Robust, Transformable, and Crystalline Single-Node Organometallic Networks Constructed from Ditopic *m*-Terphenyl Isocyanides

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S *Supporting Information*

ABSTRACT: The preparation of 3D and 2D Cu(I) coordination networks using ditopic *m*-terphenyl isocyanides is described. The incorporation of sterically encumbering substituents enables the controlled, solid-state preparation of Cu(I) tris-isocyanide nodes with a labile solvent ligand in a manner mirroring solution-phase chemistry of monomeric complexes. The protection afforded by the *m*-terphenyl groups is also shown to engender significant stability towards heat as well as acidic or basic conditions, resulting in robust single-metal-node networks that can transition from 3D to 2D extended structures.

Control over the metal coordination environment has become a defining hallmark in the evolution of porous coordination polymers (PCPs) and metal−organic frameworks (MOFs) and has given rise to significant topological and structural diversity within this class of materials.[1−4] To achieve targeted and/or emergent properties, techniques such as thermal activation, reticular linker substitution,[5,6] and post-synthetic modification[7] have been employed to create highly tailored, functional materials for applications in separations,[8] gas storage,[9] sensing,[10] and catalysis.[11] In many cases, such enhanced properties are enabled by open metal-coordination sites at the secondary building unit (SBU) or framework linker. Although recent progress in defect engineering has provided a means to consistently impart some structures with open metal sites,[12] there remain few approaches to reliably control the formation of low-coordinate metal centers within a framework material.[13] However, in molecular systems it is well established that sterically encumbering ligands can exert substantial control over the coordination number and geometry at a metal site, and this strategy has allowed for the preparation of numerous complexes possessing coordinative unsaturation.[14−16] In some cases, the increased steric profile of the ligand can additionally engender high thermal and moisture stability to the resulting complex.[17,18]

In recent years, we have extensively studied a class of encumbering, monodentate *m*-terphenyl[19] isocyanide ligands that are highly effective at controlling the coordination number and geometry of mono- and multinuclear coordination complexes.[20−25] Like the metal-ligand bonds in carboxylate- and imidazolate-based MOFs, the metal−isocyanide linkage is recognized to be robust on account of strong ligand-to-metal σ-donation and the potential for significant secondary π-

backbonding interactions.[24,26] However, multitopic isocyanides represent an under-explored linker group for coordination networks. This is despite the fact that some of the earliest reported catalytically active amorphous coordination polymers consisted of ill-defined mixtures of diaryldiisocyanides and Rh(I) single-metal nodes.[27−29] Accordingly, here we report the development of diisocyanide ligands featuring *meta*-terphenyl substituents that enable coordinative control and stabilization of highly robust crystalline coordination frameworks possessing mononuclear Cu(I) nodes. Most importantly, the same principles that allow for the manipulation of coordination geometry and number of mononuclear centers in solution[20] are shown to be transported to a solid-state network when significantly encumbering, neutral ligands are utilized as linker groups.

The ditopic *m*-terphenyl isocyanide, [CNAr^{Mes2}]_2 (Figure 1), was prepared via Suzuki-Miyaura coupling of the *para*-bromo
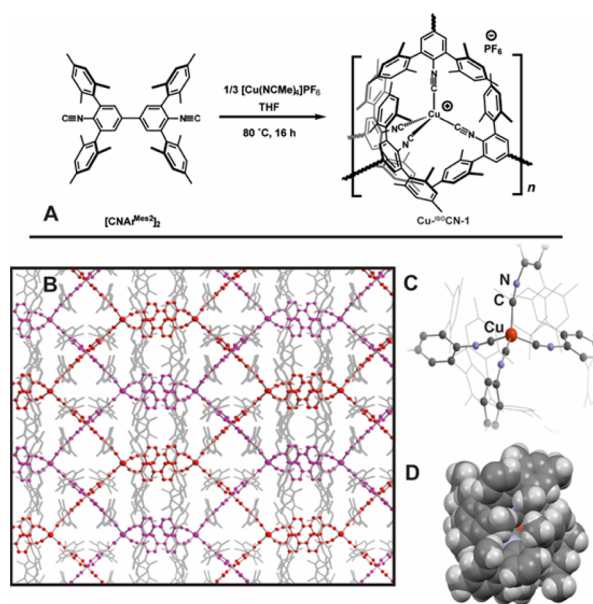

