Syntheses of the Novel Acidic and Basic Ligands and Superlattice Formation from Gold Nanoparticles through Interparticle Acid–Base Interaction

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Novel acidic or basic aryl-alkyl disulfides having phenol, benzoic acid, benzenesulfonic acid, aniline, and benzylamine groups were synthesized as protective agents for gold (Au) nanoparticles. Monodisperse Au nanoparticles passivated by these ligands were prepared using a chemical reduction technique, and self-assembled into well-ordered hexagonal close-packed (hcp) 2D superlattices on the substrate. We also present, for the first time, the formation of an aggregated multilayer of Au nanoparticles at a water–organic solvent interface by mixing separately synthesized acidic and basic Au nanoparticles. This film was definitely different from those obtained by the LB method and the conventional self-assembly method through solvent evaporation.

Chemical techniques for the preparation and size separation of organically protected metal[1–3] and semiconductor nanoparticles[4,5] have advanced rapidly over the past several years. Such nanoparticles can serve as building blocks for the creation of extended one-,[6–8] two-,[9–15] and three-dimensional[16,17] systems. Recently, two- and three-dimensional superlattices of Au and Ag nanoparticles have attracted the attention of many scientists concerning their collective electronic[18,19] and optical properties.[20,21] In such systems, the interparticle spacings[20] and periodicity[22] within the superlattices are the key determinant to control their physical properties. An acid–base interaction has been effectively used to control both the interparticle spacings and periodicity of metal nanoparticle superlattices. The acid–base mediated fabrication of ordered monolayers of Au cluster compounds was first reported by Schmid's group.[23] They utilized a strong attractive interaction between sulfonic groups on cluster surfaces and polyelectrolytes containing imino groups on a substrate to promote the self-assembly of the acidic $[Au_{55}\{PPh_2(m\text{-}C_6H_4SO_3Na)_{12}\}Cl_6]$ on a mica surface coated with poly(ethylenimine). Rotello's group has employed poly(amidoamine) (PAMAM) dendrimers to assemble Au nanoparticles functionalized with carboxylic acid through acid–base chemistry between the particle and the dendrimer.[24] Five kinds of PAMAM dendrimers with different generations (0, 1, 2, 4, 6) were used to achieve a monotonic increase in the interparticle spacing from 4.1 to 6.1 nm with increasing the generation of dendrimers. Recently, we demonstrated the novel concept based on an acid–base interaction for controlling the structure of Au nanoparticle superlattices.[15] The amino-functionalized Au nanoparticles as building blocks self-assembled into different symmetric 2D superlattices using some organic acids. The 2D superlattices of quasi-honeycomb and square structures were obtained by neutralizing the amino-functionalized Au nanoparticles with benzene-1,3,5-tricarboxylic acid and acetic acid, respectively. The acid–base interaction between acidic metal nanoparticles and basic ones seems to have a great potential for not only controlling the structure of superlattices, but also for fabricating the metal nanoparticle alloy structure, where the different kinds of metal nanoparticles passivated by acidic and basic ligands are controllably orientated alternatively (Fig. 1).

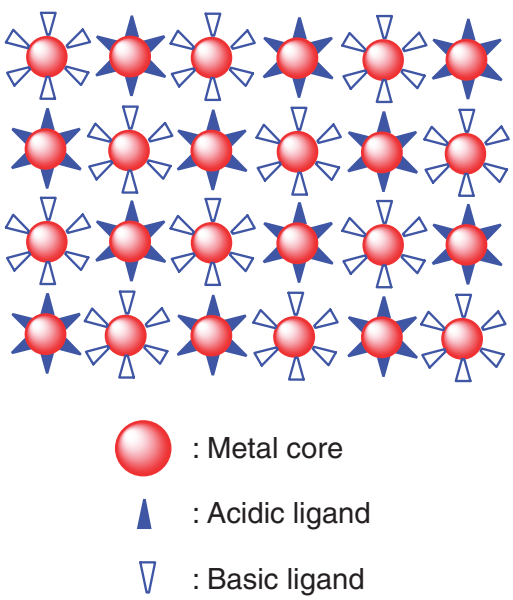

Fig. 1. Schematic illustration of acid–base interaction between acidic and basic metal nanoparticles to form the alternatively arranged superlattice.

