Supplementary Material (ESI) for Green Chemistry
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Aerobic Oxidative Esterification of Alcohols Catalyzed by Polymer-incarcerated Gold Nanoclusters under Ambient Conditions

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Electronic Supporting Information

1. General: JEOL JMN-LA400 spectrometer was used for NMR measurment. Tetramethylsilane ($\delta = 0$) was used as an internal standard for ^{1}H NMR and $CDCl_3$ ($\delta = 77.0$) for ^{13}C NMR. The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literature. ICP analysis was performed on Shimadzu ICPS-7510 equipment. GC analysis was performed on Shimadzu GC-2010 apparatus (Column = GL Science, TCWAX, 0.25 mm ID, 0.25 μm, 60.0 m; Gas pressure: 214.2 kPa; Total flow: 90.6 mL/min; Column flow: 1.86 mL/min; Velocity: 30.8 cm/sec; Purge flow: 3.0 mL/min; Sprit ratio: 46.0; Injector: 250 °C, FID: 250 °C; Column program: starting from 50.0 °C, 10 min hold, 10 °C/min to 220 °C, 5 min hold). The structures of the known compounds were confirmed by comparison with commercially available compounds or literature data. STEM images were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All STEM specimens were prepared by placing a drop of the solution on carbon-coated Cu grids and allowed to dry in air (without staining). MeOH was purchased from Wako Pure Chemical Company. Purchased MeOH was left in a cap opened bottle over 1 day to afford MeOH (wet). Purchased MeOH was distilled over Na and dried over MS3A to afford MeOH (dried or without notes). Other solvents were purchased in dried grade from Wako Pure Chemical Company and used as is. $AuClPPh_3$ was purchased from Strem Chemical Inc. $NaBH_4$ was purchased from Wako Pure Chemical Company and recrystallized from diglyme by heating according to the literature[1] and stored in a glove box. It is important to manipulate all operations under Ar atmosphere during recrystalization. Activity of catalyst and reproducibility are highly influenced by the purity and condition of $NaBH_4$ in the course of catalyst preparation.

2. Preparation of PI Au[2]

2-1. Preparation of 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol: To sodium hydride (60% in mineral oil, 5.7 g) suspended in THF (150 mL), tetraethyleneglycol (22.5 g) was added at 0 °C. After the reaction mixture was stirred for 20 min at room temperature, 1-(chloromethyl)-4-vinylbenzene (13.3 g) was added and the mixture was further stirred for 2 h. The mixture was cooled to 0 °C and diluted with diethyl ether. Saturated aqueous ammonium chloride was added to quench the reaction and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chromatography to afford 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol ether (21.6 g, 79.7%). ^{1}H NMR ($CDCl_3$) $\delta = 2.55\text{-}2.59$ (m, 1H), 3.59-3.73 (m, 16H), 4.55 (s, 2H), 5.25 (d, 1H, $J = 6.4$ Hz), 5.53 (d, 1H, $J = 18$ Hz), 6.71 (dd, 1H, $J = 11.0, 17.9$ Hz), 7.22-7.27 (m, 3H), 7.31-7.39 (m, 2H); ^{13}C NMR $\delta = 61.8$, 69.5, 70.5, 70.69, 70.74, 72.6, 73.0, 113.8, 126.3, 128.0, 136.0, 137.1, 138.0.

2-2. Preparation of 4-Vinylbenzyl glycidyl ether: To sodium hydride (60% in mineral oil, 4.0 g) suspended in DMF (200 mL), glycidol (6.6 mL) was added at 0 °C. After the reaction mixture was stirred for 1 h at 0 °C, 1-(chloromethyl)-4-vinylbenzene (7 mL) was added and the mixture was further stirred for 5 h at room temperature. The mixture was cooled to 0 °C and diluted with diethyl ether. Saturated aqueous ammonium chloride was added to quench the reaction and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The residue was purified by flash chromatography to afford 4-Vinylbenzyl glycidyl ether (7.0 g, 74%). ^{1}H NMR ($CDCl_3$) $\delta = 2.60$ (dd, 1H, $J = 2.8, 4.8$ Hz), 2.78 (dd, 1H, $J = 4.0, 4.8$ Hz), 3.17 (m, 1H), 3.42 (dd, 1H, $J = 5.6, 11.2$ Hz), 3.74 (dd, 1H, $J = 2.8, 11.2$ Hz), 4.56 (dd, 2H, $J = 10.8, 17.6$ Hz), 7.30 (d, 2H, $J = 8.0$ Hz), 7.39 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR $\delta = 40.2$, 50.7, 70.7, 72.9, 113.8, 126.2, 127.9, 136.4, 137.0, 137.4.

