

# Empirical and Theoretical Insights into the Structural Features and Host–Guest Chemistry of $M_8L_4$ Tube Architectures

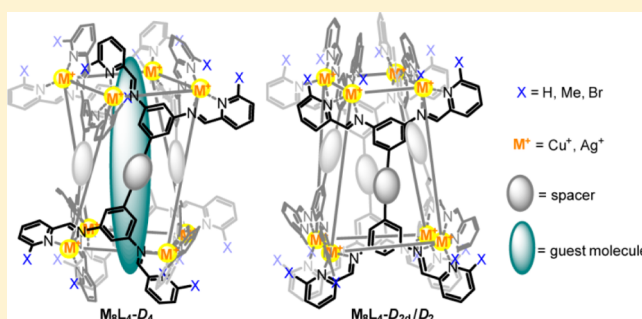
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**S** Supporting Information

**ABSTRACT:** We demonstrate a general method for the construction of  $M_8L_4$  tubular complexes via subcomponent self-assembly, starting from  $Cu^I$  or  $Ag^I$  precursors together with suitable elongated tetraamine and 2-formylpyridine sub-components. The tubular architectures were often observed as equilibrium mixtures of diastereomers having two different point symmetries ( $D_{2d}$  or  $D_2 \rightleftharpoons D_4$ ) in solution. The equilibria between diastereomers were influenced through variation in ligand length, substituents, metal ion identity, counteranion, and temperature. In the presence of dicyanoaurate(I) and  $Au^I$ , the  $D_4$ -symmetric hosts were able to bind linear  $Au(Au(CN)_2)_2^-$  (with two different configurations) as the best-fitting guest. Substitution of dicyanoargentate(I) for dicyanoaurate(I) resulted in the formation of  $Ag(Au(CN)_2)_2^-$  as the optimal guest through transmetalation. Density functional theory was employed to elucidate the host–guest chemistries of the tubes.



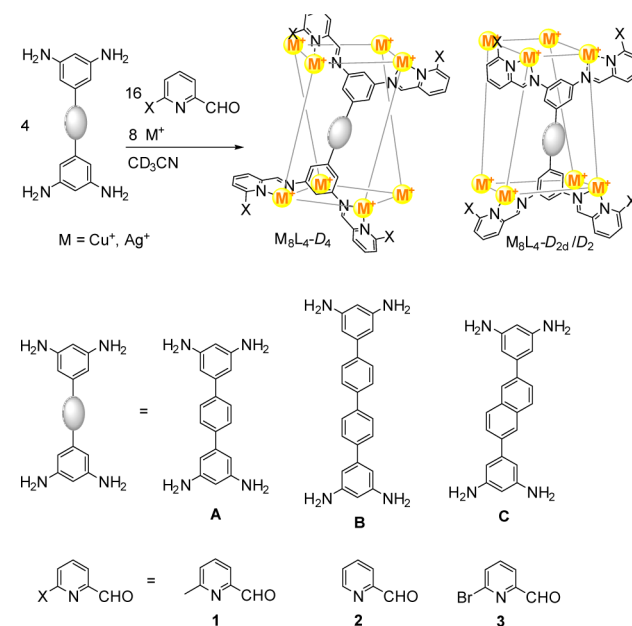
## INTRODUCTION

Metal–organic container molecules<sup>1–7</sup> have attracted interest due to their ability to isolate guest molecules in the micro-environments provided by their internal cavities. Encapsulation may alter the chemical behavior of a guest,<sup>8</sup> leading to applications in catalysis,<sup>9–14</sup> sensing,<sup>15–20</sup> stabilization,<sup>21–25</sup> and transport.<sup>26–29</sup> Subcomponent self-assembly, wherein dynamic-covalent  $C=N$ <sup>30,31</sup> and coordinative  $M \rightarrow L$  bonds are formed during the same overall process,<sup>32–35</sup> has proven particularly useful for the synthesis of metal–organic hosts.<sup>36</sup> The first such hosts had tetrahedral<sup>37–41</sup> or cubic<sup>42–46</sup> structures, with approximately spherical cavities suitable for binding compact anions and small molecules.

Newer subcomponent-self-assembled hosts have been prepared that have yet more complex structures, including pseudoicosahedra,<sup>47</sup> hexagonal<sup>48,49</sup> and pentagonal<sup>50</sup> prisms, twisted cubes,<sup>51</sup> asymmetric structures,<sup>52</sup> and tubular architectures.<sup>53</sup> Tubes represent interesting research targets due to their potential biomimetic function as molecular channels for selective transportation of ions and molecules, and as hosts for linear guests. Although many tubular organic systems have been reported,<sup>54–59</sup> the structural properties and host–guest chemistries of discrete metal–organic tubes have been less well-studied.<sup>60,61</sup>

Recently, we have reported the assembly of  $M_8L_4$  tubular capsule **1a** from the reaction of tetraamine **A**, 6-methyl-2-formylpyridine **1** and  $[Cu(MeCN)_4]BF_4$  (Scheme 1).<sup>53</sup> This tube is able to transform  $Au(CN)_2^-$  into a linear complex anion

## Scheme 1. General Synthesis of $M_8L_4$ Tubes



$NC-Au-CN-Cu-NC-Au-CN^-$ , which was not independently observed, as the optimal guest for encapsulation. Building upon

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our previous work on tube **1a**, we demonstrate how the length, shape and substituents of the ligands, the counteranions and metals can influence the stereochemistry and host–guest chemistry of the tubular complexes. Insights into the nature and origin of some of these processes are provided by density functional theory (DFT) analysis.

## RESULTS AND DISCUSSION

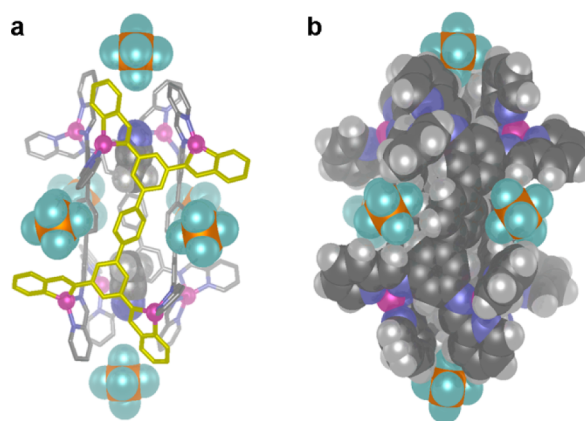
**Synthesis and Stereochemistry.** A  $M_8L_4$  tubular complex can be constructed as the uniquely observed product using elongated tetraamine **A**, **B**, or **C** (4 equiv), 2-pyridine-carboxaldehyde derivatives (16 equiv), and a suitable salt of  $Cu^I$  or  $Ag^I$  (8 equiv) in acetonitrile, as depicted in Scheme 1. Depending on the orientation of the bidentate iminopyridine binding sites, the  $M_8L_4$  tube can adopt approximate  $D_{2d}/(D_2)$  or  $D_4$  point symmetries where the metal ions define the vertices of a cuboid. As we observed earlier,<sup>53</sup> in the crystal structures of tube **1a**· $BF_4^-$ , the  $D_{2d}$  isomer has isosceles trapezoids as the long faces of the cuboid, with the shorter faces forming rectangles, whereas in the  $D_4$  isomer the cuboid approximates a right square prism in which one of the square faces is twisted with respect to the other. The  $D_4$  isomer possesses a narrow linear channel that is capable of trapping two acetonitrile molecules inside. The difference in the symmetry of the two diastereomers led to characteristic NMR peak multiplicities, allowing them to be distinguished by  $^1H$  NMR. The population of the two isomers in solution reflects their relative thermodynamic stability, which can be tuned in several ways, as summarized in Table 1.

**Table 1. Summary of Isomers Formed in Acetonitrile upon the Variation of Tetraamine, Aldehyde, and Counter Ion for  $Cu_8L_4$  Tubes**

complex	tetraamine	aldehyde	counter ion	
			$BF_4^-$	$PF_6^-$
<b>1a</b>	<b>A</b>	<b>1</b>	$D_4:D_{2d}$ 90:10%	$D_4$ only
<b>2a</b>		<b>2</b>	$D_{2d}$ only	$D_4:D_{2d}$ 52:48%
<b>3a</b>		<b>3</b>	$D_{2d}$ only	unstable
<b>1b</b>	<b>B</b>	<b>1</b>	$D_4:D_{2d}$ 1:99%	$D_4:D_{2d}$ 24:76%
<b>1c</b>	<b>C</b>	<b>1</b>	$D_2$ only	$D_4:D_2$ 6:94%

The substituent on the aldehyde subcomponent was observed to influence the stability of the tube isomers. Replacing a methyl group with a proton (aldehyde **2**) or a bromine (aldehyde **3**) at the 6 position of pyridine-2-carboxaldehyde resulted in the relative destabilization of the  $D_4$ -symmetric isomer, so that in the cases of **2a**· $BF_4^-$ , **3a**, and **1c**· $BF_4^-$ , the  $D_4$  isomer did not form in solution.

