Supplementary Information for:

Plasmon-assisted grafting of anisotropic nanoparticles – spatially selective surface modification and creation of amphiphilic nanoparticles

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Experimental

Materials.

Chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4\,H_2O$, 99.9 %), sodium citrate dihydrate (99%), silver nitrate ($AgNO_3$, 99 %), ascorbic acid (AA, 99%), hexadecyltrimethylammonium bromide (CTAB, ≥ 98%), sodium borohydride ($NaBH_4$, ≥99%), 1-iodo-3,5-bis(trifluoromethyl)benzene (98%), 3,5-Bis(trifluoromethyl)phenyl-boronic acid (≥95 %), boron trifluoride diethyl etherate (99%), 3-Chloroperbenzoic acid (≤77%), 4-aminobenzoic acid (ReagentPlus, ≥99%), tert-Butyl nitrite (90%), acetic acid (reagent grade, ≥99.7%), diethyl ether, methanol and Toluenesulfonic acid monohydrate (≥98.5%) were purchased from Sigma-Aldrich and used without further purification. Nitric acid (assay 68~70%) was purchased from PENTA. Deionized water was used throughout all experiments. 4-carboxybenzenediazonium tosylate was prepared according to [S1]. Di-[3,5-bis(trifluoromethyl)phenyl]iodonium tetrafluoroborate was prepared according to [S2].

Samples preparation

Preparation of 30 and 50 nm gold nanorods (further designated as $AuNR_1$ and $AuNR_2$). Gold nanorods were prepared using previously published but slightly modified method [S3]. The gold seeds were prepared by reduction of $HAuCl_4$ (0.25 mL, 0.01 M) in CTAB (9.75 mL, 0.1 M) solution by rapidly adding freshly prepared ice-cold NaBH4 (0.60 mL, 10 mM) at 0^oC under continuous stirring. During the first 10 minutes, the color of the solution changed from bright orange to brown.

The stirring was then turned off, and the gold seeds were used within 48 hours after preparation. In the next step, the CTAB (9.5 mL, 0.1 M) was added to a 15 mL Eppendorf tube, followed by the addition of $AgNO_3$ (50 µL for AuNRs1 or 90 µL for AuNRs2, 0.01 M), $HAuCl_4$ (0.3 mL, 0.01 M), ascorbic acid (50 µL, 0.1 M) and lastly the gold seeds (12 µL, 2,5 µM) under slow stirring. The mixtures were left undisturbed overnight (14-16 h) at RT, during which the colorless solutions turned blue for $AuNRs_1$ and purple for $AuNRs_2$. The obtained AuNRs were purified using the subsequent cycles (3x) of centrifugation (10 min, 5000 rpm (1.957 × g)). and ultrasound-assisted re-dispersion.

Preparation of 365 nm long gold nanorods. The third kind of AuNRs (designated as AuNR3) was prepared through a three-step seeding method [S4]. The initial gold seed particles were prepared into a 22 ml glass vial, where 19.8 ml of 0.025 M sodium citrate solution and 0.2 ml of 0.00025 M $HAuCl_4$ solution were added. Then 0.6 ml of a freshly prepared ice-cold solution of the $NaBH_4$ in 0.025M sodium citrate solution was added at once into the CTAB/sodium citrate solution under vigorous stirring. The color of the solution was immediately changed to orange-red. The gold seeds were used during one week after preparation.

To obtain gold nanowires, a growing solution containing 15 ml of 0.2 M CTAB and 15 ml of 0.0005 M of $HAuCl_4$ was initially prepared. In 22 ml glass vails labeled A and B was added 2.25 ml of growth solution each and 22.5 ml of this solution was added into 50 ml polypropylene tube labeled C. Then 12.5 µl of 0.1 M ascorbic acid was added in vial A and B. Into tube C 125 µl of 0.1 M ascorbic acid was added followed by addition of 50 µl concentrated nitric acid. 200 µl of the initial gold seed solution was added into vial A, and the solution was vigorously shaken for 3 seconds. After that, 200 µl of the solution in vial A was transferred to vial B and shaken for 5 seconds. Finally, 200 µl of the solution in vial B was transferred to tube C and mixed for 5 seconds. The mixture was left undisturbed overnight (12 h) at RT. The obtained nanowires were centrifuged at 5000 rpm (1.957 × g) for 10 min, the supernatant was poured out, and the precipitation was redispersed in 5 ml deionized water. This purification procedure was repeated 3 times.

Plasmon assisted IS surface grafting ($AuNRs_1$ and $AuNRs_2$). Plasmon triggering was performed using a continuous light-emitting diode (LED) source. The 660 nm LED source was used for AuNRs1 (940 mW) and 785 nm LED one for AuNRs2 (800 mW). The colloidal suspension of gold nanorods (2 mL, 3 µM) was mixed with a 1mL of a 1 mM solution of IS in a 9:1 water/methanol solvent and illuminated with LED under the continuous mixing for 2 h. The laser beam spot (ca 5 cm^2) was set up to homogeneously illuminate the surface of reaction mixture. After the modification process, AuNRs were collected by centrifugation and washed sequentially by water and a 1:1 water/methanol mixture (15 min, 5000 rpm or 1.957 × g).

Infrared assisted surface grafting by iodonium salt. An infrared light assisted modification was performed using the 150 W halogen optic lamp HLX EFR. The illumination was performed through a 1000 nm cut-off optical filter (Thorlabs), transparent for wavelength above 1 µm. The colloidal suspension of gold nanowires (2 ml, 7 µM) was mixed with a 1mL of a 1 mM solution of IS in a 9:1 water/methanol solvent and illuminated with an IR lamp under the continuous mixing for 2 h. After the modification process, AuNRs were collected by centrifugation and washed sequentially by water and a 1:1 water/methanol mixture (15 min, 5000 rpm (1.957 × g)).

Spontaneous diazonium surface grafting. An aqueous solutions of the 4-carboxybenzenediazonium tosylate (1 ml of 1 mM solution) was added to suspension of IS-grafted AuNRs (in the case of control experiments – pristine AuNRs) and stirred for 2 h in darkness. The nanoparticles were then collected by centrifugation and washed thoroughly by several centrifugation/washing cycles by water and a 1:1 water/methanol mixture (15 min, 5000 rpm (1.957 × g)).

