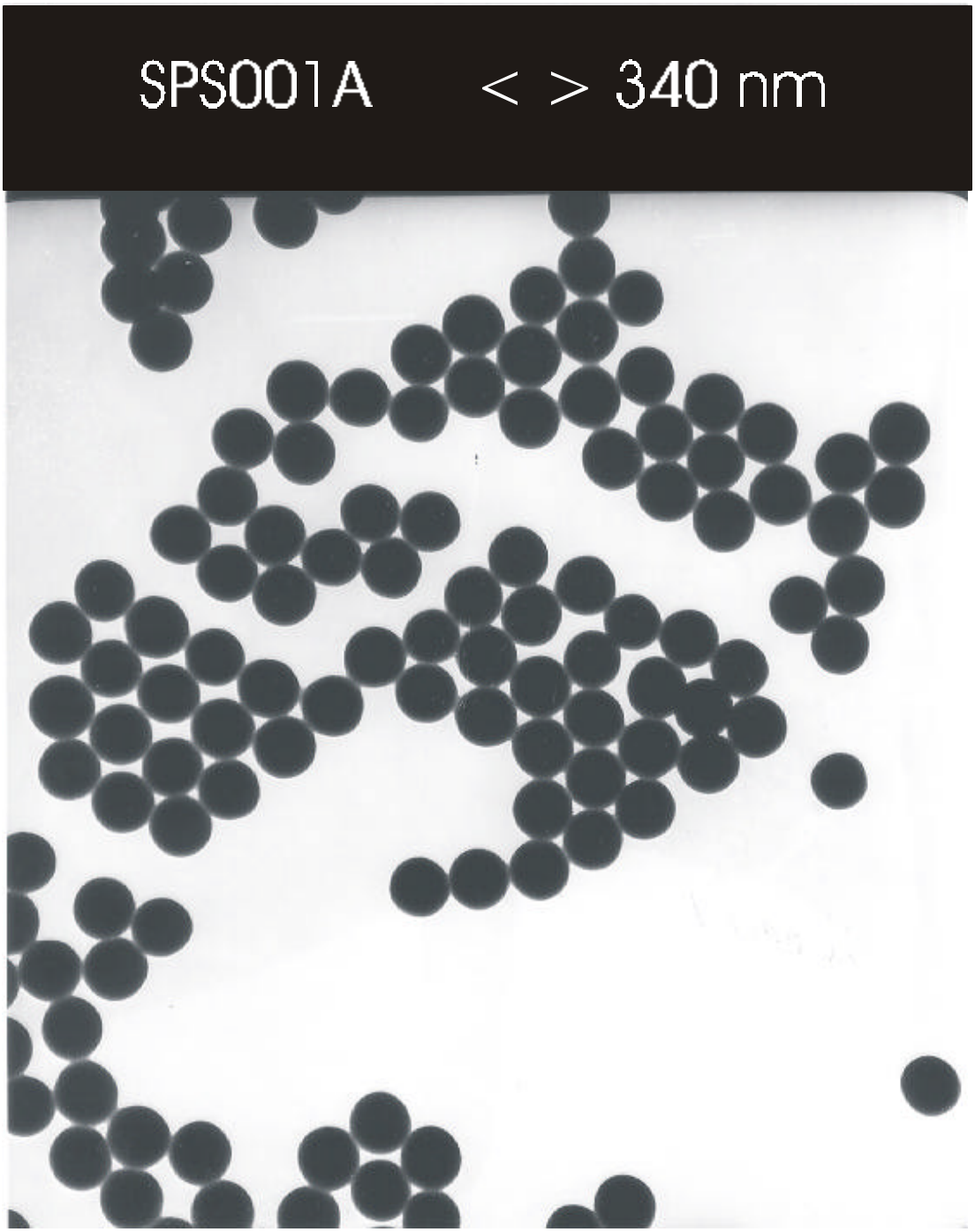
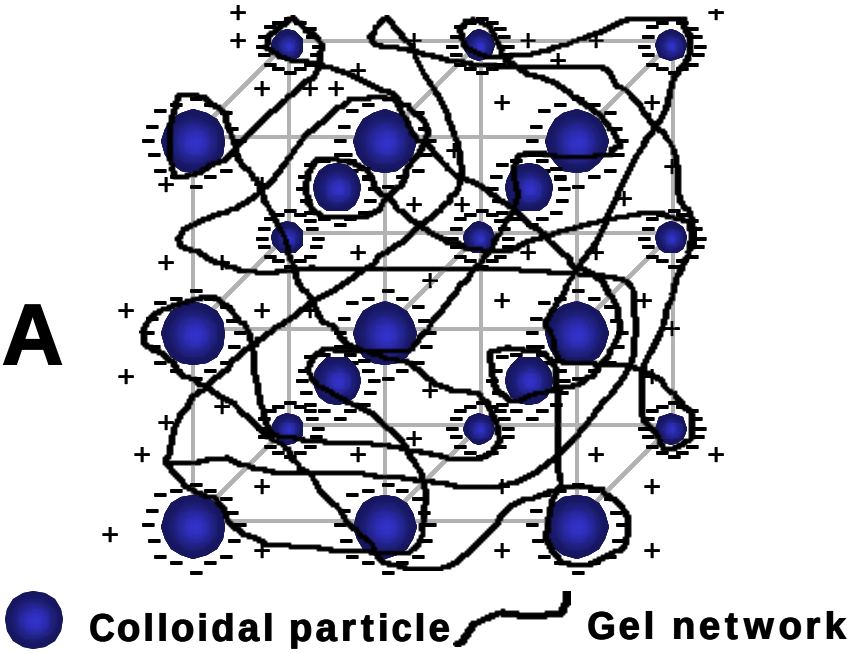
S. A. Asher, Department of Chemistry

TEM of Polystyrene Spheres
300 nm (QLS)

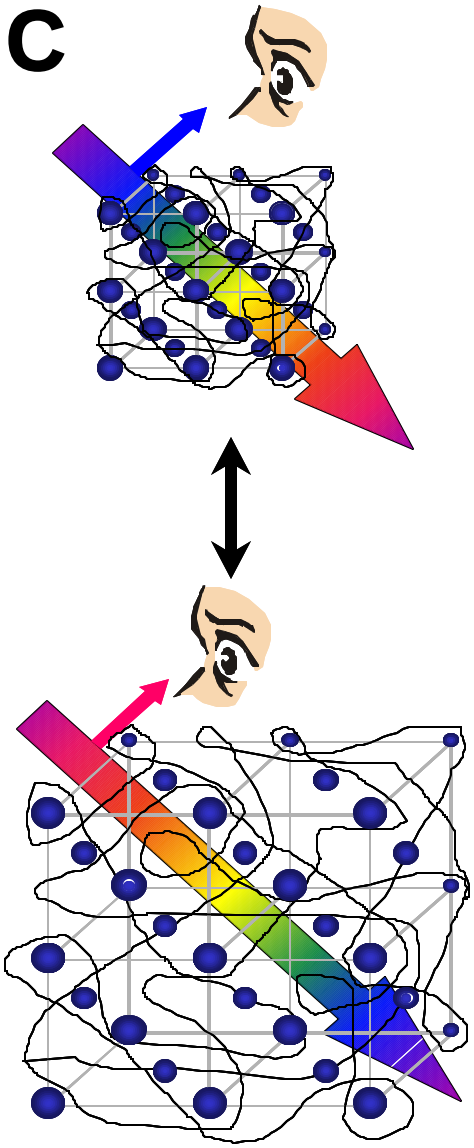


S. A. Asher, Department of Chemistry

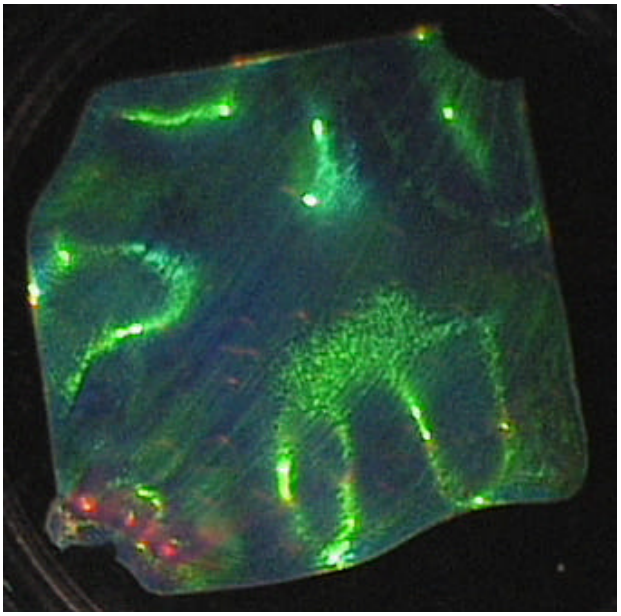
A



C



B



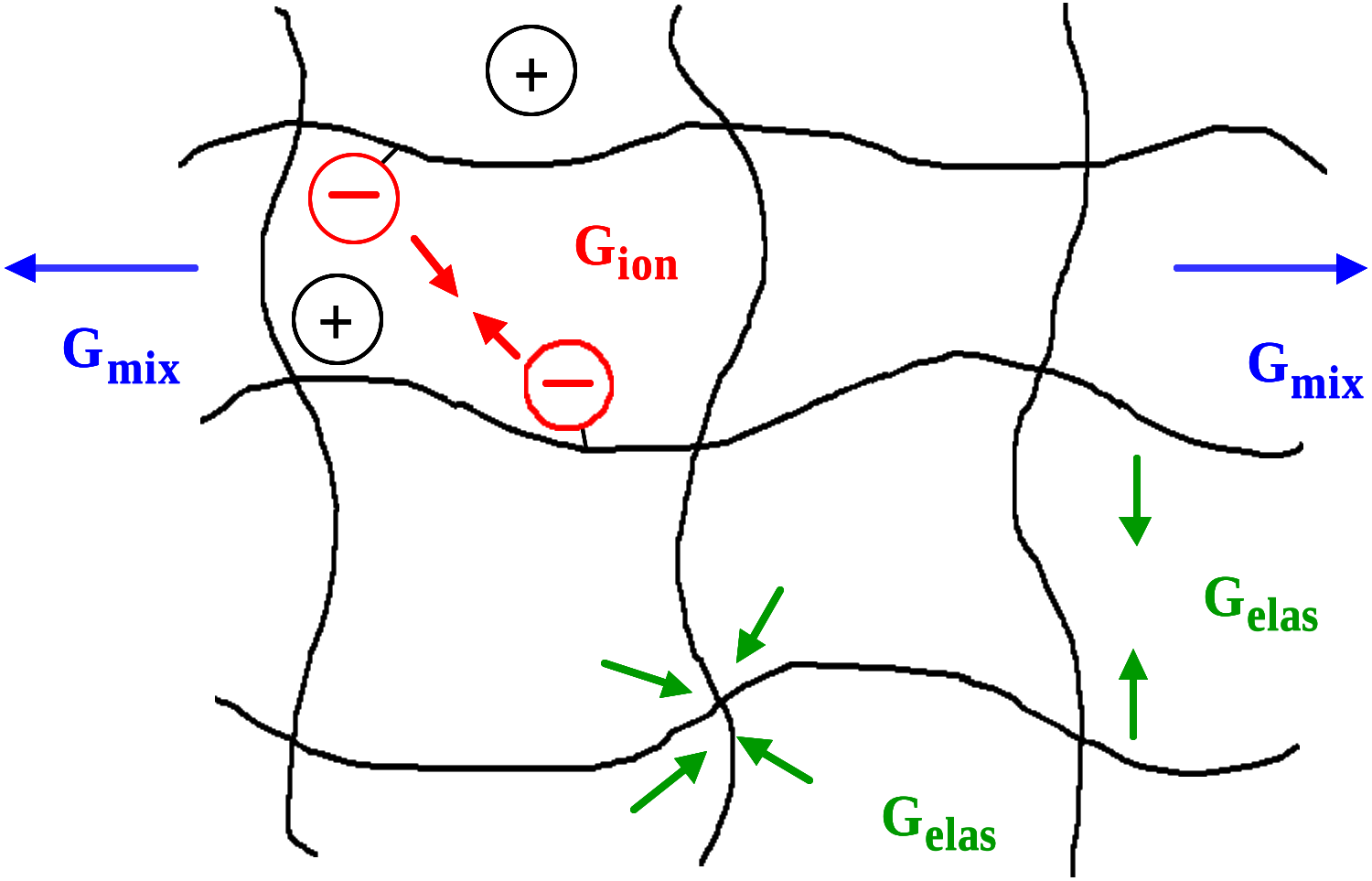
A) Polymerized crystalline colloidal array (PCCA)
B) Photograph of typical PCCA showing bright iridescence.

