Electronic Supplementary Information

A versatile platform of catechol-functionalized polysiloxanes for hybrid nanoassembly and *in situ* surface enhanced Raman scattering applications

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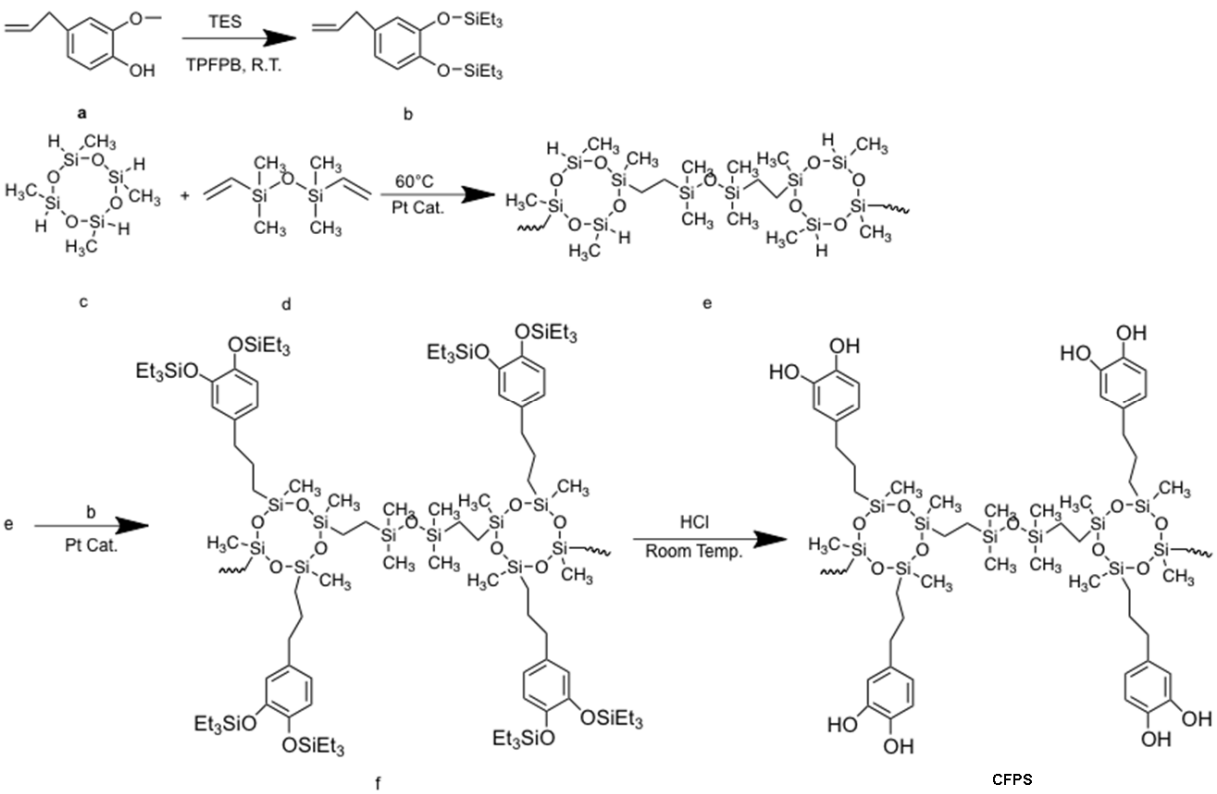


Fig. S1. Synthesis route of CFPS.

