Design of materials for storing hydrogen in quasi-molecular form

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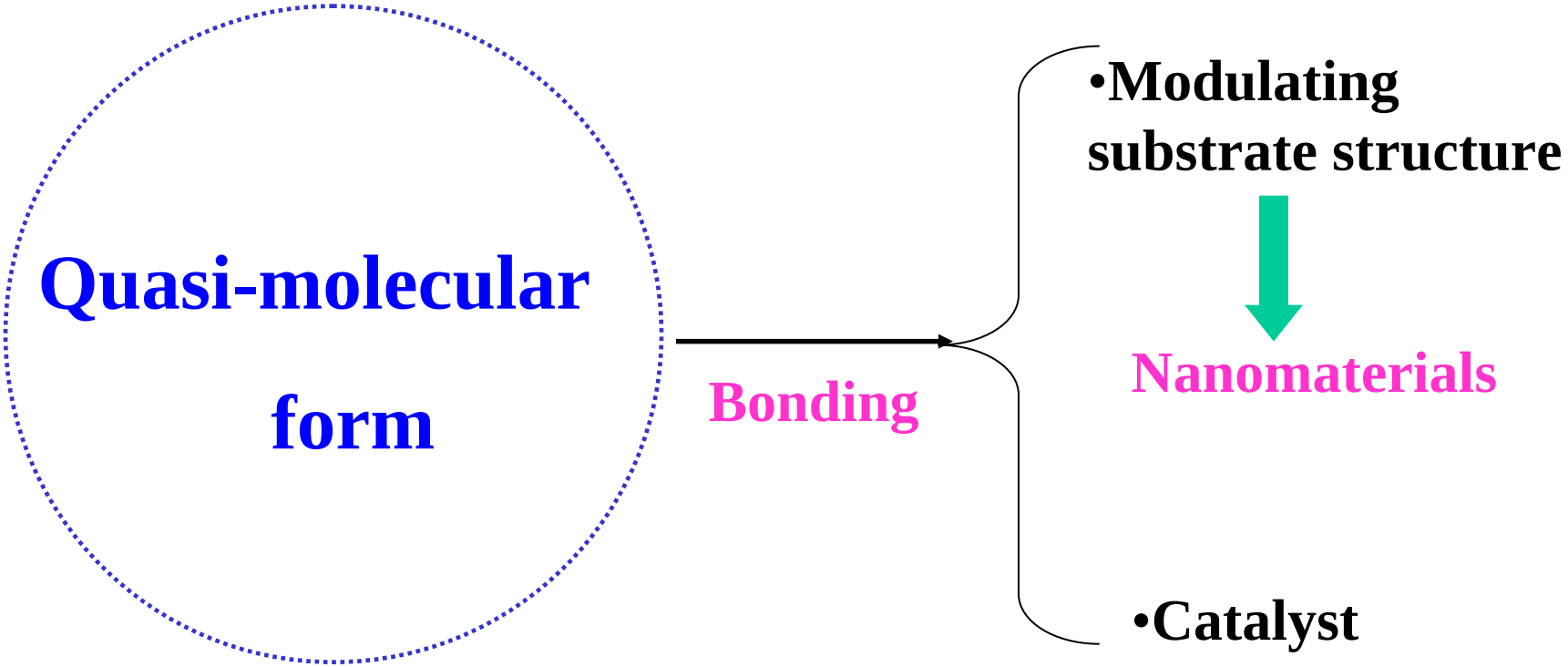
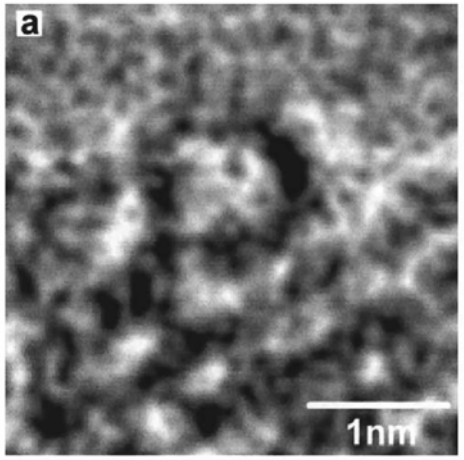
- **Atomic form** (covalent or ionic)

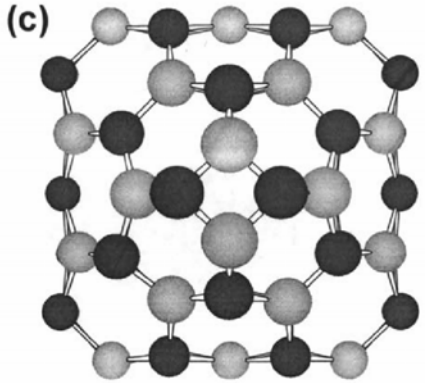


- **Molecular form** (van der Walls)

The most studied systems

1. **B-N nano structures**
2. **Carbon nano structures**
3. **Nano porous structures (MOFs)**

