	O(3)–Cd(1)–O(4)	93.13(10)	N(1)–Cd(1)–O(2)	86.31(12)
<b>Complex 6<sup>f</sup></b>					
Cd(1)–N(4)#1	2.326(4)	Cd(1)–O(2)	2.346(4)	Cd(1)–N(5)	2.390(4)
Cd(1)–N(1)	2.418(4)	Cd(1)–Cl(1)	2.523(2)	O(2)–Cd(1)–O(1)	54.02(15)
N(1)–Cd(1)–O(1)	82.02(15)	O(2)–Cd(1)–Cl(1)	154.02(12)	N(5)–Cd(1)–Cl(1)	99.12(12)
<b>Complex 7<sup>g</sup></b>					
Cd(1)–O(2)	2.292(5)	Cd(1)–N(1)	2.349(6)	Cd(1)–Cl(1)	2.535(2)
Cd(1)–O(1)	2.619(7)	Cd(1)–N(4)#1	2.294(6)	O(2)–Cd(1)–N(4)#1	97.8(2)
O(2)–Cd(1)–N(1)	87.2(2)	N(1)–Cd(1)–Cl(1)	92.34(15)	O(2)–Cd(1)–O(1)	52.5(2)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms in **1**: #1  $-x + 1, -y + 1, -z + 1$ .<sup>b</sup> Symmetry transformations used to generate equivalent atoms in **2**: #1  $-x, -y + 1, -z$ .<sup>c</sup> Symmetry transformations used to generate equivalent atoms in **3**: #1  $-x + 2, -y, -z + 1$ .<sup>d</sup> Symmetry transformations used to generate equivalent atoms in **4**: #1  $-x, -y + 2, -z$ .<sup>e</sup> Symmetry transformations used to generate equivalent atoms in **5**: #1  $-x, -y + 1, -z$ .<sup>f</sup> Symmetry transformations used to generate equivalent atoms in **6**: #1  $x + 1, y, z$ ; #2  $x - 1, y, z$ ; #3  $-x + 2, -y + 2, -z$ .<sup>g</sup> Symmetry transformations used to generate equivalent atoms in **7**: #1  $-x + 2, -y, -z$ ; #2  $-x + 2, -y + 1, -z$ ; #3  $-x + 2, -y + 1, -z + 1$ .**Fig. 1.** Perspective view with partial atom-labeling scheme of the binuclear structure of complex  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{pbbbm})_2]$  (**1**). Hydrogen atoms are omitted for clarity.

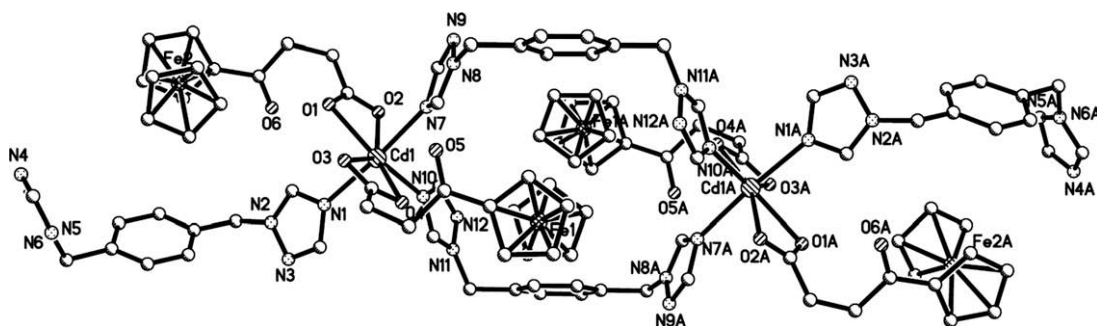
like chain, there seems to be no direct hydrogen bonding but the intramolecular edge-to-face CH/ $\pi$  interaction 2.912 Å (dihedral angle: 93.2°; H/ $\pi$ -plane separation: 2.613 Å) between intermolecular benzimidazole rings (Fig. 5a) [15]. Such  $\pi$ - $\pi$  interaction plays an important role in the forming of double ladder-like chain. An interesting feature in the two-dimensional layered supramolecular network of polymer **6** is that both types of aromatic  $\pi$ - $\pi$  stacking interactions are observed (Fig. 6). One type is the head-to-tail  $\pi$ - $\pi$  stacking interactions from intermolecular benzimidazole rings with the inter-planar separation of 3.420 Å (center-to-center separation: 3.755 Å). Another type of edge-to-face CH/ $\pi$  interactions is 2.799 Å being the dihedral angle 93.2° (H/ $\pi$ -plane separation:

2.699 Å) shorter than the mean distance (ca. 2.86 Å) of the  $\text{sp}^2\text{-CH}\cdots\pi$  reported by Suezawa et al. [15]. These two types of  $\pi$ - $\pi$  stacking interactions extend the above 1-D polymeric chains into 2-D supramolecular layers. Thus aromatic  $\pi$ - $\pi$  stacking interactions are mainly responsible for forming 2-D supramolecular layers in **6**.