For ellipsometry measurements the thin gold films were sputtered on silicon substrates and spontaneously grafted with diazonium salts (containing the -Ar(COOH) or $-Ar(CF_3)_2$) under the immersion in 1mM salts solutions for 1 h. The gold deposition was accomplished from the Au target (DC, Ar plasma; gas purity, 99.995%; pressure, 4 Pa; discharge power, 7.5 W; sputtering time, 200 s, resulting film thickness was 20 nm).

Measurement techniques

Absorption spectra of the solutions were taken on a Lambda 25 UV/Vis/NIR Spectrometer (PerkinElmer, USA) in the spectral range 300-900 nm at a scanning rate of 480 nm min^{-1} and the data collection interval of 1 nm. The solutions were measured in 1 cm quartz cells. The reference spectrum of the solvent (deionized water) was subtracted from all spectra.

TEM images of nanoparticles were obtained on a JEOL JEM-1010 transmission electron microscope with a SIS MegaView III digital camera. STEM observations and EDX analyses were performed on a JEOL JEM-2200FS electron microscope equipped with a 100 mm^2 JEOL Dry SD100GV EDX detector with a Super UTW window.

The ellipsometry measurements were performed using a Jobin Yvon ellipsometer in a 380−900 nm wavelength range under incident angle of 75°. First, the pristine gold films were measured, and their optical parameters were fitted using the Drude-Lorentz approximation in FilmWizard software. Second, the grafted gold films (with $-C_6H_4COOH$ or $-C_6H_3(CF_3)_2$ chemical moieties) were measured, and ellipsometry measurements data were fitted using the effective medium approximation (EMA) model (with the introduction of the mixture of organic materials with the Cauchy dispersion of the refractive index and voids).

The finite-difference time-domain (FDTD) electromagnetic simulation was performed by the boundary-element method, implemented in the SCUFF-EM software suit [S5], [S6]. The modeled system consists of gold nanoparticle encapsulated in the organic shell, immersed in the water. Tabulated values of gold permittivity [S7] were used directly to eliminate. inaccuracies associated with model fitting. Organic shell permittivity was measured by ellipsometry. Water was assumed to have constant purely real permittivity equal to 1.77. In all experiments, method convergence was examined by doubling the resolution (which corresponds to a four-fold increase in the number of vertices) until the relative difference in spectra became less than 1%.

Raman scattering was measured with a Lambda Solutions, Inc., (USA) Raman spectrometer with two excitation wavelengths – 785 or 532 nm. Parameters of SERS measurements were chosen to be the same for both excitation wavelength: 4.5 mW laser powers, 5 s. integration time and 50 times spectra averaging). All SERS measurements were carried out in solutionand the spectra were baseline-corrected by subtracting the spectrum of pristine AuNRs, followed manual alignment of the background.

Utilization of amphiphilic AuNRs for SERS detection

The catechol and squalene were dispersed in the water/ethanol mixture (2:1), concentration of both compounds – 0.1 mM. The previously centrifuged AuNRs2 were added in the solutions of targeted compounds by ultrasonication, kept for 2 h, separated by centrifugation, and subjected to SERS measurements.

For trapping and detection of phosphatidylcholine (PC) three different concentration of PC in water were used: above micelle formation (10^{-2}M), closed to micelle formation (10^{-3}M) and below micelle formation (10^{-4}M). The formation of micelles was checked by appearance of apparent opalescence during the transmission of laser light through the solution. The suspensions of pristine or amphiphilic AuNRs2 were added in the solutions of PC (volume ratio: 1:1), kept for 2 h, separated by centrifugation, and subjected to SERS measurements.

References

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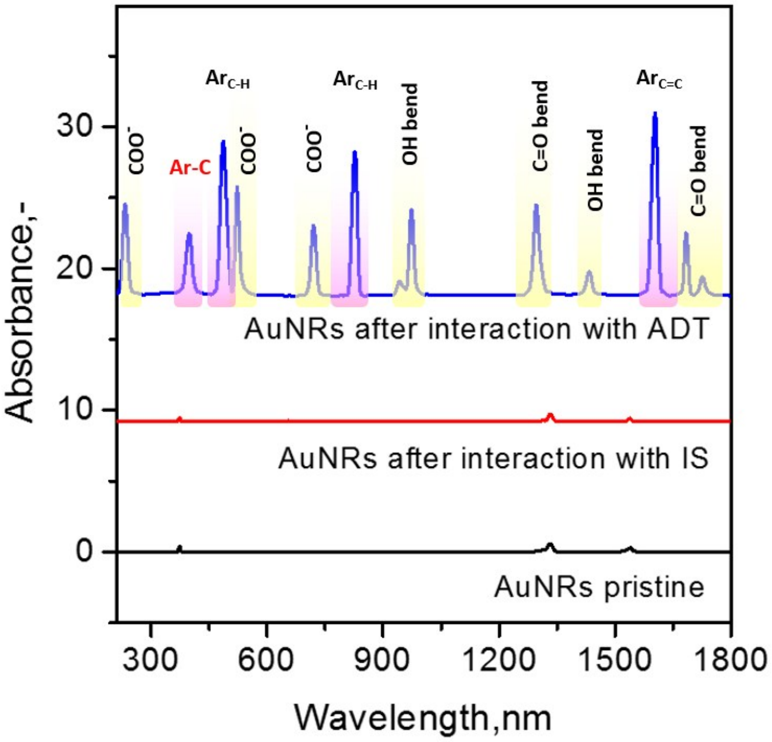

Fig. S1 Control experiments: SERS spectra of AuNRs2 before and after interaction with solution of iodonium or diazonium salts without LED illumination (reaction mixtures were kept in dark).

Discussion (Fig. S1): In the case of spontaneous interaction of IS with AuNRs no characteristic Raman vibration bands are seen, which result suggests the key role of plasmon excitation for NPs surface grafting. For diazonium salt the appearance of characteristic Raman bands indicates the ability of diazonium salt to graft the AuNRs surface in spontaneous manner.

