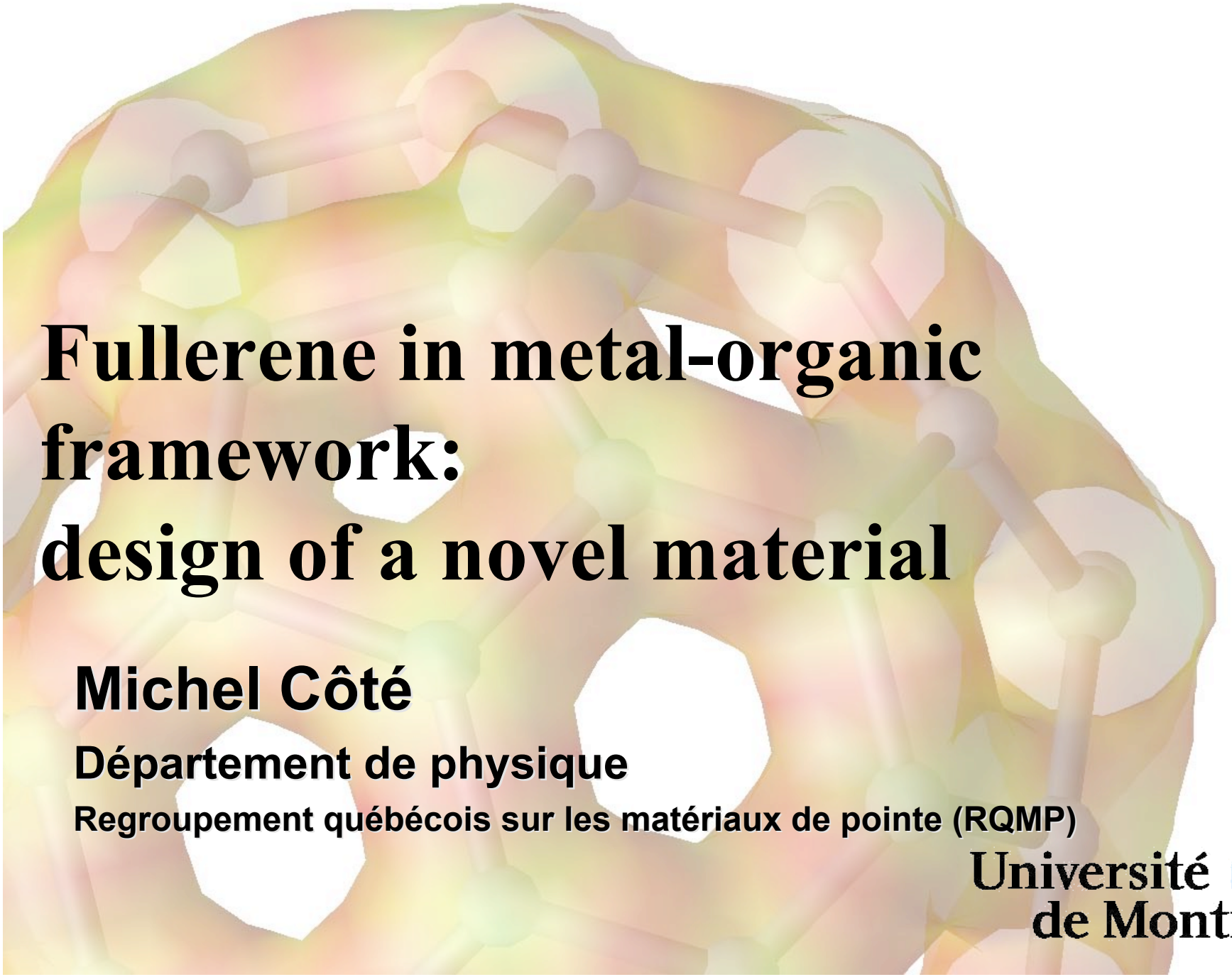


Fullerene in metal-organic framework: design of a novel material

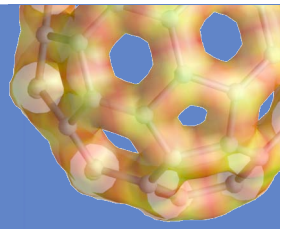
Michel Côté

Département de physique

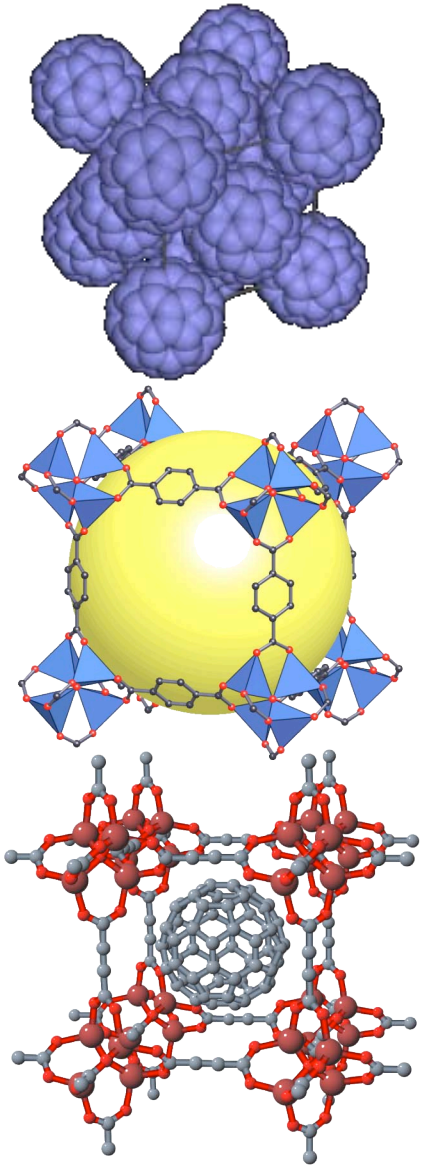
Regroupement québécois sur les matériaux de pointe (RQMP)

Université de Montréal

Outline:



- C_{60} and its crystal
  - C_{60} properties
  - Superconductivity in C60 solid
- Metal-organic-framework (MOF)
  - Structure
  - Applications
- A new compound: C_{60} and MOF
  - Design of electronic structure



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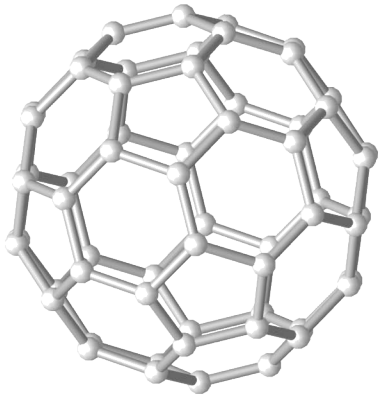
C_{60} fullerene

