

Supporting Information

Structure Determination of a Metastable $\text{Au}_{22}(\text{SAdm})_{16}$ Nanocluster and Its Spontaneous Transformation into $\text{Au}_{21}(\text{SAdm})_{15}$

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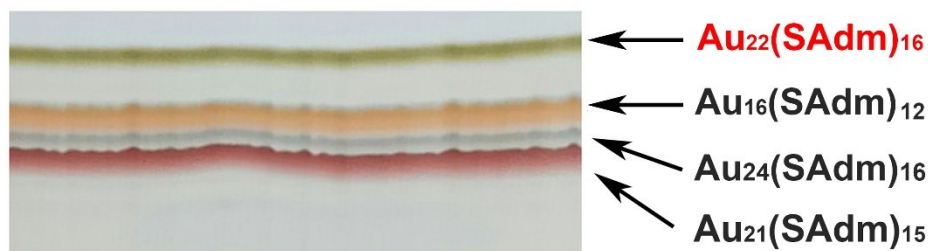


Fig. S1 Photograph of the raw product separated by TLC plate.

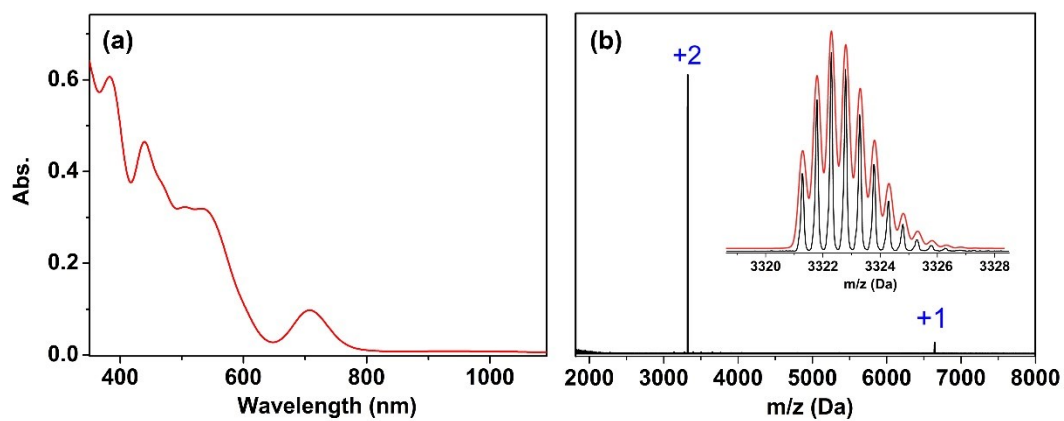


Fig. S2 UV-vis spectrum (a) and ESI-MS pattern (b) of the Au_{21} purified by TLC plate. Inset shows the calculated isotopic pattern of Au_{21} with +2 charge (red) compared with the experimental signal (black).

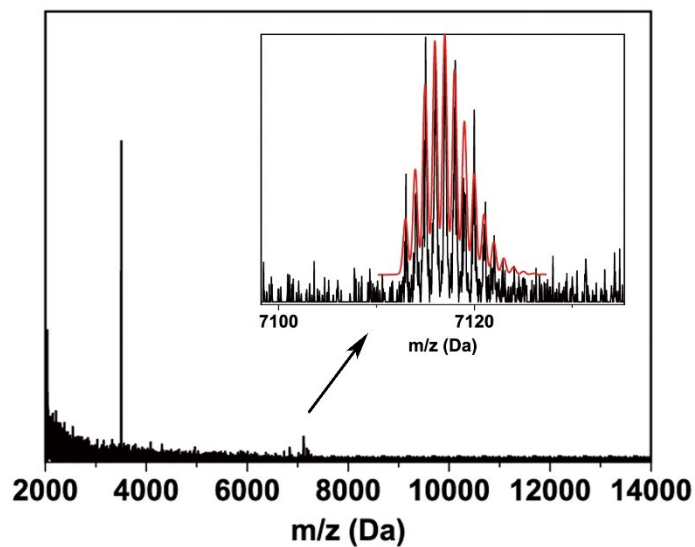


Fig. S3 ESI-MS spectrum of Au₂₂ with prolonged acquisition time showing the [Au₂₂(SAdm)₁₆ + Ag⁺] species.

