Supporting information

Functionalized Au_{22} clusters: Synthesis, characterization and patterning

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Preparation of PDMS stamp:

PDMS was prepared by mixing Sylgard 184 curing agent (Dow Corning) and its elastomer in 1:10 ratio. Prior to curing, the mixture was degassed in vacuum for 30 min. PDMS was poured onto the master (CD) and then cured in the oven at 70 °C for 6 h. The stamp was then peeled off from the master and it contained line features of 505 nm width, separated by ~ 1 μm wide channels (measured from AFM, shown in scheme 3). In order to remove any uncrosslinked low molecular weight PDMS, the stamps were cleaned using hexane and sonicated in ethanol for 20 min. Cover glass slides were cleaned by sonicating in acetone and in double-distilled water and dried under flowing argon. They were cleaned further by heating at 80 °C in piranha solution (1:2 of H_2O_2:H_2SO_4) (Caution: this mixture reacts violently with organic matter) for 10 min.

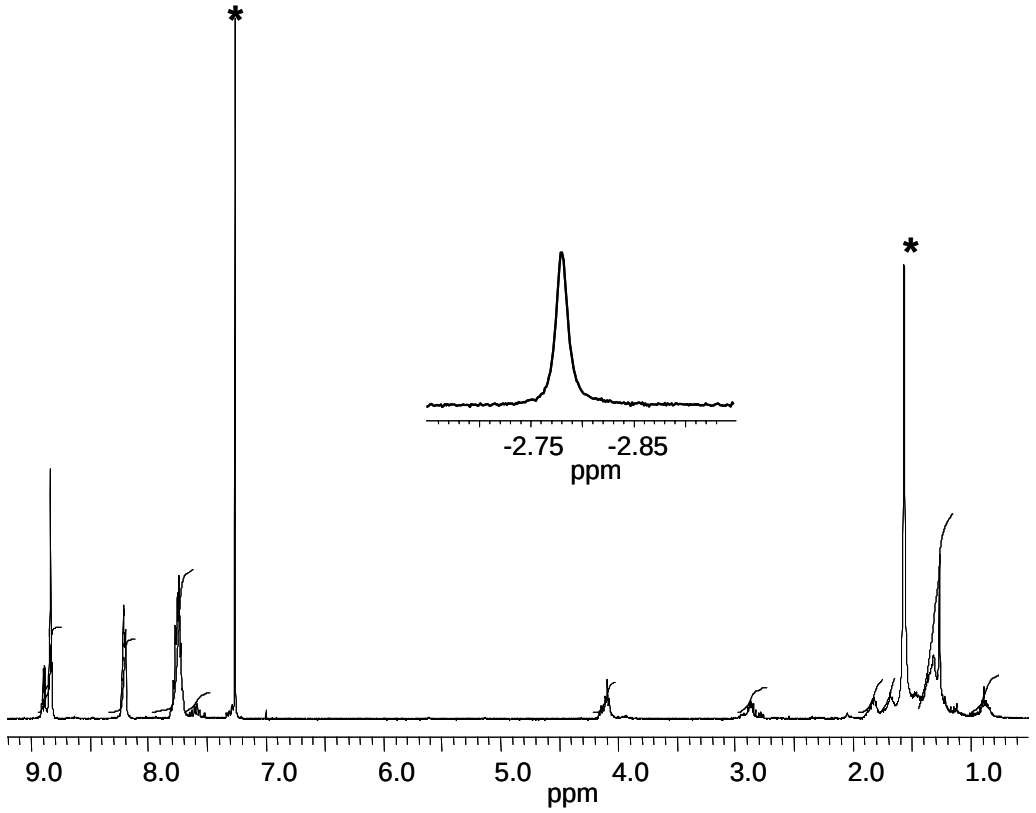

Figure S1. ^{1}H NMR of H_2TPPSH in $CDCl_3$. ^{1}H NMR in $CDCl_3$: 8.88 ppm (m, 8H, ß-pyrrole-H), 8.21 (m, 8H, o-phenyl-H), 7.75 (m, 11H, m- and p-phenyl-H), 4.08 (t, 2H, O-CH_2), 2.95 (m, 2H, (CH2-S)), 1.81 (m, 2H, CH_2), 1.70 (m, 2H, (CH_2)), 1.25-1.32 (m, 8H, $(CH2)_4$). Inset shows the expanded region for imino hydrogens, establishing the presence of free base porphyrin.

