Coupled Molecular Switches: A Redox-Responsive Ligand and the Redox-Switched Complexation of Metal Ions

Herbert Plenio* and Clemens Aberle[a]

Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday

Abstract: 1,1′-$(OC_2H_4OTos)_2$-ferrocene was treated with various diaza-[*n*]-crown-*m* (*n*/*m* = 12/4, 15/5, 18/6) to give three ferrocene cryptands (*n*/*m* = 12/4 (FcCrypt), 15/5, 18/6). The complexation of Group 1 and 2 metal ions by FcCrypt leads to large shifts in the redox potentials (up to +500 mV relative to FcCrypt) and consequently to a drastic decrease in the binding strength (up to 10^8) in the ferrocene cryptands. The redox potential of Fcpda (1,1′-*N*,*N*′-bis-(dipicol-2-ylamino)-3,3′,4,4′-tetraphenylferrocene) can be modified reversibly by complexation of Zn^{2+} (E(Fcdpa) = −0.13 V, E(Fcdpa-2Zn^{+}) = +0.66 V and E(Fcdpa-Zn^{2+}) = +0.72 V). The X-ray crystal structure of FcCrypt-Ca-$(ClO_4)_2 \cdot H_2O$ was determined; Ca^{2+} is coordinated by six oxygen (Ca^{2+}–O 238.7, 239.1, 239.5, 242.6, 243.6, 247.7 pm) and two nitrogen donors (Ca^{2+}–N 256.1, 259.2 pm) and displays a short Fe–Ca^{2+} contact (402.7 pm). The stability constants of FcCrypt-Na^+ ($\lg K = 8.32$ in CH_3CN) and FcCrypt-K^+ ($\lg K = 4.54$ in CH_3CN) were determined. The precise adjustment of complex stability and redox potentials of Fcdpa, Fcdpa-Zn^{2+}, FcCrypt (+0.12 V), and FcCrypt-Na^+ (+0.395 V) allows coupling of the redox-switchable ferrocene cryptand and the redox-responsive aminoferrocene. In a cyclic process starting from a mixture of Fcdpa$^+PF_6^-$ and FcCrypt-Na^+ the addition of $Zn(CF_3SO_3)_2$ raises the redox potential of Fcdpa$^+$ to that of Fcdpa$^+$-Zn^{2+}. This complex oxidizes FcCrypt-Na^+, while the oxidized cryptand displays a drastically reduced affinity towards Na^+, so that a mixture containing FcCrypt$^+$, Fcdpa-Zn^{2+}, and uncoordinated Na^+ results. The alkali metal ion is recomplexed after cyclam-assisted removal of Zn^{2+} from the Fcdpa-Zn^{2+} complex, since Fcdpa is oxidized by FcCrypt$^+$ with reformation of FcCrypt-Na^+. Thus two independent chemical processes—the complexation/decomplexation of Zn^{2+} and of Na^+—are linked indirectly with mediation by electron-transfer reactions.

Keywords: electrochemistry · electron transfer · molecular devices · supramolecular chemistry

Introduction

In 1992 a book with the title "*Nanosystems—Molecular Machinery, Manufacturing and Computation*" stimulated the minds of chemists, physicists, and engineers alike.[1] In a detailed analysis K. E. Drexler explained to chemists how to build upon their knowledge of bonds and molecules to manufacture nanotechnological systems, and showed engineers how to scale down their concepts of macroscopic systems to the level of molecules. Upon reading this book, however, it quickly emerges that his concept of realizing sophisticated functions on the scale of molecules appears to be far beyond the abilities of today's synthetic chemists. Nonetheless, chemists and physicists are starting to rise to this challenge, and terms like molecular switches,[2–14] molecular wires,[15] molecular ratchets,[16–18] molecular motors,[19] and molecular machines[20–26] are appearing in the literature.[27]

We are interested in molecular switches in which a characteristic property of a molecule can be reversibly switched on or off by changing the redox state of an organometallic unit that is coupled to a macrocyclic ligand.[28–31] Thus, a new property, namely, that of a switch, emerges, since the coordination of a metal cation is destabilized on oxidation of the redox-active unit, and restabilized on reduction. Such devices are rather simple, since they have only a single function. It should be possible to enhance their performance by integrating several molecules with different functions. We recently demonstrated that a new level of complexity can be reached by coupling a molecular switch with a redox-responsive ligand.[32] A redox-responsive ligand also consists of a redox-active chelating ligand. However, upon coordination of a metal ion, the redox properties of the ligand are reversibly changed, that is, a weak oxidant is converted into a strong oxidant and vice versa.[33] Consequently we have two types of switches, one which changes its binding properties towards metal ions on changing the redox

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potential, and another whose redox properties are modified on binding metal ions; this is basically the same phenomenon, but viewed under two aspects. This classification is nonetheless practical, as in different compounds one or the other property prevails.

An important feature of such an arrangement is its ability to link events which are normally completely independent of each other. Numerous examples of this are found in biochemistry, especially in signal transduction and hormone-driven processes.[34] Here we describe in some detail the individual components of such an artificial regulatory system by using a sequence of two coupled molecular switches and demonstrate the viability of such a coupled device.

Results and Discussion

The integration of a redox-responsive system and a molecular switch into a single device requires careful adjustment of the properties of the individual components. In our case the redox potentials of the substituted ferrocenes and the binding affinities of their ligating subcomponents towards metal ions must be carefully balanced. Furthermore, the switching effect and the redox response must be optimized, and for this purpose, it is advantageous to directly attach donor atoms to the redox-active unit, that is, to the cyclopentadienyl rings of ferrocene. In such oxygen- or nitrogen-substituted ferrocenes, for which we have developed efficient synthetic procedures,[35, 36] the oxidation of the ferrocene unit has a very marked influence on the binding properties of a chelating ligand,[37] or, vice versa, the coordination of metal ions strongly alters the redox potential of ferrocene.[38–40]

Beginning with an equimolar mixture of the Na^+ complex of FcCrypt and the redox-responsive ligand Fcdpa$^+PF_6^-$ (top box in Figure 1), the addition of one equivalent of $Zn(CF_3SO_3)_2$ leads to the formation of Fcdpa$^+$-Zn^{2+}. Consequently, Fcdpa$^+$ ($E = -0.13$ V) is converted to the strong oxidant Fcdpa$^+$-Zn^{2+} ($E = +0.72$ V), which is capable of quantitatively oxidizing FcCrypt-Na^+ ($E = +0.395$ V). FcCrypt$^+$ displays a drastically decreased affinity towards Na^+. Finally the ability of the ferrocene cryptand to bind Na^+ can be re-established by simply adding to the reaction mixture a strong ligand (cyclam) that can remove Zn^{2+} from Fcdpa-Zn^{2+}, so that Zn^{2+}-cyclam complex is formed. At this point, in the absence of Zn^{2+}, Fcdpa is a reductant which is oxidized by FcCrypt$^+$ ($E = +0.12$ V) present in solution, and one finally returns to the beginning (top box in Figure 1), in which Fcdpa$^+$ and FcCrypt-Na^+ coexist, and the whole process can be started over again. Hence, the presence of a Zn^{2+} salt indirectly (with mediation by electron-transfer reactions) leads to the liberation of Na^+ ions, and the absence of Zn^{2+} to the complexation of Na^+.

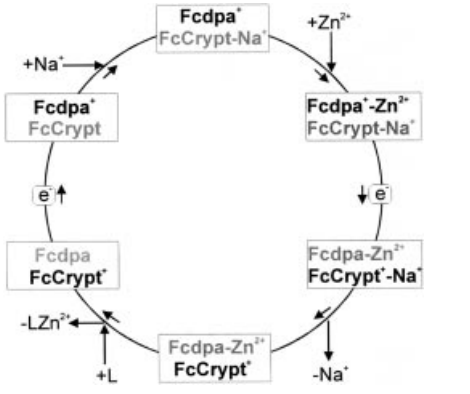
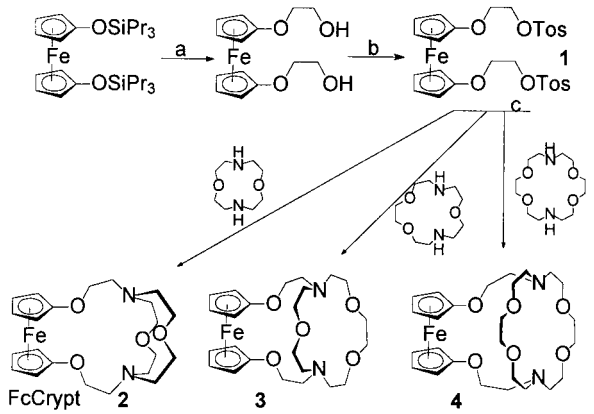


Figure 1. Electron-transfer-mediated regulation of the Na^+ concentration by addition of Zn^{2+} salt and removal of Zn^{2+} ions by addition of cyclam (L; 1,4,8,11-tetraazacyclotetradecane). The species displayed in the boxes do not necessarily correspond to isolated intermediates and mainly serve to elucidate the reaction sequence.

