A Dynamic Tricopper Double Helicate

Marie Hutin, Richard Frantz, and Jonathan R. Nitschke*[a]

Abstract: The reaction between 8-aminoquinoline, 1,10-phenantholine-2,9-dicarbaldehyde, and copper(I) tetrafluoroborate gave a quantitative yield of a tricopper double helicate. The presence of dynamic covalent imine (C=N) bonds allowed this assembly to participate in two reactions not previously known in helicate chemistry: 1) It could be prepared through subcomponent substitution from a dicopper double helicate that contained aniline residues. An electron-poor aniline was quantitatively displaced; a more electron-rich aniline competed effectively with the aminoquinoline, setting up an equilibrium between dicopper and tricopper helicates that could be displaced towards the tricopper through the addition of further copper(I). 2) Both dicopper and tricopper helicates could be prepared simultaneously from a mixture of phenanthroline dialdehyde, aniline, and aminoquinoline, which contained all possible imine condensation products in equilibrium. Following the addition of copper(I), thermodynamic equilibration on both covalent and coordinative levels eliminated all partially-formed and mixed imine ligands from the mixture, leaving the helicates as exclusive products.

Keywords: copper(I) · dynamic combinatorial chemistry · imines · self-assembly · template synthesis

Introduction

The development of subcomponent self-assembly builds upon the accomplishments of "classical" metallo-organic self-assembly[1,2] by combining it with dynamic covalent chemistry.[3,4] Subcomponent self-assembly has allowed for the creation of complex structures[5,6] from simple building blocks through the dynamic formation of two distinct hierarchical[7,8] layers of linkages: covalent (C=N) and coordinative (N→metal) bonds. As a result of the reversible nature of these connections, these structures also possess the feature of being reconfigurable through substitution chemistry on both covalent and coordinative levels,[6,9,10] with the two levels being independently addressable in certain cases.[11]

A central challenge of subcomponent self-assembly is the difficulty of simultaneously programming the two distinct self-assembly processes, or how to template[12] the formation of specific structures or collections of structures from out of large dynamic libraries[13–15] of products. It is also of interest to investigate how subcomponent substitution might be used to cleanly and selectively transform one structure into an-

other. Such transformations could permit the incorporation of function based upon structural rearrangement, as has been demonstrated in the cases of a signal-amplifying allosteric catalyst,[16] a "chain-walking" epoxidation catalyst,[17] a reversible molecular motor,[18] a fluid-transporting rotaxane surface,[19] and a molecular elevator.[20]

We report herein the results of a study into the dynamic chemistry of a new tricopper double helicate. In addition to being accessible through subcomponent self-assembly, this structure could also be quantitatively prepared through ligand-subcomponent substitution[9–11] starting from a dicopper helicate,[10,21,22] an unprecedented transformation to the best of our knowledge. Both di- and tricopper helicates could also be prepared simultaneously from a library of dynamically interconverting ligand subcomponents in a process that eliminated all mixed and partially-formed structures; this subcomponent sorting phenomenon has not been observed previously in polynuclear complexes.

Results and Discussion

Copper(I) tetrafluoroborate (3 equiv), 8-aminoquinoline (4 equiv), and 1,10-phenanthroline-2,9-dicarbaldehyde (2 equiv) reacted in dimethyl sulfoxide (DMSO) or acetonitrile solution to give a single product, **1**. Results of ESI-MS indicated $Cu_3L_2^{3+}$ stoichiometry and NMR spectra were