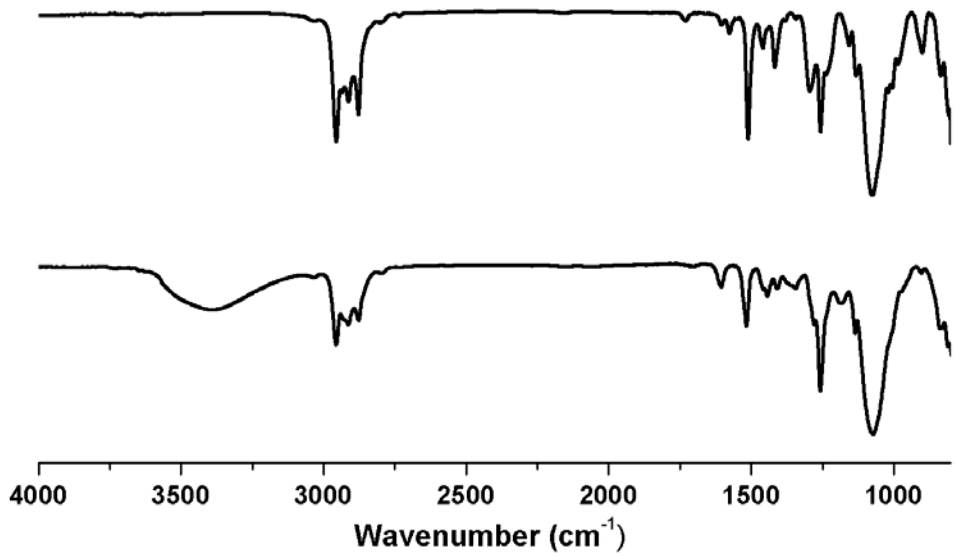


Fig. S2. FTIR spectra of CFPS (top) before and (bottom) after deprotection.

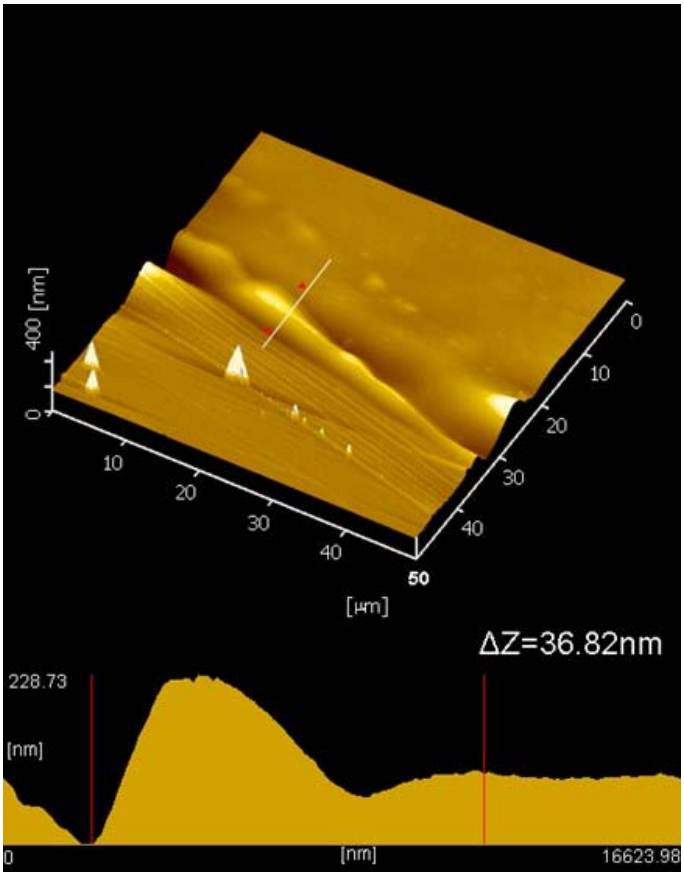
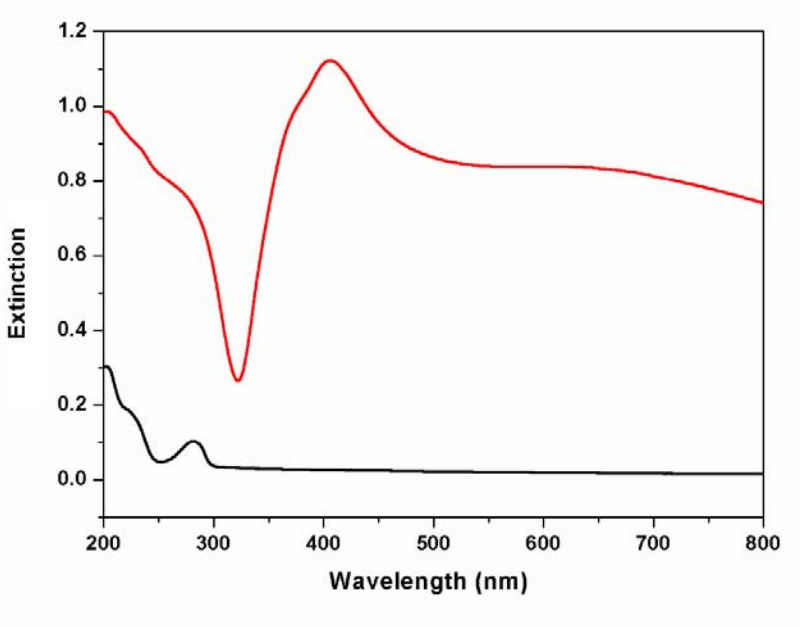


