ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 1, pp. 16–24. © Pleiades Publishing, Ltd., 2015.

Three Naphthoate-Based Cadmium(II) Complexes with Discrete Binuclear, Cyclic Tetranuclear, and Polymeric Double-Chain Motifs[1]

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Received May 29, 2014

Abstract—Three new naphthoate-based cadmium(II) complexes, $[Cd_2(Phen)_2(NA)_4]$ (**I**), $[Cd_4(H_2O)_2(2,2'\text{-}Bipy)_2(NA)_8]$ (**II**), and $[Cd_3(4,4'\text{-}Bipy)_2(NA)_6]_n$ (**III**) (NA^- = 1-naphthoate, Phen = 1,10-phenanthroline, 2,2'-Bipy = 2,2'-bipyridine, and 4,4'-Bipy = 4,4'-bipyridine), were hydrothermally synthesized by varying the *N*-heterocyclic coligands and characterized by X-ray single-crystal structure analysis (CIF files CCDC nos. 971968 (**I**), 971969 (**II**) and 971970 (**III**)). Structural analyses reveal that the former two samples are carboxylate aggregated oligomers with centrosymmetric binuclear and cyclic tetranuclear motifs. By contrast, complex **III** exhibits a polymeric one-dimensional double-chain with linear $\{Cd_3(NA)_6\}$ subunits periodically extended by pairs of ditopic 4,4'-Bipy connectors. Obviously, the mixed ligands of the self-assemble system play different roles with the core-aggregation for carboxylate group and the extension/termination of the subunit for *N*-heterocyclic coligand. Furthermore, all the three entities with higher thermal stability display strong fluorescent emissions at room temperature resulting from the NA^--based intraligand and/or ligand-to-metal charge transfer, suggesting their hopeful use as fluorescent materials.

DOI: 10.1134/S1070328415010029

INTRODUCTION

Rational design and successful preparation of functional metal complexes have always attracted intense interest mainly due to their structural and topological diversities [1, 2] as well as their potential applications in gas sorption [3], catalysis [4], magnetism [5] and luminescence [6]. In this field, mixed-ligand systems bearing polycarboxylate and bipyridyl-like binding groups and diverse metal ions have always generated lots of intriguing high-dimensional metal complexes with polynuclear metal cluster, inter-/self-penetrating and/or high-connected motifs [7–10]. Crystallographically, binding mode, number, as well as the position of the deprotonated carboxylate and pyridyl moieties can significantly dominate the fundamentally structural motif and the connectivity of the targeted complex. In particular, the unexpectedly synergistic coordination coming from the polycarboxylate group to the metal ion is observed to play more important roles for the resulting structural diversity and complexity, which has becoming one of essential factors for the targeted complexes. Many complex systems also demonstrate that the introduction of N-donor ancillary ligands, such as 2,2'-bipyridine-like chelating ligands or 4,4'-bipyridine-like bridging linkers [7, 11, 12], into metal-carboxyl coordination systems will affect the architectures of the final coordination compound. To further investigate the influence of auxiliary co-ligands on the structures and properties of carboxylate-based coordination complexes, herein, three typically *N*-heterocyclic co-ligands, 1,10-phenanthroline (Phen), 2,2'-bipyridine (2,2'-Bipy), and 4,4'-bipyridine (4,4'-Bipy), were chosen as fundamentally building blocks to self-assembly with 1-naphthoic acid (HNA) and inorganic cadmium(II) salt. The main purpose for choosing HNA as a core-ligand is that deprotonated 1-naphthoate (NA^-) with a three-atom carboxylate attached on a bulky π-conjugate skeleton can act as a functional organic ligand to generate interesting metal complexes by carboxylate coordinating with metal ion and also by weak π-π stacking interactions [13–15]. As a result, three novel NA^--based Cd(II)-complexes, $[Cd_2(Phen)_2(NA)_4]$ (**I**), $[Cd_4(H_2O)_2(2,2'\text{-}Bipy)_2(NA)_8]$ (**II**) and $[Cd_3(4,4'\text{-}Bipy)_2(NA)_6]_n$ (**III**), were hydrothermally obtained and structurally characterized. Structural analysis reveals that the former two complexes are discrete oligomers with carboxylate aggregated bi- and tetranuclear motifs. By contrast, complex **III** exhibit polymeric double-chain with linear $\{Cd_3(NA)_6\}$ subunits infinitely extended by ditopic 4,4'-Bipy connectors. Obviously, the

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carboxylate group in **I–III** is consistently responsible for the aggregation of the discrete metal ion and the *N*-heterocyclic coligand contributes to the extension and/or termination of the structural subunits. Additionally, the three solid samples with higher compositional stability up to 230°C display strong fluorescent emissions at room temperature, which is primarily resulted from the NA^--based intraligand and ligand-to-metal charge transfer.

EXPERIMENTAL

Reagents and instruments. HNA was purchased from Acros and other analytical-grade starting materials were obtained commercially and used as received without further purification. Doubly deionized water was employed for the conventional synthesis. IR spectra were collected in a range of 4000–400 cm^{-1} region on a Nicolet IR-200 spectrometer with KBr pellets. Elemental analyses for C, H, and N were determined on a PerkinElmer 2400C elemental analyzer. TGA experiments were carried out on a Shimadzu simultaneous DTG-60A thermal analysis instrument with a heating rate of 8°C min^{-1} from room temperature to 800°C under a nitrogen atmosphere (flow rate 10 mL min^{-1}). Fluorescence spectra of the polycrystalline powder samples of **I–III** were performed on a Fluorolog-3 fluorescence spectrophotometer from Horiba Jobin Yvon at room temperature.

Synthesis of I. A mixture of HNA (68.9 mg, 0.4 mmol), Phen (39.6 mg, 0.2 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (123.4 mg, 0.4 mmol), NaOH (24.0 mg, 0.6 mmol), and doubly deionized water (12.0 mL) were sealed in a 23.0 mL stainless steel vessel and heated at 160°C for 120 h under autogenous pressure. After the mixture was cooled to room temperature at the rate of 5°C h^{-1}, colorless block-shaped crystals suitable for single-crystal X-ray diffraction analysis were isolated directly, washed with ethanol, and dried in air. The yield was 35% based on HNA ligand.

