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High Thermally and Chemically Stable Nickel (II) Coordination Polymers: Tentative Studies on Their Sorption, Catalysis, and Magnetism

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ABSTACT: Five Ni(II) coordination polymers (CPs), new $\{[Ni(bitp)(bpe)_{0.5}(H_2O)_2] \cdot 0.5bpe\}_n$ (1), $\{[Ni(bitp)(bpa)_{0.5}(H_2O)_2] \cdot 0.5bpa\}_n$ (2), $\{[Ni(bitp)(4,4'-bpy)_{0.5}(H_2O)] \cdot H_2O\}_n$ (3), $\{[Ni_{1.5}(bitp)(Hbitp)(2,2'-bpy)(H_2O)] \cdot 3H_2O\}_n$ (4) and $[Ni(bitp)(bipyam)]_n$ (5), where $H_2bitp = 2$ -(benzimidazol-1-yl)terephthalic acid, bpe = 1,2-bis(4-pyridyl)ethylene, bpa = 1,2-bis(4-pyridyl)ethylane, 4,4'-bpy = 4,4'-bipyridine, 2,2'-bpy = 2,2'-bipyridine and bipyam = 2,2'-bipyridylamine, were prepared under the same hydrothermal environments except various N-donor ligands which can effectively regulate the structure of complexes. For bridging

N-donor ligands bpe (1), bpa (2) and 4,4'-bpy (3), isostructural 1-2 feature 3D layered-pillared frameworks with one-dimensional (1D) channels that house free bpe or bpa, while 3 is a wavelike 2D stacked layer with similar bridging auxiliary ligands 4,4'-bpy. But when terminal ligands 2,2'-bpy or bipyam used, 2D 4 and 1D ladder chain 5 are obtained, respectively. Interestingly, 1-5 exhibit outstanding thermostability (up to 320 °C) and chemical stabilities (against boiling water, acids, bases and organic solvents). Furthermore, based on their high thermal and chemical stability, tentative studies on the structure and property (such as adsorption, catalysis, and magnetic properties) were undertaken. The gas sorption measurements show that 1 and 2 exhibit highly adsorption selectivity of CO₂ over CH₄. The catalytic reactions demonstrate 1 - 5the catalysts role of synthesize to 3,6-di(pyridine-4-yl)-1,2,4,5-tetrazine. The magnetic analysis indicates that there presents a (ZFS) zero field splitting on the Ni (II) ions in 1–5.

INTRODUCTION

Coordination polymers (CPs) have aroused widespread concern with their diverse interesting topologies as well as their intriguing potential applications such as gas sorption and separation, heterogeneous catalysis and magnetism applications.^{1–7} Even though CPs are promising porous materials in a variety of fields, in comparison with other materials such as metal oxides, porous carbons, zeolites, silica, and heteropolyanion salts,⁸ their limited thermal and chemical stability usually hamper CP's property applications in many fields.^{9,10} Therefore, the development of novel and robust CPs under harsh conditions has motivated numerous investigations. As has

been reported, the stability of CPs can be improved by enhancing the matching level of coordination groups with metal ions.^{11–13} In other words, the complexes obtained are more stable if the coordination groups and metal ions conform well to the rule of acid-base hard-soft (HSAB) reaction. So one effective building strategy on stable CPs is to combine multi–topic carboxylate ligands with parts of divalent transitional-metal (Zn²⁺, Co²⁺, Ni²⁺, and Cu²⁺),^{14–18} thereby possibly characterizing their thermal/chemical stability as well as their properties. Now, though it is known that the CP's diverse properties are closely related to their structures and could be modulated by tailoring their structures, it is still a challenge to design and prepare the CPs with anticipated performance.¹⁹⁻²¹

The Ni(II) ion, as a nontoxic and abundant crustal element, has relatively larger radius, mutable stereochemical activity, greater electronegativity, and a high ligand-field stabilization energy (LFSE)^{22–24}, making it possible to design and prepare Ni(II)-CPs with rich topologies, high stabilities and multifarious properties.^{25,26} For example, paramagnetic Ni(II) can be used to construct Ni(II)–CPs with magnetic properties, and interestingly, the reported Ni(II)–CPs, as the rare examples of ferromagnetic coupling *via* H-bonds, exhibit the weak ferromagnetic coupling.^{27–29} In addition, the highly polar Ni(II)–CPs have been considered as a new kind of CO₂ separation and capture materials, ascribed to their high sorption affinity and capacity by framework–adsorbate interactions.^{30–33} Not only that, it is also to be observed that the coordinatively unsaturated Ni(II) is also able to function as Lewis acid to catalyze organic reactions.^{34–36} For instance, Nickel triflates have been

discovered as highly effective catalysts for the synthesis of 1,2,4,5-tetrazines.³⁷ Thus, explorations of the Ni(II)–CP's structure and property are of crucial significance for the development of advanced CPs–based materials.

