Organic/Inorganic Nanocomposites from confined polymerization

Controlling Organic Phase Architecture via Templating with the Inorganic Phase and vice versa.

http://www.cem.msu.edu/~kanatzid/

MICHIGAN STATE UNIVERSITY

Our work exploits *confined polymerization* and self-assembly,
to organize inorganic and organic building-units into nanocomposite materials with targeted structural features spanning Å to µm length scales.

The techniques involve concepts in

- supramolecular,
- host-guest inclusion
- templating
- biomimetic chemistry

our work has contributed to the idea that inorganic materials can be synthesized by molecular design, self-assembly and crystal engineering.

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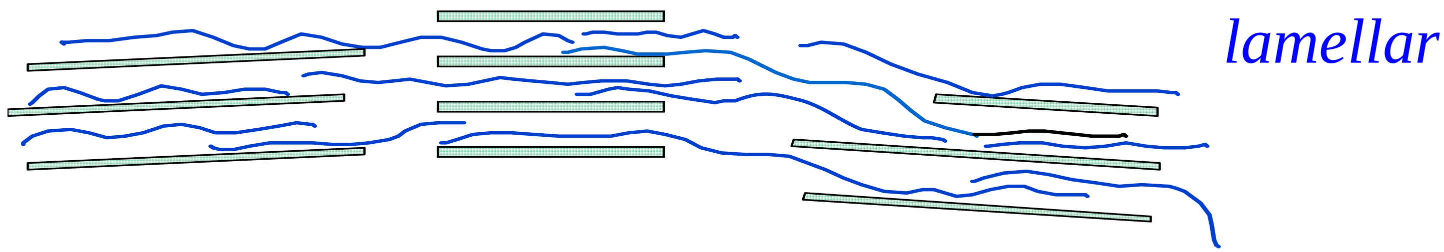
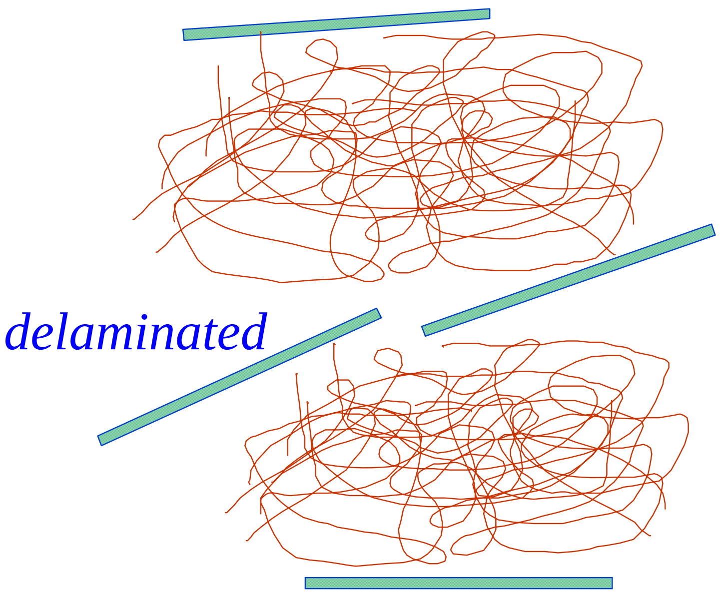
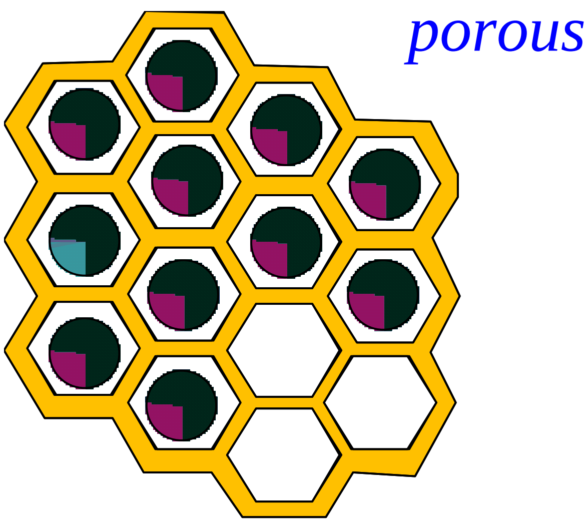
Nanocomposites of interest



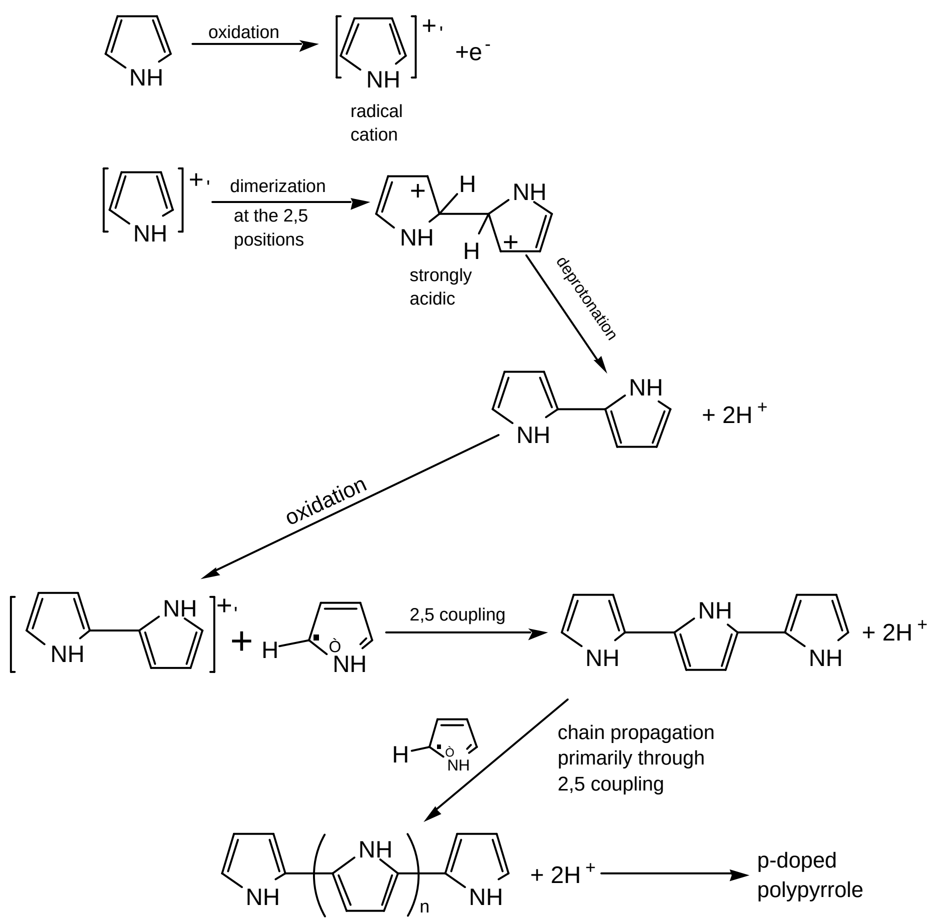




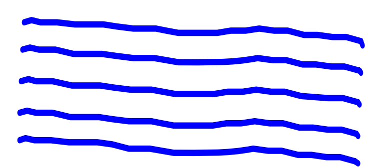
Potential Applications

- Tough structural materials
- Smart membrane systems
- Battery cathode materials
- Sensor applications
- EMI shielding
- Electronic device components

Polymerization of pyrrole

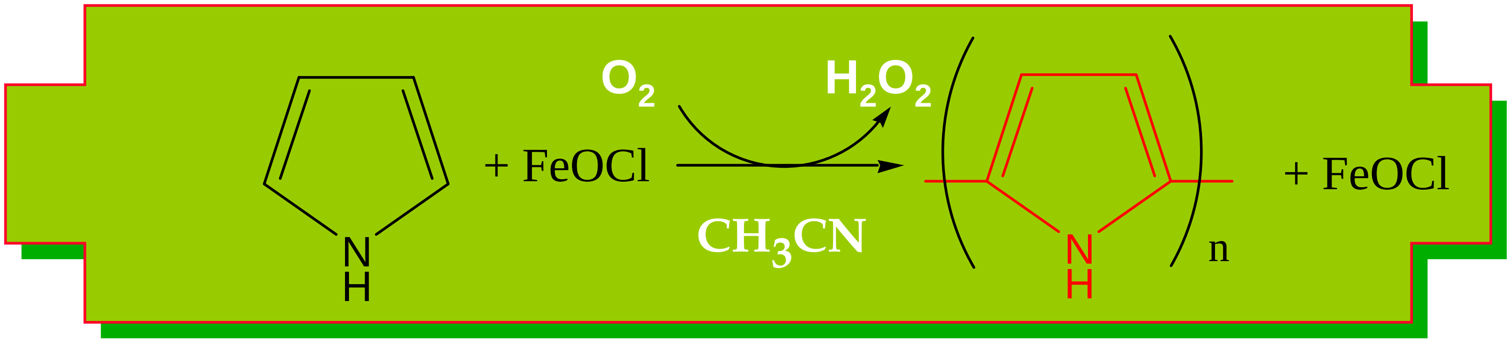


disordered
branched



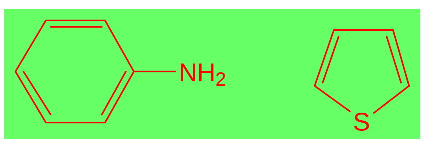
Ordered parallel

INTERCALATIVE POLYMERIZATION IN FeOCl and $V_2O_5 2H_2O$

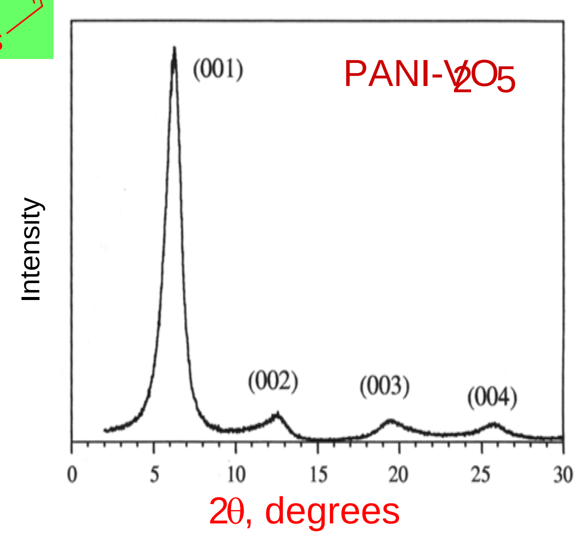


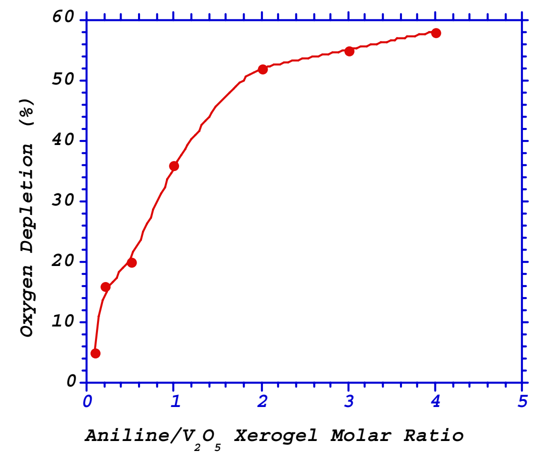
V_2O_5 Xerogel

Also



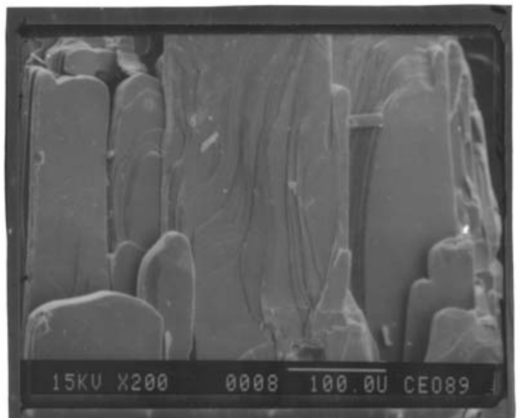
mw=5000
~55 units

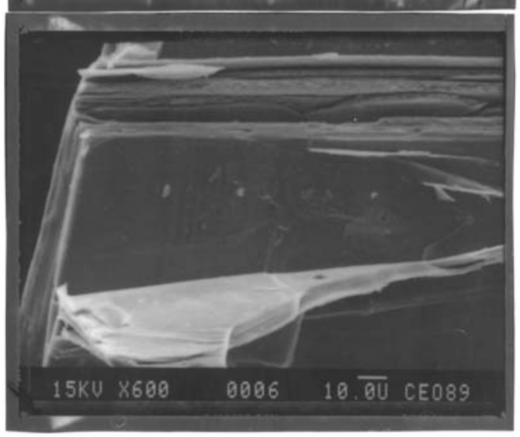


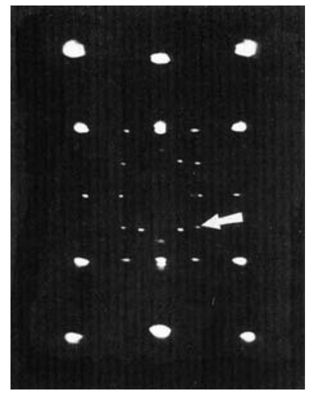


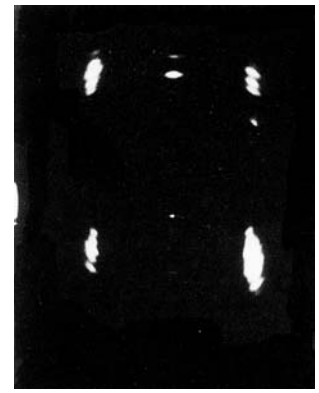
Kanatzidis, Marks et al
JACS 109, 3797 *(1987)*

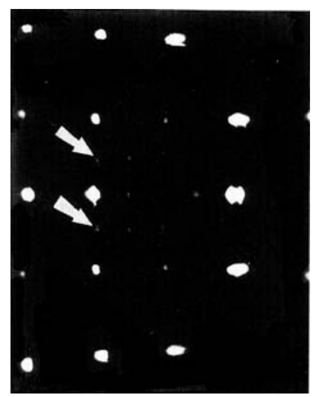
X-ray Diffraction from PANI-FeOCl “single crystal”

