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Surface mediated chiral interactions between cyclodextrins and propranolol enantiomers: a SERS and DFT study

Rares Stiufiuc,[a*] Cristian Iacovita,[a*] Gabriela Stiufiuc,[b] Ede Bodoki,[c] Vasile Chis,[b] and Constantin M. Lucaciu,[a]

[a] Department of Pharmaceutical Physics-Biophysics, Faculty of Pharmacy, "Iuliu Hatieganu" University of Medicine and Pharmacy, Pasteur 6, 400349 Cluj-Napoca, Romania. rares.stiufiuc@umfcluj.ro, cristian.iacovita@umfcluj.ro, clucaciu@umfcluj.ro.

[b] Faculty of Physics, "Babes Bolyai" University, Kogalniceanu 1, 400084 Cluj-Napoca, Romania. gabi.stiufiuc@phys.ubbcluj.ro, vasile.chis@phys.ubbcluj.ro

[c] Department of Analytical Chemistry, Faculty of Pharmacy, ''Iuliu Hatieganu'' University of Medicine and Pharmacy, Pasteur 4, 400349 Cluj-Napoca, Romania. bodokie@umfcluj.ro.

[*] Corresponding authors

Supplementary information

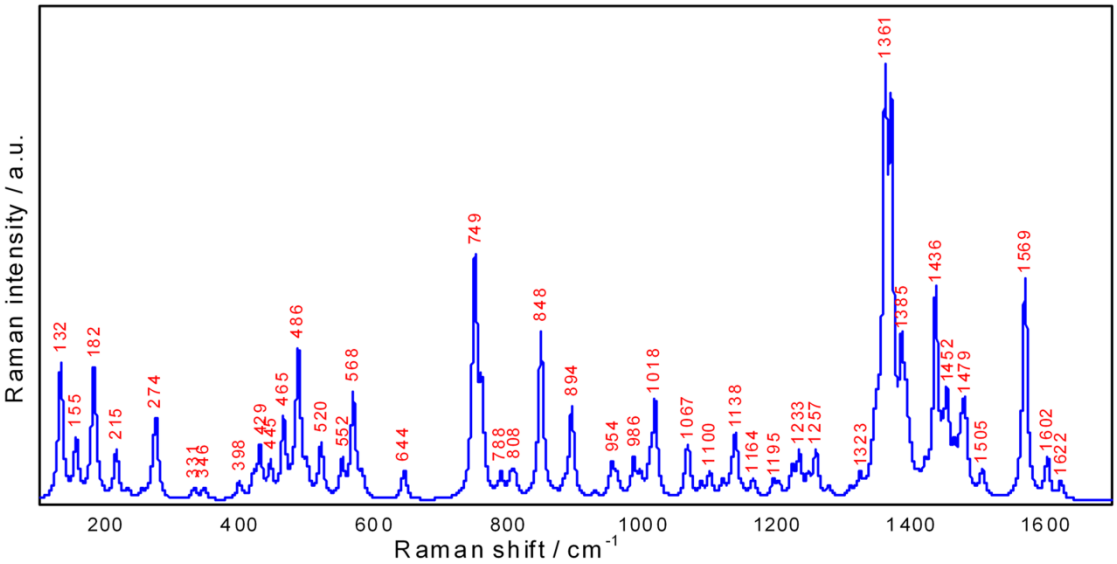

Figure SI-1. Calculated Raman spectrum of propranolol enantiomers – protonated form.

Table SI-1. Tentative assignment of vibrational bands occurring in all SER spectra based on DFT calculations.

SER spectra				Calculated Raman spectrum	
R, S-prnl on Ag colloid (cm^{-1})	R, S –prnl on Au colloid (cm^{-1})	R-prnl+βCD on Ag colloid (cm^{-1})	R-prnl+βCD on Au colloid (cm^{-1})	Calculated wavenumber (cm^{-1})	Assignments
		334		331	δ(NCC)+δ(COC)
		345		346	$\rho(CH_3)$+δ(CCC) methylethylamino chain
		434	423	429	out-of-plane deformation naphthyl+$\rho(CH_3)$
494	491			486	Symmetric longitudinal stretching - naphthyl
		518		520	δ(CCC) naphthyl + δ(CNC) methylethylamino chain
	622	622	621	641	out-of-plane deformation - naphthyl
	667	680	679	644	δ(CCC) naphthyl
737	736			749	naphthyl breathing
758	757			788	β(NH)+ δ(CNC)+$\nu(C\text{-}CH_3)$
789	789			788	out-of-plane deformation - naphthyl
	802			802	δ(CCC) naphthyl
		828		808	out-of-plane deformation - naphthyl
	869			848	$\rho(CH_3)+\rho(CH_2)$+β(NH)
		879		894	$\delta(C\text{-}(CH_3)_2)$
		912		928	$\rho(CH_2)$ methylethylamino chain
		937		954	$\rho(CH_3)$+β(CH) methylethylamino chain
	959			962	$\delta(C\text{-}(CH_3)_2)$
		982		986	ν(CN)+δ(CCC) naphthyl
1017	1018			1018	ν(CC)+ δ(CH)
1070	1068		1057	1067	δ(CCC) naphthyl +ν(CC) methylethylamino chain+$\rho(CH_3)$
1102	1098			1100	ν(CO)+ β(CH)+ δ(CCC)
	1159 1178	1168	1173	1164	ν(CN)+$\delta(C\text{-}(CH_3)_2)$ methylethylamino chain
		1203	1208	1203	δ(CCC) naphthyl +δ(CH)
1240	1240			1238	$\tau(CH_2)+\tau(NH_2)$+δ(CH) methylethylamino chain
1268	1273			1257	$\tau(CH_2)$+β(CH)+β(OH) methylethylamino chain
1296				1323	δ(CH) methylethylamino chain+$\omega(CH_2)$
1381	1382			1361	ν(CC) naphthyl+ δ(CH) +$\omega(CH_2)$
1440	1440			1436	δ(CH) naphthyl
1506	1503			1505	ν(CC)+$\delta(CH_2)$
1577	1573			1569	ν(CC)+β(CH) naphthyl

