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CHEMISTRY AND APPLICATIONS OF CYANOXIMES AND THEIR METAL COMPLEXES

by

Nikolay Gerasimchuk

Department of Chemistry

Missouri State University

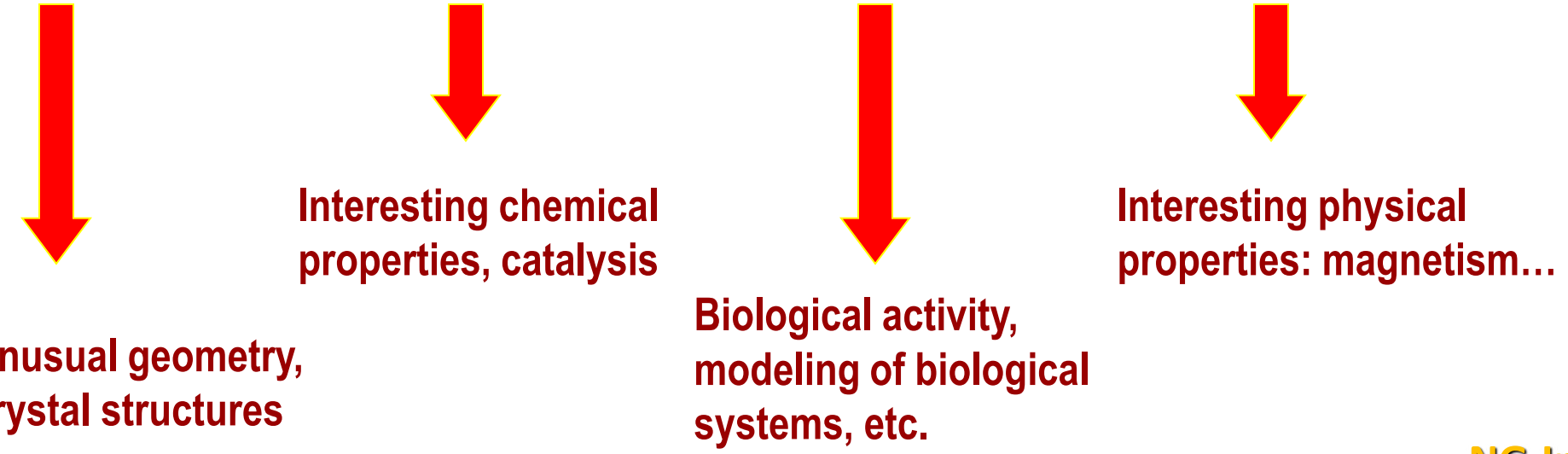
My research interests are in the area of modern inorganic chemistry.

My International designs new ligands for preparation of a variety of metal complexes for different applications.

Conventional ligand systems for coordination chemistry:

1) macrocycles: N, O-, S- crowns and their mixed donor analogs
2) aromatic macrocycles: porphyrins, phtalocyanins, texaphyrins
3) pyrazolylboranes, other tripodal ligands
4) heterocycles and heterocyclic mono-, polyamines
5) Schiff-bases

and many, many others…

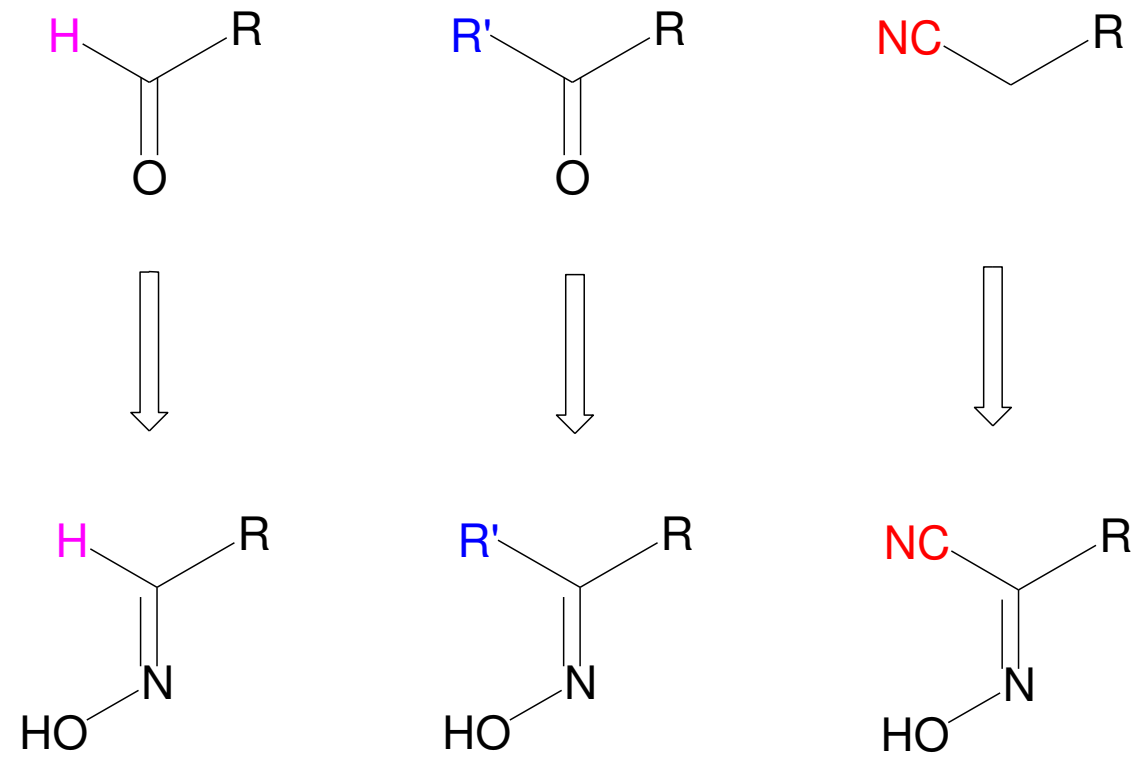


Unfortunately, many of them represent a boring set of tools…

My goal is to design universal, better set of tools for different and specific applications!

