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Reduction of a Redox-Active Ligand Drives Switching in a Cu(I) Pseudorotaxane by a Bimolecular Mechanism

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Introduction

Redox driven molecular machines1-2 are being developed as the active materials3-4 for molecular memory,5 muscles,6,7 and electron relays.8 The functional cores of some of these machines are derived from redox-responsive compounds,9,10 which often originate in the form of supramolecular complexes.1 As a consequence, the complexes can be used as a template to synthesize mechanically interlocked structures,11,12 such as catenanes and rotaxanes. Early successes involved linear motions in π-donor−acceptor rotaxanes13 and rotary motions in Cu(I/II) catenates.14 Recent efforts to enable more sophisticated functions15,16 have been directed at new and efficient syntheses

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of interlocked molecules. This goal also requires and can benefit from complementary efforts aimed at new switching modalities.

Ligand-based switching\(^7\) is an attractive yet less common alternative than that originating from changes in a metal’s oxidation state.\(^9\),\(^14\)–\(^20\) The reduction of lariat crown ethers to reversibly bind alkali metals was an early precedent\(^10\) that helped establish the fundamentals of redox switching.\(^2\),\(^10\) There have been few subsequent extensions. These include oxidation\(^21\) and deprotonation\(^22\) of the ligand as well as some proton-coupled electron transfer reactions\(^23\) and the potentiometric control\(^25\) over ligand tautomers in self-assembled monolayers. Redox-active ligands are also a part of nature’s tool box\(^25\) to deal with oxidative stress.\(^26\) The reduced thiol form of cysteine binds reversibly bind alkali metals was an early precedent\(^10\) that helped establish the fundamentals of redox switching.\(^2\),\(^10\) There have been few subsequent extensions. These include oxidation\(^21\) and deprotonation\(^22\) of the ligand as well as some proton-coupled electron transfer reactions\(^23\) and the potentiometric control\(^25\) over ligand tautomers in self-assembled monolayers. Redox-active ligands are also a part of nature’s tool box\(^25\) to deal with oxidative stress.\(^26\) The reduced thiol form of cysteine binds Zn(II) ions, while the oxidized disulphide form does not. To the best of our knowledge, however, there are no examples that are designed to employ ligand reduction to effect reversible molecular motions\(^27\) within coordination compounds.


New opportunities can be considered when utilizing ligand reduction. For instance, when the ligand’s redox state is responsible for switching instead of the metal’s, the metal ion can potentially retain its magnetic, optical, and catalytic functionality irrespective of the switch state. Furthermore, different parameters become available for tuning the switch, such as the σ-donor, π-acceptor, and steric properties of the ligand. With these ideas in mind and inspired to elaborate upon a previous report,\(^28\) we are investigating the reduction of redox-active ligands\(^29\) to drive molecular motions. (Scheme 1a).

**Design.** Within the realm of coordination chemistry, the reduced anionic form of \(N\)-heterocyclic ligands can display stronger binding affinities for metal moieties than their electrically neutral counterparts.\(^30\) When such noninnocent ligands\(^29\) are brought together with kinetically labile transition metals, the opportunity to observe chemically reversible switching is...
opened up. An early serendipitous example using a noninnocent ligand was observed for a mononuclear complex \(^{33}\) formed between the manganese(I) metal moiety \(\{\text{I}^7\text{-C}_5\text{R}_5\text{(CO)}_2\text{Mn}\}\) and the heterocyclic bridging ligand pyrazine. The dynamic behavior of this system is represented by a redox-centered scheme, or ECEC mechanism (Scheme 1b), for which an electrochemical (E) reduction initiates a chemical (C) process. Initially, reduction of the complex, M(L), generates a formal negative charge localized on the coordinated pyrazine ligand, M(L\(^-$)). As a consequence, the increased basicity of the uncoordinated nitrogen on the pyrazine drives the formation of the binuclear complex, M(L\(^-$))M, through disproportionation by reaction with 1 equiv of the unreduced parent complex and, in the process, liberates a free ligand, L. Reoxygenation of the binuclear complex, M(L\(^-$)M, is followed by comproportionation with the free ligand, L, to reform the mononuclear complex, M(L). It should be possible, therefore, to take advantage of noninnocent ligands and labile Cu(I) centers, to drive and facilitate, respectively, intermolecular switching events by ligand reduction.

