

Supporting Information

Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles

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Table S1: A summary of monolayer protected Au and Ag clusters synthesized so far.

Core	Ligand	Composition*	Focus	Synthesis method	Physical state of the product	Other measured properties**	Reference
Au ₂	Bis(diphenylphosphino)methane	[Au(Ph ₂ P) ₂ CH] ₂	Crystal structure	Solution phase	Solid	-----	¹
Au ₄	Tri-phenylphosphine, iodide	[Au ₄ (μ-I) ₂ (PPh ₃) ₄]	Crystal structure	Solution phase	Solid	-----	²
Au ₅	Bis(diphenylphosphino)methane, nitrate	[Au ₅ (dppmH) ₃ (dppm)](NO ₃) ₂	Crystal structure	Solution phase	Solid	-----	³
Au ₆	Tri-phenylphosphine, nitrate	[Au ₆ (PPh ₃) ₆](NO ₃) ₂ ·3CH ₂ Cl ₂	Crystal structure	Solution phase	Solid	-----	⁴⁻⁵
Au ₇	Tri-phenylphosphine	[Au ₇ (PPh ₃) ₇] ⁺	Crystal structure	Solution phase	Solid	³¹ P NMR, ¹ H NMR, ESR, IR	⁶
Au ₈	Tri-phenylphosphine	[Au ₈ (PPh ₃) ₈](PF ₆) ₂	Crystal structure	Solution phase	Solid	-----	⁷
Au ₈	Tri-phenylphosphine	[Au ₈ (PPh ₃) ₈](NO ₃) ₂	Crystal structure	Solution phase	Solid	Mossbauer spectroscopy	⁸
Au ₉	Tris-p-methylphenylphosphine	[Au ₉ (P(C ₆ H ₄ -p-Me) ₃) ₃] ₃ [PF ₆] ₃	Crystal structure	Solution phase	Solid	----	⁹
Au ₉	Tris-p-methylphenylphosphine	[Au ₉ (P(C ₆ H ₄ -p-Me) ₃) ₃] ₃ [BF ₄] ₃	Crystal structure	Solution phase	Solid	UV/Vis	¹⁰
Au ₁₀	Dicyclohexylphenyl phosphine, chloride	[Au ₁₀ Cl ₃ (PCy ₂ Ph) ₆](NO ₃)	Crystal structure	Solution phase	Solid	----	¹¹
Au ₁₁	Tri-phenylphosphine	Au ₁₁ (PPh ₃) ₁₀ (SCN) ₃	Crystal structure	Solution phase	Solid	----	¹²
Au ₁₁	Tris-p-chlorophenylphosphine, iodide	Au ₁₁ I ₃ [P(C ₆ H ₄ -p-Cl) ₃] ₇	Crystal structure	Solution phase	Solid	----	¹³
Au ₁₁	Tris-p-fluorophenylphosphine, iodide	Au ₁₁ I ₃ [P(C ₆ H ₄ -p-F) ₃] ₇	Crystal structure	Solution phase	Solid	----	¹⁴
Au ₁₁	3-Mercaptopropionic acid	Au ₁₁ (SCH ₂ CH ₂ COOH) ₇ (TOA) ₇	Luminescence	Brust method	Solid	UV/Vis, XPS, ESI MS	¹⁵
Au ₁₁	3-Mercaptopropionic acid	Au ₁₁ (SCH ₂ CH ₂ COO-) ₇ (TOA) ₇	Thermal stability	Brust method	Solid	SEM, UV/Vis, XRD, TGA, DSC	¹⁶
Au ₁₁	Tri-phenylphosphine, chloride	Au ₁₁ (PPh ₃) ₇ Cl ₃	Spectral diffusion in STM	Hutchison method	Solid	Tunneling spectrum, differential conductance	¹⁷
Au ₁₃	Dimethylphenylphosphine, chloride	[Au ₁₃ (PMe ₂ Ph) ₁₀ Cl ₂](PF ₆) ₃	Crystal structure	Solution phase	Solid	----	¹⁸
Au ₁₃	1,2-Bis (diphenylphosphine), chloride	[Au ₁₃ (dppe) ₅ Cl ₂] ₃	Characterization and crystal structure	Two step solution phase	Solid	ESI MS, UV/Vis, PL	¹⁹

