

Supplementary

Sensing Bisphenol A by Means of Surface-Enhanced Raman Spectroscopy and DFT Calculations to Elucidate the Enhancement Mechanism That Dominates the Spectrum

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Table S1. Experimental conditions and characterization of the different AgNPs.

AgNPs	Aqueous solution ¹		Conditions		Characterization			
	AgNO ₃	Reducing agent	T (°C)	Medium	Device	Color	Size ² (n)	Absorption maximum ³
Ag@Cit	100 mL 1 mM	2 mL 1%	Heating, 80 °C		Reflux (1h), Magnetic stirring (1h)	Greenish grey	19 ± 32 nm (82)	408 nm
Ag@HX	10 mL 10 mM	90 mL 16 mM	Room, 25 °C	Basic: 300 µL, 1 M NaOH	Magnetic stirring (15 min)	Grayish-green	42 ± 52 nm (57)	419 nm
Ag@BH	10 mL 1 mM	40 mL 3 mM	Cooling, 3 °C		Ice bath, Magnetic stirring (30 min)	Caramel	12 ± 9 nm (273)	389 nm
Ag@βCD	200 µL 10 mM	45 mL 10 mM	Heating, 60 °C	Basic: 15 mL, 10 mM NaOH	Water bath, Magnetic stirring (15 min)	Grayish-green	38 ± 17 nm (337)	419 nm

¹ volume and concentration. ² average diameter and standard deviation measured by TEM [1]. (n) Number of NPs measured. ³ UV spectroscopy [1]

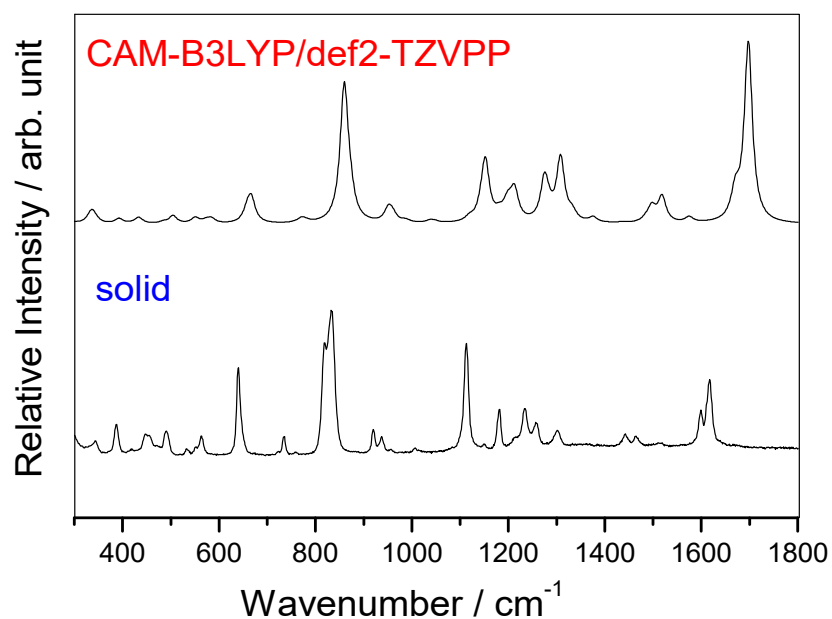


Figure S1. Experimental Raman spectrum of the BPA solid and that theoretical at CAM-B3LYP/def2-TZVPP level of calculation. The calculated wavenumbers are not scaled.

