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# Carboxylic acid functionalized *ortho*-linked oxacalix[2]benzene[2]pyrazine: synthesis, structure, hydrogen bond and metal directed self-assembly<sup>†</sup>‡

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Cyclooligomerization of 2,6-dichloropyrazine 4 and benzyl 2,3-dihydroxybenzoate 5 under microwave irradiation resulted in a racemic pair of ester functionalized ortho-linked oxacalix[2]benzene[2]pyrazine 6, which was further transformed to the corresponding racemic carboxylic acid functionalized ortho-linked oxacalix[2]benzene[2]pyrazine 3. Both enantiomers of 3 adopt 1,3-alternate conformations with their two carboxylic acid groups pointing to opposite directions in the solid state. Enantiomers of 3 form a step-like one-dimensional supramolecular polymer via intermolecular hydrogen bond interactions between the carboxylic acids for crystals obtained in methanol. No hydrogen bonds were formed between the carboxylic acids for crystals of **3** obtained in pyridine and aqueous guanidine solutions; instead, intermolecular hydrogen bonds between the carboxylic acid groups of **3** and pyridine, as well as guanidinium ions were formed. Under metal-mediated self-assembly conditions, the pyrazinyl nitrogen atoms in 3 interacted with transition metal ions, such as Ag(I), Cu(II) and Zn(II), and resulted in the formation of four new metal-containing supramolecular complexes. Metallomacrocycles 7, 8 and 9 were formed by reactions of 3 with Ag(1) or Cu(11) ions by bridging two ligands 3 in the equatorial region via M-N coordination bonds. A one-dimensional coordination polymer 10 was generated by reaction between ligand 3 and Zn(II) ions, and a cage-based structure is presented in 10 by bridging of the cyclophane units by Zn<sup>2+</sup> ions via Zn–N and Zn–O bonds.

# Introduction

Self-assembly is a widely used technology in the generation of various supramolecular aggregates.<sup>1</sup> Small molecular building blocks with well-defined geometries, encoded with hydrogen bonding, hydrophobic/hydrophilic,  $\pi$ – $\pi$  stacking, and coordination interaction motifs, are the key to the success in obtaining versatile supramolecular architectures.<sup>2</sup> Macrocyclic molecules, such as cyclodextrins,<sup>3</sup> calix[4]arenes (including resorcin[4]-arene),<sup>4</sup> and cucurbiturils,<sup>5</sup> due to their well-defined cavity structures and conformational preferences, have been intensively used

in the construction of various supramolecular objects via selfassembly. Heterocalixaromatics, structural analogues of calixarenes, have recently attracted considerable attention in the area of supramolecular chemistry.<sup>6</sup> Due to the intrinsic electronic nature of the heteroatoms, which can form various degrees of conjugation with their neighboring aromatic units, heterocalixaromatics can thus exhibit unique conformational features and versatile recognition properties.7 The incorporation of nitrogencontaining heterocycles into oxa- and aza-calixarene derivatives by Wang et al.,<sup>8</sup> Katz et al.,<sup>9</sup> Debaen et al.,<sup>10</sup> and our group<sup>11</sup> has made this class of molecules even more attractive in generating new metallosupramolecular objects with well-defined structures and recognition properties through metal-directed selfassembly. In our previous reports, we have shown that ortholinked oxacalix[2]benzene[2]pyrazine 1 and oxacalix[2]arene[2]pyrazine 2 (Chart 1) could be used to assemble discrete metalcontaining molecular cages, infinite chains of coordination cages, as well as one-dimensional coordination polymers via coordination-driven self-assembly, and some of the resulting coordination cages could act as host molecules to encapsulate guest species.<sup>12</sup> However, the studies on coordination-driven self-assembly behaviors of heterocalixaromatics are currently limited only to 1 and 2, mainly due to the synthetic difficulties encountered in obtaining these macrocycles with multiple functionalities, which thus hindered their use as molecular building blocks in constructing sophisticated metallosupramolecular

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<sup>†</sup>Dedicated to Professor Wen-Qi Chen on the occasion of his 80th birthday.

<sup>&</sup>lt;sup>‡</sup>Electronic supplementary information (ESI) available: <sup>1</sup>H and <sup>13</sup>C NMR for the new synthesized ligand. HRMS (ESI) data for 1 : 1 adduct of **3** and pyridine and complexes **7** and **8**. CCDC 825937, 825938, 825939, 825940, 825941, 825942, 825943. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11283c

objects *via* metal-directed self-assembly. Herein, we wish to report our results on the synthesis and structure of an *ortho*-linked oxacalix[2]benzene[2]pyrazine **3** bearing two carboxylic acid functions (Scheme 1) and the use of **3** in assembling various supramolecular aggregates, including hydrogen bond-driven self-assembly of a one-dimensional step-like supramolecular polymer, coordination-driven self-assembly of metallo-macrocycles and coordination polymer.

## **Experimental section**

#### General

All chemicals were used as received without further purification. Chemical reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Classic column chromatography was performed using Merck 60 (70–230 mesh) silica gel. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 500 spectrometer in the corresponding deuterized solvents. Chemical shifts are reported in parts per million *versus* tetramethylsilane. Mass spectra were recorded on a Bruker micrOTOF-Q spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on a Bruker SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ( $\lambda = 0.71073$  Å).

#### Crystal structure data collection and refinement

Intensity data were collected at 173 K or room temperature (296 K) on a diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) (Table 1). Data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by full-matrix least-



Chart 1 Molecular structures of 1 and 2.