Selection of the Components and Their Assembly. To test this hypothesis a polypyridyl-based thread and macrocycle component were selected as the building blocks to prepare redox-active pseudorotaxanes. The bridging ligand 3,6-bis(5-methyl-2-pyridine)-1,2,4,5-tetrazine (Me\(_2\)BPTZ) was selected as the thread-like noninnocent ligand. It is a dimethylated derivative of the parent BPTZ system,\(^{31}\) which has been extensively employed in the preparation of mixed-valent compounds\(^{32}\) and self-assembled into multinoiunuclear structures with a variety of metal ions.\(^{33}\) In almost all prior examples, the solid state structures of the complexes were found to prefer an \(\eta^6\) orientation even though there appears to be little preference for either \(\eta^5\) or \(\eta^4\) in the free ligand. For the purposes of redox-switching, the ligand displays an accessible reduction at \(-1\) V vs Ag/AgCl. Reduction of the coordinated ligand populates a \(\pi^*\) orbital that is primarily localized on the tetrazine core.\(^{34}\) Upon complexation, the reduction shifts increasingly closer to \(0\) V when the first and second metal moieties are bound.\(^{32a-d,1-35}\) The concept of switching with a tetrazine derivative was demonstrated recently by using reduction to turn on the binding of a dialkyl thiourea guest.\(^{36}\)

The ability to use Cu(I)-templated self-assembly to thread binucleating ligands akin to Me\(_2\)BPTZ inside polypyrrold macrocycles has been shown previously in the preparation of heteroligand \([n]\) pseudorotaxanes \((n = 2, 3, 4)^{37}\) and multicomponent architectures.\(^{38}\) The same preparation strategies\(^{37}\) have been used herein, and a similar macrocycle (M)\(^{39}\) based on 2,9-diphenyl-1,10-phenanthroline has been selected. The M is modified with a benzylic hydroxyl unit for future synthetic modifications. The redox properties of the prior Cu(I) pseudorotaxanes,\(^{37}\) when using pyridazine in place of tetrazine, were never characterized. However, the redox properties of some related Cu\(^3\) grids\(^{40}\) and of the binuclear [Cu(PPh\(_3\))\(_2\)(μ-BPTZ)-Cu(PPh\(_3\))\(_2\)]\(^{41}\) complexes have been documented.

This paper is organized into two parts that quantify (1) the stepwise formation of Cu(I) pseudorotaxanes and (2) the mechanism of reduction-induced redox switching of \([2]\)PR\(_2\). The sequential self-assembly (Scheme 2) of the \([2]\) pseudorotaxane (\([2]\)PR\(_2\)) and the \([3]\) pseudorotaxane (\([3]\)PR\(_2\)) from copper-macrocyclic Cu-M\(^+\) and thread (Me\(_2\)BPTZ) components are verified using electrospray ionization mass spectrometry (ESI-MS) and \(^{1}H\) NMR spectroscopy with the syn geometry of the \([3]\)PR\(_2\) confirmed from X-ray crystallography. UV–vis–NIR titrations reveal that the \([2]\)PR\(_2\) and \([3]\)PR\(_2\) display some of the lowest metal-to-ligand charge-transfer (MLCT) transitions for a BPTZ complex. These data were used to calculate \(K_1\) and \(K_2\) values consistent with negative cooperativity. The second


part presents the evidence in favor of the reduction-induced switching of a solution of \( \text{[2]} \text{PR}^+ \). This behavior was confirmed using variable scan-rate cyclic voltammetry (CV) from 50 to 0.2 V s\(^{-1}\). The stoichiometry of the products and net chemical reversibility were corroborated using UV-vis-NIR spectroelectrochemistry. The \(-5.1 \text{ kcal mol}^{-1}\) driving force for the reaction was found to stem from the electrostatic stabilization of the reduced ligand by two monocationic Cu\(^+\) centers. Lastly, variable concentration CVs in conjunction with digital simulations confirm that switching proceeds by a bimolecular reaction between unreduced \( \text{[2]} \text{PR}^+ \) and reduced \( \text{[3]} \text{PR}^{2+} \).

