Surface Enhanced Raman Spectroscopy of different chain length PEP+ moiety bound to Gold Nanorods

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Outline

- Introduction: Surface Plasmon Resonance (SPR) and Surface Enhanced Raman Spectroscopy (SERS)
- Au Nanorods (NRs) synthesis and functionalization
- UV-visible and TEM characterizations
- DDA calculation
- SERS measurements
- Final remarks

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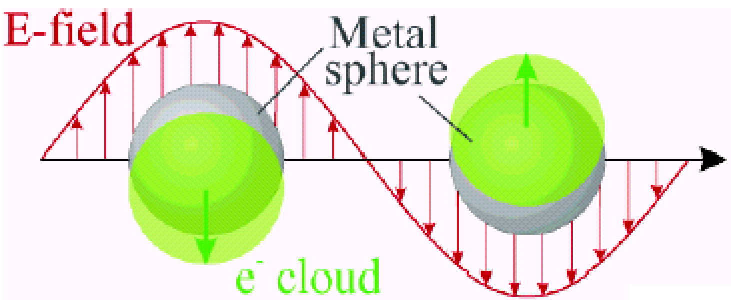
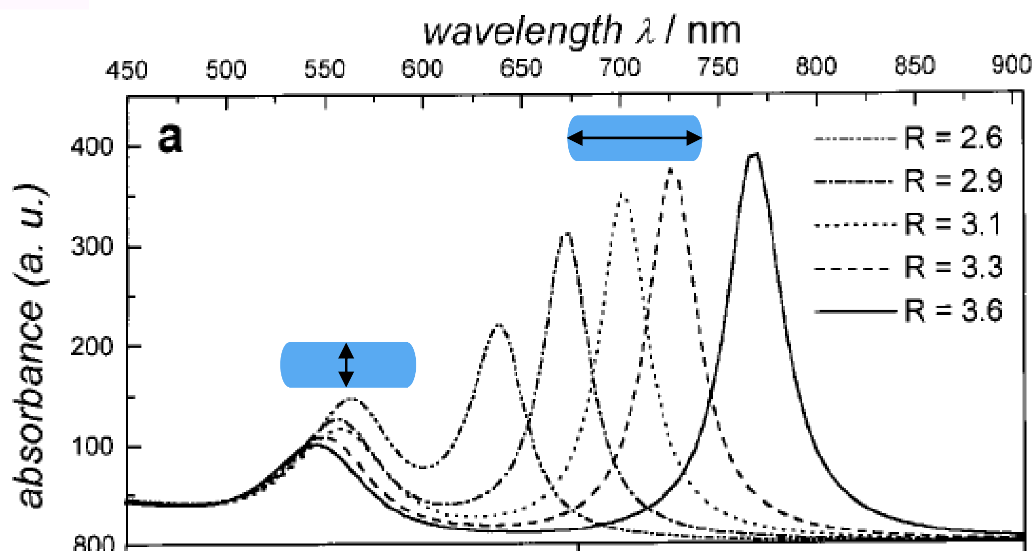
Introduction (1): SPR

SPR: coherent excitation of all free electrons within the conduction band

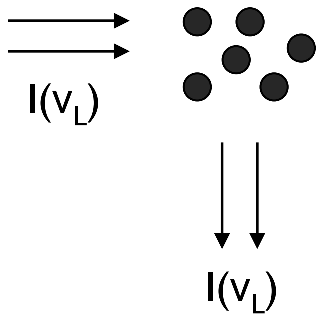


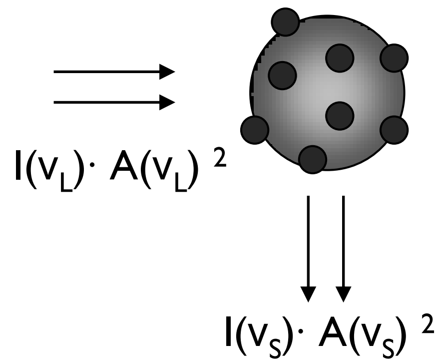
Mie theory
Gans Model

$$E_{loc} = \frac{3\varepsilon}{\varepsilon + 2\varepsilon_m} E_0$$



Introduction (2): SERS





$$I_{NRS}\left(\nu_S\right) = NI\left(\nu_S\right)\sigma^{R}_{free}$$

$$I_{SERS}\left(\nu_S\right) = N' I\left(\nu_L\right)\left|A\left(\nu_L\right)\right|^2 \left|A\left(\nu_S\right)\right|^2 \sigma^{R}_{ads}$$