C) As the hydrogels shrink and swell, the lattice spacing of the CCA locked within changes as well. Thus, the volume changes of the gel can be observed by monitoring the change in diffraction.

S.A. Asher, Department of Chemistry, University of Pittsburgh

FREE ENERGY CONTRIBUTIONS TO GEL VOLUME

$$G_{tot} = G_{mix} + G_{ion} + G_{elas}$$

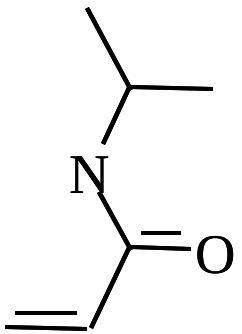


S.A. Asher, Department of Chemistry, University of Pittsburgh

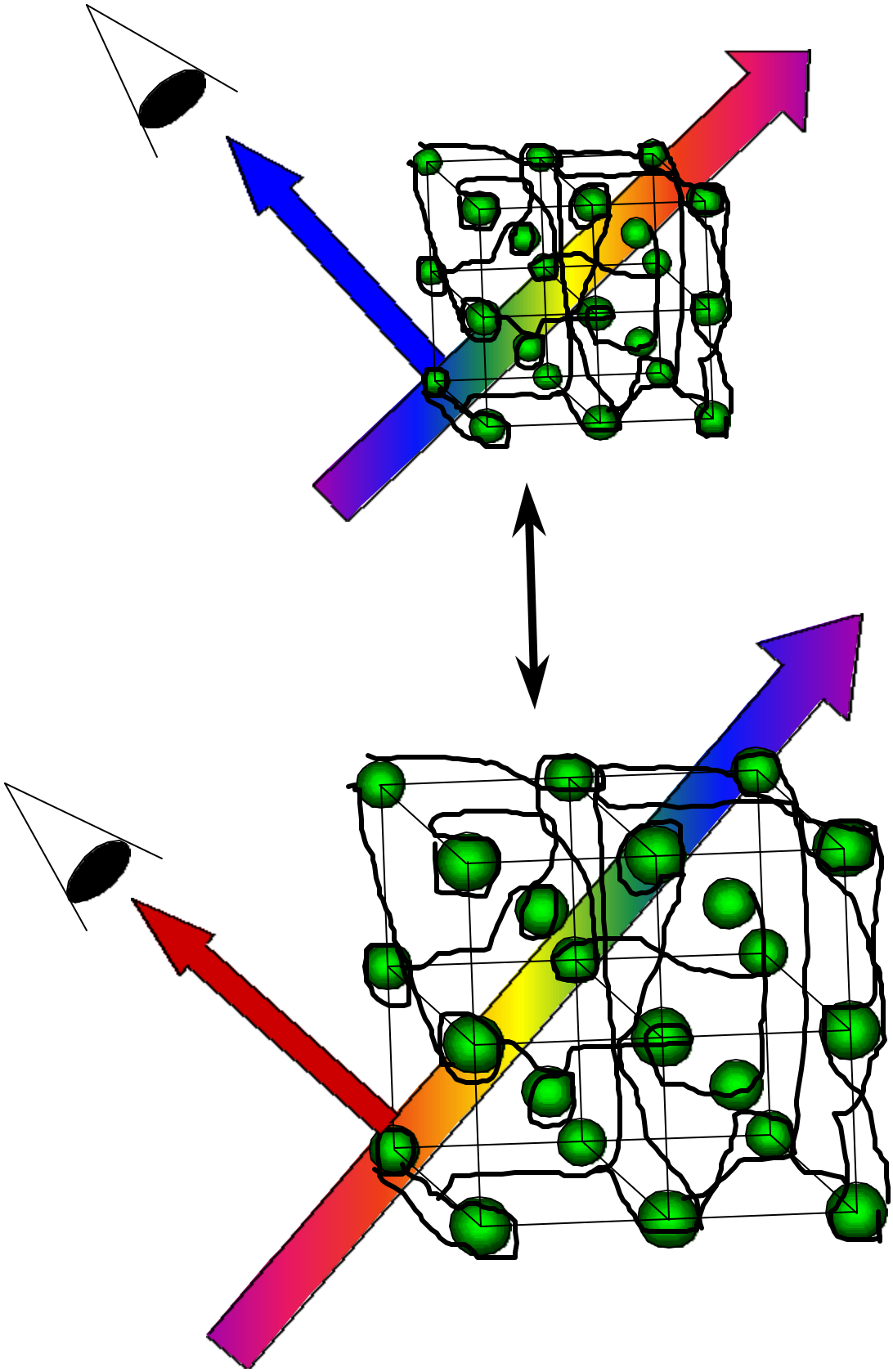
Poly(N-isopropylacrylamide) : The Driving Force

Poly(N-isopropylacrylamide) (PNIPAM) undergoes a reversible phase transition when heated above 32.1 ^{o}C. This coil-globule transition is analogous to a liquid-vapor phase transition. The recipe and synthesis conditions determine the extent of volume changes and whether they are continuous or discontinuous.

