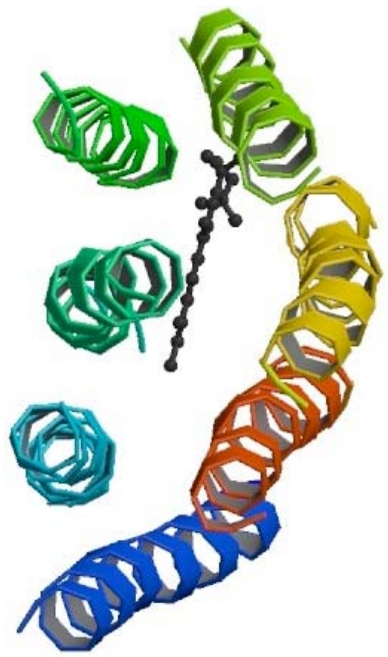
Class 01: Recent breakthroughs in structure and composition 1: The nanostructure problem

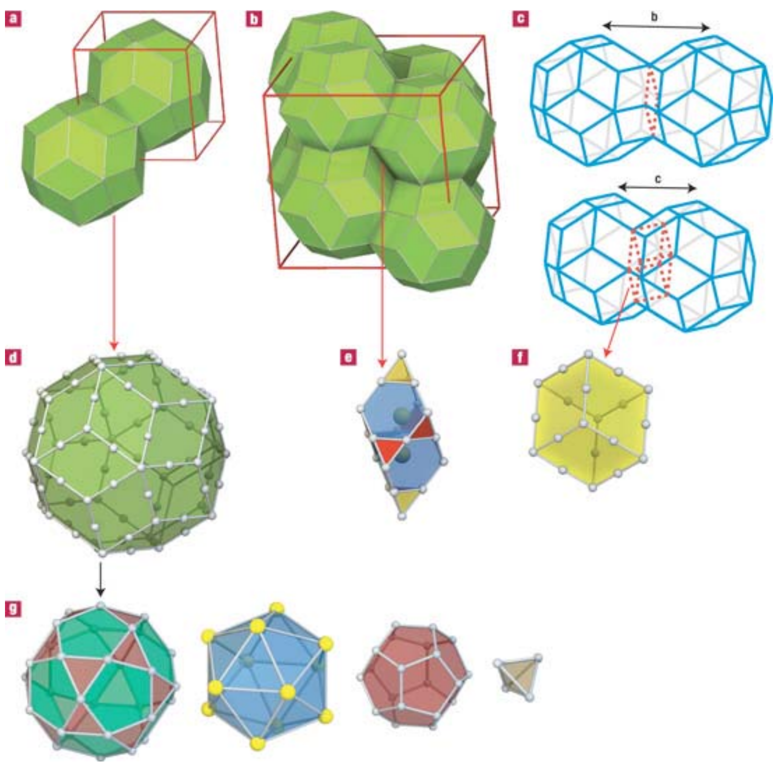
A complete understanding of structure, meaning the location of every atom with a resolution 1 Å or less, is the basis for understanding property: Whether of materials or of biologically active molecules. Obtaining "crystal structures" remains a challenge. The usual technique is X-ray diffraction, used to determine the contents of a single unit cell, with the crystal lattice acting as a diffraction amplifier.

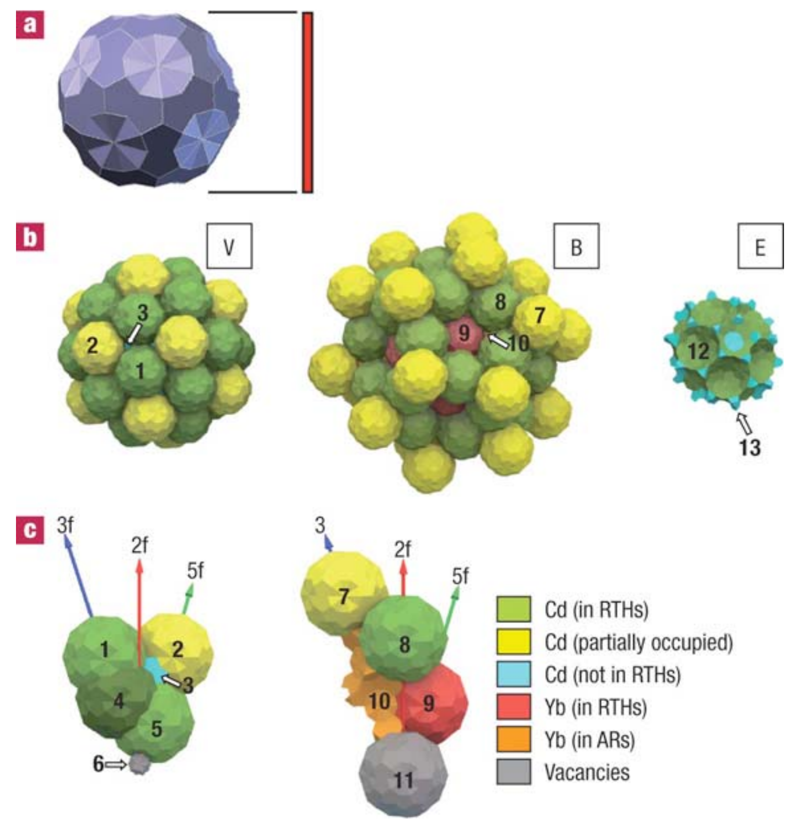


Bacteriorhodopsin from *Halobacterium salinarium* at 3.5 Å resolution.

Henderson, *et al.,* Model for the structure of bacteriorhodopsin based on high-resolution electron cryo-microscopy, *J. Mol.Biol.* **213** (1990) 899-929.