- Raman scattering is a weak effect (cross section ~10^{-30} cm^2)
- If we can increase the local fields we can obtain a larger *effective scattering cross section*
  - ✓ Higher Raman scattering (higher signal)
  - ✓ Lower detection limits (Raman scattering scales with E^4)

Introduction (3): how to increase SERS

- Resonance between the plasmon band and the laser excitation

- Distance from the metal surface

- Resonance with molecular electronic transitions

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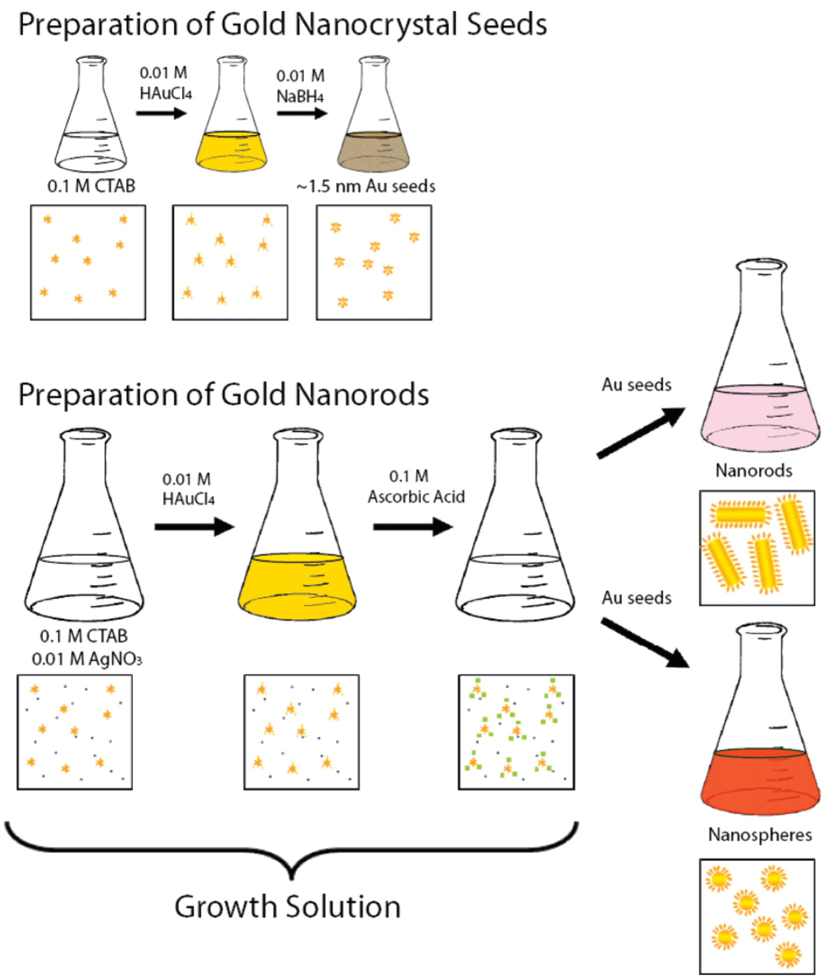
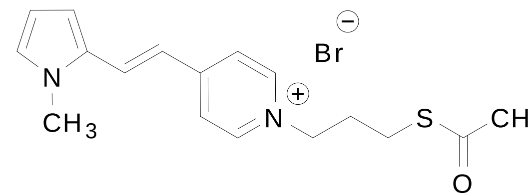
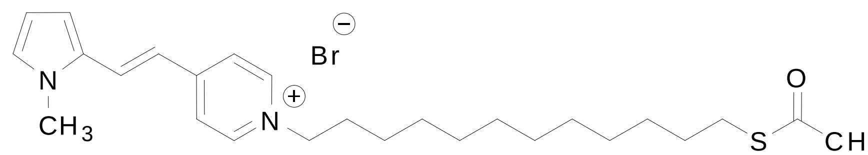
Au NRs synthesis and functionalization





PEP+C3-SAC



PEP+C12-SAC

 Smith et al *Langmuir* **2008**, 24, 644 – Placido et al *Chem. Mater.* **2009**, 21, 4192

