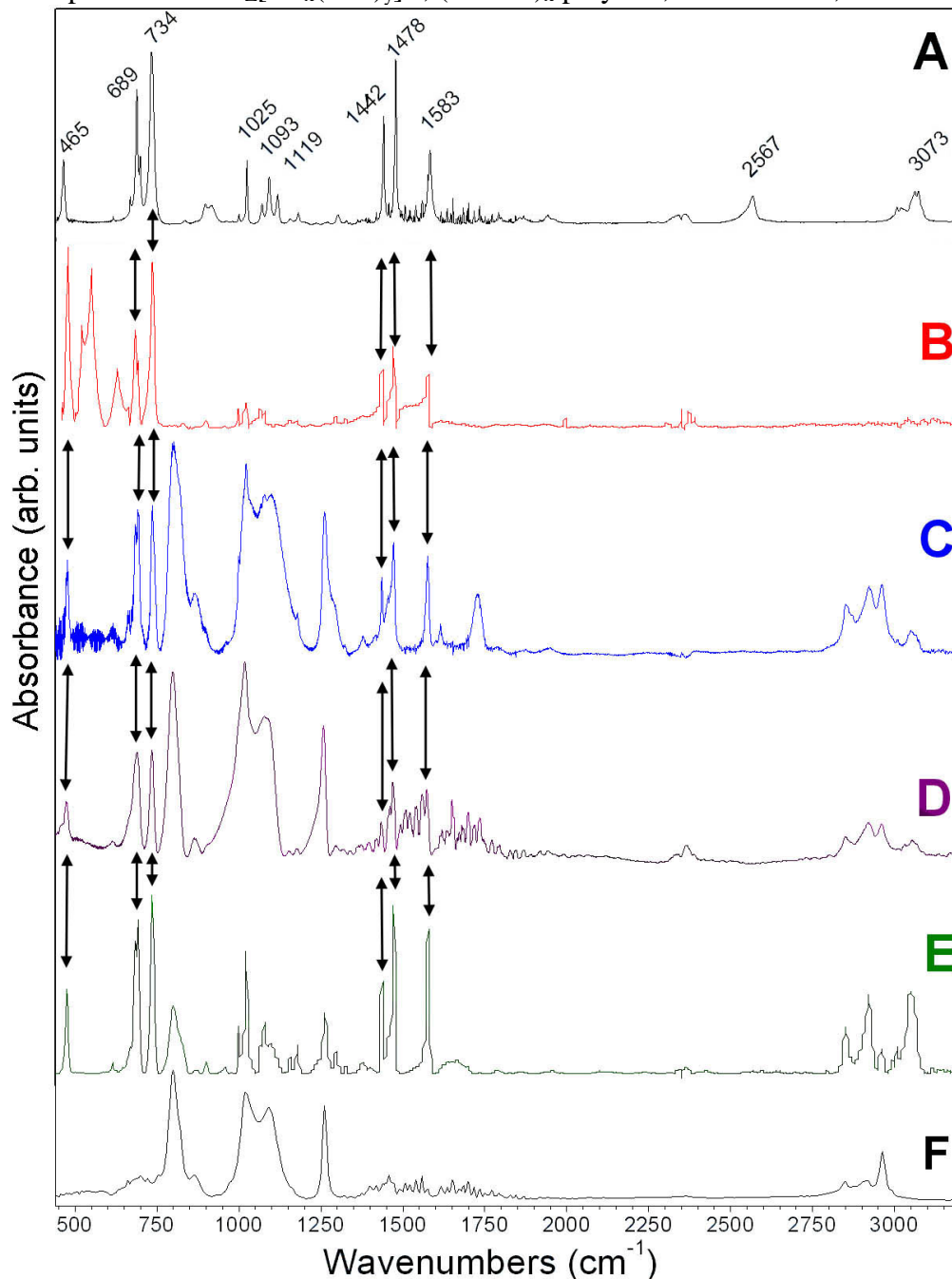
