

## Supporting Information

### **Inkjet-Printed Silver Nanoparticle Paper Detects Airborne Species from Crystalline Explosives and Their Ultratrace Residues in Open Environment**

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#### **Abstract**

This supporting information provides the calculation of mean free path  $\lambda$  and other supplement files for the main text list as follows:

Figure S1. The TNT structure-like analytes.

Figure S2. The Raman-active molecules with thiol group.

Figure S3. The SEM and TEM image of AgNPs.

Figure S4. The photos of printed AgNPs papers.

Figure S5. The optical properties of AgNPs papers with different printing layer numbers.

Figure S6. The charge-transfer complexing reaction.

Figure S7. The molecular selectivity of interaction.

Figure S8. The sensitive limit.

Figure S9. The sensitivity of PABT-modified AgNPs papers with different layer numbers.

Figure S10. The selectivity of PABT Raman enhancements.

Figure S11. SERS responses of structure-like Raman-active signal molecules to TNT.

Figure S12. The Raman enhancement vs collecting time.

Figure S13. To detect the odor of the millimeter-sized TNT crystals.

Figure S14. The Raman enhancement vs collecting time.

Figure S15. The sensitivity of AgNPs colloid modified with  $1 \times 10^{-7}$  M PABT to TNT.

Table S1. PABT vibration modes recorded by SERS spectra from the AgNPs papers.

### The calculation of mean free path $\lambda$ :

The mean free path  $\lambda$  is related to the diffusion coefficient  $D$  and the average thermal velocity  $v$ :

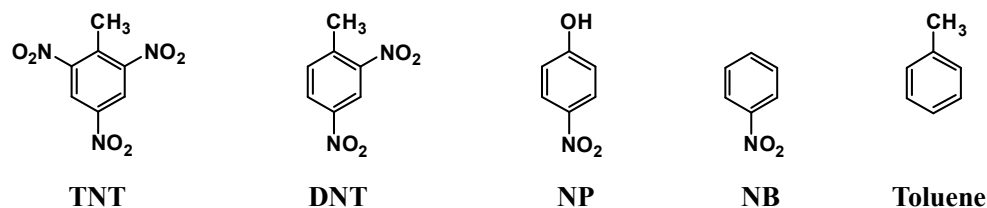
$$\lambda = \frac{3D}{v} \quad (1)$$

$$v = \sqrt{\frac{8k_B T}{\pi M}} \quad (2)$$

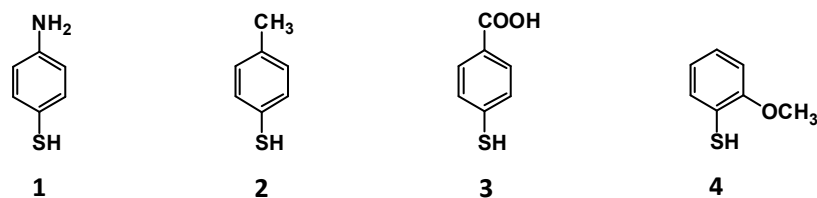
Where  $k_B$  is Boltzman's constant and  $M$  is the weight of a TNT molecule. We use an average value of the TNT diffusion coefficients reported in literature,<sup>1-3</sup>  $D = 5.59 \times 10^{-6} \text{ m}^2/\text{s}$ , and neglect its slight temperature dependence. At the room temperature of 25 °C, the mean free path  $\lambda$  calculated by the eq (1) and (2) is  $3.18 \times 10^{-6} \text{ m}$ .

