Electronic Supplementary Information:

Flow Hydrodynamics-Dependent Assembly of Polymer-Tethered Gold Nanoparticles in Microfluidic Channels

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S1. Calculation for Reynolds number (*Re*):

The *Re* number can be calculated as follows:[1, 2]

$$Re = \frac{Q\text{tot}d}{vA} \qquad \textbf{(Eq. S1)}$$

where Q_{tot} is the total volumetric flow rate, *d* represents the equivalent diameter of the square tube of MFC ($d = 1.0$ mm), *A* is the cross-sectional area of the square tube, and *v* means the kinematic viscosity of water-THF mixtures at 298 K.[3] When R_Q changes from 0.0625 to 4.0 (Q_{tot} varies from 2.125 to 10.0 mL/h), *v* alters from 1.21×10^{-6} to 0.59×10^{-6} m^2/s. Thus, *Re* ranges from 0.62 to 5.99. When R_Q is fixed to 1.0 (*v* is fixed to 0.66×10^{-6} m^2/s), we changed Q_{tot} in the range of 0.5 to 16.0 mL/h. Therefore, *Re* number ranges from 0.27 to 8.61.

S2. Simulation Details:

We used COMSOL Multiphysics 5.4 to simulate the mixing process of THF and water in a three-dimensional model. The CFD simulation process was carried out as follows: First, the three-dimensional geometric model of MFC was painted by software "Solidworks". Then, the mixing process was depicted by a single-phase flow model and a chemical species transport model. Subsequently, the geometric model, the parameters of THF and water were introduced into COMSOL Multiphysics 5.4. The laminar flow model and the diffusion coefficient of the solute was used to describe the diffusive transport. Boundary conditions were set up for conveniently obtaining the solution of CFD simulation. Besides, velocity inlet, pressure outlet, as well as non-slip wall condition were determined. Finally, the geometric model was meshed and the mixing process was calculated.

The numerical simulations were based on the steady-state incompressible Navier-Stokes equation **Eq. S3-S7** in the convective transport and diffusive transport models, as follows:

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \mathbf{u}) = 0 \qquad \textbf{(Eq. S2)}$$

$$\frac{\partial (\rho u)}{\partial t} + \mathrm{div}(\rho u \mathbf{u}) = \mathrm{div}(\mu \,\mathrm{grad}\, u) - \frac{\partial p}{\partial x} + F_x \qquad \textbf{(Eq. S3)}$$

$$\frac{\partial (\rho v)}{\partial t} + \mathrm{div}(\rho v \mathbf{u}) = \mathrm{div}(\mu \,\mathrm{grad}\, v) - \frac{\partial p}{\partial y} + F_y \qquad \textbf{(Eq. S4)}$$

$$\frac{\partial (\rho \omega)}{\partial t} + \mathrm{div}(\rho \omega \mathbf{u}) = \mathrm{div}(\mu \,\mathrm{grad}\, \omega) - \frac{\partial p}{\partial z} + F_z \qquad \textbf{(Eq. S5)}$$

$$\frac{\partial (\rho c_s)}{\partial t} + \mathrm{div}(\rho \mathbf{u} c_s) = \mathrm{div}\left(D_s \mathrm{grad}\,(p c_s)\right) + S_s \qquad \textbf{(Eq. S6)}$$

Where **Eq. S2** is the mass conservation equation, **Eq. S3-S5** are the momentum conservation equations, and **Eq. S6** is the species mass-conservation equation, encompassing the convective transport and the diffusive transport.

S3. Supporting Figures:

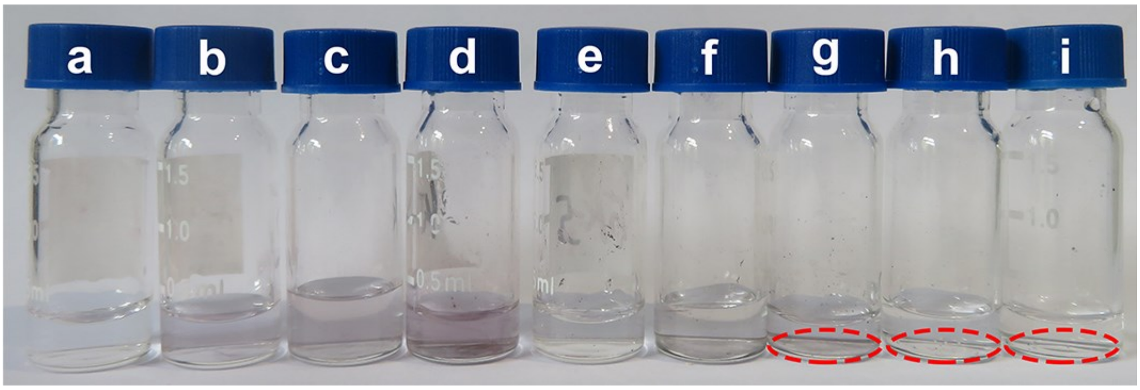

Figure S1. Photographs of the suspensions of 15-AuNP@PS_{5k} assemblies obtained at different R_Q: (a) 0.25; (b) 0.5; (c) 1.0; (d) 2.0; (e) 3.0; (f) 4.0; (g) 5.0; (h) 6.0; (i) 8.0. Red dashed circles in (g-i) indicate the precipitates.