2-3. Preparation of Copolymer 1: Styrene (2.1 g), 4-vinylbenzyl glycidyl ether (4.1 g), 2-(2-(2-(2-(4-vinylbenzyloxy)ethoxy)ethoxy)ethoxy)ethanol (6.0 g) and 2, 2'-azobis(4-methoxy)-2,4-dimethylvaleronitrile (181.2 mg) were combined in chloroform (11.0 mL). The mixture was stirred for 48 h at room. The resulting polymer solution was slowly poured into ether. The precipitated polymer was filtered and washed with ether several times and dried *in vacuo* to afford the desired copolymer (**1**, 6.86 g, 56 % yield). The molar ratio of the components was determined by ^{1}H NMR analysis (*x: y: z* = 29: 35: 36).

2-4. Preparation of PI-Au: Copolymer **1** (800.0 mg) and $NaBH_4$ (13.0 mg) were dissolved in diglyme (12 mL) at room temperature, to this solution was slowly added chlorotriphenylphosphine gold (I) (32.0 mg) with 2 mL of diglyme, then the solution turned wine red. The mixture was stirred for 3 h at room temperature and diethyl ether (50 mL) was slowly added to the mixture at room temperature. Brown coaservates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethyl ether several times and dried at room. Next, the catalyst capsules were heated at 150 ˚C for 4 h without solvent to prepare wine red solid. Thus prepared solid was washed with dichloromethane and water, crashed and dried to afford wine red powder. This powder was heated at 150 ˚C for 5 h without solvent to afford PI-Au. PI Au (10-20 mg) was heated in mixture of sulfuric acid and nitric acid at 200 ˚C, the mixture was cooled to room temperature and aqua regia was added. The amount of gold in the resulting solution was measured by ICP analysis to determine the loading of gold.

3. Typical images of PI-Au

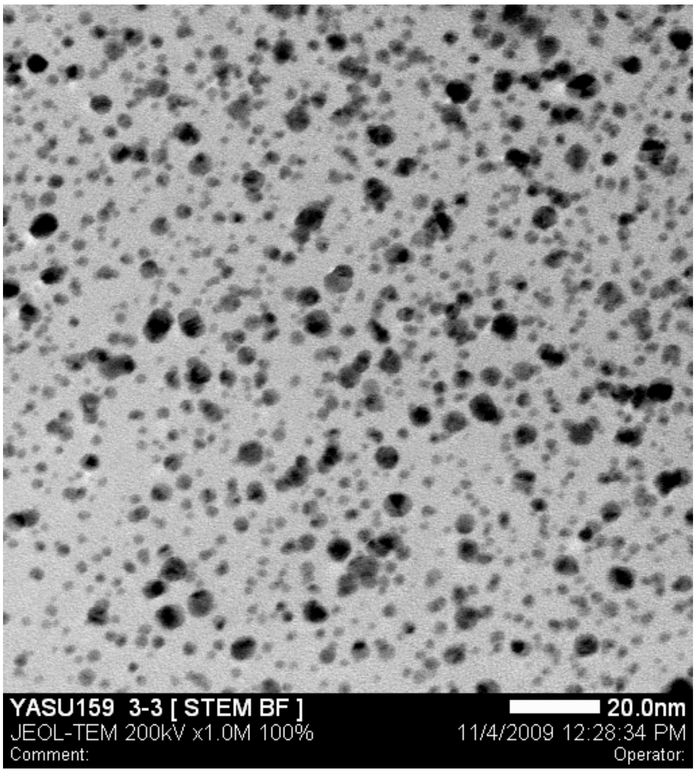

Figure S-1. PI-Au before use.

