

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/24235281>

ChemInform Abstract: Redox-Triggered Chiroptical Molecular Switches

ARTICLE *in* CHEMICAL SOCIETY REVIEWS · APRIL 2009

Impact Factor: 33.38 · DOI: 10.1039/b800412a · Source: PubMed

CITATIONS

75

READS

22

1 AUTHOR:



James W Canary

New York University

114 PUBLICATIONS 3,053 CITATIONS

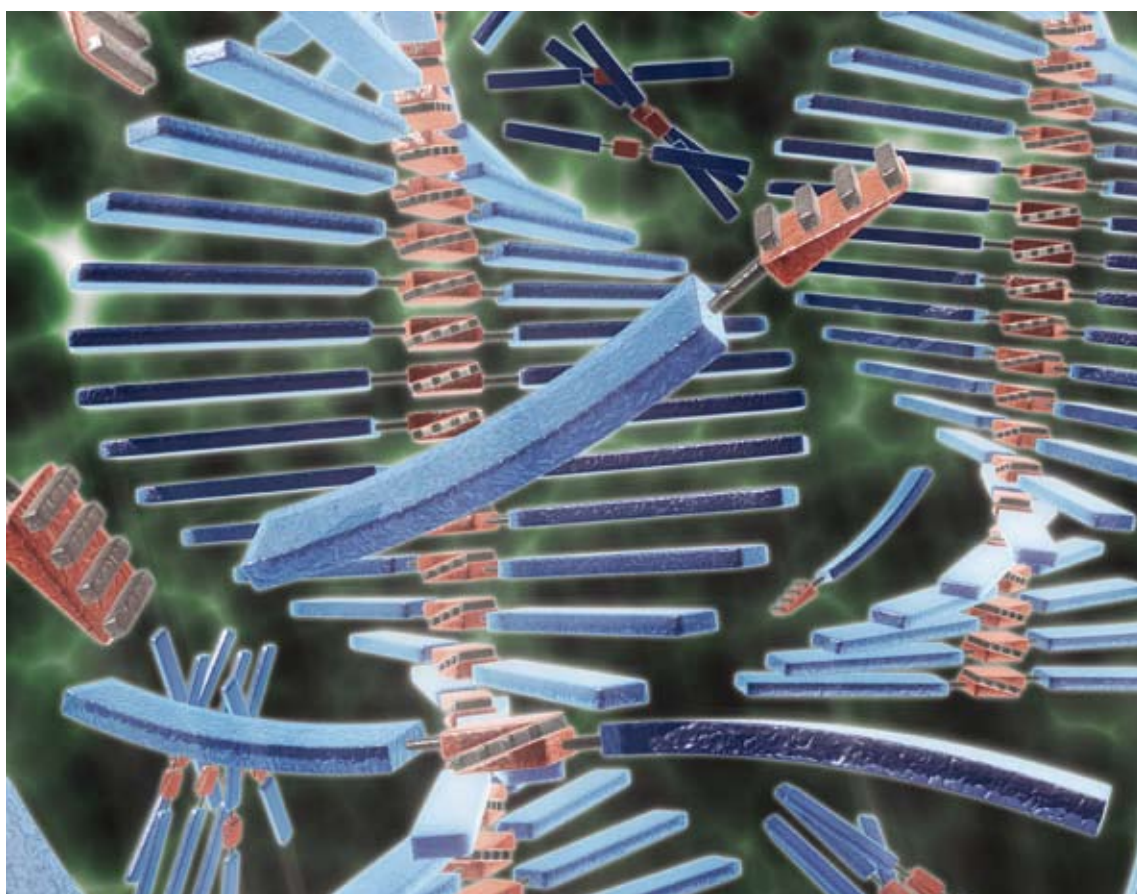
SEE PROFILE

Chem Soc Rev

This article was published as part of the
2009 Nanoscale Chirality issue

Guest Editor David Amabilino

Please take a look at the issue 3 [table of contents](#) to access
the other reviews.



Redox-triggered chiroptical molecular switches†

James W. Canary

Received 16th September 2008

First published as an Advance Article on the web 20th January 2009

DOI: 10.1039/b800412a

Efficient chiroptical molecular redox switches have been engineered that display multiple stable optically active forms, chemically reversible redox processes, and highly sensitive chiroptical responses. Systems that have been studied in this context include electro-active organic polymers, redox-active coordination complexes, and certain organic compounds that may be oxidized or reduced reversibly. Studies in this field have yielded diverse platforms that benefit from dynamic stereochemical and electronic phenomena. This *tutorial review* introduces basic design criteria for chiroptical molecular switches, summarizes examples, and provides an outlook for future work in the area.

Introduction

Recent interest in materials for optical and molecular electronic technology has led to the discovery of chiroptical molecular switches triggered by redox changes. These materials exhibit changes in their interaction with polarized light that can be modulated by oxidation or reduction. Redox-write, chiroptical-read materials may be useful for a variety of applications such as optical displays, telecommunications, or molecular electronics. The purpose of this article is to provide an introduction to this interesting topic. Related molecular switch compounds triggered by optical or other means are not included, nor are sensors or chiral electrodes whose purpose is to detect enantiomeric excess or effect asymmetric catalysis.

Polymers, coordination complexes, and small organic molecules have been engineered to display redox-dependent chiroptical responses. Redox changes may be induced by chemical oxidizing or reducing agents or may be effected by electrochemical means. Chemical reagents must be efficient

and selective, and the reagent and its oxidation products must not interfere with the optical method used for detection. Electrochemical oxidation and reduction are seemingly cleaner, but additives such as electrolytes (or accompanying impurities) must meet similar criteria. Many potential applications require adaptation to the solid state, where electrochemistry is attractive as a trigger due to the available solid-state electronic technology. Electrochemistry may offer some advantages over optical triggers, for example, where bleaching may be a problem if high energy or intense light is required.

Chiroptical spectroscopic measurements are powerful tools for the characterization of materials in this field, and may include any form of polarized light measurement.¹ Circular dichroism (CD) is the most commonly used method due to the relatively strong information content (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 (Fig. 1), with amplitude that depends on the strength of the electronic absorbance, the asymmetric distribution of electrons in the molecule, and on 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.² Two chromophores present in a molecule in close proximity to one another may interact, resulting in differentiation of the energies of the transitions (Fig. 1). 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 (λ_{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. Such exciton-coupled CD spectra are characterized by the shape of the curve, the large amplitude of the spectrum, and the correspondence of the

Department of Chemistry, New York University, New York, NY 10003, USA. E-mail: canary@nyu.edu

† Part of the nanoscale chirality themed issue.



