Supporting Information

Electronic relaxation dynamics in $[Au_{25}(SR)_{18}]^{-1}$ (R = CH_3, C_2H_5, C_3H_7, MPA, PET) thiolate-protected nanoclusters

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The electronic structure of the R=MPA system has a different pattern of excitations compared to R=H, CH_3, C_2H_5, C_3H_7. In R=MPA, the first excitation is mainly constructed from a HOMO → LUMO transition (S_1 state) which has a high weight (0.8587). Likewise, excited states 4, 5 and 6 also have one transition which has a high weight and they directly resemble the S_4, S_5 and S_6 states, respectively, that were defined for the FSSH-TDKS calculations. The other ligand systems' excited states are a mix of several excitations based on their weights as shown in Table S1 below.

Table S1. The TDDFT excitations, energy, oscillator strength, weights and most weighted transitions involved in the ~1.35 eV peak of the $[Au_{25}(SR)_{18}]^{-1}$ (R = CH_3, C_2H_5, C_3H_7, MPA, PET) clusters.

Excited states for R= CH_3	Energy (eV)	Oscillator strength	Weight	Most weighted transitions
4	1.34	0.0217	0.5339	HOMO → LUMO+1
			0.1832	HOMO-1 → LUMO
			0.1519	HOMO-2 → LUMO
			0.0943	HOMO → LUMO
			0.0122	HOMO-1 → LUMO+1
5	1.35	0.0230	0.6838	HOMO-1 → LUMO
			0.2163	HOMO → LUMO+1
			0.0418	HOMO-1 → LUMO+1
			0.027	HOMO → LUMO
6	1.37	0.0228	0.8776	HOMO-2 → LUMO+1
			0.0544	HOMO → LUMO
			0.0251	HOMO-2 → LUMO
			0.0101	HOMO → LUMO+1

Excited states for R= C_2H_5	Energy (eV)	Oscillator strength	Weight	Most weighted transitions
4	1.36	0.0235	0.5041	HOMO → LUMO+1
			0.2451	HOMO-2 → LUMO
			0.1611	HOMO → LUMO
			0.0345	HOMO-1 → LUMO+1
			0.0249	HOMO-1 → LUMO
5	1.37	0.0245	0.4358	HOMO-1 → LUMO
			0.2659	HOMO-2 → LUMO
			0.2327	HOMO → LUMO+1
			0.0234	HOMO-1 → LUMO+1
			0.0144	HOMO → LUMO
6	1.39	0.0252	0.6122	HOMO-2 → LUMO+1
			0.2615	HOMO-1 → LUMO+1
			0.0586	HOMO → LUMO
			0.0329	HOMO-2 → LUMO

Excited states for R= C_3H_7	Energy (eV)	Oscillator strength	Weight	Most weighted transitions
4	1.35	0.0244	0.4485	HOMO → LUMO+1
			0.2191	HOMO → LUMO
			0.2174	HOMO-2 → LUMO
5	1.36	0.0261	0.3531	HOMO-1 → LUMO
			0.3345	HOMO-2 → LUMO
			0.2366	HOMO → LUMO+1
6	1.38	0.0269	0.6256	HOMO-2 → LUMO+1
			0.2556	HOMO-1 → LUMO+1

Excited states for R= MPA	Energy (eV)	Oscillator strength	Weight	Most weighted transitions
1	1.13	0.0131	0.8587	HOMO → LUMO
			0.0699	HOMO → LUMO+1
			0.0222	HOMO-2 → LUMO
			0.0172	HOMO-1 → LUMO
			0.0137	HOMO-1 → LUMO+1
2	1.14	0.0012	0.7229	HOMO-1 → LUMO
			0.2606	HOMO → LUMO+1
			0.0118	HOMO-1 → LUMO+1
3	1.16	0.0062	0.6455	HOMO → LUMO+1
			0.2313	HOMO-1 → LUMO
			0.0900	HOMO → LUMO
			0.0164	HOMO-2 → LUMO+1
4	1.27	0.0220	0.9412	HOMO-1 → LUMO+1
			0.0162	HOMO-1 → LUMO
			0.0116	HOMO → LUMO
			0.0071	HOMO-2 → LUMO
			0.0044	HOMO-2 → LUMO+2
5	1.31	0.0177	0.9194	HOMO-2 → LUMO
			0.032	HOMO-2 → LUMO+1

			0.0143	HOMO → LUMO
			0.0097	HOMO-1 → LUMO+1
6	1.38	0.0176	0.9279	HOMO-2 → LUMO+1
			0.0301	HOMO-2 → LUMO

Excited states for R= PET	Energy (eV)	Oscillator strength	Weight	Most weighted transitions
4	1.35	0.0246	0.4067	HOMO-1 - LUMO
			0.3073	HOMO-1 - LUMO+1
			0.1241	HOMO - LUMO
			0.107	HOMO-2 - LUMO
			0.0313	HOMO - LUMO+1
5	1.37	0.0308	0.5929	HOMO - LUMO+1
			0.2286	HOMO-2 - LUMO
			0.0805	HOMO-1 - LUMO
			0.0361	HOMO - LUMO
			0.0267	HOMO-1 - LUMO+1
6	1.40	0.0305	0.8557	HOMO-2 - LUMO+1
			0.0615	HOMO - LUMO+1
			0.0406	HOMO-1 - LUMO

