

Cationic zinc (II) dimers and one dimensional coordination polymer from ionic carboxylic acid

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Abstract. A rare example of chelating two tetra cationic paddle-wheel zinc dimers were synthesized from the reaction between flexible imidazolium carboxylate (LH_2Br_2) and corresponding zinc precursors. A zinc coordination polymer was synthesised by treating *in situ* generation of **2** in the presence of 4,4'-bipyridine. These new molecules, dimers and polymer, were characterized by FT-IR, NMR, UV-vis, fluorescent and single crystal X-ray diffraction techniques. Zinc polymer is the first example of 1D coordination polymer constructed by tetra cationic zinc dimer as a secondary building unit in coordination polymer.

Keywords. Imidazolium carboxylate; secondary building units; zinc dimers; 4,4'-bipyridine; zinc coordination polymer.

1. Introduction

Construction of functionalized coordination polymers have attracted a lot of attention in recent decades due to their potential applications in the field of gas separation,¹ gas adsorption,² drug delivery,³ sensors,⁴ nonlinear optics,⁵ magnetic materials,⁶ conducting application,⁷ and catalysis.⁸ An important tool to design and synthesize coordination polymers is secondary building unit (SBU). To design and synthesize coordination polymers, one of the most important tool is secondary building unit (SBU). Till now, more than 150 different secondary building units have been reported for coordination polymers.⁹ In which, square shaped paddle-wheel is one of the most important building blocks in coordination polymers, where two metal atoms are bridged by four carboxylates and mostly metal atoms are in apical position. The square shaped paddle-wheel building blocks are commonly known as Zn, Cu, Rh, Ru, Mo, Ni, Co, Re, Cr, Mn, W, Pt, Mg, Al and In.⁹ Some well-known examples are MOF-5 for Zn square shaped paddle-wheel and HKUST for Cu square shaped paddle-wheel.¹⁰ Recently, Kitagawa *et al.* have reported the isostructural Ru and Rh 1D coordination polymers from corresponding paddle wheel dimers of $[\text{M}_2(4\text{-Cl-2-OMePhCO}_2)_4(\text{THF})_2]$ (M = Ru, Rh) using phenazine (phz) as a linker for the selective NO molecules tapping, which is considered as

one of the most important synthetic protocols to construct the functional materials.¹¹ However, the chelating carboxylate zinc paddle-wheel dimers are rare,¹² in particular the coordination polymers with chelating zinc carboxylate paddle wheel building block are not known. Thus, we report two new tetra cationic zinc dimers (**1** and **2**) and cationic zinc 1D coordination polymer (**3**). The structural and optical properties of **1-3** (scheme 1) were studied.

