

Water Clusters with Superatom Electronic States

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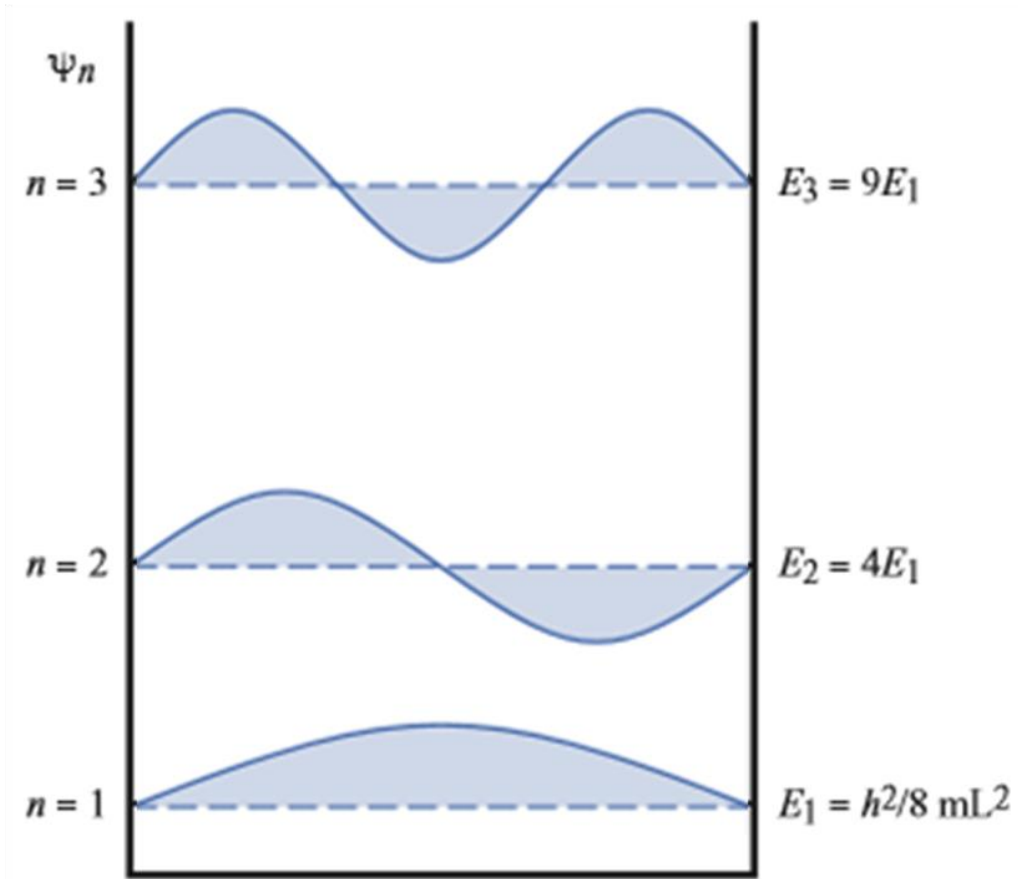
Outline

- Introduction
 - Atomic and Molecular Orbitals
 - Superatom Molecular Orbitals
 - Buckminsterfullerene C60
- Superatom Water Clusters
- Applications
 - Antimicrobial Nanostructured Water Clusters
- Synthesis of Nanostructured Water Clusters
- Acknowledgements

