

# Synthesis and Optical Characterization of Colloidal Gold Nanoparticles on Planar Substrates

EE 412 Final Presentation

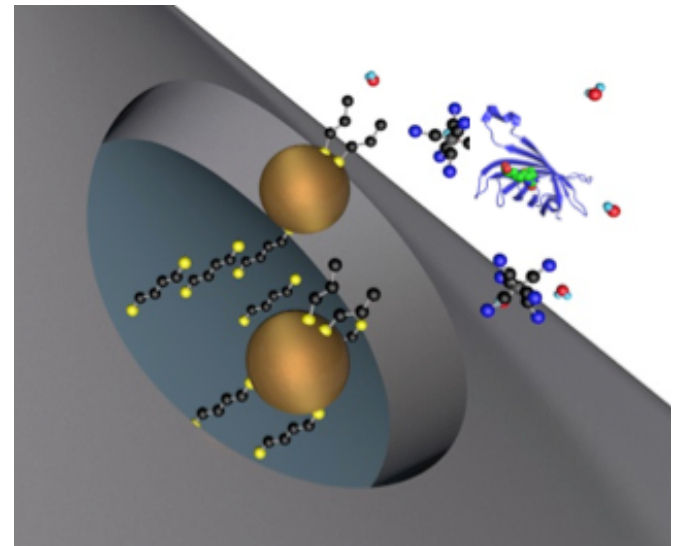
Charmaine Chia

Advisors: Dr. Michelle Rincon

Dr. Robert Chen

# Motivation

- Gold nanoparticles used as nano-electrodes in Quantum Tunneling Electronic Probe (QTEP)
  - Potential to detect electrical signatures of biomolecules in aqueous solution
  - Sensor interface:
    - Macro Pt-Ir tip
    - ~380 nm coating of hafnia
    - 500 nm hole drilled using FIB
    - 24 h functionalization of
      - Ethanedithiol
      - 10 nm gold nanoparticles (GNP)
- by immersion of tip in functionalization solution



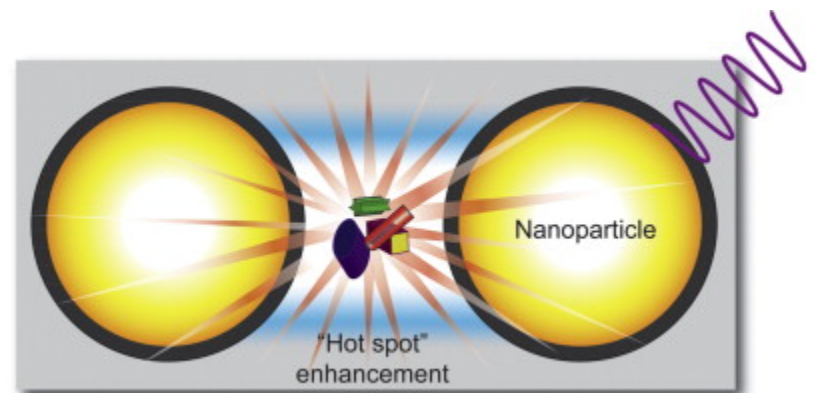
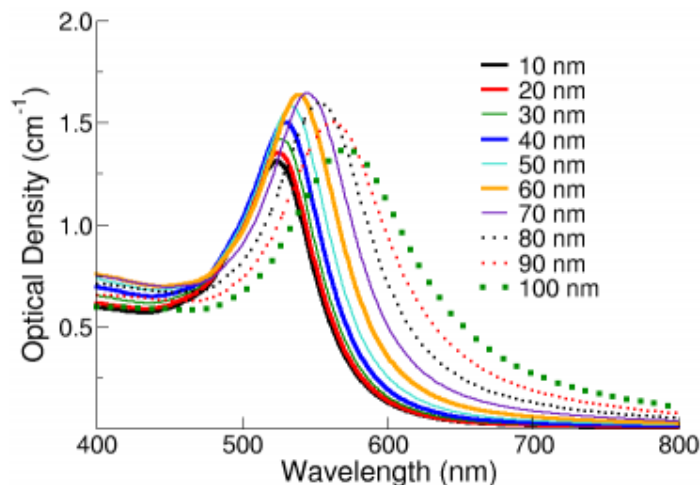
# Motivation

- Q: Can we use the unique optical properties of the GNP's as an orthogonal detection method?

## Localized Surface Plasmon Resonance (LSPR)

Collective oscillations of conduction band electrons when excited by incident light with wavelength smaller than nanoparticle size.

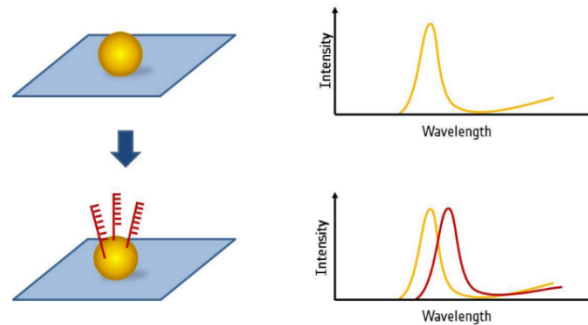
- Resonant frequency depends on the composition, size, geometry, dielectric environment and separation distance



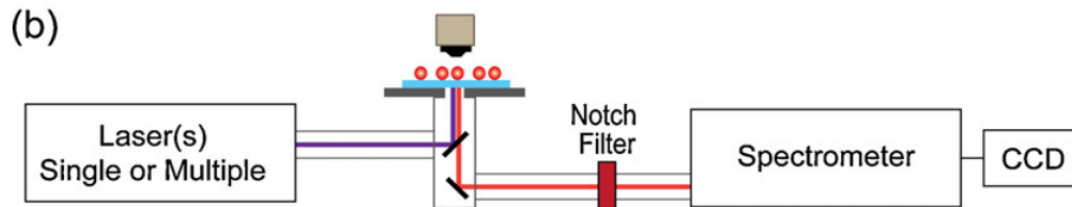
# Motivation

## LSPR in sensing

- Detection of shift in LSPR resonance when target molecule interacts with nanoparticle



- Surface enhanced spectroscopic techniques (e.g. SERS)

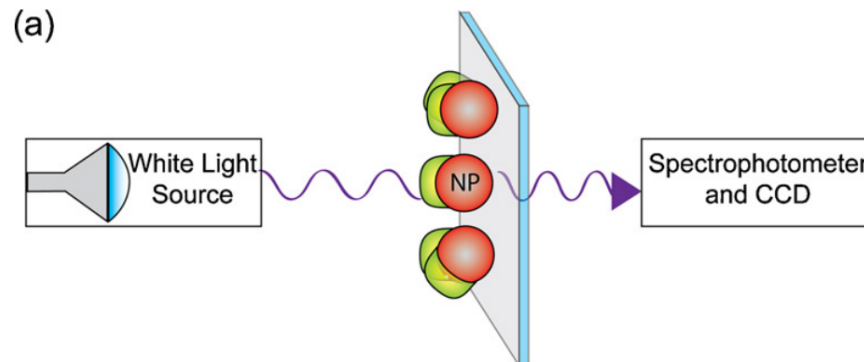


- Nanoparticle antenna (e.g for detection of fluorescence)
- Hot electron excitation of energy levels in neighboring molecules

# Project Aims

Characterize the optical properties of colloidal GNP's functionalized on platinum using the QTEP protocol

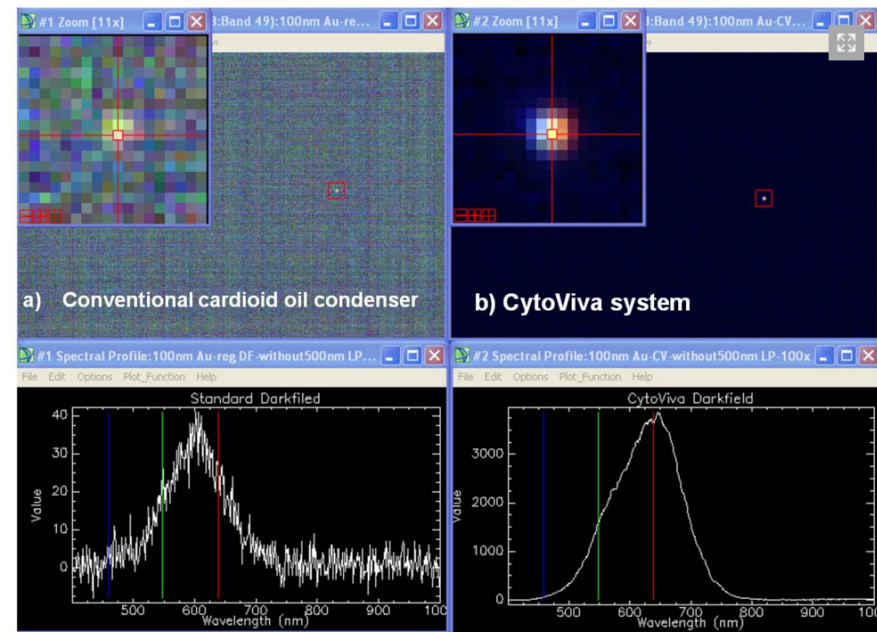
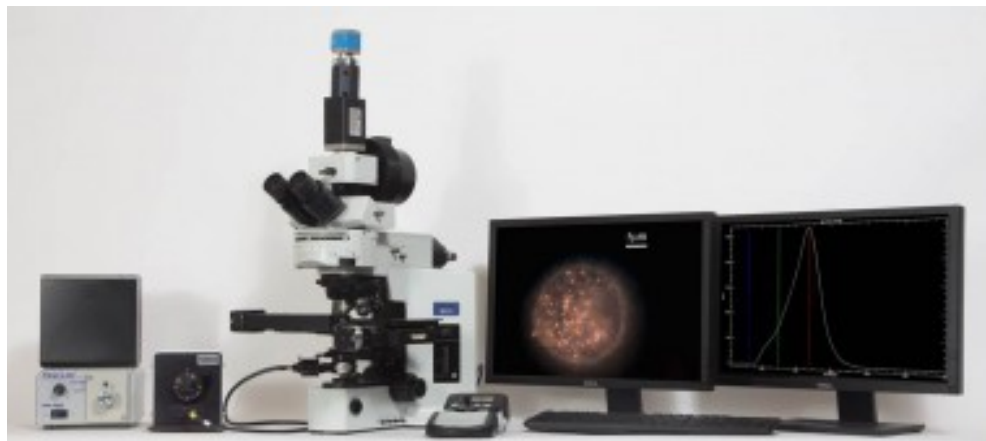
- Typically done using UV-vis spectroscopy, but this technique does not afford much spatial resolution



- Interested in capabilities of the Cytoviva Hyperspectral imaging system in nSIL

# Cytoviva Hyperspectral imaging system

- Main components: Transmission diffraction grating spectrograph + integrated camera
- Captures the optical spectrum of each pixel in the image by combining line scan motion of the microscope stage with digital imaging spectroscopy.



# Sample preparation

Choose to use planar substrate for convenience:

- Start with clean silicon wafer (wbclean)
- Thermally deposit 300 nm of oxide (thermco)
- Evaporate 10 nm of Ti, followed by 200 nm of Pt (intlvac)
- Functionalize with ethanedithiol in ethanol solution (24h).

