Electronic Supplementary Material (ESI) for Nanoscale
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Supporting Information

Self-Assembly of Thiolated Cyanine Aggregates on Au(111) and Au Nanoparticle Surfaces

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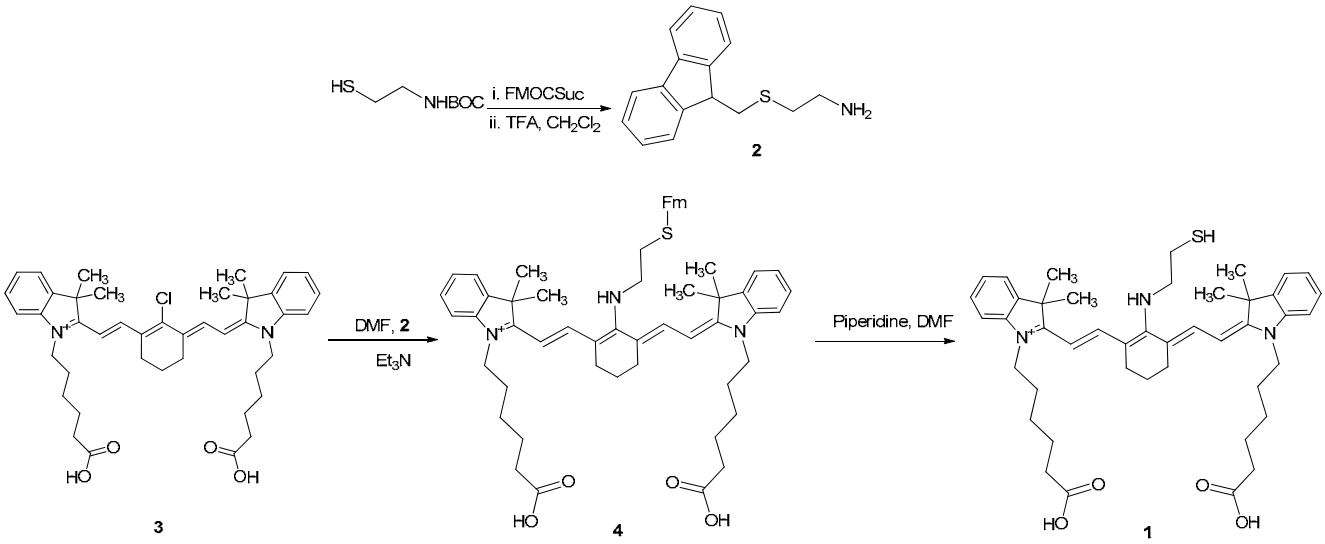
Experimental Section: Dye Synthesis

General Considerations

All starting materials for the dye synthesis were purchased from commercial sources and were used as received. ^{1}H NMR (200 MHz) spectra have been measured in a Varian Bruker AC-200 spectrometer. Mass spectra were measured with a Bruker Daltonik microTOF mass spectrometer (ESI+, ESI-). Fluorescence measurements were performed on a Cary Eclipse fluorometer. Absorption spectra were measured on a Cary 50 spectrophotometer.

Scheme S1

Synthetic scheme for compound **1**:



2-(9H-fluoren-9-ylmethylsulfanyl)ethanamine (2): Compound **2** was prepared according to procedure described by West et al.[1] Briefly, to a solution of N-Boc-cysteamine (0.3g, 1.70 mmol) in 10 mL of CH_2Cl_2 was added N-(9-Fluorenylmethoxycarbonyloxy)succinimide (Fmoc-OSu) (0.620 g, 1.86 mmol) and TEA (0.26 mL, 1.86 mmol). After stirring for 4 hours the reaction was concentrated in vacuo and purified by column chromatography (cyclohexane : ethyl Acetate = 9:1) to give .0.538 mg (89%) of the S-Fm protected thiol as a clear oil. ^{1}H NMR (200 MHz, Cl3CD) δ 7.78 (d, J = 7.7 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.49 – 7.25 (m, 4H), 4.84 (sa, 1H), 4.13 (t, J = 6.3 Hz, 1H), 3.30 (q, J = 6.2 Hz, 2H), 3.12 (d, J = 6.3 Hz, 2H), 2.64 (t, J = 6.5 Hz, 2H), 1.46 (s, 9H).The protected thiol (80mg, 0.2mmol) was treated with 0.5 mL of CH_2Cl_2 and 0.5 mL trifluoroacetic acid. After stirring for 2 hours the solvent was removed in a rotatory evaporator to afford **2** as yellow oil (57mg, quant). This product was used immediately without further purification.

