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

Supporting Information

Effects of Ligands on (De-)Enhancement of Plasmonic Excitations of Silver, Gold and Bimetallic NanoClusters: TD-DFT+TB Calculations

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Table S1 Bonding energy (in eV) based on energy decomposition energy analysis for Au(Ag)–SCH_3 bond in monometallic and bimetallic clusters, and the amount of Hirshfeld transferred charge (in |e|).

Complex	$^{1}\Delta E_{int}$	$^{2}\Delta V_{elstat}$	$^{3}\Delta E_{oi}$	$^{4}\Delta E_{Pauli}$	$^{5}\Delta q$
$Ag_{20}SCH_3^{-1}$	-2.61	-4.35	-2.75	+4.49	-0.60
$Ag_{16}Au_4SCH_3^{-1}$	-2.94	-5.75	-4.09	+6.90	-0.74
$Ag_4Au_{16}SCH_3^{-1}$	-3.02	-4.86	-2.76	+4.60	-0.67
$Au_{20}SCH_3^{-1}$	-3.47	-6.30	-4.14	+6.97	-0.80

[1]Total bonding energy, [2]Electrostatic attractive energy, [3] Total orbital interactions, [4]Total Pauli repulsion, [5]Hirshfild transferred charge from ligand to metal cluster.

Table S2 Splitting the high-intensity excited state of Ag_{20} after interaction with SCH_3.

Ag_{20}		**$Ag_{20}SCH_3$**	
Energy (eV)	***f***	**Energy (eV)**	***f***
3.89	4.63	3.93	1.72
3.89	4.63	3.94	0.92
3.89	4.63	3.98	3.28
	Sum *f* = 13.89	4.10	2.42
		4.14	3.29
		4.14	1.10
			Sum *f* =12.73

Table S3 Splitting the excited states of Au_{20} (with oscillator strength > 10^{-2}) after interaction with SCH_3.

Au_{20}		$Au_{20}SCH_3$	
Energy (eV)	***f***	**Energy (eV)**	***f***
3.2653	0.1689	3.13121	4.67E-02
3.2653	0.1689	3.1558	2.49E-02
3.2653	0.1689	3.18855	1.34E-02
3.4035	0.179	3.19227	1.02E-02
3.4035	0.179	3.20597	3.83E-02
3.4035	0.179	3.21153	2.85E-02
3.50927	9.00E-02	3.2491	1.64E-02
3.50927	9.00E-02	3.26035	2.90E-02
3.50927	9.00E-02	3.2656	2.79E-02
3.61097	5.75E-02	3.28621	1.26E-02
3.61098	5.75E-02	3.29888	2.39E-02
3.61098	5.75E-02	3.30636	4.12E-02
3.66995	2.63E-02	3.32427	5.37E-02
3.66995	2.63E-02	3.34232	7.61E-02
3.66995	2.63E-02	3.34863	9.97E-02
3.83991	1.61E-02	3.39001	1.88E-02
3.83991	1.61E-02	3.44448	2.83E-02
3.83991	1.61E-02	3.45233	0.2081
3.90001	3.16E-02	3.46108	2.46E-02
3.90001	3.16E-02	3.48406	1.21E-02
3.90001	3.16E-02	3.51251	1.50E-02
3.93979	1.54E-02	3.52735	4.85E-02
3.93979	1.54E-02	3.53951	5.10E-02
3.93979	1.54E-02	3.54513	0.102
3.9564	1.95E-02	3.54802	5.51E-02
3.9564	1.95E-02	3.5618	2.34E-02
3.9564	1.95E-02	3.57082	0.1064
	Sum *f* = 1.81	3.5749	6.64E-02
		3.58493	2.24E-02
		3.59548	6.65E-02
		3.60331	8.15E-02
		3.61291	7.18E-02
		3.61666	4.20E-02
		3.62595	2.46E-02
		3.63713	1.96E-02
		3.63901	1.35E-02
		3.64092	1.01E-02
		3.65498	1.62E-02
		3.66066	3.74E-02
		3.7147	0.1288
		3.72017	1.45E-02
		3.73067	1.55E-02
		3.7355	1.54E-02
		3.75394	1.94E-02
		3.75599	1.23E-02
		3.77378	1.73E-02
		3.82344	1.11E-02
			Sum *f* = 1.94