[a] M. Hutin, Dr. R. Frantz, Dr. J. R. Nitschke
Department of Organic Chemistry, University of Geneva
30 Quai Ernest-Ansermet, 1211 Genève 4 (Switzerland)
Fax: (+41)22-379-3215
E-mail: Jonathan.Nitschke@chiorg.unige.ch

consistent with the D_2-symmetric double-helical structure of **1** shown in Equation (1).
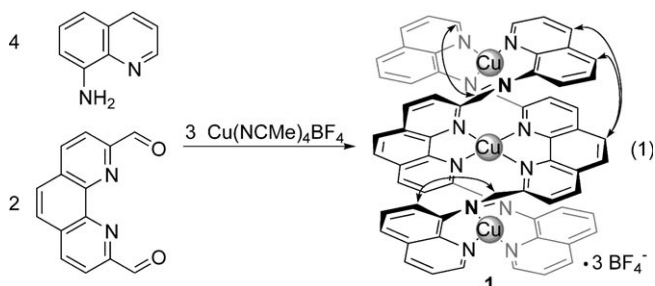
Similar helicate structures that consist of three Cu^I centers surrounded by two ligands each bearing six sp^2 nitrogen donor atoms have been reported by Constable,[23] Potts,[24] and Thummel.[25] Because we lacked crystals of sufficient quality for X-ray analysis, we based our structural assignment of **1** primarily upon NMR data. COSY, HSQC, and HMBC experiments allowed us to assign all resonances in the ^{1}H and ^{13}C NMR spectra of **1**. NOESY and ROESY experiments showed a large set of correlations, all of which were consistent with the assigned structure of **1**. The most revealing of the observed NOEs are shown as double-headed arrows in Equation (1). A correlation between the imine and 7-quinoline protons indicated that the ligand adopted the configuration shown, and correlations between protons that are spatially distant on the same ligand strand are readily explained by structure **1** as interligand correlations.[26]

The addition of Δ-TRISPHAT anion, shown to be a useful chiral shift reagent by Lacour,[27] split all observed

Abstract in French: *La réaction entre la 8-aminoquinoline, la 1,10-phenanthroline-2,9-dicarbaldehyde et le cuivre(ı) tetrafluoroborate conduit à la formation quantitative d'un double hélicate à trois cuivres. Grâce à la liaison imine (C=N) dynamique et covalente, cet assemblage participe à deux réactions nouvelles dans la chimie des hélicates : 1) L'hélicate peut être préparé par la substitution de composants à partir d'un double hélicate à deux cuivres incorporant des anilines. Une aniline pauvre en électrons est déplacée quantitativement par l'aminoquinoline ; une aniline plus riche en électrons est déplacée plus difficilement, conduisant ainsi à un équilibre entre l'hélicate à deux cuivres et celui à trois cuivres. Cet équilibre peut être déplacé vers la formation de l'hélicate à trois cuivres par l'addition d'un excès de cuivre(ı). 2) Les hélicates à deux et trois cuivres peuvent être préparés simultanément en ajoutant du cuivre(ı) à un mélange d'aminoquinoline, d'aniline et de phenanthrolinecarbaldehyde contenant tous les produits de condensation possibles à l'équilibre. Suite à cet ajout, l'équilibre thermodynamique élimine les ligands partiellement formés ou mixtes, laissant les hélicates comme uniques produits.*

signals in two, as shown in Figure 1. This observation provided clear evidence for the presence of two enantiomers, as expected for helical structure **1**.[28]
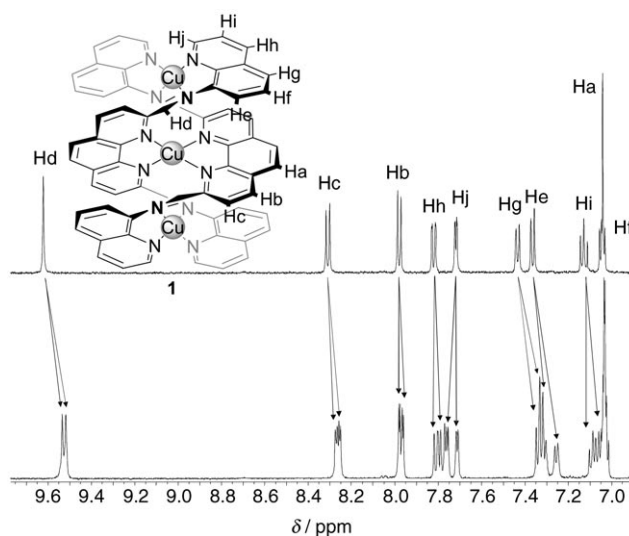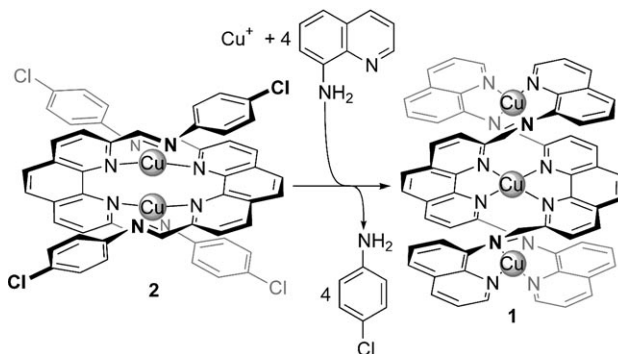

