

## Electronic Supplementary Information

### **2D Hybrid Networks of Gold Nanoparticles: Mechanoresponsive Optical Humidity Sensors**

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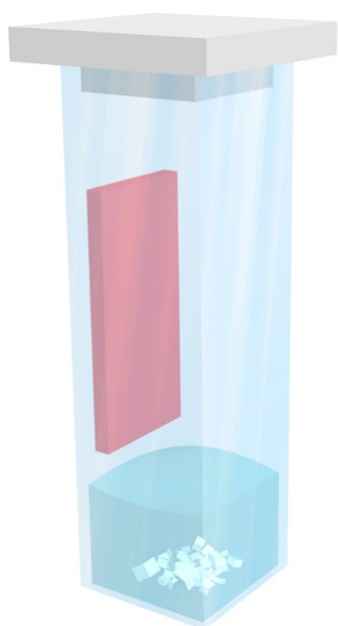
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## 1. Methods and materials

The AuNPs were synthesized with the Turkevich method by placing a 150 ml of a 2.2 mM water solution of sodium citrate di-hydrated in a 3-neck round-bottom flask. The flask was kept under Ar atmosphere and heated up to 100 °C. At this point 1 ml of a 25 mM water solution of HAuCl<sub>4</sub> was added rapidly in the flask under stirring (the solution turns yellow because of the presence of the HAuCl<sub>4</sub>). The solution was kept at 100 °C under continuous stirring for 3.5 min before being left to cool down at room temperature. The volume of the solution was kept constant during the whole reaction by using a reflux condenser.<sup>1</sup> DLS experiments were performed with a Malvern “Zetasizer Nano ZS” equipped with a 4 W  $\lambda = 633$  nm laser source. UV-Vis extinction spectra were recorded with a Jasco “V-670” UV-Vis-NIR spectrophotometer in 1 cm optical path quartz cuvettes. All the SEM images reported in this manuscript were recorded using a FEI Quanta 250 FEG microscope in high vacuum, with a spot size of 3 nm and acceleration voltage of 20 kV. Electrical I-V measurements were recorded with a Keithley source meter model “2636B” connected to a micromanipulator probe station. The substrate used for electrical characterization are 300 nm SiO<sub>2</sub>/Si with 40 nm thick gold electrodes featuring a channel length = 100 nm.

The cross-link reaction between AuNPs and commercially available SH-PEG-SH (Mw = 1000 Da, purchased by Sigma Aldrich) was performed by adding the PEG containing water solution directly in the solution in which the AuNPs were grown, without further purifications. The employed PEG:AuNPs molar ratio is set to = 3. In particular the experiments were performed by adding 30  $\mu$ l of a 1 mg/ml PEG solution to 8 ml of AuNPs solution (nominal concentration evaluated from optical extinction measurements =  $1.3 \times 10^{-8}$  M)<sup>2</sup>.

All the AuNPs 2D network-based films were prepared by drop casting 200-300  $\mu$ l (depending on the substrate’s size) of the AuNPs-PEG solution on freshly ozone cleaned substrates. After the complete evaporation of the solvent, the samples were rinsed in water multiple times to remove the residuals of sodium citrate. UV-Vis extinction spectra on films in **Fig 3c** and **4b** were recorded by placing the AuNPs films, deposited on quartz substrates, inside a 1 cm optical path quartz cuvette. By adding saturated salt solution inside the sealed cuvette, as schematized in **Fig. S1**, it was possible to record UV-Vis extinction spectra at different relative humidity conditions, with a precise control over the environment.<sup>3</sup> The first (“0% RH”) and last (“water”) points were recorded respectively by sealing the cuvette in a N<sub>2</sub> filled glovebox (0.5 ppm water) and by completely filling the cuvette with MilliQ water. The optical extinction dry-humid cycles reported in **Fig. 4a** and **S7** were recorded by placing the samples on a support and flushing a flow of humid air directly on the sample surface with a tubing system connected to a balloon inflated with humid air (~ 50-60 % RH).



Utilized salt	Relative humidity (20°C)
Lithium chloride (LiCl)	11.3 %
Magnesium chloride (MgCl <sub>2</sub> )	32.6 %
Sodium chloride (NaCl)	75.3 %
Potassium chloride (KCl)	84.3 %
Potassium sulfate (K <sub>2</sub> SO <sub>4</sub> )	97.3 %

Figure S1: schematic of the approach used to perform optical extinction measurements in controlled humid environment and table of the employed saturated salt water solutions with the corresponding equilibrium humidity.<sup>3</sup>