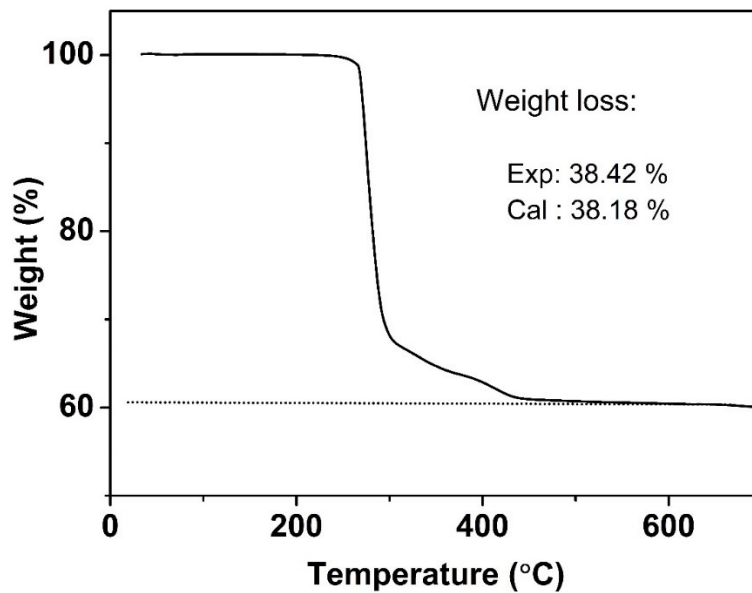


Fig. S4 TGA curve of Au₂₂.

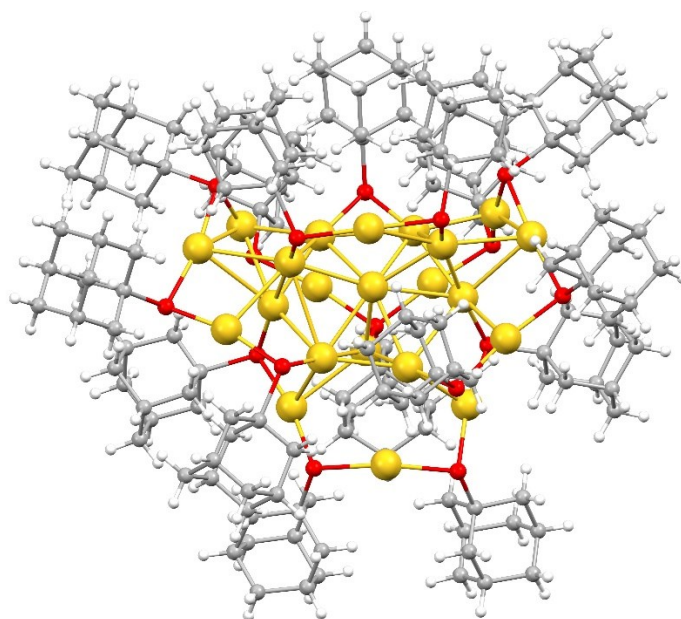


Fig. S5 Total structure of Au₂₂ (color labels: yellow = Au, red = S, gray = C, white = H).

Table S1. Crystal data for Au₂₂.

	Au ₂₂
Empirical formula	C ₁₆₀ H ₂₄₀ Au ₂₂ S ₁₆
Formula weight	7009.73
Temperature	120 K
Wavelength	1.54186 Å
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 16.3688(16)
	b = 32.3268(9)
	c = 36.999(2)
	α = 90°
	β = 97.356(7)°
	γ = 90°

Volume	19417(2)
Z	4
Density (calculated)	2.398 g/cm ³
Absorption coefficient	32.258
F(000)	12776
Crystal size	0.1 x 0.07 x 0.06 mm ³

Table S2. Comparison of bond lengths in Au₂₂ and Au₂₁.

	Au ₂₂	Au ₂₁	Diff.
Au(core)-Au(core)	2.61-3.22 Å (Avg. 2.81 Å)	2.65-3.20 Å (Avg. 2.84 Å)	-0.88%
Au(core)-Au(motif)	2.85-3.20 Å (Avg. 3.03 Å)	2.84-3.25 Å (Avg. 3.02 Å)	+0.33%
Au(core)-S(motif)	2.35-2.39 Å (Avg. 2.36 Å)	2.22-2.46 Å (Avg. 2.35 Å)	+0.42%
Au(motif)-S(motif)	2.27-2.32 Å (Avg. 2.30 Å)	2.15-2.45 Å (Avg. 2.31 Å)	-0.43%