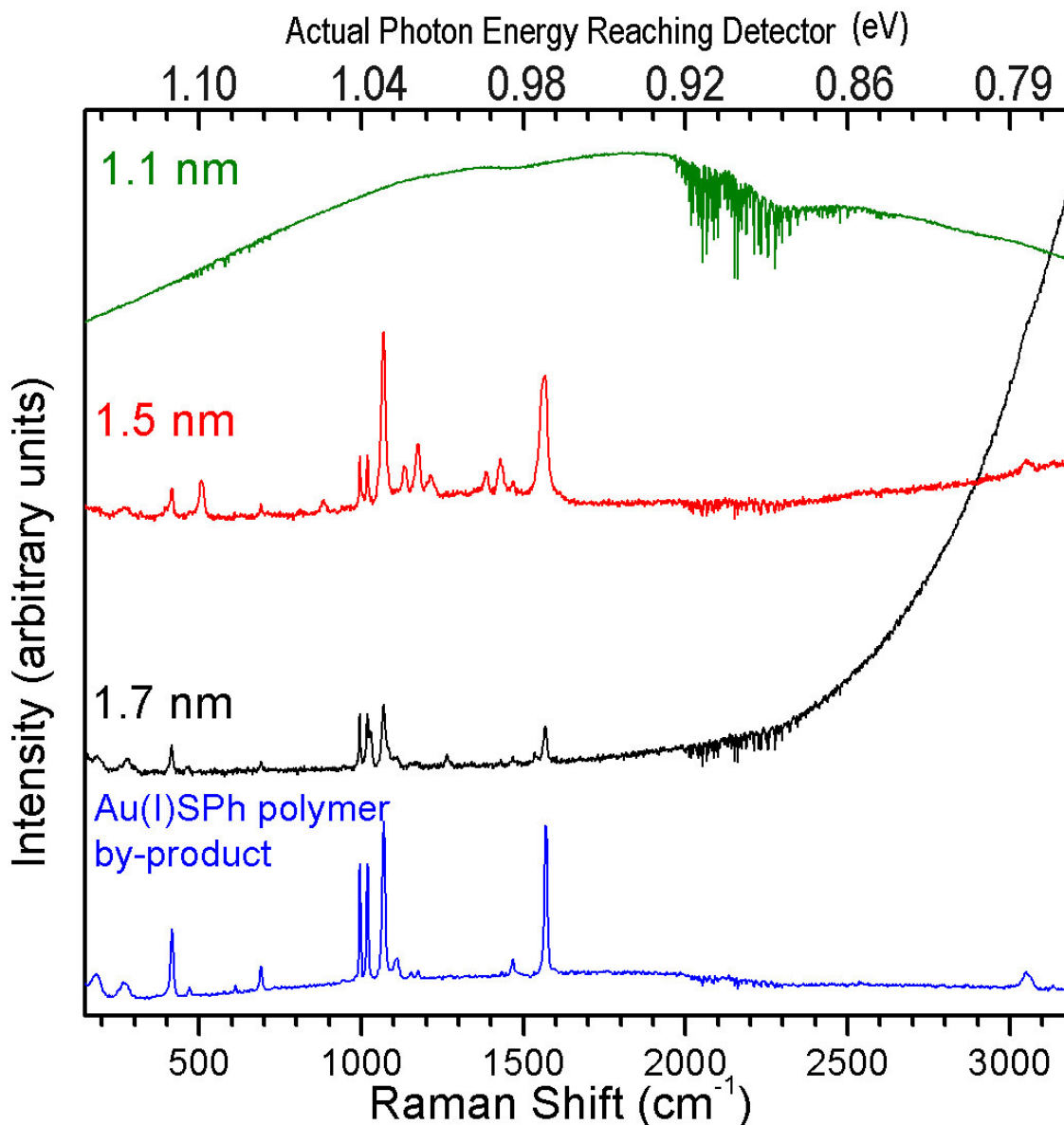


