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Electronic Supplementary Information : Single gold bipyramids on a silanized substrate as robust plasmonic sensors for liquid environments†

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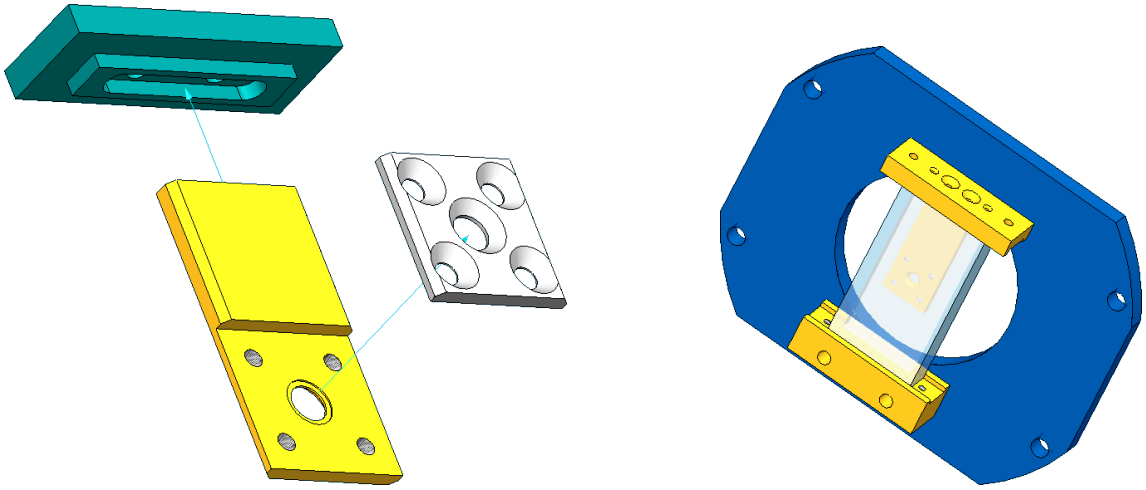
Schematic of the fluid cell



(a) dipper **(b)** dipper with cell

Fig. 1 Fluid cell.

Details on the sample preparation

Preparation of the bipyramids is a two steps approach: first the seeds are prepared and then the gold structure is grown from these seeds.

1/ Seed preparation: A mixture of 4ml $HAuCl_4$ (0.5mM), 4ml CTAC (95mM) and 72μl of HNO3 (250mM) was treated with 100μl of a freshly made $NaBH_4$ solution (50mM) under strong stirring (1000 rpm). The mixture turned from light yellow to light brown indicating the formation of the seeds. Finally, a solution of citric acid was added (16μl - 1 M) in the mixture before heating at 80-85°C for 1 hour. The final suspension of seeds can be stored at room temperature for several weeks.

2/ Growth of the Bipys : The growth solution consisted in a mixture of 40μl of $HAuCl_4$ (25mM), 4ml CTAB (47mM in water), 18μl of silver nitrate (10mM) and 60μl of 8-hydroxyquinoline (0.4M in ethanol). Once the solution turned light yellow, 40μl of gold seeds were added under stirring. The mixture was then heated at 40-45°C for 50mn.

All samples were prepared on 10 x 10 x 0.5 mm^3 SiO_2 slides. The slides are washed in a DFT4 detergent (5 % Gigapur) in order to activate their surface with the formation of OH groups. The slides are rinsed twice with distilled water to remove the excess DFT4, once with acetone to remove the water, and then once with methanol in preparation for immersion in methanol-based solutions. Each of the preceding steps is performed for 15' in an ultrasound bath at 40°C.

The glass slides are transferred to glass pill jars which prevent them from resting flat on a surface. The slides are immersed in a methanol-based silane solution (5% N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (95%), 5% 3-mercaptopropylmethyl-dimethoxysilane (95%)) and incubated at 45°C for 60' to silanize the surface. The amino derivative ensures rapid grafting of gold NPs while the thiol derivative creates strong and lasting bonds. The 50:50 ratio was chosen to optimize both aspects. The solution is then removed and the slides are rinsed 3 times with methanol to remove excess silanes before drying at 120°C for 30'.

To graft gold MNOs to the surface, 50μl of a diluted MNO solution is spread evenly over the glass substrate and left to stand for 5' before rinsing vigorously 3 times with distilled water. The slides are then stored in a new pill jar until use.

