Supporting Information

Thiol-Ubiquinone Assisted Fragmentation of Gold Nanoparticles

Sara Riaz,[a] Wei-Ma,[a] Chao Jing,[a] Mian Hasnain Nawaz,[b] Da-Wei Li*[a] and Yi-Tao Long*[a]

[a] *State Key Laboratory of Bioreactor Engineering & 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*

[b] *Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China.*

Experimental

Materials and Methods

Coenzyme Q_0 was of the best available grade (>98%) from Sigma. 4-(methylthio)phenylboronic acid was purchased from Aladdin Chemistry Co. Ltd in 97 % purity. N_2 (99.998%, prepurified) was obtained from Cryogenic Gases (Detroit, MI). THF and ethanol were supplied by Sinopharm Chemical Reagent Co. Ltd and THF was freshly distillled prior to use. $HAuCl_4.3H_2O$ was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Thioanisole, sodium citrate and other chemical reagents used for synthesis were of analytical grade, obtained from commercial suppliers and used without further purification unless otherwise noted. The gold nanoparticles solution was prepared by using Milli-Q water (Millipore Milli-Q System: Millipore, USA, 18 MΩ.cm).

Absorption spectra of the solutions were recorded by using a Ocean Optics 2000+ UV-Vis spectrophotometer. The size and shape of the gold colloids were investigated with a JEOL JEM 2100 TEM instrument operated at an accelerating voltage of 200 kV. The TEM samples were prepared by dropcasting the solutions on carbon-coated copper grids and then dried at room temperature. ^{1}HNMR spectra were recorded at 400 MHz, using BRUKER AV 400 Spectrophotometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference.

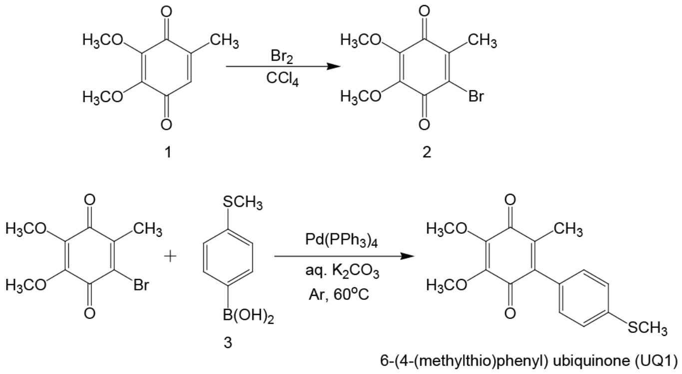
Procedures

Synthesis of 6-(4-(methylthio)phenyl) ubiquinone (UQ1)

6-(4-(methylthio)phenyl) ubiquinone **(UQ1)** was synthesized by suzuki coupling[1] of 6-bromoubiquinone **(2)**. To a stirred solution of coenzyme Q_0 **(1)** (2.0 g, 11 mmol) in 20 mL of carbon tetrachloride, was added bromine (3.4 g, 21.5 mmol) dropwise at room temperature. The reaction mixture was stirred for 4 hr, washed with water, dried with magnesium sulfate, and evaporated. It was purified by column chromatography to give 2 (74 %) as red needle crystals. ^{1}H NMR (400.0 MHz, $CDCl_3$, 298 K) δ ppm: 4.00

(s, 3H, $-OCH_3$), 4.03 (s, 3H, $-OCH_3$), 2.22 (s, 3H, $-CH_3$).

