Electronic Supporting Information for

Two Dimensional Self Assembly of Disulfide Functionalized Bis-acylurea: a Nanosheet Template for Gold Nanoparticle Arrays

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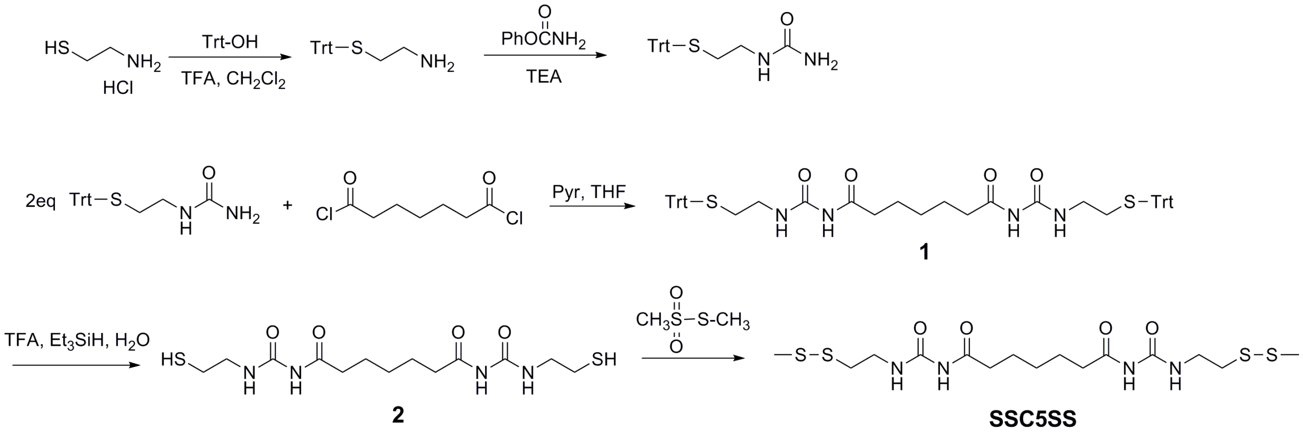
1. Experimental details

Materials and Instrumentation

All the chemicals were purchased from commercial chemical suppliers and were used without further purification. THF was dried by distillation over sodium. . NMR spectra were recorded on a 300 MHz Bruker Spectrometer. SEM was carried out using an LEO EM 1530 Gemini field emission microscope. SEM samples were prepared by drop casting gels or dispersion onto silicon wafers and drying them in vacuum over for at least 10 h. Powder XRD patterns were measured using a D500 Siemens diffractometer. UV-vis spectra were recorded using a Shimadzu UV-2012 spectrophotometer.

Synthesis



Synthesis of Trityl-*S*-mercaptoethylamine.

Trityl-*S*-mercaptoethylamine was synthesized as reported elsewhere. (J. P. O'Neil, S. R. Wilson, J. A. Katzenellenbogen *Inorg. Chem.*, **1994**, *33*, 319–323.) Triphenylmethanol (50 mmol, 13 g) was added as powder into a stirred solution of cysteamine hydrochloride (50 mmol, 5.7 g) in 58 mL of trifluoroacetic acid (TFA) at room temperature. After being stirred for 2 h, the reaction mixture was concentrated by rotary evaporation under reduced pressure. The dark oily liquid was diluted with ethyl acetate (50 mL) and the organic layer was washed with 3N NaOH (aq) (25 mL × 4), H_2O (25 mL × 2), $NaHCO_3$ (aq. sat'd, 25mL), and brine (25 mL). The aqueous washes were back-extracted with ethyl acetate (25 mL) and the combined organic extracts were dried over $MgSO_4$, followed by filtration through a celite pad. The solution was allowed to stand in a freezer to yield colorless crystalline product. Crystallization was repeated three times to give 13.2 g (82%) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.30$ (brs, 2H), 2.30 (t, 2H), 2.57 (t, 2H), 7.17-7.49 (m, 15H).

