Interconversion between a Vertically Oriented Transition Metal-Complexed Figure-of-Eight and a Horizontally Disposed One

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Ⓢ *Supporting Information*

ABSTRACT: A large ring containing two pairs of transition metal-complexing fragments with alternating bi- and tridentate chelates has been shown to behave as a bimodal figure-of-eight. When coordinated to a preferentially octahedrally coordinated Fe(II) or Cu(II) center, the height of the molecule along the coordinating axis of the tridentate ligands (vertical on the drawing) is only ~11 Å, whereas the height of the molecule along the same vertical axis is several times as large for the complex of the tetrahedrally coordinated copper(I) center. This new type of molecular machine-prototype could be used as constitutive element in muscle-like dynamic systems.

Although molecular motions in biology have been recognized as essential for decades,[1] it is only 20 years ago that molecular chemists have deliberately designed and synthesized multicomponent molecular systems in view of setting them or given parts of them in motion under the action of a signal.[2] Originally, the field of molecular machines was to a large extent derived from that of catenanes and rotaxanes.[3] Catenane- or rotaxane-based molecular machine prototypes were first proposed at the beginning of the 90s, but since then numerous such molecular systems have been reported with increasing complexity and sophistication.[4] At the end of the 90s, a few important contributions were reported by other groups using noninterlocking molecules.[5] In recent years, outstanding work has been reported toward functional molecular machines, either in the materials field or in synthetic chemistry,[6] a particularly impressive example being that of a [2]rotaxane incorporating several different stations in its axis and whose behavior is reminiscent of that of a ribosome.[7] Related to molecular machines, transition metal complexes able to undergo controlled translocation of the metal under the action of a chemical or electrochemical signal have also triggered much interest.[8]

Surprisingly, noninterlocking cyclic systems undergoing controlled large amplitude motions are very uncommon although large rings can occupy markedly different shapes, which could be interconverted with one another using an appropriate signal.[9] Such rings could certainly be used as components of muscle-like compounds able to contract or elongate in analogy with [2]rotaxane dimers acting as molecular muscles.[10]

In the present report, we would like to show that a large macrocycle (78-membered ring), incorporating two different pairs of coordinating fragments, can interact with transition metals in a bimodal way. The nature of the metal or its oxidation state will determine its binding mode to the ring. In addition, each form of the complexed ring has the shape of a figure-of-eight, with a clear crossing point between the two loops of the cycle.

The general formula of the ring is represented in Scheme 1. The bidentate and tridentate chelates are arranged in an

**Scheme 1. Four-Coordinating-Group Macrocycle 1**[a]
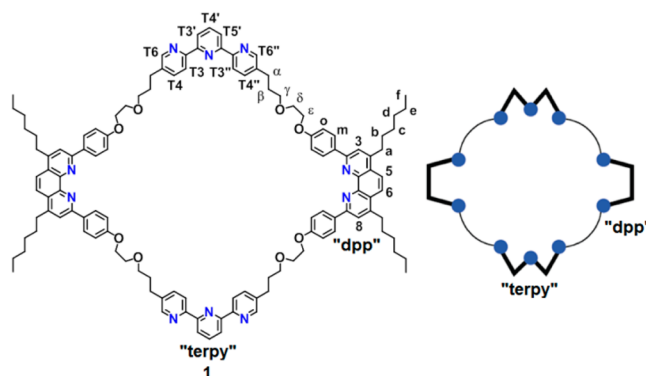
[a]The two terpy fragments are disposed on the vertical axis, and the dpp units are located on the horizontal one. Solubilizing groups are indispensable to be able to handle the compound in normal solvents. The nitrogen atoms are symbolized by blue disks on the right drawing. The target macrocyclic compound is a 78-membered ring.

alternating situation: dpp (dpp: 2,9-diphenyl-1,10-phenanthroline)−terpy (terpy: 2,2′,6′,2″-terpyridine)−dpp−terpy. The two coordinating groups used are classical chelating moieties very well adapted to tetrahedral or octahedral coordination spheres, respectively. It is thus expected that Cu(I) will form a bis-dpp complex by taking up the two dpp fragments, whereas Fe(II) will accommodate the two terpy groups, as represented in a schematic fashion in Scheme 2.

