

## Elucidation of the Bonding of a Near Infrared Dye to Hollow Gold Nanospheres – A Chalcogen Tripod

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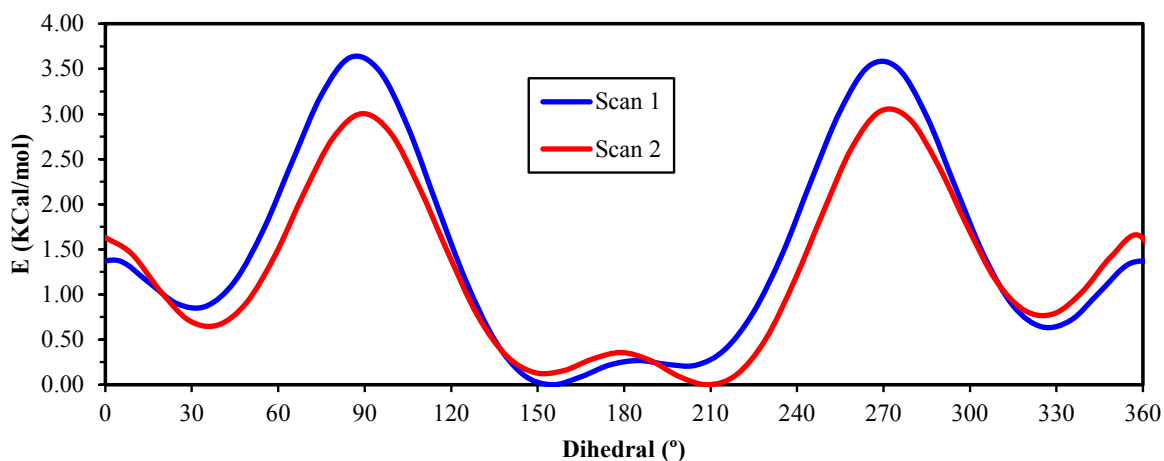
**Table S1.** Assignment of main bands ( $\text{cm}^{-1}$ ) in the resonance and SERS spectra using the corrected calculation.

Theor. Raman	Expt Raman 785 nm	SERS FT-1064 nm	SERS 1280 nm	Assignments for Dye 1
416; 424 (doublet)	415 (br) 428; 410 (sh)- 633 nm	415	416	416; Out of plane rocking movement on bridge with some selenophene 3 & 4 movement 424: Stretch of S-containing rings (C-S), (C=C), (C-H) with rocking movement on bridge (C=C), (C-H)
464; 486 (w)	472	479	478	Stretch of S-containing rings (C-S), (C=C), (C-H) and all four selenophene rings (C-Se), (C=C), (C-H) (486– selenophene rings 1 & 2)
497; 536 (w)	500 (633nm-w)	527	523	Elongation of all four selenophene rings (C-Se), (C=C), (C-H) with bending of S-containing rings (C-S), (C=C), (C-H) – out of plane (497 – selenophene rings 3 & 4)
581	568	565	559	Rocking movement on bridge (C=C), (C-H) - out of plane
607 (w)	619	620	616	Extended vibration in core (C=C), (C-H) with elongation in S-containing rings (C-S), (C=C), (C-H)
628	642	636	638 (sh)	Rocking movement on selenophene rings 1 & 3 (C-Se), (C=C), (C-H)
710	735	732	728	S-containing ring breathing mode (C-S), (C=C), (C-H); extended to selenophene rings (C-Se), (C=C), (C-H)
969 (w)	965(633nm-w)	971	965	selenophene rings (C=C), (C-H)
1041	1044	1044	1044	selenophene rings 3 & 4 (C-Se), (C=C), (C-H)
1073	1078	1073	1071	(C-H) bending in selenophene rings with rocking movement throughout bridge, core (C=C), (C-H) and Se rings (C=C)
1155; 1204	1180 (br)	1179 (br) 1223 (sh)	1177 (br)	Core (C=C), (C-H) with extension through bridge (C=C) into selenophene rings (C-

