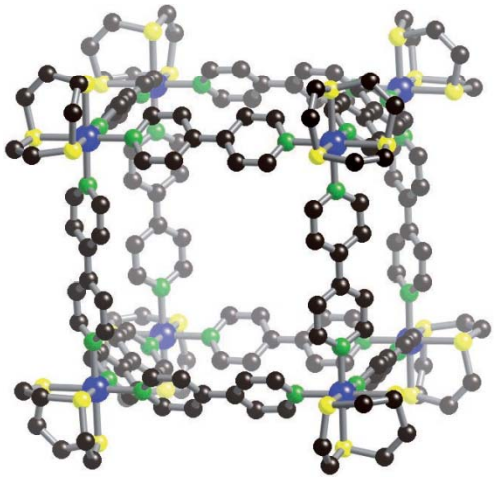
UNIVERSIDAD NACIONAL DE COLOMBIA

Seminario Internacional Nanociencia 2010, Universidad del Norte, Barranquilla, Colombia, 21-23 de octubre de 2010

Metal Organic Polyhedra, MOP & Metal Organic Frameworks, MOF



Álvaro Duarte Ruiz
Chemist , Dr. rer. nat
Associate Professor
aduarter@unal.edu.co
Department of Chemistry, Office 413
Universidad Nacional de Colombia- Bogotá D.C.


MOF nanocube: marketed by BASF as *Basolite*

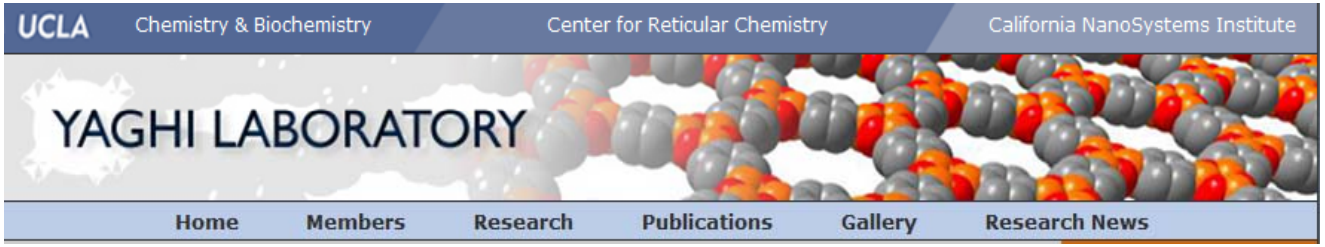
Content

1. Top researchers in the field and suggested bibliography.
2. Political Impact on Society and Economic funding from Institutions/ Industries / Research Centers.
3. Concepts of Supramolecular Chemistry and Network Solids.
4. Metal Organic Frameworks & Metal Organic Polyhedra: Synthesis and properties.
5. Applications.
6. Ongoing Research at the UNAL and PostGraduate Course.

Top Researchers in the Field

Prof. Jean-Marie Lehn, University of Strasbourg
Nobel Prize 1987, Chemistry

Prof. Makoto Fujita, The University of Tokio



Prof. Omar Yaghi, University of California L.A.

Prof. Peter Stang, The University of Utah

The Kitagawa Group

北 川 研 究 室

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University

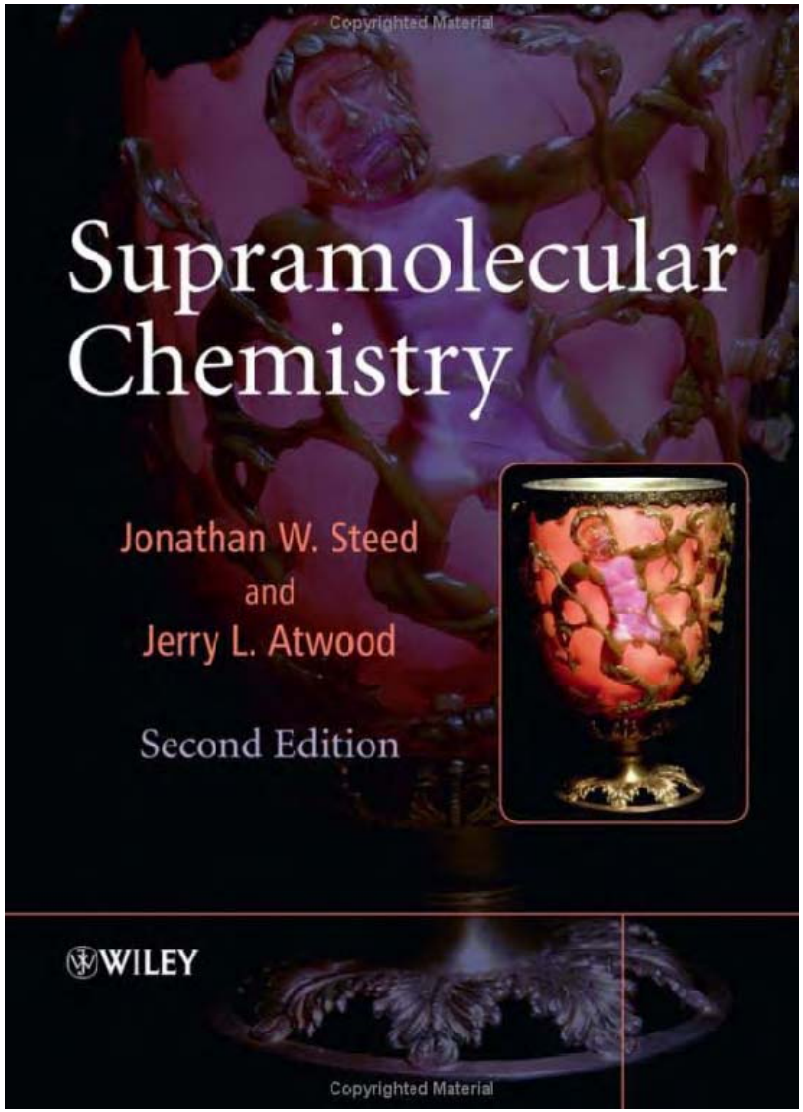
Prof. Susumu Kitagawa, Kyoto University

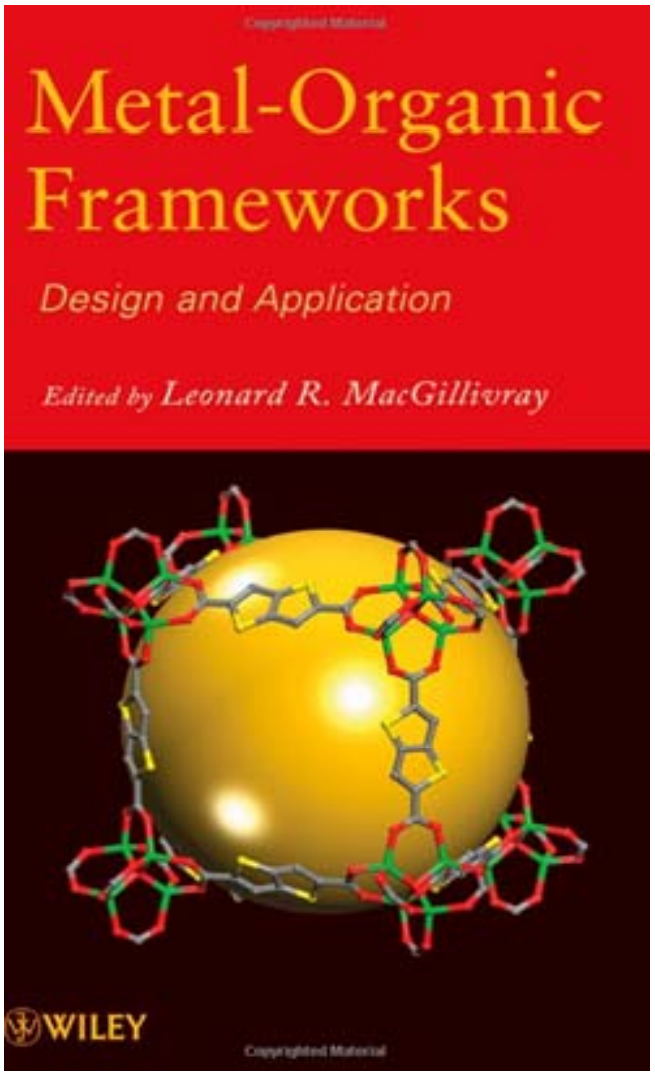
Prof. Jerry Atwood, University of Missouri

Prof. Kenneth Raymond, University of California, Berckeley

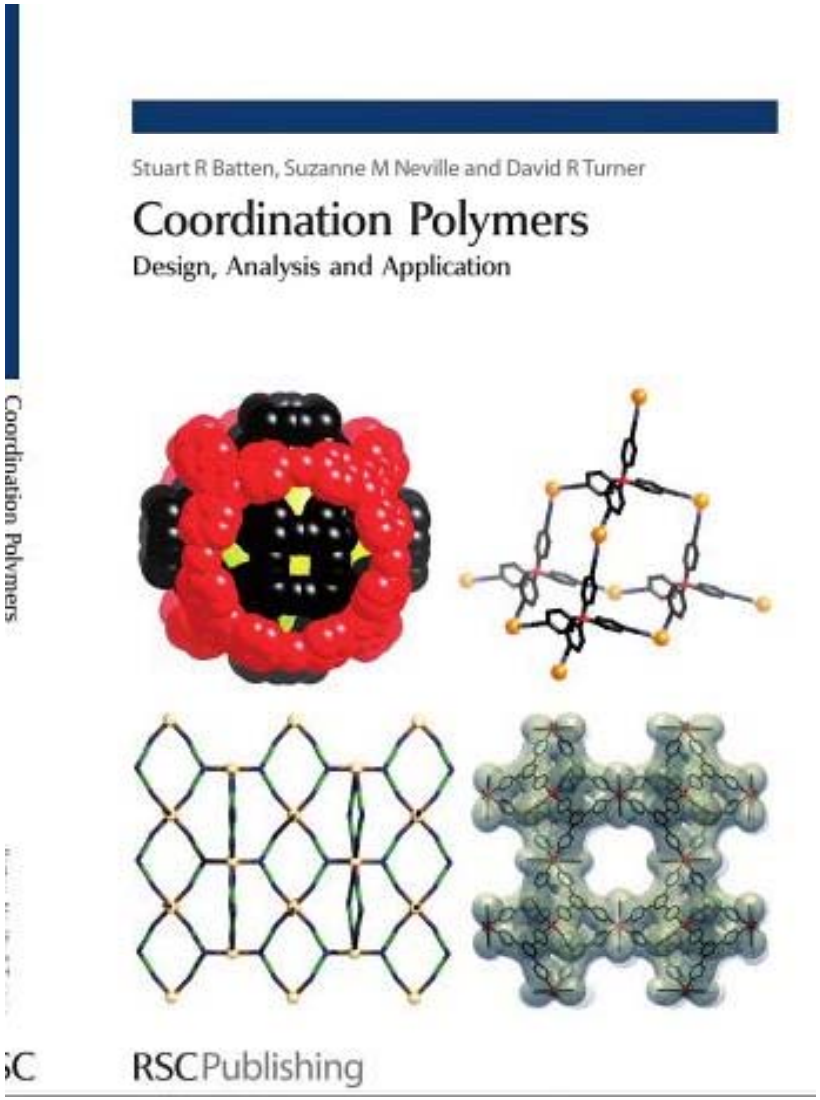
Suggested Bibliography

Books





Suggested Bibliography



Suggested Bibliography

Metal–Organic Polyhedra

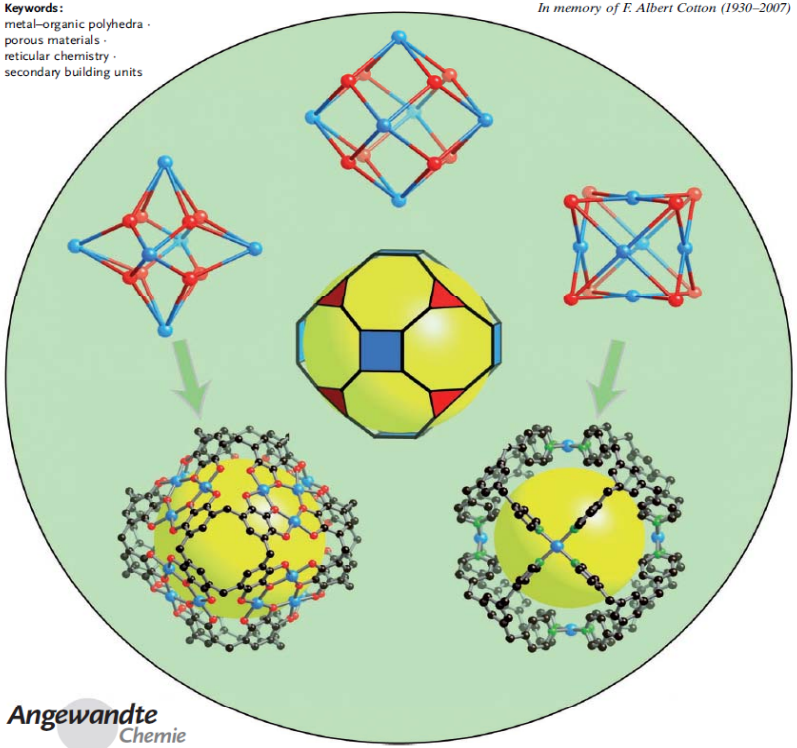
DOI: 10.1002/anie.200705008

Reticular Chemistry of Metal–Organic Polyhedra

David J. Tranchemontagne, Zheng Ni, Michael O'Keeffe, and Omar M. Yaghi**

Keywords:
metal–organic polyhedra ·
porous materials ·
reticular chemistry ·
secondary building units

In memory of F. Albert Cotton (1930–2007)



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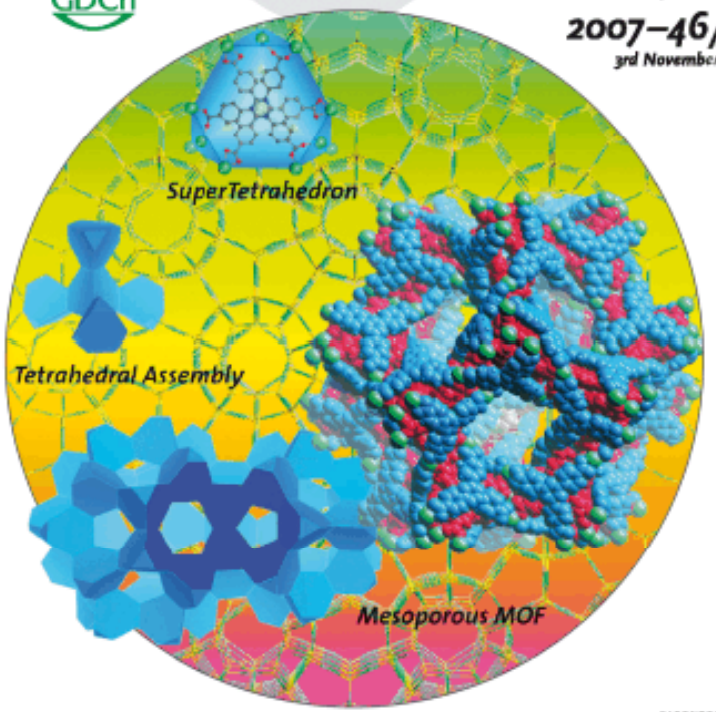
2007–46/43

3rd November Issue



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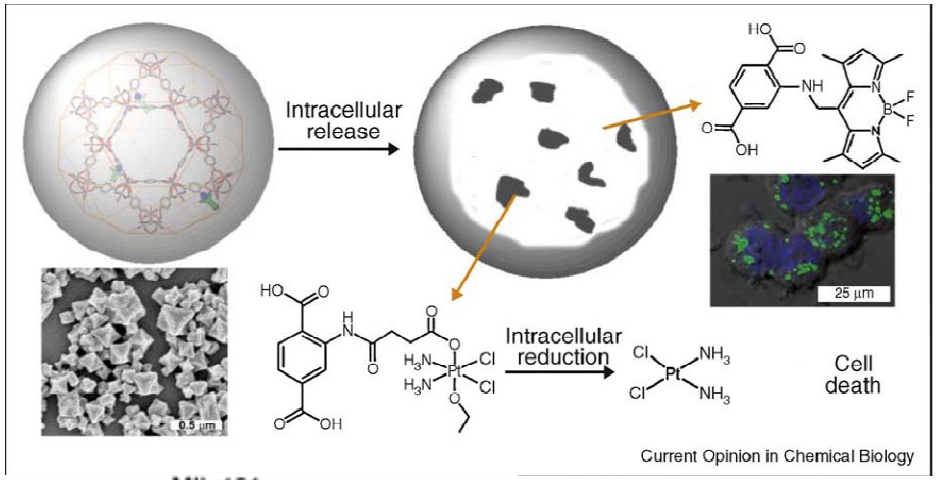
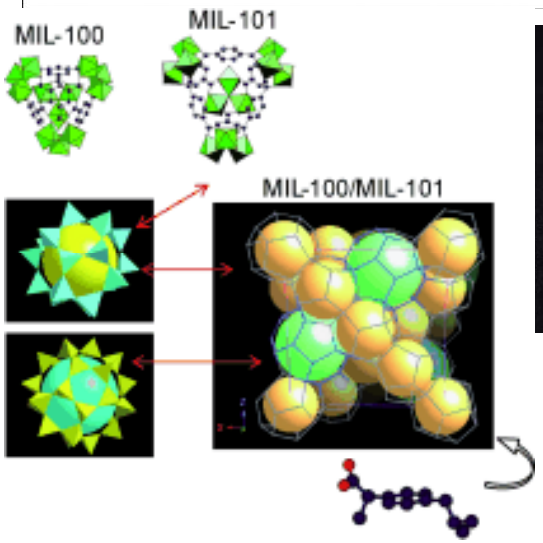
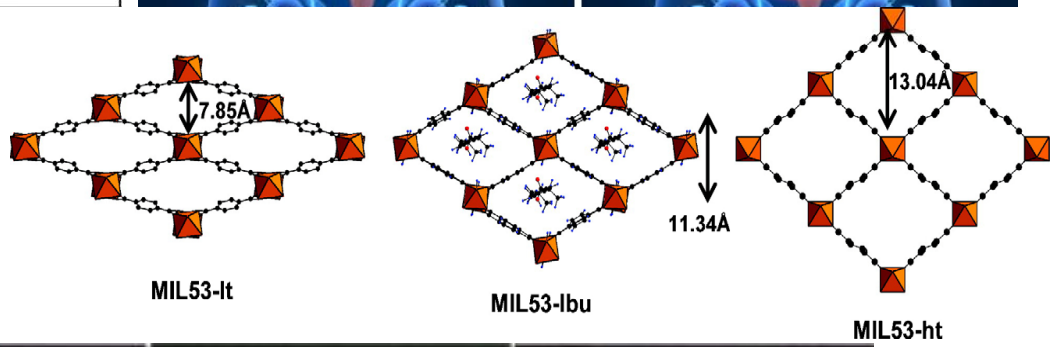
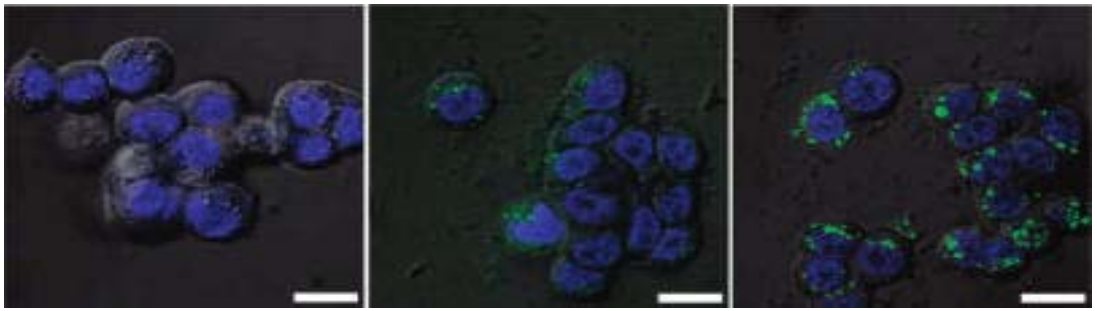
CO_2 Is Becoming a Serious Problem

Drug Delivery

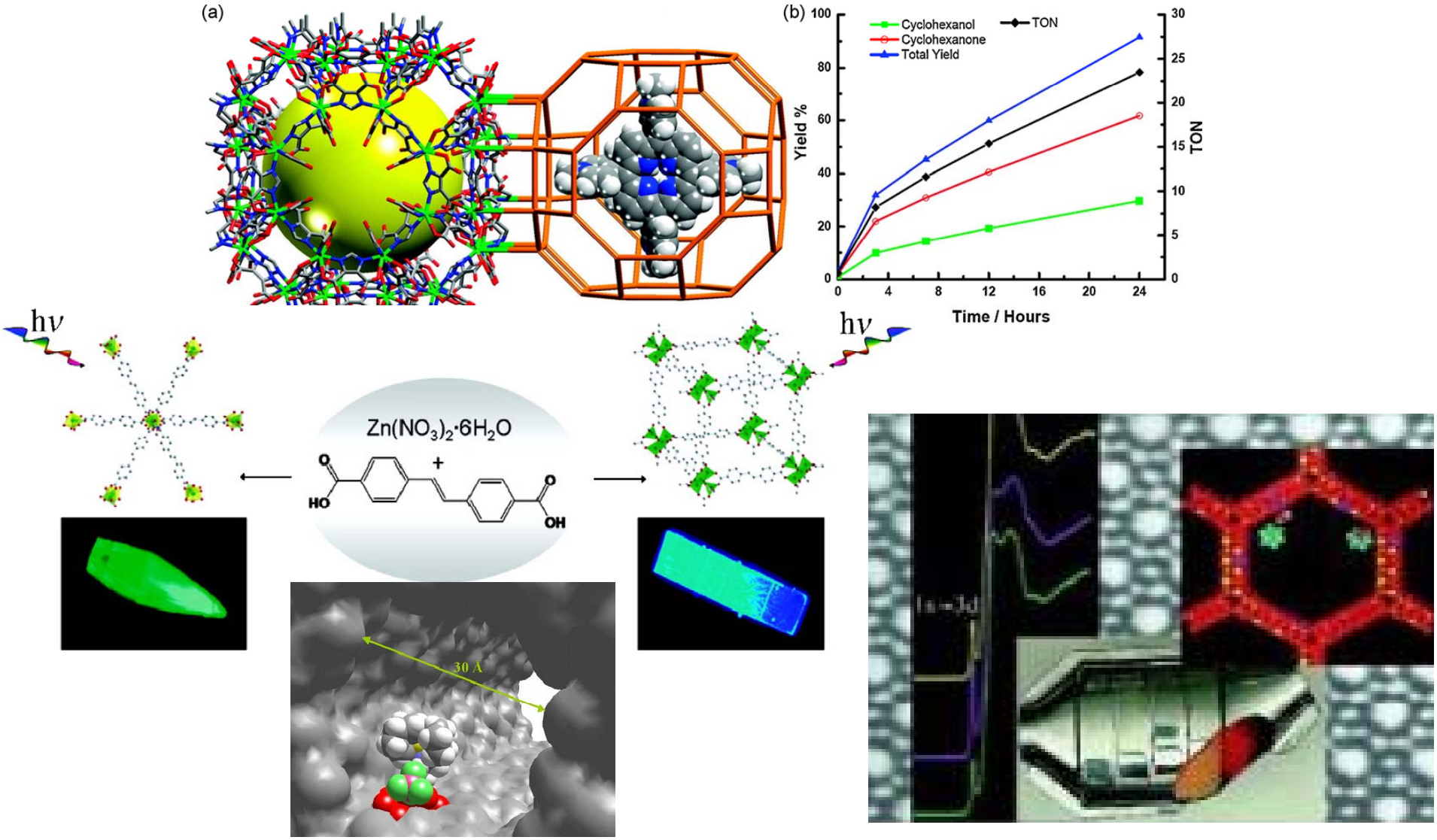








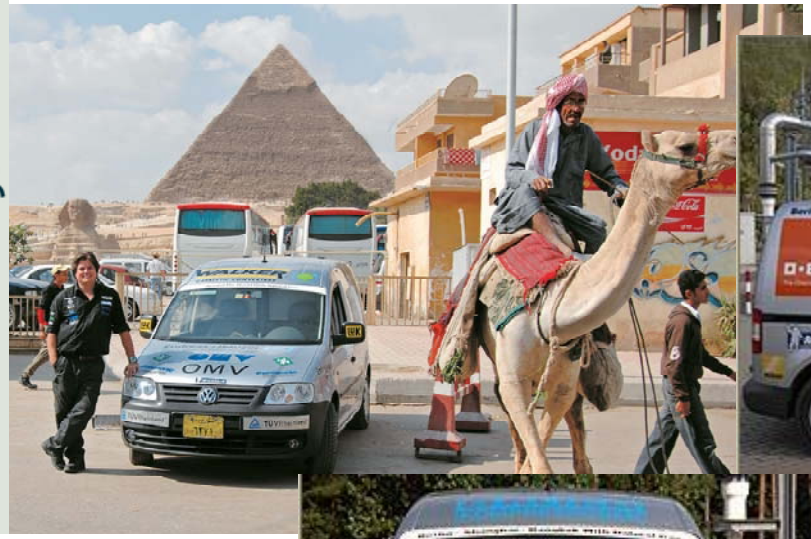
Catalysis and Sensors

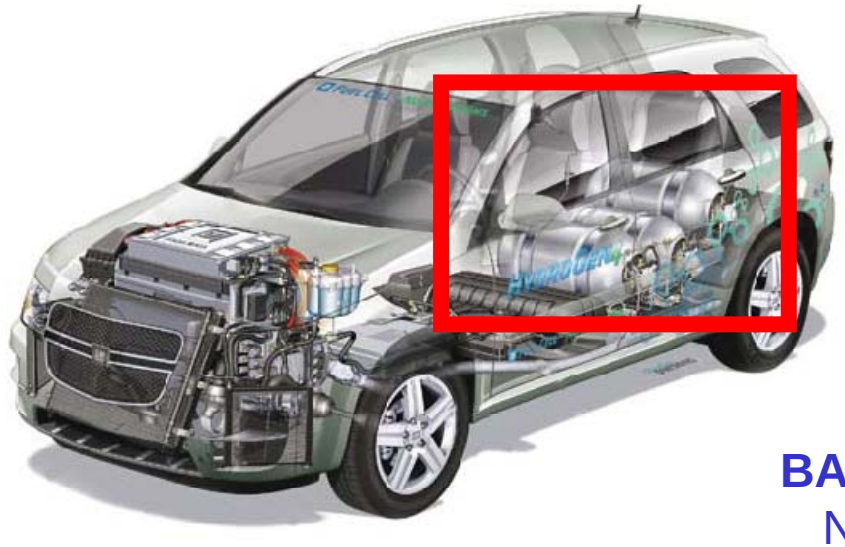


Nanotechnology Opens Gate For Innovation

AROUND THE WORLD WITH NATURAL GAS

EcoFuel World Tour





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Home > Adsorbents > BASF Adsorbent Technologies > Metal Organic Frameworks > Metal Organic Frameworks

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The Chemical Company

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- Catalyst Substrate and Intermediates
- Metal Oxide Purification Adsorbents
- Metal Organic Frameworks
  - BASOLITE MOF Information Request

Adsorbents

We make adsorbents differently

Metal Organic Frameworks

BASOLITE MOF - The World Record in Surface Area

Achieve breakthroughs in your catalysis or physisorption applications. 1 g of BASOLITE™ MOF has the surface area of several football fields and can absorb, store and release a vareity of small molecules by utilizing its huge surface area and open framework structure.

Performance compares to zeolites, silicas, aluminas and activated carbon. Let BASOLITE unlock novel surface applicatons for you.

BASOLITE A10 **Hydrophilic Aluminum MOF**

BET surface area 1100-1500 m^2/g

Reactivation at 200°C

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BASF's catalysts facility in Shanghai receives "Quality 5 Sar Award" from Hyundai Motor Company - *May 11, 2010* More

BASF showcases solutions to help extend the range of batteries at Advanced Automotive Batteries Conference - *May 10, 2010* More

Literature Download

- BASOLITE MOF Datasheet

http://www.catalysts.basf.com/Main/adsorbents/basf_adsorbent_technologies/metal_organic_frameworks

The world record in surface area

BASOLITE Metal Organic Frameworks

BASF
The Chemical Company

BASOLITE MOF Properties

	BASOLITE Properties	BET Surface Area	Sigma Aldrich #
BASOLITE A100 Aluminum terephthalate	Hydrophilic MOF Can be re-activated at 200°C	1100-1500 m²/g	688738
BASOLITE C300 Copper benzene – 1,3,5-tricarboxylate	Hydrophilic MOF Can be re-activated at 200°C	1500-2100 m²/g	688614
BASOLITE Z1200 2-Methylimidazole zinc	Organophilic ZIF (Zeolitic Imidazolate Frameworks) Can be re-activated at 100°C	1300-1800 m²/g	691348

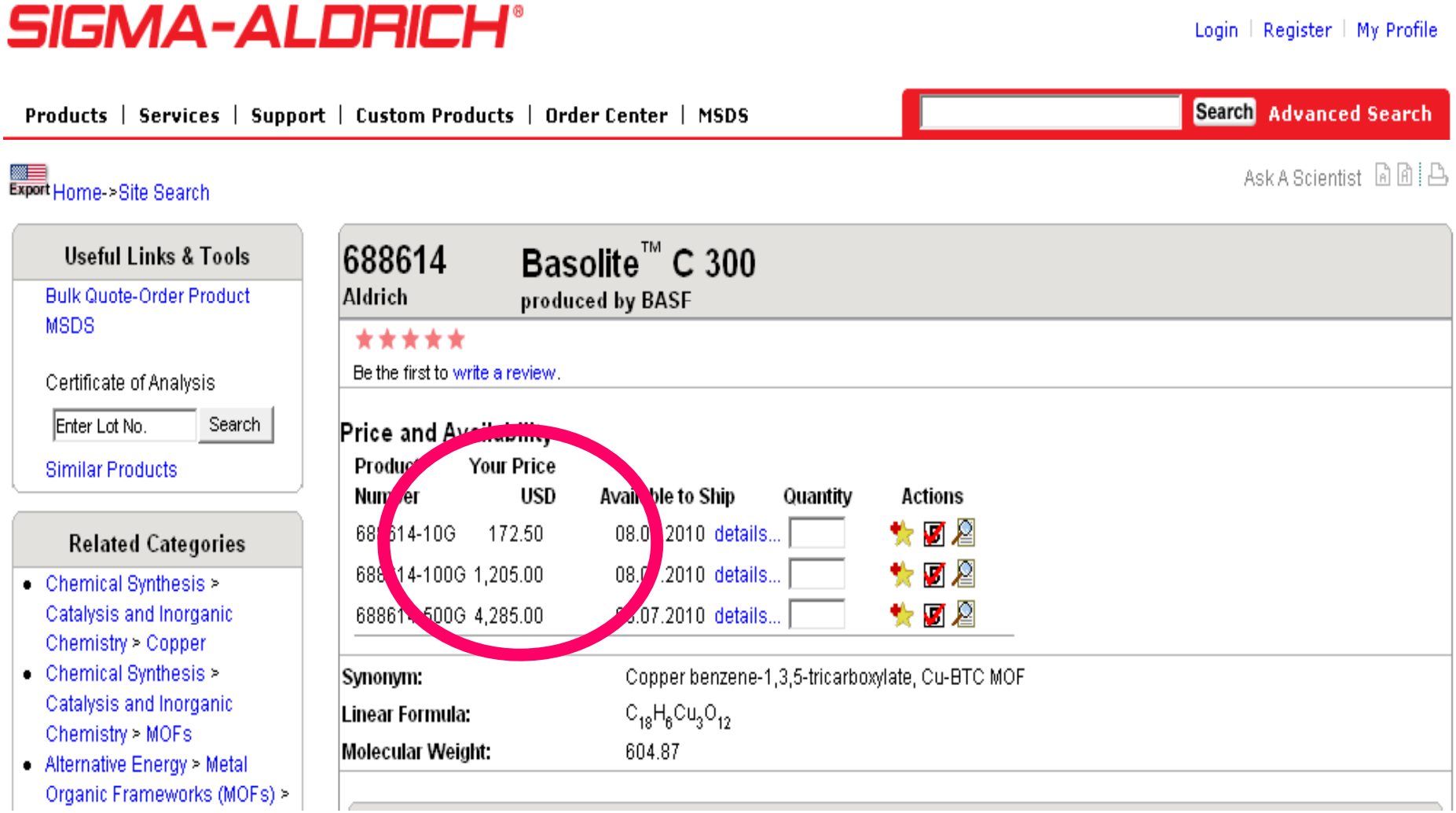
BASOLITE MOF Performance Comparisons

Current Technology	BASOLITE Performance Comparison
Zeolite	MOF have close to one order of magnitude higher surface area and no dead volume, high uptake capacity, low desorption energy and structural variety. Metal atoms are atomically dispersed for catalytic activity.
Silica	MOF have significantly higher surface areas and high uptake capacity.
Alumina	Hydrophilic MOF are available with more than one order of magnitude higher surface area, low desorption energy, reversibility and stability against water.
Active Carbon	An organophilic MOF (Z1200) is available with even higher surface area, can be reactivated and is stable at high temperatures. Custom tailored structures possible in the future.