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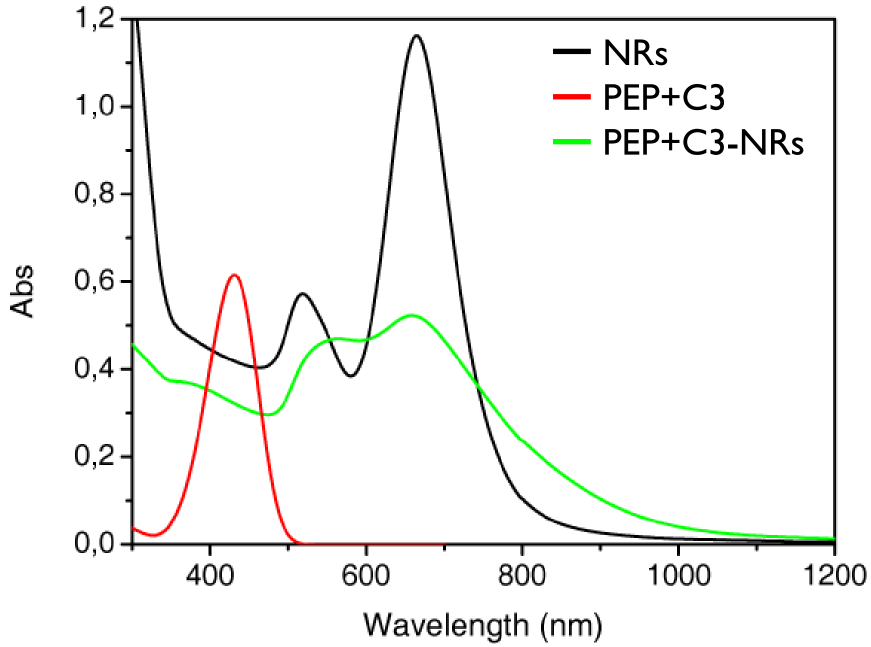
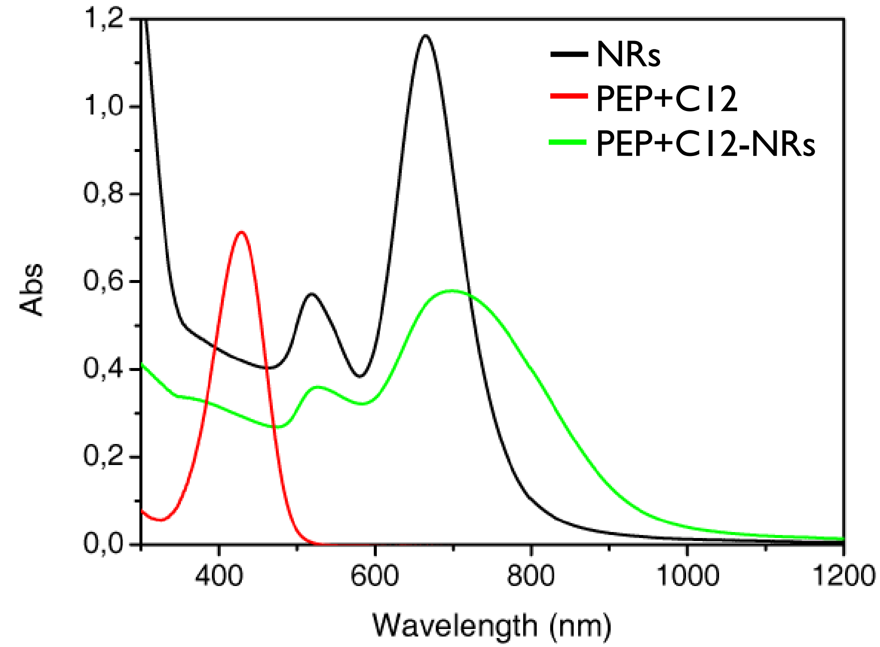
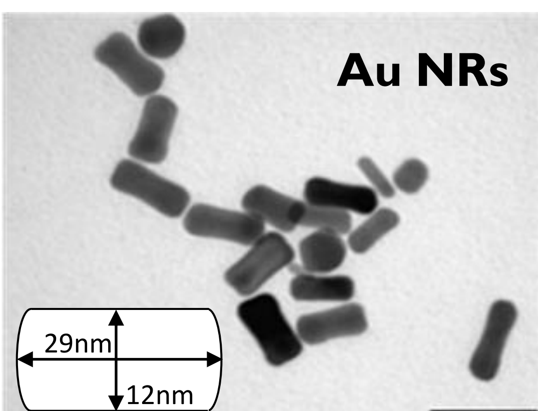
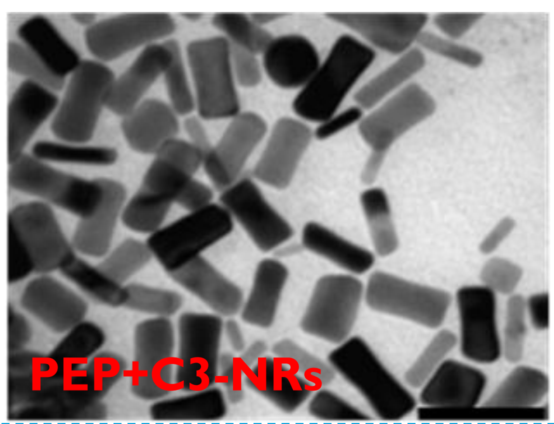
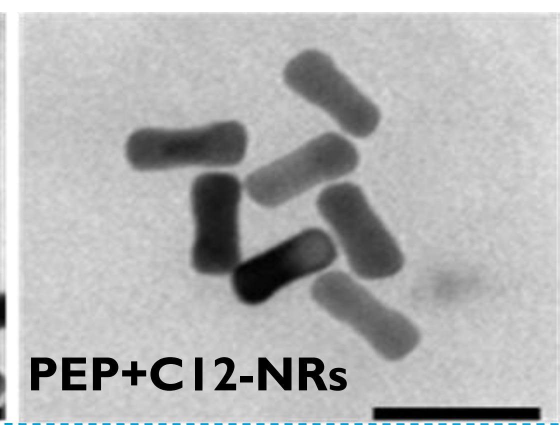
UV-visible and TEM characterizations