Synthesis of Trt-*S*-mercaptoethylurea

To a stirred mixture of Trt-*S*-mercaptoethylamine (14.5 mmol, 4.6 g) and phenyl carbamate (14.5 mmol, 2.0 g) at 60 °C in dry THF (75 mL), triethylamine (29 mmol, 4.15 mL) was added. After being stirred for 4 h, volatiles are evaporated. Crude solids were recrystallized with n-hexane and ethyl acetate to give 4.2 g (80%) of the urea. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 2.41$ (t, 2H), 2.96 (q, 2H), 4.22 (s, 2H), 4.58 (t, 1H), 7.17-7.40 (m, 15H).

Synthesis of **1**.

To a stirred solution of Trt-*S*-mercaptoethylurea (2 mmol, 0.73 g) in dry THF (75 mL) at room temperature, pyridine (3 mmol, 0.24 mL) and pimeloyl chloride (1 mmol, 0.16 mL) was sequentially added. After being stirred for 16 h under argon atmosphere, volatiles were evaporated under reduced pressure. Crude solids were recrystallized at -20 °C from a concentrated ethanol solution to provide 0.60 g (72%) of **1**. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.31$ (m, 2H), 1.61 (m, 4H), 2.23 (m, 4H), 2.37 (t, 4H), 3.05 (q, 4H), 7.11-7.40 (m, 30H), 8.43 (t, 2H), 9.03 (s, 2H).

Synthesis of **2**.

Deprotection of **1** was performed following a procedure as reported elsewhere (M. Fischler, A. Sologubenko, J. Mayer, G. Clever, G. Burley, J. Gierlich, T. Carell, U. Simom *Chem. Commun.* **2008**, 169–171.). To a stirred solution of **1** (0.90 mmol, 0.76 g) in dichloromethane (50 mL) at room temperature, TFA (25 mL), triethylsilane (2.5 mL), and H_2O (2.5 mL) were sequentially added. After being stirred for 1 h at room temperature, volatiles were evaporated under reduced pressure. The crude solid products were recrystallized from a concentrated ethanol solution to give 0.23 g (70%) of **2**. ^{1}H NMR (300 MHz, CDCl$_3$) $\delta = 1.38$ (m, 2H), 1.68 (m, 4H), 2.33 (t, 4H), 2.68 (q, 4H), 3.47 (q, 4H), 8.72 (t, 2H), 9.26 (s, 2H). ^{13}C NMR (300 MHz, D$_6$-DMSO) $\delta = 23.82$, 24.21, 28.00, 35.57, 42.26, 153.45, 174.98. MS (ESI): 387.14 (100%, M+Na), 385.13 (52%, M + Na - 2H). IR (diamond-ATR): $\nu = 3313$, 2944, 2927, 2872, 1695, 1674, 1526, 1468, 1436, 1420, 1358, 1303, 1250, 1235, 1176, 978, 840, 775 cm^{-1}.

