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Review

Transition metal-based chiroptical switches for nanoscale electronics and sensors

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Contents

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ABSTRACT

Efficient metal-based chiroptical switches have been designed that are capable of achieving multiple stable and reversible states. Studies in this field have yielded a variety of complex molecular devices whose conformations are controllable by many triggering mechanisms including pressure, solvent, counter ion, redox state, and photoinduction. Many of the systems are monitored with precision using circular dichroism spectroscopy. This review aims to provide a brief background of the development of these systems and a comprehensive overview of recently developed metal-based chiroptical switches. Potential applications in electronics and sensor technologies are discussed.

1. Introduction

Recent interest in the burgeoning fields of molecular and optical electronics has led to many exciting discoveries in the sub-field of metal-based chiroptical switches. These materials generally involve a scaffold built upon a transition metal–chelate complex that, upon exposure to an external stimulus, is capable of changing

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its interaction with polarized light. Such molecular switches, which are inherently on the nanometer size scale, could prove to play a key role in the development of future optical displays, molecular electronics, and telecommunications materials.

This article aims to give a current overview of metal-based molecular switches. Although the broader field of molecular switches is diverse and interesting [1–10], chiroptically inactive or non-metal-based switches will not be covered. Many metal-based chiroptical switches have been synthesized within the past decade [11–15]. Most of these systems include a transition metal chelated to multiple atoms of an associated chiral ligand. The conformational state of the chelation complex is altered by a multitude of triggering agents such as photochemical irradiation, reducing/oxidizing agents, counterion exchange, and others. Regardless of which trigger is used, the interconversion between states must be efficient, selective, and reversible. The mechanism may involve structural changes induced by the metal ion directly, such as in redox-triggered molecular switches, or the metal may play a structural role or participate in generation of the readout signal.

The means of analysis of these metal-based chiroptical switches is also critical. A non-destructive readout of the optically active system must be employed in order to gain accurate information about the different states of the switch. Thus, the tools used to accurately assess switching may be limited. Indeed, the presence of the metal may offer limitations on readout, such as quenching fluorescence of the organic ligand, or may offer new opportunities such as presenting additional chromophoric elements that can be monitored.

Chiroptical spectroscopic measurements are powerful tools for the characterization of materials in this field, and may include any form of polarized light measurement [16]. Circular dichroism (CD) is the most commonly used method due to the relatively strong information content of this technique as compared, for example, to single-wavelength optical rotation measurement, and the widespread availability of sensitive CD instruments. Various mechanisms may give rise to CD, including induced and exciton-coupled CD (ECCD). A typical CD spectrum will appear similar to the corresponding UV–vis absorbance spectrum, with amplitude that depends on the strength of the electronic absorbance, the asymmetric distribution of electrons in the molecule, and the coupling between these two phenomena. Unless the spectrum can be calculated explicitly, the features of an induced CD spectrum are difficult to interpret on the basis of structural changes other than by comparing to similar systems.

Exciton-coupled circular dichroism (ECCD) is particularly useful for solution studies, and was reviewed recently [17]. Two chromophores present in a molecule in close proximity to one another may interact, resulting in differentiation of the energies of the transitions. In such a case, two distinct UV–vis bands may, in principle, be observed, with the difference in energy corresponding to the difference between the two absorption maxima ($\lambda_{\max}$). In practice, UV–vis spectra are broad, and two distinct bands are seldom observed. However, in CD spectra, the two coupled absorbances display Cotton effects with opposite signs, resulting in sigmoidal shaped curves. The shape of the curve, the large amplitude of the spectrum, and the correspondence of the null in the CD spectrum characterize such exciton-coupled CD spectra with the $\lambda_{\max}$ from the UV–vis spectrum. Few other spectroscopic signals report structural aspects of molecular conformation or intermolecular association so dramatically as ECCD. By this feature, ECCD can be used as a sensitive probe of changes in molecular conformation or intermolecular association (e.g., stacking).

Although CD has often been used to obtain stereochemical information from solutions, its utility is more limited in the solid-state or aggregates. Methods for obtaining solid-state spectra are currently under development, but interpretation of CD data obtained from oriented media is very challenging and subject to error [18].

The character of the chiroptical signal is only one aspect of chiroptical switches. In general, requirements for the design of an efficient metal-based chiroptical molecular switch include: (i) stability of the optically active forms, (ii) chemical reversibility of the redox processes, (iii) high sensitivity of the chiroptical response and (iv) potential application in multimode switching. There are many systems that achieve these aims. The review will be organized by input mechanism: First, we will discuss selected examples of metal association and dissociation as a means to trigger chiroptical changes, which is a seemingly trivial means of triggering chiroptical response but for which several unique and interesting examples will be discussed. Changes in the environment of metallo-organic complexes including solvent, temperature, counter ion, and pressure will be discussed. We will mention briefly the Pfeiffer effect, a classic phenomenon that was not originally intended as a chiroptical switch yet involves chemistry that is highly relevant to metal-based chiroptical switches. Redox chemistry is particularly suited to metal-based systems, and therefore redox-triggered chiroptical molecular switches will be discussed at length. Fewer examples of optically induced metal-based chiroptical switches have been reported and these will also be presented.

2. Metal binding-induced switches

Several studies have been reported in which addition of a metal ion to an organic molecule or polymer induces a change in chiroptical properties. Since nearly any chiral ligand will display different chiroptical properties upon complexation of a metal ion, this mechanism might be considered a somewhat trivial example of a metal-based redox switch. We will limit our discussion to examples involving triggered supramolecular stereochemical behavior. A number of papers have appeared on metallofoldamers that are significant primarily from a supramolecular assembly viewpoint but have not been discussed in detail as switches [19–22].

2.1. Foundational studies: copper templated synthesis of chiral macrocycles

For example, the group led by Jean-Pierre Sauvage has provided foundational studies for the field of metal-based chiroptical molecular switches although much of their published work falls outside the scope of this article [12]. The use of copper ions to assemble molecules with unique topologies including catenanes and trefoil knots, and the study of metal ion- and redox-triggered molecular switches represent major contributions to the assembly of chiral coordination complexes and metal-based switches. Among the studies that incorporate molecular triggering phenomena and chirality in the same molecule include the synthesis and study of a phosphorus-containing [2]catenane as an example of an interlocking chiral structure [23]. As shown in Fig. 1, interlocked [2]catenanes from macrocycles with directional chirality may form enantiomeric structures. Compounds **4a/4b** showed clearly the presence of diastereomers by ^{1}H and ^{31}P NMR spectroscopy. Removal of the copper ion gave diastereomers **5a/5b** that were separated by HPLC. Although this work was not discussed from a molecular switch perspective, the addition and removal of the metal ion locks and unlocks the two rings with respect to their ability to slip through each other, which was discussed in several earlier systems described by the Sauvage laboratory [12].

2.2. Electron-switched supramolecular chiral polythiophene aggregates

In a system showing elegant complexity, Goto and Yashima reported electron-switched supramolecular chiral polythiophene

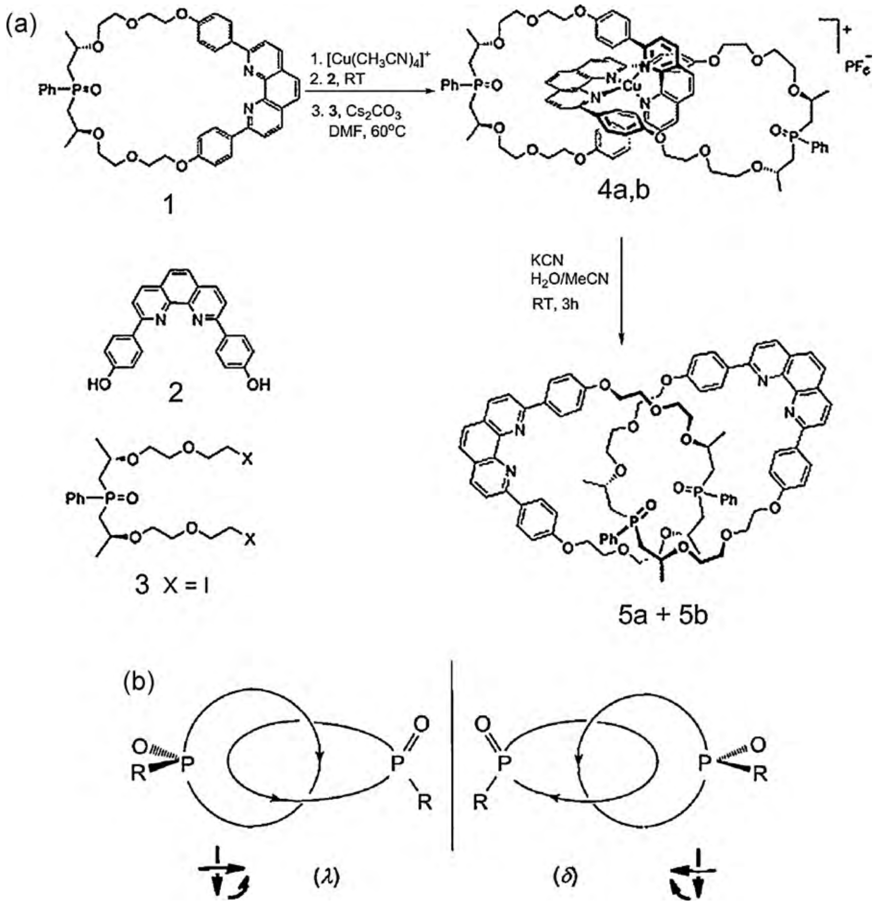

Fig. 1. (a) A chiral catenane was prepared by Cu(I) templation to form catenane 4a and b diastereomer (not shown). Removal of the Cu(I) gave a diastereomeric mixture that was separated by column chromatography. (b) Enantiomeric catenanes and stereochemical assignment. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission [23].

aggregates (Fig. 2) [24]. Polythiophene oligomers with side chains containing remote chiral centers were prepared and studied in solution. The compounds form chiral aggregates in certain solvents that exhibit-induced circular dichroism (ICD) in the π–π^* transition region. Addition of a Cu(II) salt resulted in oxidative doping of the polymer main chain and the disappearance of CD. Further addition of amines such as triethylenetetramine removed the doping by shifting the oxidation potential of the copper, extracting electrons from the polythiophene molecules and consequently regenerating the ICD signal. Doping also induced color and morphological changes as measured by electronic absorbance and atomic force microscopy (AFM). Chiral oligothiophenes have been examined for applications as circular polarized electroluminescence devices as well as enantioselective sensors, electrodes, catalysts, and adsorbents. Electron-induced triggering of polythiophenes would bring new dimensions to such devices if adaptable in the solid-state, which the authors believe is possible.

3. Environment-induced switches

Chiroptical properties of metal complexes respond to a startling variety of different triggers including counter ion, temperature, solvent, and pressure. The “Pfeiffer effect” represents a very early example of metal-based chiroptical response to an environmental trigger. The effect of external agents on the optical activity displayed by coordination complexes has been known from the early days of coordination chemistry [25,26]. In 1931, Pfeiffer and Quehl reported that the optical rotation of a solution of an optically active compound (the “environment” compound, e.g., *d*-α-bromocamphor-p-sulfonate) changes upon the addition of racemic mixtures of some optically active coordination compounds (e.g., *d,l*-[Zn(*o*-phen)3, *o*-phen = *ortho*-phenanthroline]) [27]. This effect has been explored in a variety of systems and has been reviewed several times. It may be observed in configurationally labile coordination complexes that are capable of some level of molecular recognition with chiral compounds in their environment. Many examples exist of complexes of bidentate ligands such as bipyridyl, o-phen, and 8-aminoquinoline with divalent, late transition metals such as Zn(II), Co(II), Cd(II), and others. Typical chiral environment compounds include cationic alkaloids (e.g., *d*-cinchonine, *l*-nicotine) and anionic camphor sulfonate derivatives. Originally observed by changes in optical rotation, the effect has been reinvestigated throughout the evolution of optical rotatory dispersion and circular dichroism methods and instruments [26,28]. Generally, the effect has been attributed to the observed shift of enantiomeric equilibrium due to an outer sphere association of the racemic metal complex and the chiral additive. This perturbation of the equilibrium leads to an unequal diastereomer occupation, and allowed the resolution of metal complexes that cannot be isolated by conventional separation techniques [28]. Pfeiffer phenomena have now been observed in other systems such as lanthanide and titanium complexes [29,30]. Many environment substances have now been studied, including amino acids [31], tartrates [32], and others. A very interesting example involving a chiral phosphate anion was reported [33]. Although Pfeiffer’s name does not appear frequently, papers continue to be published that discuss