Class 01: Recent breakthroughs in structure and composition 1: The nanostructure problem

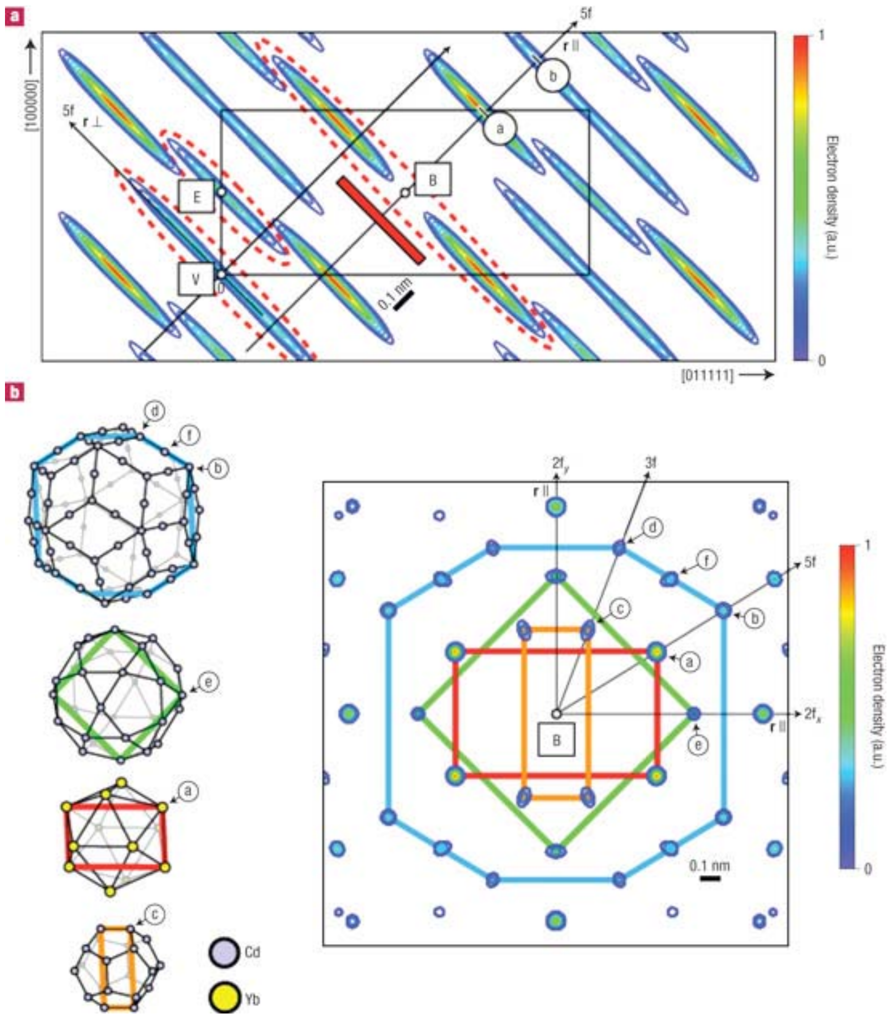




"first detailed structure solution of *i*-$YbCd_{5.7}$, one of the very few stable binary *i*-QCs, by means of X-ray structure determination. Three building units with unique atomic decorations arrange quasiperiodically and fill the space. These also serve as building units in the periodic approximant crystals."

H. Takakura, C. Pay Gómez, A. Yamamoto, M. De Boissieu, A. P. Tsai, Atomic structure of the binary icosahedral Yb–Cd quasicrystal, *Nature Mater.* **6** (2007) 58-63.

Class 01: Recent breakthroughs in structure and composition 1: The nanostructure problem



Quasicrystallography is facilitated by the existence of crystalline lattices in higher dimensional space (here in 6D) that project to the quasicrystal in lower-dimensional (3D) space. Note the 6 numbers used to index the electron density projections in the image on the left.

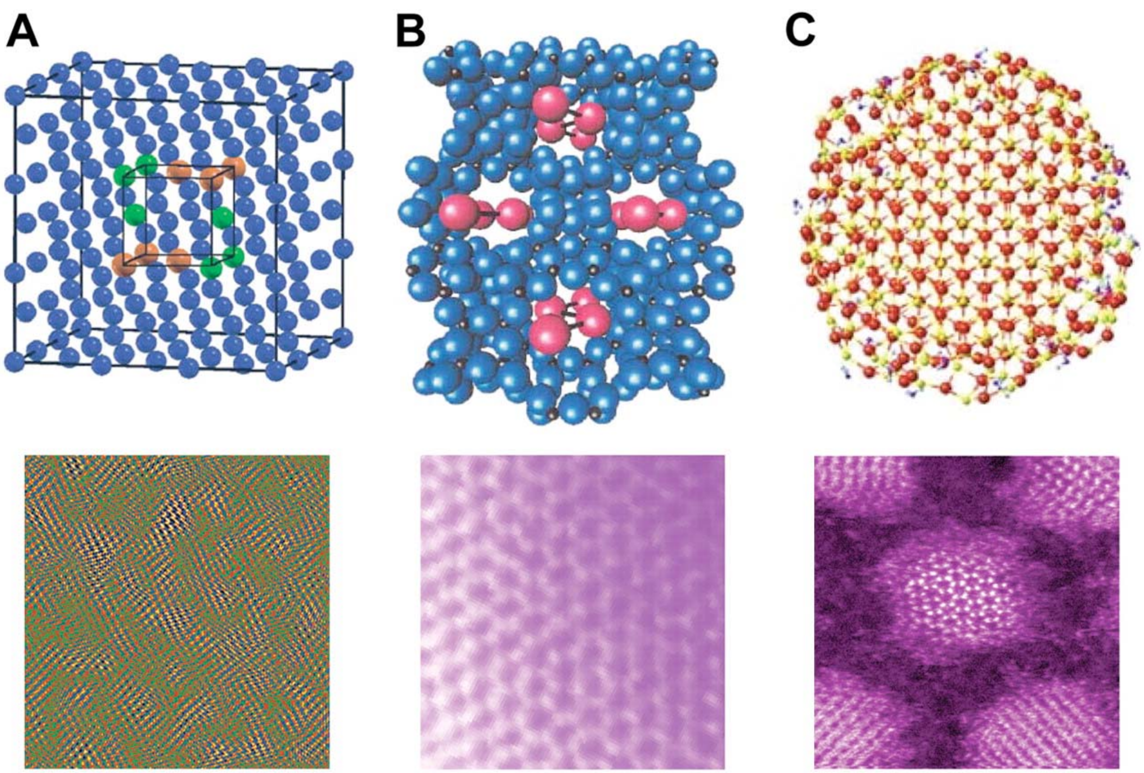
H.Takakura, C. Pay Gómez, A. Yamamoto, M. De Boissieu, A. P. Tsai, Atomic structure of the binary icosahedral Yb–Cd quasicrystal, *Nature Mater.* **6** (2007) 58-63.