Now available at ALDRICH Chemistry
sigma-aldrich.com

http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/General_Information/basf_basolite_handout_051908.Par.0001.File.tmp/basf_basolite_handout_051908.pdf

Basolite C 300 Cost



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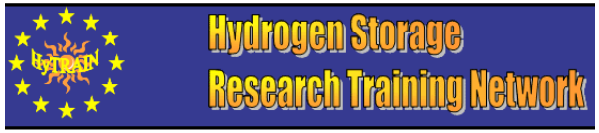
Important Sponsors of Research

NSF



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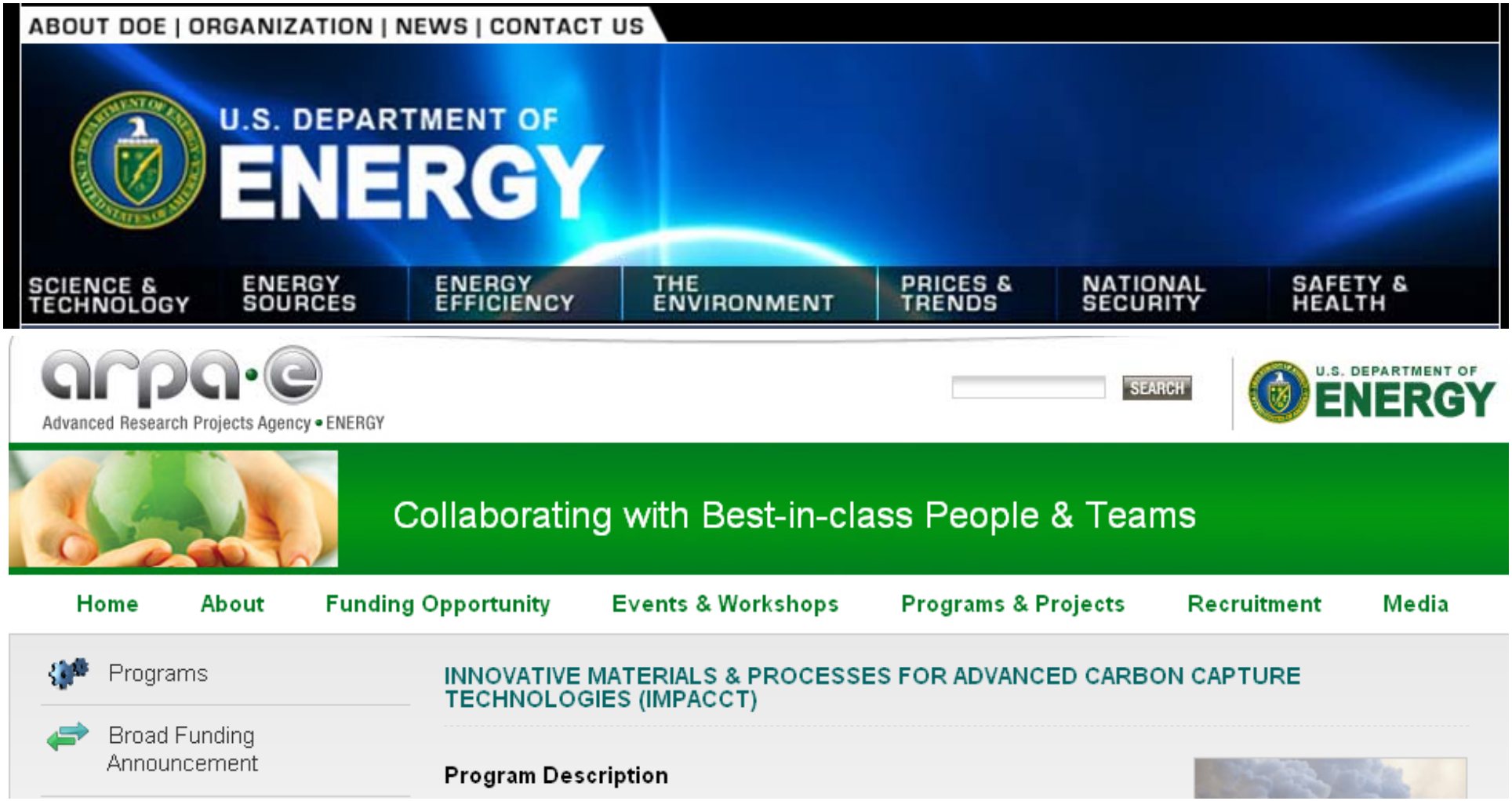
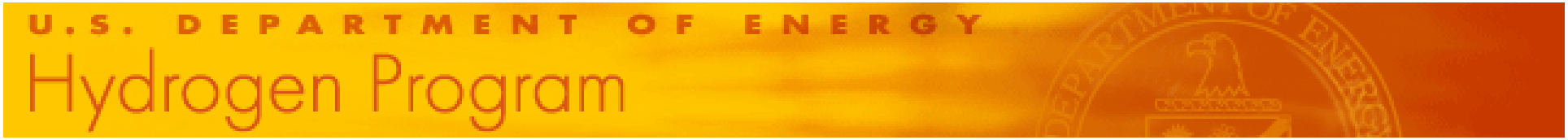


http://arpa-e.energy.gov/ProgramsProjects/IMPACCT.aspx
http://www.energy.gov/

Energy Efficiency & Renewable Energy



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Fuel Cell Technologies Program

About the Program | Program Areas | Information Resources | Financial Opportunities | Technologies | Market Transformation | Home

Hydrogen Storage

Basics
Current Technology
DOE R&D Activities

Quick Links
- Hydrogen Production
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- Fuel Cells
- Technology Validation
- Codes & Standards
- Education
- Systems Analysis

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On-board hydrogen storage for transportation applications continues to be one of the most technically challenging barriers to the widespread commercialization of hydrogen-fueled vehicles. The EERE hydrogen storage activity focuses primarily on the applied research and development (R&D) of low-pressure, materials-based technologies to allow for a driving range of more than 300 miles (500 km) while meeting packaging, cost, safety, and performance requirements to be competitive with current vehicles. While automakers have recently demonstrated progress with some prototype vehicles traveling more than 300 miles on a single fill, this driving range must be achievable across different vehicle models and without compromising space, performance, or cost. In addition, hydrogen storage will be needed for both other niche vehicular applications and off-board uses such as for stationary power generation and for hydrogen delivery and refueling infrastructure.

Since FY 2005, the hydrogen storage effort has been conducted under the framework of the National Hydrogen Storage Project. This effort includes independent projects and Centers of Excellence (CoEs) in applied hydrogen storage R&D funded by DOE/EERE and basic research projects for hydrogen storage funded by the DOE Office of Science. A new effort starting in FY 2009 is the Hydrogen Storage Engineering CoE that will provide a coordinated approach to the engineering R&D of on-board materials-based systems. The Engineering CoE is planned as a five-year effort and may produce up to three sub-scale prototype systems (based on the most promising materials under consideration) as its final output (subject to go/no-go decision points).

Crosscutting efforts on system analysis and material chemical and environmental reactivity are also included in the National Hydrogen Storage Project. The three current materials-development CoEs have been focused on specific hydrogen storage material classes: on-board reversible metal hydrides, hydrogen adsorbents, and chemical hydrogen

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NEWS

DOE Issues RFI for Fuel Cell Technical and Cost Targets for Portable Power Applications
June 1, 2010

DOE Releases Fuel Cell Pre-Solicitation Workshop Proceedings
April 7, 2010

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- NatCarb
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- Reference Shelf
- Contacts

Hydrogen & Clean Fuels

Carbon Sequestration

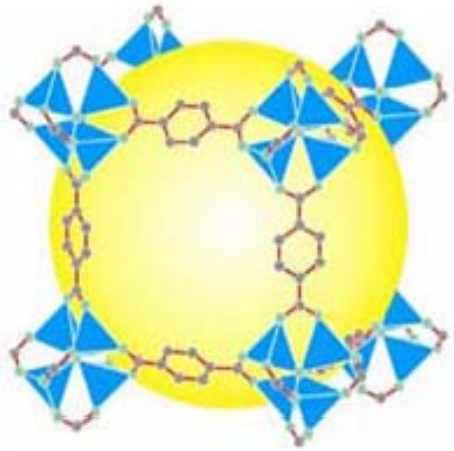
Breakthrough Concepts Project Descriptions

Carbon Dioxide Separation with Novel Microporous Metal Organic Frameworks

Project # 42121

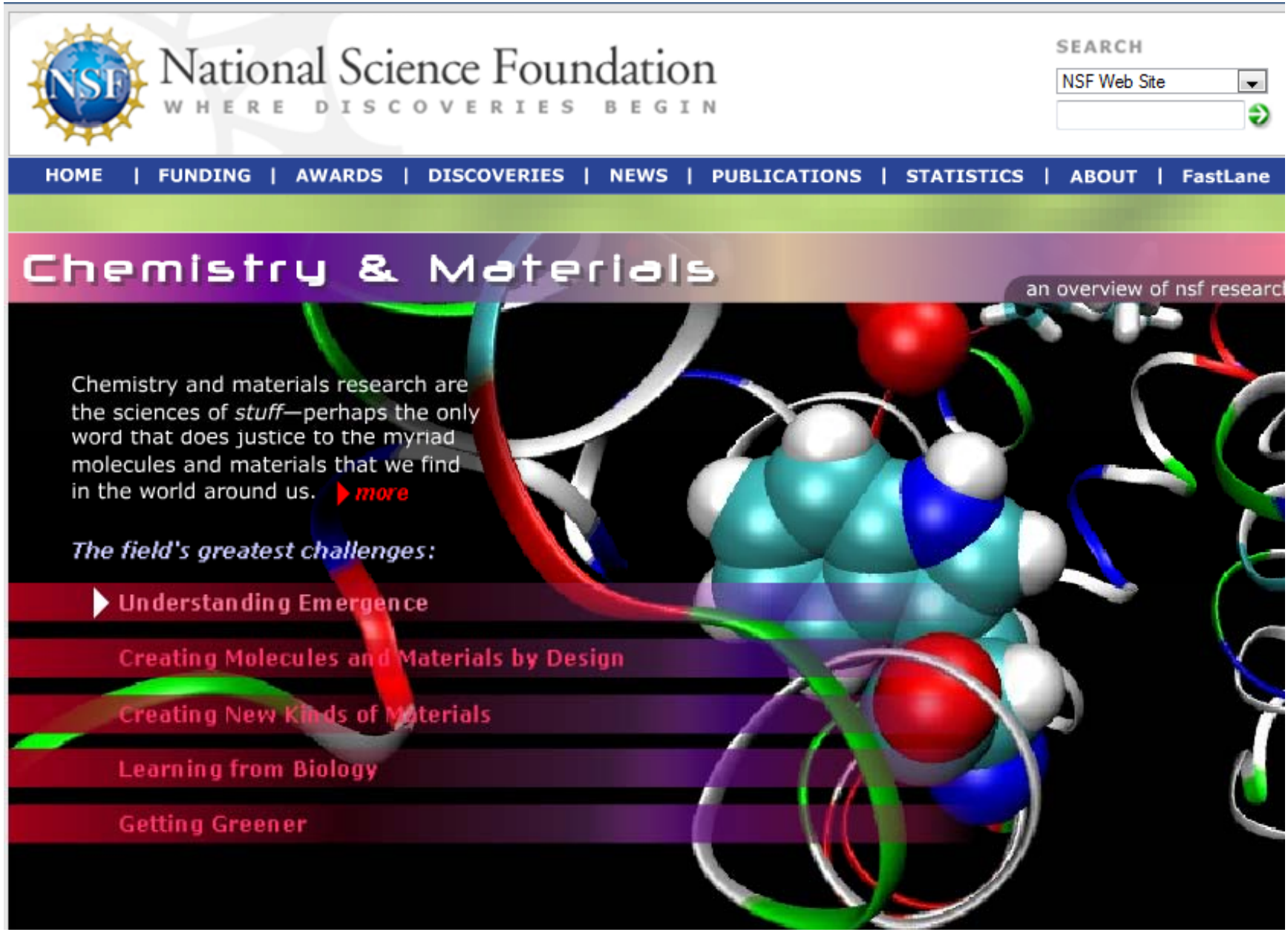
Primary Performing Organization:
UOP LLC (A Honeywell Company)

In this project, researchers will work to develop novel microporous metal organic frameworks (MOFs) as sorbents for the removal of carbon dioxide (CO_2) from flue gas and gasifier streams in coal-fueled power plants. MOFs have previously exhibited exceptional adsorption capacity for methane, hydrogen, and other gases. MOFs are hybrid organic/inorganic structures – essentially scaffolds made up of metal hubs linked together with struts of organic compounds – a structure designed to maximize surface area. MOF sorption properties can be readily tailored by modifying either the organic linker and/or the metal hub. The desired sorbent would have high selectivity, high adsorption capacity, and good adsorption/desorption rates, and would be tailored to minimize the CO_2 binding energy in the interest of reducing the energy required for regeneration.



Molecular structure of the microporous metal organic framework MOF-5.

http://www.netl.doe.gov/technologies/carbon_seq/core_rd/breakthrough/42121.html



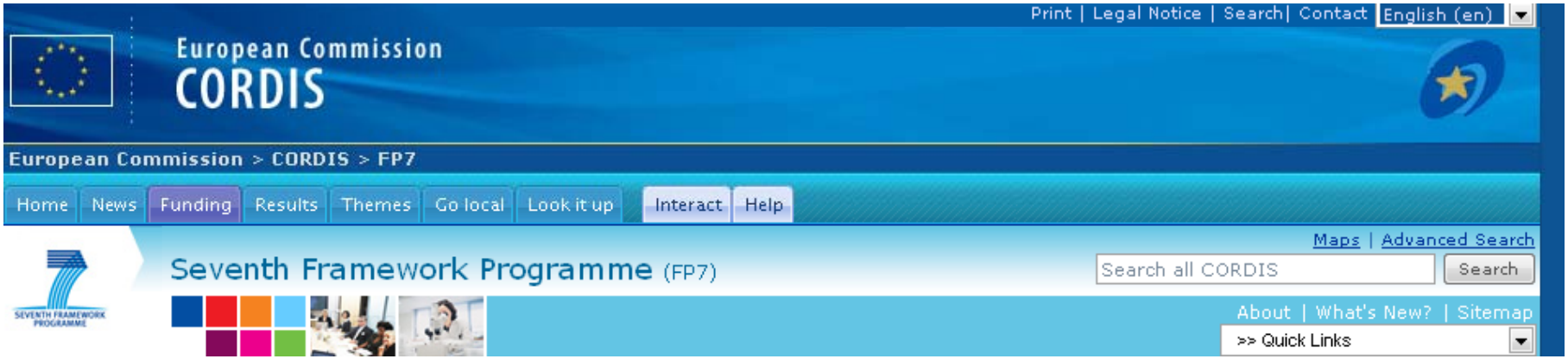
http://www.nsf.gov/news/overviews/chemistry/

Project	Funding	No Inst.	Responsible
Hydrogen Storage in Metal-Organic Frameworks. (2005-2010)	USDollars $=1`700.000	7	Omar M. Yaghi University of California L. A.
A Biomimetic Approach to Metal-Organic Frameworks with High H2 Uptake (2007-2012)	USDollars $=1`400.000	11	Hongcai Zhou Texas A&M university
Reversible Hydrogen Storage Materials – Structure, Chemistry, and Electronic Structure (2005-2010)	USDollars $=1`600000	6	Ian Robertson & Duane Johnson University of Illinois Urbana Campaign
Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching (2009-2013)	USDollars $= 1`512000	2	Angela D. Lueking, Jing Li & Milton W. Cole Penn State University Rutgers University

Project	Funding	No Inst.	Responsible
Advanced separation and storage of carbon dioxide: Design, Synthesis and Applications of Novel Nanoporous Sorbents (2006-2008) "DESANNS"	€ 3,51 Millions	7	Philip Llewellyn Institut Français du Pétrole France
Anchoring of metal-organic frameworks, MOFs, to surfaces (2006-2009) "SURMOF"	€ 2,83 Millions	7	Christof Wöll Ruhr-Universität Bochum, Germany
Functional Metal Organic Frameworks as Heterogeneous Catalysts (2006-2010) "MOFCAT"	€ 2,87 Millions	6	Richard Blom SINTEF Materials and Chemistry Norway
New materials for hydrogen powered mobile applications (2009-2012) "HYPOMAP"	€. 1,18 Millions	4	Kieschinck Ronald Jacobs University Bremen GGMBH, Germany

Project	Funding	No Inst.	Responsible
Carbon Dioxide Separation with Novel Microporous Metal OrganicFrameworks (2007-2010)	USDollars $= 2`802.000	3	Richard Willis UOP LLC, a Honeywell company
MOFs for CO2 capture, control their mesh size to improve the selectivity of adsorbing CO2 and to reduce the energy required. ("IMPACCT") (2010-)	USDollars $=1`019,874	1 So Far...	JOE Zhou Texas A&M University
Instrumentation tools and computational algorithms to accelerate the development of metal organic framework ("IMPACCT") (2010-)	USDollars $=3`663,696	1 So Far...	Jeffrey Long Lawrence Berkeley National Laboratory
MOFs integrated into fiber membranes to improve the throughput and selectivity for CO2 capture. ("IMPACCT") (2010-)	USDollars $= 1`000000	1 So Far...	Georgia Istitute of Technology

European Agencies Funding Research



http://cordis.europa.eu/fp7/home_en.html

http://cordis.europa.eu/fp6/dc/index.cfm?fuseaction=UserSite.FP6HomePage

http://erc.europa.eu/index.cfm

European Projects On MOFs

Nanotechnologies and Nano-Sciences,
Knowledge-Based Multifunctional Materials and New Production Processes and Devices

- Project partners
- R&D program
- Publications
- Useful Links

MOFCAT

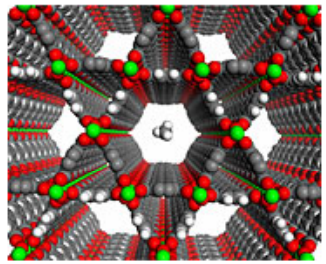
Functional Metal Organic Frameworks as Heterogeneous Catalysts

Metal Organic Frameworks (MOFs) are novel organic-inorganic crystalline materials, which promise to become a powerful and flexible family for different industrial uses within catalysis, adsorption and sensor technology, overcoming many of the limitations of Zeolites: MOFs may display extreme porosity and surface areas, and their functionalities can be tailored.

The project aims at developing reproducible and scalable synthesis procedures for known and new MOFs, and also exploiting combinatorial techniques. We want, at the molecular level, to understand the interactions governing their stability, self-assembly and adsorption properties, by means of combined experimental and theoretical modelling efforts. New routes for functionalisation to create MOF-based single-site catalysts for two emerging industrial processes will be developed and the functionalised MOFs will be exploited as catalysts in emerging industrial processes as well as more future processes such as Pt-functionalised MOFs as catalysts for C-H activation at moderate conditions. In addition, the adsorption and storage properties of selected MOFs for non-condensable gases such as hydrogen and methane will be examined.

The work packages of the project comprise the synthesis, characterisation, modelling, and testing of the materials, as well as a technology implementation plan for their production and use.

MOFCAT



http://www.sintef.no/Projectweb/MOFCAT/

DeSannS

Design Synthesis and Application of Novel Nanoporus Adsorbent Component

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LAST NEWS

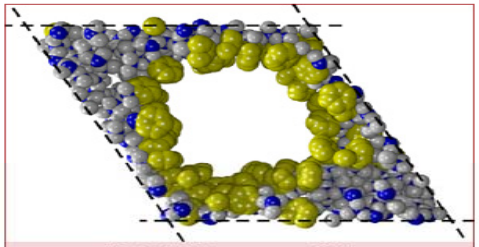
- Next DeSANNS meeting
- 9th International Conference on Fundamentals of Adsorption
- 15th International Conference of Zeolites

FP6 STREP SES6CT2005-020133

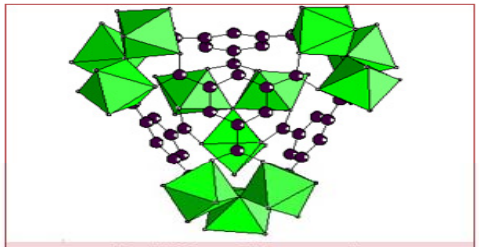
WELCOME TO THE DESANNS WEBSITE

One of the technological problems that faces society today is the environmentally friendly and economically favourable **separation, capture and storage of gases.** This is the case of **carbon dioxide** that will be critically important in the future European H_2 **based economy**. It is crucial to find a new route to **capture and store** CO_2 produced during various industrial processes with different conditions.

2 promising materials :



Periodic Mesoporous Oxide



Metal Organic Framework

RUHR-UNIVERSITÄT BOCHUM

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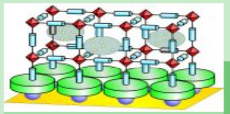

SURMOF
Mainpage

Physikalische Chemie I » Faculty of Chemistry und Biochemistry » RUB Faculties » RUB Homepage

Mainpage
Project Summary
Participants
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Scientific publications
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16.10.2009

Anchoring of metal-organic frameworks, MOFs, to surfaces

SURMOF

NMP4-CT-2006-032109

Specific Targeted Research Project (STREP)

Funding: 2.5 Mio. €

Duration: 36 months

http://www.desanns.univ-montp2.fr/index.php?option=com_content&task=view&id=1&Itemid=1

http://www.ruhr-uni-bochum.de/pc1/SURMOF/

nanoMOF

- nanoMOF
  - Project Aim
  - Applications
  - Project Partner
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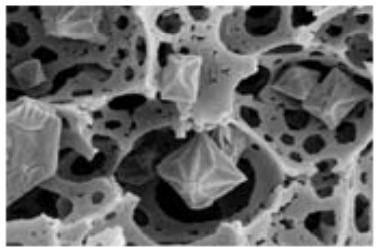
  - Intern

Fraunhofer-Gesellschaft
Fraunhofer IWS

nanoMOF - Nanoporous Metal-Organic Frameworks for production



"nanoMOF" will focus beyond discovery and integrate nanostructured MOFs into products with industrial impact within a strong cooperation of established MOF research institutions and industrial end users.

News

3rd General Assembly Meeting at the University Leuven
29th - 30th June 2010

MOF2010 conference
5th - 8th September 2010 in

TU Dresden » Fakultät Mathematik und Naturwissenschaften » Fachrichtung Chemie und Lebensmittelchemie » Metal-Organic Frameworks

FACHRICHTUNG CHEMIE UND LEBENSMITTELCHEMIE

INORGANIC CHEMISTRY | AK PROF. KASKEL | AK PROF. RUCK | AK PROF. GLOE | AK PROF. KNIEP | AK PROF. GRIN

PRIORITY PROGRAM "Porous Metal-Organic Frameworks"

- Coordinator & Contact
- Summary
- Projects and Participants

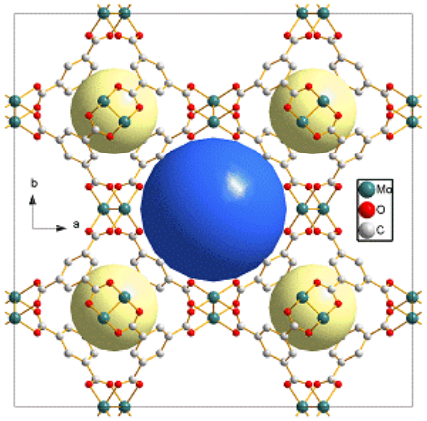
EVENTS

- Topical Workshop 2009 MOF Modelling for PhD students
- Kickoff meeting 2009
- Topical Workshop 2010 Adsorption and Diffusion in MOFs for PhD students

NEWS

SUMMARY

Metal-Organic Frameworks (MOFs)



NEWS

Calendar of events TU Dresden

CONTACT

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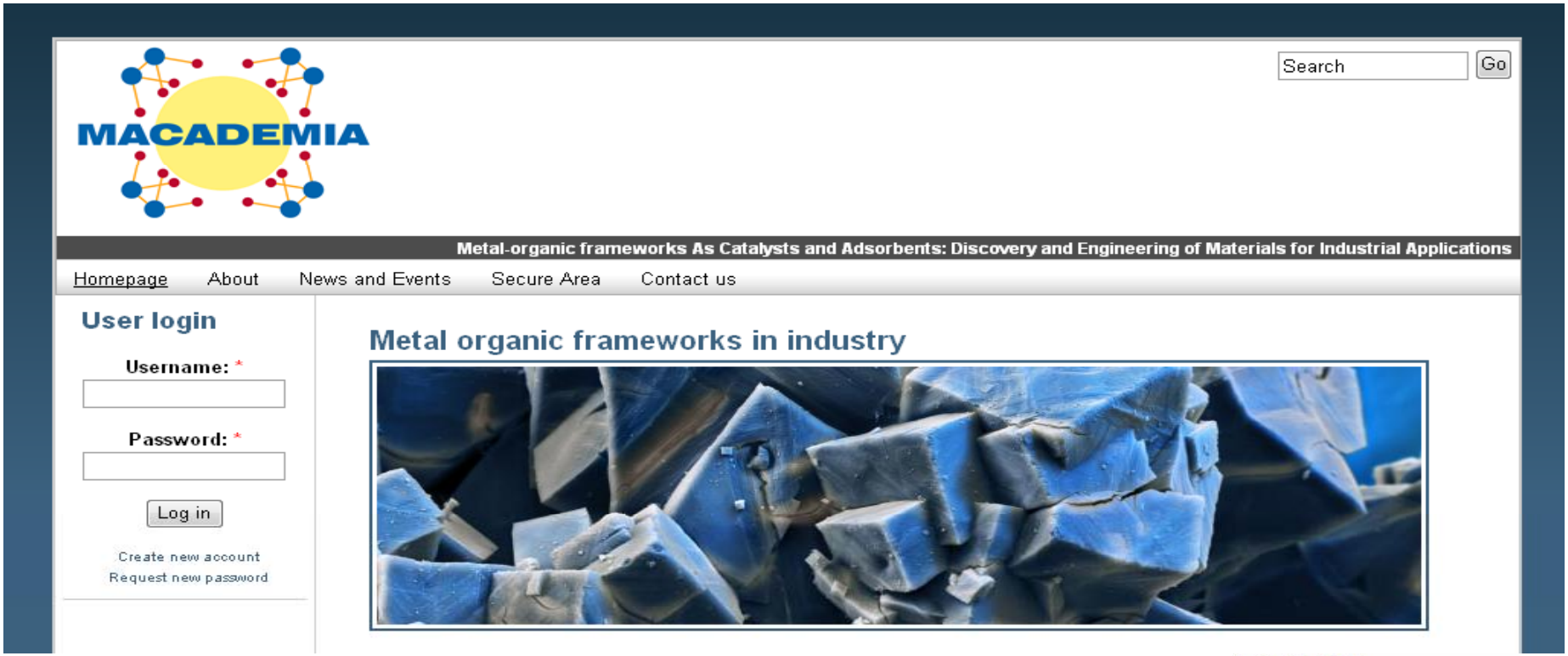
Zi. 63

Mail to:
TU Dresden
Fachrichtung Chemie
und Lebensmittelchemie

http://www.nanomof-project.eu/
http://www.metal-organic-frameworks.de/index.shtml



BASF

Christian-Albrechts-Universitaet Kiel

Faculdade de Engenharia da Universidade do Porto

Heyrovsky Institute Physical Chemistry Prague

Charles University

CNRS

Faculté Polytechnique de Mons

Imperial Consultants

Total Raffinage Marketing

University of Edinburgh

Katholieke Universiteit Leuven

Laboratoire Catalyse et Spectrochimie (LCS)

Total

Universidad Politecnica de Valencia

University of Warwick

Korean Research Institute of Chemical Technology

Laboratoire Chimie Provence

Total Petrochemicals France

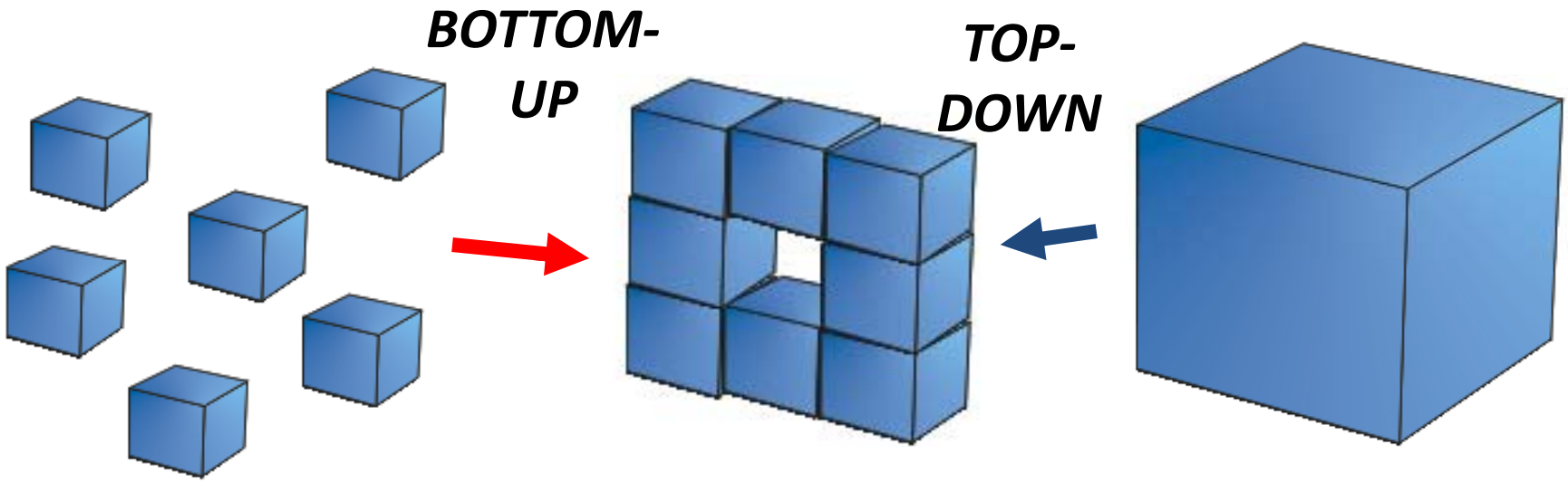
Institut Charles Gerhardt

Institut Lavoisier

Institut de Catalyse et l'Environnement (IRCE)

http://www.macademia-project.eu/

Two Approaches to Nanomaterials Frabrication



Atoms, Molecules

Nanoestructured Material

Bulk

Top Down Approach: Physical Methodologies of Nanofabrication

Bottom Up Approach: Chemical Methodologies of Molecular Self Assembly, Supramolecular Chemistry

What is the relation of Supramolecular Chemistry with Nano-Materials?

1) Design Nano-materials in a Rational Fashion from Atoms and Molecules as a Building Blocks.
2) Design different Architectures of the Materials.
3) Take Advantage of the Interaction of the Molecules within the material.

What does it mean?

-Nanosized materials (porous materials)
-Materials with new Properties (Physical & Chemical Properties) e.g. Magnetic, Thermal, reactivity, solubility

With the help of SUPRAMOLECULAR CHEMISTRY we can Understand and Study those materials

Supramolecular Chemistry

A field of chemistry related to species of greater complexity than molecules, that are held together and organized by means of intermolecular interactions. The objects of supramolecular chemistry are supermolecules and other polymolecular entities that result from the spontaneous association of a large number of components into a specific phase (membranes, vesicles, micelles, solid state structures *etc*.)

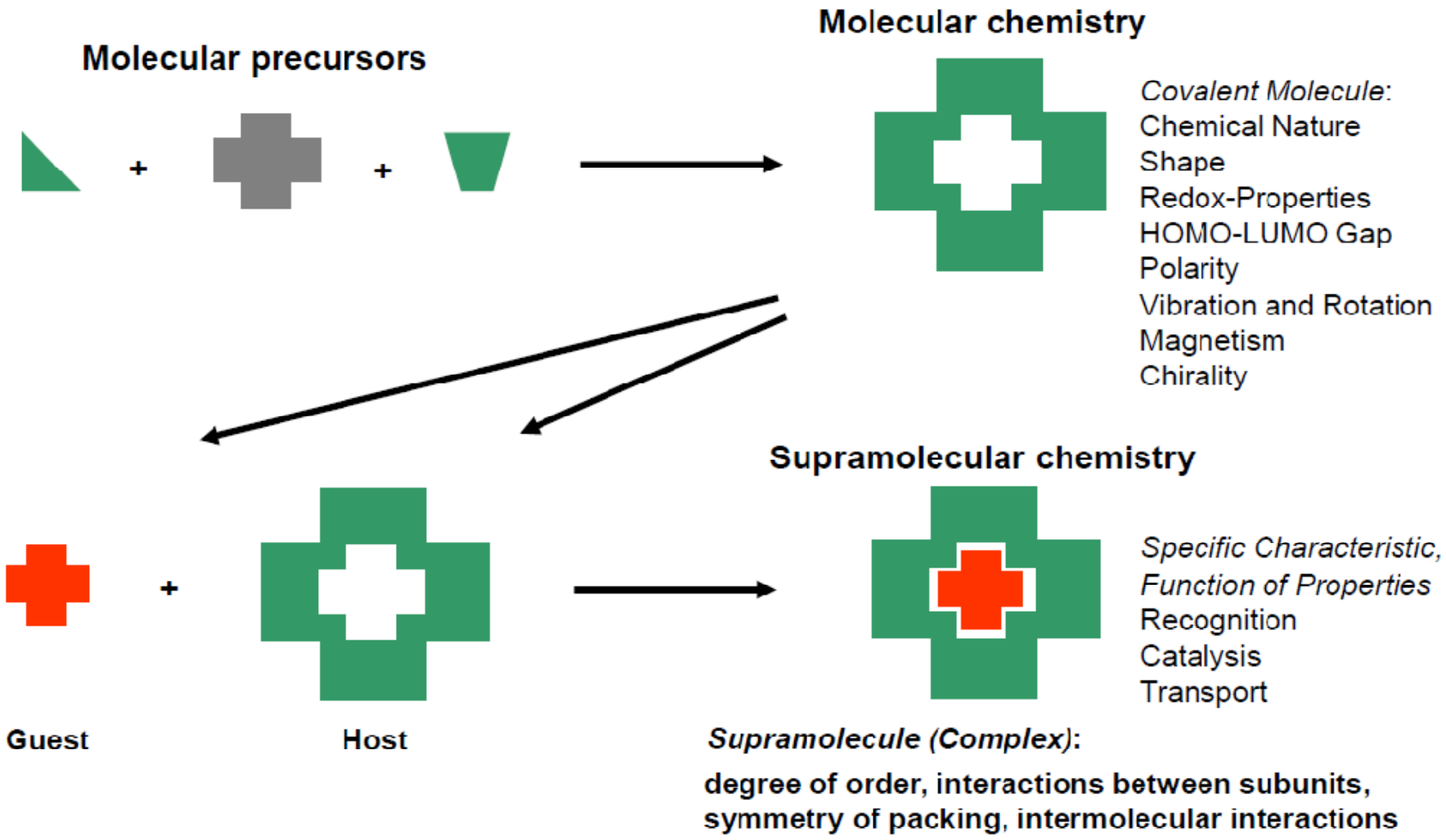
1999, *71*, 1964
IUPAC Compendium of Chemical Terminology 2006

Supramolecular Chemistry

- Self Assembly or Self Organization
- Molecular Host-Guest Chemistry
- Solid State Host-Guest Chemistry
- NanoChemistry / Nanotechnology
- Supramolecular Devices
- Interlocked & Interwoven Systems
- Crystal Engineering
- Biological Chemistry

…..And Many Other Branches

Comparison Between the Scope of Molecular And Supramolecular Chemistry



Bonding Energies

Intramolecular Bonding

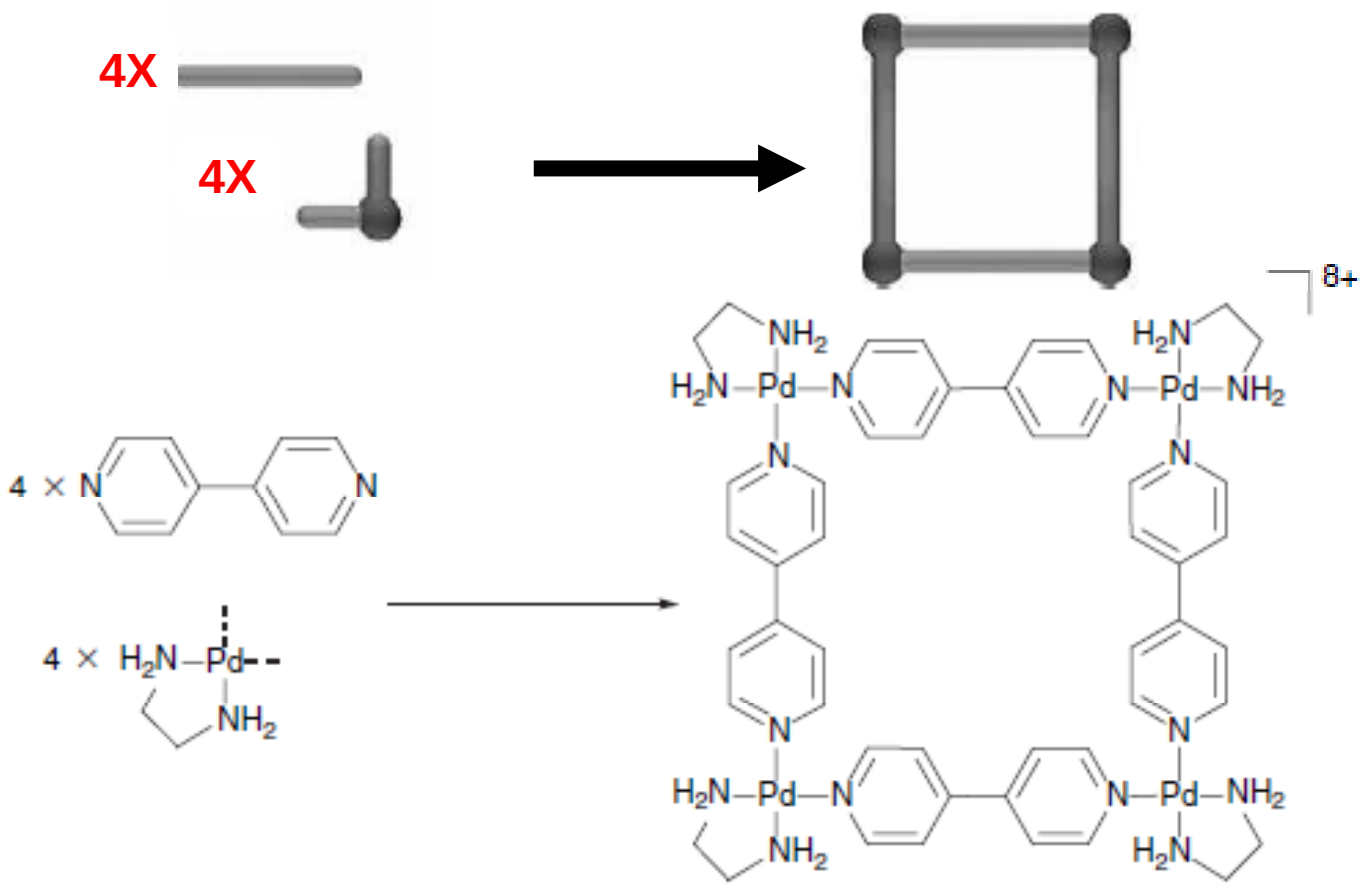
- Single Bond C-C (350 kJ/mol)
- Double Bond C=C (609 kJ/mol)
- Triple Bond N ≡N (942 kJ/mol)

Intrermolecular Bonding

- Van Der Waals (< 5kJ/mol)
- Hydrogene Bonding (4-120 kJ/mol)
- Ion-Ion (100-350 kJ/mol)
- Dipole-Dipole (5-50 kJ /mol)
- Ion-Dipole (40-200 kJ/mol)
- π- π stacking (0-50 kJ/mol)
- Cation- π (5-80 kJ/mol)

Supramolecular Chemistry is focus on Intermolecular Bonding

Supramolecular Self Assembly



Self Assembling -Square

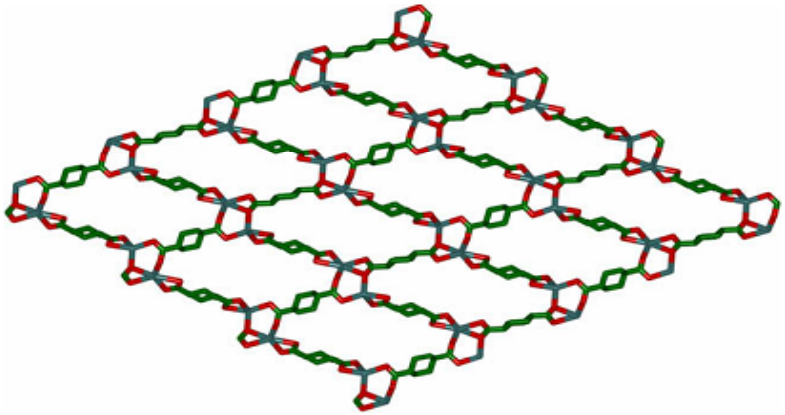
Steed Jonathan W., Turner David R.,Wallace Karl J. Core Concepts in Supramolecular Chemistry and Nanochemistry, 2007 John Wiley & Sons pp 108

Definition of a Network Solid

Is a chemical compound in which the atoms are bonded by covalent bonds in a continuous network.