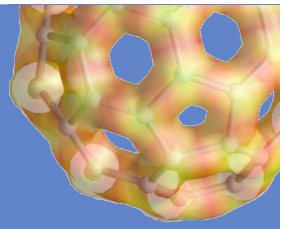


Biosphere in Montreal

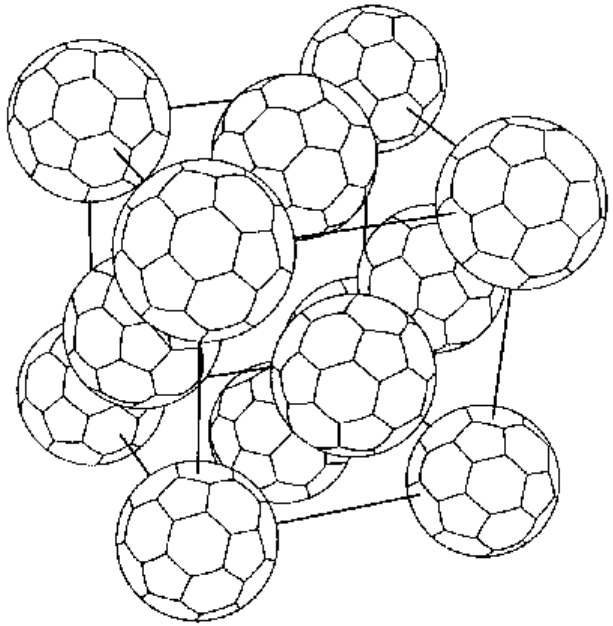
- name, *fullerenes* ou *buckyballs,* is in honor of the architect Buckminster Fuller

- discover in 1985; Nobel Prize in 1996
  Curl, Kroto and Smalley

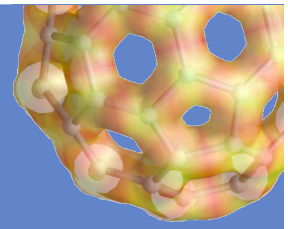
C_{60} proprieties

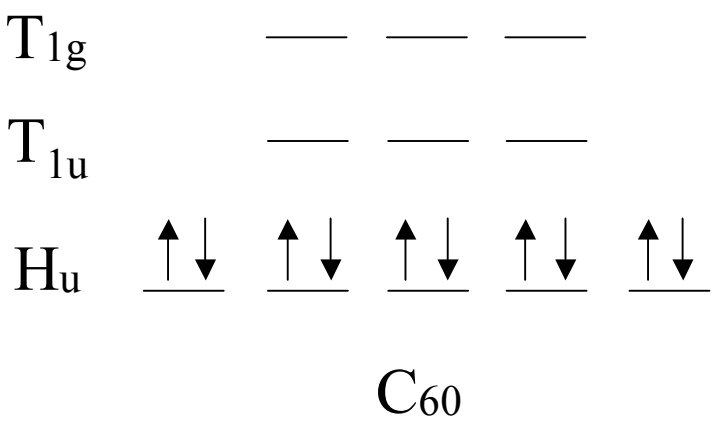


- high symmetry; icosahedral
- formation energy = 8.4 eV/atom
  For comparison graphite/diamond = 8.8 eV/atom
- very stable
  Can be thrown at 100 000 km/h at a wall without breaking.
- can form a solid



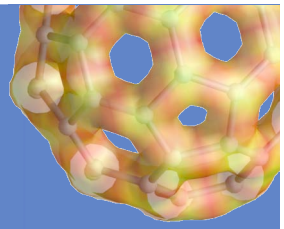
Electronic structure of C_{60}

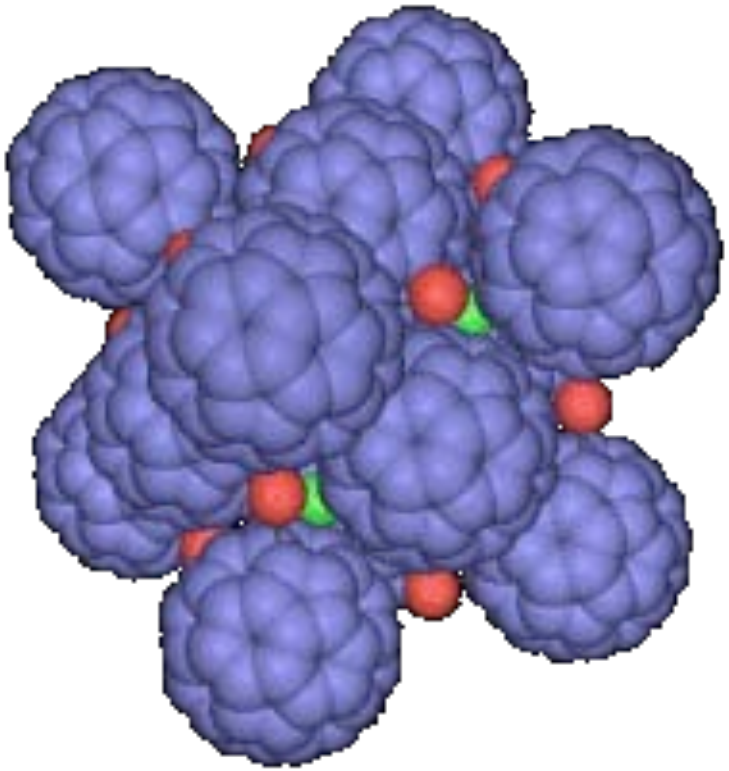




In order to make C_{60} a metal with a high electronic density of states, we want to had 3 electrons for each C_{60}, hence A_3C_{60}, where A is an alkali atom.

C_{60} metal



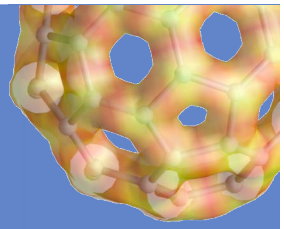


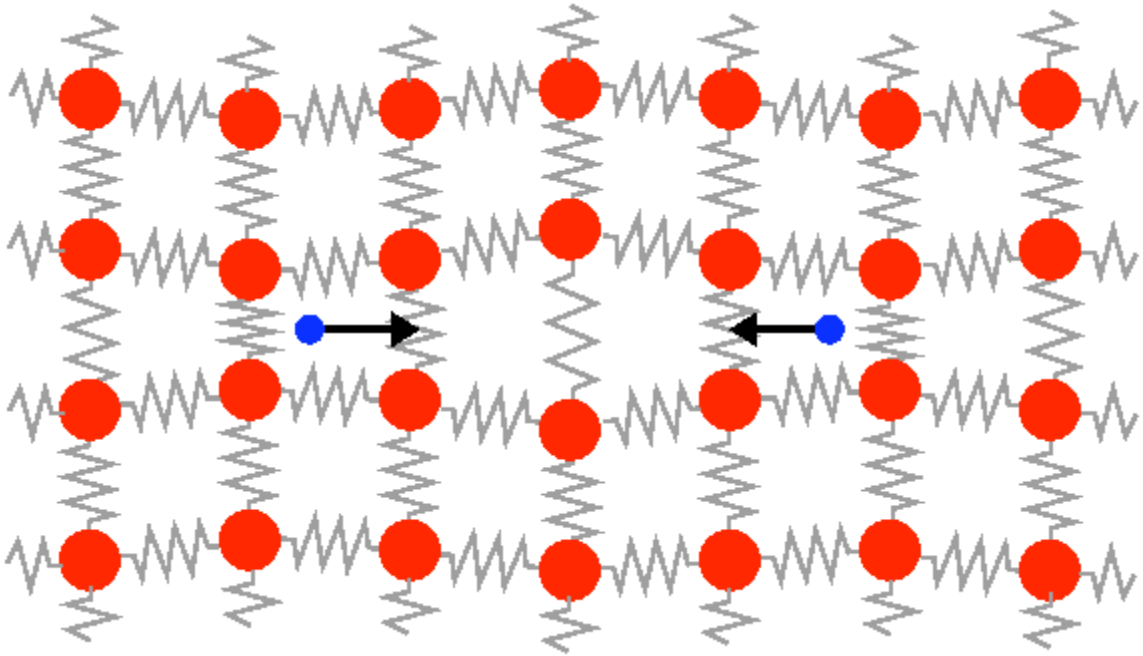
- C_{60} crystals can be doped with alkali. A_3C_{60} (A=K,Rb,Cs).

