New Routes to Nanoparticles

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ICONSAT New Delhi 16th March 2006

How To Make a Nano-Material

- **Use a clever precursor**
- Use a Physical Separation
- In Water!

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New Ways to Tellurides……..

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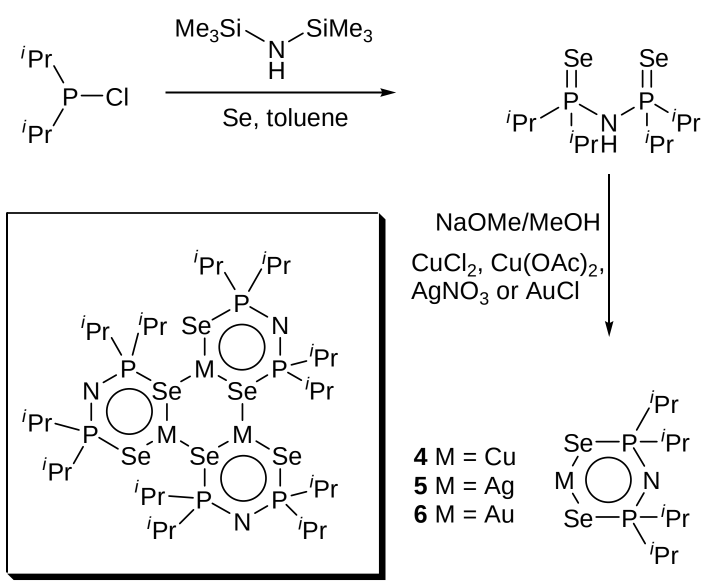
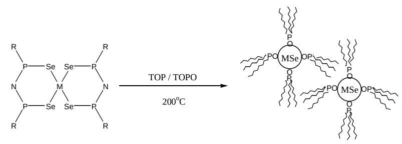


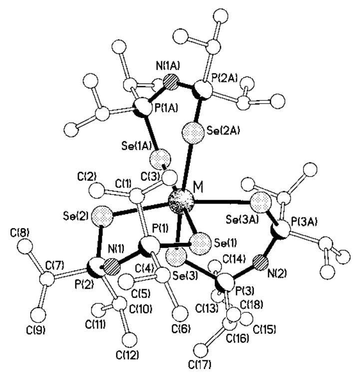
Imino-*bis*(diisopropylphosphine chalcogenide)

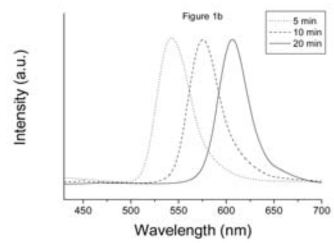
Dalton Transactions 2003, 1500-1504 J. Mater. Chem., 2004, 14, 233-237

- Efficient synthesis of *"air-stable"* M $[N(SePR_2)_2]_2$ (yields 95-99%).
- Reaction can be scaled up (~25g) without loss to quality/yield.
- *"Dot"* synthesis is convenient and efficient.



where R = ^{i}Pr or Ph and M = Cd, Zn or Hg

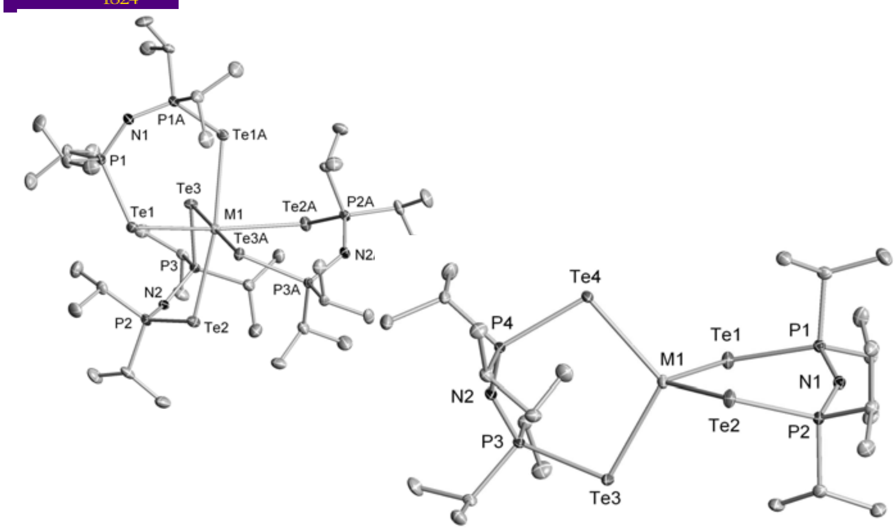




PL of CdSe by Thermolysis of $Cd[N(SeP^{i}Pr_2)_2]_2$

D.J.Crouch, P. O'Brien, M.A.Malik, P.J.Skabara and S.P. Wright, Chem. Commm., 2003 1454.

