This journal is (c) The Royal Society of Chemistry 2009

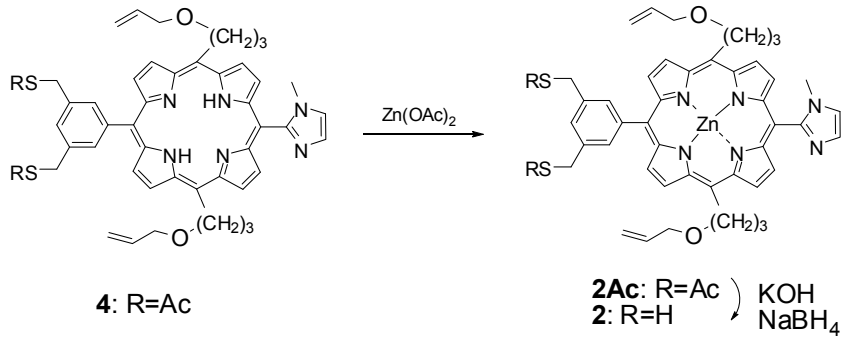
Supplementary Information

Single Supramolecular Porphyrin Wires Bridging Gold Nanoparticles

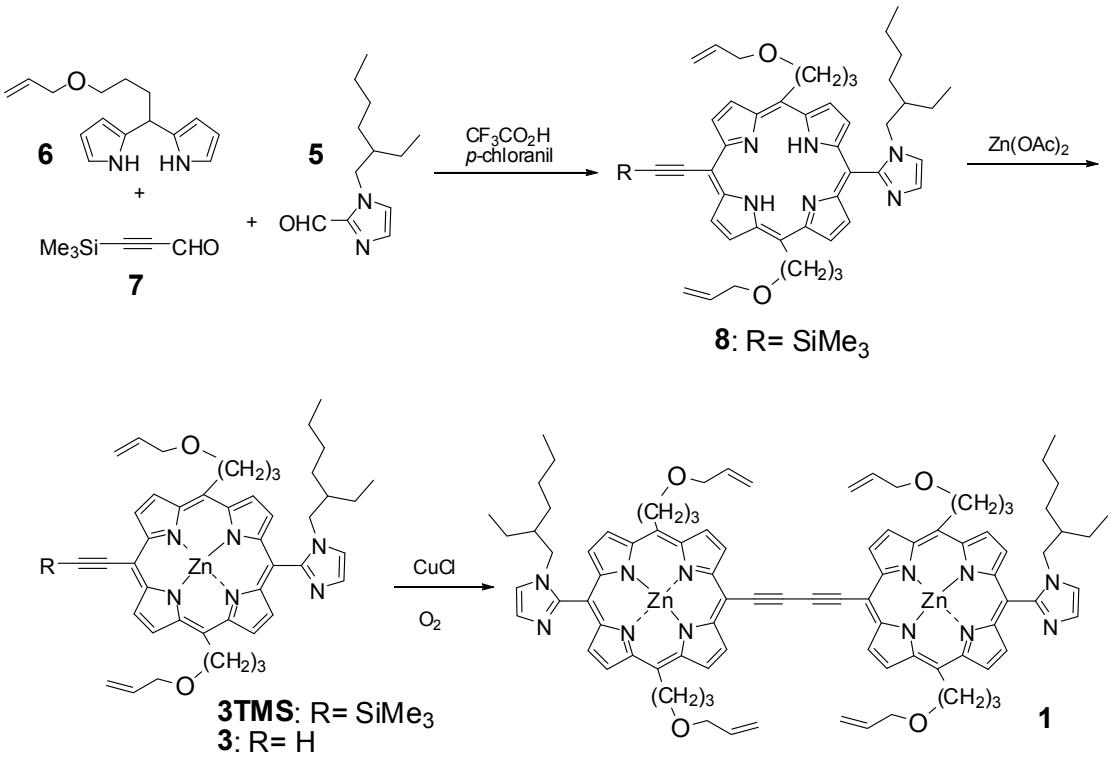
Akiharu Satake, Masakuni Fujita, Yusuke Kurimoto, and Yoshiaki Kobuke

Contents page

1. Synthetic schemes



Scheme S1. Preparation of **2**.



Scheme S2. Preparation of **1**.

2. Experimental

2.1. Syntheses of **2** and **1**.

General procedure

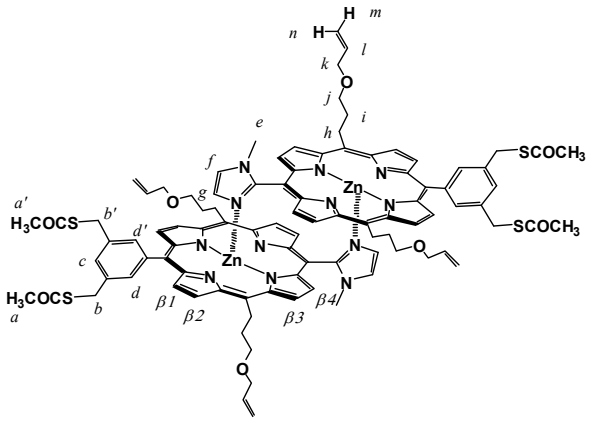
All solvents and reagents were used without further purification, except as noted below. Chloroform contained 0.5% ethanol as a stabilizer. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl radical solutions prior to use. A mixture of toluene, THF and pyridine (2:1:1 vol/vol/vol) defined as TTP solution was prepared by mixing each solvent in a flask and stirring the mixture under Ar. Triethylamine (Et_3N) was distilled from calcium hydride. NMR spectra were recorded on a JEOL Ex-270 (270 MHz) or ECP-600 (600 MHz) spectrometer in $CDCl_3$ or $(CDCl_2)_2$ with Me_4Si as an internal standard at 25°C unless otherwise noted. MALDI-TOF mass spectra were measured by Perspective Biosystems Voyager DE-STR spectrometer with dithranol as a matrix. HRMS spectra were collected by a JEOL JMS-700 for FAB method and JEOL AccuTOF (JMS-T100LC) for ESI method. UV-vis spectra were obtained from a Shimadzu UV-3100PC instrument. Fluorescence spectra were obtained from a Hitachi F-4500 instrument. Column chromatography was performed with silica gel (63-210 μm, KANTO chemical) and Aluminum oxide (activity II, 60-200 μm, basic, Merck). Flash column chromatography was performed with silica gel (40-50 μm, KANTO chemical). Gel permeation chromatography (GPC) under atmospheric pressure was carried out with Biobeads® S-X1 (BIO-RAD Lab. Inc., exclusion limit 1.4×10^4 Da) and Biobeads® S-X3 (exclusion limit 2×10^3 Da). Preparative and analytical GPC-HPLC was performed on TSK-GEL $G3000H_{HR}$ (Tosoh, exclusion limit = 6×10^4 Da) with pyridine as an eluent, and PLgel 20 μm MIXED-A column (Polymer Laboratories, exclusion limit = 4×10^7 Da) with $(CHCl_2)_2$ as an eluent. Transmission

Electron Microscope (TEM) images were obtained from a JEM-3100FEF (JEOL) on copper grids supported by elastic carbon film (Oken sho-ji, STEM100). Atomic force microscopic (AFM) images were obtained from an E-sweep+SPI4000 (SII) with dynamic force mode (DFM). Cantilever (SI-DF20, SII) and mica substrate (Nilaco) were used for the AFM measurements. A spin-coater (K-359SD-1 SPINNER, Kyowa-Riken) was used for preparation of samples. Porphyrin **4** was prepared by a similar method reported previously.[1]

