Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

In-situ Monitoring of Palladacycle-Mediated Carbonylation by Surface-Enhanced Raman Spectroscopy

Kai Hu, Da-Wei Li*, Jing Cui, Yue Cao, Yi-Tao Long*

Key Laboratory for Advanced Materials & Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China.

**E-mail: ytlong@ecust.edu.cn; daweili@ ecust.edu.cn.*

General Methods

Reagents. N,N-Dimethyl-4-nitrobenzylamine (>97%) was purchased from Accela ChemBio Co., Ltd (Shanghai, China). All other reagents were of analytical grade without further purification. Gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, >99.0%), Sodium citrate (99%) and sodium chloride (>99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium tetrachloropalladate (Na_2PdCl_4, 98%) were obtained from Aladdin-Reagent Co., Ltd (Shanghai, China). Ultrapure water (18 $M\Omega \cdot cm^{-1}$) obtained from a Mili-Q System (Billerica, MA, USA) was used throughout the work.

Apparatus. UV-vis spectra were measured by a USB2000+ spectrometer (Ocean Optics Inc., U.S.A), and Transmission electron microscopy (TEM) measurements were performed on a JEM-2100 HR-TEM (JEOL, Tokyo, Japan) equipped for analysis at an accelerating voltage of 200 kV. ^1H NMR and ^{13}C NMR spectra was taken in Dimethyl Sulfoxide-D6 at an Ultra Shield 400 spectrometer (Bruker BioSpin AG, Magnet System 400 MHz/54 mm). Mass spectra were obtained by using the ESI method of Flight mass spectrometry (MALDI-TOF, AB Sciex, 4800 Plus). Agilent 1290 liquid chromatography coupled with 6530 quadrupole-time-of-flight mass spectrometry was used for liquid chromatography/mass spectrometry (HPLC-MS) analysis. The dark-field measurements were performed on an inverted microscope (eclipse Ti−U, Nikon, Japan) that was equipped with a dark-field condenser (0.8 <NA < 0.95) and a 40 × objective lens (NA = 0.8). Raman spectra were measured at a portable Raman spectrometer (BWS415, B&W Tek Inc., USA) with a beam diameter

of 10 μm and a resolution of 5 cm^{-1}. An excitation wavelength of 785 nm was chose to induce Raman scattering. A 1.5 m bifurcated fiber probe, which was equipped with the small portable Raman spectrometer provided facile SERS detection

Synthesis of Palladacycles (PCs).[1] To a 20 mL vial was weighed N,N-Dimethyl-4-nitrobenzylamine (237 mg, 1.32 mmol, 2.00 equiv) and Na_2PdCl_4 (194 mg, 0.66 mmol, 1.00 equiv). A magnetic stir bar was added to the vial along with methanol (10 mL). The mixture was sonicated for 1 minute, then nitrogen atmosphere was established. The mixture was heated at 60 °C in the dark for 14 h. Then the precipitated was filtered off, washed with water and methanol and dried under vacuum. The product was a yellow-green solid in 63.3% yield. ^{1}H NMR (400 MHz, DMSO): δ 2.65 (s, 2.89 H)， δ 2.75 (s, 6 H), δ 4.02 (s, 0.93 H), δ 4.19 (s, 2.0 H), 7.14 (d, J = 8.4 Hz, 0.46 H), 7.33 (d, J = 8.0Hz, 1H), 7.77 (d, J = 7.6 Hz, 0.45 H), 7.93 (d, J = 8.4 Hz, 1 H), 8.14 (s, 0.46 H), 8.67 (s, 1 H). ^{13}C NMR (100 MHz, DMSO): δ 51.52, 52.04, 71.80, 72.47, 119.35, 120.87, 122.38, 123.32, 127.05, 129.21, 144.11, 145.18, 150.64, 157.05, 157.19. Mass spectrometry calcd for $C_{18}H_{22}N_4O_4Pd_2Cl_2$ $[M^+$+H] 640.9, found 641.0.

Preparation of gold nanoparticles (AuNPs). AuNPs were prepared according to the pervious reported procedures.[2] Briefly, 2.4 mL of 1.00 % $HAuCl_4$ was added into 50 mL deionized water and rapidly heated to be boiling under vigorous stirring, then 5 mL of 1.00 % trisodium citrate solution was added. The solution was held at boiling for 10 min and cooled to the room temperature. The resulting AuNPs were centrifuged at 5000 rpm for 5 min and resuspended in 50 mL deionized water for

nanoplatforms fabrication.

