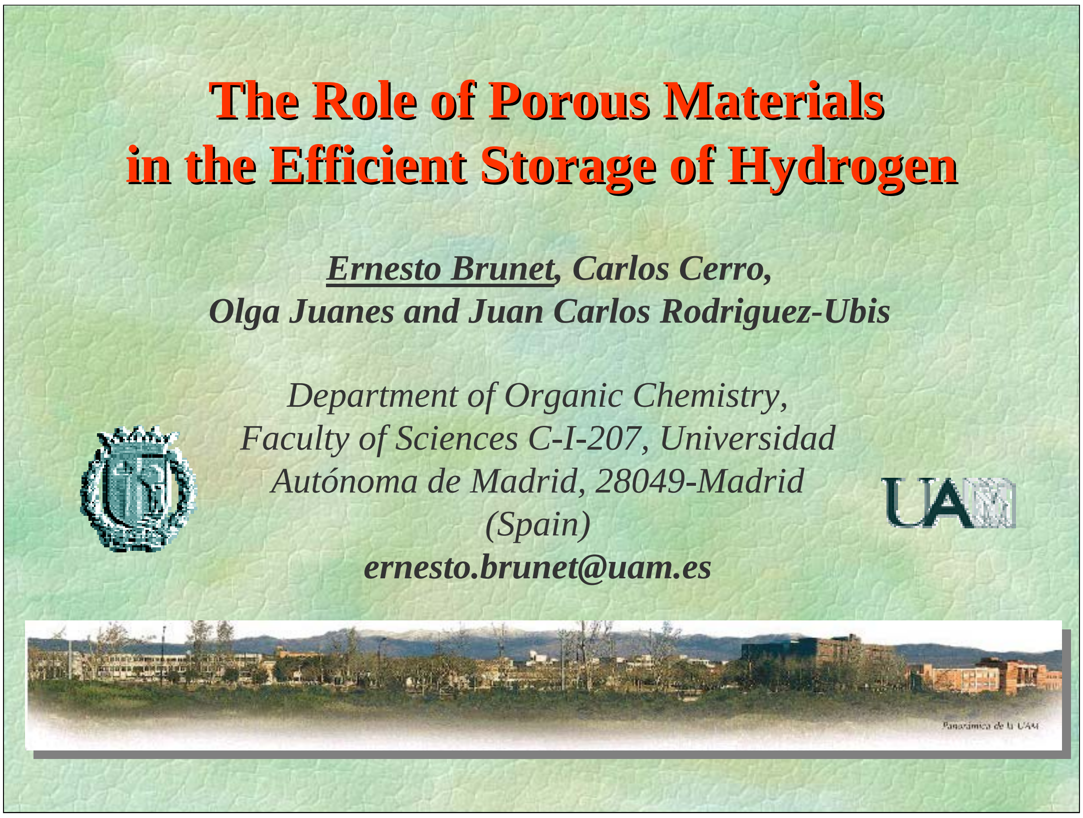

The Role of Porous Materials in the Efficient Storage of Hydrogen

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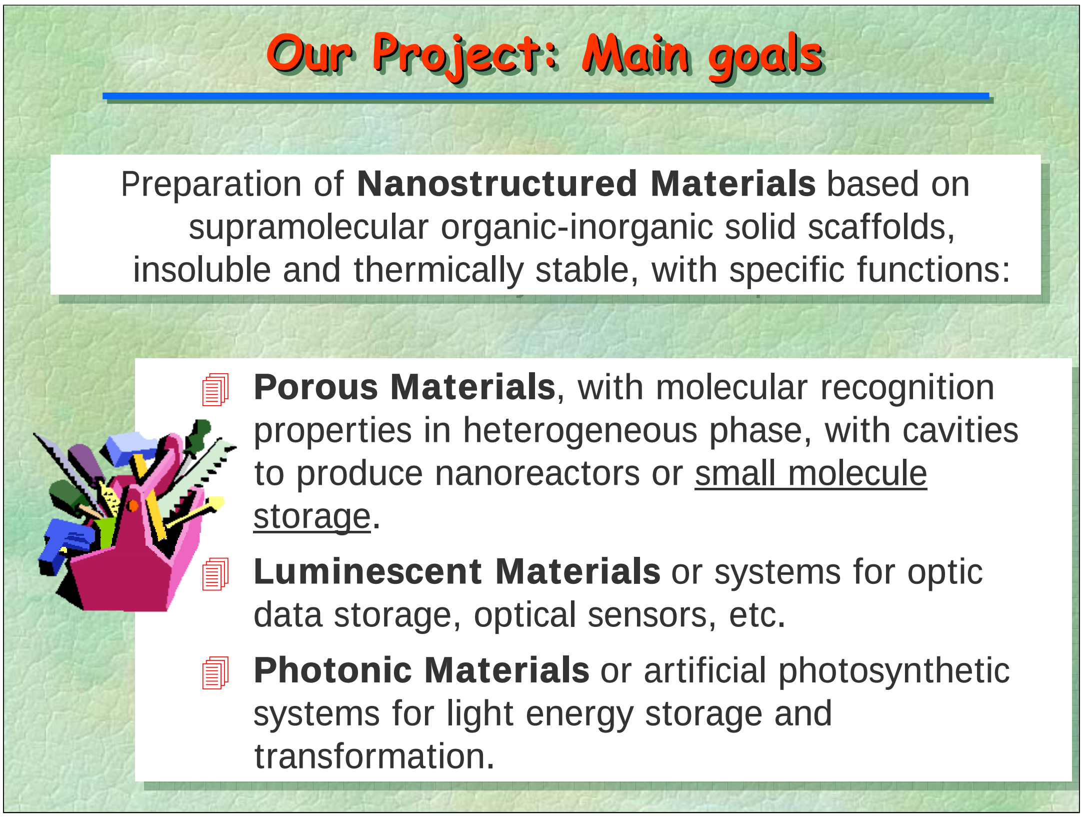
Good afternoon to everyone. I’m going to talk about the important topic of hydrogen storage, the role of porous materials to accomplish it and our modest contribution to this field.

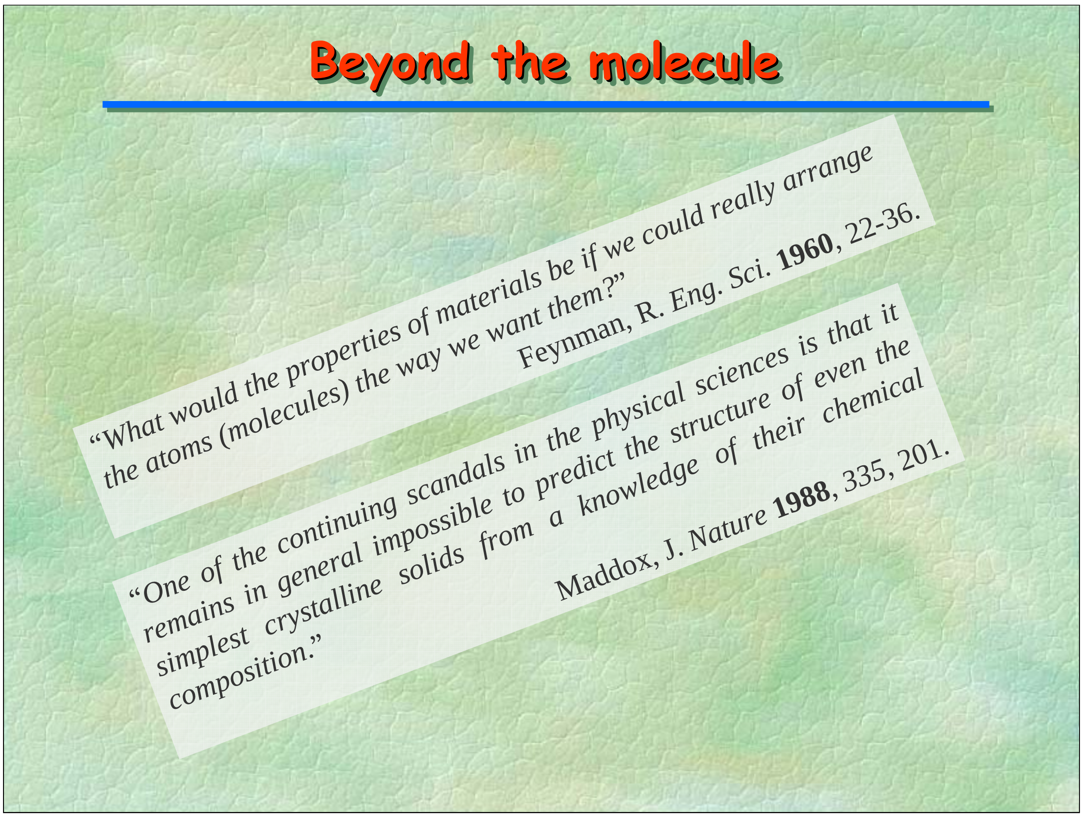


Our Project: Main goals

Preparation of **Nanostructured Materials** based on supramolecular organic-inorganic solid scaffolds, insoluble and thermically stable, with specific functions:

- **Porous Materials**, with molecular recognition properties in heterogeneous phase, with cavities to produce nanoreactors or <u>small molecule storage</u>.
- **Luminescent Materials** or systems for optic data storage, optical sensors, etc.
- **Photonic Materials** or artificial photosynthetic systems for light energy storage and transformation.

