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ARTICLE TYPE

Electronic Supplementary Information for

Novel electrochemical sugar recognition system using ruthenium complex and phenylboronic acid assembled on gold nanoparticles

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Synthesis of the complexes and ligands

Hacac-$(CH_2)_8$-I: Hacac (6.8 g, 0.068 mol), diiodoctane (25 g, 0.068 mol), and K_2CO_3 (9.4 g, 0.17 mol) were dissolved in 100 cm^3 of acetone dried over 3A molecular sieves and refluxed for 72 h. Evaporation of the solvent provided a yellow oily substance. Yield: 63.2% (14.5 g, 0.043 mol) EI-MS: *m/z* = 338.

$[Ru^{III}(acac)_2(acac\text{-}(CH_2)_8I)]$: $[Ru^{II}(acac)_2(AN)_2]$ (1.00 g, 2.62 mmol) and Hacac-$(CH_2)_8$-I (2.47 g, 7.30 mmol) were dissolved in 100 cm^3 of ethanol. The solution was refluxed for 5 h. Then, additional Hacac-$(CH_2)_8$-I (0.83 g, 2.45 mmol) was added and reflux was continued for 18.5 h. The crude product was purified by column chromatography (silica gel/BZ:AN = 20:1 v/v%). The second fraction was separated and dark red crystals were obtained by evaporation of the solvent. Yield: 9.77% (0.163 g, 0.256 mmol) FAB-MS: *m/z* = 636.5 (M^+).

$[Ru^{III}(acac)_2(acac\text{-}(CH_2)_8\,SH)]$: $[Ru^{III}(acac)_2(acac\text{-}(CH_2)_8I)]$ (0.163 g, 0.256 mmol) was dissolved in 20 cm^3 of acetonitrile and then 0.058 g (0.762 mmol) of thiourea was added. The solution was refluxed for 18 h. The crude product obtained by evaporation of the solvent was dissolved in a small amount of acetonitrile. Then, 20 cm^3 of water and ca. 5 cm^3 of 0.16 mol dm^{-3} KOH solution were added to the solution and the mixture was refluxed for 2 h. The crude product was purified by column chromatography (silica gel/hexane:ethyl acetate = 1:2 v/v%).The first fraction was separated and again purified by column chromatography (silica gel/hexane:ethyl acetate = 1:1 v/v%). Dark red crystals were obtained by evaporation of the solvent. Yield: 3.7% (5.15 mg, 9.45×10^{-6} mol) FAB-MS: *m/z* = 545.

Reagents

Sugars (D-fructose, D-glucose, and D-galactose) were purchased from Wako Pure Chemical Industries Ltd. For synthetic experiments, commercially available reagent grade solvents were used and dehydrated by molecular sieves before use. For the preparation of GNPs, $HAuCl_4 \cdot 3H_2O$ was used from Wako Pure Chemical Industries Ltd.

