Supporting Information

Dynamic Plasmonic Pixels

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Preparation of Au NR suspensions with resonance at 1100 nm:

Au NRs with longitudinal resonances at 1100 nm in water were prepared as follows: Hexadecyltrimethylammonium bromide (CTAB) was purchased from GFS chemicals. Benzyldimethylhexadecylammonium chloride (BDAC) was purchased from TCI America. $HAuCl_4$, $AgNO_3$, hydroquinone, sodium borohydride, and L-ascorbic acid were purchased from Aldrich. Two growth solutions ("A" and "B") were prepared according to the following procedure: The growth solution A was prepared by mixing $HAuCl_4$ (0.2 mL, 0.1 M), $AgNO_3$ (0.2 mL, 0.1 M), and CTAB (40 mL, 0.05 M), followed by the addition of hydroquinone solution (1 mL, 0.1 M) as a reducing agent. When the solution became clear (~10 min), an aqueous solution of $NaBH_4$ (0.01 mL, 0.01 M) was added without stirring. The as-prepared solution was left at 25 °C for 24 h. The growth solution B was prepared by mixing $HAuCl_4$ (1 mL, 0.1 M), $AgNO_3$ (0.16 mL, 0.1 M), CTAB (0.05 M), and BDAC (0.1 M) in 100 mL of water. Hydroquinone solution (5 mL, 0.1 M) was then added. The as-made solution was kept at 25 °C for 10 min. The two growth solutions A and B were mixed together and left inside an oven at 25 °C for 24 h. To remove excess surfactant, the solution was centrifuged at 12,000 rpm (24,792 $\times g$) for 20 min (50 mL Thermo Scientific Nunc centrifuge tubes, Thermo Scientific Sorvall Lynx 4000 centrifuge with Fiberlite F14-14×50cy rotor). The supernatant was decanted and discarded, and the precipitate was redispersed in 18 MΩ deionized (DI) water (EMD Millipore Milli-Q Advantage A10).

Purification and phase transfer of Au NR suspensions:

Before further purification of each type of Au NR, the temperature of the NR suspensions was raised to 30 °C in a water bath to dissolve crystallized surfactant. Excess surfactant was then removed by centrifuging 30 mL of aqueous NR suspension at 4000–4500 rpm (2754–3486 $\times g$), 30 °C for 1 h. The supernatant was decanted with a serological pipette and discarded, and the precipitate was redispersed with 1.1 mM CTAB (98%, GFS Chemicals) to 40 mL. The sample was centrifuged a second time at 4000–4500 rpm (2754–3486 $\times g$), 30 °C for 1 h; the supernatant was decanted and discarded, and the precipitate was redispersed with DI water at 30 °C to 10 mL.

The Au NRs were phase-transferred to toluene by functionalizing the NRs with thiol-terminated polystyrene (PS-thiol).[3] To 10 mL of tetrahydrofuran (THF, HPLC Grade, Fisher Scientific), 0.1 g PS-thiol (M_n = 50,000; Polymer Source, Inc.) was added and dissolved. 10 mL of Au NR suspension was placed in a 30 mL glass vial. 5 mL of the PS-thiol/THF solution was added to the Au NR, and the vial was capped and shaken for 1 min. An additional 5 mL of the PS-thiol/THF solution was then added, followed by another 1 min of shaking. The Au NRs formed flocculates on the side of the vial and in the liquid, which were allowed to settle to the bottom of the vial for 20 min. The colorless solvent was then decanted and discarded, and any remaining solvent was evaporated with the flow of dry N_2. The PS-thiol-functionalized Au NRs were redispersed in 10 mL of toluene (HPLC grade, Fisher Scientific).

The Au NRs were then purified from excess, unbound PS-thiol. To promote precipitation during centrifugation, 5 mL of 2-propanol (ACS Plus grade, Fisher Scientific) was added to 10 mL of Au NR suspension in toluene, followed by vortexing for 30 s. The sample was centrifuged at 9000 rpm (13,945 $\times g$), 30 °C for 1 h; the supernatant was decanted and discarded, and the precipitate was redispersed with toluene to 30 mL. 10 mL of 2-propanol was added, followed by vortexing for 30 s. The sample was centrifuged a second time at 9000 rpm, 30 °C for 1 h; the supernatant was decanted and discarded, and the precipitate was redispersed with toluene to 30 mL. 10 mL of 2-propanol was added, followed by vortexing for 30 s. The sample was centrifuged a third time at 9000 rpm, 30 °C for 1 h; the supernatant was decanted and discarded, and the precipitate was redispersed with toluene to the desired Au NR concentration.

Preparation of Au NR cores for Au@Ag@SiO$_2$@OTMOS NRs:

Au NR cores were prepared based on the methods of Park *et al*.[4] A seed solution was prepared by dissolving HAuCl$_4$ (≥99.9%, Aldrich, 0.025 mL, 0.1 M) in an aqueous solution (10 mL, 0.1 M) of CTAB. A freshly prepared, ice-cold NaBH$_4$ (99.99%, Aldrich) solution (0.6 mL, 0.01 M) was then added into the mixture under vigorous stirring (1 min). The seed solution was aged for 10 min before being added into the growth solution. Two growth solutions were prepared: Growth A: The growth solution was prepared by mixing HAuCl$_4$ (0.150 mL, 0.1 M), AgNO$_3$ (>99.99%, GFS Chemicals, 0.024 mL, 0.1 M), and CTAB (1.092 g, 2.99 mM) in 30 mL of DI water, followed by addition of an L-ascorbic acid (>99.0%, TCI) solution (0.159 mL, 0.1M) as a mild reducing agent. Finally, 3 mL of seed solution was added into the growth solution. The solution was kept at 25 °C for 15 min. Growth B: The solution was prepared by mixing CTAB (1.092 g, 2.99 mM), AgNO$_3$ (2.4 mL, 0.1 M), HAuCl$_4$ (15 mL, 0.1 M), and L-

ascorbic acid solution (15.9 mL, 0.1 M). The solution was kept at 25 °C for 15 min. The growth

solution B was added dropwise to growth solution A, and the Au NRs as prepared were kept at

25 °C overnight. The Au NRs had an absorption peak at ~680 nm resulting from the longitudinal

surface plasmon resonance. The as-prepared Au NRs were placed in 50 mL centrifuge tubes and

purified by centrifuging at 3000 rpm (1549 $\times g$), 30 °C for 1 h. The supernatant was decanted and

discarded, and the precipitate was redispersed to the original volume with DI water, followed by

30 s each of sonication and vortexing. The Au NRs were centrifuged a second time at 3000 rpm,

30 °C for 1 hour. The supernatant was again decanted and discarded, and the precipitate was

redispersed to the original volume with DI water, followed by 30 s each of sonication and

vortexing.

