Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information:

Structure and formation of highly luminescent protein-stabilized gold clusters

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Supplementary Figures:

Supplementary Tables:

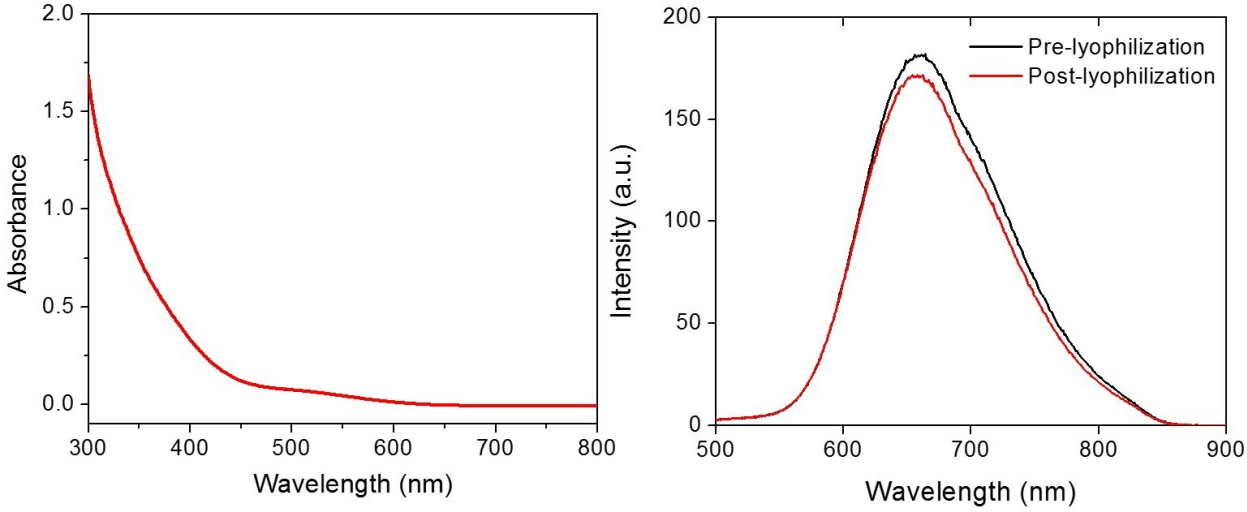

Figure S1. UV-Vis absorption of AuBSA (12 h sample) and photoluminescence (excitation @ 470 nm) of AuBSA (12 h sample) before and after lyophilisation.

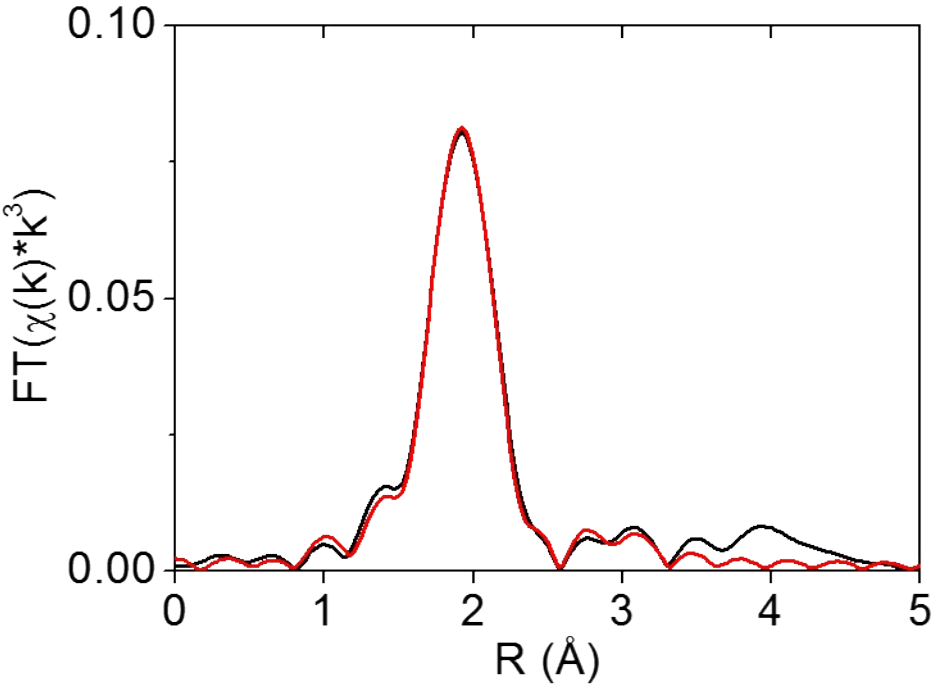

Figure S2. Two-shell Au L_3-edge EXAFS fit (red line) of AuBSA at 12 h (black line).

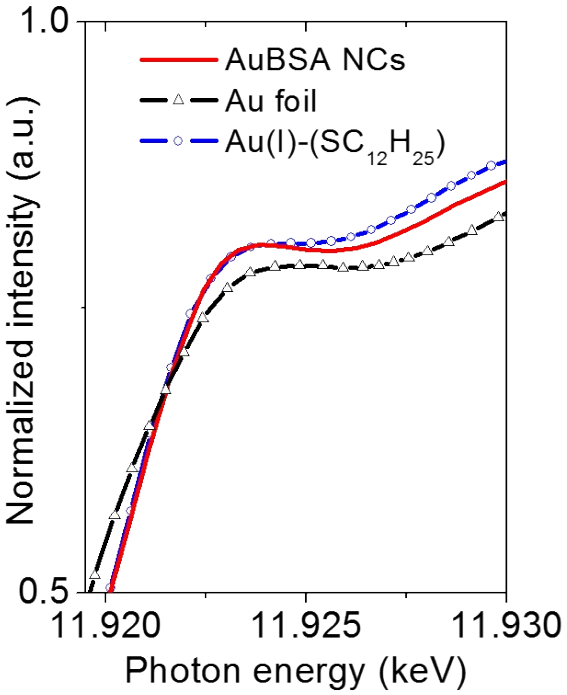

Figure S3. Au L_3-edge XANES, white-line region shown, of AuBSA with Au(I)-SR polymer and Au foil (Au(0)) references.