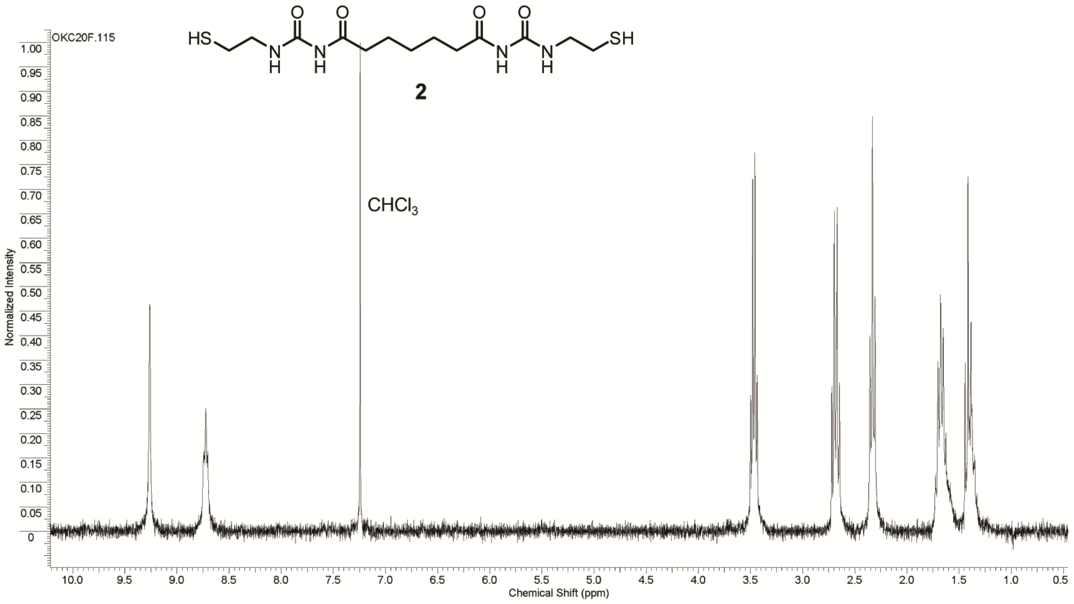


Figure S1. 1H NMR spectrum of **2** (in CDCl$_3$)

Synthesis of **SSC5SS**.

To a stirred solution of **2** (0.14 mmol, 50 mg) in absolute ethanol (25 mL) at room temperature, *S*-methyl methanethiosulfonate (0.69 mmol, 0.1 mL) was added dropwise under argon atmosphere. Using a heat gun, the reaction flask was gently heated until solids had clearly dissolved.. After being stirred for 16 h, volatiles were evaporated using rotary evaporation. The crude solids were purified by recrystallization at -20 °C from a concentrated ethanol solution to provide 54 mg (87%) of a white powder. ^{1}H NMR (300 MHz, D$_6$-DMSO) δ = 1.21 (m, 2H), 1.49 (m, 4H), 2.25 (t, 4H), 2.40 (s, 6H), 2.85 (t, 4H), 3.46 (q, 4H), 8.56 (t, 2H), 10.30 (s, 2H). ^{13}C NMR (300 MHz, D$_6$-DMSO) δ = 21.47, 22.70, 24.21, 35.57, 36.55, 38.11, 153.47, 175.01. MS (ESI): 385.13 (100%, M+Na – $(SCH_3)_2$), 479.14 (5%, M + Na). IR (diamond-ATR): ν = 3313, 2986, 2945, 2908, 2865, 1695, 1674, 1526, 1468, 1435, 1419, 1354, 1308, 1237, 973, 956, 896, 795, 718, 688 cm^{-1}.

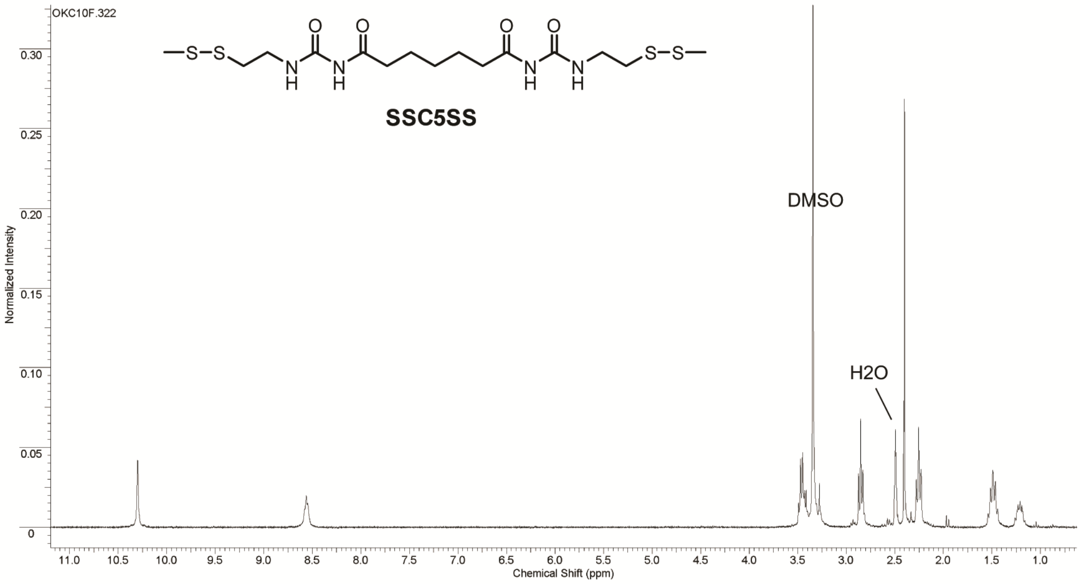


Figure S2. 1H NMR Spectrum of **SSC5SS** (in D$_6$-DMSO)

Preparation of **SSC5SS** Nanosheets.

