

Template-confined fabrication of controllable gold nanoparticles based on two-dimensional nanostructure of macrocycle

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1. Materials and Measurements

Materials. H₂AuCl₄ and NaBH₄ were purchased from Sigma-Aldrich Co. LLC., and the solvents were obtained from Beijing Chemical Reagents Co. and dried using standard methods. The chemicals involved in our experiments were of analytical grade and used without further purification. The assemblies were formed on freshly cleaned HOPG (grade ZYB, Russia) surface. Compound **1** was prepared according to literature methods [*Chem. Commun.*, 2014, 50, 9369-9371]. All reactions were carried out under nitrogen atmosphere unless otherwise noted.

Measurements. ¹H and ¹³C NMR were performed on Bruker AV-400 spectrometer with residual solvent peaks (CDCl₃: ¹H: δ= 7.26, ¹³C: δ=77.23). Maldi-TOF MS were obtained on a PerSeptive Biosystem Voyager-DE STR. STM measurements were performed on Nanoscope III (Veeco Metrology, USA) with mechanically formed Pt/Ir (80/20) tips. All images were recorded in constant current mode, and the tunnelling conditions are given in the corresponding figures captions. XPS measurements were conducted on ESCALAB250Xi spectrometer equipped with Mg K α (1253.6 eV) source.

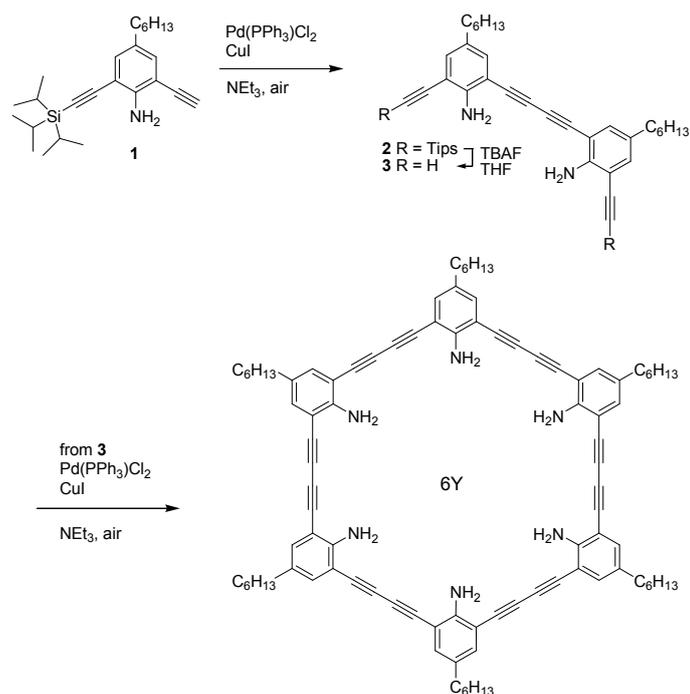
2. Synthesis of macrocycle **6Y**

The synthesis of macrocycles **6Y** was outlined in Scheme 1. Starting with the single protected compound **1**, homocoupling of **1** under Pd/Cu catalyzed variation of the oxidative acetylene coupling furnished **2** in 98.8% yield. Complete deprotection of the Tips group with TBAF in THF provided **3** in 98% yield. Homocoupling of **3** under Pd/Cu catalyzed variation under diluted concentration in THF furnished macrocycle

6Y as a brown solid in 10% yield after CC and size exclusion Chromatography (SEC).

All the compounds were characterized by ^1H NMR, ^{13}C NMR, MALDI-TOF and HR MALDI-TOF mass spectrometers.

Scheme 1. Schematically synthetic route of macrocycle **6Y**



2.1 Synthesis of 6,6'-(buta-1,3-diyne-1,4-diyl)bis(4-hexyl-2-((triisopropylsilyl)ethynyl)aniline) (**2**)

A three-necked flask was charged with **1** (2.9 g, 7.6 mmol), THF (15 ml), diisopropyl ethyl amine (2.9 g, 22.44 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.16 g, 0.228 mmol), and CuI (0.073 g, 0.38 mmol). After the reaction mixture was stirred for 1 h under air, the resulted residue was absorbed on silica gel and purified by column chromatography (CC) (hexane/ethyl acetate (200:1/v:v) as eluent) to yield **2** (2.86 g, 3.76 mmol) as a yellow oil in 98.8% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.16 (s, 2H), 7.15 (s, 2H), 4.83 (s, 4H), 2.45 (t, $J = 7.6$ Hz, 4H), 1.54 (m, 4 H), 1.31 (s, 12

H), 1.16 (s, 42H), 0.91 (t, J = 6.6 Hz, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 149.16, 133.53, 133.01, 131.66, 108.04, 105.61, 103.10, 96.58, 79.70, 78.92, 77.36, 77.04, 76.72, 34.67, 31.73, 31.42, 28.84, 22.63, 18.74, 14.11, 11.30. MALDI-TOF MS: m/z;[M]⁺, calcd for C₅₀H₇₆N₂Si₂:76132; found:761.8.