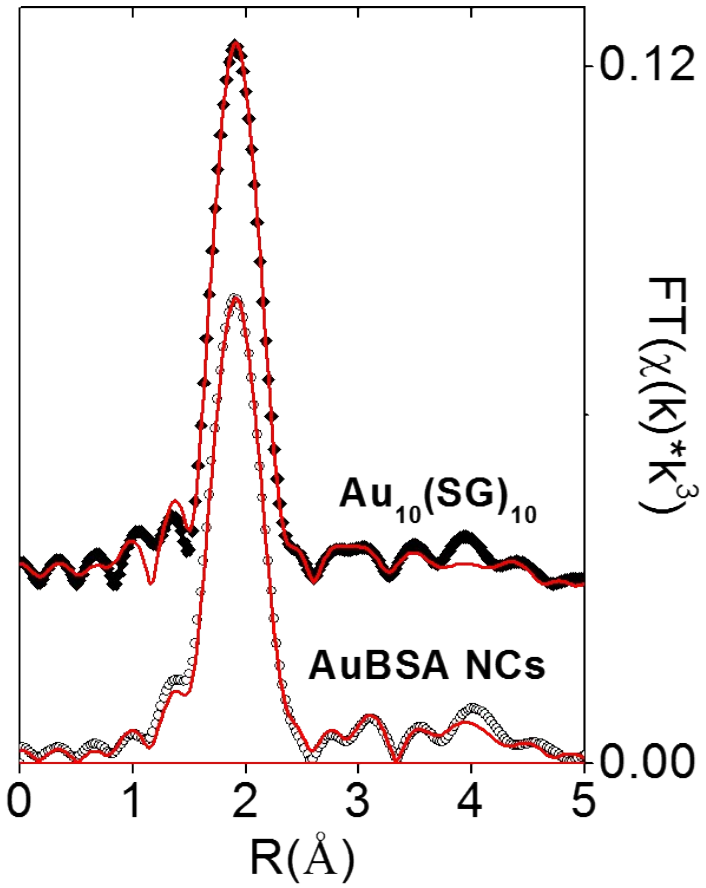

Figure S4. Multi-shell EXAFS fitting (red line) of AuBSA and $Au_{10}(SG)_{10}$.

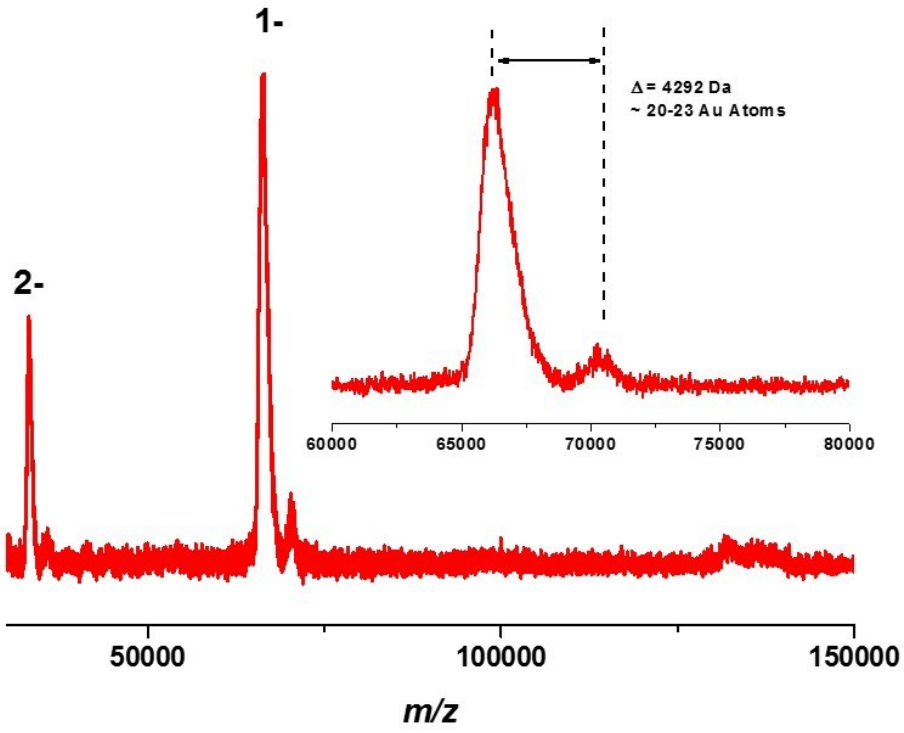

Figure S5. MALDI-TOF measurement of AuBSA in linear negative mode. The measured sample was prepared by mixing 10 μL of AuBSA aqueous solution with 100 μL of 10 mg/L sinapinic acid aqueous solution, followed by casting and drying the mixture on a testing plate.