In most cases, both  $BF_4^-$  and  $PF_6^-$  counterions allow the formation of  $M_8L_4$  tubes, and the formation of the  $D_4$  isomer is preferred when  $PF_6^-$  is present. The crystal structure of **2a**· $D_4$ · $PF_6^-$  (Figure 1) reveals that one  $PF_6^-$  anion is located at each end of the tube with one fluorine atom pointing directly into the channel, and four such anions associate at the junctions between two neighboring terphenyl ligands, which are also sandwiched between two pyridine residues. For all these anions, short contacts (2.3–2.8 Å) are observed between fluorine



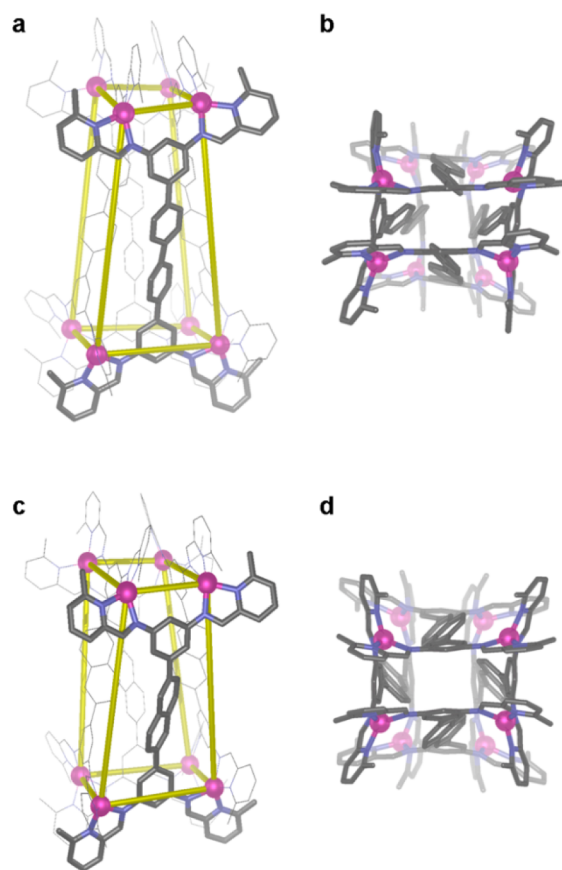
**Figure 1.** Crystal structure of **2a**· $D_4$ · $PF_6^-$ . (a) Representation of the complex with one ligand highlighted in yellow (hydrogen atoms not shown). (b) CPK representation showing the proximity between  $PF_6^-$  anions and ligand hydrogens.

atoms and protons of the complex, which may account for the extra stabilization effect brought by the  $PF_6^-$  anion.<sup>62,63</sup>

Host **2a**· $PF_6^-$  has an approximately equal distribution of both isomers in solution. The interconversion between **2a**· $D_4$ · $PF_6^-$  and **2a**· $D_{2d}$ · $PF_6^-$  could be followed by  $^1H$  NMR spectroscopy as the temperature was varied. Kinetic studies (described in the Supporting Information) revealed  $\Delta H^\ddagger = 108 \pm 7$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = 71 \pm 24$  J K<sup>-1</sup> mol<sup>-1</sup> for the isomerization from **2a**· $D_4$ · $PF_6^-$  to **2a**· $D_{2d}$ · $PF_6^-$ , and  $\Delta H^\ddagger = 58 \pm 8$  kJ mol<sup>-1</sup>, and  $\Delta S^\ddagger = -104 \pm 24$  J K<sup>-1</sup> mol<sup>-1</sup> for the reverse transformation (from **2a**· $D_{2d}$ · $PF_6^-$  to **2a**· $D_4$ · $PF_6^-$ ), which appears more entropically disfavored compared to the same process for the terphenyl congener **1a**· $BF_4^-$  ( $\Delta S = -62 \pm 21$  J K<sup>-1</sup> mol<sup>-1</sup>).<sup>53</sup> The rate constants for both transformations were identical at 283 K, marking **2a**· $D_4$  as the dominant species in solution below this temperature, and **2a**· $D_{2d}$  above.

Since the choice of counterions has been shown to have a measurable but small impact on the stereochemistry of almost all of the complexes listed in Table 1, a computational study was undertaken to determine the differential effect of including two  $PF_6^-$  counterions at the ends of the empty  $D_4$  versus the  $D_{2d}$  isomers of **1a**. A relative stabilization of the  $D_{2d}$  isomer by only 4.1 kJ mol<sup>-1</sup> was computed (see Computational Methods section for theory details), a value commensurate with the small energy changes associated with the variations in isomeric ratios discussed above.

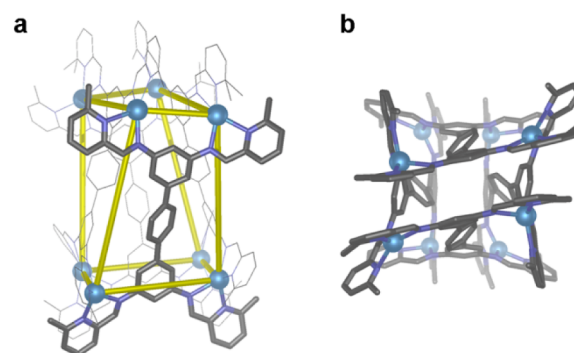
Longer ligands also disfavored the  $D_4$  isomer: the reaction between tetraamine **B** or **C**, 6-methyl-2-pyridine-carboxaldehyde **1** and  $[Cu(MeCN)_4]BF_4$  in acetonitrile produced **1b**· $D_{2d}$  and **1c**· $D_2$  as the predominant isomers, respectively (Figures S27 and S33, Supporting Information). The hexafluorophosphate anion was again found to slightly stabilize the  $D_4$  isomer; when copper(I) hexafluorophosphate was used in place of the tetrafluoroborate, the equilibrium ratios were found to be 24:76% and 6:94% for complexes **1b**· $D_4$ :**1b**· $D_{2d}$  and **1c**· $D_4$ :**1c**· $D_2$ , respectively, as revealed by their  $^1H$  NMR spectra (Figures S21 and S30, Supporting Information). Models suggested that the  $D_4$ -symmetric tubes constructed from tetraamine **B** or **C** are not long enough to accommodate a third acetonitrile molecule inside the channel, leaving instead additional empty space, and incurring an energetic penalty for doing so. Single crystals of **1b**· $BF_4^-$  and **1c**· $PF_6^-$  were isolated by vapor diffusion of diethyl ether (or diisopropyl ether) into an acetonitrile solution of the



**Figure 2.** Crystal structures of **1b**- $D_{2d}$ ·BF<sub>4</sub> (a,b) and **1c**- $D_2$ ·PF<sub>6</sub> (c,d).<sup>64</sup> (a,c) Side view; (b,d) top view. Hydrogen atoms, solvent molecules, and counterions are omitted for clarity.

respective complexes. X-ray analyses revealed the presence of **1b**- $D_{2d}$  (Figure 2a,b) and **1c**- $D_2$  (Figure 2c,d), whose structures resemble that of **1a**- $D_{2d}$ . For **1b**- $D_{2d}$  the elongation of the ligand backbone from terphenylene to quaterphenylene did not result in an increase of the width of the tube channel, but rather narrows it. The shorter faces (Figure 2b) are slightly distorted from a rectangular geometry. The average Cu–Cu distance of the shorter edge of the top and bottom faces was 5.3 Å, 0.1 Å shorter than in **1a**- $D_{2d}$ . For **1c**- $D_2$  the presence of a naphthalene spacer reduces the symmetry of the complex by removing the mirror plane that bisects the ligand. The naphthalene spacer also introduces an offset between the two terminal phenyl rings, which slightly widens the tube channel. The shorter edge of the rectangular face in **1c**- $D_2$  (5.6 Å) is 0.2 Å longer than that in **1a**- $D_{2d}$ .

Ag<sup>I</sup> can also be used in place of Cu<sup>I</sup> to form an M<sub>8</sub>L<sub>4</sub> tube. The reaction between tetraamine **A**, 6-methyl-2-pyridine-carboxaldehyde **1** and AgBF<sub>4</sub> in acetonitrile produced **4**- $D_{2d}$  as the only observed product in solution, as verified by <sup>1</sup>H NMR and MALDI-MS. Doublets were observed for the two symmetry-independent imine protons, with  $J = 5.9$  and  $7.8$  Hz due to the coupling between <sup>107/109</sup>Ag and the imine protons. Vapor diffusion of diethyl ether into an acetonitrile solution of **4**- $D_{2d}$ ·BF<sub>4</sub> allowed the isolation of single crystals suitable for X-ray analysis. The solid state structure reveals an approximate  $D_{2d}$ -symmetric M<sub>8</sub>L<sub>4</sub> topology, consistent with solution observations (Figure 3). Compared to analogous Cu<sup>I</sup> tubes (**1a**- $D_{2d}$ , **1b**- $D_{2d}$  and **1c**- $D_2$ ) **4**- $D_{2d}$ ·BF<sub>4</sub> is more distorted: the top view of **4**- $D_{2d}$ ·BF<sub>4</sub> shows that the shorter faces of the complex form a



**Figure 3.** Crystal structure of Ag<sup>I</sup> complex **4**- $D_{2d}$ ·BF<sub>4</sub>. (a) Side view highlighting one ligand in thicker stick presentation. (b) Top view showing the distortion at the Ag<sup>I</sup> centers.

parallelogram (Figure 3b), whereas those in the Cu<sup>I</sup> tubes approximate a rectangle. Furthermore the Ag<sup>I</sup> centers in **4**- $D_{2d}$ ·BF<sub>4</sub> show a greater degree of distortion from idealized tetrahedral geometry compared to the Cu<sup>I</sup> centers in **1a**- $D_{2d}$ ·BF<sub>4</sub> with N–Ag–N angles in the range 72–154° compared N–Cu–N angles of 79–138° in its Cu<sup>I</sup> analogue.