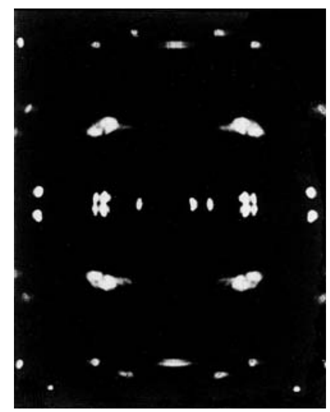




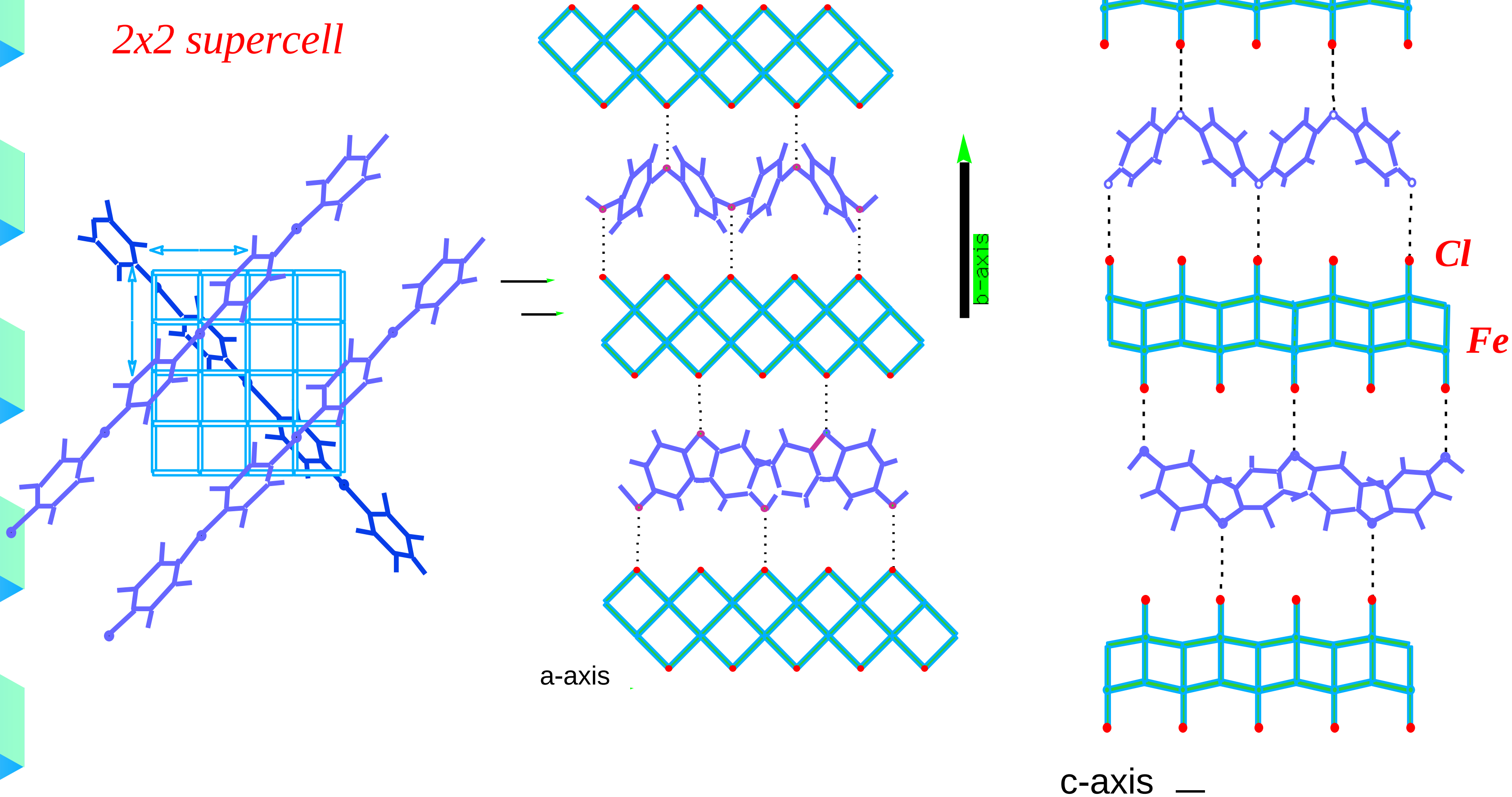




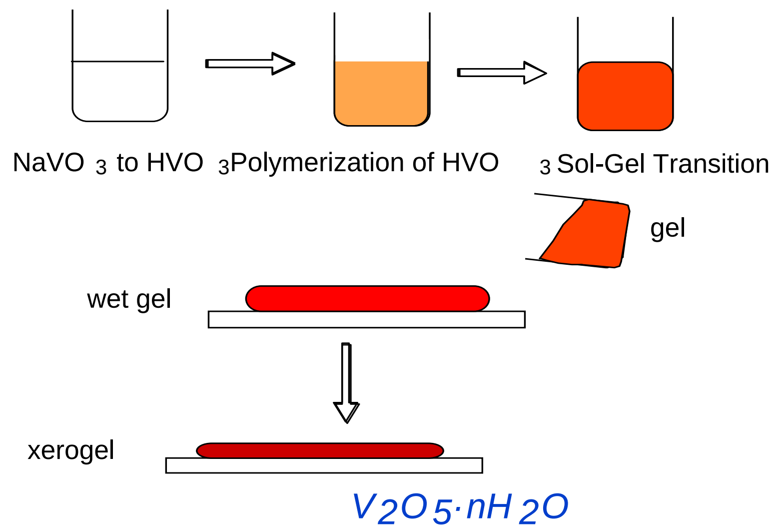


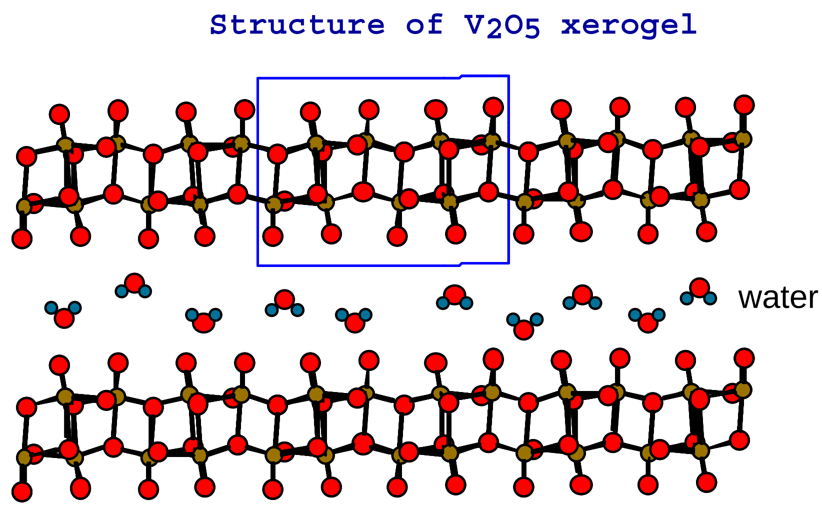


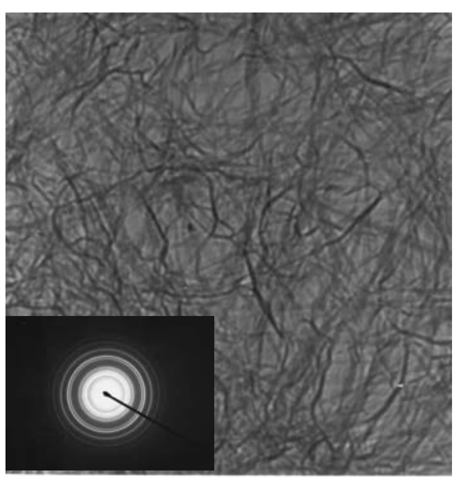
Ordering of polyaniline in FeOCl (Endotaxy)

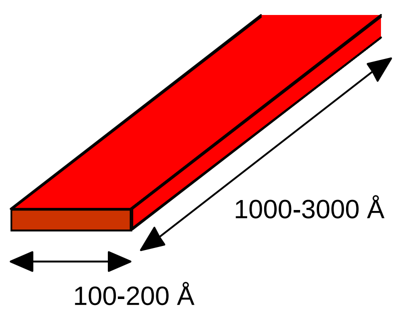


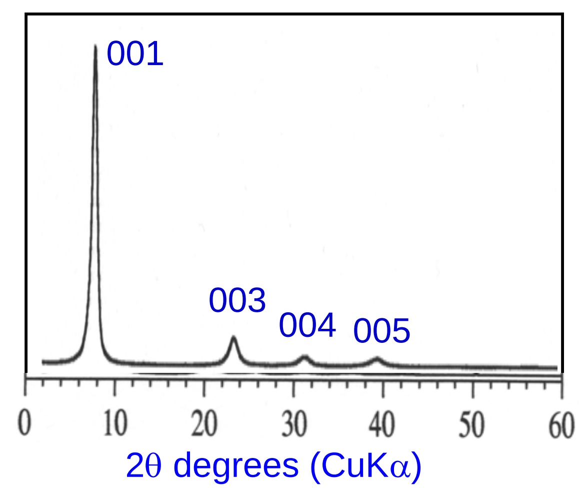
$V_2O_5 \cdot nH_2O$ xerogel











SALIENT FEATURES OF NANOCOMPOSITES

- ***Diverse Components Mixed at the Molecular Scale***
  - compound-like
  - classical composite -like
- ***Potential Polymer Chain Ordering in Intralamellar Space***
  - **polymer structure**
  - **enhanced properties**
- ***Maximization of Interface Interactions***
  - **model systems for interface studies**
  - **Interactions at interface responsible for advanced properties**
- ***Hybrid materials ….. new properties***

Layered Inorganic Compounds as Host Materials

Phyllosilicates, clays:	montmorillonite, hectorite, fluorohectorite
Oxides:	**V_2O_5 xerogel**, **MoO_3**
Oxyhalides:	**FeOCl**
Dichalcogenides:	**MoS_2**, TiS_2, **TaS_2, $NbSe_2$, WS_2**
MPS_3:	$MnPS_3$, $CdPS_3$, $NiPS_3$
metal phosphates:	**α-$Zr(HOPO_3)_2{\cdot}H_2O$, α-$Ti(HOPO_3)_2{\cdot}H_2O$, $HUO_2PO_4{\cdot}4H_2O$**
Layered Double Hydroxides:	$[Ca_2Al(OH)_6]^+[(OH){\cdot}3H_2O]^-$

Giannelis, Ruiz-Hitzky, Kanatzidis, Nazar, Lemmon, Jones, others...

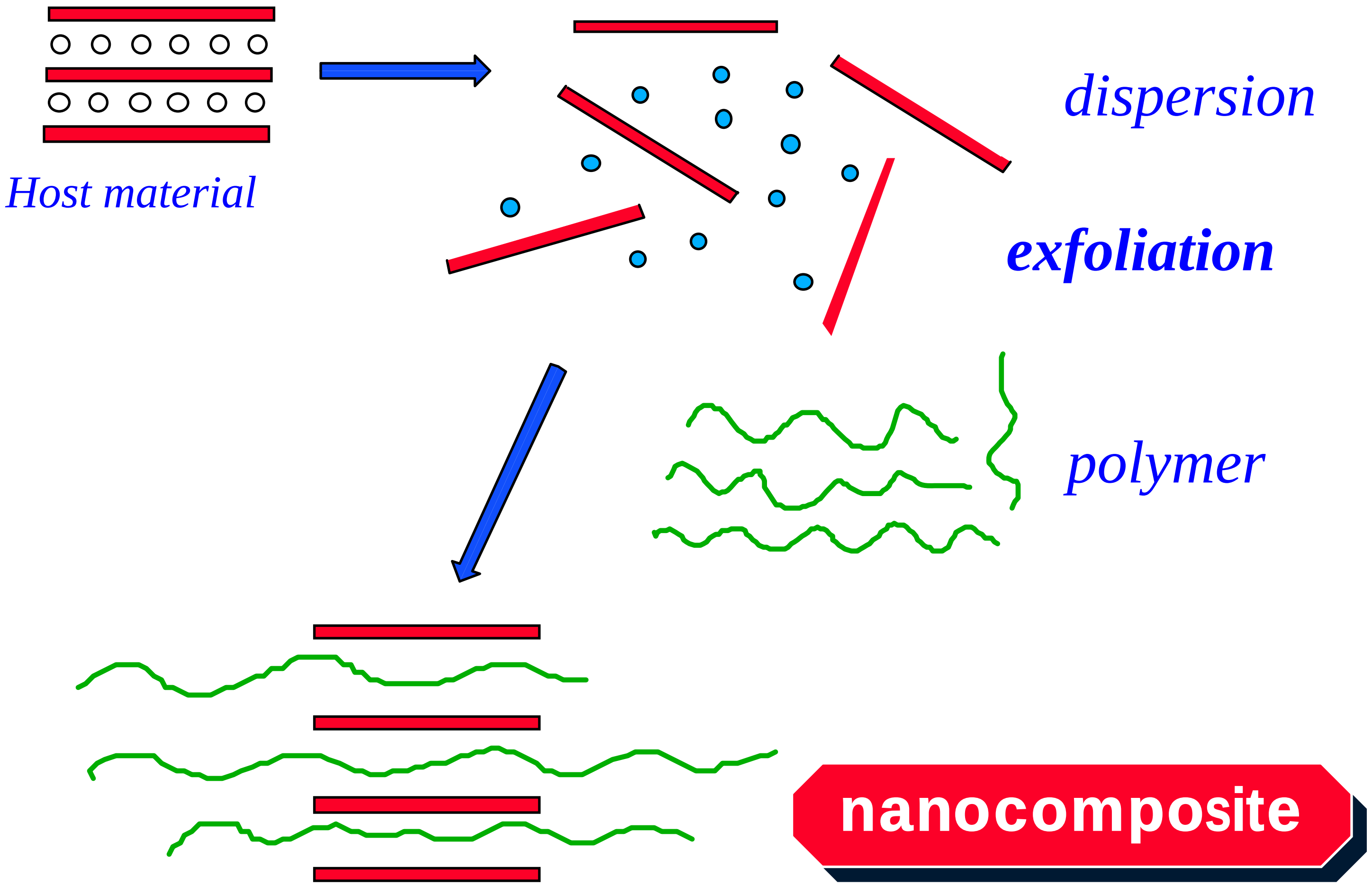
Methods for Polymer Intercalation

- *in-situ* intercalative redox polymerization
  - polypyrrole/FeOCl, PANI/V_2O_5 (Kanatzidis et al)
  - polypyrrole/zeolite (Bein et al)
  - polypyrrole/clay (Giannelis et al)
- monomer intercalation followed by induced topotactic polymerization
  - post-intercalative
  - nylon/clay (Kamigaito, Usuki et al)
  - anilinium/V_2O_5 (Kanatzidis et al)
- direct polymer intercalation (solution/solid interface)
  - PPV/MoO_3 (Nazar et al) (precursor polymer)
  - PEO/V_2O_5 (Kanatzidis et al)
  - PEO/clay (Ruiz Hitzky, Giannelis)
  - PEO/$CdPS_3$ (Clement et al)
  - PAN/zeolite (Bein et al)

...more methods

- direct polymer intercalation from the melt
  - PEO/clay, polystyrene/clay (Giannelis et al)
- polymer encapsulation by flocculation of a colloidal single layer suspension of the host
  - (nano-composite self assembly)
  - PANI/MoS_2 (Kanatzidis et al)
- simultaneous polymerization/polymer encapsulation by flocculation of a colloidal single layer suspension of the host
  - (nano-composite self assembly)
  - polypyrrole/MoS_2 (Kanatzidis et al)
- Alternating layer by layer deposition of one phase on top of another
  - Mallouk, Decher others
- Others...

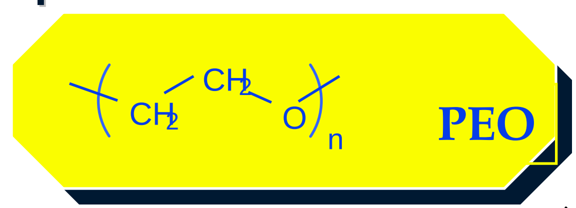
POLYMER ENCAPSULATION

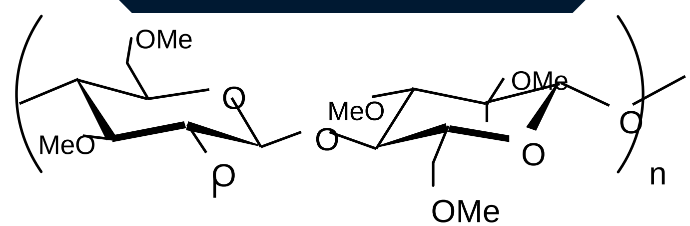


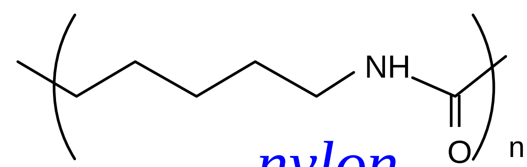
Exfoliated layers of MoS_2 , WS_2 , $NbSe_2$ and TaS_2 have been used for the first time to produce plastic-like nanocomposites

- The exfoliation method applies to a large variety of soluble polymers
  - Enables tuning of the mechanical properties in these materials

- Polyethylene
- Polyethylene-oxide, PEO
- poly(propylene glycol) ,
- methyl cellulose,
- poly(ethylenimine), PEI
- Nylon
- etc.

