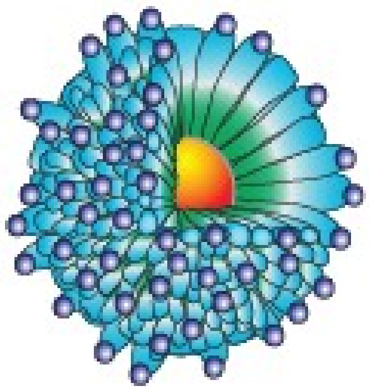
Effect of Nanomaterial Surface Properties on their Bioavailability to Cells, Fish, and Plants

Richard W. Vachet
Department of Chemistry and
Center for Hierarchical Manufacturing
University of Massachusetts Amherst

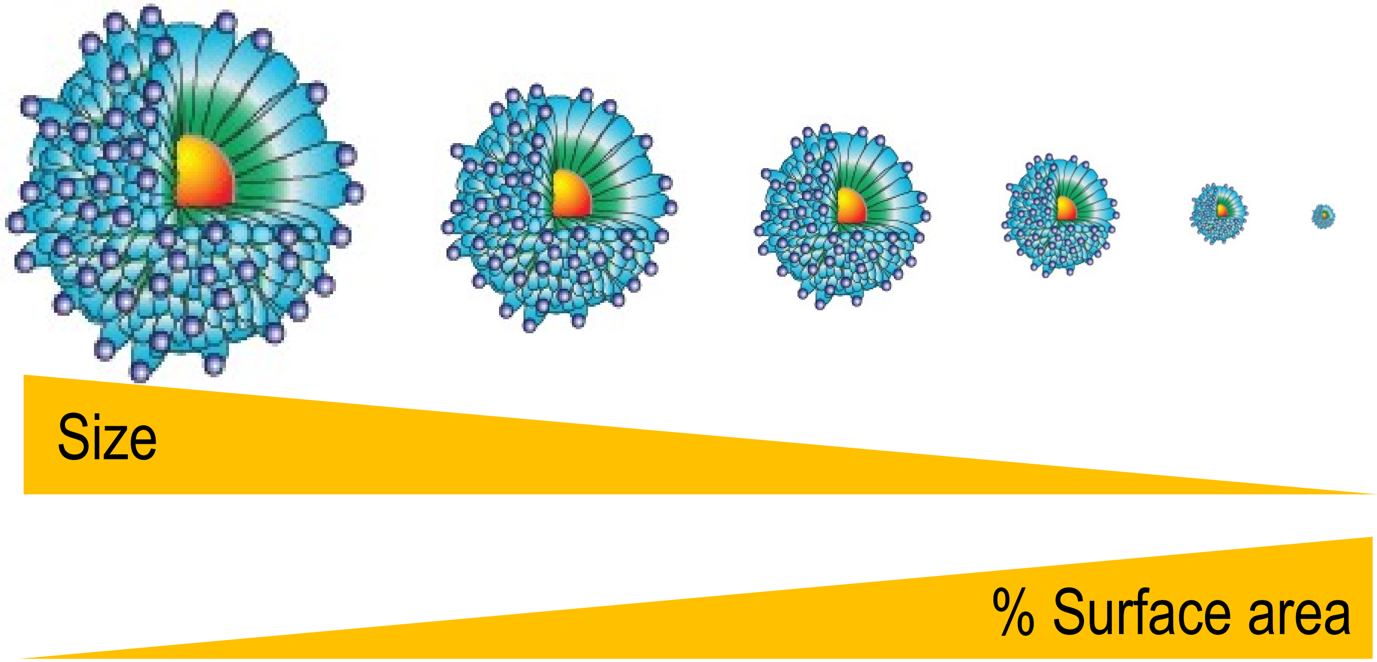
Environmental Fate, Transport, and Bioavailability of Nanomaterials



- > 1,000 commercial products with nanomaterials, ranging from electronics to cleaners to cosmetics to sporting equipment; up ~ 400% since 2006
- Increased manufacturing and use of nanomaterials will inevitably lead to their release into the environment
- What's the impact on the environment?

Effect of Nanomaterial Properties on Bioavailability

- Nanomaterial surface properties will control fate, transport, and **bioavailability**

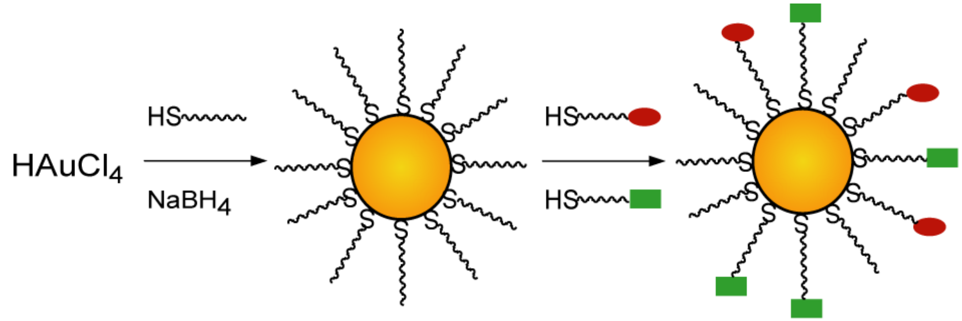


To understand how surface properties influence bioavailability:

- **Synthesize stable and well-defined nanomaterials**
- **Develop tools to track nanomaterials in complex samples**

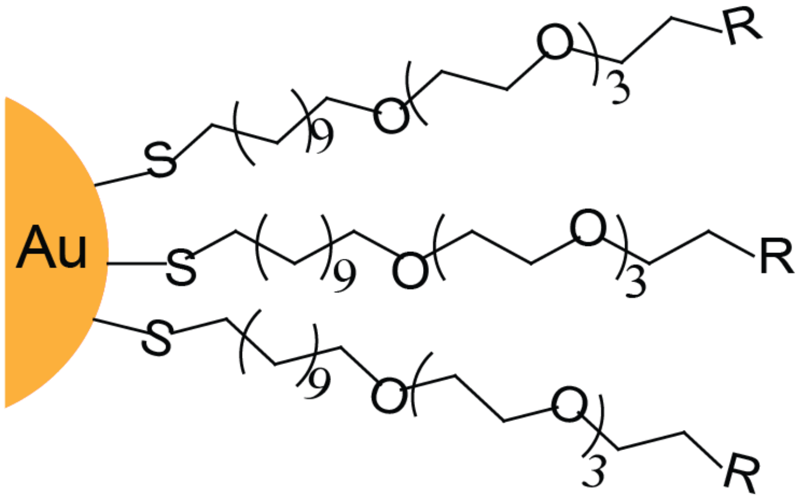
Gold Nanoparticle Models

- Easy to synthesize
- Tunable core sizes
- Core-shell design
- Well defined surface properties
- Inherently non-toxic

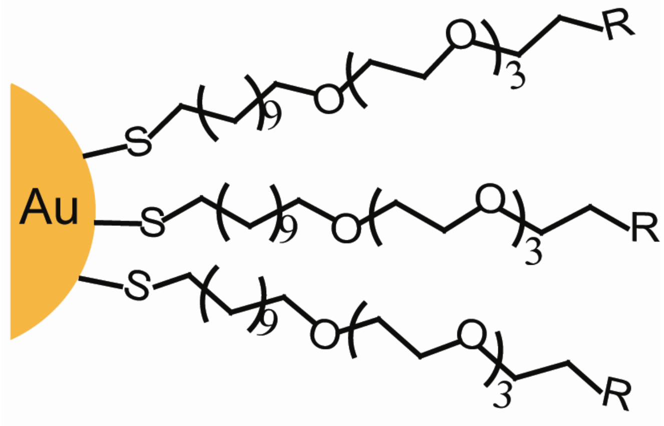


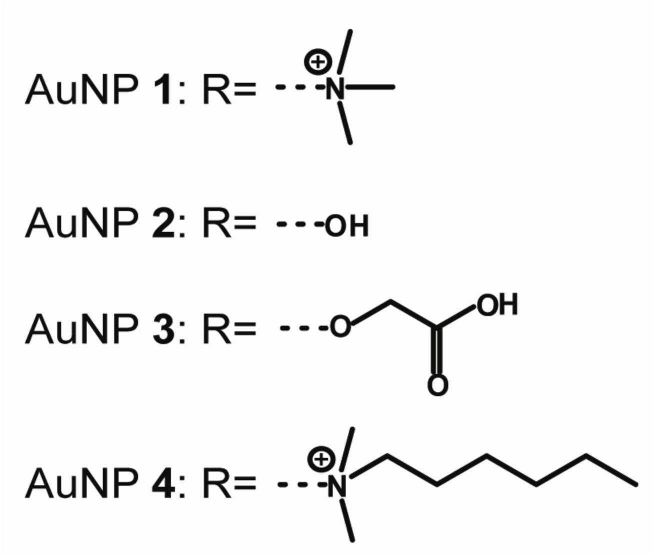
Surface Properties

- Monolayer of ligands on AuNP
- Hydrophobic layer to stabilize gold core
- TEG layer for solubility and biocompatibility
- Variable end groups define interactions