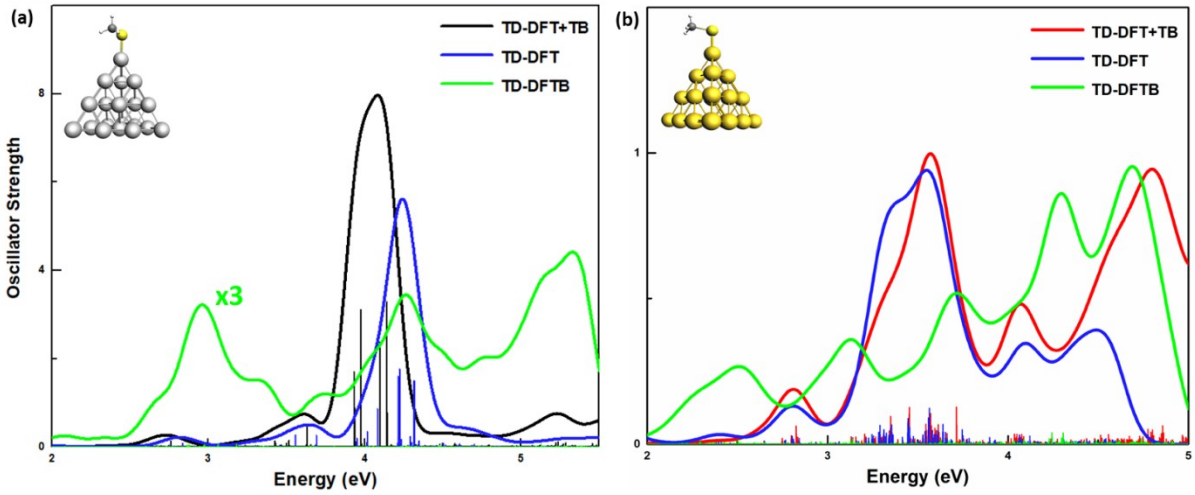

Figure S1. Absorption spectra for (a) $Ag_{20}SCH_3$, (b) $Au_{20}SCH_3$, with TD-DFT+TB, TD-DFT and TD-DFTB level of theory. Spectra have been broadened with a σ = 0.2 eV Gaussian.

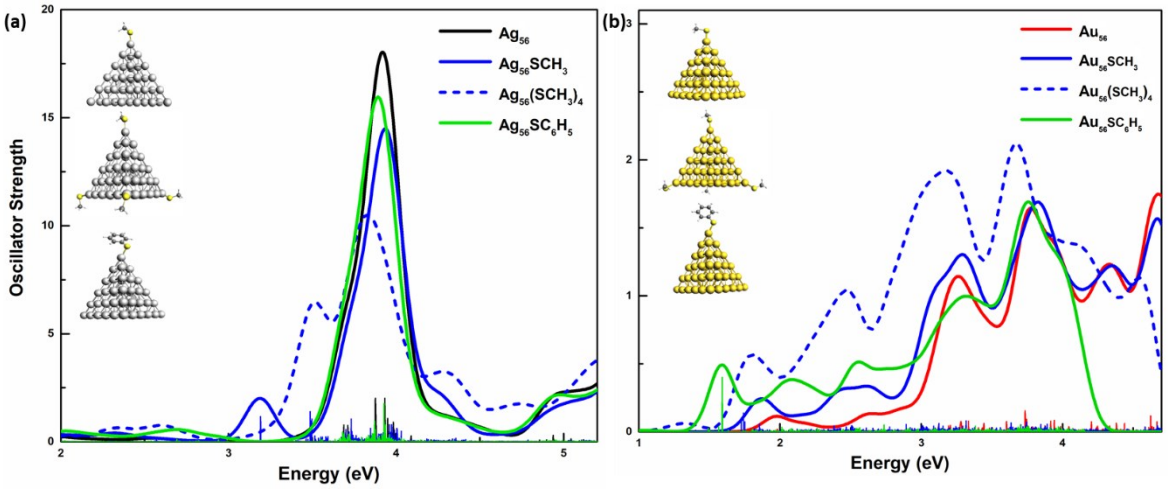

Figure S2. Calculated absorption spectra for (a) Ag_{56} and (b) Au_{56} with SCH_3 and SC_6H_5 ligands. Spectra have been broadened with a σ = 0.2 eV Gaussian.