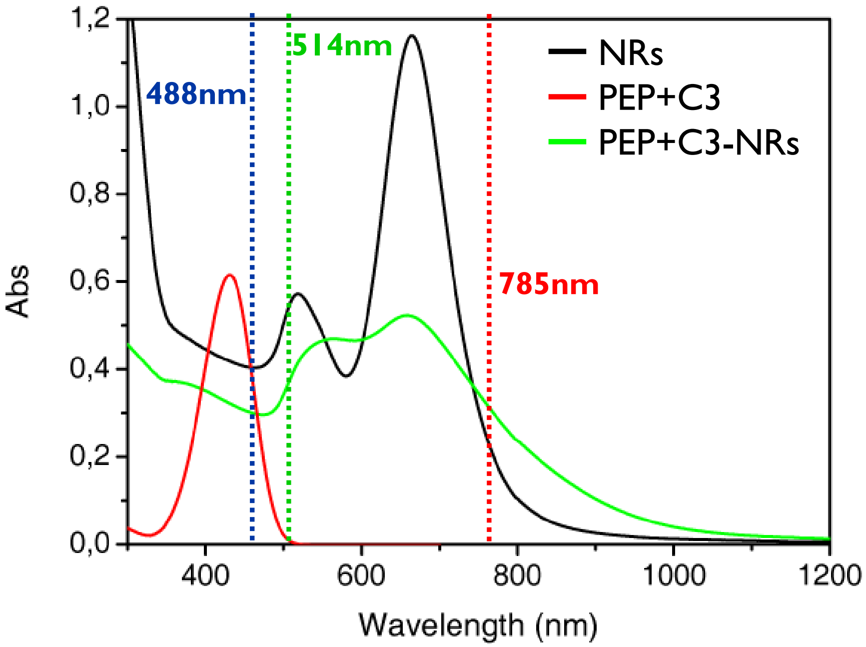


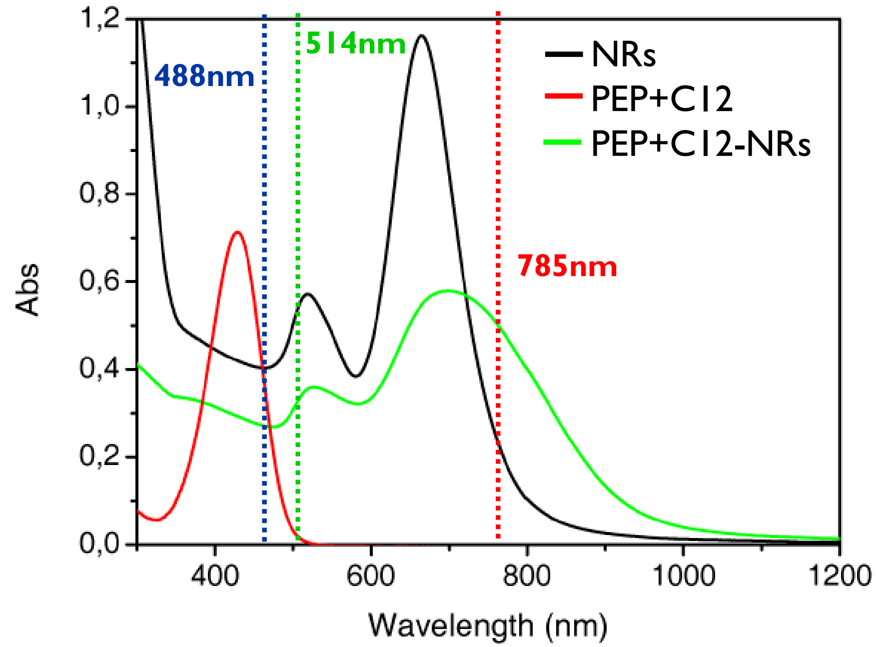


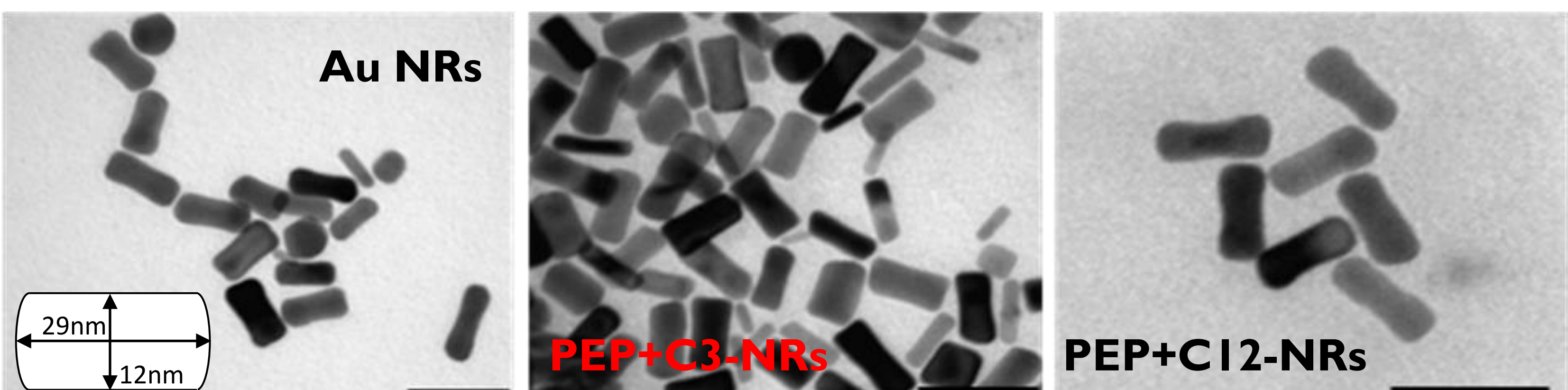