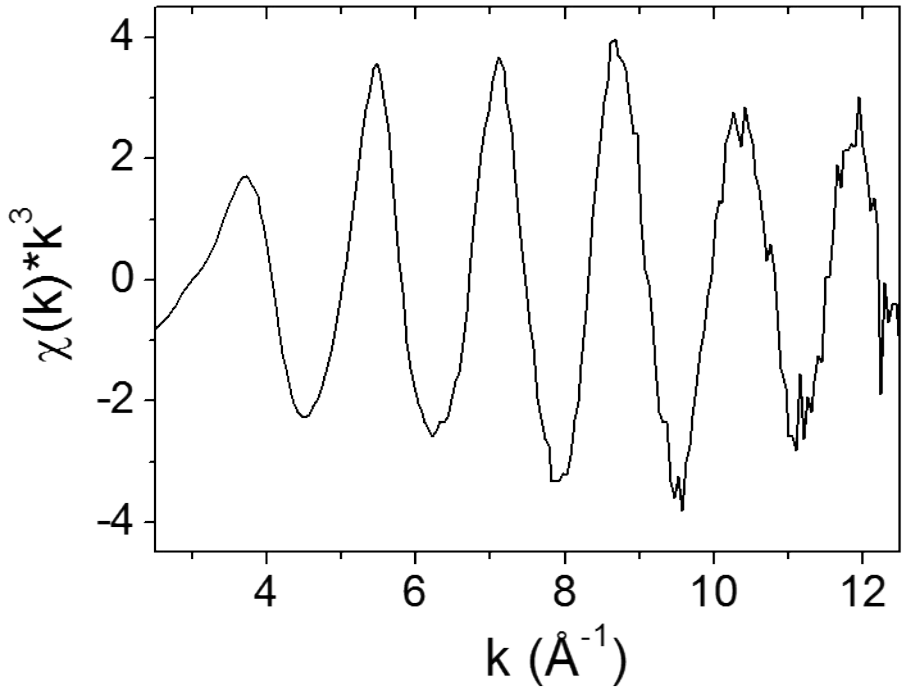

Figure S6. Au L_3-edge k^3-space spectrum of $Au_{10}(SG)_{10}$.

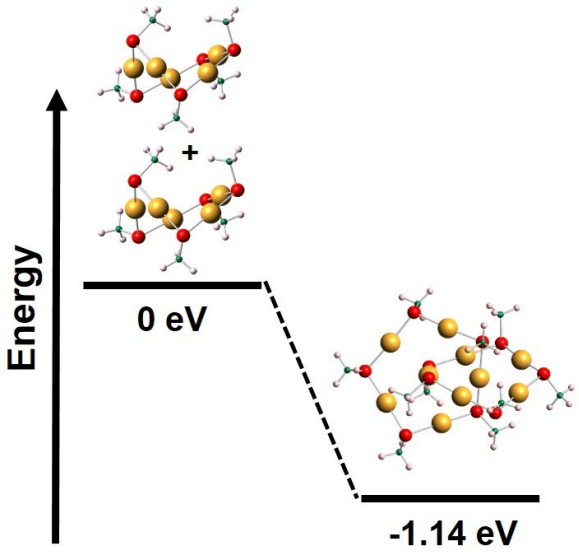

Figure S7. DFT-optimized geometries of $Au_5(SMe)_5$ and $Au_{10}(SMe)_{10}$ with relative energy difference ($Au_{10}(SMe)_{10}$ – 2 x ($Au_5(SMe)_5$).

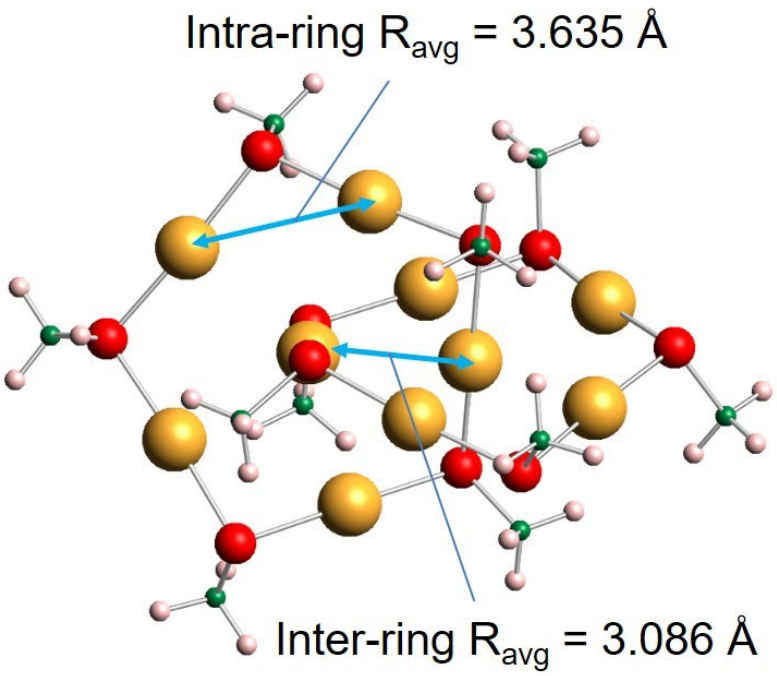

Figure S8. DFT-optimized structure of $Au_{10}(SMe)_{10}$ with average inter- and intra-ring bond distances.