James W. Canary

James W. Canary completed undergraduate studies at the University of California, Berkeley. He received his PhD under the direction of Donald Cram at the University of California at Los Angeles. He joined the New York University faculty in 1991 after completing an NIH post-doctoral fellowship with Ronald Breslow at Columbia University. Professor Canary is fascinated by stereodynamic and responsive materials including triggered chiral

materials, nucleic acid templated polymers, and biomedical imaging agents.

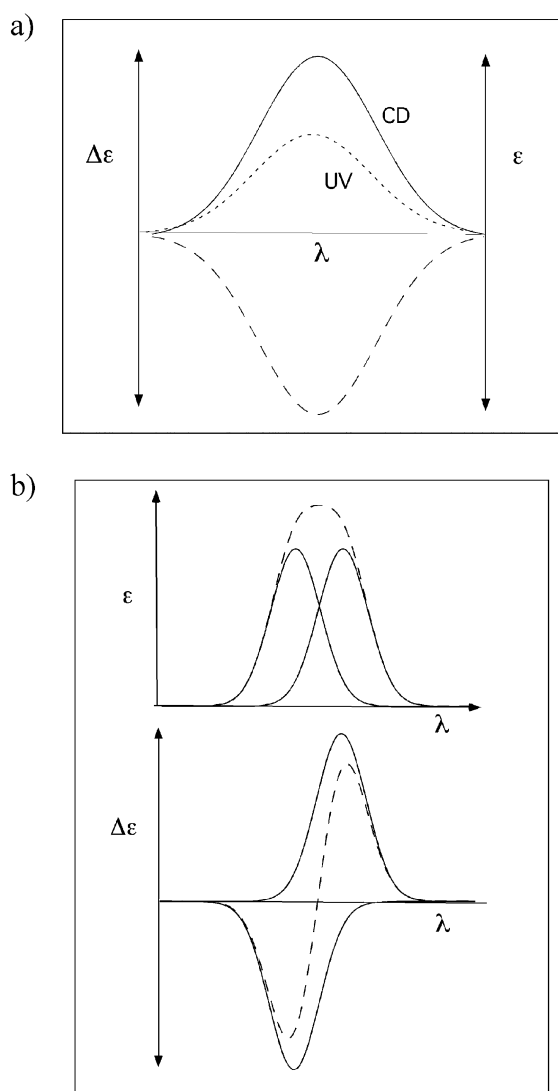


Fig. 1 (a) Circular dichroism spectra. (b) Electronic transition moments in two proximal chromophores may interact resulting in addition in the absorption spectrum but subtraction in the CD spectrum. The null in an ECCD spectrum will appear near the λ_{\max} of the UV-Vis spectrum.

null in the CD spectrum with the λ_{\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 determine stereochemical information from solutions, its utility is more limited in the solid state or aggregates. For spectra obtained from non-isotropic systems, linear dichroism and linear birefringence may dominate the spectrum, and may be misinterpreted as CD. 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.³

The character of the chiroptical signal is only one aspect of chiroptical switches. In general, requirements for the design of an efficient chiroptical molecular redox 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.⁴ Examples discussed in this paper include electro-active organic polymers, redox-active coordination complexes, and certain organic compounds that may be oxidized or reduced reversibly.

Polymers

Some electro-active organic polymers, such as polyaniline, adopt a helical conformation but can easily interconvert between two helical forms. Introduction of a conformational bias by incorporating a chiral center on the polymer backbone, adding a chiral dopant, or presenting a chiral field during synthesis may induce asymmetry in the polymer backbone. The backbone asymmetry may or may not persist in solution, depending on the polymer conformational properties. Chiral bias is often more persistent in aggregates and especially in the solid state.⁵

Polyaniline (PANI, Fig. 2) possesses a helical backbone, although bond rotations that result in interconversion of helical forms are facile. PANI can be prepared in several oxidation states; protonation of the emeraldine state results in optimal electronic properties. In one study, PANI was prepared in several oxidation states and protonated using camphor sulfonic acid.^{6,7} Thin films containing the chiral dopants gave redox-dependent CD spectra. Solutions of the polymers gave CD spectra only in solvents like *N*-methylpyrrolidone (NMP) in which some aggregation of polymer backbones persisted; stronger solvents (such as *m*-cresol) prevented aggregation and gave no CD spectra. This behavior is expected, since full solvation of the chiral ion separates it from the polymer chain, but aggregates may include chiral anions, which in turn induce asymmetric orientation of the chromophores.

In a series of studies, soluble polyaniline derivatives were prepared in the presence of anionic carbohydrate polymers including dextran sulfate⁸ and chondroitin sulfate.⁹ PANI derivatives poly(*o*-methylaniline) and poly(*o*-methoxyaniline) prepared with chondroitin sulfate gave CD spectra corresponding to electronic transitions of the polyaniline derivatives in thin films and solution. The CD spectra were responsive to redox state and pH, as well as other factors such as solvent and ionic strength. Chemical interconversion between the three common redox states of the PANI in aqueous solution gave strong changes in CD. The chiroptical properties resulted from

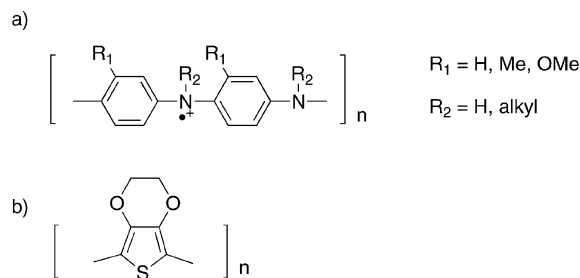


Fig. 2 Examples of electro-active organic polymers that give chiral structures with chiral dopants. (a) Polyaniline and derivatives; (b) PEDOT.

formation of intertwined intermacromolecular complexes between the PANI polymers. In addition to potential applications in chiral electrodes, the system was discussed as a chiroptical pH sensor and an electro-active, enantioselective separation material for capillary electrophoresis.

Optically active poly(3,4-ethylenedioxythiophene/hydroxypropyl cellulose) (PEDOT/HPC) was prepared by oxidative electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) in a concentrated solution of HPC.¹⁰ HPC forms a right-handed nematic liquid crystalline phase under these conditions, and allows epitaxial growth of PEDOT in a three-dimensional chiral field. The insolubility and infusibility of PEDOT/HPC effectively preserves its metastable chiral structure. The PEDOT/HPC exhibits a strong CD in thin films. It also shows electrochemical stability, and reversible color change between a dark blue reduced state and sky blue oxidized state with corresponding changes in the CD spectra. The CD of PEDOT/HPC derives from aggregation order produced by the matrix nematic liquid crystal during the polymerization. The intense optical activity of the polymer allows observation of electro-chiroptical effects.