Energy vs time at 300K for $Au_{25}(SC_2H_5)_{18}^-$

Energy vs time at 300K for $Au_{25}(SC_3H_7)_{18}^-$
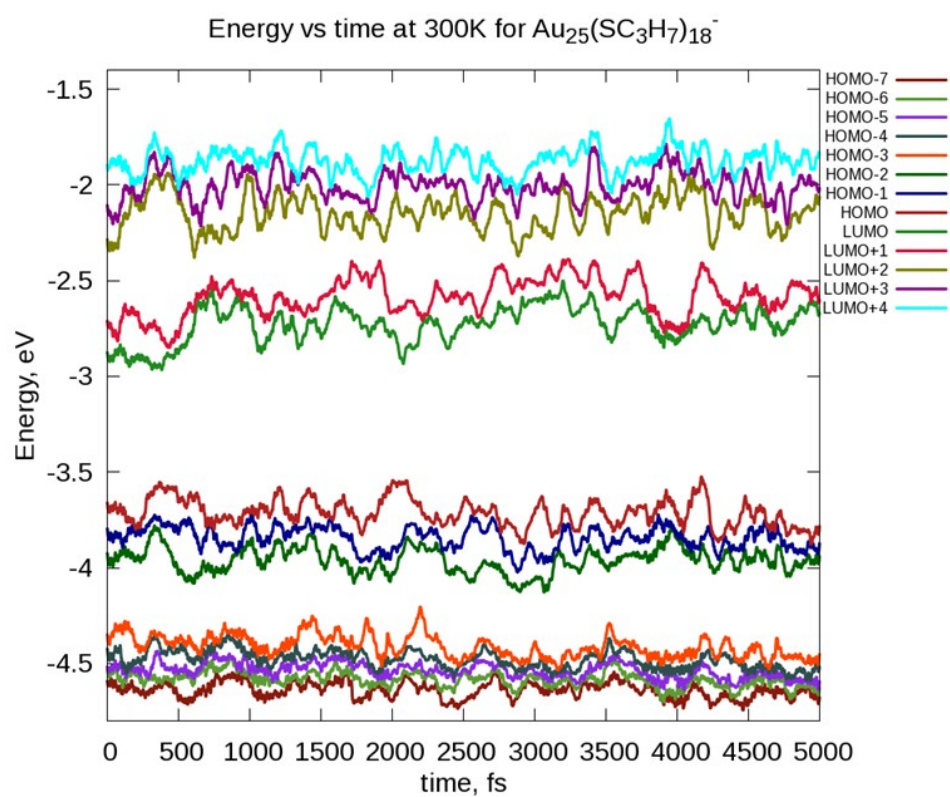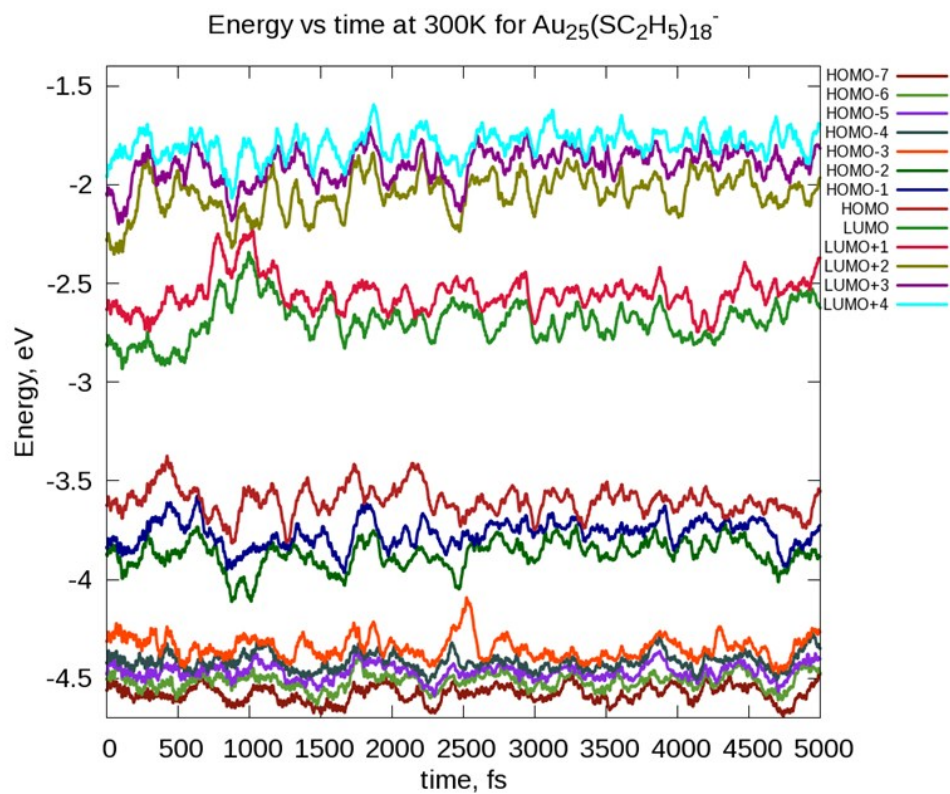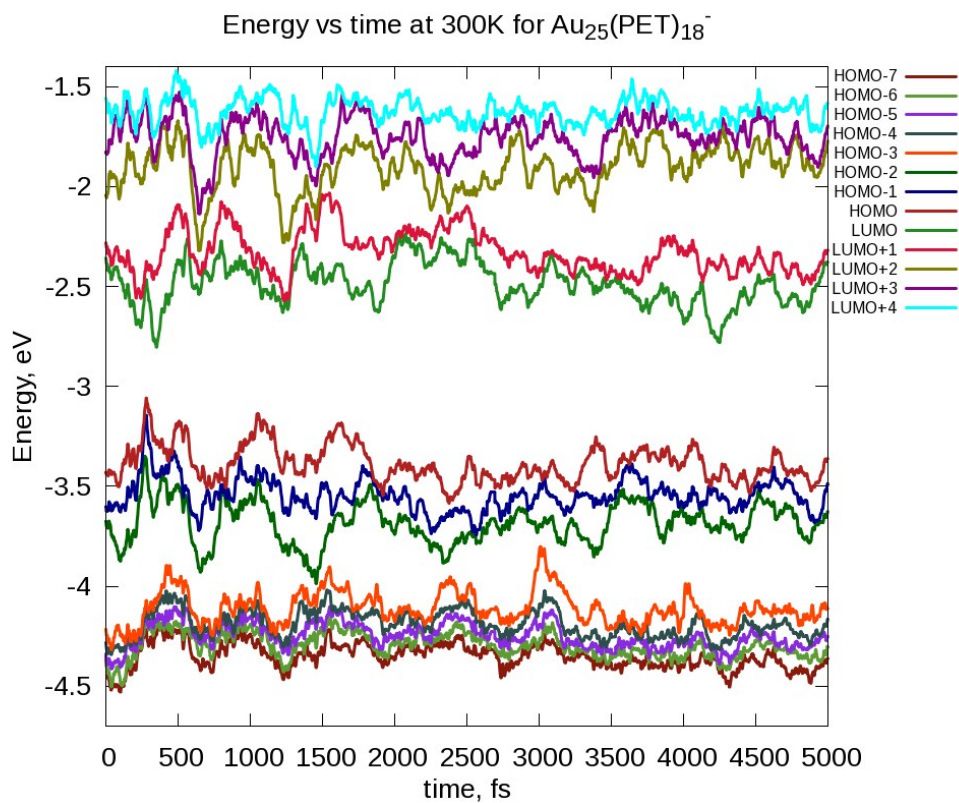
Figure S1. Orbital energy variation with time during the MD simulation for $[Au_{25}(SR)_{18}]^{-1}$ (R= C_2H_5, C_3H_7, PET).
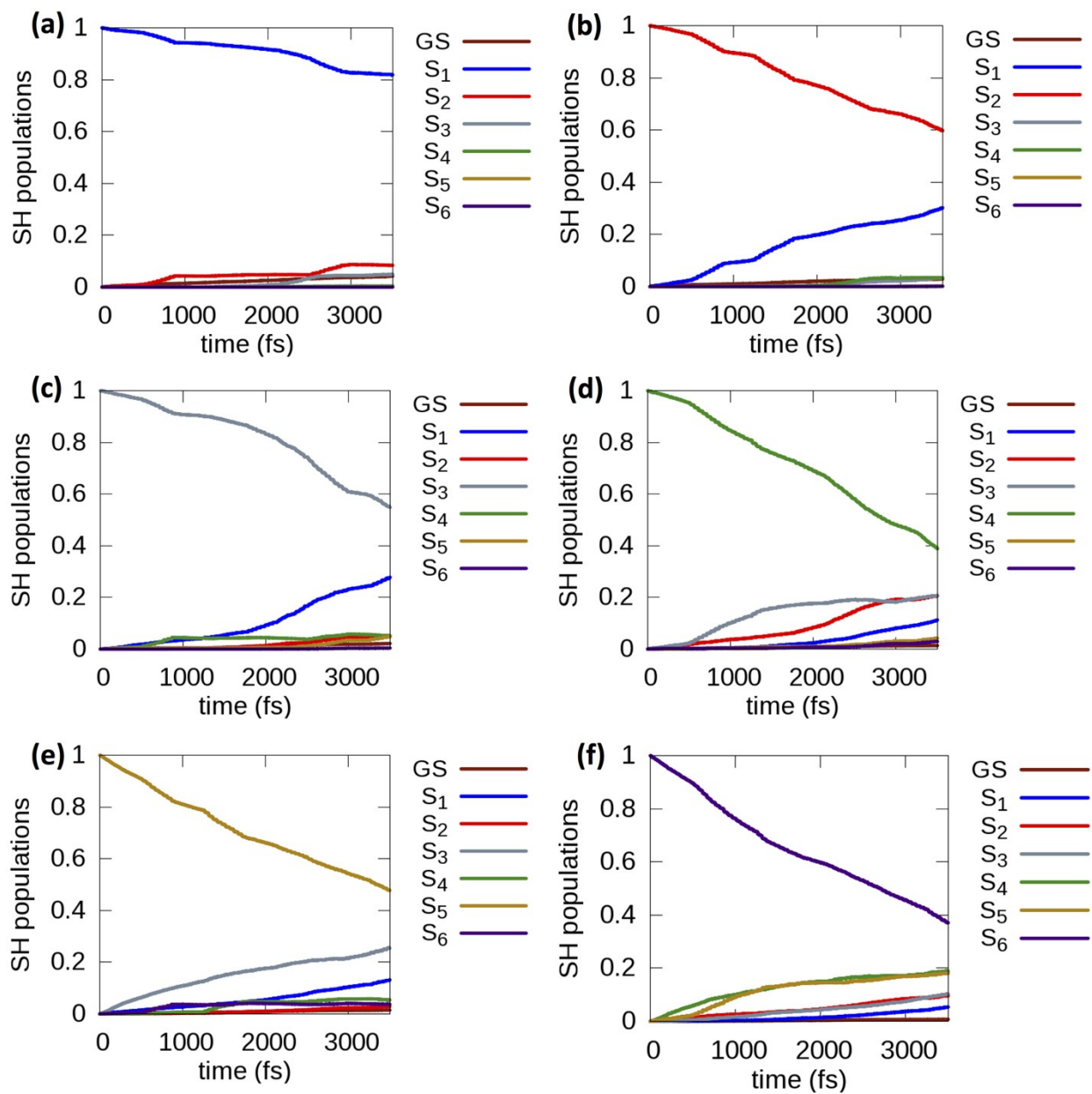
Figure S2. Evolution of the populations of S_1, S_2, S_3, S_4, S_5, S_6 states. Panels a−f are relaxations from S_1 to S_6, respectively, with the energy correction for $[Au_{25}(SCH_3)_{18}]^{-1}$.

Table S2. Individual GS growth and decay time constants, averages, and standard deviations calculated for four different MD simulations for $[Au_{25}(SCH_3)_{18}]^{-1}$.

