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Supplementary Materials

Sodium Lauryl Sulfate-Conjugated Cationic Gemini-Surfactant-Capped Gold Nanoparticles as Model System for Biomolecule Recognition

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Synthesis and Characterization of 16-s-16 gemini surfactants

Mass Spectrometry Measurements (MS). The compounds were dissolved in 50/50 mixture of acetonitrile/water (HPLC purity J. T. Baker) and diluted with the same mixture to make 5 μM solutions. Measurements were done on triple quadrupole mass spectrometer: AB-Sciex model Q-TRAP 4000, equipped with electrospray (ESI) ionization chamber. Solutions were fed with syringe pump (Harvard Apparatus) with 5 μL/min. Structure of compounds was confirmed by collisional induced dissociation in the second quadrupole and detection of fragments in the third quadrupole.

Nuclear Magnetic Resonance Spectroscopic Measurements (NMR). The compounds were dissolved in 99.95% $CDCl_3$ (~10 mg in 0.7 mL) and transferred into 5 mm NMR sample tubes (Promochem, Wesel, Germany). Spectra were measured with Topspin 1.3 on a Bruker DRX-400 AVANCE spectrometer (Bruker, Rheinstetten, Germany) at 400.13 MHz (1H) or 100.62 MHz (13C). For 1D spectra 32k data points were recorded and Fourier transformed to spectra with a range of 15 ppm (1H) and 240 ppm (13C). COSY, TOCSY, NOESY, HMQC, and HMBC spectra were measured in 128 experimental runs with 1024 data points each. Appropriate linear forward prediction, sinusoidal multiplication and Fourier transformation led to 2D-spectra with a range of 12 ppm and 220 ppm for 1H and 13C, respectively. Residual CHCl3 was used as internal standard for 1H (δH 7.24) and CDCl3 for 13C (δC 77.0) spectra.

Surface Tension Measurements. The surface tension of aqueous solutions of gemini surfactants was determined by Krüss 100K tensiometer (Krüss, Hamburg, Germany) equipped with the Wilhelmy plate at 25°C. The critical micelle concentration (CMC) and the surface tension at CMC were determined from the breakpoint in the surface tension versus. the concentration curve. The CMC was determined by reverse measurements starting from a highly concentrated aqueous solution and stepwise dilution by addition of water. The sequence of concentrations is produced automatically from an initial stock of the prepared surfactant solution. All experiments were carried out with double distillated water (72.08 mN m^{-1}).

Table S1. Values of the CMC of 16-s-16 gemini surfactants obtained by the surface tension technique and their comparison with other values reported in the bibliography.

Gemini surfactant	CMC /mM
16-3-16	0.024 (0.026)[a]
16-6-16	0.032 (0.046)[a]

(a) Data obtained from reference [56].

1. ,3-Propanediyl-bis-(dimethylhexadecylammonium bromide) (s = 3), 16-3-16

Yield = 68%. Elemental analysis (C39H84N2Br2, Mr=740.9057). Calc. for trihydrate (%): C 63.22; H 11.43; N 3.78. Found (%): C 61.78; H 10.98; N 3.67. 1H-NMR (400 MHz, $CDCl_3$, δ in ppm): 3.87 (m, 4H, N+-CH_2-CH_2-CH^2-N+); 3.49 (m, 4H, N+-CH_2-); 3.36 (s, 12H, N+-CH_3); 2.74 (m, 2H, N+-CH_2-CH_2-CH_2-N+); 1.79 (m, 4H, N+-CH_2-CH_2-); 1.38-1.24 (m, 52H, -(CH_2)13-); 0.87 (t, 6H, -CH_3). 13C NMR (100 MHz, $CDCl_3$, δ in ppm): 67.3 (N+-CH_2-); 61.6 (N+-CH_2-CH_2-CH_2-N+); 51.7 (N+-CH_3); 32.2, 29.9, 29.8, 29.8, 29.8, 29.8, 29.6, 29.6, 29.6, 29.5, 29.5, 26.7, 23.1 (-$(CH_2)_{13}$-); 23.4 (N+-CH_2-CH_2-); 19.2 (N+-CH_2-CH_2-CH_2-N+); 14.6 (-CH_3). Mass spectroscopy: (m/z) = 740.50; [M++ 79Br-]+ = 661.5; [M++ 81Br-]+ = 659.4; [(M - 2Br) / 2]+ = 289.7.

1. ,6-Hexanediyl-bis-(dimethylhexadecylammonium bromide) (s = 6), 16-6-16

Yield = 88%. Elemental analysis ($C_{42}H_{90}N_2N_2$, Mr=782.9854). Calc. for trihydrate (%): C 64.43; H 11.59; N 3.58. Found (%): C 63.72; H 11.08; N 3.60. 1H-NMR (400 MHz, $CDCl_3$, δ in ppm): 3.74 (m, 4H, N+-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N+); 3.42 (m, 4H, N+-CH_2-); 3.36 (s, 12H, N+-CH_3); 2.05 (m, 4H, N+-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N+); 1.67 (m, 4H, N+-CH_2-CH_2-); 1.61 (m, 4H, N+-CH_2-CH_2-CH_2- CH_2-CH_2-CH_2-N+); 1.37-1.24 (m, 36H, -$(CH_2)_{13}$-); 0.87 (t, 6H, -CH_3). 13C NMR (100 MHz, $CDCl_3$, δ in ppm): 65.0 (N+-CH_2-); 64.3 (N+-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N+); 51.2 (N+-CH_3); 31.9, 29.9, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 26.1, 22.6 (-$(CH_2)_{13}$-); 24.0 (N+-CH_2- CH_2-CH_2-CH_2-CH_2-CH_2-N+); 22.9 (N+-CH_2-CH_2-); 21.5 (N+-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N+); 14.1 (-CH_3). Mass spectroscopy: (m/z) = 782.5; [M++ 79Br-]+ = 703.5; [M++ 81Br-]+ = 701.3; [(M - 2Br) / 2]+ = 311.2