Figure 1. (A) Synthesis of Cu-^{ISO}CN-1. (B) Interpenetrated diamondoid lattice of Cu-^{ISO}CN-1 along the *ac* plane, with *m*-terphenyl groups displayed in wireframe and THF and [PF_6]^− omitted for clarity. (C) Cu(I) tetrakis-isocyanide node. (D) Space-filling diagram of Cu(I) tetrakis-isocyanide node of Cu-^{ISO}CN-1.

aniline 4-BrAr^{Mes2}NH$_2$ and is available in an overall 73% yield from the known aniline H$_2$NAr^{Mes2}.[30] Ditopic [CNAr^{Mes2}]$_2$ is an off-white solid with a ^{13}C{^{1}H} NMR isocyanide carbon resonance of 172.2 ppm and a ν_{CN} stretching band of 2118 cm^{-1} in C$_6$D$_6$ solution, which are similar to those of the monotopic isocyanide CNAr^{Mes2}.[20] Notably, crystallographic structure determination of [CNAr^{Mes2}]$_2$ revealed a near-planar biphenyl core with a torsion angle approaching 0° (Figure S2.7), which contrasts with the equilibrium torsion angle for unsubstituted biphenyl of 44.4°.[31] On the basis of the calculated torsional barriers in [CNAr^{Mes2}]$_2$ (2.0 kcal/mol at 0° and 3.3 kcal/mol at 90°; Table S4.1), we attribute the observed absence of torsion to be predominantly derived from crystal packing forces. Importantly, this low-barrier rotation element remains the only significant structural flexibility in the ligand, which otherwise provides a rigid, linear scaffold for the formation of coordination frameworks.

With [CNAr^{Mes2}]$_2$ in hand, we sought to examine the effect of *meta*-terphenyl substitution in coordination frameworks composed of Cu(I)-isocyanide nodes. Mechanically mixing solid [CNAr^{Mes2}]$_2$ with [Cu(MeCN)$_4$]PF$_6$, followed by addition of THF and heating at 80 °C for 16 h in a pressure tube afforded large colorless, octahedral-shaped crystals of Cu-^{ISO}CN-1 (^{ISO}CN = isocyanide coordination network). The observed isocyanide IR stretching frequency at 2118 cm^{-1} (ATR-IR) indicated little activation of the σ-bond of the isocyanide and insignificant π-backdonation, as expected for a Cu(I) isocyanide material.[20,32] Structural analysis by single crystal X-ray crystallography revealed a 2-fold interpenetrated diamondoid framework (Figure 1B) in the *Fdd2* space group composed of four-coordinate Cu(I) units of approximate tetrahedral geometry, (Houser τ_4[33] = 0.95). The [CNAr^{Mes2}]$_2$ ligands bridging the Cu(I) nodes form ca. 9.8 × 9.8 Å rectangular channels along the *a* and *c* axes and are partially occupied by *meta*-mesityl groups, which narrow the pore size to ca. 2.1 × 3.2 Å. Cu-^{ISO}CN-1 is, to our knowledge, the first structurally characterized three-dimensional framework assembled from diisocyanide building blocks.

