

Electronic Supplementary Information for

X-ray-excited optical luminescence from protein-directed Au_{~20} clusters

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Table S1. Optical properties of Au clusters, listing absolute PL quantum yields (Φ) and maximum emission wavelengths (λ_{max}) upon irradiation with 470 nm light.

	Before dialysis		After dialysis	
	Φ (%) ^a	λ_{max} (nm)	Φ (%) ^a	λ_{max} (nm)
HSA-Au	7.2	620	4.5	610
BSA-Au	5.9	620	3.3	610
Lactoferrin-Au	8.3	620	6.7	610

a. Absolute PL (Φ) when excited at 470 nm.

Table S2. Chemical yields based on ICP-AES measurements.

	Weight for measurement (mg)	Au % ^a	Chemical yield (%)
HSA-Au	8.49	6.3	86
BSA-Au	2.63	5.9	80
Lactoferrin-Au	7.05	6.4	88

a. Au content in the sample, as calculated by the following equation: Au content = (ICP result (ppm) \times Dilution Factor \times 1 mL) / Total weight (ppm = mg/L).

Table S3. Relationships between emission wavelength, energy and number of Au atoms in clusters.

Atom number of Au	Protein	Emission wavelength (nm)	Emission energy (eV)	Reference number
Au ₈	BSA	420	2.95	1
Au ₈	BSA	430	2.88	2
Au ₈	BSA	430	2.88	3
Au ₈	BSA	450	2.76	4
Au ₁₆	BSA	580	2.14	5
Au ₁₆	BSA	604	2.05	6
Au ₁₆	BSA	604	2.05	7
Au _{~20}	BSA	610	2.03	This study
Au ₂₀	BSA	620	2.00	8
Au ₂₀	BSA	650	1.91	9
Au ₂₀	BSA	660	1.88	10
Au ₂₅	BSA	630	1.97	11
Au ₂₅	BSA	635	1.95	12
Au ₂₅	BSA	640	1.94	13
Au ₂₅	BSA	650	1.91	14
Au ₂₅	BSA	650	1.91	3
Au ₂₅	BSA	660	1.88	15
Au ₃₈	BSA	650	1.91	16
Au ₃₈	BSA	660	1.88	17
Au ₃₈	BSA	660	1.88	18

Table S4. Percentages of Au(I) and Au(0) determined from XPS spectra.

	Au (0) ^a	Au (I) ^a
HSA-Au	89%	11%
BSA-Au	89%	11%
Lactoferrin-Au	85%	15%

a. Values estimated from the areas of Au 4f XPS peaks.

Table S5. Number of amino acids in individual proteins.

Protein		HSA (66.5kDa)	BSA (66.5kDa)	Lacto (80kDa)
Total amino acids		609	607	710
(a)	Arginine (R)	27	26	44
	Lysine (K)	60	60	46
	Histidine (H)	16	17	9
	Total	103 (17%)	103 (17%)	99 (14%)
(b)	Tyrosine (Y)	19	21	21
	Tryptophan (W)	2	3	10
	Total	21 (4%)	24 (4%)	31 (4%)
(c)	Cysteine (C)	35 (6%)	35 (6%)	33 (5%)

Table S6. PL lifetimes and rate constants on quenching with molecular oxygen (k_q).

	Condition	A ₁ (%)	τ_1 (μs)	A ₂ (%)	τ_2 (μs)	τ_{ave} (μs) ^a	k_q (10 ⁹ L mol ⁻¹ s ⁻¹)
BSA-Au	Air	40.63	0.19	59.37	1.96	1.24	0.57
	Ar	37.32	0.30	62.68	2.31	1.56	
HSA-Au	Air	39.22	0.18	60.78	1.83	1.18	0.57
	Ar	38.02	0.25	61.98	2.22	1.47	
Lacto-Au	Air	56.64	0.07	43.36	1.59	0.73	0.56
	Ar	55.40	0.08	44.60	1.74	0.83	

a. Individual lifetimes were obtained by fitting with a double-exponential function and averaged to obtain τ_{ave} .

