Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary materials for Solution Self-Assembly of Janus Plasmonic Nanoparticles

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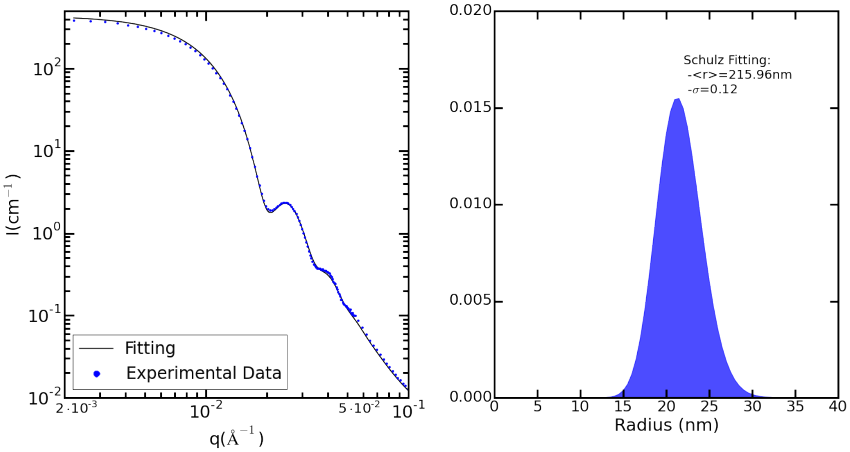

Figure S1: Left: Fitting of the SAXS signal from the gold nanoparticles using the analytical solution for spheres with a polydispersity defined by a Schulz distribution (Right).

Singular Value Decomposition

By visual inspection of the absorbance spectra as a function of time we could identify two isosbestic points? , where the absorbance remains constant over a certain period of time and indicates the presence of only two components in the system.

One such point occurs at 566 nm over the first ten hours of the kinetics (see Figure S2), as the Janus particles assemble into dimers. The absorbance then starts drifting due to the presence of the larger clusters (see the right panel in Figure 3 of the main text). After complete assembly of the particles (a process that takes about 40 h, see the left panel in Figure 3 of the main text) another isosbestic point appears at 680 nm (see Figure S3) as the dimers themselves assemble into clusters.

Singular Value Decomposition

The experimental absorbance data $A(\lambda, t)$ measured as a function of the wavelength λ and the time t can be organized as an $M \times N$ matrix A (we assume in the following that $M > N$), with M wavelength values and N time points, such that A_{ij} is the value for λ_i at t_j, where $t_1 = 0$ and $t_N = t_{\text{final}}$ (the beginning and the end of the kinetics, respectively). Using the singular value decomposition technique[?] , this matrix can be factorized into:

$$\mathsf{A} = \mathsf{U}\,\mathsf{W}\,\mathsf{V}^T \,,$$

where U and V are $M \times N$ and $N \times N$ orthogonal matrices, while W is an $N \times N$ diagonal matrix with nonnegative elements $\mathsf{W}_{ii} \geq 0$, known as singular values. The columns of U can be seen as basis vectors that, when multiplied by the time-dependent coefficients in V and weighted by the singular values, yield back the experimental absorbance spectra.

By row and column permutations, we can arrange the singular values such that $\mathsf{W}_{ii} \geq \mathsf{W}_{jj}$ for $i > j$. One can often obtain a very good approximation to A by truncating W to keep only the K largest singular values:

$$\mathsf{A} \simeq \mathsf{A}_K = \mathsf{U}\,\mathsf{W}_K\,\mathsf{V}^T \,,$$

where W_K is obtained from W by setting $\mathsf{W}_{ii} = 0$ for $i > K$.

In our case, we obtained good results with $K = 3$, hinting that only three species contribute to the absorbance over the duration of the kinetics. This conclusion is supported by the presence of the two isosbestic points discussed above. The signal of each species, $S_i(\lambda)$, $i = 1, 2, 3$ can be accurately described as a linear combination of the first three columns of U, but the combination coefficients are *a priori* unknown. It is however reasonable to identify one species as the isolated nanoparticles, which are the only species present at $t = 0$, so that $S_1(\lambda) = A(\lambda, t = 0)$. Their spectrum (in red) exhibits a single peak around 530 nm. The amplitude of this component decreases rapidly, vanishing in less than 40 hours. The second curve (in blue) can be identified as the contribution of particle dimers with a surface-to-surface distance of 2.2 nm, yielding a coupling peak at 630 nm (visible in the intermediate-time spectra). Its amplitude shows a rapid increase during the first hours followed by a slow decline. The third component (in green) is due to larger assemblies, with a wide coupling band centered around 750 nm, suggesting the particles have gotten closer together, and a bigger polydispersity in the average distance. Overall we can deduce that the heterodimers start to assemble in dimers shortly after the addition of the thiol. This is a relatively fast process, which results in a maximum concentration of dimers almost 20 h after the initiation of the process. This first step is followed by a slower one, during which the dimers are transformed in larger and more complex assemblies. This process has a longer induction time, and is much slower: as the shape of the curves makes clear, it still hasn't reached equilibrium after 72 h. The final recorded state of the system is thus a solution containing a mixture of dimers and larger clusters.