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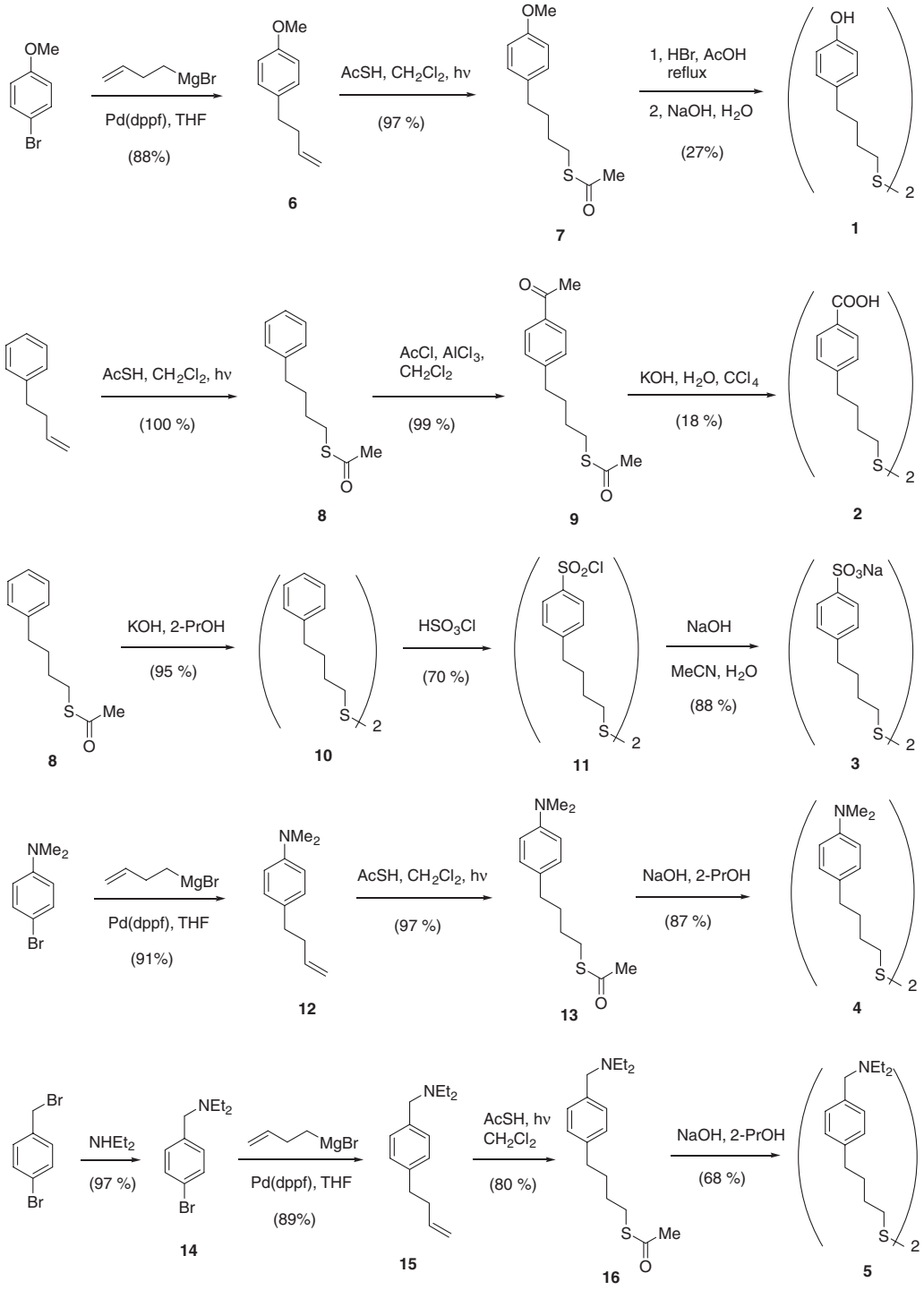
In this paper, we report on the syntheses of acidic and basic ligands having various pK_a values. Monodisperse Au nanoparticles passivated by these ligands are prepared using a chemical reduction technique, and being self-assembled into well-ordered hexagonal close-packed (hcp) 2D superlattices on a substrate. We also present, for the first time, the formation of an aggregated multilayer of Au nanoparticles at a water–organic solvent interface by mixing separately synthesized acidic and basic Au nanoparticles.

Experimental

General. The chemicals were bought from Sigma-Aldrich, Wako Pure Chemicals, Kanto Kagaku, and Tokyo Chemical Industry and used without further purification, unless otherwise noted.

Syntheses of Acidic and Basic Ligands. Various acidic (**1**–**3** in Scheme 1) and basic (**4**, **5** in Scheme 1) ligands were synthesized as follows:

(4-But-3-enyl)anisole (6). To a dispersion of *p*-bromoanisole (3.0 g, 16.0 mmol) and [$PdCl_2$(dppf)] (dppf: bis(diphenylphos-



Scheme 1.

phino)ferrocene) (392 mg, 0.48 mmol) in dried THF (50 mL), a dried THF solution (50 mL) of 4-butenylmagnesium bromide (35.3 mmol) prepared from magnesium and 4-bromobutene was added dropwise at room temperature; the solution was then refluxed for 3 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was washed with a dilute aqueous NH_4Cl solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, hexane:dichloromethane = 2:1) to give **6** (2.30 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, 2H), 6.83 (d, 2H), 5.85 (m, 1H), 5.00 (m, 2H), 3.79 (s, 3H), 2.65 (t, 2H), 2.34 (q, 2H). GC–EI-MS 162 (M^+).

***S*-4-(4-Methoxyphenylbutyl) Thioacetate (7).** A mixture of **6** (2.20 g, 13.6 mmol) and thioacetic acid (1.24 g, 16.3 mmol) in dichloromethane (50 mL) was irradiated with a 450 W medium-pressure mercury lamp for 1.5 h. After removing the solvent under a vacuum, dichloromethane was added, and the mixture was washed with saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, hexane:ethyl acetate = 2:1) to give **7** (3.14 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, 2H), 6.80 (d, 2H), 3.77 (s, 3H), 2.87 (t, 2H), 2.55 (t, 2H), 2.30 (s, 3H), 1.61 (m, 4H). GC–EI-MS 238 (M^+).

Bis[4-(4-hydroxyphenyl)butyl] Disulfide (1). An acetic acid (20 mL) solution of **7** (2.0 g, 8.4 mmol) and conc. HBr (8.0 mL, 74 mmol) was refluxed under ambient condition for 2 h. After removing the solvent under a vacuum, a 6 M aqueous NaOH solution was added, and the mixture was washed with dichloromethane. The aqueous solution was then stirred under ambient condition at room temperature for 60 h. After adding sulfuric acid to the solution, the product was extracted with dichloromethane, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, dichloromethane:ethyl acetate:methanol = 100:10:1) to give **1** (0.42 g, 27%) as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, 4H), 6.74 (d, 4H), 5.17 (s, 2H), 2.66 (t, 4H), 2.54 (t, 4H), 1.67 (m, 8H). DI-EI-MS 362 (M^+).

***S*-4-Phenylbutyl Thioacetate (8).** A mixture of 4-phenyl-1-butene (4.40 g, 33.3 mmol) and thioacetic acid (3.81 g, 50.0 mmol) in dichloromethane (50 mL) was irradiated with a 450 W medium-pressure mercury lamp for 30 min. After removing the solvent under a vacuum, dichloromethane was added, and the mixture was washed with a saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, hexane:ethyl acetate = 1:1) to give **8** (7.03 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (t, 2H), 7.16 (d, 3H), 2.88 (t, 2H), 2.62 (t, 2H), 2.31 (s, 3H), 1.64 (m, 4H). GC–EI-MS 208 (M^+).

