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Laser Desorption Ionization Mass Spectrometric Imaging of Mass Barcoded Gold Nanoparticles for Security Applications

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Supporting Information

Gold nanoparticles with the attached ligand were synthesized in a two-step method. This entailed the preparation of pentanethiol stabilized nanoparticles of approximate 2.5 nm size using the Brust method followed by a ligand exchange reaction.[1] Ligands were synthesized according to previous methods.[2] After purification, the nanoparticles were diluted to a concentration of 1μM with water, filtered through a .2μm polypropylene membrane (Puradisc 25AS, Whatman), and syringed into a virgin aftermarket Epson inkjet cartridge for printing (MIS Associates, Auburn Hills, MI USA).

Printing was done using an Epson Artisan 50 inkjet printer (Long Beach, CA USA) which was used as packaged. The substrate was loaded into the printer by taping the bottom of the substrate to the included CD tray. For our work, patterning was done by using the Print CD software provided with the Epson printer. The text was written in Arial font in Bold letters at a font size of 2 for appropriate detection. In order to print only the channel of interest, the color of the letter has to match the channel printed. To print only the magenta channel, the RGB value must be set to (255,0,255); The cyan channel, (0,255,255); the yellow channel, (255,255,0). A representative screen capture of the printed is shown in Figure S1. The ICM color management also must be turned off in the Advanced tab of the printer properties to ensure no mixing of the channels occurs. Before printing, the printheads were cleaned two times using the "Head Cleaning" function in the Maintenance tab of the printer properties to ensure that the channels were filled.

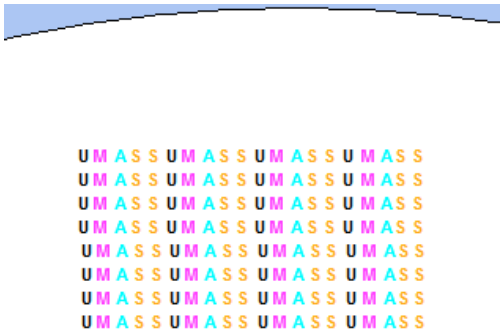

Figure S1 – Screen capture of the pattern to be printed on the substrate.

The LDI-MS image analysis was carried out on a Bruker Autoflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) (Autoflex III). The Autoflex III is equipped with a Smartbeam-laser and with the FlexImaging 2.1 software package (Bruker Daltonics, Bremen, Germany). LDI measurements were done in operating conditions as follows: ion source 1 = 19.00 kV, ion source 2 = 16.60 kV, lens voltage = 8.44 kV, reflector voltage = 20.00 kV, reflector voltage 2 = 9.69 kV, pulsed ion extraction time = 10 ns, suppression = 180 Da, and positive reflectron mode in a mass range of 100−1200 Da. The mass spectrometric imaging sequence was generated by FlexImaging 2.1 software. Imaging was performed by continuously scanning the surface in the x-direction and y-direction. The lateral resolution for the LDI-MS imaging was set to 50 µm. A total of 50 laser shots were measured per position. In general, ~ 400,000 laser shots were fired on a ~ 20 mm^2 area. The data analysis and image generation were performed in FlexImaging 2.1. The indium tin oxide (ITO) glass slides and the NALDI™ substrate were obtained from Bruker Daltonics (Billerica, MA USA) and Nanosys (Palo Alto, CA USA) respectively.

1. M. Brust, M. Walker, and D. Bethell, *J. Chem. Soc., Chem.*, 1994, 801-802.

2. C.-C. You, O. R. Miranda, B. Gider, P. S. Ghosh, I.-B. Kim, B. Erdogan, S. A. Krovi, U. H. F. Bunz, V. M. Rotello, *Nat. Nanotechnol.* 2007, **2**, 318–323.