Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information: Controlled synthesis of gold nanorod dimers with end-to-end configurations

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Contents

1 GNR assembly in bulk suspension. S-3

1.1 Control experiments. S-5

Drop-coating deposition of the GNR assemblies S-7

1.2 Deposition of the GNR assemblies between two cover slides S-8

2 Step-wise assembly of GNRs on the glass surface. S-11

3 Two-photon-excited fluorescence enhancement. S-13

References S-15

1 GNR assembly in bulk suspension.

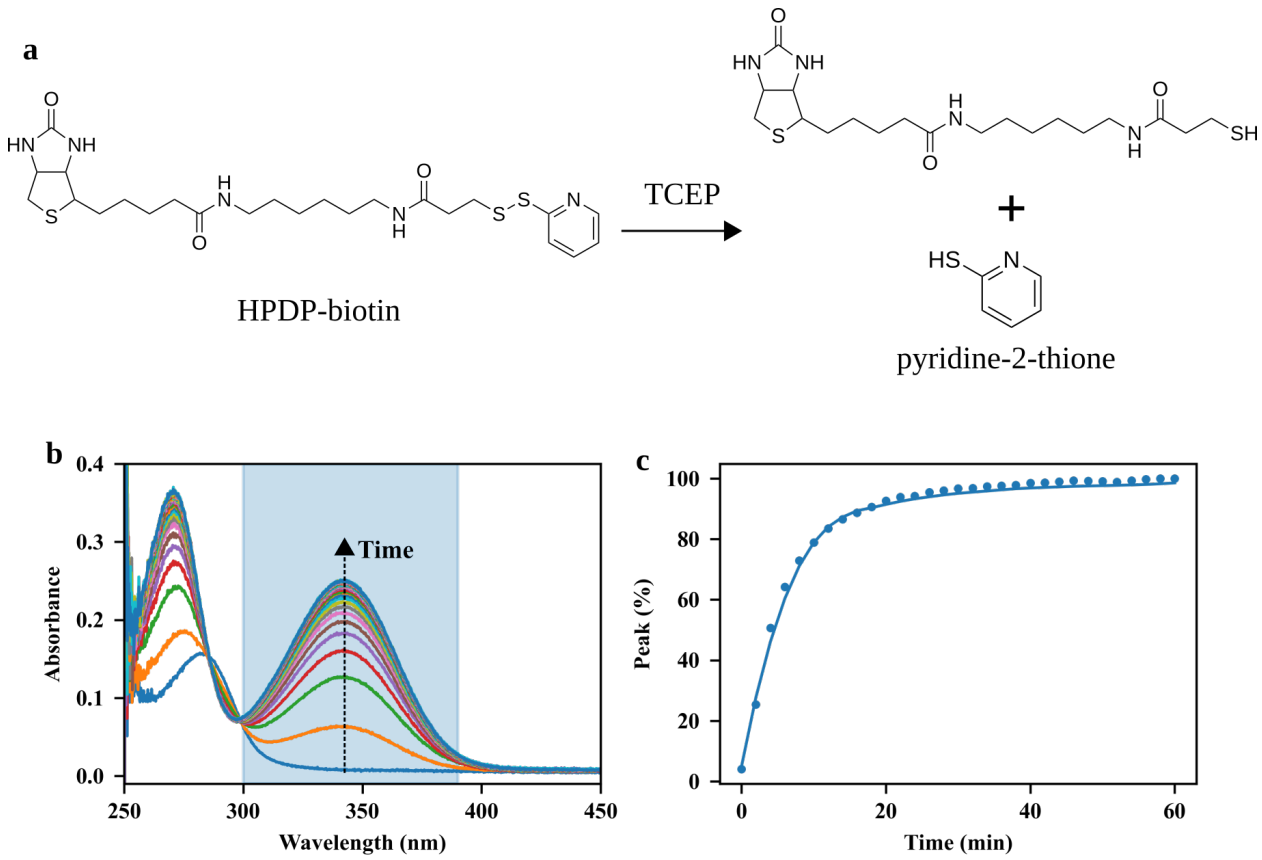

Figure S1: (a) Cleavage of the disulfide bond in HPDP-biotin by the reducing agent TCEP. (b) Spectral evolution for HPDP-biotin at the concentration of 40 μM after the addition of 40 μM TCEP. The disulfide-bond cleavage of HPDP-biotin molecules is verified by monitoring the release of pyridine-2-thione, which has a maximum absorption at 343 nm. The spectra were acquired every 2 min. (b) Time evolution for the percentage of the peak at 343 nm.

