Supporting Information

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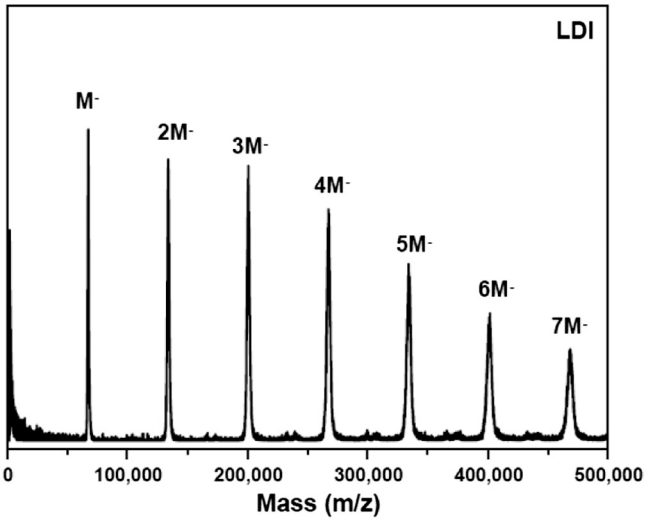
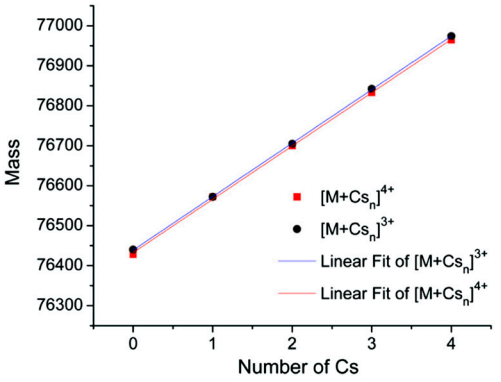


Fig. S1. Laser desorption ionization (LDI) mass spectrum of $Au_{333}(SR)_{79}$ nanoparticles in the range of 500 to 500,000 Da.



[M+Cs$_n$]$^{4+}$		
Equation	y = a + b*x	
Adj. R-Square	0.99953	
	Value	Standard Error
Intercept	76432.8	3.52727
Slope	133.28	1.44

[M+Cs$_n$]$^{3+}$		
Equation	y = a + b*x	
Adj. R-Square	0.99994	
	Value	Standard Error
Intercept	76438.92	1.28125
Slope	133.8	0.52307

Fig. S2. Linear fittings of the ESI-MS peaks of $Au_{333}(SR)_{79}$ nanoparticles. In both 4+ and 3+ ion sets, the slope of 133.28 or 133.8 corresponds to the atomic mass of Cs (standard value: 133). The intercept, 76,432.8 (standard deviation $\sigma = \pm 3.5$) or 76438.9 ($\sigma = \pm 1.28$), is the molecular mass of the nanoparticle. The lower mass $[MCs_x]^{4+}$ set offers a higher accuracy, thus, we take this set to determine the molecular mass of the nanoparticle, M = 76,432.8 ± 3.5 Da.

Table S1. The formulas corresponding to the TGA-determined organic wt% of 14.5 (allowed to fluctuate ±0.5 in order to expand the search range for the formula)

