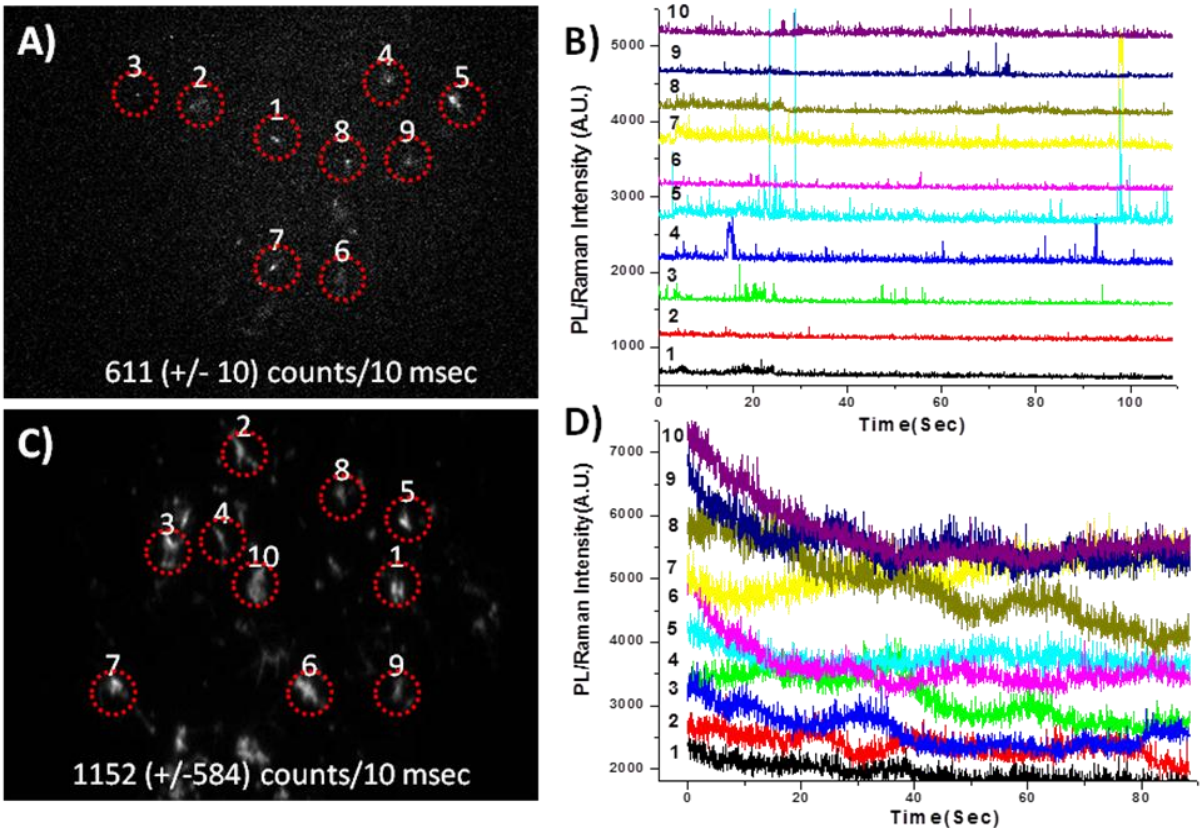
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
This journal is © The Owner Societies 2012

Supporting information

Spatial and Temporal Variation of Surface-Enhanced Raman Scattering at Ag Nanowires in Aqueous Solution

Daniel A. Clayton, Tyler E. McPherson, Caleb M. Hill, Shanlin Pan,* Mingyang Chen, and David A. Dixon*
The University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487-0336
Dehong Hu
Fundamental and Computational Science Directorate, Pacific Northwest National Laboratory, PO Box 999, Richland, WA 99352
*Corresponding Authors: span1@bama.ua.edu; dadixon@as.ua.edu

Figure S1. (A) Raman image of single Ag NWs under DI water. The mean counts of this image are 611 (+/- 10). (B) Corresponding Raman trajectories from ten selected spots of Ag NWs from (A). (C) Raman image of Ag NWs coated with a 1 mM mercaptopyridine aqueous solution. (D) Corresponding Raman trajectories of ten selected spots from (C).



This journal is © The Owner Societies 2012

Figure S2. Polarization dependence of photoluminescence background of bundles of purified Ag NWs. Image size: 50 μm×50 μm. Polarization angle of incident laser is scanned from 0 to 180 degree while the sample is fixed.

