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ORIGINAL ARTICLE

Impact of binding positions of 1,3-alternate calix[4]arene tetrabenzoic acids on geometry of coordination polymers

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Abstract

In this work, calix[4]arene was used as a building block for the preparation of 1,3-alternate calix[4]arene tetrabenzoic acids. Two structural isomers, **3A** and **3B** were obtained which have the carboxylate groups on the *para* and *meta* positions, respectively. The reaction conditions were optimized to obtain, four coordination polymers with linkers of **3A** and **3B** with Zn^{2+} and Cd^{2+} in different forms. Structural analysis of the product (**CU-SCRU1**) from **3A** with Zn^{2+} showed that it was a 1D polymeric chain. In the case of **3B** with Zn^{2+} it was a 1D polymeric chain in a zig-zag shape (**CU-SCRU2**). The free rotation of the methylene bridge allowed the carboxylate group at the *meta* position of **3B** to coordinate with the Zn^{2+} ion. In both cases, the carboxylate groups at each side of the organic linkers, **3A** and **3B**, chelated to the same metal center (Zn^{2+}) which resulted in the formation of 1D coordination polymers. However, each polymeric chain extended to a 3D framework by nonclassical hydrogen bonding and intermolecular interactions for **CU-SCRU1** and **CU-SCRU2**, respectively. The reaction of **3B** and Cd^{2+} provided coordination polymers that were suitable for structural characterization. Interestingly, two products were formed in the same reaction, **CU-SCRU3** and **CU-SCRU4**, that had different coordination structures. The structural features of these two products suggested that they exist as a 3D framework, however, the nitrogen adsorption–desorption analysis revealed that they were nonporous materials.

"Dedicated to Dr. Jacques Vicens"

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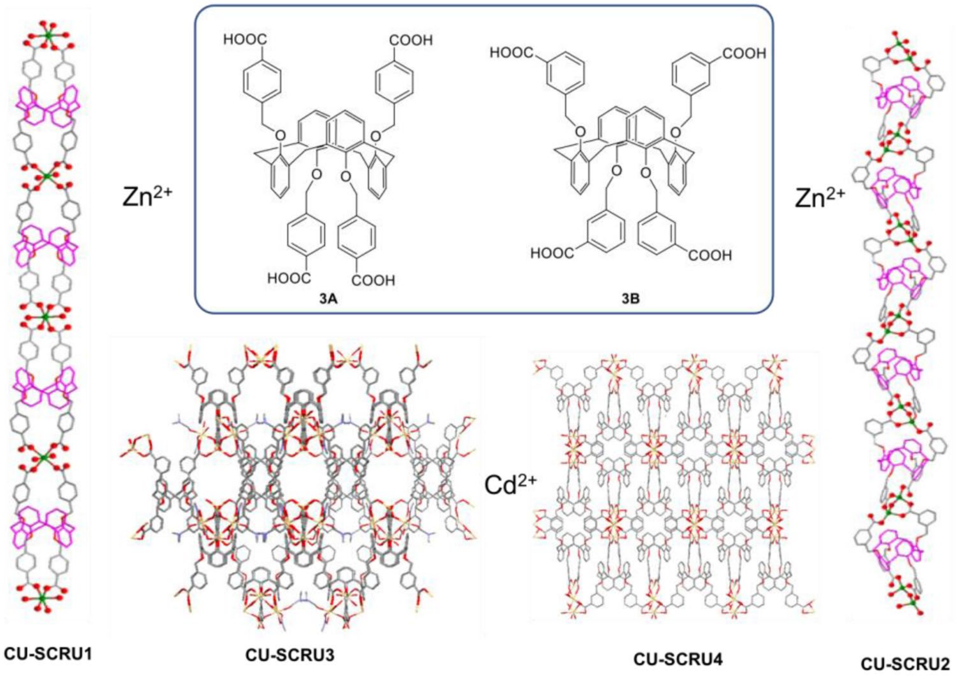
Graphic abstract



Keywords Coordination polymer · Complexation · Calix[4]arene · Crystal structure · Advanced material

Introduction

Coordination polymers are materials composed of metal ions/clusters and organic ligands bonded through coordination bonds [1]. Coordination polymers have structural features in different dimensions where 1D forms a chain [2], 2D a sheet [3], and 3D a framework [4]. The most well-known example of a 3D framework of coordination polymers is MOFs (metal–organic frameworks [5]. These MOF materials possess interesting properties such as large surface area, high pore volume, and relatively high thermal stability [6]. They are applicable in various areas [7], for example, gas storage [8], gas separation [9], and heterogeneous catalyst [10]. Recently, several new MOFs have been designed and synthesized that provide outstanding characteristics [11]. In general, the structure and property of coordination polymers depend on the organic linker and the metal ion [12]. Additionally, the reaction condition plays an important role and different conditions can result in unique product formation [13]. The organic linker is the most important factor on the polymer's structure and properties [14]. Many organic compounds have been designed, modified and applied to the synthesis of coordination polymers. The organic linker should have at least two functional groups for the formation of coordination bonds with the metal ion/cluster. Carboxylate and *N*-heteroaromatic compounds (pyridine derivatives) are the most commonly used chelating groups because of their strong coordination bonds. Over four decades, various types of organic building blocks have been successfully used as ligands in the synthesis of coordination polymers. Most of them are rigid core structure aromatic compounds which are easier to tune and to form predictions for the structure and properties of the resulting coordination polymers [15, 16]. There are fewer examples of aliphatic organic linkers due to their flexibility increasing the complexity of the obtained coordination polymers [17]. The choice of metal ion is also often investigated during optimization as it plays an important role in the formation of the products [18]. However, the chelation between metal ions and organic linkers has been well described and this can help to predict and design the coordination polymers without the need to optimize the metal ion.

Our research group used modified calix[4]arene as the building block for the development of a coordination polymer based sensor [19]. Herein, we designed and synthesized new organic linkers using calix[4]arene as a building block. Calix[4]arene is one of the most popular building blocks in supramolecular chemistry due to its cyclic cavity shape and π-electron rich structure which may provide desired properties in the new coordination polymers. Two organic linkers (**3A** and **3B**) were designed and functionalized in a 1,3-alternate conformation. **3A** and **3B** are structural isomers of each other and have the carboxylate group as the chelating group which can form strong bonds with metal ions. Herein, the synthesis of coordination polymers composing of d^{10} transition metal ions is reported.

Experimental section

Reagents

All reagents were analytical grade and used as received without further purification. Commercial grade solvents were purified by distillation. Anhydrous solvents were dried over CaH_2 and freshly distilled under nitrogen atmosphere. Calix[4]arene was prepared following literature procedures [20].

Characterization

^1H NMR spectra were obtained in $CDCl_3$ or DMSO-*d$_6$* at 400 MHz (Varian, USA). ^{13}C NMR spectra were obtained in $CDCl_3$ or DMSO-*d$_6$* at 100 MHz (Bruker, UK). Chemical shifts (δ) were reported in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) by using α-hydroxycyano cinnamic acid (CCA) as a matrix. XRD patterns were obtained by X-Ray Diffractometry, Rigaku DMAX 2200 Ultima + /Cu lamp. IR spectra were obtained by Fourier Transform Infrared Spectroscopy, Nicolet Impact 412. Nitrogen adsorption analyses were obtained by a Surface area analyzer, BELSORP-mini instrument. The morphologies of coordination polymers were obtained by Scanning Electron Microscopy, Philips XL30CP and their thermal stabilities were measured by Thermo-gravimetric Analysis, TG–DTA Perkin-Elmer Pyris diamond.