UV-visible and TEM characterizations







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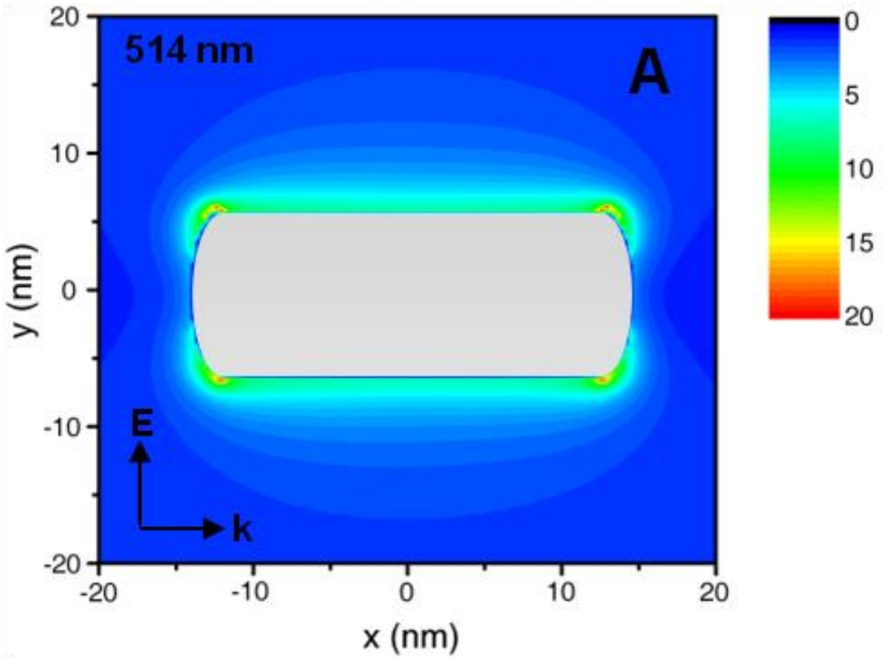
DDA calculation