In this paper, we chose the 2-(benzimidazol-1-vl) terephthalic acid (H_2 bitp) as the main ligand to react with NiCl₂·6H₂O and different auxiliary ligands under the same hydrothermal conditions. The H₂bitp, as a kind of multicarboxylate ligands, possess two carboxylic and one imidazol groups, which bound much more strongly with hard Lewis acid Ni(II) and therefore probably generate CPs with improved stability and more diverse structures.^{38,39} Five complexes, $\{[Ni(bitp)(bpe)_{0.5}(H_2O)_2] \cdot 0.5bpe\}_n$ (1), $\{[Ni(bitp)(bpa)_{0.5}(H_2O)_2] \cdot 0.5bpa\}_n$ (2), $\{[Ni(bitp)(4,4'-bpy)_{0.5}(H_2O)] \cdot H_2O\}_n$ (3), $\{[Ni_{15}(bitp)(Hbitp)(2,2'-bpy)(H_2O)] \cdot 3H_2O\}_n$ (4) and $[Ni(bitp)(bipyam)]_n$ (5), where bpe = 1,2-bis(4-pyridyl)ethylene, bpa = 1,2-bis(4-pyridyl)ethylane, 4,4'-bpy = 4,4'-bipyridine, 2,2'-bpy = 2,2'-bipyridine and bipyam = 2,2'-dipyridylamine, were obtained. In 1-5, we found that the addition of different kinds of auxiliary ligands contribute to the framework, bridging ligands bpe/bpa/4,4'-bpy helping to extend the framework into 3D or 2D structure while terminal ligands forming 2D or 1D structure instead. 1/2 are bridged by bpe/bpa into 3D layered-pillared frameworks with 1D channels housed by free bpe/bpa, while 3 exists in the form of 3D network shaped on wavelike 2D layers through hydrogen bonding interactions. Moreover, when terminal ligands are used to replace bridging ligands, 2D 4 and 1D ladder chain 5 are formed, and further self-assembled through $\pi \cdots \pi$ interactions or hydrogen bonds to obtain different 3D supramolecular frameworks. Notably, 1–5 exhibit enhanced

thermostability up to 320 °C and chemical stability, which expand their practical application. The gas adsorption properties of **1** and **2** were studied, which exhibits high CO₂ sorption heat and sorption selectivity for CO₂ over CH₄. The catalytic results demonstrate the catalysts role of **1–5**, and **2** is selected to synthesize 3,6-di(pyridine-4-yl)-1,2,4,5-tetrazine as the target catalyst. The magnetic analysis of **1–5** indicates the presence of a (ZFS) zero field splitting on the Ni(II) ions.

EXPERIMENTAL SECTION

Materials and Methods. All synthetic reagents and solvents commercial available were used directly. Elemental analyses (for carbon, hydrogen, and nitrogen) were taken on a PerkinElmer 2400C elemental analyzer. The FT-IR spectra (4000–400 cm⁻¹) were obtained on a Bruker EQUINOX–55 using KBr pellets. The Powder X-ray diffraction (PXRD) data were tested on a Bruker D8 ADVANCE X–ray powder diffractometer (Cu K α , $\lambda = 1.5418$ Å) in the angular range of 5° $\leq 2\theta \leq 50^{\circ}$. The thermal stabilities were performed in a Netzsch TG209F3 apparatus. The gas sorption isotherms of **1** and **2** were measured on a Micromeritics ASAP 2020 M adsorption instrument. Magnetizability measurements were assessed on a Quantum Design MPMS–XL–7 SQUID magnetometer.

 $\{[Ni(bitp)(bpe)_{0.5}(H_2O)_2] \cdot 0.5bpe\}_n$ (1). A mixture of H₂bitp (0.1 mmol, 28.2 mg), NiCl₂·6H₂O (0.1 mmol, 23.7 mg), bpe (0.1 mmol, 18.2 mg), NaOH (8 mg) and 10 mL H₂O was placed in a Teflonlined stainless steel vessel (25 mL), heated to 150 °C for 3 d. After it cooled to room temperature at a rate of 0.1 °C min⁻¹, dark–green block crystals of 1 with 65% (based on H₂bitp) were collected. Anal. Calcd for C₅₄H₄₄N₈Ni₂O₁₂ (1114.36 g mol⁻¹): C, 58.15; H, 3.95; N, 10.05%. Found: C, 58.67; H, 3.89; N, 9.99%. IR (KBr, cm⁻¹): 3475 *s*, 2934 *s*, 1605 *s*, 1554 *s*, 1421 *m*, 1364 *s*, 1240 *m*, 1010 *w*, 954 *m*, 906 *w*, 795 *s*, 747 *w*, 532 *s*.

 $\{[Ni(bitp)(bpa)_{0.5}(H_2O)_2] \cdot 0.5bpa\}_n$ (2). 2 is dark–green block crystal and gained by similar synthetic operation with 1, except that bpe was changed as bpa (0.1 mmol, 18.4 mg). Yield: 67% (Based on H₂bitp ligand). Anal. Calcd for C₅₄H₄₈N₈Ni₂O₁₂ (1118.39 g mol⁻¹): C, 57.94; H, 4.29; N, 10.01%. Found: C, 58.42; H, 4.33; N, 9.89%. IR (KBr, cm⁻¹): 3475 *s*, 2960 *s*, 1615 *s*, 1562 *s*, 1421 *m*, 1364 *s*, 1240 *m*, 1004 *m*, 910 *m*, 795 *s*, 747 *w*, 532 *s*.