Fig. S3. (top) AFM image of pristine CFPS film prepared on Si wafer and (bottom) cross-section of CFPS film in the top image highlighted with the white bar.



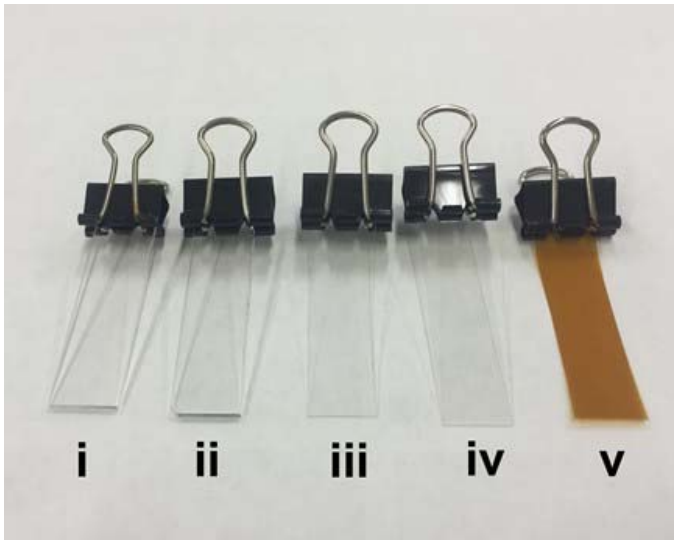


Fig. S4. (top) UV-Vis extinction spectra of CFPS film (black) and CFPS/AgNP assembly (red) on quartz. (bottom) Photograph of CFPS film coated onto (i) quartz, (ii) glass, (iii) PMMA, (iv) PET, and (v) PI substrates.

Surface energy

The surface energy of CFPS and CFPS/AgNP nanoassemblies was calculated by using Owens and Wendt formula:

$$1 + \cos\theta_1 = 2\left[\frac{\left(\gamma_s^d \gamma_{L_1}^d\right)^{1/2}}{\gamma_{L_1}} + \frac{\left(\gamma_s^p \gamma_{L_1}^p\right)^{1/2}}{\gamma_{L_1}}\right]$$

$$1 + \cos\theta_2 = 2\left[\frac{\left(\gamma_s^d \gamma_{L_2}^d\right)^{1/2}}{\gamma_{L_2}} + \frac{\left(\gamma_s^p \gamma_{L_2}^p\right)^{1/2}}{\gamma_{L_2}}\right]$$

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

In these equations, θ_i (i = 1 and 2) is contact angle. γ_s and γ_{L_i}(i=1, 2) signify the surface free energy of solid and liqud. γ_s^d ($\gamma_{L_i}^d$) and γ_s^p ($\gamma_{L_i}^p$) respectively represent the dispersive and polar components of γ_s (γ_{L_i}). Water and diiodomethane were choosen as testing liquid; γ_{water} = 72.8 mN/m (γ_{water}^d = 21.8 mN/m and γ_{water}^p = 51 mN/m), and γ_{MeI_2} = 50.8 mN/m ($\gamma_{MeI_2}^d$ = 50.8 mN/m and $\gamma_{MeI_2}^p$ = 0 mN/m). The results are summarized in Table S1.