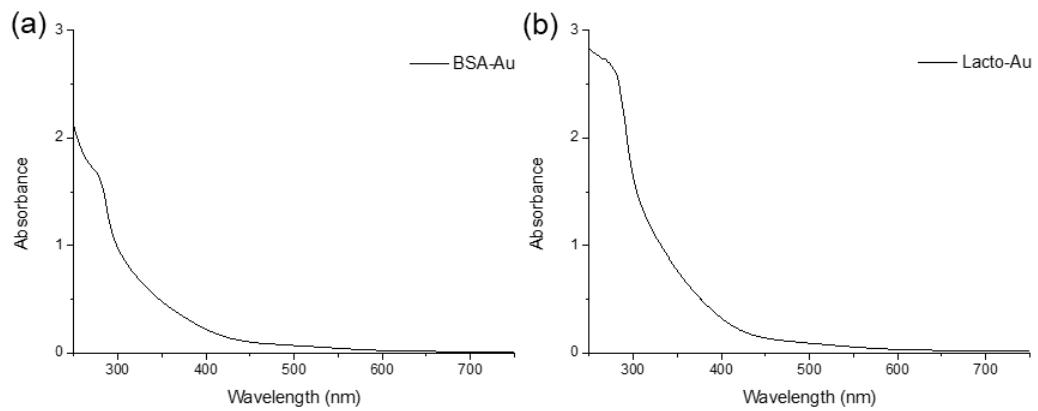


Figure S1. Absorption spectra for (a) BSA-Au, and (b) lactoferrin-Au clusters.

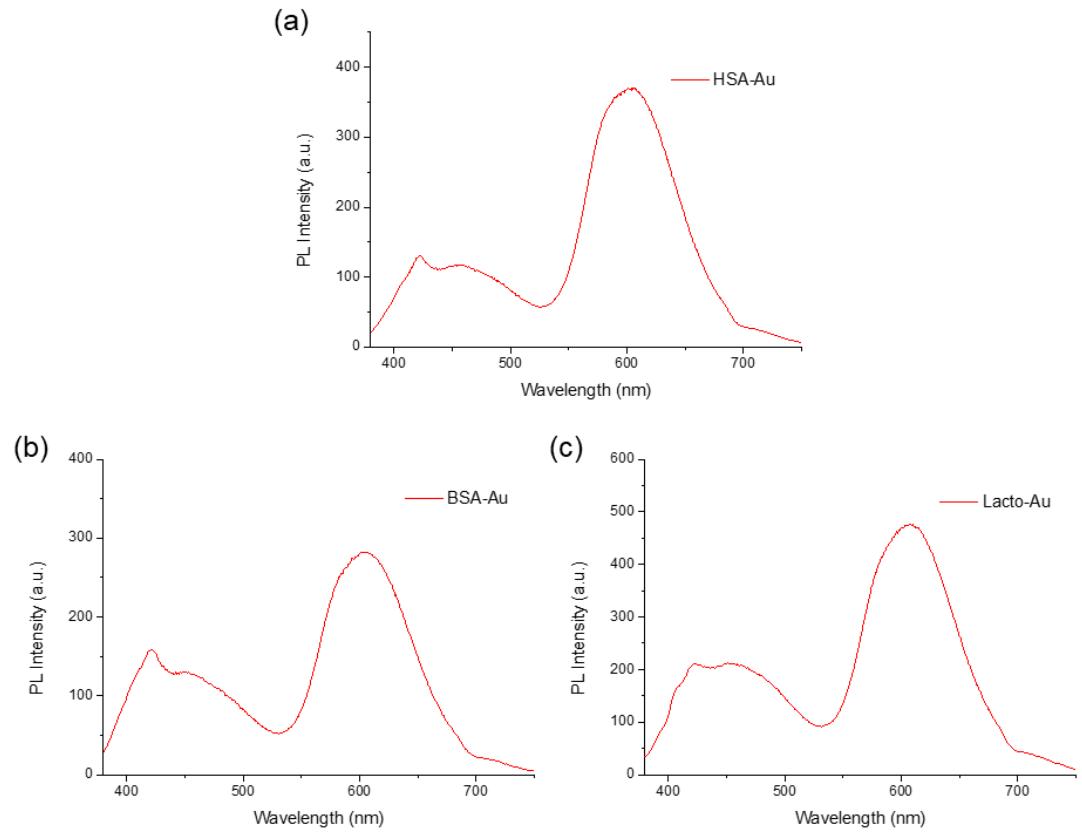


Figure S2. PL spectra for (a) HAS-Au, (b) BSA-Au, and (c) lactoferrin-Au clusters, when excited at 370 nm.