 $\{[Ni(bitp)(4,4'-bpy)_{0.5}(H_2O)] \cdot H_2O\}_n$ (3). 3 is green block crystal and gained by similar synthetic operation with 1 except that bpe was changed as 4,4'-bpy (0.1 mmol, 15.7 mg). Yield: 35% (Based on H₂bitp ligand). Anal. Calcd for C₂₀H₁₆N₃NiO₆ (453.05 g mol⁻¹): C, 52.97; H, 3.53; N, 9.27%. Found: C, 53.40; H, 3.65; N, 9.33%. IR (KBr, cm⁻¹): 3312 *s*, 1613 *m*, 1577 *m*, 1545 *s*, 1511 *s*, 1417 *m*, 1391 *s*, 1240 *m*, *w*, 815 *m*, 739 *m*, 635 *m*.

 $\{[Ni_{1.5}(bitp)(Hbitp)(2,2'-bpy)(H_2O)]\cdot 3H_2O\}_n$ (4). 4 is green block crystal and gained by similar synthetic operation with 1 except that bpe was changed as 2,2'-bpy (0.1 mmol, 15.7 g). Yield: 66% (Based on H₂bitp ligand). Anal. Calcd for $C_{80}H_{66}N_{12}Ni_3O_{24}$ (1755.52 g mol⁻¹): C, 54.73; H, 3.76; N, 9.57%. Found: C, 54.95; H, 3.62; N, 9.66%. IR (KBr, cm⁻¹): 3381 *s*, 1705 *m*, 1605 *s*, 1511 *w*, 1468 *m*, 1372 *s*, 1240 *m*, 1022 *w*, 910 *m*, 764 *s*, 515 *w*.

[*Ni(bitp)(bipyam)*]_n (5). 5 is green block crystal and gained by similar synthetic operation with 1 except that bpe was changed as bipyam (0.1 mmol, 17.1 g). Yield: 63% (Based on H₂bitp ligand). Anal. Calcd for C₂₅H₁₇N₅NiO₄ (510.14 g mol⁻¹): C, 58.80; H, 3.33; N, 13.72%. Found: C, 59.43; H, 3.23; N, 13.53%. IR (KBr, cm⁻¹): 3242 *m*, 1655 *m*, 1570 *s*, 1538 *w*, 1485 *s*, 1432 *m*, 1400 *w*, 1236 *s*, 1150 *m*, 1012 *m*, 823 *w*, 755 *s*.

Single-Crystal Structure Analysis. The X-ray diffraction data were collected at 293(2) K using a Bruker SMART APEX II CCD diffractometer equipped with Mo–K α ($\lambda = 0.71073$ Å) radiation. The structures of 1–5 were solved and refined by full–matrix least–squares procedure based on $F^{2,40,41}$ All the non–hydrogen atoms were located with anisotropic displacement parameters. And all hydrogen atoms except for water molecules were located and fixed in idealized positions. The crystal data, selected bond distances and angles for for 1–5 are presented in Table S1 and Table S2. CCDC: 1810869-1810873 for 1–5.

RESULTS AND DISCUSSION

Crystal Structures of $\{[Ni(bitp)(bpe)_{0.5}(H_2O)_2]\cdot 0.5bpe\}_n$ (1) and $\{[Ni(bitp)(bpa)_{0.5}(H_2O)_2]\cdot 0.5bpa\}_n$ (2). The complexes 1 and 2 are isostructural and isomorphous with similar auxiliary ligand (bpe for 1, bpa for 2) and only 1 with detailed discussion. X-ray diffraction data displays that 1 is 3D layered-pillared structure with 1D channels housed by free bpe and belongs to the triclinic space group P-1. The asymmetry unit of 1 contains one Ni(II) ion (a half Ni1 and a half Ni2), one bitp²⁻, a half coordinated bpe, a half bpe guest and two coordinated water (Figure 1a).

Both the Ni1 and Ni2 centers are hexa-connected. The Ni1 is surrounded by four oxygen atoms from two bitp²⁻ ligands, two coordinated water molecules (O1W) as well as two nitrogen atoms from two bitp²⁻ ligands, presenting a distorted octahedral coordination environment. Compared with Ni1, Ni2 bonds to two nitrogen atoms from two bpe ligands, four oxygen atoms from two bitp²⁻ ligands and two coordinated water molecules (O2W). The distance of water molecules between the adjacent layers (O1W…O1W, 15.015 Å) is within the length of the bpe ligand ($N_{bpe}-N_{bpe} = 9.358$ Å), compared to the distance of O2W…O2W (16.174 Å). Thus, O1W, bonded with Ni1, is used to stabilize free bpe reside in the quadrangle channels by forming strong hydrogen bonds (O1W-H1WB. N4, 2.852(2) Å). O2W, bonded with Ni2, is used to stabilize whole framework by forming strong hydrogen bonds with the coordinated water molecules (O2W-H2WB···O1W, 2.842(3) Å) and monodentate coordinated carboxylic oxygens (O2W-H2WA···O4, 2.609(9) Å). All coordinated water molecules point into the channel where the free bpe is resided, which certainly crowd the channels of 1. The distance of Ni-O and Ni-N bond is within the reported distance.^{42–44} All carboxyl groups of the H₂bitp ligand adopt one coordination mode: $\mu_1 - \eta^1: \eta^0$ (Table 1). The Ni1 centers are coordinated by bitp²⁻ ligands to form a 1D loop chain along b axis with the Ni1...Ni1 distance being 10.656 Å, the adjacent chains are further joined via Ni2-O bonds to obtain a 2D parallel layer along the bc crystal face (Figure 1b). Finally, the bridging bpe ligands serve as pillars connecting the adjacent layers together to result in a 3D network with 1D channels in which the free bpe are housed by forming strong hydrogen bonds with the coordinated water

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molecules (O1W-H1WB···N4). The bpe molecules act both as the secondary ligands as well as the guest molecules. The steric hindrance of free bpe/bpa works markedly for absence of solvent molecules in the cavity. (Figure 1c). The topological expression is a (3, 4, 4) -connected framework where the complex symbol is $(4.8^2)_2(4^2.8^2.10^2)(8.10^4.12)$, by denoting both Ni1(II) and Ni2(II) ion as four-connected nodes and bitp²⁻ as a three-connected nodes (Figure 1d).

