Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Quantitative Analysis of Charge Transfer Plasmons in Silver Nanocluster Dimers Using Semiempirical Methods

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Table S1. Composition of the strong longitudinal excited states of the end-to-end Ag_4 dimer into pure transitions. All transitions with weights > 5% are listed.

Distance (Å)	Energy (eV)	Transition	Weight (%)	CTP character
3.5	1.57	HOMO → LUMO	87.35	11.96
		HOMO-1 → LUMO+1	8.69	7.04
	2.60	HOMO-2 → LUMO	64.75	5.36
		HOMO-1 → LUMO+1	17.64	7.04
		HOMO-3 → LUMO+1	11.77	4.66
4.0	1.75	HOMO → LUMO	79.91	6.96
		HOMO-1 → LUMO+1	15.80	4.76
	2.66	HOMO-2 → LUMO	49.78	3.34
		HOMO-1 → LUMO+1	27.99	4.76
		HOMO-3 → LUMO+1	12.36	2.84
4.5	1.88	HOMO → LUMO	69.39	3.77
		HOMO-1 → LUMO+1	26.45	2.97
	2.72	HOMO-2 → LUMO	51.05	1.89
		HOMO-3 → LUMO+1	20.76	1.68
		HOMO-1 → LUMO+1	18.47	2.97
5.0	1.94	HOMO → LUMO	60.20	1.96
		HOMO-1 → LUMO+1	35.73	1.73
	2.76	HOMO-2 → LUMO	54.45	1.00
		HOMO-3 → LUMO+1	35.25	0.94
		HOMO-1 → LUMO+1	4.71	1.73

Table S2. Composition of the excited states of the end-to-end Ag_8 dimer into excitations and CTP character of the pure excitations. All excitations with weights > 5% are listed.

Distance (Å)	Energy (eV)	Transition	Weight (%)	CTP character (%)
3.5	1.06	HOMO → LUMO	70.94	8.27
		HOMO-1 → LUMO+1	19.98	3.80
	1.91	HOMO-2 → LUMO	44.98	6.38
		HOMO-1 → LUMO+1	24.13	3.80
		HOMO → LUMO+2	11.99	6.36
		HOMO-3 → LUMO+1	8.34	3.92
4.0	1.16	HOMO → LUMO	62.68	4.37
		HOMO-1 → LUMO+1	28.57	2.58
	1.98	HOMO-2 → LUMO	47.23	3.70
		HOMO-1 → LUMO+1	17.64	2.58
		HOMO-3 → LUMO+1	14.60	2.54
		HOMO → LUMO+2	8.75	3.96
4.5	1.22	HOMO → LUMO	55.79	2.22
		HOMO-1 → LUMO+1	36.09	1.60
	2.04	HOMO-2 → LUMO	52.44	1.97
		HOMO-3 → LUMO+1	29.01	1.54
		HOMO-1 → LUMO+1	6.12	1.60
5.0	1.25	HOMO → LUMO	51.40	1.13
		HOMO-1 → LUMO+1	40.82	0.93
	2.06	HOMO-2 → LUMO	50.49	1.13
		HOMO-3 → LUMO+1	38.34	0.93

Table S3. Composition of the transverse excited states of the side-by-side Ag_4 dimer into excitations and CTP character of the pure excitations. All excitations with weights > 5% are listed.