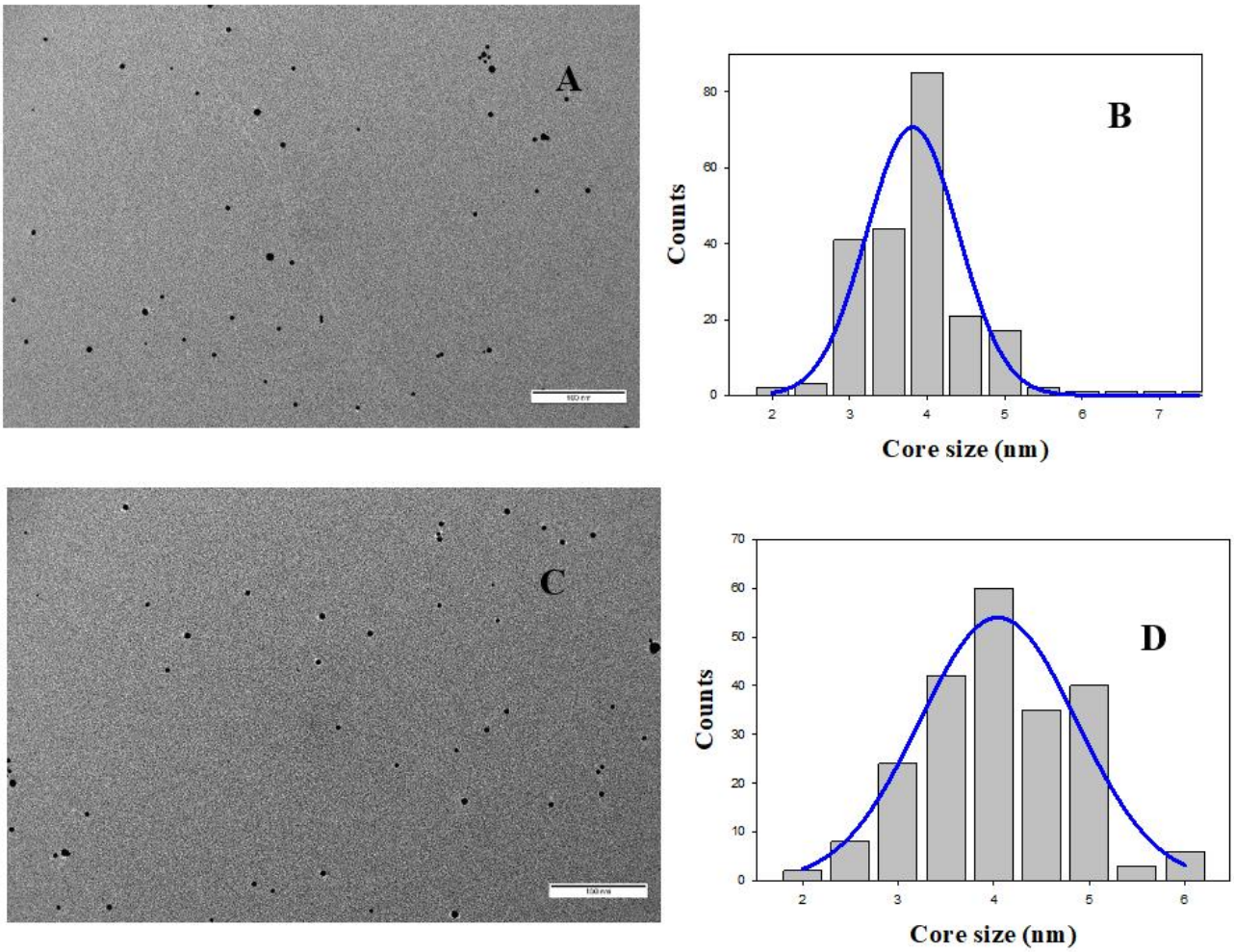

Figure S1. Example of TEM images and size distributions of Au@16-s-16 in water ($C_{Au@16\text{-}3\text{-}16}$ = 5.8 x10^{-8} M and $C_{Au@16\text{-}6\text{-}16}$ = 4.6 x10^{-8} M) for the calculation of the average size of the colloidal systems. (**A–B**) Au@16-3-16 system. (**C–D**) Au@16-6-16 system.

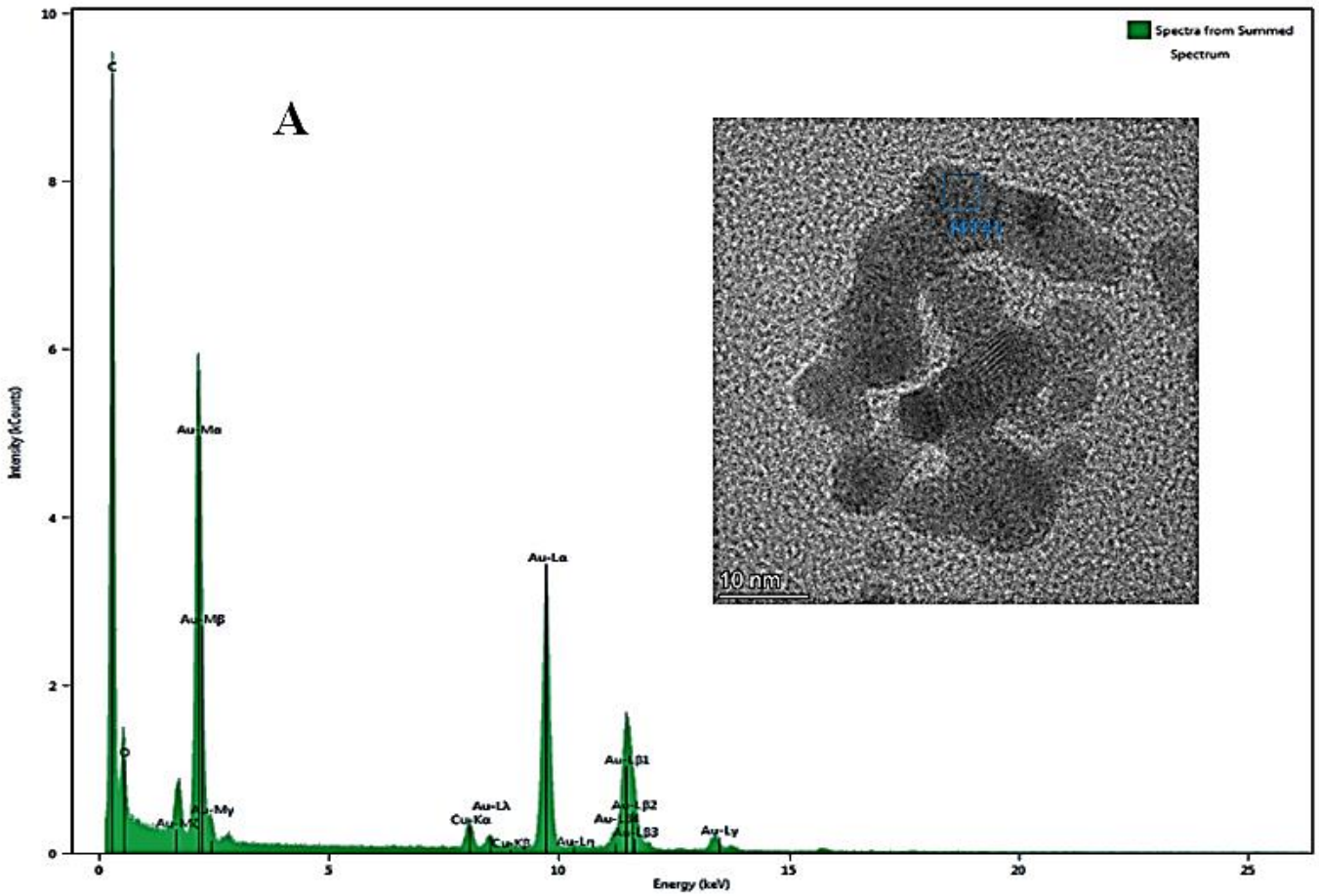

Figure S2 A. EDS spectra for Au@16-s-16/SDS complexes, the inset show TEM images of the aggregates for obtaining EDS spectra. Elemental mapping results indicate the presence of Gold elements in the samples. Au@16-3-16/SDS complex, $C_{Au@16\text{-}3\text{-}16} = 1.74 \times 10^{-8}$ M, $C_{SDS} = 3.0 \times 10^{-5}$ M.

