

Supporting Information

**Contribution of Hydrogen Bond to Charge-Transfer Induced
Surface-Enhanced Raman Scattering of the Intermolecular System
Consist of p-Aminothiophenol and Benzoic Acid**

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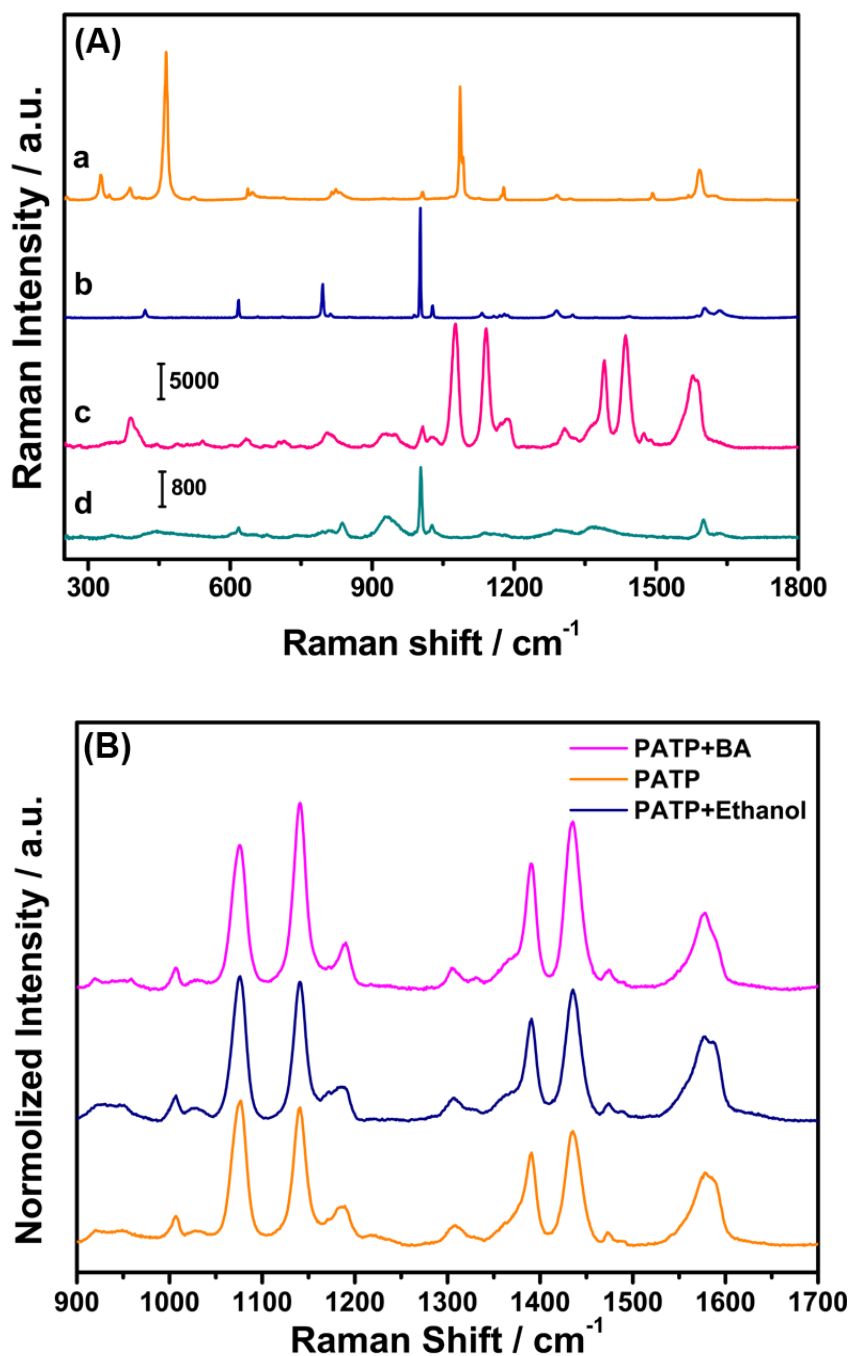


Figure S1. (A) Raman spectra of PATP (a) and BA (b). SERS spectra of PATP (c) and BA (d) in the substrate of Ag nanoparticles. (B) SERS spectra of dry substrate adsorbed PATP, substrate adsorbed PATP immersed in ethanol, and substrate adsorbed PATP immersed in BA ethanol solution.