SEM and AFM caracterisation of synthesized samples

Typical SEM images (fig. 2) realized on a synthesized sample in low vacuum show the low density and the shape of one bipyramid (about 100 nm long by 35 nm width, see inset in fig. 2). AFM images (fig. 3) were realized in a area of aggregation of bipyramids that seem to confirm the orientation of the bipyramids.Both images show the cleanness of the substrate.

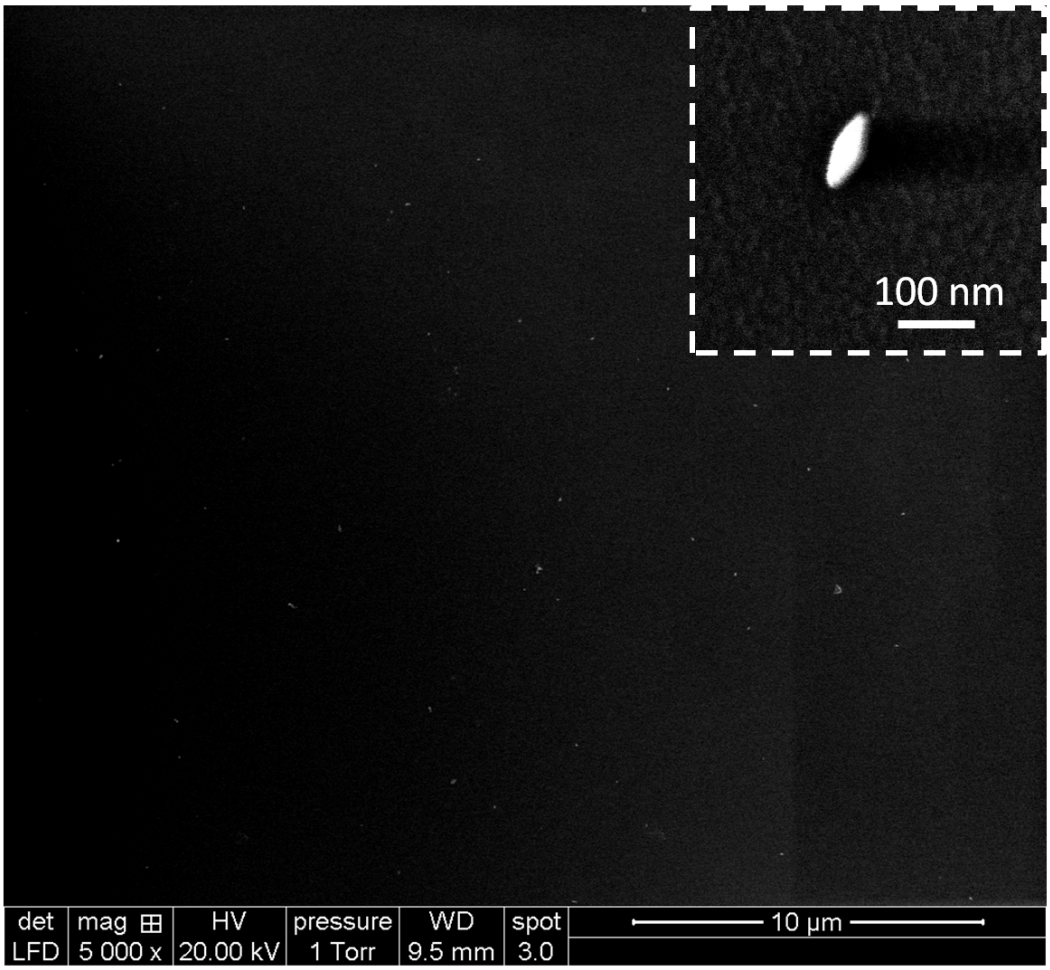


Fig. 2 SEM images of prepared samples. The average density is about one nanobipyramids for 10 square micron. Inset : zoom image on a nanobipyramid.

