

## **Supplementary Information**

### **Poly(thionine) modified screen-printed electrodes for CA19-9 detection and its properties in Raman spectroscopy**

Y. Castaño-Guerrero<sup>1,2,3</sup>, Y. Romanguera-Barcelay<sup>3,4</sup>, Felismina T.C. Moreira<sup>1,2</sup>, Walter R. Brito<sup>4</sup>, E. Fortunato<sup>5</sup>, M.G.F. Sales<sup>1,2,3,\*</sup>

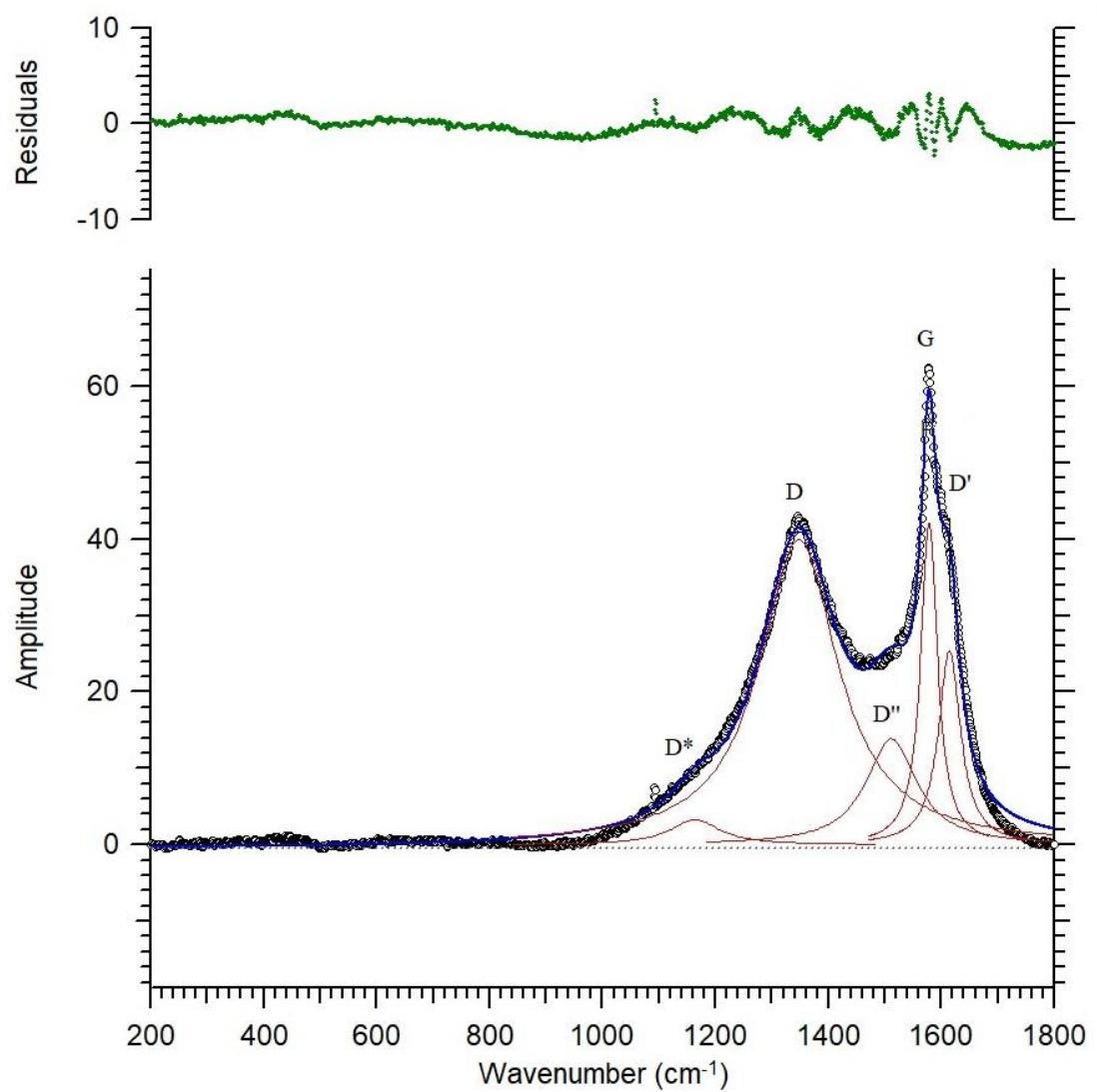
<sup>1</sup>BioMark@ISEP, Rua Dr. António Bernardino de Almeida, 431, 4249-015, Porto, Portugal;

