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Interplay of Interactions Governing the Dynamic Conversions of Acyclic and Macrocyclic Helicates

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Abstract: A rigid, helical macrocycle that contains two copper(I) ions has been synthesized through subcomponent self-assembly. Although it does not obey the "rule of coordinative saturation", this macrocycle could be prepared through subcomponent substitution starting from a tri(copper(I)) helicate, in a reaction in which copper(I) was ejected. The macrocycle was observed to readily participate in a sequence of transformations between helical structures mediated by the electronic effects of substituents, entropic effects, the conformational preferences of organic building blocks, and the coordinative preferences of the metal ion. The thermodynamic parameters governing the interconversion of an "open" helicate and the "closed" macrocycle were determined through van 't Hoff analysis, allowing quantification of the entropic driving force for macrocyclization.

Keywords: dynamic covalent chemistry · macrocyclization · self-assembly · substitution · systems chemistry

Introduction

The creation and transformation of complex structures under thermodynamic control requires a nuanced understanding of the rules, or "programming instructions,"[1] governing the self-assembly processes of interest. Intricate self-assembled structures have been created using the interplay of different kinds of interactions, such as circular helicates[2] and cages[3] (metal coordination + guest templation), Borromean[4] and Solomon[5] links (metal coordination + π-stacking + dynamic covalent[6] imine bond formation), triply interpenetrated catenanes[7] and functional monolayers[8] (metal coordination + π-stacking), strained grids[9] (metal coordination + hydrophobic interactions + dynamic covalent bonds), and multicomponent cycles and rotaxanes (metal coordination + boronate ester formation + imine bond formation). Herein we build upon these prior examples by showing how four types of interactions may act together not only upon a *single structure* but within a *system of structures*.[10] We were able to describe the evolution of this system following the addition of a subcomponent, allowing multiple sequential transformations to be executed between acyclic and macrocyclic helicates.

Results and Discussion

The products expressed by our system were observed to depend upon interactions mediated by 1) the electronic effects of substituents, 2) entropic effects, 3) the conformational preferences of organic building blocks, and 4) the coordinative preferences of copper(I). All of these effects were important, but none taken alone could allow the prediction of the product observed from a given set of building blocks.

We have previously described the self-assembly of trinuclear double helicates similar to **4**, which formed (Scheme 1) from 2,9-diformyl-1,10-phenanthroline (2 equiv), copper(I) (3 equiv), and 8-amino-quinoline **3** (4 equiv).[11] We initially reasoned that introducing bis(aminoquinoline) **1** would give rise to large architectures containing the trimetallic helicate motif of **4** as a subunit. However, when subcomponent **1** was incorporated, its preferred geometry imposed the for-

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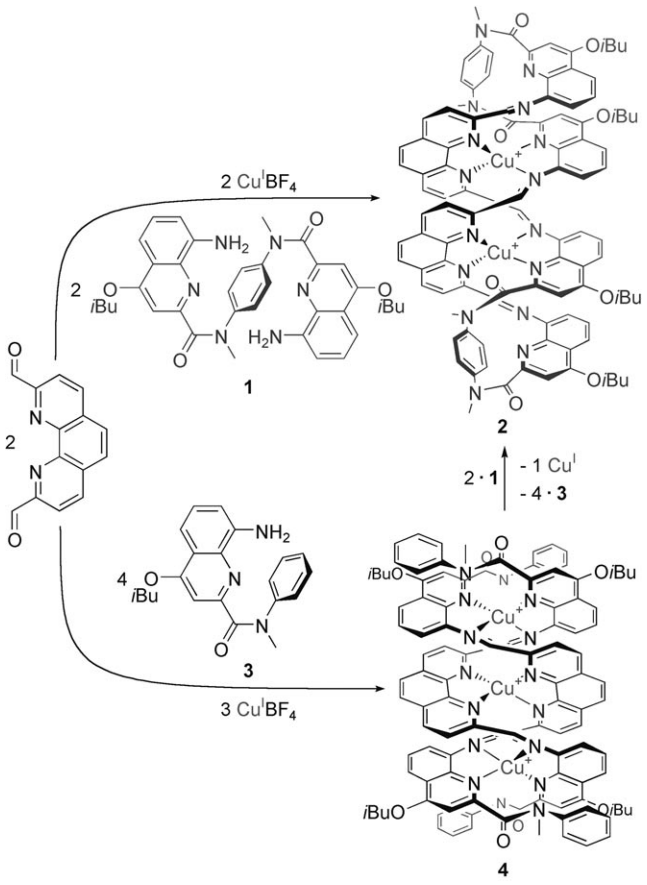


