

Facile synthesis of new divergent imidazole-containing ligands for a 1-D cobalt(II) coordination polymer



E Liu^a, Hangxing Xiong^a, Li Li^a, Chengxiong Yang^a, Zhiwei Yin^b, Anthony Chang^b, David R. Manke^c, James A. Golen^c, Guoqi Zhang^{b,*}

^a College of Chemical Engineering and Pharmacy, Jingchu University of Technology, Jingmen 448000, China

^b Department of Sciences, John Jay College and The Graduate Center, The City University of New York, New York, NY 10019, USA

^c Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, MA 02747, USA

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ABSTRACT

A new divergent ligand (**3a**) containing a triaryl core and two imidazole side-arms has been designed and synthesized. The synthetic procedure utilizes a two-step strategy, *i.e.* the Kröhnke condensation, followed by a Cu-catalyzed Ullman-type coupling. This synthetic strategy allows the facile introduction of various substituents on the 4-position of the central pyridine in the ligands, which was proved by the synthesis of a ligand analog (**3b**). The new ligands were well characterized by spectroscopic methods and X-ray structural analysis was carried out for **3a**. Reaction of **3a** with Co(NCS)₂ by a layering method afforded single crystals of a coordination polymer **5**, which was structurally characterized by X-ray diffraction. **5** is composed of two ligands and one Co(NCS)₂ in its asymmetric unit and features a 1-D coordination polymer with nano-scale metallomacrocycles. The structure of **5** is found to be quite different from all known coordination networks composed of Co(NCS)₂ and closely related divergent ligands.

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1. Introduction

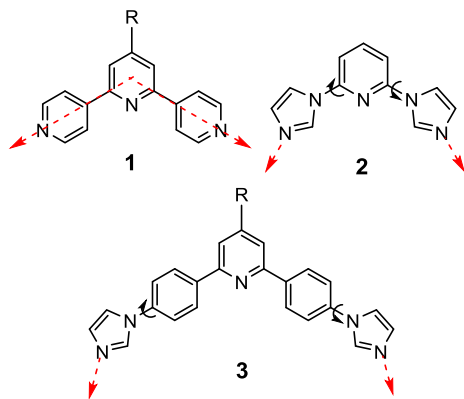
In recent years, the divergent analogues of the classical tridentate 2,2':6',2''-terpyridine (2,2':6',2''-tpy) derived ligands, 4,2':6',4''-tpy (**1**, Scheme 1) have become a popular choice for the construction of novel metal–organic coordination polymers or networks that displayed not only interesting supramolecular structures but also intriguing materials properties [1–6]. Generally, 4'-aryl-4,2':6',4''-tpys could be readily synthesized and purified in reasonable yields through the conventional one-pot Kröhnke condensation that has been employed for the preparation of a majority of 4'-aryl-2,2':6',2''-tpys [7]. A variety of transition metals (such as Zn^{II}, Cd^{II}, Hg^{II}, Cu^{II}, Co^{II} and Mn^{II} etc.) have been explored by the Constable, our and other groups through coordination-driven self-assembly to construct diverse metal–organic network structures [8–10], where the 4'-position substituent effect has been extensively studied, thanks to the easiness on ligand modification. Apparently, the divergent N-donors in 4,2':6',4''-tpys open new opportunities for the formation of more complicated supramolecular structures upon coordinating to metal ions, in comparison with the chelating N₃ cavity of 2,2':6',2''-tpys.

In search of other divergent ligand analogs to 4,2':6',4''-tpys, we found that 2,6-bis(imidazole-1-yl)pyridine (**2**, Scheme 1) bearing *N*-imidazolyl side-arms instead of 4-pyridyl group could exhibit similarly interesting coordination chemistry, even though the V-shaped N-donors in **2** adopt a smaller angle. In addition, rotations about the C–N bonds between the pyridyl core and imidazolyl arms would lead to different ligand conformations during the process of metal–ligand self-assembly, whereas rotations about the inter-ring C–C bond in 4,2':6',4''-tpy has no effect on the directionalities of the peripheral N-donors. However, up to date there were only a few metal coordination networks based upon this ligand that have been reported [11], although it was recently revealed that this compound comprises of a perfect building block for the construction of various molecular boxes and covalent macrocycles [12]. Indeed, the difficulty in modifying the pyridine core with different substituents has largely limited its applications in coordination and supramolecular chemistry.