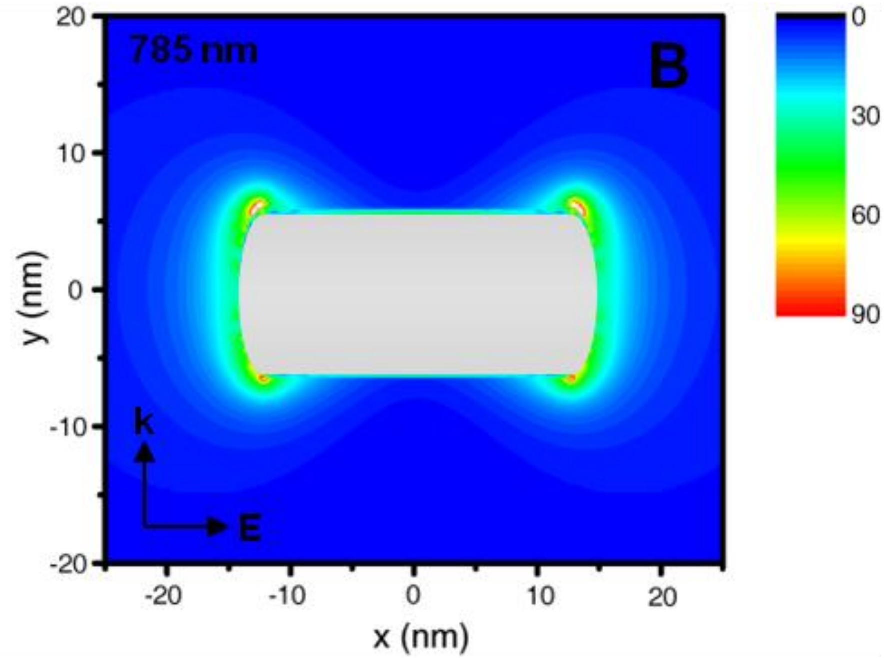
DDSCAT 7.1

Excitation of the Transverse plasmon mode



EF ~ 10^2

Excitation of the Longitudinal plasmon mode



EF ~ 10^4

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