

Cu(I/II) Redox Control of Molecular Conformation and Shape in Chiral Tripodal Ligands: Binary Exciton-Coupled Circular Dichroic States

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Abstract: This manuscript describes the design, synthesis, and characterization of a coordination complex that demonstrates reversible interconversion between two redox states that show very different chiroptical properties. Reported here are three chiral N₄-tetradentate ligands, prepared in enantiopure form by asymmetric synthesis, and their circular dichroic and other properties, as well as those of numerous Cu(I) and Cu(II) complexes. While the chiroptical spectra of the free ligands are unremarkable, the CD spectra of the complexes are very intense, and spectral features indicate that they derive from exciton coupling. Comparison of complexes with one, two, or three chromophores provides strong supportive evidence for this assignment, and semiquantitative correlation with intensity as rationalized by additivity. A Cu^I(L)/Cu^{II}(L) redox couple was identified that showed dramatically different circular dichroic properties that was further shown to be easily oxidized and reduced chemically between two states with remarkable retention of signal. A structural hypothesis for the interconversion is given and supported by a variety of spectroscopic evidence.

Introduction

Chiral organic molecules have found many applications in materials science. Current display technology benefits greatly from switchable cholesteric liquid crystals, which operate by reorientation of molecules induced by electric fields. Excellent progress has been made with these materials; soon, cholesterics may find applications in other areas of molecular electronics, including light valves, modulators, shutters, light deflectors, optical filtration, logic elements, and storage devices.¹ Many materials with second-order nonlinear optical properties possess a chiral center which guarantees noncentrosymmetry for even-ordered harmonic generation.² Recently, pioneering new phenomena have been reported such as nonlinear optical activity in second harmonic generation from chiral surfaces.³ The ability to modulate the shape and chirality-related properties of molecules seems likely to improve greatly the chances for development of new applications of chiral compounds. Development of suitable chiroptical switches will require large amplitude and easily detectable signals, reversible and fast interconversion between states, and ready adaptability to solid state technology. One promising but not yet completely successful approach has utilized photochemical reactions in which an element of chirality is inverted upon irradiation, for example, of a substituted alkene.^{4,5} Such photoswitched compounds have

provided interesting and elegant systems such as molecular motors.⁶

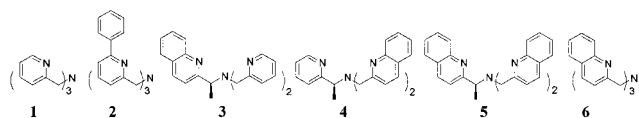
We have examined redox-induced changes in molecular shape.⁷ This strategy may offer practical advantages because many current technologies are based on electrically induced changes. Furthermore, a redox-write, chiroptical-read approach may offer significant stability and other practical advantages. Among a variety of interesting redox-switched systems,^{8–10} Sauvage et al.^{11,12} and Weiss et al.¹³ have described bistable, copper-based achiral or racemic molecular switches. Shanzer et al. described an elegant chiral system in which an Fe^{II} atom translocated between binding sites upon oxidation to Fe^{III}.¹⁴ Daub et al. have described systems in which significant changes in circular dichroism have been observed upon redox triggering.^{15,16} We have undertaken an approach that relies on

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(1) Schadt, M. *Annu. Rev. Mater. Sci.* **1997**, *27*, 305–379.
(2) Verbiest, T.; van Elshocht, S.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913–915.
(3) Verbiest, T.; Kauranen, M.; Persoons, A. *J. Mater. Chem.* **1999**, *9*, 2005–2012.

(4) Ireie, M., Ed. *Chem. Rev.* **2000**, *100*, entire issue.
(5) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789–1816.
(6) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152–155.
(7) Canary, J. W.; Zahn, S.; Chiu, Y.-H.; dos Santos, O.; Liu, J.; Zhu, L. *Enantiomer* **2000**, *5*, 397–403.
(8) Fabbri, L.; Licchelli, J.; Pallavicini, P. *Acc. Chem. Res.* **1999**, *32*, 846–853.
(9) Gokel, G. W.; De Wall, S. L. *Adv. Supramol. Chem.* **1999**, *5*, 203–235.
(10) Collier, C. P.; Wong, E. W.; Belohradsk'y, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391–394.
(11) Armaroli, N.; Balzani, V.; Collin, J.-P.; Gavina, P.; Sauvage, J.-P.; Ventura, B. *J. Am. Chem. Soc.* **1999**, *121*, 4397–4408.
(12) Blanco, J. J.; Jimenez, M. C.; Chambron, J. C.; Heitz, V.; Linke, M.; Sauvage, J. P. *Chem. Soc. Rev.* **1999**, *28*, 293–305.
(13) Wytko, J. A.; Boudon, C.; Weiss, J.; Gross, M. *Inorg. Chem.* **1996**, *35*, 4469–4477.
(14) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, *374*, 790–792.
(15) Westermeier, C.; Gallmeier, H.-C.; Komma, M.; Daub, J. *Chem. Commun.* **1999**, 2427–2428.
(16) Porsch, M.; Sigl-Seifert, G.; Daub, J. *Adv. Mater.* **1997**, *9*, 635–639.

coordination chemistry changes induced by one-electron oxidation/reduction of a copper ion.^{17,18} Such chemistry is well precedented in the inorganic literature.^{19–21}



The compounds discussed here are related to the parent ligand tris([2-pyridyl]methyl)amine, **1** (TPA). Derivatives of **1** with one arm containing a chiral center as a result of incorporating a substituent show adoption of an additional, helical chiral element upon complexation of a trigonal bipyramidal metal ion such as Cu^{II} or Zn^{II}.^{22–24} This additional, propeller-like chirality orients the heterocyclic rings in derivatives of **1** such that large signals in the circular dichroism (CD) spectrum may be observed. The helical chirality and close positioning of the heterocycles result in coupling of the chromophores if the electric transition moments are suitably placed. The result is the formation of exciton-coupled circular dichroism (ECCD) spectra of large amplitude.²⁵ The CD spectra have been analyzed and shown to reveal the absolute chirality of the chromophore pairwise orientation, and thus give the configuration of the propeller twist. The analysis has been extended to show that amines of unknown configuration may be derivatized and analyzed to give the amine absolute configuration by CD.²⁶ Previous work also showed that the ligand conformation could be mediated by the nature of the metal ion coordinated.²⁷ Exchange of a trigonal bipyramidal metal for an octahedral one such as Cd^{II} or Fe^{II} resulted in loss of the CD signal because of distortion of the propeller conformation. Recently, it was shown that coordination complexes of **3** and **5** could be used to dope nematic liquid crystals, producing cholesteric phases.²⁸