## 2. Dynamic light scattering of synthesized AuNPs

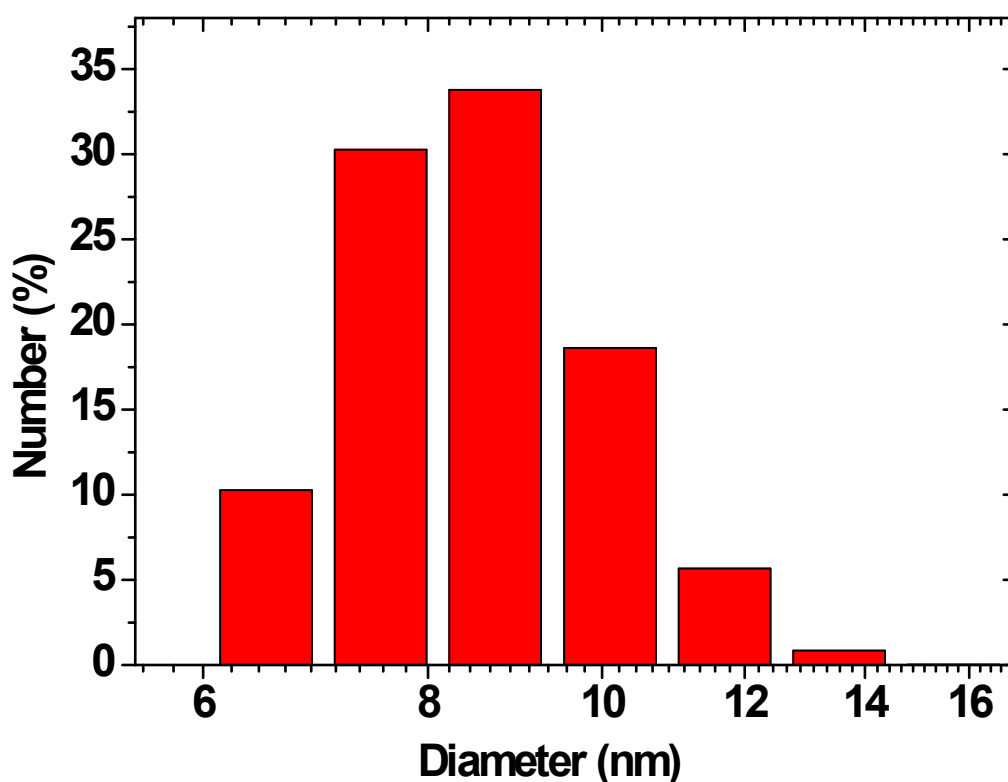


Figure S2: Dynamic light scattering measurements of the size of the as synthesized AuNPs

### 3. UV-Vis spectra of AuNPs/SH-PEG-SH solutions

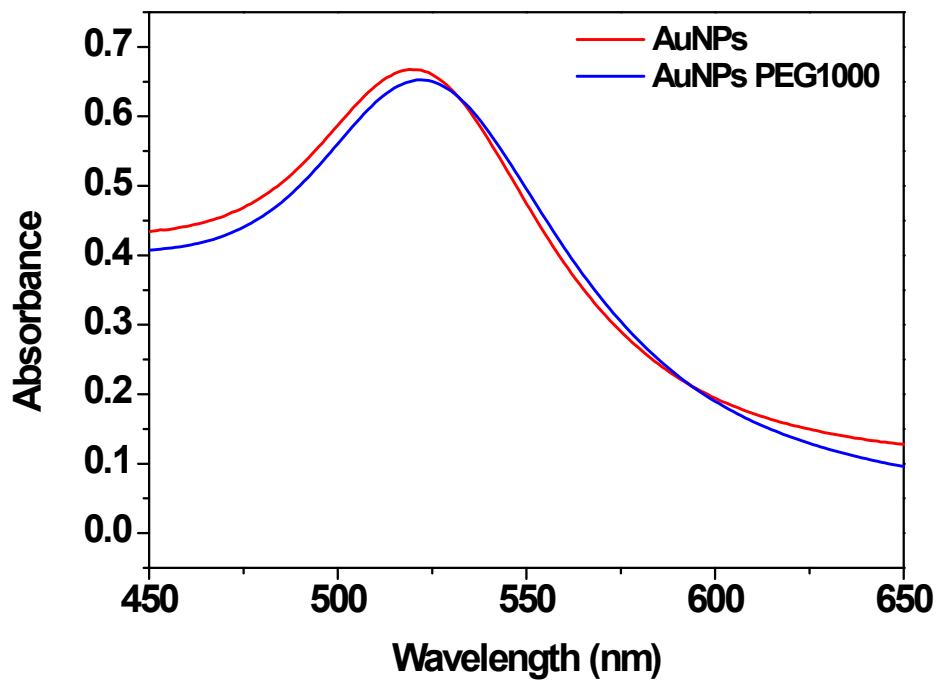


Figure S3: UV-Vis absorbance spectra of a solution of AuNPs in H<sub>2</sub>O as synthesized and after addition of the cross-linker SH-PEG-SH