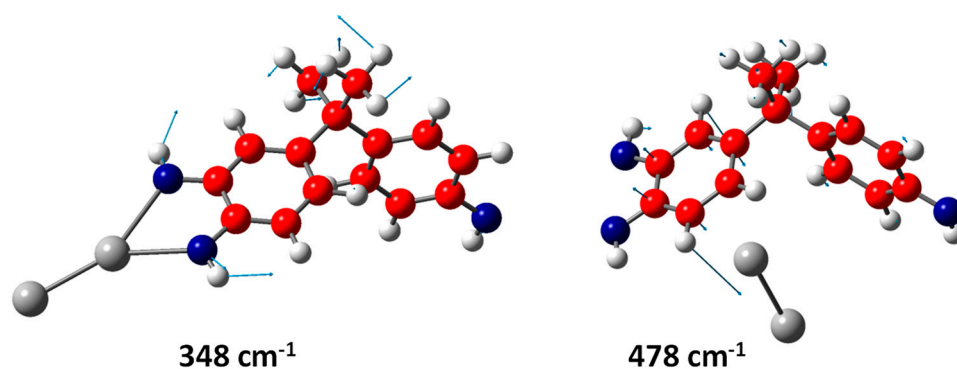


Figure S2. Vectorial representation of the vibrational motions corresponding to the two strongest SERS bands. Wavenumbers calculated at CAM-B3LYP/def2-TZVPP level.

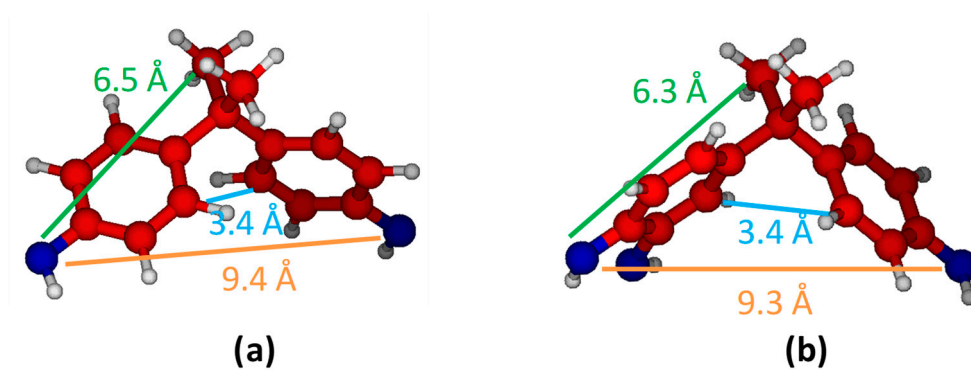


Figure S3. Optimized CAM-B3LYP/def2-TZVPP structures of isolated (a) BPA and (b) BPA(OH).

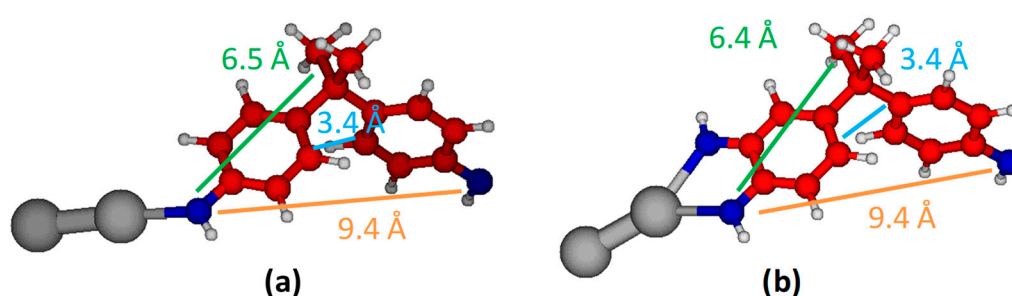


Figure S4. Optimized CAM-B3LYP/def2-TZVPP structures of (a) Ag₂-BPA and (b) Ag₂-BPA(OH) complexes in which silver atoms are coordinated through the oxygen atoms.

Table S2. TD-CAM-B3LYP/def2-TZVPP excitation energies (ΔE) and oscillator force (f) at the Franck-Condon point corresponding to the first ten singlets of isolated BPA and BPA(OH).