X-ray crystallographic analysis reveals that **7** is made of dinuclear cadmic units, linked by the double  $\text{Cl}^-$  bridges to form 1D chains. As shown in Fig. 7a, the fundamental dinuclear unit is similar to that in **1-5**. Each six-coordinated Cd(II) ion is in a octahedral environment with two oxygen atoms from one  $\eta^2\text{-FcCOC}_2\text{H}_4\text{COO}^-$  unit, two nitrogen atoms from two adjuvant ligands mbbbm and



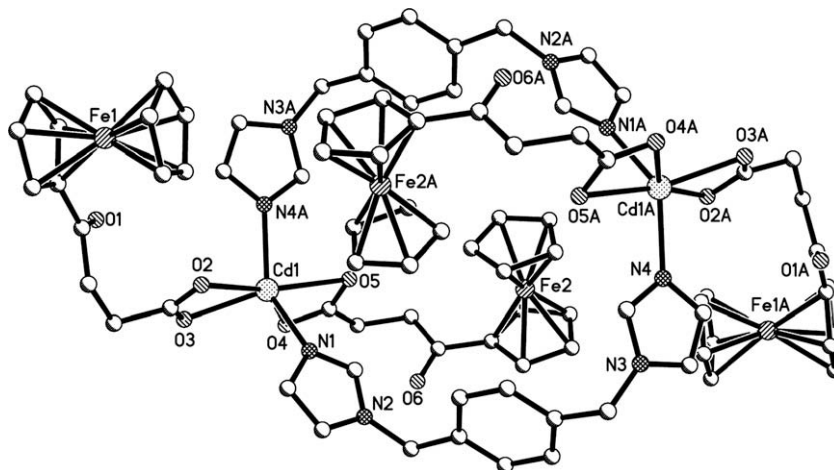
**Fig. 2.** (a) Perspective view with partial atom-labeling scheme of the binuclear structure of complex  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{pbbbm})\text{Cl}]_2$  (**2**). (b) Two-dimensional layered supramolecular network of complex **2** or **3**. The dashed lines represent the  $\pi$ - $\pi$  stacking interactions between two adjacent benzimidazole rings. Hydrogen atoms are omitted for clarity in figures (a) and (b).



