Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Helix Architecture and Helicity Switching via Dynamic Metal Coordination Chemistry

Hiroyuki Miyake[a]; Hiroshi Tsukube[a]
[a] Department of Chemistry, Graduate School of Science, Osaka City University, Osaka, Japan

To cite this Article Miyake, Hiroyuki and Tsukube, Hiroshi(2005) 'Helix Architecture and Helicity Switching via Dynamic Metal Coordination Chemistry', Supramolecular Chemistry, 17: 1, 53 — 59
To link to this Article: DOI: 10.1080/10610270412331328790
URL: http://dx.doi.org/10.1080/10610270412331328790

Supramolecular Chemistry, January–March 2005 VOL. 17 (1–2), pp. 53–59

Taylor & Francis
Taylor & Francis Group

Helix Architecture and Helicity Switching via Dynamic Metal Coordination Chemistry

HIROYUKI MIYAKE* and HIROSHI TSUKUBE

Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Received (in Austin, USA) 22 July 2004; Accepted 15 September 2004

A variety of metal complex helicates have been developed for helix architecture and helicity switching via ligand optimization. Among them, kinetically labile metal helicates offered dynamic inversion of complex helicity induced by external stimuli. They are promising candidates for excellent supramolecular devices based on dynamic metal coordination chemistry.

Keywords: Helicity; Inversion; Labile complex; Stimulus response; Duplex; Triplex

INTRODUCTION

Molecular programming toward the design of helical structures and their dynamic inversion has been actively studied for developing new nanoscaled molecular machines with biomimetic functions. Several types of foldamers, natural and artificial polymers and natural/artificial hybrid systems have been reported to give supramolecular helices [1–3]. The metal complexes also offer a promising strategy for developing structurally and functionally defined supramolecules due to their characteristic coordination geometry, redox activities and unique spectroscopic and magnetic properties. Several types of kinetically “labile metal complexes ” have successfully provided unique machine-like motion including dynamic rotations, translations, stretching and shape flipping [4–9]. In this review, we summarize the metal complex strategy toward generation and switching of helical structures, comparing them with nonmetal systems. As some labile metal helicates are demonstrated to offer dynamic inversion of their helical structures via noncovalent interaction with external signals, a new class of supramolecular sensors and switching and memory devices can be constructed using the metal helicate approach.

HELICITY INDUCTION AND HELICITY SWITCHING VIA NONMETAL COORDINATION

Nature organizes various helical architectures to offer special biological functions. For example, DNAs usually have duplex structures with right-handed helicity, but some of them form left-handed double helices upon external stimuli [10]. As illustrated in Fig. 1 [11], the right-handed double helix (B-DNA) of d(CGCGCG) is typically inverted to a left-handed double helix (Z-DNA), depending on salt concentration, temperature and other environmental factors.

As helical inversion of biopolymers is thought to trigger biological events, many efforts to mimic helical inversion phenomena have been made using organic molecules. Nakashima *et al.* typically demonstrated that achiral polysilylene polymer **1** had asymmetric helical structures upon interaction with chiral alcohols [12]. Although achiral **1** showed no circular dichroism (CD) signal, addition of (*S*)-2-butanol induced a positive CD signal around 350 nm, while (*R*)-2-butanol showed a negative signal. Xu *et al.* recently reported that right-handed helicene (*P*)-**2** bound left-handed Z-DNA more efficiently than right-handed B-DNA [13]. As (*P*)-**2** effectively converted the B-DNA to the Z-DNA form through

---

*Corresponding author. Tel.: +81-6-6605-3124. Fax: +81-6-6605-2522. E-mail: miyake@sci.osaka-cu.ac.jp

ISSN 1061-0278 print/ISSN 1029-0478 online © 2005 Taylor & Francis Ltd
DOI: 10.1080/10610270412331328790