Through analyzing the crystal structure of **1** and **2**, it could be known that the distances of layer–to–layer (11.729 Å) and Ni2…Ni2 separated by the bpe (13.508 Å) in **1** are a bit larger than that in **2**(11.675 Å and 13.504 Å), which could be ascribed to the difference in length of bpe/bpa (9.358 Å/9.214 Å). Furthermore, **1** and **2** also with different pore dimensions (10.361 × 11.729 Å² for **1**, 10.305 × 11.675 Å² for **2**, included vander Waals radius). The diverse dihedral angles between benzene ring and benzimidazole moiety (*ca.* 87.4° for **1** and 85.5° for **2**) give rise to the difference for Ni1…Ni1 nonbonding separations (10.608(3) Å for **2**).



Figure 1. (a) Coordinated environment of the Ni (II) in **1**. Symmetry codes: A = -x + 1, -y + 2, -z + 1; B = x, y + 1, z; C = -x + 1, -y + 1, -z + 1; D = -x + 1, -y, -z; E = -x + 2, -y + 1, -z. (b) The 2D layer of **1** shown down the *bc* plane. (c) The 3D framework displaying the connectivity between the layers by the bpe ligand. (d) Hydrogen bond diagram between free bpe and coordination water. (e) Schematic representation of the four–connected 3D topology network for **1**.

Crystal Structures of {[Ni(bitp)(4,4'-bpy)_{0.5}(H₂O)]·H₂O}_n (3). 3 exists as a 3D network stacked by 2D layers through hydrogen bonding interactions and falls within the C2/c space group. As seen in Figure 2a, the asymmetric unit is composed of one Ni (II) ion, one bitp^{2–} ligand, a half 4,4'-bpy linker lying at an inversion centre,

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one coordinated water molecule and one lattice water molecule. Each Ni atom is six-coordinated by four carboxylate O atoms from two bitp²⁻ ligands and two coordinated water as well as two imidazole N atoms from one bitp²⁻ ligand and one 4,4'-bpy, to construct a distorted octahedral environment (Figure 2a). The Ni–O and Ni–N bond lengths are in the range 2.070(2)–2.080(2) Å and 2.075(2)–2.165(2) Å, respectively, which are within the reported distance values.^{42–44} Each bitp²⁻ links to three Ni²⁺ ions to obtain a 1D chain with the dihedral angles between benzene ring and benzimidazole moiety are *ca*. 67.18°, in which two carboxyl groups adopt $\mu_1 - \eta^0: \eta^1$ and $\mu_1 - \eta^1: \eta^1$ coordination mode (Table 1). Adjacent chains are linked by 4,4'-bpy to obtain 2D wavelike layers along the *ab* plane (Figure 2c). Moreover, the coordinated water oxygen atom (O5) is linked with a carboxylate oxygen atom (O3) through the hydrogen bond (O5–H5A···O3 = 2.714(3) Å) to connect the adjacent 2D layers, further forming a 3D framework (Figure 2b).



Figure 2. (a) Coordinated environment of Ni (II) ions in **3**. Symmetry codes: A = x - 0.5, -y + 0.5, z - 0.5; B = -x + 0.5, -y + 0.5, -z + 1; C = -x + 0.5, -y + 1.5, -z + 1. (b) The 3D network built on hydrogen bonding interactions. (c) The 2D layer of **3** shown down the *ab* plane. (d) View of the 1D chain in **3**.

Crystal Structures of {[Ni_{1.5}(bitp)(Hbitp)(2,2'-bpy)(H₂O)]·3H₂O}_n (4). 4 falls within the triclinic space group P-1, showing a 2D network. And each asymmetric unit contains one and a half crystallographically independent Ni(II) ions (one half of Ni1 and one Ni2), one bitp²⁻ ligand, one Hbitp⁻ ligand, one 2,2'-bpy ligand, one coordinated water molecule and three lattice water molecules (Figure 3a). Ni1 is surrounded by four carboxylate O atoms from two bitp²⁻ and two coordinated water molecules as well as two imidazole N atoms from two Hbitp⁻ ligands to take on a distorted octahedral coordination environment. Ni2 shows a distorted quadrangle