Exciton-coupled CD spectra are diagnostic for changes in molecular conformation and shape in our system. The signal originates from the anisotropic interaction between adjacent nonconjugated chromophores, affording a bisignate spectrum (Figure 1). When the transition moments of the chromophores constitute a positive exciton chirality,²⁹ one obtains a positive couplet (positive longer wavelength Cotton effect, CE, and a negative shorter wavelength CE). The absolute sign and magnitude of the ECCD spectra have been placed on firm

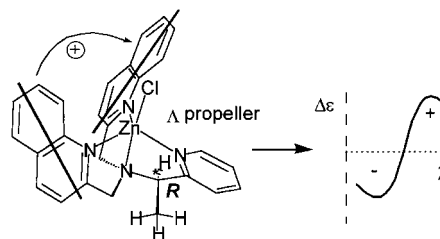


Figure 1. Structural basis for exciton-coupled circular dichroism (ECCD) spectrum of $[(\text{Zn}^{\text{II}}\text{-}(\text{R})\text{-}4)\text{Cl}]^+$.²⁴

theoretical ground, and spectra have been calculated by ab initio or semiempirical methods.²⁹ The presence of the ECCD mechanism can be recognized by the strong amplitude of the signal, the bisignate shape, and the occurrence of the null close to the λ_{max} for the electronic transition. The amplitude, A , of the signal depends on the intensity of the electronic transition and the distance and dihedral angle (max at 70°, i.e., Figure 1) between the chromophores.³⁰

The idea for a redox chiroptical switch originated from studies of the ligand tris(6-phenyl-[2-pyridyl]methyl)amine (**2**) for which crystallographic structures of both the Cu^I and the Cu^{II} complexes were obtained.³¹ Both structures showed pronounced propeller twists, but the Cu^{II} structural twist was significantly larger as a result of the expansion of the coordination sphere of the metal ion by coordination of an acetonitrile ligand. It was predicted, from examination of these structures, that the CD spectra of related chiral ligands should be modulated by redox changes that would be expected to induce changes in the dihedral angle between the chromophores. For this study, the ligands **3–5** were selected. The ligand **5** is closely related to achiral molecules reported by Karlin et al., copper complexes of which were structurally characterized and showed coordination chemistry behavior similar to that of **2**.^{32,33} The ligand conformation in the Cu^I complex of **6**³³ resembles a three-bladed propeller with pseudo C_3 symmetry. In our own previous work, quinoline ligands had given excellent CD spectra resulting from a favorable orientation of the electric transition moment corresponding to one of the observed electronic transitions.²³ Some of the results concerning ligand **5** and its copper complexes were previously communicated.¹⁷

Results and Discussion

Absorption and Circular Dichroism Spectra. The absorption spectra of ligands **3–5** and their copper perchlorate complexes in methanol display bands characteristic for quinoline and pyridine chromophores (Figure 2). All spectra are qualitatively very similar, displaying two major transitions of practically equal intensities (207 nm, 232 nm) and a band of poorly resolved peaks at 280–330 nm; these bands are blue-shifted with respect to quinoline as well as quinoline-containing intermediates used in this study. The transition bands for quinoline are at 225–227 nm ($\epsilon = 35\,000\text{--}40\,000$), 278 nm ($\epsilon = 3500$), 300 nm ($\epsilon = 2600$), and 314 nm ($\epsilon = 3000$). 2-Bromomethylquinoline presents two strong peaks of practi-

- (17) Zahn, S.; Canary, J. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 305–307.
 (18) Zahn, S.; Canary, J. W. *Science* **2000**, *288*, 1404–1407.
 (19) Xie, B.; Elder, T.; Wilson, L. J.; Stanbury, D. M. *Inorg. Chem.* **1999**, *38*, 12–19.
 (20) Ambundo, E. A.; Deydier, M.-V.; Grall, A. J.; Aguera-Vega, N.; Dressel, L. T.; Cooper, T. H.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, *38*, 4233–4242.
 (21) Ambundo, E. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **2001**, *40*, 5133–5138.
 (22) Wang, S. X.; Taratorin, A. M. *Magnetic Information Storage Technology. Electromagnetism Series*; Academic Press: New York, 1999.
 (23) Canary, J. W.; Allen, C. S.; Castagnetto, J. M.; Wang, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8484–8485.
 (24) Canary, J. W.; Allen, C. A.; Castagnetto, J. M.; Chiu, Y.-H.; Toscano, P. J.; Wang, Y. *Inorg. Chem.* **1998**, *37*, 6255–6262.
 (25) Castagnetto, J. M.; Xu, X. D.; Berova, N. D.; Canary, J. W. *Chirality* **1997**, *9*, 616–622.
 (26) Zahn, S.; Canary, J. W. *Org. Lett.* **1999**, *1*, 861–864.
 (27) Castagnetto, J. M.; Canary, J. W. *J. Chem. Soc., Chem. Commun.* **1998**, 203–204.
 (28) Zahn, S.; Proni, G.; Spada, G. P.; Canary, J. W. *Chem.-Eur. J.* **2001**, *7*, 88–93.
 (29) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.

- (30) Nakanishi, K.; Berova, N. D.; Woody, R. W., Eds. *Circular Dichroism: Principles and Applications*; VCH Publishers: New York, 1994.
 (31) Chuang, C.-L.; Lim, K.; Chen, Q.; Zubieta, J.; Canary, J. W. *Inorg. Chem.* **1995**, *34*, 2562–2568.
 (32) Wei, N.; Murthy, N. N.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 6093–6100.
 (33) Wei, N.; Murthy, N. N.; Chen, Q.; Zubieta, J.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1953–1965.