- T_c ~ 10 - 40 K linked to the enlargement of the distance between the C_{60} (10 to 10.3 Å center to center).

http://www.physik.uni-stuttgart.de/ExPhys/2.Phys.Inst./group/nmr/fullerene/fullerene_gallery.html

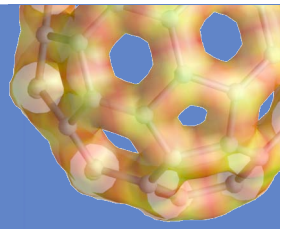
Superconductivity





• effective attraction between electrons due to motion of atoms.

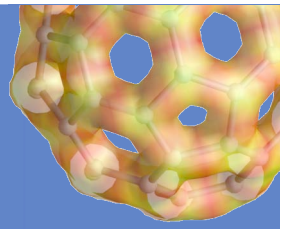
Transition Temperature

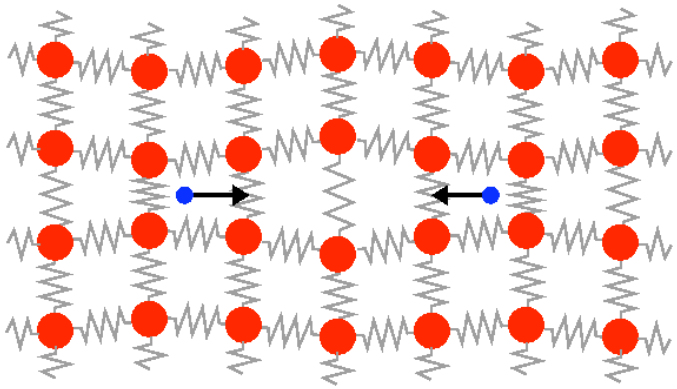


$$T_C \sim \theta_D \, e^{-1/V_{elph} D(\varepsilon_F)}$$

- The interaction responsible for the superconductivity in fullerenes is mediated via the intramolecular phonons

Electron-phonon coupling

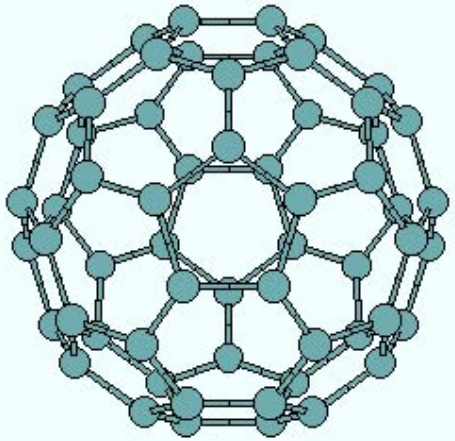


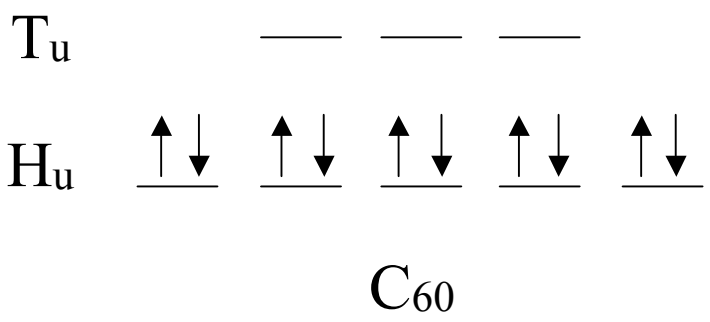


Only intramolecular modes are responsible for the coupling

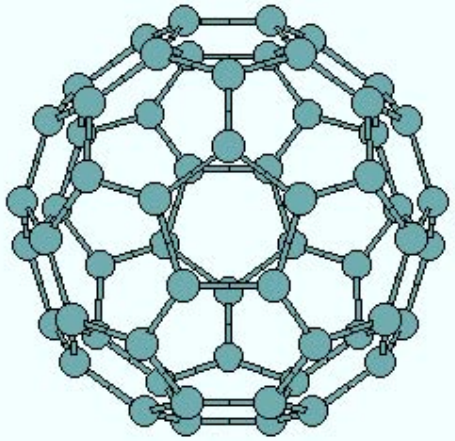
$$Vep \sim \sum_{\lambda} \frac{\left|\left\langle \psi_i \left| \varepsilon_\lambda \cdot \delta V \right| \psi_j \right\rangle\right|^2}{\omega_\lambda^2}$$

Ag mode





Hg mode



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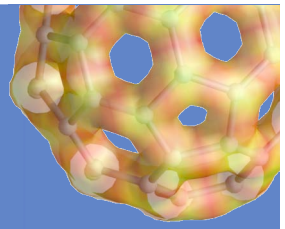
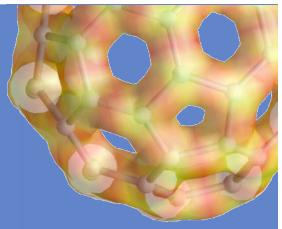


$$T_C \sim \theta_D \, e^{-1/V_{elph} D(\varepsilon_F)}$$

- The interaction responsible for the superconductivity in fullerenes is mediated via the intramolecular phonons
- When the lattice parameter changes, only the DOS at the Fermi level changes

$$D(\varepsilon_F) \sim \frac{1}{\text{Dispersion}} \sim \text{Lattice parameter}$$