For $C_{34}H_{22}N_2O_4Cd$

anal. calcd., %:	C, 64.32;	H, 3.49;	N, 4.41.
Found, %:	C, 64.30;	H, 3.45;	N, 4.35.

IR (ν, cm^{-1}): 3062 ν(C–H), 1553 $\nu_{as}(COO^-)$, 1512 $\nu_{as}(COO^-)$, 1427 $\nu_s(COO^-)$, 1407 $\nu_s(COO^-)$, 1372 $\nu_s(COO^-)$.

Synthesis of II. Colorless block-shaped crystals suitable for single-crystal X-ray diffraction analysis were obtained by adopting the similar procedures to those of **I** only with 2,2'-Bipy instead of Phen. The yield was 40% based on HNA ligand.

For $C_{54}H_{38}N_2O_9Cd_2$

anal. calcd., %:	C, 59.85;	H, 3.53;	N, 2.58.
Found, %:	C, 59.78;	H, 3.60;	N, 2.47.

IR (ν, cm^{-1}): 3257 ν_{br}(O–H), 3049 ν(C–H), 1598 $\nu_{as}(COO^-)$, 1554 $\nu_{as}(COO^-)$, 1437 $\nu_s(COO^-)$, 1407 $\nu_s(COO^-)$, 1373 $\nu_s(COO^-)$.

Synthesis of III. Colorless block-shaped crystals suitable for single-crystal X-ray diffraction analysis were obtained by adopting the similar procedures to those of **I** only with 4,4'-Bipy instead of Phen. The yield was 30% based on HNA ligand.

For $C_{86}H_{58}N_4O_{12}Cd_3$

anal. calcd., %:	C, 61.61;	H, 3.49;	N, 3.34.
Found, %:	C, 61.50;	H, 3.41;	N, 3.27.

IR (ν, cm^{-1}): 3049 ν(C–H), 1604 $\nu_{as}(COO^-)$, 1546 $\nu_{as}(COO^-)$, 1507 $\nu_{as}(COO^-)$, 1412 $\nu_s(COO^-)$, 1374 $\nu_s(COO^-)$.

X-ray diffraction analysis. Single-crystal X-ray diffraction data for **I–III** were collected on a computer-controlled Bruker APEX-II CCD diffractometer equipped with graphite-monochromated MoK_α radiation with radiation wavelength 0.71073 Å by using ω–φ scan mode at room temperature. Semiempirical multiscan absorption corrections were applied using SADABS [16] and the program SAINT [17] was used for integration of the diffraction profiles. Both structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [18]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. Details for crystallographic data were listed in Table 1, and selected bond lengths and angles were given in Table 2. Hydrogen-bonding parameters for **II** and **III** were shown in Table 3. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 971968 (**I**), 971969 (**II**) and 971970 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Phase-pure crystals of **I–III** were successfully prepared under similar hydrothermal conditions in basic medium. Obviously, the introduction of aqueous NaOH solution is to make HNA ligand deprotonation and facilitate its coordination with Cd^{2+} ion. Additionally, complexes **I–III** are air stable, insoluble in common organic solvents and can retain their crystalline integrity at ambient conditions for a considerable length of time.

In the IR spectra, a broad absorption centered at 3257 cm^{-1} for **II** is assigned to the stretch vibrations of ν(O–H) and should be associated with the presence of water molecule. Weak absorptions appeared at 3062 (for **I**) and 3049 cm^{-1} (for both **II** and **III**) could be ascribed to the C–H stretching vibrations of aromatic

Table 1. Crystallographic data and structure refinement summary for **I**–**III***

Parameter	Value		
	I	**II**	**III**
Formula weight	634.94	1083.66	1676.56
Crystal size, mm	0.21 × 0.17 × 0.12	0.28 × 0.19 × 0.16	0.32 × 0.20 × 0.14
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	12.7557(9)	12.3986(6)	10.373(3)
b, Å	14.0716(10)	16.0092(8)	12.222(3)
c, Å	15.6135(11)	22.5151(12)	15.224(4)
α, deg	90.0	90.0	74.674(3)
β, deg	108.1690(10)	100.0420(10)	75.221(3)
γ, deg	90.0	90.0	71.348(3)
V, Å^3	2662.8(3)	4400.6(4)	1732.9(7)
Z	4	4	1
ρ_{calcd}, g/cm^3	1.584	1.636	1.607
μ_{Mo}, mm^{-1}	0.864	1.030	0.983
F(000)	1280	2176	842
θ Range, deg	1.99–25.50	1.76–27.86	2.11–25.03
Range of reflection indices	$-14 \le h \le 15, -14 \le k \le 17, -18 \le l \le 15$	$-16 \le h \le 10, -21 \le k \le 20, -29 \le l \le 29$	$-10 \le h \le 12, -13 \le k \le 14, -15 \le l \le 18$
Reflections collected/unique	14727/4936	29082/10467	9425/6008
R_{int}	0.0236	0.0204	0.0268
Number of parameters refined	370	613	475
GOOF on F^2	1.064	1.057	1.014
R ($I > 2\sigma(I)$)*	$R_1 = 0.0359$, $wR_2 = 0.0943$	$R_1 = 0.0240$, $wR_2 = 0.0592$	$R_1 = 0.0457$, $wR_2 = 0.1024$
R (all data)*	0.0534/0.1005	0.0333/0.0616	0.0833/0.1158
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.231/–0.374	0.364/–0.345	1.216 /–0.803

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

ring. An absence of a characteristic band at 1675 cm^{-1} in **I**–**III** indicates the complete deprotonation of HNA ligand by NaOH [19], which is consistent with the single-crystal structural determinations. In addition, **I** shows characteristic peaks at 1553, 1512, and 1427, 1407, 1372 cm^{-1} for asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of carboxylate group. In **II**, they appear at 1598, 1554, and 1437, 1407, 1373 cm^{-1}. For **III**, the asymmetric and symmetric stretching absorptions for carboxylate group locate at 1604, 1546, 1507, and 1412, 1374 cm^{-1}. The different splits and separations between ν_{as} and ν_s indicate the coexistence of the multiple coordination modes [20]. Thus, the results of IR spectra are well agreement with those of crystal structure determinations.