Ag coating of Au NR cores:

The Au NR cores were coated with Ag, following a method based on that described by

Park *et al*.[5] Typically, six 5 mL batches of the following type were prepared in parallel to provide

a total of 30 mL. In a typical individual reaction, 184 µL of purified Au NR cores was added to 5

mL of DI water in a Fisherbrand 16×100 mm flint glass culture tube. The resulting suspension

had an absorbance at 680 nm of ~1.25 over a 1 cm path length. Then, 0.018 g of CTAB was

added, raising the CTAB concentration of the Au NR suspension to ~10 mM. The suspension

was vortexed 30 s then placed in a 30 °C water bath for 15 min to encourage CTAB dissolution.

The NR suspension was then vortexed until no undissolved CTAB could be seen. Next, 50 µL of

0.1 M $AgNO_3$ was added, and the suspension was mixed with a pipette. The suspension was then

aged at 25 °C for 30 min. During the first ~5 min of aging, the suspension became turbid. After

aging, 100 µL of 0.1 M L-ascorbic acid was added, and the suspension was

mixed with a pipette. Then, 200 µL of 0.1 M sodium hydroxide (NaOH, Fisher Scientific, ACS grade) of pH 13 was added, and the suspension was mixed with a pipette. The addition of NaOH increased the pH of the Au NR suspension from ~3.7 to ~10.0, as measured by a pH probe inserted in the tube (Mettler Toledo InLab Micro-Pro-ISM probe with FiveEasy FE20 meter). Within ~5 min, a color change toward green was observed. The suspension rested at 25 °C for at least 3 h to allow the Ag-coating reaction to complete.

The Au@Ag NRs were then purified with three centrifugation cycles as described here: The 5 mL of Au@Ag NRs from each of the six tubes was transferred to individual 50 mL centrifuge tubes, and DI water at 30 °C was added to bring the total liquid volume in each tube to 40 mL. The sample was centrifuged at 4000 rpm, 30 °C for 1 h; the supernatant was decanted and discarded, and the precipitate was redispersed with DI water to 5 mL. The 5 mL from each of the six tubes was then combined in a single tube, and 10 mL of DI water was added to bring the total volume to 40 mL. This tube was then centrifuged at 4000 rpm, 30 °C for 1 h; the supernatant was decanted and discarded, and the precipitate was redispersed to 40 mL with 1.1 mM CTAB at 30 °C. Finally, a third centrifugation was performed at 4000 rpm, 30 °C for 1 h; the supernatant was decanted and discarded, and the precipitate was redispersed to 30 mL with 1.1 mM CTAB.

SiO_2 Coating of Au@Ag NRs:

The Au@Ag NRs were overcoated with SiO_2 following a method adapted from Wu and Tracy.[6] The pH of the NR suspension was raised to 10 with the dropwise addition of 0.1 M NaOH. 10 mL of the suspension was dispensed in a 20 mL glass scintillation vial, which was placed in a water bath at 30 °C with magnetic stirring in the vial. A solution of 20 % (v/v)

tetraethyl orthosilicate (TEOS, 99.999%, Aldrich) in anhydrous methanol (99.8%, Sigma-Aldrich) was prepared and loaded in a 5 mL syringe fitted with a 30 G needle. In a typical reaction, a total of 125 µL of the TEOS solution was added dropwise to the Au@Ag NRs over a period of 5 min using a syringe pump (Fisherbrand) operating at 1.5 mL/h. The sample was stirred magnetically for 30 min and then left without stirring in the 30 °C water bath for 20 h.

The sample was removed from the water bath and vortexed for 30 s. The Au@Ag@SiO$_2$ NR suspension was divided between two 50 mL centrifuge tubes, 5 mL of NRs to each. 35 mL of methanol (ACS grade, Fisher Chemical) was added to each tube, followed by vortexing for 30 s. The sample was then centrifuged at 2951 rpm (1500 $\times g$), 30 °C for 30 min; the supernatant was decanted and discarded, and the precipitate was redispersed with methanol to 40 mL, followed by vortexing for 30 s. A second centrifugation with the same parameters was performed, and the precipitate was redispersed with methanol to 5 mL, followed by vortexing for 30 s.

Phase transfer of Au@Ag@SiO$_2$ NRs to nonpolar solvents:

In order to make the Au@Ag@SiO$_2$ NRs stable in nonpolar solvents, the SiO$_2$ surface was functionalized with octadecyltrimethoxysilane (OTMOS, 90% technical grade, Acros Organics), utilizing a method adapted from the report of Pastoriza-Santos *et al.*[7] First, 5 mL of the NR suspension in methanol was dispensed into a 2 dram (7.4 mL) glass vial and placed in a 30 °C water bath, with magnetic stirring in the vial. Then, 50 µL of 28.0–30.0% ammonium hydroxide solution (ACS grade, Oakwood Chemical) was added. Finally, 500 µL of 10 vol% OTMOS in chloroform (≥99%, Sigma-Aldrich) was added, and the solution was stirred for 24 h in the 30 °C water bath.

