Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Assembling patchy nanorods with spheres: Limitations imposed by colloidal interactions

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1. Normalized extinction spectra of as-prepared AuNP and AuNR samples

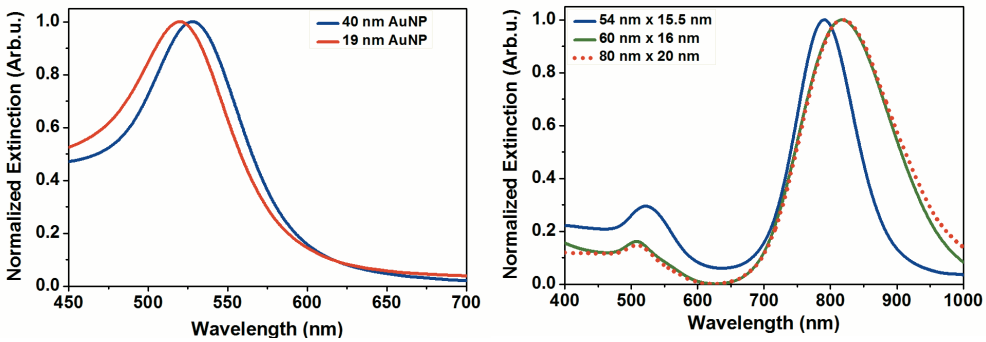


Figure S1. (a) Normalized extinction spectra of the 19 and 40 nm gold nanopheres used for the assemblies. (b) Normalized extinction spectra of the gold nanorods solution before surface modification.

2. Surface modification of the AuNRs

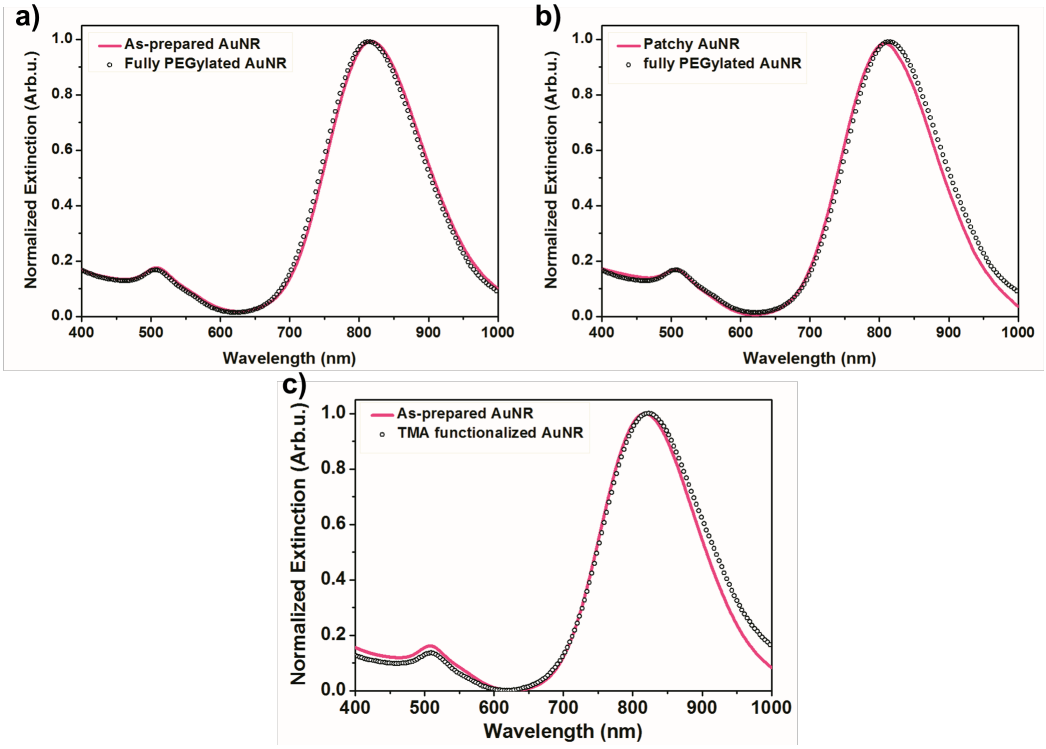


Figure S2. (a) Extinction spectra of patchy AuNRs and fully PEGylated solution as a reference. The cysteamine monolayer stays intact after PEgylation resulting in a blueshifted LSPR peak. (b) Extinction spectra of As-prepared sample and fully PEGylated AuNRs and the spectra of (c) TMA functionalized AuNR solution with the adherent as-prepared solution.