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pyramid geometry and connects with two carboxylate O atoms from one bitp²⁻ and one Hbitp⁻ and three N atoms from one 2,2'-bpy and one bitp²⁻ imidazole. All Ni-O and Ni-N bond lengths within the range of Ni-MOFs.⁴²⁻⁴⁴ Different from 1-3, the H₂bitp in **4** takes two deprotonation modes: bitp²⁻ and Hbitp⁻. The former connects to three Ni²⁺ ions in which the carboxyl groups are fully deprotonated, its dihedral angle between the benzimidazole and benzene ring is $ca. 76.04^{\circ}$ and the latter links two Ni²⁺ ions in which the carboxyl groups are partly deprotonated with the angle is $ca. 54.21^{\circ}$ (Table 1). Four Ni^{2+} ions (2Ni1 + 2Ni2) are first connected by two bitp²⁻ and two Hbitp⁻ to give a [Ni₄ (bitp)₄] square, further extended into a 1D chain. Furthermore, adjacent chains are connected via Ni2-N (from bitp²⁻) bonds to form a 2D layer (Figure 3b). The 3D network is constructed by 2D layers through weak $\pi \cdots \pi$ stacking interaction between the parallel pyridine rings, with centroid distance, vertical distance, and angle of 3.739(2) Å, 3.568(4) Å and 17.39(5)° (Figure 3c and 3d). Moreover, coordination water, carboxyl and guest water molecules housed at pores produce multiform H-bonds each other.



Figure 3. (a) Coordinated environment of Ni (II) ions in **4**. Symmetry codes: A = -x + 1, -y + 2, -z + 1; B = x, y + 1, z; C = -x + 1, -y + 1, -z + 1; D = x + 1, y, z. (b) Schematic view of the 2D structure of **4** along *c* axis. (c) The 3D network of **4**. (d) The schematic view of weak $\pi \cdots \pi$ stacking interactions between the parallel pyridine rings.

Crystal Structures of [Ni(bitp)(bipyam)]_n (5). 5 forms the triclinic space group *P*–1. The asymmetric unit contains one Ni(II) ion, one bitp^{2–} ligand and one bipyam ligand. As Figure 4a shown, Ni(II) ion displays a distorted octahedral coordination geometry definited by three oxygen atoms from two bitp^{2–} ligands and three nitrogen atoms from one bipyam ligand and one bitp^{2–} ligands. The average bond distances of Ni–O (2.085(4)–2.159(4) Å) and Ni–N (2.011(4)–2.181(4) Å) are within the reported distance values.^{42–44} Ni (II) ions are connected by $\mu_I - \eta^0 : \eta^I$ carboxyl groups and $\mu_I - \eta^1 : \eta^1$ carboxyl groups, giving a 1D ladder chain. And the dihedral angle between the benzimidazole and benzene ring is *ca*. 71.86°. Furthermore, these 1D chains are linked by the hydrogen bonding interactions to obtain a 2D layer (N4–H4…O3 2.865 Å) (Figure 4b) and 3D supramolecular framework (C17–H17…O3 3.460 Å) (Figure 4c).

(a)

Figure 4. (a) Coordinated environment of Ni (II) ions in 5. Symmetry codes: A = -x+ 1, -y + 1, -z + 1; B = -x, -y + 1, -z + 1. (b) The 2D layer of 5. (c) The 3D network of 5.

(b)

(c)

Table 1. T	The coordination	modes of H ₂ bitp	in complexes 1–5.
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Complexes	1	2	3	4		5
Coordination modes	r L	8.	J.R.	J.S.	JB.	J.R.
Dihedral angles	87.4 °	85.5°	67.18°	54.21°	76.04°	71.86°

Structural Comparison of Complexes 1–5 and the Influencing Factors.

As summarized in the Table 1, The H₂bitp ligand and auxiliary ligands lead to the structural diversities. The H₂bitp ligand exhibits three different coordination modes,

and coordinates with two or three Ni (II) ions by using the benzimidazole N atom and monodentate/chelating carboxyl groups. In addition, the dihedral angles between the benzimidazole and benzene ring show a correlation with coordination modes. It is obvious that the dihedral angles wherein the carboxylic groups uncoordinate with the metal atom or adopt a chelating mode in **3–5** are smaller than that in **1** and **2** in which the carboxylic groups coordinate in a monodentate mode. Therefore, distinct dihedral angles contribute to the different framework. And auxiliary ligands in **1–5** contribute to the structural extension. Bridging ligands bpa/bpa in **1/2** extend the 2D wavelayer into 3D network while the bridging 4,4'-bpy in **3** connect the 1D zigzag chains into 2D layers. In **4** and **5**, terminal 2,2'-bpy(for **4**) and bipyam (for **5**) ligands occupy the huge space around the Ni(II), further preventing the extension of the framework to form 2D and 1D complexes, respectively.Thus, bridging ligands help to extend the framework into 3D or 2D structure while terminal ligands form 2D or 1D structure instead.

By comparing the deprotonation of H₂bitp ligands in 1–5, it is obvious that the H₂bitp ligands are fully deprotonated in 1, 2, 3, and 5, while in 4 it is partly deprotonated or fully deprotonated. 1–3 are prepared under the same experimental condition with various straight line N–donor ligands (bpe, bpa, 4,4'-bpy for 1, 2 and 3, respectively) which result in some differences on their frameworks due to the conformation of the bitp^{2–} ligand and nature of auxiliary ligands. There are two Ni (II) ions in 1 and 2 asymmetric unit compared to the mononuclear structure of 3. In 1 and 2, both carboxylic groups adopt monodentate coordination mode, while in 3, a

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carboxylic group exist in two forms: monodentate coordination mode and bidentate chelating mode. It occupies a coordination site, hindering the extension of the framework and inducing a 2D layer. Moreover, because of the flexibility of the bitp^{2–} ligand, the dihedral angles between the benzimidazole and benzene ring is *ca*. 87.4° for **1** and 85.5° for **2** compared with the dihedral angle of 67.18° in **3**. The bpe and bpa are more flexible spacer–shaped ligand whereas 4,4'-dpy is a rigid bridging ligand. Similarly, **4** and **5** also form different structures.