Table S1. Contact angles and surface free energy for CFPS and CFPS/AgNP nanoassemblies.

	Contact angle (deg)		Surface free energy (mN/m)		
Sample	θ_{water}	θ_{MeI2}	γ_s^d	γ_s^p	γ_s
CFPS	57.4	82.1	30.04	4.78	34.82
CFPS/AgNP	56	97.4	30.87	0.422	31.292

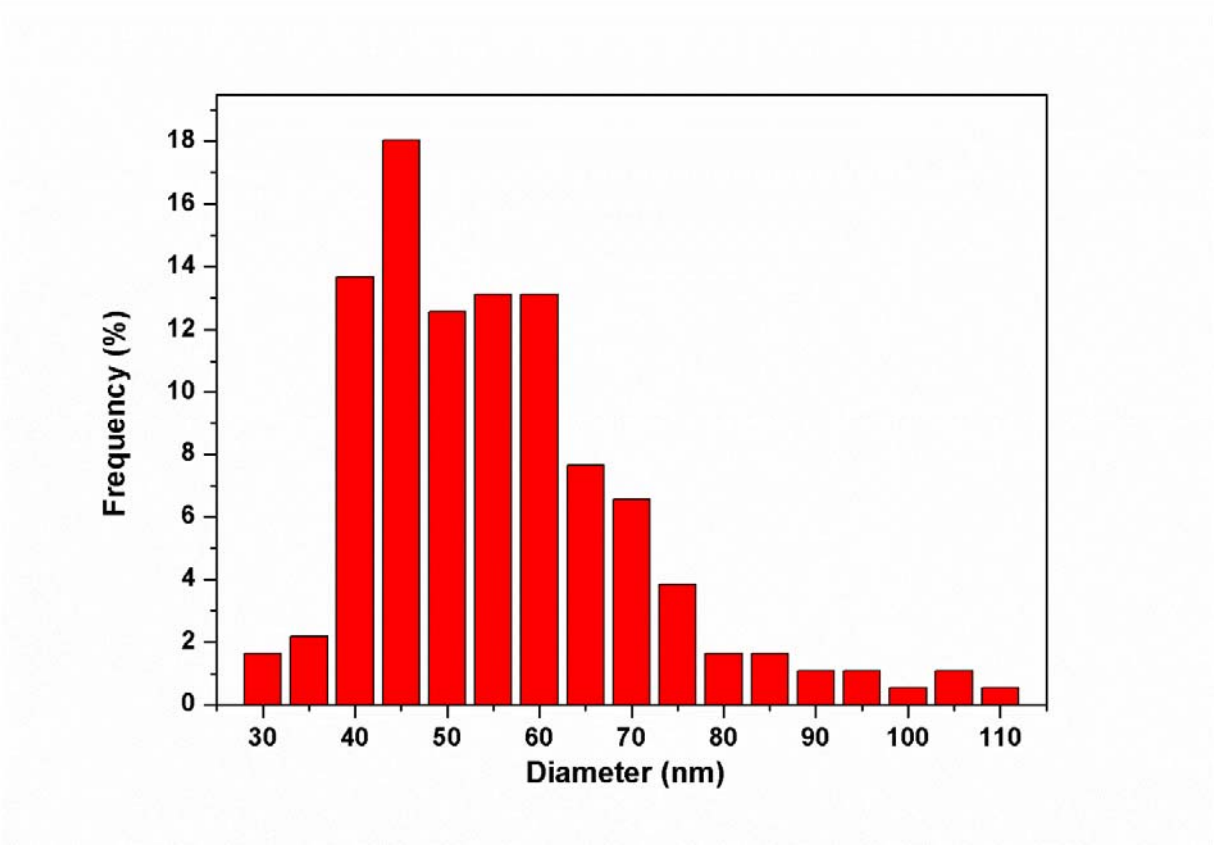


Fig. S5. Size distribution histogram of AgNPs.