|	GS growth time (ps)					
Excited state	0-5 ps	5-10 ps	10-15 ps	Different temperature ramp MD	Average	Std. Dev
S_1	24	48	44	56	**43**	14
S_2	24	64	45	61	**48**	18
S_3	44	57	38	72	**53**	15
S_4	65	68	50	73	**64**	10
S_5	35	84	56	88	**66**	25
S_6	61	78	54	99	**73**	20
	Decay time (ps)					
Excited state	0-5 ps	5-10 ps	10-15 ps	Different temperature ramp MD	Average	Std. Dev
S_1	12	13	8	13	**12**	2.3
S_2	6.0	4.4	2.7	4.3	**4.4**	1.4
S_3	7.1	3.5	2.9	5.2	**4.7**	1.9
S_4	4.6	2.3	1.9	2.6	**2.8**	1.2
S_5	4.3	2.5	2.4	3.5	**3.2**	0.9
S_6	3.7	1.9	1.8	2.4	**2.4**	0.9
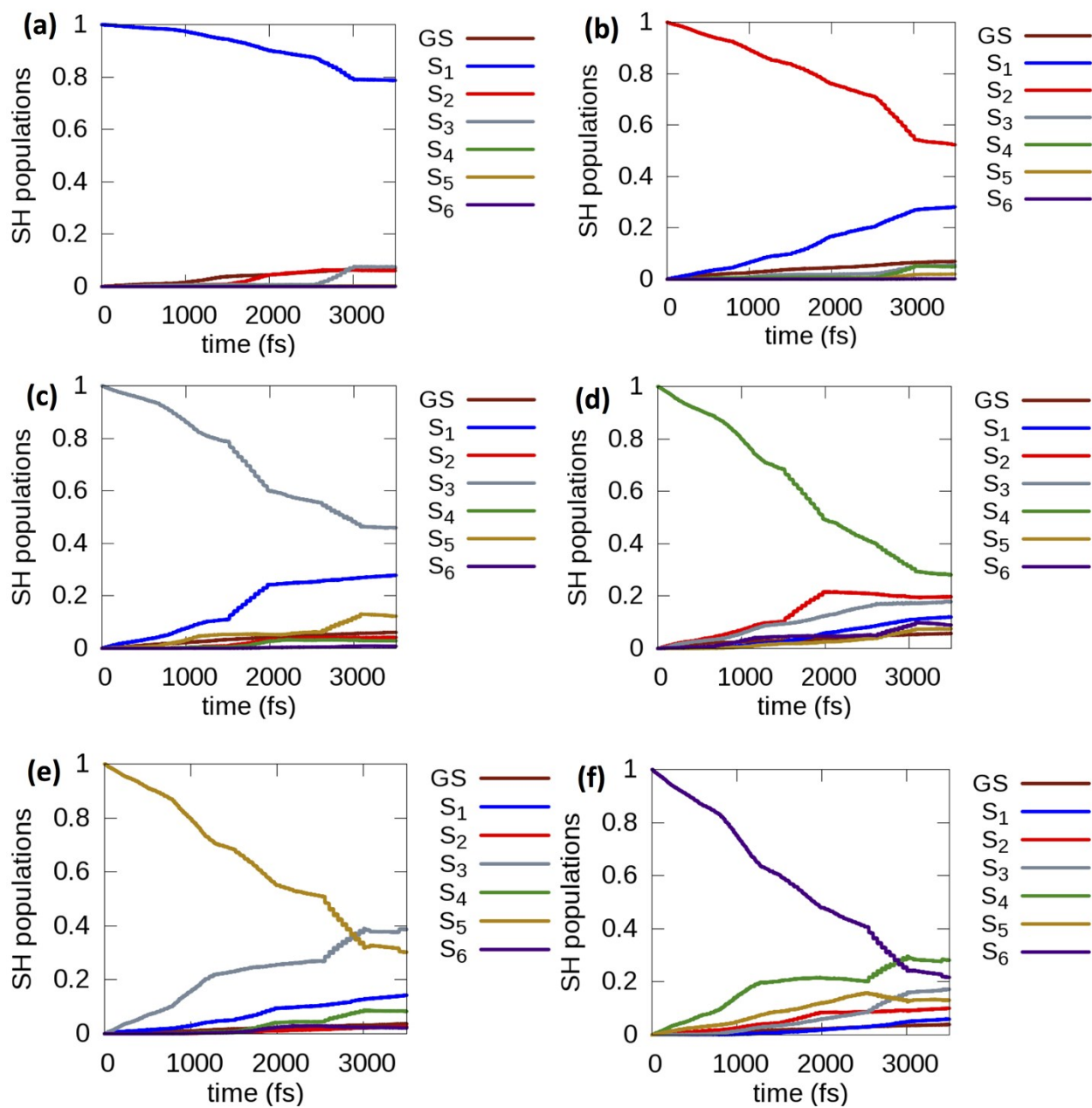
Figure S3. Evolution of the populations of the S_1, S_2, S_3, S_4, S_5, S_6 states for $[Au_{25}(SC_2H_5)_{18}]^{-1}$ without the energy correction. Panels a–f are relaxations from S_1 to S_6, respectively.
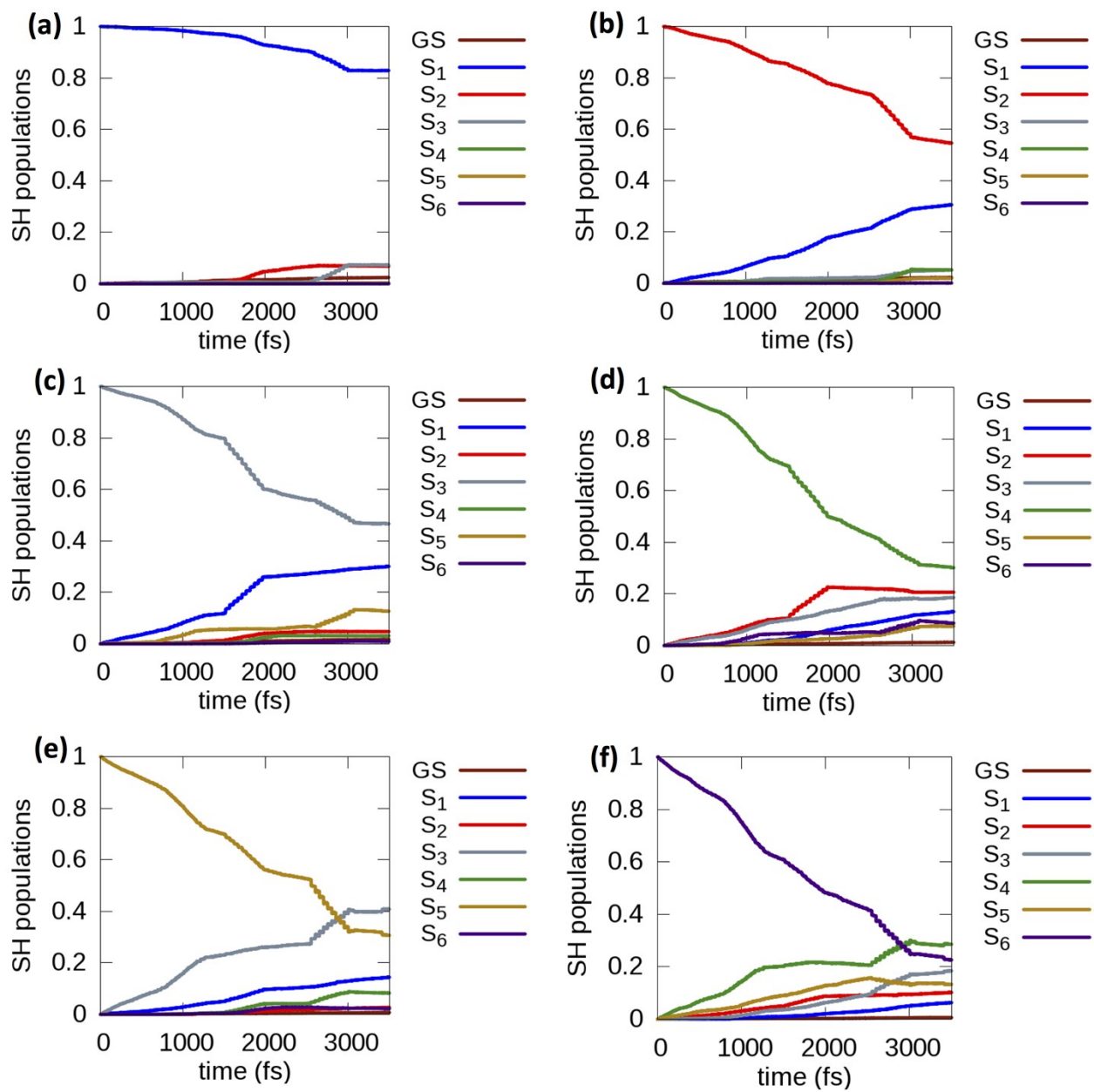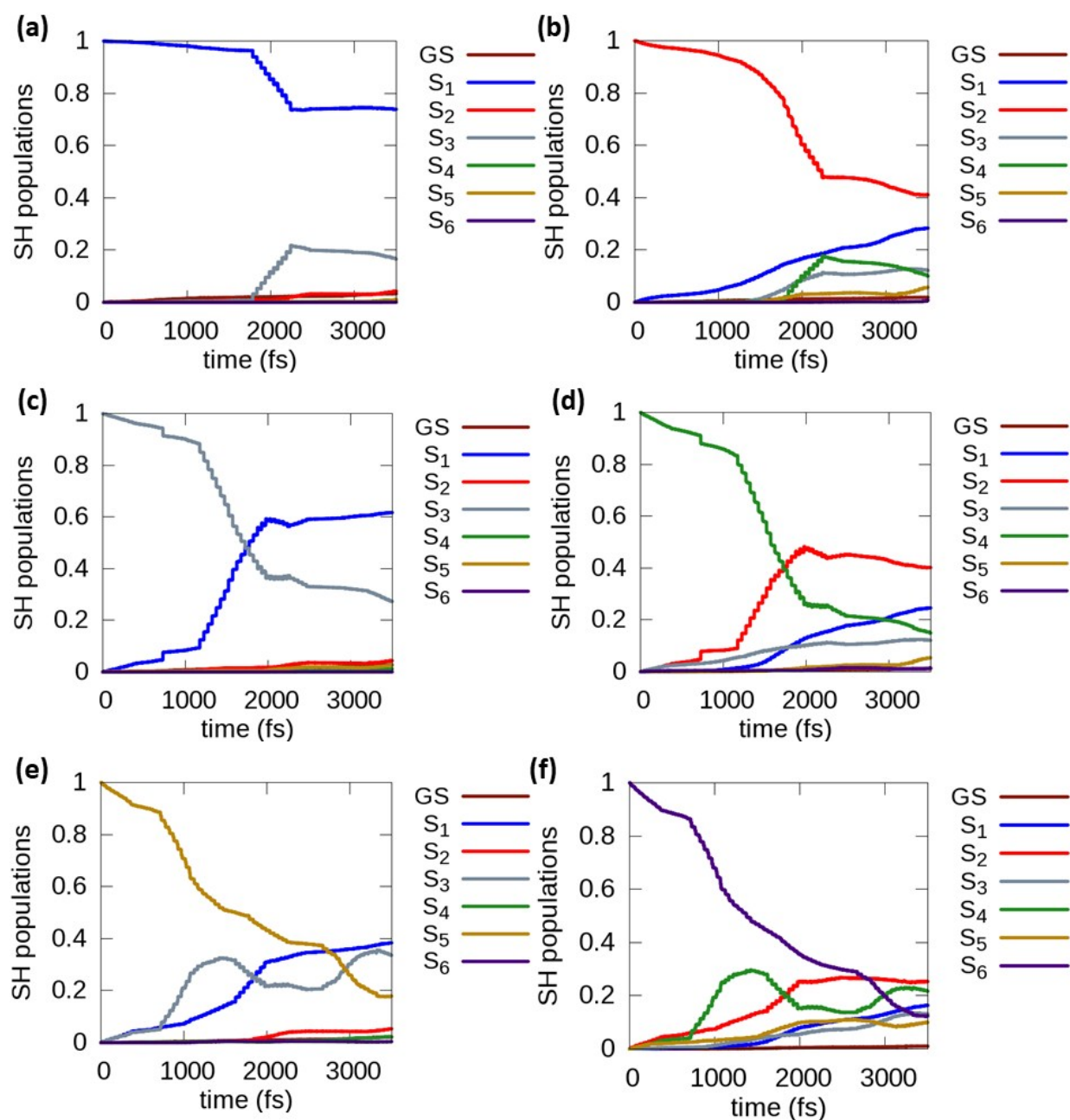
Figure S4. Evolution of the populations of the S_1, S_2, S_3, S_4, S_5, S_6 states for $[Au_{25}(SC_2H_5)_{18}]^{-1}$ with the 0.55 eV energy correction. Panels a−f are relaxations from S_1 to S_6, respectively.
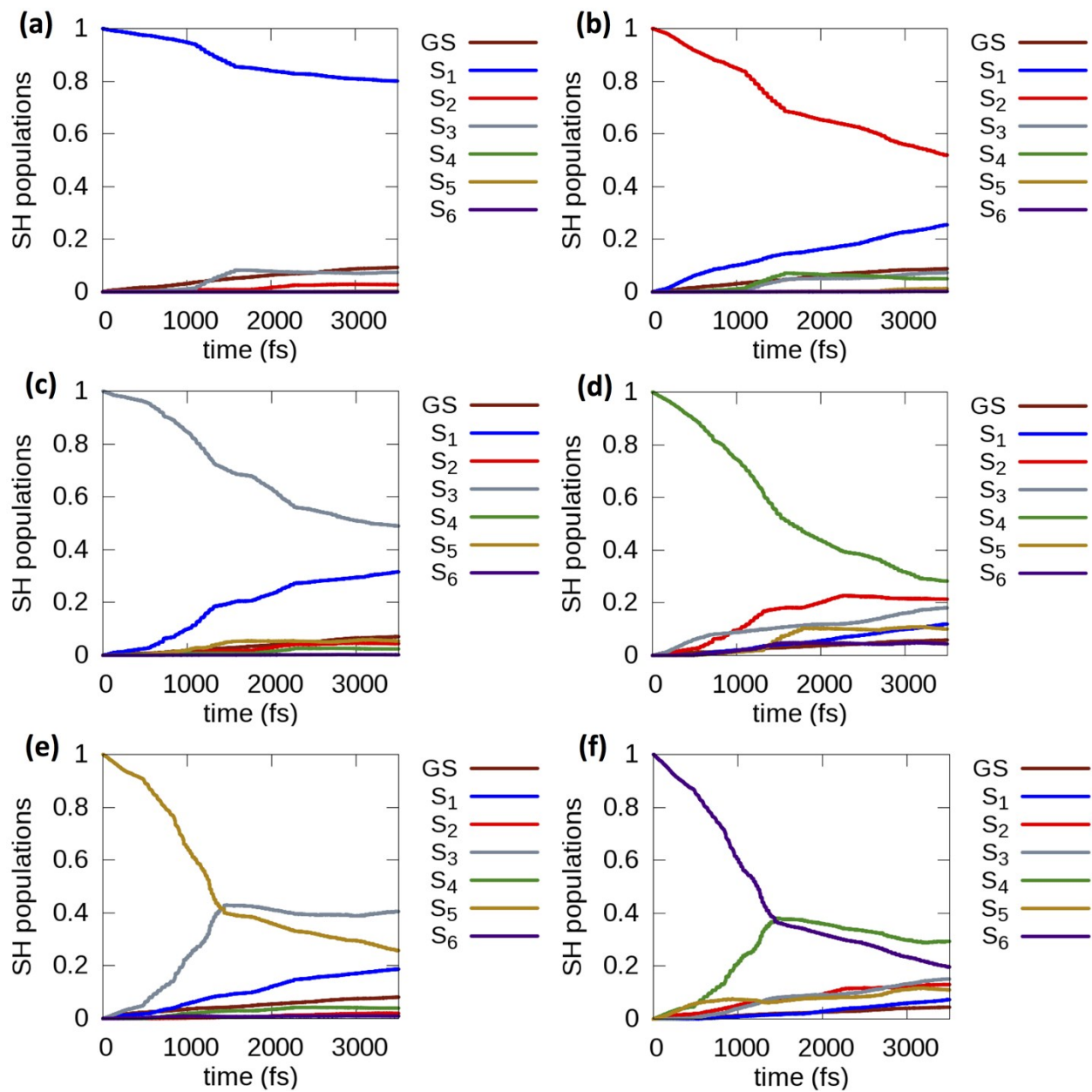
Figure S5. Evolution of the populations of the S_1, S_2, S_3, S_4, S_5, S_6 states for $[Au_{25}(SC_3H_7)_{18}]^{-1}$ without the energy correction. Panels a−f are relaxations from S_1 to S_6, respectively.
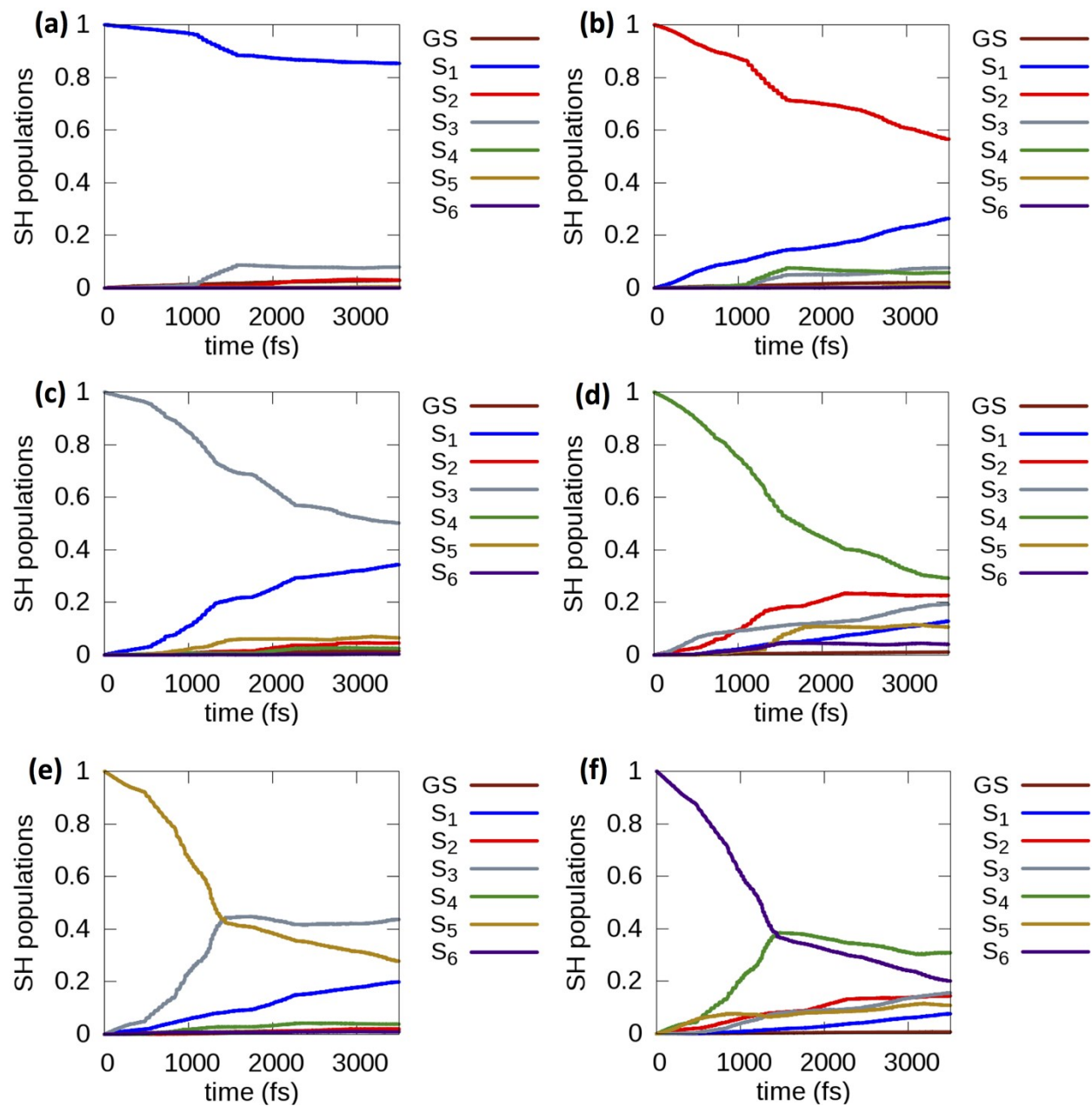
Figure S6. Evolution of the populations of the S_1, S_2, S_3, S_4, S_5, S_6 states for $[Au_{25}(SC_3H_7)_{18}]^{-1}$ with the 0.55 eV energy correction. Panels a−f are relaxations from S_1 to S_6, respectively.