BPA (C ₂)											
	S ₀ 1A	S ₁ 1B	S ₂ 2A	S ₃ 2B	S ₄ 3A	S ₅ 3B	S ₆ 4A	S ₇ 5A	S ₈ 4B	S ₉ 5B	S ₁₀ 6A
$\Delta E(\text{Si-S}_0)/\text{eV}$	0.0000	5.0608	5.1396	5.8262	5.9465	6.3346	6.3383	6.4048	6.4117	6.69	6.7884
f	0.0000	0.0607	0.0156	0.1518	0.0348	0.0003	0.0000	0.0019	0.1238	0.6743	0.0505
BPA(OH) (C ₁)											
	S ₀ A	S ₁ A	S ₂ A	S ₃ A	S ₄ A	S ₅ A	S ₆ A	S ₇ A	S ₈ A	S ₉ A	S ₁₀ A
$\Delta E(\text{Si-S}_0)/\text{eV}$	0.0000	5.0541	5.1145	5.7719	5.8702	5.9171	6.1979	6.351	6.4582	6.5939	6.6474
f	0.0000	0.0403	0.0551	0.1021	0.0068	0.0364	0.0414	0.0001	0.3121	0.3023	0.135

Table S3. TD-CAM-B3LYP/def2-TZVPP excitation energies (ΔE) and oscillator force (f) at the Franck-Condon point corresponding to the first ten singlets of the different Ag₂-BPA and Ag₂-BPA(OH) complexes coordinated through the oxygen atoms and their corresponding charges transferred (Δq).

Ag ₂ -BPA											
	S ₀	S ₁ (PL ₀)	S ₂ (PL ₁)	S ₃ (PL ₂)	S ₄ (PL ₃)	S ₅ (PL ₄)	S ₆ (PL ₅)	S ₇ (PL ₆)	S ₈ (PL ₇)	S ₉ (CT _{0F})	S ₁₀ (S ₁)
ΔE(Si-S0)/eV	0.0000	3.2494	4.2228	4.2983	4.7433	4.8802	4.915	4.9954	4.9955	5.0148	5.0871
F	0.000	0.5239	0.2991	0.3028	0.0629	0.0312	0.0297	0.0000	0.0000	0.0337	0.0492
Δq ¹		0.0171	-0.0160	-0.0211	0.0130	-0.0121	-0.0010	0.0050	0.0050	-0.7621	-0.0020
Ag ₂ -BPA(OH)											
	S ₀	S ₁ (PL ₀)	S ₂ (PL ₁)	S ₃ (PL ₂)	S ₄ (PL ₃)	S ₅ (CT _{0F})	S ₆ (PL ₄)	S ₇ (PL ₅)	S ₈ (PL ₆)	S ₉ (PL ₇)	S ₁₀ (S ₁)
ΔE(Si-S0)/eV	0.0000	3.2289	4.1904	4.2333	4.7369	4.7971	4.8098	4.8775	4.9892	4.9892	5.0405
f	0.0000	0.5493	0.2935	0.3273	0.0635	0.0037	0.0253	0.0471	0.0000	0.0001	0.1182
Δq ¹		0.0093	-0.0389	0.0177	-0.2171	-0.6429	0.0147	0.0352	0.0041	0.0042	-0.0281

¹ $q = q(\text{Si}) - q(\text{S}_0)$. Negative values indicate a charge transferred from metal-to-molecule (F: forward transition). Positive values indicate a charge transferred from molecule-to-metal (R: reverse transition).

Table S4. TD-CAM-B3LYP/def2-TZVPP excitation energies (ΔE) and oscillator force (f) at the Franck-Condon point corresponding to the first ten singlets of the different Ag₂-BPA and Ag₂-BPA(OH) complexes coordinated through one face of the aromatic ring and their corresponding charges transferred (Δq).