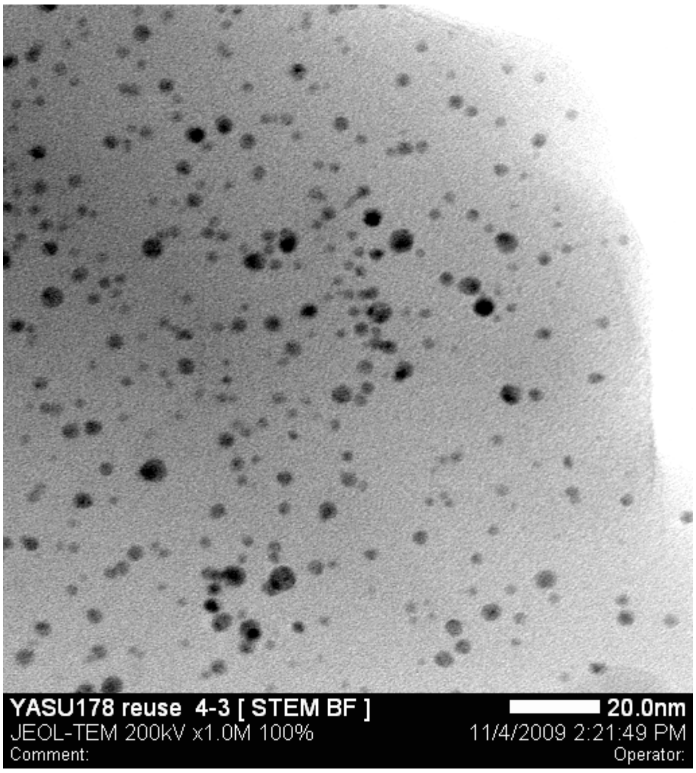

Figure S-2. PI-Au after 10th use (Table 3, Run10).

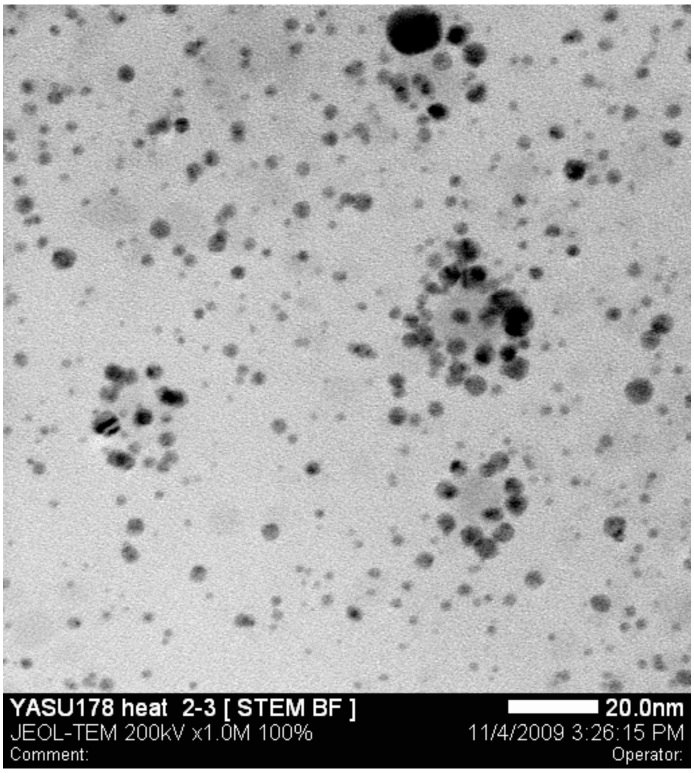

Figure S-3. PI-Au after 10th use (Table 3, Run10) then heated at 170 ˚C for 4 h.