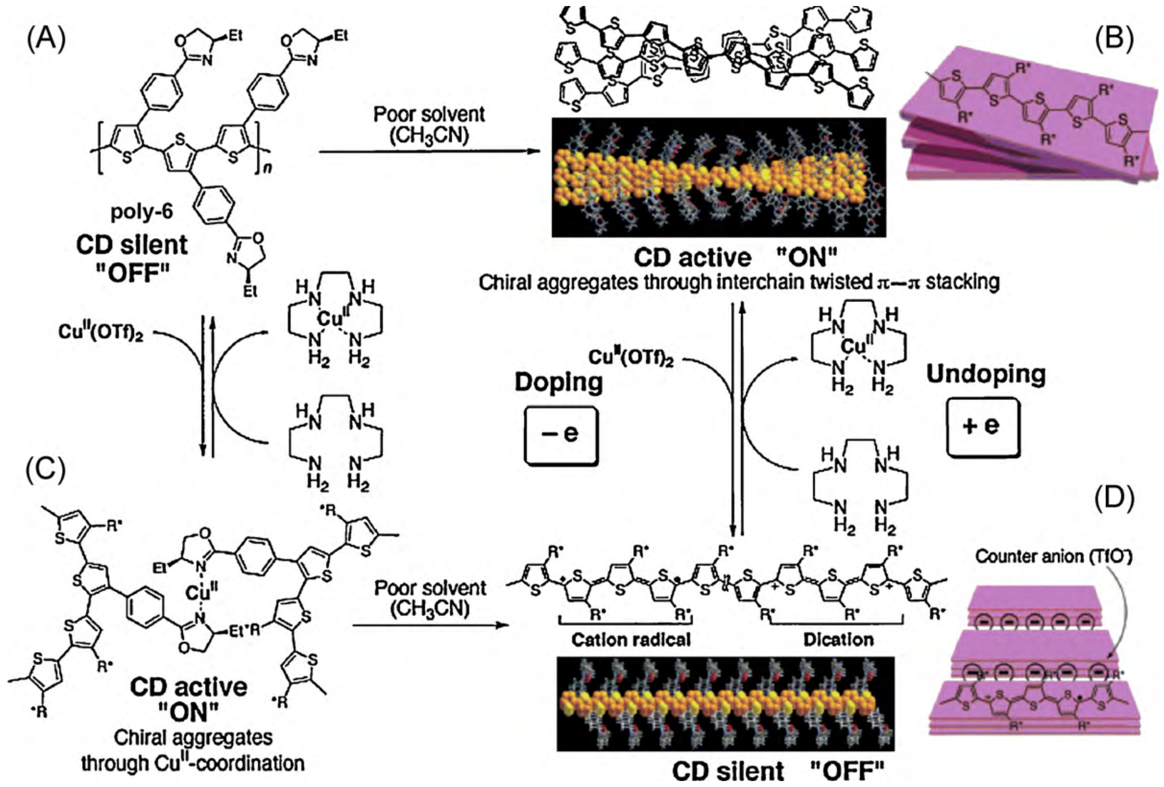

Fig. 2. Oligothiophenes containing chiral centers in side chains (poly-**6**) aggregate in poor solvents. Electron doping by adding Cu(II) results in CD-active aggregates, while undoping reversibly turns off the CD signal. Reprinted with permission [24]. Copyright 2002 American Chemical Society.

similar phenomena [34]. (Indeed, the authors are grateful to Professor Jay Siegel of the University of Zurich who brought the Pfeiffer effect to our attention.)

3.1. *Amino acid stimulated helicity of salen(Ti)Cl_2 complexes*

Schwartz et al. reported a system that is related to the Pfeiffer effect, seen in (salen)TiCl_2 complexes [35]. Salen [N,N′-ethylenebis(salicylidenaminate)] forms octahedral complexes of titanium where the ligands arrange themselves in a *trans*, pseudo-planar manner around the metal. When the salen ligands are no longer in a planar configuration, a helical twist occurs without preferential chirality as in salen complexes like (salen)Cr(oxalato)$^-$ [36], (salen)Fe(oxalato)$^-$ [36], and (salen)Co(acac) [37]. However, when chiral α-hydroxy carboxylic acids react with (salen)TiCl_2, a preferential helical twist of the complex occurs depending on the absolute configuration of the carboxylic acids (Fig. 3). The exciton-coupled π–π* transition of the azomethine chromophore in the complexes was measured with circular dichroism, and the sign of $\Delta\varepsilon$ was consistently opposite for enantiomers of carboxylate ligands. However, the amplitudes of the Cotton effects were larger for bulky substituents than for less sterically hindered ones, indicating that when the side group is large, a predominance of one diastereomer occurs. Nevertheless, the helical twist of the complexes can be predicted: a Δ-twist with (R)-carboxylic acids and a Λ-twist with (S)-carboxylic acids. This system differs from the classical Pfeiffer effect in that the host is achiral rather than racemic, and the induction involves inner sphere rather than outer sphere complexation.

3.2. *Guest controlled tripodal ligand chirality*

Supramolecular conformational bias based on host–guest complexes includes nonempirical CD approaches for the determination of the absolute configuration of primary amines [38]. Complexation of the conformational racemate [Cu(BQPA)](ClO_4)$_2$ (BQPA = N,N-bis[2-quinolyl]methyl-N-[2-pyridyl]methylamine) [39] with various chiral amines gave exciton-coupled circular dichroism (ECCD) spectra that were consistent with formation of a preferred conformational diastereomer as shown in Figs. 4 and 5. The zinc(II) complexes with solvent coordinated as the fifth ligand exhibit conformational enantiomerism, with the chirality of the molecule originating from the helical structure of the ligand when associated with the metal ion. Introduction of a chiral guest molecule may displace the solvent and create diastereomers. It was observed that left-handed guests induced a left-handed propeller conformation in the ligand (Fig. 5), yielding a positive couplet in the CD spectra [34]. The details of the CD spectral assignment are discussed later in this review article.

3.3. *Zinc porphyrin tweezers*

Much more sensitive chirality "sensing" was achieved by forming supramolecular complexes of primary chiral amines with pentanediol-linked zinc porphyrins, referred to as a "zinc porphyrin tweezer" [17,40,41], as shown in Fig. 6. Binding occurs first between the chiral primary amine and carrier molecules, which in turn bind to the bidentate zinc porphyrin. The resulting 1:1 host–guest complex generates an ECCD spectrum. Based on the sign of the couplet in the split CD spectrum, the group order (small, medium, large) in the Newman projection is determined and the absolute configuration at the chiral carbon of the monoamine can be resolved. The method is applicable to aromatic amines, cyclic and acyclic amines, amino esters, amides, and cyclic amino alcohols. This approach offers a sensitive, widely applicable nonempirical advancement for probing chirality, although the substrate profile is limited to bifunctional compounds. A

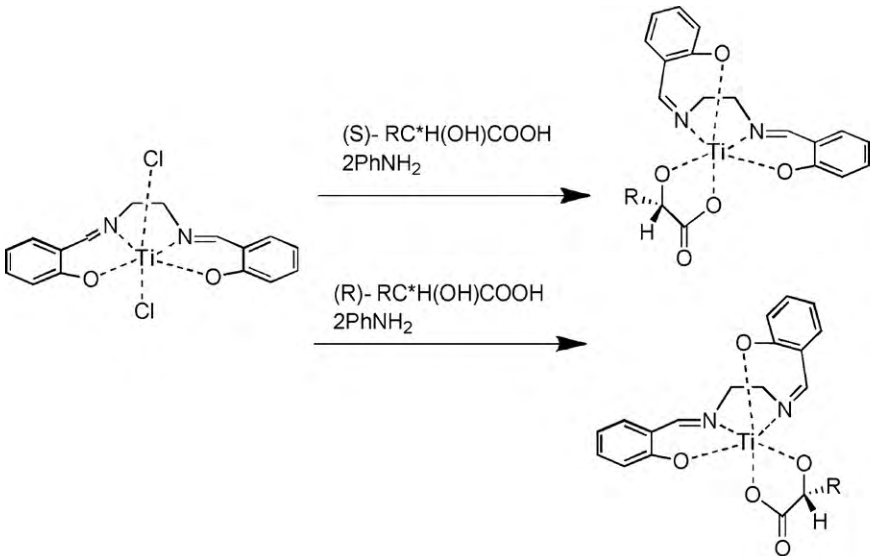

Fig. 3. (salen)TiCl$_2$ complex reacting with chiral amino acids resulting in preferential helical twists. An example of the Pfeiffer effect. Copyright 1994 American Chemical Society [35].

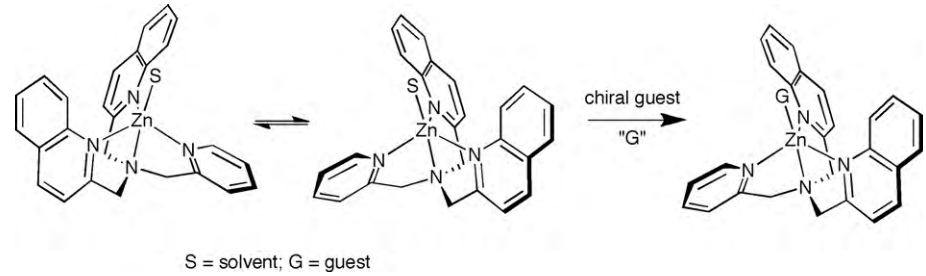

Fig. 4. Achiral Zn complex of bis(quinolylmethyl)pyridylmethylamine reacts with chiral amines to induce an ECCD spectrum [34].

variety of substrates have been examined by this and similar approaches [42].

A porphyrin dimer with a shorter ethane bridge linker was reported to display pronounced CD spectra in the presence of monofunctional amines [43,44]. Supramolecular chirality induction occurs when amines bind to the "face to face" *syn* conformation of the achiral bis(zinc porphyrin) resulting in the extended *anti*-conformer with an increased helical dislocation. These two forms are easily distinguished spectroscopically. Left and right-handed screw twists of the bis(zinc porphyrin)-amine diastereomers are due to the absolute configuration of the amines. Amines with the (*R*) absolute configuration-induced ECCD spectra with negative couplets, and amines with (*S*) absolute configuration induced the opposite handedness. The bulkier amines resulted in stronger CD signals, suggesting the role of steric factors in the mechanism of chiral induction.

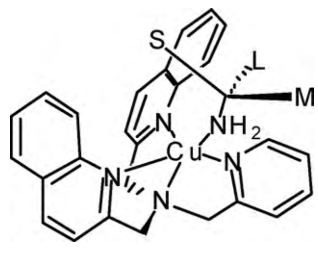

Fig. 5. Left-handed guest induces left-handed propeller twist, yielding a positive ECCD couplet [34].

3.4. Practical application of the Pfeiffer effect for analyzing chiral diamines

Recently, Anslyn took advantage of Pfeiffer phenomena to develop a rapid assay of enantiomeric excess. Chiral diamines PD, DC, DP, and MD (Fig. 7) were added to racemic copper(I) or Pd(II) complexes, resulting in circular dichroism spectra corresponding to MLCT bands of the metal complexes [45,46]. An instrument interfaced to a robotic 96-well plate allowed rapid and convenient measurement of the CD spectra of the compound library. Linear discriminate analysis of the CD spectra then determined the identification, concentration and enantiomeric excess of the diamines. This study represents a practical application of the Pfeiffer effect as a chiroptical sensor technique.

