Scientific Program

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Research Systems of Green Chemistry

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Inverse Molecular Design of Green Catalysts for Biomass Conversion

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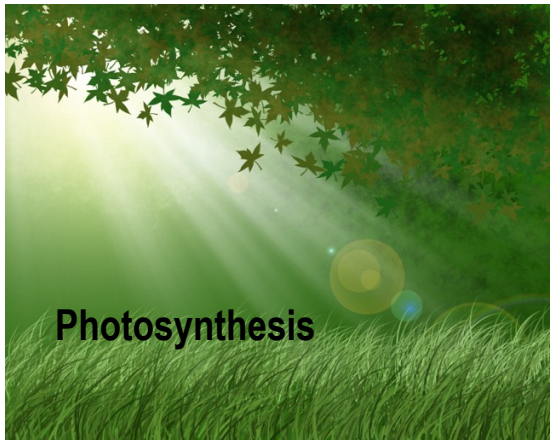
Main Campus

Orange Campus

Biomass Energy: No Extra CO_2 Emission

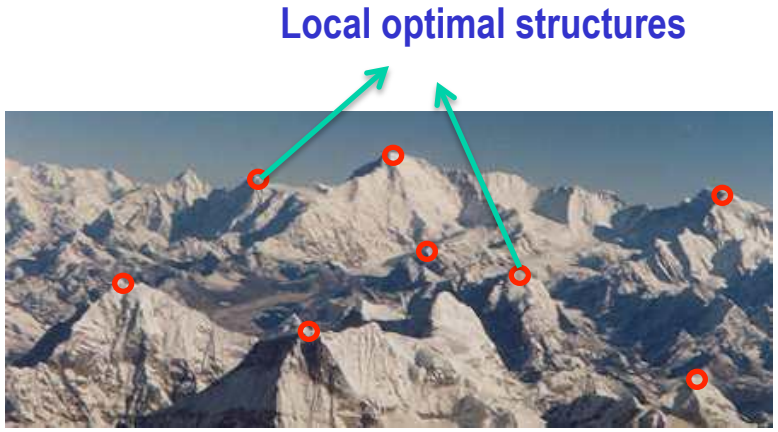
CO_2 is recycled *via* the photosynthesis of plants in nature.



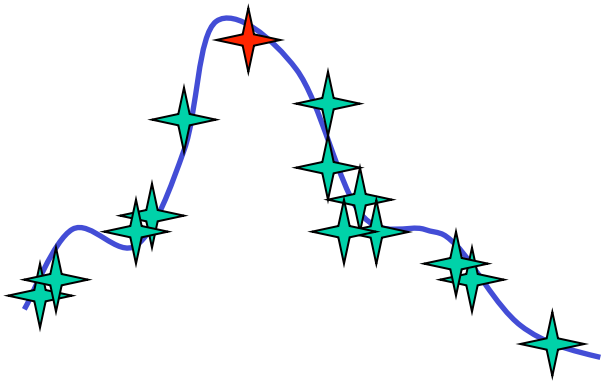
Catalysts !?

Designing efficient, robust, and cheap catalysts is the key for the development of next generation technology for biomass conversion.

How Does TB-LCAP Search for Optimum Molecules?

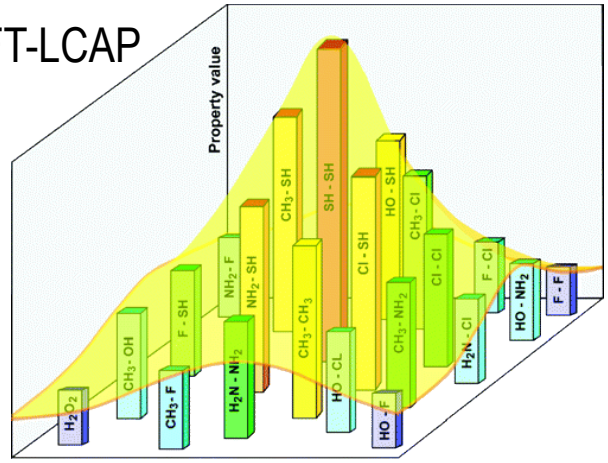


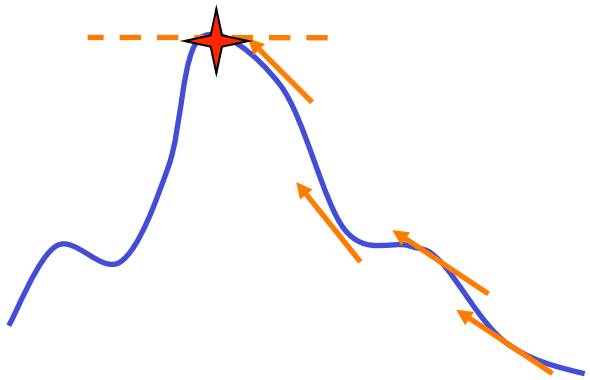
"Analog" of molecular structure-property surface



Stochastic Search

DFT-LCAP





Deterministic Search

TB-LCAP

The TB-LCAP Inverse design uses an effective and efficient way to search optimal molecules.