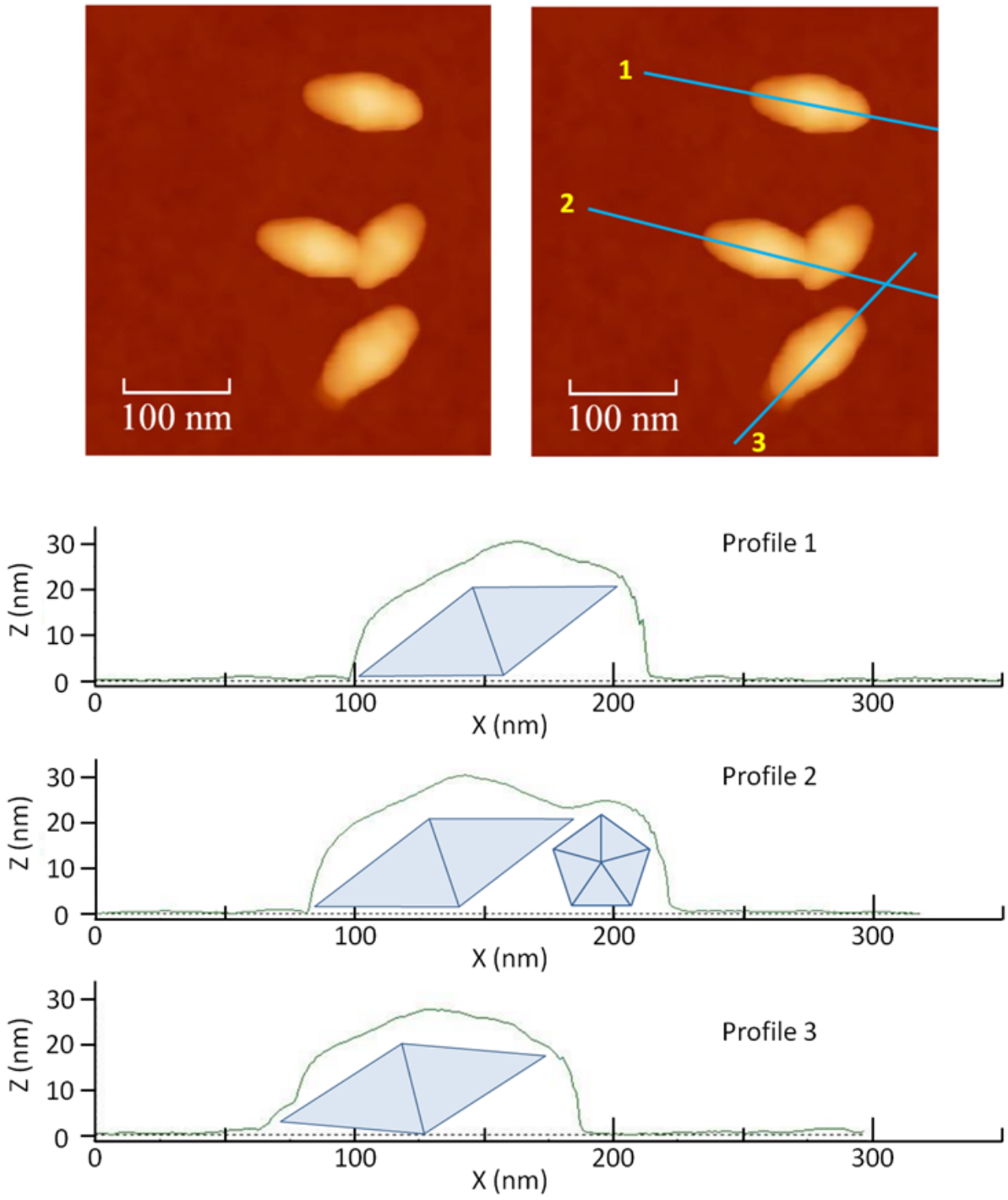
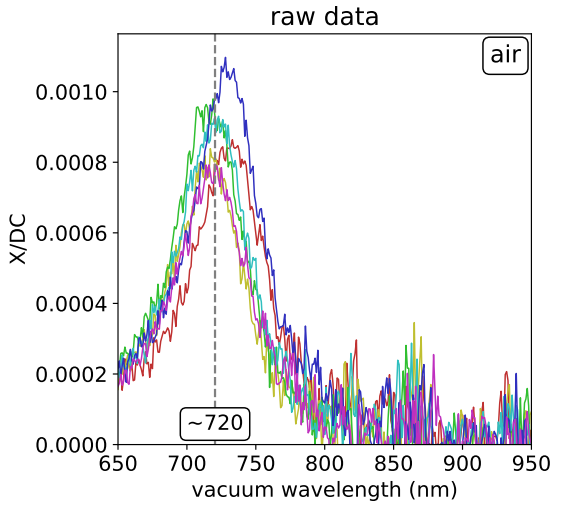
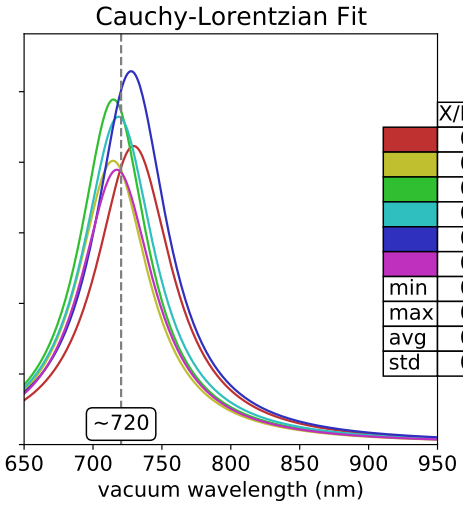