Results and Discussion

Synthesis, Self-Assembly, and Characterization. The \( \text{Me}_2\text{BPTZ} \) ligand was synthesized using the known procedures\(^{31,42} \) for 3,6-disubstituted tetrazines. The macrocycle \( \text{M} \) was prepared from a literature procedure.\(^{39} \) The equilibria (Scheme 2) can be driven close to completion when the components are mixed in solutions at concentrations that are sufficiently high to ensure tight binding conditions. For each equilibrium, this situation is fulfilled at or above \( \sim 1 \text{ mM} \). The copper macrocycle Cu-M\(^+\) was preformed by mixing equimolar ratios of Cu(MeCN)\(_4\)•PF\(_6\) and \( \text{M} \) in CH\(_2\)Cl\(_2\) at 4 mM. The self-assembly of the \( \text{[2]} \text{PR}^+ \) and \( \text{[3]} \text{PR}^{2+} \) pseudorotaxanes occurs spontaneously by mixing solutions (\( \sim 1 \text{ mM}, \text{CH}_2\text{Cl}_2\)) of appropriate stoichiometric ratios of Cu-M\(^+\) and \( \text{Me}_2\text{BPTZ} \). For the \( \text{[2]} \text{PR}^+ \), a darkly tinted purple solution was generated whereas a dark tinted green solution was produced for the \( \text{[3]} \text{PR}^{2+} \). The ESI-MS (Figure S1) was utilized to confirm the self-assembly with peaks assigned to the parent ions observed from solutions of the \( \text{[2]} \text{PR}^+ \) (M\(^+\) = 971.6 m/z) and \( \text{[3]} \text{PR}^{2+} \) (M\(^{2+}\) = 839.4 m/z). The \(^1\text{H} \) NMR spectra (Figure S2) confirm that the formation of both pseudorotaxanes proceeds in a stepwise manner through the \( \text{[2]} \text{PR}^+ \) to the \( \text{[3]} \text{PR}^{2+} \) in CD\(_2\)Cl\(_2\) on the basis of the symmetry-dependent methyl groups on the ends of the coordinated \( \text{Me}_2\text{BPTZ} \) ligand.

Figure 1. Representation of the syn conformation of two coppers in \( \text{[3]} \text{PR}^{2+} \). The crystal structure of the \( \text{[3]} \text{PR}^{2+} \) (Figure 1) reveals the syn

\(^{a}\) The wavy lines represent syn-anti isomerism of \( \text{Me}_2\text{BPTZ} \).
Reduction of Redox-Active Ligand Drives Switching

The self-assembly of [2]PR+ and [3]PR2+ was monitored using UV–vis–NIR spectroscopy under tight binding conditions by titration (Figure 2) of a concentrated solution of Me2BPTZ into a solution of Cu-M+. Consistent with the darkly tinted solutions that were observed upon mixing, both pseudorotaxanes absorb across the entire UV–vis region and out into the NIR and they show characteristic bands in their spectra. The [3]PR2+ shows absorbance peaks of medium intensity at 470 (6800), 656 (4500), 775 (4700), and 1088 (2800) nm (M⁻¹ cm⁻¹) that grow in upon addition of Me2BPTZ up to 0.5 equiv with respect to the 1 equiv of Cu-M⁺ present initially. Further addition of Me2BPTZ up to 1 equiv leads to spectroscopic changes that are assigned to the [2]PR+ pseudorotaxane with bands growing in at 437 (3500), 566 (4100), and 808 (2800) nm (M⁻¹ cm⁻¹). The ~450 nm absorption bands in the spectra of both pseudorotaxanes are assigned to Cu → phenanthroline MLCT transitions. We attribute the red-shifted 470 nm band to the π stacking between phenanthroline units. The remaining absorption bands are assigned to Cu → Me2BPTZ MLCT transitions by analogy to related binuclear complexes. The visible absorption band of the Me2BPTZ ligand itself, while absorbing at ~500 nm, is too weak (ε ~450 M⁻¹ cm⁻¹) to contribute significantly to the observed spectra. The fact that the lowest-energy electronic transition is red-shifted from 808 nm for [2]PR+ to 1088 nm for [3]PR2+ is consistent with the MLCT assignments: The additional electropositive Cu center acts to stabilize the optical acceptor orbital localized on the Me2BPTZ ligand, which is expected to be a tetrazine-localized LUMO.

