Supplementary Information

Long- and Short-Ranged Chiral Interactions in DNA-assembled Plasmonic Chains

Kevin Martens[1], Felix Binkowski[2], Linh Nguyen[1], Li Hu[3], Alexander O. Govorov[4], Sven Burger[2, 5] and Tim Liedl[1]*

[1]*Faculty of Physics, Ludwig-Maximilians-University, Geschwister-Scholl-Platz 1, D-80539 Munich, Germany*

[2]*Zuse Institute Berlin, Takustraße 7, D-14195 Berlin, Germany*

[3]*Chongqing Engineering Laboratory for Detection, Control and Integrated System, Chongqing Technology and Business University, Chongqing 400067, China*

[4]*Department of Physics and Astronomy, Nanoscale and Quantum Phenomena Institute, Ohio University, Athens, Ohio 45701, United States*

[5]*JCMwave GmbH, Bolivarallee 22, D-14050 Berlin, Germany*

** tim.liedl@lmu.de*

Materials

DNA scaffold strands (p8064) were prepared following previously described procedures.[1, 2] Unmodified staple strands (purification: desalting) were purchased from Eurofins MWG. Thiol-modified strands (purification: HPLC) were purchased from Biomers. Uranyl formate for negative TEM staining was purchased from Polysciences, Inc.. Spherical gold nanoparticles were purchased from BBI Solutions. Other chemicals were purchased from CarlRoth and Sigma-Aldrich.

Supplementary Note S1: DNA Origami Design

The left half of the dimeric origami structure (yellow part in Figure S1) was folded with an 8064 base pair (bp) scaffold strand and 126 core staple strands as well as 62 "C_4 endcap" staples, 22 staples for dimerization and 12 "handle" strands for NP assembly. The right half of the origami structure (blue part in Figure S1) was folded separately but with the same 8064 bp scaffold strand and a different set of 123 core staple strands as well as 70 C_4 endcap staples, 25 staples for dimerization and 11 handle strands for NP assembly.

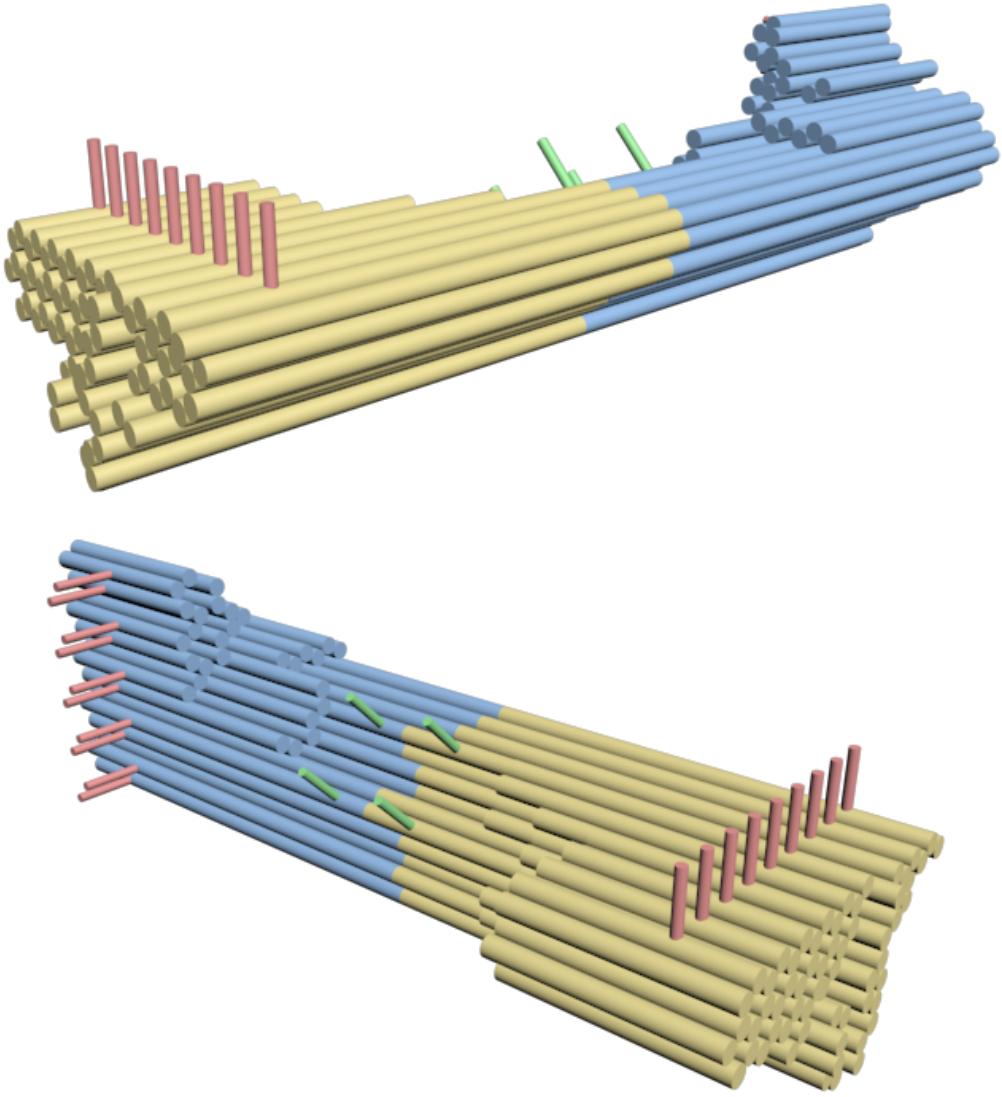

Figure S1: 3D Model of the DNA origami structure, depicting the individual halfs in blue and yellow (cylinders represent DNA helices). The handles for the NS are depicted in green as well as the handles for the NRs in red.