The elemental compositions of these clusters (Au_{25} and Au_{22}) were determined using CHNS analysis. The percentage of each element in the cluster was calculated theoretically and compared with the experimental data. The total elemental composition (empirical formula) of the cluster was determined by trial and error method. The elemental composition corresponds to $Au_{22}(SG)_{15}(H_2TPPOAS)_2]$ is in good agreement with experimentally observed composition (total CHNS %). This led to the conclusion that the as prepared cluster is having the composition of $Au_{22}[(SG)_{15}(H_2TPPOAS)_2]$.

Element	Experimental (%)	Calculated (%)
C	30.436	30.807
N	7.420	7.500
S	4.569	4.900
H	2.711	2.980

Table 1. Elemental analysis data of $Au_{22}[(SG)_{15}(H_2TPPOAS)_2]$. Total C, H, N, S % = 45.14

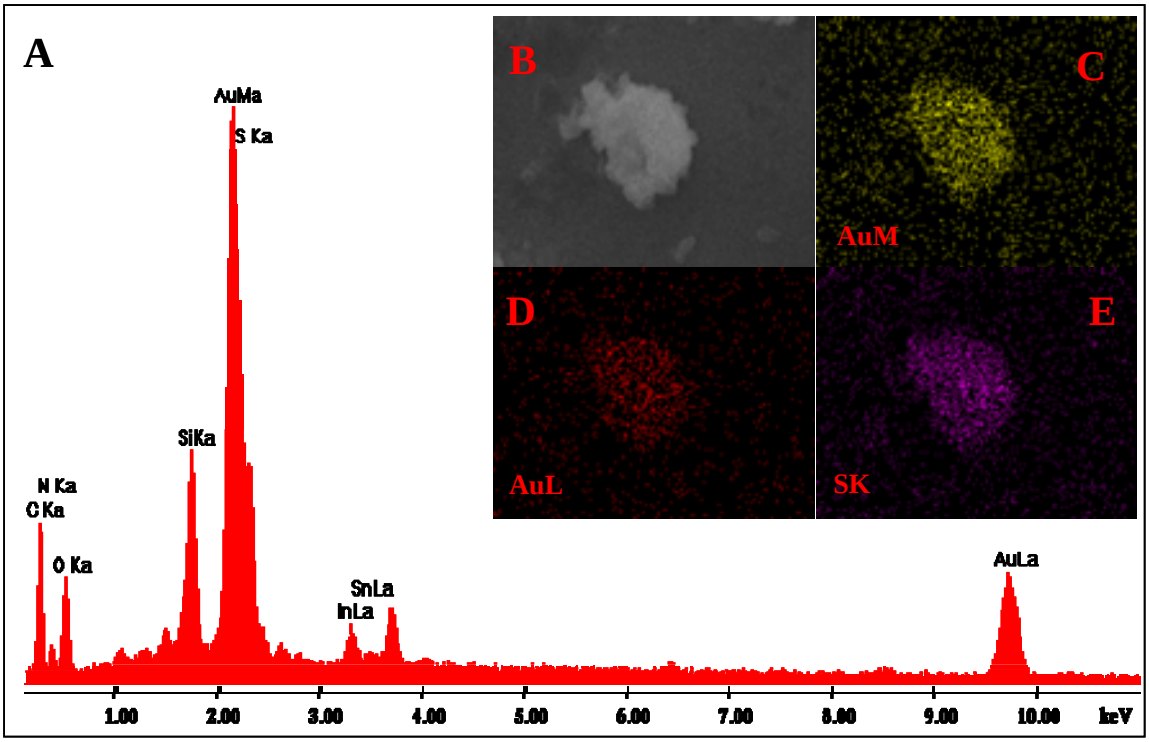

Figure S2. A. The EDAX spectrum of an aggregate of Au_{22}, collected from the area shown in B. The EDAX maps of Au Mα, Au Lα and S Kα of same area are given in C, D and E. Si, Sn and In peaks are due to the substrate used.