Au ₁₄	Tri-phenylphosphine, nitrate	[Au ₁₄ (PPh ₃) ₈ (NO ₃) ₄]	Crystal structure	Solution phase	Solid	DFT	20
Au _n (n = 10-39)	Glutathione	Au ₁₀ (SG) ₁₀ , Au ₁₅ (SG) ₁₃ , Au ₁₈ (SG) ₁₄ , Au ₂₂ (SG) ₁₆ , Au ₂₂ (SG) ₁₇ , Au ₂₅ (SG) ₁₈ , Au ₂₉ (SG) ₂₀ , Au ₃₃ (SG) ₂₂ , Au ₃₉ (SG) ₂₄	Characterization	Solution phase	Solid	TEM, FTIR, XPS, PAGE	21
Au ₁₅	Glutathione, cyclodextrin	Au ₁₅ @CD	Characterization	Two step solution phase	Solid	Lifetime, NMR, CD, DLS	22
Au ₁₅ , Au ₁₈	Glutathione	Au ₁₅ (SG) ₁₃ , Au ₁₈ (SG) ₁₄	Characterization	Two phase	Solid	UV/Vis, PL, XPS, ESI MS	23
Au ₁₈	Glutathione	Au ₁₈ (SG) ₁₄	Characterization	Solution phase	Solid	UV/Vis, PL, XPS, PAGE	24
Au ₁₈	Cyclohexylthiol	Au ₁₈ (SC ₆ H ₁₁) ₁₄	Crystal structure	Two phase ligand exchange	Solid	UV/Vis, ESI MS, TD DFT, IR, SEC, PL, ¹ HNMR	25
Au ₁₉	N,N-bis(diphenylphosphino)amine), Phenylalkyne	[Au ₁₉ (PhC≡C) ₉ (Hdppa) ₃](SbF ₆) ₂	Crystal structure	Solution phase	Solid	UV/Vis, ESI MS, ³¹ P NMR, TDDFT	26
Au ₁₉	Phenylethanethiol	Au ₁₉ (SC ₂ H ₄ Ph) ₁₃	Characterization	Solution phase	Solid	SEC, XPS, ESI MS, UV/Vis, PXRD	27
Au ₂₀	Phenylethanethiol	Au ₂₀ (SCH ₂ CH ₂ Ph) ₁₆	Characterization	Brustr method	Solid	UV/Vis, SEC, NMR	28
Au ₂₀	4-t-butylbenzenethiol	Au ₂₀ (TBBT) ₁₆	Crystal structure	Ligand exchange method	Solid	SXRD	29
Au ₂₀	tris(2-(diphenylphosphino)ethyl)phosphine	[Au ₂₀ (PP ₃) ₄]Cl ₄	Crystal structure	Two step solution phase	Solid	ESI MS, ³¹ P NMR	30
Au ₂₀	tris(2-(diphenylphosphino)ethyl)phosphine	[Au ₂₀ (PP ₃) ₄]Cl ₄	Hyperpolarizability	Two step solution phase	Solid	Hyper-Rayleigh Scattering, DFT, UV/Vis,	31
Au ₂₁	Adamentanethiol	Au ₂₁ (S-Adm) ₁₅	Crystal structure	Two step solution phase	Solid	UV/Vis, DFT	32
Au ₂₂	Glutathione, porphyrin	Au ₂₂ [(-SG) ₁₅ (-SAOPPTH ₂) ₂]	Characterization	Three step solution phase	Solid	UV/Vis, lifetime study, XPS	33
Au ₂₂	1,8-bis-(diphenylphosphino) octane	Au ₂₂ (L) ₆	Crystal structure	Solution phase	Solid	UV/Vis, ESI MS, PL	34
Au ₂₂	Glutathione	Au ₂₂ (SG) ₁₈	Characterization	CO-directed	Solid	UV/Vis, ESI MS, PL, ESI MS, DFT	35
Au ₂₃	Glutathione	Au ₂₃ (SG) ₁₈	NIR emission	Two step solution phase followed by	Solid	UV/Vis, MALDI MS, XPS, fluorescenc	36

				interfacial etching		e imaging	
Au ₂₃	Cyclohexanethiol	[Au ₂₃ (SC ₆ H ₁₁) ₁₆] ⁻	Crystal structure	One step solution phase	Solid	UV/Vis, ESI MS, DFT	³⁷
Au ₂₄	Phenylethanethiol and tri-phenylphosphine	[Au ₂₄ (PPh ₃) ₁₀ (SC ₂ H ₄ Ph) ₅ X ₂] ⁺	Crystal structure	Modified Brust method	Solid	ESI MS, UV/Vis, DFT calculation	³⁸
Au ₂₄	Benzeneselenol	Au ₂₄ (SePh) ₂₀	Crystal structure	Modified Brust method	Solid	UV/Vis	³⁹
Au ₂₄	Adamentanethiol	Au ₂₄ (SAdm) ₁₆	Crystal structure	Three step solution phase	Solid	ESI MS, UV/Vis, DFT	⁴⁰
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Solid state emission	Three step solution phase	Solid	UV/Vis, Raman	⁴¹
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Ligand etching	Two step solution phase followed by ligand etching	Solid	NMR, UV/Vis, TEM	⁴²
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Phase transfer	Two step solution phase	Solid	UV/Vis, XPS, FT IR	⁴³
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Silica embedding	Two step solution phase	Solid	UV/Vis, TEM, XPS	⁴⁴
Au ₂₅	PPh ₃ /C _n H _(2n+1) SH	Au ₂₅ (PPh ₃) ₁₀ (SC _n H _{2n+1}) ₅ Cl ₂ ²⁺	Crystal structure	Hutchison method	Solid	UV/Vis, XRD	⁴⁵
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	CO oxidation	Two step solution phase	Solid	TGA, GC	⁴⁶
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈ ⁻	Air oxidation	Two step solution phase	Solid	UV/Vis, NMR, ESI MS	⁴⁷
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	Crystal structure	Two step solution phase	Solid	UV/Vis, DFT	⁴⁸
Au ₂₅	Phenylethanethiol	[N(C ₈ H ₁₇) ₄][Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈]	Crystal structure	Modified Brust method	Solid	----	⁴⁹
Au ₂₅	Hexanethiol/PyR-SH	Au ₂₅ (C ₆ S) ₁₇ PyS	Electron transfer	Brust method	Solid	UV/Vis, steady state fluorescence, TEM	⁵⁰
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	NMR	Brust method	Solid	UV/Vis, DFT study	⁵¹
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	Electrochemical sensing	Brust method	Solution	MALDI MS, UV/Vis, TEM	⁵²
Au ₂₅	Hexanethiol	Au ₂₅ (SC ₆ H ₁₃) ₁₈	Electrochemistry	Brust method	Solution	UV/Vis, TEM	⁵³
Au ₂₅	Glutathione	[Au ₂₅ (SG) ₁₈ -6H] ⁷⁻	Electron emission	Two step solution phase	Solid	UV/Vis, ESI MS, MS/MS	⁵⁴
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈ ^{0/1-}	Electron self	Modified Brust	Solid	COSY, two dimensiona	⁵⁵