Macrocycle **1** was prepared in 17 steps from commercially available compounds. The synthesis of this macroring will be reported in a future publication. In preliminary work, no substituents were introduced at the periphery of the coordinating groups, leading to highly insoluble compounds. It thus appeared as essential to attach solubilizing groups on some of the

Scheme 2. Two States of the Figure-of-Eight[a]
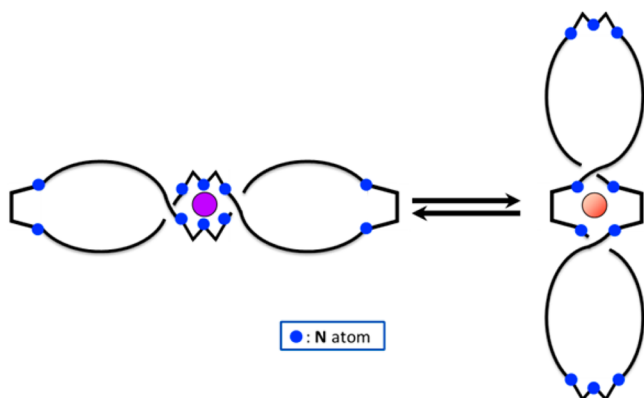
[a]"On the left, the octahedral Fe(II) complex (Fe is a purple disk) implies that the long axis is horizontal, whereas formation of the tetrahedral Cu(I) center, indicated as a red disk, imposes a long vertical axis. Alternatively, the octahedrally coordinated metal can be a copper(II) center obtained by electrochemically oxidizing the copper(I) complex. The central entanglement is represented with 2 crossings, which is in accordance with the geometrical features of the complexes involved. The coordinating nitrogen atoms are represented as small blue disks. The conversion of the copper(I) complex to the iron(II) complex via metal exchange involves compression of the ring along the vertical axis and elongation of the horizontal dimension. The same holds true for the oxidation of copper(I) to copper(II). Note that the macrocyclic complexes are chiral because of the helical arrangement of the compounds. In the present work, the complexes are racemates. Arbitrarily, the vertical axis for both forms has been selected as the straight line between the central nitrogen atoms of the two terpy nuclei.

fragments. The use of *n*-hexyl groups as solubilizing functions turned out to be particularly well suited.

Compound **1** was fully characterized by ^{1}H and ^{13}C NMR, including COSY, HR-MS (ES).[11]

The copper(I) complex $[\mathbf{1}\cdot Cu^+]\cdot[PF_6^-]$ was prepared quantitatively as a deep red solid by the reaction of macrocycle **1** with stoichiometric amount of $Cu(CH_3CN)_4PF_6$ in a dichloromethane−acetonitrile mixture. The iron(II) complex was obtained by stoichiometric addition of $Fe(OTf)_2$ in MeOH to a CH_2Cl_2 solution of free ligand **1**. Formation of the iron(II) complex $[\mathbf{1}\cdot Fe^{2+}]\cdot[OTf^-]_2$ was observed immediately as indicated by the appearance of a deep color in the solution. The complex was isolated in very good yield as an intense purple solid. After formation, the two complexes were filtered on alumina to remove possible traces of starting material. Both complexes were characterized by ^{1}H NMR, HR-MS(ES), electronic spectroscopy, and electrochemistry.[12]

Interestingly, both complexes could easily and efficiently be demetalated to afford the metal-free compound **1**. Treatment of the copper(I) complex $[\mathbf{1}\cdot Cu^+]\cdot[PF_6^-]$ by a KCN/water−acetonitrile solution at room temperature led to the free macrocycle **1** in quantitative yield. In the case of the iron(II) complex, demetalation occurred by addition of a Cs_2CO_3/DMF solution, which was heated at 70 °C during 1 h.[13] In both cases, the free ligand was obtained with a satisfactory purity without further purification.