**Host–Guest Chemistry.** In previous work, we demonstrated that tube **1a**- $D_4$ ·BF<sub>4</sub> is capable of binding the complex anion Cu(Au(CN)<sub>2</sub>)<sub>2</sub><sup>−</sup>. The Cu<sup>I</sup> ion bridges the two NC–Au–CN<sup>−</sup>, and it could be substituted by Ag<sup>I</sup> to give the Ag(Au(CN)<sub>2</sub>)<sub>2</sub><sup>−</sup> adduct of **1a**- $D_4$ ·BF<sub>4</sub>.

We have since determined DFT binding energies for these guests, and for every analogous guest with a different combination of central group-11 metal and dicyano group-11-metalate, inside of **1a** in acetonitrile continuum solvent. The results are shown in Table 2. Counterions were not included. Because of

**Table 2. Computed Energies of Incorporation of Group-11 Metal Centers (Rows) And Dicyano Ends (Columns) In kJ mol<sup>−1</sup>**

central cation	peripheral anions in N≡C–M'–C≡N–M–N≡C–M'–C≡N		
	Cu(CN) <sub>2</sub> <sup>−</sup>	Ag(CN) <sub>2</sub> <sup>−</sup>	Au(CN) <sub>2</sub> <sup>−</sup>
<i>D</i> <sub>4</sub> -host			
Cu <sup>I</sup>	−36.8	−52.7	−69.0
Ag <sup>I</sup>	−41.8	−53.1	−72.4
Au <sup>I</sup>	−116.3	−129.3	−143.9
<i>D</i> <sub>2d</sub> -host			
Cu <sup>I</sup>	<sup>a</sup>	<sup>a</sup>	2.9
Ag <sup>I</sup>	<sup>a</sup>	<sup>a</sup>	−15.1
Au <sup>I</sup>	<sup>a</sup>	<sup>a</sup>	−97.9

<sup>a</sup>These values were not determined; no such binding is observed experimentally.

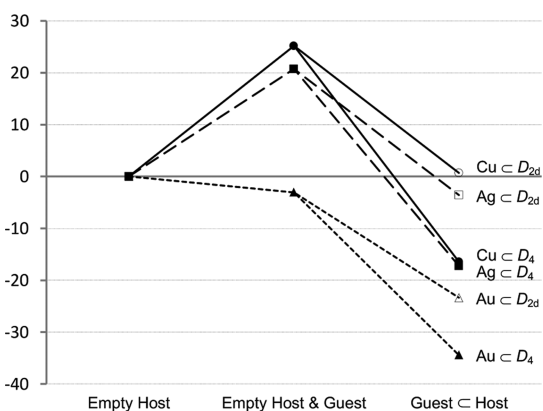
the high computational cost of optimizing the geometry of the large host–guest complexes, energies were not computed for the experimentally unobserved binding of the dicyanoargentate and dicyanocuprate guests in the  $D_{2d}$  host isomer.

Binding energies were calculated by determining the difference in energy between each host–guest complex and its corresponding separated starting compounds and acetonitrile-filled  $D_4$  host isomer at 5 μM concentrations of the host–guest complexes. For consistency with the experimental conditions employed (vide infra), free Au<sup>I</sup> was modeled as the cationic moiety of the salt Au(tmbn)<sub>2</sub>SbF<sub>6</sub> (tmbn = 2,4,6-trimethoxybenzotrile), whereas

free  $\text{Cu}^{\text{I}}$  and  $\text{Ag}^{\text{I}}$  were modeled as the tetrakis(acetonitrile) complexes.

The computed energies of binding matched the experimentally observed trend, where guests bound more strongly in the  $D_4$  isomer and larger group-11 metals bound more strongly than smaller ones. This trend is consistent, allowing for reasonable extrapolation to the binding of the  $\text{Ag}(\text{CN})_2^-$  and  $\text{Cu}(\text{CN})_2^-$  guests in the  $D_{2d}$  host isomer. It is important to note that these energies of the host–guest complexes are relative to those of the solvent-filled cage and guest precursors, not the polymeric precipitate actually observed when no host is present. This distinction is likely to explain why we still obtain negative binding energies for the  $\text{Cu}(\text{Ag}(\text{CN})_2)_2^-$  and  $\text{Ag}(\text{Ag}(\text{CN})_2)_2^-$  guests, which are not observed to bind in situ, as these energies were not calculated relative to the global energy minimum.

Contrary to our previous inference,<sup>53</sup> it seems that the trend of favoring heavier group-11 metals at the center of the complex anion is predicated not upon increased cation- $\pi$  interaction with the organic linkers of the host cage, but upon stronger intraguest binding. Figure 4 shows the DFT energetics



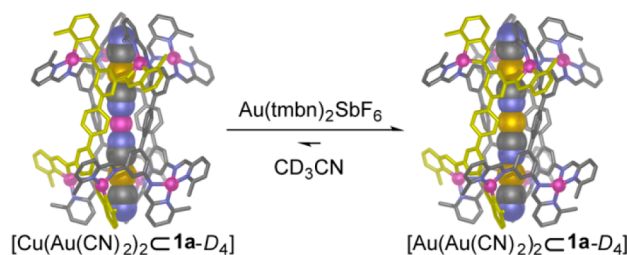
**Figure 4.** Calculated energetics for stepwise formation and incorporation of group-11 metal-centered bis-dicyanoaurates into  $1a-D_4$  (“Guest  $\subset$  Host” data from last column of Table 2, “Empty Host” for guests as their dissociated precursors).

of the stepwise formation and insertion of the bis-dicyanoaurate guests into both  $1a-D_4$  and  $1a-D_{2d}$ . For this hypothetical pathway, the global minimum energy of complex **1a** was assumed to be the  $D_4$  isomer with two incorporated acetonitrile guests, and consequently this structure was chosen as the starting material for the host cage in the second step of the pathway. By comparing the energies of guest formation to those of host–guest complexation, the role of the comparatively strong gold–nitrogen bonds in stabilizing the  $[\text{Au}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4]$  complex becomes apparent.

In keeping with our theoretical predictions, the addition of  $\text{Au}(\text{tmbn})_2\text{SbF}_6$  (1.2 equiv) to  $[\text{Cu}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4 \cdot \text{BF}_4]$  (1 equiv) led to the formation of a new host–guest complex  $[\text{Au}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4 \cdot \text{BF}_4]$  (Scheme 2), as verified by ESI-MS. A low resolution crystal structure was obtained for the product, showing that  $\text{Au}^{\text{I}}$  replaced  $\text{Cu}^{\text{I}}$  as the bridging cation within the guest.

NMR spectra of  $[\text{Au}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4 \cdot \text{BF}_4]$  revealed additional splitting: many  $^1\text{H}$  signals appeared as a set of three closely spaced peaks of roughly equal intensity. Using isotopically labeled  $\text{KAu}^{(13)\text{CN}}_2$ , in the  $^{13}\text{C}$  NMR spectrum (Figure S37, Supporting Information) the  $^{13}\text{C}$ -labeled guest

### Scheme 2. Formation of Trigold Host–Guest Complex $[\text{Au}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4] \cdot \text{BF}_4$ via Transmetalation<sup>a</sup>



<sup>a</sup>The two representations shown are X-ray crystal structures. One configuration of the trigold guest is shown.

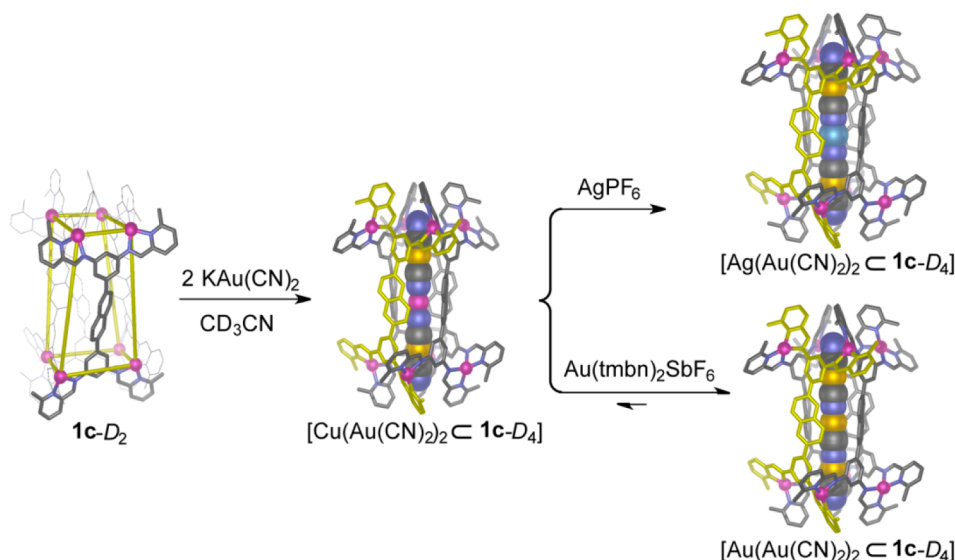
gave rise to three doublets and four singlets with different intensity, indicating the presence of multiple carbon environments.