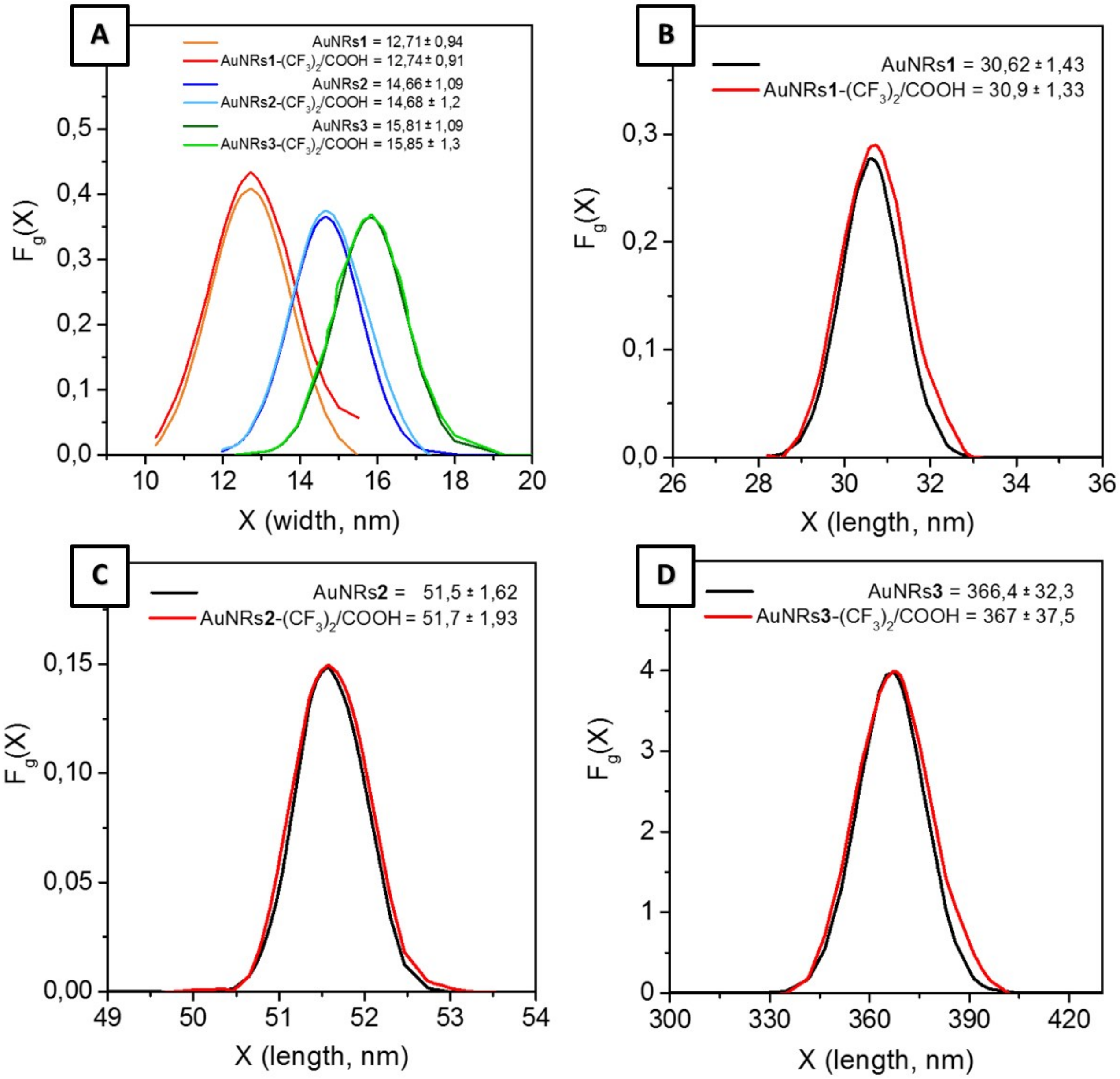

Fig. S2 Distribution of width(s) (A) and lengths of AuNRs1 (B), AuNRs2 (C), and AuNRs3 (D) estimated from TEM images before and after two-steps surface modifications (longitudinal plasmon assisted IS grafting and spontaneous diazonium salt grafting).

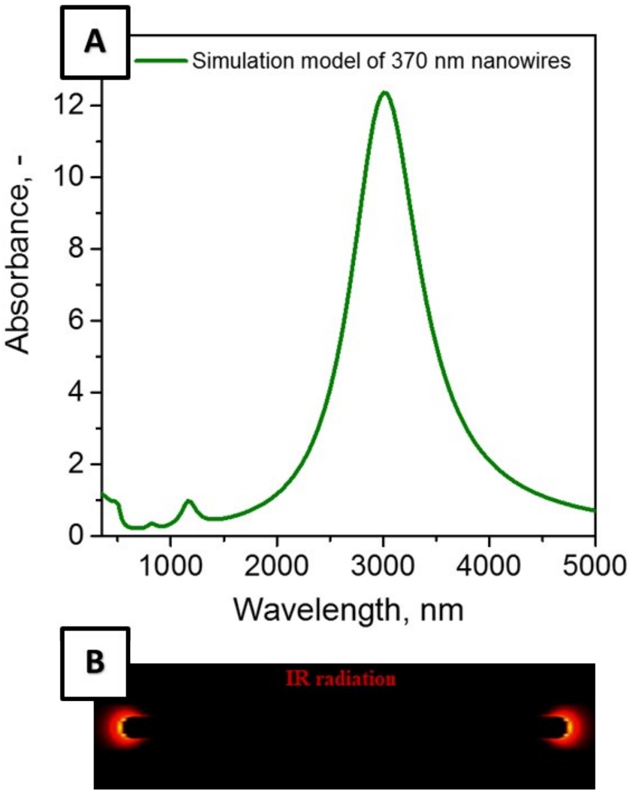

Fig. S3 A - Numerically simulated absorption spectra of AuNRs$_3$ (simulations were performed using FDTD method, parameters of AuNRs used for simulation were estimated from TEM images: length – 366.4 nm; width – 15.9 nm). B – FDTD simulated distribution of EF under the illumination of AuNR3 with 2 900 nm wavelength.