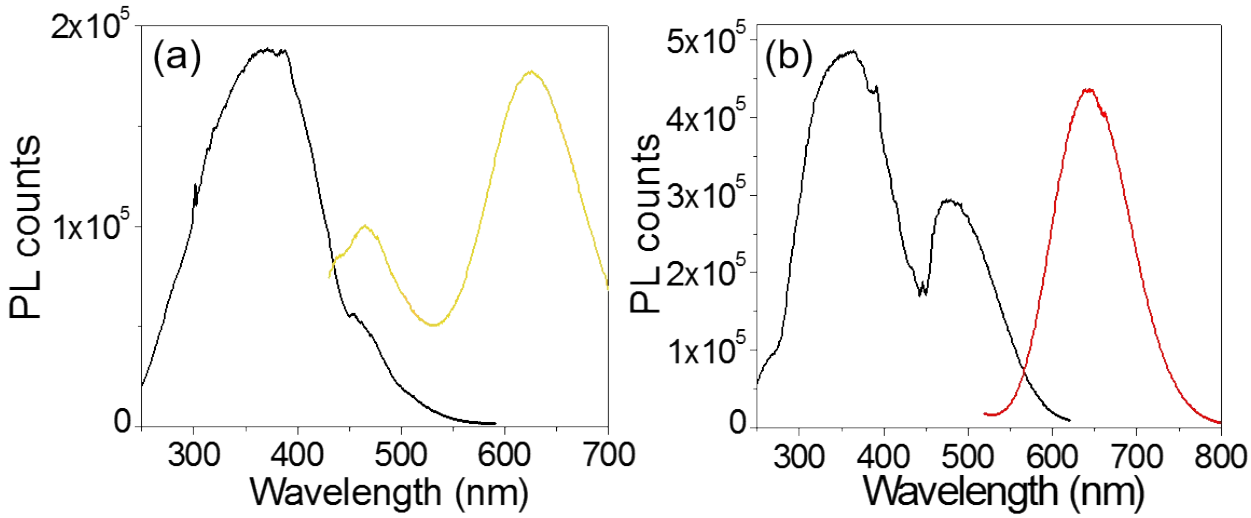

Figure S9. Photoluminescence (yellow and red lines) (excitation @ 365 nm) and excitation spectra (black line) of (a) $Au_{10}(SG)_{10}$ and (b) AuBSA.

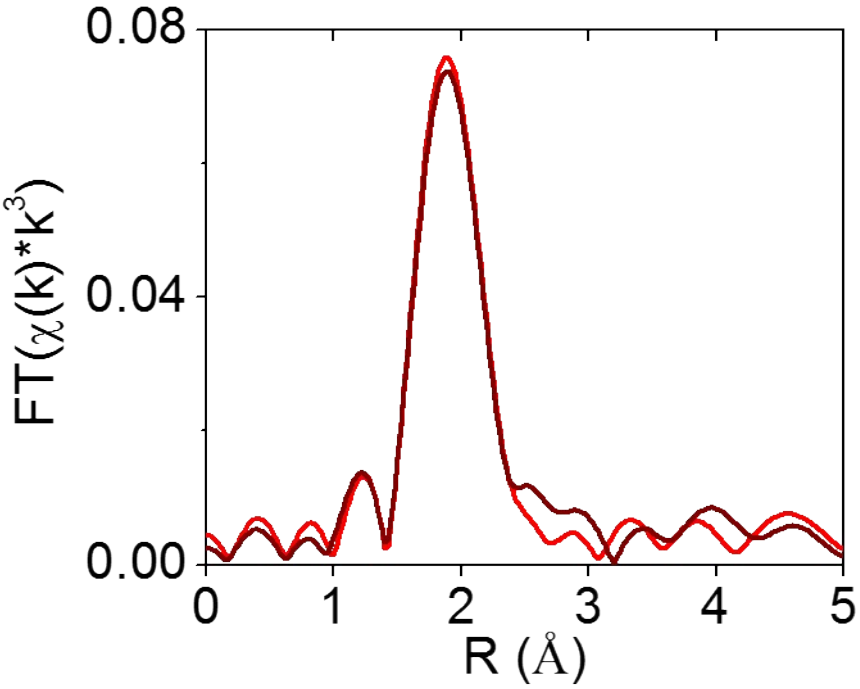

Figure S10. Au L_3-edge EXAFS of AuBSA before (red line) and after trypsin digestion (maroon line).

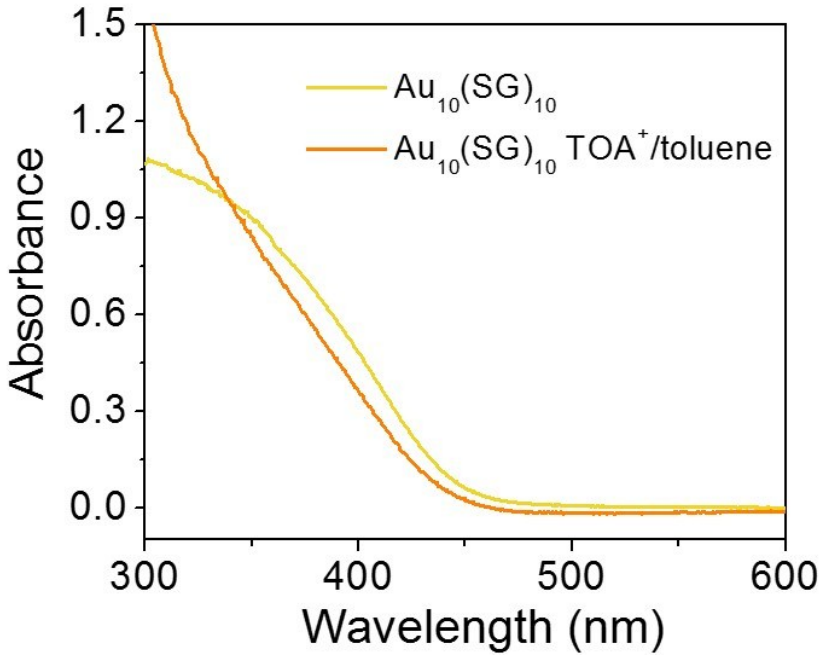

Figure S11. UV-Vis absorption of $Au_{10}(SG)_{10}$ and $Au_{10}(SG)_{10}$ after phase-transfer with TOA^+/toluene (TOA^+-$Au_{10}(SG)_{10}$ clusters were ~3X less concentrated than original $Au_{10}(SG)_{10}$ and thus, adjusted in this spectrum).