The vial was removed from the water bath and vortexed for 30 s to release any clumps of material from the sides of the vial. The solids were allowed to settle to the bottom of the vial for 15 min, after which the top 4 mL of solvent was decanted and discarded. After adding 4 mL of methanol, the sample was vortexed for 30 s and allowed to settle for 15 min. The top 4 mL of solvent was again decanted and discarded, 4 mL of methanol was added, and the sample was vortexed for 30 s then allowed to settle for 15 min. For the third time, the top 4 mL of solvent was decanted and discarded. Then, 5 mL of heptane (HPLC grade, Fisher Chemical) was added and the sample vortexed for 30 s. The sample phase-separated into two fractions: a colorless methanol phase at the bottom and a heptane phase containing the NRs on top, pictured in Supporting Information Figure S8. Both phases were then extracted into a 10 mL syringe fitted with a 20 G needle and the phases allowed to separate within the syringe. The methanol phase was dispensed from the bottom of the syringe and discarded, and the heptane phase containing the NRs was dispensed into a 15 mL centrifuge tube (Thermo Scientific Nunc). The sample was centrifuged at 3453 rpm (2400 $\times g$), 35 °C for 30 min (Eppendorf 5810R centrifuge). The supernatant was decanted and discarded, and the precipitate was redispersed with heptane to 1 mL. The Au@Ag@SiO$_2$@OTMOS NRs in heptane were kept above 25 °C to avoid reversible clouding.

Simulations:

Simulations were performed using the commercial finite-element simulation software COMSOL Multiphysics.[8] An electromagnetic plane wave comprising the relevant wavelength range was simulated as incident on NRs of variable material compositions and dimensions. The core NRs were modeled as hemispherical-capped cylinders. The Au, Au@Ag, and

Au@Ag@SiO$_2$ NRs were modeled by applying shells to the base Au NR with H$_2$O, methanol, toluene, or heptane as the surrounding medium. Complex optical material properties of Au, Ag, SiO$_2$, methanol, and heptane were interpolated *via* commonly cited published data,[9-12] with the refractive index of H$_2$O set at 1.33 and toluene at 1.475. Two NR orientations were modeled, complete parallel alignment with the direction of plane wave propagation ($S = 1$) and perpendicular alignment ($S = -1/2$), the combination of which can model the random alignment situation ($S = 0$).

Each model simulated a quarter-NR by establishing perfect electric conductor (PEC) and perfect magnetic conductor (PMC) boundary conditions along the two perpendicular walls bisecting the NR. This reduction of the total model volume made it possible to implement a finer tetrahedral mesh without prohibitively increasing the computation time. Scattering boundary conditions and perfectly matched layers were applied to the remaining model boundaries to prevent erroneous boundary scattering.

The absorption cross-section was calculated by integrating the resistive losses over the volume(s) of the NR(@shells), $ACS = 4 \iiint emw.Qrh \ / \ S$, where the factor of four takes into account that only ¼ of a NR is modeled, $emw.Qrh$ is the built-in resistive losses function, $S = E_0^2/(2Z_0 n)$, where E_0 is the incident electric field, Z_0 is the characteristic impedance of vacuum, and n is the refractive index of the medium. The scattering was found by integrating the time average Poynting vector components of the scattered field through each non-mirror boundary, $scPoav = (emw.relPoavx \cdot onx) + (emw.relPoavy \cdot ony) + (emw.relPoavz \cdot onz)$ where onx, ony, and onz are normal vectors to the boundary surfaces. The scattering was thus $SCS = 4 \iint scPoav/S\_in$. The extinction cross-section was taken to be the sum of calculated absorption and scattering, $ECS = ACS + SCS$.

Considering the calculated extinction spectrum in the $S = 1$ orientation as longitudinal, L, and that in the $S = -1/2$ orientation as transverse, T, the simulated spectra were combined *via* the equation $ECS_{Unaligned} = 1/3(L + 2T)$ where $ECS_{Unaligned}$ is the extinction spectrum for the unaligned case $(S = 0)$.[3] Thus, the model was used to produce spectra for fully aligned and randomly oriented nanorod suspensions.

Each computation was performed with the incident wavelength swept from 200 to 1200 nm in 5 nm increments. Extinction spectra were plotted for Au@Ag in H_2O and Au@Ag@SiO_2 in methanol for Ag layer thickness swept from 0 to 10 nm to encompass the TEM-measured value of 4 nm. Similarly, the SiO_2 layer thickness was held constant at the TEM-measured value of 27 nm. The core Au NR dimensions were held constant at 20×55 nm, also based on experimental measurements.

References:

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a

b

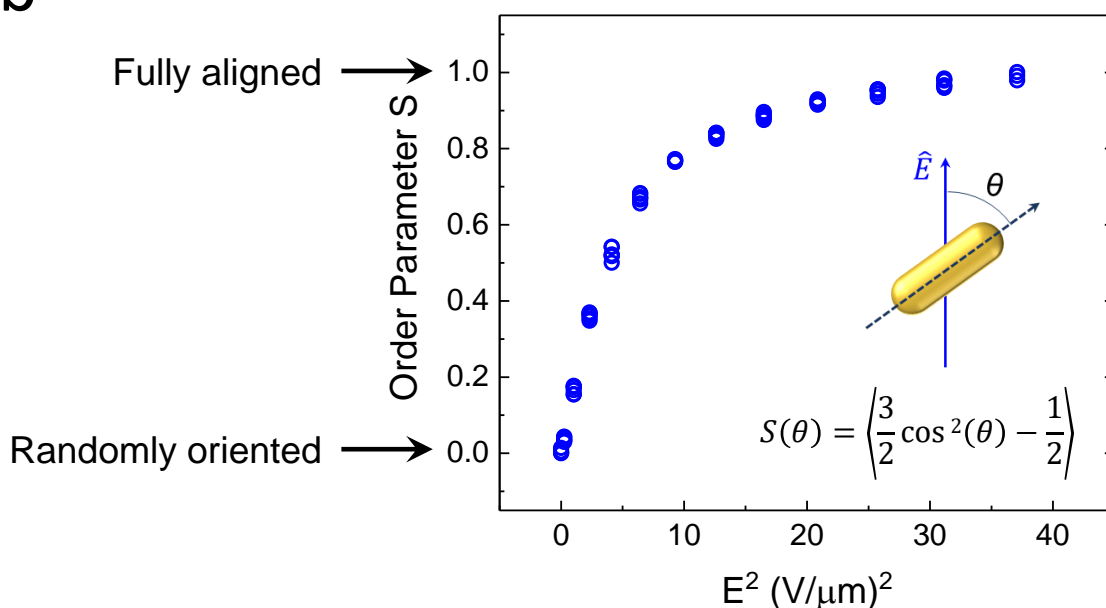$$S(\theta) = \left\langle \frac{3}{2}\cos^2(\theta) - \frac{1}{2} \right\rangle$$
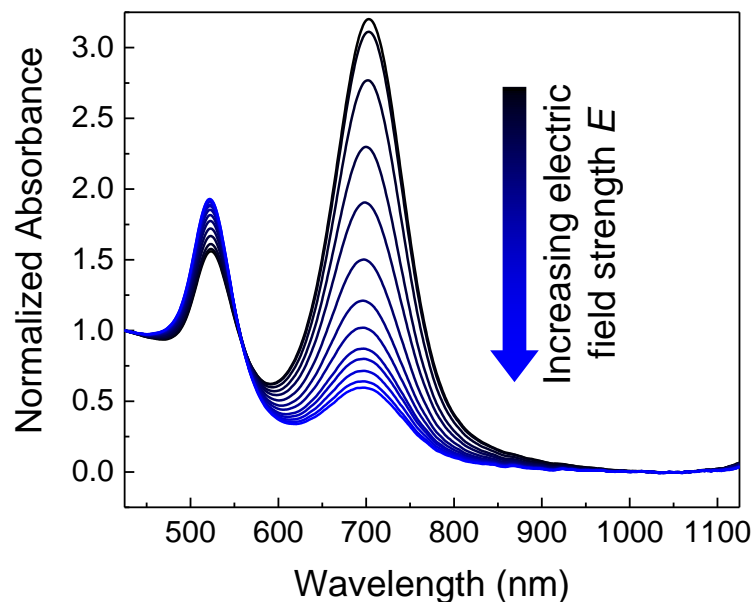
Figure S1. (a) Extinction spectra of Au NRs aligned under electric field strengths from 0–6.1 V/μm. (b) Orientational order parameter, S, extracted from the spectra of (a) as a function of the square of the electric field strength. Θ represents the angle between the NR long axis and the applied electric field, and the braces indicate the ensemble average.
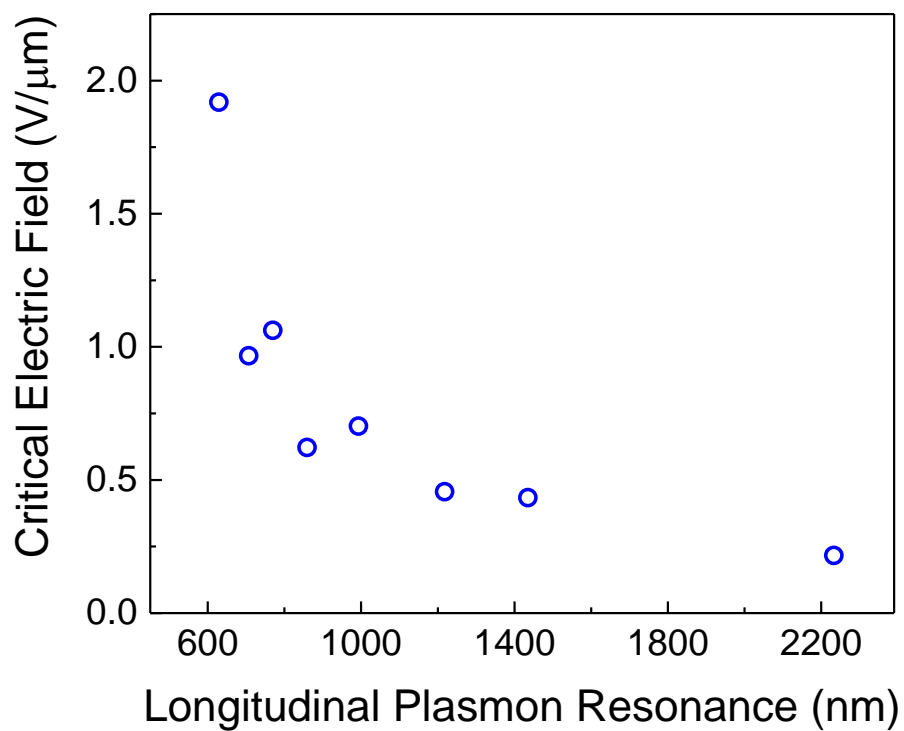
Figure S2. Critical electric field strength as a function of the longitudinal plasmon resonance of Au NRs with different aspect ratios.
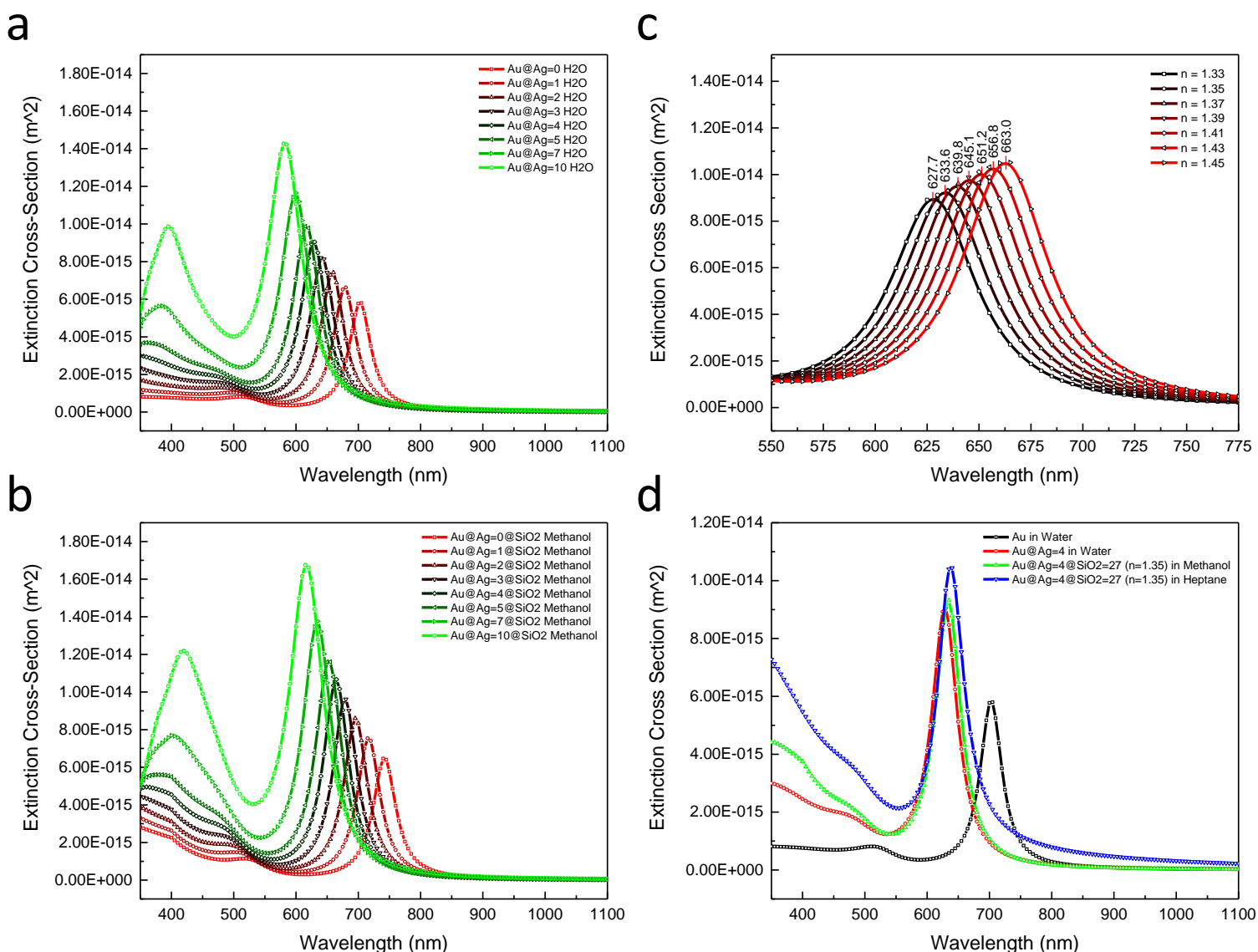
Figure S3. Simulated extinction spectra of Au@Ag NRs with the indicated Ag thicknesses (in nm), (a) without a SiO_2 shell, suspended in water