	1620	1616	1616	1602	ν(CC) naphthyl
			1671		$\delta(NH_2)$
ν – stretching, β – XH bending (X=C, N, O), *δ* – bending, *ρ* – rocking, *τ* – twisting, *ω* – wagging, *γ* – out of plane bending					

Table SI-2 Geometrical parameters characteristic for the geometry of R-βCD and S-βCD inclusion complexes (distances in Å, angles in degrees):

Geometrical parameter	βCD-R	βCD-S
distance[X_{CD}-C*]	5.829	6.522
angle[P_{mean}(CD),P_{mean}(naphthyl)]	76.8	27.1
distance[$X_{naphthyl}$-P_{mean}(CD)]	1.467	1.587
C*- chiral carbon of the enantiomer, X_{CD}-centroid defined by the oxygen atoms linking the glucopyranose units, P_{mean}(CD)-mean plane defined by the oxygen atoms linking the glucopyranose units, P_{mean}(naphthyl)-average plane of the naphthyl group, $X_{naphthyl}$-centroid of the naphthyl group		

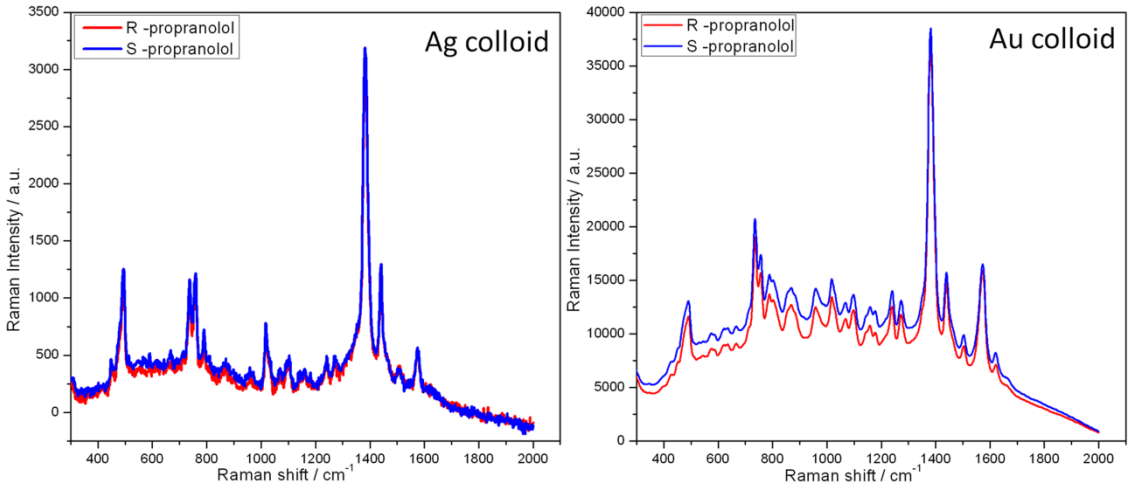

Figure SI-2. SER spectra of pure R- and S- propranolol on silver and gold colloids.

