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Syntheses, Structures and Properties of Nickel(II) and Manganese(II) Coordination Polymers Based on V-shaped Bis-imidazole and Aromatic Carboxylate Ligands

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1	Syntheses, Structures and Properties of Nickel(II) and Manganese(II)
2	Coordination Polymers Based on V-shaped Bis-imidazole and
3	Aromatic Carboxylate Ligands
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10	
11	ABSTRACT
12	Using V-shaped mixed ligands bis-imidazole and aromatic carboxylic acids, five new
13	coordination polymers namely, $\{[Ni(B-im)(Br-a)Cl] \cdot H_2O\}_n$ (1),
14	{ $[Ni(B-im)(I-a)(H_2O)_2] \cdot 0.5H_2O$ } _n (2), $[Ni(B-im)(I-a)(H_2O)_2]_n$ (3),
15	$[Ni(B-im)(M-a)(H_2O)_2]_n$ (4) and $\{[Mn_2(B-im)_2(I-a)_2] \cdot 2H_2O\}_n$ (5) $[B-im =$
16	1,1'-(5-methyl-1,3-phenylene)bis(1H-imidazole), Br-a = 5-bromonicotinic acid, I-a =
17	isophthalic acid and M-a = 5-methylisophthalic acid] were solvothermally synthesized
18	and fully characterized by IR spectra, element analyses, X-ray powder and
19	single-crystal diffractions, and thermogravimetric analyses. Complexes 1 and 2
20	feature polymeric macrocyclic chain structures containing interesting nanotubular
21	channels, which are constructed by bridging 30-membered macrocyclic [Ni ₃ (B-im) ₃]
22	subunits with Br-a ligands and by bridging folded 20-membered macrocyclic
23	$[Ni_2(B-im)_2]$ subunits with I-a ligands, respectively. Isomorphic complexes 3 and 4
24	represent double-chain structures containing folded 18-membered macrocyclic
25	$[Ni_2(B-im)(I-a)]$ subunits and $[Ni_2(B-im)(M-a)]$ subunits, respectively. Complex 5 is a
26	2D porous coordination polymer containing novel chiral four-stranded Mn(II) chains
27	consisting of two (B-im)-bridged aspiral chiral chains and two (I-a)-bridged
28	heterochiral coaxial 21-helical chains. The results of thermal gravimetric analyses

- 29 suggest that the dehydrated frameworks of **1–5** are stable up to 320 °C. Additionally,
- 30 the magnetism of complexes **3** and **5** were also investigated.
- 31

32 Keywords: Coordination polymer; Crystal structure; V-shaped mixed ligand system;

- 33 Metal-organic nanotube; Magnetism
- 34

35 **1. Introduction**

Over the last several decades there has been much interest in the area of crystal 36 engineering of metal-organic frameworks (MOFs) in view of their potential 37 applications in adsorption [1], photochemical area [2], catalysis [3], and magnetism [4] 38 39 as well as their variety of intriguing architectures [5]. As is known to all, the structures 40 of coordination polymers determine their properties, which has stimulated extensive study upon the internal structure-function relationship [6]. To get novel structures with 41 42 unique performances, much effort has been devoted to controlling the assembled 43 motifs via selecting suitable organic ligands, metal ions, and building blocks [7–12]. 44 The N-containing heterocyclic ligands are studied most frequently not only due to their 45 strong coordination ability of nitrogen atoms with most transition metal ions by 46 coordination bonds, but also due to their rigid skeleton structures and abundant 47 recognition sites for further assembling into higher-dimensional multifunctional 48 supramolecular frameworks through hydrogen bonds, $\pi \cdots \pi$ stacking and Van der 49 Waals' force [13, 14]. Besides, ligands including polycarboxylic groups possess strong 50 coordination ability and diverse coordination models, which makes them being a kind 51 of popular multifunctional ligands [15].

Although the N-containing heterocyclic ligands and aromatic carboxylic acid ligands have been studied a lot, systematic investigation upon the collaborative effect of a mixed ligand system including V-shaped bis-imidazole and aromatic carboxylate ligands in the fabrication of novel MOFs has been reported a little [16]. In this context, a V-shaped molecule 1,1'-(5-methyl-1,3-phenylene)bis(1H-imidazole) (B-im) was choicely selected as the main ligand. The main ligand B-im is a typical angular ditopic

58 linker featuring a semi-rigid skeleton with two extrorse bites, and thereby may have a 59 trend to bridge metal ions into macrocycles or helixes. And meanwhile, V-shaped 60 aromatic carboxylic acids such as 5-bromonicotinic acid (Br-a), isophthalic acid (I-a) 61 and 5-methylisophthalic acid (M-a) which have different symmetric structures and 62 functional groups (see Scheme 1) were introduced as the auxiliary ligands. Through 63 solvothermal reactions of nickel(II) and manganese(II) salts with above mentioned V-shaped ligands, respectively, five new MOFs, namely, $\{[Ni(B-im)(Br-a)Cl] \cdot H_2O\}_n$ 64 $\{[Ni(B-im)(I-a)(H_2O)_2] \cdot 0.5H_2O\}_n$ (2), $[Ni(B-im)(I-a)(H_2O)_2]_n$ 65 (1), (3), $[Ni(B-im)(M-a)(H_2O)_2]_n$ (4) and $\{[Mn_2(B-im)_2(I-a)_2] \cdot 2H_2O\}_n$ (5) were obtained and 66 67 fully characterized by IR spectra, element analyses, X-ray powder and single-crystal 68 diffractions, and thermogravimetric analyses. Additionally, the magnetic properties for

69 crystalline compounds **3** and **5** were also investigated.