			exchange dynamics	method		I Raman	
Au ₂₅	Dodecanthiol	Au ₂₅ (SC ₁₂ H ₂₅) ₁₈	Alcohol oxidation	Modified Brust method	Solid	GC MS, TGA, ICP	⁵⁶
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Core etching	One step solution phase	Solution	XPS, TEM, UV/Vis	⁵⁷
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	Dithiol cross-linking	Brust method	Solution	MALDI MS, DFT	⁵⁸
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈ ⁻	Ion mobility mass spectrometry	Brust method	Solid	MS/MS	⁵⁹
Au ₂₅	Diocetyl diselenide	Au ₂₅ (SeC ₈ H ₁₇) ₁₈	Characterization	Brust method	Solid	UV/Vis, TGA, XPS, XRD	⁶⁰
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	High yield synthesis	Two step solution phase	Solid	UV/Vis, DLS, TGA	⁶¹
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Ligand exchange	Hutchison method followed by Ligand exchange	Solid	ESI MS, TEM, UV/Vis	⁶²
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	Ligand exchange	One step solution phase	Solution	UV/Vis, CD	⁶³
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	Size evolution study	One step solution phase	Solution	UV/Vis, MALDI TOF	⁶⁴
Au ₂₅	Cysteine	Au ₂₅ (Cys) ₁₈	CO-directed synthesis	One step solution phase	Solid	UV/Vis, ESI MS	⁶⁵
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	Magnetic circular dichroism study	Two step solution phase	Solid	TDDFT, UV/Vis	⁶⁶
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Size dependent properties	One step solution phase	Solid	TEM, XRD, UV/Vis	⁶⁷
Au ₂₅	Hexanethiol	Au ₂₅ (SC ₆ H ₁₃) ₁₈	Origin of magic stability	Schiffrin method	Solid	ESI MS, UV/Vis, DFT	⁶⁸
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	NMR and mass spectrometry	One step solution phase	Solid	UV/Vis, TEM, ESI MS	⁶⁹
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	FRET	Two step solution phase	Solid	UV/Vis, IR, NMR, LDI	⁷⁰
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Reactivity	Two step solution phase	Solid	FT-IR, TEM, UV/Vis	⁷¹
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	EPR	Two step solution phase	Solid	DFT	⁷²
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	NMR	One step solution	Solid	TGA, UV/Vis,	⁷³

				phase		MALDI MS, etc.	
Au ₂₅	BSA	Au ₂₅ @BSA	Temperature-dependent luminescence	One step solution phase	Solution	UV/Vis, lifetime measurements	⁷⁴
Au ₂₅	Hexanethiol	Au ₂₅ (SC ₆ H ₁₃) ₁₈	Temperature-dependent absorbance	Brust method	Solid	----	⁷⁵
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	EXAFS	Brust method	Solid	XANES	⁷⁶
Au ₂₅	Glutathione/ Hexanethiol	Au ₂₅ (SG) ₁₈ / Au ₂₅ (SC ₆ H ₁₃) ₁₈	Luminescence	Brust method	Solid	UV/Vis, PL, luminescence decay	⁷⁷
Au ₂₅	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈	¹ HNMR	Modified Brust method	Solid	COSY, Raman	⁵⁵
Au ₂₅	Glutathione	Au ₂₅ (SG) ₁₈	Single molecule mass spectrometry	Two step solution phase	Solid	Nanopore detection, nanopore blockade analysis, ESI MS	⁷⁸
Au ₂₅	6-mercaptohexanoic Acid	Au ₂₅ (MHA) ₁₈	Self-assembly	One step solution phase	Solid	UV/Vis, ESI MS, TEM, FESEM, XRD	⁷⁹
Au ₂₅ , Au ₄	2-methacryloyloxyethyl Phosphorylcholine	Au ₂₅ (MPC) ₁₈ and Au ₄ (MPC) ₄	Optical properties	Solution phase	Solid	ESI MS, UV/Vis, MALDI FT-ICR, XPS, TG, PL	⁸⁰
Au ₂₅	Phenylethanethiol, Butanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈ , Au ₂₅ (BT) ₁₈	TLC	Solution phase	Solid	UV/Vis, MALDI MS	⁸¹
Au ₂₅	4-(tert-butyl)-benzyl mercaptan,	Au ₂₅ (SBB) ₁₈	Luminescence enhancement	Solution phase	Solid	UV/Vis, PL, MALDI MS, ESI MS, TG, TEM, XPS	⁸²
Au ₂₈	Glutathione	Au ₂₈ (SG) ₁₄ [#]	Optical properties	Two step solution phase	Solid	UV/Vis, ESI MS, MALDI MS, CD, PAGE	⁸³
Au ₂₈	Glutathione	Au ₂₈ (SG) ₁₄ [#]	Isolation	Two step solution phase	Solid	UV/Vis, ESI MS, MALDI MS, PXRD, ¹³ C NMR	⁸⁴
Au ₂₈	Glutathione	Au ₂₈ (SG) ₁₄ [#]	Luminescence	Two step solution phase	Solid	UV/Vis, PL, Decay lifetime	⁸⁵