Remetalation was also carried out almost quantitatively showing that metal exchange is nearly quantitative and can be performed under reasonably mild chemical conditions. This metal exchange process, although high-yielding, is certainly less

promising in terms of molecular machinery than an electro-chemically or photochemically driven process (Figure 1).
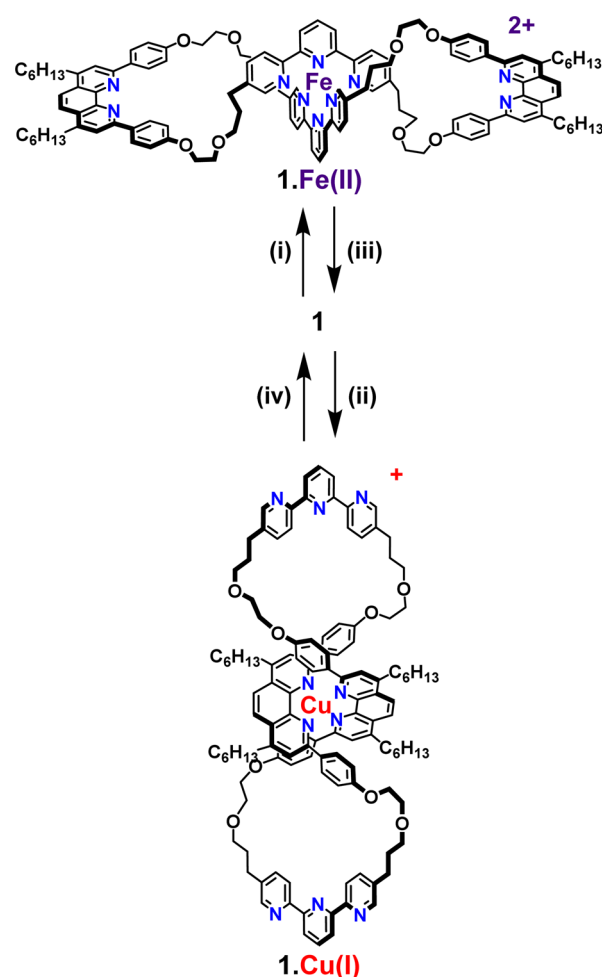

Figure 1. Metalation−demetalation−remetalation, $\mathbf{1}\cdot Fe(II)−\mathbf{1}−\mathbf{1}\cdot Cu$-(I): (i) $Fe(OTf)_2$, CH_2Cl_2/MeOH, rt, 5 min, 97%; (ii) $[Cu(CH_3CN)_4]$-PF_6, CH_2Cl_2/CH_3CN, rt, 5 min, 99%; (iii) Cs_2CO_3, DMF, 70 °C, 1 h, 96%; (iv) KCN, water/CH_3CN, rt, 12 h, 95%. The Fe(II) and Cu(I) complexes were isolated as racemates. From literature structural data or CPK models, one can estimate the dimensions of the figure-of-eight in each situation. As far as the vertical axis is concerned, the "thickness" of the iron(II) complex can be estimated as the distance between the two 4′ hydrogen atoms: d(4′-4′) ~11 Å.[14] The height of the copper(I) complex is much larger: d(4′-4′) ~30 Å according to CPK models.

The copper(I) complex involves the dpp fragments, which clearly fit in together, as shown by the strong upfield shift of the m protons. As in related complexes,[15] the m protons of a given dpp unit are located in the shielding region of the 1,10-phenanthroline nucleus belonging to the other dpp fragment. In the free ligand, the doublet of the m protons is centered at 7.13 ppm, whereas the signal of the same protons is found at 6.14 ppm in the copper(I) complex. Interestingly, the m protons of the iron(II) complex resonate at a normal chemical shift (6.94 ppm), indicating that the dpp fragments in the Fe(II) complex are not interacting with the metal center and are not in an intertwined arrangement (Figure 2).