Single-crystal X-ray diffraction analyses show that complex **I** exhibits a centrosymmetric binuclear structure bridged by a pair of the carboxylate group from two NA$^-$ ligands. As shown in Fig. 1a, the asymmetric unit of **I** consists of one crystallographically independent Cd^{2+} ion, one neutral Phen molecule and a pair of unique NA$^-$ anion in different binding modes. The sole Cd^{2+} ion in **I** is seven-coordinated in a distorted pentagonal-bipyramidal coordination geometry defined by two N atoms from one chelating Phen ligand and five carboxylate O donors from three individual NA$^-$ anions. The Cd–O$_{carboxylate}$ and Cd–N distances are in the region of 2.317 to 2.547 Å (Table 2), falling into the normal range of Cd(II)-based complexes with mixed carboxylate and/or pyridyl ligands [21, 22].

Table 2. Selected bond lengths (Å) and angles (deg) for **I**–**III***

Bond	*d*, Å	Bond	*d*, Å
I			
Cd(1)–O(1)	2.364(3)	Cd(1)–O(2)	2.367(3)
Cd(1)–O(3)	2.547(3)	Cd(1)–O(4)	2.417(3)
Cd(1)–N(1)	2.354(3)	Cd(1)–N(2)	2.382(3)
Cd(1)–O(3)^{i}	2.317(3)		
II			
Cd(1)–N(1)	2.3224(15)	Cd(1)–N(2)	2.3367(15)
Cd(1)–O(4)	2.2816(13)	Cd(1)–O(6)	2.3124(13)
Cd(1)–O(8)	2.2747(13)	Cd(1)–O(1*w*)^{i}	2.3848(13)
Cd(2)–O(1)	2.2056(13)	Cd(2)–O(3)	2.3021(13)
Cd(2)–O(5)	2.4087(16)	Cd(2)–O(6)	2.3881(14)
Cd(2)–O(7)	2.2192(12)	Cd(2)–O(1*w*)^{i}	2.4253(13)
III			
Cd(1)–O(1)	2.209(5)	Cd(1)–O(5)^{ii}	2.357(5)
Cd(1)–N(2)	2.293(4)	Cd(2)–O(6)	2.307(4)
Cd(2)–O(2)^{iv}	2.203(5)	Cd(2)–N(1)	2.288(4)
Cd(2)–O(3)	2.296(5)	Cd(2)–O(4)	2.400(4)
Cd(2)–O(5)	2.530(6)		
Angle	**w, deg**	**Angle**	**w, deg**
I			
O(3)^{i}Cd(1)N(1)	90.50(10)	O(3)^{i}Cd(1)O(1)	146.58(10)
N(1)Cd(1)O(1)	122.34(10)	O(3)^{i}Cd(1)O(2)	92.76(10)
O(4)Cd(1)O(3)	51.93(10)	O(1)Cd(1)O(2)	55.05(9)
O(3)^{i}Cd(1)N(2)	91.43(10)	N(1)Cd(1)N(2)	70.15(10)
O(1)Cd(1)N(2)	94.13(10)	O(2)Cd(1)N(2)	85.16(10)
O(3)^{i}Cd(1)O(4)	107.39(11)	N(1)Cd(1)O(4)	82.51(11)
O(1)Cd(1)O(4)	84.92(11)	O(2)Cd(1)O(4)	119.67(11)
N(2)Cd(1)O(4)	146.98(10)	O(3)^{i}Cd(1)O(3)	73.87(10)
N(1)Cd(1)O(3)	121.28(10)	O(1)Cd(1)O(3)	91.73(9)
O(2)Cd(1)O(3)	83.17(10)		
II			
O(8)Cd(1)O(4)	91.45(5)	O(8)Cd(1)O(6)	148.97(5)
O(4)Cd(1)O(6)	87.87(5)	O(8)Cd(1)N(1)	113.54(5)
O(4)Cd(1)N(1)	85.60(5)	O(6)Cd(1)N(1)	97.35(5)
O(8)Cd(1)N(2)	100.20(5)	O(6)Cd(1)O(1*w*)^{i}	71.85(5)
O(6)Cd(1)N(2)	92.33(5)	N(1)Cd(1)N(2)	71.02(5)
O(8)Cd(1)O(1*w*)^{i}	79.35(5)	O(4)Cd(1)O(1*w*)^{i}	110.18(5)
N(2)Cd(1)O(1*w*)^{i}	92.16(5)	O(1)Cd(2)O(7)	92.72(5)
O(1)Cd(2)O(6)	93.37(5)	O(7)Cd(2)O(3)	87.83(5)
O(3)Cd(2)O(6)	90.87(5)	O(1)Cd(2)O(5)	100.68(6)
O(7)Cd(2)O(5)	102.47(5)	O(3)Cd(2)O(5)	91.06(5)
O(6)Cd(2)O(5)	54.30(5)	O(1)Cd(2)O(1*w*)^{i}	89.41(5)
O(7)Cd(2)O(1*w*)^{i}	132.66(5)	O(3)Cd(2)O(1*w*)^{i}	81.34(5)
O(6)Cd(2)O(1*w*)^{i}	69.87(4)	O(5)Cd(2)O(1*w*)^{i}	123.54(5)
III			
O(1)^{i}Cd(1)N(2)	89.10(19)	O(1)Cd(1)N(2)	90.90(19)
O(1)^{i}Cd(1)O(5)^{iii}	92.1(3)	O(1)^{i}Cd(1)O(5)^{ii}	87.9(3)
N(2)Cd(1)O(5)^{ii}	93.55(16)	N(2)^{i}Cd(1)O(5)^{ii}	86.45(16)
O(2)^{iv}Cd(2)O(3)	97.9(3)	N(1)Cd(2)O(3)	90.74(19)
O(2)^{iv}Cd(2)N(1)	102.7(2)	N(1)Cd(2)O(6)	90.38(16)
O(3)Cd(2)O(6)	104.5(2)	O(2)^{iv}Cd(2)O(4)	93.1(2)
N(1)Cd(2)O(4)	143.61(18)	O(3)Cd(2)O(4)	54.35(18)
O(6)Cd(2)O(4)	89.31(16)	O(2)^{iv}Cd(2)O(5)	101.7(2)
N(1)Cd(2)O(5)	119.18(17)	O(3)Cd(2)O(5)	138.9(2)
O(6)Cd(2)O(5)	52.39(16)	O(4)Cd(2)O(5)	88.60(17)