### References

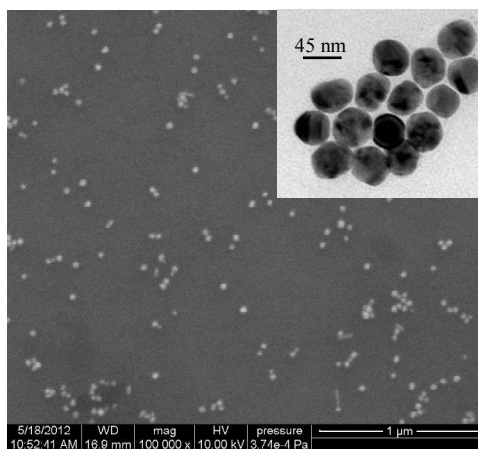
1. McKone, T. E.; Daniels, J. I. *Regul. Toxicol. Pharmacol.* **1991**, *13*, 36-61.
2. Phelan, J. M.; Webb, S. W. *Sandia Report SAND97-1426*, Sandia National Laboratories: Albuquerque, NM. June **1997**.
3. Rosenblatt, D. H.; Burrows, E. P.; Mitchell, W. R.; Parmer, D. L. *In the handbook of environmental chemistry*. Hutzinger, O., Ed. Springer-Verlag: Berlin, **1989**, pp 195-234.



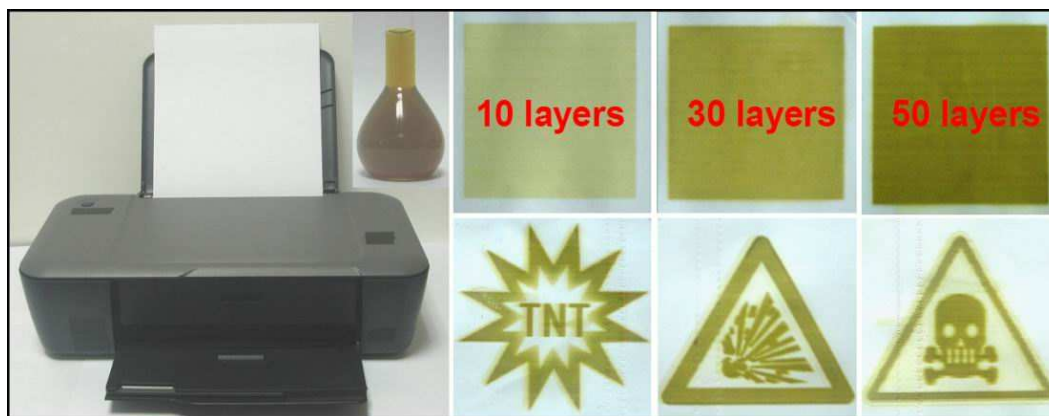
**Figure S1.** The structure-like analytes. 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), nitro phenol (NP), nitro benzene (NB) and toluene.



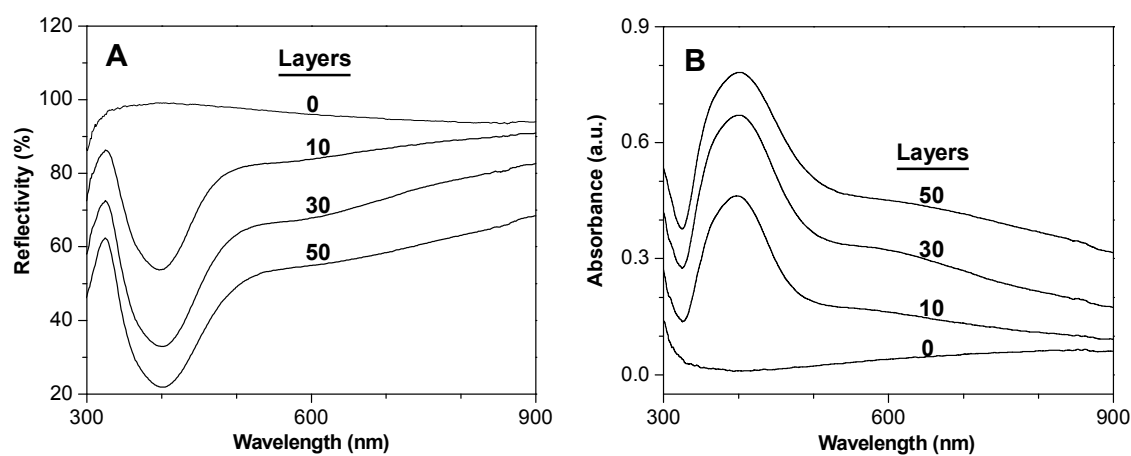
**Figure S2.** The Raman-active molecules with thiol group. (1) *p*-aminobenzenethiol, (2) 4-mercaptotoluene, (3) 4-mercaptobenzoic acid and (4) 2-methoxybenzenethiol.