Ag ₂ -BPA (external face)										
	S ₀	S ₁ (PL ₀)	S ₂ (CT _{0F})	S ₃ (PL ₁)	S ₄ (CT _{1F})	S ₅ (CT _{2F})	S ₆ (CT _{3F})	S ₇ (S ₁ ,CT _{4R})	S ₈ (PL ₂)	S ₉ (PL ₃) S ₁₀ (PL ₄)
$\Delta E(\text{Si-S}_0)/\text{eV}$	0.0000	3.2761	3.8303	4.1665	4.5585	4.7031	4.8710	4.9235	4.9952	5.0431 5.0432
f	0.000	0.5198	0.0832	0.2114	0.1569	0.0117	0.1007	0.0692	0.0043	0.0002 0.0003
Δq^1		0.0270	-0.4695	-0.0384	-0.2673	-0.2113	-0.0942	0.1222	0.0341	0.0125 0.0123
Ag ₂ -BPA(OH) (external face)										
	S ₀	S ₁ (PL ₀)	S ₂ (CT _{0F})	S ₃ (PL ₁)	S ₄ (CT _{1F})	S ₅ (CT _{2R})	S ₆ (CT _{3R})	S ₇ (S ₁ ,CT _{4F})	S ₈ (PL ₂)	S ₉ (PL ₃) S ₁₀ (PL ₄)
$\Delta E(\text{Si-S}_0)/\text{eV}$	0.0000	3.2743	3.9192	4.1423	4.6064	4.6229	4.8130	4.8676	4.9916	5.0430 5.0431
f	0.0000	0.5271	0.1036	0.2053	0.0788	0.0925	0.0542	0.0667	0.0211	0.0004 0.0001
Δq^1		0.0303	-0.3785	-0.0338	-0.2366	0.0340	0.0247	-0.1004	0.0233	0.0120 0.0124
Ag ₂ -BPA (internal face)										
	S ₀	S ₁ (PL ₀)	S ₂ (CT _{0F})	S ₃ (PL ₁)	S ₄ (CT _{1F})	S ₅ (CT _{2F})	S ₆ (CT _{3F})	S ₇ (S ₁)	S ₈ (CT _{4R})	S ₉ (PL ₃) S ₁₀ (PL ₄)
$\Delta E(\text{Si-S}_0)/\text{eV}$	0.0000	3.2706	3.8696	4.1681	4.5562	4.6848	4.8755	4.9160	4.9949	5.0479 5.0483
f	0.000	0.4413	0.1038	0.2253	0.1999	0.0011	0.0741	0.0899	0.0144	0.0041 0.0013
Δq^1		0.0280	-0.4717	-0.0522	-0.2497	-0.1445	-0.1525	0.0949	0.0417	0.0126 0.0134
Ag ₂ -BPA(OH) (internal face)										
	S ₀	S ₁ (PL ₀)	S ₂ (CT _{0F})	S ₃ (PL ₁)	S ₄ (CT _{1F})	S ₅ (CT _{2R})	S ₆ (CT _{3F})	S ₇ (S ₁)	S ₈ (PL ₃)	S ₉ (CT _{4F}) S ₁₀ (PL ₄)
$\Delta E(\text{Si-S}_0)/\text{eV}$	0.0000	3.2485	3.9758	4.1479	4.5286	4.6039	4.7673	4.8491	4.9691	5.0157 5.0429
f	0.0000	0.4648	0.1464	0.1870	0.0563	0.1288	0.0059	0.0225	0.0590	0.0321 0.0002
Δq^1		0.0212	-0.3190	-0.0740	-0.1822	0.0808	-0.1891	0.0622	-0.0160	-0.1755 0.0106

¹ $q = q(\text{Si}) - q(\text{S}_0)$. Negative values indicate a charge transferred from metal-to-molecule (F: forward transition). Positive values indicate a charge transferred from molecule-to-metal (R: reverse transition).