*Synthesis of **2Ac***

To a solution of free base porphyrin **4** (10.6 mg, 12.6 μmol), 1 mL of methanol solution saturated by $Zn(OAc)_2$ was added. After stirring the mixture for 2 h, water was added, and the organic layer was extracted with chloroform. The chloroform layer was washed with distilled water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was reprecipitated from chloroform and hexane, and purified further by silica gel column chromatography ($CHCl_3$/acetone=10/1) to give purple solid (10.4 mg, 91%). TLC: Rf = 0.89 ($CHCl_3$/MeOH = 16/1); MALDI-TOF mass (dithranol): *m/z* 901. 7 $(M+H)^+$; HRMS (FAB, *m*-NBA as a matrix) *m/z* 901.2536 $(M+H)^+$, calcd for $C_{48}H_{49}N_6O_4S_2Zn$ 901.2548; UV-vis of dimeric **2Ac** ($CHCl_3$): λ_{max}/nm (Abs) 413.5 (0.0919), 437.5 (0.1137), 565.0 (0.0099), 619.0 (0.0065); Fluorescence of dimeric **2Ac** ($CHCl_3$) excited at 438 nm: λ_{max}/nm 624.4, 681.4; ^1H NMR of dimeric **2Ac** (600 MHz, $CDCl_3$) δ 9.65 (d, 2H, *J* = 4.4 Hz, *β1*), 9.00 (d, 2H, *J* = 4.4 Hz, *β2*), 8.96 (d, 2H, *J* = 4.4 Hz, *β3*), 8.47 (dd, 1H, *J* = 1.6, 1.4 Hz, *d'*), 7.94 (dd, 1H, *J* = 1.6, 1.4 Hz, *d*), 7.71 (t, 1H, *J* = 1.6 Hz, *c*), 6.20 (ddt, 2H, *J* = 17.2, 10.5, 5.4, *l*), 5.54 (d, 1H, *J* = 1.9 Hz, *f*), 5.53 (ddt, 2H, *J* = 17.2, 3.0, 1.6 Hz, *n*), 5.41 (d, 2H, *J* = 4.4

Hz, *β4*), 5.34 (ddt, 2H, *J* = 10.5, 1.6, 1.3 Hz, *m*), 5.25-5.21 (m, 4H, *i*), 4.61 (s, 2H, *b'*), 4.42 (s, 2H, *b*), 4.24 (ddd, 4H, *J* = 5.4, 3.0, 1.3 Hz, *k*), 3.98-3.91 (m, 4H, *h*), 3.14-2.96 (m, 4H, *j*), 2.56 (s, 3H, *a'*), 2.41 (s, 3H, *a*), 2.10 (d, 1H, *J* = 1.9 Hz, *g*), 1.68 (s, 3H, *e*).



Synthesis of ***1-(2-ethylhexyl) imidazole***

To a suspension of NaH (60% oil suspended, 1.2 g, 30 mmol) in THF (40 mL), imidazole (1.7 g, 25 mmol) was added at 0 °C. After stirring for 10 min, 1-bromo-2-ethylhexane (6.7 mL, 32.5 mmol) and potassium iodide (0.82 g, 5 mmol) were subsequently added. The mixture was refluxed for 6.5 h. Water was added to the mixture. The organic layer was extracted with ethyl acetate (50 mL × 2). The solution was adjusted to pH 1 with 3 M HCl solution. The imidazole derivatives were protonated and transferred to the aqueous layer. The organic layer was separated, and the aqueous layer was adjusted to pH 10 with solid Na_2CO_3. The imidazole derivatives were deprotonated and extracted with ethyl acetate (50 mL × 3). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($CHCl_3$/Methanol = 9/1) to give a title compound (3.99 g, 88%) as a colorless oil. TLC ($CHCl_3$/methanol = 9/1): Rf 0.5; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (s, 1H, Im_2), 7.05

(s, 1H, Im_4), 6.87 (s, 1H, Im_5), 3.82 (d, 2H, J = 6.9 Hz), 1.74-1.64 (m, 2H), 1.29-1.21 (m, 8H), 0.92-0.87 (m, 6H).

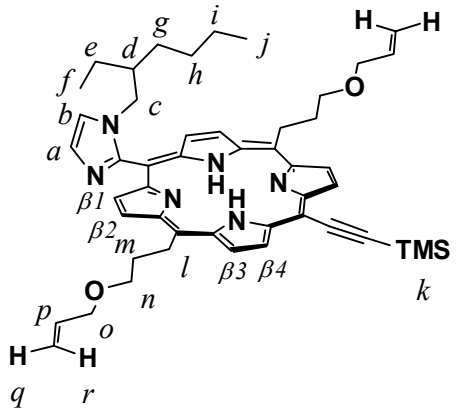
Synthesis of ***1-(2-ethylhexyl) imidazole-2-carboxaldehyde*** **5**

To a solution of ***1-(2-ethylhexyl) imidazole*** (3.0 g, 16.6 mmol) in dry THF (20 mL), *n*-BuLi (in hexane, 1.58 M, 15.8 mL, 25 mmol) was slowly added at -78 °C. After 10 min, dry DMF (3.9 mL, 49.8 mmol) was added at -78 °C. After 1 h, water was added to the mixture. The title compound was extracted, dried, and concentrated by the similar method for ***1-(2-ethylhexyl) imidazole***. The residue was distilled (39 Pa, 85 °C) to give *aldehyde* **5** (1.8 g, 52%). This sample included starting material ***1-(2-ethylhexyl) imidazole*** (3%), but this was used in the next reaction. TLC ($CHCl_3$/methanol = 9/1): Rf 0.5; ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.81 (d, 1H, J = 0.8 Hz, CHO), 7.28 (d, 1H, J = 1.0 Hz Im_4), 7.13 (s, 1H, Im_5), 4.29 (d, 2H, J = 7.4 Hz), 1.78 (ttt, 1H, J = 12.7, 5.9, 1.0 Hz), 1.34-1.17 (m, 8H), 0.89-0.87 (m, 6H).

Synthesis of **5,15-bis(3-allyloxypropyl)-10-(1-(2-ethylhexyl)-2-imidazolyl)-20-(2-trimethylsilylethynyl)porphyrin 8**

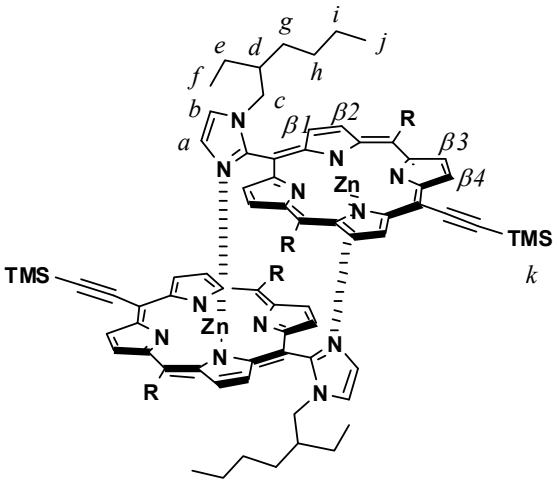
A mixture of imidazolecarboxaldehyde **5** (330 mg, 1.58 mmol) and allyloxypropyldipyrromethane[2] (772 mg, 3.16 mmol) in $CHCl_3$ (530 mL) was degassed by three freeze-pump-thaw cycles. Trimethylsilylethynal (200 mg, 1.58 mmol) was added to the mixture. Subsequently, a solution of trifluoroacetic acid (352 μL, 4.74 mmol) in $CHCl_3$ (2 mL) was added slowly to the mixture. After stirring the mixture at rt for 5 h, 1,4-chloranil (1.55 g, 6.32 mmol) was added. The mixture was stirred for 8 h. Triethylamine (658 μl, 4.74 mmol) was added for neutralization of the mixture. The