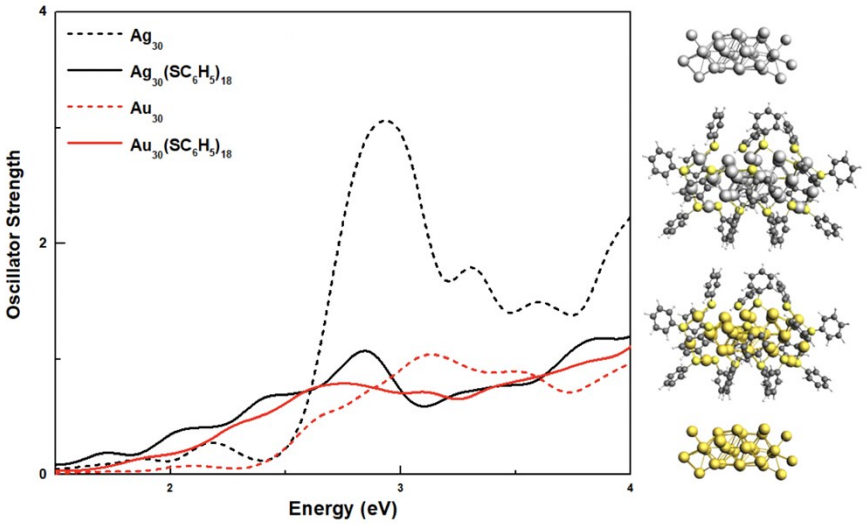

Figure S3. Calculated TD-DFT+TB absorption spectra for Ag_{30}, $Ag_{30}(SC_6H_5)_{18}$, Au_{30}, and $Au_{30}(SC_6H_5)_{18}$. Spectra have been broadened with a σ = 0.2 eV Gaussian.

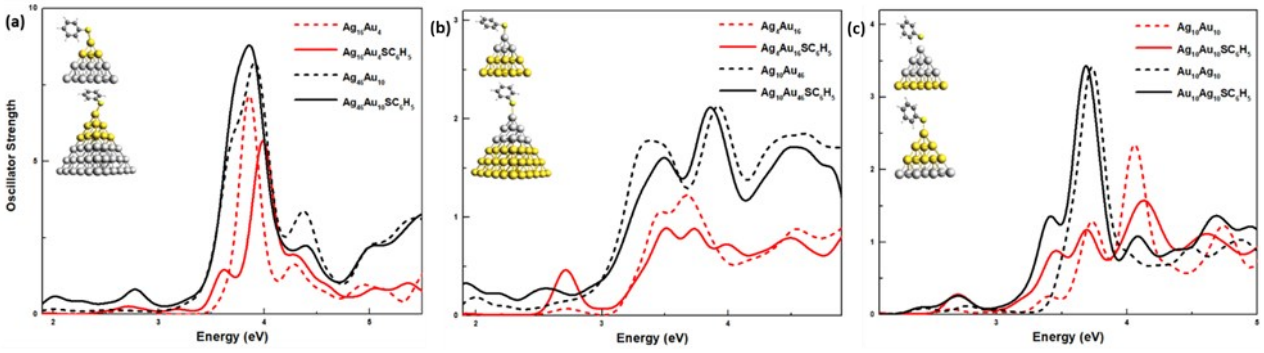

Figure S4. Calculated absorption spectra for (a) $Ag_{16}Au_4SC_6H_5$ and $Ag_{46}Au_{10}SC_6H_5$ (b) $Ag_4Au_{16}SC_6H_5$ and $Ag_{10}Au_{46}SC_6H_5$, and (c) $Ag_{10}Au_{10}SC_6H_5$ and $Au_{10}Ag_{10}SC_6H_5$. Spectra have been broadened with a σ = 0.2 eV Gaussian.