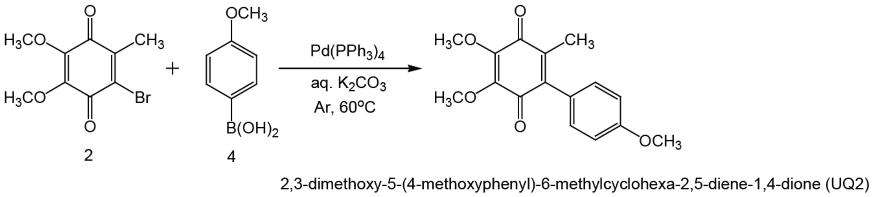
To a mixture of 4-(methylthio)phenylboronic acid **3** (0.07 g, 0.42 mmol), K_2CO_3 (0.26 g, 1.92 mmol) and 5 mol % $Pd(PPh_3)_4$ (0.022 g, 0.0192 mmol) in THF:H_2O (2:1), a solution of 6-bromoubiquinone **2** in THF (2 mL) was added dropwise. The reaction mixture was kept for stirring at 60°C for 12 hr. The progress of the reaction was monitored by TLC, it was washed with ethyl acetate followed by brine, dried with sodium sulphate (anhydrous) and evaporated. The product was purified by column chromatography to afford orange red crystals of **UQ1** in 40% yield. ^1H NMR (400.0 MHz, $CDCl_3$, 298 K) δ ppm: 1.96 (s, 3H, $-CH_3$), 2.52 (s, 3H, $-SCH_3$), 4.02 (s, 3H, $-OCH_3$), 4.06 (s, 3H, $-OCH_3$), 7.08 (d, 2H, ArH), 7.29 (d, 2H, ArH).



Scheme 1S Synthesis of 6-(4-(methylthio)phenyl) ubiquinone **(UQ1)**

Synthesis of 2,3-dimethoxy-5-(4-methoxyphenyl)-6-methylcyclohexa-2,5-diene-1,4-dione (UQ2)

To a mixture of 4-methoxyphenylboronic acid **4** (0.069 g, 0.46 mmol), K_2CO_3 (0.26 g, 1.92 mmol) and 5 mol % $Pd(PPh_3)_4$ (0.022 g, 0.0192 mmol) in THF:H_2O (2:1), a solution of 6-bromoubiquinone **2** in THF (2 mL) was added dropwise. The reaction mixture was kept for stirring at 60°C for 12 hr. The progress of the reaction was monitored by TLC, it was washed with ethyl acetate followed by brine, dried with sodium sulphate (anhydrous) and evaporated. The product was purified by column chromatography to afford dark red crystals of **UQ2** in 70% yield. ^1H NMR (400.0 MHz, $CDCl_3$, 298 K) δ ppm: 1.98 (s, 3H, $-CH_3$), 3.85 (s, 3H, $-OCH_3$), 4.01 (s, 3H, $-OCH_3$), 4.06 (s, 3H, $-OCH_3$), 6.96 (d, 2H, ArH), 7.10 (d, 2H, ArH).



Scheme 2S Synthesis of 2,3-dimethoxy-5-(4-methoxyphenyl)-6-methylcyclohexa-2,5-diene-1,4-dione **(UQ2)**

Synthesis of Gold Nanoparticles

The gold nanoparticles (ca. 20 ± 2 nm) were synthesized by modified citrate reduction method.[2] All the glassware were dipped overnight in aqua regia (HCl:HNO_3 in a ratio of 3:1) and washed with plenty of water followed by sonication in milliQ water for at least 5 minutes. 50 mL of the aqueous solution of $HAuCl_4$ (0.01% wt %) was heated to boil under vigorous stirring. Then, 1 mL of aqueous sodium citrate (10 % wt%) was added at once in the boiling solution which resulted in a rapid color change from yellow to deep red within few minutes. It was kept boiling for further 10 minutes to ensure complete reduction of $HAuCl_4$. The solution was cooled to room temperature before using it for UV-Vis and TEM analysis.

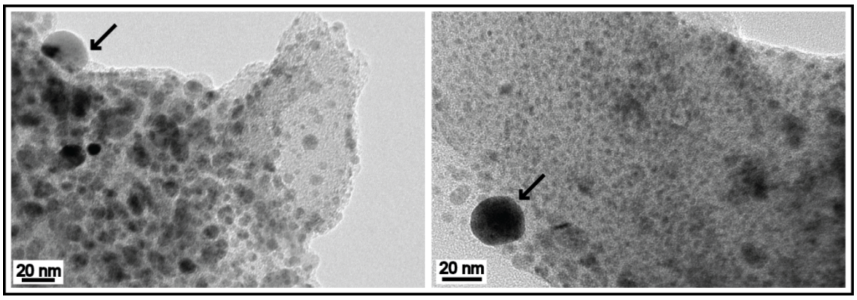


Fig. 1S HRTEM micrographs of AuNPs capped with UQ1, showing a few original particles along with fragments.

