

Determine the Ni–Ni Bonding Strength in Metal-String Complexes Using Head-to-Head Nanorods and Electrochemical Surface Enhanced Raman Spectroscopy

Bo-Han Wu,^a Li-Yen Hung,^a Jheng-Yang Chung,^a Shie-Ming Peng,^b I-Chia Chen^{a*}

^aDepartment of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan, Republic of China

^bDepartment of Chemistry, National Taiwan University, Taipei, 106, Taiwan, Republic of China

Table of Contents

1. Figure S1: Full SERS Spectra of (a) AuNR(CTAC), (b) AuNR(CTAB), (c) AuNS(CTAB), and (d) AuNS(citrate) Ni ₃ (dpa) ₄ (NCS) ₂ in solution and (e) full Raman spectrum of Ni ₃ (dpa) ₄ (NCS) ₂ in solid crystals. Asterisk denotes bands from acetonitrile.....	S2
2. Figure S2: Cyclic voltammogram of (a) Ni ₃ (dpa) ₄ (NCS) ₂ and (b) Ni ₃ (dpa) ₄ Cl ₂	S2
3. Figure S3: ECSERS spectra of Ni ₃ (dpa) ₄ (NCS) ₂	S3
4. Figure S4: (a) Solid-state Raman, (b) ECSERS at +1.3 V, and (c) AuNP SERS of Ni ₃ (dpa) ₄ Cl ₂	S4
5. Figure S5: Absorption spectra of Ni ₃ (dpa) ₄ Cl ₂ with varied applied voltages	S5
6. Figure S6: SEM image of AuNR(CTAB) with Ni ₃ (dpa) ₄ (NCS) ₂	S5
7. Figure S7: SERS of Ni ₃ (dpa) ₄ (NCS) ₂ in (a) AuNR(CTAC) and (b) AuNR(CTAB)	S6
8. Figure S8. Full Raman spectra of (a) [Ni ₂ (TPG) ₄]BF ₄ , (b) Ni ₂ (TPG) ₄ , and (c) HTPG	S7