The nanostructure problem.

The Problem with Determining Atomic Structure at the Nanoscale

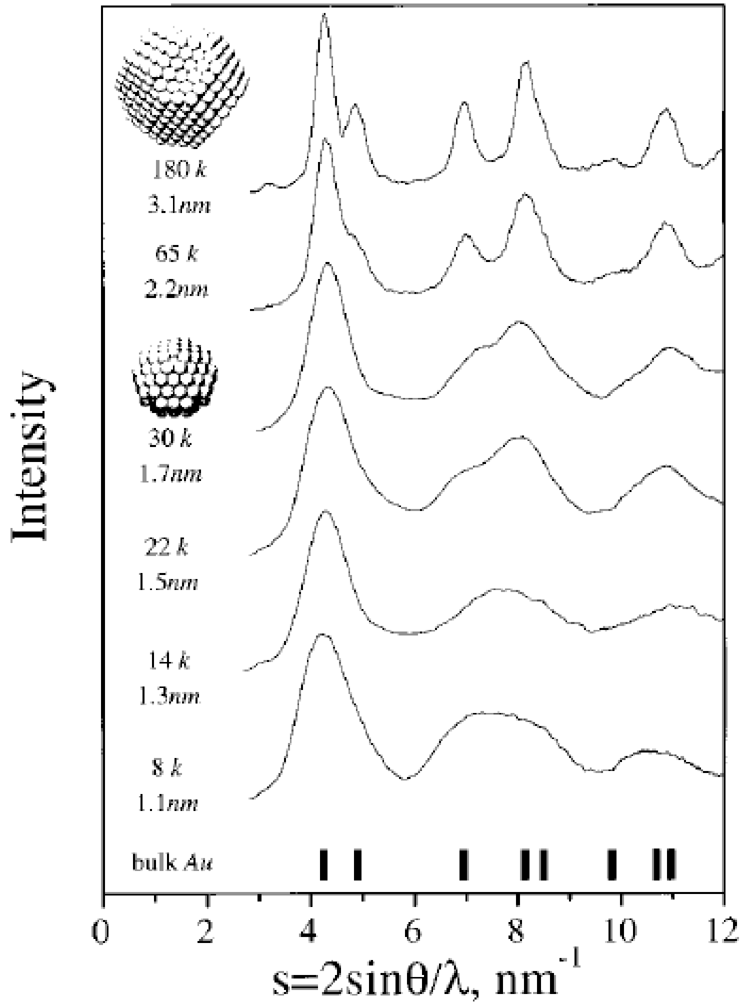
Simon J. L. Billinge[1]* and Igor Levin[2]

Science, **316** (2007) 561-563.



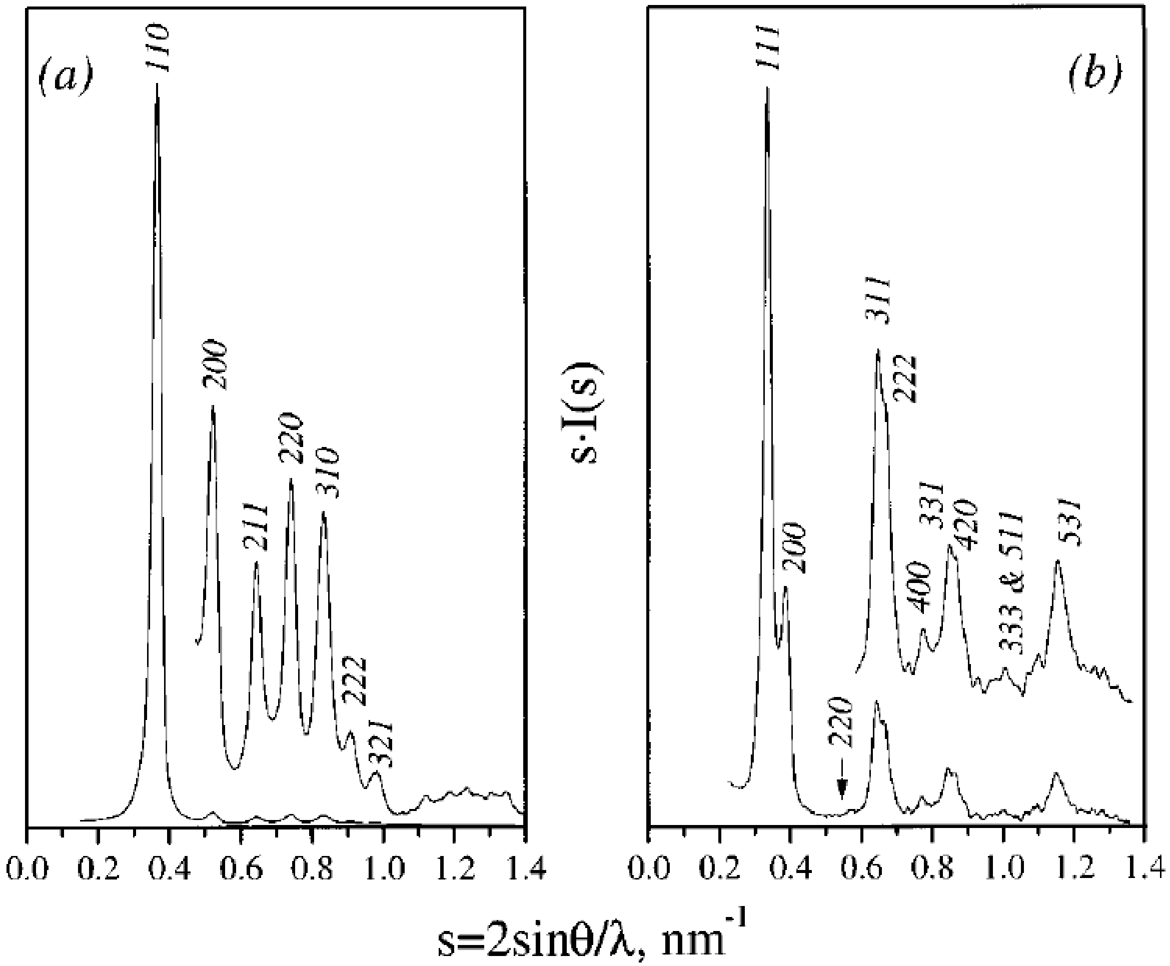
A, B, and C, are examples respectively of nanoscale precipitates in a bulk crystal, of a molecule in a porous crystal and a nanoparticle. The models and corresponding micrographs (below).