Distance (Å)	Energy (eV)	Transition	Weight (%)	CTP character (%)
3.5	3.51	HOMO-1 → LUMO+4	79.28	20.34
		HOMO-2 → LUMO	8.39	33.85
		HOMO → LUMO +1	4.94	44.50
	2.68	HOMO-2 → LUMO	74.17	33.85
		HOMO-1 → LUMO+4	14.68	20.34
		HOMO → LUMO +1	7.14	44.50
	1.87	HOMO → LUMO +1	84.66	44.50
		HOMO-2 → LUMO	12.01	33.85
4.0	3.96	HOMO-1 → LUMO+4	50.48	16.98
		HOMO → LUMO +6	40.56	13.59
	4.17	HOMO-3 → LUMO+1	69.72	1.01
		HOMO-2 → LUMO +3	15.9	0.39
4.5	4.51	HOMO → LUMO +7	23.53	9.73
		HOMO-2 → LUMO+4	22.33	12.39
		HOMO-10 → LUMO	17.92	1.18
		HOMO-11 → LUMO+1	10.97	0.97
		HOMO-4 → LUMO+2	8.40	1.14
		HOMO-5 → LUMO+3	6.71	1.00
	4.28	HOMO-1 → LUMO +3	69.87	0.13
		HOMO-3 → LUMO+1	6.51	0.70
		HOMO → LUMO+2	5.52	0.03
5.0	4.87	HOMO → LUMO+8	32.28	6.27
		HOMO-2 → LUMO +4	23.48	7.25
		HOMO-19 → LUMO+1	5.77	0.20
5.5	5.13	HOMO → LUMO+9	41.10	3.66
		HOMO-2 → LUMO+6	26.50	4.85
		HOMO-1 → LUMO+15	12.62	3.67
		HOMO-3 → LUMO+10	7.71	4.86
6.0	5.22	HOMO → LUMO+10	39.76	1.97
		HOMO-2 → LUMO+6	23.48	2.66
		HOMO-1 → LUMO+15	21.32	1.95
		HOMO-3 → LUMO+9	12.30	2.66

Table S4. Composition of the transverse excited states of the side-by-side Ag_8 dimer into excitations and CTP character of the pure excitations. All excitations with weights > 5% are listed.

Distance (Å)	Energy (eV)	Transition	Weight (%)	CTP character (%)
3.5	3.62	HOMO-3 → LUMO+7	28.28	22.31
		HOMO-1 → LUMO+5	24.11	3.97
		HOMO-2 → LUMO +8	19.26	19.94
		HOMO → LUMO+11	14.20	17.64
	3.77	HOMO-6 → LUMO	51.67	4.82
		HOMO-5 → LUMO+2	18.69	2.38
		HOMO-1 → LUMO+5	5.02	3.97
	3.42	HOMO-1 → LUMO+5	41.53	3.97
		HOMO-4 → LUMO+4	9.40	0.91
		HOMO → LUMO+10	7.51	1.70
		HOMO-3 → LUMO+7	7.03	22.31
		HOMO-2 → LUMO+8	6.35	19.94
		HOMO-3 → LUMO+3	5.16	0.90
	2.03	HOMO → LUMO+3	71.25	0.65
		HOMO-1 → LUMO+2	10.54	42.27
		HOMO-2 → LUMO+1	7.62	1.48
	2.15	HOMO-1 → LUMO+2	81.53	42.27
		HOMO → LUMO+3	9.95	0.65
	2.49	HOMO-4 → LUMO	89.29	35.26
		HOMO-5 → LUMO+2	3.52	2.38
4.0	4.09	HOMO-4 → LUMO+7	26.62	18.35
		HOMO-2 → LUMO+9	18.66	16.34
		HOMO-1 → LUMO+11	14.13	14.32
		HOMO-1 → LUMO+10	9.92	0.93
		HOMO-2 → LUMO+6	9.20	0.16
		HOMO-4 → LUMO+4	5.11	0.88
	2.00	HOMO-3 → LUMO	60.05	41.98
		HOMO-2 → LUMO+1	17.61	1.62
		HOMO → LUMO+2	14.12	48.98
	1.54	HOMO → LUMO+2	78.19	48.98
		HOMO-3 → LUMO	16.67	41.98
4.5	4.57	HOMO-4 → LUMO+8	15.21	13.55
		HOMO-3 → LUMO+10	12.13	11.93
		HOMO → LUMO+18	10.98	9.05
		HOMO-1 → LUMO+12	10.10	10.49
		HOMO-1 → LUMO+9	6.10	0.23
		HOMO-4 → LUMO+4	6.05	0.26
		HOMO → LUMO +13	5.30	0.43
	4.47	HOMO-35 → LUMO+1	11.05	0.71