Combining the strengths of UMIST and The Victoria University of Manchester



T. Chivers, DJ. Eisler, JS Ritch, Dalton Trans. 2005, 2675.

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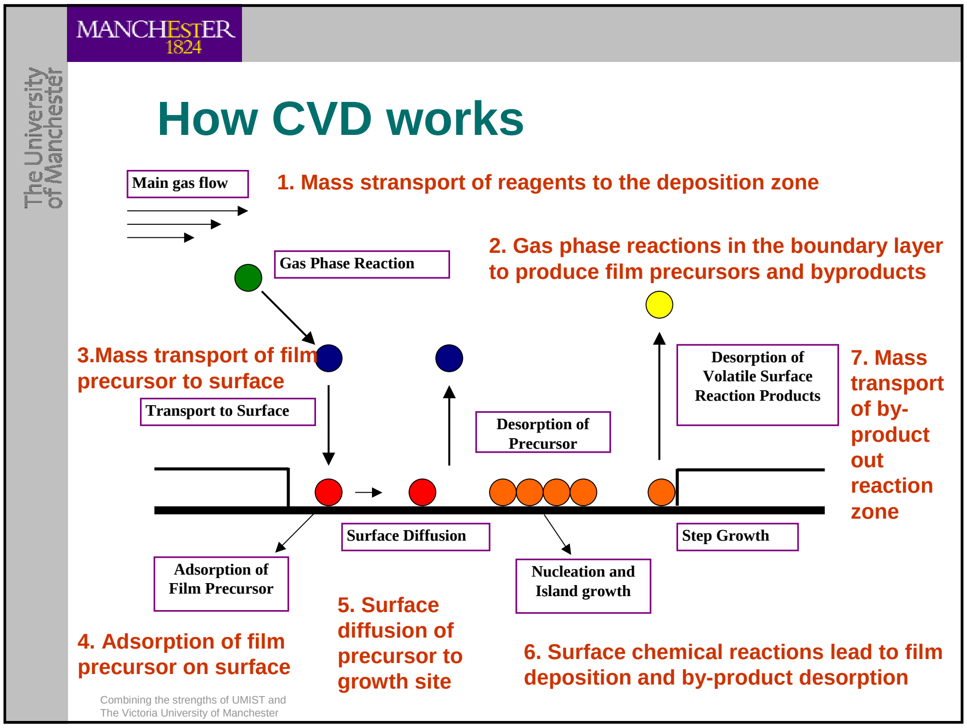
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How CVD works
Main gas flow
1. Mass stransport of reagents to the deposition zone
Gas Phase Reaction
2. Gas phase reactions in the boundary layer to produce film precursors and byproducts
3.Mass transport of film precursor to surface
Transport to Surface
Desorption of Precursor
Desorption of Volatile Surface Reaction Products
7. Mass transport of by-product out reaction zone
Surface Diffusion
Step Growth
Adsorption of Film Precursor
Nucleation and Island growth
4. Adsorption of film precursor on surface
5. Surface diffusion of precursor to growth site
6. Surface chemical reactions lead to film deposition and by-product desorption
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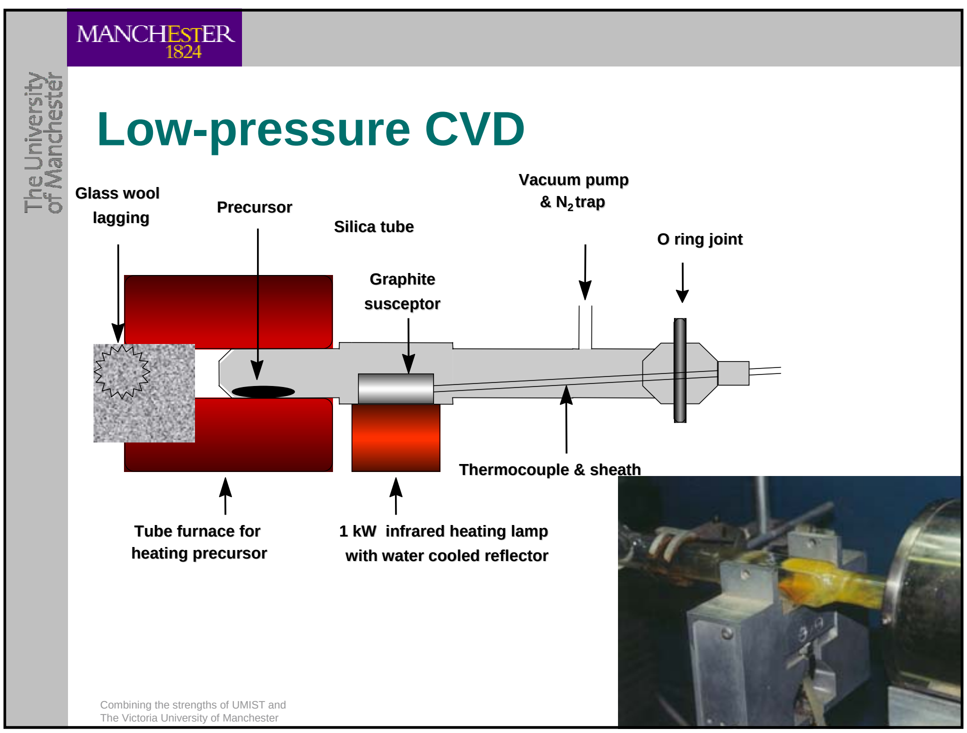
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Low-pressure CVD
Glass wool lagging
Precursor
Silica tube
Vacuum pump & N_2 trap
O ring joint
Graphite susceptor
Thermocouple & sheath
Tube furnace for heating precursor
1 kW infrared heating lamp with water cooled reflector
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What makes for a good precursor?

- **Volatility**
- **Clean decomposition**
- **Stability under delivery conditions**
- **Compatibility with other precursors**
- **Freedom from adventitious impurities**

Conventional route

- **Highly toxic and/or oxygen or moisture sensitive gases *e.g*. H_2S, H_2Se, NH_3, PH_3, AsH_3, SiH_4 etc.**
- **Environment and safety conditions: particularly important for industrial processes.**

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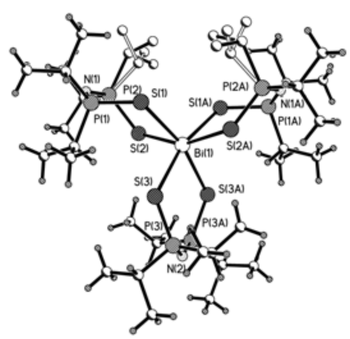

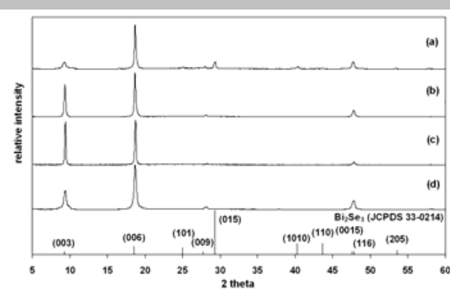

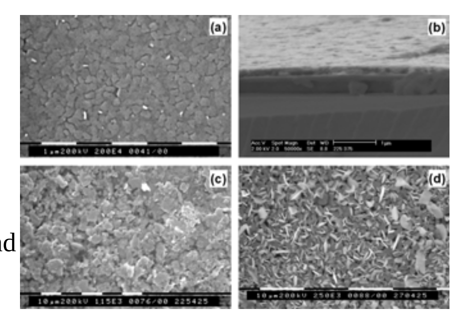

films grown by LP-MOCVD of $Bi[(SeP^{i}Pr_2)_2N]_3$ at

(a) T_{prec} = 275 °C, T_{subs} = 425 °C,
(b) T_{prec} = 225 °C, T_{subs} = 425 °C,
(c) T_{prec} = 225 °C, T_{subs} = 400 °C and
(d) T_{prec} = 225 °C, T_{subs} = 375 °C.