In the Fe(II) complex, the upfield shift undergone by the 6 and 6″ protons is spectacular. In the free molecule and in its copper(I) complex, these protons resonate at normal positions (8.55−8.46 ppm). These values are in deep contrast with the
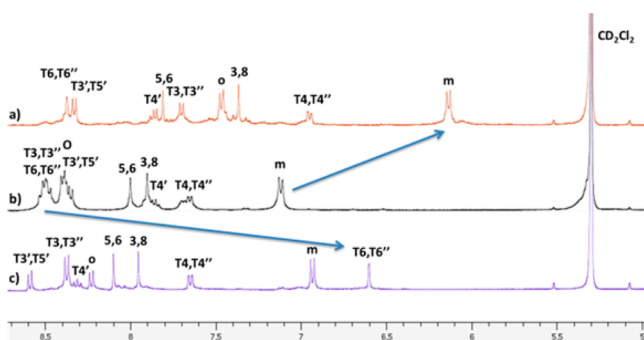
Figure 2. Partial ^1H NMR spectra in CD_2Cl_2 of (a) copper(I) complex $[\mathbf{1}\cdot Cu^{2+}]\cdot[OTf^-]_2$; (b) free macrocyclic ligand **1**; (c) $[\mathbf{1}\cdot Fe^{2+}]\cdot[OTf^-]_2$. Atom numbering is indicated in Figure 1. Full assignment of the signals shows the very significant difference between the spectra of the three compounds and thus the drastic geometrical changes undergone by the organic backbone by metalating the metal-free ring by copper(I) or by iron(II), both complexes having completely different shapes.

chemical shift of the iron(II) complex $[\mathbf{1}\cdot Fe^{2+}]\cdot[OTf^-]_2$ 6 and 6″ protons whose signal is centered around 6.61 ppm. In this case, the terpy fragment exerts a very strong ring current effect, which induces a large upfield shift onto the 6 and 6″ protons belonging to the other terpy. This upfield shift is even enhanced by the fact that a metal-coordinated terpy is distorted, leading to a "pinched" conformation bringing the 6 and 6″ protons to close proximity of the other terpy nucleus. The strong upfield shift of protons 6 and 6″ is analogous to that found in a related figure-of-eight bis-terpy Fe(II) complex previously reported by our group.[16]

The cyclic voltammogram of Figure 3 tends to indicate that after oxidation of the 4-coordinate complex at +0.65 V in the
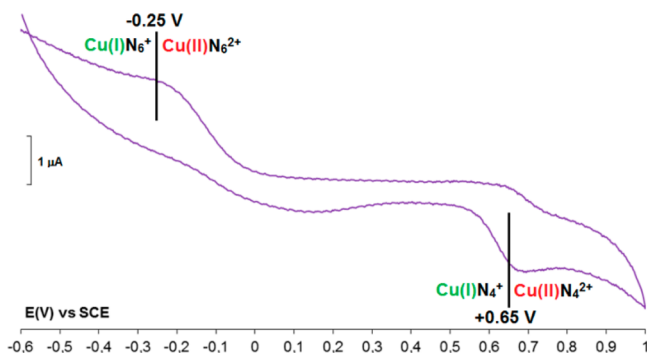

Figure 3. Cyclic voltammogram of $[\mathbf{1}\cdot Cu^+]\cdot[PF_6^-]$ in CH_3CN. Supporting electrolyte: 0.1 M $nBu_4N^+\cdot PF_6^-$; Pt electrode, SCE, 20 mV/s, −0.6 to +1 V. The anodic scan shows mostly oxidation of the 4-coordinate copper(I) complex to copper(II) with an oxidation wave around +0.65 V. The reductive scan (+1 to −0.6 V) shows a relatively intense wave around −0.25 V, indicative of a 6-coordinate copper(II) complex.

course of the −0.6 V to +1 V scan, the unstable copper(II) complex obtained rearranges. Indeed, by inverting the scan potential at +1 V and by scanning from +1 to −0.6 V, the main wave is observed at a negative potential (−0.25 V). It corresponds to reduction of a 6-coordinate copper(II) complex to copper(I). A related behavior has already been observed with copper-complexed catenanes,[2c,17] although in these previous examples, rearrangement of the thermodynamically unstable copper(II) complexes obtained as transient species was much slower than in the present noninterlocking system. A similar

behavior was observed by increasing the scan rate from 20 to 200 mV/s. These electrochemical experiments clearly establish that a fast rearrangement of the bis-dpp copper(II) complex to a bis-terpy complex takes place. In other words, contraction or extension of the copper-complexed figure-of-eight can be driven by an electrochemical signal. The height of $[\mathbf{1}\cdot Cu(II)^{2+}]$ is very similar to that of the Fe(II) analogous complex (as drawn in Figure 2) and is expected to be small (∼11 Å), whereas that of the copper(I) complex is probably close to 30 Å.