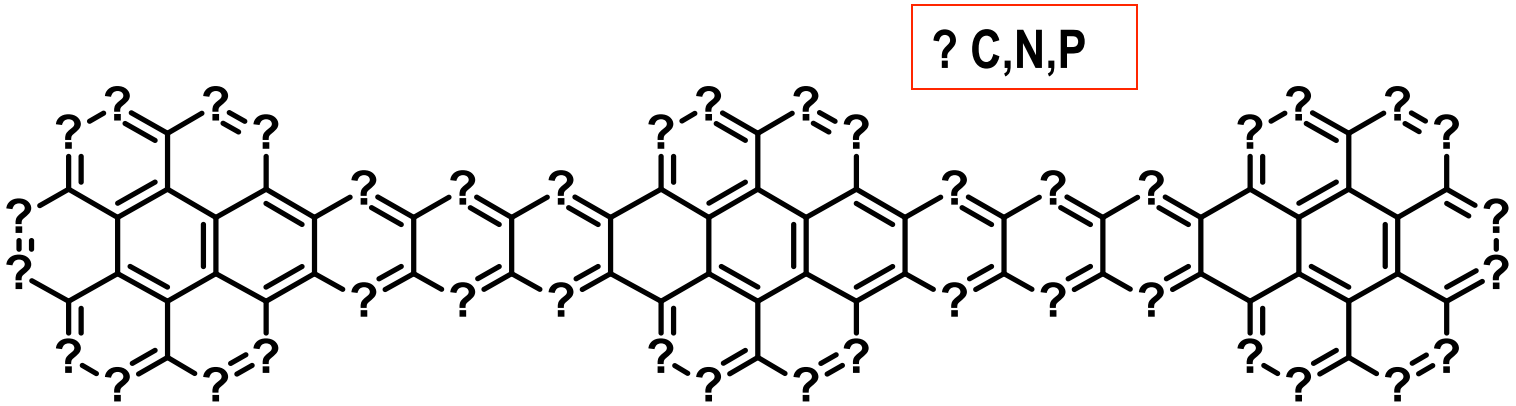
Mingliang Wang, Xiangqian Hu, David N. Beratan, Weitao Yang, *J. Am. Chem. Soc.* **2006**, *128*(10), 3228-3232.

Dequan Xiao, Weitao Yang, and David N. Beratan, *J. Chem. Phys.*, *129*(4), **2008**, 044106.

Advantage of TB-LCAP

Dequan Xiao, Weitao Yang, and David N. Beratan, *J. Chem. Phys.*, *129*(4), **2008**, 044106.

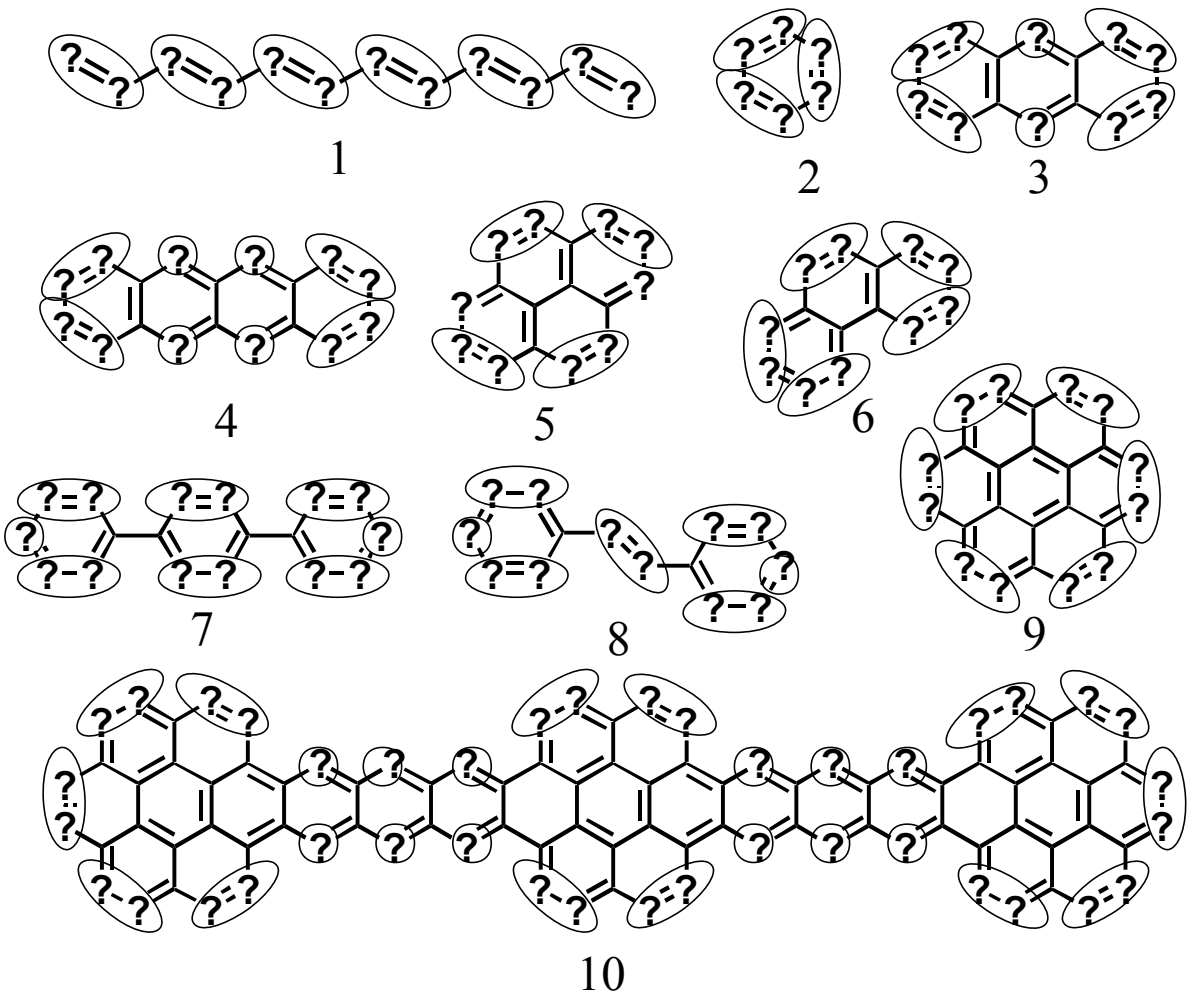
An example molecular framework:



N sites: 40
M types: 3

Exhaustive enumeration cost: $N^M=10^{19}$
TB-LCAP search cost: **$10\text{-}10^4$**

Optimizing NLO Materials



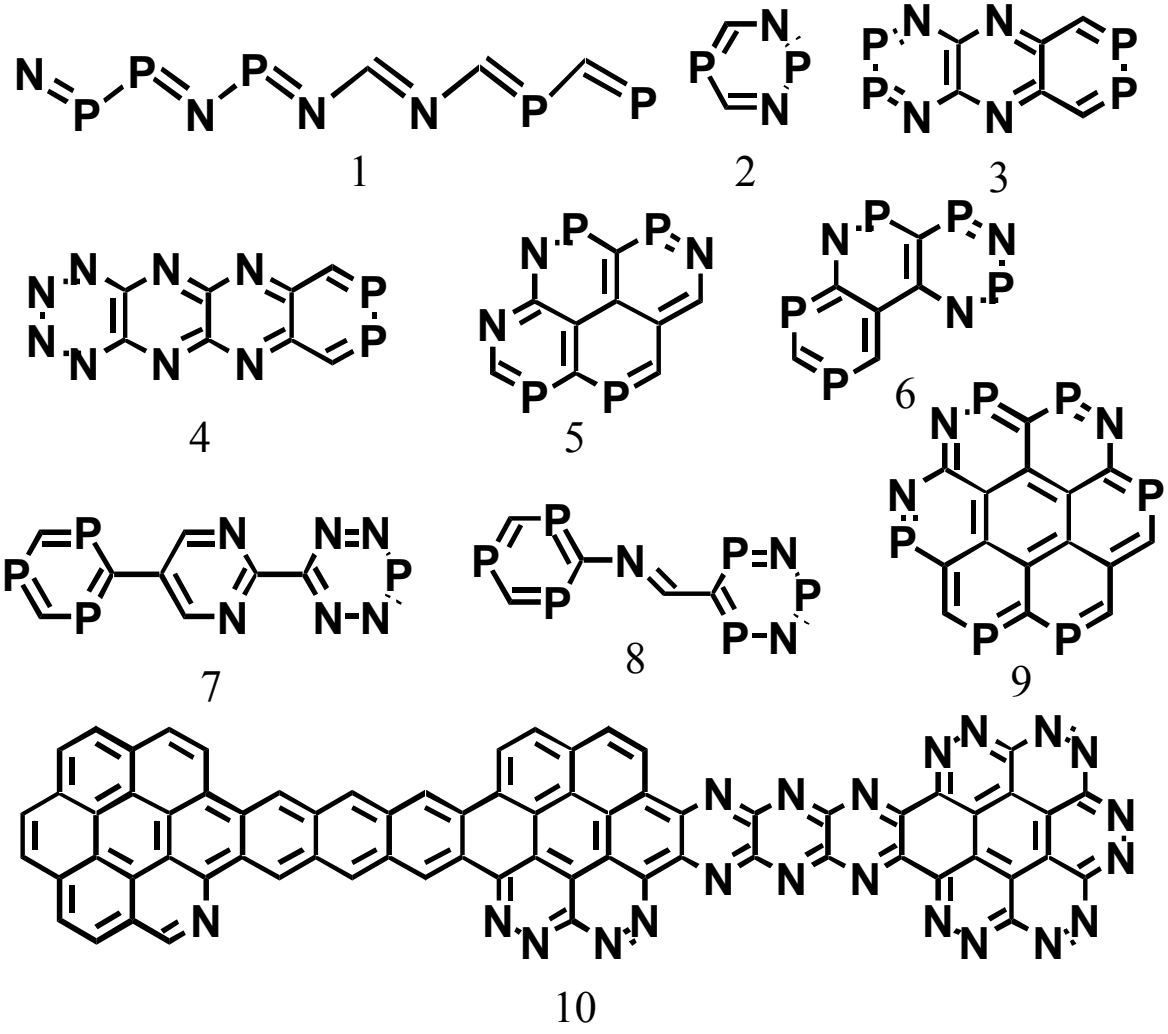
Candidate functional groups:

C, N, P,

CC, CN, NC, CP, PC, NN, NP, PN

Dequan Xiao, Weitao Yang, and David N. Beratan, *J. Chem. Phys.*, *129*(4), **2008**, 044106.