2.2 Synthesis of 6,6'-(buta-1,3-diyne-1,4-diyl)bis(2-ethynyl-4-hexylaniline) (3)

To a stirred solution of **2** (1.9 g, 2.495 mmol) in THF (20 ml) was added a solution of TBAF (0.044 g, 0.14 mmol) in THF (2 ml). The mixture was stirred for 30 minutes under air. After removal of the solvent, the residue was chromatographed (silica gel, hexane/ethyl acetate (40:1/v:v)) to furnish **3** (1.08 g, 2.44 mmol) as a yellow oil in 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.16 (s, 4H), 4.78 (s, 4H), 3.40 (s, 2H), 2.42 (t, J = 7.3 Hz, 4H), 1.54 (s, 4H), 1.28 (s, 12H), 0.88 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 149.22, 133.95, 133.59, 131.76, 106.42, 105.76, 82.82, 80.07, 79.58, 78.97, 34.57, 31.69, 31.29, 28.74, 22.59, 14.09. MALDI-TOF MS: m/z;[M]⁺, calcd for C₃₂H₃₆N₂: 448.63; found: 448.53.

2.3 Synthesis of macrocycle 6Y

To a degassed solution of Pd(PPh₃)₂Cl₂ (0.032 g, 0.0446 mmol) in dry THF (1400 ml), CuI (0.0187 g, 0.098 mmol), diisopropyl ethyl amine (1.0 g, 3.5 mmol), was dropped a solution of **3** (0.4 g, 0.892 mmol) in THF (500 mL) over 10 h. The reaction mixture was further stirred under air at rt. for 4 days. The resulted reaction mixture was absorbed on silica gel and purified by column chromatography (CC) (hexane/ethyl acetate (15:1/v:v) as eluent) and further subjected to Size exclusion chromatography (Bio-bead, toluene as eluent) to yield **6Y** (0.040 g, 0.0336 mmol) as

a yellow oil in 10% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.14 (s, 12H), 4.76 (s, 12H), 2.43 (t, $J = 7.6$ Hz, 12H), 1.53 (m, 12H), 1.30 (s, 36H), 0.90 (t, $J = 6.7$ Hz, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 150.25, 133.75, 132.03, 106.05, 79.45, 79.23, 34.57, 31.68, 31.19, 28.76, 22.58, 14.08. MALDI-TOF HRMS: m/z ; $[\text{M}+\text{H}]^+$, calcd for $\text{C}_{96}\text{H}_{103}\text{N}_6$: 1339.8216; found:1339.8230.

3. Formation of AuNPs on Surface

6Y was dissolved in ethanol with the concentration less than 10^{-4} M, and then a droplet of solution was deposited onto freshly cleaved HOPG surface. After evaporation of solvent, the STM images were recorded at the surface. A drop of HAuCl_4 (1 μL , 10^{-3} g/L) was added onto the HOPG surface when the assembled structure of **6Y** was obtained. After standing for 15 minutes, the reacted samples were repeatedly washed with ethanol/water mixed solution for several times. And then, 0.4 μL of NaBH_4 with concentration of 10^{-3} g/L was added onto the surface. The STM measurement was conducted again after washing the surface for several times following the same procedure as mentioned above.