Dalton Transactions 2003, 1500-1504

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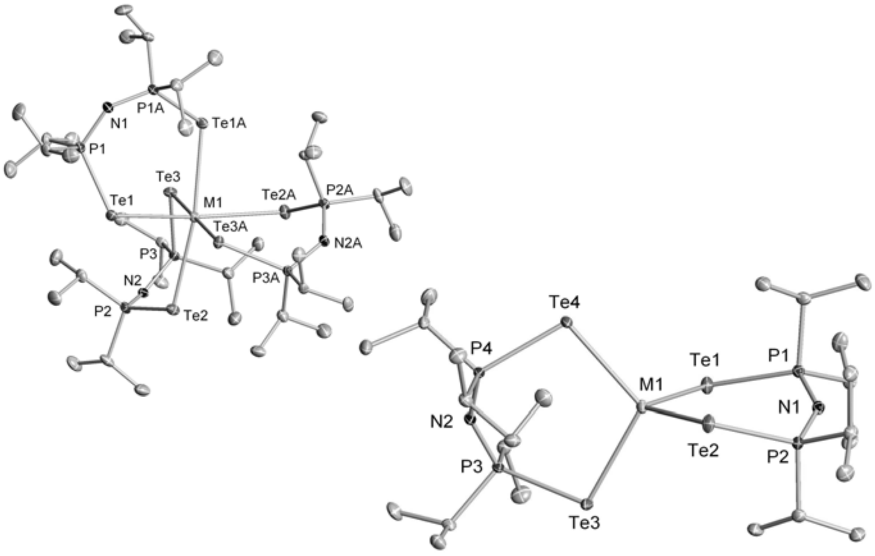

T. Chivers, DJ. Eisler, JS Ritch, Dalton Trans. 2005, 2675.

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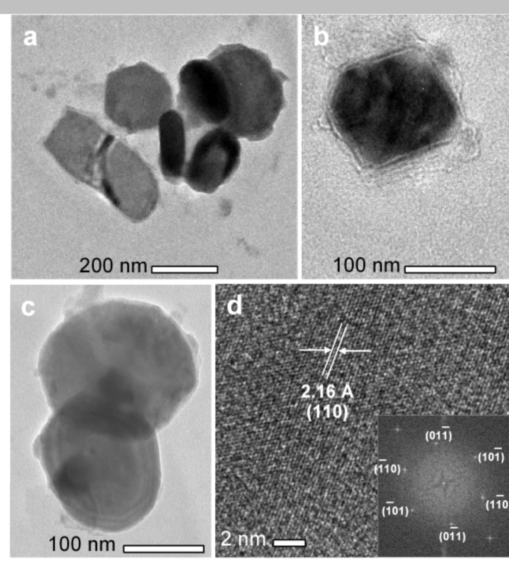
TEM Pictures of Sb_2Te_3



HRTEM and FFT (inset) of the films grown at 475 ºC

J. Amer. Chem.Soc. In press 2006.

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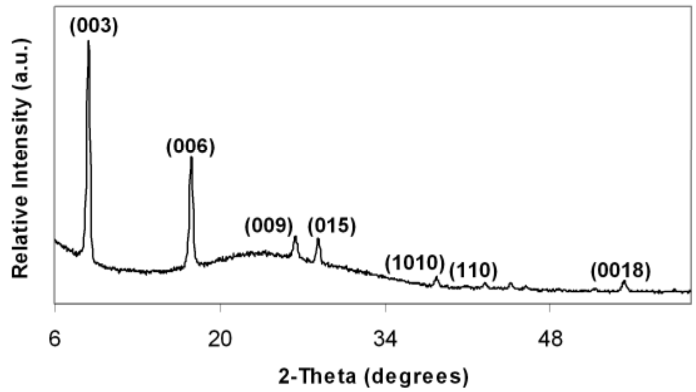

. X-ray diffraction pattern of rhombohedral Sb_2Te_3

thin films deposited at 475 ^{o}C

using a dynamic argon flow rate of 240 sccm.

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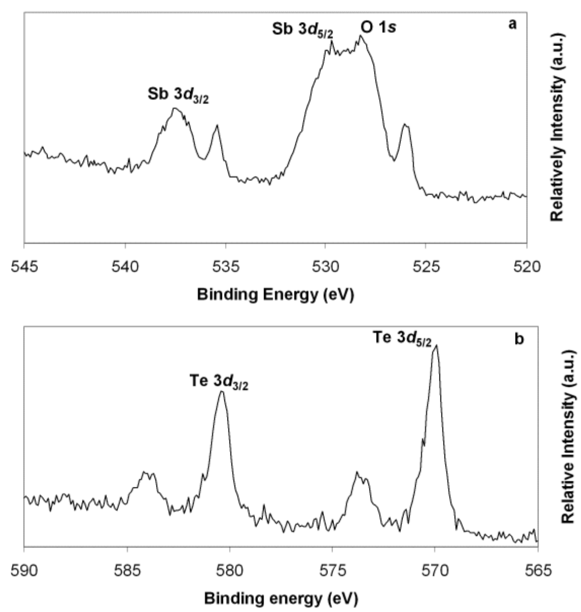

Survey XPS scan for

(a) Te and

(b) Sb

films grown at 475 ^{o}C.

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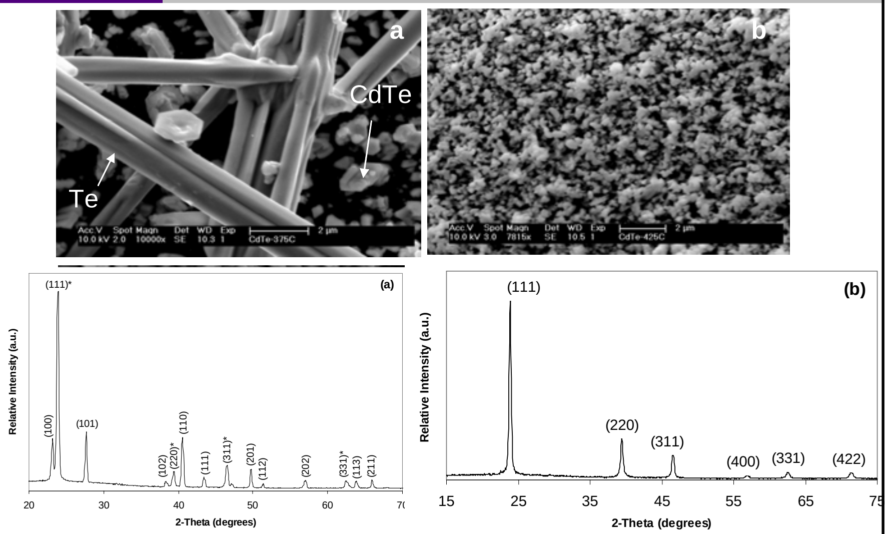

SEMs of (a) CdTe and Te deposited at 375°C; CdTe deposited at (b) 425°C.

J. Mater. Chem., 2006, 16, 966 – 969

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Just when you thought you understood!