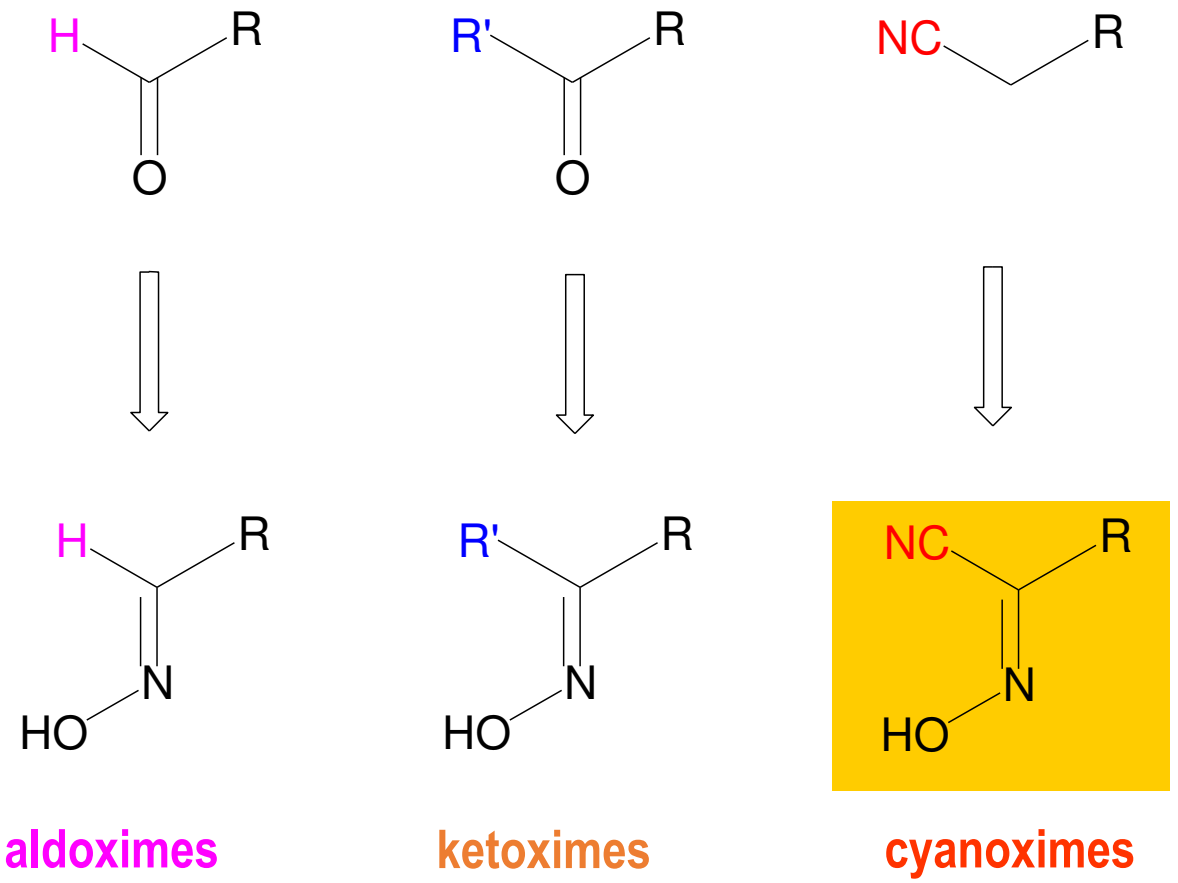
My choice of ligands is oximes, but not the usual ones!

Types of oxime and their precursors.

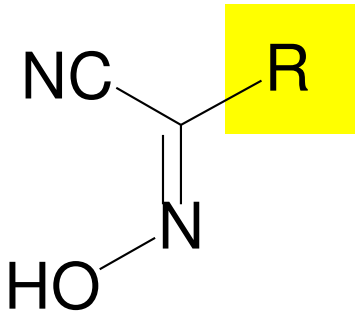


aldoximes ketoximes cyanoximes

Types of oximes and their precursors.



Cyanoximes

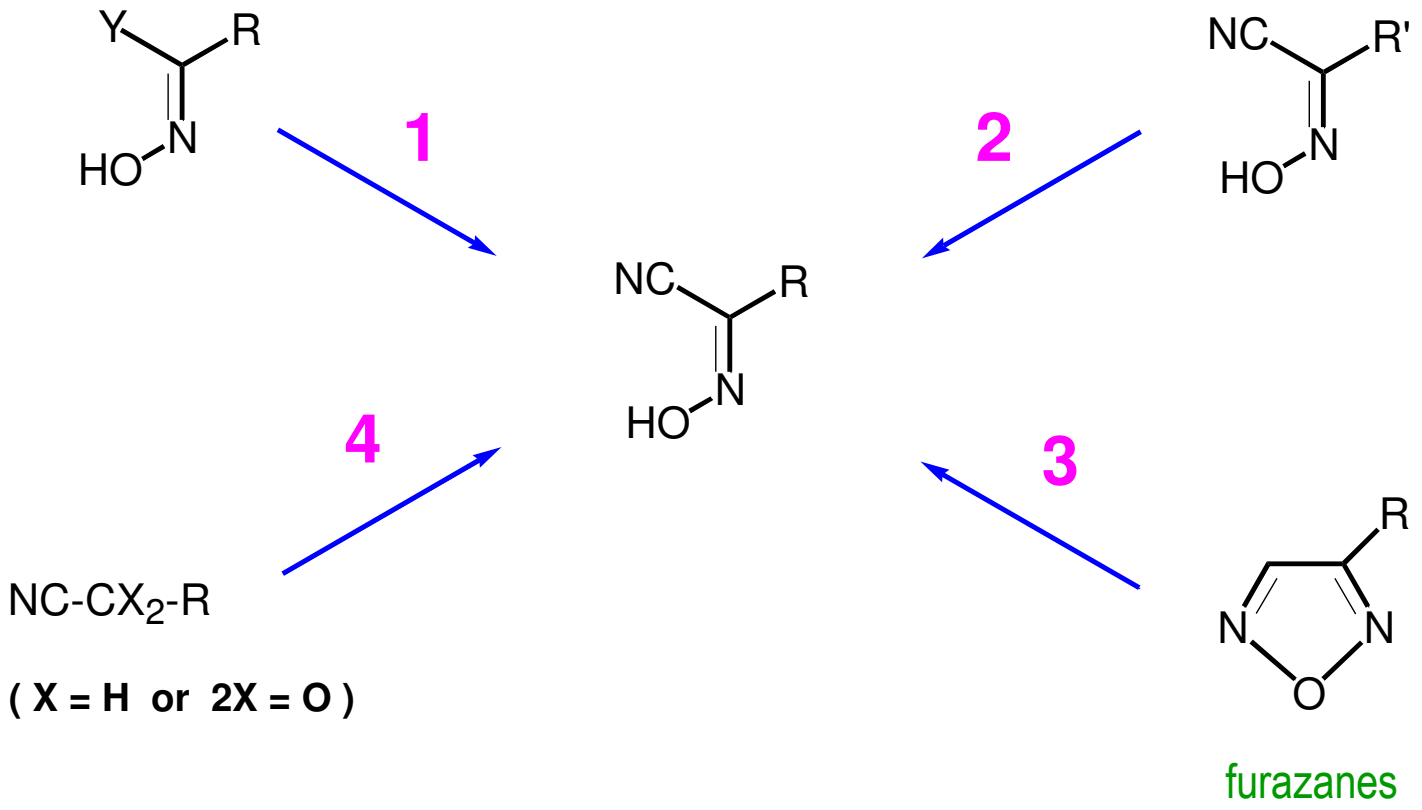


R - electronwithdrawing International

presence of the CN-International :

- significantly increases acidity of the oxime (100 - 10,000 times) which makes cyanoximes better ligands
- provides adequate solubility in organic and aqueous media (as CH_3CN, $CH_2(CN)_2$, $(CN)_2$)
- helps in crystallization of ligands and metal complexes
- allows further chemical modification of the ligand (hydrolysis, and formation of amides, carboxylic acids; addition of H_2S, H_2Se)