There are no individual molecules and the entire crystal may be considered a macromolecule.

Covalent crystal model diamond

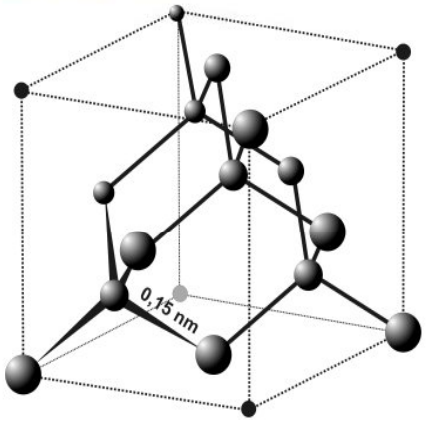


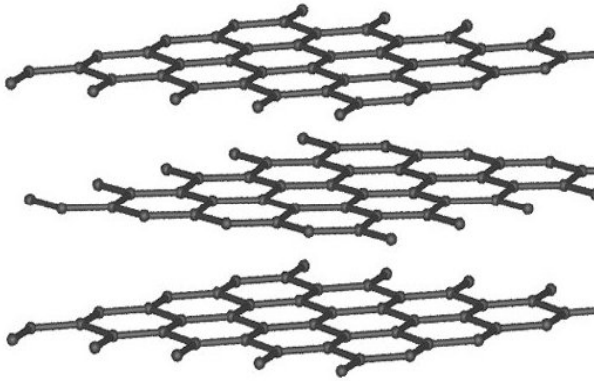
3D topology network connected by Cd atoms and Acid Carboxymethilphophonate

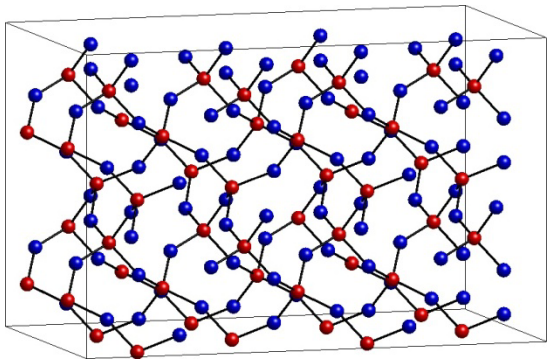
Formulas as those for ionic compounds; simple ratios of the component atoms represented by a formula unit.

Inorganica Chimica Acta, 2009, **362**, 1605–1610

Examples of Network Solids







Diamond

Graphite

Quartz, SiO_2

Network Solids

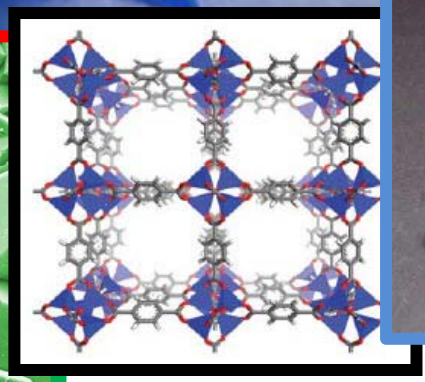
Diamond

Citrine

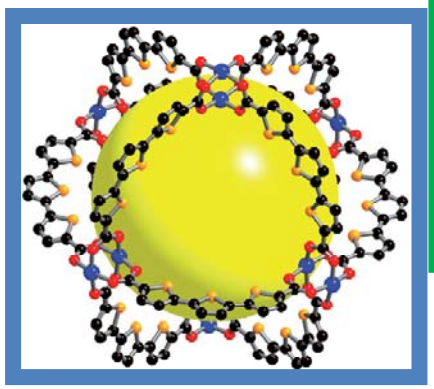
Cupper Sulfate Crystal

Quartz

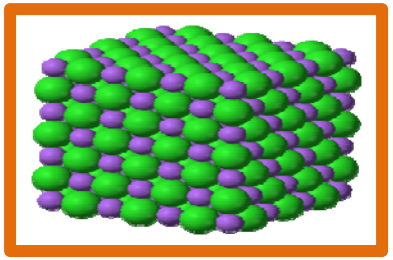
'Nanocubes' of MOF materials. (Courtesy of BASF.)



Metal Organic Framework MOF 5



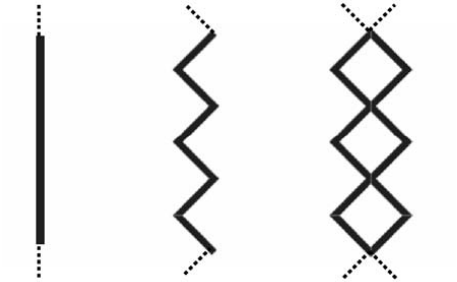
Metal Organic Polyhedra MOP 28



Crystal Structure of NaCl

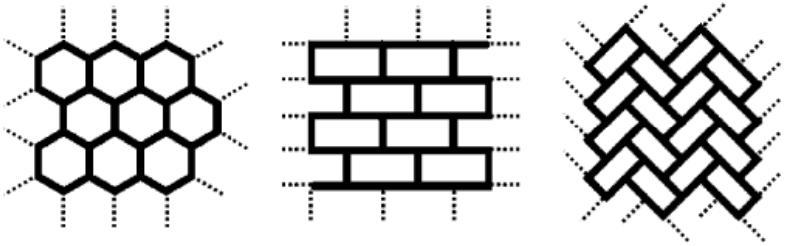
Dimensionality of Network Solids

1D



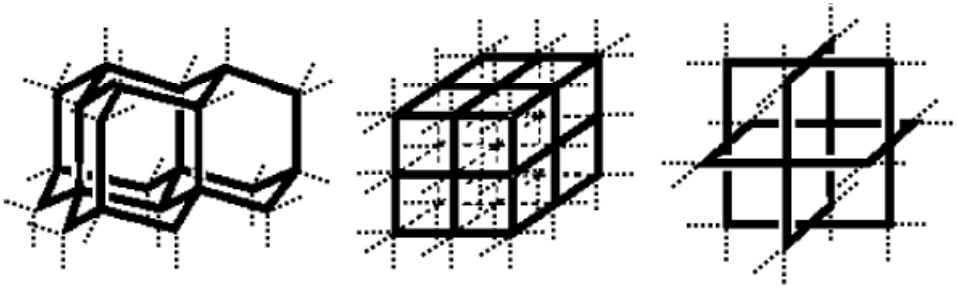
Lineal Zig-Zag Double Helix

2D



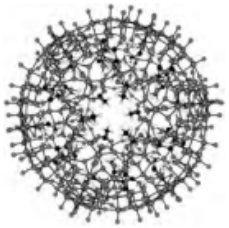
HoneyComb Wall Intercalated Birks

3D



Diamond Octahedral NbO

0 D



Coordination Cluster

Morphology & Composition are required to properly describe the material

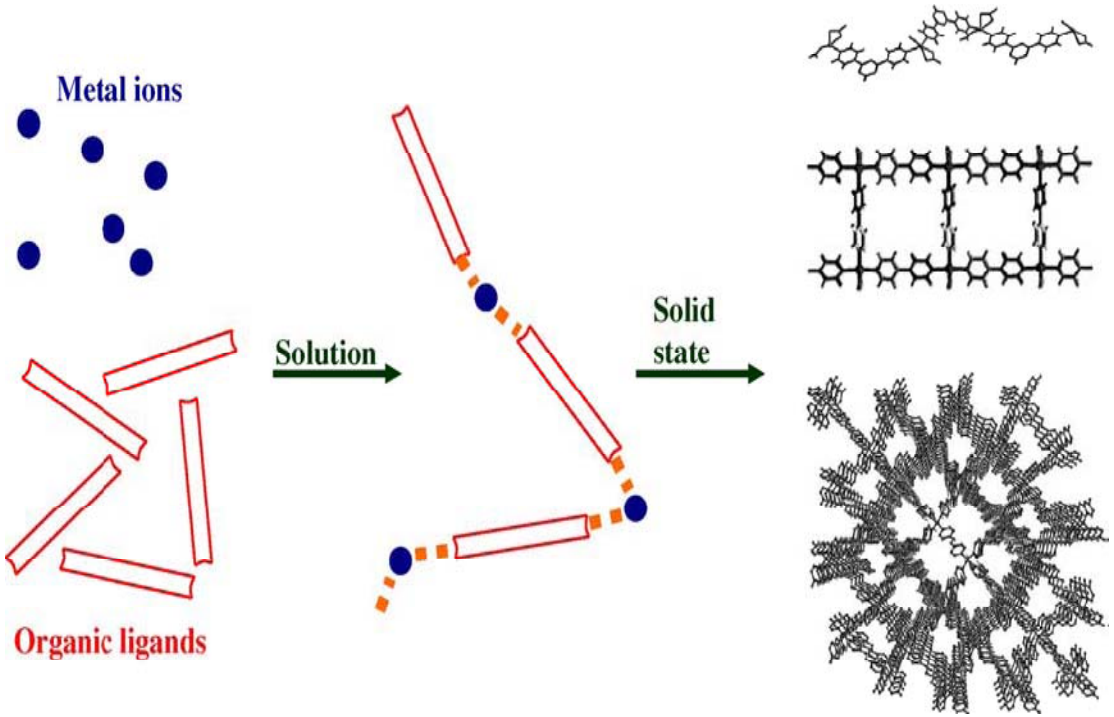
Chem. Rev. 2001, **101**, 1629−1658

Coord. Chem. Rev., 2006, **250**, 2127-2157

Coordination Polymers

Coordination polymer Bonding:

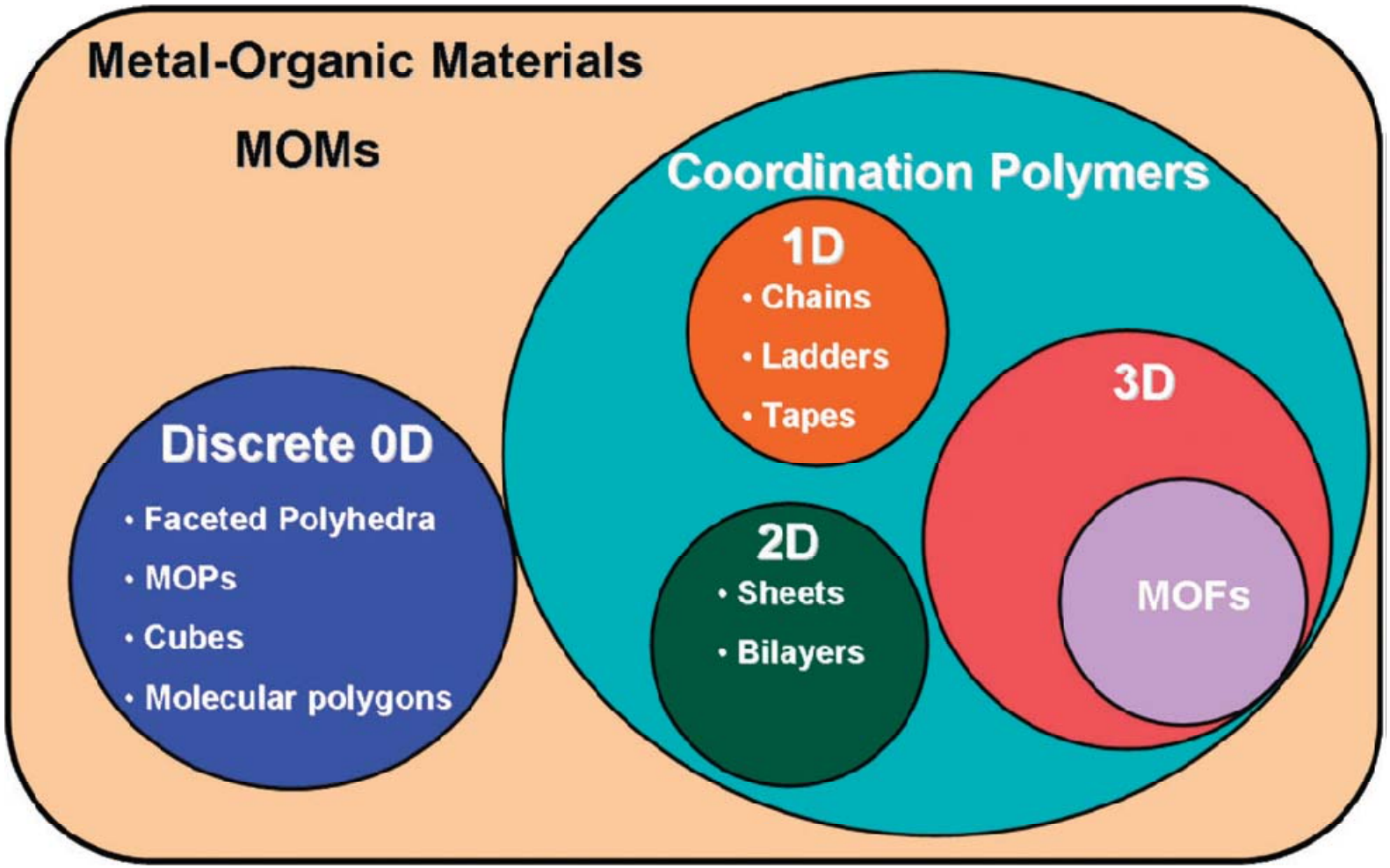
Ligand- Coordination Metal- Ligand



Any reticular structure can be obtained by controlling the ligand architecture and central ions coordination geometry

Coordination Chemistry Reviews, 2006, **250**, 2127–2157

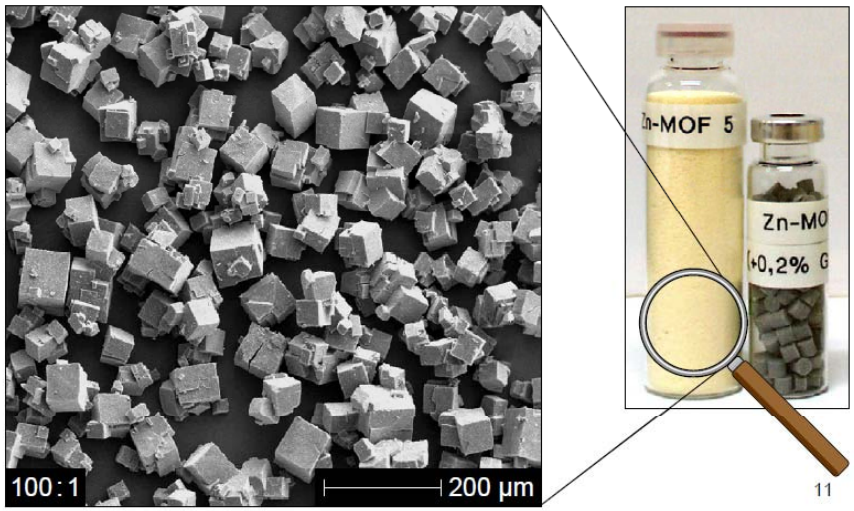
Metal Organic Materials

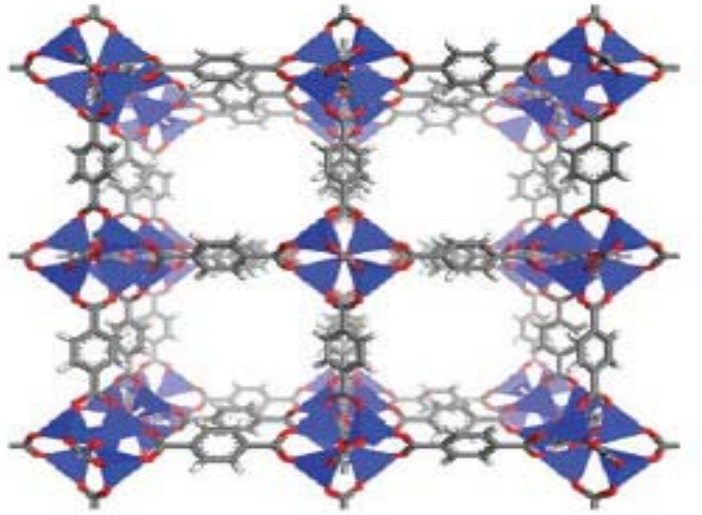


Chem. Soc. Rev., 2009, **38**, 1400–1417

Metal–Organic Frameworks (MOFs)

Metal–organic frameworks (MOFs) are extended porous structures composed of transition metal ions (or clusters) that are linked by organic bridges. They are prepared as crystalline solids by solution reactions of metal ion salts with organic linkers.





J. Mater. Chem., 2006, **16**, 626–636

Nature Materials, 2007, **6**, 92 - 93

Main MOF`s Characteristics

Basically MOFs are/have:

- Crystalline & Porous Materials.
- Thermal stability.
- Well-defined structures.
- Low density.
- High surface area (1000-4500 m^2/g)
- Chemically-tunable structures.
- Morphological properties can be modified.
- They are “easily” synthesized.
- MOFs are frecuently air-sensitive.
- Not stable under Chemical attack (e.g. Solvents)

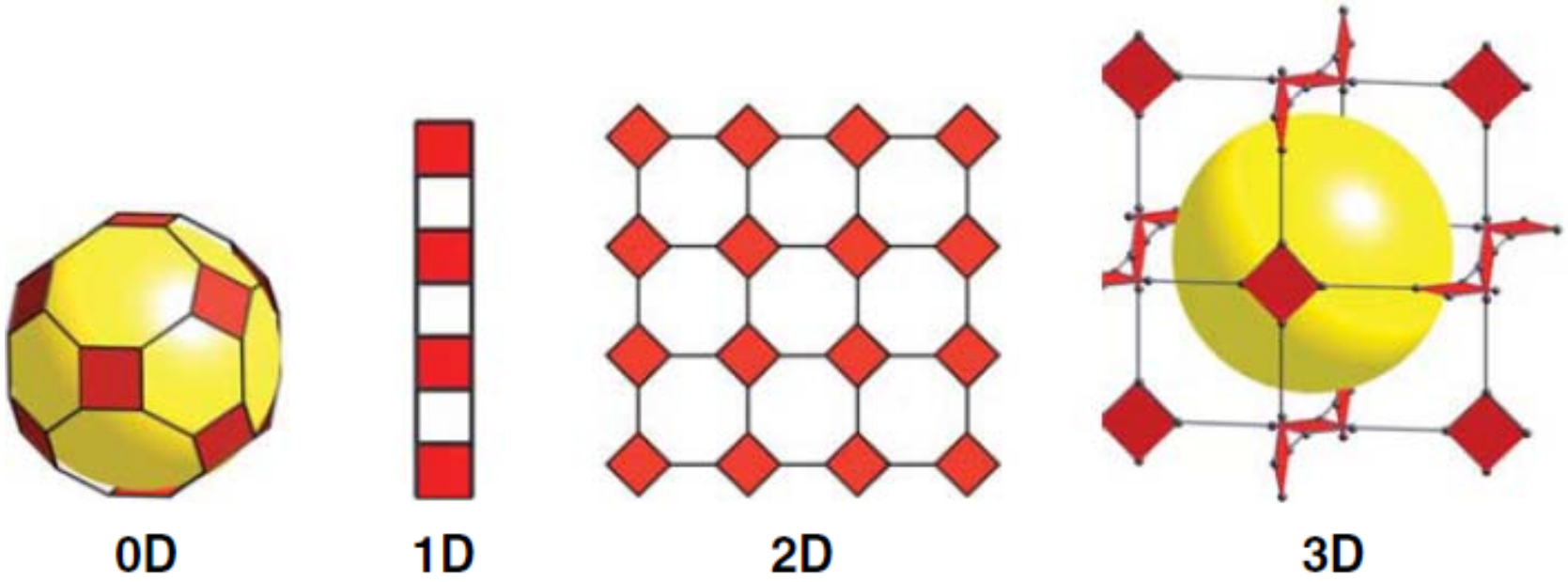
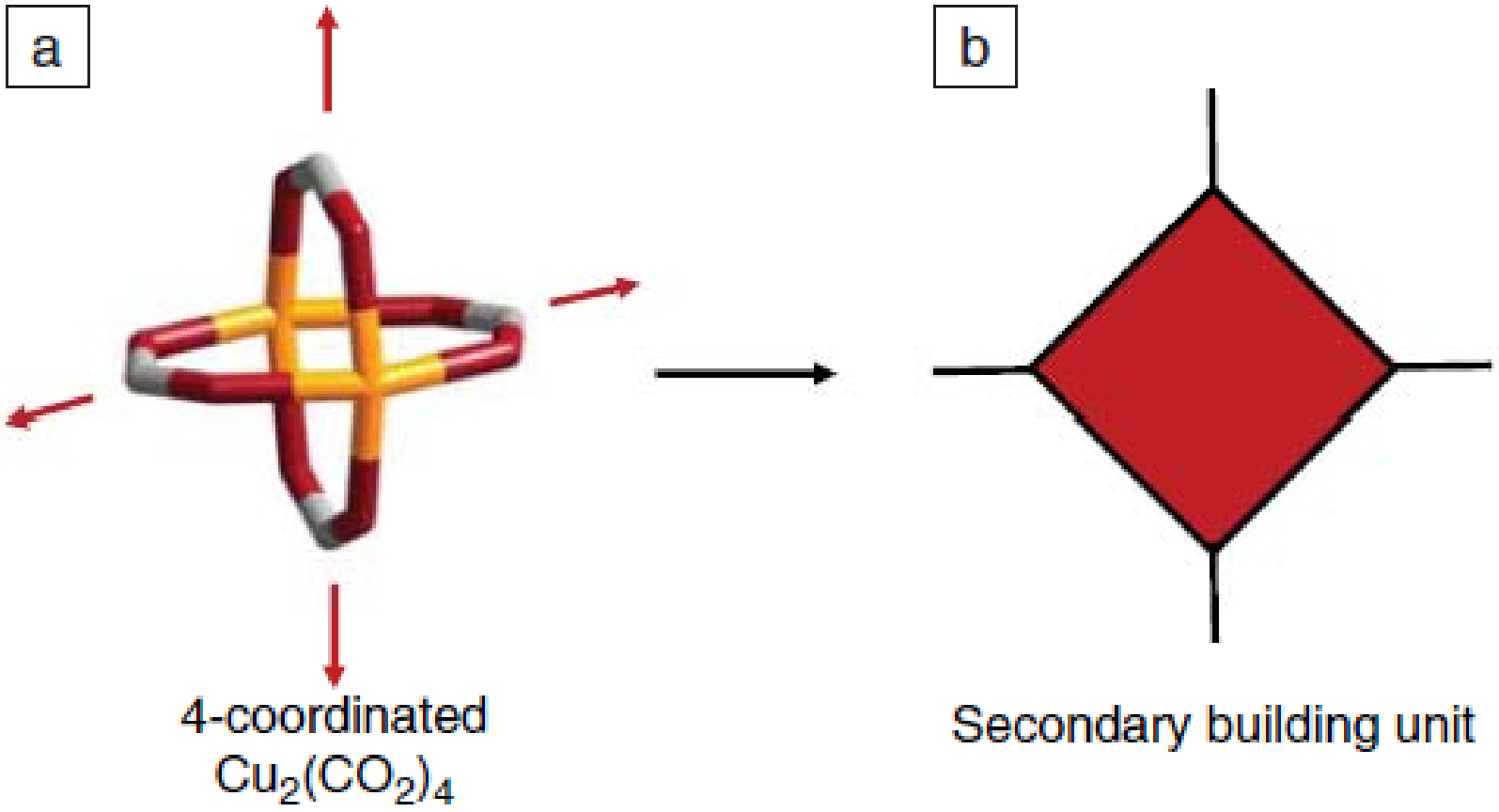
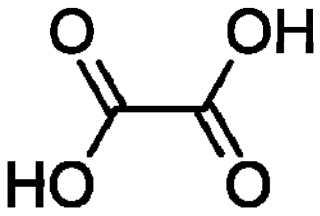


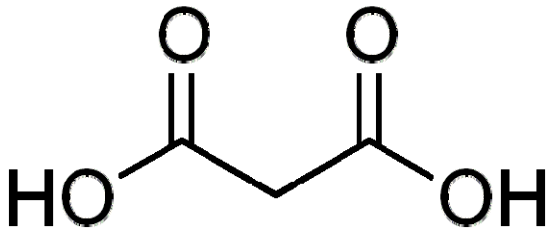
Figure 1. Design of nanoparticles (0D), chains (1D), sheets (2D), and networks (3D). All these structures are composed of intersections that are square in shape (red), which are connected by ditopic linkers (black). The dimensionality of linked square units is controlled by use of precise linker geometry.

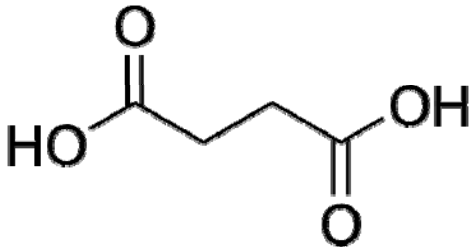
Secondary building unit (SBU)