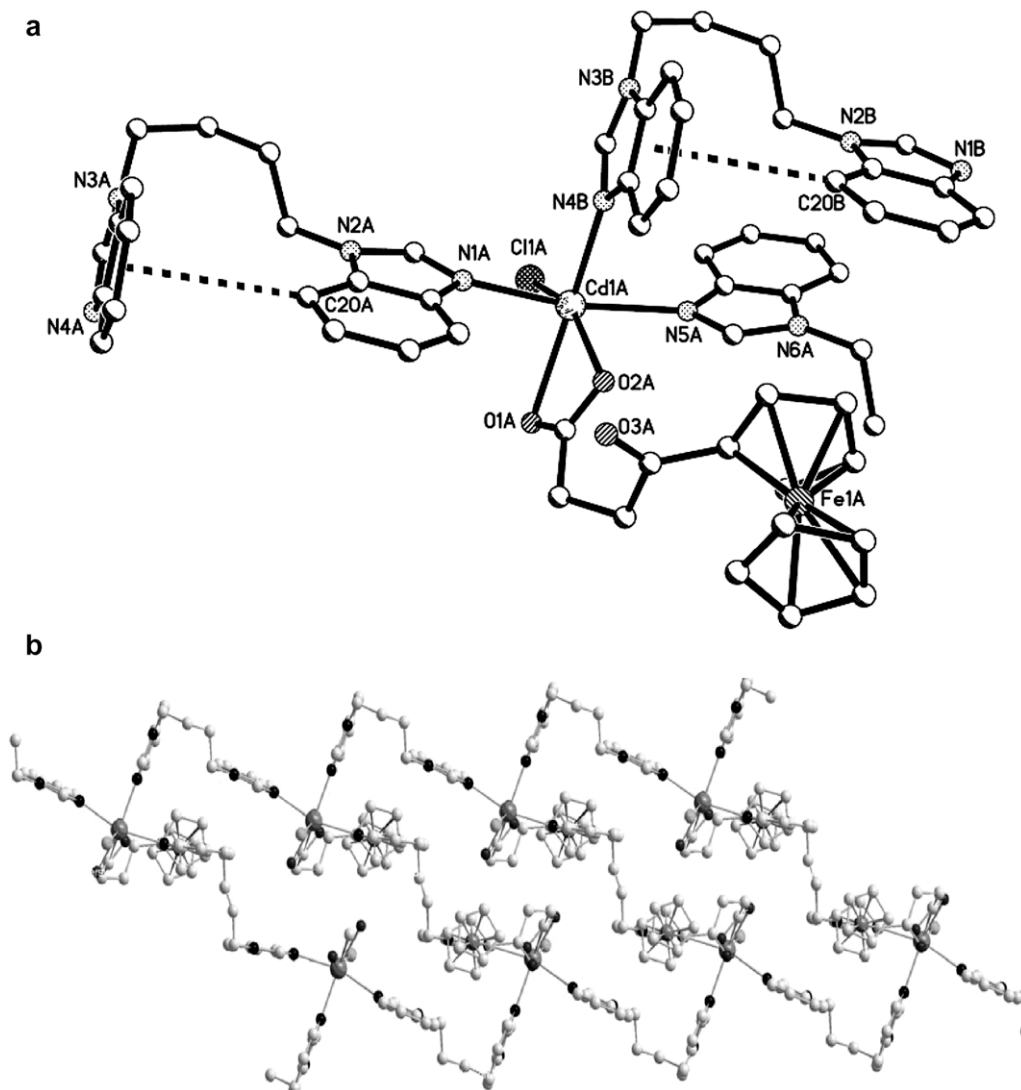
**Fig. 3.** Perspective view with partial atom-labeling scheme of the binuclear structure of complex  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{btbx})_2] \cdot (\text{CH}_3\text{OH})_{0.5}$  (**4**). Hydrogen atoms and solvent molecules are omitted for clarity.

two chlorine anions. The chlorine anion competes with  $\text{FcCOC}_2\text{H}_4\text{COO}^-$  ligand and participates in coordination. The Cd–Cl bond lengths are 2.662(2) and 2.525(2) Å, respectively. The adju-

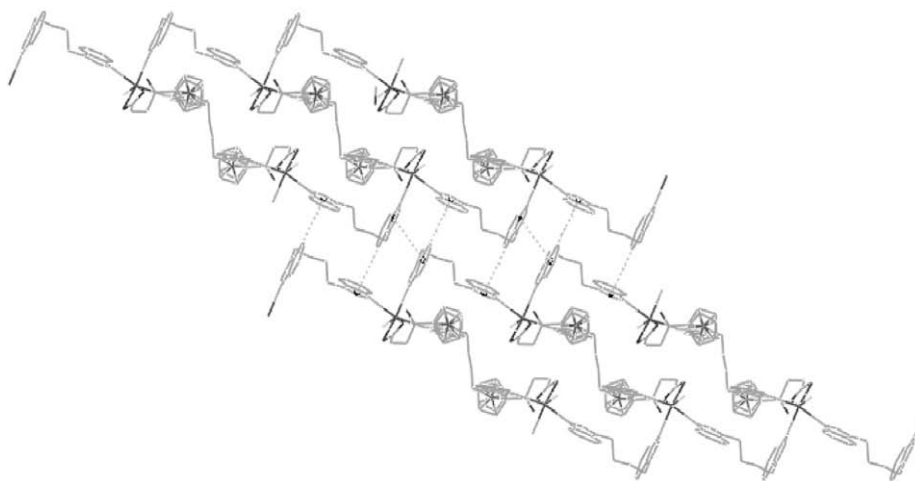
vant ligand mbbbm and chlorine anions alternately link Cd(II) ions to an infinite 1-D chain-like structure (Fig. 7a). In complex **7**, no obvious hydrogen bonds exist in 1-D chain or between two adja-