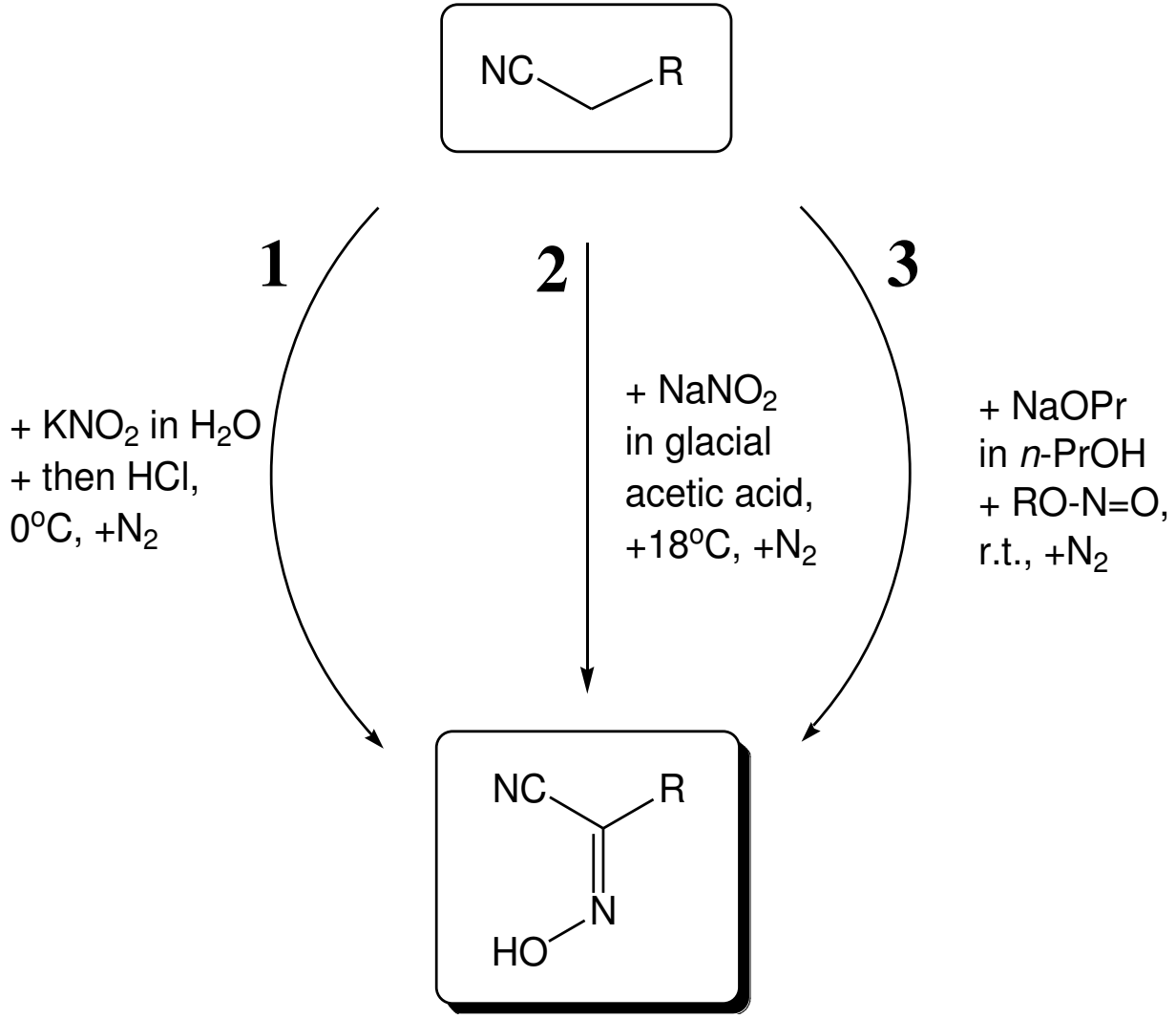
Cyanoximes preparation: general methods.



Sov. Progr. Chem., **1986,** 52, N°7, p.686.

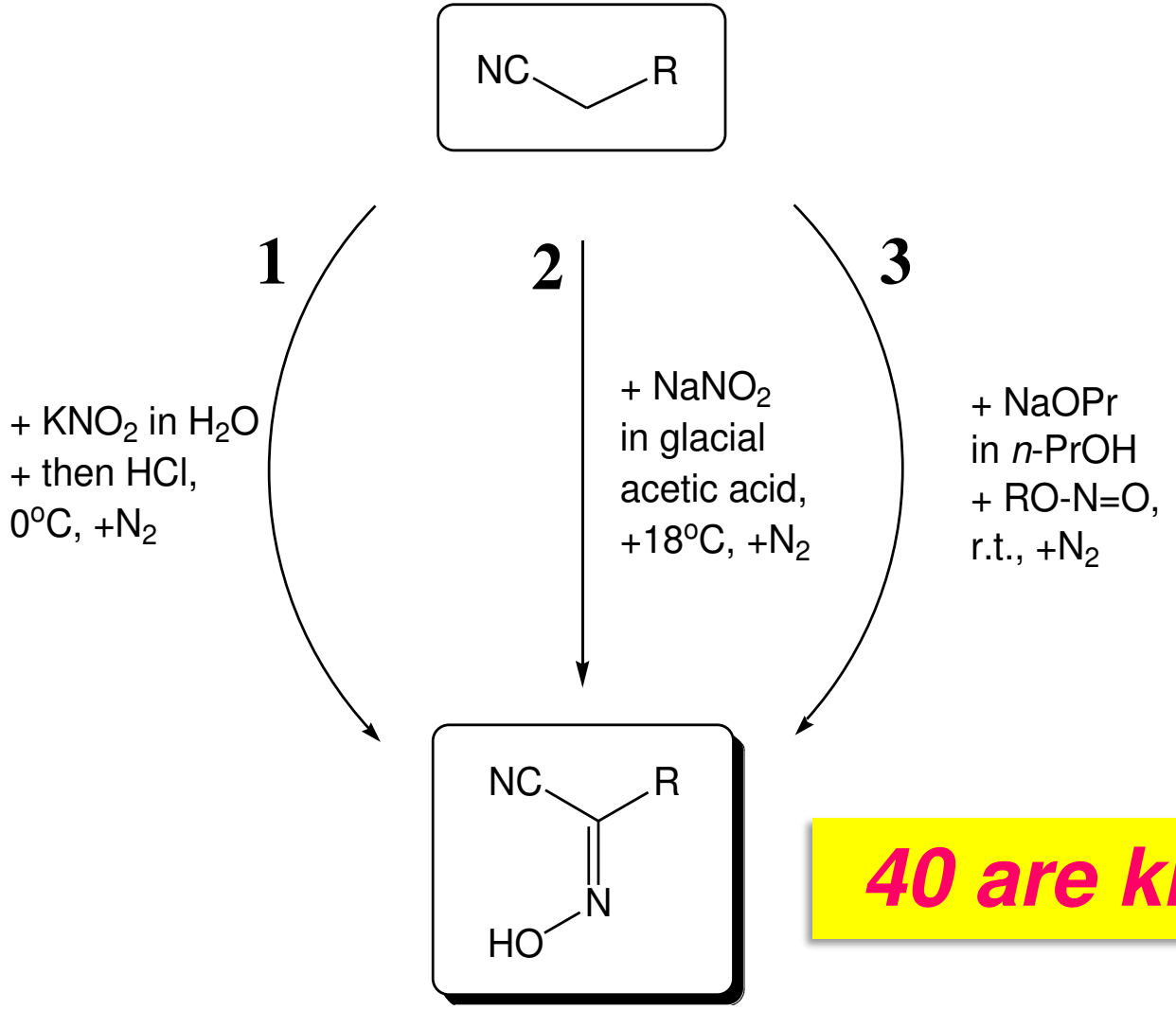
Dokl. Acad. Nauk UkSSR, **1989,** B, N°4, p.37.

