Supporting Information for

Charge Transfer Interactions of Pyrazine with Ag$_{12}$ Clusters——
Towards Precise SERS Chemical Mechanism

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**Fig. S1** A typical X-ray photoelectron surveys spectrum of the as-prepared Ag$_{12}$ NCs.

**Fig. S2** Exclusion experiments showing no Raman interference of Ag$_{12}$ NCs (a), and the ligand H$_2$SMA (b). Also, the DFT-calculated Raman activity display rather weak signal in the region lower than 2000 cm$^{-1}$ (c), which is in sharp contrast to its IR activity.

**Fig. S3** Optimized isomers geometries of bare Ag$_{12}$ (a) Ag$_{12}$C$_1$, (e) Ag$_{12}$C$_1$, (b/c/d) Ag$_{12}$(SCH$_3$)$_6$ and (f/g/h) Ag$_{12}$(SCH$_3$)$_6$. The energy of Ag$_{12}$C$_1$ is set as zero reference (energy = 0.00 eV).

**Fig. S4** Calculated Raman spectra of the other models: (a) Ag$_{12}$-pyrazine-Ag$_{12}$, (b) edge-adsorbed Ag$_{12}$(SCH$_3$)$_6$-pyrazine.

**Table S1** Natural population analysis (NPA) charge distribution of Ag$_{12}$(SCH$_3$)$_6$, pyrazine, bottom- and edge- adsorbed pyrazine on the cluster.
We have examined the binding energy on bottom-adsorbed and edge-adsorbed Ag\textsubscript{12}(SCH\textsubscript{3})\textsubscript{6}-pyrazine complex, as listed in Table S2. The total binding energy is calculated using the equation \( \Delta E = E_{\text{complex}} - E_{\text{pyrazine}} - E_{\text{Ag}} \), where \( E_{\text{complex}} \), \( E_{\text{pyrazine}} \), and \( E_{\text{Ag}} \) denote the total energy of Ag\textsubscript{12}(SCH\textsubscript{3})\textsubscript{6}-pyrazine complex, a pyrazine molecule and Ag\textsubscript{12}(SCH\textsubscript{3})\textsubscript{6} cluster, respectively. As results, bottom-adsorbed Ag\textsubscript{12}(SCH\textsubscript{3})\textsubscript{6}-pyrazine complex shows a larger binding energy (6.75 kcal mol\(^{-1}\)) than the edge-adsorbed Ag\textsubscript{12}(SCH\textsubscript{3})\textsubscript{6}-pyrazine complex (4.63 kcal mol\(^{-1}\)).

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Meanwhile, the length Ag-N bond of edge-adsorbed Ag\textsubscript{12}(SCH\textsubscript{3})\textsubscript{6}-pyrazine complex is larger (2.52 Å) than that of the bottom-adsorbed complex (2.43 Å).

<table>
<thead>
<tr>
<th>Complex</th>
<th>( q_{\text{pyrazine}\rightarrow\text{cluster}} )</th>
<th>R(Ag-N)</th>
<th>( \Delta E ) (Kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom-adsorbed</td>
<td>0.305</td>
<td>2.43</td>
<td>-6.75</td>
</tr>
<tr>
<td>Edge-adsorbed</td>
<td>0.177</td>
<td>2.52</td>
<td>-4.63</td>
</tr>
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</table>
As supplementary information, we have also calculated the deformation density and Milliken charge distribution of edge-adsorbed Ag\(_{12}\)(SCH\(_3\))\(_6\)-pyrazine, as shown in Fig. S5.

**Fig. S5** (a) The calculated deformation density (\(\Delta \rho = \rho^{\text{complex}} - \rho^{\text{Ag}_{12}} - \rho^{\text{pyrazine}}\)) isosurfaces in the edge-adsorbed Ag\(_{12}\)(SCH\(_3\))\(_6\)-pyrazine, with an isosurface value of 0.0001 a.u. The enhanced density is in green and the depletion density in red. (b) Mulliken charge distribution in the edge-adsorbed Ag\(_{12}\)(SCH\(_3\))\(_6\)-pyrazine.

**Fig. S6** Natural bond orbital (NBO) donor-acceptor (overlap) interactions in the edge-adsorbed Ag\(_{12}\)(SCH\(_3\))\(_6\)-pyrazine between Ag\(_{12}\)(SCH\(_3\))\(_6\) and pyrazine. The positive and negative donor orbitals are yellow and purple; the positive and negative acceptor orbitals are green and blue.
Table S3 Second-order perturbation theory analysis of Fock matrix in NBO basis for pyrazine and Ag_{12}(SCH_3)_6-pyrazine complex.
Fig. S7 Orbital interaction diagram for edge-adsorbed Ag$_{12}$(SCH$_3$)$_6$-pyrazine formed upon interaction of the Ag$_{12}$(SCH$_3$)$_6$ (frag. 1) and pyrazine (frag. 2).

Table S4 Charge decomposition analysis (CDA) of the Ag$_{12}$(SCH$_3$)$_6$-pyrazine complex.