Supporting Information

The Role of Herzberg-Teller Vibronic Coupling on Surface-enhanced Resonance Raman Spectra of 4,4'-diaminotolane with Nearly Close Molecular and Charge-transfer Transitions

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Table S1. The parameters of SERS spectra acquisition.

Laser line	Laser power	Confocal hole/ Pinhole	Diffraction grating	Spectral resolution	Accumulation time[a]	Number of acquisitions
nm	mW	μm	gr/mm	cm^{-1}	s	
488	20	150	1800	2	20(60)	2
514	20	150	1800	2	20(60)	2
532	20	25x1000	1200	5	20(60)	2
633	20	150	1800	1	20(60)	2
785	20	25x1000	1200	3	20(60)	2

[a] for the spectra measured on silver; in brackets - for the spectra measured on gold.

Table S2. Vibrational frequency (in cm^{-1}), dimensionless displacement and transition dipole-moment derivatives (in a.u.) for $S_8^{Ag_6-comp}$and $S_9^{DAT-comp}$transitions.

ω_k	$\Delta_k^{S_8}$	$\Delta_k^{S_9}$	$(\Delta\mu_{S_8}/\Delta Q_k)_0$	$(\Delta\mu_{S_9}/\Delta Q_k)_0$
455.9	0.10	0.04	8.98E-08	3.51E-06
482.5	0.04	0.04	1.99E-06	2.27E-05
506.4	0.02	0.19	3.06E-07	3.29E-08
523.6	0.01	0.18	6.01E-07	4.09E-07
532.2	0.01	0.17	5.45E-07	5.52E-06
609.9	0.09	0.17	1.38E-07	3.62E-06
692.4	0.02	0.33	1.65E-06	7.60E-06
751.7	0.23	0.09	4.46E-07	9.37E-06
783.9	0.11	0.05	1.46E-06	7.59E-07
791.4	0.21	0.04	5.79E-07	1.81E-05
799.2	0.66	0.20	3.67E-06	1.70E-04
833.3	0.07	0.04	1.33E-08	3.86E-07
872.4	0.00	0.04	1.01E-05	3.57E-05
893.6	0.01	0.09	2.32E-07	1.61E-06
894.7	0.01	0.20	1.06E-06	2.37E-06
976.2	0.01	0.19	1.88E-06	1.05E-04
980.4	0.04	0.32	2.23E-06	1.00E-04
1105.6	0.35	0.27	1.31E-04	2.68E-03
1142.3	0.03	0.01	6.36E-06	4.53E-05
1149.7	0.06	0.32	5.91E-06	7.79E-05
1204.9	0.05	0.05	9.47E-06	3.00E-05
1262.3	0.07	0.04	2.16E-06	4.30E-05
1457.7	0.04	0.10	4.19E-05	1.44E-03
1480.6	0.01	0.07	1.98E-06	4.46E-05
1561.9	0.52	0.53	9.40E-05	1.19E-03
1565.4	0.24	0.17	1.28E-04	2.43E-03
1571.1	0.12	0.14	8.67E-05	1.07E-03
1582.4	0.04	0.23	1.23E-05	4.18E-04
2168.4	0.33	0.54	8.35E-04	2.70E-02