The goals of our current project on the preparation of nanostructured materials is three fold: porous materials… luminescent materials… photonic materials…



Beyond the molecule

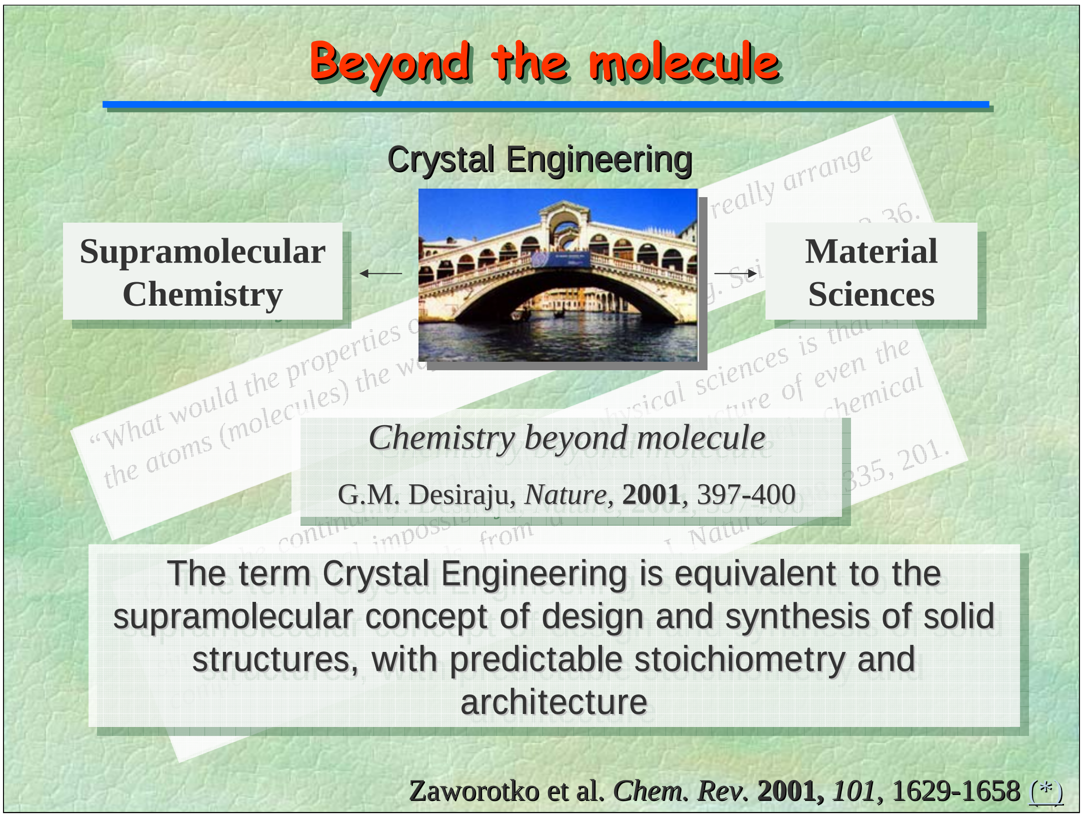
“What would the properties of materials be if we could really arrange the atoms (molecules) the way we want them?”

Feynman, R. Eng. Sci. **1960**, 22-36.

“One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition.”

Maddox, J. Nature **1988**, 335, 201.

The design of a solid material is still difficult today because the provocative opinions of Feynman and Maddox still hold almost untouched. To help solve these problems new trends has come.



Beyond the molecule

Crystal Engineering

Supramolecular Chemistry ← → **Material Sciences**

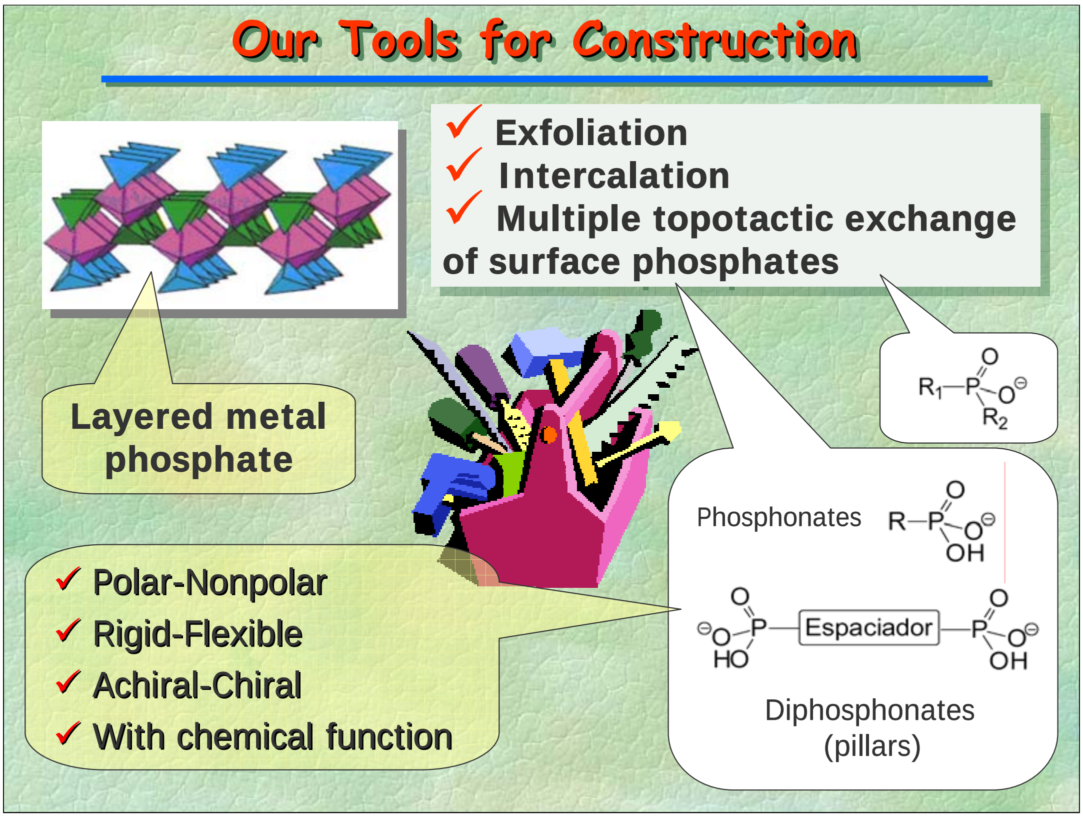
Chemistry beyond molecule

G.M. Desiraju, *Nature*, **2001**, 397-400

The term Crystal Engineering is equivalent to the supramolecular concept of design and synthesis of solid structures, with predictable stoichiometry and architecture

Zaworotko et al. *Chem. Rev.* **2001,** *101*, 1629-1658 (*)

For instance, crystal engineering laying a bridge between the concepts of supramolecular chemistry, chemistry beyond the molecule, and material sciences. The term Crystal Engineering is thus equivalent to the supramolecular concept of design and synthesis of solid structures, with predictable stoichiometry and architecture



Our Tools for Construction

- ✓ Exfoliation
- ✓ Intercalation
- ✓ Multiple topotactic exchange of surface phosphates

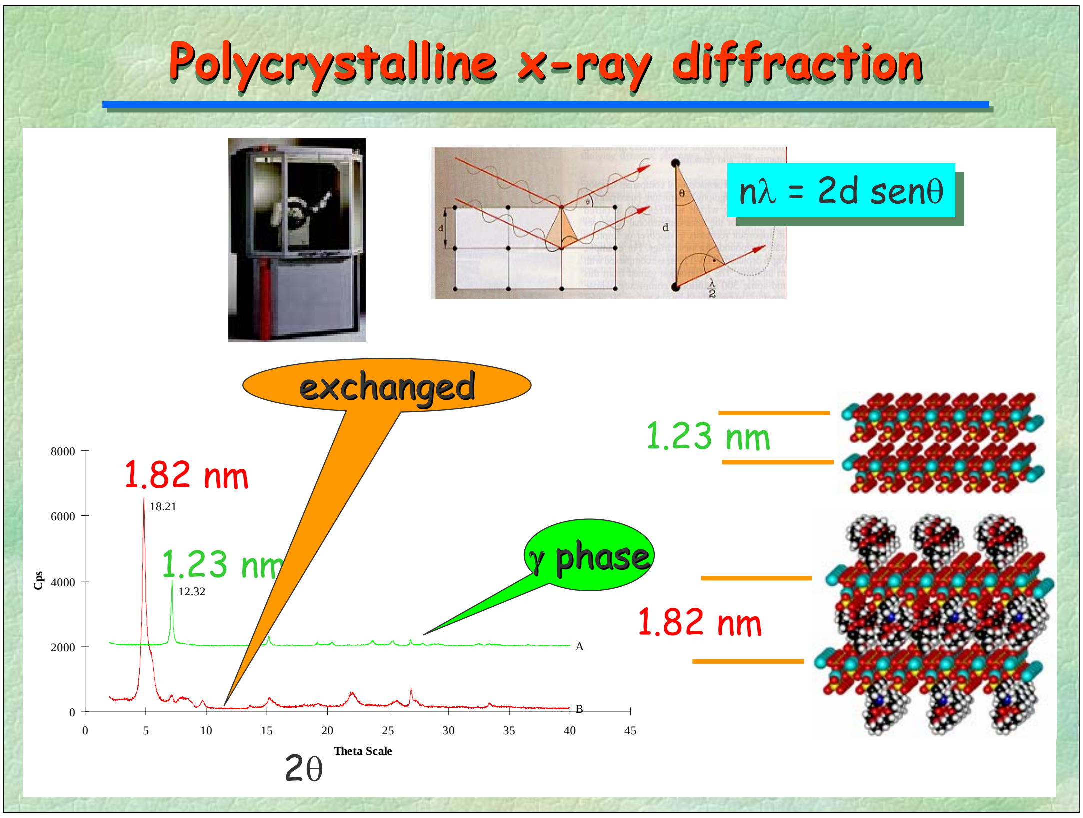
Layered metal phosphate

- ✓ Polar-Nonpolar
- ✓ Rigid-Flexible
- ✓ Achiral-Chiral
- ✓ With chemical function