Characterization of Model AuNPs



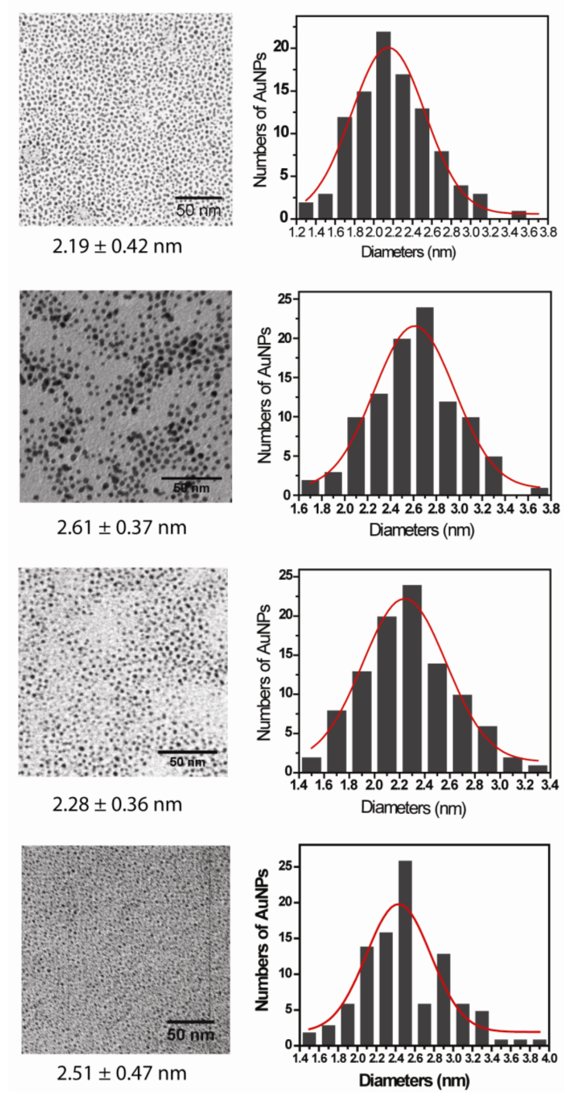


AuNP 1

AuNP 2

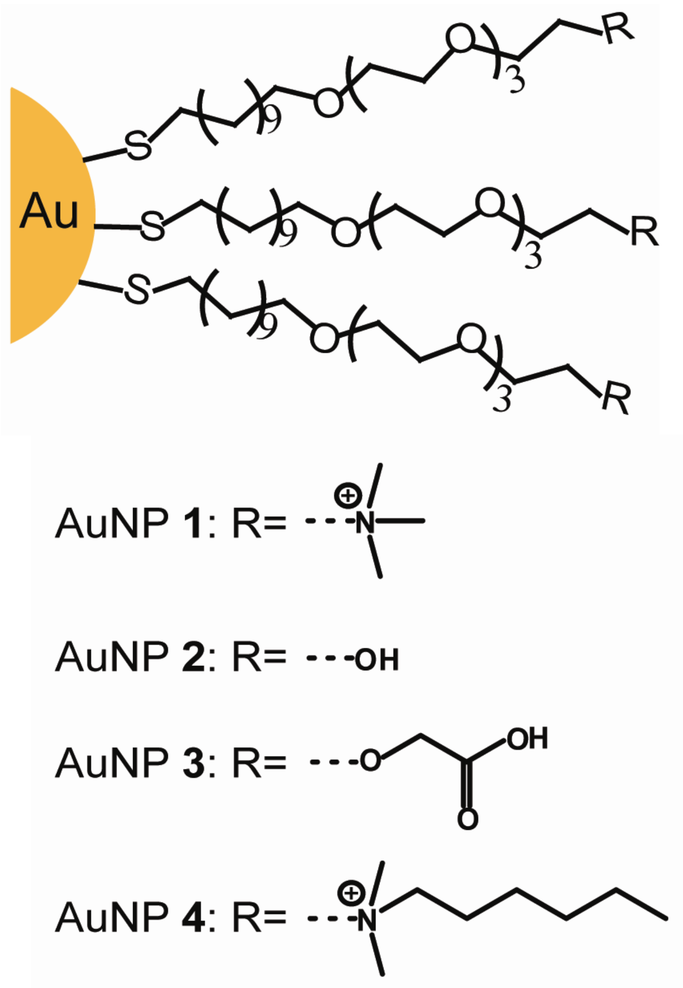
AuNP 3

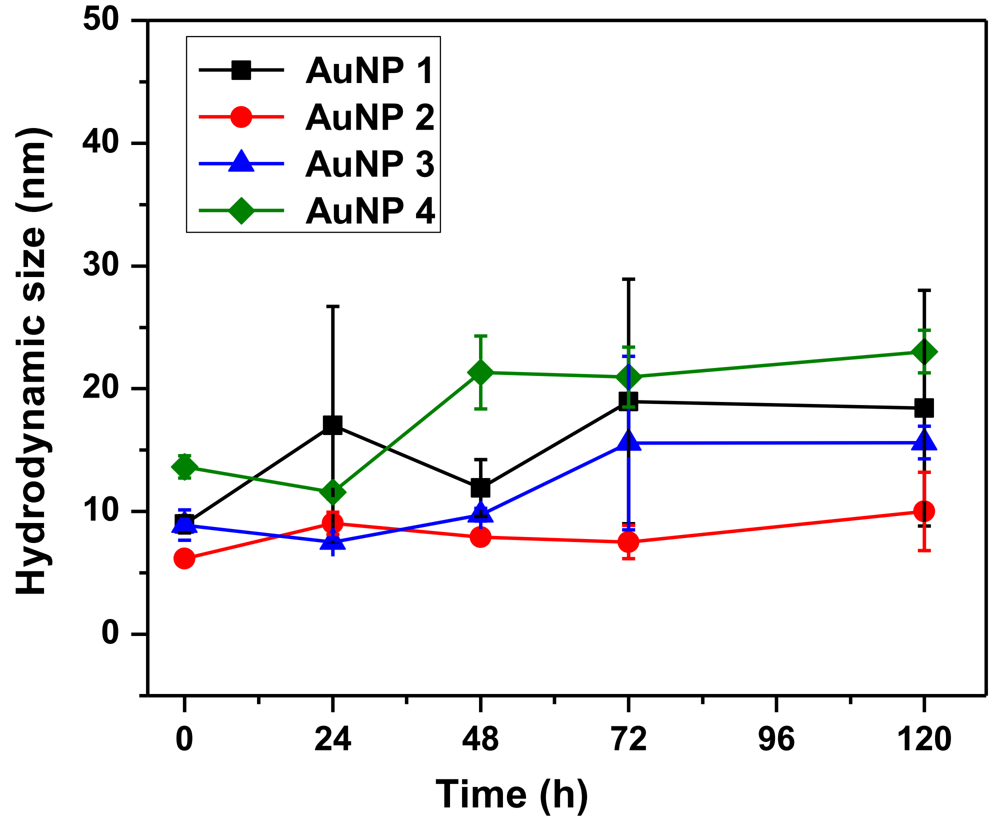
AuNP 4



AuNPs: 2 – 2.5 nm core diameters (by TEM)