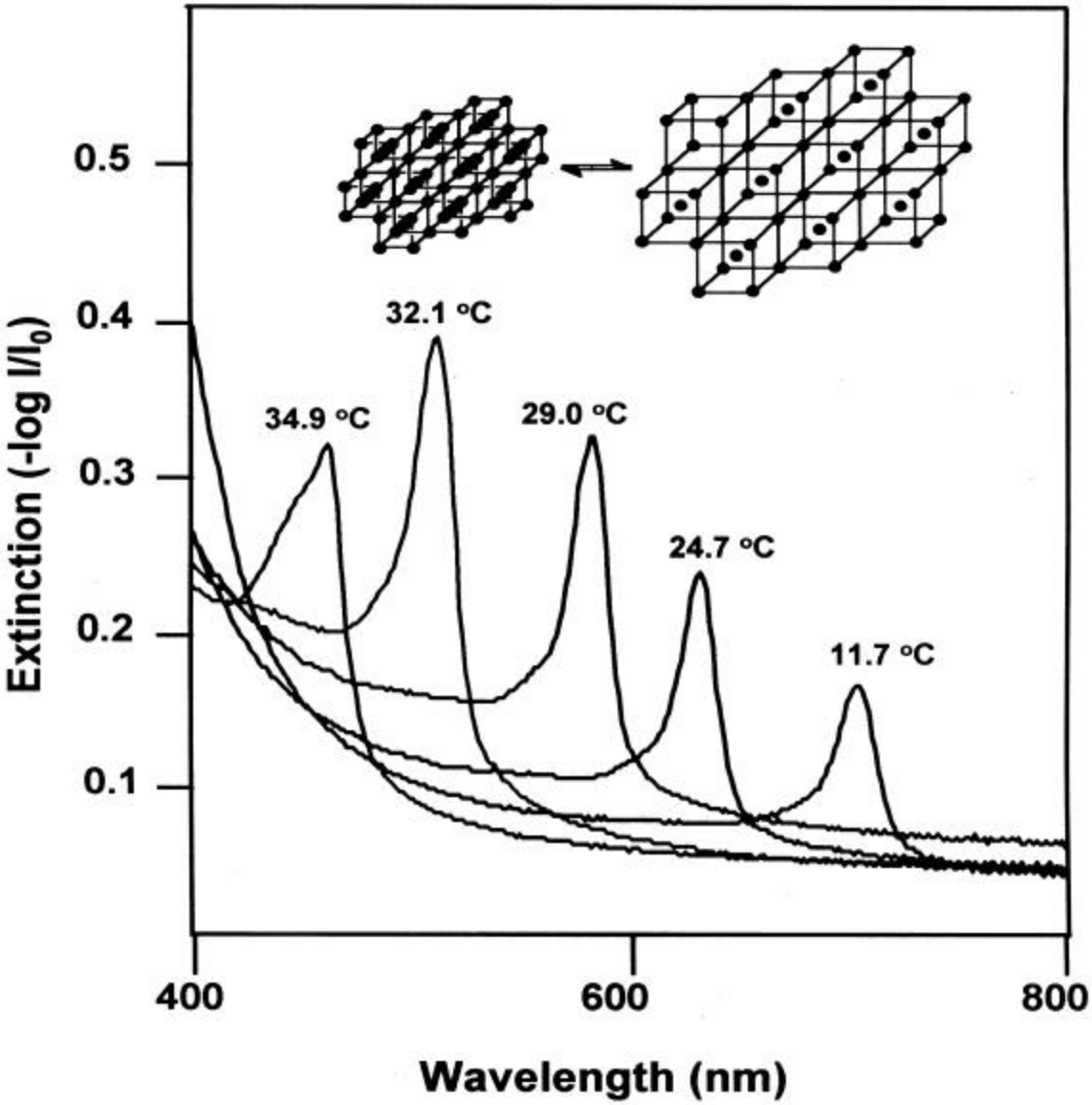
<u>Chemical Structure of NIPAM</u>



S. A. Asher, Department of Chemistry



S. A. Asher, Department of Chemistry

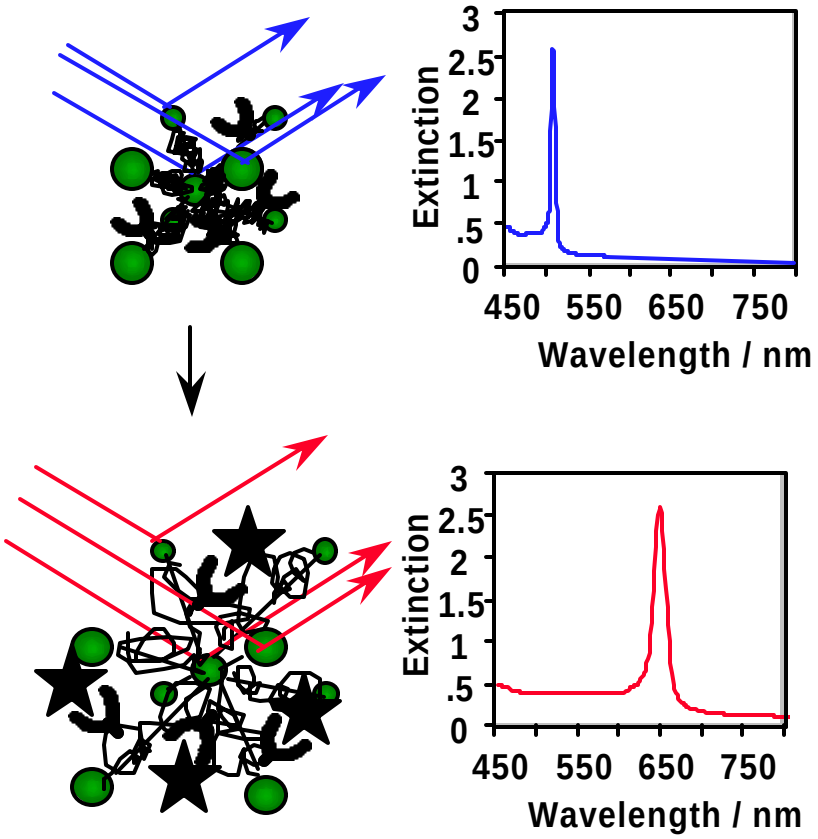


Wavelength selective reflector tuned across the visible spectrum

S. A. Asher, Department of Chemistry

Diffracting Materials for Chemical Sensing

S. A. Asher, Department of Chemistry



Polystyrene colloid.

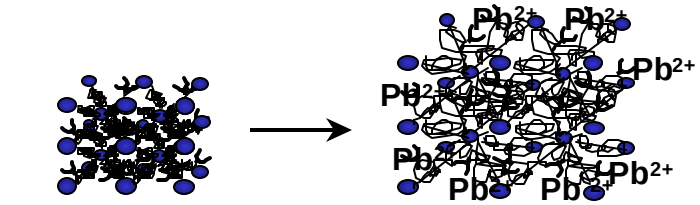
Side group capable of molecular recognition.

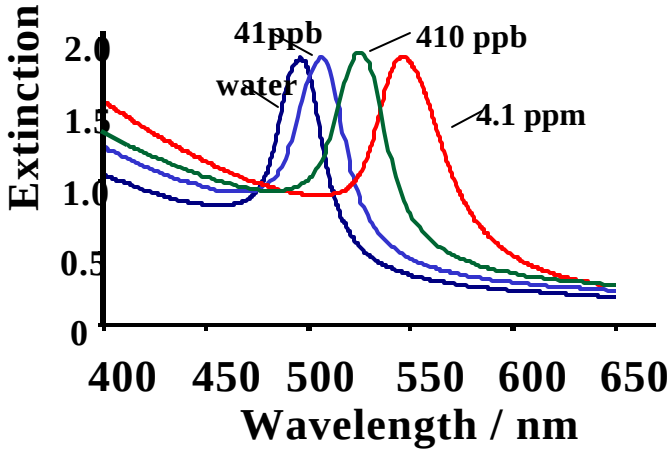
Substrate to be recognized.

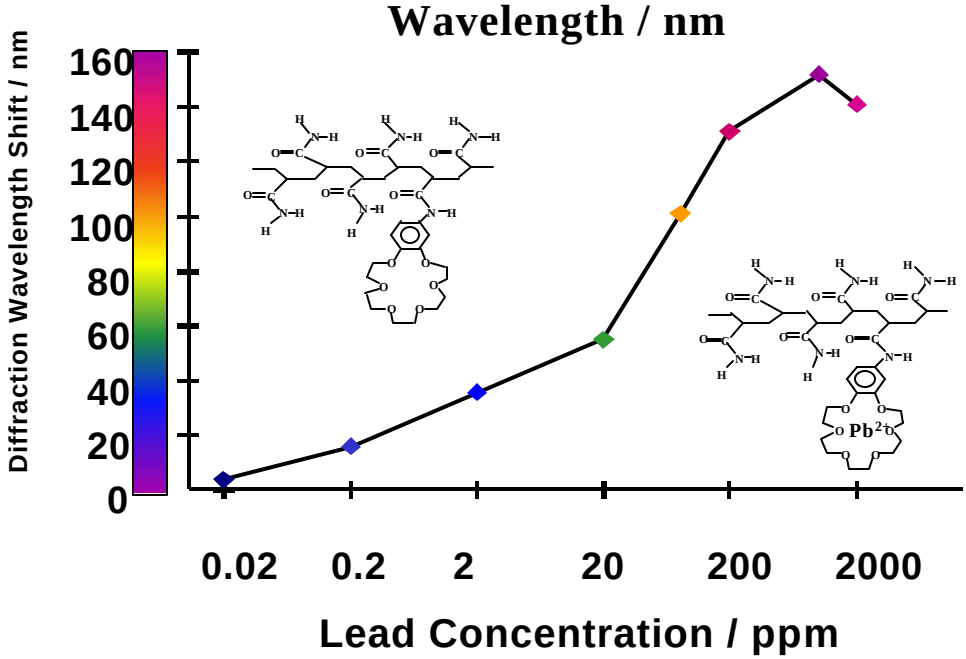
Hydrogel matrix.

S. A. Asher, Department of Chemistry

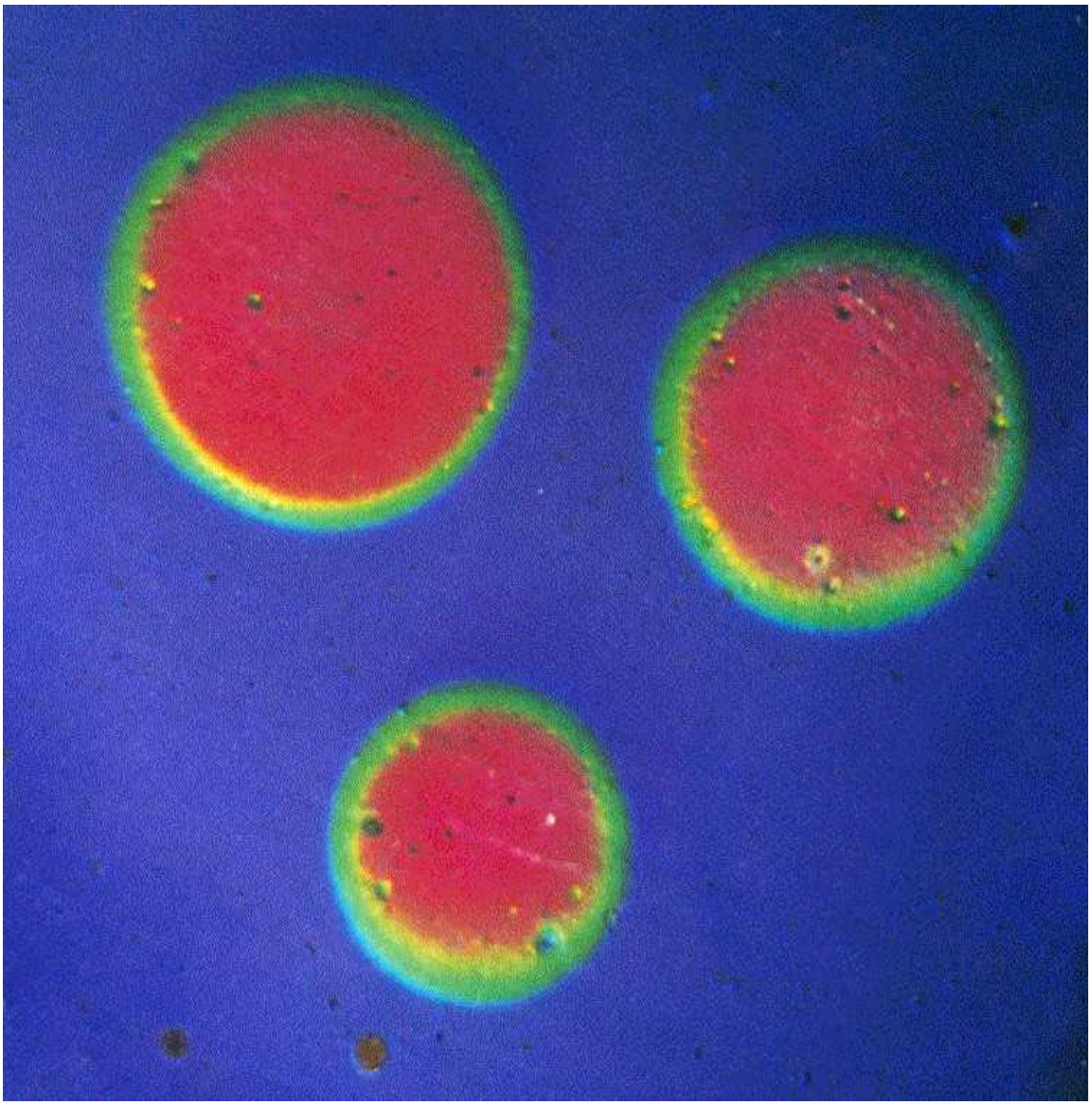
We constructed cation and anion sensors by attaching chelating agents to the PCCA. Chelation of the analyte ion results in immobilization of the counterion which results in an osmotic pressure which swells the gel and red shifts the diffraction in proportion to the analyte concentration.