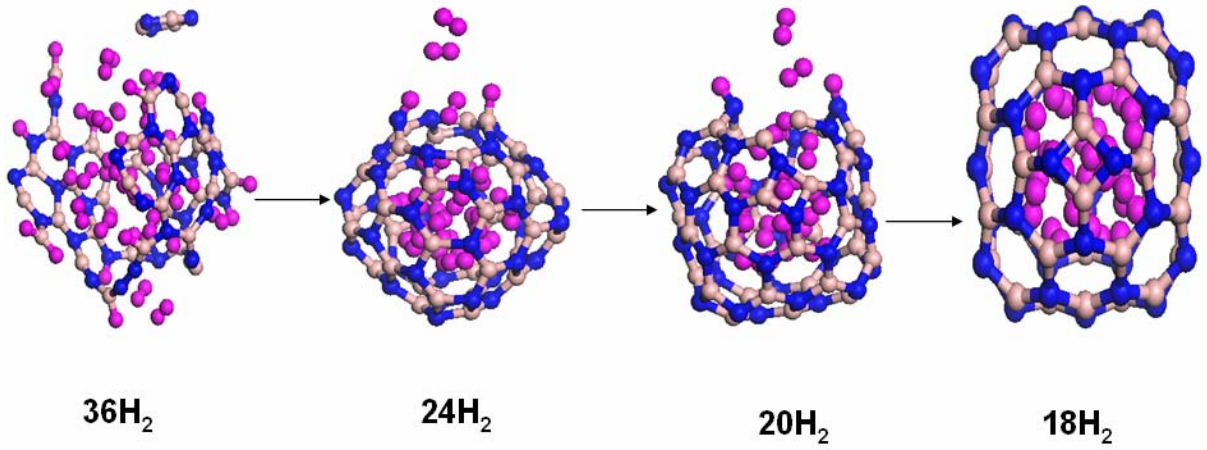




Experimental synthesis of $B_{36}N_{36}$ cage

How many H_2 can be inserted inside the cage ?

T=0K



4% wt

T=300K

thermal stability?

$18H_2@B36N36$ —0.4 ps.→ **$4H_2$ escaped out of the cage**

$13H_2@B36N36$ —1.3 ps.→ **$3H_2$ escaped out of the cage**

Storage of Molecular Hydrogen in B–N Cage: Energetics and Thermal Stability

Qiang Sun,* Qian Wang, and Puru Jena

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2005
Vol. 5, No. 7
1273–1277

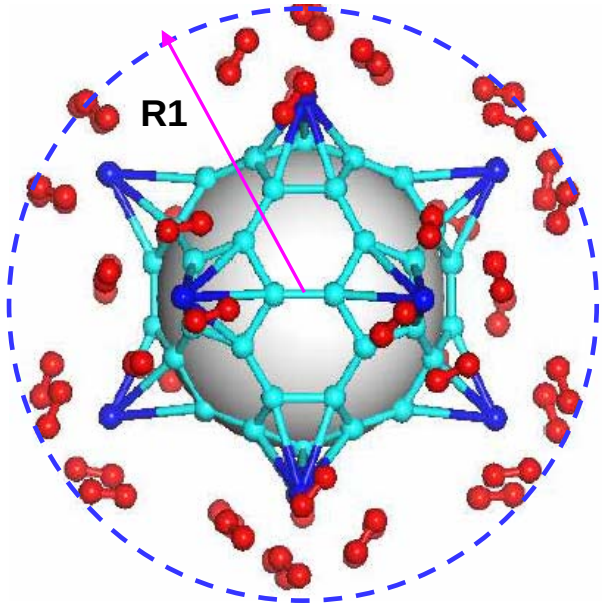
The problems for nano carbon

Nano carbon –H_2 interation too weak

Transition metal doping is needed for improving the absorption-→ **strong d-d interations**
→ **clustering problem**