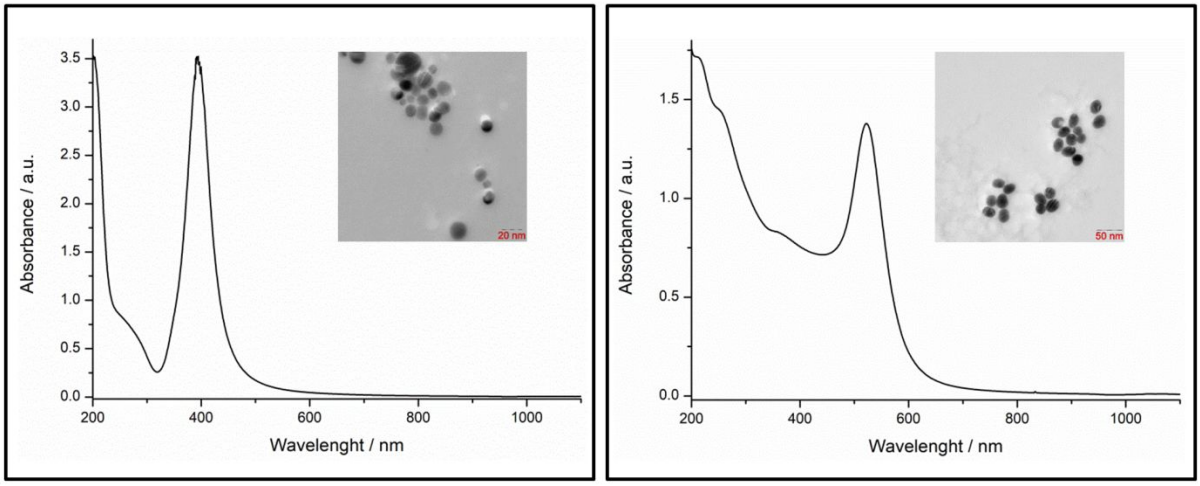

Figure S1. The UV-Vis spectra and TEM images of obtained silver (left) and gold (right) colloids.

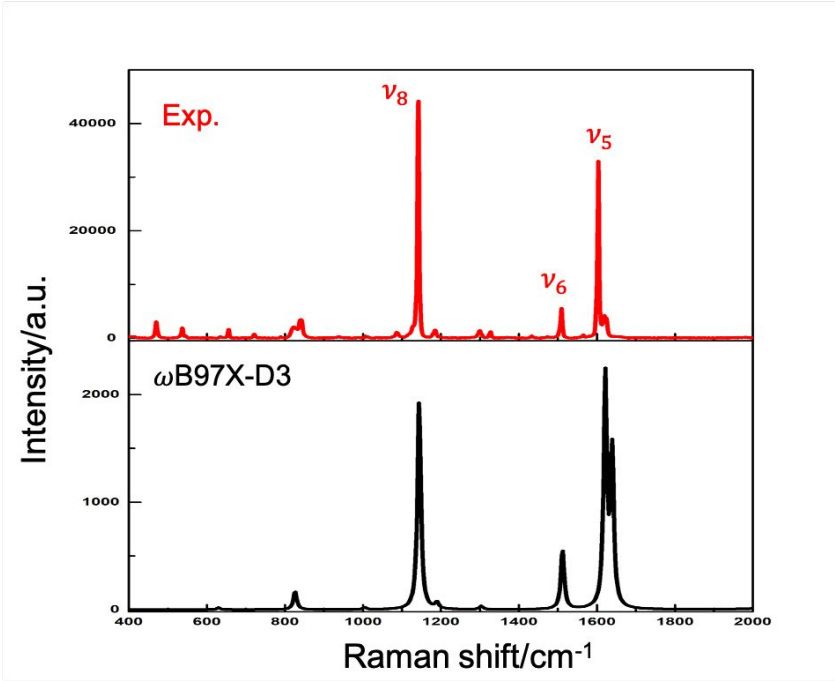

Figure S2. Comparison of the experimental and calculated normal Raman spectra of DAT.