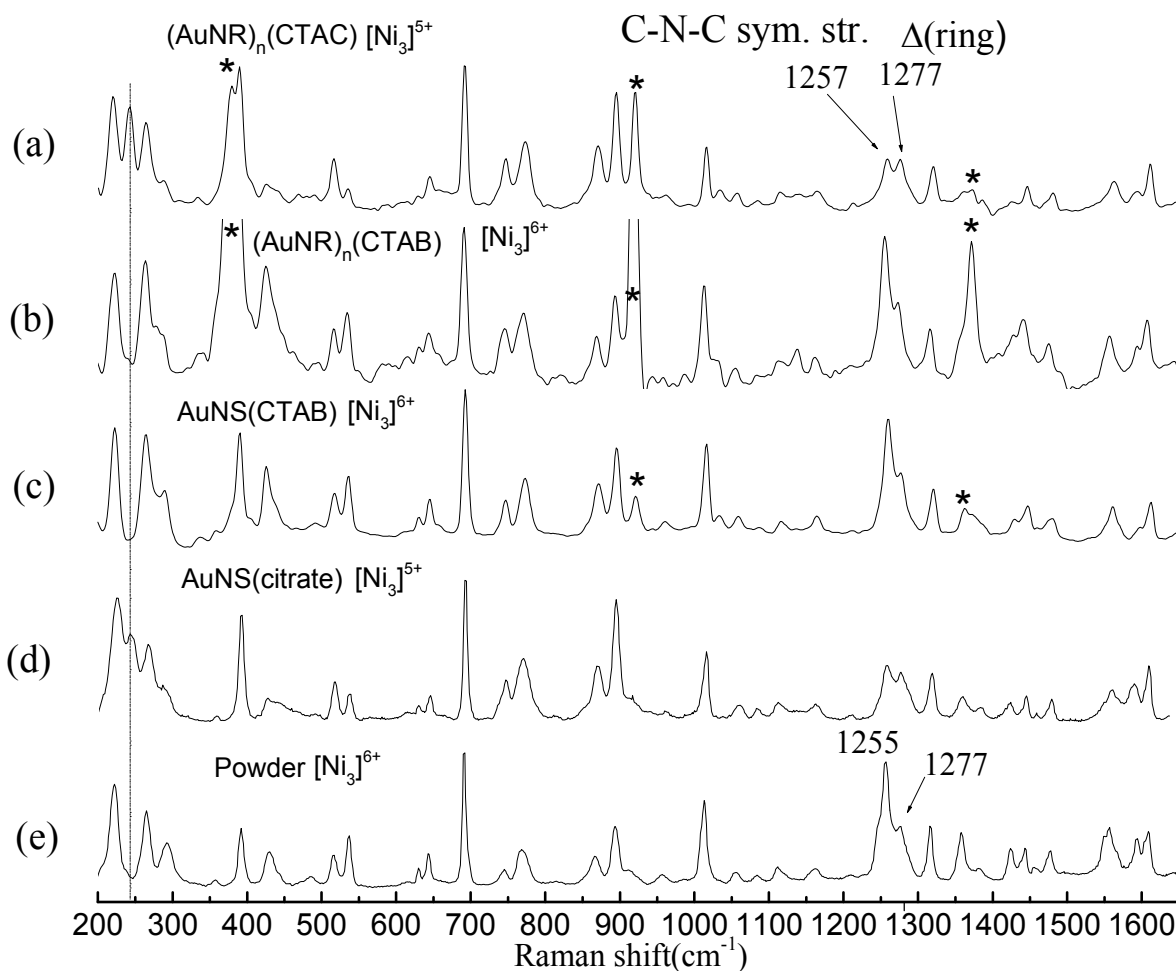


Figure S1. Full SERS Spectra of (a) AuNR(CTAC), (b) AuNR(CTAB), (c) AuNS(CTAB) and (d) AuNS(citrate) $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$ in solution and (e) full Raman spectrum of $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$ in solid crystals. Asterisk denotes band from acetonitrile.

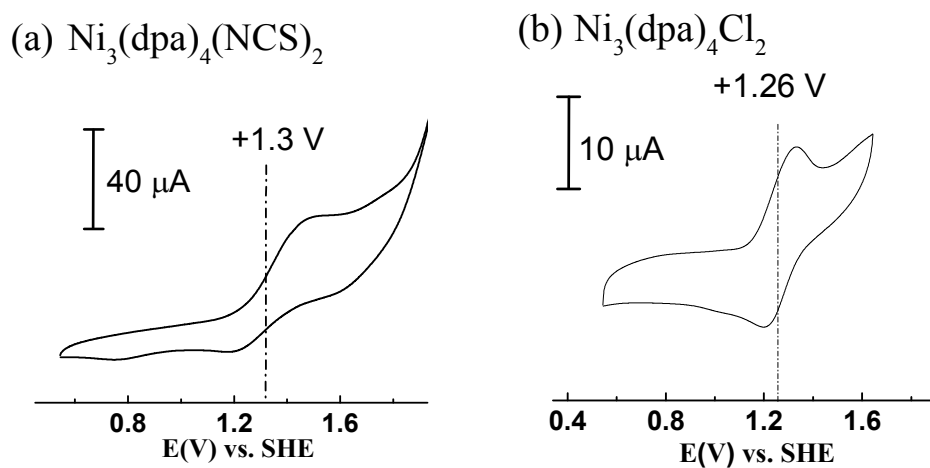


Figure S2. Cyclic voltammogram of (a) $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$ and (b) $\text{Ni}_3(\text{dpa})_4\text{Cl}_2$ adsorbed on AuNPs in 0.1 M TBAP/DCM.