These MLCT bands are lower in energy compared to most other complexes with the BPTZ ligand. This situation is attributed to a small energy difference (∆Eredox = Eox − Ered) between the metal oxidation (Supporting Information) and ligand reduction (vide infra) potentials. The redox energy separations for [2]PR+ (∆Eredox = 1.50 V) and [3]PR2+ (∆Eredox = 1.40 V) in CH2Cl2 do not entirely account for the energies of the MLCT bands at 1.53 and 1.14 eV, respectively. The larger discrepancy between the redox and optical energies for the [3]PR2+ suggests that the electronic configuration of the MLCT excited state [CuII(Me2BPTZ)CuI]+ is not effectively approximated by the corresponding oxidation states: [CuII(Me2BPTZ)CuI]+ and [CuII(Me2BPTZ)CuI]. The kinetically inert binuclear complex [Fe(CN)₆](µ-BPTZ)Fe(CN)₆]⁺ is the only other example with a low energy MLCT transition showing a shoulder at 1085 nm (1.1 eV, MeCN) and a correspondingly small energy difference between reduction (~0.51 V) and oxidation (~0.35 V) of ∆Eredox = 0.86 eV.

The binding constants Kₐ, K₁, and K₂ (Scheme 2) were determined from UV–vis–NIR titration data recorded at 50 μM (CH2Cl2, 298 K) by using an equilibrium-restricted factor analysis approach (Supporting Information, Section S.6).

![Figure 2](image_url)
Initially, the raw titration data were analyzed using an unrestricted factor analysis to confirm that there are only three absorbing species present in the data set at wavelengths longer than 450 nm, i.e., Me$_2$BPTZ, [2]PR$^+$, and [3]PR$^{2+}$. Modeling of the equilibria in Scheme 2 using HySS$^{46}$ verified the importance of including the equilibrium for formation of Cu-M$^+$: Cu$^+$ + M = Cu-M$^+$. This 1:1 association constant was determined in a separate titration (Supporting Information) to be $\Delta G_a = -6.9 \pm 1$ kcal mol$^{-1}$ (298 K, CH$_2$Cl$_2$). A minimized fit of the titration data for the pseudorotaxanes provided $\Delta G_a = -7.1 \pm 1$, $\Delta G_i = -12.2 \pm 1.5$ and $\Delta G_2 = -8.9 \pm 0.5$ kcal mol$^{-1}$. The similarity between $\Delta G_i$ values for separate sets of titration data supports the accuracy of the binding constants. These data indicate that the binding of Cu-M$^+$ to Me$_2$BPTZ operates with negative cooperativity; $^{47}$ the ratio $K_1/K_2 = 400$ is much greater than 4. Presumably the $\pi$ stacking in the crystal structure of [3]PR$^{2+}$ goes some way towards alleviating any steric and electrostatic repulsions between the two Cu-M$^+$ moieties.

Reduction Electrochemistry. The reduction CVs of Me$_2$BPTZ, [2]PR$^+$, and [3]PR$^{2+}$ (Figure 3) were recorded at fast scan rates (50 V s$^{-1}$) to characterize the half-wave potentials ($E_{1/2}$). These scan rates prevent any reduction-induced switching to occur in the case of [2]PR$^+$. The CVs were recorded during a titration of Cu-M$^+$ into Me$_2$BPTZ showing the stepwise formation of [2]PR$^+$ and then [3]PR$^{2+}$ (Figure S4) that corresponds closely to the procedure as a function of scan rate (50 V s$^{-1}$). Figure 3a and (b). $\Delta S$ compensation was used at faster scan rates, and each scan is background subtracted. The presence of an EC mechanism stimulated by the reduction of [2]PR$^+$ is evident from the variable scan rate CVs. Substantive changes are evident in the CVs when the scan rate is slowed down (Figure 4a and b); (i) A redox couple for the free Me$_2$BPTZ grows in at $E_{1/2} = -0.960$, $-0.650$, and $-0.285$ V (vs Ag/AgCl in CH$_2$Cl$_2$) for Me$_2$BPTZ, [2]PR$^+$, and [3]PR$^{2+}$, respectively. Both Me$_2$BPTZ and [3]PR$^{2+}$ show one process as a function of scan rate (50 $- 0.2$ V s$^{-1}$, Figure S5). Coulometry (Table S2) confirms that each reduction is a one-electron process. The peak intensities of [2]PR$^+$ and [3]PR$^{2+}$ are lower than that of Me$_2$BPTZ on account of their lower diffusion coefficients as confirmed by $^1$H NMR analysis (Figure S6). The shifts in $E_{1/2}$ values upon complexation conform to the behavior of kinetically inert BPTZ binuclear complexes. $^{32a-g,35}$ The ligand-based reduction, and consequently the LUMO, is stabilized by 310 and 365 mV upon coordination of the first and then monocationic Cu-M$^+$ moieties. The stabilization energy is therefore attributed$^{30}$ largely to the Coulombic attraction between the tetrazine-localized anion and the monocationic Cu(I) ions.