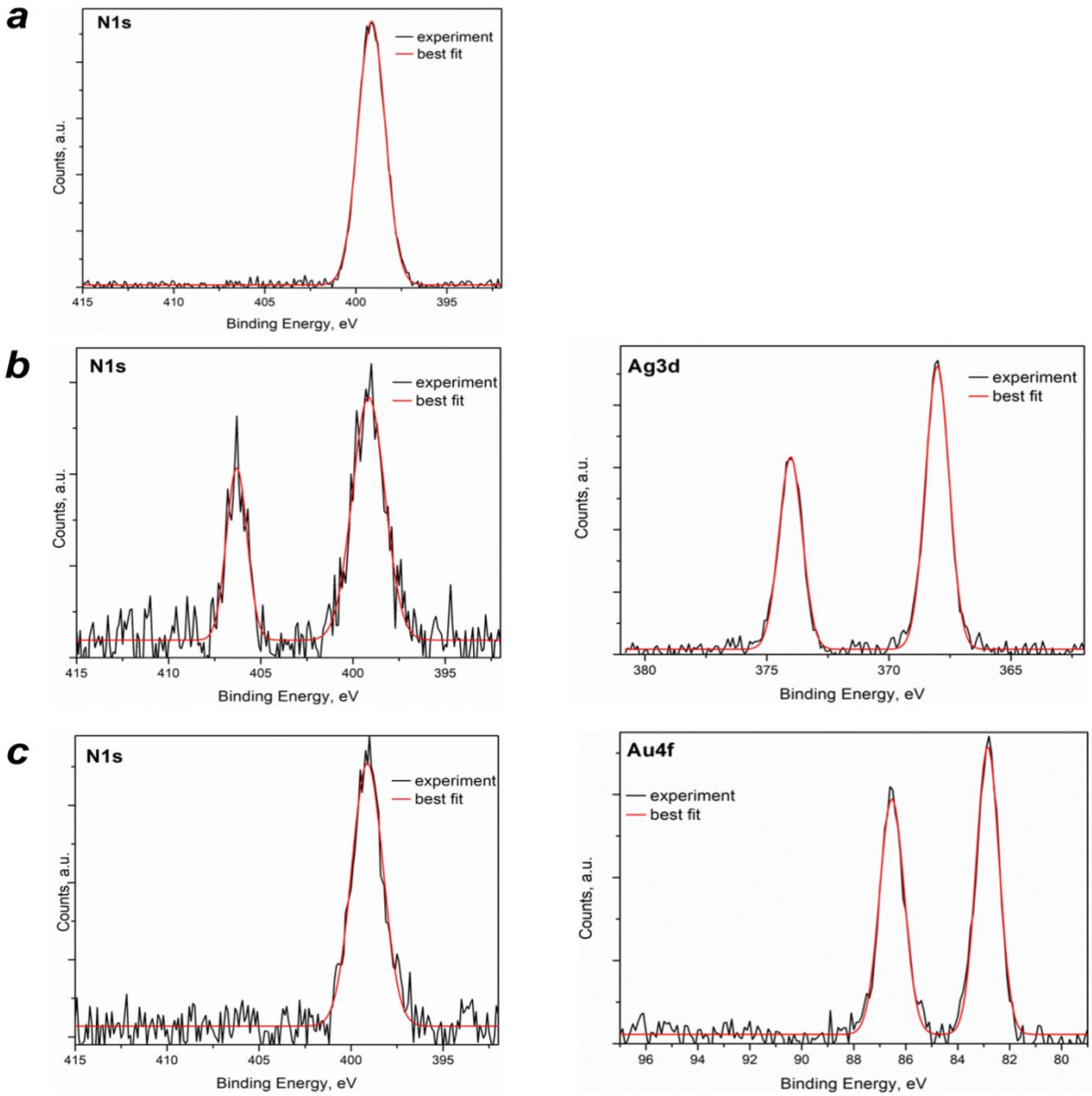

Figure S3. The XPS spectra of N1s, Ag3d and Au4f core levels for solid DAT (a), DAT in silver colloid (b) and DAT in gold colloid (c). In the N1s range of DAT in silver colloid, the peak near 407 eV corresponds to nitrate anions remaining after nanoparticles synthesis.