Figure 1. ^{1}H NMR signals of **1** (top trace) split into two (bottom trace) following the addition of the enantiodifferentiation agent Δ-TRISPHAT anion.

The use of 8-aminoquinoline together with 1,10-phenanthroline-2,9-dicarbaldehyde may be considered to program[1] the formation of this tricopper helicate: The bis-(imine)ligand formed by the condensation of these two starting materials possesses six nitrogen donor atoms, and two such ligands are well suited to generate a helicate containing three pseudotetrahedral copper(ı) ions.[23–25] If 4-chloroaniline was used in place of 8-aminoquinoline, the resulting self-assembled ligand contained only four nitrogen donors. Thus, the structure generated in the presence of Cu^I was dicopper helicate **2** (Scheme 1), of a structure type initially reported by Ziessel.[21] We have previously detailed the preparation through subcomponent self-assembly of helicates structurally similar to **2**.[10]

The addition of 8-aminoquinoline (4 equiv) and copper(ı) tetrafluoroborate (1 equiv) to a solution of dinuclear heli-

Scheme 1. Substitution of aminoquinoline for chloroaniline, generating trimetallic **1** from dimetallic **2**.

cate **2** resulted in quantitative subcomponent substitution, as shown in Scheme 1. If the reaction was conducted in acetonitrile solution, helicate **1** and 4-chloroaniline were the only observed products after 1 h at 323 K. However, in DMSO solution, the reaction had reached only 17 % completion after 6 h at 323 K. After 48 h, the reaction had run its course in DMSO, with no further signals of **2** being visible in the NMR spectrum. The electron-poor 4-chloroaniline (Hammett $\sigma_{para} = 0.37$ for −Cl)[29] thereby served as an excellent leaving group in the subcomponent-substitution reaction.

Acetonitrile appears to facilitate the dynamic equilibration necessary for the strict (thermodynamic) self-assembly[30] process. This solvent effect could be a consequence of the fact that acetonitrile is a good ligand for copper(I): following dissociation of one "arm" of a chelating ligand, acetonitrile could coordinate to the vacant metal site, blocking the immediate reassociation of the chelating ligand and allowing covalent imine exchange to occur on the dissociated part of the ligand away from the crowded coordination sphere of the metal.

If the subcomponent-substitution reaction shown in Scheme 1 was conducted in acetonitrile in the absence of additional copper(I), the reaction still proceeded. Substitution stopped only after **2** had been entirely consumed, to give **1** in 66 % yield (limited only by the availability of CuI). Thus, the formation of **1** appeared to be preferred over the formation of alternative structures, such as a helicate containing the ligands of **1**, but only two copper ions. Although such a dicopper structure would suffer from less Coulombic repulsion than would a tricopper structure, the preorganization of the ligands by two metal ions should render the insertion of a third metal ion highly entropically favorable.[31]

Helicates have proven themselves to be extremely fruitful systems for the study of dynamic behavior in self-assembly.[32] Constable[23] and Potts[24] have described the preparation of oligopyridines capable of accommodating a variable number of copper(I) ions in helical structures. Lehn has described circular helicates whose nuclearity may be changed as a function of template anion,[33] a system that expresses different helicate structures as a function of the metal ions present,[34] and a helicate that dynamically expands and contracts as a function of pH.[35] Albrecht[15] and Raymond[36] have described systems in which a tetrahedron or helicate may be selected as product based on template or solvent effects, and Albrecht and Schalley have also studied a system in which the dynamic forces holding the two halves of a hierarchically self-assembled helicate may be quantified.[7] We have investigated a system in which arylamines replaced alkylamines within dinuclear helicates based upon pKa differences.[10] We are not aware, however, of a precedent for the covalent and supramolecular transformation of one helicate into another of different nuclearity and bearing different ligands.