#### Synthesis of ester functionalized *ortho*-linked oxacalix[2]benzene-[2]pyrazine 6

2.6-Dichloropyrazine 4 (488 mg, 3.28 mmol), benzyl 2.3-dihydroxybenzoate 5 (800 mg, 3.28 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (3.21 g, 9.84 mmol) were stirred in DMSO (20 mL) under microwave conditions (160 °C, 30 min). The reaction mixture was poured into 50 mL of water, extracted with ethyl acetate ( $3 \times 20$  mL). The combined extracts were washed with water and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the crude product was purified by chromatography on a silica gel column (petroleum ether-ethyl acetate 10:1). Compound 6 was obtained as white powder. Yield: 80 mg (3.8%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (s, 1H), 7.78 (s, 1H), 7.68 (d, J = 7.9, 1H), 7.35–7.32 (m, 3H), 7.17–7.16 (m, 2H), 7.05 (t, J = 8.0, 1H), 6.86 (d, J = 7.9, 1H), 5.14 (dd,  $J_1 = 12.0$ ,  $J_2 = 31$ , 2H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 163.79, 156.75, 156.44, 146.35, 144.96, 135.27, 128.55, 128.48, 128.43, 128.40, 126.09, 126.01, 125.61, 66.82; HRMS (ESI):  $C_{36}H_{24}N_4O_8Na^+$  m/z calcd 663.1486, found 663.1452.

#### Synthesis of acid functionalized *ortho*-linked oxacalix[2]benzene-[2]pyrazine 3

Compound **6** (2 g, 3 mmol) was dissolved in methanol (200 mL) and hydrogenated in the presence of 10% palladium on charcoal (50 mg). The product **3** was obtained by filtering the palladium on charcoal. Yield: 1.2 g (83%). White powder. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  12.90 (s, 1H), 8.13 (s, 1H), 7.99 (s, 1H), 7.65–7.63 (m, 1H), 7.34 (dd,  $J_1 = 1.0, J_2 = 8.0, 1H$ ), 7.27–7.24 (m, 1H); <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  164.61, 156.59, 156.33, 145.73, 144.01, 128.29, 127.97, 126.42, 126.23, 126.09, 125.50; HRMS (ESI): C<sub>22</sub>H<sub>11</sub>N<sub>4</sub>O<sub>8</sub><sup>-</sup> *m/z* calcd 459.0571, found 458.9823.

#### Synthesis of [Ag<sub>2</sub>(3)<sub>2</sub>·2ACN] 7

Compound **3** (23 mg, 0.05 mmol) and AgBF<sub>4</sub> (29.2 mg, 0.15 mmol) were dissolved in a mixture of *N*-methylpyrrolidone (480  $\mu$ L) and acetonitrile (120  $\mu$ L) under heating. X-ray quality single crystals of complex **7** were obtained by slow diffusion of



Scheme 1 Synthesis of carboxylic acid functionalized *ortho*-linked oxacalix[2]benzene[2]pyrazine 3 (the isomeric structures of 3 are shown in Fig. 1).

	Summary of crystal data and refinement results for complexes 3, 7, 8, 9 and 10
	Table 1

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Complex no:	3	<b>3</b> + pyridine	Guanidinum salts of <b>3</b>	7	8	6	10
Formula Molecular weight T/K Crystal system Space group d/A	$\begin{array}{c} C_{44}H_{24}N_8O_{16}\\ 920,71\\ 173(2)\\ 173(2)\\ 71\\ 71\\ 71\\ 71\\ 10,7260(2)\\ 11,785(2)\\ 11,785(2)\\ 11,785(2)\\ 11,785(2)\\ 10,74450(10)\\ 104,4450(10)\\ 104,4450(10)\\ 104,4450(10)\\ 1957,10(5)\\ 1957,10(5)\\ 1957,10(5)\\ 1957,10(5)\\ 1957,10(5)\\ 1957,10(5)\\ 1957,10(5)\\ 1957,10(5)\\ 100,100\\ 100,$	$\begin{array}{c} C_{32}H_{22}N_6O_8\\ 618.56\\ 173(2)\\ \text{Monoclinic}\\ P2(1)/c\\ 15.8522(6)\\ 12.9196(5)\\ 12.9196(5)\\ 12.9196(5)\\ 14.5605(5)\\ 95.9900(10)\\ 95.9900(10)\\ 90\\ 95.9900(10)\\ 90\\ 90\\ 90\\ 90\\ 90\\ 90\\ 90\\ 90\\ 90\\ 90$	$\begin{array}{c} C_{12}H_{11}N_{5}O_{4}\\ 289,26\\ 296(2)\\ Orthorhombic\\ Fdd2\\ 17.3714(7)\\ 24.5657(6)\\ 12.4327(3)\\ 90\\ 90\\ 90\\ 90\\ 5305.5(3)\\ 8\\ 8\\ 8\\ 1.491\\ 1.491\\ 1.491\\ 2.342\\ 0.512\\ 0.112\\ 1.491\\ 1.53\\ 0.122\\ 3.42\\ 0.0235\\ 0.025\\ 0.025\\ 0.025\\ 0.025\\ 0.025\\ 0.02$	$\begin{array}{c} C_{34}H_{3.3}A_{2}BF_{4}N_{7}O_{10}\\ 894.35\\ 173(2)\\ Monoclinic\\ P2(1)/c\\ 18.4288(8)\\ 14.022(6)\\ 14.022(6)\\ 14.9352(6)\\ 0.0\\ 101.3390(10)\\ 90\\ 101.3390(10)\\ 90\\ 3783.6(3)\\ 2\\ 2\\ 2\\ 1.035\\ 0.618\\ 6622\\ 6662\\ 66$	$\begin{array}{c} C_{64}H_{72}Cl_4Cu_5N_{12}O_{26}\\ 1694.22\\ 173(2)\\ Triclinic\\ 9.3423(3);\\ 9.3423(3);\\ 13.8845(4)\\ 15.2876(4)\\ 15.2876(4)\\ 85.990(4)\\ 71.108(2)\\ 71.$	$\begin{array}{c} C_{9,6}H_{s4}Cl_4Cu_2N_{16}O_{32}\\ 2212,43\\ 173(2)\\ 0rthorhombic\\ 20,2076(6)\\ 15,5977(5)\\ 31.7601(10)\\ 90\\ 90\\ 90\\ 90\\ 90\\ 10.010.5(5)\\ 1.46\\ 8.32\\ 0.36\times 0.28\times 0.22\\ 0.12\\ 1.46\\ 8.322\\ 0.622\\ 112.590\\ 883220(672\\ 1.05\\ 0.0616\\ 0.0616\\ 0.0616\end{array}$	$\begin{array}{c} C_{49}H_{40}ZnN_8O_{21}\\ 1142.28\\ 173(2)\\ Monoclinic\\ P2(1)/c\\ 17.9503(8)\\ 13.7307(5)\\ 90\\ 13.7307(5)\\ 13.7307(5)\\ 109.4960(10)\\ 90\\ 109.4960(10)\\ 90\\ 109.4960(10)\\ 90\\ 109.4960(10)\\ 90\\ 60.598\\ 54.979\\ 8552\\ 85520/707\\ 1.060\\ 0.0368\\ 0.006\\ $
Final $R_1$ , $wR_2$ R indices (all data) Largest diff. peak and hole/e $Å^{-3}$	0.0364, 0.0988 0.0474, 0.1079 0.517, -0.485	0.0403, 0.1002 0.0551, 0.1151 0.457, -0.361	0.0236, 0.0638 0.0243, 0.0646 0.131, -0.124	0.0350, 0.0913 0.0375, 0.0946 1.084, -0.604	0.0399, 0.1074 0.0448, 0.1115 1.012, -0.662	0.0787, 0.2244 0.1010, 0.2534 1.271, -0.837	0.0479, 0.1228 0.0640, 0.1391 1.199, —0.709