Characterization of Model AuNPs

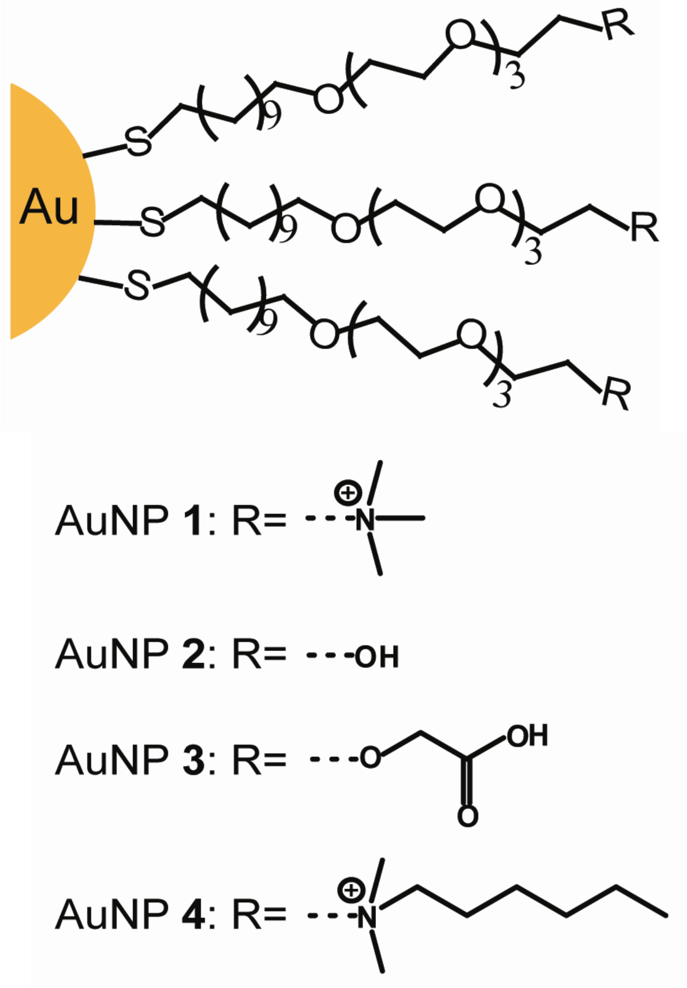


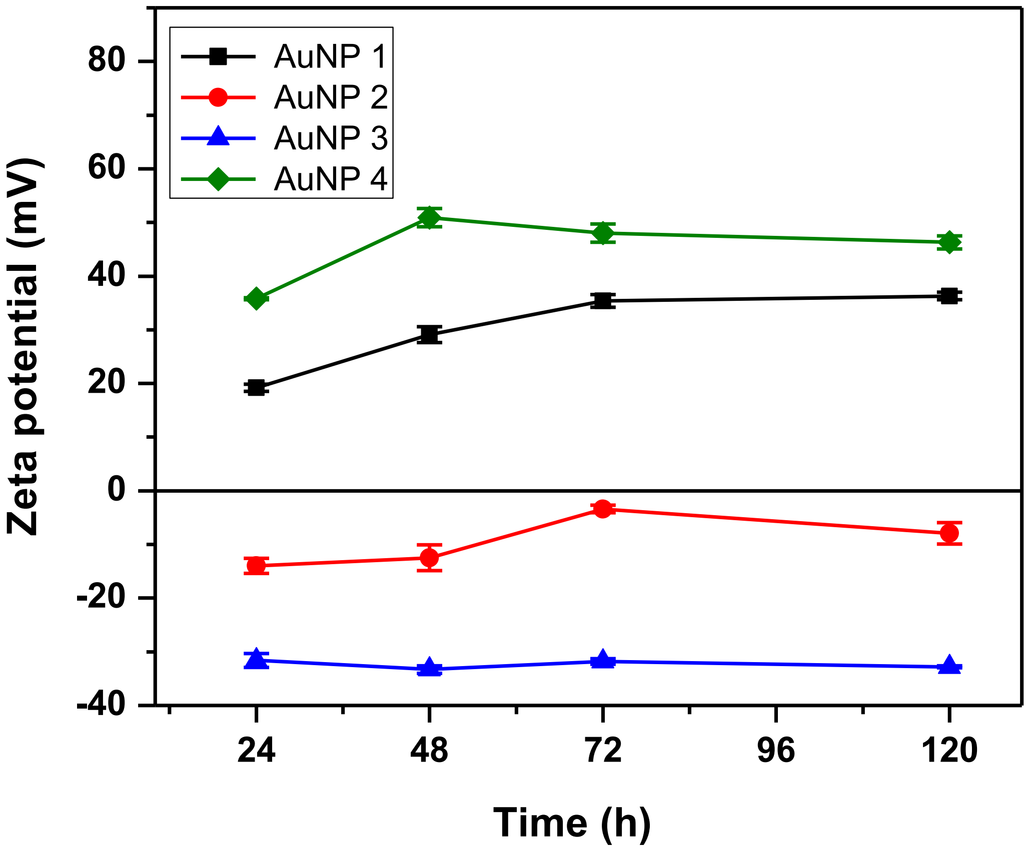


AuNPs: 7 – 20 nm core-shell diameters (by DLS)

Stable over 5 days in solution

Characterization of Model AuNPs





AuNPs: expected surface charge in solution

Influence of Surface Properties on Nanoparticle Bioavailability to Fish

Japanese medaka (*Oryzias latipes*)

Why Medaka?

• thrive in a variety of environments (i.e. pH, dissolved O_2, temperature, dissolved organic carbon) and these factors may influence bioavailability of NPs

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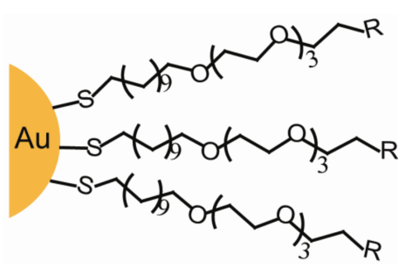

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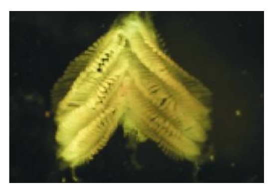

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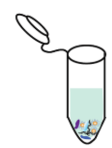
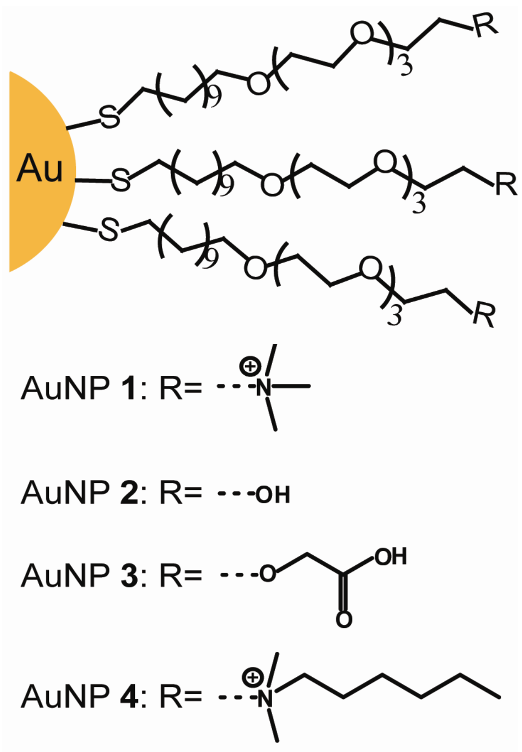
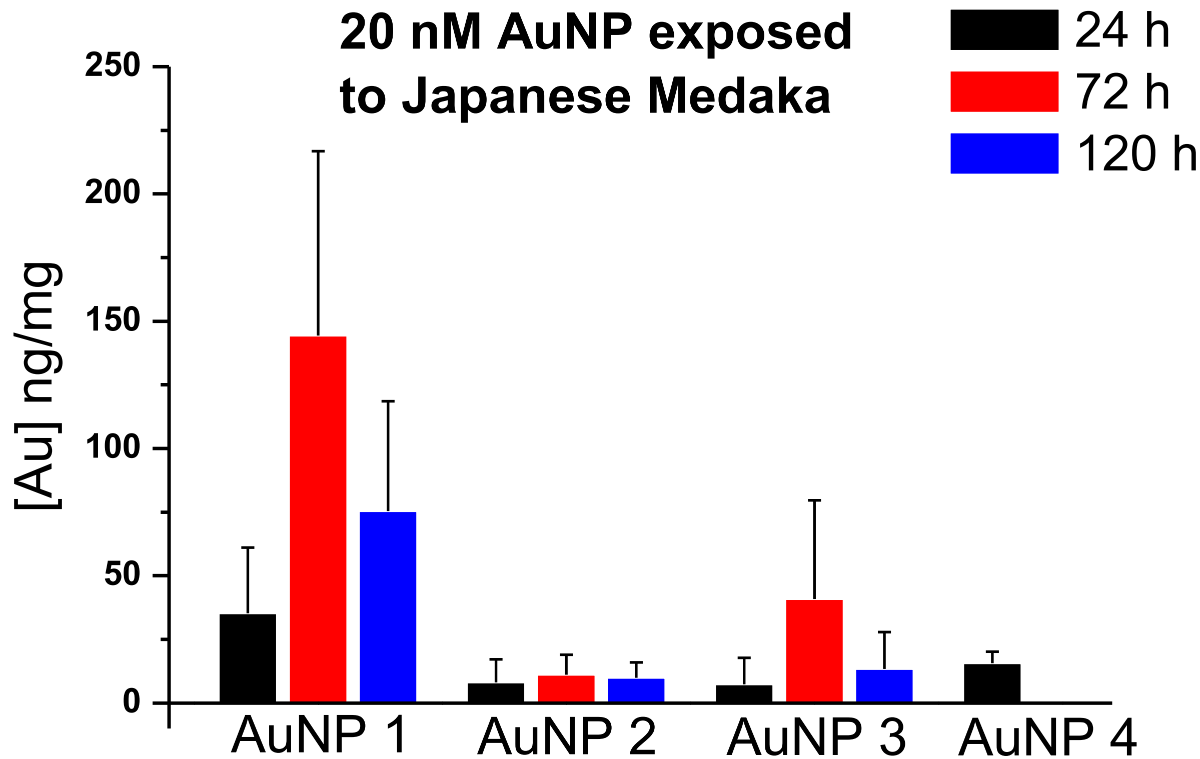
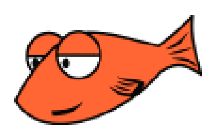