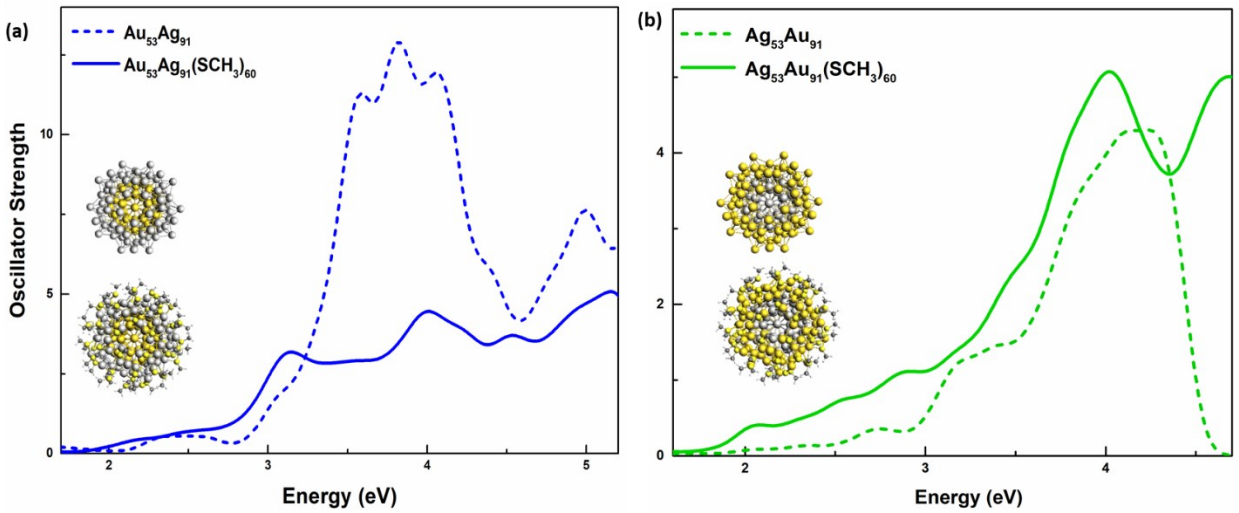

Figure S5. Calculated absorption spectra for (a) $Au_{53}Ag_{91}(SCH_3)_{60}$ and $Au_{53}Ag_{91}$(b) Ag_{53} $Au_{91}(SCH_3)_{60}$ and $Ag_{53}Au_{91}$. Spectra have been broadened with a σ = 0.2 eV Gaussian.

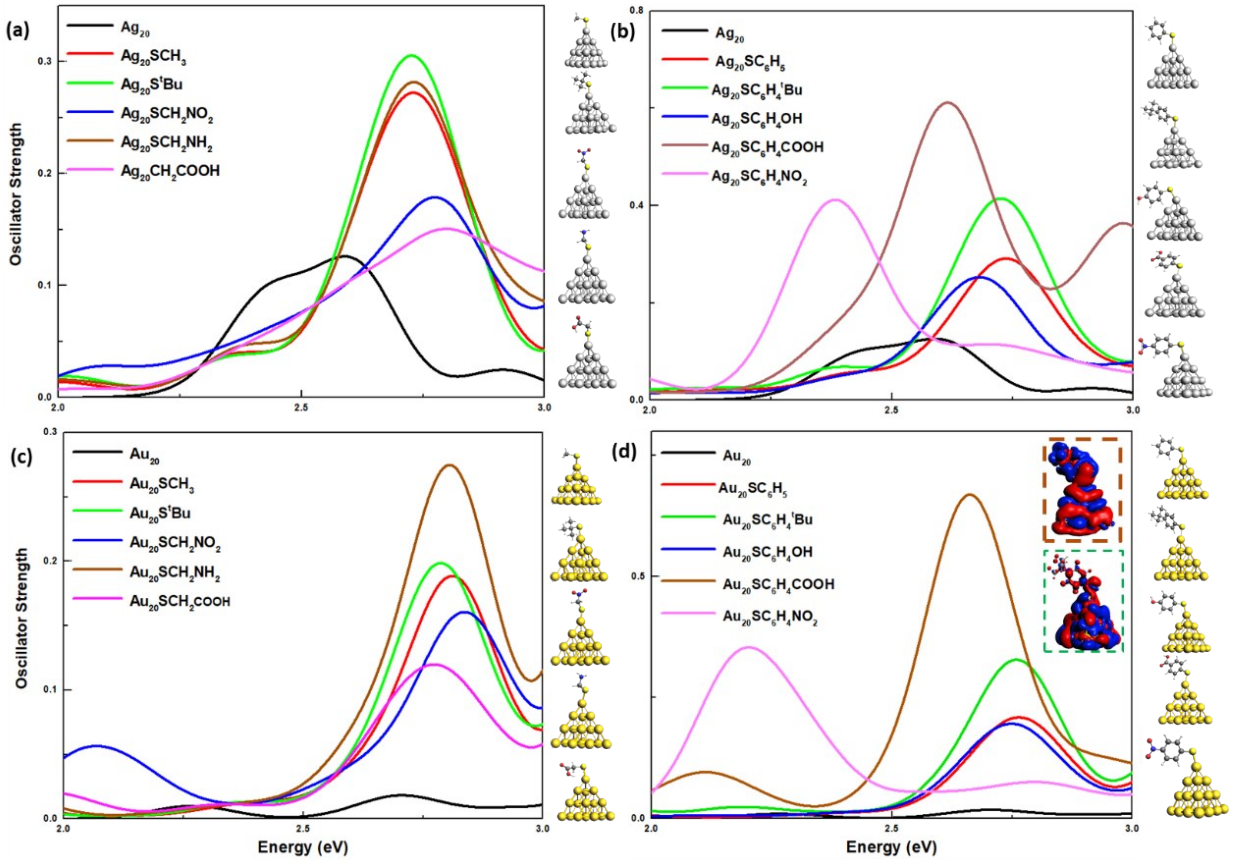

Figure S6. Calculated TD-DFT+TB absorption spectra for Ag_{20} (a, b) and Au_{20} (c, d) with different donor and acceptor functional groups in the range of 2 to 3 eV. Spectra have been broadened with a σ = 0.2 eV Gaussian.