Synthesis of the substituted ferrocenes: The synthesis of FcCrypt is straightforward (Scheme 1) but differs from that of the 1,1′2,2′tetraphenyl-substituted analogue reported recently.[37, 41] In the final step the reaction of tosylate **1** with

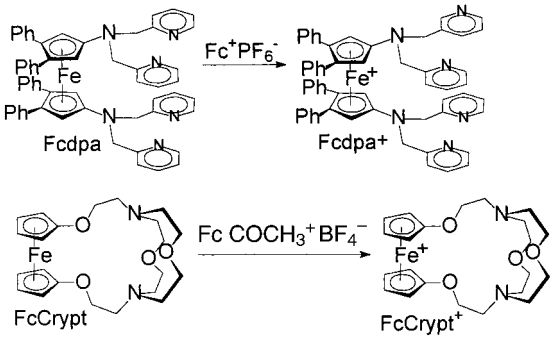


Scheme 1. Syntheses of the ferrocene cryptands. Reagents and conditions: a) TBAF, BrC_2H_4OH; b) NaH, TsCl; c) N_2–[12]crown-4, N_2–[15]crown-5, or N_2–[18]crown-6. TBAF = tetrabutylammonium fluoride.

various diaza-[n]-crown-m ($n = 12$, $m = 4$; $n = 15$, $m = 5$; $n = 18$, $m = 6$) in the presence of a templating base (Na_2CO_3) gives ferrocene cryptands **2**–**4**. Metal complexes of FcCrypt are prepared quantitatively by simply mixing the appropriate alkali or alkaline earth metal triflate with the ligand in acetonitrile solution.

The aminoferrocene Fcdpa was available from a previous study;[38] the synthesis of Fcdpa-Zn^{2+} and Fcdpa-2Zn^{2+} complexes is straightforward. Fcdpa and FcCrypt can be oxidized easily with Fc$^+PF_6^-$ or acetyl-Fc$^+BF_4^-$ to afford the salts of Fcdpa$^+$ and FcCrypt$^+$ (Scheme 2). The oxidized aminoferrocene Fcdpa$^+$ is much more stable than FcCrypt$^+$.

Electrochemistry: *FcCrypt and its metal complexes*: To a good approximation, the difference in redox potentials between FcCrypt and its complexes of Group 1 and 2 metal ions $\Delta E = E(\text{FcCrypt-M}^{n+}) - E(\text{FcCrypt})$ determines the redox switching effect, which is the ratio of the stability constants K_{red} and K_{ox} for the complexation of M^{n+} by FcCrypt and FcCrypt$^+$.[42] The redox potentials of ferrocene cryptands **2**–**4** and their alkali and alkaline metal ion complexes were determined by cyclic voltammetry in CH_3CN (Table 1). The anodic shift of the Fe^{II}/Fe^{III} redox potential is most pronounced when the size



Scheme 2. Oxidation of Fcdpa and FcCrypt to the corresponding ferrocenium salts. $Fc^+ = (C_5H_5)_2Fe^+$.

Table 1. Redox potentials of FcCrypt and its metal complexes in CH_3CN at ambient temperature (scan rate 50 – 100 mV s^{-1}, redox potentials are given to within ± 5 mV).

	FcCrypt **2**		FcCrypt **3**		FcCrypt **4**	
	E [V]	ΔE [mV]	E [V]	ΔE [mV]	E [V]	ΔE [mV]
FcCrypt	0.150	–	0.165	–	0.165	–
+ Li^+	0.360	+210	0.315	+150	0.267	+100
+ Na^+	0.395	+245	0.362	+200	0.293	+125
+ K^+	0.290	+140	0.375	+210	0.350	+185
+ Rb^+	0.205	+55	0.378	+215	0.370	+205
+ Cs^+	0.175	+25	0.315	+150	0.333	+165
+ Ca^{2+}	0.620	+470	0.667	+500	0.360	+195
+ Sr^{2+}	0.620	+470	0.530	+365	0.385	+220
+ Ba^{2+}	0.550	+400	0.555	+390	0.487	+325
+ H^+	0.300	+150	–	–	–	–
+ $2H^+$	0.430	+280	–	–	–	–

of the metal ion and that of the cavity are complementary to each other, which for **2** appears to be the case for metal ions roughly of the size of Na^+, Ca^{2+}, and Sr^{2+}. The larger ferrocene cryptands **3** and **4** display larger values of ΔE only with correspondingly larger cations. For example, the complexes of **2**, **3**, and **4** with Cs^+ show a ΔE of 25, 150, and 165 mV, respectively, while the ΔE of K^+ complexes with the same ligands are 140, 210, and 185 mV. The ΔE of Cs^+ complexes peak for the largest cryptand **4**, while for the medium-sized K^+, the highest shifts in the redox potential are found for the medium-sized cryptand **3**. The ΔE value of +500 mV on complexation of Ca^{2+} or Sr^{2+} should lead to a decrease in the complexation stability constant of about 4×10^8 ($\Delta \lg K = 8.6$) for Ca^{2+} and Sr^{2+}. In all cases the interaction between the metal centers is much larger than would be expected for a simple electrostatic interaction[43–45] (see below).

It is interesting to compare the anodic shifts observed upon ligation of metal ions by the present ferrocene cryptands with those described previously by us. These ligands only differ in having four phenyl rings attached to the ferrocene unit.[37] The redox-switching effects observed in the ferrocene cryptands described here are much more pronounced. This was unexpected, and we believe that in the electron-richer ferrocenes described here, the donor ability of the two oxygen atoms directly attached to the metallocene is increased. This idea is supported by the fact that the absence of the four phenyl groups in the ferrocene cryptands **2**, **3**, and **4**, lowers the redox potential of ferrocene by about 130 mV relative to the tetraphenylferrocene cryptands.

With regard to the pronounced switching effects, we were surprised to observe fully reversible electrochemical behavior for all metal complexes. We therefore investigated the electrochemistry of FcCrypt-Ca^{2+} and FcCrypt-Sr^{2+} more closely at scan rates of 5 – 5000 mV s^{-1}. However, in all cases we only observed a single reversible redox wave at half-wave potentials corresponding to the oxidation and reduction of the FcCrypt-Ca^{2+} complex. An EC process, which should occur once the decomplexation of the metal ion is faster than the time scale of the electrochemical experiment, was not found. There appear to be two possible explanations for the unexpected electrochemical behavior: 1) The decomplexation of the metal ions is too slow to be observable on the time scale of the cyclic-voltammetry experiment, which is limited by the fact that oxidized product diffuses away from the electrode surface. 2) The metal ion is not fully decoordinated from FcCrypt, but only changes its location within the macrocycle, whereby its distance from the iron atom increases; this could be an extremely fast process. Note that Gokel and Kaifer et al. already discussed this problem in some detail for other ferrocene cryptands, which display much smaller redox-switching effects.[12] It was argued there that the absence of an EC process is due to a significant remaining complexation strength of the ferrocene cryptand after oxidation.