S. A. Asher, Department of Chemistry



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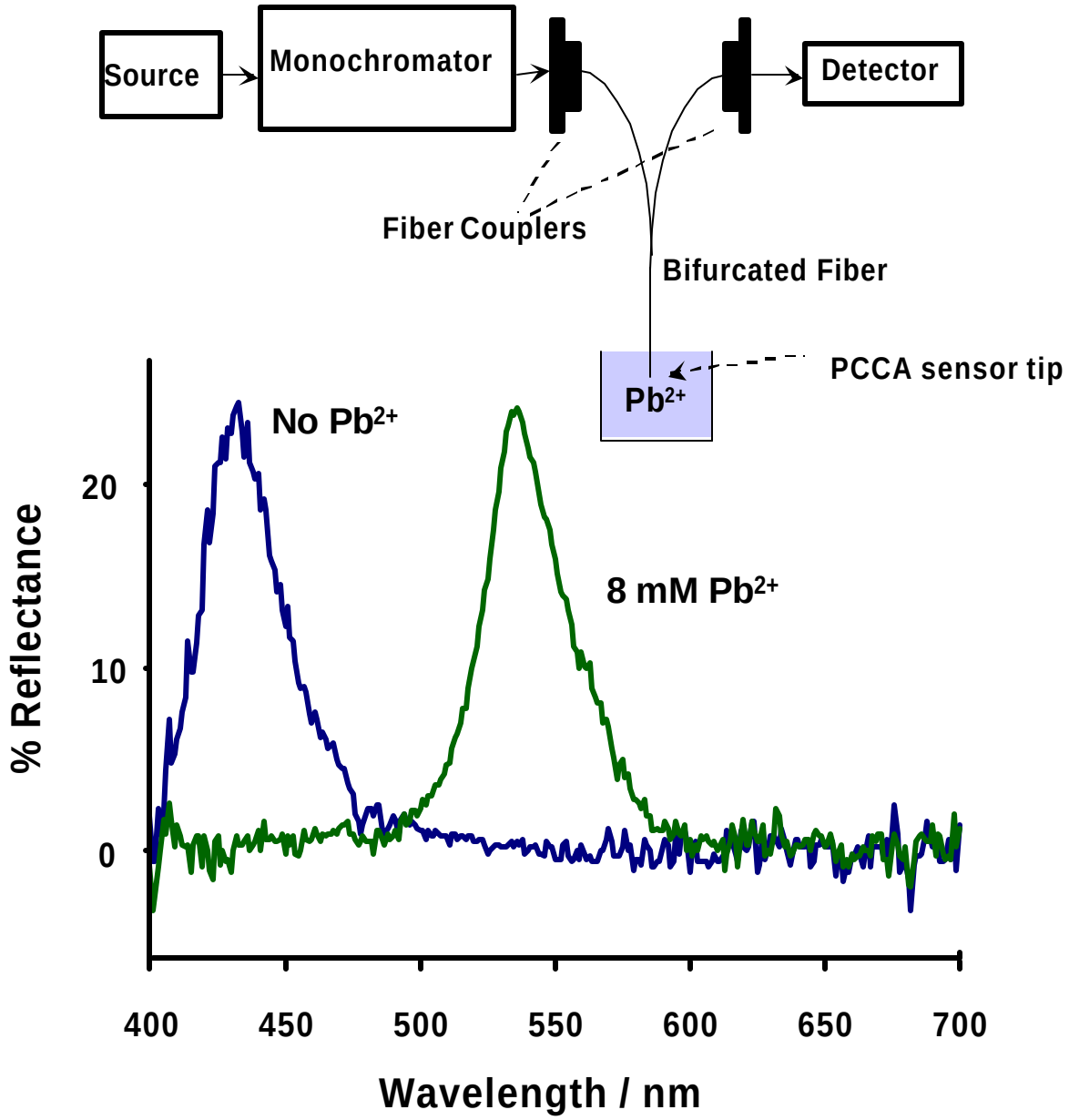

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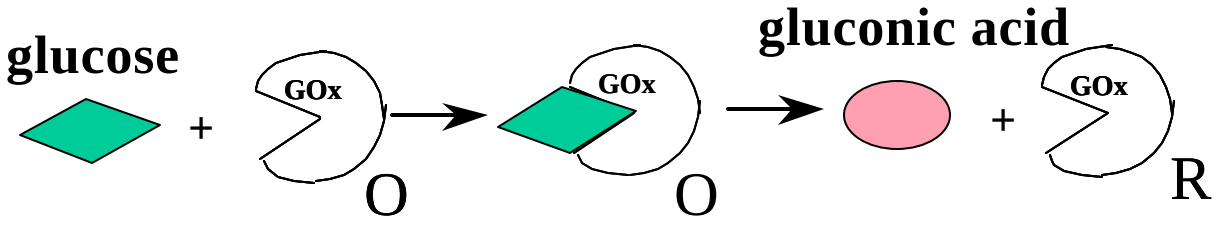
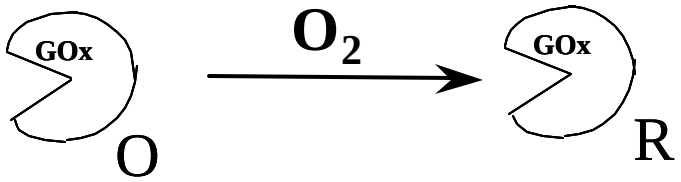
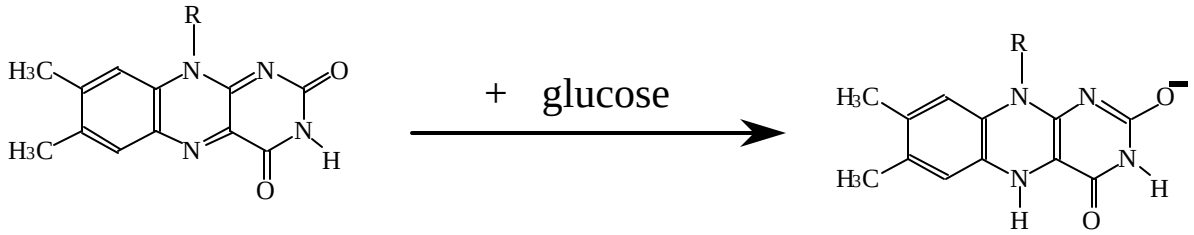
Glucose Oxidase Reaction Mechanism

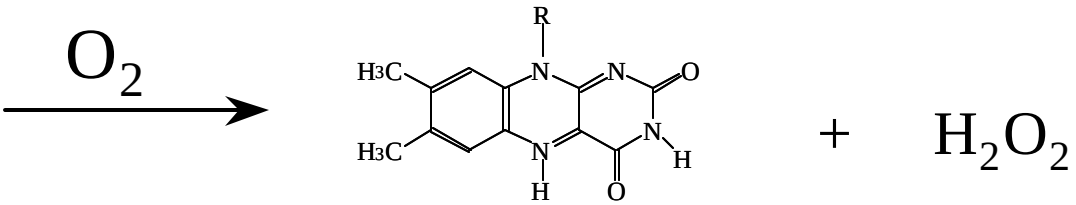






Oxidized Flavin

Reduced Flavin



Oxidized Flavin

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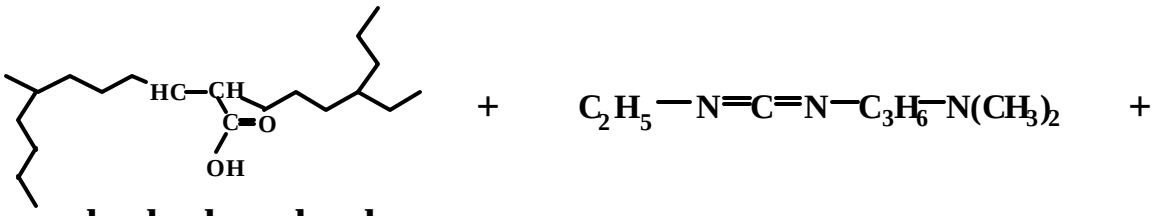
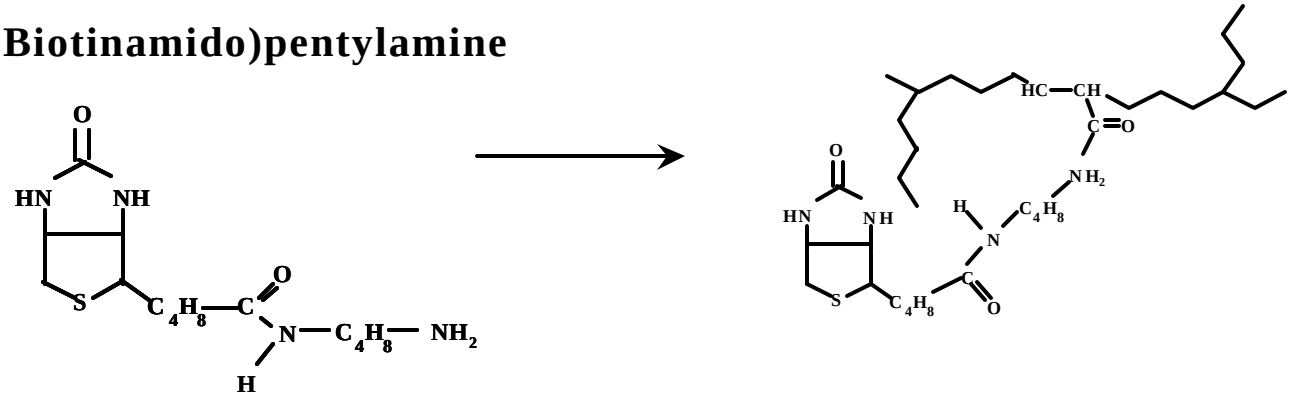
1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide

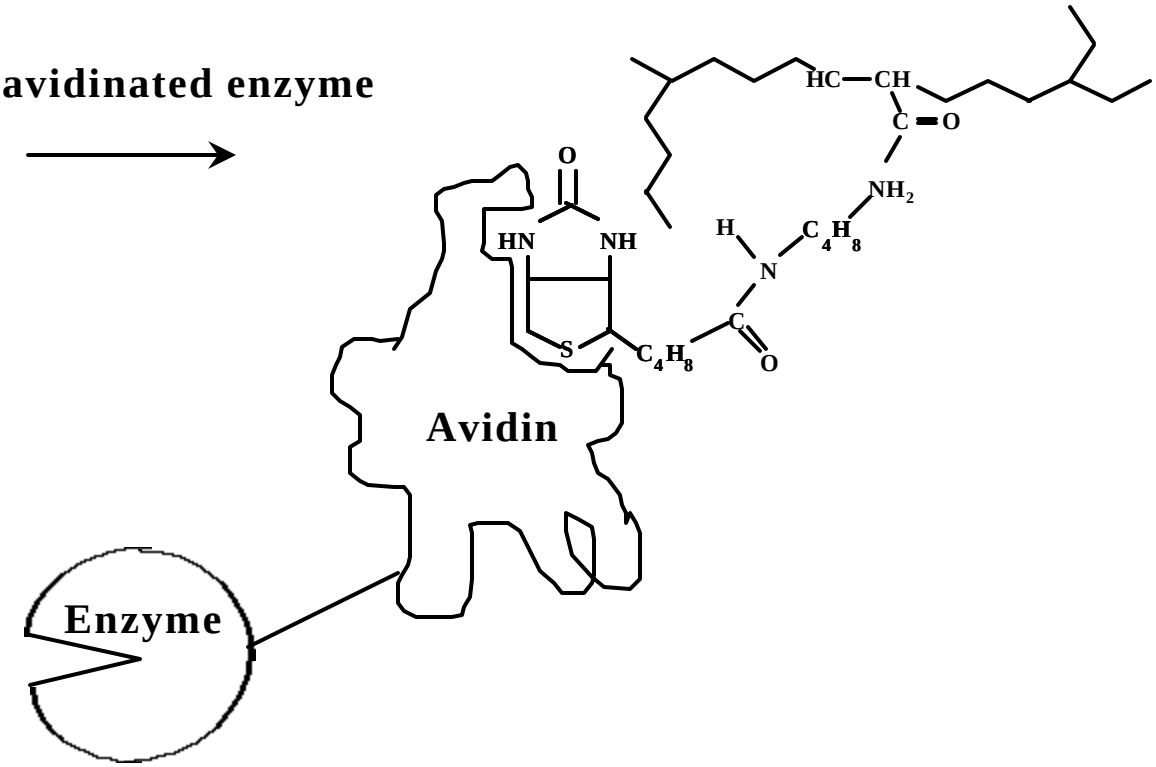


hydrolyzed gel

5-(Biotinamido)pentylamine



+ avidinated enzyme



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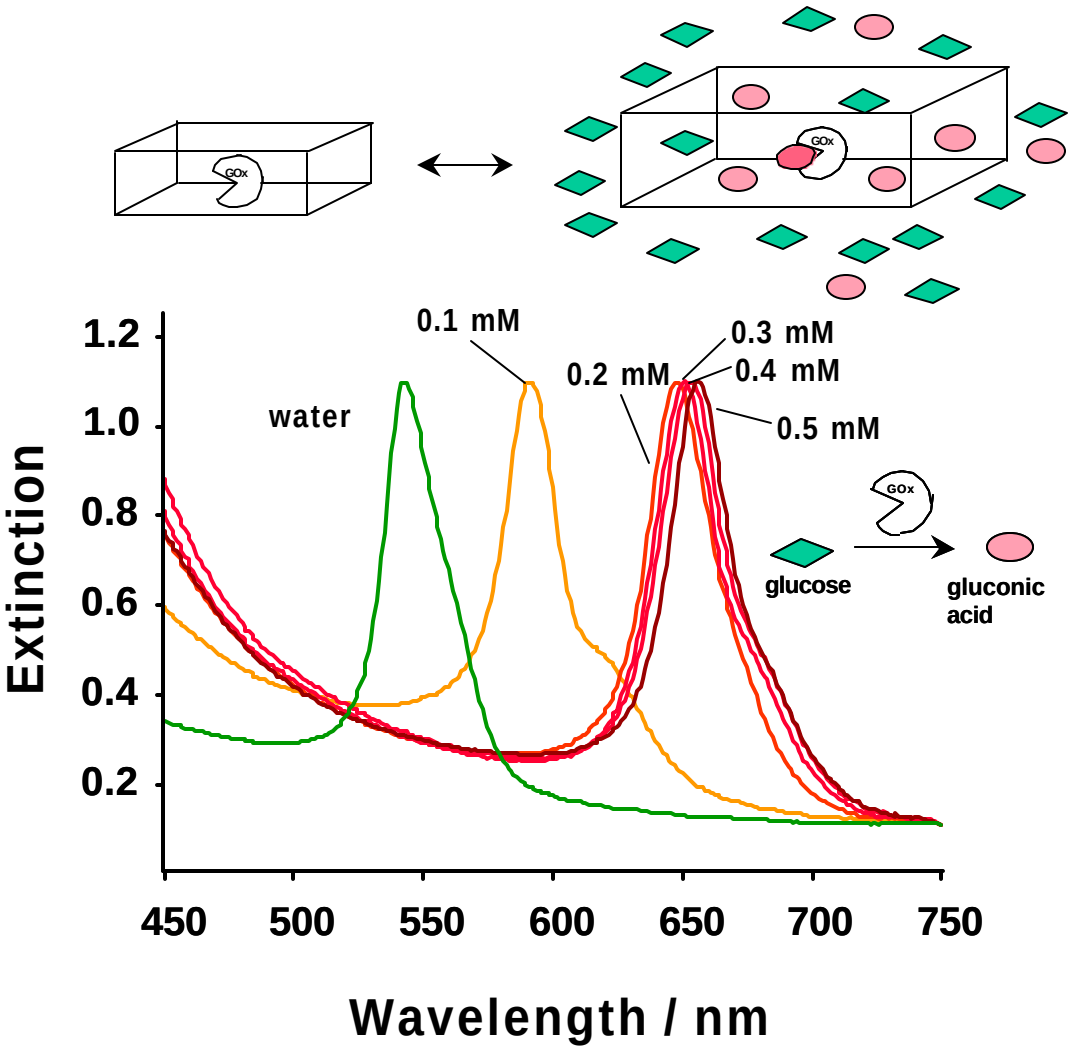
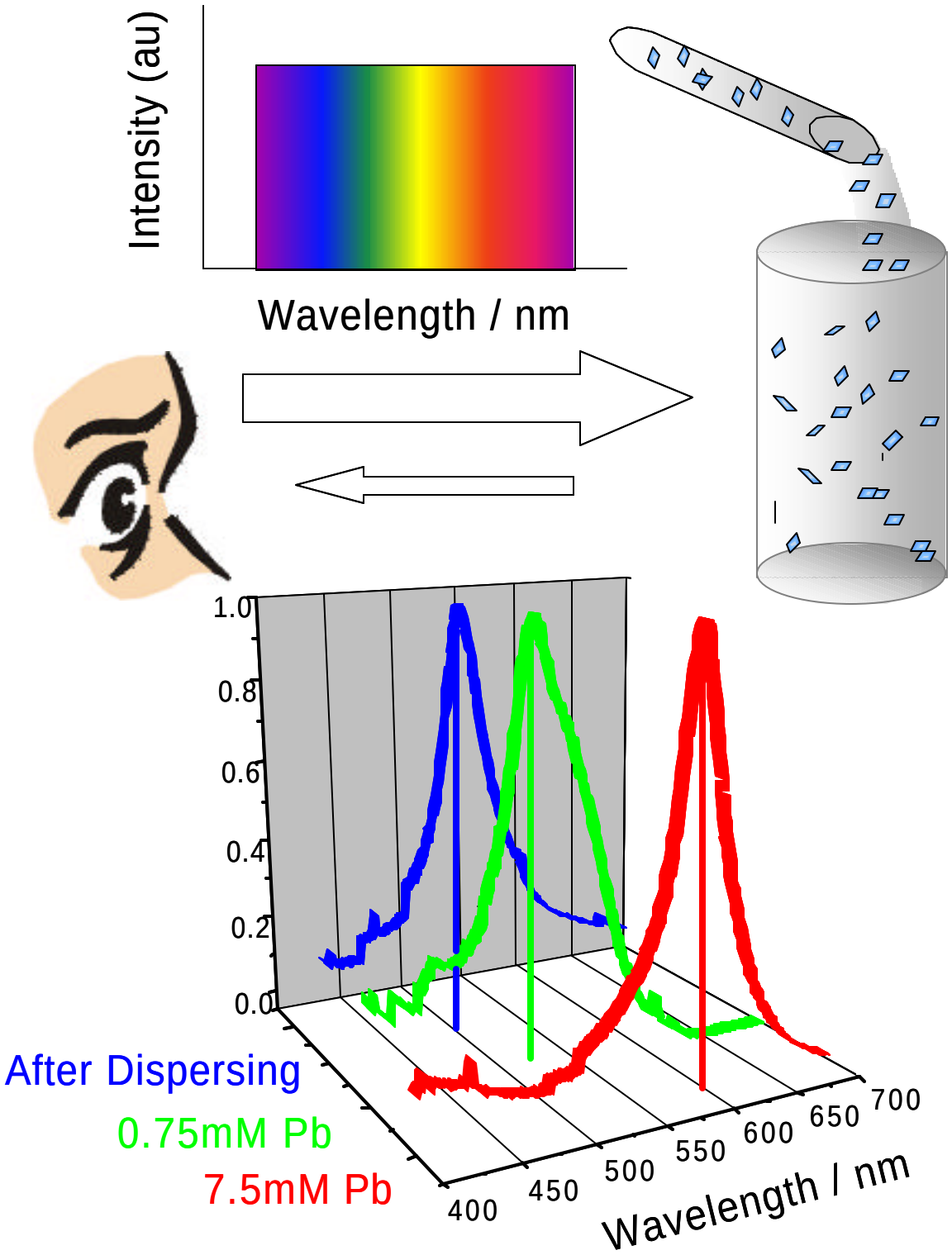


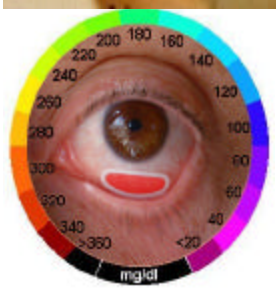
Gel Particulate Colorimetric Reagent



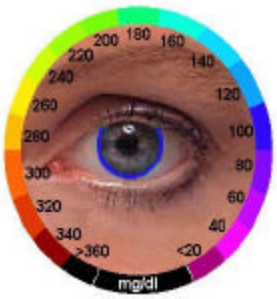
S. A. Asher, Department of Chemistry

Chemical (glucose) Sensing Fantasies

Fig. 1 Concept for glucose sensing device for tear fluid and for implants. The color diffracted defines the glucose concentration.



Glucoview™
Ocular Insert



Glucoview™
Diagnostic Contact Lens

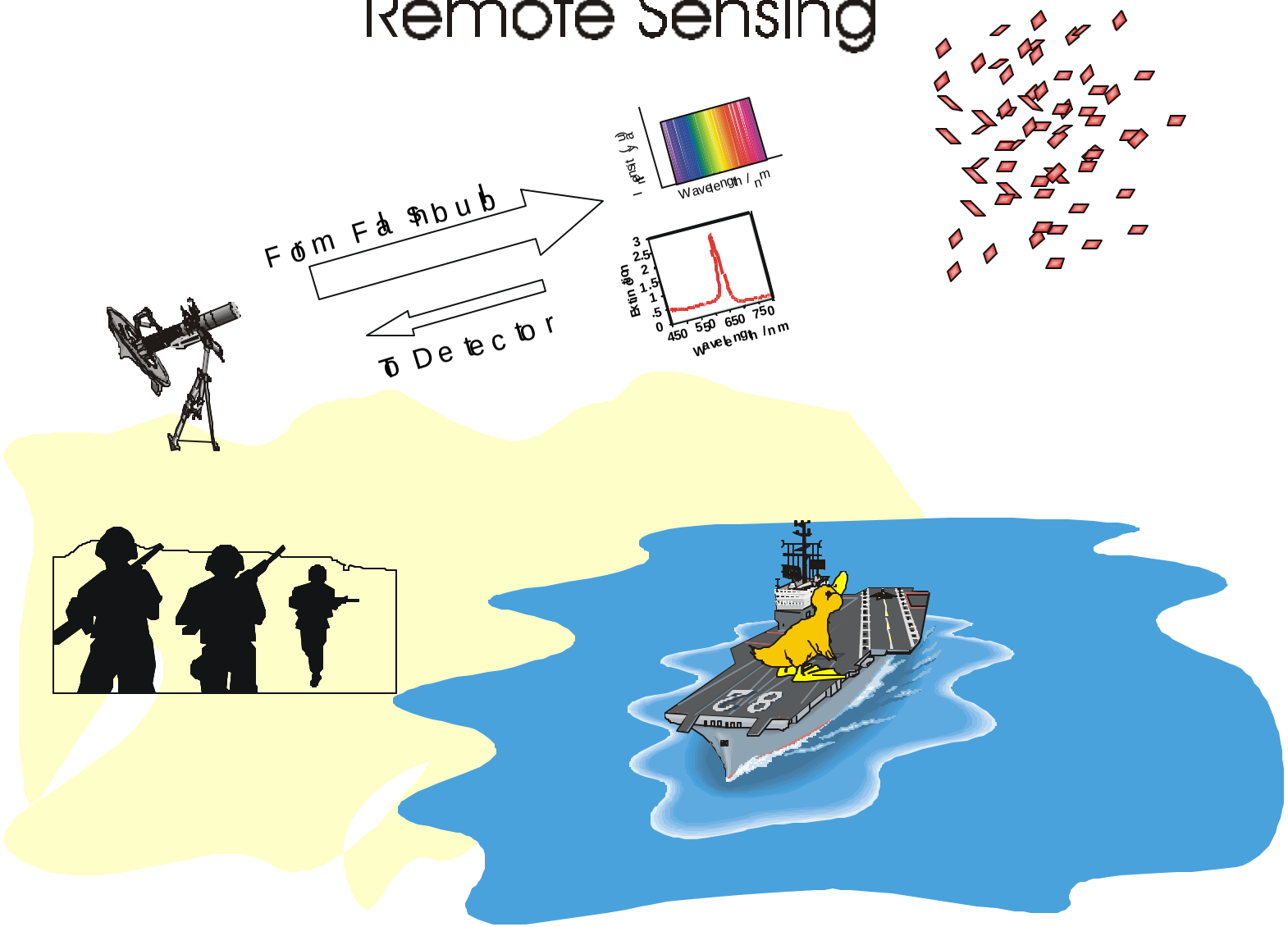
Glucoview™
Subcutaneous Insert

S. A. Asher, Department of Chemistry

PCCA Sensing Array for Glucose, pH, Recreational Pharmaceuticals and Alcohol, Stress Hormones, etc.