benzene into the above solution at room temperature in a dark environment (10 mg, 22%). IR (KBr): 3484, 3072, 2932, 2889, 2491, 1952, 1707, 1635, 1551, 1509, 1451, 1410, 1290, 1264, 1186, 1119, 1081, 1041, 935, 854, 777, 745, 663, 635, 599, 528, 485, 456 cm<sup>-1</sup>; ESI-MS: m/z 567.1, 795.2, 1027.2, 1035.0. Anal. calcd for C<sub>68</sub>H<sub>66</sub>N<sub>14</sub>O<sub>20</sub>Ag<sub>2</sub>B<sub>2</sub>F<sub>8</sub>: C, 45.66; H, 3.72; N, 10.96. Found: C, 45.29; H, 3.88; N, 10.34.

## Synthesis of [Cu<sub>2</sub>(3)<sub>2</sub>Cl<sub>4</sub>]·2NMP 8

Compound **3** (23 mg, 0.05 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (36 mg, 0.15 mmol) were mixed in *N*-methylpyrrolidone (480 µL) and acetonitrile (240 µL). The resulting blue–green slurry turned clear upon addition of HCl (2%, 160 µL). X-ray quality single crystals of complex **8** were obtained by slow diffusion of benzene into the above solution at room temperature (20 mg, 48%). IR (KBr): 3429, 3099, 2931, 2512, 1708, 1645, 1605, 1546, 1506, 1451, 1411, 1332, 1257, 1194, 1144, 1078, 1046, 1012, 942, 856, 774, 749, 664, 530, 489 cm<sup>-1</sup>. ESI-MS: *m*/*z* 532.2, 720.2, 754.3. Anal. calcd for  $C_{54}H_{48}N_{10}O_{21}Cu_2Cl_4$ : C, 44.98; H, 3.36; N, 9.71. Found: C, 44.53; H, 3.39; N, 9.99.

## Synthesis of [Cu<sub>2</sub>(3)<sub>2</sub>Cl<sub>4</sub>]·(3)<sub>2</sub> 9

Compound **3** (6 mg, 0.0125 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (6.4 mg, 0.0375 mmol) were dissolved in methanol (20 mL). X-ray quality single crystals of complex **9** were obtained by slow evaporation of methanol at room temperature (4 mg, 30%). IR (KBr): 3439, 3085, 1728, 1636, 1583, 1551, 1454, 1416, 1320, 1267, 1189, 1145, 1075, 1044, 1010, 956, 852, 803, 767, 648, 513, 401 cm<sup>-1</sup>. Anal. calcd for C<sub>44</sub>H<sub>24</sub>Cl<sub>2</sub>CuN<sub>8</sub>O<sub>16</sub>: C, 50.08; H, 2.29; N, 10.62. Found: C, 49.94; H, 1.24; N, 9.86.

# Synthesis of [Zn(3)<sub>2</sub>·2MeOH]<sub>n</sub> 10

Compound **3** (23 mg, 0.05 mmol) and Zn(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (52 mg, 0.15 mmol) were dissolved in methanol (4 mL). X-ray quality single crystals of complex **10** were obtained by slow evaporation of methanol at room temperature (12 mg, 43%). IR (KBr): 1646, 1610, 1583, 1554, 1448, 1425, 1398, 1334, 1304, 1271, 1250, 1188, 1149, 1074, 1046, 1011, 952, 846, 767 cm<sup>-1</sup>. Anal. calcd for  $C_{44}H_{24}N_8O_{16}Zn$ : C, 53.59; H, 2.45; N, 11.36. Found: C, 51.08; H, 2.05; N, 10.08.