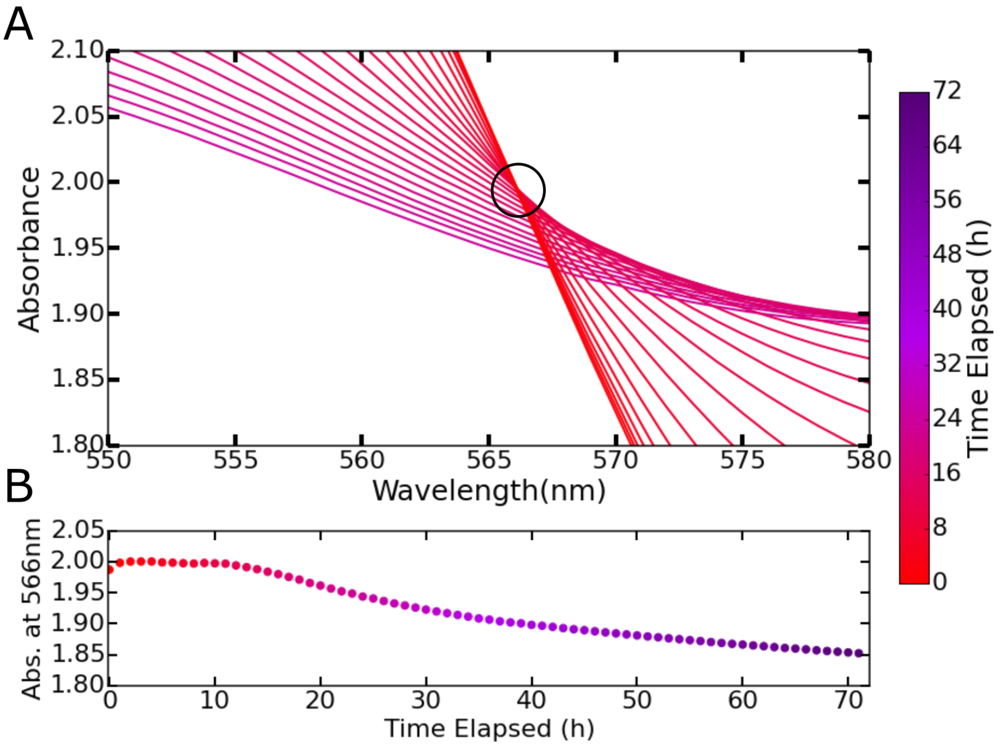

Figure S2: A) Detail of the evolution of the UV-Visible spectra shown in Figure 2 of the main text, with the first 25 spectra shown. B) The intensity of the spectra at 566 nm over the same period of time shows the presence of an isosbestic point for the first ten hours.

