Coordination Polymers Based on Substituted Terpyridine Ligands: Synthesis, Structural Diversity, and Highly Efficient and Selective Catalytic Oxidation of Benzylic C–H Bonds

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ABSTRACT: Reaction of two related rigid terpyridine ligands, 4′-(4-cyanophenyl)-2,6′,4-terpyridine (L1) and its derivative, 4′-(4-carboxyphenyl)-2,6′,4-terpyridine (L2), with transition metal ions (Co2+ or Cu2+/Cu+), afforded four novel coordination compounds: Co(L1)Cl2 (1), Co2(L1)2Cl6 (2), Cu(L1)2(CN)6 (3), and [Cu2(L1)2(H2O)6]Cl6 (4). Crystal structure analysis reveals that 1 is comprised of single-stranded 2 helices, which is compared with the structure of compound 2. 3 shows a three-dimensional (3D) 4-fold interpenetration structure. 4 exhibits a one-dimensional gridlike belt structure, which further builds 3D supramolecular architecture via π−π stacking interactions. These novel coordination compounds show excellent catalytic activity for the oxidation of benzylic C−H bonds. Notably, compound 4 shows the best catalytic properties for the oxidation of benzylic hydrocarbons up to 99% conversion and 99% selectivity.

INTRODUCTION

Functionalization of C−H bonds is a powerful tool for generating high-value chemical feedstock from less expensive raw materials and has become a central challenge in modern organic chemistry. Despite the high conversion rate, many benzylic C−H bond oxidation reactions reported to date rely on homogeneous catalysts, and thus, the recyclability and reusability of these specially designed catalysts can be problematic. Design of the heterogeneous molecular catalysts containing catalytic active sites has proven to be the most valuable strategy for solving this problem.

Copper and cobalt compounds have been extensively investigated as oxidation catalyst for oxidation of benzylic C−H bonds. In these catalysts, metal centers, which are usually coordinated to the N-donor or O-donor ligands such as pyrimidine, imidazole, porphyrins, bipyridines, phenanthrolines, and poly(carboxylic acid)s and acted as catalytic active sites, played a crucial role in the catalytic reaction. For example, Su et al. report a polycatenated three-dimensional (3D) Cu(II) square-grid metal–organic framework (MOF), [Cu2(bped)2(H2O)2(SiF6)] [bped = meso-1,2-bis(4-pyridyl)-1,2-ethanediol], which displays adsorption behaviors and efficient catalytic activities.

Multipyridyl ligands of 4,2’-6’,4-terpyridine are a well-known class of ligands that have some advantages for constructing MOFs, especially the ligands with additional function such as 4-X-C6H4 (X = C≡CH, COOH, Br, SMe, or NMe2) groups incorporated at position 4′. The type of MOF had potential applications in the area of catalysis, luminescence, gas uptake, magnetism, and biochemical activities. Wen and Ke et al. have reported two porous cadmium(II) frameworks with a polytopic 4-(4-carboxyphenyl)-2,6′,4-terpyridine to offer two kinds of cobalt frameworks, (4,4) and (6,3) nets, respectively. Afterward, this bridging co-ligand coordinated with Zn(II),Co(II), or Mn(II) results in different kinds of interpenetration, polycatenane, interdigitation, polythread, and other species. However, coordination compounds with terpyridine...
ligands have rarely been investigated in the oxidation catalytic reactions.87

Herein, we successfully prepared four coordination polymers, Co(L1)L1Cl6 (1), Co(L2)L1Cl6 (2), Cu(L2)L14(CN)9 (3), and [Cu(L2)L1(H2O)4]4H2O (4), through a hydrothermal method. The dimensionalities of the entire architectures of the four compounds vary from one-dimensional (1D) to 3D, and we found that the solvent and subtle temperature changes have a profound impact on the self-assembly of polymeric networks. We also successfully employed the four coordination polymers as highly efficient catalysts for the oxidation of benzylic hydrocarbons up to 99% conversion and 99% selectivity.