***S*-4-(4-Acetylphenylbutyl) Thioacetate (9).** After trichloroaluminum anhydride (2.82 g, 21.1 mmol) was dissolved with dry dichloromethane (20 mL), the mixture was cooled to 0 °C with an ice-water bath. Acetyl chloride (0.9 g, 11.5 mmol) was added to the solution, and the mixture was stirred at 0 °C for 10 min. To the solution, **8** (2.0 g, 9.60 mmol) was added dropwise within 10 min at 0 °C, and the solution was contentiously stirred at 0 °C for 3 h. Water (10 mL) was carefully added dropwise to the solution, and 6 M sulfuric acid (10 mL) was then added to dissolve the aluminum hydroxide. The solution was extracted with dichloromethane, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, dichloromethane:ethyl acetate = 100:1) to give **9** (2.39 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H), 7.23 (d, 2H), 2.89 (t, 2H), 2.68 (t, 2H), 2.58 (s, 3H), 2.32 (s, 3H), 1.65 (m, 4H). GC–EI-MS 250 (M^+).

Bis[4-(4-carboxyphenyl)butyl] Disulfide (2). To a mixture of tetrachloromethane (20 mL) and potassium hydroxide (10 g) in water (20 mL), **9** (1.80 g, 7.19 mmol) was added, and the solution was vigorously stirred for 12 h at room temperature. The organic phase was removed, and sulfuric acid was then added to the water phase. The resulting precipitate was filtered off, washed with water and hexane to give **2** (270 mg, 18%). ^{1}H NMR (300 MHz, CD_3OD) δ 7.96 (d, 4H), 7.32 (d, 4H), 2.71 (m, 8H), 1.73 (m, 8H). DI-EI-MS 418 (M^+).

Bis(4-phenyl)butyl] Disulfide (10). 2-Propanol (20 mL) solution of **8** (3.0 g, 14.4 mmol) and KOH (660 mg, 10.0 mmol) was stirred under ambient condition at room temperature for 17 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was then washed with a diluted aqueous NaOH solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, hexane:ethyl acetate = 2:1) to give **10** (2.25 g, 95%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.18 (m, 6H), 2.66 (m, 8H), 1.71 (m, 8H). GC-EI-MS 330 (M^+).

Bis[4-(4-chlorosulfonylphenyl)butyl] Disulfide (11). Chlorosulfuric acid (8.7 g, 74.4 mmol) was added dropwise into a solution of **10** (1.23 g, 3.72 mmol) in dry dichloromethane (20 mL) under cooling with an ice-water bath; the solution was then stirred at room temperature for 1.5 h. The solution was poured into crushed ice, extracted with dichloromethane, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, dichloromethane) to give **11** (1.38 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, 4H), 7.42 (d, 4H), 2.76 (t, 4H), 2.68 (t, 4H), 1.75 (m, 8H). DI-EI-MS 526 (M^+).

Disodium Bis[4-(4-sulfonatophenyl)butyl] Disulfide (3). To an acetonitrile solution (40 mL) of **11** (1.35 g, 2.56 mmol), a sodium hydroxide (0.56 g, 14.4 mmol) aqueous solution (30 mL) was added, and the solution was then stirred at room temperature for 16 h. The solution was concentrated under reduced pressure, purified by column chromatography (ODS silica, water:methanol = 1:1) to give **3** (1.20 g, 88%). ^{1}H NMR (300 MHz, DMSO) δ 7.44 (d, 4H), 7.07 (d, 4H), 3.53 (s, 4H), 2.61 (t, 4H), 2.49 (t, 4H), 1.54 (m, 8H).

4-(4-But-3-enyl)-*N*,*N*-dimethylaniline (12). To a dispersion of *p*-bromo-*N*,*N*-dimethylaniline (2.0 g, 10.0 mmol) and [$PdCl_2$-(dppf)] (82 mg, 0.1 mmol) in dried THF (30 mL), a dried THF solution (50 mL) of 4-butenylmagnesium bromide (22.0 mmol), prepared from magnesium and 4-bromobutene, was added dropwise at room temperature. The solution was then refluxed for 6 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was washed with a dilute aqueous NH_4Cl solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, hexane:dichloromethane = 1:1) to give **12** (1.60 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, 2H), 6.68 (d, 2H), 5.86 (m, 1H), 5.00 (m, 2H), 2.89 (s, 6H), 2.61 (t, 2H), 2.33 (q, 2H). GC–EI-MS 175 (M^+).

***S*-4-(4-Dimethylaminophenyl)butyl Thioacetate (13).** A mixture of **12** (1.54 g, 8.79 mmol) and thioacetic acid (3.13 mL, 44.0 mmol) in dichloromethane (70 mL) was irradiated by a 450 W medium-pressure mercury lamp for 1.5 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was washed with a saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, dichloromethane: ethyl acetate = 10:1) to give **13** (2.15 g, 97%). ^{1}H NMR (300

MHz, $CDCl_3$) δ 7.05 (d, 2H), 6.68 (d, 2H), 2.91 (s, 6H), 2.89 (t, 2H), 2.53 (t, 2H), 2.32 (s, 3H), 1.62 (m, 4H). GC–EI-MS 251 (M^+).

Bis[4-(4-dimethylaminophenyl)butyl] Disulfide (4). A 2-propanol solution (20 mL) of **13** (1.09 g, 4.34 mmol) and NaOH (0.48 g, 12.0 mmol) was stirred under ambient condition for 34 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was washed with a dilute aqueous NaOH solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, dichloromethane:ethyl acetate = 20:1) to give **4** (0.79 g, 87%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, 4H), 6.69 (d, 4H), 2.90 (s, 12H), 2.68 (t, 4H), 2.54 (t, 4H), 1.67 (m, 8H). GC–EI-MS 416 (M^+).

