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SERS-active carboxymethyl cellulose-based gold nanoparticles: High-stability in hypersaline solution and selective response in the Hofmeister series.

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Abstract: Gold nanoparticles (AuNP) were directly synthesized with sodium carboxymethyl cellulose (CMC) by a simple one- pot procedure, exhibing a surprising protection against salt-induced aggregation. The AuNP@CMC nanoparticles are reactive towards thiol ligands such as 4-mercaptopyridine (4MPy) and 2,4,6-trimercapto-1,3,5-triazine (TMT) indicating a labile character for the CMC coating. Aggregation can be promoted by those ligands combined with salt induced effects along Hofmeister series, allowing to explore the local enhanced electric fields (hot spots) in surface enhanced Raman (SERS) sensors. Such behavior is selective for the several salts within the Hofmeister series, exposing the role of the ligand exchange dynamics in the system.

Keywords: Gold nanoparticles, carboxymethyl cellulose, hypersaline solution, ligand exchange, SERS.

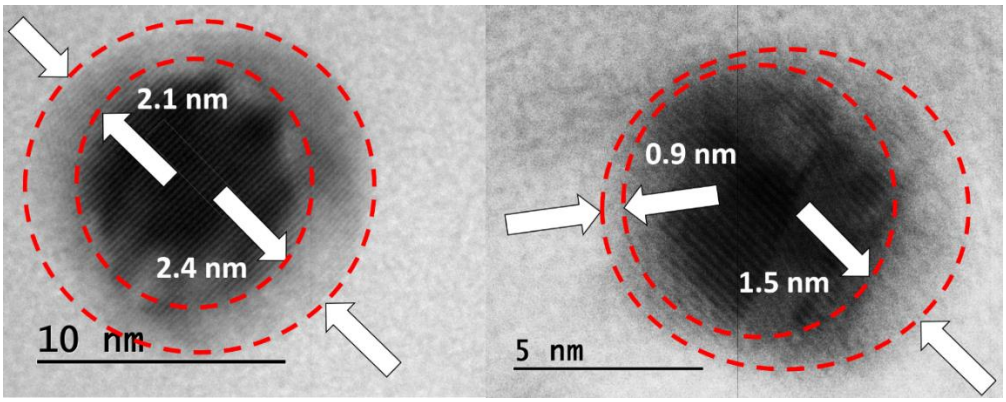

Figure S1. Overfocused HRTEM micrographies of AuNP@CMC highlighting the inhomogeneous coating with the mean size of 1.7 ± 1.1 nm.

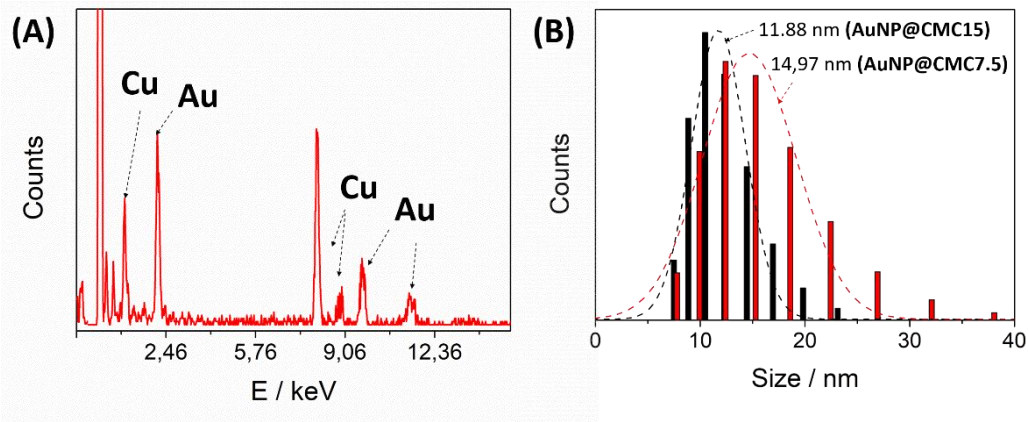

Figure S2. (A) Energy-Dispersive X-ray Spectroscopy (EDS) measurement of AuNP@CMC7.5 and AuNP@CMC15 confirming the presence of gold (present in the nanoparticles) and copper (presented in the grid). (B) DLS measurement for both above-mentioned samples showing a similar size histogram.