* Symmetry codes: $^{i}\ 1-x, 1-y, 1-z$ (**I**); $^{i}\ 1-x, -y, 2-z$ (**II**); $^{i}\ 1-x, 2-y, -z$; $^{ii}\ 1-x, 1-y, -z$; $^{iii}\ x-1, y+1, z$; $^{iv}\ x+1, y-1, z$ (**III**).

Table 3. Geometric parameters of hydrogen bonds for **II** and **III***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
II				
O(1*wA*)–H(1*wA*)···O(2)	0.86	1.70	2.558(4)	174
O(1*wA*)–H(2*wA*)···O(3)^i	0.88	1.85	2.728(1)	173
C(5)–H(5*A*)···O(7)^{ii}	0.93	2.40	3.297(3)	163
III				
C(37)–H(37)···O(3)^i	0.93	2.59	3.258(2)	130

* Symmetry codes: ^{i} 1 – *x*, –*y*, –*z*; ^{ii} 1/2 – *x*, *y* – 1/2, 1/2 – *z* (**II**); ^{i} 1 – *x*, 1 – *y*, –*z* (**III**).

Acting as a typically bidentate chelating ligand, neutral Phen molecule binds Cd^{2+} ion in an asymmetric bidentate mode with two Cd–N bond distances slightly different from each other (Table 2). By contrast, the two unique NA^- ligands in **I** adopt two different binding modes. One presents its carboxylate group to aggregate adjacent metal ions in a chelating-bridging fashion, generating a binuclear structure with the Cd···Cd distance of 3.8908(3) Å. Instead, the second carboxylate group belonging to the other NA^- ligand exhibit a bidentate chelating fashion to complete the coordination sphere of the Cd^{2+} ion.

Each centrosymmetric binuclear molecules of **I** interacts with six neighbors through weak intermolecular C–H···π and π···π stacking interactions (Fig. 1b). The distances of H and C atoms to the center (Cg) of phenyl moiety of NA^- ligand are 2.8679 and 3.7415 Å, and the involved angle CHCg is 157°. The π···π stacking interaction are produced between phenyl and quinolinyl rings of Phen ligand with the centroid-to-centroid distance of ~3.528 Å. The periodic arrangement of the discrete binuclear units of **I** can topologically lead to a 6-connected α-Po-type ($4^{12}6^3$) network (Fig. 1c), in which the inter-molecular distances are 10.9758(5) and 12.7557(9) Å, respectively, separated by C–H···π and π···π interactions.

Complex **II** with the formula of $[Cd_4(H_2O)_2(2,2'\text{-}Bipy)_2(NA)_8]$ possesses a cyclic tetranuclear entity, although it also crystallizes from the same space group as **I**. The asymmetric unit of **II** contains two crystallographically independent Cd(II) octahedra, four NA^- anions, one neutral 2,2'-Bipy ligand, and one coordinated water molecule. Both of the Cd^{2+} ions in **II** are hexa-coordinated in N_2O_4 (for Cd(1)) and O_6 (for Cd(2)) donor sets. The octahedron of Cd(1) is completed by one chelating 2,2'-Bipy ligand, three carboxylate O atoms from three isolated NA^- anions, and one bridging water molecule. By contrast, the consistent O donors of Cd(2) ion belong to one water bridging molecule and four carboxylate groups from four NA^- ligands. The Cd–O and Cd–N distances fall in the normal range (Table 2) and are comparable to those Cd(II)-based complexes with carboxylate and bipyridyl ligands [21, 22].

Analogous to the Phen molecule in **I**, the neutral 2,2'-Bipy ligand in **II** adopts a asymmetrically bidentate chelating mode to complete the coordination octahedron of Cd(1) ion. The four unique NA^- anions in **II** adopt three kinds of coordination modes: terminally monodentate, bidentate bridging, and chelating-bridging fashions. As shown in Fig. 2a, the unique Cd(1) and Cd(2) ions are three-fold bridged by one bridging water molecule and two carboxylate group of NA^- ligands in bidentate bridging and bridging-chelating modes, which are further connected together by the third bidentate bridging NA^- ligand, leading to a cyclic tetranuclear subunit with the intermetallic separations of 3.5225(2) and 4.7543(3) Å for Cd(1)···Cd(2) and Cd(2)···Cd(1*A*). The cyclic tetranuclear molecule is further consolidated by the intramolecular hydrogen-bonding interactions between the coordinated water molecule and the deprotonated carboxylate group of NA^- ligand (Table 3 and Fig. 2b).

As shown in Fig. 2c, each discrete tetranuclear unit of **II** are connected with six neighbors by weak intermolecular C–H···π and C–H···O interactions, also generating a 6-connected α-Po-type ($4^{12}6^3$) network (Fig. 2d). The distance of H atom *d*(H···Cg) and C-donor *d*(C···Cg) of the pyridyl group to the center of benzene ring (Cg) are 2.7464 and 3.5949 Å, and the angle is 152.1° (Fig. 2c, Table 3).

