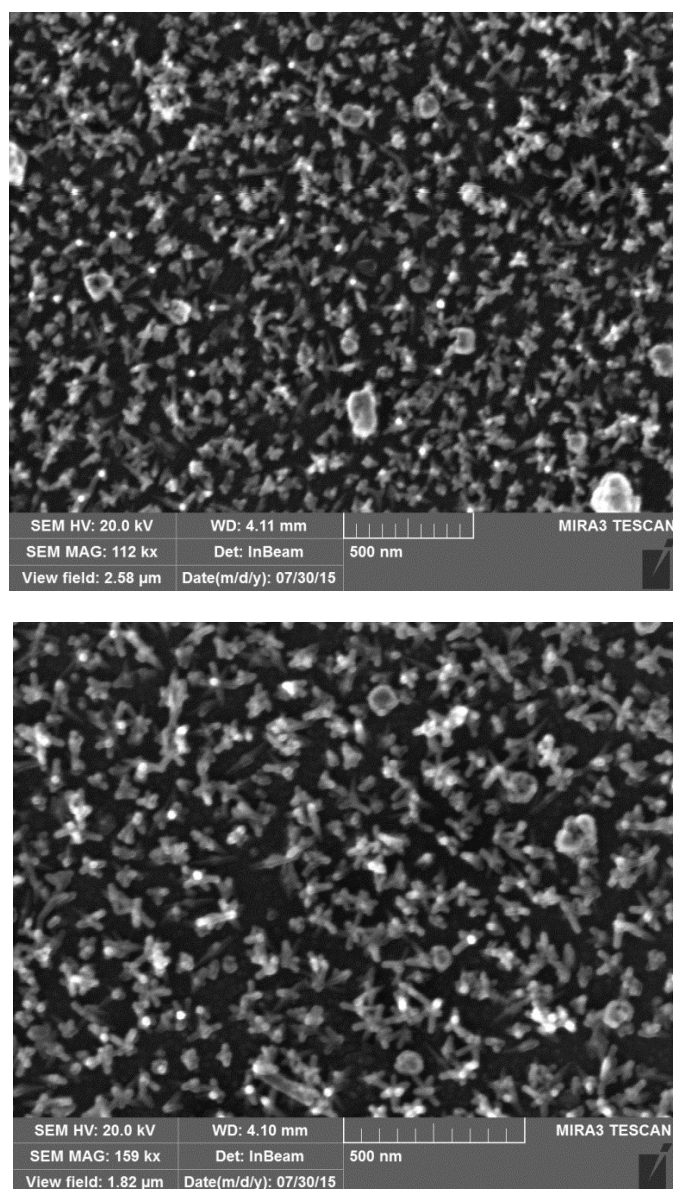


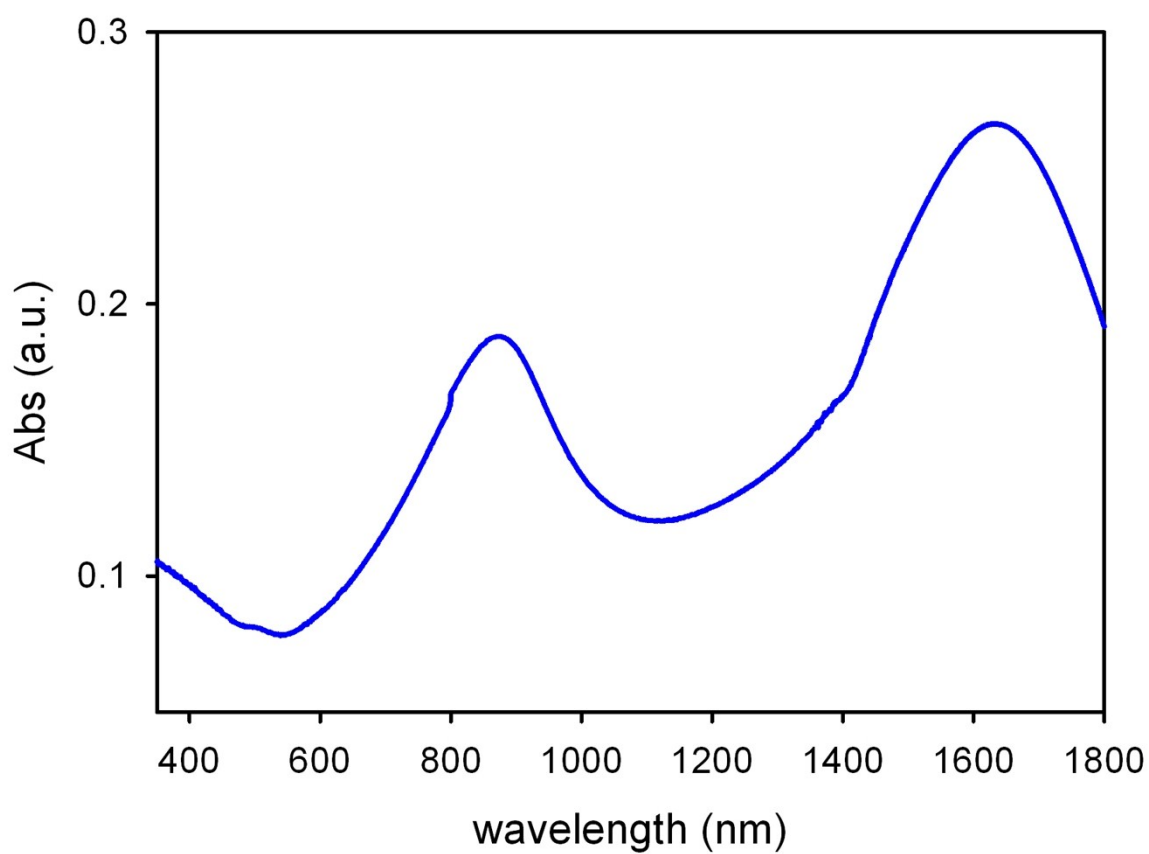
## A bistren cryptand with a remote thioether function: Cu(II) complexation in solution and on the surface of gold nanostars

