Electronic Supplementary Information

Real-Time Monitoring of Plasmon Induced Dissociative Electron Transfer to the Potential DNA Radiosensitizer 8-Bromoadenine

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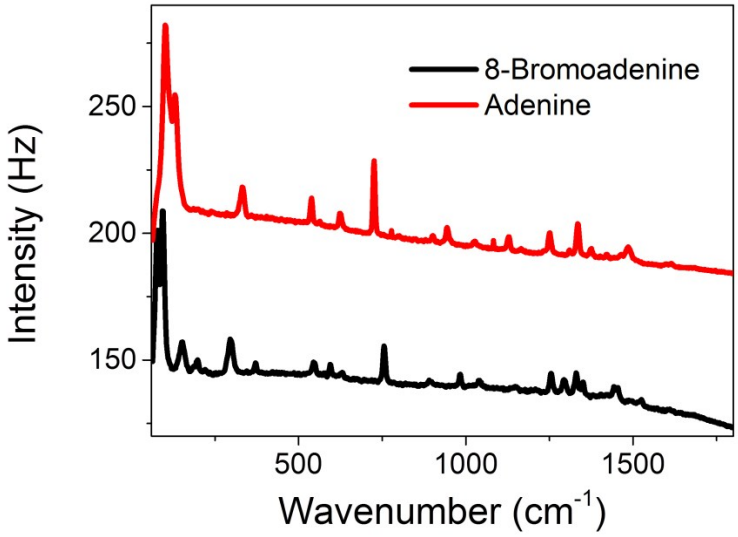

Figure S1: Raman spectra of ^{8Br}A and A powder taken with a 785 nm laser.

NRS 8BrA	SERS ^{8Br}A	Description[1]	NRS Adenine	SERS Adenine	Description [2]
79			102		
93			128		
151			331	337	Δ(C6-C5-N7) - Δ(N1-C6-N6) + Δ(N3-C4-N9)
196			538		Δ(N1-C6-C5) + Δ(C2-N3-C4)
220w			562	565	Γ(N1-C2-N3) + γ(C2-H) - γ(C8-H)
296	299	τ(C4-C5), γ(C8-Br), τ(Pyr ring)	624	628	Δ(C4-C5-N7) - Δ(C4-N9-C8) + Δ (N1-C6-N6)

344	357	Δ(C6-N10), ν(C8-Br), δ(C8-Br), α(Im ring)	725	735	Pyr + Im ring breathing
371			777		ω(NH2)
545	568	δ(Pyr Ring), δ(C8-Br), δ(C6-N10)	900	916	Δ(N1-C2-N3) + Δ(C8-N9-C5)
594		τ(Pyr Ring), τ(Im Ring), γ(C6-N10)	944	968	Δ(N7-C8-N9); γ(N9-H)
628	635	δ(Im Ring), δ(Pyr Ring), ν(C5-C6)	1026	1043	t(NH2); ν(C6-N1)
755	767	Pyr + Im ring breathing	1082	1080	
892		δ(Pyr Ring), ν(C5-N7)	1127	1121	δ(C8-H); ν(C3-N3) + ν(C4-N9) - ν(C5-C6) - ν(C5-N7)
982	984	r(NH2), ν(C6-N1), ν(C2-N1)	1164	1174	δ(C8-H) - δ(N9-H); ν(C8-N9) + (C5-N7) - ν(C4-N9) - ν(C4-N3) - ν(C2-N3)
1040	1032	ν(C8-N9), δ(N9-H), ν(C4-N9)	1250	1267	δ(C8-H) + δ(N9-H); ν(C2-N3) + ν(C8-N7) + ν(C2-N1) - ν(C5-N7) - ν(C4-N9)
1146w	1150	δ(N9-H), ν(C4-N3), δ(Im ring), ν(C4-N9)	1310		δ(C2-H); ν(C2-N3) + ν(C5-N7) - ν(C8-N7) - ν(C4-N9)
1205w			1334	1329	δ(C2-H); ν(C2-N3) + ν (C5-N7) - ν(C8-N7) - ν(C4-N9)
1255	1246	ν(C5-N7), r(NH2), ν(C2-N3), ν(C2-N1)	1374		δ(N9-H); δ(C8-H); ν(C8-N9) + ν(C4-C5) + ν(C2-N3) + ν(C6-N1) - ν(C5-C6) - ν(C2-N1) - ν(C4-N3) - ν(C8-N7)
1294		ν(C2-N3), ν(C5-N7)	1421	1410	ν(C4-N9) + ν(C8-N7) + ν(C6-N1) - ν(C4-C5) - ν(C4-N3) - ν(C8-N9)
1330	1332	δ(C2-H), ν(C6-N10), ν(C8-N9), ν(C2-N1)	1465	1465	δ(N9-H) - δ(C8-H) + δ(C2-H); ν(C8-N9) + ν(C2-N1) + ν(C6-N1) - ν(C2-N3) - ν(C8-N7) - ν(C6-N6)
1447	1432	ν(C8-N7)	1614w	1597	α(NH2); δ(N9-H); ν(C4-C5) + ν(C2-N1) - ν(C5-C6) - ν(C6-N1) - ν(C4-N3) - ν(C2-N3)
1488	1464	δ(C2-H), ν(C6-N1), ν(C6-N10), δ(NH2)			
1520	1552	Δ(NH2), ν(C4-C5), ν(C5-C6)			