Thermal and Chemical Stability. The PXRD patterns of complexes 1–5 were determined and shown in Figure S1. the experimental PXRD patterns were in good match with the simulated, which conformed the phase pureness of the samples. It is considerable for the chemical stability of CPs in organic solvents, acid, base and moisture/water,^{45,46} which is quite important in many fields. However, as most CPs are unstable in acids and bases or even in moist air, the chemical stability of CPs are always an obstacle for their application. It is worth mentioning that the chemical stability of 1–5 are determined by immersing samples in dichloromethane, methanol, N, N-dimethylformamide, N-methyl-2-pyrrolidone, ether, acetonitrile, ethanediol, alcohol or water at least for 7 days. The PXRD indicate that the crystal frameworks of 1-5 can remain their completeness (Figure S2). The difference in diffraction intensity between the experimental and simulated PXRD is mainly ascribed to nonrandom orientation of crystallites. The slight peak shift could be due to the solvent effect. ⁴⁷ As shown in Figure S3, 1–5 can well maintain their crystallinity when immersed in the boiling water, boiling methanol, which reveal quite high

resistance toward these treatments. Furthermore, this is also true for crystals of 1–5 upon immersed in acidic or basic aqueous solutions with the pH range of 3–12 for at least 7 days, and the PXRD confirmed that the high chemical stability of 1–5. Although some reported CPs with high stability, such as PCN–225, NO₂–tagged UiO–66 and pyrazole–based Ni(II)–CPs,^{48–50} seldom porous CPs have been reported to maintain the integrities in the acidic and basic aqueous solutions in such broad pH range.

Careful analyses of five Ni (II)–CPs in this work, the high chemical stability could be attributed to the following factors: first, the carboxylic group as a hard Lewis base, imidazol group as a boundary base which bound much more strongly with hard Lewis acid Ni(II) and thus conform to the HSAB reaction rule. Second, the rigid bitp^{2–} ligand, uniform and dense assembly structure also contributes a lot to its stability. Last, the open channels in **1** and **2** are largely occupied by guest molecules and coordinated water molecules, which essentially provide a solvophilic condition for capturing polar organic solvents and water molecules, thereby effectively preventing their attacks on inorganic nodes. ^{51,52}

The TGA data were performed in a flowing of N_2 environment during 30–800 °C. As shown in Figure 5, 1–5 are thermally stable up to 320 °C. The sample lose weight of 6.89% (for 1) and 6.78% (for 2) in the temperature range of 115–142 °C (for 1) and 35–125 °C(for 2), corresponding to the release of two coordinated water molecules (6.46% for 1, and 6.43% for 2), and then a half of free bpe/bpa ligand start to break down until 358 °C or 280 °C with the loss of 16.25% for 1 (calcd. 16.33%) and 16.44% for **2** (calcd. 16.45%), respectively. And accompanying with the decomposition of the framework. The result shows that **1** is more stable than **2**, which is possible ascribed to that the bpe is a rigid N-donor while bpa is a flexible one. Different from **1** and **2**, **3** and **4** exhibit a weight reduction of 8.27% and 8.23% in the range of 116-252 °C and 30–165 °C, assigning to the decrease of the coordinated and free water molecules (calcd. 7.95% and 8.21%). Then it is a platform until 320 °C, and the structure begins to topple down. There is no solvent molecule in **5**, therefore, the TG curve exhibits platform before 380 °C, showing high thermal stability, and then followed by the framework's fall down.



Figure 5. TGA curves of complexes 1–5.

IR Spectra. As shown in Figure S6, complexes **1–5** have similar infrared spectra, and present characteristic absorption band of the bitp^{2–} and auxiliary ligands. The IR spectra of **1–5** with major absorption peaks at 1550–1625 cm⁻¹ and 1350–1450 cm⁻¹ could be attributed to the asymmetric and symmetric stretching vibrations of carboxylic groups, representing the presence of the coordinated –COO group.^{53,54} The broad absorption bands at 2900–3475 cm⁻¹ of **1–4** are in line with the asymmetric vibration of v_{OH}, indicating the existence of H₂O molecules. The weak peak at 3424

cm⁻¹ in **5** could be ascribed to the moisture in the air.⁵⁵The separation of 241 cm⁻¹ (for **1**), 251 cm⁻¹ (for **2**) and 233 cm⁻¹ (for **4**) between these two bands [vas(COO⁻¹) – vs(COO⁻¹)] is typical of monodentate coordination of carboxylate group.^{56,57} $\Delta v = 186$ cm⁻¹ for **3** and 170 cm⁻¹ for **5** are assigned to the stretching modes of the chelating carboxylate. For **4**, the existence of the medium peak at 1705 cm⁻¹ attributable to the C=O vibration of the –COOH group conforms the partial deprotonation of the dicarboxylic ligand.^{58,59} Furthermore, the sharp absorption bands at 1543–1545 and 1445–1460 cm⁻¹ correspond to the characteristic absorption of the C=C and C=N in the benzimidazole. Absorption region at 600–1300 cm⁻¹ stemming from N–donor ligands *viz.* bpa, bpe, bpy and bipyam are similar to those observed for N ligands.⁶⁰

Gas Sorption Properties. The excellent thermal and chemical stability of complexes 1 and 2 encourage us to evaluate its porosity. The samples of 1 and 2 was activated by heating 1 and 2 at 200 °C for 5 h under a high vacuum. PXRD patterns still closely matched the simulated patterns of 1 and 2, indicating that the samples after activated retained the intact host frameworks of 1 and 2.