Fcdpa-Zn^{2+} and Fcdpa-Co^{2+} complexes: Closer inspection revealed that the electrochemistry of the redox-responsive ligand Fcdpa and its Zn^{2+} complexes is much more complicated than anticipated previously.[32] The cyclic voltammogram of Fcdpa (E = – 0.13 V) is reversible and straightforward. For Fcdpa-2 Zn^{2+} the redox potential can be determined with reasonable accuracy, even though the shape of the curve and the separation of the two half-waves indicate incomplete electrochemical reversibility. For a 1/1 stoichiometry of Fcdpa and Zn^{2+} the CV is less obvious. A substoichiometric situation is depicted in Figure 2.[46] An EC process appears to generate

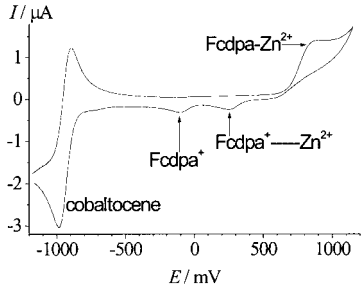


Figure 2. Cyclic voltammogram of Fcdpa with 0.8 equiv Zn^{2+} in CH_3CN at – 30 °C to illustrate the EC process upon oxidation of the close Fcdpa-Zn^{2+} isomer.

two species from the initial complex $Fcdpa^+$-Zn^{2+}. One is Fcdpa, and the other seems to be another Fcdpa-Zn^{2+} complex.[47] Apparently, two different isomers of Fcdpa-Zn^{2+} exist. The CV of both species could be determined in independent CV experiments only approximately: $E_{qrev} =$ 0.28 and 0.72 V. By using substoichiometric amounts of Zn^{2+} it is possible to obtain quasireversible redox curves ($E_a - E_c \geq$ 110 mV) for one isomer, while at higher Zn^{2+} concentrations

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(ca. 1.0–1.2 equiv) a quasireversible CV curve ($E_a - E_c \geq 100$ mV) is observed for the other isomer. Nonetheless, we are confident that the two Fcdpa-Zn^{2+} complexes differ with respect to the relative orientation of Zn^{2+} and the ferrocenyl unit. One isomer presumably has a short Fe–Zn^{2+} distance (Fcdpa$\cdot\cdot Zn^{2+}$), and in the other Fe and Zn^{2+} appear to be well separated (Fcdpa$\cdots\cdots Zn^{2+}$). Figure 3 shows two possible isomers of Fcdpa-Zn^{2+} with their respective redox potentials.

Since the electrochemistry of Fcdpa-Zn^{2+} is very complicated, we tried to obtain more information by investigating the related Fcdpa-Co^{2+} complexes. Again we observe two different isomers at slightly different potentials, and the CV curves are only quasireversible ($E_a - E_c = 100$ mV). Consequently, we now feel more comfortable in considering the same two types of isomers as for the Zn^{2+} complex. However, a detailed study of the mechanisms or even calculations are far beyond the scope of this study. Despite some deficiencies in understanding the electrochemistry of Fcdpa and Zn^{2+}, there is little doubt about the most important conclusion: The 1/1 complex Fcdpa-Zn^{2+} is already able to oxidize FcCrypt-Na^+. Consequently, we prefer to use Fcdpa-Zn^{2+} instead of Fcdpa-2Zn^{2+}[32] as the redox-responsive component of our system of coupled molecular switches. In Figure 4 all complexes needed for the coupled molecular devices are arranged according to their redox potentials, and this proves the thermodynamic feasibility of this complex system.

UV/Vis spectra of Fcdpa and FcCrypt metal complexes: The UV/Vis spectra of the d^5 and d^6 species Fcdpa, Fcdpa$^+$, Fcdpa-Zn^{2+}, Fcdpa-2Zn^{2+}, Fcdpa$^+$-Zn^{2+}, and Fcdpa$^+$-2Zn^{2+} are shown in Figure 5. Typical for ferrocenes are high-energy bands around 280 nm corresponding to a $\pi-\pi^*$ transition, while the less intense bands at about 360 and 430 nm are Laporte forbidden d–d bands; the spectra of the oxidized ferrocenes are also normal.[48] The most significant difference between the spectra of the N- and O-substituted ferrocenes are the d–d band extinction coefficients, which are 5–10 times larger in the former.

The large anodic shifts in the ferrocene redox potential upon coordination of metal ions by FcCrypt prompted us to investigate whether the coordination of metal ions by FcCrypt has an effect on the UV/VIS spectra. The following metal complexes were studied, and the coordination of metal ions indeed causes small spectral changes in the low-intensity d–d

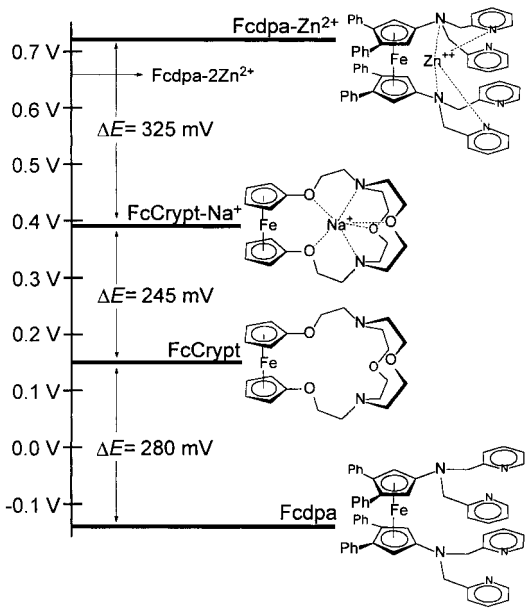


Figure 4. Ordering of the redox potentials of Fcdpa, Fcdpa-Zn^{2+}, Fcdpa-2Zn^{2+}, FcCrypt, and FcCrypt-Na^+.

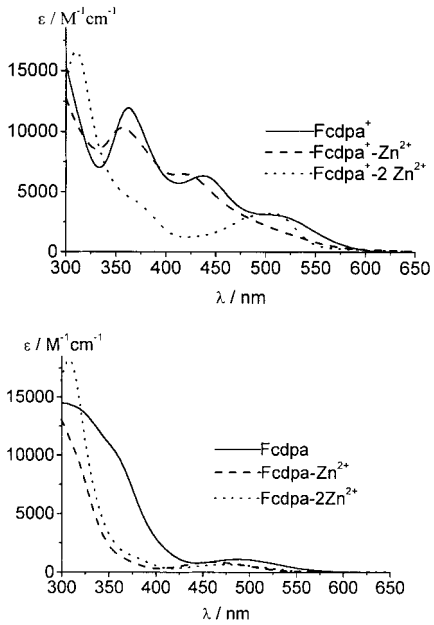


Figure 5. UV/Vis spectra of Fcdpa, Fcdpa-Zn^{2+}, Fcdpa-2Zn^{2+}, Fcdpa$^+$, Fcdpa$^+$-Zn^{2+}, and Fcdpa$^+$-2Zn^{2+} in CH_3CN ($c = 10^{-4}$ mol dm^{-3}).

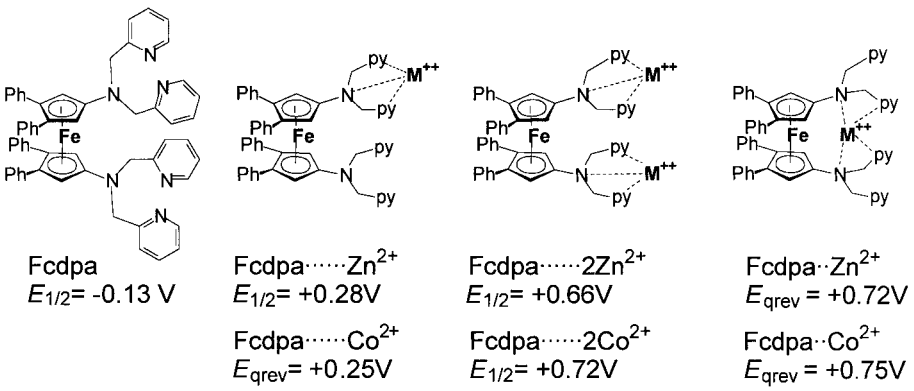


Figure 3. Redox potentials of Fcdpa-Zn^{2+}, Fcdpa-2Zn^{2+}, Fcdpa-Co^{2+}, and Fcdpa-2Co^{2+}.