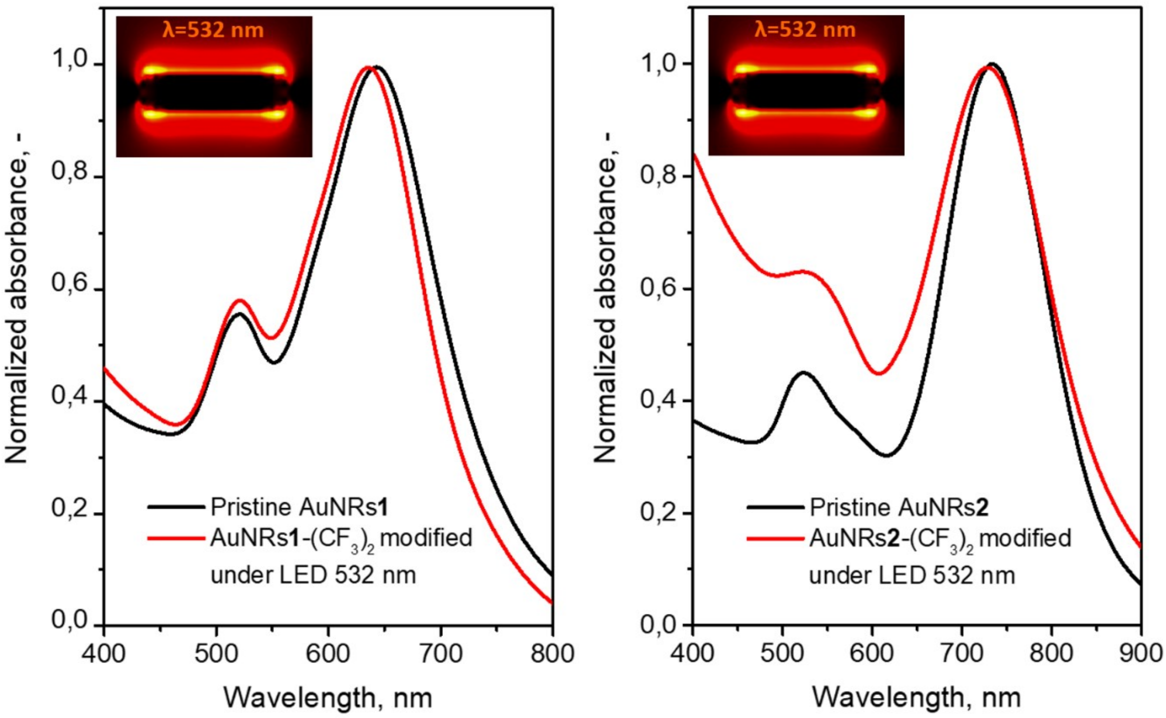

Fig. S4 The comparison of UV-Vis spectra of AuNRs1 and AuNRs2 taken before and after the surface modification induced by transverse plasmonic mode excitation in the solution of IS. Inserts show the FDTD simulated distribution of EF under the excitation of transverse plasmon resonances.

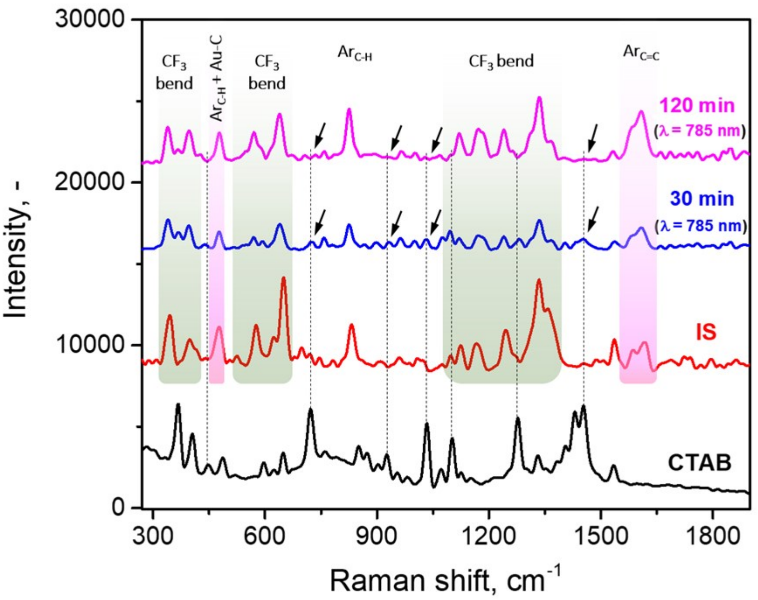

Fig. S5 SERS spectra of AuNRs1 measured after the different times on first stage modification (illumination with 785 nm wavelength in the solution of IS). The black arrow shows the spectra position of the CTAB characteristic peak and indicate their gradual disappearance during the plasmon-assisted CTAB substitution by -Ar(CF_3)$_2$.

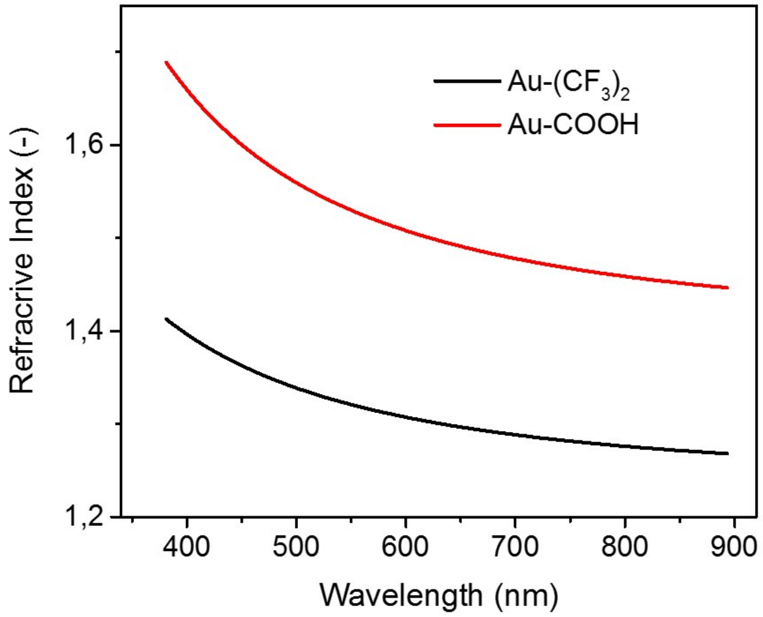

Fig. S6 Real part of refractive index of -Ar-$(CF_3)_2$ and -Ar-COOH organic layers spontaneously grafted to thin gold films using diazonium approach.