# **Results and discussion**

# Synthesis of carboxylic acids functionalized *ortho*-linked oxacalix[2]benzene[2]pyrazine 3

The synthesis of ester functionalized *ortho*-linked oxacalix[2]benzene[2]pyrazine **6** could not be isolated by straightforward heating of **4** and **5** in DMSO in the presence of  $Cs_2CO_3$  as in the conventional synthesis of unsubstituted *ortho*-linked oxacalix[2]benzene[2]pyrazine reported previously.<sup>11a</sup> We thus examined numerous reaction conditions, and fortunately, compound **6** was isolated in 3.8% yield as a pair of isomers by heating the reaction mixture of **4** and **5** in DMSO in the presence of  $Cs_2CO_3$  at 160 °C for 30 min under microwave irradiation. Followed by Pd



**Fig. 1** Crystal structure of the isomeric pair of **3** obtained in methanol (top), pyridine (middle) and aqueous guanidine solution (bottom). Color code: O (red), N (blue), and C (gray).

catalyzed hydrogenation of 6, an isomeric pair of compound 3 was thus obtained, as shown in Scheme 1 (the two isomeric pairs of 3 and 6 could not be distinguished in the 2-D drawing, however, the isomeric structure of 3 can be viewed in the crystal structure, as seen in Fig. 1; for detailed synthetic procedure, see Experimental section).

#### Structure and conformation of 3

Previous studies revealed that replacing the methylene groups by heteroatoms in the bridging positions of calix[4]arenes resulted in heteocalix[4] aromatics with mainly 1,3-alternate conformations.<sup>8a,10b,14</sup> An ortho-linked oxacalix[2]benzene[2]pyrazine 1 was also found to adopt a 1,3-alternate conformation.<sup>11a</sup> In order to analyze solvent influences on the intermolecular hydrogen bond interaction patterns between the carboxylic acid functions of 3, single crystals of 3 of X-ray diffraction quality were grown in methanol, pyridine and aqueous guanidine solutions. It was found that both isomers of 3 (obtained in all three solvents) adopt 1,3-alternate conformations, and the ratio between the two isomers is 1:1 in all three cases. Compound 3 was found to cocrystallize with pyridine and guanidinium ions (discussed in later section), but not in the case of methanol. The structures of the isomeric pair of 3 obtained in the above mentioned three solvents are shown in Fig. 1. The bridging oxygen atoms in macrocycle 3 are found to be conjugated with pyrazine rings with an average C-O bond distance of 1.36 Å, while no conjugation exists between the bridging oxygen atoms and the phenyl planes (average C-O bond distance: 1.39 Å). The two carboxylic acid groups in 3 are pointing in opposite directions. Small differences were found in dihedral angles (4.5°, 12.7° and 10.5°) and their



Fig. 2 Formation of a one-dimensional step-like polymer *via* intermolecular hydrogen bond interactions between the carboxylic acid functions of a single enantiomer **3** obtained in methanol. Color code: O (red), N (blue), and C (gray).

corresponding centroid-to-centroid distances (4.60 Å, 4.86 Å and 4.80 Å) between the face-to-face oriented pair of phenyl planes of 3 obtained from methanol, pyridine and aqueous guanidinium solutions, respectively. For the pair of pyrazinyl rings in 3, different trans-annular N····N distances between the two upper rim nitrogen atoms (5.74 Å, 5.25 Å, and 4.04 Å), as well as the two lower rim nitrogen atoms (2.85 Å, 2.85 Å, and 2.88 Å) were found for 3 obtained in methanol, pyridine, and aqueous guanidinium solution, thus creating different dihedral angles between the pair of pyrazinyl rings (70.2°, 51.2°, and 24.3° for 3 obtained in methanol, pyridine, and aqueous guanidinium solution, respectively). The two torsional angles between the carboxylate planes and their connecting phenyl rings are found to be different for 3 obtained in methanol (10.4° and 12.9°) and in pyridine (2.8° and 6.3°), while both torsional angles are 37.0° between the carboxylate planes and their connecting phenyl rings for 3 obtained in aqueous guanidine solution.

#### Molecular interactions and self-assemblies of 3

Carboxylic acids are known to form dimers via hydrogen bond interactions in methanol.<sup>15</sup> In the presence of organic bases, such as pyridine and guanidinium ions, the hydrogen bonds between the carboxylic acids are broken, instead, new hydrogen bonds (or ion pairs) between the carboxylic acid functions and organic bases are formed. In the present study, both isomers of compound 3 are found equally presented in the single crystals grown in the three solvent systems. Molecular crystal structure of compound 3, grown in methanol, reveals a typical hydrogen-bonded pattern for carboxylic acids. The intermolecular hydrogen bond interactions between the carboxylic acid functions of 3 (O---O distance: 2.63–2.65 Å) resulted in a one-dimensional stepped polymeric chain-like topology, and each polymeric chain is enantiomerically pure, as shown in Fig. 2 (also see Fig. S1<sup>‡</sup>). No hydrogen bond interactions exist between the carboxylic acid groups and the pyrazinyl nitrogen atoms in the crystals of 3 grown in methanol.



Fig. 3 Intermolecular hydrogen bond interactions between the carboxylic acid groups of a pair of isomers 3 and pyridines. Color code: O (red), N (blue), and C (gray).