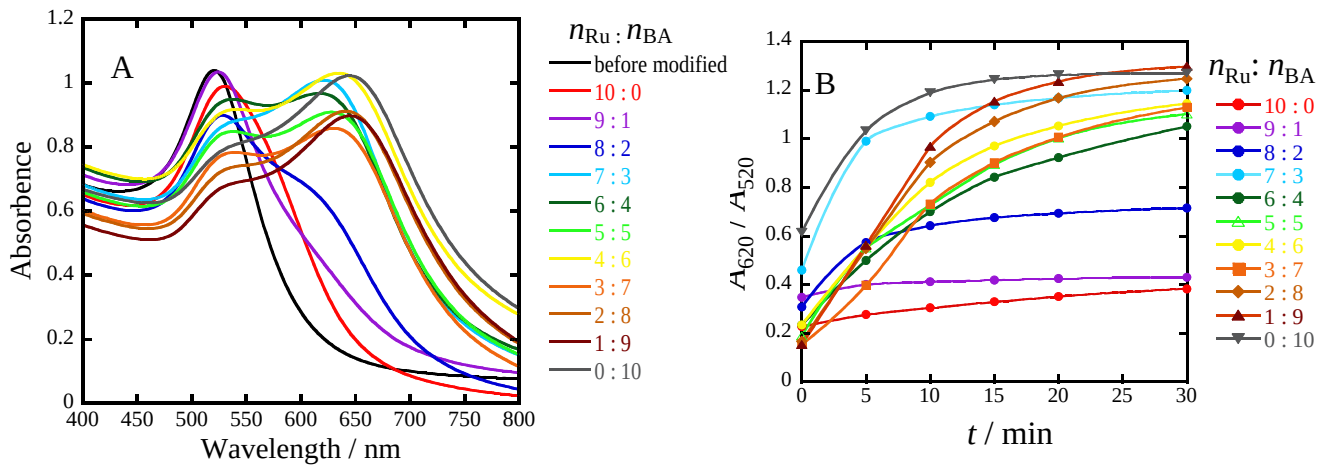

Fig. S1 A) UV-vis spectra of **GNP**s modified with various ratios of **Ru0** and **B0**. B) Time dependence of $\Delta(A_{620}/A_{520})$ of **GNP** before modification with **Ru0** and **B0** at **Ru0**:**B0** = 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10.

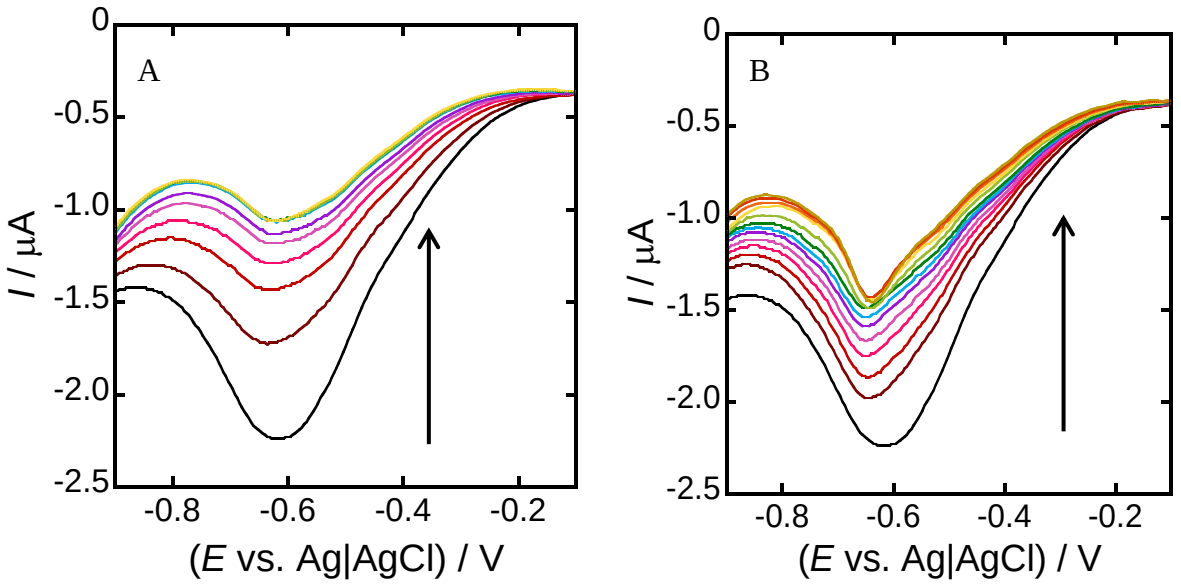

Fig. S2 DPV of **Ru8**/**B10**/**GNP** complexes in 0.1 mol dm^{-3} $NaClO_4$-(H_2O:EtOH = 3:1) at glassy carbon electrode (ϕ = 3 mm) under Ar with addition of D-fructose (A) and D-galactose (B). [D-fructose]: A; 0, 0.5, 1.0, 2.5, 5.0, 7.5,10, 25, 50 μmol dm^{-3}, B; 0, 0.5, 1.0, 2.5, 5.0, 7.5,10, 25, 50, 100, 150 μmol dm^{-3}.

