Supporting Information

Supporting Information for the paper entitled "Tunability mechanism of Surface-Enhanced Raman Scattering of Pyridine on MAg (M=Cu, Ag, Au) Diatomic Clusters via N-Ag bonding" by Lei Chen, Yang Gao, Haoran Xu, Zhigang Wang, Zhengqiang Li, Rui-Qin Zhang.

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Table S1. The calculated binding properties before and after pyridine molecule interaction with metal clusters using the TDDFT method at the BP86/TZP level.

Configuration	ΔE_{bind}	Q(Py-Ag)	Ag-M	exp	R(N-Ag)	HOMO	LUMO	Band gap
Cu-Ag			2.38	2.37[a]		-4.990	-3.278	1.71
Cu-Ag-Py	-16.97	0.083	2.37		2.21	-3.880	-2.801	1.08
AgAg			2.57	2.53[a]		-5.378	-3.328	2.05
Ag$_2$-Py	-15.35[b]	0.098	2.57		2.25[b]	-4.303	-2.825	1.48
AuAg			2.54	2.53[a]		-5.825	-3.695	2.13
Au-Ag-Py	-21.20	0.087	2.52		2.17	-4.728	-3.016	1.71

R(N-Ag) in unit Å represents the bond length between N and Ag atoms; R(Ag-M) in unit Å represents the distance between two metal atoms before and

10 after adsorption; Q(Py→M) in units of electron charge represents the ground state charge transfer between the pyridine and the metal cluster; HOMO in unit eV represents the highest occupied molecular orbital; LUMO in unit eV represents the lowest unoccupied molecular orbital; Band gap in unit eV represents the difference between HOMO and LUMO; and the total binding energy $\triangle$Ebind is in units of Kcal/mol, calculated based on the equation $\triangle E_{bind} = E_{pyridine} + E_{cluster} - E_{Py\text{-}cluster}$; [a] Reference 28, [b] Reference 31

The binding properties of pyridine interacting with AuAg/CuAg/Ag$_2$ clusters are presented in Table S1, including bond distance,

15 charge transfer, band gap and other data for comparison. The calculated distance of the N-Ag bond is 2.21 Å in the CuAg-Py and 2.17 Å in the AuAg-Py complex as presented in Table S1. Compared to the value 2.25 Å in the Ag$_2$-Py complex, the distance of the N-Ag complex is shortened by 0.04 Å and 0.08 Å, respectively. The binding energy analysis indicates that the CuAg-Py and AuAg-Py complexes, which are based on heteronuclear clusters, are more stable than the Ag$_2$-Py complex. The calculated values are -16.97 Kcal/mol for CuAg-Py complex and -21.20 Kcal/mol for AuAg-Py complex. Among all of the three complexes, the AuAg-Py has the

20 strongest interaction with the biggest binding energy and the smallest bond length of R (N-M) in the ground state. The data in Table S1 indicates that, before and after the pyridine adsorption on metal clusters, there is no evident difference in the distance between two metal atoms. As to the bare metal diatomic clusters, the bond distances agree well with the experimental values as shown in Table S1. Charge transfer analysis shows that, compared to AuAg-Py and CuAg-Py complexes, there is the maximum amount of charge transfer from pyridine to Ag$_2$ cluster with the value of 0.098 e among these three complexes. For these three complexes, the binding energy order is

25 AuAg-Py＞CuAg-Py＞Ag$_2$-Py, the charge transfer order is Ag$_2$-Py＞AuAg-Py＞CuAg-Py, and the R(N-M) order is Ag$_2$-Py＞CuAg-Py＞AuAg-Py. In the case of M=Cu, the binding energy of pyridine adsorbed on the AgCu cluster are calculated to be -26.29 Kcal/mol for the Ag-Cu-Py complex and -19.67 Kcal/mol for the Cu-Ag-Py complex, respectively. It is obvious that the former conformation is more stable than the latter; and the binding energy difference between the two configurations is -6.62 Kcal/mol. In the case of M=Au, the binding energy of pyridine interacting with AuAg cluster is calculated to be -17.35 Kcal/mol for the Ag-Au-Py complex and -21.20

Kcal/mol for the Au-Ag-Py complex, respectively, and the binding energy difference between those two configurations is -3.75 Kcal/mol.