Au ₂₈	4-tert-butylbenzenethiol	Au ₂₈ (TBBT) ₂₀	Crystal structure	Two step solution phase	Solid	HPLC, ESI MS, CD, calculation	⁸⁶
Au ₂₉	Glutathione	Au ₂₉ (SG) ₁₈	Characterization	CO-directed	Solid	UV/Vis, ESI MS	⁸⁷
Au ₃₀ , Au ₃₉ , Au ₆₅ , Au ₆₇	1-adamantanethiol (AdSH), cyclohexanethiol (CySH), n-hexanethiol (C6SH).	Au ₃₀ (SAd) ₁₈ , Au ₃₉ (SAd) ₂₃ , Au ₆₅ (SCy) ₃₀ , and Au ₆₇ (SCy) ₃₀	Characterization	Modified Brust method	Solid	UV/Vis, TEM, PL, MALDI MS	⁸⁸
Au ₃₀	tert-butanethiol, 1-adamantanethiol	Au ₃₀ (S-t-C ₄ H ₉) ₁₈ , Au ₃₀ (SAd) ₁₈	Characterization	Two step solution phase	Solid	ESI MS, MALDI MS, UV/Vis, PXRD, ¹ H NMR	⁸⁹
Au ₃₀	tert-butanethiol	Au ₃₀ S(S-t-Bu) ₁₈	Crystal structure	On pot THF method	Solid	UV/Vis, ESI MS, CD, DFT	⁹⁰
Au ₃₆	Thiophenol	Au ₃₆ (SPh) ₂₃	Characterization	Two step solution phase	Solid	UV/Vis, NMR	⁹¹
Au ₃₆	4-tert-butylbenzenethiol	Au ₃₆ (SPh-tBu) ₂₄	Crystal structure	Two step solution phase followed by ligand etching	Solid	ESI MS, TGA, PDOS	⁹²
Au ₃₈	Dodecanethiol	Au ₃₈ (SC ₁₂ H ₂₅) ₂₄	Photoemission	Two step solution phase	Solid	STM, TEM, UV/Vis, MALDI MS	⁹³
Au ₃₈	Butanethiol/hexanethiol/octanethiol/decanethiol/dodecanethiol	Au ₃₈ (SR) ₂₄ *	Characterization	Modified Brust method	Solid	DPV, TEM, UV/Vis	⁹⁴
Au ₃₈	Butanethiol/hexanethiol/octanethiol/decanethiol/dodecanethiol/Hexadecanethiol	Au ₃₈ (SR) ₂₄	Characterization	Modified Brust method	Solid	FT-IR, XANES, TEM	⁹⁵
Au ₃₈	Dodecanethiol	Au ₃₈ (SC ₁₂ H ₂₅) ₂₄	Characterization	Two step solution phase	Solid	LDI, NMR, TGA	⁹⁶
Au ₃₈ /Au ₄₀	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ /Au ₄₀ (SCH ₂ CH ₂ Ph) ₂₄	Ligand exchange	Two step solution phase	Solid	CD, MALDI MS, UV/Vis	⁹⁷
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ *	Effects of oxidative electronic charging	Brust method	Solid	DPV, NMR, UV/Vis	⁹⁸
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ *	Electron transfer	Brust method	Solid	CV, ET	⁹⁹
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄	Pd-doping	One step solution phase	Solid	SEC, XPS, UV/Vis	¹⁰⁰
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ *	Reactivity with PPh ₃	Brust method	Solid	UV/Vis, ¹ H NMR, ³¹ P	¹⁰¹