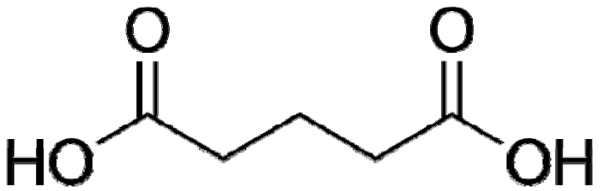


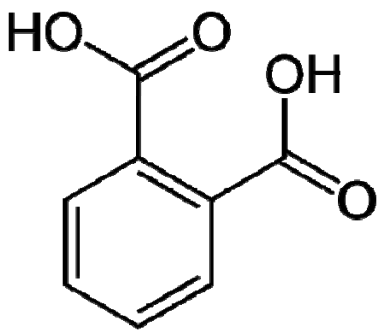
Common ligands in MOFs

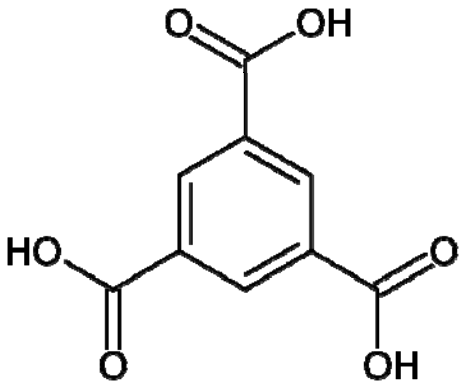


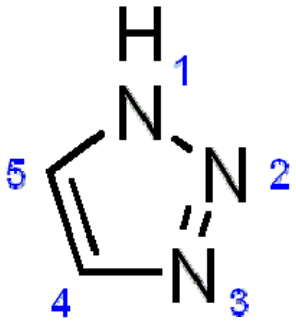


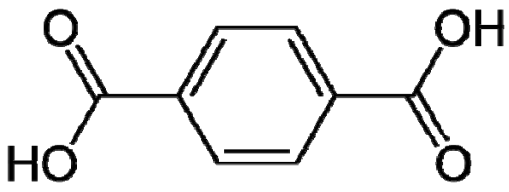




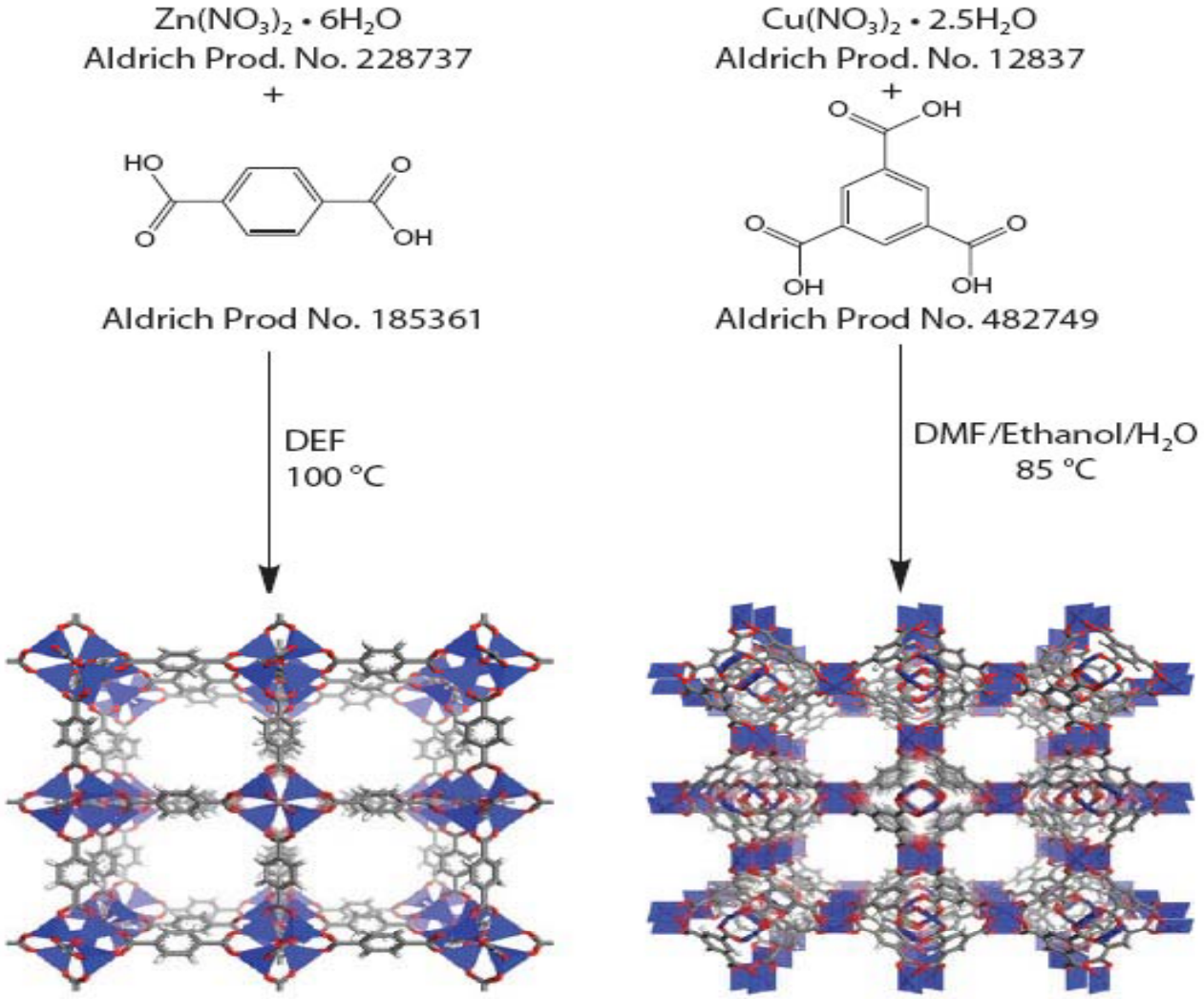






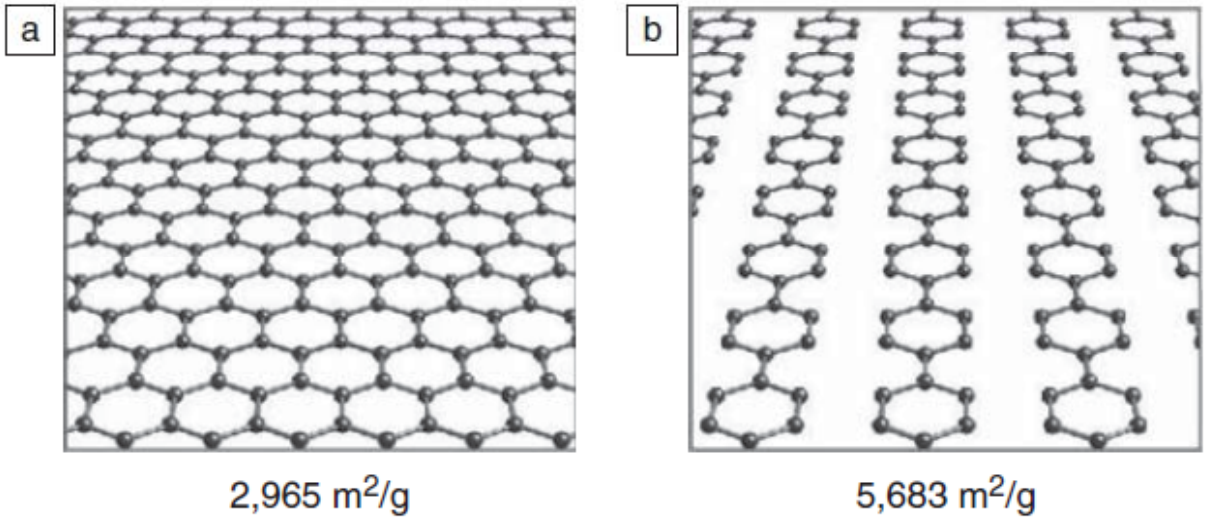


Ligand-Metal Dependant Geometry

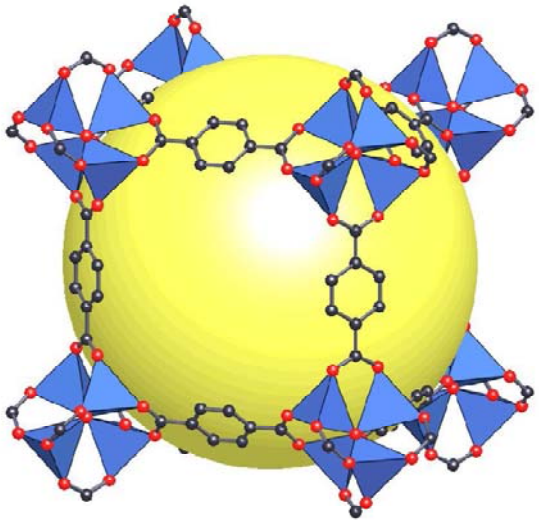


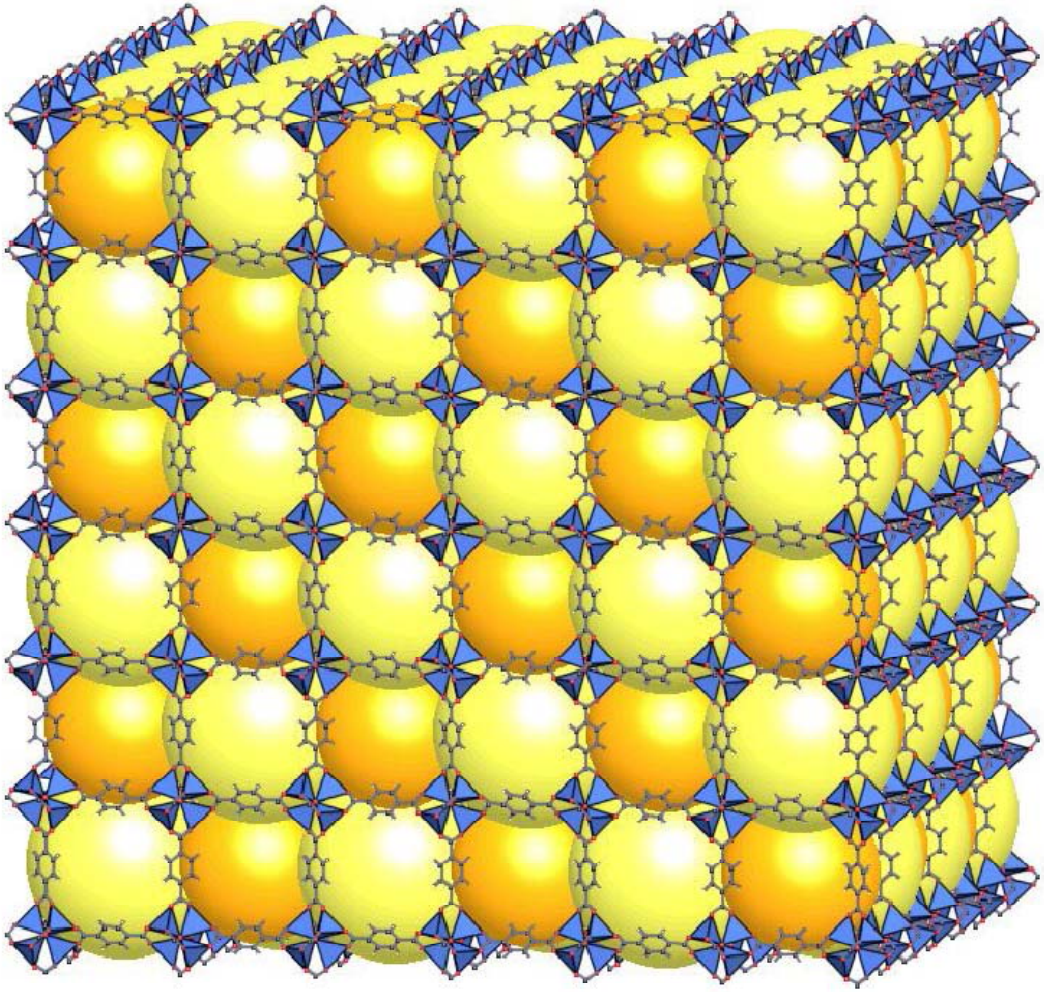
Sigma Aldrich http://www.sigmaaldrich.com/materials-science/alternative-energy-materials/metal-organic-frameworks.html

Calculated surface area of a hypothetical layer of graphite



Metal–Organic Frameworks Model





Nature, 1999, **402**, November,276-279

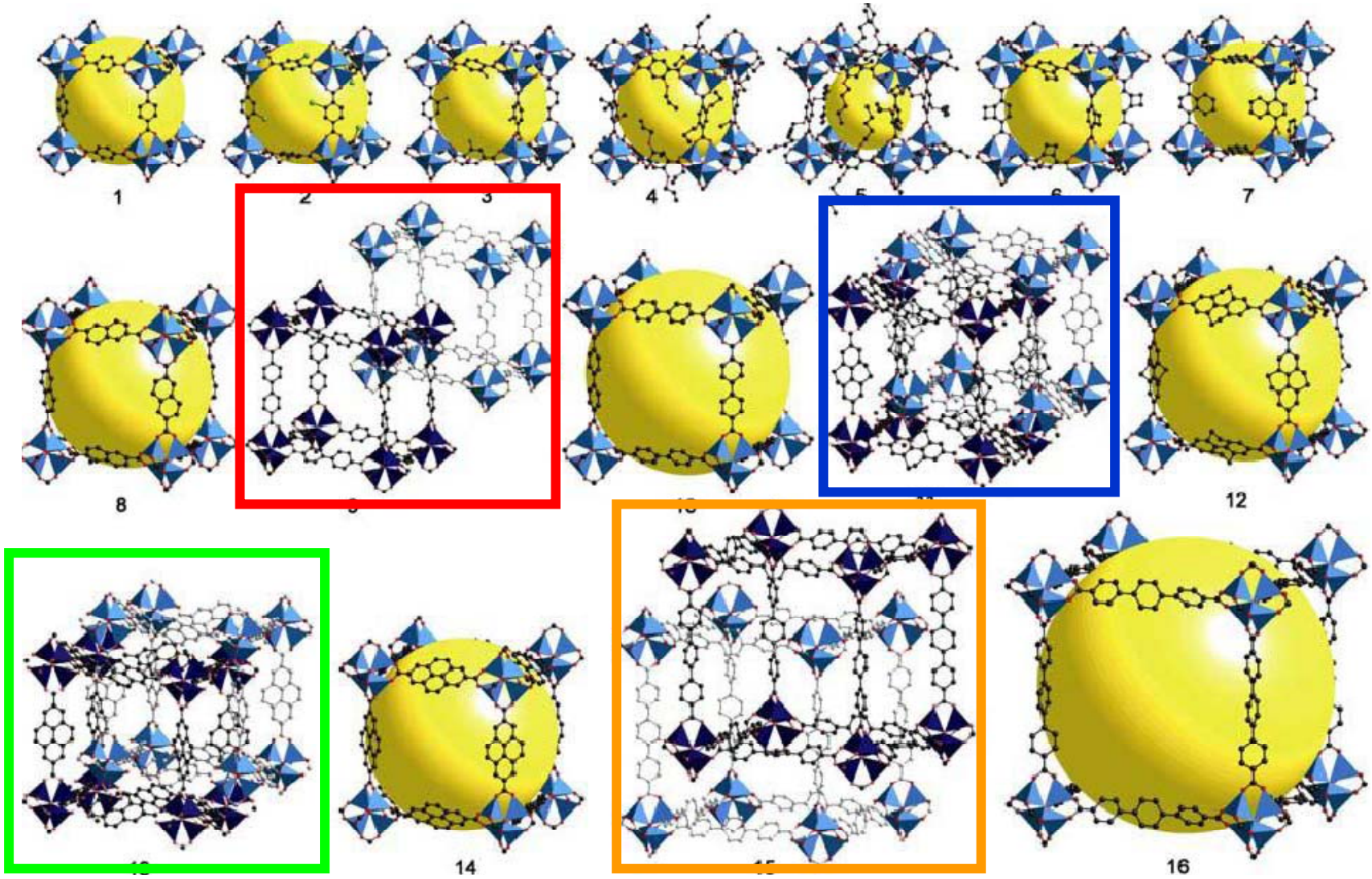
J. Mater. Chem., 2006, **16**, 626–636

MOFs Industrial Production

CH&EN News “Heading To Market With MOFs” http://pubs.acs.org/cen/coverstory/86/8634cover.html

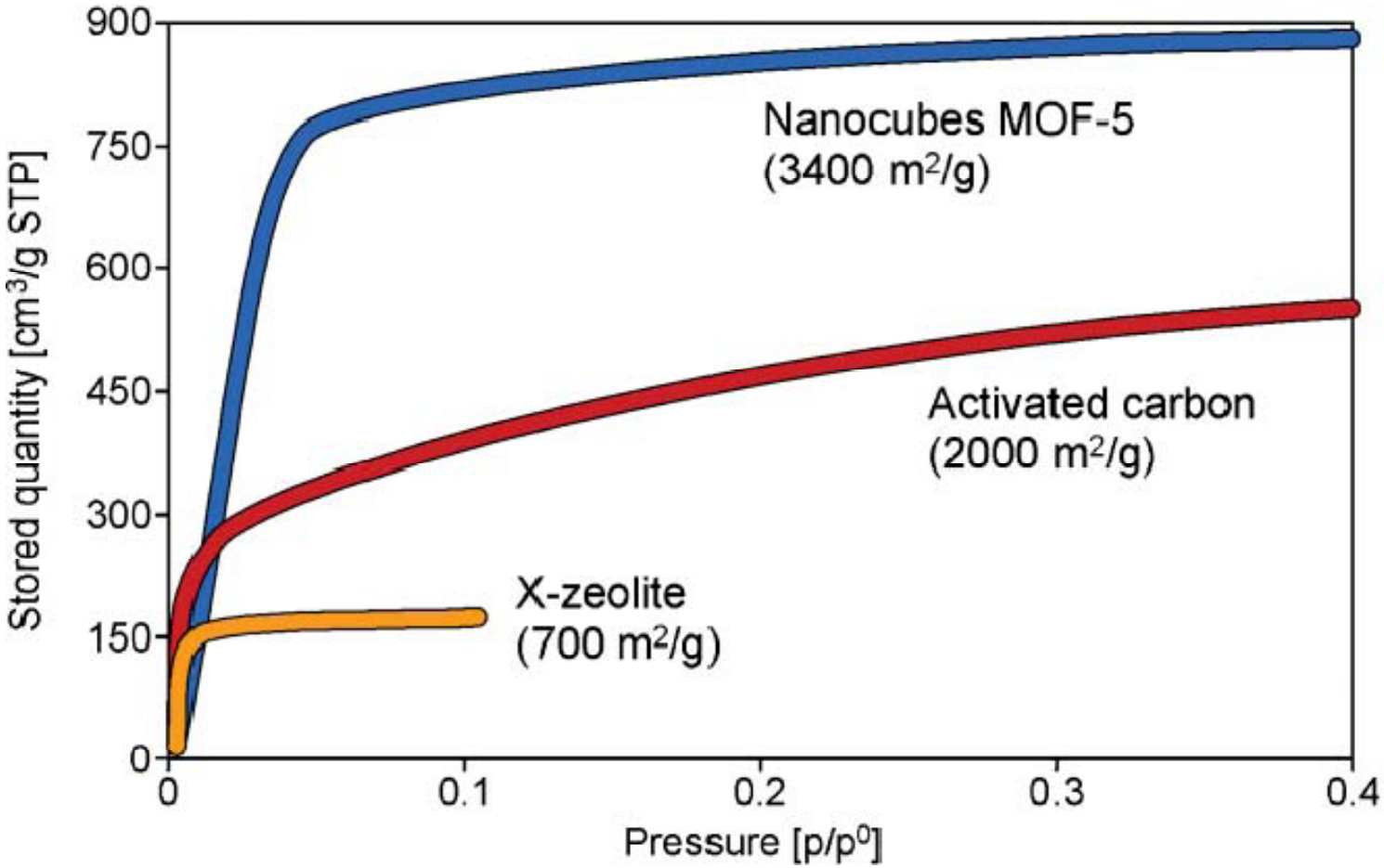
Adapted from Dr Omar Yaghi (UCLA) and Dr Ulrich Mueller (BASF) Lectures 2010

Different Pore Size Varying Ligands



Science, 2002, **295** No. 5554, 469-472

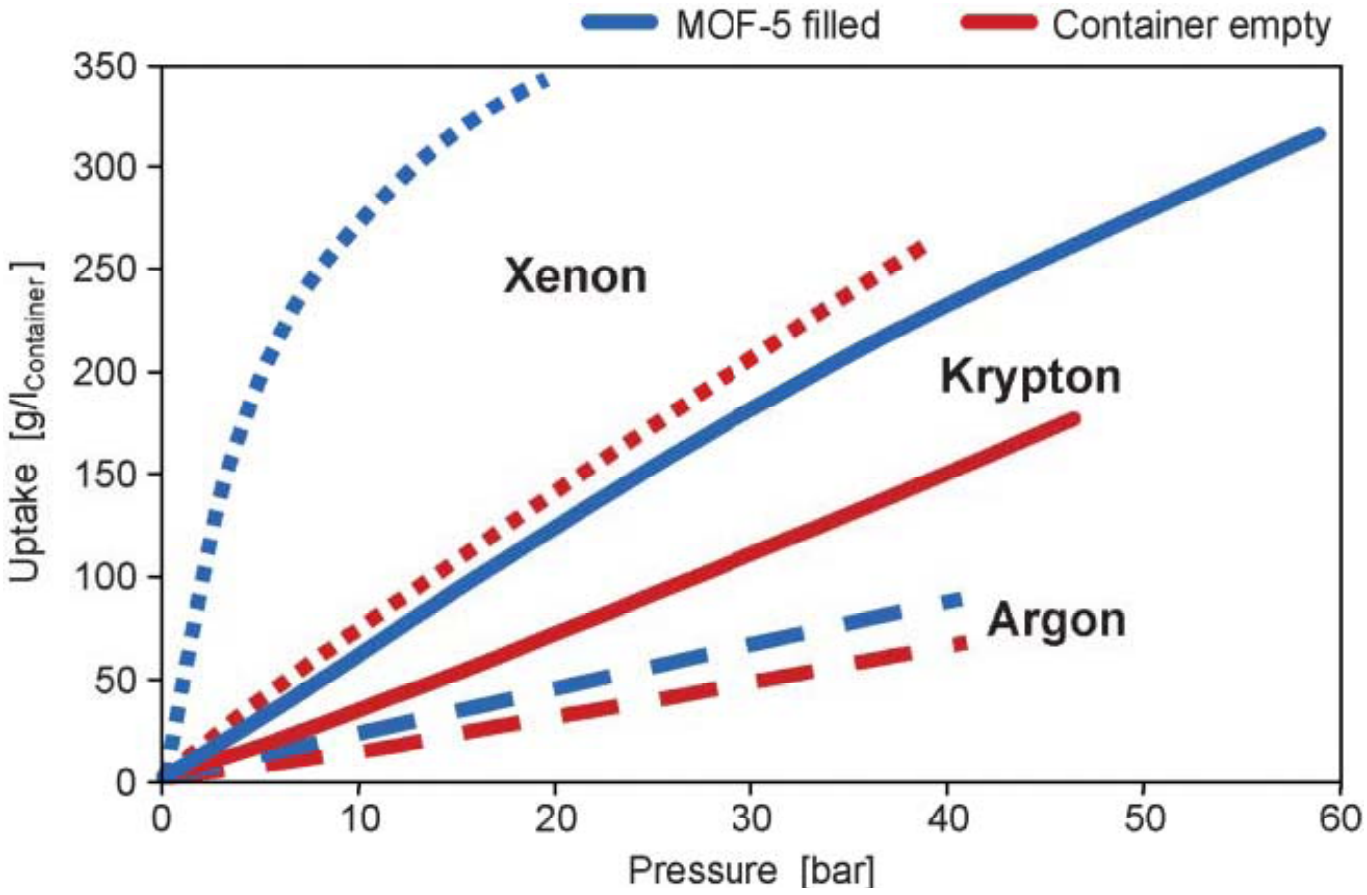
Materials for Argonne Storage



Adsorption isotherms of argon at 87 K on MOF-5 compared to activated carbon and zeolite X.

J. Mater. Chem., 2006, **16**, 626–636

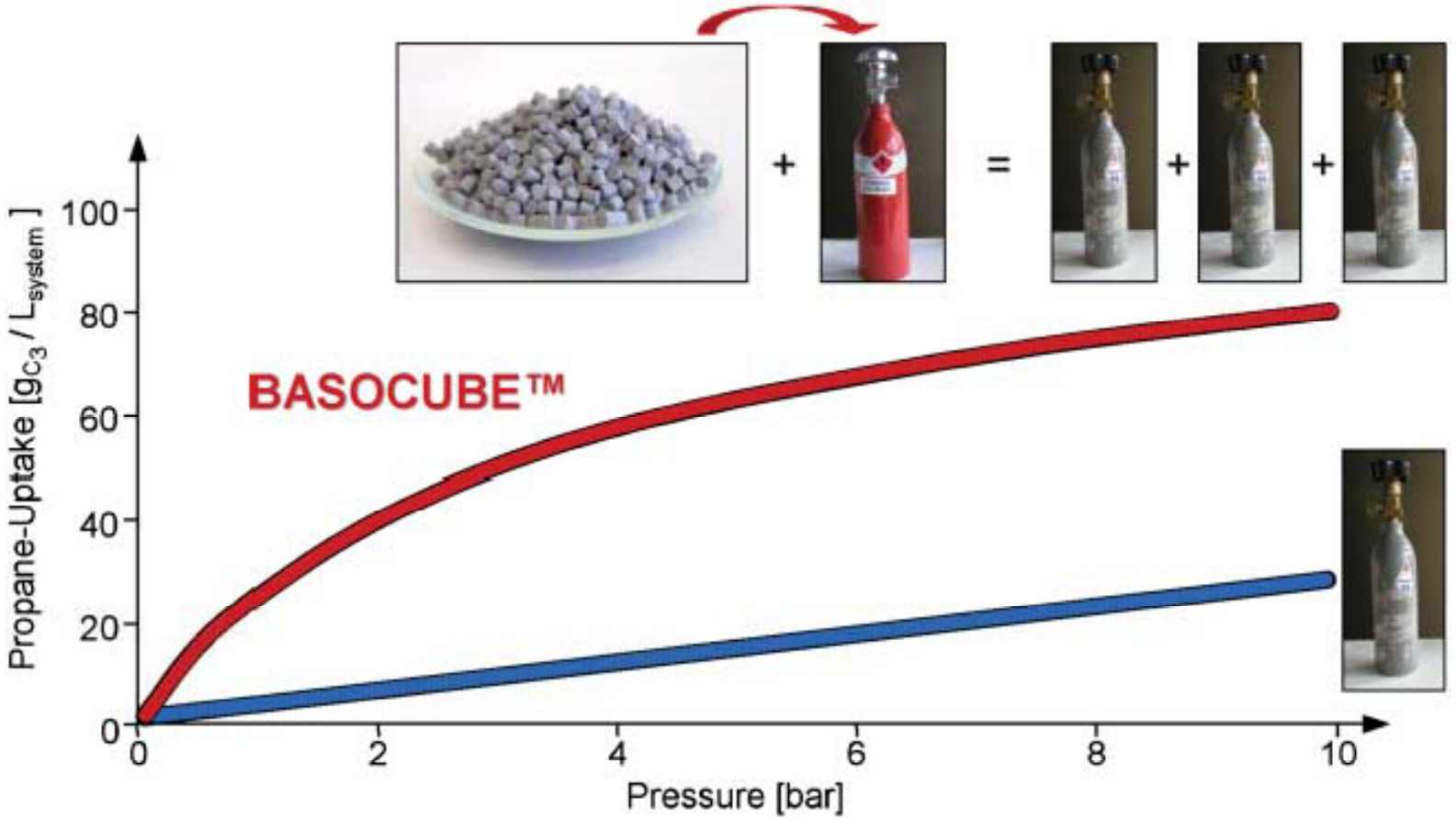
Uptake increases when MOF is used



Compression curves of rare gases Ar, Kr, Xe and comparison over inflation curves into MOF-5-filled gas containers at Room Temperature (298K)

J. Mater. Chem., 2006, **16**, 626–636

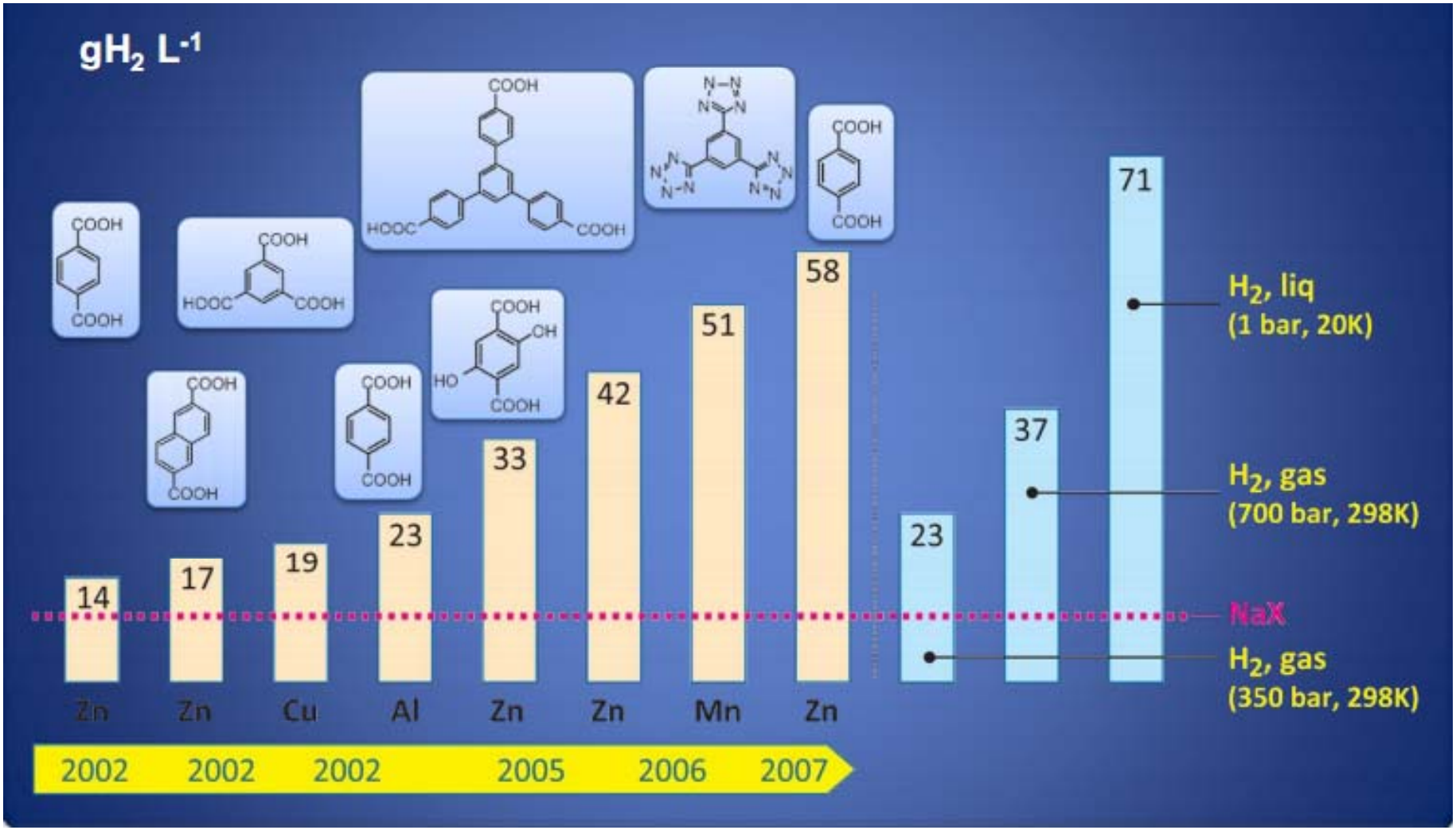
Uptake increases when MOF is used



Compression of propane into gas container with and without MOF-filling (MOF-5 tablets in lecture bottles, room temperature 298K).

J. Mater. Chem., 2006, **16**, 626–636

Gas Storage on MOFs (Hydrogen) 77K



Taken From Dr. Yaghi Lecture 2010 New Orleans USA.

MRS Bulletin, **2009**, 34, 682-690

The USDOE 2010 targets for a hydrogen storage system are

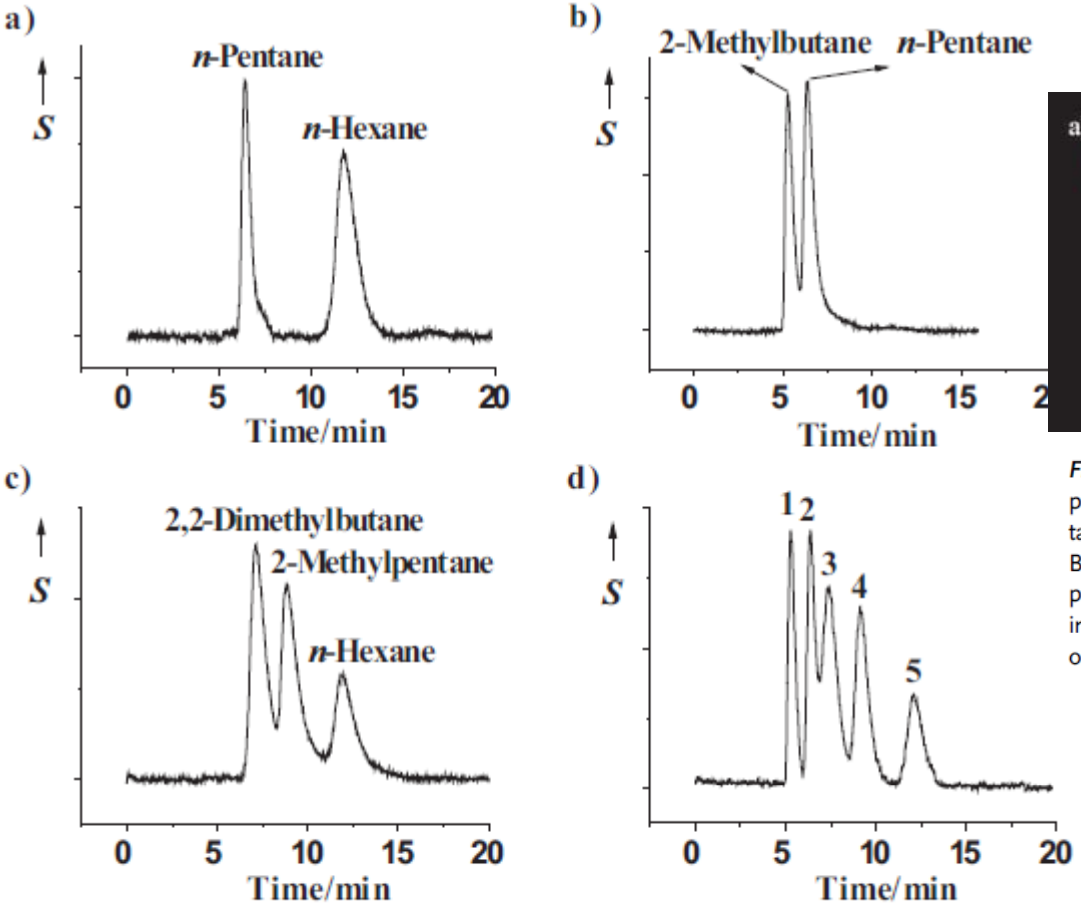
1) a capacity of 45 g H_2 per L,
2) a refueling time of 10 min or less,
3) a lifetime of 1000 refueling cycles
4) an ability to operate within the temperature range 30 to 50 °C.[1]

MOFs Applications

Properties and Applications

A Microporous Metal–Organic Framework for Gas-Chromatographic Separation of Alkanes**

Banglin Chen, Chengdu Liang, Jun Yang, Damacio S. Contreras, Yvette L. Clancy, Emil B. Lobkovsky, Omar M. Yaghi, and Sheng Dai**



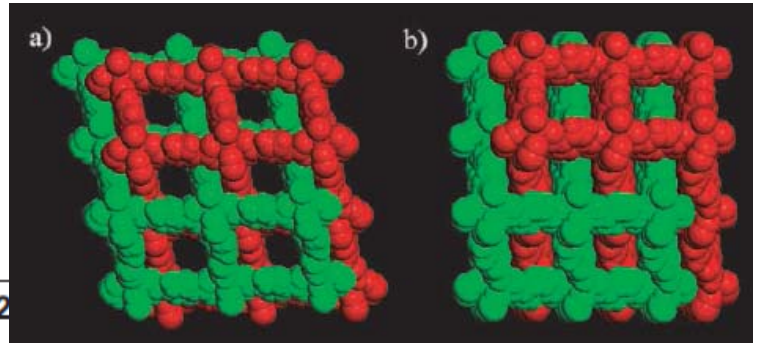


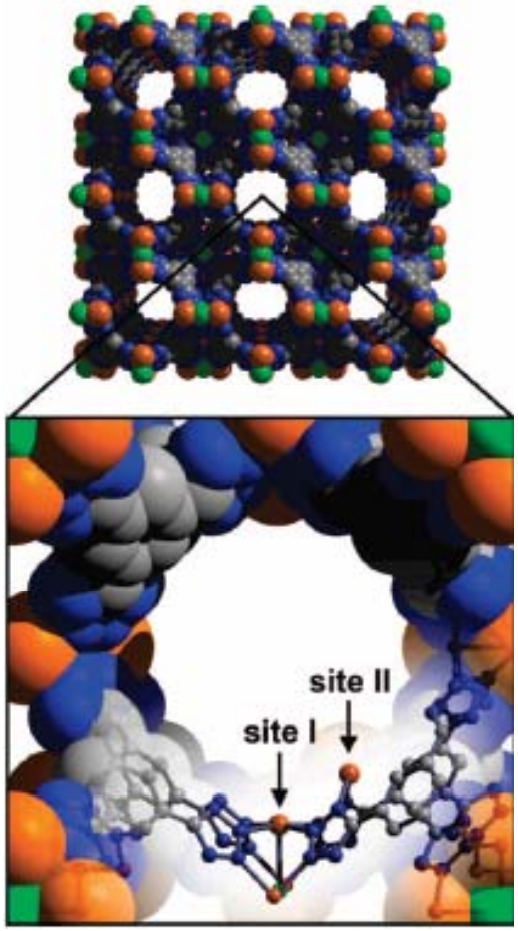
Figure 1. Space-filling representations of the structures of a) the open phase $Zn(BDC)(4,4'\text{-Bipy})_{0.5}\cdot(DMF)(H_2O)_{0.5}$ (MOF-508a), which contains 1D channels of 4.0×4.0 Å, and b) the dense phase $Zn(BDC)(4,4'\text{-Bipy})_{0.5}$ (MOF-508b), viewed along the rectangular diagonal of the paddle-wheel clusters. The two interpenetrating frameworks are shown in red and green. The disordered guest molecules in MOF-508a are omitted for clarity.

Angew. Chem. Int. Ed. **2006**, *45*, 1390–1393

Size-Selective Lewis Acid Catalysis in a Microporous Metal-Organic Framework with Exposed Mn^{2+} Coordination Sites

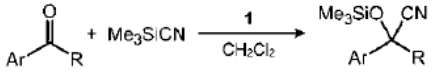
Satoshi Horike, Mircea Dincă, Kentaro Tamaki, and Jeffrey R. Long*
Department of Chemistry, University of California, Berkeley, California 94720

$Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2$



2100 m^2/g

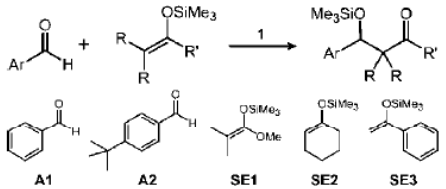
Table 1. Results for the Cyanosilylation of Carbonyl Substrates in the Presence of **1**[a]



entry	Ar	R	time (h)	yield (%)[b]
1	phenyl	H	9	98
2	1-naphthyl	H	9	90
3	4-phenoxyphenyl	H	9	19
4	biphenyl	H	9	18
5	phenyl	CH_3	24	28
6	biphenyl	CH_3	24	1

[a] Reaction conditions: Me_3SiCN (3 mmol), aldehyde/ketone (1.5 mmol), CH_2Cl_2 (5 mL), **1** (0.04 g, 0.006 mmol), room temperature, under N_2. [b] Determined by ^1H NMR based on the carbonyl substrate.