Scheme 1. Syntheses of dicopper macrocycle **2** (2·diformylphenanthroline + 2·**1** + 2·Cu^{I} → **2**) and tricopper helicate **4** (2·diformylphenanthroline + 4·**3** + 3·Cu^{I} → **4**), and the transformation of **4** into **2** upon addition of **1** (**4** + 2·**1** → **1** + 4·**3** + Cu^{I}).

mation of a stable product structure **2** (Scheme 1), wherein all ligand nitrogen atoms were *not* bound to metal ions. This demanding subcomponent could be introduced and removed quantitatively following selection rules based upon substituent electronic effects,[12,13] allowing the system to be switched back and forth between obeying and disobeying the rule of coordinative saturation. This rule,[14] which postulates that the most stable structure will have all ligand donor atoms bound to a metal ion and all metal ions coordinatively saturated, has been broken in exceptional cases,[15] but its expression has not previously been switched on and off within a system.

Even though only four of the six ligand nitrogen atoms of macrocycle **2** are bound to copper(I) ions, we observed no tendency for the subcomponents of **2** to form coordinatively saturated structures. No changes to the ^{1}H NMR spectrum of **2** were noted following either the addition of excess copper tetrafluoroborate (4 equiv) or excess **1** (4 equiv) followed by heating to 393 K for 12 h. The reaction of helicate **4** (1 equiv) with **1** (2 equiv) resulted in quantitative conversion to **2** with ejection of **3** (4 equiv) and Cu^{I}: Remarkably, coordinative saturation does not render **4** stable with respect to **2**, despite the similarity of their constituent subcomponents.

Single crystals of **2** were grown by diffusion of benzene into a nitromethane solution. Two views of the X-ray crystal structure of **2** are presented in Figure 1. NMR spectra of **2** in solution, including NOESY and COSY data, were consistent with the solid-state structure (see the Supporting Information).

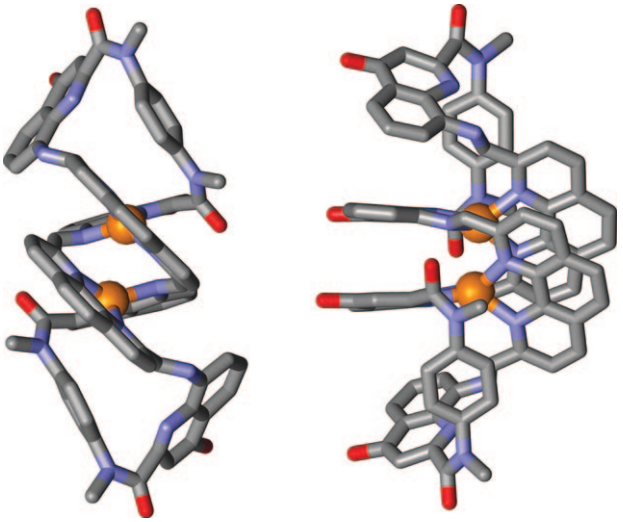
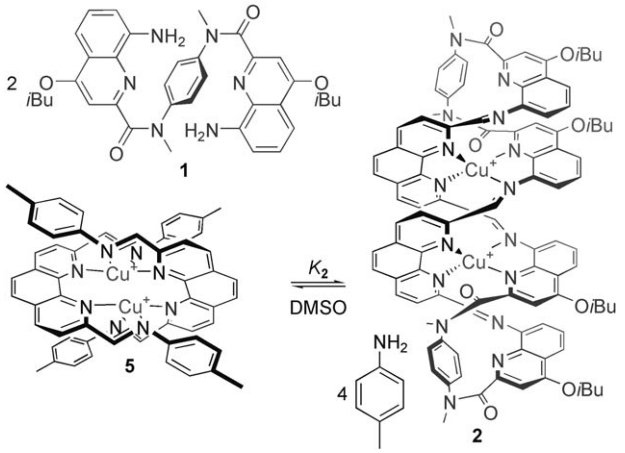


Figure 1. Two views of the crystal structure of macrocycle **2**: C gray, N violet, O red, Cu orange; hydrogen atoms, *i*Bu groups, counterions, and molecules of solvent of crystallization are not shown.