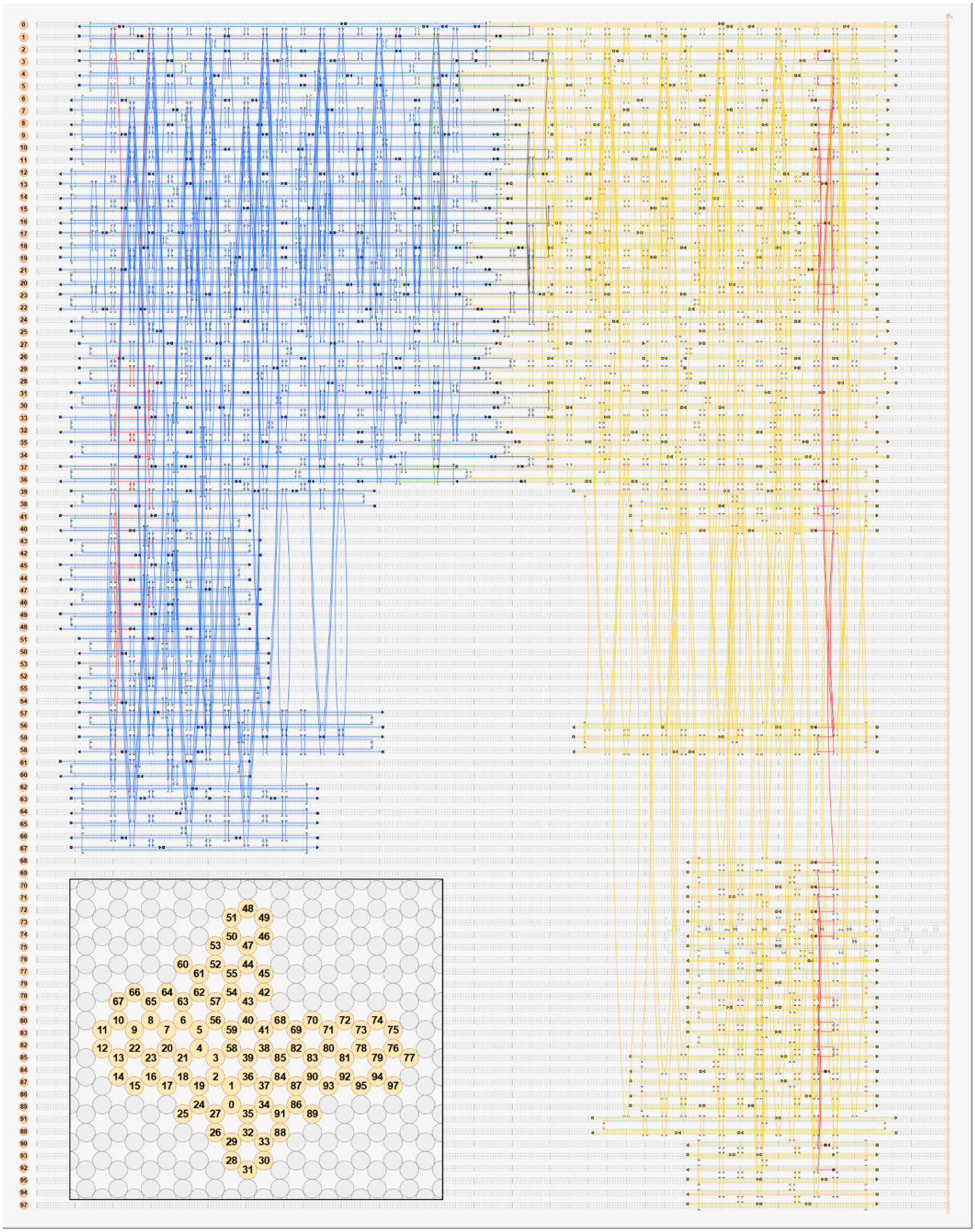

Figure S2: Cadnano design of the DNA origami structure, depicting the individual halves in blue and yellow as well as the handles for the NS in green and the handles for the NRs in red. The staples that connect the individual sides are depicted in black.

Supplementary Note S2: DNA Origami Synthesis

The scaffold was used during folding at a concentration of 16 nM with 160 nM core and endcap staples plus 200 nM dimer and handle staples. 1X TE and 28 mM $MgCl_2$ were added as buffer solution. The two solutions containing the two mixtures were heated up to 65°C and then cooled down to room temperature over the course of 24 h. Subsequently the left side of the origami and the right side were combined in equal amounts and left to dimerize over 48 h. Dimer origamis were purified using gel electrophoresis with 0.7% agarose gel in a buffer of 1X TAE, 11 mM $MgCl_2$ and 0.05‰ Roti Stain as intercalating dye. The gel was run for 2.5 h at 70 V, before the origami dimer band was cut out under UV light and afterwards squeezed to redisperse the sample in buffer.

Table S1: Left half DNA origami protocol.

Component	**Concentration**	**Amount**	**End Concentration**
Scaffold 8064	100 nM	16 µL	16nM
Core Staples	397 nM	40.3 µL	160nM
Endcap Staples	806 nM	19.9 µL	160nM
Dimere Staples	2273 nM	8.8 µL	200nM
Handles	4167 nM	4.8 µL	200nM
TE	20X	5 µL	1X
MgCl2	1 M	2.8 µL	28mM
H2O	-	2.4 µL	-
Total	**100 nM**	**100 µL**	

Table S2: Right half DNA origami protocol.

Component	**Concentration**	**Amount**	**End Concentration**
Scaffold 8064	100 nM	16 µL	16nM
Core Staples	407 nM	39.3 µL	160nM
Endcap Staples	714 nM	22.4 µL	160nM
Dimere Staples	2000 nM	10 µL	200nM
Handles	4545 nM	4.4 µL	200nM
TE	20X	5 µL	1X
MgCl2	1 M	2.8 µL	28mM
H2O	-	0.1 µL	-
Total	**100 nM**	**100 µL**	

For TEM analysis, samples were incubated for 15 min on copper grids (Ted Pella Inc., Redding, USA) before being dabbed off with a filter paper and subsequently stained with 2% uranyl format in two steps. In the first step the uranyl format solution only quickly washes the grid, in the second step it is left to incubate for 15 s before being dabbed off. Images were taken with a JEOL JEM 1011 electron microscope at 80 kV.