How does one locate every atom in the absence of perfect crystallinity ?



Evolution of the wide-angle diffraction patterns of gold nanoparticles as a function of diameter and of average atomic mass. The nanoparticles were prepared by reducing Au^{3+} in the presence of thiols, and the materials was precipitated out using non-solvents.

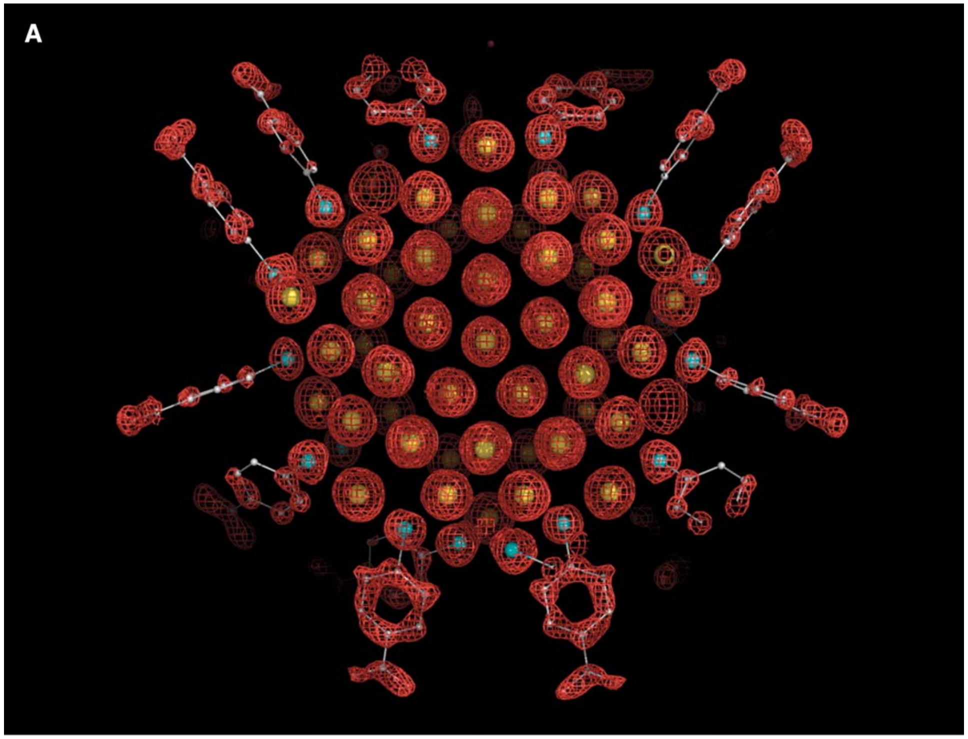
Whetten *et al.*, Crystal structures of molecular gold nanocrystal arrays, *Acc. Chem. Res.* **32** (1999) 397-406.

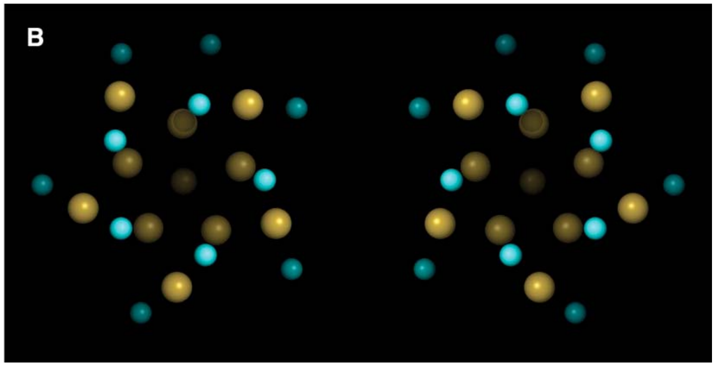


Interestingly, apart from the wide-angle reflections, the collected solids also showed small-angle peaks corresponding to correlations between nanoparticles. “Crystals of nanocrystals”. No correlations found however between the small- wide-angle scattering (no satellite reflections).

Whetten *et al.*, Crystal structures of molecular gold nanocrystal arrays, *Acc. Chem. Res.* **32** (1999) 397-406.