Development of the Meyer reaction for synthesis of cyanoximes.



J. Coord. Chem., **2004,** 57, 1205

Development of the Meyer reaction for synthesis of cyanoximes.



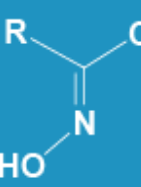
40 are known

J. Coord. Chem., **2004,** 57, 1205

Visible light insensitive
Ag(I) complexes

2

cyanoximes



3

1

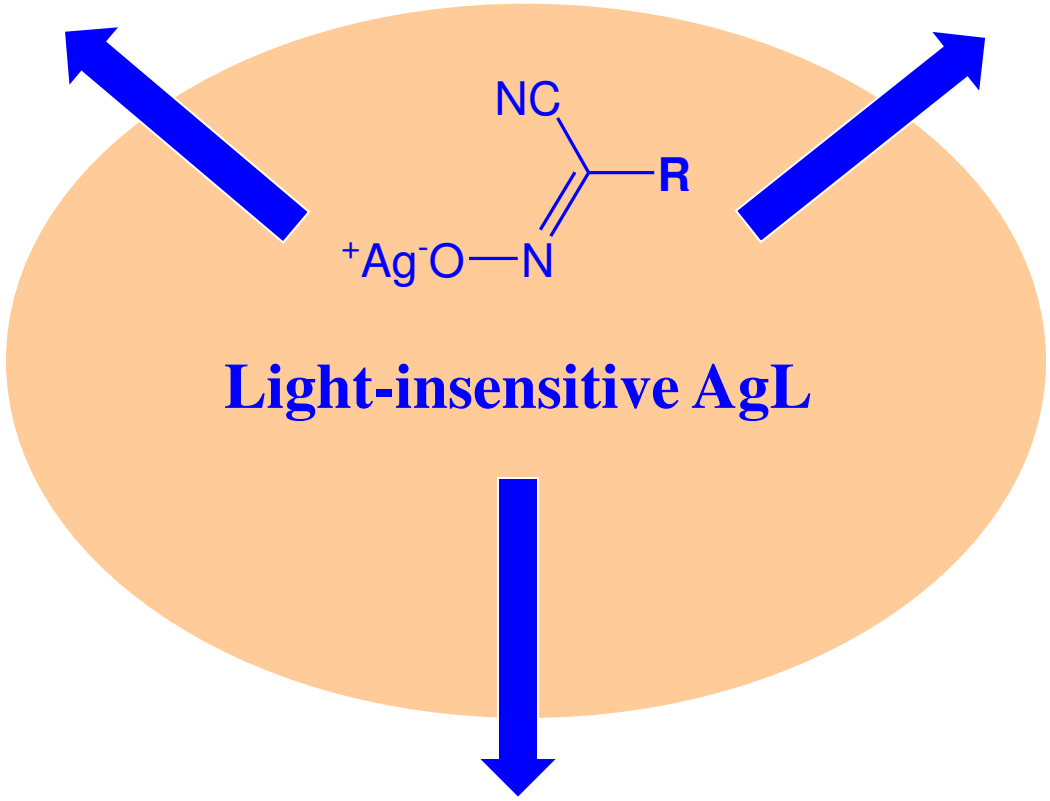
One dimensional
coordination polymers (Pt, Tl)

New cytotoxic Pd(II)/Pt(II)
compounds

Applications of silver(I) cyanoximates.

Battery-less
detectors of UV-radiation

Non-electrical sensors of
gases industrial importance



Antimicrobial compounds as
additives to implants adhesives

Polymers. **2011**, *3*, 2

The sensor works in a passive-mode, *without batteries*, and changes color similarly to pH paper!

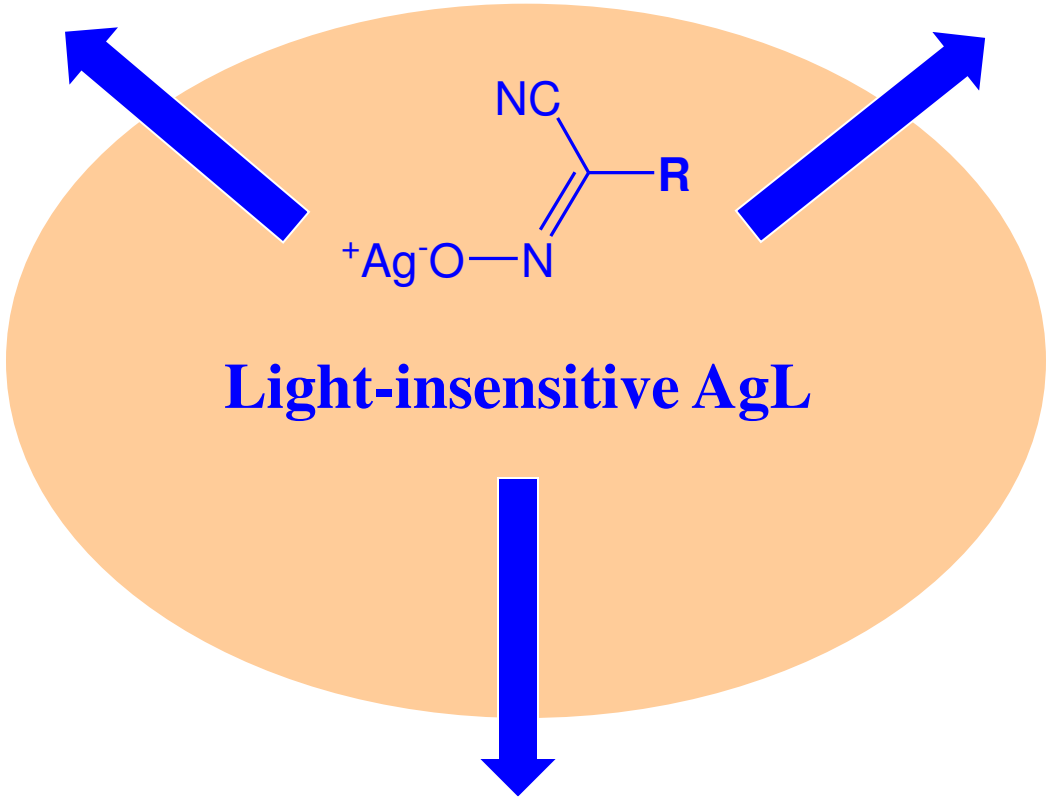
The sensor can be used as ***area detector*** for measurements of the UV-radiation fields in:

- habitable space objects,
- manufacturing sites with intensive welding (cars, other metal constructions),
- manufacturing of printed circuit boards (electronics, computers, etc.)