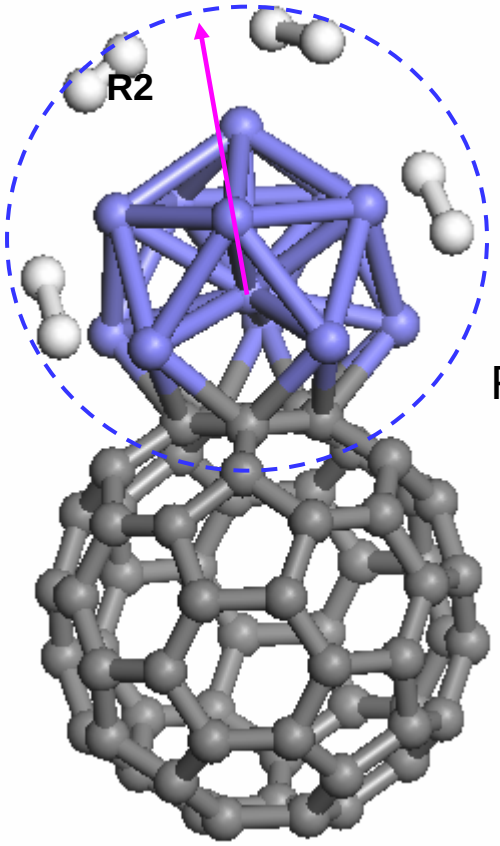
e.g. Ti12C60

Li12C60



R1=6.7

$S1 = 4 \pi R_1^2$



R2=4.8

$S2 = 4 \pi R_2^2 \times 3/4$

$$\frac{S2}{S1} = \frac{3}{4}(R2/R1)^2 = 38\%$$

H2 storage = 38% x8% = 3 wt %

J|A|C|S COMMUNICATIONS

Published on Web 10/04/2005

Clustering of Ti on a C_{60} Surface and Its Effect on Hydrogen Storage

Qiang Sun,† Qian Wang,† Puru Jena,*,† and Yoshiyuki Kawazoe‡

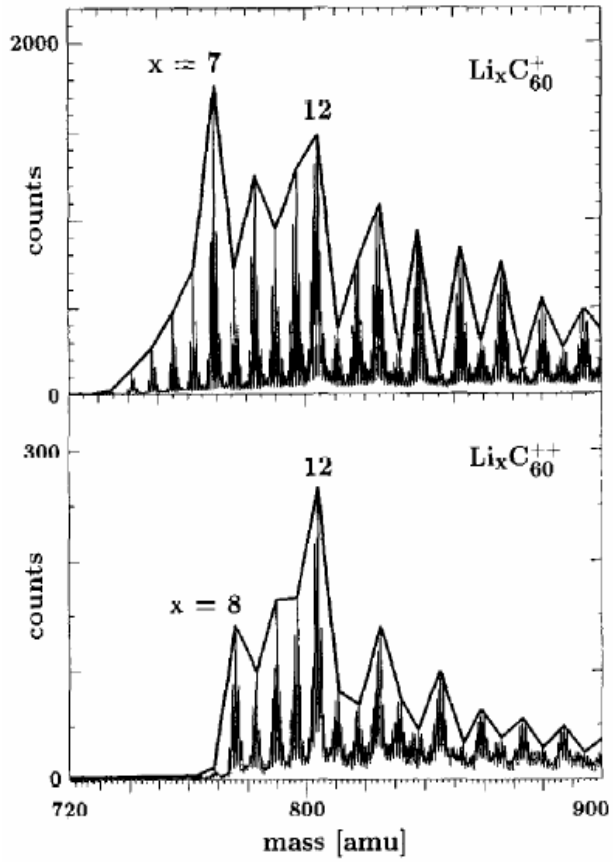
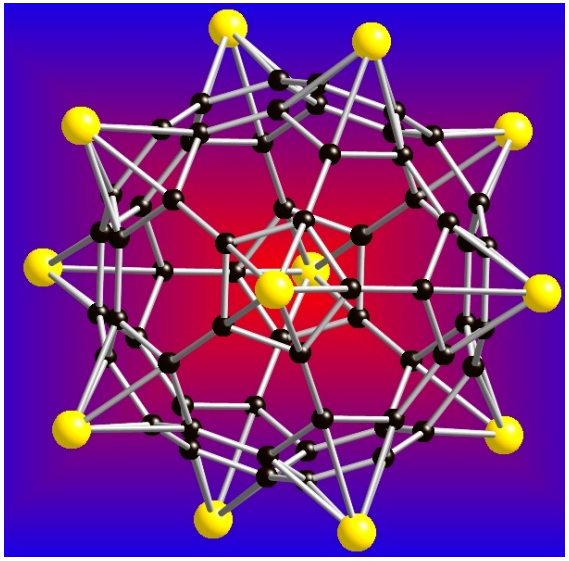
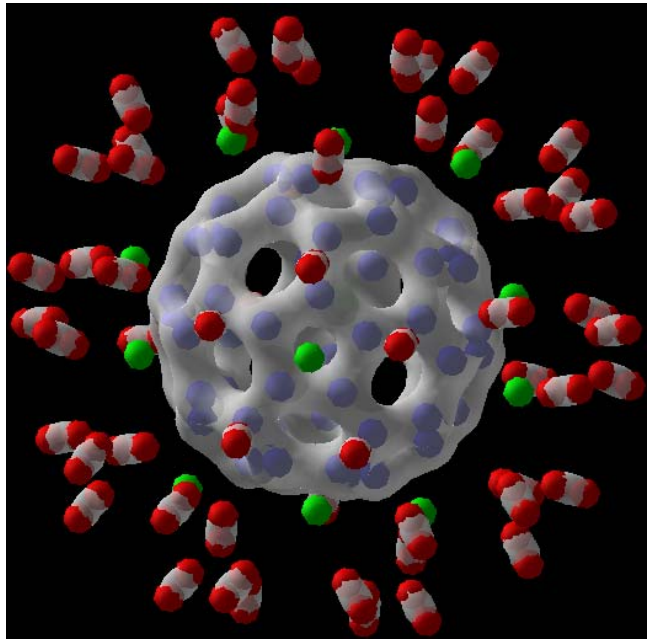


Fig. 9. Mass spectra of singly (top) and doubly (bottom) ionized $C_{60}Li_x$ clusters: note the prominent features at $x = 7$ for singly ionized and $x = 8$ for doubly ionized clusters and at $x = 12$ in both spectra.



$Li_{12}C_{60}$



$60H_2$-$Li_{12}C_{60}$

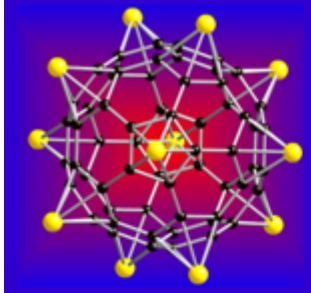
Weight percent: 15%

Interaction energy: 4.50eV → 0.075eV/H2

J|A|C|S
ARTICLES
Published on Web 07/06/2006

First-Principles Study of Hydrogen Storage on $Li_{12}C_{60}$

Qiang Sun,*,†,‡ Puru Jena,‡ Qian Wang,‡ and Manuel Marquez§



INTERNATIONAL SYMPOSIUM ON MATERIALS ISSUES IN A HYDROGEN ECONOMY

November 12-15, 2007 Richmond, Virginia, USA

SCOPE

This Symposium will address fundamental materials issues concerning the production, storage, and use of hydrogen, as well as those of safety, education, and economics. It will bring together researchers from Physics, Chemistry, Materials Science, Engineering, and Economics to share their ideas and results, to delineate outstanding problems, and to guide future research. There will be no parallel sessions so that the participants can take part in the discussion of every issue central to the hydrogen economy. In addition to the invited speakers, the oral sessions will include selected hot topics to be chosen from contributed abstracts. Participants can also present their research in two poster sessions.

TOPICS

Production - Thermo-chemical, photoelectro-chemical, nuclear, biomass, and photo-biological

Storage - Liquid, compressed gas and solid state (complex light metal hydrides, zeolites, clathrates, metal-organic frameworks, carbon and boron-nitride based nanostructures, and chemical hydrides)

Fuel cells - Polymer electrolyte and hydro-carbon membranes

Cross-cutting – Catalysis and nanostructures

Education, Safety and Economics

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http://www.has.vcu.edu/phy/ishe

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Key Question:

Can we find a system

- **Avoid clustering of transition metal atoms**
- **Keep the binding in Kubas type**