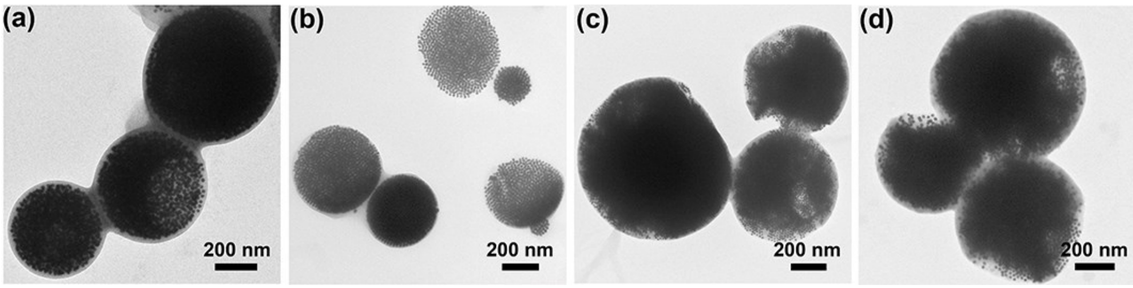

Figure S2. TEM images of 15-AuNP@PS_{5k} assemblies obtained in bulky solution at different volumetric ratios of AuNP@PS THF to water: (a) 0.25; (b) 0.5; (c) 1.0; (d) 2.0.