Molecular crystals of **3**, grown in pyridine, revealed no intermolecular hydrogen bonds between the carboxylic acid functions being formed, instead, the intermolecular hydrogen bonds between the carboxylic acid groups of **3** and pyridinyl nitrogen atoms were observed (O····N distance: 2.60 Å and 2.63 Å), shown in Fig. 3. <sup>1</sup>H NMR spectrum of the dissolved co-crystals of **3** and pyridine in CDCl<sub>3</sub> shows a downfield peak at 15.4 ppm for –COOH proton, suggesting the existence of intermolecular hydrogen bonding interactions between the carboxylic acid groups and pyridine in solution; ESI-MS results demonstrate the presence of 1:1 adducts of **3** and pyridine in solution with a signal at m/z 540.5266 (ESI<sup>‡</sup>).

The crystals of the guanidinium salt of **3** were obtained by slow evaporation of its aqueous solution. Guanidinium ions and **3** formed a 2 : 1 adduct in which each guanidinium ion formed an ion pair with one carboxylic acid function in **3** (Fig. 4 and Fig. S2<sup>‡</sup>). Each guanidinium ion is found hydrogen-bonded to three carboxylate groups (N····O distances: 2.85–2.96 Å) and a pyrazinyl nitrogen atom (N····N distance: 3.03 Å) from four independent molecules of **3**. The similar length of the three C–N bond distances in the guanidinium unit (1.31 Å–1.33 Å) indicates its complete protonation. The disappearance of the acid protons in the <sup>1</sup>H NMR spectrum of the guanidinium salt of **3** in CDCl<sub>3</sub> also demonstrates the complete deprotonation of the carboxylic acid functions of **3** in its aqueous guanidine solution.

# Self-assembled metallosupramolecular cages and coordination polymers based on 3

As shown in Fig. 1, the two upper rim nitrogen atoms of the face-to-face oriented pyrazinyl rings in **3** are directed outward relative to the central cavity of the oxacalix[4]arene ligand, and the adjustable dihedral angle between the two pyrazinyl rings could make them easy to fit the coordination geometrical requirements adopted by different transition metal ions, leading to the formation of coordination supramolecular cages and polymers *via* metal–ligand coordinative interactions.<sup>12</sup> On the other hand,



Fig. 4 Intermolecular hydrogen bond pattern between a guanidinium ion and three carboxylic acid groups, a pyrazinyl nitrogen atom from four independent molecules of 3. Color code: O (red), N (blue), and C (gray).

the carboxylic acid groups in **3** could also participate in the interactions with metal ions or solvent molecules. We thus envisioned that under metal-directed self-assembly conditions, the interactions between the cyclophane ligand **3** and metal ions, such as Ag(1), Cu( $\pi$ ) and Zn( $\pi$ ), could potentially generate more sophisticated supramolecular architectures. In the following section of this paper, the results of metal-directed self-assembly based on **3** in *N*-methylpyrrolidone (NMP) and methanol are discussed.

Due to the extremely low solubility of **3** in nonpolar solvents, the polar solvent NMP was first employed in the self-assembly process. A discrete silver-containing molecular cage **7** was prepared by dissolving  $AgBF_4$  and **3** in NMP and acetonitrile. Single crystals of the cage complex **7** suitable for X-ray analysis



**Fig. 5** Crystal structure of **7** shows the Ag-containing coordination cage formed by an isomeric pair of ligand **3**. Color code: Ag (green), O (red), N (blue), C (gray), B (brown) and F (yellow).

were obtained by slow diffusion of benzene into the reaction mixture at ambient temperature in a dark environment. <sup>1</sup>H NMR study revealed that cage 7 does not survive in coordinating solvents like DMSO-d<sub>6</sub>, acetonitrile-d<sub>3</sub> and DMF-d<sub>7</sub>, and complex 7 was insoluble in nonpolar solvents, such as benzene-d<sub>6</sub>, CDCl<sub>3</sub> and CD<sub>3</sub>NO<sub>2</sub>, thus preventing the study of the solution properties of complex 7 by NMR techniques. ESI-MS study was carried out in NMP, signals at m/z 567.1, 795.2, 1027.2 and 1035.0, which can be assigned to  $[Ag(3)]^+$  or  $[Ag_2(3)_2]^{2+}$ ,  $[Ag_2(\mathbf{3}^-)\cdot\mathbf{3}ACN]^+$ ,  $[Ag(\mathbf{3})_2]^+$  and  $[Ag_2(\mathbf{3}^-)\cdot NMP]^+$  (ACN = acetonitrile, NMP = N-methylpyrrolidone), respectively, are observed (ESI<sup>±</sup>). These results demonstrate the presence of silver complexes in solution, similar to silver complexes formed by silver ions and pyrazinyl-based oxacalix[2]benzene[2]pyrazine ligands,<sup>12</sup> as well as pyridinyl-based cyclotriveratrylene ligands in solution.<sup>16</sup> The ESI-MS results suggest that the cage complex 7 was formed by these silver complex species in the crystallization process.

Single crystal X-ray diffraction analysis unambiguously established the cage-based structure of  $[Ag_2(3)_2 \cdot 2ACN]$  7. Shown in Fig. 5, an isomeric pair of ligand 3 is bridged by two  $Ag^+$  ions in the equatorial region, resulting in the formation of the rhomboidal molecular cage 7. This result suggests the existence of an assembly process of chiral self-discrimination in the system. Each Ag(I) ion in 7 is five coordinated and adopts a distorted trigonal bipyramidal arrangement, the silver centre is occupied by three nitrogen atoms (two from pyrazinyl nitrogen atoms of 3, one from a coordinated acetonitrile) and two fluorine atoms (from two weakly coordinated BF4- anions). The three Ag-N bonds (Ag– $N_{pv}$  = 2.25(1) and 2.29(1) Å, and Ag– $N_{CMe}$  = 2.27 (1) Å) form a nonequivalent trigonal plane, with the N<sub>pv</sub>-Ag-N<sub>py</sub> and two N<sub>py</sub>-Ag-NCMe angles of 130.3(1)°, 122.0(1)° and 107.7(1)°, respectively. The coordinated acetonitrile is pointing outward relative to the Ag-containing cage center (Ag-Ag-NCMe angle: 170.5°). The two weakly coordinated fluorine atoms (Ag-F distances: 2.68 Å and 2.77 Å) occupy the opposite apical positions of the trigonal bipyramidal with a F-Ag-F angle