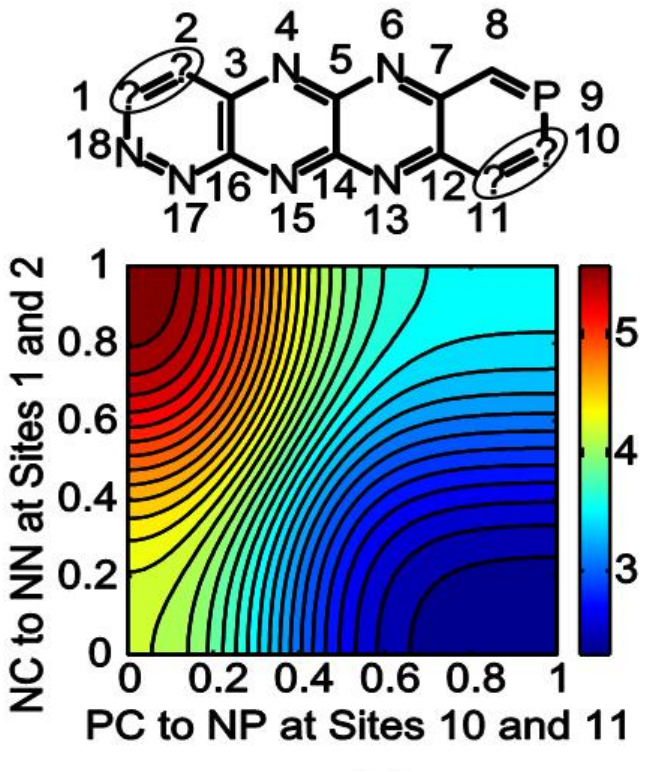
Structures with Maximum Hyperpolarizabilities



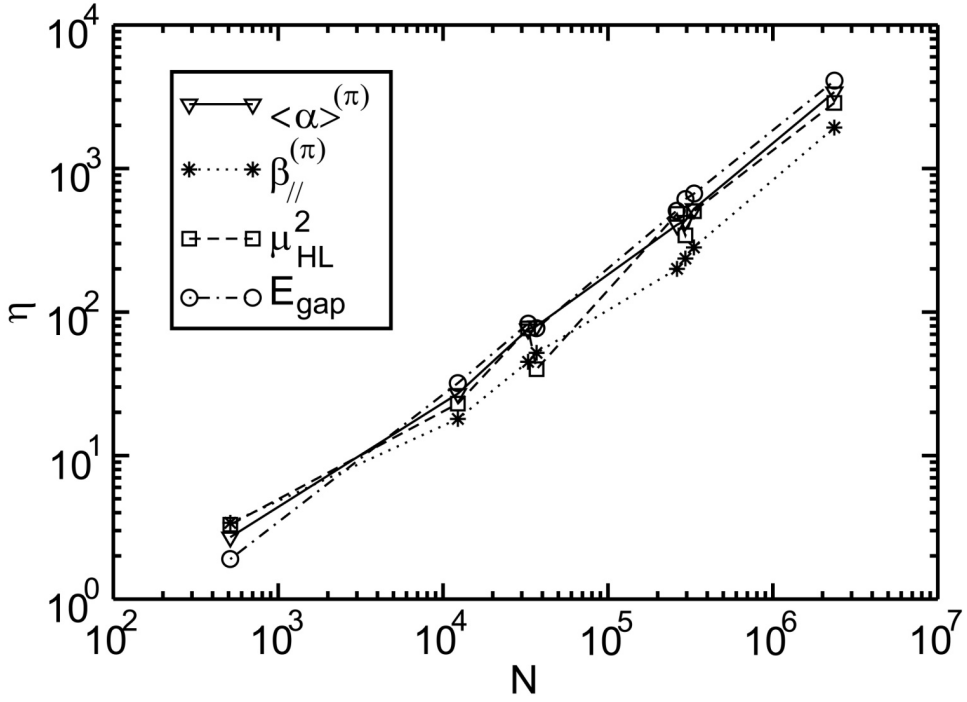
Dequan Xiao, Weitao Yang, and David N. Beratan, *J. Chem. Phys.*, *129*(4), **2008**, 044106.