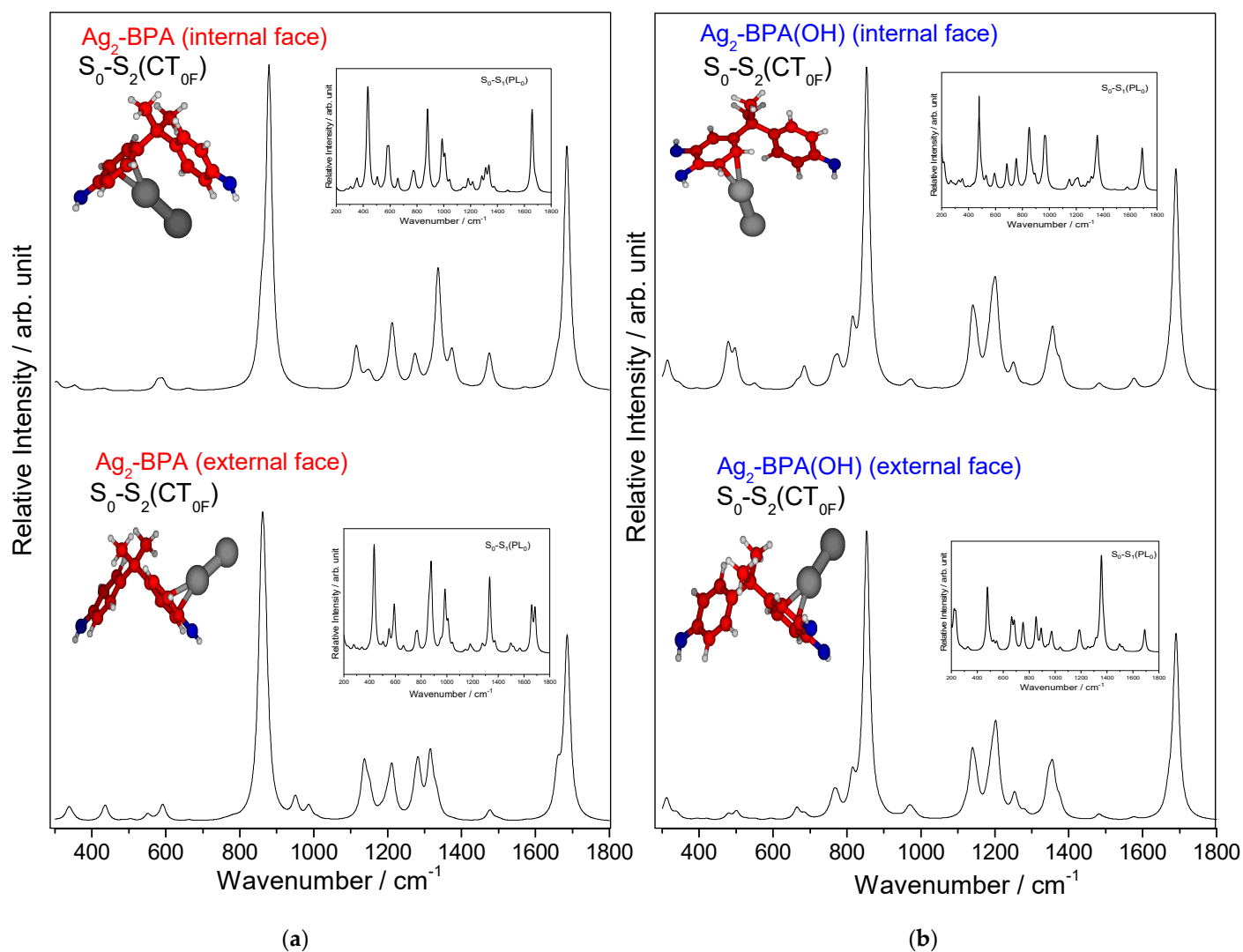


Figure S5. CAM-B3LYP/def2-TZVPP resonance Raman spectra to the first charge transfer (CT) state of (a) $\text{Ag}_2\text{-BPA}$ and (b) $\text{Ag}_2\text{-BPA(OH)}$ complexes in which silver atoms are coordinated through internal and external ring face. The insets show the resonance Raman spectra to the first plasmon-like (PL) state.

Reference

- de Souza, M.L.; Otero, J.C.; López-Tocón, I. Comparative Performance of Citrate, Borohydride, Hydroxylamine and β -Cyclodextrin Silver Sols for Detecting Ibuprofen and Caffeine Pollutants by Means of Surface-Enhanced Raman Spectroscopy. *Nanomaterials* **2020**, *10*, 2339. <https://doi.org/10.3390/NANO10122339>.