Complex **III** exhibits one-dimensional (1D) double chain with linear trinuclear subunits extended by pairs of 4,4'-Bipy ligands. The asymmetric unit of **III** contains one and a half crystallographically independent Cd(II) sites, three NA^- anions in three binding modes, and one neutral 4,4'-Bipy ligand. Locating at an inversion center, the unique Cd(1) ion in **III** is hexacoordinated in an elongated octahedral geometry (Fig. 3a). The equatorial plane of the Cd(1) ion is defined by two carboxylate O and two pyridyl N donors, and the axial positions are occupied by two carboxylate O donors from two centrosymmetric NA^- anions. The bond length of the axial Cd–O is 0.15 Å

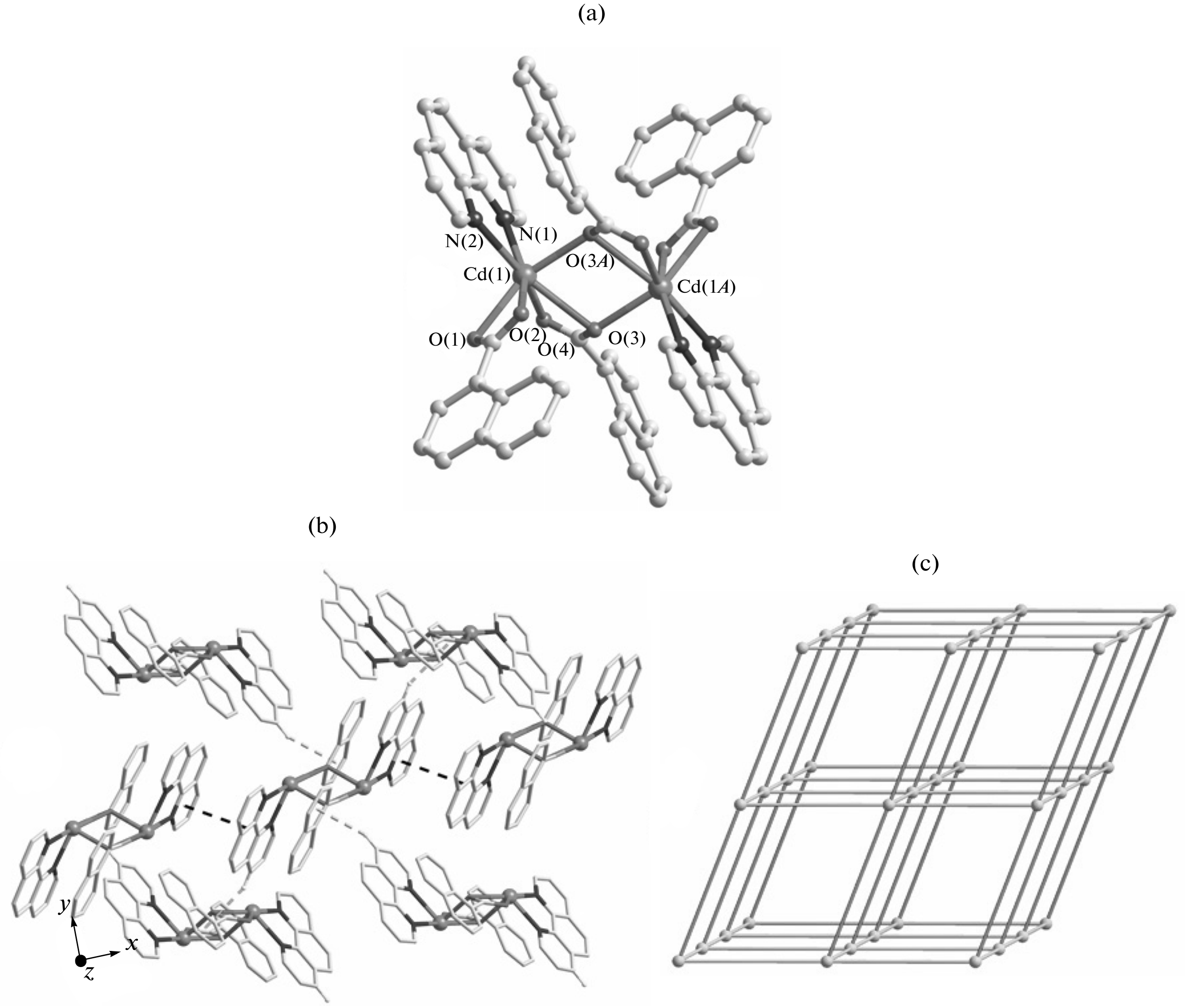

Fig. 1. Binuclear structure of **I** (a) (hydrogen atoms were omitted for clarity. Symmetry codes: $A = 1 - x, 1 - y, 1 - z$); intermolecular connectivity of **I** by weak C–H···π and π···π stacking interactions (b) (bidentate chelating NA^- ligands were omitted for clarity); topological representation for the 3D supramolecular network of **I** (c).

longer than those in the equatorial plane (Table 2). Suited at a general position, the Cd(2) ion is bound to five carboxylate O and one pyridyl N donors from three separate NA^- anions and one neutral 4,4'-Bipy ligand, assuming a slightly distorted CdO_5N octahedron with the Cd–O and Cd–N distance comparable with those in **I** and **II** (Table 2).

The central Cd(1) ion connects with two external Cd(2) and Cd(2*C*) ions through two pairs of carboxylate groups in bidentate bridging and chelating-bridging modes, generating a linear $\{Cd_3(NA)_6\}$ subunit with the Cd(1)···Cd(2) separation of 3.9084(9) Å. The individual Cd_3^{II} subunits are periodically extended by pairs of ditopic 4,4'-Bipy connectors, generating a 1D double chain of **III** (Fig. 3b). The nearest inter-subunit Cd(1)···Cd(2) separation is 11.646(2) Å spanned by 4,4'-Bipy ligand.

As shown in Fig. 3c, each 1D chain of **III** interacts with four neighbours by interchain C–H···O (Table 3) and C–H···π aromatic interactions, leading to a 3D supramolecular network of **III** with the interchain nearest Cd(1)···Cd(1) distance of 10.373(3) and 15.224(4) Å. Notably, both the C–H···O and C–H···π interaction are produced between the NA^- ligands. The distances of H atom and C–donor to the center of benzene ring (Cg) are 2.7184 Å and 3.4589 Å, and the angle of HCCg is 137°.