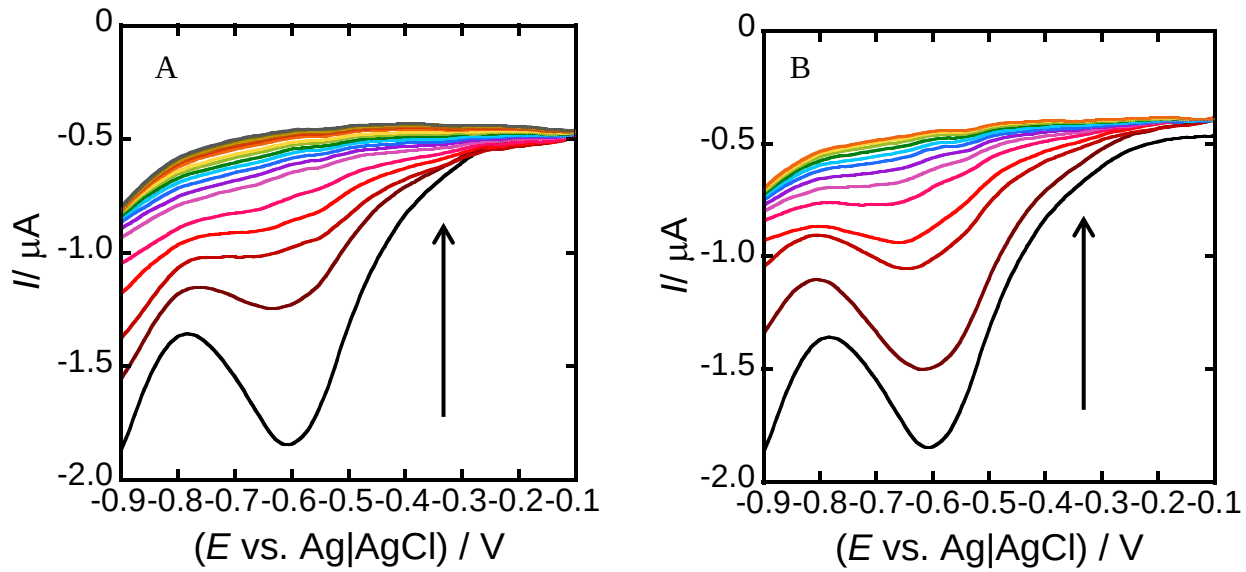

Fig. S3 DPV of **Ru0**/**B0**/**GNP** complexes in 0.1 mol dm^{-3} $NaClO_4$-(H_2O:EtOH = 3:1) at a glassy carbon electrode (ϕ = 3 mm) under Ar upon the addition of D-fructose (A) or D-galactose (B). [D-fructose]: A; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100, 150, 250, 500 μmol dm^{-3}, B; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100, 150, 250, 500 μmol dm^{-3}.

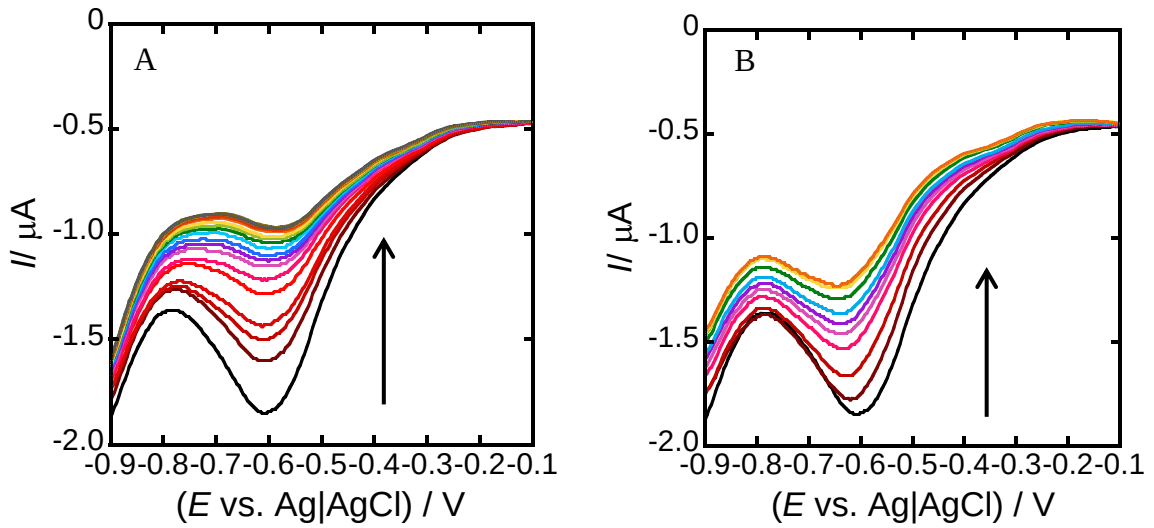

Fig. S4 DPV of **Ru0**/**B10**/**GNP** complexes in 0.1 mol dm^{-3} $NaClO_4$-(H_2O:EtOH = 3:1) at a glassy carbon electrode (ϕ = 3 mm) under Ar upon the addition of D-fructose (A) or D-galactose (B). [D-fructose]: A; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100, 150, 250, 500, 750 μmol dm^{-3}, B; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100 μmol dm^{-3}.