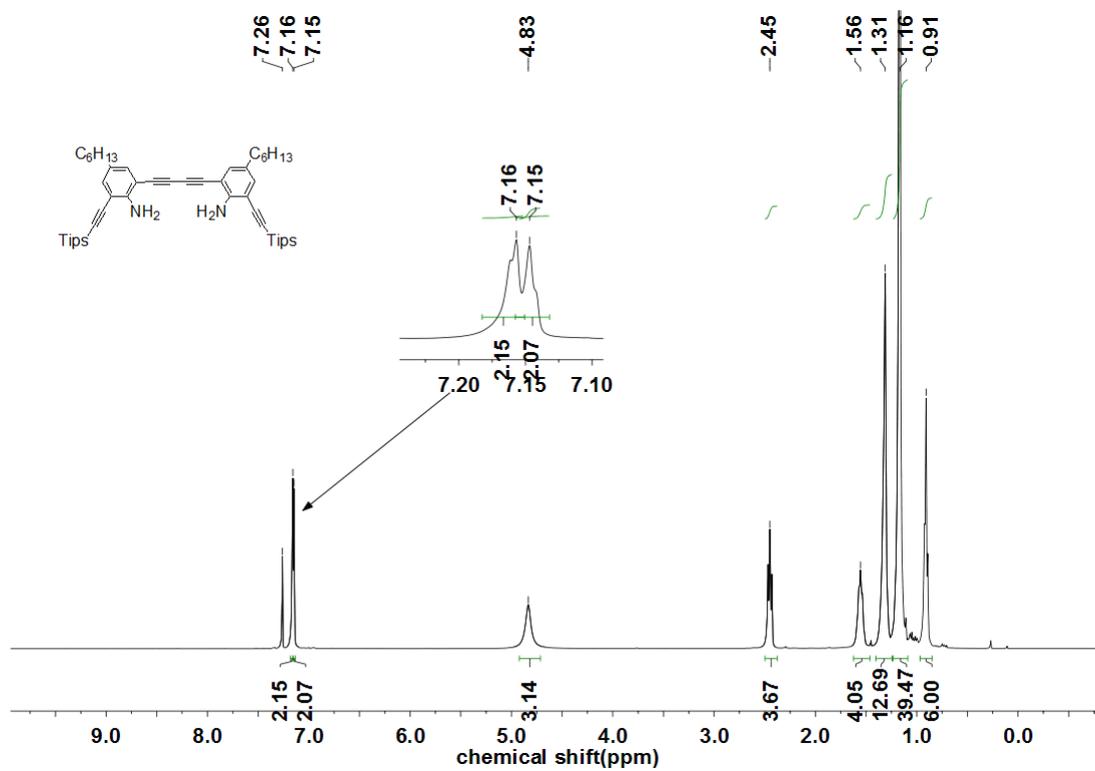


Figure S1. ¹H NMR of compound 2.

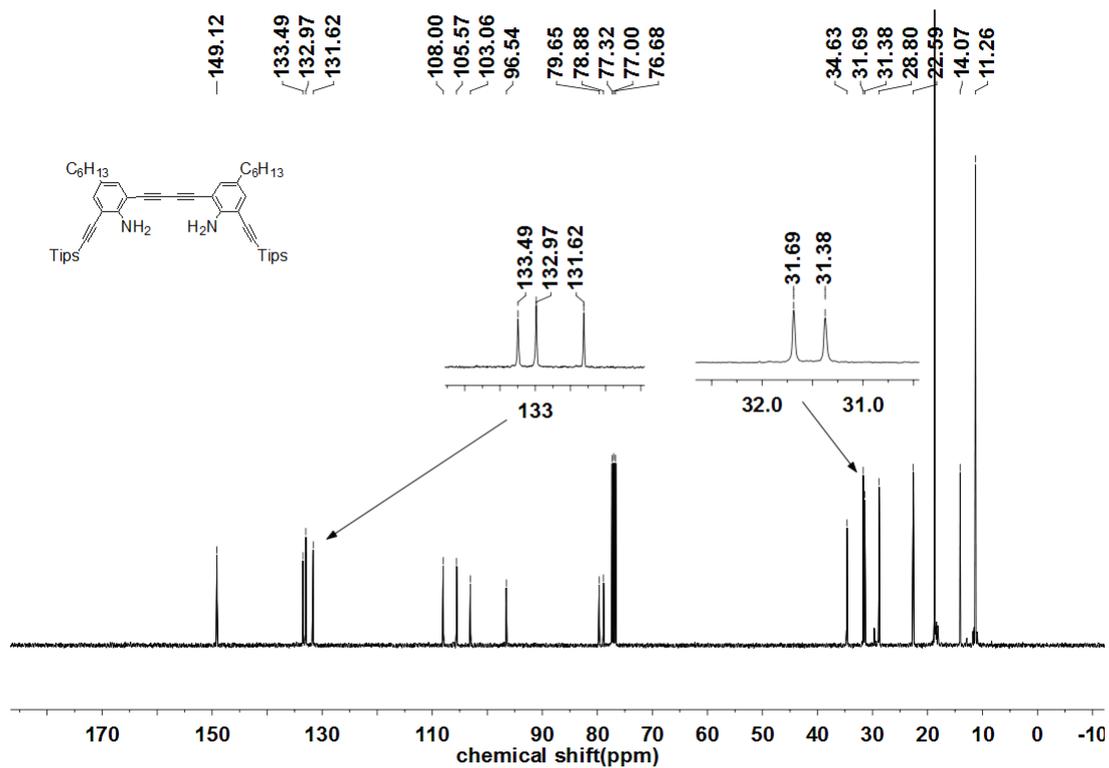


Figure S2. ^{13}C NMR of compound 2.