HARD SOFT ACID BASE theory (HSAB)

The Klopman equation describes the energetic change that occurs when two species approach each other in the course of a reaction and begin to interact, as their associated molecular orbitals begin to overlap with each other and atoms bearing partial charges begin to experience attractive or repulsive electrostatic forces. This relationship provides a mathematical basis for the key assumptions of frontier molecular orbital theory and hard soft acid base (HSAB) theory. Conceptually, it highlights the importance of considering both electrostatic interactions and orbital interactions when rationalizing the selectivity or reactivity of a chemical process. The following schematic image summarize the above explanation.

$$\Delta E = \underbrace{\left(-\sum_{a,b}(q_a + q_b)\beta_{ab}S_{ab}\right)}_{(1)} + \underbrace{\left(\sum_{k<\ell}\frac{Q_k Q_\ell}{\varepsilon R_{k\ell}}\right)}_{(2)} + \underbrace{\left(\sum_{r}^{\text{occ.}}\sum_{s}^{\text{unocc.}} - \sum_{s}^{\text{occ.}}\sum_{r}^{\text{unocc.}}\frac{2(\sum_{a,b} c_{ra}c_{sb}\beta_{ab})^2}{E_r - E_s}\right)}_{(3)}$$

Figure S3. Schematic image summarizing the Klopman equation and its respective terms

The first term describes the closed-shell repulsion of the occupied molecular orbitals of the reactants (q_a = is the electron population in atomic orbital *a*; β_{ab}, S_{ab} = resonance and overlap integrals for the interaction of atomic orbitals *a* and *b*). The second term describes the Coulombic attraction or repulsion between the atoms of the reactants (Qk = is the total charge on atom *k*, and R_{kl} is the local dielectric constant). Finally, the third term accounts for all possible interactions between the occupied and unoccupied molecular orbitals of the reactants (c_{ra} = the coefficient of atomic orbital *a* in molecular orbital *r*; E_r = the energy of molecular orbital *r*). Although conceptually useful, the Klopman equation seldom serves as the basis for energetic analysis in modern quantum chemical calculations. Because of the difference in MO energies appearing in the denominator of the third term, energetically close orbitals make the biggest contribution. Besides, analysis can often be simplified by considering only the highest occupied and lowest unoccupied molecular orbitals of the reactants (the HOMO-LUMO interaction in frontier molecular orbital theory, see in the next page). The relative contributions of the second and third terms play an important role in justifying hard soft acid base theory (HSAB), with hard-hard interactions governed by the ionic term and soft-soft interactions governed by the covalent term.[1,2]

HOMO-LUMO theory

Generally speaking, HOMO and LUMO are types of molecular orbitals. The acronyms stand for *highest occupied molecular orbital* and *lowest unoccupied molecular orbital*, respectively as following schematic image shows. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap ($H_{Ho} - H_{Lu}$) and it can be used to predict the strength and stability of transition metal complexes.[3]

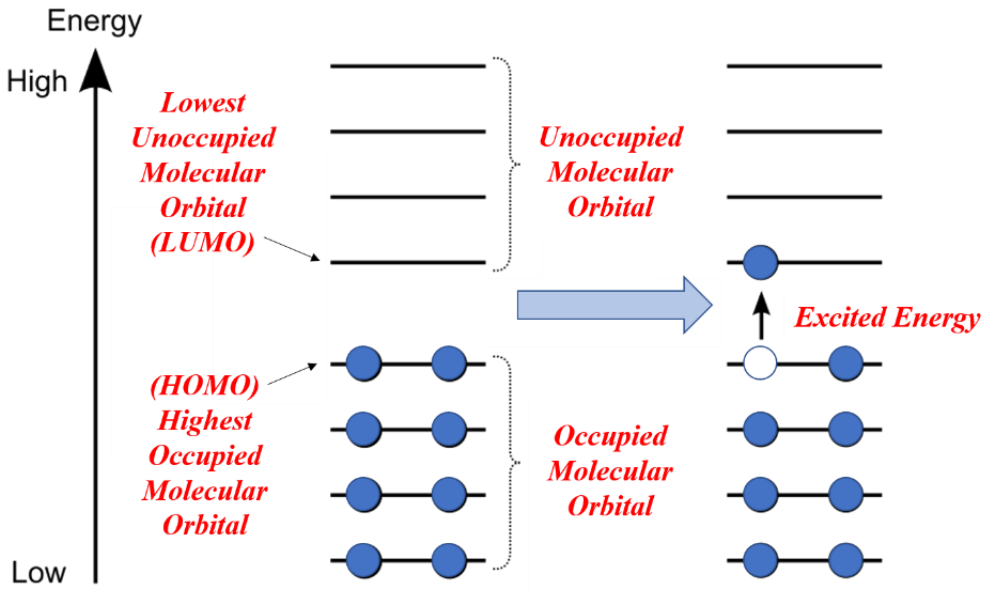

Figure S4. Diagram of the HOMO and LUMO of a general molecule. Each circle represents an electron in an orbital; When light is absorbed by an electron in the HOMO, it goes to the LUMO.