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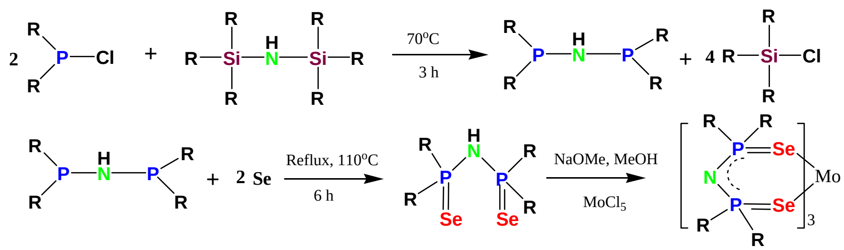
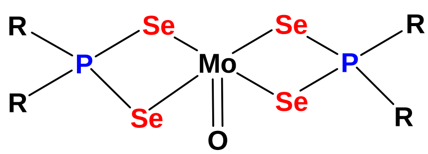
Mo Complex from Woollins' Reagent



Obtained product



May not get Wollins Reagent, but the "Wrong Ligand"

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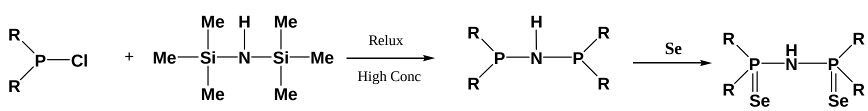
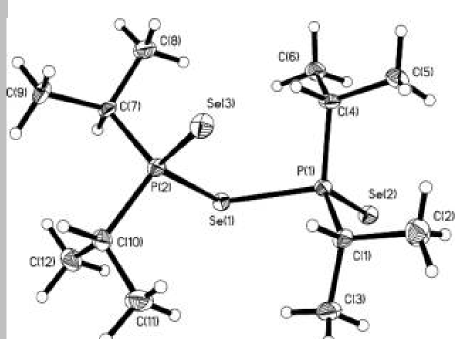
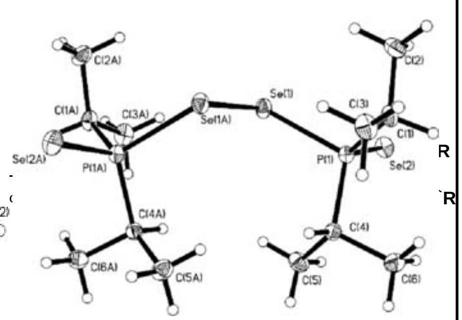
MAIN PRODUCT







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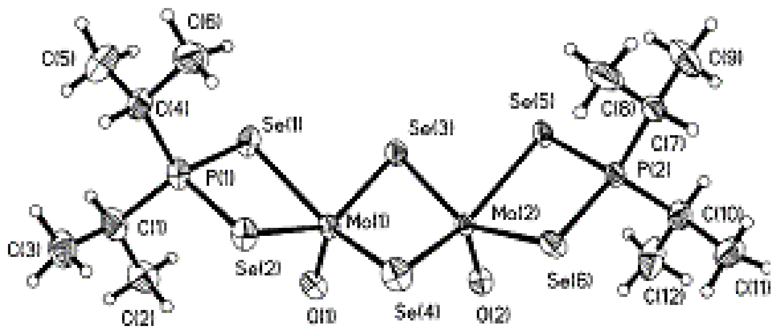
$[Mo_2O_2Se_2(Se_2P^iPr_2)_2]\ MoCl_5$ and $[^iPr_2PSe]_2Se$



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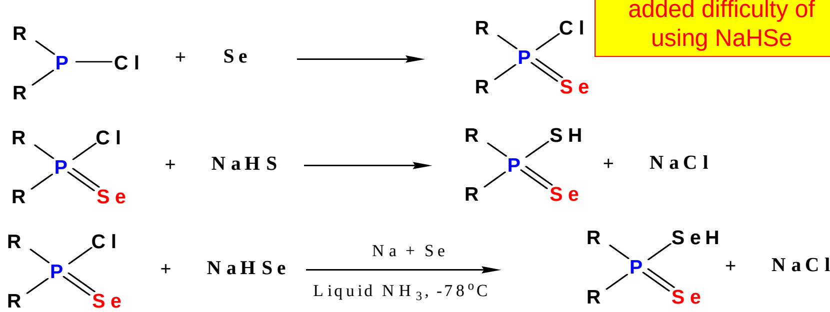
DIALKYLDICHALCOGENOPHOSPHINATES

Previous Work

Not-reproducible with added difficulty of using NaHSe



Unstable, never isolated, used *in situ* to make metal complexes, no solid state characterization

*References: (a) J. Inorg. Nucl. Chem. 1974, **36,** 472-5; (b) Angw. Chem. 1969, 8, 89. (c) Polyhedron 1991, 10, 2641.*

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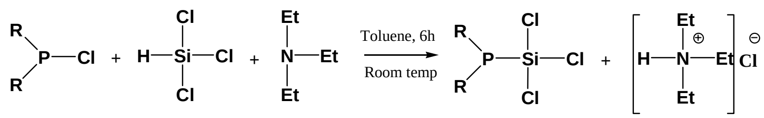
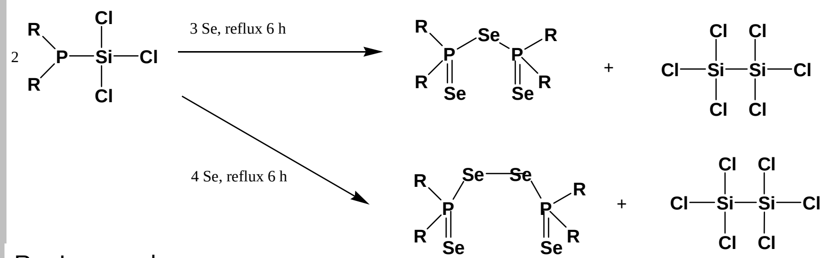
Novel Synthetic Route *(1)*

STEP 1: BENKESER REACTION



STEP 2: INSERT Se



R = Isopropyl

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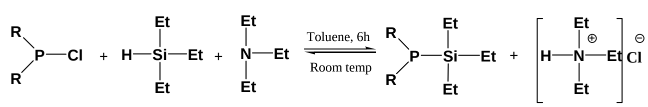
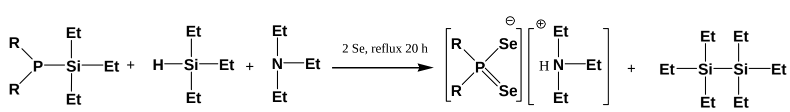
Novel Synthetic Route *(2)*

- Alternatively, use excess Lewis Base NEt_3 to stabilize ionic species e.g. $[(^iPr)_2PSe_2]$
- $HSiCl_3/NEt_3$: did not work due to the formation of $[HNEt_3^+][SiCl_3^-]$
- $HSiEt_3/NEt_3$: worked