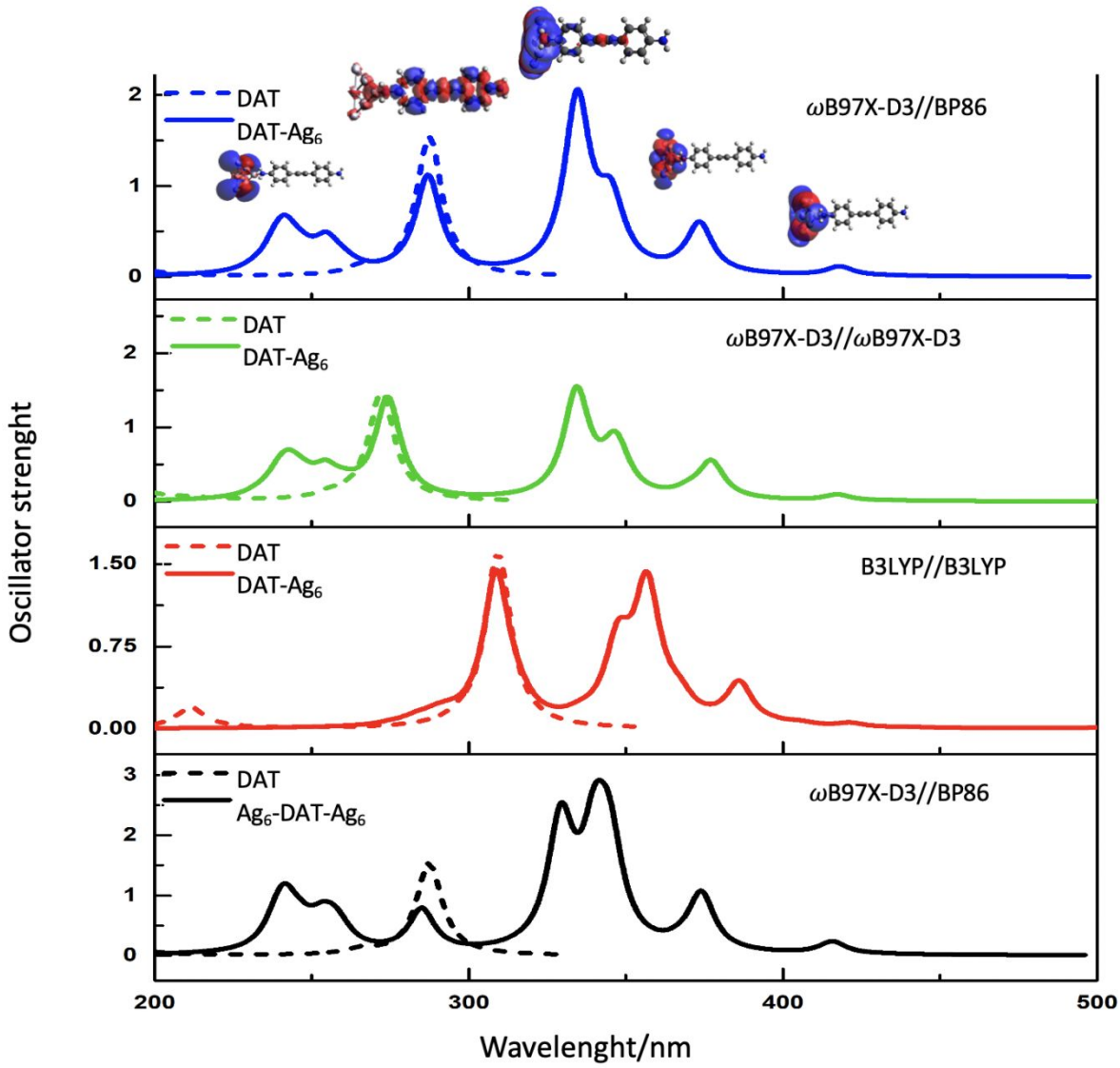

Figure S4. The calculated UV-Vis absorption spectra for DAT and DAT-Ag_6 with different DFT functionals. The spectra have been broadened with σ = 15 nm Lorentzian.

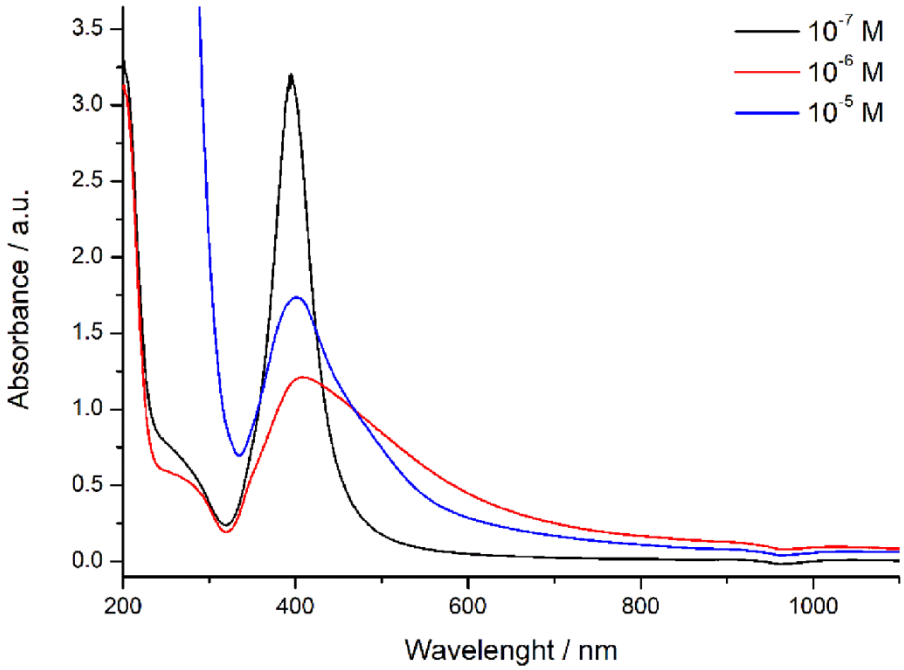

Figure S5. The UV-Vis absorption spectra of silver colloid with indicated concentrations of DAT.

