Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting Information on

Time-dependent Emission Stokes Shift in Au, Ag and Au/Ag Fluorescent Nanoclusters : Evidence of Multiple Emissive States

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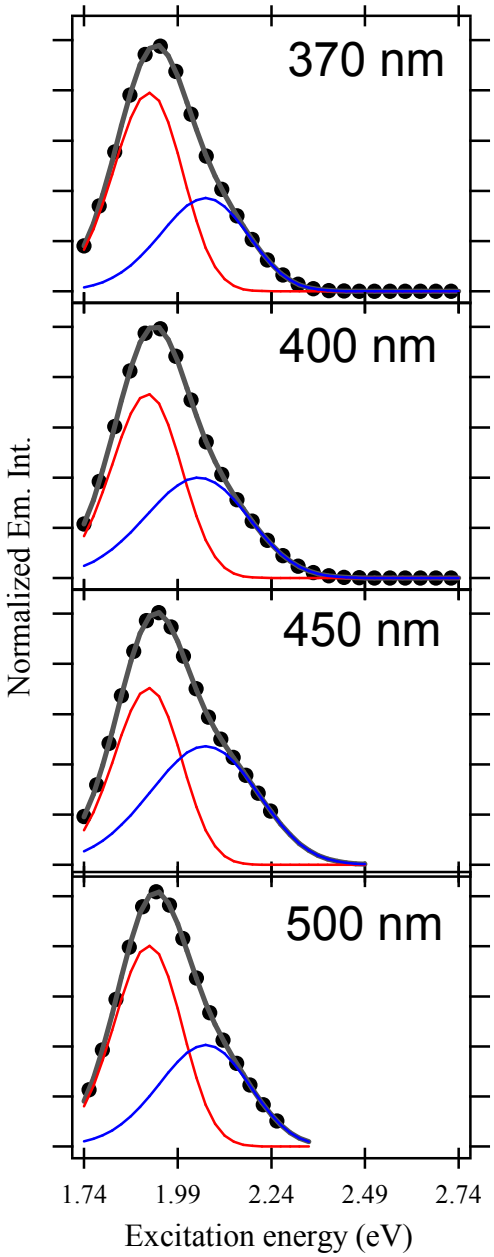

Figure SF1. Normalized emission spectrum of Au nanoclusters at different excitation wavelengths (as indicated) plotted along with the component peaks obtained by double lognormal fitting. Markers black solid line represent the original and fitted spectra respectively. Blue and red lines stand for the deconvoluted components.

