

A FAMILY OF “UMPOLUNG” MOLECULAR CONTAINERS FOR THE INCLUSION OF XENON AND OTHER GASES

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For two decades, ^{129}Xe has received increasing attention as a potent tracer for MRI imaging and NMR-based sensing due to its enormous chemical shift range and the availability of laser polarization techniques that enhance nuclear polarization, and thereby sensitivity, by several orders of magnitude. Emerging biosensing technologies based upon delivery of the noble gas to biomolecular targets have been supported by several proof-of-concept experiments.¹ Notably, the delivery mechanism for these technologies necessarily relies upon a supramolecular recognition event—the inclusion/binding/encapsulation of ^{129}Xe atoms by functionalized hosts. To date, cryptophane molecular containers—most notably derivatives of cryptophane-**222** (Figure 1; $n = 2$, $R = \text{OCH}_3$) and cryptophane-**111** ($n = 1$, $R = \text{H}$)—are by far the most promising host candidates as they display the highest known thermodynamic affinities for xenon.

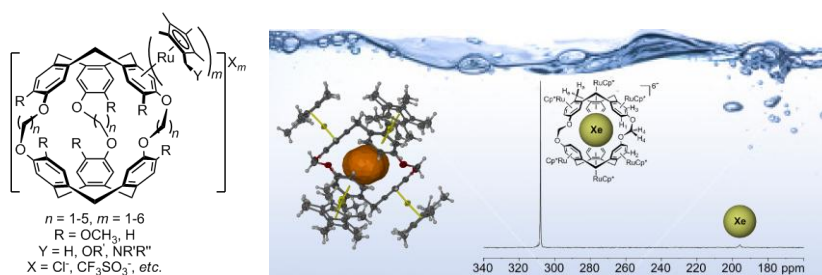


Figure 1. (left) A family of metal-functionalized cryptophanes for the encapsulation of anions, small molecules, and gases. (right) Aqueous encapsulation of xenon within a metal-functionalized cryptophane-**111** derivative.

The presentation will focus on our progress concerning the development of a family of metal-functionalized “umpolung” cryptophanes, as outlined in Figure 1,²⁻⁴ for the encapsulation of xenon and other gases.³ One of these hosts, a hexametalated derivative of cryptophane-**111**, equals the highest known binding affinity for xenon. The cationic transitional metal moieties induce an enormous downfield NMR chemical shift of the encapsulated ^{129}Xe atoms, greatly broadening the practical chemical shift range made available by cryptophane hosts. The results suggest that it is possible, using only a couple of optimized host skeletons, to create a large family of hosts with comparably high xenon affinities, but whose ^{129}Xe NMR frequency responses span nearly the entire known chemical shift range for xenon (0-350 ppm).

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