Au ₃₈ / Au ₄₀	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ / Au ₄₀ (SCH ₂ CH ₂ Ph) ₂₄	Isolation through size exclusion chromatography	Two step solution phase followed by ligand exchange	Solution	NMR UV/Vis, TEM, MALDI MS	¹⁰²
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄	Electrochemical properties	One step solution phase followed by ligand exchange	Solid	ESI MS, TGA, SEC	¹⁰³
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄	Structure and bonding by X-ray absorption spectroscopy	One step solution phase followed by ligand exchange	Solid	Simulated XANES, EXAFS	¹⁰⁴
Au ₃₈	Hexanethiol	Au ₃₈ (SC ₆ H ₁₃) ₂₄	Solvent dependent stability	Brust-Schiffrin two-phase Method	Solution	LDI-TOF MS, CV	¹⁰⁵
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄	Crystal structure	Modified Brust method	Solid	LDI MS, ESI MS	¹⁰⁶
Au ₃₈	X-benzenethiol, X= nitro/bromo/hydroxy	Au ₃₈ (SPhX) ₂₄ [*]	Substituent effects	Two phase Brust method followed by ligand exchange	Solution	OSWV, ¹ H NMR, UV/Vis	¹⁰⁷
Au ₃₈	Phenylethanethiol	Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ [*]	Characterization	Brust two-phase method	Solid	NMR, TGA, TEM	¹⁰⁸
Au ₃₈	Hexanethiol	Au ₃₈ (SC ₆ H ₁₃) ₂₂ ^S	Characterization	Brust-Schiffrin two-phase method	Solid	DPV, SWV, MALDI MS	¹⁰⁹
Au ₃₈	Dodecanethiol	Au ₃₈ (SC ₁₂ H ₂₅) ₂₄	Catalysis	Modified Brust method	Solid	MALDI MS, FT-IR, XAS	¹¹⁰
Au ₃₈	Hexanethiol	Au ₃₈ (SC ₆ H ₁₃) ₂₂ ^S	Temperature dependent emission	Brust-Schiffrin two-phase method	Solid	Gaussian fitting, Luminescence decay	¹¹¹
Au ₃₉	Tri-phenylphosphine	[(Ph ₃ P) ₁₄ Au ₃₉ Cl ₆] ₂	Crystal structure	Modified Hutchison method	Solid	-	¹¹²
Au ₄₀	Phenylethanethiol	Au ₄₀ (SCH ₂ CH ₂ Ph) ₂₄	Isolation	3 step solution phase	Solid	UV/Vis, MALDI MS, ESI	¹¹³
Au ₄₀	Phenylethanethiol	Au ₄₀ (SCH ₂ CH ₂ Ph) ₂₄	Enantiomers separation	Two step solution phase	Solid	UV/Vis, MALDI MS, CD	¹¹⁴
Au ₄₀	2-methylbenzenethiol	Au ₄₀ (o-MBT) ₂₄	Crystal structure	Two step solution phase	Solid	DFT	¹¹⁵
Au ₄₁	S-Eind	Au ₄₁ (S-Eind) ₁₂	Binding motif	Brust method	Solid	MALDI MS, TEM, XPS,	¹¹⁶

Au ₄₄	Thiophenol	TOA ₂ Au ₄₄ (SPh) ₂₈	Characterization	Two step solution phase	Solid	EXAFS, XRD, MALDI TOF MS, NMR	117
Au ₄₄	4-tert-butylbenzenethiol, 2,4-dimethylbenzenethiol	Au ₄₄ (TBBT) ₂₈ , Au ₄₄ (2,4-DMBT) ₂₆	Single crystal	Modified Brust method	Solid	UV/Vis, XPS, ESI MS, DFT	118
Au ₅₂	4-tert-butylbenzenethiol	Au ₅₂ (TBBT) ₃₂	Crystal structure	Two step solution phase	Solid	DFT	115
Au ₅₅	Octadecanethiol	Au ₅₅ (SC ₁₈) ₃₂	Isolation	Brust method	Solid	UV/Vis, LDI, TEM	119
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Application in microelectronics	Schmid method	Solid	STM, SET	120
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Interfacial synthesis	Schmid method	Solid	TEM	121
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Characterization	Schmid method	Solid	NMR, IR, Mössbauer spectroscopy	122
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Ligand exchange	Schmid method	Solid	IR, NMR, UV/Vis	123
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	STM study	Schmid method	Solid	-	124
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Direct Atomic Imaging	Schmid method	Solid	STEM, HAADF TEM	125
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Double layer formation on silicon wafer barrier film	Schmid method	Solid	AFM, SEM	126
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Electrical properties	Schmid method	Solid	Resistances, AFM	127
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	3D assembly and electrical properties	Schmid method	Solid	I-curve, AFM, computational study	128
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Superstructure property	Schmid method	Solid	SEM, FT-IR, SAXRD	129
Au ₅₅	Triphenylphosphine	Au ₅₅ (Ph ₂ PC ₆ H ₄ SO ₃ H) ₁₂ Cl ₆	2D monolayer formation	Schmid method	Solid	TEM	130
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Oxidation resistant property	Schmid method	Solid	AFM, XPS	131
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Quasi 1 D arrangements	Schmid method	Solid	Diode behavior, SEM	132-133
Au ₅₅	Triphenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Metallic properties	Schmid method	Solid	STM, tunneling spectra, conductivity	134