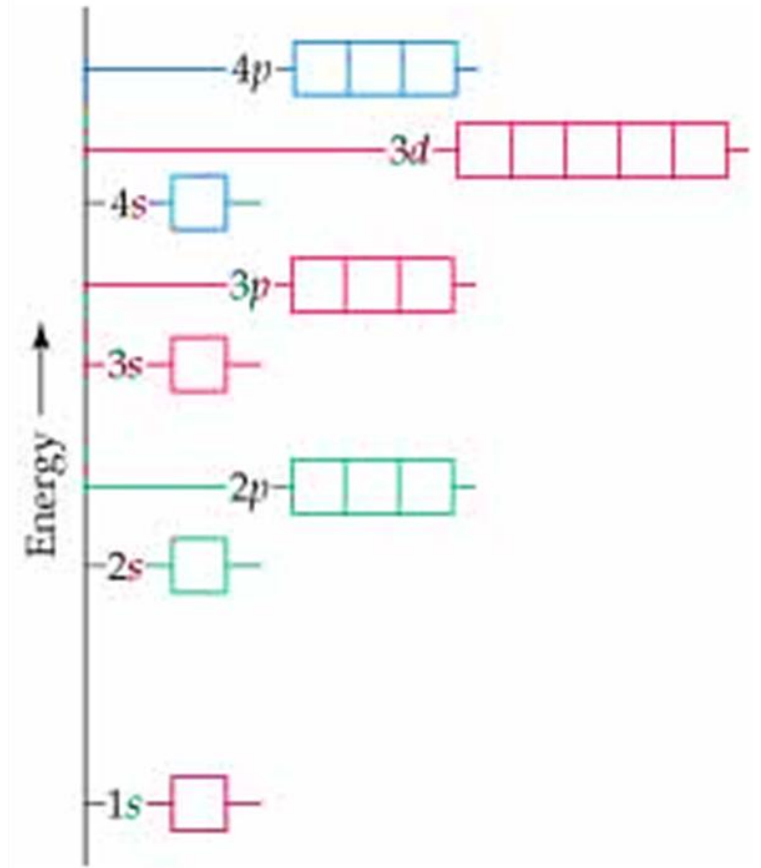
Atomic Orbitals

The Schrodinger Equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)$$

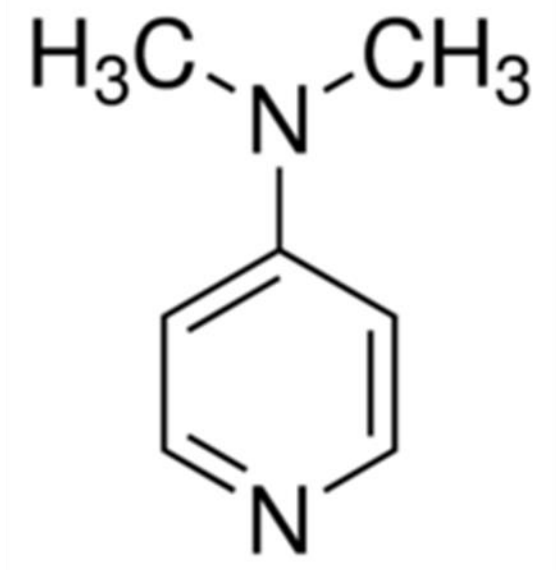


Particle in a Box

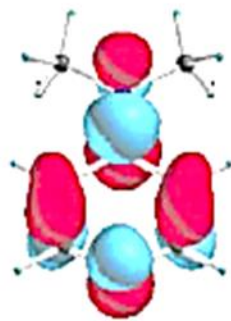


Hydrogen Atom

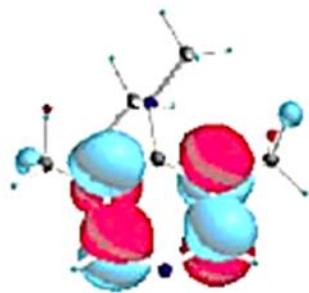
Molecular Orbitals



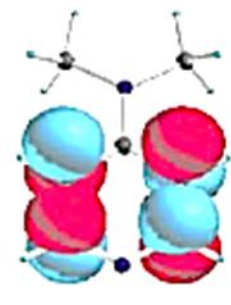
LUMO+1: π^*



LUMO+1: π^*



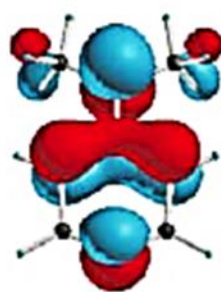
LUMO: π^*



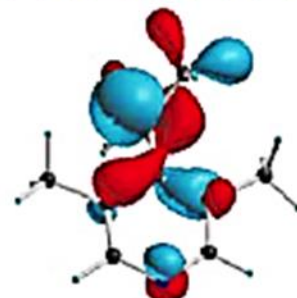
LUMO: π^*



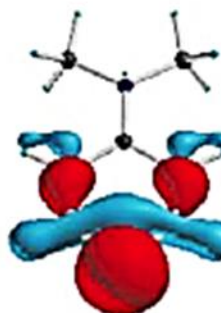
HOMO: π



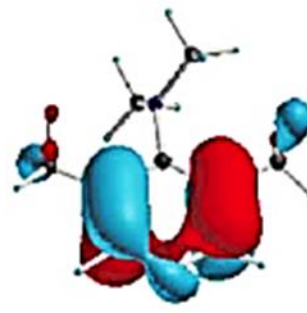
HOMO: π



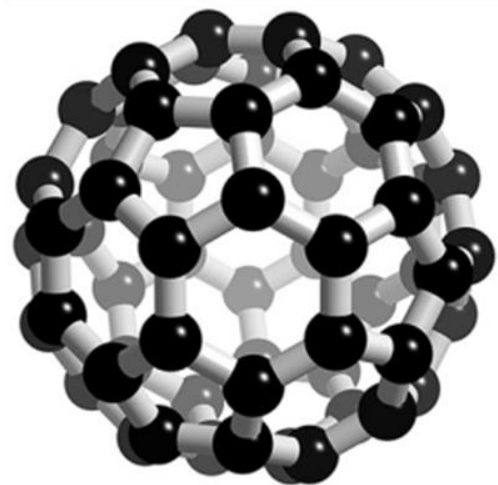
HOMO-1: n_{N}



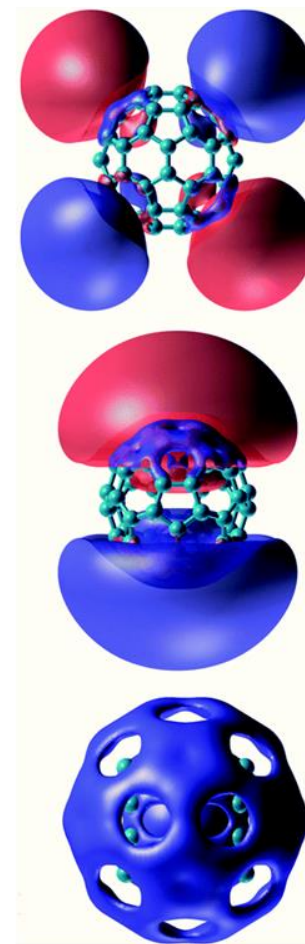
HOMO-1: π



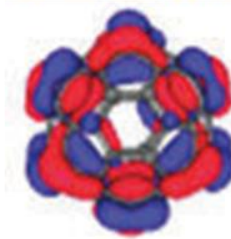
Superatom Molecular Orbitals



Buckminsterfullerene C₆₀



Lowest Unoccupied
Molecular Orbital
(LUMO)

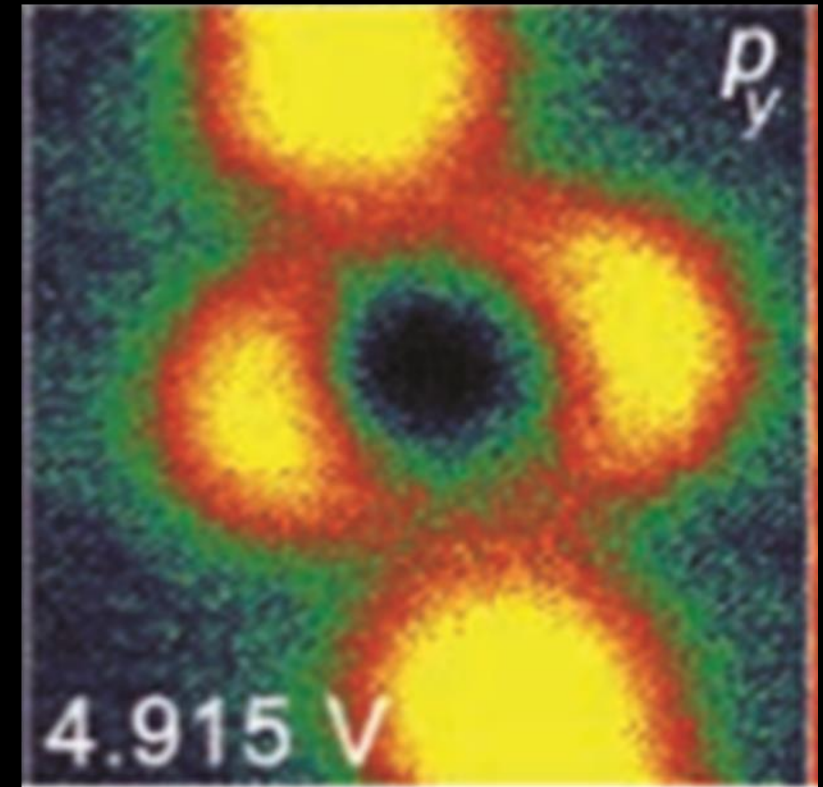
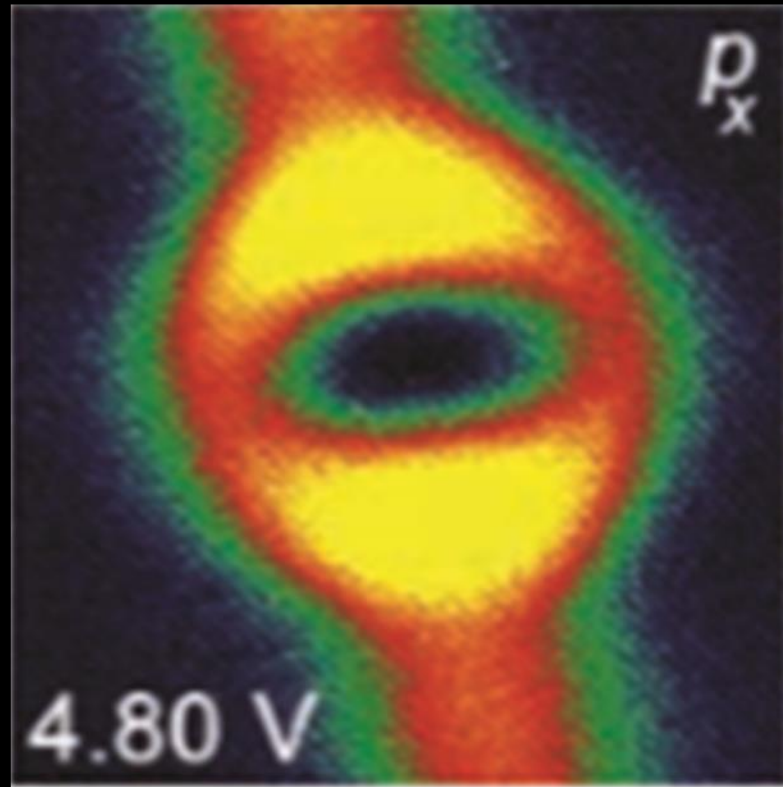
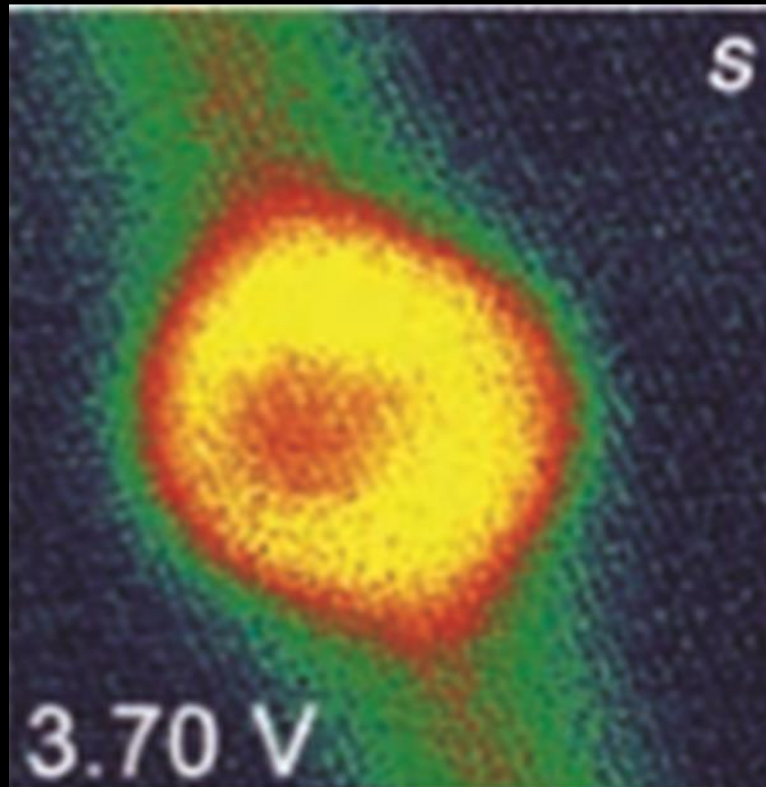


Highest Occupied
Molecular Orbital
(HOMO)

Feng, M. et al. *Science*, **2008**, 320, 359.