Apparently, the structural determinations clearly reveal that the oligomeric subunits (centrosymmetric binuclear, cyclic tetranuclear as well as the linear trinuclear motifs) in **I**–**III** are exclusively generated by

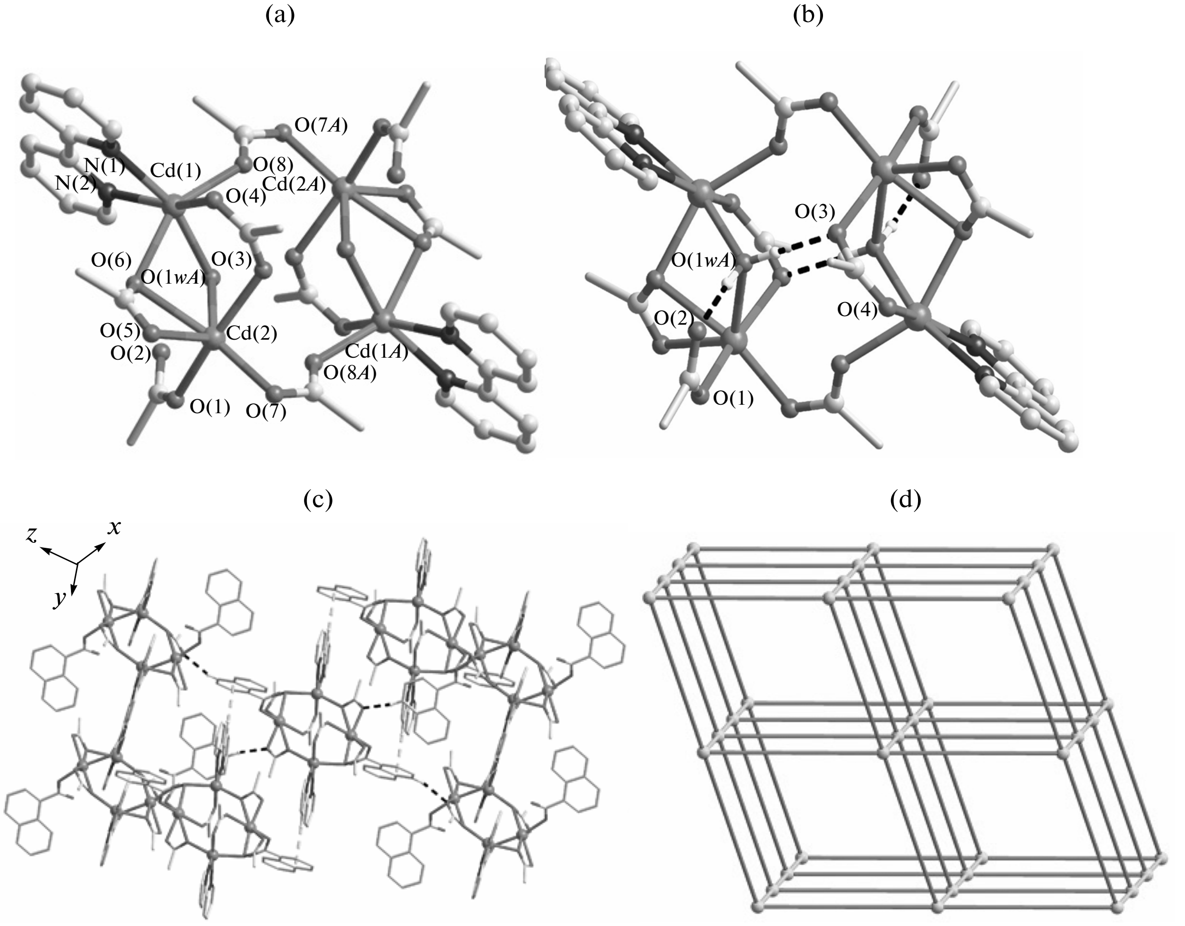

Fig. 2. Tetranuclear entity of **II** (a) (hydrogen atoms were omitted for clarity. Symmetry codes: $A = 1 - x, -y, 2 - z$); intramolecular O–H···O hydrogen-bonding interactions in **II** (b) (symmetry codes: $A = 1 - x, -y, 2 - z$); linkage of the tetranuclear structures of **II** by weak C–H···π and C–H···O interactions (c); topological representation for the 3D supramolecular network of **II** (d).

carboxylate substitute of NA^- ligand and the *N*-heterocyclic coligand govern the blocking or the extension of the subunits through the chelating or bridging mode.

TGA experiments of **I**–**III** were carried out to explore their thermal stability and the results were presented in Fig. 4. As a result, **I** can be thermally stable up to 267°C and is followed by a continuous two-step weight-loss stage between 267 and 483°C. The obvious weight-loss stage is corresponding to the broken of the binuclear motif and the decomposition of the mixed ligands. The remained substance beyond 483°C is calculated to be CdO (obsd. 21.4%, calcd. 20.2%). The release of the coordinated water molecule in **II** is ranged from 130 to 190°C (obsd. 1.63%, calcd. 1.67%). The secondly weight-loss process of **II** for the continuous release of 2,2'-Bipy and NA^- ligands is between 230 and 452°C, leading CdO as the final product (obsd. 23.2%, calcd. 23.7%). The TG curve of **III** indicates only one weight-loss stage in the region of 294 and 449°C, ascribing to the decomposition of deprotonated NA^- anions and 4,4'-Bipy ligand. The final product of **III** above 449°C is CdO (obsd. 22.7%, calcd. 23.0%).