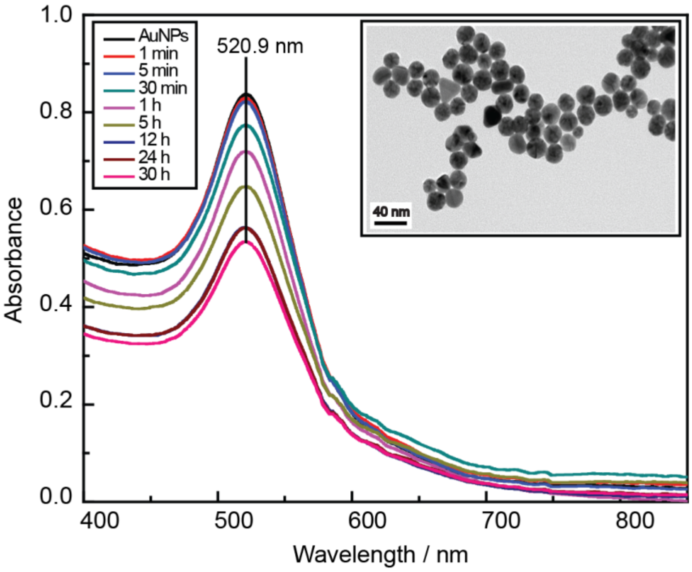


Fig. 2S UV-vis spectra of AuNPs modified with UQ2 (1 mmol), inset shows corresponding HRTEM image of AuNPs after 30 h of modification with UQ2.

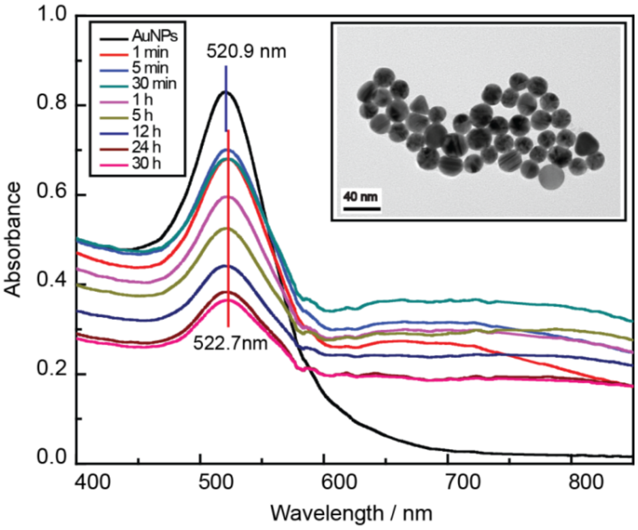


Fig. 3S UV-vis spectra of AuNPs modified with TA (1 mmol), inset shows corresponding HRTEM image of AuNPs after 30 h of modification with TA.