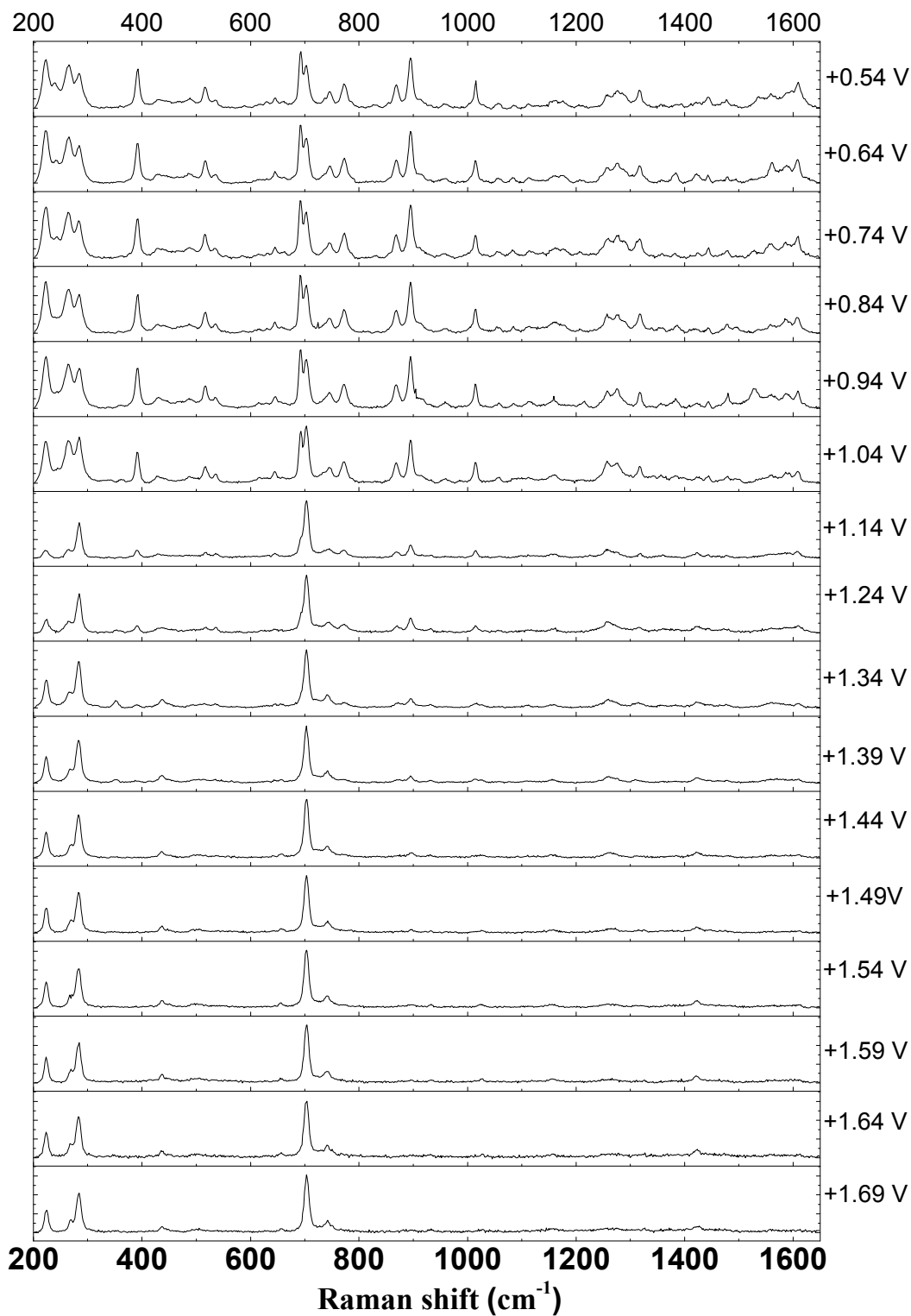


Figure S3. Full ECSERS spectra of $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$ from 0.54 V– +1.69 V.