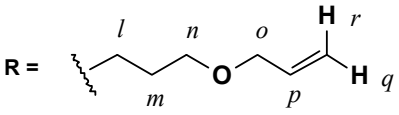
mixture was concentrated to ca. 5 mL under reduced pressure. Silica gel (ca. 3 g) was added to the mixture to be adsorbed. The mixture was dried under reduced pressure, and the residue was placed on a silica gel column chromatography. The mixture was eluted by $CHCl_3$/Acetone = 10/1. Fractions including the target compound were purified by additional two column chromatographies using Al_2O_3 (activity II, $CHCl_3$) and flash SiO_2 ($CHCl_3$/MeOH = 20/1)) to give porphyrin **8** as a purple solid (63 mg, 5.1 %). Purity was checked by TLC and ^{1}H NMR. TLC Rf = 0.70 ($CHCl_3$/MeOH = 10/1); MALDI-TOF (dithranol) *m/z* 781.5 $(M+H)^+$, calcd for $C_{48}H_{60}N_6O_2Si$ 780.5; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.74 (d, 2H, *J* = 4.7 Hz, *β4*, *β4'*), 9.52 (d, 2H, *J* = 4.7 Hz, *β3*, *β3'*), 9.43 (d, 2H, *J* = 4.4 Hz, *β2*, *β2'*), 8.76 (d, 1H, *J* = 4.4 Hz, *β1* or *β1'*), 8.75 (d, 1H, *J* = 4.4 Hz, *β1* or *β1'*), 7.69 (d, 1H, *J* = 1.4 Hz, *a* or *b*), 7.47 (d, 1H, *J* = 1.4 Hz, *a* or *b*), 6.09 (ddt, 2H, *J* = 17.3, 10.4, 5.5 Hz, *p*), 5.42 (ddt, 2H, *J* = 17.3, 2.9, 1.6 Hz, *r*), 5.27 (ddt, 2H, *J* = 10.4, 2.9, 1.0 Hz, *q*), 5.04 (t, 4H, *J* = 7.7 Hz, *l*), 4.07 (ddd, 4H, *J* = 5.5, 1.6, 1.0 Hz, *o*), 3.64-3.61 (m, 4H, *n*), 3.59 (d, 2H, *J* = 7.4 Hz, *c*), 2.76 (tt, 4H, *J* = 7.7, 5.7 Hz, *m*), 1.32-1.31 (m, 1H, *d*), 0.92-0.33 (m, 8H, *e*, *g*, *h*, *i*), 0.65 (s, 9H, *k*), 0.20 (t, 3H, *J* = 7.4 Hz, *f* or *j*), 0.19 (t, 3H, *J* = 7.4 Hz, *f* or *j*), -2.44 (s, 2H, NH).



Synthesis of ***5,15-bis(3-allyloxypropyl)-10-(1-(2-ethylhexyl)-2-imidazolyl)-20-(2-trimethylsilylethynyl)porphyrinatozinc(II) 3TMS***

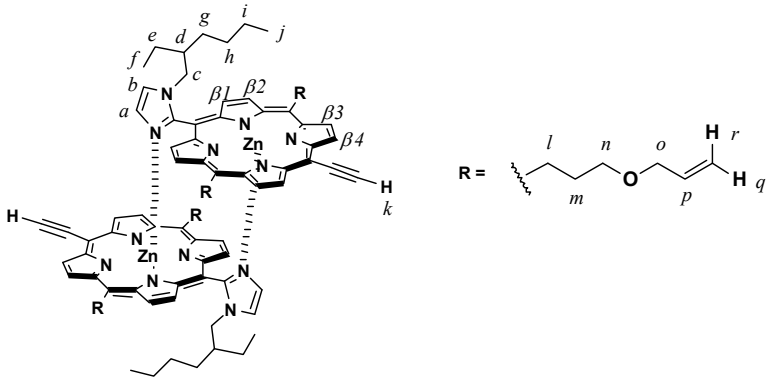
Porphyrinatozinc(II) **3TMS** was prepared from **8** (10 mg, 12.8 μmol) by the similar method for porphyrinatozinc(II) **2Ac**. Some impurities were detected in the crude sample by ^{1}H NMR (4.49, 2.20, and 1.45 ppm). The mixture was used for the next reaction. TLC: Rf = 0.77 ($CHCl_3$/MeOH = 50/1); MALDI-TOF mass (dithranol) *m/z* 843.6 $(M+H)^+$, calcd for $C_{48}H_{58}N_6O_2SiZn$ 842.4; ^{1}H NMR of dimeric **3TMS** (600 MHz, $CDCl_3$, mixture of isomers) δ 9.90 (d, 4H, *J* = 4.1 Hz, *β4*), 9.69 (d, 2H, *J* = 4.1 Hz, two of four *β3*), 9.68 (d, 2H, *J* = 4.1 Hz, two of four *β3*), 8.87 (d, 1H, *J* = 4.1 Hz, one of four *β2*), 8.86 (d, 1H, *J* = 4.7 Hz, one of four *β2*), 8.85 (d, 1H, *J* = 4.7 Hz, one of four *β2*), 8.84 (d, 1H, *J* = 4.1 Hz, one of four *β2*), 6.22-6.19 (m, 4H, *p*), 5.54 (ddt, 4H, *J* = 17.2, 3.3, 1.4 Hz, *q*), 5.49 (d, 2H, *J* = 1.9 Hz, *b*), 5.39 (d, 1H, *J* = 4.1 Hz, one of four *β1*), 5.38 (d, 1H, *J* = 4.7 Hz, one of four *β1*), 5.36-5.34 (m, 6H, two of four *β1*, *r*), 5.19 (br, 8H, *l*), 4.23 (ddd, 8H, *J* = 7.2, 5.4, 1.4 Hz, *o*), 3.92–3.89 (m, 8H, *n*), 3.11–2.94 (m, 8H, *m*), 2.00 (d, 2H, *J* = 1.9 Hz, *a*), 1.77–1.70 (m, 4H, *c*), 0.74 (s, 18H, *k*), 0.07–0.43 (m, 18H, *d*, *e*, *g*, *h*, *i*), –0.27 (t, 6H, *J* = 7.1 Hz, *f* or *j*), –0.53 (t, 6H, *J* = 7.3 Hz, *f* or *j*).


a
b
c
d
e
f
g
h
i
j
k
β1
β2
β3
β4
R
TMS
Zn
N


R =
l
m
n
o
p
q
r
O
H

Synthesis of ***5,15-bis(3-allyloxypropyl)-10-(1-(2-ethylhexyl)-2-imidazolyl)-20-ethynylporphyrinatozinc(II) 3***

To a degassed solution of **3TMS** (10.3 mg, 12.2 μmol) in $CHCl_3$ (2.5 ml), tetrabutylammonium fluoride (TBAF, 1 M in THF, 37 μl, 37 μmol) was added. The mixture was stirred for 1 h at rt. After usual work up process, the crude material was purified by gel permeation chromatography (Bio Beads S-X3, ϕ 1×100 cm, toluene) to give **3** (6.3 mg, 67%) as a green solid. TLC: Rf = 0.81 ($CHCl_3$/MeOH = 50/1); MALDI-TOF mass (dithranol) *m/z* 771.6 $(M+H)^+$, calcd for $C_{45}H_{50}N_6O_2Zn$ 770.3; ^1H NMR of dimeric **3** (600 MHz, $CDCl_3$, mixture of isomers) δ 9.93 (d, 4H, *J* = 4.4 Hz, *β4*), 9.72 (d, 2H, *J* = 4.4 Hz, two of four *β3*), 9.72 (d, 2H, *J* = 4.4 Hz, two of four *β3*), 8.88 (d, 1H, *J* = 4.4 Hz, one of four *β2*), 8.87 (d, 1H, *J* = 4.4 Hz, one of four *β2*), 8.86 (d, 1H, *J* = 4.4 Hz, one of four *β2*), 8.86 (d, 1H, *J* = 4.4 Hz, one of four *β2*), 6.24–6.17 (m, 4H, *p*), 5.56-5.52 (m, 4H, *q*), 5.49 (d, 2H, *J* = 2.2 Hz, *b*), 5.40 (d, 1H, *J* = 4.4 Hz, one of four *β1*), 5.39 (d, 1H, *J* = 4.4 Hz, one of four *β1*), 5.37–5.36 (m, 6H, two of four *β1*, *r*), 5.25–5.16 (m, 8H, *l*), 4.29 (s, 2H, *k*), 4.23 (ddd, 8H, *J* = 7.4, 5.8, 1.2 Hz, *o*), 3.94–3.85 (m, 8H, *n*), 3.11–2.95 (m, 8H, *m*), 1.99 (d, 2H, *J* = 2.2 Hz, *a*), 1.77–1.70 (m, 4H, *c*), 0.10–0.45 (m, 18H, *d*, *e*, *g*, *h*, *i*), –0.24 (t, 6H, *J* = 7.3 Hz, *f* or *j*), –0.57 (t, 6H, *J* = 7.4 Hz, *f* or *j*).