4. Esterification in methanol catalyzed by PI-Au

4-1. A typical procedure for aerobic oxidation of alcohols catalyzed by PI-Au: *p*-Methyl benzyl alcohol (30.5 mg, 0.25 mmol), K_2CO_3 (17.3 mg, 0.125 mmol) , PI-Au (0.072 mmol/g, 1 mol%), methanol (2.0 mL), and water (4 μL) were combined in a round-bottomed flask. After the mixture was for 24 h under O_2 atmosphere at room temperature, the catalyst was collected by filtration and washed with dichloromethane using KIRIYAMAROHTO® funnel. The aqueous layer was added to brine (40 ml) and the whole aqueous layer was extracted with dichloromethane (20~30 mL). The yield was determined by GC analysis with reference to an internal standard (IS = anisole).

4-2. Recovery and reuse of PI-Au (Table 3, entry 7): *p*-Methyl benzyl alcohol (18.8 mg, 0.15 mmol), K_2CO_3 (9.8 mg, 0.07 mmol), PI-Au (0.057 mmol/g, 1 mol%), methanol (1.2 mL), and water (2.5 μL) were combined in a round-bottomed flask. After the mixture was stirred for 24 h under O_2 atmosphere at room temperature, the catalyst was collected by filtration and washed with dichloromethane using KIRIYAMAROHTO® funnel. The aqueous layer was added to brine (40 ml), and the whole aqueous layeer was extracted with methylene chloride (20~30 mL). The yield was determined by GC analysis with reference to an internal standard (IS = anisole). The filtered catalyst was dried *in vacuo* and heated at 170 °C for 4 h without solvent under atmospheric air conditions. The catalyst (24.8 mg) was collected. (Ca. 1-3 mg of catalyst was trapped by filtration paper in every use.)

4-3. Reaction profiles of oxidation of *p*-methyl benzyl alcohol catalyzed by PI-Au: *p*-Methyl benzyl alcohol (152.6 mg, 1.25 mmol), K_2CO_3 (86.3 mg, 0.62 mmol) , PI-Au (0.057 mmol/g, 1 mol%), anisole (98.2 mg) as an internal standard, methanol (10 mL), and water (20 μL) were combined in a round-bottomed flask and were stirred under O_2 atmosphere at room temperature. On each time, approximately 20 mL of the reactant was taken out from the reactor to a microtube by microsyringe through a septum fitted with the reactor. The microtube to which brine (0.5 ml) and diethyl ether (0.5 ml) were added was shaken. Then, the ether layer was taken for GC analysis. The yields of the starting material, *p*-tolualdehyde and *p*-toluic acid methyl ester were plotted against the reaction time (Figure 1a). The natural logarithm of density of the starting material was plotted against the reaction time (Figure S-4). The rate constant was determined from gradient of analogous curve.