70

71 **2. Experimental section**

72 2.1. General information and materials

73 All chemicals purchased were of reagent grades or better and used without further 74 purification. Element analyses were performed with a Carlo-Erba 1106 elemental analyzer. IR spectra (KBr pellets) were recorded on a Nicolet NEXUS 470 FT-IR 75 spectrophotometer from 400 to 4000 cm⁻¹. Thermal analysis curves were scanned 76 under air on a STA 409 PC thermal analyzer. The powered X-ray diffraction (PXRD) 77 patterns of the samples were recorded by a RIGAKU-DMAX2500 X-ray 78 79 diffractometer with Cu-K α radiation. The temperature-dependent magnetic 80 measurements were determined on a Quantum Design SQUID-XL7 magnetometer. 81 Diamagnetic corrections were made using Pascal's constants.

2.2. Syntheses

82

83 2.2.1. Synthesis of $\{[Ni(B-im)(Br-a)Cl] \cdot H_2O\}_n$ (1)

A mixture of B-im (0.05 mmol, 0.0112 g), Br-a (0.05 mmol, 0.0101 g), NiCl₂·6H₂O
(0.05 mmol, 0.0119 g), NaOH (0.05 mmol, 0.002 g), CH₃OH (4 mL) and H₂O (4 mL)
was stirred at room temperature for half an hour, and then sealed into a 25 mL
Teflon-lined stainless autoclave. The autoclave was heated in an oven at 80 °C for 3 d

and then gradually cooled to room temperature. Green prismatic crystals of **1** were collected, washed with ethanol, and dried naturally. Yield: 58% (based on Ni). Selected IR (KBr, cm⁻¹): 3450 (s), 3136 (m), 1608 (s), 1549 (m), 1510 (m), 1441 (m), 1390 (s), 1283 (m), 1127 (m), 1070 (m), 752 (m), 657 (m). Anal. Calcd. for $C_{19}H_{17}BrClN_5O_3Ni$ (%): C, 42.46; H, 3.19; N, 13.03. Found (%): C, 42.80; H, 3.18; N, 13.13.

94 2.2.2. Synthesis of $\{[Ni(B-im)(I-a)(H_2O)_2] \cdot 0.5H_2O\}_n$ (2)

A procedure identical to that for **1** was followed to prepare green needle crystals **2**, except that Br-a (0.05 mmol, 0.0101 g) and NaOH (0.05 mmol, 0.002 g) were replaced by I-a (0.05 mmol, 0.0084 g) and NaOH (0.1 mmol, 0.004 g), respectively. For **2**, Yield: 62% (based on Ni). Selected IR (KBr, cm⁻¹): 3442 (s), 3130 (m), 1609 (s), 1509 (s), 1367 (s), 1242 (m), 1110 (m), 1075 (m), 742 (m), 709 (m), 654 (m), 423 (m). Anal. Calcd. for $C_{21}H_{21}N_4O_{6.5}Ni$ (%): C, 51.25; H, 4.30; N, 11.39. Found (%): C, 51.47; H, 4.27; N, 11.31.

102 2.2.3. Synthesis of $[Ni(B-im)(I-a)(H_2O)_2]_n(3)$

103 A mixture of B-im (0.05 mmol, 0.0112 g), I-a (0.05 mmol, 0.0084 g), NiSO₄· $6H_2O$ 104 (0.05 mmol, 0.0131 g), NaOH (0.1 mmol, 0.004 g), CH₃OH (1 mL) and H₂O (7 mL) 105 was stirred at room temperature for half an hour, and then sealed into a 25 mL 106 Teflon-lined stainless autoclave. The autoclave was heated in an oven at 120 °C for 4 107 d and then gradually cooled to room temperature. Green rod-shaped crystals 3 were 108 collected, washed with ethanol, and dried naturally. Yield: 78% (based on Ni). Selected IR (KBr, cm⁻¹): 3455 (m), 3139 (w), 1609 (s), 1509 (s), 1367 (s), 1287 (m), 109 1247 (m), 1111 (m), 1074 (m), 938 (m), 828 (m), 744 (s), 708 (s), 653 (m), 427 (m). 110 111 Calcd. for C₂₁H₂₀N₄O₆Ni (%): C, 52.21; H, 4.17; N, 11.60. Found (%): C, 51.98; H, 112 4.15; N, 11.69.

113 2.2.4. Synthesis of $[Ni(B-im)(M-a)(H_2O)_2]_n$ (4)

A procedure identical to that for 2 was followed to prepare green needle crystals 4,
except that I-a (0.05 mmol, 0.0084 g) was replaced by M-a (0.05 mmol, 0.009 g). For
4, Yield: 43% (based on Ni). Selected IR (KBr, cm⁻¹): 3462 (m), 3147 (m), 3130 (m),
1612 (s), 1539 (s), 1500 (s), 1434 (m), 1363 (s), 1283 (m), 1247 (m), 1108 (m), 1067

- 118 (m), 935 (m), 857 (m), 836 (m), 750 (m), 717 (s), 654 (m). Calcd. for $C_{22}H_{22}N_4O_6N_1$
- 119 (%): C, 53.21; H, 4.46; N, 11.27. Found (%): C, 53.52; H, 4.58; N, 11.32.
- 120 2.2.5. Synthesis of $\{[Mn_2(B-im)_2(I-a)_2] \cdot 2H_2O\}_n$ (5)