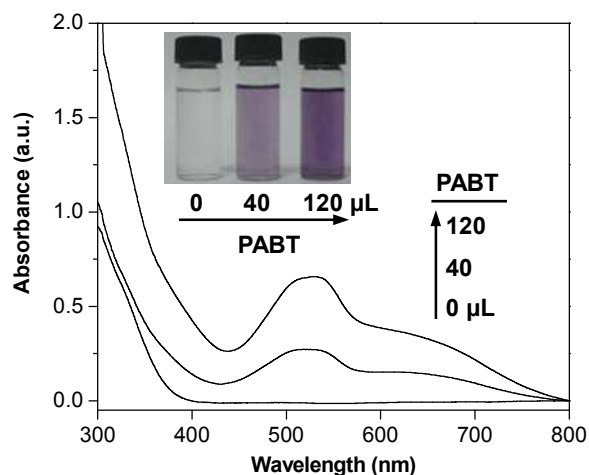
**Figure S3.** The SEM and TEM image of AgNPs. The AgNPs have an average size of  $\sim 45$  nm and show monodispersed morphology.



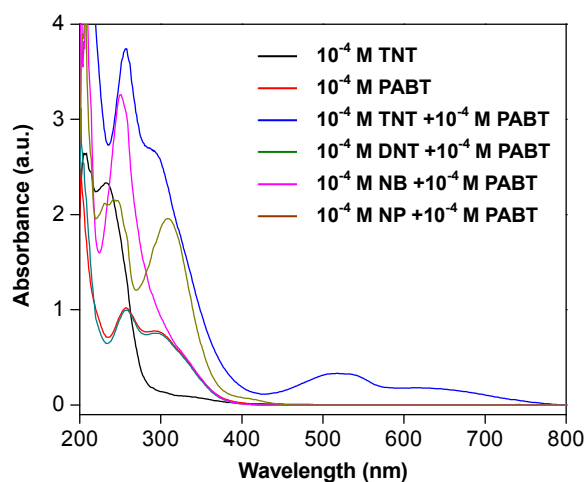
**Figure S4.** The photos of printed AgNPs papers. The AgNPs colloid was used as “ink” and printed by a commercial inkjet printer. The different layers (upper) and the various “signs” or “words” (bottom) on hydrophilic cellulose paper were shown in the images.



**Figure S5.** The optical properties of AgNPs papers with different printing layer numbers. (A) The reflection spectra of AgNPs papers. (B) The corresponding absorption spectra obtained by the transformation of reflection spectra.



**Figure S6.** The charge-transfer complexing reaction. A new visible absorption ranging from 415-800 nm with a peak at 529 nm appears upon the addition of 0.01 M PABT into 4 mL TNT solution (0.1 mM). The absorption intensifies with the increment of PABT amount. Meanwhile, the corresponding color of solution changes gradually from colorless into purple.