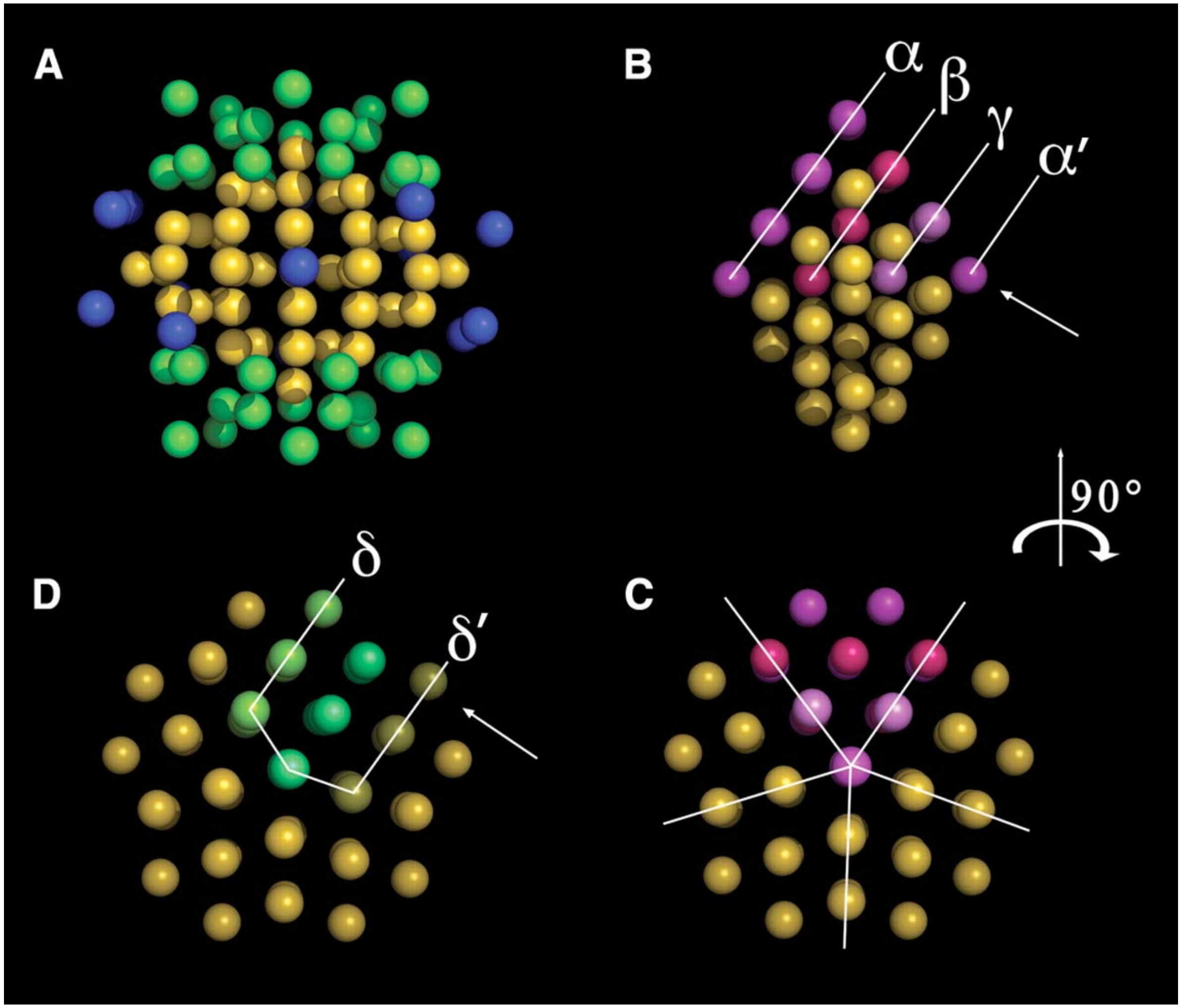
Enter the biochemists.





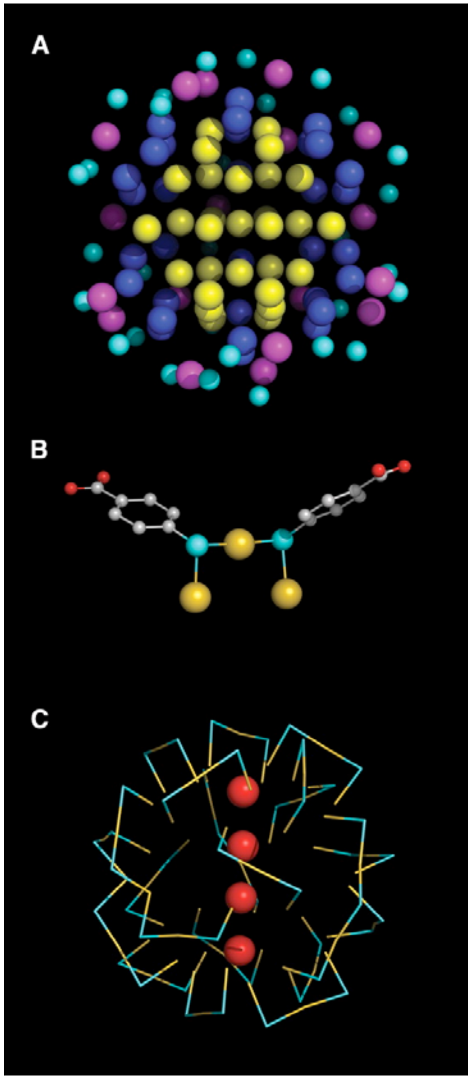
p-mercaptobenzoic (*p*-MBA) acid capped gold nanoparticles: 102 gold atoms, and 44 (*p*-MBA)

Jadzinsky *et al.*, Structure of a thiol monolayer-protected gold nanoparticle at 1.1 A resolution, *Science* **318** (2007) 430-433.