The reaction of helicate **3** (1 equiv) with 8-aminoquinoline (4 equiv) and copper tetrafluoroborate (1 equiv) in acetonitrile resulted in only 18 % conversion to **1**, the equilibrium

being established after 90 h at 323 K. The electron-rich 4-methoxyaniline (Hammett $\sigma_{para} = -0.27$ for −OMe)[29] competed effectively with the 8-aminoquinolines, which allowed both helicates to coexist in the presence of free subcomponents at equilibrium.

The addition of copper(I) naturally pushed the equilibrium shown in Scheme 2 further to the right: following the addition of three additional equivalents of copper(I) tetrafluoroborate, the percentage of **1** present increased from 18 to 26 % within 22 h at 323 K.
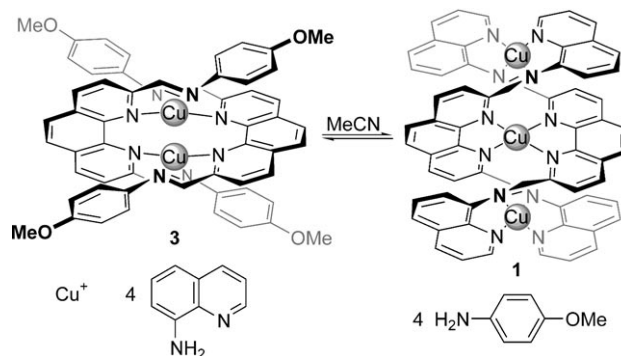
Scheme 2. Equilibrium between **3** and **1** in the presence of free subcomponents.

The failure of any intermediates to appear in the **2**-to-**1** and **3**-to-**1** transformations led us to suspect that dicopper and tricopper double helicates might be synthesized side-by-side from a mixed set of ligand subcomponents.[11] Following the mixing of 4-chloroaniline, 8-aminoquinoline, and 1,10-phenanthroline-2,9-dicarbaldehyde (4 equiv each) in acetonitrile, a dynamic library[4,13,37] of products formed (Scheme 3). NMR spectra indicated that this library was composed of numerous imine condensation products in dynamic equilibrium with the starting materials. Following the addition of copper(I) tetrafluoroborate (5 equiv), this library collapsed within 80 h at room temperature to give helicates **1** and **2** as the uniquely templated products.

