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Based Coordination Polymers**

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## COMMUNICATION

# Synthesis of Atomically Precise Single-Crystalline Ru<sub>2</sub>-Based Coordination Polymers

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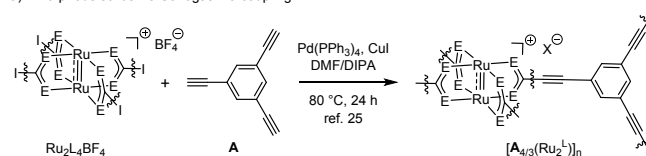
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Methods to incorporate kinetically inert metal nodes and highly basic ligands into single-crystalline metal-organic frameworks (MOFs) are scarce, which prevents synthesis and systematic variation of many potential heterogeneous catalyst materials. Here we demonstrate that metallopolymerization of kinetically inert Ru<sub>2</sub> metallomonomers via labile Ag–N bonds provides access to a family of atomically precise single-crystalline Ru<sub>2</sub>-based coordination polymers with varied network topology and primary coordination sphere.

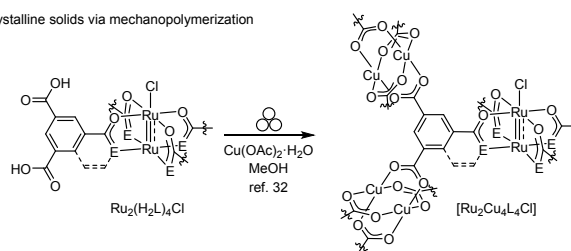
Metal-organic frameworks (MOFs) have attracted significant attention as platforms for heterogeneous catalysis in part due to the diversity of metal geometries and cluster sizes that can be incorporated within the extended crystal lattices of these materials.<sup>1,2</sup> Reticular synthetic logic enables systematic variation of structural parameters during MOF synthesis.<sup>3-6</sup> While access to single-crystalline materials facilitates characterization of catalyst structure,<sup>7</sup> observation of reactive species,<sup>8-10</sup> and systematic modulation of substrate diffusivity,<sup>11-15</sup> obtaining single-crystalline materials requires that the lattice be constructed via reversible metal–ligand (M–L) bond formation. As a result, it is challenging to incorporate kinetically inert metal ions into highly crystalline materials.<sup>16,17</sup> A less appreciated ramification of the need for reversible M–L bonding is that the primary coordination sphere of lattice ions is frequently limited to weak-field donors, which can engage in rapid exchange.<sup>18</sup> In contrast, a much wider variety of ligand donorities are routinely utilized in homogeneous catalysis.<sup>19-23</sup> Development of methods that enable systematic variation of the primary coordination sphere of lattice ions are needed to access the full array of potential MOF catalysts.

We have been interested in Ru<sub>2</sub>-based MOFs as platforms for nitrogen-atom and nitrene-transfer catalysis.<sup>15, 24-26</sup> Due to

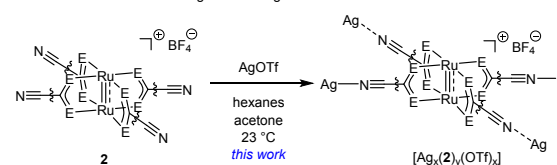
a) Amorphous solids via Sonogashira coupling



b) Microcrystalline solids via mechanopolymerization



c) Single-crystalline materials via reversible Ag–nitrile linkage



**Figure 1.** Previous metallopolymerization chemistry based on a) Sonogashira coupling reaction of halogenated Ru<sub>2</sub> complexes with polyalkynes or b) mechanopolymerization synthesis of carboxylated Ru<sub>2</sub> complexes with Cu(OAc)<sub>2</sub> resulted in amorphous solids or microcrystalline powders, respectively. c) Here, we report the synthesis of single-crystalline heterobimetallic materials based on systematically variable kinetically inert metallomonomers and reversibly generated Ag–nitrile linkages.