Constructed from the d^{10}-configuration metal ion and bulky π-conjugated NA^- ligand, complexes **I**–**III** can be hopefully applied as luminescent materials [23]. The emissions of the three solid-state samples were thus measured at room temperature, together with free HNA and Phen ligands for comparison. As shown in Fig. 5, upon excitation at 370 nm, complex **I** exhibits an intense luminescent peak at 421 nm and a broad band with the maximum peak at ~575 nm. Two broad emissions centered at 421 and 575 nm that are similar to **I** can also be observed for **III** upon excited at 345 nm. For **II**, an obviously strong emission occurs at 421 nm upon excitation at 370 nm. Under comparable conditions, free HNA species gives a broad emission at 420 nm upon excitation at 345 nm, and Phen molecule displays intense emissions at 392, 381, 404, and 428 nm ($\lambda_{ex} = 265$ nm). Therefore, the observed luminescence at ca. 421 nm for **I**–**III** should be assigned to

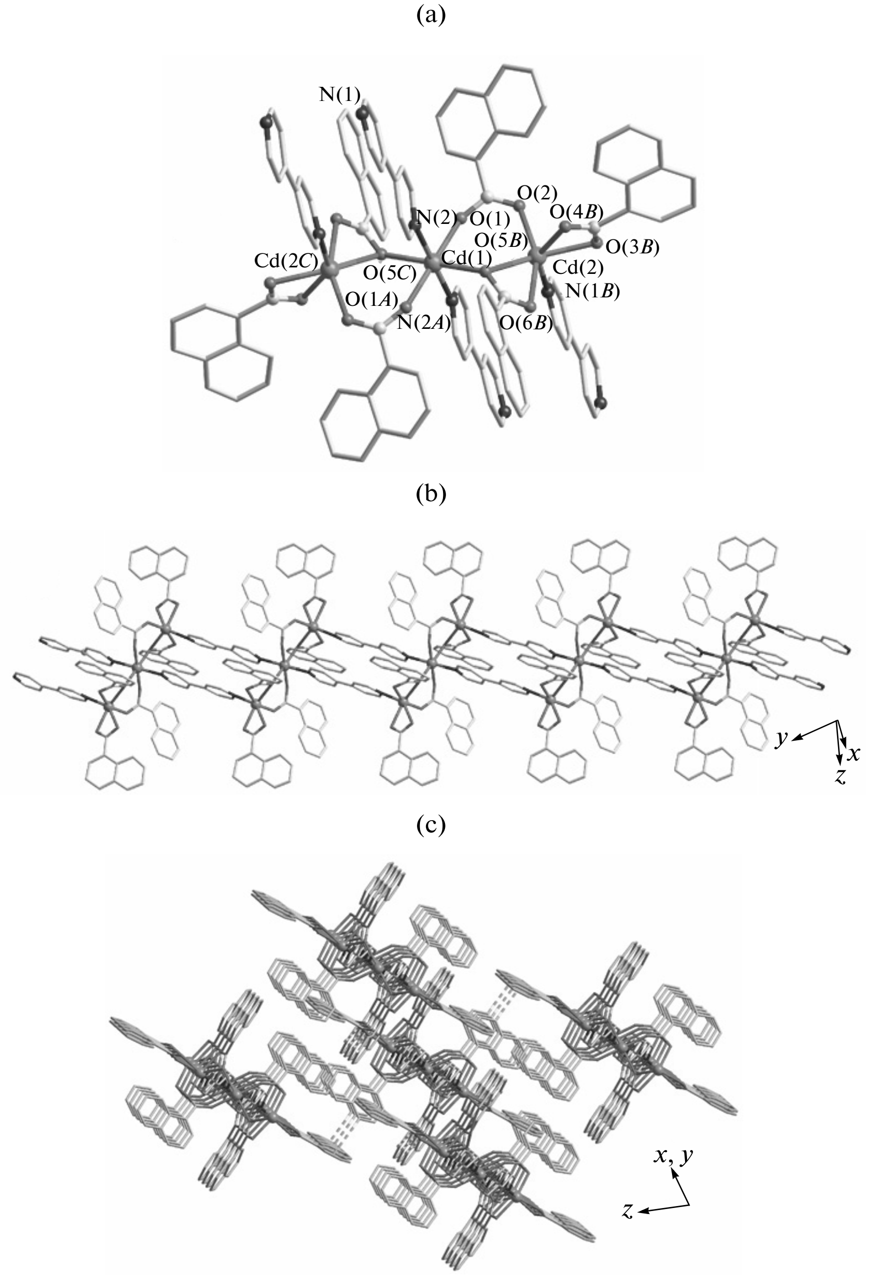

Fig. 3. Local Cd$_3^{II}$ subunit of **III** (a) (hydrogen atoms are omitted for clarity. Symmetry codes: $A = -x, 2 - y, -z$; $B = x - 1, y + 1, z$; $C = 1 - x, 1 - y, -z$); 1D double chain of **III** with linear Cd$_3^{II}$ subunits extended by 4,4'-Bipy connectors (b); non-covalent 3D architecture of **III** by interchain C–H···O and C–H···π interactions (c).

the intraligand electronic transfer of NA$^-$ anion, in which the slight difference is probably resulted from the deprotonation of HNA and the coordination behavior of NA$^-$ to Cd^{2+} ion. Compared with the fluorescent of HNA, the new broad band for **I** and **III** are probably originated from ligand-to-metal charge-transfer (LMCT) due to the formation of the discrete or polymeric metal complexes [24].