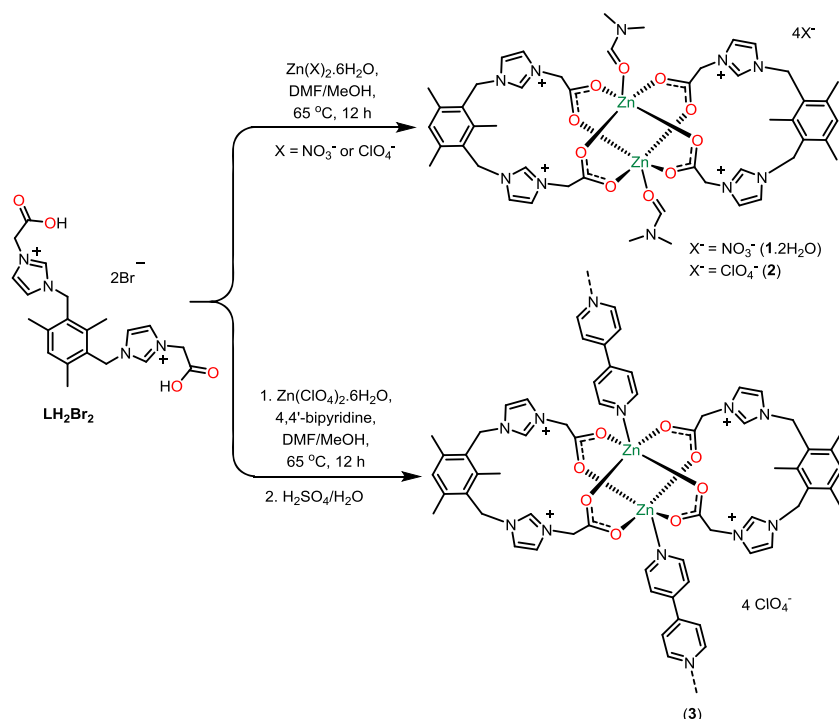
2. Experimental

2.1 General considerations

The solvents were purchased from commercial sources and purified according to standard procedures.¹³ Unless otherwise stated, the chemicals were purchased from commercial sources. LH_2Br_2 was prepared as reported.¹⁴ FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25°C, unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. The UV-vis spectra were measured on a T90+ UV-visible spectrophotometer. The fluorescent emission spectra were measured on a Horiba Scientific fluorescence spectrophotometer. The crystal structures of **1-3** were measured on an Oxford Xcalibur 2 diffractometer. Data were collected at 150 K. Using Olex2,¹⁵ the

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This paper is dedicated to Professor S S Krishnamurthy.



Scheme 1. Synthesis of 1-3.

structures were solved with the ShelXS¹⁶ structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimization. In **1**, hydrogen atoms for water molecule were not included during the final refinement. Some of the perchlorate anions in **2** and **3** are disordered. Therefore, the complete refinement was not possible for **2** and **3**.

2.2 Synthesis of 1

LH₂Br₂ (0.1 g, 0.179 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.054 g, 0.181 mmol) were taken into schlenk tube and added 1:1 DMF and MeOH (2 mL). The reaction mixture was heated at 65 °C under stirring condition for 12 h. After ten days, colourless crystals were formed and washed with MeOH then dried under vacuum. Yield: 24% (based on $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. (%) for $\text{C}_{48}\text{H}_{66}\text{N}_{14}\text{O}_{24}\text{Zn}_2$ (1353.87): C, 42.58; H, 4.91; N, 14.48; found: C, 42.3; H, 5.1; N, 14.3. ¹H NMR (400 MHz, D₂O): δ 8.47 (s, 2H, Im H), 7.92 (s, 1H, DMF CH) 7.44 and 7.35 (s, 2 × 2H, 2 × Im H), 7.25 (s, 1H, Ar H), 5.51 (s, 4H, Mes CH₂N), 4.73 (s, 4H, CH₂), 3.00 (s, 3H, DMF CH₃), 2.84 (s, 3H, DMF CH₃), 2.34 (s, 6H, Mes CH₃), 2.21 (s, 3H, Mes CH₃) ppm. ¹³C NMR (100 MHz, D₂O): δ 172.13 (DMF C = O), 164.94 (C = O), 140.85 (Ar C), 139.18 (Ar C), 135.87 (Im C), 131.36 (Ar C), 127.70 (Ar C), 123.78 (Im C), 121.57 (Im C), 52.02 (DMF CH₃), 47.70

(Mes CH₂), 36.89 (CH₂), 31.36 (DMF CH₃), 18.88 (Mes CH₃), 14.64 (Mes CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3144 (w), 3107 (w), 3067 (w), 1683 (w), 1648 (s), 1567 (m), 1447 (m), 1409 (m), 1383 (w), 1333 (s), 1234 (w), 1155 (s), 1130 (w), 1103 (w), 1041 (w), 1019 (w), 979 (w) cm⁻¹.