Figure S7. Evolution of the populations of the S_1, S_2, S_3, S_4, S_5, S_6 states for $[Au_{25}(MPA)_{18}]^{-1}$ with the 0.55 eV energy correction. Panels a−f are relaxations from S_1 to S_6, respectively.
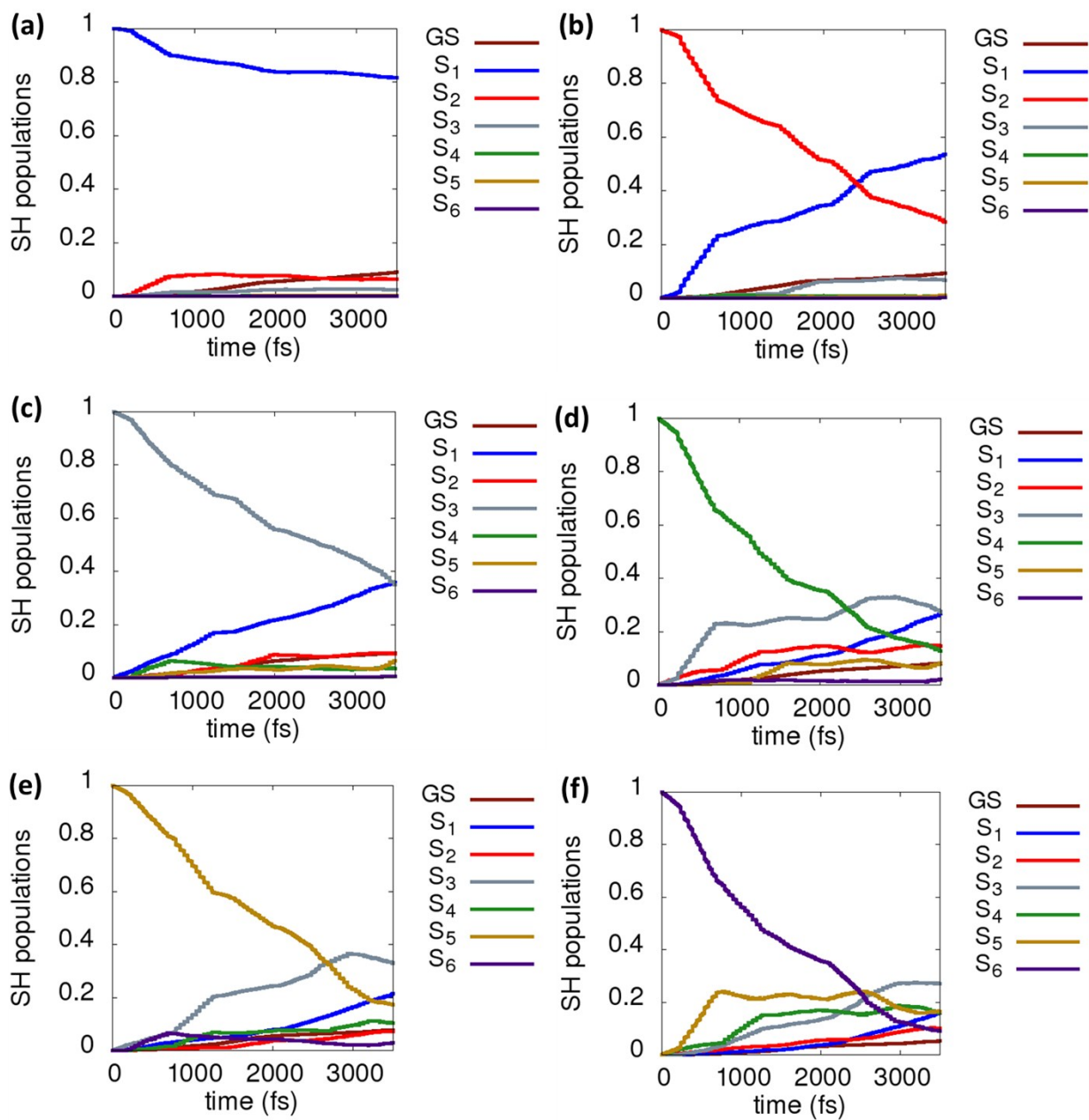
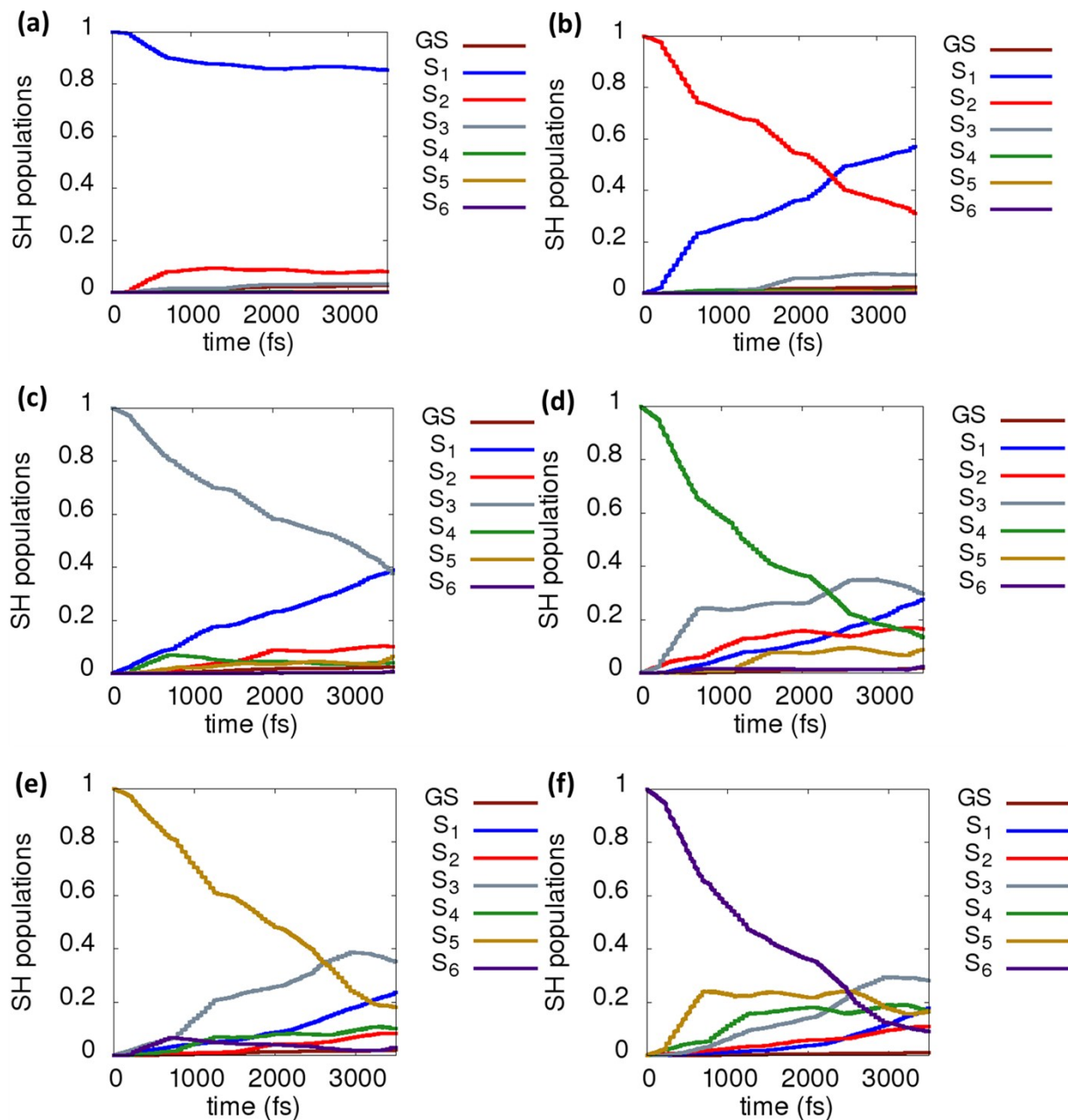**Figure S8**. Evolution of the populations of the S_1, S_2, S_3, S_4, S_5, S_6 states for $[Au_{25}(MPA)_{18}]^{-1}$ without the energy correction. Panels a−f are relaxations from S_1 to S_6, respectively.