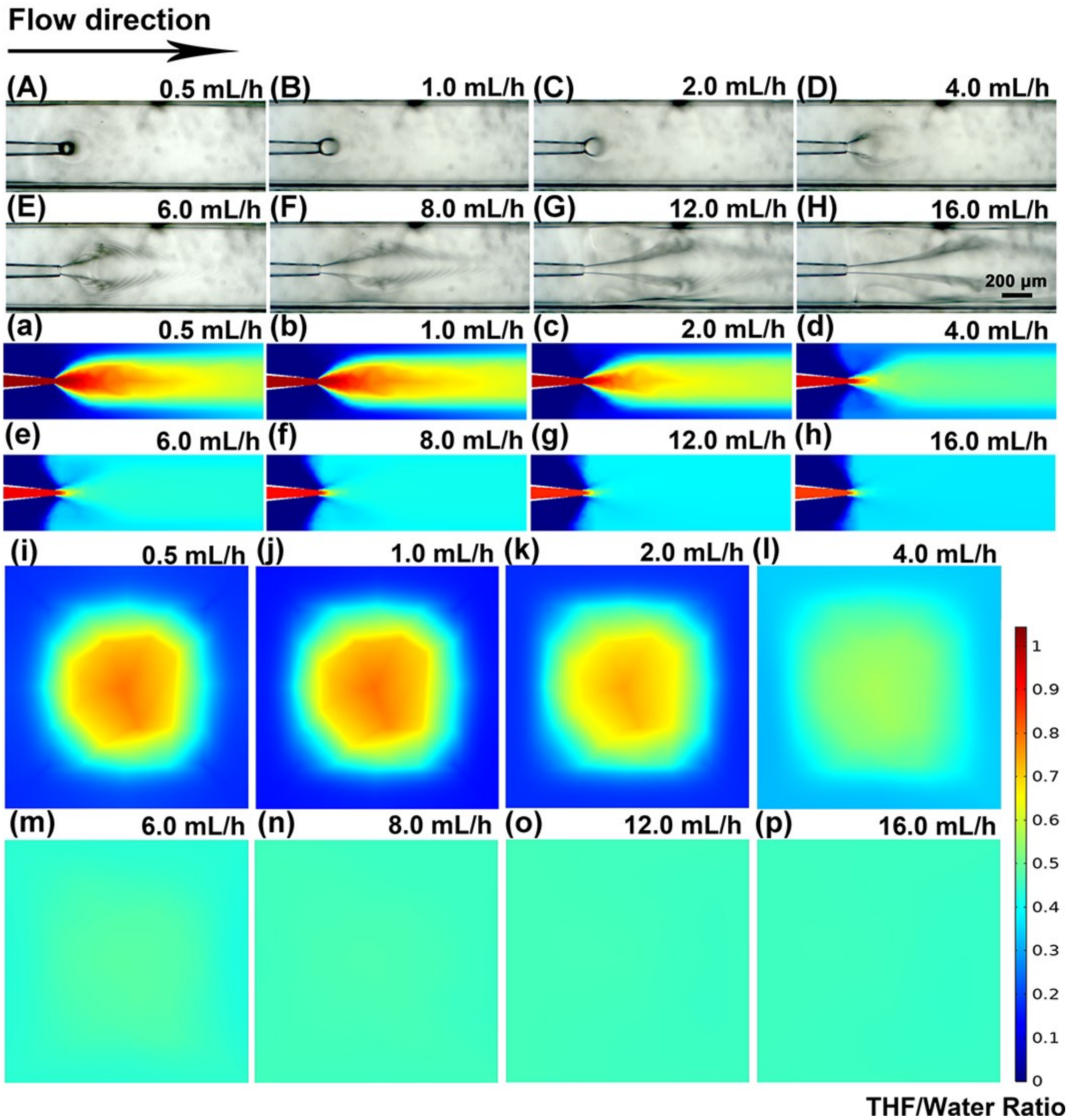

Figure S3. (A-H) Optical microscopy images of solvents mixing patterns; (a-h) simulation results of the concentration distribution of THF in the microfluidic channels; and (i-p) cross-sectional images of simulated concentration distribution of THF in the microfluidic channels at different $Q_{tot,}$ while R_Q was fixed to 1.0. The cross-sectional images were collected 1 mm away from the orifice.

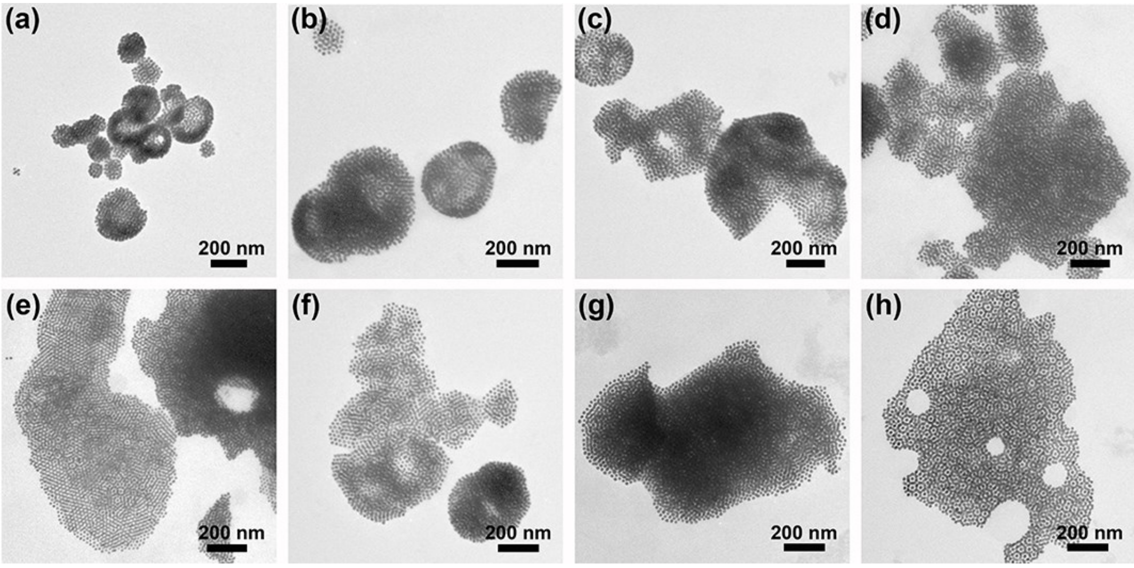

Figure S4. TEM images of the 15-AuNP@PS_{5k} assemblies at different Q_{tot}: (a) 0.5; (b) 1.0; (c) 2.0; (d) 4.0; (e) 6.0; (f) 8.0; (g) 12.0; (h) 16.0 mL/h. R_Q was fixed to 0.25.