<sup>2</sup>CEB, Centre of Biological Engineering, University of Minho, Braga, Portugal;

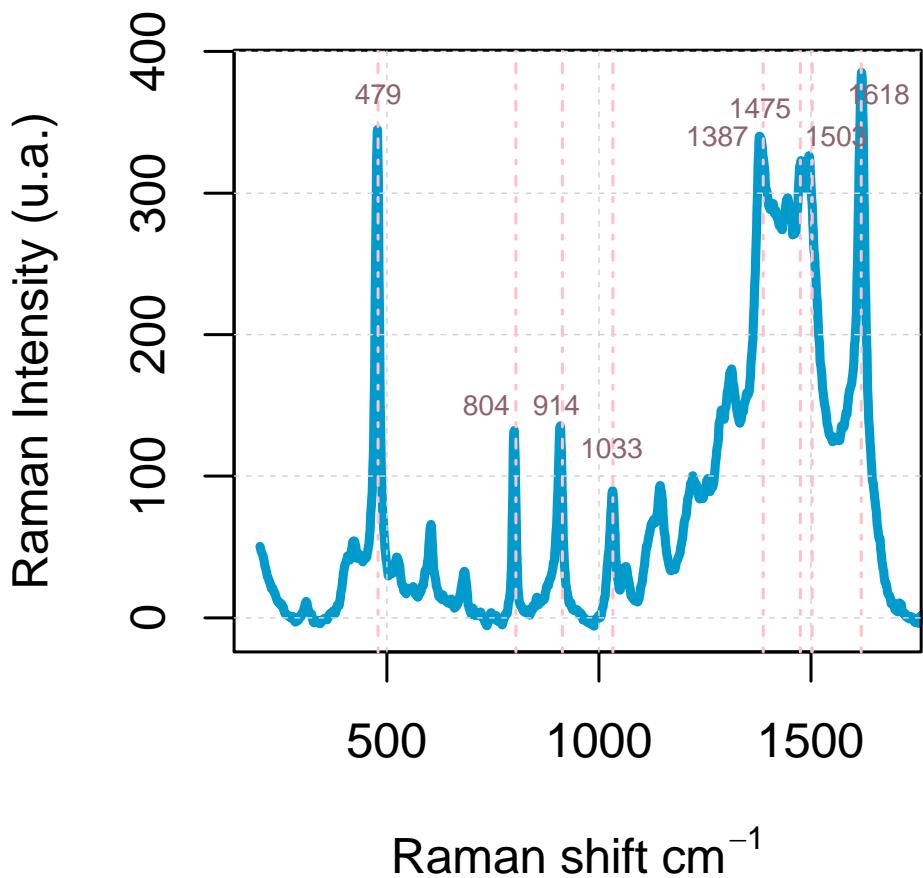
<sup>3</sup>BioMark@UC, Rua Sílvio Lima 3030-790, Coimbra, Portugal;

<sup>4</sup>Department of Physics and Department of Chemistry (LABEL), Federal University of Amazonas, Manaus, 69067-005, Amazonas, Brazil;