Figure 3. Fast scan-rate (50 V s$^{-1}$) CVs of Me$_2$BPTZ (red), [2]PR$^+$ (purple), and [3]PR$^{2+}$ (green) at 0, 0.9, and 2.0 equiv of Cu-M$^+$ added to Me$_2$BPTZ at constant concentration: 1 mM was maintained by using Ar bubbling to control the solution volume in CH$_2$Cl$_2$, glassy carbon, 0.1 M TBAPF$_6$. $\Delta S$ compensation was applied.

Figure 4. CVs of [2]PR$^+$ recorded as a function of decreasing scan rates (see open arrows) for scans down to (a) $-1.4$ V (25 red), 10, 7.5, 5, 4, 2, 1.5, and 1 (blue) V s$^{-1}$ and (b) $-0.8$ V (10 red), 7.5, 5, 3, 2, 1.5, and 1 (blue) V s$^{-1}$). (c) CVs recorded at 0.2 V s$^{-1}$ with different clipping voltages. Asterisked peak (*) is assigned to the anti isomer of [3]PR$^+$ (see Supporting Information). Conditions: 1:1 molar mixture of Cu-M$^+$:Me$_2$BPTZ at 1 mM, 0.1 TBAPF$_6$, Ar degassed CH$_2$Cl$_2$, Pt counter electrode, for the CVs in (a) and (b). $\Delta S$ compensation was used at faster scan rates, and each scan is background subtracted.

References:


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peak for \( [2]PR^0 \) and the enhanced reoxidation peak for the reduced \( [3]PR^- \). When the CV is clipped at \(-0.45\) V, the voltammetric wave for the \( [3]PR^- \) in the reverse scan was observed to be lower than if the CV was switched at \(-0.85\) V. These results confirm that the production of \( [3]PR^- \) occurs after reduction of \( [2]PR^+ \).

All of these CV experiments confirm that the population of the reduced \( [3]PR^- \) is increased after the voltammetric wave for reduction of \( [2]PR^+ \).

UV–vis–NIR Spectroelectrochemistry. To examine the stoichiometry of the electrochemically driven formation of \( [3]PR^- \) from \( [2]PR^+ \), spectroelectrochemistry studies were conducted. This technique\(^{48} \) allows for the simultaneous collection of UV–vis–NIR spectra while executing electrochemistry experiments, thus allowing for the \textit{in situ} visualization of changes in the distribution of molecular species and redox states as reflected by the characteristic absorptions bands. On the basis of Scheme 1, it is predicted that electrolysis of a solution of \( [2]PR^+ \) within the thin layer of the spectroelectrochemistry cell will show the conversion of 1 equiv of \( [2]PR^+ \) into 0.5 equiv of \( [3]PR^- \) and 0.5 equiv of \( Me_2BPTZ \).

The spectroelectrochemistry of the \( [3]PR^{2+} \) system (Figure 5a) was conducted to provide the marker bands of reduced \( [3]PR^- \). The corresponding thin-layer and slow scan rate CV (0.25 mV s\(^{-1}\)) displayed one reversible process (I/I\(_s\) \( \sim \) 1), and the major spectroscopic changes were observed to follow the onset of Faradaic current. During the reduction, a bleach of the three MLCT bands corresponding to the Cu(I) \( \rightarrow \) Me\(_2\)BPTZ transitions were observed simultaneously with an increase in intensity in the band at 470 nm (Figure 5a) assigned to the Cu \( \rightarrow \) phenanthroline MLCT band. The small increase in intensity of the 470 nm band and the absence of any additional transitions in the vis-to-NIR region down to 3200 nm suggests that the coordinated Me\(_2\)BPTZ\(^-\) ligand anion absorbs light at \( \sim 470 \) nm consistent with related complexes.\(^{32,3,m,49} \) The spectroelectrochemistry of the Me\(_2\)BPTZ ligand alone indicated that the reduced ligand was not stable for the scale of the experiment. Using the characteristic spectra of \( [3]PR^- \), the response of the \( [2]PR^+ \) was analyzed by spectroelectrochemistry.