TB-LCAP Hypersurface & Search Efficiency

Hypersurface



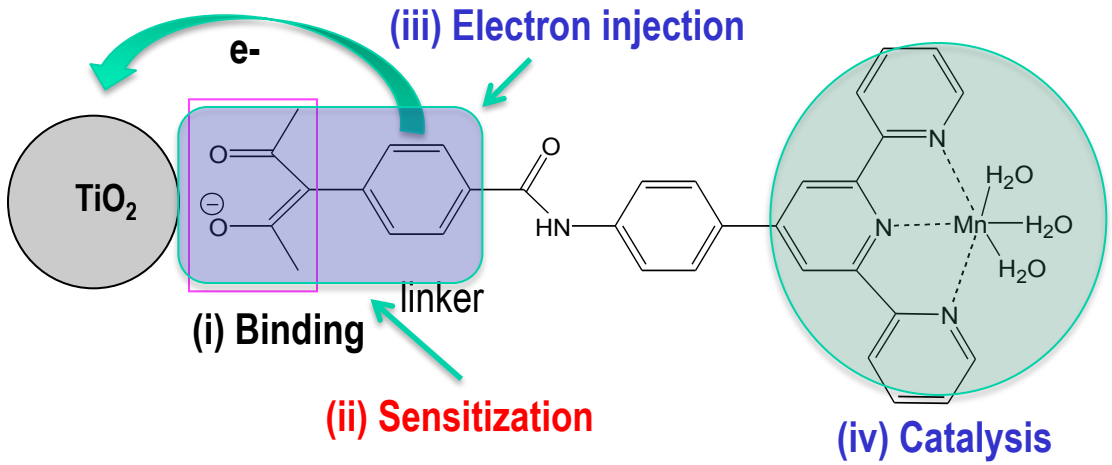
Efficiency

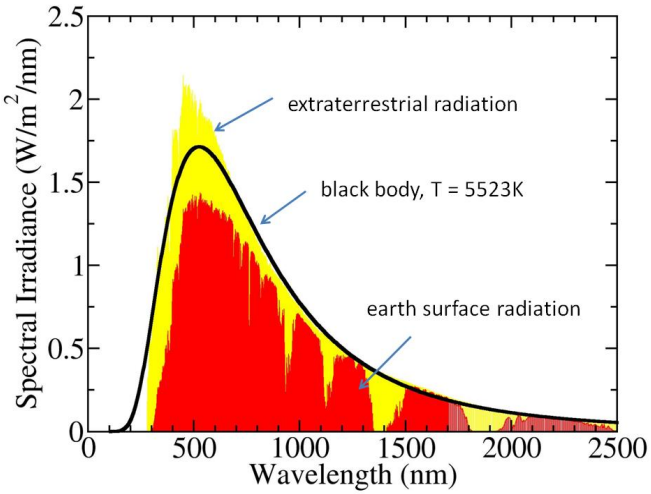


Dequan Xiao, Weitao Yang, and David N. Beratan, *J. Chem. Phys.*, *129*(4), **2008**, 044106.

Optimizing Photoabsorption

A prototype photocatalyst used by the Yale Solar Energy Group.

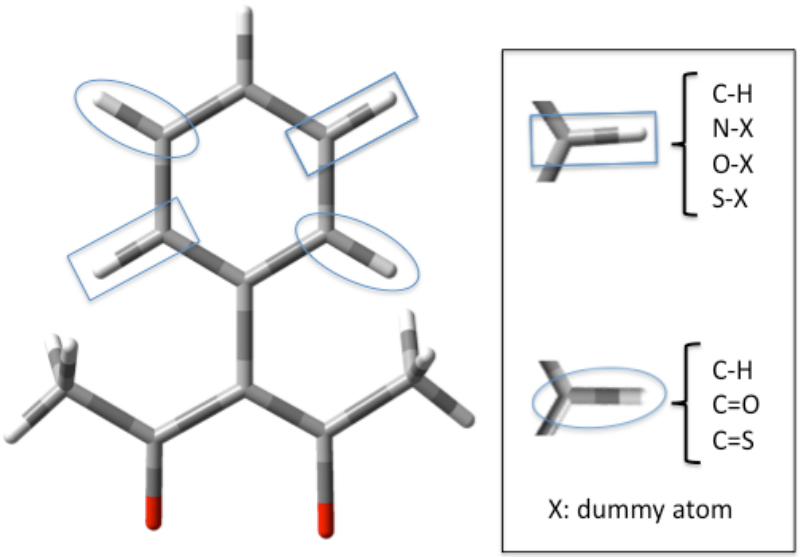




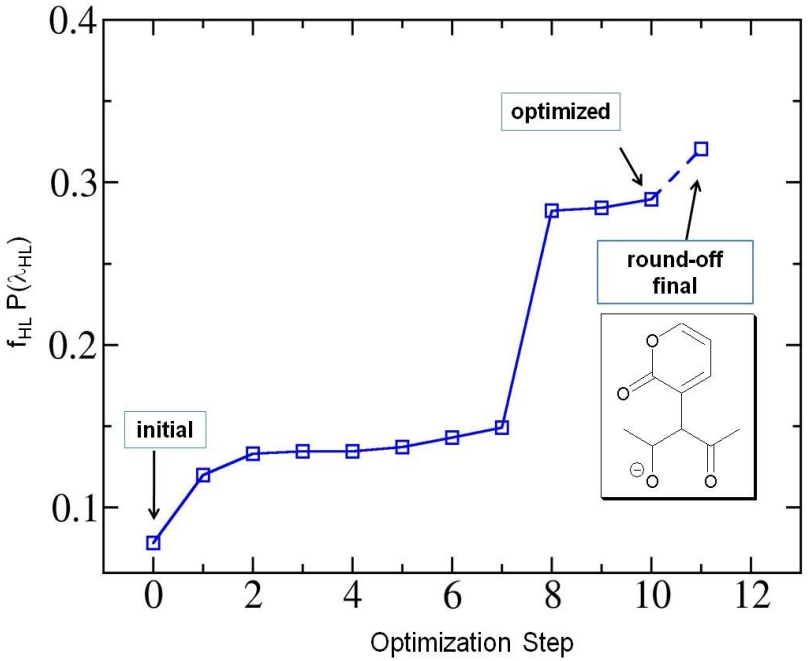
Target Molecular Property:
Photoabsorption

Search Framework

Dequan Xiao, Lauren A. Martini, Robert C. Snoeberger III, Robert H. Crabtree, and Vicotr S. Batista, *J. Am. Chem. Soc.*, *133*(23), **2011**, 9014-9022.



Molecular framework



Search path

The phenyl-acac molecular framework includes 144 possible chemical structures.