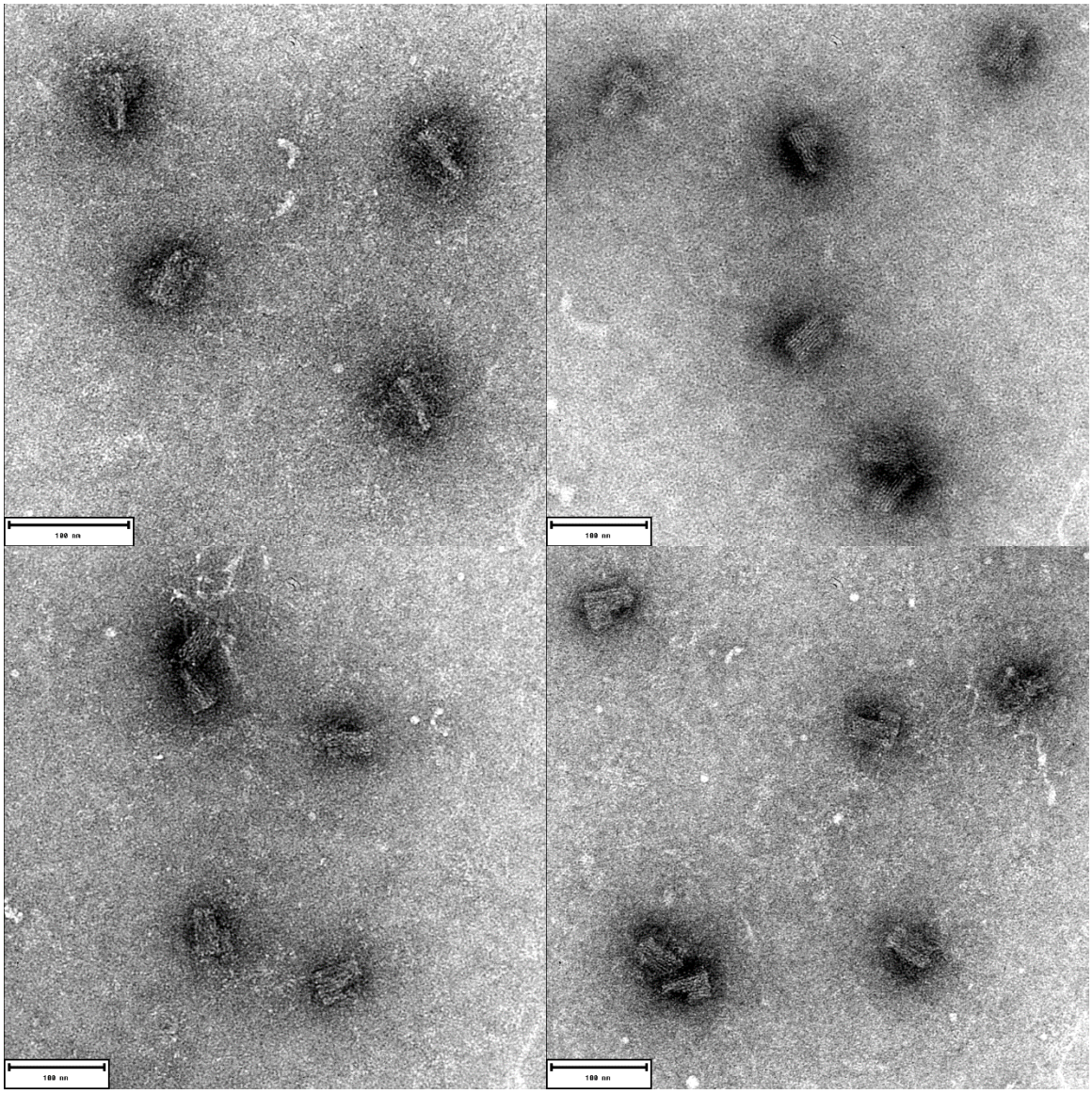

Figure S3: Electron micrographs of the left half of the DNA origami after gel electrophoresis purification