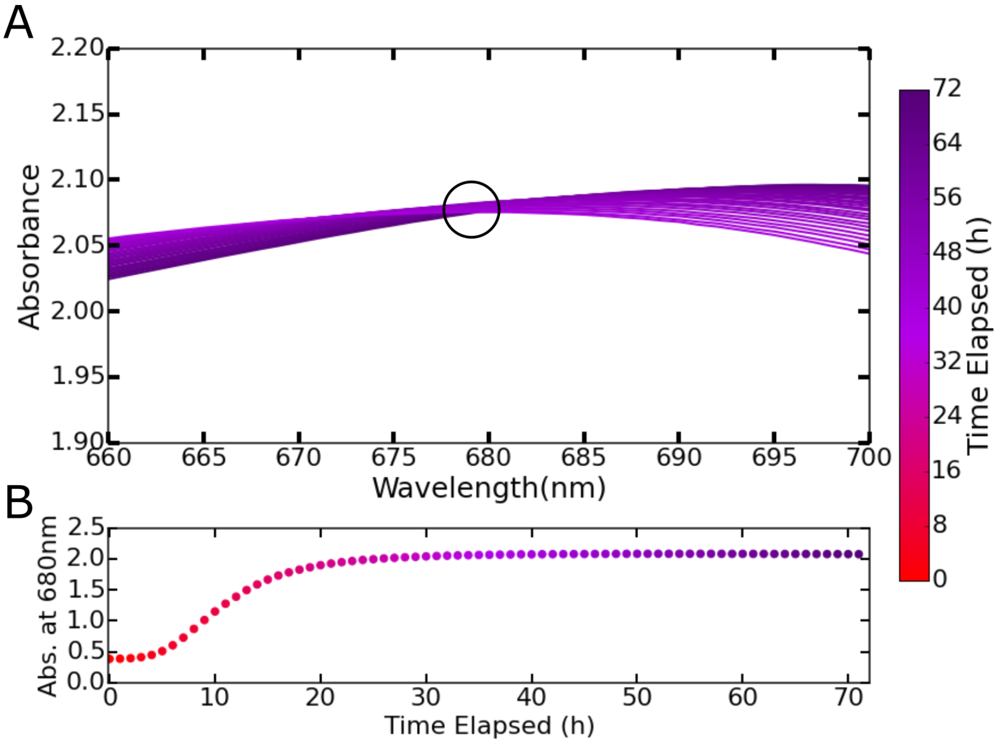

Figure S3: A) Detail of the evolution of the UV-Visible spectra shown in Figure 2 of the main text, with the last 30 spectra shown. B) The intensity of the spectra at 680 nm over the same period of time shows the presence of an isosbestic point after about 40 hours.

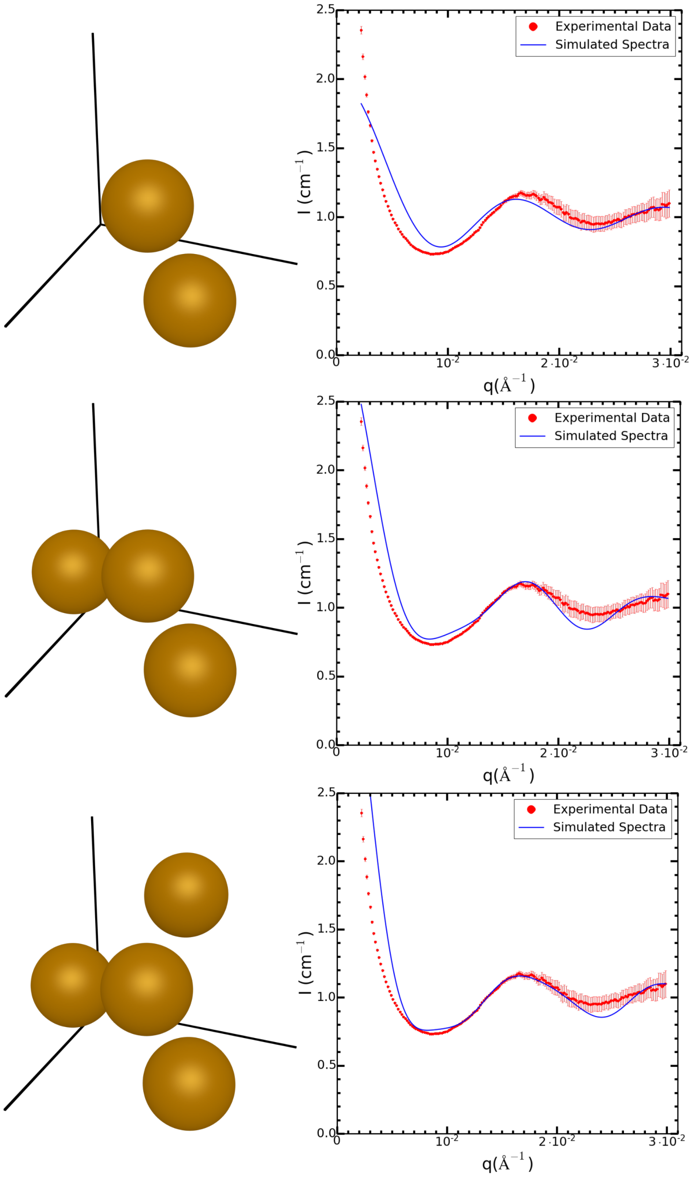

Figure S4: Example of the different steps through which the fitting algorithm goes through to find cluster structures which are compatible withthe structure factor obtained by SAXS measurements. The first column shows the rendering of the position of hte spheres while the right one shows the comparison between the experimenta data (*red dots*), and the simulated curve (*blue line*)