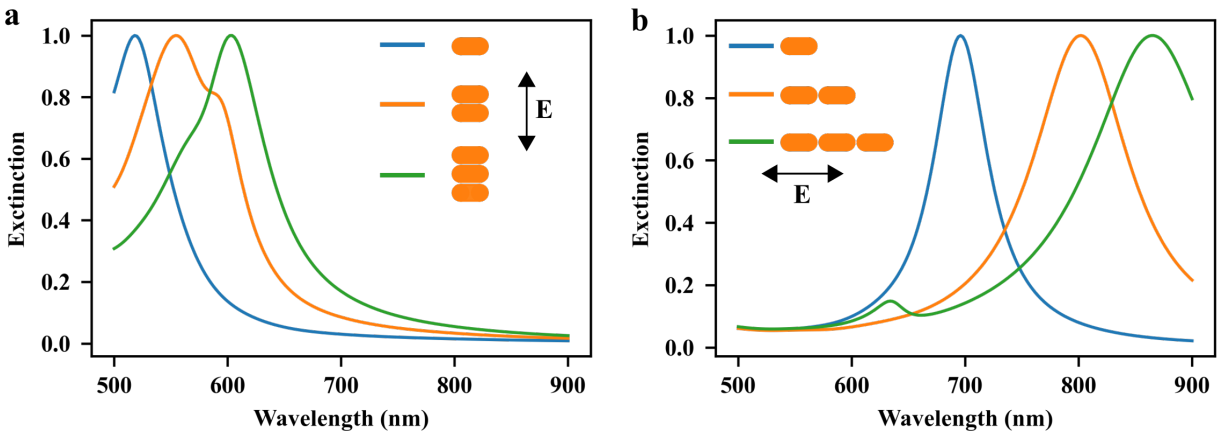

Figure S2: Simulated extinction spectra for GNRs of different morphologies. (a) The extinction spectra excited transversely for a single GNR (blue), a side-by-side GNR dimer (orange), and a side-by-side trimer(green). (b) The extinction spectra excited longitudinally for a single GNR (blue), an end-to-end GNR dimer (orange), and an end-to-end trimer (green). Each GNR was modeled as a spherically capped cylinder with the dimensions of 40 nm $\times$ 97 nm. The interparticle gap was set as 5 nm. The simulations were performed by using a boundary element method.[S1–S3]The dielectric permittivity for gold was taken from Johnson and Christy,[S4] and the refractive index of the ambient medium was taken as 1.33.

1.1 Control experiments.

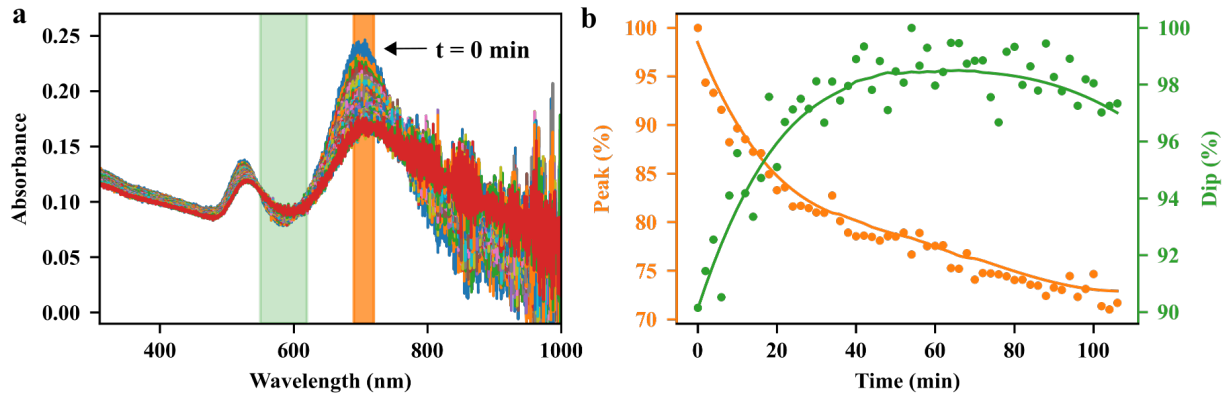

Figure S3: (a) Spectral evolution for GNRs in the presence of the HPDP-biotin, streptavidin, and TCEP. The assembly was triggered by adding the mixture without centrifugal filtering. (b) Time evolution of the percentage of the longitudinal plasmon peaks (orange line with dots), and the percentage of the dips (green line with dots) in the special window indicated by the green shadow in (a). The spectra were acquired every 2 min.

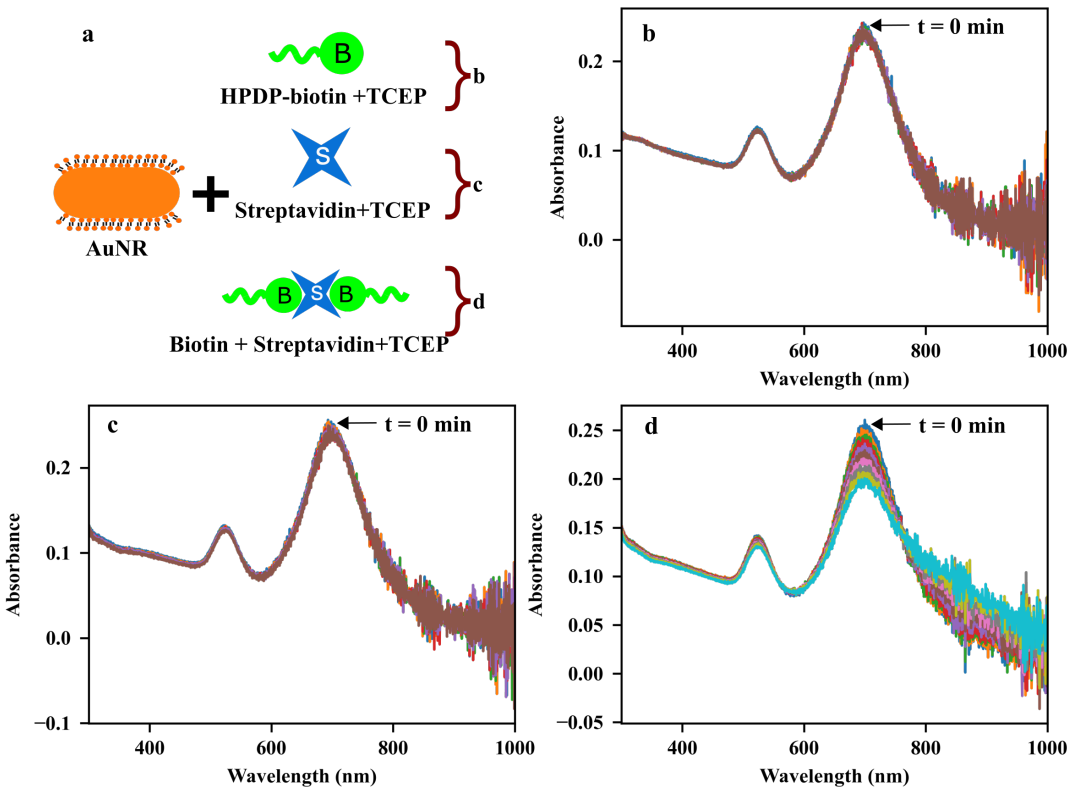

Figure S4: Control experiments: (a) Schematic showing the different linker molecules used for the experiment. (b, c, d) Time evolution of the extinction spectra when the linker is only biotin and TCEP (b), only streptavidin and TCEP (c), and when the linker molecule is biotin-streptavidin and TCEP (d). The TCEP concentration for (b) and (c) was 100 μM. The spectra were acquired every 10 min for 2 hours.