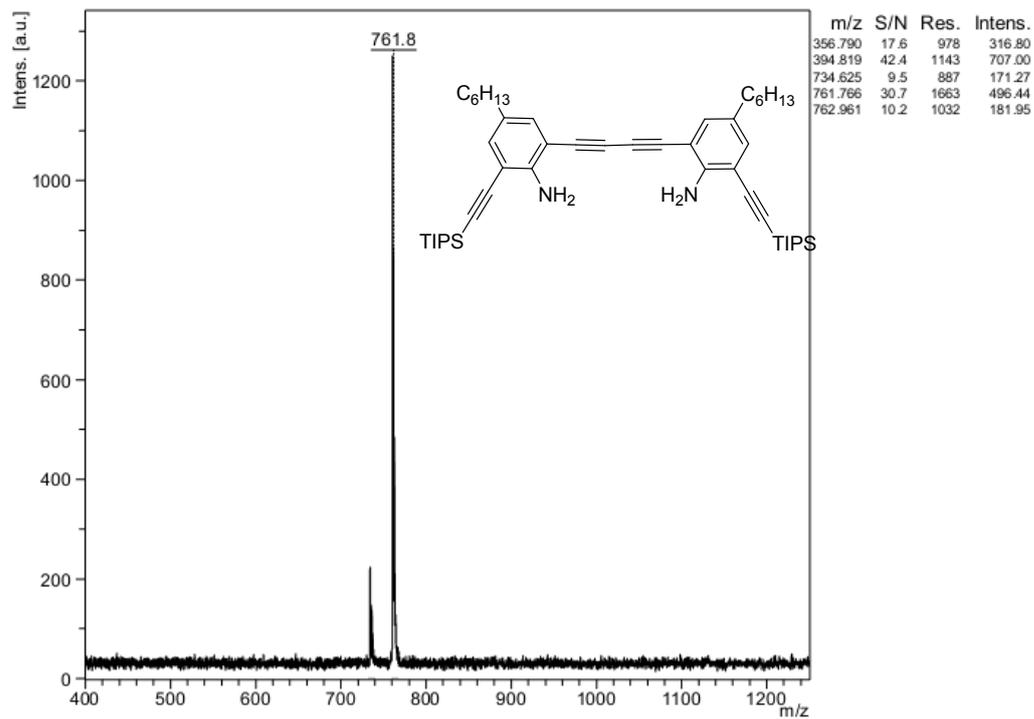


Figure S3. MALDI-TOF of compound 2.

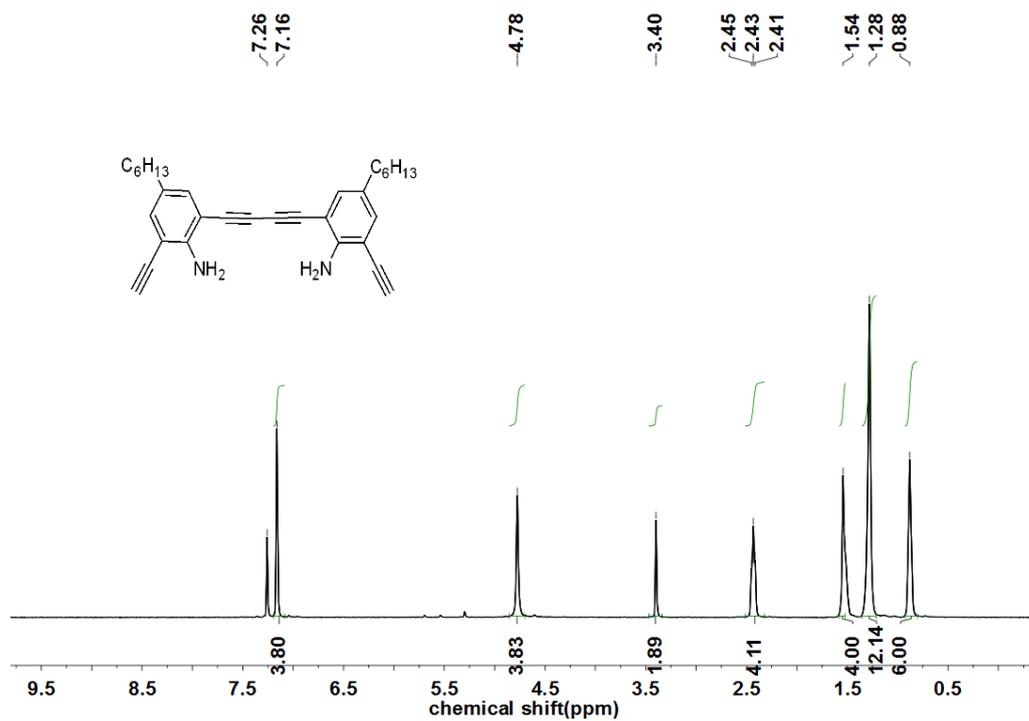


Figure S4. ¹H NMR of compound 3.