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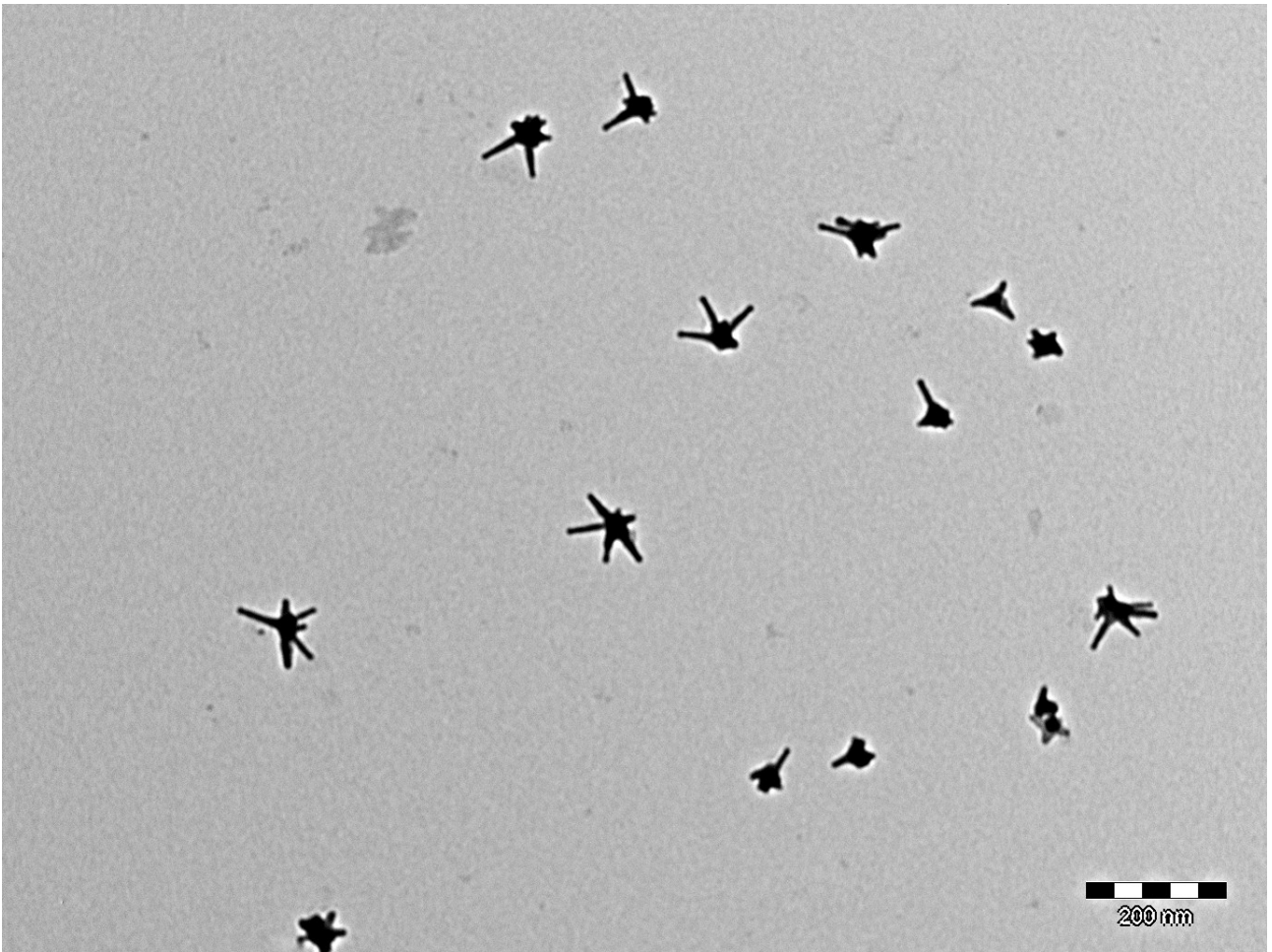
### Electronic Supporting Information