Subcutaneous Sensors

Remote Sensing



Collaborators:

Professor Rob Coalson	University of Pittsburgh
Professor Ajay Sood	Indian Institute of Science
Dr. Rasu Kesavamoorthy	Indira Gandhi Centre for Atomic Research
Professor Craig Wilcox	University of Pittsburgh

Graduate Students:

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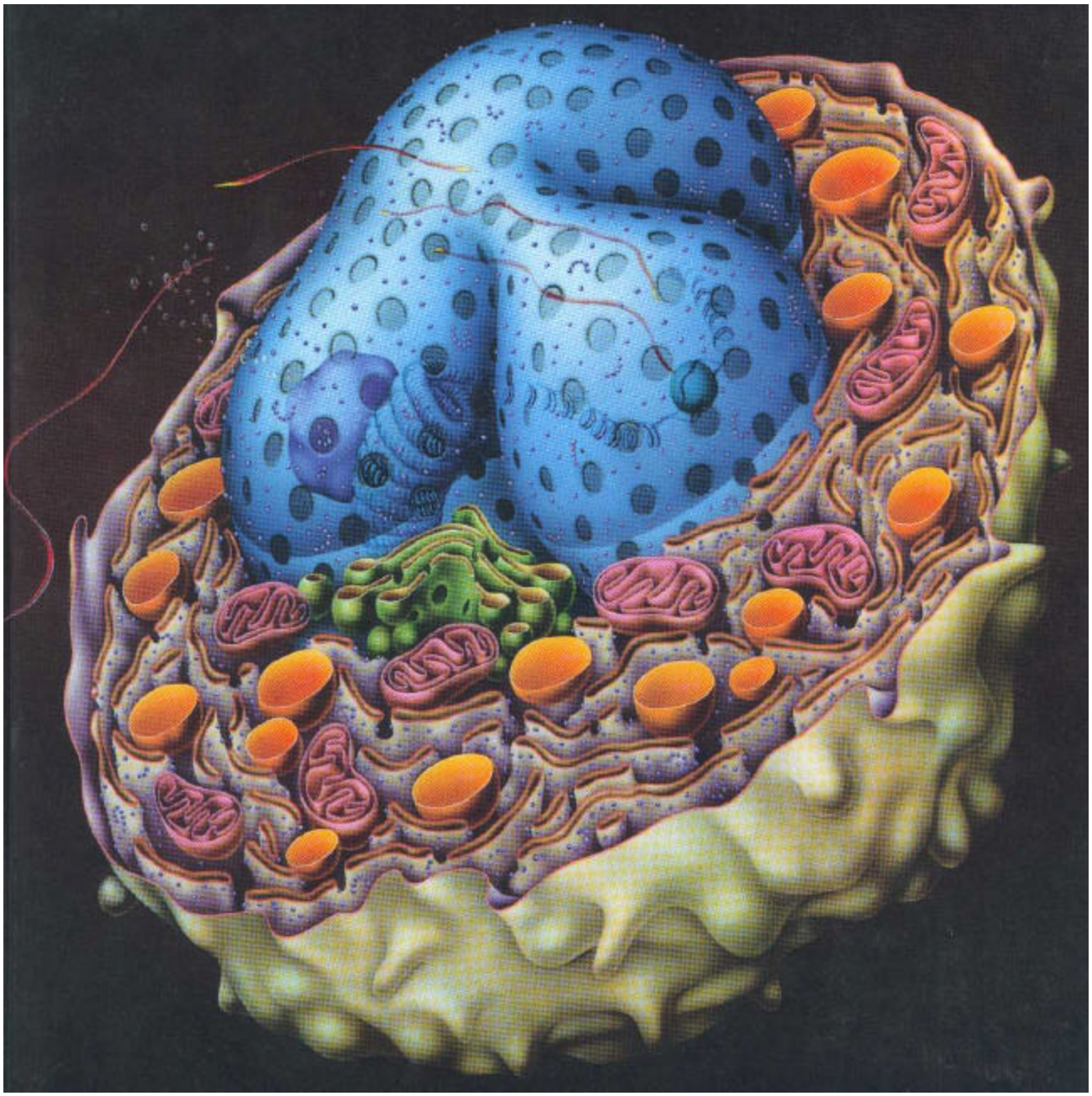
Dr. Perry Flaugh	Sun Oil
Dr. Jim Conners	Institute of Paper Chemistry
Charles Brnardic	Eli Lilly
Zhijun Wu	Monsanto
Dr. John Holtz	Katz School of Business
Guisheng Pan	Colgate Palmolive
Dr. Lei Liu	PraxAir
Jesse Weissman	UniLever
Hua Zhang	
Jonathan Keim	
Marta Kamenjicki	
Michael Baltusavich	
Chad Reese	

Post Docs:

Dr. Sesh Jagannathan	Eastman Kodak
Dr. Panos Photinos	S. Oregon State University
Dr. Song-Yuan Chang	EM Industries
Dr. Albert Tse	Reichhold Chemical
Dr. Hari Sunkara	DuPont
Dr. Calum Munro	PPG Industries, Inc.
Kangtaek Lee	Inje University, Korea
Wei Wang	
Igor Lednev	
Ying Wang	
Serban Peteu	
Xu Xiangling	

Funding:

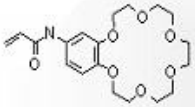
ARMY	NSF
ONR	NIH
DARPA	



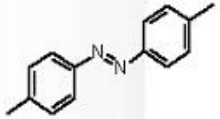
Hierarchically Assembled Intelligent Materials for Chemical Sensing and Electro-optics

Asher Research Group, University of Pittsburgh

Molecules



Molecular Recognition



Photochromics

Nanoscopic

CdS Ag

Au Fe_3O_4

Photonic and Magnetic Quantum Dots

Mesoscopic

Colloidal Particles

Macromolecules

Hydrogel Networks

Responsive Materials For

- Optical Limiters and Switches
- Chemical Sensors
- Optical Memory
- Magneto – Optical Transducers

Chemical Sensing Applications

- In vivo Clinical Sensors
- Point of Care Sensors
- Environmental Sensors
- Biological and Chemical Agents
- Remote Atmospheric Sensing

Optical Materials

- Optical Limiters for eye and sensor Protection
- Photonic Materials for Optical Switching and Memory
- Display Device Applications

Application of Nanoscience for Chemical Sensing

Science (2000) ***289***: 1757
Scanometric DNA Array Detection with Nanoparticle Probes

T.A. Taton, **C.A. Mirkin**, and R.L. Letsinger
Northwestern University, Evanston, IL

Science (2000) ***287***: 622
Nanotube Molecular Wires as Chemical Sensors

J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, **H. Dai**
Stanford University, Stanford, CA 94305

Science (1997) ***278***: 840
A Porous Silicon-Based Optical Interferometric Biosensor

V.S.-Y. Lin, K. Motesharei, K.-P.S. Dancil, **M.J. Sailor**, M.R. Ghadiri
University of California, San Diego, La Jolla, CA
The Scripps Research Institute, La Jolla, CA

Science (2001) ***291***: 443
NANOMATERIALS: Stretching the Mold

T.E. Mallouk
Pennsylvania State University, University Park, PA

J.Am. Chem. Soc. (1997) ***119***: 11306
Diffusion-Limited Size-Selective Ion Sensing Based on SAM-Supported Peptide Nanotubes (SAM – Self-assembled monolayers)

K. Motesharei and M.R. Ghadiri
The Scripps Research Institute, La Jolla, CA

. c

Nanosynthesis for Materials Development

Nanosynthesis can fill a gap in our capabilities.

Atoms. —Chemical synthesis→ Functional molecules.

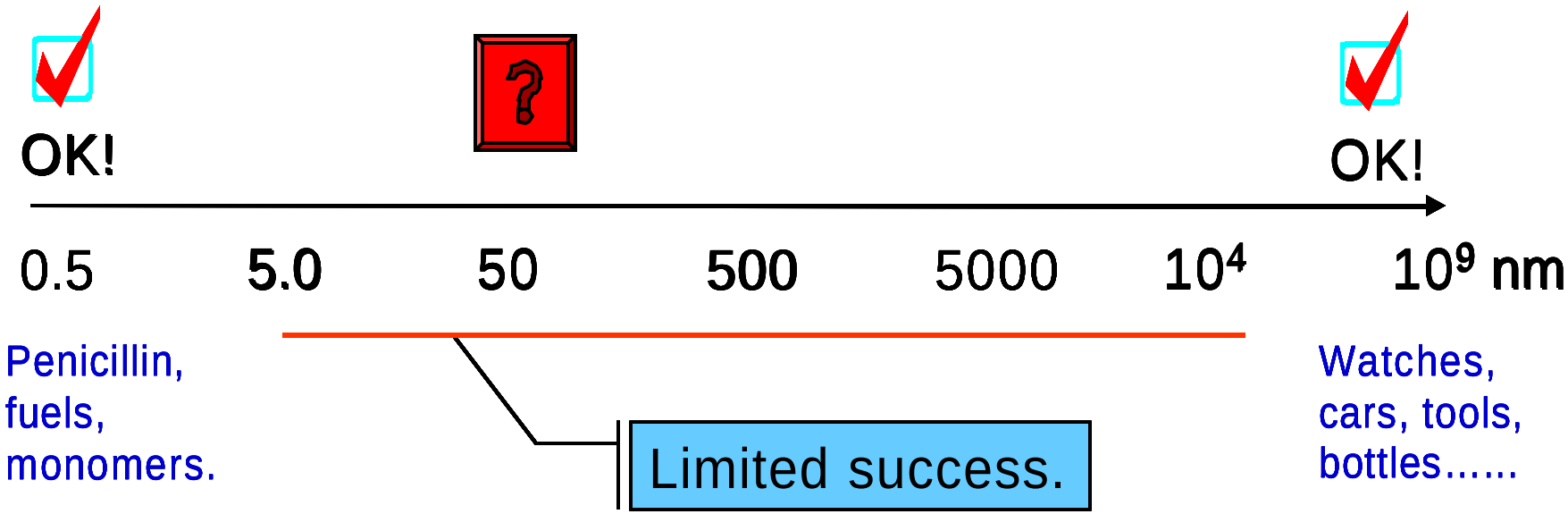
Nanofragments. —"Nano synthesis"→ Functional nanodevices.