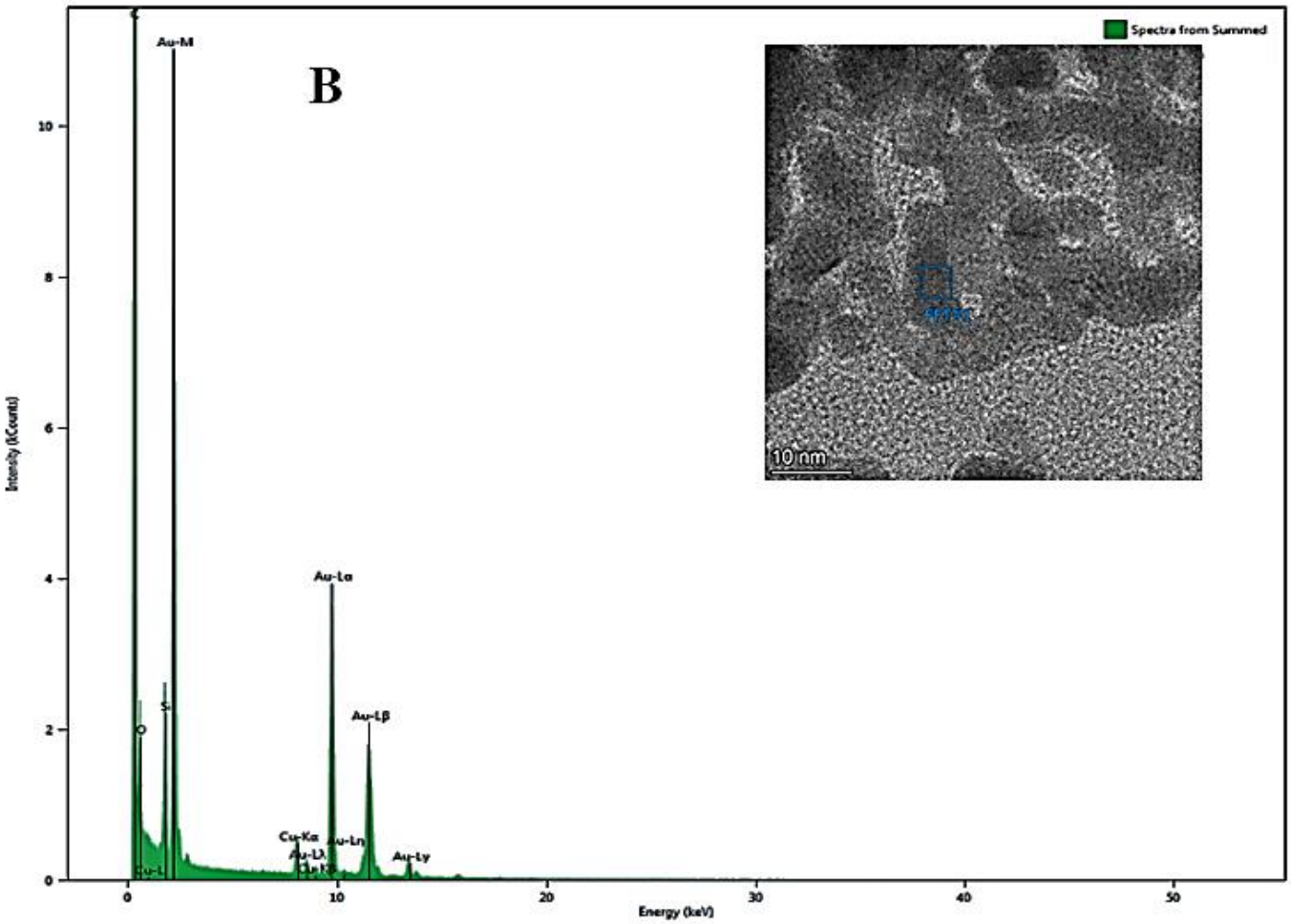

Figure S2 B. EDS spectra for Au@16-s-16/SDS complexes, the inset show TEM images of the aggregates for obtaining EDS spectra. Elemental mapping results indicate the presence of Gold elements in the samples. Au@16-6-16/SDS complex, $C_{Au@16\text{-}6\text{-}16} = 1.38 \times 10^{-8}$ M, $C_{SDS} = 3.0 \times 10^{-5}$ M.

