Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

$Au_{144-x}Pd_x(SR)_{60}$ nanomolecules

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Synthesis of $Au_{144-x}Pd_x(SR)_{60}$ nanomolecules: The nanoparticles were synthesized by using two phase Brust[1] method as described earlier.[2] Aqueous solution (30mL) containing $HAuCl_4$ and K_2PdCl_4 (total metal concentration was set to 30mM) was mixed with toluene solution (30 mL) of tetraoctylammonium bromide, TOABr (1.1 mmol). The initial mole ratios of Au : Pd precursors were 1 : 0, 1 : 0.1, 1 : 0.33, 1 : 1 or 1 : 1.5. After stirring for 30 min, the organic phase was separated and phenylethane thiol (10 mmol) was added and further stirred for 30 min at room temperature. This solution was cooled in an ice bath for 30 min. An aqueous solution of $NaBH_4$ (20 mmol, 20 mL) cooled to 0 ^oC, was rapidly added to the reaction mixture under vigorous stirring. After 3 h, the organic layer was separated from aqueous layer and evaporated to dryness. The product was washed with methanol to remove excess starting materials and by-products. The residual mixture was extracted with toluene. 20mg of this product was dissolved in 0.5mL of toluene and etched with excess phenylethane thiol (0.5 mL) at 80^0C under stirring. The pure $(AuPd)_{144}(SR)_{60}$ fractions isolated from size exclusion chromatography[3] and solvent fractionation.

Optical absorption spectroscopy: UV-Visible spectra were obtained in toluene solutions using ShimadzuUV-1601 spectrophotometer/UVprobe 2.0 software in 300–1100 nm range.

MALDI mass spectrometry: MALDI mass spectra were acquired with a Bruker Daltonics Autoflex mass spectrometer using DCTB matrix at optimal laser fluence.[4] Spectral analyses were done using Bruker Daltonics flexAnalysis version 3.0.

ESI mass spectrometry: ESI mass spectra were obtained from a Waters Synapt mass spectrometer in THF solution in positive mode. ESI calibration was performed with 50 : 50 isopropanol : water solution of NaI.

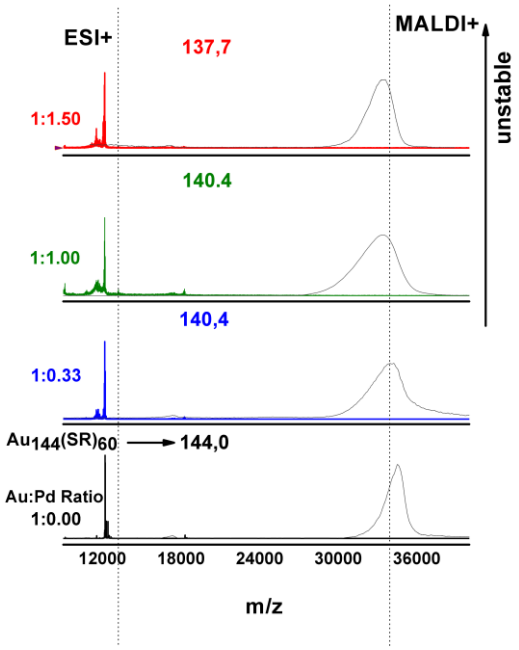

Figure S1. The 3+ peak of ESI mass spectra plotted with MALDI mass spectra in grey (positive mode) of $Au_{144-x}Pd_x(SR)_{60}$ NM's for Au : Pd precursor ratios of 1 : 0 (black), 1 : 0.33 (blue), 1 : 1.00 (green) and 1 : 1.50 (Red) in the starting material. The MALDI peaks are significantly broader and slightly lower in mass due to fragmentation from the loss of ligands. Toluene solution of the NM's were mixed with DCTB[4] matrix in toluene and air dried in steel plate for MS analysis.

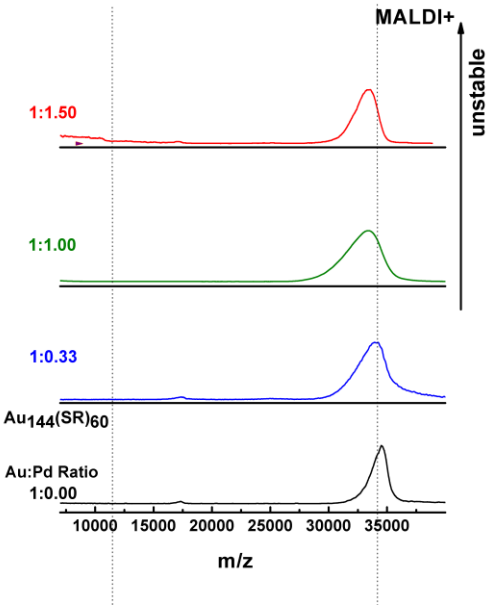

Figure S2. MALDI mass spectra in (positive mode) of $Au_{144-x}Pd_x(SR)_{60}$ NM's for Au : Pd precursor ratios of 1 : 0 (black), 1 : 0.33 (blue), 1 : 1.00 (green) and 1 : 1.50 (Red) in the starting material. Toluene solution of the NM's were mixed with DCTB[4] matrix in toluene and air dried in steel plate for MS analysis.

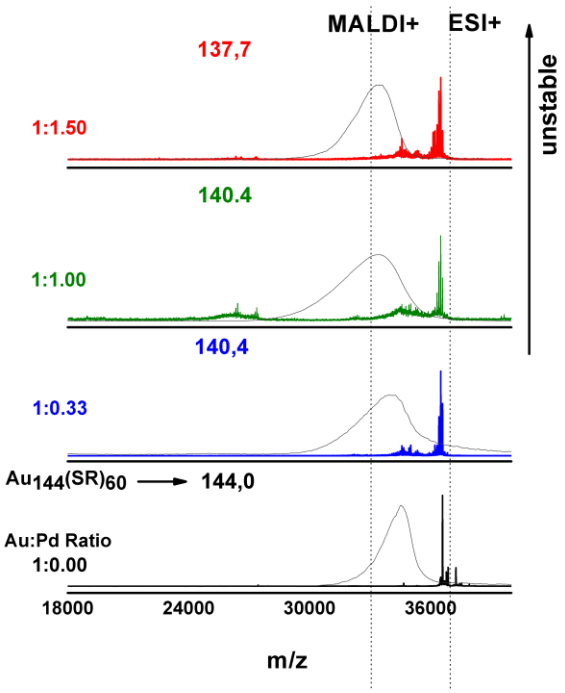

Figure S3. The deconvoluted ESI mass spectra of the 3+ peak plotted with MALDI mass spectra in grey (positive mode) of $Au_{144-x}Pd_x(SR)_{60}$ nm's for Au : Pd precursor ratios of 1 : 0 (black), 1 : 0.33 (blue), 1 : 1.00 (green) and 1 : 1.50 (Red) in the starting material. The MALDI peaks are significantly broader and slightly lower in mass due to fragmentation from the loss of ligands. Toluene solution of the nm's were mixed with DCTB[4] matrix in toluene and air dried in steel plate for MS analysis.

References:

(1) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *Journal of the Chemical Society, Chemical Communications* 1994, *0*, 801.
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(3) Knoppe, S.; Boudon, J.; Dolamic, I.; Dass, A.; Bürgi, T. *Analytical Chemistry* 2011, *83*, 5056.
(4) Dass, A.; Stevenson, A.; Dubay, G. R.; Tracy, J. B.; Murray, R. W. *Journal of the American Chemical Society* 2008, *130*, 5940.