

Supporting Information

Stabilizing Single Molecular Raman Behaviour of a Nonbonding Molecule on Ag Nanoparticles

Zhixun Luo¹, Yi Luo^{2,3}, Jie Li⁴, Kai Liu², Hongbing Fu¹, Ying Ma¹, Jiannian Yao^{1*}

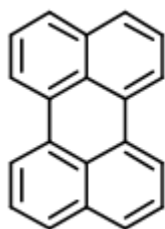
¹Key Laboratory of Photochemistry, Institute of Chemistry, the Chinese Academy of Science, Beijing, 100080, People's Republic of China

²Department of Theoretical Chemistry, Royal Institute of Technology, AlbaNova, S-106 91 Stockholm, Sweden

³Hefei National Laboratory of Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

⁴Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China

1, Material



(Perylene, C₂₀H₁₂)



(Pyrene, C₁₆H₁₀)

Perylene and pyrene (sublimed, 99.5% purity, Sigma-Aldrich) molecules can be physically adsorbed on metal substrate. Owing to its strong π - π absorption bands, it is usually difficult to obtain population-averaged Raman spectra with a 514.5 excitation, especially the rather strong fluorescence of perylene. They do not mix with water, while the good solvent CHCl₃/CHCl₂ has strong Raman peaks that would interfere with the characteristic Raman modes. They are the harmful matters in our environment and are very difficult to detect effectively at low concentration, i.e. no trace-analysis of them has been reported.

2 , Method

Low-temperature stage:

The low-temperature setup, as one of the accessories of the Raman instrument, is provided by *Renishaw Company*. The sample stage actually can burden a low temperature up to -190°C (by liquid nitrogen). We choose a relatively proper temperature at -150°C for all the low-temperature measurements.

THMS600/HSF91 STAGE CONNECTIONS

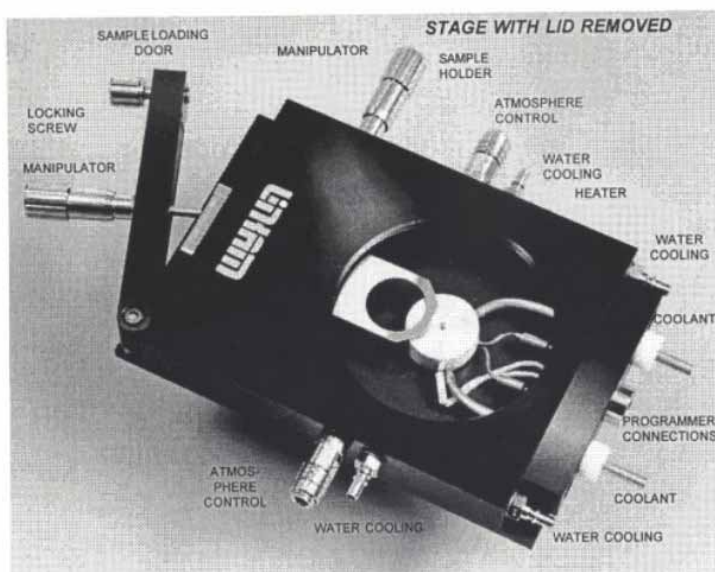


Fig.s1. Sketch photos of the low-temperature stage connections with Raman instruments.

Characterization of Ag colloid:

Ag nanoparticle synthesis: The Ag colloid was prepared according to the method of *P.C. Lee* and *D. Meisel*. 90 mg of Ag nitrate were dissolved in 500 ml deionized water and the solution was heated to boiling. Then 10 ml of a 1% trisodium-citrate aqueous solution was dropped into the boiling Ag nitrate solution (one drop per second for the first one-third, and three seconds a drop for the two-third, then ten second a drop), accompanied with vigorously stirring. After that, the mixed solution was kept boiling for 10 min. Gray Ag colloid was finally obtained, which could be stable for several weeks, with size distribution mainly centred on 90nm. DLS analysis shows that the Combined Zeta Potential of the Ag colloid is about -34.93mV, with Std. Error of 5.43, and combined Rel. Residual is 0.0419.