3.5. Anion controlled switching of amide complexes

There are several interesting examples of chiroptical metalloswitches triggered by interaction with anions. Yano et al. reported chiral inversion [47] induced around a seven-coordinated cobalt center by interaction between sugars and sulfate anions. New cage-type cobalt(II) complexes that consist of N-glycosides from mannose-type aldoses and tris(2-aminoethyl)amine (tren), [Co((aldose)$_3$ tren)]X$_2$·nH$_2$O (where X = Cl$^-$, Br$^-$) and [Co((aldose)$_3$ tren)]SO$_4$·nH$_2$O exhibited C_3 helical configuration inversion around the Co(II) center. The complexes that contain the SO$_4$$^{2-}$ counteranion give opposite CD bands than the complexes with halogen anions. Furthermore, the CD spectral characteristics of [Co((aldose)$_3$ tren)]X$_2$·nH$_2$O where (X = Cl$^-$, Br$^-$) changed dramat-

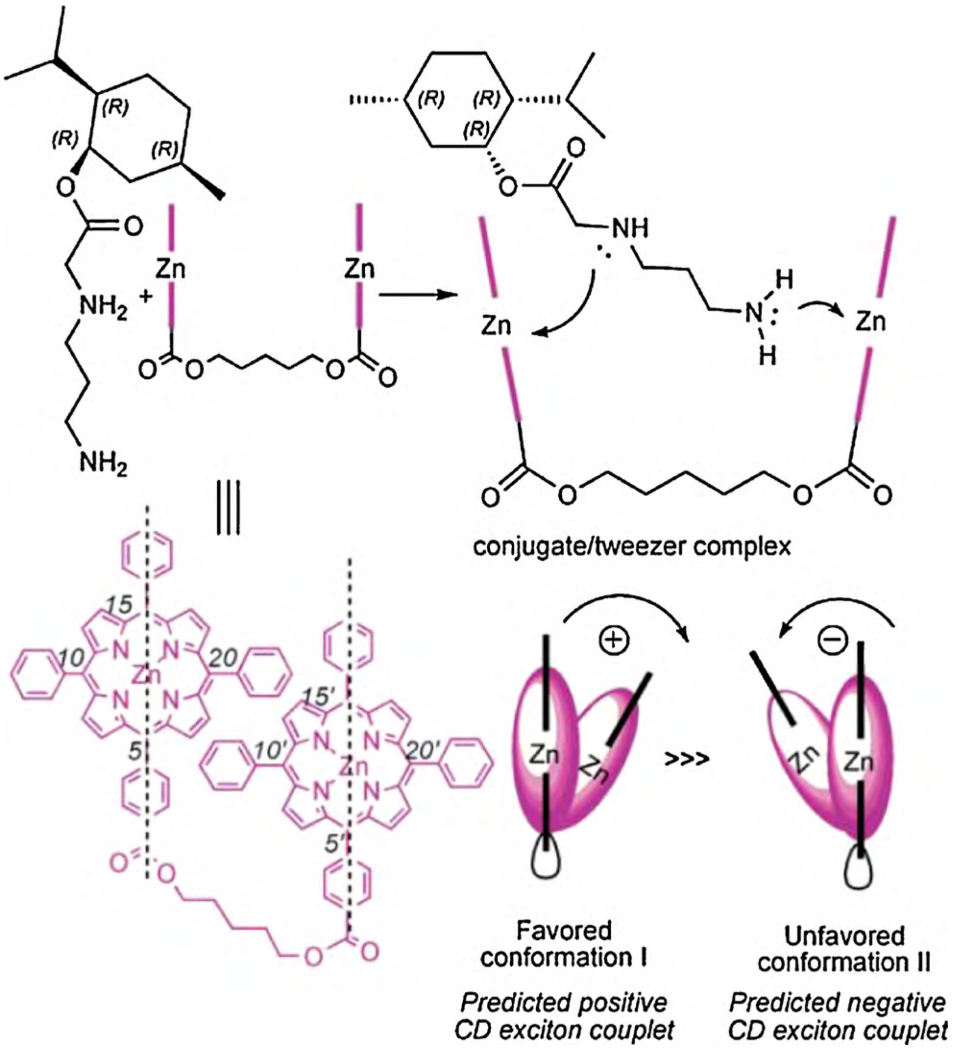

Fig. 6. Macrocyclic 1:1 host–guest complex formed between guest and host. Reproduced by permission of The Royal Society of Chemistry [17,41].

ically with the addition of sulfate anions, and even inverted at high sulfate concentrations, suggesting ion pair formation which was confirmed by a crystal structure. When sulfate ion is embedded into the cavity of the sugar hydroxyl groups, the complex adopts a Δ configuration, while the complex with the halogen anion exhibits a Λ configuration. When the sulfate anion approaches the sugar complex, the electrostatic attraction between the doubly negative and positive charges of the sulfate anion and complex cation causes the

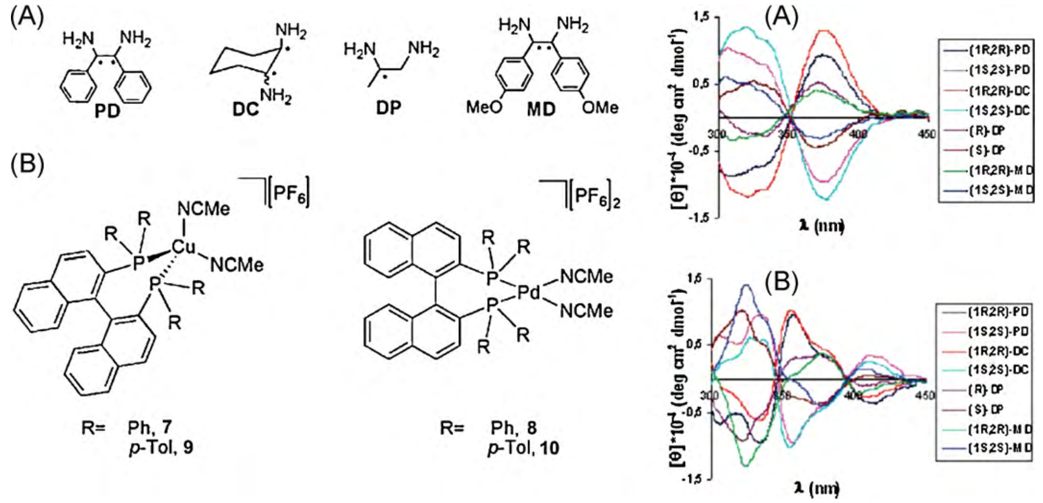

Fig. 7. Structures of chiral diamines, racemic metal complexes, and CD spectra of adducts [45,46]. Copyright 2008 American Chemical Society.

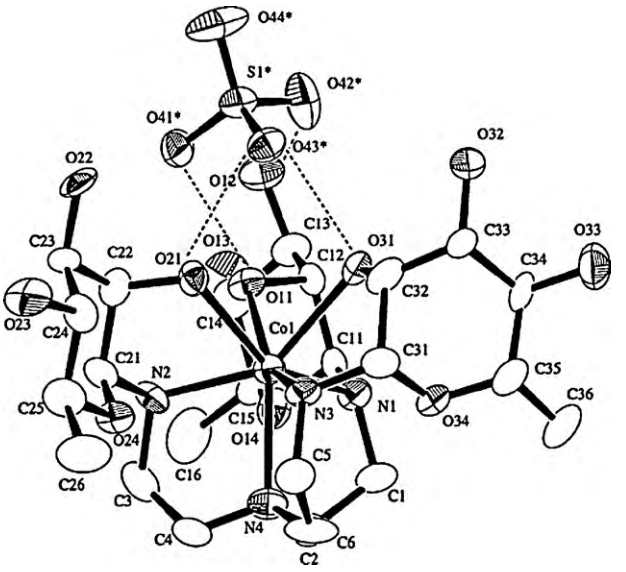

Fig. 8. ORTEP drawing of [Co((L-Rha)$_3$tren)]SO_4 showing the interaction between complex cation and sulfate anion. The sulfate anion situates itself into the complex cation cavity along the C_3 axis. Rha = 6-deoxy-L-mannose [47]. Copyright 1997 American Chemical Society.

hydrogen bonds between the ligands to be interrupted and brings about a chiral inversion due to the sulfate embedding into the large complex cavity (Fig. 8). Reversibility was exhibited when the sulfate ions were removed and replaced with halide ions.

Initial work by Miyake et al. established that the helicity of a chiral tetradentate ligand chelated to Co(II) was readily inverted by the addition of nitrate anion (Fig. 9) [48]. Preliminary studies suggest that two molecules of nitrate serve to invert the helicity of the ligand. Chelation of the first equivalent to the Co(II) center displaces the two tertiary nitrogens of the bound ligand, while the second equivalent of nitrate disrupts hydrogen bonding of the amide to solvent [49]. Circular dichroism studies indicated that the initial L11-Co(ClO_4)$_2$ complex exhibited a positive CD signal in the range of the d–d transition (around 530 nm) in CH_3CN/CH_2Cl_2 = 1/9 (Fig. 10). Upon gradual addition of Bu_4NNO_3 the sense of the d–d transition in the observed CD spectra changes from positive to negative.

These early findings by Miyake led to the synthesis of a chemical device designed to exhibit dual mode motions [50]. This time, a modified version of chiral tetradentate ligand (Fig. 11) including 2,5-dimethoxybenzene moieties attached through amide

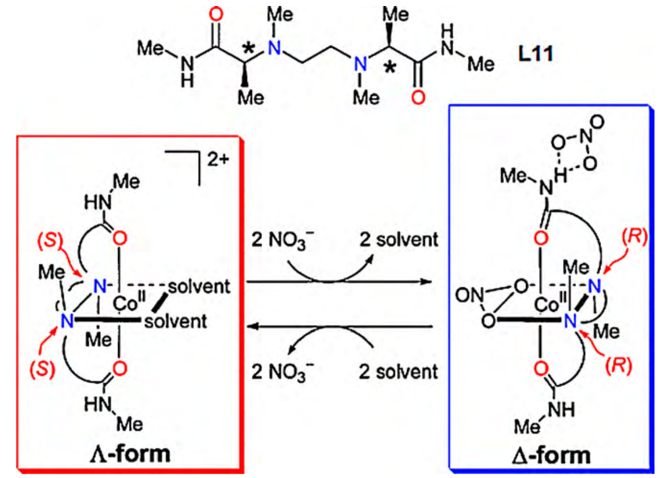

Fig. 9. Helicity inversion in L11–Co(II) complex [49]. Reproduced by permission of The Royal Society of Chemistry.

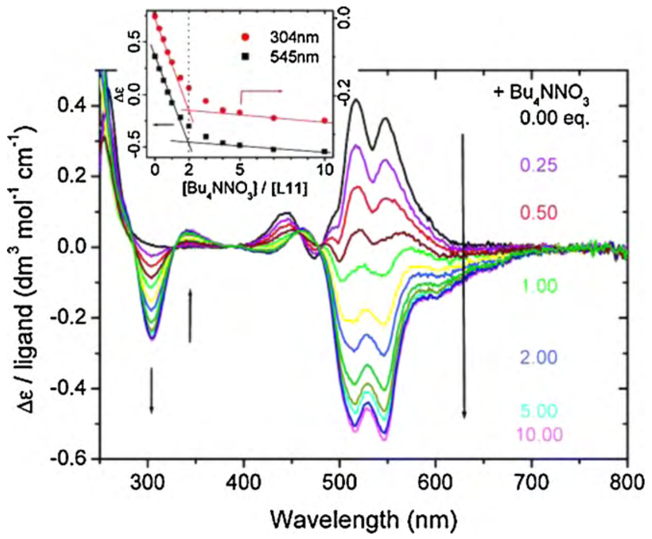

Fig. 10. CD spectral changes of 1:1 mixture of L11 and Co(ClO_4)$_2$·6H_2O (black) upon the addition of Bu_4NNO_3 in CH_3CN/CH_2Cl_2 1/9 at room temperature. (Inset) Titration profiles of the CD amplitudes at 304 and 545 nm. [L11] = [Co(ClO_4)$_2$·6H_2O] 1.5 × 10^{-3} mol dm^{-3} [48]. Copyright 2004 American Chemical Society.