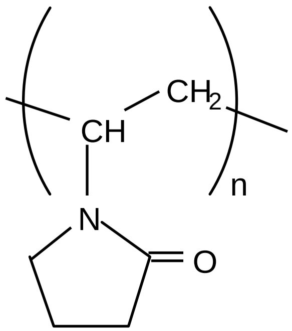


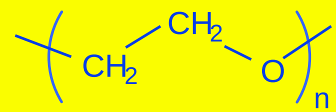




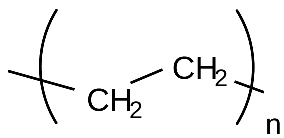
nylon

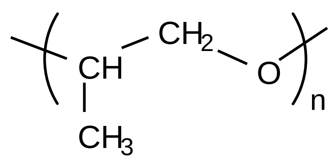
Some Encapsulated Polymers

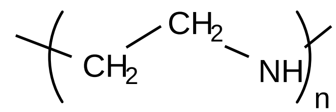


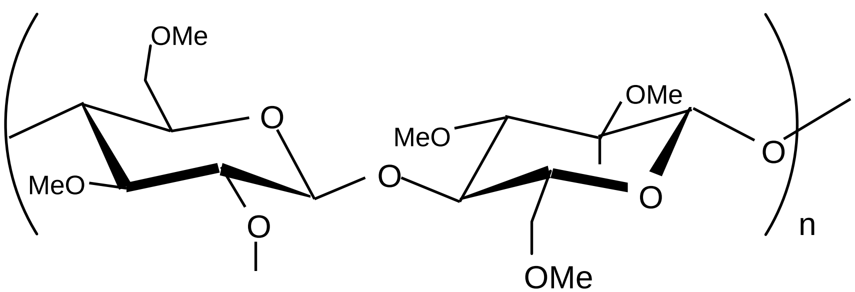


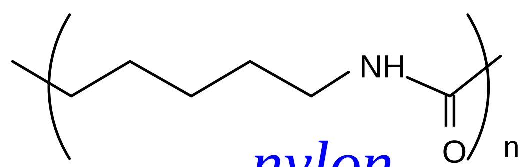
PEO



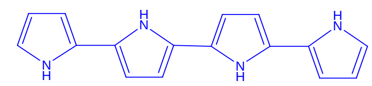




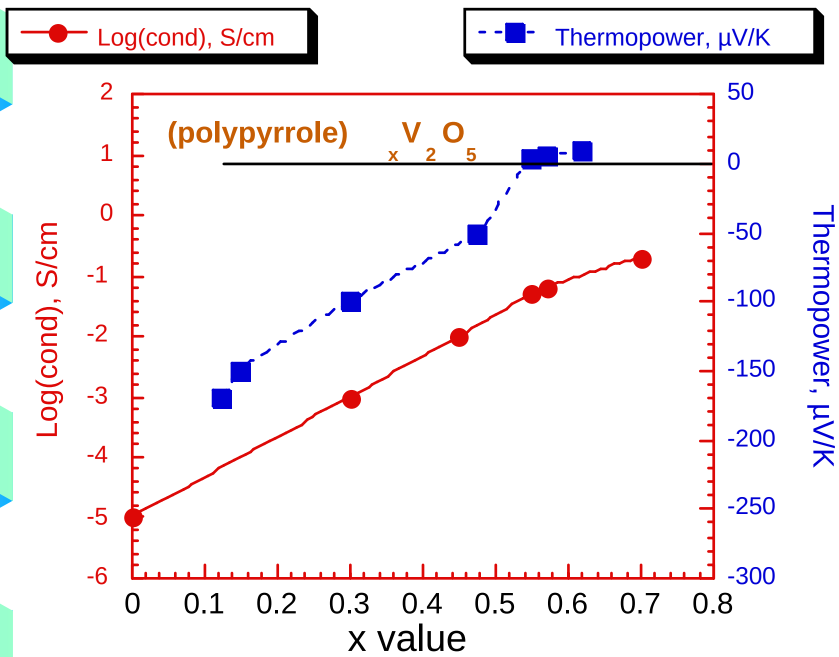


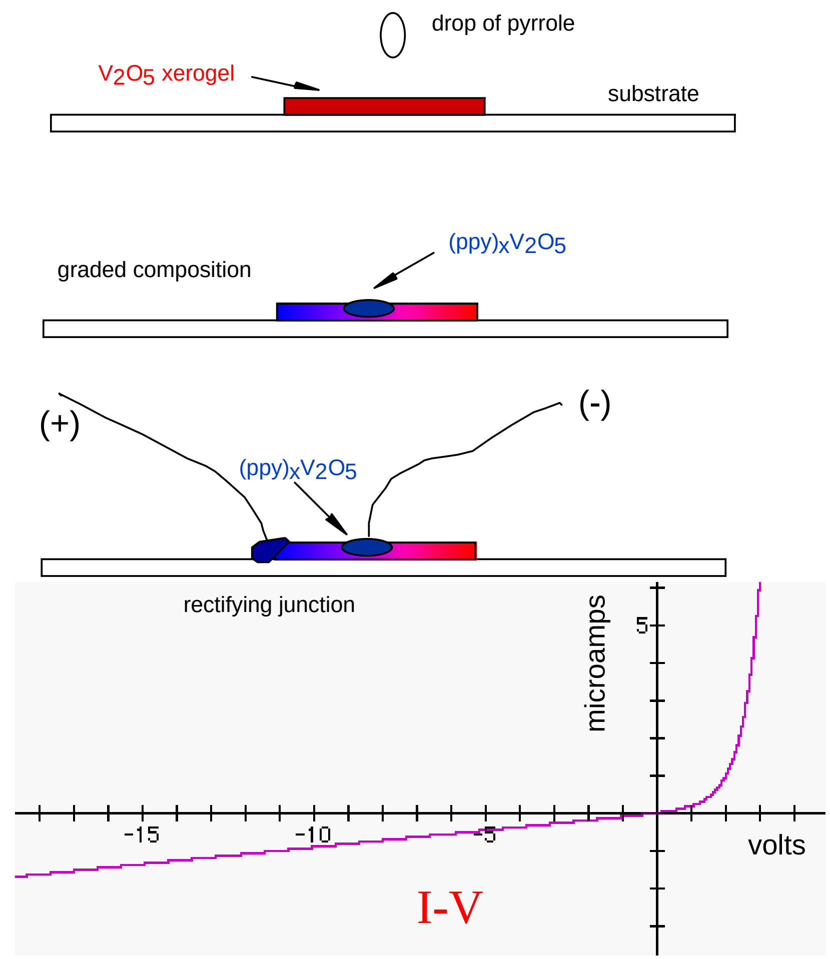


nylon



Rectifying polypyrrole/ V_2O_5 xerogel junctions





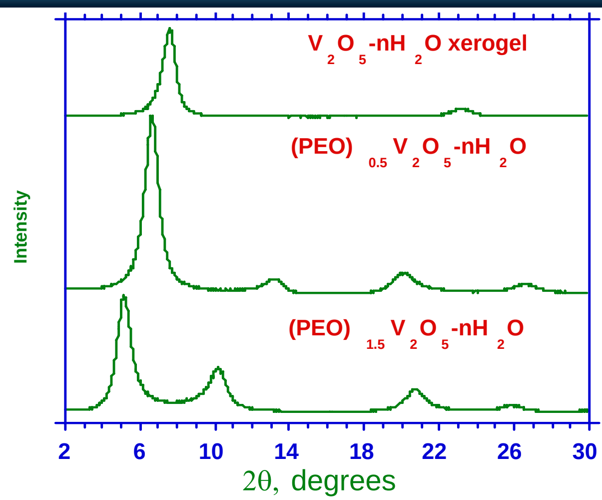
$(polypyrrole)_xV_2O_5$

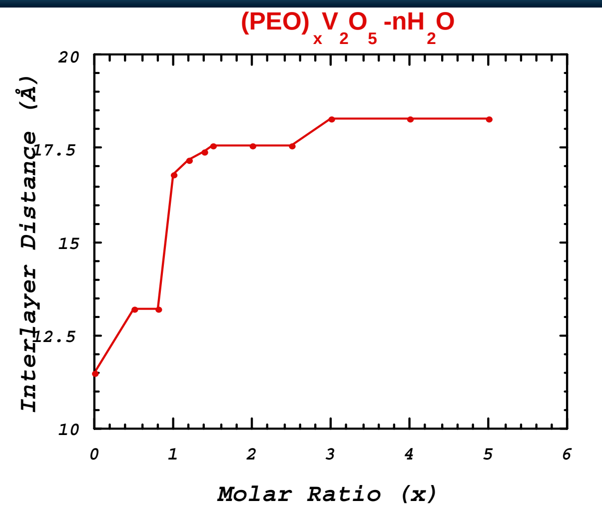
Conductivity type changes with x

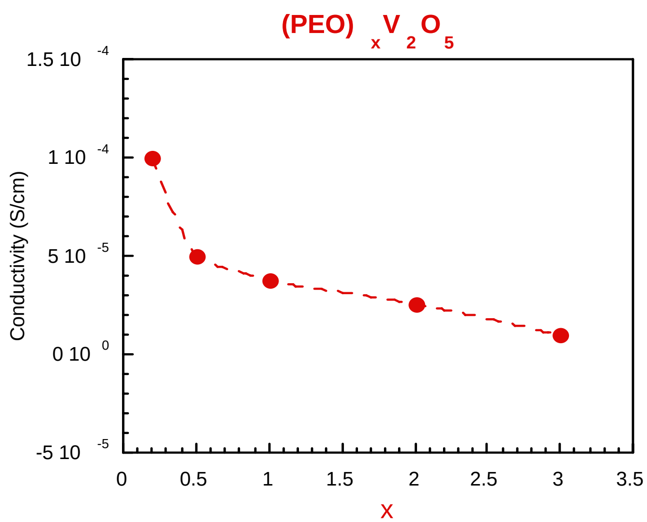
At low x system is n-type

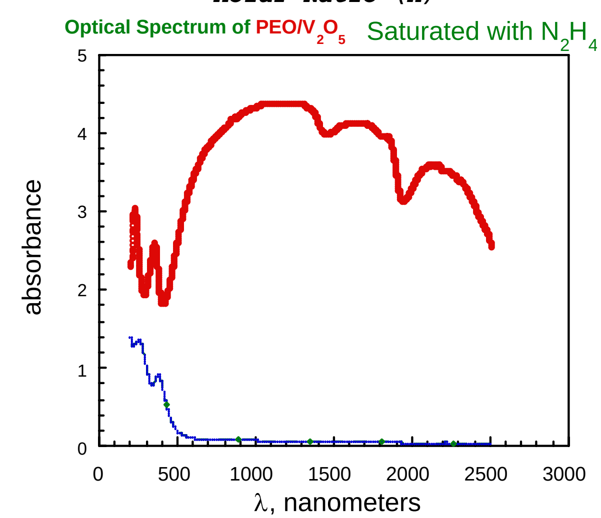
At high x system is p-type

$(PEO)_xV_2O_5$ nanocomposites



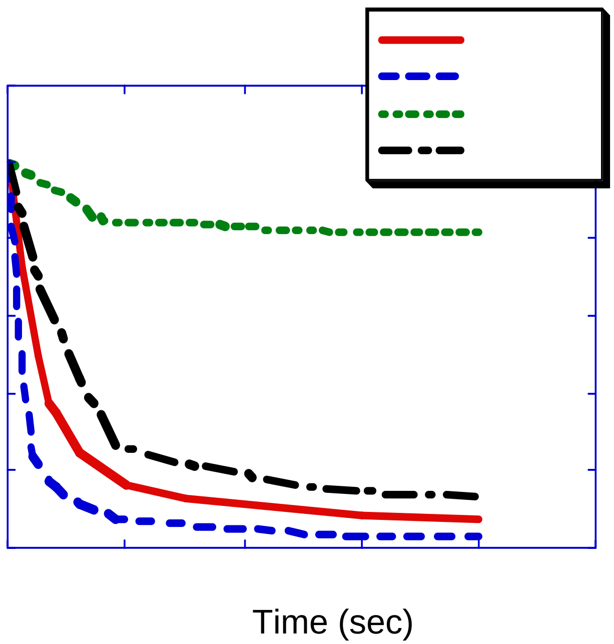




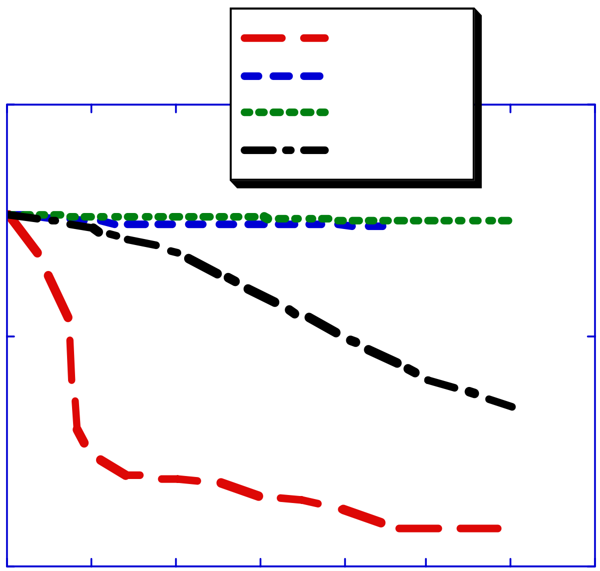


$(PEO)_xV_2O_5$ as a sensitive N_2H_4 sensor

Response to N_2H_4

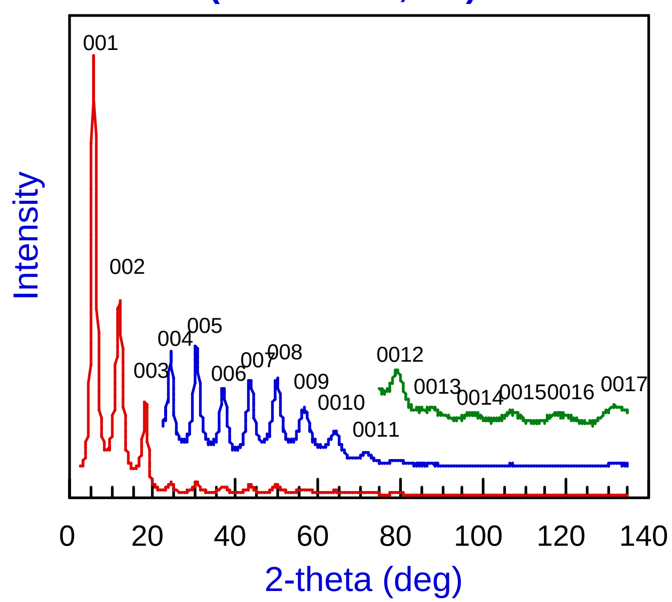


Response to NH_3

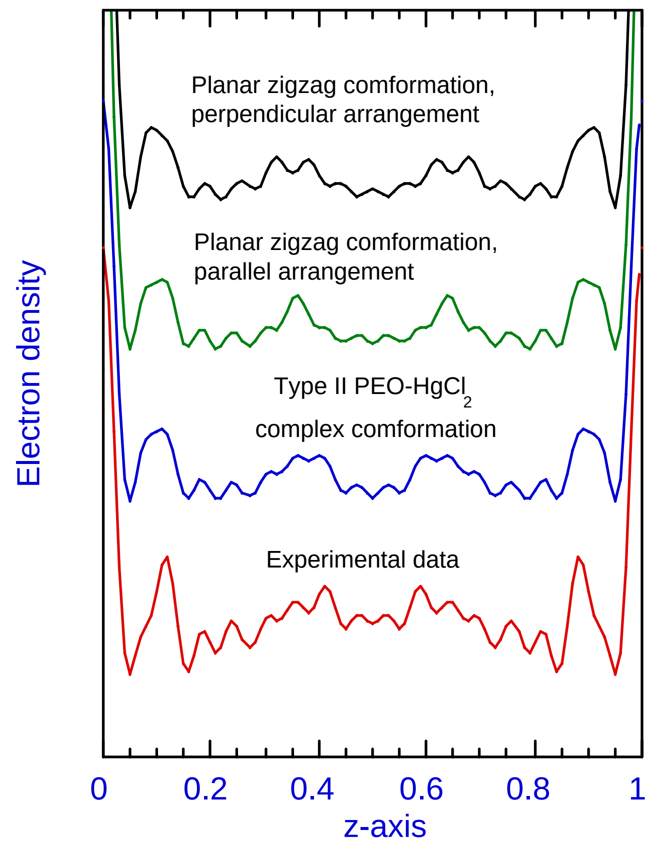


Highly oriented films

XRD Pattern of Li_xTaS_2•PEO Film
(M.W. = 100,000)

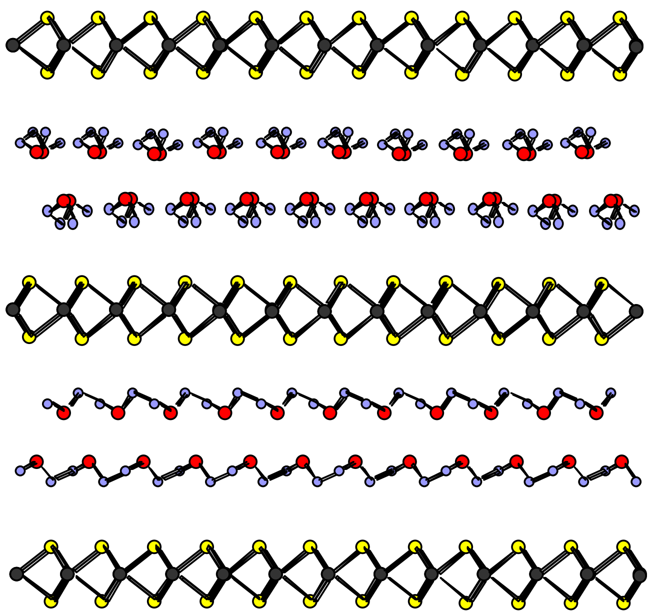


One-Dimensional Electron-Density
Maps of Li_xTaS_2¥PEO Nanocomposite

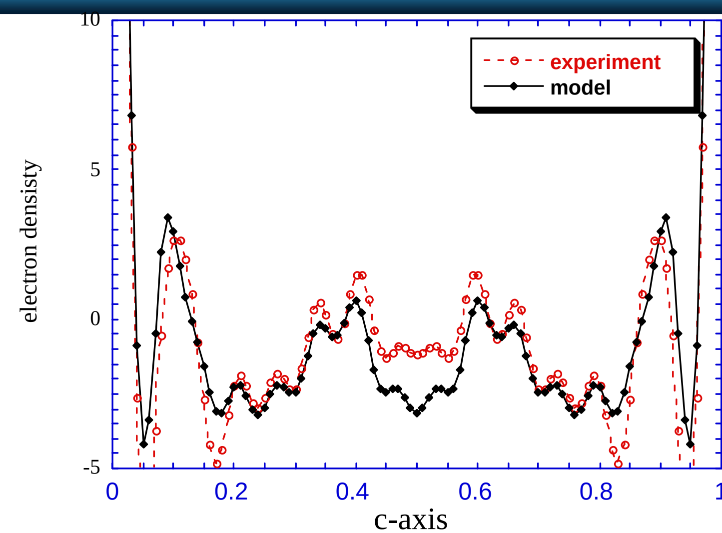


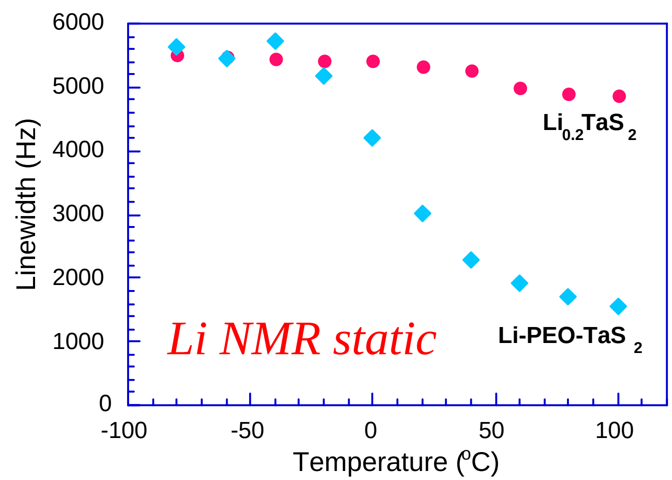
PEO conformation in TaS_2 and $NbSe_2$ and Li-ion mobility