Goto and Yashima reported electron-switched supramolecular chiral polythiophene aggregates (Fig. 3).¹¹ 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 AFM. Chiral oligothiophenes have been examined for applications as circular polarized electroluminescence devices, and enantioselective sensors, electrodes, catalysts, and adsorbents. Electron-induced triggering of polythiophenes would bring new dimensions to such applications if applicable in the solid state, which the authors believe is possible.

An interesting system was reported by Amabilino and co-workers, who described a helical poly(isocyanide) with chiral tetrathiafulvalene (TTF) side chains, as illustrated in Fig. 4.¹² The polymer showed reversible interconversion between three univalent and two very broad mixed-valence redox states. Each of these states showed distinctive CD spectra. These properties could not be produced by the monomer. The remarkable number of distinct states demonstrates the advantage of assembling redox systems in macromolecules.

The redox-dependent chiroptical properties provide valuable information about the behavior of the polymers in aggregates and in solution. Additionally, these chiral, electro-active organic polymers offer potential applications as chiral electrodes, circularly polarized electroluminescence and electro-active chiral materials such as magneto-optics or Kerr cells for light shutters. Very interesting concepts have been demonstrated including cooperative response to chiral information, and memory of helicity.

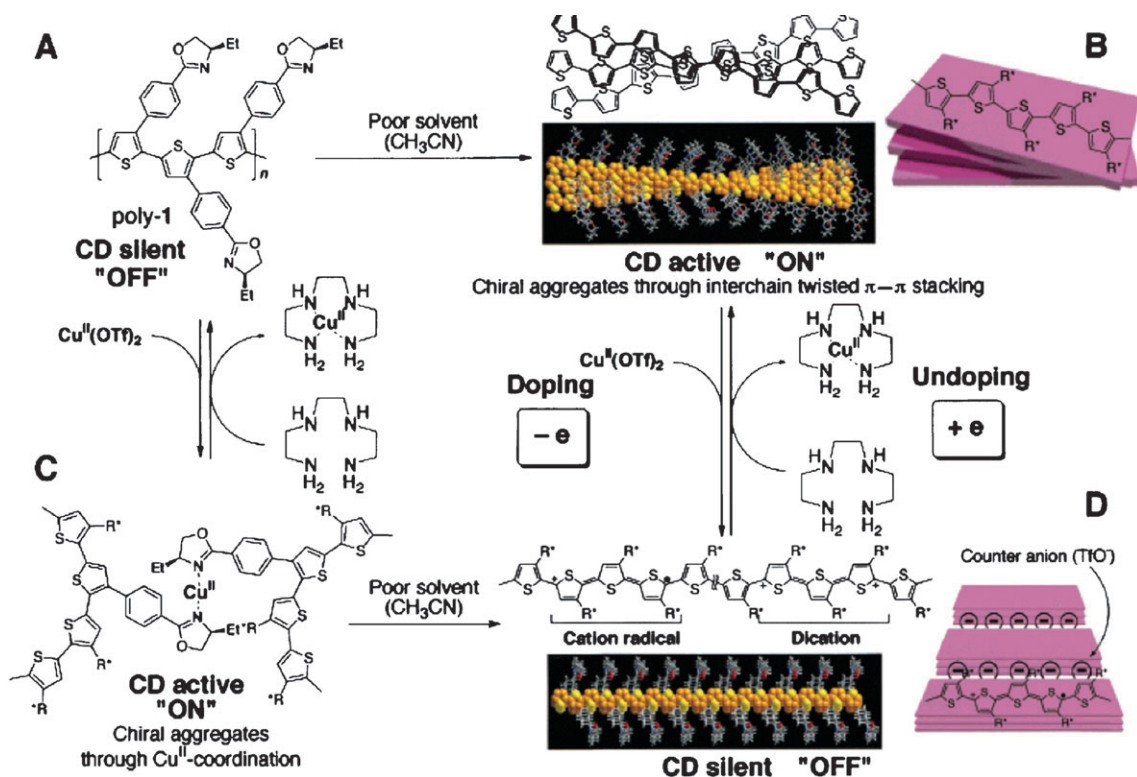


Fig. 3 Oligothiophenes containing chiral centers in side chains (poly-1) aggregate in poor solvents. Electron doping by adding Cu(II) results in CD active aggregates, while undoping reversibly turns off the CD signal. Reprinted with permission.¹¹ Copyright 2002 American Chemical Society.

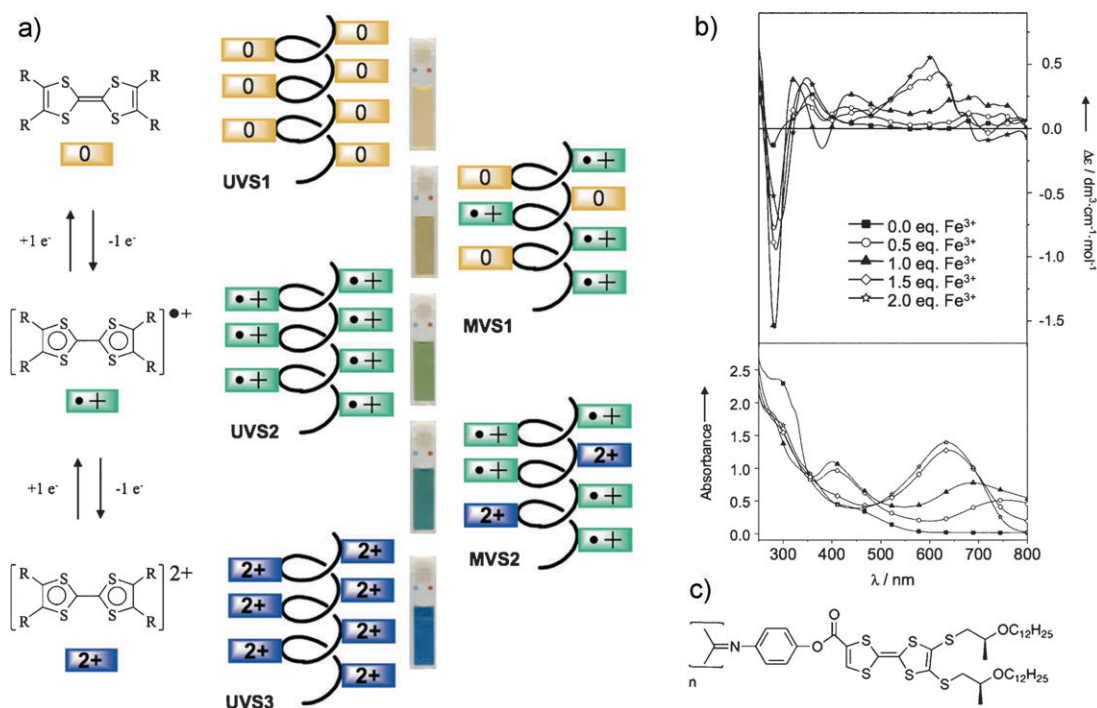


Fig. 4 (a) Helical polymers containing TTF units in five redox states, each with unique CD spectra (b). (c) Chemical structure of the polymers. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.¹²

Metal-based 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.