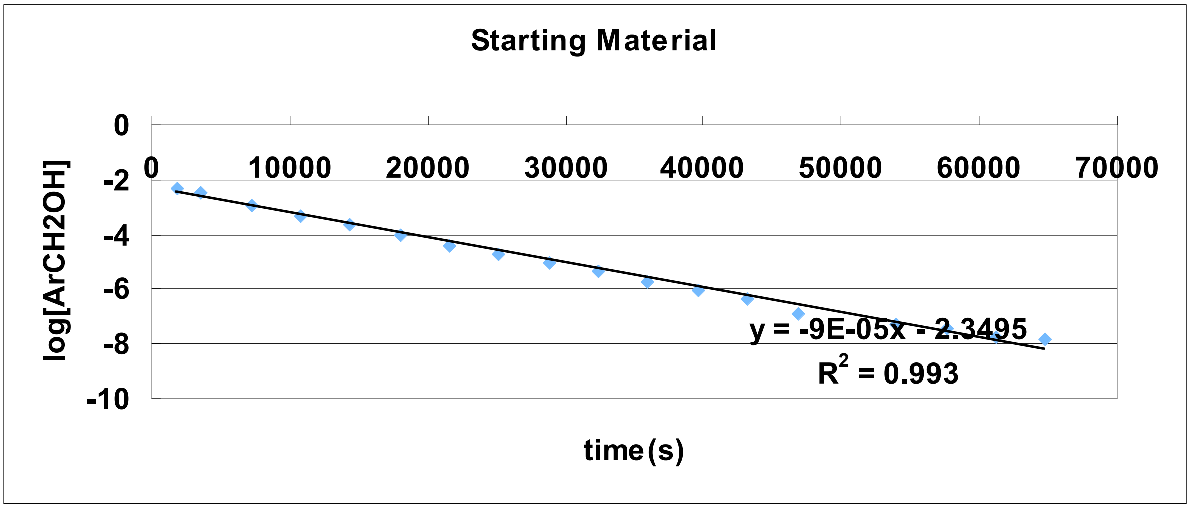

Figure S-4

4-4. NMR spectrum of a reaction system in deuterium solvent: Tolualdehyde (29.4 mg, 0.25 mmol), K_2CO_3 (17.7 mg, 0.125 mmol), CD_3OD (2.0 mL), and D_2O (4 μL) were combined in a round-bottomed flask. After the mixture was stirred for 1 h in air at room temperature, NMR spectrum of the reaction solution was taken (Figure S-5).

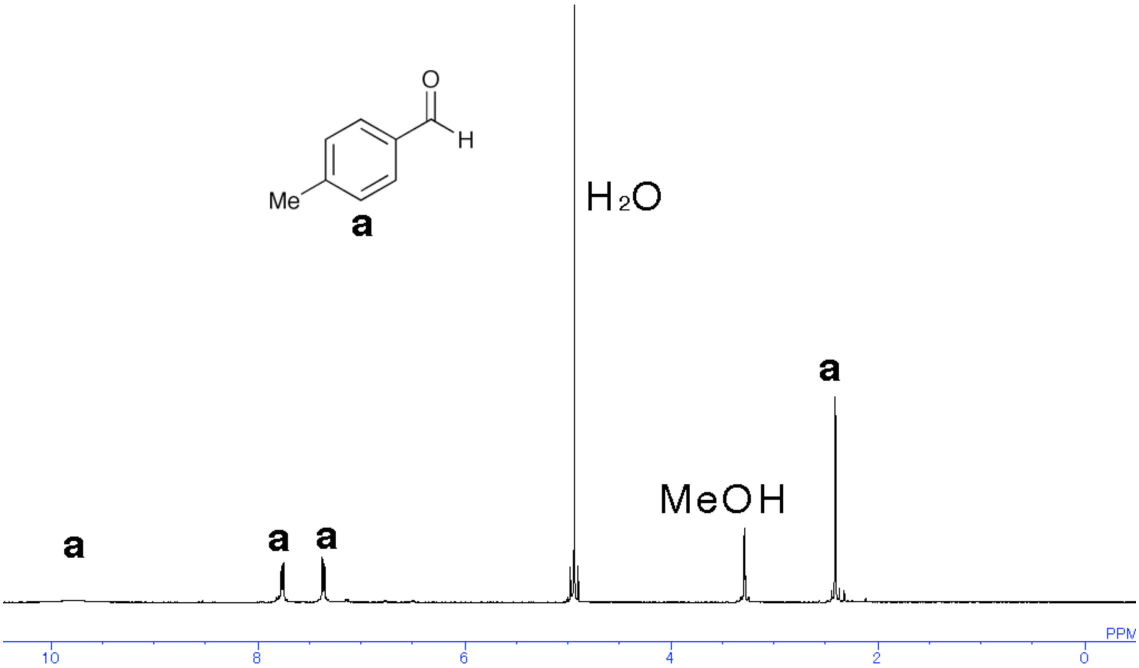

Figure S-5

References

1) H. C. Brown, E. J. Mead, B. C. S. Rao, *J. Am. Chem. Soc.* 1955, **77**, 6209.

2) H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi, *Angew. Chem., Int. Ed.* 2007, **46**, 4151.