Li -PEO-TaS_2



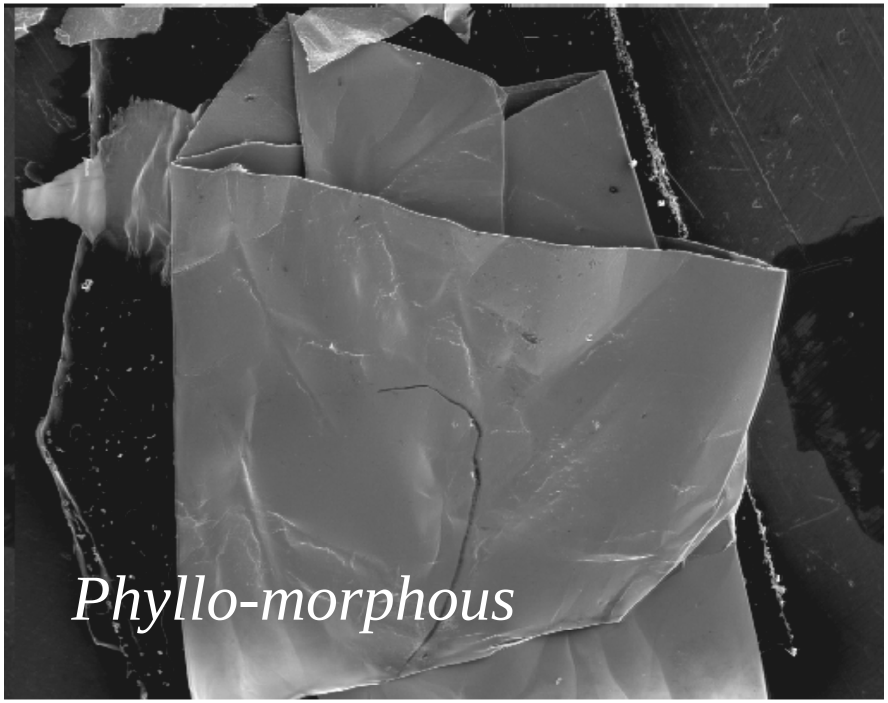
Type-II PEO-$HgCl_2$ complex



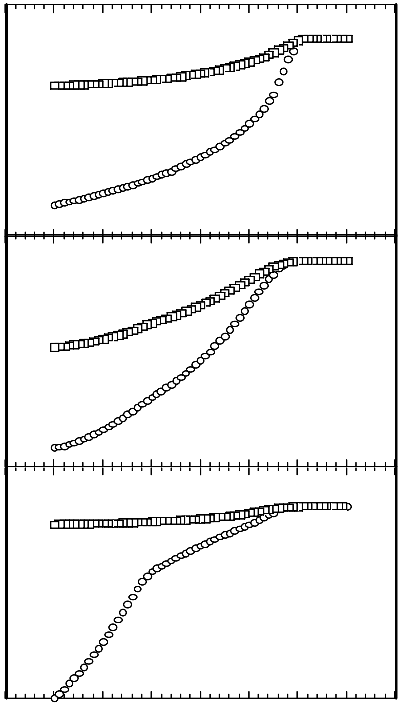


Superconductivity in TaS_2 and $NbSe_2$

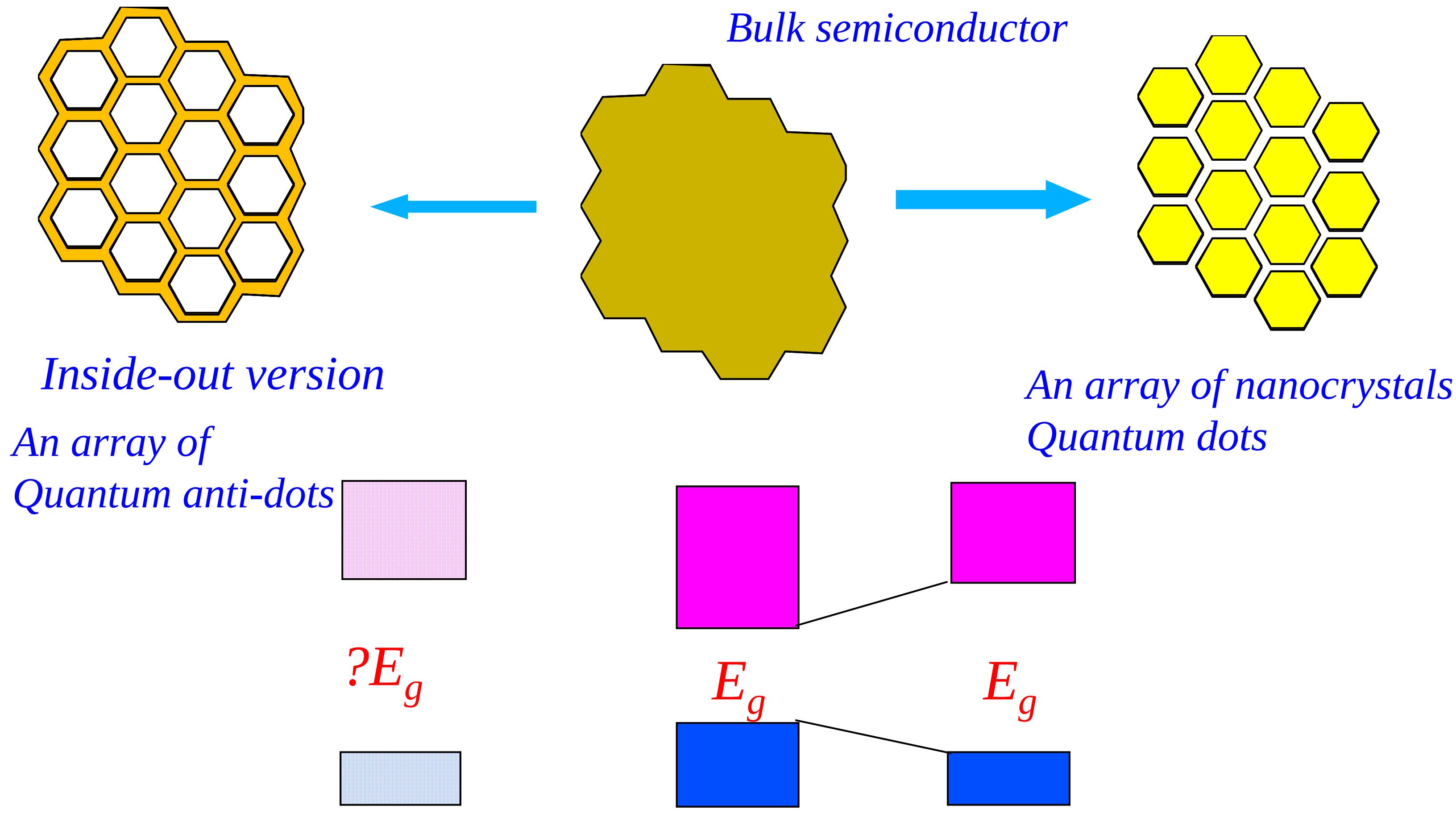
Free standing film of TaS_2



Meissner effect in $NbSe_2$



Porous Semiconductors (non-oxidic): A challenge



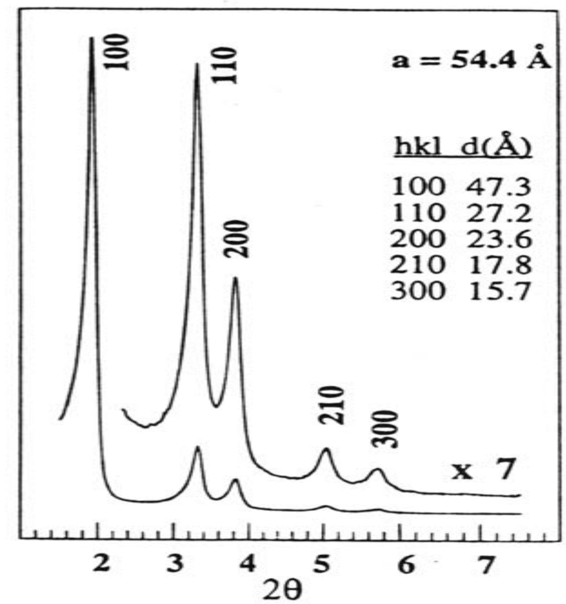
Mesoporous Oxides via Liquid Crystal Template Route

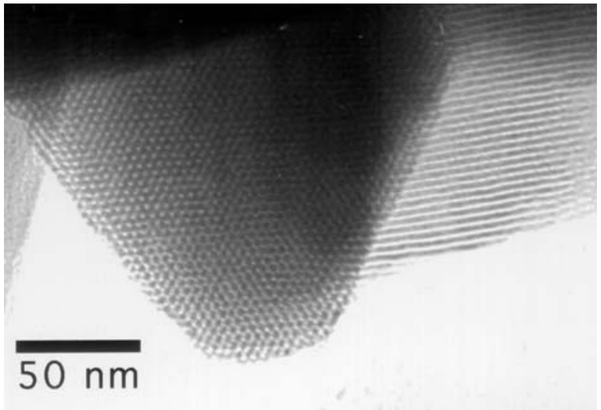
- Major Breakthrough ca 1989: general synthetic strategy to ordered mesoporous silicates by Mobil[1] (MCM-41, MCM-48 etc), opened the pathway for novel hybrid solids.
- Many mesoporous metal oxides have been synthesized based on MCM-X materials[2,3].

ZrO_2, V_2O_5, SnO_2, TiO_2

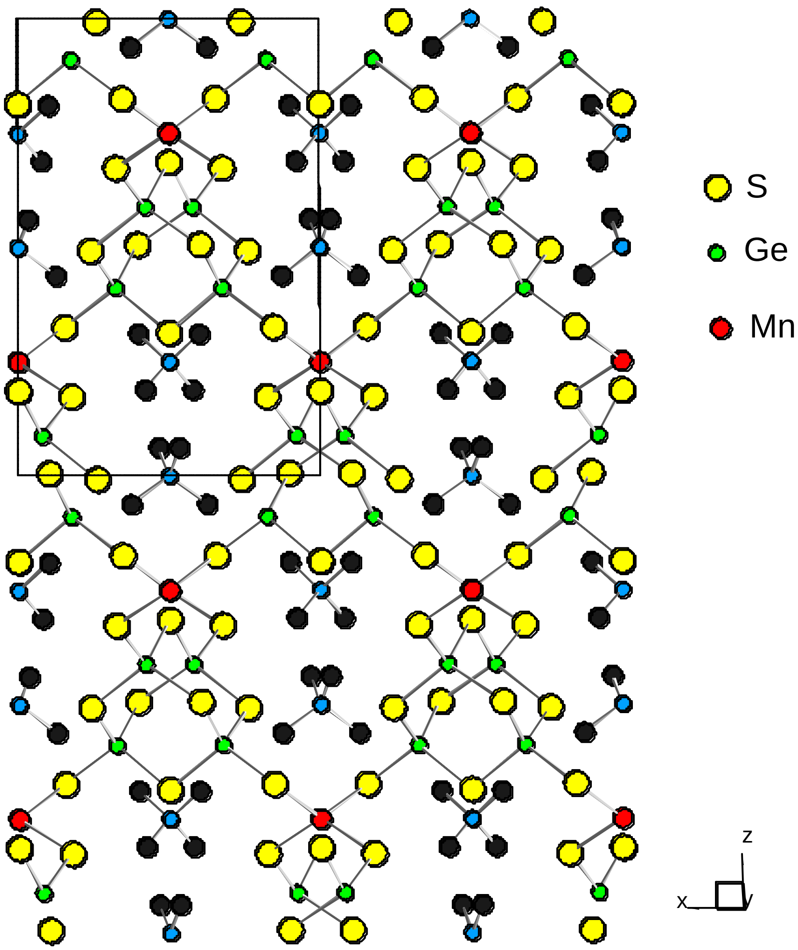
1. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* **1992,** 359, 710.

G. D. Stucky et al, *Chem. Mater*. **1996**, 8, 1147

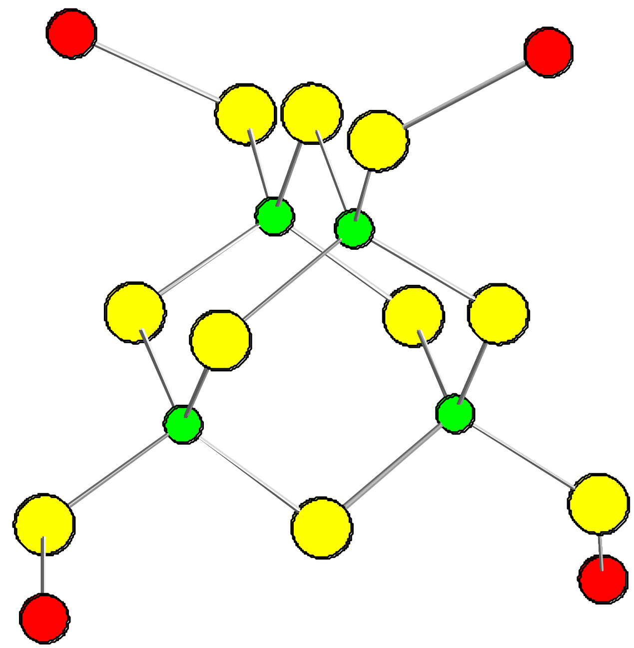




Adamantane based frameworks

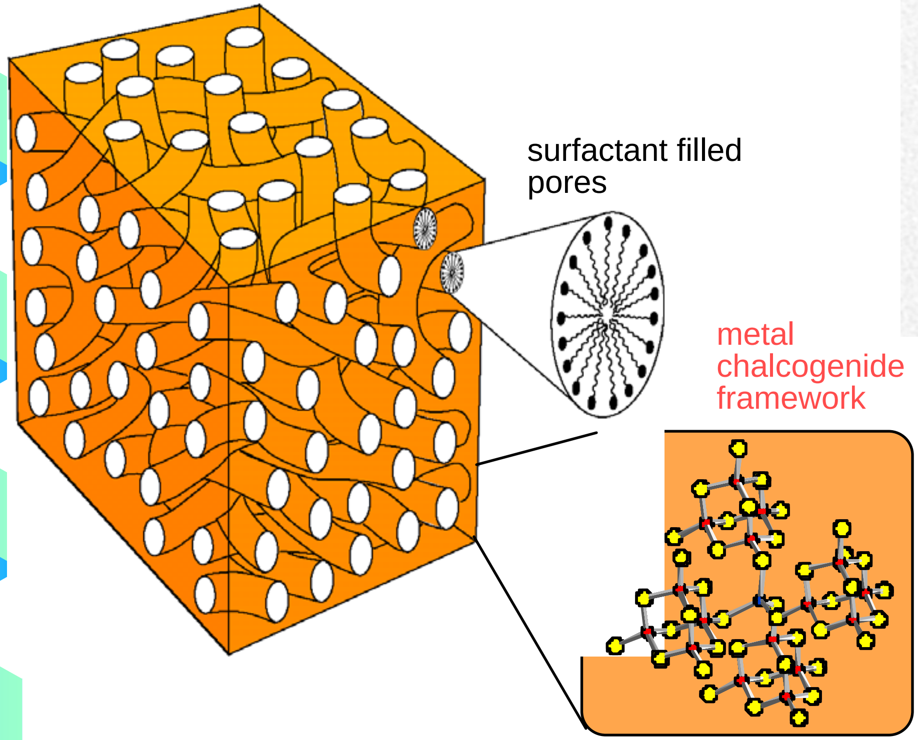


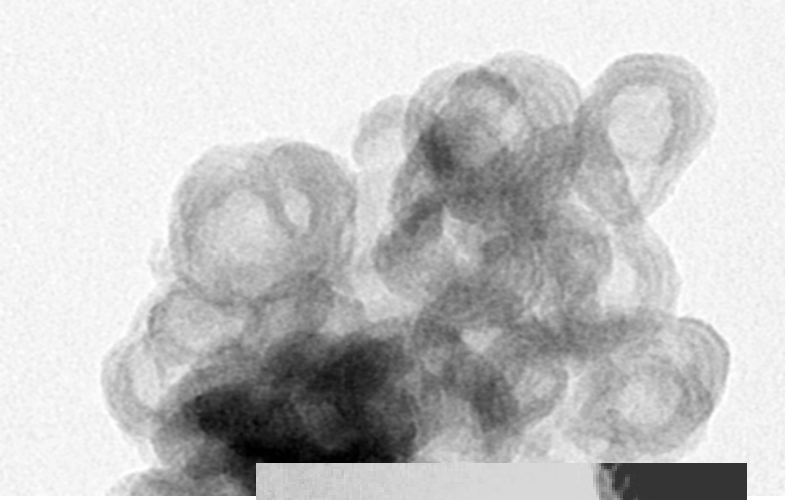
$(Me_4N)_2MnGe_4S_{10}$ microporous

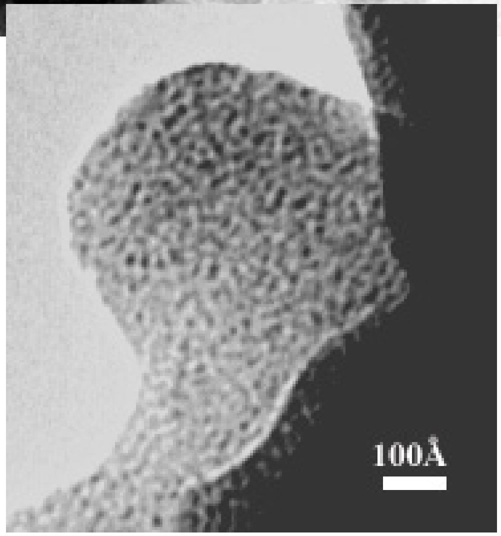


Yaghi et al
Ozin et al

Mesostructured Wormholes ~35 Å







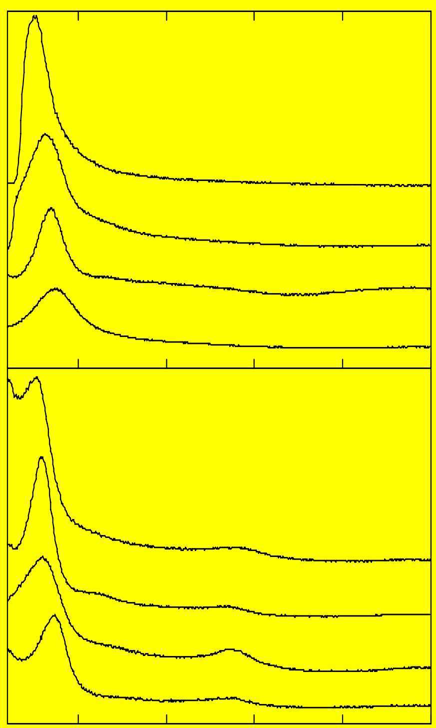
Kanatzidis et al *Advanced Mater*. 2000, 12, 85-91

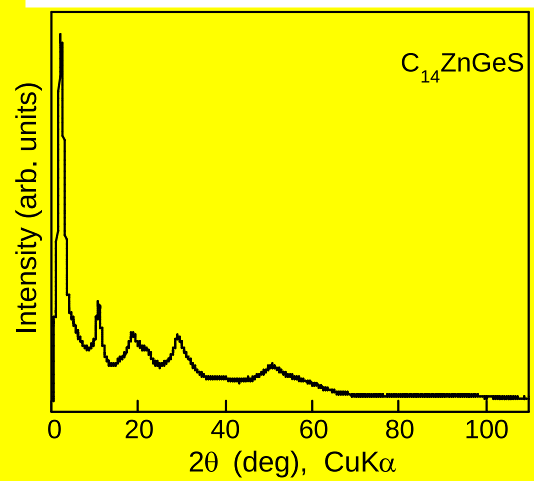
$(R\text{-}NMe_3)_2M(Ge_4Q_{10})$ Q= S, Se