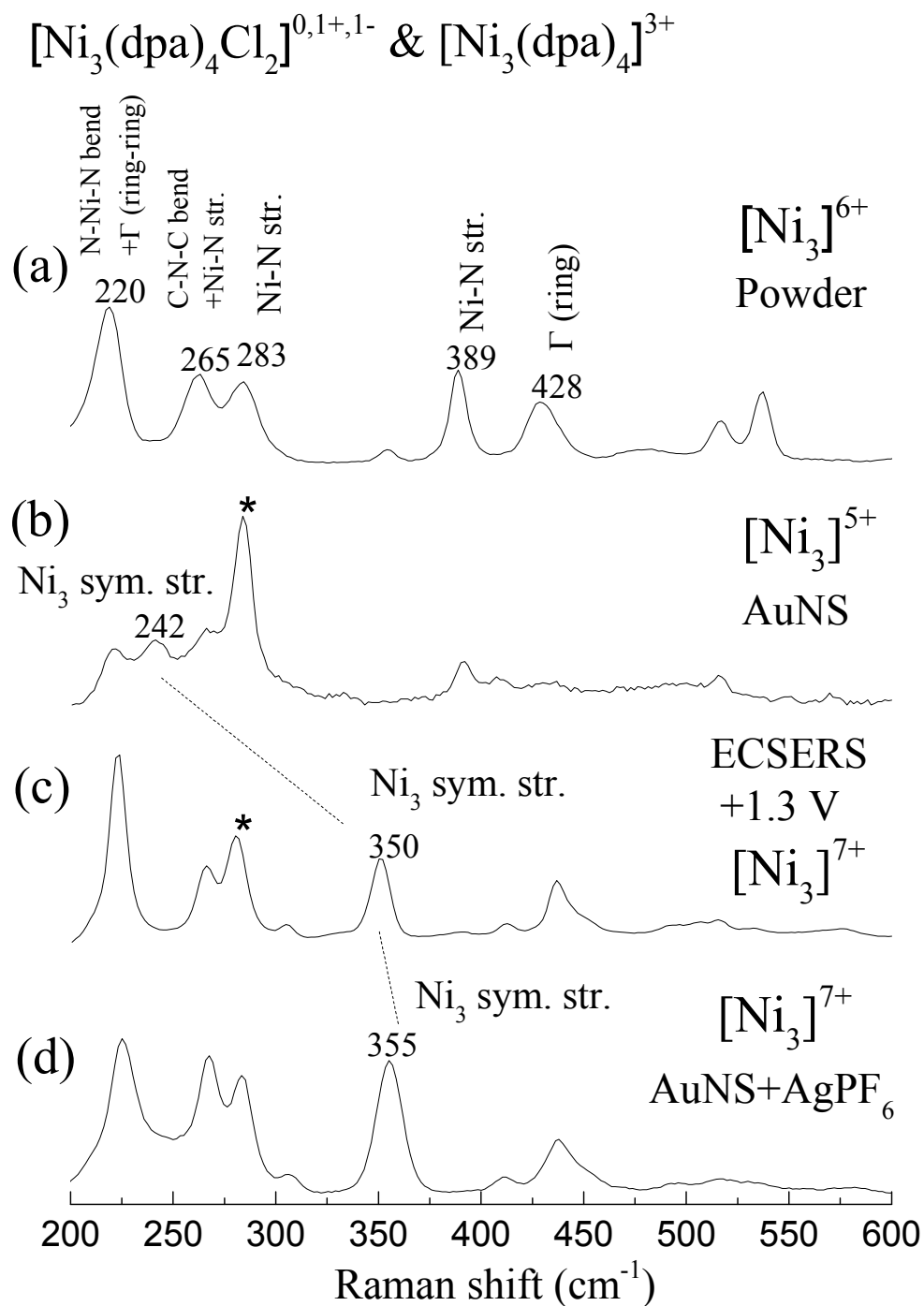


Figure S4. (a) Solid state Raman curve, (b) AuNP SERS, (c) ECSERS at +1.3 V, and (d) AuNP SERS with AgPF₆ added of $\text{Ni}_3(\text{dpa})_4\text{Cl}_2$. Asterisk sign denotes bands from dichloromethane (DCM). The assigned $[\text{Ni}_3]$ core is as indicated.