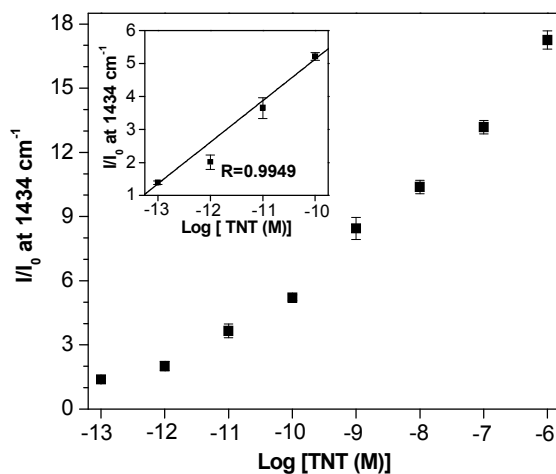


**Figure S7.** The molecular selectivity of interaction. After the addition of TNT, DNT, NB and NP into PABT solution, the UV-vis absorption spectra show that only TNT leads to the appearance of a new visible absorption, suggesting that other structure-like molecules DNT, NB and NP cannot form the charge-transfer complex with PABT.

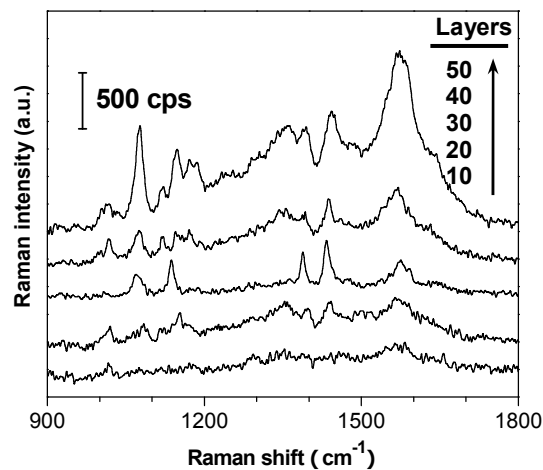
**Table S1.** PABT vibration modes recorded spectra from the AgNPs papers.

1008	$\gamma_{CC} + \gamma_{CCC} (\nu_{18a})$	by SERS
1078	$\nu_{CS} (\nu_{7a})$	
1142	$\delta_{CH} (\nu_{9b})$	
1192	$\delta_{CH} (\nu_{9a})$	
1307	$\nu_{CC} + \delta_{CH} (\nu_{14})$	
1392	$\delta_{CH} + \nu_{CC} (\nu_3)$	
1434	$\nu_{CC} + \delta_{CH} (\nu_{19b})$	
1578	$\nu_{CC} (\nu_{8a})$	

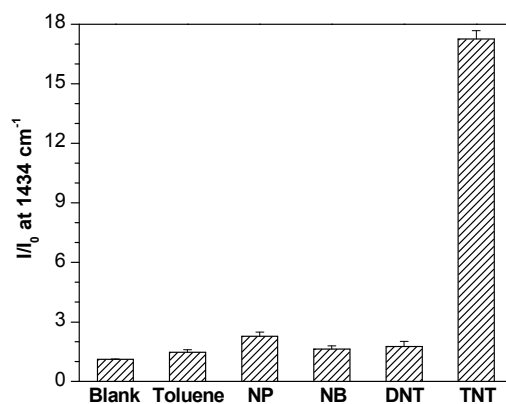
Approximate description the modes of PABT ( $\nu$ , stretch;  $\delta$  and  $\gamma$ , bend).