The sensor can be further developed as a self-adhesive film/strip that can be easily removed from the surface at any time!

Battery-less
detectors of UV-radiation

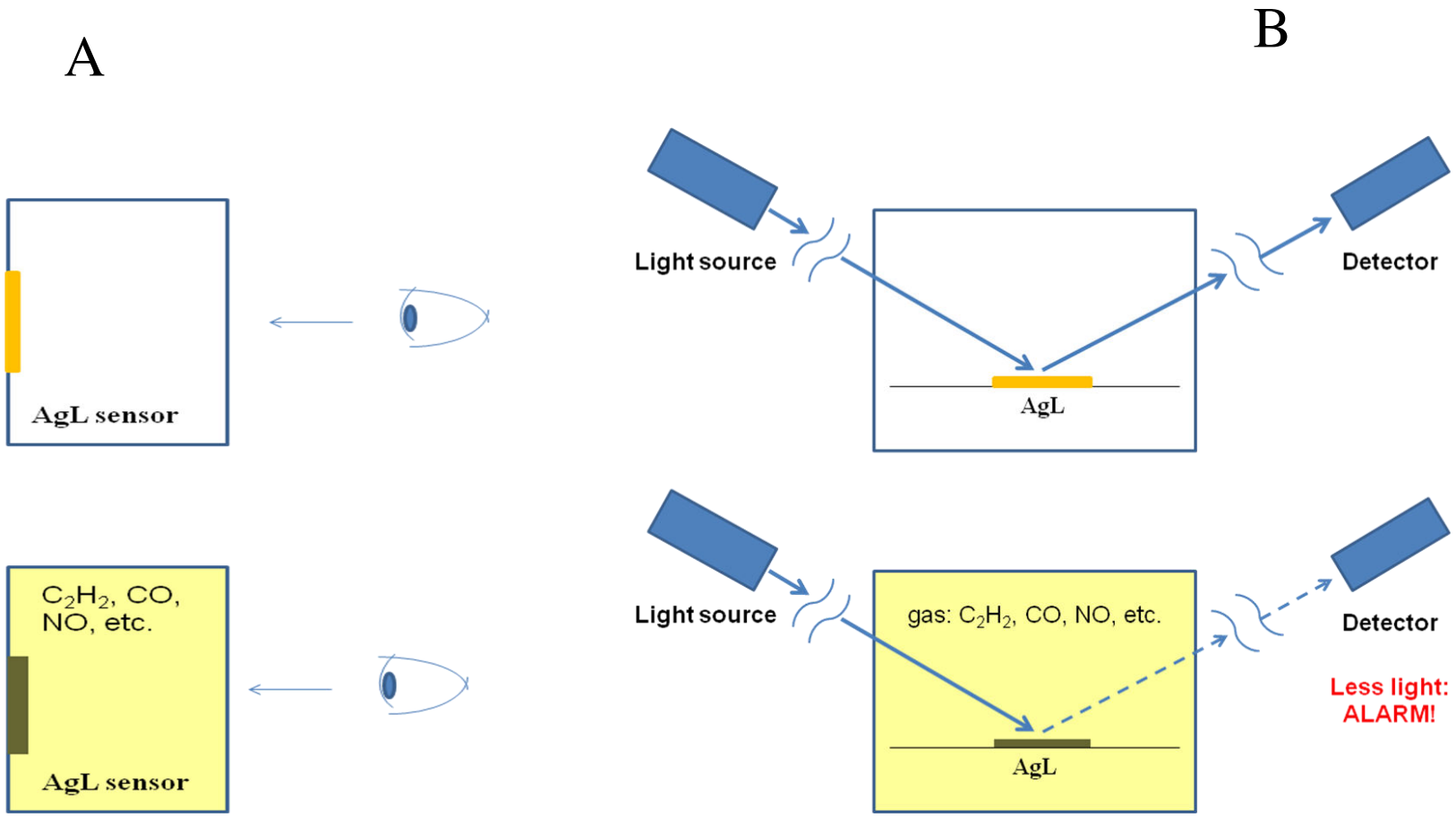
Non-electrical sensors of
gases industrial importance



Antimicrobial compounds as
additives to implants adhesives

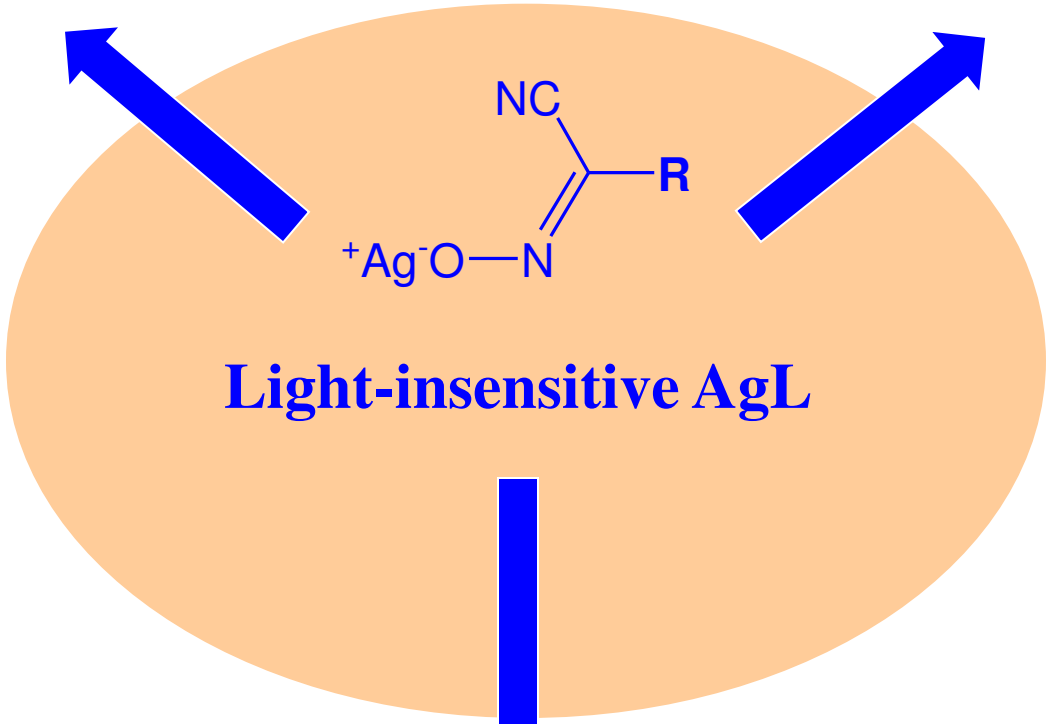
Polymers. **2011**, *3*, 2

Schematic diagram for the *visual inspection* (A), *<u>or</u> quantitative measurements* using the optoelectronic pair (B) working in closed, illumined premises.