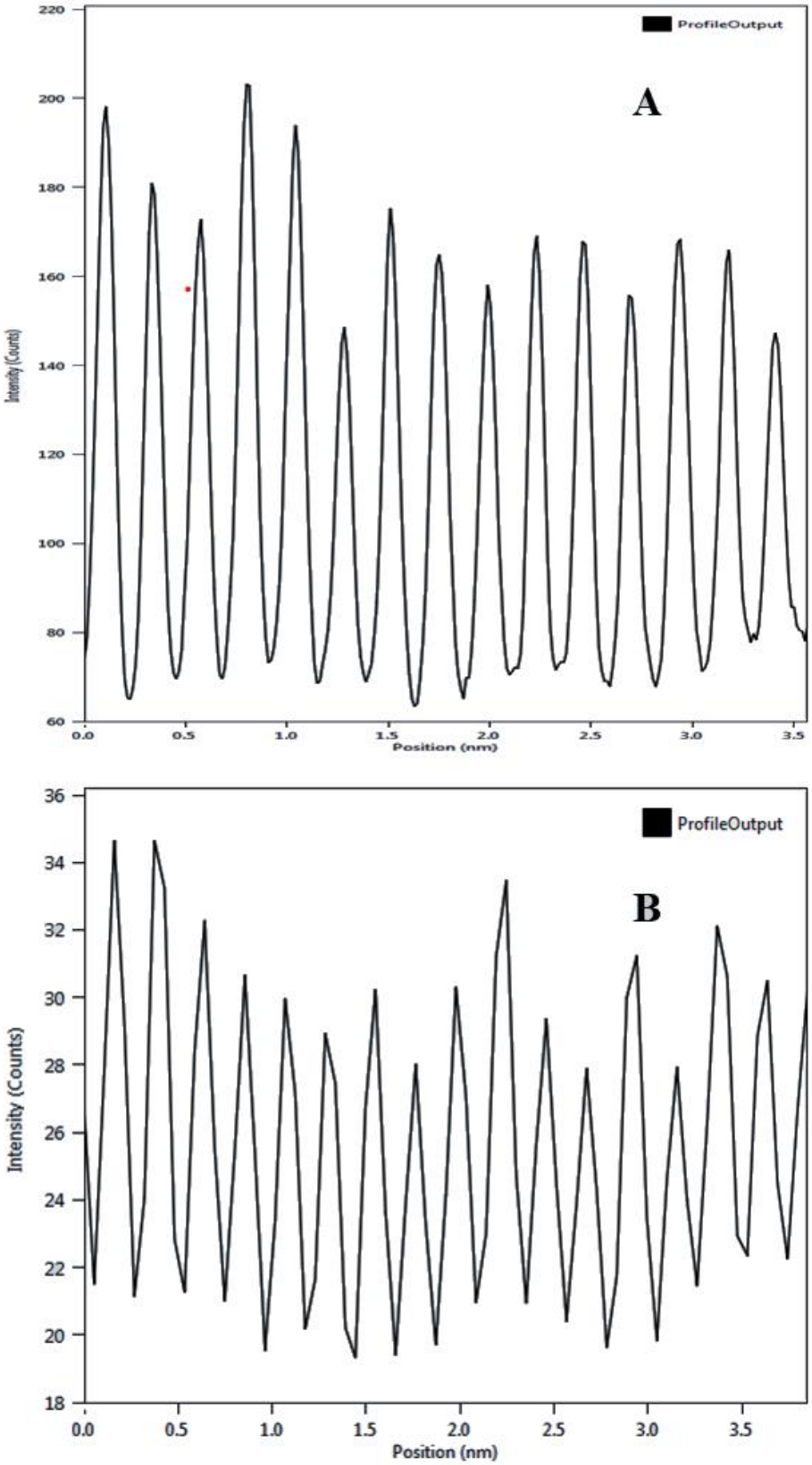

Figure S3. Intensity (counts) versus position (nm) profiles for Au@16-s-16/SDS complexes showing the d spacing among gold atoms. (**A**) Au@16-3-16/SDS complex, $C_{Au@16\text{-}3\text{-}16} = 1.74 \times 10^{-8}$ M, $C_{SDS} = 3.0 \times 10^{-5}$ M. (**B**) Au@16-6-16/SDS complex, $C_{Au@16\text{-}6\text{-}16} = 1.38 \times 10^{-8}$ M, $C_{SDS} = 3.0 \times 10^{-5}$ M.

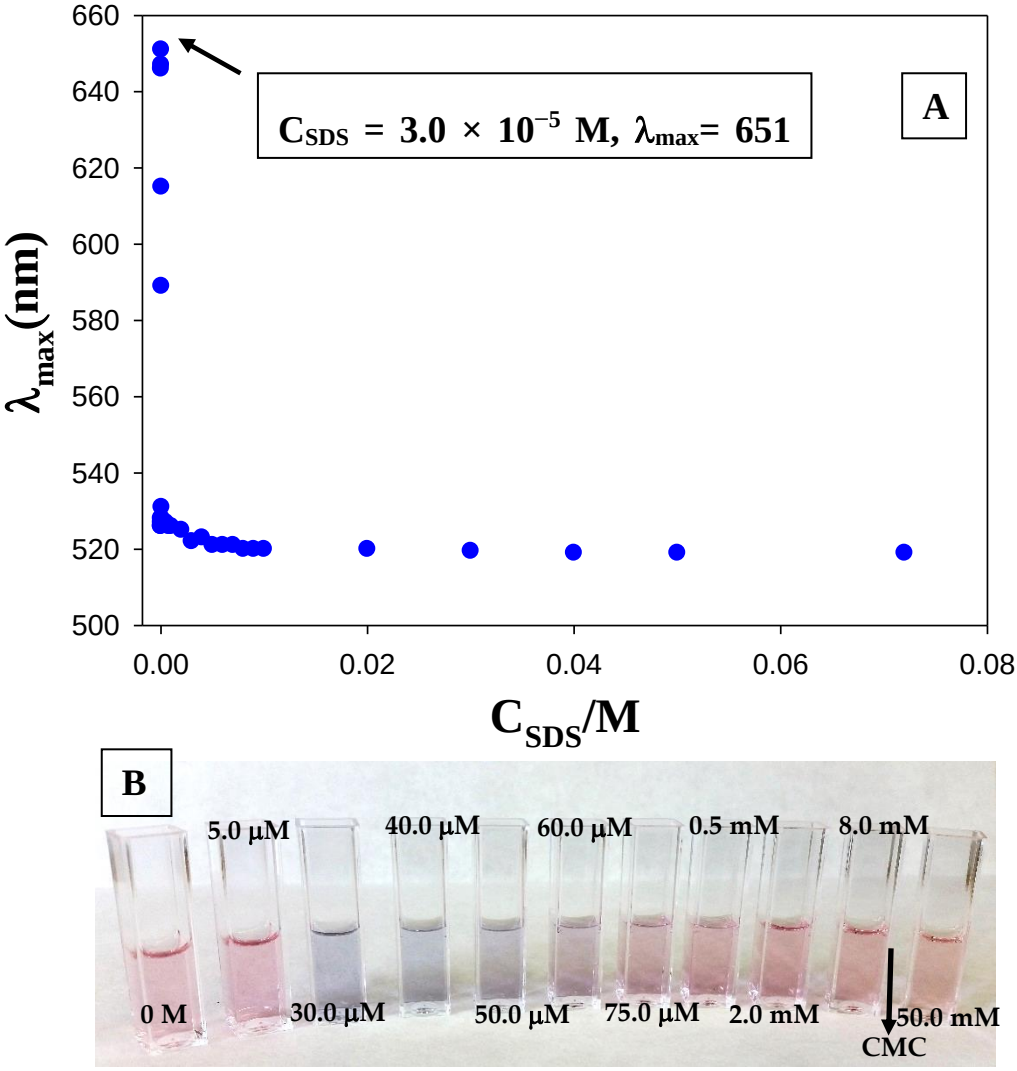

Figure S4. (**A**) Maximum wavelength for the aggregation of the system Au@16-3-16/SDS determination by following the changes of the maximum wavelength of the SPR as a function of C_{SDS} concentration. (**B**) A series of diluted SDS surfactant solutions with added gold nanoparticles covered with 16-3-16 gemini surfactant, where 200 μl of Au@16-3-16 of 1.74 × 10^{-7} M solution was diluted with 1800 μl of SDS solutions of appropriate concentrations; the arrow bars indicate the surfactant concentration at which aggregation is maximum and the approximate obtained CMC value.

