Supporting Information

A Non-ionic Surfactant Based Catalyst Tablet: A Reusable Gold-NHC catalyst system for alkyne hydration reactions

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1. Experimental Section

1.1. Materials and Instrumentation

Otherwise noted all chemical purchased from Sigma-Aldrich and used as received. Dichloromethane (CH_2Cl_2) was dried using P_2O_5 and distilled under nitrogen atmosphere prior to use. Synperonic®F108 (20 % polyoxypropylene and 80 % polyoxyethylene content, M_n: 16000 Da measured against PMMA standart in THF) were purchased from Sigma-Aldrich and used as received. Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]gold(I) was purchased from Sigma-Aldrich and used as received. Number average molar masses (M_n) were determined by a size exclusion chromatography (SEC) system LC-20A from Shimadzu equipped with a SIL-20A auto-sampler, RID-10A and a refractive index detector. The analysis was performed on the following column system operating on THF (flow rate 1 mL/min) at 40°C: main-column PSS SDV analytical (5 µm, 300 mm × 8.0 mm, 10,000 Å) and a PSS SDV analytical pre-column (5 µm, 50 mm × 8.0 mm). The calibration was created using narrow linear poly(methylmethacrylate)
standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981,000 Da. GC-MS analysis were performed using Shimadzu GC-MS QP2010-Plus equipped with Restek Rxi-5Sil column (30m x 0.25 mm x 0.25 µm) with a constant helium flow rate of 1 ml/min. vent. Dynamic light scattering (DLS) analysis was carried out using a Malvern Seta-Sizer Nano-ZS90 with a fixed scattering angle 90°. High contrast transmission electron microscopy (TEM) images were recorded at METU Central Lab (Ankara) with an FEI Tecnai G2 Spirit Bio(TWIN) TEM at 120 kV using carbon filmed coated copper grids. Samples were stabilized on copper tape then were analyzed by Thermo K-alpha monochromatic high performance X-ray photoelectron spectrometer.

1.2. Synthesis of Au-1@Syn catalyst tablets

A Schlenk reactor was charged with Synperonic®F108 (1.00g) and stirred magnetically with a magnetic stirbar u under nitrogen atmosphere at 70 °C. After Synperonic®F108 melted completely, 1,3-Bis(2,6-diisopropylphenyl-imidazol-2-ylidene)gold(I) chloride [(IPr]AuCl] (Au-1, 0.010 g, 0.0161 mmol in 100 µL of CH_2Cl_2) was added dropwise to the melted Synperonic®F108 in Schlenk reactor. The reaction mixture was continuously stirred under positive nitrogen flow until all CH_2Cl_2 spurred away from the reaction mixture. The hot mixture was poured into plastic molds and slowly cooled in a vacuum oven at 25 °C. Catalyst tablets (80 (± 5.2) mg, 1.29 µmol Au) were denoted as Au-1@Syn. Samples for TEM imaging were prepared by using a methanol/water (v/v: 1/1, 50 mL) and Au-1@Syn (0.01 g) mixture. The mixture was drop-casted on carbon filmed coated copper grids.

1.3. Representative Procedure for Alkyne Hydration Reactions

A 20 mg (0.325 µmol Au) portion of Au-1@Syn tablet was weighted into a Schlenk reactor and methanol (1 mL) and distilled water (1 mL) was added to the reactor and stirred continuously with a magnetic stir bar at room temperature until a homogenous solution is formed. Alkyne substrate (0.325 mmol) was added to the reactor and stirred for five minutes at 1000 rpm until a stable emulsion is formed and concentrated sulfuric acid (0.094 mmol, 5 µL) was added to the reaction media to initiate the reaction. The reaction mixture was stirred at 80 °C. Aliquots taken from the reaction mixture was analyzed by GC-MS. Once all the alkyne is consumed, the reaction mixture was cooled to room temperature and extracted with diethyl ether to separate the product. Diethyl ether phase was washed with water and organic solvent was removed by rotary evaporator to isolated the final product.