and (b) with a 27 nm SiO_2 shell (n=1.45), suspended in methanol. (c) Simulated extinction spectra of Au@Ag@SiO_2 NRs in methanol, where the refractive index of the 27 nm mesoporous SiO_2 shell has the indicated values and the Ag thickness is 4 nm. (d) Simulated extinction spectra of the indicated NRs, illustrating the sequence of spectral shifts from the initial Au NRs in H_2O to the final Au@Ag@SiO_2 NRs in heptane. The functionalization of the SiO_2 shell with OTMOS is not explicitly considered in the simulation.
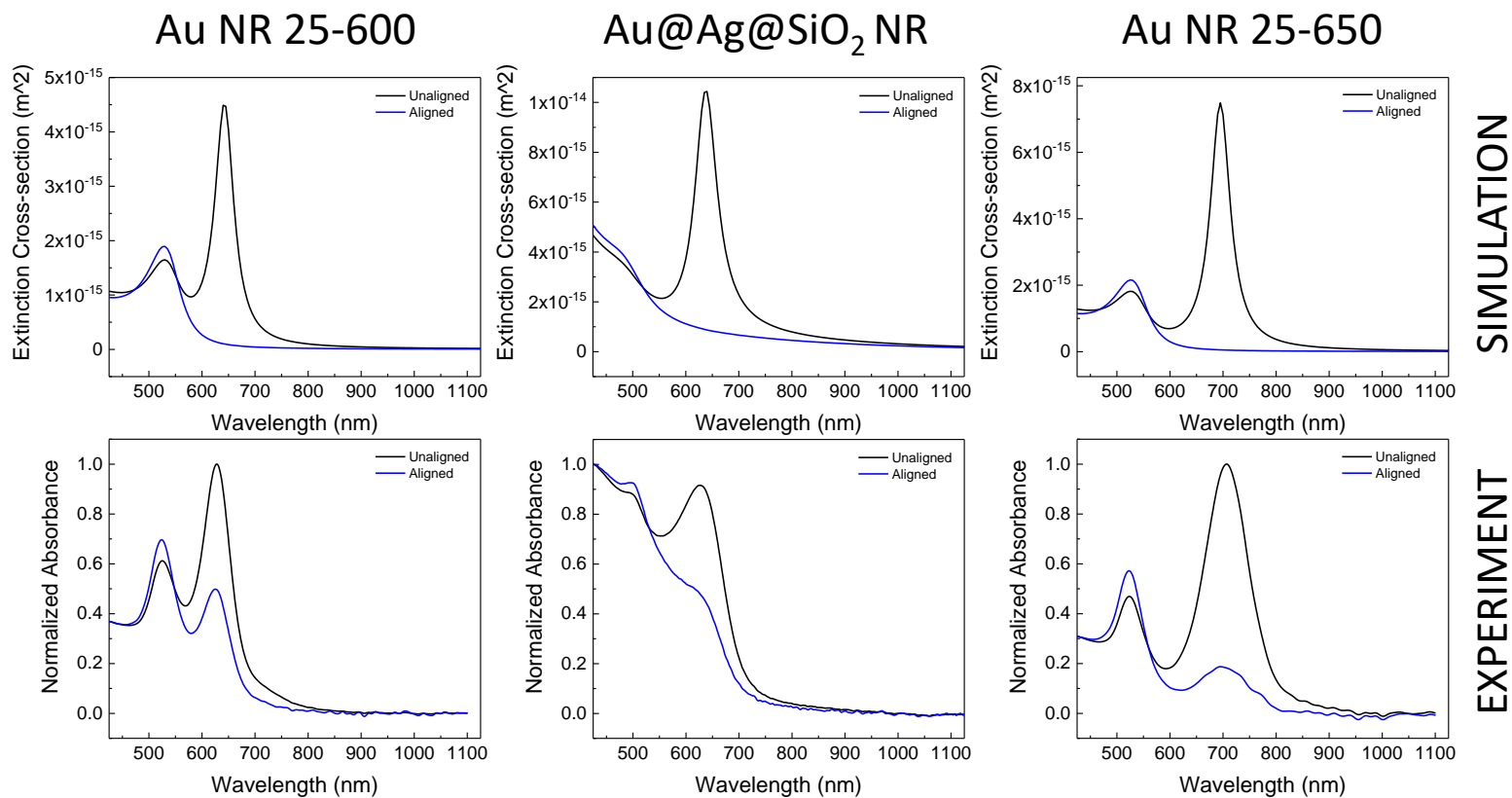
Figure S4. Simulated (top row) and experimental (bottom row) extinction spectra of the indicated NRs in unaligned and aligned states.
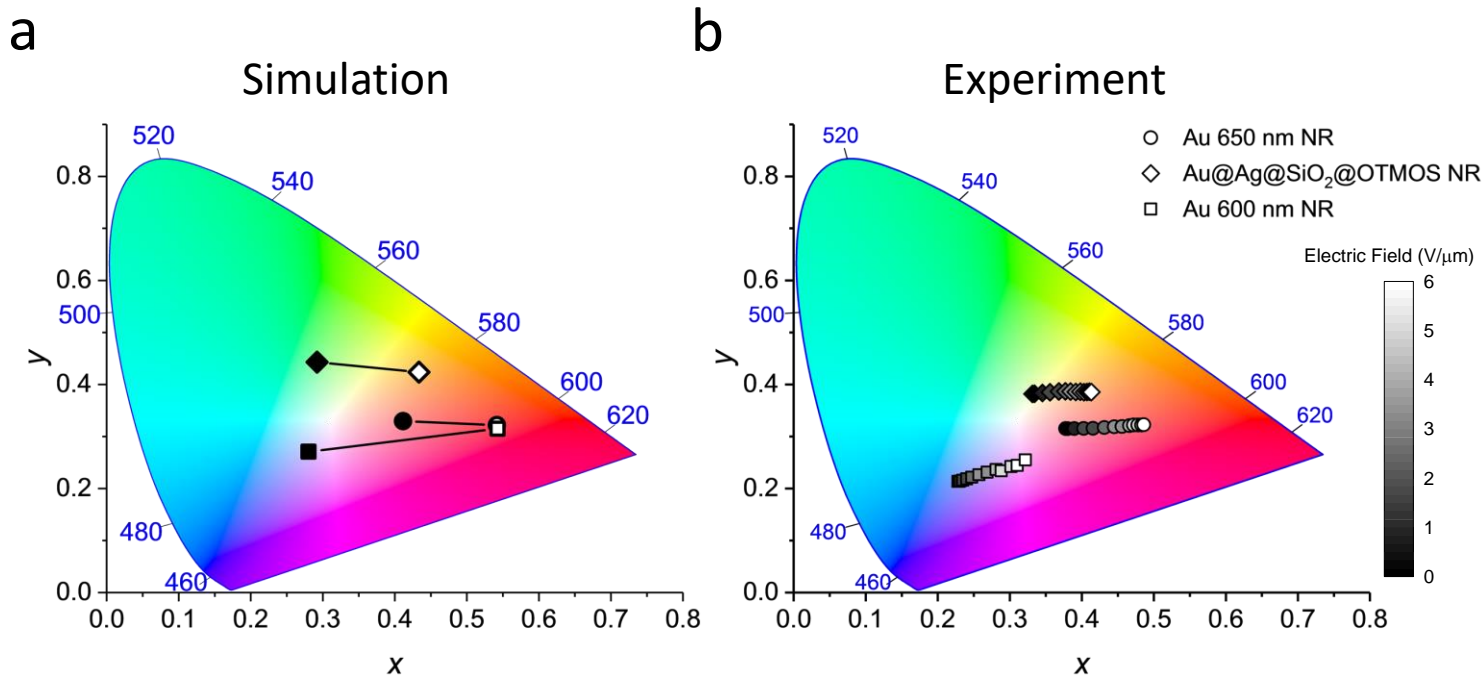
Figure S5. (a) Simulated and (b) experimental CIE 1931 chromaticity diagrams for Au 25-600, Au@Ag@SiO$_2$@OTMOS, and Au 25-650 NRs. Filled and open symbols in (a) are for unaligned and perfectly aligned states, respectively. The data in (b) is the same as Figure 4b, reproduced here for comparison.