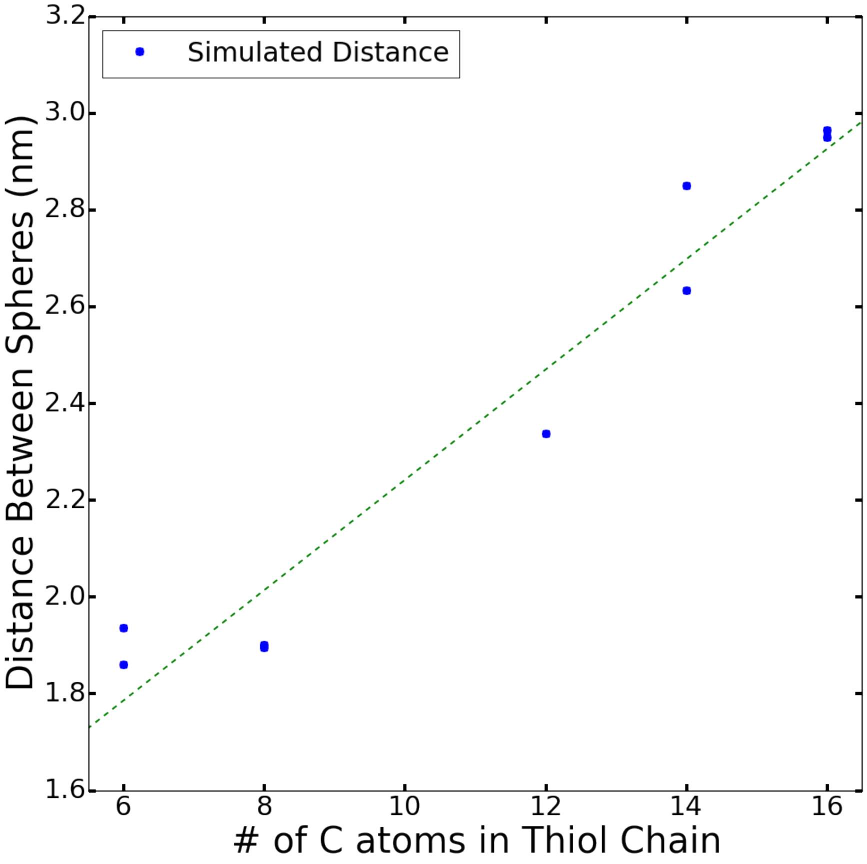

Figure S5: Average distance between first neighbors as calculated using the sequential addition algorithm. Multiple samples were prepared using different thiols (6C,8C,12C,14C,16C). The resulting data points were fit using a simple linear relationship (*green dotted line*). The fit returned a slope of 0.11 nm per CH_2 group, while the length of a single C-C bond in a chain accounts for an additional 0.1256 nm in a trans-trans conformation, indicating that the carbon chains are interpenetrated.

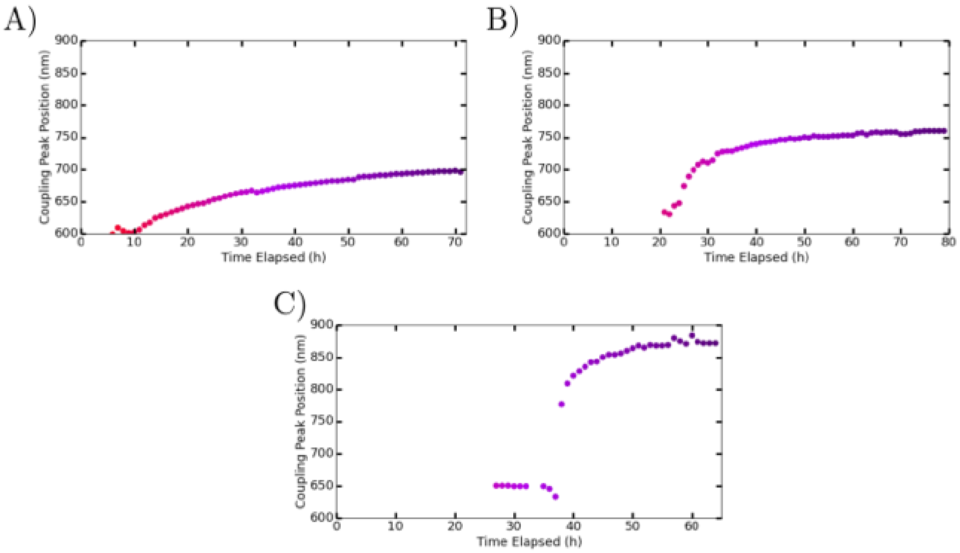

Figure S6: Evolution with time of the position of the coupling plasmon for assemblies prepared using three different thiols. A) Hexadecane thiol, B) Dodecanethiol, and C) Decanethiol. As the thiol becomes shorter, the final position of the coupling plasmon shifts towards longer wavelengths.