Fig. 3 AFM images of prepared samples and profiles along the long axis of bipyramids. Bipyramid shapes (about 100 nm by 35nm) have been added in the profiles as guidelines to illustrate the orientation of the nanobipyramids.

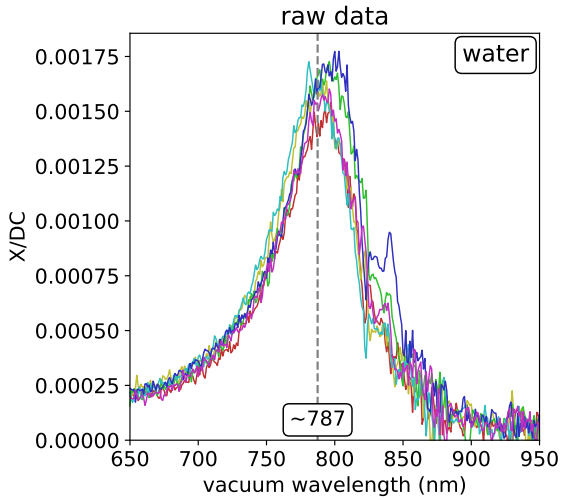
Extinction spectra and SMS maps of the 6 studied BPs in different media (air, water, or water+glycerol)

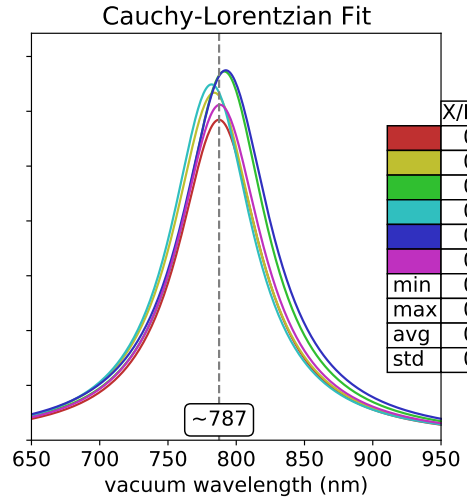




	X/DC max	λ_{max} (nm)	Γ (nm)	λ_{max}/Γ
	0.0008	730	66	11.0
	0.0008	715	63	11.4
	0.0010	715	59	12.0
	0.0009	719	63	11.5
	0.0011	728	63	11.6
	0.0008	717	64	11.2
min	0.0008	715	59	11.0
max	0.0011	730	66	12.0
avg	0.0009	720	63	11.5
std	0.0001	6	2	0.3