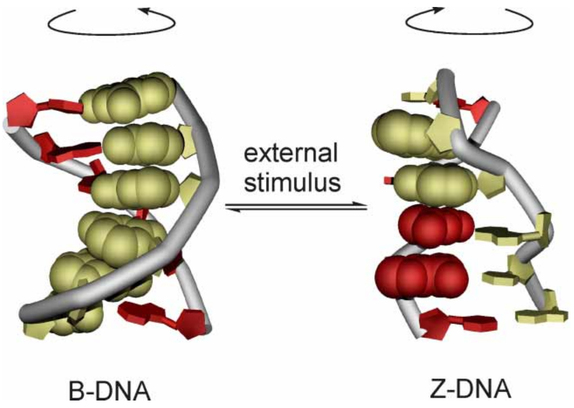
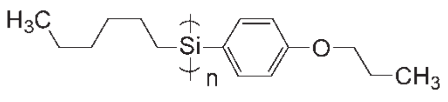


FIGURE 1 Double-helix structures of DNA d(CGCGCG).

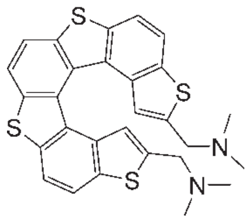
noncovalent interaction, a new route was proposed for the biological switching functions of Z-DNA.

METAL COMPLEX STRATEGY FOR HELIX ARCHITECTURE

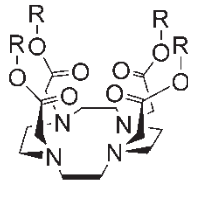
A variety of metal complexes with bipyridine and related heteroaromatic ligands are known to form duplex and triplex helicates [14–19]. Imbert *et al.* designed a hybrid-type ligand **3** that included a bidentate coordinating site for the 3d metal cation and a tridentate site for the 4f metal cation. This formed a bimetallic triplex-stranded helicate in which the Cr^{3+} cation was coordinated by three bidentate sites and the Ln^{3+} (Nd^{3+} and Yb^{3+}) cation was coordinated by three tridentate sites [20]. The resulting triplex interestingly exhibited extended lifetimes of lanthanide-based near-infrared luminescence in the millisecond range via a Cr$^{3+} \rightarrow$ Ln^{3+} energy-transfer mechanism (Fig. 2). Shinoda *et al.* systematically synthesized ester-armed cyclens **4**, which formed octadentate Na^{+} complexes, to offer quadruplicated helical geometry [21,22]. A further combination of octadentate complex and chiral ligand cyclen realized the integration of helical metal complexes at the supramolecular level.



1



2



4

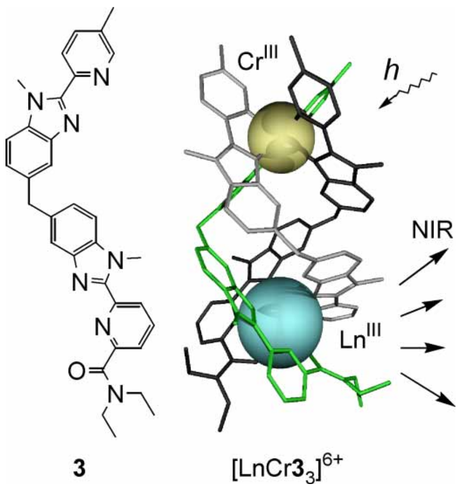


FIGURE 2 Bimetallic triplex architecture exhibiting long lifetime near-infrared luminescence.