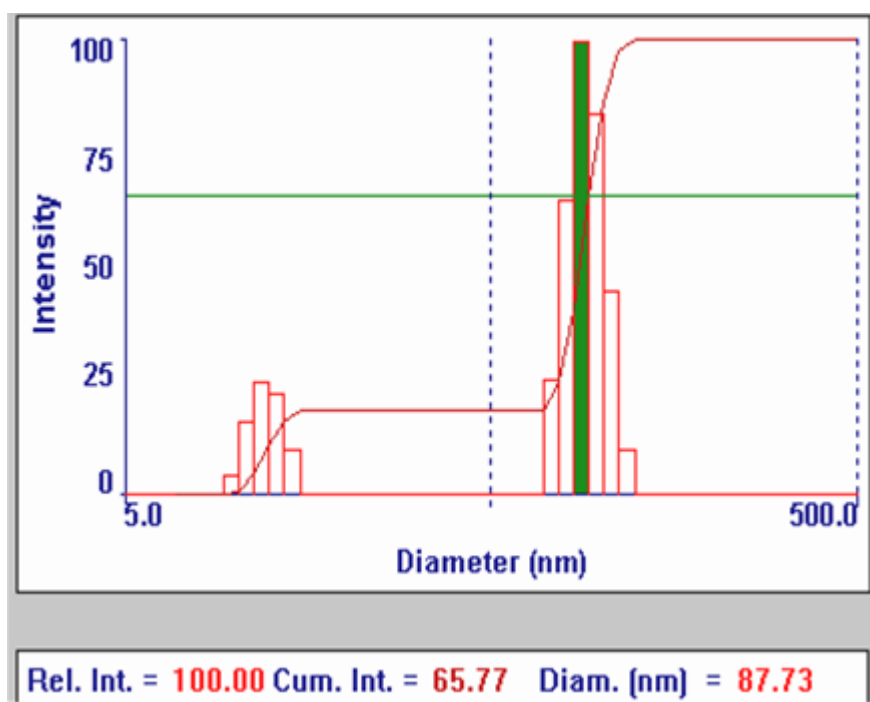


Fig.s2. Dimension distribution of colloidal Ag nanoparticles prepared by the redox method mentioned in the text

Assembly of colloidal Ag nanoparticles:

Cover glasses were cleaned with ethanol and deionized water, dried in vacuum; then place these dried cover glass into sample boxes and lean a tiny angle (ca. 5°), drop on the Ag colloid gradually on the cover glasses with tiny shaking. After dried again, the above well prepared colloidal Ag nanoparticles were uniformly assembled on cover-glass to act as SERS substrates.

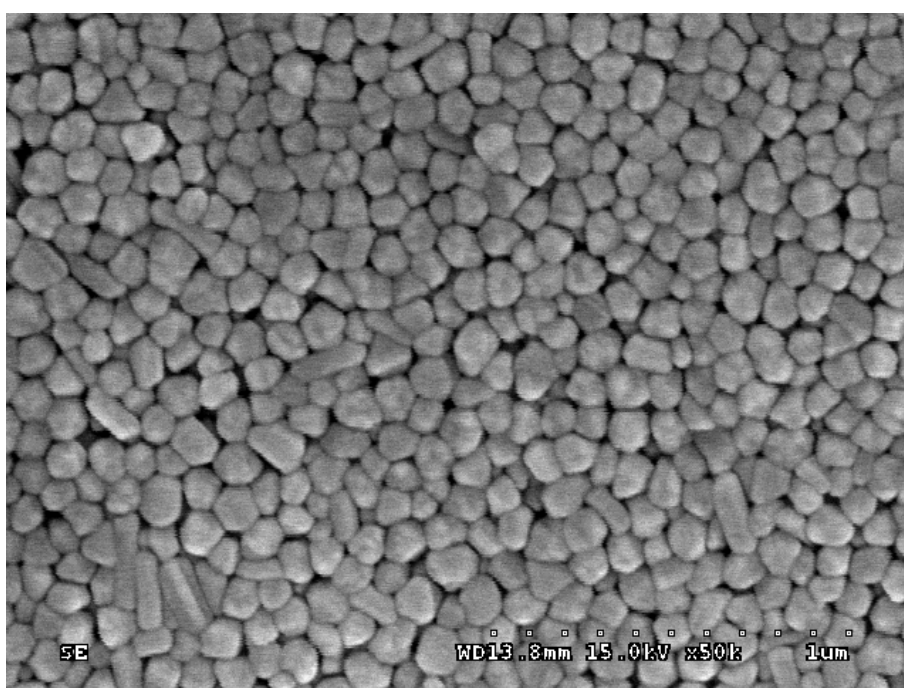


Fig.s3. SEM image of the Ag nanoparticles assembled on cover-glass as SERS substrate

Method: The morphology and size of the sample were examined by field emission scanning electron microscopy (FESEM, Hitachi S-4300). All AFM images were obtained on Seiko SPM3800; the TEM images were done on a JOEL JSM-6301F. All Raman spectra were collected by a Renishaw H13325 spectrophotometer, laser excitation is at 514.5nm.