2.3 Synthesis of 2

Compound **2** was synthesized similar manner as **1** using **LH₂Br₂** (0.1 g, 0.179 mmol) and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.067 g, 0.180 mmol). Colourless crystals were formed after seven days and washed with MeOH then dried under vacuum. Yield: 63% (based on $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. (%) for $\text{C}_{48}\text{H}_{62}\text{N}_{10}\text{O}_{26}\text{Cl}_4\text{Zn}_2$ (1467.62): C, 39.28; H, 4.26; N, 9.54; found: C, 39.3; H, 4.2; N, 9.6. ¹H NMR (400 MHz, D₂O): δ 8.45 (s, 2H, Im H), 7.91 (s, 1H, DMF CH) 7.43 and 7.35 (s, 2 × 2H, 2 × Im H), 7.24 (s, 1H, Ar H), 5.50 (s, 4H, Mes CH₂N), 4.73 (s, 4H, CH₂), 2.99 (s, 3H, DMF CH₃), 2.84 (s, 3H, DMF CH₃), 2.33 (s, 6H, Mes CH₃), 2.21 (s, 3H, Mes CH₃) ppm. ¹³C NMR (100 MHz, D₂O): δ 172.16 (DMF C = O), 164.94 (C = O), 140.84 (Ar C), 139.19 (Ar C), 135.85 (Im C), 131.38 (Ar C), 127.70 (Ar C), 123.80 (Im C), 121.60 (Im C), 52.02 (DMF CH₃), 47.72 (Mes CH₂), 36.90 (CH₂), 31.37 (DMF CH₃), 18.91 (Mes CH₃), 14.67 (Mes CH₃) ppm. FT-IR (neat): $\bar{\nu}$ = 3147 (w), 3120 (w), 1691 (m), 1647 (s),

1571(m), 1448 (m), 1409 (s), 1382 (m), 1336 (w), 1317 (m), 1155 (m), 1068 (s), 977 (w), 936 (w) cm^{-1} .

2.4 Synthesis of **3**

LH₂Br₂ (0.1 g, 0.179 mmol), 4,4'-bipyridine (0.028 g, 0.179 mmol) and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.067 g, 0.180 mmol) were taken into schlenk tube and added 1:1 DMF and MeOH (2 mL). The reaction mixture was heated at 65°C under stirring condition for 12 h and resultant solid was dissolved in 1:2 H₂O and H₂SO₄ (2 mL). After one week, colourless crystals were formed and washed with MeOH then dried under high vacuum. Yield: 42% (based on $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. (%) for $\text{C}_{52}\text{H}_{56}\text{Cl}_4\text{N}_{10}\text{O}_{24}\text{Zn}_2$ (1477.63): C, 42.27; H, 3.82; N, 9.48; found: C, 42.1; H, 3.8; N, 9.4. FT-IR (neat): $\bar{\nu} = 3460$ (br), 3087 (m), 3061 (w), 2995 (w), 2523 (br), 2347 (w), 2194 (w), 2164 (w), 2123 (w), 2020 (w), 1998 (w), 1952 (w), 1935 (w), 1627 (s), 1485 (s), 1370 (m), 1239 (m), 1205 (w), 1109 (m), 1064 (w), 1041(m), 983 (m) cm^{-1} .

3. Results and Discussion

3.1 Synthesis and characterization of **1** and **2**

The zinc dimers **1** and **2** were synthesized from corresponding zinc metal salts and **LH₂Br₂** in DMF/MeOH at 65°C (scheme 1). Compounds **1** and **2** were formed as colourless crystals and insoluble in almost all organic solvents. Compounds **1** and **2** were characterized by FT-IR, multinuclear (¹H and ¹³C) NMR, UV-vis and fluorescent spectroscopy. In FT-IR, **1** displayed the coordinated COO asymmetric stretching frequency at 1648 cm^{-1} and COO symmetric stretching frequency at 1409 cm^{-1} . In FT-IR, the presence of non-coordinating NO_3^- ions in **1** was confirmed through stretching frequency at 1333 cm^{-1} . Similarly the presence of ClO_4^- ions in **2** was supported by FT-IR stretching frequency of 1068 cm^{-1} . The bridging COO group was evidenced by FT-IR stretching frequency at 1647 and 1409 cm^{-1} . In ¹H NMR, the N-CH-N proton of **1** and **2** are slightly upfield (δ 8.47 ppm for **1** and 8.45 ppm for **2**) shifted compared to that of **LH₂Br₂** (δ 8.59 ppm). The ¹³C NMR chemical shift value of C=O for **1** and **2** are slightly upfield (δ 164.9 ppm for **1** and **2**) shifted compared to that of **LH₂Br₂** (δ 169.9 ppm). In compounds **1** and **2**, the presence of two coordinated DMF molecules are confirmed by ¹H NMR and ¹³C NMR.