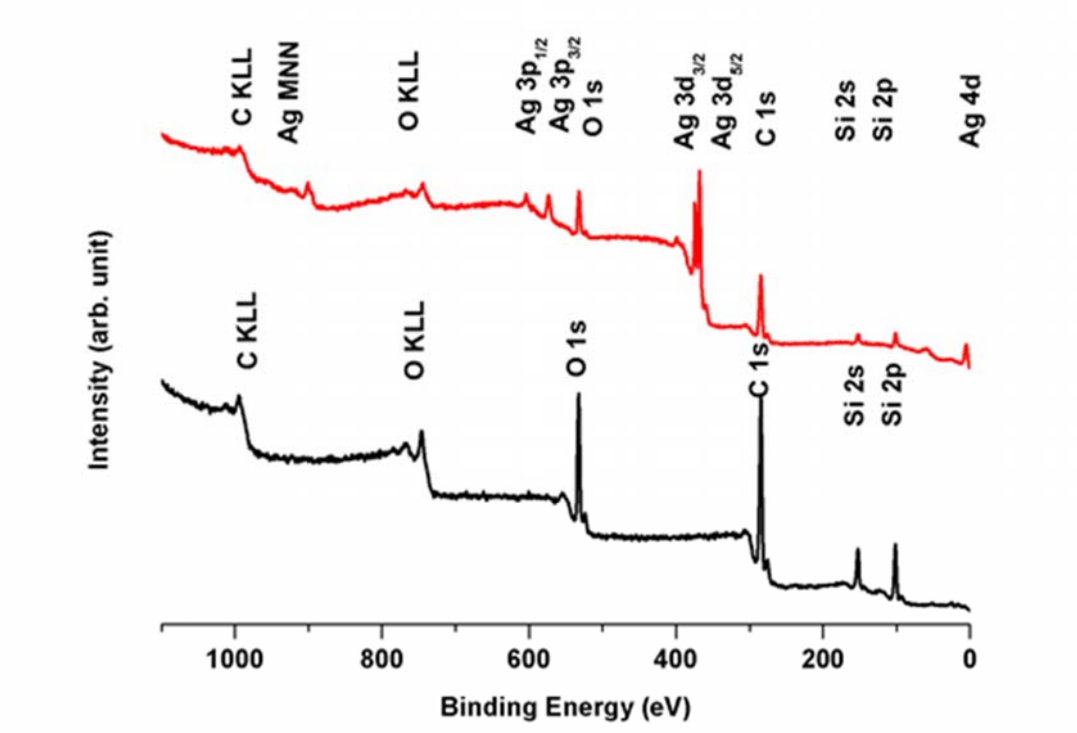


Fig. S6. XPS spectra of CFPS film (black) and CFPS/AgNP nanoassembly (red).