Battery-less
detectors of UV-radiation

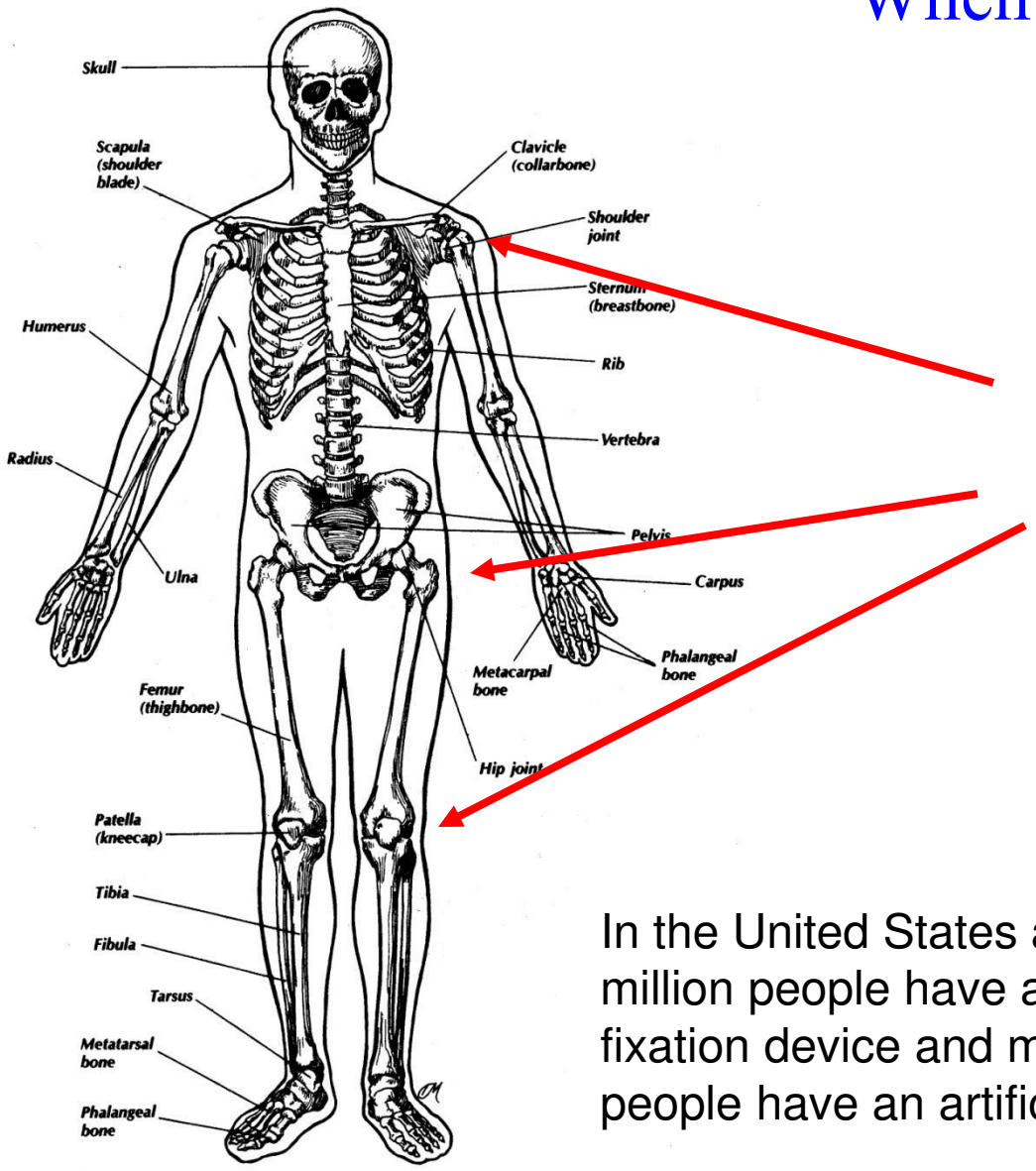
Non-electrical sensors of
gases industrial importance