Attempts at thermal activation (50 to 125 °C, 25 °C intervals) of Cu-^{ISO}CN-1 for gas sorption analysis repeatedly generated samples with distinctly broadened IR spectra in the isocyanide region (Figure S1.11). Holding a solid sample of Cu-^{ISO}CN-1 at 125 °C for 1.5 d resulted in a significant change in its ATR-IR spectrum and produced a discernible shift in ν_{CN} to ca. 2149 cm^{-1} (Figure 2), indicating increased σ-donation from the isocyanides to the Cu(I) center.[34] Furthermore, PXRD analysis of Cu-^{ISO}CN-1 after thermolysis (Figure S1.13) showed that an alternate crystalline phase of lower symmetry was being accessed. In our initial report on mononuclear Cu(I) complexes supported by the monodentate isocyanide CNAr^{Mes2},[20] tetrakis-isocyanide species were not observed in solution by traditional spectroscopic methods, even in the presence of additional equivalents of free CNAr^{Mes2}. This suggested that tris-CNAr^{Mes2} coordination is kinetically preferred, and is attributed to the steric profile of the flanking mesityl rings. However, within coordination frameworks, kinetically "trapped," metastable coordination sites can occur due to the specific set of synthetic conditions employed,[35−38] which can transform under thermal conditions to provide the corresponding thermodynamically preferred framework.[39] Accordingly, the transformation of Cu-^{ISO}CN-1 in the solid-state indicates steric destabilization of the framework, despite the stability often observed in interpenetrated diamondoid
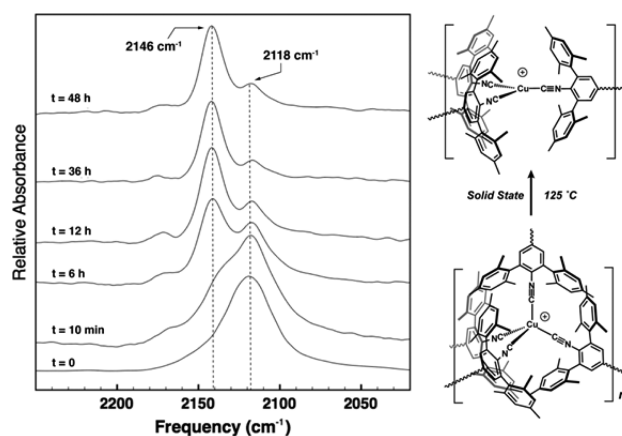

Figure 2. Stacked ATR-IR spectra for the thermolysis of Cu-^{ISO}CN-1 in the solid state at 125 °C over the course of 2 days. After 36 h, no further changes in relative ν_{CN} intensity were observed. The residual band centered at 2118 cm^{-1} after 48 h of heating is free [CNAr^{Mes2}]$_2$ present in the solid-state sample.

networks.[40] Indeed, substantial congestion is observed in the space-filling diagram of the Cu(I) tetrakis-isocyanide node (Figure 1, D), revealing significant steric pressures from the presence of *m*-terphenyl substituents. Consequently, the alleviation of this congestion could then enable the formation of lower-coordinate Cu(I) nodes, similar to that observed for mononuclear species in solution.

In an effort to further investigate this solid-state transformation,[41,42] we found that heating of a suspension of Cu-^{ISO}CN-1 in THF at 100 °C in a sealed pressure tube for 5 days followed by slow cooling provided large colorless block crystals of this new phase, denoted Cu-^{ISO}CN-2. The solid-state IR spectrum of Cu-^{ISO}CN-2 displayed a single strong absorbance at 2146 cm^{-1}, which is consistent with the band observed upon heating solid Cu-^{ISO}CN-1 and is suggestive of a tris-isocyanide arrangement about the Cu(I) center (Figure 2).[34] Additionally, analysis of the mother liquor indicated the presence of free [CNAr^{Mes2}]$_2$, thereby indicating linker ejection en route to the formation of Cu(I) centers featuring fewer isocyanide ligands than found in the original network. These coordination properties were confirmed by structural analysis of Cu-^{ISO}CN-2 by single-crystal X-ray crystallography, which reveals a 2-fold interpenetrated framework composed of overlapping 2D sheets (Figure 3). The 2D sheets conform to a hexagonal pattern (*hcb* net) with Cu(I) tris-isocyanide nodes capped by a coordinated THF molecule. Like Cu-^{ISO}CN-1, small rectangular channels (ca. 11 × 10 Å) are formed along the *b* axis that are partly occupied by the *m*-terphenyl groups, creating smaller channels (ca. 4.5 × 5.1 Å). This 3D to 2D transformation of Cu-^{ISO}CN-1 to Cu-^{ISO}CN-2 is noteworthy, as it represents a significant lattice rearrangement concurrent with alteration of the metal coordination environment. Although the precise mechanism of this transformation is unknown at this time, this result nonetheless demonstrates that the generation of metal nodes with labile solvent ligands as the thermodynamically preferred product can be done in a straightforward manner using encumbering, multitopic *m*-terphenyl isocyanides. As such, we targeted the *in situ* formation of a porous framework composed of Cu(I) tris-isocyanide nodes via a direct approach.