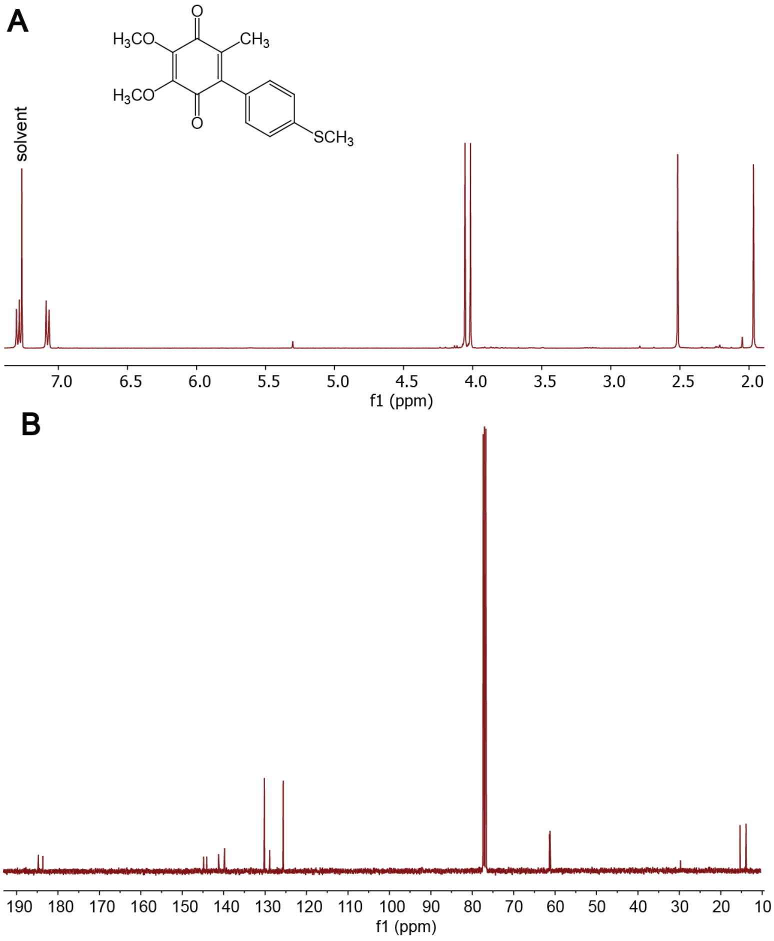


Fig. 4S ^{1}H NMR spectrum of UQ1 (A) ^{13}CNMR spectrum of UQ1 (B)

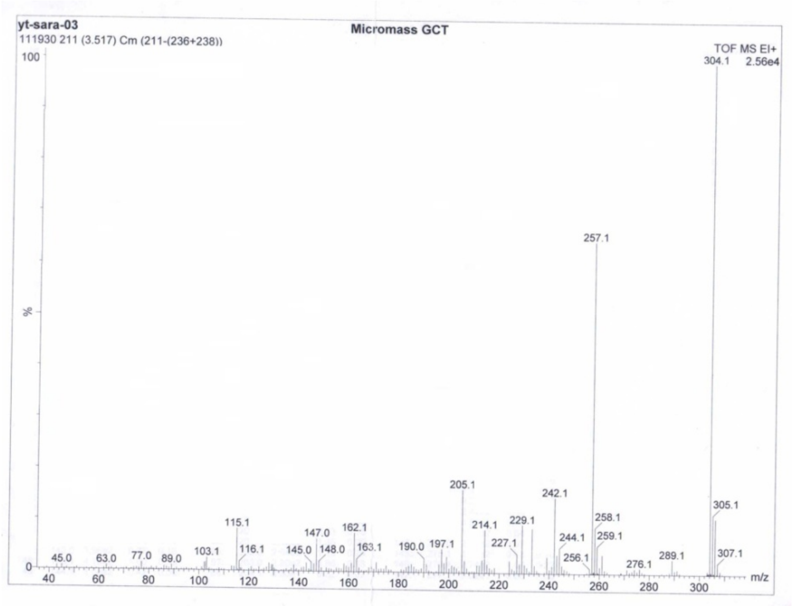


Fig. 5S Mass spectrum of compound UQ1

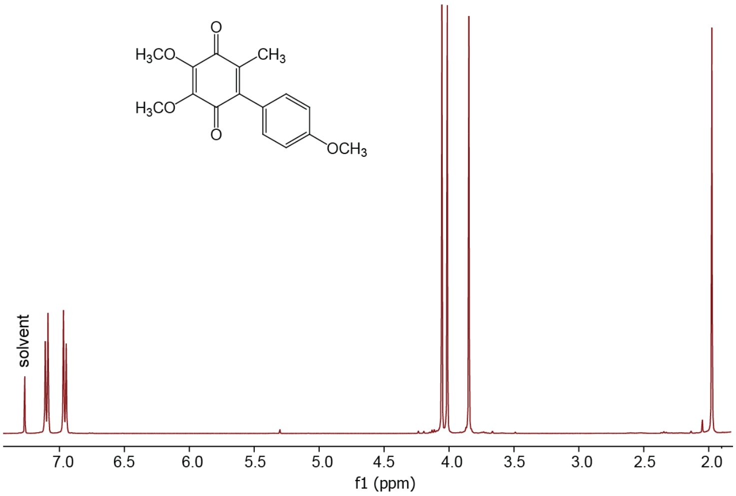


Fig. 6S ^{1}HNMR spectrum of compound UQ2

References

1. Wei-Ma, Hao Zhou, Yi-Lun Ying, Da-Wei Li, Guo-Rong Chen, Yi-Tao Long, Hong-Yuan Chen, *Tetrahedron*, 2011, **67**, 5990-6000.
2. S. Techane, D. R. Baer and D. G. Castner, *Anal. Chem*. 2011, **83**, 6704–6712.