Synthesis of ***1,4–bis(5,15–bis(3–allyloxypropyl)–10–(1–(2–ethylhexyl)–2–imidazolyl)–porphyrinatozinc)butadiyne 1***

In a small test tube, a mixture of ethynylporphyirnatozinc **3** (3.2 mg, 4.14 μmol) and CuCl (1.2 mg, 12.4 μmol) in pyridine (0.3 mL) was stirred vigorously with bubbling of oxygen. After 7.5 h, water was added to the mixture. The organic layer was extracted with a mixture of chloroform/pyridine (1/1), washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was reprecipitated in pyridine and diethylether, and purified by recycle gel permeation chromatography (column: Tosoh $G3000H_{HR}$, eluent: pyridine) to give **1** (0.6 mg, 19 %) as a brown solid. MALDI-TOF mass (dithranol) *m/z* 1542.9 $(M+H)^+$; HRMS (ESI with methanol) *m/z* 770.32892 $(M+2H)^{2+}$, calcd for $C_{90}H_{98}N_{12}O_4Zn_2$ 770.32867 (2+ ion); UV-vis in pyridine as a monomeric form λ_{max} / nm ($\varepsilon/M^{-1}cm^{-1}$): 456 (86000), 488.5 (47000), 578.5 (4800), 662.5 (16000), 723.5 (19000) (Fig. S1).

Preparation of polymeric **1**

Since bisporphyrin **1** tends to afford insoluble aggregates partially after long standing, samples of polymeric **1** were prepared as follows: **1** (417 μg, 0.27 μmol) was dissolved in pyridine, and the solvent was evaporated under reduced pressure. To the residue, $(CHCl_2)_2$ (1 mL) was added under argon atmosphere. The mixture was slowly stirred at 0 °C. Some insoluble precipitate was filtered on a filter paper (Advantec®, type 5B). The filtrate (ca. 0.27 mM as a monomeric unit) was diluted before UV-vis and fluorescence measurements. UV-vis in tetrachloroethane λ_{max}/nm (Abs) : 432.8 (0.1724), 463.4 (0.2083), 503.6 (0.3637), 579.2 (0.0363), 682.8 (0.0642), 747.2 (0.2529) (Fig. S1); Fluorescence in Tetrachloroethane λ_{ex} : 463 nm, λ_{max}/nm: 751.4.

*Preparation of AFM sample of polymeric **1***

A solution of **1** was deposited on a freshly peeled mica surface. The mica substrate was rotated in spincoater (150 rpm, then 250 rpm for 5 min.) The substrate was dried at 40 °C under reduced pressure for 5 h. AFM images were shown in Fig. 4.

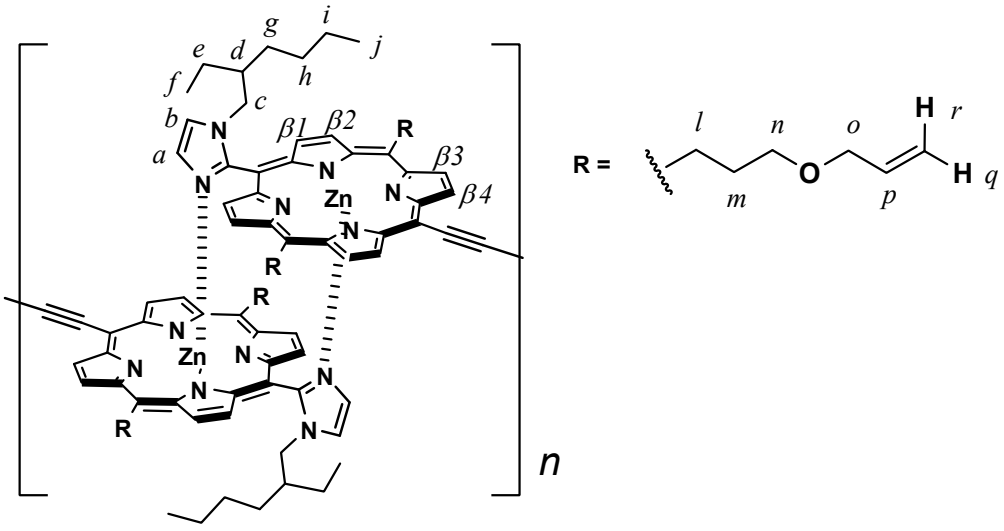
*Gel permeation analysis of polymeric **1***

Polymeric **1** (3×10^{-4} M^{-1}) in $(CHCl_2)_2$ was analyzed on GPC (PLgel 20 μm MIXED-A). The chromatogram shows two peaks at 5.74 and 9.05 min (Fig. S2). The relative ratio of the integrated peaks depended on the concentration of sample, so that the former peak increased on injecting more concentrated samples. Thus, the former and latter peaks are supposed to be aggregated and isolated supramolecular wires. The average molecular weight of the latter peak was determined as approximately 130,000 Da on the basis of polystyrene standard, which corresponds to ca. 100 mer of **1**. Osuka reported that one-dimensional giant porphyrin arrays ($\log M_w > 4$) eluted much faster than polystyrene standards of the same molecular weight,[3] thus the value, 100 mer, may be overestimated in harmony with the estimated value from AFM (38 mer).

*Preparation of ^{1}H NMR sample of polymeric **1***

A solution of **1** (1.1 mg, 0.71 μmol) in $(CDCl_2)_2$ (0.4 mL) was stirred for 6 h. Precipitates were filtered on cotton, and the filtrate was used for measurement. ^{1}H NMR (600 MHz, $(CDCl_2)_2$) δ 10.31 (br, 4H, *β4*), 9.89 (br, 4H, *β3*), 8.94 (br, 4H, *β2*), 6.29-6.23 (m, 4H, *p*), 5.70 (br, 2H, *b*), 5.60 (dd, 4H, J = 17.4, 3.6 Hz, *q*), 5.52 (br, 4H, *β1*), 5.41 (dd, 4H, J = 9.3, 3.6 Hz, *r*), 5.28 (br, 8H, *l*), 4.30 (br, 8H, *o*), 3.98-3.96 (m, 8H,

n), 3.14-3.12 (m, 8H, *m*), 2.27 (br, 2H, *a*), 1.78 (br, 4H, *c*), 0.26–0.21 (m, 24H, *d*, *e*, *f* or *j*, *g*, *h*, *i*), –0.41 (br, 6H, *f* or *j*). (Fig. 3)



2.2. Preparation of AuNP and its derivatives.

Preparation of gold nanoparticle (AuNP)

Gold nanoparticles were prepared by a similar method reported previously.[4] To a solution of $HAuCl_4 \cdot 4H_2O$ (100 mg, 243 μmol, 1 eq) in distilled water (8 mL), tetraoctylammonium bromide (TOAB) (584 mg, 1.07 mmol, 4.4 eq) in toluene (20 ml) was added, and the mixture was stirred vigorously. A $NaBH_4$ solution (100 mg, 2.65 mmol, 11 eq in 0.7 ml water) was added slowly to the mixture, and the mixture was stirred for 20 min. The mixture was adjusted to pH 7 with 1M H_2SO_4 aqueous solution, and the organic layer was extracted with toluene. The organic layer was washed with distilled water (5 times), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give dark purple solid (730 mg). This solid sample can be stored for a few months in freezer.

*Preparation of gold nanoparticle functionalized by **2** (AuNP-**2**)*

Since bisthiol **2** was easily oxidized by air, deprotection of **2Ac** were carried out under Ar atmosphere. Degassed solvents saturated by Ar were used in this procedure. To a solution of bisacetylthiol **2Ac** (25 μg, 27.7 nmol, 1 eq) in THF (0.2 mL), a mixture of potassium hydoxide (50 μg, 886 nmol, 32 eq) and $NaBH_4$ (2.5 μg, 66.5 nmol, 2.4 eq) in methanol (0.4 mL) was added. The mixture was stirred for 30 min at 60 °C. Toluene (0.3 mL) and water (0.3 mL) were added to the mixture, and the mixture was stirred vigorously for 5 min. After standing for a while, the mixture was separated into two phases. The upper toluene solution contained bisthiol **2** which was immediately used for functionalization of AuNP.