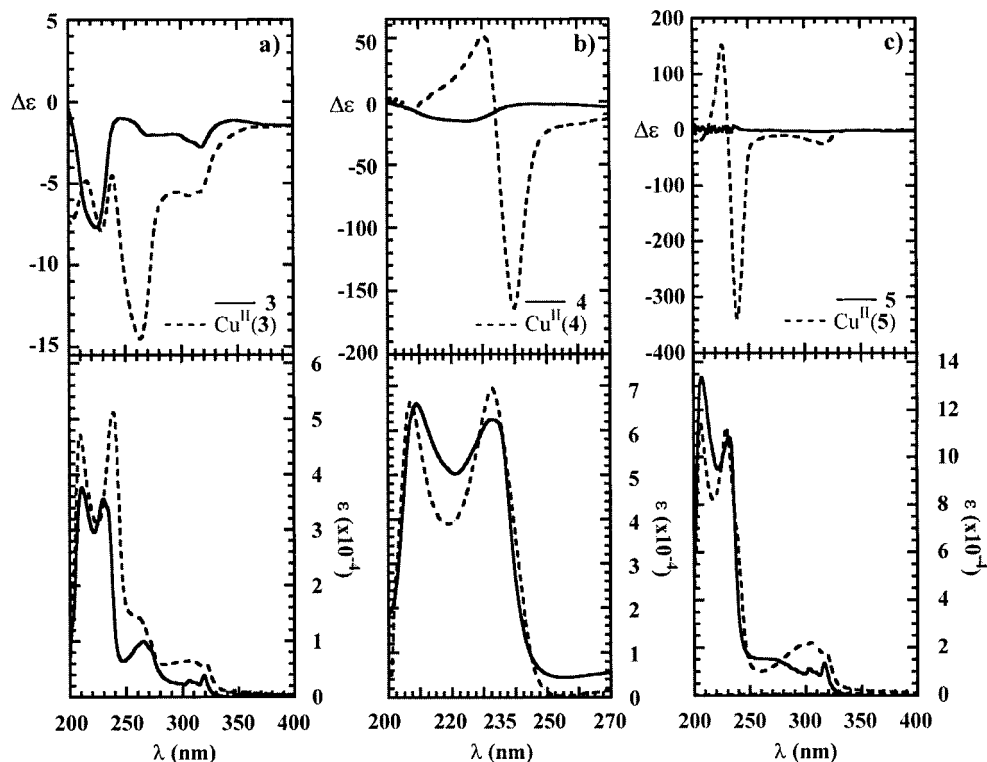


Figure 2. Circular dichroism (upper part) and absorption (lower part) spectra of complex $[\text{Cu}^{\text{II}}(\text{L})]^{2+}$ (dashed line) and ligand **L** (solid line). UV-vis (5 mM) and CD spectra (0.3 mM) were measured at room temperature in methanol. ϵ and $\Delta\epsilon$ units are $\text{L mol}^{-1} \text{cm}^{-1}$. (a) **L** = 3. (b) **L** = 4. (c) **L** = 5.

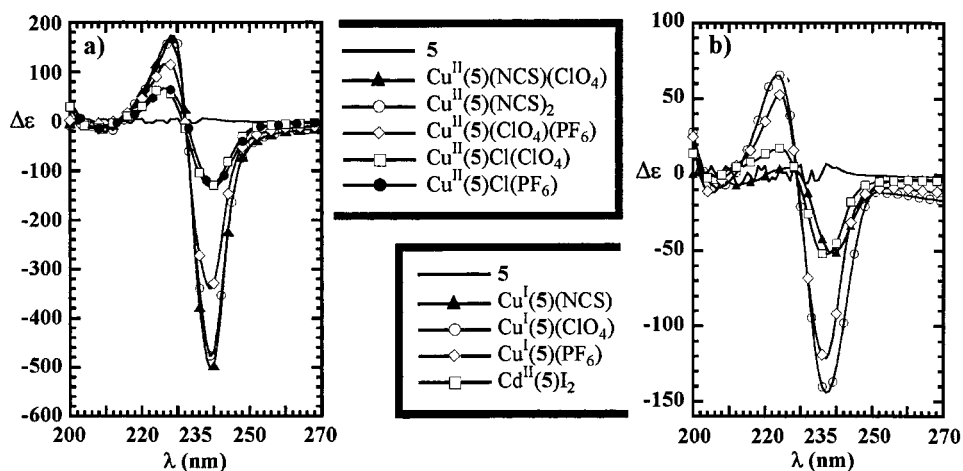


Figure 3. Circular dichroism spectra in methanol. Formulas represent elemental composition as determined by combustion analysis of the isolated complexes. (a) Ligand **5** and Cu^{II} complexes. (b) Ligand **5** and Cu^{I} complexes and Cd^{II} complex. $\Delta\epsilon$ unit is $\text{L mol}^{-1} \text{cm}^{-1}$.

cally equal intensities, one at 207 nm ($\epsilon = 59\,000$), and another at 233 nm ($\epsilon = 57\,000$), and a band of peaks at 250–325 nm. *R*-(+)-1-(2-Quinoly)-ethyl-amine exhibits a strong, relatively broad peak at 207–208 nm ($\epsilon = 40\,000$), a broad shoulder at 230 nm ($\epsilon = 17\,000$), as well as a band of poorly resolved transitions at 320–330 nm ($\epsilon = 3500\text{--}4000$). Quantitatively, the spectra of **3–5** differ because of the varying number of the quinoline moieties ($\epsilon = 35\,000\text{--}40\,000$) in the ligands. The spectra of the copper complexes show small shifts with respect to the free ligand that depend on the nature of the metal ion. The absorption maxima near 230 nm for $\text{Cu}^{\text{II}}(\mathbf{3})$ shift to longer wavelengths, whereas $\text{Cu}^{\text{II}}(\mathbf{4})$ and $\text{Cu}^{\text{II}}(\mathbf{5})$ show small shifts toward shorter wavelength.