Au ₅₅	Tri-phenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Temperature dependent impedance study	Schmid method	Solid	y curve Conducting mechanism, SEM	135
Au ₅₅	Phenylethanethiol	Au ₅₅ (SCH ₂ CH ₂ Ph) ₃₁	Characterization	Two step solution phase followed by ligand exchange	Solid	UV/Vis, MALDI MS, XRD	136
Au ₅₅	Tri-phenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Application as a quantum dots	Schmid method	Solid	Quantum mechanical calculation	137
Au ₅₅	Tri-phenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Diode behavior	Schmid method	Solid	SEM	138
Au ₅₅	Tri-phenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	Electronic interaction	Schmid method	Solid	TEM, AFM	139
Au ₅₅	Tri-phenylphosphine	Au ₅₅ (PPh ₃) ₁₂ Cl ₆	TEM and SAXD study	Schmid method	Solid	-	140
Au ₆₀	Tri-phenylphosphine, benzeneselenol	[Au ₆₀ Se ₂ (Ph ₃ P) ₁₀ (SeR) ₁₅] ⁺	Crystal structure	Modified Brust method	Solid	UV/Vis, ESI MS, MALDI MS, DPV,	141
Au ₆₇	Phenylethanethiol/ Hexanethiol	Au ₆₇ (SR) ₃₅	Characterization	Three step solution phase method	Solid	MALDI MS, ESI MS, UV/Vis, DPV, NMR, DFT, PDOS	142
Au ₆₈	Phenylethanethiol	Au ₆₈ (SCH ₂ CH ₂ Ph) ₃₄	Characterization	One step solution phase	Solid	UV/Vis	143
Au ₇₅	Hexanethiol	Au ₇₅ (SC ₆ H ₁₃) ₄₀	Characterization	Thiol exchange process	Solid	UV/Vis, HPLC, NMR, MALDI MS, CV, TGA	144
Au ₉₂	4-tert-butylbenzenethiol	Au ₉₂ (TBBT) ₄₄	Single Crystal	Two step solution phase	Solid	ESI MS, UV/Vis	145
Au ₁₀₁	Tri-phenylphosphine	Au ₁₀₁ (PPh ₃) ₂₁ Cl ₅	Ligand Exchange	Hutchison method	Solid	FTIR, NMR, XPS, TEM, DLS	146
Au ₁₀₂	p-Mercaptobenzoic acid	Au ₁₀₂ (p-MBA) ₄₄	Crystal structure	One step solution phase	Solid	-	147
Au ₁₃₀	4-methylbenzenethiol	Au ₁₃₀ (p-MBT) ₅₀	Crystal structure	Two step size focusing	Solid	¹ H NMR, COSY, HSQC, DFT,	148
Au ₁₃₃	4-tert-butylbenzenethiol	Au ₁₃₃ (SPh-tBu) ₅₂	Crystal structure	Three step solution	Solid	MALDI MS, ESI	149

				phase		MS, SAXS, UV/Vis, DPV	
Au ₁₃₀ / Au ₁₈₇	Dodecanethiol	Au ₁₃₀ (SC ₁₂ H ₂₅) ₅₀ / Au ₁₈₇ (SC ₁₂ H ₂₅) ₆₈	Characteri- zation	Brust method	Solid	XRD, HRTEM, HPLC, LDI	¹⁵⁰
Au _{144- 146}	Butanethiol, hexanethiol, dodecanethiol, and benzylthiol	Au ₁₄₄₋₁₄₆ (SR) ₅₀₋₆₀	Characteri- zation	Brust method	Solid	NMR, SEM, XPS, SEM, SA XRD	¹⁵¹
Au ₁₄₄	C _n H _{2n+1} SH (n = 48)	Au ₁₄₄ (SR) ₆₀	Characteri- zation	Two step solution phase	Solid	TGA, XRD, MALDI MS, ESI MS	¹⁵²
Au ₂₅ , Au ₃₈ , Au ₁₄₄	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈ , Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ , Au ₁₄₄ (SCH ₂ CH ₂ Ph) ₆₀	FT IR	Modified Brust methods	Solid	UV/Vis, MALDI MS,	¹⁵³
Au ₂₅ , Au ₃₈ , Au ₄₀ , Au ₁₄₄	Phenylethanethiol	Au ₂₅ (SCH ₂ CH ₂ Ph) ₁₈ , Au ₃₈ (SCH ₂ CH ₂ Ph) ₂₄ , Au ₄₀ (SCH ₂ CH ₂ Ph) ₂₄ , Au ₁₄₄ (SCH ₂ CH ₂ Ph) ₆₀	Far- infrared spectroscopy	Modified Brust methods	Solid	UV/Vis, MALDI MS, DFT	¹⁵⁴
Au ₂₂₅	Hexanethiol	Au ₂₂₅ [S(CH ₂) ₅ CH ₃] ₇₅	Characteri- zation	Brust method	Solid	UV/Vis, TEM, TGA, HPLC, OSWV	¹⁵⁵
Au ₃₂₉	Phenylethanethiol	Au ₃₂₉ (SCH ₂ CH ₂ Ph) ₈₄	Characteri- zation	Brust method	Solid	UV/Vis, MALDI MS, ESI MS, HAADF- STEM, SAXS, PXRD, PDF	¹⁵⁶
Au ₃₃₃	Phenylethanethiol	Au ₃₃₃ (SCH ₂ CH ₂ Ph) ₇₉	Characteri- zation	Brust method	Solid	UV/Vis, XRD, TEM, LDI, MALDI MS	¹⁵⁷
Au _{~940±2 0}	Phenylethanethiol	Au _{~940±20} (SR) _{~160±4}	Characteri- zation	Modified Brust method, 3 steps	Solid	UV/Vis, MALDI MS, ESI MS, HAADF- STEM, SAXS, PXRD, PDF	¹⁵⁸
Ag ₇	2,3- dimercaptosuccinic acid	Ag ₇ (DMSA) ₄	Characteri- zation	One step solution phase method	Solid	TEM, MALDI MS	¹⁵⁹
Ag ₇ /Ag ₈	Mercaptosuccinic acid	Ag ₇ (H ₂ MSA) ₇ /Ag ₈ (H ₂ MSA) ₈	Characteri- zation	Interfacial method/Prad eep	Solid	UV/Vis, TEM, PAGE, PL, XPS, LDI	¹⁶⁰
Ag ₉	Mercaptosuccinic acid	Ag ₉ (H ₂ MSA) ₇	Characteri- zation	Solid state route/Prad eep	Solid	UV/Vis, TEM,	¹⁶¹