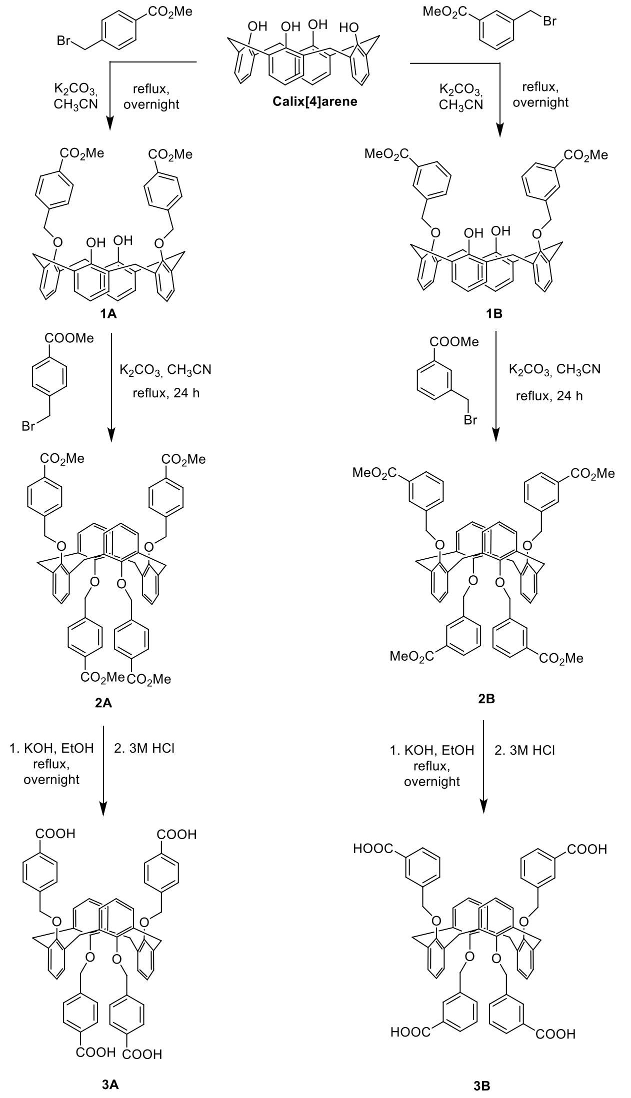
Procedures

Scheme 1.

Synthesis of organic linkers, 1,3-alternate calix[4]arene tetrabenzolic acids, 3A and 3B

The organic linkers 3A and 3B were synthesized following the procedure in scheme 1.

Synthesis of 1,3-calix[4]arene di(methyl-p-benzoate) (*1A*) Calix[4]arene (0.53 g, 1.25 mmol) and potassium carbonate (K_2CO_3) (0.69 g, 6.25 mmol) were placed into a 100 mL two-necked round-bottom flask containing dried acetonitrile (30 mL). The resulting mixture was refluxed under nitrogen atmosphere for 1 h. Then, a solution of methyl-4-(bromomethyl) benzoate (0.57 g, 2.50 mmol) in dried acetonitrile (10 mL) was added and the reaction mixture was allowed to reflux overnight. The reaction was cooled to room temperature. Potassium carbonate was separated by filtration, and the filtrate was dried under vacuum. The crude product was dissolved in dichloromethane (30 mL) and then washed with aqueous 3 M HCl (10 mL), water and brine, respectively. The organic phase was dried over anhydrous Na_2SO_4 and concentrated to one -third of the volume under vacuum. The product was precipitated by methanol. The resulting white solid was filtered and washed with methanol to obtain the desired product (**1A**) (0.66 g, 73%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.98 (4H, d, *J* = 8.0 Hz), 7.81 (4H, d, *J* = 6.4 Hz), 7.06 (4H, d, *J* = 7.6 Hz), 6.91 (4H, d, *J* = 7.2 Hz), 6.78 (2H, t, *J* = 7.6 Hz), 6.66 (2H, t, *J* = 7.6 Hz), 5.13 (4H, s), 5.28 (4H, d, *J* = 13.2 Hz), 3.92 (6H, s), 3.36



Scheme 1 Synthetic pathways of 1,3-alternate calix[4]arene tetrabenzoic acids (**3A** and **3B**)

(4H, d, *J* = 13.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.8, 153.2, 151.7, 141.8, 133.0, 130.1, 129.8, 129.2, 128.6, 127.8, 126.9, 125.7, 119.2, 77.6, 52.1, 31.4; IR (Nujol): ν_{max} 3373, 2924, 1722, 1463, 1279, 1197,1108, 1018, 756.

Synthesis of 1,3-calix[4]-arene di(methyl-m-benzoate) (1B) **1B** was synthesized following the synthetic method as described for **1A** but methyl-3-(bromomethyl) benzoate (0.57 g, 2.50 mmol) was used as a reagent instead of methyl-4-(bromomethyl)benzoate. 1,3-Calix[4]-arene di(methyl-*m*-benzoate) (**1B**) was obtained as a white solid. (0.62 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.16 (2H, s), 8.02 (4H, t, *J* = 7.2 Hz), 7.73 (2H, s), 7.32 (2H, t, *J* = 7.6 Hz), 7.04 (4H, d, *J* = 7.6 Hz), 6.88 (4H, d, *J* = 7.6 Hz), 6.76 (2H, t, *J* = 7.4 Hz), 6.66 (2H, t, *J* = 7.4 Hz), 5.11 (8H, s), 4.50 (4H, d, *J* = 12.8 Hz), 3.87 (12H, s), 3.33 (4H, d, *J* = 13.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 166.8, 153.3, 151.7, 137.2, 133.1, 132.2, 130.4, 129.3, 129.2, 129.1, 128.6, 128.5, 127.9, 125.6, 119.1, 77.8, 52.2, 31.4; IR (Nujol): ν_{max} 3394, 2949, 1721, 1590, 1465, 1287, 1202, 1087, 747.