As shown in figure 1, the solution state and solid state UV-vis absorption spectra are not comparable. The UV-visible absorption spectra of **1** and **2** were measured in water at room temperature, and displayed the λ_{max} at

203 nm. The λ_{max} of **1** and **2** are almost comparable with **LH₂Br₂** ($\lambda_{\text{max}} = 202$ nm) and this is mainly due to π to π^* transitions of ligand (figure 1a). The solid UV-vis absorption spectrum of **1** showed the almost comparable absorption wavelength with **LH₂Br₂** at 216, 224 and 271 nm except 305 nm. Similarly, the solid UV-vis absorption spectrum of **2** showed the comparable absorption wavelength with **LH₂Br₂** at 239 and 274 nm (figure 1b). The fluorescent emission spectra of **1** and **2** were measured in water at excitation wavelength of 370 nm. A typical two sets of emission wavelengths (401 nm, 424 nm for **1** and 400 nm, 424 nm for **2**) were observed with strong intensity compared to **LH₂Br₂** (figure 1c). In addition, molecule **2** showed an additional emission at 445 nm with weak intensity. In solid fluorescent emission spectra, **1** and **2** showed the corresponding emission wavelengths at 439 and 440 nm. The fluorescent intensity of **LH₂Br₂** is much higher than **1** and **2** (figure 1d).

3.2 Single crystal X-ray structure of **1** and **2**

Compound **1** crystallized in the triclinic space group $P\bar{1}$. Data collection parameters are listed in table 1. The selected bond lengths and bond angles are presented in table 2. The molecular structure of **1** is depicted in figure 2. Molecule **1** is the first tetracationic zinc dimer with a 'paddle-wheel' structure (figure 3a). Asymmetric unit of **1** contains one zinc atom, two half part of **L**, one coordinated molecule of DMF, one lattice H₂O and two NO_3^- anions.

The geometry of zinc(II) is a square pyramidal (figure 3b). The coordination environment around each zinc is fulfilled by four carboxylate moieties of two **LH₂Br₂** and oxygen atoms of DMF. In each zinc centre, the four carboxylate oxygen atoms are arranged nearly in the basal plane while the oxygen atoms of DMF and a Zn(II) centre are in the apical position (figure 3a and b). The core structure of **1** is comparable with that of $[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{10}\text{S}_6\text{Zn}_2]$.^{12a} The Zn and Zn separation distance is 2.969(7) Å, which is slightly longer than that of $[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{10}\text{S}_6\text{Zn}_2]$ (2.943(5) Å).^{12a} The Zn(1)–O_{COO} bond lengths are in the range of 2.025(2) to 2.067(2) Å. Notably, the Zn(1)–O(5)_{DMF} bond length (1.969(2) Å) is shorter than that of Zn(1)–O_{COO}. The O_{COO}–Zn(1)–O_{COO} angle falls in the range of 86.66(9)° to 159.46(9)° and O_{DMF}–Zn(1)–O_{COO} angle falls in the range of 95.03(9)° to 105.68(9)°. Therefore, the overall structural features of **1** are slightly different from the known similar class of neutral zinc carboxylate dimer.

Compound **2** crystallized in the triclinic space group $P\bar{1}$. Data collection parameters are listed in table 1. The