Ag ₁₁	Glutathione	Ag ₁₁ (SG) ₇	Characterization	p One step solution phase	Solid	NMR ESI MS, MS/MS, UV/Vis, PAGE, DFT	162
Ag ₁₄	3,4-difluorobenzenethiol, Triphenylphosphine	Ag ₁₄ (SC ₆ H ₃ F ₂) ₁₂ (PPH ₃) ₈	Crystal structure	One step solution phase method	Solid	UV/Vis, PL, ³¹ P NMR	163
Ag ₁₅	BVA	Ag ₁₅ @BVA	Characterization	Modified Xie method	Solution	XPS, EDAX, TEM	164
Ag ₁₅ , Ag ₃₁	Glutathione	Ag ₃₁ (SG) ₁₉ and Ag ₁₅ (SG) ₁₁	Characterization	Cyclic reduction method	Powder	UV/Vis, PL, ESI MS, Lifetime, DFT	165
Ag ₁₆ , Ag ₃₂	1,2-bis(diphenylphosphino)ethane, 3,4-difluorothiophenol, 4-(trifluoromethyl)thiophenol	Ag ₁₆ (DPPE) ₄ (SC ₆ H ₃ F ₂) ₁₄ and [Ag ₃₂ (DPPE) ₅ (SC ₆ H ₃ F ₂) ₂₄] ²⁻	Crystal structure	Two step solution phase	Solid	UV/Vis, photoemission	166
Ag ₁₈ , Ag ₂₅ , Ag ₂₆	Triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, tris(4-fluorophenyl)phosphine	[Ag ₁₈ H ₁₆ (TPP) ₁₀] ²⁺ , [Ag ₂₅ H ₂₂ (DPPE) ₈] ³⁺ , and [Ag ₂₆ H ₂₂ (TFPP) ₁₃] ²⁺	Characterization	One step solution phase	Solid	UV/Vis, ESI MS, 1H NMR, 2H NMR, 31 P NMR, XRS, XPS	167
Ag ₂₁	Dithiophosphate	[Ag ₂₁ [S ₂ P(OiPr) ₂] ₁₂] ⁺	Crystal structure	One step solution phase	Solid	ESI MS, DFT, UV/Vis, XPS, NMR	168
Ag ₂₅	Dimehylbenzenethiol	Ag ₂₅ (DMBT) ₁₈ (PPH ₄) ⁺	Crystal structure	Solution phase	Solid	UV/Vis, ESI MS, DFT, PL	169
Ag ₂₉	Benzenedithiol	Ag ₂₉ (BDT) ₁₂ (TPP) ₄	Crystal structure	Solution phase	Solid	UV/Vis, ESI MS, PL, DFT	170
Ag ₃₀	Captopril	Ag ₃₀ (Capt) ₁₈	Characterization	One step solution phase	Solid	UV/Vis, ESI MS, PAGE, TEM, ¹ HNMR, COSY	171
Ag ₃₂	Glutathione	Ag ₃₂ (SG) ₁₉	Characterization	One step solution phase	Solid	UV/Vis, PAGE	172
Ag ₃₂	Glutathione, N-(2-mercaptopropionyl) glycine	Ag ₃₂ (SG) ₁₉ , Ag ₃₂ (MPG) ₁₉	NMR	Solid state route/Pradeep	Solid	UV/Vis, PAGE, ESI MS, MALDI MS	173
Ag ₄₄	4-fluorothiophenol or 2-naphthalenethiol	Ag ₄₄ (SR) ₃₀ ⁴⁻	Characterization	Multiple temperature controlled	Solution	Sedimentation, UV/Vis,	174

