Shape-controllable gold nanocrystallization using an amphiphilic polythiophene

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1. General

Transmission electron microscopy (TEM) was carried out using JEOL JEM-2000FX and JEM-1010 electron microscopes. High-resolution TEM and EDX mapping were performed using JEOL JEM-3200FS. Field emission scanning electron microscopy (FE-SEM) was carried out using JEOL JSM-7500F electron microscope. The intensity data of X-ray diffraction (XRD) was collected by Rigaku RINT-TTR III powder diffractometer. Absorption spectra were obtained on Shimadzu UV-3100PC spectrophotometer. KEYENCE VN-8000 nanoscale hybrid microscope was used for recording AFM image. The electric conductivity was evaluated using ADVANTEST R6551 digital multimeter.

2. Preparation of gold nanocrystals

Gold nanocrystals were prepared as follows: 1) an aqueous solution of $\mathbf{1_{poly}}$ (2.3×10^{-4} M/unit) and HAuCl₄ (2.0×10^{-4} M) was allowed to stand for 24 h at room temperature; 2) an aqueous solution of $\mathbf{1_{poly}}$ (2.3×10^{-5} M/unit) and 2.0×10^{-3} M of HAuCl₄ was allowed to stand for 24 h at room temperature; 3) a CH₃CN solution containing $\mathbf{1_{poly}}$ (4.7×10^{-3} M/unit) and HAuCl₄ (4.0×10^{-2} M) at room temperature for 24 h. These solutions containing gold nanocrystals with no further purification were analyzed by several techniques involving microscopic apparatus as well as EDX.

3. XRD measurement

X-ray diffraction (XRD) was carried out where obtained nanoplate exhibited several peaks which are assigned as {111}, {200}, {220}, {311} and {222} facets of fcc lattice, respectively. The intensity ratio of {200} to {111} is 0.33, being lower than that of the standard value (JCPDS). This finding means that the nanoplates obtained in this work are mainly dominated by {111} facet which supports the result of SAED pattern.
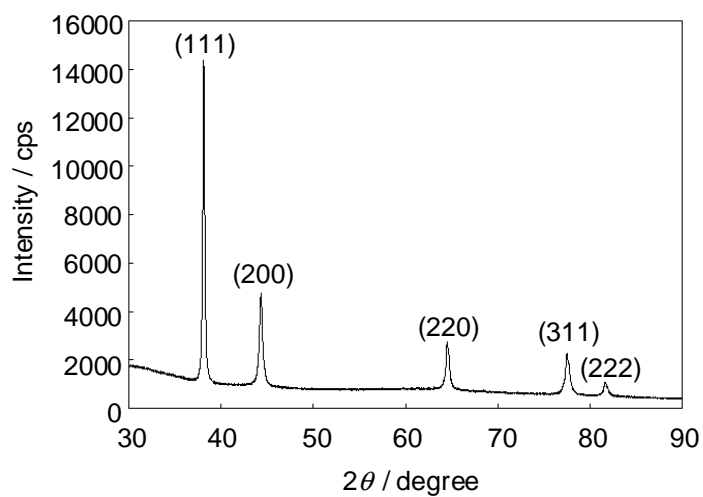
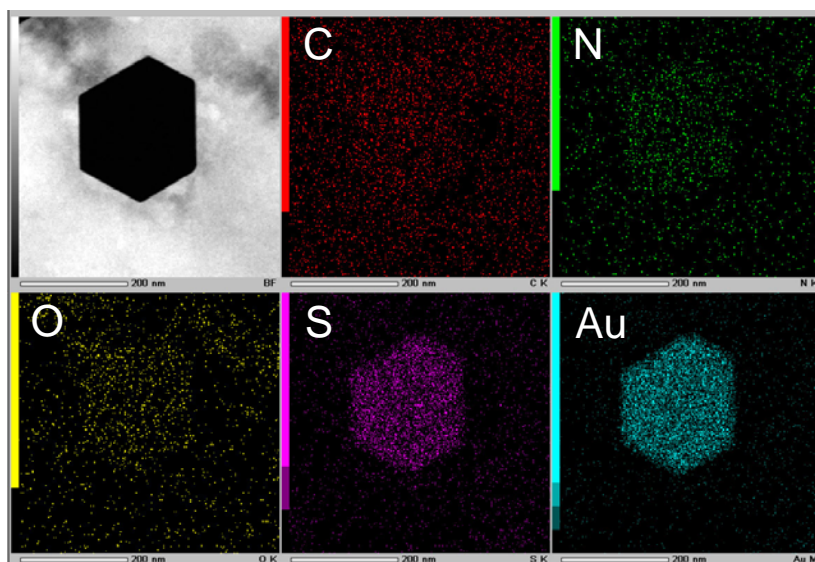**Fig. S1** XRD pattern of obtained gold nanoplates.