METAL COMPLEX STRATEGY FOR HELICITY INDUCTION

More refined molecular programming has been achieved by the use of chirality. Because the direction of the helical structure can be controlled by a suitable combination of chiral ligands and metal centers, there are two possible approaches to control the helical structures of the metal complexes. Figure 3 illustrates schematically the uses of ligand chirality and complex helicity for helicity induction, where "ligand chirality" is defined as the chirality of the additional ligand to give the twisted geometry between two chromophoric groups (Fig. 3a) and "complex helicity" is the chirality at the metal center, which can trigger supramolecular helicity (Fig. 3b). As the direction of "complex helicity" is determined by the chirality of the coordinating ligand, it can be

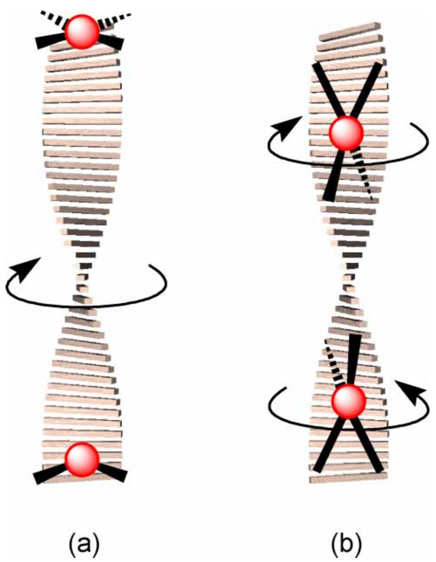
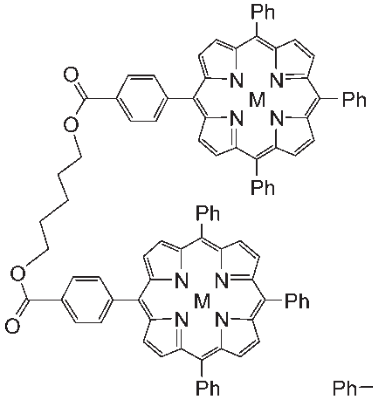
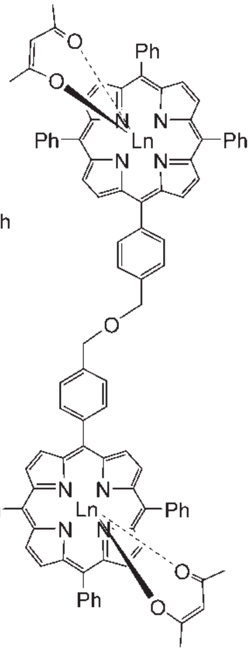


FIGURE 3 Molecular programming based on (a) ligand chirality and (b) complex helicity.

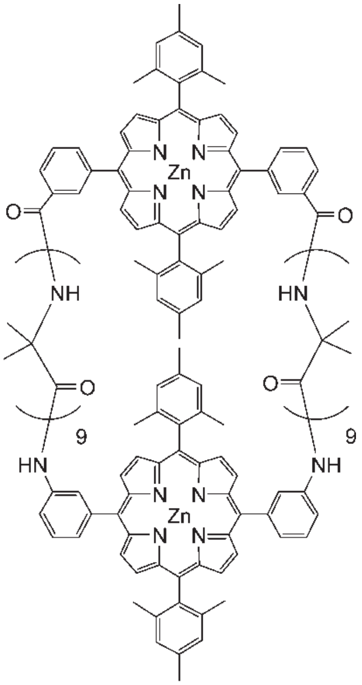
switched by interaction of external stimuli with the metal center and/or the ligand.



5 (M = Zn, Mg)



6 (Ln = Yb, Gd)



7

The helical sense of bisporphyrin-metal complexes **5**–**7** was programmed in which a chiral external ligand asymmetrically bridged two metal centers ("ligand chirality", see Fig. 3a). When the bisporphyrin complex **5** including Zn^{2+} or Mg^{2+} was bound by a chiral amine or amide, the twisted geometry between the two porphyrin rings was asymmetrically fixed [23]. The bisporphyrin complex is achiral, but chirality of the external bidentate ligand induced supramolecular chirality. The zwitterionic cystine worked as an effective external chiral ligand in the cases of bisporphyrinates **6** including Yb^{3+} and Gd^{3+} [24], and the helical oligopeptide with two pyridyl binding sites operated well in the bisporphyrin **7** system [25]. In these bisporphyrin-metal complexes, the directions of their helices were significantly controlled by the chirality of external ligands. As the metal porphyrinates are chromophoric, the generated helical structures gave intense induced CD signals around the porphyrin Soret bands, which offered CD chirality sensing of external stimuli.