Reduction of a solution containing the \( [2]PR^+ \) (Figure S11) is expected to show absorption bands corresponding to the sum of (a) 0.5 equiv of the reduced \( [3]PR^- \) species plus (b) 0.5 equiv of the unreacted Me\(_2\)BPTZ ligand. The spectrum generated after reduction of \( [2]PR^+ \) (Figure 5b) coincides with our expectations: The 470 nm band is at half the intensity as it was for reduction of an equimolar solution of \( [3]PR^{2+} \).

Thermodynamics of Switching. The CVs and spectroelectrochemistry are consistent with an ECCE mechanism (Scheme 3).\(^{3,28} \) Upon reduction \((E_2)\) of 0.5 equiv of the \( [2]PR^+ \), a supramolecular disproportionation\(^{50,51} \) reaction \((K_0^*)\) takes place between the reduced \( [2]PR^- \) and neutral \( [2]PR^0 \) forms to generate the reduced \( [3]PR^- \) pseudorotaxane and free Me\(_2\)BPTZ ligand. Consistent with this idea, both liberated Me\(_2\)BPTZ and reduced \( [3]PR^- \) were observed in the CVs. During the reverse sweep of the CV, reoxidation \((E_3)\) of the \( [3]PR^- \) species takes place initiating disproportionation \((1/K_0 = K_1/K_2)\) between the neutral \( [3]PR^{2+} \) and free Me\(_2\)BPTZ to regenerate the \( [2]PR^+ \) species. We know from binding studies \((\textit{vide supra})\) that the inequality \( K_1 > K_2 \) will drive this disproportionation reaction.

The driving force of reduction-induced switching \((K_0^*)\) can be quantified on the basis of the ladder scheme\(^{39} \) (Scheme 4), the known half-wave potentials \( E_2 \) and \( E_3 \), and the stepwise formation constants \( K_1 \) and \( K_2 \). The reduction-induced switching is represented by a supramolecular disproportionation.

\[
[2]PR^+ + Me_2BPTZ + Cu-M' \rightarrow \frac{1}{K_1} [2]PR^+ + Cu-M'
\]

\[
[3]PR^- + Me_2BPTZ \rightarrow \frac{K_1}{K_2} [3]PR^- + Me_2BPTZ
\]

The thermodynamic expression for eq 3 can be formulated (Section S.14) as:

\[
\Delta G(K_0^*) = F(E_3 - E_2) + \Delta G(K_0)
\]

All of the factors in eq 4 are known and lead to a calculated driving force for the reduction-induced switching reaction of \( \Delta G(K_0^*) = -5.1 \text{ kcal mol}^{-1} \).

The thermodynamic description given in eq 4 allows for the driving and restraining forces to be examined. The major driving force, \( E_3 - E_2 \), is the difference in electrochemical energy (365 mV) between the reduction potentials for \( [3]PR^{2+} \) and \( [2]PR^0 \). This energy represents the enhanced stabilization of the ligand-localized anion by two monocationic Cu(I) centers.


rather than just one and corresponds to 8.4 kcal mol\(^{-1}\). In opposition to this is the energy cost involved in the disproportionation reaction in the neutral state (\(K_D\)) of 3.3 kcal mol\(^{-1}\), which is characteristic of negative cooperativity.

**Kinetics and Mechanism of Switching.** Digital simulations (Figure 6 and Section S.15) of the variable scan rate and variable concentration (3.8, 1.9, 0.95, 0.48, and 0.24 mM) CV data were conducted to characterize the mechanism of switching. The CVs were simulated assuming two limiting cases for the supramolecular disproportionation: either a dissociation–association or bimolecular mechanism (Scheme 5). The known values for \(E_2\), \(K_1\), \(K_2\), and \(K_D^*\) were used in the simulations. The higher nuclearity species surrounding [3][PR]\(^{**+}\) were not included in the simulations.

For switching when a dissociation–association mechanism (eqs 5–7) was assumed, it was possible to use a common set of parameters to simulate the CV for a given concentration. However, these parameters failed to account for the effect of concentration on the CVs: It was found that the shape of the simulated CVs did not change with concentration (Figure 6b).