These two structures were the smallest ones that could be constructed from the available self-assembled ligands, while simultaneously ensuring that all copper(I) ions were tetracoordinate, and that all nitrogen atoms were bound to copper. The mixed imine ligand, which contains both aminoquinoline and chloroaniline residues, possesses five donor atoms and, therefore, would not be able to self-assemble into a coordinatively saturated structure without dimerizing into an entropically-disfavored L_4Cu_5 assembly.[38] Enthalpy (coordinative saturation) and entropy (avoidance of larger structures when possible) thereby worked together to direct the two hierarchical levels[7,8] of this simultaneous self-assembly process. Figure 2 shows ^{1}H NMR spectra of the mixture shown in Scheme 3 before and after the addition of copper(I).
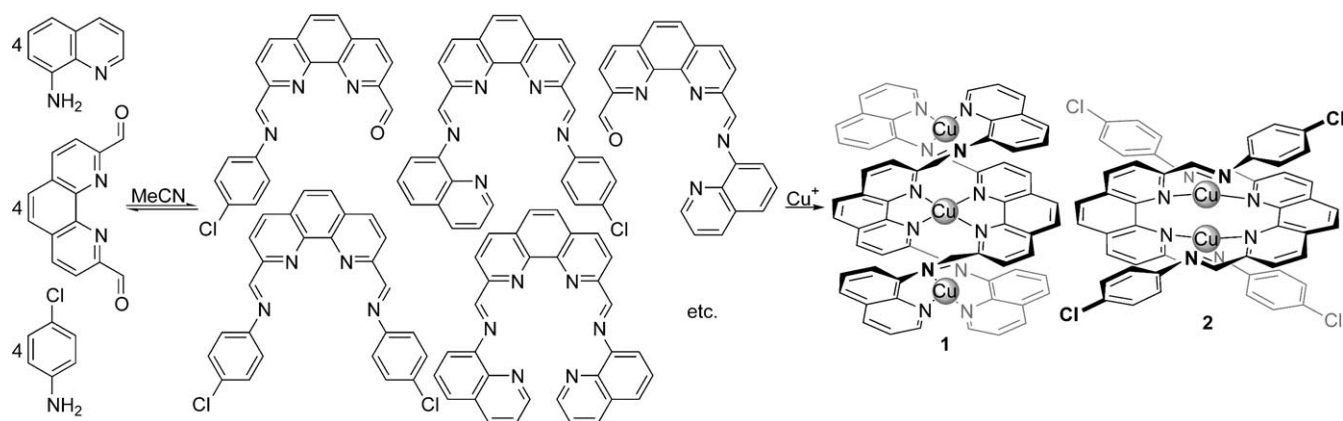
Scheme 3. Simplification of a dynamic library of ligands through the templated formation of helicates **1** and **2**.
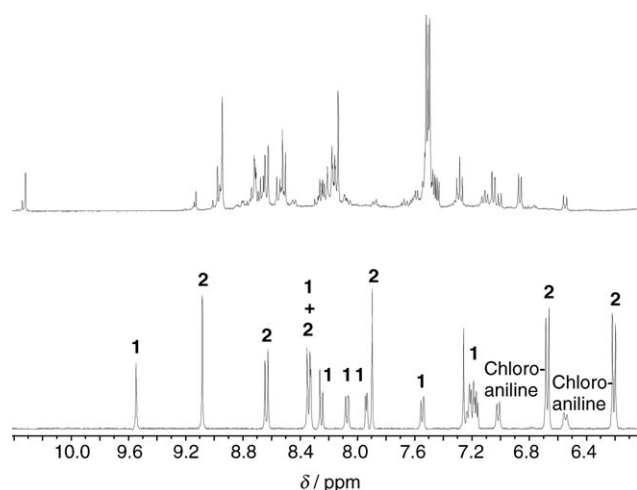

Figure 2. Clean conversion of the dynamic library shown in Scheme 3 (top trace) into a mixture of **1** and **2** (bottom trace) following the addition of copper(ɪ).

NMR spectra revealed that the same dynamic library of ligands formed in DMSO solution, and both **1** and **2** were identified in the spectrum 24 h after the addition of copper(ɪ) tetrafluoroborate. However, **1** and **2** together accounted for only 38% of the total mass of ligand subcomponents present (as measured by ^{1}H integration against an internal standard). The rest of the subcomponents were observed as numerous minor peaks that diminished slightly following heating to 323 K over five days, at which point **1** and **2** accounted for 50% of the total mass. Because there was no change in the NMR spectrum of a mixture of **1** and **2** heated to 323 K for four days, we concluded that the minor peaks correspond to kinetic products that rearranged only with difficulty into the thermodynamic products **1** and **2** in DMSO. These observations reinforced the hypothesis that acetonitrile accelerates the dynamic equilibration process, in the same manner as was observed during the conversion of **2** to **1**.