Three fluorescent Cd(II)-naphtholate complexes with oligomeric binuclear, cyclic tetranuclear, and infinite double-chain motifs were hydrothermally synthesized by incorporating with *N*-heterocyclic coligands. Structural analysis reveals that the carboxylate group attached on the naphthalene ring is significantly dominate the formation of the oligonuclear substructure and the *N*-heterocyclic coligand is responsible for the extension or termination of the local subunits. Due

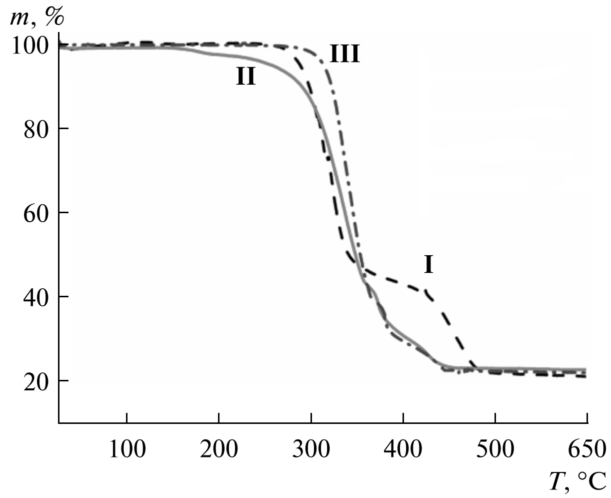

Fig. 4. TG curves for **I**–**III**.

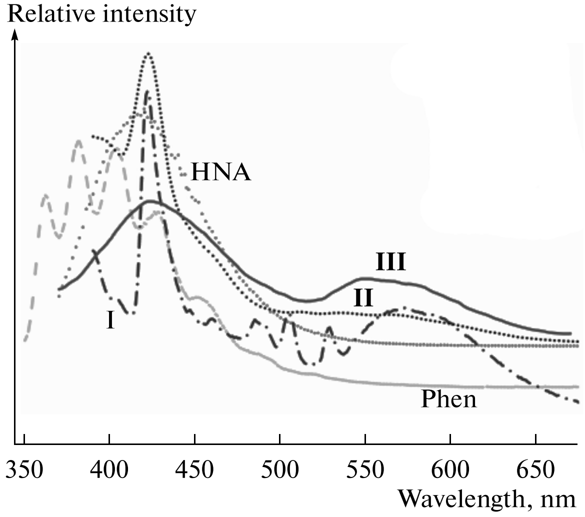

Fig. 5. Solid-state emissions of **I**–**III** and free ligands in the solid state at room temperature.

to the NA^--involved intraligand and ligand-to-metal charge transfer, the three complexes with good thermal stability exhibit two strong emissions with different intensity, suggest their potential applications as luminescent materials.

ACKNOWLEDGMENTS

This present work was supported by the Science Foundation of Shaanxi University of Technology (SLGQD13-4), the National Natural Science Foundation of China (Grants 21171129, 21173157, and 21373132), and Tianjin Municipal Education Commission (2012ZD02), which are gratefully acknowledged.

REFERENCES

1. Luo, L., Chen, K., Liu, Q., et al., *Cryst. Growth Des.*, 2013, vol. 13, no. 6, p. 2312.
2. Yang, J.X., Zhang, X., Cheng, J.K., et al., *Cryst. Growth Des.*, 2012, vol. 12, no. 1, p. 333.
3. Suh, M.P., Park, H.J., Prasad, T.K., et al., *Chem. Rev.*, 2012, vol. 112, no. 2, p. 782.
4. Ma, L., Falkowski, J.M., Abney, C., et al., *Nature Chem.*, 2010, vol. 2, no. 10, p. 838.
5. Coates, C.M., Fiedler, S.R., McCullough, T.L., et al., *Inorg. Chem.*, 2010, vol. 49, no. 4, p. 481.
6. Zhang, J.P., Zhang, Y.B., Lin, J.B., et al., *Chem. Rev.*, 2011, vol. 112, no. 2, p. 1001.
7. Ye, B.H., Tong, M.L., and Chen, X.M., *Coord. Chem. Rev.*, 2005, vol. 249, nos. 5–6, p. 545.
8. Go, Y.B., Wang, X.Q., Anokhina, E.V., et al., *Inorg. Chem.*, 2005, vol. 44, no. 23, p. 8265.
9. Han, Z.B. and Zhang, G.X., *CrystEngComm*, 2010, vol. 12, no. 2, p. 348.
10. Lin, Q.P., Wu, T., Bu, X.H., et al., *Dalton Trans.*, 2012, vol. 41, no. 13, p. 3620.
11. Liu, G.X., Huang, Y.Q., Chu, Q., et al., *Cryst. Growth Des.*, 2008, vol. 8, no. 9, p. 3233.
12. Dong, M.M., He, L.L., Fan, Y.J., et al., *Cryst. Growth Des.*, 2013, vol. 13, no. 8, p. 3353.
13. Yang, E.C., Dai, P.X., Wang, X.G., et al., *Transition Met. Chem.*, 2007, vol. 32, no. 2, p. 28.
14. Yang, E.C., Dai, P.X., Wang, X.G., et al., *Z. Anorg. Allg. Chem.*, 2009, vol. 635, no. 2, p. 346.
15. Hou, Z.J., Wang, X.G., Dai, P.X., et al., *Chin. J. Struc. Chem.*, 2012, vol. 31, no. 9, p. 1295.
16. Sheldrick, G.M., *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, Göttingen (Germany): Univ. of Göttingen, 1996.
17. *SAINT, Software Reference Manual, Madison* (WI, USA): Bruker AXS, 1998.
18. Sheldrick, G.M., *SHELXTL, Structure Determination Software Programs*, Madison (WI, USA): Bruker Analytical X-ray System, Inc., 2001.
19. Bellamy, L.J., *The Infra-Red Spectra of Complex Molecules*, New York: John Wiley & Sons, Inc., 1958.
20. Cao, R., Shi, Q., Sun, D.F., et al., *Inorg. Chem.*, 2002, vol. 41, no. 23, p. 6161.
21. Zou, R.Q., Bu, X.H., and Zhang, R.H., *Inorg. Chem.*, 2004, vol. 43, no. 17, p. 5382.
22. Yang, E.C., Dai, P.X., Wang, X.G., et al., *Z. Anorg. Allg. Chem.*, 2007, vol. 633, no. 4, p. 615.
23. Yam, W.-W.V. and Lo K.K.-W., *Chem. Soc. Rev.*, 1999, vol. 28, no. 5, p. 323.
24. Chen, W., Wang, J.Y., Chen, C., et al., *Inorg. Chem.*, 2003, vol. 42, no. 4, p. 944.