121 A mixture of B-im (0.05 mmol, 0.0112 g), I-a (0.05 mmol, 0.0084 g), MnCl₂ (0.05 mmol, 0.0099 g), NaOH (0.1 mmol, 0.004 g), CH₃CN (3 mL) and H₂O (5 mL) was 122 123 stirred at room temperature for half an hour, and then sealed into a 25 mL Teflon-lined stainless autoclave. The autoclave was heated in an oven at 110 °C for 4 d and then 124 gradually cooled to room temperature. Pale yellow block crystals 5 were collected, 125 126 washed with CH₃CN, and dried naturally. Yield: 63% (based on Mn). Selected IR (KBr, cm⁻¹): 3423 (s), 3138 (w), 1604 (s), 1545 (s), 1505 (s), 1385 (s), 1239 (m), 1112 127 (m), 1067 (m), 1025 (m), 933 (m), 815 (m), 755 (s), 710 (m), 651 (m). Calcd. for 128 129 C₄₂H₃₆N₈O₁₀Mn₂(%): C, 54.67; H, 3.93; N, 12.14. Found (%): C, 54.39; H, 3.86; N, 130 12.09.

131 2.3. X-ray structure determination

Crystallographic data were collected on an Oxford Xcalibur Gemini diffractometer 132 with an Eos detector at 293(3) K using Cu K α radiation ($\lambda = 1.5418$ Å) except for **3** 133 using Mo K α radiation ($\lambda = 0.71073$ Å). Raw data collection and reduction were done 134 using CrysAlisPro software. Empirical absorption correction using spherical 135 136 harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Structures were solved by direct methods and refined by full-matrix least-squares on F² using 137 138 SHELXTL [17]. The non-hydrogen atoms were refined with anisotropic thermal 139 parameters. The carbon H atoms were included in geometric positions and given 140 thermal parameters setting to $1.2 \times U_{eq}$ of the attached atoms. Lattice water H atoms 141 in 5 were not added owing to their disorder. The other water H atoms in those 142 compounds were located from different maps and their positions were fixed during 143 the refinement such that they remained in chemically meaningful positions. Crystal 144 data are summarized in detail in Table 1 while the selected bond lengths and bond 145 angles are listed in Table 2.

146

147 **3. Results and discussion**

148 *3.1. Syntheses and IR spectra*

Compounds 1–5 were solvothermally prepared at a lower temperature range of 80–120 °C using mixed solvents of H₂O and CH₃OH for 1–4 and mixed solvents of H₂O and CH₃CN for 5. The total solvent volume in all the reactions was controlled in 8 mL while the ratios of two mixed solvents were carefully adjusted to fit the initial syntheses of the exhibited compounds perfectly. In all the reactions the equivalent amount of NaOH was added for the full deprotonation of the aromatic carboxylic acids used.

156 In the IR spectra of 1-5, the broad absorptions around 3420-3462 cm⁻¹ are ascribed 157 to O-H stretching vibration of water molecule, and the weaker absorptions around 3136–3156 cm^{-1} are characteristic stretching vibration of C–H in aromatic rings. 158 There is no strong absorption peak around 1700 cm^{-1} for the -COOH stretch, 159 implying that the carboxylic groups in all the compounds are completely deprotonated. 160 161 Characteristic bands of carboxylates for asymmetric stretches $[v_{as}(COO^{-})]$ are at 1608 cm^{-1} for 1, 1609 cm^{-1} for 2 and 3, 1612 cm^{-1} for 4, and 1545 and 1604 cm^{-1} for 5. 162 163 Characteristic bands of carboxylates for symmetric stretches $[v_s(COO^{-})]$ appear at 1390 cm⁻¹ for 1, 1367 cm⁻¹ for 2 and 3, 1363 cm⁻¹ for 4, and 1365 cm⁻¹ for 5. The 164 obviously different values of $\Delta v = v_{as}(COO^{-}) - v_{as}(COO^{-})$ suggest the different 165 166 coordination environment of the carboxylates in 1–5 [18]. Notably, the values of Δv for 2-4 are similar and lager (in a range from 242 to 249 cm⁻¹), suggesting a 167 unidentate coordination mode of carboxylates in each complex. As for 5, the splitting 168 of $v_{as}(COO^{-})$ indicates the different coordination environment of carboxylates. In 169 170 conclusion, the IR data are good agreement with the X-ray analyses.

171 *3.2. Crystal Structures*

Compound 1 crystallizes in the hexagonal $P6_{3}mc$ space group with a Flack parameter of 0.03(3). The asymmetrical unit of 1 consists of one-half Ni, one-half B-im, one-half Br-a, one-half Cl⁻, and one-half free water molecule. As shown in Fig. 1, the central Ni atom adopts a distorted octahedral geometry ligated by one terminal Cl atom, two O atoms from the chelating carboxyl group of one Br-a ligand and three nitrogen atoms from two B-im ligands and another Br-a ligand (The Ni–Cl bond is

178 2.356(2) Å while the Ni–N and Ni–O bonds range from 2.084(3) to 2.225(4) Å).