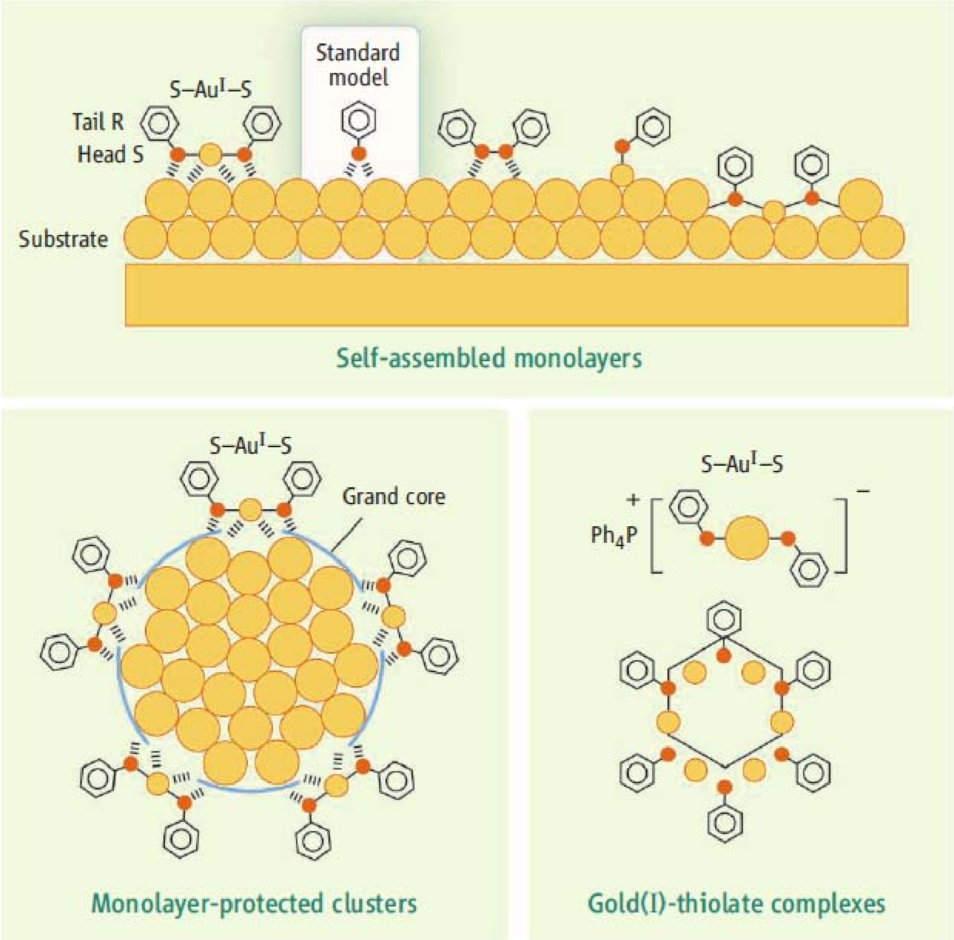


Many ways of looking at the gold core, including as 5 twinned *fcc* units seen in C.

Jadzinsky *et al.*, Structure of a thiol monolayer-protected gold nanoparticle at 1.1 A resolution, *Science* **318** (2007) 430-433.



A surprise: The mode by which the thiol binds.



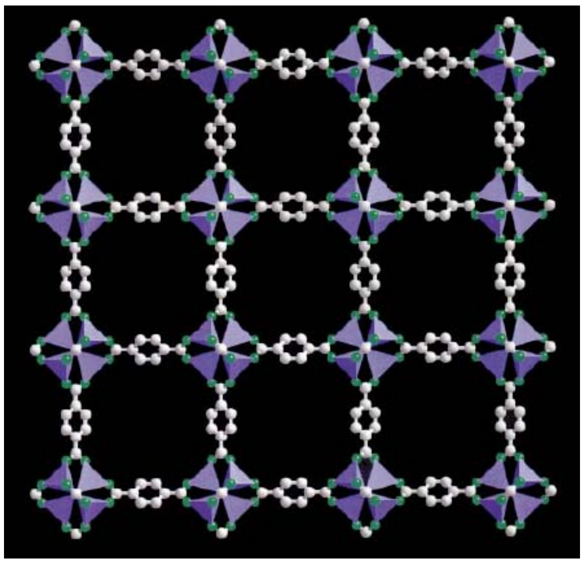
Jadzinsky *et al.*, Structure of a thiol monolayer-protected gold nanoparticle at 1.1 A resolution, *Science* **318** (2007) 430-433; Whetten and Price, *Science* **318** (2007) 407-408.

Organic-inorganic framework solids: MOF-5

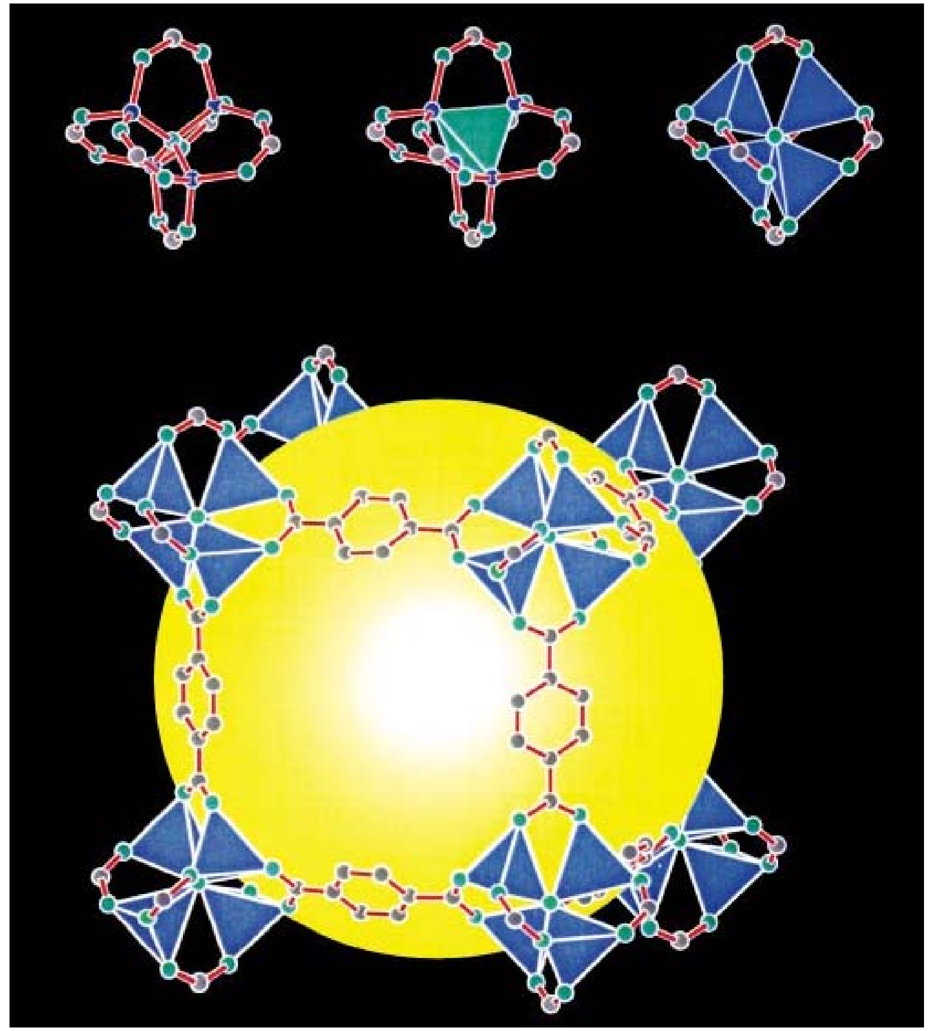
Design and synthesis of an exceptionally stable and highly porous metal-organic framework

Hailian Li*, Mohamed Eddaoudi†, M. O'Keeffe* & O. M. Yaghi†

Nature **402** (1999) 276-279.