4-Bromo-*N*,*N*-diethylbenzylamine (14). 4-Bromobenzyl bromide (10.0 g, 39.0 mmol) was added to diethylamine (50 mL) at room temperature, and the solution was refluxed for 1 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was then washed with dilute aqueous NaOH solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (activated alumina, ethyl acetate) to give **14** (10.0 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, 2H), 7.21 (d, 2H), 3.50 (s, 2H), 2.49 (q, 4H), 1.02 (t, 6H). GC–MS 241 (M^+).

4-(4-But-3-enyl)-*N*,*N*-diethylbenzylamine (15). To a dispersion of **14** (2.0 g, 8.3 mmol) and [$PdCl_2$(dppf)] (67 mg, 83 μmol) in dried THF (50 mL), a dried THF solution (50 mL) of 4-butenylmagnesium bromide (18 mmol), prepared from magnesium and 4-bromobutene, was added dropwise at room temperature. The solution was then refluxed for 1.5 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was washed with a dilute aqueous NH_4Cl solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, hexane:ethyl acetate = 1:1 then ethyl acetate:diethylamine = 10:1) to give **15** (1.60 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, 2H), 7.12 (d, 2H), 5.86 (m, 1H), 5.00 (m, 2H), 3.50 (s, 2H), 2.68 (t, 2H), 2.50 (q, 4H), 2.38 (q, 2H), 1.04 (t, 6H). GC–MS 217 (M^+).

***S*-[4-(4-Diethylaminomethylphenyl)butyl] Thioacetate (16).** A mixture of **15** (1.60 g, 7.36 mmol) and thioacetic acid (2.8 mL, 39 mmol) in dichloromethane (50 mL) was irradiated with a 450 W medium-pressure mercury lamp for 4 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was washed with a saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (silica gel, hexane:ethyl acetate = 1:1 then ethyl acetate:diethylamine = 100:1) to give **16** (1.73 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, 2H), 7.10 (d, 2H), 3.53 (s, 2H), 2.89 (t, 2H), 2.60 (t, 2H), 2.52 (q, 4H), 2.32 (s, 3H), 1.65 (m, 4H), 1.04 (t, 6H). GC–MS 293 (M^+).

Bis[4-(4-diethylaminomethylphenyl)butyl] Disulfide (5). A 2-propanol solution (20 mL) of **16** (1.70 g, 5.79 mmol) and KOH (0.66 g, 10.0 mmol) was stirred under ambient condition at room temperature for 26 h. After removing the solvent under a vacuum, dichloromethane was added and the mixture was washed with a dilute aqueous NaOH solution, dried over Na_2SO_4, and evaporated to concentration. The product was purified by column chromatography (activated alumina, dichloromethane:diethylamine = 100:1) to give **5** (0.98 g, 68%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, 4H), 7.10 (d, 4H), 3.53 (s, 4H), 2.68 (t, 4H), 2.61 (t, 4H), 2.51 (q, 8H), 1.70 (m, 8H), 1.04 (t, 12H). GC–MS 501 (M^+).

Preparation of Au Nanoparticles. Various acidic and basic ligand-protected Au nanoparticles were synthesized as follows:

Ligand 1-Protected Au (1–Au) Nanoparticles. Brust's two-phase reaction was modified to synthesize **1**–Au nanoparticles. To a mixture of *o*-dichlorobenzene (*o*-DCB, 30 mL), acetic acid (0.1 mL), **1** (10.0 μmol), and $HAuCl_4 \cdot 4H_2O$ (10.0 μmol) in water (15 mL), tetraoctylammonium bromide (11 mg, 20.0 μmol) was added and the mixture was vigorously stirred for 5 min. Under vigorous stirring, a $NaBH_4$ (100 μmol) aqueous solution (5 mL) was swiftly added to the solution, and continuously stirred for 30 min to obtain **1**–Au nanoparticles as a precipitate. The resulting precipitate of **1**–Au nanoparticles was filtered off, washed with water and *o*-DCB, and then dissolved into a few mL of *N*,*N*-dimethylacetamide (DMAc).

Ligand 2-Protected Au (2–Au) Nanoparticles. To a MeOH/H_2O (44 mL/1 mL) mixed solution of **2** (5.0 μmol) and $HAuCl_4 \cdot 4H_2O$ (10.0 μmol), a $NaBH_4$ (100 μmol) methanol solution (5 mL) was swiftly added under vigorous stirring. The solution was continuously stirred for 30 min to give **2**–Au nanoparticles.

Ligand 3-Protected Au (3–Au) Nanoparticles. To a MeOH/DMAc/AcOH (44 mL/1 mL/0.1 mL) mixed solution of **3** (5.0 μmol) and $HAuCl_4 \cdot 4H_2O$ (10.0 μmol), a $NaBH_4$ (100 μmol) methanol solution (5 mL) was swiftly added under vigorous stirring. The solution was continuously stirred for 30 min to give a methanol solution of **3**–Au nanoparticles. Water was added to precipitate the **3**–Au nanoparticles and the **3**–Au nanoparticles were filtered off, followed by being redispersed in methanol (2.0 mM in a concentration based on the Au atom).

Ligand 4-Protected Au (4–Au) Nanoparticles. To a DMAc solution (45 mL) of **4** (10.0 μmol) and $HAuCl_4 \cdot 4H_2O$ (10.0 μmol), $NaBH_4$ (100 μmol) methanol solution (5 mL) was swiftly added under vigorous stirring. The solution was continuously stirred for 30 min to give **4**–Au nanoparticles. Water was added to precipitate the **4**–Au nanoparticles, and the **4**–Au nanoparticles were then filtered off, followed by being redispersed in DMAc (2.0 mM in a concentration based on the Au atom).

Ligand 5-Protected Au (5–Au) Nanoparticles. To a DMAc solution (45 mL) of **5** (5.0 μmol) and $HAuCl_4 \cdot 4H_2O$ (10.0 μmol), $NaBH_4$ (100 μmol) methanol solution (5 mL) was swiftly added under vigorous stirring. The solution was continuously stirred for 30 min to give **5**–Au nanoparticles. After water was added to precipitate the **5**–Au nanoparticles, the **5**–Au nanoparticles were filtered off, followed by being redispersed in ethyl acetate (2.0 mM in concentration based on the Au atom).