transition: FcCrypt $\lambda = 433.5$ nm ($\varepsilon = 139$ dm^3 mol^{-1} cm^{-1}), FcCrypt-Na^+ 422.5 (151), FcCrypt-K^+ 433.5 (155), FcCrypt-Ca^{2+} 417.5 (141), FcCrypt-Sr^{2+} 424.5 (133), FcCrypt-Ba^{2+} 435.5 (157), FcCrypt-La^{3+} 423.5 (140), FcCrypt-Y^{3+} 419.5 (145); ($c = 10^{-3}$ mol dm^{-3} in CH_3CN). The extinction coefficients are virtually constant throughout the series of metal complexes. This implies that the symmetry of the ferrocene moiety

is not perturbed significantly, that is, the cyclopentadienyl rings retain their coplanar orientation.[49] This is also supported by the solid-state structure of FcCrypt-Ca$(ClO_4)_2$, in which a Cp – Cp interplanar angle of only 5.6° was found. The maximum of the d – d transition, however, is changed upon coordination of a metal ion, and in most cases a small hypsochromic shift is observed. Clearly, the energy of the d – d splitting is increased, and this can either be caused by a lowering of the HOMO (a'_{1g}) energy or by an increase in the LUMO (e^*_{1g}) energy. Explaining this is not easy, but there are speculations in the literature about possible donor – acceptor interactions between filled d orbitals on the iron atom of ferrocene with other metal atoms near by.[50–53]

X-ray crystal structure of FcCrypt-Ca$(ClO_4)_2$: To better understand the very large redox switching effects observed in complexes of FcCrypt we determined the crystal structure of the Ca^{2+} complex, since for the alkali and alkaline earth metal ions, the largest anodic redox shift is observed with this cation.

In the solid state, Ca^{2+} is coordinated by four O atoms with Ca^{2+}–O distances of 238.7(5) – 243.6(5) pm and two N atoms (Ca^{2+}–N 256.1(8), 259.2(7) pm) of the cryptand (Figure 6). Two slightly longer Ca^{2+}–O distances to the perchlorate counterion (247.7(19) pm) and a single water molecule (262.6(6) pm) are also present, and the result is a coordination number of eight for Ca^{2+}. The metal ion appears to be slightly too large for the cavity of FcCrypt, since the Ca–O distances are rather short (cf. [2.2.1]cryptand-Ca^{2+}: Ca–O 249 – 255 pm).[54]

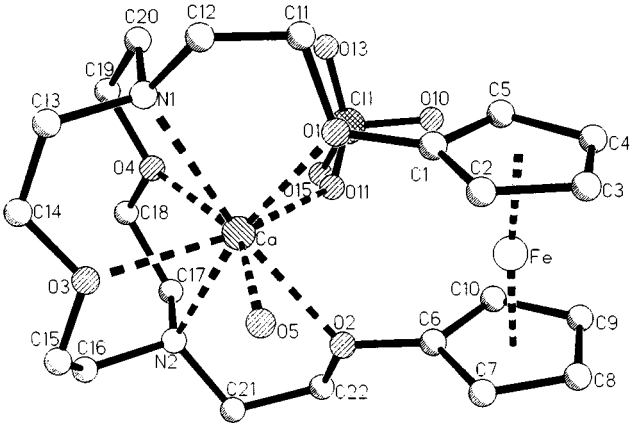
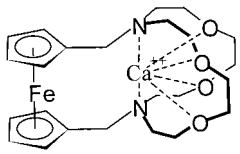


Figure 6. Crystal structure of FcCrypt-Ca$(ClO_4)_2$. Selected bond lengths and interatomic distances [pm]: Ca–O1 238.7(5), Ca–O2 239.5(6), Ca–O3 239.1(7), Ca–O4 243.6(5), C–O5 242.6(6), Ca–O11 247.7(19), Ca–N1 256.1(8), Ca–N2 259.2(7), Fe–Ca 402.7(6).

The most significant feature in this crystal structure is the Fe–Ca^{2+} distance (402.7 pm), since it should determine the degree of Coulomb interaction between the metal centers and contribute to the shift of the ferrocene redox potential.[55] However, the Fe–Ca^{2+} distance in the related ferrocene cryptate **5** is even shorter (365.8 pm).[56] This difference may not appear spectacular, but the anodic shift in the redox potential upon Ca^{2+} complexation is much smaller in this complex ($\Delta E = +274$ mV)[57] than in FcCrypt-Ca^{2+} ($\Delta E =$



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Scheme 3.

$+500$ mV). Why is this the case? In most, but not all,[29, 31, 58] of the ferrocene crown ethers reported previously, the electronic interaction between the metal centers is mainly electrostatic, as the donor atoms (site of metal ion complexation) are separated from the redox-active group by an insulating CH_2 group, as in **5**. Consequently, a more efficient mechanism must be operative in complexes of FcCrypt. This can be attributed to the direct bonding of Ca^{2+} to the two oxygen atoms directly attached to the ferrocenyl unit, which effectively mediate the transfer of electron density between the two metal centers.[59]

Stabilities of metal complexes of FcCrypt and Fcdpa: An important question that influences the coupling of the molecular switches is whether FcCrypt preferentially coordinates Na^+ or Zn^{2+}. This was investigated by ^1H NMR spectroscopic competition experiments. All ^1H NMR titrations were carried out in CD_3CN[60] at concentrations of 10^{-3} mol L^{-1}. First, we investigated the reaction of $Zn(CF_3SO_3)_2$ with FcCrypt, which results in the protonation of the nitrogen atoms and not in the coordination of the metal ion. This suggests a low stability of the Zn^{2+} complex of FcCrypt. In a competition experiment we then determined which species exist when FcCrypt, $Zn(CF_3SO_3)_2$, and $NaCF_3SO_3$ are present in a 1/1/1.5 ratio. The ^1H NMR spectrum shows a mixture of FcCrypt-H^+ and FcCrypt-Na^+ (ca. 3/1). After addition of 0.01 mL of [D_5]pyridine (ca. 10 equiv), FcCrypt-Na^+ is present exclusively. From these results, we conclude the following order of stabilities: FcCrypt-H^+ > FcCrypt-Na^+ ≫ FcCrypt-Zn^{2+}. However, mixing Fcdpa, $Zn(CF_3SO_3)_2$, FcCrypt, and $NaCF_3SO_3$ leads to exclusive formation of the respective metal complexes. The Na^+ stability constant of FcCrypt was determined with an ion-selective electrode to be $\lg K = 8.32$ (in CH_3CN; $\lg K = 6.56$ in CH_3OH), which is weaker than that of the[2.2.1]cryptand.[61] Due to the well-defined cavity, Na^+ is coordinated with high selectivity with respect to K^+ ($\lg K = 4.54$ in CH_3CN, 3.26 in CH_3OH). It would have been interesting to also determine the stability constant of FcCrypt$^+$ complexes. Evaluation of titration experiments with a Na^+-selective electrode gave a $\lg K < 2$ in CH_3CN. However, due to the limited stability of the oxidized ferrocene cryptand in solution, these data are not very reliable.

The stability constants of Fcdpa-Zn^{2+} ($K > 10^8$), Fcdpa-2Zn^{2+} ($K_2 \approx 6 \times 10^5$), Fcdpa$^+$-$Zn^{2+}$ ($K = 7.5 \times 10^4$), and Fcdpa$^+$-2Zn^{2+} ($K = 2500$) in CH_3CN were determined by UV/Vis spectral titrations.[62]

The coupled switches: *Titration experiments*: Even in a simplified approach which does not take into account the complexation of metal ions by cyclam or protonation by adventitious water, the sheer number of species involved

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(FcCrypt, $FcCrypt^+$, FcCrypt-Na^+, $FcCrypt^+$-Na^+, Fcdpa, $Fcdpa^+$, Fcdpa-Zn^{2+}, Fcdpa-2Zn^{2+}, $Fcdpa^+$-Zn^{2+}, $Fcdpa^+$-2Zn^{2+}, Na^+, Zn^{2+}) makes it difficult to fully understand the chemical equilibria and the kinetics of the coupled switches described here. We therefore did not attempt to quantitatively evaluate the complete reaction system at a given Zn^{2+} concentration, but instead restricted ourselves to performing experiments which unequivocally prove the presence of certain species in dependence on the actual amount of Zn^{2+} present in the reaction system. Our understanding of the reaction sequence is aided by a number of simplifications: The differences between the redox potentials are always equal to or larger than 250 mV; hence, the redox reactions are considered to be quantitative. Based on the association constants, the complexation of Na^+ by FcCrypt and that of Zn^{2+} by Fcdpa and $Fcdpa^+$ are also regarded as quantitative. In the given mixture of reactants, cyclam quantitatively removes Zn^{2+} from Fcdpa-Zn^{2+}.