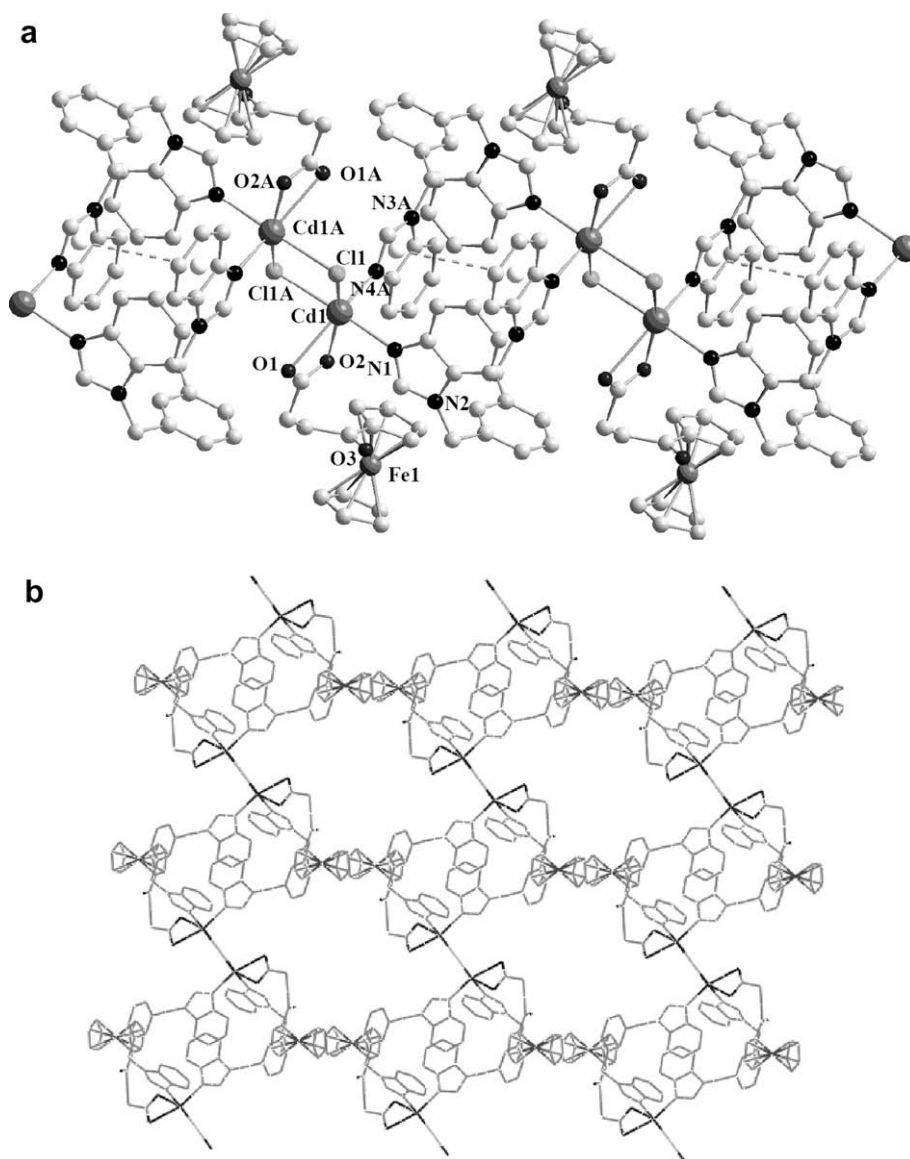
**Fig. 4.** Perspective view with partial atom-labeling scheme of the binuclear structure of complex  $[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})_2(\text{bix})]_2 \cdot (\text{H}_2\text{O})$  (**5**). Hydrogen atoms and solvent molecules are omitted for clarity.



**Fig. 5.** (a) Perspective view of the repeating unit in polymer  $\{[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{bbbm})_{1.5}\text{Cl}] \cdot (\text{CH}_3\text{OH})_{0.5}\}_n$  (**6**) with partial atom-labeling scheme (Hydrogen atoms and solvent molecules are omitted for clarity). The dashed lines represent the  $\pi$ - $\pi$  stacking interactions of edge-to-face between two adjacent benzimidazole rings in a chain. (b) One-dimensional double ladder-like chain structure of polymer **6** with hydrogen atoms and solvent molecules being omitted for clarity.



**Fig. 6.** Two-dimensional layered supramolecular network of polymer **6** with hydrogen atoms and solvent molecules being omitted for clarity. The dashed lines represent the  $\pi$ - $\pi$  stacking interactions of edge-to-face and face-to-face between two chains.