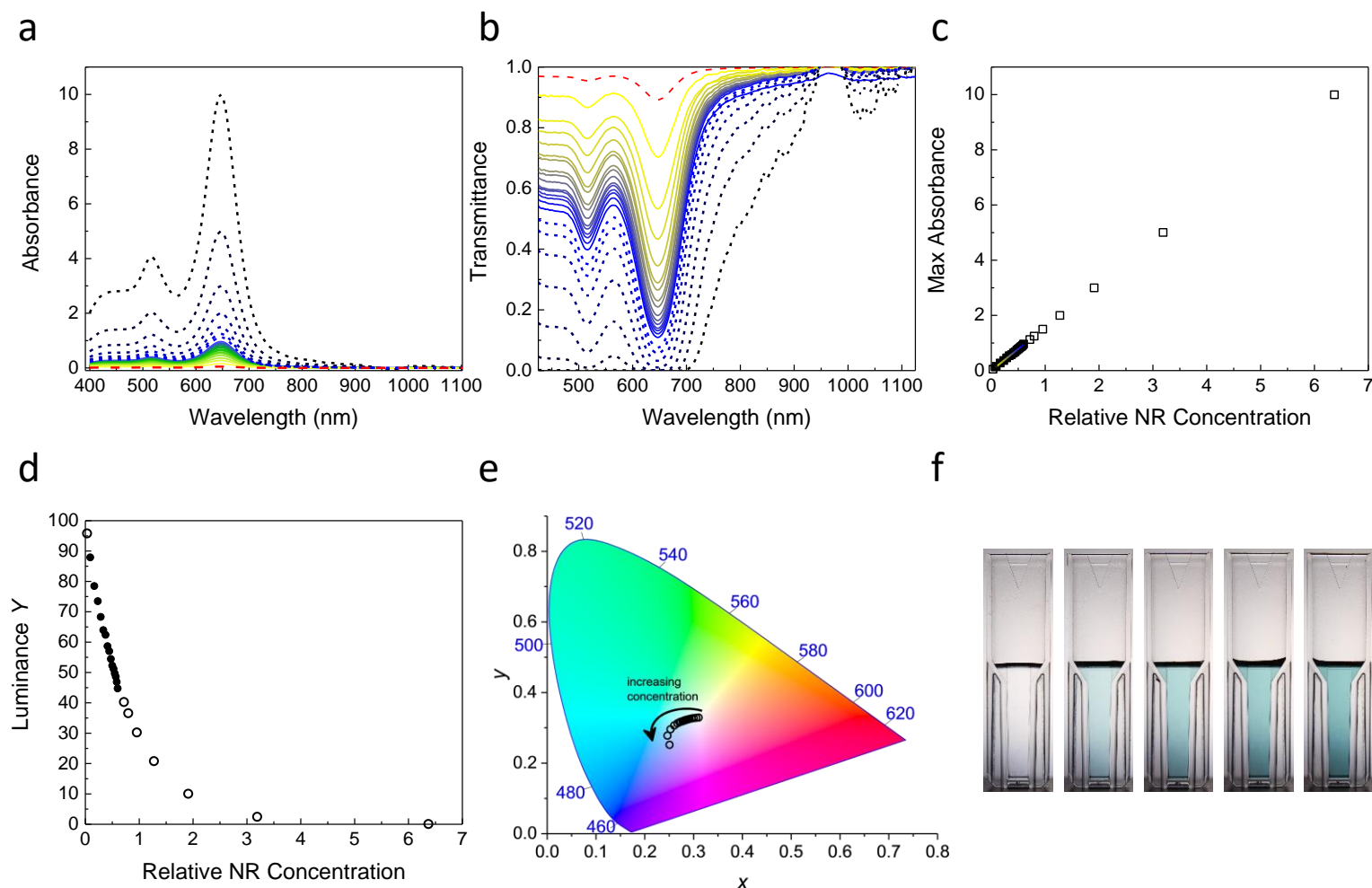
Figure S6. (a) Absorption and (b) transmission spectra of Au NR suspensions of the same type (Au NR 25-650 in water) but prepared with different concentrations. Solid curves are from experimentally measured data, and the dashed curves are extrapolations to higher and lower concentrations. (c) Maximum absorbance at the plasmon resonance for NR suspensions of different concentrations relative to the as-received concentration. (d) CIE 1931 luminance *Y* and (e) chromaticity *x,y* values calculated from the spectra in (b) using a D65 standard illuminant and a 2° observer. Solid and open data markers in (c–e) are for experimental and extrapolated data, respectively. (f) Photographs of five of the NR suspensions measured, increasing in concentration from left to right. The width of each cuvette is 1 cm.