#### 4. Electrical characterization

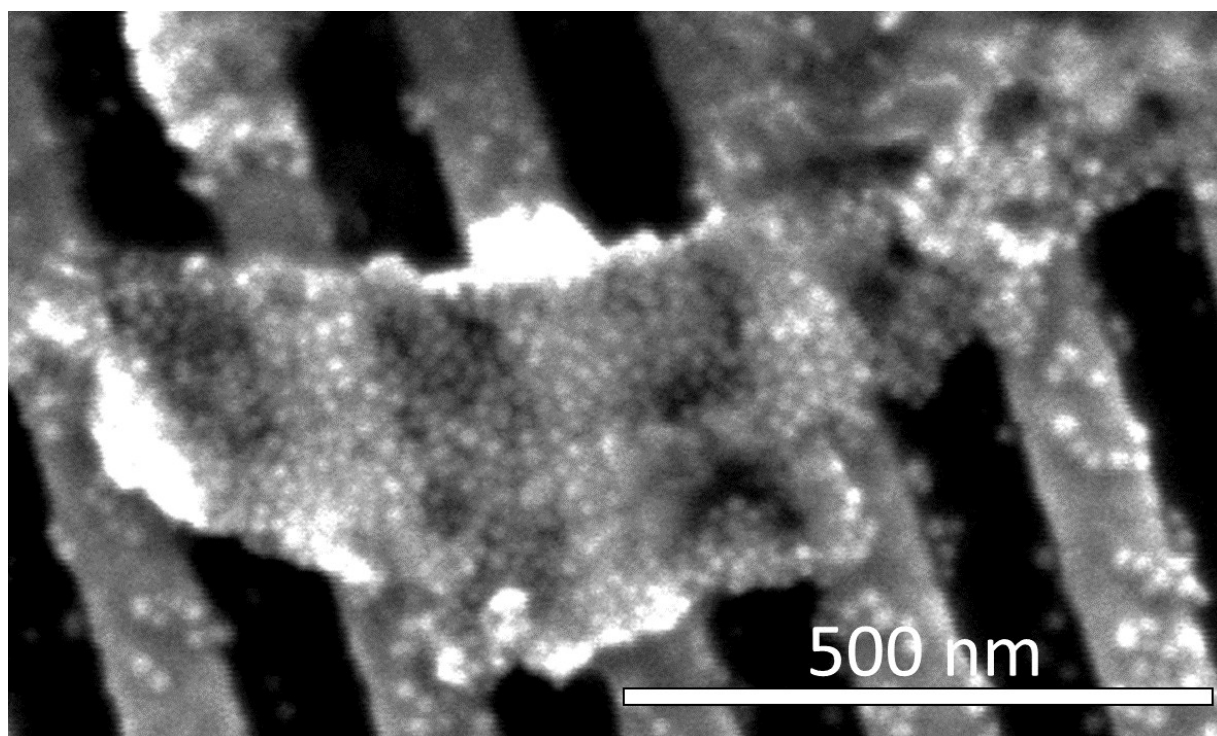


Figure S4: Example of SEM image of SiO<sub>2</sub> supported short channel (100 nm) Au electrodes bridged by a single domain of AuNPs network.