Cast shapes and small assemblies. —Manufacturing→ Functional machines.

C. Wilcox, Department of Chemistry

Nanosynthesis for Materials Development

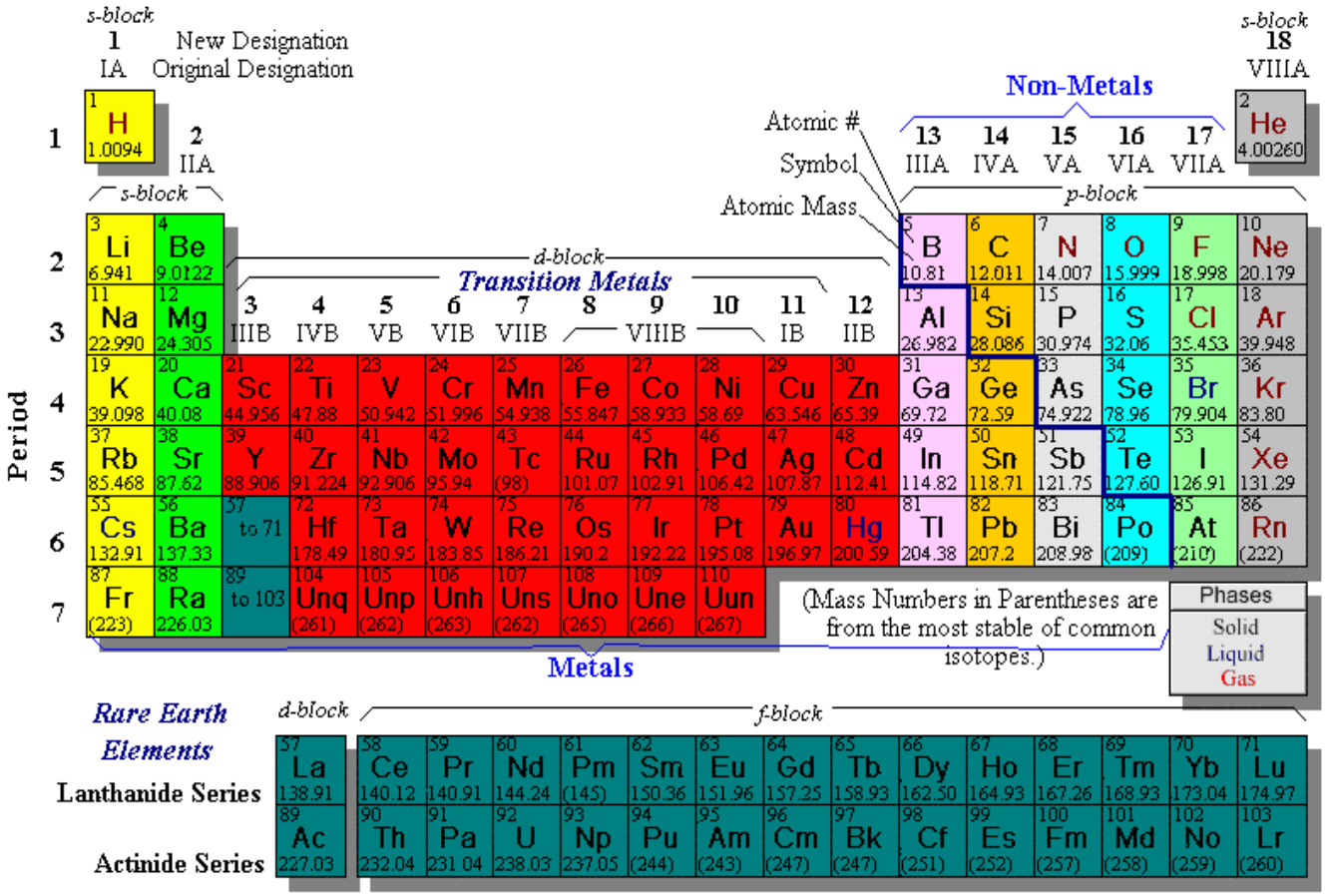
Current status in production according to scale.



<u>The goal of this subproject is to fill in the middle.</u>

S. A. Asher, Department of Chemistry

Periodic Table of the Elements



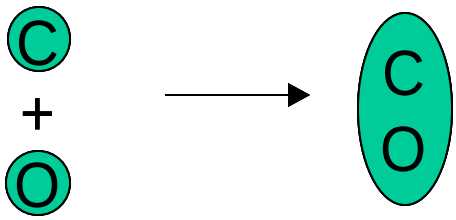
From Hyper Chemistry on the Web! http://library.thinkquest.org/2690/ptable/ptable.html

C. Wilcox, Department of Chemistry

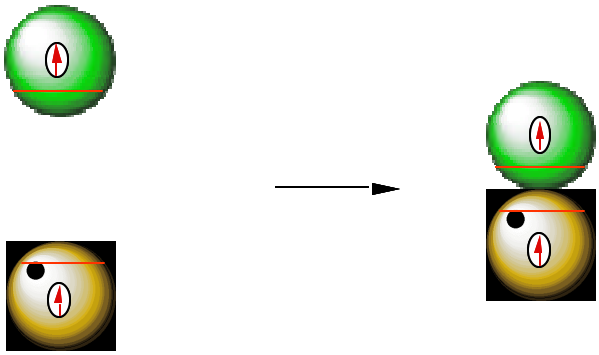
Nanotech: Process and Materials Development

The “Diatomic Molecule” of Nanosynthesis.

Chemical synthesis



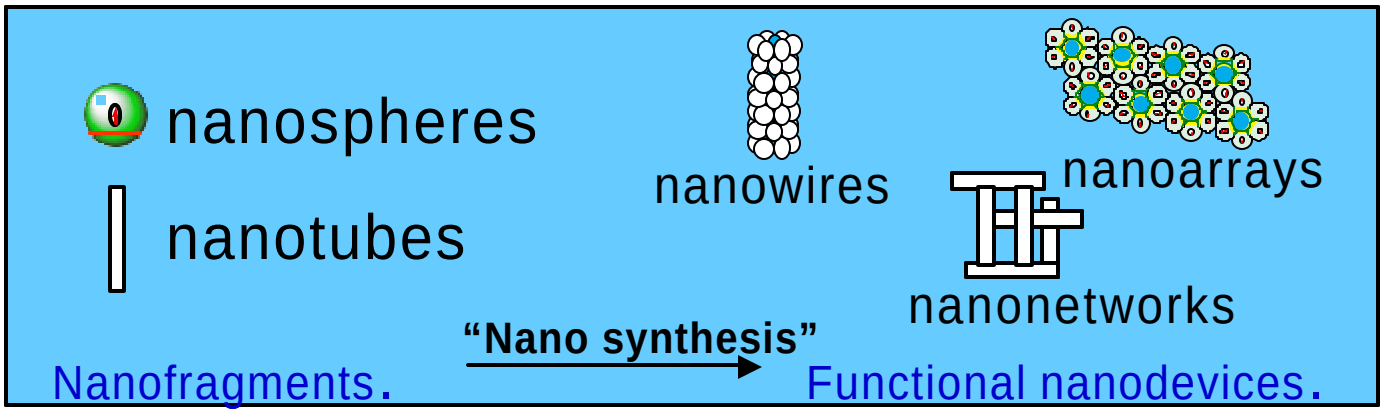
Nano synthesis



Rational control of microsphere assembly.

C. Wilcox, Department of Chemistry

Nanosynthesis for Materials Development



What do we need to succeed?

Anisotropic building blocks. (atoms, molecules)
Bonding strategies - nanoadhesives. (bonding)
Techniques for handling - dispersion. (solvation)
Separation and purification methods

Payoff: <u>Unlimited capacity to prepare mesoscale structures.</u>

S. A. Asher, Department of Chemistry

Crystalline Colloidal Self-Assembly:

MOTIF

FOR

CREATING SUBMICRON

PERIODIC SMART MATERIALS

S. A. Asher, Department of Chemistry

CRYSTALLINE COLLOIDAL ARRAYS CONTAINING MOLECULAR RECOGNITION AGENTS: CHEMICAL SENSING MATERIALS

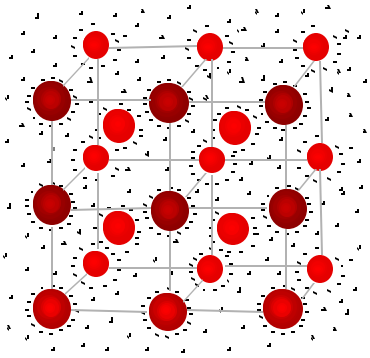
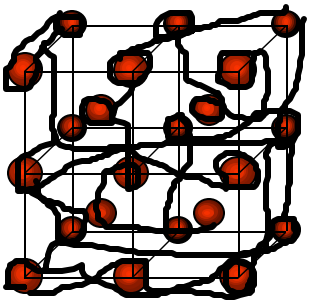
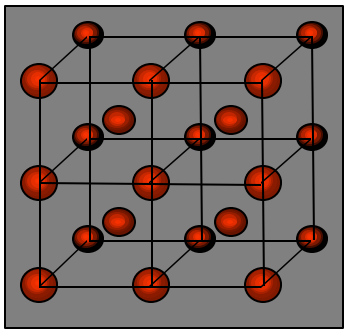
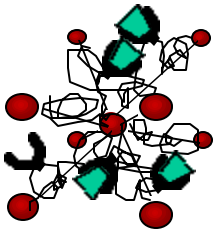
A MOTIF FOR SENSING

ALL, MANY, SOME, A FEW

CHEMICAL SPECIES

S. A. Asher, Department of Chemistry

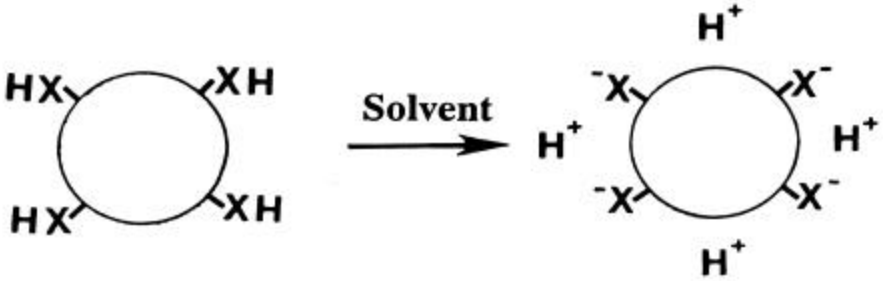
Mesoscopically Periodic Materials

CCA	PCCA	SCCA	IPCCA
			
Self-Assembling Diffracting Structure	Hydrogel Volume Phase Transition	Rigid 3-D Periodic Materials	Electronically Chemically Thermally Responsive Materials
Fragile	Robust Tunable Spacings	Rugged	Smart Materials
Optical Filters	Optical Filters NLO Switches Optical Limiters	Optical Filters NLO Switches Optical Limiters	Agile Optical Filters Chemical Sensing Display Devices