Table 1: Assignment NRS bands of A and ^{8Br}A observed in the present experiment and comparison to values reported previously. ω: wagging; δ: in-plane deformation; Δ: in-plane ring deformation of skeletal atoms; γ: out-of-plane deformation; Γ: out-of-plane ring deformation of skeletal atoms; α: scissoring; τ: torsion; t: twisting; ν: stretching; r: rocking; Pyr: pyrimidine; Im: Imidazol. Atoms are labeled according to Fig. 1a.

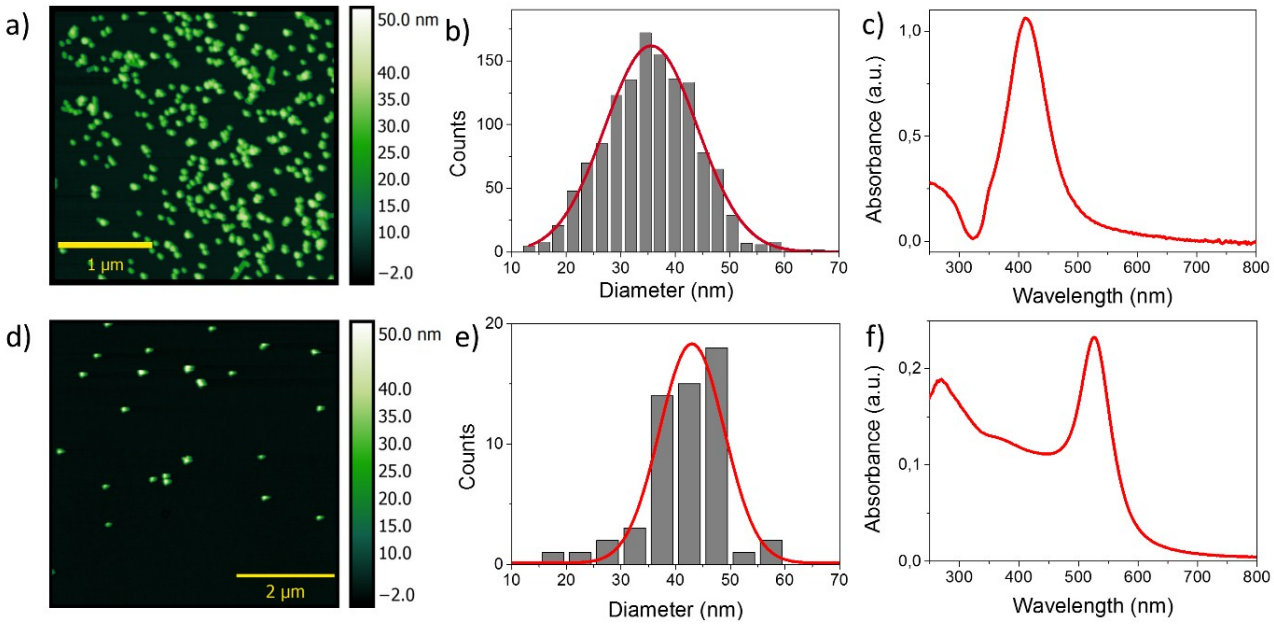

Figure S2: a) AFM image of AgNP, b) Size distribution of AgNP, c) UV-Vis-Absorbtion spectra of AgNP, d) AFM image of AuNP, e) Size distribution of AgNP, f) UV-Vis-Absorbtion spectra of AgNP.