Fabrication of AuNPs/PCs. Under stirring, a freshly prepared saturated palladacycles (PCs) solution was added dropwise to the prepared AuNPs at a 1:1 PCs solution/ AuNPs colloid volume ratio, which facilitated uniform distributions of the PCs on the gold particle surface. After 10 min, excess PCs were removed by three rounds of centrifugation (5000 rpm, 5 min) and resuspension in deionized water. Thus, the AuNPs/PCs nanoplatforms were obtained for monitoring experiments.

Measurement with Dark-Field Microscopy and Scattering Spectroscopy. The AuNPs-functionalized slide was immobilized on a platform, using ultrapure water as the medium and the white light source, a 100w halogen lamp was used to excite the AuNPs and generate plasmon resonance scattering light. The dark-field color images were recorded by a true-color digital camera (Nikon DS-fi, Japan). A monochromator (Acton SP230i, PI) equipped with a grating (grating density, 300 lines/mm; blazed wavelength, 500 nm) was used to split the scattering light of the AuNPs recorded by a spectrometer CCD (CASCADE 512B, Roper Scientific, PI) to obtain the scattering spectra. PC solution was added into the medium water. Record the plasmon resonance scattering spectra of the AuNPs after assembling PC molecules on their surfaces at different time.

Density Functional Theory (DFT) calculations. In order to verify the formation of carboxyl-contained 4-nitro-N,N-dimethlybenzylamine, we performed DFT calculations using Gaussian 09[2] suite of program at the level of B3LYP/6-311++g (d, p) to simulate its Raman spectra for the further understanding of the experimental

results. Regarding the effect of the aqueous environment, the integral equation formalism version of polarizable continuum model (IEF-PCM)[3] implemented in Gaussian 09 were included for the geometry optimization and the vibrational frequencies calculations of the most stable geometry structure. The Raman shifts were obtained based on all the calculated vibrational frequencies scaled by the factor of 0.967[4] according to basis set and the utilized functional. The vibrational modes corresponding to the calculated peaks were subsequently analyzed