The thermodynamic feasibility of coupling the redox switches displayed in Figure 1 is based on the ordering of the redox potentials in Figure 3. A ^{1}H NMR titration and a UV/Vis titration were performed to determine whether the reactions depicted in Figure 1 actually take place, that is, whether they are kinetically feasible within a given time frame. In both experiments a solution of one equivalent of $Zn(CF_3SO_3)_2$ in CD_3CN (CH_3CN) was added stepwise to a mixture of $Fcpda^+PF_6^-$ and FcCrypt-Na^+ in CD_3CN (CH_3CN), followed by one equivalent of cyclam. The UV/Vis experiment is ideal for observing species associated with Fcdpa and $Fcdpa^+$, but due to the small extinction coefficients it is not suitable for the detection of species derived from FcCrypt. For this purpose a ^{1}H NMR titration experiment is ideal. We found that one equivalent of Zn^{2+} salt is already sufficient to initiate the reaction sequence depicted in Figure 1.

In the NMR titration experiment, the ^{1}H NMR spectrum of the initial mixture of $Fcdpa^+PF_6^-$ and FcCrypt-$NaCF_3SO_3$ shows sharp peaks associated with diamagnetic FcCrpyt-Na^+ and broader lines associated with paramagnetic $Fcdpa^+$ (Figure 7). Even $Fcdpa^+$ can be identified with some confidence, since its pyridine signals are only slightly broadened

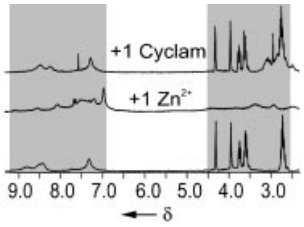

Figure 7. ^{1}H NMR titration experiment of $Fcdpa^+PF_6^-$ and FcCrypt-$NaCF_3SO_3$ in CD_3CN with one equivalent of $Zn(CF_3SO_3)_2$ in CD_3CN ($c = 10^{-4}$ mol dm^{-3}) and one equivalent of cyclam in $CDCl_3$.

in the NMR spectrum. On addition of Zn^{2+} the spectrum changes, and with one equivalent of Zn^{2+} the signals of $FcCrypt^+$ and Fcdpa-Zn^{2+} can be identified, even though the signals of the latter are exchange-broadened. After addition of one equivalent of cyclam, the initial spectrum for a mixture of FcCrypt-Na^+ and $Fcdpa^+$ reappears.

A UV/Vis titration experiment can be used to identify Fcdpa-Zn^{2+} and $Fcdpa^+$ due to their characteristic spectra, while the bands of FcCrypt and related species are hidden under the very intense bands of the aminoferrocene. In this experiment (Figure 8), $Zn(CF_3SO_3)_2$ was added stepwise (0.1 equiv of Zn^{2+} salt per addition), and as can be seen by comparison with Figure 5, the spectral maxima of the UV/Vis

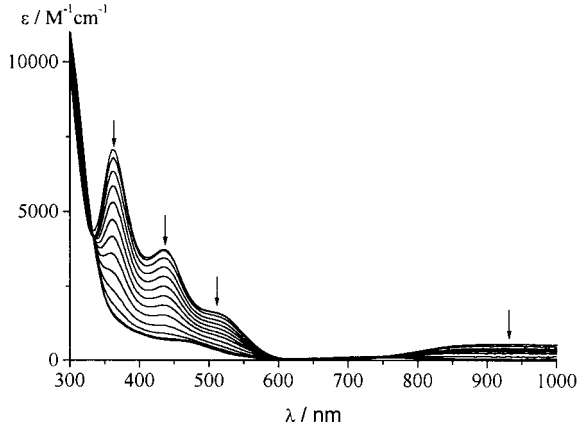

Figure 8. UV/VIS spectra of the titration of $Fcdpa^+PF_6^-$ and FcCrypt-$NaCF_3SO_3$ with $Zn(CF_3SO_3)_2$ in CH_3CN ($c = 10^{-4}$ mol dm^{-3}). Arrows indicate absorptions that decreased during the experiment. The initial UV/Vis spectrum is that of $Fcdpa^+$; the final one, after addition of one equivalent of $Zn(CF_3SO_3)_2$, is that of Fcdpa-$Zn(CF_3SO_3)_2$.

spectrum prior to addition of Zn^{2+} largely conforms to the electronic spectrum of $Fcdpa^+$. On addition of Zn^{2+} the peaks corresponding to $Fcdpa^+$ slowly disappear, and new bands grow at 275, 305, and 475 nm, which are characteristic of Fcdpa-Zn^{2+}. After addition of one equivalent of cyclam, the original UV/Vis spectrum is observed. This sequence of adding Zn^{2+} salt and cyclam, that is, the complete cycle of reactions displayed in Figure 1, was repeated up to six times with a single batch to demonstrate the reversibility of all reactions involved in the cycle. Indeed, after six consecutive cycles, the UV/Vis spectrum of the reaction mixture still had about 75 % of the intensity prior to the first cycle.

Apart from the thermodynamic feasibility of the cycle described in Figure 1 all of the reactions involved must be fast enough to permit their complete equilibration within a reasonable period of time. A first qualitative result of the hand-mixing titration experiments (UV/Vis or ^{1}H NMR) concerning the kinetics of the reactions is the absence of any induction period for complex formation. This was not surprising, since Zn^{2+} and Na^+ typically undergo rapid complexation/decomplexation reactions.[63] Furthermore, Nelsen et al. and Hupp et al. demonstrated that self-exchange reactions involving ferrocene/ferrocenium typically are very fast (on the order of 10^7 dm^3 mol^{-1} s^{-1}).[64, 65]

We were interested in obtaining at least a qualitative picture of the dynamics of the sequence of reactions involved, and therefore investigated the dynamics of the above reactions by stopped-flow kinetics. To realize pseudo-first-order conditions, a tenfold excess of $Zn(CF_3SO_3)_2$ in CH_3CN and a solution of $Fcdpa^+PF_6^-$ and FcCrypt-$NaCF_3SO_3$ in CH_3CN were injected into a stopped-flow cell. However, all

spectroscopic changes leading to Fcdpa-Zn^{2+} and $FcCrypt^{+}$ are complete even before the first spectrum is recorded (i.e., <10 ms).[66]

Conclusion

Single molecular devices can only accomplish fairly simple tasks. The integration of several such units into a coupled device permits the realization of more complex functions reminiscent of a regulatory event. Two independent chemical processes—the complexation/decomplexation of Zn^{2+} in a redox-responsive ligand (Fcdpa) and the complexation/decomplexation of Na^{+} in a redox-switched ligand (FcCrypt)—have been linked in a cyclic and highly reversible process. On addition of Zn^{2+} to $Fcdpa^{+}$ the complexation of the metal ion by the aminoferrocene produces the strong oxidizing agent $Fcdpa^{+}$-Zn^{2+}, which is able to remove an electron from FcCrypt-Na^{+}; this redox event leads to an oxidized ferrocene cryptand, the ability of which to complex Na^{+} is drastically reduced; upon removal of Zn^{2+} from its Fcdpa complex by an even stronger ligand (cyclam), the reducing agent Fcdpa is produced, which easily loses an electron to $FcCrypt^{+}$ to give FcCrypt, whose strong binding capacity for Na^{+} is thus restored. A single cycle is now complete and can be started over again by addition of Zn^{2+}. Clearly, electron-transfer reactions mediate between the two separate reactions and tie the complexation of Zn^{2+} to the decomplexation of Na^{+}, and vice versa. The energy which drives this process is the complexation of Zn^{2+} by Fcdpa and its removal by the strong ligand cyclam.

This may appear to be a complicated procedure for achieving something simple, namely, the complexation/decomplexation of Na^{+}. However, we should ask ourselves why cells also prefer such an indirect and entangled strategy to perform most of their chemical reactions. A simple answer is that such complications add flexibility. Any of the intermediate steps through which two chemical events are coupled may be inhibited or enhanced by various other chemical or physical stimuli. It is this apparently simple detail which infers the capacity to adapt to changing environmental conditions in a highly flexible manner.