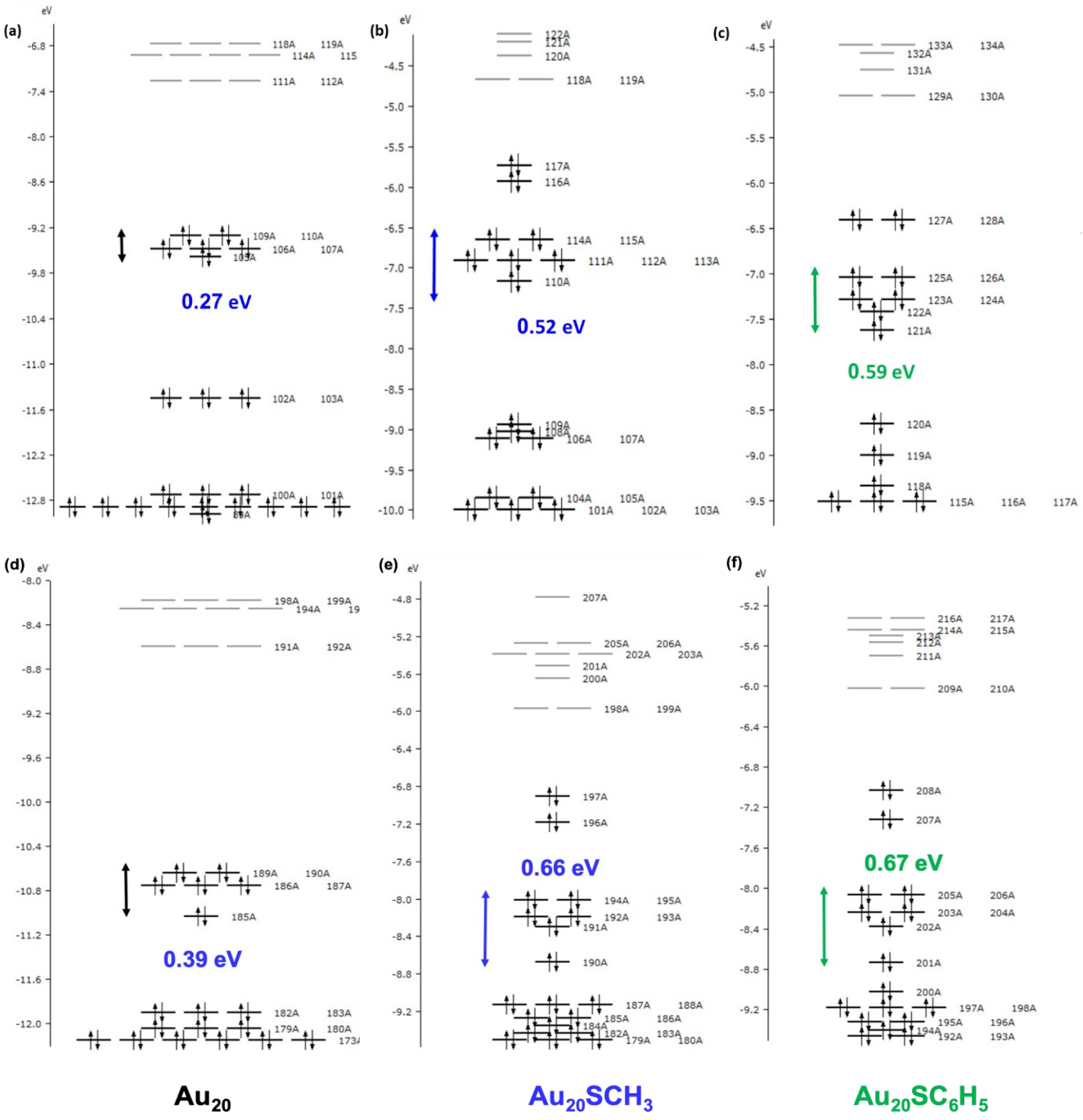

Figure S7. Level of energy for molecular orbitals of (a) Ag_{20}, (b) $Ag_{20}SCH_3$, (c) $Ag_{20}SC_6H_5$, (d) Au_{20}, (e) $Au_{20}SCH_3$, and (f) $Au_{20}SC_6H_5$.