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Silver Nanoclusters: Controlled Synthesis, Structures and Photoluminescence

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Table S1. Crystal Structures of Some Ag NCs.

Formula	Core		Shell	Ag…Ag bonds		Number of free electrons	Ref.
	composition	geometry	composition	bond dist (Å)	average bond dist (Å)		
Thiol-Protected Ag NCs							
$[Ag_{25}(SPhMe_2)_{18}]^{-}$	Ag_{13}	icosahedron	$Ag_{12}(SPhMe_2)_{18}$	2.749−3.221	2.910	8	23
$[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$	Ag_{13}	icosahedron	$Ag_{16}S_{24}P_4$	2.755−3.158	2.955	8	24
$[Ag_{34}S_2(PhCH_2S)_{18}(CF_3CO_2)_9]$	Ag_{13}	icosahedron	$[Ag_{21}S_2(PhCH_2S)_{18}(CF_3CO_2)_9]$	2.719–3.190	2.963	3	140
$[Ag_{44}(SR)_{30}]^{4-}$	$Ag_{12}@Ag_{20}$	icosahedron@ dodecahedron	$Ag_{12}(SR)_{30}$	2.812–3.223	2.957	18	25,26
$Ag_{50}(dppm)_6(SR)_{30}$	$Ag_{12}@Ag_{20}$	icosahedron@ dodecahedron	$Ag_{18}(dppm)_6(SR)_{30}$	2.764–3.049	2.910	20	60
$[Ag_{62}S_{12}(SBu^t)_{32}]^{2+}$	Ag_{14}	face-centered cube	$Ag_{48}(SBu^t)_{32}$	2.845–3.228	3.056	4	64

$[Ag_{62}S_{13}(SBu^t)_{32}]^{2+}$	$S@Ag_{14}$	twisty face-centered cube	$Ag_{48}(SBu^t)_{32}$	2.876–3.220	3.064	2	66
$[Ag_{46}S_7(SPhMe_2)_{24}]^+$	$Ag_6S@Ag_{32}$	face-centered cube	$Ag_8S_6(SPhMe_2)_{24}$	2.744–2.963	2.905	7	67
$Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8$	Ag_{14}	face-centered cube	$Ag_8(SC_6H_3F_2)_{12}(PPh_3)_8$	2.810−2.850	2.830	2	68
$Ag_{23}(PPh_3)_8(SC_2H_4Ph)_{18}$	Ag_{11}	helical face-centered cube	$Ag_{12}(PPh_3)_8(SC_2H_4Ph)_{18}$	2.744–3.225	2.905	5	69
$[Ag_{38}(SPhF_2)_{26}(PPh_3)_8$	Ag_{28}	fcc close-packing	$Ag_{10}(SPhF_2)_{26}(PPh_3)_8$	2.724–3.225	2.937	12	70
$[Ag_{63}(SPhF_2)_{36}(PR'_3)_8]^+$	Ag_{47}	fcc close-packing	$Ag_{16}(SPhF_2)_{36}(PR'_3)_8$	2.832–3.204	2.919	26	71
$[Ag_{67}(SPhMe_2)_{32}(PPh_3)_8]^{3+}$	Ag_{23}	Ag_{13} cuboctahedron sharing with Ag_8 crowns to form Ag_{21} metal core, which is again connected with two Ag atoms	$[Ag_{44}(SPhMe_2)_{32}(PPh_3)_8]$	2.846−3.048,	2.9195	32	75
$[Ag_{46}(SPhMe_2)_{24}(PPh_3)_8](NO_3)_2$	Ag_{14}	face-centered cube	$[Ag_{32}(SPhMe_2)_{24}(PPh_3)_8]$	2.770–3.218	3.037	20	73,74
$[Ag_{43}(SPhMe_2)_{25}(PPh_3)_4]$	$Ag_{12}@Ag_{20}$	icosahedron@ dodecahedron	Ag_2S_5P, Ag_4S_8P, Ag_2S_4P and Ag_3S_6P, and $SPhMe_2$			18	73
$[Ag_{40}(SPhMe_2)_{24}(PPh_3)_8](NO_3)_2$	Ag_8	cube	$[Ag_{32}(SPhMe_2)_{24}(PPh_3)_8]$	2.770–3.218	3.037	14	73,74
$Ag_{40}(SPhMe_2)_{24}(PPh_3)_8H_{12}$	Ag_8	cube	$[Ag_{32}(SPhMe_2)_{24}(PPh_3)_8]$		3.197	2	76
$Ag_{16}(SC_6H_3F_2)_{14}(dppe)_4$	Ag_8	nearly rhombus Ag_4 unit capped by two Ag_2 units above and below the rhombus	$[Ag_8(dppe)_4(SC_6H_3F_2)_{14}]$	2.694−3.040	2.845	2	80
$[Ag_{32}(dppe)_5(SC_6H_3CF_3)_{24}]^{2-}$	Ag_{22}	pentagon face-sharing bi(pentagonal antiprism) Ag_{17} unit	$[Ag_{10}(dppe)_5(SC_6H_3F_2)_{24}]^{14-}$	2.657−3.089	2.917	10	80