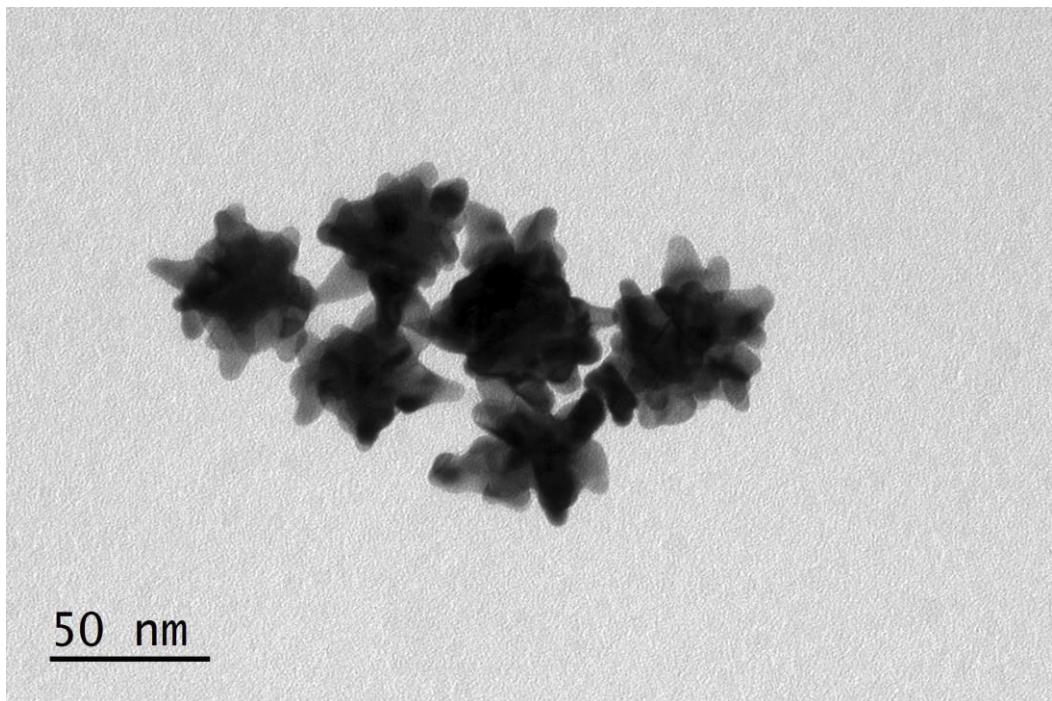
<sup>5</sup>CENIMAT|i3N, Departamento de Ciéncia de Materiais, Faculdade de Ciéncias e Tecnologia, Universidade NOVA de Lisboa, Lisboa, and CEMOP/UNINOVA, Campus da Caparica, Caparica, Portugal.



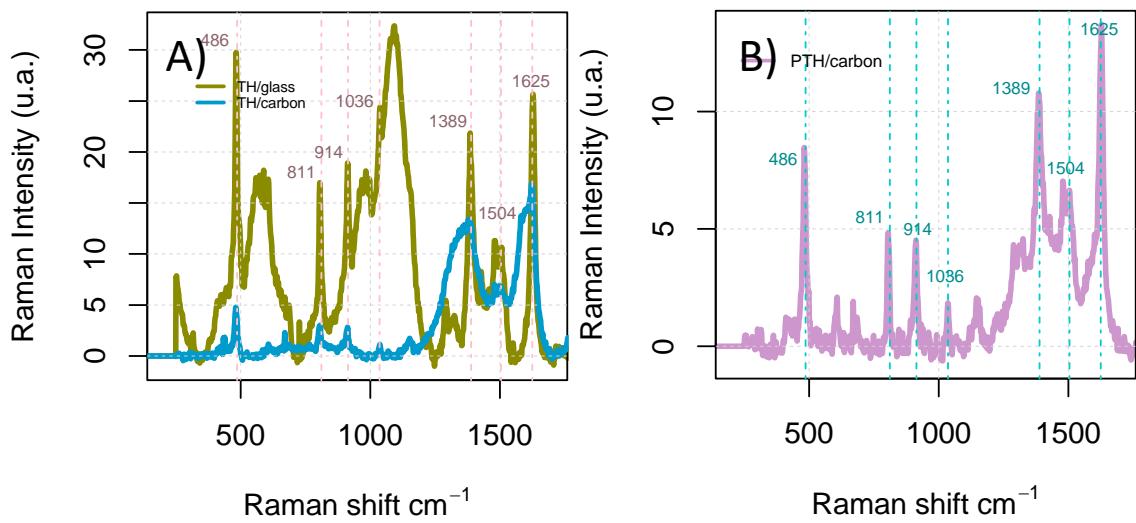
**Figure S1.** Raman spectra of the carbon electrode at room temperature, signaling peaks G, D, D', D'' and D\*.