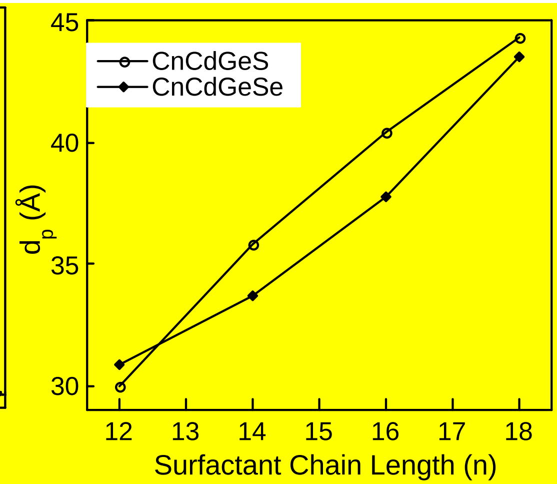
Non-periodic inorganic framework

Diffuse scattering

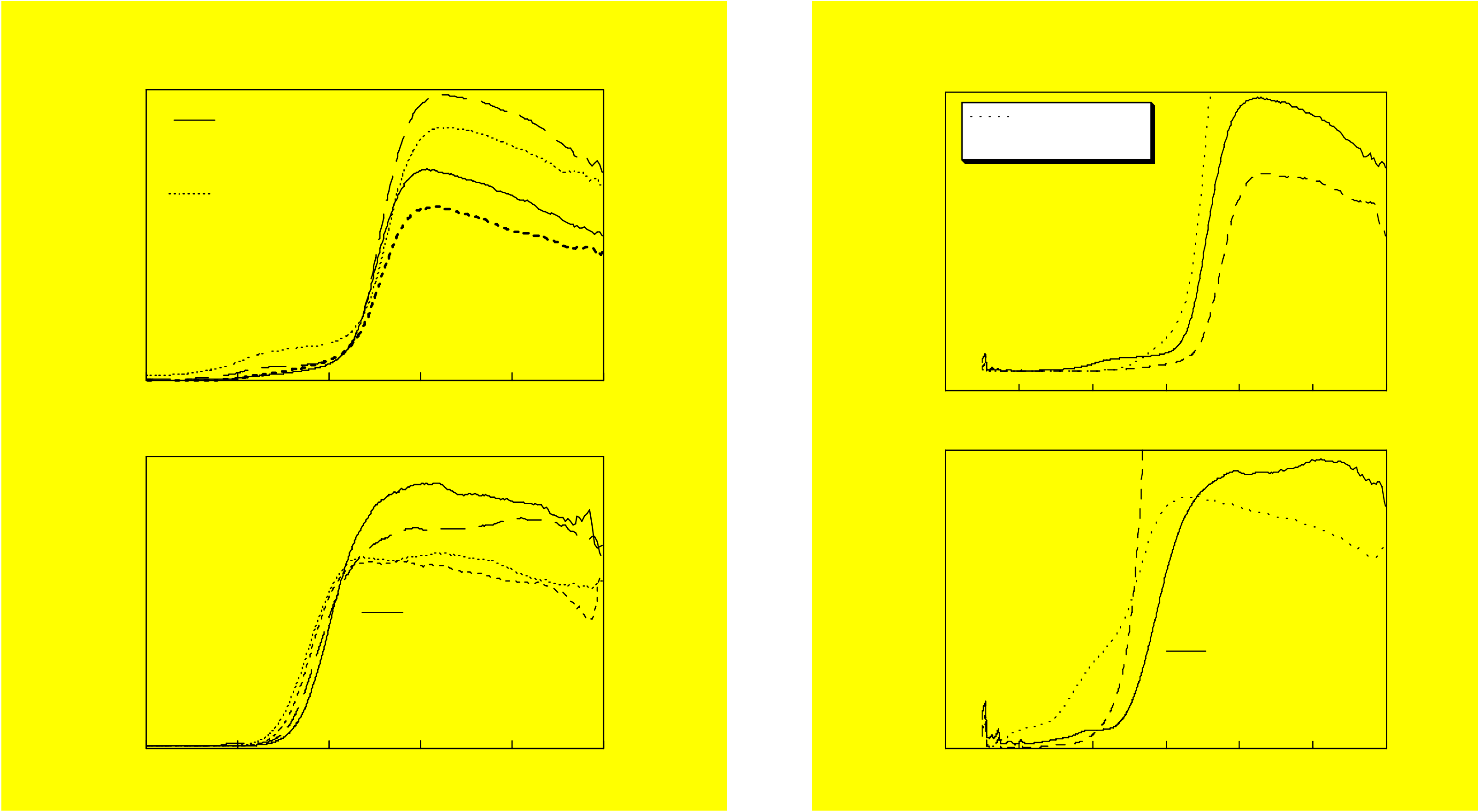
Adjustable pore size



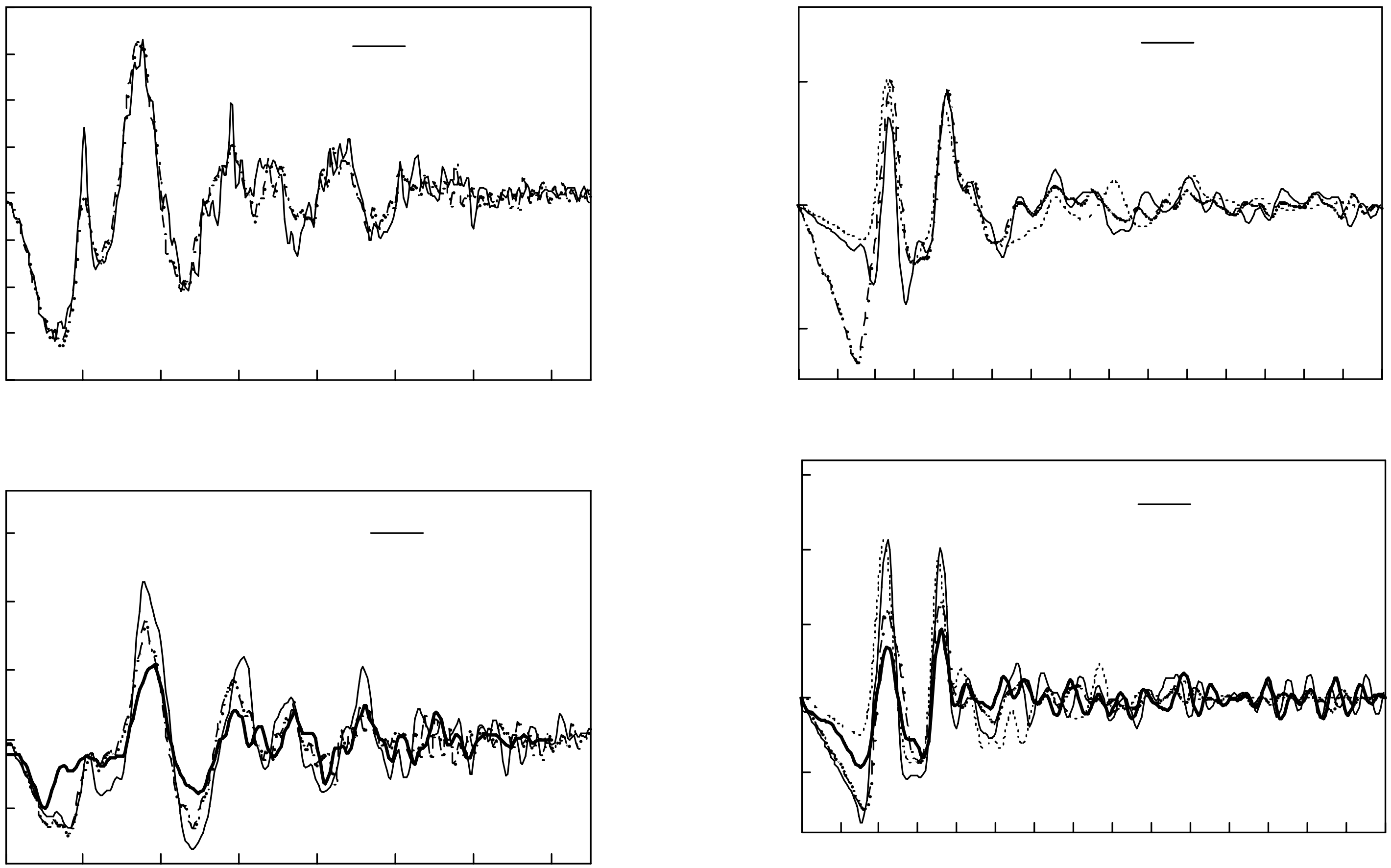




Optical Properties



Diffuse scattering and Pair Distribution Functions (with S. J. L. Billinge, M. F. Thorpe)



Influence of solvent

- In water: *$(R\text{-}NMe_3)_2MGe_4Q_{10}$*
  - Disordered wormhole
- In formamide: *$(R\text{-}NME_3)_{2\text{-}x}M_{1+x}Ge_4Q_{10+\delta}$*
  - Ordered hexagonal, cubic

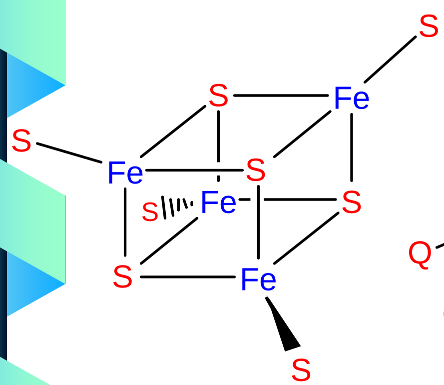
$$[Ge_4Q_{10}]^{4-} \rightleftharpoons [Ge_4Q_{10-x}]^{z-} + xQ^{2-}$$

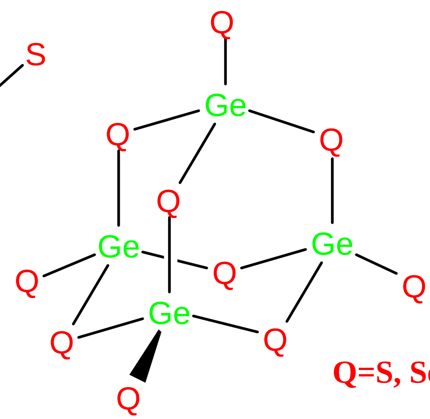
$$2[SnSe_4]^{4-} \rightleftharpoons [Sn_2Se_6]^{4-} + 2Se^{2-}$$

Biologically inspired nanocomposites (Fe_4S_4 ferredoxinoids)

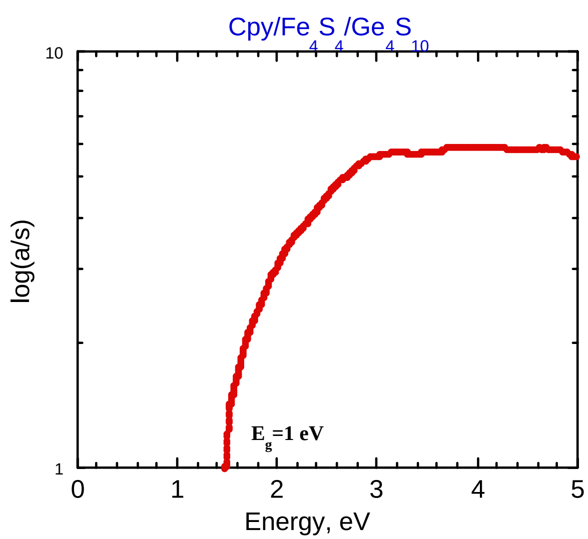
Fe4S4-MSU-1 and Fe4S4-M SU-2

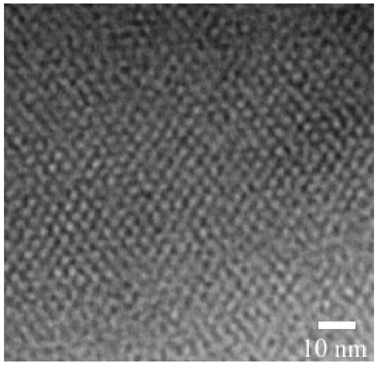
Angew Chemie 2000, 39, 4558

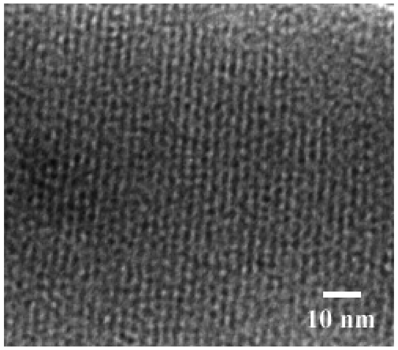


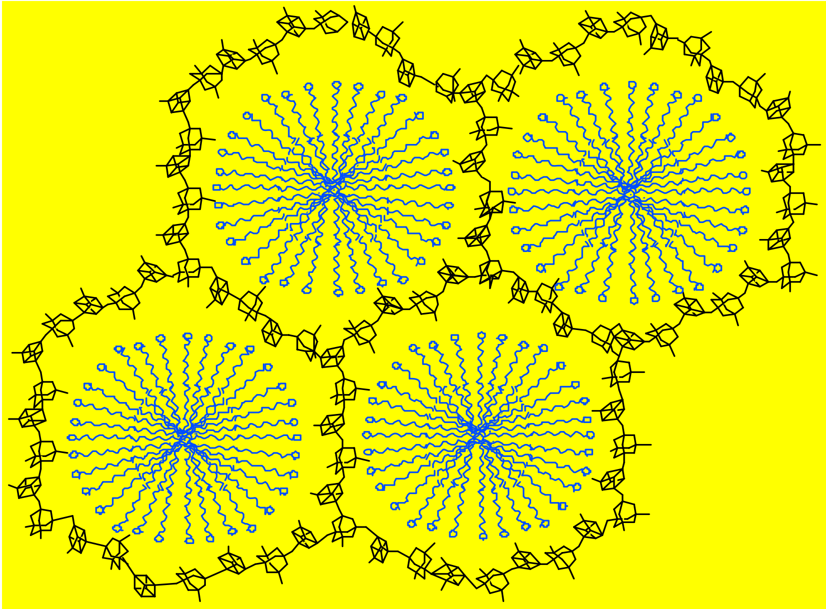


Q=S, Se



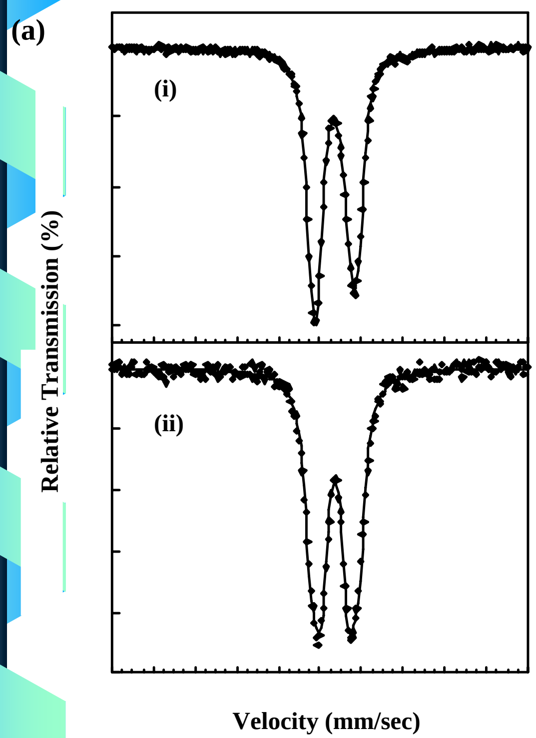




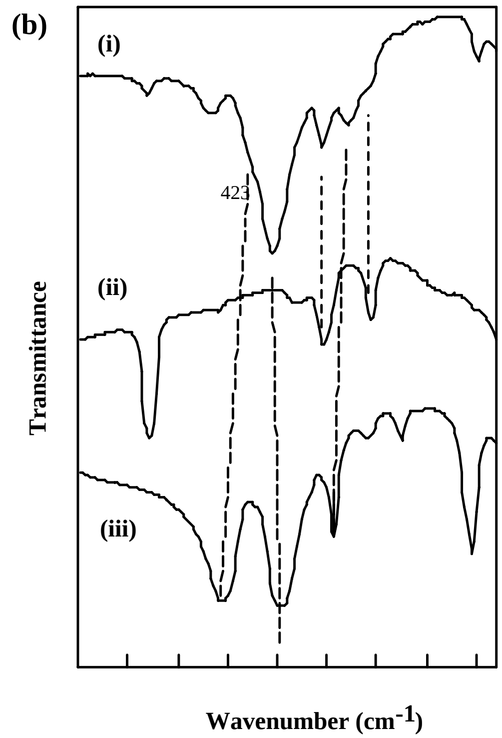


Characterization of Fe4S4-MSU-1 and Fe4S4-MSU-2

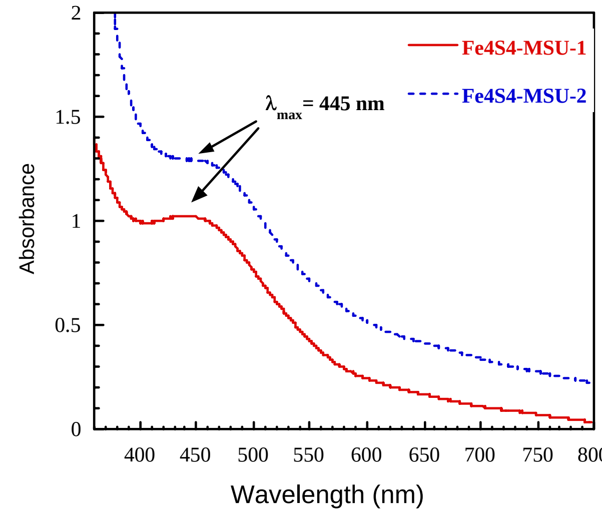
Fe Mössbauer



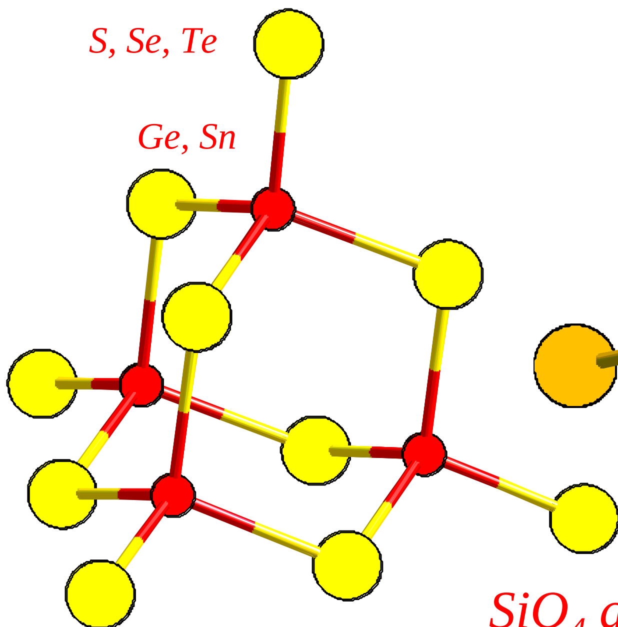
Infrared spectroscopy

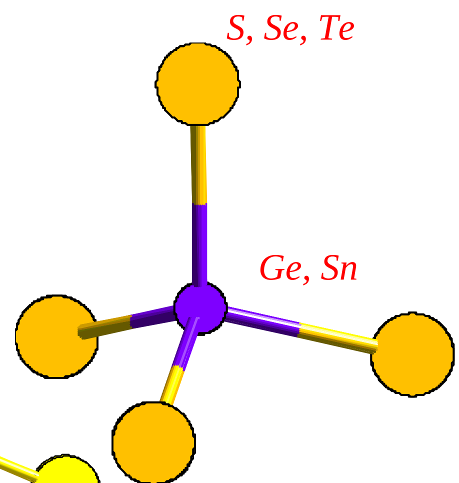


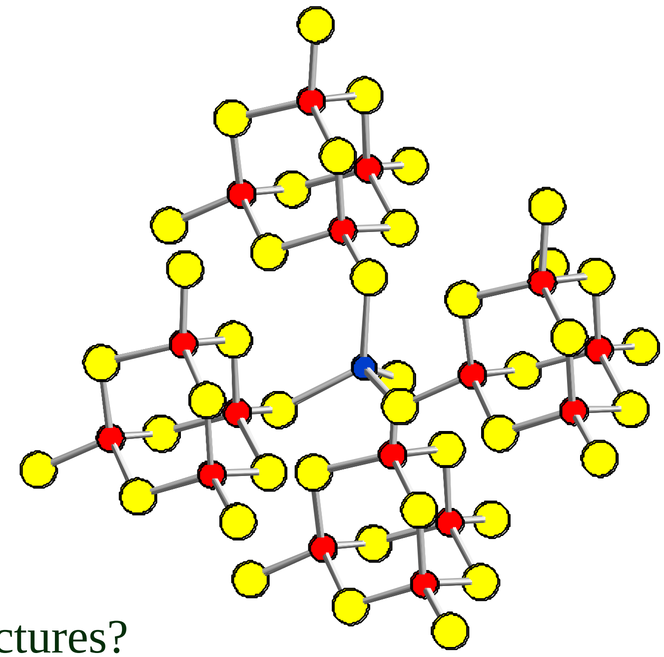
Fe_4S_4 cluster extraction UV/vis spectra



Mesostructured Non-Oxidic Solids Based on the Tetrahedral Clusters and Metal Ions







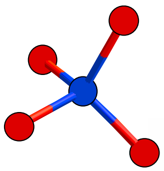
SiO_4 analogs

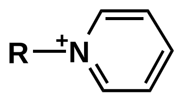
topologically similar structures?