→ ICP/MS

Influence of Surface Properties on Nanoparticle Bioavailability to Fish

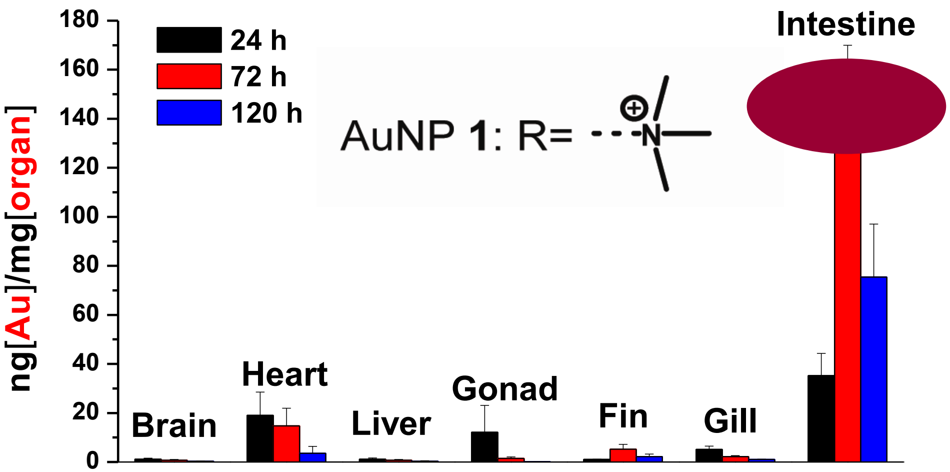


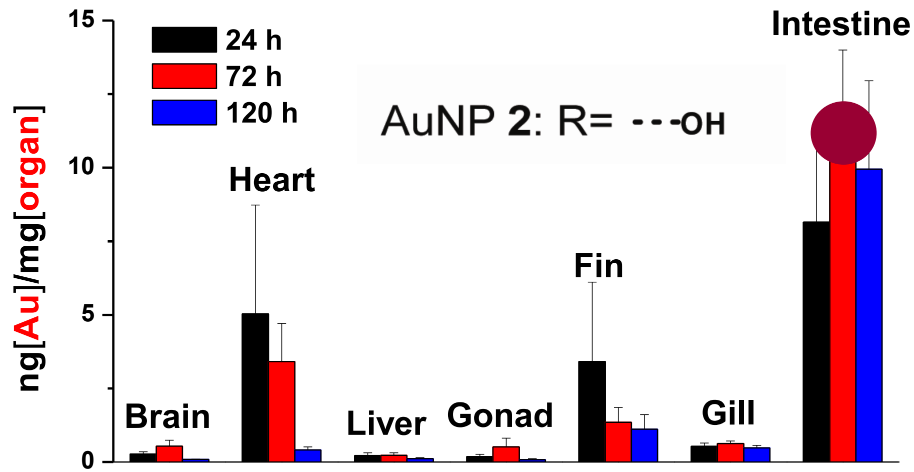


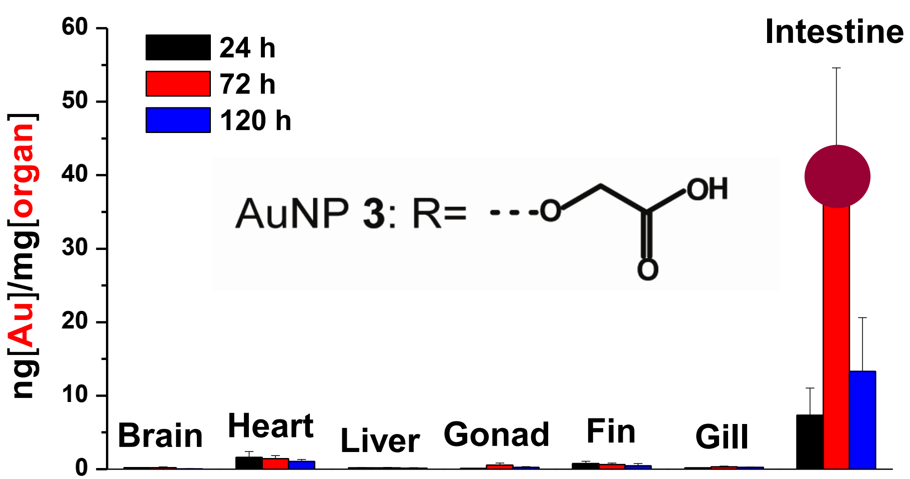
AuNP 1-3 →  **Fish are healthy for entire exposure**

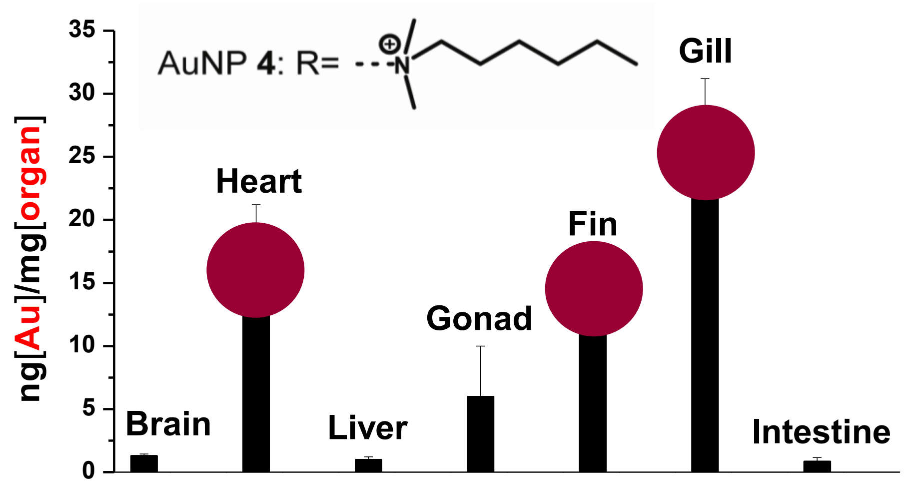
AuNP 4 →  **Killed all fish within 24 hours of exposure**