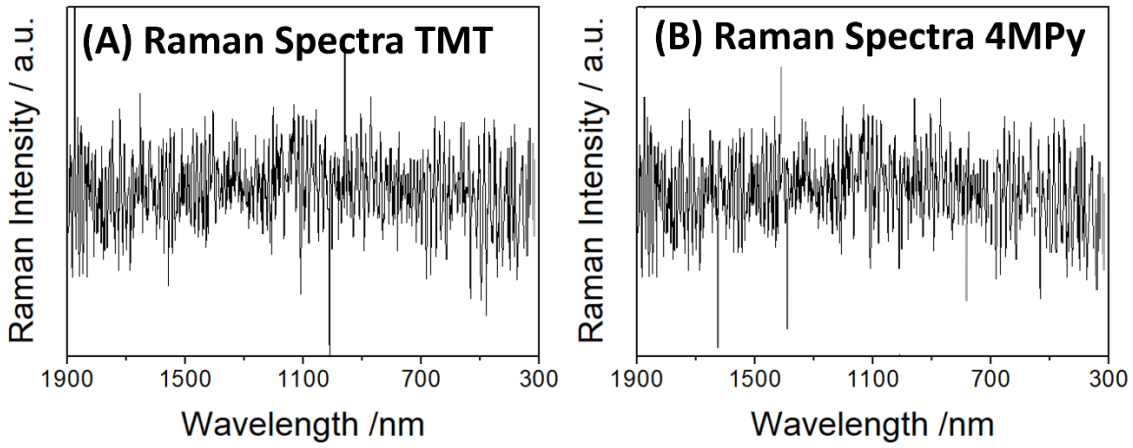

Figure S5. (A) Raman spectrum of TMT. (B) Raman spectrum of 4MPy. The studied ligands do not show any kind of Raman signal.

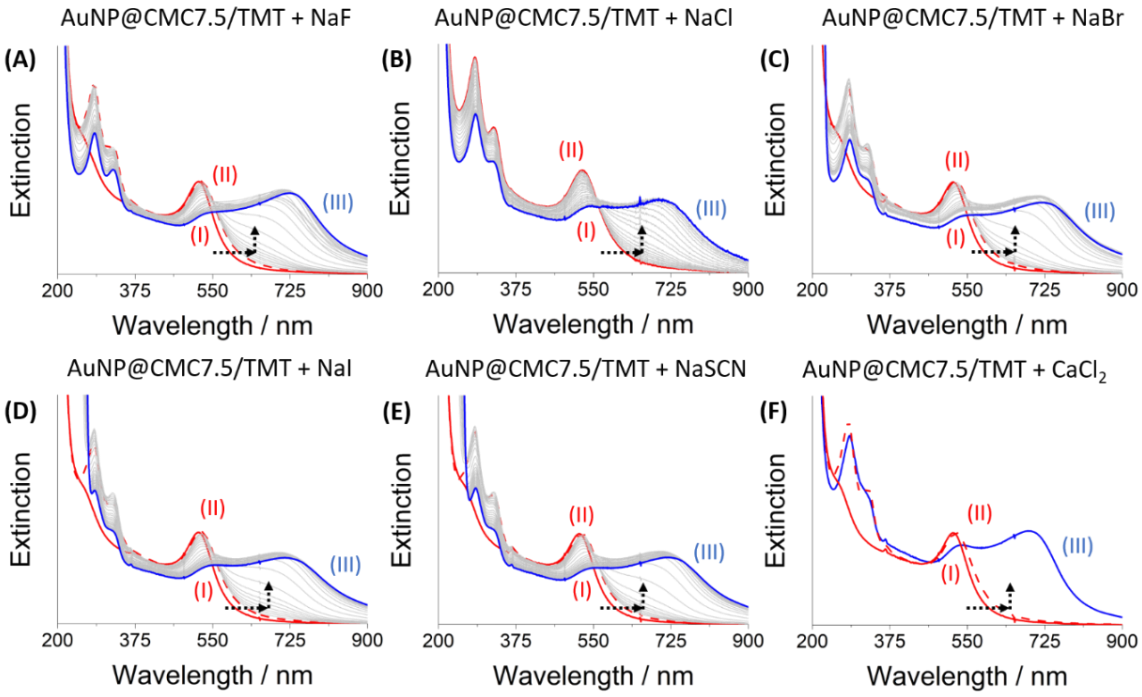

Figure S6. (A) SPR band before (I, solid red line) and after (II, dashed red line) adding TMT in the AuNP@CMC7.5 and after adding 500 μL of NaF 4.0 mol.L^{-1} in the same system (III, blue line) proving the agglomeration process. (B-E) Same thing changing the salt (NaCl, NaBr, NaI and NaSCN). (F) In that system, it was not necessary to add 500 μL of $CaCl_2$. After the first addition of that, the system was agglomerated.