To a degassed solution of AuNP (100 mg) in THF (10 mL), the toluene solution of **2**

was added. The mixture was stirred for 24 h, and black precipitates were formed on the glass wall. To the mixture, 1-octanethiol (19.3 μl, 111 μmol, 4000 eq) and pyridine (10.2 ml) were added, and the mixture was stirred for 48 h. Most of the black precipitate was dissolved to give a brown-colored solution. After small precipitates were filtered on cotton, the filtrate was concentrated under reduced pressure by approximately 0.1 mL. (Sample should not be concentrated completely. If do, it was never dissolved in the same solvent.) The concentrated sample was purified by atmospheric gel permeation chromatography (column: diameter 1 cm, height 100 cm) on Bio-Beads S-X1 with TTP solution as an eluent. AuNP-**2** composite was obtained as a TTP solution from the initial fractions. The AuNP-**2** solution in TTP should not be concentrated to avoid irreversible aggregation. The solution was directly deposited on copper grid covered with elastic carbon film and mica substrate for TEM and AFM measurements, respectively.

Preparation of TEM sample

Ethanol (2 μL) was dropped on a copper grid covered with elastic carbon film prior to use, and the above AuNP-**2** solution in TTP (2 μL) was deposited immediately on the same face. The grid was dried at 40 °C under reduced pressure (ca. 1 kPa) for 5 h. The TEM image was shown in Fig. S3. The average diameter was determined as 4.6 nm.

*Estimation of amounts of porphyrin **2** on AuNP-**2***

UV-vis spectra of AuNP-**2**, AuNP, and **2Ac** were measured in TTP solution (Fig. S4). Amounts of porphyrin **2** on AuNP-**2** were estimated from the UV-vis spectra.

(1) As a standard, an extinction coefficient of porphyrin **2Ac** in the range of 22000-24000 cm^{-1} (416-454 nm) was determined as 3×10^8 $M^{-1}cm^{-1}$. If light absorption

of porphyrin **2** occurs only on a hemisphere of the irradiation side in AuNP-**2**, the concentration of the porphyrin moiety was determined as 4×10^{-8} M from the UV-vis spectrum of Fig. S4.

(2) Gold nanoparticle of 4.6 nm diameter is composed of approximately 3000 gold atoms. An extinction coefficient of approximately 4000 $M^{-1}cm^{-1}$ per gold atom at the plasmon maximum is reported previously.[5] The concentration of gold nanoparticle as mean diameter 4.6 nm was estimated as 1×10^{-8} M from the UV-vis spectrum of Fig. S4.

(3) From the estimations (1) and (2), it is concluded that *four molecules of porphyrin **2** exist on each 4.6 nm gold nanoparticle*.

*Composition of AuNP-**2** and **1** on mica substrate*

A TTP solution of AuNP-**2** (3 μL, 1.3×10^{-8} M as a gold nanoparticle, $\varepsilon = 1.2 \times 10^{7}$ $M^{-1}cm^{-1}particle^{-1}$ at the plasmon maximum) was deposited on a mica substrate freshly peeled. The substrate was rotated in a spincoater (from 150 to 250 rpm) for 5 min, and dried under vacuum at 40 °C for 5 h. A 3 μL aliquot of a $(CHCl_2)_2$ solution of **1** (Abs. 0.2 at 463 nm, 7.0 μM) was deposited on the mica substrate precoated by AuNP-**2**. The substrate was rotated in a spincoater (150 rpm, then 250 rpm for 5 min.), and dried at 40 °C under vacuum for 5 h. Collected AFM images are shown in Figs. 5, 6, S5A, and S6.

As a control experiment, gold nanoparticles coated by only octanethiol were used instead of AuNP-**2**. After deposition of **1**, AFM image was collected. (Fig S5B)

3. References

[1] M. Morisue and Y. Kobuke, *Chem. Eur. J.* **2008**, *14*, 4993.

[2] A. Ohashi, A. Satake, Y. Kobuke, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 365.

[3] N. Aratani, A. Takagi, Y. Yanagawa, T. Matsumoto, T. Kawai, Z. S. Yoon, D. Kim and A. Osuka, *Chem. Eur. J.* **2005**, *11*, 3389.

[4] a) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.* **1994**, 801. b) J. Fink, C. J. Kiely, D. Bethell and D. J. Schiffrin, *Chem. Mater.* **1998**, *10*, 922. c) G. Harada, H. Sakurai, M. M. Matsushita, A. Izuoka and T. Sugawara, *Chem. Lett.* **2002**, 1030.

[5] S. Link, Z. L. Wang and M. A. El-Sayed, *J. Phys. Chem. B.* 1999, *103*, 3529.

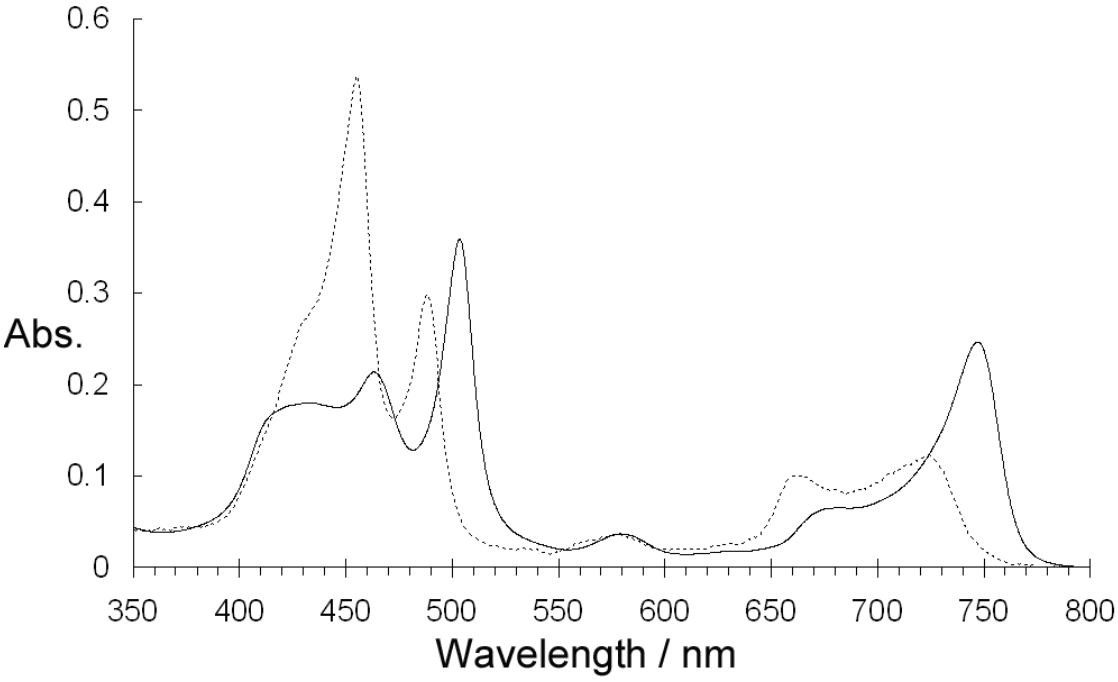


Fig. S1. UV-vis spectra of (solid) polymeric **1** in tetrachloroethane and (dotted) monomeric **1** in pyridine (normalized at 555 nm)