Synthesis of 1,3-alternate calix[4]arene tetra(methyl-p-benzoate) (*2A*): A solution of 1,3-calix[4]arene di(methyl-*p*-benzoate) (**1A**) (0.43 g, 0.60 mmol) and potassium carbonate (K_2CO_3) (1.38 g, 10.00 mmol) in dried acetonitrile (30 mL) was placed into a 100 mL two-necked round-bottom flask. The mixture was refluxed under a nitrogen atmosphere for 1 h. Then, a solution of methyl-4-(bromomethyl) benzoate (0.30 g, 1.32 mmol) in dried acetonitrile (10 mL) was added. The reaction mixture was refluxed for 2 days. The potassium carbonate was then filtered off and the filtrate was placed into the rotary evaporator to remove the solvent. The crude extract was then dissolved with dichloromethane (30 mL) and washed with 3 M HCl (10 mL), water and brine, respectively. The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent removed under vacuum to one-third of the volume. The desired product (**2A**) was obtained as a white solid (0.35 g, 57%) by precipitation with methanol. ^{1}H NMR (400 MHz, DMSO-d_6) *δ*: 8.15 (8H, d, *J* = 7.6 Hz), 7.20 (8H, d, *J* = 7.6 Hz), 6.66 (8H, d, *J* = 7.6 Hz), 6.45 (4H, t, *J* = 7.4 Hz), 4.92 (8H, s), 4.05 (12H, s), 3.63 (8H, s); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 167.2, 155.5, 143.0, 133.9, 131.1, 129.2, 129.1, 126.5, 122.7, 71.2, 52.2, 37.4; IR (Nujol): ν_{max} 2949, 1718, 1613, 1452, 1287, 1196, 1107, 1020, 754. MALDI-TOF mass(m/z): Anal. caled for [C64H58O12 + Na +]: 1041.382, found 1039.513.

Synthesis of 1,3-alternate calix[4]arene tetra(methyl-m-benzoate) (*2B*): Following the synthetic method as described for **2A**, **2B** was achieved by using **1B** (0.70 g, 1.00 mmol) and methyl-3-(bromomethyl) benzoate (0.50 g, 2.20 mmol) as starting materials. 1,3-Alternate calix[4]arene tetra(methyl-*m*-benzoate) (**2B**) was obtained as a white solid (0.58 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.05 (4H, d, *J* = 7.6 Hz), 7.95 (4H, s), 7.50 (4H, d, *J* = 8.0 Hz), 7.33 (4H, d, *J* = 7.2 Hz), 6.68 (8H, d, *J* = 7.2 Hz), 6.46 (4H, t, *J* = 7.6 Hz), 4.86 (8H, s), 3.97 (12H, s), 3.57(8H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.2, 155.7, 138.4, 133.8, 132.2, 131.1, 129.9, 128.4, 128.2, 127.7, 122.4, 71.9, 52.1, 37.1; IR (Nujol): ν_{max} 2949, 1721, 1588, 1454, 1367, 1286, 1200, 1092, 747. MALDI-TOF mass (m/z): Anal. caled for [$C_{64}H_{58}O_{12} + Na^+$]: 1041.382, found 1039.787.

Synthesis of 1,3-alternate calix[4]arene tetra-p-benzoic acid (*3A*): A solution of 1,3-alternate calix[4]arene tetra(methyl-*p*-benzoate) (**2A**) (1.02 g, 1.00 mmol) in ethanol (30 mL) in a 100 mL two-necked round-bottom flask was gently heated until **2A** was completely soluble. Then, a solution of potassium hydroxide (5.60 g, 100.00 mmol) in water (10 mL) was added. The resulting mixture was refluxed until completion (TLC analysis). The reaction mixture was concentrated under reduced pressure and then acidified by aqueous 3 M HCl (30 mL). The precipitate was filtered and washed with water to yield the desired product **3A** (0.87 g, 90%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.93 (4H, s), 8.00 (8H, d, *J* = 7.6 Hz), 7.23 (8H, d, *J* = 7.6 Hz), 6.59 (8H, d, *J* = 7.6 Hz), 6.28 (4H, d, *J* = 7.0 Hz), 4.86 (4H, s); 3.59 (4H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 167.3, 155.6, 143.1, 133.7, 130.4, 129.5, 128.6, 126.9, 121.7, 71.0, 36.5; FT-IR (KBr pellet) ν/cm^{-1}: 3466, 2915, 1682, 1453, 1418, 1279, 1195, 1092, 1034, 757. MALDI-TOF mass (m/z): Anal. caled for [$C_{60}H_{50}O_{12} + Na^+$]: 985.320, found 983.657.

Synthesis of 1,3-alternate calix[4]arene tetra-m-benzoic acid (*3B*): 1,3-Alternate calix[4]arene tetra-*m*-benzoic acid (**3B**) was obtained by the same procedure used for the synthesis of **3A** but **2B** (0.31 g, 0.30 mmol) was used as a starting material instead of **2A**. The desired product was obtained as a white precipitate (0.26 g, 90% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.88 (4H, s), 7.89 (4H, d, *J* = 9.2 Hz), 7.42 (4H, d, *J* = 7.4 Hz), 7.22 (4H, d, *J* = 7.6 Hz), 6.60 (8H, d, *J* = 7.6 Hz), 6.26 (4H, t, *J* = 7.2 Hz), 4.74 (8H, s), 3.52 (8H, s); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 167.4, 155.5, 138.4, 133.6, 132.2, 130.4, 130.2, 127.9, 127.8, 121.6, 71.4, 36.4; FT-IR (KBr pellet) ν/cm^{-1}: 3432, 2917, 1691, 1588, 1456, 1409, 1303, 1250, 1200, 1090, 748. MALDI-TOF mass (m/z): Anal. caled for [$C_{60}H_{50}O_{12} + Na^+$]: 985.320, found 983.616.

Synthesis of coordination polymers

Synthesis of coordination polymers from *3A* and Zn(II) ion A solvothermal reaction was carried out with the organic linker **3A** and $Zn(NO_3)_2.6H_2O$ in a mixed solvent of DMF and DEF (diethylfomamide) (1:1, v/v) that was placed in a 10 mL vial and sealed. It was kept at 90 °C in an oven for

48 h, then cooled to room temperature over 12 h. and colorless needle-like crystals were obtained (**CU-SCRU1**).

Synthesis of coordination polymers from *3B* and Zn(II)ion A solvothermal reaction was carried out with the organic linker **3B** and Zn(NO$_3$)$_2$.6H$_2$O in 100 mL of a Teflon-lined stainless steel vessel containing a mixture of DMF:DEF (1:1, v/v, 30 mL) as solvents. The mixture was heated to 150 °C in 6 h and kept at this temperature for 48 h. After cooling to room temperature for 24 h, cubic colorless crystals were obtained (**SCRU-CU2**).

Synthesis of coordination polymers from *3B* and Cd(II) ion The organic linker **3B** with Cd(NO$_3$)$_2$.4H$_2$O was dissolved in a mixture of DMF and DEF (1:1, v/v) in a 10 mL vial and sealed. The reaction vessel was kept at 90 °C in the oven for 48 h, then cooled to room temperature over 12 h which yielded colorless polyhedral crystals (**CU-SCRU3** and **CU-SCRU4**).

Results and discussion

Synthesis of 1,3-alternate calix[4]arene tetra-benzoic acids, *3A* and *3B*.