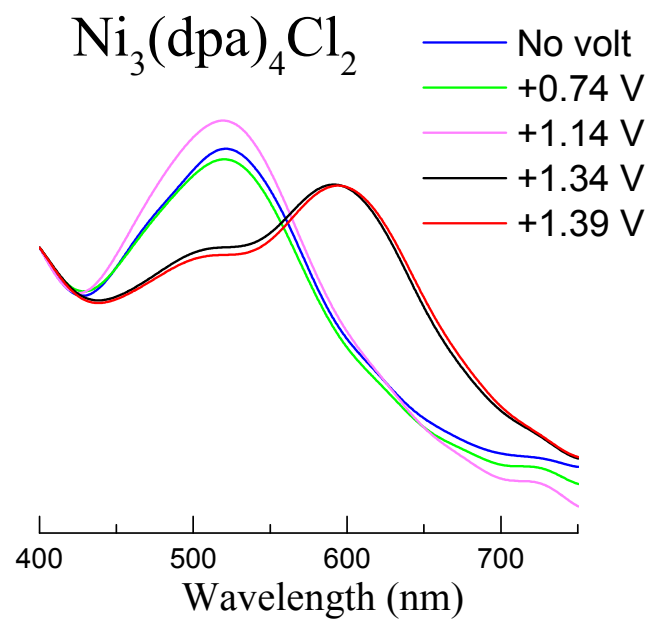


Figure S5. Absorption spectra of $\text{Ni}_3(\text{dpa})_4\text{Cl}_2$ without and with applied voltage at +0.74, +1.14, +1.34, +1.39 V in 0.1 M TBAP/DCM.

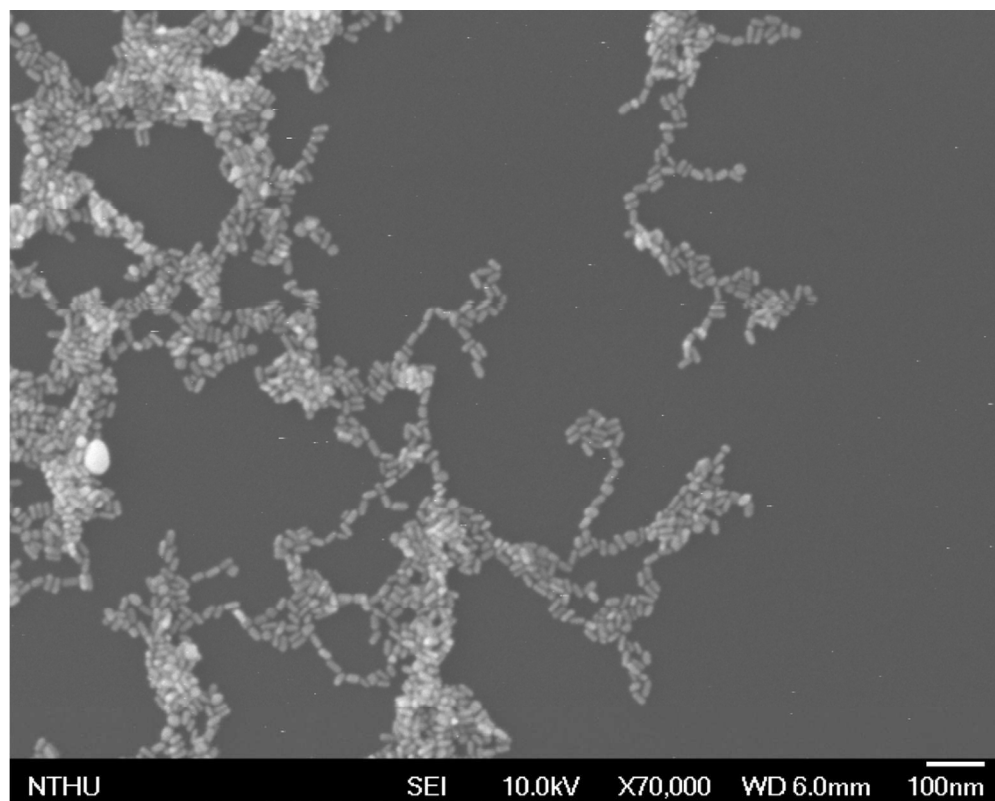


Figure S6. SEM image of AuNR(CTAB) with $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$ as the bridging molecules. The scale bar is 100 nm.