Table 2. Results for the Mukaiyama–Aldol Reaction in the Presence of **1**[a]



entry	aldehyde	silyl enolate	time (h)	solvent	yield (%)[b]
1	**A1**	**SE1**	99	CH_2Cl_2	63
2	**A2**	**SE1**	99	CH_2Cl_2	24
3	**A1**	**SE2**	99	CH_2Cl_2	< 1
4	**A1**	**SE3**	99	CH_2Cl_2	< 1
5[c]	**A1**	**SE1**	6	DMF	8[d]
6[c]	**A1**	**SE1**	6	DMF	51

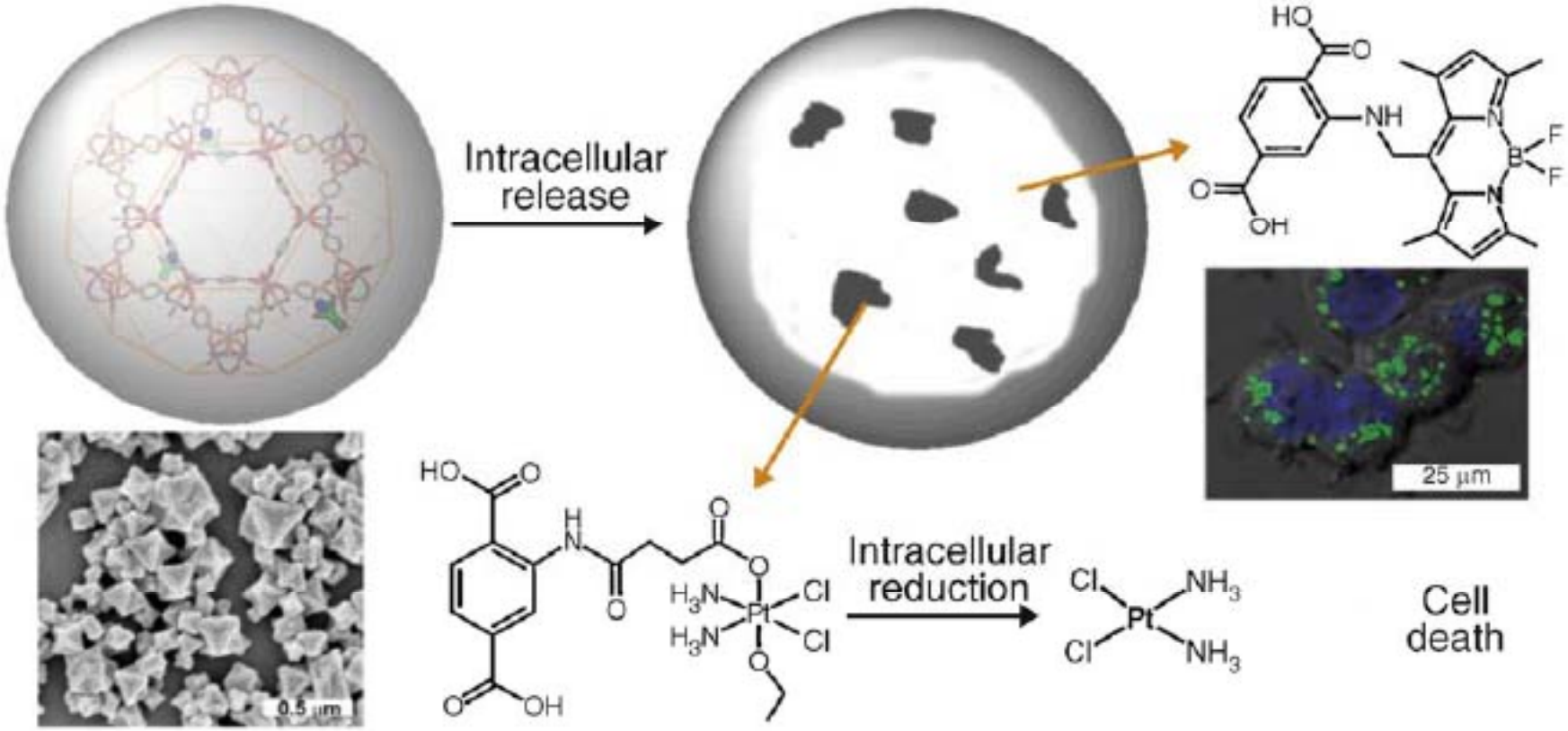
[a] Reaction conditions: silyl enolate (2 mmol), aldehyde (1 mmol), solvent(5 mL), **1** (0.04 g, 0.006 mmol), room temperature, under N_2. [b] Determined by ^1H NMR based on the aldehyde. [c] Reaction at −45 °C. [d] No catalyst added.

J. Am. Chem. Soc. 2008, **130**, 5854

Metal–organic frameworks as potential drug carriers

Rachel C Huxford, Joseph Della Rocca and Wenbin Lin

Absorber y liberar: Ibuprofeno, Procainamida, Oxido Nítrico
Encapsular tanto el “imaging agent” y el “therapeutic agent”



NanoMIL-101 can be loaded both with an optical imaging agent and cisplatin prodrug. Simultaneous release of the fluorophore and cisplatin prodrug allows real-time monitoring of the drug delivery by optical imaging.

Current Opinion in Chemical Biology 2010, **14**:262–268

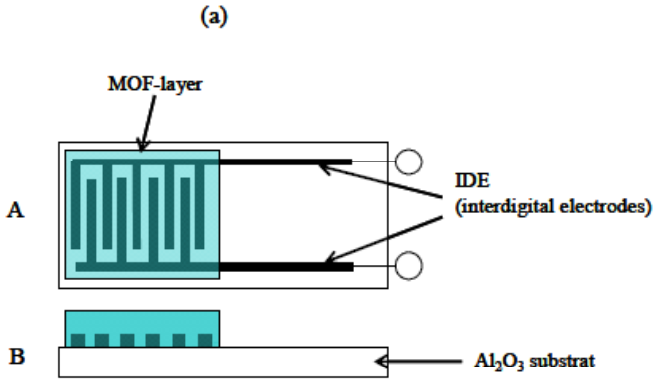
Metal-Organic Frameworks for Sensing Applications in the Gas Phase

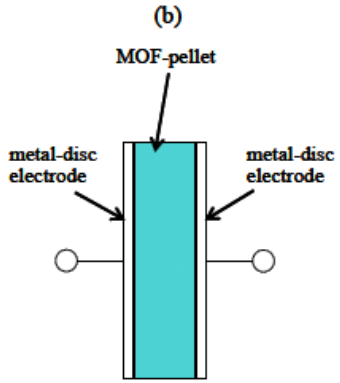
Sensors **2009**, *9*, 1574-1589;

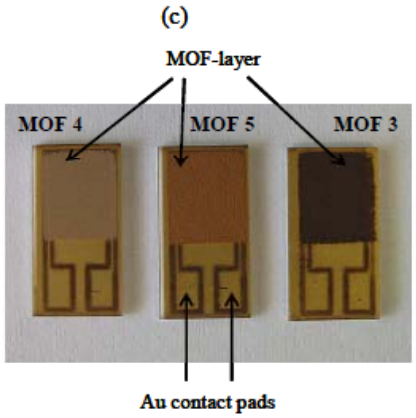
long-term stable water vapor sensor

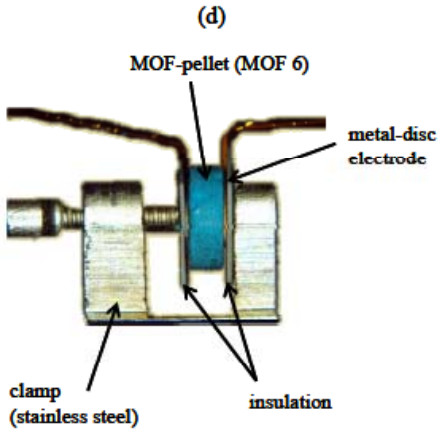
120 °C-240 °C
O_2, CO_2, C_3H_8, H_2
H_2O, Etanol, Metanol

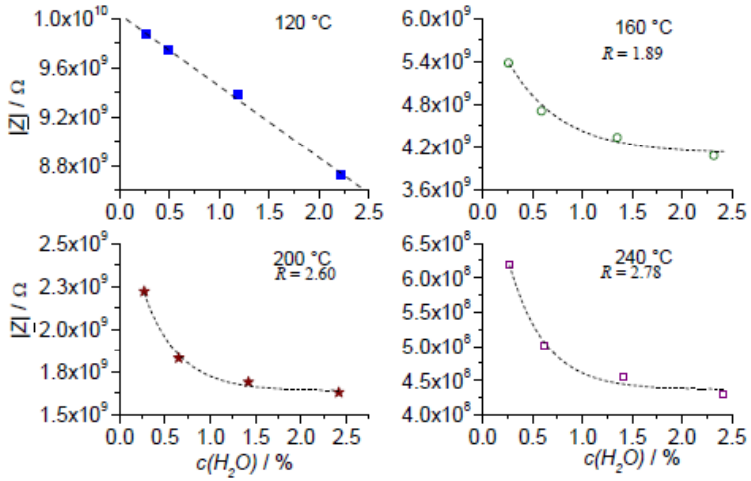
Al-terephthalate-MOF (Al-BDC, Basolite™ A100),
Fe-1,3,5-benzenetricarboxylate-MOF (Fe-BTC),
Cu-1,3,5-benzenetricarboxylate-MOF (Cu-BTC).



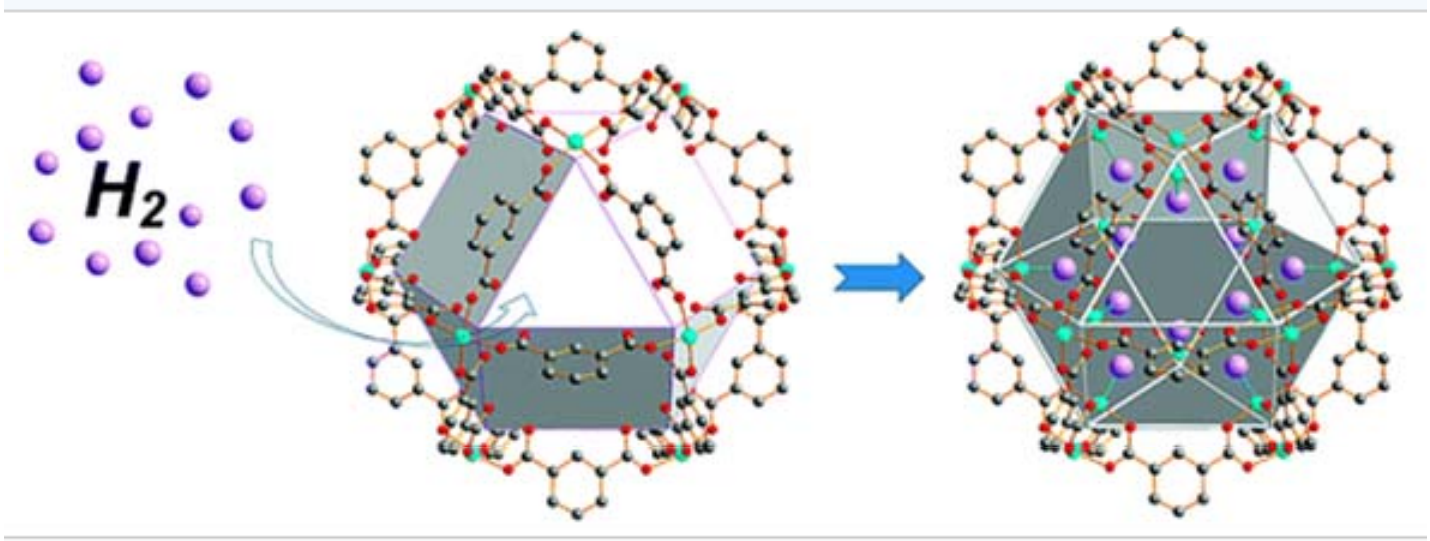






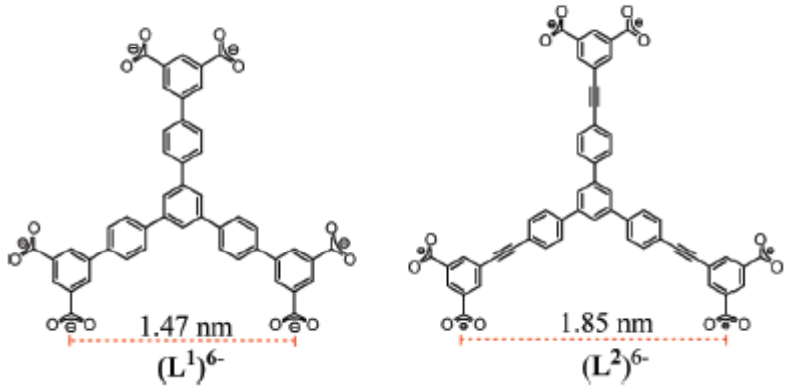


Metal–Organic Polyhedral Frameworks: High H_2 Adsorption Capacities and Neutron Powder Diffraction Studies



$[Cu_3(C_{54}H_{24}O_{12})(H_2O)_3]\cdot 16DMF\cdot 26H_2O$,

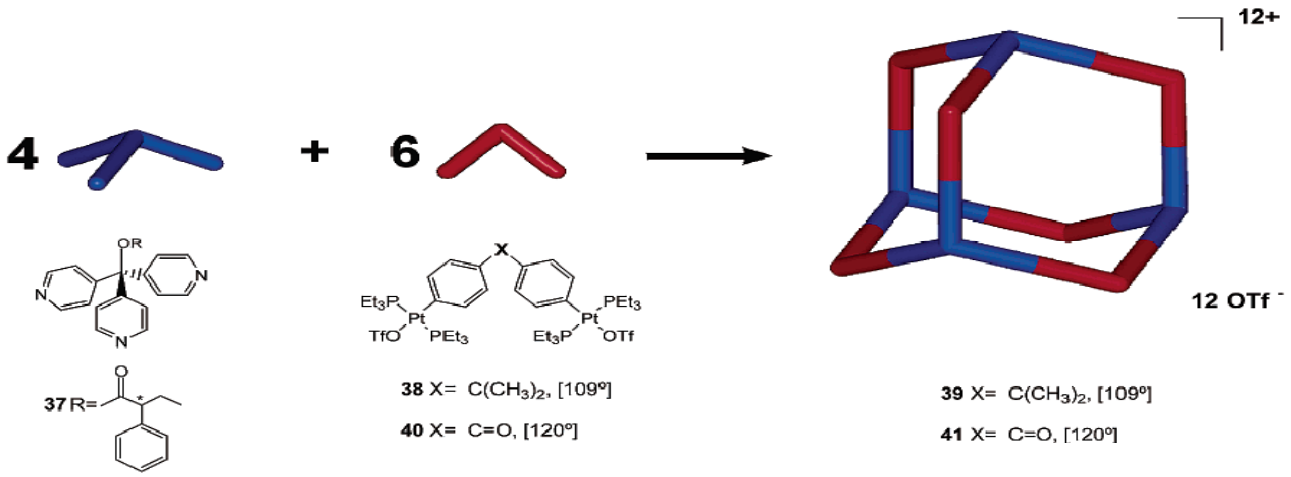
4664 m2 / g
9.2 wt % a 77 K, 50 bar



J. Am. Chem. Soc., **2010**, *132* (12), pp 4092–4094

Metal-Organic Polyhedra (MOPs)

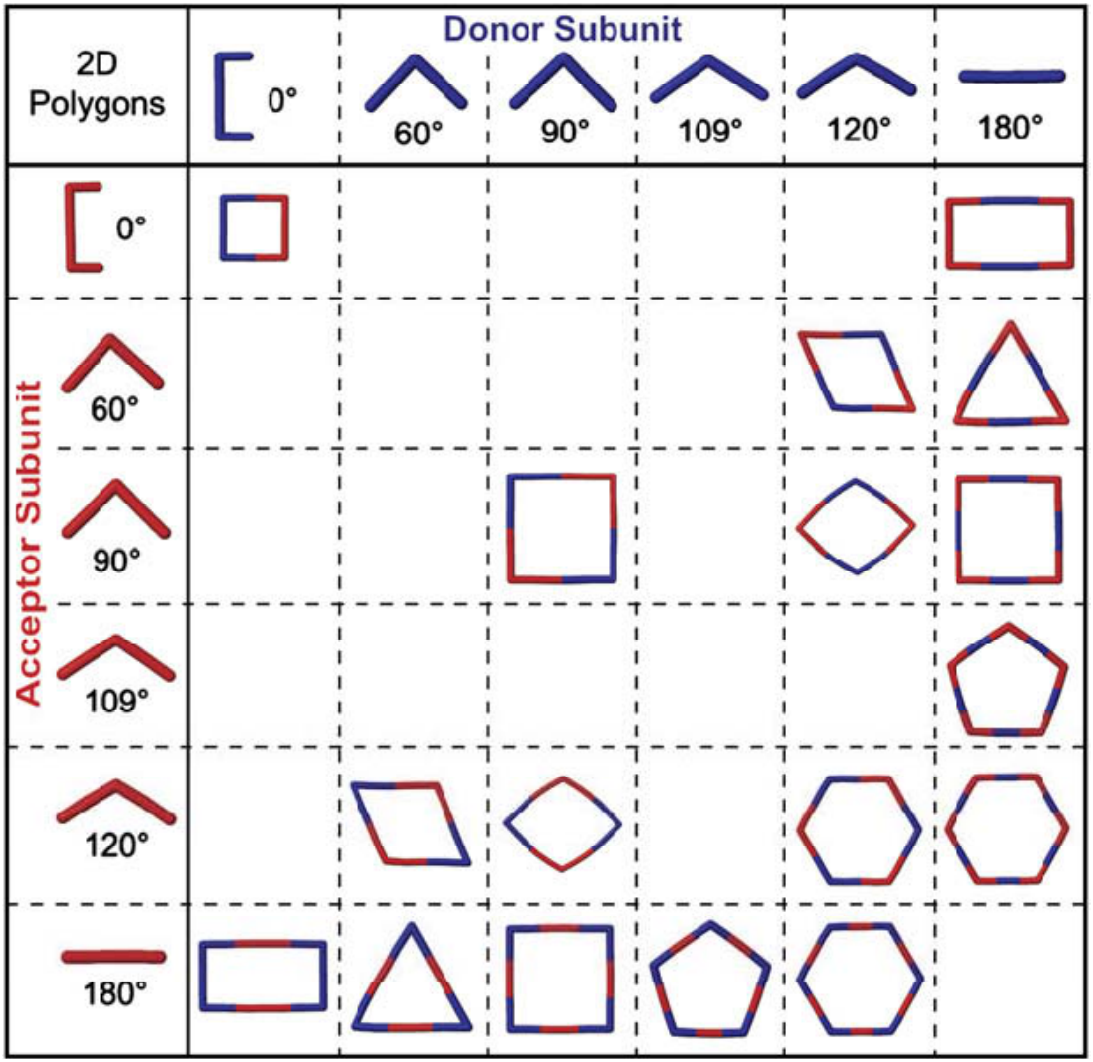
Metal-organic polyhedra (MOPs), are discrete metal-organic molecular assemblies. They are useful as host molecules that can provide tailorable internal volume in terms of metrics, functionality, and active metal sites. As a result, these materials are potentially useful for a variety of applications, such as highly selective guest inclusion and gas storage, and as nanoscale reaction vessels.



J. Am. Chem. Soc., 1999, **121**, 10434-10435
Acc. Chem. Res. 2002, **35**, 972-983

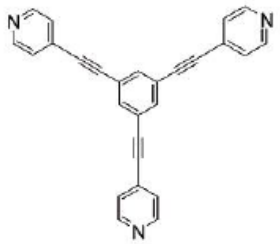
Self Assembled of Adamantanoids

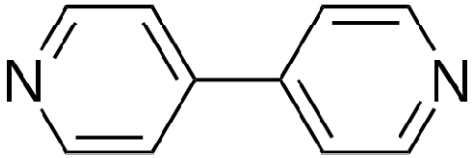
Supramolecular Polygons

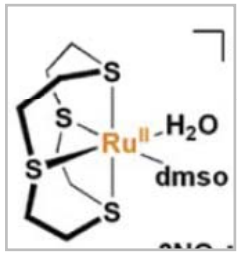


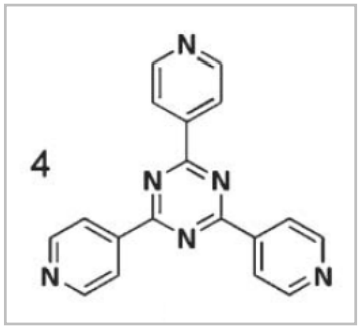
Tetrahedron 64 (2008) 11495–11503

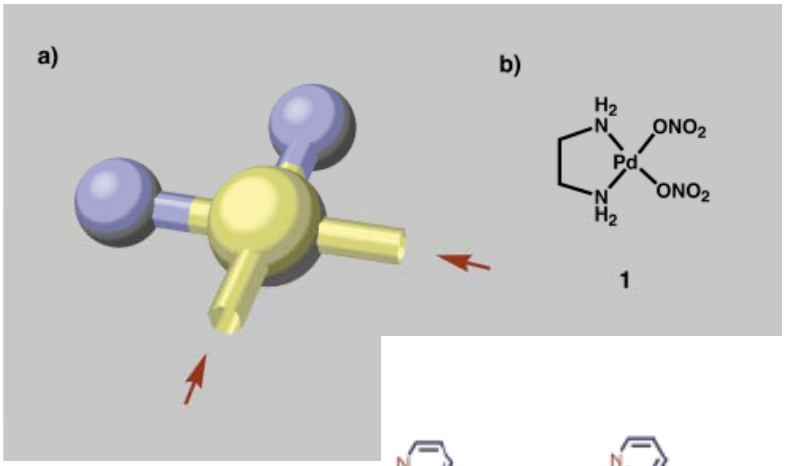
Common ligands & SBCs in MOPs

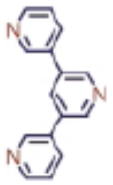


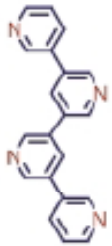


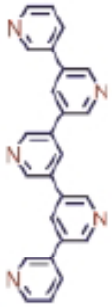


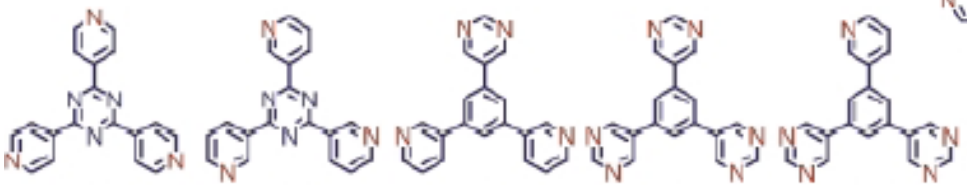












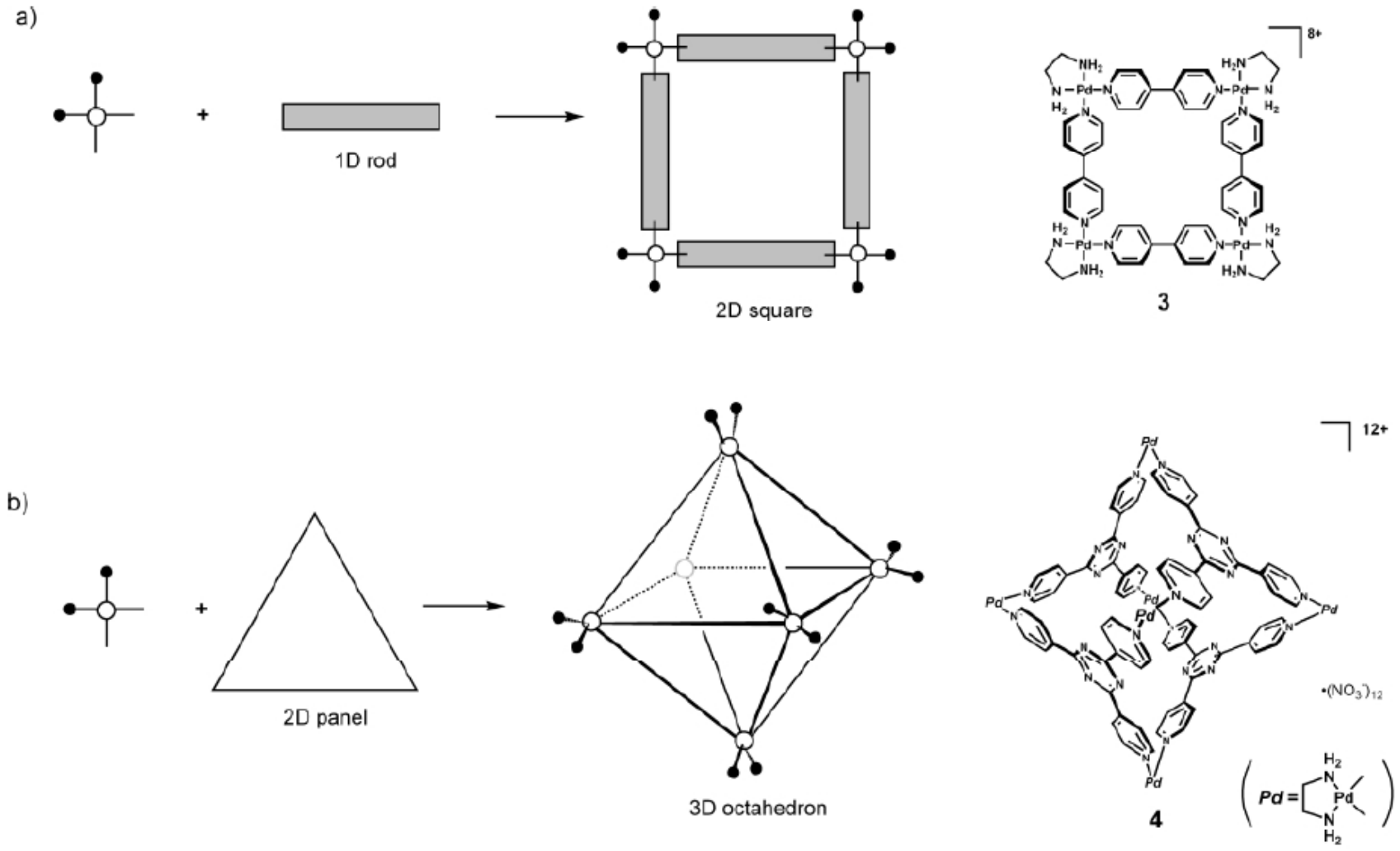
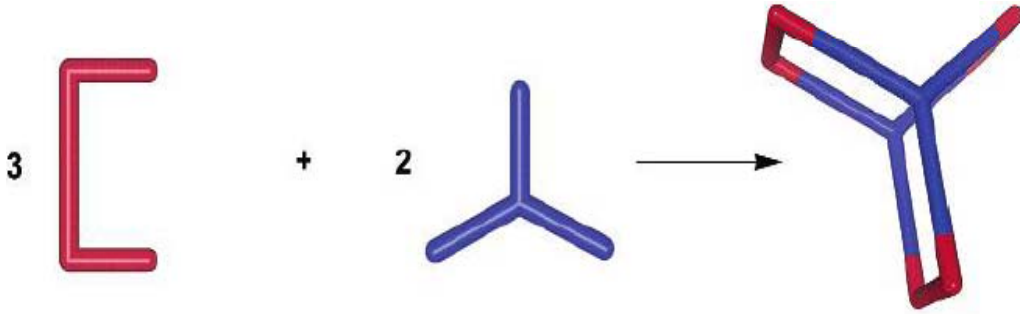
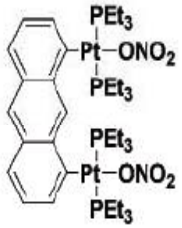


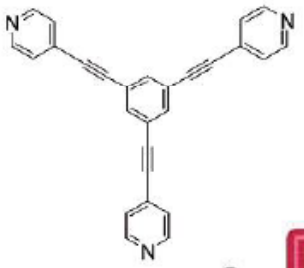
Fig. 2 (a) Schematic representation of molecular paneling: (a) from 1D-rods to 2D-molecules and (b) from 2D-panels to 3D-molecules.

Some Other Molecular Polyhedra

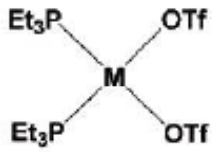
Self Assembly of NonDistorted Trigonal Prisms



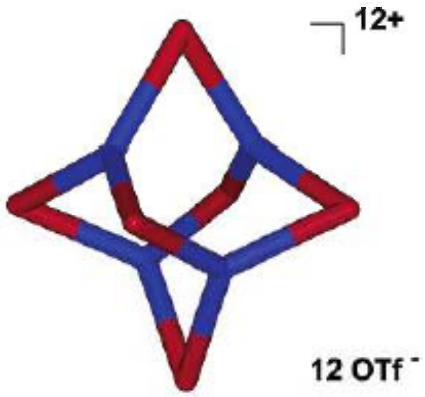




Self Assembly of Truncated Tetrahedra



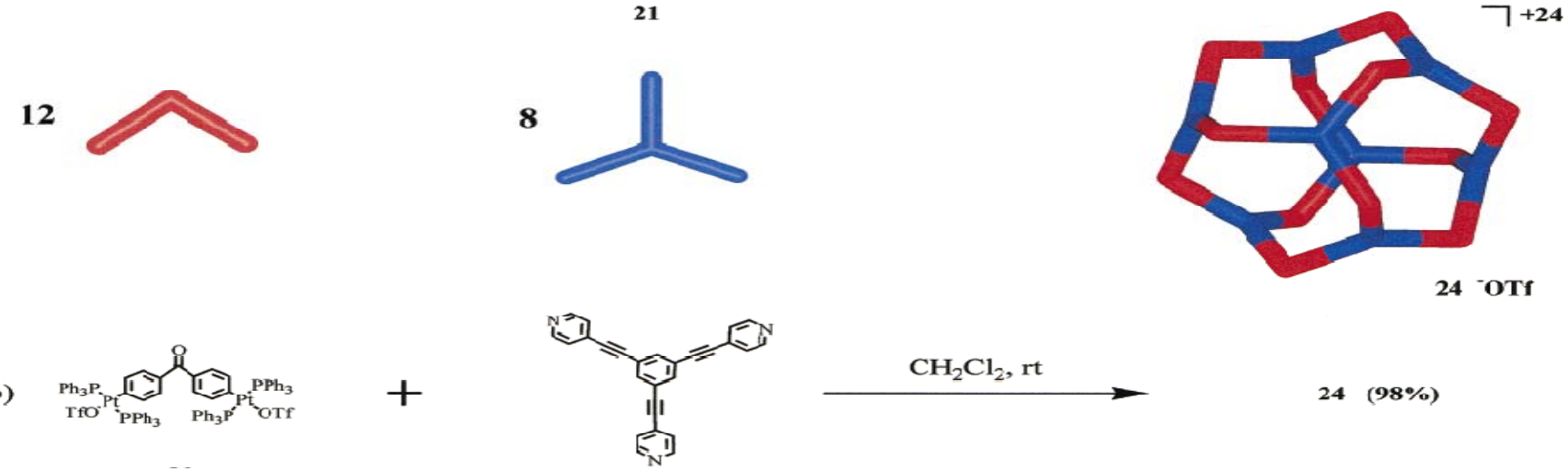
1: M = Pt
2: M = Pd



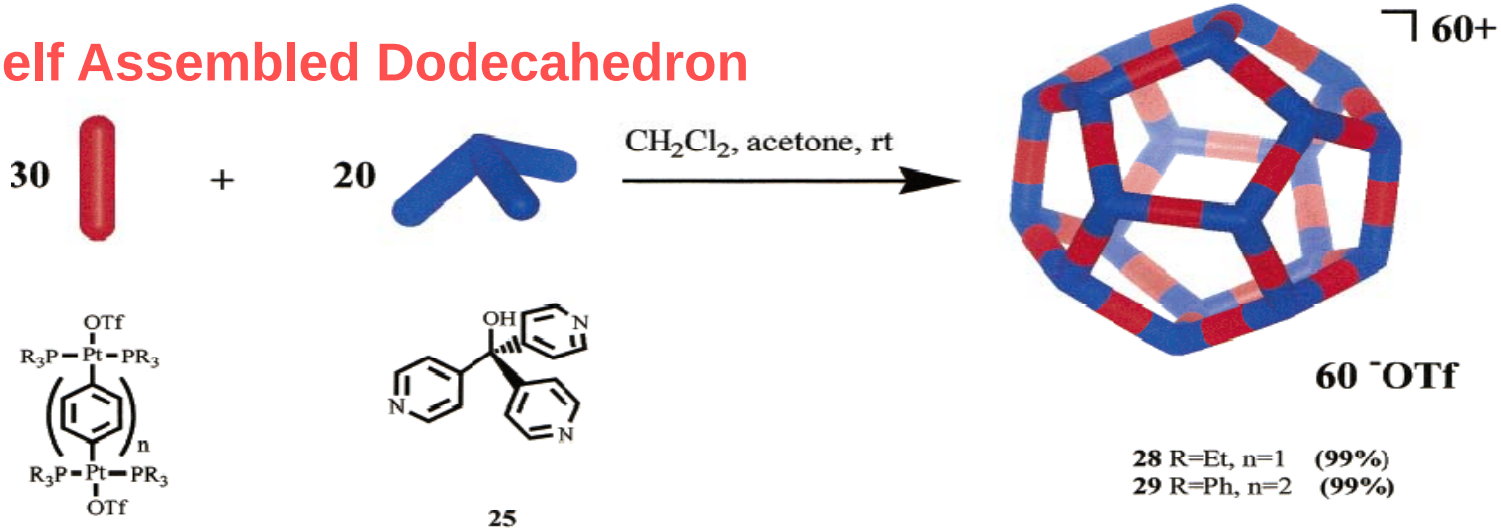
Acc. Chem. Res. 2002, **35**, 972-983

Some Other Molecular Polyhedra

Self Assembled of Cubocahedra



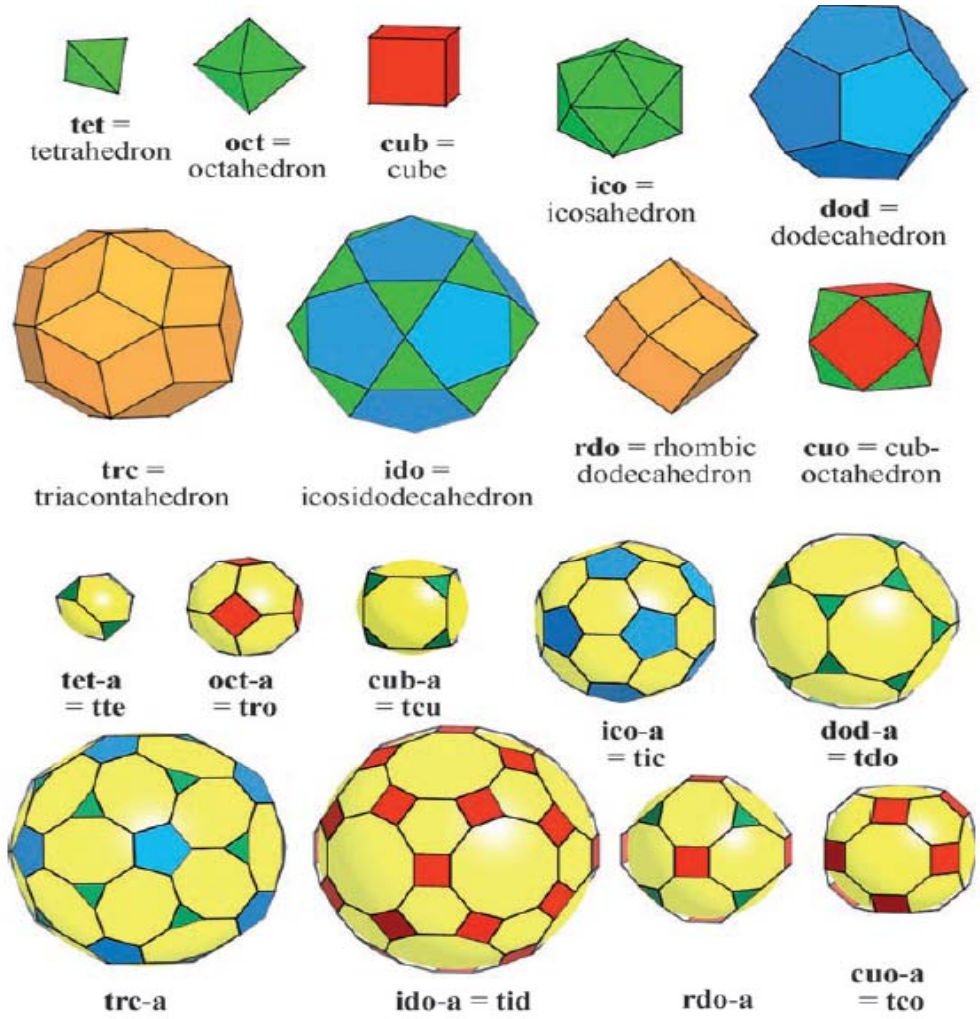
Self Assembled Dodecahedron



Acc. Chem. Res. 2002, **35**, 972-983

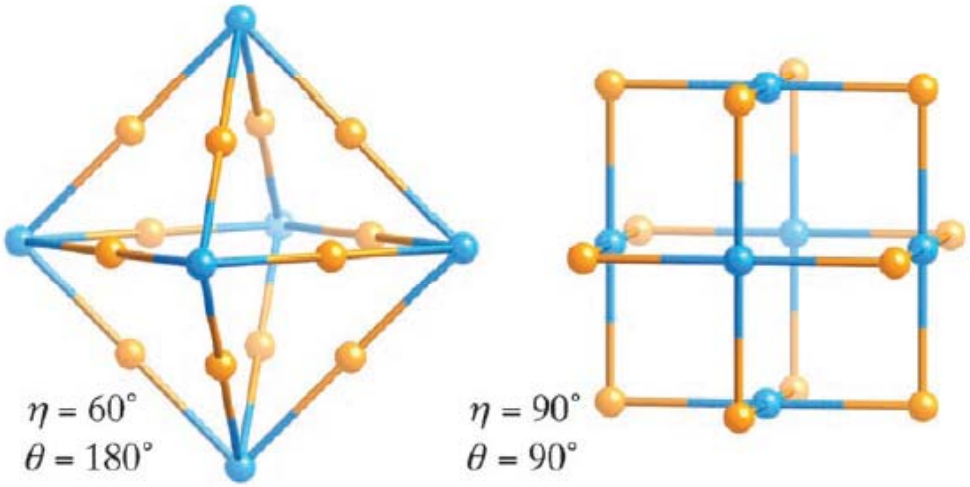
Polyhedra Designs

The process of obtaining Polyhedra when replacing the original vertices by a polygon with the number of sides equal to the valence of those vertices.