STEP 1: BENKESER REACTION



STEP 2: INSERT Se



R= Isopropyl; Phenyl

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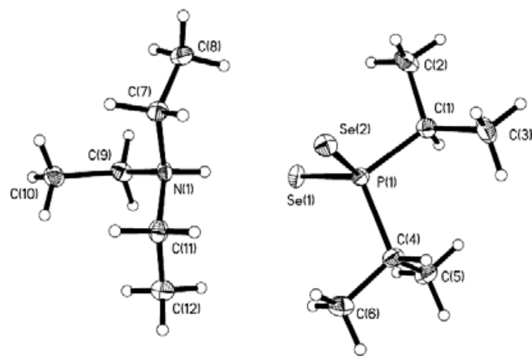
Crystal Structures



[$^{i}Pr_2PSe_2$][$HNEt_3$]   Yield = ~ 85%

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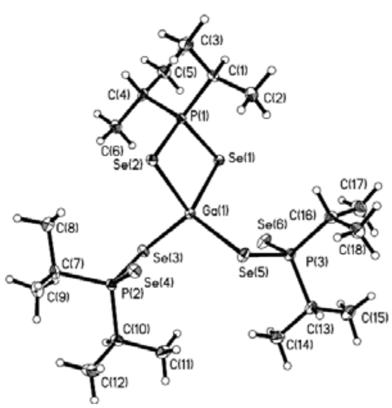
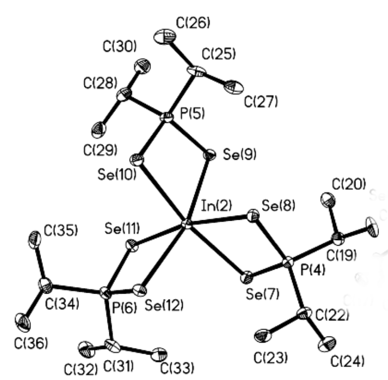
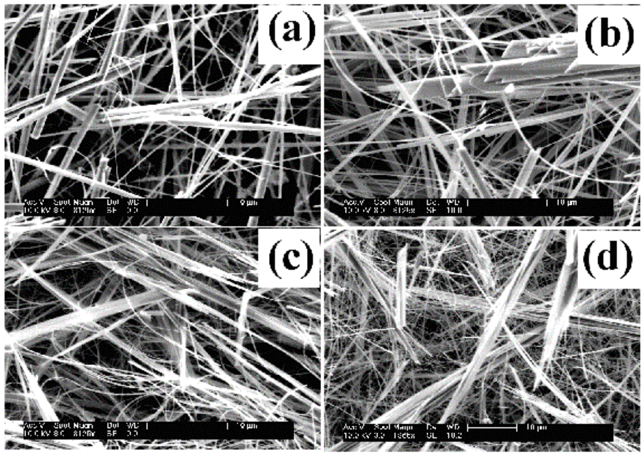
Group 13 complexes





$$n\,[R_2PX_2]^- \quad + \quad M^{n+} \quad \underset{\text{Room Temp.}}{\overset{\text{MeOH}}{\rightleftharpoons}} \quad [R_2PX_2]_nM$$

R = Ph; ^{i}Pr X = S; Se M^{n+} = In^{3+}; Ga^{3+}



Micrograph of rhobohedral Sb_2Se_3 grown on glass at

(a) 400 ºC (b) 425 ºC (c) 450 ºC (d) 475 ºC from

(b) $[Sb(Se_2P^iPr_2)_3]$ with an Ar flow rate of 180 sccm

How To Make a Nano-Material

- Use a clever precursor
- **Use a Physical Separation**
- In Water!

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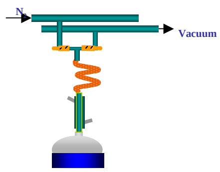
TECHNIQUES

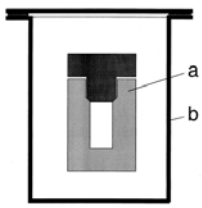
Schlenk Techniques



Strategies learnt from previous studies:

- High temperature/ Inert atmosphere
- Single precursor
- Single surfactant ➔spherical particules
- Mixture of surfactants ➔ anisotropy

Solvothermal/Hydrothermal



➔ **Comparable results**

➔ **Advantage: Use of low cost and less toxic solvents**

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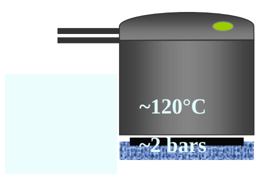
WHAT ABOUT « COOKING » NANOPARTICLES ?



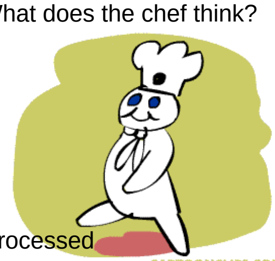
Using a pressure-cooker…

PRECURSOR + SURFACTANT

↓ ?

NANOPARTICLES

What does the chef think?



Make Mine Soft Solvothermal Processed

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PRECURSORS

[(2,2'-bipyridyl)M(SC(C_6H_5))$_2$] with =O on the C of the SC group

M= Cd, Pb

BCT: Bipyridyl Cadmium Thiocarbamate

BLT: Bipyridyl Lead Thiocarbamate

[Pb(S_2(P(C_6H_5)$_2$)$_2$N)$_2$]

SPIROL: Spirobicyclic Lead

➔Air stable compounds

Zhang, Chin and Vittal, J.Chem Phys B., 2004, 108, 18569

Thiobenzoic acid complexes under reflux

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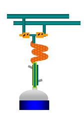
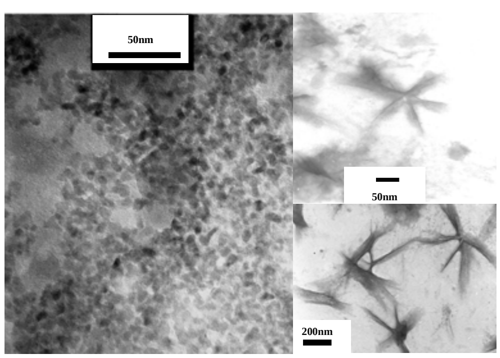
CADMIUM SULPHIDE NANOPARTICLES