**Figure S1** – SEM images of a GNS SAM (Type II surface)

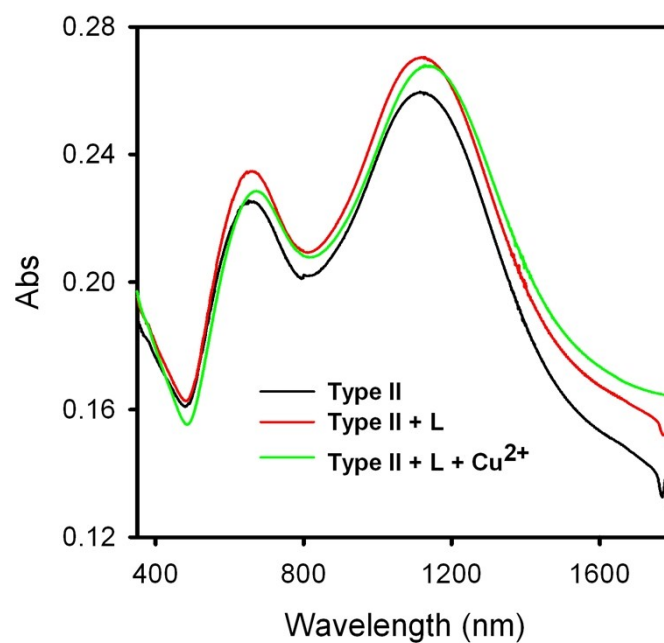


**Figure S2** - UV-Vis-NIR extinction spectrum of a GNS colloidal solution in water

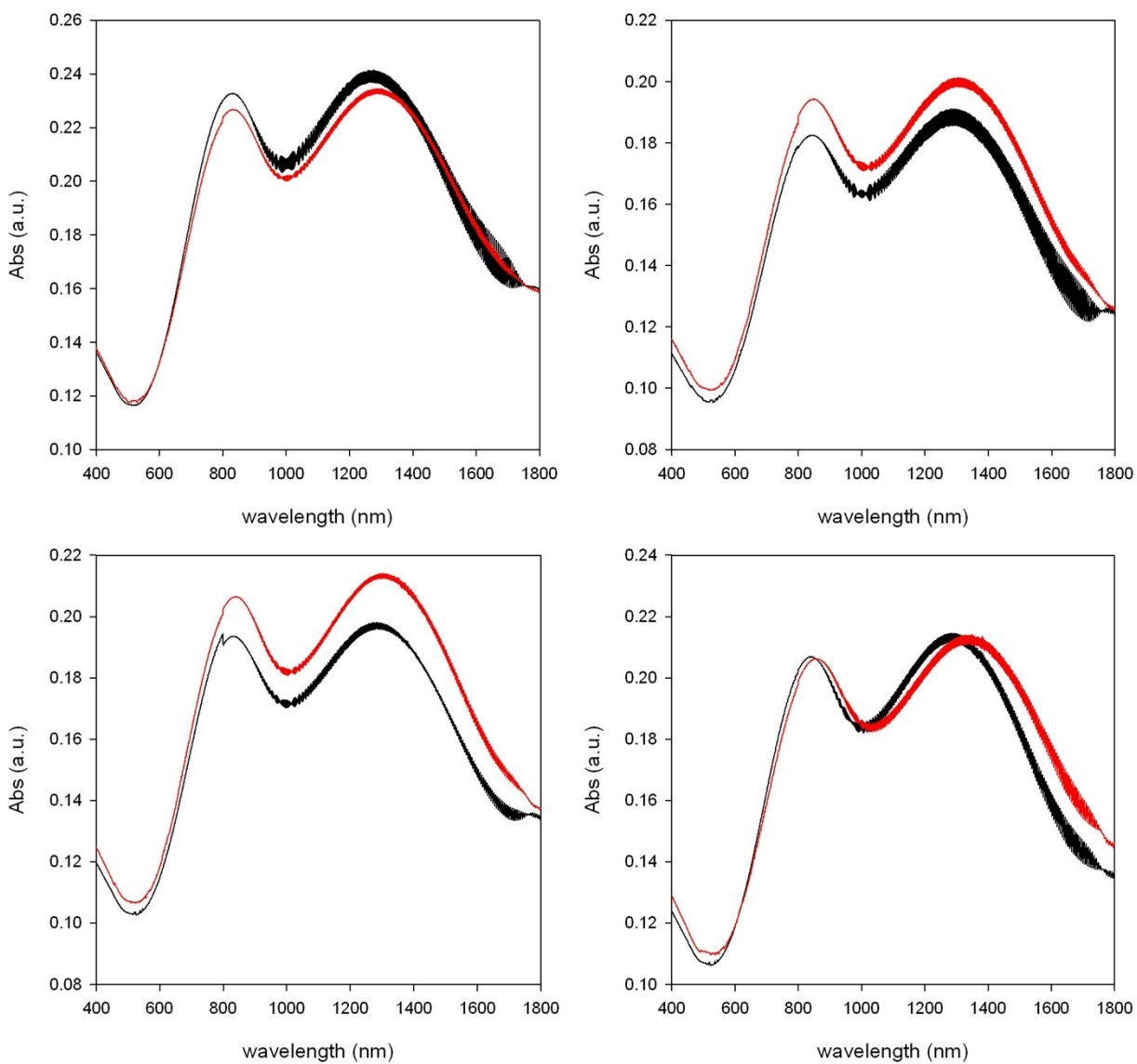


**Figure S3** – TEM image of a TEM colloid used for coating (the image in Figure 2B, main text, is a detail taken from this larger image)