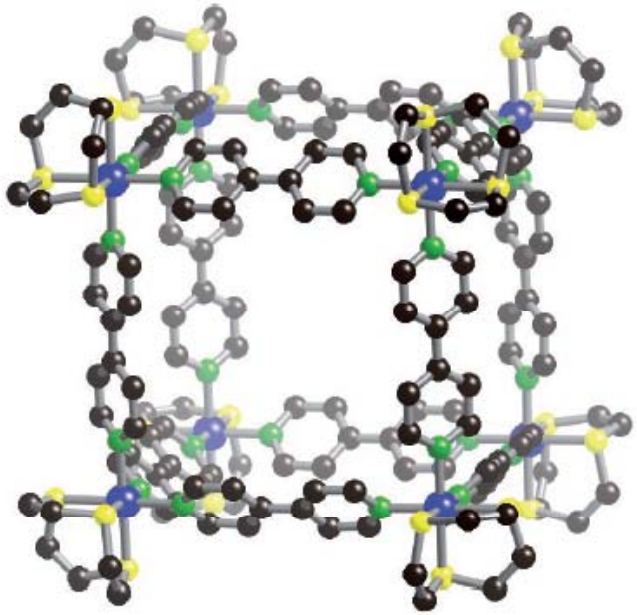


The nine edge-transitive convex polyhedra.

Angew. Chem. Int. Ed. 2008, **47**, 5136 –5147



Two configurations of six tetravalent SBUs linked to form an octahedron

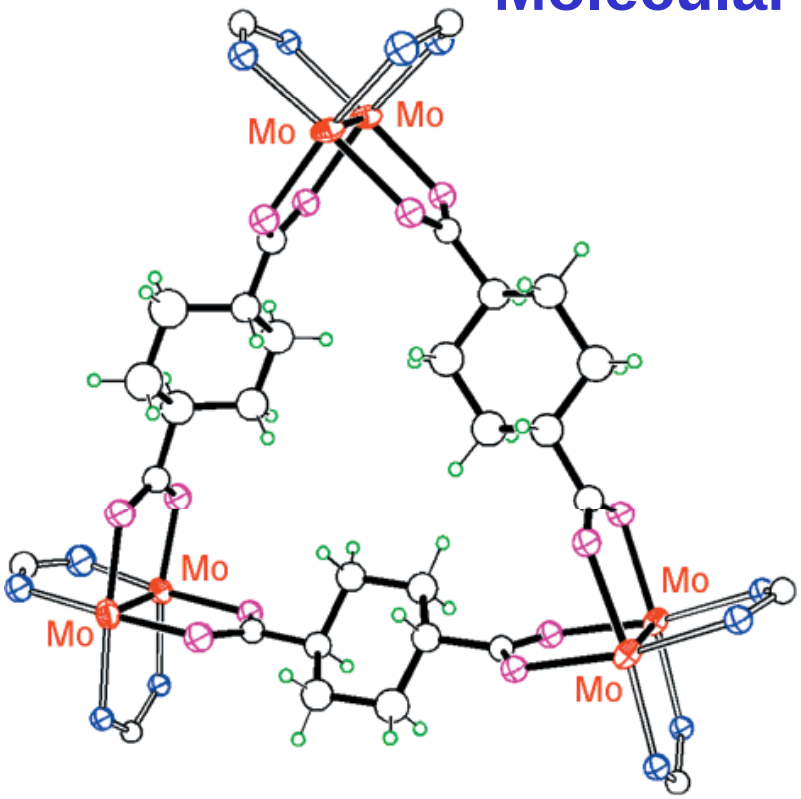


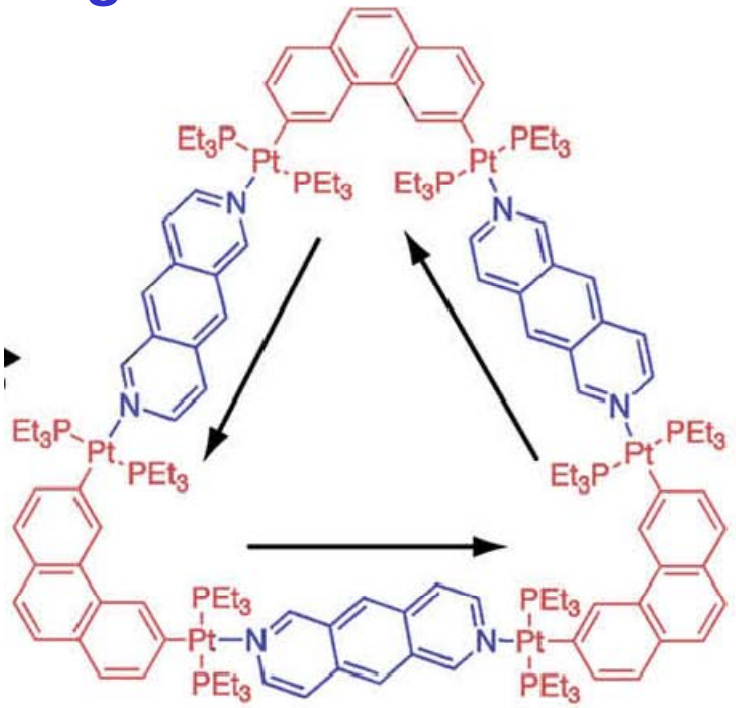
Construction of a cube, The model of the simple cubic structure [L8Ru8(bpy)12]16+ (L=1,4,7-trithionane; bpy=4,4'-bipyridine) proposed based on NMR evidence. (Ru blue, C black, N green, S yellow).

Angew. Chem. Int. Ed. 2008, **47**, 5136 –5147

Molecular Polygons

Molecular Triangles





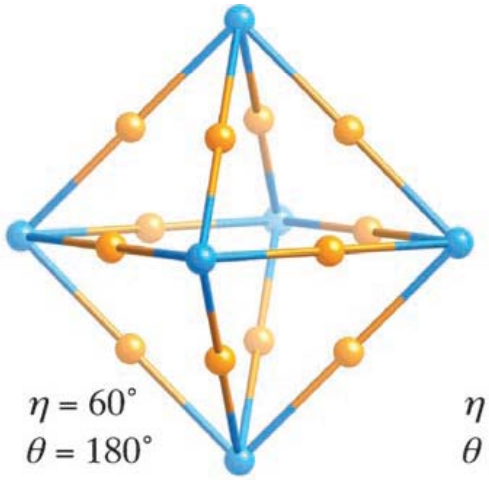
(A) The core of the molecular triangle 21 showing three [*cis*-Mo2(DAniF)2]3[*eq,eq*-1,4-O2CC6H10CO2]3Mo2 units linked by three cyclohexanedicarboxylate anions.

(B) Molecular Triangle

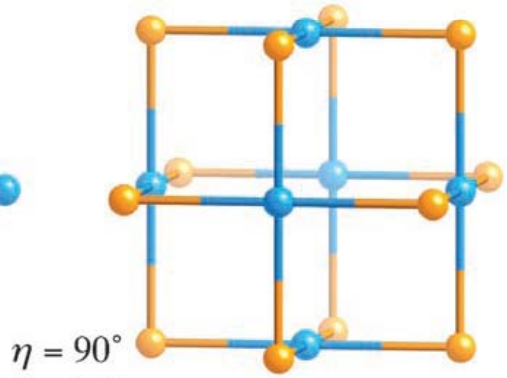
Acc. Chem. Res. 2001, **34** No 10, 759-771

Acc. Chem. Res. 2005, **38**, 371-380

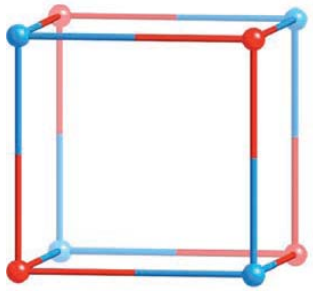
MOPs



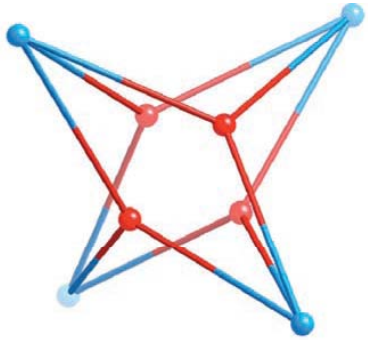
$\eta = 60^\circ$
$\theta = 180^\circ$



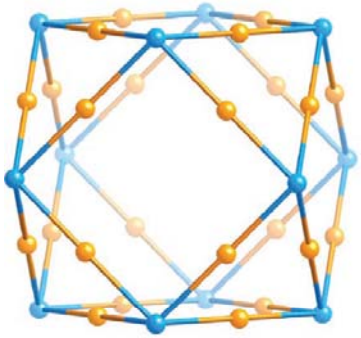
$\eta = 90^\circ$
$\theta = 90^\circ$

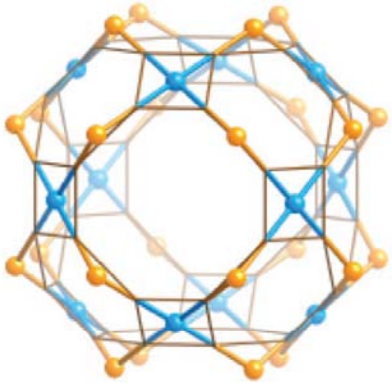


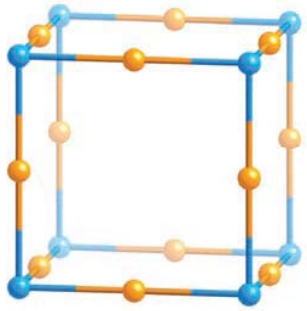
$\eta_1 = 90^\circ, \eta_2 = 90^\circ$



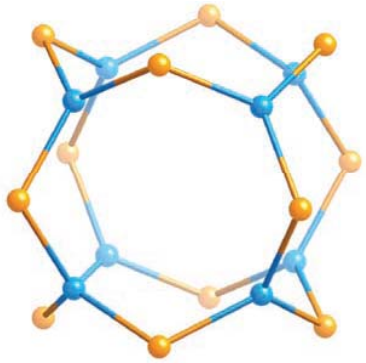
$\eta_1 = 120^\circ, \eta_2 = 33.6^\circ$







$\eta = 90^\circ, \theta = 180^\circ$

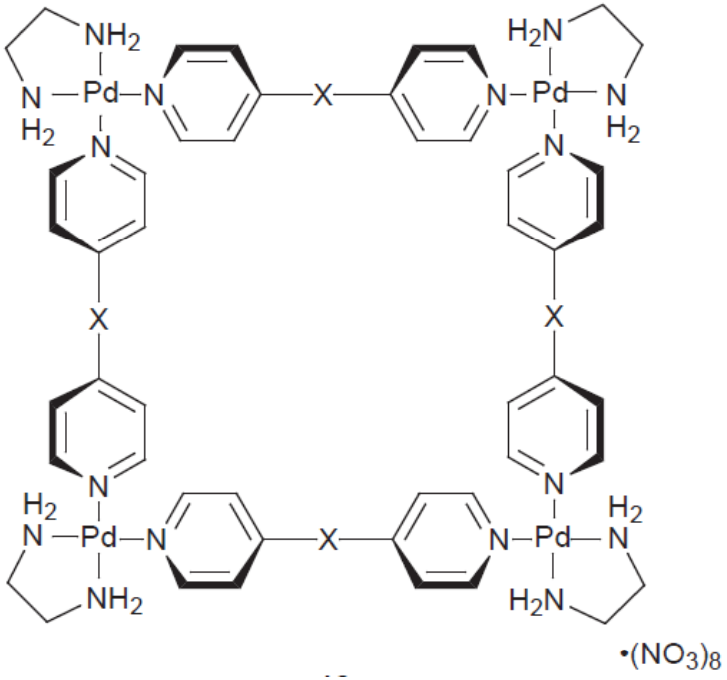


$\eta = 120^\circ, \theta = 109.5^\circ$

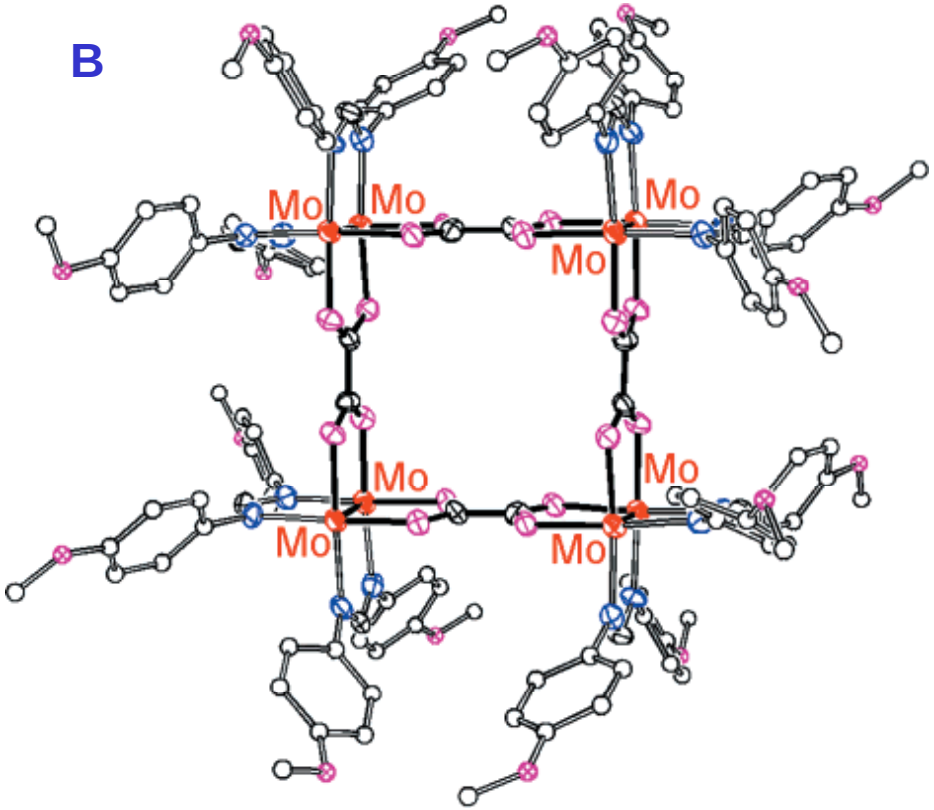
Molecular Polygons

Molecular Squares

A



B



(A) Molecular square of bipyridine ligands and ethylenediamine coordinating the Pd.
(B) Structure of the molecular square, showing four Mo2 units linked by four oxalate anions.

Acc. Chem. Res. 2001, **34** No 10, 759-771

Acc. Chem. Res. 2005, **38** No 4, 371-380

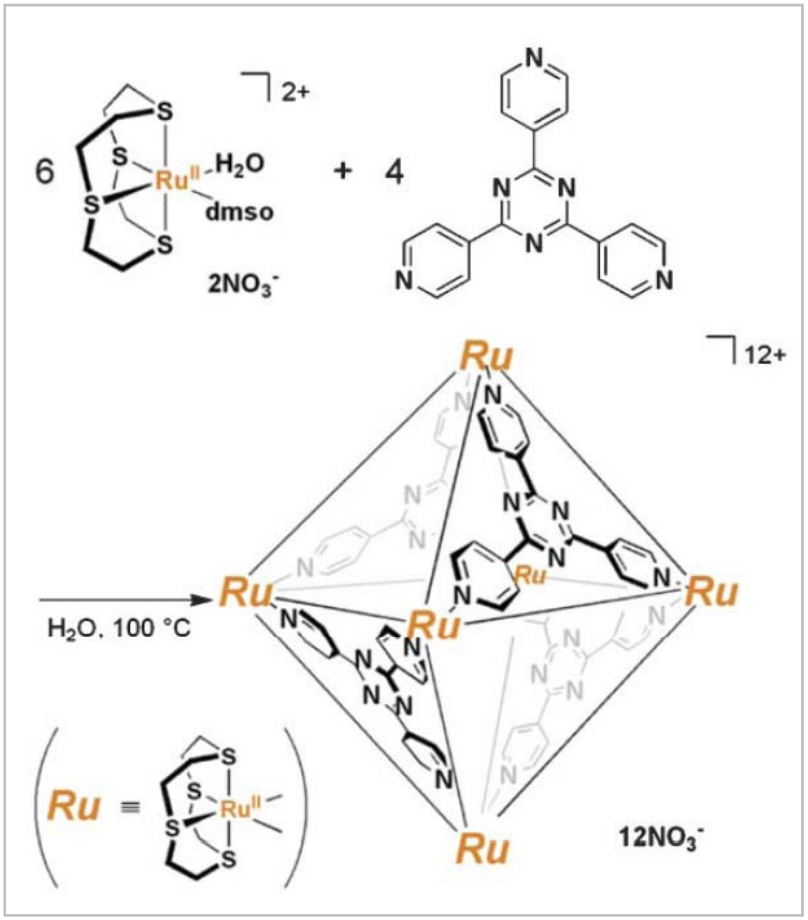
Chem. Soc. Rev., 1998, **27**, 417 - 425

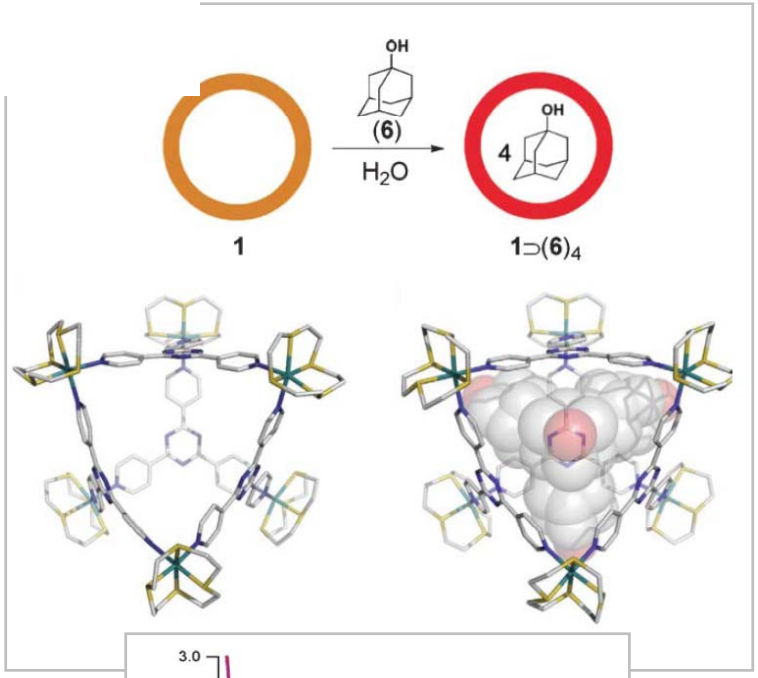
MOPs Applications

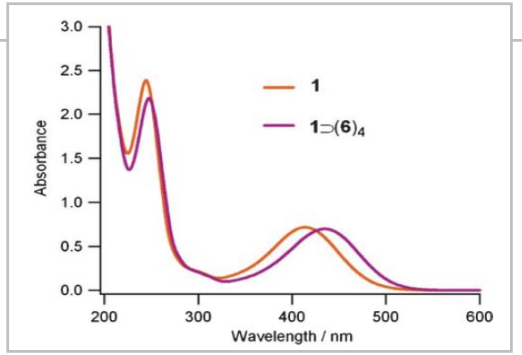
Host-Guest interactions

Ru(II)-cornered coordination cage that senses guest inclusion by color change†

Ken-ichi Yamashita, Masaki Kawano and Makoto Fujita*







Yamashita, K.; Kawano, M.; Fujita, M. Ru(II)-cornered coordination cage that senses guest inclusion by color change. *Chem. Commun*. **2007**, 4102–4103

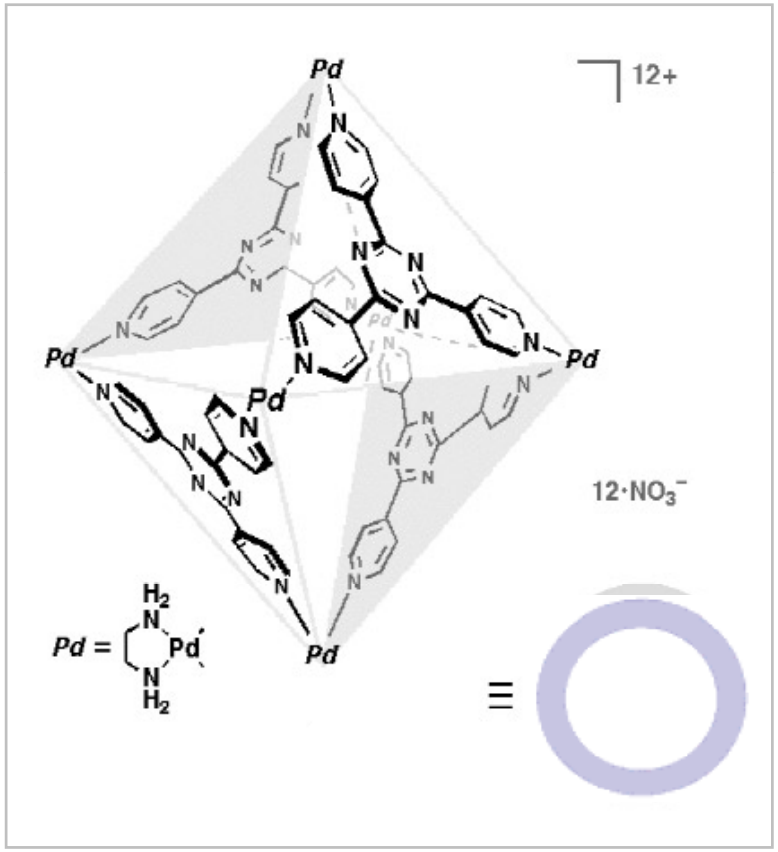
Fotochemical Nanoreactors

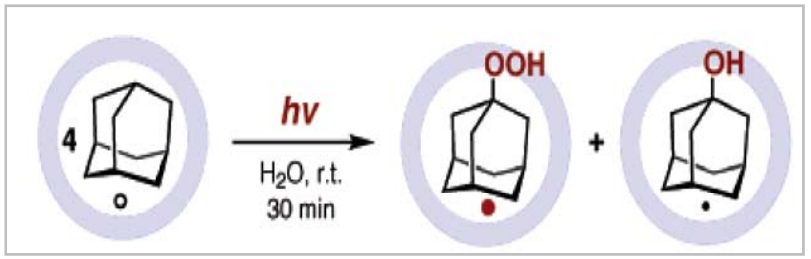
Alkane Oxidation via Photochemical Excitation of a Self-Assembled Molecular Cage

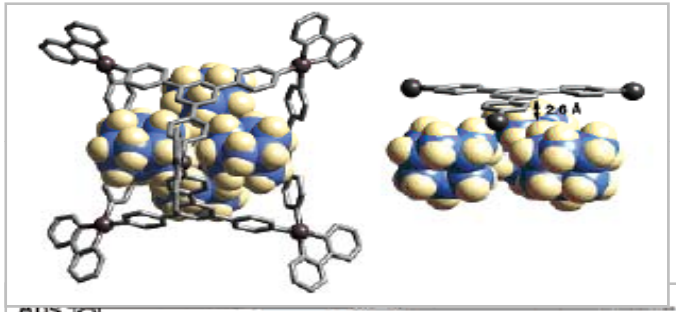
Michito Yoshizawa,† Sachiko Miyagi,† Masaki Kawano,† Katsuya Ishiguro,‡ and Makoto Fujita*,†

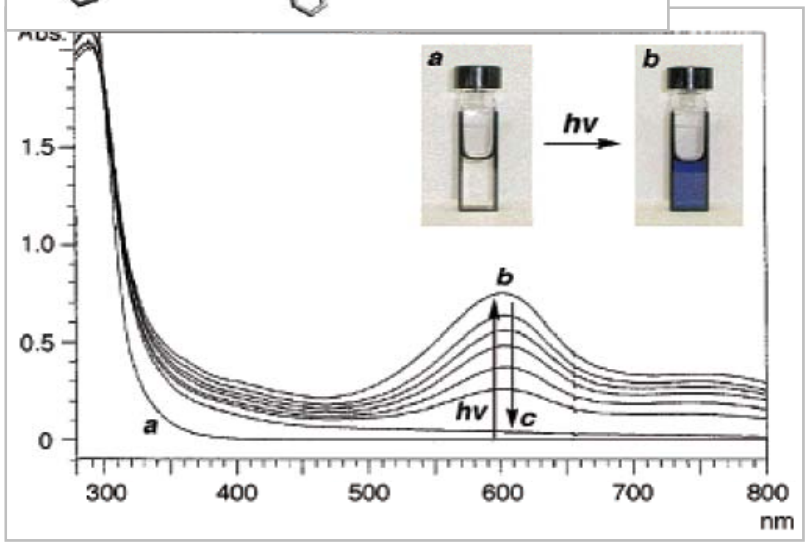
Department of Applied Chemistry, School of Engineering, The University of Tokyo, and CREST, Japan Science and Technology Corporation (JST), Bunkyo-ku, Tokyo 113-8656, Japan, and Department of Chemistry, Yamaguchi University, Yamaguchi-shi, Yamaguchi 753-8512, Japan

Received April 25, 2004; E-mail: mfujita@appchem.t.u-tokyo.ac.jp







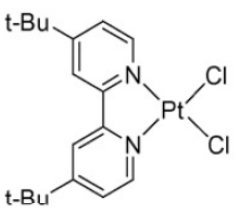


Yoshizawa, M.; Miyagi, S.; Kawano, M.; Ishiguro, K.; Fujita, M. Alkane Oxidation via Photochemical Excitation of a Self-Assembled Molecular Cage. *J. Am. Chem. Soc.* **2004**, 126, 9172-9173.

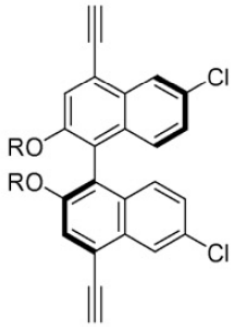
Luminiscent Metallocicles

Self-assembly of discrete metallosupramolecular luminophores

Michael W. Cooke, Daniel Chartrand, Garry S. Hanan*

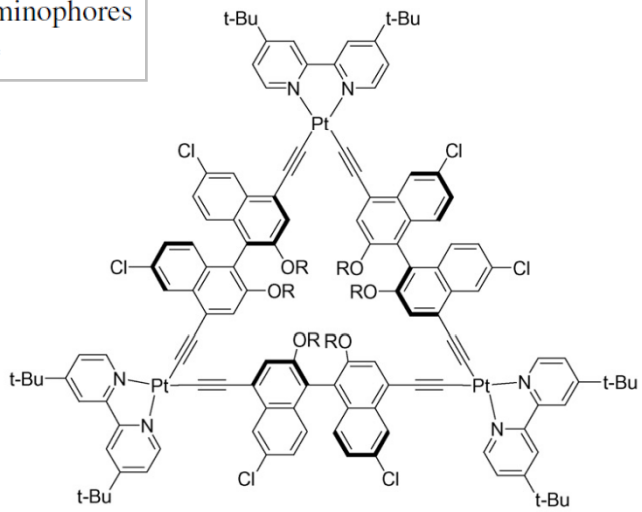


+



L_1, R = Ac
L_2, R = Et

CuI
Et_2N



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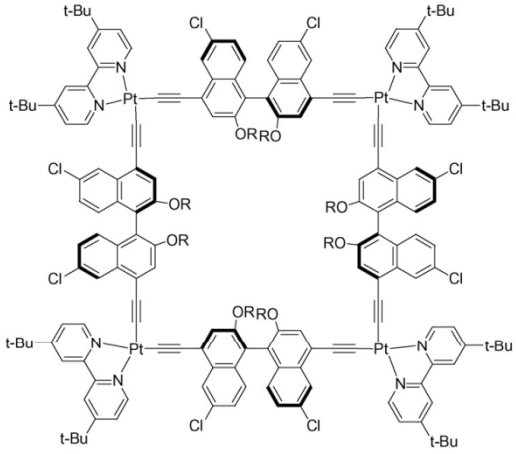
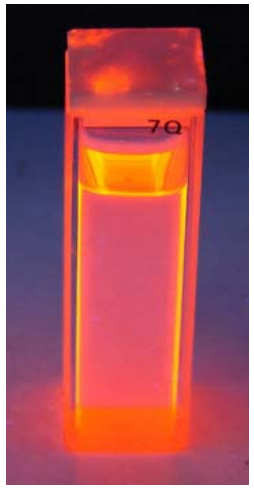


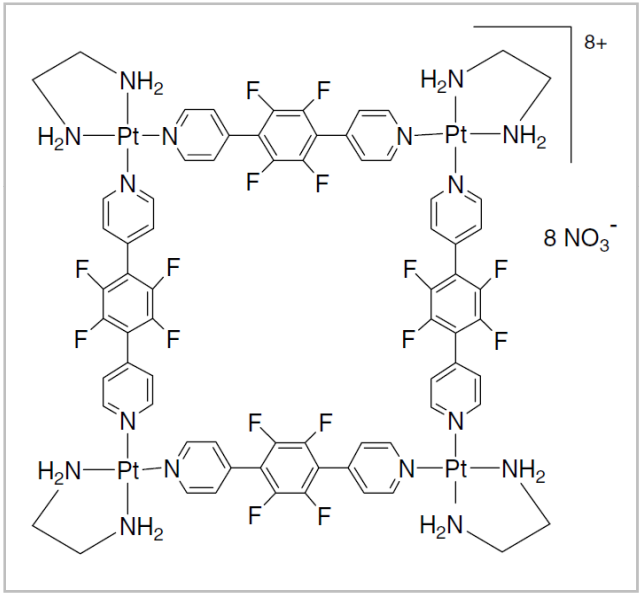


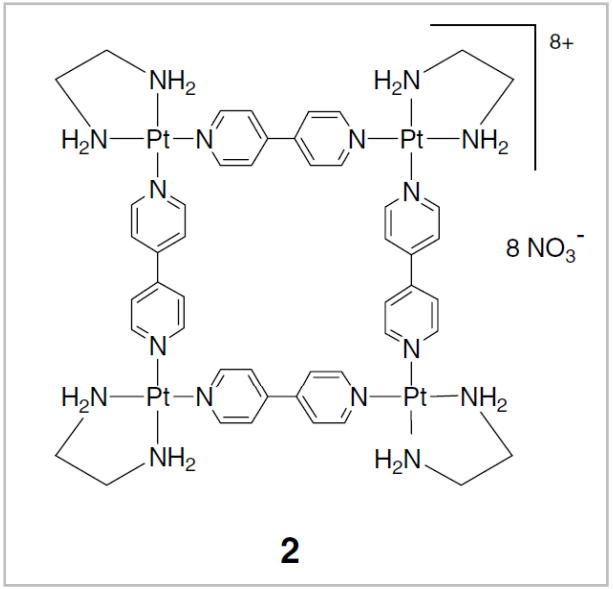
Cooke, M.; Chartrand, D.; Hanan, G. Self-assembly of discrete metallosupramolecular luminophores. *Coord. Chem. Rev*. **2008**, 252, 903–921.