## EXPERIMENTAL SECTION

### Materials and Methods.

All of the chemicals and solvents were commercially available without further purification. L1 was synthesized by a modification of the literature methods,88 and L2 was readily obtained through the hydrolysis of L1. IR spectra were recorded with KBr pellets on a Nicolet 170S Fourier transform infrared spectrometer (FT-IR) in the range of 4000–400 cm−1. Powder X-ray diffraction data (PXRD) were collected on a Bruker SMART APEX-CCD instrument using Cu Kα radiation (λ = 1.5406Å). Thermal gravimetric analyses (TGA) were performed in a nitrogen atmosphere on a Q50TGA instrument at a heating rate of 10 ⁰C min⁻¹. The syntheses of compounds 1–4 are shown in Scheme 1.

### Scheme 1. Syntheses of Compounds 1–4

#### Synthesis of Ligand L1.

Ligand L1 was prepared by the procedure of Beves with a slight modification.89 4-Acetylpyridine (4.84 g, 40.0 mmol) was added to the mixture. Subsequently, the reaction mixture was heated at 160 °C for 3 days, and then slowly cooled to room temperature. After the solution had been filtered, blue strip crystalline products were collected by filtration, blue hexagonal plate crystals of L1 were prepared with a procedure analogous to that of I, except that reaction temperature was decreased to 100 °C. Yield: 24.2%. Anal. Calcd for C22H15N3O2 (%): C, 74.78; H, 4.30; N, 10.14. Found: C, 73.31; H, 4.37; N, 10.01. FT-IR (KBr pellet, cm⁻¹): 2973(w), 2225(w), 2126(m), 1599(s), 1541(w), 1488(m), 1396(m), 1174(m), 1137(w), 1002(s), 822(m), 540(w), 444(m).

#### Synthesis of Co(L1)L1Cl6 (2).

A mixture of Cu(NO3)2·3H2O (7.25 mg, 0.03 mmol), L1 (10.0 mg, 0.03 mmol), and acetonitrile (8 mL) were sealed in a 16 mL Te-sealed on-lined autoclave, heated at 160 °C for 3 days, and then slowly cooled to room temperature. After the solution had been filtered, blue strip crystalline products of 4 were obtained. Yield: 10.2%. Anal. Calcd for C12H4CuN6O2 (%): C, 63.75; H, 4.30; N, 10.14. Found: C, 63.31; H, 4.37; N, 9.95. FT-IR (KBr pellet, cm⁻¹): 3431(s), 1617(w), 1595(m), 1551(s), 1384(s), 1217(w), 1063(m), 847(w), 784(m), 696(m), 632(m), 512(m).

#### General Procedure for Catalyzed Oxidation of Benzyl Hydrocarbons.

Benzyl hydrocarbons (0.125 mmol), 70% tert-butyl hydroperoxide (TBHP) (0.3125 mmol), and catalyst (4 mol%) were placed into a Schlenk tube, and then chlorobenzene (1 mL) was added to the mixture. Subsequently, the reaction mixture was heated to 80 °C in a Waters parallel reactor and maintained 24 h while the mixture was being stirred. After the oxidation reaction, the mixture was cooled to room temperature. Then the resulting mixture was analyzed by GC–MS and GC using naphthalene as an external standard.

#### Determination of the Crystal Structure.

The X-ray single-crystal data for compounds were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. All the data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the o-scaling algorithm. The structures of all compounds were determined by direct methods and refined by full-matrix least-squares methods with SHELXL-97. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms are placed in calculated positions. For 2, we used the SQUEEZE command in the refine process as the solvent molecules cannot be accurately determined because of the dispersibility of the electron cloud density. The crystallographic data are listed in Table 1. Important bond lengths and bond angles are listed in Table S1 of the Supporting Information.
RESULTS AND DISCUSSION

Syntheses. Ligand L1 was synthesized using the reaction of cyanobenzaldehyde with 2 equiv of 4-acetylpyridine under basic conditions. Then, L1 was hydrolyzed to ligand L2 with a carboxyl group under acidic conditions. The ligands are poorly soluble in solvent at room temperature, so we adopted a solvothermal method that can promote the solubility of ligands. In this system, the self-assembly process is obviously affected by various factors such as reaction temperature, metal ions, and coordinated disposition of the ligands. As we expected, the benzonitrile group of L1 is not coordinated in the assembly process, whereas the carboxyphenyl of L2 is connected with metal ions through oxygen atoms, which greatly affects the resulting structures and properties.

Description of the Structures. Description of the Structure of Co(L1)Cl2 (1).