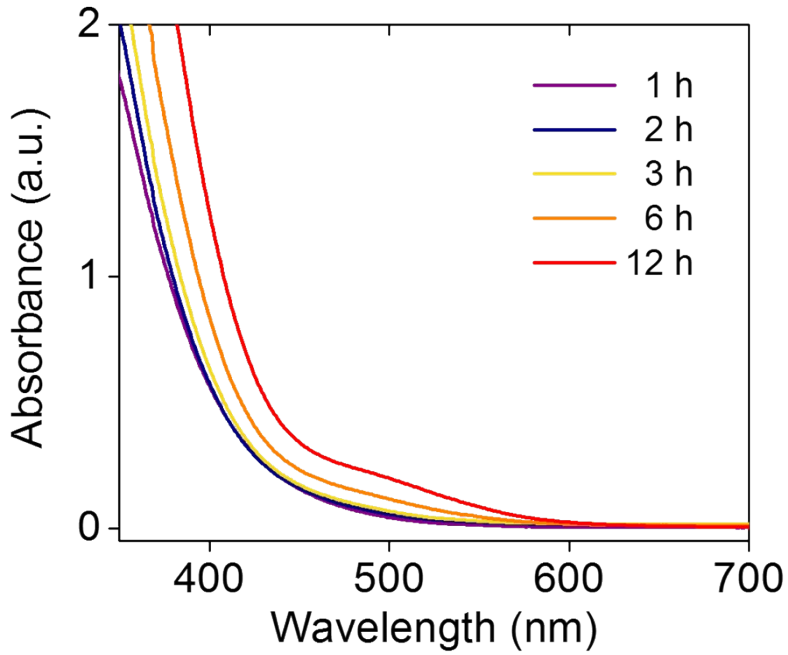

Figure S12. UV-Vis absorbance spectra at various time points during the synthesis of AuBSA clusters.

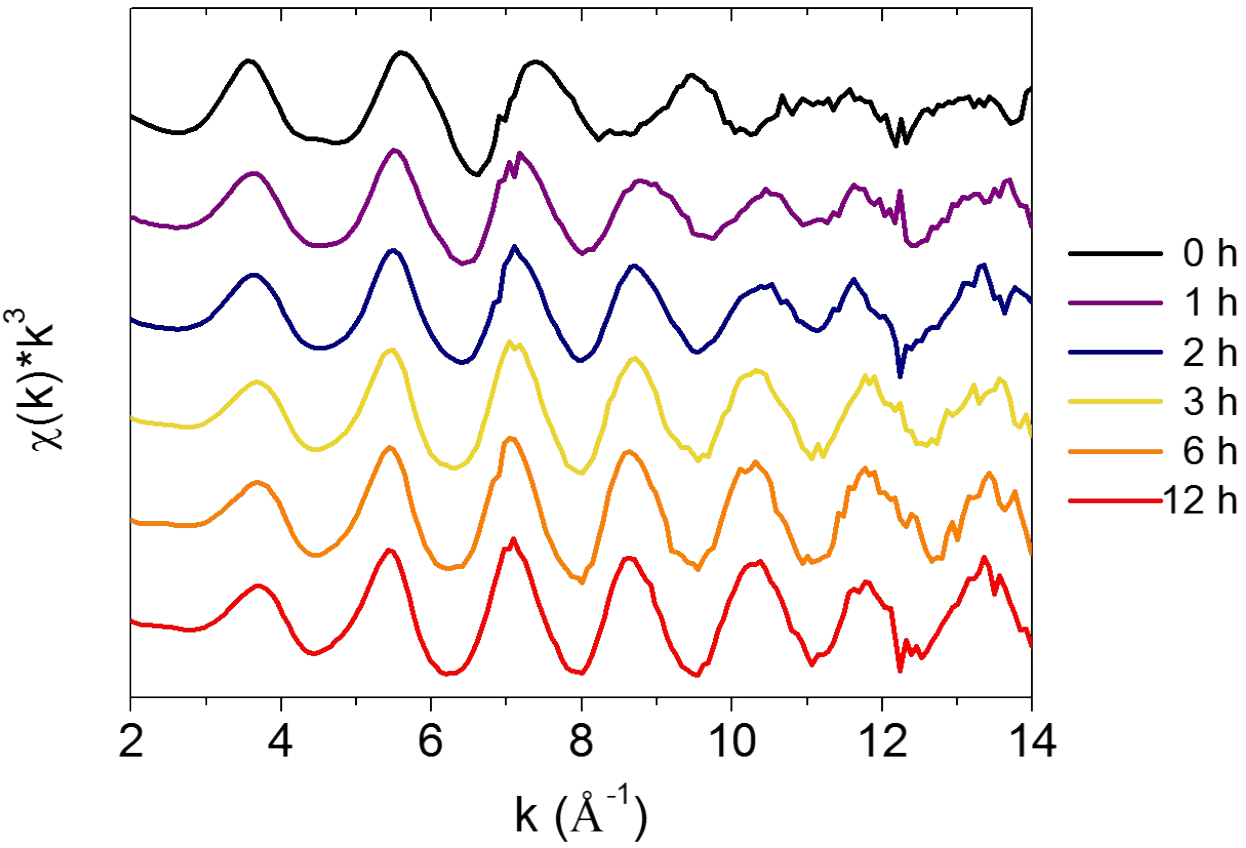

Figure S13. Au L_3-edge k^3-space of time-dependent AuBSA samples.