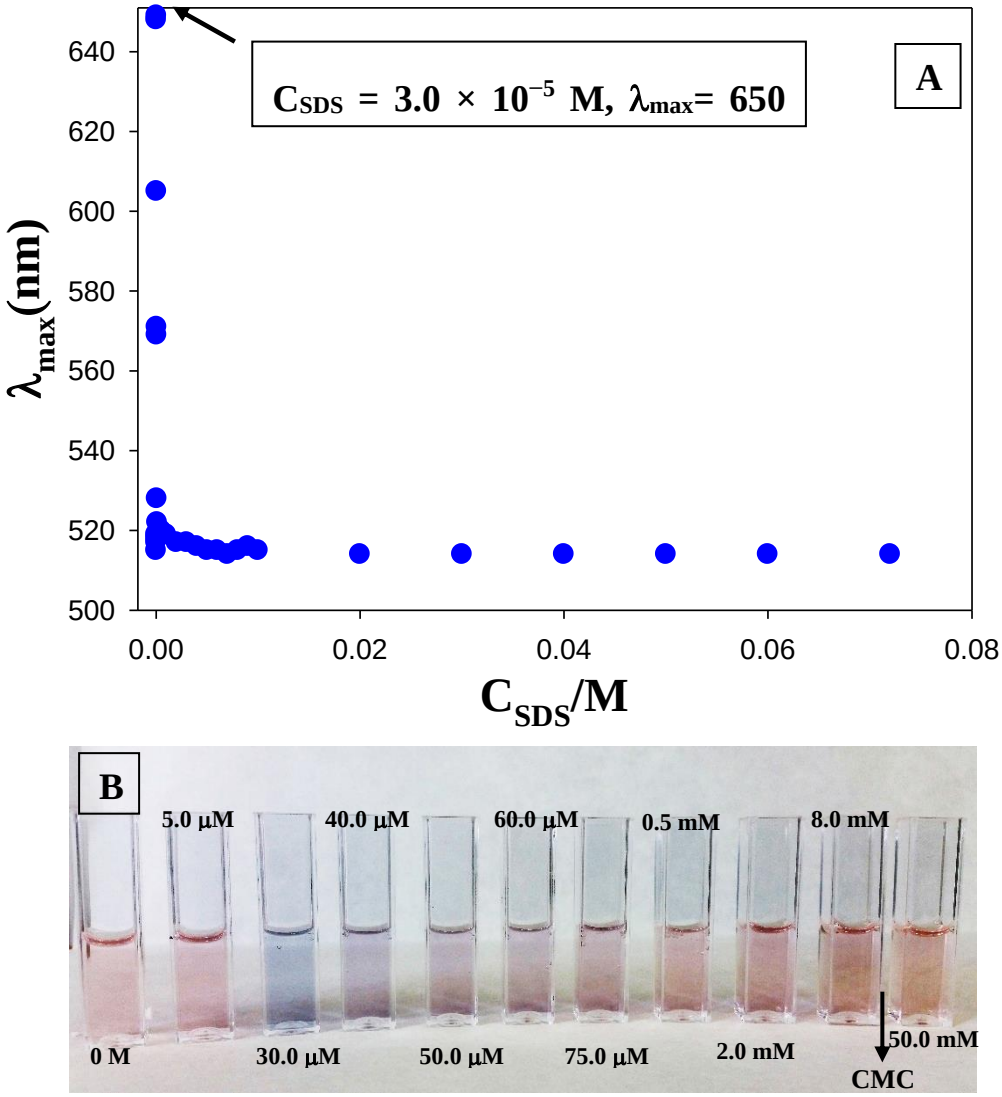

Figure S5. (**A**) Maximum wavelength for the aggregation of the system Au@16-6-16/SDS determination by following the changes of the maximum wavelength of the SPR as a function of C_{SDS} concentration. (**B**) A series of diluted SDS surfactant solutions with added gold nanoparticles covered with 16-6-16 gemini surfactant, where 200 µl of Au@16-3-16 of 1.38 × 10^{-7} M solution was diluted with 1800 µl of SDS solutions of appropriate concentrations; the arrow bars indicate the surfactant concentration at which aggregation is maximum and the approximate obtained CMC value.

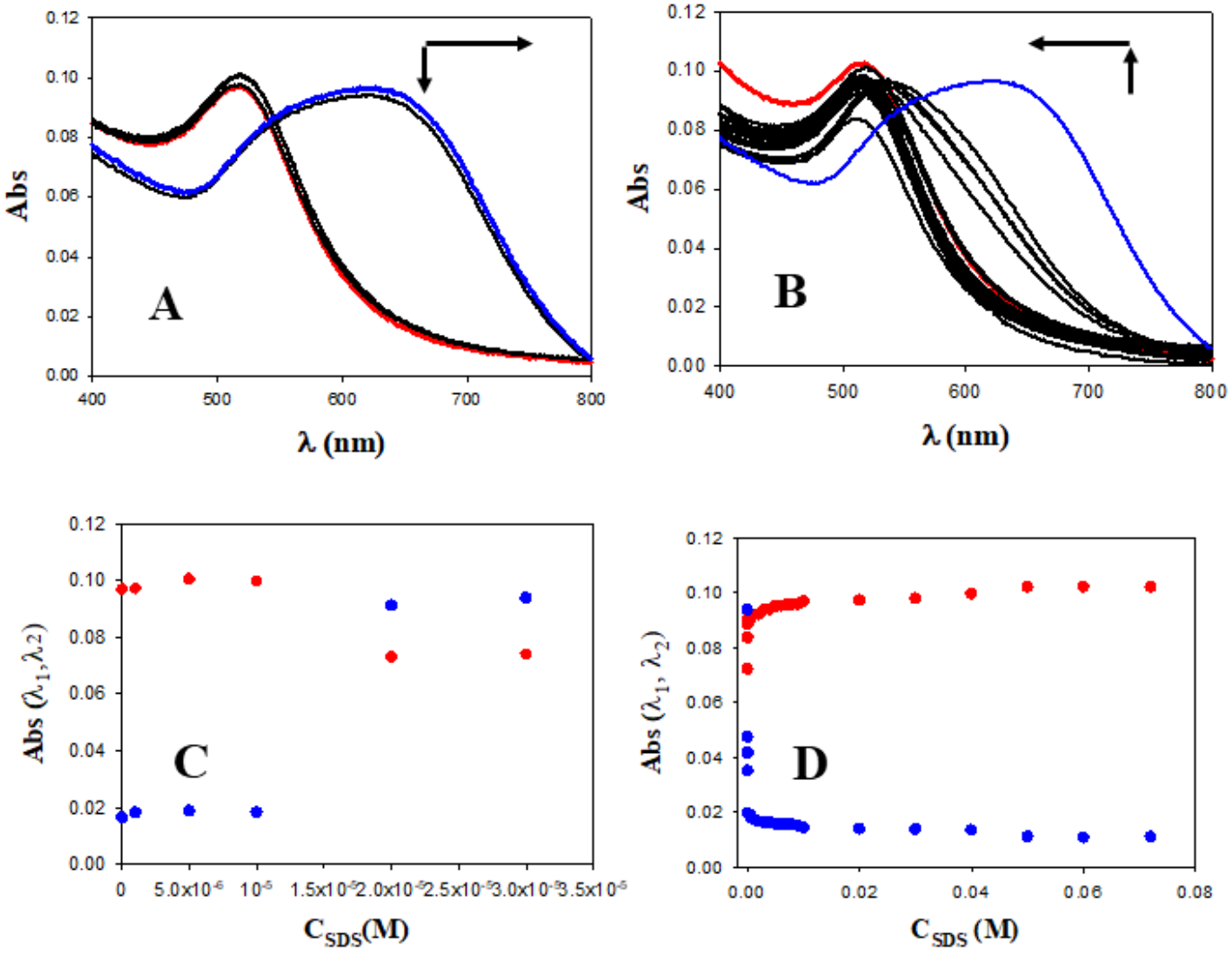

Figure S6. Absorbance titration of Au@16-6-16/SDS system at a fixed gold nanoparticle concentration and its corresponding absorbance intensities at λ_1 = 516 nm (in red, non-aggregated gold nanoparticles maximum wavelength) and λ_2 = 650 nm wavelengths (in blue, aggregated gold nanoparticle maximum wavelength). $C_{Au@16\text{-}6\text{-}16} = 1.38 \times 10^{-8}$ M in all the experiments. (**A**) Aggregation experiments. Red spectrum, C_{SDS} = 0 μM; blue spectrum, C_{SDS} = 30.0 μM; black spectra arrows direction, C_{SDS} = 1.0, 5.0, 10.0 and 20.0 μM. (**B**) Disaggregation experiments. Red spectrum, C_{SDS} = 0.07 M; blue spectrum, C_{SDS} = 30.0 μM; black spectra arrows direction, C_{SDS}= 40.0 μM, 50.0 μM, 60.0 μM, 75.0 μM, 10.0 mM, 50.0 mM, 75.0 mM, 1.0 mM, 2.0 mM, 3.0 mM, 4.0 mM, 5.0 mM, 6.0 mM, 7.0 mM, 8.0 mM, 9.0 mM, 0.01 M, 0.02 M, 0.03 M, 0.04 M, 0.05 M and 0.06 M. (**C**) Absorbance intensities of aggregation experiments in Figure A. (**D**) Absorbance intensities of disaggregation experiments in Figure B.

