

Project 54791

Managing Tight Binding Receptors for New Separations Technologies DOE EMSPAward No. 545791 (9/15/96--9/14/00)

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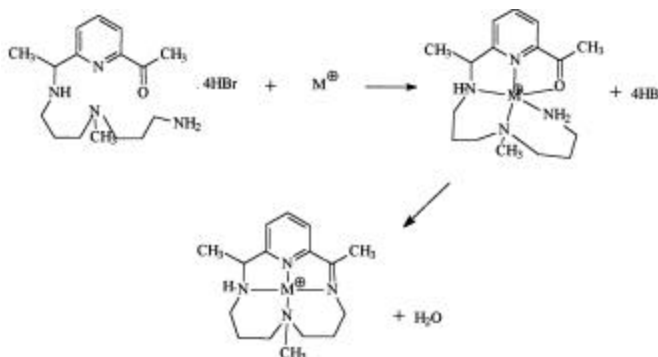
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This program is directed at establishing the fundamental principles that will make the most strongly binding ligands and their complexes available to separations technologies. The ultimate powerful ligands can capture metal ions in the most competitive of circumstances. Ultra tight-binding ligands can remove metal ions from mineralized sites, take them away from lesser ligands, and even capture metal ions from extremely dilute solutions. Further, these feats offer the possibility of solving some of the most serious environmental challenges that cannot be met by existing technologies: decontamination of metal surfaces, removal of metal contaminations from soils, separation of very low concentrations of radioactive metal ions from nuclear waste, capturing of contaminating metal ions from extremely dilute solutions. Despite their promise, extremely stable complexes are rarely used in separations because their great stabilities are accompanied by very slow rates of complex formation and dissociation. Specifically, this program has attacked this limitation in two ways: (1) seeking basic scientific ways of overcoming the natural molecular lethargy of ultra tight-binding ligands and (2) developing a new technology that functions despite the slowness of the metal binding reactions. The three basic concept areas of this program are: replace slow equilibrium formation and dissociation of ultra tight-binding complexes by (1) *switch-binding of templating ligands*, and (2) *switch-release* of photo reactive ligands, and (3) Create a slow separations technology based on imprinted polymers (e.g., a soil poultice)

(1) *Switch-binding of templating ligands*

ligands. **Figure 1** shows our Generation 1 switch-binding ligand and the template ring closing. Both the synthesis and quantitative characterization of the new family of ligands were challenging because the target molecule, by design, reacts with itself. These problems were overcome and template ring closure upon contacting nickel(II) in aqueous solutions was proven by isolation of the macrocyclic nickel complex (isolated yield, 82%), and solution studies. Kinetic studies on the acid destruction of the complex showed the stabilization expected for a macrocyclic complex. As expected, two

rate processes occur during switch-binding to nickel(II); rapid first complexation on the millisecond time scale, followed by a slower process in which the chelation process is completed. Our preliminary analysis gives the rate constant for the critical final macrocyclization step $k_2 = 6.05(±0.48) \times 10^{-2} \text{ s}^{-1}$. A very similar linear ligand that cannot cyclize gave $k_2 = 3.07(±0.21) \times 10^{-2} \text{ s}^{-1}$. Equally important, comparison of the rate constants for our switch-binding reaction with those for complex formation using similar macrocycles shows that the new ligands bind more rapidly by a factor of two or three orders of magnitude. The result suggests that switch-binding macrocycle formation may be as fast or faster than ordinary chelation. These studies have already provided a proof of concept for the switch-binding principle. A second generation of switch-binding ligands has been designed and synthesized in which the ring closing reaction is amide or ester formation.