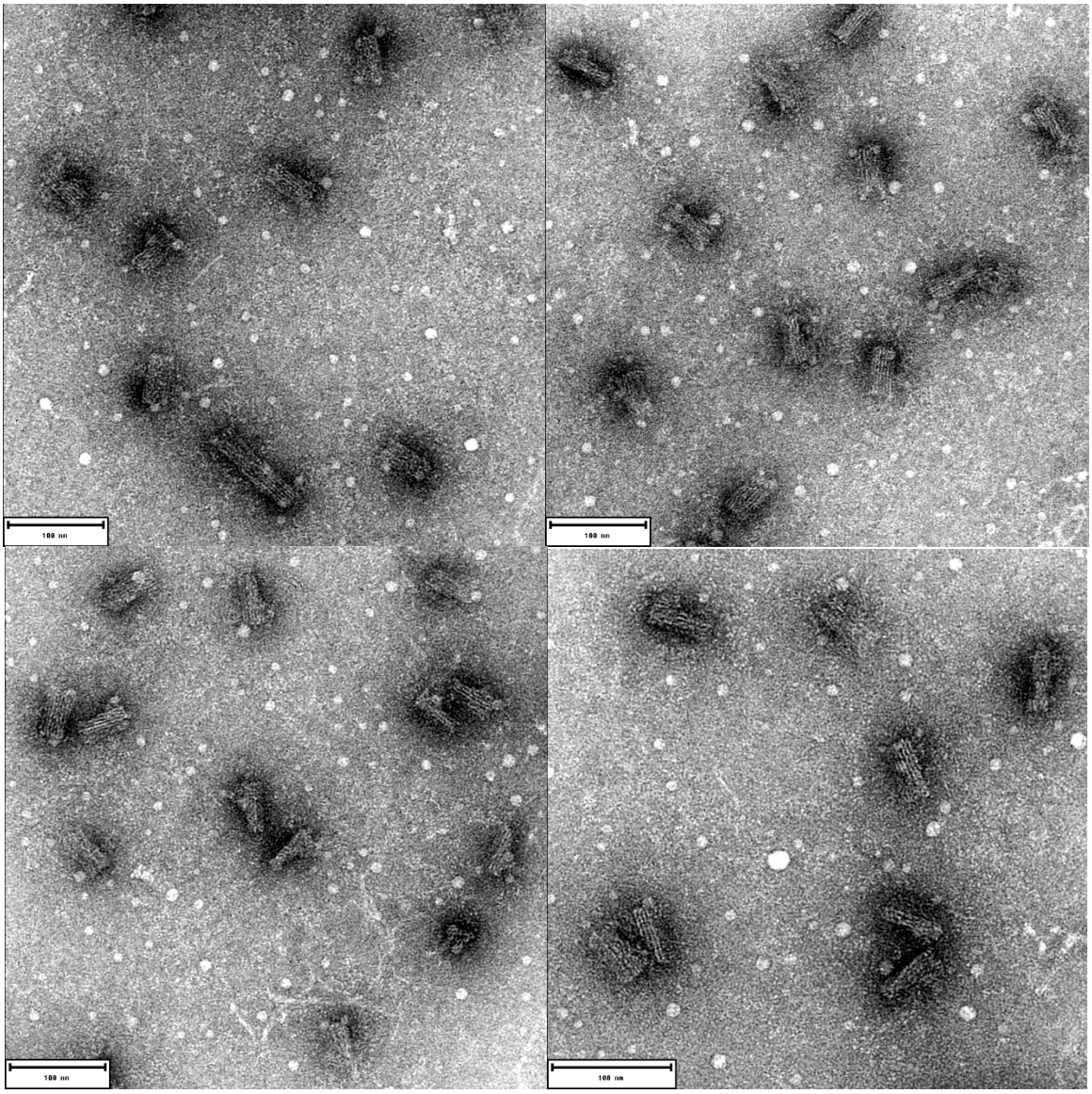

Figure S4: Electron micrographs of the right half of the DNA origami after gel electrophoresis purification