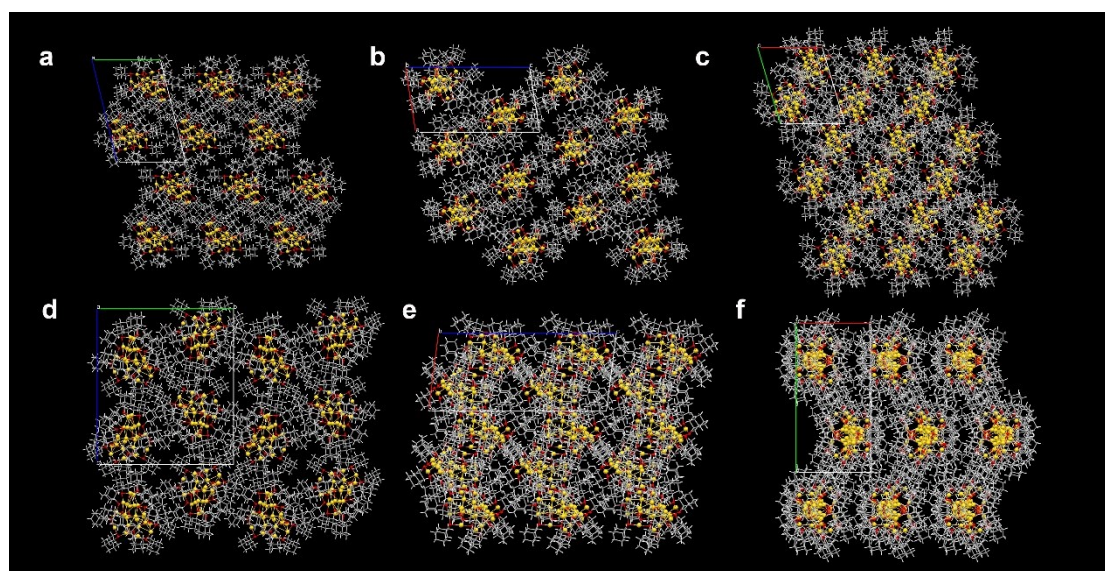


Fig. S6 Packing mode of Au₂₁ viewed from the a axle (a), b axle (b) and c axle (c) and Au₂₂ viewed from the a axle (d), b axle (e) and c axle (f). (color labels: yellow = Au; red = S; grey = C; white = H).

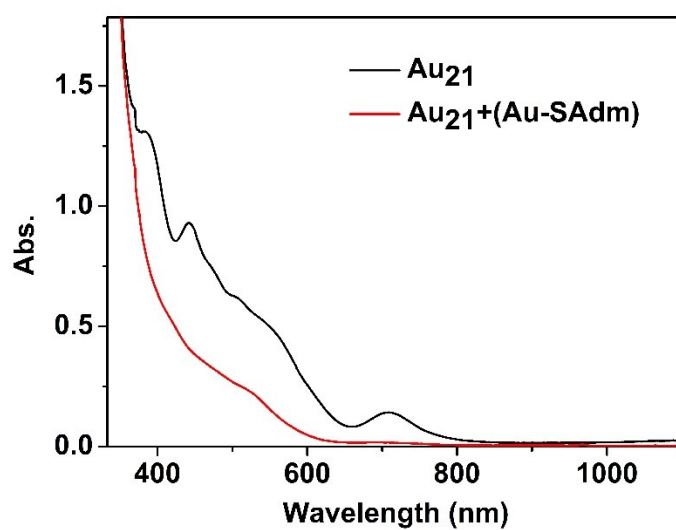


Fig. S7 UV-vis spectra of Au₂₁ (black curve) and Au₂₁ reacting with Au-SAdm complex for 12 h (red curve).

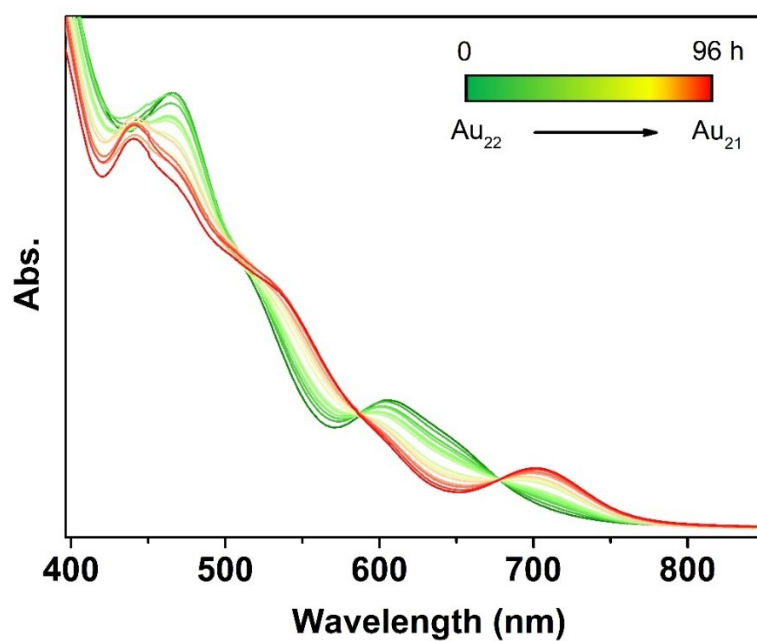


Fig. S8 Time-dependent UV-vis spectra of Au₂₂ in n-Hex.