Rinse with ethanol followed by DI water (using micropipette).

- Functionalize with GNP in aqueous solution with salt buffer, varying:

- **Size** (10, 50, 100 nm)
- **Concentration of GNP**  
(1x, 8x, 10x, 18x, 100x, 500x, 1000x dilution)
- **Functionalization time** (2h, 24h)

Rinse with DI water.

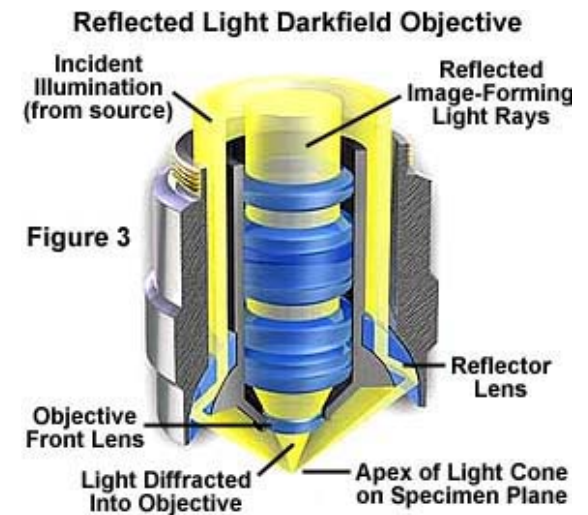


# Initial Cytoviva characterization

- Started out with bright-field reflectance mode
- Too bright → Attempted to use neutral density filter and to deposit a thinner Pt film (2 nm Ti, 5 nm Pt) to reduce reflectance

- Switched to **dark-field** objectives

- Occluding disk placed in the path of the light traveling through vertical illuminator so only the peripheral rays of light reach the deflecting mirror
- This excludes the unscattered beam from the image



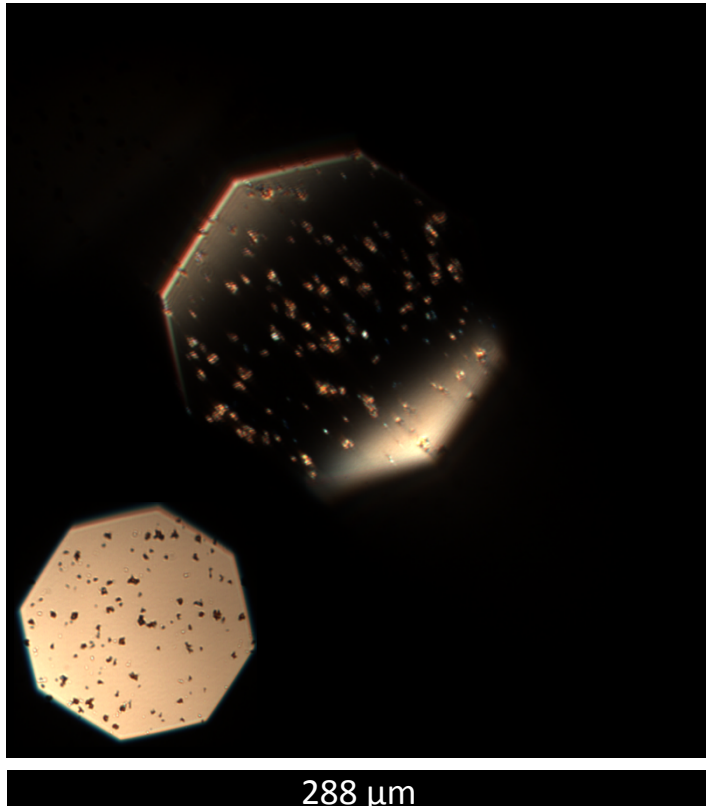
- Only managed to obtain dark-field image when slide controlling light to eyepiece / camera was in a midway position to shade out more light



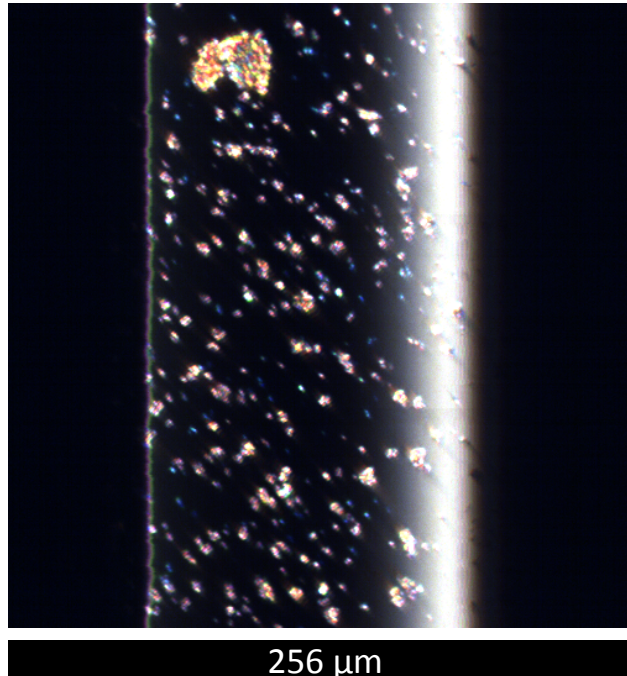
# Pt → ethanedithiol → GNP

*50nm GNP, 24h, 1x dilution*

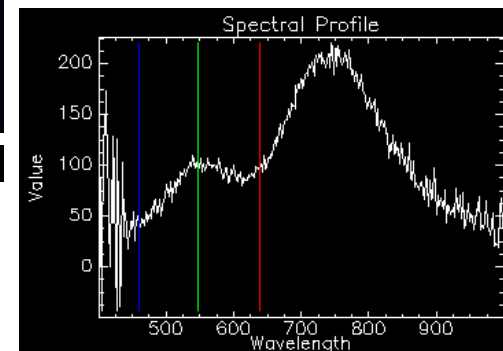
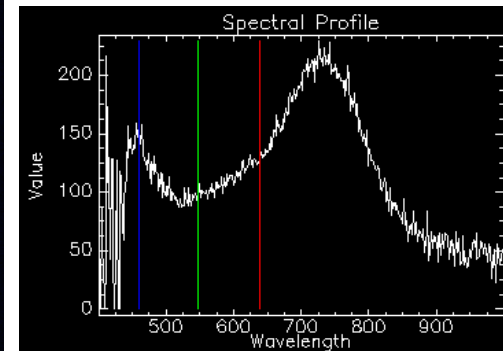
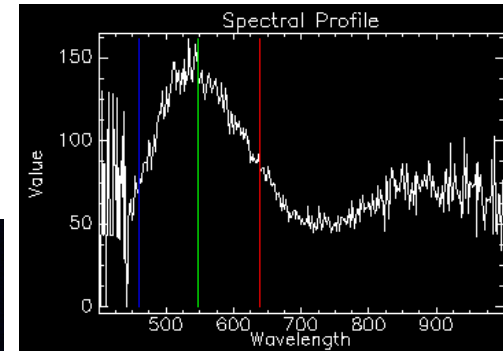
Optical image



Hyperspectral image



Sample spectra

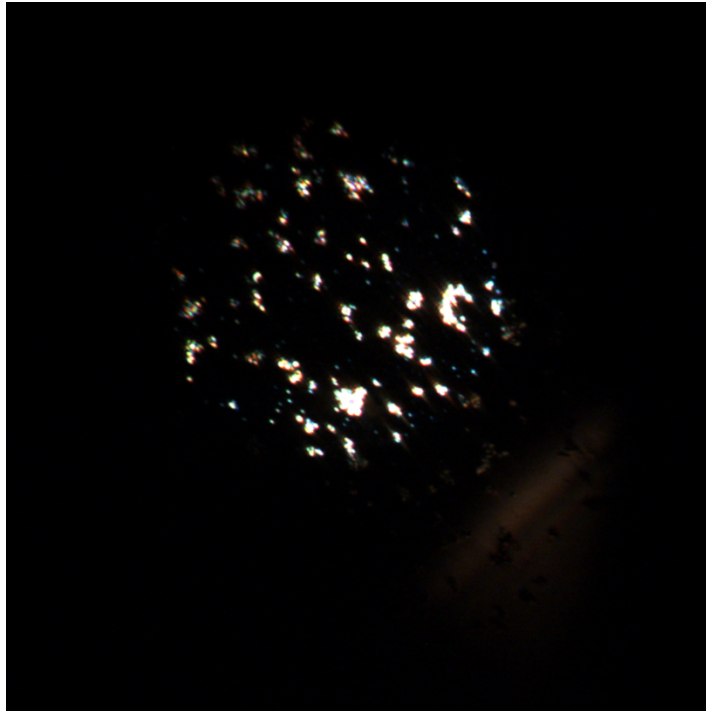


Main peaks seem to occur at: ~460, 550, 750 nm

# Pt $\rightarrow$ ethanedithiol $\rightarrow$ GNP

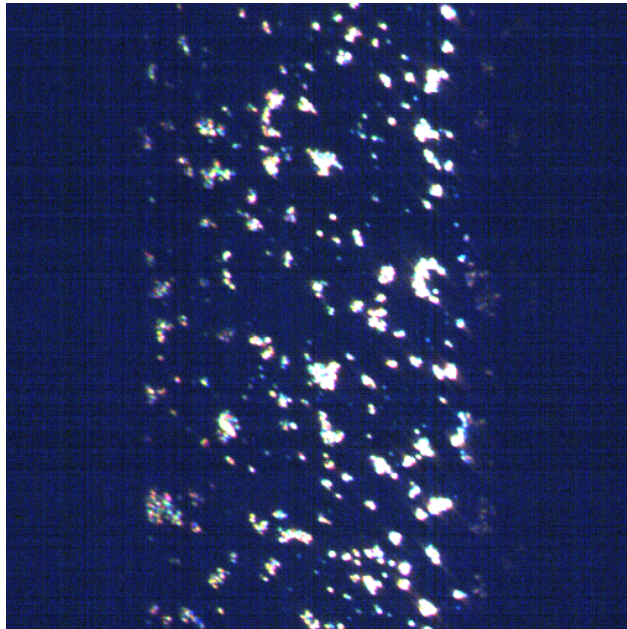
*50nm GNP, 2h, 8x dilution*

Optical image

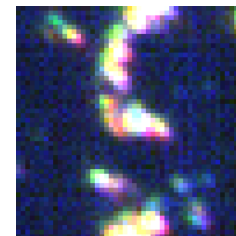


288  $\mu\text{m}$

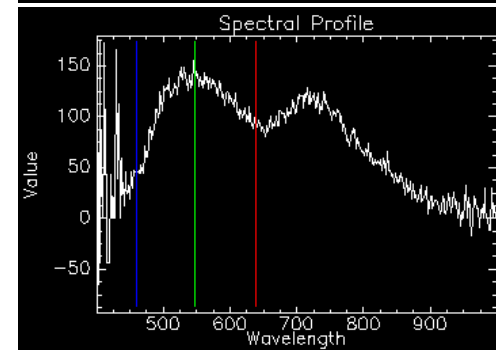
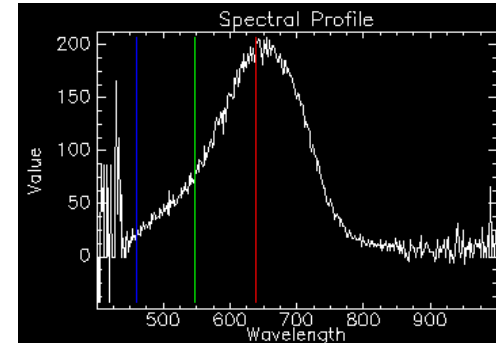
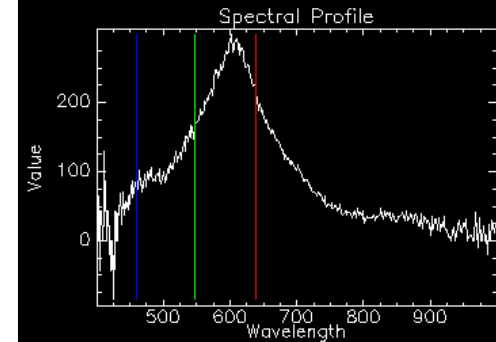
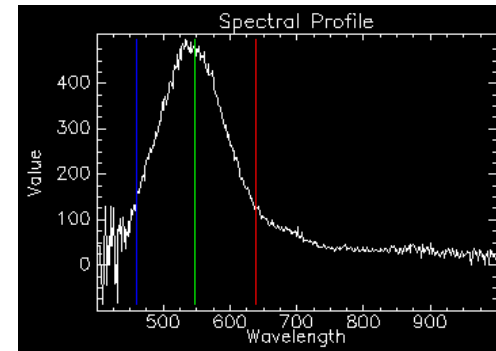
Hyperspectral image