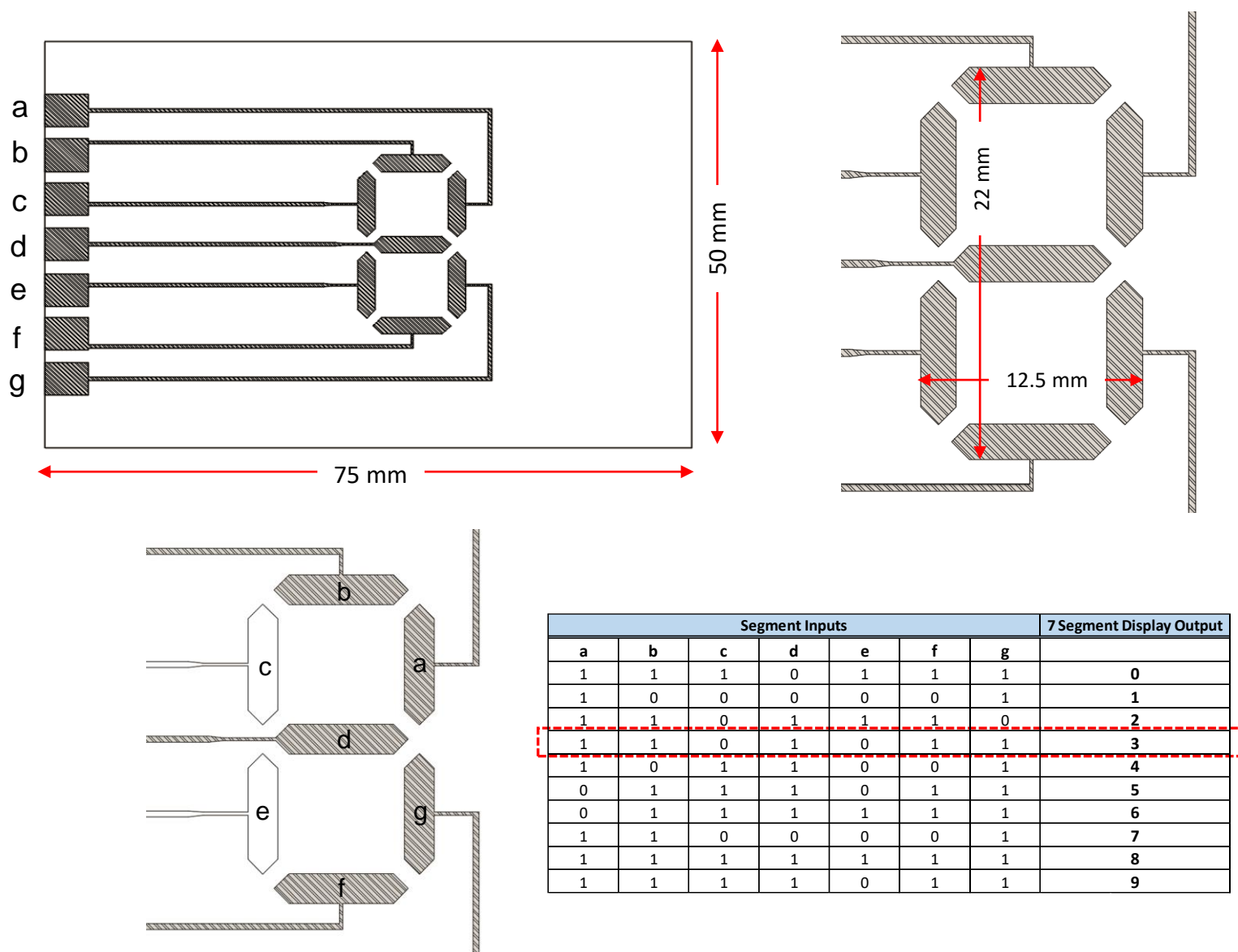| Segment Inputs							7 Segment Display Output
a	b	c	d	e	f	g	
1	1	1	0	1	1	1	0
1	0	0	0	0	0	1	1
1	1	0	1	1	1	0	2
1	1	0	1	0	1	1	3
1	0	1	1	0	0	1	4
0	1	1	1	0	1	1	5
0	1	1	1	1	1	1	6
1	1	0	0	0	0	1	7
1	1	1	1	1	1	1	8
1	1	1	1	0	1	1	9