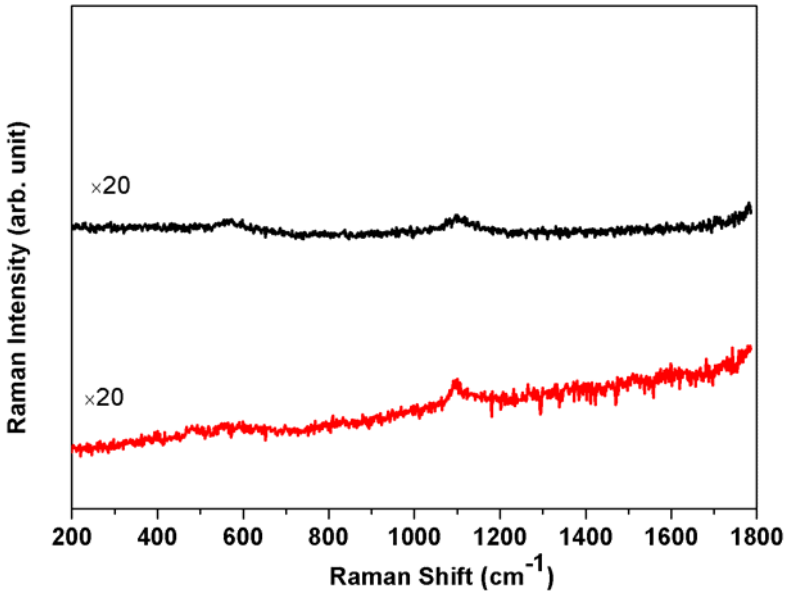


Fig. S7. Raman spectra of pristine CFPS (red) and CFPS/AgNP nanoassembly (black).

Calculation of enhancement factors for CFPS/AgNP nanoassemblies

We conducted calculations using a method similar to that described in an earlier report.[S1] For a solid PATP sample, because the spot activated by the laser was a 1-μm-diameter circle, and because the depth that the laser could reach was around 20 μm, according to the density (1.18 g/cm^3) and molecular weight (125.19) of solid PATP, the number of PATP molecules activated in the bulk solid (N_{bulk}) can be determined as shown below.

$$N_{bulk} = \frac{\pi\left(\frac{d_{spot}}{2}\right)^2 D\rho_{PATP}N_A}{M_{r,PATP}}$$

Therein, d_{spot} stands for the diameter of circular laser spot, D signifies the depth of the incident laser beneath the surface of PATP solid, ρ_{PATP} and $M_{r,\,PATP}$ respectively denote the density and molecular weight of PATP, and N_A represents the Avogadro constant. The N_{bulk} was determined as 8.91×10^{10}.

For the PATP molecules adsorbed onto the CFPS/AgNP nanoassembly film, we assumed that the PATP molecules take a vertical orientation on the surface and that the area occupied by a single PATP molecule is regarded as equal to the cross-sectional area of the molecule.[S2] Reportedly, each PATP molecule occupies an area S_{PATP} = 0.20 nm^2 on the Ag surface.[S3] According to the surface morphology of CFPS/AgNP, different sample footprint areas covered by AgNP are 4%, 10%, 63%, and 71% respectively. The number of PATP molecules activated on the surface of CFPS/AgNP, i.e. N_{surf}, is calculated as shown below.

$$N_{surf} = \frac{\pi\left(\frac{d_{spot}}{2}\right)^2}{S_{PATP}} A_{cover\ ratio}$$

Then Raman scattering intensities at 1582 cm^{-1} and 1444 cm^{-1} are used to calculate EF of a_1 and b_2 vibration according to the following equation.