A weighed amount (~ 10 mg) of **SSC5SS** was dissolved in ethanol (~ 1 mL) by heating it gently with a heat gun. White precipitates, which were formed upon cooling to room temperature, were filtered and dried under vacuum.

Synthesis of AuNPs.

The gold colloid solution was prepared following a procedure as reported elsewhere (K. C. Grabar, R. G. Freeman, M. B. Hommer, M. J. Natan *Anal. Chem.* **1995**, *67*, 735–743.). All glassware used was thoroughly cleaned in aqua regia (3 parts HCl, 1 part HNO_3), rinsed with Millipore H_2O (18.2 MΩ/cm), and oven-dried prior to use. To a boiling aqueous solution of 0.01% $HAuCl_4 \times 3H_2O$ (100 mL), 2.5 mL of 1% sodium citrate aqueous solution was added with vigorous stirring. When the color change of the solution into wine-red was perceived, heating was stopped and the reaction flask was cooled to room temperature. SEM image indicated an average diameter of 19 nm ± 3 nm. The colloid solution was stored in a refrigerator and used for immobilization experiments after adjusted to pH 10 using 0.5 NaOH (aq).

Immobilization of AuNPs on **SSC5SS** Nanosheets.

SSC5SS nanosheets (2.0 mg) were well dispersed in 2.0 mL H_2O by ultrasonication for 1 min. The mixture was divided into 5 portions, then transferred into five vials. To the vials, 0.1, 0.2, 0.3, 0.4, and 2.5 (excess) mL of gold colloid solutions were added, respectively, then the vials were shaken overnight at room temperature. The wine red color of the dispersed solution turned purple red within hours, finally purple blue. In the case where an excess amount of gold colloid solution was used, the solution remained wine red after 1 d. The products were purified by centrifugation with H_2O for at least 5 times.

Site-Directed Immobilization of AuNPs on **SSC5SS** Nanosheets on a Layer-By-Layer (LBL) Film.

A negatively charged LBL film was prepared on a glass slide. The substrate was cleaned by treatment with a Piranha solution, and negatively charged by the RCA treatment, as reported by others (H. J. Park, J. Kim, J. Y. Chang, P. Theato *Langmuir* **2008** *24* 10467-10473.). The negatively charged substrate was immersed in a 3.5 wt% poly(allylamine hydrochloride) (PAH; M_w= 70 000 g/mol) aqueous solution for 20 min, rinsed with water 3 times, and then dried with nitrogen. The substrate was then immersed into a 3.5 wt% poly(sodium 4-styrene sulfonate) (PSS; M_w= 70 000 g/mol) aqueous solution for 20 min and subjected to the same rinsing and drying procedures. This cycle was repeated twice again to prepare the negatively charged film, [$(PAH/PSS)_3$], on the substrate. Onto the film, a **SSC5SS** dispersion in ethanol was dropped, then allowed to dryness under ambient atmosphere. After annealed for 1 min at 80 ^{o}C, the substrate was thoroughly washed with ethanol and water, and then dried with nitrogen. For the immobilization of AuNPs, the substrate was immersed into a gold colloid solution at room temperature. After 1 d, the substrate was washed thoroughly with plenty of water, then dried under vacuum.