Shanzer reported a molecular redox switch based on chemical triggering of iron translocation in triple-stranded helical complexes (Fig. 5).¹³ The elegant 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 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, and could be observed by UV-Vis or CD spectroscopy.

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.¹⁴

Work in our laboratories began with the observation that tripodal, N_4 -ligands form stable coordination complexes with divalent metal cations.¹⁵ In the case of $Zn(II)$ and $Cu(II)$, the ligand, otherwise conformationally mobile with many

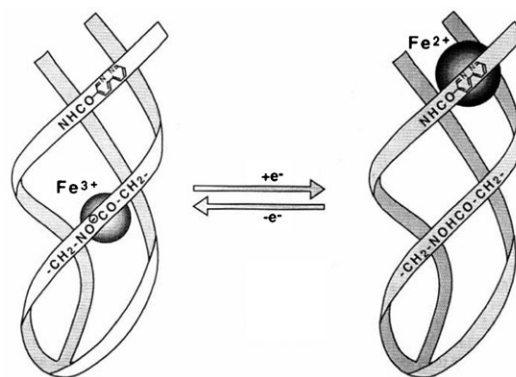


Fig. 5 Tripodal ligand containing two binding sites. $Fe(II)$ binds preferentially to the tris(bipyridine) site while $Fe(III)$ selects the tris(hydroxamate) ligation site. Change of metal ion oxidation state results in translocation of the metal ion from one site to another. Reprinted by permission from Macmillan Publishers Ltd: Copyright 1995.¹³

conformations, wraps around the metal ion to form a propeller-like complex. In ligand **1** (Fig. 6), 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,¹⁶ with few exceptions, established the relationship between the chiral carbon center and the propeller configuration.¹⁷

Exciton-coupled circular dichroism² (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.¹⁸ It was confirmed that $Cu(II)$ and

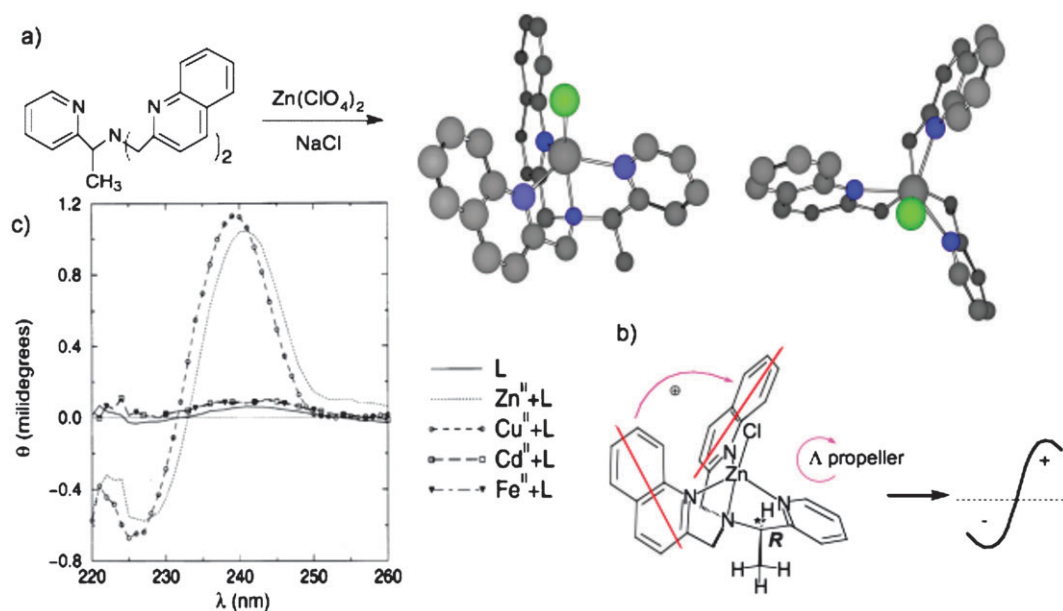


Fig. 6 (a) Conformationally mobile ligand wraps around Zn^{2+} ion to form propeller-like complex as shown by X-ray crystallography (two views shown); (b) prediction of positive ECCD couple; (c) CD spectra of perchlorate complexes where Zn^{2+} and Cu^{2+} show strong amplitude compared to free ligand (L) and Cd^{2+} and Fe^{2+} complexes which are octahedral and distort propeller conformation.¹⁶

Zn(II) complexes showed ECCD spectra consistent with solid-state propeller-like structures. As shown in Fig. 6, 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 $\pi-\pi^*$ 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.¹⁹ The tris(quinoline) compound in Fig. 7 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 affect 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

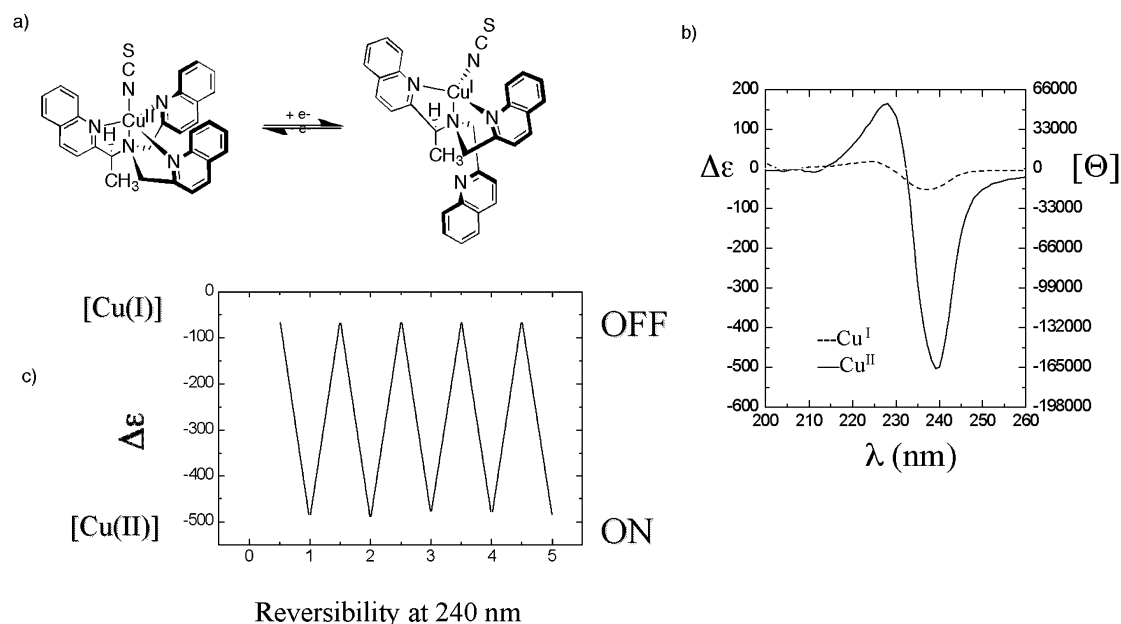


Fig. 7 On/off chiroptical molecular switch. (a) One-electron reduction results in dissociation of an arm of the tripodal ligand; (b) CD spectra of Cu^+ and Cu^{2+} complexes; (c) oxidation and reduction cycles with ascorbate and persulfate.²⁰