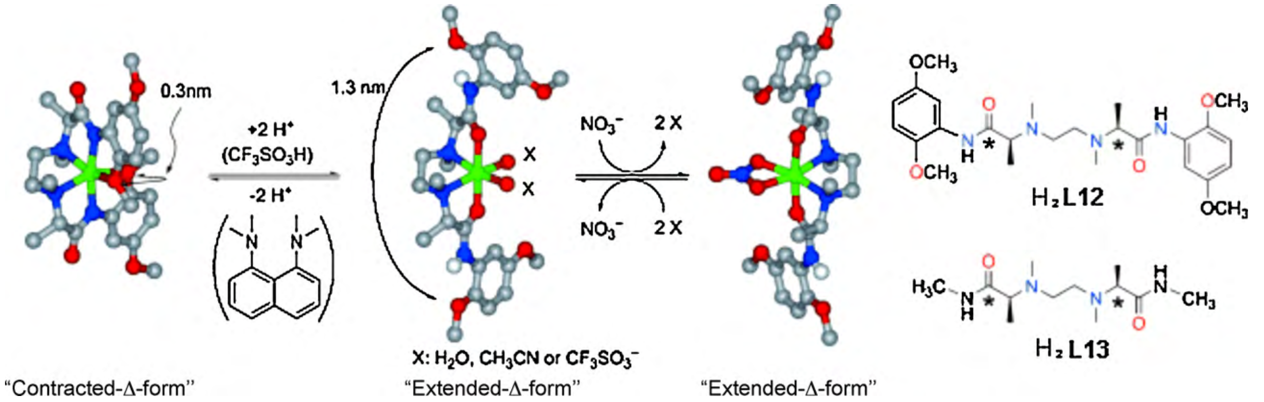

Fig. 11. Stretching and inverting dual motions of the Co^{II} complex. Crystal structures of [Co(**L12**)](left) and [Co (H$_2$**L12**) (CF_3SO_3) (H_2O)] (CF_3SO_3)·($CHCl_3$) (middle), and DFT-optimized structure of [Co(H$_2$**L12**)(NO_3)]$^+$ (right) are illustrated. Most hydrogen atoms, solvent molecules, and $CF_3SO_3^-$ ions are omitted for clarity [50]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

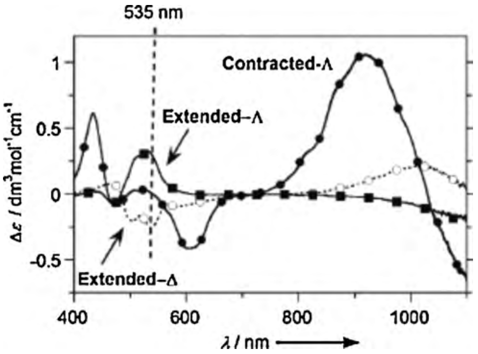

Fig. 12. CD spectra of [Co(H_2**L12**)(CF_3SO_3)(H_2O)] (CF_3SO_3)·($CHCl_3$) (■), [Co(**L12**)] (●) and [Co(H_2**L12**) (CF_3SO_3) (H_2O)](CF_3SO_3)·($CHCl_3$) in the presence of five equivalents of Bu_4NNO_3 (○) in $CH_3CN/CHCl_3$ (1/9) at room temperature [50] Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

linkages to the terminals of the ligand was employed. An acid–base reaction of the corresponding cobalt complex triggers an interconversion of coordinating atoms between amide nitrogen atoms and amide oxygen atoms, which causes a stretching (extension/contraction) molecular mode. Inversion of helicity (again from Λ to Δ) after addition of five equivalents of Bu_4NNO_3 accounts for the second device mode. CD studies of the [Co(**L12**)] complex in $CH_3CN/CHCl_3 = 1/9$ exhibit positive signals at 433 nm and 918 nm and negative signals at 474 nm, 607 nm, and 1100 nm, which correspond to the contracted-Λ-form (Fig. 12). Two equivalents of CF_3SO_3H (to form [Co(H_2L12)(CF_3SO_3)(H_2O)](CF_3SO_3)·($CHCl_3$) then caused a rapid signal shift from 0 nm to positive in the 530 nm region (ca. 5 s) which indicated a switch to the extended-Λ-form. The helicity inversion caused by addition of five equivalents of Bu_4NNO_3 gave rise to a negative CD signal around 530 nm. The similarity of this CD signal shift to the original H_2L13 ligand study supports the assertion that helicity is changed in the device.

Reversibility of the extended and contracted state by acid–base chemistry was carried out on the complex using N,N,N′,N′-tetramethyl-1,8-naphthalenediamine as a proton sponge and triflouromethanesulfonic acid. Circular dichroism signals remained consistent after many deprotonation/protonation cycles, proving that robust reversibility was established (Fig. 13). Such a kinetically labile Co(II) complex provides for a dynamic dual mode switch that could potentially be required for sophisticated supramolecular switching devices.

Recently, similar peptide helix inversion by nitrate anion was shown to occur in analogous Ni^{II} and Zn^{II} complexes [51]. Selection between Zn^{II}, Co^{II}, or Ni^{II} allowed tuning of the rate of the inversion process to occur on a time scale from milliseconds (Zn^{II}) to hours (Ni^{II}). The estimated half-lifetime ($\log \tau_{1/2}$) of these metallopeptide complexes showed a linear correlation with the water exchange lifetime of the aqueous metal cations.

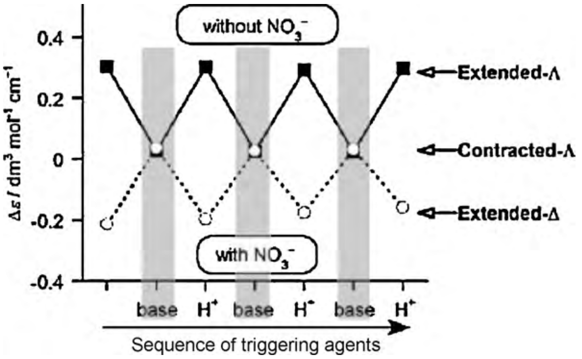

Fig. 13. Protonation/deprotonation-induced reversible switching of the contracted-Λ/extended-Λ (■) and contracted-Λ/extended-Δ (○) process observed by CD spectra at 535 nm in $CH_3CN/CHCl_3$ (1/9). H⁺: CF_3SO_3H; base: 1,8-bis(dimethylamino)-naphthalene [50]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

3.6. Solvent controlled switching of metal complexes

In another novel study, the Lisowski group has examined chiroptical switches involving lanthanide complexes of chiral hexaazamacrocycles [52]. The hexaazamacrocycle L14 shown in Fig. 14 was designed to complex large lanthanides such as Yb(III) and Eu(III). Upon addition of $Yb(NO_3)_3{\cdot}5H_2O$ in acetonitrile, it was observed that the chiral ligand L14 wrapped around the Yb in a helical Λ-form corresponding to the (RRRR)-(SRSR) L14 isomer. Crystal structure studies of $[YbL14(NO_3)_2]_2$-$[Yb(NO_3)_5](NO_3)_4{\cdot}5CH_3CN$ show an improper torsion angle C2-C4-C15-C17 of −13.3° which is unusually high for a lanthanide(III) hexaazamacrocycle complex. Solvation of the same complex in water, though, leads to ligand reorganization presenting a sharp shift in helicity as evidenced by an improper torsion angle C2-C4-C15-C17 of 87.2° for the (RRRR)-(SSSS) isomer. CD studies confirm helicity inversion by solvent effects, demonstrating quantitative conversion of Λ-form complex to Δ-form complex in 144 h.

The proposed mechanism of inversion (Fig. 14) involves an initial exchange of hydrate into a 10-coordinate metal inner sphere, which is followed by slow ligand reorganization into an 8-coordinate sphere. Lisowski argues that the "squeezed" (RRRR)-(SSSS) isomer is more capable of accommodating smaller water axial ligands whereas the "open" (RRRR)-(SRSR) isomer preferentially binds the bulkier nitrate ligand in the axial position [53]. The study as a whole represents a rare case of reversible solvent-induced helicity inversion for a metal-based complex.

Recent reports from Nitschke offer an alternative copper(I)-based solvent-triggered molecular switch [54]. The initial synthesis of the chiral Cu(I) complex in methanol resulted in an equal mixture of both P and M-diastereomers which was characterized by a weak circular dichroism spectrum bearing similarities to that of the free ligand. A featureless CD spectrum in the ligand's metal-to-ligand charge transfer (MLCT) band further established that there was no net diastereomeric excess formed. A stark contrast was then found when the Cu(I) complex was dissolved in dichloromethane-d_2 and the CD spectrum revealed a positive Cotton effect in the MLCT region. Combined studies of CD and NMR suggest that the Cu(I) complex (Fig. 15) fully converts to the P diastereomer in nonpolar dichloromethane. Similar studies in DMSO then showed that the M-diastereomer of the complex (Fig. 15) exists in 20% excess, setting the stage for a reversible metal-based chiroptical molecular switch. The solvent-induced conformational exchange was reasoned to be dominated by hydrogen bonding effects.

A weakly polar solvent such as dichloromethane is reasoned to only weakly interact with the hydroxyl groups of the ligand, allowing for intramolecular hydrogen bonding. Such hydrogen bonding serves to rigidify the structure and lock the complex into the P conformation. Polar solvents such as DMSO, though, interact strongly with the ligand hydroxyl group and push the hydroxyl groups apart, leading to a preference for the M conformation. The authors hypothesize that such a reversible solvent-triggered complex could serve as a means to control stereoselectivity in future metal-catalyzed reactions.

3.7. Biological and pressure-based switches

Pressure also can induce chiroptical responses in chiral metal complexes. Octahedral chiral Δ and Λ-tris-[cyclic O,O′,1(*R*), 2(*R*)-dimethylethylene dithiophosphato]chromium (II) complexes

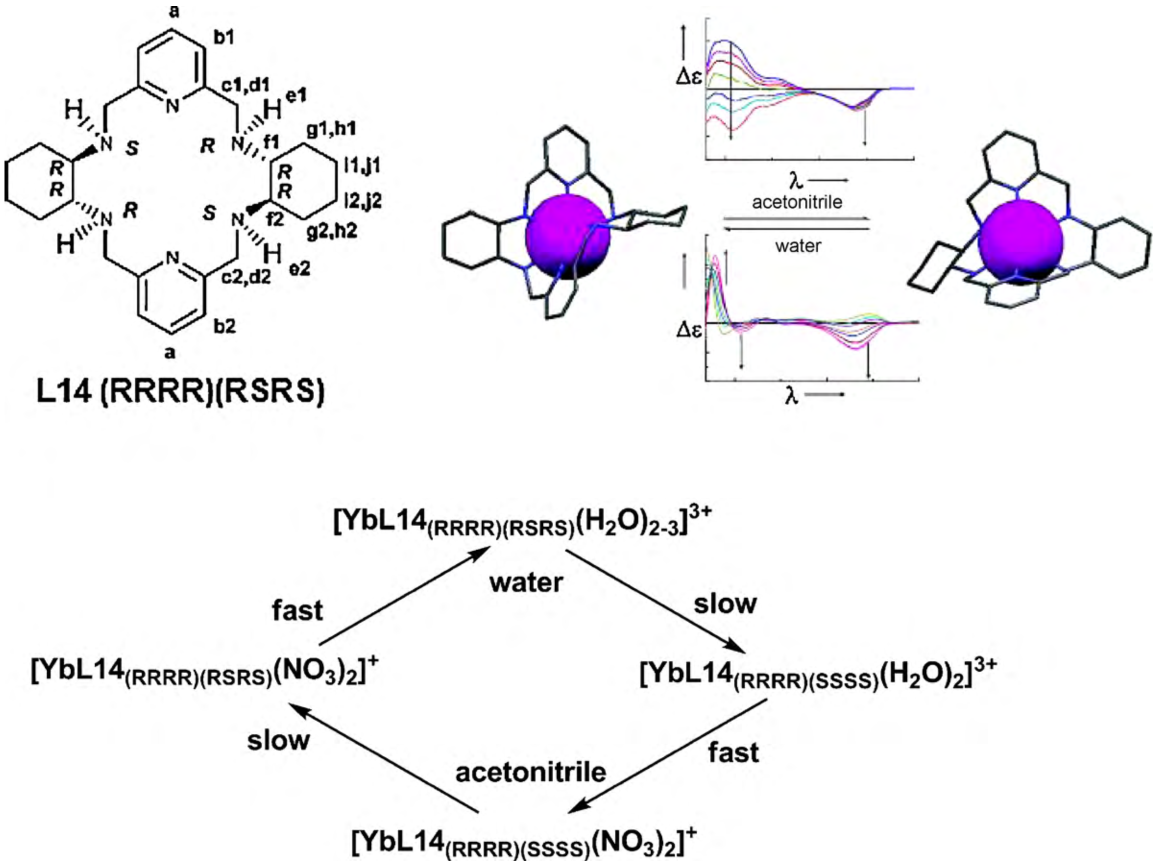

Fig. 14. (Top left) Structures of one of the chiral macrocycle isomer L14(RRRR)(RSRS). (Bottom) Proposed mechanism of helicity inversion of the (RRRR)(RSRS) and (RRRR)(SSSS) isomers of the macrocycle L in its Yb(III) complexes. (Top right) Solvent-induced reversible helicity inversion with accompanying CD spectra [52]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

demonstrated inversion from the Δ form to the Λ form by means of pressure, the Λ form being more stable at high pressures [55,56]. When the applied pressure exceeded 2.5 GPa, the CD band obtained from polycrystalline Nujol samples inverted from negative to positive. The cycle was reversible as demonstrated by applying repeating pressure cycles. Pressure experiments with various ratios of Δ and Λ diastereomers confirmed inversion of helicity, however, the transition pressure varied and was dependent on the amount of Δ-diastereomer present in the sample. Mechanistic explanation of the pressure-induced chirality inversion could involve bond breaking or trigonal twisting around the metal center.