Phosphonates

Diphosphonates (pillars)

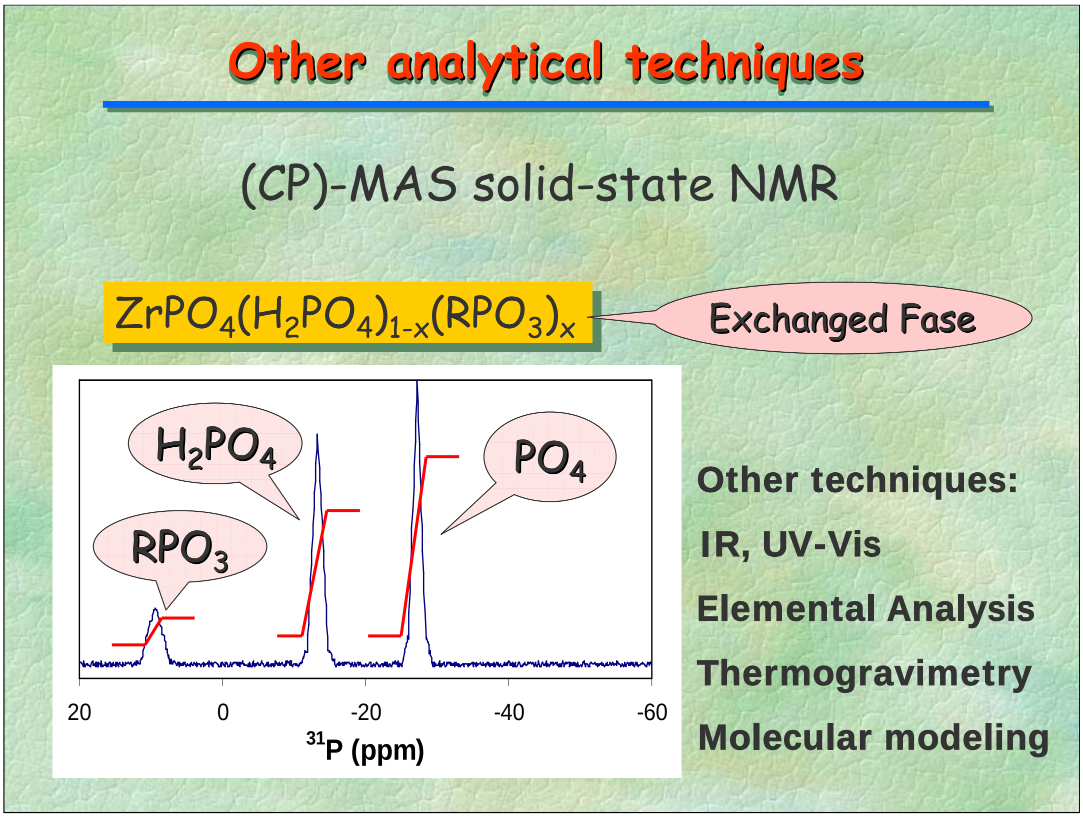
On these grounds we have developed a conceptual bottom-up approach based on the organic-inorganic structures built from layered metal phosphates. The exfoliated layers of the inorganic salt are either intercalated with organic compounds by weak interactions or the surface phosphates exchanged and the organic phosphonates covalently incorporated between the layers. This exchange occurs topotactically so, the layered structure is preserved. And it can be performed in a multiple fashion thus incorporating different organic moieties between the layers. These organic moieties can be in principle whatever you imagine, for simple polar or non-polar compounds, rigid or flexible chains, with intrinsic or extrinsic chiral properties or with any desired chemical function. The main limitation of this approach would be just the imagination of the researcher.



Polycrystalline x-ray diffraction

$n\lambda = 2d\ sen\theta$

Characterization of these materials is accomplished by polycristalline x-ray diffraction among other techniques.



Other analytical techniques

(CP)-MAS solid-state NMR

$ZrPO_4(H_2PO_4)_{1-x}(RPO_3)_x$

Exchanged Fase

Other techniques:

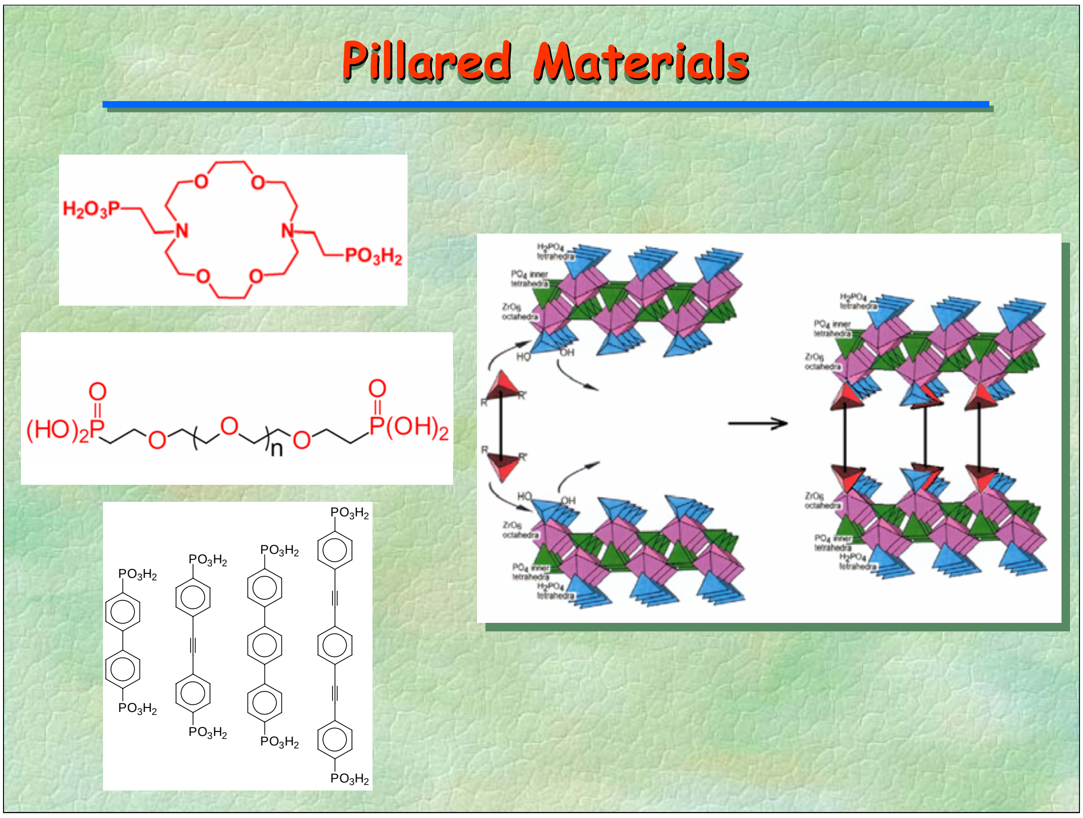
IR, UV-Vis

Elemental Analysis

Thermogravimetry

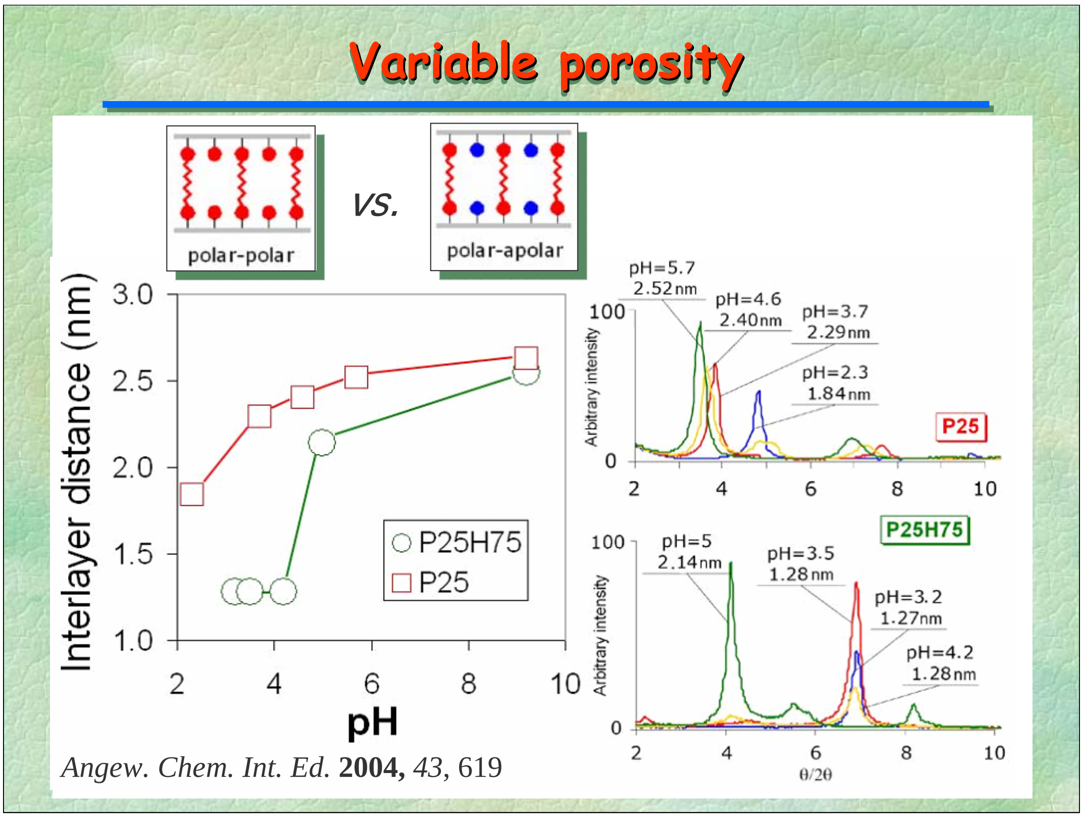
Molecular modeling

To the help of characterization of course solid-state NMR also comes, as well as other techniques like absorption spectroscopy, elemental analysis or thermogravimetry among others. Unfortunately, one cannot get single crystals from these layered materials and all the pieces of evidence have to be gathered by molecular modeling to reveal the final structure.



