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Redox-Switched Exciton-Coupled Circular Dichroism: A Novel Strategy for Binary Molecular Switching**

Steffen Zahn and James W. Canary*

A recent and exciting prospect in the area of information technology lies in the development of molecular switches that operate with efficiency, reversibility, and resistance to fatigue.[1] The development of electrochemical switches has recently attracted much attention due to possible applications such as data storage.[2–8] Redox switches require a) components whose structures and physical properties can be turned on or off electrochemically,[3, 6–8] and b) sufficiently different optical spectra that allow the individual states to be addressed.[2, 4] Here we describe a method for generating a redox switch through redox control of the ligand conformation. This approach resulted in a novel molecular switch with reproducible redox-dependent optical properties; the switch should be easily adaptable to solid-state technology.

Our molecular redox switch is based on a) complexes in which a single metal center can exist in two different oxidation states, and b) chiral ligands having easily distinguishable optical properties. Copper(II) complexes are particularly suitable since they show fast ligand exchange, which potentiates fast signal interchange. The ligand (*S*)-*N*,*N*-bis[(2-quinolyl)methyl]-1-(2-quinolyl)ethylamine, (*S*)-α-MeTQA, was selected for this study because of the steric hindrance and strong chromophoric properties presented by the 2-quinolyl groups and the expected optimal chromophoric orientation provided by the propellerlike geometry of the complexes. Reduction of the sterically hindered Cu^{II} complex was anticipated to result in a change in the orientation of the 2-quinolyl arms with respect to the central axis (Scheme 1). Since the exciton-coupled circular dichroism (ECCD) signal generated from these complexes is critically dependent upon the distance and dihedral angle between the planar chromophores,[9] the magnitude of the ECCD spectrum was expected to vary with the oxidation state of the copper ion.

The preparation of the ligand (*S*)-α-MeTQA began with the asymmetric synthesis of (*S*)-2-(1-aminoethyl)quinoline from the 2-aminomethylquinoline imine of (+)-pinanone.[10] A single recrystallization of the L-(+)-tartrate salt of the chiral primary amine yielded the desired product with 99.7% *ee* in 19% overall yield. Alkylation of the enantiomerically pure amine with 2-bromomethylquinoline provided (*S*)-α-MeTQA in 81% yield. Copper complexes **1** and **2** were prepared by mixing homogeneous solutions of the ligand and the appropriate salt.[11, 12] The UV/Vis spectrum of **2** shows a

$[Cu^{I}\{(S)\text{-}\alpha\text{-MeTQA}\}](PF_6)$ **1**

$[Cu^{II}\{(S)\text{-}\alpha\text{-MeTQA}\}](ClO_4)(PF_6)$ **2**

d–d transition at 691 nm ($\varepsilon = 202$), which is consistent with a coordination geometry for the Cu^{II} ion that is closer to a square pyramid than the desired trigonal bipyramid.[11, 13] However, addition of one equivalent of NH_4NCS (to yield **4**) resulted in two d–d bands (719 nm, $\varepsilon = 202$; 867 nm, $\varepsilon = 296$); this indicates trigonal-bipyramidal geometry.[13] The color change of **4** from turquoise to green-yellow is due to a ligand-to-metal charge transfer (LMCT) at 420 nm ($\varepsilon = 445$).[14] Cyclic voltammograms of the copper complexes in acetonitrile or dimethylformamide were well-behaved and displayed single quasi-reversible one-electron redox waves ($i_{pa}/i_{pc} \approx 1$).[15]

The CD spectra of **1** ($A = 174$) and **2** ($A = 455$) displayed bisignate curves with remarkably large amplitudes (that is, large positive and negative Cotton effects).[16] The split CD

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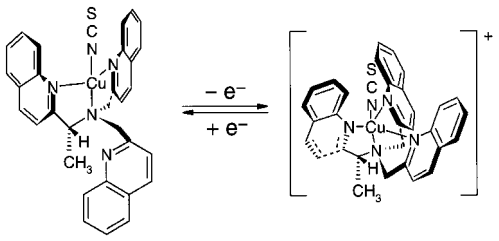