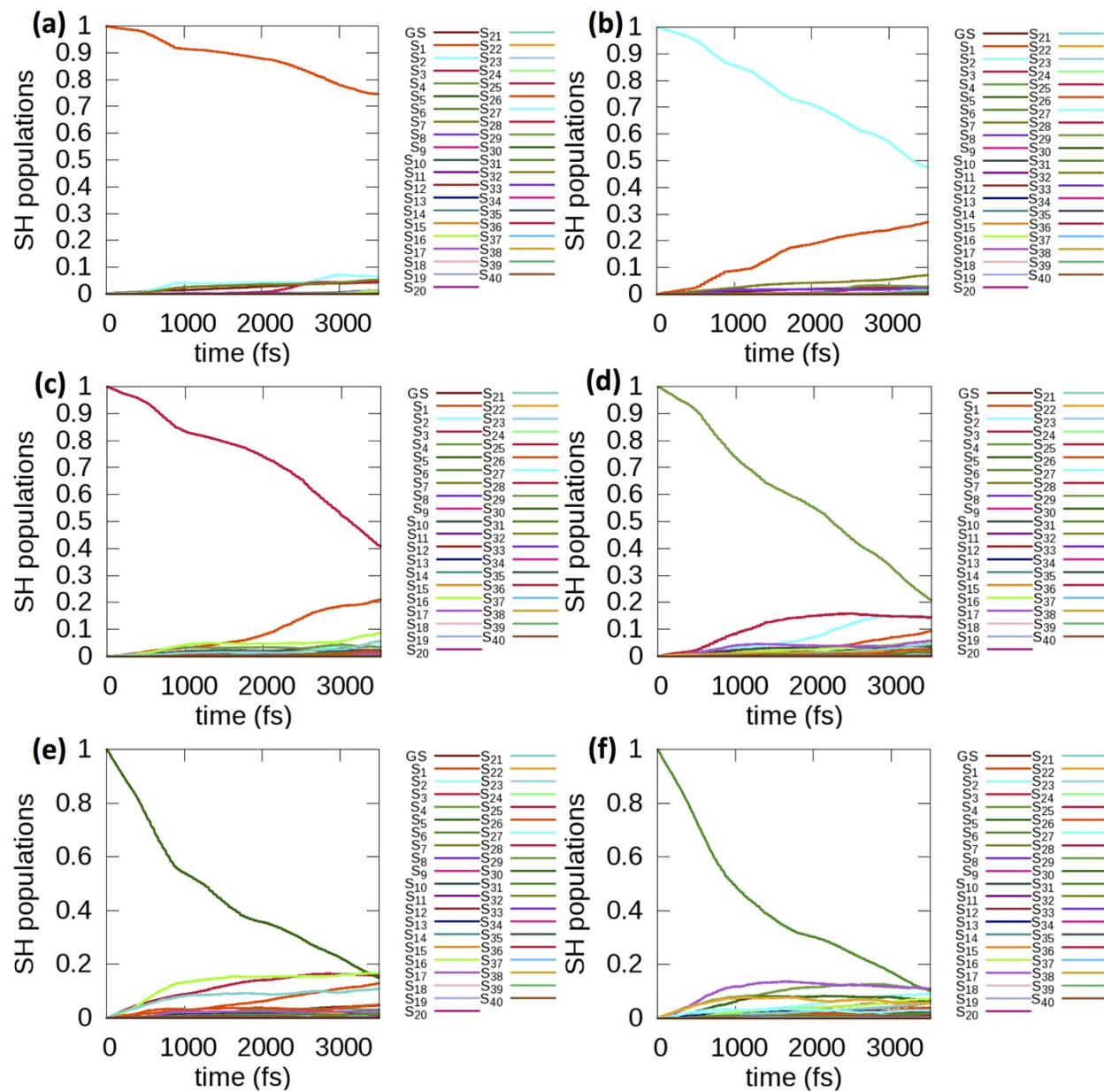**Figure S9**. Evolution of the populations of the S_1, S_2, S_3, S_4, S_5, S_6 states for $[Au_{25}(MPA)_{18}]^{-1}$ with the 0.55 eV energy correction. Panels a–f are relaxations from S_1 to S_6, respectively.

Table S3. GS growth times calculated for ligated clusters with the 0.55 eV energy correction.

Excited state	GS growth times (ps) with correction					
	H	CH_3	C_2H_5	C_3H_7	MPA	PET
S_1	313	77	129	102	99	118
S_2	365	105	136	139	175	128
S_3	441	168	184	207	128	140
S_4	690	258	257	277	298	212
S_5	750	215	476	184	188	176
S_6	1429	477	566	473	395	346

Table S4. Decay times calculated for ligated clusters with the 0.55 eV energy correction.

Excited state	Decay times (ps) with correction					
	H	CH_3	C_2H_5	C_3H_7	MPA	PET
S_1	18	18	22	18	12	16
S_2	3.3	7.4	7.0	5.9	4.5	3.1
S_3	3.1	7.8	4.6	4.6	2.9	3.9
S_4	1.9	4.7	3.2	2.7	2.2	1.9
S_5	2.6	4.9	3.5	2.3	2.4	2.6
S_6	1.9	3.8	2.7	1.9	2.1	1.7

