

Gold Raspberry-Like Colloidosomes Prepared at the Water-Nitromethane Interface

Evgeny Smirnov,¹ Pekka Peljo,¹ and Hubert H. Girault^{1,}*

¹ Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne, Rue de l'Industrie 17, CH-1951 Sion, Switzerland.

Table of Contents

| Description | Page |
|--|------|
| SI-1: Chemical analysis (EDX) of a colloidosome sample | 3 |
| SI-2: Investigation of colloidosomes with confocal fluorescence microscopy | 4 |
| SI-3: UV-Vis spectra of TTF and TTF ⁺ | 6 |

SI-1. Chemical analysis (EDX) of a colloidosome sample

EDX spectra from colloidosomes were recorded from different places of the sample, as demonstrated in **Figure S1**. Data summarized in the **Table S1** below the image shows presence of both sulfur and gold in colloidosomes and significant amount of sulfur, but negligible amount of gold in another places of the interest. Notably, small amount of gold calculated based on EDX spectra in the case of Spectra 2-4 is below the limit of detection for EDX-analysis and likely caused by mathematical errors in fitting of EDX-spectra or single particles accidentally caught in the electron beam.

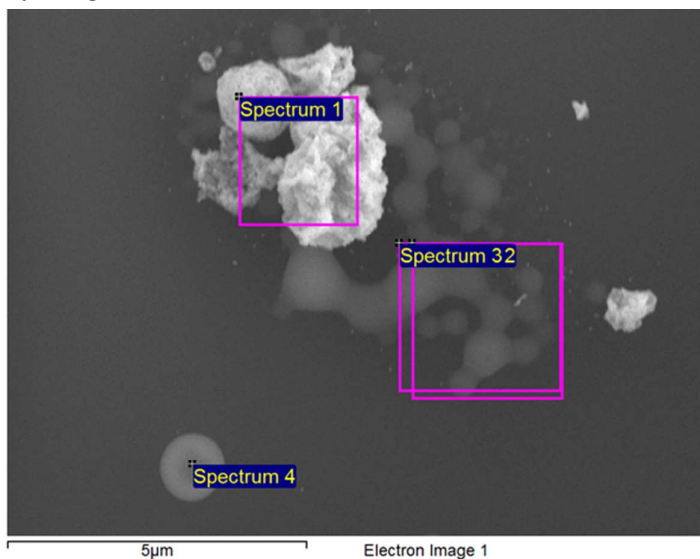


Figure S1. SEM image of a colloidosome sample and marked regions where EDX probing was carried out.

Table S1. Semi-quantitative EDX analysis results of colloidosomes and empty TTF-spheres obtained during draining-off process.

| | Si | S | Au |
|------------|-------|-------|-------|
| Spectrum 1 | 60.27 | 14.89 | 24.84 |
| Spectrum 2 | 91.76 | 7.98 | 0.27 |
| Spectrum 3 | 93.01 | 6.84 | 0.15 |
| Spectrum 4 | 92.17 | 7.73 | 0.10 |

SI-2. Investigation of colloidosomes with confocal fluorescence microscopy

In order to avoid fluorescence overlapping between coumarine dye, TTF and AuNPs, very low concentration of TTF (0.1 mM) was used. The blurring green color in top-left panel in Figure S2 is most likely due to tiny amount of coumarine dye migrated with nitromethane molecules into the aqueous phase during extraction process.

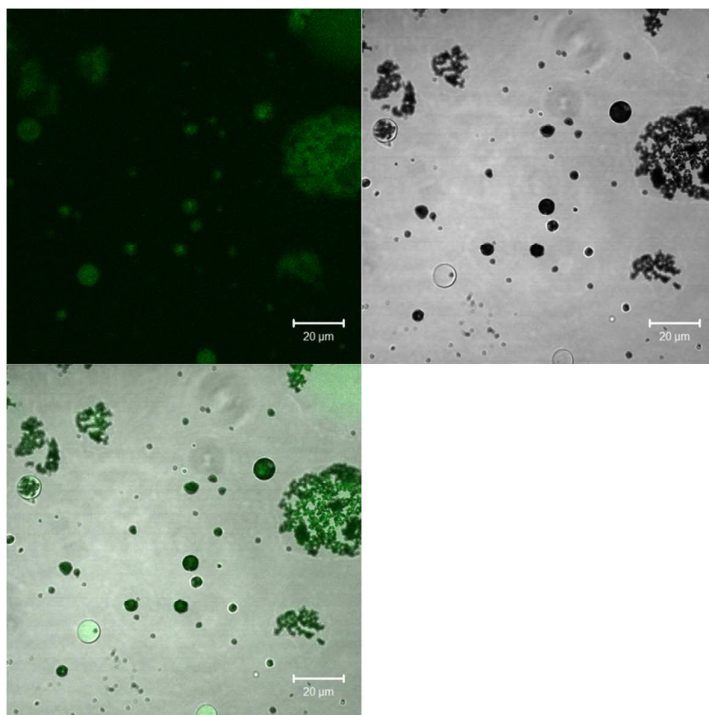


Figure S2. Confocal fluorescence microscopy images of obtained colloidosomes at water – nitromethane interface. Top-left panel – an image from fluorescence channel, top-right panel – regular confocal microscopy channel, bottom-right image – combined image.

To calculate colloidosomes size distribution, colloidosomes were tracked, measured and analysed on confocal fluorescence microscopy images. For each nanoparticle sizes used in the work we analysed from 100 up to 170 separate colloidosomes. The obtained distributions are present in **Figure S3**.