In continuation with our recent work on transition metal chemistry based on the divergent ligands, 4'-aryl-4,2':6',4''-tpys and other N-rich analogs [9,13], we were interested in further modifying these ligands by varying the angle between the V-shaped N coordination sites through the introduction of imidazolyl side-arms. We envisaged that one could construct the triaryl core similar to 4,2':6',4''-tpy by taking advantage of the easiness of modifi-

* Corresponding author.

E-mail address: guozhang@jjay.cuny.edu (G. Zhang).



Scheme 1. Structures and various metal coordination directionalities of divergent ligands **1**–**3**.

cation on the 4-position of central pyridine through one-pot Kröhnke condensation, and then imidazolyl units can be readily anchored on the *para*-position of the side phenyl rings, should halo-substituents were present in the phenyl rings of the starting materials. Therefore, we report herein the successful synthesis of a novel divergent ligand bearing imidazolyl side-arms with a larger distance being between the divergent N-donating sites (Scheme 1). It is revealed that the R substituents in the 4-position of the central pyridine core can be readily altered as we anticipated. The application of this type of ligands in the synthesis of metal–organic coordination polymers/networks has been demonstrated through the synthesis and X-ray structural characterization of a one-dimensional (1-D) cobalt(II) coordination polymer containing nano-scale metallomacrocyclic motifs.

2. Experimental

2.1. General

Solvents and reagents were purchased from Fisher Scientific or Sigma–Aldrich in the US. All reactions were performed under ambient conditions (no inert atmosphere). FT-IR spectra were measured on a Shimadzu 8400S instrument with solid samples using a Golden Gate ATR accessory. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TG-50 analyzer under N₂ atmosphere with a heating rate of 20 °C/min. ¹H and ¹³C NMR spectra were obtained at room temperature on a Bruker III 500 MHz spectrometer with TMS as an internal standard. High resolution mass spectra were recorded on an Agilent 6550 iFunnel ESI-QTOF-LC/MS instrument. Elemental Analyses were performed by Midwest Microlab LLC in Indianapolis.

2.2. Synthesis of **4a**

In a 250 mL round-bottom flask equipped with a magnetic stirrer, 4-bromoacetophenone (3.94 g, 20.0 mmol) was added to a solution of benzaldehyde (1.06 g, 10.0 mmol) in EtOH (80 mL). KOH pellets (0.84 g, 15 mmol) were then added, followed by aqueous NH₃ (28%, 50 mL). The resulting reaction mixture was heated to 70 °C upon rigorous stirring for 24 h. The suspension was cooled to room temperature and filtered. Off-white solid was collected, washed with EtOH and dried in a desiccator over P₂O₅. Yield: 2.60 g (56%). ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 8.0 Hz, 4 H), 7.90 (s, 2 H), 7.76 (d, *J* = 7.5 Hz, 2 H), 7.68 (d, *J* = 8.5 Hz, 4 H), 7.59–7.53 (m, 3 H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 156.39, 150.88, 138.54, 137.91, 131.93, 129.35, 129.26, 128.77, 127.22,

123.83, 117.36 ppm. HR-MS (ESI, positive): *m/z* 465.9621 [M+H]⁺ (the only peak, calc. 465.9629).

2.3. Synthesis of **4b**

4b was synthesized according to the same procedure as for **4a**, except the replacement of benzaldehyde with pyridine-4-carboxaldehyde (1.06 g, 10.0 mmol). Off-white solid of **4b** was collected in 52% yield (2.42 g). ¹H NMR (500 MHz, CDCl₃) δ 8.84 (s, 2 H), 8.09 (d, *J* = 8.5 Hz, 4 H), 7.90 (s, 2 H), 7.69 (m, 6 H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 156.99, 150.38, 147.75, 146.48, 137.66, 132.04, 128.66, 124.12, 121.83, 116.74 ppm. Anal. Calcd. for C₂₂H₁₄Br₂N₂: C, 56.68; H, 3.03; N, 6.01. Found: C, 56.59; H, 3.01; N, 6.18%.