Examination of the coordination vectors[16] of the unbound nitrogen atoms of **2** revealed that they are not well situated either to chelate or bridge. The degrees of freedom available to the system are limited by the rigidity of subcomponent **1** and the preferred *trans*-orientation of the carbonyl and N-phenyl vectors of its tertiary amide groups.[17] Operating within these constraints, we infer that the system of diformylphenanthroline, **1**, and Cu^{I}, minimizes strain and maximizes entropy by breaking the rule of coordinative saturation in generating **2**.

Bis(aminoquinoline) **1** was observed to react with helicate **5**[12] (Scheme 2), with the equilibrium not strongly favoring either side. This system was thus more amenable to thermodynamic analysis than the transformation of **4** into **2** (Scheme 1), where the equilibrium lay strongly on the side of **2**. Van 't Hoff analysis of the system of Scheme 2 provided quantitative insight as to the effects of entropy and enthalpy on substitution reactions involving **2**. The equilibrium composition of the product mixture of the reaction between **1** and helicate **5** was measured from 373 K to 403 K, and a linear least-squares fit of ln(K) versus T^{-1} (see the Supporting Information) yielded the values of $\Delta H° = 81\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S° = 0.193\ \mathrm{kJ\,mol^{-1}\,K^{-1}}$. The system of Scheme 2 is thus balanced between enthalpy, which favors incorporation of the *p*-toluidine subcomponent during the formation of **5**, and entropy, which favors the increase in number of parti-



Scheme 2. Equilibrium between helicate **5** and macrocycle **2** ($2\cdot\mathbf{1} + \mathbf{5} \rightleftharpoons 4\cdot p$-toluidine $+$ **2**).

cles during the formation of macrocycle **2** (three species going to five). Similar effects presumably govern the formation of **2** from **4** (Scheme 1), although this system is more complicated to analyze because the equilibrium lay strongly on the side of **2** and because of potential interactions between liberated Cu^{I} and the solvent and with liberated **3**.

In prior work[12] we had investigated how substituent effects can generate an enthalpic driving force for imine exchange. The Hammett equation[18] was observed to quantitatively predict the degree to which a less electron-rich amine residue was displaced by a more electron-rich amine within the imine ligands of a metal complex. Although the Hammett equation appears an unsuitable tool to quantify the behavior of the systems incorporating diamines because of the importance of entropy in these equilibria, we reasoned that the balanced nature of the equilibrium between **5** and **2** would allow **1** to displace electron-poor anilines that *p*-toluidine (Hammett $\sigma_{para} = -0.17$)[18] is able to displace,[12] and that **1** would in turn be displaced by electron-rich anilines that displace *p*-toluidine.

We thus designed the sequence of transformations shown in Scheme 3. Each step was observed to occur in $>95\,\%$ yield and the entire sequence could be carried out within the same reaction flask. The corresponding NMR spectra are presented in Figure 2. The presence of additional Cu^{I} did not result in the formation of products incorporating **1** that obeyed the rule of coordinative saturation.