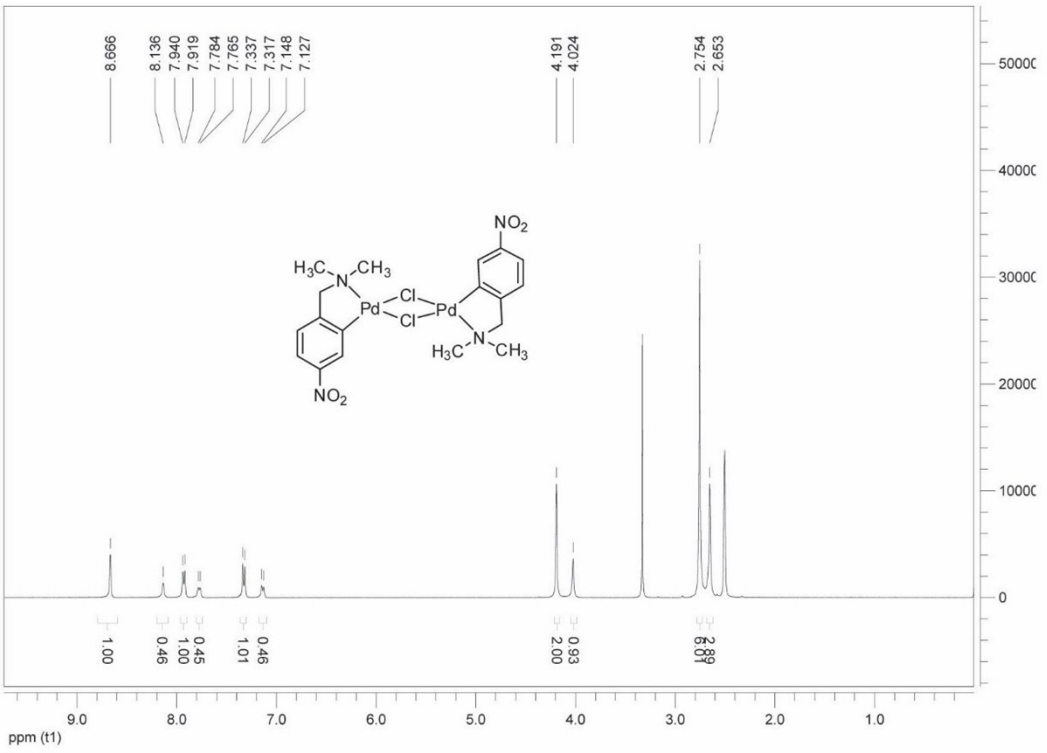

Figure S1. [1]H NMR spectrum of palladacycles (PCs) in DMSO-d6

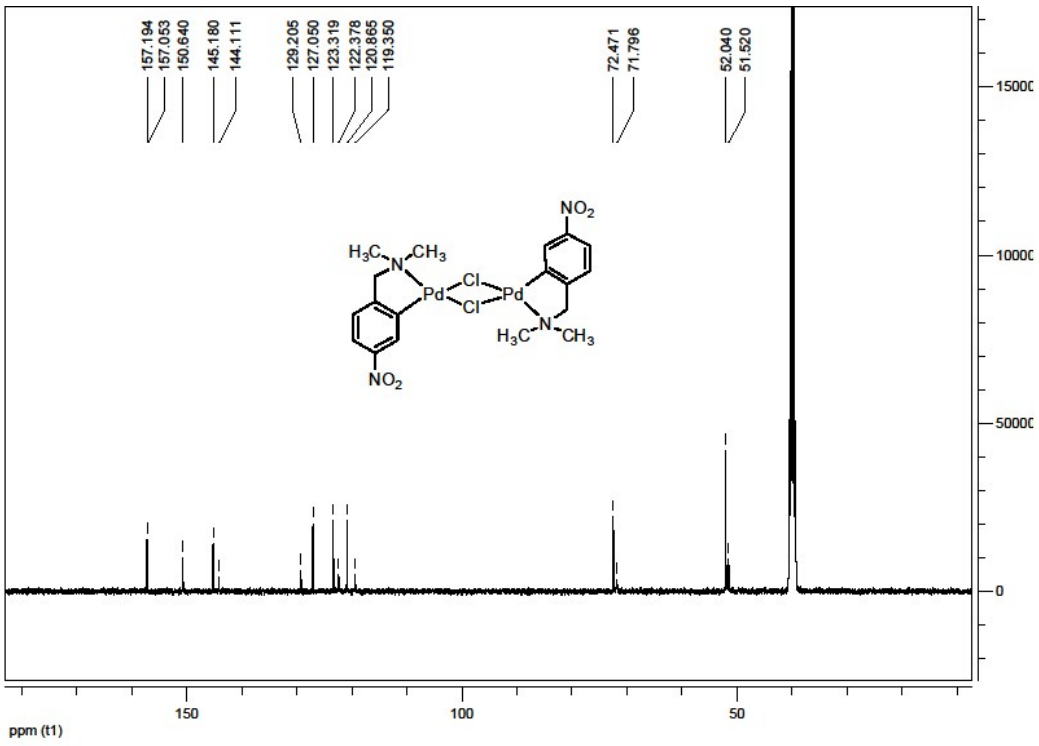