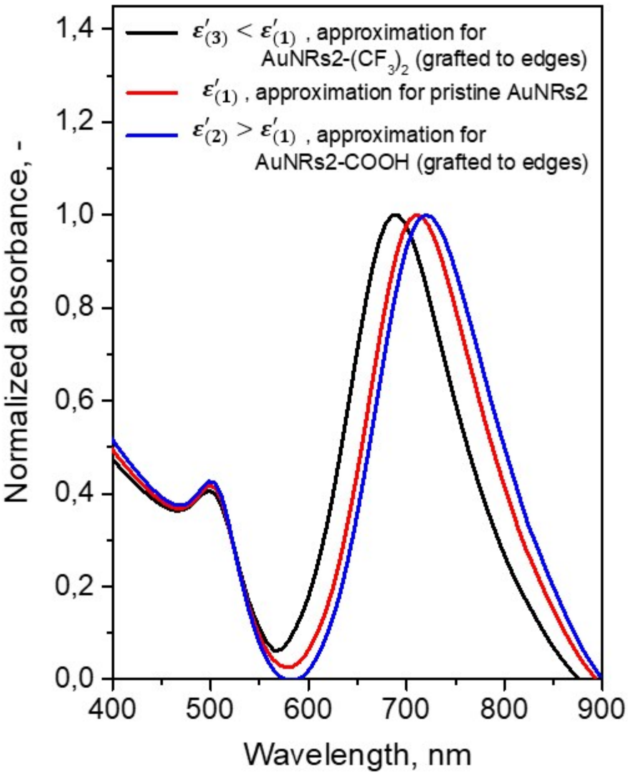

Fig. S7 Results of numerical simulation of AuNRs UV-Vis absorption spectra as a function of surface grafting of the AuNRs edges with -C_6H_4COOH $\varepsilon'_{(2)} > \varepsilon'_{(1)}$ and $C_6H_3(CF_3)_2$ $\varepsilon'_{(3)} < \varepsilon'_{(1)}$ chemical moieties ($\varepsilon'_{(1)}$, $\varepsilon'_{(2)}$, and $\varepsilon'_{(3)}$ represents the real part of the dielectric function of surrounding environments, approximated from the ellipsometry measurements). Please, note that the ellipsometry was performed at air, while the real spectra, presented in the main manuscript text, were taken in underwater conditions. So that obtained results should be considered as only qualitative ones.

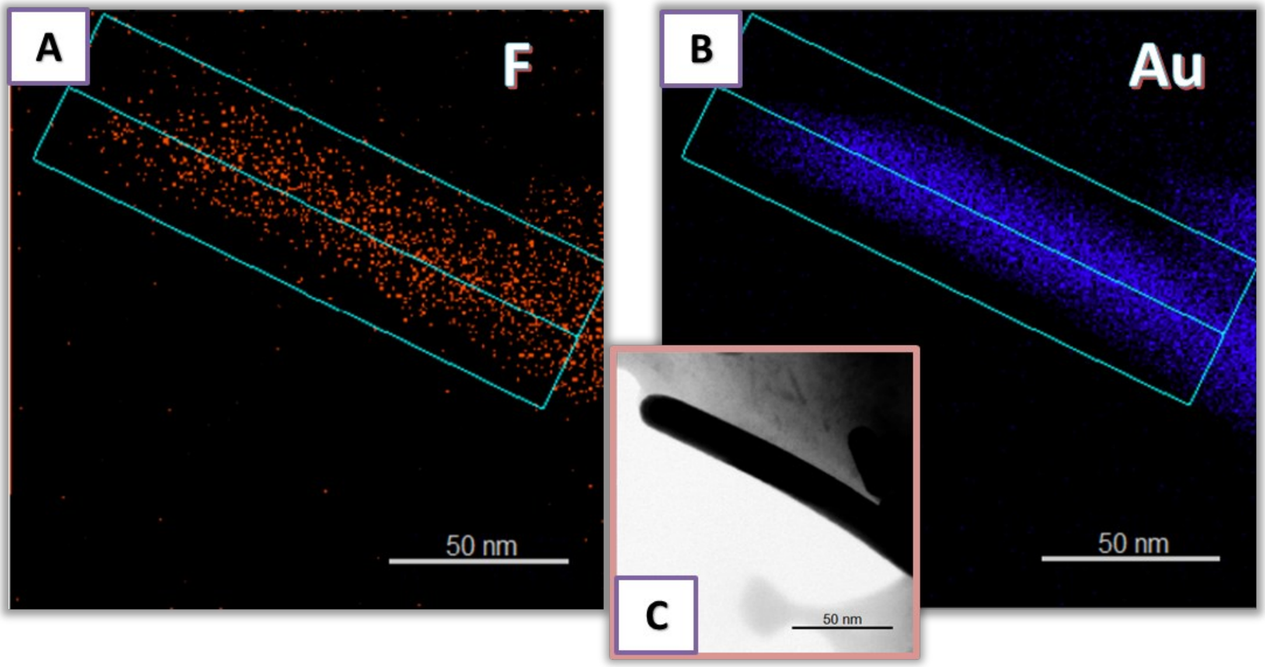

Fig. S8 STEM/EDX measurements of fluorine (A) and gold (B) distributions after the illumination of AuNRs3 in the solution of iodonium salt with 532 nm LED wavelength (i.e. excitation of transverse plasmonic mode). (C) corresponding STEM image.