METAL COMPLEX STRATEGY FOR HELICITY SWITCHING

The helicity of metal complexes has been effectively inverted and switched by dynamic ligand rearrangements, coupled with coordination from achiral species and redox reactions of the metal center. Chambers *et al.* reported that the coordinating counteranions altered the helical direction of the octahedral Co^{3+} complex. When the isolated Λ *cis*-α $[Co^{III}(\mathbf{8})Cl_2]ClO_4$ complex reacted with sodium oxalate in hot water, Δ *cis*-α $[Co^{III}(\mathbf{8})(ox)]ClO_4$ was obtained [26]. Although the helicity of the Co^{3+} complex was inverted by external stimulus, the inert complex properties yielded very slow processes. By contrast, "labile Co^{2+} complexes" exhibited dynamic ligand exchange kinetics and offered dynamic helicity inversion. We recently demonstrated that the helical sense of the "labile Co^{2+} complex" with the chiral tetradentate ligand **9** was rapidly inverted upon the addition of the achiral NO_3^- anion [27]. The crystal structure of $[Co^{II}(\mathbf{9})(MeOH)_2](ClO_4)_2$ revealed that the Co^{2+} center was coordinated by two amine nitrogen atoms and two amide oxygen atoms of the ligand and two methanol oxygen atoms from the solvent to form the Λ *cis*-α configuration (Fig. 4a). The ^1H NMR spectrum showed that all signals appeared in the paramagnetic range with C_2 symmetrical patterns (major isomer/minor isomer = 97.5/2.5). This indicates that the asymmetric helical structure was retained in the solution. This complex exhibited a positive CD signal in the range of d–d transition. As the sign of the CD signal was notably reversed by addition of NO_3^- (Fig. 5), the helicity around the Co^{2+} center was inverted from the Λ to the Δ form. Two equivalents of NO_3^- were required for complete inversion of the CD signals (inset of Fig. 5). The $Co(NO_3)_2$ complex with ligand

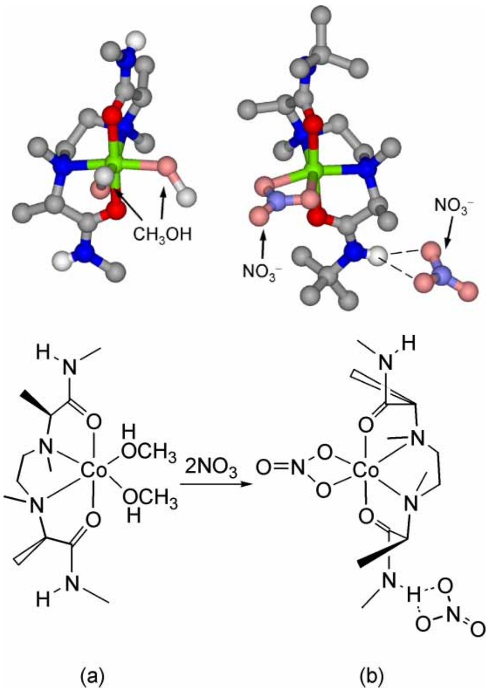
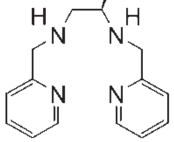


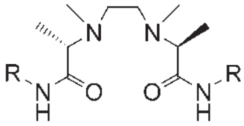
FIGURE 4 Helicity inversion of Λ *cis*-α $[Co(\mathbf{9})(MeOH)_2](ClO_4)_2$ (a) to the corresponding Δ form (b).

10 was isolated, in which one NO_3^- coordinated with the Co^{2+} center in a bidentate chelate fashion and the other NO_3^- hydrogen bonded with the amide hydrogen. Thus, the cooperative action of two NO_3^- anions was thought to stabilize the Δ form more effectively than the corresponding Λ form (Fig. 4b).