Tc vs lattice parameter



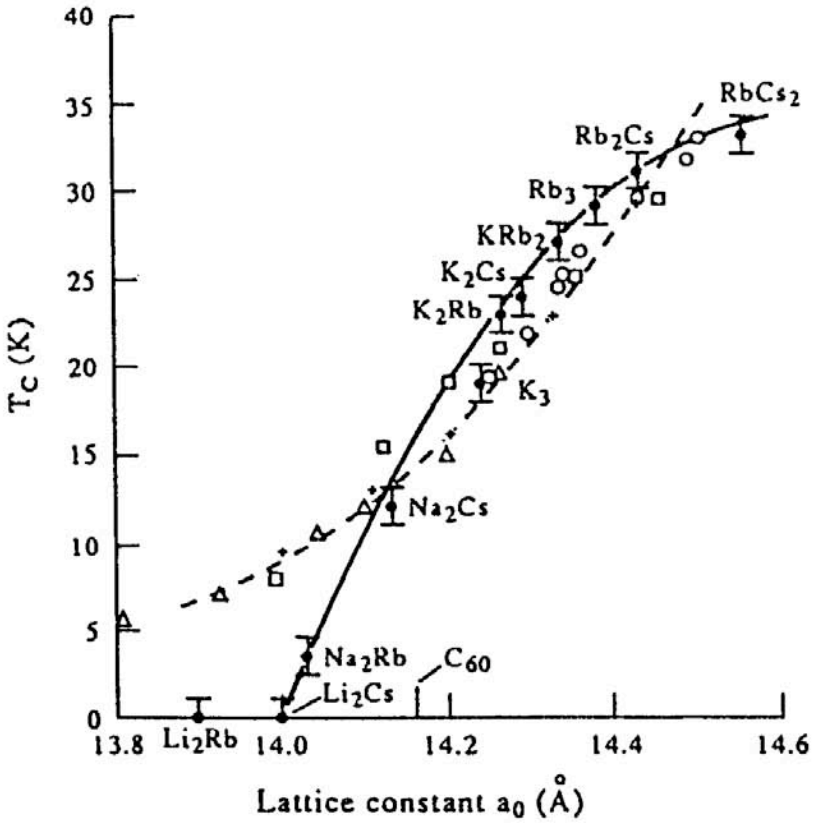
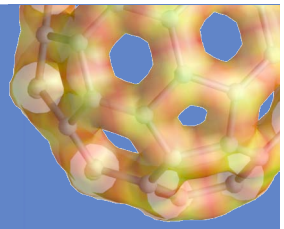
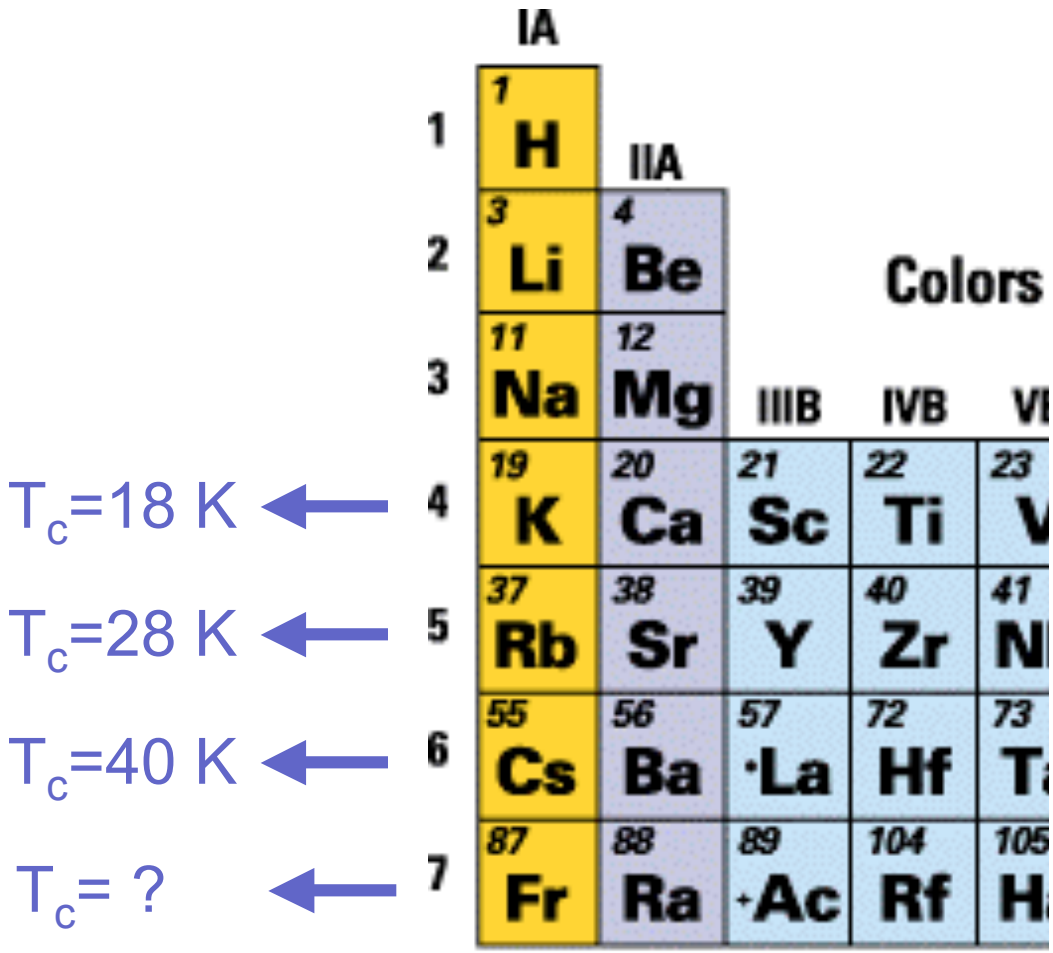


Fig. 10.14. The relationship between T_c and the lattice parameter a_0 for A_3C_{60} (A: Li, Na, K, Rb, Cs and their binary alloys) superconductors. Open triangles and squares are from pressure experiments, and the dotted line represents the T_c-a_0 relationship expected from the simple BCS theory using the density of states due to LDA calculations. The *solid line* is a guide for the eyes. From [10.48]

Source: T. Ishiguro, K. Yamaji, G. Saito, "Organic Super-conductors"

Alkali atoms





Fr half-life = 22 minutes

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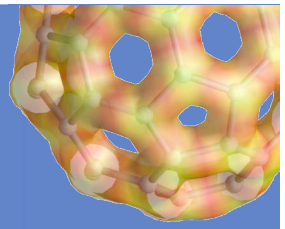
Outline:



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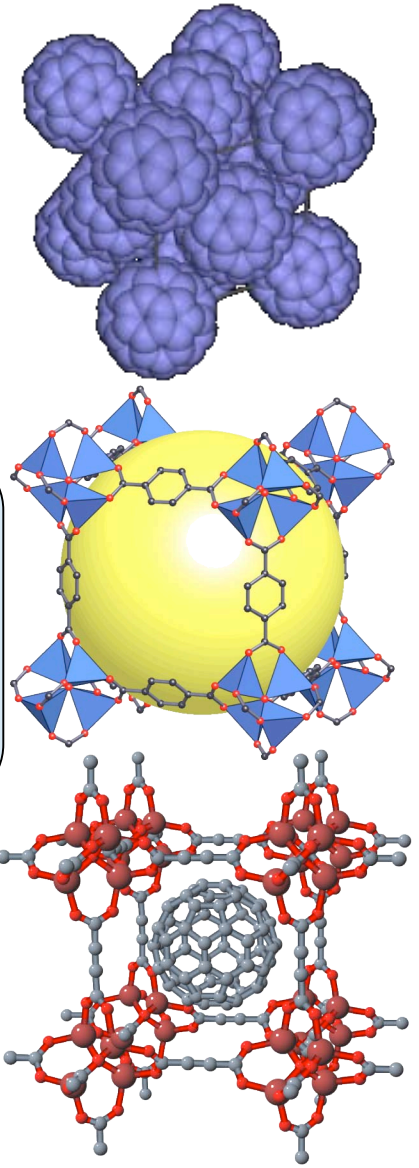

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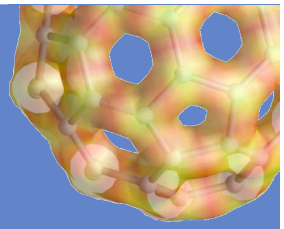
Hydrogen storage



Fuel cell:

⇒ the problem of hydrogen storage

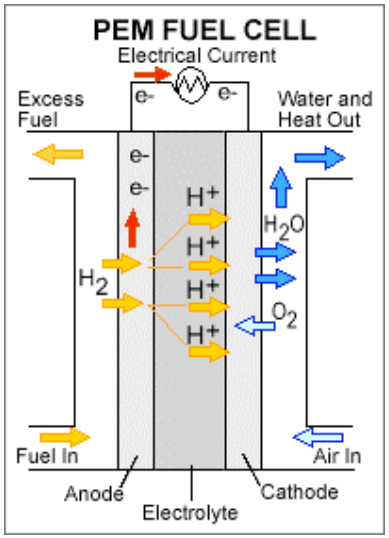
Present material capacity:

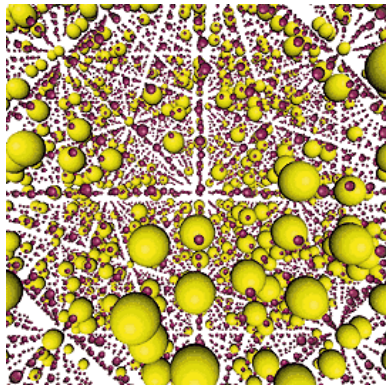
⇒ 2 to 4 % of their weight in hydrogen

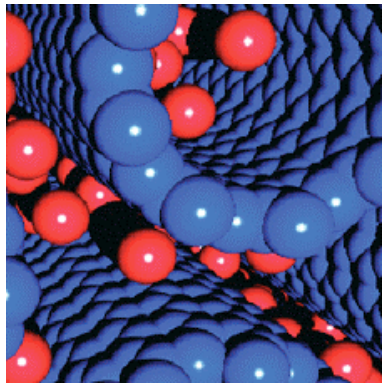
DOE goal:

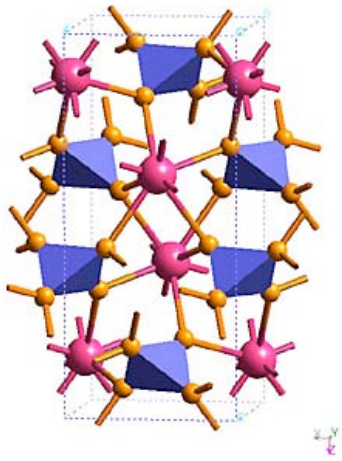
⇒ 6.5 % of their weight

⇒ 1.2 billion US$ in research funding









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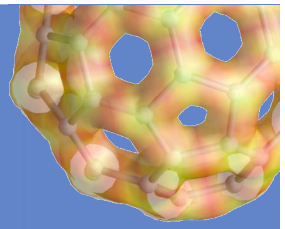
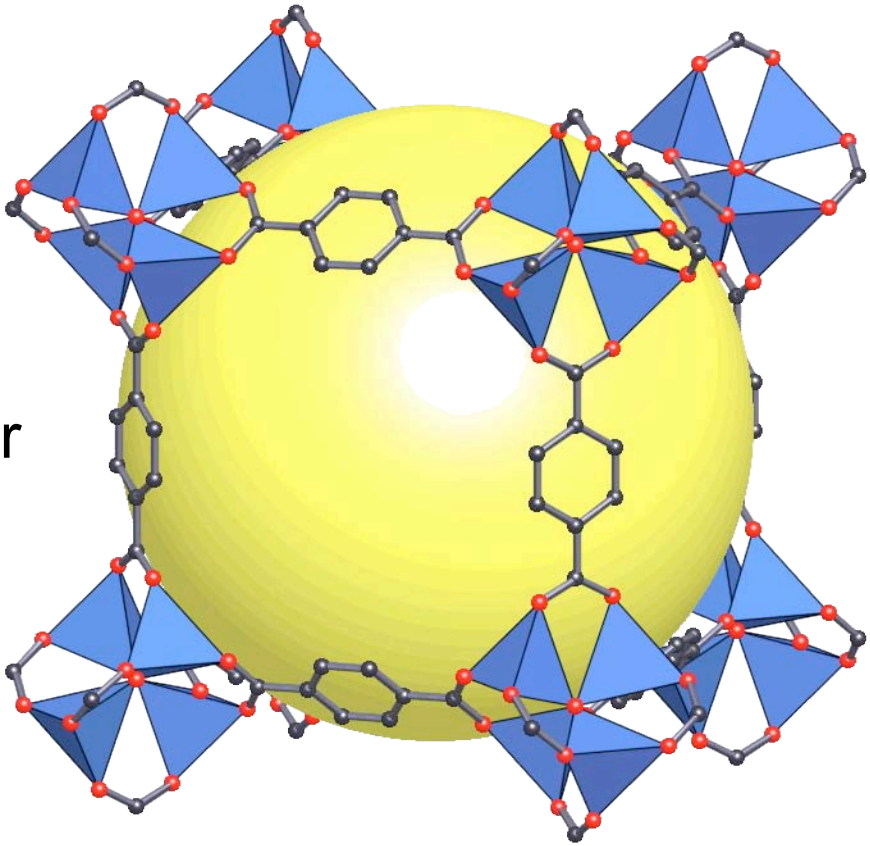
Metal-Organic Framework (MOF)



$Zn_4O(BDC)_3$ BDC=1,4-benzenedicarboxylate

- 4.5 weight % of H_2 at 78 K and 0.8 bar
- 0.5% at RT and 10 bar
- 1% at RT and 20 bar



Rosi et al., Science **300** (2003)
Yaghi's group, Chemistry, Michigan University.

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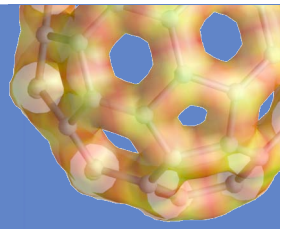
Outline:



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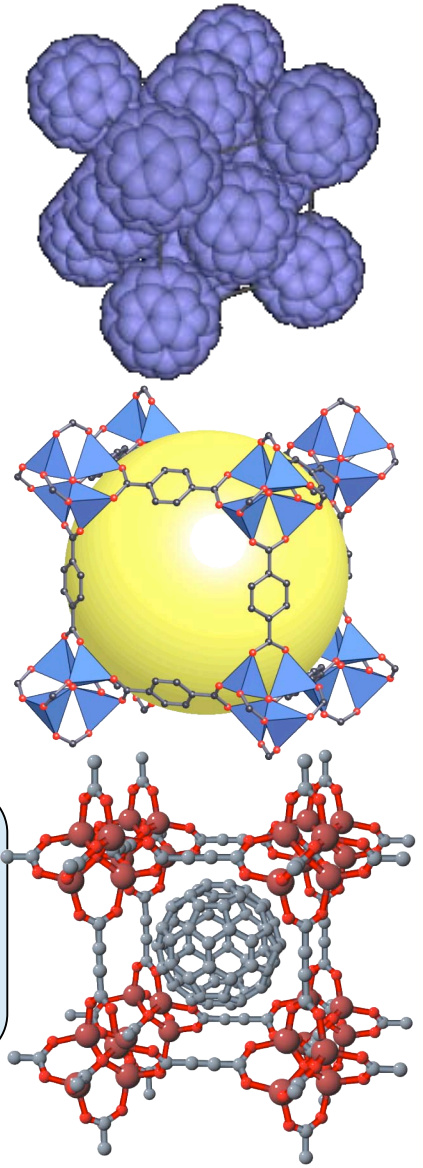

