Supporting Information

Raman and SERS Spectroscopy of Cucurbit[n]urils

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1 Peak frequencies for all CB[n]

The Raman frequencies for various peaks observed experimentally and calculated using Spartan ’08 (HF and scaled by a factor 0.9) are given below in Table S1.

Table S1. Raman frequencies (in cm^{-1}) for all CB[n]

CB[5]		CB[6]		CB[7]		CB[8]	
Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated
452	458	443	446	441	440	437	437
655	644	655	644	655	646	654	646
826	830	827	833	829	833	832	834
881	886	893	897	899	903	908	908
1378	1360	1383	1362	1378	1362	1380	1361
1419	1417	1417	1421	1421	1420	1424	1425
1745	1746	1742	1743	1745	1742	1745	1742

2 Movies of vibration modes

Movies of the 450, 830 and 880 cm^{-1} vibration modes of CB[5] obtained from Spartan'08 are included. The amplitude of the vibrations is exaggerated for clarity.

3 SERS spectra of CB[n] on Klarite™

SERS spectra were recorded using CB[n] solutions in 20% DCl in D_2O on Klarite™. Only 1 µl of their 1 mM solutions was placed on the SERS surface with a quartz cover glass on top. The spectrum of each of the CB[n] was easily recorded within 10 s at modest laser powers. Furthermore, the SERS effect is highly localized near surfaces and decays exponentially with increasing distance from a surface. Therefore, only those molecules which are on or near the SERS surface experience the enhancement effect. Thus, even after washing the excess solutions off the surface, the SERS spectra of the physisorbed CB[n] could be recorded with the peak intensities showing only a slight decrease of about 10%. It is noted that the SERS spectra show fewer peaks compared to the Raman spectra. This could be due to the imposition of additional surface selection rules in SERS. Moreover, CB[5] shows higher intensities of peaks than others indicating stronger adsorption on the surface and also slightly higher surface coverage due to its smaller size. We also observe that the SERS peaks are broader than their Raman counterparts, possibly due to weak interaction of molecular orbitals with the metal surface in the solution.

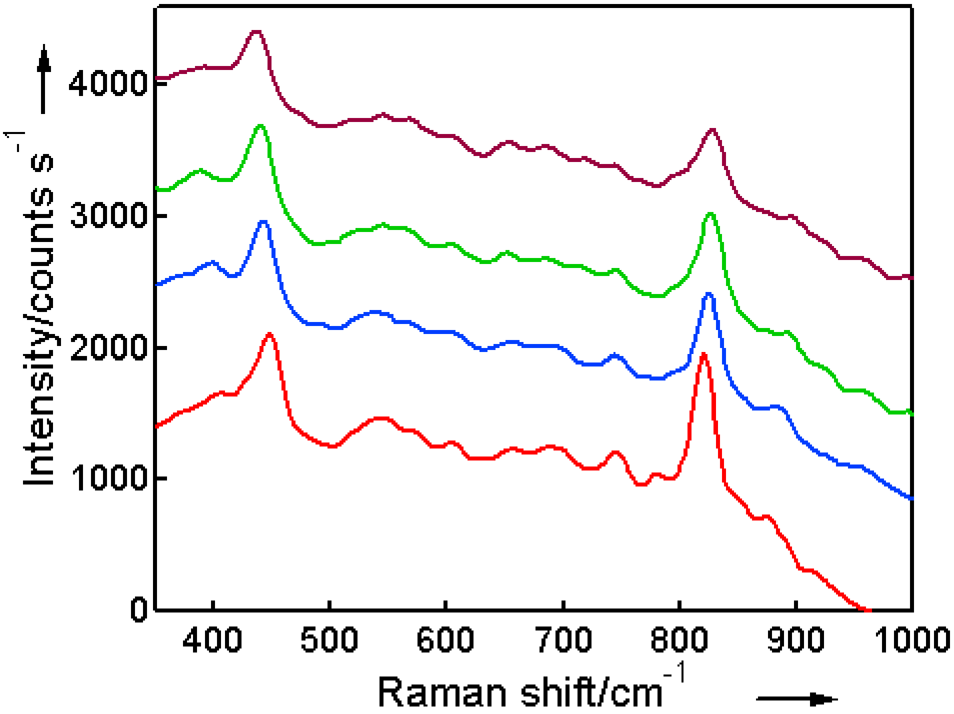

Fig. S1. SERS spectra of CB[n] solutions recorded on Klarite™. The spectra are: -- CB[5], -- CB[6], -- CB[7] and –CB[8]. Acquisition conditions: 785 nm excitation, single 10 s scan, laser power: 2.8 mW.