The synthesis of 1,3-alternate calix[4]arene tetrabenzoic acids, **3A**, and **3B** involved three reaction steps. In the first step, calix[4]arene reacted with methyl-4-(bromomethyl) benzoate or methyl-3-(bromomethyl) benzoate in dry CH$_3$CN by using K$_2$CO$_3$ as base to selectively provided 1,3-calix[4]arene di(methyl-*p*-benzoate) (**1A**) or 1,3-calix[4] arene di(methyl-*m*-benzoate) (**1B**) in good yields of 73% and 69%, respectively. In the second step, the reaction of **1A** or **1B** with methyl-4-(bromomethyl) benzoate or methyl-3-(bromomethyl) benzoate in the presence of K$_2$CO$_3$ provided the desired conformation of the products, 1,3-alternate calix[4]arene tetra(methyl-*p*-benzoate) (**2A**) or 1,3-alternate calix[4]arene tetra(methyl-*m*-benzoate) (**2B**) in moderate yields, 57% and 56% respectively. The 1,3-alternate conformations of **2A** and **2B** were confirmed by singlet signals of methylene bridge protons at 3.63 and 3.57 ppm, respectively. The products obtained in each step were easily precipitated in CH$_2$Cl$_2$/MeOH. In the final step, compound **2A** or **2B** was hydrolyzed under refluxing condition in the presence of excess KOH and then acidified by HCl to provide 1,3-alternate calix[4]arene tetra-*p*-benzoic acid (**3A**), 92% yield, or 1,3-alternate calix[4]arene tetra-*m*-benzoic acid (**3B**), 90% yield. The single crystals of **2B** and **3A** were obtained as shown in Fig. 1.

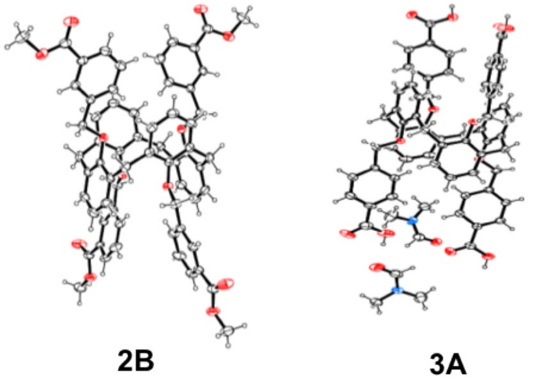


Fig. 1 Crystal structures of compound **2B** and **3A** (ORTEP draws of **2B** and **3A** displacement ellipsoids are scaled to the 25% probability level)

Synthesis of coordination polymers.

Synthesis of coordination polymers by organic linkers, **3A** and **3B,** were successfully carried out under optimized conditions to provide four single crystals from three reactions which meant that there were two types of coordination polymers formed in the same reaction.

Coordination polymers, *CU-SCRU1* and *CU-SCRU2*.

The optimal reaction conditions of the reaction between 1,3-alternate calix[4]arene tetra-*p*-benzoic acid (**3A**) or 1,3-alternate calix[4]arene tetra-*m*-benzoic acid (**3B**) and Zn(II) ion provided the 1D coordination polymers, named **CU-SCRU1** (**3A**-Zn) and **CU-SCRU2** (**3B**-Zn), respectively.

Single-crystal X-ray diffraction analysis showed that **CU-SCRU1** was composed of two kinds of crystallographically independent Zn(II) ions. The Zn1(II) ion which exhibits octahedral coordination geometry with four monodentate carboxylate oxygen atoms in the equatorial positions and two oxygen atoms from DMF molecules in the axial positions (Fig. 2). The Zn1-O bond lengths were in the range of 2.047–2.128 Å.

The coordination environment of the Zn2(II) ion is the same as the Zn1(II) ion with the Zn2-O bond lengths being in the range of 2.040–2.134 Å.

The coordination geometry of Zn1(II) and Zn2(II) ions are perpendicular to each other. The structure of **CU-SCRU1** extends in a 1D linear chain by coordination bonds as displayed in Fig. 3. The 2D and 3D structures of **CU-SCRU1** were formed by 1D-polymeric chains with weak intermolecular interaction (nonclassical H-bonding).

The **CU-SCRU2** was composed of two kinds of crystallographically independent Zn(II) ions. Both the Zn1(II) ion and the Zn2(II) ion were in a tetrahedral geometry composed of three oxygen atoms from three carboxylic groups

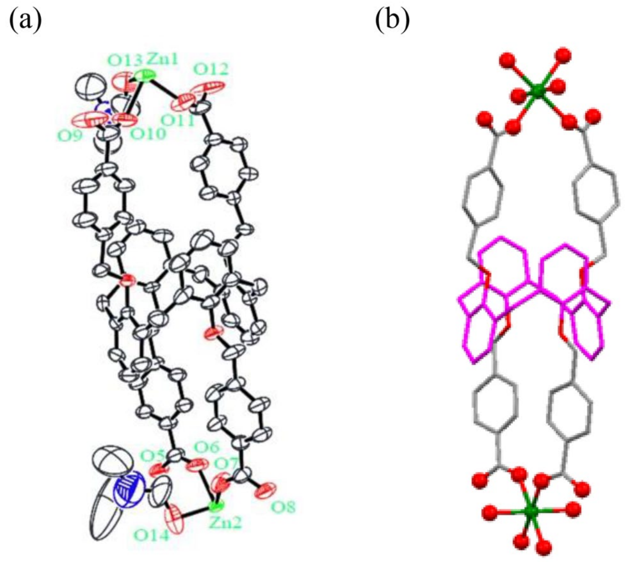


Fig. 2 Coordination environment of **CU-SCRU1**; (**a**) the asymmetric unit and the related coordination atoms are labeled as follows with the hydrogen atoms omitted for clarity: green, Zn1 and Zn2; red, O; blue, N; black, C. (**b**) Zn(II) ion located in an octahedral geometry, image generated by Mercury

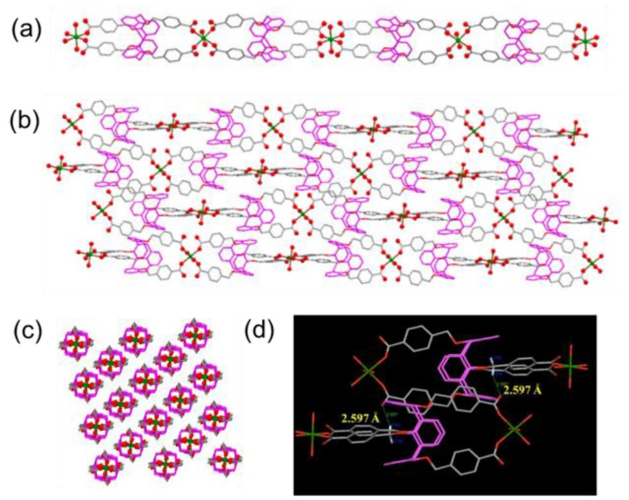


Fig. 3 (**a**) Overall 1D polymeric chain of **CU-SCRU1**. (**b**) Side view 2D structure of **CU-SCRU1** (**c**) Top view of the 3D structure of **CU-SCRU1**. (**d**) Non-classical H-bonding between 1D-polymeric chains of **CU-SCRU1** (Images are generated by Mercury)

in chelating monodentate mode and one oxygen atom in a bridging mode between the Zn1(II) ion and the Zn2(II) ion (see Fig. 4). For the Zn1(II) ion, the bond lengths of Zn1-O were in the range of 1.938–1.992 Å and the bond angle of the tetrahedral geometry was 98.9–123.2°. In the case of the Zn2(II) ion, the Zn2-O bond lengths were in the range 1.907–2.007 Å and their bond angles lied between