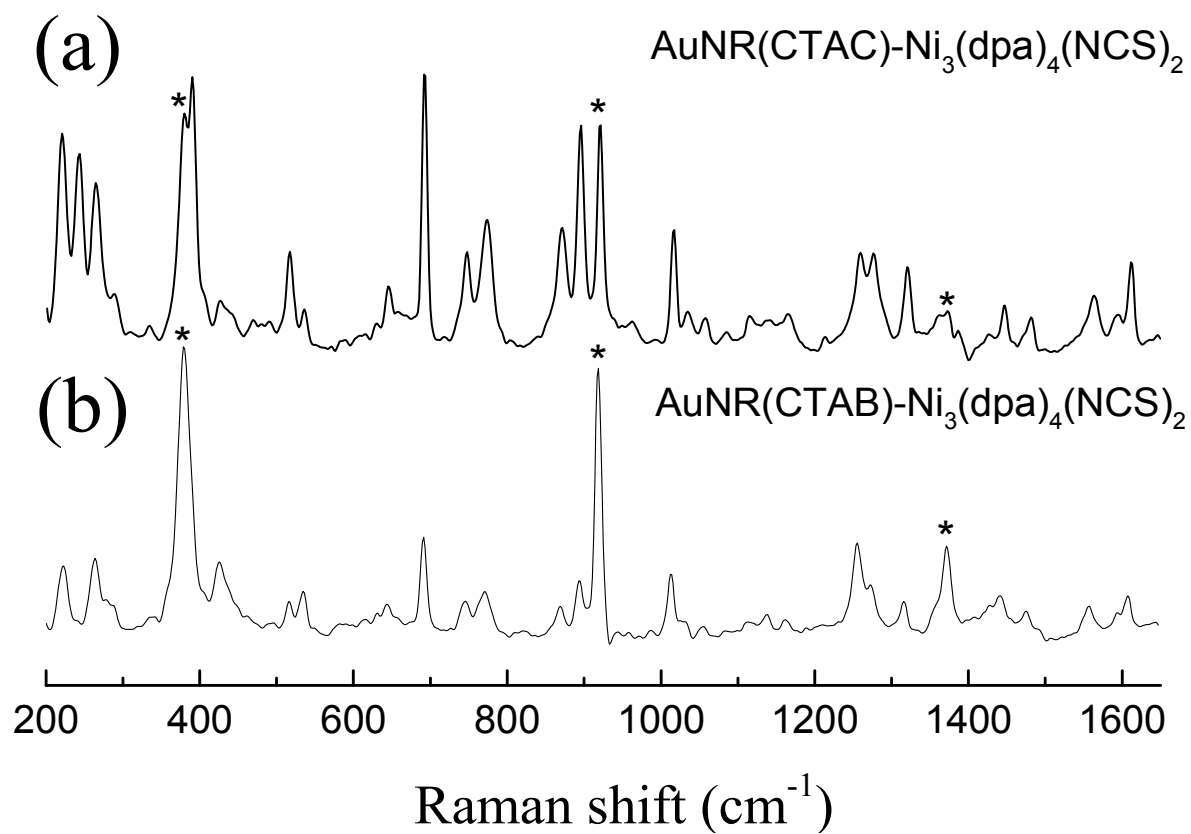


Figure S7. SERS of $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$ in (a) $\text{AuNR}(\text{CTAC})$ and (b) $\text{AuNR}(\text{CTAB})$. Asterisk denotes band from acetonitrile.