**Fig. 7.** (a) One-dimensional chain-like structure of polymer  $\{[\text{Cd}(\eta^2\text{-FcCOC}_2\text{H}_4\text{COO})(\text{mbbbm})\text{Cl}] \cdot (\text{H}_2\text{O})_{2.75}\}_n$  (**7**) with partial atom-labeling scheme. The dashed lines represent the  $\pi$ - $\pi$  stacking interactions between two adjacent benzimidazole rings in a chain. (b) Two-dimensional layered supramolecular network of polymer **7** along  $c$  axis. Hydrogen atoms and solvent molecules are omitted for clarity in figures (a) and (b).



cent 1-D chains. In a 1-D chain, the intramolecular head-to-tail  $\pi$ - $\pi$  stacking interactions between two adjacent benzimidazole rings give rise to inter-planar separation of 3.523 Å and a center-to-center separation of 4.066 Å (Fig. 7a). And between two adjacent chains, such 1-D chains were further assembled by similar  $\pi$ - $\pi$  interactions with the inter-planar separation of 3.376 Å (center-to-center separation: 3.655 Å) to form an infinite 2-D supramolecular network (Fig. 7b). These foregoing facts specify that the  $\pi$ - $\pi$  interactions are very important in all seven complexes, where they contribute significantly to molecular self-assembly processes.

### 3.4. Roles of adjuvant ligands and anions

The structures of complexes **1–7** show that the adjuvant ligands and anions are important in the construction of molecular architecture of metal complexes. In **1**, **4** and **5**, ferrocenesuccinate ligands participate in coordination but the nitrate anion and acetate anion don't coordinate. While, in complexes **2**, **3**, **6** and **7**, the chlorine or iodine anions participate in coordination, which indicates that they have a little stronger coordination capability than nitrate anion and acetate anion. In polymer **7**, the chlorine anion acts as adjuvant ligand and binds to two adjacent Cd(II) ions. While in **2** and **6**, the chloride anion binds to the Cd(II) ion as terminal modes. Generally, the counterions can show different coordination modes in the structure, such as, bridging the metal ions, or coordinating with metal ions as terminal coligands [16]. Furthermore, by utilizing different adjuvant ligands btx and bix, we obtained dimers **4** and **5**. Interestingly, two adjuvant ligands (bix and btx) are similar but the structures are different. Analysis of the crystal structures of **1–5** and **7** revealed that the Cd–N bond lengths [ranging from 2.217(3) to 2.394(6) Å] and the N–Cd1–N bond angles [ranging from 94.71(2)° to 135.79(13)°] have some differences due to the steric hinderance effect of different adjuvant ligands. In these structures, all the Cd1 ions are connected by the adjuvant ligands in *cis*-conformation forming dimeric structures. Such *cis*-conformation of the adjuvant ligands is easy to form various  $\pi$ - $\pi$  interactions, where they have contributed significantly to the formations of those solid structures. While in **6**, due to strong flexible nature of bbbm ligand [N–Cd1–N bond angles: 81.44(15)–83.60(15)°], a 1-D double ladder-like chain structure was obtained. That is to say, adjuvant ligands play a controlling role on building the molecular structures. Thus, selection of appropriate adjuvant ligands and anions would be a good method to construct new coordination complexes. It should be pointed out that the reaction conditions (solvent, temperature, and metal–ligand ratio) keep constant in these self-assembly processes.

### 3.5. Electrochemistry properties

The electrochemical behaviors of coordination complexes **1–7** have been studied by cyclic voltammetry and differential pulse voltammogram in DMF solutions (ca.  $5.0 \times 10^{-4}$  M total Fc concentrations) containing 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. As shown in Fig. 8a, all these complexes and ferrocenesuccinate exhibit an irreversible redox wave with inordinately large peak to peak separation ( $\Delta E_p$ ) and anodic to cathodic peak current ratio ( $i_a/i_c$ ), which is attributed to substrate deposition at the working electrode. Similar phenomena have been observed for several ferrocenecarboxylate containing complexes [17]. It can be seen from solution-state differential pulse voltammograms (Fig. 8b) that all these complexes show a single peak, which can be assigned to the electron-transfer process of the ferrocenyl moiety. Relative to ferrocene ( $E_{1/2} = 0.544$  V in DMF solution), the half-wave potential ( $E_{1/2}$ ) of the ferrocenyl carboxylate ligand FcCOC<sub>2</sub>H<sub>4</sub>COOH (0.716) is shifted to higher potential. It is because that the electron-withdrawing ability of the carbonyl and carboxyl groups serves to raise