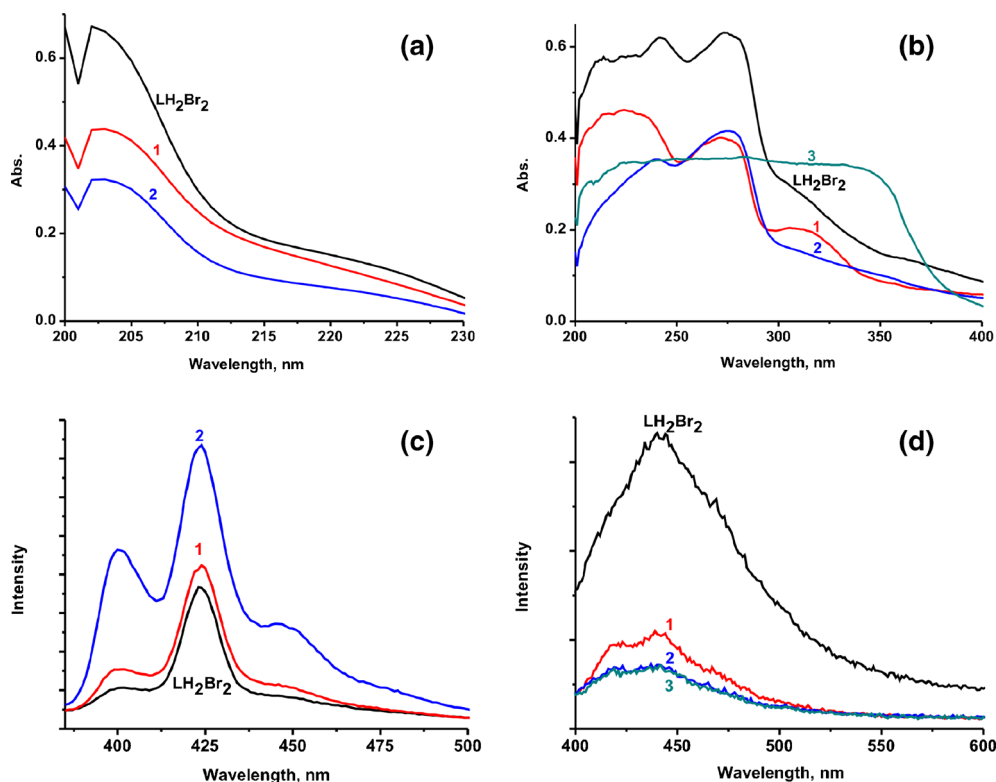


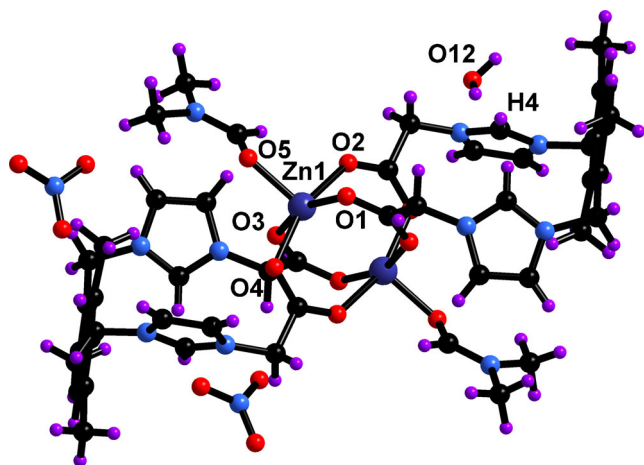
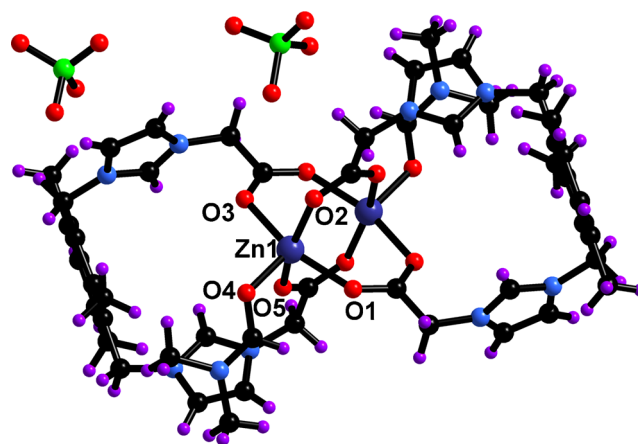
Figure 1. (a) The UV-vis absorption spectra of LH_2Br_2 , **1** and **2** in water at rt (1.6×10^{-6} M). (b) The solid-state UV-vis absorption of **1-3** and LH_2Br_2 at rt. (c) The fluorescent spectra of LH_2Br_2 , **1** and **2** in water at rt with excitation wavelength of 370 nm (1.6×10^{-6} M). (d) The solid-state fluorescent spectra of **1-3** and LH_2Br_2 .