Preparation of SM-SERS sample:

20uL target solution is deposited on a cover-glass to form a sample area of Φ 0.5cm or so. The use of cover-glass supported samples makes it possible to apply the low temperature set-up with THMS600/HSF91 stage connections.

Substrate characterization:

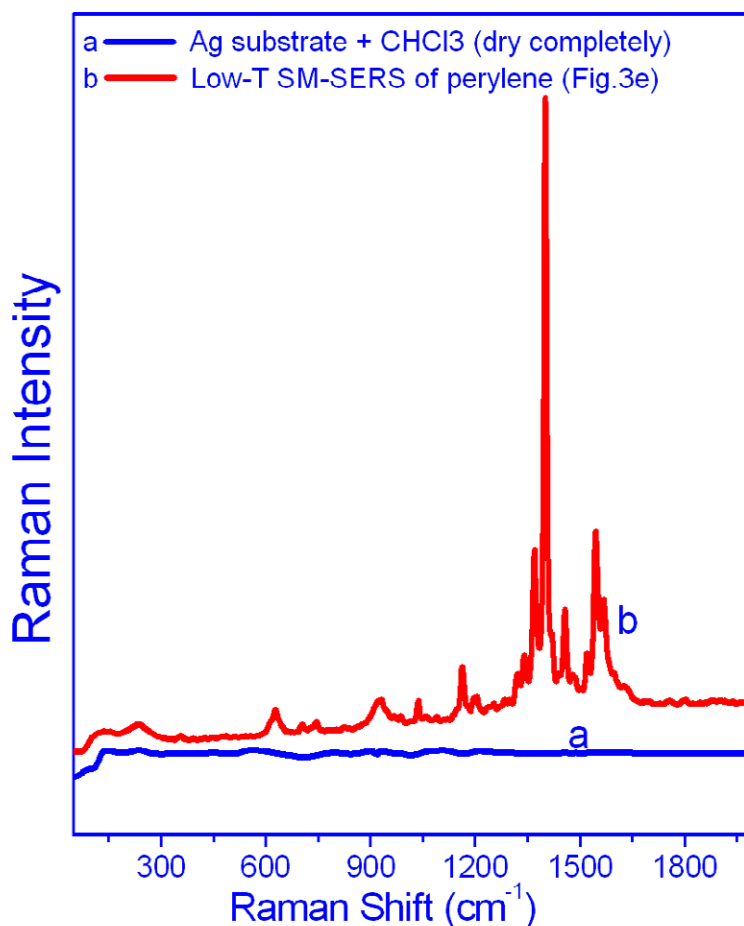


Fig.s4. (a) Raman spectrum of the above Ag substrate (with only CHCl₃ solvent media on, dry completely); (b) compared with the sample signal of SM-SERS of perylene on the same substrate (refer to Fig. 2e)