Experimental Section

Commercially available solvents and reagents were purified according to literature procedures. All reactions were carried out under a nitrogen or argon atmosphere. Chromatography was performed on silica MN60. NMR spectra were recorded at 300 K with a Bruker Avance (^{1}H NMR 200 MHz, ^{13}C NMR 50.3 MHz) spectrometer. ^{1}H NMR spectra were referenced to residual undeuterated solvent, and ^{13}C NMR spectra to the solvent signals: $CDCl_3$ ($\delta(^1H)=7.26$, $\delta(^{13}C)=77.0$), C_6D_6 ($\delta(^1H)=7.16$, $\delta(^{13}C)=128.0$), CD_3CN ($\delta(^1H)=1.93$, $\delta(^{13}C)=1.30$). For the purpose of ^{1}H NMR signal assignment, CpH denotes a proton attached to the sp^2 C atom of cyclopentadiene or to the C atoms of an η^5-cyclopentadienyl ring in a ferrocene. Mass spectra: Finnigan MAT3800. IR spectra: Bruker IFS-25: solid materials as KBr tablets. UV/Vis spectra: Jasco V570. Rapid-scan UV/Vis measurements were performed on a home-built stopped-flow apparatus and a custom-made diode array from J&M. Elemental analyses: Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg. Cyclic voltammetry: The standard electrochemical instrumentation consisted of an EG&G 273A-2 potentiostat–galvanostat. All cyclic voltammograms were recorded in dry CH_3CN under an argon atmosphere at ambient temperature. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as counterelectrode. The pseudoreference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of cobaltocenium perchlorate (-0.94 V vs. Ag/AgCl) or ferrocene ($+0.40$ V vs. Ag/AgCl). NBu_4PF_6 (0.1 mol dm^{-3}) was used as supporting electrolyte. The abbreviation Fc is indiscriminately used for ferrocene, ferrocenyl, or ferrocenediyl. Starting materials were commercially available or synthesized according to literature procedures: $Fc^{+}BF_4^{-}$,[67] $FcCOCH_3{}^{+}PF_6^{-}$,[67] diaza-[12]crown-4,[68] Fcdpa,[38] 1,1′-Fc-$(OSi\,i\!Pr_3)_2$.[37]

1,1′-$(OC_2H_4OH)_2$-Ferrocene: TBAF · 3 H_2O (9.45 g, 30 mmol) was added to a mixture of 1,1′-bis(triisopropylsiloxy)ferrocene (4.4 g, 9.85 mmol), 1-bromo-2-ethanol (13.9 mL, 197 mmol) and K_2CO_3 (27.1 g, 197 mmol) in CH_3CN (300 mL), and the reaction mixture refluxed overnight. The solution was filtered, the solvent evaporated, and the crude product suspended in cyclohexane/ethyl acetate (1/1). This suspension was applied to silica gel and eluted under argon with cyclohexane/ethyl acetate (1/1) to remove impurities. The product was eluted with pure ethyl acetate. Yield: 1.6 g (4.80 mmol), 49 %, orange powder. ^{1}H NMR (C_6D_6): $\delta=2.17$ (br, 2H; OH), 3.28 (m, 8H; CH_2), 3.44 ("t", $J=2$ Hz, 4H; FcH), 3.75 ("t", $J=2$ Hz, 4H; FcH); ^{13}C NMR (C_6D_6): $\delta=56.75$, 61.60, 62.63, 72.47, 127.04; EI-MS: m/z: 306.

1,1′-$(OC_2H_4OTs)_2$-Ferrocene: 1,1′-$(OC_2H_4OH)_2$-Ferrocene (1.6 g, 4.80 mmol) and tosyl chloride 9.15 g (48.0 mmol) were dissolved in CH_2Cl_2 (300 mL), and the solution was cooled to 0 °C. Freshly powdered KOH 10.75g (192.0 mmol) was added in several portions while holding the temperature of the reaction mixture at close to 0 °C. The reaction mixture was stirred for a further 3 h and then poured onto ice (300 g). The organic and aqueous layers were separated. The aqueous solution was extracted with CH_2Cl_2 (2×50 mL), and the combined organic layers washed with aqueous NaOH (3×50 mL) and water (100 mL). Drying over $MgSO_4$, filtration, and evaporation of the solvent gave a crude product, which was purified by chromatography (cyclohexane/ethyl acetate 3/2). Yield: 2.86 g (4.65 mmol), 97 %, yellow powder. ^{1}H NMR (C_6D_6): $\delta=7.81$ (d, $J=8$ Hz, 4H; ArH), 6.75 (d, $J=8$ Hz, 4H; ArH), 4.05 (m, 4H; CH_2OFc), 3.95 (s, 4H; FcH), 3.69 (s, 4H; FcH), 3.61 (m, 4H; CH_2OTs), 1.83 (s, 6H; CH_3). ^{13}C NMR (C_6D_6): $\delta=21.15$, 56.54, 62.82, 68.17, 68.64, 127.71, 128.03, 128.35, 129.93. FD-MS: m/z: 615 [M^+] (100 %).

General procedure for the synthesis of the ferrocene cryptands 2–4: 1,1′-$(OC_2H_4OTs)_2$-Ferrocene (1 equiv), diaza crown ether (1 equiv), and base (10 equiv) were refluxed in CH_3CN overnight. The suspension was filtered, and the solvent evaporated. The crude product was purified by chromatography (ethyl acetate/Et_2NH 10/1).

1,1′-(*O*,*O*′-Diethoxy(1,7)-4,10-dioxa-1,7-diazacyclododecane)ferrocene (2): Scale: 1,1′-bis(2-tosylethoxy)ferrocene (500 mg, 0.81 mmol), diaza-[12]crown-4 (150 mg, 0.81 mmol), Na_2CO_3 (860 mg, 8.15 mmol). Yield: 245 mg (0.55 mmol) 68 %, orange powder. ^{1}H NMR (CD_3CN): $\delta=2.56$–2.67 (m, 4H; NCH_2), 2.73–2.89 (m, 8H; NCH_2), 3.50–3.59 (m, 4H; OCH_2), 3.66–3.77 (m, 4H; OCH_2), 3.84 ("t", $J=1.9$ Hz, 4H; C_5H_4), 3.92 (t, $J=7.5$ Hz, 4H; OCH_2), 4.09 ("t", $J=1.9$ Hz, 4H; C_5H_4). ^{13}C NMR (CD_3CN): $\delta=55.85$, 55.87, 57.03, 62.63, 71.32, 71.44, 128.42; elemental analysis (%) calcd for $C_{22}H_{32}FeN_2O_4$ (444.36): C 59.47, H 7.26, N 6.30; found: 58.61, H 7.70, N 5.97.

1,1′-(*O*,*O*′-Diethoxy(1,7)-4,10,13-trioxa-1,7-diazacyclopentadecane)ferrocene (3): Scale: 1,1′-$(OC_2H_4OTs)_2$-ferrocene (235 mg, 0.38 mmol), diaza-[15]crown-5 (81 mg, 0.38 mmol), K_2CO_3 (526 mg, 3.81 mmol). Yield: 112 mg (0.23 mmol), 61 %, orange powder. ^{1}H NMR ($CDCl_3$): $\delta=2.57$–2.81 (m, 12H; NCH_2), 3.53–3.61 (m, 12H; OCH_2), 3.78 ("t", $J=1.9$ Hz, 4H; C_5H_4), 3.86 (t, $J=7.5$ Hz, 4H; $FcOCH_2$), 4.01 ("t", $J=1.9$ Hz, 4H; C_5H_4); ^{13}C NMR ($CDCl_3$): $\delta=55.04$, 56.74, 56.90, 62.00, 69.92, 70.08, 70.12, 71.01, 127.27.