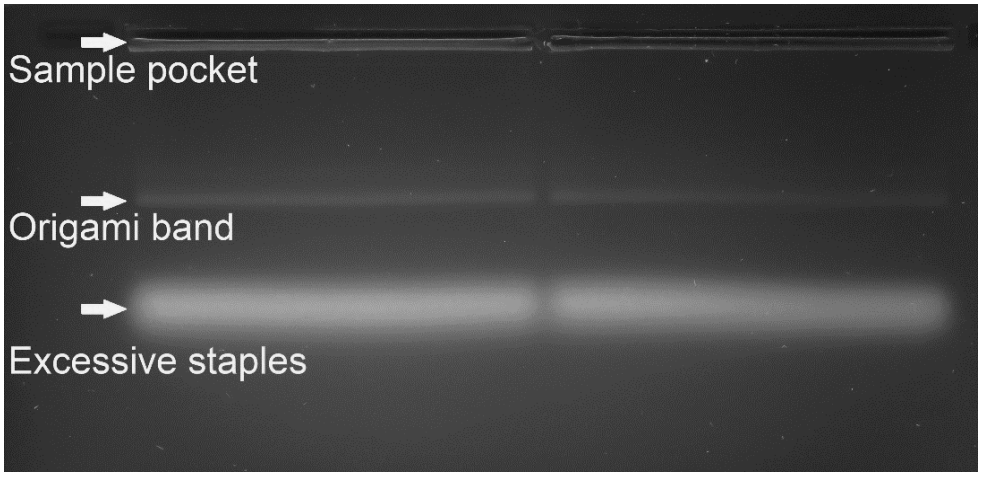

Figure S5: Gel electrophoresis band of DNA origami structure after dimerization

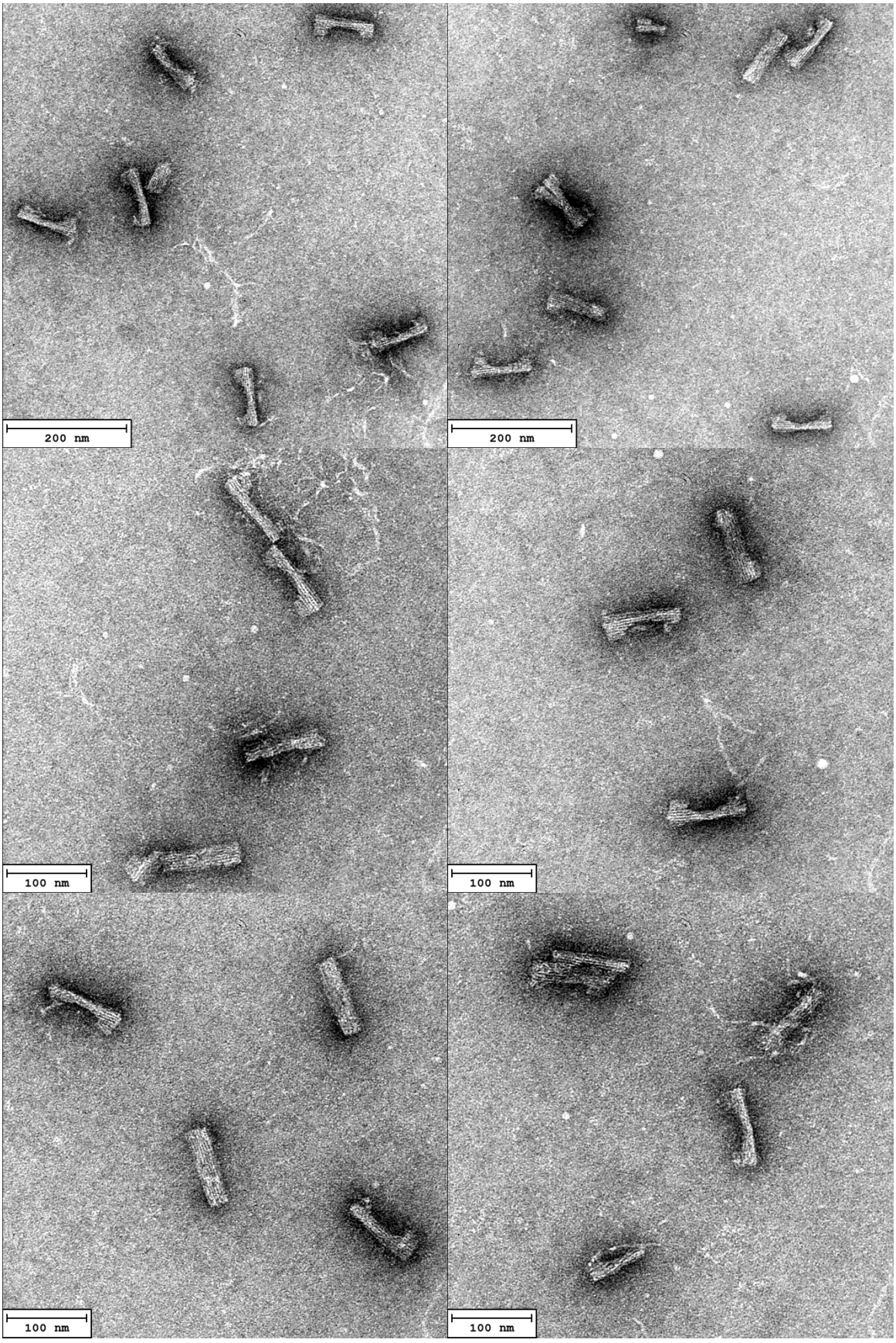

Figure S6: Electron micrographs of the complete DNA origami structure (purified)

Supplementary Note S3: DNA Origami-Nanoparticles Assembly Synthesis

40 nm NSs were incubated at an optical density (OD) of 4 with 10 mM thiol-modified DNA oligonucleotides, previously activated with TCEP, and 0.02% SDS. NR synthesis was performed following the protocol of Ye et al. [3] 60 nm x 23 nm NRs were incubated at OD 1.4 with 5 mM thiol-modified DNA oligonucleotides and 0.1% SDS. Samples were frozen, thawed and purified using gel electrophoresis with a 0.7% agarose gel in a buffer of 1X TAE, 11 mM $MgCl_2$, run for 1.5 h at 120 V. Subsequently the correct monomer bands were cut and squeezed to redisperse in buffer.

For the synthesis of the NR– –NR sample, NRs were added to the origami structures in a ratio of 10:1 in a buffer of 1X TAE, 11 mM MgCl2 plus 500 mM NaCl and incubated for 24 h. The sample was purified using gel electrophoresis with a 0.7% agarose gel in a buffer of 1X TAE, 11 mM $MgCl_2$, run for 1.5 h at 70 V. The band of the structures was cut out and squeezed. For the NR–NS–NR sample, first NSs were incubated with the DNA origami in a ratio of 5:1 in a buffer of 1X TAE, 11 mM $MgCl_2$ plus 500 mM NaCl for 24 h. Afterwards NRs were added in a ratio of 10:1 to the origami, and incubated in the same buffer for 24 h. The samples were purified using gel electrophoresis with a 0.7% agarose gel in a buffer of 1X TAE, 11 mM $MgCl_2$, run for 1.5 h at 70 V. The structure bands were cut out, squeezed and identified by TEM.

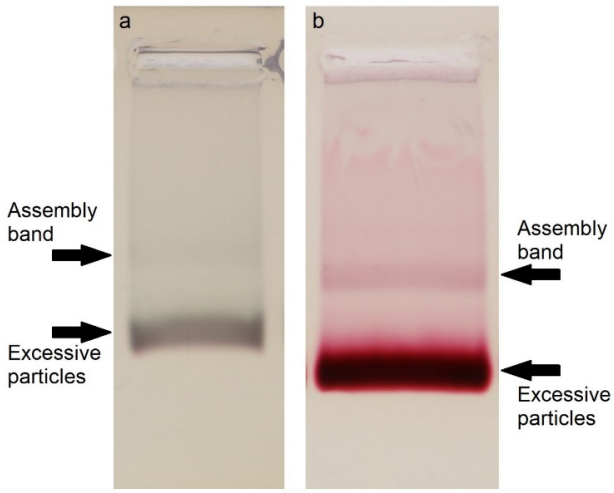

Figure S7: Gel electrophoresis bands of samples with a) the NR– –NR arrangement and (b) the NR–NS–NR arrangement