1.4. The reusability experiments

A 20 mg (0.325 μmol Au) portion of Au-1@Syn tablet was weighted into a Schlenk reactor and methanol (1 mL) and distilled water (1 mL) was added to the reactor and stirred continuously with a magnetic stir bar at room temperature until a homogenous solution is formed. Phenylacetylene (0.325 mmol, 36 μL) was added to the reactor and stirred for five minutes at 1000 rpm until a stable emulsion is formed and concentrated sulfuric acid (0.094 mmol, 5 μL) was added to the reaction media to initiate the reaction. The reaction mixture was stirred at 80 °C. Aliquots taken from the reaction mixture was analyzed by GC-MS. Once all the alkyne is consumed, the reaction mixture was cooled to room temperature and extracted with diethyl ether (5 mL) to separate the product. The water phase of the extraction mixture is separated and taken to a Schlenk reactor. The aqueous mixture is diluted with 1 mL of methanol and the reactor was charged with phenylacetylene (0.325 mmol, 36 μL) and reaction mixture is heated to 80 °C. Once the conversion of phenylacetylene has reached a plateau, the product and the catalyst was separated using the above mentioned method.

2. Experimental Data

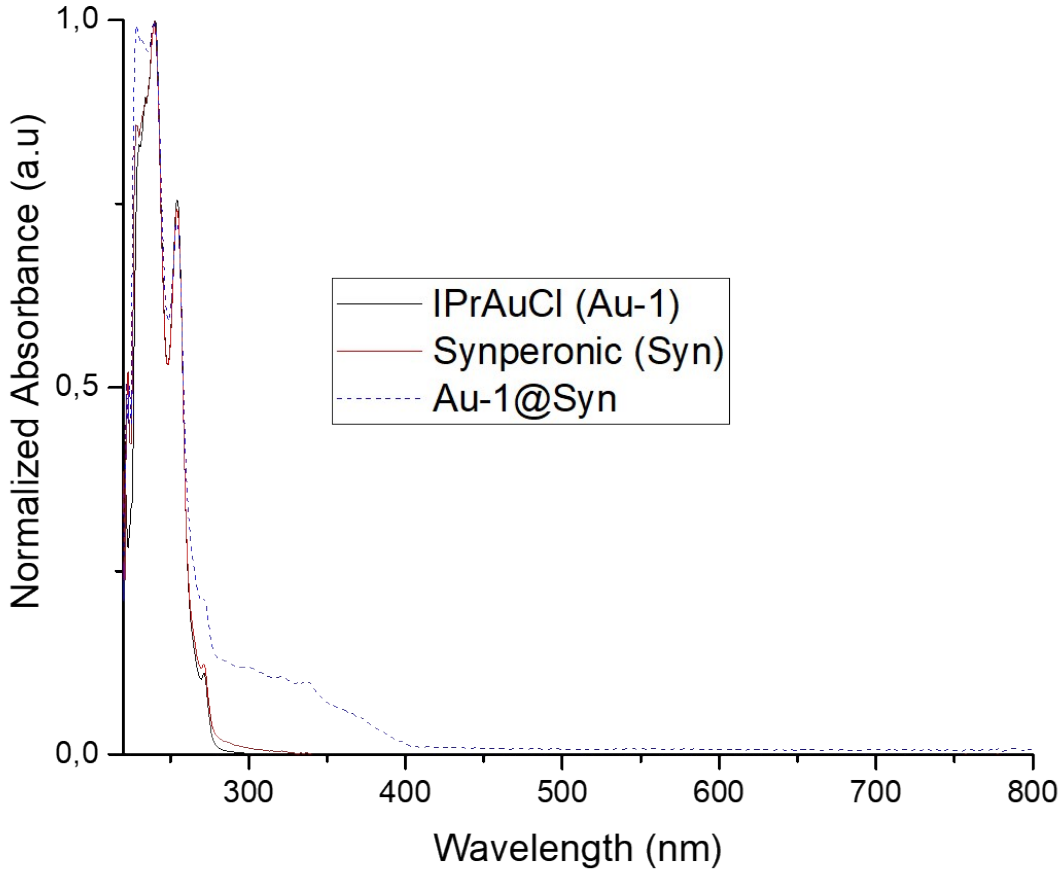

Figure S1. UV-Vis spectrums of catalyst tablets in CH_2Cl_2.