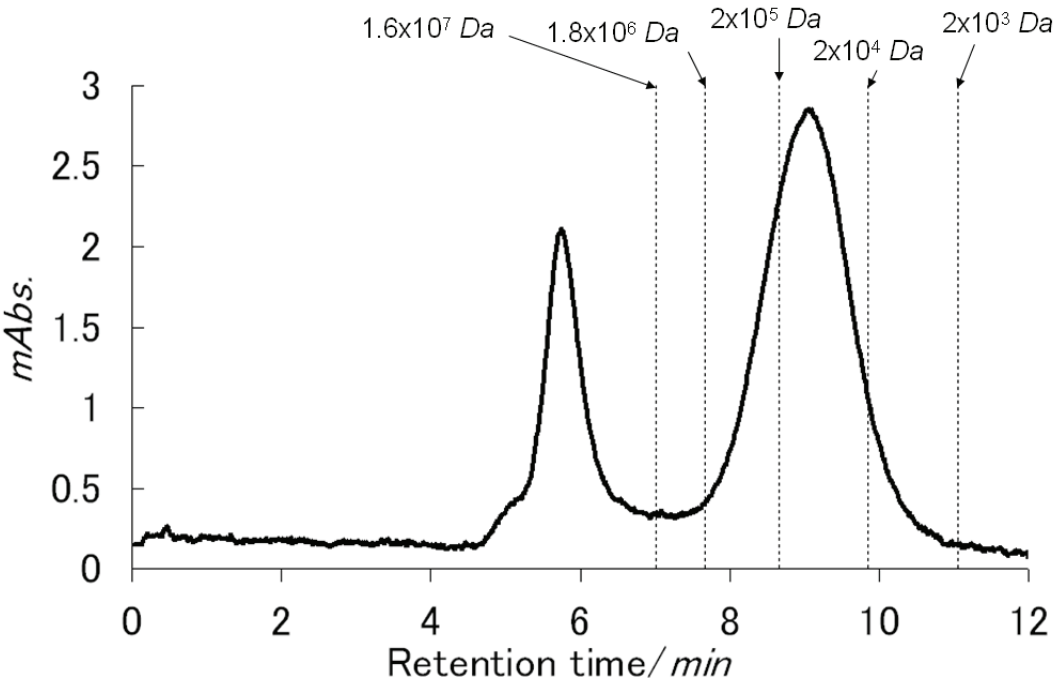


Fig. S2. GPC chart of **1** (column: PLgel MIXED-A, Polymer Laboratories, exclusion limit: 4×10^7 Da, eluent: tetrachloroethane, monitored at 462 nm), dotted lines: retention times of standard polystyrenes (1.6×10^7, 1.8×10^6, 2×10^5, 2×10^4, 2×10^3 Da)

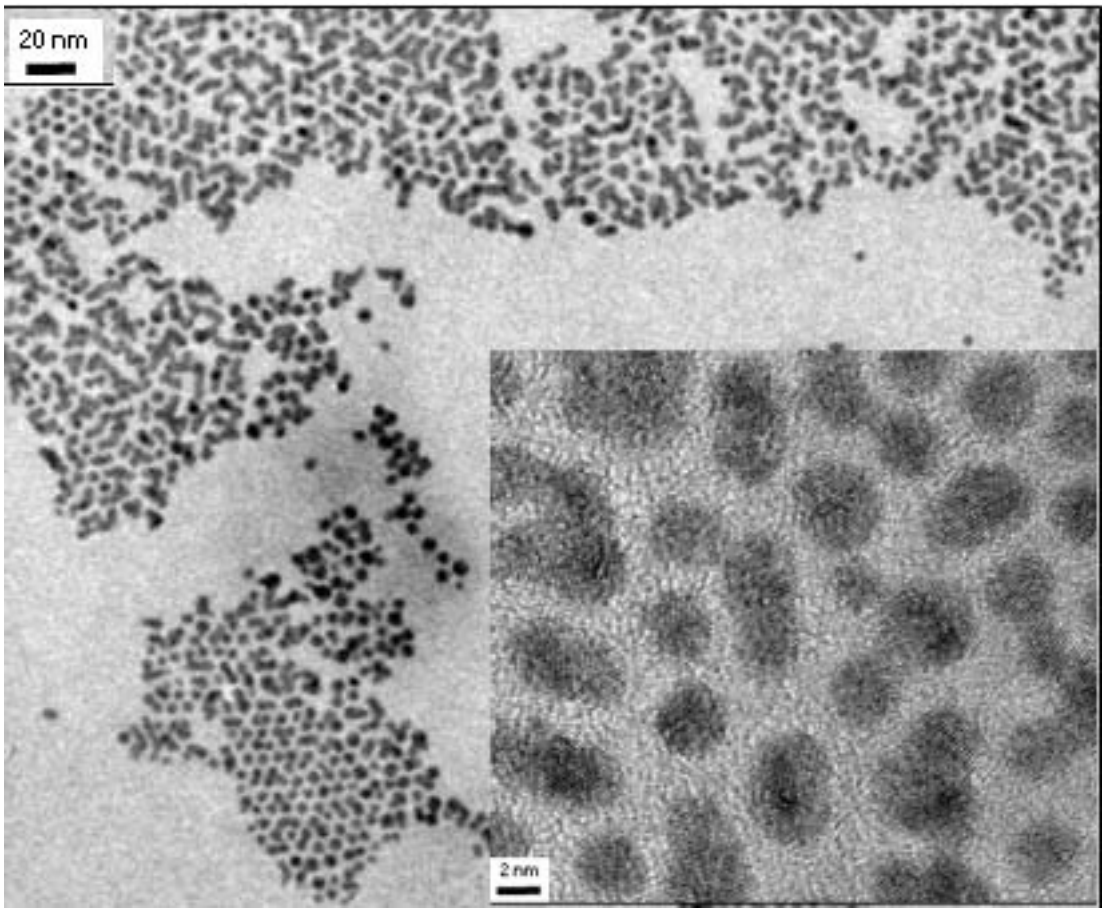


Fig. S3. TEM image of AuNP-**2** (scale bars: 20 nm and 2 nm (inset))

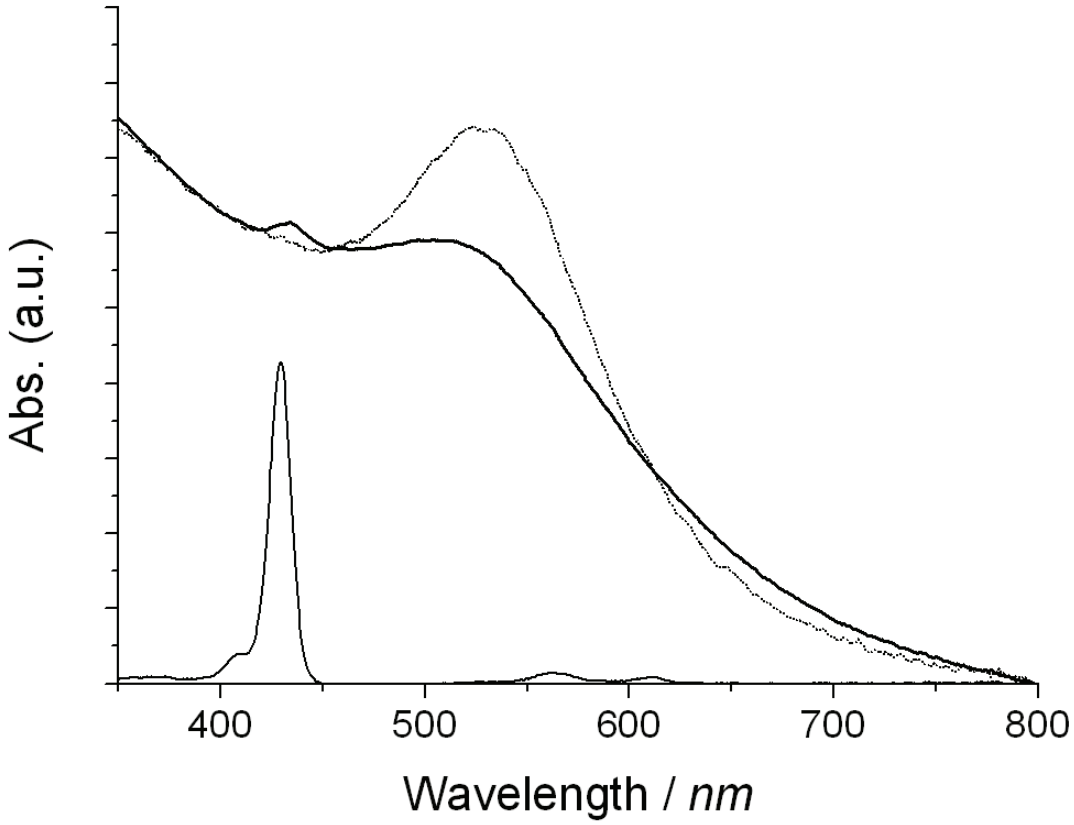


Fig. S4. UV-vis spectra of (solid) porphyrin **2Ac** in $CHCl_3$, (dotted) non-functionalized AuNP, and (bold) functionalized AuNP-**2** (The last two spectra were normalized at 415 nm.)