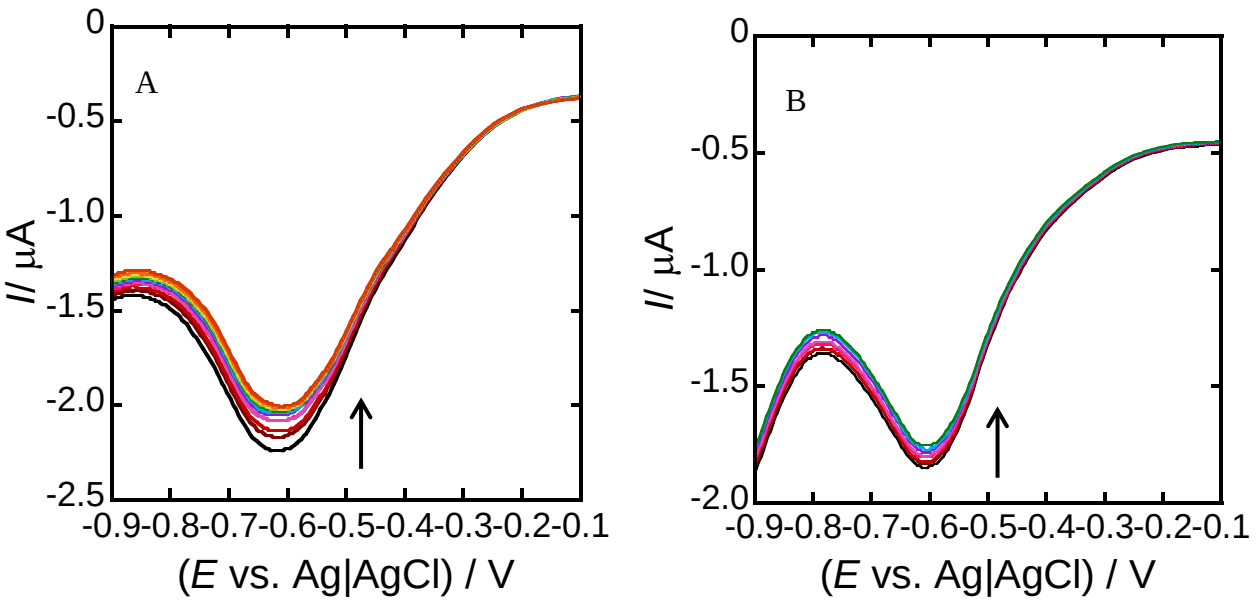

Fig. S5 DPV of **Ru8**/**B0**/**GNP** complexes in 0.1 mol dm^{-3} $NaClO_4$-(H_2O:EtOH = 3:1) at a glassy carbon electrode (ϕ = 3 mm) under Ar following the addition of D-fructose (A) or D-galactose (B). [D-fructose]: A; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100, 150, 250 μmol dm^{-3}, B; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100, 150, 250 μmol dm^{-3}.