		that is side-capped by one Ag atom and one near-square Ag_4 unit at the opposite direction					
$Ag_{78}(dppp)_6(SR)_{42}$ $Ag_{78}(R/S\text{-}bdpp)_6(SR)_{42}$	$Ag@Ag_{21}$	three mutually inter-penetrating icosahedron	$Ag_{44}(dppp)_6(SR)_{42}$	2.760-3.078	2.869	36	81
$[Ag_{32}(dppm)_5(SAdm)_{13}Cl_8]^{3+}$	Ag_{13}	icosahedron	$[Ag_{19}(dppm)_5(SAdm)_{13}Cl_8]$	2.721–3.316	3.023	8	82
$[Ag_{45}(dppm)_4(S^tBu)_{16}Br_{12}]^{3+}$	Ag_{23}	two Ag_{13} icosahedron fused the three face sharing Ag atoms	$[Ag_{22}(dppm)_4(SBut)_{16}Br_{12}]$	2.716–3.049	2.897	14	82
$Ag_{33}(SCH_2CH_2Ph)_{24}(PPh_3)_4$	Ag_{13}	icosahedron	$Ag_{20}(SCH_2CH_2Ph)_{24}(PPh_3)_4$	2.780–3.083	2.933	9	83
$[Ag_{22}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4]^{2+}$	Ag_{10}	combination of two perpendicularly connected Ag_5 distorted trigonal bipyramidal units	$Ag_{12}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4$	2.757–3.168	2.862	4	89
Alkynyl-Protected Ag CNs							
$[Ag_{19}(dppm)_3(PhC{\equiv}C)_{14}]^{3+}$	Ag_{13}	anticuboctahedron	$[Ag_6(dppm)_3(PhC{\equiv}C)_{14}]$	2.867–3.228	3.014	2	93
$[Ag_{25}(dpppe)_3(MeOPhC{\equiv}C)_{20}]^{3+}$	Ag_{13}	anticuboctahedron	$[Ag_{12}(dpppe)_3(MeOPhC{\equiv}C)_{20}]$	2.877–3.489	3.024	2	93
$[Ag_{34}(BTCA)_3(^tBuC{\equiv}C)_9(tfa)_4(CH_3OH)_3]^+$	Ag_{13}	icosahedron	$[Ag_{21}(BTCA)_3(^tBuC{\equiv}C)_9(tfa)_4(CH_3OH)_3]$	2.795–3.078	2.945	8	94
$[Ag_{35}(H_2BTCA)_2(BTCA)(^tBuC{\equiv}C)_{16}]^{3+}$	Ag_{13}	icosahedron	$[Ag_{22}(H_2BTCA)_2(BTCA)(^tBuC{\equiv}C)_{16}]$	2.702–3.230	2.931	8	95
$Ag_{48}(^tBuC{\equiv}C)_{20}(CrO_4)_7$	Ag_{23}	two classic Ag_{13} icosahedron connected by sharing one apical	$Ag_{25}(^tBuC{\equiv}C)_{20}(CrO_4)_7$	2.722–3.434	2.912	14	97