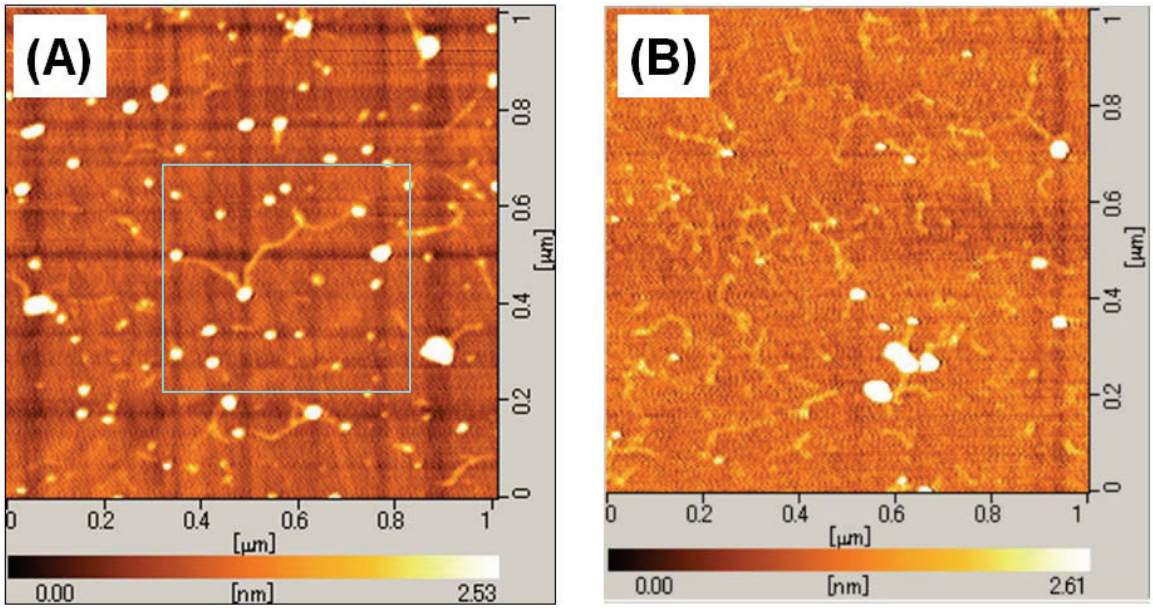


Fig. S5. AFM image of (A) AuNP-**2** with **1** (Square part is enlarged in Fig. S6.) and (B) AuNP functionalized by only octanethiol with **1**

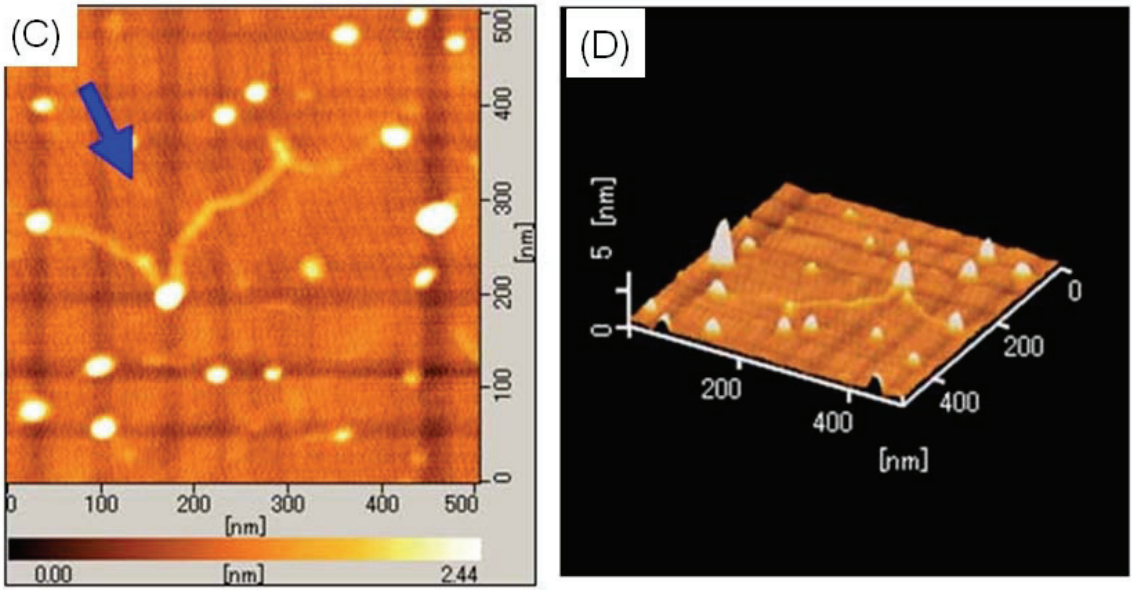


Fig. S6. (C) Enlarged AFM image of AuNP-**2** with **1** (Square part in Fig. S5 (A)) and (D) 3D image of (C) (watching from the direction of blue arrow)