256  $\mu\text{m}$

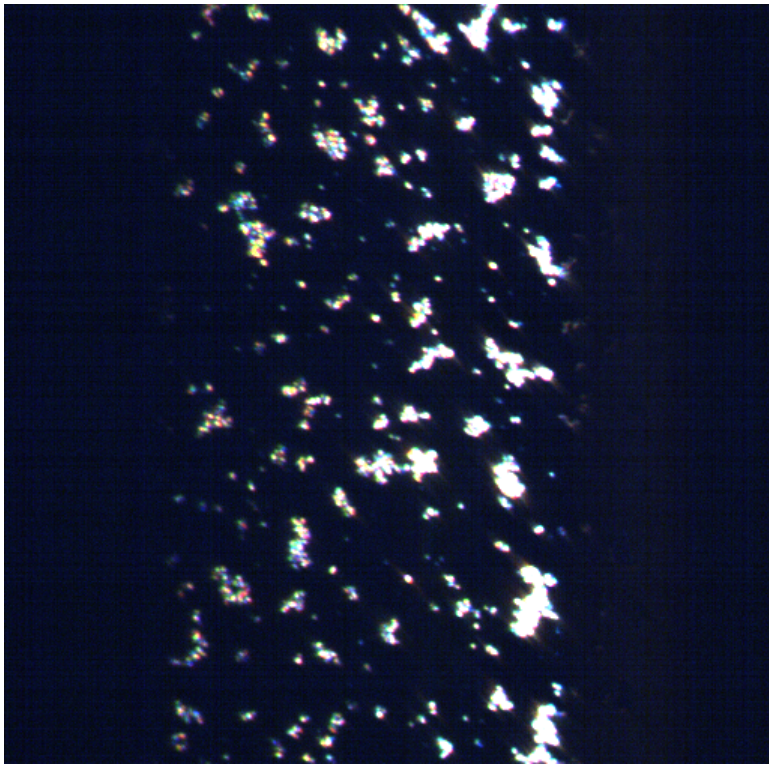


But also intermediate frequencies depending on position.



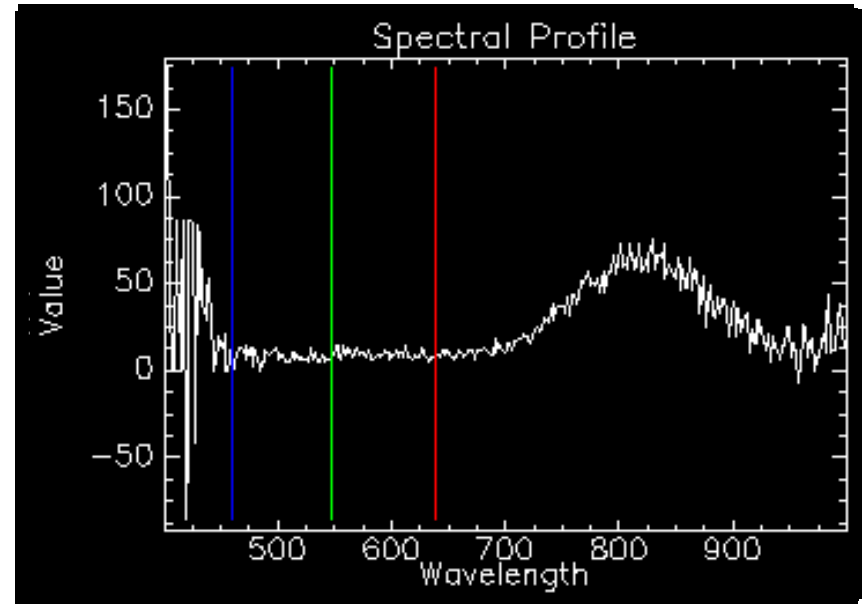
Pt  $\rightarrow$  ethanedithiol  $\rightarrow$  GNP

*50nm GNP, 24h, 8x dilution*



256  $\mu\text{m}$

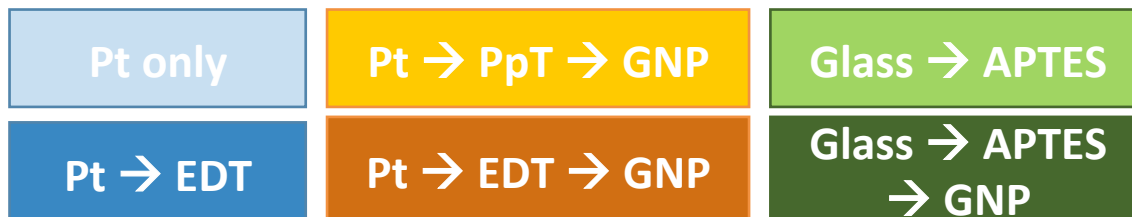
Evolution of spectra across a clump



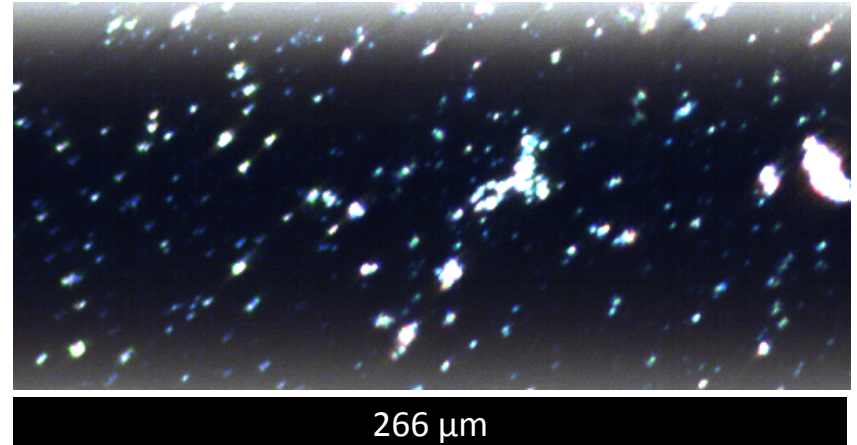
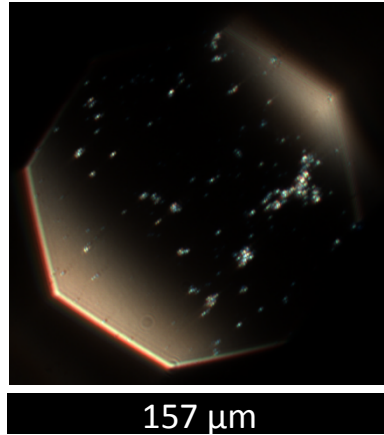
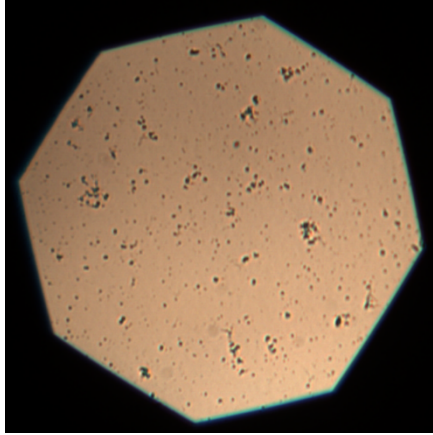
**For reference: GNP resonance peak at  $d \sim 50$  nm is around 550 nm**

# Questions raised...

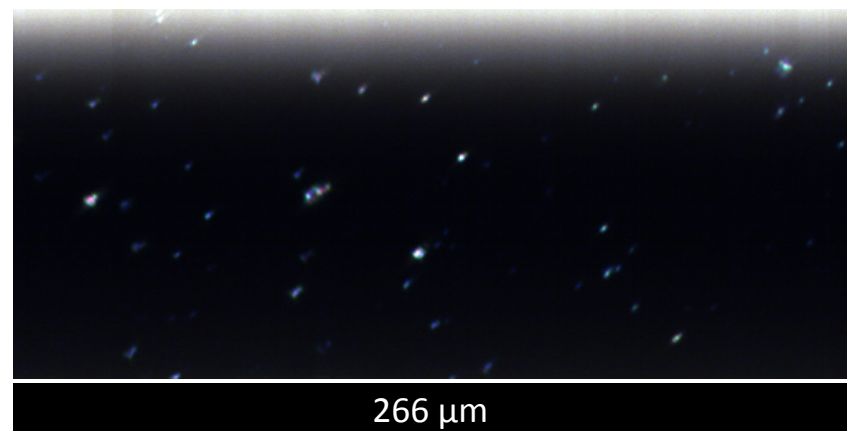
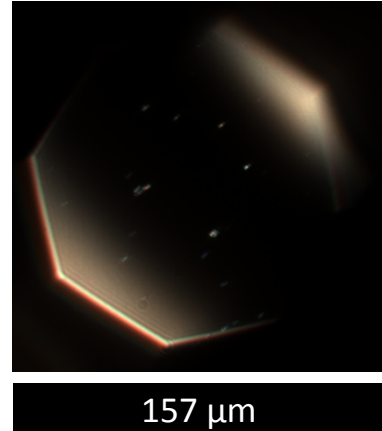
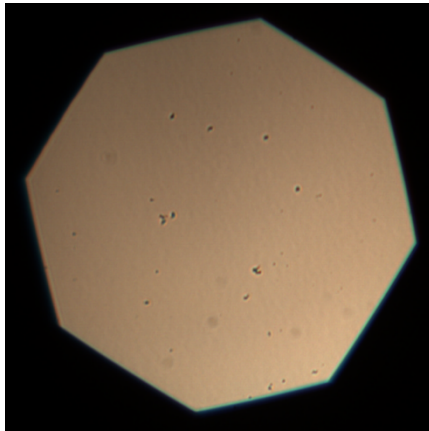
- What causes the distinct peaks?
  - Different materials within clump?
  - Distinct resonance modes of coupled NP's?
- Why do is peak shifting observed?
  - Different particle or gap size (between adjacent particles)?
  - **Chromatic aberration** at boundaries between sub-particles in clump?  
"Fringes" of color along boundaries that separate dark and bright parts of the image, because each color in the optical spectrum cannot be focused at a single common point.
- What are the clusters?
  - Nanoparticles? Crystallized salt? Impurities?
- Can we separate the contributions due to the Pt substrate and ethanedithiol (EDT) functionalization step?
- Are the GNP's attached to the substrate? What do GNP's look like?
- Need more controls and alternative imaging techniques:



Pt → ethanedithiol

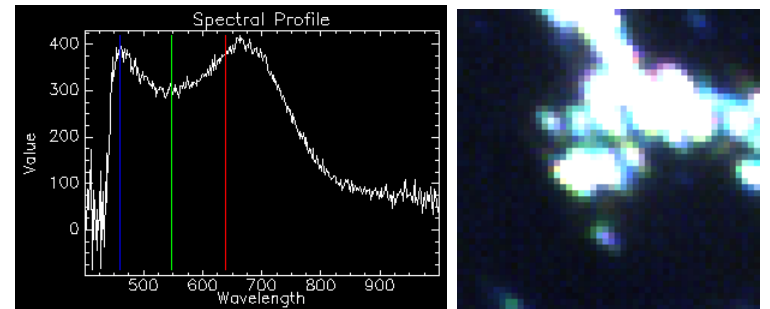
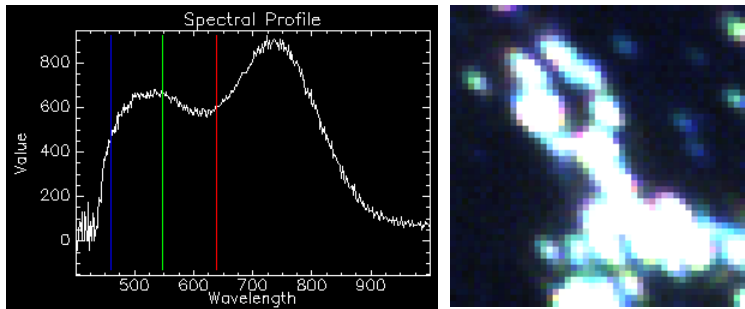
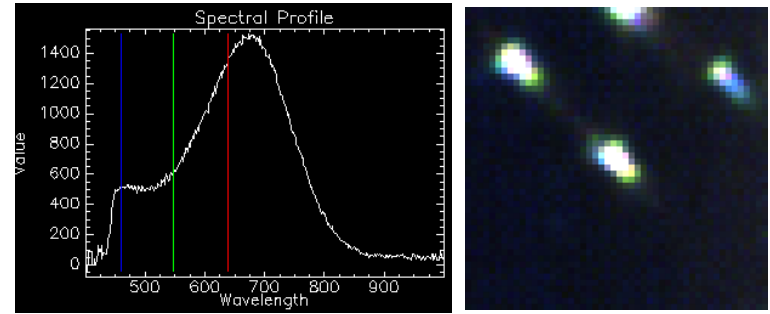
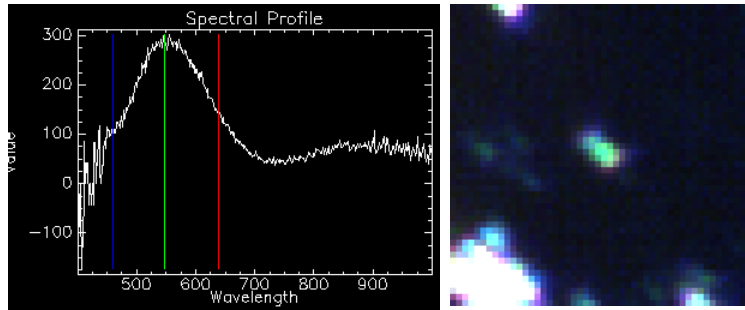


Pt → ethanedithiol → water

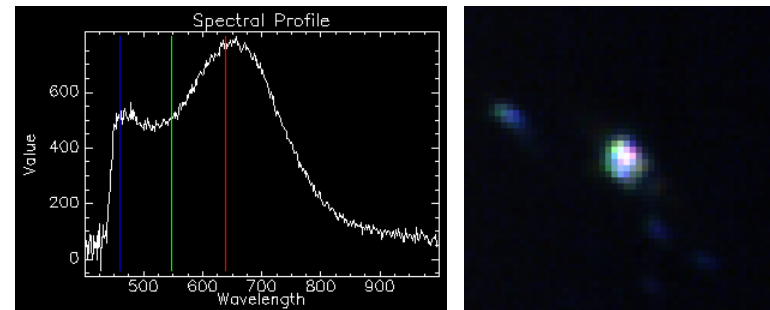
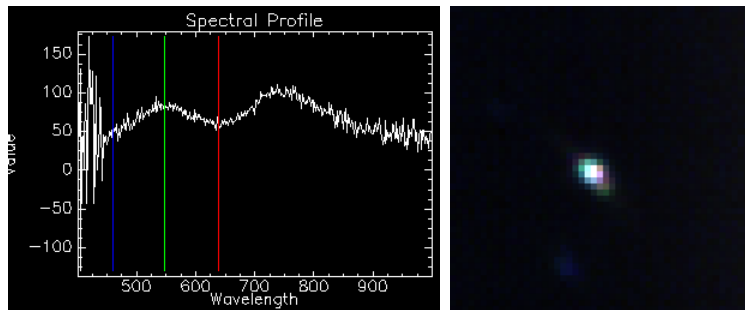


Clumps also observed. But less clumping if surface was kept covered by DI water after EDT functionalization.

Pt → ethanedithiol

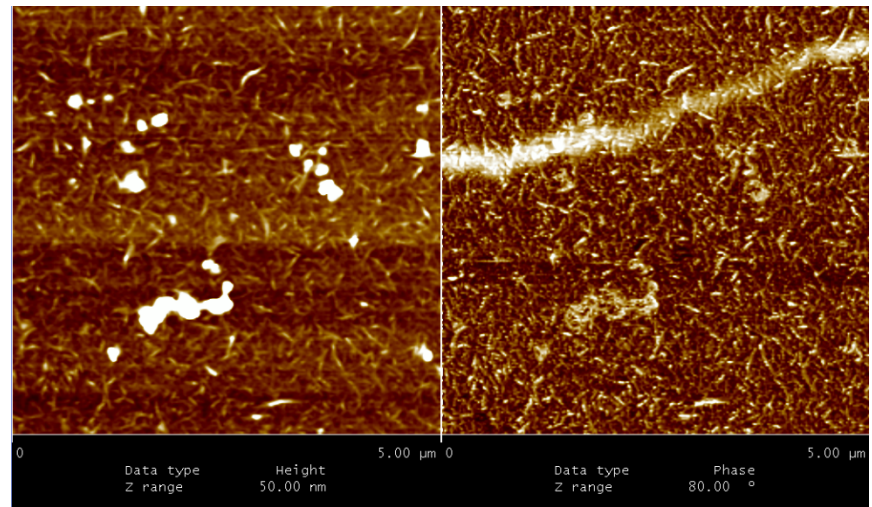
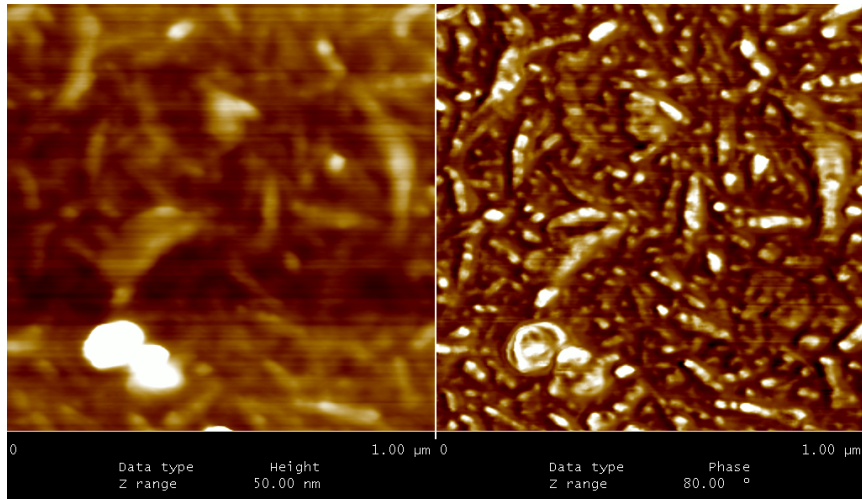


Pt → ethanedithiol → water

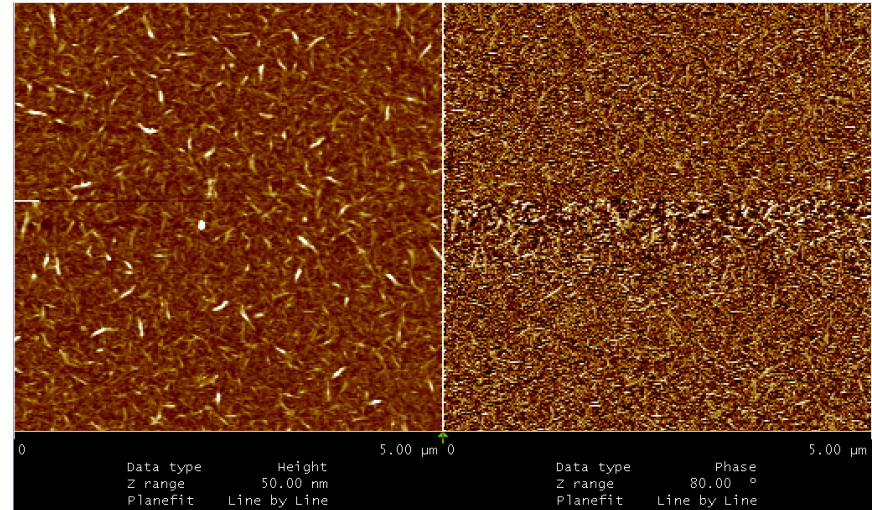
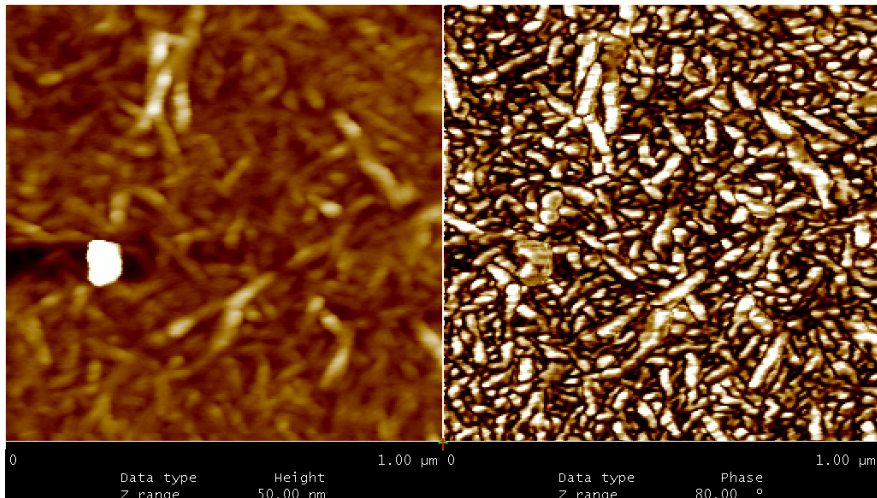