The geometrical analogy between copper(II) and iron(II) in terpy complexes supports the idea that the copper(II) complex $[\mathbf{1}\cdot Cu^{2+}]\cdot[OTf^-]_2$ is a bis-terpy complex.

In conclusion, a new metal-complexed figure-of-eight has been synthesized and shown to be a dynamic system. The compound can be contracted or elongated using a chemical signal (metal exchange) or an electrochemical process (Cu^{II}/Cu^I). The contraction and elongations processes are concerted in the sense that each process triggers an opposite process in an orthogonal direction (8 is converted to ∞ and vice versa). Interestingly, figure-of-eight complexes could also be used in contraction/extension of oligomers or polymers thus leading to muscle-like species. We also note that transition metal-driven threading of the free loops of the copper- or iron-complexed figure-of-eight by various coordinating fragments could lead to novel topologies.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Additional analytical data of compounds **1**, $[\mathbf{1}\cdot Fe^{2+}]\cdot[OTf^-]_2$, $[\mathbf{1}\cdot Cu^+]\cdot[PF_6^-]$, and $[\mathbf{1}\cdot Cu^{2+}]\cdot[OTf^-]_2$. 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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■ REFERENCES

(1) (a) Howard, J. *Annu. Rev. Physiol.* **1996**, *58*, 703. (b) Horwich, A. L.; Farr, G. W.; Fenton, W. A. *Chem. Rev.* **2006**, *106*, 1917. (c) Asbury, C. L.; Fehr, A. N.; Block, S. M. *Science* **2003**, *302*, 2130. (d) Vale, R. D.; Milligan, R. A. *Science* **2000**, *288* (5463), 88. (e) Bath, J.; Turberfield, A. J. *Nat. Nanotechnol.* **2007**, *2*, 275. (f) Noji, H.; Yasuda, R.; Yoshida, M.; Kinosita, K. *Nature* **1997**, *386*, 299. (g) Walker, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2308.

(2) (a) Ballardini, R.; Balzani, V.; Gandolfi, M. T.; Prodi, L.; Venturi, M.; Philp, D.; Ricketts, H. G.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **1993**, *32*, 1301. (b) Bissell, R. A.; Cordova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133. (c) Livoreil, A.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 9399.

(3) (a) Catenanes, Rotaxanes, and Knots. In *Organic Chemistry*; Schill, G., Ed.; Academic Press: New York, 1971; Vol. *22*. (b) Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795. (c) Hunter, C. *J. Am. Chem. Soc.* **1992**, *114*, 5303. (d) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725. (e) Vögtle, F.; Dünnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451. (f) Hamilton, D. G.; Feeder, N.; Prodi, L.; Teat, S. J.; Clegg, W.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1998**, *120*, 1096.

(g) Dietrich-Buchecker, C.; Sauvage, J.-P. *Molecular Catenanes, Rotaxanes and Knots. A Journey Through the World of Molecular Topology*; Wiley-VCH: Weinheim, 1999. (h) Fujita, M. *Acc. Chem. Res.* **1999**, *32*, 53. (i) Harada, H. *Acc. Chem. Res.* **2001**, *34*, 456. (j) Kim, K. *Chem. Soc. Rev.* **2002**, *31*, 96. (k) Felder, T.; Schalley, C. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 2258. (l) Loren, J. C.; Gantzel, P.; Linden, A.; Siegel, J. S. *Org. Biomol. Chem.* **2005**, *3*, 3105. (m) Lankshear, M. D.; Beer, P. D. *Acc. Chem. Res.* **2007**, *40*, 657. (n) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72. (o) Megiatto, J. D., Jr.; Schuster, D. I. *J. Am. Chem. Soc.* **2008**, *130*, 12872. (p) Faiz, J. A.; Heitz, V.; Sauvage, J.-P. *Chem. Soc. Rev.* **2009**, *38*, 422. (q) Li, S.; Taura, D.; Hashidzume, A.; Harada, A. *Chem.—Asian J.* **2010**, *5*, 2281. (r) Nakatani, Y.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2010**, *49*, 5463. (s) Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. *Chem. Rev.* **2011**, *111*, 5434. (t) Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurney, R. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 9260.