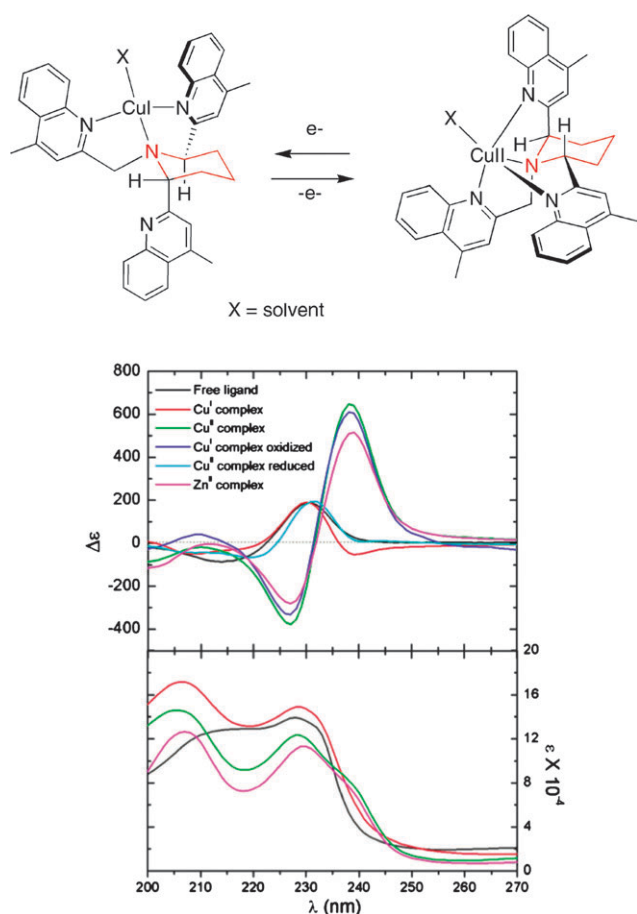


Fig. 8 Redox-triggered inversion of one chair form of a piperidine ring into the other chair and corresponding CD (top) and UV-Vis (bottom) spectra. Adapted with permission.²³ Copyright 2006 American Chemical Society.

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.²⁰ 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 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.²¹ 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.²² 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. 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. 8).²³ In this case, the rigidity of the ligand provided control over which chair form of the piperidine was adopted. In the Cu(I) oxidation state, the ligand adopts a relatively stable cyclohexane chair form 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 substituent. 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 ¹H NMR experiments.

In these studies, ECCD serves 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.²

Systematic exploration by Steffen Zahn of amino acid derivatives^{24,25} led to the discovery of a molecule that inverts helicity and ECCD sign upon one-electron redox change.²⁶ A ligand derived from the amino acid methionine forms a tetradentate complex with Cu(II) involving three nitrogen atoms and a carboxylate (Fig. 9). In this system, the propeller twist of the molecule is dictated by the asymmetric carbon center by virtue of a gearing mechanism among 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 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.²⁷

Closer scrutiny of the mechanism of this interesting transformation is warranted. One possible scheme is shown in Fig. 10. 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

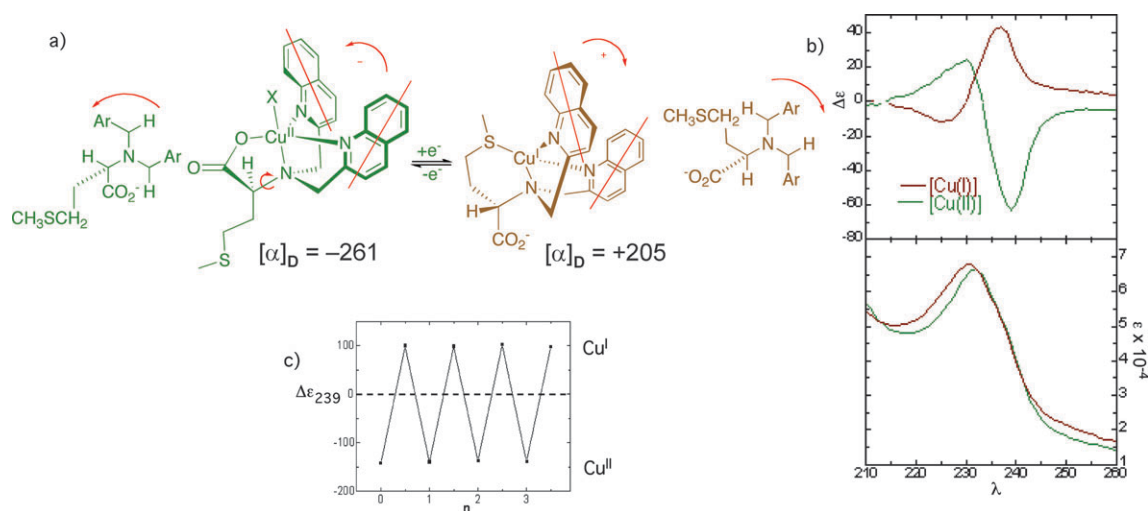


Fig. 9 Redox-induced inversion of helicity. (a) As a result of the presence of gearing among the three arms of the tripod near the sterically crowded tertiary amine of the ligand, a pivot about a C–N bond results in the inversion of the propeller; (b) CD and UV-Vis spectra of Cu^+ and Cu^{2+} oxidation states; (c) chemical cycling with ascorbate and persulfate.^{26,27}

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} .²⁸ A potential candidate for the slow step in the reaction is the substitution reaction proceeding from P_3 to P_4 . The rate of this reaction would depend greatly on the solvent used, but only acetonitrile has been employed in rate studies by SECM.

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. 9 gives inversion of ECCD upon reduction with thiosulfate ion or ascorbate.²⁹ 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.³⁰

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.³¹ As shown in Fig. 11, a 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.

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.