3. Room temperature spectra

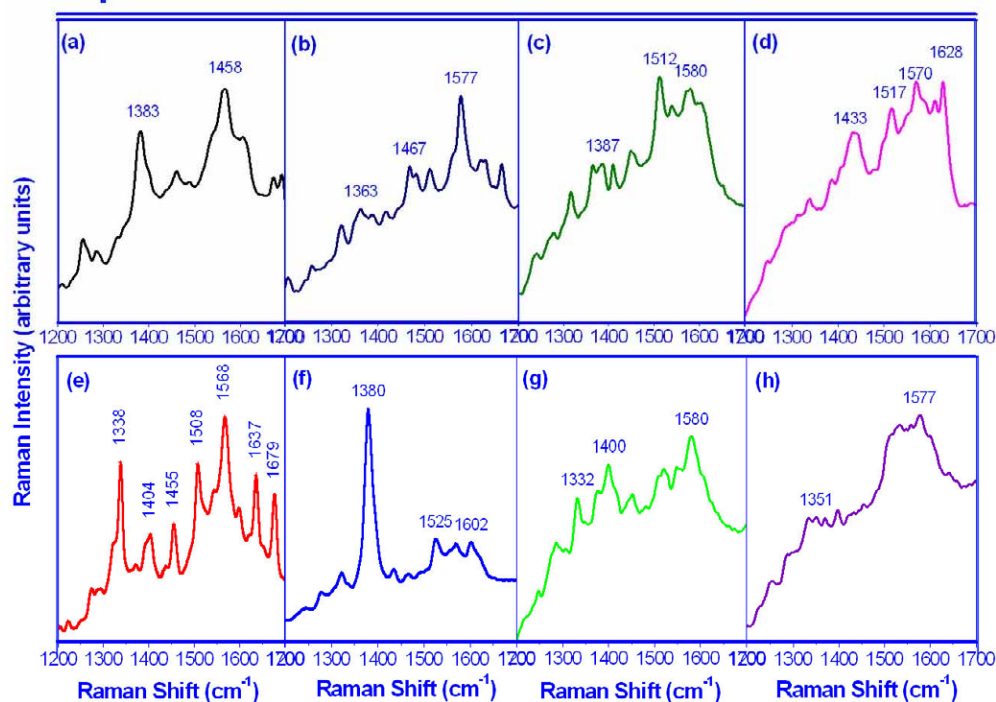


Fig.s5 Time dependent Raman spectra of perylene (10^{-15} M) on Ag-coated cover-glass at room-temperature, performed at the same ‘hot-spot’ with a relative weaker laser power (75%, 15mw), all the spectra were collected sequentially in every 1.5 minutes.

We can examine laser induced thermal effects by reducing the laser power. The spectra are collected continuously at every 1.5 minutes on the same ‘hot-spot’. Although the spectral-fluctuation is still very strong, few interesting observations are worth to mention. It can be seen that the spectra obtained at higher laser power have been largely reproduced and the spectral features do not become broader after long radiation time although the background goes up considerably. It is interesting to note that the spectrum shown in Fig. s5f is much cleaner than the rest and is dominated by a peak around 1380cm^{-1} . The spectra which were taken before and after Fig. s5f show more similarities on the spectral profiles. These seem to indicate that the laser power is not the major thermal sources for the spectral-fluctuation and the single molecular motion is reversible or directly by a certain force rather than the random thermal diffusion.

4, Estimation

In 20uL of 10^{-15} M dilute solution, the number of perylene molecules can be estimated as:

$$N = 10^{-15} \text{ Mol/L} \cdot 20 \times 10^{-6} \text{ L} \cdot 6.02 \times 10^{23} \text{ Mol}^{-1} = 1.2 \times 10^4 \quad (1)$$

When 20uL solution is deposited on a glass cover slip to form a sample area of Φ 0.5cm, with a laser focus-spot of Φ 1um, the statistical probability for a “hot-spot” to host a single perylene molecule is:

$$p = 1.2 \times 10^4 \times \left(\frac{10^{-6}}{0.5 \times 10^{-2}} \right)^2 = 4.8 \times 10^{-4} \quad (2)$$

So it is rather difficult to find a SM-SERS “hot-spot” with this ultra-low concentration sample. It is noted that this estimation is based on the assumption of uniform monodispersity of molecules.

To evaluate Raman enhancement factor of the system, we employed

$$G = \frac{I_{SERS}}{N_{surf}} / \frac{I_{Raman}}{N_{bulk}} \quad (3)$$

Here the former part represents the SERS intensity contributed by perylene molecules adsorbed on substrate, and the latter part represents the normal Raman intensity of the species in solution. Choosing a main mode of perylene molecule from SM-SERS spectra as the reference, an enhancement factor, G , of 2.5×10^{18} could be obtained, indicating that it is possible to probe the Raman signal of a single molecule.

5, Calculated Raman spectra of the perylene molecule

All calculations were carried out using density functional theory at B3LYP level with Lanl2dz basis sets as implemented in Gaussian03 package. The models were configured with Gaussview software with optimized geometry. Two Ag10 clusters placed a few nanometer (0.6~2nm, respectively) were assumed to represent the Ag nanoparticle pair, the distances between Ag atoms were set to be 2.82 Å. Optimized geometry of perylene was used for all calculations