Drop-coating deposition of the GNR assemblies

Scanning electron micrographs (SEM) were captured by an Apreo SEM (ThermoFisher Scientific). An accelerating voltage of 5 kV and a current of 13 pA were used for the scanning of images at a working distance of 10 mm from the pole piece of the SEM. To prevent charging inside SEM, GNR samples were sputtered with a Pt/Pd target inside a Cressington sputter coater to get a 2 nm thick film of the target on the sample.

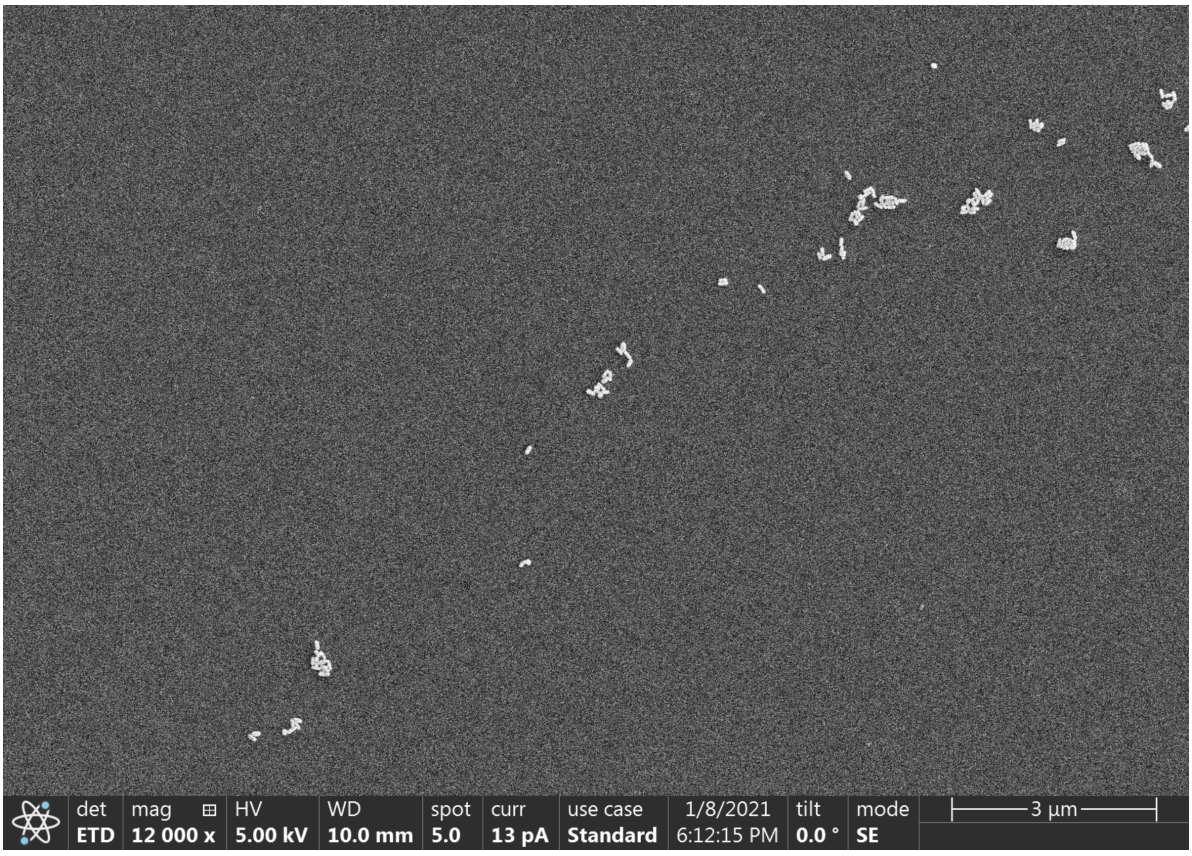

Figure S5: SEM images of GNR assemblies on a glass slide. The assembly was triggered by adding the dithiolated streptavidin-biotin compounds to the GNR suspension. The assemblies were deposited onto the glass slide by drop-casting.