Hydrogen storage using silsesquioxanes (SQ)

$$[RSiO_{3/2}]_n$$

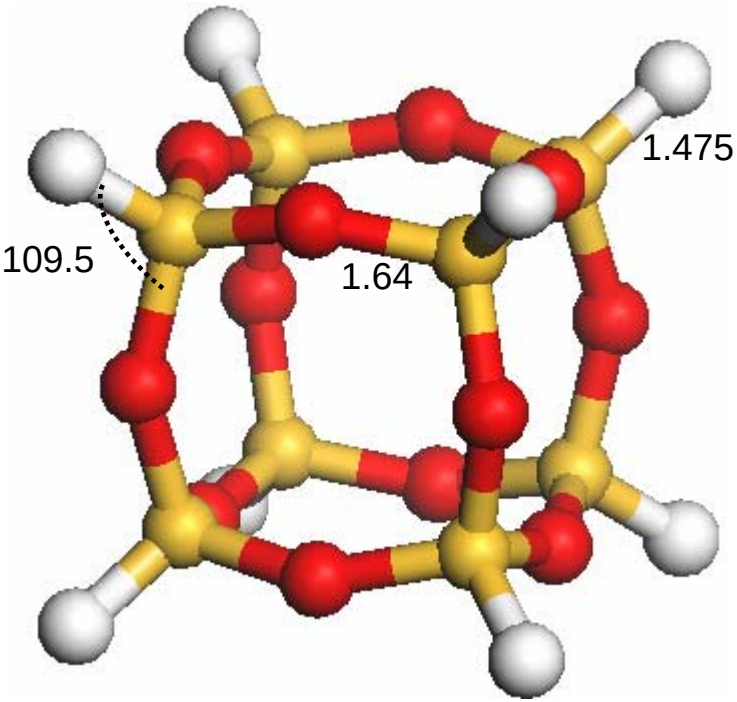
functional group

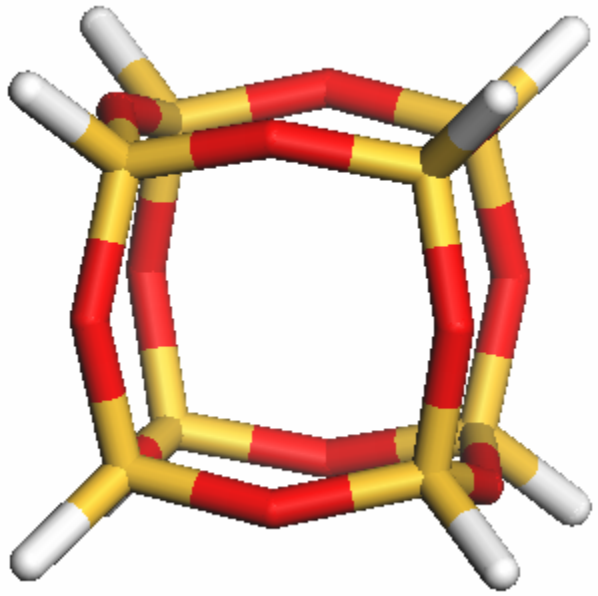
Chem. Mater. **2007,** *19,* 3074—3078

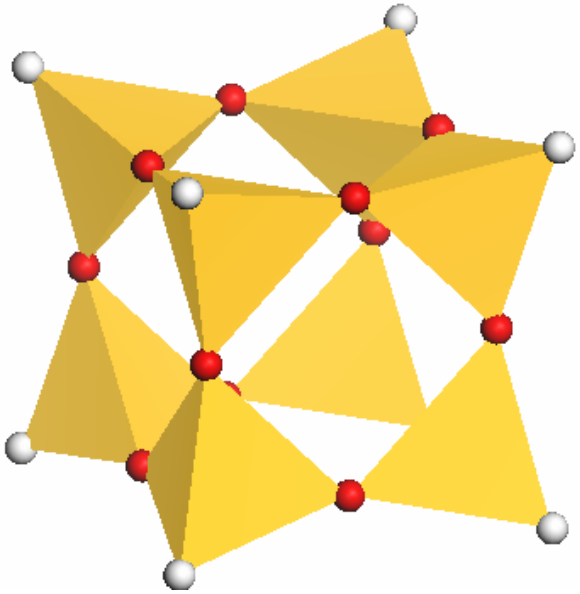
Hydrogen Storage in Organometallic Structures Grafted on Silsesquioxanes