4 SERS with different CB[5] concentrations (detection limit)

The SERS peak intensities were found to depend on the concentrations. The figure below shows the dependence of the 450 cm^{-1} peak intensity with concentration. A 10 *ppb* level of CB[5] could be easily detected with SERS. A log dependence of the intensity of the CB[n] peaks is probably due to kinetics of the adsorption process. In the study by An *et al.* monolayers of CB[n] were formed on a gold surface by overnight soaking[1], however, here the process was undertaken over a few minutes.

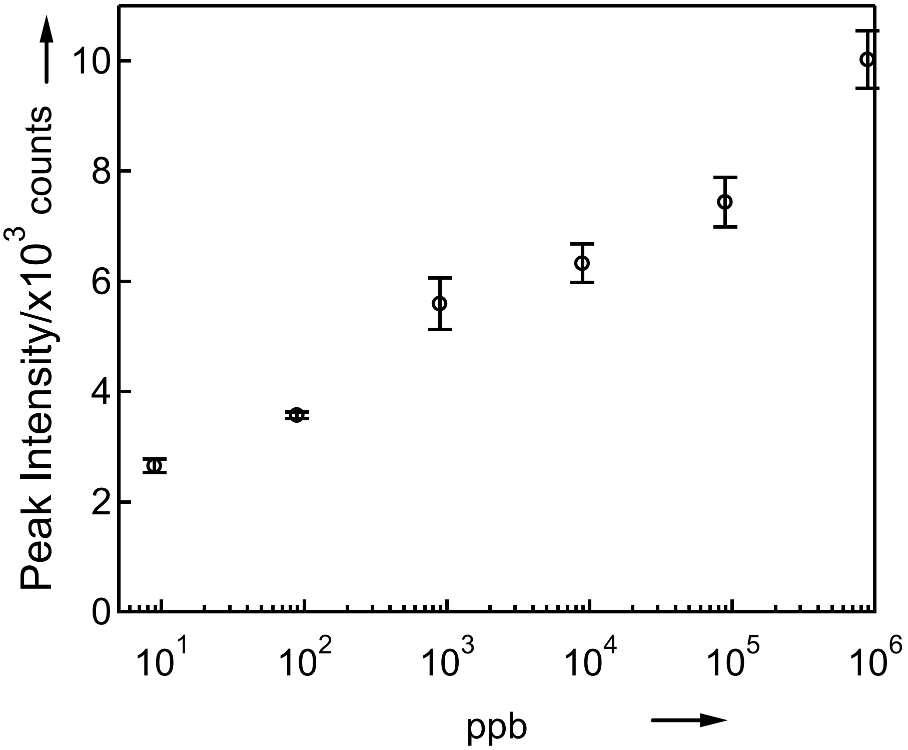

Fig. S2. SERS peak intensity with concentration. The SERS spectra were recorded on Klarite™ using 1 µl of each concentration. The solutions were prepared by serial dilution of 1 mM stock solution. Acquisition conditions: 785 nm excitation, laser power: 2.8 mW.

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[1] Q. An, G. Li, C. Tao, Y. Li, Y. Wu and W. Zhang, Chem. Commun., 2008.

5 Size of CB[n]-gold nanoparticle conjugates

The size of the different nanoparticle conjugates used in the paper for SERS were characterized with TEM. The mean sizes and standard deviation are given below in Table S2.

Table S2. Mean size of CB[n] gold nanoparticle of conjugates

Sample	**Mean size ± standard deviation / nm**
CB[5]-AuNPs	3.6 ± 1.0
CB[6]-AuNPs	8.5 ± 2.6
CB[7]-AuNPs	3.5 ± 1.1