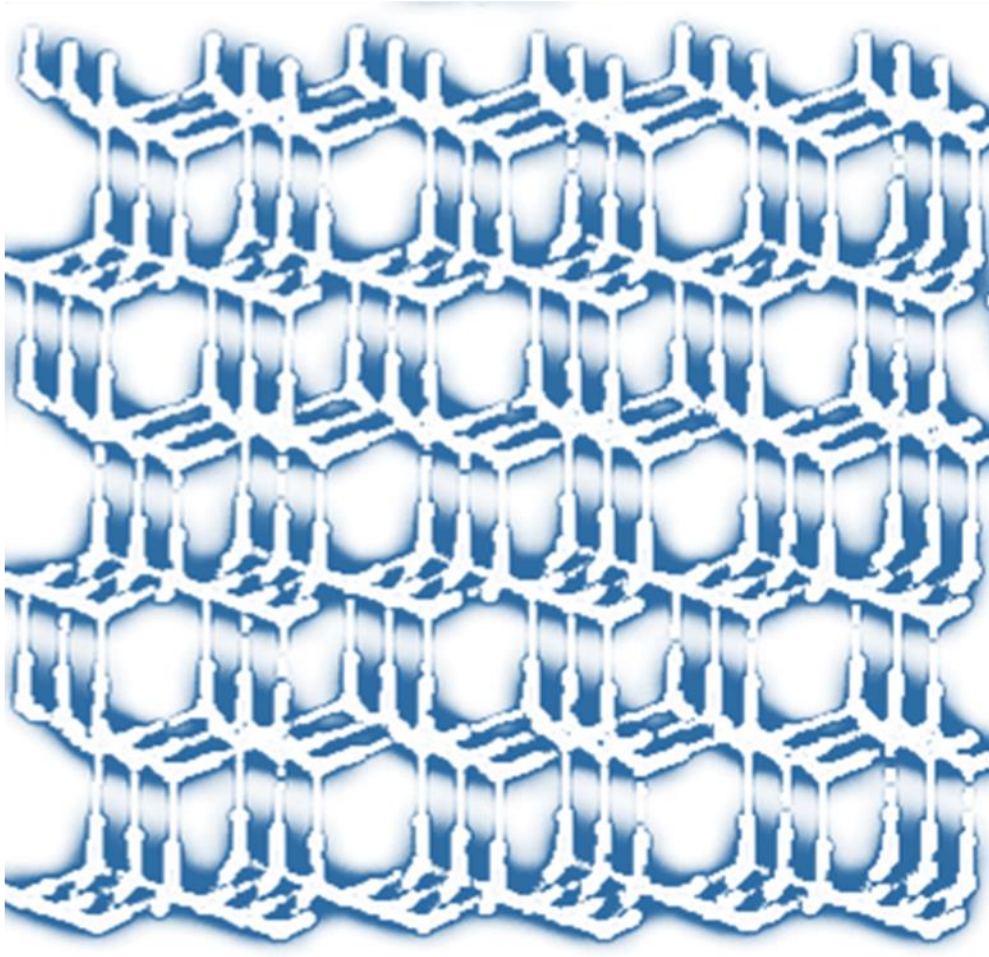
Prof. Hrvoje Petek (U. of Pittsburgh)