Designing Hydrogenolysis Catalysts for Biomass Conversion

A heterogeneous catalyst framework: hydrotalcite with doped metal oxides

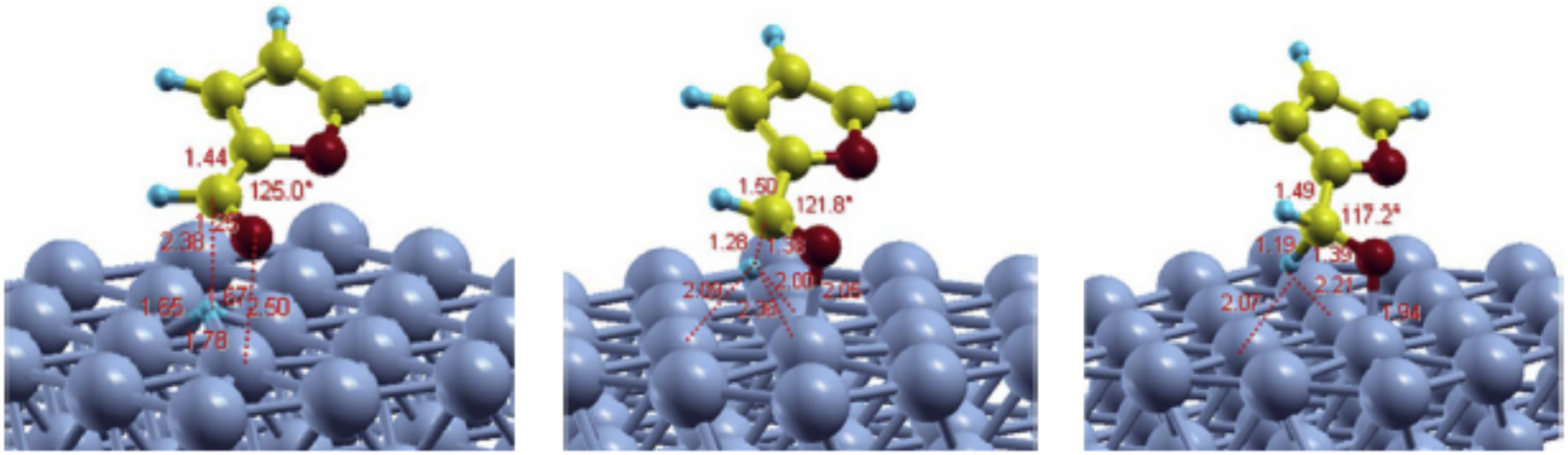
$[Mg_6Al_2(OH)_{16}CO_3.4H_2O]$
Hydrotalcite

+ Cu → Porous metallic oxides

catalyst

Katalin Barta, Theodore D. Matson, Makayla L. Fettig, Susannah L. Scott, Alexiei V. Iretskii, and Peter C. Ford, *Green Chem*. **2010**, *12*, 1640-1647.

Typical Hydrogenation Mechanism



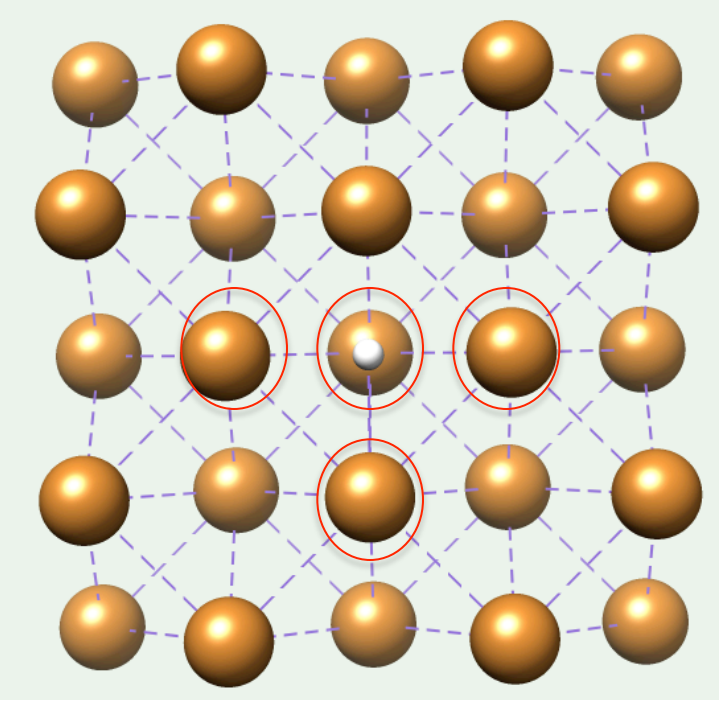
Reactant **TS** **Intermediate**

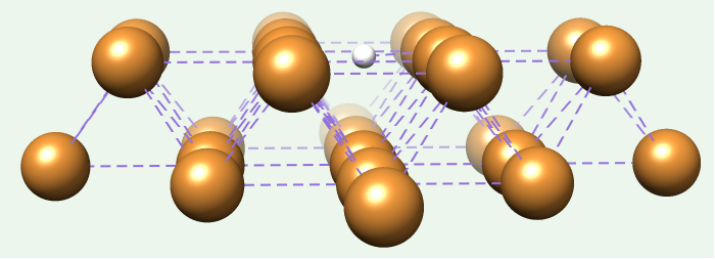
In terms of inverse molecular design, our goal is to search for a particular metal-doped Cu-surface with maximum binding energy (negative values) to H-atoms.

Surapas Sitthisa, Tawan Sooknoi, Yuguang Ma, Perla B. Balbuena, and Daniel E. Resasco, *J. Catal.*, **2011**, *277*, 1-13.

Search Framework

We choose the Cu lattice as the search framework.