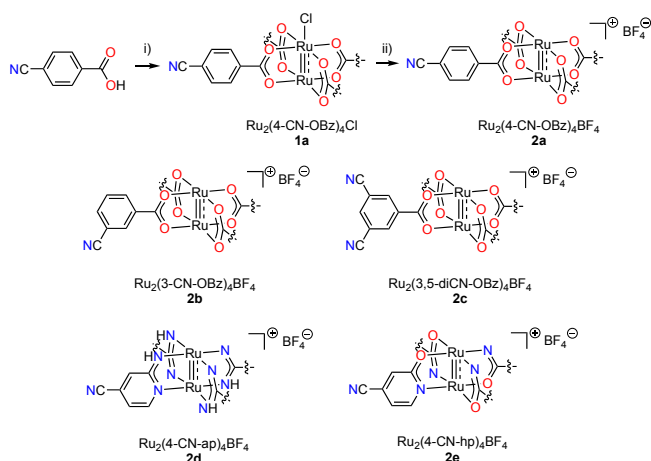
the slow ligand exchange kinetics characteristic of Ru<sup>2+</sup> and Ru<sup>3+</sup>,<sup>27-29</sup> as well as potential formation of Ru metal<sup>30</sup> or RuO<sub>2</sub> under solvothermal conditions, the family of available Ru<sub>2</sub>-based MOFs is extremely limited: Only [Ru<sub>6</sub>(btc)<sub>4</sub>Cl<sub>3</sub>] is available from solvothermal methods and only as a microcrystalline powder (btc = 1,3,5-benzenetricarboxylate).<sup>30,31</sup> To provide access to new Ru<sub>2</sub>-based materials, we have been developing metallopolymerization chemistry in which pre-synthesized metallomonomers featuring peripheral functionality are polymerized under conditions in which the metallomonomers are kinetically stable (Figure 1).<sup>25,32</sup> The metallopolymerization

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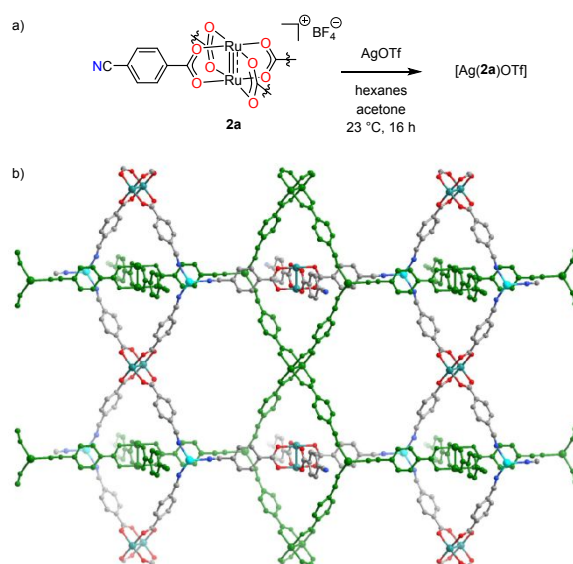
Electronic Supplementary Information (ESI) available: Experimental details, spectra, X-ray crystallographic information, and additional figures and tables. CCDC 2011428–2011433. See DOI: 10.1039/x0xx00000x

strategy enables systematic variation of both network topology and the primary coordination sphere of lattice ions by rational perturbation of the molecular structure of the constituent metallomonomers. We previously demonstrated metallopolymerization via Sonogashira coupling of halogenated  $Ru_2$  complexes with polyalkynes (Figure 1a)<sup>25</sup> and via mechanochemical reaction of carboxylated  $Ru_2$  complexes with the  $Cu(OAc)_2$  salt provided amorphous and microcrystalline porous solids, respectively (Figure 1b).<sup>32</sup> In neither case were single-crystalline materials available. Inspired by classic reports of coordination polymers based on Ag–nitrile linkages,<sup>33–36</sup> here we report the metallopolymerization of a family of  $Ru_2$  complexes featuring peripheral nitrile substituents with  $Ag^+$ . This synthetic strategy provides access to a family of single-crystalline  $Ru_2$ -based materials, in which both network topology and primary coordination sphere of lattice ions can be systematically manipulated (Figure 1c).