Notably, a simple alteration in the synthetic protocol provided a new coordination polymer composed solely of
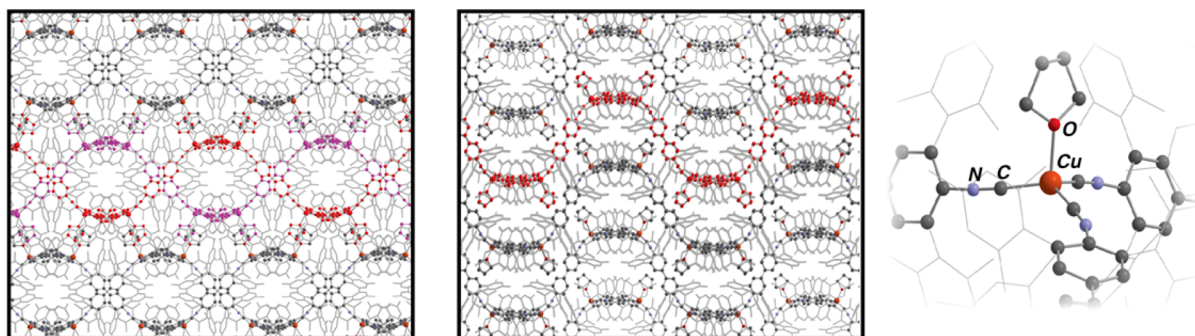
Figure 3. (Left) View down the *c* axis of Cu-^{ISO}CN-2. (Middle) View of Cu-^{ISO}CN-3 down the *ac* plane. Free solvent and $[PF_6]^-$ anions have been removed for clarity. (Right) $[Cu(THF)([CNAr^{Mes2}]_2)_3]^+$ node of Cu-^{ISO}CN-3, similar to that found in Cu-^{ISO}CN-2.

Cu(I) tris-isocyanide nodes. Addition of a dilute solution of $[CNAr^{Mes2}]_2$ to dissolved $[Cu(MeCN)_4]PF_6$ produced an amorphous, off-white polymer with a single isocyanide band centered at 2145 cm^{-1}. Heating of this polymer at 100 °C for 24 h followed by slow cooling over 16 h generated Cu-^{ISO}CN-3 as a colorless crystalline solid. Analysis by single crystal X-ray crystallography showed a stacked-layer, noninterpenetrated 2D coordination network ($P2_1/n$ space group) with a matching *hcb* net to Cu-^{ISO}CN-2 (Figure 3). The honeycomb network is composed of pyramidalized (C−Cu-centroid = 12.7°) tris-isocyanide Cu(I) nodes with an apically bound THF molecule, similar to that of the interpenetrated framework of Cu-^{ISO}CN-2. However, this THF is pointed inward to long, narrow rectangular channels (ca. 23.1 × 3.7 Å) along the *a* axis. Accordingly, this spatial orientation of bound THF in Cu-^{ISO}CN-3, coupled with known solution-phase lability of the THF ligand in the monomeric species $[(THF)Cu-(CNAr^{Mes2})_3]^+$,[20] prompted us to further investigate the physical properties of this material.

Purification of Cu-^{ISO}CN-3 involves three cycles of slow stirring in THF followed by centrifugation and removal of the supernatant, and provides Cu-^{ISO}CN-3 as a free-flowing microcrystalline solid. Thermogravimetric analysis (Figure S3.4) reveals a small mass loss at 281 °C, attributable to shallow-depth THF loss, followed by decomposition at 487 °C, which demonstrates the remarkably high thermal stability of the framework. Surface area analysis after activation at 200 °C by N_2 showed negligible adsorption; however, further analysis with CO_2 provided a Langmuir value of 200 m^2/g. Although many materials outcompete Cu-^{ISO}CN-3 in measured internal surface area, this Langmuir value is comparable to some zeolitic materials[43] and as such we believe this result supports the viability of *meta*-substituent incorporation into bridging ligands without greatly sacrificing material performance.