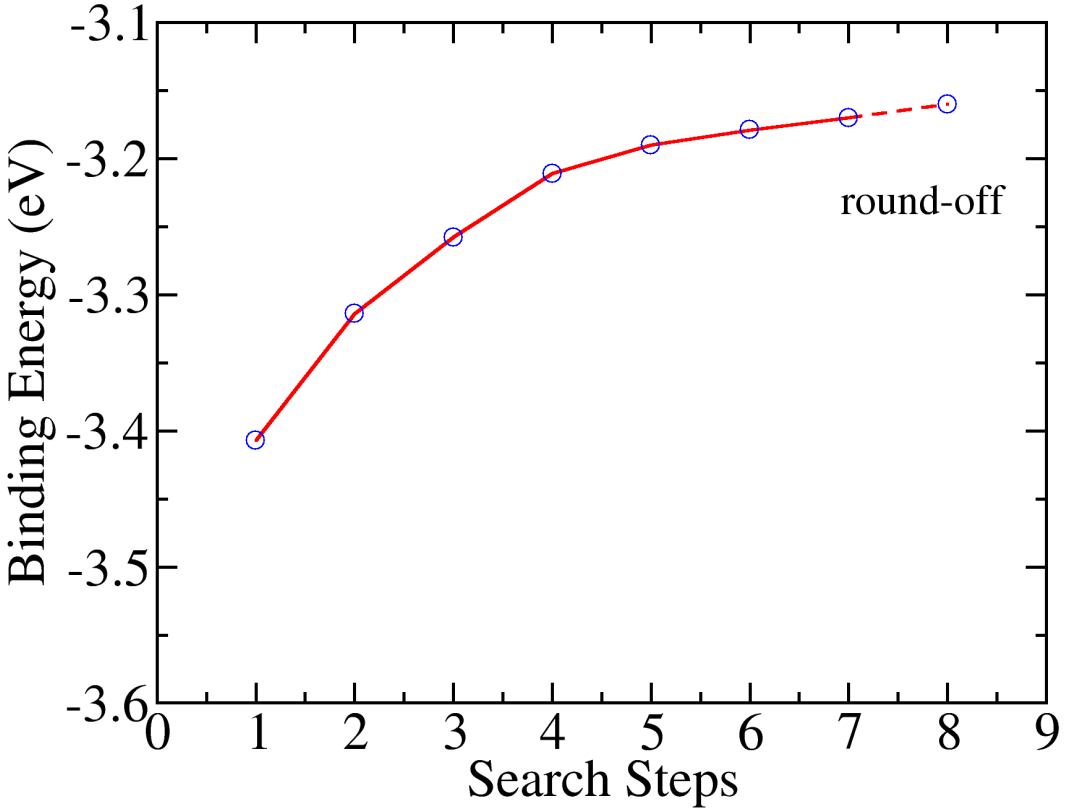
denotes flexible sites

Option 1: Cu, Ni, Co

Option 2: Cu, Ru, Pd

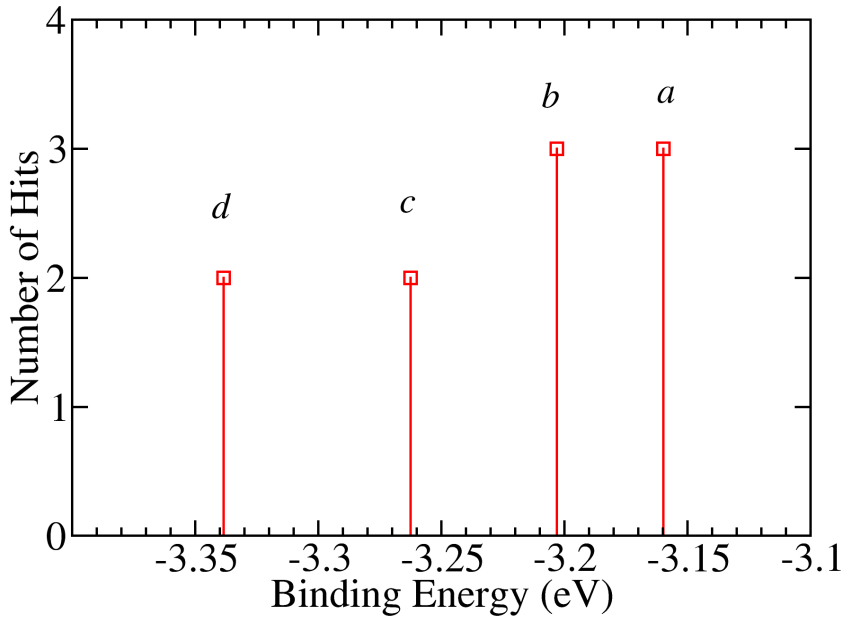
Raphael Gagne, Amanda Rindgen, and Dequan Xiao, *manuscript*, submitted.

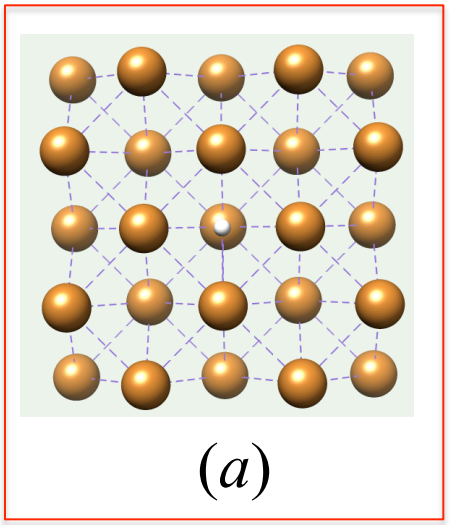
Search for Catalysts with Low Binding Affinity to H-Atoms, Option 1: Cu, Ni, and Co

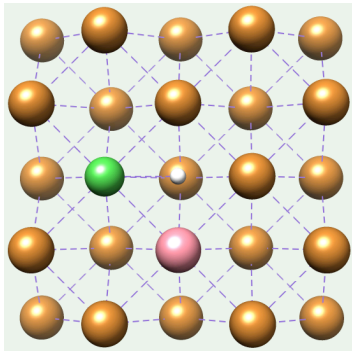


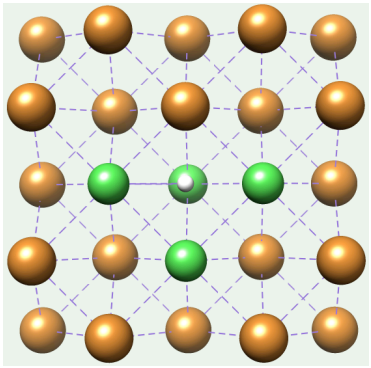
Raphael Gagne, Amanda Rindgen, and Dequan Xiao, *manuscript*, submitted.