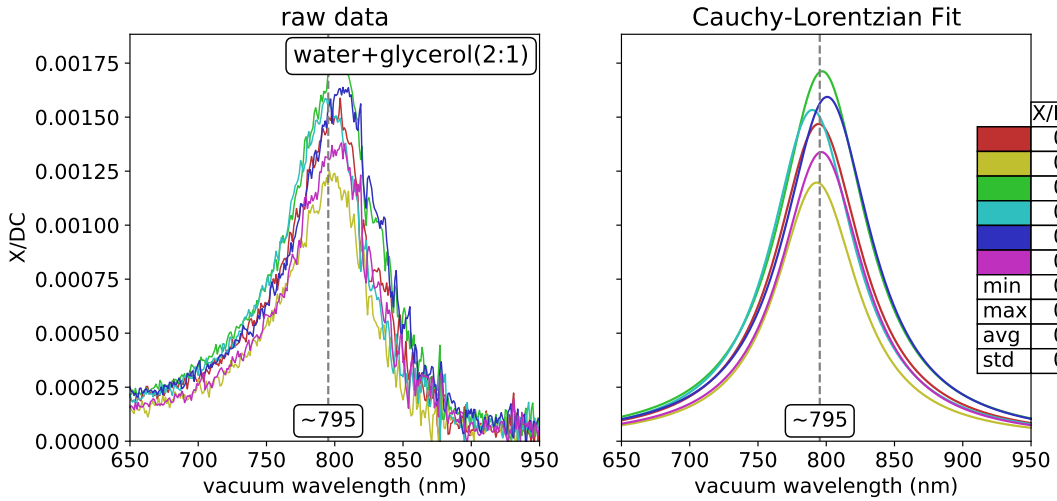
Fig. 4 Raw spectra in air before immersion in water.





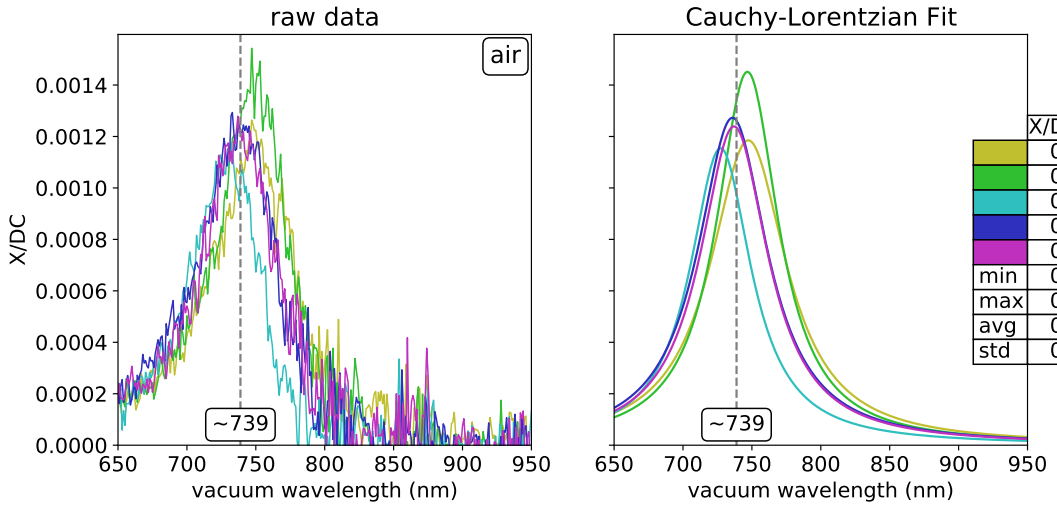
	X/DC max	λ_{max} (nm)	Γ (nm)	λ_{max}/Γ
	0.0015	787	73	10.7
	0.0016	784	74	10.5
	0.0017	791	74	10.7
	0.0016	782	72	10.8
	0.0017	792	78	10.1
	0.0015	788	75	10.5
min	0.0015	782	72	10.1
max	0.0017	792	78	10.8
avg	0.0016	787	74	10.6
std	0.0001	4	2	0.2

Fig. 5 Raw spectra in water.