# Comparison of AFM images

Pt → Ethanedithiol



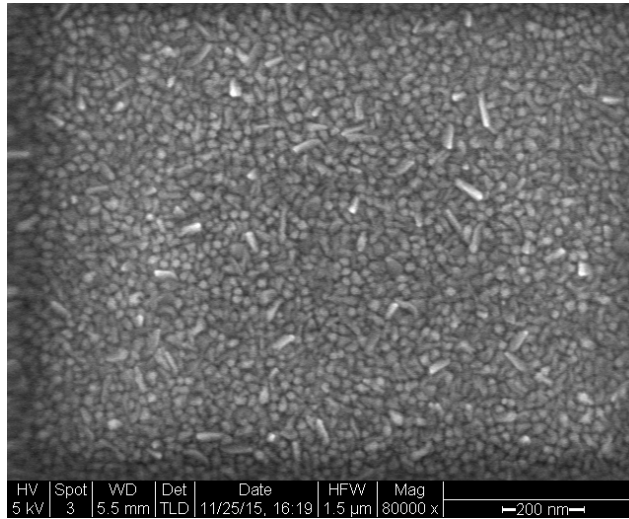
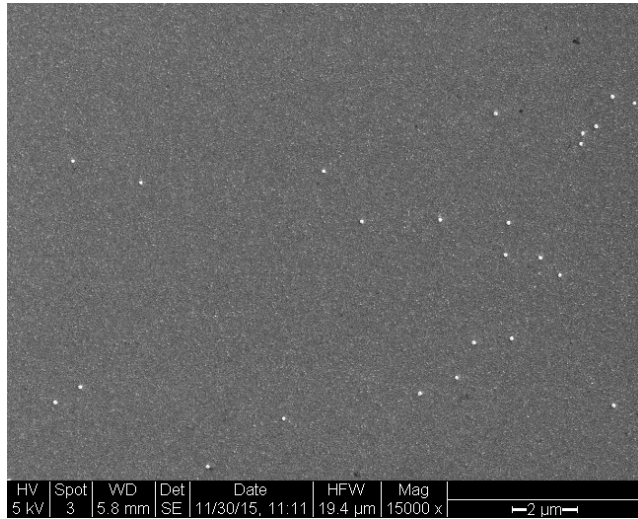
Pt → Ethanedithiol → GNP



Similar rod-like structures in background. Pt → EDT seems

# Comparison of SEM images

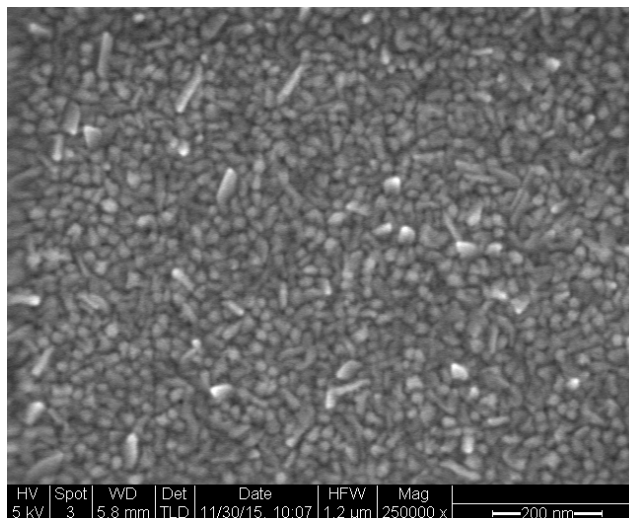
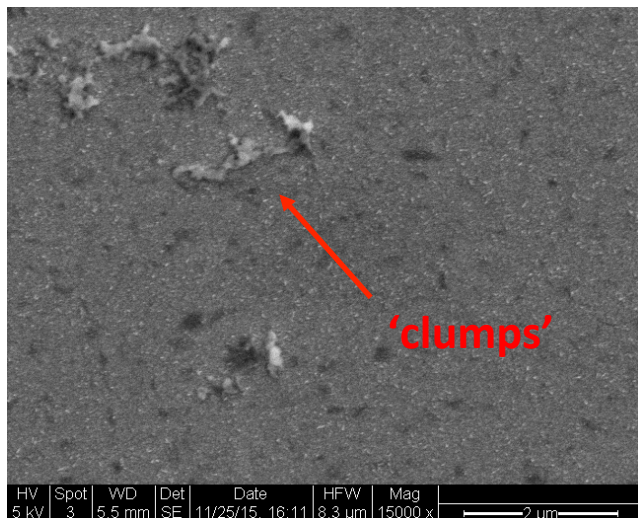
Pt only



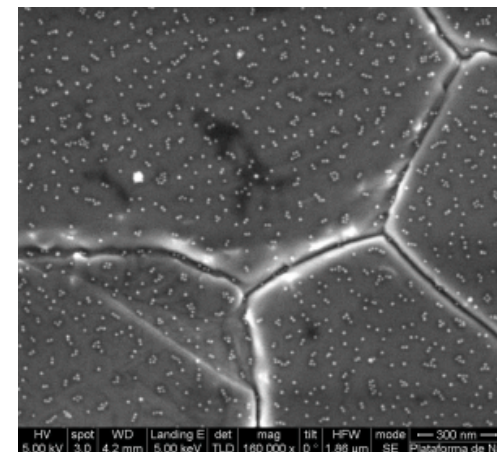
Same rod-like background.

Pt substrate does not show any bright clumps in Cytoviva

Pt → EDT → GNP



**Ex: GNP aggregation on DNA origami**





# Observations

- Rod-like background doesn't show up under Cytoviva, but the clumps do.
- Hard to resolve from Cytoviva data if clumps on ***Pt* → *EDT*** and ***Pt* → *EDT* → *GNP*** are the same.  
But they appear to have similar structure in optical image.
  - If same, they might be a byproduct of EDT functionalization
  - If not, it's possible that the clumps on ***Pt* → *EDT* → *GNP*** may be GNP's
- But the clumps on the substrates functionalized with gold don't seem to be composed of units with spherical morphology, as GNP typically appear.
  - Possible that interaction with the Pt surface may have changed its appearance – e.g. GNP's may be embedded → but unlikely

We might not be observing any GNP's on the functionalized  
substrates

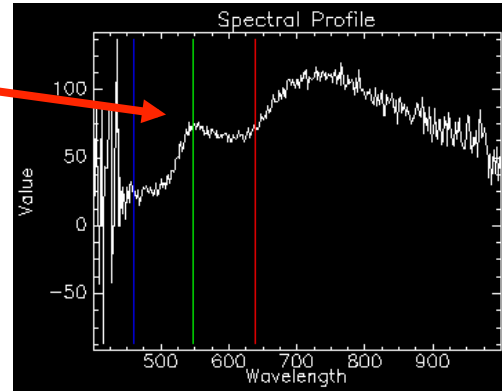
# For Ref: Functionalized glass slides

Glass slide → APTES / ethanol → GNP

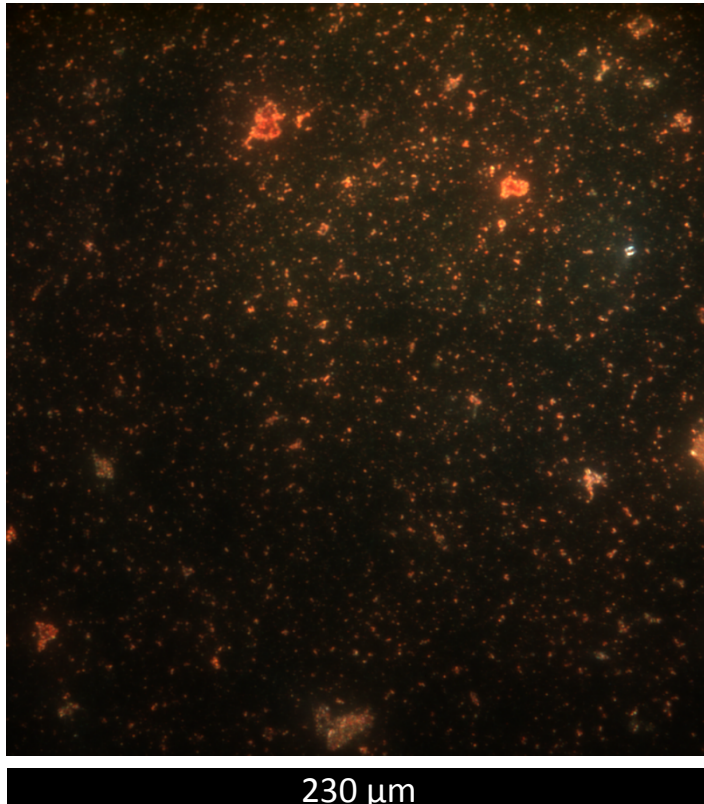
50nm GNP, 24h

Consistent peak at 550 nm  
observed over 'green' region.  
Indicative of uniform attachment  
of 50 nm GNP's

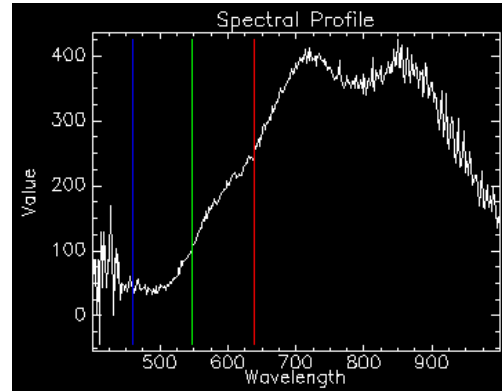
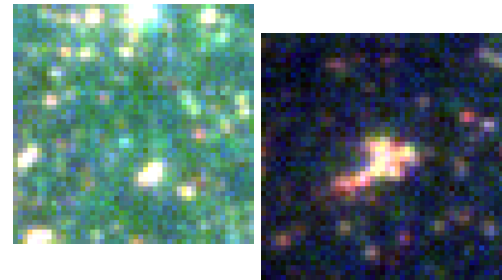
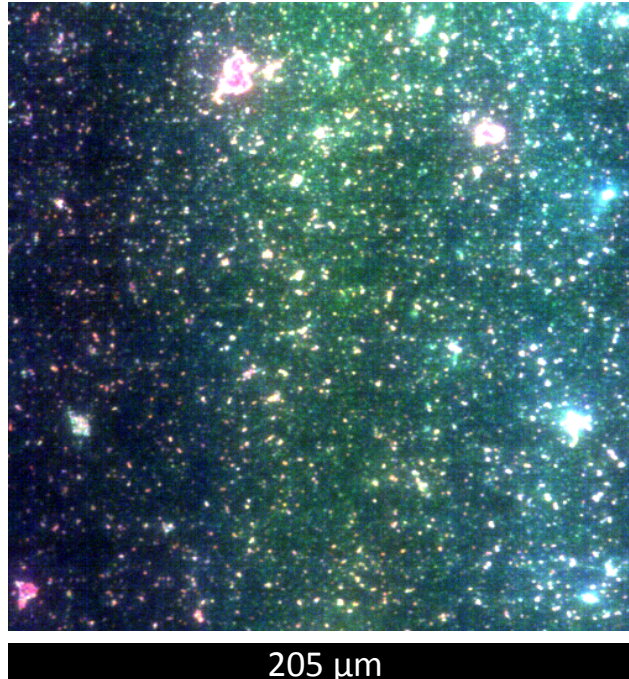
Sample spectra