$Zn_4O(BDC)_3$



Formed by crystallizing benzenedicarboxylic (BDC) acid with zinc ions under slightly oxidizing conditions. Cubic, a = 25.67 Å, density near 0.6 gcm^{-3}, surface area 2900 m^2g^{-1}.

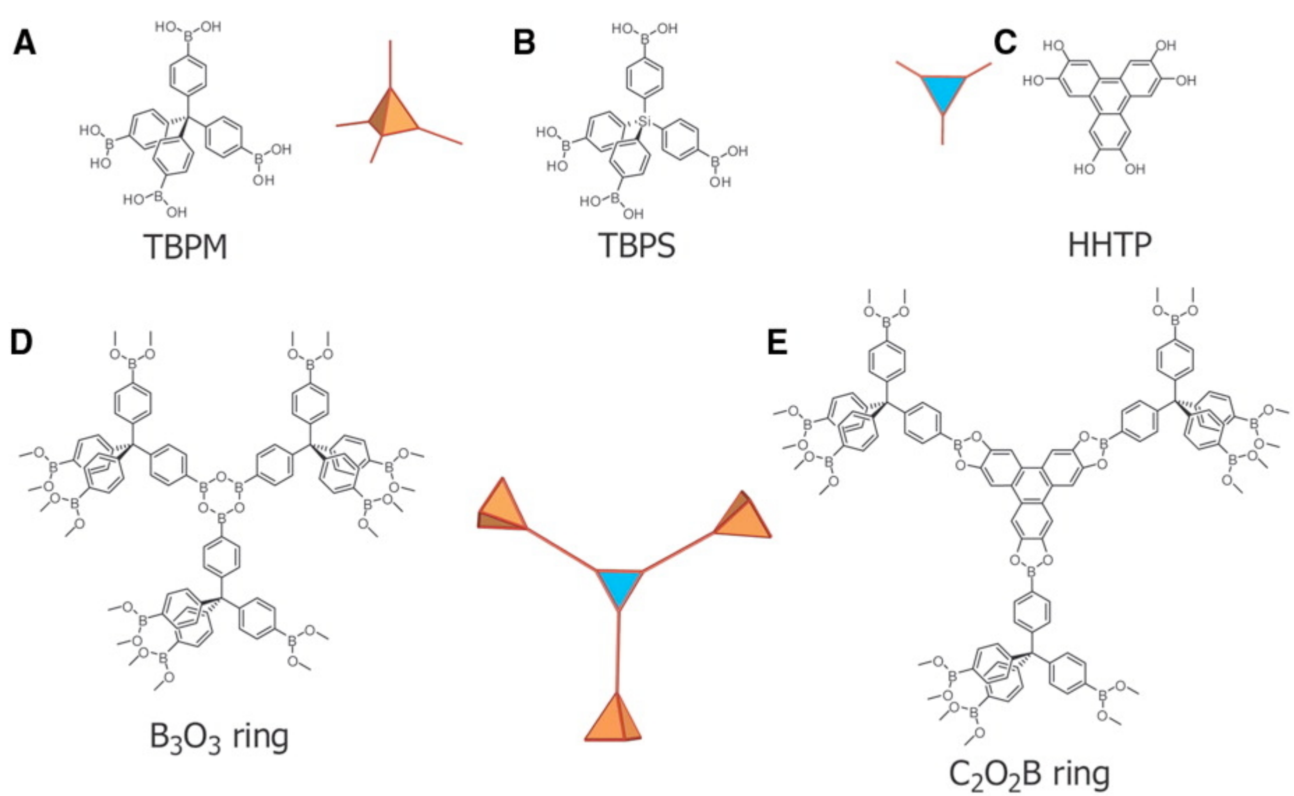
Can a similar all-organic solid be prepared -- a 3D organic polymer ?

Designed Synthesis of 3D Covalent Organic Frameworks

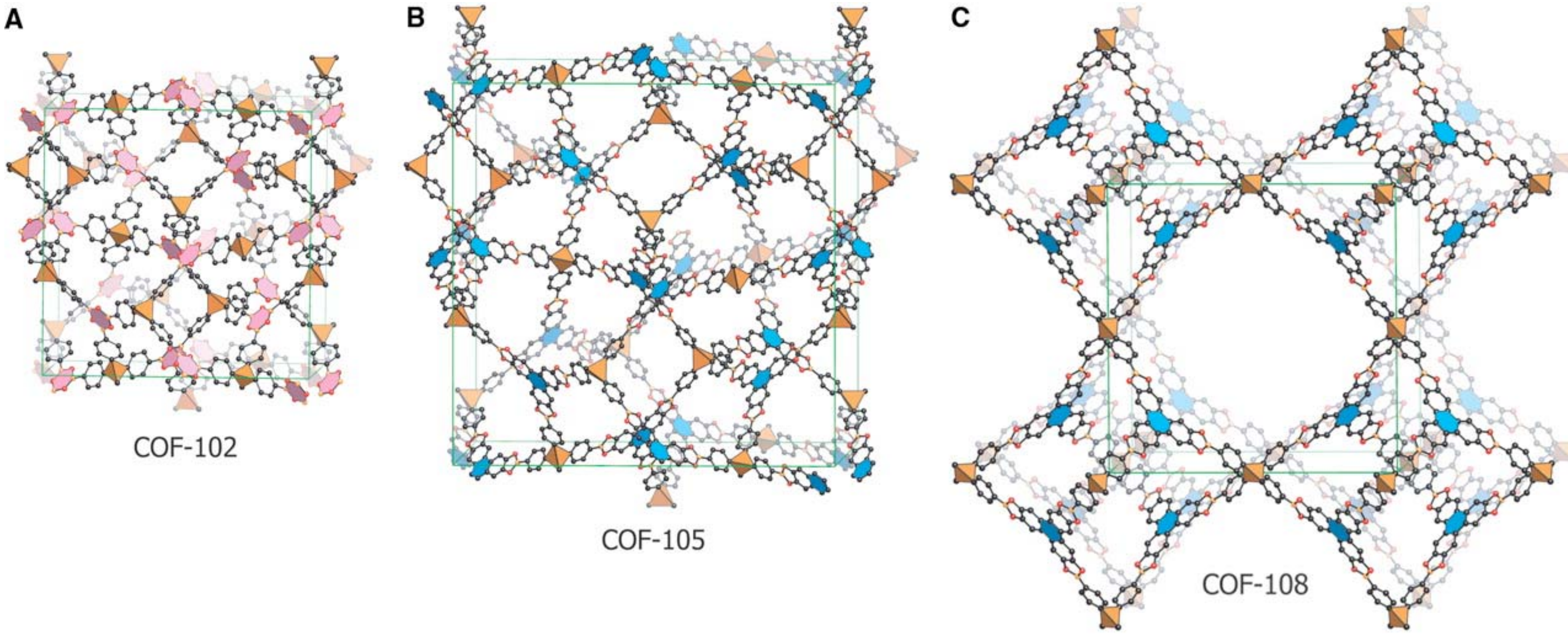
Hani M. El-Kaderi,[1] Joseph R. Hunt,[1] José L. Mendoza-Cortés,[1] Adrien P. Côté,[1] Robert E. Taylor,[1] Michael O'Keeffe,[2] Omar M. Yaghi[1]*