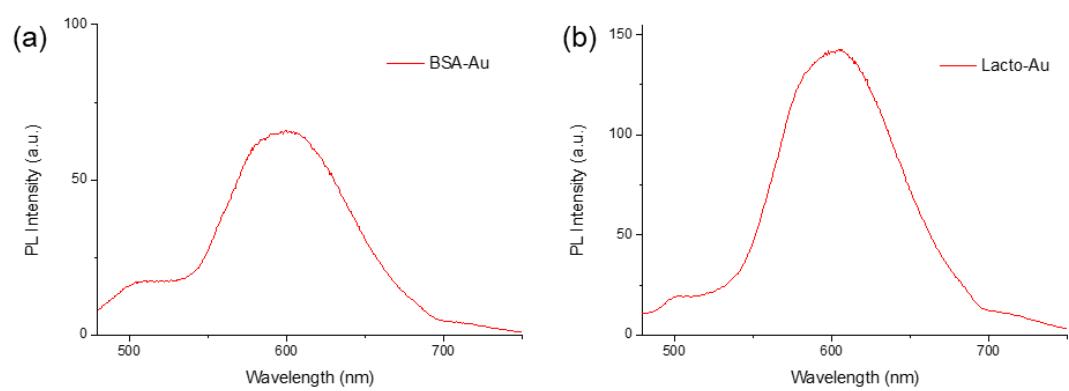


Figure S3. PL spectra for (a) BSA-Au, and (b) lactoferrin-Au clusters when excited at 470 nm.

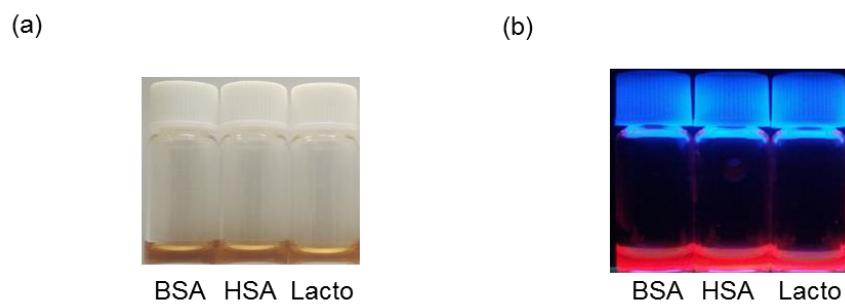


Figure S4. Photographs of Au cluster samples (a) under natural light and (b) UV light irradiation. From left, BSA-Au, HSA-Au, lactoferrin-Au.

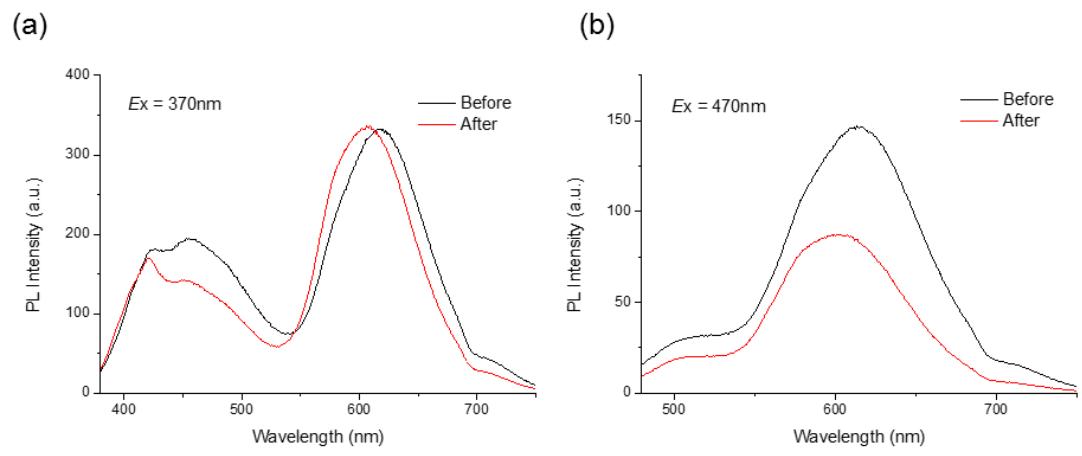


Figure S5. PL spectra of BSA-Au clusters before and after dialysis when excited at (a) 370 nm and (b) 470 nm.

