Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Tailoring the interaction between a gold nanocluster and a fluorescent dye by cluster size: creating a toolbox of range-adjustable pH sensors

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Extinction coefficient measurement of Au_{25}(*p*-MBA)$_{18}$ and Au_{250}(*p*-MBA)$_n$ nanoclusters

The extinction coefficient of Au_{25}(*p*-MBA)$_{18}$ and Au_{250}(*p*-MBA)$_n$ was obtained by using the Beer-Lambert equation (1);

$A = \varepsilon \times b \times c \#(1)$

where **A** is the absorbance of the sample, **ε** is the extinction coefficient ($M^{-1}cm^{-1}$), **b** is the optical path length (1 cm), and **c** is the molar concentration (M). The absorbance was divided by the optical path length (b) and the molar concentration (c), as in equation (2);

$A/(b \times c) = \varepsilon \#(2)$

Note that we have used the composition of Au_{25}(*p*-MBA)$_{18}$ and Au_{250}(*p*-MBA)$_{75}$ to calculate the molar weight for each solution's molar concentration.[1] The samples were each prepared in a 1.5 mL 0.01 M NaOH aqueous solution. A known amount of the dried cluster was added to the solution and re-dissolved. After measuring the absorbance, the values were divided by molar concentration (c) and optical path length (b) to obtain a spectrum of extinction coefficient as a function of the wavelength.

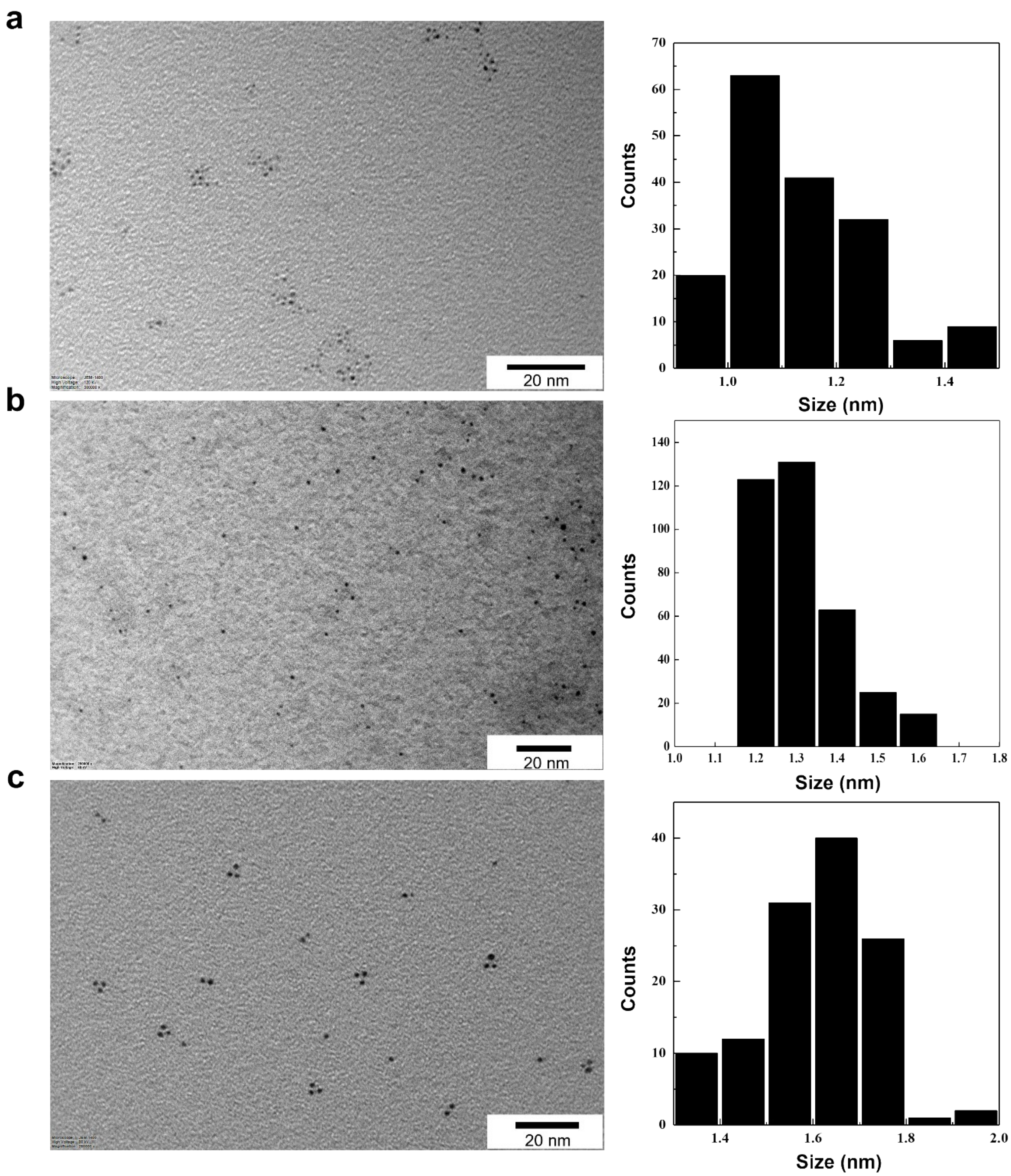

Figure S1 TEM images of the synthesized a) Au_{25}, b) Au_{102}, and c) Au_{250} nanocluster. (Scale = 20 nm) The histograms of the core size distribution is displayed on the right side of each image.