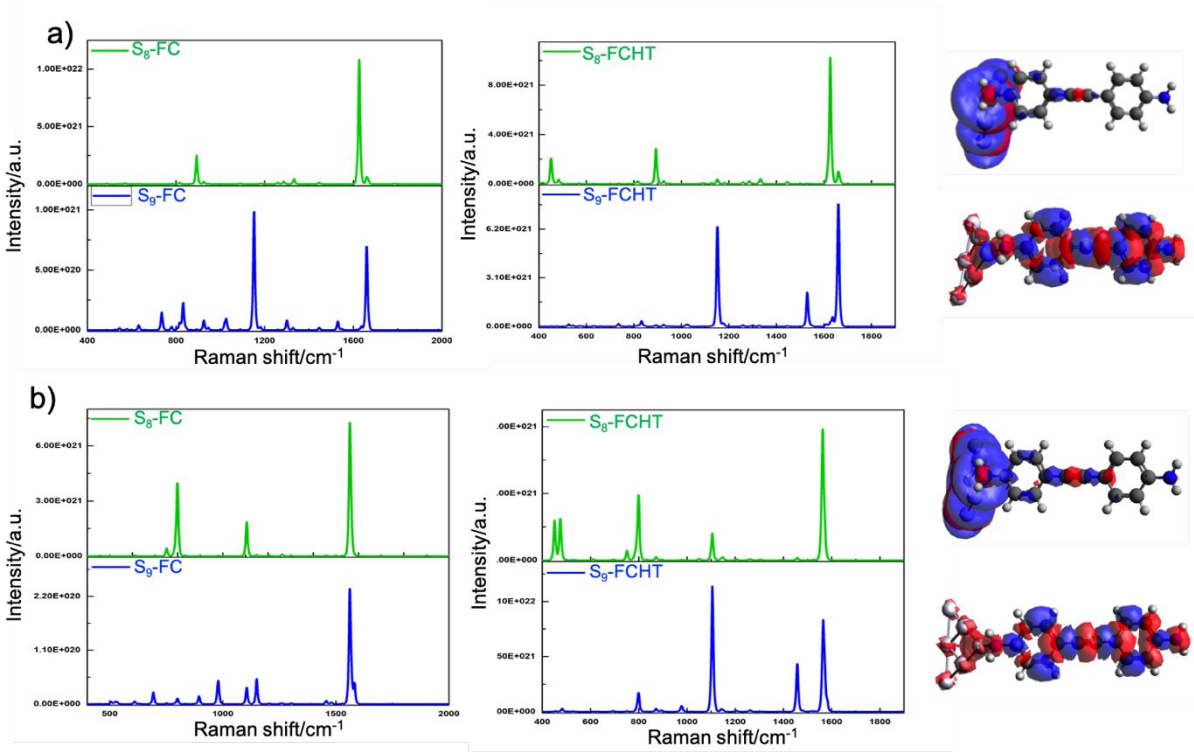

Figure S6. The calculated SERS spectra of DAT–Ag_6 including Herzberg-Teller term, using incident light wavelength equals to 410 nm (3.02 eV) at a) ωB97X-D3//ωB97X-D3 and b) ωB97X-D3//BP86 level of theory.