		HOMO-6 → LUMO+4	8.43	0.58
		HOMO-16 → LUMO+3	6.41	1.17
		HOMO-1 → LUMO+10	6.20	0.23
		HOMO-34 → LUMO+2	6.15	0.73
		HOMO → LUMO+14	5.63	0.43
		HOMO-4 → LUMO+5	5.33	0.26
5.0	5.01	HOMO → LUMO +19	21.24	5.81
		HOMO-5 → LUMO+9	20.52	8.83
		HOMO-2 → LUMO+15	17.19	6.77
		HOMO-3 → LUMO+11	16.49	7.76
5.5	5.24	HOMO-7 → LUMO+5	14.57	0.06
		HOMO → LUMO+25	12.65	3.36
		HOMO-5 → LUMO+10	9.11	5.32
		HOMO → LUMO+12	8.96	0.02
		HOMO-2 → LUMO+17	8.41	3.95
		HOMO-4 → LUMO+11	7.59	4.54
		HOMO-6 → LUMO+7	5.80	0.02
6.0	5.35	HOMO → LUMO+26	21.96	1.77
		HOMO-6 → LUMO+10	14.61	2.90
		HOMO-2 → LUMO+19	13.97	2.12
		HOMO-4 → LUMO+13	11.56	2.46
		HOMO-1 → LUMO+29	11.40	1.66
		HOMO-3 → LUMO+25	7.50	2.13
		HOMO-7 → LUMO+18	7.09	2.89
		HOMO-5 → LUMO+20	5.90	2.48

Table S5. Breakdown of the main absorption states in the side-by-side Ag_{31}^{+} dimers with their excited-state energies and oscillator strengths. States listed meet the criteria of oscillator strength: > 2.0 for longitudinal states, > 1.5 for in-plane transverse states, and the two highest for out-of-plane transverse states.

Distance (Å)	Longitudinal		In-plane Transverse		Out-of-plane Transverse	
	Energy (eV)	Oscillator Strength (f)	Energy (eV)	Oscillator Strength (f)	Energy (eV)	Oscillator Strength (f)
3.5	3.59	3.927	3.39	2.663	4.84	2.604
	3.61	4.891	3.77	4.613	5.23	6.141
	3.65	5.731	3.78	2.052		
4.0	3.59	4.590	3.61	1.609	4.82	4.902
	3.71	2.556	3.83	2.161	5.20	1.647
	3.73	3.920	3.89	1.542		
4.5	3.48	9.949	3.82	2.751	4.79	2.611
	3.71	2.392	4.04	2.276	4.82	1.972
5.0	3.30	2.527	4.05	2.363	4.28	4.913
	3.70	21.664	4.16	3.453	4.80	8.554
5.5	3.68	10.900	4.12	2.577	4.28	6.556
	3.69	11.551	4.28	4.196	4.79	10.185
			4.64	2.194		
6.0	3.67	7.675	3.94	2.167	4.28	7.714
	3.68	18.298	4.15	1.810	4.79	11.455
			4.32	1.939		
			4.64	1.908		

Table S6. Breakdown of the main absorption states in the side-by-side Ag_{31}^{+} dimers with their excited-state energies and oscillator strengths. Two states with highest oscillator strengths from each transition category are listed.

Distance (Å)	Longitudinal		In-plane Transverse		Out-of-plane Transverse	
	Energy (eV)	Oscillator Strength (f)	Energy (eV)	Oscillator Strength (f)	Energy (eV)	Oscillator Strength (f)
3.5	3.60	11.545	3.45	4.806	4.78	3.754
	3.71	4.692	3.79	3.882	4.90	2.901
4.0	3.57	9.591	3.78	2.860	4.86	3.934
	3.66	7.485	3.79	3.843	5.20	4.817
4.5	3.68	14.284	3.63	1.509	4.30	4.500
	3.71	6.304	3.75	1.729	4.79	11.514
5.0	3.67	11.593	3.88	3.255	4.29	3.870
	3.69	12.811	4.24	4.536	4.79	11.663
5.5	3.67	18.618	3.91	1.669	4.29	8.795
	3.68	7.867	4.31	4.301	4.79	11.350
6.0	3.66	23.547	4.35	3.567	4.28	9.747
	3.68	3.571	4.75	2.624	4.79	11.098