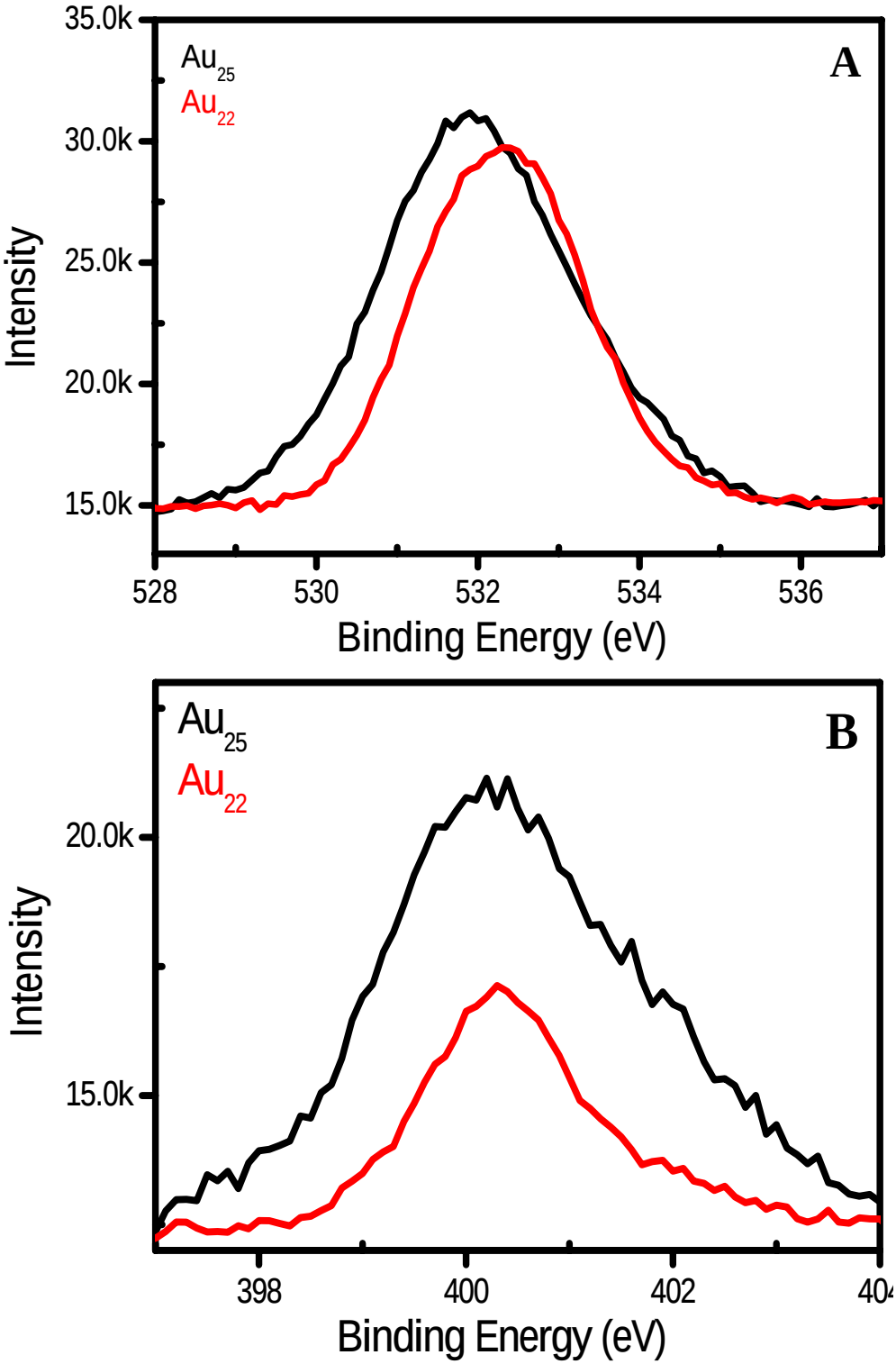

Figure S3. O1s (A) and N1s (B) core level photoelectron spectra of Au_{25}, and Au_{22}, respectively.