The CD spectra of **3–5** and their Cu^{II} complexes are shown in Figure 2. The relative intensity of the spectra of the free

ligands is relatively weak. Complexation with Cu^{II} gives rise to ECCD spectra for the copper complexes of ligands **4** and **5**. The data suggest that the longitudinal transition at 232 nm is responsible for the characteristic bisignate curves in the spectra. The complex $\text{Cu}^{\text{II}}(\mathbf{3})$ displays a very weak spectrum, with no indication of exciton coupling.^{24,25} Although its UV-vis spectrum is very similar to those of the other copper complexes, the CD spectra are entirely different. The complex $\text{Cu}^{\text{II}}(\mathbf{4})$ gives rise to a strong ECCD couplet. Introducing a third quinoline moiety in $\text{Cu}^{\text{II}}(\mathbf{5})$ resulted in a qualitatively identical ECCD spectrum but with even stronger amplitude.

Figure 3 shows the spectra of several complexes of ligand **5**. The amplitudes are dependent on the oxidation state of the metal and the presence of coordinating anions. These factors will be discussed in the next two sections.

Table 1. Comparison of the Magnitude of Induced Cotton Effects and Amplitudes of Cu^{II} Complexes with Their Corresponding Visible Spectra Data^a

complexes	$\Delta\epsilon_{\text{max data}}$			$\epsilon_{\text{max data}}$	
	$\Delta\epsilon$	ϵ	λ	ϵ	λ
[Cu ^{II} (5)NCS]	0.49	384	425	390	420
	-0.92	131	698	133	712
	0.61	186	858	190	884
	0.54	187	907		
[Cu ^{II} (5)(CH ₃ OH)]	-0.23	119	660	120	668
	0.27	85	840		
	0.19	77	907		
	-0.22	143	745	182	680
[Cu ^{II} (5)Cl]	0.07	86	846		
	0.10	76	913		

^a Spectra are of 0.3 mM methanol solutions prepared from solids with the indicated elemental composition.

Electrodichroic Couple Cu^{II}(5)/Cu^I(5). The Cu^I complexes of ligand **5** were expected to show significantly reduced CD signal amplitude as a result of a reduced dihedral angle between the quinoline chromophores. The calculated dihedral angle between the chromophores in Cu^{II}(5) is about 21.3° and 15.4° in Cu^I(5) (Supporting Information). The change in ligand twist arises from the larger metal ion radius and longer coordinate N–Cu bonds and from the lower coordination number of the metal ion complex. These factors reduce the total steric interaction between the quinoline arms in the Cu^I complex, via rotation about the CH₂–C_{quinoline} bond.

Ascorbic acid was used to reduce Cu^{II}(5). Reduction was rapid, as observed by the quick color change from green to yellow, and the resulting CD spectrum was identical to that of a solution prepared from isolated [Cu^I(5)](PF₆). Addition of 1 equiv of ammonium persulfate resulted in a sluggish change in the CD spectrum. Heating at 45 °C for about 10 min yielded a spectrum similar to that of the solution prepared from isolated complex Cu^{II}(5)(ClO₄)(PF₆). Subsequent reduction resulted in a yellow solution, and the CD spectrum was again identical to that of Cu^I(5)(PF₆).

Thus, the redox couple Cu^{II}(5)/Cu^I(5) gave the expected variation in circular dichroism amplitude, consistent with the original hypothesis that led to this study. The amplitude nearly tripled upon oxidation to Cu^{II}(5). However, interconversion between the two states was sluggish, so it was decided to examine the effect of counterions.

Influence of Coordinating Anions. Counterions in these complexes may or may not influence the CD spectra. Clearly, strongly coordinating anions such as SCN⁻ will coordinate to the metal center, providing an influence upon the CD spectrum that will result from the electronic influence on the metal ion and steric interactions with the ligand. The effect of anions on the metal is significant because of the possibility for Cu^{II} to adopt square pyramidal (sq py) or trigonal bipyramidal (tbp) coordination geometries. Only the latter geometry is expected to afford an intense ECCD spectrum.²⁴ The sq py versus tbp character was estimated according to Karlin's UV–vis trends, developed for very similar complexes (Table 1).^{32,34} The two limiting structures are shown in Figure 4 with achiral ligand **6**,^{32,34} in which **7a** represents a complex in which the Cu ion

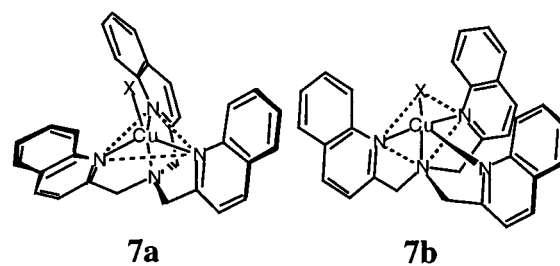


Figure 4. Depiction of potential geometries of [Cu^{II}(6)X] complexes with trigonal bipyramidal and square pyramidal copper ion, enforcing C₃ and C_σ ligand conformations, respectively. X = coordinating anion or solvent.

adopts tbp geometry, which in turn enforces a ligand conformation with approximate C₃ symmetry. When the Cu^{II} ion adopts sq py geometry, a distorted, T-like ligand conformation with approximate C_σ symmetry is adopted, as in **7b**.³⁵ In this structure, two quinolyl rings are nearly coplanar. This geometry allows only for very poor interaction of the dipole moments of the chromophores, yielding a weak ECCD signal.

The complex Cu^{II}(5)(NCS) gave electronic spectra with absorbance in the d–d region at 712 (133) and 884 (190) nm. The ratio of extinction coefficients is 0.70, indicating tbp Cu^{II}.^{32,34} This complex gives correspondingly intense CD spectra (Figure 3). Examination of CPK models showed that in a trigonal bipyramidal environment, complex [Cu^{II}(5)(NCS)] should possess a pseudo C₃ axis with the quinoline donors in a nearly perfect three-bladed propeller arrangement giving rise to three strong excitonic interactions.

The complex [Cu^{II}(5)(CH₃OH)] shows d–d transitions at 668 (120) with a shoulder at 820 (86) nm. The extinction coefficient ratio of 1.39 suggests a geometry that is intermediate between **7a** and **7b**, or a mixture of solution structures in which the ligand may exist in both conformations. This analysis agrees with the intermediate amplitude of the CD spectra for this complex. The solution structure of [Cu^{II}(5)Cl] gives a peak in the visible spectrum at 680 (218) nm, with a shoulder at 1050 (90) nm, suggesting a predominantly C_σ conformation.³² This complex gives weak amplitude CD spectra.