1. M. Wachhold, K.K. Rangan, S.J.L. Billinge, V. Petkov, J. Heising, M.G. Kanatzidis, *Adv. Mater.* **2000,** 12(2) 85-91.
2. K. K. Rangan, S. J. L. Billinge, V. Petkov, J. Heising, M. G. Kanatzidis, *Chem. Mater.* **1999**, 10, 2629.
3. M.J. MacLachlan, N. Coombs, G.A. Ozin, *Nature* **1999**, 397, 681**.**

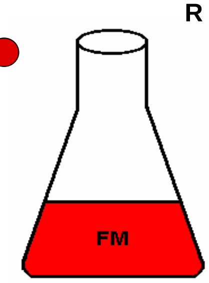
Synthesis

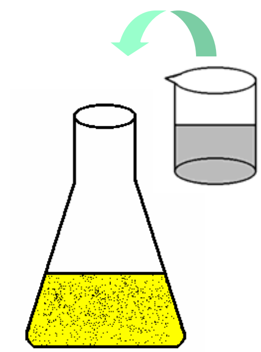
Mesostructured Chalcogenide Phases





R : $CH_3-(CH_2)_{15}-$





Supramolecular organization

Formamide : 20 ml

Surfactant : 10 mmol

K_4SnSe_4 : 1 mmol

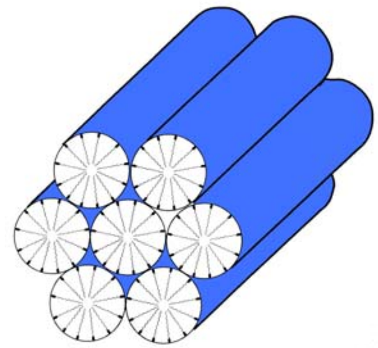
Temperature : 75 °C

Slow addition of M^{2+}/FM solution

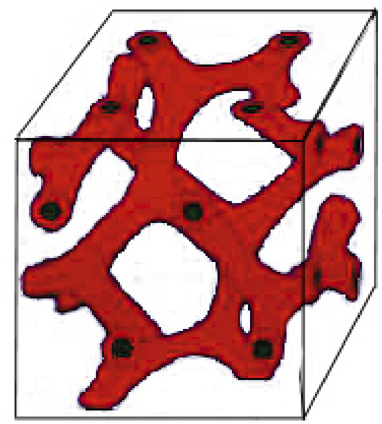
M^{2+} : Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}

Immediate precipitation

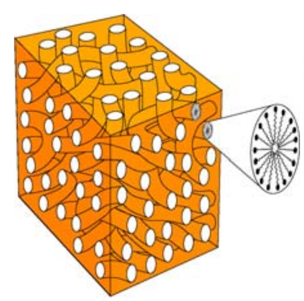
aging for 24h



hexagonal



cubic

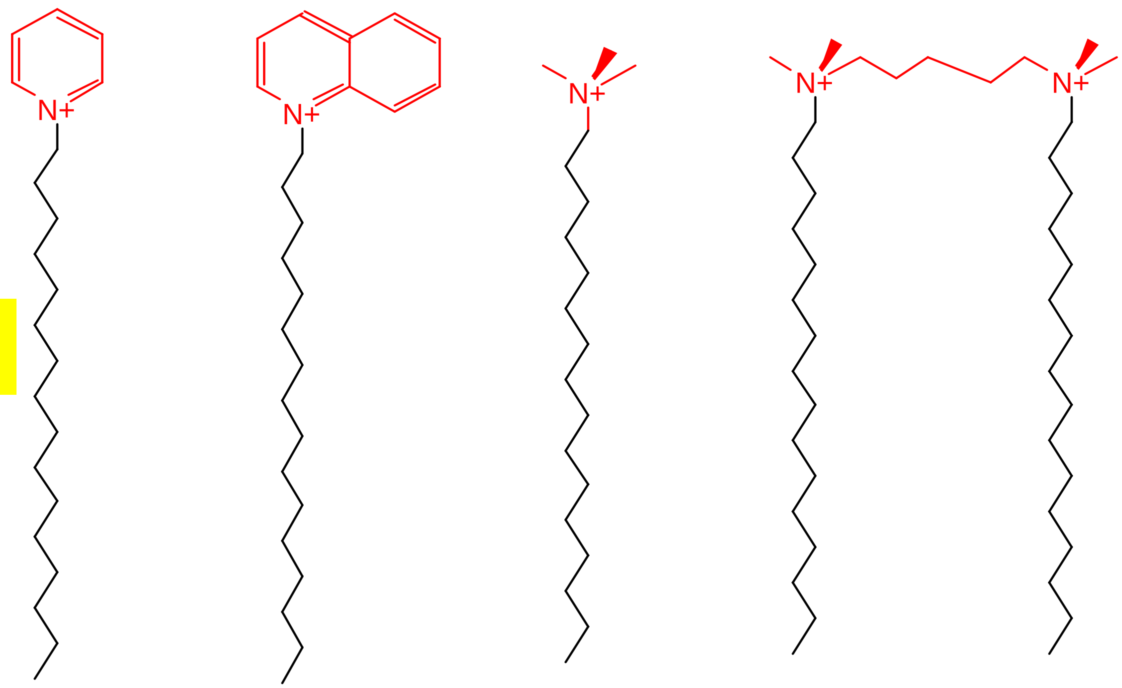


wormhole

Surfactants set the stage for inorganic framework assembly

Examples

$R=C_nH_{2n+1}$

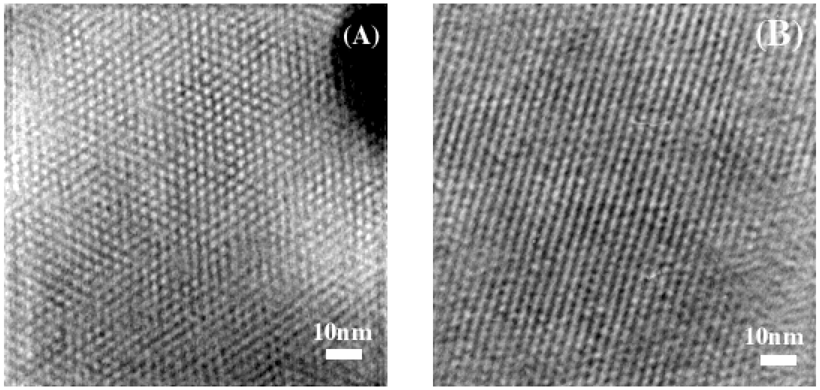


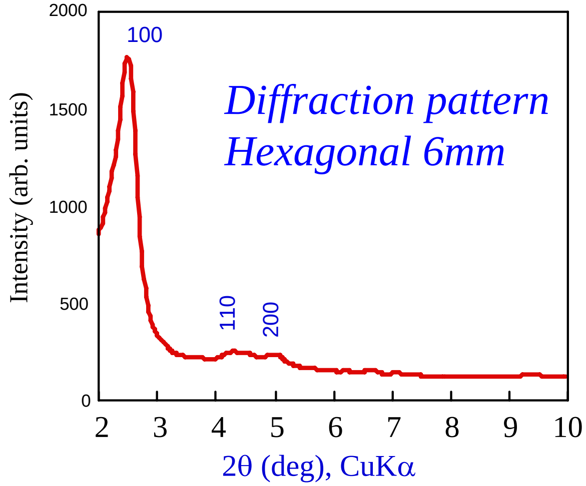
R-pyridinium *R-quinolinium* *R-TMA-* *Gemini-$C_{n\text{-}s\text{-}n}$*