Low Temperature STM on C60

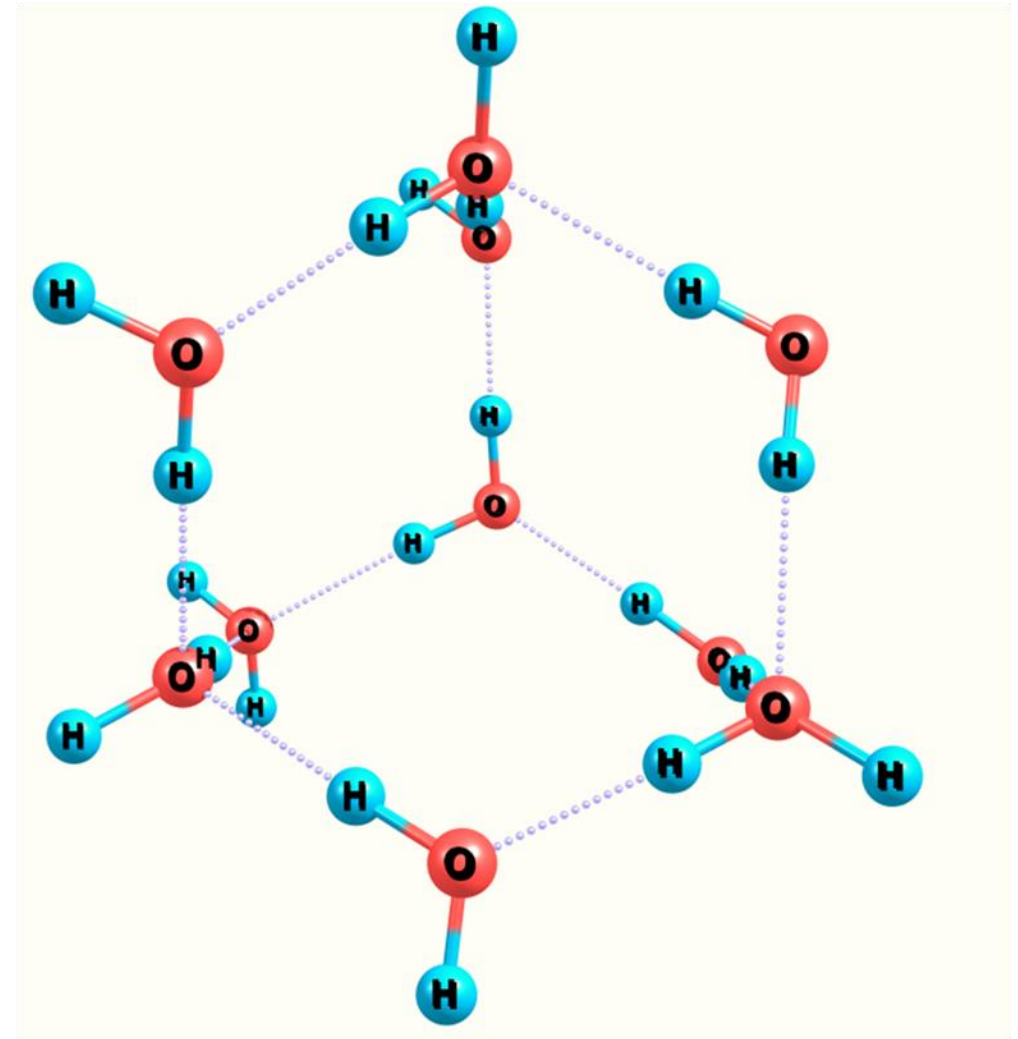


Superatom Electronic State in Nanostructured Water

Ic – type Hexagonal ice



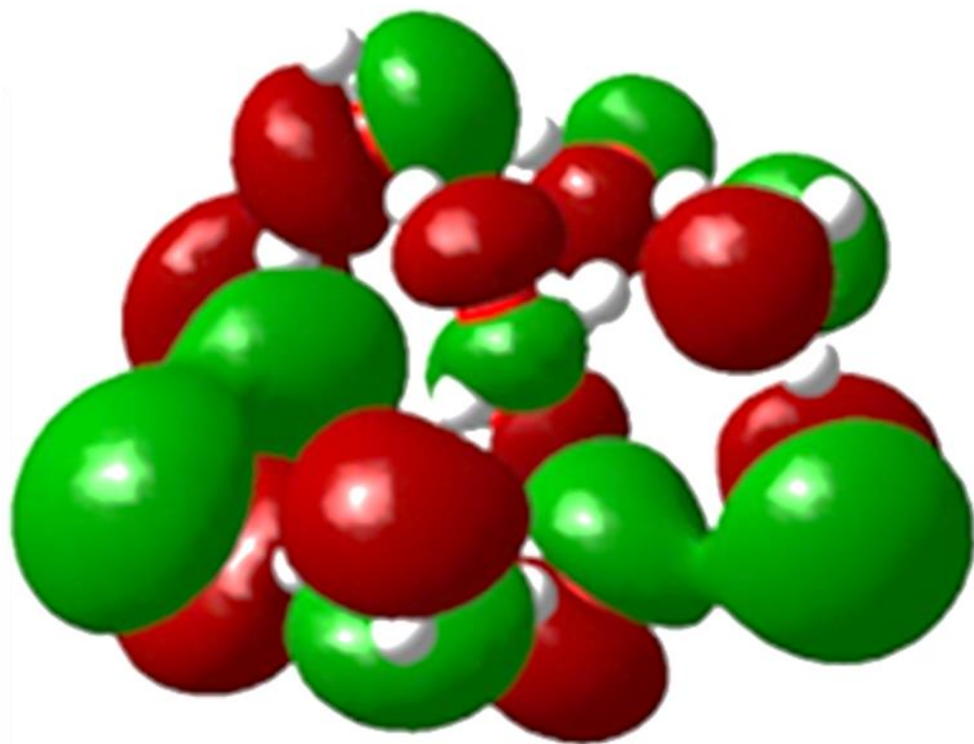
Space group P63/mmc; symmetry D6h



Superatom Electronic States in the Adamantanoid Water Cluster

Cluster optimized
at MP2/6-
311++G(d,p)-PCM
plotted at 0.01 au
isosurface

$E = -50.04$ kcal/mol

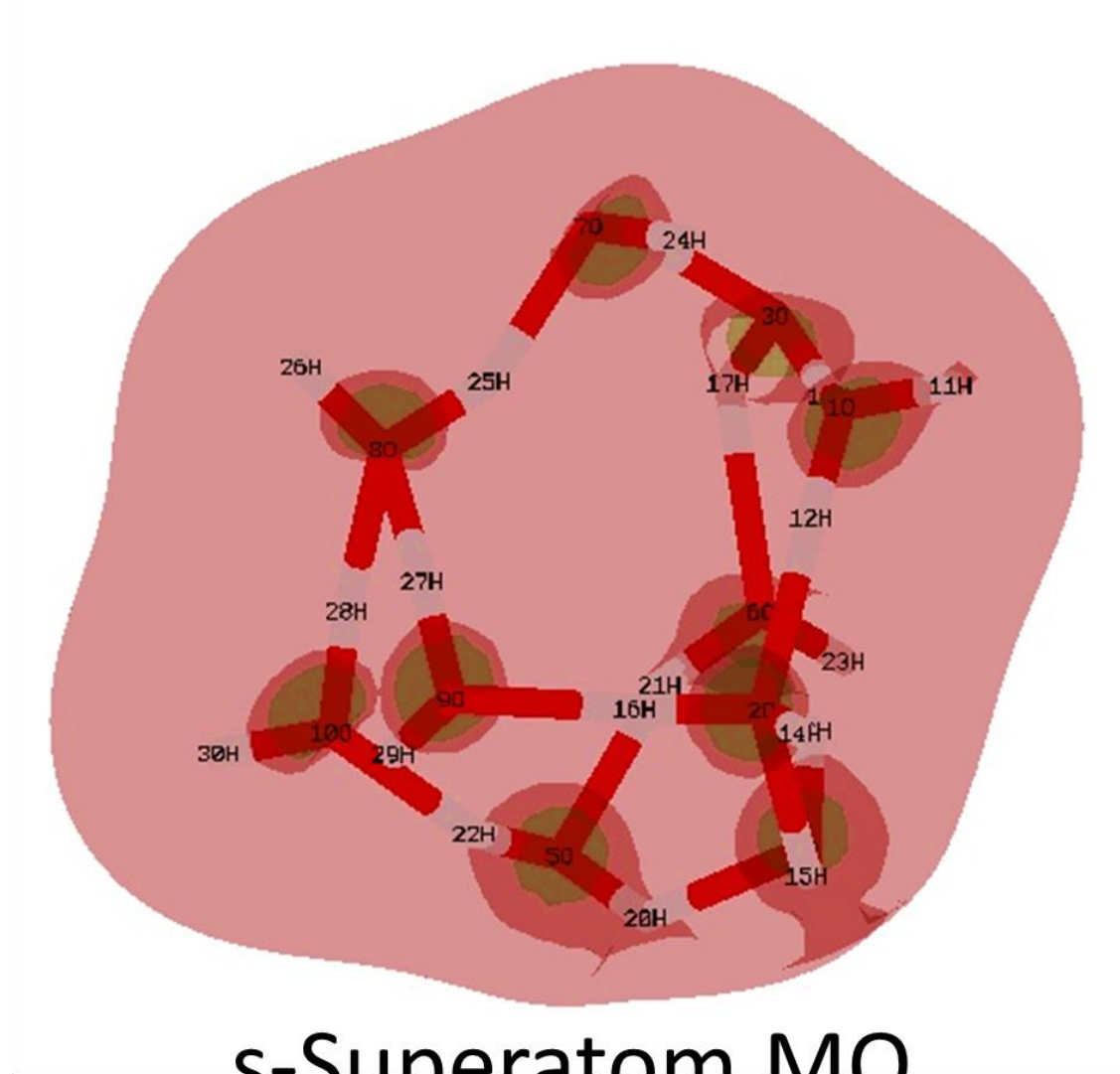


Highest Occupied
Molecular Orbital
(HOMO)

Superatom Electronic States in the Adamantanoid Water Cluster

LUMOs of $(\text{H}_2\text{O})_{10}$ cluster optimized at MP2/6-311++G(d,p)-PCM plotted at 0.01 au isosurface

$E = -0.0392 \text{ eV}$
LUMO

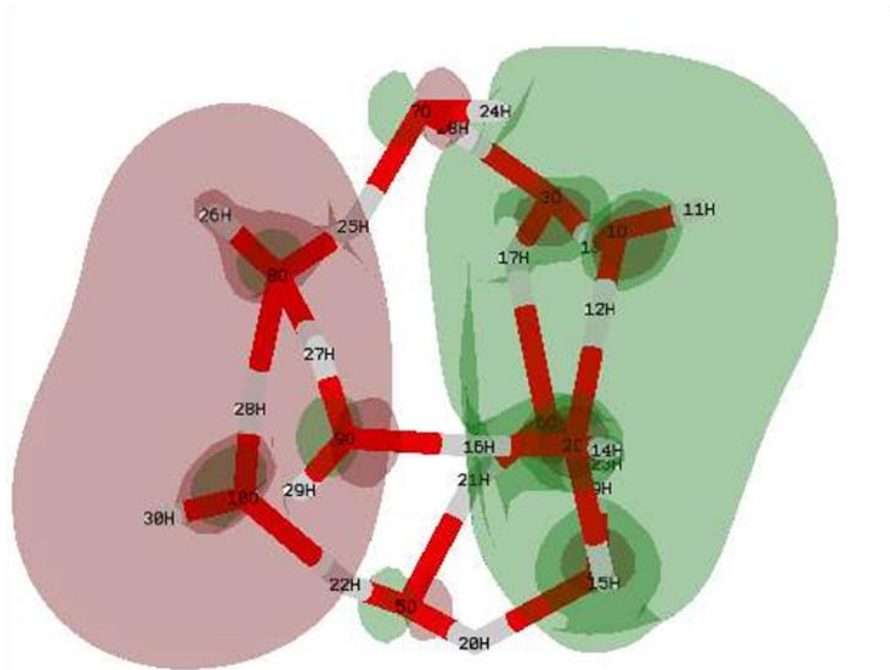


s-Superatom MO

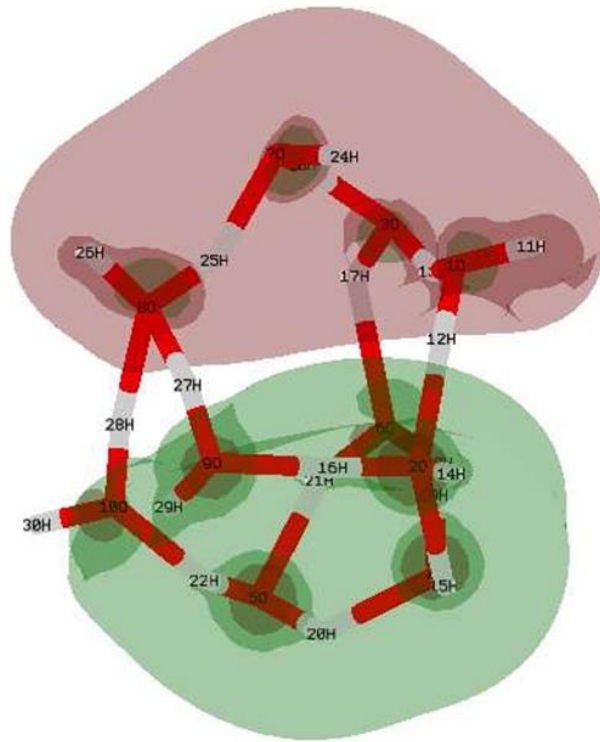
Lowest Unoccupied Molecular Orbital (LUMO)



Superatom Electronic States in the Adamantanoid Water Cluster

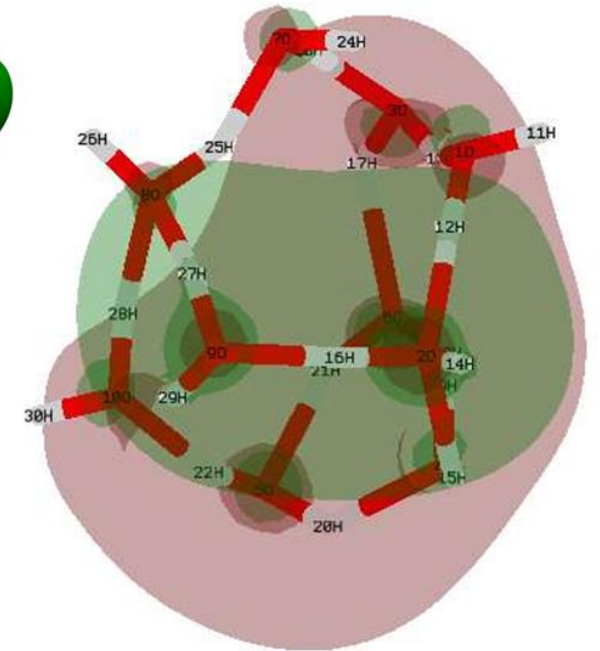
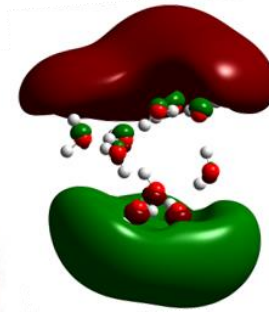