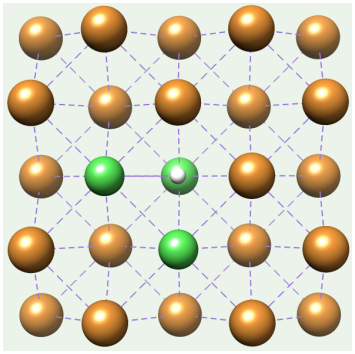
Results after 10 Searches





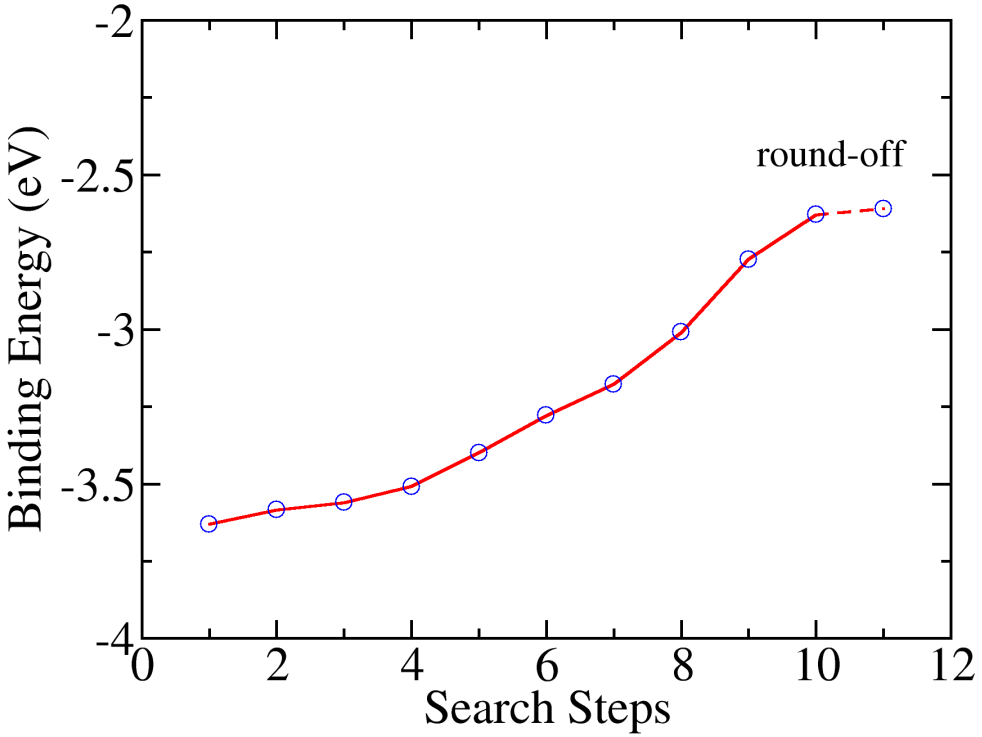


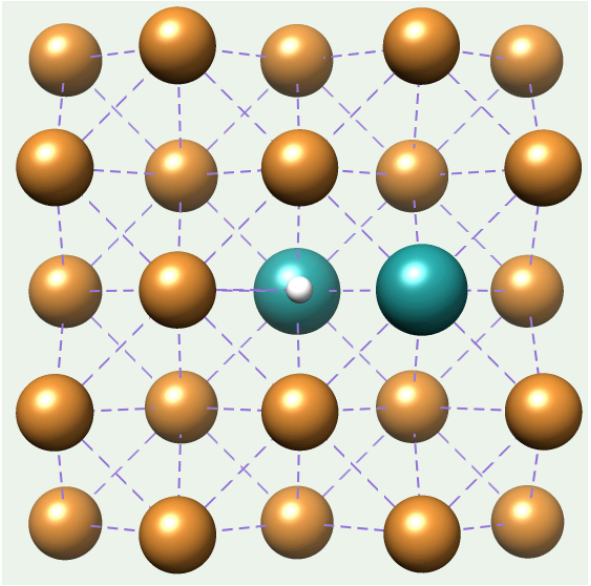




Raphael Gagne, Amanda Rindgen, and Dequan Xiao, *manuscript*, submitted.

Option 2: Cu, Ru and Pd





Ru doped Cu

Raphael Gagne, Amanda Rindgen, and Dequan Xiao, *manuscript*, submitted.

Conclusions

- The TB-LCAP inverse molecular design methods have been developed by me (with my coauthors) in the past years to successfully search for optimal nonlinear optical materials and photosensitizers. This is the first successful application of TB-LCAP for the design of biomass catalysts.
- The TB-LCAP search indicates that doping noble metals such as Ru or Pd onto Cu surfaces will favor the release of bound H-atoms on the surface, thus favors the hydrogenolysis of biomass molecules. This finding is consistent with the knowledge of hydrogenation catalysts in the literature.
- The TB-LCAP search also indicates that doping non-noble metals Ni or Co could not improve the efficiency of the hydrogenolysis of biomass molecules. However, other non-noble metals can be introduced to improve the catalytic efficiency.

Acknowledgement

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