$$\mathrm{EF} = \frac{N_{bulk} I_{surf}}{N_{surf} I_{bulk}}$$

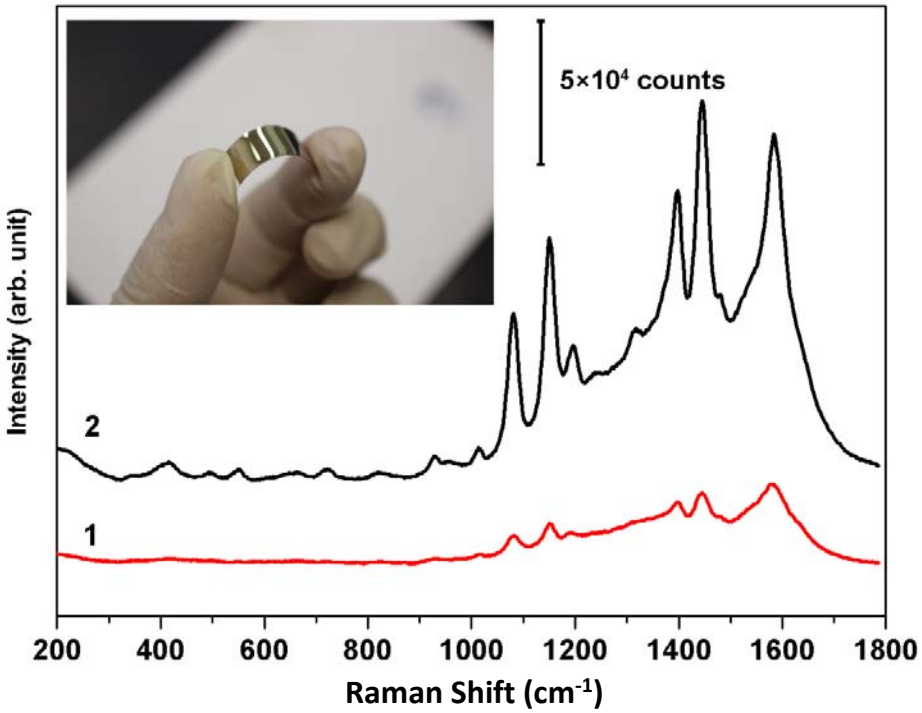


Fig. S8. PMMA based flexible CFPS/AgNP substrate on the left corner and Line 1 and Line 2 enhancement signal using 0.1 nM and 1 mM PATP ethanol solution, respectively, on PMMA based flexible CFPS/AgNP substrate.

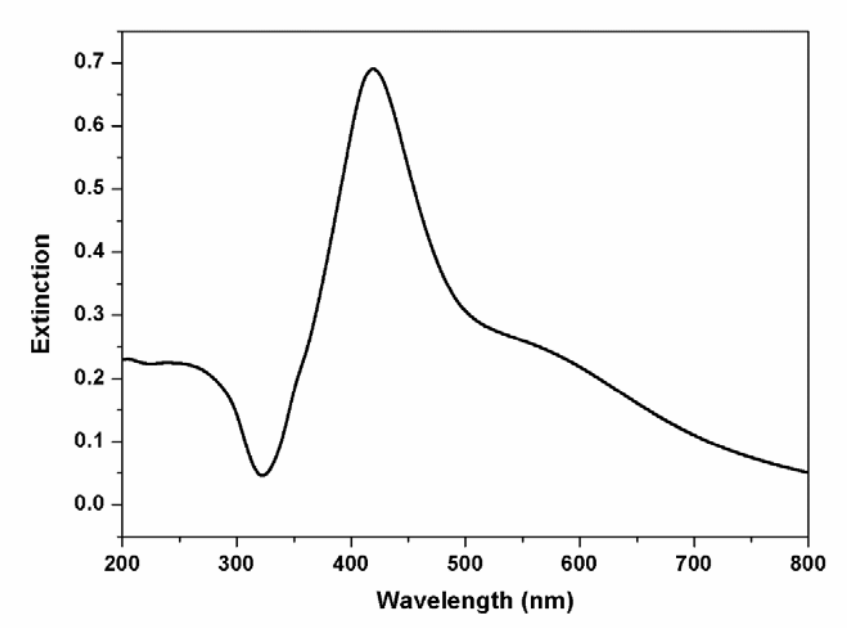


Fig. S9. Extinction spectrum of Ag NPs in solution (0.5 mgL^{-1}).