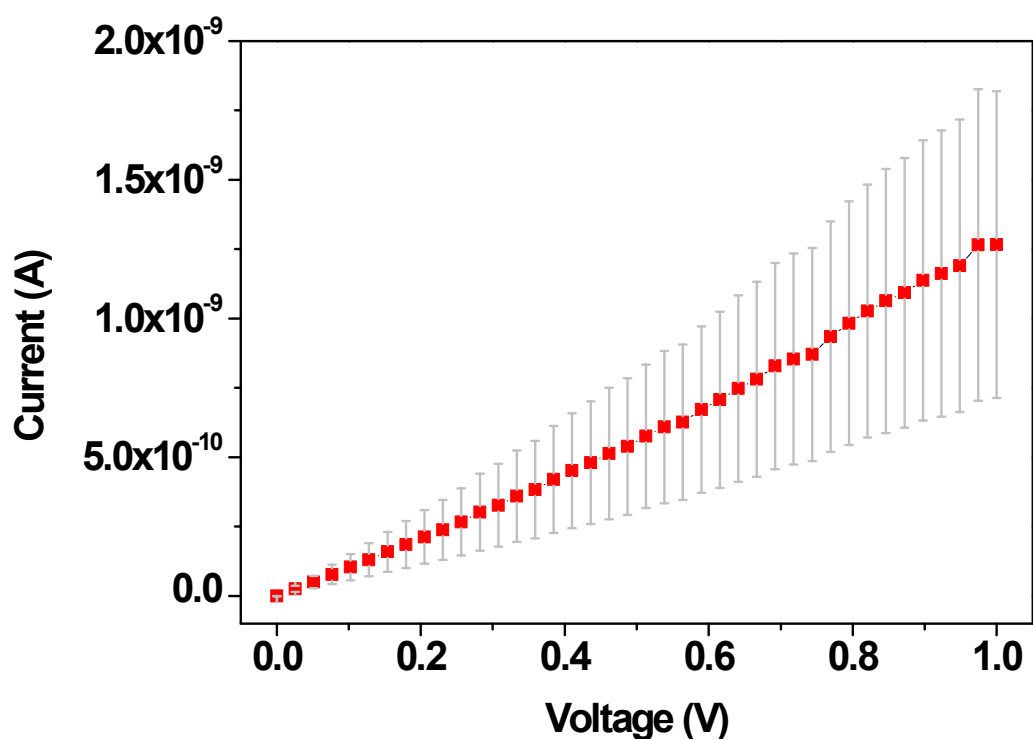


Figure S5: I-V characteristics of short channel two-terminal devices of 2D AuNPs networks (average resistance 772 M $\Omega$ ).

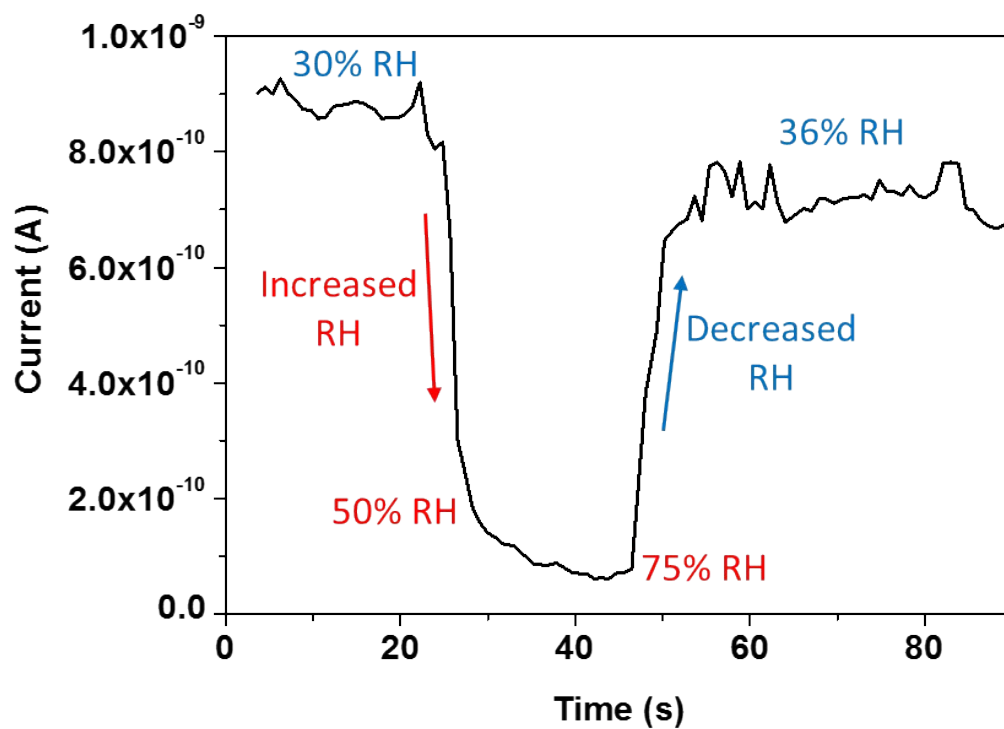


Figure S6: Electrical two-terminal device response to the increased humidity on 2D AuNPs networks.