Figure S10. Evolution of the populations of states initially excited into S_1, S_2, S_3, S_4, S_5, S_6 (a-f, respectively) for $[Au_{25}(SCH_3)_{18}]^{-1}$ with the 0.55 eV energy correction in the presence of higher excited states.
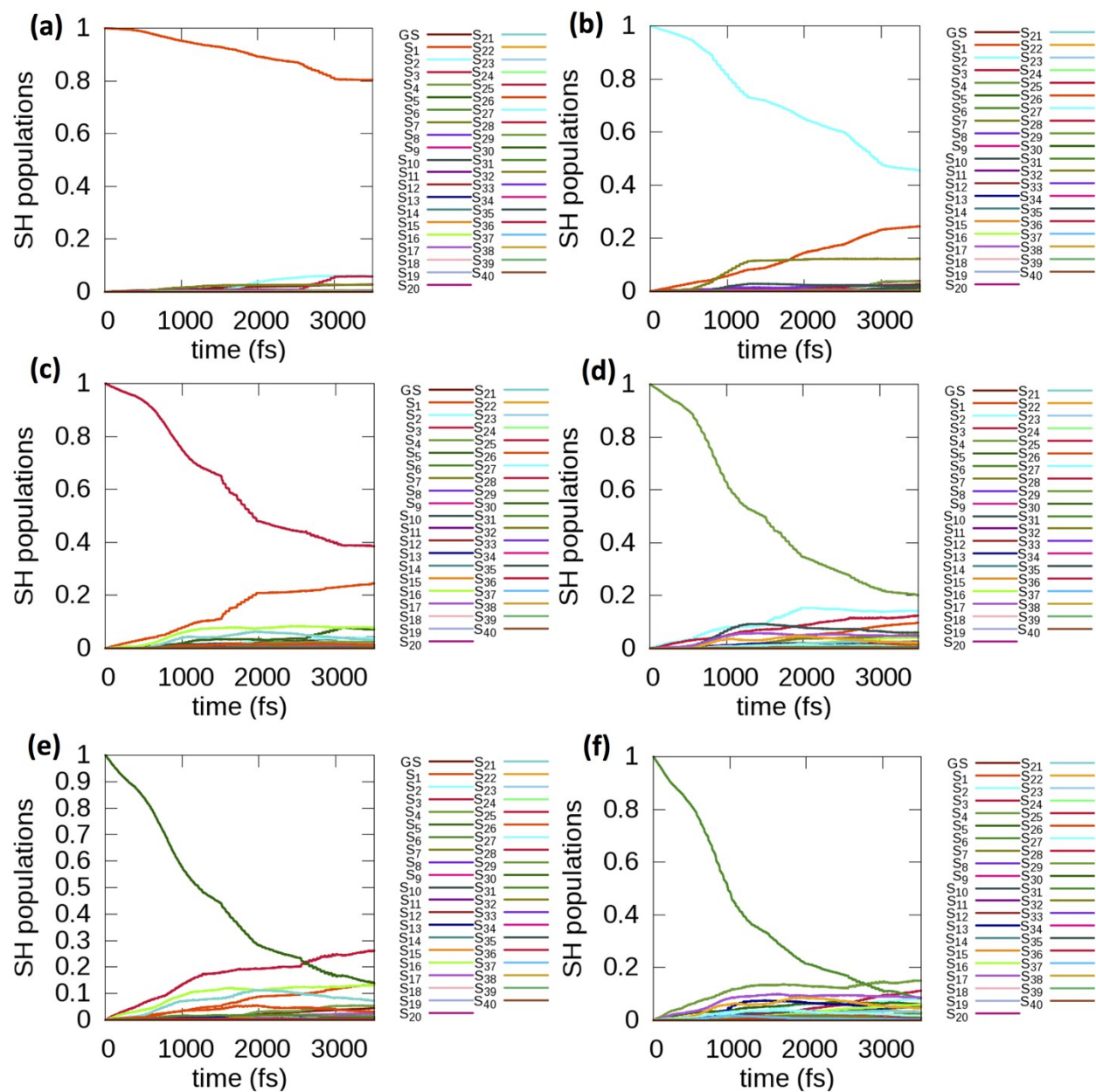
Figure S11. Evolution of the populations of states initially excited into S_1, S_2, S_3, S_4, S_5, S_6 (a-f, respectively) for $[Au_{25}(SC_2H_5)_{18}]^{-1}$ with the 0.55 eV energy correction in the presence of higher excited states.
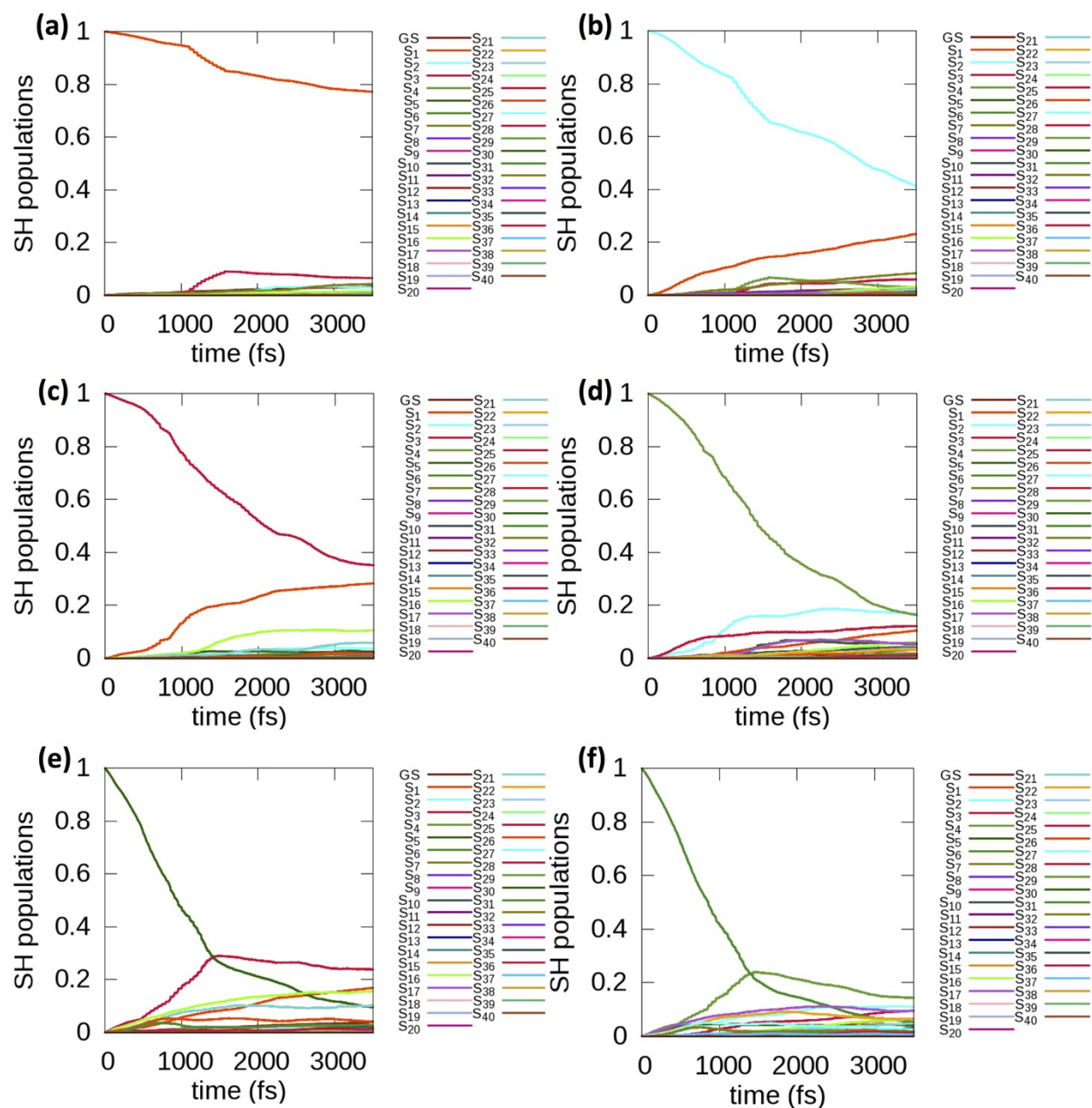
Figure S12. Evolution of the populations of states initially excited into S_1, S_2, S_3, S_4, S_5, S_6 (a-f, respectively) for $[Au_{25}(SC_3H_7)_{18}]^{-1}$ with the 0.55 eV energy correction in the presence of higher excited states.

**Table S5**. Decay time constants obtained for $[Au_{25}(SR)_{18}]^{-1}$ (R = CH_3, C_2H_5, C_3H_7, MPA, PET) nanoclusters for S_1-S_{40} states. The subscript "a" – The PET decay times were calculated without adding the 0.55 eV correction to the S_1-S_6 states.

Decay time (ps)					
Excited state	methyl	ethyl	propyl	MPA	PET[a]
S_1	14	17	12	11	14
S_2	5.6	4.6	4.2	2.8	2.9
S_3	5.8	3.2	3.3	2.0	3.9
S_4	3.1	2.1	2.1	1.5	1.9
S_5	1.9	1.8	1.3	1.0	2.8
S_6	1.6	1.4	1.1	0.9	1.7
S_7	8.0	13	11	8.6	8.3
S_8	1.6	2.0	2.0	1.9	2.3
S_9	1.4	1.6	1.4	1.1	2.2
S_{10}	3.7	3.7	3.8	2.3	2.7
S_{11}	1.4	1.3	1.4	1.3	1.4
S_{12}	1.5	1.2	1.1	0.9	1.7
S_{13}	3.7	3.3	2.3	1.5	2.4
S_{14}	1.5	1.5	1.2	0.8	1.4
S_{15}	1.5	1.1	1.0	0.7	1.5
S_{16}	3.5	2.4	3.9	4.1	2.6
S_{17}	2.3	2.2	2.7	2.3	1.5
S_{18}	2.2	2.1	2.6	2.2	2.3
S_{19}	1.0	1.0	1.3	0.9	1.2
S_{20}	1.1	0.9	1.0	0.7	1.2
S_{21}	1.8	1.3	1.6	1.4	1.3
S_{22}	1.3	1.3	1.3	1.2	0.9
S_{23}	1.4	1.2	1.5	0.9	1.2
S_{24}	0.7	0.6	0.8	0.6	0.8
S_{25}	0.8	0.6	0.6	0.5	0.8
S_{26}	1.0	1.0	1.0	1.1	0.9
S_{27}	0.8	0.9	0.9	0.9	0.7
S_{28}	0.9	1.0	0.9	0.9	0.9
S_{29}	0.6	0.6	0.6	0.6	0.6
S_{30}	0.7	0.6	0.5	0.5	0.7
S_{31}	0.9	1.0	0.8	0.9	0.7
S_{32}	0.8	1.1	0.8	0.9	0.6
S_{33}	0.8	1.0	0.8	0.7	0.8