179 In 1, three V-shaped B-im ligands bridge three Ni nodes into a 30-membered 180 macrocyclic $[Ni_3(B-im)_3]$ subunit (SBU). In the SBU, the three Ni nodes are coplanar 181 and uniformly separated by 9.7025(9) Å. Owing to the obvious distortion of the 182 methylbenzene groups in the B-im ligands from the Ni₃ plane, the SBU looks like a 183 plate where three free water molecules are located through complicated $C-H\cdots O$ and 184 $O-H\cdots Cl$ hydrogen-bonding interactions ($C9\cdots O3 = 3.447(7)$ Å, $O3\cdots Cl1 = 3.305(3)$ Å; see Fig. 2a). Intriguingly, three Br-a ligands pillared adjacent SBUs through 185 186 carboxyl O atoms chelating the Ni centers in one SBU and pyridyl N atoms 187 coordinating the Ni centers in the other, and thereby forming a novel 1D polymeric metal-organic nanotube 1 with the diameter of the opening being about 12 Å (see Fig. 188 189 2b). In the nanotube the distance between the adjacent Ni₃ planes of $[Ni_3(B-im)_3]$ SBUs separated by pillars Br-a is 7.739(1) Å. The nanotube has C_{3y} symmetry, and 190 extends along c-axis. In comparison with the limited 1D polymeric metal-organic 191 192 nanotubes being reported so far, the 1D nanotubular structure with the higher 193 symmetry in 1 is particularly rare [19]. In 1 those 1D nanotubes array parallelly, and 194 every nanotube interdigitates with three adjacent nanotubes through the mutual 195 insertion of B-im ligands into the tubular cavities (see Fig. S1). Clearly, this deep 196 insertion of B-im ligands reduces the effective free volume of the nanotubes.

197 Complex 2 crystallizes in the orthorhombic *Imcm* space group, and its 198 asymmetrical unit consists of one-half Ni, one-half B-im, one-half I-a, two one-half 199 coordinated water molecules, and a quarter of lattice water molecule. The Ni atom is 200 six-coordinated by two nitrogen atoms (N1 and N1A) from two B-im, two oxygen 201 atoms (O1 and O1A) from two I-a, and two oxygen atoms (O3 and O4) from two 202 coordinated water molecules, and thus forming a slightly distorted octahedron 203 geometry with N1, N1A, O1 and O1A in the equatorial plane and O3 and O4 at axial 204 positions (Fig. 3a). A mirror plane m containing the O3 and O4 divides the 205 coordination geometry into two equivalent parts. The Ni–N and Ni–O bonds range 206 from 2.085(2) to 2.118(3) Å.



7 In 2, two B-im ligands link two Ni ions into a folded 20-membered macrocyclic

208 $[Ni_2(B-im)_2]$ SBU which is also halved by the mirror plane *m* containing the O3 and 209 O4 (Fig. 3b). Each SBU is bonded by four I-a ligands, and those SBUs are further 210 interconnected by the I-a ligands through the monodentate bridging of their two 211 carboxyl groups forming a zigzag polymeric chain in which all the SBUs cap the up 212 and down vertices of the zigzag (Fig. 4a). In particular, the chain structure of 2 213 consists of another kind of greater 36-membered macrocycle $[Ni_4(B-im)_2(I-a)_2]$ 214 formed by two I-a ligands bridging two macrocyclic [Ni₂(B-im)₂] SBUs. In the 215 resulting 36-membered macrocycle $[Ni_4(B-im)_2(I-a)_2]$ the four Ni centers are 216 completely coplanar and form a rectangle with the length and width being 10.979 and 9.025 Å, respectively, and the dihedral angle between the two adjacent Ni₄ planes 217 218 being 115.68° (Fig. 4a). Interestingly, when viewed along the *a*-axis, the chain 219 exhibits an oval or quadrangular pore which extends along the chain so that the chain 220 can be thought as a metal-organic polymeric nanotube (Fig. 4b). Indeed, the nanotube 221 2 is irregular in comparison with the nanotube 1. The dimensions of the nanotube 222 approximate to the sizes of the rectangle of the Ni₄.

223 In 2, every coordination water molecule O3 forms three intrachain hydrogen bonds: 224 As a donor hydrogen-bonding two the uncoordinated carboxyl O2 ($O3 \cdots O2 = 2.654(2)$) Å), as an acceptor capturing the lattice water molecule O5 in the larger oval pore 2.2.5 $[Ni_4(B-im)_2(I-a)_2]$ (O5...O3 = 2.947(4) Å). Additionally, every coordination water 226 227 molecule O4 forms two interchain hydrogen bonds with the coordinated carboxyl O1 (O4...O1D = 2.741(3) Å, D = x, -y+1/2, -z+3/2), through which extends those 228 229 nanotubes into a 3D supramolecular architecture (Fig. 5). Notably, those zigzag 230 polymeric chains interdigitate along *b*-axis with their 20-membered macrocyclic 231 $[Ni_2(B-im)_2]$ SBUs inserting into adjacent nanotubes, in which there are obviously 232 interchain $\pi \cdots \pi$ interactions between benzene rings of B-im (centroid-to-centroid 233 distance = 3.771(2) Å, Fig. S2). Such stacking sharply reduces the effective free 234 volume of the nanotubes.