Figure S2. [13]C NMR spectrum of palladacycles (PCs) in DMSO-d6

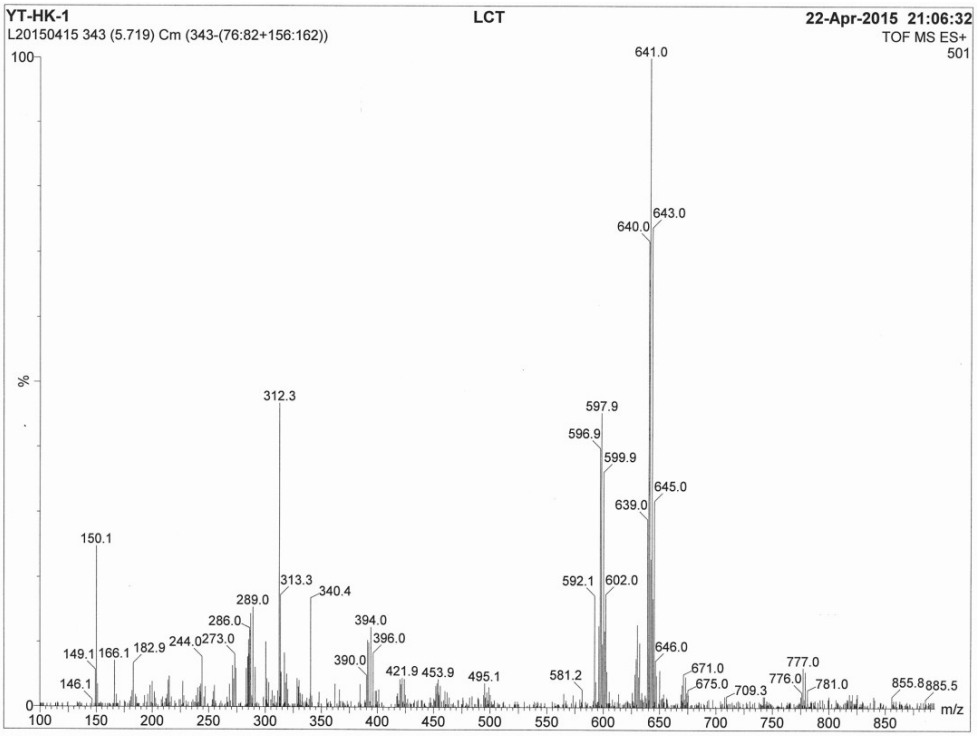

Figure S3. Mass spectrum of palladacycles (PCs)