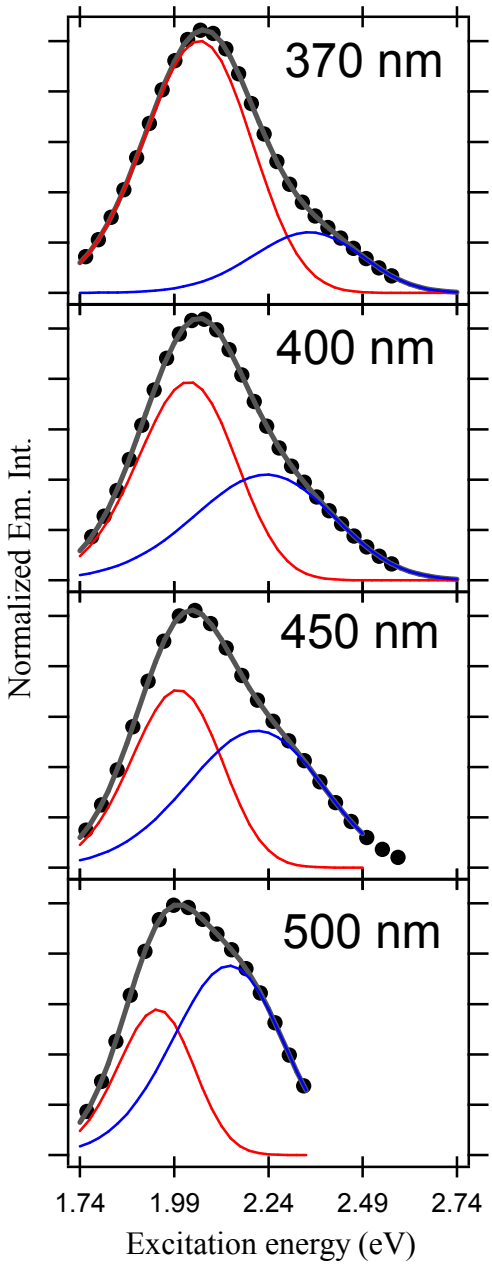

Figure SF2. Normalized emission spectrum of Au/Ag nanoclusters at different excitation wavelengths (as indicated) plotted along with the component peaks obtained by double lognormal fitting. Markers black solid line represent the original and fitted spectra respectively. Blue and red lines stand for the deconvoluted components.

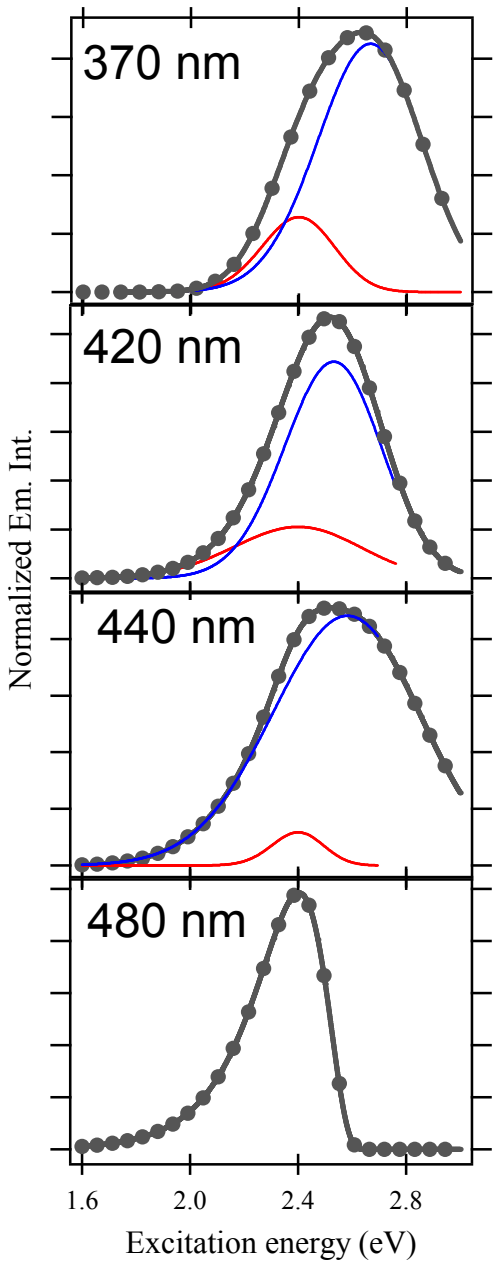

Figure SF3. Normalized emission spectrum of Ag nanoclusters at different excitation wavelengths (as indicated) plotted along with the component peaks obtained by double/single lognormal fitting. Markers black solid line represent the original and fitted spectra respectively. Blue and red lines stand for the deconvoluted components.