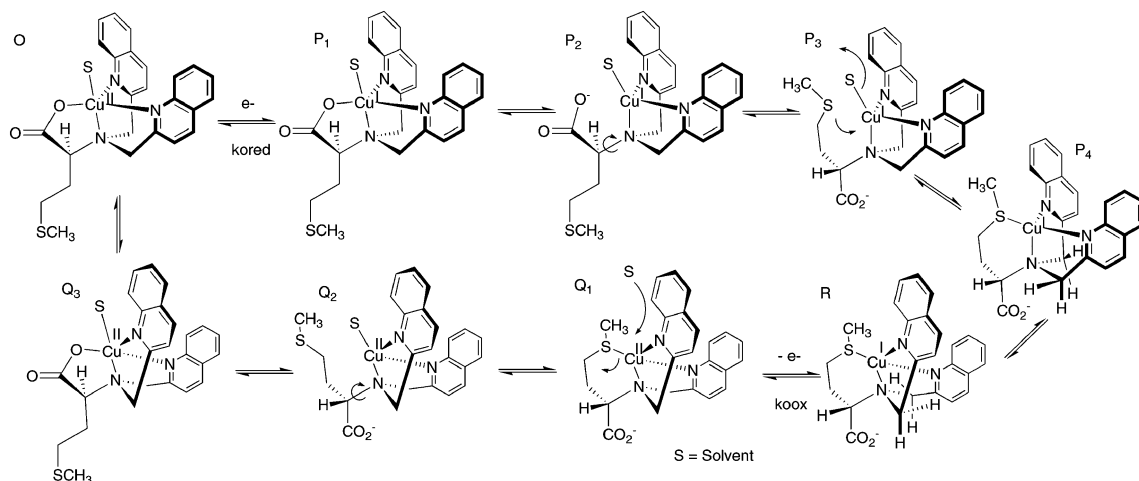


Fig. 10 A possible mechanism of reorganization of Cu^+ and Cu^{2+} complexes.

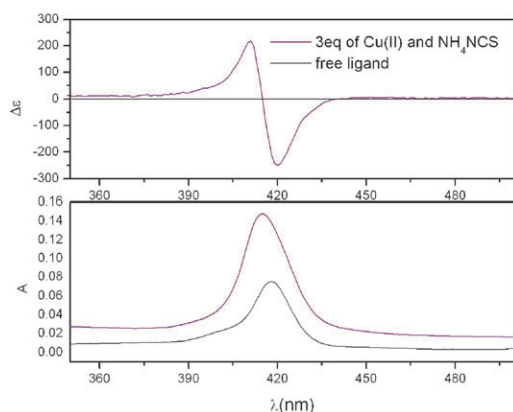


Fig. 11 Redox-triggered reorientation of porphyrins. Adapted with permission.³¹ Copyright 2007 American Chemical Society.

Organic systems

Certain organic molecules can also display useful redox changes, and some of these have been studied as redox-triggered chiroptical molecular switches. In such cases, one-electron redox chemistry that produces bistable compounds is challenging due to the necessary involvement of open-shell species. Two-electron redox reactions may avoid this issue.

Organic radical anions have been studied as chiroptical redox switches. Daub used spectroelectrochemical measurements to show that pyrene functionalized *trans*-1,2-substituted cyclohexanes, as shown in Fig. 12, are excellent chiroptical switches due to intramolecular exciton coupling which leads to split CD.⁴ The two pyrene moieties were weakly coupled in the ground state, but formation of the radical anions of both pyrene units led to strong CD spectra around 500 nm, corresponding to the absorption of the pyrene radical anion. Interestingly, the corresponding bis-amide compound did not show a significant CD spectrum in the reduced state. The system gave a reversible cyclic voltammogram, and beautiful spectroelectrochemical data were obtained by scanning over the reduction wave at $E_{1/2} = -2120$ mV vs. ferrocene. Reduction of chromophores was also undertaken by the groups of Grimme and Daub with derivatives of boron dipyrromethene (BDP). The BDP is a very interesting and useful chromophore due to its excellent optical properties, especially fluorescence. The bis-BDP compound shown in Fig. 12b yielded a strong CD spectrum at 495 nm for the neutral molecule that was examined by quantum mechanical calculations and shown to involve coupling but weak splitting of the two chromophores. Reduction of the compound resulted in disappearance of the 495 nm band, and no CD spectrum was observed for the radical anion. The system acted as a highly reversible on/off chiroptical molecular switch.³² Relevant applications discussed for this system include sensors, circular-polarized photoluminescence, electrochemiluminescence, organic light-emitting diodes, and light-emitting diodes powered by spin-polarized carriers.

Recently, a series of aromatic imides showed strong electronic changes but weaker CD changes as a function of oxidation state.³³ Stronger CD responses were obtained by incorporating naphthalenetetracarboxylate diimides into chiral organogels

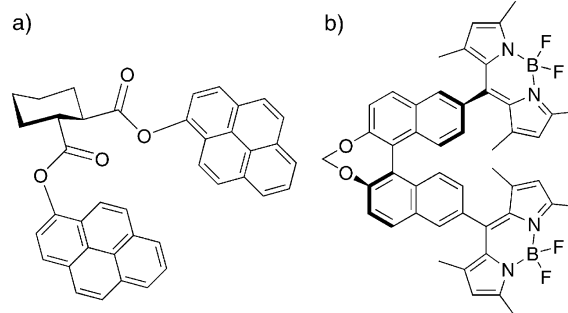
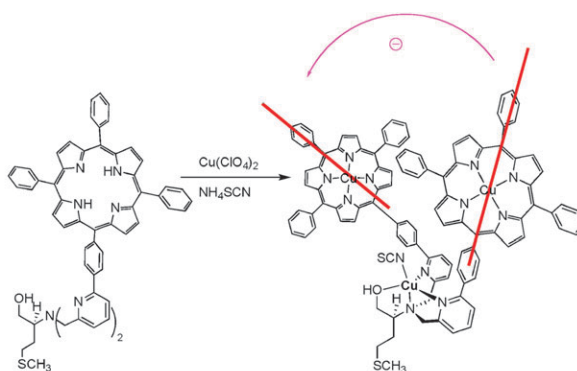


Fig. 12 One electron reduction of each chromophore results in strong changes in CD spectra. (a) Bis-pyrene and (b) bis-boron dipyrromethene.

(Fig. 13).³⁴ In this medium, a variety of data pointed to stacking of the chromophores into supramolecular assemblies. The redox-active gels exhibited reversible and drastic changes in circular dichroism as the aromatic moieties were switched between neutral, radical anion, and dianion states. The largest CD signal was obtained when the stacked naphthalene diimide chromophores were reduced to the radical anion state. The optical response was observed over a wide spectral range, including near infrared (1310–1550 nm).