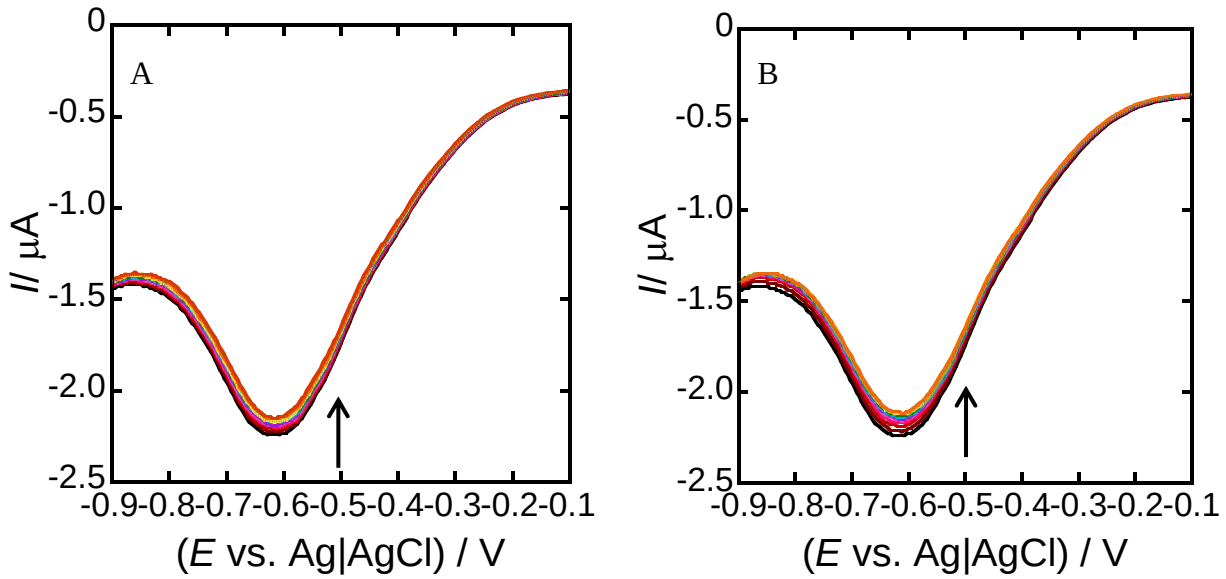

Fig. S6 DPV of **Ru8**/**GNP** complexes in 0.1 mol dm^{-3} $NaClO_4$-(H_2O:EtOH = 3:1) at a glassy carbon electrode (ϕ = 3 mm) under Ar following the addition of D-fructose (A) or D-galactose (B). [D-fructose]: A; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100, 150, 250 μmol dm^{-3}, B; 0, 0.5, 1.0, 2.5, 5.0, 7.5, 10, 25, 50, 100, 150, 250 μmol dm^{-3}.

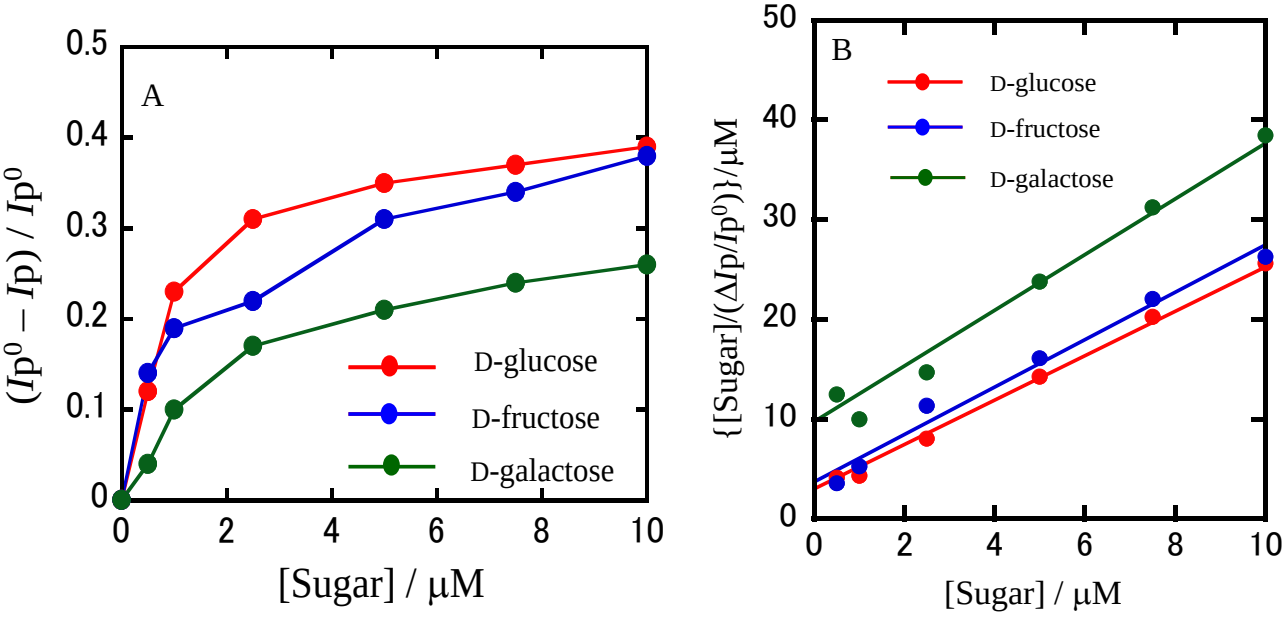

Fig. S7 A plot of {(Ip^0 – Ip)/Ip^0 *vs.* [Sugar] (A) and a plot of {[Sugar]/($\Delta Ip/Ip^0$)} *vs.* [Sugar] (B) for the **Ru0**/**B10**/**GNP** complex