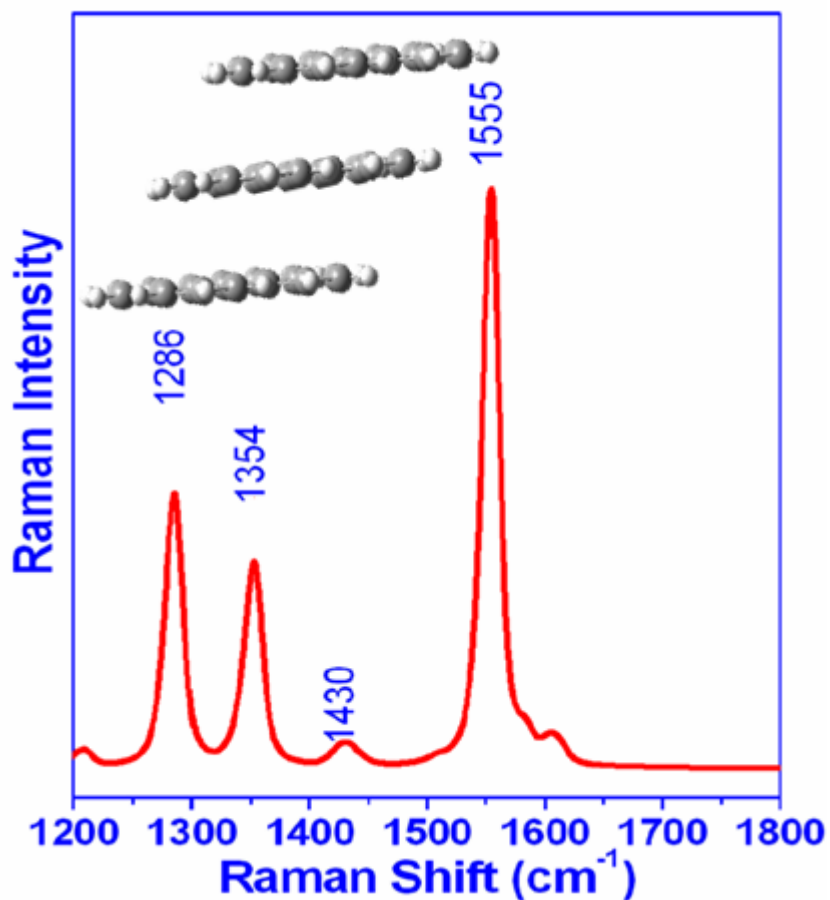


Fig.s6 Calculated Raman Spectrum of three π - π stacking perylene molecules, which also show three main Raman active modes.

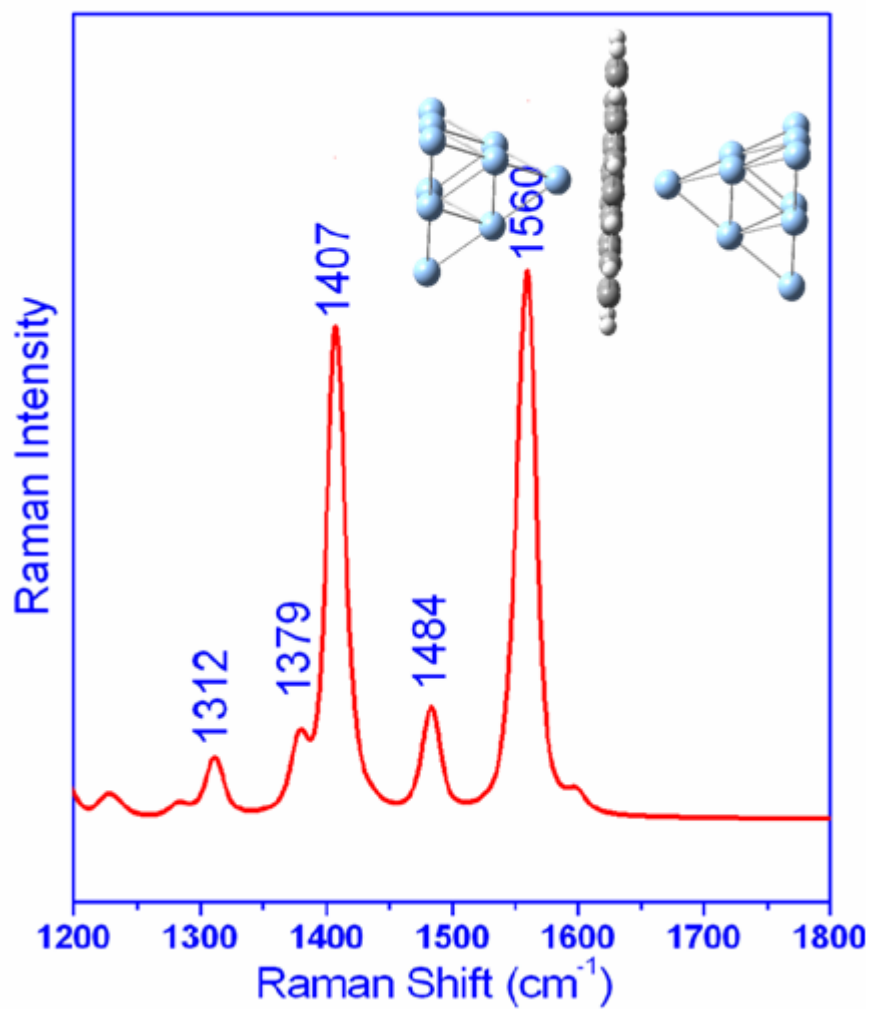


Fig.s7 Calculated spectrum for a perylene molecule trapped in two triangle Ag clusters whose tips are separated by 0.6nm.