Influence of Surface Properties on Nanoparticle Bio-Distribution









Statistically significant; one-way ANOVA: $p < 0.01$

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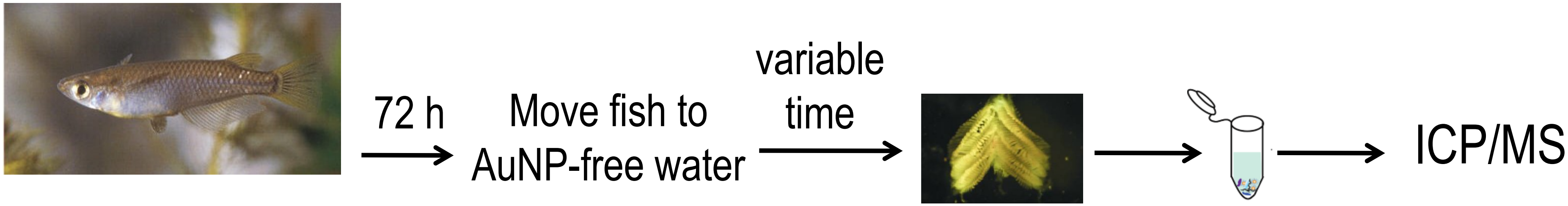
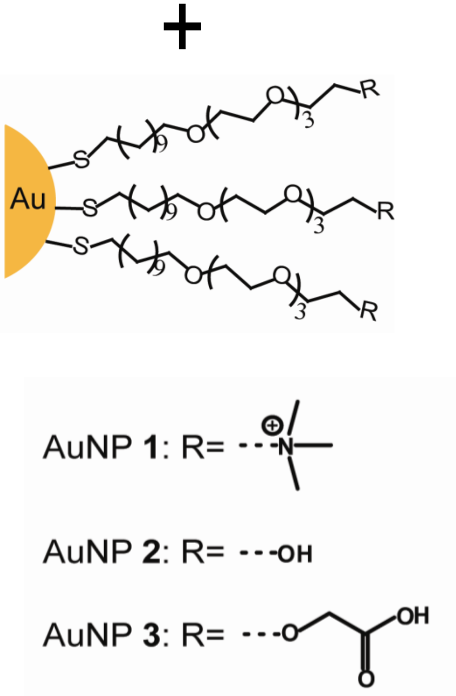
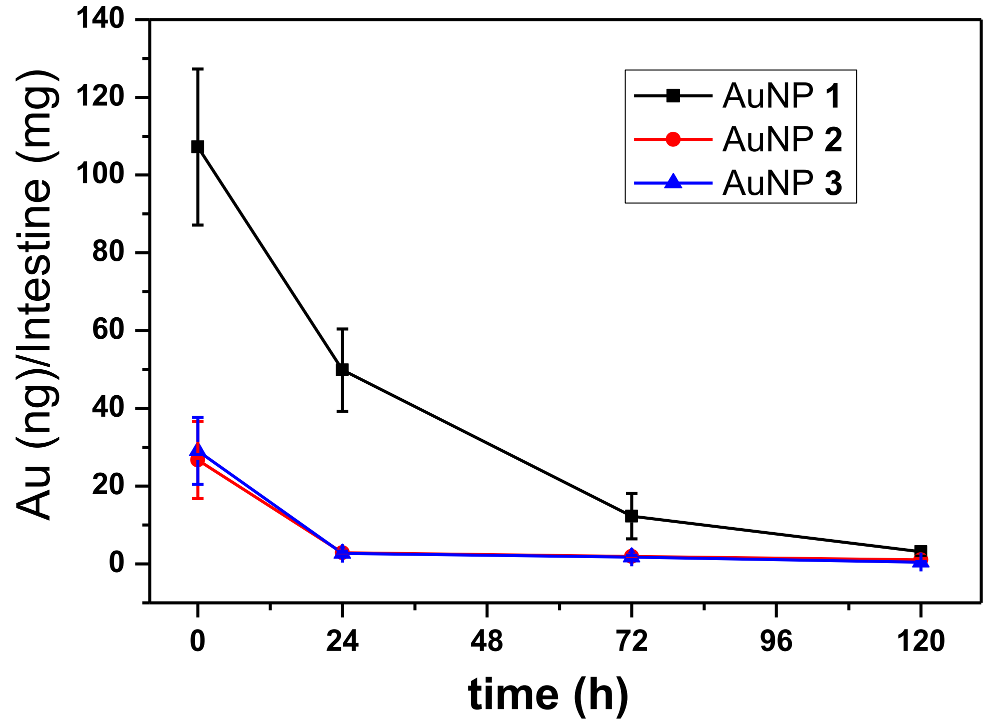
Clearance of AuNPs 1-3 from Intestines







AuNPs 1-3 cleared from intestines

Tentative conclusion: NPs with hydrophilic surfaces are less toxic and more sustainable nanomaterials

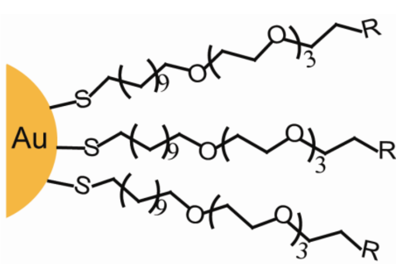
Influence of Surface Properties on Nanoparticle Bioavailability to Plants

rice
• food staple

radish
• edible roots

pumpkin
• popular crop

ryegrass
• important pasture crop



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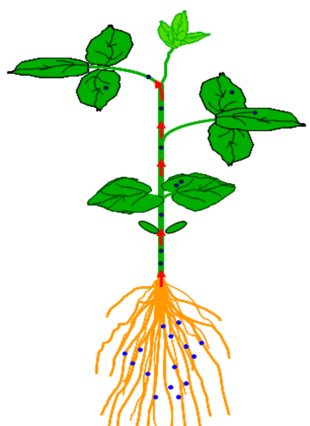
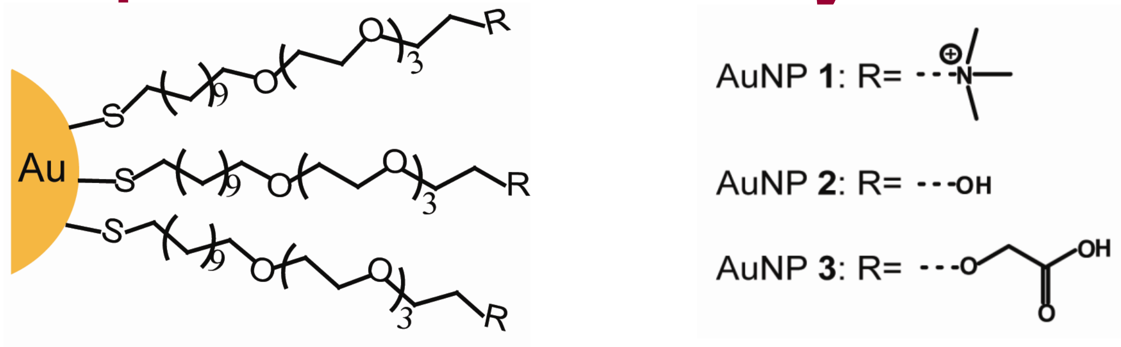


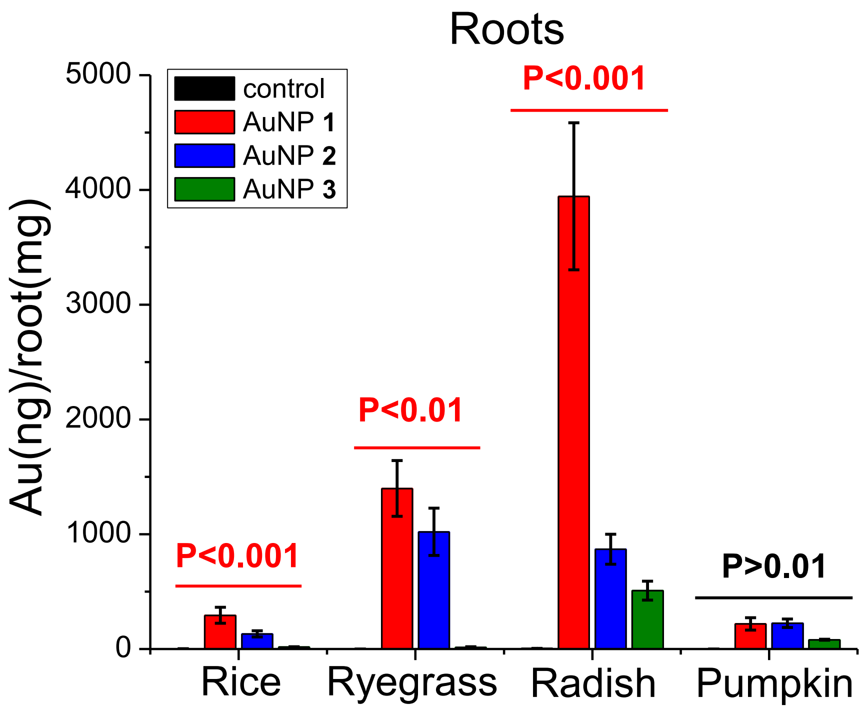
harvest roots and leaves/shoots after 5 days →