Table 1. Structural parameters of **1-3**.

Parameters	1	2	3
Empirical formula	$\text{C}_{48}\text{H}_{62}\text{N}_{14}\text{O}_{24}\text{Zn}_2$	$\text{C}_{48}\text{H}_{62}\text{Cl}_4\text{N}_{10}\text{O}_{26}\text{Zn}_2$	$\text{C}_{52}\text{H}_{56}\text{Cl}_5\text{N}_{10}\text{O}_{28}\text{Zn}_2$
Formula weight	1349.90	1467.68	1577.13
Temperature (K)	150	150	150
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	9.8562(8)	9.8818(12)	11.3785(6)
$b/\text{\AA}$	10.9897(9)	10.8661(11)	11.7799(6)
$c/\text{\AA}$	14.8662(6)	15.3988(19)	13.7768(5)
$\alpha/^\circ$	93.136(5)	90.332(9)	71.415(5)
$\beta/^\circ$	92.944(5)	90.724(10)	66.956(5)
$\gamma/^\circ$	113.362(7)	111.427(11)	78.817(4)
Volume (\AA^3)	1471.3(2)	1539.0(3)	1605.57(15)
Z	1	1	1
$\rho_{\text{calc}}/\text{mg mm}^{-3}$	1.5234	1.5835	1.6310
Absorption coefficient (mm^{-1})	1.812	3.349	3.658
$F(000)$	699.4	756.9	808.4
Data collected	10579	6144	11867
Unique data	5521	4474	6024
R_{int}	0.0249	0.0272	0.0327
GOF on F^2	1.049	1.048	1.794
$R_1(I > 2s(I))$	0.0549	0.0840	0.1347
$wR_2(I > 2s(I))$	0.0159	0.2343	0.4133
R_1 values (all data)	0.0583	0.0867	0.1483
wR_2 values (all data)	0.1589	0.2344	0.4133

Table 2. Bond lengths and angles of compounds **1**, **2** and **3**.

	$[\text{C}_{42}\text{H}_{38}\text{N}_6\text{O}_{10}\text{S}_6\text{Zn}_2]^{12a}$	1	2	3
		Bond lengths (Å)		
Zn to Zn	2.943(5)	2.969(7)	2.966(12)	2.998(11)
Zn–O _{DMF}	1.982(15)	1.969(2)	1.962(4)	-
Zn–O _{COO}	2.027(16)–2.044(16)	2.025(2)–2.067(2)	2.034(4)–2.074(4)	2.030(5)–2.059(5)
Zn–N	-	-	-	2.035(6)
		Bond angles (°)		
O _{COO} –Zn–O _{COO}	85.74(7)–159.86(7)	86.66(9)–159.46(9)	86.53(16)–159.54(16)	87.2(2)–158.6(2)
O _{DMF} –Zn–O _{COO}	99.34(7)–100.89(7)	95.03(9)–105.68(9)	93.61(16)–106.85(17)	-
N–Zn–O _{COO}	-	-	-	95.9(2)–105.4(2)

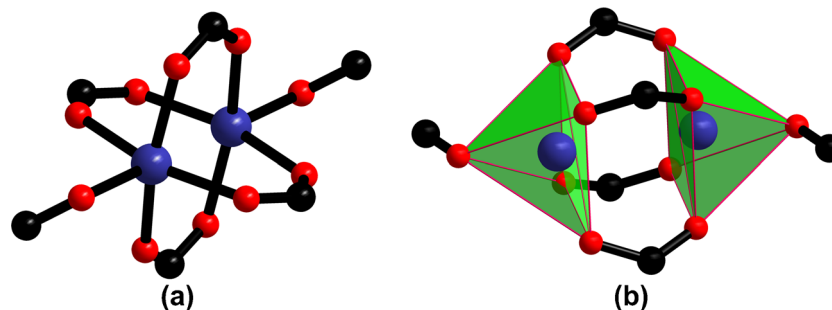
**Figure 2.** Molecular structure of **1**.**Figure 4.** Molecular structure of **2**.