**Fig. 6** Crystal structure of **8** shows a Cu-containing coordination cage self-assembled based on an isomeric pair of **3**. Color code: Cu (deep red), O (red), N (blue), C (gray) and Cl (green).

of 172.5°. The equal coordination environments of the two Ag centres in 7 indicate the highly symmetrical nature of the cage complex. The two crystallographically equivalent Ag<sup>+</sup> ions in this  $[Ag_2(3)_2]$ -based cage are separated by 6.76 Å, which is shorter than the Ag···Ag distance (7.87 Å) of the similar cage complex  $[Ag_2(1)_2]$ .<sup>12</sup> In the  $[Ag_2(1)_2]$ -based cage, the cage void was occupied by a hydrophobic methyl group from an acetonitrile coordinated to a neighboring cage.<sup>12</sup> However, this is not the case in 7; the void of the present cage  $[Ag_2(3)_2]$  7 is found unfilled by any guest molecules, as its two opposite openings are blocked by acetonitriles coordinated to its neighboring cage complexes (Fig. S3<sup> $\pm$ </sup>). In [Ag<sub>2</sub>(3)<sub>2</sub>]-based cage 7, the eight pyrazinyl nitrogen atoms and the two silver centres form a plane with a deviation of 0.021 Å. The nitrogen atoms of the two coordinated acetonitriles are found located on opposite sides the plane (0.07 Å). The dihedral angle between the two pyrazinyl rings of ligand 3 in cage 7 is 41.8°, while the dihedral angle and the corresponding centroid-centroid distance between the pair of phenyl planes of ligand 3 in cage 7 are 15.7° and 4.91 Å, respectively. No intermolecular hydrogen bonds between the carboxylic acid groups (carboxylic acids dimers) of ligands 3 in 7 were formed. Instead, each carboxylic acid function in 7 is found hydrogen bonded to a NMP molecule (Fig. 5). All attempts to generate  $[Ag_2(3)_2]$ -based cage complex in methanol failed, as crystals of ligand 3 were obtained in all attempts.

The Cu-based cage complex  $[Cu_2(3)_2Cl_4]$ ·2NMP **8** was prepared by mixing Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and **3** in NMP and acetonitrile, the resulting blue–green slurry turned clear upon addition of 2% aqueous HCl. Single crystals of complex **8** were obtained by slow diffusion of benzene into the reaction mixture at room temperature. Due to the electronic effect of the paramagnetic Cu<sup>2+</sup> ion, broad peaks for pyrazinyl protons are given in the <sup>1</sup>H NMR spectrum of **8** in DMF-d<sub>7</sub>, which contrast the sharp peaks in the <sup>1</sup>H NMR spectrum of the free ligand **3** (ESI‡). ESI-MS shows peaks at *m*/*z* 532.2, 720.2 and 754.3 for the NMP solution of complex **8**, we could only assign the signal at 720.2 to [Cu-(**3**<sup>-</sup>)·2NMP]<sup>+</sup>, and the other signals remain to be correctly assigned to their corresponding complex species (ESI‡). The crystal structure of **8**, determined at 173 K, revealed a similar cage-based topology to that of **7**, shown in Fig. 6. The cage



**Fig. 7** Molecular structure of complex **9** shows a similar  $[Cu_2(3')_2Cl_4]$  cage-based structural motif similar to that of **8**, but the two apical positions of the square pyramidal Cu(II) centres are occupied by a racemic pair of ligand **3'** in **9**, instead of two NMP ligands in complex **8**. Selected bond angles (°): Cl–Cu–Cl, 166.7; N–Cu–Cl, 88.0, 88.8, 90.3, 90.6°; N<sub>api</sub>–Cu–N, 91.9, 98.3; N<sub>api</sub>–Cu–Cl, 94.0, 99.3; N<sub>api</sub>–Cu–Cu, 156.5. Color code: Cu (deep red), O (red), N (blue), C (gray) and Cl (green).

complex 8 was assembled by bridging a pair of isomeric 3 via coordinative interactions with two Cu<sup>2+</sup> ions in the equatorial region, suggesting an assembly process of chiral self-discrimination. Each Cu<sup>2+</sup> ion adopts a distorted square pyramidal arrangement, in which the Cu<sup>2+</sup> centre is occupied by two pyrazinyl nitrogen atoms from the isomeric pair of cage forming ligands 3, two chloride atoms, and an oxygen atom from a coordinated solvent molecule of NMP. As a result, the two Cu-N bonds (2.03(1) Å) and the two Cu–Cl bonds (2.27(1) Å, 2.30(1) Å) form a distorted tetragonal plane with the four N-Cu-Cl angles of 87.6(1)°, 88.2(1)°, 89.7(1)° and 90.7(1)°, respectively. The coordinated NMP occupies the apical position of the tetragonal pyramidal with a Cu–O bond distance of 2.20(1) Å, two O-Cu-N angles of 92.4(1)° and 103.2(1)°, and two O-Cu-Cl angles of  $94.4(1)^{\circ}$  and  $99.6(1)^{\circ}$ , respectively. The two coordinated NMP molecules in cage complex 8 are directed outward relative to the cage center with two equal O-Cu-Cu angles of 150.1°. The equal coordination environment of the two Cu centres indicates the high symmetric nature of the cage 8. The two crystallographically equivalent  $Cu^{2+}$  cations in cage 8 are separated by only 4.95 Å, which is shorter than that of a similar Cu-based cage  $[Cu_2(1)_2]$  (Cu-Cu distance: 5.66 Å),<sup>12b</sup> as well as the Ag-based cage  $[Ag_2(3)_2]$  7 (Ag--Ag distance: 6.76 Å). As a result, the two coordinated pyrazinyl rings in each Cu<sup>2+</sup> centre in 8 are almost in one plane with a N-Cu-N angle of 164.3(1)°. The Cl-Cu-Cl angle is 166.0(1)°. No guest molecules could fill in the narrow cage void of 8. The dihedral angle between the two pyrazinyl rings of ligand 3 in 8 is 30.0°, while the dihedral angle and the corresponding centroid-centroid distance between the pair of phenyl planes of ligand 3 in 8 are 35.5° and 5.53 Å, respectively. Similar to complex 7, an equatorial plane is formed by the eight pyrazinyl nitrogen atoms and the two copper atoms with a deviation of 0.08 Å, and the two coordinated oxygen atoms from NMPs are found located on the opposite sides of the