→ ICP/MS

Influence of Surface Properties on Nanoparticle Bioavailability to Plants

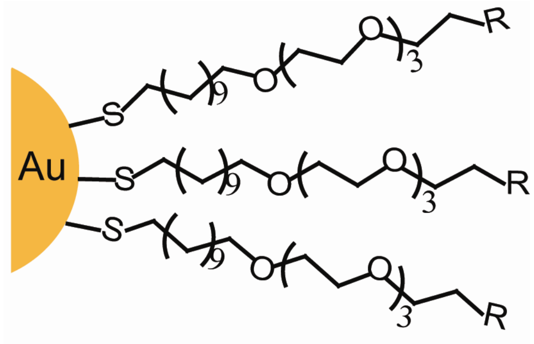
80 nM of AuNP

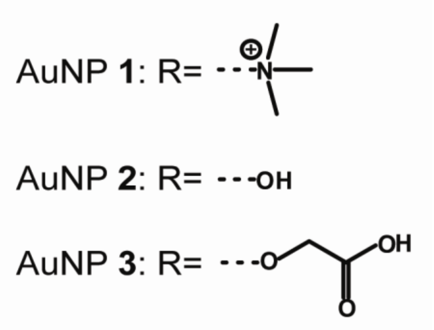


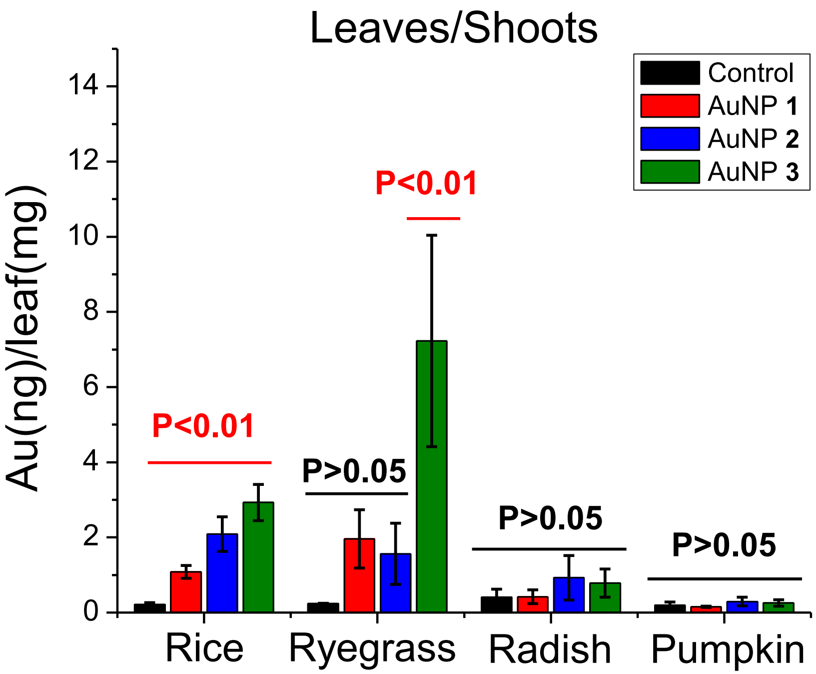


- **AuNPs 1 associates with roots most significantly**
- **Radish has most NPs in roots**
- **Pumpkin has least NPs in roots**
- **Separate studies show 90% of NPs in radish roots are on surface**

Influence of Surface Properties on Nanoparticle Bioavailability to Plants





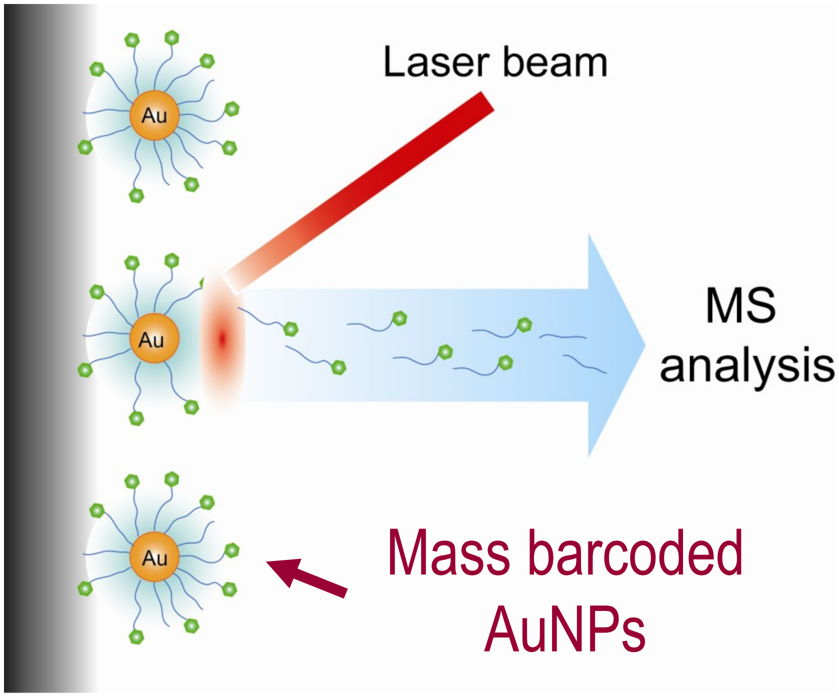


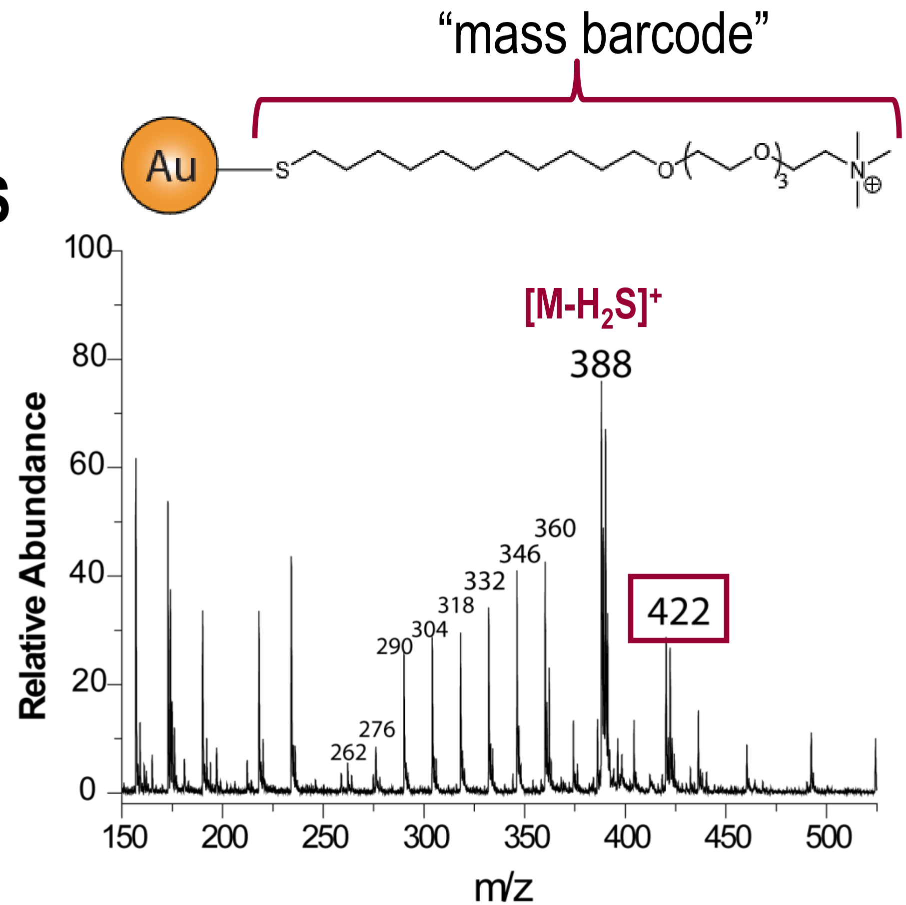
- **AuNPs 3 is most taken up into leaves/shoots of rice and ryegrass; AuNP 1 is generally the least**
- **Each AuNP type goes into rice shoots**
- **No significant uptake into radish or pumpkin**