To further test the role of the ligand conformation in the determination of the intensity of the CD signal, we isolated cadmium complex Cd(5)I₂. This metal ion is known to form six-coordinate, octahedral complexes with related ligands, and would enforce a C_σ ligand conformation.³⁵ The CD spectrum is indeed weak (Figure 2b).

Addition of thiocyanate to a solution of Cu^{II}(5) in methanol gave rise to a significantly stronger amplitude signal. Using more than 1 equiv of thiocyanate did not change the magnitude of the signal further. Similar manipulation of the CD spectrum of Cu^I(5) resulted in reduced CD amplitudes.

Electrodichroic Couple Cu^{II}(5)(NCS)/Cu^I(5)(NCS). Among the variety of counterions that were investigated, it was found that addition of thiocyanate gave an increase in the CD amplitude for Cu^{II}(5) and a decrease in that for Cu^I(5) (Figure 3). The resulting complexes Cu^{II}(5)(NCS)(ClO₄) and Cu^I(5)(NCS) were isolated and characterized by elemental analysis. The UV–vis spectrum of Cu^{II}(5)(NCS) displayed a new maximum at about 420 nm. Additionally, the d–d bands

(34) Zubieta, J.; Karlin, K. D.; Hayes, J. C. *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Adenine Press: Albany, NY, 1983.

(35) Allen, C. S.; Chuang, C.-L.; Cornebise, M.; Canary, J. W. *Inorg. Chim. Acta* **1995**, *239*, 29–37.

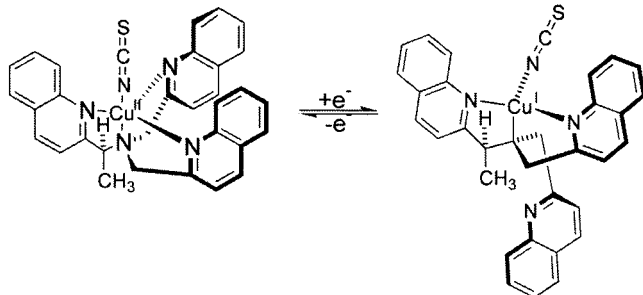


Figure 5. Proposed structures for $[\text{Cu}^{\text{II}}(\mathbf{5})\text{NCS}]$ and $[\text{Cu}^{\text{I}}(\mathbf{5})\text{NCS}]$.

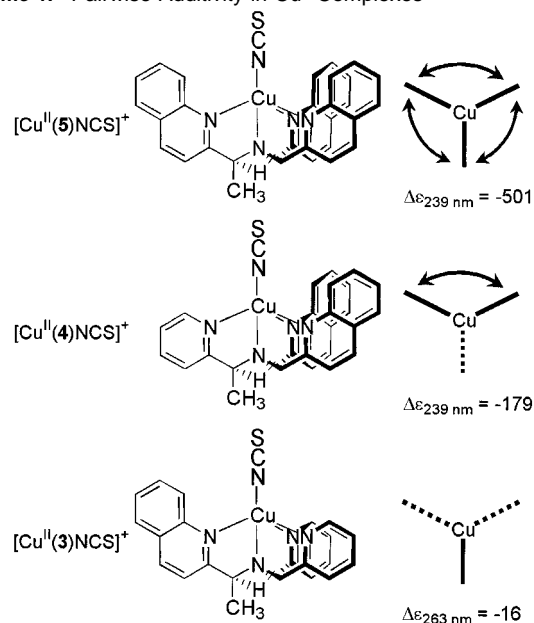
changed significantly (Table 1). The ratio of CD intensity at 240 nm between the two complexes is a factor of 10.

To assess the ability of the system to behave as a reversible switch, redox cycling studies were conducted in solution and monitored by CD and UV/vis spectroscopy. Similar to system $\text{Cu}^{\text{II}}(\mathbf{5})/\text{Cu}^{\text{I}}(\mathbf{5})$, addition of ascorbic acid to $\text{Cu}^{\text{II}}(\mathbf{5})\text{(NCS)}$ generated UV/vis and CD spectra that were identical to those of independently isolated $\text{Cu}^{\text{I}}(\mathbf{5})\text{(NCS)}$. The reverse process was initiated by the action of ammonium persulfate. The resulting spectra indicated the loss of thiocyanate, which is attributed to oxidation under these rather drastic conditions. Therefore, additional thiocyanate was added, which resulted in spectral features similar to complex $\text{Cu}^{\text{II}}(\mathbf{5})\text{(NCS)}$. Redox studies required the addition of up to 6 equiv of thiocyanate to correct for oxidation. With these conditions employed, the redox cycle became totally reversible. This process was repeated four more times without observing significantly reduced intensity, demonstrating the superb reversibility and reproducibility of the chiroptical signal.¹⁷

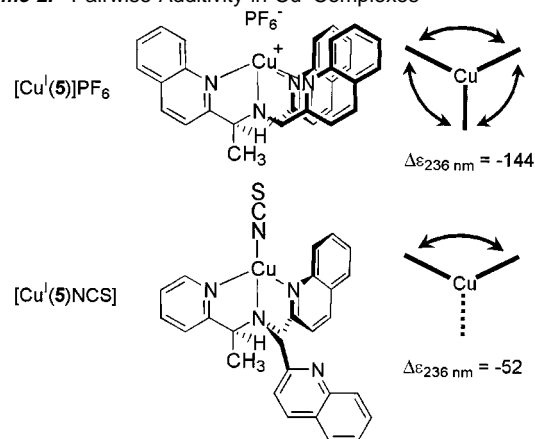
Additivity of the CD Spectra. The difference in intensity between $\text{Cu}^{\text{II}}(\mathbf{5})\text{(NCS)}$ and $\text{Cu}^{\text{I}}(\mathbf{5})\text{(NCS)}$ is larger than can be rationalized by a simple twisting/untwisting mechanism. Examination of the CD intensities led to the hypothesis that the Cu^{I} complex does not maintain tetradentate coordination of the trisquinoline ligand in solution, but loses coordination of one quinoline nitrogen. Examination of models indicates that such an event would result in the dissociated arm positioning one quinoline remote from the other two quinolines. The mechanism in Figure 5 shows the Cu^{II} state with three quinolines coordinated and the Cu^{I} state with only two ligated to the copper ion in the presence of the strongly coordinating SCN^- anion. The Cu^{II} would then allow for three pairwise interactions between the quinolines, and the Cu^{I} state would allow only one such coupling. Because the additivity of CD couplets is well established,^{29,36,37} we suggest that the amplitude of the Cu^{I} state is diminished by a factor of 3 because of dissociation of a quinoline arm. This factor, combined with the smaller twist of the overall ligand in the less sterically congested coordination environment, results in the remarkable difference in CD amplitude. The dissociation hypothesis is testable by examination of the spectral intensities of complexes of ligands **3**–**5**.