As adjusted the reaction conditions of **2**, i.e., changing the ratio of water and methanol and the reaction temperature from 1:1 and 80 °C to 1:7 and 120 °C, or followed the same reaction procedure for **2** only using M-a instead of I-a, isomorphic

238 complexes **3** and **4** were obtained, respectively. For terseness only the structure of **4** is 239 discussed in detail. The coordination environment around Ni in **3** is given in Fig. S3. 240 Complex 4 crystallized in the orthorhombic *Pnma* space group. The asymmetric 241 unit of 4 contains one-half Ni, one-half B-im ligand, one-half M-a ligand and one 242 coordinated water molecule. The six-coordinated Ni atom located at an inversion 243 center *i* is in a slightly distorted octahedron geometry ligated by two nitrogen atoms 244 (N1 and N1A) from two B-im and two oxygen atoms (O1 and O1A) from two Ma^{2-} in 245 the equatorial plane, and by two oxygen atoms (O3 and O3A) from two terminal 246 water molecules at axial positions (Fig. 6). The Ni–N bonds are 2.076(2) Å while 247 Ni–O bonds cover a range of 2.074(1)-2.121(1) Å. In 4 two Ni ions are bonded by a 248 B-im bridge and a M-a bridge to form another folded 18-membered macrocyclic 249 [Ni(B-im)(M-a)] SBU which is halved by a mirror plane *m* perpendicular to the 250 straight line connecting the two Ni atoms. Those SBUs are further interconnected 251 through sharing common metal nodes, and thereby resulting in the 1D 252 double-stranded chain architecture in 4 (Fig. 6). Every chain further interacts with 253 adjacent chains through $\pi \cdots \pi$ interactions between the benzene rings of B-im from adjacent chains (centroid-to-centroid distance = 3.681(2) Å) and C-H $\cdots \pi$ interactions 254 255 occurring from the methyls of M-a and B-im to the benzene rings of the M-a ligands 256 in adjacent chains (C-to-centroid distances being 3.456(4) and 3.407(3) Å, respectively), and in this way to produce a 3D supramolecular framework in 4 (Fig. 257 258 S4).

Complex **5** crystallizes in the orthorhombic $Pna2_1$ space group with a Flack parameter of 0.484(8). The asymmetrical unit of **5** consists of two Mn, two B-im, two I-a and two free water molecules. In **5**, the two crystallographically independent Mn1 and Mn2 centers adopt five-coordinated patterns, and are located in distorted trigonal bipyramid geometries with three carboxyl O atoms from two different I-a forming the equatorial plane and two N atoms occupying the vertex positions (Fig. 7). The Mn–N and Mn–O bonds cover a normal range from 2.034(5)–2.263(5) Å [20].

266 Complex **5** features a 2D porous coordination polymer containing novel chiral 267 four-stranded Mn(II) chains consisting of two (B-im)-bridged aspiral chiral chains and

268 two (I-a)-bridged heterochiral coaxial 2_1 -helical chains (Fig. 8). In 5, deprotonated I-a 269 ligands have two coordination modes: One half as bis-monodentate bridges like those 270 found in 2 and 3, and the other half as four-connected bridges in a μ_4 -kO:kO':kO'':kO''' 271 coordination mode. Every four-connected I-a uses its every carboxyl group bridging 272 the crystallographically independent Mn1 and Mn2, and in this way it results in a 273 double-stranded chain structure containing two (I-a)-bridged heterochiral coaxial 274 2_1 -helical chains [namely, -(Mn1)-(I-a)-(Mn1)- and -(Mn2)-(I-a)-(Mn2)- helixes] 275 along c-axis with the 2_1 helical pitches being 19.1087(3) Å (Fig. 8a). Along the 276 double-stranded chain structure, the crystallographically independent Mn1 and Mn2 277 are also linked by B-im ligands into two almost parallel (B-im)-bridged aspiral chiral 278 chains, and thereby forming the novel chiral four-stranded Mn(II) chain (Fig. 8a). 279 Those four-stranded Mn(II) chains are further connected by the bis-monodentate 280 bridges I-a to form the 2D polymer 5. In crystal structure, those 2D layers pack up 281 along *b*-axis through the interdigitation of B-im between adjacent layers (Fig. S5).

282 3.3. Thermogravimetric analysis (TGA) and Powder X-ray diffraction (PXRD)

283 To evaluate the thermal stability of compounds 1-5, their thermal gravimetric analyses were carried out under air atmosphere with a heating rate of 10 °C min⁻¹ and 284 285 the results are given in Fig. S6. For complex 1, the dehydration process occurred from 286 room temperature to 167 °C with a weight loss of 2.61% corresponding to the 287 removal of the lattice water molecules (calcd 3.35%), and then a successive mass loss 288 occurred from 362 to 700 °C, indicating the complete decomposition of the compound. 289 As for the resulting residue of 14.67%, it is presumed to be NiO (calcd 13.90%). For 2, 290 the slow dehydration process occurred from room temperature to 232 °C with a 291 weight loss of 8.28% corresponding to the release of the lattice and coordinated water 292 molecules (calcd 9.15%), and then a successive sharp mass loss followed up to 350 °C. 293 The remaining residue of 16.00% is considered to be NiO (calcd 15.18%). Below 294 100 °C the isostructural compounds 3 and 4 are stable. The dehydration processes 295 occurred at 124–224 °C for 3 with a weight loss of 7.32 (calcd 7.46%) and at 296 107-159°C for 4 with a weight loss of 6.35 (calcd7.25%). The dehydrated 297 frameworks of **3** and **4** are stable up to 354°C and 392 °C, respectively. For compound

5, the dehydration process occurred at 57–147 °C with a weight loss of 4.18% corresponding to the removal of the lattice water molecules (calcd 3.90%), and then a successive mass loss occurred from 320 to 520 °C, indicating the complete decomposition of the dehydrated framework of **5**. As for the resulting residue of 19.50%, it is presumed to be MnO_2 (calcd18.84%).