Mori and Inoue investigated the chiroptical properties of modified tetraarylethylenes in various oxidation states.³⁵ Radical cations and dications were generated reversibly in quantitative yields by electrochemical means. Neutral, radical cationic and dicationic tetraarylethylenes with attached chiral centers displayed distinctly different chiroptical properties and visible color changes, reflecting the alteration in twist angle and bond length of the chromophores. The compounds showed durability upon repeated redox cycles, suggesting application as switches and memory devices working on ternary logic.

The Suzuki group found that dihydro[5]helicenes containing two electron-donating spiro rings undergo reversible C–C bond breaking to give binaphthyl dications (Fig. 14a).³⁶ This interesting chemistry was accompanied by drastic changes in the electronic and CD spectra with the appearance of absorbances associated with the dications. An interesting

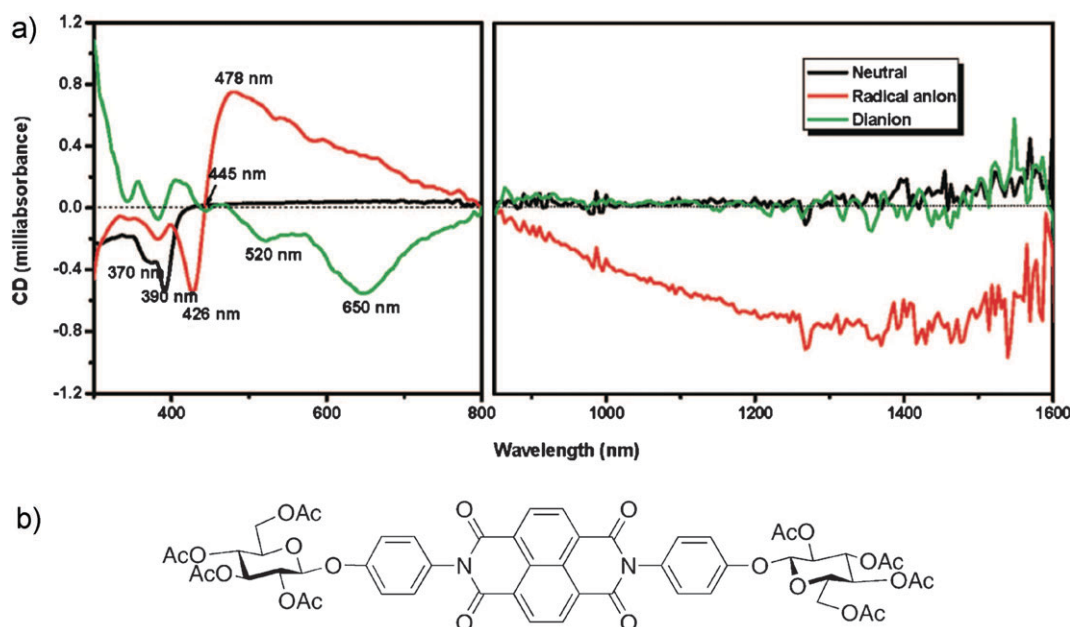


Fig. 13 Visible and near infrared (NIR) circular dichroism spectra (a) of organogels composed of naphthalene diimides attached to glucopyranoside derivatives (b). Reprinted (“Adapted” or “in part”) with permission from Ref. 34. Copyright 2008 American Chemical Society.

variation involved a biphenyl system where the helical chirality was induced by a remote carbon center in a *sec*-butyl group (Fig. 14b).³⁷ In this system, increasing diastereomeric excess and CD amplitude were observed with decreasing solvent polarity, which was rationalized as driving increased steric bias as a result of enhanced intramolecular π - π interactions. Several variations of redox-dependent C-C bond breaking systems have been reported, and this interesting area was reviewed recently.³⁸ Potential applications discussed for these compounds include unimolecular memory storage.

Fukui *et al.* reported a conceptually novel system in which optically active bis(catecholketal)s undergo conformational

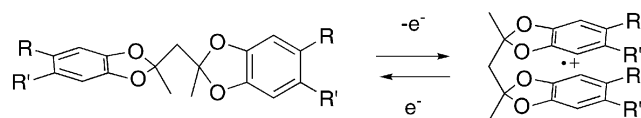


Fig. 15 Bis(catecholketal)s interconvert between extended and folded conformations upon one-electron redox change.

changes upon one electron oxidation.³⁹ The neutral molecule adopted an extended conformation but the radical cation folded as shown in Fig. 15. The conformational analysis was bolstered by theoretical calculation of the CD spectra coupled with conformational population analysis.

Electrochromic systems involving organic radical cations have also been generated from cationic starting states. Molecules based on axially dissymmetric 1,1'-binaphthyl and electrochromic viologens were prepared and characterized.⁴⁰ The compounds showed reversible changes in their absorption and CD spectra when reduced electrochemically to the viologene state. In this case, the mechanism of the CD change was purely electronic in origin.

Organic molecules have now been engineered to demonstrate chiroptical response by either oxidation or reduction with one or two electrons. Bistable states have been achieved by incorporating high delocalization of charge and/or spin. Some of these systems might be expected to offer fast switching rates and the opportunity to easily tailor optical and electrochemical properties.

Outlook

Polymers, coordination complexes, and organic molecules have been shown to act as chiroptical molecular switches. Helical polymers with chiral substituents or dopants may adopt asymmetric conformations or aggregates that give rise to strong circular dichroism spectra. This response may be

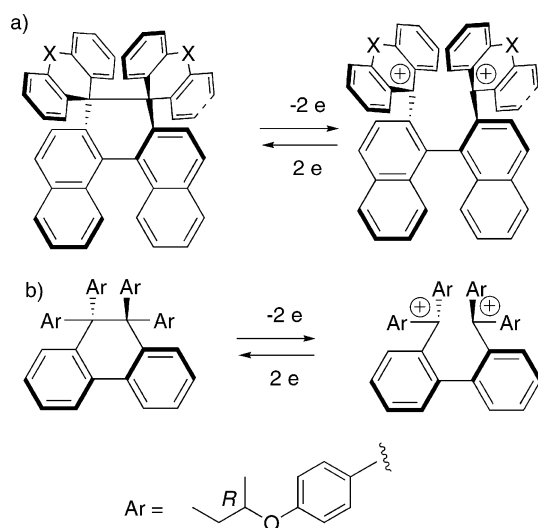


Fig. 14 Two-electron oxidation/reduction results in the reversible formation/breakage of a covalent carbon-carbon bond. (a) Binaphthyl system; (b) biphenyl system where chirality is induced by remote chiral carbon center.

highly sensitive to the oxidation state of the polymer, and thus the chiroptical properties may be switched between two or more states. Coordination complexes may exhibit strong changes in chiroptical spectra as a result of electronic changes at the metal or conformational changes in a chromophoric ligand. Organic molecules may be reduced or oxidized by one or two electron processes to yield molecules with substantially changed electronic properties or conformation.