We initiated these investigations by preparing a family of  $Ru_2[II,III]$  complexes (**2**, Figure 2) featuring peripheral nitrile groups in which both the substitution pattern (*i.e.*, 3- vs. 4-monosubstitution and 3,5-disubstitution) and the primary coordination sphere (*i.e.* carboxylate, 2-oxypyridinate, and 2-aminopyridinate) were varied. These metallomonomers were synthesized by thermally promoted ligand exchange between  $Ru_2(OAc)_4Cl$  and the appropriate ligand. Ligand exchange was monitored by mass spectrometry (*i.e.*  $m/z$  value that corresponded to  $[Ru_2L_4]^+$ ) and  $^1H$  NMR spectroscopy. The  $^1H$  NMR spectra of **2a**, **2b**, and **2c** display the appropriate number of paramagnetically shifted signals, which is similar to the  $^1H$  NMR data obtained for  $Ru_2(OBz)_4BF_4$ .<sup>24</sup> Neither 2-aminopyridinate- nor 2-oxypyridinate- based  $Ru_2L_4BF_4$  complexes (**2d** and **2e**) display well-defined  $^1H$  NMR signals when measured in  $d_6$ -DMSO at 295 K, which is similar to  $^1H$  NMR data of iodinated analogues we reported previously.<sup>25</sup>  $Ru_2L_4Cl$  complexes often display poor solubility due to the formation of  $[-Ru-Ru-Cl-]_n$  chains,<sup>25,37,38</sup> and consistent with this, complexes **1** display poor solubility in many common solvents. Treatment



**Figure 2.** A two-step synthetic procedure based on ligand exchange followed by anion exchange, affords a family of soluble metallomonomers (**2**). Conditions: i) **1a–1b**: MeOH/ $H_2O$ , 90 °C; **1c**: PhCl, 150 °C, 14 h; **1d–1e**: PhCl, 155 °C, 24 h. ii) **2a–2b**: MeOH, 23 °C, 24 h; **2c**: THF, 23 °C, 24 h; **2d**: THF, 23 °C, 24 h; **2e**: MeOH, 65 °C, 24 h. THF = tetrahydrofuran, ap = aminopyridinate, hp = hydroxypyridinate.

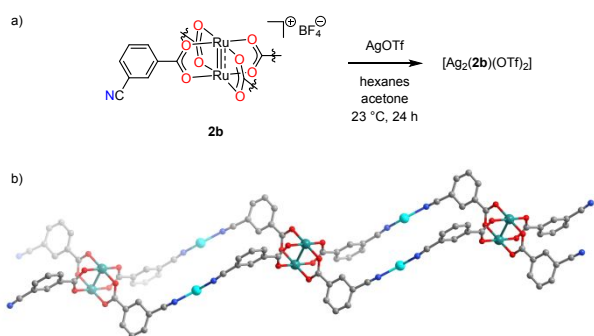


**Figure 3.** a) Diffusion of hexanes into an acetone solution of  $Ru_2(4-CN-OBz)_4BF_4$  (**2a**) and  $AgOTf$  affords orange-colored block-shaped crystals of  $[Ag(2a)OTf]$ . b) A two-dimensional extended coordination polymer of  $[Ag(2a)OTf]$  was revealed by SCXRD. The second interpenetrated layer is marked green.

of complexes **1** with  $AgBF_4$  afforded  $[Ru_2L_4]BF_4$  complexes **2**, which displayed significantly enhanced solubility. The anion exchange process was characterized by the appearance of a broad B–F IR stretching mode at  $1020\text{ cm}^{-1}$  (Figures S1–S5). The molecular structure of  $Ru_2(4-CN-OBz)_4BF_4$  (**2a**) was established by single-crystal X-ray diffraction (SCXRD, Figure S6).

With access to a suite of soluble  $Ru_2$  complexes featuring peripheral nitrile substituents, we investigated metallopolymerization chemistry in the presence of silver trifluoromethanesulfonate ( $AgOTf$ ). Diffusion of hexanes into a solution of  $Ru_2(4-CN-OBz)_4BF_4$  (**2a**) and  $AgOTf$  in acetone afforded orange-colored block-shaped crystals (Figure 3a). SCXRD analysis revealed a two-dimensional (2D) layered structure in which there are two different coordination modes for metallomonomers incorporated into the framework: one metallomonomer is coordinated to four  $Ag(I)$  nodes via each of the nitrile substituents while the other metallomonomer is coordinated to two  $Ag(I)$  nodes via trans-disposed nitriles (the other two nitriles are not coordinated to  $Ag(I)$ ); Figure 3b). Each  $Ag(I)$  ion in the coordination polymer is trigonally coordinated with an average  $Ag-N$  distance of  $2.06\text{ \AA}$  and the average  $N-Ag-N$  angle  $111.7^\circ$ . The extended 2D layer (Figure S7) is singly interpenetrated by another layer (Figure 3c). Topologically,  $[Ag(2a)OTf]$  is described as a 3,4-connected **bex** net, in which each  $Ag(I)$  ion serves as the 3-connected node and the 4-connected metallomonomer as the second node. Attempts to generate this structure by solvothermal combination of 4-cyanobenzoic acid,  $Ru_2(OAc)_4Cl$ , and  $AgOTf$  were unsuccessful due to formation of  $Ag$  mirror.<sup>39</sup>