## 5. High speed cycles showing reversible optical plasmonic shift

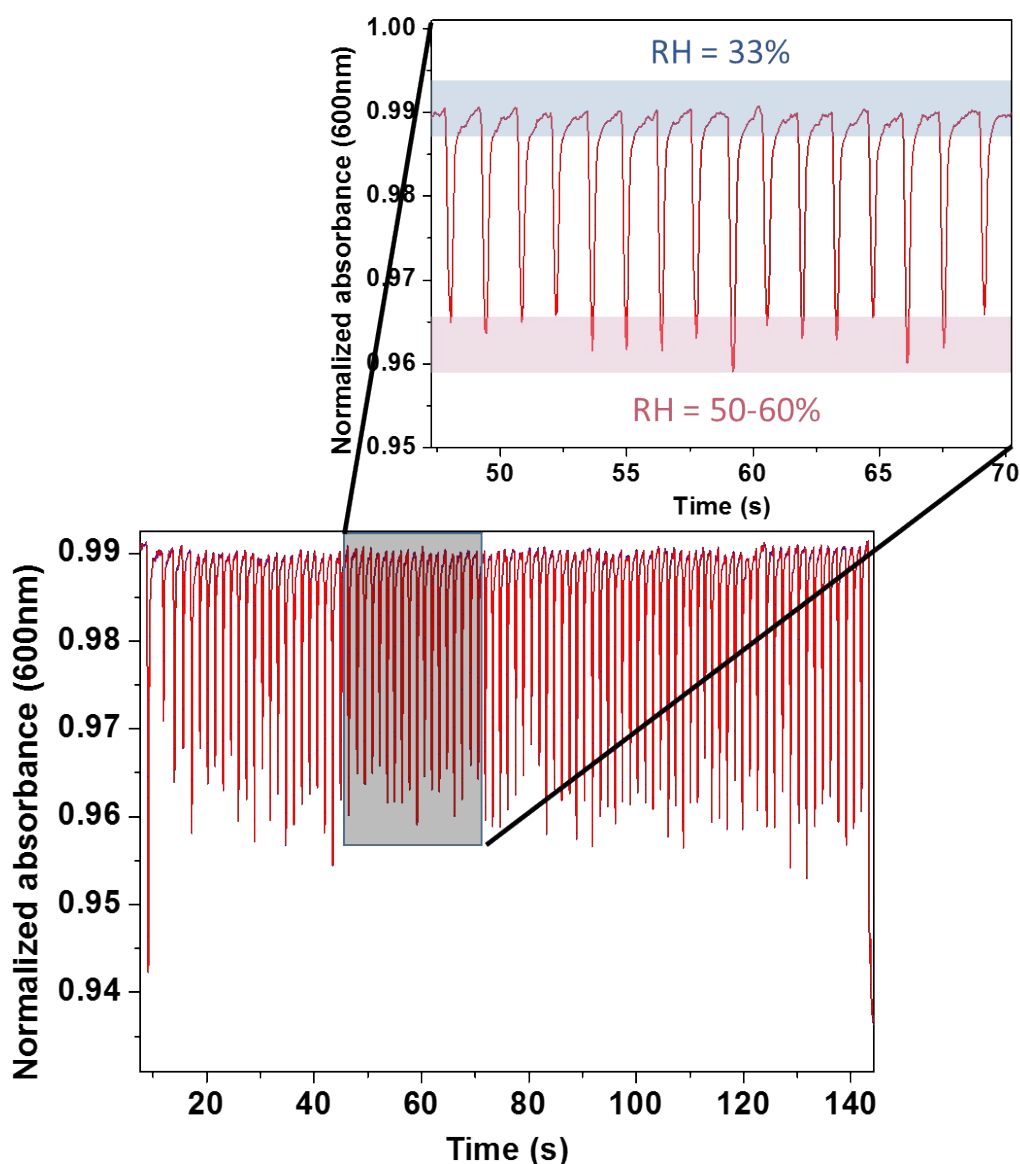


Figure S7: Cycles of dry and humid environment to test response speed and reversibility of the plasmonic wavelength shift using pulses of humid air.

## 6. DDA simulations

We implemented a discrete dipole approximation (DDA) method in order to calculate the extinction spectra of hexagonal clusters made of 7 Au nanoparticles (NPs). The calculating resolution (i.e. minimum distance between 2 discretizing dipoles) is set to 1 nm and the diameter of each AuNP is fixed at 9 nm. In the experiments, the AuNPs are cross linked with a self-assembled monolayer of di-thiolated linkers (see Fig.2 in the main text) which 2D network swells as the humidity increases. In the simulations, we account for such a PEG backbone through a effective refractive index that evolves as a function of the adsorbed humidity as

$$n_{eff} = \alpha n_{back} + (1 - \alpha)n_{H_2O}$$

where  $n_{back} \sim 1.78$  is fixed in such a way as to corresponds to the background refractive index of the PEG-AuNP network – see main text. The refractive index of pure water is set to  $n_{H_2O} = 1.33$ .

The critical point is to evaluate the impact of humidity on the  $\alpha$  coefficient with corresponds to the water loss/uptake within the PEG chains around the particles. The amount of water desorbed/adsorbed at different RH conditions was extracted by experimental literature data on water sorption isotherms in bulk PEGs, reported in Ref.<sup>4</sup> (**Fig. S8**).

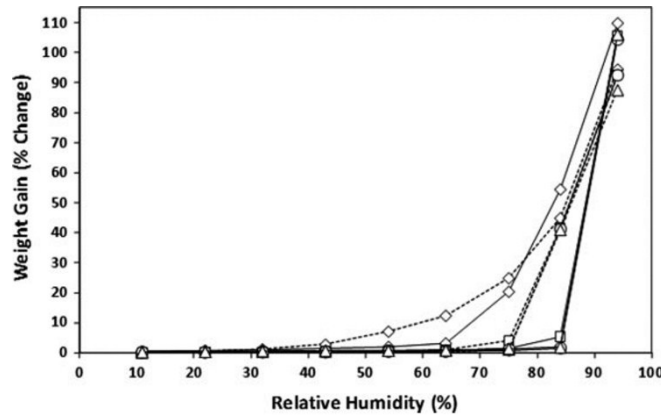


Figure S8: Vapor sorption isotherms of various MW PEGs measured by automated gravimetric moisture analysis at each relative humidity. ( $\diamond$ ) PEG 1450, ( $\square$ ) PEG 3350, ( $\circ$ ) PEG 6000, ( $\Delta$ ) PEG 8000. Solid lines (-) and dashed lines (- -) are isotherms measured at 25° C and 40° C respectively. Reprinted from Ref.<sup>4</sup>