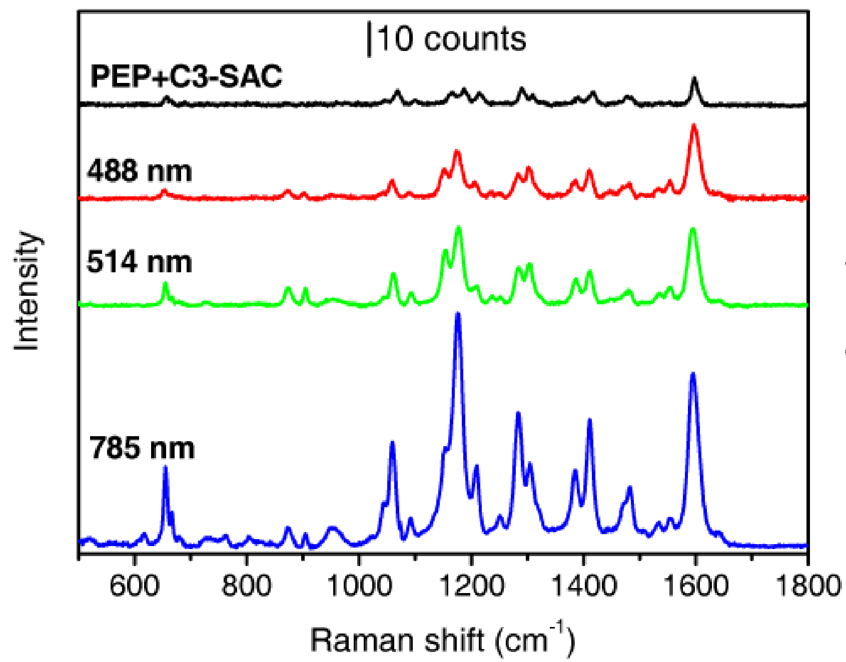
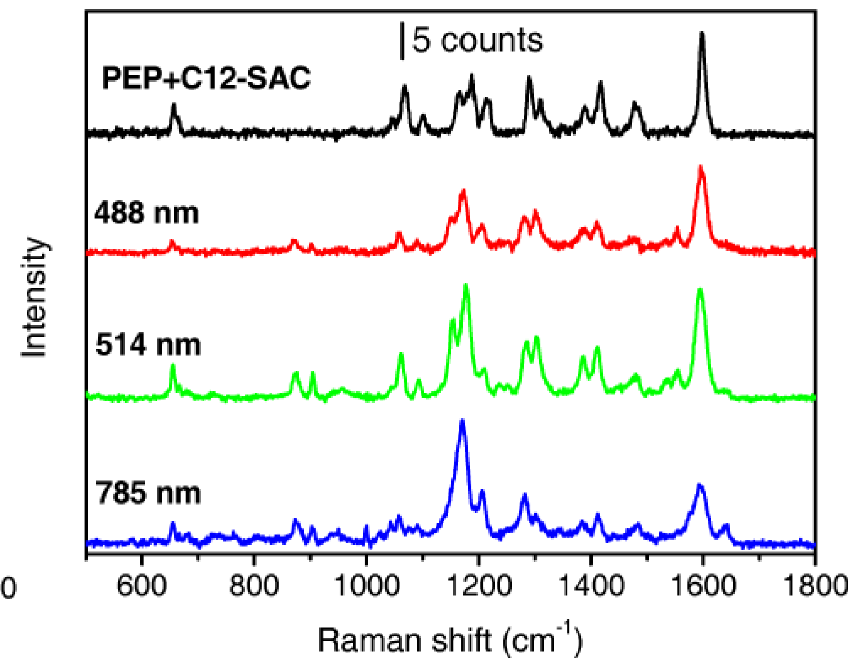
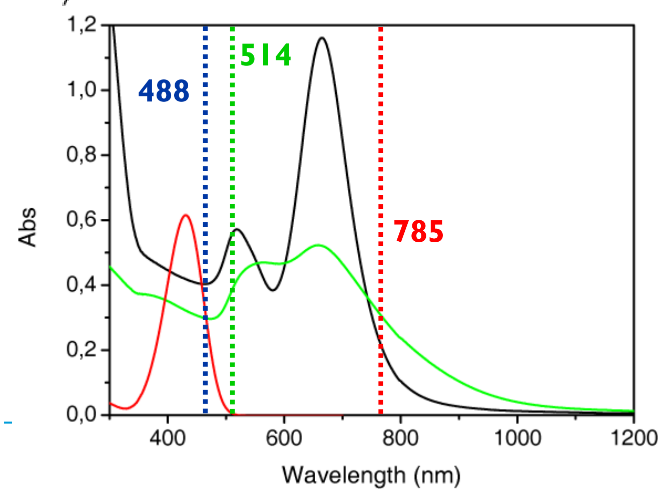
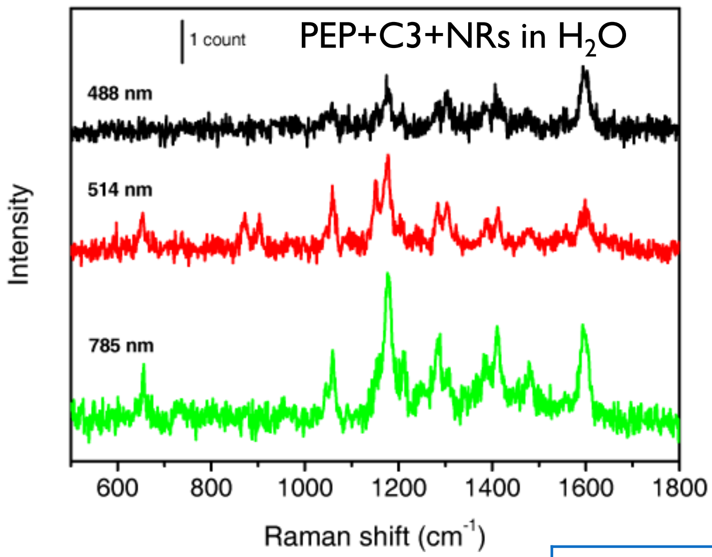
SERS (1): PEP+C3 and PEP+C12