Table 1. Crystallographic Data for Compounds 1–4

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Figure 1. (a) Coordination mode of the L1 ligand and the coordination geometries of the CoII cations in compound 1 (symmetry code: A 1/2 – x, y – 1/2, 1/2 – z). (b) Scheme of the one-dimensional helical chain of 1 with a 21 axis (yellow). (c) π-π stacking interactions between the pyridyl rings of neighboring ligands. (d) Weak interactions of π-π interactions and hydrogen bonding interactions between C= N and the pyridyl or benzene rings in 1. Color scheme: Co, light blue; N, dark blue; Cl, green; C, black. H atoms have been omitted for the sake of clarity.

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Co$^{2+}$ cations via the terminal N-donors of pyridyl groups, leaving the nitrile group uncoordinated; thus, L$^1$ acts as a bidentate bridging linker, leading to a one-dimensional 2 helical chain with the a pitch of 16.7 Å and a Co···Co distance along the chain of 12.727(1) Å (Figure 1b). Various weak interactions are also found in the packing structure, involving π···π interactions among pyridyl rings of L$^1$ from adjacent helices in an offset face-to-face stacking fashion (centroid–centroid distances of 3.619 and 3.708 Å), weak interactions of the nitrile groups and pyridyl rings of L$^1$ via face-to-face stacking interaction (distance of 3.589 Å), and C–H···N weak hydrogen bonding interaction (distances of 3.260 and 3.284 Å), as shown in panels c and d of Figure 1.

**Description of the Structure of Co$_2$(L$^1$)$_2$Cl$_3$ (2).** Compound 2 crystallizes in trigonal space group P$\overline{3}$21 with its asymmetric unit consisting of two crystallographically independent cobalt ions, one and one-half L$^2$ ligands, and three Cl$^-$ anions (shown in Figure 2a). In this structure, the cobalt centers also adopt four-coordinated tetragonal geometry defined by two Cl$^-$ anions and two pyridyl nitrogen atoms from L$^1$ to form helical chains with a Co···Co distance of 12.540(1) Å (Figure 2c). Because the procedures for 1 and 2 are almost the same except for the temperature, they seem to show

![Figure 2](image_url)

Figure 2. (a) Coordination mode of the L$^1$ ligand and the coordination geometries of the Co$^{2+}$ cations in compound 2. (b) π···π stacking interactions between the pyridyl rings and C≡N of neighboring ligands. (c) One-dimensional helix topology in 2 that runs along the ac axis. Color scheme: Co, light blue; N, blue; Cl, green; C, black. H atoms have been omitted for the sake of clarity.

![Figure 3](image_url)

Figure 3. (a) Scheme of the asymmetric unit in 3 showing the coordination mode of the L$^1$ ligand and the coordination geometries of the Cu$^+$ cations in compound 3. (b) Tetranuclear cuprous ring. (c) Octanuclear cuprous ring. (d) Perspective view of the quadruple interdigitated architecture in 3 along the ac axis (the connectivity of the neighboring Cu is drawn by a line, and the ligands have been omitted). Color scheme: Cu, light blue; C, black. H atoms have been omitted for the sake of clarity. The μ$_2$-CN$^-$ bonds are colored pink.
comparable chainlike structures, but in fact, they are distinct from each other. Compound 2 shows a more complicated helical structure. A 32 axis in 2 instead of a 21 axis in 1 runs along the oc direction (Figure 2c). In 1, two neighboring L1 ligands are arranged in the same orientations and positions, while the spatial directions of alternate L1 in 2 are different, which can be ascribed to two types of crystallographically independent cobalt ions and L2 in 2. Similar to 1, the π–π stacking interactions between the pyridyl rings or C≡N (centroid–centroid distances of 3.801 and 3.960 Å) in neighboring chains sustain the interdigitated structure (Figure 2b).