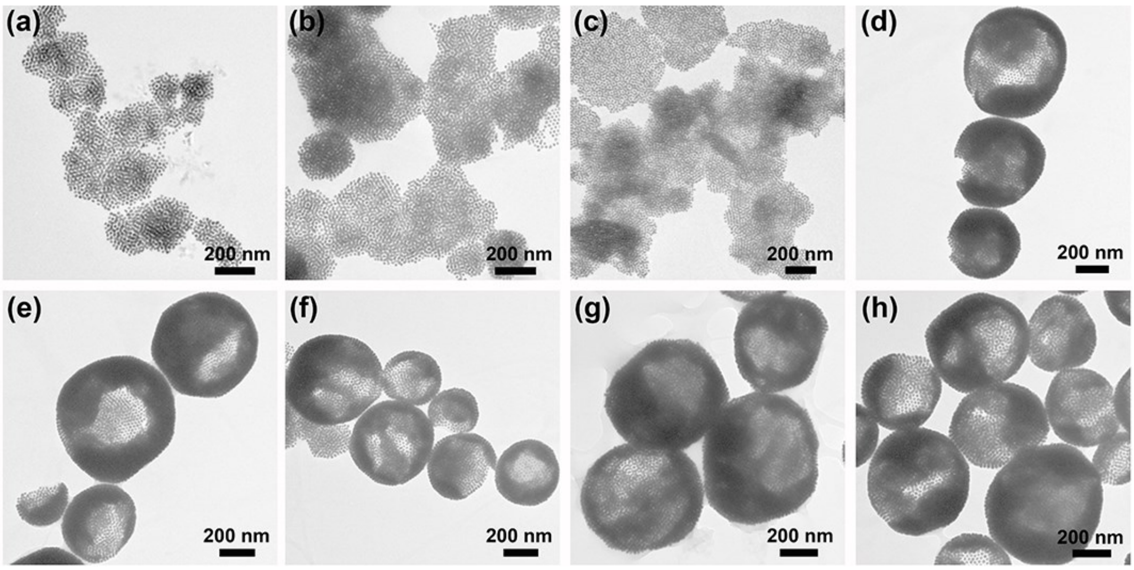

Figure S5. TEM images of the 15-AuNP@PS_{5k} assemblies at different Q_{tot}: (a) 0.5; (b) 1.0; (c) 2.0; (d) 4.0; (e) 6.0; (f) 8.0; (g) 12.0; (h) 16.0 mL/h. R_Q was fixed to 3.0.

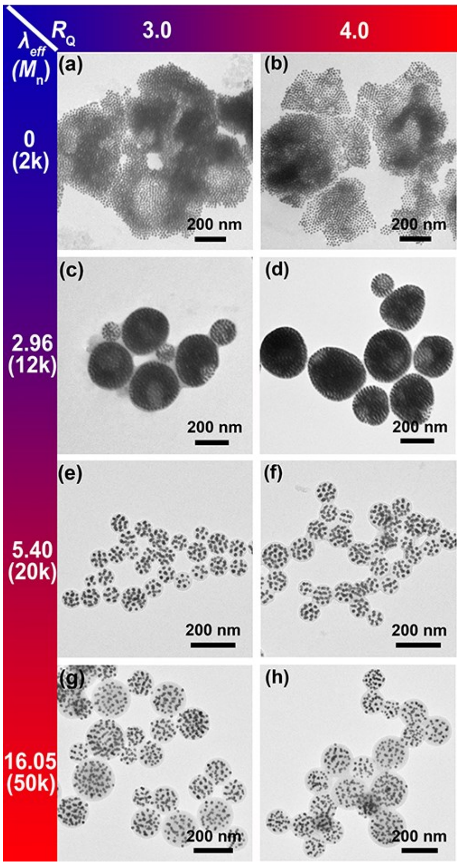

Figure S6. TEM images of 15-AuNP@PS assemblies at high R_Q. Q_{water} was fixed to 2.0 mL/h.

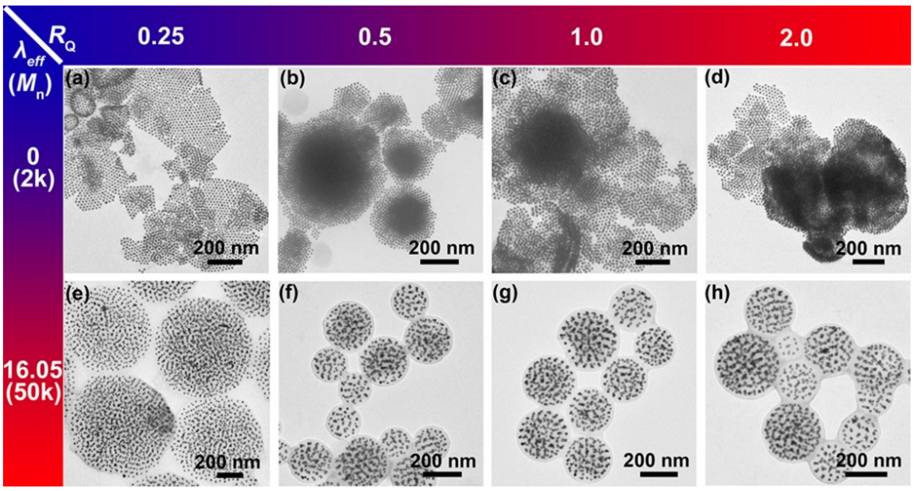

Figure S7. TEM images of 15-AuNP@PS assemblies at different R_Q. Q_{water} was fixed to 2.0 mL/h.