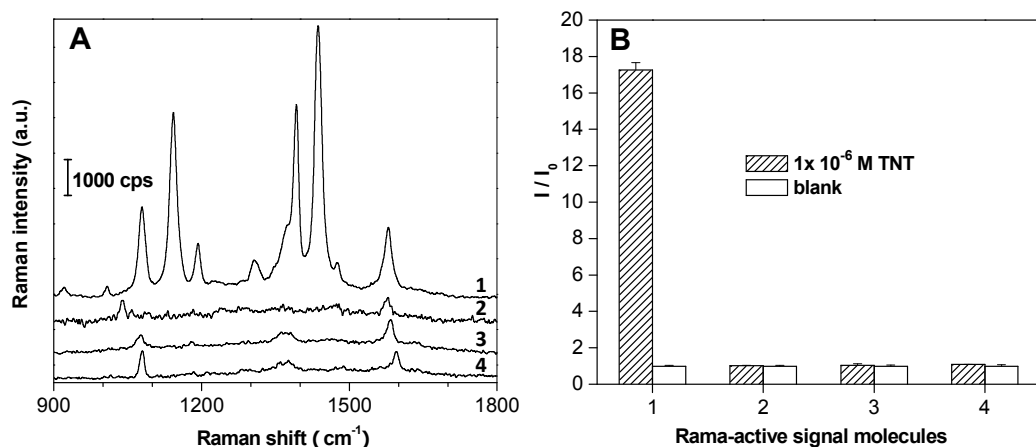
**Figure S8.** The sensitive limit. The Raman enhancement ( $I/I_0$  at  $1434\text{ cm}^{-1}$ ) correlates with the logarithm of TNT concentrations. The linear regression equation is  $y = 17.712 + 1.258x$ , and thus deduces a theoretical detection limit of  $1.1 \times 10^{-14}\text{ M}$  TNT based on  $3\sigma$  of the blank signals. Here,  $I$  and  $I_0$  represent the Raman intensities at  $1434\text{ cm}^{-1}$  after the addition of TNT analyte and pure ethanol, respectively.



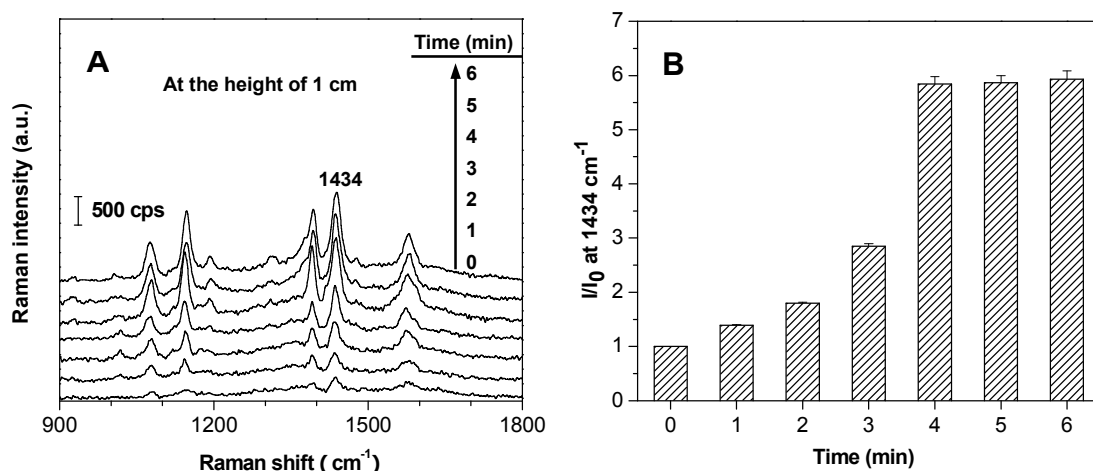
**Figure S9.** The sensitivity of PABT-modified AgNPs papers with different layer numbers. Raman spectra were taken from the PABT-modified AgNPs papers after  $1 \times 10^{-13}$  M TNT ethanol was added.



**Figure S10.** The selectivity of PABT Raman enhancements. The Raman enhancement of PABT ( $I/I_0$  at  $1434 \text{ cm}^{-1}$ ) after the additions of  $1.0 \times 10^{-6}$  M toluene, nitrophenol (NP), nitrobenzene (NB), dinitrotoluene (DNT) and TNT ( $I$  and  $I_0$  represent the Raman intensity in the presence and absence of analytes, respectively).