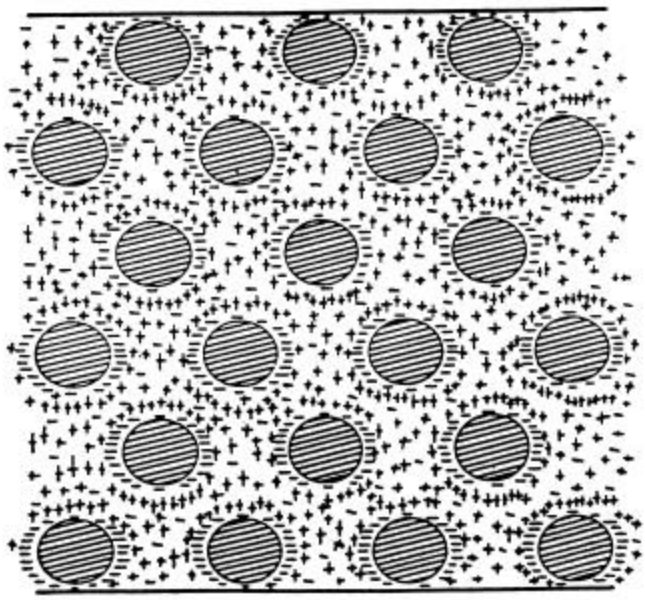
S. A. Asher, Department of Chemistry

Crystalline Colloidal Arrays

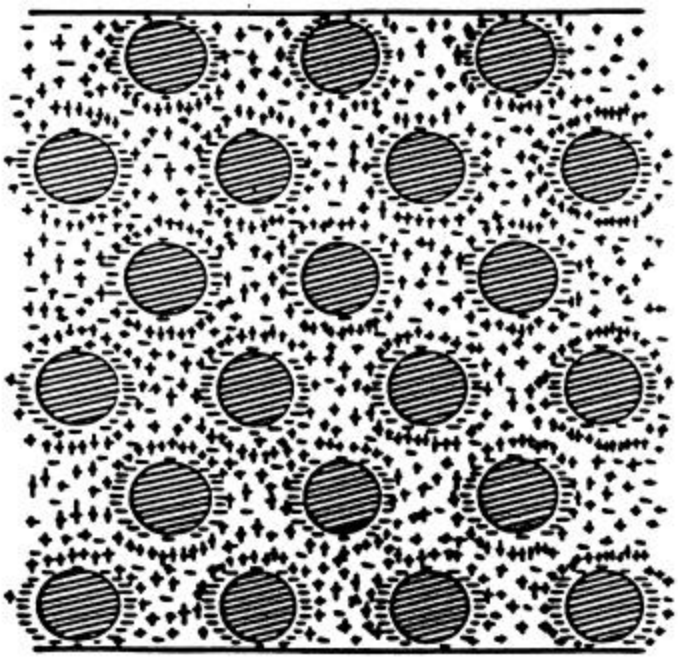
1. Fabricated From Colloidal Particles



2. Particles Self Assemble Into 3-D Ordered Crystal Structure



For 10^{13} spheres/cc <==> Crystalline Colloidal Array



Spacings only depend upon the Particle Number Density and Crystal Structure.

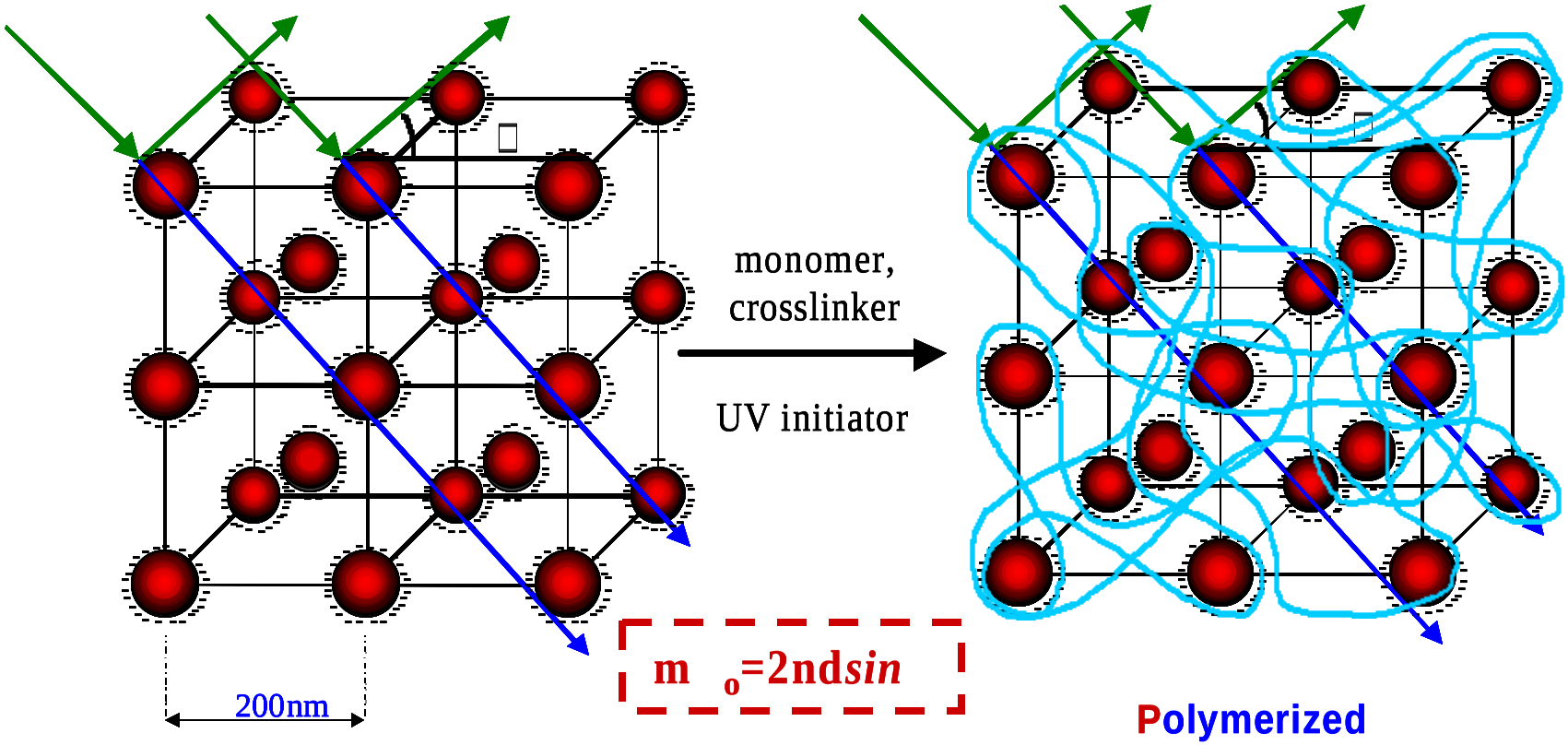
Bragg Diffraction occurs with Phenomenal Efficiency

Transmittance < 10^{-8} for 0.5 mm Thickness

- **Dynamical Diffraction Limit**

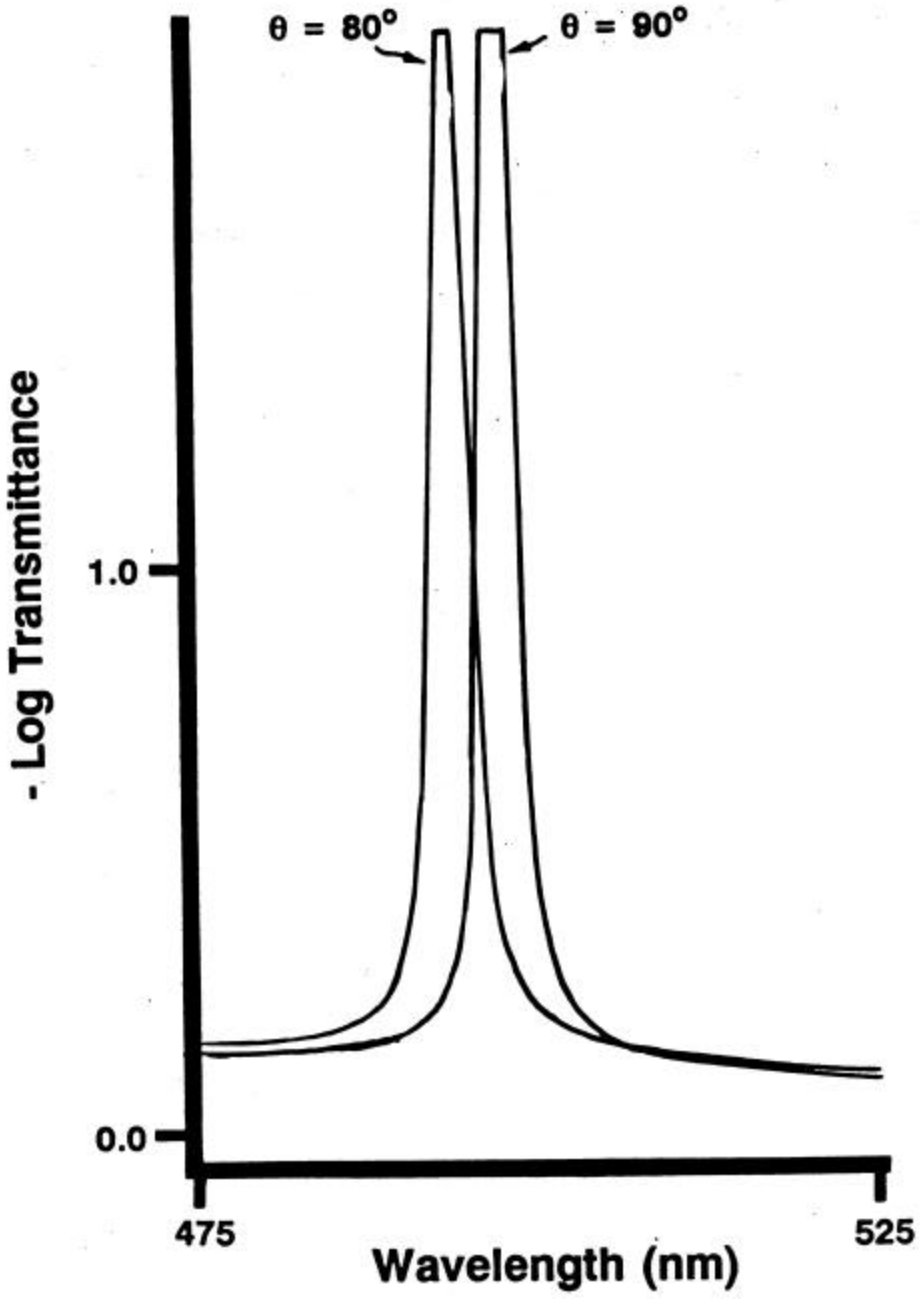
S.A. Asher, Department of Chemistry, University of Pittsburgh

Introduction



$m_o = 2nd\sin$

Crystalline Colloidal Array

Polymerized Crystalline Colloidal Array

S. A. Asher, Department of Chemistry