Pillared Materials

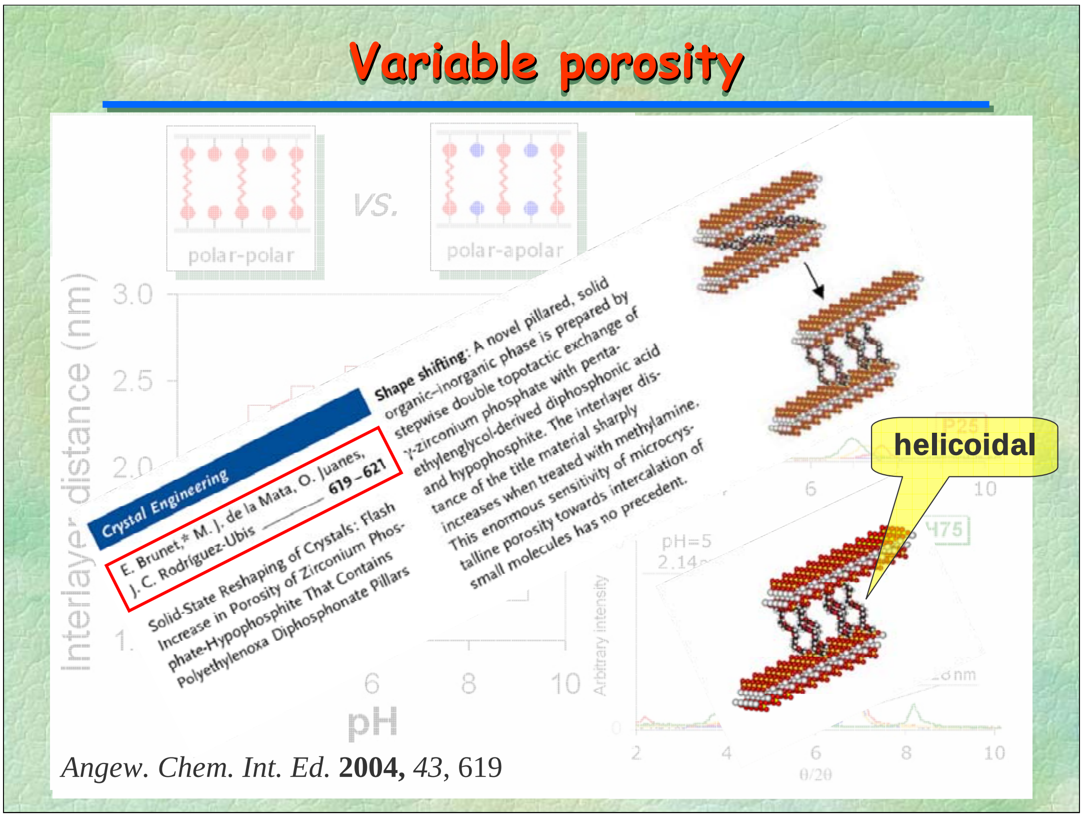
With the layered salts of zirconium phosphate we’ve been able to obtain layered materials with a large variety of diphosphonates as those displayed in the slide.



Variable porosity

Angew. Chem. Int. Ed. **2004,** *43*, 619

For instance, in recent work we were able to build a composite with huge porosity changes sensitive to pH variations in aqueous dispersion.



Variable porosity

Crystal Engineering

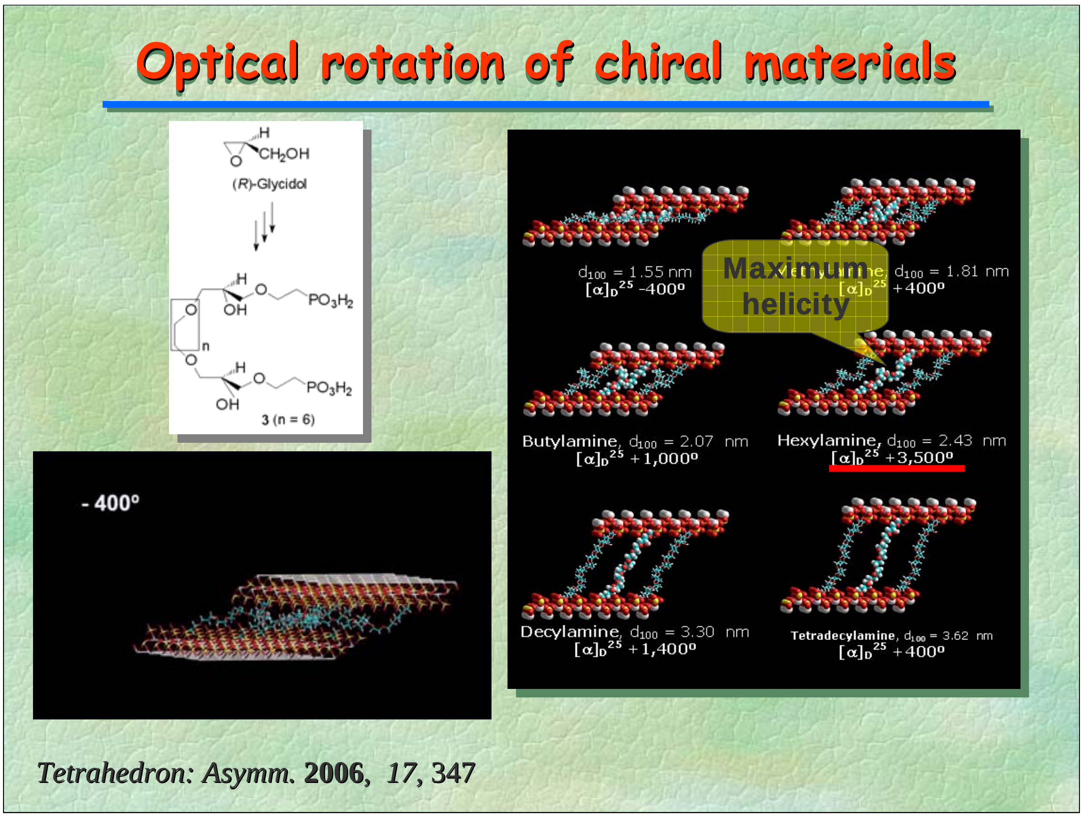
E. Brunet,* M. J. de la Mata, O. Juanes,
J. C. Rodríguez-Ubis ______ **619–621**

Solid-State Reshaping of Crystals: Flash Increase in Porosity of Zirconium Phosphate-Hypophosphite That Contains Polyethylenoxa Diphosphonate Pillars

Shape shifting: A novel pillared, solid organic–inorganic phase is prepared by stepwise double topotactic exchange of γ-zirconium phosphate with pentaethylenglycol-derived diphosphonic acid and hypophosphite. The interlayer distance of the title material sharply increases when treated with methylamine. This enormous sensitivity of microcrystalline porosity towards intercalation of small molecules has no precedent.

Angew. Chem. Int. Ed. **2004,** *43*, 619

Polycristalline X-ray diffraction studies suggested that the polyethylenoxa chains adopted an helicoidal arrangement, opening the possibility of observing supramolecular chiralty in the solid state which we demonstrated for the first time in a further study by means of the synthesis of polyethylenoxa chains containing stereocenters.