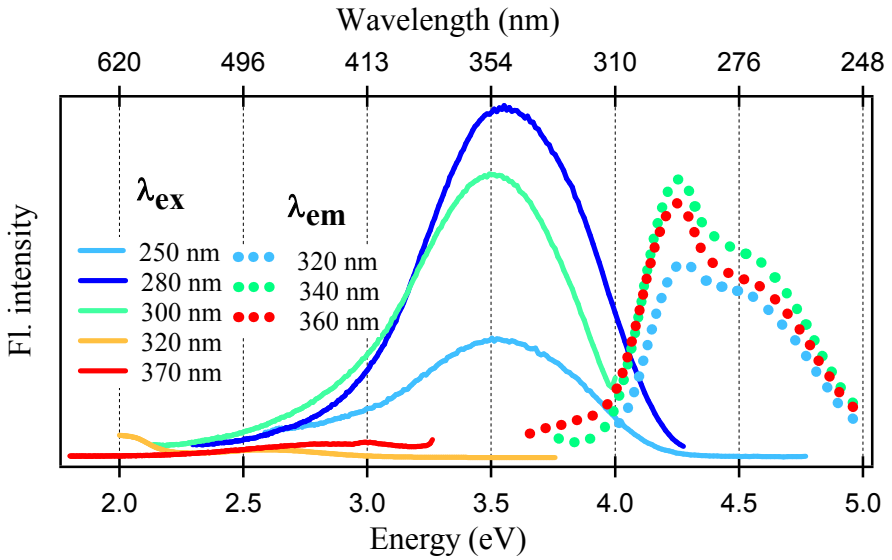

Figure SF4. Emission spectra (solid curves) and excitation spectra (dotted curves) of BSA at different excitation (λ_{ex}) and emission (λ_{em}) wavelengths respectively, as indicated.

Table ST1. Emission and excitation peak positions of the nanoclusters at different excitation and emission energies (obtained from lognormal fitting)*			
i) Au nanoclusters			
λ_{ex} (nm)	**Low energy emission peak (eV)**	**High energy emission peak (eV)**	**χ^2**
370	1.91	2.06	0.054
400	1.91	2.05	0.082
420	1.90	2.05	0.086
440	1.91	2.06	0.087
450	1.91	2.06	0.091
460	1.92	2.06	0.088
480	1.92	2.06	0.082
500	1.91	2.06	0.076
520	1.91	2.06	0.077
550	1.89	2.04	0.073
λ_{em} (nm)	**Excitation peak (eV)**		
580	2.53		0.032
600	2.49		0.011
620	2.48		0.012
640	2.44		0.017
660	2.42		0.029
680	2.41		0.052
700	2.39		0.156
ii) Au/Ag nanoclusters			
λ_{ex} (nm)	**Low energy emission peak (eV)**	**High energy emission peak (eV)**	**χ^2**
370	2.06	2.35	.811
400	2.03	2.23	.758
420	2.02	2.23	.684
440	2.01	2.22	.599
450	2.00	2.21	.420
460	1.99	2.19	.476
480	1.97	2.18	.411
500	1.95	2.14	.275
520	1.93	2.10	.294

Au/Ag nanoclusters			
λ_{em} (nm)	**Low energy excitation peak (eV)**	**High energy excitation peak (eV)**	**χ^2**
480	2.78	2.95	0.024
500	2.62	2.91	0.036
520	2.62	2.92	0.081
540	2.65	2.92	0.056
560	2.35	2.81	0.139
580	2.32	2.81	0.155
600	2.32	2.81	0.173
620	2.31	2.80	0.157
640	2.31	2.78	0.117
660	2.29	2.76	0.191
680	2.29	2.75	0.181
ii) Ag nanoclusters			
λ_{ex} (nm)	**Low energyemission peak (eV)**	**High energy emission peak (eV)**	**χ^2**
370	2.40	2.67	1.069
400	2.40	2.58	0.874
420	2.40	2.53	0.528
440	2.40	2.53	2.551
450	2.41	2.54	0.262
460	2.40	2.54	0.259
480	2.40	-	0.257
λ_{em} (nm)	**Excitation peak (eV)**		
420	3.23		0.220
440	3.07		0.182
460	2.95		0.094
480	2.82		0.052
500	2.76		0.034
520	2.72		0.061
540	2.70		0.083
560	2.69		0.398
580	2.69		1.063
600	2.68		1.990

* The exact peak positions of various components in any given spectrum were determined by deconvoluting the spectrum with lognormal fitting (see Results and Discussion). The emission (or excitation) peak positions of the deconvoluted components are listed against their corresponding excitation (or emission) energies, respectively, in Table ST1.