New Measurement Methods

New Method

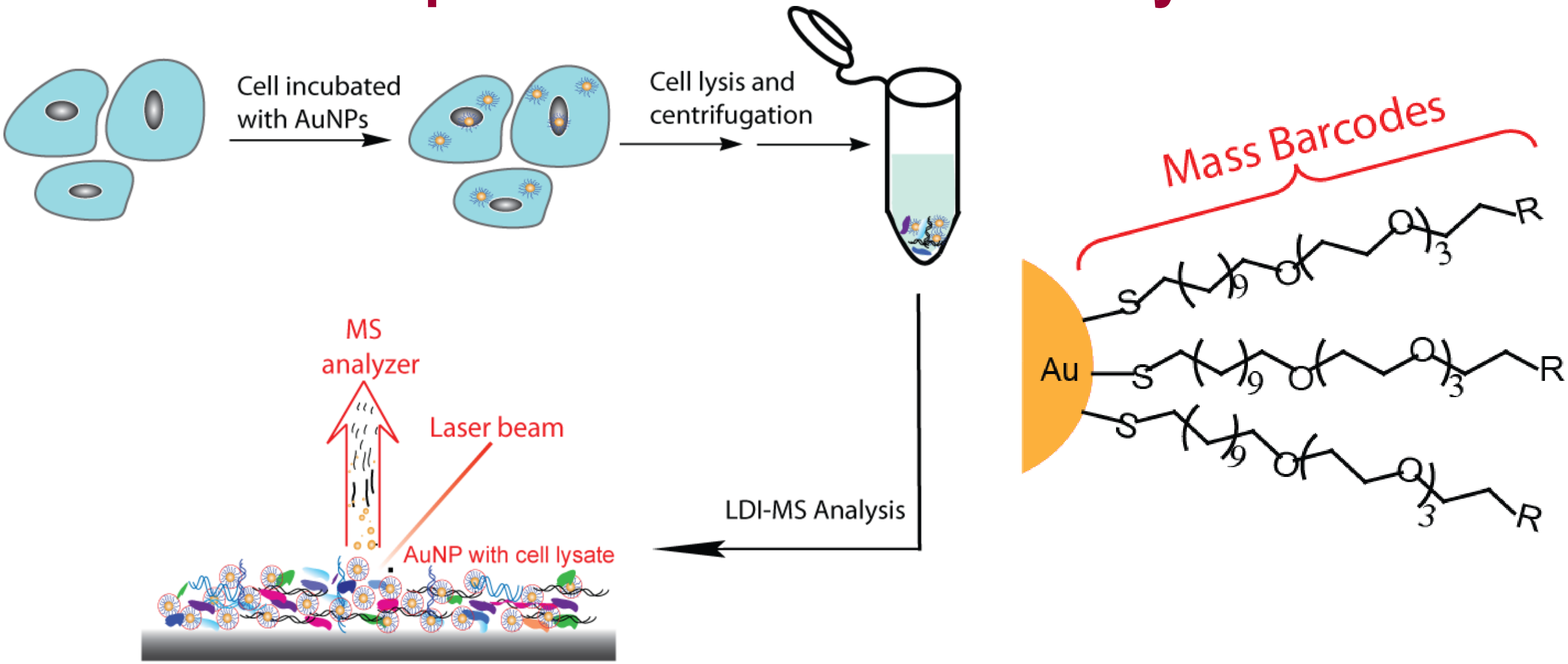
measure "mass barcodes" with laser desorption/ionization (LDI) MS

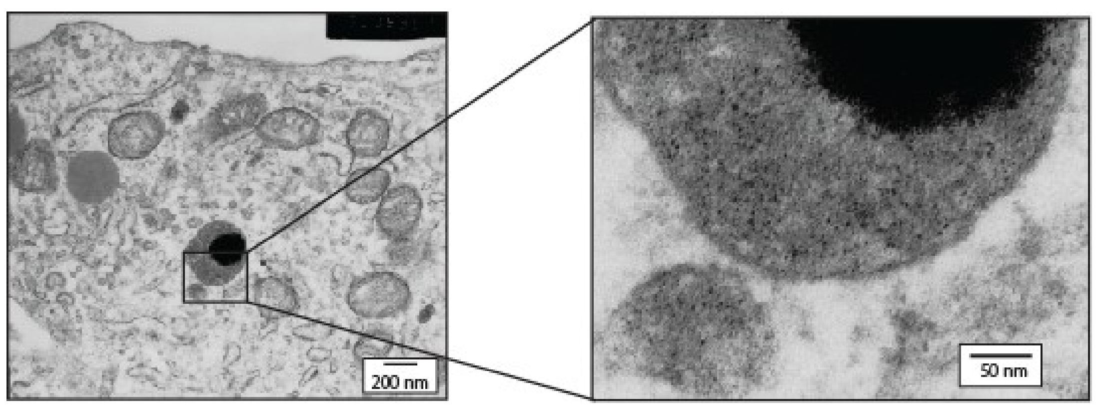




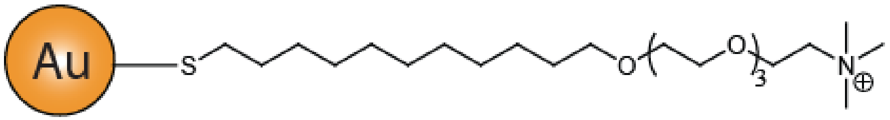
- Gold core acts as energy reservoir: upon laser irradiation, AuNPs absorb laser energy and monolayer is desorbed and ionized
- Mass spectrum contains intact ligands, ligand fragments and disulfide ions

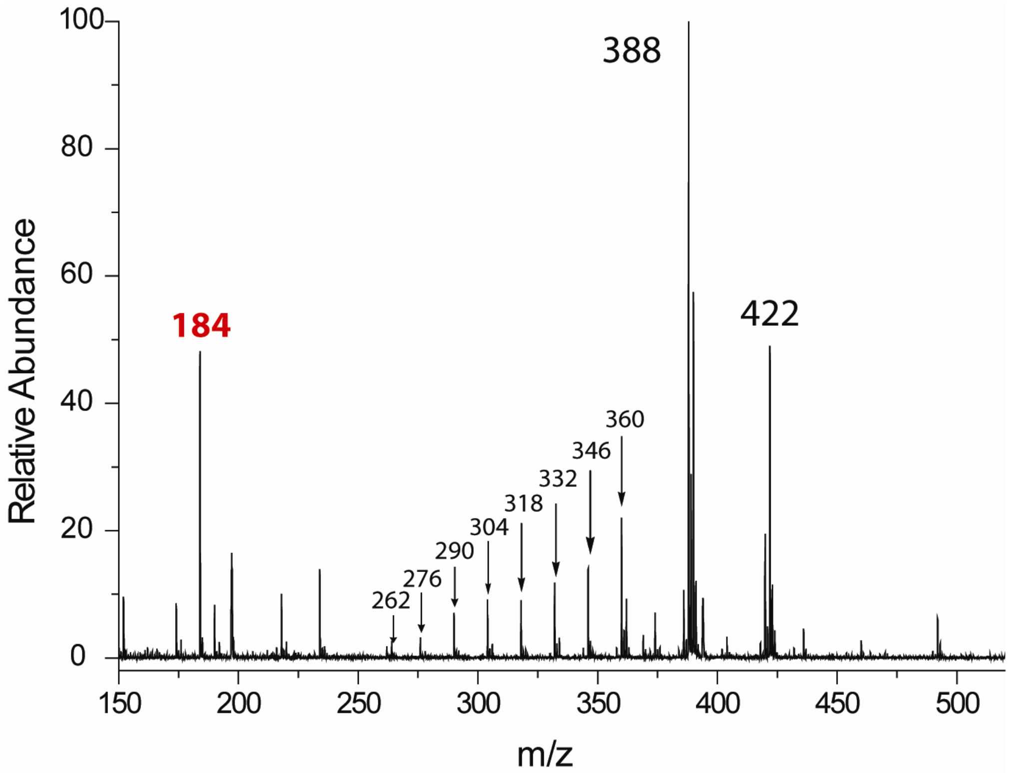
Cellular Uptake of AuNPs Studied by LDI-MS