Description of the Structure of Cu9(L1)4.5(CN)9 (3). As shown in Figure 3a, compound 3 crystallizes in orthorhombic space group Pbcn with its asymmetric unit comprising nine CuI ions, four and one-half L1 ligands, and nine cyanide ions. The existence of cyanide ions can be proven by 2126 cm⁻¹ of the bridged CN⁻ stretching in IR, which is in agreement with the previously reported result. Despite the absence of CN⁻ anions in the reactant system, they probably originate from the decomposition of solvent acetonitrile and/or L1 at high temperature and simultaneously reduced Cu²⁺ to Cu⁺. Similarly, the XPS experiments were conducted for testing the charge of cooper in compound 3. Thus, Figure S2 of the Supporting Information shows plots of the Cu 2p³/₂ (931.14 eV) and Cu 2p 1/₂ (950.97 eV) photoelectron being in agreement with those previously reported and discussed in the literature for Cu⁺. In this structure, each copper ion is bridged by two C/N atoms of CN⁻ and one pyridyl nitrogen atom of L1 to form a distorted triangular coordination geometry. As a rigid "V" type connector, each L1 ligand combines with two CuI ions via two pyridyl groups, leaving the nitrile group uncoordinated. Also, the CN⁻ anion acts as a linear μ₂-ligand bridging cuprous ions. As shown in panels b and c of Figure 3, μ₂-L1/CN⁻ connectors and three-connected cuprous node construct two types of ring motifs: tetranuclear and octanuclear cuprous rings. The tetranuclear cuprous ring is comprised of two L1 ligands and two CN⁻ and four cuprous ions, and the Cu···Cu distance is 4.857 Å along the CN⁻ and 13.136 Å along L1. Meanwhile, two L1 ligands and six CN⁻ and eight cuprous ions construct an elliptical octanuclear ring, whose longest Cu···Cu distance is 23.485 Å. In this way, the two ring motifs connect with each other to construct a 3D network with large hexagonal channels (see Figure S3 of the Supporting Information). Notably, the large size void in the layer structure provides the possibility of the ultimate generation of the entanglement. As shown in Figure 3d, the structure is reinforced by a 4-fold interpenetration to a resultant stable close structure.

Description of the Structure of [Cu3(L2)6(H2O)6]·4H₂O (4). The reaction between L2 and Cu(CH₃COO)₂·H₂O afforded blue strip crystals of 4 that crystallize in triclinic space group P1. In the asymmetric unit, there are one and one-half copper ions and three L2 ligands. As shown in Figure 4a, each CuI forms a distorted CuN₅O₃ tetragonal pyramid geometry with two nitrogen atoms and two oxygen atoms from four L2 ligands.
occupying the equatorial positions and one oxygen atom from a coordinated H₂O filling the axial position. While the Cu²⁺ center adopts a distorted octahedral geometry defined by two pyridyl nitrogen atoms and two carboxylate oxygen atoms from two nonequivalent L² ligands, two oxygen atoms form a water molecule occupying the axial position. It is worth noting that the axial position is occupied by a water molecule via the weak coordination interaction with the Jahn–Tellar effect of Cu²⁺ (with the Cu–O distance being 2.305 and 2.481 Å), which makes them potential active sites for further catalytic activity.

In this structure, each L² ligand acts as a bridging linker to connect Cu(II) centers using one of the pyridine terminal nitrogen atoms and the carboxylate oxygen atom to form a gridlike infinite 1D chain with a minimal Cu···Cu distance of 14.288 Å (Figure 4a). Unlike compound 3, (a) the introduction of -COOH instead of -C≡N yields a new bridging mode of this ligand. (b) Without the acetonitrile in the reaction system, the oxidation state of Cu is +2 in 4. As depicted in panels b and c of Figure 4, although the residual pyridyl rings and phenyl rings are not engaged in coordination, it bears the offset face-to-face π···π stacking interactions with their corresponding rings of adjacent chains with centroid–centroid distances of 3.537, 3.883, and 3.811 Å, which further aggregated the 3D network.

**Table 2. Oxidation of Various Benzyl Hydrocarbons Catalyzed by 4**

| Entry | Substrates | Products | Conv. (%) | Selec. (%)
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*Reaction conditions: benzylic hydrocarbons (0.125 mmol), compound 4 (4 μmol), TBHP (0.3125 mmol), chlorobenzene (1 mL), 80 °C, 24 h.*

*Selectivity to ketones. The byproducts are corresponding alcohols.

Thermal Stability and Powder XRD. To investigate the thermal stability of compounds 1–4, thermal gravimetric analyses (TGAs) were conducted in the temperature range of 25–800 °C under a nitrogen atmosphere (in Figure S4 of the Supporting Information). Their main skeletons are stable until 300–500 °C and show excellent thermal stability. The collapse temperature is ~460 °C for 1, ~440 °C for 2, ~360 °C for 3, and ~290 °C for 4. In particular, for compound 4, there’s a weight loss before 79 °C (observed 7.41%, theoretical 7.85%), which can be attributed to the release of lattice water molecules.