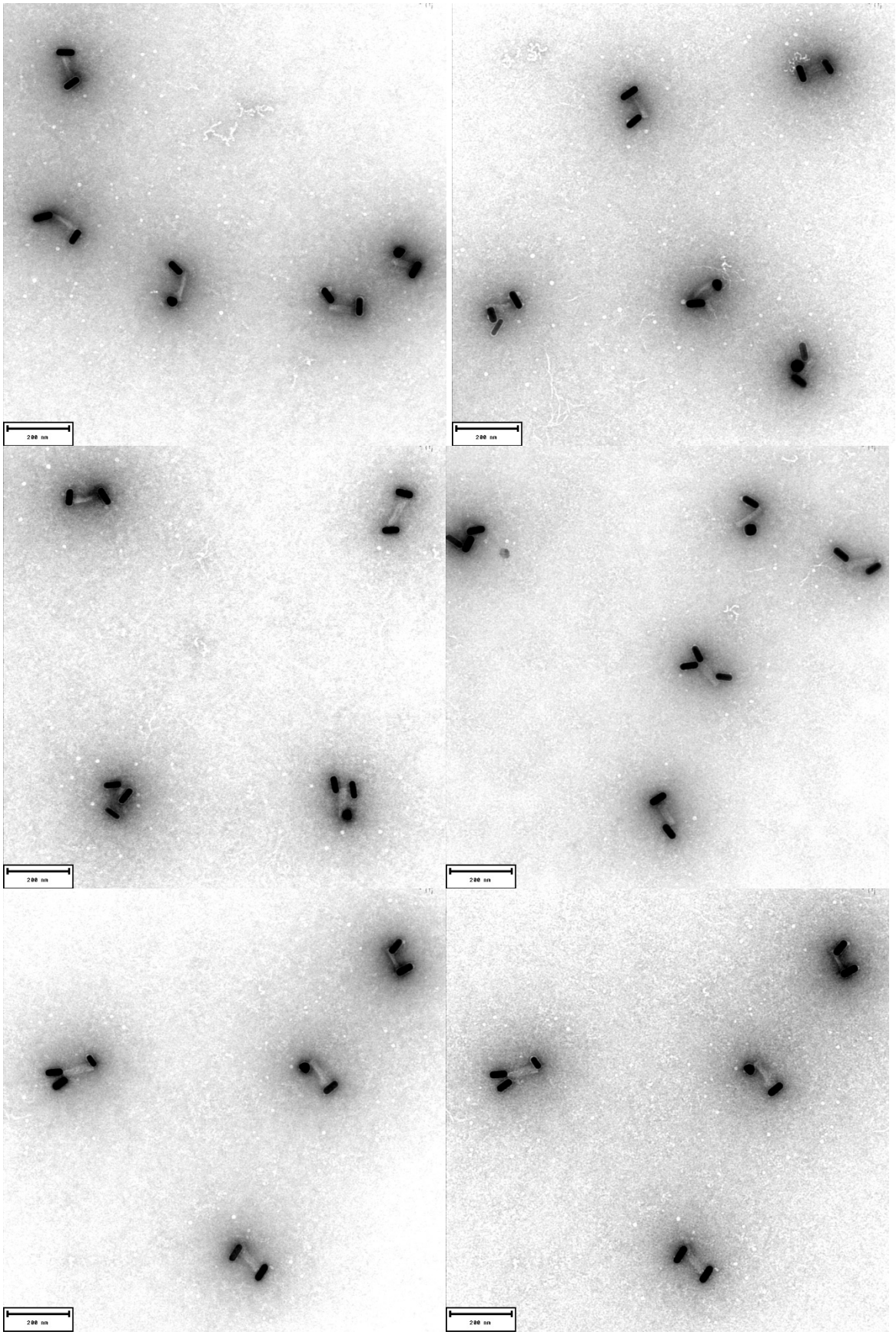

Figure S8: Electron micrographs of the NR– –NR arrangement

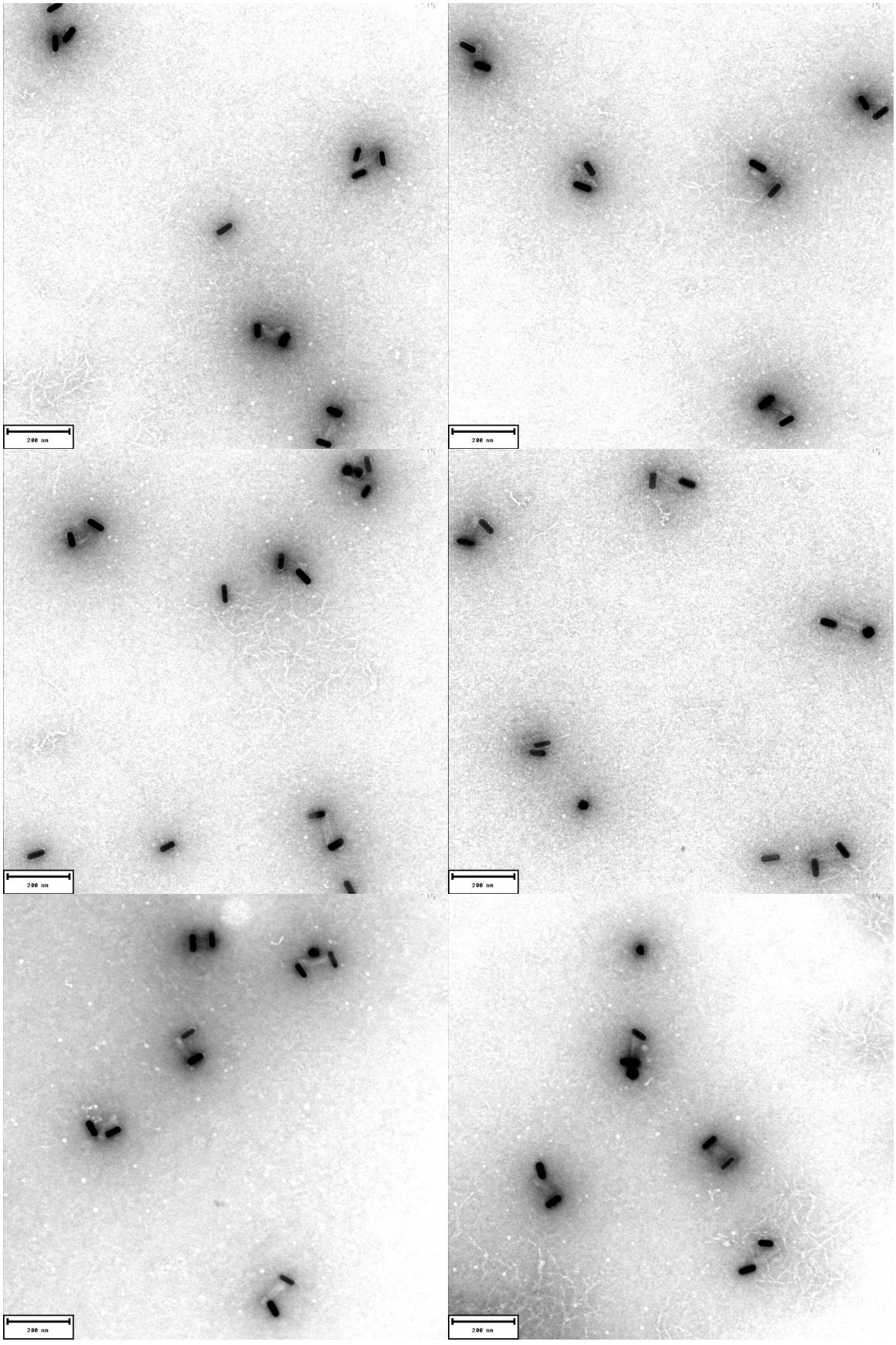

Figure S9: Electron micrographs of the NR– –NR arrangement

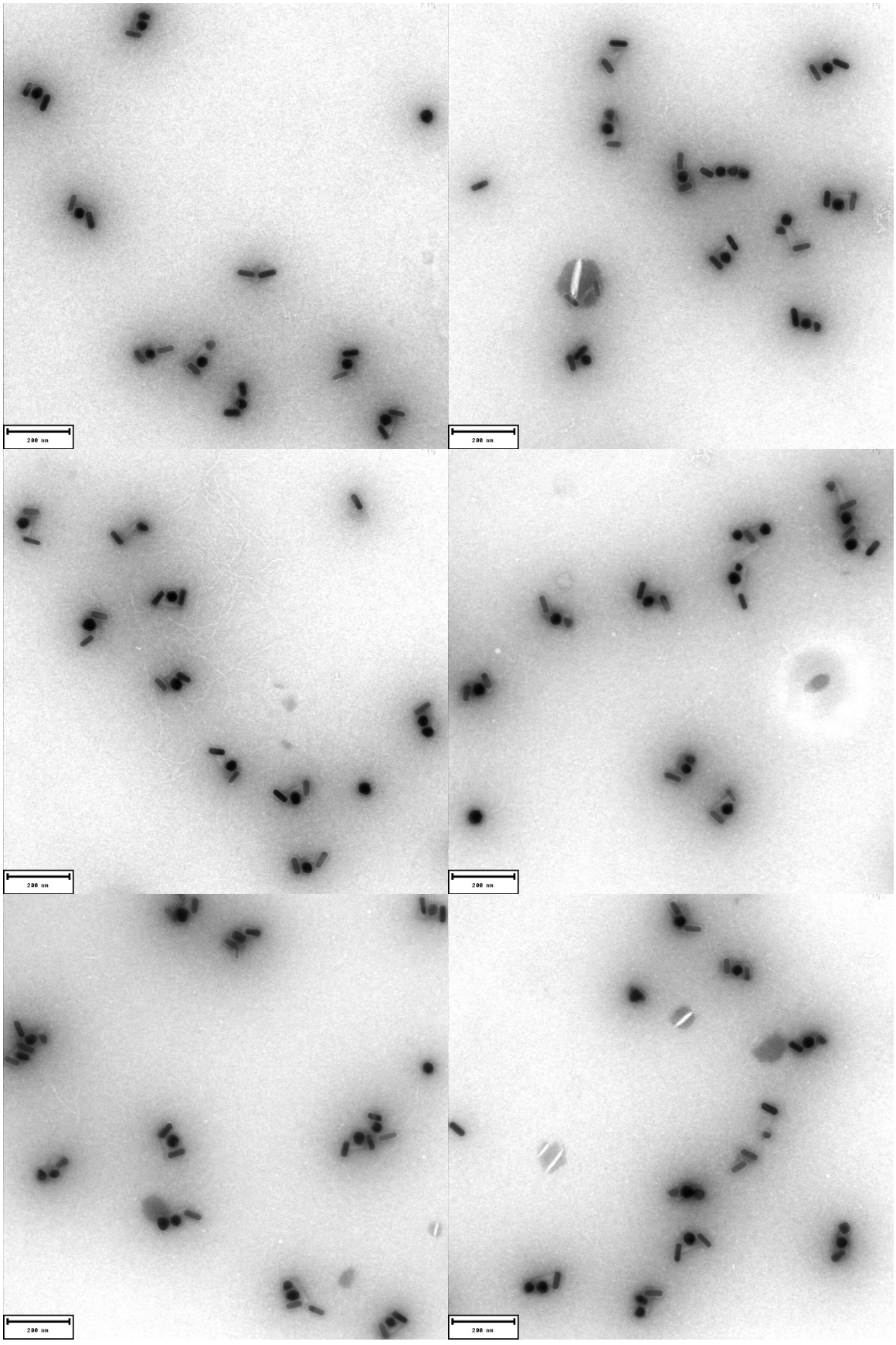

Figure S10: Electron micrographs of NR–NS–NR sample

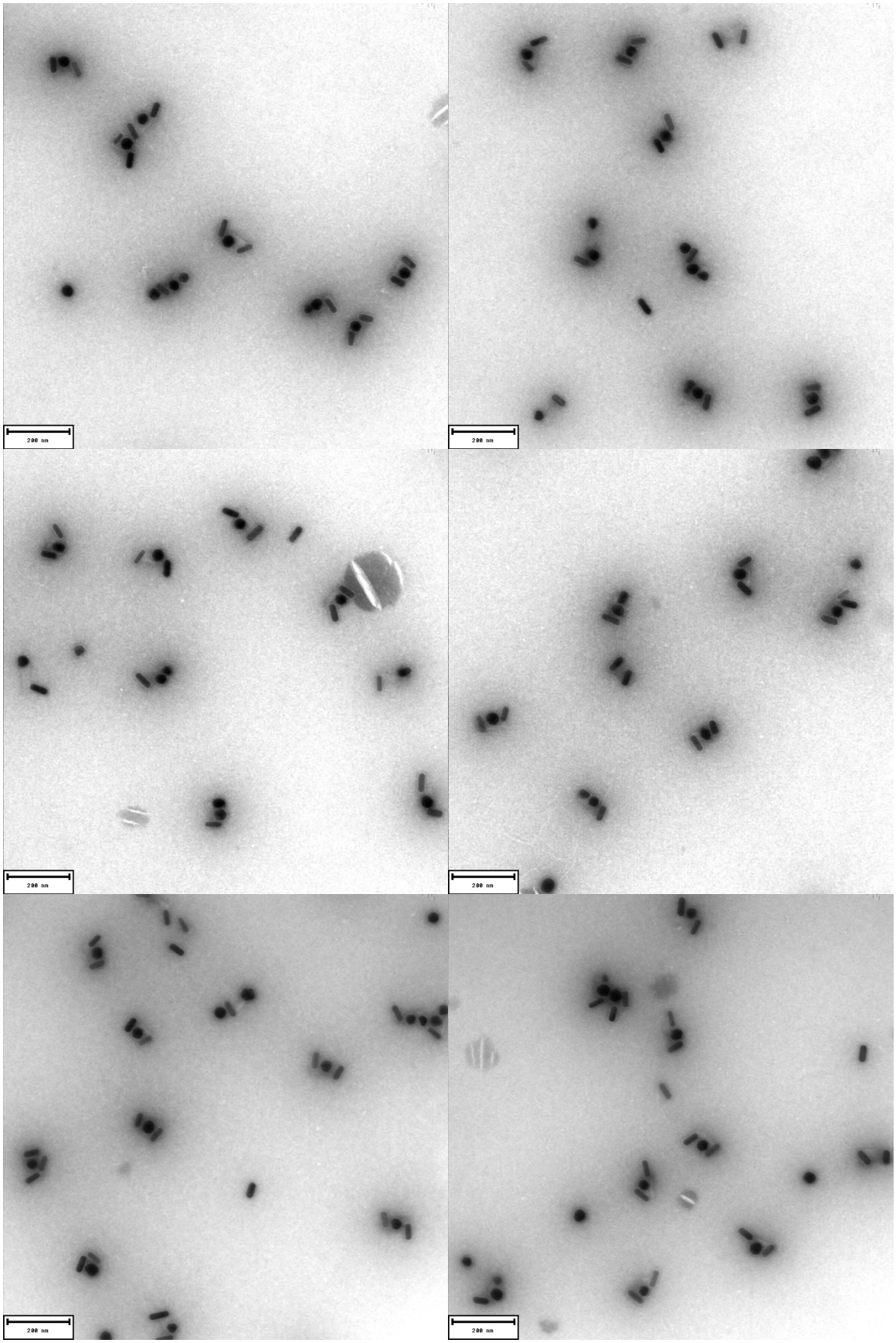

Figure S11: Electron micrographs of NR–NS–NR sample

Table S3: NR– –NR Synthesis Assembly Statistics.

Assembly	Number	Percentage
NR– –	3	< 3 %
NR– –NR	113	57.5 ±7 %
NS– –NR	27	14 ±4.5 %
NS– –NS	1	< 1.5 %
NR– –2NR	30	15.5 ±5 %
NR–NS–NR	7	3.5 ±2.5 %
NR–NR–NS	8	4 ±2.5 %
NR–NS–NS	3	< 3 %
NS–NR–NS	1	< 1.5 %
NR–NR–NR–NR	2	< 2 %
NR–NR–NS–NS	1	< 1.5 %
Total	**196**	**100 %**

Table S4: NR– –NR Synthesis Particle Statistics.

Particle	Number	Percentage
NS	54	12 ±3 %
NR	390	88 ±3 %
Total	**444**	**100 %**

Table S5: NR–NS–NR Synthesis Assembly Statistics.

Assembly	Number	Percentage
NR– –NR	28	9 ±3 %
NS– –NR	11	3.5 ±2 %
NS– –NS	3	< 2 %
NR– –2NR	4	1.5 ±1 %
NR–NS–NR	160	51 ±5.5 %
NS– –2NR	8	2.5 ±1.5 %
NR–NS–NS	57	18 ±4.5 %
NS–NR–NS	4	1.5 ±1 %
NS–NS–NS	5	1.5 ±1.5 %
NR–2NS–NR	5	1.5 ±1.5 %
NR–NR–2NR	3	< 2 %
NS–NS–2NR	3	< 2 %
NR–NS–NR–NS	7	2 ±1.5 %
NR–NS–2NR	7	2 ±1.5 %
NR–NS–2NS	4	1.5 ±1 %
NS–NR–2NS	3	< 2 %
NS–NR–3NS	1	< 0.5 %
Total	**313**	**100 %**

Table S6: NR– –NR Synthesis Particle Statistics.

Particle	Number	Percentage
NS	354	41 ±3 %
NR	577	59 ±3 %
Total	**931**	**100 %**