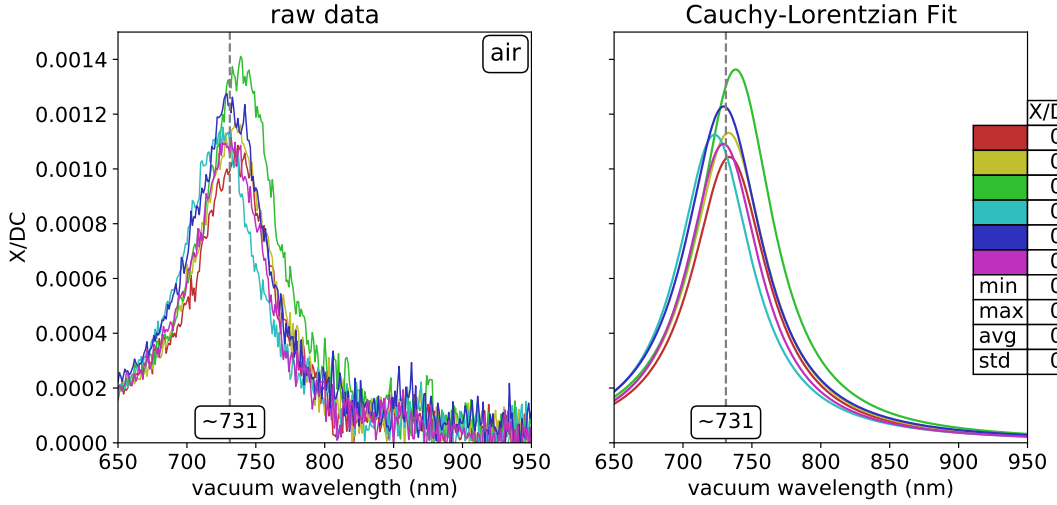
	X/DC max	λ_{max} (nm)	Γ (nm)	λ_{max}/Γ
	0.0015	794	77	10.4
	0.0012	793	73	10.8
	0.0017	797	78	10.2
	0.0015	790	75	10.6
	0.0016	801	79	10.2
	0.0013	796	74	10.7
min	0.0012	790	73	10.2
max	0.0017	801	79	10.8
avg	0.0015	795	76	10.5
std	0.0002	3	2	0.2

Fig. 6 Raw spectra in the 2:1 volumetric mix of water and glycerol.



	X/DC max	λ_{max} (nm)	Γ (nm)	λ_{max}/Γ
	0.0012	747	67	11.1
	0.0015	747	55	13.6
	0.0012	727	54	13.4
	0.0013	736	62	11.9
	0.0012	737	60	12.3
min	0.0012	727	54	11.1
max	0.0015	747	67	13.6
avg	0.0013	739	60	12.5
std	0.0001	8	5	0.9

Fig. 7 Raw spectra in air after immersion in water+glycerol.



	X/DC max	λ_{max} (nm)	Γ (nm)	λ_{max}/Γ
	0.0010	734	67	11.0
	0.0011	733	67	11.0
	0.0014	738	66	11.2
	0.0011	723	65	11.1
	0.0012	730	68	10.8
	0.0011	729	64	11.4
min	0.0010	723	64	10.8
max	0.0014	738	68	11.4
avg	0.0012	731	66	11.1
std	0.0001	5	1	0.2

Fig. 8 Raw spectra in air after 8 months of dry storage.

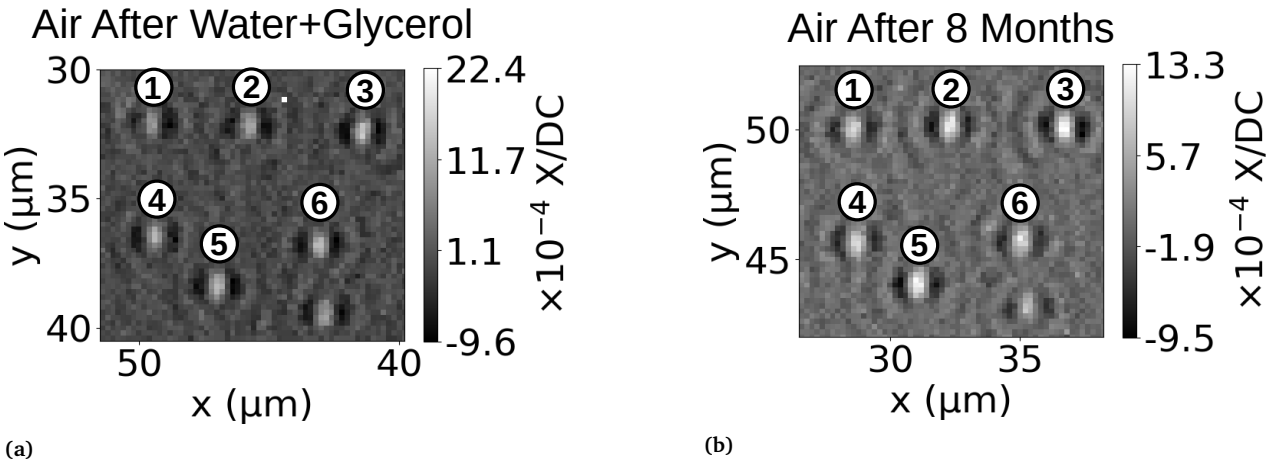


Fig. 9 Corresponding SMS maps of the 6 BPs for the peaks shown in figure 6 of the article.