(4) Machines and catenanes: (a) Stoddart, J. F. *Acc. Chem. Res.* **2001**, *34*, 409. (Special Issue on Molecular Machines) and references therein. (b) Molecular Machines and Motors. In *Structure and Bonding*; Sauvage, J.-P., Ed.; Springer: Berlin, 2001. (c) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72. (d) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines—Concepts and Perspectives for the Nanoworld*; Wiley-VCH: Weinheim, 2008. (e) Durot, S.; Reviriego, F.; Sauvage, J.-P. *Dalton Trans.* **2010**, *39*, 10557. (f) Davidson, G. J. E.; Sharma, S.; Loeb, S. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4938.

(5) Noninterlocking machines: (a) Kelly, T. R.; De Silva, H.; Silva, R. A. *Nature* **1999**, *401*, 150. (b) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, H.; Feringa, B. L. *Nature* **1999**, *401*, 152. (c) Zahn, S.; Canary, J. W. *Science* **2000**, *288*, 1404. (d) Kinbara, K.; Aida, T. *Chem. Rev.* **2005**, *105*, 1377. (e) Azov, V. A.; Schlegel, A.; Diederich, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 4635. (f) Carella, A.; Coudret, C.; Guirado, G.; Rapenne, G.; Vives, G.; Launay, J.-P. *Dalton Trans.* **2007**, 177. (g) Kinbara, K.; Muraoka, T.; Aida, T. *Org. Biomol. Chem.* **2008**, *6*, 1871. (h) Klok, M.; Boyle, N.; Pryce, M. T.; Meetsma, A.; Browne, W. R.; Feringa, B. L. *J. Am. Chem. Soc.* **2008**, *130*, 10484. (i) Iordache, A.; Oltean, M.; Milet, A.; Thomas, F.; Baptiste, B.; Saint-Aman, E.; Bucher, C. *J. Am. Chem. Soc.* **2012**, *134*, 2653. (j) Lang, T.; Graf, E.; Kyritsakas, N.; Hosseini, M. W. *Chem.—Eur. J.* **2012**, *18*, 10419.

(6) Functional machines: (a) Balzani, V.; Clemente-Leon, M.; Credi, A.; Ferrer, B.; Venturi, M.; Flood, A. H.; Stoddart, J. F. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 1178. (b) Berna, J.; Leigh, D. A.; Lubomska, M.; Mendoza, S. M.; Perez, E. M.; Rudolf, P.; Teobaldi, G.; Zerbetto, F. *Nat. Mater.* **2005**, *4*, 704. (c) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172. (d) Eelkema, R.; Pollard, M. M.; Vicario, J.; Katsonis, N.; Ramon, B. S.; Bastiaansen, C. W. M.; Broer, D. J.; Feringa, B. L. *Nature* **2006**, *440*, 163. (e) Green, J. E.; Wook Choi, J.; Boukai, A.; Bunimovich, Y.; Johnston-Halperin, E.; DeIonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shik Shin, Y.; Tseng, H.-R.; Stoddart, J. F.; Heath, J. R. *Nature* **2007**, *445*, 414. (f) Koçer, A.; Walko, M.; Meijberg, W.; Feringa, B. L. *Science* **2005**, *309*, 755. (g) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174. (h) Nguyen, T. D.; Liu, Y.; Saha, S.; Leung, K. C.-F.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2007**, *129*, 626.