Optical image



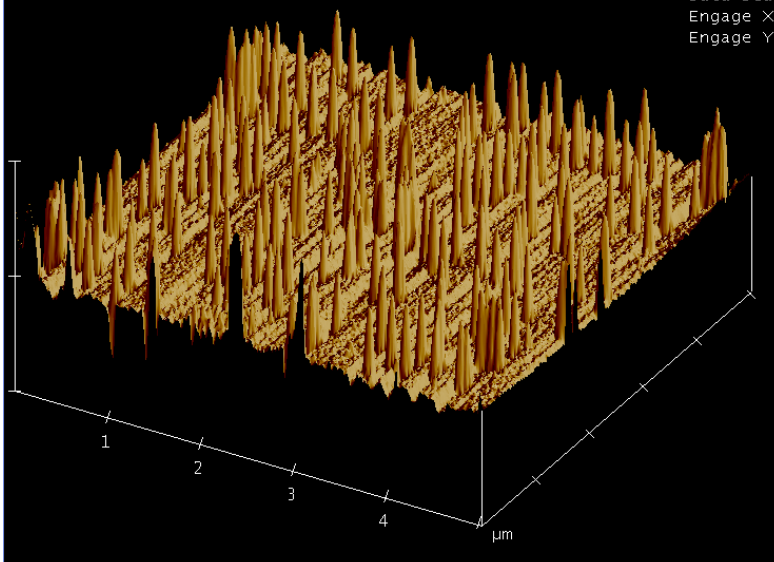
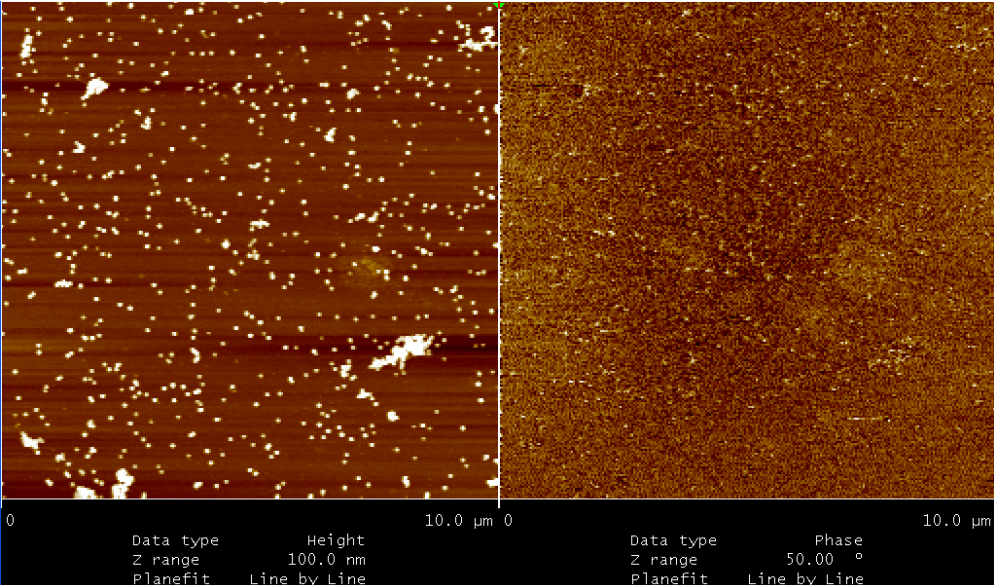
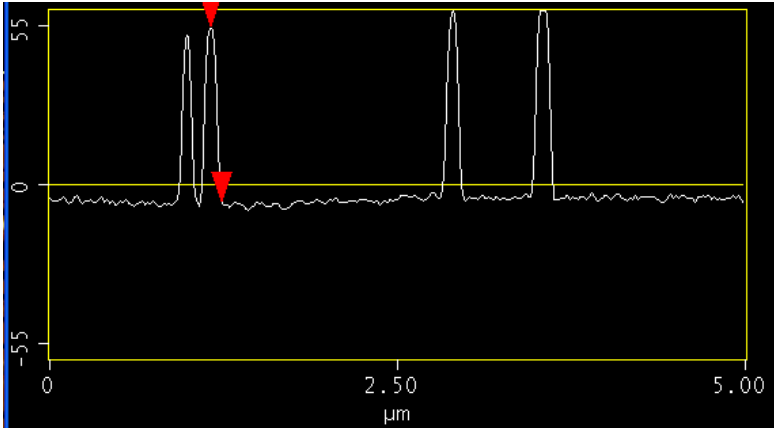
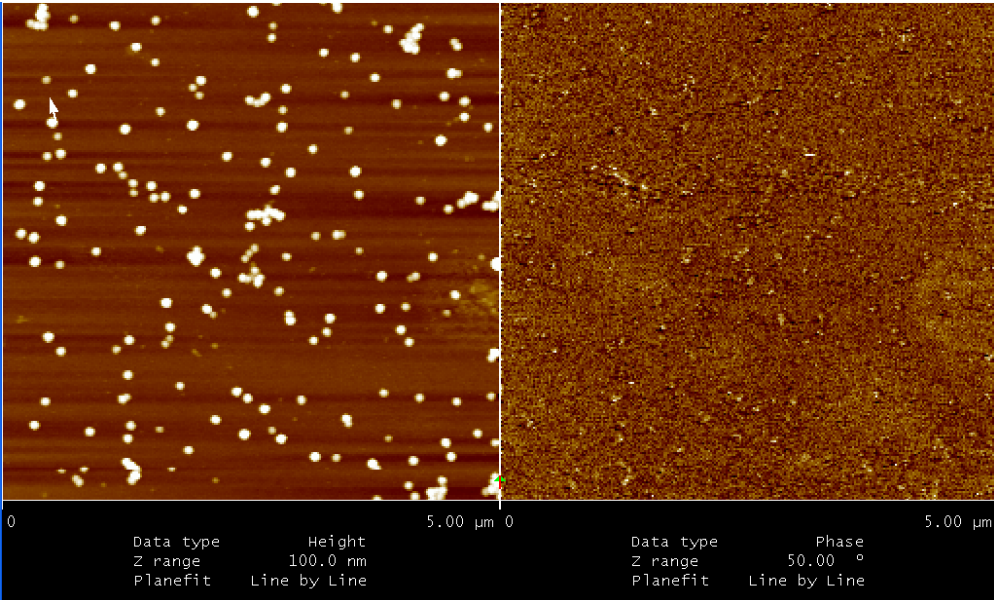
Hyperspectral image



# Functionalized glass slides

Glass slide → APTES / ethanol → GNP

...so nothing wrong with the nanoparticle solution!



# Functionalized glass slides

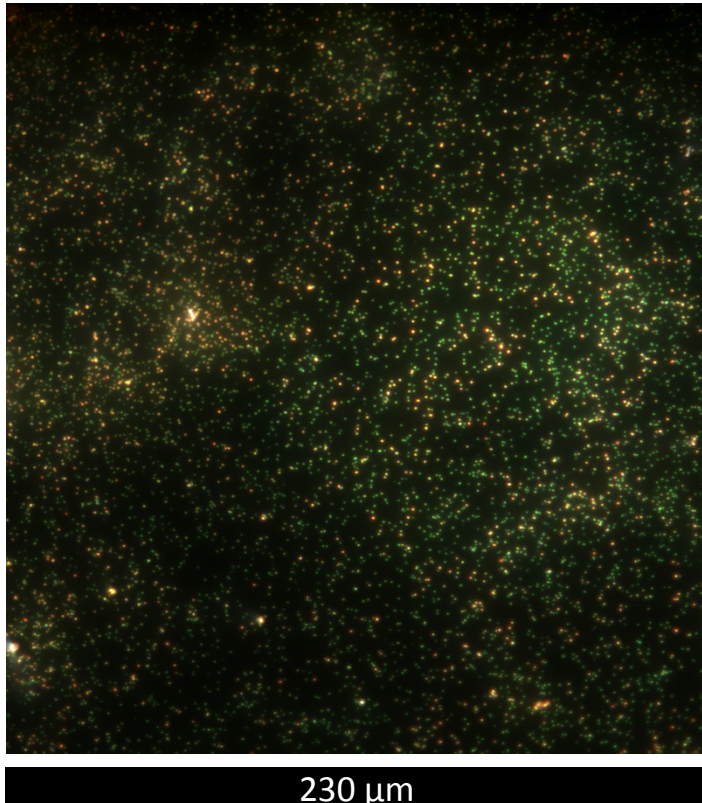
Glass slide → APTES / ethanol → GNP

100nm GNP, 24h

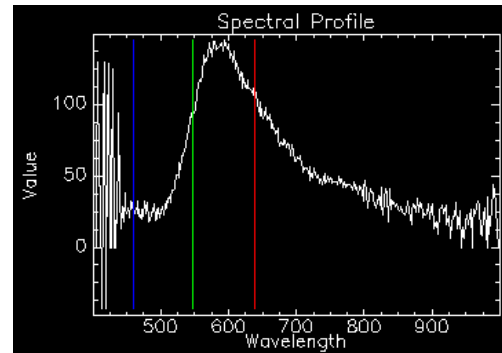
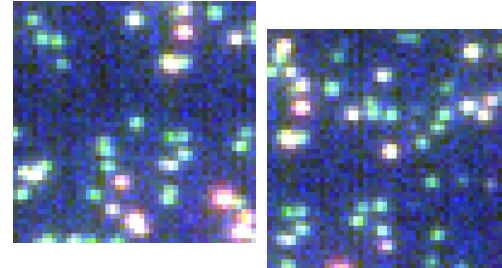
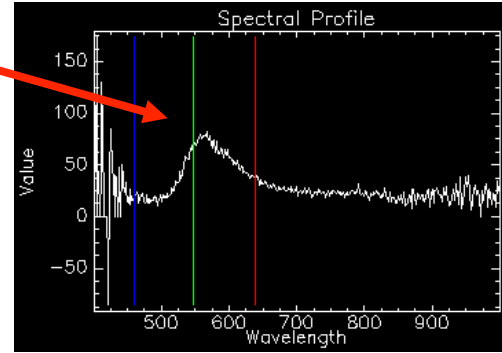
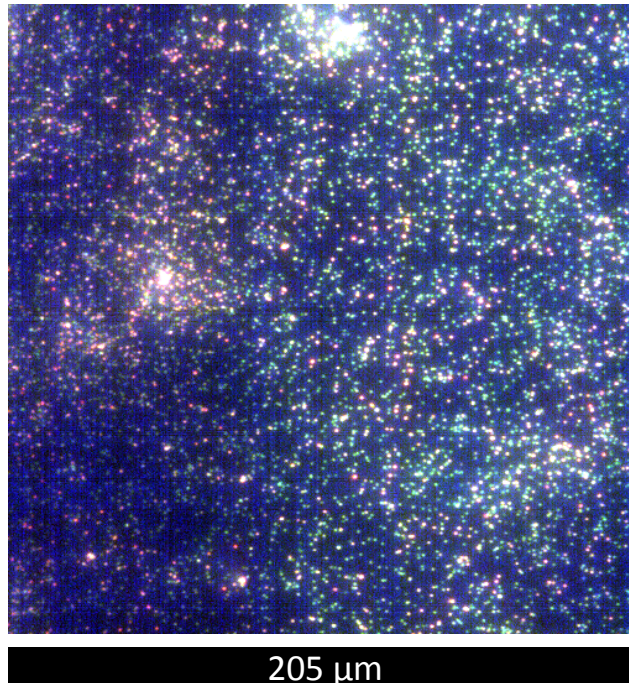
Consistent peak at ~570 nm  
observed over 'green' region.  
Indicative of uniform attachment  
of 100 nm GNP's