Anticancer Metalocycles

DNA interaction and antiproliferative behavior of the water soluble platinum supramolecular squares $[(en)Pt(N–N)]_4(NO_3)_8$ (en = ethylenediamine, N–N = 4,4′-bipyridine or 1,4-bis(4-pyridyl)tetrafluorobenzene)

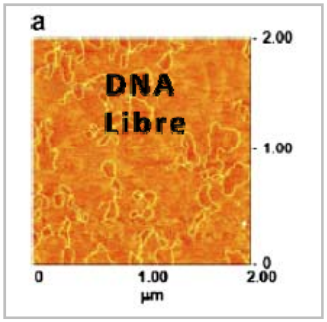
Mounia Mounir [a], Julia Lorenzo [b], Montserrat Ferrer [a,*], Maria J. Prieto [c], Oriol Rossell [a], Francesc X. Avilès [b], Virtudes Moreno [a,*]

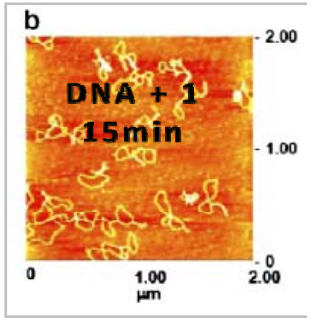


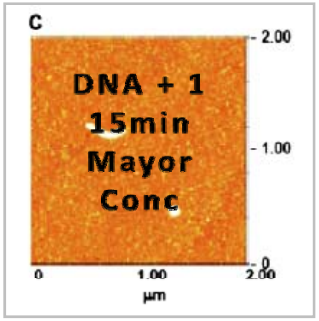


2

Tapping mode atomic force microscopy (TMAFM)







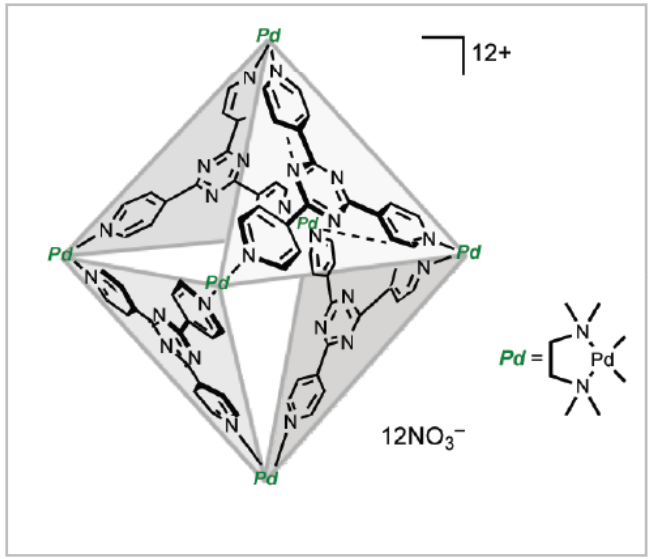
Complex	IC_{50} (µM) 24 h	IC_{50} (µM) 72 h
1	4.85 ± 1.01	5.26 ± 1.77
2	2.87 ± 1.06	2.78 ± 1.11
Cisplatin	15.61 ± 1.15	2.15 ± 1.01

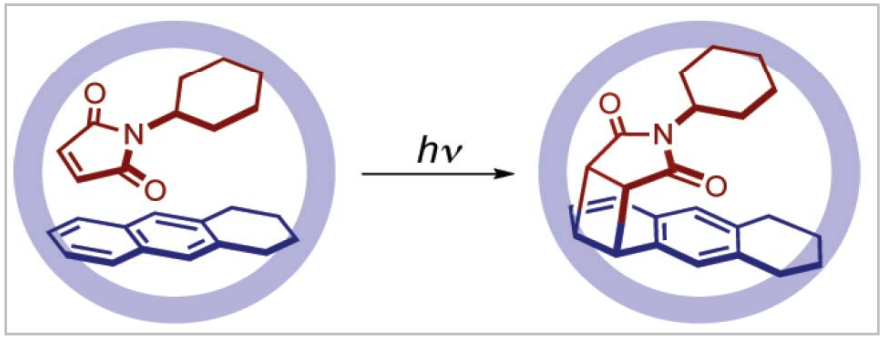
Mounir, M.; Lorenzo, J.; Ferrer, M.; Prieto, M.; Rossell, O.; Avile`s, F.; Moreno, V. DNA interaction and antiproliferative behavior of the water soluble platinum supramolecular squares $[(en)Pt(N–N)]_4(NO_3)_8$ (en = ethylenediamine, N–N = 4,4´-bipyridine or 1,4-bis(4-pyridyl)tetrafluorobenzene). *J. Inorg Biochem.* ***2007****, 101, 660–666.*

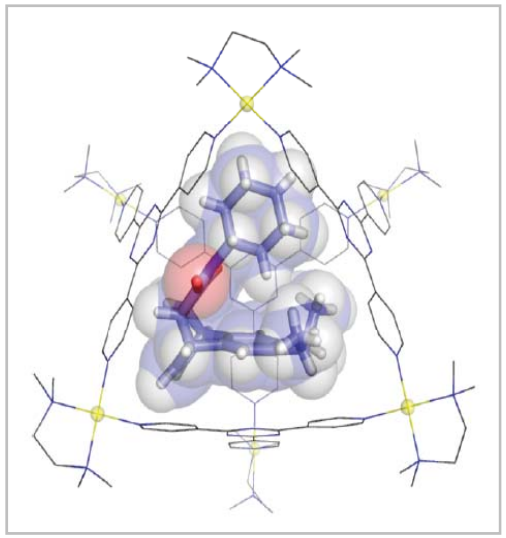
Catalytic Nanoreactor

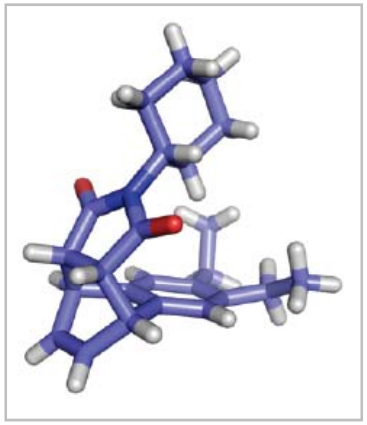
Naphthalene Diels–Alder in a Self-Assembled Molecular Flask

Takashi Murase, Shinnosuke Horiuchi, and Makoto Fujita*









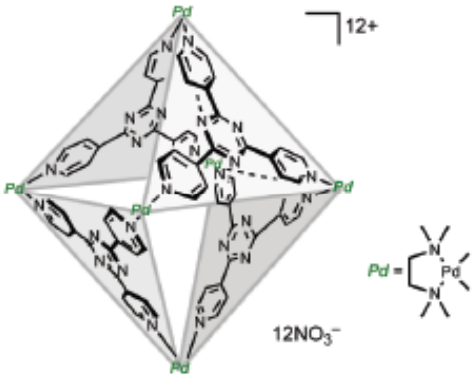
Product	Yield (%)	Rate constant ($\times 10^{-5}$ s^{-1})
4a (R = H)	0	–[c]
4b (R = Me)	8	–[c]
4c (R = Et)	60	4.1
4d (R = *n*-Pr)	64	6.2
4e (R,R = $-(CH_2)_4-$)	62	2.8
4f (R,R = $-O(CH_2)_2O-$)	0	–[c]

Murase, T.; Horiuchi, S.; Fujita, M. Naphthalene Diels-Alder in a Self-Assembled Molecular Flask. *J. Am. Chem. Soc*. **2010**, 132, 2866–2867.

Catalytic Nanoreactor

Naphthalene Diels–Alder in a Self-Assembled Molecular Flask

Takashi Murase, Shinnosuke Horiuchi, and Makoto Fujita*



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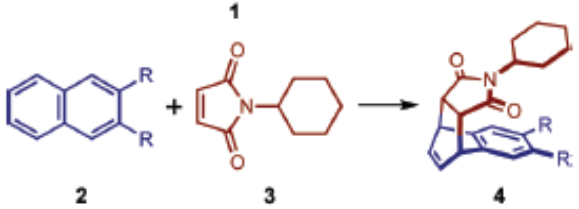
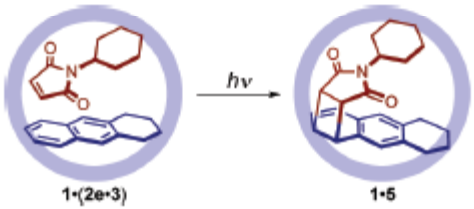


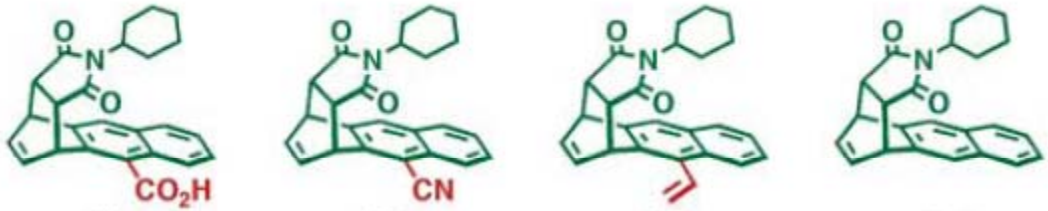
2 3 4

Induce una alta regioselectividad !

Scheme 1. Photocycloaddition of Naphthalene **2e** with Maleimide **3** within Cage **1**



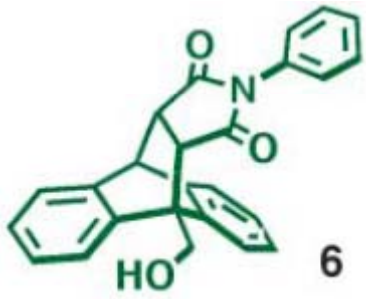
1•(2e•3) 1•5



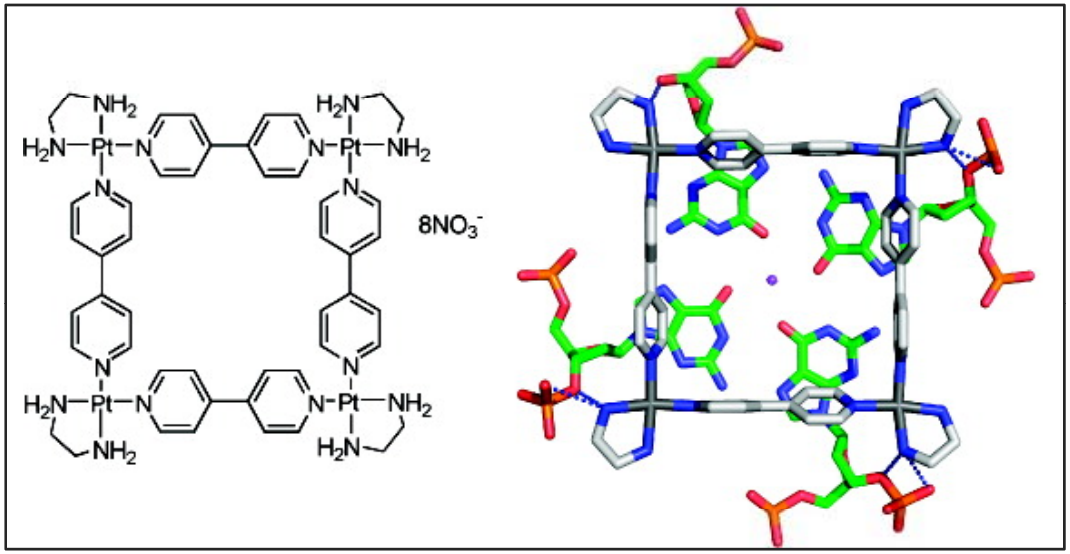
92% 88% 80% 55%

J. AM. CHEM. SOC. 2010, *132*, 2866–2867

SCIENCE VOL 312 14 APRIL 2006

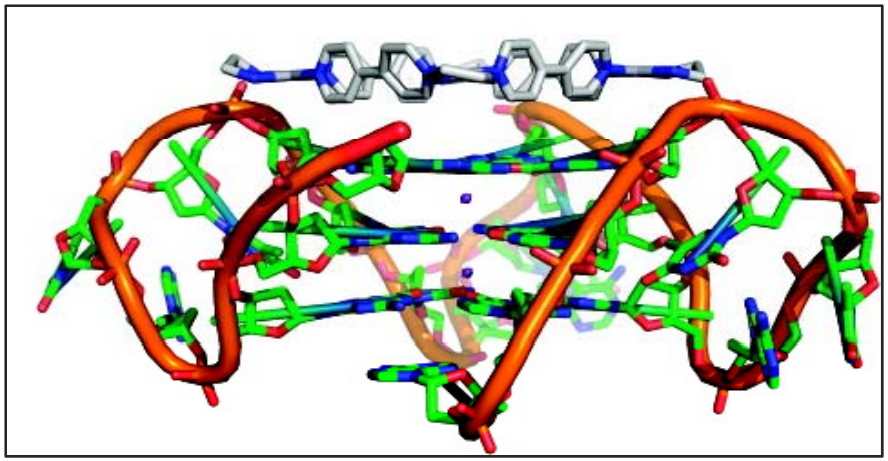


6



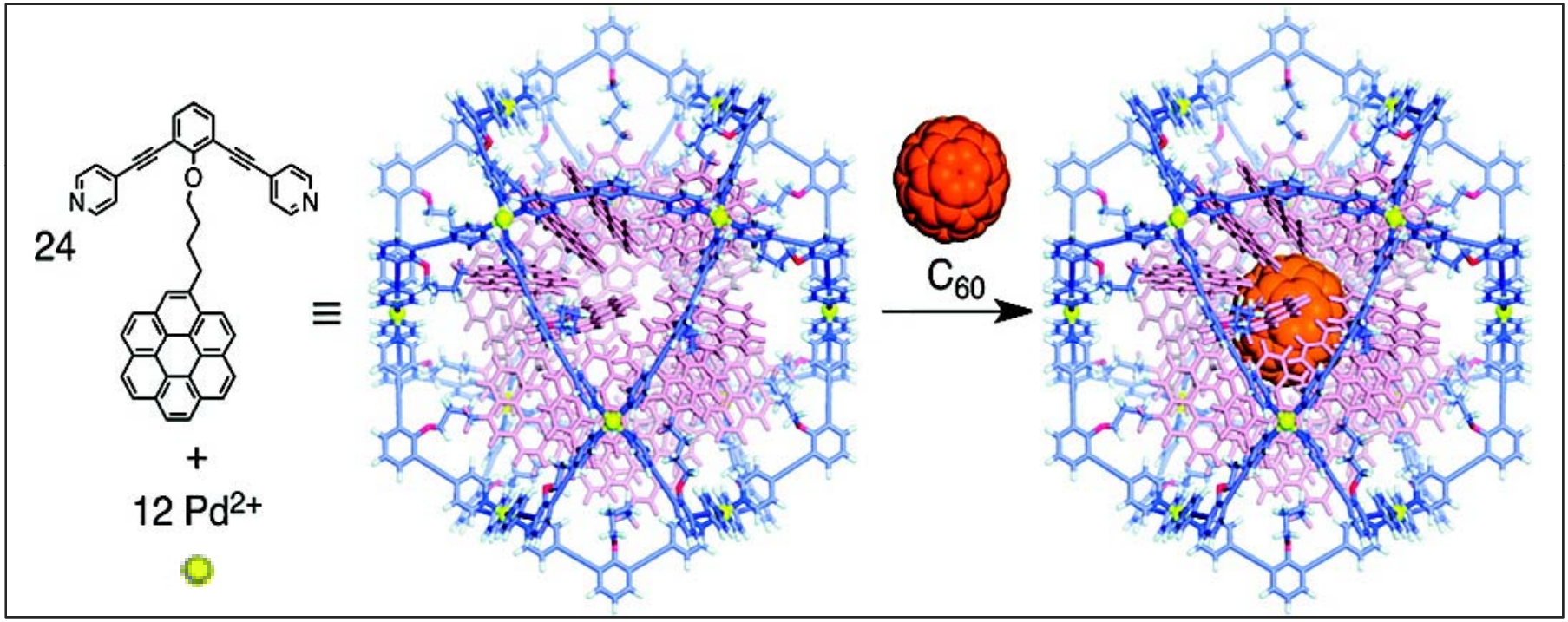
Metalociclos Cuadrados Anticancerígenos

Capacidad del cuadrado de Fujita de inhibir el crecimiento y propagación de algunas células cancerígenas a través de mecanismos de ensamblaje con su DNA y RNA



Kieltyka, R.; Englebienne, P.; Fakhoury, J.; Autexier, C.; Moitessier, N.; Sleiman, H. *J. Am. Chem. Soc.* **2008**, 130, 10040-10041.

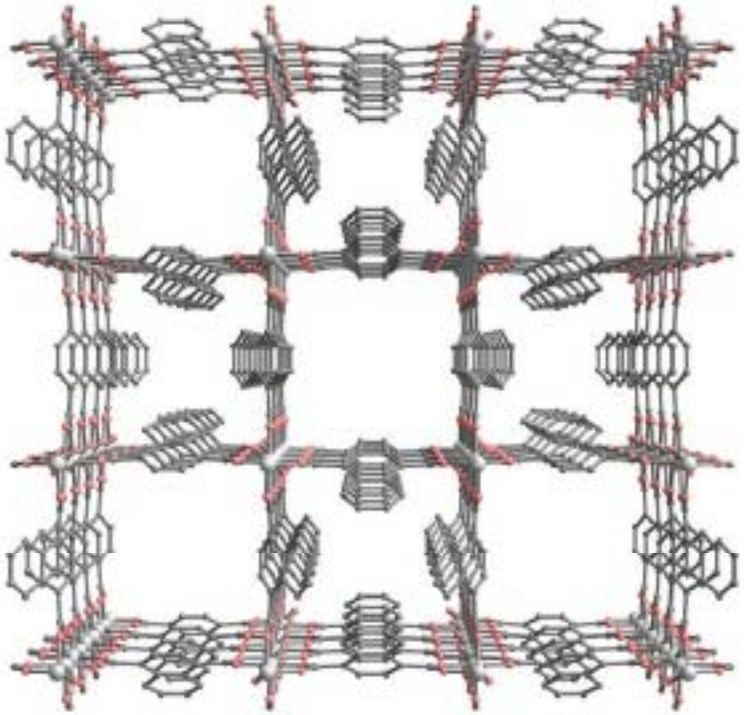
Nanoesferas de Coordinacion



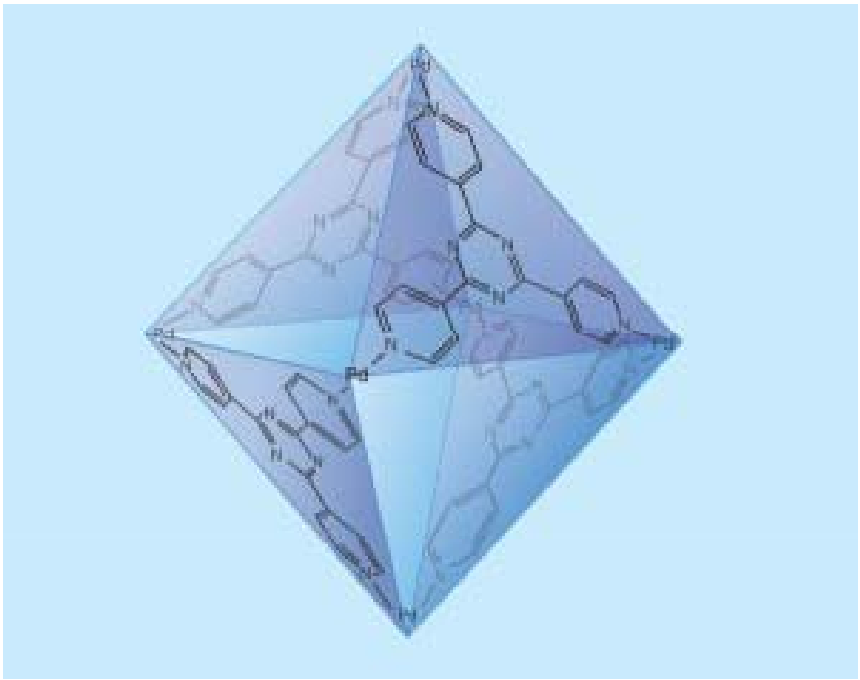
Nanoesferas de coordinación endofuncionalizadas con coronandos que tienen la propiedad de reconocer selectivamente Fullerenos C_{60} incrementando su solubilidad en solventes orgánicos

Suzuki , K.; Takao, K.; Sato, S.; Fujita, M.. *J. Am. Chem. Soc.* **2010**, 132, 2544-2545.

Metal Organic Frameworks & Metal Organic Polyhedra



Example of a Standard MOF



Example of a MOP

Frequent Applications

MOF

- Molecular sieves
- Sensors
- Gas absorption/storage
- Gas separation/purification
- Ion exchange
- Size-selective separation
- Heterogeneous catalysis
- Potential drug carriers

MOP

- Nanoscale reaction vessels
- Catalysis
- Cancer treatment
- Metallosupramolecular
- Luminophores
- Molecular recognition
- Sensors

Actividades en la UN

1. Curso de posgrado (Química Supramolecular y Nanomateriales)
2. Cátedra de sede José Celestino Mutis, I-2011, Nanotecnología
3. Nuevos materiales: Fullerenos y Nanotubos de Carbono
4. Química Supramoleculares (cuadrados, polímeros de coordinación)
5. Síntesis de ftalocianinas
6. Síntesis de MOF & caracterización de COLTAN

UNIVERSIDAD NACIONAL DE COLOMBIA

Nanotecnología: el tamaño sí importa!

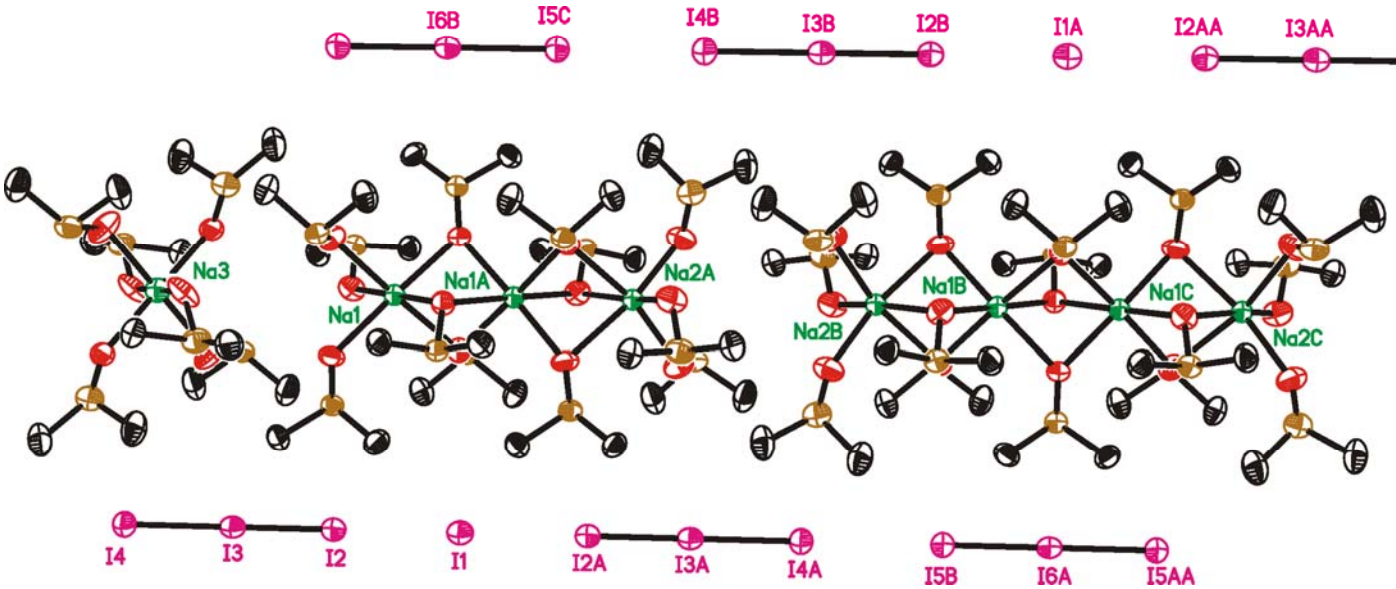
Cátedra de Sede, José Celestino Mutis I-2011

Facultades de
Ciencias (Alvaro Duarte Ruiz, Jairo Giraldo y Eduardo Posada),
Medicina (Dianney Clavijo y Ciro Casadiego)
Ingeniería (Alberto Delgado y Hugo Zea).

Synthesis and structure of $[Na_4(DMSO)_{15}][(I_3)_3(I)]$. Self-assembly of hexacoordinated sodium.

Nelson Nuñez-Dallos[†], Luis Garzón-Tovar[†], Álvaro Duarte-Ruiz[*†], Klaus Wurst[‡], Eliseo Avella-Moreno[†] and Fernando Gómez-Baquero[§]

[†]Departamento de Química, Universidad Nacional de Colombia, Ciudad Universitaria, Bogotá Kr 30 No 45-03, Colombia, [‡]Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, 6020, Innrain 52a, Innsbruck, Austria, and the [§]College of Nanoscale Science and Engineering, University at Albany SUNY.



Inorganic Chemistry
including bioinorganic chemistry

Ongoing Research At the UN

Síntesis del complejo

En presencia de Hidróxido de sodio (NaOH):

Reacción 1

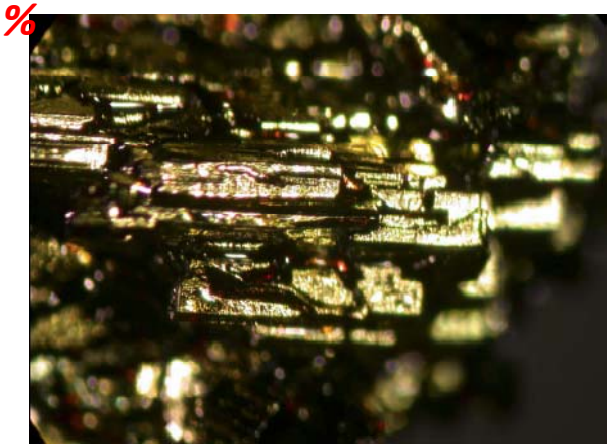
$$16(CH_3)_2SO + 4NaOH + 10CH_3I \rightarrow [Na_4(DMSO)_{15}]^{4+}[(I)(I_3)_3]^{4-} + 2CH_3OH + 2CH_3OCH_3 + CH_3SCH_3 + 2C_2H_6 + H_2O$$

P.M. 2532,88 g/mol

Rendimiento: 28.2%

Reacción 2

$$(CH_3)_2SO + CH_3I \rightarrow [(CH_3)_3SO]^+I^-$$ ***Rendimiento: 13.1%***

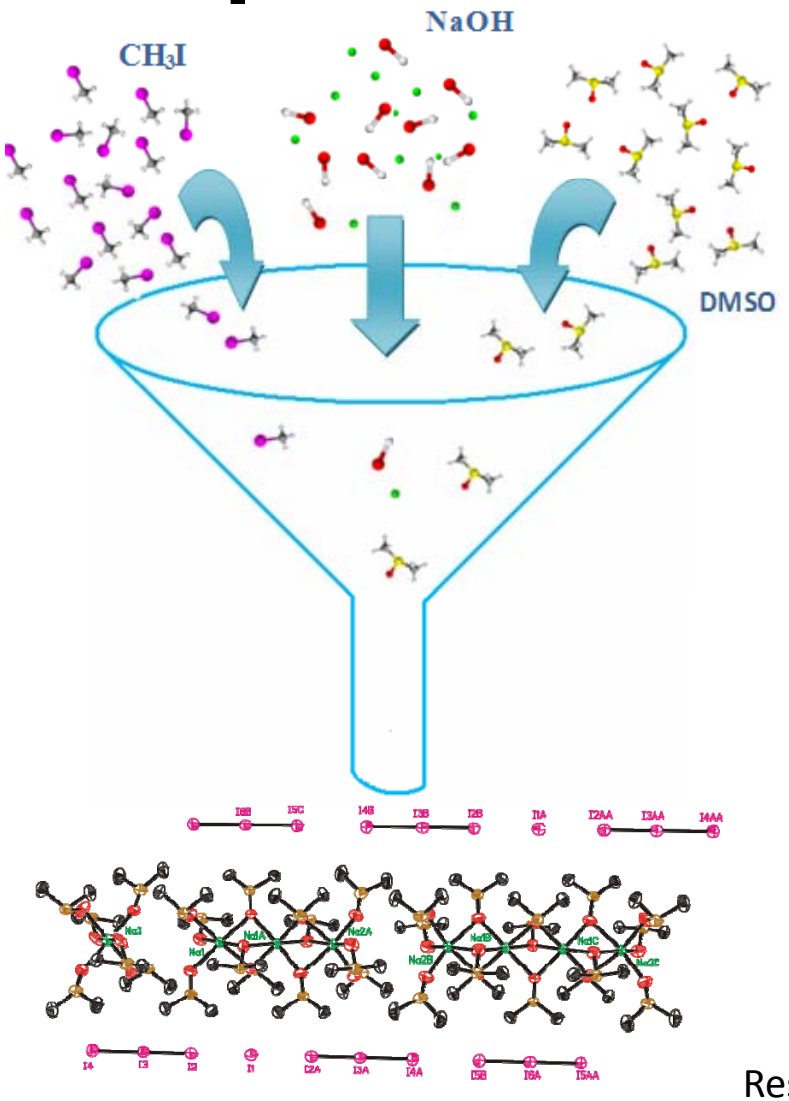


En ausencia de Hidróxido de sodio:

Reacción 2

$$(CH_3)_2SO + CH_3I \rightarrow [(CH_3)_3SO]^+I^-$$

Supramolecular Self Assembly



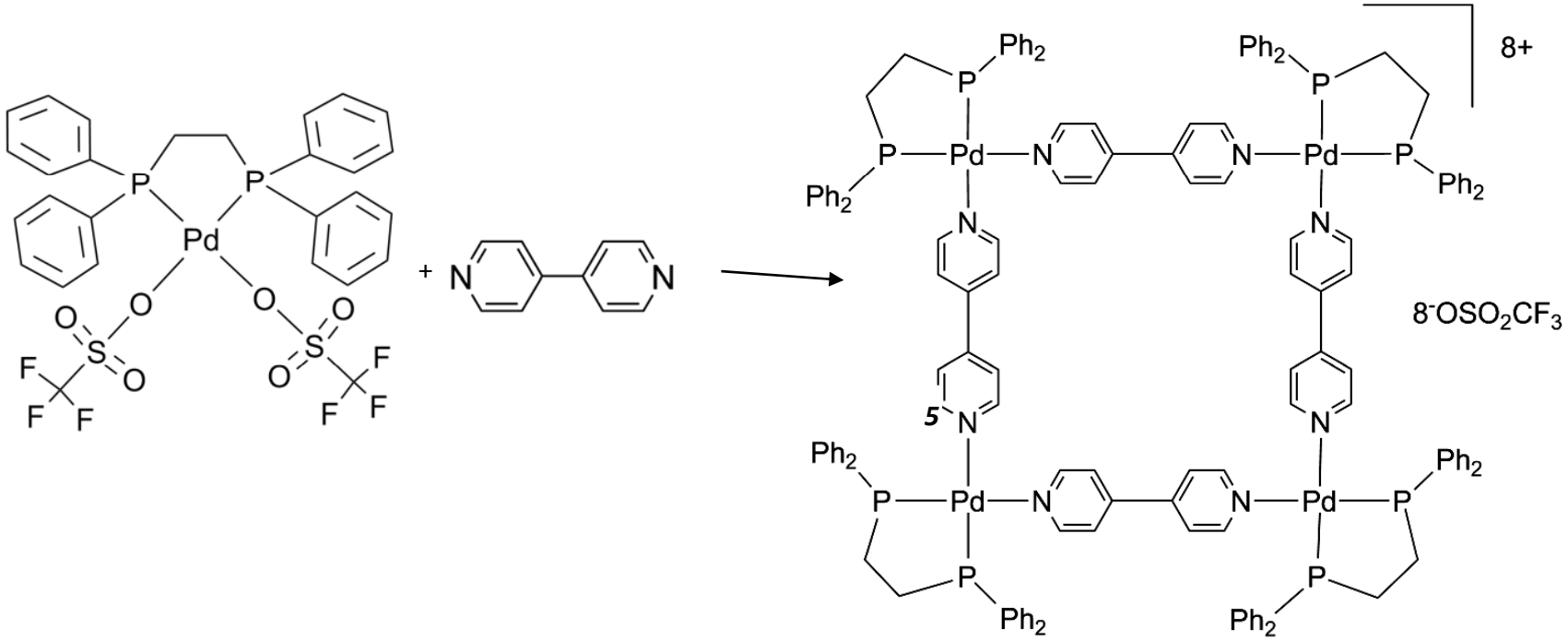
$[Na_4(DMSO)_{15}]^{4+}[(I)(I_3)_3]^{4-}$

1. Organized Structure
2. Weak Interactions
3. Reversibility
4. Thermodinamic Stability

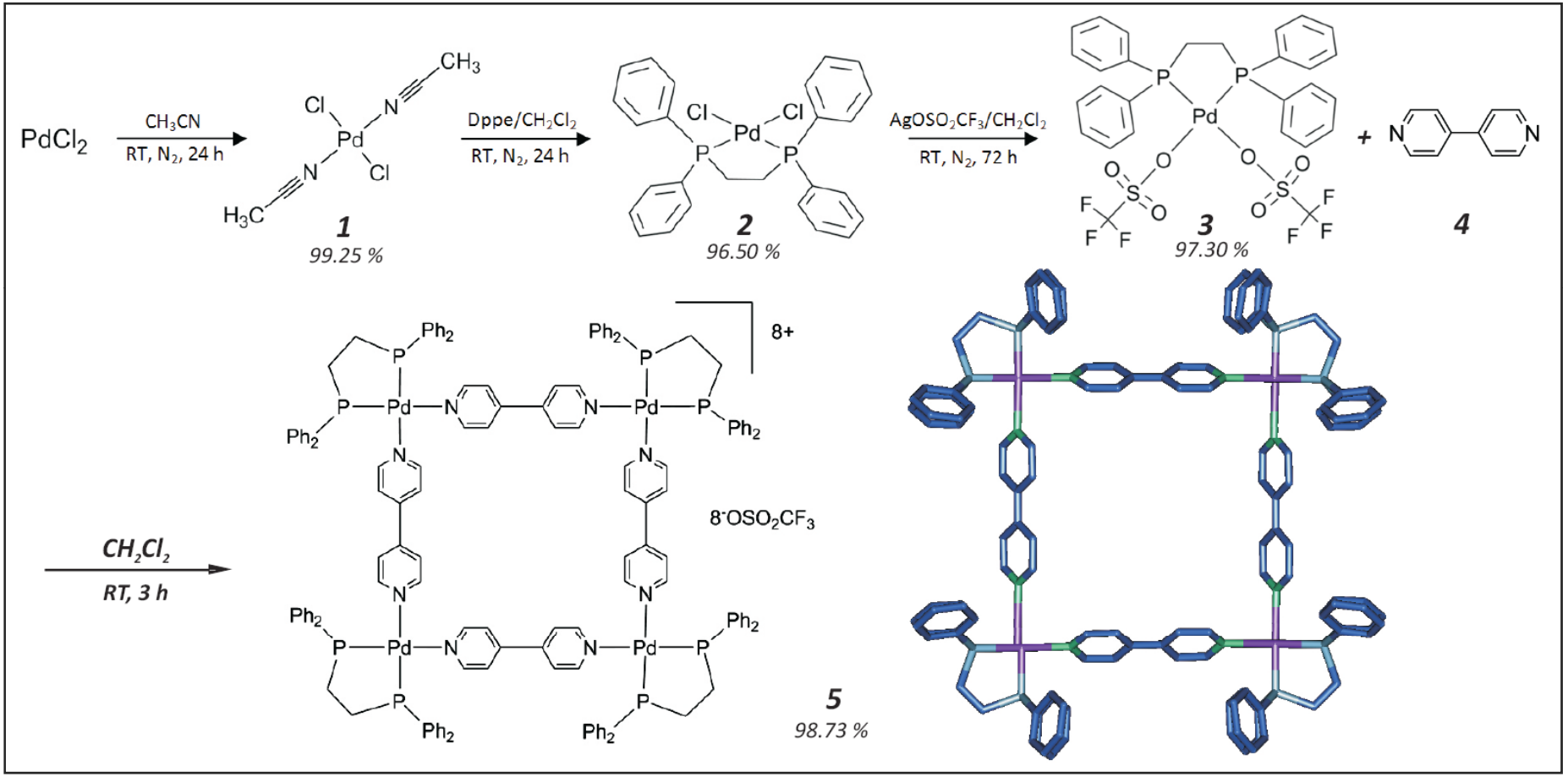
Research Group: Nuevos Materiales Fullerenos y Nanotubos de Carbono. Departamento de Química, Universidad Nacional de Colombia. Alvaro Duarte

ENSAMBLAJE DE CUADRADOS SUPRAMOLECULARES

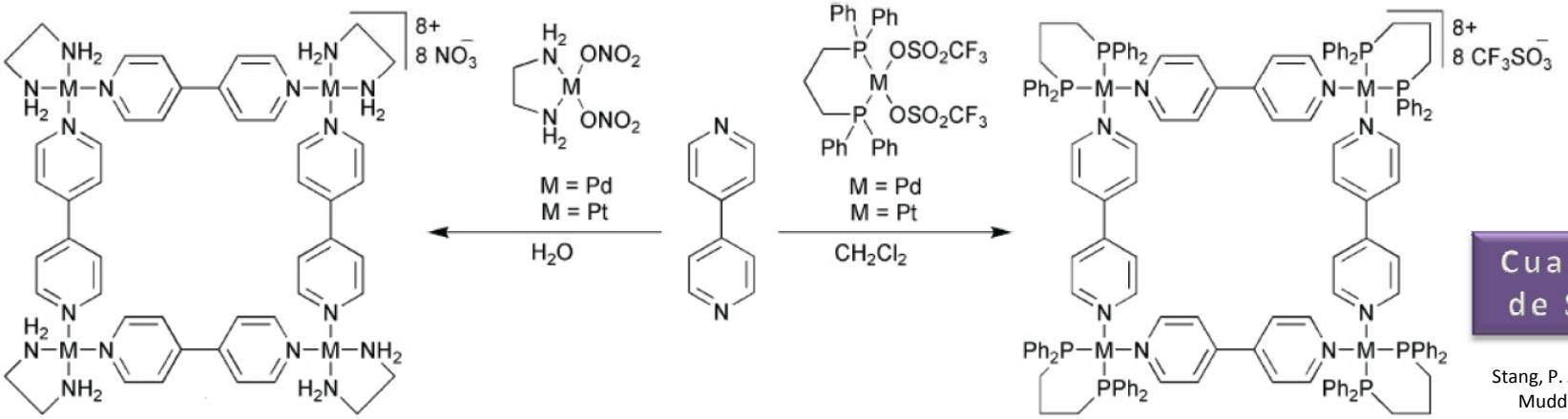
Julián Camilo Posada



Etapas de la síntesis Cuadrado Supramolecular

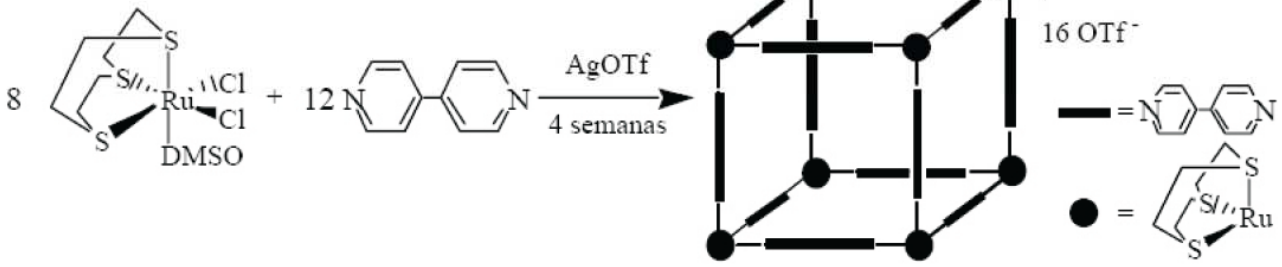


Metalomacrociclos Cuadrados



Cuadrado de Fujita

Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112, 5645-5647.*



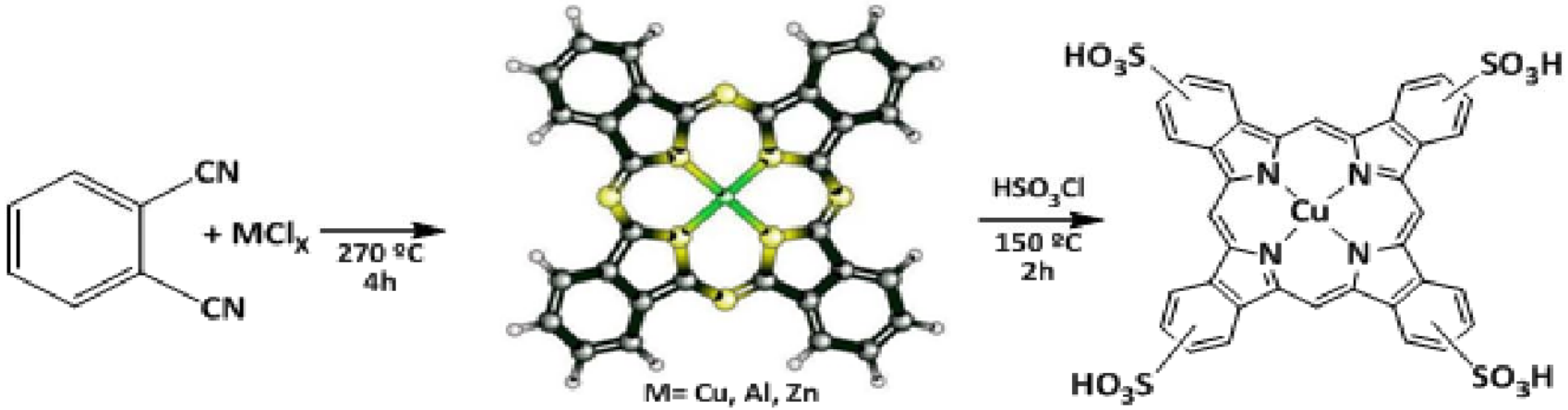
Cuadrado de Stang

Stang, P. J.; Olenyuk, B.; Muddiman, D. C.; Smith, R. D. *Organometallics.* **1997**, 16, 3094-3096.