selected bond lengths and bond angles are presented in table 2. The molecular structure of **2** is shown in figure 4. The single crystal X-ray structure of **2** is isostructural with **1**. Thus, the structure feature of **2** has not been discussed in detail. However, the structural parameters of **1** and **2** are significantly different. These are differing by the counter ion and lattice water molecule. In **2**, the Zn and Zn separation distance (2.966(12) Å) is nearly comparable with that of **1**. The Zn(1)–O_{COO} bond lengths are in the range from 2.033(4) to 2.074(4) Å. Notably, the Zn(1)–O(5)_{DMF} bond length (1.962(4) Å) is shorter than that of

Zn(1)–O_{COO}. The O_{COO}–Zn(1)–O_{COO} angle falls in the range of 86.53(16) to 159.54(16)° and O_{DMF}–Zn(1)–O_{COO} angle falls in the range of 93.61(16) to 106.85(16)°.

3.3 Synthesis and characterization of **3**

The zinc polymer **3** was synthesized from the reaction of Zn(ClO₄)₂·6H₂O, 4,4'-bipyridine and **LH₂Br₂** in 1:1 of DMF/MeOH at 65°C for 12 h (scheme 1). The reaction between Zn(NO₃)₂·6H₂O, **LH₂Br₂** and 4,4'-bipyridine in DMF/MeOH mixture gave white

**Figure 3.** (a) Core unit of isostructural zinc dimers **1** and **2** (b) polyhedron view of **1** and **2**.

precipitate, which was dissolved in concentrated sulfuric acid and water in 1:2 ratio to isolate a known $[\text{ZnBr}_2(\mu\text{-bpy})]_\infty$ coordination polymer without **L**.¹⁷ Compound **3** is insoluble in almost all organic solvents. The compound **3** was characterized by FT-IR, UV-vis and fluorescent spectroscopy. In FT-IR, **3** displayed the bridging COO stretching frequency from 1627 and 1485 cm^{-1} . The band at 1041 cm^{-1} is associated with ClO_4^- stretching vibrations. The solid UV-visible absorption spectrum of **3** was measured at room temperature, and displayed the absorption wavelength in the range of 209–353 nm as a broad peak (figure 1b). This is mainly due to the π to π^* and n to π^* transitions

of ligand and 4,4'-bipyridine. In solid fluorescent emission spectrum, **3** showed corresponding emission wavelength at 442 nm and fluorescent intensity of **3** is decreases compared to **2** and LH_2Br_2 (figure 1d).

3.4 Single crystal X-ray structure of **3**

Compound **3** crystallized in the triclinic space group $P\bar{1}$. Data collection parameters are listed in table 1. The selected bond lengths and bond angles are presented in table 2. The solid state structure of **3** is shown in figure 5. The molecule **3** contains Zn dimer paddle wheel unit of **2**, two 4,4'-bipyridine and four