Sample spectra

Optical image (Dage)



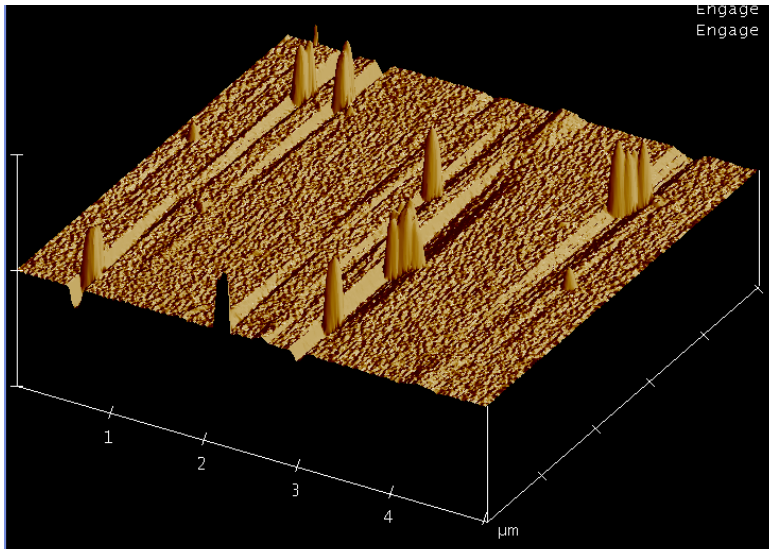
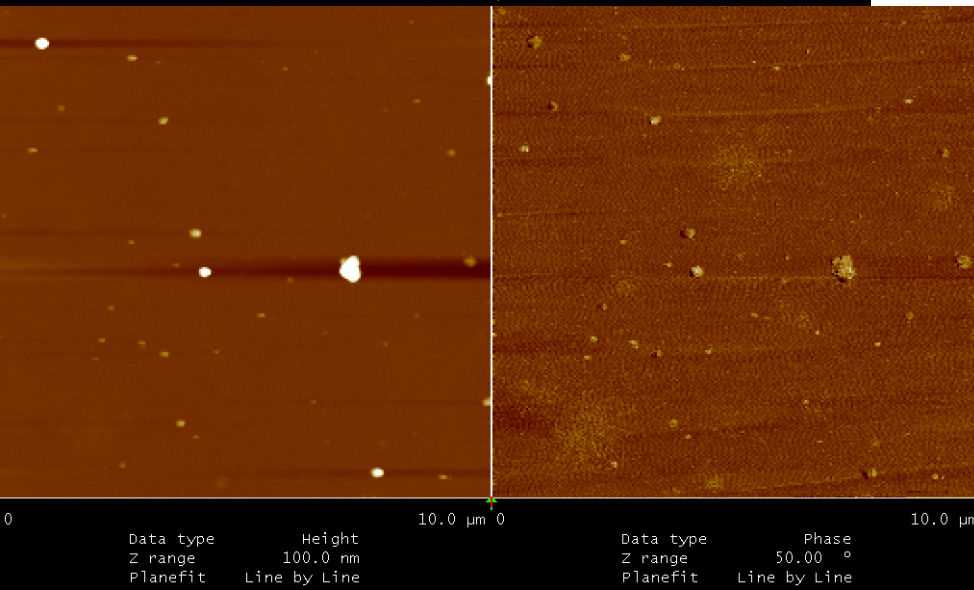
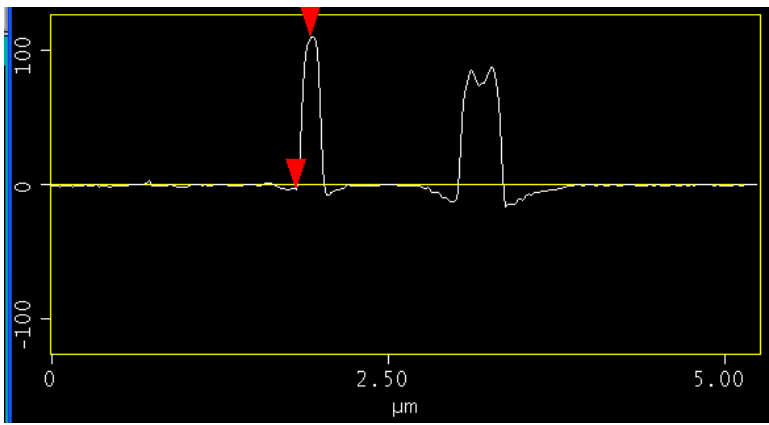
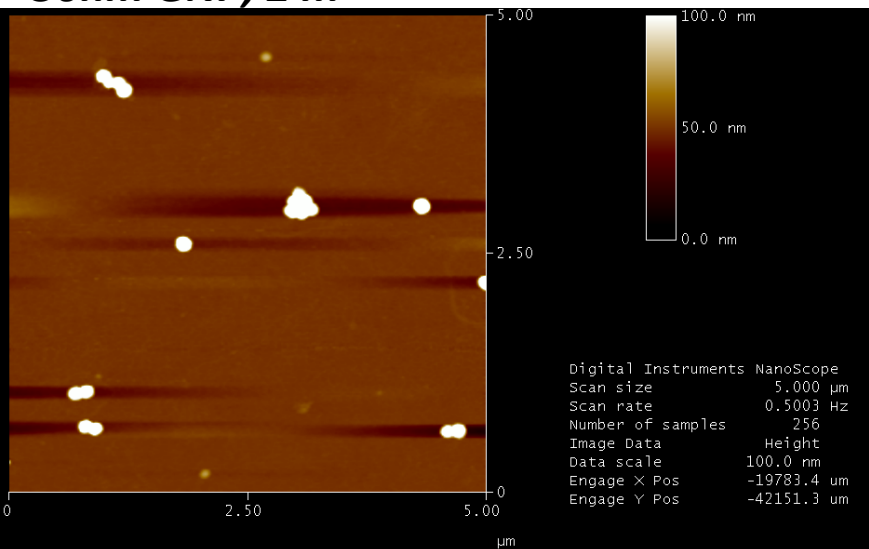
Hyperspectral image (Andor)



# Functionalized glass slides

Glass slide → APTES / ethanol → GNP

**50nm GNP, 24h**

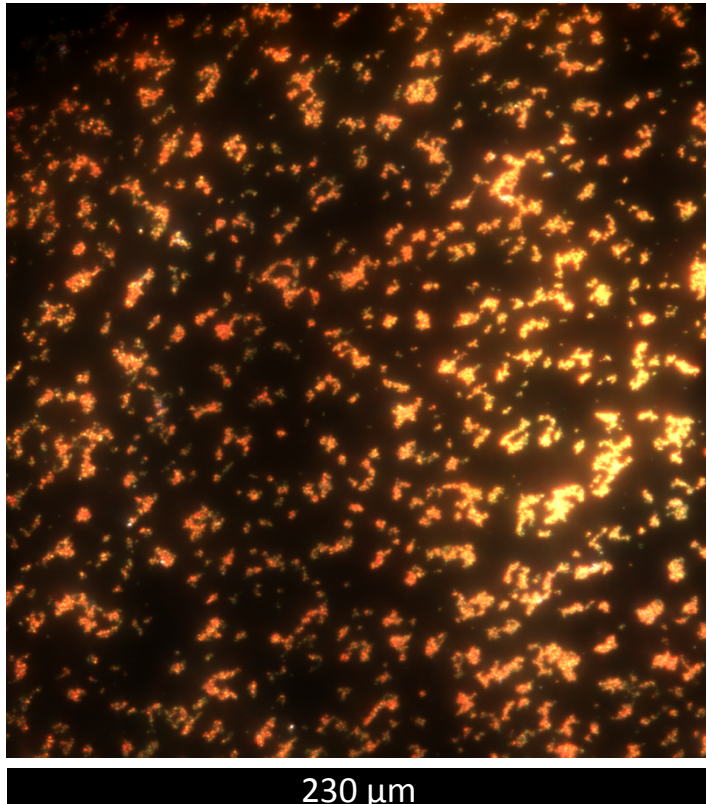


# Functionalized glass slides

Glass slide → APTES / methanol → GNP

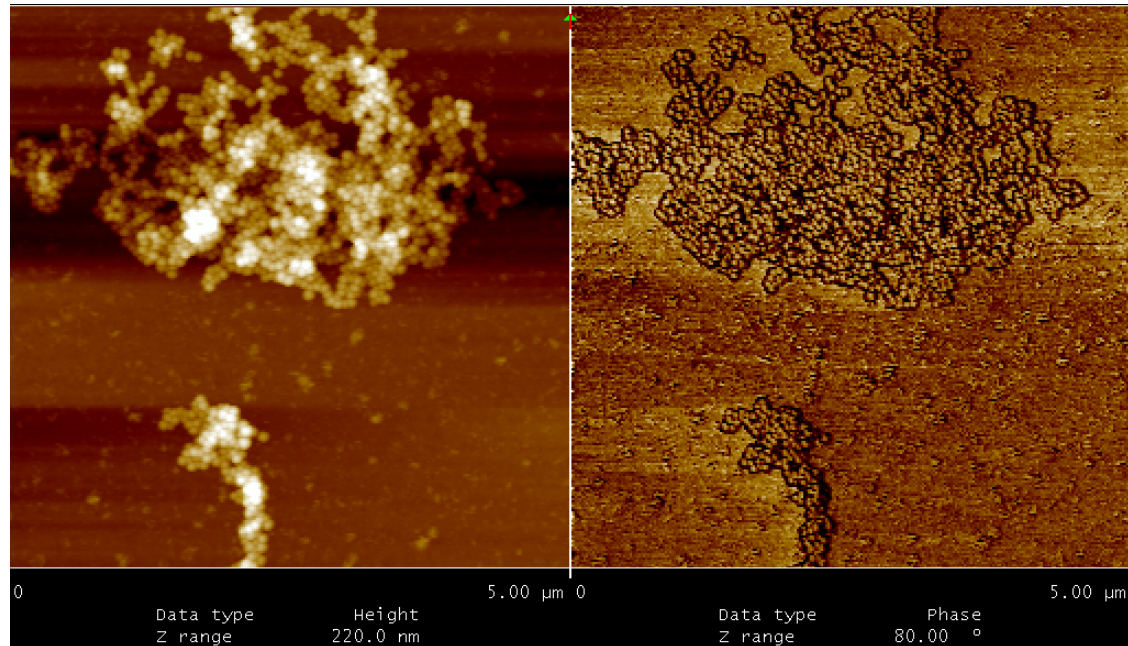
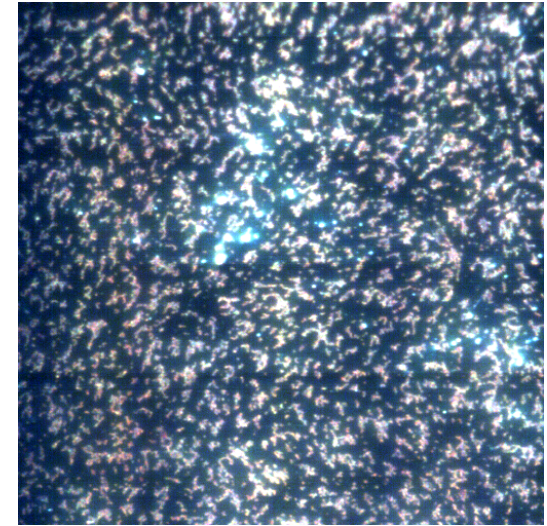
*5nm GNP, 24h, 18x dilution*