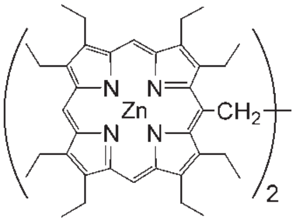
The interaction between achiral species and coordinating ligands also induced helicity inversion of the metal helicates. Yano *et al.* reported that a "labile Co^{2+} complex" with the sugar-based heptadentate tripodal ligand **11** reversibly changed its helical structure ($\Lambda \rightleftharpoons \Delta$) in the presence of the SO_4^{2-} anion (Fig. 6) [28]. The multiple hydrogen-bonding formation between the SO_4^{2-} anion and OH groups of the sugar ligand regulated the direction of the sugar units and changed the helicity around the Co^{2+} center. The solvent also acted as an effective stimuli to invert the helical sense of the bisporphyrin metal complex [29,30]. Borovkov *et al.* reported that the coordination of a chiral amino acid ester with the zinc bisporphyrin complex **12** provided a supramolecular helical structure. This showed that the sign of the CD signal depended on the nature of the solvent, and the interaction of the solvent with the polar substituent of the coordinating amino acid ester was thought to be important.



8



9 R = Me
10 R = ${}^tBu$



12

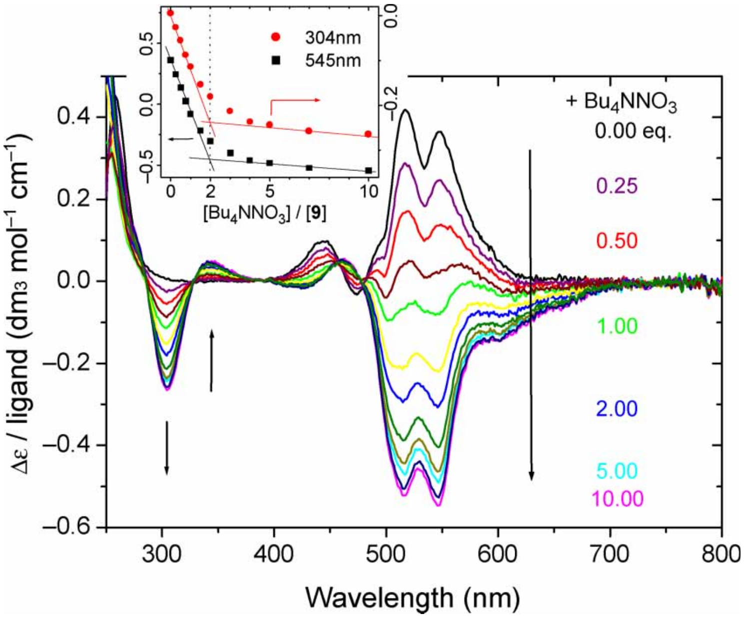


FIGURE 5 CD spectral changes of a 1:1 mixture of **9** and $Co(ClO_4)_2{\cdot}2H_2O$ upon the addition of Bu_4NNO_3 in CH_3CN/CH_2Cl_2 (1/9). Inset: Titration profiles of the CD amplitudes at 304 and 545 nm.