2. Optical microscope images of supramolecular structures prepared from **2** and **SSC5SS**

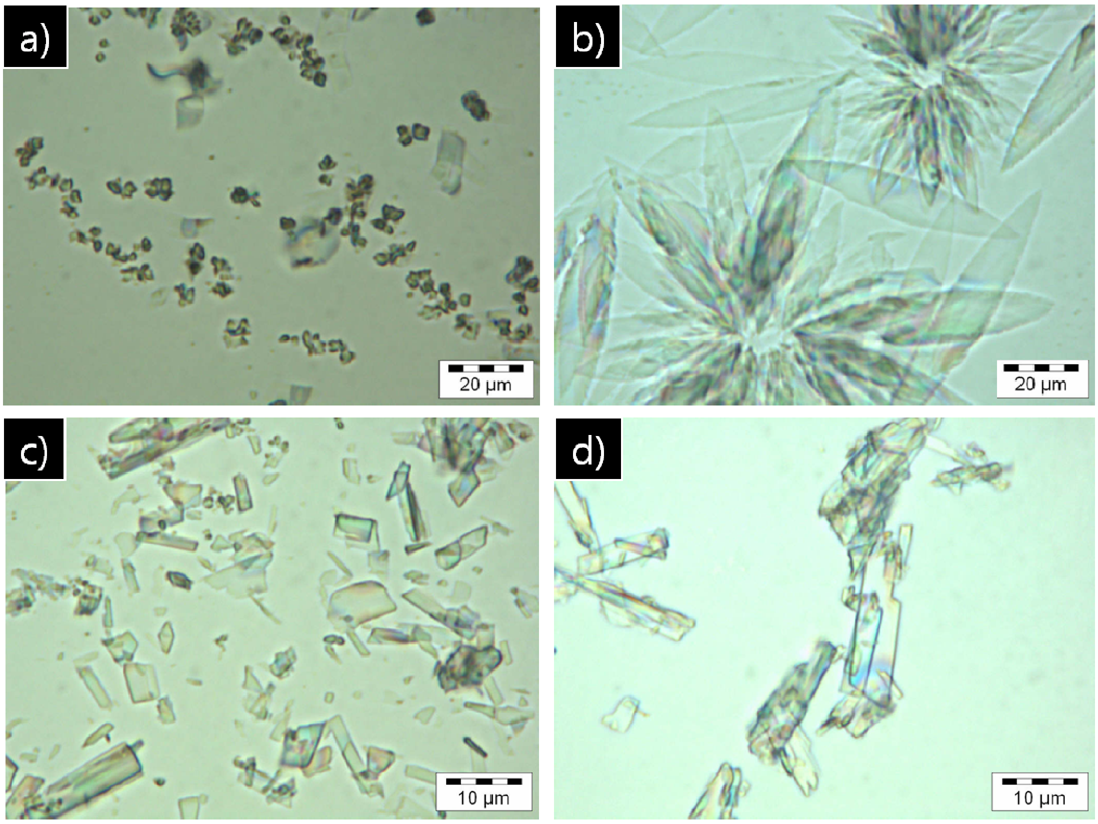


Figure S3. (a and b) Optical microscope images of **2.** Irregular and leaflet-shaped crystals are observed. (c and d) Optical microscope images of **SSC5SS** nanosheets