Antimicrobial compounds as
additives to implants adhesives

Polymers. **2011**, *3*, 2

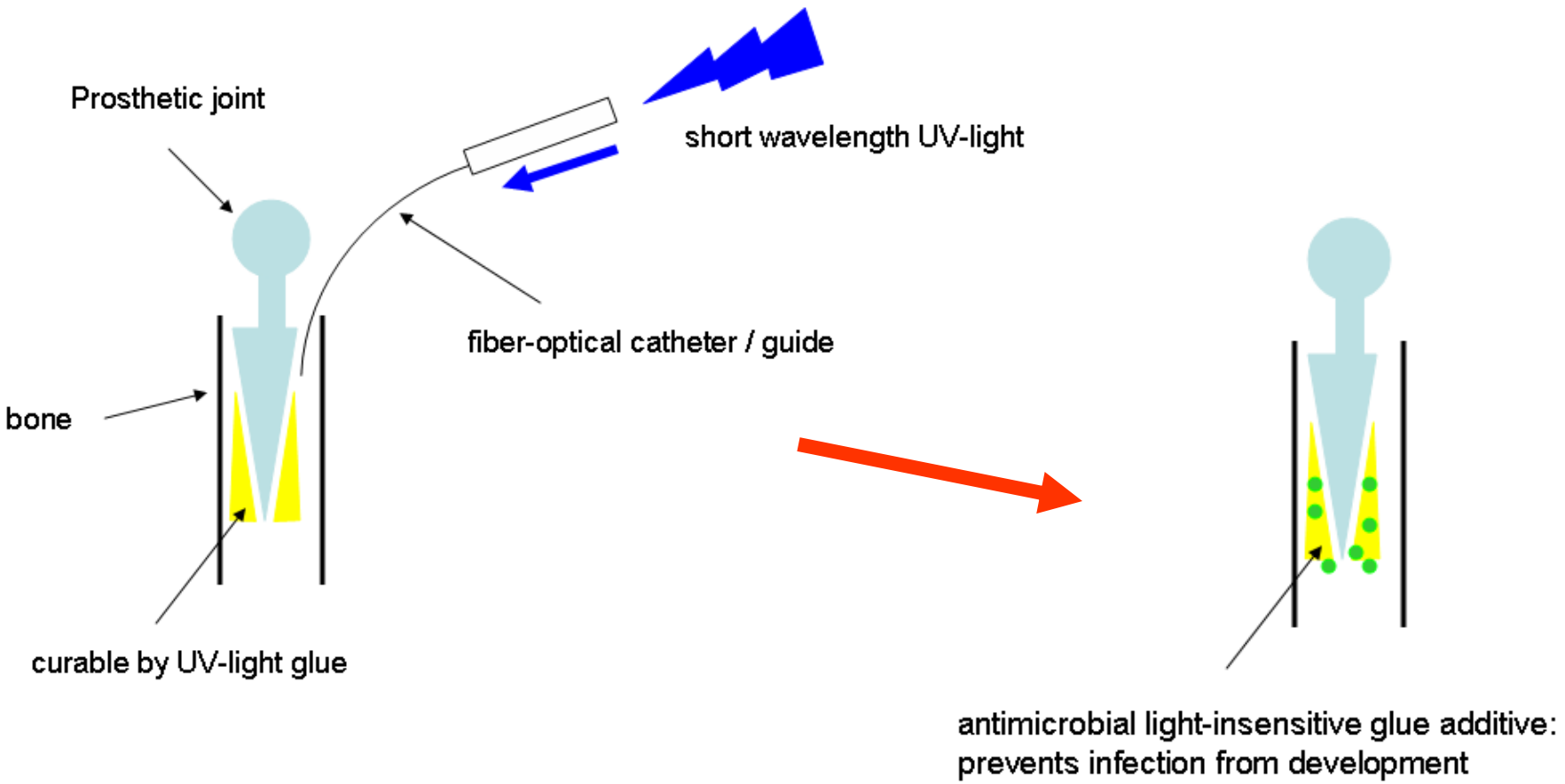
When we get old…

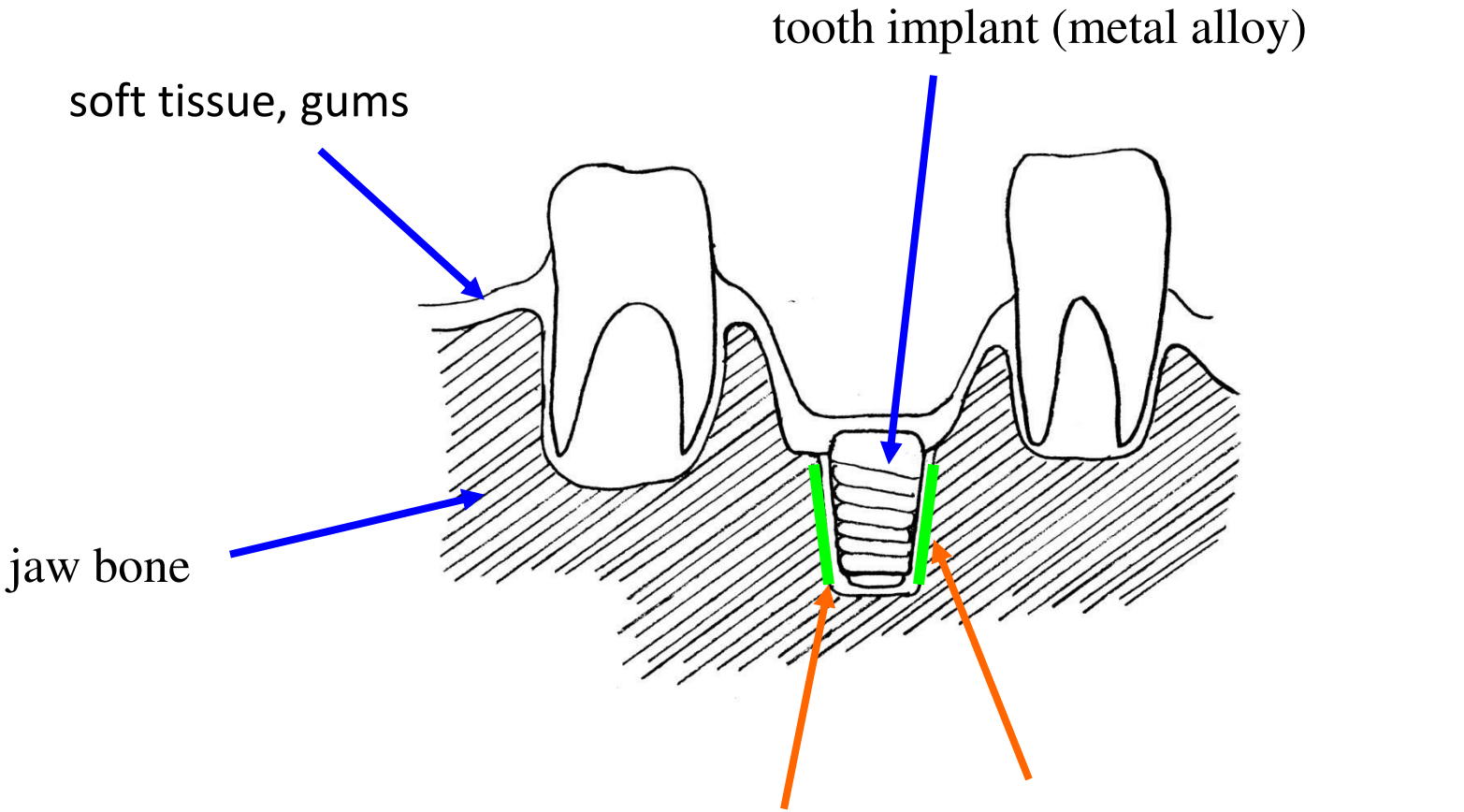


Joint
replacement therapy

In the United States alone, more than 4.4 million people have at least one internal fixation device and more than 1.3 million people have an artificial joint

Artificial joints: insertion





The US patents applications:

"Visible light-insensitive Silver(I) cyanoximates as antimicrobial additives into polymeric light curable composites used during introduction of indwelling medical devices"

Full patent, October 2012

"Antimicrobial, thermally and visible light stable silver(I) cyanoximates that inhibit biofilm formation."

Provisional patent, November 2013

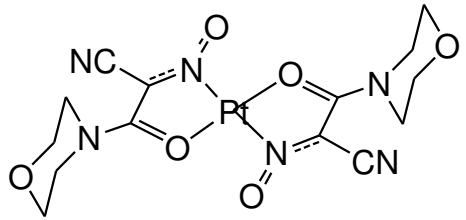
Claims are:

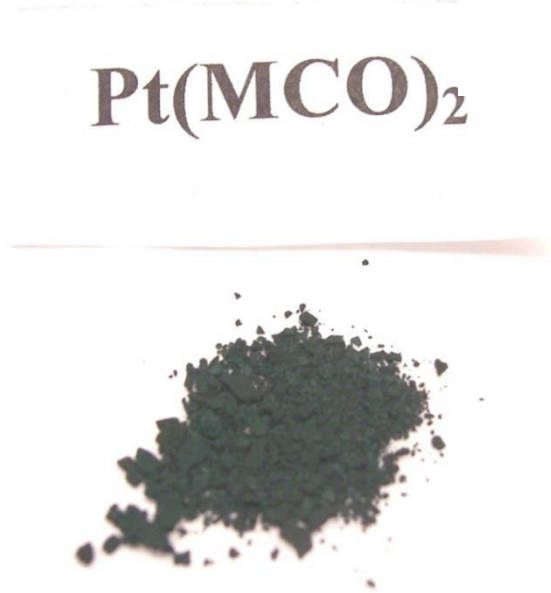
1) Water insoluble (can't leach out)
2) Easily survive minutes of curing light
3) Demonstrate antimicrobial activity
4) Thermally stable up to 150°C