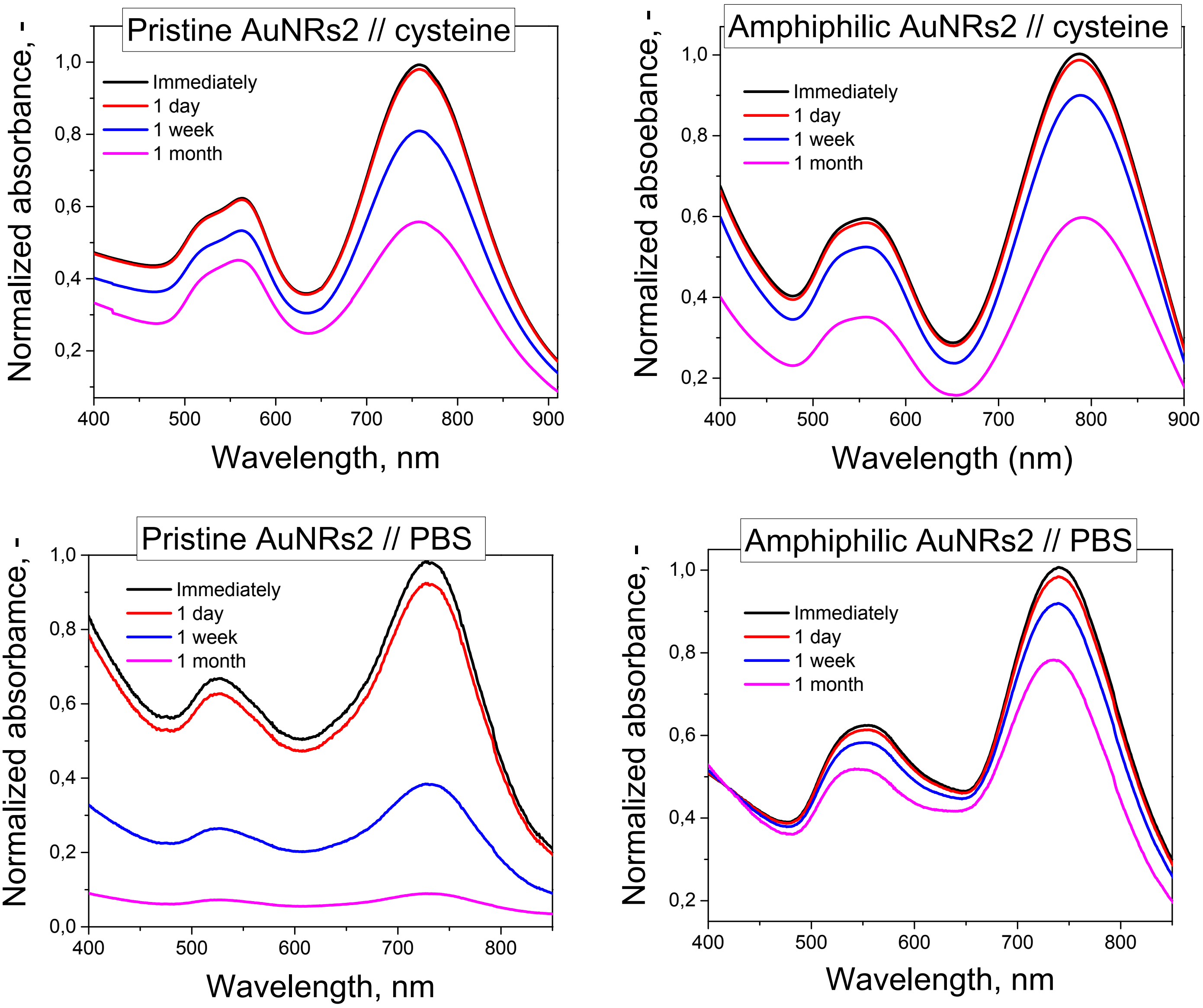

Fig. S9 UV-Vis spectra of pristine and amphiphilic AuNRs2 measured after different times in the solution of cysteine (1 mM) and PBS (1 mM).

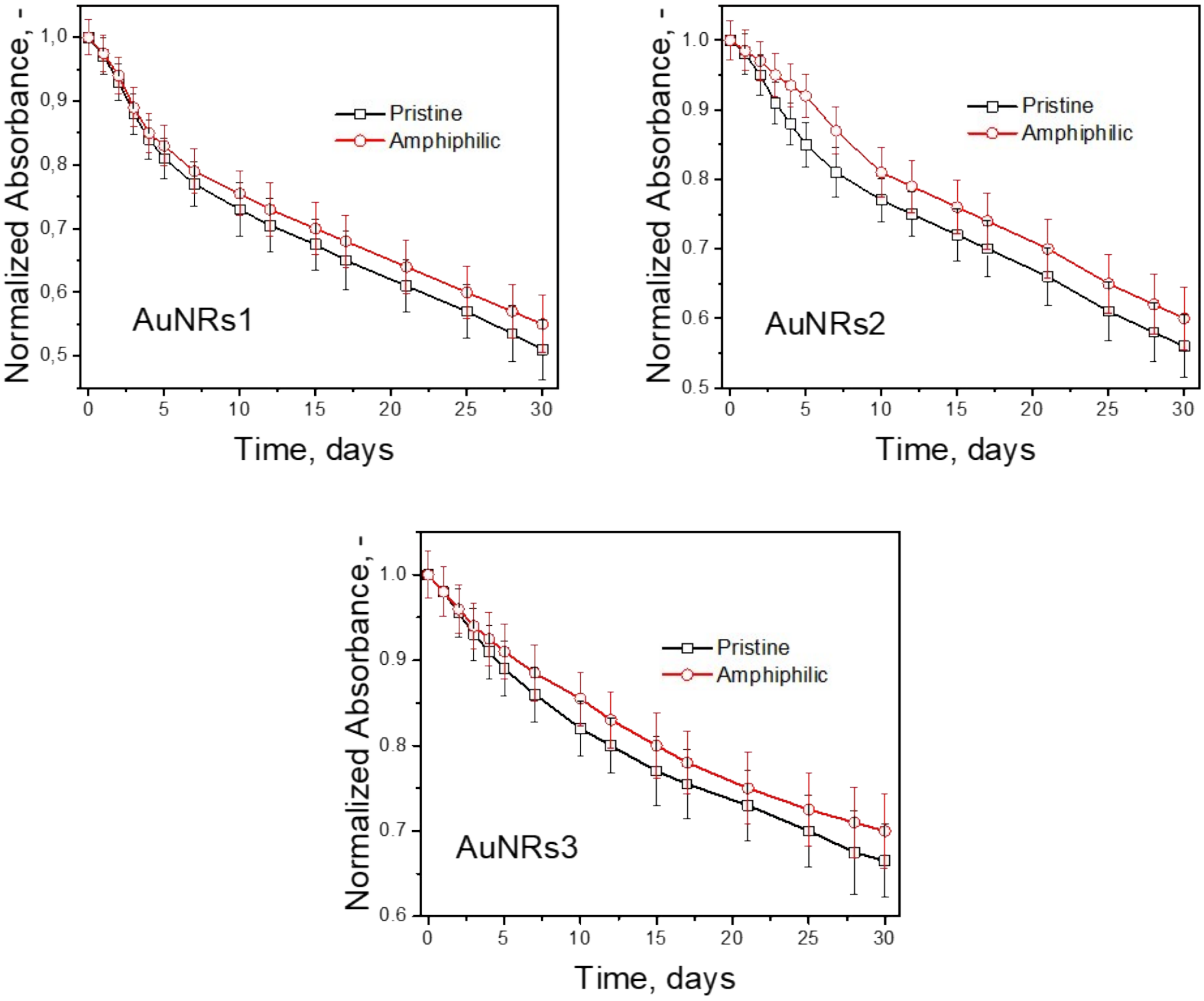

Fig. S10 Stability of pristine and amphiphilic AuNRs in cysteine (1 mM) solution, estimated from intensity decrease of longitudinal AuNRs1 (A) and AuNRs2 (B) or transverse AuNRs3 (C) plasmon absorption bands.