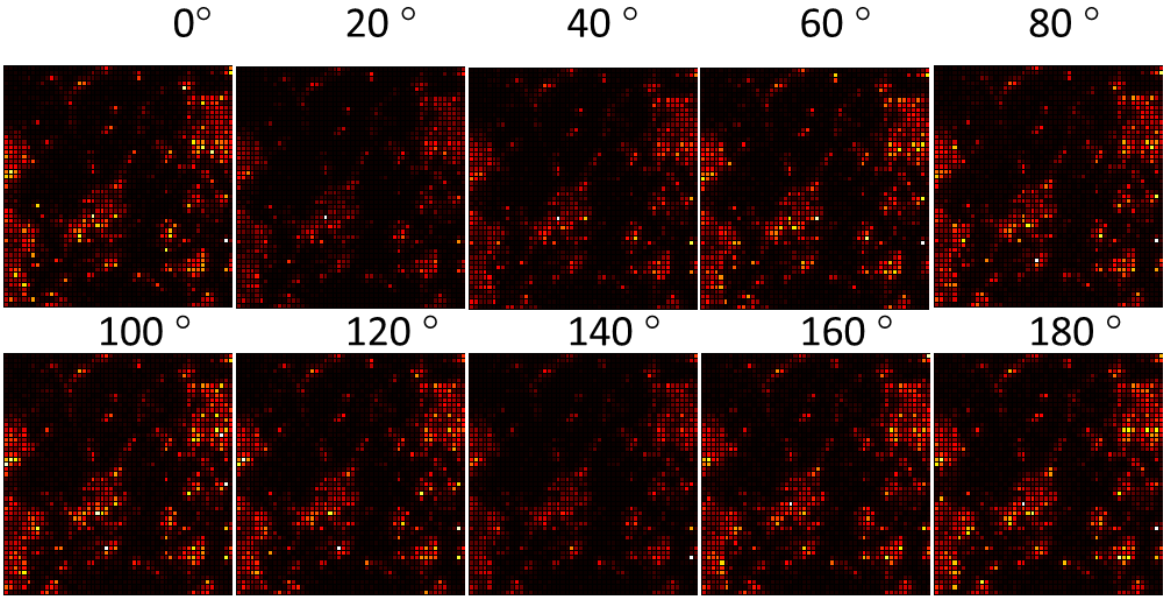


Figure S3. The simulated local field intensity of two 80 nm crossed silver nanowires at the xy plane (z=0) with linearly polarized incident light in the Z direction. The simulated silver nanowires have length of 400 nm, 400 nm and 1600 nm, filled by dipoles with a dipole-dipole distance of 2.25 nm, 4.5 nm, and 4.5 nm respectively. Wavelength: 488 nm, polarization angles 0^o (A and B), 45^o (C and D), and 90^o (E and F). B, D and F are 3D representation of the local field intensity for the 2D plots A, C, and E, respectively. Field intensity is summed along the Z direction and projected onto the XY plane.