The Parker group has recently utilized the chiral environment of drug site II of serum albumin to induce helicity inversion in complexes of terbium and europium (III) [57]. It was found that chiral complex (SSS)-Δ-$[Tb.L^{15}]^{+3}$ changed helicity to (SSS)-Λ-$[Tb.L^{15}]^{+3}$ upon addition of human or bovine serum albumin. Convincing data was supplied by circularly polarized emission (Fig. 16). When the Δ-isomer is exposed to BSA or HSA, there is an inversion of the sign of emission and 35% reduction of the signal intensity. The authors explain that the emission spectra “are consistent with the inversion of the helicity of the complex in the protein-bound form” [58]. Parallel experiments were run using the Λ-isomer, but no change in emission spectra was found. These results give one of the few immediately biologically relevant examples of a metal-based chiroptical molecular switch. The system could potentially allow protein association to be tracked *in vitro* in real time.

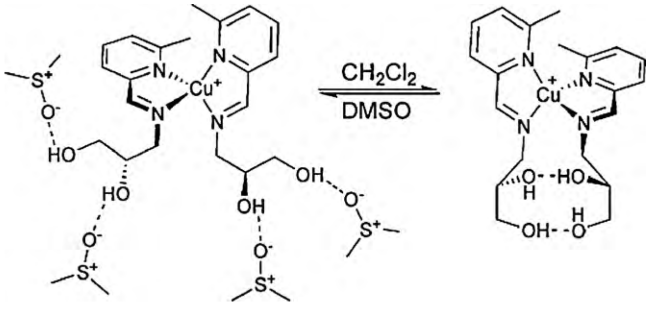

Fig. 15. Postulated structures in DMSO (left, M predominating) and CH_2Cl_2 (right, P exclusively) [54]. Reproduced by permission of The Royal Society of Chemistry.

4. Redox-triggered systems

The rich coordination chemistry literature offers many avenues for entry into the design of redox-sensitive metal complexes that display rich chiroptical spectra. Redox-active metal ions themselves often show useful electronic spectral changes. However, changes in CD spectra of the organic ligand are also very useful, particularly in complexes that display ECCD.

4.1. Iron translocation in triple-stranded helical complexes

Professor Aviram Shanzer of the Weizmann Institute reported the first published example of a redox-mediated chiroptical redox switch. The system was based on chemical triggering of iron translocation in triple-stranded helical complexes (Fig. 17) [59]. The design accommodated a single metal ion in one of two sites, either a “hard” binding N_3O_3 cavity presenting three hydroxamate moieties or a “soft” N_6-cavity with three bipyridyl ligands. Chemical reduction of Fe(III) to Fe(II) induced the metal to translocate from the

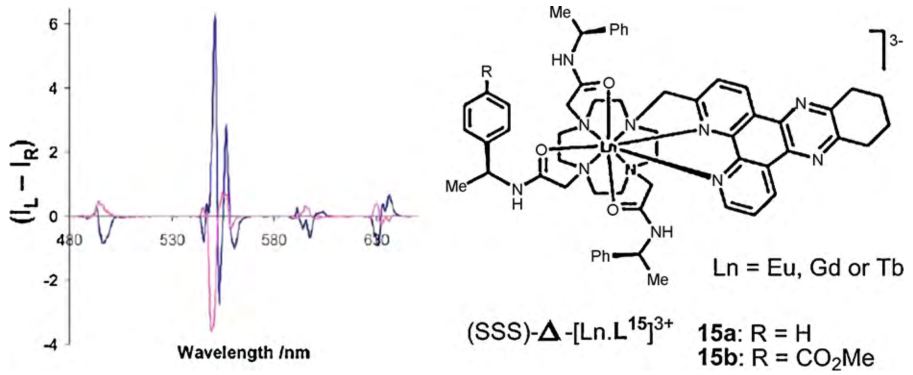

Fig. 16. Left: CPL spectra for (SSS)-Δ-$[Tb.L^{15b}]^{3+}$ (blue) and in the presence of added BSA (red) (295 K, D_2O, λ_{exc} 348 nm, 15 μM complex, 30 μM protein; relative $(I_L + I_R) = 60$ on this scale). Right: Chiral lanthanide metal-ligand complex used to bind human or bovine serum albumin in "drug site II" [57]. Reproduced by permission of The Royal Society of Chemistry.

hydroxamate binding site to a bipyridyl site, as the "softer" Fe(II) favored the site with more nitrogen ligands. Redox switching of the complex was induced by reduction with ascorbate and oxidation with ammonium persulfate. Pronounced differences in UV–vis and CD spectra were observed corresponding to changes in absorbance associated with Fe(II) vs. Fe(III) electronic spectra. A split CD spectrum in the UV region was observed that was three times more intense for the Fe(II) state, suggesting exciton interactions involving the bipyridyl moieties. Reduction was rapid, and oxidation gave the Fe(II) absorbance spectrum after a few minutes (several hours were required to achieve the original Fe(III) CD spectrum). The fact that metal exchange did not occur between control compounds with single metal binding sites suggested intramolecular translocation reaction. Variation of the structure resulted in significantly different translocation rates. Although outside the scope of this article, a related, achiral Cu(I/II)-based system was reported in collaboration with the Albrecht-Gary laboratory that included a detailed mechanistic analysis [60]. In a recent review of translocation systems [15], it was noted that metal translocation rates vary from hours to hundreds of milliseconds, depending on the ligand and metal used. Other interesting achiral Cu(I/II) redox-triggered conformational switches have been described [61].

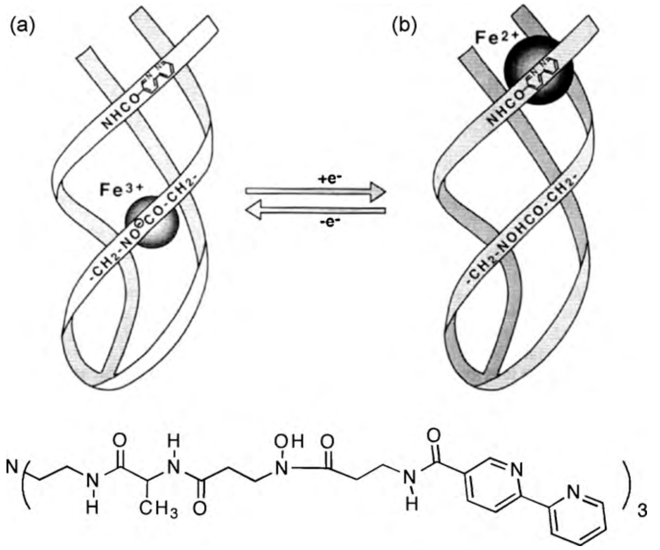

Fig. 17. Tripodal ligand containing two binding sites. Fe(II) binds preferentially to the tris(piperidine) site while Fe(III) selects the tris(hydroxamate) ligation site. Change of metal ion oxidation state results in translocation of the metal ion from one site to another [59]. Reprinted by permission from Macmillan Publishers Ltd. Copyright 1995.

4.2. Chiroptical tripodal ligands

The development of redox-triggered chiroptical switches in the Canary laboratories began with the observation that tripodal, N_4-ligands form stable coordination complexes with divalent metal cations [62,63]. In the case of Zn(II) and Cu(II), the ligand, otherwise conformationally mobile with many conformations, wraps around the metal ion to form a propeller-like complex. In ligand **L16** (Fig. 18), there exists a single stereogenic center on one of the tripod arms. This stereocenter dictates the helicity of the propeller formed by the planes of the heterocycles. A number of crystallographic structures [64], with few exceptions, established the relationship between the chiral carbon center and the propeller configuration [65]. Exciton-coupled circular dichroism [17] (ECCD) established the preponderance of a single propeller conformation in solution, and tested whether the same configuration was present relative to the carbon center as had been observed in solid-state studies [66]. It was confirmed that Cu(II) and Zn(II) complexes showed ECCD spectra consistent with solid-state propeller-like structures. As shown in Fig. 18, the conformationally mobile free ligand gives a relatively weak CD spectrum, while Zn(II) and Cu(II) complexes afford the characteristic ECCD spectra. This method allows one to assign the absolute configuration of the orientation of the π–π^* transition moment giving rise to the couplet, from which was deduced the sense of the propeller twist in solution.

The dependence of ECCD upon the strength of the electronic transition moment, the proximity of the coupled transitions, and the angle between them led to the development of several interesting chiroptical molecular switches. An on/off system was studied involving a tripodal ligand containing three quinoline moieties [67]. The tris(quinoline) compound in Fig. 19 forms a coordination complex with Cu(II) involving the coordination of four nitrogen atoms and affording an exceptionally intense split CD spectrum that results from the additive effect of three ECCD couplets in one molecule. Reduction to the Cu(I) complex in the presence of strongly coordinating thiocyanate ion gave dissociation of one quinoline arm. This resulted in a much weaker ECCD spectrum due to two factors: (1) the dissociation of one quinoline reduces the number of ECCD couplets from three to one; and (2) the less sterically crowded environment around the copper ion allows unwinding of the ligand and reduces the magnitude of the dihedral angle and therefore diminishes the amplitude of the ECCD couplet. The overall effect is a very large difference in ECCD amplitude between Cu(I) and Cu(II) states. Dependence of the ECCD amplitude on the counter ion supported the structural assignment [68]. The complex is highly reversible chemically upon oxidation of the Cu(I) complex with ammonium persulfate and reduction of the Cu(II) complex with sodium ascorbate. Temperature-dependent ^1H

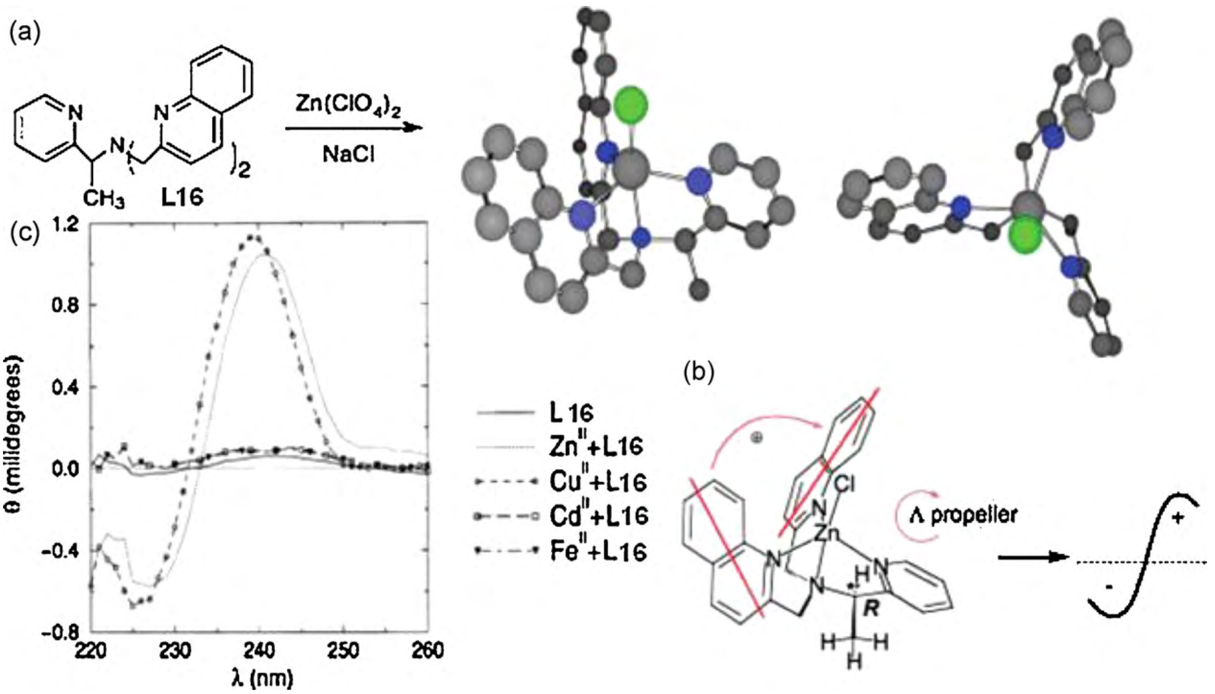

Fig. 18. (a) Conformationally mobile ligand wraps around Zn^{2+} ion to form propeller-like complex as shown by X-ray crystallography (two views shown); (b) prediction of positive ECCD couplet; (c) CD spectra of perchlorate complexes where Zn^{2+} and Cu^{2+} show strong amplitude compared to free ligand (L16) and Cd^{2+} and Fe^{2+} complexes which are octahedral and distort propeller conformation [62,63].