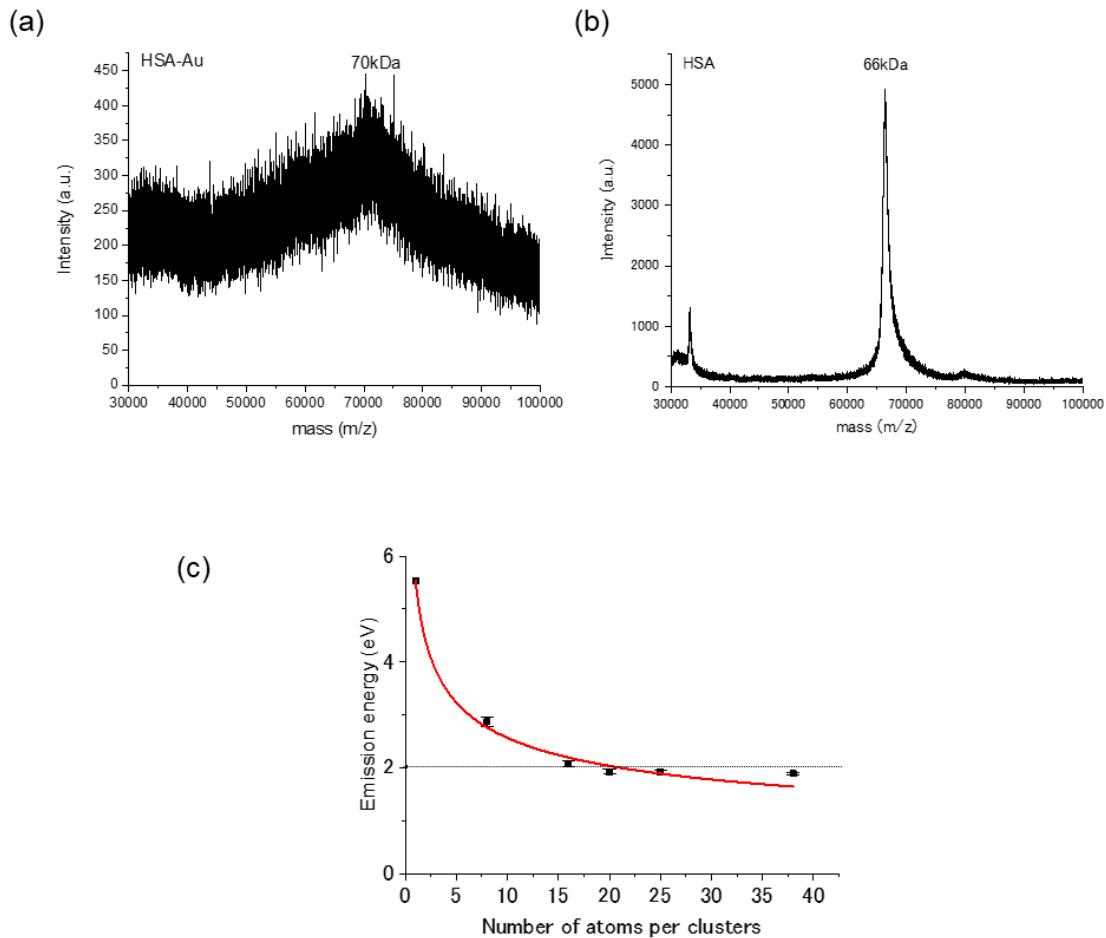


Figure S6. MALDI-mass spectra for (a) HSA-Au and (b) HAS. (c) Correlation between the number of Au atoms per cluster and the PL energy, as determined from previously published data shown in Table S3. The curve was fitted with $E = E_f/N^{1/3}$, where E is emission energy, E_f is the Fermi energy of an Au atom (5.5eV) and N is the number of Au atoms per cluster.