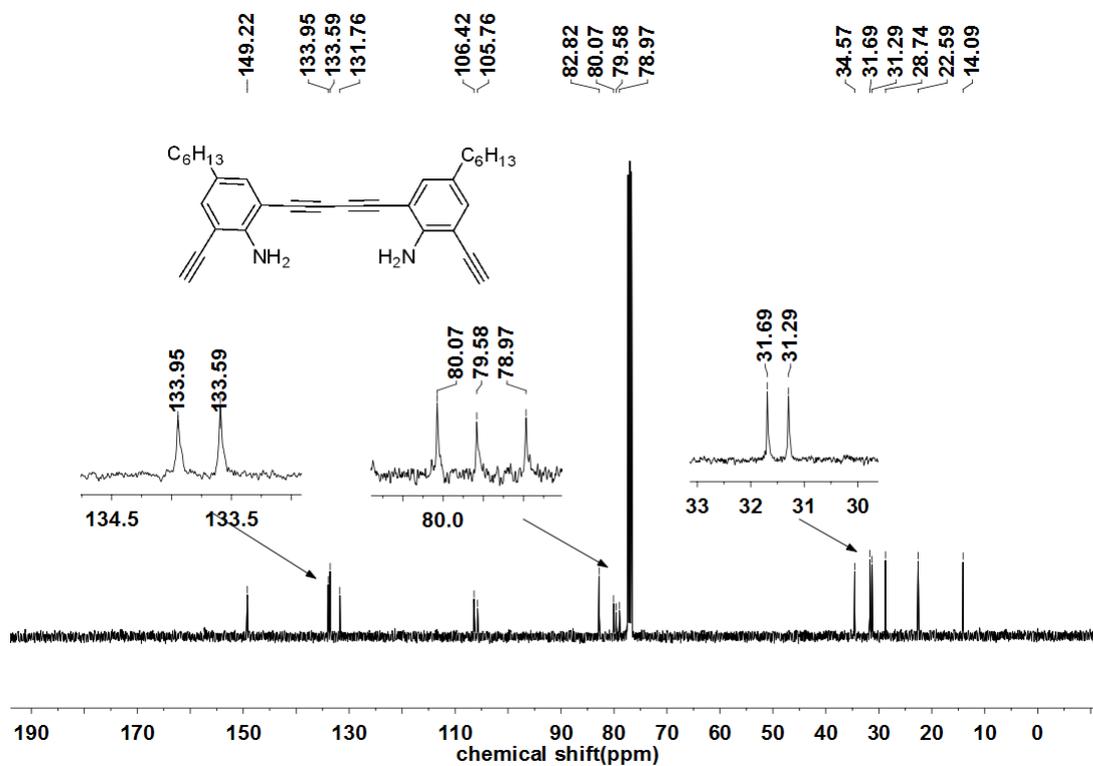


Figure S5. ¹³C NMR of compound 3.

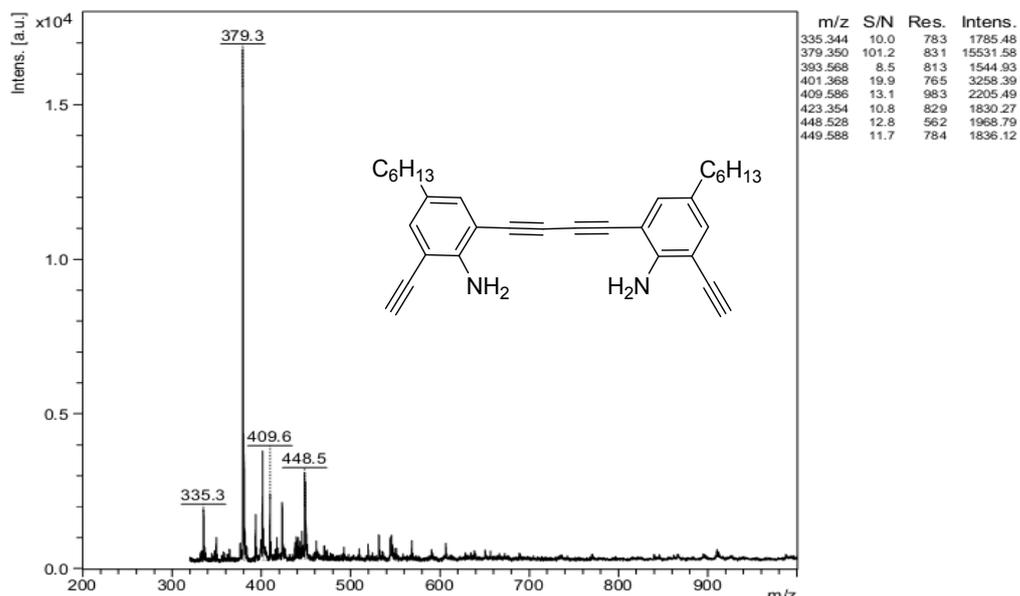


Figure S6. MOLDI-TOF of compound 3.