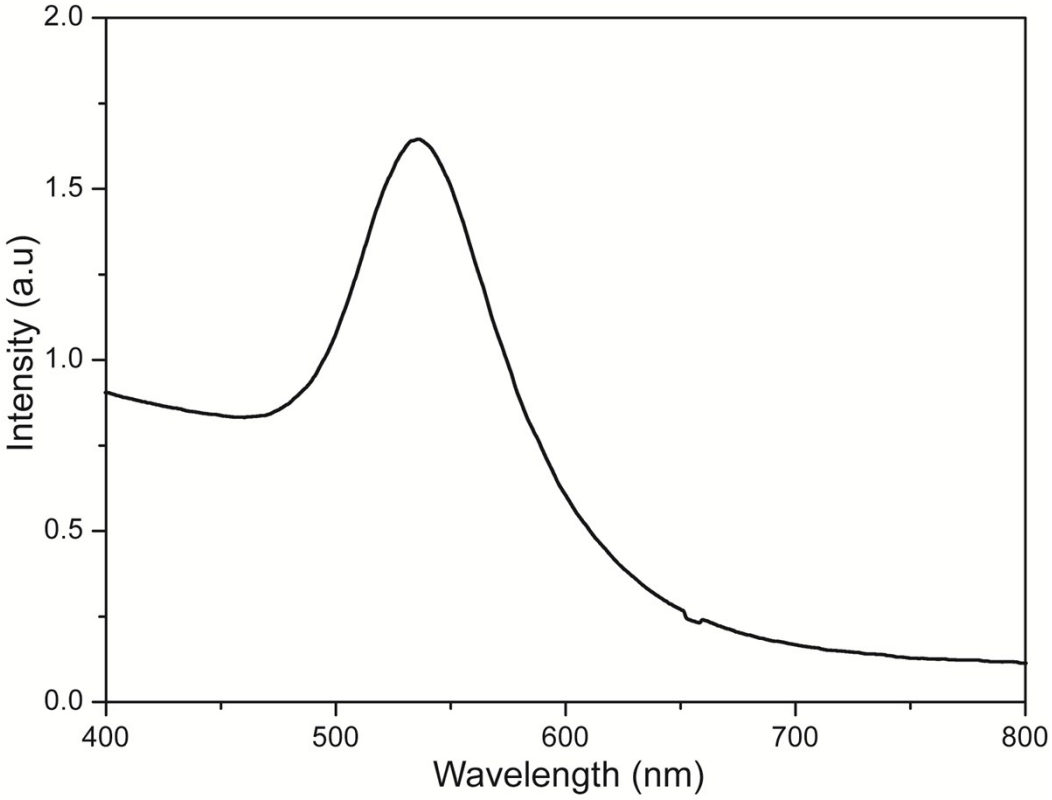

Figure S4. UV-vis spectra of AuNPs/PCs nanoplatforms

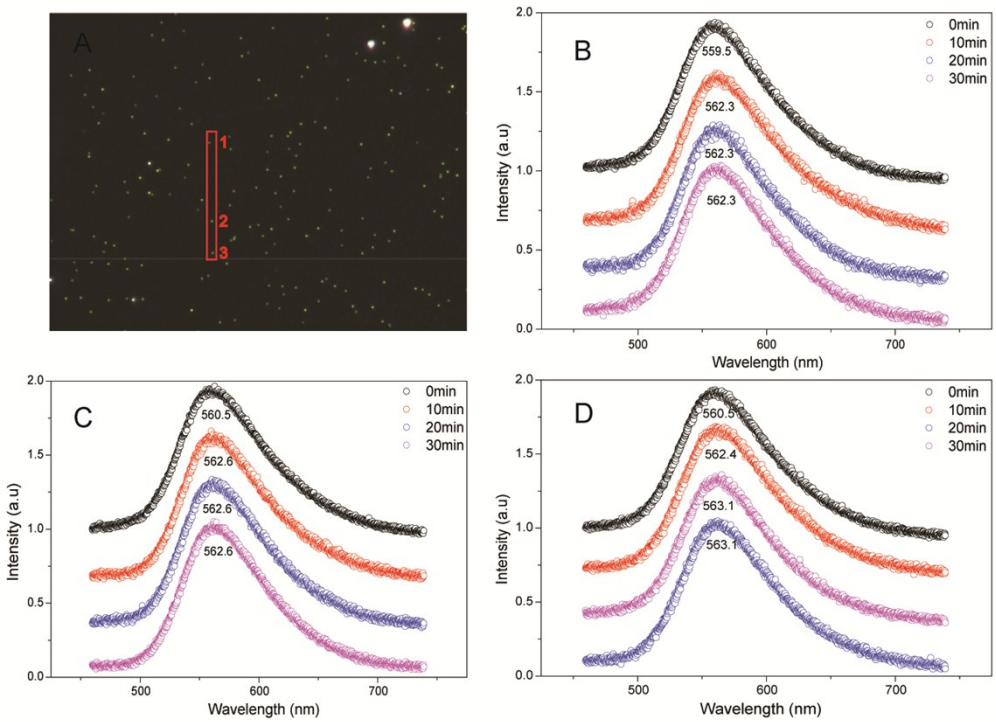

Figure S5. (A) Dark-field images of three randomly selected AuNPs (1-3). (B-D) The corresponding plasmon resonance scattering spectra of the three AuNPs (1-3) after assembling PC molecules on their surfaces at different time.