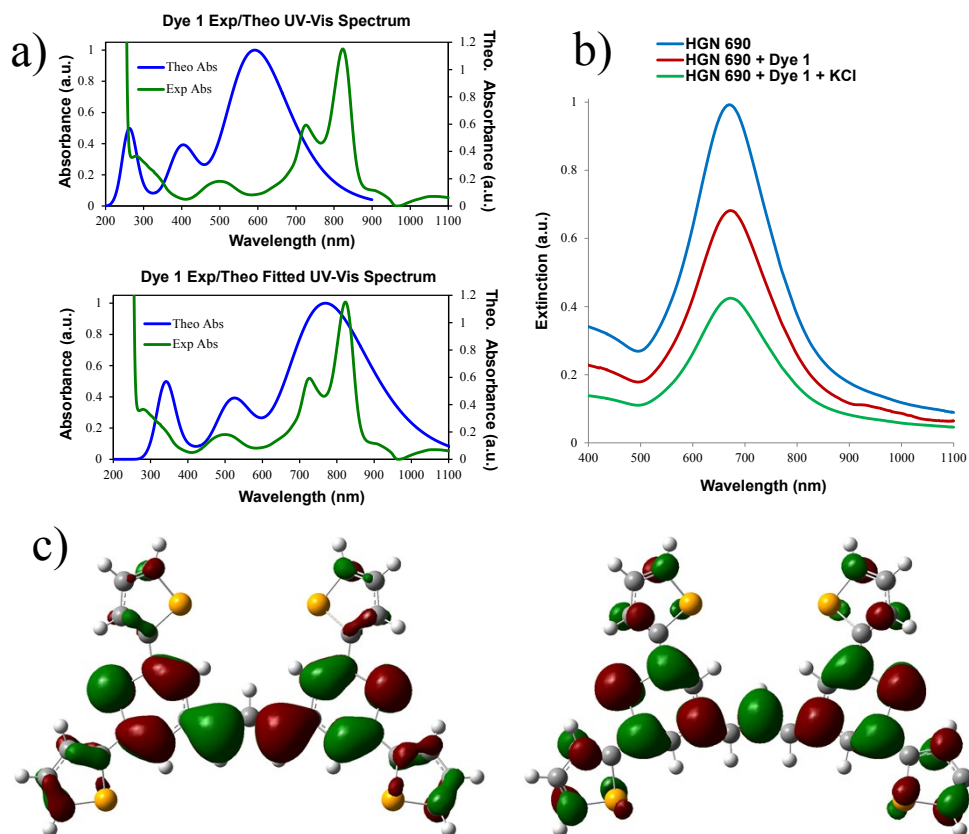
			1200 (sh)	Se), (C=C), (C-H)
1263; 1288	1246 1297	1287	1265(sh) 1288	Bridge (C=C) to selenophene rings 2 & 4 with less movement in selenophene 1 (C-Se), (C=C), (C-H)
1362 (w)	1360 (w)	1370	1372	Core (C=C), (C-H) extending to (C=C) bridge to selenophene rings 3 & 4 (C-Se), (C-H)
1416	1425; 1417 (sh)	1425	1423	selenophene ring (C-Se), (C=C), (C-H) to S-containing ring movement (C-S), (C=C), (C-H) (mainly selenophene 1 & 2) and core (C=C)
1470;	1487	1489	1485	Core (C=C), (C-H) and S-containing rings (C-S), (C=C), (C-H) with extension to selenophene rings (C-Se), (C=C), (C-H)
1500; 1518	1507; 1535	1530 (sh)	1526 (w)	Core (C=C), (C-H) and selenophene rings (C-Se), (C=C), (C-H); (1518 – selenophene rings 3 & 4; 1500 – selenophene rings 1 & 2)
1588	1595	1588	1587	Core (C=C), (C-H) and S-containing rings (C-S), (C=C), (C-H)