Compound **3** was synthesized according to the general method described by Zhang et al.[2]

Compound **2**: To a solution of **3** (100mg, 0.13 mmol) in 2ml of anhydrous DMF was added **2** and 50 µL of TEA, then the reaction mixture was stirred for 4 hours protected from light. The solvent was evaporated by vacuum not over 40 °C to get a dark blue solid. The product was purified by column chromatography, using Sephadex LH-20 column (20 x 1500 mm) and methanol as solvent. Affording 95mg (75%) of a dark blue solid. ^{1}H NMR (200 MHz,

MeOD) δ 7.84 (d, J = 13.6 Hz, 2H), 7.74 (d, J = 7.3 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.51 – 7.17 (m, 8H), 7.09 (t, J = 7.8 Hz, 4H), 5.86 (d, J = 12.4 Hz, 2H), 4.24 – 3.99 (m, 5H), 3.93 (t, J = 6.1 Hz, 2H), 3.25 – 3.02 (m, 4H), 2.57 (t, J = 6.2 Hz, 2H), 2.28 (t, J = 6.0 Hz, 4H), 1.88 – 1.14 (m, 26H). HRMS (ESI+) Calcd for ([M+nH])+, 902.4925; Found, 902.4939.

Compound **1**: Compound **2** (95mg, 0.10mmol) was dissolved in 2 mL of anhydrous DMF and 1 mL of freshly distilled pyperidine , the resulting solution was stirred for 7 hours protected from light. The solvent was removed in *vacuo*, and then purified on C18-RP column using methanol-water (80:20) as eluent to afford the desired product (40mg, 55%) of the product. ^{1}H NMR (200 MHz, MeOD) δ 7.83 (d, J = 13.0 Hz, 2H), 7.36 (d, J = 7.1 Hz, 2H), 7.28 (d, J = 7.3 Hz, 2H), 7.08 (t, J = 7.3 Hz, 4H), 5.86 (d, J = 12.9 Hz, 2H), 4.10 (t, J = 5.9 Hz, 4H), 3.96 (t, J = 6.0 Hz, 2H), 3.12 (t, J = 6.1 Hz, 2H), 2.52 (t, J = 5.9 Hz, 4H), 2.23 (t, J = 5.9 Hz, 4H), 1.88 – 1.24 (m, 26H). HRMS (ESI+) Calcd, 723.4064; Found, 723.4057.

Computational details

The computations of the geometry for the thiolated cyanine dye were performed using DFT with Gaussian03 package[3]. The DFT was treated according to Becke's three parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP)[4], and all calculations were performed without any symmetry constraints by using polarized split-valence 6-31G* basis sets.

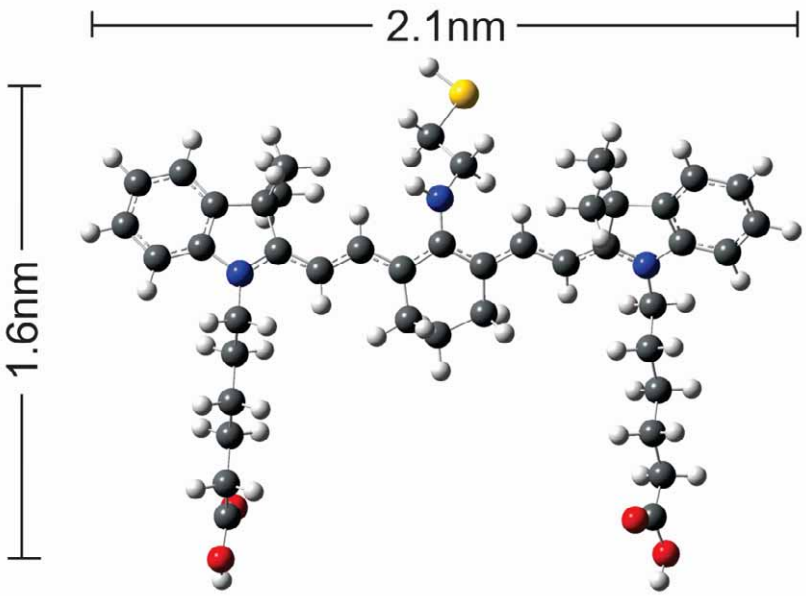


Figure S1. Optimized geometrical structure of the thiolated cyanine dye. Blue: N; Yellow: S; ~~the~~ Red: O; Dark: C; White: H).