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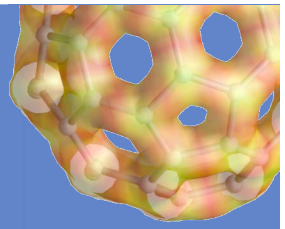
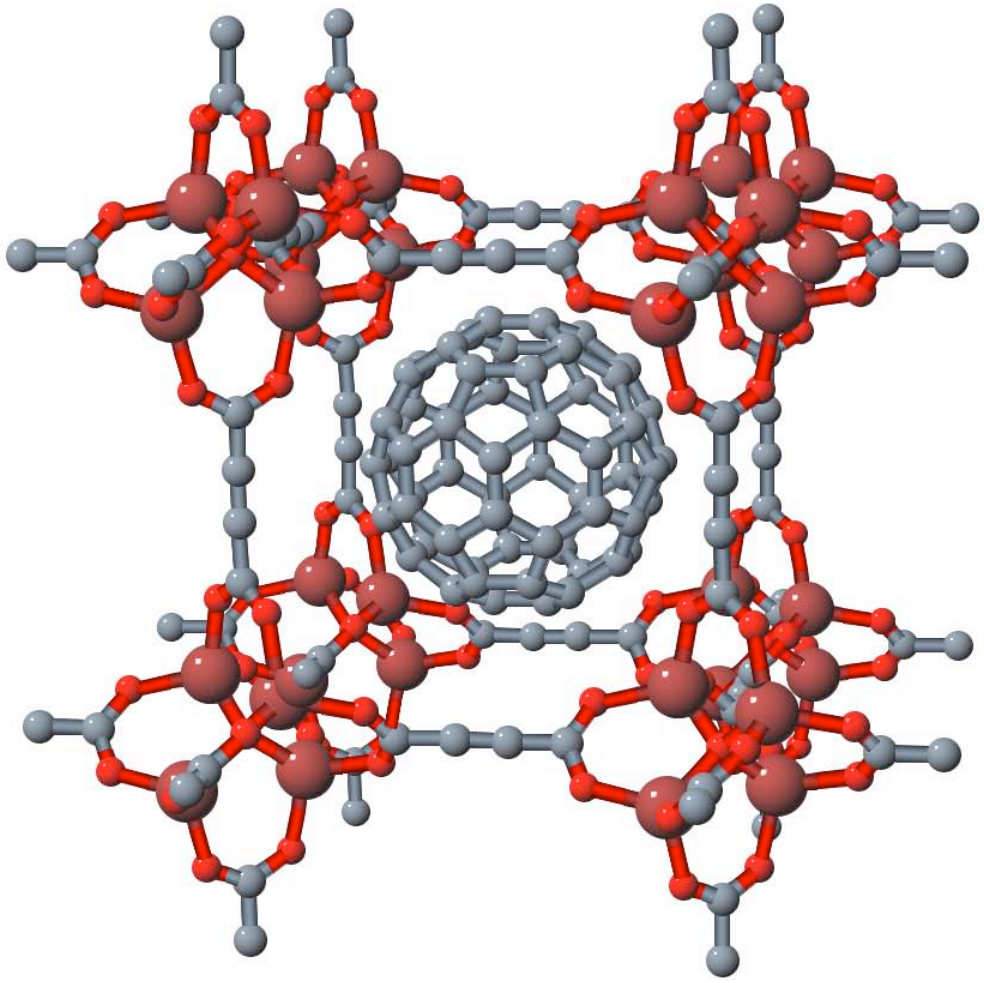
Material Design





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Design of a novel material

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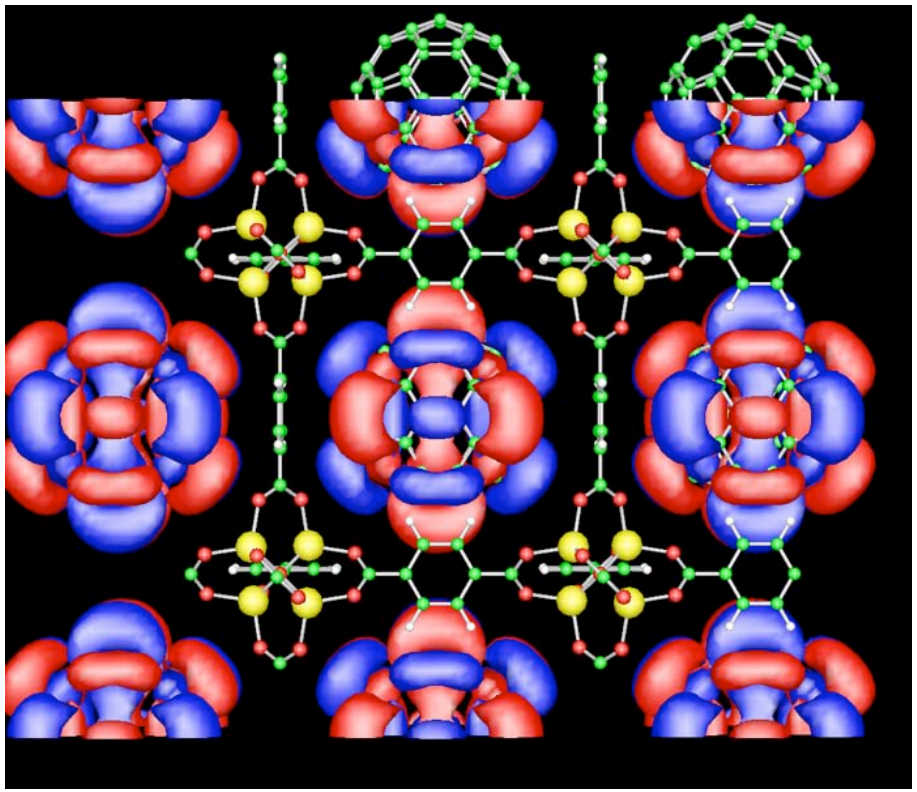
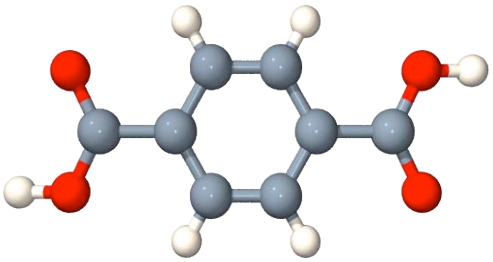
MOF-5C_{60}



- ΔE=0.87 eV
- New cubic structure for C_{60}
- Center to center distance of 12.9 Å between the C_{60}
- Need to reduce the size of the organic linker 1,4-benzenedicarboxylic



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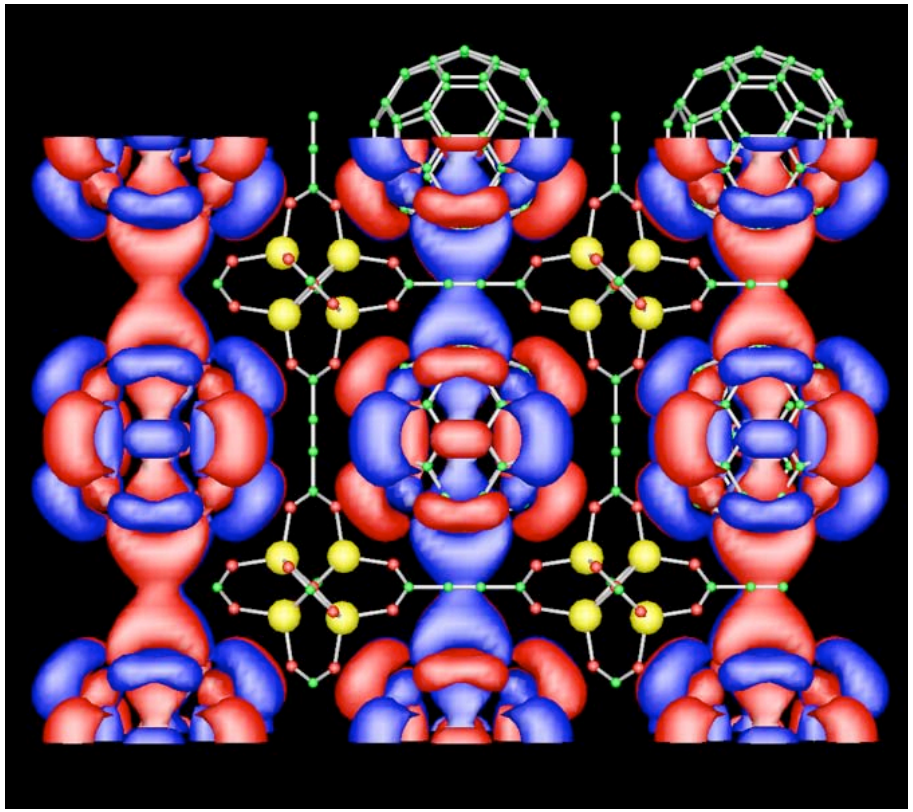
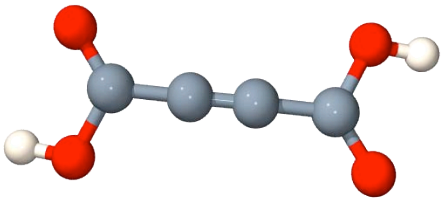