4. EDX mapping

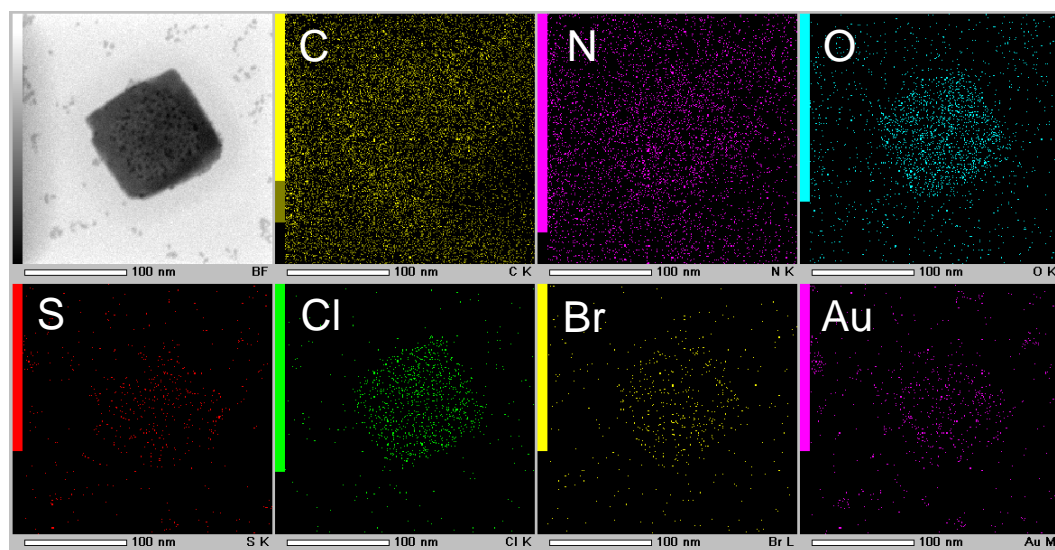**Fig. S2** TEM and EDX-mapping images of obtained **1$_{poly}$**-hybrid gold nanoplate.

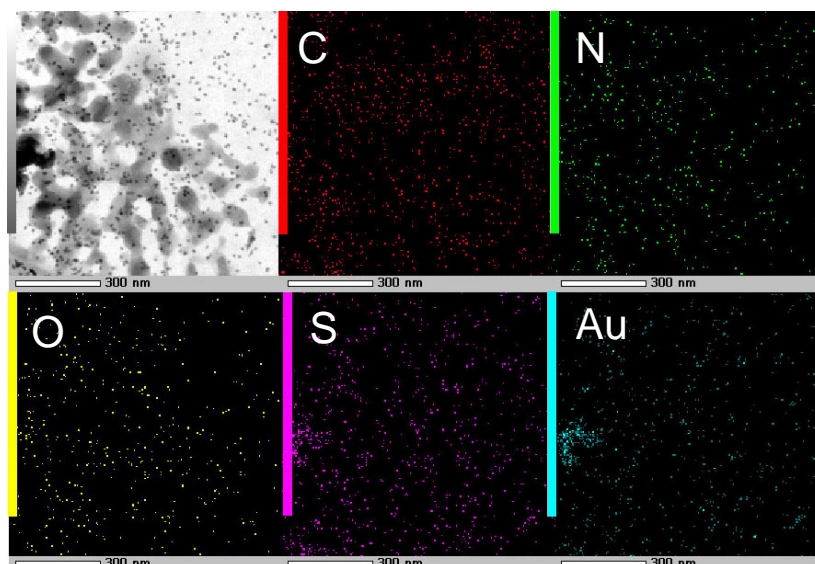**Fig. S3** TEM and EDX-mapping images of obtained **1$_{poly}$**-hybrid gold nanocube.

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Fig. S4 TEM and EDX-mapping images of **1poly**-hybrid gold nanoparticles with an average of spherical diameter of (7.7 ± 1.6) nm.

5. Concentration-dependency of gold nanocrystallization in CH₃CN

In order to estimate the effect of the bulk solvent on the morphology, we carried out the nanocrystallization with several different concentrations of reactants in CH_3CN at room temperature.