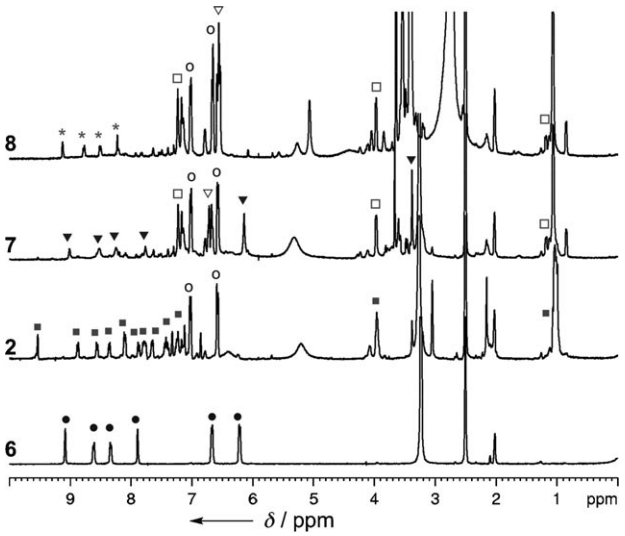
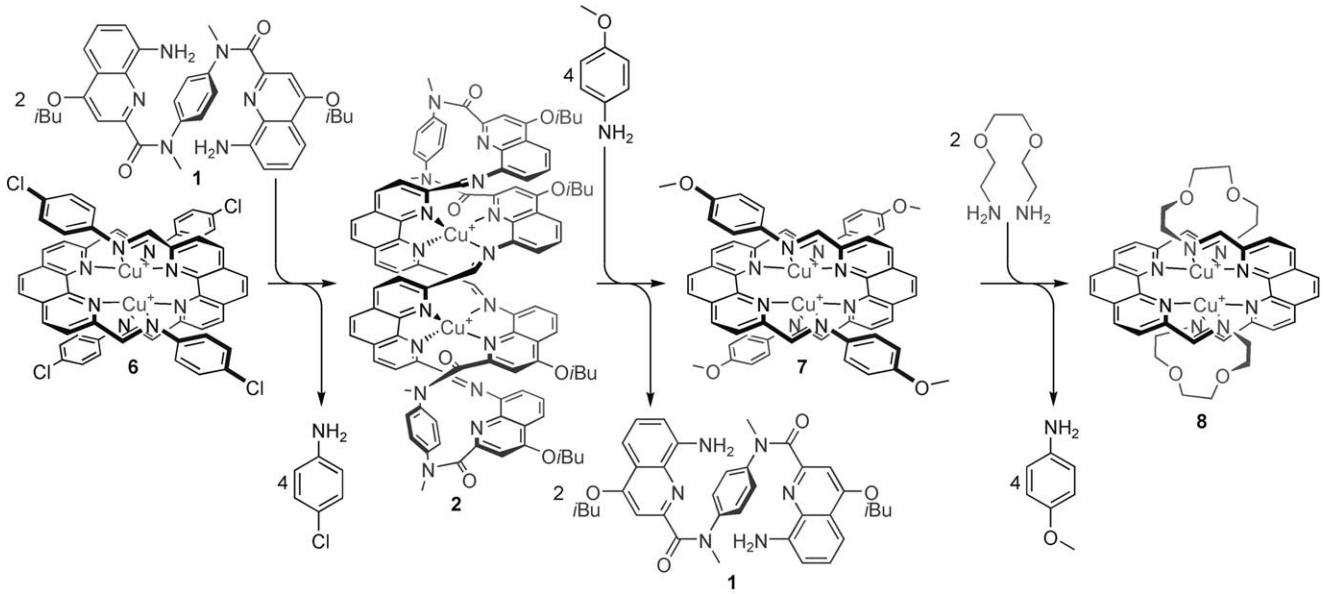


Figure 2. ^{1}H NMR spectra of four-stage transformation shown in Scheme 3: ● = helicate **6**, o = *p*-chloroaniline, ■ = macrocycle **2**, □ = diaminoquinoline **1**, ▼ = helicate **7**, ▽ = *p*-methoxyaniline, * = macrocycle **8**.



Scheme 3. Four-stage subcomponent substitution sequence incorporating **2** ($\mathbf{6} + 2\cdot\mathbf{1} \rightarrow \mathbf{2} + 4\cdot p$-chloroaniline; $\mathbf{2} + 4\cdot p$-methoxyaniline $\rightarrow \mathbf{7} + 2\cdot\mathbf{1}$; $\mathbf{7} + 2\cdot$(ethylenedioxy)bis(ethylamine) $\rightarrow \mathbf{8} + 4\cdot p$-methoxyaniline).