Figure S7. Schematic and dimensions of the seven-segment numerical indicator. The table provides the segment input states corresponding to each numeral.
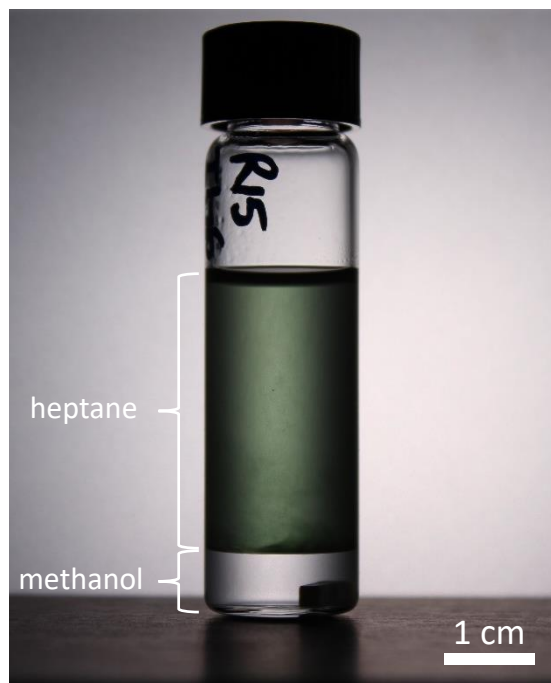
Figure S8. Photograph of the phase transfer of Au@Ag@SiO$_2$ NRs from methanol to heptane, showing the phase-separated fractions following functionalization with OTMOS.
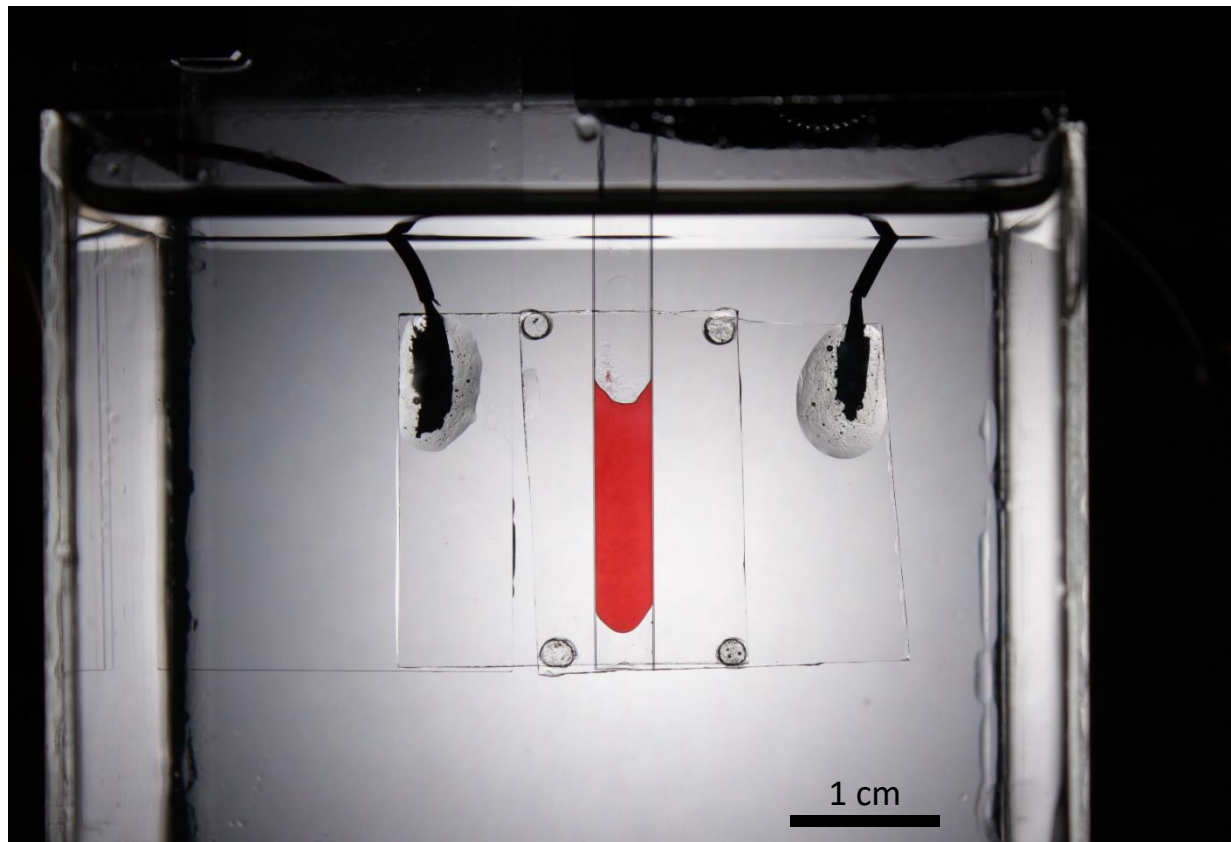
Figure S9. Photograph of experimental apparatus for observing NR alignment. The NR suspension is loaded in a rectangular capillary that is mounted between ITO-coated glass slides to which electrical leads are soldered with indium. The mount is immersed in silicone transformer oil to prevent dielectric breakdown.