- ΔE=1.02 eV
- Keep the simple cubic structure for the C_{60}
- Center to center distance of 11.3 Å between the C_{60}
- The organic acid 2-butynediodic in the synthesis of the MOF



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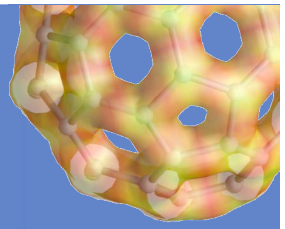
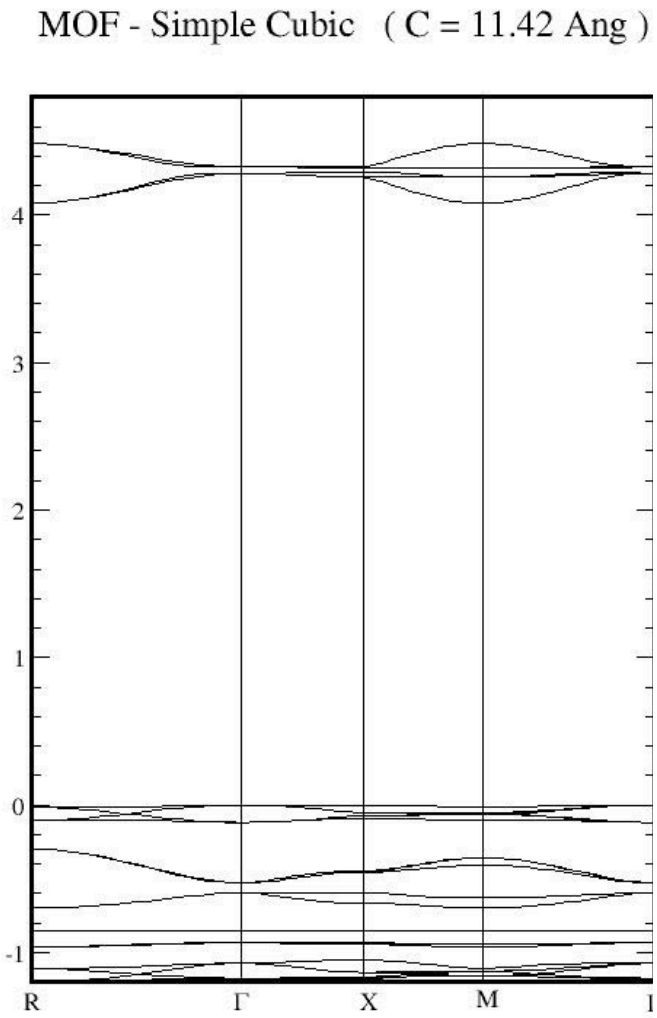
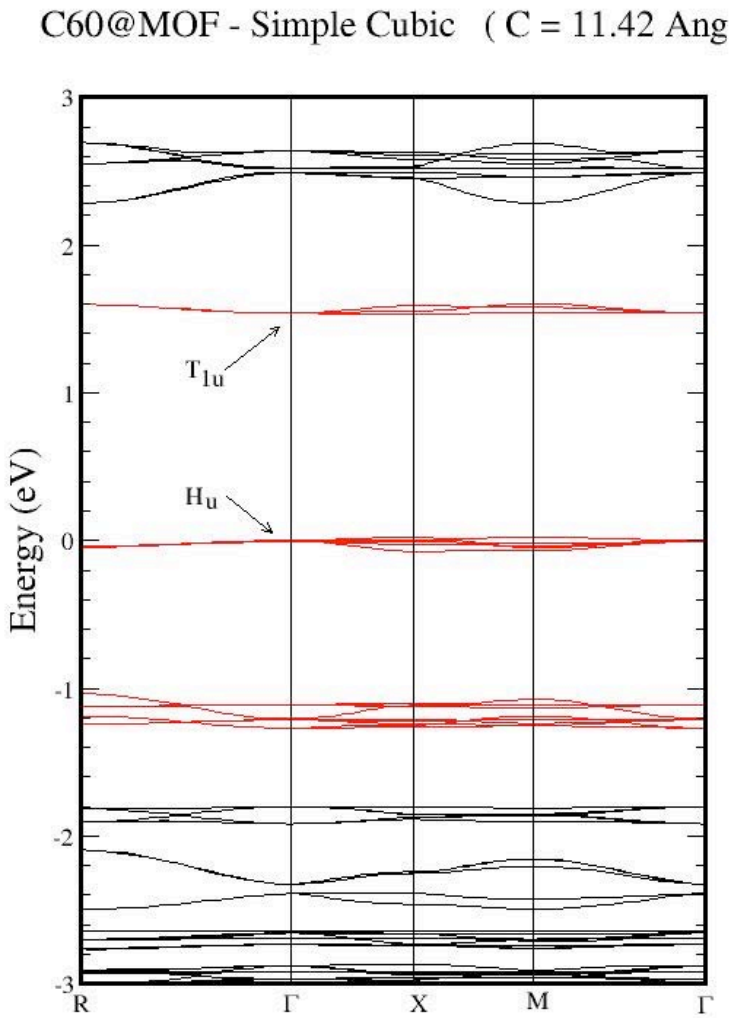
$MOFC_4C_{60}$ band structure