The substantial geometrical changes required during the conversion of **6** to **2** and **2** to **7** are reflected in the slower kinetics of these transformations ($t_{1/2}$ = ca. 12 h at 393 K) than in the transformation of **7** to **8** ($t_{1/2}$ = ca. 5 min at 393 K). We attribute this difference in activation energy to the extensive rearrangement necessary—involving the breakage and reforming of six nitrogen-copper linkages—to convert the coordination environments of **6** to **2** or **2** to **7**.

With the exception of **2**, all of the products shown in Schemes 1–3 obey the rule of coordinative saturation, having four ligand nitrogen atoms per copper ion. The presence of subcomponent **1** thus causes this "rule" to be broken upon its incorporation, only to be reinstated following this subcomponent's ejection. Thus, to determine whether the system will follow this rule, it is necessary to know not only whether **1** is present, but also whether another subcomponent is present with a greater affinity for complex formation (such as 4-methoxyaniline). The first condition must be true, and the second false, for the system to exist in the state of coordinative unsaturation exemplified by **2**.

Conclusions

The system encompassing helicates **2**, **4**, **5**, **6**, **7**, and **8** is thus governed by substituent and entropic effects, acting together to determine which subcomponent will be incorporated into the favored product. The rule of coordinative saturation[14] dictates the structure of this product, except when this product incorporates **1**: the preferred geometry of this subcomponent then favors the structure of **2**. We are currently investigating new structures built around the novel dicopper double-helicate core of **2**, as well as developing new ways to use linear free energy relationships to quantitatively predict the outcome of reassembly reactions involving diamines and higher-order multitopic amines.

Experimental Section

General: All reactions were carried out in dry glassware with an argon overpressure. Unless otherwise noted, all reagents were purchased from Aldrich or Acros and used without further purification; 1,10-phenanthroline-2,9-dicarbaldehyde[19] was prepared according to the literature. NMR spectra were recorded on Bruker Aspect 300, Bruker DRX-400, Bruker Avance 500 Cryo, and Bruker 500 TCI-ATM Cryo Spectrometers.

Macrocycle 2: Into a Teflon-capped NMR tube, 2,9-diformyl-1,10-phenanthroline (1.07 mg, 4.78 mmol), **1** (2.97 mg, 4.78 mmol), $[Cu(CH_3CN)_4]BF_4$ (2.26 mg, 7.18 mmol), CD_3CN (0.1 mL), and CD_2Cl_2 (0.4 mL) were added. The tube was sealed and the solution was purged of dioxygen by three vacuum/argon-fill cycles. The dark brown solution was left at 323 K overnight, following which **2** was observed as the unique product by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, 243 K, CD_2Cl_2/CD_3CN, referenced to $CHDCl_2$ at 5.32 ppm, *a*-*h* and *a*′-*h*′ refer to resonances that have been assigned to protons in the structure of **2**; see the Supporting Information for assignments): δ = 9.09 (s, 2H, *d*), 8.69 (d, J = 8.05 Hz, 2H, *b*′), 8.42 (d, J = 8.36 Hz, 2H, *c*′), 8.18 (d, J = 8.05 Hz, 2H, *b*), 7.96 (d, J = 8.36 Hz, 2H, *c*), 7.92 (d, J = 9.26 Hz, 2H, *a*′), 7.75 (d, J = 9.32 Hz, 2H, *a*), 7.72 (d, J = 8.43 Hz, 2H, *g*′) 7.68 (d, J = 7.55 Hz, 2H, *g*), 7.50 (d, J = 6.52 Hz, 2H, *e*), 7.47 (d, J = 8.89 Hz, 2H, *e*′), 7.37 (t, J = 8.32 Hz, 2H, *f*′), 7.07 (s, 2H, *h*), 6.99 (t, J = 7.89 Hz, 2H, *f*), 6.88 (s, 2H, *h*′), 6.73 (s, 2H, *d*′), 6.39 (dd, J = 8.72 Hz, $J_{2'}$ = 1.94 Hz, 2H, Ph_1), 6.19 (dd, J = 8.72 Hz, $J_{2'}$ = 1.94 Hz, 2H, Ph_2), 6.08 (dd, J = 8.72 Hz, $J_{2'}$ = 1.94 Hz, 2H, Ph_3), 4.98 (dd, J = 8.72 Hz, $J_{2'}$ = 1.94 Hz, 2H, Ph_4), 3.87 (m, 8H, $OCH_2CH(CH_3)_2$), 3.01 (s, 3H, NH_3), 1.15 (t, 4H, $OCH_2CH(CH_3)_2$), 1.08 ppm (m, 24H, $OCH_2CH(CH_3)_2$); ^{13}C NMR (125 MHz, 300 K, CD_2Cl_2): δ = 168.51, 166.28, 164.19, 163.27, 162.48, 156.56, 155.84, 154.66, 151.66, 151.09, 149.00, 143.77, 141.66, 141.33, 140.91, 140.05, 138.94, 138.62, 138.29, 137.76, 139.98, 129.94, 128.45, 128.23, 126.67, 126.31, 124.74, 123.86, 122.84, 122.43, 120.83, 120.78, 120.53, 118.90, 103.24, 101.97, 76.38, 75.41, 67.95, 38.91, 36.19, 29.92, 28.44, 28.23, 25.84, 19.13, 19.05, 18.95, 18.84 ppm; ESI-MS: *m/z*: 884.24 (2^{2+}).