Preparation of an Aggregated Network of Au Nanoparticles through an Acid–Base Interaction. To a mixture of a 2.0 mM **5**–Au ethyl acetate solution (100 μL) and water (300 μL) in a polypropylene test tube, a 2.0 mM **3**–Au methanol solution (100 μL) was added, and the mixture was vigorously shaken. An aggregated layer formed at an ethyl acetate–water interface was poured onto 100 mL of water. The resulting film was transferred onto a polyvinylformal-coated TEM grid, using a horizontal lifting method in which a TEM grid was carefully contacted horizontally with the film.

Measurements. Samples for transmission electron microscopy (TEM) were prepared by dropping Au nanoparticle solutions onto amorphous carbon-coated Cu grids. TEM images were taken at an accelerating voltage of 100 kV on a Hitachi H-7100. The particle sizes of Au nanoparticles were estimated by counting two hundred particles from TEM images. The mean interparticle spacing was obtained by a direct measurement of individual spacings within a well-ordered hcp domain. NMR (^{1}H, 300 MHz) spectra were obtained in $CDCl_3$, CD_3OD or DMSO-d_6 on a Varian 300 MHz spec-

trometer model Gemini. The chemical shifts are reported in ppm, relative to tetramethylsilane (δ 0.00). GC and DI EI-mass analyses were carried out on a Shimadzu QP-5050 mass spectrometer. UV–vis spectra were obtained on a Hitachi U-3310 spectrophotometer in the 350–800 nm range. Powder X-ray diffraction (XRD) of the Au nanoparticles was performed using Cu Kα radiation (1.540 Å) on a MAC science M18XHF-SRA.

Results and Discussion

General Remarks on Ligand Syntheses. In order to demonstrate our new concept for the formation of novel 2D nanoparticle superlattices based on the acid–base interaction, acidic (**1**–**3**) and basic (**4**, **5**) ligands of various pK_a values were synthesized. These ligands were designed to have three functional groups, that is, disulfide groups to coordinate with the surface Au atoms of the nanoparticles, benzene rings endowing solubility with Au nanoparticles, and acidic or basic groups to provide the reactive sites.

Terminal olefin **6** was synthesized using a cross-coupling reaction over a Pd catalyst between a Grignard reagent and *p*-bromoanisol (Scheme 1). The Ni(dppf)-catalyzed cross-coupling reaction failed in this case. The photo radical addition of thioacetic acid to the olefin **6** proceeded smoothly in almost equivalent yield to give thioester **7**. Since this process did not require any radical initiator reagent, the reaction was very clean and the product was easily purified by short silica-gel column chromatography. The thioester **7** was treated with boiling HBr in acetic acid; then, the auto-oxidation of thiol gave the phenol-derivative **1** in an overall yield of 23%. Thioester **8** was synthesized under the same condition as thioester **7**. Then, the standard Friedel–Crafts acylation provided acetophenone **9**. A two-phase haloform reaction in CCl_4 and aqueous KOH gave the benzoic acid-derivative **2** in an overall yield of 18%. Disulfide **10** was synthesized through mild methanolysis and auto-oxidation of thioester **8**. A subsequent chlorosulfuric acid treatment at room temperature gave sulfonyl chloride **11**, which was hydrolyzed to give **3** in an overall yield of 59%. Olefin **12** was synthesized through a cross-coupling reaction over a Pd catalyst under the same condition as that of **6**. The subsequent photo radical addition of thioacetic acid and mild alcoholysis gave aniline-derivative **4** in an overall yield of 77%. The standard substitution of *p*-bromomethylbromobenzene with diethylamine and a following similar introduction of alkyldisulfide gave the benzylamine-derivative **5** in an overall yield of 47%. In this case, two or more equivalents of thioacetic acid were required during the photo radical addition to olefin **15** due to salt formation between benzylamine and thioacetic acid. For the syntheses of aryl-alkyl disulfides, our three-step approach, that is, the cross coupling, photo radical addition of thioacetic acid, and alcoholysis, is a quite useful synthetic route.

Formation and Characterization of Au Nanoparticles. All of the Au nanoparticles protected by ligands **1**–**5** were synthesized by the chemical reduction of Au(III) to Au(0) with $NaBH_4$ as a reducing agent in the presence of 0.5–1 equivalents of ligands to Au species. The Au nanoparticles were purified with poor solvents, and then dissolved into a proper solvent to prepare a solution containing only pure Au nanoparticles. The reaction conditions, mean diameters and standard deviations of the obtained Au nanoparticles are given in Table 1.

The **1**–Au nanoparticles were synthesized using a modified Brust's method.[25] The addition of AcOH is requisite to produce monodisperse Au nanoparticles, by preventing the formation of phenolate.[26] The Au nanoparticles obtained at a molar ratio of **1**/Au = 1 were 2.1 ± 0.3 nm in size. Although the phenol-derivative **1** could be dissolved in *o*-DCB, the resulted **1**–Au nanoparticles were not soluble in both *o*-DCB and water, indicating that the nanoparticles started to precipitate when their size reached a certain diameter. This in-situ size-selective precipitation technique was quite effective for **1**–Au nanoparticles. The **1**–Au nanoparticles could be dissolved into some polar solvents, like MeOH and DMAc. When benzoic acid **2** was used as a protective ligand, the monodisperse Au nanoparticles with sizes of 2.3 ± 0.3 nm were successfully obtained at a molar ratio of **3**/Au = 0.5 in a MeOH/H_2O mixed solvent. The **2**–Au nanoparticles could be dissolved into some polar solvents, like MeOH, ethyleneglycol, and DMAc. For the sulfonate-derivative **3**, **3**–Au nanoparticles prepared at a molar ratio of **3**/Au = 0.5 in water had a mean diameter of 1.8 nm with a large size distribution, presumably because a micelle formation of the ligands in water confines the disulfide groups inside the micelles and suppresses the uniform protection of nanoparticles. For the amine-derivatives **4** and **5**, monodisperse Au nanoparticles were easily obtained in a MeOH/DMAc mixed solvent; their sizes were 2.1 ± 0.2 nm and 2.4 ± 0.2 nm, respectively. Espe-