FTIR Spectra of $\text{TOA}_Z[\text{Au}_x(\text{SPh})_y]^{Z-}$, $(\text{AuSPh})_x$ polymer, benzenethiol, and TOABr



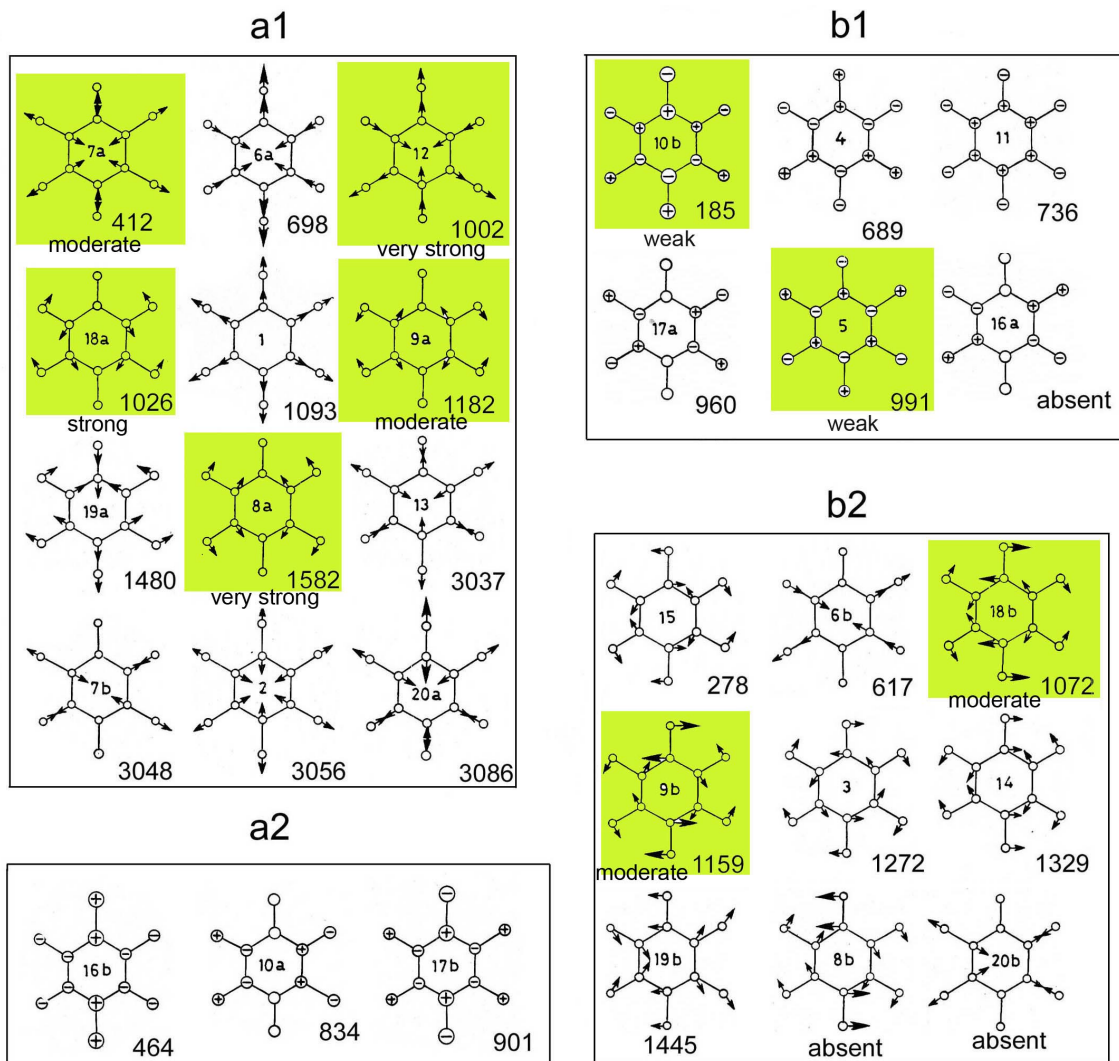
FTIR spectra of (A) Benzenethiol (B) $(\text{AuSPh})_x$ (C) 1.5 nm $\sim[\text{TOA}]_6[\text{Au}_{140}(\text{SPh})_{62}]$ (D) 1.7 nm $\sim[\text{TOA}]_3[\text{Au}_{140}(\text{SPh})_{78}]$ (E) $[\text{TOA}]_2[\text{Au}_{44}(\text{SPh})_{28}]$ and (F) TOABr. Arrows indicate the shared spectral features between the benzenethiolate containing species. Spectra were prepared as dry, thin, optically translucent films deposited on a KBr disk from toluene. A Nicolet 520 FT-IR spectrometer at a resolution of 2 cm^{-1} over 128 scans with background subtraction and slope correction was utilized for these spectra.

Full Raman Spectra for $\text{Au}_x(\text{Benzenethiolate})_y$ MPCs.