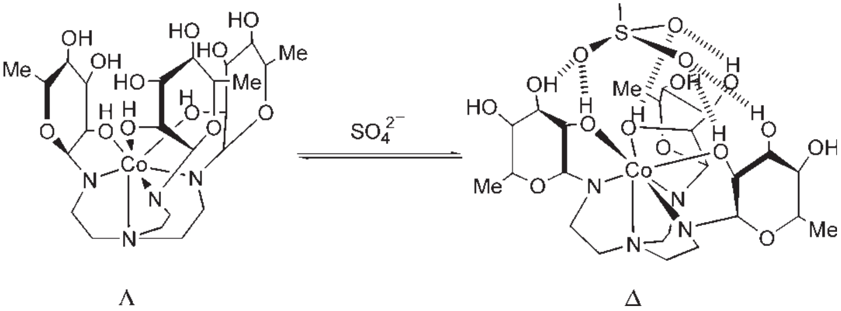
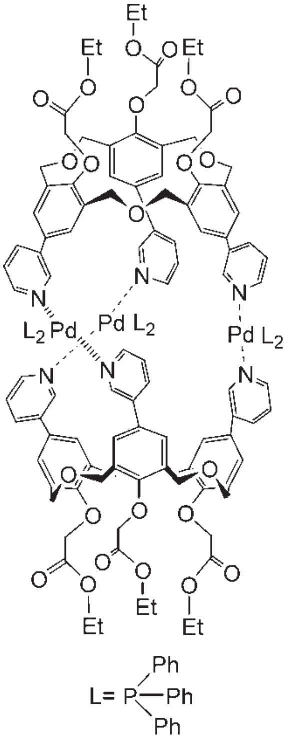


FIGURE 6 Helicity inversion of Co^{2+} complex with **11**.

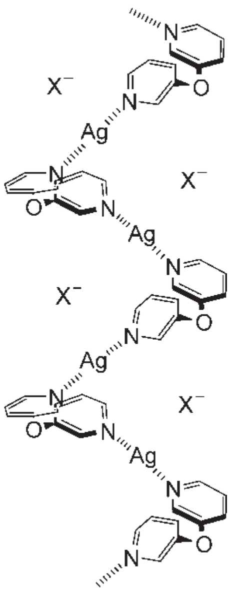
Electrochemical control of metal complex helicity was successfully developed by Canary and coworkers (Fig. 7). The hard Cu^{2+} ion favored coordination from the hard $-CO_2^-$ group of the ligand **13**, while the soft Cu$^+$ ion preferred the soft methionine sulfur atom. As reduction of the hard Cu^{2+} to the soft Cu$^+$ ion switched the metal coordination site, the asymmetric arrangement of the two quinoline chromophores was altered [31,32].

METAL COMPLEX STRATEGY FOR HELICAL MOLECULAR MACHINES

Helical molecules often exhibited dynamic equilibrium between left-handed (*M*) and right-handed (*P*) helical structures, and have the potential to be unique molecular machines. Hiraoka *et al.* recently designed a sandwich-shaped Ag$^+$ complex with the disk-shaped ligand **14**, in which a fast flip motion occurred between the helical structures [(*P*) $\rightleftharpoons$ (*M*)] (Fig. 8) [33]. The motion rate decreased considerably with an increase in the ring size of the ligand (**14** → **15**). Ikeda *et al.* constructed a capsule-like molecule of homooxacalix[3]aryl ester-Pd^{2+} complex **16**. This had a helical structure and showed dynamic helical flipping motion, which could be controlled by the inclusion of chiral guest molecules [34]. A smart molecular spring was developed by Jung *et al.* [35]. When the skew-shaped ligand Py$_2$O (3,3′-oxybispyridine) complexed a Ag$^+$ cation in a linear coordination fashion, polymeric helices [Ag(Py$_2$O)]X(X = NO$_3^-$, BF$_4^-$, ClO$_4^-$ and PF$_6^-$) **17** were formed. The pitch of the helix was reversibly stretched by counteranion exchange and the large PF$_6^-$ anion exhibited a larger pitch than the smaller NO$_3^-$ anion [35].