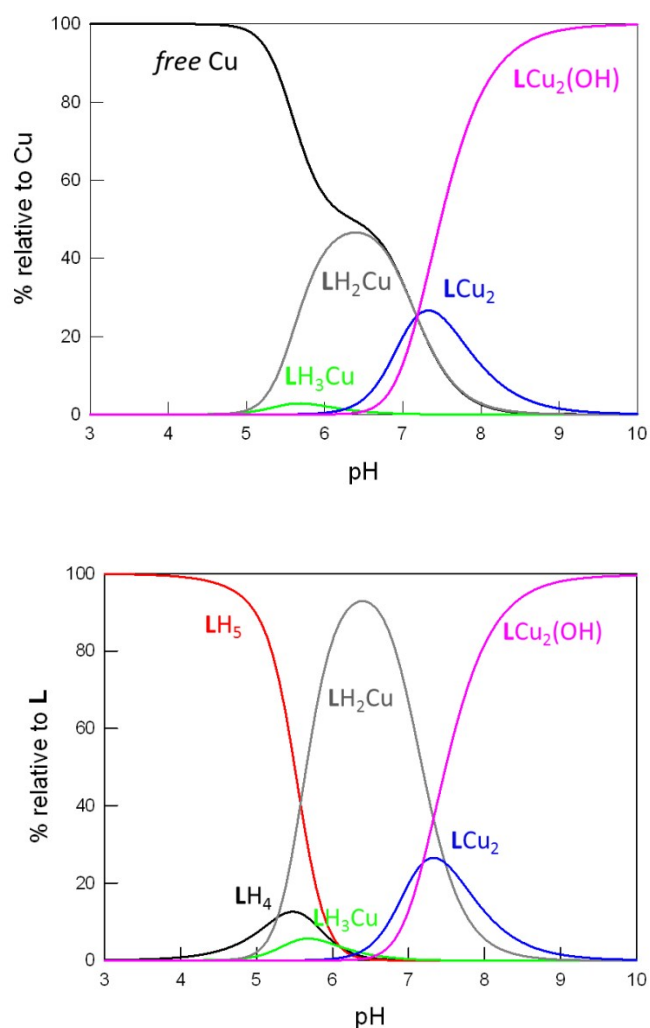
TSA (two-step functionalization approach)



**Figure S4A:** extinction spectrum of a slide undergoing TSA, i.e. of a Type II slide, of the slide after addition of L and of the same after further treatment with Cu<sup>2+</sup>.



**Figure S4B:** extinction spectra of 4 different Type II slides (only GNS on PEI) before (black) and after (red) the immersion in a  $10^{-4}$  M solution of  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ , evidencing the red shift of the GNS LSPRs on contact with  $\text{Cu}^{2+}$  cations.



**Figure S5:** Distribution diagrams relative to Cu and L, calculated at the experimental conditions of the Cu<sup>2+</sup> release in water from Type III surfaces (*i.e.* [L] = 0.667 μM and [Cu<sup>2+</sup>]=1.33 μM). Both diagrams have been obtained by considering the protonation and complexation constants reported in Table 1.

The hypothesized 0.667 μM concentration for the [Cu<sub>2</sub>L]<sup>4+</sup> complex is obtained considering the surface of the slides (2.2x2.6 cm), that are functionalized on both sides (total surface = 11.44 cm<sup>2</sup>). The surface concentration of the complex is 1/2 of that of Cu<sup>2+</sup> with the SSA (see Table 2, main text), *i.e.* 0.175 nmol/cm<sup>2</sup>. This leads to 2.002 nmol of complex. The volume of solution in contact with such moles is 3.0 mL. 2.002x10<sup>-9</sup>/0.003 gives the used 6.67x10<sup>-7</sup> molar concentration.