3. Powder X-ray diffraction patterns of **BuC5Bu** and **SSC5SS**

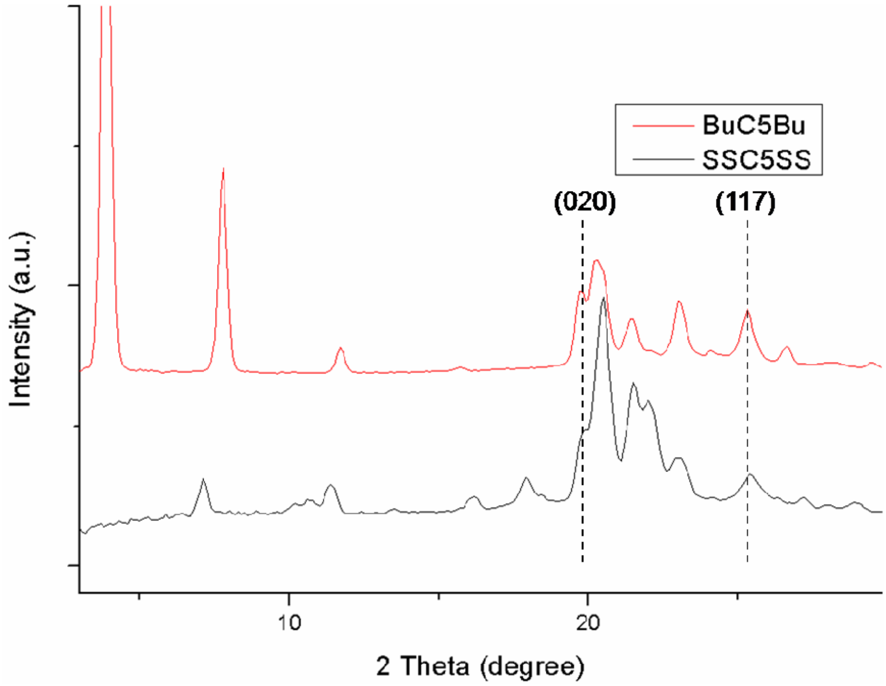


Figure S4. Powdery XRD patterns of **BuC5Bu** and **SSC5SS**. In the small angle region, reflections corresponding to (*f*00) planes are seen. The layer *d*-spacings of **BuC5Bu** and **SSC5SS** were determined to be 22.9 and 24.0 Å, respectively. In the wide angle region, reflections at d values of 4.49 Å and 3.51 Å, corresponding to intermolecular distances between alkyl chains are seen.

4. UV-Vis spectra of AuNP immobilized **SSC5SS** nanosheets

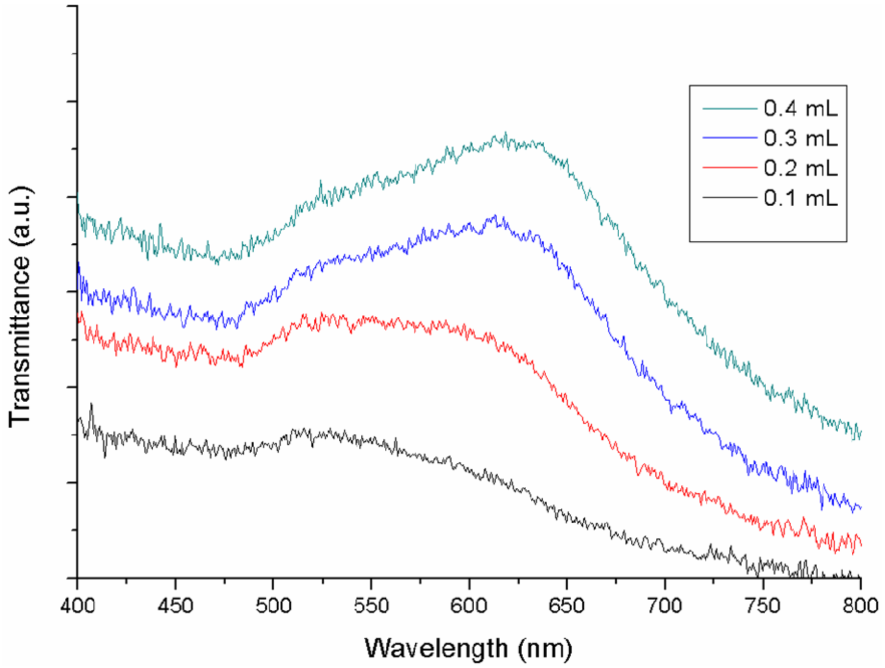


Figure S5. UV-Vis spectra of the dispersed solutions of AuNP immobilized **SSC5SS** nanosheets in H_2O. The absorption band at 520 nm is the characteristic plasmon band of AuNPs. The absorption band at ~630 nm, that increases with an increasing amount of AuNPs, indicates the formation of superlattices of AuNPs.