Cubo de Roche

Roche, S.; Haslam, C.; Adams, H.; Heath, S. L.; Thomas, J. A. *Chem. Commun.* **1998**, 1681–1682.

Ftalocianinas



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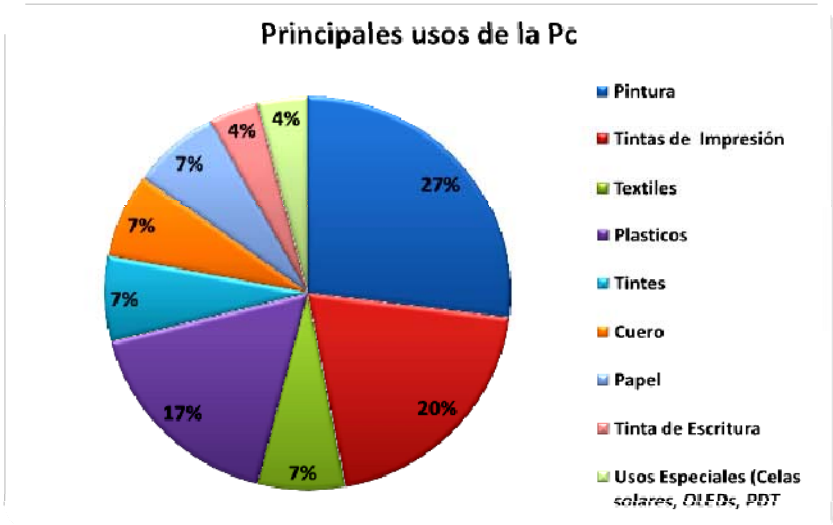
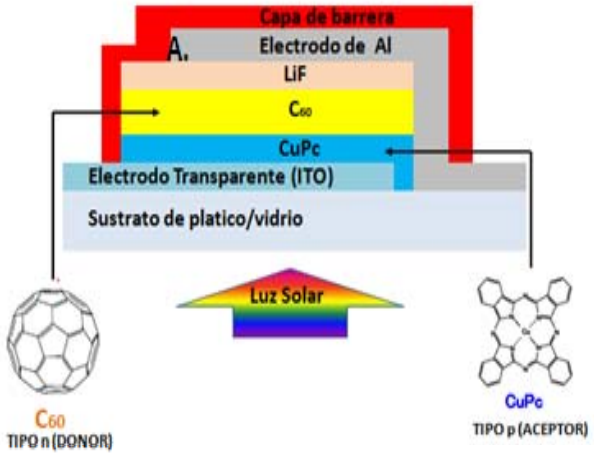
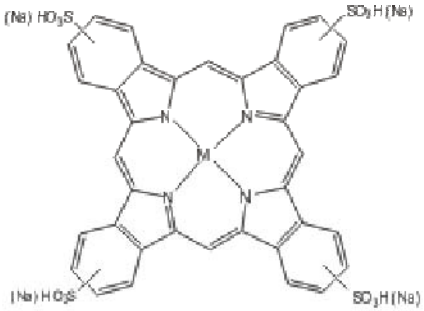


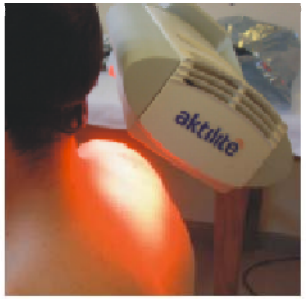
Aplicaciones

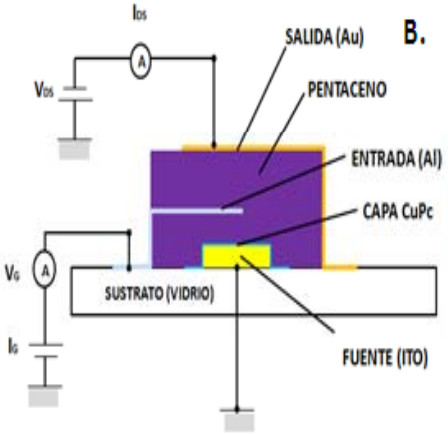


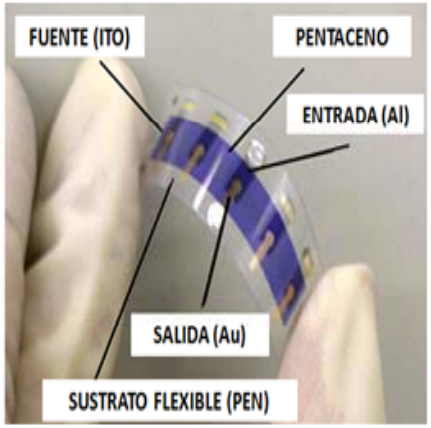
Modelo convencional OPV

M. Altamente Integrado OPV









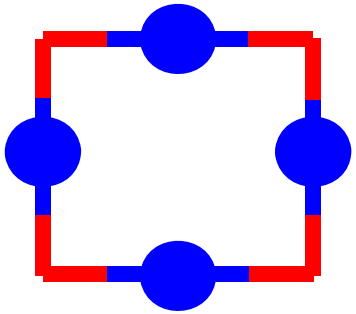
Resultados del Tratamiento de PDT con "Photosens®" basados en la investigación en Rusia (1998 – 2004)

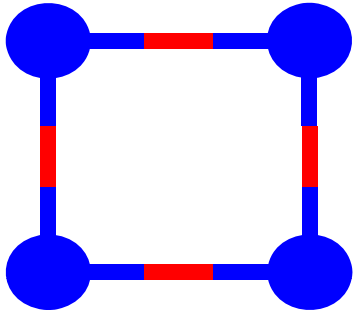
	Pacientes	Regresión Total	Regresión Parcial	Estabilización	Sin efectos
Piel, faringe, lengua, labios, mucosas, cavidad oral, cáncer de estómago y esófago, la vulva, vejiga urinaria, etc	1509	1014 (67%)	414 (27%)	72 (5%)	9 (1%)
Cáncer de mama y melanoma, pleuritis malignas del estómago y el esófago cáncer de III-IV etapas	880	209 (24%)	359 (41%)	272 (31%)	40 (4%)

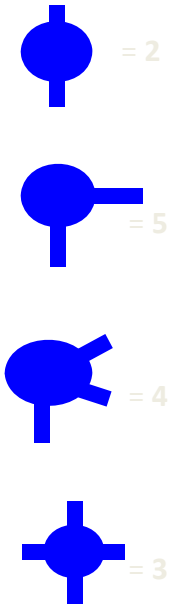
Supramolecular Self Assembly

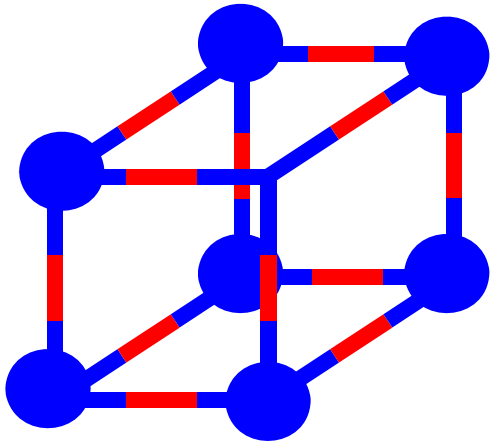
= *cis*-$Pt(OTf)_2(PEt_2)_2$

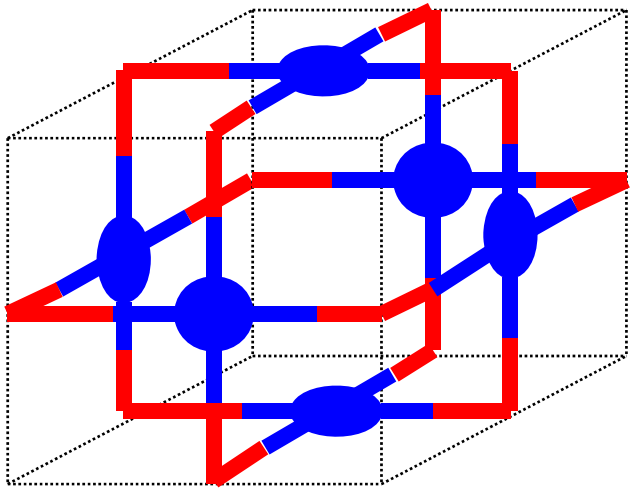
= *trans*-$Pt(OTf)_2(PEt_2)_2$







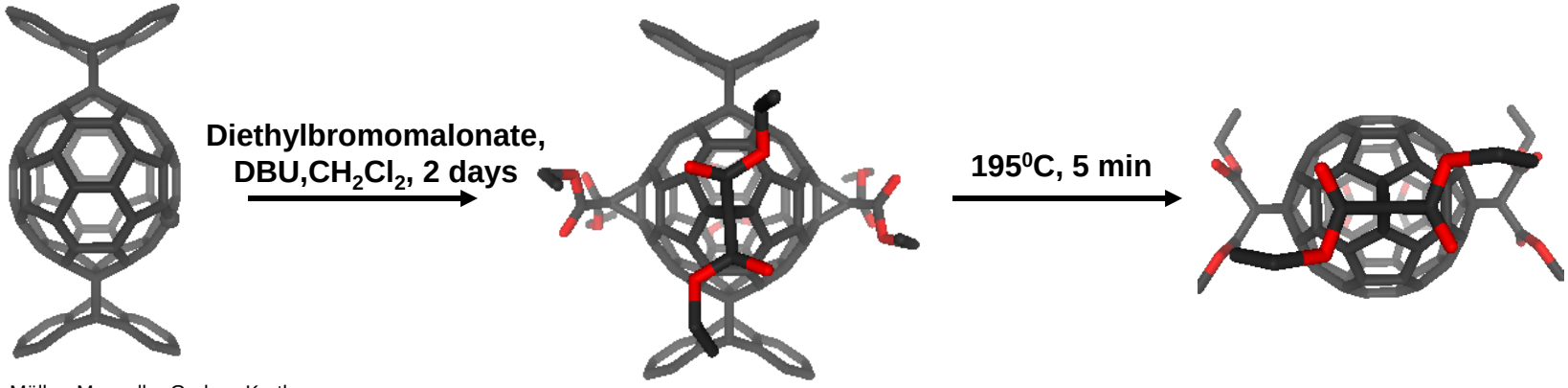




Prof. Luis Echegoyen, Texas University

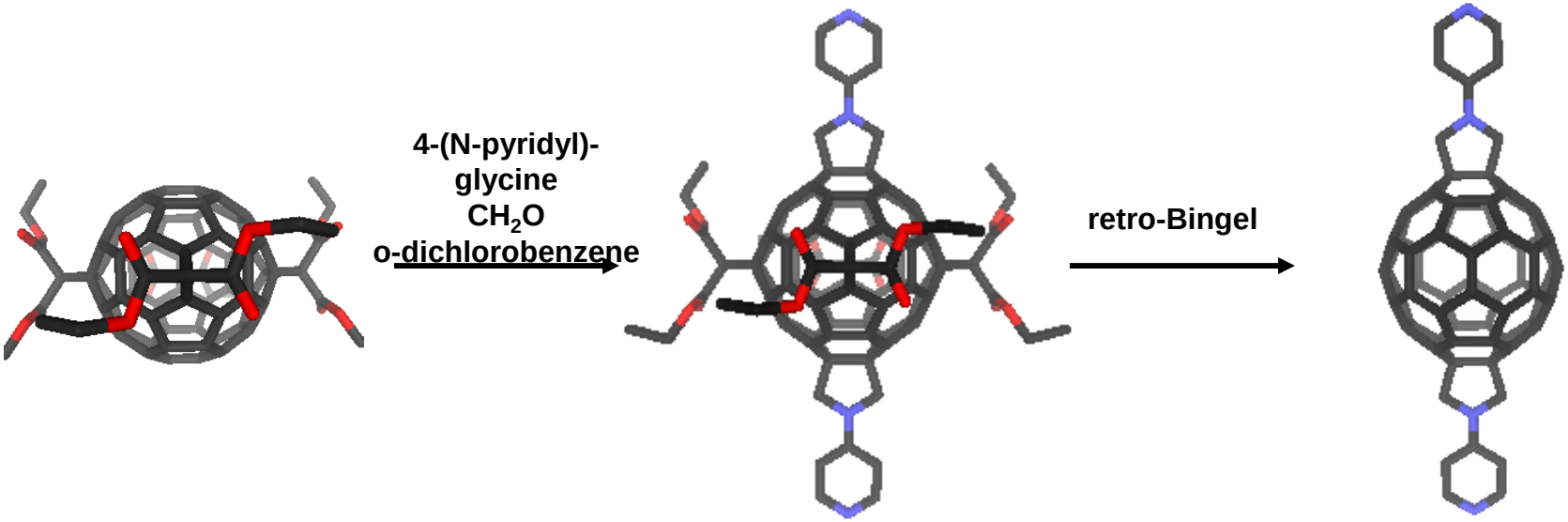
Synthesis of *trans*-1 Bis-N-Pyridyl Pyrrolidinofullerene

Orthogonal Transposition : Protection-Deprotection



Kräutler, Müller, Maynollo, Gruber, Kratky, Ochsenbein, Schwzenbach, Bürgi, *Angew. Chem. Int. Ed.* **1996**, *35*, 1204

Krautler . B. et. al *J. Am. Chem. Soc*. **1997**, 119, 9317-9318

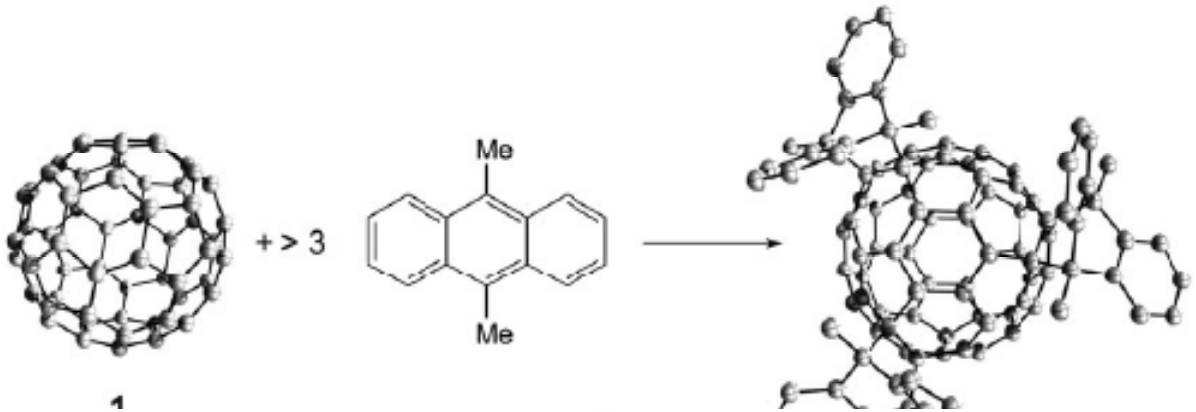


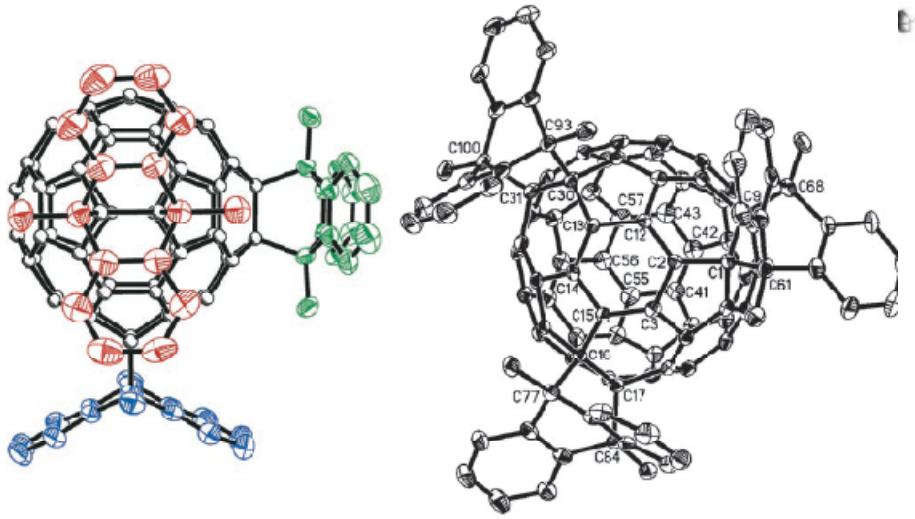
The Orthogonal (*e*,*e*,*e*)-Tris-Adduct of 9,10-Dimethylanthracene with C_{60}-Fullerene: A Hidden Cornerstone of Fullerene Chemistry

Preliminary Communication

by **Alvaro Duarte-Ruiz**[a][b], **Klaus Wurst**[c], and **Bernhard Kräutler***[a]

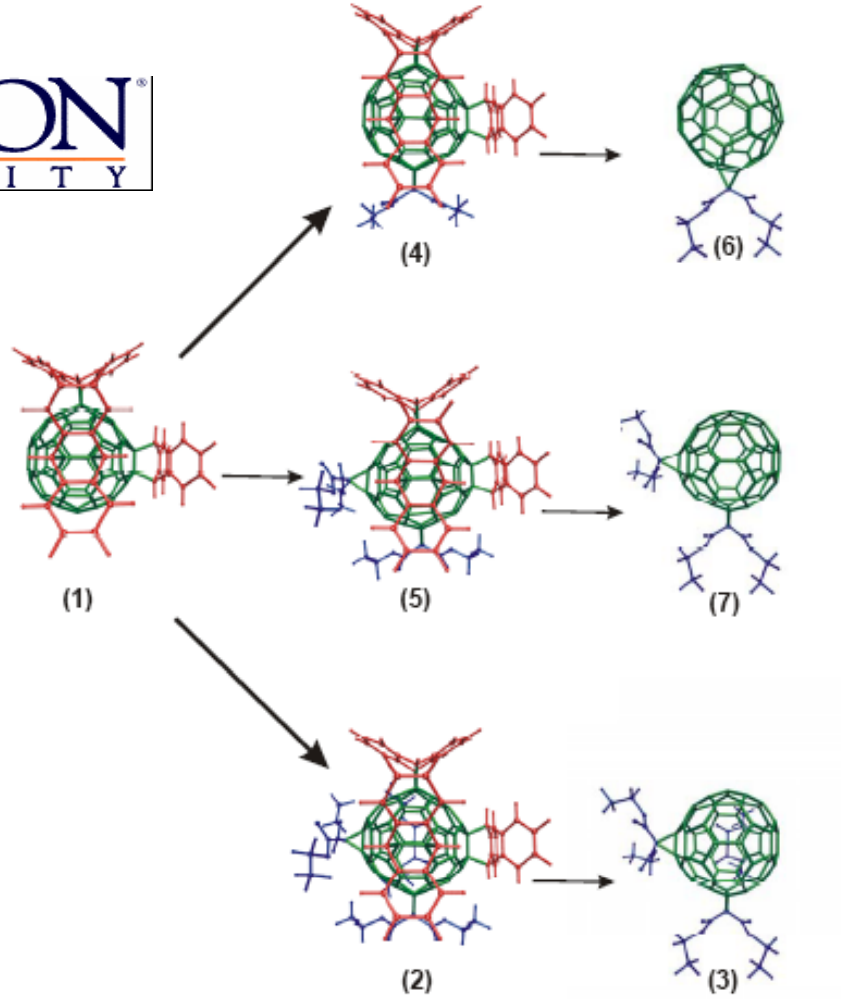
Helvetica Chimica Acta, 91, 2008, 1401





Preparation of an Equatorial Trisadduct of C_{60} by a New Protection-Deprotection

Duarte-Ruiz Alvaro, Echegoyen Luis, *J. Mex. Chem. Soc.* 2009, 53 (3), 168



Thanks For your Attention!

I hope to see you guys in the next Course of Supramolecular Chemistry !

Do you Have any Questions?

Special Thanks to:

Ing. César López

Ing. Hugo Zea

Julian Camilo Posada

Jessica Orrego

Nelson Núñez

Luis Garzón

Paulo Torres

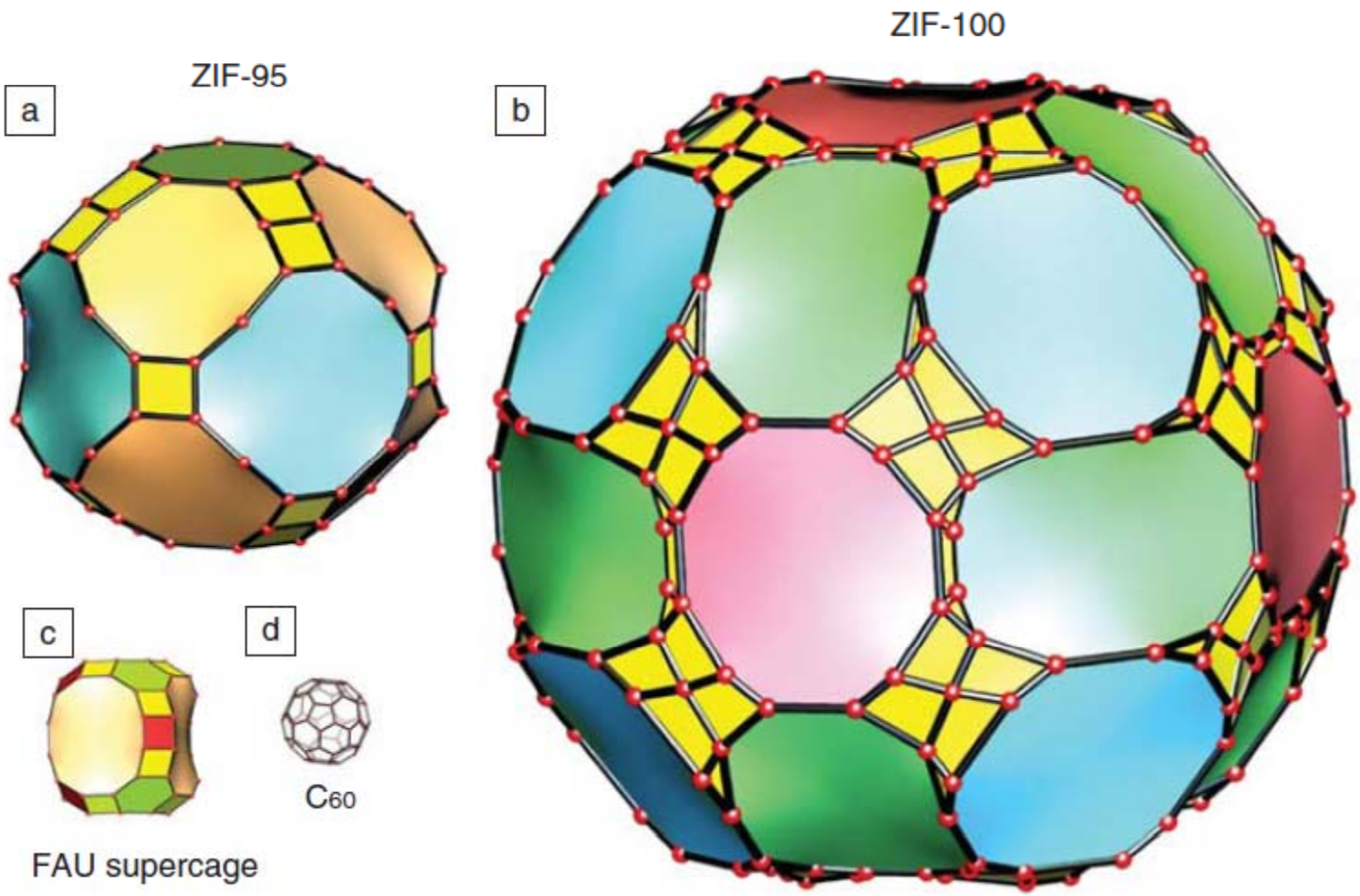
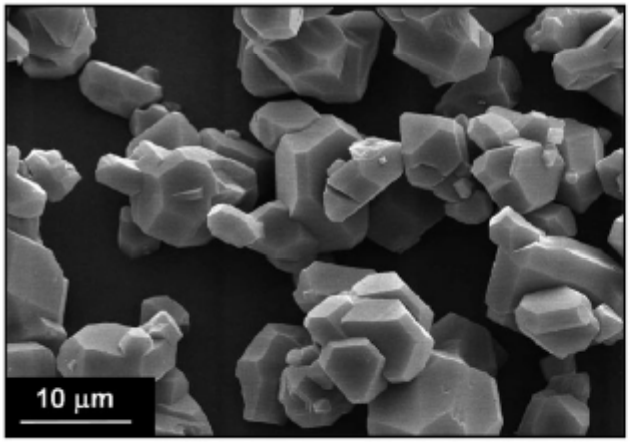
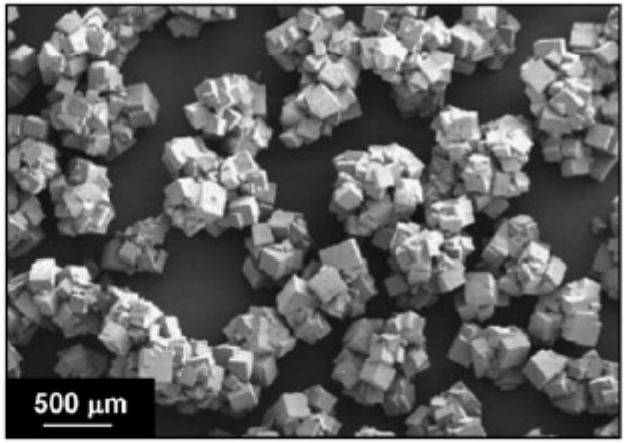


Figure 15. Size comparison of (a) POZ B in ZIF-95, (b) MOZ in ZIF-100, (c) super cage in faujasite (FAU), and (d) C_{60}. The MOZ cage has a 35.6 angstroms inner sphere diameter. All the cages are shown in ball and stick diagrams (Zn, red spheres in (a) and (b); Si/Al, red spheres in (c); C, red spheres in (d)). Different tilings are shown in different colors.

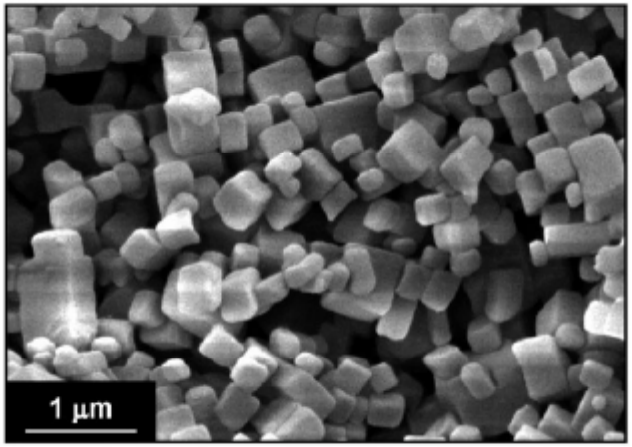
Morphology of crystals from different MOF samples



Cu-BTC-MOF (Basolite C300)

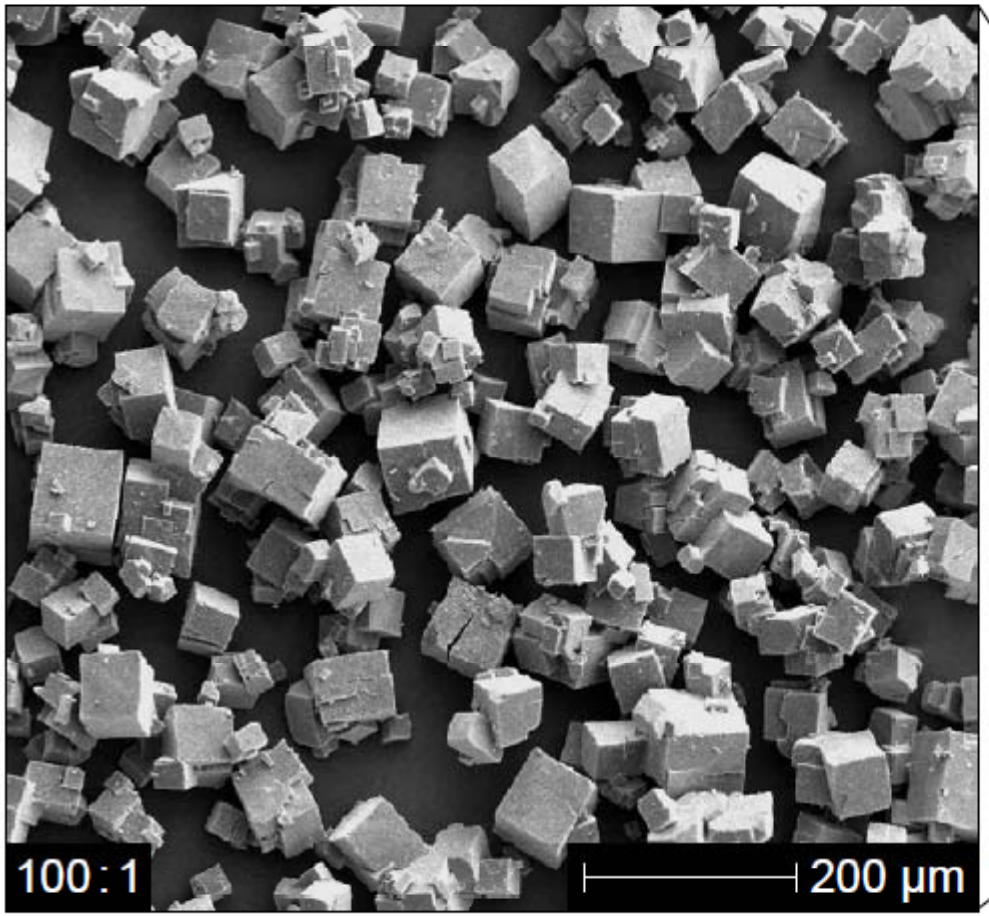


MOF-5



MOF-5 with nm-size particles

MOFs at the Electronic Microscope



11

J. Mater. Chem., 2006, **16**, 626–636

Synthetic Approaches

Solvothermal:

The most used method; Reactants are dissolved (in organic solvents of high boiling point) at high temperature during long times (days). The morphology leads to big crystals. The main problem is to avoid damage in thermolabile linkers.

Microwaves:

Fast method, reaction time around a few seconds (or min). Reaction temperature might be high (above 100ºC). The morphology is almost always a fine powder, not big crystals. The main problem is the purification of the crystals.

Ultrasonic:

Reaction time is reasonable (from minutes to hours). Reaction temperature is kept low (about 45ºC). No control over the morphology of the material. Easy purification in most cases.

Electrochemical:

Very Fast, Room temperature, High control over the morphology of the material. The main problem is the inclusion of conductive salts on the material.

Dr. Omar Yaghi On MOFs