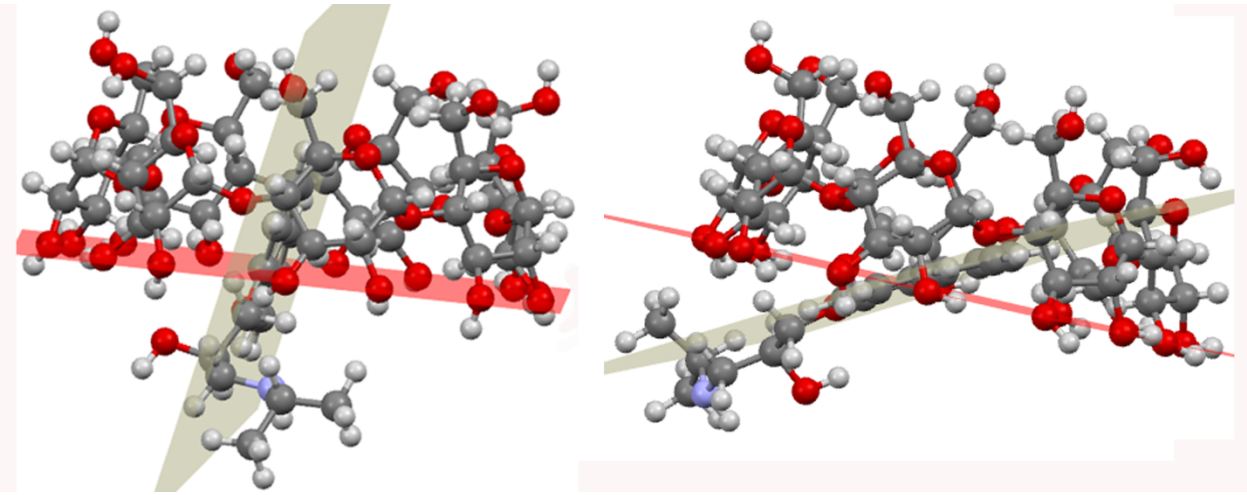

Figure SI-3. B3LYP-D/6-31G(d) optimized geometries of R-βCD and S-βCD complexes. The planes of naphthyl group of both propranolol enantiomers and of the oxygen atoms on the wider rim of βCD are highlighted with gray and red colors, respectively.

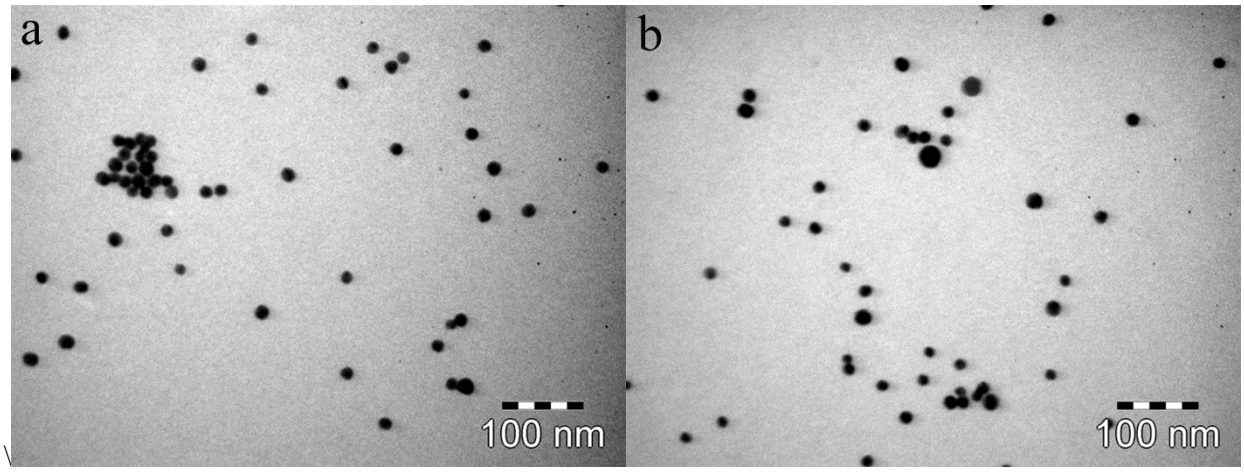

Figure SI-4. Large scale TEM images of silver (a) and gold (b) nanoparticles employed as SERS substrates.

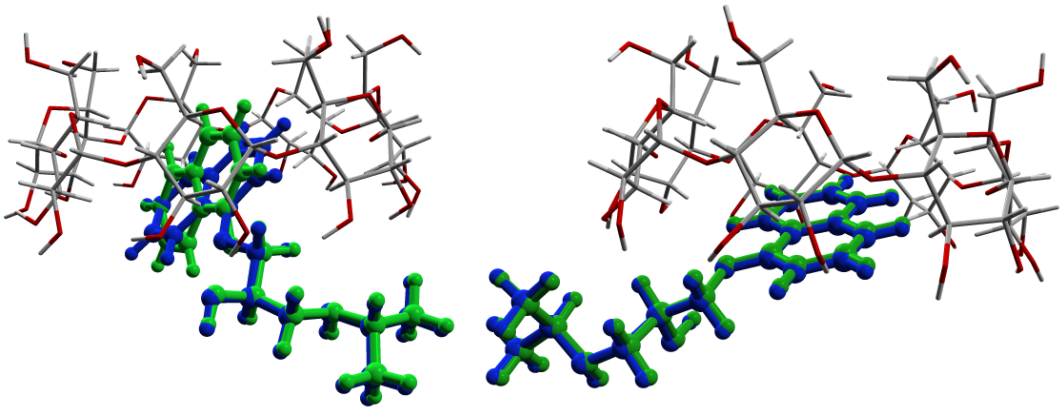

Figure SI-5 B3LYP-D/6-31G(d) (green color) and B97-D/6-31G(d) (blue color) optimized geometries of R- (left) and S- propranolol (right) inside the β-CD cavity.