3 4

Scheme 1. The redox system [Cu^{I}{(*S*)-α-MeTQA}](NCS) (**3**)/[Cu^{II}{(*S*)-α-MeTQA}(NCS)]$^{+}$ (**4**). The structure of **3** was determined from ^{1}H NMR spectra at various temperatures, CD spectra, and comparison with structural data for analogous complexes.[13, 20] The geometrical arrangement of **4** is supported by CD and VIS spectroscopic data and comparison of structurally related Cu^{II} complexes.[15]

curve, the coincidence of the inflection point with the λ_{max} of the low-energy absorption band of the UV/Vis spectrum, and the large intensity of the signal are consistent with an exciton-coupling mechanism. Adding NH_4NCS to solutions of **1** and **2** resulted in a weaker signal for **3** ($A = 70$) and a stronger signal for **4** ($A = 670$, Figure 1). The intensity for **4** was such that it

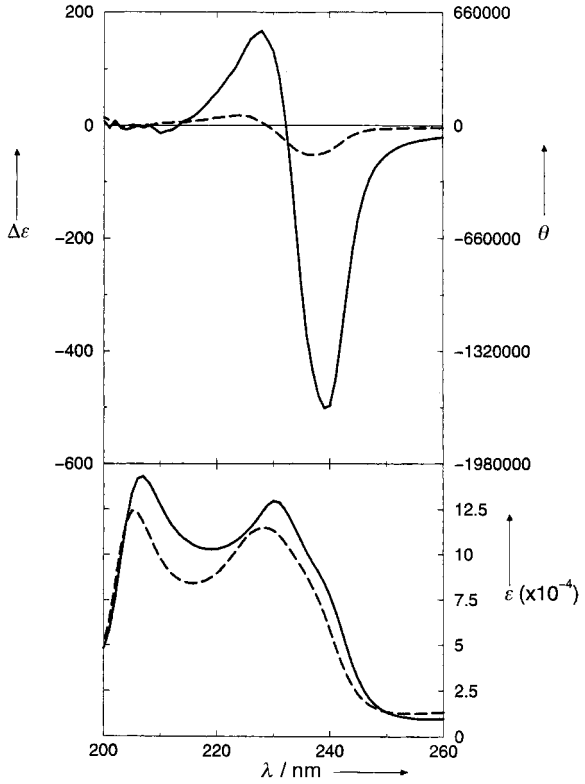

Figure 1. Circular dichroism (top) and UV/Vis spectra (bottom) of complexes **3** (dashed lines) and **4** (solid lines). UV/Vis (5 μM) and CD spectra (0.3 mM) were measured at room temperature in methanol. ε and $\Delta\varepsilon$ are given in L mol^{-1} cm^{-1}.

was possible to obtain good spectra at concentrations as low as 700 nM. Films of complex **4** prepared on quartz exhibited a CD curve that is similar in pattern and sign to that shown in Figure 1 but even more intense than that observed in methanol, as estimated by comparison with the isotropic absorption spectrum of the film. The large variation in intensity of the CD spectra of **3** and **4** was also maintained in the film.

Quantitative analysis of the CD spectra[17] of Cu^{I} complexes **1** and **3** suggest that addition of NCS^{-} displaces one quinoline arm of the ligand, which is similar to the behavior of other closely related tripodal Cu^{I} complexes.[11] Consequently, **3** provides one couplet, whereas **1** provides three couplets that together afford a much more intense spectrum. The substantially stronger intensities of **2** and **4**, compared with analogous bis(quinoline) ligands,[18] are also consistent with tetradentate coordination of the Cu^{II} ion.

To assess the ability of systems **1**/**2** and **3**/**4** to behave as reversable switches, redox cycling studies were conducted in solution and monitored by CD and UV/Vis spectroscopy. Reduction of **2** with ascorbic acid immediately gave CD and UV/Vis spectra identical to those of **1**. Reaction of **1** with ammonium persulfate was more sluggish and required 10 min at 50 °C in order to achieve the CD signal of **2**. This process was repeated three times; each cycle gave a less intense UV/Vis absorption band for **1**. However, in the presence of NCS^{-} much better results were obtained (Figure 2). Treatment of **4**