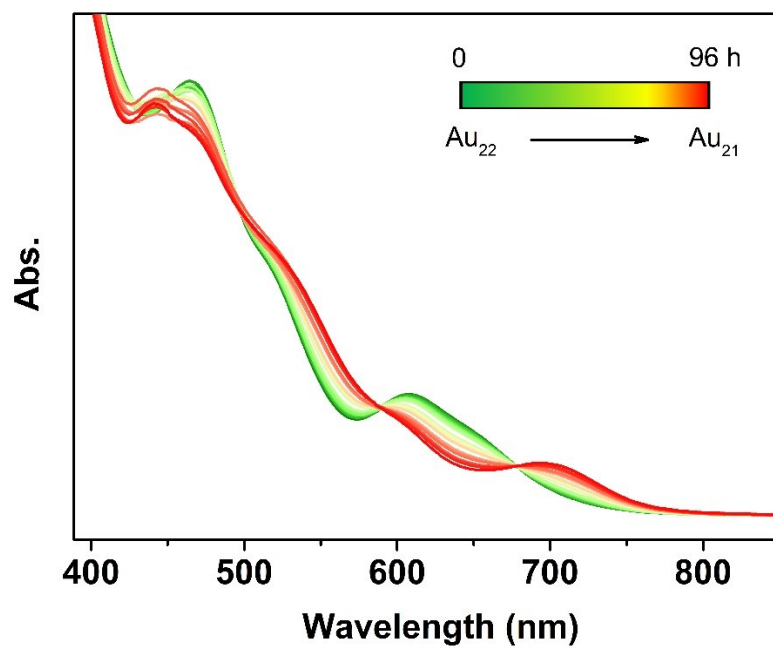


Fig. S9 Time-dependent UV-vis spectra of Au₂₂ in toluene.

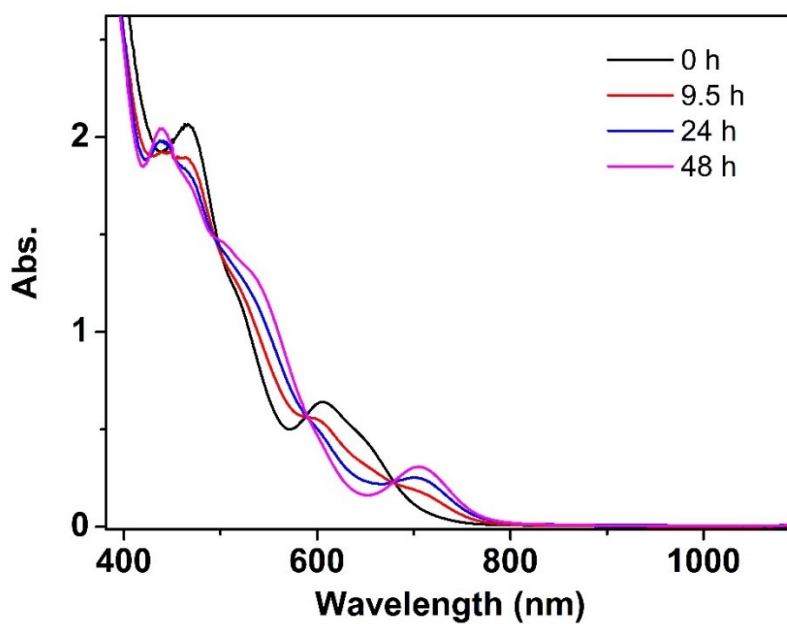


Fig. S10 Time-dependent UV-vis spectra of Au₂₂ in deoxidized CHCl₃ under N₂ atmosphere.