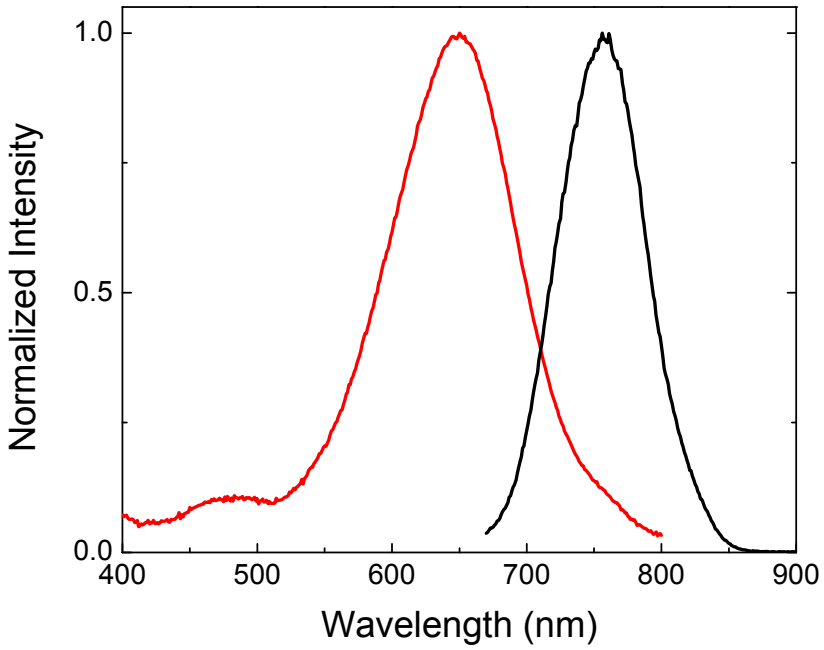


*Figure S2. Normalized absorption (red line) and emission (black line) spectra of compound **1** in PBS.*

Gold Nanoparticles (AuNP) preparation and post modification with CNN (AuNP-CNN).

AuNP stabilized in citrate buffer.

Gold nanoparticles (AuNP) were synthesized by the standard method introduced by Turkevich et al [5] and refined by Frens.[6] Briefly, the reduction of a gold hydrochlorate solution has been initiated by sodium tris-citrate (Merck) by bringing gold solution to a boil in a reactor, which is heated by a bath thermostat. The liquid was vigorously stirred. After the solution started to boil, preheated citrate solution was added. After 15 min the liquid was extracted and cooled to room temperature.

AuNP stabilized in citrate buffer pH 7.5 were characterized by UV- vis spectra and Transmission Electron Microscopy (TEM). Figure S3.a shows the UV visible spectra of AuNP stabilized in citrate buffer pH 7.5. The absorption (surface Plasmon resonance) peak is

obtained at 520 nm which matches well with others results. Figure S3.b shows the Size Distribution Function and the inset is TEM image of AuNPs stabilized in citrate buffer pH 7.5. The size distribution was performed using ImageJ software, an average size of 12 ± 1 nm was determined over 230 particles.

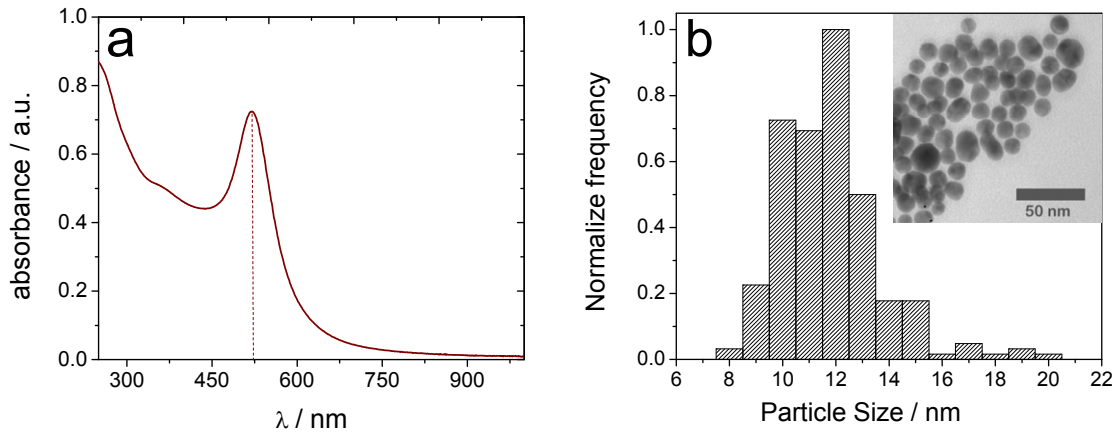


Figure S3. Characterization of the AuNPs stabilized in citrate buffer pH 7.5. (a) UV-visible spectra. (b) Size distribution function. Inset: TEM image of the AuNPs.