1.2 Deposition of the GNR assemblies between two cover slides

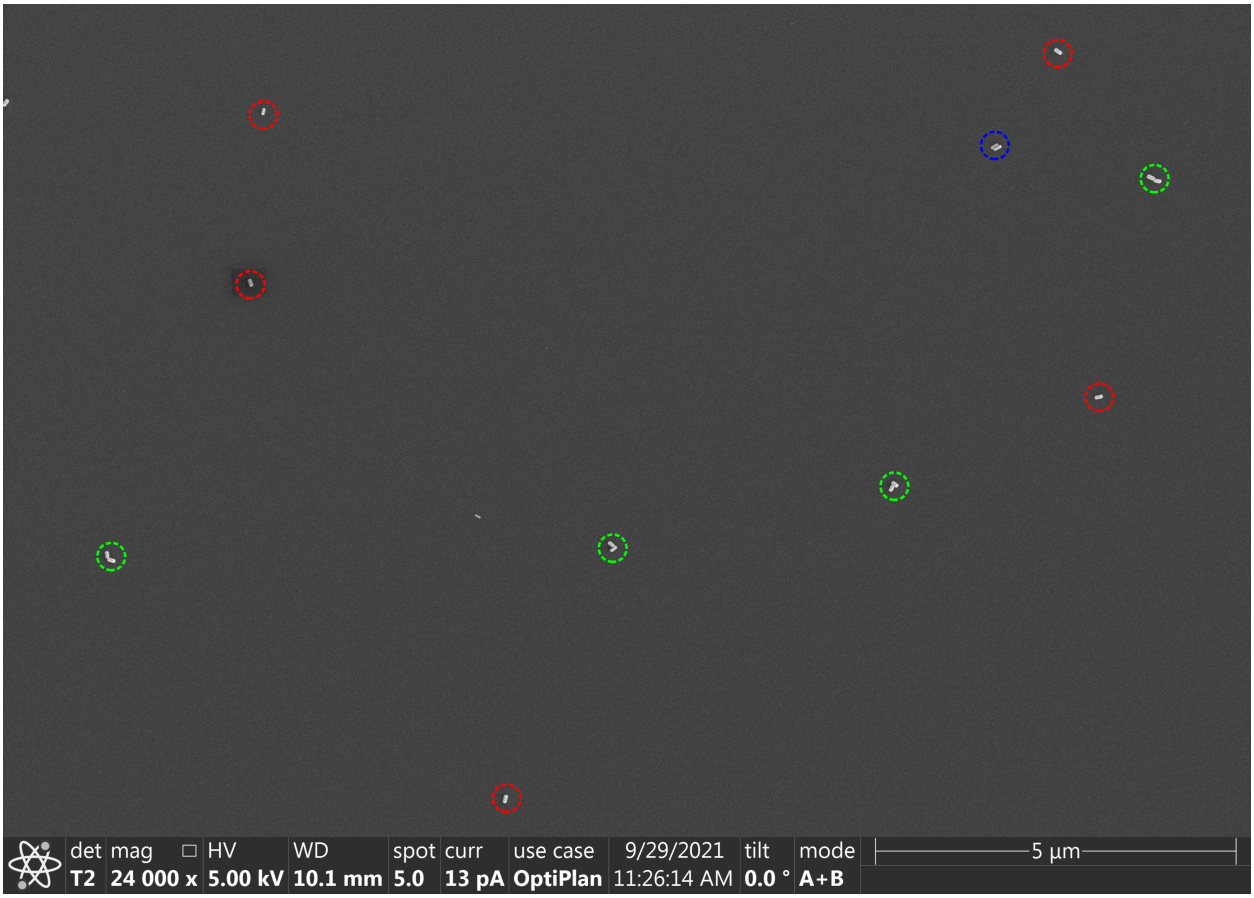

Figure S6: SEM images of GNR assemblies on a glass slide. The assembly was triggered by adding the dithiolated streptavidin-biotin compounds to the GNR suspension. The assemblies were deposited onto the glass slides and dried between two cover slides. The assemblies of different morphologies are highlighted by colored circles: end-to-end GNR dimer: green, single GNR: red, side-by-side GNR dimer: blue, and clusters: orange.

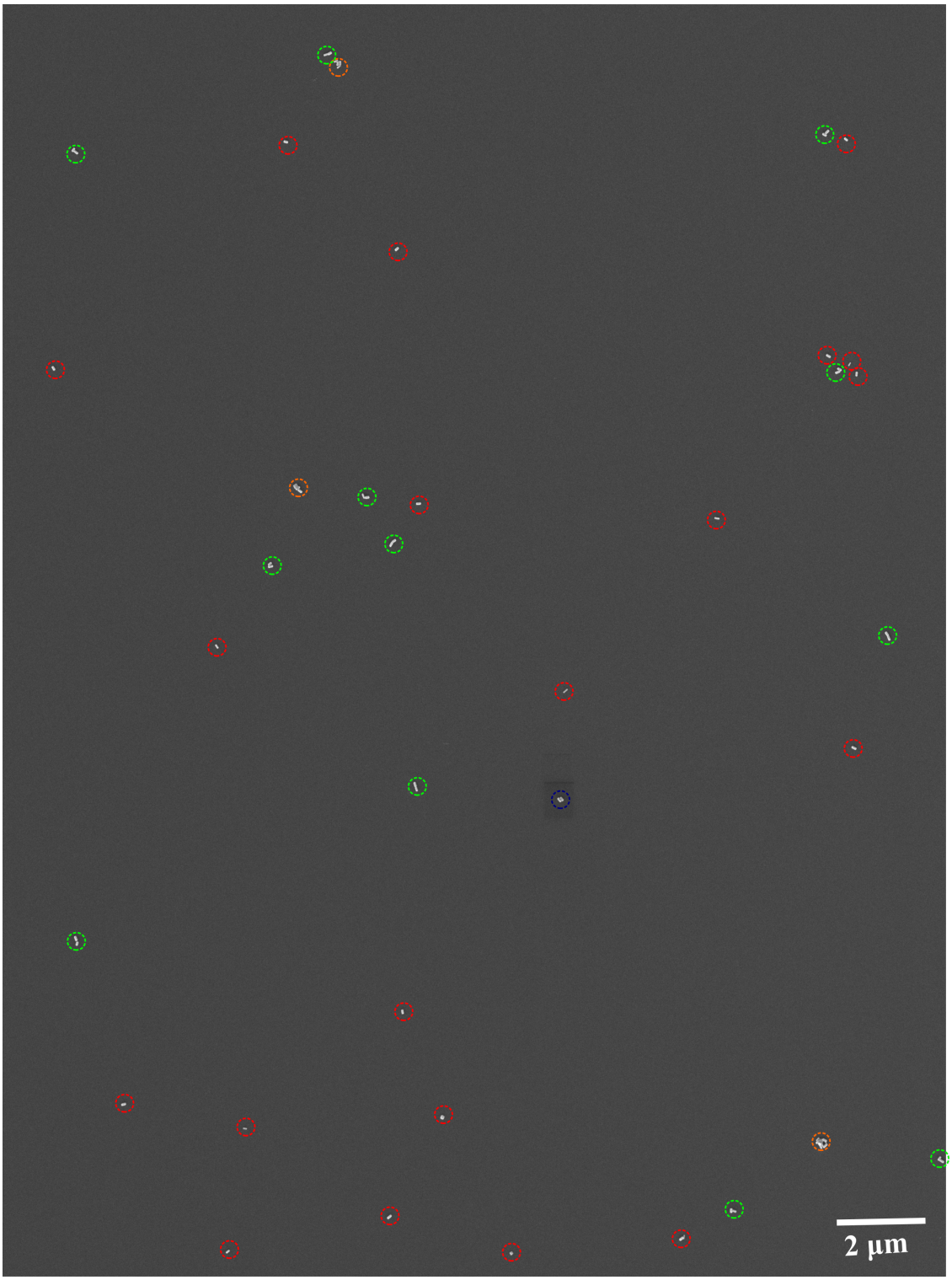

Figure S7: SEM images of GNR assemblies on the same glass slide as figure S6. The assemblies of different morphologies are highlighted by colored circles: end-to-end GNR dimer: green, single GNR: red, side-by-side GNR dimer: blue, and clusters: orange.