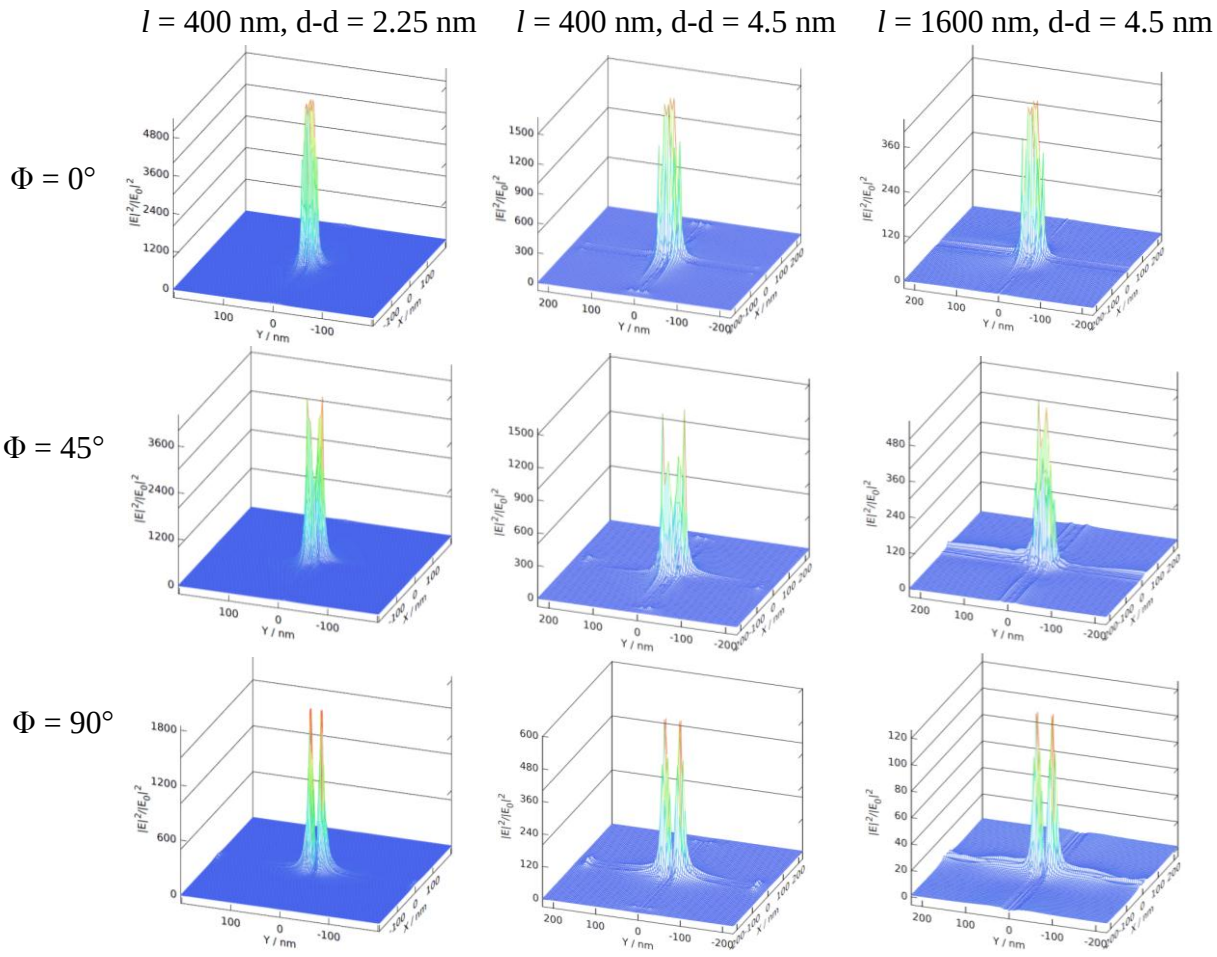


Figure S4. (A) Raman spectrum of adenine enhanced by (1) single, (2) adjacent, (3) crossed, and (4) connecting NWs (B) Raman spectrum of cytosine enhanced by (1) crossed and (2) single Ag NW (C) Raman spectrum of guanine enhanced by three pairs of crossed Ag NWs located at three different sites (1-3) of the Ag nanowire sample (D) Time evolution of Raman spectrum of thymine enhanced by two crossed Ag NWs.