Qiang Sun,*,†,‡,§ Qian Wang,‡ Puru Jena,‡ B. V. Reddy,|| and Manuel Marquez||

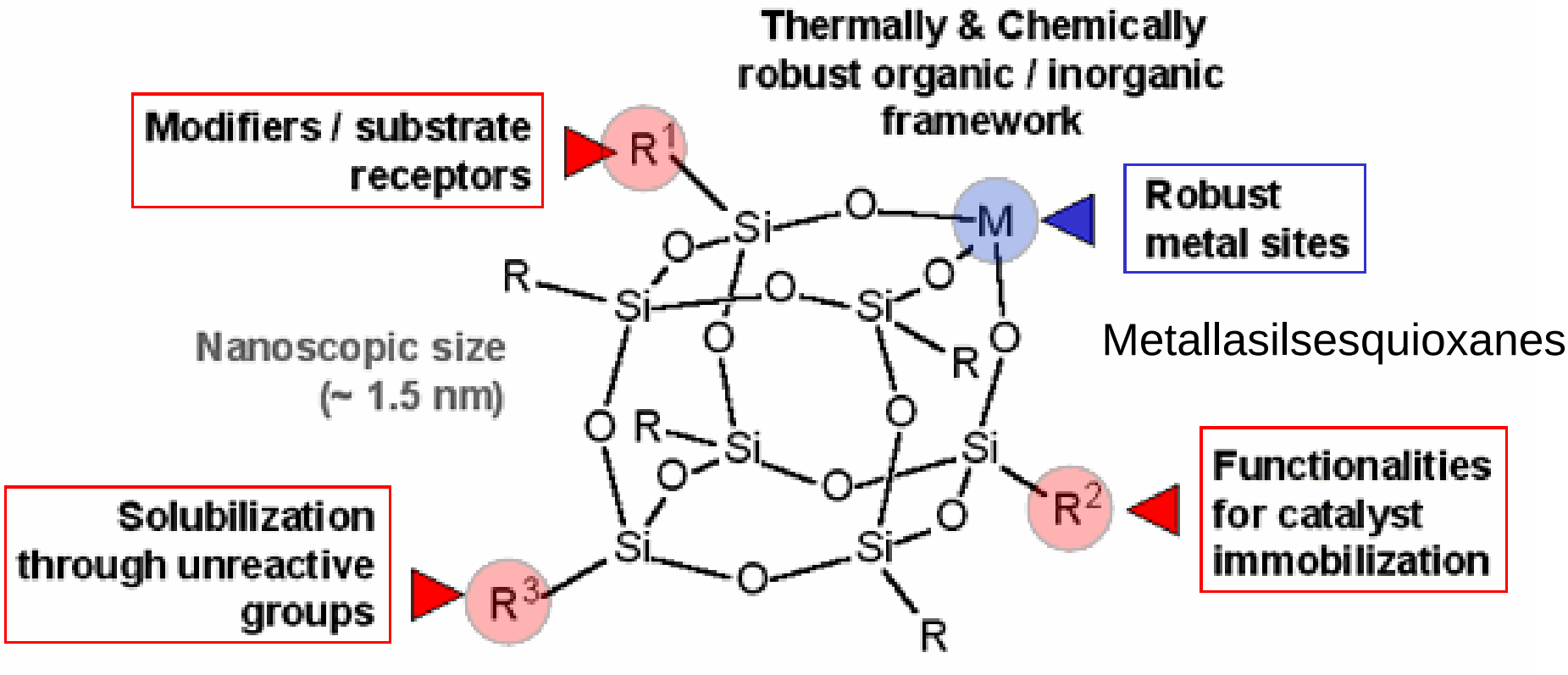
$H_8Si_8O_{12}$





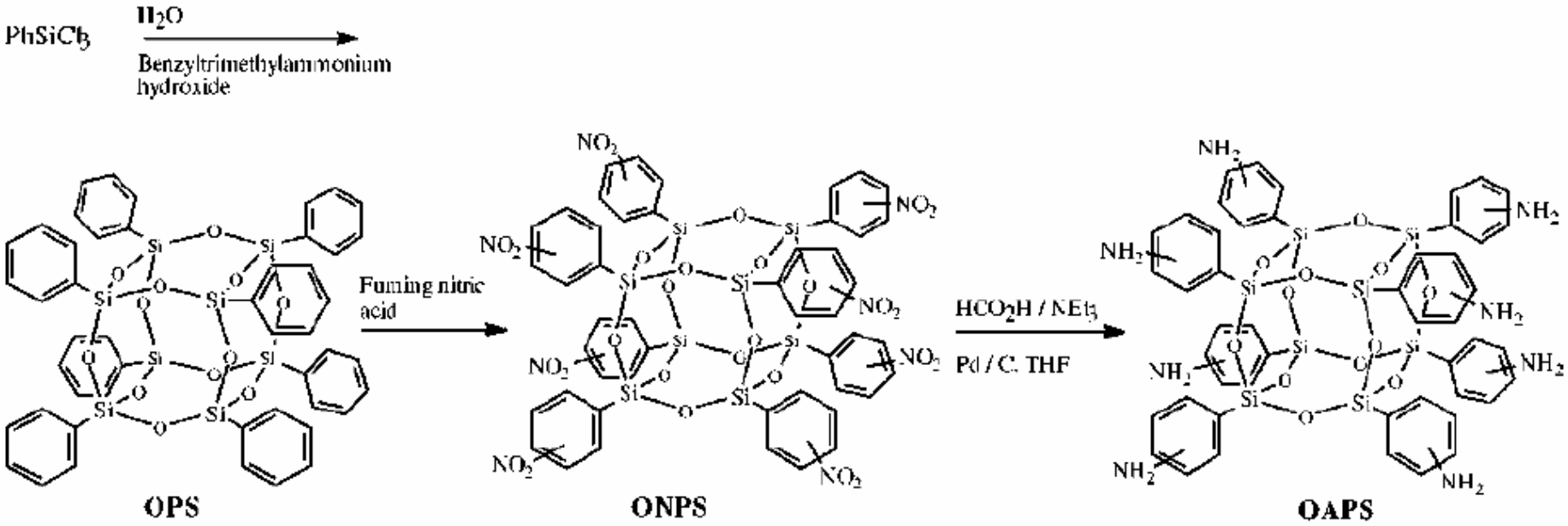


O_h symmetry

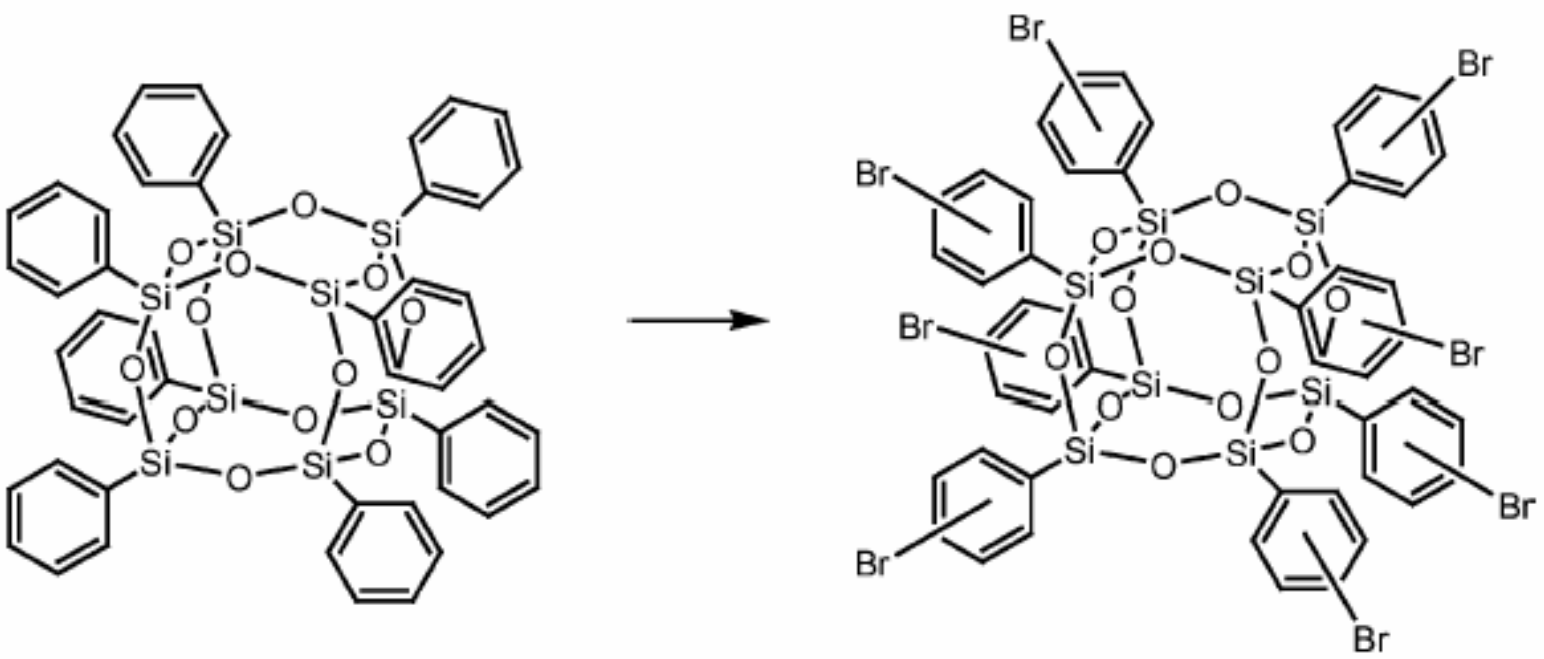


Since their discovery and isolation in 1946, many stoichiometrically well-defined POSS™ frameworks have been reported with synthetically useful functional groups.

Scheme 1



J. Am. Chem. Soc. **2001,** *123,* 12416−12417



Scheme 1. Schematic synthesis of a brominated octaphenylsilsesquioxane.