AuNP-CNN

AuNPs stabilized in citrate buffer of pH 7.5 and thiolated CNN solution in the same buffer were mixed in a 1:1000 molar ratio in order to replace the citrate capping by the thiolated CNN SAM. In order to reach this ratio we calculated an approximated molar absorption coefficient of AuNPs using Mie Method.[7] A value of 0.145 x 10^{-9} M^{-1} cm^{-1} was obtained, in well agreement with previously reported values.[7][8] Using this value we prepare a mix of AuNP:CNN in a 1:1000 ratio and the solutions were left overnight at room temperature in the dark. Modified AuNPs with CNN (AuNP-CNN) were separated from the excess CNN solution by several centrifugation steps at 4^0C. First, the reaction mix was centrifugated (3200 g, 60 mins.) and the pellet was resuspended in citrate buffer pH 7.5 before a second centrifugation step (4600 g, 60 mins.). This washing step was repeated three times at 7600 g, 60 mins. Supernatant solutions were stored and UV visible spectra were performed in order to follow the cleaning process. After the second centrifugation step at 4600 g no CNN was detected by UV visible spectroscopy of the supernatant solution. The AuNP-CNN was characterized by UV-vis and particle size was determined by analysis from TEM images. Figure S4a shows UV visible spectra of purified AuNPs-CNN (red solid line). In order to easily comparison, original AuNPs stabilized in citrate buffer pH 7.5 is also introducing (pink

dash line). Both UV visible spectra of AuNP-CNN and AuNP stabilized in citrate buffer show the same feature with the maximum peak position at 520 nm, indicating the procedure does not affect the nanoparticle nature. In addition AuNP-CNN UV visible spectra also shows a small shoulder at 800 nm corresponding to CNN molecules of the AuNP capping, but due to strong absorption extinction coefficient of AuNP it is not easily to observe. In the MS Raman Spectra of AuNP-CNN result the clear evidence of successful AuNP modification with CNN dye. On the other hand Figure S4b show particle size distribution and the inset is a zoom of the TEM image of AuNP-CNN. The size distribution was performed using ImageJ software by measuring 190 nanoparticles without using any algorithm. An average particle size of 12± 1 nm was determined, this value correspond to same obtained for AuNP stabilized in citrate buffer with slightly difference in the size distribution plot (see Figure S3.b). These results show that the procedure used to AuNP post functionalization with CNN does not disturb the morphology of the original AuNPs.

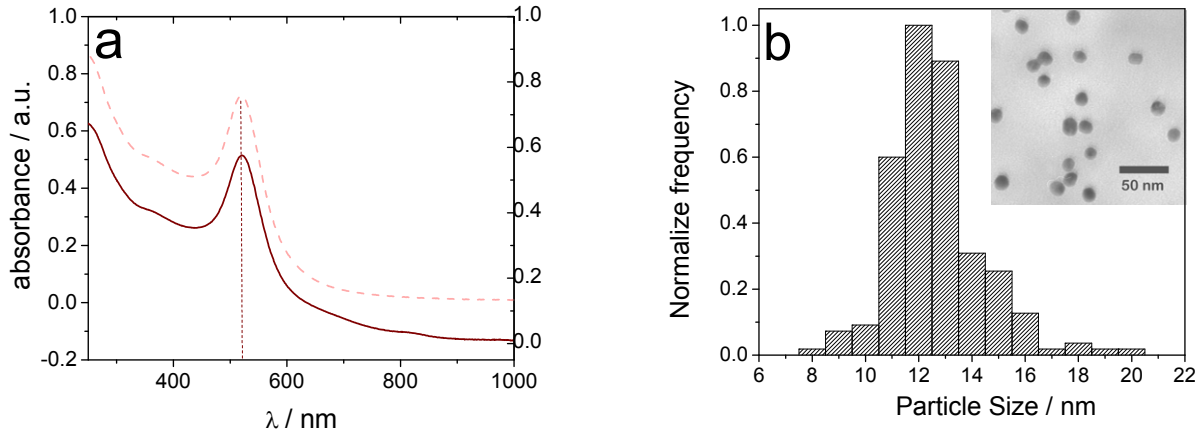


Figure S4. Characterization (a) UV visible spectra of AuNPs-CNN in citrate buffer pH 7.5 (red solid line) and AuNPs stabilized in citrate buffer pH 7.5 (pink dash line) (b) Size distribution function of AuNPs-CN . Inset: TEM image of AuNPs-CNN in citrate buffer pH 7.5

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