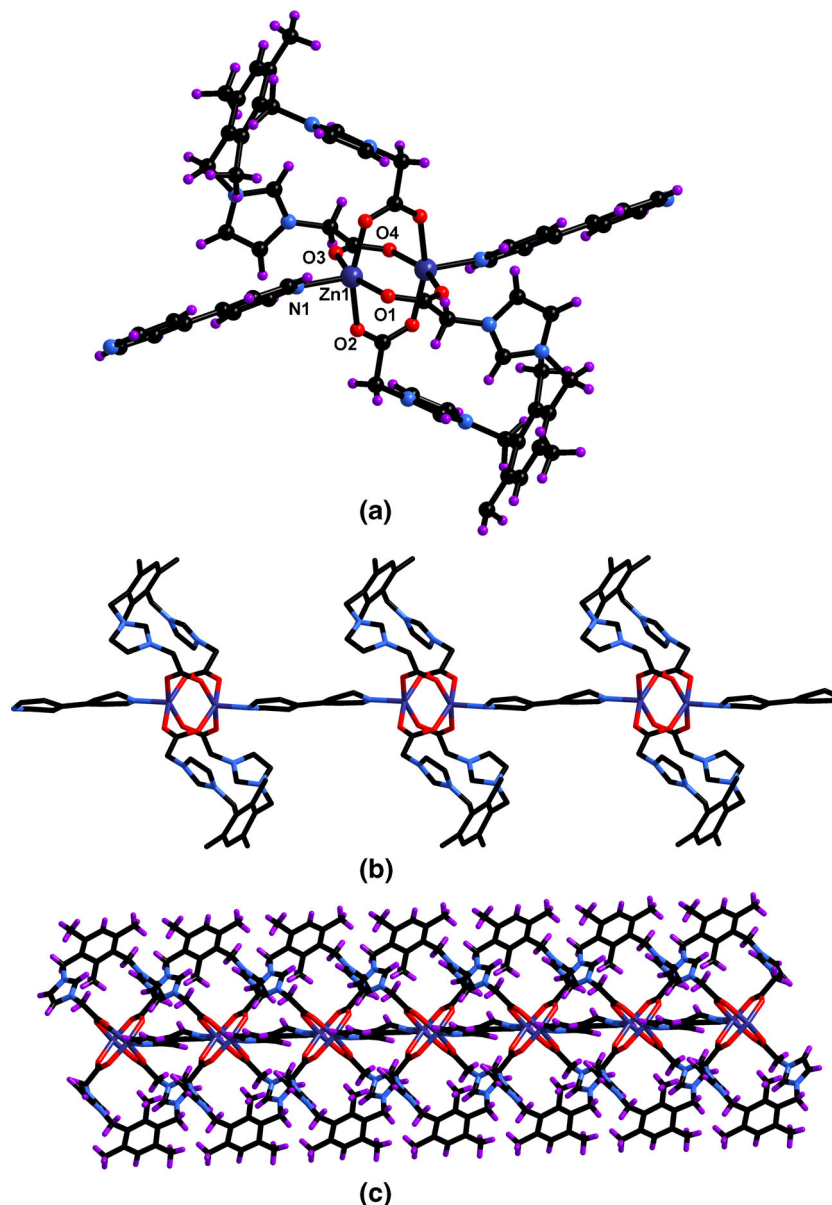


Figure 5. (a) The coordination environment of Zn(II) in compound **3**. (b) 1D chain of **3** view along a axis. Hydrogen atoms and ClO_4^- ions have been omitted for clarity. (c) View of connectivity between square-paddle wheel unit and 4,4'-bipyridine.

uncoordinated ClO_4^- anions. The molecule **3** is a 1D coordination polymer consisting of $[\text{LZn}]_2$ core connected by 4,4'-bipyridine. The Zn and Zn separation distance is 2.998(11) Å, which is slightly longer than that of **1** and **2**. The Zn– O_{COO} bond lengths are in the range of 2.030(5) to 2.059(5) Å. The Zn–N bond length is 2.035(6) Å. The $\text{O}_{\text{COO}}\text{--Zn--O}_{\text{COO}}$ angle falls in the range of 87.2(2)° to 158.6(2)°. The N–Zn– O_{COO} angle falls in the range of 95.9(2)° to 105.4(2)°.

4. Conclusion

In summary, the new tetra cationic zinc dimers (**1** and **2**) and zinc 1D coordination polymer (**3**) were synthesized and characterized by FT-IR, NMR, UV-vis, fluorescent and single crystal X-ray diffraction techniques. The zinc dimers **1** and **2** are rare examples of chelating tetra cationic zinc dimers. Compound **3** is the first example of 1D coordination polymer constructed by zinc dimer core unit connected by 4,4'-bipyridine and the charge is balanced by ClO_4^- anions. The construction of porous coordination network using tetra cationic zinc dimers is in progress.

Supplementary Information

CCDC 994145-994147 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk

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