Table 1. Reaction Conditions and Particle Sizes of the Au Nanoparticles Protected by the Ligand **1**–**5**

Ligand No.	Ligand /mmol	$HAuCl_4$ /mmol	$NaBH_4$ /mmol	Solvent /mL		Particle size /nm
1	10	10	100	*o*-DCB H_2O AcOH	30 20 0.1	2.1 ± 0.3
2	5	10	100	MeOH H_2O	49 1	2.3 ± 0.3
3	5	10	100	H_2O	50	1.8 ± 0.6
4	10	10	100	DMAc MeOH	45 5	2.1 ± 0.2
5	5	10	100	DMAc MeOH	45 5	2.4 ± 0.2

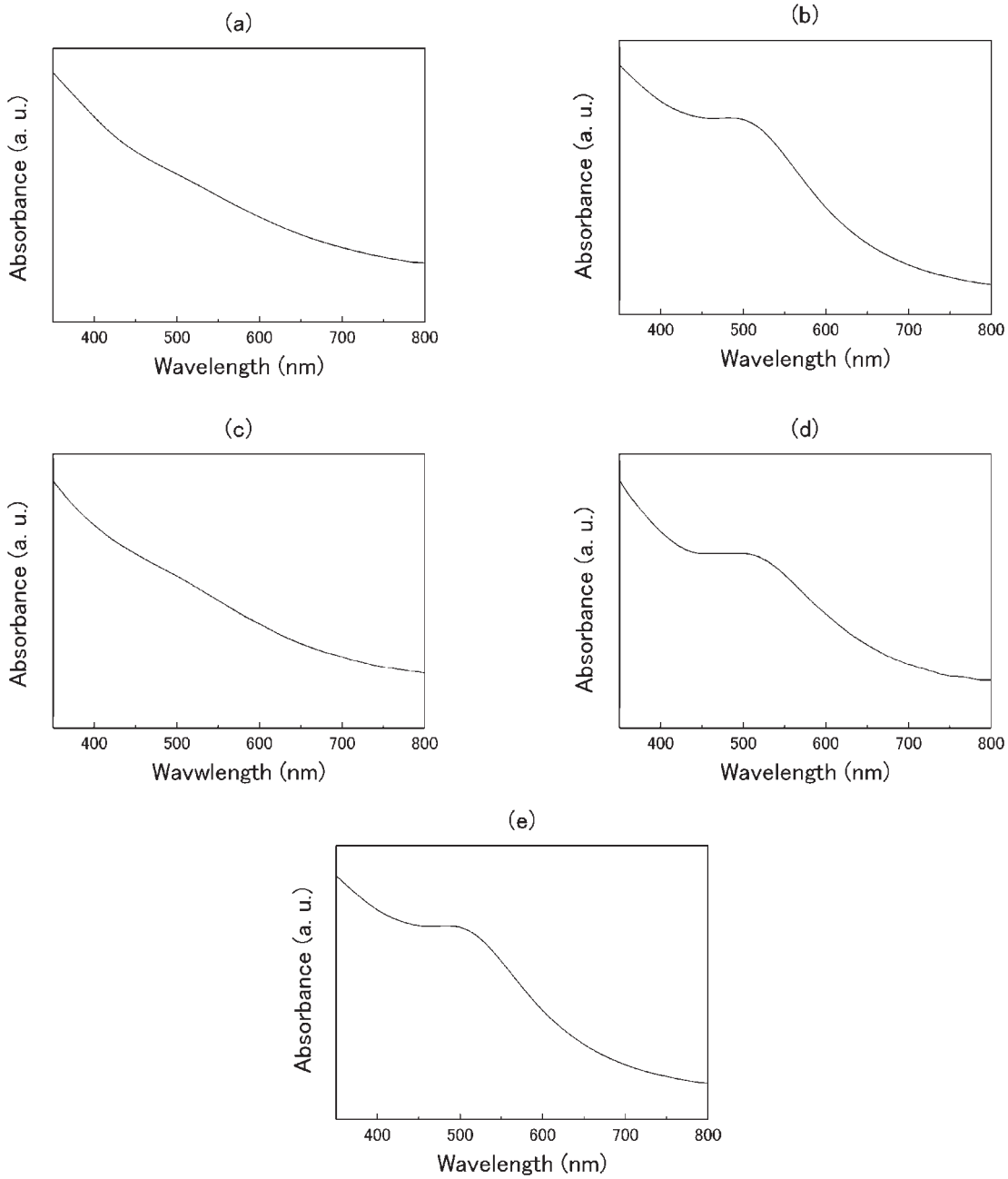


Fig. 2. UV–vis spectra of (a) **1**–Au, (b) **2**–Au, (c) **3**–Au, (d) **4**–Au, and (e) **5**–Au nanoparticles.

cially, the **5**–Au nanoparticles were highly soluble in both polar solvents, like DMAc, and non-polar solvents, like toluene.

Figure 2 shows UV–vis spectra of the Au nanoparticles. The broad tailing absorptions were observed in the range from the UV to visible regions in all cases, due to the formation of a band structure, indicating the formation of Au nanoparticles. Small surface plasmon resonances at ~520 nm were observed from all Au nanoparticles, which means the formation of very small Au nanoparticles.[27] Especially, small surface resonances of **1**–Au and **3**–Au reflect their quite small sizes. The powder X-ray diffraction patterns of **5**–Au in Fig. 3 revealed that the **5**–Au have the typical face-centered-cubic (fcc) structure for Au, and that the particle size calculated from the full width at half maximum of the (111) peak with Scherrer's equation is in good agreement with the mean diameter obtained from the TEM observation. Other Au nanoparticles were also identified to have fcc structures in a similar fashion.