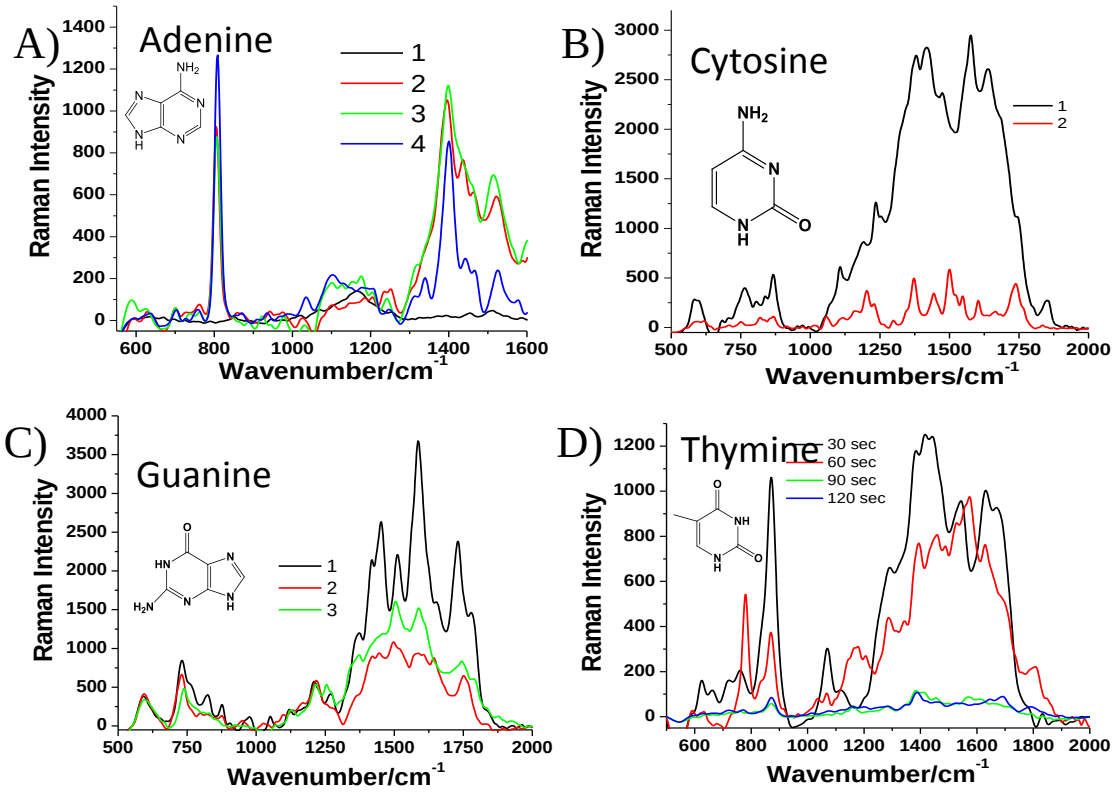


Table S1. Raman Spectra Assignments (Frequencies in cm^{-1}) Based on DFT Calculations at the B3LYP/ aug-cc-pVDZ Level.

Mercaptopyridine

DFT[a]	Experimental	Assignment
1005 (28)	1049.74	ring stretch/deformation
1084 (8)	---	ring stretch/deformation
1121 (18)	1139.179	C-S str
1234 (7)	1255.087	CCH bend

1280(3)	---	ring stretch/deformation
1332 (4)	1323.129	CCH bend
---	1537.362	Unassigned
1610 (15)	1620.094	C=C str
---	1751.934	Unassigned
---	1830.802	Unassigned

Adenine

Calculation	Experimental	Assignment
723 (28)	---	ring stretch
820 (1)	804.693	ring torsion
857 (1)	---	CH out-plane wag on 5-ring
896 (2)	---	N-C-N bend
942 (4)	---	5-ring stretch
1005 (5)	1025.737	NH_2 rock
1078 (10)	---	mix of CNH bend and NC str
1238 (11)	---	mix of ring breath and NH_2 rock
1264 (22)	1251.183	ring stretch + CN str
1335 (10)	---	ring stretch + CN str
1356 (18)	---	ring stretch + CN str
1366 (72)	---	ring stretch
1416 (25)	1396.409	NCH bend + CN str
1434 (4)	1440.000	CC str + CN str (on bridging C)
1498 (13)	---	CN str
1513 (82)	1522.234	CN str (in 5-ring)
1605 (4)	---	NH_2 bend (scissor)

1636 (24)	1618.222	CN and CC str
1660 (8)	---	C-NH_2 str

Cytosine

Calculation	Experimental	Assignment
768 (31)	---	ring stretch
---	823.152	Unassigned
---	1068.000	Unassigned
1120 (10)	---	CCH bend + CNH bend + CC str + CN str
1208 (8)	1202.234	CCH bend + CNH bend + CC str + CN str
1261 (15)	---	CN str
---	1300.000	Unassigned
1350 (6)	1373.334	CC str + CCH bend
1439 (6)	1450.000	CC str + CN str
1498 (5)	1499.492	C-NH_2 str
1566 (21)	---	ring str kekule
1626 (10)	1605.111	NH_2 scissor
1684 (16)	1668.000	CC str
1757 (33)	1739.026	CO str

Guanine

Calculation	Experimental	Assignment
625 (28)	---	ring stretch
---	730.475	in phase ring stretching
---	823.000	Unassigned

945 (6)	---	CN_2 bend
---	975.520	NH str + NC str
1043 (4)	---	CN str
1065 (7)	---	CN str
---	1210.080	CN str + NH str
1301 (21)	1272.000	NCH bend
1328 (5)	---	NCH bend
1360 (6)	1368.000	CC + CN str on the bridging C
1384 (96)	---	CN str + CNH bend
1438 (16)	1451.920	CC + CN str
1509 (124)	1513.000	CN str
1553 (27)	1586.350	CN str
1602 (16)	---	NH_2 scissor mixed with other str
1609 (98)	---	NH_2 scissor mixed with other str
1652 (52)	---	NH_2 scissor mixed with other str
1782 (51)	1731.640	CO str
---	2226.000	Unassigned