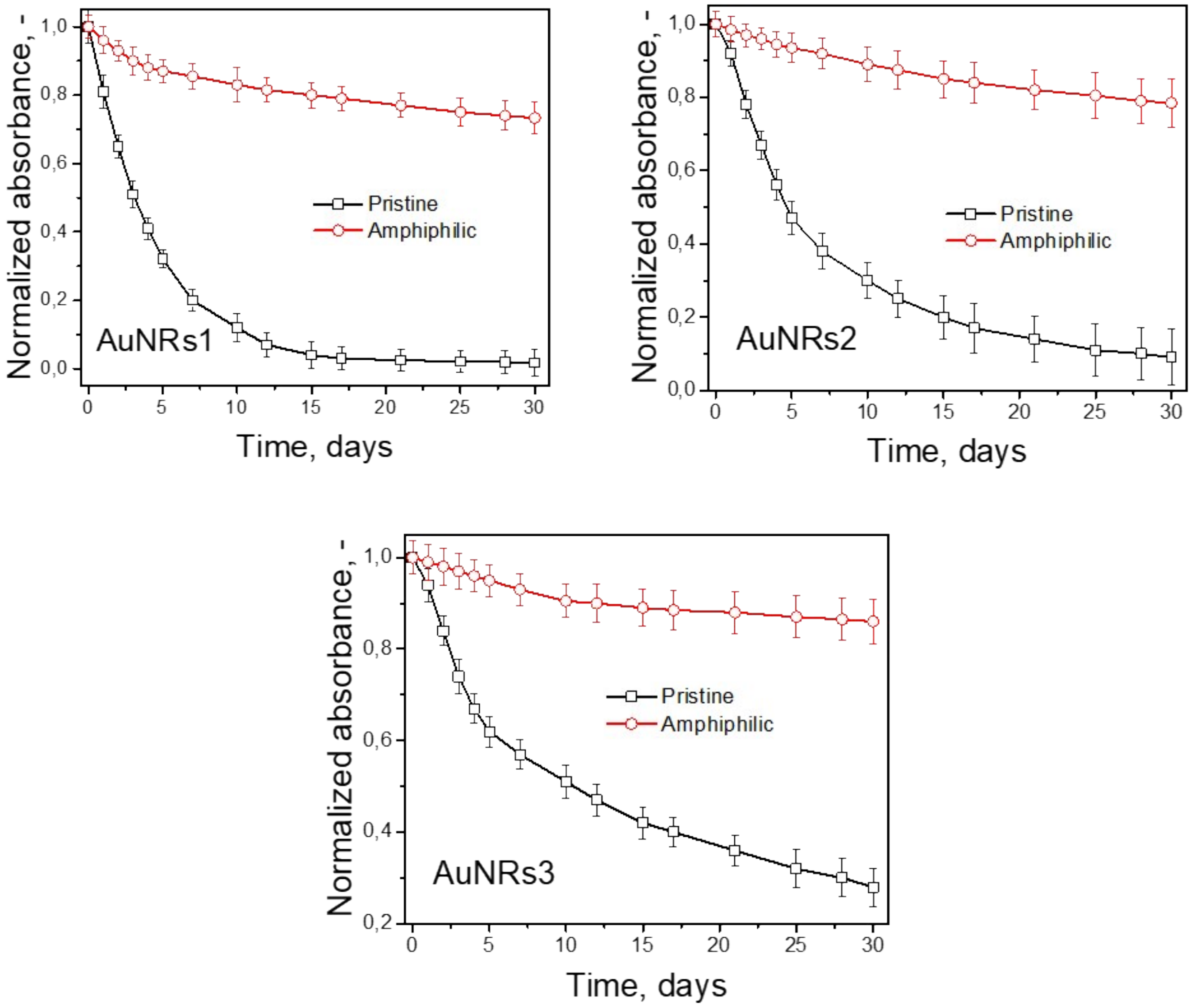

Fig. S11 Stability of pristine and amphiphilic AuNRs in PBS (1 mM) solution estimated from intensity decrease of longitudinal AuNRs1 (A) and AuNRs2 (B) or transverse AuNRs3 (C) plasmon absorption bands.