X-ray crystal structure of 2: A thin needle-shaped crystal of compound **2** was mounted on a cryoloop using Paratone-N oil as cryoprotectant. Data were collected at 213 K on a R-axis Rapid-S goniometer equiped with a Rigaku MM07 $Cu_{K\alpha}$ rotating anode (λ = 1.54178 Å). The IP camera on this setup is of size 460 mm × 256 mm with an angle range of −60 to +144 degrees. The camera length is fixed at 127.4 mm. The crystal belongs to the triclinic $P\bar{1}$ space group with unit cell parameters a = 17.19, b = 19.63, c = 21.21 Å with angles α = 93.13, β = 100.15, and γ = 105.47°. V = 6751.3(4) A^3, ρ_{calcd} = 1.272 g cm^{-3}, μ = 1.033 mm^{-1}, Z = 2, reflections collected: 89919, independent reflections: 23046 (R_{int} = 0.1735), final R indices [$I > 2\sigma(I)$]: $R1$ = 0.1653, $wR2$ = 0.3776, R indices (all data) $R1$ = 0.3250, $wR2$ = 0.4646. The structure was solved by direct methods using SHELXD and refined with SHELXL-97.[20] Seven benzene molecules and two BF_4^- ions were located in the density map. The poor quality of the refinement and data collection statistics are a consequence of the large number of disordered solvent molecules, the relatively large size of the complex and the very small size of the crystal collected ($0.1 \times 0.1 \times 0.025$ mm^3). CCDC-718066 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Four-step transformation of Scheme 3: Into a Teflon-capped NMR tube, **6** (2.32 mg, 2.23 mmol), **1** (2.77 mg, 4.47 mmol), CD_3CN (0.1 mL), and $[D_6]$DMSO (0.4 mL) were added. The tube was sealed and the solution was purged of dioxygen by three vacuum/argon-fill cycles, and heated for 12 h at 393 K, after which **2** and *p*-chloroaniline were the only species observed in solution by ^{1}H NMR spectroscopy. *p*-Methoxyaniline (1.10 mg, 8.94 mmol) was added to this solution and the tube was purged of dioxygen by three vacuum/argon fill cycles. The solution was heated to 393 K for five days, after which **7** and **1** were the only products observed by NMR spectroscopy. To this solution 2,2′-(ethylenedioxy)bis(ethylamine) (1.32 mg, 8.94 mmol) was added. The tube was sealed and the solution was purged of dioxygen by three vacuum/argon-fill cycles, and heated for 5 min at 393 K, to afford **8**, *p*-methoxyaniline and **1** as the unique products sobserved by ^{1}H NMR spectroscopy.