Table ST2. Fitting parameters for fluorescence time-profiles							χ^2
i) Au nanoclusters							
λ_{em} (nm)	**τ_1 (ns)**	**a_1(%)**	**τ_2 (ns)**	**a_2(%)**	**τ_3 (ns)**	**a_3(%)**	
550	0.27	50	1.55	38	7	12	4.00
570	0.30	52	1.80	38	10	10	4.02
580	0.30	53	2.00	38	13	09	3.96
590	0.34	54	2.25	37	17	09	3.55
600	0.37	53	2.40	36	22	11	3.02
610	0.36	52	2.50	35	28	13	3.15
620	0.53	54	3.30	29	39	17	2.88
630	0.50	53	3.30	27	46	20	3.00
640	0.55	49	3.75	27	50	24	3.08
650	0.45	44	2.95	29	48	27	3.84
660	0.65	48	4.90	22	62	30	4.22
680	1.00	48	10.75	13	92	39	4.56
700	0.80	41	8.05	15	100	44	4.76
Au/Ag nanoclusters							
λ_{em} (nm)	**τ_1 (ns)**	**a_1(%)**	**τ_2 (ns)**	**a_2(%)**	**τ_3 (ns)**	**a_3(%)**	
520	0.24	55	1.60	36	7	10	4.06
530	0.26	55	1.80	36	10	08	3.94
540	0.28	57	2.10	36	13	07	3.83
550	0.32	57	2.30	35	16	07	3.68
570	0.33	55	2.40	36	22	09	3.34
580	0.35	56	2.60	34	25	10	3.18
590	0.34	55	2.60	34	28	11	2.98
600	0.35	55	2.60	33	28	12	3.29
610	0.33	55	2.70	32	31	13	3.71
620	0.37	56	3.00	31	34	13	3.96
630	0.32	50	2.34	35	30	15	4.33
640	0.27	54	2.52	32	31	15	4.84
660	0.31	54	2.64	31	32	16	4.97
680	0.28	56	2.60	29	30	15	5.05

iii) Ag nanoclusters							
λ_{em} (nm)	**τ_1 (ns)**	**a_1(%)**	**τ_2 (ns)**	**a_2(%)**	**τ_3 (ns)**	**a_3(%)**	**χ^2**
420	0.16	61	0.91	27	5	12	3.48
440	0.16	77	2.85	16	7	07	3.21
450	0.18	70	2.48	20	7	10	3.06
470	0.18	70	2.76	21	7	09	2.94
480	0.18	68	2.73	24	8	08	2.67
490	0.19	70	2.96	22	8	08	2.25
510	0.19	70	3.11	21	8	09	2.86
520	0.19	68	3.00	23	8	09	2.88
530	0.17	71	3.29	23	8	06	3.27
540	0.19	72	3.26	21	8	07	3.56
560	0.18	73	3.27	22	9	05	3.82
580	0.16	73	2.79	22	9	05	3.79

Table ST3. Emission maxima and Stokes shift for the nanoclusters		
i) Au nanoclusters		
Time (ns)	**υ_{max}(t) (cm^{-1})**	**υ_{max}(t=0)-υ_{max}(t) (cm^{-1})**
0	16450	750
10	15700	
ii) Au/Ag nanoclusters		
Time (ns)	**υ_{max}(t)**	**υ_{max}(t=0)-υ_{max}(t) (cm^{-1})**
0	18100	1400
10	16700	
iii) Ag nanoclusters		
Time (ns)	**υ_{max}(t)**	**υ_{max}(t=0)-υ_{max}(t) (cm^{-1})**
0	21300	200
10	21100	