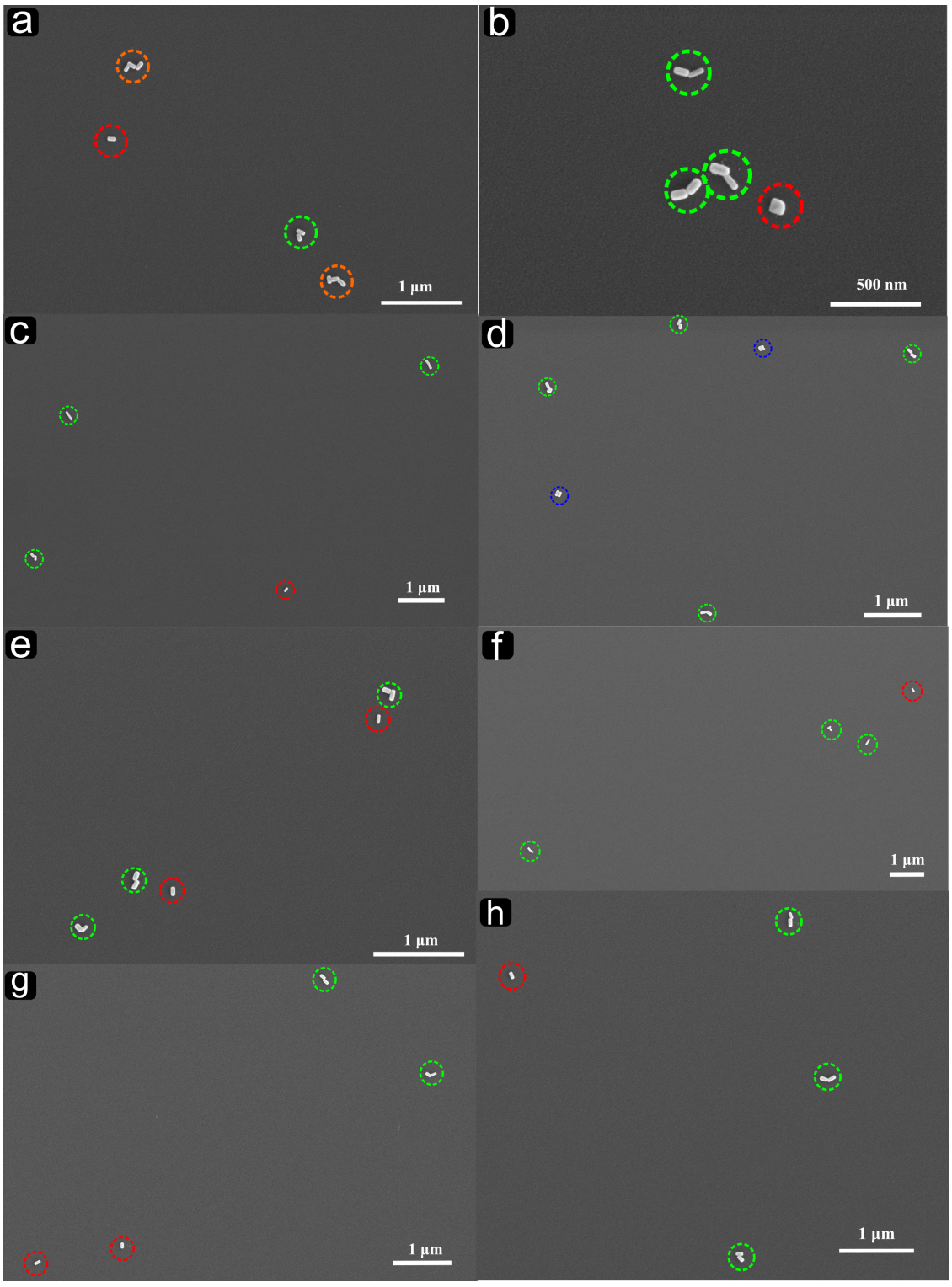

Figure S8: SEM images of GNR assemblies on the same glass slide as figure S6. (a-h) These SEM images are of different areas from the same sample. The assemblies of different morphologies are highlighted by colored circles: end-to-end GNR dimer: green, single GNR: red, side-by-side GNR dimer: blue, and clusters: orange.