$E = 0.0526 \text{ eV}$
LUMO +1



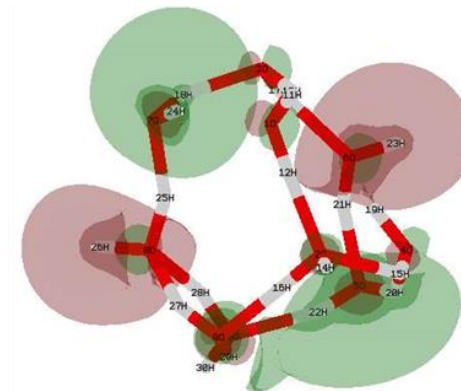
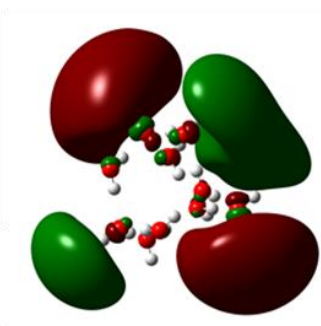
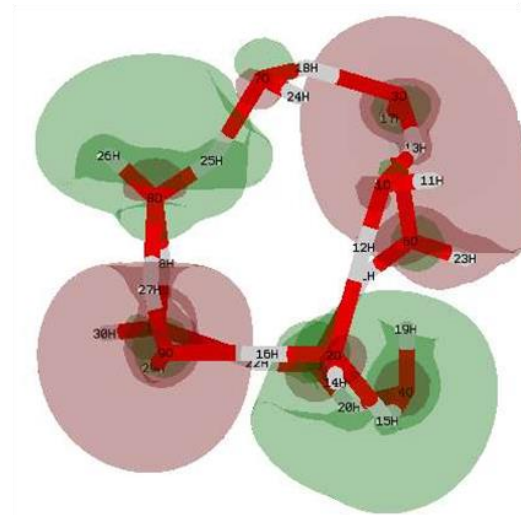
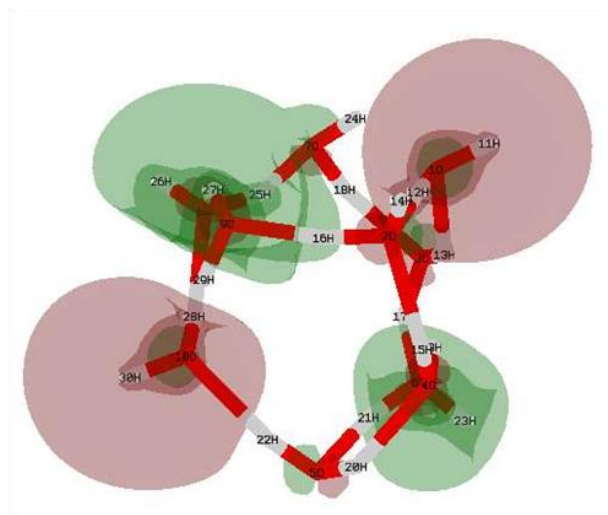
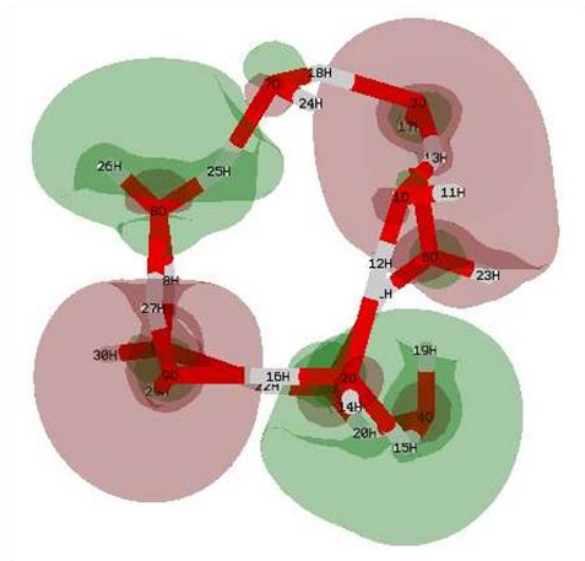
$E = 0.0579 \text{ eV}$
LUMO +2

p-Superatom MO



$E = 0.0644 \text{ eV}$
LUMO +3

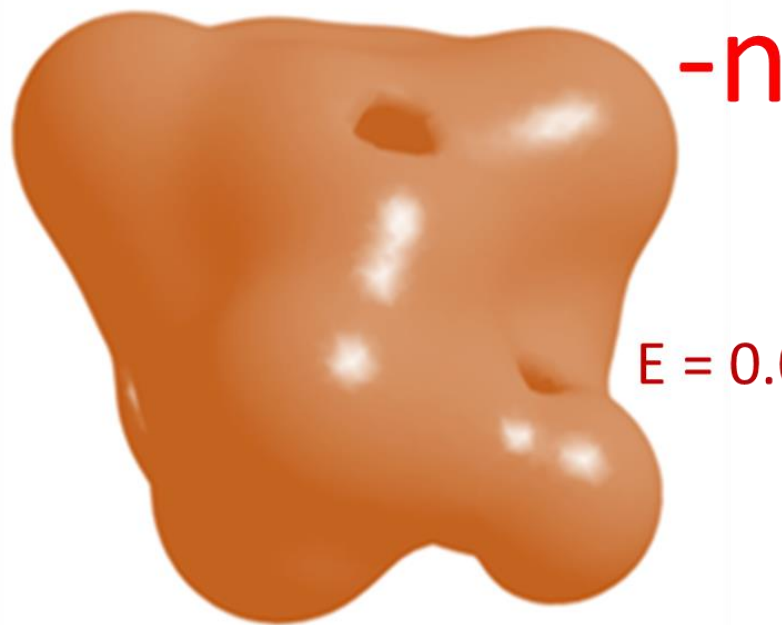
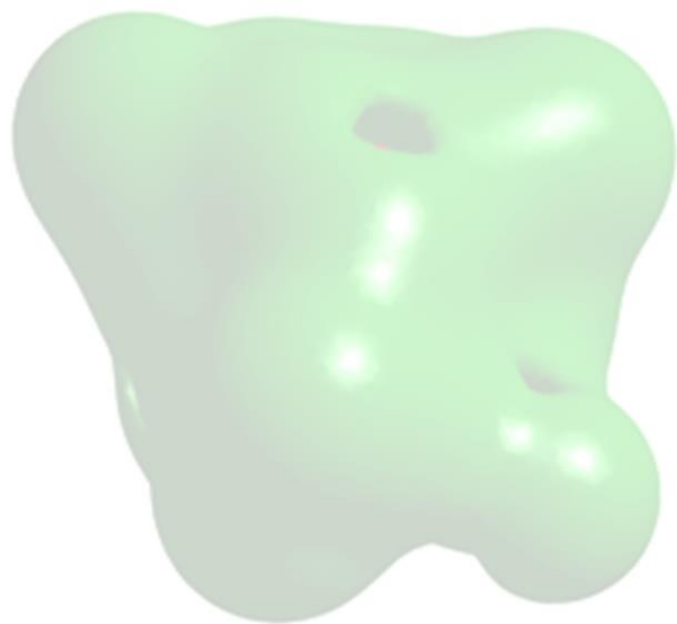
Superatom Electronic States in the Adamantanoid Water Cluster