5. Microscope images

(1) AuNP immobilized nanosheets

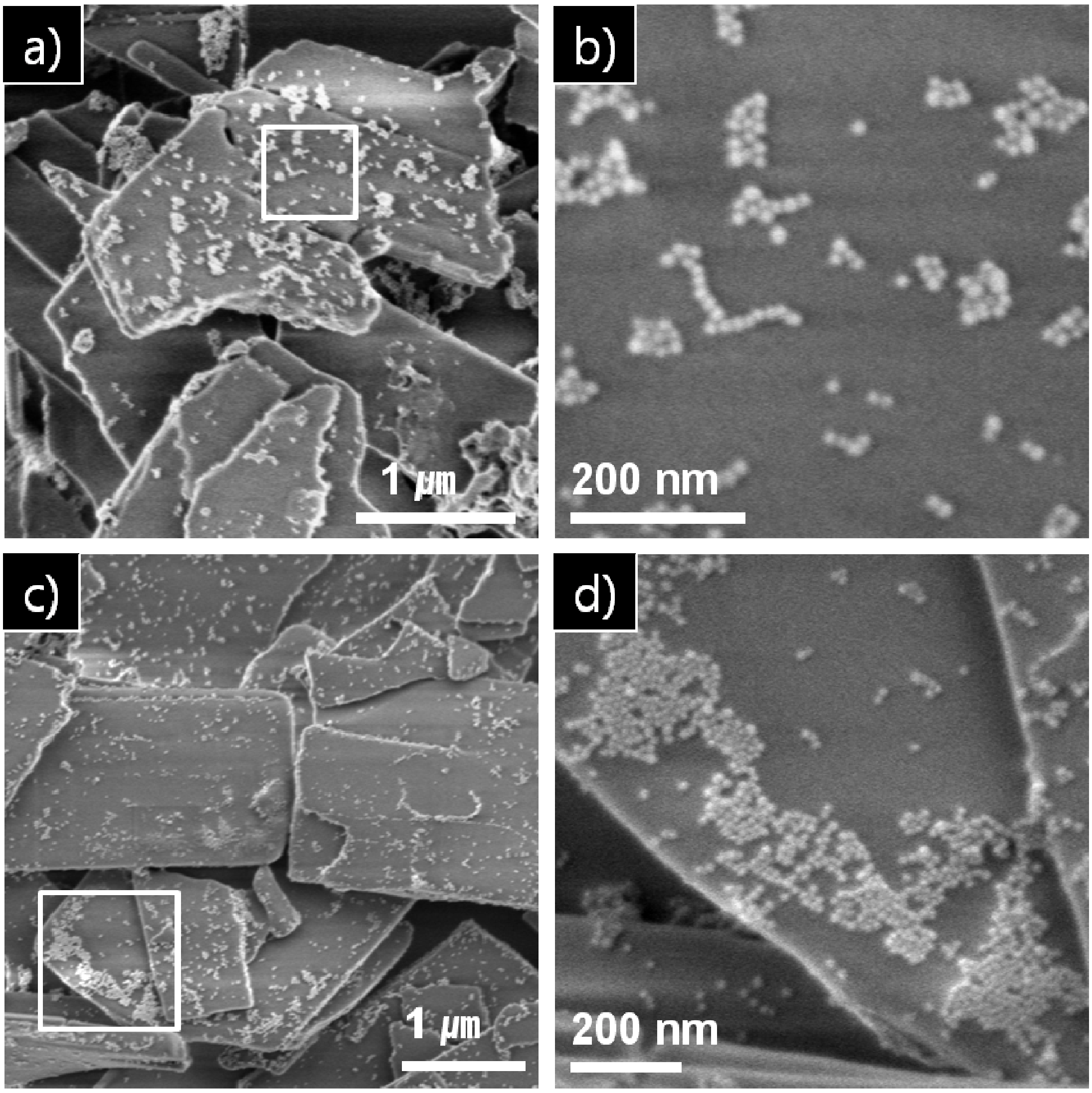


Figure S6. AuNP immobilized **SSC5SS** nanosheets, prepared through the addition of (a and b) 0.3 mL and (c and d) 0.4 mL of gold colloid solutions to 0.4 mg of **SSC5SS** nanosheets, respectively.