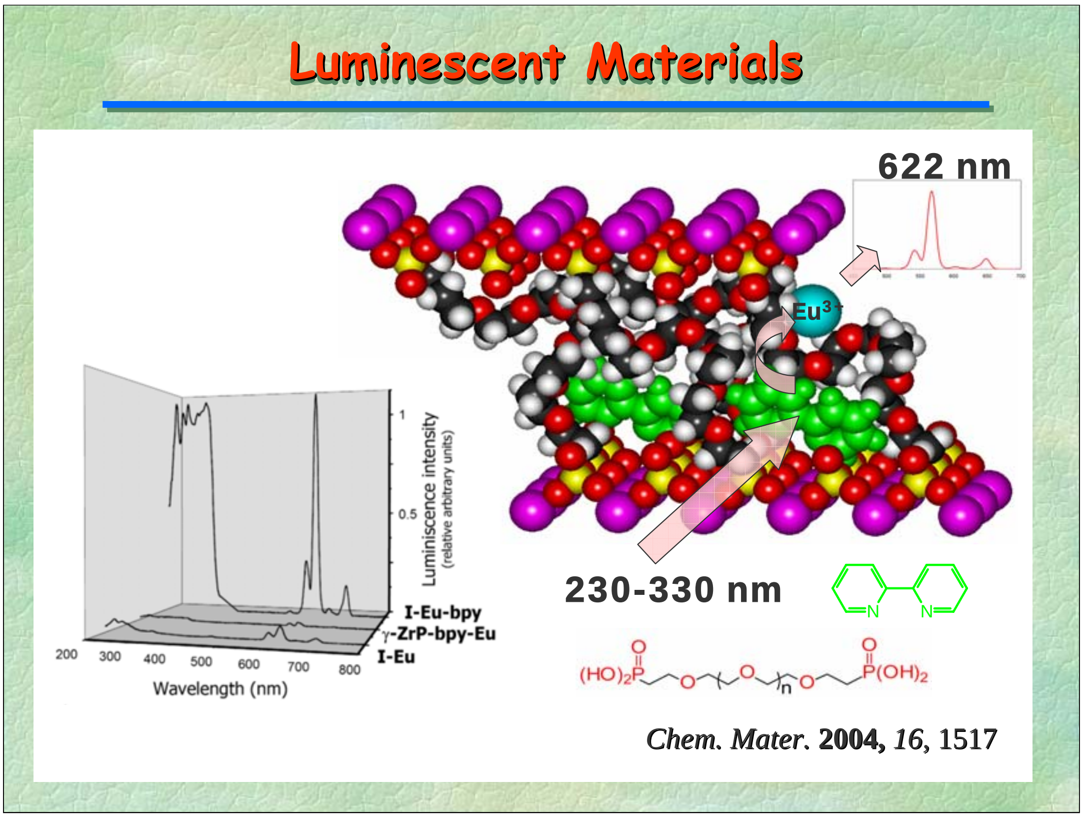


Optical rotation of chiral materials

Tetrahedron: Asymm. **2006**, *17*, 347

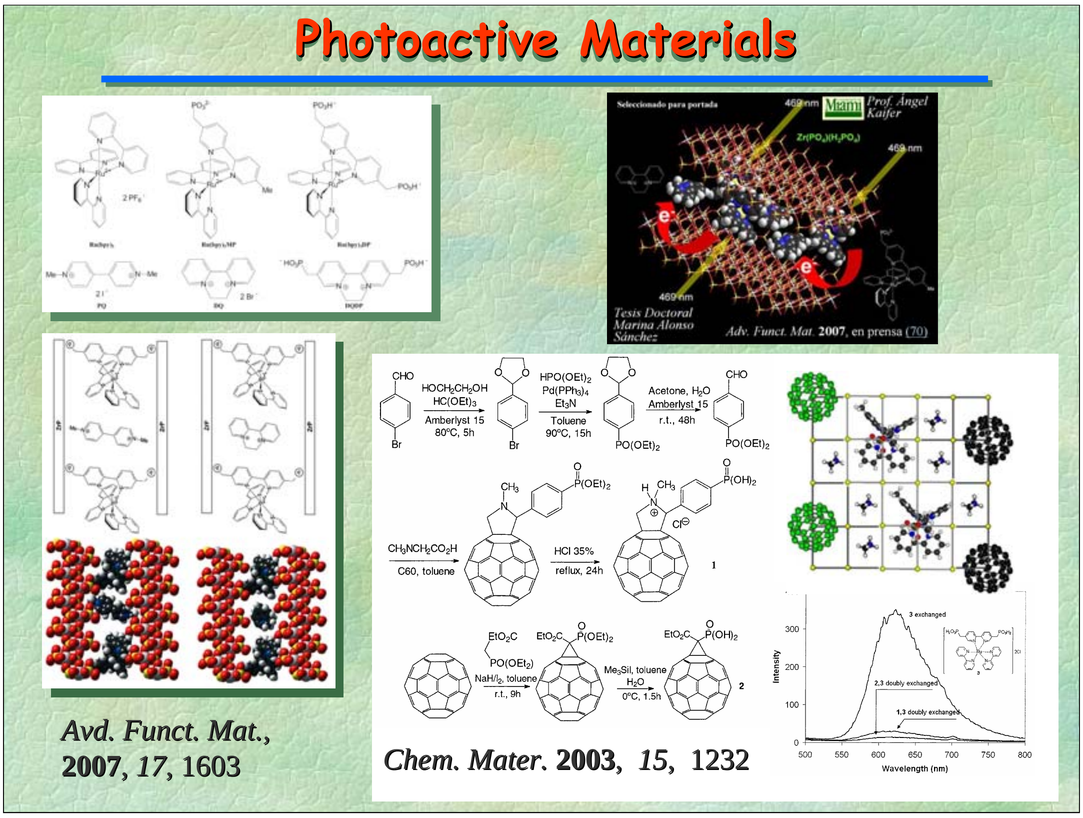
We thus observed huge changes of the optical rotation of the material in bulk dispersions in water occasioned by the simple intercalation of alkyl amines of increasing length. The animated Figure shows the molecular mechanics simulation of a couple of organic-inorganic layers showing how the optical rotation qualitatively correlates to the helicity of the organic chains with increasing interlayer distance. This is the most plausible explanation of the large optical rotation changes observed experimentally.

Luminescent Materials



Chem. Mater. **2004**, *16*, 1517

These materials containing polyethylenoxa pillars were also converted into highly luminescent materials by simple lanthanide ion exchange and the intercalation of simple sensitizers as bipyridine. We expect these materials to be the starting point to prepare luminescent solids as signaling devices for an wide range of different organic species.

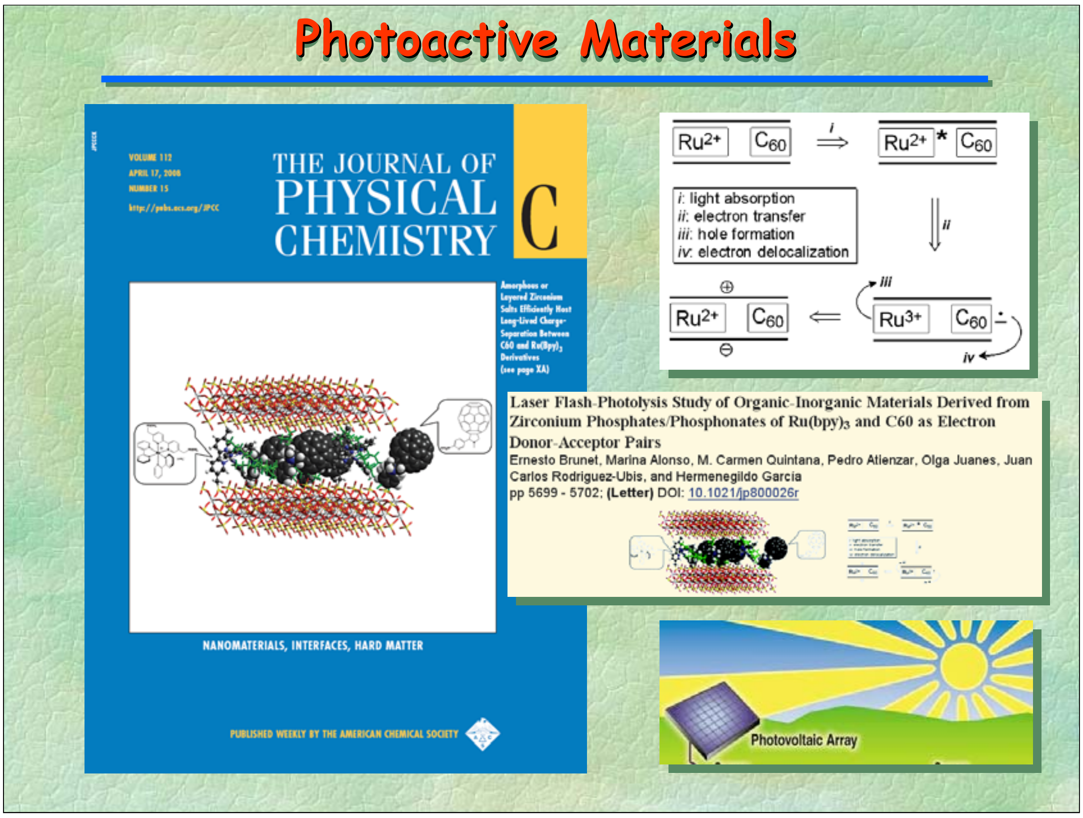


Photoactive Materials

Avd. Funct. Mat., **2007**, *17*, 1603

Chem. Mater. **2003**, *15*, 1232

We have been also capable of introducing, within the layers of the inorganic salt, electron donor and acceptor species as the classical ruthenium trisbipy and viologens or fullerene. The quenching of the luminescence of the ruthenium complex marks the accomplishment of the sought charge transfer between the active species.



