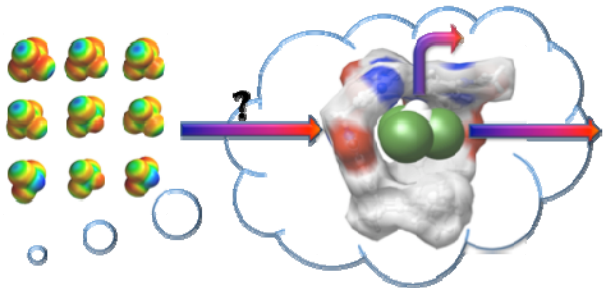
Gated Molecular Baskets

Jovica D Badjic
Assistant Professor
Department of Chemistry
Ohio State University
Columbus, OH 43228 USA

The isolation of a guest molecule inside a host allows the tailoring of its local environment and properties. The stabilization of reactive intermediates, the promotion of chemical transformations, and the modulation of conformational dynamics have thus been investigated in confined environments. The incorporation of dynamic elements of design into artificial hosts has been recognized as mandatory for increasing the efficiency of any encapsulation-based catalyst. In that vein, the constrictive binding has been defined as the activation energy needed for a guest to leave the host. Interestingly, a high constrictive binding is critical for stabilizing reactive intermediates but detrimental for promoting chemical reactions. The quandary can be addressed by examining the kinetic stability of the encapsulation complexes, i.e., the interdependence between the host's conformational dynamics and the encapsulation kinetics. Accordingly, our research program is focused on understanding working mechanisms of basket-like hosts capable to fold and control the kinetic stability of incarcerated guests (see Figure).[1] The folding process is mediated by *intramolecular* hydrogen bonding[2-3] or metal-to-ligand coordination[4] of the heterocyclic "flaps" appended to the basket rim. The kinetic stability of a guest has been dictated by (a) its coordination to the metal cation, or (b) rapid opening and closing of the hydrogen bonding 'flaps". In this way, the guest exchange is restricted by the baskets' conformational behavior, allowing us to examine the relationship between the molecular exchange kinetics and the host's dynamics. The control of chemical reactivity and the chirality transfer are also investigated in such synchronized and dynamic environments.



1. Maslak, V.; Yan, Z.; Xia, S.; Gallucci, J.; Hadad, C. M.; Badjić, J. D. Design, synthesis, and conformational dynamics of a gated molecular basket, *J. Am. Chem. Soc.* **2006**, *128*, 5887-5894.
2. Wang, B-Y.; Bao, X.; Yan, Z.; Maslak, V.; Hadad, C. M.; Badjić, J. D. A 3-fold Butterfly Valve in Command of the Encapsulation's Kinetic Stability. Molecular Baskets at Work. *J. Am. Chem. Soc.* **2008**, *130*,15127-15133.
3. Wang, B-Y.; Bao, X.; Stojanovic, S.; Hadad, C. M.; Badjić, J. D. Encapsulation of Guests within a Gated Molecular Basket: Thermodynamics and Selectivity. *Org. Lett.* **2008**, *10*, 5361-5364.
4. Rieth, S.; Yan, Z.; Xia, S.; Hadad, C. M.; Badjić, J. D. Molecular Encapsulation via Metal-to-Ligand Coordination in a Cu(I)-Folded Molecular Basket. *J. Org. Chem.* **2008**, *73*, 5100-5109.