This curves directly yields the  $(1-\alpha)/\alpha$  water “weight gain” ratio as a function of the relative humidity between the PEG and water refractive indices which can be nicely fitted by an exponential function. The resulting evolution of the effective refractive index is then injected in the simulation and the concomitant evolution of the interparticles distance is included in such a way as to give a best fit relation between the relative humidity  $R$  and the experimental spectral position  $\lambda$  of the network’s optical absorption peak as:

$$\lambda = -0.077 * \exp(-R/ -15.58) + 596.19$$

This fit, shown on Fig. S9, immediately reveals that merely accounting for the influence of the relative humidity on effective refractive index changes is not sufficient in order to reproduce the actual spectral evolutions gathered in Fig. 4 (b) of the main text. To do, it is also important to progressively increase the interparticle distances as the relative humidity increases, in relation with the progressive swelling of the PEG 2D network. Combined with the modification of the effective refractive index changes, the progressive contraction of the PEG chains turns out to be an essential spectral parameter, starting from a maximal interparticle distance of 8 nm up to the minimal distance of 4 nm. This is clearly seen on the agreement shown in Fig. S10 between the evolutions of the broadband extinction spectra experimentally recorded and numerically evaluated.



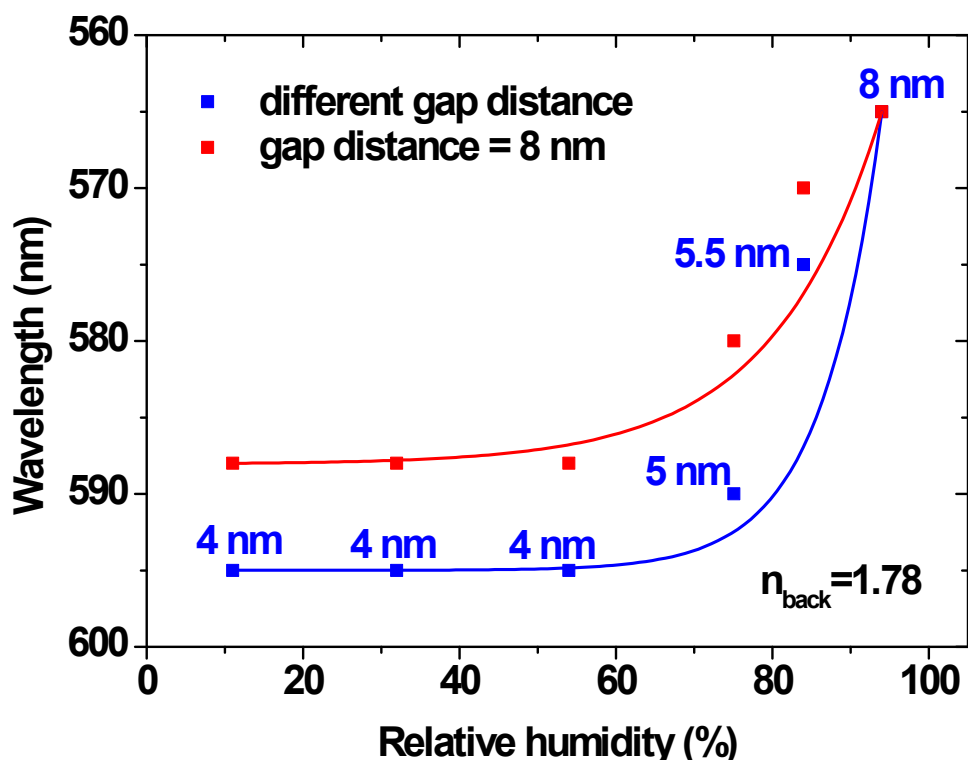


Figure S9: Evolution of the absorption peak of a 7 AuNPs hexagonal cluster simulated by a DDA approach. Comparison between the simulated optical response of AuNPs networks upon exposure to moisture accounting for solely changes in the background refractive index (red) and in both background refractive index and ligand chain length (i.e. interparticle distances) as a function of the relative humidity. This simulated curve is to be compared with the experimental data shown in Fig. 4 (b) in the main text.