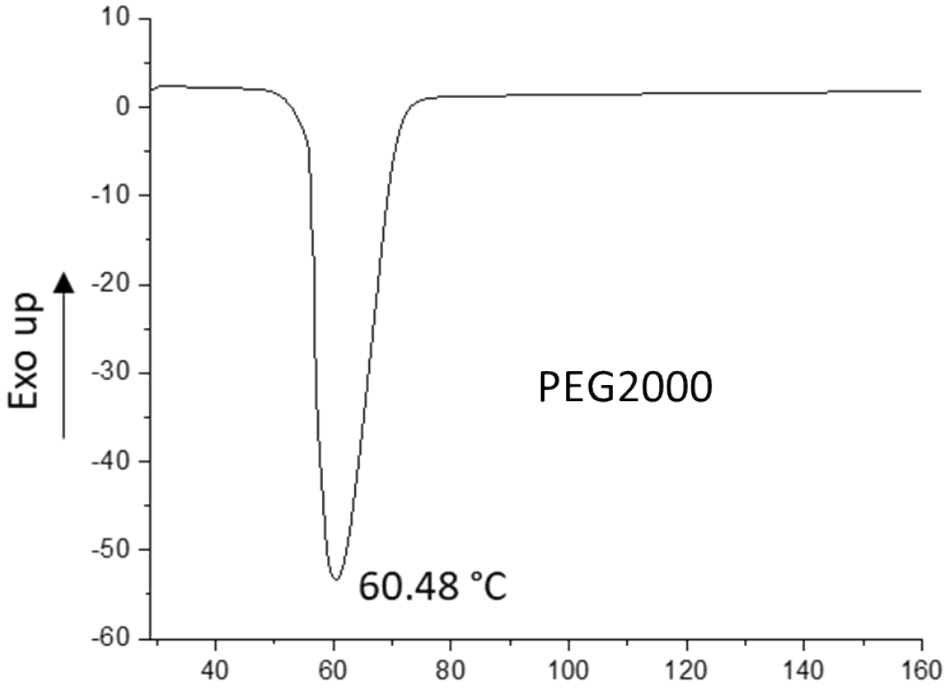

Figure S2. DSC thermogram of PEG2000

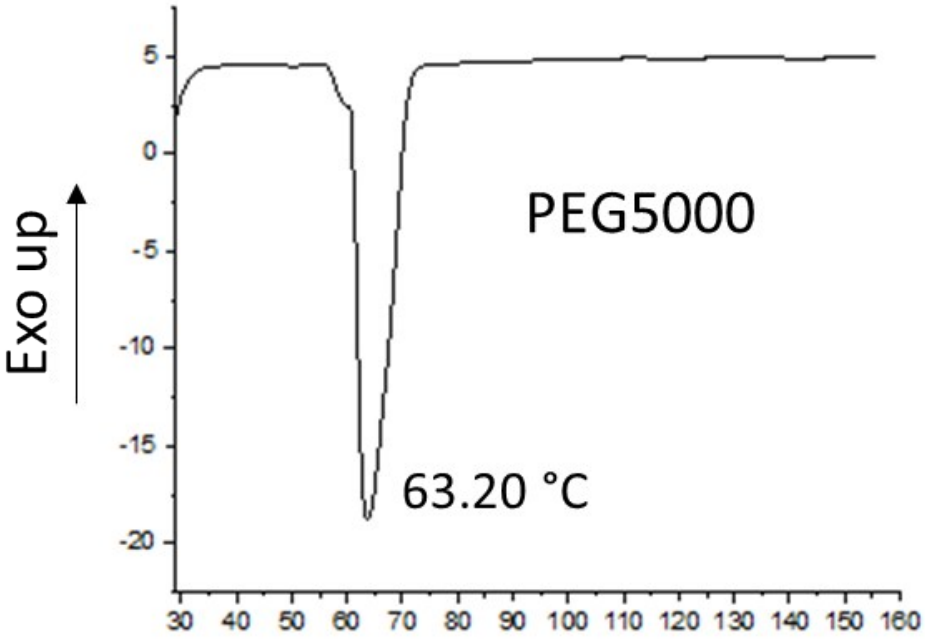

Figure S3. DSC thermogram of PEG5000