Apart from the thermal stability, the phase purity of the prepared crystal materials 1–5 were determined by powered X-ray diffraction (PXRD) measurements, and the experimental and simulated PXRD patterns of those compounds are shown in Figs. S7–S11. The calculated PXRD patterns from the single-crystal X-ray diffraction data are in agreement with the observed ones, indicating the phase purity of those synthesized crystalline products. The differences in intensity may be due to the preferred orientation of the powder samples.

310 3.3. Magnetic Properties

311 Compounds based on carboxylate-bridged paramagnetic metal ions usually display interesting magnetism [21], and thus the temperature-dependent magnetic 312 313 susceptibilities (χ_M) of polycrystalline samples 3 and 5 were measured at a field of 314 1000 G in the temperature range of 2–300 K, respectively. The corresponding graphs of χ_M vs T and $\chi_M T$ vs T are shown in Figs. 9–10. For **3**, the $\chi_M T$ of 1.29 cm³ mol⁻¹ K 315 316 per Ni(II) at room temperature is higher than the expected spin-only value of 1.00cm³ mol^{-1} K per Ni(II) (S =1, g = 2), revealing a significant orbital contribution which 317 always causes zero-field splitting. The linear decrease of the $\chi_M T$, from room 318 319 temperature dawn to ca 50 K, is strange and seems to be the signature of a TIP contribution. Upon cooling, the $\chi_M T$ values gradually decrease to 1.23 cm³ mol⁻¹ K at 320 22 K. As the temperature is lowered the $\chi_{\rm M}T$ values slightly increase to 1.24 cm³ 321 322 mol^{-1} K at 9 K, and then abruptly decrease to 1.11 cm³ mol⁻¹ K at 2 K. By eliminating the TIP contribution, the data rather suggest a ferromagnetic coupling of the Ni(II) 323 324 ions. The magnetic behavior of $\mathbf{3}$ can be explained by large zero-field splitting, as 325 well as a weak ferromagnetic interaction under the molecular field approximation. 326 The best fit of eqn. (1) to the data was achieved with g = 2.14, D/k = 6.74 K, $\theta = 0.82$, TIP = 121×10^{-5} and $R = 1.1 \times 10^{-6} (R = \sum (\chi_{obsd} - \chi_{cacld})^2 / \sum \chi_{obsd}^2)$. 327

328
$$\boldsymbol{\mathcal{X}}_{M} = \frac{2Ng^{2}\boldsymbol{\beta}^{2}}{3k(T-\boldsymbol{\theta})} \left[\frac{2kT/D - 2kT\exp(-D/kT)/D + \exp(-D/kT)}{1 + 2\exp(-D/kT)} \right] + \text{TIP}$$
(1)

For **5**, the $\chi_{\rm M}T$ of 4.32 cm³ mol⁻¹ K per Mn(II) at room temperature is similar to the expected spin-only value of 4.38 cm³ mol⁻¹ K per Mn(II) (*S* =5/2, *g* = 2). Upon cooling, the $\chi_{\rm M}T$ values decrease slowly from 300 to 25K, and quickly decrease to the minimum 1.86 cm³ mol⁻¹ K at 2 K. This phenomenon is typical for antiferromagnetic interactions. Besides, the $1/\chi_{\rm M}$ vs *T* plot follows the Curie–Weiss law with a negative Weiss constant ($\theta = -2.38$ K; Fig. S12), indicating weakly antiferromagnetic interactions between Mn(II) ions.

336

337 **3. Conclusion**

In summary, we have solvothermally synthesized five new nickel(II) and 338 339 manganese(II) MOFs with the mixed V-shaped ligands bis-imidazole and aromatic 340 carboxylates. In particular, the assemblies of transition metal nickel(II) with the mixed V-shaped B-im and Br-a or I-a contribute to the formation of novel metal-organic 341 342 polymeric nanotubes owing to the interestingly sorted-recognition and hierarchical 343 assembly between nickel(II) ions and the V-shaped ligands bis-imidazole B-im and 344 carboxylates Br-a or I-a through coordination interactions. In addition, the structure 345 architectures of those MOFs are obviously influenced by reaction conditions, and 346 especially by the auxiliary aromatic carboxylates ligands used. The results of thermal 347 gravimetric analyses suggest that the dehydrated frameworks of 1-5 are stable up to 320 °C. 348

349 A

Appendix A. Supplementary material

350 CCDC 1465489–1465493 contains the supplementary crystallographic data for 1–5, 351 respectively. These data be obtained free of charge can via 352 http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge 353 Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 354 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Other supporting information 355 contains Figs. S1–S12.