$E = 0.0781$ to 0.0992 eV

d-Superatom MO

Superatom Electronic States in the Adamantanoid Water Cluster



$E = 0.04980 \text{ eV}$

$\Delta = 0.4398 \text{ eV} = 2,819 \text{ nm (Near IR)}$

Electron affinity = -26.82 kcal/mol

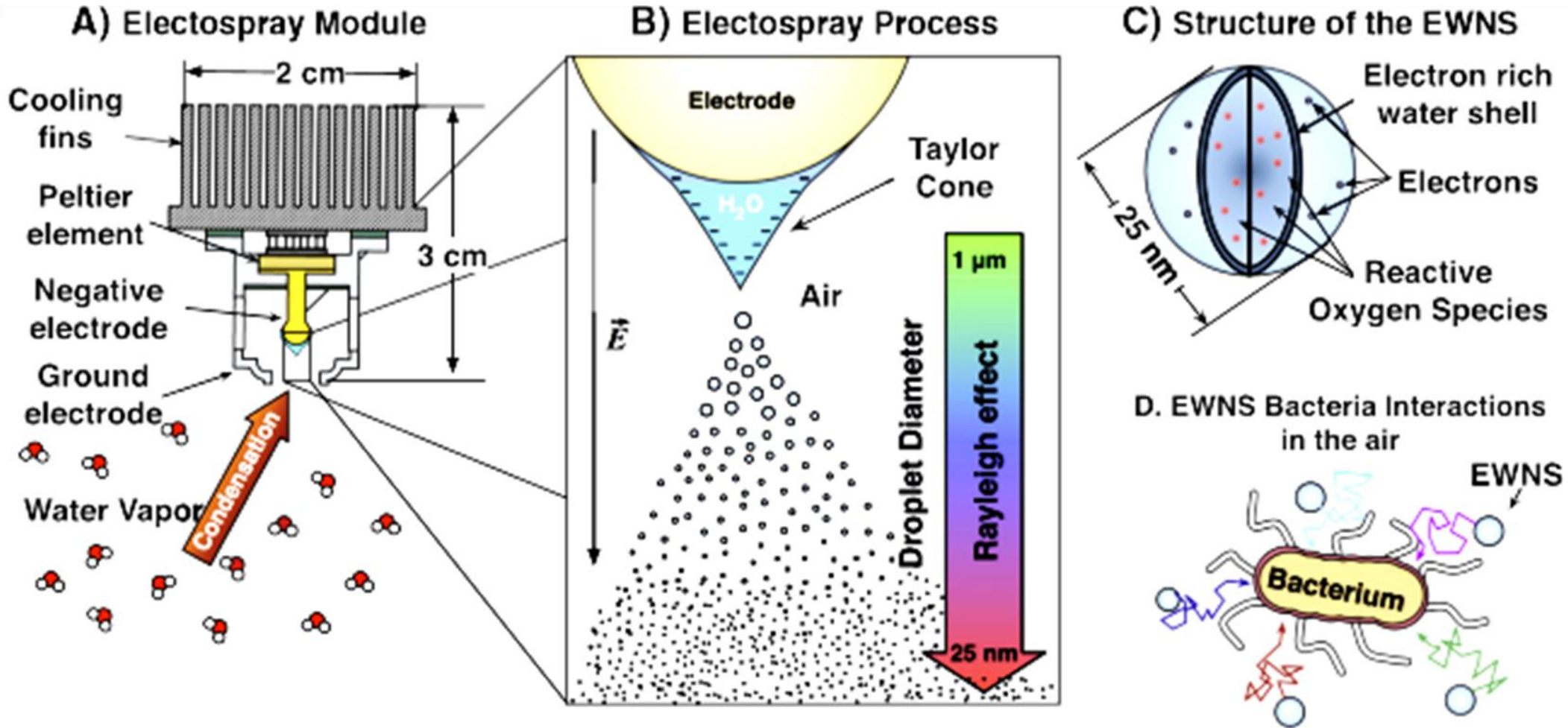
Applications of Nanostructured Water Clusters

Prof. Philip Demokritou (Harvard U.)

Pyrgiotakis, G., et al. *Nanomedicine Nanotech. Biol. and Med.*, **2014**, *10*, 1175.
Environ. Sci. Tech. **2015**, *49*, 3737.

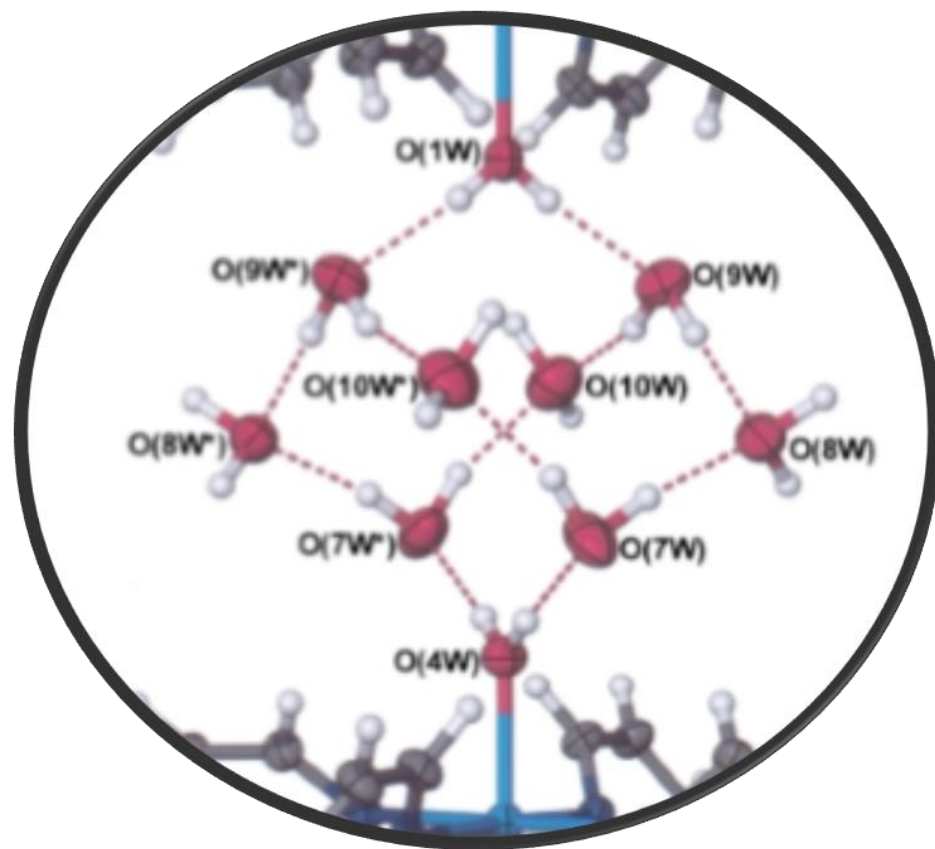
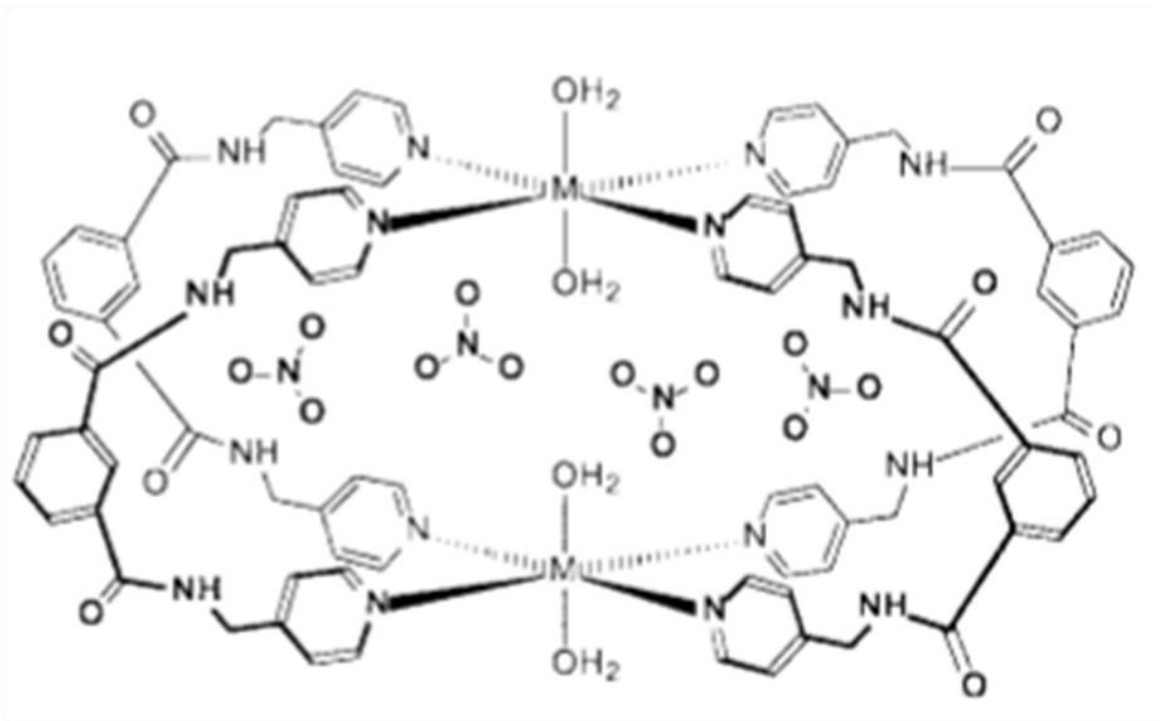
Peltier Electrode