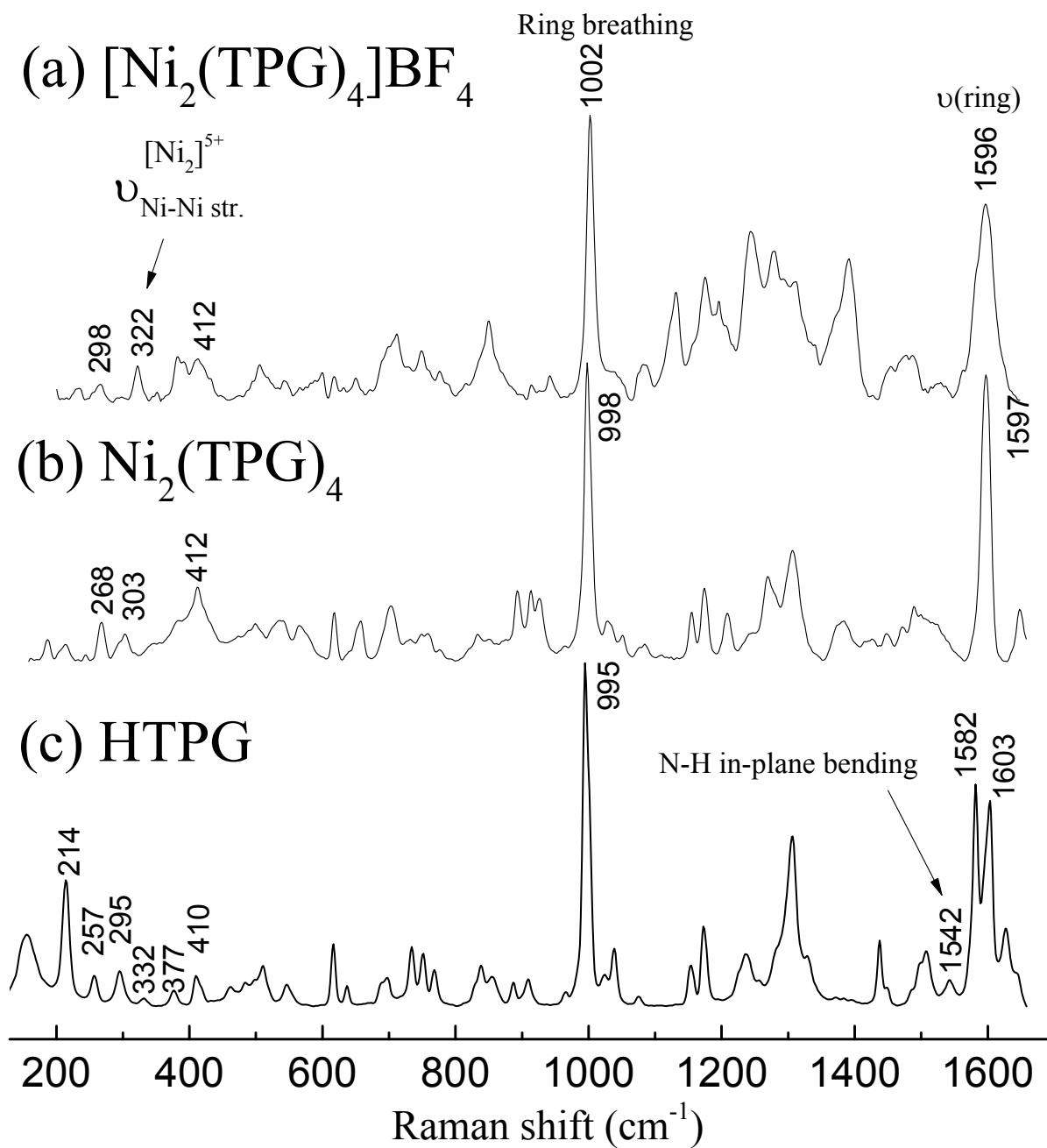


Figure S8. Full Raman spectra of (a) $[\text{Ni}_2(\text{TPG})_4]\text{BF}_4$, (b) $\text{Ni}_2(\text{TPG})_4$, and (c) HTPG with 633 nm excitation.