Figure 6. CO_2 and CH_4 adsorption isotherms for 1 (a) and 2 (b) for CH_4 and CO_2 at 298 K and 273K.



Figure 7. Pressure-dependent selectivities of 1 (a) and 2 (b) over CH_4 calculated by the IAST method.

Complexes **1** and **2** exhibit very small N₂ uptake (25 cm³ g⁻¹ at 101.325 kPa) at 77 K. This could be ascribed to structural shrinkage arising from the free bpe/bpa ligands in 1D channel after desolvation, which leads to the blocked diffusion.⁶¹ At 273 and 298 K, **1** and **2** are almost nonadsorptive for CH₄ (18.2 and 7.8 cm³ g⁻¹ for **1**, 11.9 and 7.7 cm³ g⁻¹ for **2**) but moderate of CO₂ is captured (58.1 and 40.1 cm³ g⁻¹ for **1**, 39.4 and 33.8 cm³ g⁻¹ for **2**) (Figure 6), demonstrating their vital gas adsorption selectivity of CO₂ over CH₄ and N₂. During separation, the selectivity of different components in the mixture is a key factor for the adsorbents, and the selectivity for CO₂ capture was calculated by ideal adsorbed solution theory (IAST).^{62,63} For CO₂/CH₄ mixtures with general feed compositions of land fill gas (CO₂/CH₄ = 50/50), the CO₂/CH₄ selectivities calculated at 1 atm were 29.3 for **1** and 11.0 for **2**, respectively (Figure 7). The notable selectivity for CO₂ over N₂ and CH₄ highlight the potential of **1** and **2** for CO₂ capture after postcombustion and in gas separation processes.

According to the adsorption isotherms of CO₂ at 273K and 298K, the adsorption affinity of **1** and **2** for CO₂ could be assessed by the adsorption isotherms(Q_{st}) calculated by the adsorption data. (Figure S11). The Q_{st} is 35.3 kJ mol⁻¹ for **1** and

22.8 kJ mol⁻¹ for **2** at zero loading, implying that the possible strong framework–CO₂ interactions might exist, thereby resulting in the apparent selectivity for CO₂. The Q_{st} for **1** remains essentially unchanged with the increase of pressure, the Q_{st} for **2** slowly decreased remaining up to 8.4 kJ mol⁻¹ at maximum loading. The key factors for high Q_{st} over CO₂ in **1** and **2** as follows: first, CO₂ could be directly extracted by the uncoordinated N atoms in bpe/bpa through dipole–quadrupole interactions with a larger quadrupole moment and a higher polarizability value (29.1 × 10⁻²⁵ cm⁻³) over CH₄ (25.9 × 10⁻²⁵ cm⁻³) and N₂ (17.4 × 10⁻²⁵ cm⁻³). Second, the steric hindrance of free bpe/bpa crowds the pores of **1** to some degree, strengthening the network–CO₂ interactions. Moreover, CO₂ molecules are tightly bound together in small channels, resulting in CO₂–CO₂ interactions and providing appropriate contributions to Q_{st} .⁶⁴

Catalysis Properties. Based on our particular interest on the synthesis and application potential of tetrazines and inspiring by their synthetic routes using Lewis acids Ni(II)/Zn(II) triflates as catalysts,³⁷ we try to look for a new effective catalyst, especially the Ni(II)-MOFs catalyst, to easily prepare tetrazines from nitriles and hydrazine hydrate, for anhydrous hydrazine is limited commercial availability in China due to safety concerns. Here in, our first tentative studies are reported.

To explore the catalytic effect of 1-5, the catalytic experiment of 4-cyanopyridine with hydrazine hydrate for the synthesis of 3,6-di(pyridine-4-yl)-1,2,4,5-tetrazine was performed. The reaction was conducted by mixing 4-cyanopyridine (1 mmol), hydrazine hydrate (5 mmol), and the nickel catalysts (2.5 mol%) in ethanol at 78 °C and stirring the mixture for 24 h. (Table 2, entry 1–6). Remarkably, in the absence of

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catalyst, the products could not be obtained. And it was found that the yields of tetrazine catalyzed by complex 1-5 are not good (about 15%). For optimizing the reaction conditions, we therefore selected 2 as the target catalyst. Concentration of the catalysts and different solvents were screened. When the same reaction was performed in ethanol at 78 °C at the catalyst 2 loading of 0.5, 1, 1.5, 2 and 2.5 (mol%), the catalyst 2 (0.5 mol%) show superior activity (Table 2, entry 7-11). Several solvents were also screened for this reaction, and ethanol was seen to be the best under above-selected reaction conditions (Table 2, entry 12-17). Thus, our optimized conditions as follows: complex 2 as the catalyst (0.5 mol%) and ethanol as the solvent, reaction temperature at 78°C. The characterization data for the 3,6-di(pyridine-4-yl)-1,2,4,5-tetrazine are given in the Supporting Information. Though it was found that the yield of tetrazine catalyzed by complex 1-5 are not good and similar to the other reported, 65-67 the results showed the catalysts role of 1–5. This tentative study not only provides the possibility that MOFs can catalyze the synthesis of tetrazine, but also lays a foundation for our further exploration and even hopeful discovery of efficient MOFs as the catalysts to prepare tetrazine.