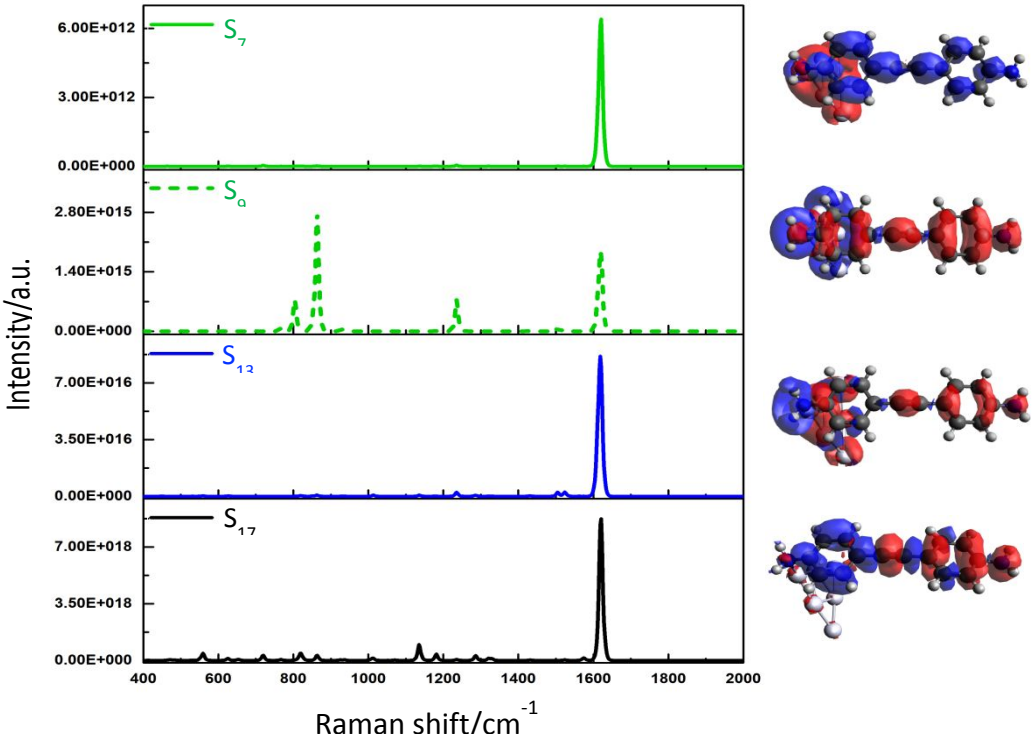

Figure S7. The calculated SERS spectra of DAT–Ag_6 including Herzberg-Teller term, using incident light wavelength equals to 417 nm (2.97 eV) at B3LYP level of theory.

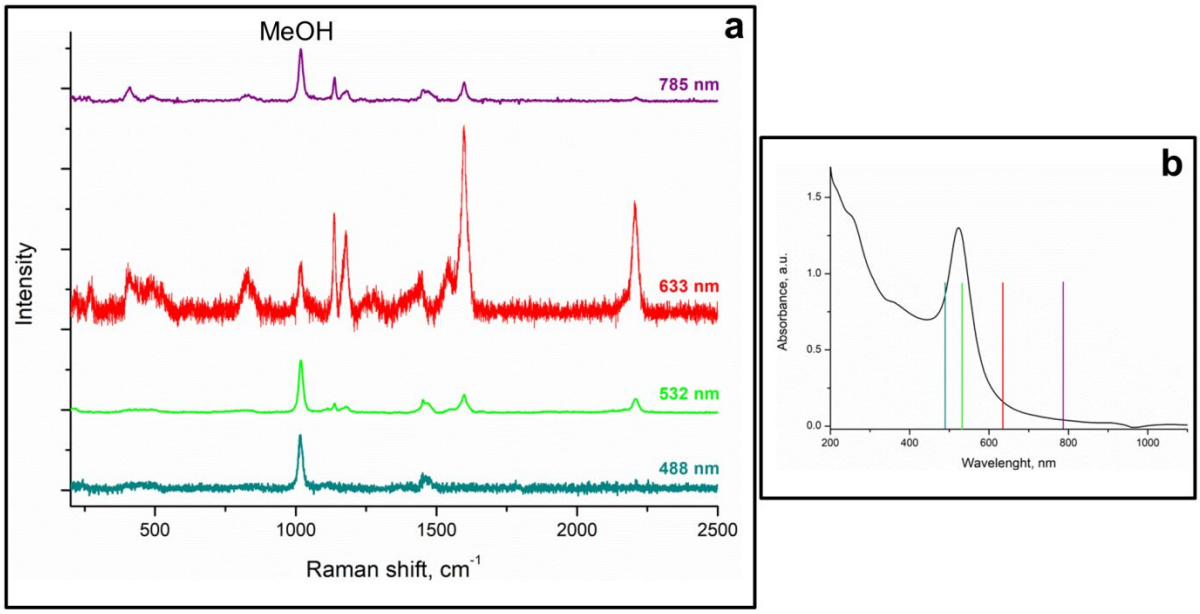

Figure S8. (a) The SERS spectra of DAT in gold colloid at the indicated excitation wavelengths. The spectra were baseline subtracted and normalized on the methanol band at 1018 cm^{-1} (b) the UV-Vis spectrum of gold colloid with DAT (10^{-6} M). The excitation wavelengths used in the SERS measurements are indicated as the vertical lines.