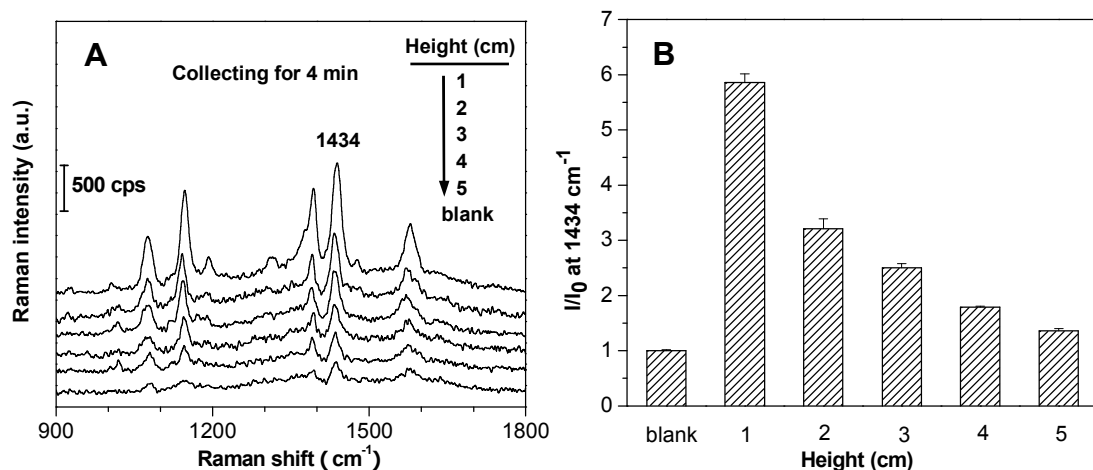


**Figure S11.** SERS responses of structure-like Raman-active signal molecules to TNT. AgNPs papers were individually modified with (1) PABT, (2) 2-methoxybenzenethiol, (3) 4-mercaptotoluene and (4) 4-mercaptobenzoic acid. (A) After dropping 5  $\mu\text{L}$  of  $1.0 \times 10^{-6}$  M TNT solution on these papers, Raman spectra show that only PABT exhibits the remarkable Raman enhancement due to the specific complexing reaction. (B) The obtained Raman enhancement ( $I/I_0$ ) by the intensity of the strongest peak on the above four AgNPs papers. The strongest peaks of PABT, 2-methoxybenzenethiol, 4-mercaptotoluene and 4-mercaptobenzoic acid are at  $1434$ ,  $1041$ ,  $1083$  and  $1587$   $\text{cm}^{-1}$ , respectively.

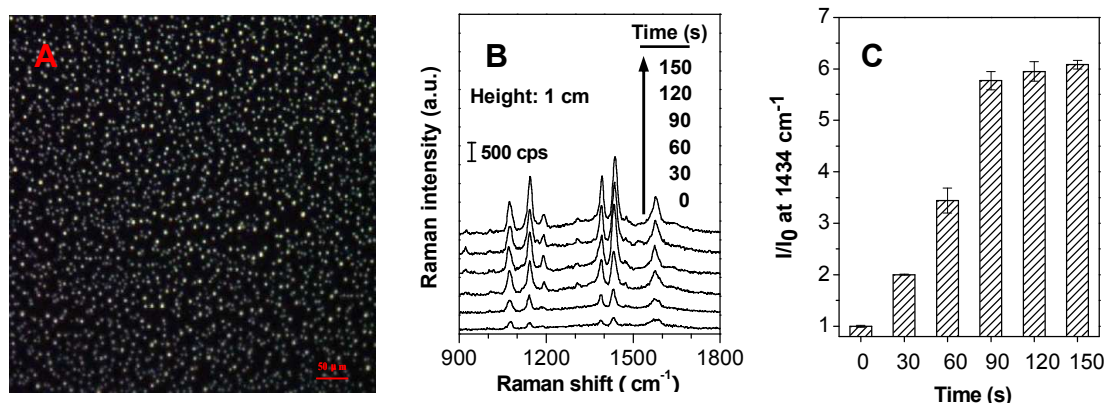


**Figure S12.** The Raman enhancement vs collecting time. The AgNPs papers were located at the height of 1 cm to collect the vapor of millimeter-sized TNT crystals while the laser illuminated the TNT crystals. (A) The SERS spectra of PABT obtained from the paper at the collecting time as indicated. (B) The Raman enhancements ( $I/I_0$  at  $1434$   $\text{cm}^{-1}$ ) vs the collecting time. The data show that the SERS intensity reaches the largest value after 4 min because the modified PABT molecules are completely saturated by TNT.