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417 418 **Captions for the Scheme and Figures:** 419 Scheme 1. Schematic representation of the selected V-shaped bis-imidazole and aromatic 420 carboxylic acid ligands. Fig. 1. Coordination environment of Ni(II) atom in 1. Symmetry codes: A = x, x-y, z; B = 1-y, x-y, z421 422 z, C = x, y, z+1; E = 1-y, 1-x, z.423 Fig. 2. (a) 30-membered macrocyclic [Ni₃(B-im)₃] SBU in 1, showing the intricate interactions 424 between the SBU and the captured water molecule. (b) View of the 1D polymeric metal-organic 425 nanotube 1. 426 Fig. 3. (a) Coordination environment of Ni(II) atom in 2. (b) View of 20-membered macrocyclic 427 [Ni₂(B-im)₂] SBU in **2**. Symmetry codes: A = -x+3/2, y, z. 428 Fig. 4. (a) 1D zigzag polymeric chain with the macrocyclic $[Ni_2(B-im)_2]$ SBUs capping the up and 429 down vertices, showing greater 36-membered macrocycle [Ni₄(B-im)₂(I-a)₂] formed by two I-a 430 ligands bridging two macrocyclic [[Ni₂(B-im)₂] SBUs. (b) View of the nanotube extending along 431 *a*-axis in **2**. 432 Fig. 5. View of 3D supramolecular network in 2 formed by interchain hydrogen bonds, with the 433 coordinated and lattice water molecules O3 and O5 being omitted for clarity. 434 Fig. 6. View of double-strand chain in 4 with hydrogen atoms being omitted for clarity, showing 435 the coordination environment of Ni(II) and 18-membered macrocyclic [Ni₂(B-im)(M-a)] SBU. 436 Symmetry codes: A = 2-x, 1-y, 1-z; B = x, 3/2-y, z, C = 2-x, y-1/2, 1-z. 437 **Fig. 7.** Coordination environment of Mn(II) in **5**. Symmetry codes: A = x-1, y, z. 438 Fig. 8. (a) View of novel chiral four-stranded Mn(II) chain consisting of two (B-im)-bridged 439 aspiral chiral chains and two (I-a)-bridged heterochiral coaxial 2₁-helical chains. (b) 2D porous 440 polymeric structure in 5. 441 **Fig. 9.** $\chi_{\rm M}$ (**■**) and $\chi_{\rm M}T$ (\circ) *vs T* with the theoretical fit (–) for **3**. 442 **Fig. 10.** χ_{M} (**■**) and $\chi_{M}T$ (\circ) *vs T* for **5**. 443 444 445 446

Table 1

Crystal date and structure refinement for complexes 1–5.

Compounds	1	2	3	4	5
Formula	C ₁₉ H ₁₇ BrClN ₅ NiO ₃	$C_{21}H_{21}N_4NO_{6.5}$	$C_{21}H_{20}N_4NiO_6$	$C_{21}H_{20}N_4NiO_6$	C ₄₂ H ₃₆ Mn ₂ N ₈ O ₁₀
<i>T /</i> K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Hexagonal	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 6 ₃ <i>mc</i>	Imcm	Pnma	Pnma	$Pna2_1$
<i>a /</i> Å	21.9372(4)	18.5892(4)	6.7623(2)	6.8518(2)	14.4770(2)
<i>b </i> Å	21.9372(4)	8.8087(2)	17.4552(6)	17.3501(5)	15.4690(3)
<i>c</i> / Å	7.7390(1)	27.4440(7)	17.3632(7)	17.4764(5)	19.1087(3)
α/°	90	90	90	90	90
βI°	90	90	90	90	90
γ/°	120	90	90	90	90
$V/\text{\AA}^3$	3225.36(9)	4493.9(2)	2049.5(1)	2077.6(1)	4279.3(1)
Ζ	6	8	4	4	4
$D_{\rm c}$ / g cm ⁻³	1.660	1.455	1.566	1.589	1.432
GOF	1.146	1.067	1.020	1.096	1.061
<i>R</i> 1	0.0374	0.0483	0.0346	0.0355	0.0548
$wR2\;(I\!\!>\!\!2\sigma\;(I))$	0.0950	0.1389	0.0792	0.0904	0.1449
Largest diff.	0.563	1.120	0.260	0.325	1.162
peak and hole	-0.341	-0.294	-0.348	-0.394	-0.354



457 **Table 2**

458

Selected bond distances (Å) and angles (°) for complexes 1–5.

			1				
	Ni1–N2	2.084(3)	Ni1–N2A	2.084(3)	Ni1–N1	2.086(5)	
	Ni1-O1C	2.102(4)	Ni1-O2C	2.225(4)	Ni1-Cl1	2.356(2)	Ó
	N2A-Ni1-N2	175.7(2)	N2A-Ni1-N1	89.0(1)	N2-Ni1-N1	89.0(1)	X
	N2A-Ni1-O1C	88.1(1)	N2-Ni1-O1C	88.1(1)	N1-Ni1-O1C	92.7(2)	
	N2A-Ni1-O2C	90.0(1)	N2-Ni1-O2C	90.0(1)	N1-Ni1-O2C	154.3(2)	
	O1C-Ni1-O2C	61.6(1)	N2A-Ni1-Cl1	92.05(9)	N2-Ni1-Cl1	92.1(1)	
	N1-Ni1-Cl1	99.7(1)	O1C-Ni1-Cl1	167.6(1)	O2C-Ni1-Cl1	106.0(1)	
			2				
	Ni1-O1	2.085(2)	Ni1-O1A	2.085(2)	Ni1-N1	2.087(2)	
	Ni1–N1A	2.087(2)	Ni1-04	2.088(3)	Ni1–O3	2.118(3)	
	01-Ni1-01A	89.3(1)	O1-Ni1-N1	177.34(9)	O1A-Ni1-N1	91.31(8)	
	O1-Ni1-N1A	91.31(8)	O1A-Ni1-N1A	177.34(9)	N1–Ni1–N1A	88.0(1)	
	01-Ni1-O4	86.64(8)	01A-Ni1-04	86.64(8)	N1-Ni1-O4	90.80(9)	
	N1A-Ni1-O4	90.80(9)	01-Ni1-O3	91.28(8)	01A-Ni1-O3	91.28(7)	
	N1-Ni1-O3	91.30(8)	N1A-Ni1-O3	91.30(8)	04-Ni1-O3	177.1(1)	
			3				
	Ni1–N1A	2.067(2)	Ni1-N1	2.067(2)	Ni1-O3	2.086(2)	
	Ni1–O3A	2.086(2)	Ni1-O1	2.121(2)	Ni1-O1A	2.121(2)	
	N1A-Ni1-N1	180.0	N1A-Ni1-O3	90.76(7)	N1-Ni1-O3	89.24(7)	
6	N1A–Ni1–O3A	89.24(7)	N1-Ni1-O3A	90.76(7)	03-Ni1-03A	180.0	
	N1A-Ni1-O1	89.99(7)	N1-Ni1-O1	90.00(7)	03-Ni1-O1	92.41(6)	
V	O3A-NA-O1	87.59(6)	N1A-Ni1-O1A	90.01(7)	N1-Ni1-O1A	89.99(7)	
	O3-Ni1-O1A	87.59(6)	O3A-Ni1-O1A	92.41(6)	01-Ni1-O1A	180.0	
	4						
	Ni1–O3A	2.074(2)	Ni1–O3	2.074(2)	Ni1–N1	2.076(2)	
	Ni1–N1A	2.076(2)	Ni1–O1A	2.121(1)	Ni1-O1	2.121(1)	