An additivity relation was found for the intensities of the first Cotton effects of ECCD curves, as illustrated in Scheme 1. The $\text{Cu}^{\text{II}}\text{(NCS)}$ complex of ligand **5** displays nearly 3 times the $\Delta\epsilon$ intensity of that of ligand **4**, while the analogous complex of **3** displays a miniscule signal. These data are consistent with the

Scheme 1. Pairwise Additivity in Cu^{II} Complexes



Scheme 2. Pairwise Additivity in Cu^{I} Complexes



expectation of three pairwise interactions for **5**, one for **4**, and none for **3**. A similar additivity was observed for the Cu^{I} complexes (Scheme 2). The $\text{Cu}^{\text{I}}(\mathbf{5})$ structure is postulated on the basis of a published X-ray structure of a similar complex.³³ Thus, the three quinoline chromophores are proximal in this complex and are available for three pairwise interactions; the conformation is similar to that of $\text{Cu}^{\text{II}}(\mathbf{5})\text{(NCS)}$ except for lack of a coordinating anion and the larger metal ion radius, both of which would give less of a twist and thus weaker overall coupling. Addition of NCS^- results in dissociation of one of the three arms in a dynamic, rapidly exchanging process, affording averaged CD spectra. Overall, the relative signal intensity is again about $1/3$ of that of the fully coordinated complex.

Other Structural Data. Repeated attempts failed to produce crystals suitable for X-ray diffraction. Karlin previously reported a structure for a closely related Cu^{I} complex obtained from acetonitrile,³⁸ which showed coordination of an acetonitrile molecule and tridentate coordination of the tetradentate ligand with one quinoline arm dissociated. Other examples of tripod

(36) Kauzmann, W.; Clough, F. B.; Tobias, I. *Tetrahedron* **1961**, *13*, 57–105.

(37) Liu, H. W.; Nakanishi, K. *J. Am. Chem. Soc.* **1981**, *103*, 5591–5593.

(38) Tyecklár, Z.; Jacobson, R. R.; Wei, N.; Murthy, N. N.; Zubieta, J.; Karlin, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2677–2689.

Table 2. Comparison of the Infrared Spectrum in the C–N and C–S Stretching Regions of Selected Cu^{II} Complexes^a

complexes	$\nu_{\text{C-N}}$	$\nu_{\text{C-S}}$ region
[Cu ^{II} (5)NCS](ClO ₄)	2083 s	826
		779
		749
[Cu ^{II} (5)NCS](SCN)	2088 s 2050 s	826
		779
		750
[Cu ^{II} (5)Cl](PF ₆)		827
		781
		750
[Cu ^I (5)NCS]	2108 s 2081 s	828
		780
		756

^a Spectra taken as KBr pellets of solids with indicated elemental composition.

arm dissociation are available.³⁹ Elongation of the bond between the copper ion and the tertiary amine nitrogen is another possibility demonstrated by Karlin,³⁸ but would not account for the changes in the CD spectra.

¹H NMR spectroscopy provided information consistent with the proposed ligand conformations. In CD₂Cl₂, Cu^I(5) displays four doublets in the 5–4 ppm region that originate from the four diastereotopic methylene protons. This contrasts the situation with the free ligand, which shows rapid inversion of the tertiary amine nitrogen atom, affording an AB pattern. The observed couplings suggest a strongly bound metal ion, with inversion of the nitrogen atom blocked by coordination to the metal. The ¹H NMR spectrum of Cu^I(5)PF₆ in CD₃CN resembled an AB quartet type pattern, suggesting inversion of the tertiary nitrogen. The ¹H NMR of Cu^I(5)(NCS) in CD₃CN displayed a very broad peak in the methylene proton region at room temperature. Upon lowering the temperature to 10 °C, it split into two broad peaks of equal intensity. Raising the temperature to 50 °C resulted in a sharper single transition for the methylene protons.

An attempt was made to distinguish N- versus S-coordination of the thiocyanate ligand by infrared spectroscopy (Table 2). The infrared spectrum of the thiocyanate ion is characterized by three fundamental modes, the C–N stretch ν_1 which occurs near 2050 cm⁻¹, the doubly degenerate bending mode ν_2 near 480 cm⁻¹, and the C–S stretch ν_3 at about 750 cm⁻¹. The wavelength of the C–S stretching frequencies has been found to be a useful guide to the mode of bonding of the thiocyanate ligand.^{40–43} Relative to that in ionic thiocyanate, the C–S stretching frequency increases in isothiocyanato complexes (M–NCS) to 780–860 cm⁻¹ and is reduced in thiocyanato complexes (M–SCN) to 690–720 cm⁻¹. Similarly, the C–N stretching frequency increases in isothiocyanato complexes (M–NCS) to 2080–2140 cm⁻¹ and lies for thiocyanato complexes (M–SCN) in the 2020–2070 cm⁻¹ region.^{40–43} We were unable to see C–S bands in the IR spectra of our complexes. The region 690–720 was devoid of peaks, but the 780–860 region contained strong absorptions that were assigned to the quinoline

moieties, and no additional peaks assignable to NCS were apparent. Control compound [Cu^{II}(5)Cl]PF₆ gave peaks at 828, 780, and 750 cm⁻¹, and very similar (and no additional) frequencies were observed for [Cu^{II}(5)(NCS)](ClO₄), [Cu^{II}(5)(NCS)]NCS, and [Cu^I(5)(NCS)]. A similar problem with overlapping bands was observed in IR spectra of the complex Cu^{II}(quinoline)₂(NCS)₂.⁴⁴ The lack of apparent C–S stretching vibrations also excludes bridged structures (M–SCN–M) which should give multiplets in this region.^{45,46}