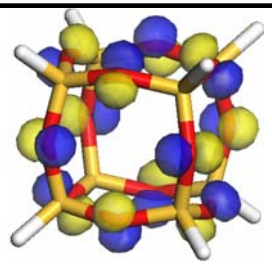
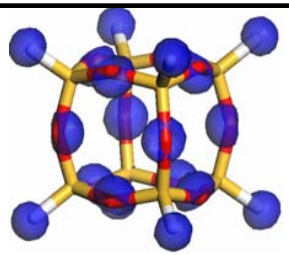
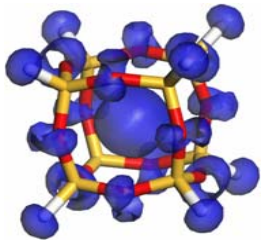
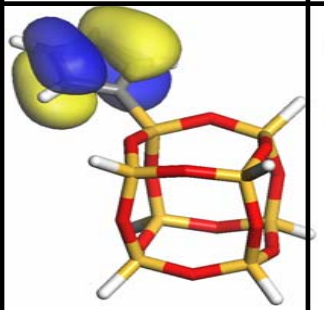
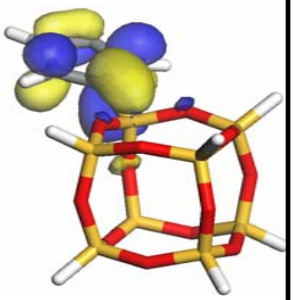
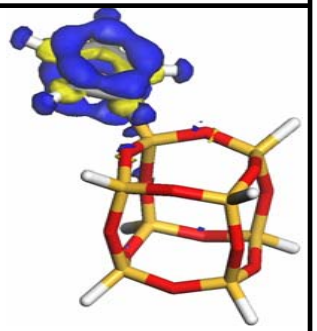
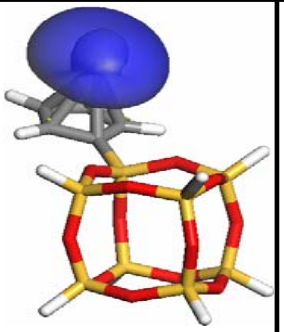
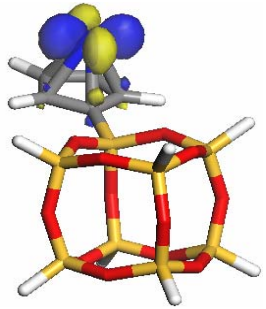
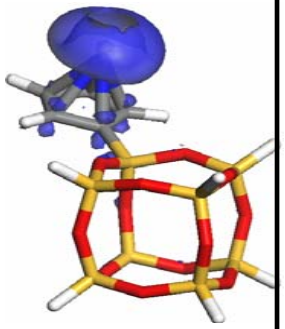
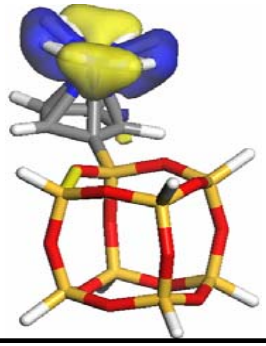
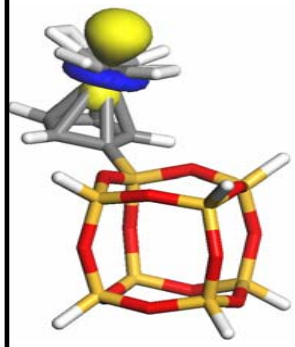
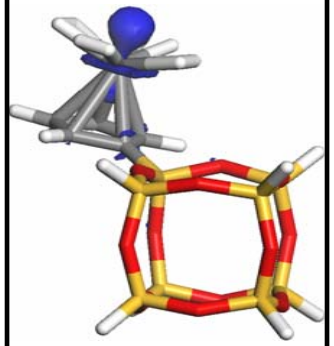
Silicon Chemistry **3:** 43–49, 2006.
DOI: 10.1007/s11201-005-9000-5