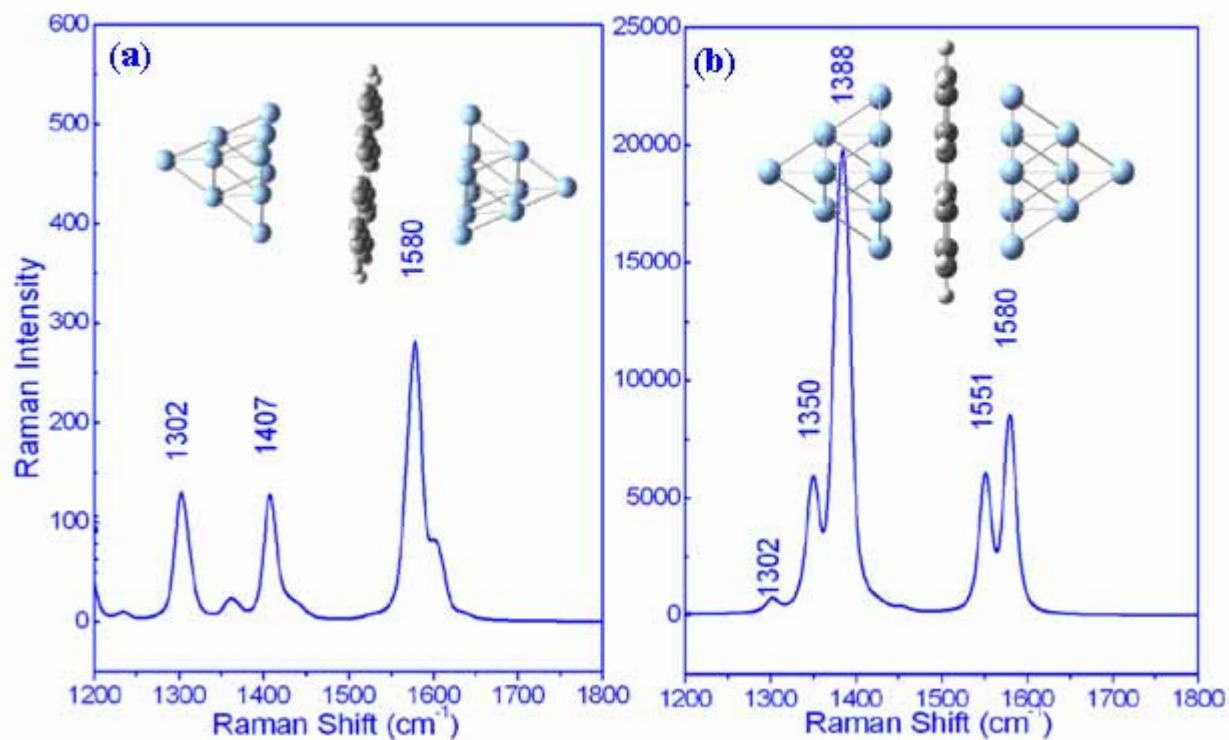


Fig.s8 Calculated Raman spectra of a perylene molecule trapped in the middle of two triangle AgB₁₀B clusters whose bases are separated by a distances of (a) 0.8 nm and (b) 0.6 nm.

4. Extend experiments

SM-SERS spectra of another nonbonding molecule pyrene

(A) Room temperature spectra:

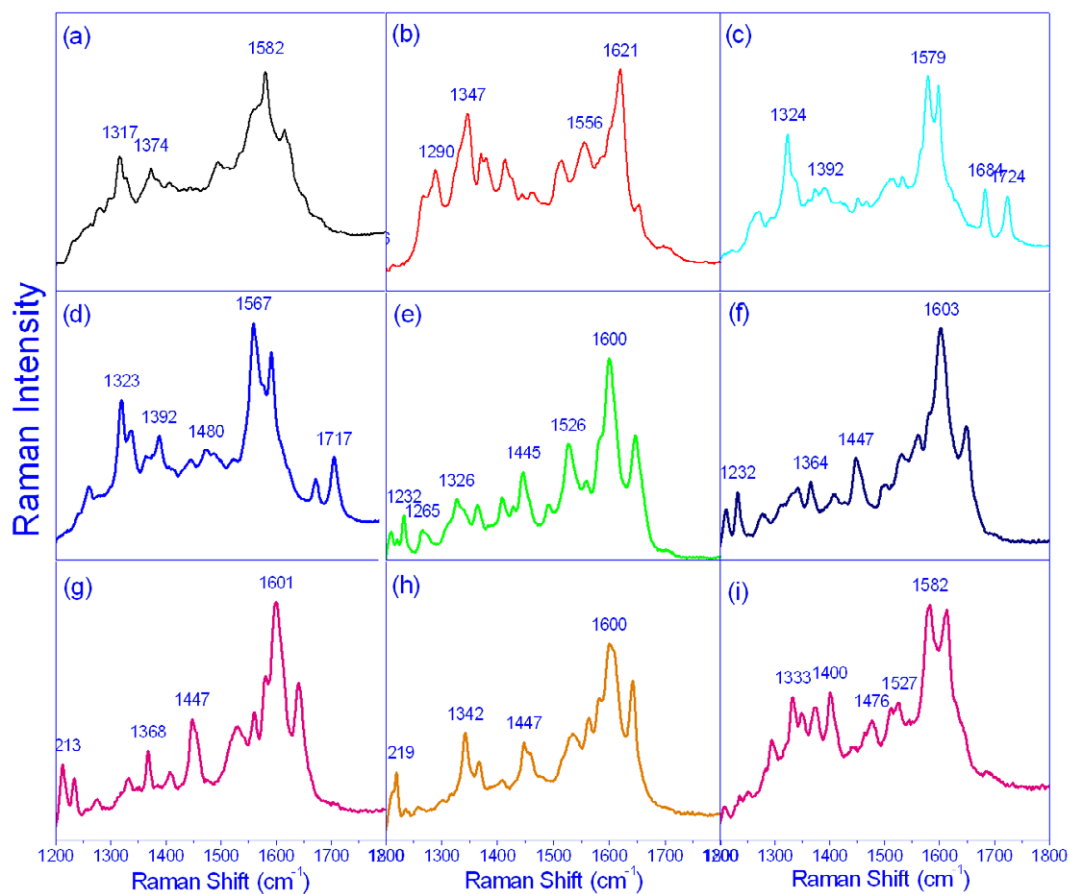


Fig.s9 Time dependent Raman spectra of pyrene (10^{-15} M) on Ag-coated cover-glass at room-temperature, performed at the same 'hot-spot' with a relative weaker laser power (75%), all the spectra were collected sequentially in every 1.5 minutes

(B) Low temperature spectra:

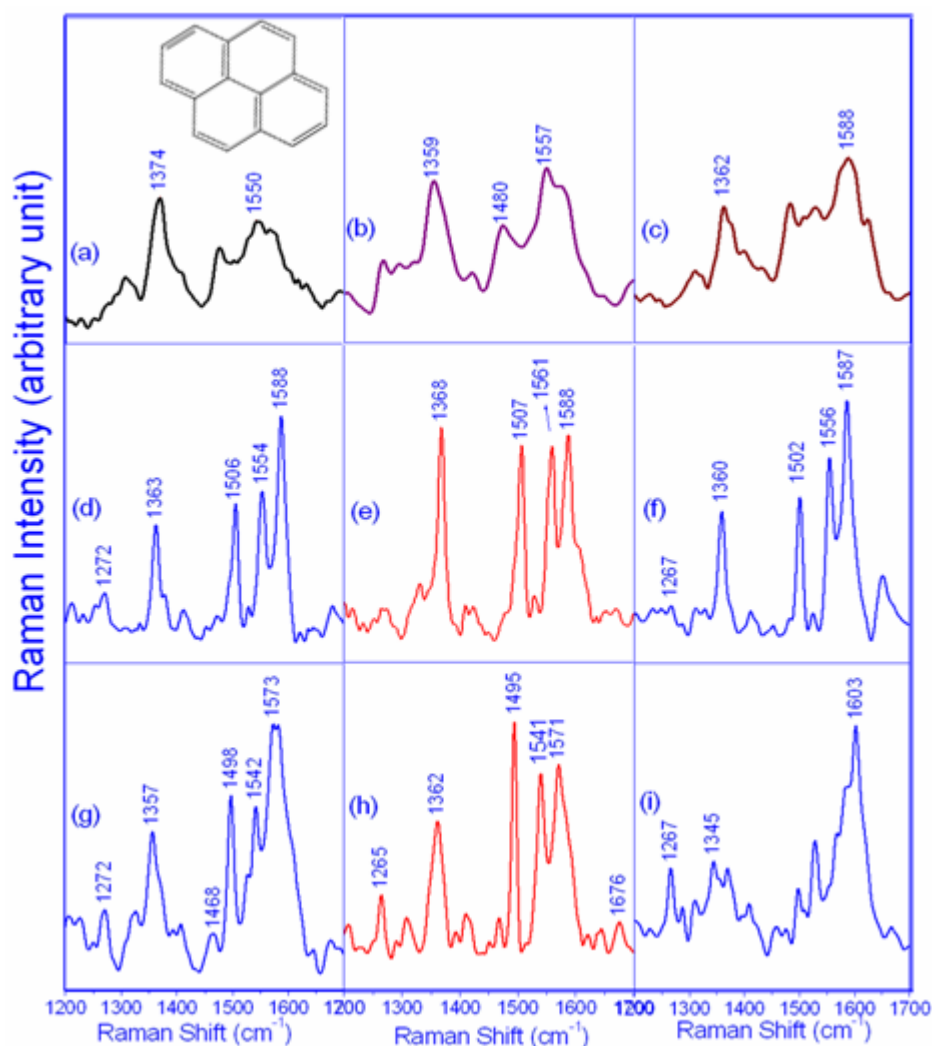


Fig.s10 Time-dependent Raman spectra of pyrene (10^{-15} M) on Ag-coated cover-glass at -150°C , collected sequentially in every 1.5 minutes. All measurements were performed at the same ‘hot-spot’ with a relative weaker laser power (15mw)

A brief summary: Low temperature spectra of pyrene molecule also show less spectral-fluctuation than room-temperature spectra do and sudden changes occur with time evolution. It can be concluded that the SM-SERS of the pyrene molecule present similar behaviours as a perylene molecule does. The single molecular motion is not controlled by the spontaneous thermal effect, but mainly driven by a well-defined force as discussed in the main text.

Further useful references:

1. J. Jiang, K. Bosnick, M. Maillard and L. Brus, *J. Phys. Chem. B*, 2003, **107**, 9964-9972.
2. P. J. Moyer, J. Schmidt, L. M. Eng and A. J. Meixner, *J. Am. Chem. Soc.*, 2000, **122**, 5409.
3. Y. Sawai, B. Takimoto, H. Nabika, K. Ajito and K. Murakoshi, *J. Am. Chem. Soc.*, 2007, **129**, 1658.
4. A. Otto, *J. Raman Spectrosc.* 2002, **33**, 593.
5. L. Peyser-Capadona, J. Zheng, J. I. Gonzalez, T. H. Lee, S. A. Patel and R. M. Dickson, *Phys. Rev. Lett.*, 2005, **94**.
6. M. W. Shao, L. Lu, H. Wang, S. Wang, M. L. Zhang, D. D. D. Ma and S.T. Lee, *Chem. Commun.*, 2008, 2310-2312.
7. T. Lemma and R.F. Aroca, *J. Raman Spectrosc.*, 2002, **33**, 197.
8. Z. J. Wang and L. J. Rothberg, *J. Phys. Chem. B*, 2005, **109**, 3387-3391.
9. P. C. Andersen, M. L. Jacobson and K. L. Rowlen, *J. Phys. Chem. B*, 2004, **108** 2148.
10. K. F. Domke, D. Zhang and B. Pettinger, *J. Phys. Chem. C*, 2007, **111**, 8611.
11. M. Futamata, F. Maruyama and M. Ishikawa, *J. Phys. Chem. B*, 2004, **108**, 13119-13127.
12. E. C. Le Ru, P. G. Etchegoin and M. Meyer, *J. Chem. Phys.*, 2006, **125**.
13. C. M. Ruan, W. Wang and B. H. Gu, *J. Raman Spectrosc.*, 2007, **38**, 568.
14. S. Sasic, T. Itoh and Y. Ozaki, *J. Raman Spectrosc.*, 2005, **36**, 593.
15. A. Weiss and G. Haran, *J. Phys. Chem. B*, 2001, **105**, 12348-12354.
16. Z. H. Zhou, G. Y. Wang and Z. Z. Xu, *Appl. Phys. Lett.*, 2006, **88**, 34104.
17. M. Moskovits, *Rev. Mod. Phys.*, 1985, **57**, 783.
18. Z. T. Deng, et. al., *Phys. Rev. Lett.*, 2006, **96**, 156102.