The  $^{13}\text{C}$  NMR spectra of the labeled host–guest complexes  $[\text{Cu}(\text{Au}^{(13)\text{CN}})_2 \subset 1a-D_4]$  and  $[\text{Ag}(\text{Au}^{(13)\text{CN}})_2 \subset 1a-D_4]$  exhibited a pair of characteristic doublets with  $J_{\text{C-C}} = 47$  Hz for the guest signals, consistent with conservation of the NC-Au-CN aurocyanide configurations within the complex anion guests. Similar signals were not observed in the  $^{13}\text{C}$  NMR spectrum for  $[\text{Au}(\text{Au}^{(13)\text{CN}})_2 \subset 1a-D_4]$ . This observation indicates that in  $[\text{Au}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4]$ , the guest configuration is different from that in  $[\text{Cu}(\text{Au}^{(13)\text{CN}})_2 \subset 1a-D_4]$  and  $[\text{Ag}(\text{Au}^{(13)\text{CN}})_2 \subset 1a-D_4]$ . We thus infer that the conformation NC-Au-CN-Au-CN-Au-CN<sup>-</sup> is not adopted by the guest in  $[\text{Au}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4]$ . Our data were consistent with the guest adopting the conformations NC-Au-CN-Au-CN-Au-CN<sup>-</sup> and NC-Au-CN-Au-CN-Au-CN<sup>-</sup>, in which each gold(I) center is bonded to at least one carbon atom.

DFT calculations of the relative energies of the free complex anions in continuum acetonitrile solvent predict NC-Au-CN-Au-CN-Au-CN<sup>-</sup> and NC-Au-CN-Au-CN-Au-CN<sup>-</sup> to be more stable than NC-Au-CN-Au-CN-Au-CN<sup>-</sup> by 15.5 and 14.6  $\text{kJ mol}^{-1}$ , respectively. Thus, to have one gold atom *not* coordinated by at least one cyanide carbon atom is disfavored energetically. In so far as only two complex anion isomers are predicted to dominate in the absence of encapsulation, and assuming that binding energies are similar for the different complex anion isomers, upon guest binding we expect to observe close to a 2:1 statistical distribution of NC-Au-CN-Au-CN-Au-CN<sup>-</sup>, and NC-Au-CN-Au-CN-Au-CN<sup>-</sup>. We thus infer the tripling of host signals in the NMR to result from *one* set of signals associated with binding of NC-Au-CN-Au-CN-Au-CN<sup>-</sup> and *two* sets of signals associated with binding of the asymmetric complex anion NC-Au-CN-Au-CN-Au-CN<sup>-</sup>, which results in desymmetrization of the two ends of the tube. The presence of multiple conformations is mirrored in the solid-state behavior of group-11 cyanides.<sup>65</sup>

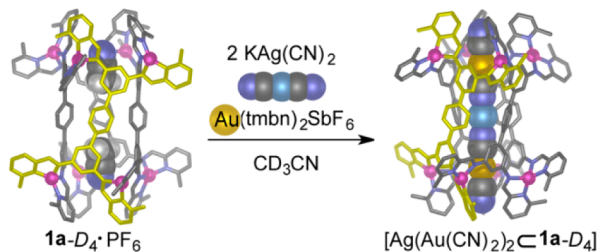
The titration of  $\text{Au}(\text{tmbn})_2\text{SbF}_6$  into an acetonitrile solution of  $[\text{Cu}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4 \cdot \text{BF}_4]$  allowed the stability constant of  $1.6 \times 10^{11} \text{ M}^{-3}$  for  $[\text{Au}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4 \cdot \text{BF}_4]$  to be determined, 129 times greater than that of  $[\text{Cu}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4 \cdot \text{BF}_4]$  and 3.7-fold higher than  $[\text{Ag}(\text{Au}(\text{CN})_2)_2 \subset 1a-D_4 \cdot \text{BF}_4]$ .

Tetraphenyl tube **1b**-PF<sub>6</sub> did not form any host–guest complex in the presence of  $\text{KAu}(\text{CN})_2$ , which suggests the energy gained by trapping the guest  $\text{Cu}(\text{Au}(\text{CN})_2)_2^-$  is not enough to compensate energy lost during isomerization from **1b**- $D_{2d}$  to **1b**- $D_4$ . In contrast, for naphthalene-based tube **1c**-PF<sub>6</sub> the addition of  $\text{KAu}(\text{CN})_2$  resulted in a rapid and clean

Scheme 3. Formation of Host–Guest Complexes from  $1c \cdot PF_6$ ,<sup>a</sup>

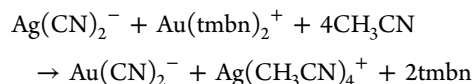
transformation to  $[Cu(Au(CN)_2)_2 \subset 1c-D_4]$  (Scheme 3), despite the low abundance of  $1c-D_4$  in solution. The crystal structure of the product confirmed the encapsulation of  $Cu(Au(CN)_2)_2^-$  within  $1c-D_4$ , consistent with NMR and ESI-MS observations. The central  $Cu^I$  within the guest could be replaced by  $Ag^I$  or  $Au^I$  in a similar way to the analogous terphenyl tube  $[Cu(Au(CN)_2)_2 \subset 1a-D_4]$  (Scheme 3).

Linear dicyanoargentate,  $Ag(CN)_2^-$ , has very similar dimensions to  $Au(CN)_2^-$ , yet no host–guest complex formation was observed when  $1a \cdot PF_6$  was treated with  $Ag(CN)_2^-$  in the presence of either  $Cu^I$  or  $Ag^I$ . In contrast, when  $Au^I$  was added, a new  $D_4$ -symmetric complex was rapidly generated. This new product was not the expected  $[Au(Ag(CN)_2)_2 \subset 1a-D_4] \cdot PF_6$ , but a transmetalated product  $[Ag(Au(CN)_2)_2 \subset 1a-D_4] \cdot PF_6$ , as verified by NMR and ESI-MS (Scheme 4). In the absence

Scheme 4. Formation of  $[Ag(Au(CN)_2)_2 \subset 1a-D_4] \cdot PF_6$  via Transmetalation between  $Ag(CN)_2^-$  and  $Au^I$ 

of the host  $1a \cdot PF_6$ , mixing  $Ag(CN)_2^-$  with  $Au^I$  resulted in the formation of white precipitate, which we infer to be the polymeric mixed-metal cyanide.<sup>66,67</sup> Host  $1a \cdot PF_6$  therefore acts as a solubilizing carrier, allowing the encapsulated guest to be studied using routine spectroscopic methods.

The lack of observed binding of  $[Au(Ag(CN)_2)_2]^-$  in  $1a$  can be explained computationally. DFT calculations show that while the fully formed guest  $Au(Ag(CN)_2)_2^-$  is predicted to bind to  $1a-D_4$  more strongly than  $Ag(Au(CN)_2)_2^-$  (by  $56.9 \text{ kJ mol}^{-1}$ , see Table 2), the transmetalation of dicyanoargentate to dicyanoaurate by the pathway



is predicted to be exoergic by  $146.4 \text{ kJ mol}^{-1}$ , making the  $[Ag(Au(CN)_2)_2 \subset 1a-D_4]$  complex more enthalpically favorable than its gold bis-dicyanoargentate counterpart by  $235.6 \text{ kJ mol}^{-1}$ .

## CONCLUSION

In this study we have developed a general synthetic procedure for  $M_8L_4$  tubular complexes using tetraamines with two 3,5-diaminophenylene moieties connected by a suitable spacer. This technique allows facile investigations into the influences of subtle changes in any of the subcomponents on the complex structure. The  $M_8L_4$  tubes are present in solution as either  $D_4$ -symmetric or  $D_{2d}/D_2$ -symmetric isomers, which are in dynamic equilibrium. The  $D_4$  isomer, which is the only one observed to bind guests, is more stabilized when  $PF_6^-$  is present as the counteranion, whereas the  $D_{2d}/D_2$  isomer is stabilized by the elongation of the ligand or the introduction of an offset between tube termini. Further systemic adaptation is revealed in the host–guest chemistry of the tubes. Dicyanoaurate is a necessary subcomponent of all guests that we observe to be bound by any tube, and the system will undertake to transform guests in order to achieve an optimal host–guest complex through guest recombination or transmetalation. This work therefore builds upon and contributes to fundamental studies of systems chemistry,<sup>68</sup> specifically the dynamic response of a system to external stimuli, as is required in the design and creation of increasingly complex molecular machines.<sup>69–73</sup> The design of a system that is specifically adapted to bind gold cyanides may also be of relevance to the mining industry,<sup>74</sup> and the ability to specifically bind linear guests may allow for their catalytic transformation, as has been observed in other systems.<sup>9–14</sup>

## EXPERIMENTAL SECTION

**Computational Methods.** All calculations employed the PBE-D3<sup>75,76</sup> functional as implemented in the ADF 2013 software package.<sup>77–79</sup> TZP basis sets with large frozen cores were employed for metal atoms, and DZP basis sets for the organic linkers.<sup>80</sup>

The zero-order regular approximation (ZORA) was employed to account for scalar relativistic effects.<sup>81–83</sup>

Empty cages and host–guest complexes were first optimized in the gas phase, and final energies were computed from single-point calculations on these minima including acetonitrile solvation effects computed from the COSMO continuum solvent model.<sup>84</sup> When representative host–guest complexes were subjected to reoptimization including solvation effects, their energies were observed to fluctuate but not to decrease (or converge, because of apparent numerical noise), on which basis we concluded that for the large cage structures, solvated single-point calculations on gas-phase geometries were sufficiently accurate for our purposes. The geometries of small molecule guests and guest precursors, however, were optimized including acetonitrile solvation effects. Because of the size of the host structures, no frequency calculations were performed, and consequently the theoretical energies reported in this paper include no thermal corrections.