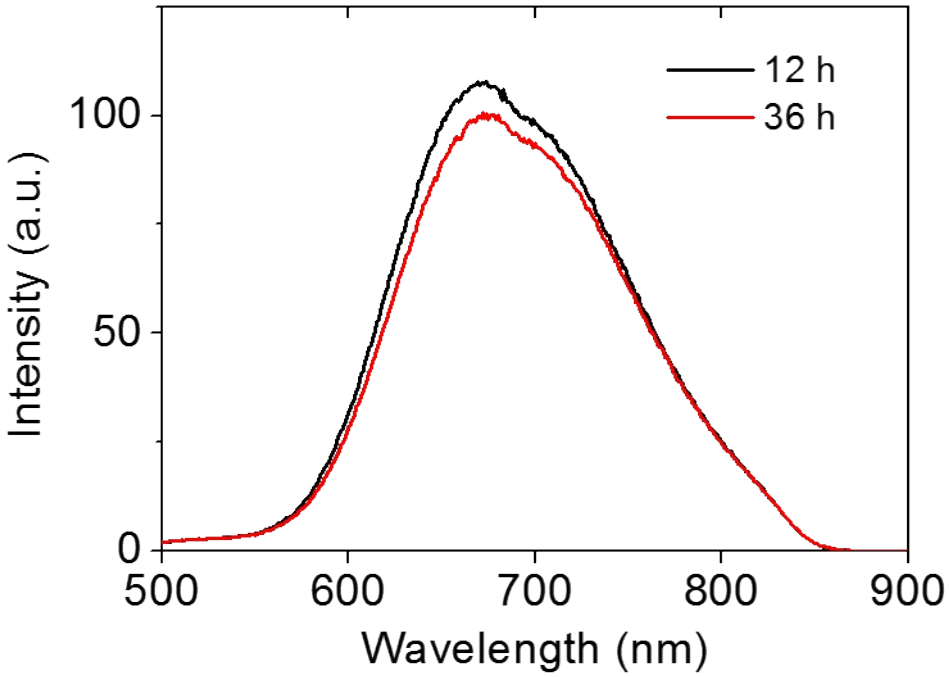

Figure S14. Photoluminescence of AuBSA at 12 and 36 h (excitation @ 470 nm).

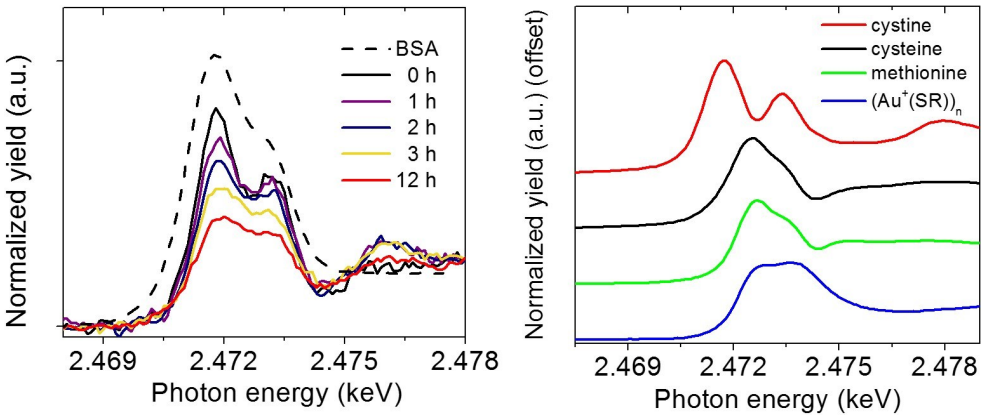

Figure S15. S K-edge XANES of AuBSA throughout protein-directed synthesis (6 h sample not shown due to oxide contamination) and standard material references.

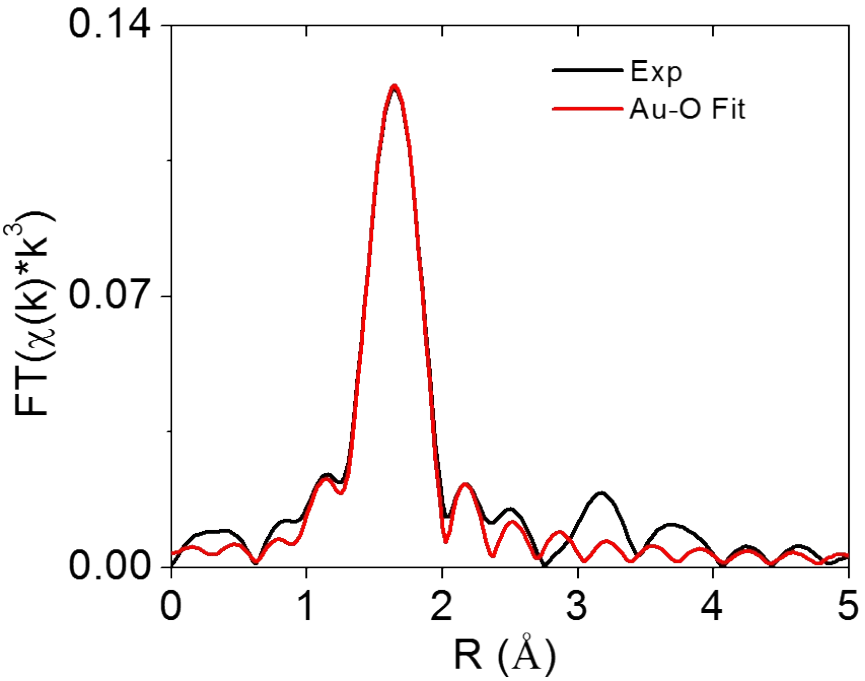

Figure S16. Au L_3-edge EXAFS of $Au(OH)_3$ reference material with fitted Au-O scattering shell. Fit parameters: CN = 3.4(3), R = 2.005(4) Å, σ^2= 0.0015(6) Å^2, E_0 shift = 6.4(7) eV.