Simulation of the switching assuming a bimolecular mechanism (eqs 5 and 8) gave rise to a more satisfactory reproduction of the experimental data for all concentrations (Figure 6c).\(^{52}\) Therefore, the switching proceeds through a bimolecular pathway with a second-order rate constant, \(k_d = 12,000\) s\(^{-1}\) M\(^{-1}\).

The overall rate of switching is governed by the rate law:

\[
\text{Rate} = (K_{E2}) k_d [2][PR]^{**+}\]  

\(^{(9)}\)

This form of the rate law has two implications. First, assuming a diffusion-limited bimolecular rate constant of \(\sim 10^{9}\) M\(^{-1}\) s\(^{-1}\), only 1 in every 100 000 collisions is successful. This situation is consistent with the need to break Cu–N metal–ligand bonds and to attain an appropriate orientation for a successful reaction. Second, the rate depends upon the position of equilibrium (\(K_{E2}\)) for the charge-transfer reaction eq 5. For an electrochemical reaction, where the electrode is a reservoir of electrons, a maximum rate of switching can be attained when the applied potential (\(E_{ap}\)) is equal to \(E_2\) such that \(K_{E2} = 1\) and there will be equal concentrations of unreduced [2][PR]\(^+\) to react with reduced [3][PR]\(^+\) to react with reduced [3][PR]\(^+\).

\(^{(52)}\) Two additional mechanisms were inspected. (a) A solvent assisted pathway stemming from the MeCN introduced into the solution from the [Cu(MeCN)]\(_4\)PF\(_6\) salt. CVs obtained from solutions with up to 400 equiv of MeCN in CH\(_2\)Cl\(_2\) (2.5% \(v/v\)) were not adequately simulated using a common set of parameters for the solvent-assisted pathway. Furthermore, physically meaningless rate constants of \(k_d > 10^{11}\) M\(^{-1}\) s\(^{-1}\), were required. (b) A bimolecular pathway via [2][PR]\(^+\) = [3][PR]\(^+\) + Me\(_2\)BPTZ\(^-\), was not able to reproduce the experimental CVs.
[2]PR\(^0\). When using 0.5 equiv of a strong reductant a maximum rate would be predicted to occur if \(K_1 \gg 1\).

Conclusions

The electrochemical reduction of the tetrazine-based redox-active ligand and the high lability of Cu(I) provide the means to create a reversible supramolecular switch that exchanges between two- and three-component pseudorotaxanes. The [2]- and [3]pseudorotaxanes were formed, respectively, from 1:1 and 2:1 molar ratios of the copper-macrocycle and the 3,6-bis(5-methyl-2-pyridine)-1,2,4,5-tetrazine bridging ligand in sequential steps consistent with \(K_1 = 8.9 \times 10^8 \, \text{M}^{-1}\) and \(K_2 = 3.1 \times 10^6 \, \text{M}^{-1}\). The scan-rate dependence of [2]PR\(^+\) indicates that the generation of 0.5 equiv of a ligand-centered anion provides the electrostatic driving force (−8.4 kcal mol\(^{-1}\) = 365 mV) to overcome the negative cooperativity (+3.3 kcal mol\(^{-1}\)) to form the reduced [3]pseudorotaxane [3]PR\(^+\) (−5.1 kcal mol\(^{-1}\)). The stoichiometry of the switching event (2[2]PR\(^+\) + e\(^-\) → [3]PR\(^+\) + Me\(_2\)BPTZ) and its chemical reversibility was verified using in situ UV−vis−NIR spectroscopic measurements of the electrochemically reduced solution. The concentration dependence of the CVs and their digital simulations provided a means to verify that the reduced [3]PR\(^+\) is generated by a bimolecular reaction between reduced [2]PR\(^0\) and unreduced [2]PR\(^+\) with a second-order rate constant of \(k_d = 12 \, 000 \, \text{s}^{-1} \, \text{M}^{-1}\). This proof-of-principle demonstration opens up the possibility to develop new classes of Cu(I) molecular machines on the basis of ligand reductions.

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Supporting Information Available: Syntheses, experimental procedures, modeling, tables of X-ray crystallography, UV−vis−NIR and electrochemistry data, and electrochemical studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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