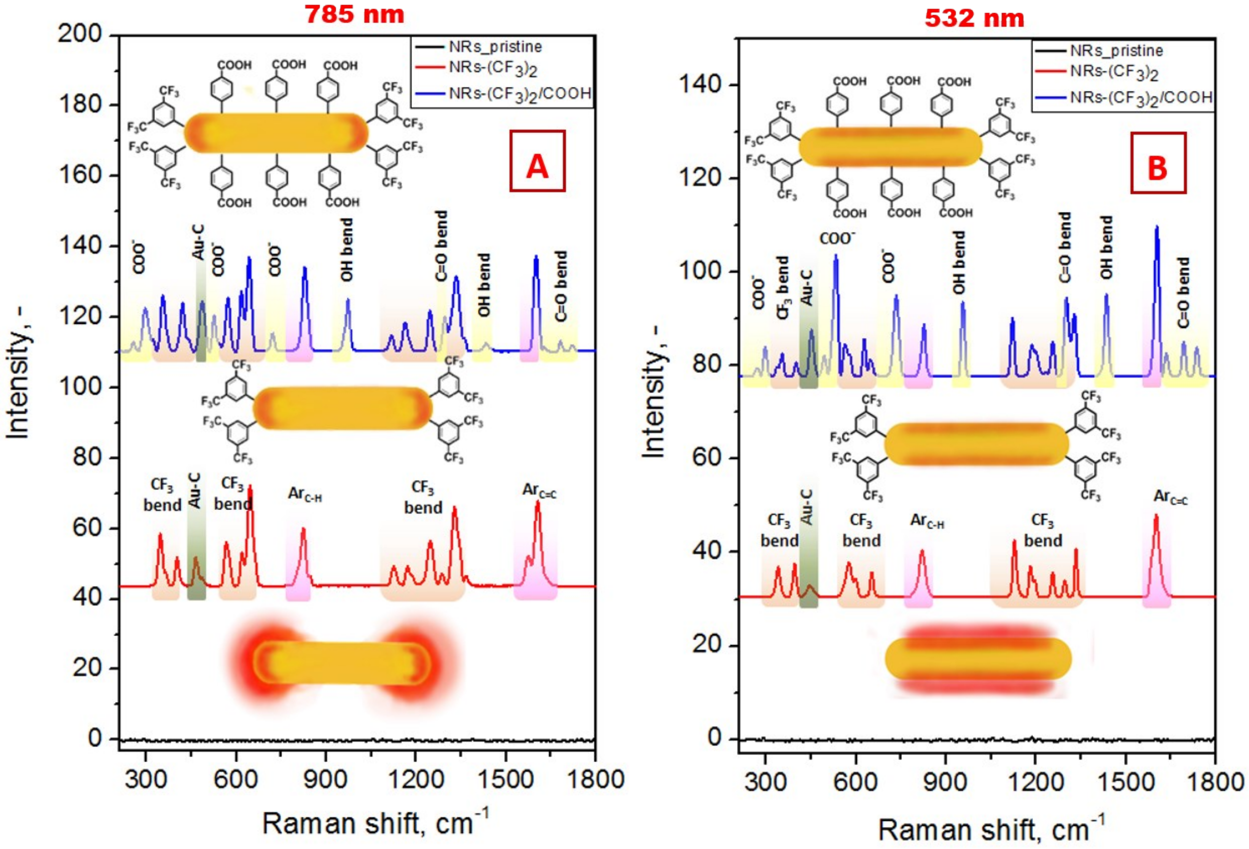

Fig. S12 SERS spectra, measured at two wavelengths on AuNRs2 grafted with Ar-$(CF_3)_2$ (AuNRs edges) and Ar-COOH (AuNRs lateral sides). Spectra were baseline corrected to remove "noise" CTAB signal.

Table SI

Characteristic peak intensities of-Ar-COOH and Ar-$(CF_3)_2$ chemical moieties as a function of SERS excitation wavelength and their position on AuNRs surface.

Sample	**Excitation wavelength** (nm)	**Peak intensity** (-)
-COOH (1015 cm^{-1}) **AuNRs lateral sides**	**785**	**9**
	532	**18**
-CF_3 (660 cm^{-1}) AuNRs edges	**785**	**26**
	532	**6**

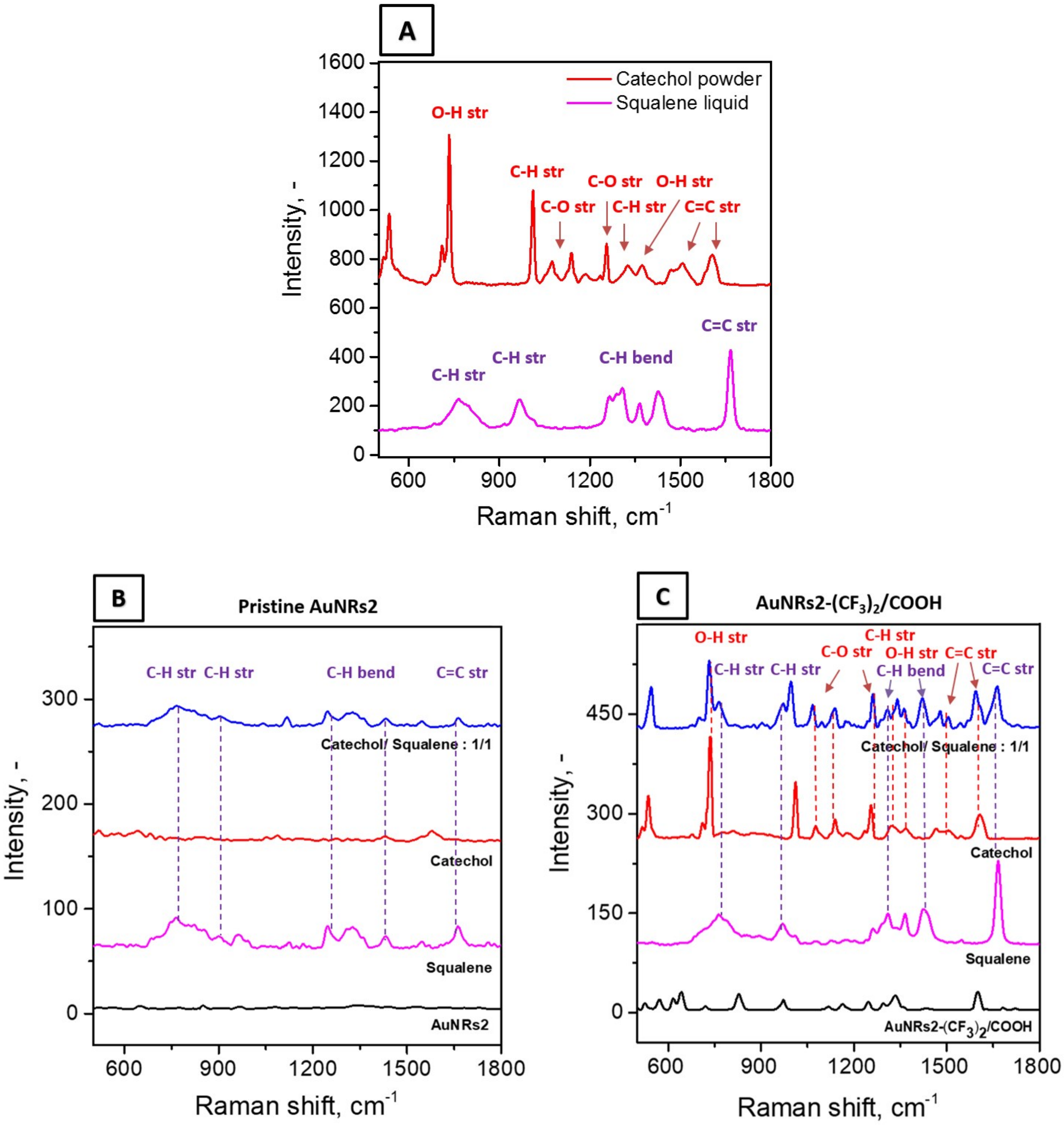

Fig. S13 (A) Raman spectra of catechol and squalene, measured in "bulk-mode". Catechol (concentration – 0.1 mM) and squalene (concentration – 0.1 mM) entrapping from water/ethanol solution and SERS-based discrimination using the pristine (B) and amphiphilic (C) AuNRs2. Spectra of catechol and squalene in (C) were baseline corrected to remove the signal from grafted to AuNRs chemical groups.