Photoactive Materials

JPCCCK

VOLUME 112
APRIL 17, 2008
NUMBER 15
http://pubs.acs.org/JPCC

THE JOURNAL OF
PHYSICAL
CHEMISTRY
C

Amorphous or Layered Zirconium Salts Efficiently Host Long-Lived Charge-Separation Between C60 and $Ru(Bpy)_3$ Derivatives (see page XA)

NANOMATERIALS, INTERFACES, HARD MATTER

PUBLISHED WEEKLY BY THE AMERICAN CHEMICAL SOCIETY

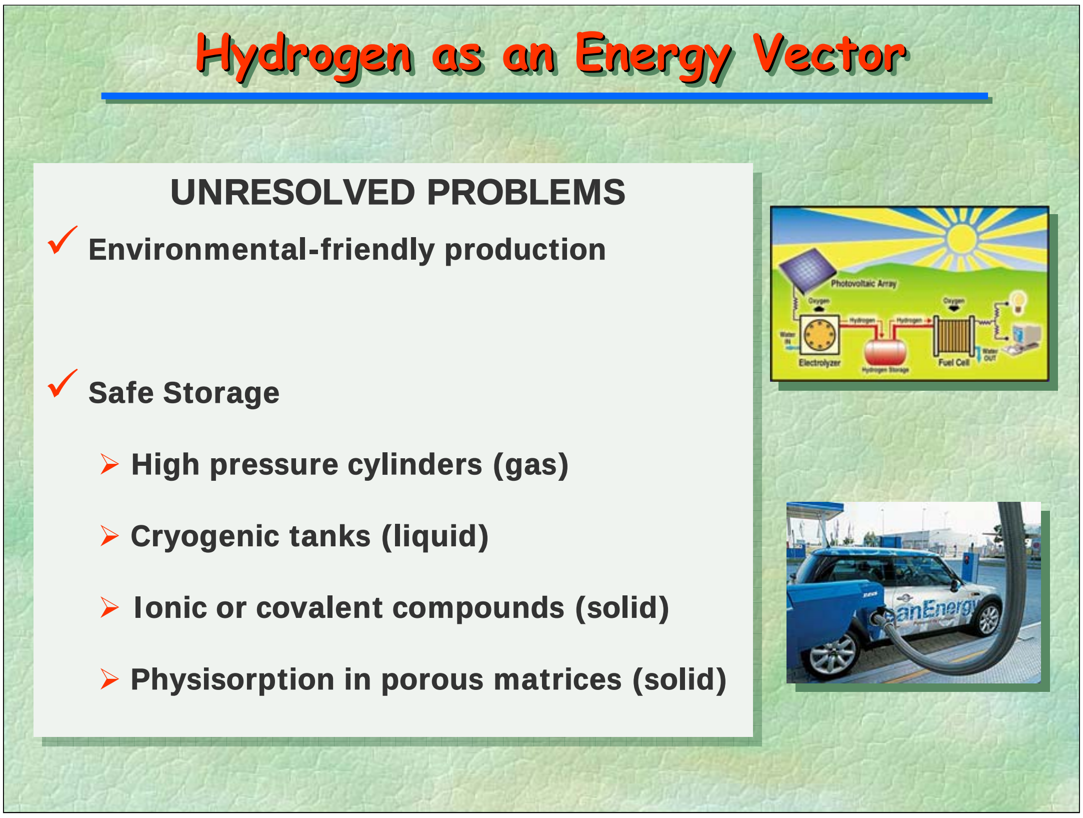
i: light absorption
ii: electron transfer
iii: hole formation
iv: electron delocalization

Laser Flash-Photolysis Study of Organic-Inorganic Materials Derived from Zirconium Phosphates/Phosphonates of $Ru(bpy)_3$ and C60 as Electron Donor-Acceptor Pairs

Ernesto Brunet, Marina Alonso, M. Carmen Quintana, Pedro Atienzar, Olga Juanes, Juan Carlos Rodriguez-Ubis, and Hermenegildo Garcia

pp 5699 - 5702; **(Letter)** DOI: 10.1021/jp800026r

Very recently, flash photolysis revealed some of these materials to have outstanding properties in that the separation of charges is long lived and the initially thought inert inorganic layer resulted semiconducting thus driving the separated electrons and/or holes along the material. Very preliminary results showed that these powders can be arranged as solar cells with promising efficiency.



Hydrogen as an Energy Vector

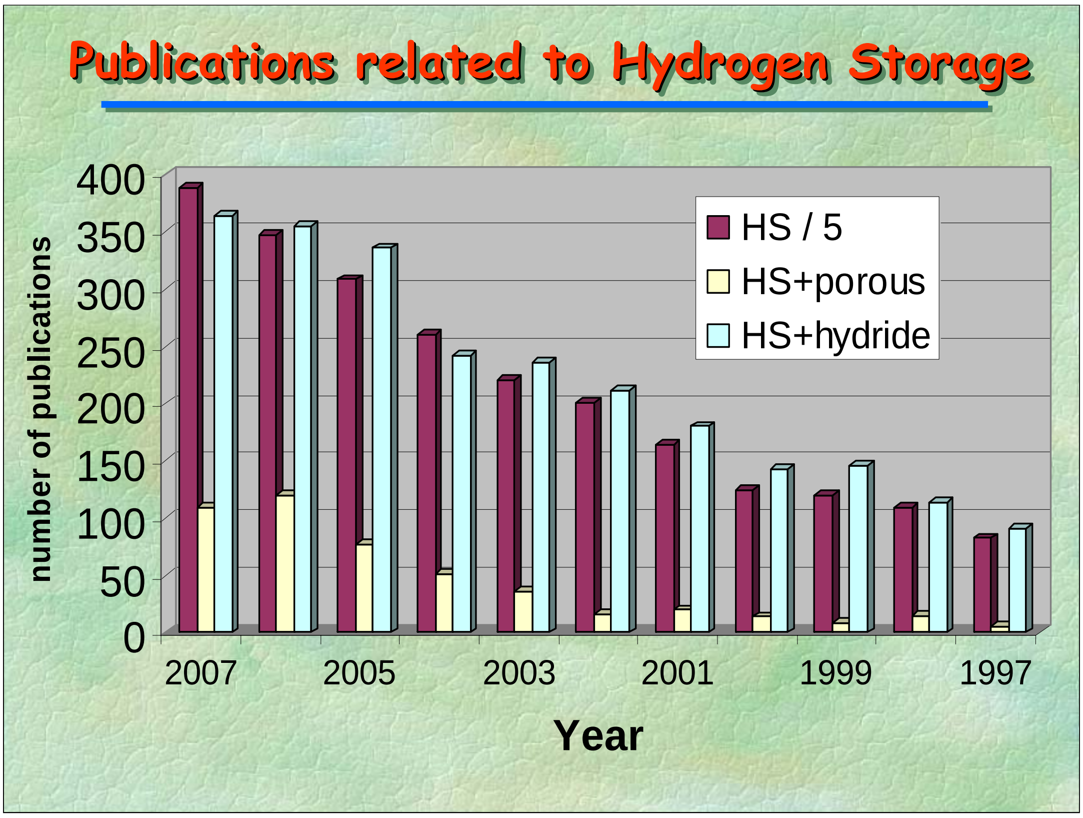
UNRESOLVED PROBLEMS

✓ **Environmental-friendly production**

✓ **Safe Storage**

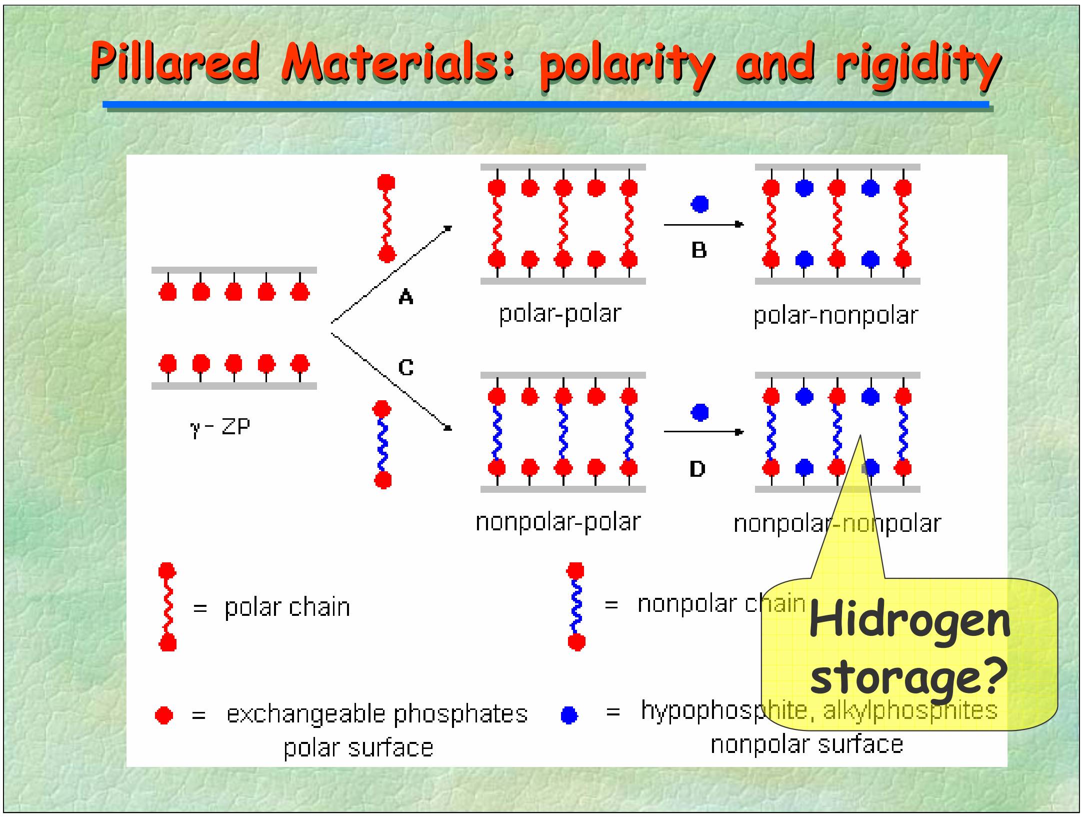
- **High pressure cylinders (gas)**
- **Cryogenic tanks (liquid)**
- **Ionic or covalent compounds (solid)**
- **Physisorption in porous matrices (solid)**

But after this huge digression concerning our recent results in different areas, let’s stick to the point of hydrogen storage. Hydrogen is a very appealing energy vector: the release of its energy does not involve the noxious carbon dioxide. Yet, it is becoming a well known fact by our society that two problems must be solved if hydrogen is to be efficient and safely used as the clean energy carrier of the future: *i*) its environmental-friendly production and *ii*) its safe storage and transportation. Although there are already many reasonably useful technical approaches, neither of the two problems is nowadays at a level of resolution which would make the use of hydrogen routinely possible. Concerning the second one, hydrogen storage may be attained by at least four main methods: *i*) in high-pressure cylinders as a gas, *ii*) as a liquid in cryogenic tanks as a liquid, *iii*) chemisorbed in ionic or covalent compounds as a solid, and *iv*) by *physisorption* in porous matrices as sorbed gas in a solid.