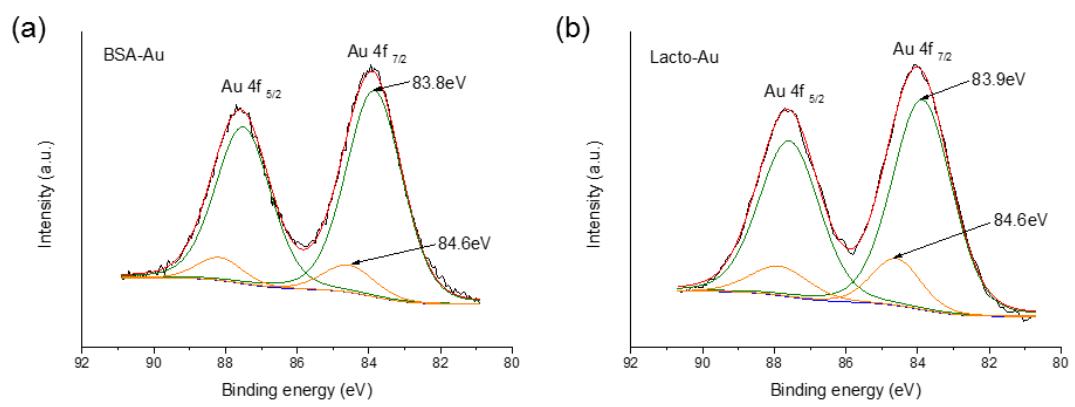


Figure S7. Au 4f XPS spectra for (a) BSA-Au, and (b) lactoferrin-Au clusters.

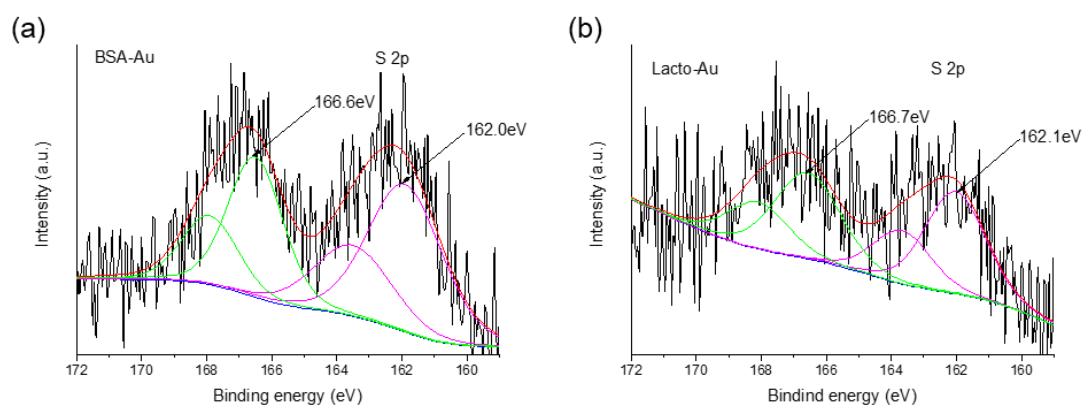


Figure S8. S 2p XPS spectra for (a) BSA-Au and (b) lactoferrin-Au clusters.