1,1′-(*O*,*O*′-Diethoxy(1,10)-4,7,13,16-tetraoxa-1,10-diazacyclooctadecane)-ferrocene (4): Scale: 1,1′-$(OC_2H_4OTs)_2$-ferrocene (292 mg, 0.47 mmol), diaza-[18]crown-6 (125 mg, 0.47 mmol), K_2CO_3 658 mg (4.76 mmol). Yield: 96 mg (0.18 mmol) 38 %, orange powder. ^{1}H NMR ($CDCl_3$): $\delta=2.72$–2.86 (m, 12H; NCH_2), 3.56–3.60 (m, 16H; OCH_2), 3.87 ("t", $J=1.9$ Hz, 4H; C_5H_4), 3.99 (t, $J=7.6$ Hz, 4H; $FcOCH_2$), 4.12 ("t", $J=1.9$ Hz, 4H; C_5H_4);

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^{13}C NMR ($CDCl_3$): $\delta = 54.54$, 54.62, 54.86, 62.06, 62.36, 62.66, 69.41, 69.96, 70.87, 71.00, 126.74.

Syntheses of metal complexes of FcCrypt: The alkali and alkaline earth metal ion complexes of FcCrypt were prepared by mixing stoichiometric amounts of the ligand and the metal salt in acetonitrile. Evaporation of the solvent gave the pure metal complexes. FcCrypt-$NaClO_4$: ^{1}H NMR (CD_3CN): $\delta = 2.58-2.87$ (m, NCH_2, 12H), 3.51–3.63 (m, 8H; OCH_2), 3.74 (t, $J = 5.0$ Hz, 4H; OCH_2), 3.94 ("t", $J = 1.9$ Hz, 4H; CpH), 4.31 ("t", $J = 1.9$ Hz, 4H; CpH); ^{13}C NMR (CD_3CN): $\delta = 53.31$, 56.87, 61.41, 64.81, 67.60, 73.19, 125.77; FcCrypt-$Ca(ClO_4)_2$: ^{1}H NMR (CD_3CN): $\delta = 2.59-2.92$ (m, 12H; NCH_2), 3.55–3.75 (m, 8H; OCH_2), 3.78 (t, $J = 5.4$ Hz, 4H; $FcOCH_2$), 3.91 (s, 4H; CpH), 4.34 (s, 4H; CpH); ^{13}C NMR (CD_3CN): $\delta =$ 53.20, 56.92, 62.85, 65.59, 68.99, 75.95, 124.28.

Protonation of FcCrypt: HBF_4 (1 or 2 equiv, 50% in diethyl ether) was added to one equivalent of FcCrypt in acetonitrile. FcCrypt-H^+: ^{1}H NMR (CD_3CN): $\delta = 3.06-3.11$ (m, 12H), 3.18 (t, $J = 5.6$ Hz, CH_2N, 4H), 3.68–3.78 (m, OCH_2, 8H), 3.90 (br s, CpH, 4H), 4.06 (t, $J = 5.5$ Hz, CH_2OFc, 4H), 4.9 (br, NH, 1H). FcCrypt-2H^+: ^{1}H NMR (CD_3CN): $\delta = 3.54-3.73$ (m, 12H), 3.86–4.06 (m, 16H), 4.25 (br, FcH, 4H), 6.15 (br, NH, 2H). ^{13}C NMR (CD_3CN): $\delta = 54.99$, 57.92, 58.65, 64.42, 66.25, 126.85.

Synthesis of Fcdpa-Zn$(CF_3SO_3)_2$: Stoichiometric amounts of Fcdpa and $Zn(CF_3SO_3)_2$ were dissolved in CH_3CN and stirred for 5 min. The ^{1}H NMR of this complex in CD_3CN displays very broad signals over a large temperature range.

Synthesis of Fcdpa-2 Zn$(CF_3SO_3)_2$: Stoichiometric amounts of Fcdpa and $Zn(CF_3SO_3)_2$ were dissolved in CH_3CN and stirred for 5 min. After evaporation of the solvent, the complex can be isolated in quantitative yield or recrystallized from CH_3CN/Et_2O to obtain single crystals. ^{1}H NMR (CD_3CN): $\delta = 4.01-4.50$ (m, 12H), 7.20–7.35 (m, ArH, 20H), 7.66 (t, pyH, 4H), 8.17 (t, pyH, 4H), 8.60 (d, pyH, 4H). ^{13}C NMR (CD_3CN): $\delta = 59.06$, 63.88, 84.78, 112.22, 125.40, 126.27, 128.30, 129.43, 130.81, 136.03, 142.79, 148.77, 156.98; elemental analysis (%) calcd for Fcdpa-2 $Zn(CF_3SO_3)_2 \cdot 4H_2O$: $C_{62}H_{56}F_{12}FeN_6O_{16}S_4Zn_2$ (1684.8): C 44.22, H 3.35, N 4.99; found: C 44.27, H 3.25, N 4.57.

Synthesis of Fcdpa$^+PF_6^-$: A mixture of Fcdpa (884 mg, 1.0 mmol) and $Fc^+PF_6^-$ (340 mg, 1.02 mmol) in CH_2Cl_2 (40 mL) was stirred for 30 min. The volatile substances were evaporated, and the residue washed with diethyl ether to remove ferrocene. The orange-red residue was recrystallized from CH_3CN. Yield: 649 mg (63%). The product was stored at -20°C. Elemental analysis (%) calcd for $C_{58}H_{48}F_6FeN_6P$ (1029.91): C 67.64, H 4.70, N 8.16; found: C 65.66, H 4.83, N 7.68.

FcCrypt$^+BF_4^-$ was synthesized by adding 1.02 equivalents of acetyl-$Fc^+BF_4^-$ to a solution of FcCrypt in CH_2Cl_2. The solvent was removed and the residue washed with diethyl ether until the extract was colorless.

Crystal structure analysis:[69] $C_{22}H_{34}CaCl_2FeN_2O_{13}$, $M_r = 701.35$; $T =$ 293(2) K; $\lambda = 0.71069$ Å; monoclinic, space group $P2_1$; $a = 8.630(2)$, $b =$ 17.683(4), $c = 10.434(2)$ Å, $\beta = 113.15(3)^\circ$, $V = 1464.1(6)$ Å^3; $Z = 2$; $\rho_{calcd} =$ 1.550 Mg m^{-3}; $\mu = 0.934$ mm^{-1}; $F(000) = 708$; crystal dimensions $0.6 \times 0.4 \times$ 0.2 mm; θ range: 2.85–26.0°; index ranges: h −10/9, k 0/21, l 0/12; reflections collected/unique: 3116/2958; $R_{int} = 0.0317$; completeness to $2\theta(26.0)$: 99.4%; refinement method: full-matrix least-squares on F^2; data/restraints/parameters: 2958/22/368; GOF on F^2: 1.080; final R indices ($I > 2\sigma(I)$): $R1 = 0.0599$, $wR2 = 0.1646$; R indices (all data): $R1 = 0.0641$, $wR2 = 0.1693$; absolute structure parameter: −0.04(4); max./min. residual electron density: +0.729/−0.459 e Å^3. The crystal structure of FcCrypt-$Ca(ClO_4)_2$ was solved and refined in the acentric space group $P2_1$, including absolute structure parameters; thus, the choice of enantiomorph was correct. All non-hydrogen atoms except for the oxygen atoms attached to the second, uncoordinated perchlorate anion were refined anisotropically. Both perchlorate ions are disordered; the uncoordinated one was restrained to a perfect tetrahedron with equal Cl–O and O–O distances.