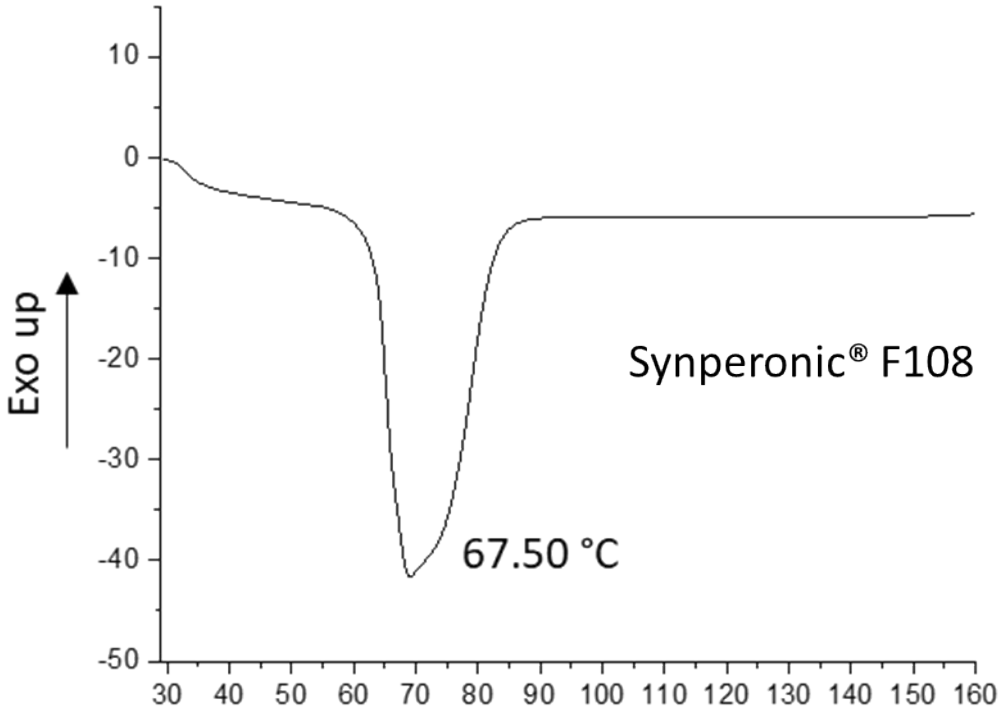

Figure S4. DSC thermogram of Synperonic®F108

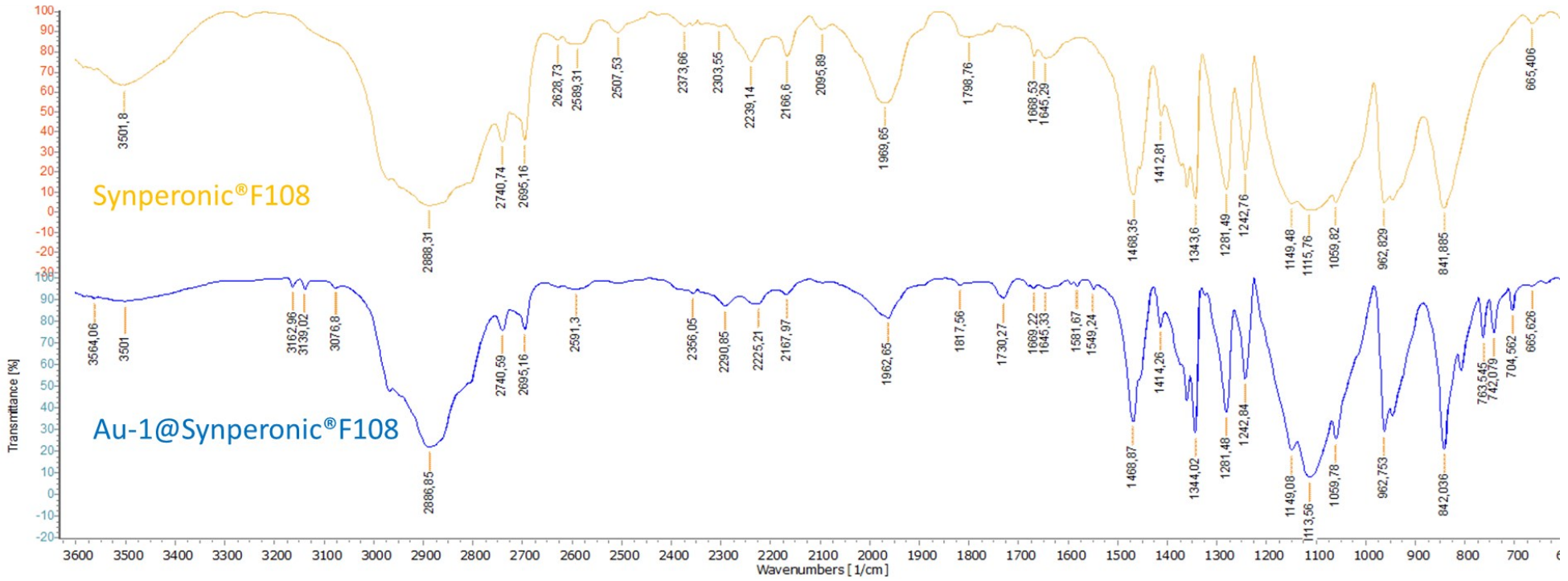

Figure S5. FTIR spectrum of Synperonic®F108 and Au-1@Synperonic®F108 