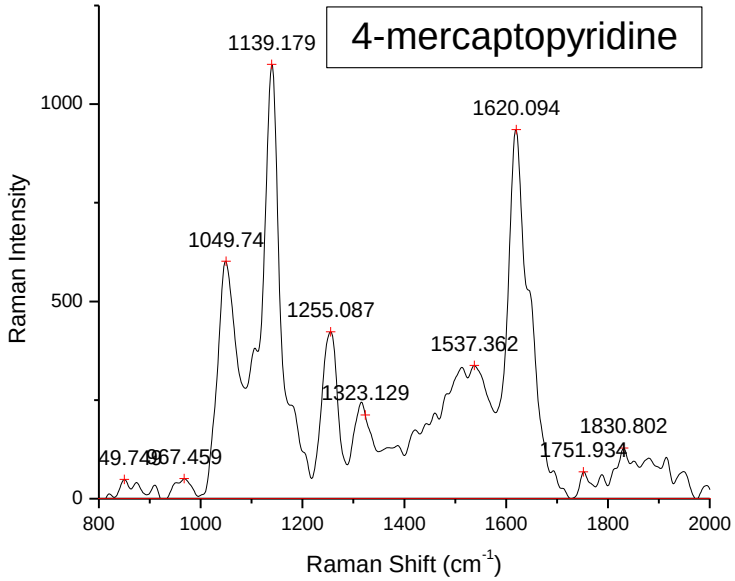
Thymine

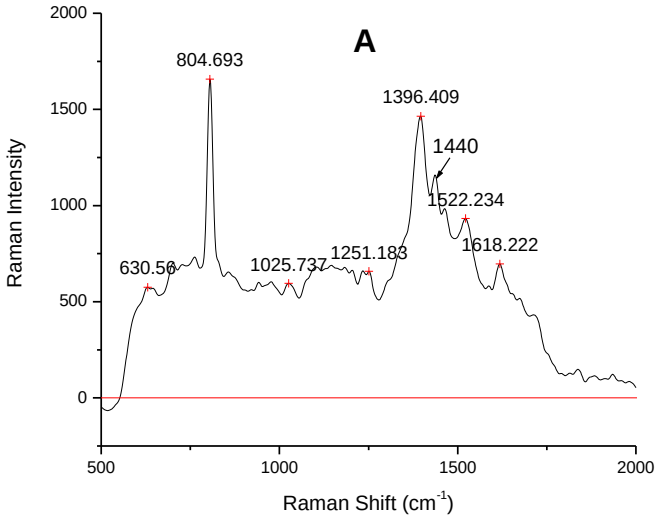
Calculation	Experimental	Assignment
---	623.000	Unassigned
735 (18)	723, 759	ring stretch
802 (5)	---	ring str
---	872.193	CN str + NH str + CC str
963 (5)	---	ring str
910 (1)	---	CH out-plane wag

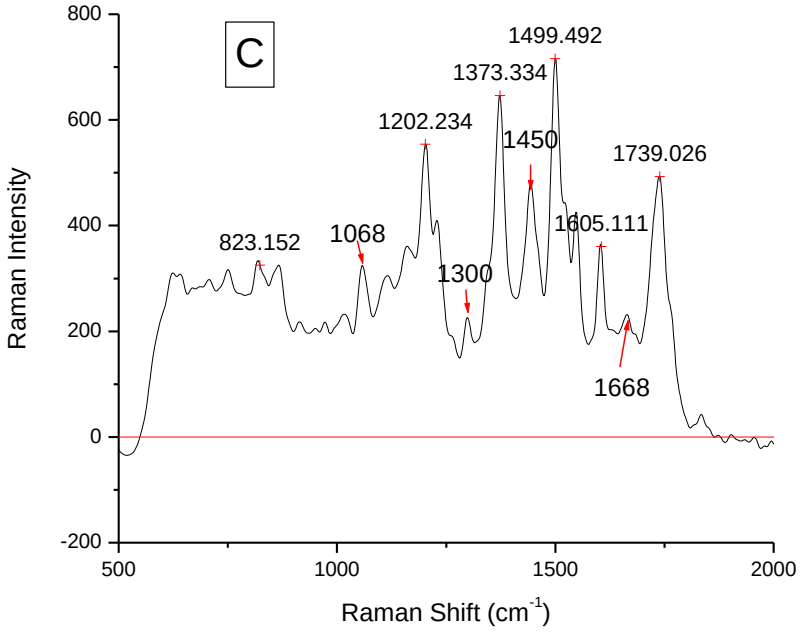
---	1069.690	CCH3 rocking
---	1286.000	ring str + CH bend
1367 (29)	---	CC str + CCH bend
1406 (9)	1413.680	CH_3 deformation
1495 (21)	---	CN str + CNH bend
---	1547.000	Unassigned
---	1629.450	Unassigned
1700 (40)	1668.000	CC str + CCH bend
1743 (53)	---	CO str
1787 (22)	---	CO str (C in -NCN-)
---	1832.000	Unassigned