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[1] K. E. Drexler, *Nanosystems—Molecular Machinery, Manufacturing and Computation*, Wiley, New York **1992**.
[2] S. Blanc, P. Yakirevitch, E. Leize, M. Meyer, J. Libman, A. Van Dorsselaer, A.-M. Albrecht-Gary, A. Shanzer, *J. Am. Chem. Soc.* **1997**, *119*, 4934.
[3] P. R. Ashton, R. Ballardini, V. Balzani, A. Credi, K. R. Dress, E. Ishow, C. J. Kleverlaan, O. Kocian, J. A. Preece, N. Spencer, J. F. Stoddart, M. Venturi, S. Wenger, *Chem. Eur. J.* **2000**, *6*, 3558.
[4] N. P. M. Huck, W. F. Jager, B. Delange, B. L. Feringa, *Science* **1996**, *273*, 1686.
[5] P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem.* **1994**, *106*, 2109; *Angew. Chem. Int. Ed.* **1994**, *33*, 2024.
[6] M. P. Debreczeny, W. A. Svec, M. R. Wasielewski, *Science* **1996**, *274*, 584.
[7] A. Doron, M. Portnoy, M. Liondagan, E. Katz, I. Willner, *J. Am. Chem. Soc.* **1996**, *118*, 8937.
[8] D. Gosztola, M. P. Niemczyk, M. R. Wasielewski, *J. Am. Chem. Soc.* **1998**, *120*, 5118.
[9] A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515.
[10] L. Bergonzi, L. Fabrizzi, M. Licchelli, C. Mangano, *Coord. Chem. Rev.* **1998**, *170*, 31.
[11] R. T. Hembre, J. S. McQueen, V. W. Day, *J. Am. Chem. Soc.* **1996**, *118*, 798.
[12] J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L. Atwood, B. C. Lynn, A. E. Kaifer, G. W. Gokel, *J. Am. Chem. Soc.* **1992**, *114*, 10583.
[13] R. Deans, A. Niemz, E. C. Breinlinger, V. M. Rotello, *J. Am. Chem. Soc.* **1997**, *119*, 10863.
[14] C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172.
[15] G. M. Tsivgoulis, J.-M. Lehn, *Adv. Mater.* **1997**, *9*, 39.
[16] T. R. Kelly, I. Tellitu, J. P. Sestelo, *Angew. Chem.* **1997**, *109*, 1969; *Angew. Chem. Int. Ed.* **1997**, *36*, 1866.
[17] T. R. Kelly, J. P. Sestelo, J. Tellitu, *J. Org. Chem.* **1998**, *63*, 3655.
[18] A. P. Davis, *Angew. Chem.* **1998**, *110*, 953; *Angew. Chem. Int. Ed.* **1998**, *37*, 909.
[19] J. Howard, *Nature* **1997**, *389*, 561.
[20] V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2000**, *39*, 3349.
[21] B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, *100*, 1789.
[22] P. R. Ashton, R. Ballardini, V. Balzani, E. C. Constable, A. Credi, O. Kocian, S. J. Langford, J. A. Preece, L. Prodi, E. R. Schofield, N. Spencer, J. F. Stoddart, S. Wenger, *Chem. Eur. J.* **1998**, *4*, 2413.
[23] P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gómez-López, M.-V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 11932.
[24] T. R. Kelly, H. De Silva, R. A. Silva, *Nature* **1999**, *401*, 150.
[25] J.-P. Collin, P. Gaviña, V. Heitz, J.-P. Sauvage, *Eur. J. Inorg. Chem.* **1998**, *1*, 1.
[26] P. R. Ashton, V. Balzani, O. Kocian, L. Prodi, N. Spencer, J. F. Stoddart, *J. Am. Chem. Soc.* **1998**, *120*, 11190.
[27] J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, **1995**.
[28] The term switch, even though used within the community, may be somewhat misleading; according to the laws of thermodynamics there can only be a certain increase or decrease in the binding affinity as expressed by a change in the stability constant K for the equilibrium under observation.
[29] P. D. Beer, *Adv. Inorg. Chem.* **1992**, *39*, 79.
[30] V. Amendola, L. Fabrizzi, M. Licchelli, C. Mangano, P. Pallavincini, L. Parodi, A. Poggi, *Coord. Chem. Rev.* **1999**, *192*, 649.
[31] F. C. J. M. van Veggel, W. Verboom, D. N. Reinhoudt, *Chem. Rev.* **1994**, *94*, 279.
[32] H. Plenio, C. Aberle, *Angew. Chem.* **1998**, *110*, 1467; *Angew. Chem. Int. Ed.* **1998**, *37*, 1397.
[33] H. Plenio, C. Aberle, *Chem. Commun.* **1998**, 2697.
[34] G. Krauss, *Biochemie der Regulation und Signaltransduktion*, Wiley-VCH, Weinheim, **1997**.
[35] H. Plenio, C. Aberle, *Chem. Commun.* **1996**, 2123.

[36] H. Plenio, D. Burth, *Angew. Chem.* **1995**, *107*, 881; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 800.
[37] H. Plenio, C. Aberle, *Organometallics* **1997**, *16*, 5950.
[38] H. Plenio, D. Burth, *Organometallics* **1996**, *15*, 4054.
[39] H. Plenio, D. Burth, O*rganometallics* **1996**, *15*, 1151.
[40] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877.
[41] The tetraphenyl-substituted ferrocene cryptand is not usable in combination with Fcdpa because the redox potential of its Na^+ complex is about 100 mV too high and therefore too close to that of Fcpda-2 Zn^{2+} to effect a quantitative redox reaction.
[42] S. R. Miller, D. A. Gustowski, Z. Chen, G. W. Gokel, L. Echegoyen, A. E. Kaifer, *Anal. Chem.* **1988**, *60*, 2021.
[43] H. Plenio, J. Yang, R. Diodone, J. Heinze, *Inorg. Chem.* **1994**, *33*, 4098.
[44] H. Plenio, R. Diodone, *Inorg. Chem.* **1995**, *34*, 3964.
[45] A. Benito, R. Martinez-Máñez, J. Soto, M. J. L. Tendero, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 2175.
[46] The oxidation is at a very anodic potential of ca. 0.8 V. However, from electrochemical simulations with DIGISIM we found that for EC processes with very fast chemical reactions the oxidation potentials can be shifted anodically, as observed here.
[47] The assigment of another Fcdpa-Zn^{2+} complex rests on the fact that by using substoichiometric amounts of Zn^{2+} this complex can be probed directly. It is, however, very unlikely that a protonated species is observed instead.
[48] Y. S. Sohn, D. N. Hendrickson, H. B. Gray, *J. Am. Chem. Soc.* **1971**, *93*, 3603.
[49] R. Rulkens, D. P. Gates, D. Balaishis, J. K. Pudelski, D. F. McIntosh, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **1997**, *119*, 10976.
[50] J. Silver, *J. Chem. Soc. Dalton Trans.* **1990**, 3513.
[51] S. Akabori, Y. Habata, Y. Sakamoto, M. Sato, S. Ebine, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 537.
[52] D. Seyferth, B. W. Hames, T. G. Rucker, M. Cowie, S. D. Raymond, *Organometallics* **1983**, *2*, 472.
[53] M. Cowie, R. S. Dickson, *J. Organomet. Chem.* **1987**, *326*, 269.
[54] A. V. Bajaj, N. S. Poonia, *Coord. Chem. Rev.* **1988**, *87*, 55.
[55] H. Plenio, C. Aberle, Y. Al Shihadeh, J. M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto, *Chem. Eur. J.* **2001**, *7*, 2848.
[56] H. Plenio, R. Diodone, *J. Organomet. Chem.* **1995**, *492*, 73.
[57] J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L. Atwood, B. C. Lynn, A. E. Kaifer, G. W. Gokel, *J. Am. Chem. Soc.* **1992**, *114*, 10583.
[58] C. D. Hall, S. Y. F. Chu, *J. Organomet. Chem.* **1995**, *498*, 221.
[59] T. Saji, *Chem. Lett.* **1986**, 275.
[60] The NMR solvent CD_3CN was used as received and contains about 0.1 % water, as estimated from a comparison of the ^1H NMR integrals of HDO and CD_2HCN.
[61] R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, D. Sen, *Chem. Rev.* **1985**, *85*, 271.
[62] Values for K larger than 10^5 are less reliable, as it is not possible to do the UV/Vis measurements in a reliable concentration range of $1/K$ [mol L^{-1}] and due to the weakness of the appropriate bands for evaluation.
[63] R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, VCH, Weinheim **1991**.
[64] S. F. Nelsen, L. J. Chen, M. T. Ramm, G. T. Voy, D. R. Powell, M. A. Accola, T. R. Seehafer, J. J. Sabelko, J. R. Pladziewicz, *J. Org. Chem.* **1996**, *61*, 1405.
[65] R. M. Nielson, L. A. Lyon, J. T. Hupp, *Inorg. Chem.* **1996**, *35*, 970.
[66] To further slow down the reaction, a 1/1/1 stoichiometry of the same reaction partners was mixed in a stopped-flow cell. Here the sequence of reactions is complete after about 1 s.
[67] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877.
[68] P. L. Anelli, F. Montanari, S. Quici, G. Ciani, A. Sironi, *J. Org. Chem.* **1988**, *53*, 5292.
[69] Crystal data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153271. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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