tablets (recorded using KBr pellets)

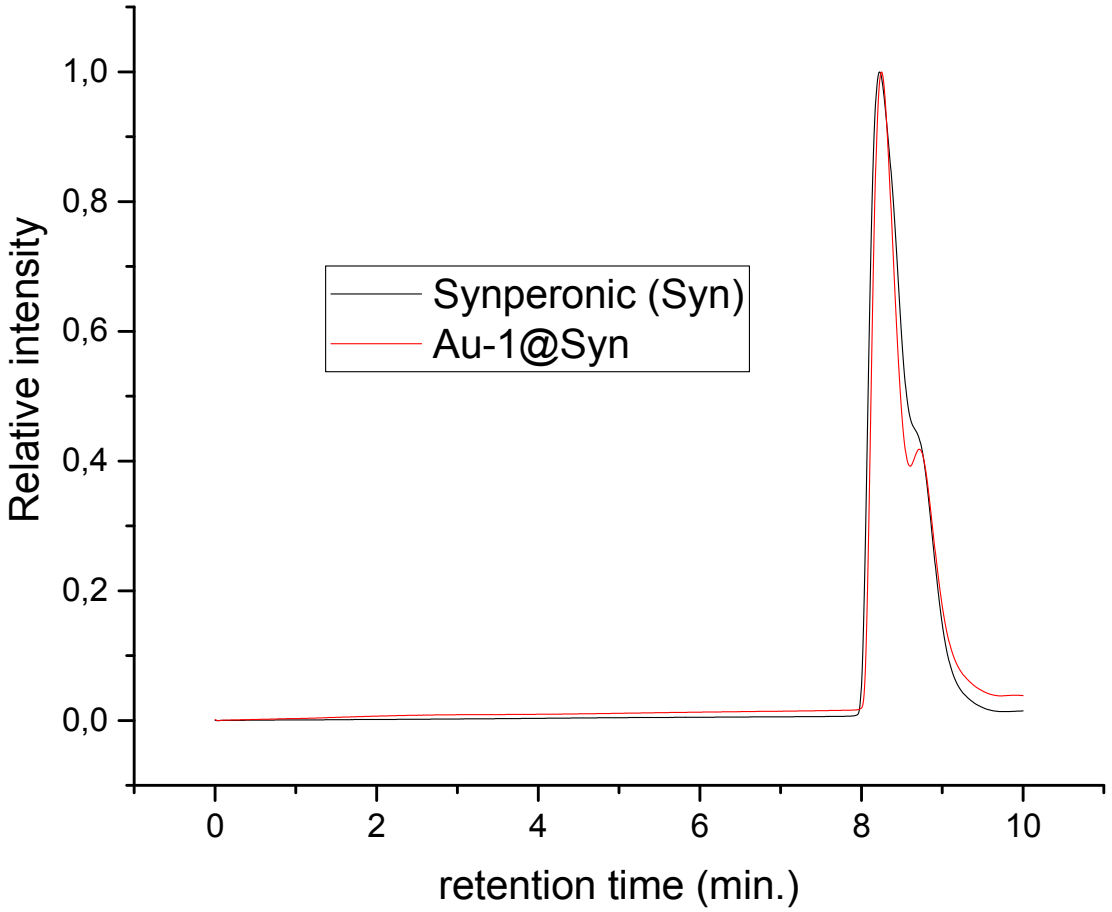
Relative intensity
1,0
0,8
0,6
0,4
0,2
0,0
0
2
4
6
8
10
retention time (min.)
Synperonic (Syn)
Au-1@Syn