Conclusion

The parallel self-assembly of **1** and **2** builds upon the self-recognition studies of Lehn and Krämer[39] and Raymond,[40] which demonstrated that different helicates could self-assemble together in solution. In the present case, however, the dynamic interchange observed between the potential ligands means that the "self" is defined only at the moment of self-assembly.[41] The two distinct hierarchical layers of self-assembly, covalent (C=N) and coordinative (N→Cu), grant the present system more degrees of freedom than are present in a purely supramolecular system. The ability to apply these degrees of freedom rationally and in parallel allows one to envisage the rapid construction of larger self-assembled systems, in which the "programs" directing the assembly of these systems serve as "subroutines" in the assembly of architectures that bear the necessary degree of complexity to serve a useful function.[19, 42]

The present study thereby serves as a point of departure for the creation of architectures containing **1** as a structural element; for example, models suggest that the use of a bis-aminoquinoline building block in which the two aminoquinolines were linked by a flexible alkyl chain might result in the exclusive formation of a knot[43] built around **1** as a structure-determining motif. The successful simultaneous preparation of **1** and **2** also indicates that these moieties might be incorporated together into a larger structure. The use of a bifunctional aminoquinoline–aniline building block could also facilitate the emergence[44] of architectures of considerable topological complexity.

Experimental Section

Preparation of helicate 1: 8-Aminoquinoline (40.9 mg, 0.284 mmol), 1,10-phenanthroline-2,9-dicarbaldehyde (33.5 mg, 0.142 mmol), and [Cu-(NCMe)$_4$]BF$_4$ (66.9 mg, 0.213 mmol) were added to a 50-mL Schlenk flask. Methanol (5 mL) was added, the flask was sealed, and the atmosphere was purified of dioxygen by performing three evacuation/argon-fill cycles. The reaction mixture was stirred at RT overnight. The supernatant was removed by cannula-filtration and the product was dried under dynamic vacuum, giving an isolated yield of 84 mg (82%) of brown microcrystalline **1**, shown by NMR spectroscopy to be pure. ^{1}H NMR (500 MHz, 298 K, [D$_6$]DMSO): $\delta = 9.53$ (s, imine, 4H), 8.31 (d, $J = 8$ Hz, 4H; 3,8-phenanthroline), 8.22 (d, $J = 8$ Hz, 4H; 4,7-phenanthroline), 8.03 (d, $J = 8$ Hz, 4H; 4-aminoquinoline), 7.93 (dd, $J = 4$ Hz, $J' = 1$ Hz, 4H; 2-aminoquinoline), 7.51 (d, $J = 8$ Hz, 4H; 5-aminoquinoline), 7.22 (m, 2 × 4H; 5,6-phenanthroline, 7-aminoquinoline), 7.15 ppm (m, 2 × 4H; 3-aminoquinoline, 6-aminoquinoline); ^{13}C NMR (125.77 MHz, 298 K, [D$_6$]DMSO): $\delta = 155.4$, 149.7, 149.0, 141.1, 139.8, 138.9, 136.7, 128.7, 128.3, 127.4, 127.3, 126.5, 125.9, 122.5, 116.1 ppm; ESI-MS: m/z (%): 389.4 (100) [**1**]$^{3+}$, 1341.6 (5) [**1**+2BF$_4$]$^+$.

Preparation of helicate 2: 4-Chloroaniline (54.2 mg, 0.425 mmol), 1,10-phenanthroline-2,9-dicarbaldehyde (50.2 mg, 0.213 mmol), and [Cu-(NCMe)$_4$]BF$_4$ (66.8 mg, 0.212 mmol) were added to a 50-mL Schlenk flask. Methanol (5 mL) was added, the flask was sealed, and the atmosphere was purified of dioxygen by performing three evacuation/argon-fill cycles, giving immediately a homogeneous orange solution. The reaction was stirred at RT overnight, during which time the solution turned green. Volatile components were evaporated to give 124 mg (97.4%) of green microcrystalline **2**, shown by NMR spectroscopy to be pure. ^{1}H NMR (500 MHz, 298 K, [D$_6$]DMSO): $\delta = 9.09$ (s, 4H; imine), 8.64 (d, $J = 8.0$ Hz, 4H; 4,7-phenanthroline), 8.34 (d, $J = 8.0$ Hz, 4H; 3,8-phenanthroline), 7.90 (s, 4H; 5,6-phenanthroline), 6.67 (d, $J = 8.5$ Hz, 8H; phenylene β to Cl), 6.20 ppm (d, $J = 8.5$ Hz, 8H; phenylene β to N); ^{13}C NMR (125.77 MHz, 298 K, [D$_6$]DMSO): $\delta = 159.73$, 148.17, 143.40, 139.76, 137.09, 132.29, 131.61, 128.08, 127.51, 126.83, 122.54 ppm; ESI-MS: m/z (%): 519.3 (100) [**2**]$^{2+}$, 1123.2 (7) [**2**+BF$_4$]$^+$.