Cu-^{ISO}CN-3 is stable under atmospheric conditions indefinitely, but is readily dissolved by strongly polar aprotic solvents such as DMF and acetone. However, Cu-^{ISO}CN-3 shows marked stability in H_2O and other protic polar solvents, such as MeOH and ^{i}PrOH. Cu-^{ISO}CN-3 also displays remarkable stability toward 1 N HCl, 1 N HNO$_3$, and 1 N NaOH (2 days, 293 K), conditions which typically lead to the decomposition of transition metal-isocyanide complexes as well as many carboxylate-based MOFs.[44] Analysis of Cu-^{ISO}CN-3 soaked in these solvents by ATR-IR demonstrates retention of the tris-isocyanide Cu(I) nodes within the framework, while PXRD analysis confirms preservation of crystallinity within Cu-^{ISO}CN-3 (Figure 4). We attribute the slight attenuation (∼8 cm^{-1}) in the IR spectra of soaked Cu-^{ISO}CN-3 to the formation of new
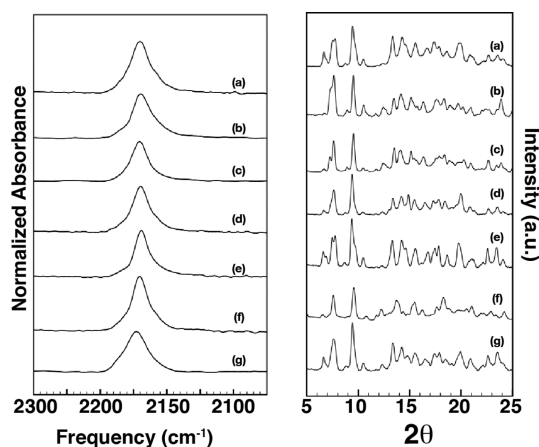

Figure 4. ATR-IR (left) and PXRD (right) of Cu-^{ISO}CN-3 after 2 day exposure to (a) 1 N NaOH, (b) 1 N HCl, (c) 1 N HNO$_3$, (d) ^{i}PrOH, (e) MeOH, (f) H_2O. Shown in g: as-prepared Cu-^{ISO}CN-3.

solvento species upon exchange with THF. Importantly, gas sorption analyses of Cu-^{ISO}CN-3 soaked in 1 N HNO$_3$ and 1 N NaOH showed only minor diminishment in measured surface area (158 m^2/g and 133 m^2/g, respectively) after activation at 200 °C. This stability can be correlated to the high observed hydrophobicity (contact angle > 120°) for Cu-^{ISO}CN-3, likely derived from the presence of the encumbering mesityl groups. These data demonstrate significant stability can be gained from the inclusion of sterically protecting groups about the metal center for single-node coordination networks.[44]

In summary, we have demonstrated that linear, ditopic isocyanides can function as effective metal linkers in the construction of 3D and 2D coordination networks. Importantly, the inclusion of sterically encumbering *m*-mesityl substituents on the central biphenyl linker forces the thermodynamically favorable formation of a 2D infinite sheet consisting of solvated tris-isocyanide Cu(I) nodes over that of a tetrakis-isocyanide 3D framework. This result mirrors the solution-phase chemistry observed for Cu(I) *m*-terphenyl isocyanides, enabling a predictive ability when designing new low-coordinate coordination polymers. In addition, the steric protection afforded by the *m*-terphenyl framework confers significant thermal and aqueous stability to the extended network. This is exceptional among coordination solids containing single metal ion nodes, as structural stability in MOFs is often attributed to high nuclearity SBUs with high connectivity using high oxidation state, strongly Lewis acid metal ions with hard Lewis basic ligands. Accordingly, the

application of this ligand system in the development of other frameworks constructed from low-coordinate metal nodes is underway.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10460.

> Synthetic procedures, computations, physical measurements (PDF)
> Crystallographic details (CIF)

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Notes

The authors declare the following competing financial interest(s): A provisional patent has been filed by J.S.F. and D.W.A. on part of the work reported.

■ ACKNOWLEDGMENTS

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