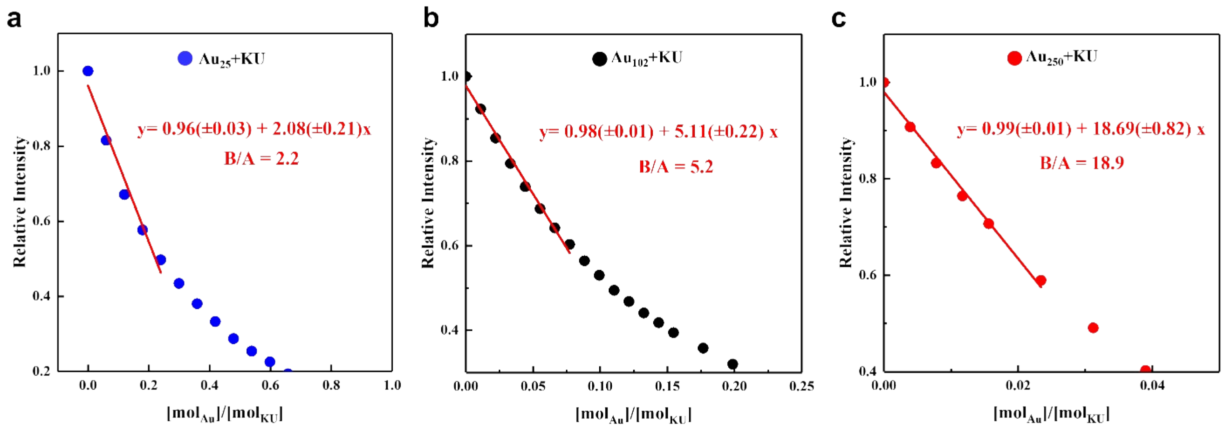

Figure S2 The linear fit to the intensity points in the initial range ($[mol_{Au}]/[mol_{KU}] < 0.1$) of the titration curve. y = A + Bx was used as a linear fit (red line), the approximate number of the bound KU with one gold nanocluster is determined by the B/A ratio. The fitting parameters and the bound KU numbers are listed in the figure.