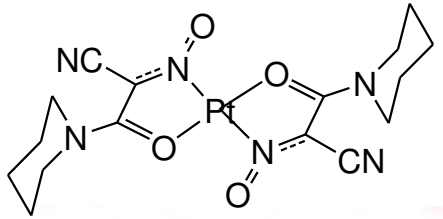
3

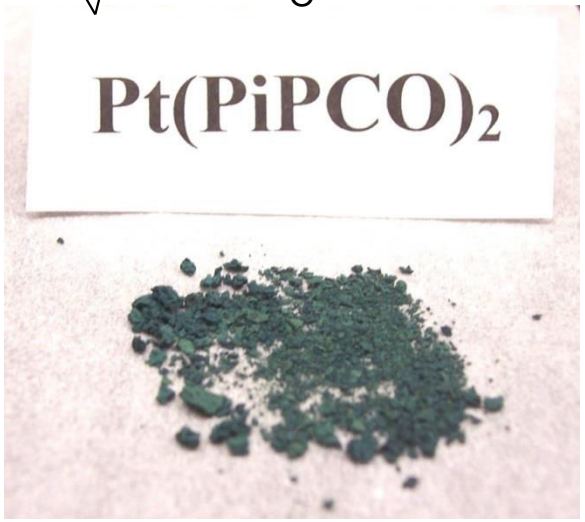
1D conducting coordination polymers

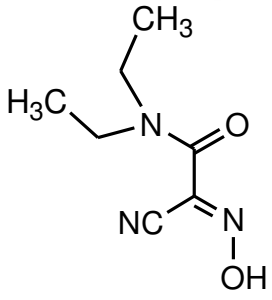
- *Pt(II/IV) mixed valence “poker chips” stacks*



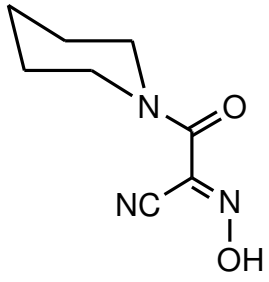




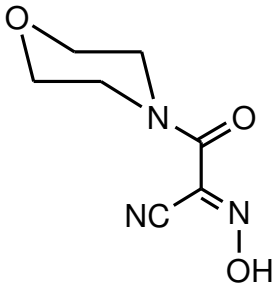




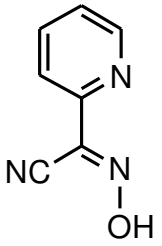
HDECO



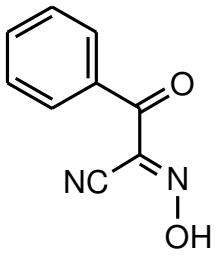
HPiPCO



HMCO

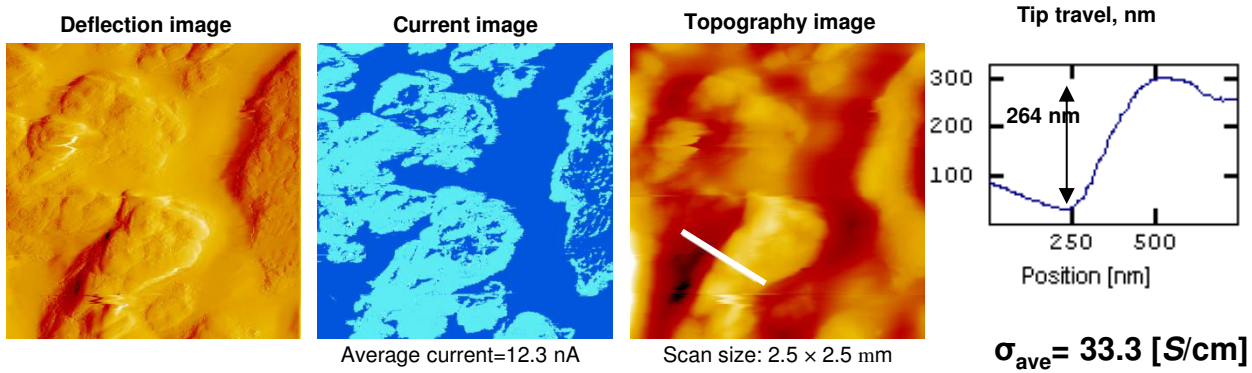


H2PCO



HBCO

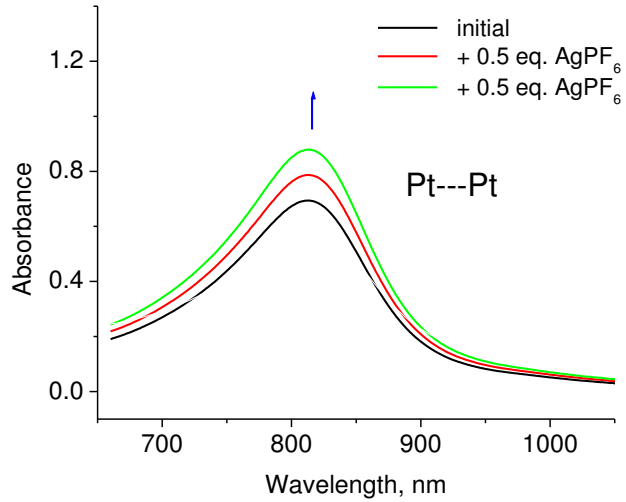
Electrical conductivity of solid samples (AFM method)

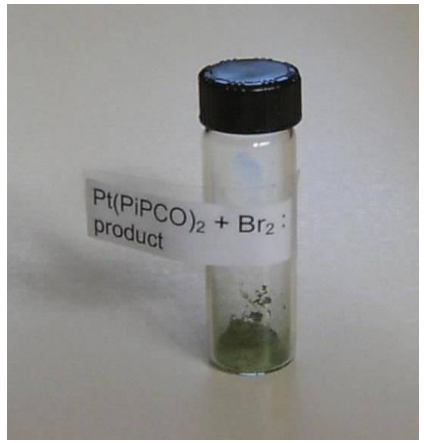


σ_{ave}= 33.3 [*S*/cm] $Pt(MCO)_2$

σ_{ave}= 22.8 [*S*/cm] $Pt(PiPCO)_2$

$Pt^{2+} + Ag^{+} \rightarrow Pt^{4+} + Ag^{0}$





σ_{ave}= 805 [*S*/cm]

mixed valence species: Pt(II/IV) !

Heat dissipation is the most pressing problem in miniature electronic devices…

Potential applications:

- molecular electronics:
  thin, conducting films that can be deposited from solutions

Chemical Sciences Related Journals

- Journal of Thermodynamics & Catalysis
- Journal of Plant Biochemistry & Physiology
- Organic Chemistry: Current Research

Chemical Sciences
Related Conferences

- Medicinal Chemistry & Computer Aided Drug Designing
- 3rd International Conference on Medicinal Chemistry & Computer Aided Drug Designing

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