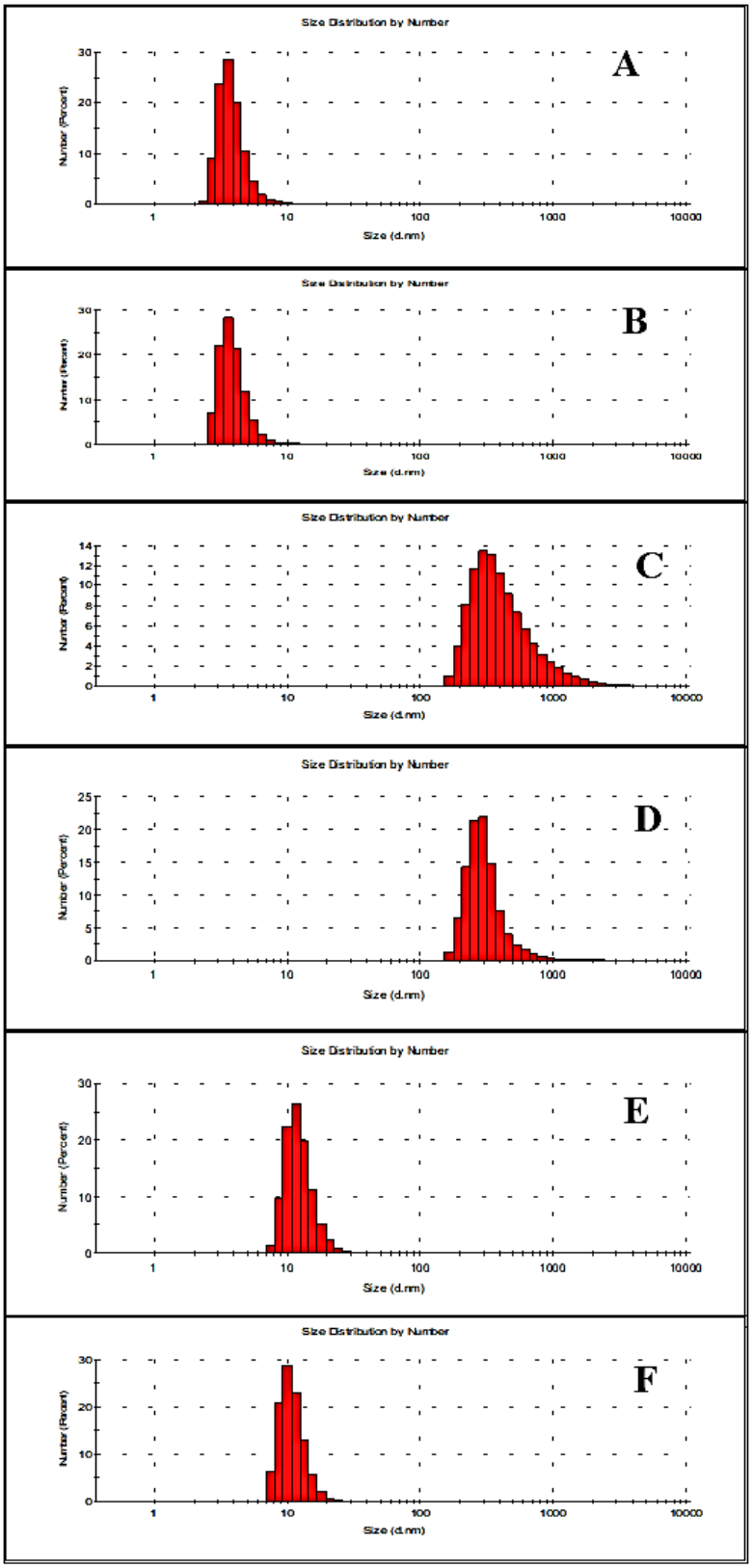

Figure S7. DLS hydrodynamic size distribution by number for Au@16-s-16/SDS complexes at different C_{SDS} concentrations. (**A**) Au@16-3-16, C_{SDS} = 0 M, (**B**) Au@16-6-16, C_{SDS} = 0 M, (**C**) Au@16-3-16, C_{SDS} = 5.0 × 10^{-5} M, (**D**) Au@16-6-16, C_{SDS} = 5.0 × 10^{-5} M, (**E**) Au@16-3-16, C_{SDS} = 1.0 × 10^{-3} M, and (**F**) Au@16-6-16, C_{SDS} = 1.0 × 10^{-3} M.