S$_{34}$	0.6	0.6	0.6	0.5	0.6
S$_{35}$	0.7	0.6	0.5	0.4	0.6
S$_{36}$	1.2	1.0	1.0	0.7	0.7
S$_{37}$	1.1	0.9	0.9	0.7	0.6
S$_{38}$	1.2	0.9	0.9	0.6	0.7
S$_{39}$	0.8	0.6	0.7	0.4	0.6
S$_{40}$	0.9	0.6	0.6	0.4	0.6
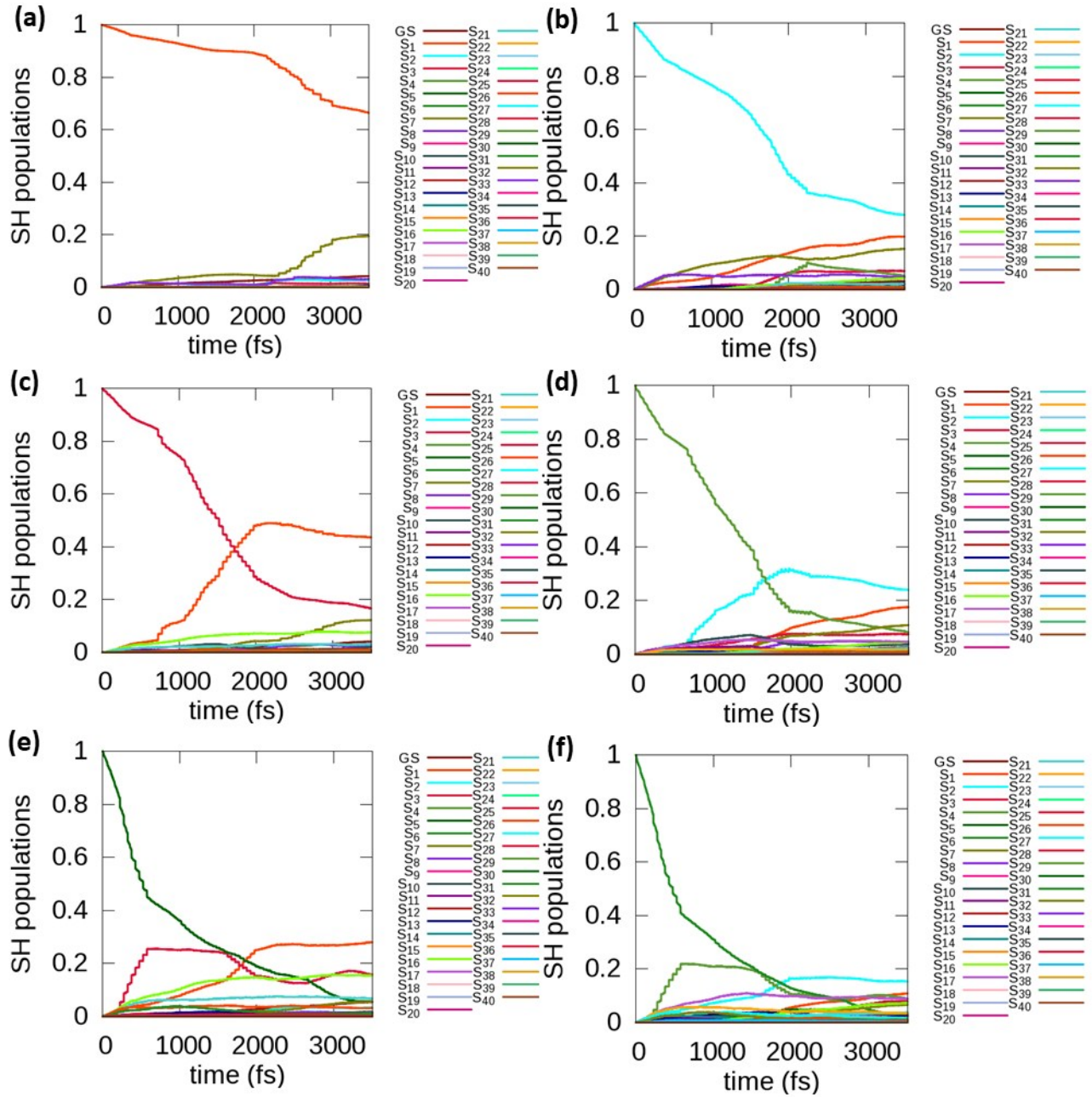
Figure S13. Evolution of the populations of states initially excited into S_1, S_2, S_3, S_4, S_5, S_6 (a-f, respectively) for $[Au_{25}(MPA)_{18}]^{-1}$ with the 0.55 eV energy correction in the presence of higher excited states.
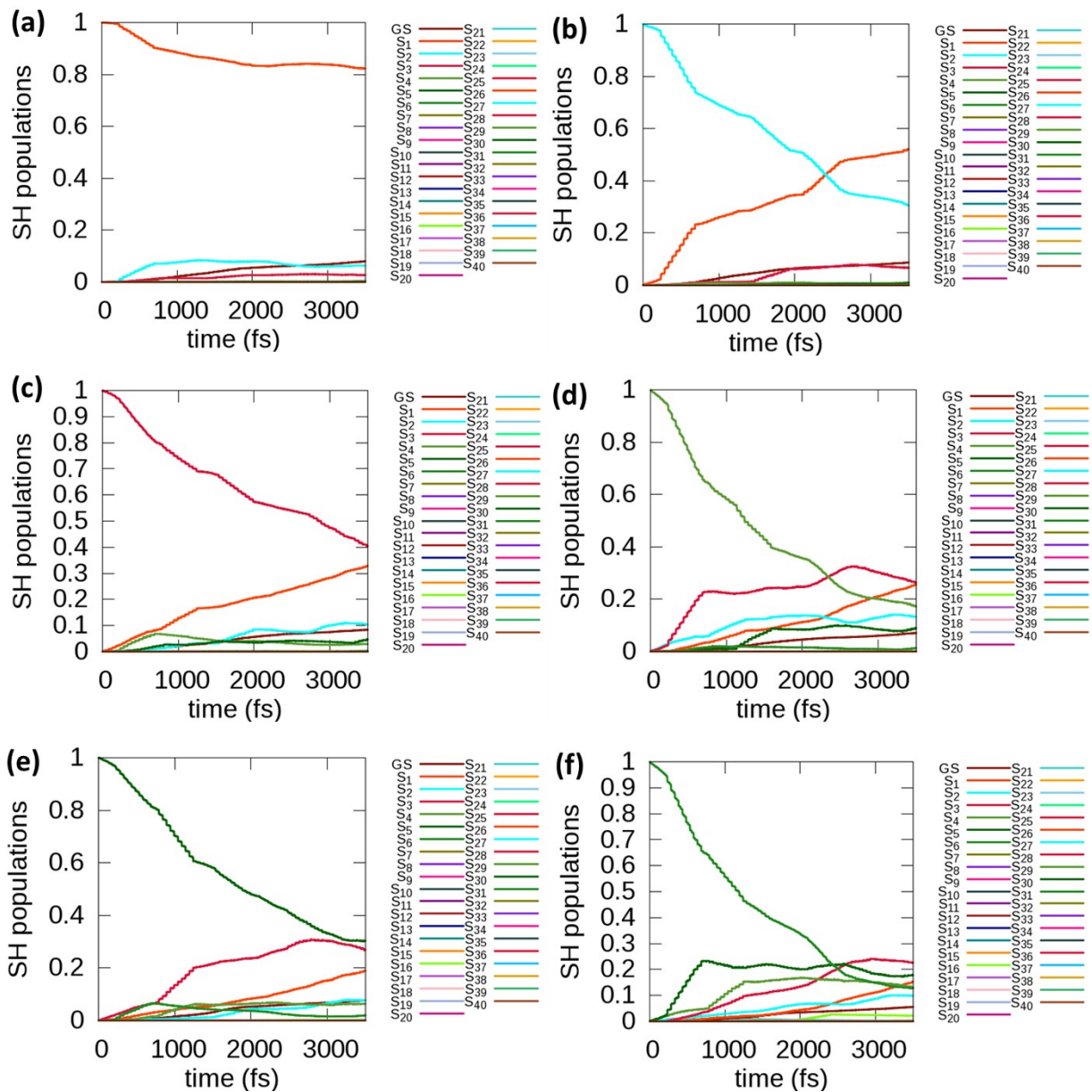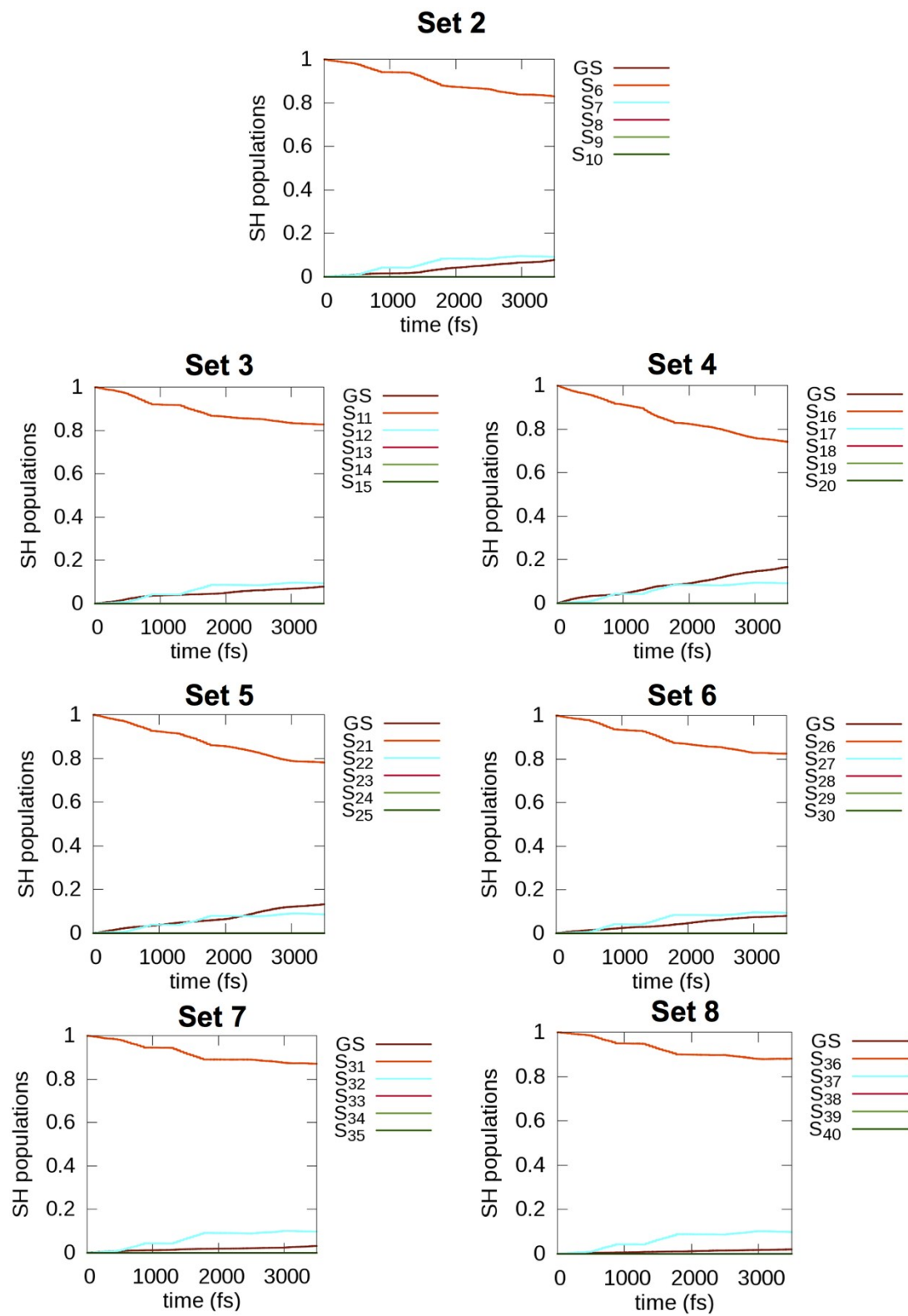

Figure S14. Evolution of the populations of states initially excited into S_1, S_2, S_3, S_4, S_5, S_6 (a-f, respectively) for $[Au_{25}(PET)_{18}]^{-1}$ (without the 0.55 eV energy correction) in the presence of higher excited states

Table S6. Excited states considered during separate electron and hole relaxations.