Synthesis of 4: Into a Teflon-capped NMR tube, 2,9-diformyl-1,10-phenanthroline (1.87 mg, 7.94 mmol), **3** (5.55 mg, 15.9 mmol), $[Cu(CH_3CN)_4]BF_4$ (3.75 mg, 11.9 mmol), CD_3CN (0.1 mL), and CD_2Cl_2 (0.4 mL) were added. The tube was sealed and the solution was purged from dioxygen by three vacuum/argon-fill cycles. The dark brown solution was left at 323 K overnight, resulting in the formation of **3** in quantitative yield, as observed by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, 300 K, CD_2Cl_2/CD_3CN, referenced to $CHDCl_2$ at 5.32 ppm): δ = 9.29 (s, 4H, imine), 8.05 (br s, 4H, phenanthroline), 7.93 (br s, 4H, phenanthroline), 7.31 (br s, 4H, phenanthroline), 7.19 (br m, 4H, AQ), 7.13–7.09 (br m, 12H AQ), 6.85 (br s, 12H, AQ), 6.73 (br s, 8H, Ph), 6.53 (br s, 8H, Ph), 5.94 (br s, 4H, Ph), 3.91 (d, 4H, $ROCH_2CH(CH_3)_2$), 3.59 (br s, 4H, $ROCH_2CH(CH_3)_2$), 1.18 ppm (br s, 24H, $ROCH_2CH(CH_3)_2$); ESI-MS: *m/z*: 662.8 (4^{3+}).

Synthesis of 2 from 4: Into a Teflon-capped NMR tube, 2,9-diformyl-1,10-phenanthroline (1.87 mg, 7.94 mmol), **3** (5.55 mg, 15.9 mmol), $[Cu(CH_3CN)_4]BF_4$ (3.75 mg, 11.9 mmol), CD_3CN (0.1 mL), and CD_2Cl_2 (0.4 mL) were added. The tube was sealed and the solution was purged from dioxygen by three vacuum/argon-fill cycles. The dark brown solution was left at 323 K overnight, resulting in the formation of **4** in quantitative yield, as observed by ^{1}H NMR spectroscopy. Compound **1**

(4.01 mg, 6.61 mmol) was added into the NMR tube. The solution was purged of dioxygen again, then heated at 323 K for 2.5 h, after which all volatiles were removed under dynamic vacuum and CD_3CN (0.2 mL) and [D_6]DMSO (0.2 mL) were added. The reaction was heated at 353 K for five days, then at 393 K for seven days, after which the reaction came to completion. The reaction was monitored by ^{1}H NMR spectroscopy and ESI-MS. ^{1}H NMR (400 MHz, 300 K, CD_3CN/[D_6]DMSO, referenced to CD_2HCN at 1.94 ppm): $\delta = 9.54$ (s, 2H, *d*), 8.88 (d, $J = 7.18$ Hz, 2H, *b′*), 8.57 (d, $J = 8.38$ Hz, 2H, *c′*), 8.36 (d, $J = 7.18$ Hz, 2H, *b*), 8.11 (d, $J = 8.38$ Hz, 2H, *c*), 7.88 (d, $J = 8.38$ Hz, 2H, *a′*), 7.79 (d, $J = 7.18$ Hz, 2H, *a*), 7.75 (d, $J = 7.18$ Hz, 2H, *g′*), 7.65 (d, broad, 2H, *g*), 7.63 (d, broad, 2H, *e*), 7.45 (m, 6H, *e′, f, h*), 7.24–7.07 (m, **3** and **2**), 6.77 (broad, 8H, phenyl), 3.92 (m, 8H, $OCH_2CH(CH_3)_2$), 3.01 (s, 3H, NH_3), 1.15 (t, 4H, $OCH_2CH(CH_3)_2$), 1.00 ppm (m, 24H, $OCH_2CH(CH_3)_2$); ESI-MS: *m/z*: 350.19 (**3**$^+$), 411.09 (**3**·Cu^+), 884.24 (**2**$^{2+}$).

Equilibrium between 5 and 2: Into a Teflon-capped NMR tube, **5** (3.39 mg, 3.55 mmol), **1** (4.39 mg, 7.10 mmol), CD_3CN (0.1 mL), and [D_6]DMSO (0.4 mL) were added. The tube was sealed and the solution was purged of dioxygen by three vacuum/argon-fill cycles. The temperature was increased from 373 K to 403 K in 10 degree intervals, being kept for 96 h at each interval. The reaction was monitored by ^{1}H NMR spectroscopy; when the integrations of the imine peaks did not change over time with respect to the TMS peak, the reaction was considered to be at equilibrium.