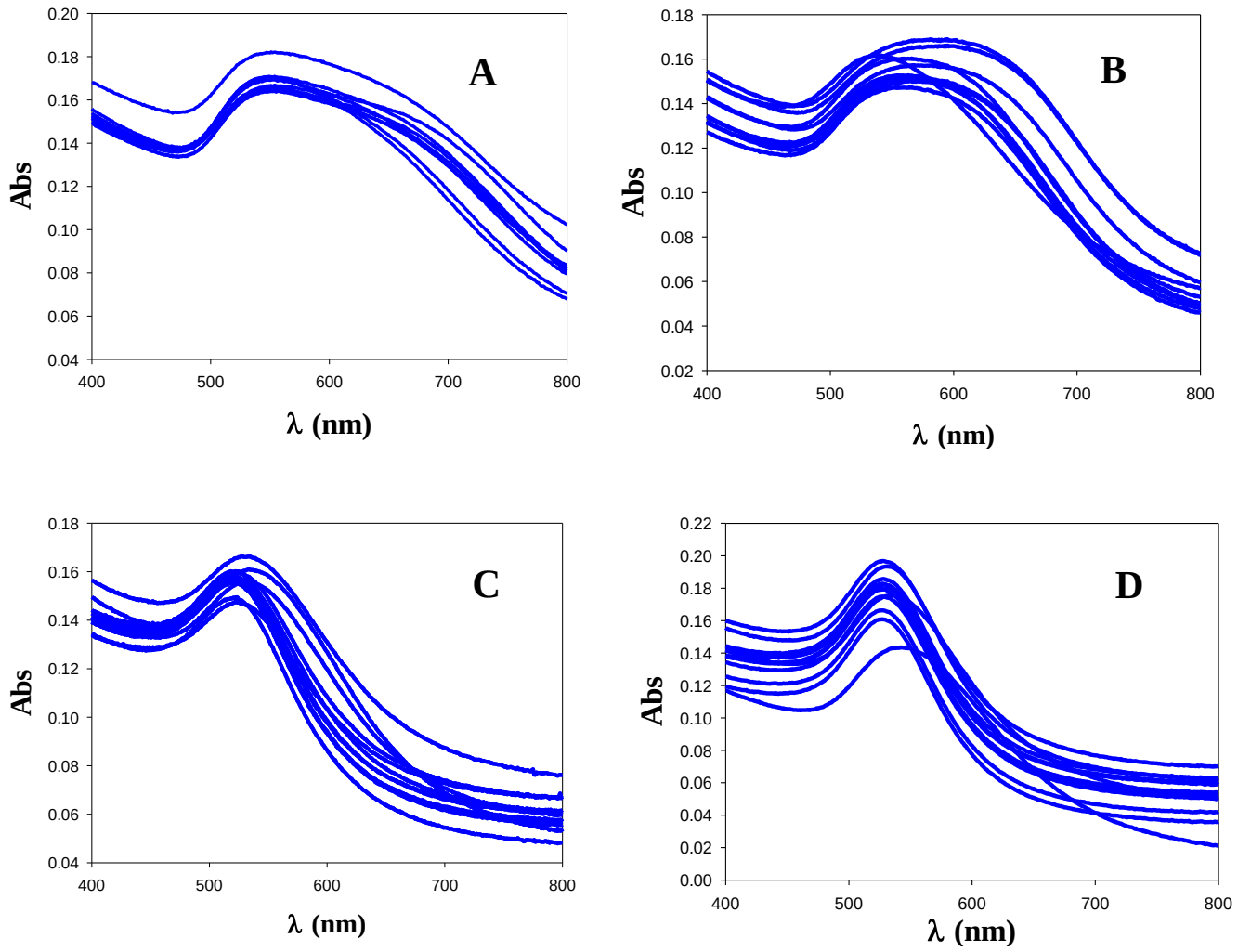

Figure S8. Absorbance titration of aggregated Au@16-s-16/SDS systems at different $C_{biopolymer}$ concentrations, the range of concentrations explored are similar as those described in figures 5 and 6 of the main text. (**A**) Au@16-3-16/SDS/DNA system, (**B**) Au@16-6-16/SDS/DNA system, (**C**) Au@16-3-16/Lysozyme/SDS system and (**D**) Au@16-6-16/Lysozyme/SDS system. (**A-B**) method of addition A. (**C–D**) method of addition B.

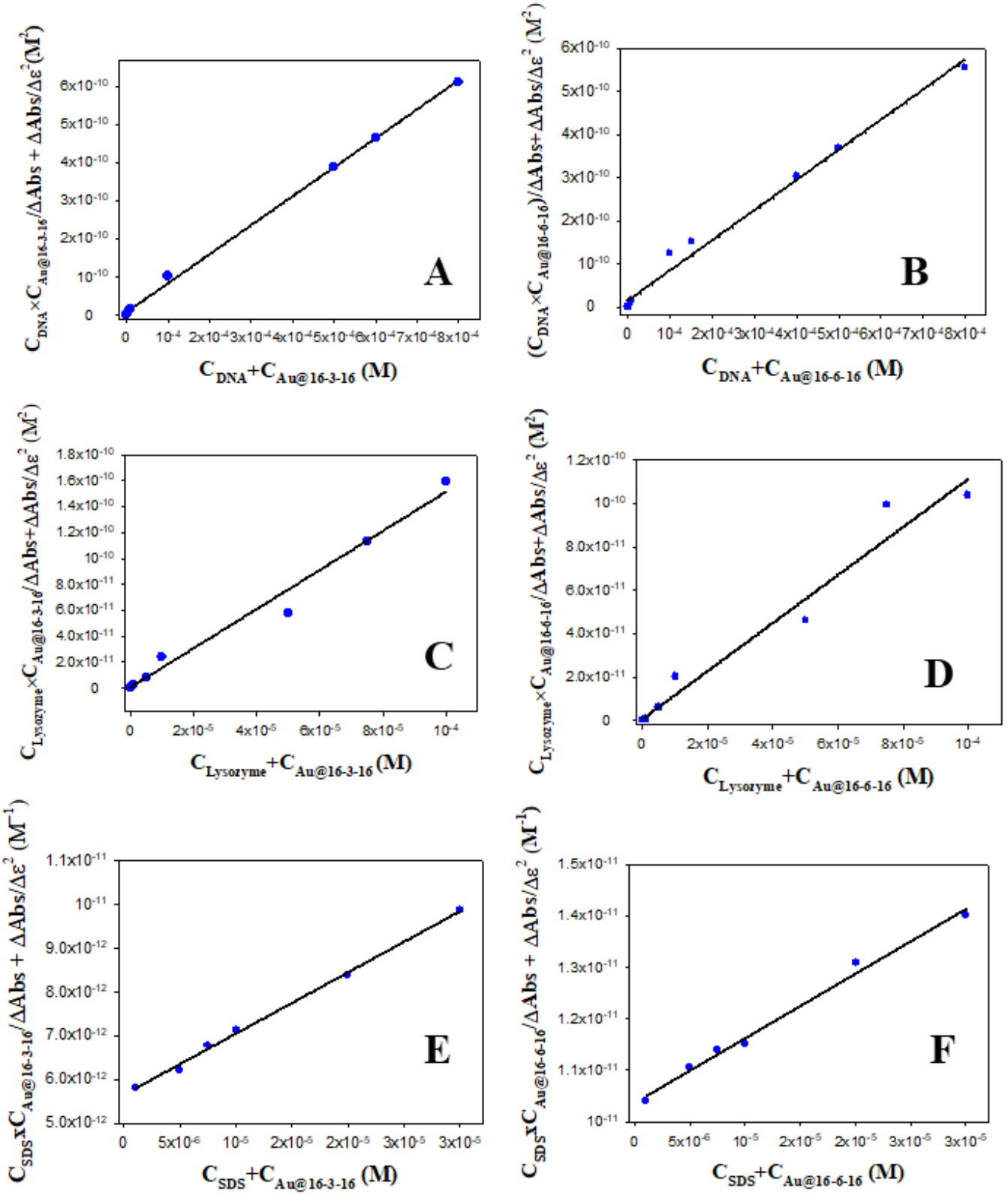

Figure S9. Analysis of the absorbance titration data for Au@16-s-16/biopolymer systems in water, T = 298.2 K. Data are fitted according to the Hildebrand Benesi model (eqn (2)). (**A**) Au@16-3-16/DNA system, $C_{Au@16-3-16} = 1.74 \times 10^{-8}$ M, $\lambda = 525$ nm. (**B**) Au@16-6-16/DNA system, $C_{Au@16-6-16} = 1.38 \times 10^{-8}$ M, $\lambda = 516$ nm. (**C**) Au@16-3-16/Lysozyme system, $C_{Au@16-3-16} = 1.74 \times 10^{-8}$ M, $\lambda = 525$ nm. (**D**) Au@16-6-16/Lysozyme system, $C_{Au@16-6-16} = 1.38 \times 10^{-8}$ M, $\lambda = 516$ nm. (**E**) Au@16-3-16/SDS system, $C_{Au@16-3-16} = 1.74 \times 10^{-8}$ M, $\lambda = 525$ nm. (**F**) Au@16-6-16/SDS system, $C_{Au@16-6-16} = 1.38 \times 10^{-8}$ M, $\lambda = 516$ nm.