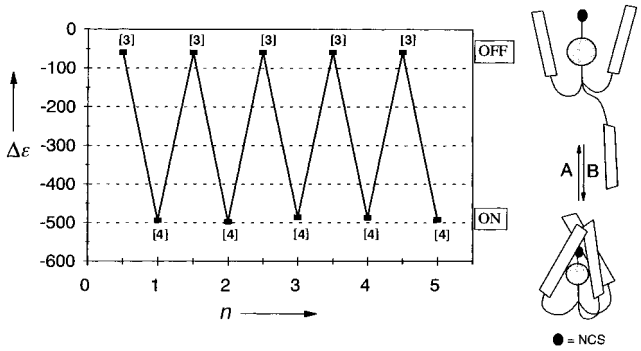

Figure 2. Left: Plot of $\Delta\varepsilon$ vs. the number of cycles n at 240 nm in methanol. The reduction of **4** to **3** proceeded with ascorbic acid, whereas **3** was oxidized back to **4** with ammonium persulfate. The average difference in signal intensity between **3** and **4** is $\Delta\Delta\varepsilon_{240} = 430$. $\Delta\Delta\varepsilon_{240}$ is the absolute difference in the $\Delta\varepsilon$ values for the binary system at 240 nm ($\Delta\Delta\varepsilon_{240} = |\Delta\varepsilon_{240(on)}| - |\Delta\varepsilon_{240(off)}|$). Right: Schematic representation of dynamic behavior of complexes **3** and **4** that leads to different arrangements of the chromophores and thus to distinct ECCD signal intensities representing the "on" and "off" states of the molecular switch. A = reduction, B = oxidation.

with ascorbic acid resulted in a CD spectrum that is identical to that of **3**, whereas oxidation of **3** with ammonium persulfate produced the CD signal of **4** immediately at room temperature.[19] Up to five cycles were carried out without a significant decrease in signal intensity; this demonstrates the superb reversibility and reproducibility of the chiroptical signal.

The magnitude of the changes in the chiroptical properties of the system **3**/**4** is quite remarkable ($\Delta\Delta\varepsilon_{240} = 430$). The low energetic barrier for the change in coordination geometry in the system **3**/**4**, its rapid response, its high signal intensities, and its stability on multiple cycling support the adaptability of

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this type of coordination complex to real applications which depend on easily distinguished "on" and "off" signals. Studies on the immobilization of these complexes on appropriate conducting surfaces are underway.

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[16] Amplitude (A): difference in the $\Delta\varepsilon$ values for the two extrema of split CD curves ($A = |\Delta\varepsilon_{1C.E.}| + |\Delta\varepsilon_{2C.E.}|$).
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Isocyanate-Based Dendritic Building Blocks: Combinatorial Tier Construction and Macromolecular-Property Modification**

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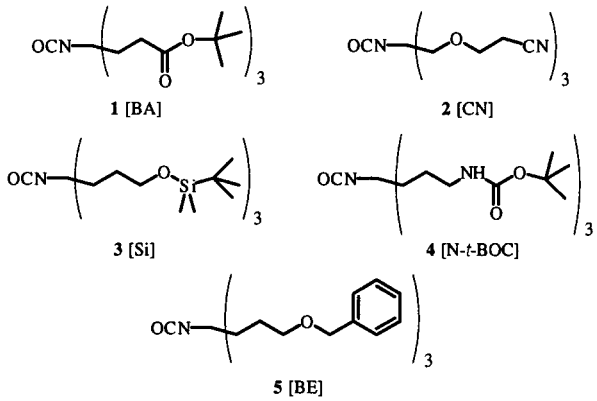
In the current development of dendritic chemistry[1] the application of iterative technology is being examined from many different perspectives. These areas include the use of dendrimers and related materials as unimolecular micelles,[2] ordered network building blocks,[3] chromatography additives,[4] cancer therapeutics,[5] and electrically conducting materials.[6] Central to the construction of these macromolecular assemblies is the design and tuning of properties such as solubility, viscosity, and reactivity for specific applications. Hence it is desirable to design synthetic methods for the ready introduction of functionally diverse terminal groups.

Recently we reported the synthesis of the stable isocyanate triester **1** and its use as a building block in the rapid "dendrimerization" of protic materials and surfaces.[7] In addition, we disclosed the syntheses of the related branched



monomers[8] **2** – **5**. Each of these monomers possesses a triad of protected functional groups, an sp^3 C-branching center and a reactive isocyanate moiety. We herein report on the concept of the rapid modification of properties through combinatorial synthesis analogous to that used for the discovery of novel solid-state materials,[9] biologically active substrates,[10] and artificial receptors.[11] While dendrimers have recently been employed[12] and touted[13,14] as vehicles for the generation of standard small-molecule libraries, our combinatorial method relies on mixtures of AB_3-type monomers having varying compositions of different, yet mutually compatible building

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