Acknowledgements

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[1] J. M. Lehn, *Chem. Eur. J.* **2000**, *6*, 2097–2102.
[2] B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem.* **1996**, *108*, 1987–1990; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838–1840.
[3] R. L. Paul, Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4883–4888.
[4] K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308–1312.
[5] C. D. Pentecost, K. S. Chichak, A. J. Peters, G. W. V. Cave, J. F. Stoddart, S. J. Cantrill, *Angew. Chem.* **2007**, *119*, 222–226; *Angew. Chem. Int. Ed.* **2007**, *46*, 218–222.
[6] S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938–993; *Angew. Chem. Int. Ed.* **2002**, *41*, 898–952.
[7] M. Fujita, N. Fujita, K. Ogura, K. Yamaguchi, *Nature* **1999**, *400*, 52–55.
[8] M. Altman, O. Zenkina, G. Evmenenko, P. Dutta, M. E. van der Boom, *J. Am. Chem. Soc.* **2008**, *130*, 5040–5041.
[9] J. R. Nitschke, M. Hutin, G. Bernardinelli, *Angew. Chem.* **2004**, *116*, 6892–6895; *Angew. Chem. Int. Ed.* **2004**, *43*, 6724–6727.
[10] a) R. F. Ludlow, S. Otto, *Chem. Soc. Rev.* **2008**, *37*, 101–108; b) M. Kindermann, I. Stahl, M. Reimold, W. M. Pankau, G. von Kiedrowski, *Angew. Chem.* **2005**, *117*, 6908–6913; *Angew. Chem. Int. Ed.* **2005**, *44*, 6750–6755; c) L. Jullien, A. Lemarchand, S. Charier, O. Ruel, J. B. Baudin, *J. Phys. Chem. B* **2003**, *107*, 9905–9917; d) P. Mukhopadhyay, P. Y. Zavalij, L. Isaacs, *J. Am. Chem. Soc.* **2006**, *128*, 14093–14102.
[11] M. Hutin, R. Franz, J. R. Nitschke, *Chem. Eur. J.* **2006**, *12*, 4077–4082.
[12] D. Schultz, J. R. Nitschke, *J. Am. Chem. Soc.* **2006**, *128*, 9887–9892.
[13] a) P. R. Ashton, M. C. T. Fyfe, S. K. Hickingbottom, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Chem. Soc. Perkin Trans. 2* **1998**, 2117–2128; b) W. D. Kerber, D. L. Nelsen, P. S. White, M. R. Gagne, *Dalton Trans.* **2005**, 1948–1951.
[14] a) D. Schultz, J. R. Nitschke, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 11191–11195; b) J. R. Nitschke, *Acc. Chem. Res.* **2007**, *40*, 103–112; c) R. J. Sarma, J. R. Nitschke, *Angew. Chem.* **2008**, *120*, 383–386; *Angew. Chem. Int. Ed.* **2008**, *47*, 377–380.
[15] a) S. Toyota, C. R. Woods, M. Benaglia, R. Haldimann, K. Warnmark, K. Hardcastle, J. S. Siegel, *Angew. Chem.* **2001**, *113*, 773–776; *Angew. Chem. Int. Ed.* **2001**, *40*, 751–754; b) P. N. W. Baxter, J. M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4510–4517.
[16] D. L. Caulder, C. Brueckner, R. E. Powers, S. Koenig, T. N. Parac, J. A. Leary, K. N. Raymond, *J. Am. Chem. Soc.* **2001**, *123*, 8923–8938.
[17] A. Itai, Y. Toriumi, S. Saito, H. Kagechika, K. Shudo, *J. Am. Chem. Soc.* **1992**, *114*, 10649–10650.
[18] L. P. Hammett, *Chem. Rev.* **1935**, *17*, 125–136.
[19] A. Angeloff, J.-C. Daran, J. Bernadou, B. Meunier, *Eur. J. Inorg. Chem.* **2000**, 1985–1996.
[20] G. M. Sheldrick in Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, **1998**.

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