2 Step-wise assembly of GNRs on the glass surface.

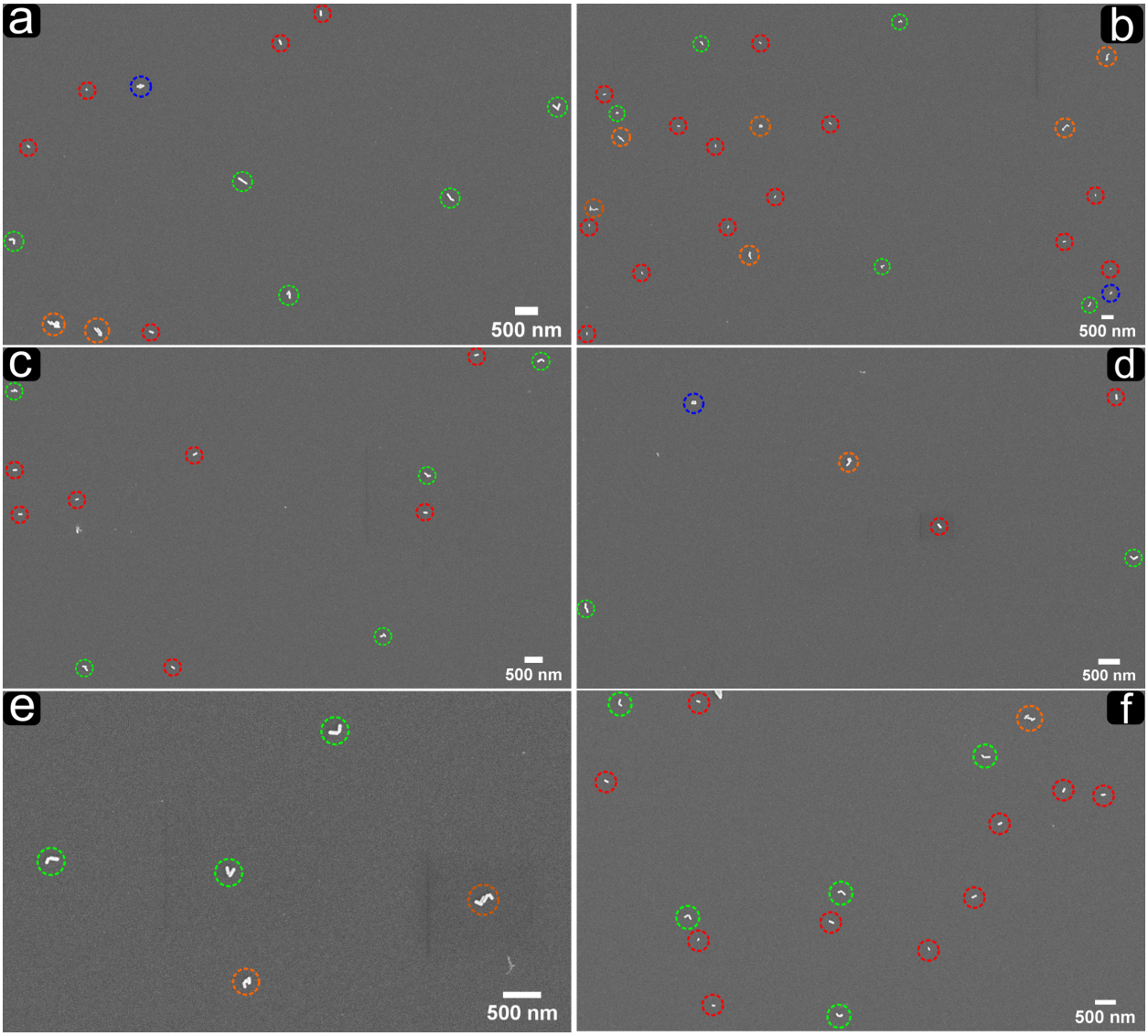

Figure S9: SEM images of GNR assemblies on a glass slide. The sample was prepared using the step-wise assembly method. (a-f) These SEM images are of different areas from the same sample. The assemblies of different morphologies are highlighted by colored circles: end-to-end GNR dimer: green, single GNR: red, side-by-side GNR dimer: blue, and clusters: orange.