(7) Lewandowski, B.; De Bo, G.; Ward, J. W.; Papmeyer, M.; Kuschel, S.; Aldegunde, M. J.; Gramlich, P. M. E.; Heckmann, D.; Goldup, S. M.; D'Souza, D. M.; Fernandes, A. E.; Leigh, D. A. *Science* **2013**, *339*, 189.

(8) (a) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, *374*, 790. (b) Amendola, V.; Fabbrizzi, L.; Mangano, C.; Pallavicini, P. *Acc. Chem. Res.* **2001**, *34*, 488. (c) Fabbrizzi, L.; Foti, F.; Patroni, S.; Pallavicini, P.; Taglietti, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5073.

(9) Two early examples of controlled ring expansion or contraction are the following ones: (a) Ueno, A.; Yoshimura, H.; Saka, R.; Osa, T. *J. Am. Chem. Soc.* **1979**, *101*, 2779. (b) Shinkai, S.; Honda, Y.; Kusano, Y.; Manabe, O. *Chem. Commun.* **1982**, 848. (c) A remarkable example of a single ring able to fold up in two distinct ways under the action of given chemical signals was reported a few years ago. It is based on the pH-driven translocation of Cu^{2+} ions between different coordination sites. The same process can occur by coordinating imidazole to the dicopper(II) complex of the ring: Fabbrizzi, L.; Foti, F.; Patroni, S.; Pallavicini, P.; Taglietti, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5073.

(10) (a) Jimenez, M.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3284. (b) Jimenez, M.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Commun.* **2003**, 1613. (c) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddart, W. A.; Ho, C.-M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745. (d) Wu, J.; Leung, K. C.-F.; Benitez, D.; Han, J.-Y.; Cantrill, S. J.; Fang, L.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 7470. (e) Stadler, A.-M.; Kyritsakas, N.; Graff, R.; Lehn, J.-M. *Chem.—Eur. J.* **2006**, *12*, 4503. (f) Tsukagoshi, S.; Miyawaki, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *Org. Lett.* **2007**, *9*, 1053. (g) Coutrot, F.; Romuald, C.; Busseron, E. *Org. Lett.* **2008**, *10*, 3741. (h) Dawson, R. E.; Lincoln, S. F.; Easton, C. J. *Chem. Commun.* **2008**, 3980. (i) Chuang, C.-J.; Li, W.-S.; Lai, C.-C.; Liu, Y.-H.; Peng, S.-M.; Chao, I.; Chiu, S.-H. *Org. Lett.* **2009**, *11*, 385. (j) Du, G.; Moulin, E.; Jouault, N.; Buhler, E.; Giuseppone, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 12504. (k) Ikeda, T.; Mamiya, J.-I.; Yu, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 506. (l) Bléger, D.; Liebig, T.; Thiermann, R.; Maskos, M.; Rabe, J. P.; Hecht, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 12559.

(11) Compound 1: ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) δ = 8.55−8.46 (m, 8H, $H_{T3,T3'',T6,T6''}$), 8.43−8.33 (m, 12H, $H_{O,T3',T5'}$), 8.01−7.83 (m, 10H, $H_{3,5,6,8,T4'}$), 7.71−7.62 (m, 4H, $H_{T4,T4''}$), 7.13 (d, ^3J = 8.7 Hz, 8H, H_m), 4.20 (t, ^3J = 4.3 Hz, 8H, H_ε), 3.79 (t, ^3J = 4.7 Hz, 8H, H_δ), 3.59−3.44 (m, 8H, H_γ), 3.16 (t, ^3J = 7.4 Hz, 8H, H_a), 2.75 (t, ^3J = 7.2 Hz, 8H, H_α), 2.00−1.88 (m, 8H, H_β), 1.87−1.76 (m, 8H, H_b), 1.54−1.44 (m, 8H, H_c), 1.40−1.29 (m, 16H, $H_{d,e}$), 0.90 (t, ^3J = 6.7 Hz, 12H, H_f); ^{13}C NMR ($CD2Cl2$, 100 MHz, 25 °C) δ = 160.4, 155.8, 155.5, 154.3, 149.8, 149.6, 147.1, 138.1, 137.2, 137.1, 133.0, 129.1, 126.6, 121.5, 120.9, 120.7, 120.6, 119.4, 119.3, 115.1, 70.3, 69.7, 67.9, 33.3, 32.1, 31.2, 30.9, 29.8, 29.5, 23.0, 14.3; HR-MS (ES) cald for $C_{122}H_{134}N_{10}O_8$ 1868.0459 $[M + H]^+$, found 1868.0402.