**General Methods.** Unless otherwise specified, all starting materials were purchased from commercial sources and used as supplied. Chromatographic separations were performed on silica gel 60 (particle size: 0.040–0.063 mm) purchased from Aldrich. TLC was performed on silica gel 60 F254 plates purchased from Merck and visualized under ultraviolet light (254 nm). NMR spectra were recorded on a Bruker DRX-400 and Bruker Avance 500 Cryo. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and are reported relative to acetonitrile-*d*<sub>3</sub> at 1.94 ppm at 298 K unless otherwise noted. Low resolution electrospray ionization mass spectra (ESI-MS) were obtained on a Micromass Quattro LC, infused from a Harvard Syringe Pump at a rate of 10  $\mu$ L per minute. MALDI was carried out by the EPSRC National MS Service Centre at Swansea. Building blocks [1,1':4,1''-terphenyl]-3,3'',5,5''-tetraamine **A** and Au(tmbn)<sub>2</sub>SbF<sub>6</sub> were synthesized following literature procedures.<sup>53,85</sup>

**Synthesis and Characterization of Metal Complexes.** **1a**·PF<sub>6</sub>. To a Schlenk tube was added **A** (80 mg, 27.5 mmol, 4 equiv), 6-methyl-2-pyridinecarboxaldehyde (133.5 mg, 110.2 mmol, 16 equiv), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (205 mg, 55.1 mmol, 8 equiv) and acetonitrile (15 mL). The solution was degassed by three evacuation/nitrogen fill cycles and stirred at room temperature for 12 h. A dark pink solution resulted. The desired product **1a**·PF<sub>6</sub> was precipitated by adding diethyl ether into the reaction mixture, and was isolated by filtration as a black solid (200 mg, 65%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz) 9.31 (8H, s, imine H), 8.59 (8H, t, J 8.00, py-H), 8.07–8.05 (16H, d, py-H), 7.91 (8H, d, J 8.00, py-H), 7.77 (8H, d, J 7.50, py-H), 7.67 (8H, m, py-H), 7.65 (8H, s, Ph-H), 7.63 (8H, s, imine H), 6.89 (16H, s, Ph-H), 6.82 (16H, s, Ph-H), 2.52 (24H, s, CH<sub>3</sub>), 2.44 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.50, 161.38, 161.02, 159.35, 150.87, 150.31, 150.20, 149.99, 143.82, 140.44, 139.67, 139.64, 131.57, 130.23, 128.55, 127.80, 126.99, 123.55, 115.42, 26.42, 25.88; ESI-MS [1a(PF<sub>6</sub>)<sub>2</sub>]<sup>6+</sup> 601.76, [1a(PF<sub>6</sub>)<sub>3</sub>]<sup>5+</sup> 751.08, [1a(PF<sub>6</sub>)<sub>4</sub>]<sup>4+</sup> 975.15, [1a(PF<sub>6</sub>)<sub>5</sub>]<sup>3+</sup> 1348.58. Found: C, 48.60; H, 3.48; N, 9.80%. Calc. for C<sub>184</sub>H<sub>152</sub>Cu<sub>8</sub>F<sub>48</sub>N<sub>32</sub>P<sub>8</sub>·3H<sub>2</sub>O: C, 48.75; H, 3.51; N, 9.89%.

**2a**·PF<sub>6</sub>. To a Schlenk tube was added **A** (10 mg, 34.4  $\mu$ mol, 4 equiv), 2-pyridinecarboxaldehyde (13.1  $\mu$ L, 0.13 mmol, 16 equiv), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (25.6 mg, 68.8 mmol, 8 equiv) and acetonitrile (5 mL). The solution was stirred at room temperature for 12 h to give a dark pink solution. Diethyl ether was added into the reaction mixture; the resulting mixture was centrifuged, and the solvent was decanted. The solid was dried under a vacuum to give the desired product **2a**·PF<sub>6</sub> as dark pink solid (16.6 mg, 45%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz) 9.67 (8H, br, imine H), 9.33 (8H, s, imine H), 9.29 (8H, s, imine H), 8.87 (8H, d, J 4.70, Ar-H), 8.65 (8H, dt, J 7.90, 1.25, py-H), 8.62 (8H, d, J 4.85, Ar-H), 8.30–7.89 (24H, Ar-H), 7.80 (8H, s, Ph-H), 7.75 (8H, t, J 6.43, py-H), 7.65 (8H, s, Ph-H), 7.60 (8H, t, J 5.78, py-H), 7.56 (8H, br, py-H), 7.65 (8H, s, Ph-H), 7.19 (8H, d, J 1.25, Ph-H), 7.00 (8H, d, J 7.85, Ph-H), 6.97 (8H, s, Ph-H), 6.94 (8H, s, Ph-H), 6.84 (8H, s, Ph-H), 6.71 (8H, d, J 7.80, Ph-H); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.57, 162.20, 160.82, 159.05, 151.94, 151.64, 151.52, 151.41, 151.21, 150.76, 150.32, 150.19, 149.95, 149.75, 147.81, 144.97, 144.08, 143.91, 140.70, 140.20, 139.90, 139.76, 139.70, 139.65, 131.71, 130.67, 130.32, 130.24, 130.05, 129.80, 129.63, 129.47, 128.68, 128.15, 123.95, 123.78, 120.16, 118.92, 115.05; ESI-MS [2a(PF<sub>6</sub>)<sub>4</sub>]<sup>4+</sup> 918.57,

[2a(PF<sub>6</sub>)<sub>5</sub>]<sup>3+</sup> 1272.64. Found: C, 47.11; H, 7.03; N, 10.35%. Calc. for C<sub>168</sub>H<sub>120</sub>Cu<sub>8</sub>F<sub>48</sub>N<sub>32</sub>P<sub>8</sub>·2H<sub>2</sub>O: C, 47.02; H, 2.91; N, 10.45%.

**General Synthetic Procedure for 2a·BF<sub>4</sub> and 3a·BF<sub>4</sub>.** To a Schlenk flask was added [1,1':4,1''-terphenyl]-3,3'',5,5''-tetraamine **A** (4 equiv), suitable 2-pyridinecarboxaldehyde (16 equiv), Cu(CH<sub>3</sub>CN)<sub>4</sub>BF<sub>4</sub> (8 equiv) and acetonitrile. The solution was degassed by three evacuation/nitrogen fill cycles and stirred at room temperature for 24 h. The product was purified by recrystallization: diethyl ether was diffused into an acetonitrile solution of the complex. The desired complex was isolated by filtration as a black solid.

**2a**·BF<sub>4</sub>: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz) 9.778 (8H, s, imine H), 9.483 (8H, s, imine H), 8.500 (4H, s, Ph-H), 8.319 (8H, d, J 4.8, py-H), 8.225 (16H, py-H), 8.066 (24H, py-H), 7.946 (4H, s, Ph-H), 7.565 (16H, py-H), 7.175 (8H, s, Ph-H), 7.056 (8H, d, J 8.0, Ph-H), 6.701 (8H, d, J 8.0, Ph-H); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.34, 158.96, 151.59, 151.54, 150.19, 149.82, 149.76, 147.72, 145.08, 143.94, 140.12, 139.93, 139.60, 139.58, 130.29, 130.05, 129.97, 129.91, 129.67, 127.99, 127.95, 124.26, 120.13, 106.75; MALDI-MS [2a(BF<sub>4</sub>)<sub>7</sub>]<sup>+</sup> 3701.4. Found: C, 49.70; H, 3.17; N, 10.84%. Calc. for C<sub>168</sub>H<sub>120</sub>B<sub>8</sub>Cu<sub>8</sub>F<sub>32</sub>N<sub>32</sub>·14H<sub>2</sub>O: C, 49.92; H, 3.69; N, 11.09%.

**3a**·BF<sub>4</sub>: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz) 9.783 (8H, s, imine H), 9.464 (8H, s, imine H), 8.599 (4H, s, Ph-H), 8.260 (8H, d, J 7.5, py-H), 8.136 (8H, d, py-H), 8.113 (8H, s, Ph-H), 7.991 (8H, t, J 7.5, py-H), 7.980 (8H, t, J 7.5, py-H), 7.822 (8H, d, J 7.5, py-H), 7.756 (8H, d, J 7.5, py-H), 7.322 (8H, s, Ph-H), 7.172 (8H, d, br, Ph-H), 6.784 (8H, d, J 7.0, Ph-H); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.05, 157.83, 152.80, 152.75, 149.77, 146.69, 145.38, 144.11, 142.84, 142.69, 142.52, 141.98, 139.90, 139.29, 134.15, 134.08, 129.64, 129.38, 129.07, 127.95, 123.72, 120.38, 106.47; MALDI-MS [3a(BF<sub>4</sub>)<sub>7</sub>]<sup>+</sup> 4964.1. Found: C, 39.15; H, 2.22; N, 8.58%. Calc. for C<sub>168</sub>H<sub>104</sub>B<sub>8</sub>Br<sub>16</sub>Cu<sub>8</sub>F<sub>32</sub>N<sub>32</sub>·6H<sub>2</sub>O: C, 39.10; H, 2.27; N, 8.69%.