		Ag atom but missing two vertexes at two pole sites					
$[Ag_{51}(^{t}BuC{\equiv}C)_{32}]^{+}$	$Ag@Ag_{14}$	hexacapped body centered cube	$Ag_{32}(^{t}BuC{\equiv}C)_{32}$	2.695–3.383	2.872	18	36
$[Ag_{74}(C{\equiv}CPh)_{44}]^{2+}$	$Ag_4@Ag_{22}$	fusion of four centered Ag_{13} icosahedrons by sharing the Ag_4 tetrahedron	$Ag_{48}(C{\equiv}CPh)_{44}$	2.722–3.222	2.941	28	35
$(C_7H_{17}ClN)_3[Ag_{112}Cl_6(C{\equiv}CAr)_{51}]$	$Ag_{13}@Ag_{42}@Ag_{48}$	icosahedron@ Mackay polyhedron	$[Ag_9Cl_6(C{\equiv}CAr)_{51}]$	2.716–3.442	2.921	58	96
Other Ligand-Protected Ag NCs							
$[Ag_{20}\{S_2P(OR)_2\}_{12}]$	Ag_{13}	icosahedron	$[Ag_7\{S_2P(OR)_2\}_{12}]$	2.793–3.009	2.912	8	99
$[Ag_{21}\{S_2P(O^{i}Pr)_2\}_{12}]^{+}$	Ag_{13}	icosahedron	$[Ag_8\{S_2P(O^{i}Pr)_2\}_{12}]$	2.754–2.998	2.911	8	98
$[Ag_{20}\{Se_2P(O^{i}Pr)_2\}_{12}]$	Ag_{13}	icosahedron	$[Ag_7\{Se_2P(OR)_2\}_{12}]$	2.751–3.010	2.965	8	100
$[Ag_{21}\{Se_2P(OEt)_2\}_{12}]^{+}$	Ag_{13}	icosahedron	$[Ag_8\{Se_2P(OR)_2\}_{12}]$	2.756–3.018	2.911	8	100
$[Ag_{21}(dpa)_{12}]^{+}$	Ag_{13}	icosahedron	$[Ag_8(dpa)_{12}]$	2.757–2.832	2.790	8	101
$[Ag_{22}(dpa)_{12}]^{2+}$	Ag_{13}	icosahedron	$[Ag_9(dpa)_{12}]$	2.770–3.168	2.933	8	101
$[Ag_{15}(Ntriphos)_4(Cl_4)]^{3+}$	$Ag@Ag_8$	body-centered cube	$Ag_6(Ntriphos)_4(Cl_4)$	2.570–3.160	2.891	8	102
$Ag_{28}(dppb)_6(MoO_4)_4$	Ag_4	tetrahedron	$Ag_{24}(dppb)_6(MoO_4)_4$	2.681–3.230	2.887	20	103
$[Ag_{27}(Si_2W_{18}O_{66})_3]^{17+}$	Ag_{27}	fusion of five octahedral $\{Ag_6\}$ units	$(Si_2W_{18}O_{66})_3$	2.710–3.020	2.842	10	106

Table S2. Optical Properties of some Ag NCs.

Formula	UV-vis absorption (nm)	Photoluminescence		State	Ref.
		Ex. (nm)	Em. (nm)		
$Ag_{14}(SC_6H_3F_2)_{12}(PPh_3)_8$	368, 530	360	420, 536 nm	liquid	68
$Ag_{16}(dppe)_4(SC_6H_3F_2)_{14}$	485	360	440		80
$\{Ag_{32}(dppe)_5(SC_6H_3CF_3)_{24}\}^{2-}$	485, 550	360	440		80
$[Ag_{20}\{S_2P(OR)_2\}_{12}]$	443, 492, 540	425	950		99
$[Ag_{21}\{S_2P(O^iPr)_2\}_{12}]^+$	425, 482, 540	435	921		98
$[Ag_{22}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4]^{2+}$	368, 512, 670	-	670		89
$Ag_{23}(PPh_3)_8(SC_2H_4Ph)_{18}$	527	350, 467, 540	800		69
$[Ag_{25}(SPhMe_2)_{18}]^-$	410, 490, 675		850		23
$Ag_{29}(BDT)_{12}(TPP)_4$	477, 513	450	659	liquid	24
			715	solid	
$Ag_{33}(SCH_2CH_2Ph)_{24}(PPh_3)_4$	460, 540	530, 600, 700	765, 810	liquid	83
$[Ag_{46}S_7(SPhMe_2)_{24}]^+$	430, 514, 651	325	550	liquid	67
			620	solid	
$Ag_{48}(^t\text{BuC}\equiv\text{C})_{20}(CrO_4)_7$	309, 397, 491	288	420	liquid	97
$[Ag_{51}(^t\text{BuC}\equiv\text{C})_{32}]^+$	383, 484, 642	372	418, 436, 466	CH_2Cl_2	36
		378	413, 437, 469	$CHCl_3$	
		436	570	CH_3CN	
		444	656	CH_3OH	
$[Ag_{67}(SPhMe_2)_{32}(PPh_3)_8]^{3+}$	425, 697	490	820	liquid	75