Bromination of octaphenylsilsesquioxane

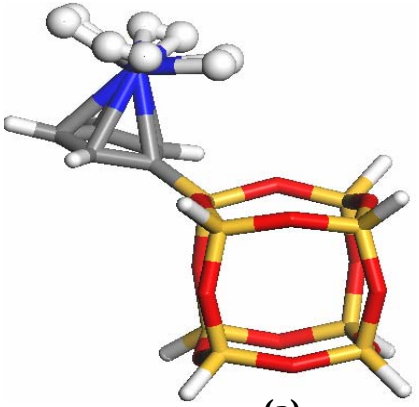
Christoph Erben*, Hans Grade & Gregory D. Goddard
GE Global Research Center, One Research Circle, Niskayuna, NY 12309, USA

Hydrogen storage in SQ

-- electronic structure analysis

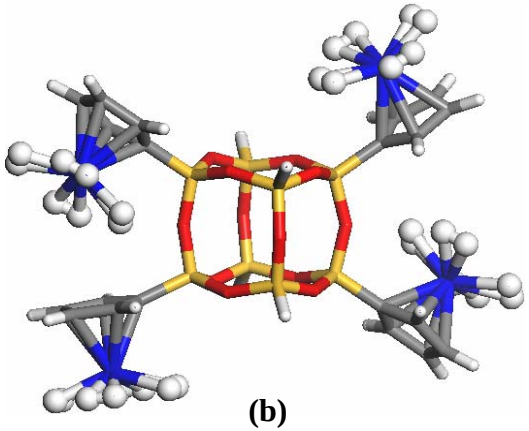
	HOMO	LUMO	Fukui
$H_8Si_{12}O_8$			
C_5H_4- $H_7Si_{12}O_8$			
ScC_5H_4- $H_7Si_{12}O_8$			
$4H_2$- ScC_5H_4- $H_7Si_{12}O_8$			

Assembling Cp-M units by grafting on SQ for hydrogen storage



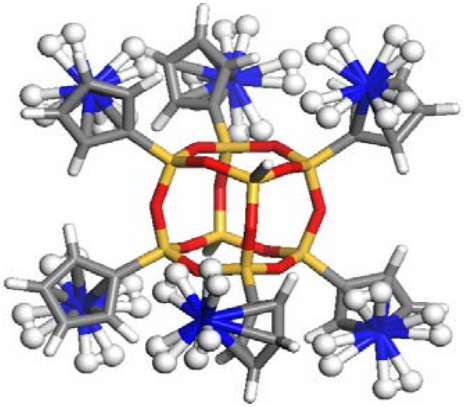
(a)

wt = 1.50%
E =0.68 eV/H_2
r1 = 0.848 Å
r2 =1.995Å



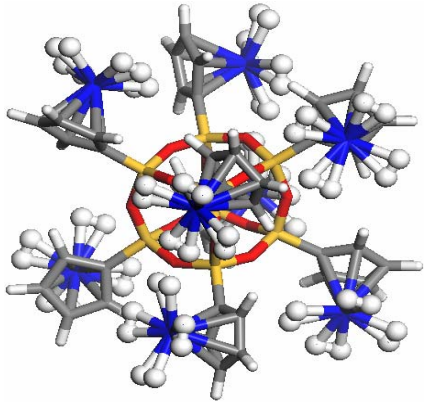
(b)