Preparation of helicate 3: A combination of 4-methoxyaniline (28.4 mg, 0.231 mmol), 1,10-phenanthroline-2,9-dicarbaldehyde (27.2 mg, 0.115 mmol), and [Cu(NCMe)$_4$]BF$_4$ (36.3 mg, 0.115 mmol) was added to a 50 mL Schlenk flask. Methanol (5 mL) was added, the flask was sealed, and the atmosphere was purified of dioxygen by performing three evacuation/argon-fill cycles, giving immediately a homogeneous orange solution. The reaction was stirred at RT overnight, during which time the solution turned green. Volatile components were evaporated to give 66 mg (96%) of green microcrystalline **3**, shown by results of NMR spectroscopy to be pure. ^{1}H NMR (500 MHz, 298 K, [D$_6$]DMSO): $\delta = 9.03$ (s, 4H; imine), 8.55 (d, $J = 8.0$ Hz, 4H; 4,7-phenanthroline), 8.26 (d, $J = 8.0$ Hz, 4H; 3,8-phenanthroline), 7.78 (s, 4H; 5,6-phenanthroline), 6.13 (m, 16H; phenylene), 3.58 ppm (s, 12H; methyl); ^{13}C NMR (125.77 MHz, 298 K, [D$_6$]DMSO): $\delta = 158.85$, 156.02, 148.02, 140.13, 137.82, 136.51, 131.19, 127.19, 125.91, 122.30, 113.25, 55.28 ppm; ESI-MS: m/z (%): 509.1 (66) [**3**]$^{2+}$, 1106.2 (11) [**3**+BF$_4$]$^+$.

Use of Δ-TRISPHAT to observe the two enantiomers of 1: A combination of 1 mg of **1**, 0.15 mL of CD$_3$CN, and 0.55 mL of CD$_2$Cl$_2$ was added to an NMR tube with a Teflon screw-cap. The sample was deoxygenated by performing three vacuum/argon-fill cycles. Portions of tetrabutylammonium Δ-TRISPHAT were then added and ^{1}H NMR spectra were recorded. All signals in the ^{1}H NMR spectra were observed to split cleanly and reached the separation shown in Figure 1 following the addition of 8.7 equiv of TRISPHAT.

Preparation of 1 from 2: A combination of **2** (8.2 mg, 0.007 mmol), 8-aminoquinoline (4.1 mg, 0.028 mmol), [Cu(NCMe)$_4$]BF$_4$ (2.2 mg, 0.007 mmol), and CD$_3$CN (0.5 mL) was added to an NMR tube with a Teflon screw-cap. The resulting dark-green solution was deoxygenated by performing three vacuum/argon-fill cycles. After 1 h at 323 K, the color had turned dark brown, and the ^{1}H NMR spectrum contained signals corresponding to a mixture of **1** and 4-chloroaniline only.

Simultaneous preparation of 1 and 2: A combination of 1,10-phenanthroline-2,9-dicarbaldehyde (4.6 mg, 0.019 mmol), 4-chloroaniline (2.5 mg, 0.019 mmol), 8-aminoquinoline (2.8 mg, 0.019 mmol), [Cu(NCMe)$_4$]BF$_4$

(7.5 mg, 0.024 mmol), and CD$_3$CN (0.4 mL) was added to an NMR tube with a Teflon screw-cap. The solution was deoxygenated by performing three vacuum/argon-fill cycles, giving immediately a dark-brown homogeneous solution. After 80 h at RT, **1** and **2** were the only products observed by ^{1}H NMR spectroscopy.

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