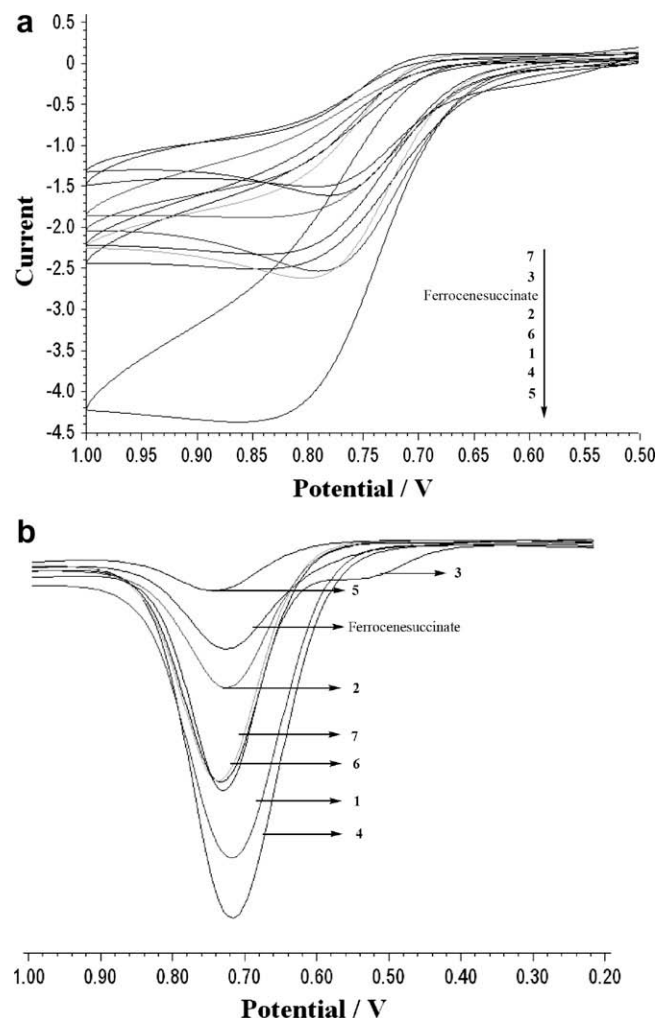


Fig. 8. Cyclic voltammograms (a) and differential pulse voltammograms (b) of complexes **1–7** and ferrocenesuccinate ( $5.0 \times 10^{-4}$  M) in DMF solution containing *n*-Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M).

the potential above that of free ferrocene [17]. Compared with those of ferrocenyl carboxylate ligands FcCH=CHCOOH (0.620 V in DMF solution) and *m*-FcC<sub>6</sub>H<sub>4</sub>COOH (0.562 V in DMF solution), the half-wave potential of FcCOC<sub>2</sub>H<sub>4</sub>COOH (0.716 V) is also shifted to higher potential. The origin of the behavior can be traced back to the presence of the conjugated double bond and phenyl ring between the electroactive ferrocenyl and carboxyl group. The electron-donating ability of the conjugated double bond and phenyl ring groups serves to partially counteract the electron-withdrawing inductive effect of the carboxyl group and central metal ions [17–18]. Therefore, it is easy to understand that the half-wave potential of FcCOC<sub>2</sub>H<sub>4</sub>COOH is higher than those of above-mentioned ligands. Furthermore, the solution-state differential pulse voltammograms (Fig. 8b) of **1–7** show a single peak with a half-wave potential ( $E_{1/2}$  vs. SCE) at 0.736 V for **1**, 0.724 V for **2**, 0.728 V for **3**, 0.720 V for **4**, 0.744 V for **5**, 0.732 V for **6** and 0.740 V for **7**, respectively. In contrast with that of FcCOC<sub>2</sub>H<sub>4</sub>COOH (0.716 V), the half-wave potentials of **1–7** are all shifted to slightly higher potential. It is apparent that the central metal ions in these complexes have some influence on the half-wave potential of the ferrocenyl moieties, and the electron-withdrawing nature of the coordinated metal centers make the ferrocene unit harder to oxidize [19–20]. At the same time, the N-containing adjuvant ligands which have different electron-withdrawing natures and coordination geometries also have

some influence on the half-wave potential of the ferrocenyl moieties, so the half-wave potentials of these Cd(II) complexes display some differences. In a short, the incorporations of the carboxyl group, metal ions and N-containing adjuvant ligands make FeII/FeIII oxidation potential of ferrocene-containing complexes all have some positive shifts.

### Acknowledgments

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.12.025](https://doi.org/10.1016/j.jorganchem.2008.12.025).

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