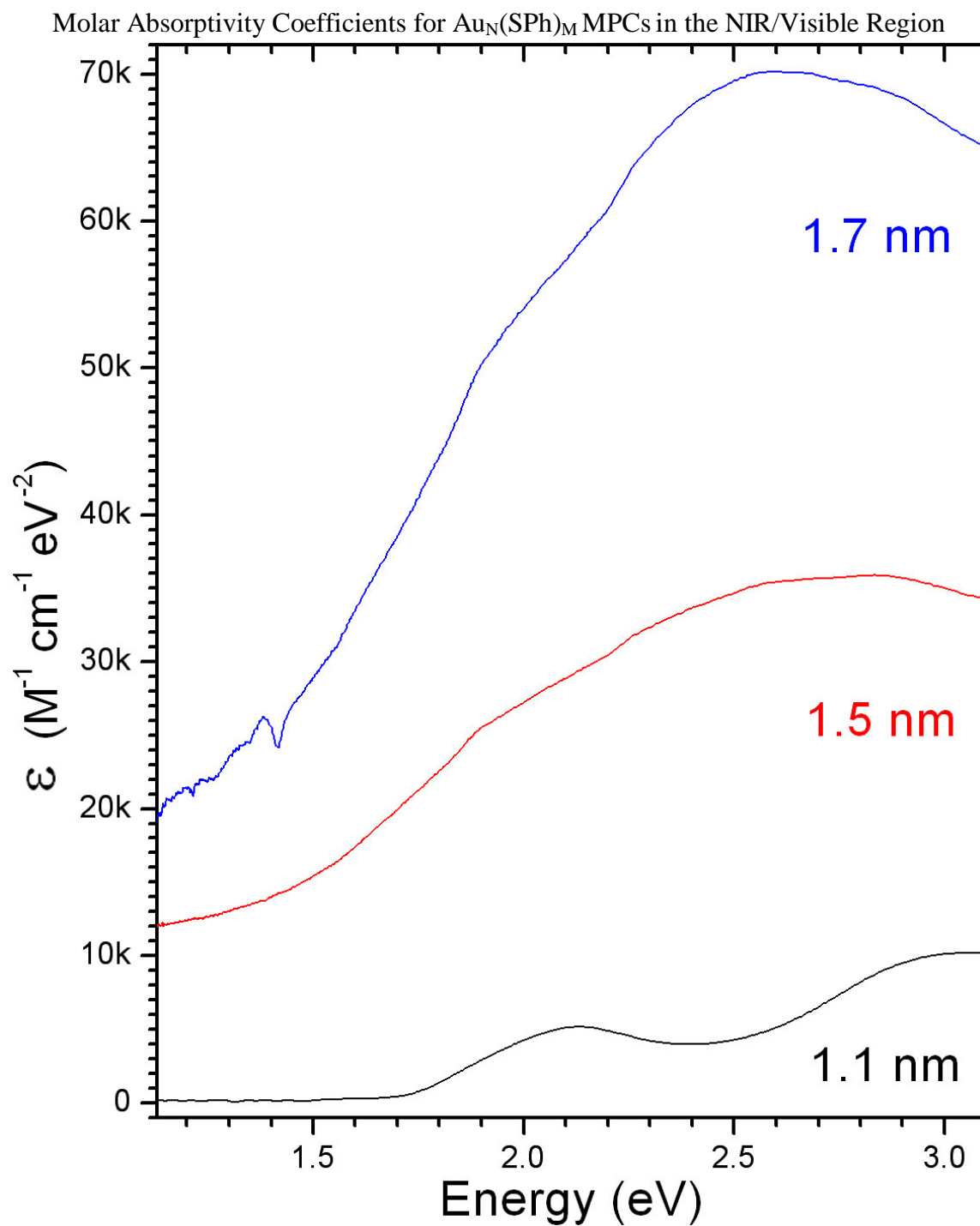


Full Raman spectra of Stokes region for $\text{Au}_N(\text{SPh})_M$ MPCs and $(\text{Au}:\text{SPh})_x$ polymer. Only fluorescence was observed in the high optical bandgap (~ 1.6 eV) 1.1 nm clusters. It is quite possible that this strong emission is merely obscuring the spectral features intrinsic to benzenethiolate. We were unable to find conditions to disfavor fluorescence, as the lowest power setting obtainable on the instrument was 10 mW.

