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1. Experimental Raman and SERS Spectra

a)



Figure-SI 1: a) Showcase overlay of a Raman spectrum for ligand a) L^1 in acetonitrile and b) L^2 in acetone and a spectrum of the correspondent solvent. The "derivative" like bands in the analyte spectrum have their origin in the subtraction of the solvent bands. For further investigation we have set our focus on the parts of the spectrum with a minimal superimposition (marked by grey boxes).



Figure-SI 2: SERS spectra of deposition of the substrate a) ligand L^1 and b) double cage $[3BF_4@Pd_4L_8](BF_4)_5$ on a nanostructured and on an flat gold surface showing an enhancement of the signals when the nanostructured Au surface is used. Recording time was 10 s.



Figure-SI 3: Experimental Raman spectra in solution (acetone) and of a solid for the ligand L^2 and SERS spectra on an Au coated surface in the ranges of 1000-1200 cm⁻¹, 1480-1680 cm⁻¹ and 2100-2300 cm⁻¹. The auxiliary dashed lines are referenced to the middle spectrum. * denotes the residual signal arising from solvent subtraction.



Figure-SI 4: Experimental Raman spectra in solution (acetone) and of a solid for the double cage $[3BF_4@Pd_4L_8](BF_4)_5$ and SERS spectra on an Au coated surface in the ranges of 1000-1200 cm⁻¹, 1480-1680 cm⁻¹ and 2100-2300 cm⁻¹. The auxiliary dashed lines are referenced to the middle spectrum. * denotes the residual signal arising from solvent subtraction.



Figure-SI 5: Comparison between the experimental Raman spectra in solution (acetone) of the ligands L^n and their corresponding double cages $[3BF_4@Pd_4L^n_8](BF_4)_5$ with a) n = 1, b) n= 2 and c) n=3 and SERS spectra on an Au coated surface in the ranges of 1000-1200 cm⁻¹, 1480-1680 cm⁻¹ and 2100-2300 cm⁻¹. * denotes the residual signal arising from solvent subtraction.



Figure-SI 6: Experimental Raman spectra in solution (acetone) of the ligands L^{1-3} and SERS spectra on an Au coated surface in the ranges of 1000-1200 cm⁻¹, 1480-1680 cm⁻¹ and 2100-2300 cm⁻¹. The auxiliary dashed lines are referenced to the spectrum of ligand L^2 . * denotes the residual signal arising from solvent subtraction.



Figure-SI 7: Experimental Raman spectra in solution (acetone) of the self-assembled cages $[3BF_4@Pd_4L^n_3](BF_4)_5$ with n = 1-3 and SERS spectra on an Au coated surface in the ranges of 1000-1200 cm⁻¹, 1480-1680 cm⁻¹ and 2100-2300 cm⁻¹. The auxiliary dashed lines are referenced to the spectrum of ligand $[3BF_4@Pd_4L^2_3](BF_4)_5$. * denotes the residual signal arising from solvent subtraction.

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		449 w		441 w		527 vw						668 vw
		602 w		600 w		600 w		599 w		692 vw		691 vw
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Experimental intensity description: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder.

^a This work.



2. Calculated vibrational spectra for the ligands Lⁿ with n =1-3

Figure-SI 8: Calculated vibrational modes with the highest intensity for the ligand L^1 .



Figure-SI 9: Calculated vibrational modes with the highest intensity for the ligand L^2 with the oxygen in axial position.



Figure-SI 10: Calculated vibrational modes with the highest intensity for the ligand L^3 .



Figure-SI 11: Scaling methods for the calculated spectrum of the ligand $\boldsymbol{L}^{\! 1}$.



Figure-SI 12: Calculated vibrational spectra using a solvent (acetonitrile) and in vacuum for the ligand L^1 vs. experimental spectra in solution (acetonitrile and acetone) and on Au surface (SERS). The range 200-1800 cm⁻¹ of the calculated spectra was enlarged by a factor of 4.4.



Figure-SI 13: Calculated vibrational spectra using a solvent (acetonitrile) and in vacuum for the ligand L^2 with variation of the oxygen position vs. experimental spectra in solution (acetone) and on Au surface (SERS). The range 200-1800 cm⁻¹ of the calculated spectra was enlarged by a factor of 4.2 for the oxygen in axial position and 4.5 for equatorial position.



Figure-SI 14: Calculated vibrational spectra using a solvent (acetonitrile) and in vacuum for the ligand L^3 vs. experimental spectra in solution (acetone) and on Au surface (SERS). The range 200-1800 cm⁻¹ of the calculated spectra was enlarged by a factor of 4.1.



3. Calculated vibrational spectra for the cages [3BF₄@Pd₄Lⁿ₈](BF₄)₅ with n =1-3

Figure-SI 15: Calculated vibrational spectra using different approaches such as i) defined distance between the pyridine atoms (abbr. constraints), ii) protonation of the ligand at the pyridine arms, iii) combination of defined distance and protonation, iv) protonation and solvation (acetonitrile), v) combination of defined distance, protonation and solvation, vi) a model of a monomeric cage $[Pd_2L_4^1]$ and vii) a model of a monomeric cage $[Pd_2L_4^1]$ and vii) a model of a monomeric cage $[Pd_2L_4^1]$ with a C4 symmetry as a simplified model for the double cage $[3BF_4@Pd_4L_8^1](BF_4)_5$ vs. experimental spectra in solution (acetonitrile and acetone) and in solid state (SERS).



Figure-SI 16: Calculated vibrational spectra using different approaches such as i) defined distance between the pyridine atoms (abbr. constraints), ii) protonation of the ligand at the pyridine arms, iii) combination of defined distance and protonation, iv) protonation and solvation (acetonitrile), v) combination of defined distance, protonation and solvation as a simplified model for the double cage $[3BF_4@Pd_4L^2_8](BF_4)_5$ vs. experimental spectra in solution (acetone) and in solid state (SERS). The calculations were done for two possible positions of the oxygen atom (equatorial and axial orientation).



Figure-SI 17: Calculated vibrational spectra using different approaches such as i) protonation of the ligand at the pyridine arm, ii) combination of protonation and solvation (acetonitrile), iii) defined distance between the pyridine atoms (abbr. constraints) and iv) combination of defined distance and protonation as a simplified model for the double cage $[3BF_4@Pd_4L^3_8](BF_4)_5 vs.$ experimental spectra in solution (acetone) and in solid state (SERS).



Figure-SI 18: Calculated vibrational spectra using different solvation models¹ for the ligands L^n with n = 1, 2 (O = axial) and 3. CPCM (conductor polarizable continuum model)² and the IEFPCM (integral equation formalism polarizable continuum model)³.

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³ G. Scalmani and M. J. Frisch, "Continuous surface charge polarizable continuum models of solvation. I. General formalism," *J. Chem. Phys.*, 2010, **132**, 114110.