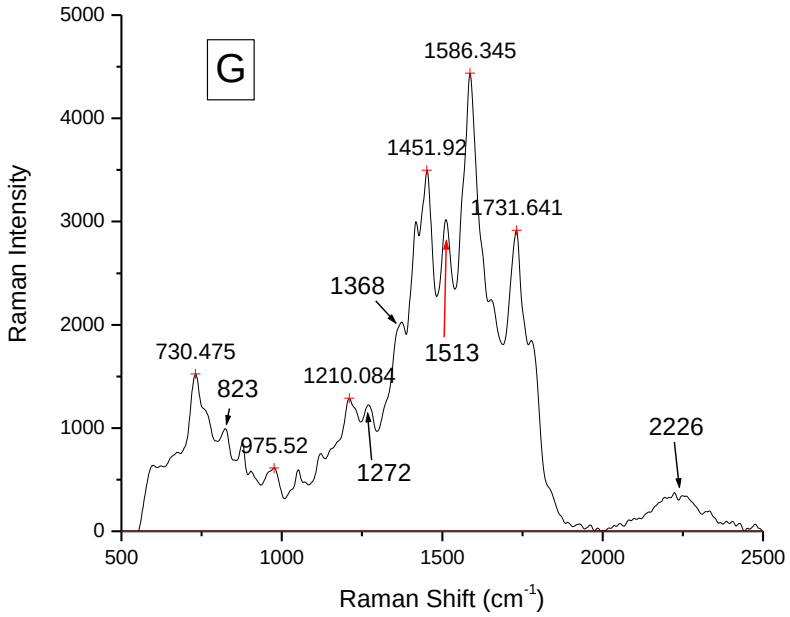
[a] Values in parentheses are the Raman activity in $Å^4$/amu.

Figure S5. Background corrected SERS spectra of 4-mercapropyridine, adenine, cytosine, guanine and thymine and Raman peak positions used to compare with calculated Rama spectra.




A
804.693
1396.409
1440
1522.234
1618.222
630.56
1025.737
1251.183
Raman Intensity
Raman Shift (cm-1)


C
1499.492
1373.334
1202.234
1450
1739.026
1605.111
823.152
1068
1300
1668
Raman Intensity
Raman Shift (cm-1)