3. **Ratio of the van der Waals attraction for the tip and side located nanospheres at a nanorod [1]:**

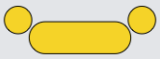
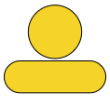
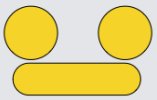
$$U_{vdW}^{tip} = \frac{-A}{6\delta} * \frac{a * a_R}{(a + a_R)}$$

$$U_{vdW}^{side} = \frac{-A}{6\delta} * \left(\frac{a_R * a^2}{(a + a_R)}\right)^{1/2}$$

where a and a_r refer to the sphere and rod radii, respectively. A is the Hamaker constant and δ is the gap between the particles. For the relative ratio of the van der Waals interaction this reduces to:

$$\frac{U_{vdW}^{side}}{U_{vdW}^{tip}} = \sqrt{1 + \frac{a}{a_R}}$$

Table S1. Summary of the sphere-to-rod size ratio, the electrophoretic mobility (μ_{el}), and the ratio of the van der Waals attraction of the side and tip location of the nanospheres for the different structures.

	D_{NP}/D_{ROD}	μ_{el} (μm*cm/Vs)	$U(vdW)_{SIDE}$ / $U(vdW)_{TIP}$
	1.2	NP: -2.4 ROD: 1.0	1.49
	2.5	NP: -2.7 ROD: 1.0	1.86
	2.0	NP: -2.7 ROD: 1.0	1.68

4. **Effect of assembly sequence on the evolving bulk spectrum:**

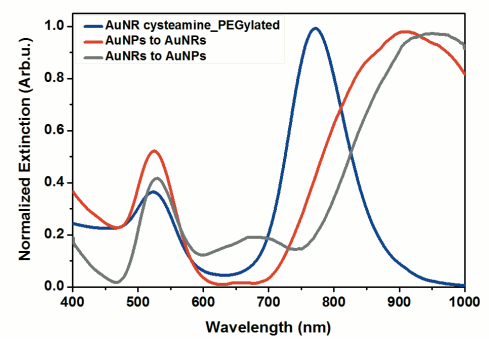


Figure S3. The effect of the assembly sequence, i.e. the nanorod/nanosphere ratio causes significant difference in the extinction spectra. When adding nanospheres to the nanorods (nanorod/nanosphere » 1) the spheres can induce chain assembly resulting in a larger redshift and broadening of the longitudinal LSPR peak.

5. Optical simulation results:

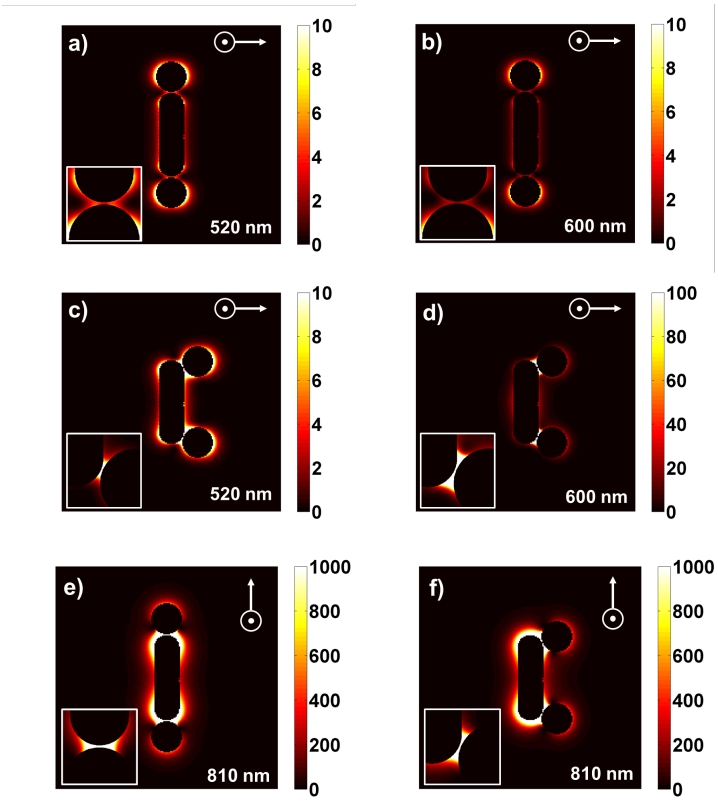


Figure S4. Selected near-field (E^2/E_0^2) maps for the assembled structures where the particles are located on the same side of the nanorods: transversal (a-d) and longitudinal (e-f) excitation. For figures (c, e, f) the inset has a color scale range one order of magnitude higher than the original image to better highlight the confined nature of the coupled mode.