5 kV



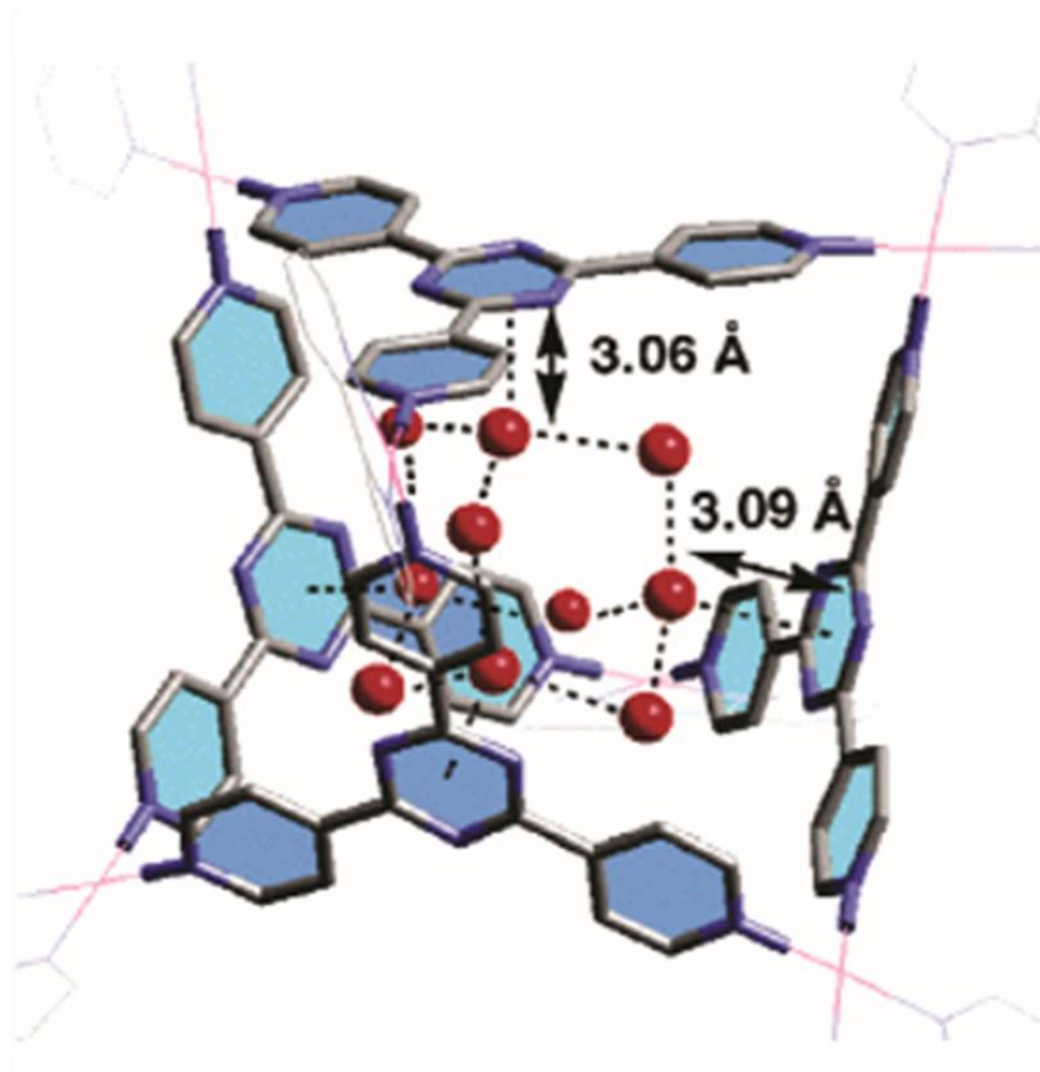
Isolation of Nanostructured Water Clusters

Isolation of Nanostructured Water Clusters



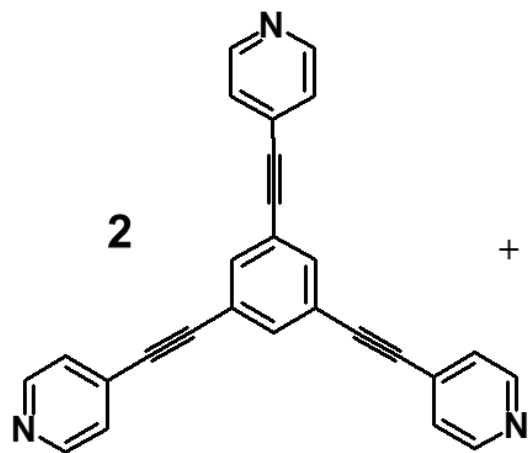
Barbour L. J., et al. *Chem. Comm.* **2000**, 859.

Isolation of Nanostructured Water Clusters

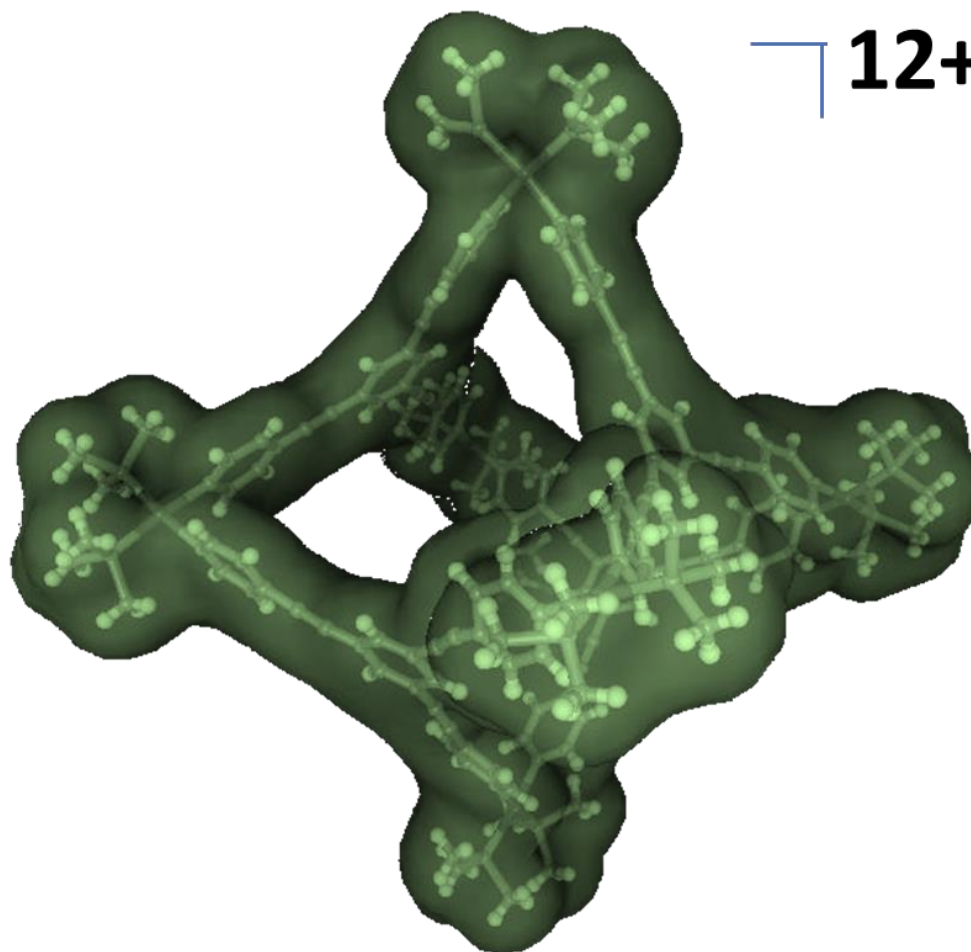
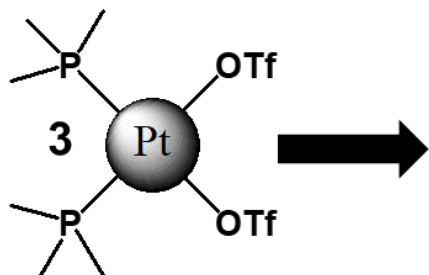


Yoshizawa, M., et al. *J. Am. Chem. Soc.* **2005**, 127, 2798.