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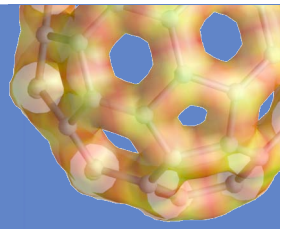
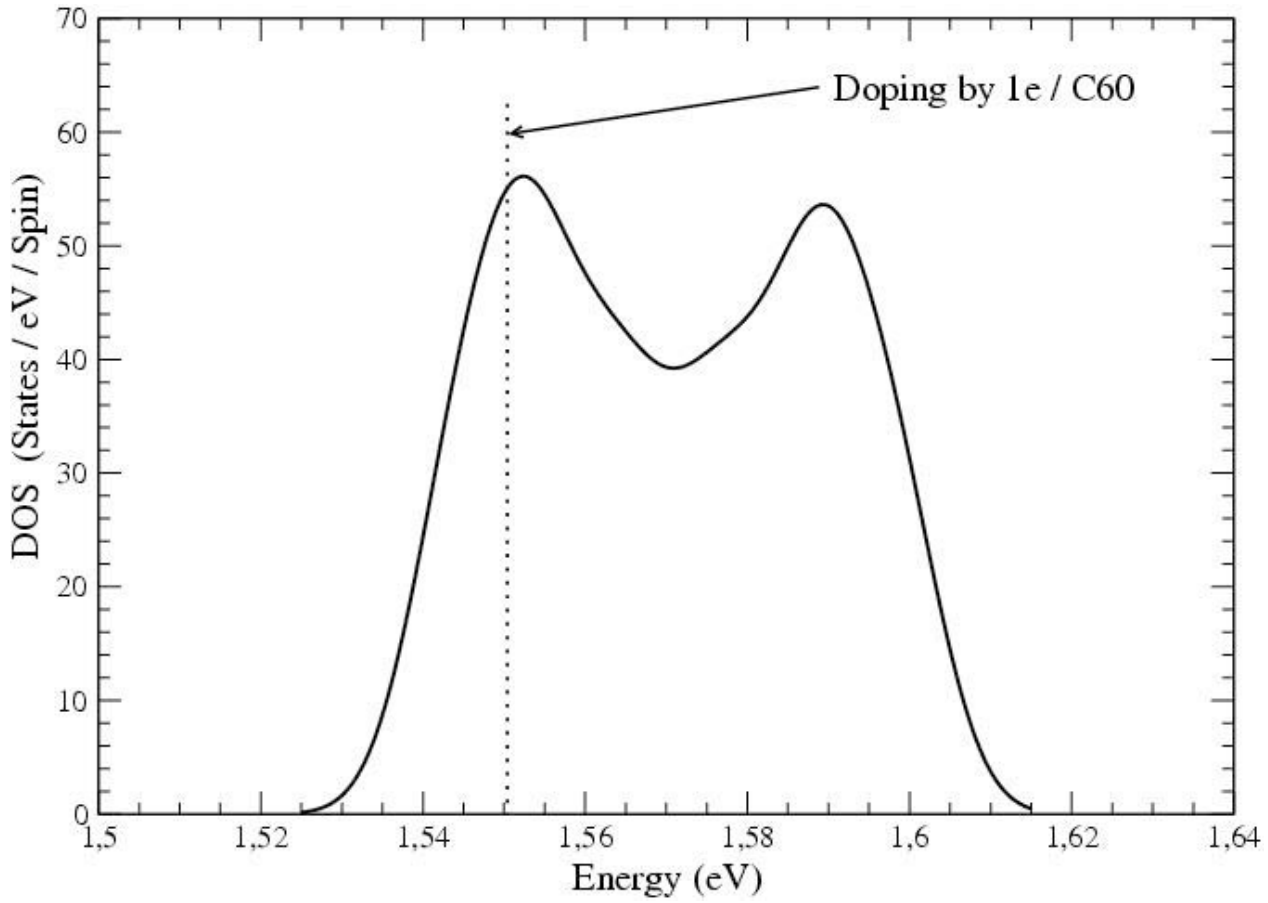
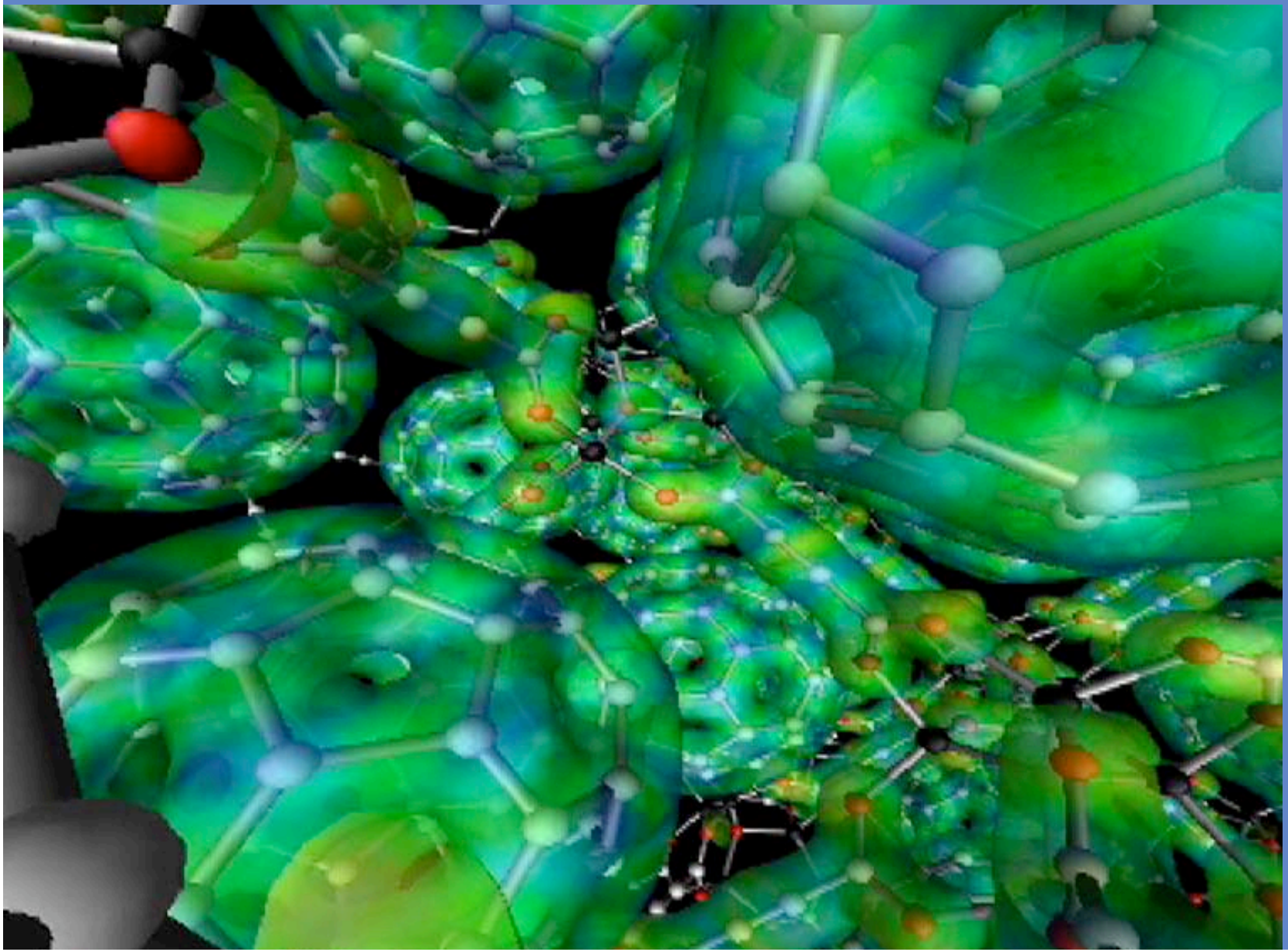
Density of states

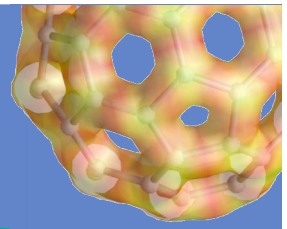




Solid FCC C_{60}: 15 states/eV/spin

A look at the charge density…





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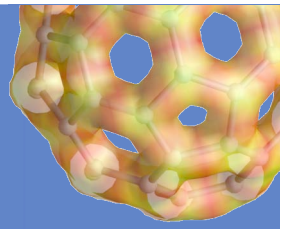
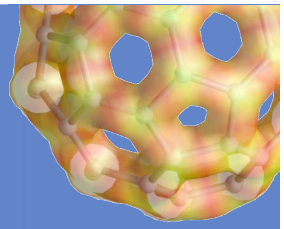
Conclusion:



- Electronic properties can be tailor with the combinaison of MOF and C60.
- Many new possibilities remain to be explore.
- The synthesis has started.

For more details see: PRL (95) 146403 (2005)

Members of the group



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