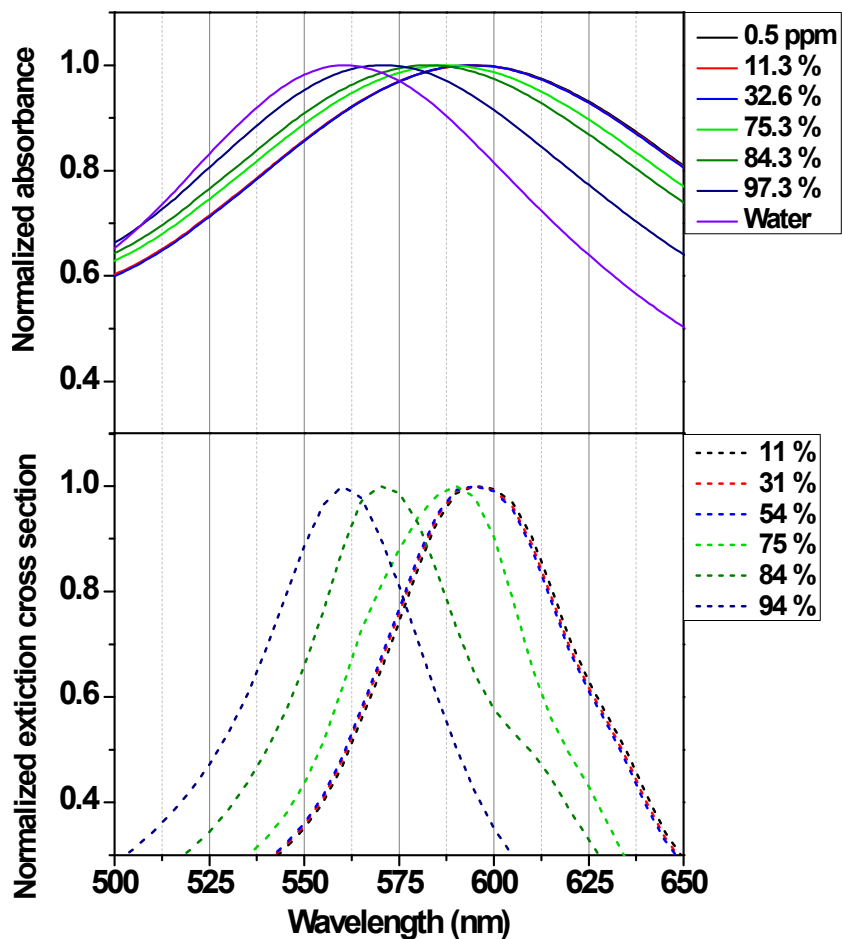


Figure S10: Comparison between experimental (top) and simulated (bottom) extinction spectra of AuNPs/PEG network exposed to different humidity levels.