NMR studies of this system led to the conclusion that the two arms lacking the chiral carbon center are in rapid equilibrium between associated and dissociated states at room temperature, but slow on the ^1H NMR time scale at low temperature [69]. The arm containing the chiral carbon center, however, remains coordinated.

Such tripodal ligands were found to act as chemosensor molecules; their ability to torque a nematic into a cholesteric liquid crystalline phase increased upon complexation with copper ion [70]. Changes in overall shape of the complexes induced by different metals and counter ions were transferred sensitively to the supramolecular level, observed by proportionate changes in the degree of twisting. Redox changes (Cu(I)/Cu(II)) also gave large changes in twisting power. The handedness of the induced cholesteric phase was related to the stereochemistry of the ligand.

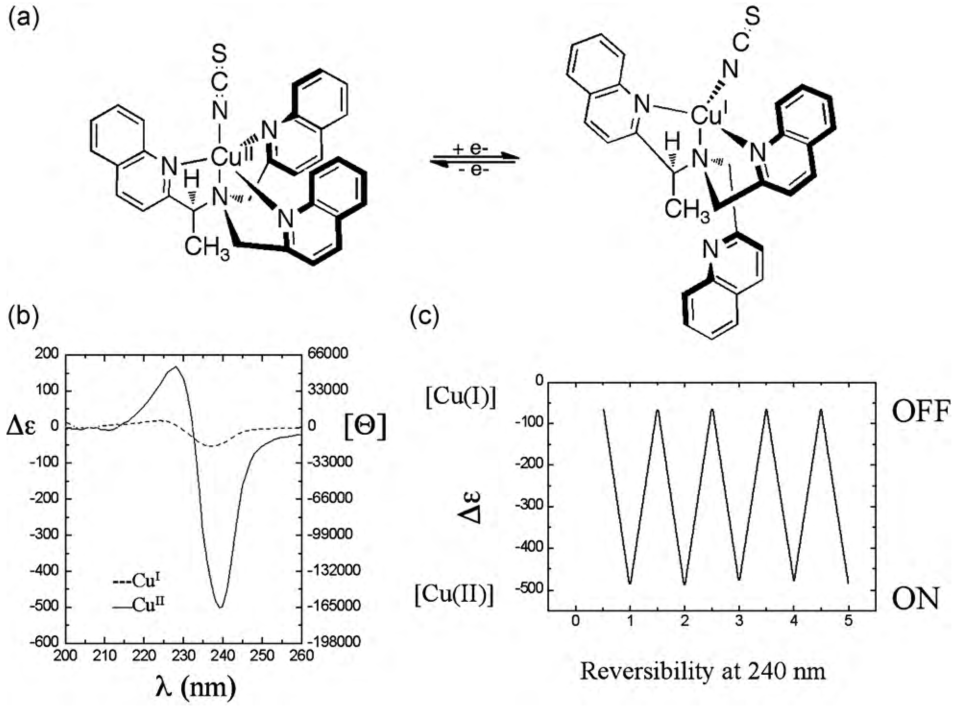

Fig. 19. On/off chiroptical molecular switch. (a) One-electron reduction results in dissociation of an arm of the tripodal ligand; (b) CD spectra of Cu^+ and Cu^{2+} complexes; (c) oxidation and reduction cycles with ascorbate and persulfate [67].

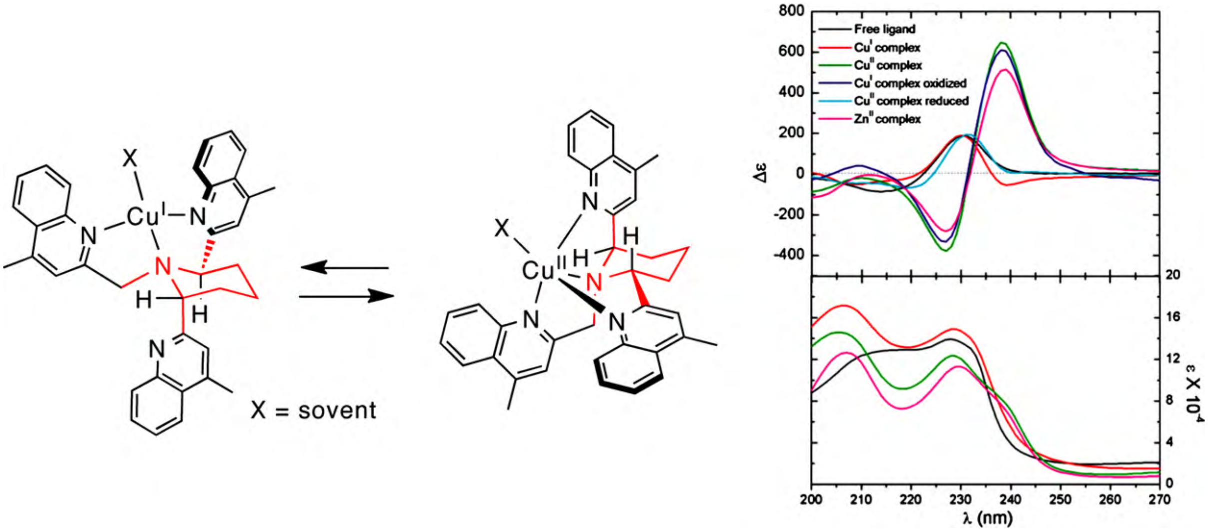

Fig. 20. Redox-triggered inversion of one chair form of a piperidine ring into the other chair and corresponding CD (top) and UV–vis (bottom) spectra [71].

Interestingly, a direct correlation was observed between helical twisting power and ECCD amplitude, consistent with each technique responding proportionately to the relative twist of the planes of the nitrogen heterocycles.

Another related complex containing two chiral carbon centers within a piperidine ring was reported (Fig. 20) [71]. In this case, the rigidity of the ligand provided control as to which chair form of the piperidine was adopted. In the Cu(I) oxidation state, the ligand adopts a relatively stable cyclohexane chair conformation, with two equatorial and one axial substituent. This conformation places one pyridine moiety remote from the metal ion, but this is accommodated by the lower coordination number of the Cu(I) ion. In the Cu(II) state, strong binding to the higher-coordination number ion brings all three pyridines into association, which forces the piperidine to adopt a higher energy chair with two axial and one equatorial substituents. The ECCD spectrum of the Cu(II) complex showed the largest amplitude of any complex in this series, but the Cu(I) spectrum did not give an ECCD spectrum. In this case, the Cu(I) structure was characterized by a series of ^{1}H NMR experiments.

In these studies, ECCD served as a tool to gauge not only the configuration of the propeller conformation but also the degree of twist of the molecule. Relatively few spectroscopic probes are available to report 3D molecular geometry, so it may be expected that this technique should be broadly applicable for the characterization of solution species [17].

Systematic exploration by Steffen Zahn of amino acid derivatives [72,73] led to the discovery of a molecule that inverts helicity and ECCD sign upon one-electron redox change [74]. A ligand derived from the amino acid methionine forms a tetradentate complex with Cu(II) involving three nitrogen atoms and a carboxylate (Fig. 21). In this system, the propeller twist of the molecule is dictated by the asymmetric carbon center by virtue of a gearing mechanism between the methine and methylene carbon atoms, and can be visualized when viewing down the bond between the tertiary amine nitrogen atom and the Cu(II) ion. Upon reduction to Cu(I), the ligand reorganizes and the sulfide moiety replaces the carboxylate, which is expected due to the preference of Cu(I) for this type of coordination. The reorganization requires a pivot about the bond between the tertiary nitrogen atom and the asymmetric

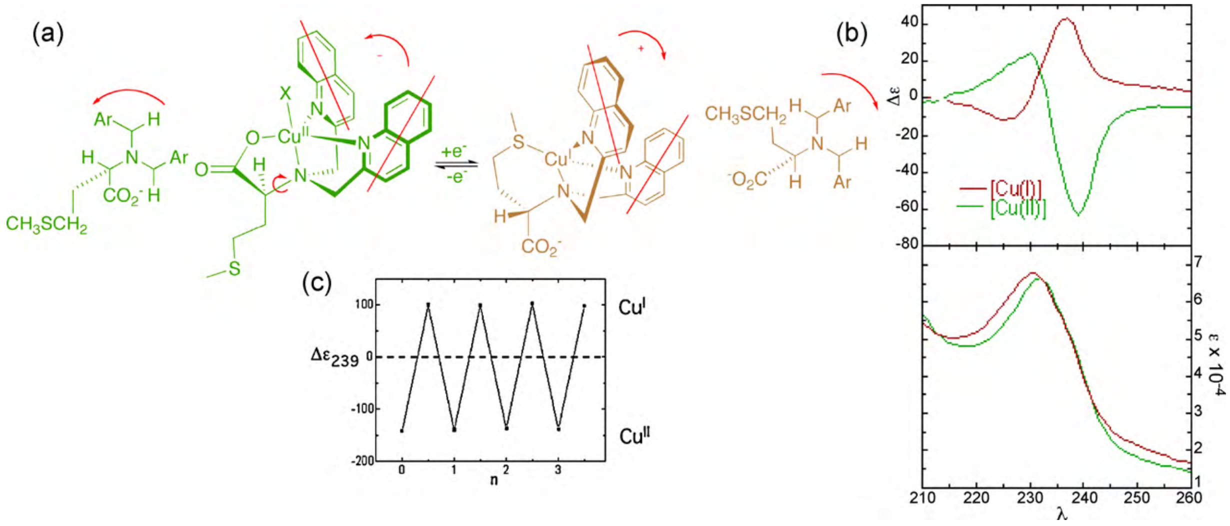

Fig. 21. Redox-induced inversion of helicity. (a) As a result of the presence of gearing among the three arms of the tripod near the sterically crowded tertiary amine of the ligand, a pivot about a C–N bond results in the inversion of the propeller; (b) CD and UV–vis spectra of Cu^+ and Cu^{2+} oxidation states; (c) chemical cycling with ascorbate and persulfate [74].

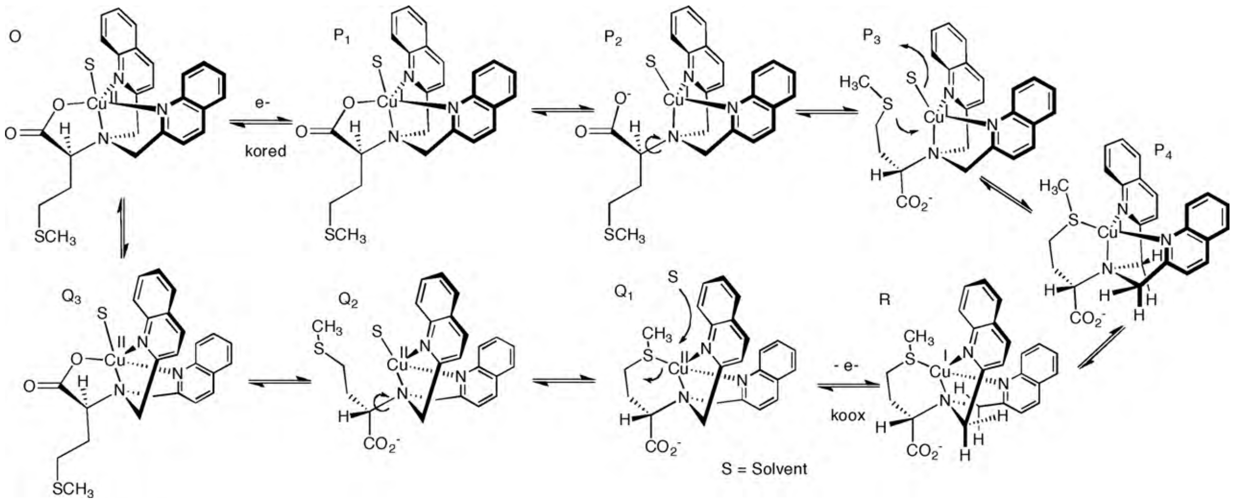

Fig. 22. A possible mechanism for reorganization of Cu^+ and Cu^{2+} complexes [63].

carbon atom. This pivot destroys the gear previously mentioned; to retain the geared conformation, the two methylene carbon groups flip, which in turn inverts the helical orientation of the two quinoline moieties, and therefore, the ECCD spectrum. The CD spectrum appears to give mirror images for the Cu(I) vs. Cu(II) complexes. The switching was reversible with cyclical additions of ascorbate and ammonium persulfate. Crystallographic data supported the structural assignments [75].