SERS (2): PEP+C3 and PEP+C12, EF



$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{M_{PEP+}}{M_{NR-PEP+}}$$

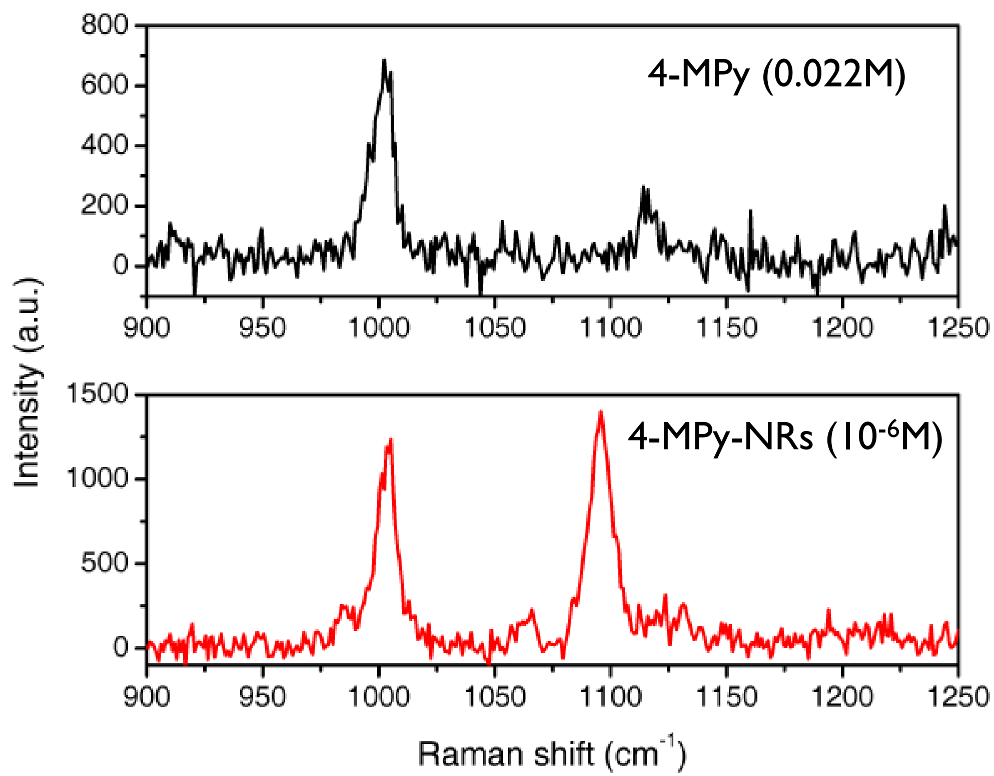
(cm^{-1})	EF@785 nm (PEP+C3-NRs)	EF@785 nm (PEP+C12-NRs)	Assignments
655	1.7×10^4	1.5×10^4	Ring CH out-of-plane def and bend.
1069	1.2×10^4	1.1×10^4	Ring CH in-plane bend (pyridinium)
1180	1.8×10^4	1.0×10^4	Ring CH in-plane bend (pyridinium)
1289	1.1×10^4	-	N-C ring str (pyrrole)
1415	9.7×10^3	-	Ring vib (pyrrole)

SERS (3): using 4-MPy to evaluate EF

- λ_{laser} = 514 nm, no Raman signal from 4-MPy-NRs

- λ_{laser} = 785 nm

(cm^{-1})	EF@785 nm	Assignments
1004	4.0×10^4	ν(C–C) ring breathing mode
1119	1.2×10^5	ν(C–S) ring breathing mode



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Final remarks

- Effect of the alkyl chain length.
- Effect of the laser resonance: 488-nm (PEP+ electronic transition), 514-nm (PEP+ electronic transition and transverse plasmon mode), 785-nm (longitudinal plasmon mode).
- DDA calculation: EF about 10^4 and 10^2 for the longitudinal and the transverse plasmon modes.
- Higher amplification when the laser excitation wavelength is resonant with either the plasmon modes. For the 514-nm laser excitation, strong contribution to the amplification due to the resonance with the absorption band of the dye.
- EF using 4-MPy: at 514-nm, no signal; at 785-nm 10^4.
- Lowering the detection limit controlling the resonance condition with either plasmon modes and electronic transitions of molecules.

Acknowledgements

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