**1b**·PF<sub>6</sub>. To a Schlenk tube was added **B**, [1,1':4,1''-4''-quaterphenyl]-3,3''',5,5''''-tetraamine (30 mg, 0.08 mmol, 4 equiv), 6-methyl-2-pyridinecarboxaldehyde (39.7 mg, 0.32 mmol, 16 equiv), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (61 mg, 0.16 mmol, 8 equiv) and acetonitrile (10 mL). The solution was degassed by three evacuation/nitrogen fill cycles and stirred at room temperature for 12 h. A dark pink solution resulted. The product was purified by recrystallization: diisopropyl ether was diffused into an acetonitrile solution of the complex. The desired product **1b**·PF<sub>6</sub> was isolated by filtration as a black solid (55 mg, 56%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz) the solution is a mixture of two isomers, *D*<sub>4</sub>:*D*<sub>2d</sub> = 13:87%, as shown in Figure S21 (Supporting Information), 10.30 (8H, s, br, imine H), 9.39 (8H, s, imine H), 9.17 (8H, s, imine H), 8.55 (4H, br, Ph-H), 8.58 (8H, t, J 7.75, py-H), 8.53 (4H, br, Ph-H), 8.10 (s, Ar-H), 8.06 (m, br, Ar-H), 7.99 (m, Ar-H), 7.92 (m, Ar-H), 7.83 (m, br, Ar-H), 7.77 (8H, d, J 7.40, Ph-H), 7.71 (8H, d, J 7.85, Ph-H), 7.67 (8H, s, Ar-H), 7.61 (8H, d, J 6.75, Ph-H), 7.57 (8H, d, J 6.75, Ph-H), 7.48 (8H, d, J 7.05, py-H), 7.38 (8H, d, J 7.45, py-H), 7.27 (8H, d, J 7.35, Ph-H), 7.21 (8H, s, Ph-H), 7.13 (8H, d, J 7.00, Ph-H), 6.90 (8H, s, Ph-H), 6.66 (8H, d, J 7.05, Ph-H), 6.52 (8H, d, J 7.25, Ph-H), 2.55 (24H, s, CH<sub>3</sub>), 2.47 (24H, s, CH<sub>3</sub>), 2.08 (24H, s, CH<sub>3</sub>), 1.72 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 163.19, 162.58, 162.36, 161.70, 160.96, 160.53, 159.53, 159.42, 158.68, 151.48, 150.91, 150.71, 150.29, 150.22, 150.03, 149.95, 147.85, 144.70, 144.57, 143.91, 140.49, 140.24, 139.69, 139.49, 139.46, 139.41, 139.35, 138.35, 131.59, 130.37, 130.09, 129.43, 129.37, 128.67, 128.51, 128.40, 128.27, 127.71, 127.60, 127.33, 127.26, 127.10, 124.36, 123.66, 119.76, 119.12, 114.88, 26.41, 25.99, 24.92, 23.88; ESI-MS [1b]<sup>8+</sup> 452.96, [1b(PF<sub>6</sub>)<sub>2</sub>]<sup>7+</sup> 538.53, [1b(PF<sub>6</sub>)<sub>3</sub>]<sup>6+</sup> 652.22, [1b(PF<sub>6</sub>)<sub>4</sub>]<sup>5+</sup> 811.71, [1b(PF<sub>6</sub>)<sub>5</sub>]<sup>4+</sup> 1051.12. Found: C, 52.91; H, 3.87; N, 9.50%. Calc. for C<sub>208</sub>H<sub>168</sub>Cu<sub>8</sub>F<sub>48</sub>N<sub>32</sub>P<sub>8</sub>·2C<sub>6</sub>H<sub>4</sub>O (diisopropyl ether): C, 52.97; H, 3.69; N, 8.99%.

**1b**·BF<sub>4</sub>. To a NMR tube was added **B**, [1,1':4,1''-4''-quaterphenyl]-3,3''',5,5''''-tetraamine (8 mg, 0.02 mmol, 4 equiv), 6-methyl-2-pyridinecarboxaldehyde (10.5 mg, 0.08 mmol, 16 equiv), Cu(CH<sub>3</sub>CN)<sub>4</sub>BF<sub>4</sub> (13.7 mg, 0.04 mmol, 8 equiv) and acetonitrile (1 mL). The resulting dark pink solution was kept at 50 °C for 12 h. Diethyl ether was added into the reaction mixture; the resulting mixture was centrifuged, and the solvent was decanted. The solid was dried under a high vacuum to give the desired product **1b**·BF<sub>4</sub> as

a dark pink solid (22.2 mg, 94%). **1b-D<sub>4</sub>:1b-D<sub>2d</sub>** = 99:1%, calculated from the integration of CH<sub>3</sub> signals in the <sup>1</sup>H NMR spectrum (i.e., peaks at 2.55, 2.48 ppm). NMR data for D<sub>2d</sub> isomer reported here: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz) 9.76 (8H, s, imine H), 9.39 (8H, s, imine H), 8.46 (4H, s, Ph-H), 8.09–8.03 (20H, Ar-H), 7.99–7.92 (24H, Ar-H), 7.61–7.54 (16H, Ar-H), 7.46 (8H, s, Ph-H), 7.44 (8H, s, Ph-H), 7.23 (8H, d, J 8.08, Ph-H), 7.15 (8H, s, Ph-H), 6.49 (8H, d, J 8.08, Ph-H), 2.13 (24H, s, CH<sub>3</sub>), 1.70 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.54, 159.47, 159.26, 158.98, 150.85, 150.85, 149.81, 147.61, 144.65, 144.24, 140.22, 139.65, 139.36, 139.21, 139.09, 138.44, 130.06, 129.72, 129.34, 128.67, 128.31, 128.11, 127.81, 127.58, 127.31, 127.25, 124.23, 119.65, 106.89, 25.01, 23.74; ESI-MS [**1b**]<sup>8+</sup> 439.92, [**1b**(BF<sub>4</sub>)<sub>2</sub>]<sup>7+</sup> 515.24, [**1b**(BF<sub>4</sub>)<sub>3</sub>]<sup>6+</sup> 615.43, [**1b**(BF<sub>4</sub>)<sub>3</sub>]<sup>5+</sup> 755.93, [**1b**(BF<sub>4</sub>)<sub>4</sub>]<sup>4+</sup> 966.81, [**1b**(BF<sub>4</sub>)<sub>5</sub>]<sup>3+</sup> 1317.78. Found: C, 55.84; H, 3.96; N, 10.00%. Calc. for C<sub>208</sub>H<sub>168</sub>Cu<sub>8</sub>F<sub>32</sub>N<sub>32</sub>B<sub>8</sub>·12H<sub>2</sub>O: C, 55.09; H, 4.27; N, 9.88%.

**1c-PF<sub>6</sub>**. To a Schlenk tube was added **C**, 5,5'-(naphthalene-2,6-diyl)bis(benzene-1,3-diamine) (20 mg, 0.06 mmol, 4 equiv), 6-methyl-2-pyridinecarboxaldehyde (28.5 mg, 0.23 mmol, 16 equiv), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (44 mg, 0.12 mmol, 8 equiv) and acetonitrile (5 mL). The solution was degassed by three evacuation/nitrogen fill cycles and stirred at room temperature for 12 h. A dark pink solution resulted. The product was precipitated by adding diethyl ether into the reaction mixture and was isolated by filtration as dark pink solid (20 mg, 29%). **1c-D<sub>2</sub>:1c-D<sub>4</sub>** = 96:4%, calculated from the integration of CH<sub>3</sub> signals in the <sup>1</sup>H NMR spectrum (i.e., peaks at 2.54, 2.46 ppm). NMR data for D<sub>2</sub> isomer reported here: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz) 9.84 (8H, br, imine H), 9.40 (8H, s, imine H), 8.54 (4H, br, Ar-H), 8.22 (4H, br, Ar-H), 8.12 (4H, s, Ph-H), 8.00–7.91 (36H, Ar-H), 7.86 (4H, d, J 8.32, naph-H), 7.73 (4H, d, J 8.36, naph-H), 7.48–7.37 (28H, Ar-H), 7.00 (4H, s, naph-H), 6.68 (4H, d, J 8.68, naph-H), 6.47 (4H, d, J 8.28, naph-H), 2.13 (24H, s, CH<sub>3</sub>, overlapping with H<sub>2</sub>O signals), 1.73 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.46, 160.04, 159.55, 159.01, 151.15, 151.01, 149.93, 147.99, 145.10, 143.62, 140.07, 139.79, 137.73, 137.09, 133.61, 133.48, 130.26, 130.20, 129.95, 129.74, 128.23, 128.07, 127.65, 127.08, 126.33, 125.33, 124.53, 119.88, 107.81, 26.39, 25.93, 24.98, 23.79; ESI-MS [**1c**]<sup>8+</sup> 439.95, [**1c**(PF<sub>6</sub>)<sub>2</sub>]<sup>7+</sup> 523.48, [**1c**(PF<sub>6</sub>)<sub>2</sub>]<sup>6+</sup> 634.87, [**1c**(PF<sub>6</sub>)<sub>3</sub>]<sup>5+</sup> 790.91, [**1c**(PF<sub>6</sub>)<sub>4</sub>]<sup>4+</sup> 1024.77, [**1c**(PF<sub>6</sub>)<sub>5</sub>]<sup>3+</sup> 1414.65. Found: C, 50.29; H, 3.45; N, 9.20%. Calc. for C<sub>200</sub>H<sub>160</sub>Cu<sub>8</sub>F<sub>48</sub>N<sub>32</sub>P<sub>8</sub>·5H<sub>2</sub>O: C, 50.36; H, 3.59; N, 9.40%.