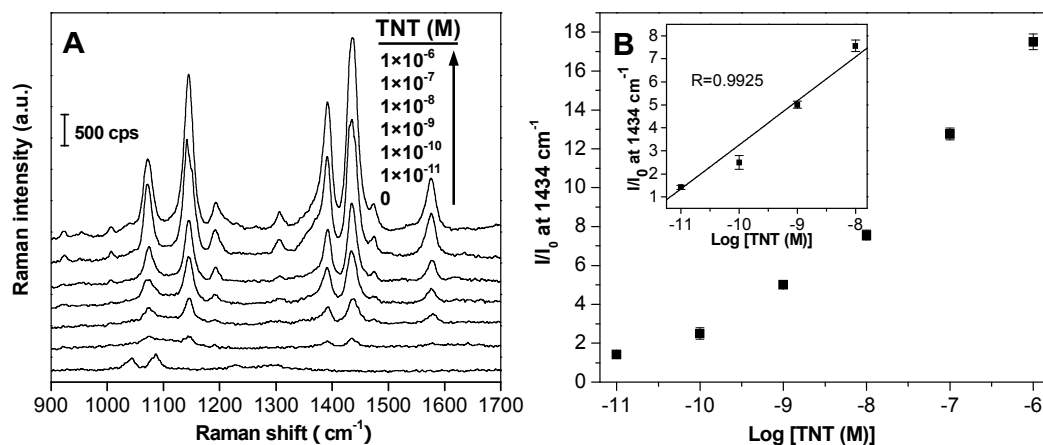




**Figure S13.** To detect the odor of the millimeter-sized TNT crystals. The needle-like TNT crystals were placed on a piece of metal slide, and illuminated with a beam of continuous near-infrared laser (1064 nm) with a low energy of 5 w and a spot of 1-mm diameter. The shape of TNT crystals was still kept under the low energy, and the AgNPs paper was located at a defined height upper the TNT crystals to collect the vapor of TNT. (A) Raman spectra obtained from the AgNPs papers at different heights to collect for 4 min. (B) The Raman enhancements ( $I/I_0$  at 1434 cm<sup>-1</sup>) vs the heights.



**Figure S14.** The Raman enhancement vs collecting time. The AgNPs papers were located at the height of 1 cm to collect the vapor of TNT microcrystals (7-8 μm) while the laser illuminated TNT microcrystals. (A) The image of the TNT microcrystals by an optical microscope to magnify by 500 folds. (B) The SERS spectra of PABT obtained from the paper at the collecting time as indicated. (C) The Raman enhancements ( $I/I_0$  at 1434 cm<sup>-1</sup>) vs the collecting time. The data show that the SERS intensity reaches the largest value after 90 s because the modified PABT molecules are completely saturated by TNT.



**Figure S15.** The sensitivity of AgNPs colloid modified with  $1 \times 10^{-7}$  M PABT to TNT. (A) Significant Raman enhancements of PABT were observed upon the addition of TNT solution with different concentrations into the PABT-modified AgNPs colloid. (B) The Raman enhancement ( $I/I_0$  at 1434 cm<sup>-1</sup>) correlates with the logarithm of TNT concentrations, and  $I$  and  $I_0$  represent the Raman intensities at 1434 cm<sup>-1</sup> after the addition of TNT analyte and pure water, respectively. The linear regression equation is  $y = 22.357 + 1.909x$ , and thus deduces a theoretical detection limit of  $2.5 \times 10^{-12}$  M TNT based on  $3\sigma$  of the blank signals.