(2) AuNP immobilized nanosheets with an excess amount of AuNPs

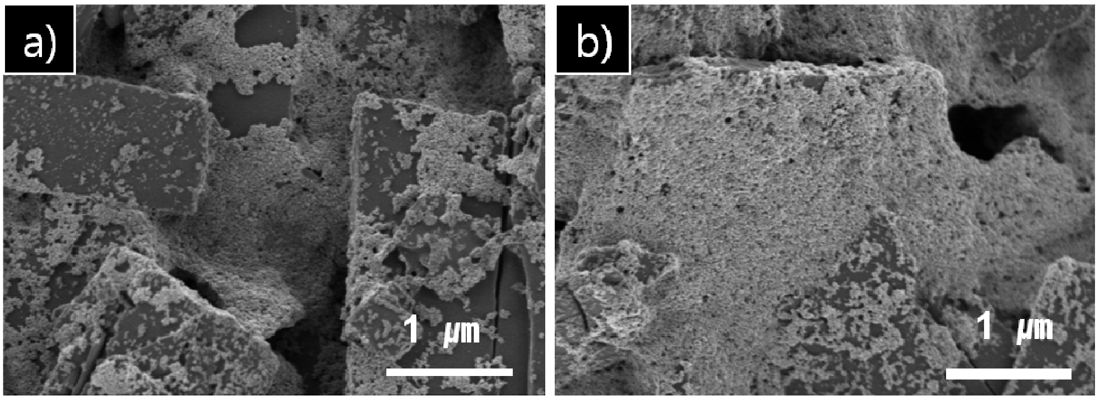


Figure S7. AuNP immobilized **SSC5SS** nanosheets, prepared through the addition of 2.5 mL of a gold colloid solution to 0.4 mg of **SSC5SS** nanosheets.

(3) Site-directed Immobilization of AuNPs on **SSC5SS** using a Layer-By-Layer film

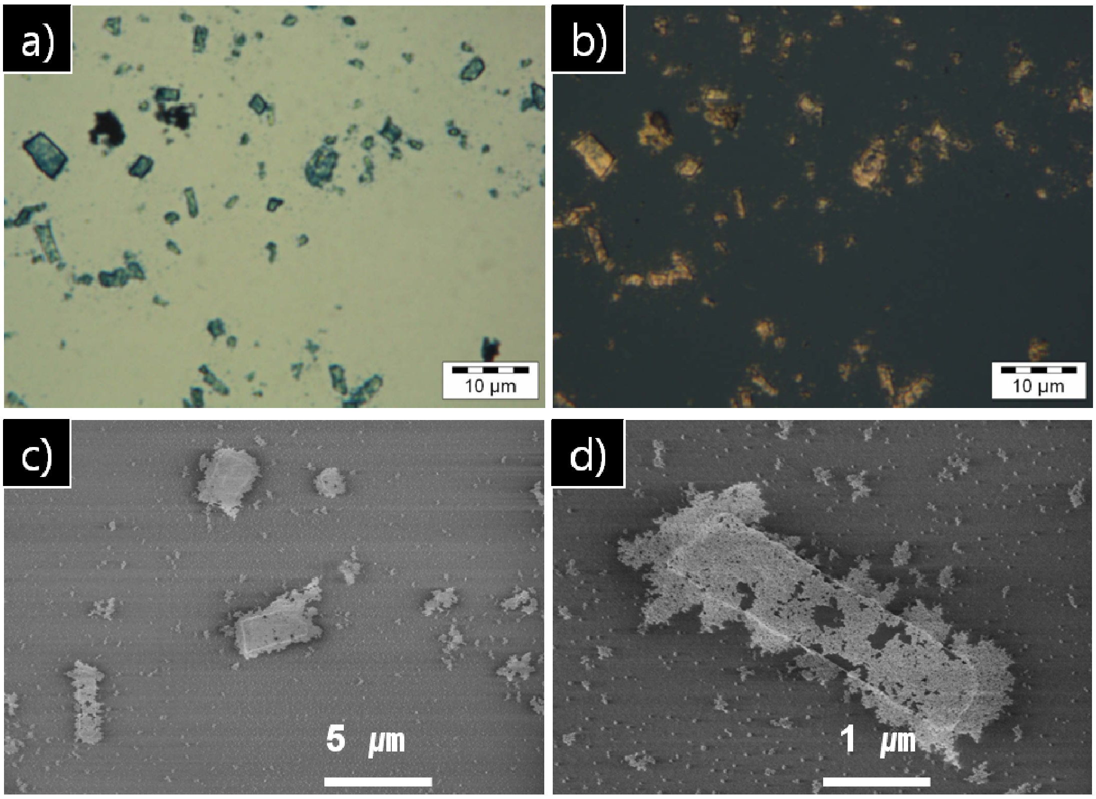


Figure S8. AuNP immobilized **SSC5SS** nanosheets on a negatively charged LBL film. Optical microscope images in (a) transmission mode and (b) reflection mode; (c and d) SEM images.