Furthermore, the powder X-ray diffraction patterns of compounds 1–4 are illustrated in Figure S5 of the Supporting Information, which confirm the purities of the bulky crystalline samples 1–4 between the simulated ones and as-synthesized products.

**Oxidation Catalytic Test.** With the aim of understanding the catalytic property of these coordination polymers for developing a new oxidation system in organic chemistry, we selected the oxidation of diphenylmethane to benzophenone as a model reaction (Scheme 2).

The primary results suggest that all four compounds can promote the catalytic oxidation of diphenylmethane, leading to benzophenone and diphenylmethanol with preferable selectivity of the carbonyl product. Optimization of the reaction conditions was achieved by selectively evaluating effects of different diphenylmethane:4 molar ratios, oxidant:4 molar ratios, and solvents (Table S2 of the Supporting Information). As depicted in Table S2 of the Supporting Information, on the basis of the oxidation of diphenylmethane, 2.5 equiv of TBHP and 4 μmol of catalyst in chlorobenzene for 24 h are appropriate conditions for all catalytic reactions. Under the same conditions, we note that compounds 1–3 showed moderate activities while 4 presented superior activity toward the oxidation reaction, giving a 94.5% conversion and 92.6% selectivity in chlorobenzene at 80 °C for 24 h (Figure 5). These results show that compound 4 can facilitate the oxidation of diphenylmethane and serve as a highly efficient and selective catalyst. Indeed, compound 4 outperforms many effective catalysts reported to date in terms of yield, i.e., nanosized coordination cages [Cu⁰(bpna)₂(H₂O)₄(SiF₆)]₁₀ [Cu₄L₄]₄X
[L = 1,3,5-tris(1-benzylbenzimidazol-2-yl)benzene, X = ClO4, OTs, or OTf]11 NHPI/Cu@PILC12 [Co2(BTC)2(HCOO)]e−(DMF)], H2O,13 even noble Pd@N-doped carbon,14 etc.

Furthermore, control catalytic experiments of the catalytic oxidation of diphenylmethane were performed on L2 and Cu(CH3COO)2-H2O under the same reaction conditions. The conversion was 8.71% for the former and 75.8% for the latter. On the basis of the facts mentioned above, we conclude that the introduction of L2 into the catalytic system changes the coordination environment of the Cu ions and the cooperation between Cu4 centers and organic ligands in the catalyst of 4 probably produces a synergistic effect and thus enhances the oxidative capacity of copper centers in the catalytic process.

Following the success of diphenylmethane oxidation and evaluation of the scope and limitations of the current procedure, oxidation reactions with an array of benzylic hydrocarbons were examined using compound 4. A compilation of results for the oxidation of various benzylic-alkanes with large molecules, along with the corresponding ketones, is presented in Table 2. It is noteworthy that, without any further optimization, the oxidation of fluorene, the derivatives of the fluorene, and xanthene proceeded smoothly with high catalytic activity (>99% conversion, >99% selectivity for ketones). These preliminary results show that these coordination polymers based on substituted terpyridine, especially compound 4, can facilitate the oxidation of benzyl-alkanes and serve as highly efficient and selective catalysts.

**CONCLUSIONS**

In this paper, four coordination compounds were successfully synthesized by two types of substituted terpyridine ligands, L1 and L2, with transition metal Co and Cu ions under solvothermal conditions. These compounds possess different architectures such as 1D helix or gridlike chain and 3D interpenetration network, which demonstrates that a change in temperature and metal ions has played a crucial role in the self-assembly process. Meanwhile, all the compounds show good thermal stabilities. In addition, compound 4 exhibits excellent oxidation catalytic properties toward benzyl-alkanes. The good catalytic properties along with the high thermal stability make these compounds potentially applicable under more rigorous reactions, especially as heterogeneous catalysts.

**ASSOCIATED CONTENT**

Supporting Information
Crystallographic data in CIF format, PXRD for simulated and as-synthesized samples, TG curves for all compounds, XPS for compound 3 and selective oxidation of diphenylmethane by 4 using TBHP oxidant. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b00008.

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Notes
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**REFERENCES**