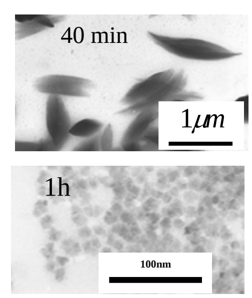


Inert atmosphere

Aerobic conditions

120°C





In HDA

1hr at 120°C

In thioglycerol, NaOH and water

1hr at 100°C

In alkaline water

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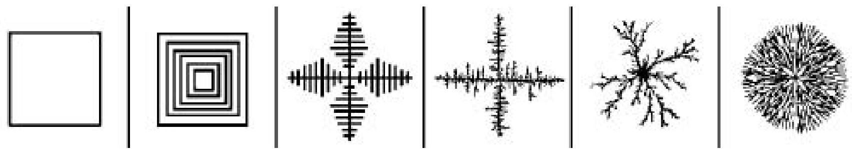
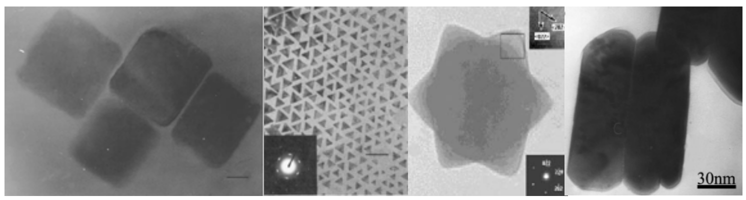
LEAD SULPHIDE NANOPARTICLES



Polyhedral | Skeletal | Single-crystalline ordered dendrite | Partially disordered dendrite | Disordered polycrystalline dendrite | Dense branching morphology

A Few examples



O'Brien et al. *J.Mater.Chem, 1997*

Yang and Fendler *J. Phys.Chem, 1995*

Sheon et al. *J. Am.Chem. Soc, 2002*

Wang et al. *J.Phys.Chem.B, 2006*

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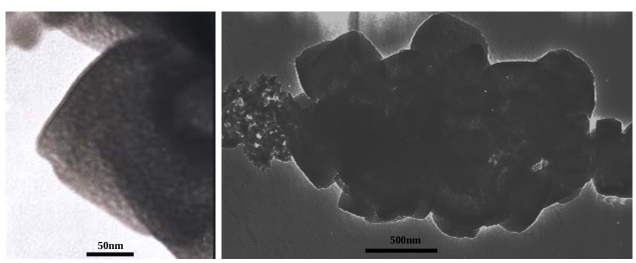
Cubic PbS made in alkaline aqueous solutions



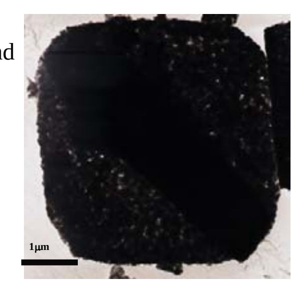
2,2'-bipyridyl)Pb(SO)C(C6H5)$_2$)

➔Cubic PbS aggregating

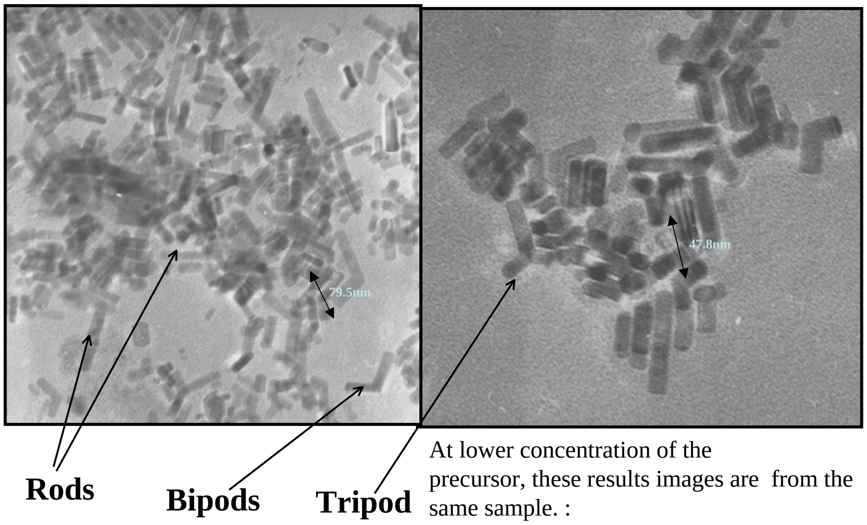
Basic 1-thioglycerol (TG) solution (pH~9) and left to react in the pressure-cooker (120ºC, 2 bars) for 10min.

[Precursor]=2.6 x 10-2 mol/L

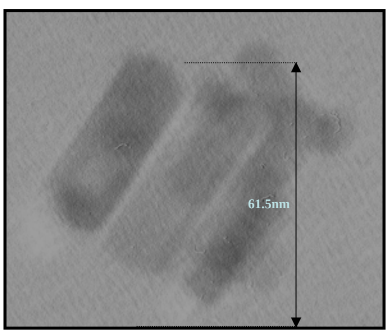
Volume ratio TG/Water= 1/5

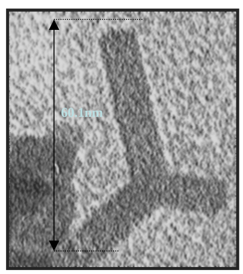


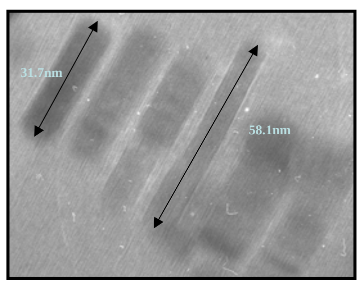
PbS rods, bipods and tripods



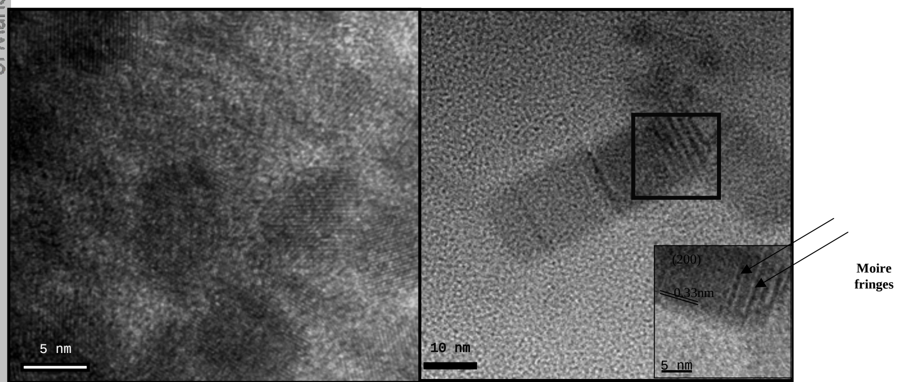
At lower concentration of the precursor, these results images are from the same sample. :
[Precursor]=7.8 x 10-3 mol/L
Volume ratio TG/Water= 1/5
Reaction time: 10min, T=120ºC, P=2bars