Closer scrutiny of the mechanism of this interesting transformation is warranted. One possible scheme is shown in Fig. 22. The characterized oxidized (O) and reduced (R) states are shown. The Cu(II) ion in O is five-coordinate, while that in R is four-coordinate. Transformation between these two states involves redox change of the metal ion, reduction of the coordination number of the metal by loss of a coordinating solvent molecule (typically acetonitrile under the conditions of the experiment), dissociation of a ligating group, reorganization of the ligand, and coordination of a different ligating group from the ligand. A mechanistic study with scanning electrochemical microscopy (SECM) revealed a slow step in acetonitrile solution for the reduction of O, with a rate of 25 s^{-1} [76]. A potential candidate for the slow step in the reaction is the substitution reaction proceeding from P3 to P4. The rate of this reaction would depend greatly on the solvent used, but only acetonitrile has been employed in rate studies by SECM.

Further supportive evidence for the assumptions underlying this mechanism was obtained by studying a metal complex with three different arms (Fig. 23) [77]. First, the complex shown in Fig. 23 gives no ECCD spectrum due to the lack of a second quinoline chromophore. The free ligand gave a single set of peaks in the aromatic region of the ^1H NMR spectrum, but the Zn(II) complex gave two sets of peaks of equal intensity. This is consistent with a 1:1 mixture of diastereomers associated with the chirality of the tertiary amine when coordinated to the Zn(II) ion. In DMSO solvent, coalescence was observed at about 100 °C, consistent with the configurational stability of the complex associated with difficulty in inverting the tertiary amine nitrogen atom. Although the spectra were generally characterized by broad peaks, the analogous Cu(I) complex gave only a single set of peaks at room temperature, but additional peaks were apparent at lower temperature. This study brings to light the stereochemical complexity of these molecules. In addition to the chirality of the carbon center of the amino acid moiety and the helicity of the propeller twist of the molecule, both the Zn(II) ion and the tertiary amine are also chiral.

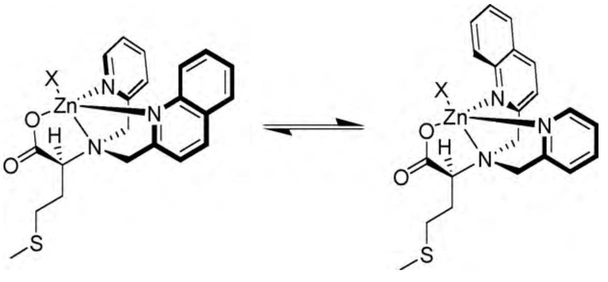

Fig. 23. Two diastereomers of Zn^{II} complex in dynamic exchange [78].

Attempts to observe one-electron redox switching of methionine derivatives with other metals has been largely unsuccessful. The only promising metal besides Cu(I)/Cu(II) is Co(II), which upon substitution for Cu(II) in the complex shown in Fig. 21, gives inversion of ECCD upon reduction with thiosulfate ion or ascorbate [78]. However, the Cu(I)/Cu(II) complexes of other tripodal ligands also give inversion of the ECCD spectrum including derivatives of methioninol and S-methylcysteine [79].

4.3. Redox-triggered porphyrin tweezers

Recently, a redox-triggered porphyrin tweezer was reported in an attempt to develop materials with optical properties in the visible region of the electromagnetic spectrum [80]. As shown in Fig. 24, bis(porphyrin) methioninol derivative gave a strong ECCD couplet upon metallation with Cu(II). The free ligand and Cu(I) complex did not give ECCD. The absence of an ECCD couplet in the Cu(I) complex was rationalized as resulting from relatively weak association of the metal under the conditions studied. The Cu(II) complex, however, showed very strong amplitude, affording an on/off chiroptical molecular switch. Other, non-chiral electrochemically responsive dimeric porphyrin systems have been reported where the redox changes occurred within the porphyrin moieties [81].

4.4. Dinuclear ruthenium complexes

A system showing strong changes in near-infrared (NIR) CD spectra was reported recently [82]. NIR techniques are of interest for several reasons, including the benefit of lower incident light energy on organic materials and greater transparency of NIR light in biological applications. Building on earlier studies of organic-based systems [83–85], the Wang laboratory studied known dinuclear ruthenium complexes with 1,2-dicarbonylhydrazizo bridging ligands (Fig. 25) that are highly electrochromic with absorption bands

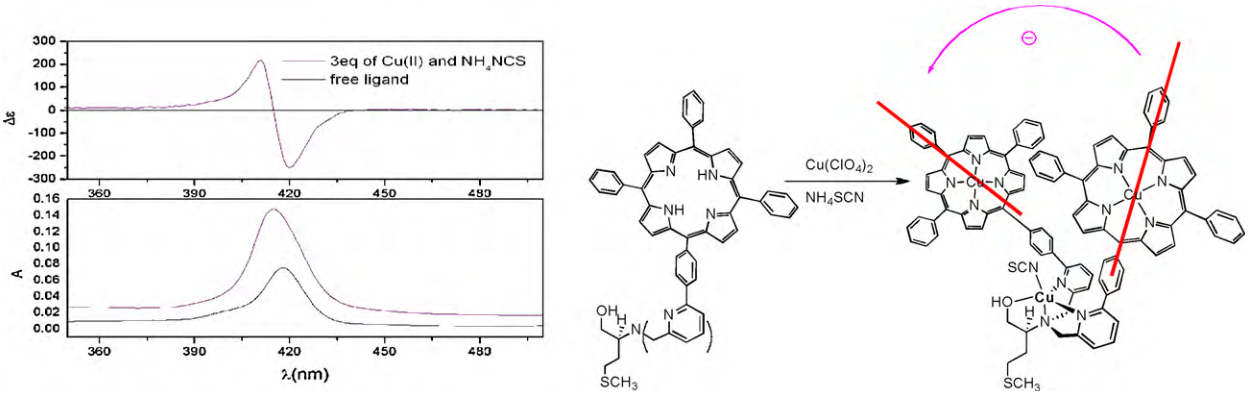

Fig. 24. Redox-triggered reorientation of porphyrins [80].

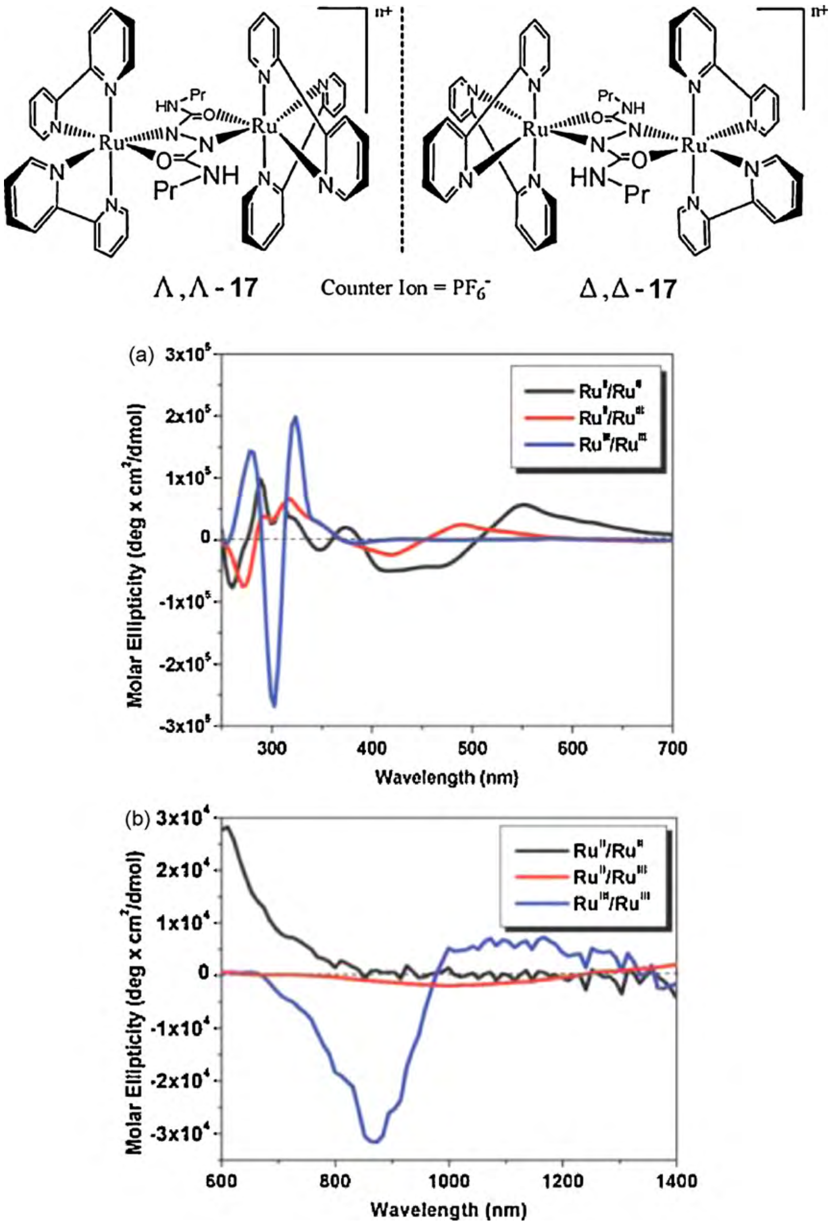

Fig. 25. Λ,Λ-isomer of a diruthenium complex. Circular dichroism spectra obtained in the UV–vis and near-infrared wavelength regimes indicate three stable states readily interconverted electrochemically [82]. Reproduced by permission of The Royal Society of Chemistry.

near 500, 900, and 1200–1600 nm. Cyclic voltammetry data showed two widely separated redox potentials, indicating ready access to the diruthenium(II), mixed-valence, and diruthenium(III) oxidation states. Ligand-centered transitions in the UV region and redox-sensitive MLCT bands in the visible region dominate the CD spectra shown in Fig. 25. A prominent band near 1115 nm observed in the Ru(II)/Ru(III) state, due to metal–metal charge transfer (MMCT), did not give a strong Cotton effect in the CD spectrum. The Ru(III)/Ru(III) state gave a strong MLCT band at 900 nm that gave a relatively strong Cotton effect in the CD spectrum. Reversible redox switch behavior was demonstrated by monitoring the CD signal at 890 nm and cycling up to seven times electrochemically between the Ru(II)/Ru(II) and Ru(III)/Ru(III) states.

A variety of systems have thus been examined for redox-active metal ion triggered chiroptical molecular switches. The mechanisms reported involve translocation of a metal ion, changes of lability of ligand rearrangement, or inner sphere ligand rearrangement resulting from change in coordination number or hardness of the metal. The changes in amplitude of observed CD spectra can be dramatic, even leading to complete inversion of the sign of the ECCD couplet.

5. Photochemically triggered chiral metal switches

Among many interesting studies, the Aida group reported a redox-triggered system in which chemical or photo-reduction of a chiral cerium bisporphyrinate double–decker complex resulted in racemization by acceleration of the porphyrin ligand rotation. They further showed that oxidation of a chiral zirconium complex resulted in deceleration of acid-induced racemization [86].

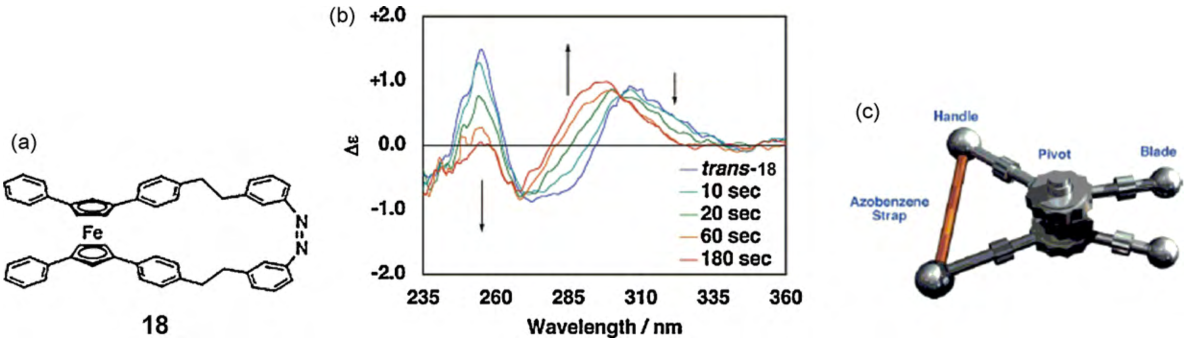

Fig. 26. (a) Structural representation of Aida's azobenzene controlled "molecular scissors." (b) Circular dichroism (CD) spectral changes of *trans*-**18** (3.5×10^{-5} mol dm^{-3}) in THF at 20 °C upon irradiation with UV light (λ = 350 nm). (c) Graphic conceptualization of the "molecular scissors" showing the strap, handle, pivot, and blade [87]. Copyright 2003 American Chemical Society.

