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**Supporting Information** 

## Gold nanostars as SERS-active substrates for FT-Raman spectroscopy

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Fig S1 – Extinction spectra recorded on fresh SF-NSs and one day after.



Fig S2 – Absorption spectrum of  $1.6 \times 10^{-6}$  M NF8 in H<sub>2</sub>O:EtOH 10:1 at different CTAB concentrations.



Core diameter	<u>Tip angle</u>	Branch length	<u>Tip radius</u>	<u>Circumscribed</u> <u>circonference diameter</u>
Peak: 39 nm	Peak: 9°	Peak: 27 nm	Peak: 3 nm	Peak: 120 nm
σ⁻: 17 nm	σ⁻: 5°	σ-: 10 nm	σ⁻:1 nm	σ-: 28 nm
$\sigma^+$ : 29 nm	σ+:11°	$\sigma^+$ : 15 nm	$\sigma^+$ : 1 nm	$\sigma^+$ : 36 nm

Fig S3 – Structural features of *SF-NSs* obtained by Log-normal fitting of the statistical distributions.

Fig S4 – Structural features of *CTAB-NSs* obtained by Log-normal fitting of the statistical distributions.

Core diameter	<u>Tip angle</u>	Branch length	<u>Tip radius</u>	Circumscribed circonference diameter
Peak: 76 nm	Peak: 23°	Peak: 53 nm	Peak: 5 nm	Peak: 179 nm
σ <sup>-</sup> : 9 nm	σ <sup>-</sup> : 7°	σ <sup>-</sup> : 14 nm	σ <sup>-</sup> : 1 nm	σ <sup>-</sup> : 29 nm
σ <sup>+</sup> : 10 nm	σ <sup>+</sup> : 10°	σ <sup>+</sup> : 20 nm	σ <sup>+</sup> : 1 nm	σ <sup>+</sup> : 34 nm

Fig S5 – Dependence of the SERS signal of NF8 (measured as the integrated area of the band at 1400 cm<sup>-1</sup>) on the NF8 concentration (log scale).



Fig S6 – UV-vis spectra of a) supernatant solutions of Au-NSs incubated with  $1.6 \times 10^{-6}$  M NF8; b) NF8 in the supernatant of C4 sample compared with that taken from the original solution (50 mM CTAB); c) NF8 in the supernatant of D4 sample compared with that taken from the original solution (5 mM CTAB).



		SF-NSs (54 tips)	CTAB-NSs (26 tips)
Portion ( 1/8 ) of the modelled structure			
Single nanostar	tips surface (nm <sup>2</sup> )	2789	3250
	total surface (nm <sup>2</sup> )	37490	83278
	volume (nm <sup>3</sup> )	629900	101480
NSs density: nanoparticles/ml		1.7×10 <sup>10</sup>	2.4×10 <sup>9</sup>
1 ml of solution	tips surface (nm <sup>2</sup> )	4.7×10 <sup>13</sup>	7.8×10 <sup>12</sup>
	total metallic surface (nm <sup>2</sup> )	6.4×10 <sup>14</sup>	2.4×10 <sup>14</sup>