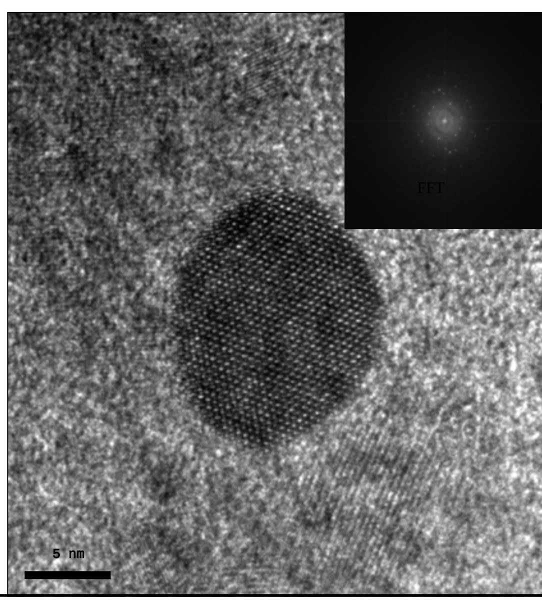


PbS nanorods

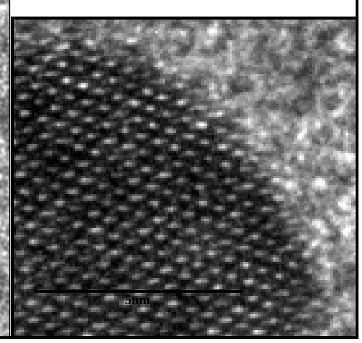


By decreasing the ratio surfactant/waterb and the concentration (to one fifth), we get these much smaller particles, with good crystallinity and narrow size distribution Exact conditions: [Precursor]=1.5 x 10-3 mol/L Volume ratio TG/Water= 1/10Reaction time: 5min, T=120ºC, P=2bars

PbS QDs



➔Face centered cubic PbS



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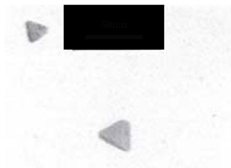
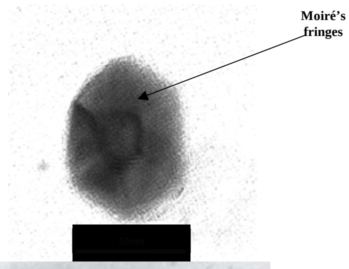
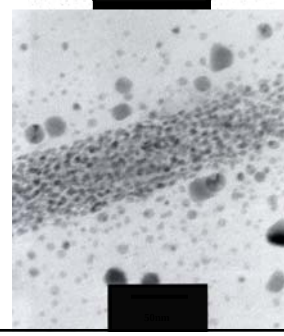
Triangular and pyramidal/bipyramidal PbS…





Pb(S2(P(C6H5)2)2N)2

The only difference here is the choice of precursor.
The hexagonal pyramid or bipyramid was not confirmed by SEM. These morphologies are minor species in the sample distribution. The exact conditions of their formation is not known at this stage.Exact conditions:
[Precursor]= 2.5 x 10-2 mol/L
Volume ratio TG/Water= 1/5
Reaction time: 10min, T=120ºC, P=2bars



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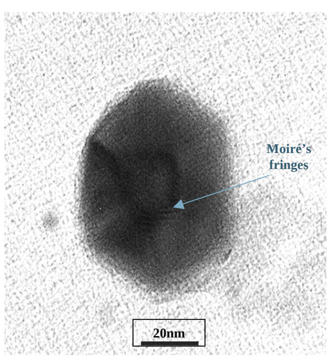