Comparing the band gap of the Ag_2-Py with the value of 1.48 eV, we found that the transition energies from HOMO to LUMO of the CuAg-Py are much lower with the value of 1.08 eV, while it is much higher for the AuAg-Py with the value of 1.71 eV. So the

5 introduction of heteromuclear atom significantly changes the properties of the pyridine-metal complex. The band gaps of the pyridine molecule adsorbed on metal clusters change with the different composition of mixed metal clusters. There are significantly differences in energy levels of molecular orbitals (MOs) including the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO). The HOMO level is -3.88 eV for CuAg-Py, -4.30 eV for Ag_2-Py and -4.73 eV for AuAg-Py. The LUMO level is -2.80 eV for CuAg-Py, -2.83 eV for Ag_2-Py and -3.02 eV for AuAg-Py. The HOMO levels, together with LUMO levels, are in the following
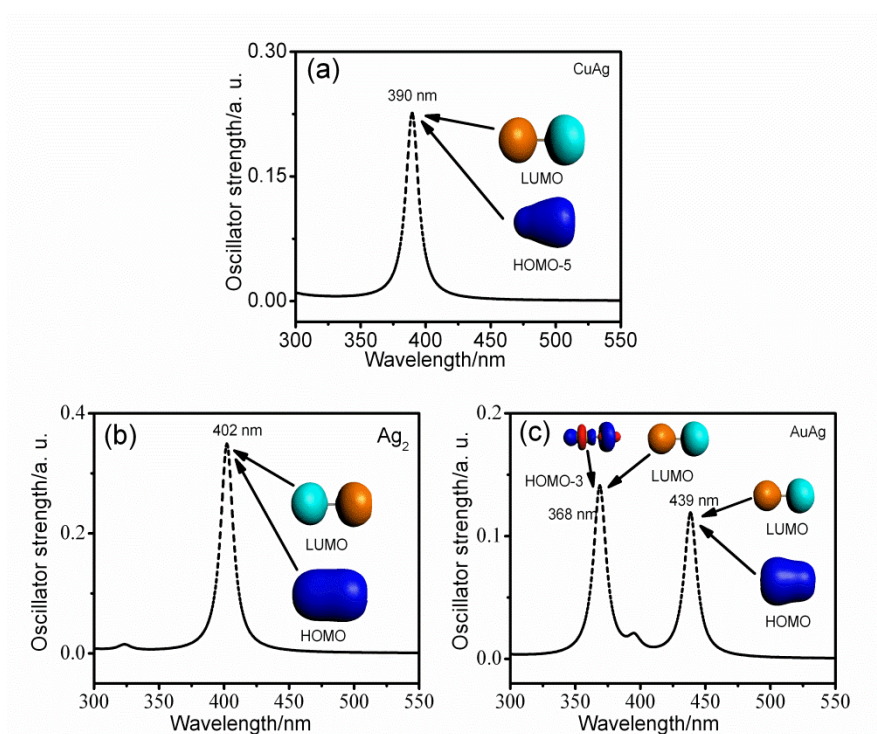
10 sequence: CuAg-Py＞Ag_2-Py＞AuAg-Py.

Figure. S1 UV-Visible absorption spectra of CuAg, Ag_2, and AuAg clusters in the range 300 to 550 nm and molecular orbital analysis of absorption peaks.

Figure S1 shows absorption spectra of bare metal clusters Ag_2, AuAg, and CuAg in the range 300 to 550 nm by TDDFT calculations.

15 For Ag_2 and AgAu clusters, the transition energies for low singlet states ($S_0 \rightarrow S_1$) are calculated to be 3.08 and 2.83 eV, respectively, which correspond to absorption peaks at 402 nm for Ag_2 and 439 nm for AgAu. The calculated results agree well with the experimental values, which are 2.8 eV for Ag_2 and 2.73 eV for AgAu clusters,[28] respectively. For CuAg cluster, the maximum absorption peak is calculated to be 3.18 eV (390 nm), which is consistent with experimental value 3.20 eV.[28] To further understand the electronic behavior of various transitions, the molecular orbitals are analysed and presented in Figure S1. For the CuAg cluster, the strongest peak is located

20 at 390 nm, which could be ascribed to the electronic transitions of HOMO-5$\rightarrow$LUMO, and Figure S1(a) indicates that this peak is mainly

caused by electronic transitions from the Ag atom to the whole cluster as a result of polarization between the Cu and Ag atoms. For the Ag$_2$ cluster, the strongest peak at 402 nm could be ascribed to electronic transitions from HOMO to LOMO, as shown in Figure S1(b), and the two Ag atoms make equal contributions to this peak. For AuAg, there are two strong peaks, located at 368 and 439 nm, and the corresponding electronic transitions are from HOMO-3 to LUMO and from HOMO to LUMO, respectively. Figure S1(c) indicates that contributions from the Au and Ag atoms are different on account of polarization between these two atoms.