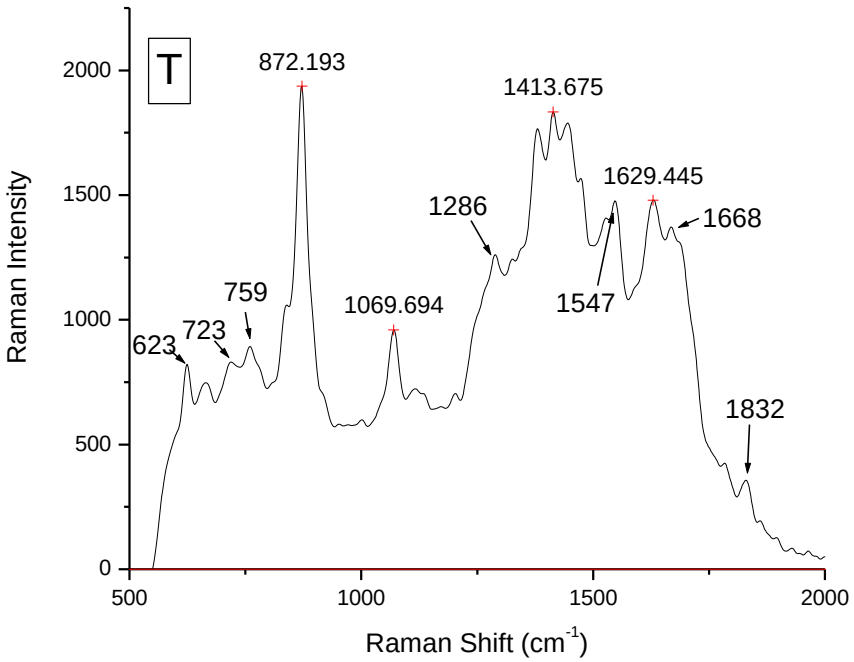


Table S2. Optimized geometry and total energy 4-mercapropyridine, adenine, cytosine, guanine and thymine for Rama spectra calculation.

Mercaptopyridine E=-646.522454

C	-1.623448	-1.142870	0.004082

C	-1.623448	1.142870	0.004082
C	-0.225648	1.200511	-0.008328
C	0.491081	0.000000	-0.006557
C	-0.225649	-1.200512	-0.008328
H	-2.206854	-2.066951	0.007458
H	-2.206854	2.066951	0.007458
H	0.290497	2.159566	-0.019427
H	0.290497	-2.159566	-0.019426
N	-2.321928	0.000000	0.012342
S	2.301519	0.000000	-0.077378
H	2.504570	0.000004	1.265879

Adenine E=-467.389513

C	0.179000	-0.520909	0.000096
C	0.711852	0.774286	0.000071
C	-1.295250	1.702876	-0.000006
C	-1.230585	-0.609556	-0.000040
C	2.293830	-0.777836	-0.000085
H	-1.929496	2.590643	0.000017
H	3.295714	-1.194826	0.000032
H	2.776779	1.316605	0.000063
N	1.183105	-1.477773	0.000030
N	2.078095	0.586785	-0.000066
N	0.023523	1.923980	0.000075
N	-1.949437	0.527831	-0.000068
N	-1.883492	-1.797657	-0.000303
H	-2.891467	-1.804739	0.000861
H	-1.367176	-2.663014	0.001142

Cytosine E=-394.996140

C	1.185891	-0.528665	-0.000016
N	-0.081467	-1.052692	-0.000020
C	-1.133623	-0.251297	-0.000007
C	-1.050533	1.187933	0.000019
C	0.204881	1.715148	0.000007
N	1.283463	0.893620	-0.000027
H	-1.932566	1.822795	0.000004
H	0.399199	2.786985	0.000012
O	2.221886	-1.178972	0.000038
H	2.226325	1.260773	0.000043
N	-2.358369	-0.843547	-0.000127
H	-3.210044	-0.307409	0.000531
H	-2.403088	-1.851745	0.000308

Guanine E=-542.639000

C	0.855756	0.506673	0.006455
C	0.530678	-0.852498	-0.000318
C	-1.674675	-0.567792	-0.002059
C	-0.214231	1.471840	0.002155
C	2.720659	-0.529408	0.000872
H	-2.275109	1.414739	-0.061446
H	3.775359	-0.783040	-0.000977
H	1.862915	-2.507772	-0.007620
N	1.736127	-1.505331	-0.003339
N	2.227769	0.683759	0.006533
O	-0.198140	2.691583	-0.002294
N	-0.694574	-1.441422	0.007763

N	-1.478873	0.789556	-0.003921
N	-2.977771	-1.010793	-0.065473
H	-3.078990	-2.003275	0.101616
H	-3.696933	-0.436585	0.353226

Thymine E=-454.206700

C	-0.239258	-1.483550	-0.000127
C	-1.158510	-0.488419	-0.000038
C	1.679676	0.027017	-0.000001
N	1.120876	-1.243127	-0.000263
H	-0.521722	-2.535440	0.000078
H	1.087957	1.981150	0.000430
C	-0.672442	0.897201	-0.000163
O	-1.384663	1.891741	-0.000158
C	-2.641863	-0.719494	0.000275
H	-3.108646	-0.257116	0.881223
H	-3.108920	-0.257559	-0.880772
H	-2.872820	-1.792191	0.000555
H	1.784056	-2.005623	-0.000268
N	0.727940	1.032791	-0.000007
O	2.883760	0.226085	0.000278

Figure S6. EDX spectrum of gold nanoparticle modified silver NWs showing the presence of gold on surface.