Moving the position of nitrile substituent from 4- to 3- on the metallomonomer (*i.e.* **2b**) changes the resultant structure from two-fold interpenetrated 2-D sheets to self-assembled 1-D chains. A crystallization reaction between  $Ru_2(3-CN-OBz)_4BF_4$

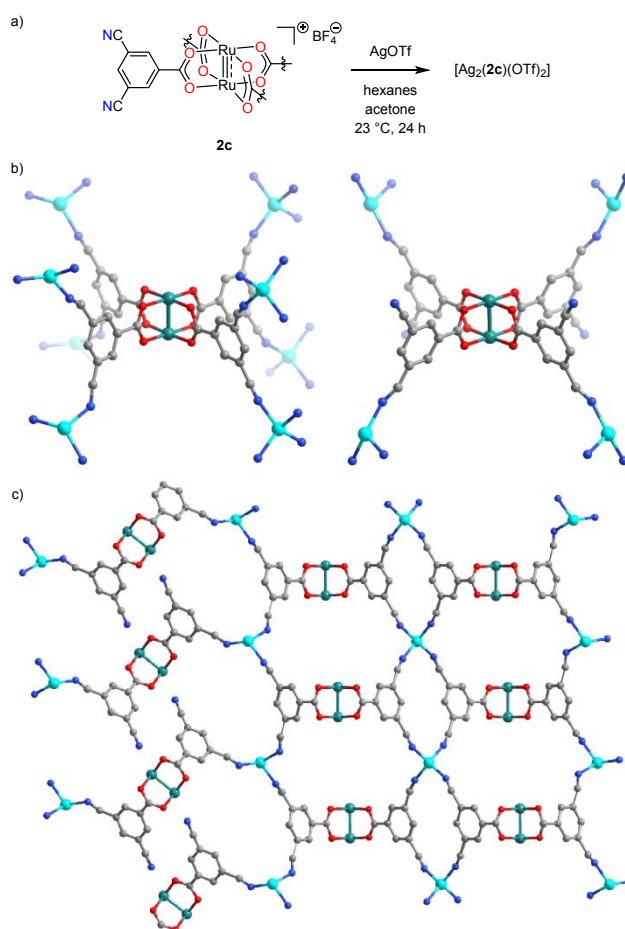


**Figure 4.** a) Diffusion of hexanes into an acetone solution of  $\text{Ru}_2(3\text{-CN-OBz})_4\text{BF}_4$  (**2b**) and AgOTf affords orange-colored crystals of  $[\text{Ag}_2(\mathbf{2b})(\text{OTf})_2]$ . b) Pairwise directionality of the nitrile substituents gives rise to the observed double-chain structure.

(**2b**) and AgOTf afforded a solid in which each Ag(I) ion is two-coordinate, bound to nitrogens of two nitrile groups at distances of 2.11(2) and 2.18(2) Å with a N–Ag–N angle of 151.5(6)° (Figure 4a). The nitrile ligands display pairwise directionality, with two *cis*-disposed nitrile pointing up and the other two *cis*-disposed nitriles pointing down. This alternating directionality gives rise to the infinite double-chain structure illustrated in Figure 4b.