Publications related to Hydrogen Storage

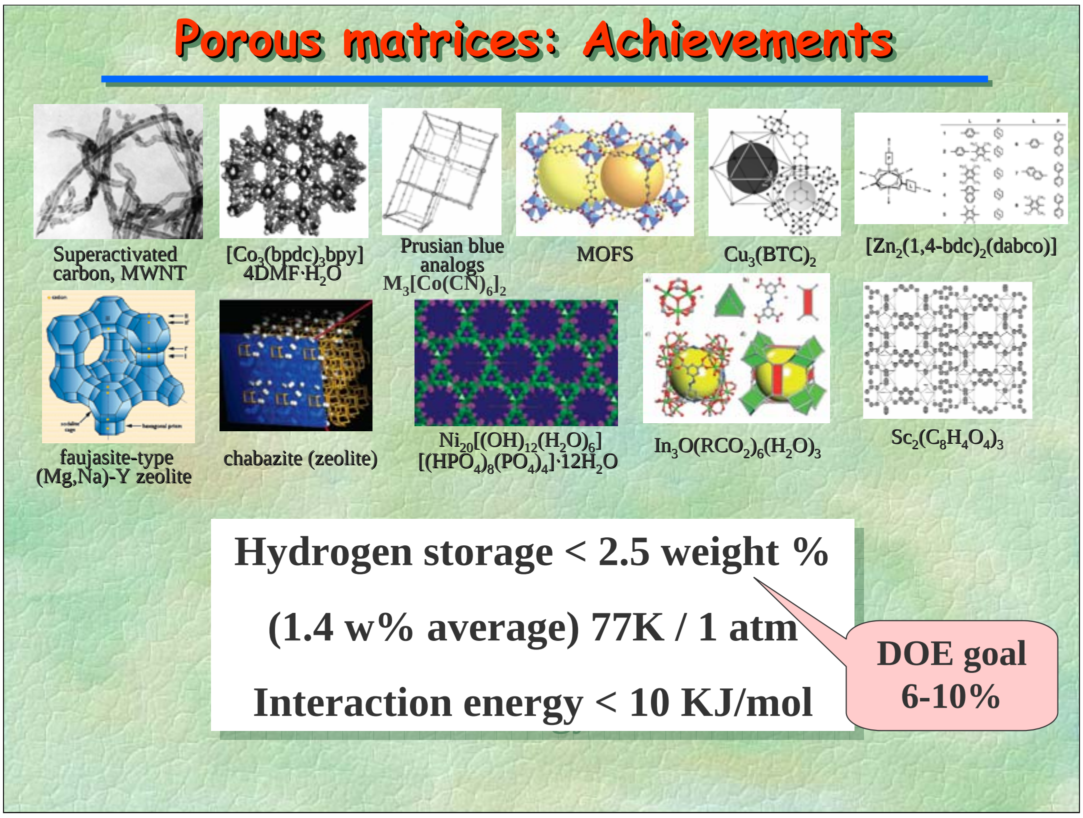
The storage of hydrogen is clearly a hot topic of research since the publications containing the term “Hydrogen Storage” have dramatically increased in the last decade, reaching in the last year the number of almost 2000 papers of which more than a third are patents. When one crosses the term “Hydrogen Storage” with “porous” the number of papers, negligible ten years ago, have also observed a boost in recent times, although the number of investigations related to chemisorption is much larger.



Pillared Materials: polarity and rigidity

Hidrogen storage?

After reading some literature the question became obvious to us. Would it be possible to store hydrogen in systems like ours?



Porous matrices: Achievements

Superactivated carbon, MWNT

$[Co_3(bpdc)_3bpy] \cdot 4DMF \cdot H_2O$

Prusian blue analogs $M_3[Co(CN)_6]_2$

MOFS

$Cu_3(BTC)_2$

$[Zn_2(1,4\text{-}bdc)_2(dabco)]$

faujasite-type (Mg,Na)-Y zeolite

chabazite (zeolite)

$Ni_{20}[(OH)_{12}(H_2O)_6][(HPO_4)_8(PO_4)_4] \cdot 12H_2O$

$In_3O(RCO_2)_6(H_2O)_3$

$Sc_2(C_8H_4O_4)_3$

Hydrogen storage < 2.5 weight %

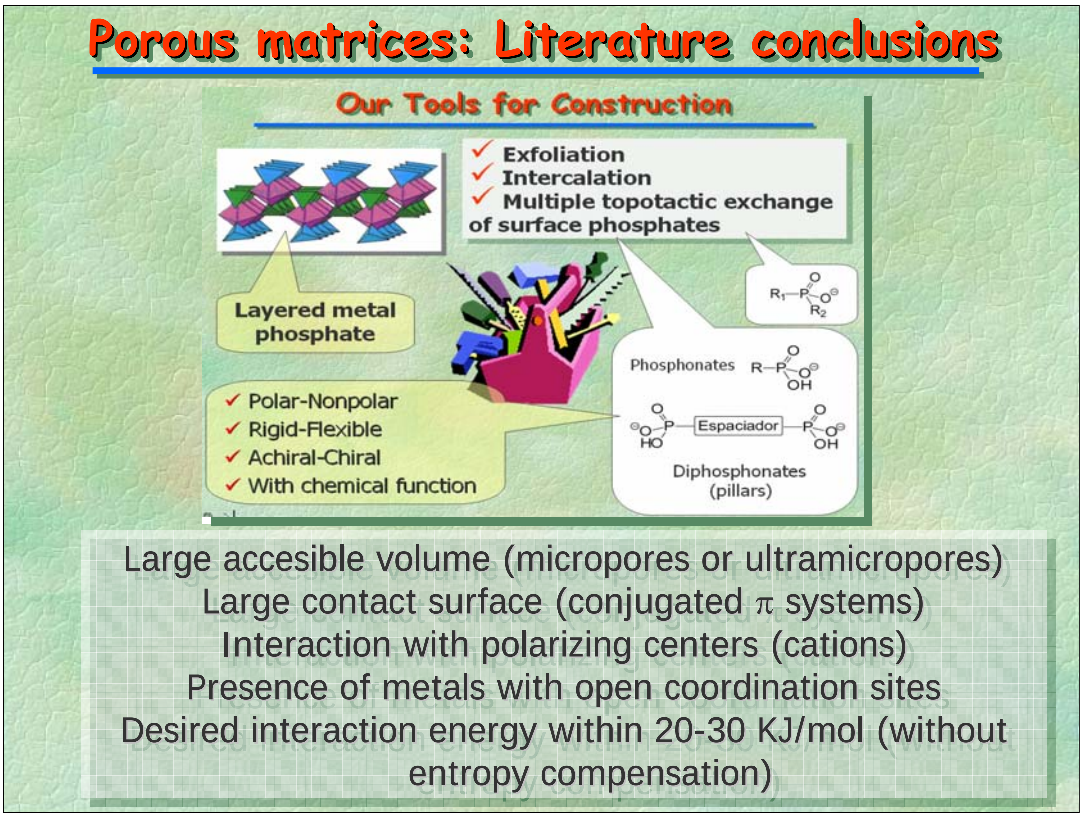
(1.4 w% average) 77K / 1 atm

Interaction energy < 10 KJ/mol

DOE goal 6-10%

The thorough revision of the literature allows one to find numerous organic, inorganic and hybrid systems in which the storage of hydrogen has been tested. From the delusion concerning carbon nanotubes to the very cleverly designed systems with almost unbelievable specific surface areas higher than 5000 m2/g.

But to the best of my knowledge, all the systems found in the literature up to today showed an average of 1.4 weight % of sorbed hydrogen at the usual conditions of measurement, namely nitrogen boiling point and 1 atm, and a limit of 2-3 weight % of sorbed hydrogen appears to be very difficult to be overcome and still far apart from The Department of Energy of the States’ goal. The interaction of the hydrogen molecules with the different systems has been measured to be very weak, below 10 KJ/mol.