**1c-BF<sub>4</sub>**. To a NMR tube was added **C**, 5,5'-(naphthalene-2,6-diyl)bis(benzene-1,3-diamine) (6 mg, 17.6 μmol, 4 equiv), 6-methyl-2-pyridinecarboxaldehyde (8.5 mg, 70.5 μmol, 16 equiv), Cu(CH<sub>3</sub>CN)<sub>4</sub>BF<sub>4</sub> (11 mg, 35.2 μmol, 8 equiv) and acetonitrile (1 mL). The resulting dark pink solution was kept at 50 °C for 12 h. Diethyl ether was added into the reaction mixture; the resulting mixture was centrifuged, and the solvent was decanted. The solid was dried under a high vacuum to give the desired product **1c-BF<sub>4</sub>** as a dark pink solid (14.4 mg, 77%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz) 9.78 (8H, s, imine H), 9.43 (8H, s, imine H), 8.51 (4H, s, Ph-H), 8.13–8.09 (12H, py-H), 8.00–7.93 (32H, Ar-H), 7.87 (4H, d, J 8.36, naph-H), 7.75 (4H, d, J 8.28, naph-H), 7.47 (8H, s, Ph-H), 7.45 (8H, s, Ph-H), 7.41 (4H, s, naph-H), 7.35 (8H, s, naph-H), 6.66 (4H, d, J 8.36, naph-H), 6.48 (4H, d, J 8.36, naph-H), 2.14 (24H, s, CH<sub>3</sub>), 1.72 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.58, 159.58, 159.49, 159.08, 150.97, 150.83, 149.86, 147.88, 145.00, 143.68, 140.27, 139.74, 137.73, 136.90, 133.54, 133.42, 130.25, 130.12, 129.84, 127.90, 127.80, 127.61, 127.02, 126.95, 126.35, 125.23, 124.41, 119.83, 107.25, 24.98, 23.70; ESI-MS [**1c**]<sup>8+</sup> 452.91, [**1c**(BF<sub>4</sub>)<sub>2</sub>]<sup>7+</sup> 530.29, [**1c**(BF<sub>4</sub>)<sub>2</sub>]<sup>6+</sup> 632.81, [**1c**(BF<sub>4</sub>)<sub>3</sub>]<sup>5+</sup> 776.73, [**1c**(BF<sub>4</sub>)<sub>4</sub>]<sup>4+</sup> 992.65, [**1c**(BF<sub>4</sub>)<sub>5</sub>]<sup>3+</sup> 1352.19. Found: C, 53.84; H, 3.98; N, 10.09%. Calc. for C<sub>200</sub>H<sub>160</sub>Cu<sub>8</sub>F<sub>32</sub>N<sub>32</sub>B<sub>8</sub>·14H<sub>2</sub>O: C, 53.78; H, 4.24; N, 10.03%.

**[Au(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]·BF<sub>4</sub>**. [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]·BF<sub>4</sub> (6.6 mg, 1.5 μmol, 1 equiv), Au(tmbn)<sub>2</sub>SbF<sub>6</sub> (1.4 mg, 1.7 μmol, 1.1 equiv) and MeCN (0.35 mL) were mixed in a NMR tube. The tube was rotated on a turner at room temperature for 12 h. Diethyl ether was then added, and the product was collected by filtration as a plum-colored solid (4 mg, 59%). <sup>1</sup>H NMR revealed the presence of [Au(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]·BF<sub>4</sub>, [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]·BF<sub>4</sub> and 1a·BF<sub>4</sub> in a ratio of 87:9:4%. Further addition of Au(tmbn)<sub>2</sub>SbF<sub>6</sub> did not increase the amount of the desired product but produced more **1a**. Characterization data for

[Au(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]·BF<sub>4</sub>: <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz) 9.44–9.38 (8H, imine H), 8.44–8.39 (8H, py-H), 8.05–7.79 (48H, Ar-H), 7.62 (8H, br, Ar-H), 7.30–7.13 (16H, Ar-H), 7.04–6.95 (16H, Ar-H), 2.50 (24H, s, CH<sub>3</sub>), 2.39 (24H, br, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) peaks split from one carbon signal are grouped in parentheses (161.48, 161.41, 161.34), 160.53, 160.08, 159.28, 151.53, (151.03, 150.98), 150.54, (149.59, 149.56, 149.52), (149.14, 149.10), (143.48, 143.19, 143.02), 139.61, 139.45, 138.86, 138.60, 138.43, 131.06, 130.62, 129.95, (129.15, 129.06, 128.90), 128.05, 127.53, (124.65, 124.42, 124.29), 117.74, 114.94, 26.19, 25.88; guest signals 152.0 (d, J 10.0), 152.5 (d, J 13.75), 152.8 (d, J 12.8), 149.24, 135.86, 135.44, 134.77; ESI-MS [Au(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (BF<sub>4</sub>)<sub>2</sub>]<sup>6+</sup> 683.52, [Au(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (BF<sub>4</sub>)<sub>2</sub>]<sup>5+</sup> 837.51, [Au(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (BF<sub>4</sub>)<sub>3</sub>]<sup>4+</sup> 1068.79, [Au(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (BF<sub>4</sub>)<sub>4</sub>]<sup>3+</sup> 1453.69.

**[Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]·PF<sub>6</sub>**. **1a**·PF<sub>6</sub> (30 mg, 7 μmol, 1 equiv), KAu(CN)<sub>2</sub> (4.1 mg, 14 μmol, 2 equiv), Cu(NCMe)<sub>4</sub>PF<sub>6</sub> (2.6 mg, 7 μmol, 1 equiv) and MeCN (5 mL) were mixed in a vial. The reaction mixture was stirred at room temperature for 12 h. Diethyl ether was then added, and the desired complex [Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]·PF<sub>6</sub> was collected by filtration as a plum colored solid (38 mg, 70%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz) 9.32 (8H, s, imine H), 8.39 (8H, t, J 7.76, Ph-H), 8.06–8.00 (24H, Ar-H), 7.83 (8H, d, J 7.96, py-H), 7.80 (8H, d, J 7.60, py-H), 7.74 (8H, s, Ph-H), 7.65 (8H, dd, J 6.72, 2.16, py-H), 7.11 (16H, s, Ph-H), 6.98 (16H, d, J 1.12, Ph-H), 2.49 (24H, s, CH<sub>3</sub>), 2.39 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 161.40, 160.93, 160.09, 159.30, 150.96, 150.53, 149.66, 149.37, 143.48, 139.56, 130.60, 130.04, 128.79, 128.15, 127.51, 124.83, 115.15, 26.21, 25.77; ESI-MS [Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a]<sup>7+</sup> 560.72, [Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (PF<sub>6</sub>)<sub>2</sub>]<sup>6+</sup> 678.22, [Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (PF<sub>6</sub>)<sub>2</sub>]<sup>5+</sup> 842.87, [Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (PF<sub>6</sub>)<sub>3</sub>]<sup>4+</sup> 1090.03, [Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1a (PF<sub>6</sub>)<sub>4</sub>]<sup>3+</sup> 1501.61; Found: C, 43.56; H, 3.08; N, 9.66%. Calc. for C<sub>188</sub>H<sub>152</sub>Ag<sub>2</sub>Cu<sub>8</sub>F<sub>42</sub>N<sub>36</sub>P<sub>7</sub>·13H<sub>2</sub>O: C, 43.64; H, 3.47; N, 9.74%.

**[Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c]·PF<sub>6</sub>**. **1c**·PF<sub>6</sub> (50 mg, 10.7 mmol, 1 equiv), KAu(CN)<sub>2</sub> (6.1 mg, 21.4 mmol, 2 equiv), Cu(NCMe)<sub>4</sub>PF<sub>6</sub> (4.0 mg, 10.7 mmol, 1 equiv) and MeCN (5 mL) were mixed in a Schlenk flask. The reaction mixture was stirred at room temperature for 5 h. Diethyl ether was added into the reaction mixture; the resulting mixture was centrifuged, and the solvent was decanted. The solid was dried under a high vacuum to give the desired product [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c]·PF<sub>6</sub> as a dark pinkish-red solid (30 mg, 86%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz) 9.27 (8H, s, imine-H), 8.59 (8H, t, J 7.48, py-H), 8.06 (8H, t, J 7.68, py-H), 8.04 (8H, s, imine-H), 7.96 (8H, d, J 6.40, py-H), 7.94 (8H, d, J 7.20, py-H), 7.87 (8H, d, J 7.88, py-H), 7.69 (8H, d, J 8.04, py-H), 7.67 (8H, s, Ph-H), 7.45 (8H, s, Ph-H), 7.04 (8H, s, naph-H), 6.90 (16H, s, naph-H), 6.80 (8H, s, Ph-H), 2.50 (24H, s, CH<sub>3</sub>), 2.49 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 161.97, 161.28, 160.47, 159.32, (Guest signals 153.29, 152.91, d, J<sub>C-Au-C</sub> 47.8, 151.42, 151.04, d, J<sub>C-Au-C</sub> 47.8) 150.95, 150.86, 150.85, 150.08, 149.53, 144.06, 140.27, 139.55, 137.39, 133.41, 130.94, 130.10, 129.98, 127.74, 127.53, 127.49, 126.85, 123.88, 118.25, 115.38, 26.48, 25.73; ESI-MS [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C L<sub>4</sub>Cu<sub>8</sub>]<sup>7+</sup> 583.05, [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c(PF<sub>6</sub>)<sub>2</sub>]<sup>6+</sup> 704.37, [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c(PF<sub>6</sub>)<sub>2</sub>]<sup>5+</sup> 874.26, [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c(PF<sub>6</sub>)<sub>3</sub>]<sup>4+</sup> 1129.01, [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c(PF<sub>6</sub>)<sub>4</sub>]<sup>3+</sup> 1553.50. Found: C, 45.50; H, 3.15; N, 9.22%. Calc. for C<sub>204</sub>H<sub>160</sub>Cu<sub>8</sub>Au<sub>2</sub>F<sub>42</sub>N<sub>36</sub>P<sub>7</sub>·15H<sub>2</sub>O: C, 45.66; H, 3.57; N, 9.40%.