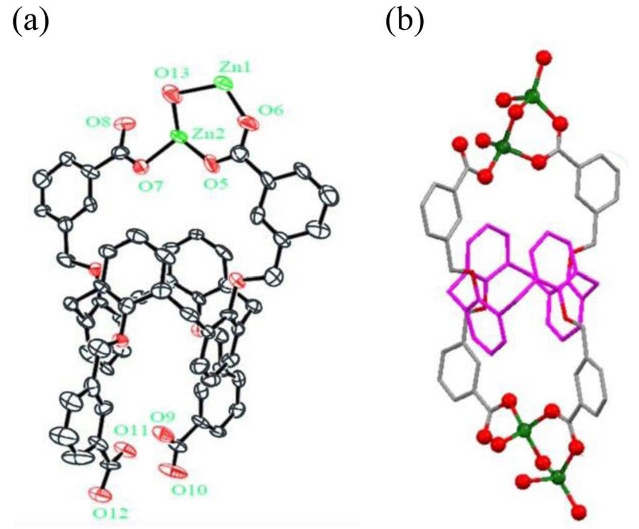


Fig. 4 (**a**) Coordination environment of **CU-SCRU2**; the asymmetric unit and the related coordination atoms are labeled as follows with the hydrogen atoms omitted for clarity: green, Zn1 and Zn2; red, O; blue, N; black, C. (**b**) The tetrahedral coordination modes of the Zn(II) ion in the complex **CU-SCRU2**

Table 1 Selected bond lengths (Å) and bond angles (deg) for **CU-SCRU1**[1] and **CU-SCRU2**[2]

CU-SCRU1	CU-SCRU2
O(10)-Zn(1) 2.128(7)	Zn(1)-Zn(2) 2.936(2)
O(11)-Zn(1) 2.047(8)	O(6)-Zn(1) 1.970(10)
O(13)-Zn(1) 2.068(9)	Zn(1)-O(9)#2 1.938(9)
O(6)-Zn(2) 2.134(6)	Zn(1)-O(11)#2 1.992(9)
O(7)-Zn(2) 2.062(7)	O(13)-Zn(1) 1.957(10)
O(14)-Zn(2) 2.040(9)	O(5)-Zn(2) 2.007(9)
O(11)#1-Zn(1)-O(11) 180.0(7)	O(7)-Zn(2) 1.907(8)
O(11)#1-Zn(1)-O(13)#1 92.9(4)	Zn(2)-O(12)#2 1.999(10)
O(11)-Zn(1)-O(13)#1 87.1(4)	O(13)-Zn(2) 1.927(10)
O(13)#1-Zn(1)-O(13) 180.0(4)	Zn(2)-O(13)-Zn(1) 98.2(5)
O(11)#1-Zn(1)-O(10) 95.6(3)	O(9)#2-Zn(1)-O(13) 123.2(4)
O(11)-Zn(1)-O(10) 84.4(3)	O(9)#2-Zn(1)-O(6) 111.8(4)
O(13)#1-Zn(1)-O(10) 91.5(3)	O(13)-Zn(1)-O(6) 110.8(4)
O(13)-Zn(1)-O(10) 88.5(3)	O(9)#2-Zn(1)-O(11)#2 107.8(4)
O(10)-Zn(1)-O(10)#1 180.0(2)	O(13)-Zn(1)-O(11)#2 100.8(4)
O(14)#2-Zn(2)-O(14) 180.0(3)	O(6)-Zn(1)-O(11)#2 98.9(4)
O(14)-Zn(2)-O(7)#2 90.5(4)	O(7)-Zn(2)-O(13) 123.8(4)
O(14)-Zn(2)-O(7) 89.5(4)	O(7)-Zn(2)-O(12)#2 115.4(4)
O(7)#2-Zn(2)-O(7) 180.0(1)	O(13)-Zn(2)-O(12)#2 105.8(4)
O(14)#2-Zn(2)-O(6)#2 89.9(4)	O(7)-Zn(2)-O(5) 103.9(4)
O(14)-Zn(2)-O(6)#2 90.1(4)	O(13)-Zn(2)-O(5) 106.6(4)
O(7)-Zn(2)-O(6)#2 94.6(3)	O(12)#2-Zn(2)-O(5) 97.9(4)
O(14)-Zn(2)-O(6) 89.9(4)	
O(7)-Zn(2)-O(6) 85.4(3)	
O(6)#2-Zn(2)-O(6) 180.0(2)	

[1] Symmetry transformations used to generate equivalent atoms: #1 -x + 1,-y,-z #2 -x, y + 2,z + 1

[2] Symmetry transformations used to generate equivalent atoms: #1 -x + 1,-y,-z #2 -x,-y + 2,-z + 1

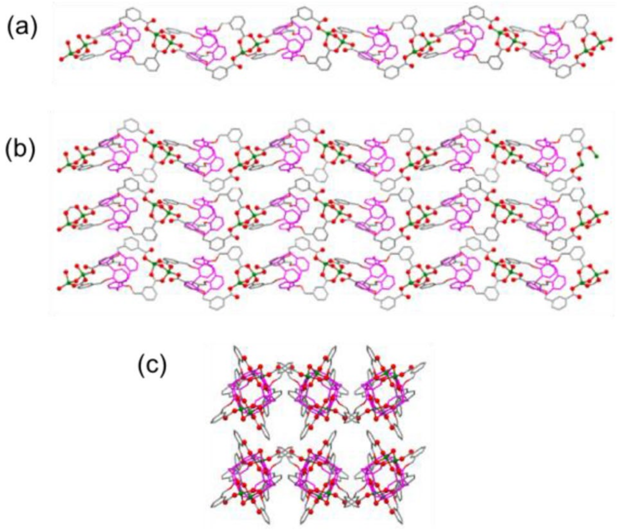


Fig. 5 (**a**) Overall 1D polymeric chain of **CU-SCRU2**. (**b**) Side view 2D structure of **CU-SCRU2** (**c**) Top view of the 3D structure of **CU-SCRU2**. (Images are generated by Mercury)

103.9° and 115.4°. Selected bond lengths and bond angles are listed in Table 1.

The structure of **CU-SCRU2** was a 1D zig-zag polymeric chain which was extended by coordination bonds as shown in Fig. 5. The 2D and 3D structures of the **CU-SCRU2** were extended by weak intermolecular interactions.

Comparing the coordination geometries of the Zn(II) ions in the complex of **CU-SCRU1** and **CU-SCRU2**, they possess octahedral and tetrahedral coordination geometry, respectively which might result from the different positions of the carboxylic acid groups on the organic linkers **3A** and **3B** and their different synthesis conditions as mentioned previously.

Coordination polymers, *CU-SCRU3* and *CU-SCRU4*.