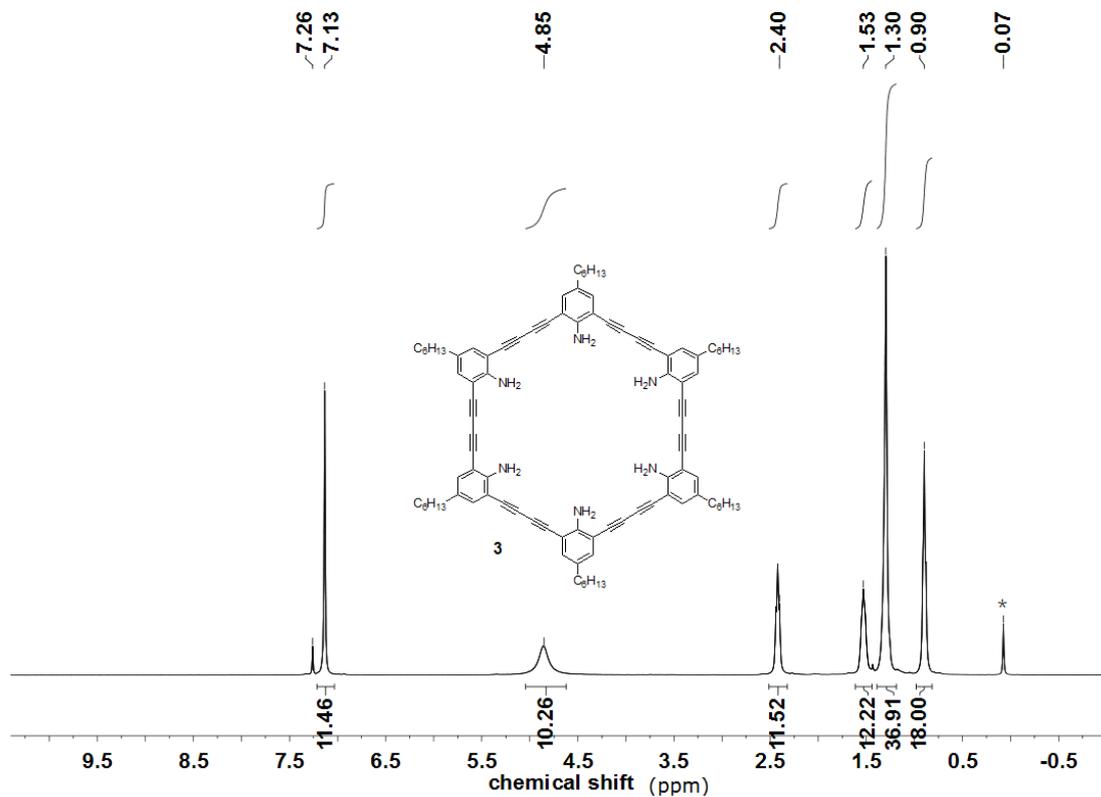


Figure S7. ^1H NMR of **6Y** (Peak with * label is from the proton resonance of grease).