An extended 3-D network was accessed by expanding the connectivity of the metallomonomer from 4 to 8 (*i.e.*, utilized metallomonomer **2c** in place of **2a** or **2b**). Metallopolymerization of  $\text{Ru}_2(3,5\text{-diCN-OBz})_4\text{BF}_4$  (**2c**) with AgOTf afforded dark orange single crystals (Figure 5a). SCXRD analysis of  $[\text{Ag}_2(\mathbf{2c})(\text{OTf})_2]$  revealed a two-fold interpenetrated 3-D network. Two types of Ag(I) nodes were observed in this structure: one Ag(I) node is trigonally coordinated by three nitriles; the other Ag(I) adopts tetrahedral coordination geometry with four nitriles. There are two distinct metallomonomer connectivities: one metallomonomer is coordinated to Ag(I) via all eight nitriles (see Figure 5b left); the other metallomonomer is coordinated to Ag(I) via four nitriles (one from each 3,5-dicyanobenzoate motif, see Figure 5b right). This results to an expanded 3-D network (Figure 5c), which is interpenetrated by another network (Figure S8a). The new 3,4,4,8-connected (4 nodal) net topology can be described by point symbology as  $(4^2.6)_4(4^2.8^4)(4^6)(4^9.6^{10}.8^9)_2$ , if the two types of metallomonomers are simplified as 8-connected and 4-connected nodes and the two kinds of Ag(I) ions serve as 3-connected and 4-connected nodes (See further discussion in Figures S8b-c).<sup>40</sup>

The modularity of the developed metallopolymerization strategy enables systematic variation of the primary coordination sphere of lattice-confined  $\text{Ru}_2$  sites within single-crystalline materials. Metallopolymerization of  $\text{Ru}_2(4\text{-CN-}n\text{ap})_4\text{BF}_4$  (**2d**) with AgOTf affords a 2-D sheet in which each nitrile of the metallomonomer is linearly coordinated Ag(I) nodes (Figure S9). Metallopolymerization of  $\text{Ru}_2(4\text{-CN-hp})_4\text{BF}_4$  (**2e**) with AgOTf affords an extended material comprised of 3-D networks (Figure S10). 3-D connectivity arises from axial binding of a hydroxypyridine ligand to the apical site of the  $\text{Ru}_2$  node, thus affording the dimensionally expanded network.



**Figure 5.** a) Diffusion of hexanes into an acetone solution of  $\text{Ru}_2(3,5\text{-diCN-OBz})_4\text{BF}_4$  (**2c**) and AgOTf affords dark orange-colored crystals of  $[\text{Ag}_2(\mathbf{2c})(\text{OTf})_2]$ . b) A three-dimensional extended coordination polymer was revealed by SCXRD. Two types of Ag(I) nodes and two kinds of the metallomonomers are observed in the structure. c) An extended network is viewed from *b* axis without the interpenetrating net. The non-coordinated nitrile groups are visible in this direction.

While the facility of Ag–nitrile reversibility provides access to single-crystalline materials, the resulting materials are not highly robust. Powder X-ray diffraction (PXRD) analysis of the developed materials  $[\text{Ag}_x(\mathbf{2}),y(\text{OTf})_z]$  reveals the family of polymers to be sensitive to desolvation, which gives rise to network collapse and amorphization (Figure S11). In addition, the materials completely dissolve upon exposure to MeCN. These observations are consistent with previous reports of Ag nitrile-based coordination polymers,<sup>41–44</sup> and highlights a critical design challenge for the development of broadly useful metallopolymerization chemistry: A delicate balance between the requirement for strong M–L linkages to provide network stability to the resulting materials while simultaneously having sufficient M–L lability to access single-crystalline materials. Modifying the charge of the  $\text{Ru}_2$  linkers, which would presumably modulate the donicity of the nitrile substituents, may provide a route to more stable materials.

In summary, we describe a synthetic strategy to incorporate kinetically inert  $\text{Ru}_2$  nodes into single-crystalline coordination polymers, which takes advantages of the facile Ag–N bond formation between nitrile groups of metallomonomers and

Ag(I) under self-assembly conditions. By modulating the geometry and connectivity of the metallomonomers, the resultant structures can be varied from 1-D chains to 2-D sheets and 3-D networks. The modularity of the metallopolymerization strategy enables the primary coordination sphere of lattice-bound Ru<sub>2</sub> nodes to be systematically varied within single-crystalline, atomically precise materials. We expect that further development of metallopolymerization concepts will result in new opportunities to rationally access robust catalyst platforms.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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