Optical image



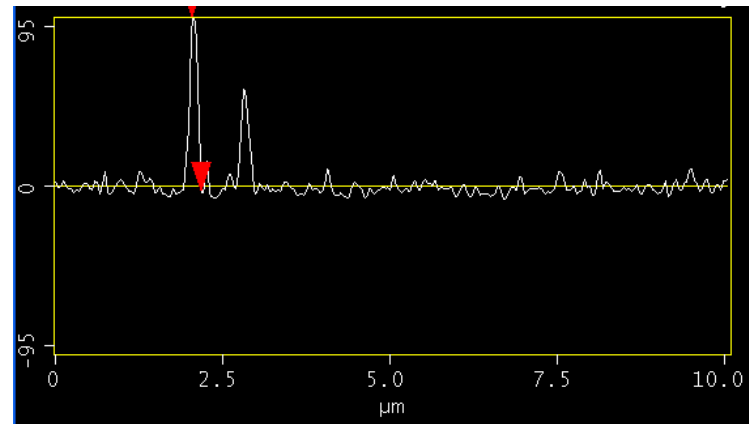
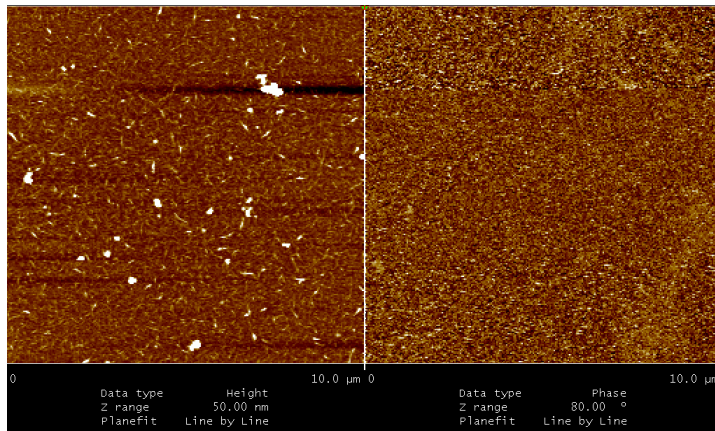
GNP Clustering!

Hyperspectral image



# Conclusions

- The Cytoviva images for Pt → EDT → GNP don't vary much for the splits done for different concentrations / sizes / functionalization times
- Rod-like background seen in AFM and SEM seems to come from the platinum
- Clumps are likely due to some impurity associated with the ethanedithiol functionalization, or salt crystals from left over from the nanoparticle buffer solution
- But possibility they may be GNP clusters



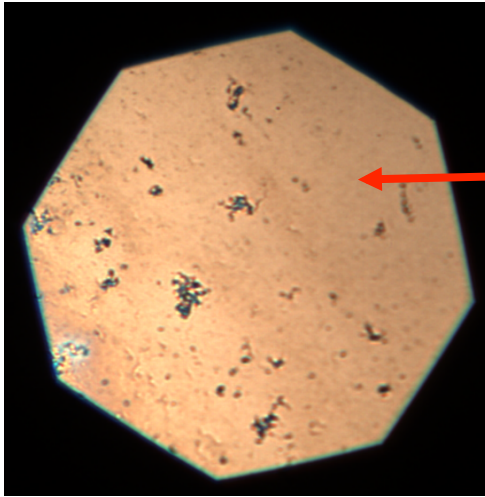
# Conclusions

- This may be due to ineffectiveness of ethanedithiol functionalization step: the high concentration combined with planar substrate may encourage bonding of both thiol groups to the Pt substrate
- Suggested future experiments:
  - Dilute ethanedithiol concentration
  - Use EDT coated GNP instead of trying to form monolayer on Pt
  - Try a different linker molecule to form an SAM on planar Pt

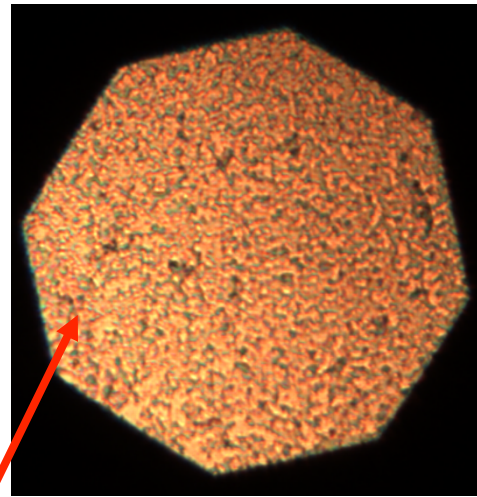


# Pt → GNP (solution left to evaporate)

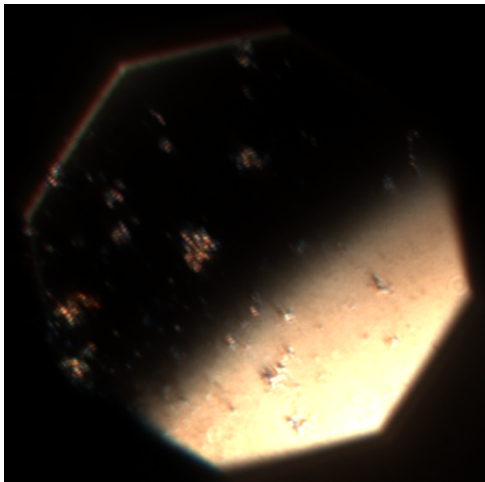
No clumps observed in the middle of the well → water evaporates from middle outwards to periphery, may have 'dragged' colloids and salt along with it leaving them deposited at the rim.



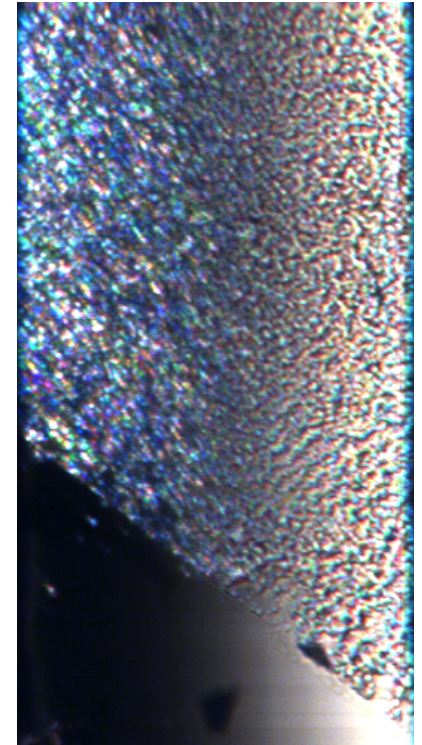
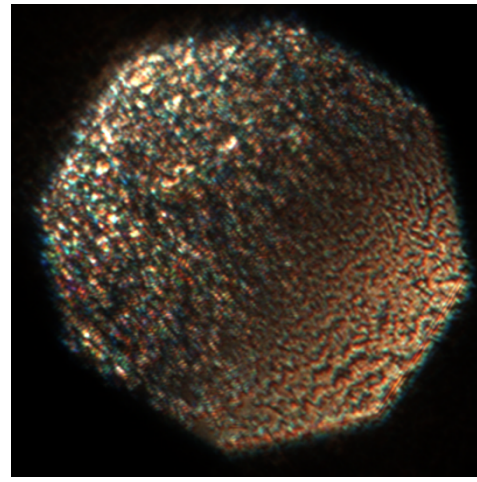
Just inside of rim. Similar to structures found with EDT step



Dense structures present in the rim, as imaged under microscope.



Border of well shows a defined 'rim'.



# Conclusions

- Succeeded in obtaining dark field hyperspectral data from Cytoviva in both reflectance and transmittance modes, and showing that GNP's can be distinguished (when they are there)
- Technique can be applied to future characterization of GNP's
- Demonstrated the limitations of this method of functionalization of GNP's on planar Pt, as well as of interpretation of Cytoviva data
- Lesson: Always check the starting assumptions!

Thank you!

			<b>CYTOVIVA IMAGING</b>		<b>AFM</b>	<b>SEM</b>	
			<i>Dark field Reflectance</i>	<i>Dark field Transmission</i>	<b>IMAGING</b>	<b>IMAGING</b>	
Pt only							
Pt → EDT	Left in air						
	Left in water						
Pt → PpT → GNP							
Pt → ethanol → GNP		1x dilution					
Pt → EDT → GNP	10 nm NP 24h	1x dilution					
		10x dilution					
		100x dilution					
		10 <sup>3</sup> x dilution					
	50 nm NP 24h	1x dilution					
		8x dilution					
		10x dilution					
		18x dilution					
		100x dilution					
		10 <sup>3</sup> x dilution					
	50 nm NP 2h	1x dilution					
		8x dilution					
		18x dilution					

EDT = Ethanedithiol in ethanol solution

Ppt = Propanethiol in ethanol solution

			CYTOVIVA IMAGING		AFM	SEM
			<i>Dark field Reflectance</i>	<i>Dark field Transmission</i>	IMAGING	IMAGING
Glass						
Glass → APTES / methanol						
Glass → APTES / methanol → GNP	50 nm NP 24h	1x dilution				
		8x dilution				
		18x dilution				
	50 nm NP 2h	1x dilution				
		8x dilution				
		18x dilution				
100 nm NP 24 h	1x dilution					
100 nm NP 2h	1x dilution					
Glass → APTES / ethanol						
Glass → APTES / ethanol → GNP	50 nm NP 24h	1x dilution				
		8x dilution				
		18x dilution				
	50 nm NP 2h	1x dilution				
		8x dilution				
		18x dilution				
100 nm NP 24 h	1x dilution					
100 nm NP 2h	1x dilution					

APTES = (3-Aminopropyl)triethoxysilane