	NCN	NH ₂ NH ₂ •H ₂ O catalyst solution T (°C)		N	
Entry	Catalyst (mol %)	Solution	Time (h)	<i>T</i> (°C)	Yield ^b (%)
1	none	EtOH	24	78	0
2	CP1	EtOH	24	78	16
3	CP 2	EtOH	24	78	18
4	CP 3	EtOH	24	78	15
5	CP4	EtOH	24	78	14
6	CP5	EtOH	24	78	14
7	CP 2 (2.5%)	EtOH	24	78	18
8	CP 2 (2%)	EtOH	24	78	19
9	CP 2 (1.5%)	EtOH	24	78	24
10	CP2 (1%)	EtOH	24	78	26
11	CP 2 (0.5%)	EtOH	24	78	26
12	CP 2	H_2O	24	Reflux	9
13	CP 2	MeOH	24	Reflux	15
14	CP 2	EtOH	24	Reflux	26
15	CP 2	Toluene	24	Reflux	17
16	CP 2	DMF	24	Reflux	18
17	CP 2	Chlorobenzene	24	Reflux	24

Table 2. Optimization of reaction condition ^a

^a Reaction conditions: 4-cyanopyridine (1 mmol), N_2H_4 ·H₂O (5 mmol), catalyst (0.005mmol), solvent (5 mL), 78°C (oil bath) for 24 h. ^b Isolated yield.

Magnetism. The static magnetic moments of polycrystalline sample of 1–5 were characterized in the temperature range of 2 to 300 K at 1000 Oe. As shown in Figure S12, complexes 1–5 possess similar curve trends. $\chi_m T$ values are stable at around 20 K, after which it then drops sharply to a minimum value at 2.0 K. The decrease at low temperatures indicates the presence of a (ZFS) zero field splitting on the Ni(II) ions and/or a weak antiferromagnetic interactions between Ni(II) ions. The susceptibility data obey the Curie–Weiss law with C = 1.23(1) cm³ K mol⁻¹, $\theta = -0.58(1)$ K for 1, C = 1.22(1) cm³ K mol⁻¹, $\theta = -0.88(1)$ K for 2, C = 1.19(1) cm³ K mol⁻¹, $\theta = -0.50(1)$ K for 3, C = 1.31(1) cm³ K mol⁻¹, $\theta = -1.41(1)$ K for 4, and C = 1.25(1) cm³ K mol⁻¹, $\theta = -0.50(1)$ K

 -1.07(1) K for **5**, respectively. Owing to that the Ni(II) ions are well isolated in the structures, the coupling between Ni(II) ions are neglectable, the magnetic susceptibility measurements were fitted using the program Phi.⁶⁸ As described by the spin Hamiltonian, $\hat{H} = D\hat{S}_z^2 + g\mu_B\hat{S}_zH$, where *D* is the axial ZFS parameter, *S* is the spin of Ni(II), *g* is the Lande factor, μ_B is the Bohr magneton and *H* is the magnetic field. The best fitting give D = 6.3(2) cm⁻¹, and g = 2.21(1) for **1**, D = 6.1(2) cm⁻¹, and g = 2.18(1) for **2**, D = 5.2(1) cm⁻¹, and g = 2.17(1) for **3**, D = 9.0(3) cm⁻¹, and g = 2.28(1) for **4**, and D = 5.3(1) cm⁻¹, and g = 2.22(1) for **5**.

CONCLUSIONS

In summary, under the same experimental environments except various N-donor ligands, we have successfully synthesized five novel Ni-CPs, ranging from 1D ladder chains, 2D layers to 3D layered-Pillared structure, suggesting that the coordination modes of H₂bitp ligand, structure of N-donor ligand contribute to the final structures. 1-5 exhibit enhanced thermostability up to 320 °C and chemical stabilities against common organic solvents, boiling water, acids and bases relative to most CPs, which expands their practical application. Furthermore, gas sorption measurements for 1 and 2 display a high absorption selectivity of CO_2 over CH_4 . The catalytic results demonstrate that 1-5 can be used as catalysts to synthesize 3,6-di(pyridine-4-yl)-1,2,4,5-tetrazine. The tentative studies put forward the possibility that coordination polymers as catalysts to prepare tetrazines. The magnetic analysis of 1-5 indicates the presence of a (ZFS) zero field splitting on the Ni(II) ions.

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ASSOCIATED CONTENT

Supporting Information. Crystallographic data, PXRD patterns, IR spectra, sorption patterns, magnetic curves and additional synthetic procedure. This material is available free of charge on the ACS Publications website.

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High Thermally and Chemically Stable Nickel (II) Coordination Polymers: Tentative Studies on Their Sorption, Catalysis, and Magnetism

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Five high thermally and chemically stable nickel (II) coordination polymers have been successfully synthesized. Furthermore, tentative studies on the structure and property (such as adsorption, catalysis, and magnetism) were undertaken.