## 7. Supplementary SEM images

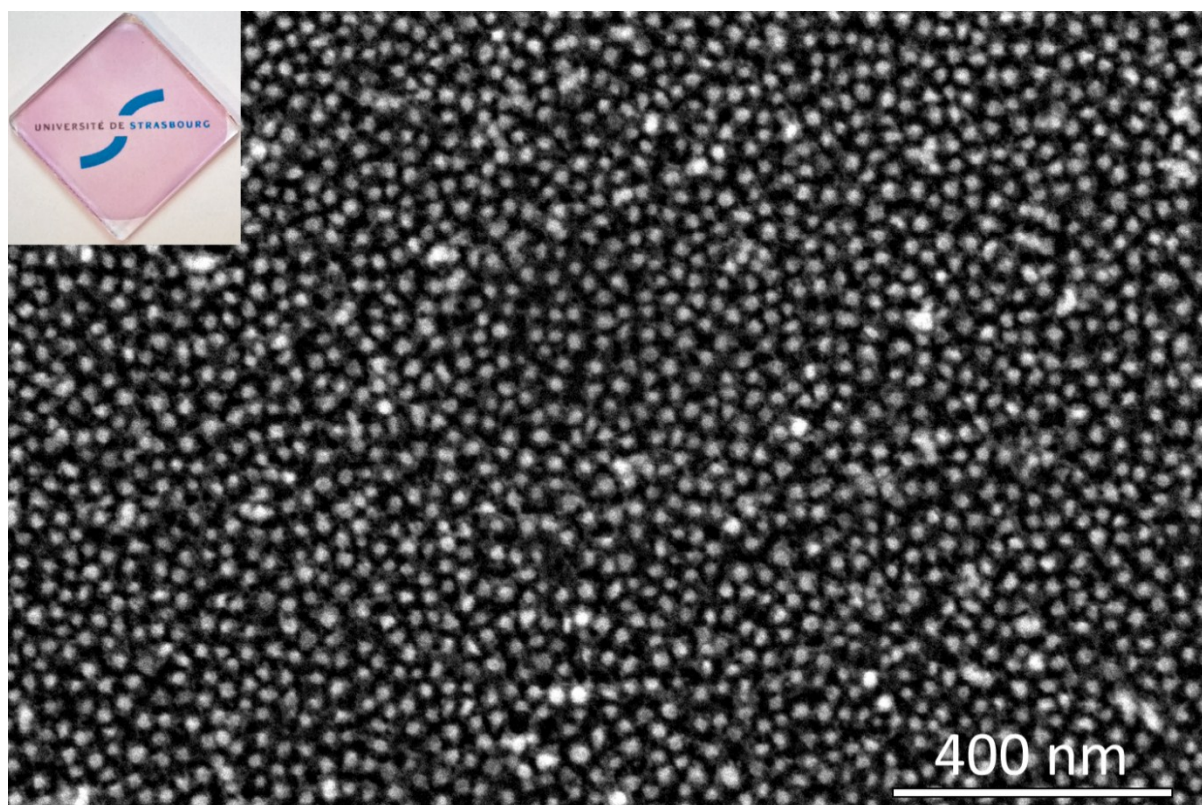


Figure S10: SEM image of disordered and disconnected AuNPs monolayer used as reference (employed substrate: native Si). Inset showing an optical image of a similar film on quartz.

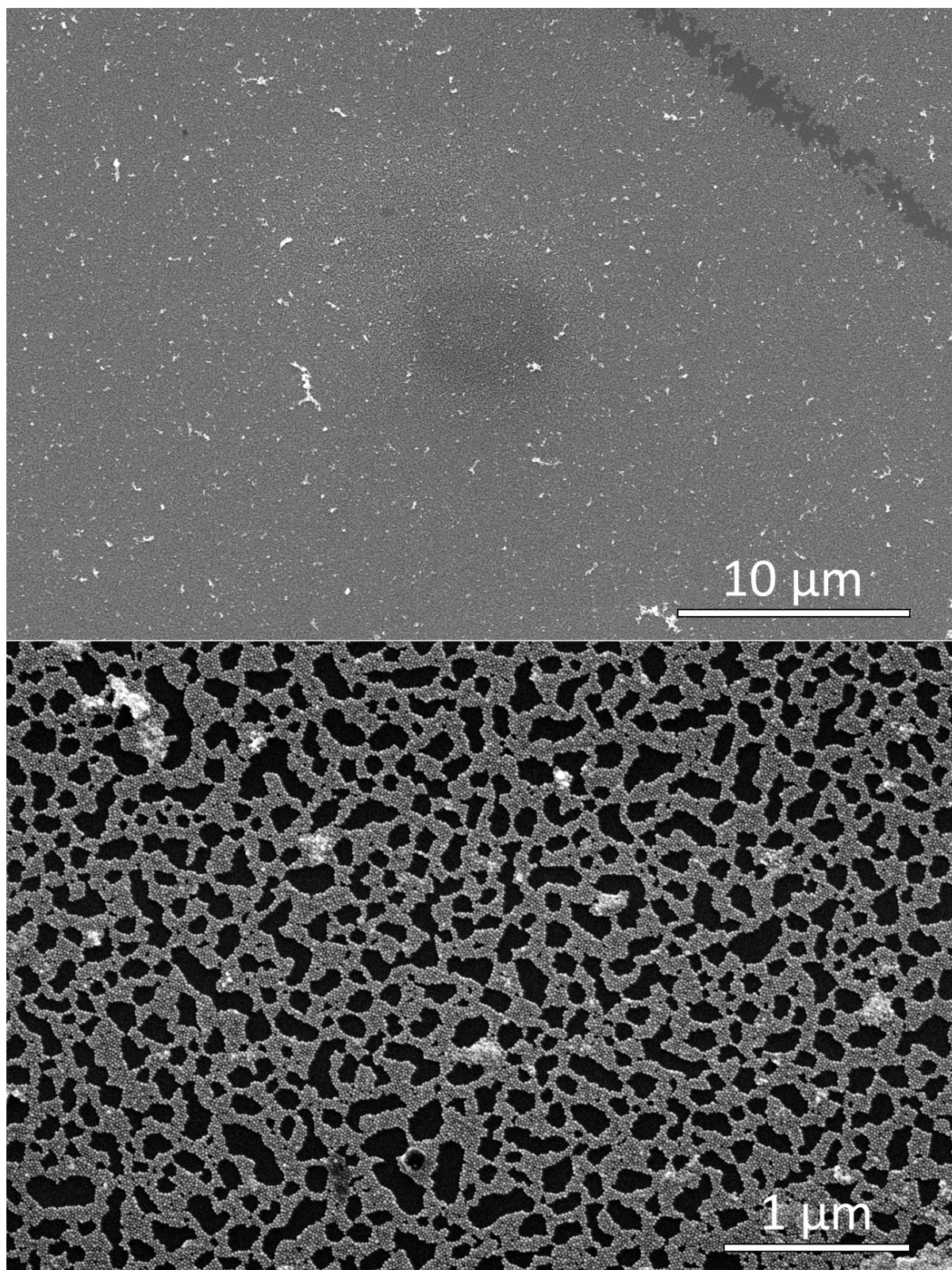


Figure S11: Large scale SEM images showing the uniformity of the 2D AuNPs-PEG network. (Substrate: native Si)

## 8. Supplementary references

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