sh = shoulder; br = broad; w=weak

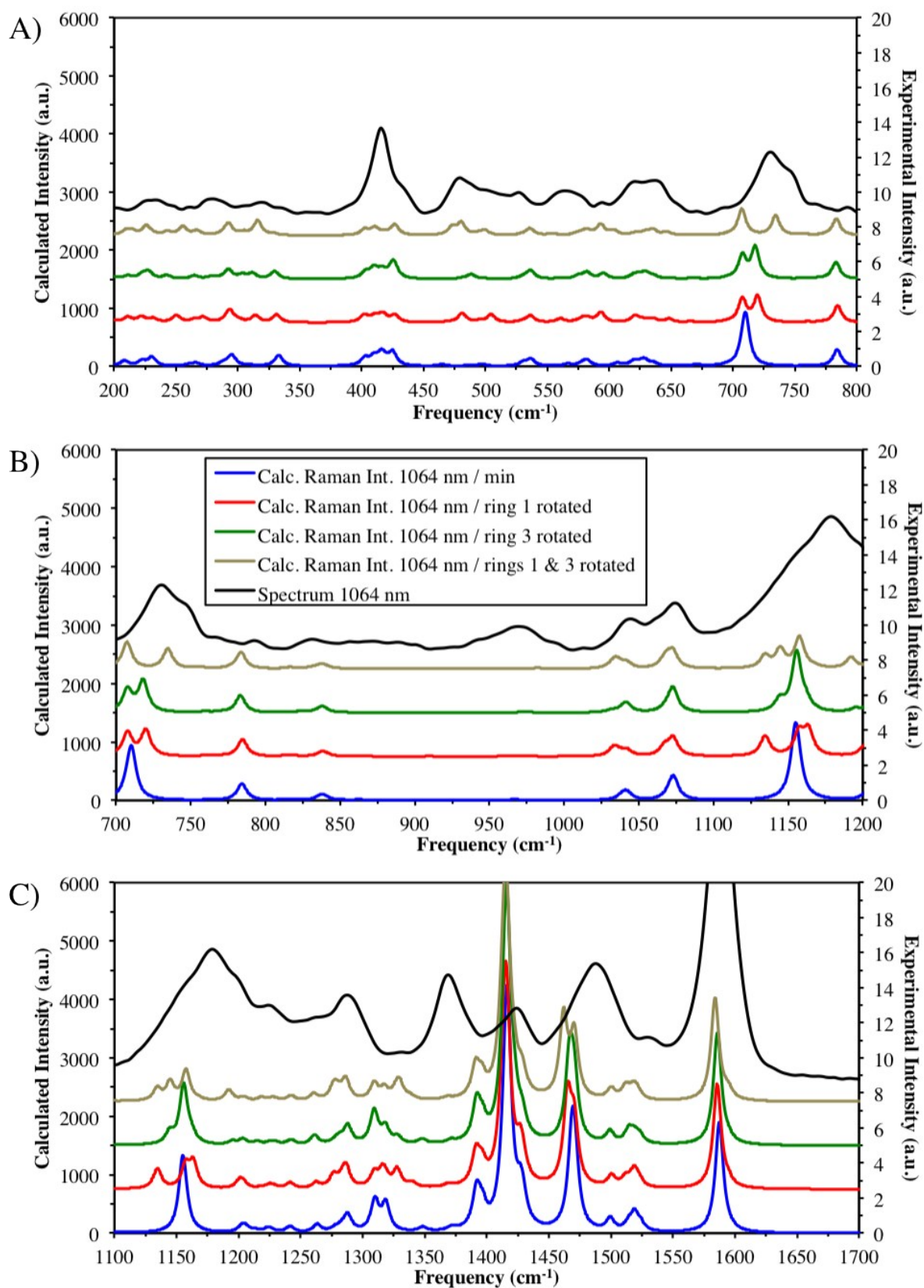
## Torsions



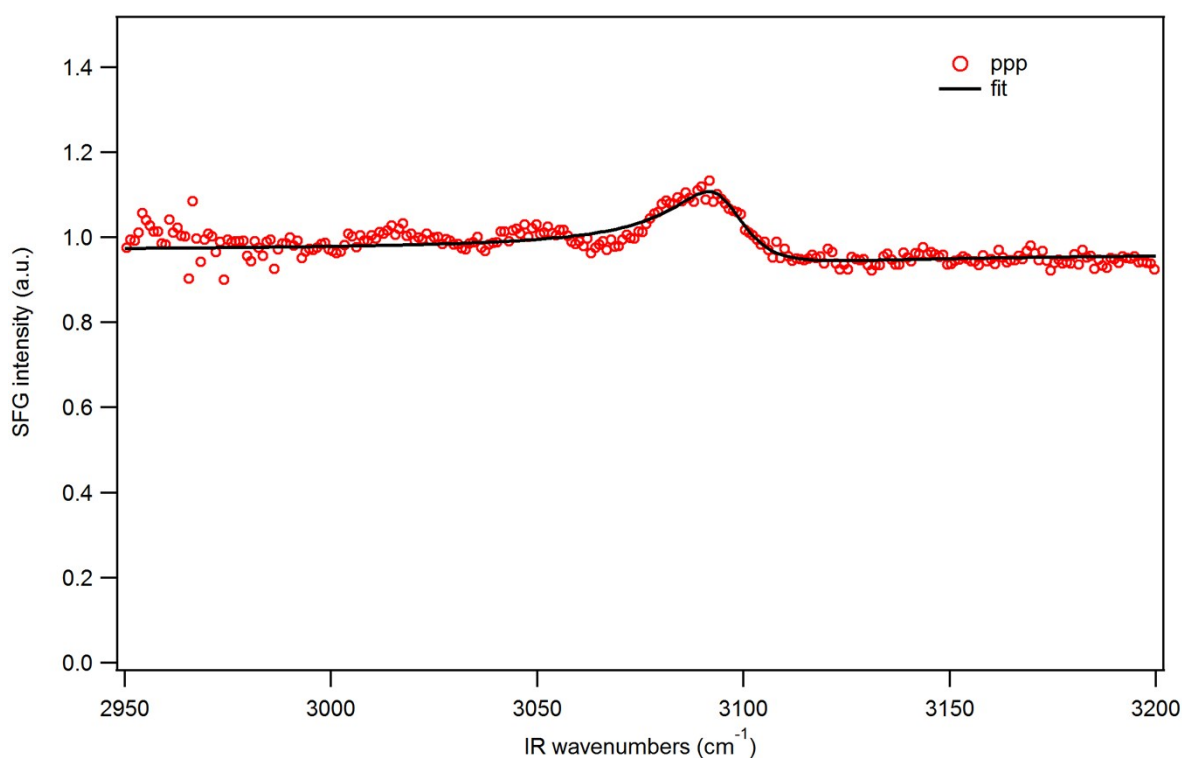
**Figure S1.** Torsion angles demonstrating the barriers to rotation of the rings is ~4 kcal. Scan 1 = Se - C - C - S; scan 2 = Se - C - C - S.



**Figure S2.** a) Calculated (blue) and experimental (green) spectra for dye **1** b) extinction spectrum for the HGN alone, with dye **1** added and with the labelled HGN aggregated c) electron density of the  $\pi$  (left) and  $\pi^*$  (right) orbitals which give rise to the 826 nm band in a) and b).



**Figure S3.** Expanded theoretical and experimental 1064-nm Raman spectra.



**Figure S4.** A single weak spectral feature in the ppp SFG spectrum is observed at 3098  $\text{cm}^{-1}$  and attributed to the various C-H stretches of dye-1.

**Table S2. Refractive index of gold and the interface**

refractive index	Gold <sup>1</sup>	n' (interface) <sup>2,3</sup>
IR at 1600 $\text{cm}^{-1}$	$4.599 + 42.577i$	1.7-2
visible at 694 nm	$0.135 + 4.070 i$	1.7-2
SFG at 625 nm	$0.167 + 3.475 i$	1.7-2

## References

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