Advances in spectroscopy have enabled many studies in this field. Quantum mechanical calculation of CD spectra coupled with conformational population analysis is beginning to play a significant role in extending the utility of chiroptical spectroscopy as a probe of structural changes in these systems. As theory, software, and hardware continue to improve rapidly, such evaluations will become even more widespread and useful.

Most studies in this area have been done in solution, but many interesting potential practical applications would most likely require solid-state materials. Polymer systems appear to be naturally suited for solid-state application. Addressable solid-state materials remain a challenge for this and other areas. New technology for detecting chiroptical properties and conformational changes at surfaces will provide new avenues for research and may lead to new opportunities for practical application.

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, and several of the available systems are poised to make a genuine contribution.

Acknowledgements

We are grateful to the National Science Foundation for generous support of our work in this area.

References

- 1 K. Nakanishi, N. Berova and R. Woody, *Circular Dichroism: Principles and Applications*, Wiley-VCH, New York, 2000.
- 2 N. Berova, L. Di Bari and G. Pescitelli, *Chem. Soc. Rev.*, 2007, **36**, 914–931.
- 3 T. Harada, H. Hayakawa and R. Kuroda, *Rev. Sci. Instrum.*, 2008, **79**, 073103.
- 4 C. Westermeier, H. C. Gallmeier, M. Komma and J. Daub, *Chem. Commun.*, 1999, 2427–2428.
- 5 J. Cornelissen, A. E. Rowan, R. J. M. Nolte and N. Sommerdijk, *Chem. Rev.*, 2001, **101**, 4039–4070.
- 6 K. Levon, K. C. Park and C. Cai, *Synth. Met.*, 1997, **84**, 335–338.
- 7 L. A. P. Kane-Maguire, I. D. Norris and G. G. Wallace, *Synth. Met.*, 1999, **101**, 817–818.
- 8 G. L. Yuan and N. Kuramoto, *Macromolecules*, 2003, **36**, 7939–7945.
- 9 G.-L. Yuan and N. Kuramoto, *Macromol. Chem. Phys.*, 2004, **205**, 1744–1751.
- 10 H. Goto and K. Akagi, *Chem. Mater.*, 2006, **18**, 255–262.
- 11 H. Goto and E. Yashima, *J. Am. Chem. Soc.*, 2002, **124**, 7943–7949.
- 12 E. Gomar-Nadal, J. Veciana, C. Rovira and D. B. Amabilino, *Adv. Mater.*, 2005, **17**, 2095–2098.
- 13 L. Zelikovich, J. Libman and A. Shanzer, *Nature*, 1995, **374**, 790–792.
- 14 K. Tashiro, K. Konishi and T. Aida, *J. Am. Chem. Soc.*, 2000, **122**, 7921–7926.
- 15 J. W. Canary, C. S. Allen, J. M. Castagnetto and Y. H. Wang, *J. Am. Chem. Soc.*, 1995, **117**, 8484–8485.
- 16 J. W. Canary, C. S. Allen, J. M. Castagnetto, Y. H. Chiu, P. J. Toscano and Y. H. Wang, *Inorg. Chem.*, 1998, **37**, 6255–6262.
- 17 X. D. Xu, K. J. Maresca, D. Das, S. Zahn, J. Zubietta and J. W. Canary, *Chem.-Eur. J.*, 2002, **8**, 5679–5683.
- 18 J. M. Castagnetto, X. D. Xu, N. D. Berova and J. W. Canary, *Chirality*, 1997, **9**, 616–622.
- 19 S. Zahn and J. W. Canary, *Angew. Chem., Int. Ed.*, 1998, **37**, 305–307.
- 20 S. Zahn and J. W. Canary, *J. Am. Chem. Soc.*, 2002, **124**, 9204–9211.
- 21 J. Zhang, K. Siu, C. H. Lin and J. W. Canary, *New J. Chem.*, 2005, **29**, 1147–1151.
- 22 S. Zahn, G. Proni, G. P. Spada and J. W. Canary, *Chem.-Eur. J.*, 2001, **7**, 88–93.
- 23 J. Zhang and J. W. Canary, *Org. Lett.*, 2006, **8**, 3907–3910.
- 24 S. Zahn and J. W. Canary, *Org. Lett.*, 1999, **1**, 861–864.
- 25 A. E. Holmes, S. Zahn and J. W. Canary, *Chirality*, 2002, **14**, 471–477.
- 26 S. Zahn and J. W. Canary, *Science*, 2000, **288**, 1404–1407.
- 27 S. Zahn, D. Das and J. W. Canary, *Inorg. Chem.*, 2006, **45**, 6056–6063.
- 28 H. S. Barcena, B. Liu, M. V. Mirkin and J. W. Canary, *Inorg. Chem.*, 2005, **44**, 7652–7660.
- 29 D. Das, Z. H. Dai, A. Holmes and J. W. Canary, *Chirality*, 2008, **20**, 585–591.
- 30 H. S. Barcena, A. E. Holmes, S. Zahn and J. W. Canary, *Org. Lett.*, 2003, **5**, 709–711.
- 31 A. E. Holmes, D. Das and J. W. Canary, *J. Am. Chem. Soc.*, 2007, **129**, 1506–1507.
- 32 G. Beer, C. Niederaalt, S. Grimme and J. Daub, *Angew. Chem., Int. Ed.*, 2000, **39**, 3252–3255.
- 33 E. K. Todd, S. Wang, X. Wan and Z. Y. Wang, *Tetrahedron Lett.*, 2005, **46**, 587–590.
- 34 J. Zheng, W. Qiao, X. Wan, J. P. Gao and Z. Y. Wang, *Chem. Mater.*, 2008, **20**, 6163–6168.
- 35 T. Mori and Y. Inoue, *J. Phys. Chem. A*, 2005, **109**, 2728–2740.
- 36 J. Nishida, T. Suzuki, M. Ohkita and T. Tsuji, *Angew. Chem., Int. Ed.*, 2001, **40**, 3251–3254.
- 37 T. Suzuki, T. Iwai, E. Ohta, H. Kawai and K. Fujiwara, *Tetrahedron Lett.*, 2007, **48**, 3599–3603.
- 38 T. Suzuki, E. Ohta, H. Kawai, K. Fujiwara and T. Fukushima, *Synlett*, 2007, 851–869.
- 39 M. Fukui, T. Mori, Y. Inoue and R. Rathore, *Org. Lett.*, 2007, **9**, 3977–3980.
- 40 J. Deng, N. Song, Q. Zhou and Z. Su, *Org. Lett.*, 2007, **9**, 5393–5396.