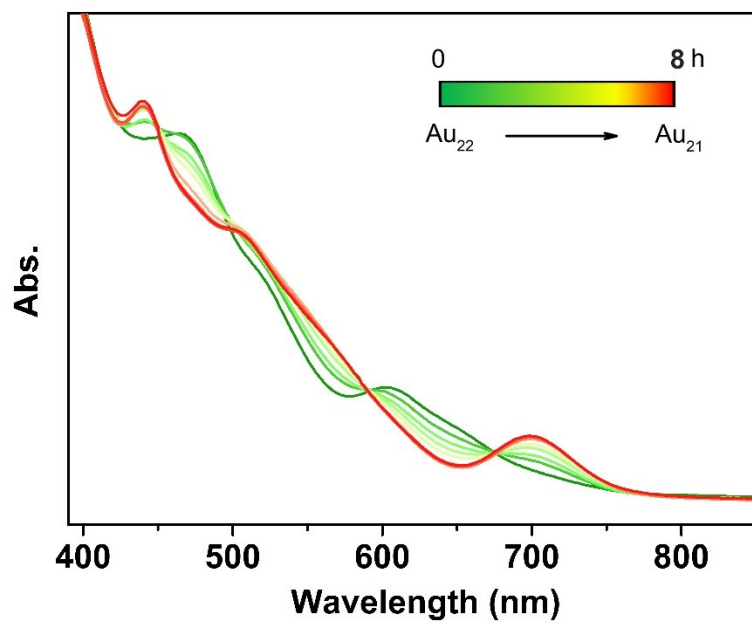


Fig. S11 Time-dependent UV-vis spectra of Au₂₂ in CHCl₃/EtOH.

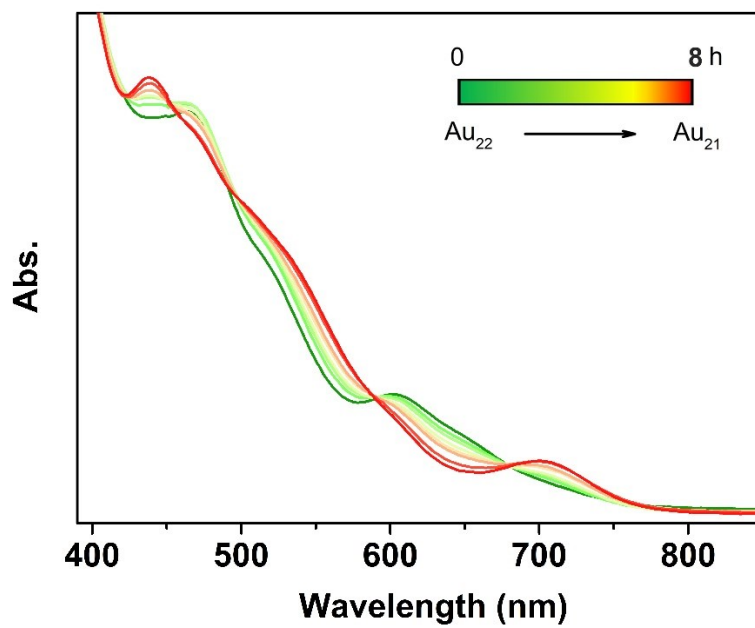


Fig. S12 Time-dependent UV-vis spectra of Au₂₂ in CHCl₃/Et₂O.

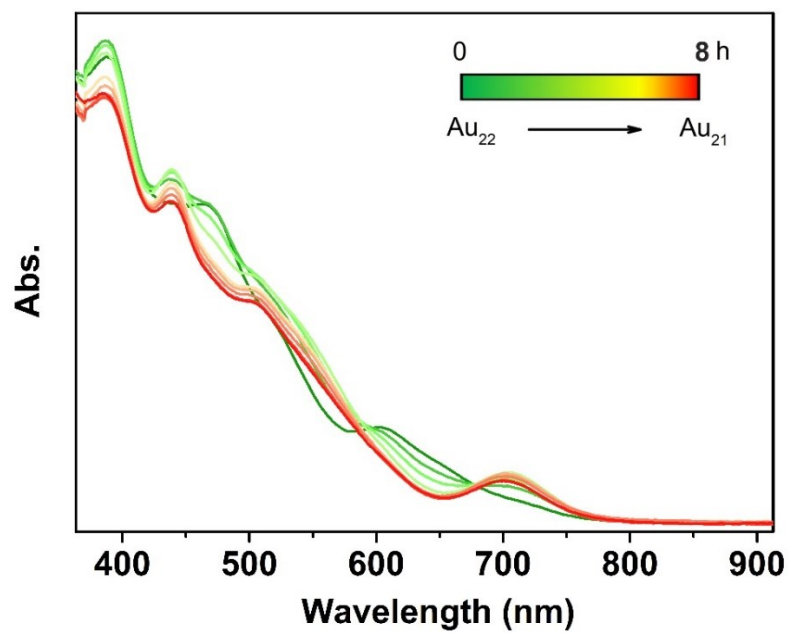


Fig. S13 Time-dependent UV-vis spectra of Au₂₂ in CHCl₃/MeCN.