The C–N stretching frequency is less diagnostic, as the frequency changes are smaller and more complex; indeed, either isothiocyanato or strongly bonded thiocyanato coordination may give increased vibrational frequency. The complex [Cu^{II}(5)(NCS)](ClO₄) gives a single peak at 2083 cm⁻¹, while that for [Cu^{II}(5)(NCS)]SCN gives two peaks at 2088 and 2050 cm⁻¹. The latter spectrum is consistent with the presence of one uncoordinated or weakly coordinated ion.⁴⁰ Interestingly, the complex [Cu^I(5)(NCS)] also showed two bands (2108, 2081 cm⁻¹), consistent with decoordination of a ligand arm because either the chiral arm or one of the achiral arms may decoordinate, likely giving two discreet species with differing IR spectra.

Cyclic voltammetry measurements quantified the redox behavior of the complexes. The half wave potentials of the Cu^{II} complexes measured by cyclic voltammetry (CV) were determined in acetonitrile to be as follows (mV; $E_{1/2}$, ΔE_p , i_{pa}/i_{pc}): Cu^{II}(5)(CF₃SO₃)₂ –45.7, 138, 0.80; Cu^{II}(5)(ClO₄)(PF₆) –49.9, 145, 0.87; Cu^{II}(5)(NCS)(ClO₄) –310.75, 125.7, 0.83. In DMF the values were Cu^{II}(5)Cl(PF₆) –385, 118, 0.82; Cu^{II}(5)(ClO₄)(PF₆) –256, 198, 1.0; Cu^{II}(5)(NCS)(ClO₄) –340, 91.4, 0.97. The CVs were well behaved and displayed single quasi-reversible one electron redox wave with i_{pa}/i_{pc} varying over the range 0.80–1.00. Peak separations were less than 145 mV (MeCN) and 199 mV (DMF) at a scan rate of 50 mV/s. The ferrocene/ferrocenium couple under the same conditions exhibited $\Delta E_p = 98.67$ mV and $E_{1/2} = 45.6$ mV versus Ag/AgNO₃ (MeCN) and $\Delta E_p = 228$ mV and $E_{1/2} = 43$ mV versus Ag/AgNO₃ (DMF). Typical scans are provided as Supporting Information.

The complexes gave voltammograms in which the half wave potentials varied significantly. In acetonitrile, three copper complexes were probed. The data suggest that in the presence of noncoordinating counteranion, acetonitrile binds to the copper center as is evident by the half wave potentials of solutions prepared from the triflate complex and Cu^{II}(5)(ClO₄)(PF₆). When the acetonitrile donor was replaced by the strong donor thiocyanate Cu^{II}(5)(NCS), the Cu^{II}/Cu^I redox couple became more negative, consistent with a more thermodynamically stable Cu^{II} species. The same results and trends in redox potentials were observed in dimethylformamide solution, where the complexes exhibited generally more negative half-wave potentials. Complex [Cu^{II}(5)Cl](PF₆) featuring the “hard” anionic chloride ligand displays the most negative value. Furthermore, the quite negative $E_{1/2}$ values for [Cu^{II}(5)NCS](ClO₄) as compared to those of [Cu^{II}(5)](ClO₄)(PF₆) in DMF and MeCN suggest that the “hard” nitrogen of thiocyanate rather than the “soft” sulfur binds to the copper center, although rearrangement of the anion cannot be excluded. In addition, the large

(39) Chen, Z.; Karasek, N.; Craig, D. C.; Colbran, S. B. *J. Chem. Soc., Dalton Trans.* **2000**, 3445–3452.

(40) Raymond, K. N.; Basolo, F. *Inorg. Chem.* **1966**, *5*, 1632–1633.

(41) Farago, M. E.; James, J. M. *Inorg. Chem.* **1965**, *4*, 1706–1711.

(42) Dessy, G.; Fares, V.; Imperatori, P.; Morpurgo, G. O. *J. Chem. Soc., Dalton Trans.* **1985**, 1285–1288.

(43) Morpurgo, G. O.; Dessy, G.; Fares, V. *J. Chem. Soc., Dalton Trans.* **1984**, 785–791.

(44) Clark, R. J. K.; Williams, C. S. *Spectrochim. Acta* **1966**, *22*, 1081–1090.

(45) Dockum, B. W.; Reiff, W. M. *Inorg. Chem.* **1982**, *21*, 2613–2619.

(46) Dockum, B. W.; Eisman, G. A.; Witten, E. H.; Reiff, W. M. *Inorg. Chem.* **1983**, *22*, 150–156.

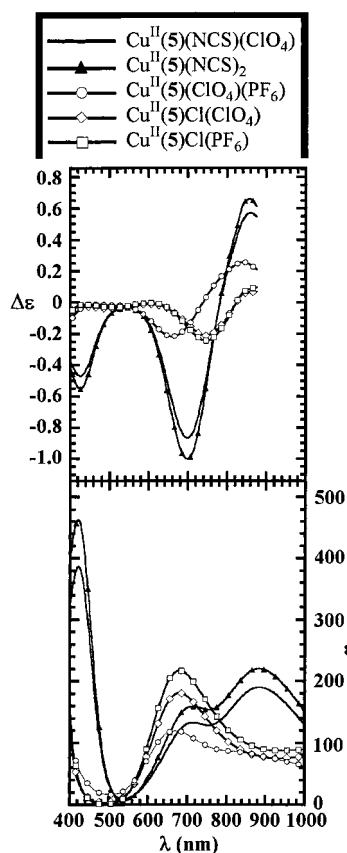


Figure 6. Induced circular dichroism (upper part) and absorption (lower part) spectra of Cu^{II} complexes. Vis (2 mM; 400–1000 nm) and CD spectra (2 mM; 400–875 nm) were measured at room temperature in acetonitrile. Formulas represent elemental composition as determined by combustion analysis of the isolated complexes. ϵ and $\Delta\epsilon$ units are $\text{L mol}^{-1} \text{cm}^{-1}$.

differences in solvent dielectric constants could also explain the more negative nature of the observed data in DMF. It should also be noted that, because the observed redox processes require changes in both oxidation state and coordination number, the mechanism of the redox change may not be the same in each solvent.