2.4. Synthesis of **3a**

To a 100 mL Pyrex tube was added a mixture of **4a** (1.00 g, 2.16 mmol), imidazole (2.94 g, 43.2 mmol), Cu₂O (0.030 g, 0.2 mmol), CuSO₄ (0.070 mg, 0.2 mmol) and K₂CO₃ (3.00 g, 21.6 mmol) under Ar atmosphere, and then anhydrous DMF (10 mL) was added. The suspension was heated to reflux and stirred overnight. The reaction mixture was cooled to room temperature and filtered, the solid was washed with CH₂Cl₂ (10 mL × 2). Water (100 mL) was added to the filtrate which was then extracted with CH₂Cl₂ (50 mL × 2). The organic layer was collected and washed with water for three times. The solution was dried over anhydrous Na₂SO₄ and filtered. The solvent was removed under reduced pressure. The product was purified through a flash column chromatography (eluent: ethyl acetate/methanol = 1:10, v/v) to give a white solid. Colorless single crystals were obtained by slow evaporation of a CH₂Cl₂–MeOH of **3a** at room temperature. Yield: 0.86 g (91%). FT-IR (solid, cm^{−1}): 1610m, 1548w, 1522s, 1484s, 1396m, 1301s, 1247s, 1186w, 1110w, 1053s, 961w, 901w, 817s, 773s, 727m, 700m, 654s. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 6.0 Hz, 4 H), 8.00 (s, 2 H), 7.94 (s, 2 H), 7.76 (d, *J* = 4.8 Hz, 2 H), 7.58–7.52 (m, 7 H), 7.38 (s, 2 H), 7.27 (s, 2 H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.22, 150.84, 138.60, 138.59, 137.90, 135.50, 130.46, 139.36, 129.36, 129.28, 128.66, 127.19, 121.52, 118.16, 117.40 ppm. HR-MS (ESI, positive): *m/z* 462.1692 [M+Na]⁺ (calc. 462.1695), 440.1873 [M+H]⁺ (base peak, calc. 440.1875).

2.5. Synthesis of **3b**

3b was prepared according to the same procedure as for **3a**, except the use of **4b** (1.01 g, 2.16 mmol) as the precursor. **3b** was isolated as white solid in 76% yield (0.72 g) after column chromatography. FT-IR (solid, cm^{−1}): 1740m, 1592s, 1521s, 1484m, 1397m, 1302s, 1246m, 1112w, 1053s, 962m, 902w, 825s, 727m, 654m, 622m. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, *J* = 6.0 Hz, 2 H), 8.35 (d, *J* = 8.8 Hz, 4 H), 7.99 (s, 2 H), 7.95 (s, 2 H), 7.68 (d, *J* = 6.0 Hz, 2 H), 7.59 (d, *J* = 8.8 Hz, 4 H), 7.39 (s, 2 H), 7.27 (s, 2 H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.69, 150.81, 148.06, 146.01, 138.19, 137.93, 135.51, 130.70, 128.68, 121.63, 121.51, 118.06, 116.94 ppm. HR-MS (ESI, positive): *m/z* 463.1664 [M+Na]⁺ (calc. 463.1647), 441.1828 [M+H]⁺ (base peak, calc. 441.1828).

2.6. Synthesis of **5**

A solution of **3a** (43.9 mg, 0.100 mmol) dissolved in MeOH/CH₂Cl₂ (10 mL, 1: 4, v/v) was placed in a long test tube. A mixture of MeOH and CH₂Cl₂ (6 mL, 1: 1, v/v) was then layered on the top of this solution, followed by another solution of Co(NCS)₂ (17.5 mg, 0.100 mmol) in MeOH (10 mL). The tube was sealed

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