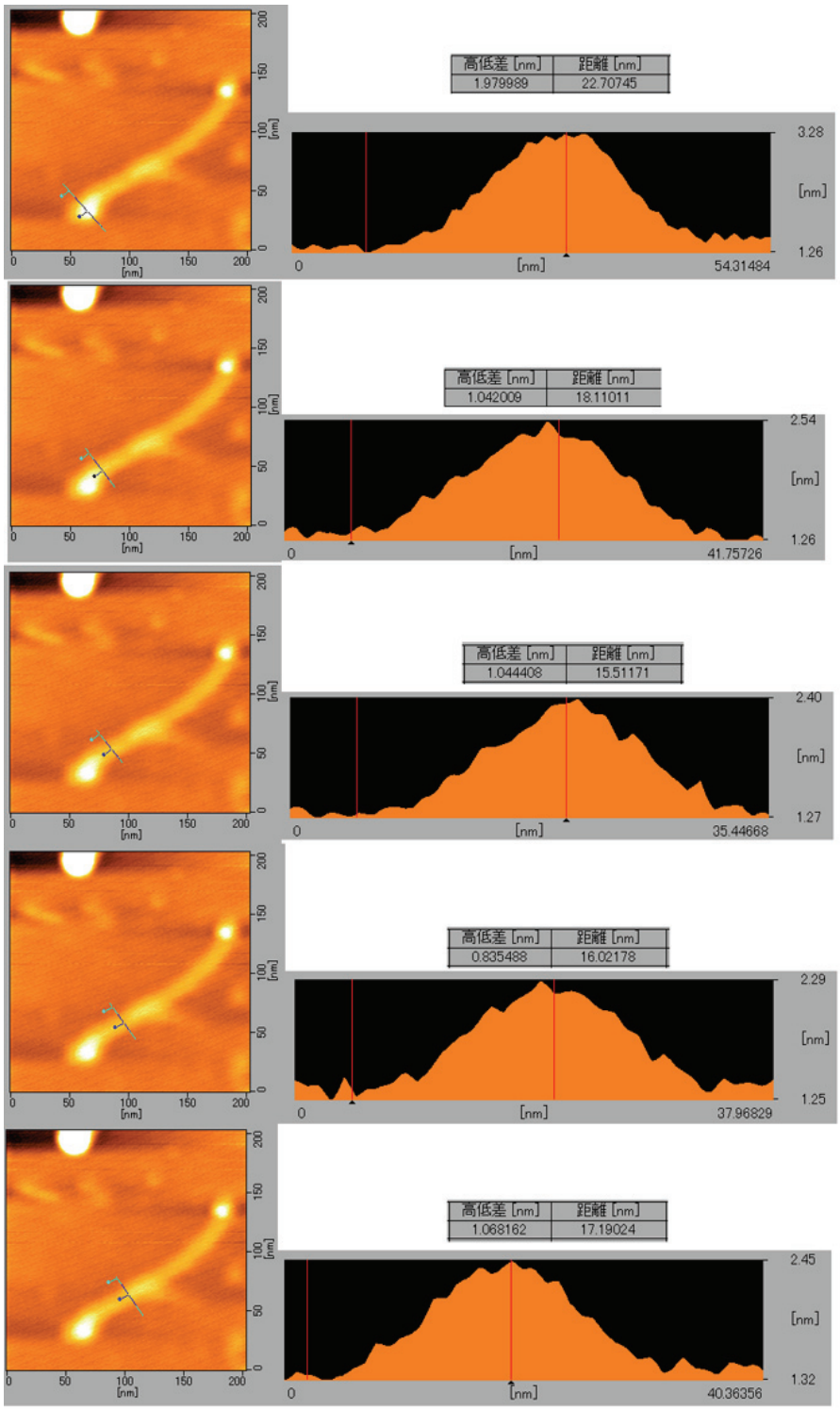


Fig. S7. Cross-sections of the nanowire in **Fig. 6**.

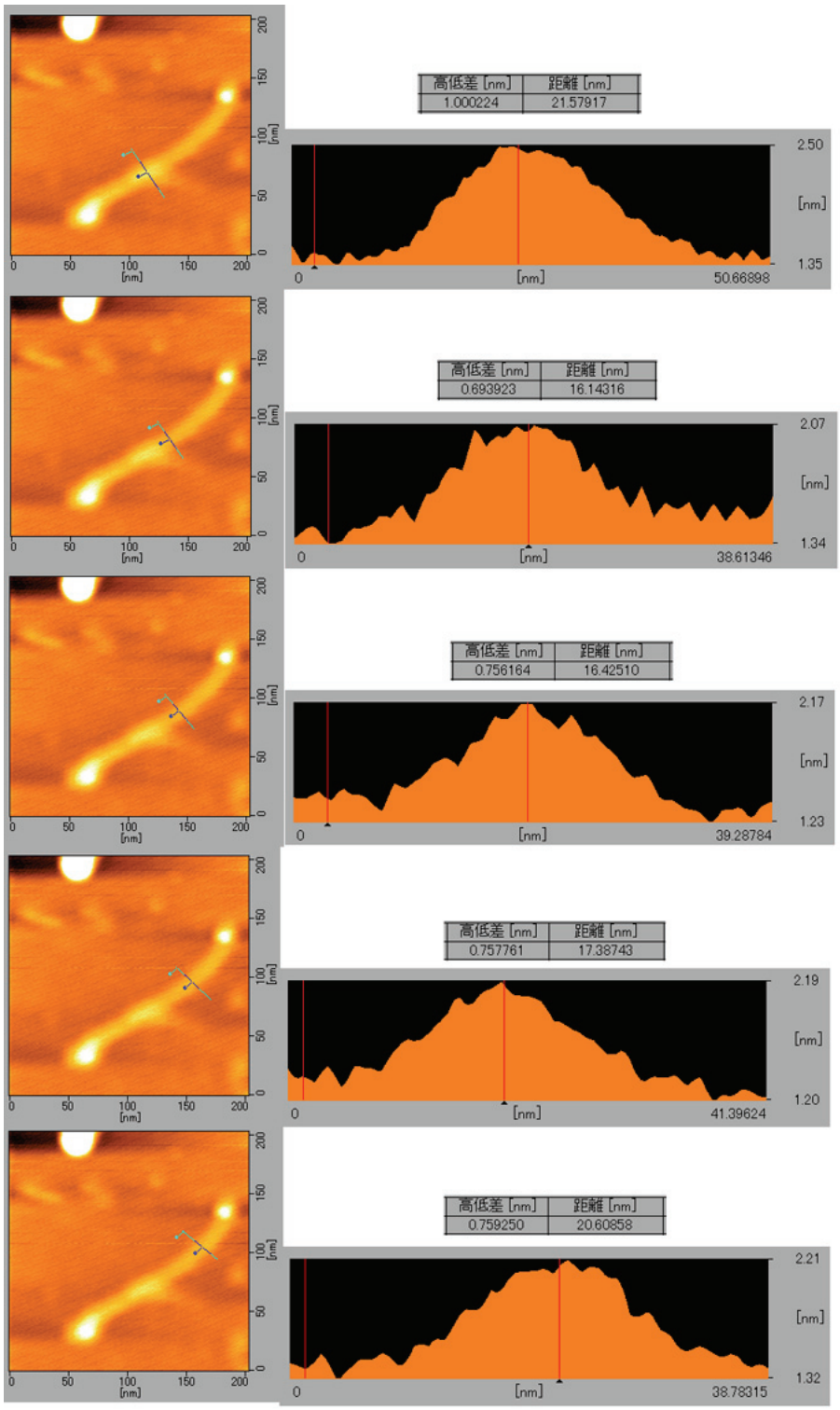


Fig. S8. Cross-sections of the nanowire in **Fig. 6**. (continued from **Fig. S7**)

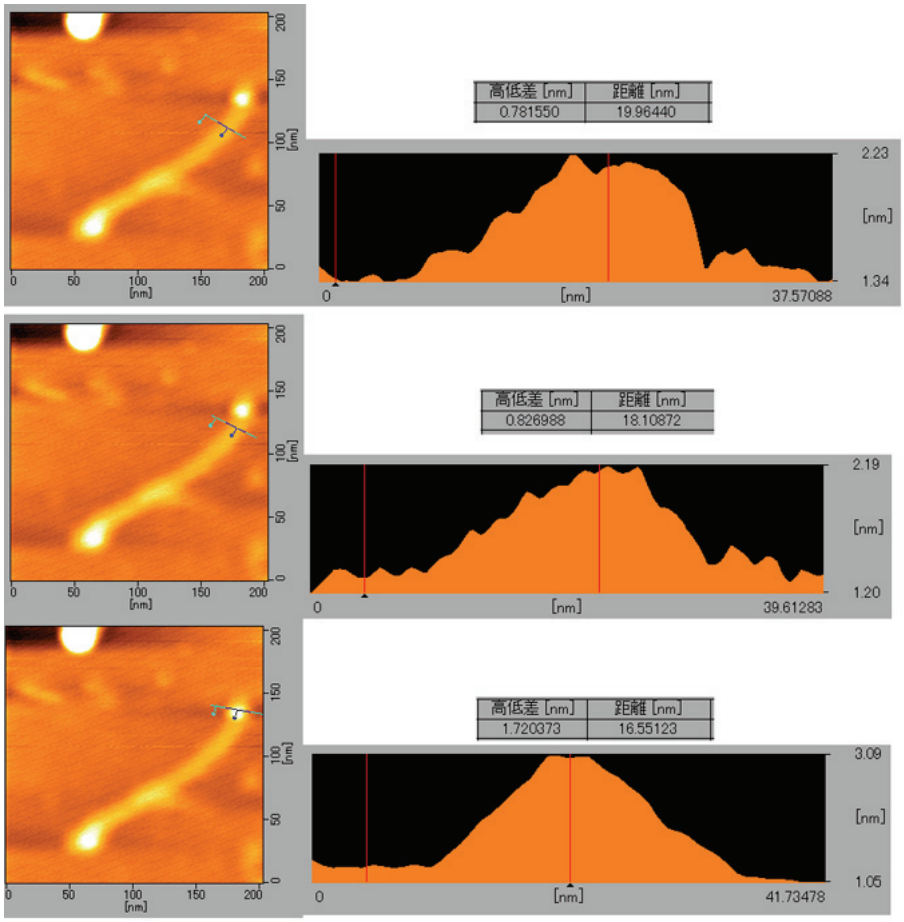


Fig. S9. Cross-sections of the nanowire in **Fig. 6**. (continued from **Fig. S8**)