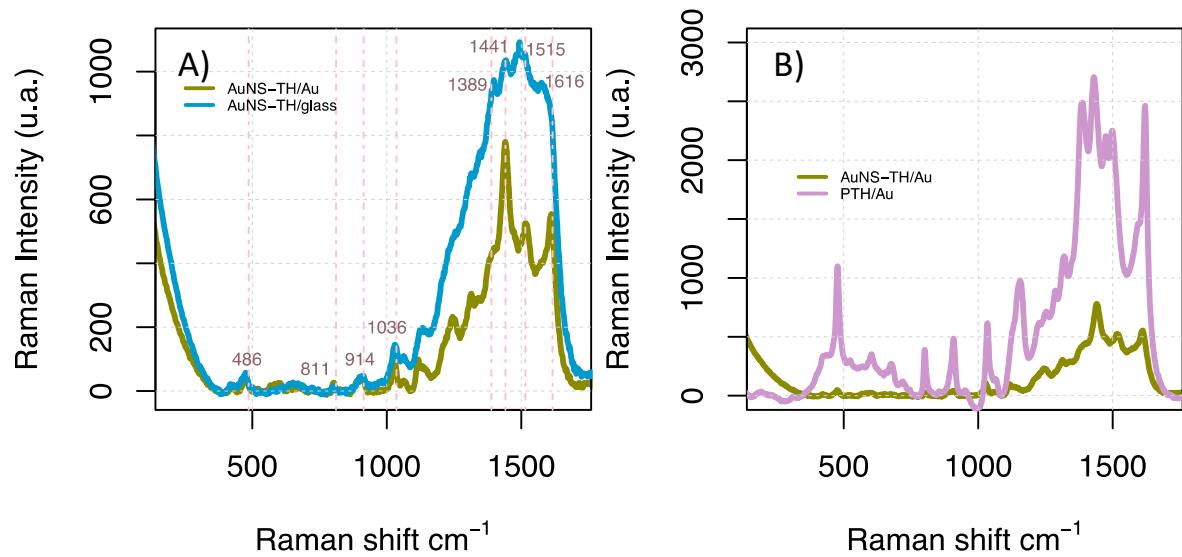
**Figure S2:** SERS spectra of TH powder showing the most relevant peaks.



**Figure S3.** TEM images of AuNS.



**Figure S4.** Raman spectra of TH, A) (blue) on carbon electrodes and (green) on glass, both substrates drops with TH, B) (pink) spectra of PTH on carbon substrate.



**Figure S5.** SERS spectra of A) TH/AuNS, (blue) on glass and (green) on gold, B) (pink) spectra of PTH on gold substrate.

**Table S1:** Information about ratio between intensities and amplitude of carbon bands, D, D'', and G.

Carbon band	Frequency (cm <sup>-1</sup> )	Intensity, I (a.u)	FWHM (cm <sup>-1</sup> )	Area (A)	I <sub>D''</sub> /I <sub>G</sub>	A <sub>D''</sub> /A <sub>G</sub>	I <sub>D</sub> /I <sub>G</sub>	A <sub>D</sub> /A <sub>G</sub>
D	1350	39,76	169,34	10575,5				
D''	1512	13,84	109,22	2374,9				
G	1579	42,04	35,73	2359,7				
					0,33	1,01	0,94	4,48
Carbon+T H band	Frequency (cm <sup>-1</sup> )	Intensity (I) (a.u)	FWHM (cm <sup>-1</sup> )	Area (A)	I <sub>D''</sub> /I <sub>G</sub>	A <sub>D''</sub> /A <sub>G</sub>	I <sub>D</sub> /I <sub>G</sub>	A <sub>D</sub> /A <sub>G</sub>
D	1350	72,68	190,68	21769,3				
D''	1504	30,62	101,12	4871,44				
G	1580	70,18	44,79	4937,025				
					0,43	0,99	1,04	4,41