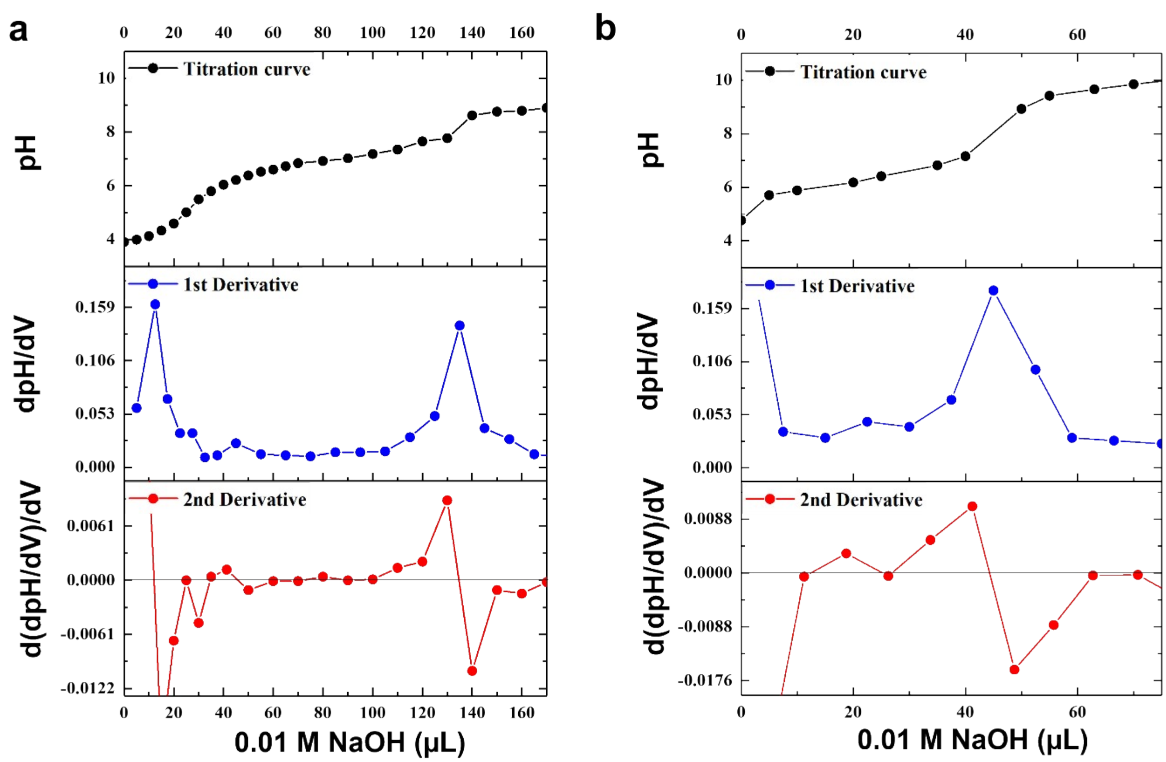

Figure S3 Acid-base titration (Top), first derivative (dpH/dV, middle), and second derivative (d(dpH/dV)/dV, bottom) curve of a) Au_{25} and b) Au_{250} nanocluster. The equivalence point and pKa were evaluated by the second derivative value. The parameters are listed in Table S1.

	$Au_{25}pMBA_{18}$	$Au_{250}pMBA_n$
Equivalence (µL)	**134.51**	**44.27**
½ Equivalence (µL)	**67.26**	**22.13**
pKa	**6.82**	**6.29**

Table S1 Parameters from the acid-base titration curve. The equivalence point was obtained by the second derivative curve and the pKa value was determined by the half point of the equivalence point.