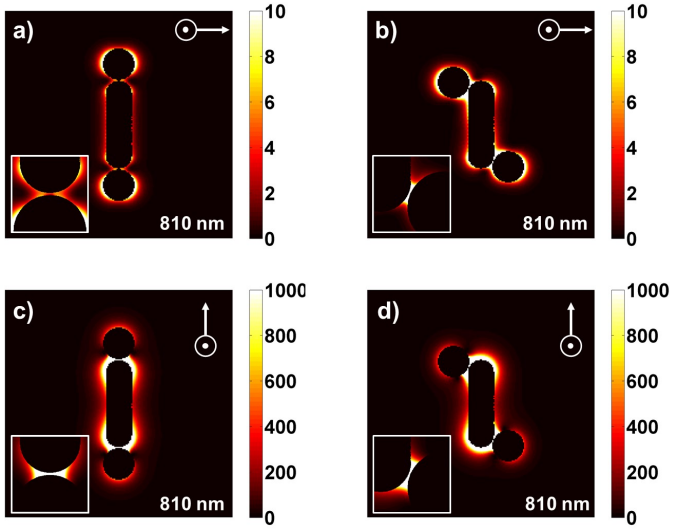


Figure S5. Selected near-field (E^2/E_0^2) maps for the assembled structures where the particles are located on the opposite side of the nanorods: transversal (a-b) and longitudinal (c-d) excitation. For figures (c-d) the inset has a color scale range one

order of magnitude higher than the original image to better highlight the confined nature of the coupled mode.

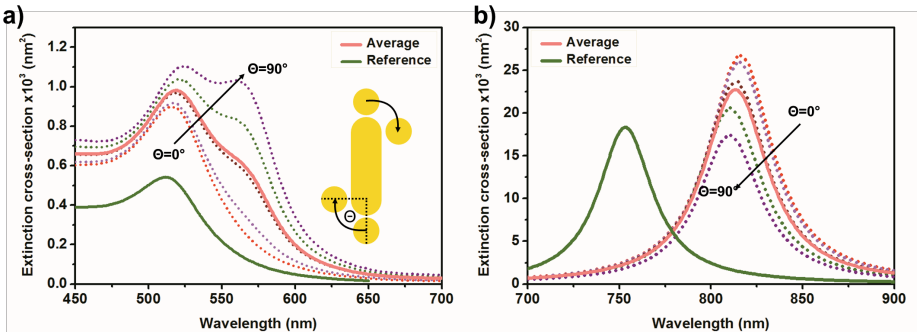


Figure S6. Transversal (a) and longitudinal (b) excitation of an assembled structure where the nanospheres are displaced towards the opposite sides of the nanorods. The two nanospheres are moved along the tip perimeter in 22.5° steps from 0° to 90° compared to the long axis of the nanorod, maintaining a gap size of 1 nm. The dotted curves are already averaged for light propagation direction parallel and perpendicular to the plane of sphere displacement, while the solid 'Average' curve represents averaging over the different angular positions. The transversal and longitudinal extinction without nanospheres is also shown as 'Reference'.

6. SEM images related to assembly experiments with 40 nm spheres:

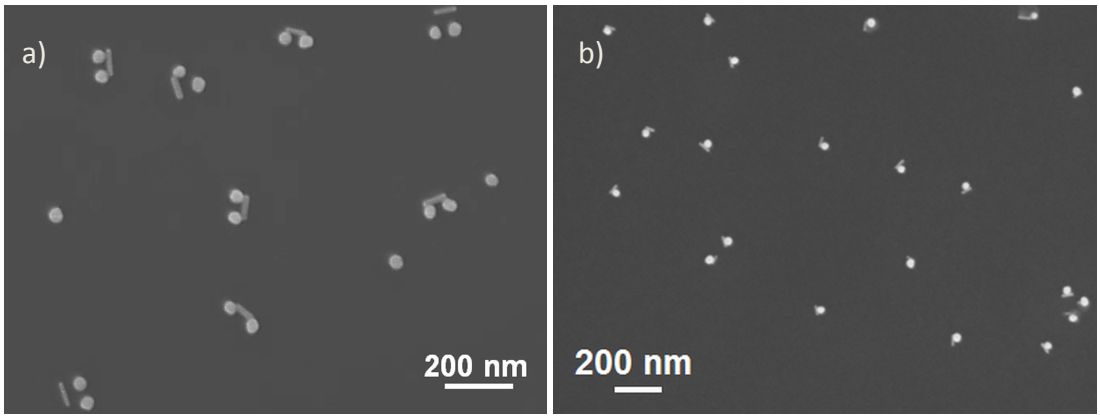


Figure S7. SEM images about the assembly experiments with 40nm AuNPs. The dimension of the rods are 80x21 nm (a) and 60x16 nm (b).