plane (1.24 Å). The carboxylic acid functions in 8 were found hydrogen-bonded with either a NMP or a water molecule.

Reaction of CuCl<sub>2</sub>·2H<sub>2</sub>O and ligand 3 in methanol resulted in a Cu-based cage complex 9, which has a ligand : Cu(II) ratio of 2:1. The crystals of complex 9 were insoluble, so the solution properties of the complex could not be investigated. Due to the quality of the single crystal, we were only able to get a dataset that did not allow for high-quality refinement, but could be used to confirm the basic structural motif of 9. As show in Fig. 7, complex 9 contains a similar  $[Cu_2(3')_2Cl_4]$ -based (3' = dimethyl esters of 3) cage motif to that of 8. However, structural changes for ligands 3 were found in complex 9, as the carboxylic acid functions of 3 in 9 have been transformed to methyl ester groups in methanol solution. Also different from 8, the two apically coordinated NMP molecules in 8 were replaced by an isomeric pair of ligands 3' in 9. Each Cu(II) centre in 9 is coordinated by three pyrazinyl nitrogen atoms and two chloride anions, and adopts a distorted square pyramidal arrangement. The two Cu-N bonds (2.05(1) Å, 2.06(1) Å) and the two Cu-Cl bonds (2.26(2) Å, 2.28(1) Å) around each Cu(II) centre in cage  $[Cu_2(3')_2Cl_4]$ form a distorted tetragonal plane, and the two pyrazine rings around each Cu(II) centre in  $[Cu_2(3')_2Cl_4]$  are almost in one plane with a N-Cu-N angle of 169.7(2)°. The Cu-N bond distances of the apically coordinated ligands 3' are 2.34(1) Å, which are longer than the Cu-N bond distances in the  $[Cu_2(3)_2Cl_4]$  cage motif (2.02–2.05 Å in 8 and 9). Only one upper rim nitrogen atom of the apically coordinated ligand 3' participates in the coordinative interaction with the copper centre, while the other one remains free. The Cu-Cu distance in 9 is 4.43 Å, which is shorter than that in 8 (4.95 Å). Such a short Cu-Cu distance resulted in a smaller dihedral angle between the pair of pyrazinyl rings in the  $[Cu_2(3')_2Cl_4]$  cage in 9 (24.1°, it is 30.0° in 8). The dihedral angle and the corresponding centroid-centroid distance between the pair of phenyl planes

of  $[Cu_2(3')_2Cl_4]$  cage in 9 are 30.1° and 5.34 Å, respectively. In the two apically coordinated ligands 3', the dihedral angle between the pair of pyrazine rings is 48.9°, the dihedral angle and the corresponding centroid–centroid distance between the pair of phenyl planes are 9.3° and 4.74 Å, respectively. Similar to 8, the eight pyrazinyl nitrogen atoms in  $[Cu_2(3')_2Cl_4]$  cage in 9 and the two copper atoms form a plane with a deviation of 0.03 Å. The two apically coordinated pyrazinyl nitrogen atoms of ligands 3' are located on the opposite sides of the plane  $(1.02 \text{ Å}; \text{ESI}^+_2)$ .