O3A-Ni1-O3	180.0	O3A-Ni1-N1	89.06(7)	03-Ni1-N1	90.94(7)		
O3A-Ni1-N1A	90.94(7)	O3-Ni1-N1A	89.06(7)	N1-Ni1-N1A	180.0		
O3A-Ni1-O1A	91.54(6)	O3-Ni1-O1A	88.46(6)	N1-Ni1-O1A	90.54(7)		
N1A-Ni1-O1A	89.46(7)	O3A-Ni1-O1	88.46(6)	03-Ni1-O1	91.54(6)		
N1-Ni1-O1	89.46(7)	N1A-Ni1-O1	90.54(7)	01A-Ni1-01	180.0		
5							
Mn1–O8A	2.034(5)	Mn1–O4B	2.100(4)	Mn1–O1	2.186(4)		
Mn1-N1	2.240(5)	Mn1–N5	2.263(5)	Mn2-O5	2.181(5)		
Mn2–O3B	2.196(4)	Mn2–N8C	2.203(5)	Mn2–O2	2.204(5)		
Mn2-N4B	2.221(5)						
O8A-Mn1-O4B	118.8(3)	O8A-Mn1-O1	109.6(3)	O4B-Mn1-O1	131.3(2)		
O8A-Mn1-N1	95.1(2)	O4B-Mn1-N1	85.0(2)	O1-Mn1-N1	85.6(2)		
O8A-Mn1-N5	85.3(2)	O4B-Mn1-N5	89.9(2)	O1-Mn1-N5	99.5(2)		
N1-Mn1-N5	174.4(2)	O5-Mn2-O3B	141.3(2)	O5-Mn2-N8C	89.3(2)		
O3B-Mn2-N8C	100.7(2)	O5-Mn2-O2	96.7(2)	O3C-Mn2-O2	120.9(2)		
N8C-Mn2-O2	86.9(2)	O5-Mn2-N4B	87.9(2)	O3B-Mn2-N4E	3 86.3(2)		
N8C-Mn2-N4B	171.8(2)	O2-Mn2-N4B	85.8(2)				

1−*y*, *z*+1/2 for **5**.



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- 494 Fig. 5. View of 3D supramolecular network in 2 formed by interchain hydrogen bonds, with the
- 495 coordinated and lattice water molecules O3 and O5 being omitted for clarity.

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- 498 Fig. 6. View of double-strand chain in 4 with hydrogen atoms being omitted for clarity, showing
- the coordination environment of Ni(II) and 18-membered macrocyclic [Ni₂(B-im)(M-a)] SBU.

500 Symmetry codes:
$$A = 2-x$$
, $1-y$, $1-z$; $B = x$, $3/2-y$, z , $C = 2-x$, $y-1/2$, $1-z$.

501





Fig. 7. Coordination environment of Mn(II) in **5**. Symmetry codes: A = x-1, *y*, *z*.

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508 Fig. 8. (a) View of novel chiral four-stranded Mn(II) chain consisting of two (B-im)-bridged 509 aspiral chiral chains and two (I-a)-bridged heterochiral coaxial 21-helical chains. (b) 2D porous 510 polymeric structure in 5. Symmetry codes: B = 1-x, 1-y, z-1/2; C = 1-x, 1-y, z+1/2; D = x, y, z-1; 511 E = 1-x, 1-y, z-3/2

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528	
529	Synopsis
530	Syntheses, Structures and Properties of Nickel(II) and Manganese(II)
531	Coordination Polymers Based on V-shaped Bis-imidazole and
532	Aromatic Carboxylate Ligands
533	Lu-Lu Lv ^a , Li-Jun Zhang ^b , Hong Zhao ^a , Ben-Lai Wu ^{a,} *
534	
535	A serial of Ni(II) and Mn(II) coordination polymers based on V-shaped mixed ligands
536	bis-imidazole and aromatic carboxylic acids were solvothermally synthesized and
537	fully characterized. Intriguingly, sorted-recognition and hierarchical assembly
538	between Ni(II) and mixed ligands result in novel nanotubes.
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543 **Research Highlights**

- 544 > Ni(II) and Mn(II) MOFs based on V-shaped mixed ligands are synthesized.
- 545 > Sorted-recognition and hierarchical assembly between Ni(II) and mixed ligands result in novel
- 546 nanotubes.
- Acceleration