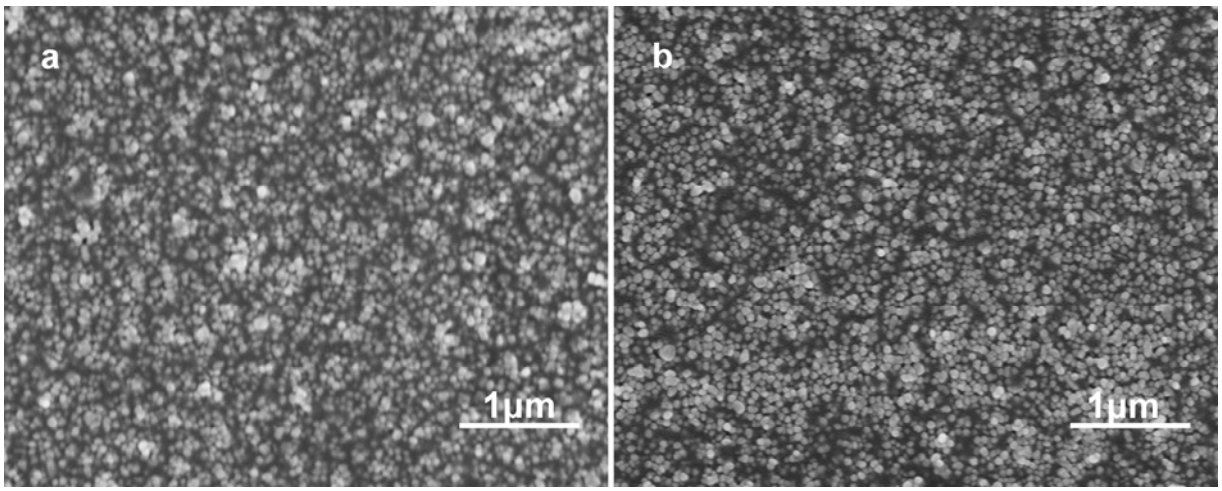


Fig. S10. CFPS/AgNP nanoassembly substrate (a) before and (b) after in-situ testing. No surface morphology change was visible.

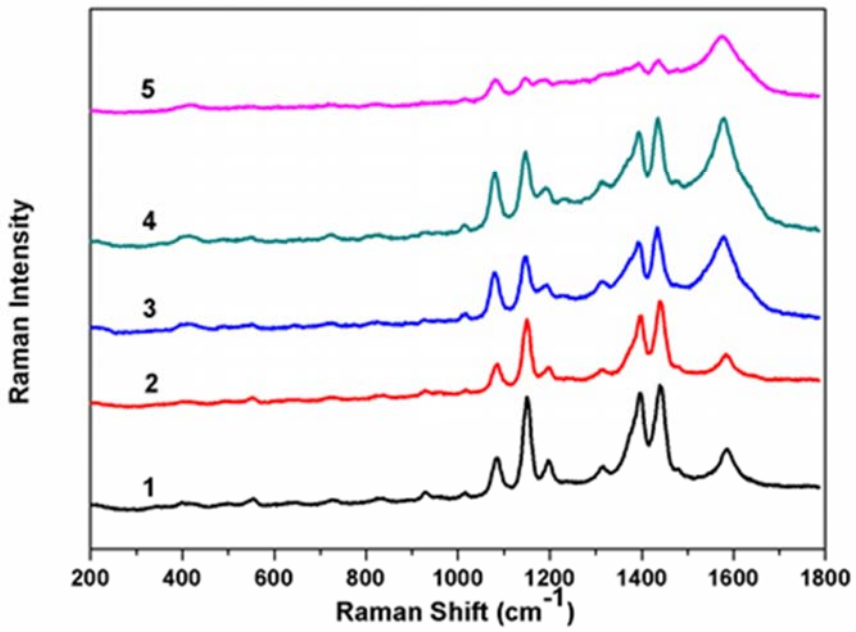


Fig. S11. Raman spectra of PATP molecules on CFPS/AgNPs nanoassemblies at different temperatures. Line 1-5 were measured respectively at 30, 70, 150, 180, and 190°C in Ar atmosphere. The signal was decreased at 190°C. A temperature controlled microscope stage (model 10033, JAPAN HIGH TECH) was used and samples were kept for 30 min before testing at each temperature.

References

[S1] Hong, G.; Li, C.; Qi, L. *Adv. Fun. Mat*. **2010**, *20*, 3774.

[S2] Lu, Z.; Ruan, W.; Yang, J.; Xu, W.; Zhao, C.; Zhao, B. *J. Raman Spectrosc*. **2009**, *40*, 112.

[S3] Wang, Y.; Zou, X.; Ren, W.; Wang, W.; Wang, E. *J. Phys. Chem. C* **2007**, *111*, 3259.