16



17

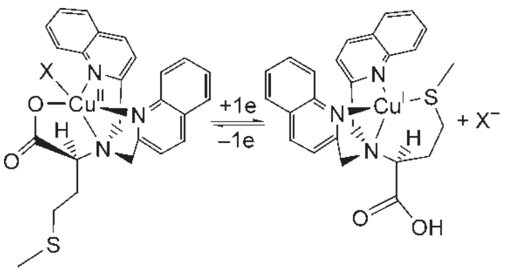
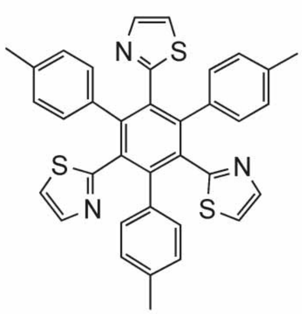


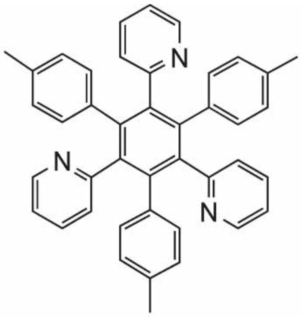
FIGURE 7 Helicity inversion of complex with **13**.

CONCLUSIONS

We have highlighted helicity induction and helicity switching systems involving metal coordination. Several types of kinetically labile metal complexes exhibit dynamic helicity switching phenomena. The external stimuli effectively invert their helicity in a few minutes. Supramolecular machines have been designed using the metal complex strategy. Further



14



15

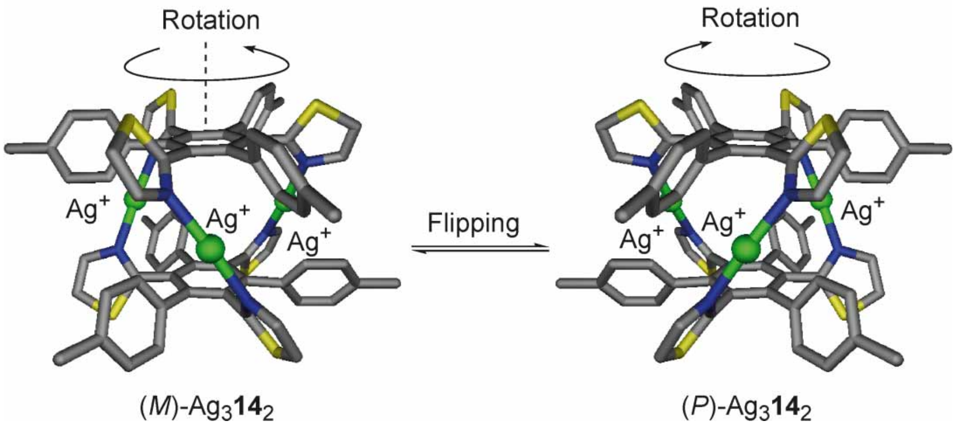


FIGURE 8 Flip motion between (*P*)- and (*M*)-helical structures in $Ag_3\mathbf{14}_2$ complex.

ligand architecture can provide various types of helical metal complexes with fascinating functions, some of which may be applicable as a new series of supramolecular machines.

Acknowledgements

We are grateful for Grant-in-Aids for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan and from the Japan Society for the Promotion of Science. Financial support from the Inoue Foundation for Science is also appreciated. Appreciation is also expressed to Kagakudojin, Wiley-VCH and the American Chemical Society for their permission to use Figs. 1–5 and 8.