Cellular Uptake of AuNP 1 Studied by LDI-MS





- LDI mass spectrum of COS-1 cell lysate after uptake of AuNP **1**
  - m/z 422 corresponds to the molecular ion (M^+) of ligand
  - m/z 184 is the head-group fragment of phosphatidylcholine
  - 100 pM (x 10^{-12} M) AuNP in cell culture can be detected

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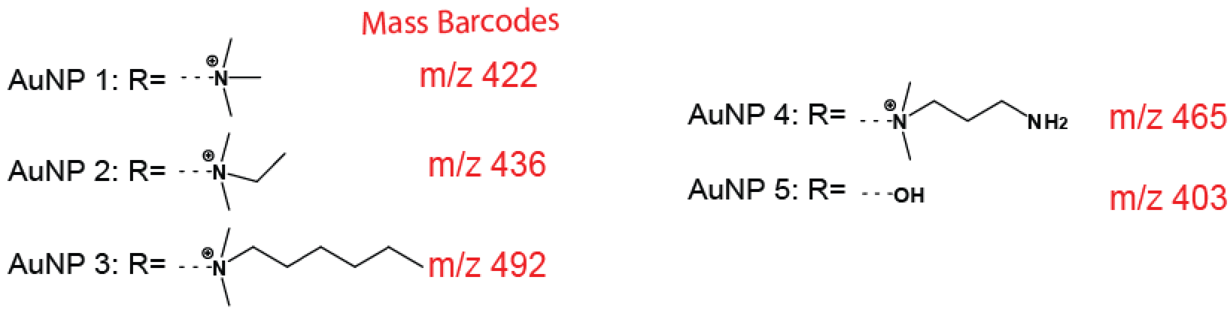
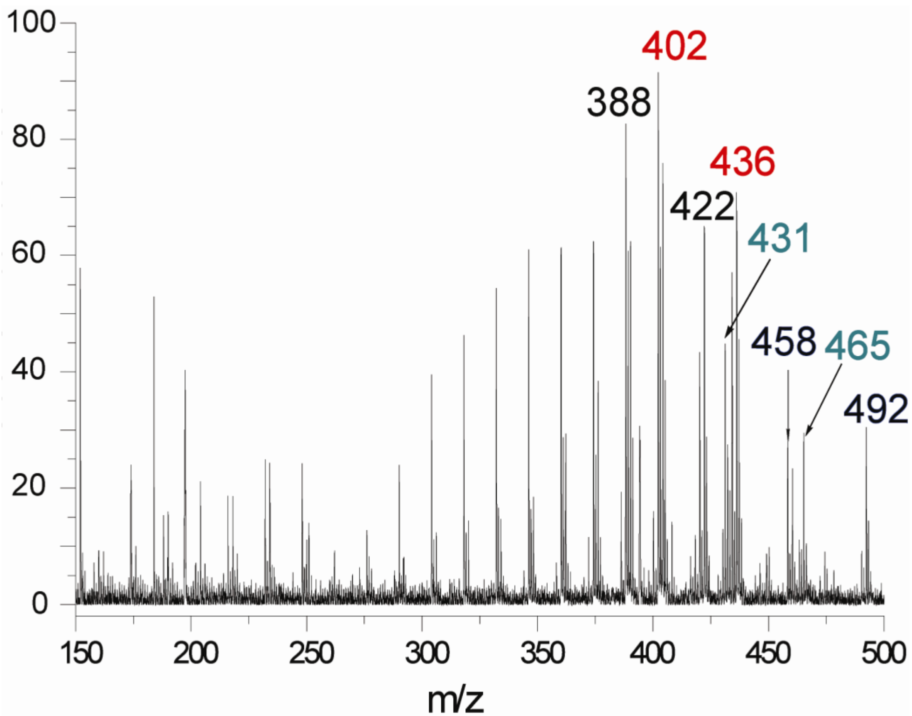
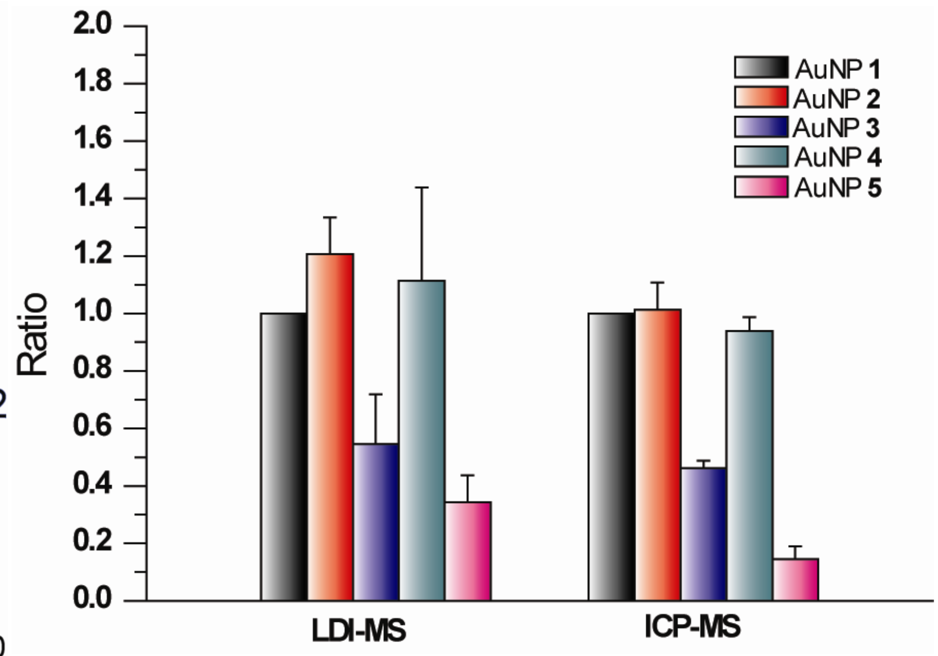
Multiplexed Tracking of AuNP Cellular Uptake by LDI-MS



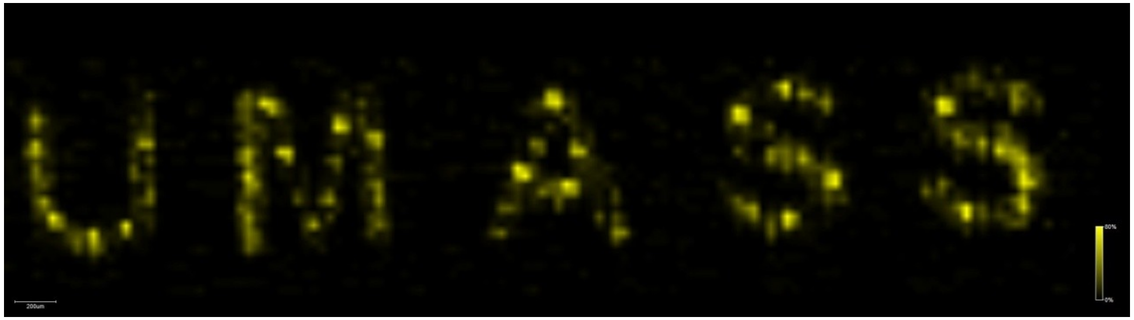




- Different "mass barcodes" for each AuNP facilitates multiplexed tracking by LDI-MS
  - Multiplexed tracking provides side-by-side comparison of AuNP uptake

Summary

- Functionalized AuNPs are good models for investigating the effect of surface chemistry on NP bioavailability.
- NP bioavailability experiments with fish and cells indicate that NPs with positively-charged surfaces are accumulated about 10x more than neutral or negative NPs.
- Hydrophilic NPs are less toxic to fish than hydrophobic NPs, and nanomaterials with such surfaces may lead to more sustainable nanomaterials
- NP bioavailability to plants is species dependent and uptake into leaves has a surface charge dependency that differs from fish and cells.
- **Future work will seek to image NPs in tissues and understand possible NP transformations *in vivo*.**



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