**[Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c]·PF<sub>6</sub>**. To [Cu(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c-D<sub>4</sub>]<sub>2</sub>·PF<sub>6</sub> (5 mg, 0.98 μmol, 1 equiv) was added a stock solution of AgPF<sub>6</sub> (0.3 mg, 1.2 μmol, 1.2 equiv of stock solution prepared using 37 mg AgPF<sub>6</sub> and 0.5 mL CD<sub>3</sub>CN). The resulting solution was heated at 40 °C for 4 h. Diethyl ether was added into the reaction mixture, which was centrifuged, and then the solvent was decanted. The solid was dried under a high vacuum to give the desired product [Ag(Au(CN)<sub>2</sub>)<sub>2</sub> C 1c]·PF<sub>6</sub> as a dark pinkish-red solid (5.3 mg, 96%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz) 9.26 (8H, s, imine H), 8.56 (8H, t, J 7.77, py-H), 8.06 (16H, imine-H and py-H), 7.96 (8H, d, J 7.60, py-H), 7.94 (8H, d, J 7.60, py-H), 7.87 (8H, d, J 7.90, py-H), 7.69 (8H, d, J 7.55, py-H), 7.65 (8H, s, Ph-H), 7.46 (8H, s, naph-H), 7.04 (8H, s, Ph-H), 6.90–6.87 (16H, m, naph-H), 6.82 (8H, s, Ph-H), 2.50 (24H, s, CH<sub>3</sub>), 2.48 (24H, s, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 162.04, 161.32, 160.40, 159.36, 150.97, 150.83, 150.05, 149.57, 144.09, 140.19, 139.57,

137.59, 133.40, 130.91, 130.13, 129.51, 127.96, 127.77, 127.54, 127.03, 124.06, 115.37, 26.47, 25.75 (Guest signals 153.1, dd,  $J_{C-Au-C}$ ,  $C-N-Ag$  47.1, 26.0, and 152.3, d,  $J_{C-Au-C}$  46.8); ESI-MS  $[Ag(Au(CN)_2)_2 \subset 1c]^{7+}$  589.40,  $[Ag(Au(CN)_2)_2 \subset 1c(PF_6)]^{6+}$  711.55,  $[Ag(Au(CN)_2)_2 \subset 1c(PF_6)_2]^{5+}$  883.05,  $[Ag(Au(CN)_2)_2 \subset 1c(PF_6)_3]^{4+}$  1140.01,  $[Ag(Au(CN)_2)_2 \subset 1c(PF_6)_4]^{3+}$  1568.57. Found: C, 46.35; H, 3.07; N, 9.87%. Calc. for  $C_{204}H_{160}AgCu_8Au_2F_{42}N_{36}P_7 \cdot 7H_2O$ : C, 46.52; H, 3.33; N, 9.57%.

**[Au(Au(CN)<sub>2</sub>)<sub>2</sub> ⊂ 1c]·PF<sub>6</sub>.** To  $[Cu(Au(CN)_2)_2 \subset 1c-D_4] \cdot PF_6$  (6.2 mg, 1.2 μmol, 1 equiv) in CD<sub>3</sub>CN (0.35 mL) in a j-young tube was added Au(tmbn)<sub>2</sub>SbF<sub>6</sub> (1.2 mg, 1.5 μmol, 1.2 equiv). The tube was rotated on a turner at room temperature for 12 h. <sup>1</sup>H NMR showed 50% of the starting material was converted to  $[Au(Au(CN)_2)_2 \subset 1c] \cdot PF_6$ . Further addition of Au(tmbn)<sub>2</sub>SbF<sub>6</sub> did not increase the amount of the desired product but converted left over  $[Cu(Au(CN)_2)_2 \subset 1c] \cdot PF_6$  into 1c-D<sub>2</sub>; ESI-MS  $[Au(Au(CN)_2)_2 \subset 1c]^{7+}$  602.06,  $[Au(Au(CN)_2)_2 \subset 1c(PF_6)]^{6+}$  726.60,  $[Ag(Au(CN)_2)_2 \subset 1c(PF_6)_2]^{5+}$  900.87,  $[Ag(Au(CN)_2)_2 \subset 1c(PF_6)_3]^{4+}$  1162.46,  $[Ag(Au(CN)_2)_2 \subset 1c(PF_6)_4]^{3+}$  1598.41.

**4·BF<sub>4</sub>.** To a NMR tube were added [1,1':4',1''-terphenyl]-3,3'',5,5''-tetraamine A (1.5 mg, 5.2 μmol, 4 equiv), 6-methyl-2-pyridinecarboxaldehyde (2.5 mg, 20.7 μmol, 16 equiv), and acetonitrile (0.5 mL). The resulting mixture was heated at 50 °C overnight before AgBF<sub>4</sub> (2.0 mg, 10.3 μmol, 8 equiv) was added. The tube was turned at room temperature overnight. A bright yellow solution resulted. The product was purified by recrystallization: diethyl ether was diffused into an acetonitrile solution of the complex. The desired product 4·BF<sub>4</sub> was isolated by filtration as yellow crystals (4.4 mg, 78%): <sup>1</sup>H NMR (CD<sub>3</sub>CN, 500 MHz) 9.45 (8H, d,  $J_{Ag-H}$  5.9, imine H), 9.33 (8H, d,  $J_{Ag-H}$  7.8, imine H), 8.33 (4H, t, Ph-H), 8.06 (4H, t, J 1.75, Ph-H), 8.05–8.03 (16H, d, J 4.7, py-H), 7.96 (8H, s, Ph-H), 7.93 (8H, t, J 7.7, py-H), 7.87 (8H, d, J 7.6, py-H), 7.54–7.51 (16H, py-H), 7.27–7.26 (16H, Ph-H), 6.66 (8H, d, J 7.9, Ph-H), 2.51 (24H, CH<sub>3</sub>), 2.07 (24H, CH<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 125 MHz) 163.71, 160.76, 160.30, 159.63, 150.10, 149.54, 149.21, 147.98, 144.43, 143.70, 141.22, 140.54, 140.27, 139.84, 130.01, 129.54, 129.17, 128.97, 128.90, 128.81, 128.67, 128.13, 125.59, 118.81, 27.18, 25.58; MALDI-MS using DCTB (2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile) matrix observed 4280.6, calc. for  $[L_4Cu_8(BF_4)_7]^+$  4281.94. Found: C, 49.35; H, 3.43; N, 9.51%. Calc. for  $C_{184}H_{152}B_8Ag_8F_{32}N_{32} \cdot 5H_2O$ : C, 49.36; H, 3.66; N, 10.05%.

**Transmetalation.** A stock solution was prepared using 18-crown-6 (6.2 mg, 23.4 μmol, 1.01 equiv), KAg(CN)<sub>2</sub> (4.6 mg, 23.1 μmol, 1 equiv) and CD<sub>3</sub>CN (0.35 mL). To 1a·PF<sub>6</sub> (4 mg, 0.9 μmol, 1 equiv) in CD<sub>3</sub>CN (0.4 mL) in a NMR tube were added KAg(CN)<sub>2</sub> (0.37 mg, 1.8 μmol, 2 equiv, 28 μL stock solution) and Au(tmbn)<sub>2</sub>SbF<sub>6</sub> (0.77 mg, 0.9 μmol, 1 equiv). The tube was rotated on a turner at room temperature for 12 h. <sup>1</sup>H NMR and ESI-MS showed the formation of  $[Ag(Au(CN)_2)_2 \subset 1a-D_4] \cdot PF_6$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

Synthesis and characterization for tetraamine B and C, NMR spectra for 1a·PF<sub>6</sub>, 2a·BF<sub>4</sub>, 2a·PF<sub>6</sub>, 3a·BF<sub>4</sub>, 1b·BF<sub>4</sub>, 1b·PF<sub>6</sub>, 1c·BF<sub>4</sub>, 1c·PF<sub>6</sub>, 4·BF<sub>4</sub>,  $[Au(Au(CN)_2)_2 \subset 1a] \cdot BF_4$ ,  $[Ag(Au(CN)_2)_2 \subset 1a] \cdot PF_6$ ,  $[Cu(Au(CN)_2)_2 \subset 1c] \cdot PF_6$ ,  $[Ag(Au(CN)_2)_2 \subset 1c] \cdot PF_6$ , and  $[Au(Au(CN)_2)_2 \subset 1c] \cdot PF_6$ , kinetic study of isomerization for 1b·BF<sub>4</sub>, calculation of binding constants for Au(Au(CN)<sub>2</sub>)<sub>2</sub>, and crystallographic data (CIF). Crystallographic data has been deposited with the CCDC (numbers 846046, 955699, and 905144–905149). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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