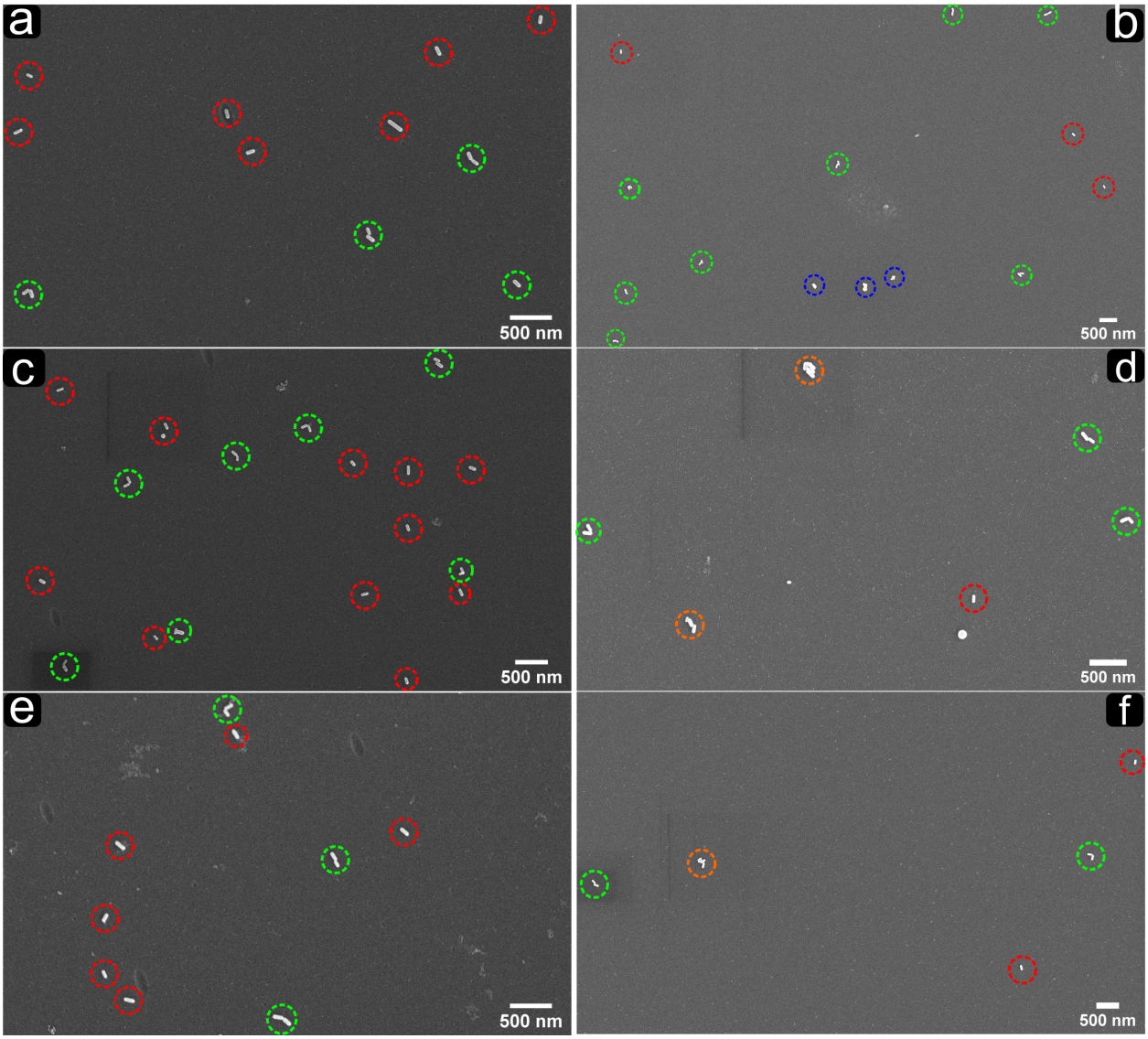

Figure S10: SEM images from two different samples prepared by using the step-wise assembly method. (a, c, e) Assemblies of different areas from the first sample. (b, d, f) SEM images from the second sample. The assemblies of different morphologies are highlighted by colored circles: end-to-end GNR dimer: green, single GNR: red, side-by-side GNR dimer: blue, and clusters: orange.

3 Two-photon-excited fluorescence enhancement.

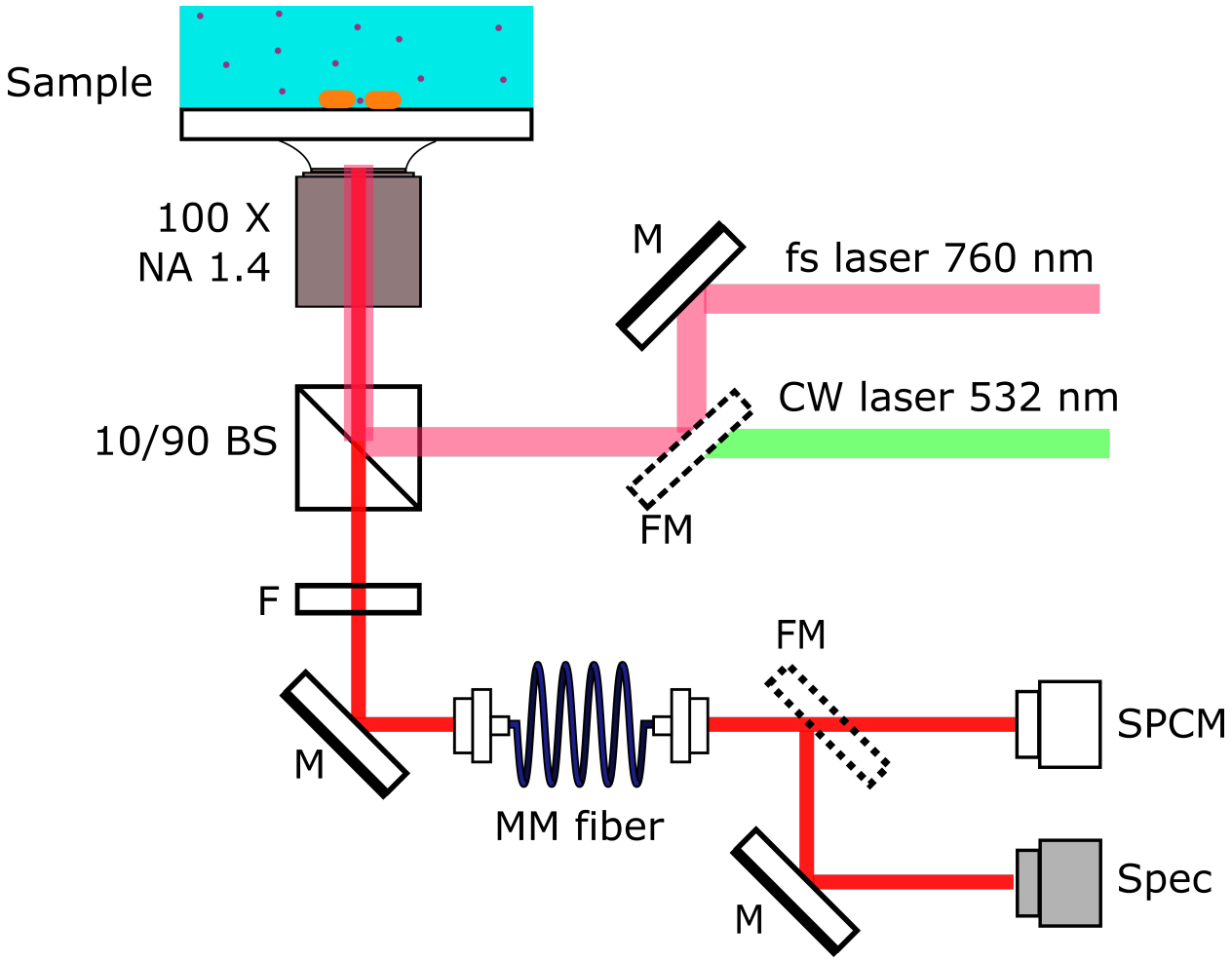

Figure S11: Schematic representation of the experimental setup for two-photon excited fluorescence measurements. BS - Beam splitter, F - Filters, M - Mirror, DM - Dichroic mirror, FM - Film mirror, MM fiber - multimode fiber, SPCM - single-photon counting module, Spec - Spectrometer.[S5]