Coordination polymer  $[Zn(3)_2 \cdot (MeOH)_2]$  10 was prepared by dissolving  $Zn(BF_4)_2$  and 3 in methanol (see Experimental section). Single crystals of 10 suitable for X-ray diffraction analysis were obtained by slow evaporation of its methanol solution. No proton shifts were observed in the <sup>1</sup>H NMR spectra of 10 relative to the free ligand 3 in solvents like DMSO, methanold<sub>4</sub>, acetonitrile-d<sub>3</sub> and DMF-d<sub>7</sub>, suggesting that complex 10 did not survive in these solvents. The extremely low solubility of 10 in benzene-d<sub>6</sub>, CDCl<sub>3</sub> and CD<sub>3</sub>NO<sub>2</sub>, prevented the further characterization of its solution behavior by NMR techniques. ESI-MS data of 10 have not shown any signals related to  $Zn^{2+}$ complexes of ligand 3, possibly due to the polymeric nature of complex 10. The crystal structure of 10 was determined by single crystal X-ray techniques at 173 K. As shown in Fig. 8, the structure of 10 reveals the formation of a one-dimensional coordination polymer with a 2:1 stoichiometry between ligand 3 and  $Zn^{2+}$  ion, and no  $[Zn_2(3)_2]$  cage-based structural motif, similar to that of 7, 8 and 9, presents in 10. However, a different  $[Zn_2(3)_2]$  cage-based structural motif is present in the coordination polymer 10. Each cage was formed by bridging a pair of enantiomerically pure ligand 3 by two  $Zn^{2+}$  ions via Zn-N and Zn-O coordination bonds (Fig. 8). Viewed along the polymeric chain, it is found that the polymeric chain is formed by the alternation of two different enantiomerically pure  $[Zn_2(3)_2]$ -based cages, resulting in the racemic coordination polymer. In the polymeric structure of 10, each ligand 3 has only one exo-nitrogen atom participating in the coordinative interaction with a  $Zn^{2+}$ cation, while the other one remains free; and one carboxylic acid function was deprotonated and connected to a second Zn<sup>2+</sup> cation through a Zn-O bond. The free carboxylic acid function of ligand 3 in 10 is hydrogen-bonded to a methanol molecule  $(d_{\Omega\dots\Omega} = 2.57$  Å, Fig. 8). The Zn<sup>2+</sup> centre is six-coordinated and adopts a distorted octahedral coordination environment, in which four out of the six coordination sites are occupied by independent ligands 3 through two Zn-O (carboxvlate) bonds (Zn-O bond distances: 2.10(1) and 2.07(1) Å) and two Zn-N bonds (Zn–N distances: 2.26(1), and 2.25(1) Å), the remaining two coordination sites are occupied by two methanol molecules via Zn–O bonds (Zn–O bond distances: 2.09(1) and 2.06(1) Å). As a result, the four coordinated oxygen atoms form a distorted tetragonal plane, and the two pyrazinyl nitrogen atoms occupy the two apical positions of the bipyramidal with a N-Zn-N bond angle of 177.4(1)°. The two carboxylate oxygen atoms occupy the opposite sides of the  $Zn^{2+}$  centre with an O–Zn–O bond angle of 177.9(1)°. Similarly, the two coordinated methanolic oxygen atoms are positioned in the opposite sides of the  $Zn^{2+}$ centre with an O–Zn–O bond angle of  $178.7(1)^{\circ}$ . The Zn<sup>2+</sup> ions in the polymeric chain are separated by 6.89 Å and are arranged with Zn-Zn-Zn angles of 169.8°. The 1.3-alternate



Fig. 8 Polymeric structure of 10 formed by the interaction of  $Zn^{2+}$  ions and 3 (top), two enantiomerically different  $[Zn_2(3)_2]$ -based cage units in coordination polymer 10 (bottom). Color code: Zn (green), O (red), N (blue) and C (gray).

conformation of ligand **3** is retained in the coordination polymer **10**. The dihedral angle between the pair of pyrazine rings of **3** in **10** is 49.6°, while the dihedral angle and its corresponding centroid–centroid distance between the pair of phenyl planes of **3** in **10** are 13.5° and 4.85 Å, respectively. The torsional angle between the phenyl ring and the uncoordinated carboxylic acid plane is 26.2°, while the coordinated carboxylate plane has a torsional angle of 34.8° with its connecting phenyl ring. Methanol molecules were found trapped in the crystal lattice (ESI<sup>‡</sup>).

As shown in Fig. 5–8, the 1,3-alternate conformation of ligand **3** was preserved upon the formation of supramolecular complexes **7**, **8**, **9** and **10**. However, due to the different electronic structures and coordination preferences adopted by different metal ions, the modes of interaction between those metal ions and ligand **3** could be completely different. Therefore, under different coordination-driven self-assembly conditions, ligand **3** could change its coordination modes (M–N or M–O bonds) and adjust its conformational orientation to fulfil the geometric requirements adopted by those metal ions, facilitating the formation of the resulting metallosupramolecular complexes **7**, **8**, **9** and **10**.

In summary, we have successfully synthesized a carboxylic acid functionalized ortho-linked oxacalix[2]arene[2]pyrazine 3 by employing microwave irradiation. Compound 3 was found to exist as a pair of isomers and each isomer adopts a 1,3-alternate conformation with its two carboxylic acid groups pointing in opposite directions. Crystallographic studies revealed the different intermolecular hydrogen bond interaction patterns for crystals of 3 grown in different solvents (methanol, pyridine and aqueous guanidine solution). Under coordination-driven self-assembly conditions, the interactions of racemic 3 with  $Ag^+$  and  $Cu^{2+}$ resulted in the formation of discrete cage-based metallosupramolecules 7, 8 and 9 in a chiral self-discrimination manner by bridging the pair of isomeric ligands 3 via Ag-N and Cu-N coordination bonds in the solid state. However, in the case of  $Zn^{2+}$  ions, a coordination polymer 10 was generated. In polymeric complex 10, dinuclear Zn-containing metallomacrocycles (formed by bridging two enantiomerically pure ligands 3 via Zn-N and Zn-O bonds) act as basic structural motifs of the coordination polymer; different enantiomers of dinuclear Zncontaining metallomacrocycles are alternated in the polymeric chain. The Ag<sup>+</sup> ion in cage complex 7 is found in a five coordination environment and adopts a distorted trigonal bipyramidal geometry; the  $Cu^{2+}$  ions in the cage complexes 8 and 9 are also five-coordinated, but adopt distorted square pyramidal arrangements; the  $Zn^{2+}$  ions in coordination polymer 10 are six-coordinated and adopt octahedral coordination environments. The differing electronic structures and coordination preferences of these metal ions are believed to play a major role in determining the molecular geometries of the resulting supramolecular complexes. The studies on the metal-mediated self-assembly based on oxacalix[n]arene[n]hetarenes, as well as guest recognition and inclusion, are currently ongoing in our laboratory. New results will be reported in due course.

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