Fabrication of Au Nanoparticle Superlattices. Generally, the monodisperse nanoparticles have a strong tendency to form self-assembled superstructures, so-called superlattices, during evaporation of the solvent. The solutions of Au nanoparticles were dropped on amorphous carbon-coated TEM grids, which were immediately covered with glass lids to slowly evaporate the solvent. Figure 4 shows TEM images of Au nanoparticles protected by ligands **1**, **2**, **4**, and **5**. TEM observations revealed that these monodisperse Au nanoparticles formed self-assembled hcp 2D superlattices, where the mean interparticle spacings were estimated to be ~1.4 nm in any superlattices. By taking the length of these ligand molecules to be ~1.3 nm into consideration, this result suggests that each Au nanoparticle

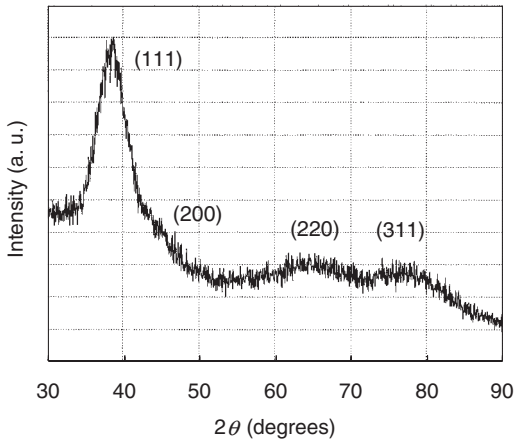


Fig. 3. XRD diffraction pattern of **5**–Au nanoparticles.

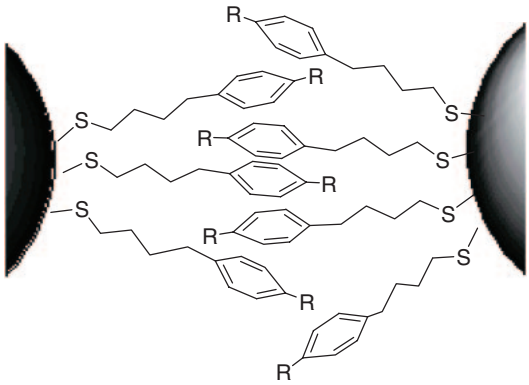


Fig. 5. Schematic illustration of interligand π–π interaction, where R stands for acidic or basic group.

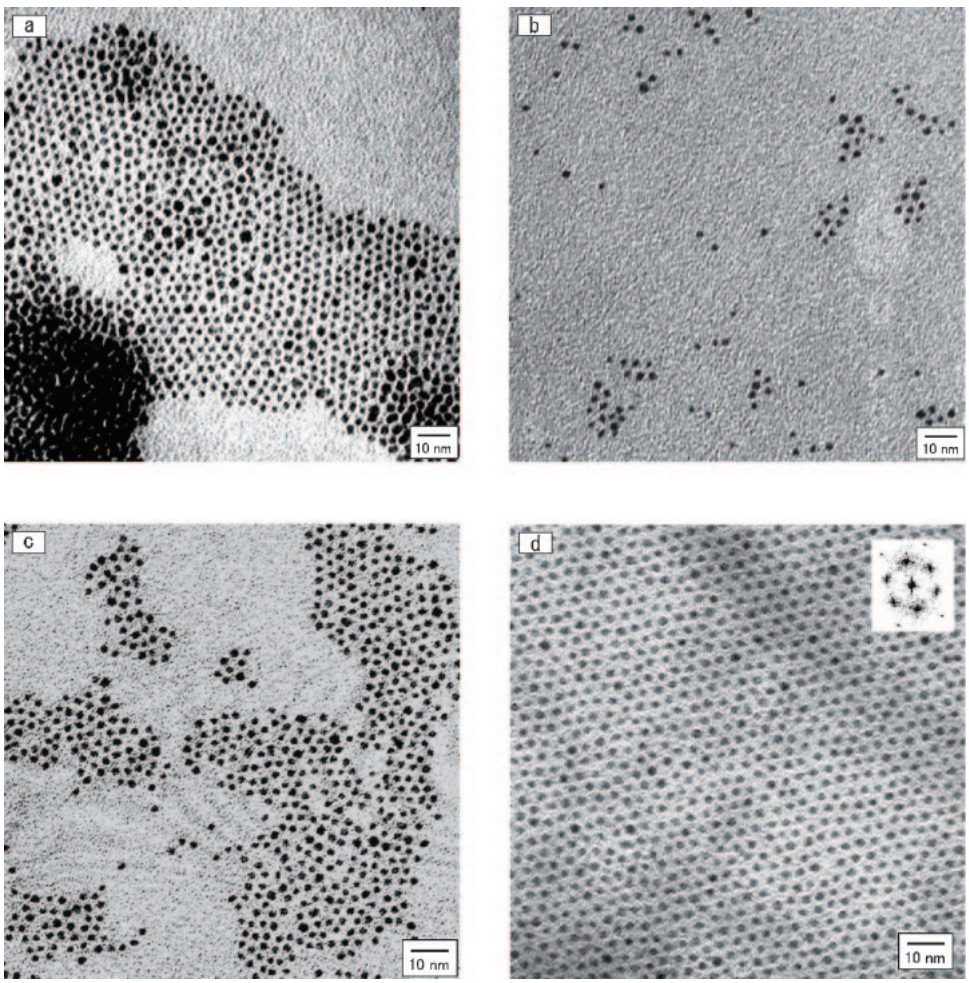


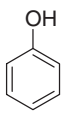
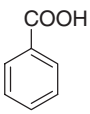
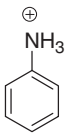
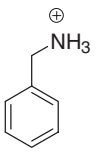
Fig. 4. TEM image of (a) **1**–Au, (b) **2**–Au, (c) **4**–Au, and (d) **5**–Au nanoparticles. The inset in (d) stands for the FFT image.

is stabilized by the ligand monolayer, and that the protective ligands are interpenetrating each other as the result of an aromatic interaction between the benzene rings of adjacent particles (Fig. 5). Actually, the interparticle spacing is estimated to be ~1.4 nm, regardless of the kind of terminal functional groups from Fig. 5, in which the alkyl chains are thought to have an all-trans conformation in the dry state.[8] Especially, we could obtain nearly perfect hcp superlattices for ligand **5**.