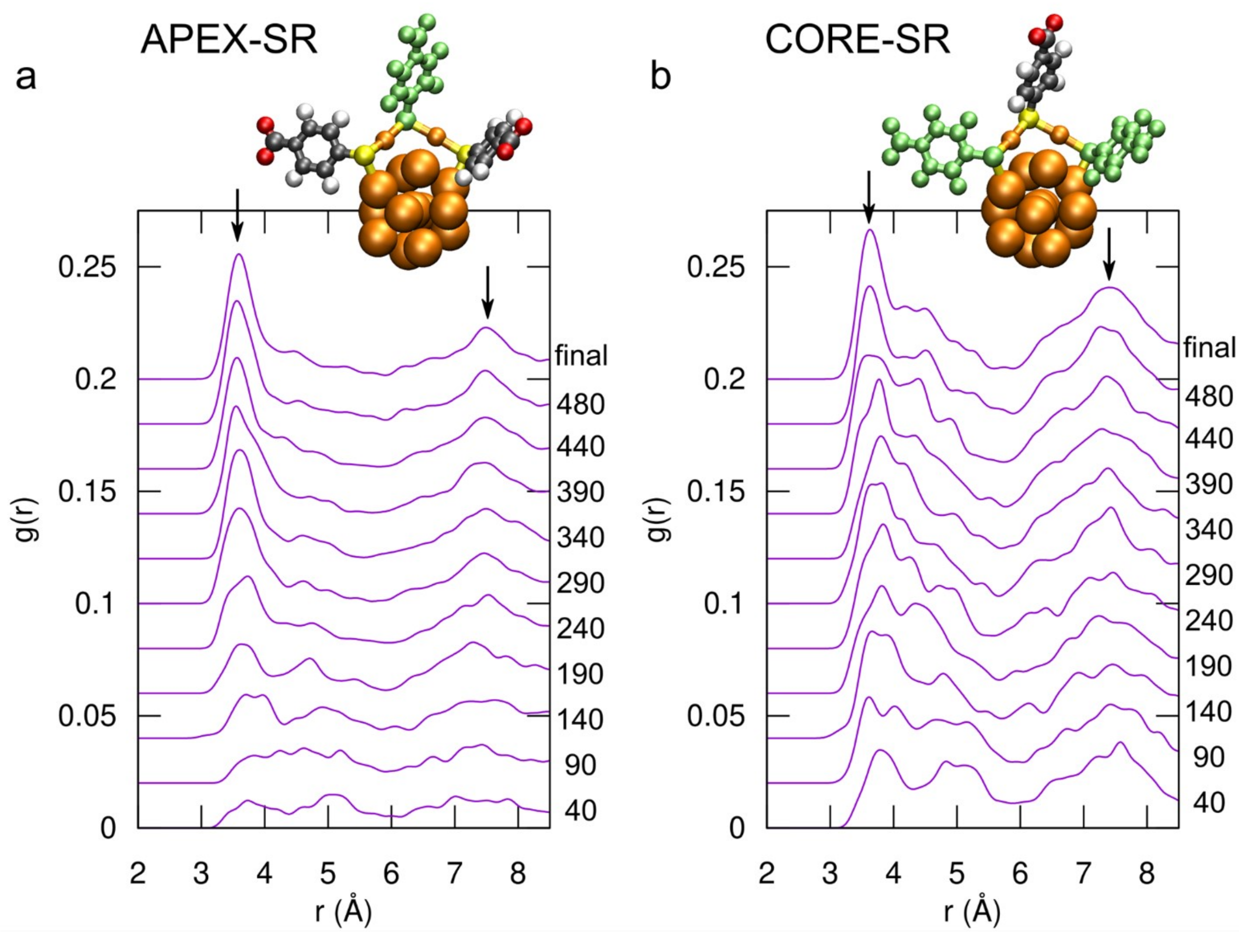

Figure S4 Pair correlation function g(r) of phenyl rings of a) apex and b) core ligands on Au_{25}. Each curve is plotted per one ligand as a moving average over 40 snapshots frames (500 snapshots extracted from 100 ns MD-trajectory). Arrows denote the peaks that are characteristic for the nearest neighbor and second nearest neighbor distances due to π-π stacking.

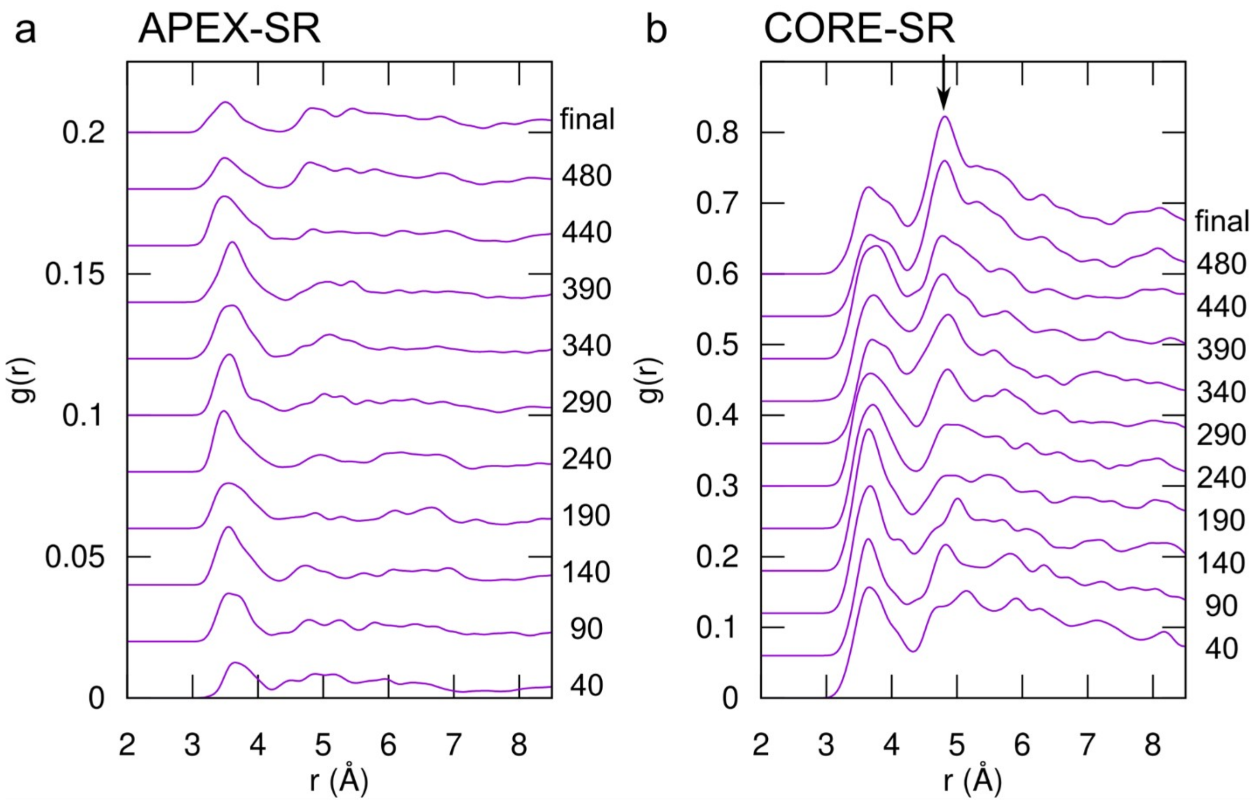

Figure S5 The same as in Fig. S4 but for Au_{102}. Arrow denotes the peak that is characteristic for the nearest neighbor distance due to T stacked ligands.

Reference

1 K. Sokołowska, *et al*., Towards controlled synthesis of water-soluble gold nanoclusters: synthesis and analysis, *J. Phys. Chem. C*, 2019, **123**, 2602−2612