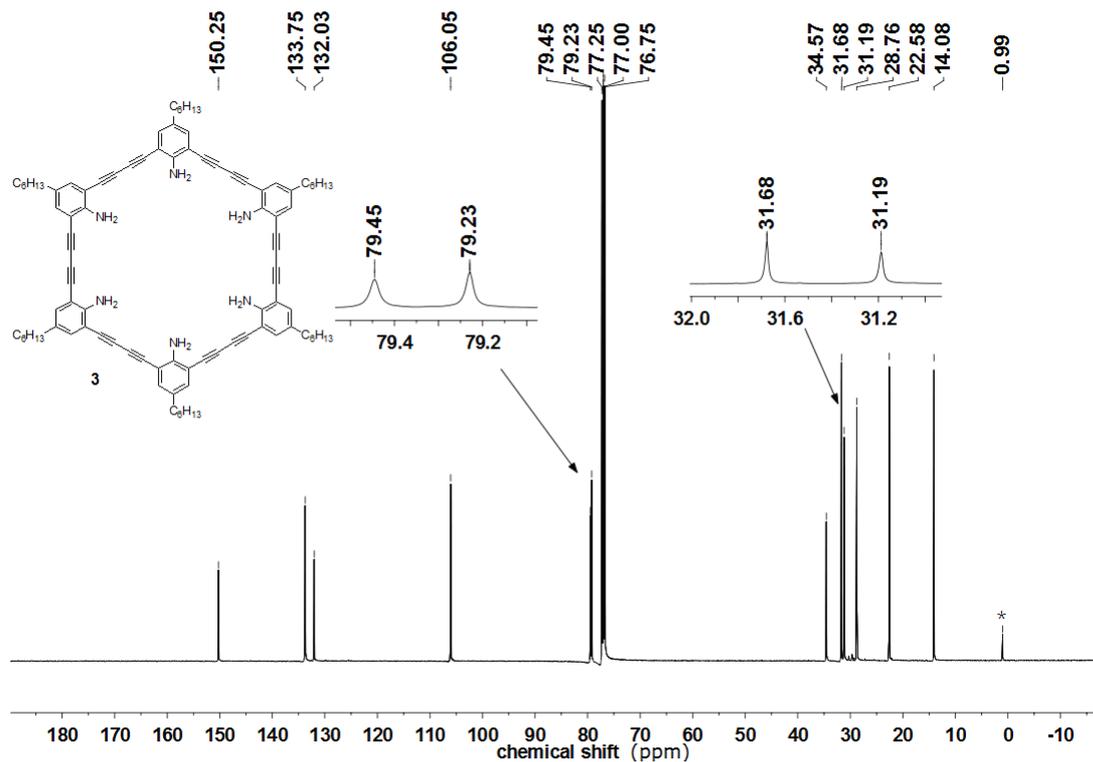


Figure S8. ^{13}C NMR of **6Y** (Peak with * label is from the carbon resonance of grease).

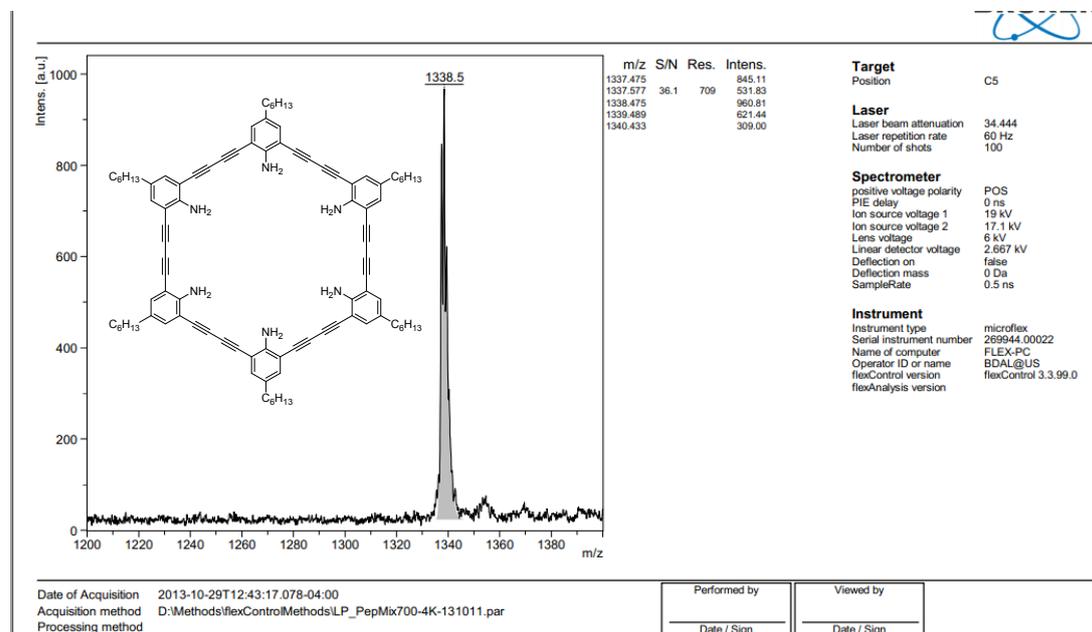


Figure S9. MOLDI-TOF spectrum of **6Y**

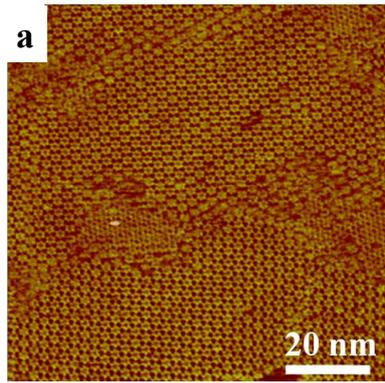


Figure S10. Large-scale STM images of 6Y on HOPG surface. Imaging conditions: $I_{set} = 400 \text{ pA}$, $V_{bias} = 460 \text{ mV}$.