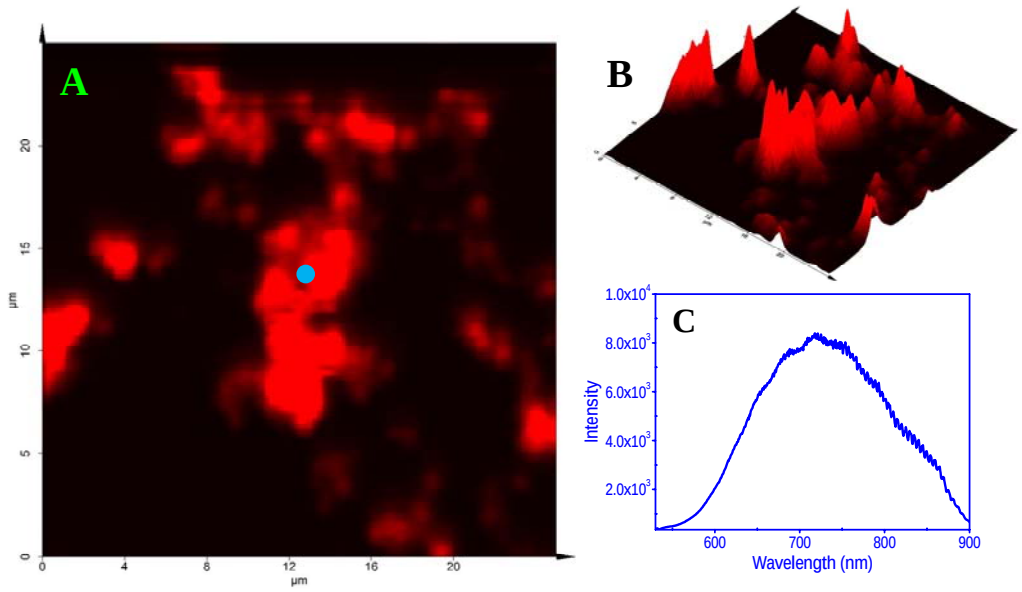

Figure S4. (A) Inherent solid state fluorescence image of an Au_{22} aggregate. (B) 3D image of the same area. (C) Fluorescence spectrum collected from the area, marked in A with a blue dot.