(12) (a) Compound $[1·Cu(I)^+]·[PF_6^-]$: ^{1}H NMR (CD_2Cl_2, 400 MHz, 25°C) δ = 8.34 (s, 4H, $H_{T6,T6'}$), 8.33 (d, ^3J = 8.0 Hz, 4H, $H_{T3',T5'}$), 7.87 (t, ^3J = 7.4 Hz, 2H, $H_{T4'}$), 7.81 (s, 4H, $H_{5,6}$), 7.70 (d, ^3J = 8.0 Hz, 4H, $H_{T3-T3''}$), 7.47 (d, ^3J = 8.4 Hz, 8H, H_o), 7.34 (s, 4H, $H_{3,8}$), 6.95 (d, ^3J = 8.2 Hz, 4H, $H_{T4,T4''}$), 6.14 (d, ^3J = 8.4 Hz, 8H, H_m), 3.85−3.69 (m, 8H, H_ε), 3.61−3.46 (m, 8H, H_δ), 3.36−3.19 (m, 8H, H_γ), 2.97−2.74 (m, 8H, H_a), 2.44 (t, ^3J = 7.3 Hz, 8H, H_α), 1.75−1.61 (m, 16H, $H_{b,\beta}$), 1.47−1.41 (m, 8H, H_c), 1.38−1.31 (m, 16H, $H_{d,e}$), 0.93 (t, ^3J = 6.7 Hz, 12H, H_f); HR-MS (ES) cald for $C_{122}H_{134}CuN_{10}O_8^+$ 965.487 $[M + H]^+/2$, found 965.485. (b) Compound $[1·Fe(II)^{2+}]·[OTf]_2$: ^{1}H NMR (CD_2Cl_2, 400 MHz, 25°C) δ = 8.59 (d, ^3J = 8.0 Hz, 4H, $H_{T3',T5'}$), 8.38 (d, ^3J = 8.4 Hz, 8H, $H_{T3,T3''}$), 8.32 (t, ^3J = 8.0 Hz, 2H, $H_{T4'}$), 8.23 (d, ^3J = 8.0 Hz, 4H, H_o), 8.10 (s, 4H, $H_{5,6}$), 7.96 (s, 4H, $H_{3,8}$), 7.65 (d, ^3J = 8.4 Hz, 4H, $H_{T4,T4''}$), 6.94 (d, ^3J = 8.6 Hz, 8H, H_m), 6.61 (s, 4H, $H_{T6,T6''}$), 3.96 (t, ^3J = 4.0 Hz, 8H, H_ε), 3.63−3.47 (m, 8H, H_δ), 3.30−3.16 (m, 16H, $H_{\gamma,a}$), 3.12−3.05 (m, 8H, H_α), 2.38−2.29 (m, 8H, H_β), 1.93−1.82 (m, 8H, H_b), 1.55−1.49 (m, 8H, H_c), 1.44−1.32 (m, 16H, $H_{d,e}$), 0.92 (t, ^3J = 6.8 Hz, 12H, H_f); HR-MS (ES) cald for $C_{122}H_{134}FeN_{10}O_8^{2+}$ 961.4863 M/2, found 961.4880.

(13) Prikhod'ko, A. I.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2009**, *131*, 6794.

(14) Nakayama, Y.; Baba, Y.; Yasuda, H.; Kawakita, K.; Ueyama, N. *Macromolecules* **2003**, *36*, 7953.

(15) (a) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Tetrahedron* **1983**, *24*, 5095. (b) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1984**, *106*, 3043.

(16) Belfrekh, N.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Inorg. Chem.* **2000**, *39*, 5169.

(17) Cárdenas, D. J.; Livoreil, A.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 11980.