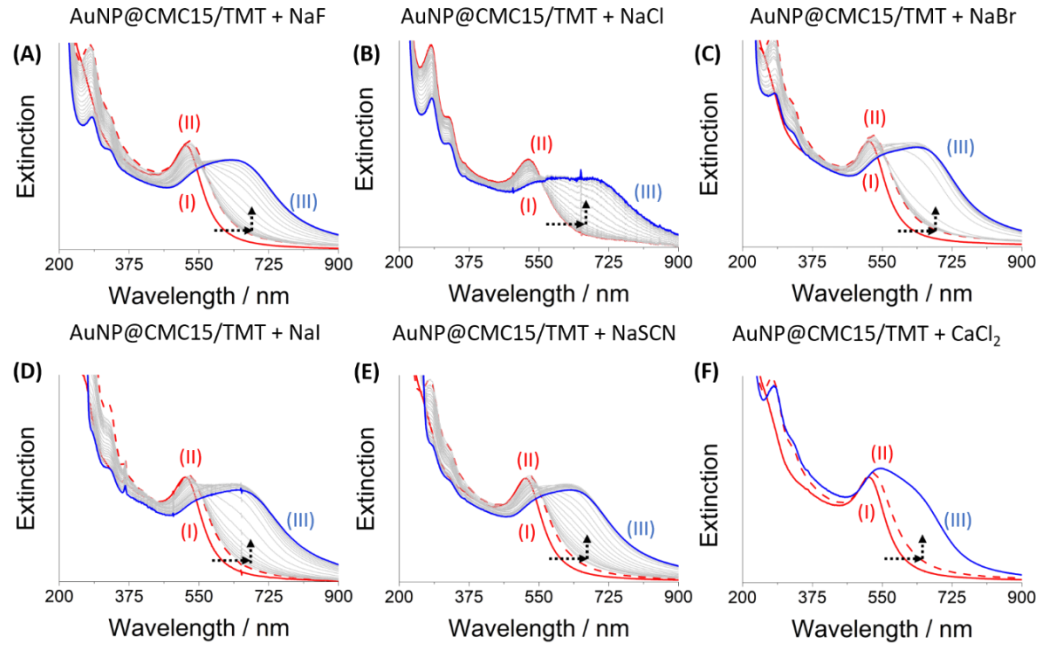

Figure S7. (A) SPR band before (I) and after (II) adding TMT in the AuNP@CMC7.5 and after adding 500 μL of NaF 4.0 mol.L^{-1} in the same system (III, blue line) proving the agglomeration process. (B-E) Same thing changing the salt (NaCl, NaBr, NaI and NaSCN). (F) In that system, it was not necessary to add 500 μL of $CaCl_2$. After the first addition of that, the system was agglomerated.