Fig. S1 (a) and (b) show the normal Raman spectra of PATP and BA, respectively, in the solid state. The control experiment was carried out as well, in which the SERS spectra of PATP and BA were obtained in the substrate of Ag nanoparticles (Fig (c)

and (d)). All the conditions here were the same as the experiment conditions above. What's more, both (c) and (d) spectra were measured in the same laser power and exposure time in order to compare exactly.

In our experiment, we immersed the substrate coated with PATP molecules in the BA ethanol solution. Although ethanol contains alcohol hydroxyl group that would also form H-bond with the amine in PATP, it doesn't contain benzene ring structure, which cannot form the aromatic conjugation system with PATP like the BA molecule. Thus, the effect of ethanol on PATP is quite insignificant compared with BA. And that is why H-bonding not observed obviously. It also can be confirmed from the Figure S 1(B)

Theoretical data in this work were obtained by DFT method of B3LYP which is the hybrid of Becke's three-parameter exchange functional^{1,2} with the Lee–Yang–Parr correlation functional.³ The triple split valence basis set of 6-31G** was adapted. All calculations were carried out with the aid of the Gaussian 09 program⁴.

When a BA molecule is introduced to the system, the carboxyl group becomes close to the amino group of PATP by forming the H-bonding. Moreover, the BA molecule is perpendicular to the plane of the PATP molecule. The highest occupied molecular orbital (HOMO) of the system containing both BA and PATP molecules is primarily located in the PATP. Above all, the energy value of the lowest unoccupied molecular orbital (LUMO) is lower than the value of single PATP. The energy level gap between the Fermi energy level of silver and the energy level of LUMO becomes smaller. As mentioned above, the existence of BA in the system decreases the energy gap, which would be conducive to the CT from the Fermi energy level of silver nanoparticles to LUMO of the adsorbed molecules. Therefore, there would be more matched excited states, such as LUMO+3 and LUMO+4, which CT excitations reflect transitions from the Fermi level of the silver substrate to LUMO+3 and LUMO+4 of the dimer system, respectively. The calculated energy levels are presented in Table S1.

Since the dimer models adopted in the calculations were just the normal forms of PATP and BA, it may be slightly different from the experiment. While, the fact is that the PATP molecules should be in the form of sulfenium anions ($\text{NH}_2\text{C}_6\text{H}_4\text{S}^-$) or para-amino phenylthiyl radicals ($\text{NH}_2\text{C}_6\text{H}_4\text{S}\cdot$) when they are adsorbed onto the surface of Ag nanoparticles. It is some difference in our calculations from the experiments. The energy gap of the PATP in the experiment system is narrower (about 4.13 eV) in fact.⁵ However, we just discussed about the influence on the energy level of PATP when the BA molecule was introduced, and this difference would be negligible in this sense. The results of the calculation further demonstrate the contribution of H-bond between the two molecules to this system.

Table S1. The frontier orbital energies of PATP monomer and PATP-BA dimer calculated at the B3LYP/6-31G** level.

The unoccupied molecular orbital	$E_{\text{PATP}}(\text{eV})$	$E_{(\text{PATP}+\text{BA})}(\text{eV})$
LUMO	-0.676	-1.788
LUMO+1	-0.572	-0.796
LUMO+2	-0.0822	-0.751
LUMO+3	0.243	-0.711
LUMO+4	0.510	-0.133

Table S2. Degree of charge transfer (p_{CT}) of the PATP in the Ag/PATP/BA system at 1141, 1390, and 1435 cm^{-1} as a function of the negative log of the BA concentration with excitation at 633 nm.

$-\text{Log}[\text{BA}(\text{mol/mL})]$	1141 cm^{-1}	1390 cm^{-1}	1435 cm^{-1}
9	0.506	0.403	0.468
7	0.522	0.408	0.479
5	0.542	0.445	0.520
4	0.552	0.448	0.521
3	0.563	0.457	0.529
2	0.569	0.475	0.547

Table S3. Degree of charge transfer (p_{CT}) of the PATP in the Ag/PATP/BA system at 1141, 1390, and 1435 cm^{-1} as a function of the substituents on BA with 633-nm

excitation.

Classification	1141 cm⁻¹	1390 cm⁻¹	1435 cm⁻¹
p-Cyanobenzoic acid	0.552	0.435	0.529
Benzoic acid	0.634	0.555	0.627
p-Hydroxybenzoic acid	0.663	0.567	0.645

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