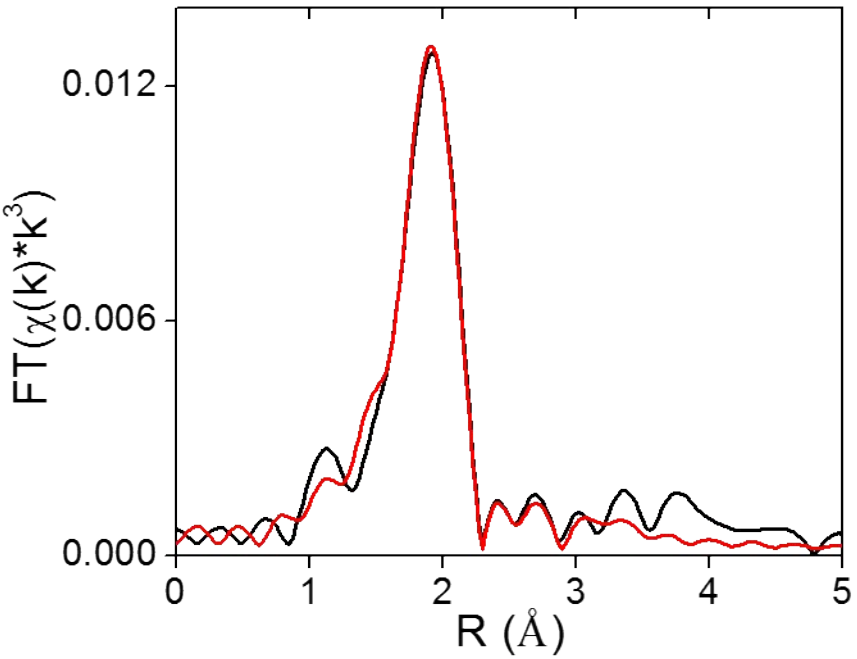

Figure S17. Au L_3-edge EXAFS and two-shell fit (red line) of AuBSA at 36 h.

Table S1. EXAFS fitting results for red luminescent AuBSA clusters.

	Parameters	AuBSA
Au-S	CN	2.2(1)
	R (Å)	2.321(8)
	σ^2 (Å^2)	0.0036(3)
	ΔE_0 (eV)	1.1(3)
Au-Au	CN	0.8(5)
	R (Å)	3.02(2)
	σ^2 (Å^2)	0.011(4)
	ΔE_0 (eV)	1.1(3)

Table S2. Multi-shell EXAFS fitting results for AuBSA and $Au_{10}(SG)_{10}$ clusters.

	Parameters	Au-S	Au-Au	Au-C	Au-Au
AuBSA	CN	2	1.8	2	2
	R (Å)	2.31(2)	3.02(3)	3.27(8)	3.67(7)
	σ^2 (Å^2)	0.0035(3)	0.016(3)	0.02(1)	0.019(9)
	ΔE_0 (eV)	2.4(4)	2.4(4)	2.4(4)	2.4(4)
$Au_{10}(SG)_{10}$	CN	2	1.8	2	2
	R (Å)	2.303(1)	3.04(2)	3.26(2)	3.57(1)
	σ^2 (Å^2)	0.00263(6)	0.016(2)	0.006(2)	0.0122(9)
	ΔE_0 (eV)	2.2(3)	2.2(3)	2.2(3)	2.2(3)

Table S3. Cartesian coordinates for the DFT-optimized structure of $Au_{10}(SCH_3)_{10}$.

Atom	X	Y	Z
Au	0.39138	2.353788	-1.7165
Au	4.116035	-1.52182	0.759526
Au	0.772002	-2.36357	1.719624
Au	-1.54957	-0.06795	0.119839
S	-1.77571	1.487185	-1.65802
S	2.508475	3.329841	-1.88283
S	2.878313	-3.35652	1.523111
S	-1.28023	-1.32357	2.106828
C	3.411418	-3.59527	3.240845
H	4.453258	-3.92024	3.242516
H	2.794657	-4.37401	3.69263
H	3.318027	-2.67948	3.824167
C	2.480443	4.617283	-0.60263
H	3.465036	5.086403	-0.55802
H	2.23244	4.204499	0.375217
H	1.739833	5.369645	-0.88003
C	-1.98981	0.597982	-3.21902
H	-1.14781	-0.06065	-3.43255
H	-2.09088	1.331173	-4.02136
H	-2.90722	0.007886	-3.15495
C	-2.49969	-2.65915	2.126016
H	-2.39416	-3.32119	1.267139
H	-2.36523	-3.23524	3.043477
H	-3.50009	-2.2216	2.123231
Au	3.929491	1.713482	-0.96456
S	5.460183	0.227394	-0.00237
C	6.382842	-0.47731	-1.39599
H	6.991382	0.311752	-1.84126
H	5.720219	-0.88698	-2.15807
H	7.039338	-1.26579	-1.02391
Au	-4.11488	-1.52322	-0.76121
Au	1.549047	-0.06744	-0.11761
Au	-0.39305	2.352682	1.71749
Au	-3.9305	1.712232	0.963839
S	-5.45984	0.225834	-8.1E-05
S	-2.87586	-3.35715	-1.52416
S	1.774766	1.487146	1.660256
S	-2.51035	3.32886	1.883163
C	1.988512	0.597242	3.220904
H	2.905881	0.007122	3.156716
H	1.146396	-0.06144	3.433839
H	2.089351	1.329921	4.023728
C	-3.40766	-3.59595	-3.24231