Number of Au	Number of SR	Calculated Mass (Da)	Deviation from experiment (Da)	Calculated Organic wt%	Deviation from experiment (wt%)
328	84	76,131.6	−301.2	15.1	0.6
328	85	76,268.8	−164.0	15.3	0.8
328	86	76,406.1	−26.7	15.4	0.9
328	87	76,543.3	110.5	15.6	1.1
328	88	76,680.5	247.7	15.7	1.2
329	83	76,191.3	−241.5	14.9	0.4
329	84	76,328.5	−104.3	15.1	0.6
329	85	76,465.7	32.9	15.2	0.7
329	86	76,603.1	170.3	15.4	0.9
329	87	76,740.3	307.5	15.5	1.0
330	81	76,113.9	−318.9	14.6	0.1
330	82	76,251.1	−181.7	14.7	0.2
330	83	76,388.3	−44.5	14.9	0.4
330	84	76,525.5	92.7	15.1	0.6
330	85	76,662.7	229.9	15.2	0.7
331	80	76,173.7	−259.1	14.4	−0.1
331	81	76,310.9	−121.9	14.6	0.05
331	82	76,448.1	15.3	14.7	0.2
331	83	76,585.3	152.5	14.9	0.4
331	84	76,722.5	289.7	15.0	0.5
332	78	76,096.1	−336.7	14.1	−0.4
332	79	76,233.3	−199.5	14.2	−0.3
332	80	76,370.5	−62.3	14.4	−0.1
332	81	76,507.8	75.0	14.5	0.01
332	82	76,645.0	212.2	14.7	0.2
333	77	76,155.9	−276.9	13.9	−0.6
333	78	76,293.1	−139.7	14.0	−0.5
333	**79**	**76,430.3**	**−2.5**	**14.2**	**−0.3**
333	80	76,567.5	134.7	14.3	−0.2
333	81	76,704.8	272.0	14.5	−0.02
334	76	76,215.6	−217.2	13.7	−0.8
334	77	76,352.9	−79.9	13.8	−0.7
334	78	76,490.1	57.3	14.0	−0.5
334	79	76,627.3	194.5	14.1	−0.4
335	75	76,275.4	−157.4	13.5	−1.0
335	76	76,412.6	−20.2	13.6	−0.9
335	77	76,549.8	117.0	13.8	−0.7

Note that the m/z ~ 19,107 being the monoadduct of $[MCs_1]^{4+}$ can be ruled out by taking into consideration the result of thermogravimetric analysis. Should the m/z ~ 19,107 peak be $[M\text{-}Cs_1]^{4+}$, then the molecular mass = 19,107 × 4 − 133 = 76,295. From the above table, one finds a matched formula of $Au_{333}(SR)_{78}$ (theoretical mass: 76,293), but the calculated weight loss (14.0%) is too much deviated from the experimental value of 14.5%. The 0.5% deviation falls out of the error range of TGA (< ± 0.3%).

Table S2. The calculated *n*th zeros of spherical Bessel functions $j_{l+1/2}(\beta r)$ of the first kind

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$	$l = 6$	$l = 7$	$l = 8$	$l = 9$	$l = 10$	$l = 11$	$l = 12$
0th zero	3.14	4.49	5.76	6.99	8.18	9.36	10.5	11.66	12.79	13.91	15.0	16.14	17.25
1st zero	6.28	7.73	9.09	10.4	11.7	13.0	14.2	15.43	16.64	17.84	19.0	22.20	21.37
2nd zero	9.42	10.9	12.3	13.7	15.0	16.4	17.6	18.92	20.18	21.43	22.66	23.89	25.10
3rd zero	12.6	14.1	15.5	16.9	18.3	19.7	21.0	22.30	23.59	24.87	26.14	27.40	28.65
4th zero	15.7	17.2	18.7	20.1	21.5	22.9	24.3	25.60	26.93	28.24	29.53	30.82	32.1
5th zero	18.8	20.4	21.9	23.3	24.7	26.1	27.5	28.87	30.22	31.55	32.87	34.18	35.48
6th zero	22.0	23.5	25.0	26.5	27.9	29.3	30.7	32.11	33.47	34.83	36.17	37.50	38.81

According to these $\alpha_{n,l}$ values, electron orbitals are constructed, for example, the smallest $\alpha_{n,l}$ is 3.14 for $(n,l) = (0,0)$, labeled 1*s* in analogy with atomic orbital, the next $\alpha_{n,l}$ value is 4.49 for $(n,l) = (0,1)$, labeled 1*p*, and so on. The as-constructed orbitals are as follows:

1*s*, 1*p*, 1*d*, 2*s*, 1*f*, 2*p*, 1*g*, 2*d*, 1*h*, 3*s*, 2*f*, 1*i*, 3*p*, 1*j*, 2*g*, 3*d*, 4*s*, 1*k*, 2*h*, 3*f*, 1*l*, 4*p* .....