Ag ₄₄	5-mercapto-2-nitrobenzoic acid	Ag ₄₄ (MNBA) ₃₀ ⁴⁻	Scalable synthesis	process One pot solution phase	Solid	TEM, UV/Vis, ESI MS	175
Ag ₄₄	5-mercapto-2-nitrobenzoic acid	Ag ₄₄ (MNBA) ₃₀ ⁴⁻	Surface modification	One pot solution phase	Solid	UV/Vis, FTIR, UPS/IPES, XPS, TEM, DFT	176
Ag ₄₄	p-Flurothiophenol, 3,4-difluorothiophenol, 4-(trifluoromethyl)thiophenol	Ag ₄₄ (SR) ₃₀ ⁴⁻	Crystal structure	One step solution phase	solid	UV/Vis, PDOS, calculation	177
Ag ₄₄	4-Mercaptobenzoic acid	Na ₄ Ag ₄₄ (MBA) ₃₀	Crystal structure	Three step solution phase	Solid	UV/Vis, ESI MS, MS/MS	178
Ag ₄₄	Benzeneselenol	Ag ₄₄ (SePh) ₃₀ ⁴⁻	Characterization	Solid state route/Pradeep	Solution	ESI MS, UV/Vis, SEM/EDAX, ¹ HNMR, HRTEM, PDOS	179
Ag ₄₄	Benzeneselenol	Ag ₄₄ (SePh) ₃₀ ⁴⁻	Reversibility	Solution phase	Solution	UV/Vis, ESI MS, RAMAN, LDI MS, SEM/DAX	180
Ag ₄₄	4-Mercaptobenzoic acid	M ₄ Ag ₄₄ (MBA) ₃₀	Stability and optical properties	Three step solution phase	Solid	IR, ESI MS, ¹ HNMR, TG, DOS	181
Ag ₄₄	4-Mercaptobenzoic acid	M ₄ Ag ₄₄ (MBA) ₃₀	Orthogonal assembly of Ag ₄₄ -TeNW composite	Three step solution phase	Solid	IR, ESI MS, ¹ HNMR, TG, DOS	182
Ag ₄₄	4-Mercaptobenzoic acid	M ₄ Ag ₄₄ (MBA) ₃₀	Janus cluster	Three step solution phase	Solid	Raman, UV/Vis, ESI MS, TEM	183
Ag ₄₄ , Ag ₃₅	4-fluorothiophenol, Glutathione	Ag ₄₄ (4-FTP) ₃₀ , Ag ₃₅ (SG) ₁₈	Ligand exchange	Solid state route, solution phase	Solid	ESI MS, UV/Vis, MALDI MS, EDAX	184
Ag ₅₅	4-tert-butylbenzyl mercaptan, Phenylethanethiol	Ag ₅₅ (BBS) ₃₁ , Ag ₅₅ (PET) ₃₁	Characterization	Solid state route/Pradeep	Solution	ESI MS, MALDI MS, UV/Vis, SAXS, TG, XRD	185
Ag ₆₇	2-4-dimethylbenzenethiol, triphenylphosphine	[Ag ₆₇ (SPhMe ₂) ₃₂ (PPh ₃) ₈] ³⁺	Crystal structure	Two step solution phase	Solid	UV/Vis, ESI MS, DFT, ³¹ P NMR, ¹ H NMR	186
Ag ₆₈	4-tert-butylbenzyl mercaptan	Ag ₆₈ (SBB) ₃₄	Characterization	Miscibility principle/pradeep	Powder	MALDI MS, UV/Vis,	187

						XPS, FT IR, XRD, TG	
Ag ₇₅	Glutathione	~Ag ₇₅ (SG) ₄₀	Characterization	High temperature solution phase route/Pradeep	Solution	NMR, UV/Vis, TEM, PL, MALDI MS	¹⁸⁸
Ag ₁₃₆ , Ag ₃₇₄	4-tert-butylbenzenethiolate	[Ag ₁₃₆ (SR) ₆₄ Cl ₃ Ag _{0.45}] ⁻ , [Ag ₃₇₄ (SR) ₁₁₃ Br ₂ Cl ₂]	Crystal structure	Two step solution phase	Solid	UV/Vis, HRTEM, TDDFT, PDOS	¹⁸⁹
Ag ₁₄₀	4-tert-butylbenzyl mercaptan	Ag ₁₄₀ BBT ₅₃	Characterization	Modified Brust method	Solid	Electrochemistry, TEM, HPLC, etc.	¹⁹⁰
Ag ₁₅₂	Phenylethanethiol	Ag ₁₅₂ (SCH ₂ CH ₂ Ph) ₆₀	Characterization	Solid state route/Pradeep	Solution	SAXS, HPLC, TEM, SEM, MALDI MS	¹⁹¹
Ag ₁₅₂	Phenylethanethiol	Ag ₁₅₂ (SCH ₂ CH ₂ Ph) ₆₀	SERS	Solid state route/Pradeep	Solution	MALDI MS, Raman, SEM/EDAX	¹⁹²
Ag ₂₈₀	4-(tert-butyl)benzyl mercaptan	~Ag ₂₈₀ (SBB) ₁₂₀	Characterization	Modified Brust method	Solid	TEM, XRD, XPS	¹⁹³

^{*},[#], and [§] These clusters were wrongly assigned in the original reports, the correct assignments are Au₂₅(SR)₁₈ (for ^{*} and [#]) and Au₃₈(SR)₂₄ (for [§]), respectively.

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