References

[1] Rowan, A. E.; Nolte, R. J. M. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 63.
[2] Huc, I. *Eur. J. Org. Chem.* **2004**, 17.
[3] Yashima, E.; Maeda, K.; Nishimura, T. *Chem. Eur. J.* **2004**, *10*, 42.
[4] Dietrich-Buchecker, C.; Jimenez-Molero, M. C.; Sartor, V.; Sauvage, J.-P. *Pure Appl. Chem.* **2003**, *75*, 1383.
[5] Chambron, J.-C.; Collin, J.-P.; Heitz, V.; Jouvenot, D.; Kern, J.-M.; Mobian, P.; Pomeranc, D.; Sauvage, J.-P.; Eur *J. Org. Chem.* **2004**, 1627.
[6] Collin, J.-P.; Dietrich-Buchecker, C.; Gaviña, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477.
[7] Barboiu, M.; Prodi, L.; Montalti, M.; Zaccheroni, N.; Kyritsakas, N.; Lehn, J.-M. *Chem. Eur. J.* **2004**, *10*, 2953.
[8] Petitjean, A.; Khoury, R. G.; Kyritsakas, N.; Lehn, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 6637.
[9] Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3348.
[10] Rich, A.; Zhang, S. *Nat. Rev. Genet.* **2003**, *4*, 566.
[11] Lam, S. L.; Au-Yeung, S. C. F. *J. Mol. Biol.* **1997**, *266*, 745.
[12] Nakashima, H.; Koe, J. R.; Torimitsu, K.; Fujiki, M. *J. Am. Chem. Soc.* **2001**, *123*, 4847.
[13] Xu, Y.; Zhang, Y. X.; Sugiyama, H.; Umano, T.; Osuga, H.; Tanaka, K. *J. Am. Chem. Soc.* **2004**, *126*, 6566.
[14] Lehn, J.-M. *Science* **2002**, *295*, 2400.
[15] Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005.
[16] Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457.
[17] Knof, U.; von Zelewsky, A. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 302.
[18] Barboiu, M.; Vaughan, G.; Kyritsakas, N.; Lehn, J.-M. *Chem. Eur. J.* **2003**, *9*, 763.
[19] Barboiu, M.; Lehn, J.-M. *Proc. Natl Acad. Sci. USA* **2002**, *99*, 5201.
[20] Imbert, D.; Cantuel, M.; Bünzli, J.-C. G.; Bernardinelli, G.; Piguet, C. *J. Am. Chem. Soc.* **2003**, *125*, 15698.
[21] Shinoda, S.; Nishimura, T.; Tadokoro, M.; Tsukube, H. *J. Org. Chem.* **2001**, *66*, 6104.
[22] Shinoda, S.; Okazaki, T.; Nishimura, T.; Hori, K.; Tsukube, H. *Chem. Commun.* **2001**, 976.
[23] Proni, G.; Pescitelli, G.; Huang, X.; Nakanishi, K.; Berova, N. *J. Am. Chem. Soc.* **2003**, *125*, 12914.
[24] Tsukube, H.; Tameshige, N.; Shinoda, S.; Unno, S.; Tamiaki, H. *Chem. Commun.* **2002**, 2574.
[25] Guo, Y.-M.; Oike, H.; Aida, T. *J. Am. Chem. Soc.* **2004**, *126*, 716.

[26] Chambers, J. A.; Goodwin, T. J.; Mulqi, M. W.; Williams, P. A. *Inorg. Chim. Acta* **1983**, *75*, 241.

[27] Miyake, H.; Yoshida, K.; Sugimoto, H.; Tsukube, H. *J. Am. Chem. Soc.* **2004**, *126*, 6524.

[28] Yano, S.; Nakagoshi, M.; Teratani, A.; Kato, M.; Onaka, T.; Iida, M.; Tanase, T.; Yamamoto, Y.; Uekusa, H.; Ohashi, Y. *Inorg. Chem.* **1997**, *36*, 4187.

[29] Borovkov, V. V.; Hembury, G. A.; Inoue, Y. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 5310.

[30] Borovkov, V. V.; Hembury, G. A.; Inoue, Y. *Acc. Chem. Res.* **2004**, *37*, 449.

[31] Zahn, S.; Canary, J. W. *Science* **2000**, *288*, 1404.

[32] Barcena, H. S.; Holmes, A. E.; Zahn, S.; Canary, J. W. *Org. Lett.* **2003**, *5*, 709.

[33] Hiraoka, S.; Harano, K.; Tanaka, T.; Shiro, M.; Shionoya, M. *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 5182.

[34] Ikeda, A.; Udzu, H.; Zhong, Z.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 3872.

[35] Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, J. K.; Chae, H. K. *J. Am. Chem. Soc.* **2000**, *122*, 9921.