1) An acetonitirile solution of **1poly** (2.3×10^{-4} M/unit) and $HAuCl_4$ (2.0×10^{-4} M) was allowed to stand for 2 weeks at room temperature. The obtained sample was deposited on carbon-coated copper grid.
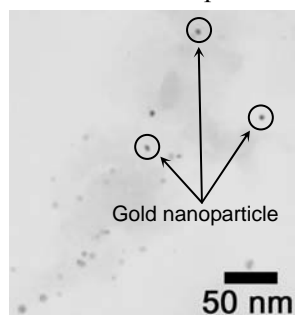

Fig. S5 TEM image of gold nanoparticles with an average of spherical diameter of (4.8 ± 0.82) nm.

2) An acetonitirile solution of **1poly** (4.7×10^{-3} M/unit) and $HAuCl_4$ (4.0×10^{-3} M) was allowed to stand for 24 h at room temperature. The obtained sample was deposited on carbon-coated copper grid.
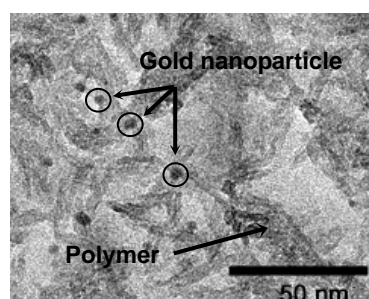

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Fig. S6 TEM image of gold nanoparticles with an average of spherical diameter of (2.7 ± 0.67) nm.

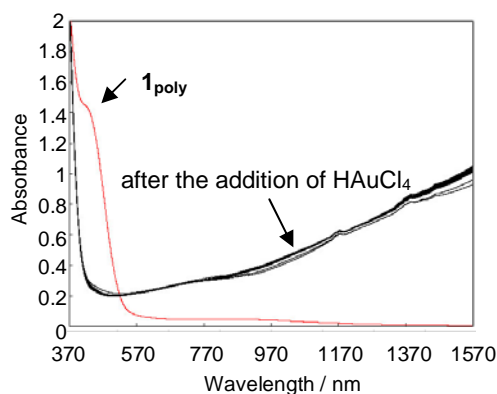## 6. Absorption spectra of 1_{poly} with HAuCl$_4$ in CH$_3$CN

Fig. S7 Absorption spectra of 1_{poly} (**-**), and 1_{poly} with HAuCl$_4$ (**-**) in CH$_3$CN at 25 °C. The black lines were measured at 4, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 240, 300, 360, 420, 1440, 2880 min after the addition of HAuCl$_4$. $[1_{poly}] = 2.3 \times 10^{-4}$ M/unit. $[HAuCl_4] = 2.0 \times 10^{-4}$ M.

7. The control experiment of gold nanocrystallization using monomer (1)

An aqueous solution of **1** $(2.3 \times 10^{-4}$ M) and HAuCl$_4$ $(2.0 \times 10^{-4}$ M) was allowed to stand for 24 h at room temperature. The obtained sample was deposited on carbon-coated copper grid.
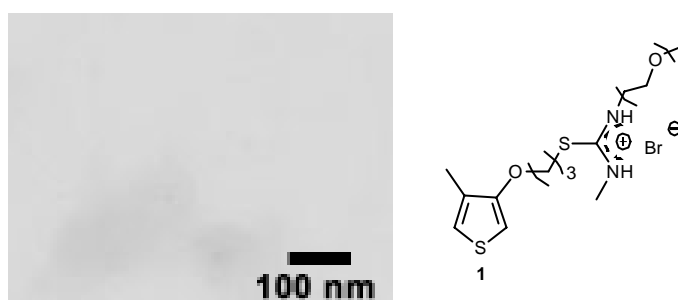

Fig. S8 TEM image of sample prepared from the monomer **1** and HAuCl$_4$. $[1] = 2.3 \times 10^{-4}$ M. $[HAuCl_4] = 2.0 \times 10^{-4}$ M.

8. Estimation of the electric conductivity

Electric conductivities were measured by the two-probe techniques using fine gold wires attached to spin-coated films with carbon paste. Thickness of the films was estimated by AFM measurement.

Table S1 Electric conductivities (σ) of the films.

Film	Thickness (nm)	Iodine-doping	σ (S/cm)
1_{poly}/Au nanoparticle hybrid film prepared from CH$_3$CN-based solution	127	No	3.4×10^{-3}
1_{poly}/Au nanoparticle hybrid film prepared from CH$_3$CN-based solution	127	Yes	4.2×10^{-2}
1_{poly}	94	No	$-^a$
1_{poly}	94	Yes	3.1×10^{-3}

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[a]The resistance is too large to estimate the σ value.