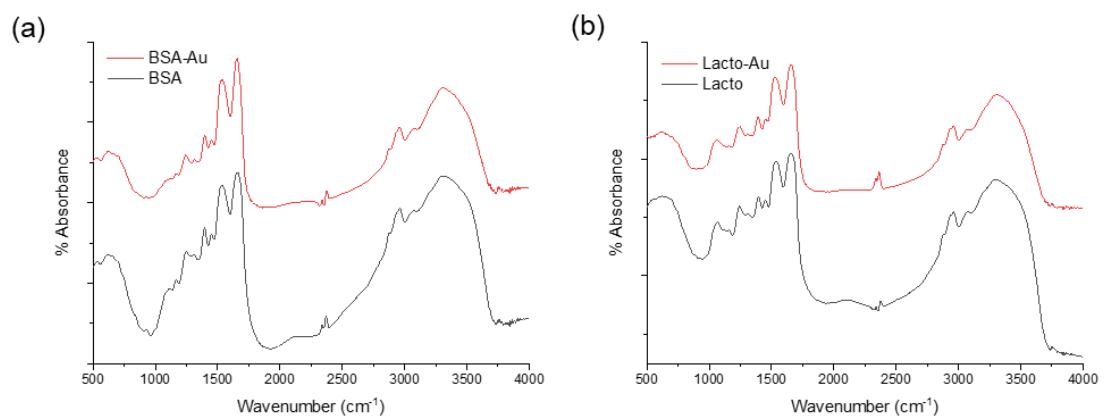


Figure S9. FT-IR spectra for (a) BSA and BSA-Au, and (b) lactoferrin and lactoferrin-Au.

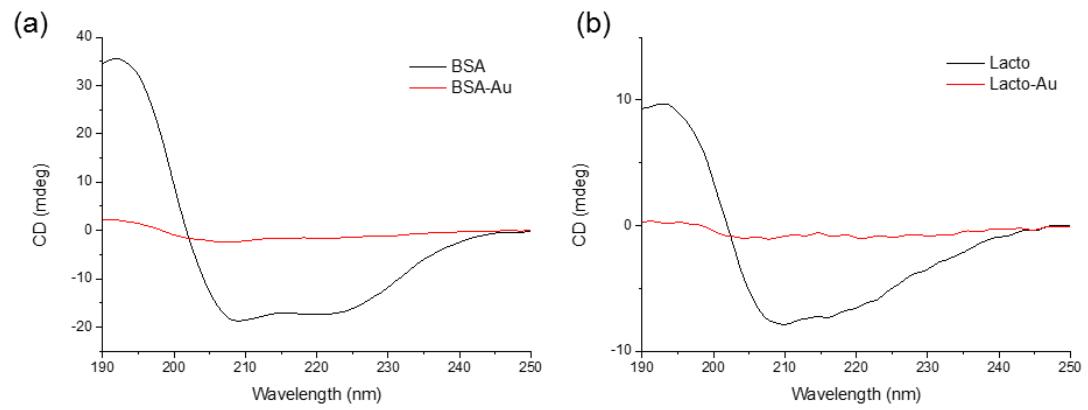


Figure S10. CD spectra for (a) BSA and BSA-Au, and (b) lactoferrin and lactoferrin-Au.