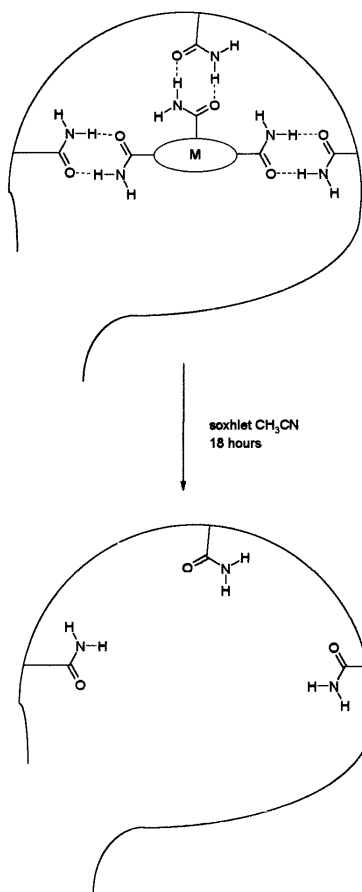
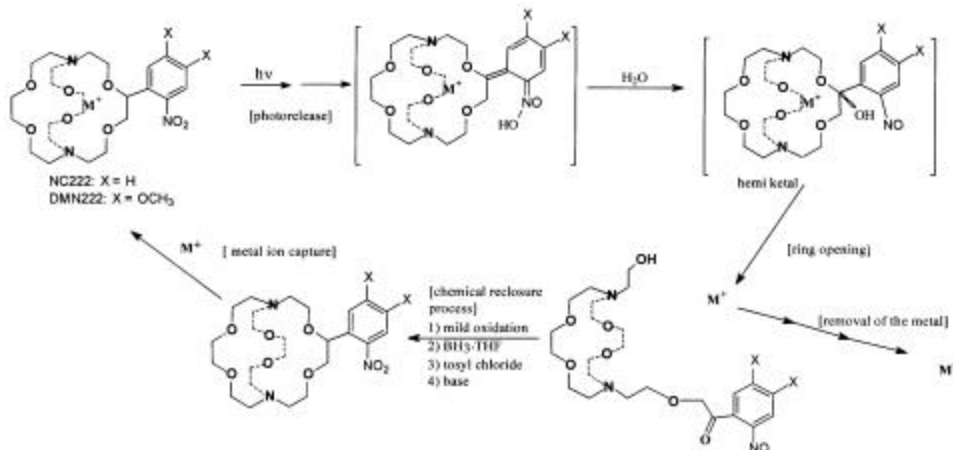


Switch-release of the Metal Ion.

The synthesis of an *o*-nitrobenzyl substituted cryptand (**Figure 2**) has been achieved, in an overall yield of 38%, by modifications of a known reaction sequence and the preliminary photochemistry examined.

Upon photolysis, the cryptand

was converted to the open macrocycle in quantitative yield following the typical photochemical sequence of *o*-nitrobenzyl derivatives. Further studies will determine the photo efficiency for this transformation, the effects of different metal ions on the nature of the reaction products and on the dissociation constants. Recyclization of the photolyzed product back to the cryptand by sequential oxidation of the nitroso group, reduction of the carbonyl and cyclization is under study.



obtained when a counter ion was also included in the polymer.

A Soil Poultrice based on Imprinted Macroporous Polymers.

This proposed new slow-binding technology mimics the manner in which certain microbes bring iron into their cells from minerals in the soil. An extremely tight-binding ligand is excreted through the cell membrane of the microorganism; it diffuses into the soil and slowly dissolves iron from the abundant oxide. The complex then diffuses back into the cell. To mimic these natural systems our **Asoil poultrice** makes use of youthful materials called **Atemplated macroporous polymers** which contain highly selective receptors. Casting the polymer in the presence of their target molecules locks in a structure favoring their binding. In this system, a solution of the selected ligand is sprayed on the contaminated soil, the ligand extracts the contaminant and polymer beads selectively adsorb the metal/ligand complex, thereby removing the insoluble contaminant from the soil. The active monomer was acrylamide, highly crosslinked with ethylene glycol dimethacrylate to produce polymers with mesopores (20-500D diameter). Amide groups are known to favor rebinding to templated polymers so the favored target complex had the ligand of **structure 1**. The mode of interaction is shown in **Figure 3**.

The new polymers were characterized by infrared spectroscopy, polymer swelling, and surface area/porosity measurements. For samples of good porosity, rebinding equaled the best expected results for selective hydrogen-binding sites. Extremely promising results were