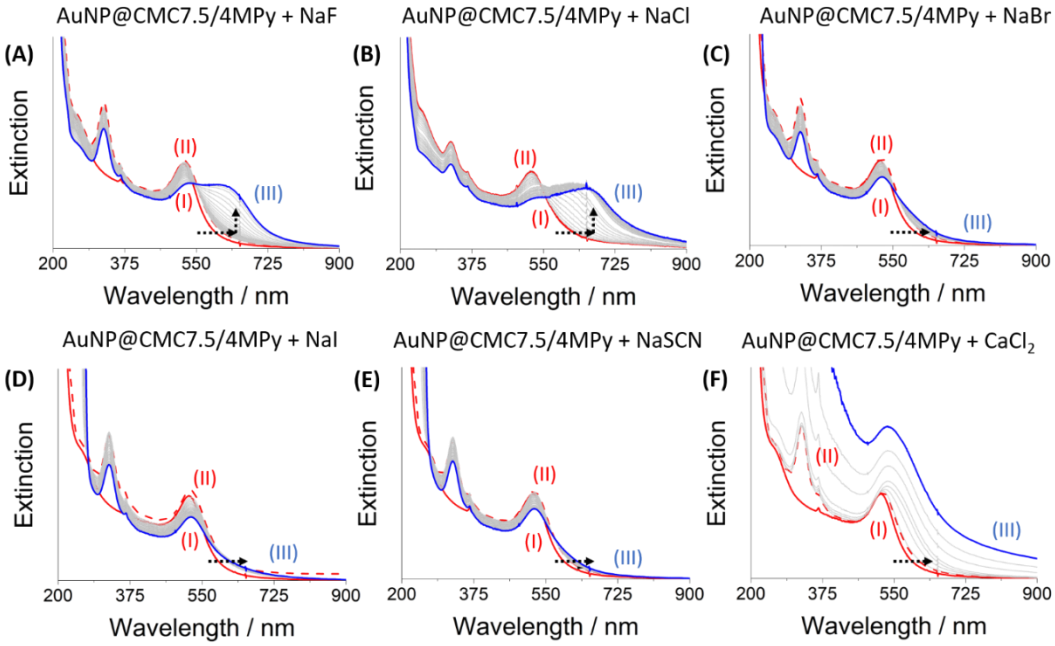

Figure S8. (A) SPR band before (I, solid red line) and after (II, dashed red line) adding 4MPy in the AuNP@CMC7.5 and after adding 500 μL of NaF 4.0 mol.L^{-1} in the same system (III, blue line) proving the agglomeration process. (B-E) Same thing changing the salt (NaCl, NaBr, NaI and NaSCN). (F) In that system, the baseline increasing disturbed our interpretation so we decided to add just six aliquots of $CaCl_2$ 4.0 mol.L^{-1}.

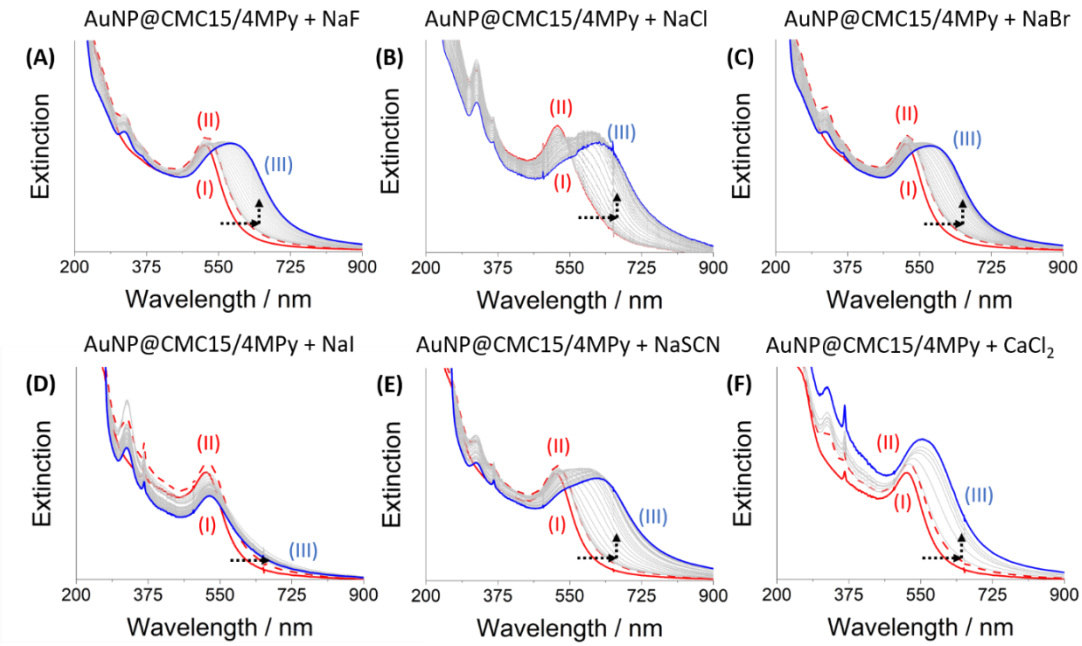

Figure S9. (A) SPR band before (I, solid red line) and after (II, dashed red line) adding 4MPy in the AuNP@CMC15 and after adding 500 μL of NaF 2.0 mol.L^{-1} in the same system (III, blue line) proving the agglomeration process. (B-E) Same thing changing the salt (NaCl, NaBr, NaI and NaSCN). (F) In that system, the baseline increasing disturbed our interpretation so we decided to add just six aliquots of $CaCl_2$ 4.0 mol.L^{-1}.

References

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2 L. Salem, *J. Am. Chem. Soc., 1968, 90(3), 543-552.*

3. J. S. Griffith and L.E. Orgel. *Q. Rev. Chem. Soc.* 1957, 11, 381-383.