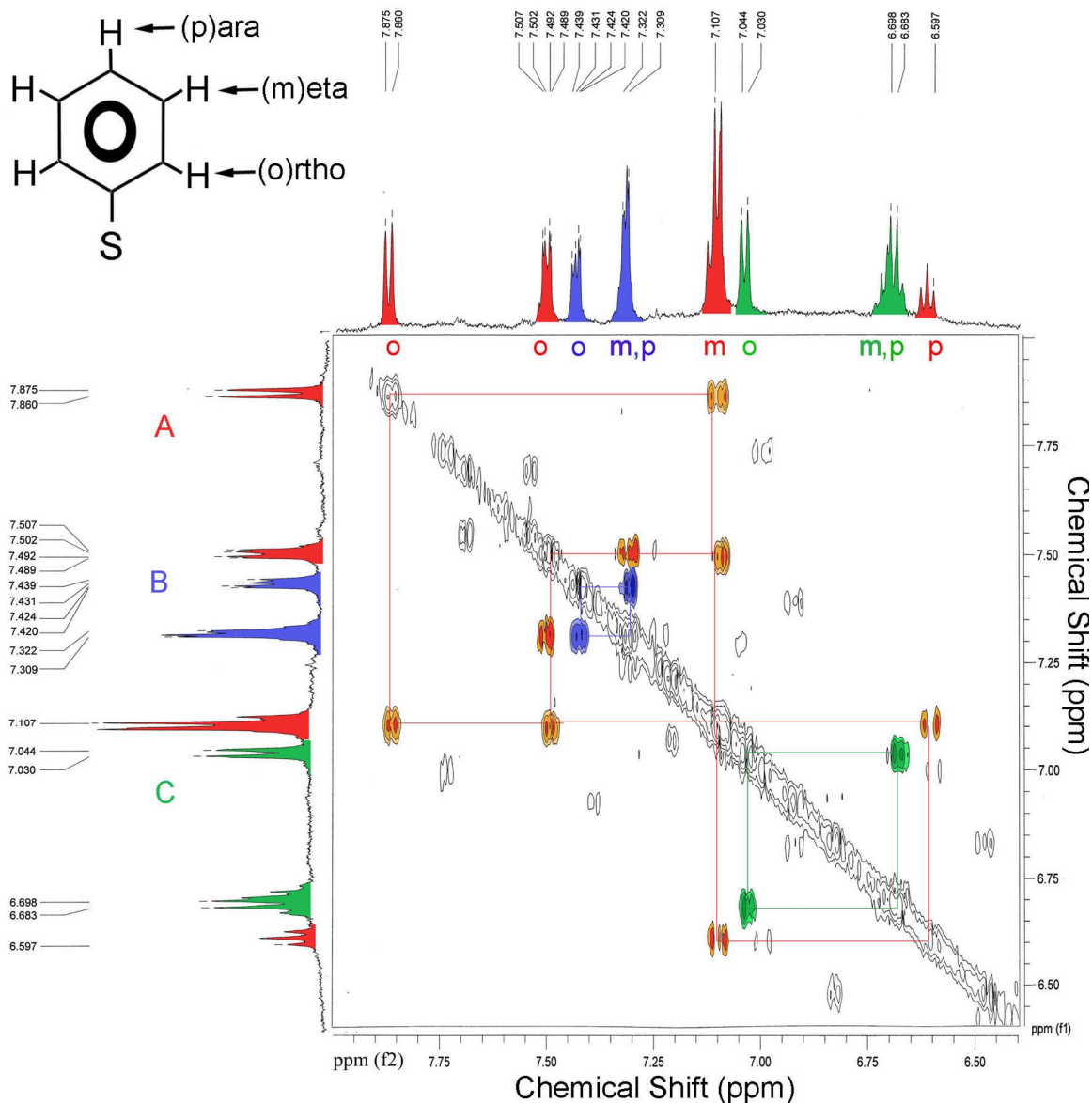
Benzenethiol Vibrational Modes



Dominant vibrational modes observed are highlighted in yellow with expected relative intensities for benzenethiol. Image adapted from Varsanyi, G. *Assignments for Vibrational Spectra of 700 Benzene Derivatives Vol. 1*, John Wiley & Sons, New York (1974)



Molar absorptivity coefficients shown are from 1.1 eV (1100 nm) to 3.1 eV (400 nm).

2-D COSY ^1H -NMR of $[\text{Au}_{44}(\text{SPh})_{28}]^{2-}$ 

Three distinct binding modes are evident from this spectrum, labeled A, B and C. Peak area integration estimates the benzenethiolates corresponding to each binding mode as follows: **A-14**, **B-7**, **C-7**.