The pK_a values for the representative acid compounds corresponding to ligands **1**, **2**, **4**, and **5** in water are given in Table 2. In order to realize our concept involving superlattice formation through an acid–base interaction between the adjacent nanoparticles, acidic **2**–Au and basic **5**–Au nanoparticles were chosen as candidates. The pK_a values of benzoic acid (4.19) and benzylammonium cation (9.35) imply that nearly perfect salt formation can be achieved when acidic **2**–Au and basic **5**–Au

are mixed. When a methanol solution of **2**–Au nanoparticles and an ethyl acetate solution of **5**–Au nanoparticles were mixed, a black precipitate was formed, which had no solubility for any neutral solvents. When 100 μL of a 20 mM methanol solution of **2**–Au nanoparticles was added to a mixture of 100 μL of a 20 mM ethylacetate solution of **5**–Au nanoparticles and 300 μL of water, vigorous shaking of the solution led to the formation of a film consisting of an aggregation of **2**–Au and **5**–Au nanoparticles at the organic solvent–water interface. During vigorous stirring of a bi-phase mixture of an organic solvent and water, small droplets of organic solvent were formed in water, and the aggregates of **2**–Au and **5**–Au nanoparticles formed in the organic phase were gathered at the interface between water and the organic phase in order to diminish the interface free energy. The mixture was then poured into a large amount of water to place the film at an air–water interface. The film at an interface could be visibly recognized to be spread in a few cm^2 regime. The obtained film was transferred onto a polyvinylformal-coated TEM grid for a TEM observation. Figure 6 presents a representative TEM image of the film formed at an air–water interface, which indicates that the film had a widely-spread network structure consisting of a multilayer of Au nanoparticles with many defects. The inset in Fig. 6 shows a magnified image of aggregated layers. Besides the nanoparticle monolayer around the edge of the aggregate, many linear structures formed by placing the nanoparticles at two-fold saddle sites of nanoparticle underlayer were observed. Therefore, these aggregates are likely to consist of predominant bi-layers with a small number of multilayers of Au nanoparticles. The acidic **2**–Au or basic **5**–Au nanoparticles themselves surely do not form the aggregates, and moreover when the weaker acid–base interactions, except for the combination of **2**–Au and **5**–Au nanoparticles, were employed, film formation was not observed. These results strongly indicate that this film is definitely different from those obtained by the LB method and the conventional self-assembly method through solvent evaporation. This simple method would allow us to easily obtain not only conductive film of metal nanoparticles, but also an alloyed metal film containing different kinds of metal nanoparticles as novel non-linear optical materials. An investigation on the detailed structure involving whether each particle is alternatively placed within the film is in progress.

Table 2. The pK_a Values for the Representative Acidic Compounds Corresponding to the Ligands **1**, **2**, **4**, and **5** in Water

Acid compound				
pK_a	9.89	4.19	4.63	9.35

Conclusion

Here, we have reported on useful synthetic routes of various acidic and basic ligands, **1**–**5**, for Au nanoparticles. Monodisperse Au nanoparticles protected by ligands **1**, **2**, **4**, and **5** were successfully prepared through the chemical reduction of the Au ion in the presence of the ligands. These nanoparticles had a strong tendency to self-assemble into hcp 2D superlattices due to their monodispersity. When the organic solutions of acidic **2**–Au and basic **5**–Au nanoparticles were mixed with water, a film consisting of the aggregated multilayer of Au nanoparticles was easily obtained at the organic solvent–water interface by the acid–base interaction, which would enable us to construct complex patterns of different kinds of nanoparticles.

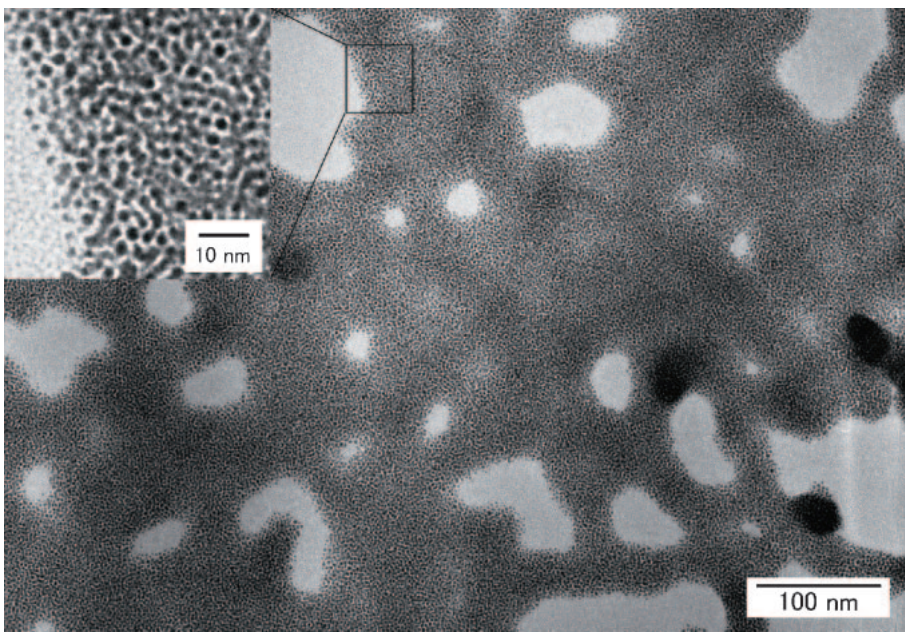


Fig. 6. TEM image of the aggregated multilayer of the **2**–Au and **5**–Au nanoparticles. The inset shows the magnified image of the aggregated multilayer.

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