$CP/M/Ge_4S_{10}$ (CPMGeS) M=Ga, In

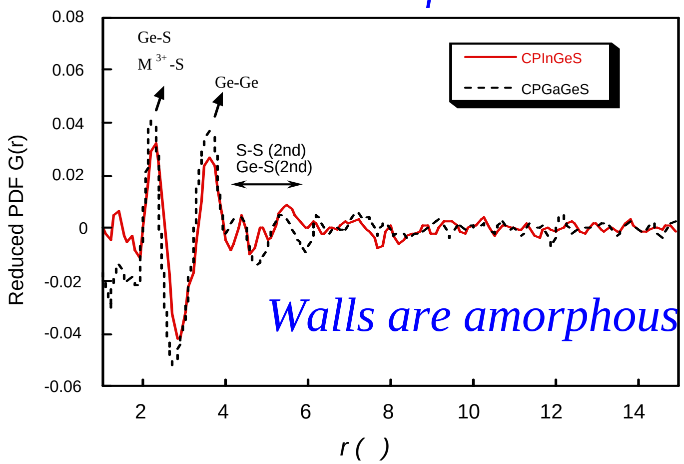
J. Am. Chem. Soc. 2000, *122*, 10230

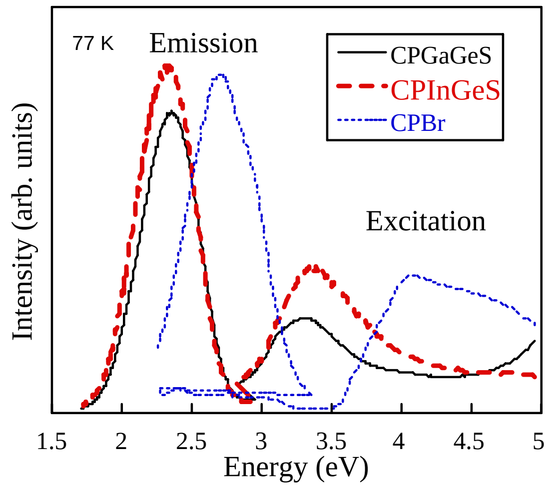
TEM images



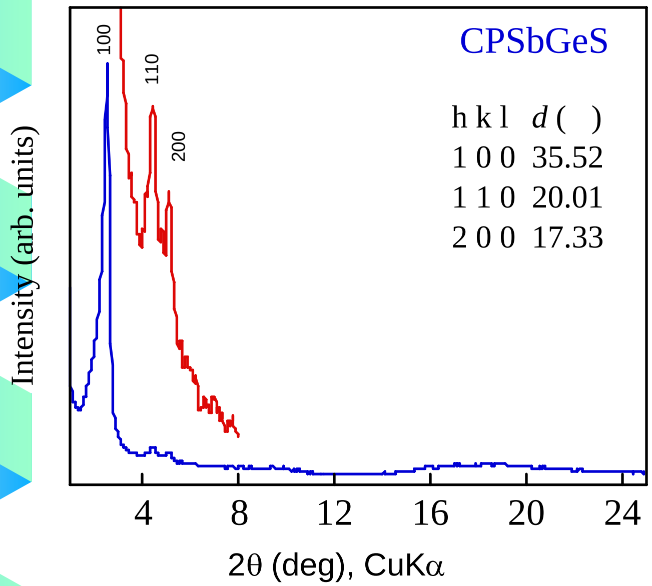


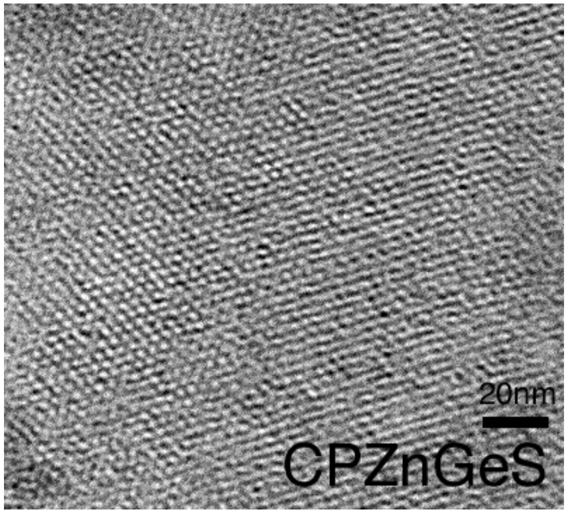
Radial distribution function

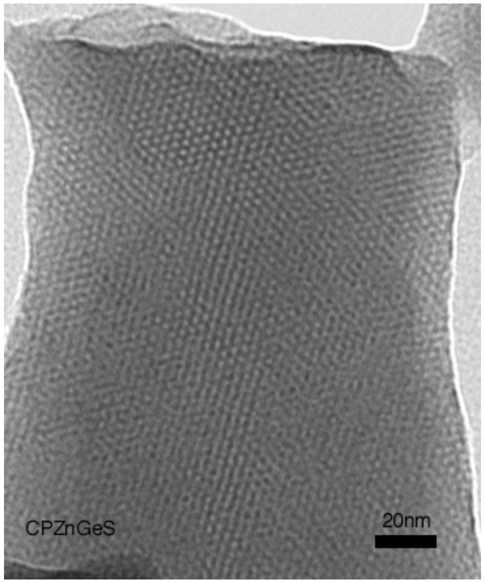




CPMGeS materials: CP/M/Ge_4S_{10}

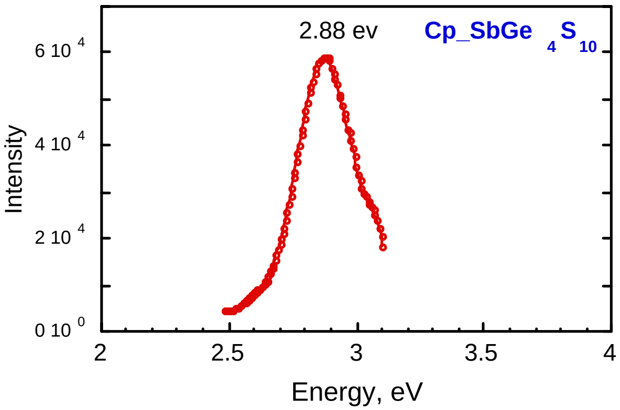




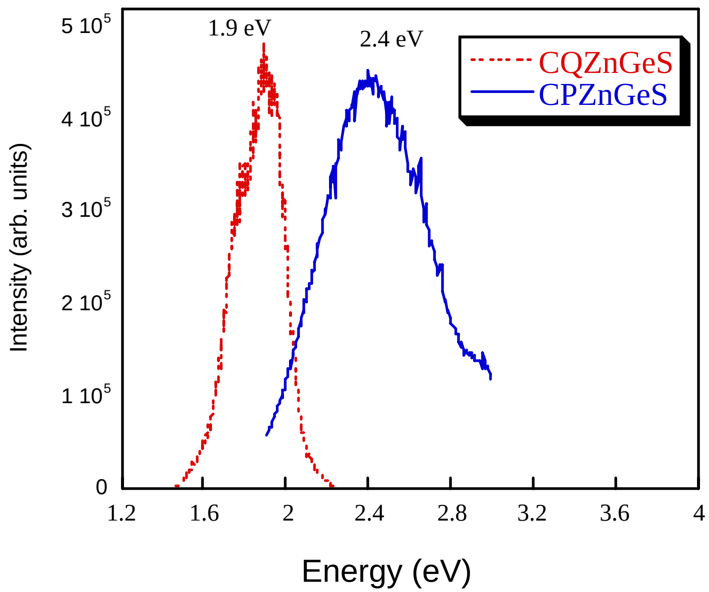


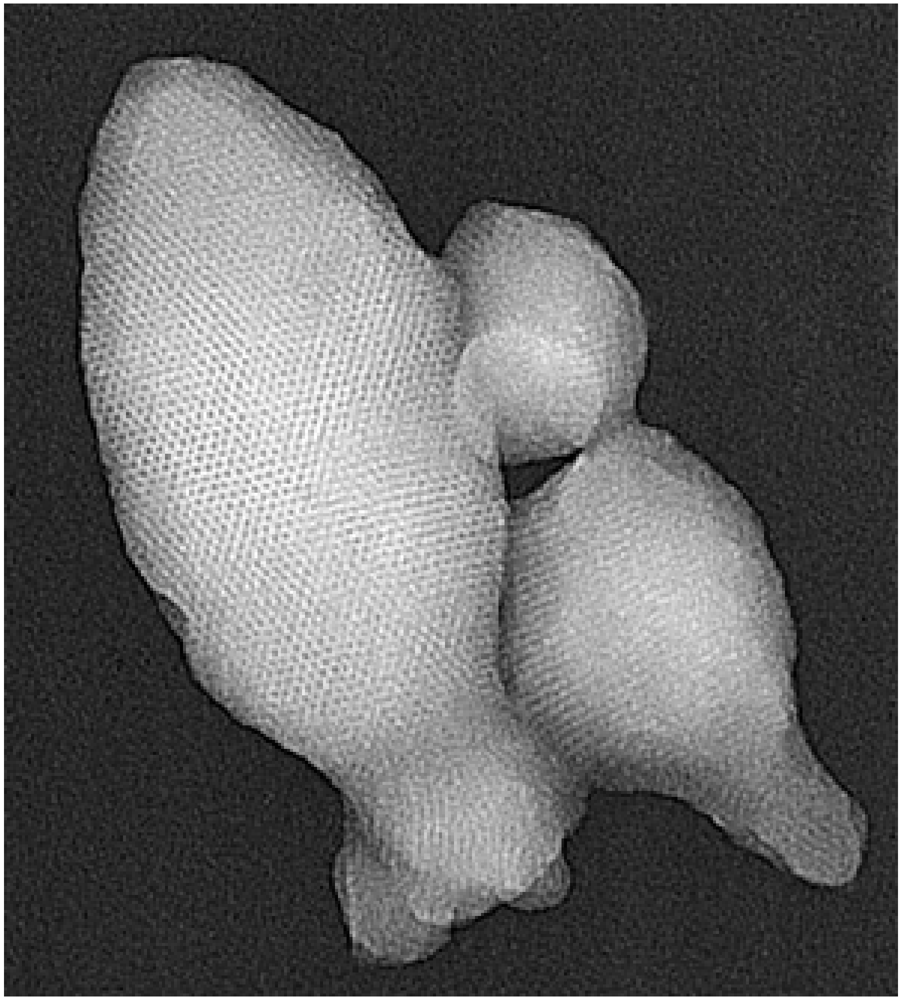
$(CP)_2M_{1+x}(Ge_4S_{10})S_x$

M=Zn, Cd, Hg, Sb, In, Ga



Hexagonal CPZnGeS



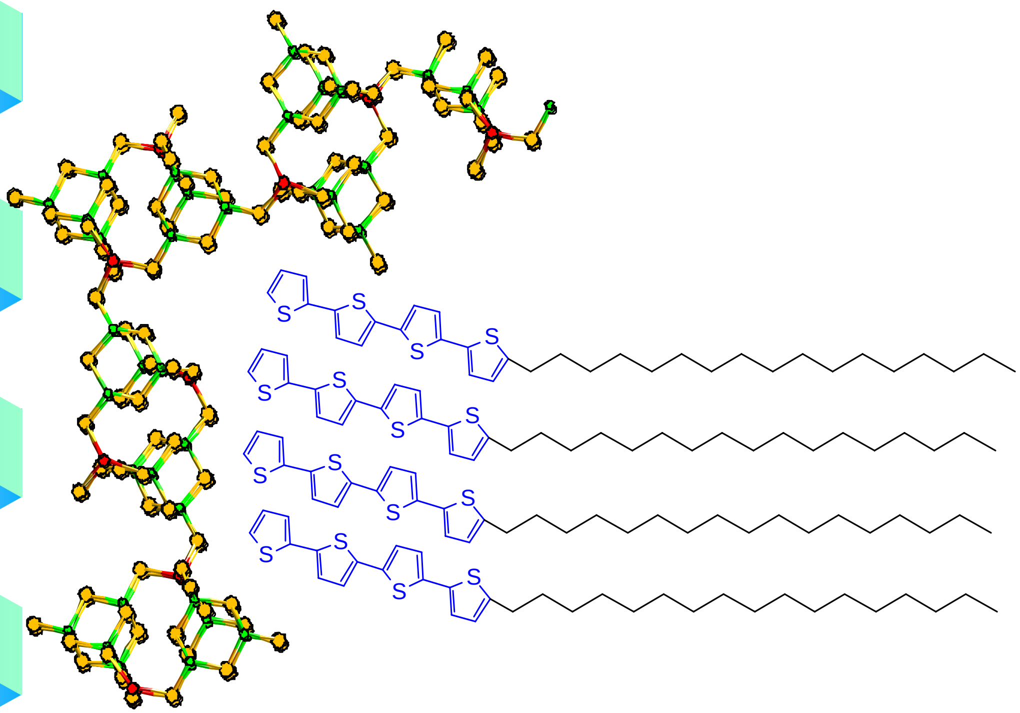


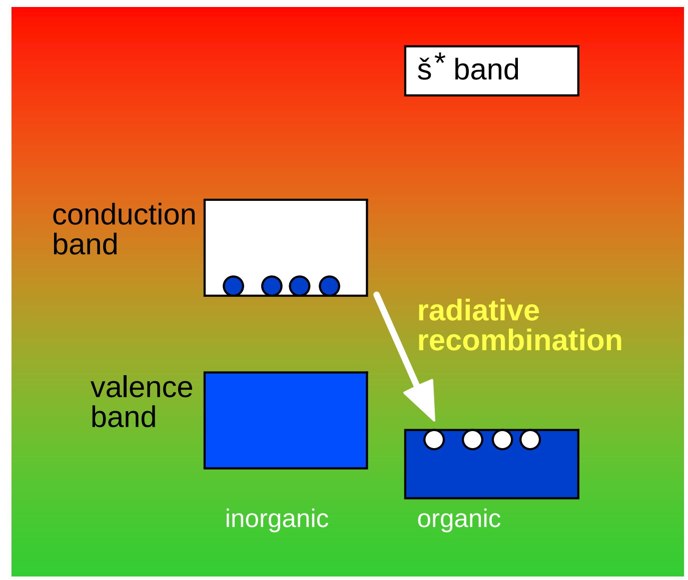
$(CP)_2Zn_2(Ge_4S_{10})S$

Thermally stable up to 220 ^oC

Perhaps we don't want to remove the surfactant!

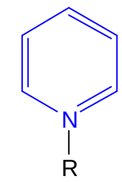
- Add functionality to the surfactant
  - Electronically active head groups or tails

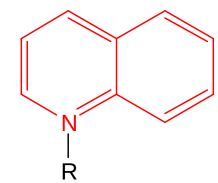


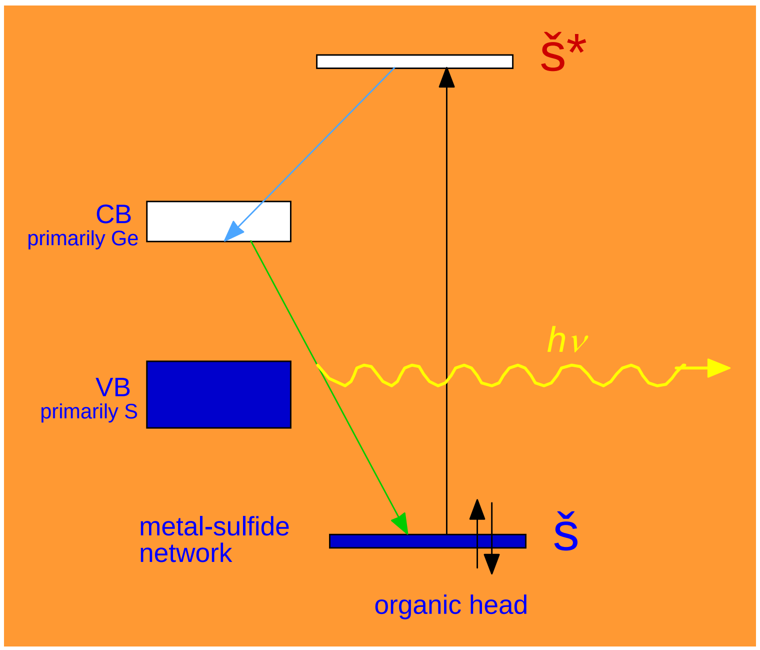


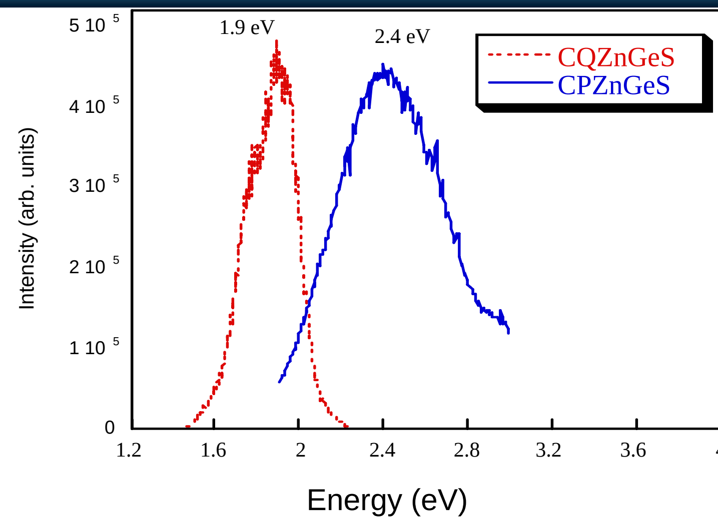
electroluminescence

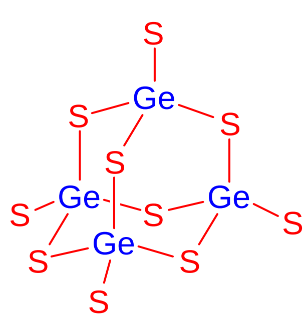
Photoluminescence

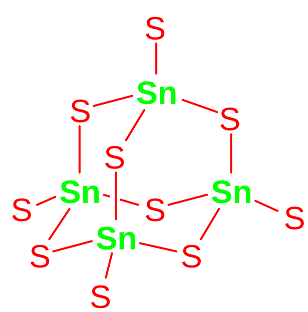


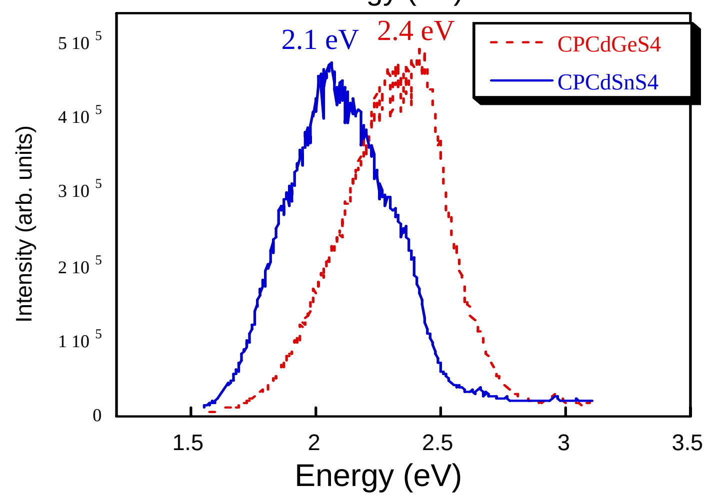










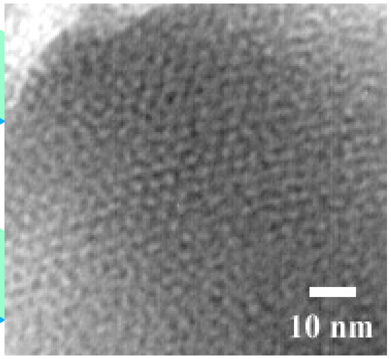


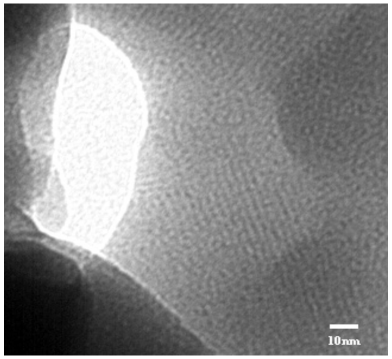
Chemical Formula : $(CP)_{4-2x}M_xSnSe_4$ (1.0<x<1.3)

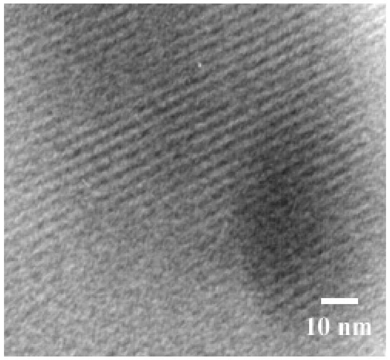
Sample	$Sn:Se_4$	$M:Se_4$	% C, H, N	$M:Se_4$ Calc.	Color
Mn	1.01	0.90	44.71, 7.10, 2.25	1.03	Orange
Fe	0.91	1.22	38.40, 6.23, 2.05	1.28	Dark-brown
Co	0.98	0.94	48.35, 6.64, 2.36	1.19	Dark-brown
Zn (cubic)	0.99	0.86	40.28, 6.17, 2.18	1.20	Yellow-orange
Zn (Hex)	0.96	0.85	41.58, 6.44,2.29	1.15	Yellow
Cd	0.92	1.23	36.90, 6.01, 2.28	1.23	Yellow
Hg	1.03	1.09	34.65, 5.52, 1.92	1.20	Dark orange

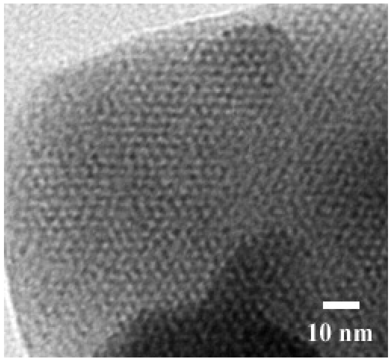
Transmission Electron Microscopy

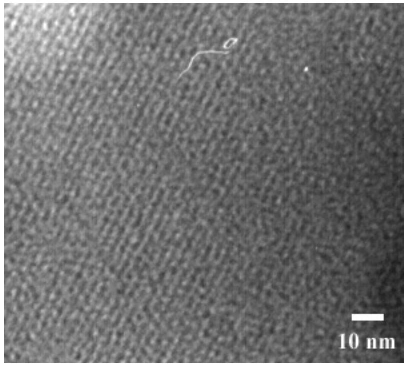
Surf / Zn^{2+} / $SnSe_4$







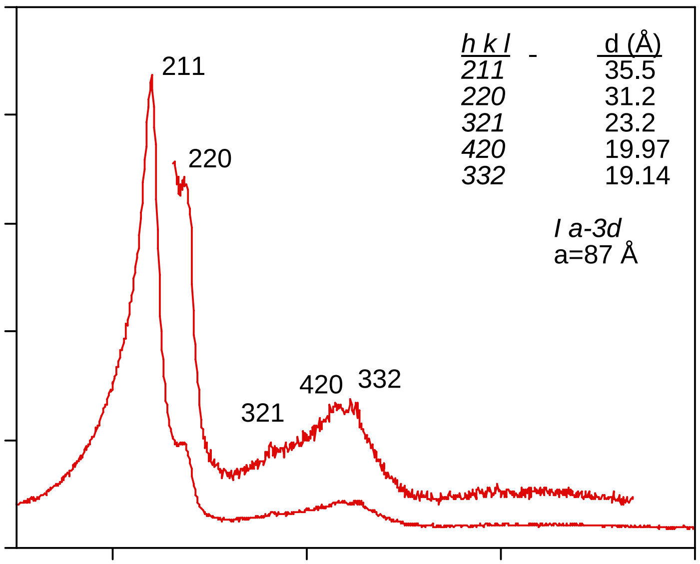


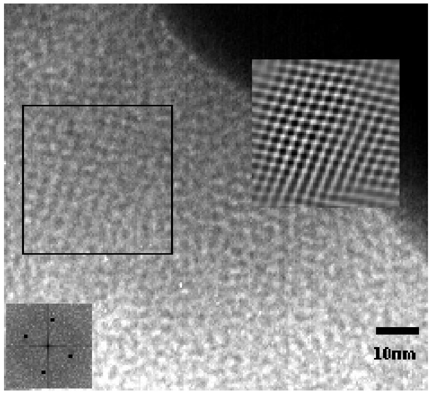


Surf / Hg^{2+} / $SnSe_4$

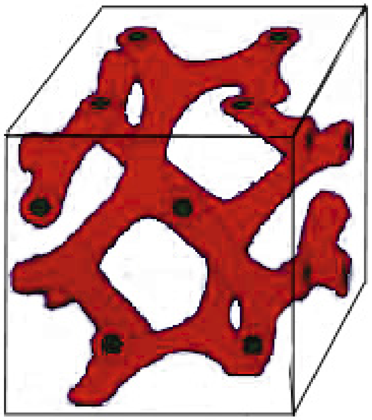
Cubic mesoporous chalcogenide $CPZnSnSe_4$