Supplementary Note S4: CD and Extinction Measurements

Samples were measured with a Chirascan circular dichroism spectrometer (Applied Photophysics, Surrey, UK) in cuvettes with 3 mm pathlengths. Spectra were collected in 0.5 nm steps with 0.3 s for each step. 3 measurements were made an averaged for the NR– –NR sample.

Supplementary Note S5: Numerical Simulations

For solving Maxwell's equations we use a higher-order finite-element method (FEM), implemented in the solver JCMsuite.[4] The geometry is discretized using a tetrahedral mesh with curvilinear mesh elements along the curved surfaces of the NPs. Transparent boundary conditions are realized by using perfectly matched layers. We use tabulated material data for NP material Au[40] and a constant refractive index of 1.4 for the background material. High numerical accuracy is ensured by using a conservative setting of the numerical parameters (polynomial degree of the FEM ansatz functions of p=2 and mesh element edge size smaller than 7 nm for the NPs and 14 nm for background material). The absorbed electromagnetic field energy and the electromagnetic field energy scattered outwards, corresponding to each circular polarized source term (left-hand circular polarization, LCP, and right-hand circular polarization, RCP), are obtained in post-processes. The extinction is given by the sum of absorption and scattering for both polarization directions, LCP and RCP, and for all six

directions of incidence. The CD (g-factor) is given by the difference between absorption and scattering for LCP and absorption and scattering for RCP, and is normalized to the extinction maximum of the respective wavelength spectrum. Field patterns for visualization purposes (Fig. 3e, f) are obtained by exporting the computed near-fields on specific cross-sections, and a summation of the exported fields over all source terms at a specific wavelength. For performing numerical parameter studies as shown in Fig. 4, the physical quantities of the project are parameterized, and a scripting language (Matlab) is used to automatically generate the input files and to distribute the FEM computations to various threads on a workstation for parallel computation of the parameter- and wavelength-scans.

References

1 Douglas, S. M. et al. Self-assembly of DNA into nanoscale three-dimensional shapes. *Nature* **459**, 414-418 (2009).

2 Douglas, S. M., Chou, J. J. & Shih, W. M. DNA-nanotube-induced alignment of membrane proteins for NMR structure determination. *PNAS* **104**, 6644-6648 (2007).

3 Ye, X. et al. Improved size-tunable synthesis of monodisperse gold nanorods through the use of aromatic additives. *ACS Nano* **6**, 2804-2817 (2012).

4 Pomplun, J., Burger, S., Zschiedrich, L. & Schmidt, F. Adaptive finite element method for simulation of optical nano structures. *Phys. Status Solidi B* **244**, 3419-3434 (2007).