H	-2.79001	-4.37412	-3.69386
H	-3.31458	-2.67995	-3.82536
H	-4.44926	-3.92171	-3.24477
C	-6.38332	-0.4793	1.392797
H	-5.72109	-0.88898	2.155216
H	-7.03941	-1.26785	1.020129
H	-6.99232	0.309553	1.837803
C	-2.48167	4.616571	0.603254
H	-1.74112	5.368818	0.881123
H	-2.23328	4.203993	-0.37458
H	-3.4662	5.085805	0.558285
Au	-0.77037	-2.36233	-1.71983
S	1.280856	-1.32027	-2.10646
C	2.501383	-2.65483	-2.128
H	2.367036	-3.22974	-3.04621
H	2.396753	-3.31814	-1.26998
H	3.501408	-2.21643	-2.12499

Table S4. Excited-state photoluminescence decay lifetime components and quantum yield (Rhodamine B in EtOH as reference) measurements.

	t_1(ns)	t_2(ns)	t_3(ns)	t_{avg}(ns)	QY(%)
$Au_{10}(SG)_{10}$	15 ± 5 (74.3%)	150 ± 30 (16.4%)	890 ± 80 (9.3%)	120 ns	0.48
$Au_{10}(SG)_{10}$ -rigidified	35 ± 8 (54.6%)	150 ± 40 (28.5%)	880 ± 90 (16.9%)	210 ns	5.0
AuBSA	30 ± 6 (22.4%%)	350 ± 50 (21.7%)	1760 ± 120 (55.8%)	1065 ns	6.8

Table S5. EXAFS refinement results for the time-dependent study of AuBSA cluster formation. Values not reported "-" were unobtainable due to fitting constraints or the absence of that scattering path.

	Parameters	0 h	1 h	2 h	3 h	6 h	12 h	36 h
Au-O	CN	2.8(2)	0.9(2)	0.6(4)	-	-	-	
	R (Å)	2.02(1)	2.04(2)	2.0(1)	-	-	-	
	σ^2 (Å^2)	0.0059(6)	0.002(2)	0.006(5)	-	-	-	
	ΔE_0 (eV)	6(1)	5(4)	2(3)	-	-	-	
Au-S	CN	-	1.1(1)	1.4(2)	2.3(1)	2.2(1)	2.2(1)	2.16(8)
	R (Å)	-	2.31(1)	2.31(2)	2.31(1)	2.323(5)	2.321(8)	2.321(2)
	σ^2 (Å^2)	-	0.003(1)	0.003(2)	0.0046(5)	0.0039(3)	0.0036(3)	0.0036(3)
	ΔE_0 (eV)	-	4(2)	2(3)	2(1)	1.7(4)	1.1(3)	0.9(4)
Au-Au	CN	-	-	-	2(1)	1.3(8)	0.8(5)	0.9(5)
	R (Å)	-	-	-	3.02(2)	3.03(2)	3.02(2)	3.02(1)
	σ^2 (Å^2)	-	-	-	0.018(6)	0.015(5)	0.011(4)	0.012(4)
	ΔE_0 (eV)	-	-	-	2(1)	1.7(4)	1.1(3)	0.9(4)

Table S6. Formation energy DFT calculations for the conversion of $AuCl_3$ to $Au(OH)_3$.

$AuCl_3 + 3OH^- \rightarrow Au(OH)_3 + 3Cl^-$	
Individual Reaction Steps	**(Products - Reactants) Total energy (SCF+XDM) /eV**
$AuCl_3 + OH^- \rightarrow AuCl_2OH + Cl^-$	-1.96 eV
$AuCl_2OH + OH^- \rightarrow AuCl(OH)_2 + Cl^-$	-1.86 eV
$AuCl(OH)_2 + OH^- \rightarrow Au(OH)_3 + Cl^-$	-1.82 eV

Table S7. Formation energy DFT calculations for the conversion of $AuCl_4^-$ to $Au(OH)_4^-$.

$AuCl_4^- + 4OH^- \rightarrow Au(OH)_4^- + 4Cl^-$	
Individual Reaction Steps	**(Products - Reactants) Total energy (SCF+XDM) /eV**
$AuCl_4^- + OH^- \rightarrow AuCl_3OH^- + Cl^-$	-1.75 eV
$AuCl_3OH^- + OH^- \rightarrow$ *cis*-$AuCl_2(OH)_2^- + Cl^-$ $AuCl_3OH^- + OH^- \rightarrow$ *trans*-$AuCl_2(OH)_2^- + Cl^-$	-1.73 eV -1.69 eV
cis-AuCl2$(OH)_2^-$ + OH- → $AuCl(OH)_3^-$ +Cl^- *trans*-AuCl2$(OH)_2^-$ + OH- → $AuCl(OH)_3^-$ +Cl^-	-1.64 eV -1.67 eV
$AuCl(OH)_3^- + OH^- \rightarrow Au(OH)_4^- + Cl^-$	-1.40 eV

Table S8. Formation energy DFT calculations for the conversion of $AuCl_3$ and $Au(OH)_3$ to their anionic complex form.

Reaction	**(Products - Reactants) Total energy (SCF+XDM) /eV**
$Au(OH)_3 + OH^- > Au(OH)_4^-$	-4.60 eV
$AuCl_3 + Cl^- \rightarrow AuCl_4^-$	-3.73 eV