With suitable reaction conditions, the coordination between the organic linker **3B** and the Cd(II) ion provided colorless polyhedral crystals which were characterized by single-crystal X-ray diffraction analysis. Interestingly, there were two crystal structures (**CU-SCRU3** and **CU-SCRU4**) formed in the same reaction. This phenomenon might be explained by the free rotation of the methylene bridge in organic linkers **3A** and **3B** resulting in different coordination polymer structures [21]. From the crystal structure of **CU-SCRU3**, as shown in Fig. 6, two Cd(II) ions showed different coordination environments. The Cd1(II) ion was at the center of an octahedral geometry, formed from four carboxylate oxygen atoms and two oxygen atoms from the solvent (DMF). However, the Cd2(II) ion formed a six-coordinated twisted octahedral geometry, surrounded by six oxygen atoms from three different **3B** anions. Selected bond lengths and bond angles of **CU-SCRU3** and **CU-SCRU4** are listed in Table 2.

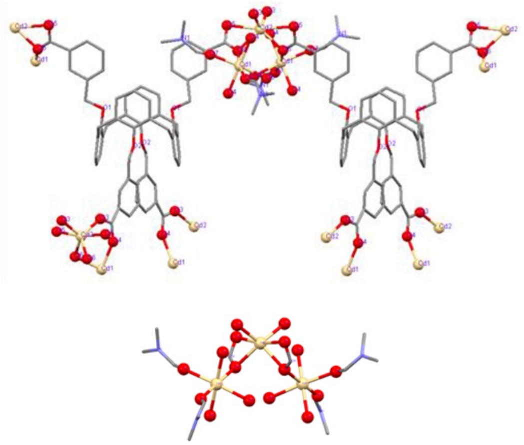


Fig. 6 Coordination environment of **CU-SCRU3**. (Images are generated by Mercury)

The structure of **CU-SCRU3** featured a 3D framework as displayed in Fig. 7

The crystal structure of **CU-SCRU4** is shown in Fig. 8 which was also composed of two kinds of crystallographically independent Cd(II) ions. The Cd1(II) ion was in a distorted octahedral geometry completed by six oxygen atoms from four carboxylic groups in chelating/bridging monodentate, bidentate and bis-bidentate modes. The coordination environment of Cd2(II) forms an octahedral geometry built from two oxygen atoms from water molecules and four oxygen atoms from four carboxylic groups in chelating/bridging monodentate, bidentate and bis-bidentate fashions.

The structure of **CU-SCRU4** also features in a 3D framework as illustrate in Fig. 9.

In comparison to **CU-SCRU2,** two carboxylate groups on each side of the **3B** ligand chelated to Zn(II) ion which made its structure a 1D polymeric chain. However, in **CU-SCRU3** and **CU-SCRU4**, the carboxylate groups had different chelating manners. The Cd(II) ions shared a coordination bond with a carboxylate from other organic linkers which made them form a 3D structure. It should be noted that the organic linkers contain a free rotation of -CH_2 that can increase the complexity of the formation of coordination polymers. However, the nitrogen adsorption–desorption study showed that they were nonporous material as demonstrated in Figs. 10 and 11.

In summary, new organic linkers, 1,3-alternate calix[4]arene tetrabenzoic acids, **3A** and **3B** were synthesized using simple synthetic pathways. The optimized reaction condition in the synthesis of the coordination polymer between **3A/3B** with Zn(II) and Cd(II) provided four single-crystals. The coordination polymer structure from **3A** and Zn(II) resulted in a 1D straight polymeric chain

Table 2 Selected Bond Lengths (Å) and Bond Angles (deg) for **CU-SCRU3**[1] and **CU-SCRU4**[2]

CU-SCRU3	CU-SCRU4
O(4)-Cd(1) 2.20(2)	Cd1-O(5) 2.489(14)
O(6)-Cd(1) 2.290(15)	Cd1-O(6) 2.307(10)
O(7)-Cd(1) 2.09(4)	Cd1-O(14)#6 2.128(17)
Cd(1)-O(7)#3 2.09(4)	Cd1-O(10)#7 2.136(17)
Cd(1)-O(4)#3 2.20(2)	Cd1-O(8)#8 2.291(11)
Cd(1)-O(6)#3 2.290(15)	Cd1-O(7)#8 2.521(14)
Cd(2)-O(3)#3 2.29(2)	Cd2-O(9)#6 2.244(15)
Cd(2)-O(3)#4 2.29(2)	Cd2-O(8)#9 2.263(13)
Cd(2)-O(5)#5 2.505(16)	Cd2-O(11)#5 2.276(16)
O(5)-Cd(2) 2.505(16)	Cd2-O(6) 2.300(14)
O(6)-Cd(2) 2.299(12)	Cd2-O(12) 2.48(2)
Cd(2)-O(6)#5 2.299(12)	Cd2- O(13) 2.44(3)
Cd(1)-O(6)-Cd(2) 112.2(7)	O(5)-Cd1-O(7)#8 172.3(4)
O(7)#3-Cd(1)-O(7) 85(3)	O(6)-Cd1-O(5) 53.0(4)
O(7)-Cd(1)-O(4)#3 86.3(16)	O(8)#8-Cd1-O(6) 93.7(4)
O(7)-Cd(1)-O(4) 88.3(13)	O(8)#8-Cd1-O(7)#8 55.0(4)
O(4)#3-Cd(1)-O(4) 173(2)	O(10)#7-Cd1-O(5) 88.9(6)
O(7)#3-Cd(1)-O(6) 96.5(14)	O(10)#7-Cd1-O(6) 133.9(8)
O(7)-Cd(1)-O(6) 170.4(11)	O(10)#7-Cd1-O(7)#8 86.8(6)
O(4)#3-Cd(1)-O(6) 84.2(12)	O(14)#6-Cd1-O(5) 88.4(7)
O(4)-Cd(1)-O(6) 101.2(7)	O(14)#6-Cd1-O(8)#8 133.4(9)
O(6)-Cd(1)-O(6)#3 84.1(6)	O(14)#6-Cd1-O(10)#7 108.8(11)
O(3)#3-Cd(2)-O(3)#4 118.1(19)	O(9)#6-Cd2-O(11)#5 177.2(8)
O(3)#3-Cd(2)-O(6) 93.8(7)	O(8)#9-Cd2-O(6) 83.8 (4)
O(3)#4-Cd(2)-O(6) 129.6(9)	O(8)#9-Cd2-O(13) 171.4(6)
O(6)-Cd(2)-O(6)#5 93.8(6)	O(11)#5-Cd2-O(13) 92.5 (8)
O(3)#3-Cd(2)-O(5) 89.5(6)	O(6)-Cd2-O(13) 90.3(7)
O(3)#4-Cd(2)-O(5) 85.4(6)	O(9)#6-Cd2-O(12) 93.5(8)
O(6)-Cd(2)-O(5) 55.0(5)	O(8)#9-Cd2-O(12) 89.6(6)
O(6)#5-Cd(2)-O(5) 133.7(5)	O(6)-Cd2-O(12) 171.5(5)
O(5)-Cd(2)-O(5)#5 170.1(5)	O(13)-Cd2-O(12) 96.8(9)

[1] Symmetry transformations used to generate equivalent atoms:

#1 -x + 7/4,-y + 3/4,z #2 -x + 2,-y + 1,-z #3 x,-y + 5/4,-z + 1/4 #4 -x + 5/4,y,-z + 1/4