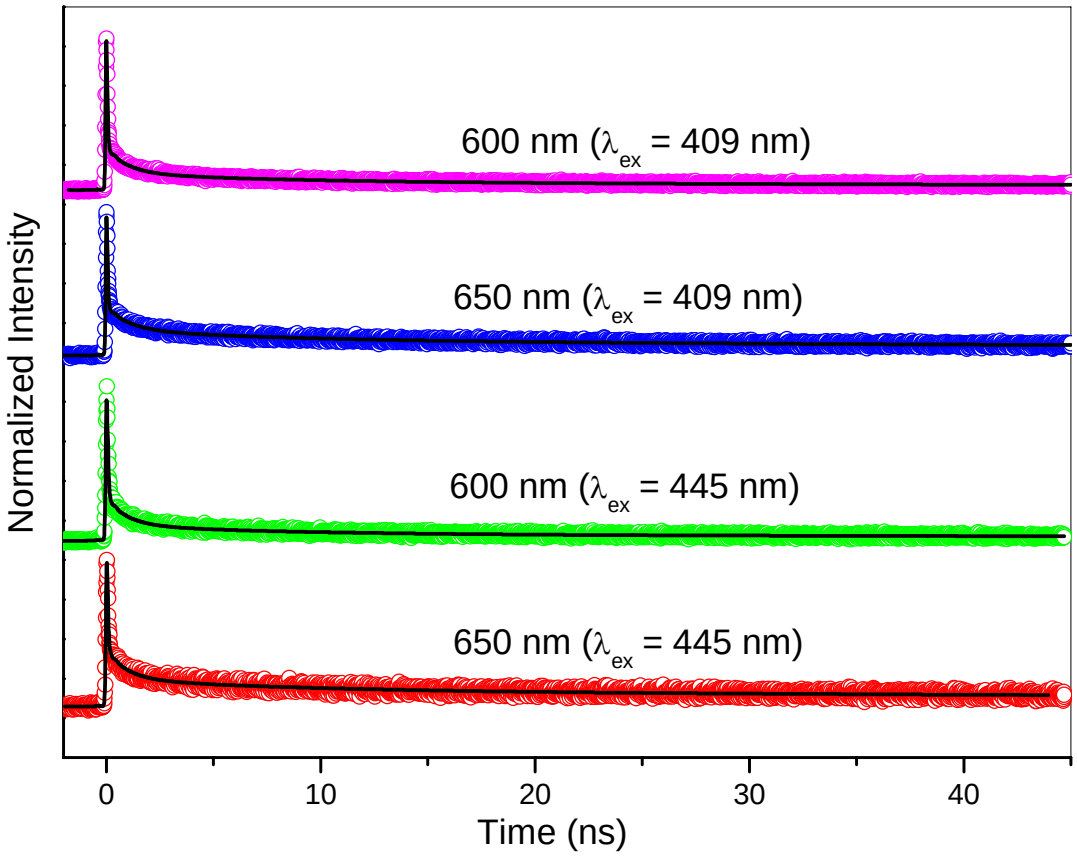

Figure S5. Fluorescence transients of porphyrin anchored Au_{22} at 600nm and 650 nm (λ_{ex} =409 nm) and 600 nm and 650 nm (λ_{ex} =445 nm).

Wavelength used for Fl. Decay (nm)	τ_1(%) (ns)	τ_2(%) (ns)	τ_3(%) (ns)	τ_4(%) (ns)
Excitation wavelength: 409 nm				
600	0.04 (90.1%)	0.97 (5.8%)	8.5 (2.3%)	124.4 (1.8%)
650	0.04 (87.6%)	1.02 (5.8%)	8.5 (3.0%)	129.7 (3.6%)
Excitation wavelength: 445 nm				
600	0.04 (91.2%)	0.96 (5.5%)	8.5 (2.1%)	162.0 (1.2%)
650	0.03 (88.4%)	0.92 (5.8%)	9.0 (2.6%)	152.4 (3.2%)

Table 2. Lifetime values of porphyrin anchored Au_{22} at 600 nm (λ_{ex} =409 nm) and 600 nm and 650 nm (λ_{ex} =445 nm)

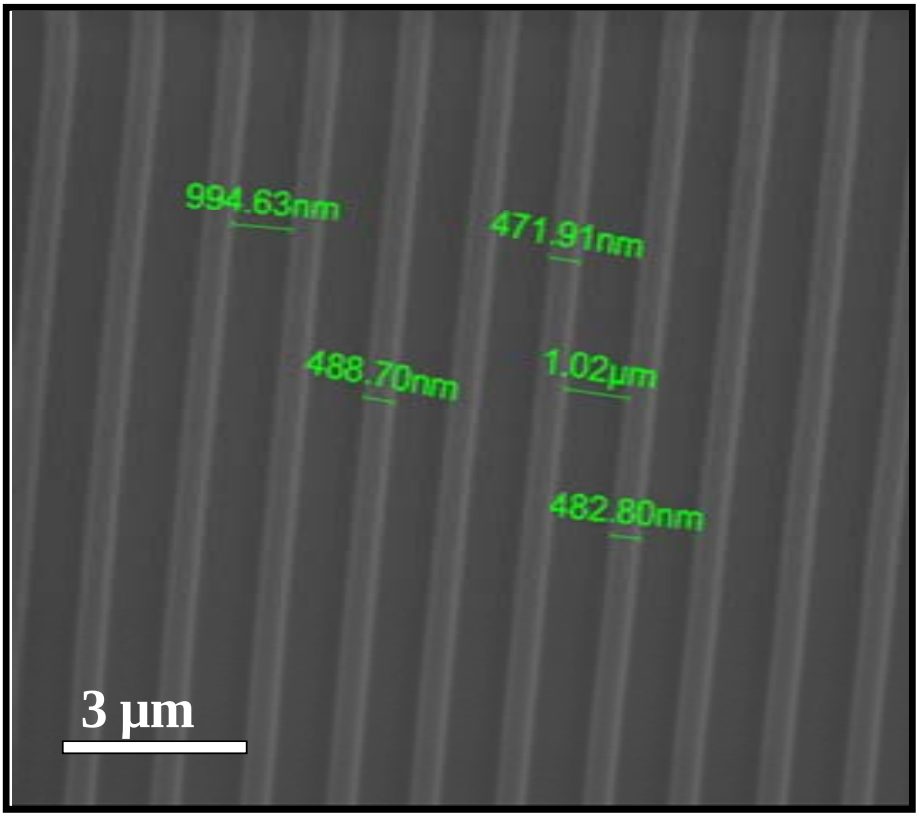

Figure S6. FESEM image of the PDMS stamp showing a line width of around 470-490 nm. The spacing between two lines is in the range of 1 µm.