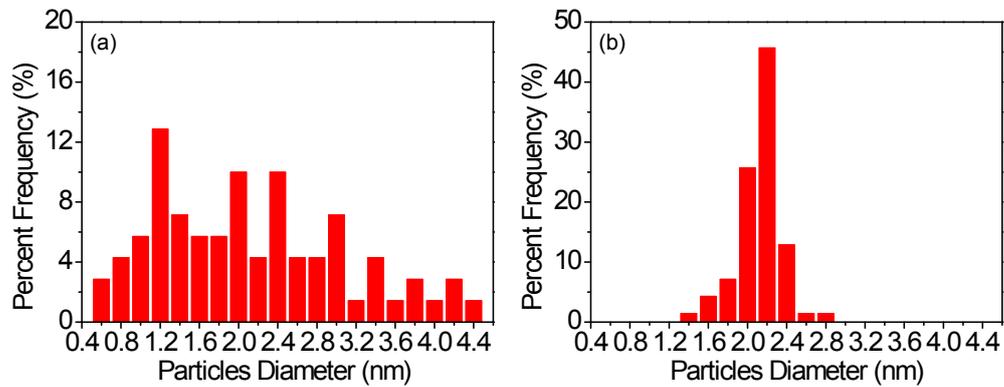


Figure S11. AuPNs size distribution before and after washing with ethanol/water mixed solution.

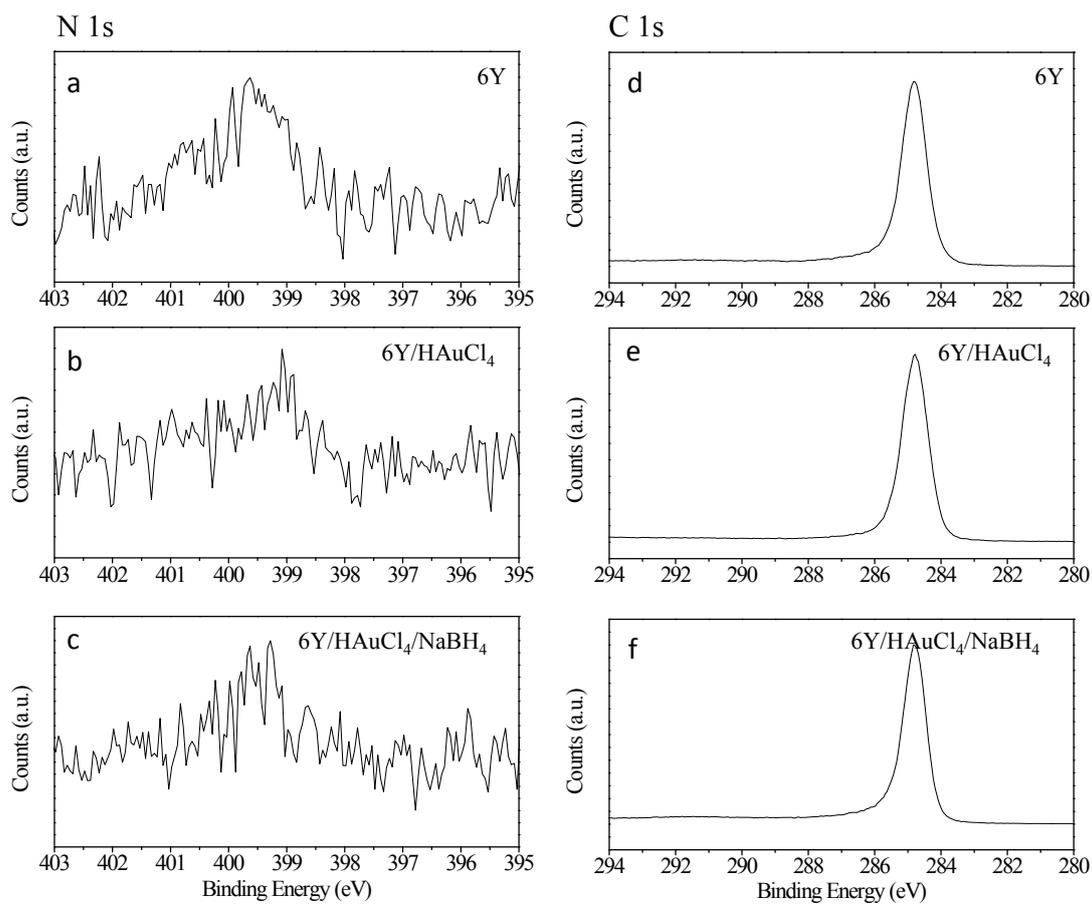


Figure S12. N 1s and C 1s regions of the XPS spectrum of **6Y**, **6Y/HAuCl₄** and **6Y/HAuCl₄/NaBH₄** samples.