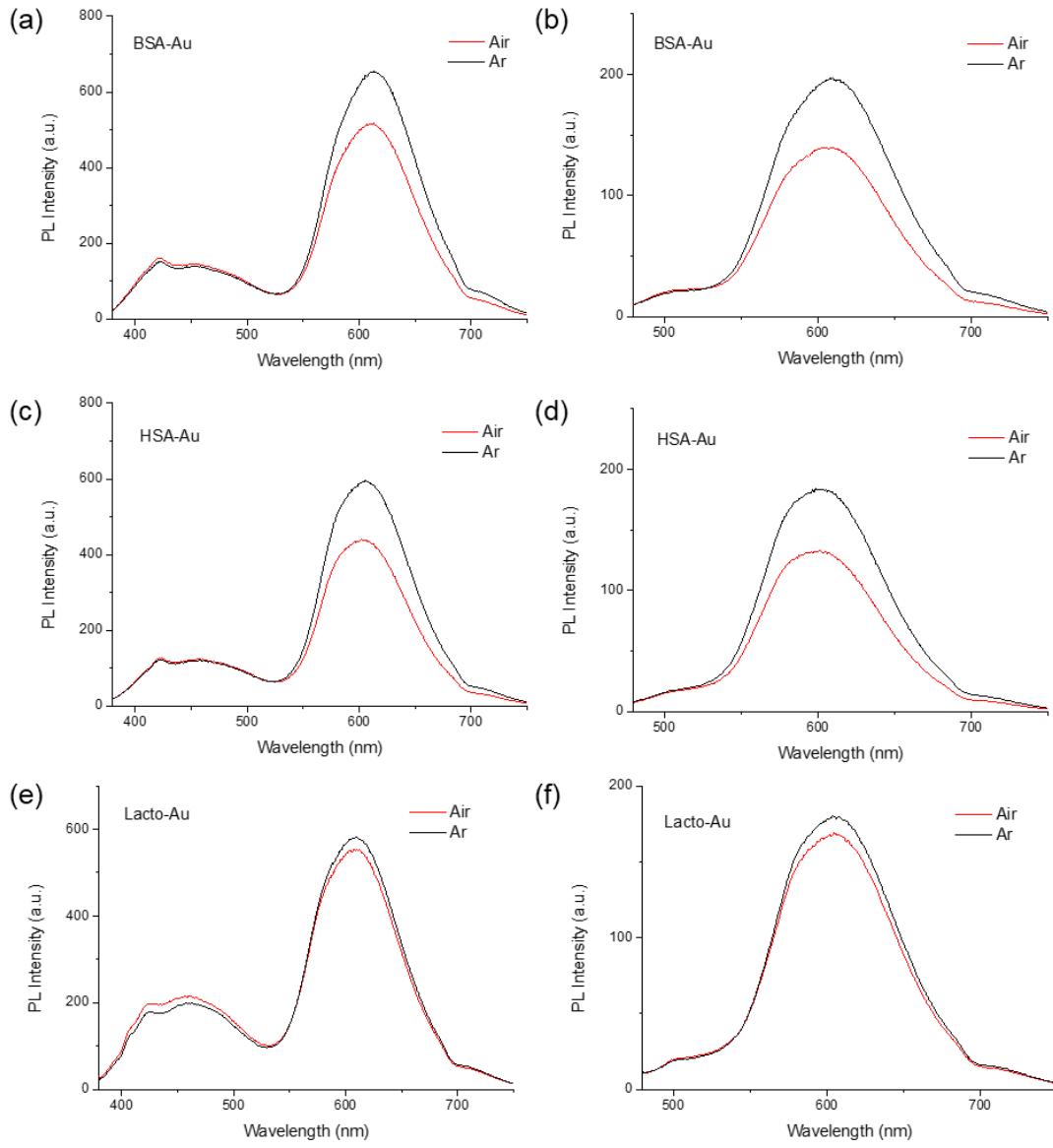


Figure S11. Oxygen dependence of PL. (a and b) BSA-Au excited at 370 nm and at 470 nm, respectively. (c and d) HSA-Au excited at 370 nm and 470 nm, respectively. (e and f) Lactoferrin-Au excited at 370 nm and at 470 nm, respectively. Experiments were carried out under argon (black) or air (red) atmospheres.

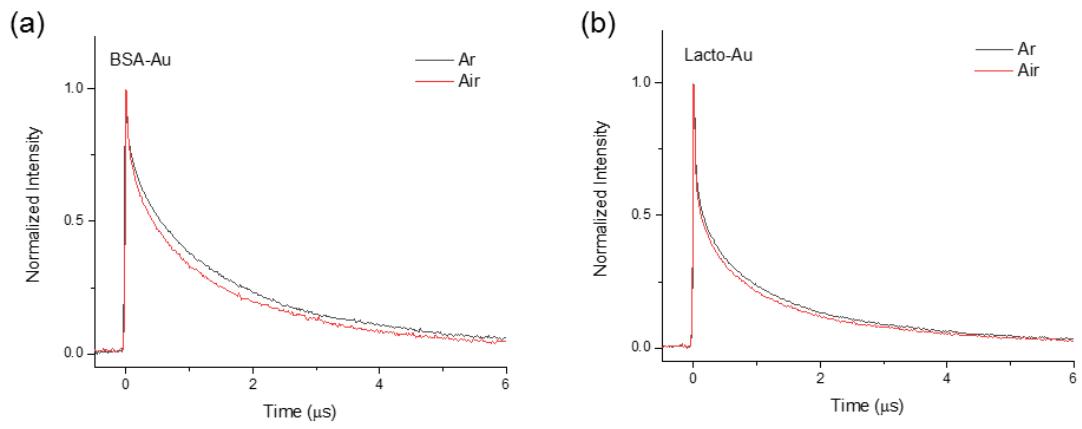


Figure S12. PL decay curves for (a) BSA-Au, and (b) lactoferrin-Au at 640 nm upon irradiation with 355 nm laser-light. Experiments were carried out under argon (black) or air (red) atmospheres.

Supporting references.

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