#5 -x + 5/4,-y + 5/4,z

[2] Symmetry transformations used to generate equivalent atoms:

#1 x + 1/2,y + 1/2,z #2 -x + 1/2,y + 1/2,-z + 1/2 #3 x,-y + 2,z + 1/2 #4 x + 1,-y + 2,z + 1/2

#5 -x + 1,-y + 2,-z + 1 #6 x,-y + 2,z-1/2 #7 x-1,-y + 2,z-1/2 #8 x-1/2,y-1/2,z

#9 -x + 1/2,y-1/2,-z + 1/2

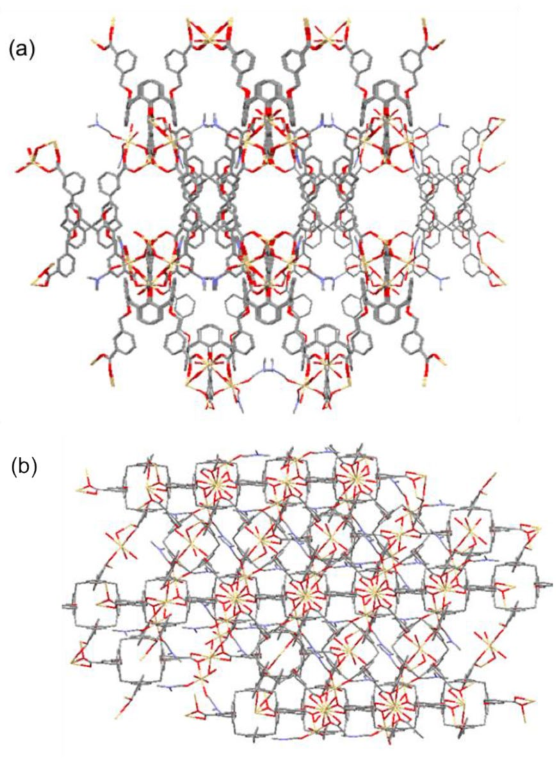


Fig. 7 Overall 3D framework of **CU-SCRU3** generated by Mercury. (**a**) View along the *a*-axis, (**b**) View along the *c*-axis

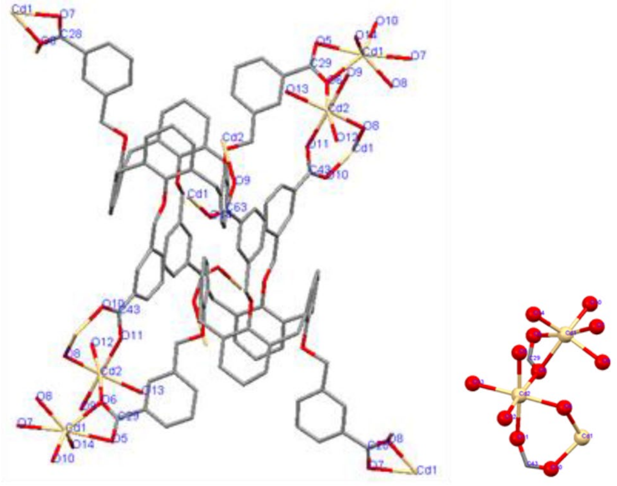


Fig. 8 Coordination environment of **CU-SCRU4** (Images are generated by Mercury)

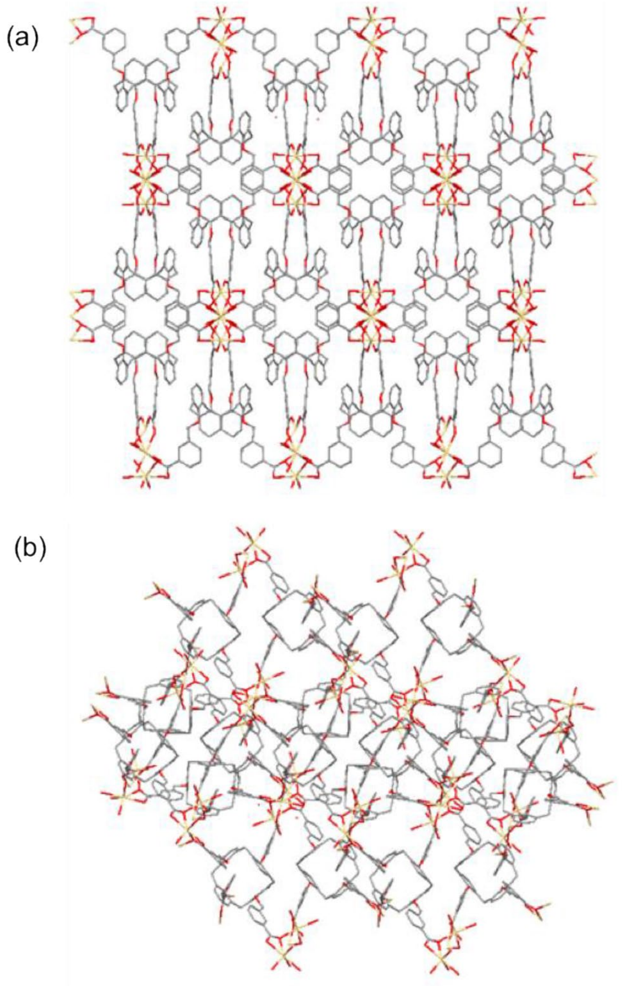


Fig. 9 Overall 3D framework of **CU-SCRU4** generated by Mercury. (**a**) View along the *a*-axis, (**b**) View along the *c*-axis

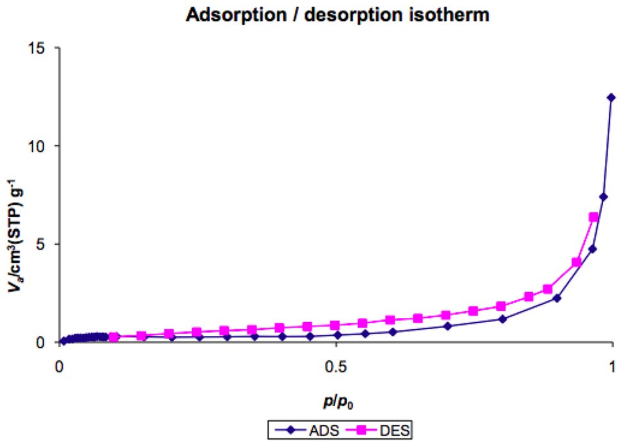


Fig. 10 The nitrogen adsorption–desorption isotherms of bulk coordination polymers (**CU-SCRU3** and **CU-SCRU4**)

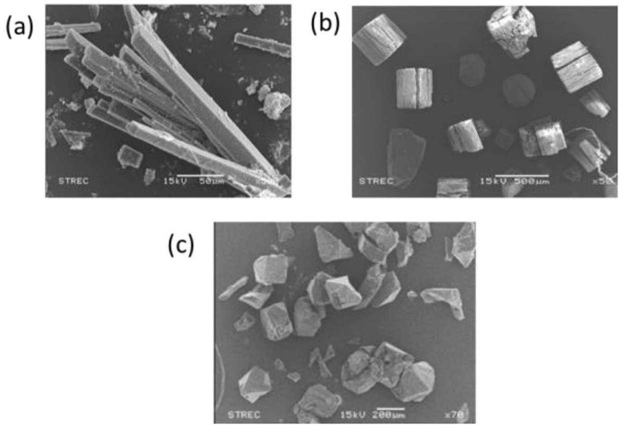


Fig. 11 SEM images of coordination polymers, (**a**) **CU-SCRU1**, (**b**) **CU-SCRU2**, (**c**) **CU-SCRU3** and **CU-SCRU4**)

while **3B** with Zn(II) yielded a 1D coordination polymer in a zig-zag shape. It is important to note that organic linkers which contain moieties that are not preorganized to coordinate with the metal ion might result in the formation of various structures such as the case of organic linker **3B** with Cd(II). In this case, two different non-porous single crystals in the same reaction were produced, **CU-SCRU3**, and **CU-SCRU4**.