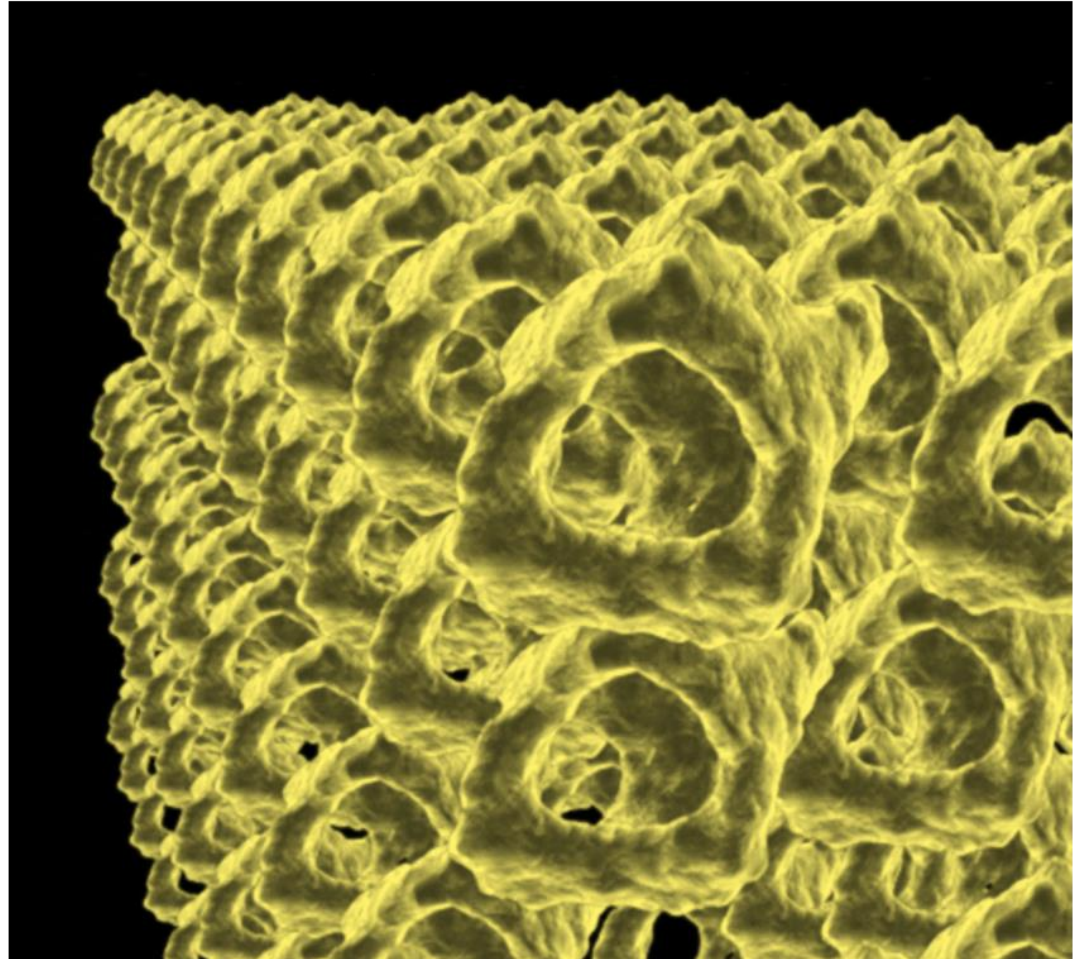
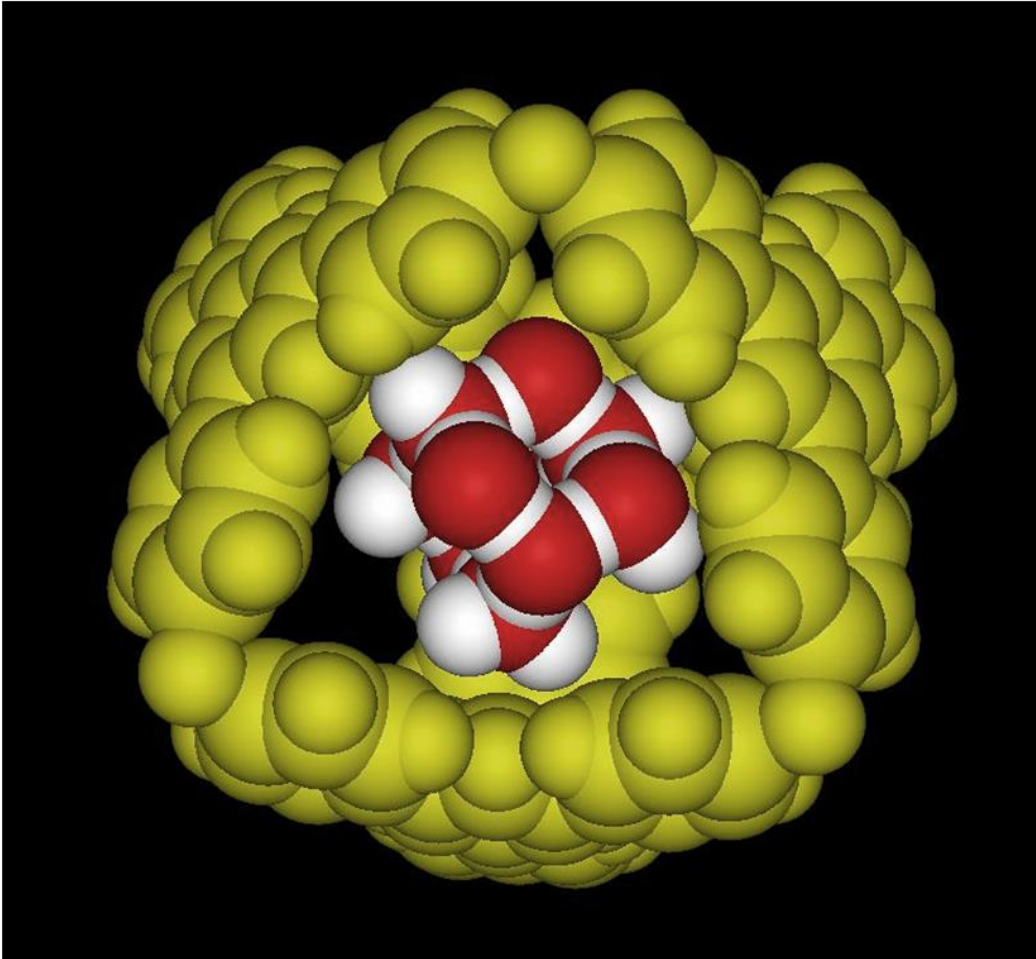
Self-assembled Capsule for Nanostructured Water Clusters



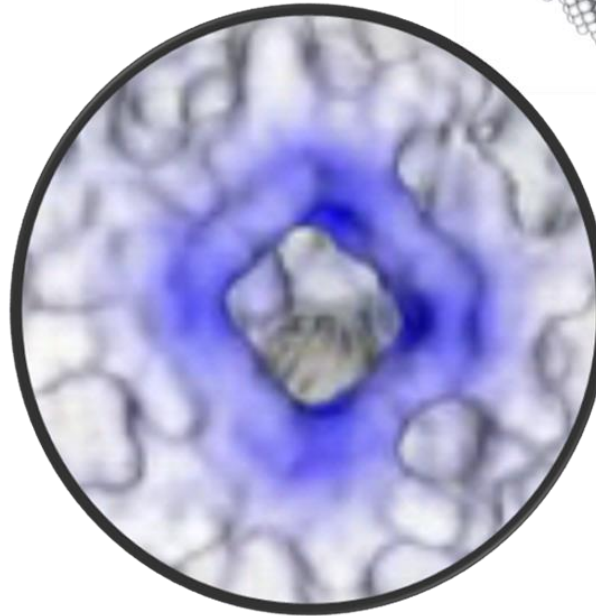
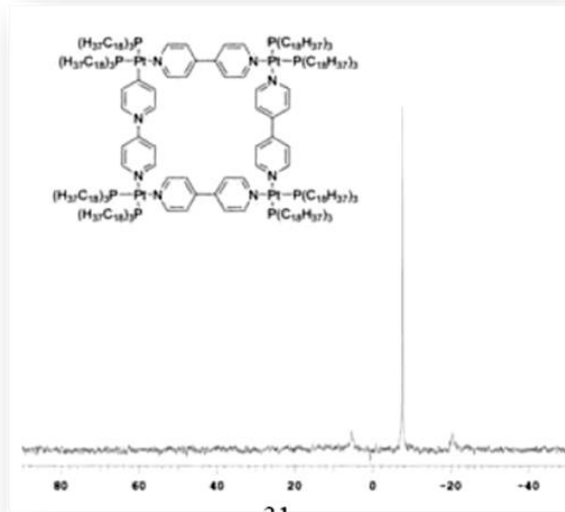
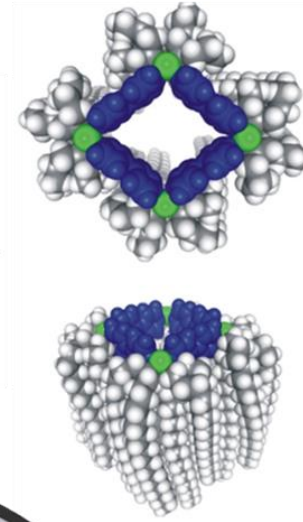
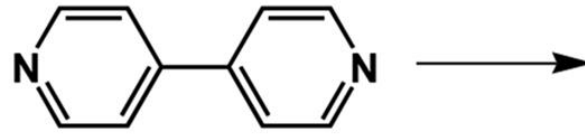
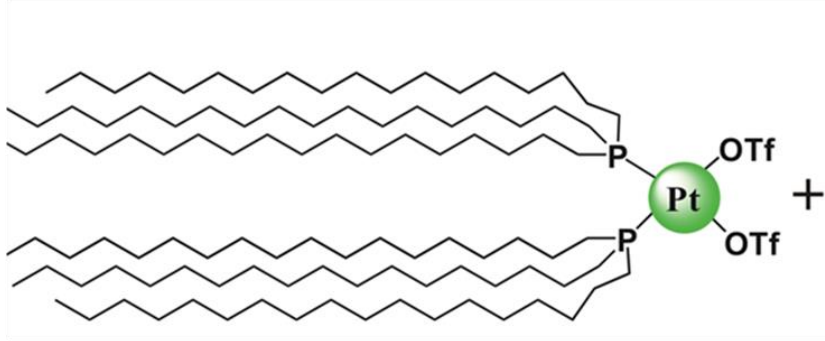
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Advanced materials for the pre-formation of water nanoclusters



Self-assembled 1 nm pores for Nanostructured Water Clusters



Summary

- Nanostructured water allows for the emergence of Superatom Electronic States with important electronic and optical properties
- DFT calculations predict high electron affinity in Superatom Molecular Orbitals
- Nanostructured water can form within hydrophobic cavities
- Novel nanostructured water clusters may play key roles in biology and advanced materials

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