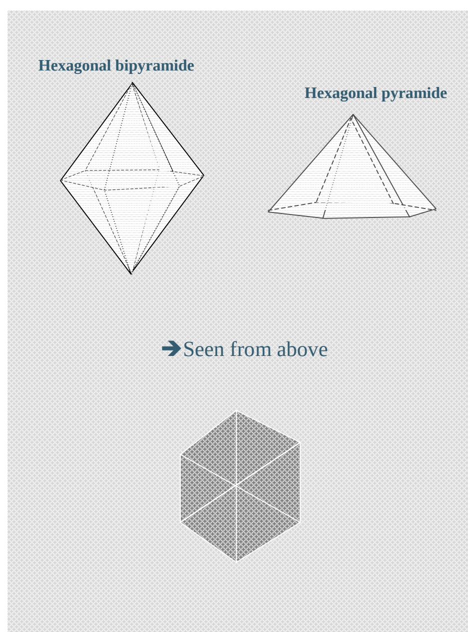

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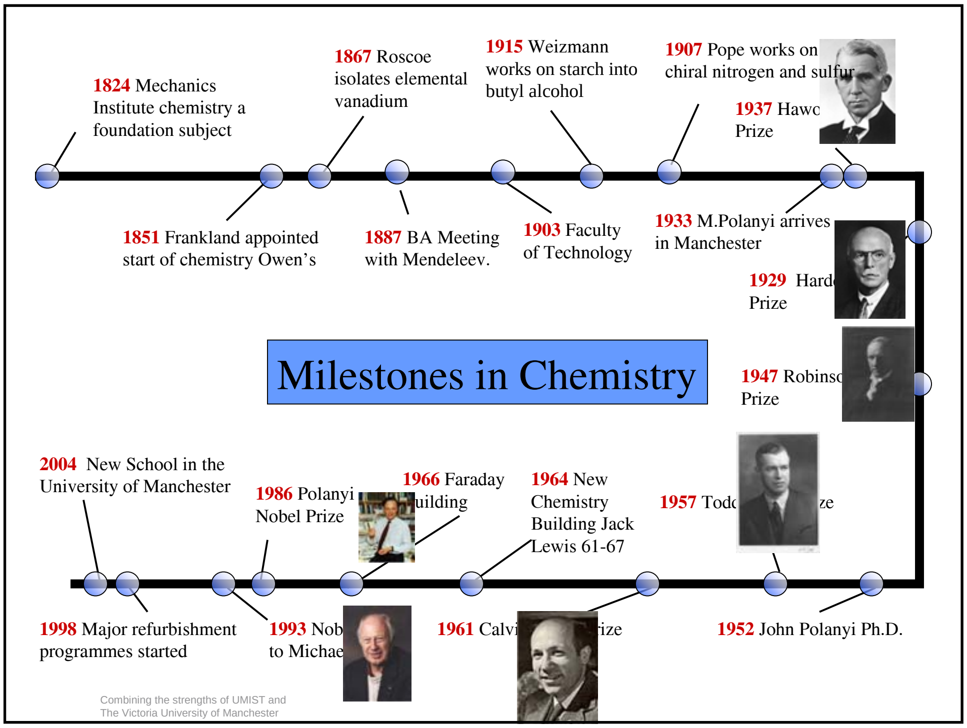
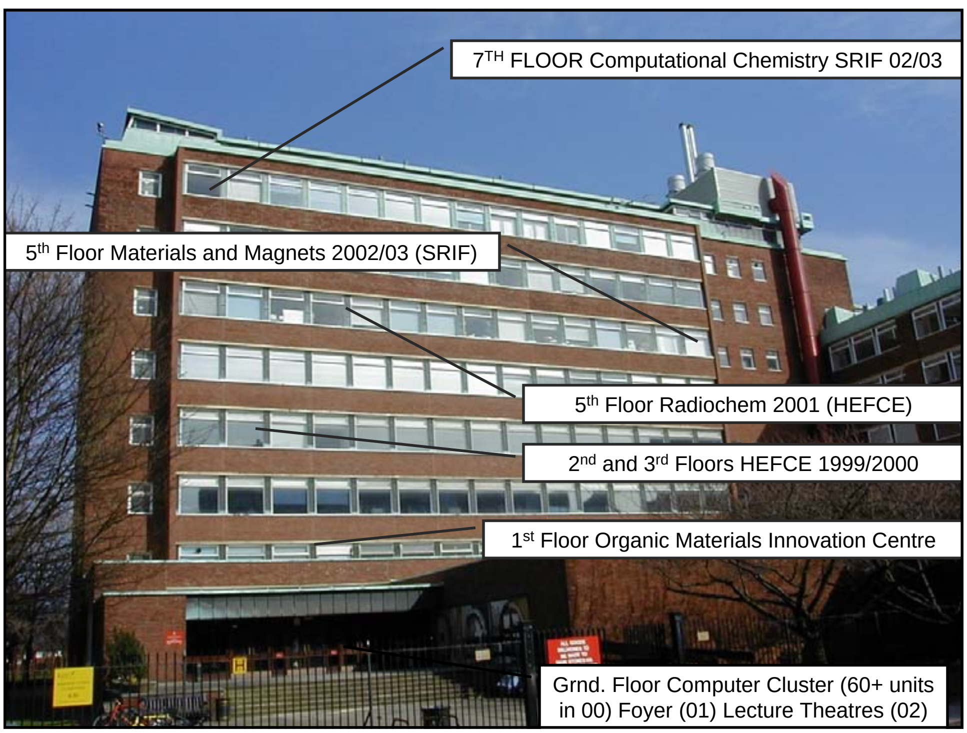
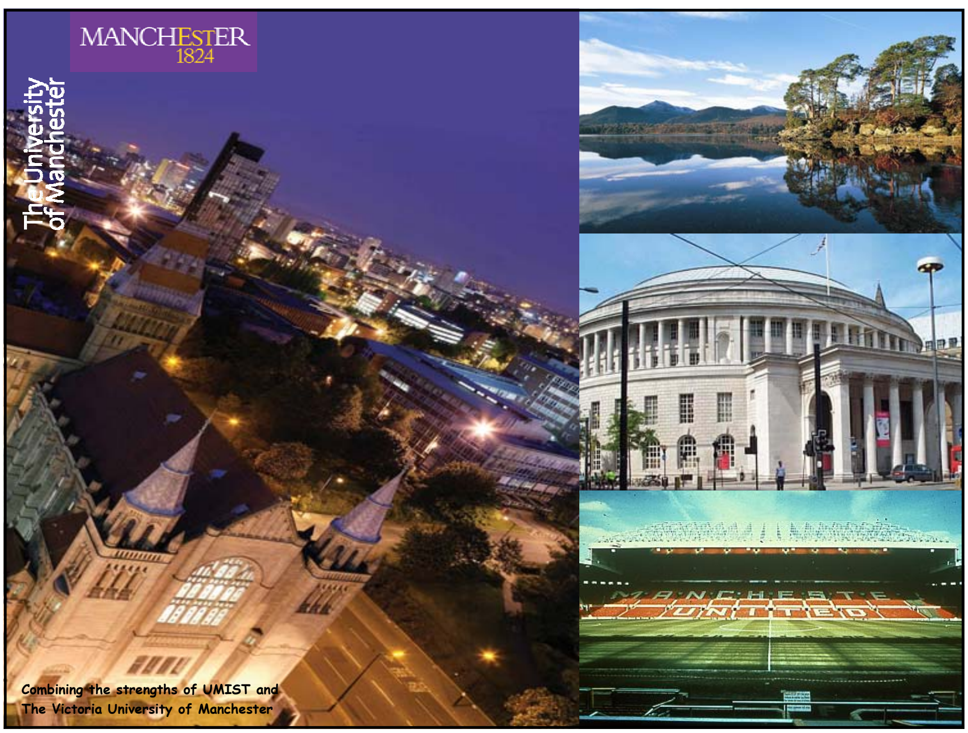
A New University for the 21st Century

- Established on 1st October 2004
- Royal Charter granted on 22nd October 2004
- 34 000 students from over 150 countries (1/3 postgraduate)
- 2000 academic staff & 1200 research staff
- £504M turnover (2004-5)
- £300M capital investment programme
- Manchester 2015 Agenda launched


Milestones in Chemistry
1824 Mechanics Institute chemistry a foundation subject
1851 Frankland appointed start of chemistry Owen's
1867 Roscoe isolates elemental vanadium
1887 BA Meeting with Mendeleev.
1915 Weizmann works on starch into butyl alcohol
1903 Faculty of Technology
1907 Pope works on chiral nitrogen and sulfur
1937 Hawc
Prize
1933 M.Polanyi arrives in Manchester
1929 Hard
Prize
1947 Robinso
Prize
2004 New School in the University of Manchester
1986 Polanyi Nobel Prize
1966 Faraday
uilding
1964 New Chemistry Building Jack Lewis 61-67
1957 Todd
ze
1998 Major refurbishment programmes started
1993 Nob
to Michae
1961 Calvi
ize
1952 John Polanyi Ph.D.
Combining the strengths of UMIST and
The Victoria University of Manchester


7TH FLOOR Computational Chemistry SRIF 02/03
5th Floor Materials and Magnets 2002/03 (SRIF)
5th Floor Radiochem 2001 (HEFCE)
2nd and 3rd Floors HEFCE 1999/2000
1st Floor Organic Materials Innovation Centre
Grnd. Floor Computer Cluster (60+ units in 00) Foyer (01) Lecture Theatres (02)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