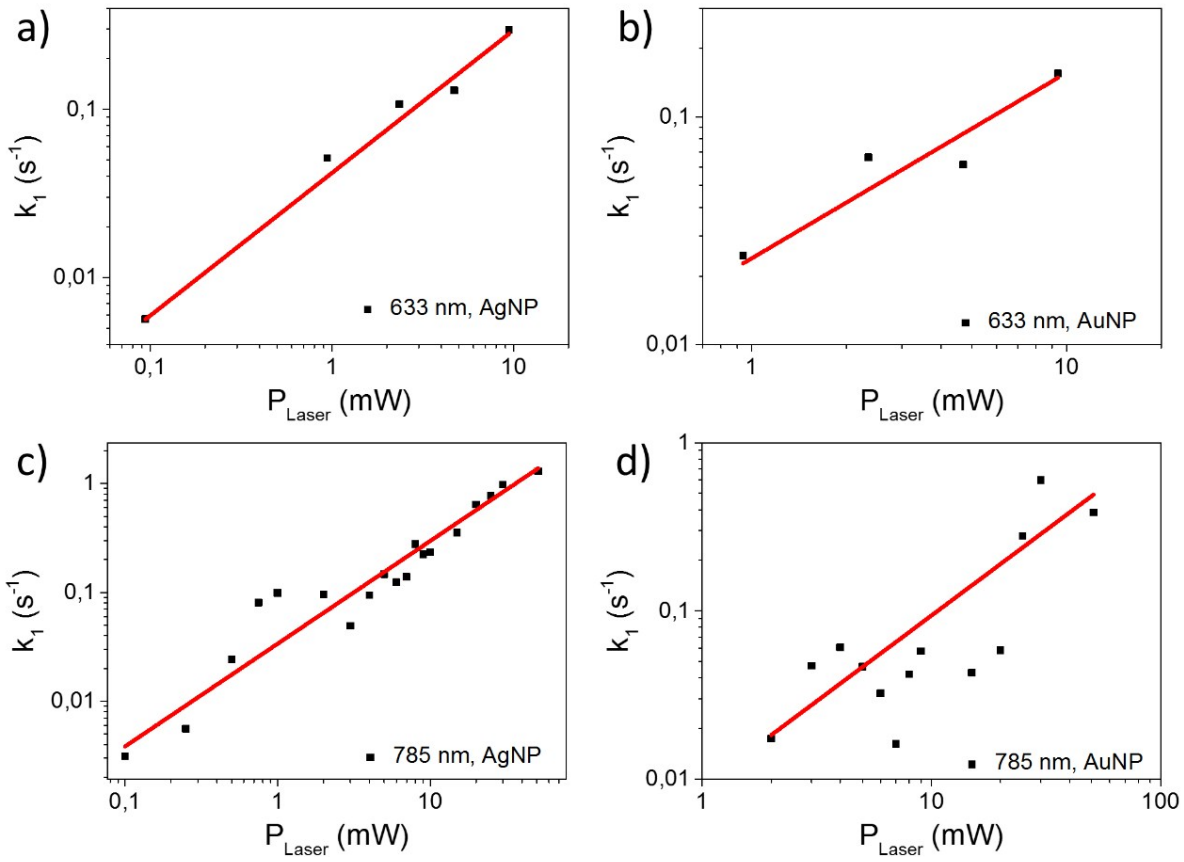

Figure S3: Rate constant k_1 as a function of the incident laser power fitted by a power law function a) AgNP with 633 nm laser, b) AuNP with 633 nm laser, c) AgNP with785 nm laser, d) AuNP with 785 nm laser.

Laser wavelength	AgNP	AuNP
532	0.92 ± 0.09	
633	0.85 ± 0.14	0.82 ± 0.24
785	0.94 ± 0.06	1.02 ± 0.31

Table 2: Power law exponents determined for $k_1 = a \cdot P^b$.

Decrease (cm^{-1})	Increase (cm^{-1})
299	337
575	392
767	628
1387	681
1433	735
1500	968
1525	1043
1620	1080
	1121
	1174
	1223
	1267
	1329
	1410
	1465
	1516
	1538
	1575
	1597

Table 3: Increasing and decreasing Raman bands of ^{8Br}A on AgNP under irradiation with a 532 nm laser.

1 Y.-L. Chen, D.-Y. Wu and Z.-Q. Tian, *J. Phys. Chem. A*, 2016, **120**, 4049–4058.

2 R. P. Lopes, R. Valero, J. Tomkinson, M. P. M. Marques and L. A. E. Batista de Carvalho, *New J. Chem.*, 2013, **37**, 2691.