Calculated extinction cross-section of a tilted gold bipyramid on a substrate with or without a layer of silane in various media (air, water, water+glycerol) using the finite element method

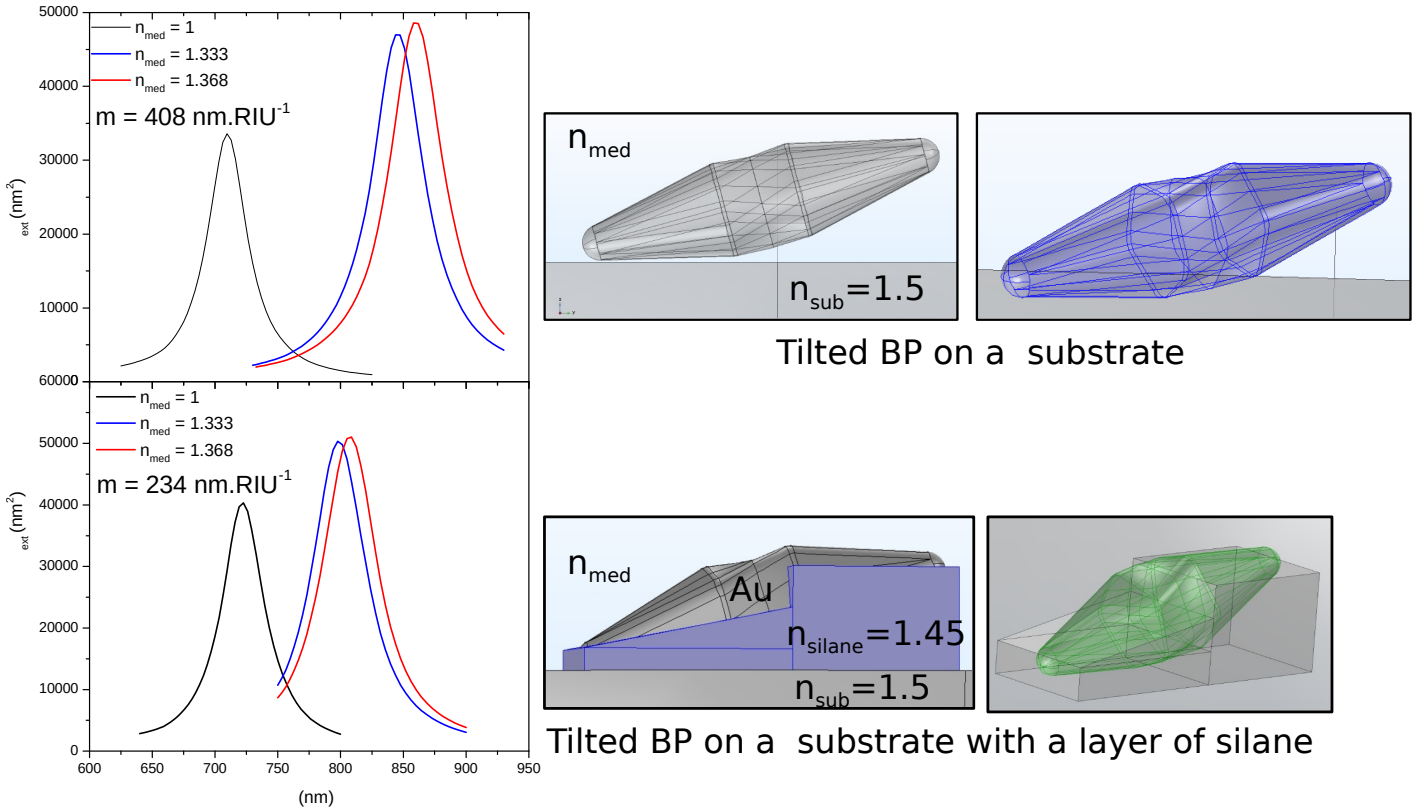


Fig. 10 finite element method simulations.