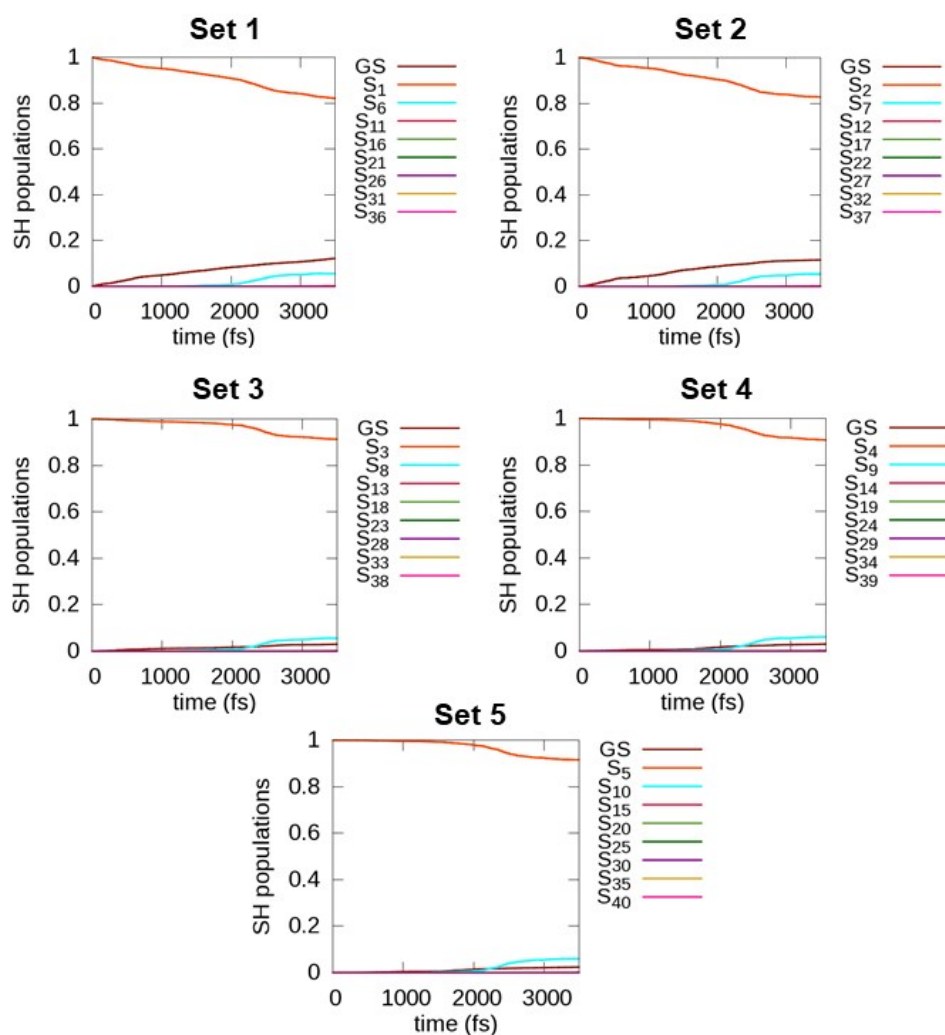| Excited state	Transition	Excited state	Transition
S_1	HOMO → LUMO	S_{21}	HOMO-4 → LUMO
S_2	HOMO → LUMO+1	S_{22}	HOMO-4 → LUMO+1
S_3	HOMO → LUMO+2	S_{23}	HOMO-4 → LUMO+2
S_4	HOMO → LUMO+3	S_{24}	HOMO-4 → LUMO+3
S_5	HOMO → LUMO+4	S_{25}	HOMO-4 → LUMO+4
S_6	HOMO-1 → LUMO	S_{26}	HOMO-5 → LUMO
S_7	HOMO-1 → LUMO+1	S_{27}	HOMO-5 → LUMO+1
S_8	HOMO-1 → LUMO+2	S_{28}	HOMO-5 → LUMO+2
S_9	HOMO-1 → LUMO+3	S_{29}	HOMO-5 → LUMO+3
S_{10}	HOMO-1 → LUMO+4	S_{30}	HOMO-5 → LUMO+4
S_{11}	HOMO-2 → LUMO	S_{31}	HOMO-6 → LUMO
S_{12}	HOMO-2 → LUMO+1	S_{32}	HOMO-6 → LUMO+1
S_{13}	HOMO-2 → LUMO+2	S_{33}	HOMO-6 → LUMO+2
S_{14}	HOMO-2 → LUMO+3	S_{34}	HOMO-6 → LUMO+3
S_{15}	HOMO-2 → LUMO+4	S_{35}	HOMO-6 → LUMO+4
S_{16}	HOMO-3 → LUMO	S_{36}	HOMO-7 → LUMO
S_{17}	HOMO-3 → LUMO+1	S_{37}	HOMO-7 → LUMO+1
S_{18}	HOMO-3 → LUMO+2	S_{38}	HOMO-7 → LUMO+2
S_{19}	HOMO-3 → LUMO+3	S_{39}	HOMO-7 → LUMO+3
S_{20}	HOMO-3 → LUMO+4	S_{40}	HOMO-7 → LUMO+4

Figure S15. Evolution of the populations of S_6, S_{11}, S_{16}, S_{21}, S_{26}, S_{31}, S_{36} states from the set 2 to set 8 electron relaxations respectively in $[Au_{25}(SCH_3)_{18}]^{-1}$.

Table S7. Calculated decay time constants for the eight electron relaxation sets.

Excited state	Transition	Decay time (ps) - Trial 1	Decay time (ps) - Trial 2
set 1 (hole created in HOMO)			
S_1	HOMO → LUMO	13	13
S_2	HOMO → LUMO+1	6.9	7.1
S_3	HOMO → LUMO+2	6.9	6.7
S_4	HOMO → LUMO+3	1.7	1.7
S_5	HOMO → LUMO+4	1.8	1.8
set 2 (hole created in HOMO-1)			
S_6	HOMO-1 → LUMO	17	17
S_7	HOMO-1 → LUMO+1	8.6	8.6
S_8	HOMO-1 → LUMO+2	6.9	6.7
S_9	HOMO-1 → LUMO+3	1.7	1.7
S_{10}	HOMO-1 → LUMO+4	1.8	1.8
set 3 (hole created in HOMO-2)			
S_{11}	HOMO-2 → LUMO	16	16
S_{12}	HOMO-2 → LUMO+1	8.7	8.7
S_{13}	HOMO-2 → LUMO+2	6.9	6.9
S_{14}	HOMO-2 → LUMO+3	1.7	1.7
S_{15}	HOMO-2 → LUMO+4	1.8	1.8
set 4 (hole created in HOMO-3)			
S_{16}	HOMO-3 → LUMO	11	11
S_{17}	HOMO-3 → LUMO+1	7.9	7.7
S_{18}	HOMO-3 → LUMO+2	6.7	6.8
S_{19}	HOMO-3 → LUMO+3	1.7	1.7
S_{20}	HOMO-3 → LUMO+4	1.7	1.7
set 5 (hole created in HOMO-4)			
S_{21}	HOMO-4 → LUMO	13	13
S_{22}	HOMO-4 → LUMO+1	8.7	8.5
S_{23}	HOMO-4 → LUMO+2	6.6	6.5
S_{24}	HOMO-4 → LUMO+3	1.7	1.7
S_{25}	HOMO-4 → LUMO+4	1.8	1.7
set 6 (hole created in HOMO-5)			
S_{26}	HOMO-5 → LUMO	16	16
S_{27}	HOMO-5 → LUMO+1	9.2	9.5
S_{28}	HOMO-5 → LUMO+2	6.4	6.6
S_{29}	HOMO-5 → LUMO+3	1.7	1.7
S_{30}	HOMO-5 → LUMO+4	1.7	1.7
set 7 (hole created in HOMO-6)			
S_{31}	HOMO-6 → LUMO	21	21

S_{32}	HOMO-6 → LUMO+1	9.5	9.6
S_{33}	HOMO-6 → LUMO+2	6.5	6.5
S_{34}	HOMO-6 → LUMO+3	1.6	1.6
S_{35}	HOMO-6 → LUMO+4	1.7	1.7
set 8 (hole created in HOMO-7)			
S_{36}	HOMO-7 → LUMO	23	23
S_{37}	HOMO-7 → LUMO+1	9.8	10
S_{38}	HOMO-7 → LUMO+2	6.1	6.2
S_{39}	HOMO-7 → LUMO+3	1.6	1.6
S_{40}	HOMO-7 → LUMO+4	1.6	1.7

Figure S16. Evolution of the populations of S_1, S_2, S_3, S_4, S_5 states from the set 1 to set 5 hole relaxations, respectively, in $[Au_{25}(SCH_3)_{18}]^{-1}$.

Table S8. Calculated decay time constants for the five hole relaxation sets.

Excited state	Transition	Decay time (ps) -Trial 1	Decay time (ps) -Trial 2
set 1 (electron excited into LUMO)			
S_1	HOMO → LUMO	18	20
S_6	HOMO-1 → LUMO	8.9	8.7
S_{11}	HOMO-2 → LUMO	5.7	5.6
S_{16}	HOMO-3 → LUMO	2.7	2.7
S_{21}	HOMO-4 → LUMO	1.6	1.6
S_{26}	HOMO-5 → LUMO	1.0	1.0
S_{31}	HOMO-6 → LUMO	1.0	1.0
S_{36}	HOMO-7 → LUMO	1.3	1.3
set 2 (electron excited into LUMO+1)			
S_2	HOMO → LUMO+1	18	17
S_7	HOMO-1 → LUMO+1	9.5	9.4
S_{12}	HOMO-2 → LUMO+1	6.3	6.1
S_{17}	HOMO-3 → LUMO+1	3.0	2.9
S_{22}	HOMO-4 → LUMO+1	1.7	1.7
S_{27}	HOMO-5 → LUMO+1	1.0	1.0
S_{32}	HOMO-6 → LUMO+1	1.0	1.0
S_{37}	HOMO-7 → LUMO+1	1.3	1.3
set 3 (electron excited into LUMO+2)			
S_3	HOMO → LUMO+2	46	45
S_8	HOMO-1 → LUMO+2	11	11
S_{13}	HOMO-2 → LUMO+2	6.5	6.4
S_{18}	HOMO-3 → LUMO+2	3.1	3.0
S_{23}	HOMO-4 → LUMO+2	1.8	1.7
S_{28}	HOMO-5 → LUMO+2	1.0	1.0
S_{33}	HOMO-6 → LUMO+2	1.0	1.0
S_{38}	HOMO-7 → LUMO+2	1.3	1.3
set 4 (electron excited into LUMO+3)			
S_4	HOMO → LUMO+3	44	42
S_8	HOMO-1 → LUMO+3	10	11
S_{14}	HOMO-2 → LUMO+3	6.7	6.6
S_{18}	HOMO-3 → LUMO+3	3.0	3.0
S_{24}	HOMO-4 → LUMO+3	1.7	1.7
S_{28}	HOMO-5 → LUMO+3	1.0	1.0
S_{34}	HOMO-6 → LUMO+3	1.0	0.9
S_{38}	HOMO-7 → LUMO+3	1.2	1.3
set 5 (electron excited into LUMO+4)			
S_5	HOMO → LUMO+4	49	48
S_{10}	HOMO-1 → LUMO+4	11	11

S_{15}	HOMO-2 → LUMO+4	6.4	6.5
S_{20}	HOMO-3 → LUMO+4	2.9	2.9
S_{25}	HOMO-4 → LUMO+4	1.6	1.7
S_{30}	HOMO-5 → LUMO+4	1.0	1.0
S_{35}	HOMO-6 → LUMO+4	1.0	1.0
S_{40}	HOMO-7 → LUMO+4	1.2	1.2