Induced Circular Dichroism Spectra. Induced circular dichroism (ICD) spectra were examined to further elucidate the structures of the complexes with varying counterions. In general, $d-d$ transitions in Cu^{II} complexes give rise to weaker electronic spectra than do the $\pi-\pi^*$ transitions in the quinoline ligands. As compared to other metal chromophores, the Cu^{II} complexes of **5** show pronounced ICD spectra. Figure 6 presents the visible ICD and isotropic absorbance spectra of Cu^{II} complexes of **5**. Numerical data for the absorption and CD bands of the optically active Cu^{II} complexes are summarized in Table 1. The two solutions prepared from $[\text{Cu}^{\text{II}}(\mathbf{5})(\text{NCS})](\text{ClO}_4)$ and $[\text{Cu}^{\text{II}}(\mathbf{5})(\text{NCS})](\text{SCN})$ exhibited one CD peak at 425 nm. These transitions have been assigned to the charge-transfer transition between the metal d orbital and the ligand (NCS) π orbital. In this case, an electron jumps from a largely localized orbital of the ligand (NCS) to the metal orbital.⁴⁷ The main feature of charge-transfer bands in absorption spectra is their relatively high intensity as compared with that of the $d-d$ transitions, a result of their electric dipole character. The ICD of such bands

may therefore be expected to occur through the electric induction mechanism and thus have the same sign as the CD of the inducing transition in the chiral species.

The CD spectra of $\text{Cu}^{\text{II}}(\mathbf{5})(\text{NCS})$ showed additional well-resolved features at 700 nm (negative CE) and 860 nm (positive CE). A change in the nature of the coordinating anion results in a significant perturbation of the spectral features in this region. The ligand field transitions observed in the CD and the absorption spectra for the Cu^{II} complexes are summarized in Table 1. Comparison between the CD and visible spectra shows the origin of the transitions and aids in the determination of the visible absorption bands as the visible spectrum is not as well resolved as the parent spectrum.

The fact that different CD spectra were observed for $\text{Cu}^{\text{II}}(\mathbf{5})$ and $\text{Cu}^{\text{II}}(\mathbf{5})\text{Cl}$, despite the similarity of their absorption spectra, and that $\text{Cu}^{\text{II}}(\mathbf{5})(\text{NCS})$ seems to be completely different is worthy of further discussion. In general, the optical activity in the $d-d$ transition of dissymmetric metal complexes has been interpreted in terms of the mixing of the d orbitals with some ungerade orbitals of the central metal ion and/or ligand molecules.⁴⁸ Thus, the different CD spectra may be ascribed to the assumption that the mixing of the d orbitals with ungerade orbitals in $\text{Cu}^{\text{II}}(\mathbf{5})$ is different from those in $\text{Cu}^{\text{II}}(\mathbf{5})\text{Cl}$. From a different point of view, the differences in the ICD spectra are also likely because of the different preferred dissymmetric conformations of the complexes. This in turn gives rise to different crystal fields, which are characterized by their individual energy levels. Thus, the position of the shorter wavelength ICD $d-d$ transition maximum differs and must be specific. The 3-fold stronger ICD signal of $\text{Cu}^{\text{II}}(\mathbf{5})(\text{NCS})$ as compared to the other complexes may be attributed to the presence of the charge-transfer band. Schipper noted that if a charge-transfer state is especially intense or nearby energetically, then the corresponding $d-d$ band may be considerably stronger in the ICD spectrum.⁴⁹

Conclusion

Development of practical chiroptical switches will require large amplitude and easily detectable signals, reversible and fast interconversion between states, and ready adaptability to solid state technology. In this work, we have successfully accomplished the first three of these goals. Compounds $\text{Cu}^{\text{II}}(\mathbf{5})(\text{NCS})$ and $\text{Cu}^{\text{II}}(\mathbf{5})\text{NCS}$ are easily interconverted with chemical reagents and give sufficiently large $\Delta\Delta\epsilon$. Key to the success of this system has been the employment of a metal ion to control the topology of a bound multidentate ligand. Copper has been ideal for this study because of its fast ligand exchange properties, potentially fast electron-transfer kinetics, stereoelectronic structure and corresponding sensitivity to coordinating anions, and stability to the environment. Much work remains to be done before it can be ascertained whether these molecules may be employed in practical systems, but the proof of principle has been provided, and new avenues of research have been created.

Experimental Section

General Methods.²⁴ Infrared spectra (IR) were recorded on a Matteson Instruments Polaris FT-IR spectrometer as KBr disks. A Kratos MALDI-TOF I mass spectrometer using the matrix α -ACHC and an extraction voltage of 4 kV was used for mass spectrometry.

(47) Herve, M.; Garnier, A.; Tosi, L.; Steinbuch, M. *Eur. J. Biochem.* **1981**, *116*, 177–183.

(48) Moffitt, W. *J. Chem. Phys.* **1956**, *25*, 1189–1198.

(49) Schipper, P. E. *J. Am. Chem. Soc.* **1976**, *98*, 7938–7944.

Absorption spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Circular dichroism spectra were acquired in methanol (unless otherwise specified) with an AVIV Model 60 DS, 62 DS, or 202 SF spectropolarimeter. Electroanalytical measurements were performed using an EG&G Model 273 potentiostat. Cyclic voltammetry experiments were carried out in a standard three-electrode apparatus with a glassy carbon working electrode, a nonaqueous reference electrode (0.1 M AgNO₃ in acetonitrile), and a platinum wire auxiliary electrode. Experiments were run in 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte in acetonitrile. Synthesis schemes and procedures are included in the Supporting Information. The various metal complexes were prepared by precipitation protocols. Purity was established by elemental analysis.

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Supporting Information Available: Synthetic procedures and characterization data for new compounds, variable temperature NMR data, cyclic voltammograms, and computational details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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