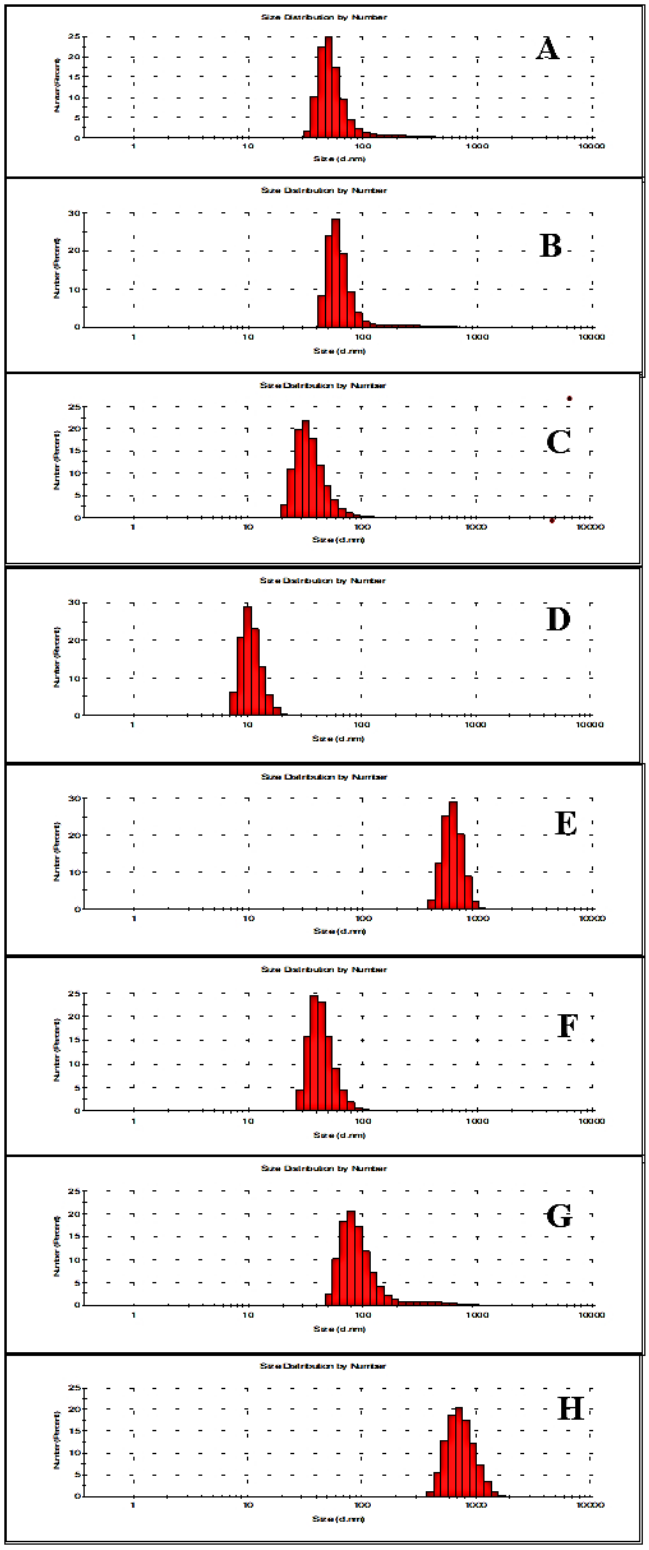

Figure S10. DLS hydrodynamic size distribution by number for Au@16-s-16 nanocomplexes at different $C_{biopolymer}$ concentrations, C_{SDS} = 5.0 × 10^{-5} M in all the experiments. (**A**) Au@16-3-16, C_{DNA} = 1.0 × 10^{-6} M. (**B**) Au@16-6-16, C_{DNA} = 1.0 × 10^{-6} M. (**C**) Au@16-3-16, C_{DNA} = 5.0 × 10^{-4} M. (**D**) Au@16-6-16, C_{DNA} = 5.0 × 10^{-4} M. (**E**) Au@16-3-16, $C_{Lysozyme}$ = 5.0 × 10^{-8} M. (**F**) Au@16-6-16, $C_{Lysozyme}$ = 5.0 × 10^{-8} M. (**G**) Au@16-3-16, $C_{Lysozyme}$ = 1.0 × 10^{-4} M. (H) Au@16-6-16, $C_{Lysozyme}$ = 1.0 × 10^{-4} M.

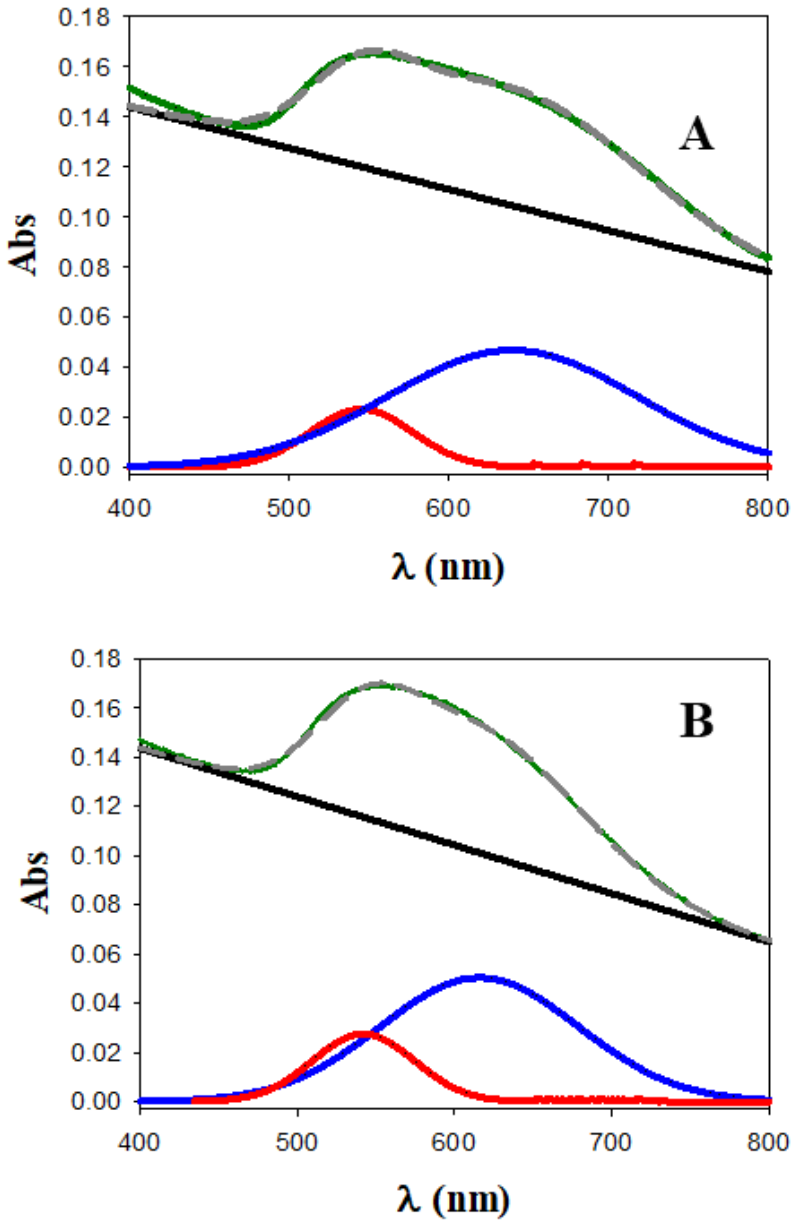

Figure S11. Examples of deconvolution of experimental spectra obtained in the presence of biomolecules. Grey long dash line corresponds to simulated data and green solid line to experimental data. The absorbance peak assigned to non-aggregated particles fraction is marked in red, while the aggregated nanoparticle fractions are marked in blue. The green line designates the linear function used to correct the background absorption. (**A**) Au@16-3-16/DNA/SDS system, C_{DNA} =1.0×10^{-7} M; (**B**) Au@16-6-16/Lysozyme/SDS system, $C_{Lysozyme}$ =5.0×10^{-7} M.