Figure S6. Size exclusion chromatogram (SEC) of Synperonic®F108 and Au-1@Synperonic®F108 tablets in THF (flow rate: 1 mL/min. measured against PMMA standarts)

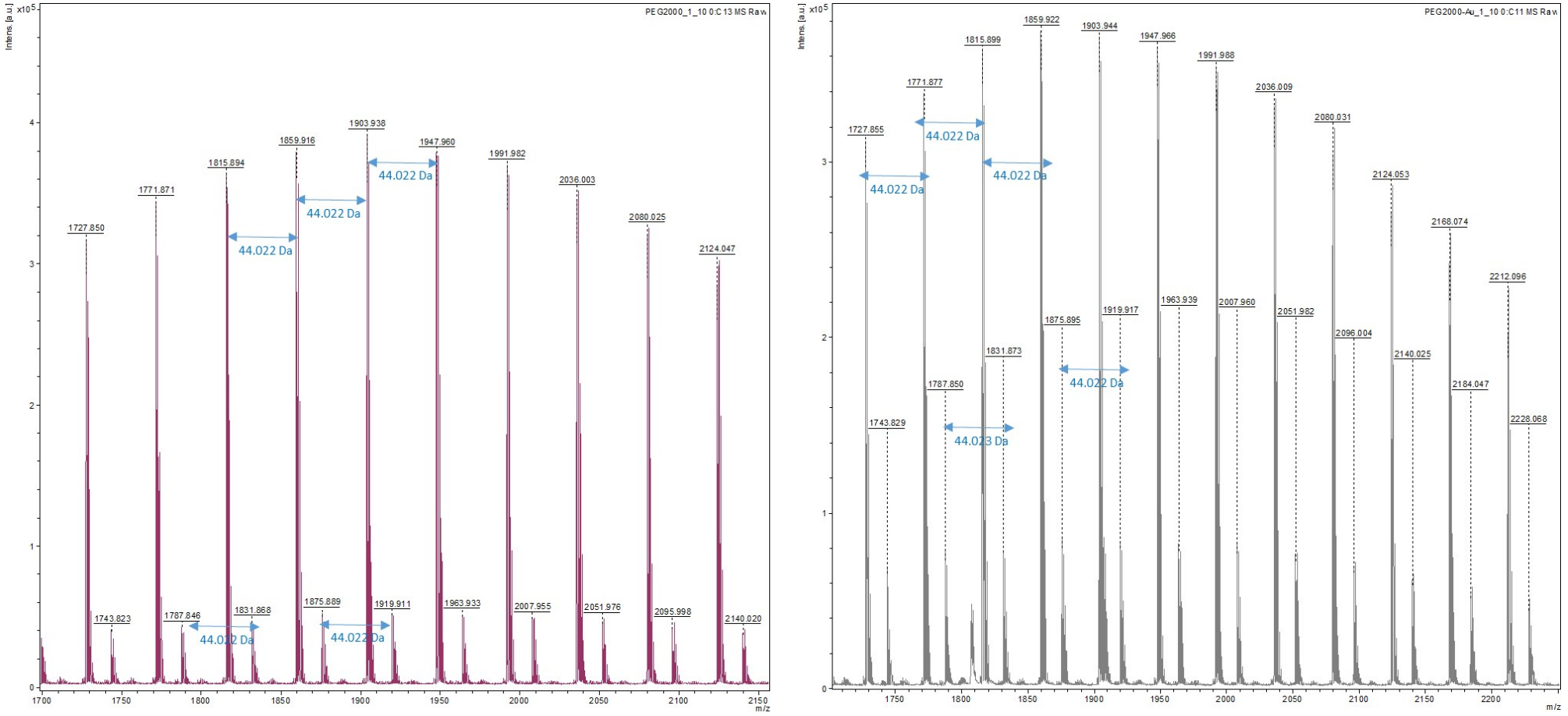

Figure S7. The detailed MALDI ToF-MS spectrum of PEG2000 and Au-1@PEG2000