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References

1. Janiak, C.: Engineering coordination polymers towards applications. Dalton Trans. **14**, 2781–2804 (2003). https://doi.org/10.1039/B305705B
2. Golenya, I.A., Gumienna-Kontecka, E., Haukka, M., Korsun, O.M., Kalugin, O.N., Fritsky, I.O.: Copper(ii) complexes of 3- and 4-picolinehydroxamic acids: from mononuclear compounds to 1D- and 2D-coordination polymers. CrystEngComm **16**(10), 1904–1918 (2014). https://doi.org/10.1039/C3CE42343C
3. Datta, A., Das, K., Massera, C., Clegg, J.K., Pfrunder, M.C., Garribba, E., Huang, J.-H., Sinha, C., Maji, T.K., Akitsu, T., Orita, S.: A 2-D coordination polymer incorporating cobalt(ii), 2-sulfoterephthalate and the flexible bridging ligand 1,3-di(4-pyridyl) propane. Inorg. Chem. Front. **2**(2), 157–163 (2015). https://doi.org/10.1039/C4QI00201F
4. Chen, S.-C., Zhang, Z.-H., Zhou, Y.-S., Zhou, W.-Y., Li, Y.-Z., He, M.-Y., Chen, Q., Du, M.: Alkali-metal-templated assemblies of new 3D lead(II) tetrachloroterephthalate coordination frameworks. Cryst. Growth Des. **11**(9), 4190–4197 (2011). https://doi.org/10.1021/cg200785g

5. Li, H., Eddaoudi, M., O'Keeffe, M., Yaghi, O.M.: Design and synthesis of an exceptionally stable and highly porous metal-organic framework. Nature **402**, 276–279 (1999)
6. Makal, T.A., Wang, X., Zhou, H.-C.: Tuning the moisture and thermal stability of metal-organic frameworks through incorporation of pendant hydrophobic groups. Cryst. Growth Des. **13**(11), 4760–4768 (2013). https://doi.org/10.1021/cg4009224
7. Mueller, U., Schubert, M., Teich, F., Puetter, H., Schierle-Arndt, K., Pastré, J.: Metal organic frameworks-prospective industrial applications. J. Mater. Chem. **16**, 626–636 (2006). https://doi.org/10.1039/B511962F
8. Düren, T., Bae, Y.S., Snurr, R.Q.: Using molecular simulation to characterize metal organic frameworks for adsorption applications. Chem. Soc. Rev. **38**, 1237–1247 (2009). https://doi.org/10.1039/B803498M
9. Keskin, S., Sholl, D.S.: Screening metal-organic framework materials for membrane-based methane/carbon dioxide separations. J. Phys. Chem. C **111**, 14055–14059 (2007). https://doi.org/10.1021/jp075290l
10. Mlinar, A.N., Keitz, B.K., Gygi, D., Bloch, E.D., Long, J.R., Bell, A.T.: Selective propene oligomerization with nickel(II)-based metal-organic frameworks. ACS Catal. **4**(3), 717–721 (2014). https://doi.org/10.1021/cs401189a
11. Cui, Y., Li, B., He, H., Zhou, W., Chen, B., Qian, G.: Metal-organic frameworks as platforms for functional materials. Acc. Chem. Res. **49**(3), 483–493 (2016). https://doi.org/10.1021/acs.accounts.5b00530
12. Chen, W., Fan, R., Zhang, H., Dong, Y., Wang, P., Yang, Y.: Tunable white-light emission PMMA-supported film materials containing lanthanide coordination polymers: preparation, characterization, and properties. Dalton Trans. **46**(13), 4265–4277 (2017). https://doi.org/10.1039/C7DT00218A
13. Wang, P., Fan, R.-Q., Yang, Y.-L., Liu, X.-R., Xiao, P., Li, X.-Y., Hasi, W., Cao, W.-W.: 1-D Helical chain, 2-D layered network and 3-D Porous lanthanide–organic frameworks based on multiple coordination sites of benzimidazole-5,6-dicarboxylic Acid: synthesis, crystal structure photoluminescence and thermal stability. CrystEngComm **15**(22), 4489–4506 (2013). https://doi.org/10.1039/C3CE40184G
14. Eddaoudi, M., Li, H., Yaghi, O.M.: Highly porous and stable metal-organic frameworks: structure design and sorption properties. J. Am. Chem. Soc. **122**(7), 1391–1397 (2000). https://doi.org/10.1021/ja9933386
15. Frost, H., Snurr, R.Q.: Design requirements for metal-organic frameworks as hydrogen storage materials. J. Phys. Chem. C **111**(50), 18794–18803 (2007). https://doi.org/10.1021/jp076657p
16. Farha, O.K., Malliakas, C.D., Kanatzidis, M.G., Hupp, J.T.: Control over catenation in metal−organic frameworks via rational design of the organic building block. J. Amer. Chem. Soc. **132**(3), 950–952 (2010). https://doi.org/10.1021/ja909519e
17. Aulakh, D., Varghese, J.R., Wriedt, M.: A new design strategy to access zwitterionic metal-organic frameworks from anionic viologen derivates. Inorg. Chem. **54**(4), 1756–1764 (2015). https://doi.org/10.1021/ic5026813
18. Xu, X., Lu, Y., Wang, E., Ma, Y., Bai, X.: Metal-controlled assembly of coordination polymers with the flexible ligand 1,1'-Biphenyl-2,2'-dicarboxylate acid. Cryst. Growth Des. **6**(9), 2029–2035 (2006). https://doi.org/10.1021/cg050671e
19. Thiampanya, P., Muangsin, N., Pulpoka, B.: Azocalix[4]arene strapped Calix[4]pyrrole: a confirmable fluoride sensor. Org. Lett. **14**(16), 4050–4053 (2012). https://doi.org/10.1021/ol301684r
20. Gutsche, C.D., Levine, J.A.: Calix[4]arenes. 6. Synthesis of a functionalizable Calix[4]arene in a conformationlly rigid cone conformation. J. Am. Chem. Soc. **104**(9), 2652–2653 (1982)
21. Makal, T.A., Yakovenko, A.A., Zhou, H.-C.: Isomerism in metal-organic frameworks: "framework isomers." J. Phys. Chem. Lett. **2**(14), 1682–1689 (2011). https://doi.org/10.1021/jz200424h

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