Porous matrices: Literature conclusions

Our Tools for Construction

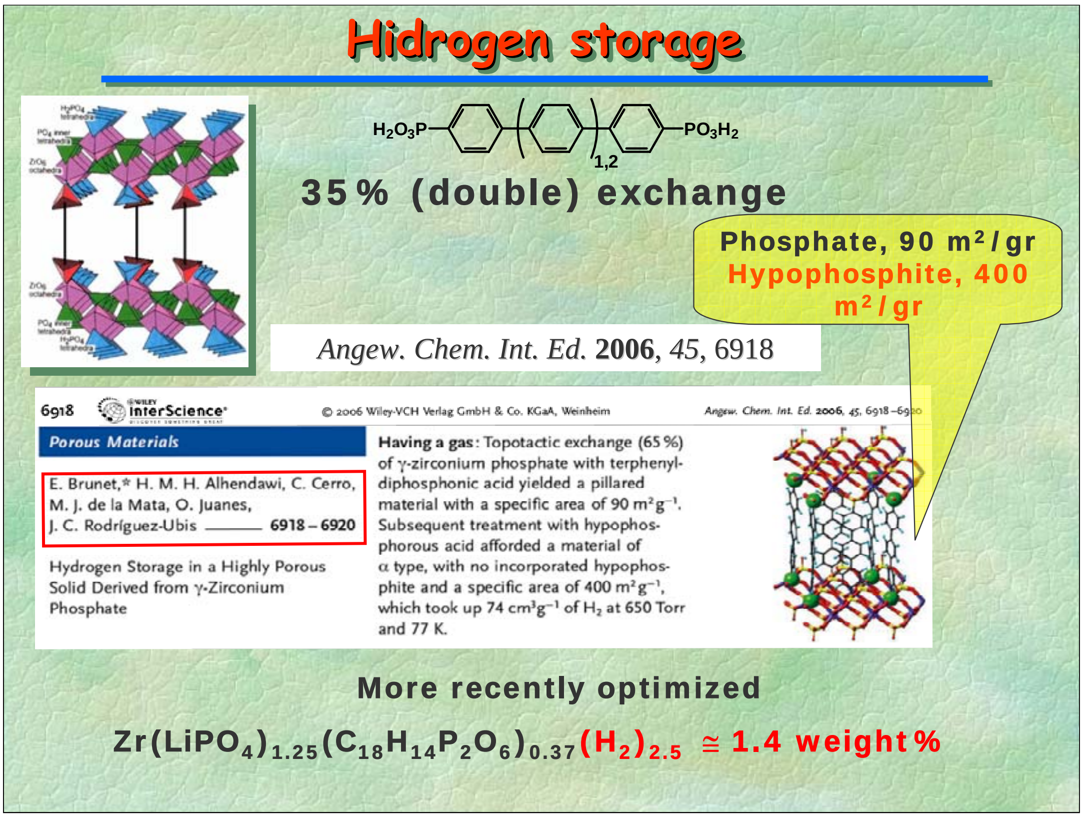
- ✓ Exfoliation
- ✓ Intercalation
- ✓ Multiple topotactic exchange of surface phosphates

Layered metal phosphate

- ✓ Polar-Nonpolar
- ✓ Rigid-Flexible
- ✓ Achiral-Chiral
- ✓ With chemical function

Large accesible volume (micropores or ultramicropores)
Large contact surface (conjugated π systems)
Interaction with polarizing centers (cations)
Presence of metals with open coordination sites
Desired interaction energy within 20-30 KJ/mol (without entropy compensation)

The Figure shows the relationship between the specific surface areas and the weight % of hydrgen storage at the mentioned conditions. Although a lot of effort has been placed in the design of very hollow structures, the results have been a bit deceptive because a very large surface area appears not to secure high hydrogen storage values. The analysis of the different structures points to the conclusion that a large accessible volume is desirable but by means of micropores or ultramicropores and therefore presenting a large internal contact surface to the elusive hydrogen molecules. Some interesting theoretical studies and experimental ones on zeolites also points to the benefit of having polarizing centers, namely small cations as for instance Li+. Also the presence of transition metals with open coordination sites appears to be important. However, all these envisaged conditions have not been achieved yet together in a material with the aim of attaining the desired goal of an interaction energy of 20-30 KJ/mol without entropy compensation. (CLICK) We believe that our already mentioned set of tools might allow us to design appropriate materials for hydrogen storage.



Hidrogen storage

35% (double) exchange

Phosphate, 90 m^2/gr
Hypophosphite, 400 m^2/gr

Angew. Chem. Int. Ed. **2006**, *45*, 6918

6918 InterScience® © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim *Angew. Chem. Int. Ed.* **2006**, *45*, 6918–6920

Porous Materials

E. Brunet,* H. M. H. Alhendawi, C. Cerro,
M. J. de la Mata, O. Juanes,
J. C. Rodríguez-Ubis ——— **6918 – 6920**

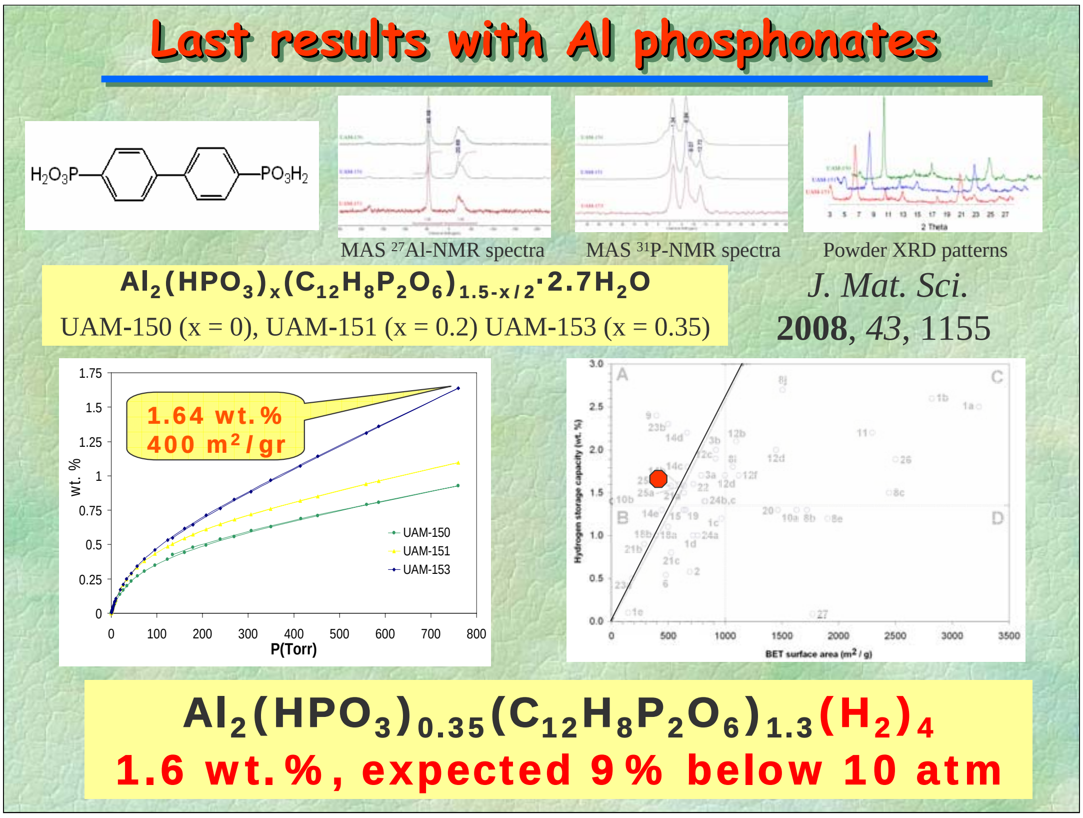
Hydrogen Storage in a Highly Porous Solid Derived from γ-Zirconium Phosphate

Having a gas: Topotactic exchange (65%) of γ-zirconium phosphate with terphenyldiphosphonic acid yielded a pillared material with a specific area of 90 m^2g^{-1}. Subsequent treatment with hypophosphorous acid afforded a material of α type, with no incorporated hypophosphite and a specific area of 400 m^2g^{-1}, which took up 74 cm^3g^{-1} of H_2 at 650 Torr and 77 K.

More recently optimized

$Zr(LiPO_4)_{1.25}(C_{18}H_{14}P_2O_6)_{0.37}(H_2)_{2.5} \cong$ **1.4 weight%**

Unfortunately our results have been very modest. Despite that, we were able to publish in Angew our first result, which proofs the hotness of the topic. By using rigid diphosphonates derived for polyphenyl chains and the exchange of protons by lithium ions we reached the decent value of 1.4 weight % with relatively small surface areas.



Last results with Al phosphonates

MAS ^{27}Al-NMR spectra MAS ^{31}P-NMR spectra Powder XRD patterns

$Al_2(HPO_3)_x(C_{12}H_8P_2O_6)_{1.5-x/2}\cdot 2.7H_2O$

UAM-150 (x = 0), UAM-151 (x = 0.2) UAM-153 (x = 0.35)

J. Mat. Sci.
2008, *43*, 1155

1.64 wt.%
400 m^2/gr

$Al_2(HPO_3)_{0.35}(C_{12}H_8P_2O_6)_{1.3}(H_2)_4$

1.6 wt.%, expected 9% below 10 atm

Using Al phosphates containing different amounts of phosphite we were closer to 2 weight %. But importantly, the slope of the hydrogen isotherm at 77K and 1 atm suggests that the DOE goal could be reached at as low pressures as 10-15 atm. You may take into account that hydrogen in cylinders at 200-400 atm represents less that 4% of the whole pressurized arrangement. Therefore the solid sorbent would highly alleviate the hazard of a very high pressure.

Conclusion and Acknowledgements

We continue the work under a high stress of pessimism

Juan Carlos Rodríguez Ubis
Olga Juanes Recio

Susana Jabardo
Manuel Huelva
Raquel Vázquez
María José de la Mata
José Antonio Martín

Marina Alonso
Carlos Cerro
Rosa Sedano
Hussein MH AlHendawi
Laura Jiménez

Although we are trying to work hard in this field, I must admit that the obtained results put us under a high stress of pessimism. My acknowledgement to all my collaborators through all these years, to the financing sources and to you for your kind attention.