Science **316** (2007) 268-272.

The trick: To get the material to form a crystalline compound rather than amorphous goop.



Class 01: Recent breakthroughs in structure and composition 2: 3D organic polymers (COFs)



Crystal structures of the different Covalent Organic Frameworks (COFs) obtained by modeling and comparing experimental and simulated powder diffraction patterns.

"Because these materials are entirely constructed from strong covalent bonds (C-C, C-O, C-B, and B-O), they have high thermal stabilities (400° to 500°C), and they also have high surface areas (3472 and 4210 $m^2\ g^{-1}$ for COF-102 and COF-103, respectively) and extremely low densities (0.17 g cm^{-1})."

Science **316** (2007) 268-272.

The enumeration of reticular structures: A mathematical exercise.

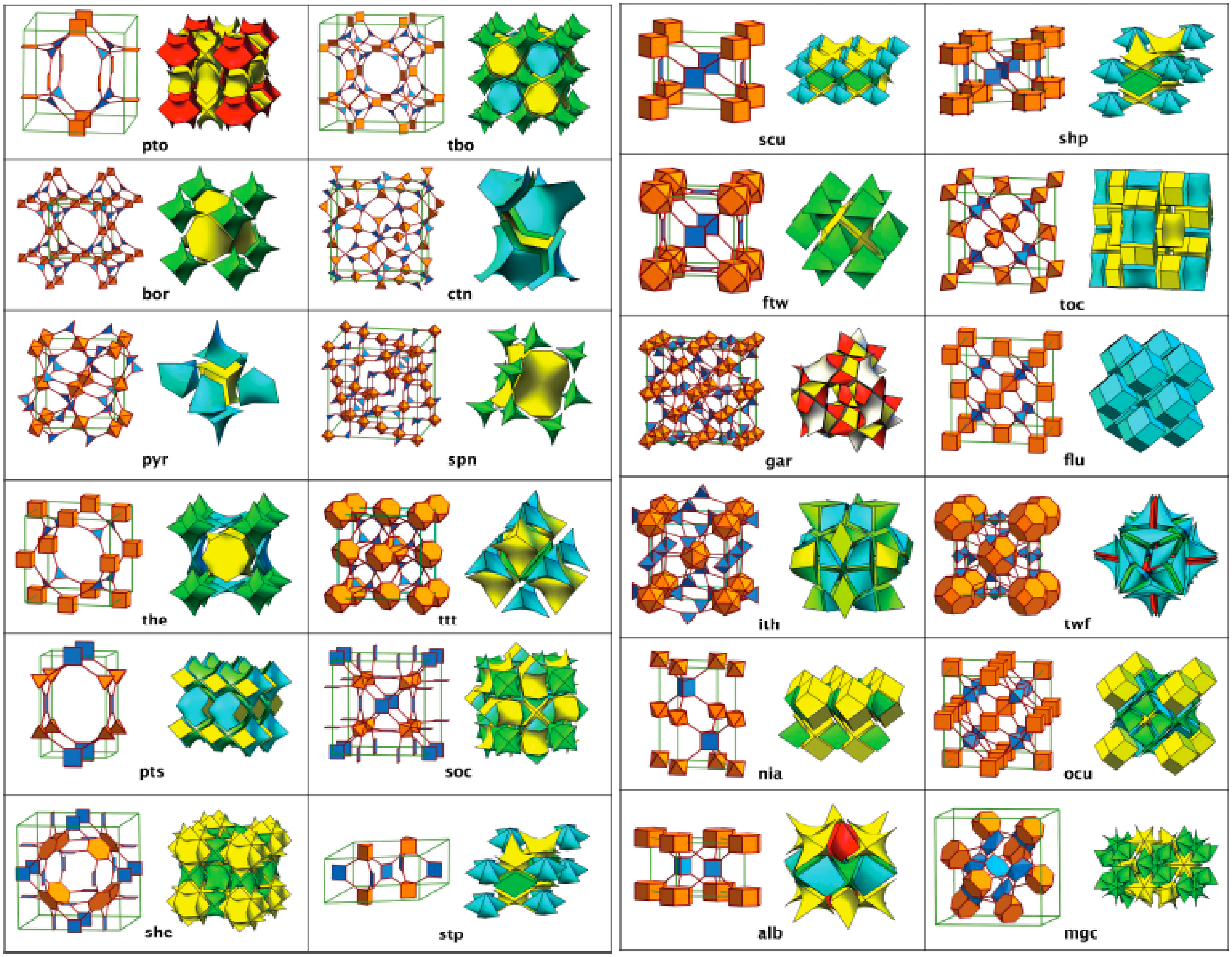
Three-periodic nets and tilings: edge-transitive binodal structures

Olaf Delgado-Friedrichs,[a] Michael O'Keeffe[a]* and Omar M. Yaghi[b]

Acta Crystallogr. A **62** (2006) 350–355.

"28 three-periodic nets with two kinds of vertex and one kind of edge are identified. Some of their crystallographic properties and their natural tilings are described. Restrictions on site symmetry and coordination number of such nets are discussed and examples of their occurrence in crystal structures are given."

Class 01: Recent breakthroughs in structure and composition 2: 3D organic polymers (COFs)



Acta Crystallogr. A **62** (2006) 350–355.