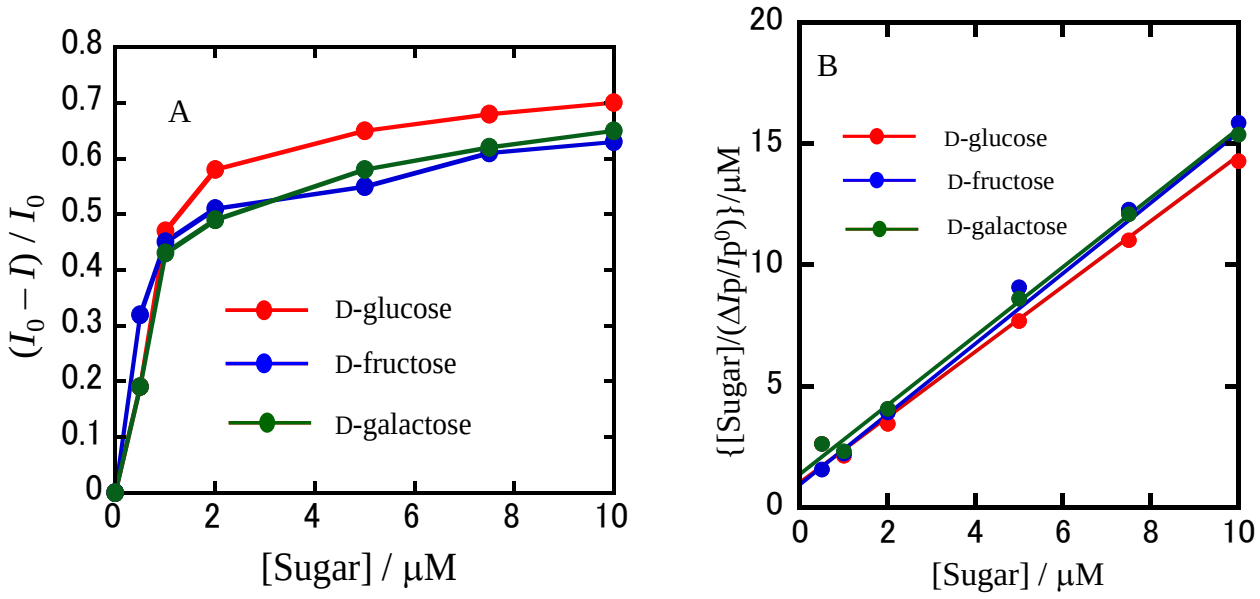

Figure S8. A plot of {($Ip^0 - Ip$)/Ip^0 *vs.* [Sugar] (A) and a plot of {[Sugar]/($\Delta Ip/Ip^0$)} *vs.* [Sugar] (B) for the **Ru0/B0/GNP** complex

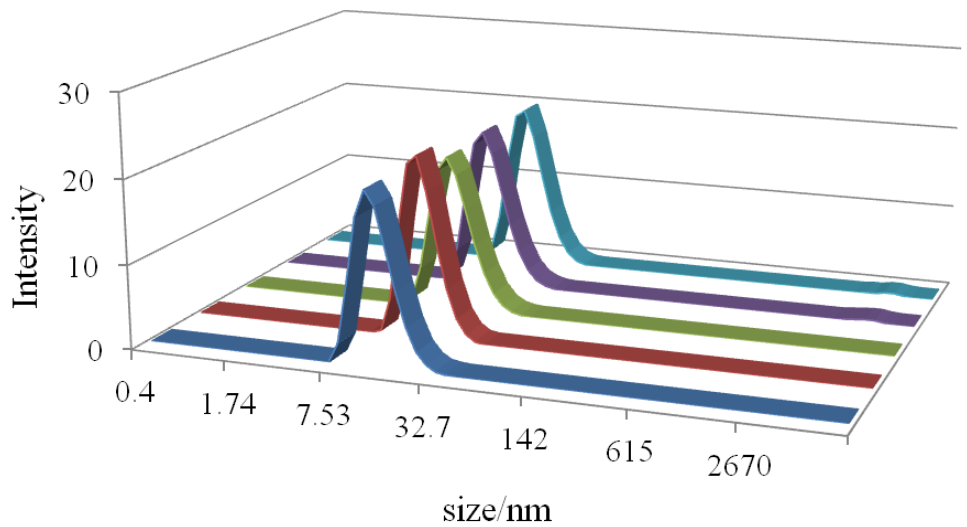

Fig. S9 Particle diameter measurement of gold nanoparticles by DLS by using Zetasizer Nano-ZS (Malvern Instrument Ltd.).