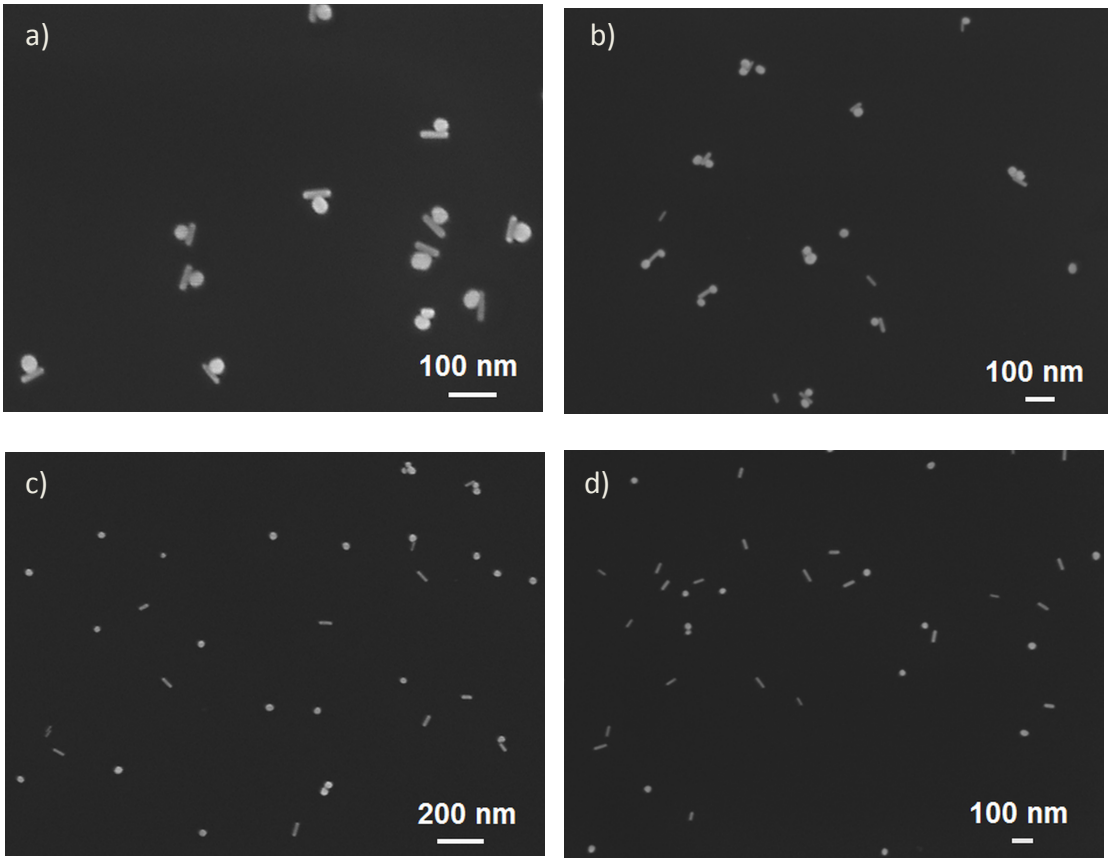


Figure S8. SEM images of the assembly experiments (60x16 nm AuNRs with 40nm AuNPs) performed at different K_2SO_4 concentrations: 0 mM (a); 2.5 mM (b); 5 mM (c); 10 mM (d).

7. Colloidal interaction energy:

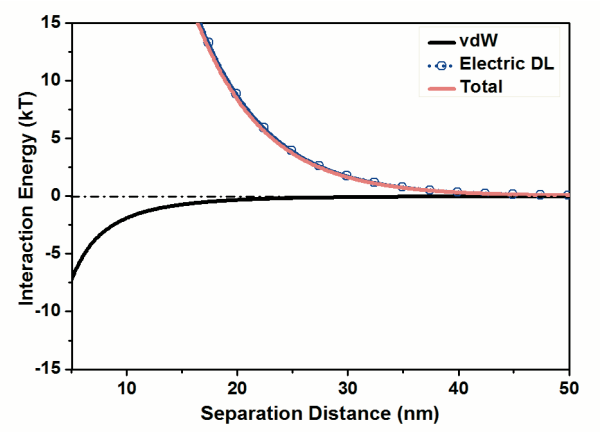


Figure S9. Pair interaction potential calculated between two 40 nm gold nanoparticles. [2]

References:

1. D. A. Walker, C. E. Wilmer, B. Kowalczyk, K. J. M. Bishop and B. A. Grzybowski, *Nano Letters*, 2010, **10**, 2275–2280.
2. D. Zámbó, G. Z. Radnóczi and A. Deák, *Langmuir*, 2015, **31**, 2662–2668.