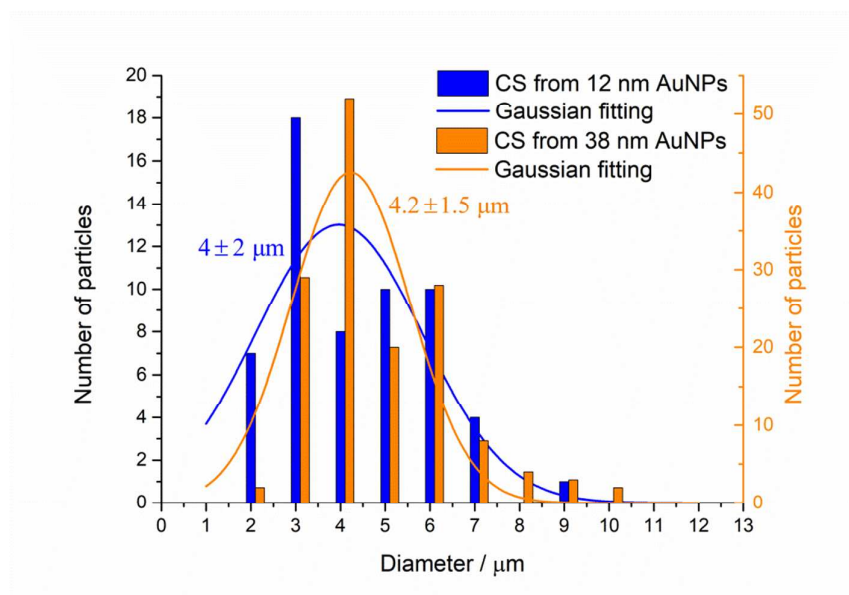


Figure S3. Colloidosomes size distribution based on the obtained confocal fluorescence microscopy images.

SI-3. UV-Vis spectra of TTF and TTF⁺

To clarify the origin of the peak at *ca.* 1000 nm in UV-Vis-NIR spectra of colloidosomes, the blank measurements were carried out. The record data is present in Figure S4. TTF possess almost zero absorption above 500 nm, where TTF⁺ has two distinguishable peaks at *ca.* 450 nm and *ca.* 580 nm. There is negligible absorbance between 900 and 1000 nm for both cases.

The procedure to extract TTF⁺ was as the following. Firstly, 1 mL of 1 mM solution of TCNQ in TFT or MeNO₂ was mixed with 1 mL of 1 mM of TTF in a vial forming TTF-TCNQ charge transfer complex. The colour of the obtained solutions was yellow in the case of TFT and yellow-greenish in the case of MeNO₂. Secondly, to polarize a liquid-liquid interface chemical and extract TTF⁺ on top of the organic phase 1.5 ml of water and 0.5 ml of 1 mM BACl and 10 mM LiCl were added. After short shaking, two colorized phases were separated: brownish aqueous due to the presence of TTF⁺Cl⁻ and turquoise organic due to TCNQ⁻BA⁺. Finally, the aqueous phase was isolated from the vial into a 10 mm QC cuvette and examined with UV-Vis-NIR-spectrometer.

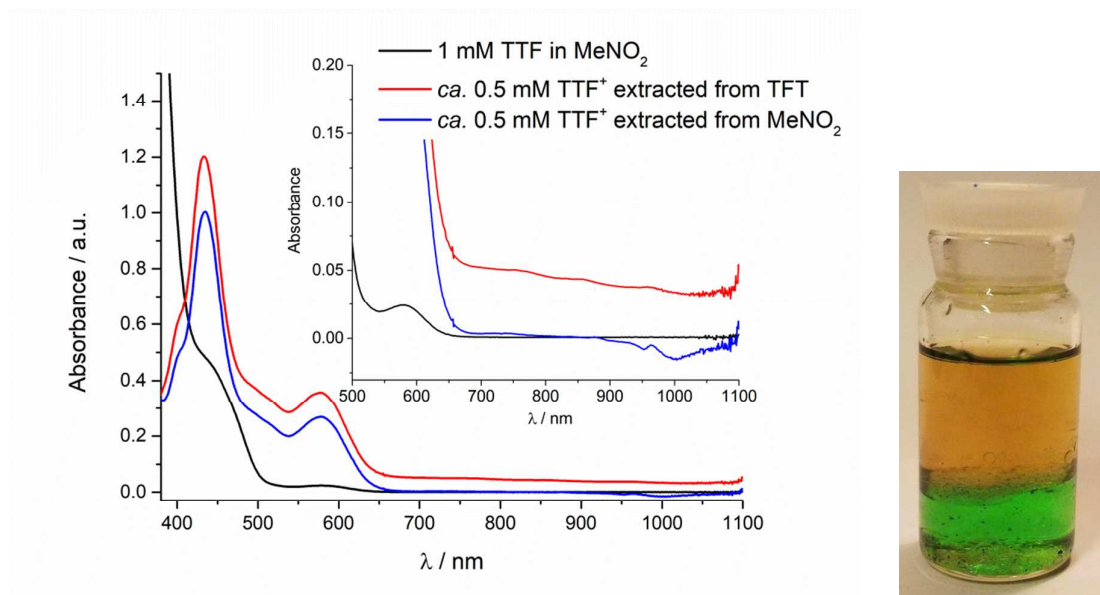


Figure S4. UV-Vis spectra of TTF in MeNO₂ and TTF⁺ extracted to the aqueous phase from w-TFT and w-MeNO₂ interfaces. Inlet: the same spectra magnified in the range of 500 to 1100 nm. On the right: a photograph of a biphasic system after TTF⁺ extraction is present.