wt = 3.70%
E =0.67 eV/H_2
r1 = 0.850 Å
r2 =1.996Å



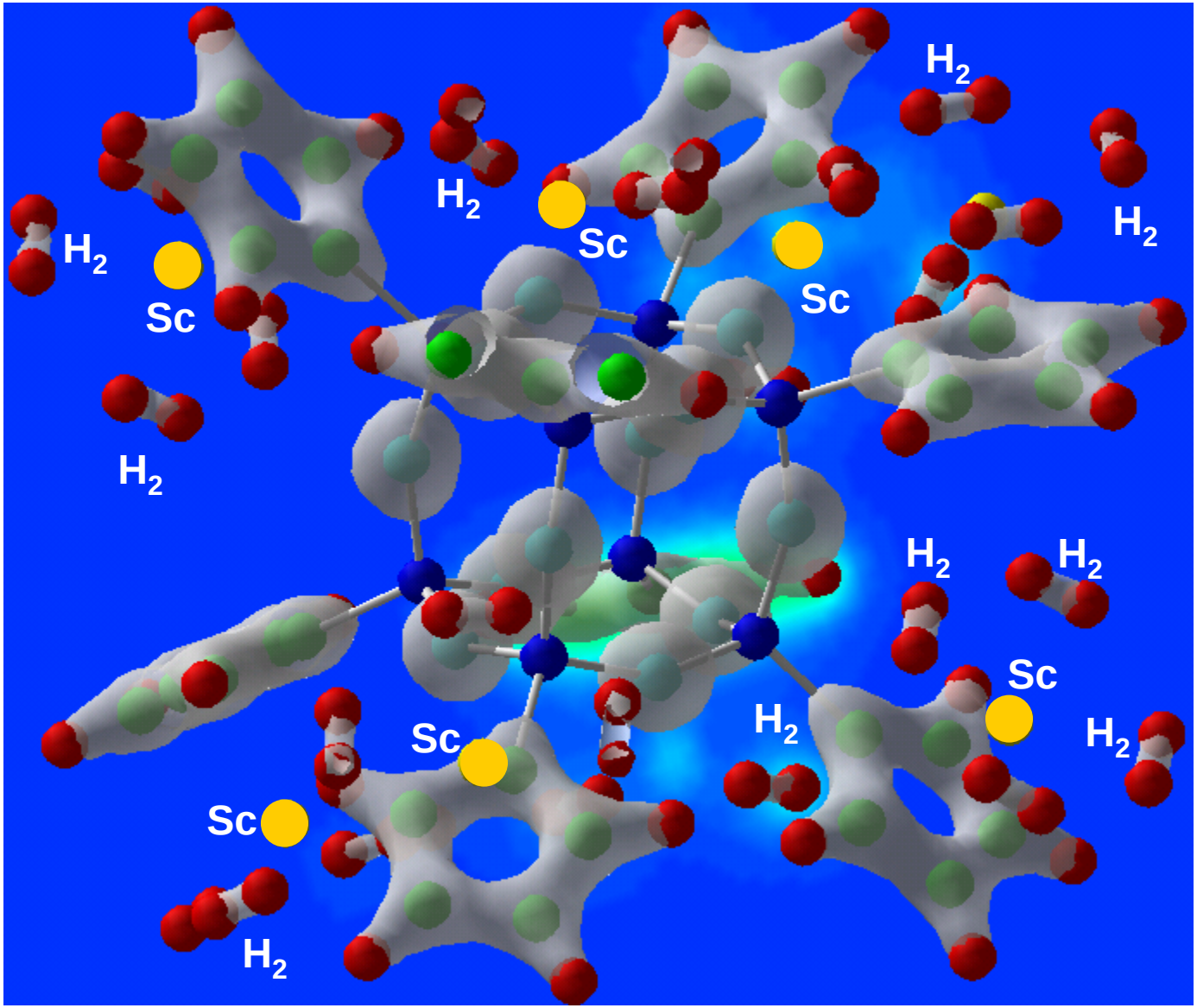
(c)

wt = 4.50%
E =0.66 eV/H_2
r1 = 0.851 Å
r2 =1.998 Å



(d)

wt = 5.0%
E =0.64 eV/H_2
r1 = 0.850 Å
r2 =2.001 Å



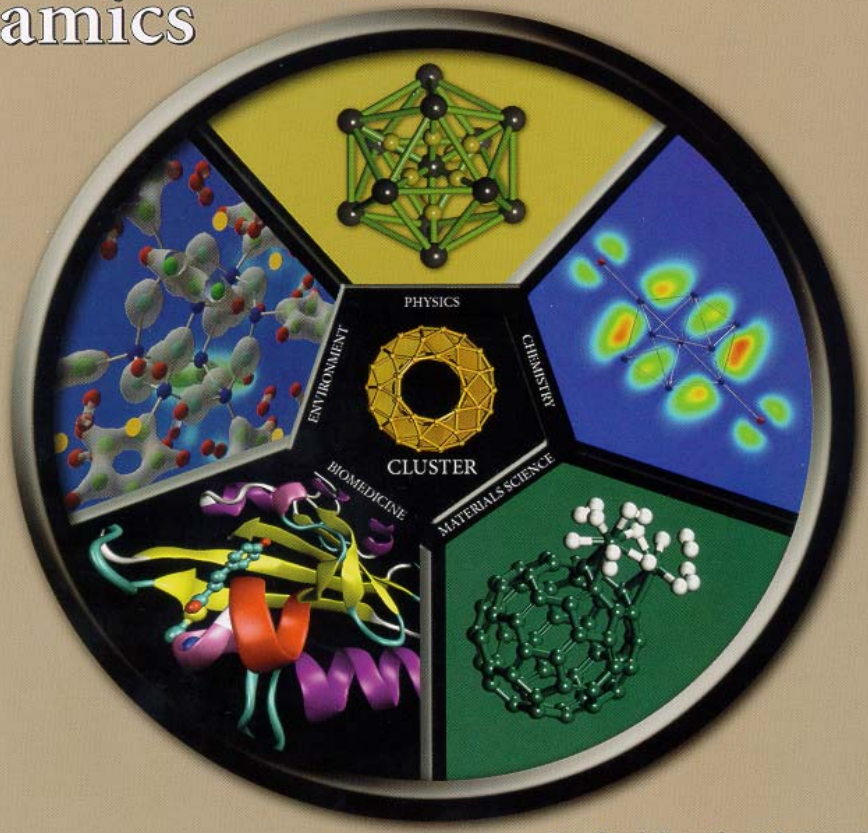
Charge density isosurface

July 11, 2006 | vol. 103 | no. 28 | pp. 10529–10824

PNAS

Proceedings of the National Academy of Sciences of the United States of America www.pnas.org

Multidisciplinary cluster dynamics



Synthesizing phosphatase inhibitors

Fraternal birth order and sexual orientation

Lipid trafficking in chloroplasts

Cluster Chemistry and Dynamics Special Feature

Summary

1. **Pure BN system is not good for H storage**
2. **Transition metal atoms prefer to clustering**
3. **Li coating can avoid clustering, but the absorption is weak**
4. **Grafting metal complex on SQ is very promising**

- It is easy to manipulate and synthesize
- The Kubas interaction can be kept (the absorption energy ~ 0.62 eV/ H_2)
- The weight percentage is 5 %

References:

Q. Sun, Q. Wang, P. Jena, *Nano Letters* 5 (2005) 1273

Q. Sun , Q. Wang, P. Jena, *et al.*, *J. Am. Chem. Soc.* 127 (2005) 14582

Q. Sun, P. Jena, Q. Wang, *et al.*, *J. Am. Chem. Soc*. 128 (2006) 9742

Q. Sun, Q. Wang, P. Jena, *et al.*, *Chem. Mater*. 19 (2007) 3074

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- Tohoku University, Japan