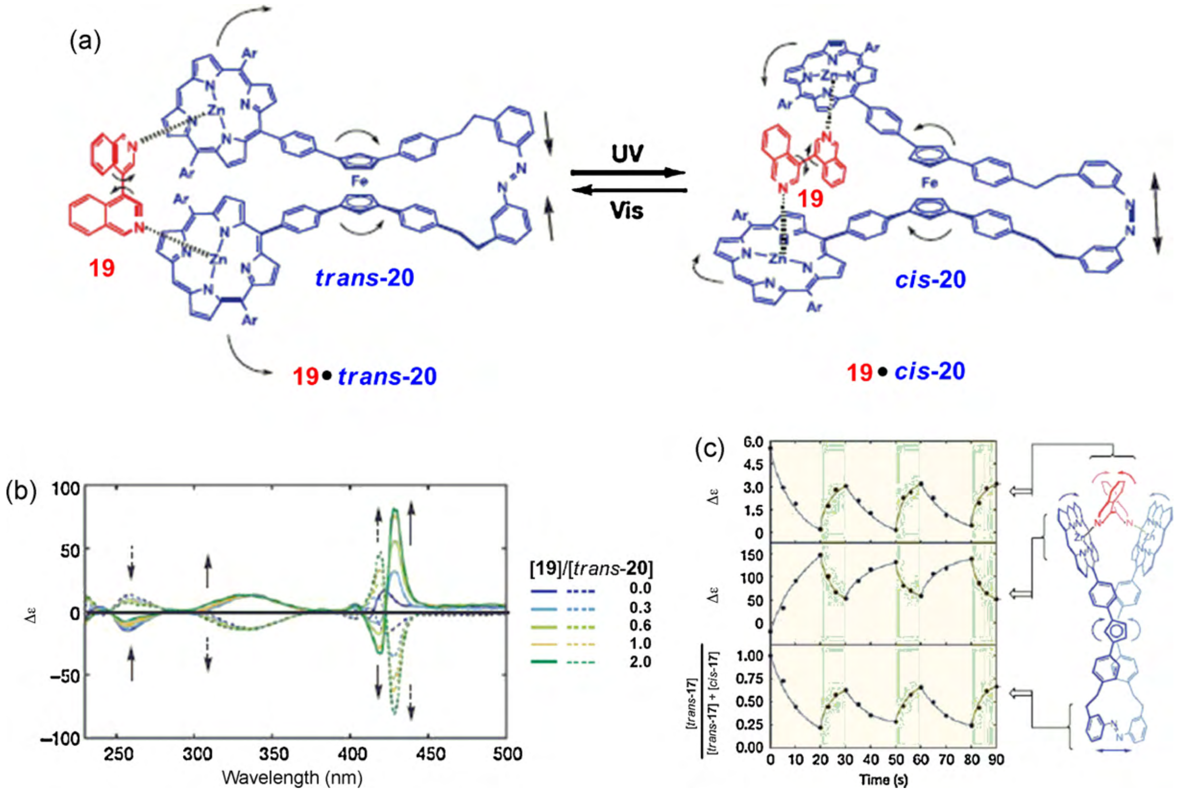

Fig. 27. (a) Schematic representation of photoisomerization of a 1:1 complex of molecular pedal **20** with rotary guest **19** (**19**·**20**). Ar, 4-decyloxyphenyl. Arrows indicate the directions of interlocked motions. (b) CD spectral changes of **trans-20** in CH_2Cl_2 (1.1×10^{-5} M) at 20 °C upon titration with **19**. (c) Circular dichroism (CD) visualization of the motions of guest-binding molecular pedals **19**·(+)-**20** and **19**·(−)-**20** triggered by light [88]. Reprinted by permission from Macmillan Publishers Ltd. Copyright 2006.

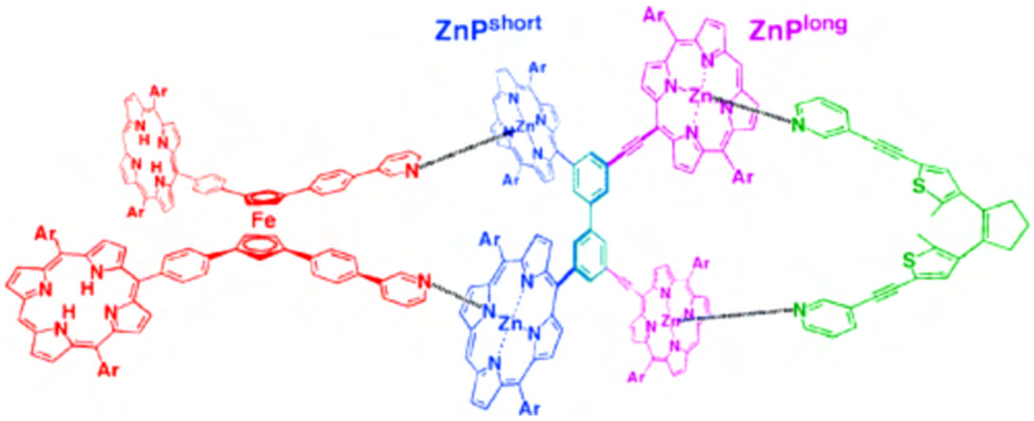

Fig. 28. Structural representation of a ternary complex designed to communicate conformational information using a pyridine-appended dithienylethene bridge [89]. Copyright 2008 American Chemical Society.

5.1. Azobenzene-based molecular scissors

The Aida group looked into the synthesis of other complex light-triggered chiroptical molecular switches. Life-sized scissors having a handle, pivot, and blades inspired the preliminary design of a pair of molecular "scissors" [87]. The chemical equivalents to these three units were found to be azobenzene as the handle, ferrocene as a pivot, and phenyl groups as the blades (Fig. 26a and c). The operation of the molecular scissor is quite elegant. Under standard conditions, the azobenzene handle is predominantly in the trans state leading to "closed" blades. Upon irradiation of UV light, the azobenzene undergoes isomerization to the cis-isomer, which then causes a slight rotation of the cyclopentadienyl rings of the ferrocene pivot. This finally moves the attached phenyl rings away from one another, leading to an "open" scissor state. The scissors' chirality (due to the planar 1,1′,3,3′-tetrasubstituted ferrocene) allows both open and closed states to be seen using circular dichroism (Fig. 26b). The authors explain that the trans-to-cis-isomerization of [CD(−)280]-trans-**18** upon UV-irradiation ($\lambda = 350$ nm) after 180 s gave rise to CD spectral changes at 240–300 nm due to the major adsorption of the tetraarylferrocene unit. Upon irradiation with visible light ($\lambda > 400$ nm), a reverse spectral change occurred, where the system quickly reached a photostationary state in 15 s. Effective reversibility was also exhibited by the system upon sequential irradiation with UV and visible light.

5.2. Host controlled guest chirality

Further research into Aida's molecular "scissors" proved that they could be applied to the field of host–guest chemistry [88]. When metallated porphyrins were attached to the 4-position of the phenyl blades, it was found that a diisoquinoline guest was able to chelate to the zinc porphyrin units. Upon irradiation of the host–guest complex with UV light ($\lambda = 350 \pm 10$ nm), the trans-azobenzene unit again isomerizes to the cis-isomer, causing a long distance conformational twist of the diisoquinoline guest (Fig. 27). The guest molecule (**19**) in solution is initially achiral due to its conformational freedom, but when added to the host molecule (*trans*-**20**) it binds in a nonplanar CD-active chiral geometry. Overlap of CD bands (275–350 nm) from the host molecule required that differential CD spectra be used to examine the motion of the guest (Fig. 27b). Irradiation with UV light caused the Cotton effects at 270–350 nm of the guest (**19**) to diminish and then vanish. It

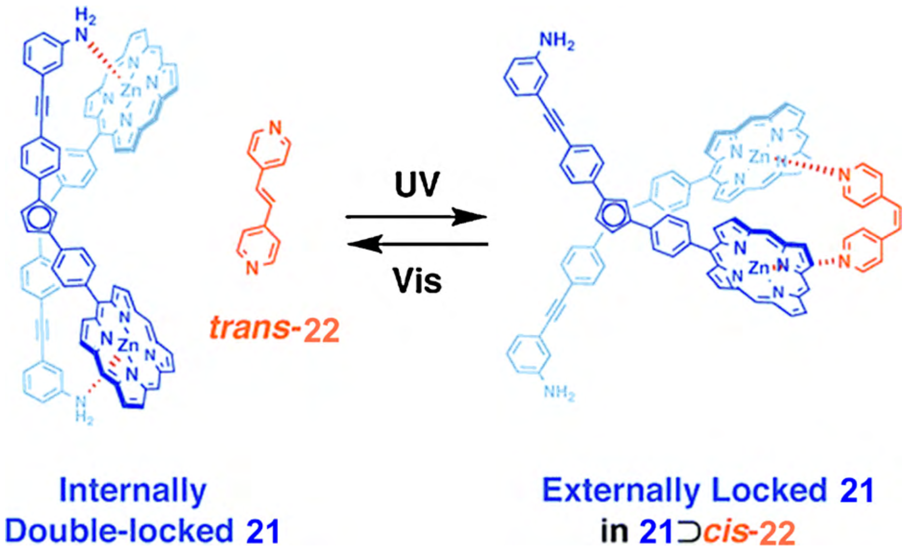

Fig. 29. Molecular structures of internally double-locked **21** and externally locked **21**⊃***cis*-22**, and schematic representation of the self-locking operation in response to photochemical isomerization of **22** [90]. Reproduced by permission of The Royal Society of Chemistry.

is reasoned that the disappearance of the CD band is caused by the guest molecule being forced into a nearly planar state when bound to the cis-isomer of the host compound. Sequential irradiation of host–guest complex (**19**·*trans*-**20**) with UV and visible light proves that the complex is controllably reversible (Fig. 27c). This represents the first instance of a "molecular machine" causing chirality manipulation in a controllable and reversible manner.

5.3. Chirality transfer via ternary complex

Recently, Aida et al. have created many similar compounds incorporating the molecular scissor as a basis for more elaborate and complex systems. Such systems include a ternary compound (Fig. 28), which includes a pyridine-appended dithienylethene derivative as a photochromic module that can again be used to transfer conformational information with UV and visible light as a trigger [89].

Extension of the pivotal ferrocene has also been adopted in reversible self-locking compounds shown in Fig. 29. In the presence of trans-1,2-bispyridine ethylene, the zinc porphyrin moieties coordinate intramolecularly with the anilines to "lock" the molecule internally [90]. UV light is then used to isomerize to the cis-1,2-bispyridine ethylene that is then capable of coordinating to the zinc porphyrin units, "locking" the molecules externally (Fig. 29). The process is again shown to be reversible by alternating UV and visible light irradiation. Such discoveries by Aida et al. could help to controllably transmit chiral and mechanical information through long molecular distances.

6. Prospects

The future of metal-based chiroptical switches is bright, given the high degree of control available, a multitude of triggering mechanisms, and the relative ease of analysis. With the large number of recently discovered systems these chiroptical switches could potentially be used for applications including optical displays, complex molecular electronics, chiral resolution, and conformational control of noncovalently bound compounds.

The Pfeiffer effect and metal ion templated synthesis provided early chemistry relevant to more recently developed metal-based chiroptical switches. Environment-responsive switches have been developed using a large variety of metals and ligands triggered by pressure, counter ion alteration, light, and solvent changes. Redox-triggered switches have been explored primarily using a tripodal ligand motif. Diazobenzene-ferrocene systems were designed to reliably switch the conformations of a set of "molecular scissors," which were then used in an array of interesting and complex supramolecular machines. Polymer systems have been explored illustrated by the use of metal dopants to cause chiroptical changes in oligothiophene polymers.

Circular dichroism experiments were used in nearly all experiments to analyze the conformational changes of the chiral compounds. Although other analytical techniques such as NMR are used to study these systems, it is readily apparent that CD experiments provide accurate and dependable readout for chiral metal-based switches. Most metal-based chiroptical switches were studied in solution phase, but the development of solid phase switches in this field is receiving increased attention.

The studies in this area have provided much stimulating new chemistry and exemplify the power of modern molecular design and solution characterization techniques. There is no doubt that there are many more opportunities to develop even more imaginative systems. Many applications for these materials have been discussed, especially in the areas of electronics and sensors, and several of the available systems are poised to make a genuine contribution.

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