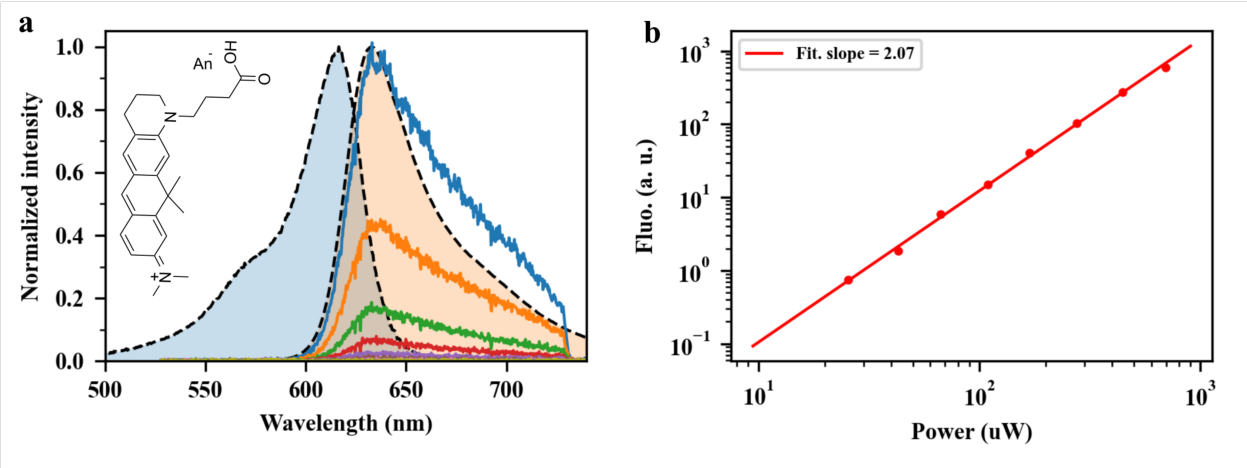

Figure S12: Spectral and power dependence measurement of ATTO 610 dye (a) The blue- and orange-shaded bands with dashed outlines represent the normalized one-photon absorption (blue-dashed) and emission (orange-dashed) spectra of ATTO 610, respectively. The solid lines give the emission spectra of 4 μM ATTO 610 excited by $\sim$ 220 fs laser pulses at 760 nm with different powers as depicted in (b). The integration time for recording each spectrum was set as 120 s. The inset shows the chemical structure of ATTO 610. (b) Power dependence of the emission integrated over wavelengths ranging from 555 nm to 728 nm, excited at the wavelength of 760 nm. The power law fit shows perfect quadratic dependence of the emission on the excitation power.

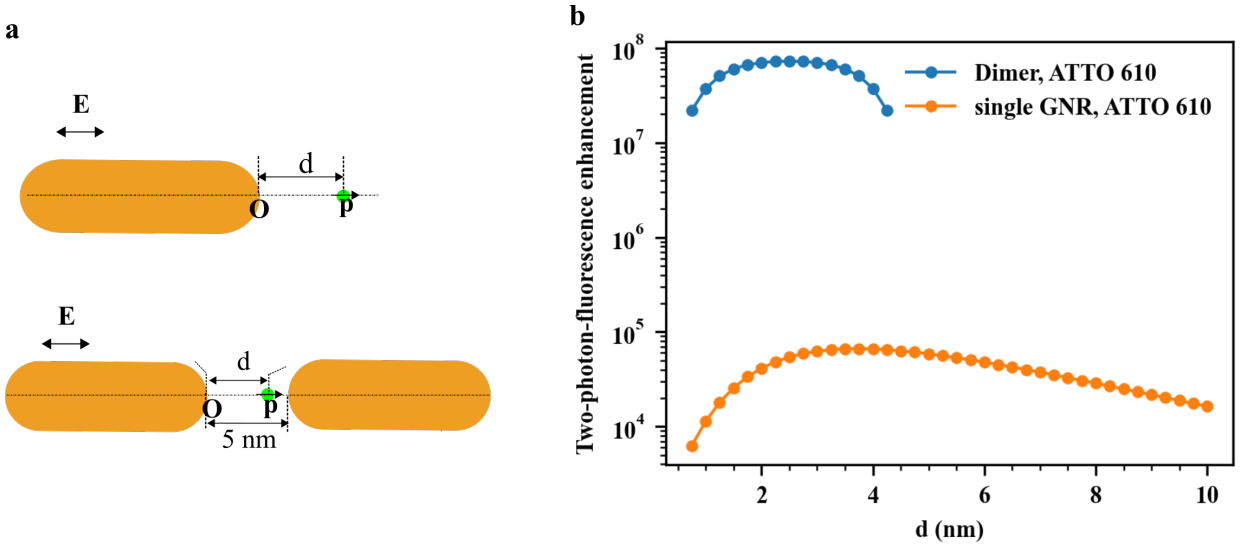

Figure S13: Simulation of two-photon-excited fluorescence enhancement of ATTO 610 by a single GNR and by a GNR dimer. (a) The schematics used for the numerical simulations. (b) The two-photon-excitation enhancement by a single GNR (orange) and by a GNR dimer (blue) as functions of position of the molecule. In the simulations, the size for the single GNR was set at 40 nm $\times$ 115 nm, and the sizes for the GNRs within the dimer were set at 40 nm $\times$ 90 nm, both of which give the plasmon resonance of 760 nm.

References

(S1) Homer Reid, M. T.; Johnson, S. G. Efficient Computation of Power, Force, and Torque in BEM Scattering Calculations. *ArXiv e-prints* **2013**,

(S2) `http://github.com/homerreid/scuff-EM`.

(S3) Reid, M. T. H.; Johnson, S. G. Efficient Computation of Power, Force, and Torque in BEM Scattering Calculations. *IEEE Transactions on Antennas and Propagation* **2015**, *63*, 3588–3598.

(S4) Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Physical Review B* **1972**, *6*, 4370–4379.

(S5) Zhang, W.; Caldarola, M.; Lu, X.; Orrit, M. Plasmonic Enhancement of Two-Photon-Excited Luminescence of Single Quantum Dots by Individual Gold Nanorods. *ACS Photonics* **2018**, *5*, 2960–2968.