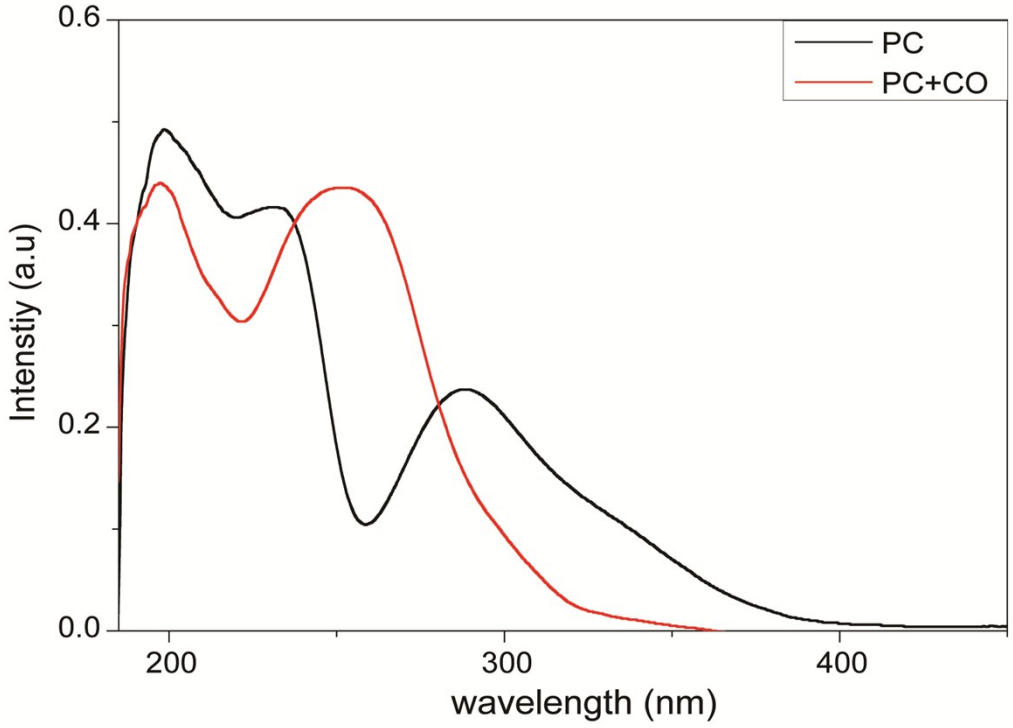

Figure S6. UV spectra of PC before and after reacting with saturated CO solution

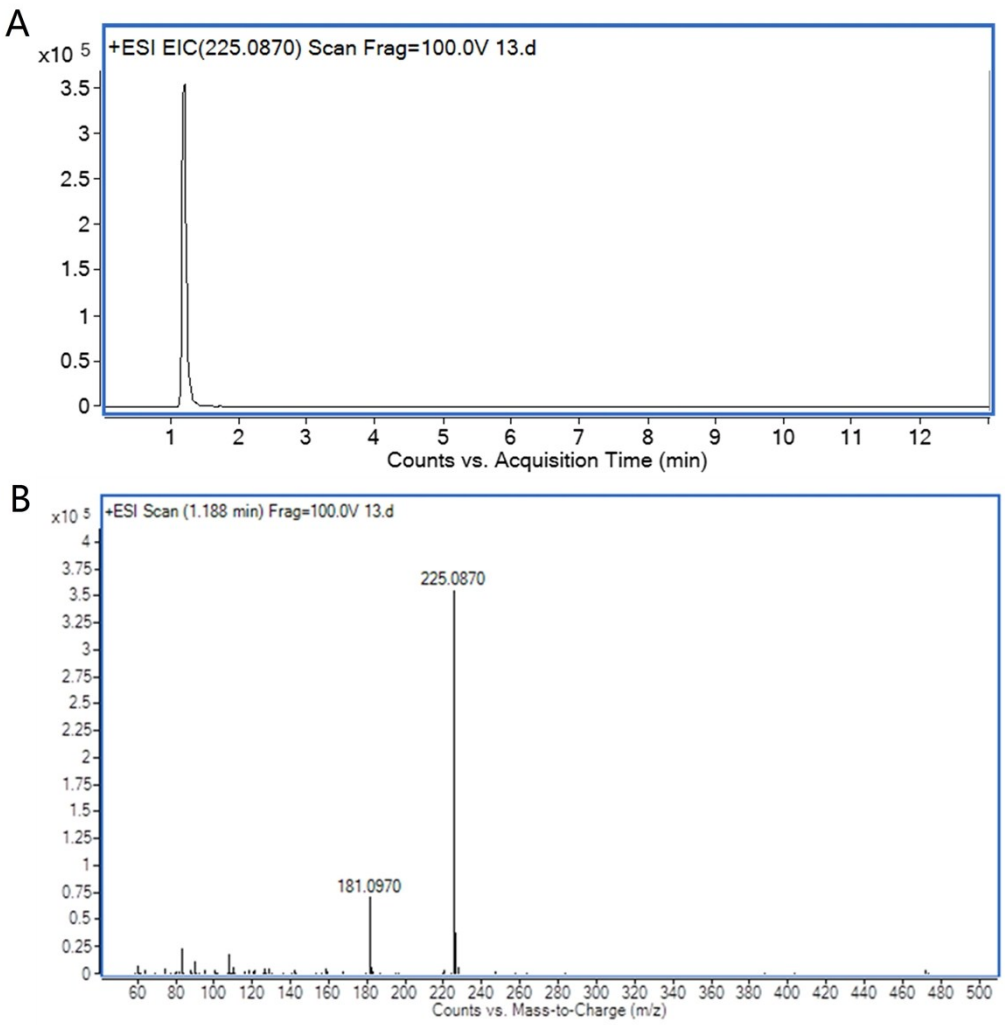

Figure S7. HPLC-MS analysis of the products of 90min reaction between the synthesized palladacycles and saturated CO. (A) The HPLC chromatogram of the product after the reaction PC with CO. (B). The high-resolution Mass spectra of the product eluted at 1.188 min.

Table S1. SERS Spectral data of AuNPs/PCs after reacting with CO and Raman spectral data of calcuate with DFT for 2-carboxyl-4-nitro-N,N-dimethylbenzylamine (CNDBA) corresponding to band assignments

DFT(cm^{-1})	SERS (cm^{-1})	Assignment
821	875	C-N stretch, Ar-C(CH_2) stretch, Ar in-plane bending
1029	1032	Ar (C-H) out-of-plane wag
1119	1104	Ar-N(NO_2) stretch, Ar (C-C-C) stretch, Ar (C-H) rock
1201	1196	Ar in-plane bending, Ar (C-H) rock, Ar-C(COOH) stretch
1333	1338	Ar (C-C) stretch, Ar-COO^- rock, Ar (C-H) rock
1365		COOH rock, Ar-COO^- rock, Ar (C-C) stretch

References

1. A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909-913.
2. B. W. Michel, A. R. Lippert and C. J. Chang, *J. Am. Chem. Soc*., 2012, **134**, 15668-15671.