X-ray diffraction pattern



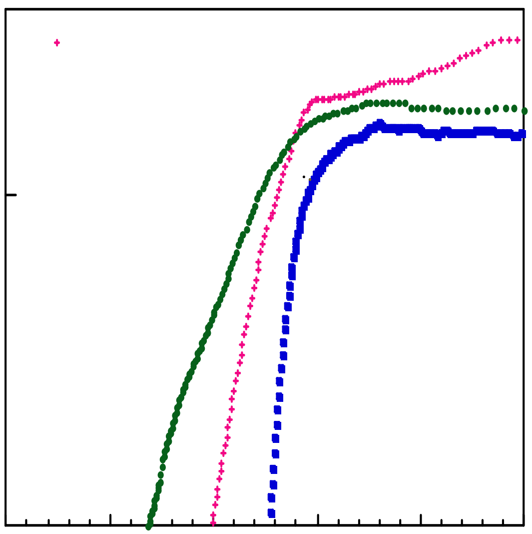


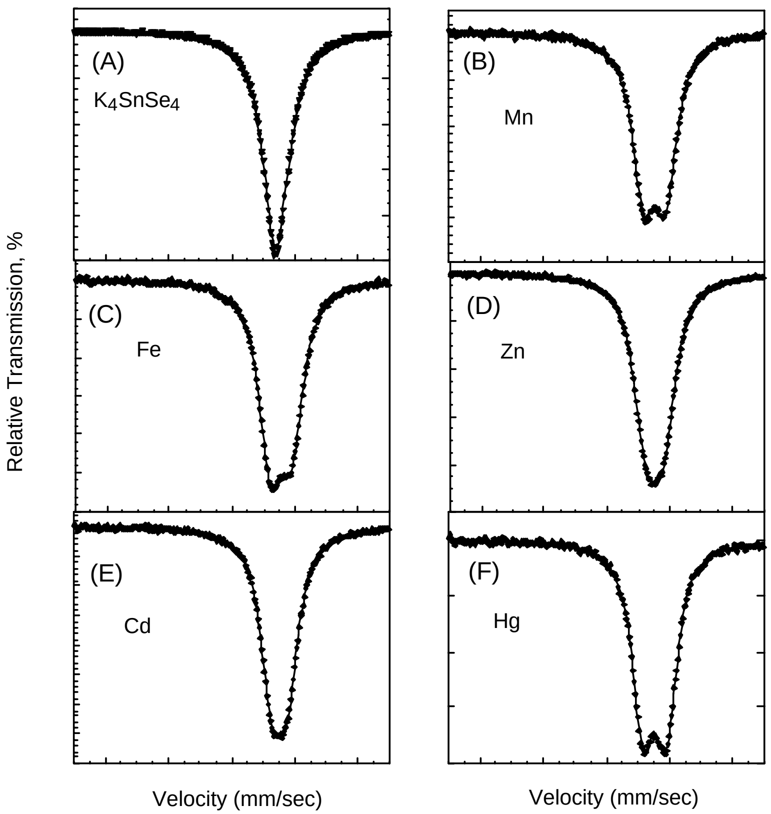
Ia-3d



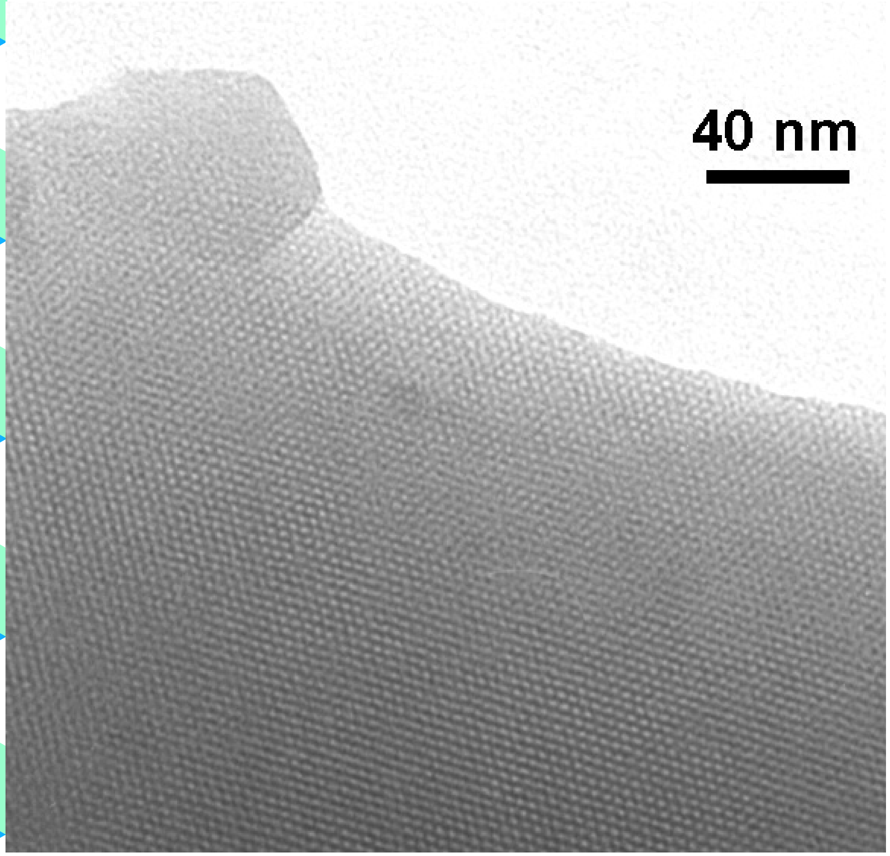
P. N. Trikalitis, K. K. Rangan, T. Bakas and M. G. Kanatzidis, *Nature* 2001, 410, 671-675.

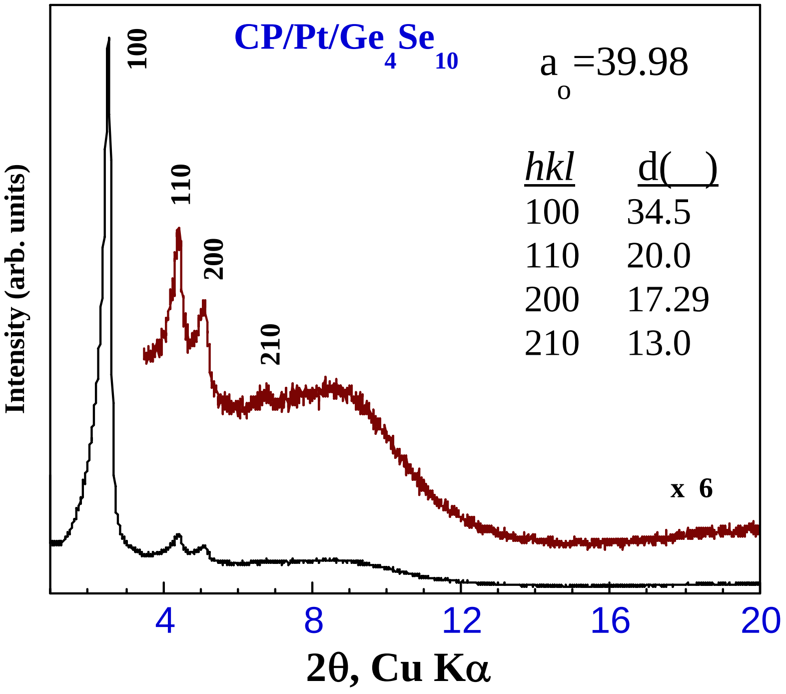
Band-gaps and Sn Mössbauer Spectroscopy



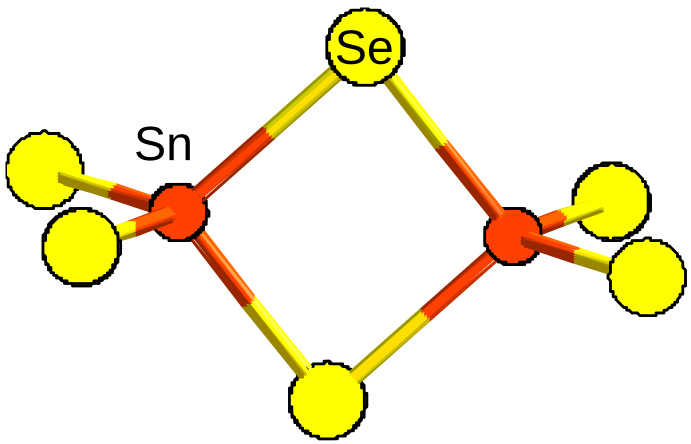


Highly ordered CP-$PtGe_4Se_{10}$

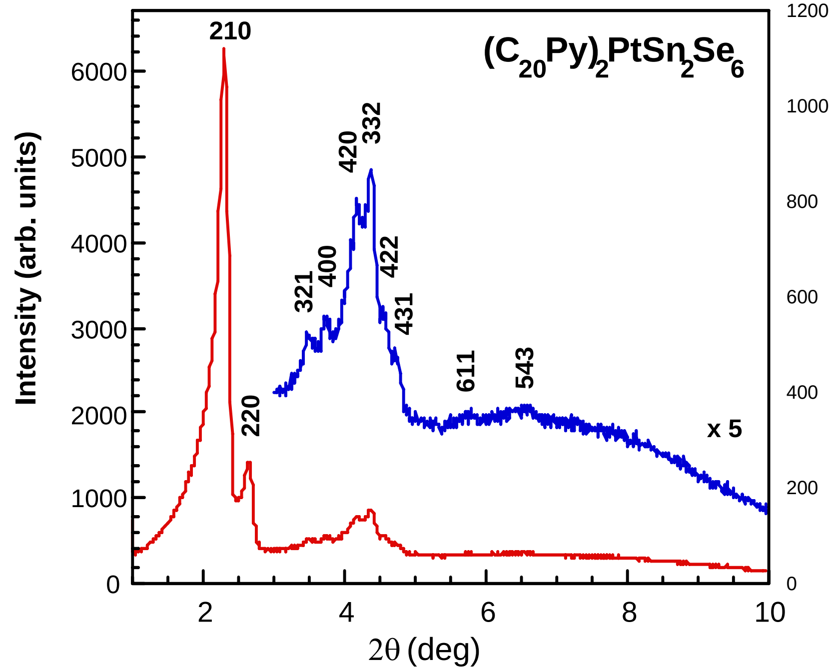




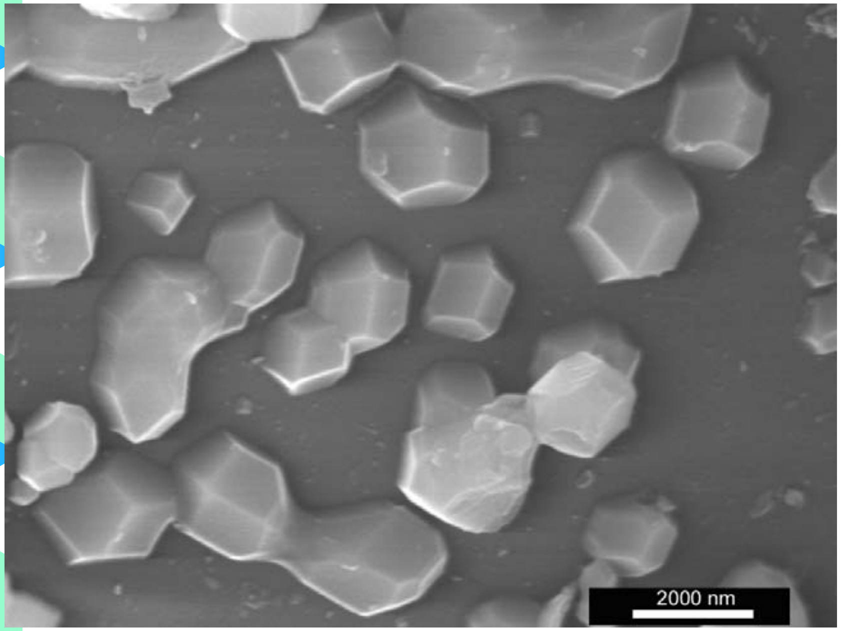
The system Pt^{2+} / $[Sn_2Se_6]^{4-}$

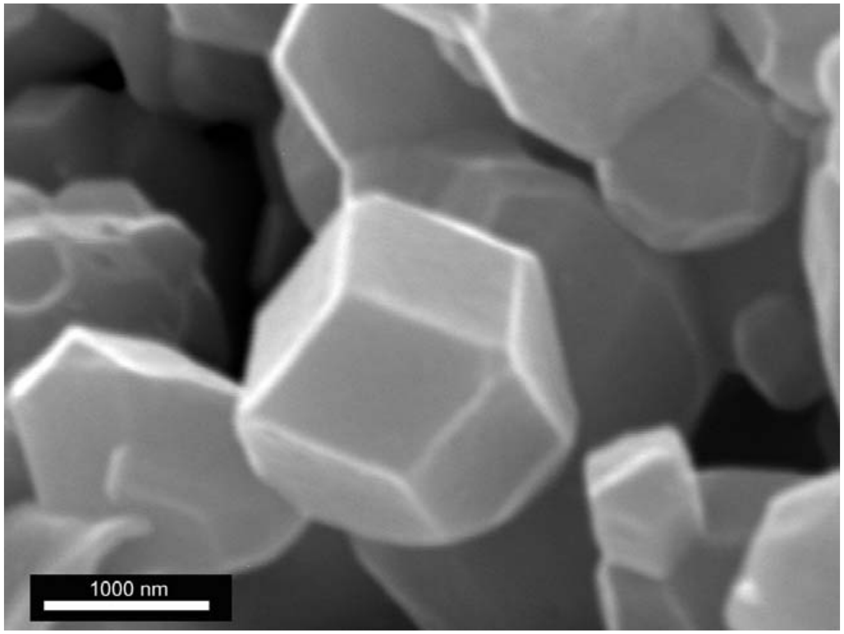


$[PtCl_4]^{2-}$ + $[Sn_2Se_6]^{4-}$

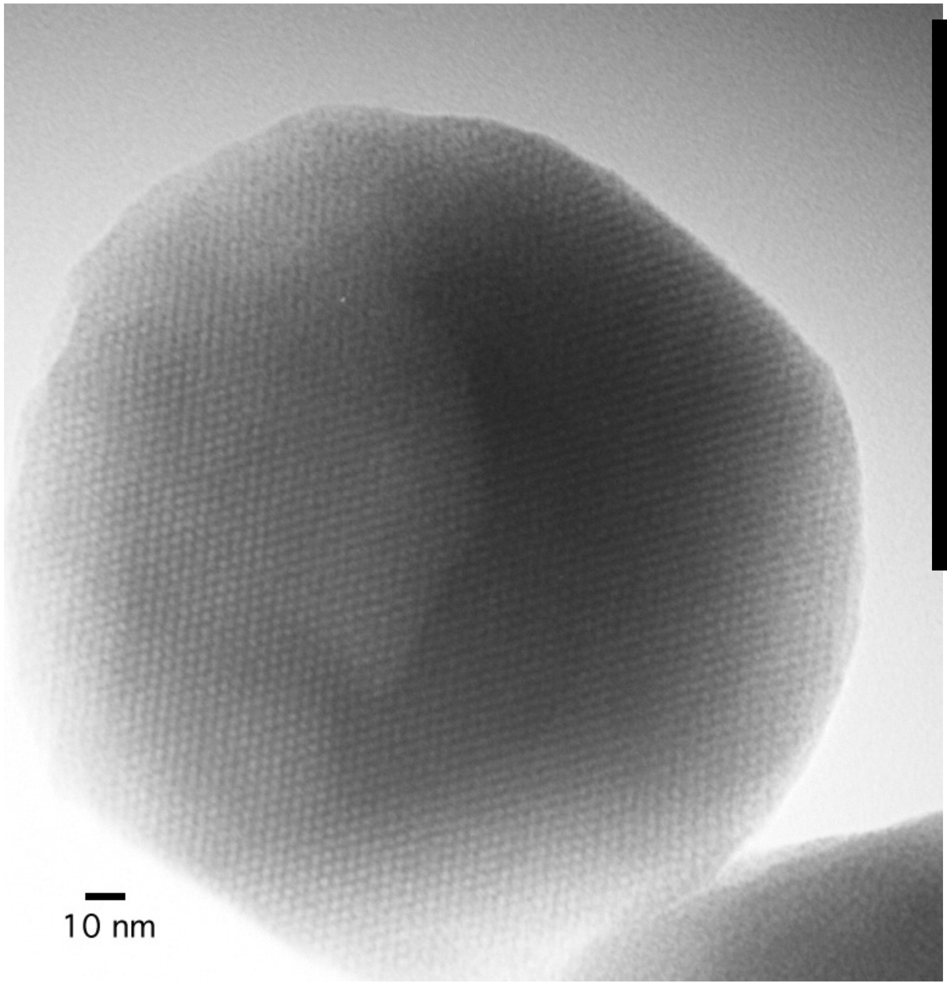


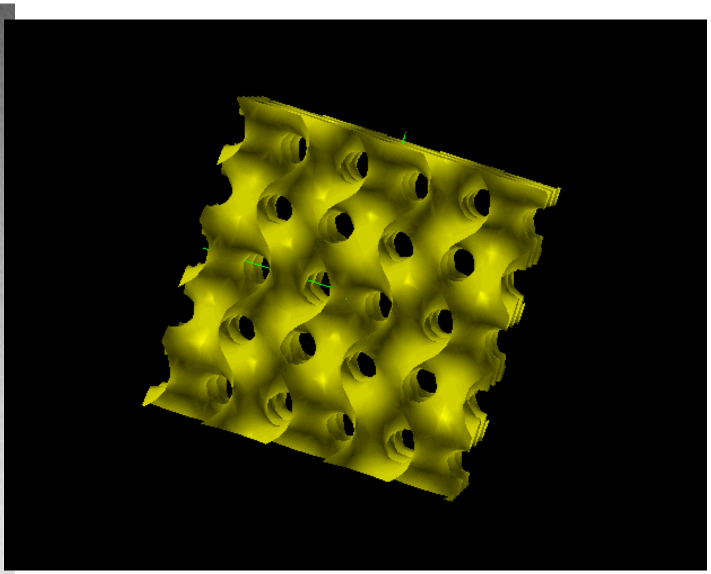
Single Crystals!...?





TEM of a Cubosome: [110] direction





Unit cell edge: 95Å
V=857,375 $Å^3$
Density 1.8 g/cm3
~34000 atoms per cell

Conclusions

- Lamellar nanocomposites with electrically conductive and conventional polymers are large class of novel materials
- Conductive polymers can be encapsulated in porous solids directly by *in situ* intercalative redox polymerization
- Exfoliated solids are superior for the synthesis of polymer nanocomposites via encapsulative precipitation
- The physical properties of lamellar nanocomposites are affected by the intercalated polymers.

Conclusions

- It is possible to construct organically templated structures with heavier SiO_4-analogs to produce semiconducting solids with well-defined mesopores.
- The surfactant templated supramolecular assembly of the $[SnSe_4]^{4-}$ and $[Ge_4Q_{10}]^{4-}$ anions with transition metals leads to mesostructured materials of the general formulae *CPMGeQ* and $(CP)_{4-2x}M_xSnSe_4$ (M=Mn, Fe, Co, Zn, Cd, Hg).
- The *c*-$(CP)_{4-2x}Zn_xSnSe_4$ represents the first example of cubic, non-oxidic mesophase.
- Non-oxidic solids promise to produce functional mesostructured materials with novel electronic and photonic properties.
- Further work involving other chalcogenide building blocks e.g. $[GeSe_4]^{4-}$, $[GeTe_4]^{4-}$, $[SnTe_4]^{4-}$ and other metals ions e.g. Ag^+, Pb^{2+}, Bi^{3+}, Sb^{3+} is needed.

Students/Research Associates

- Dr. Pantelis Trikalitis
- Dr. Kasthuri K Rangan
- Chung-Guey Wu
- Yu-Ju Liu

- **Dr. Carl R. Kannewurf (NWU)**
- Prof. Thomas Bakas, Ioannina, Greece (Mössbauer)
- Prof. V Papaefthymiou, Ioannina, Greece (Mössbauer)

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