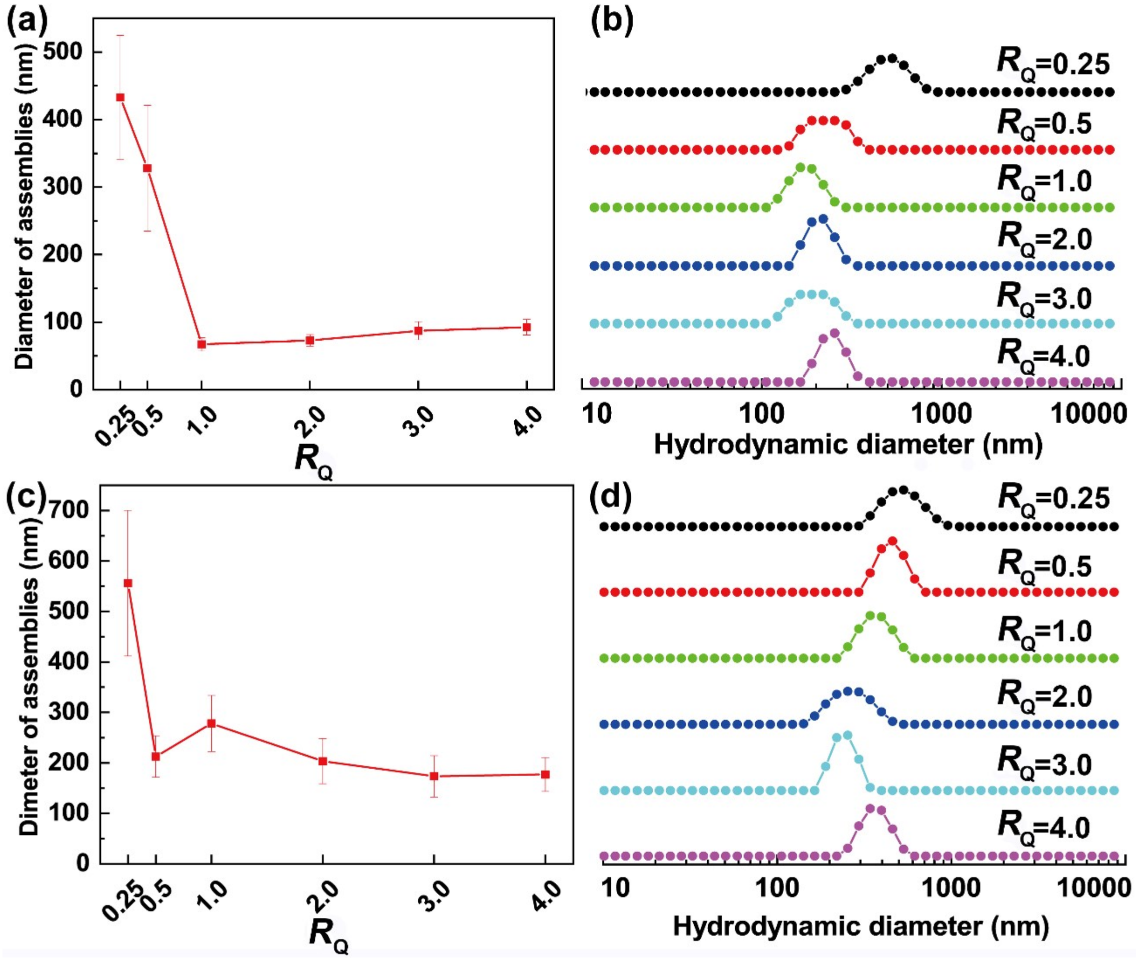

Figure S8. (a) and (c) Plots showing the size of 15-AuNP@PS_{20k} and 15-AuNP@PS_{50k} assemblies at different R_Q. The size of assemblies was obtained by measuring more than 100 assemblies. (b) and (d) DLS profiles showing the hydrodynamic diameters of 15-AuNP@PS_{20k} and 15-AuNP@PS_{50k} assemblies at different R_Q. Q_{water} was fixed to 2.0 mL/h.

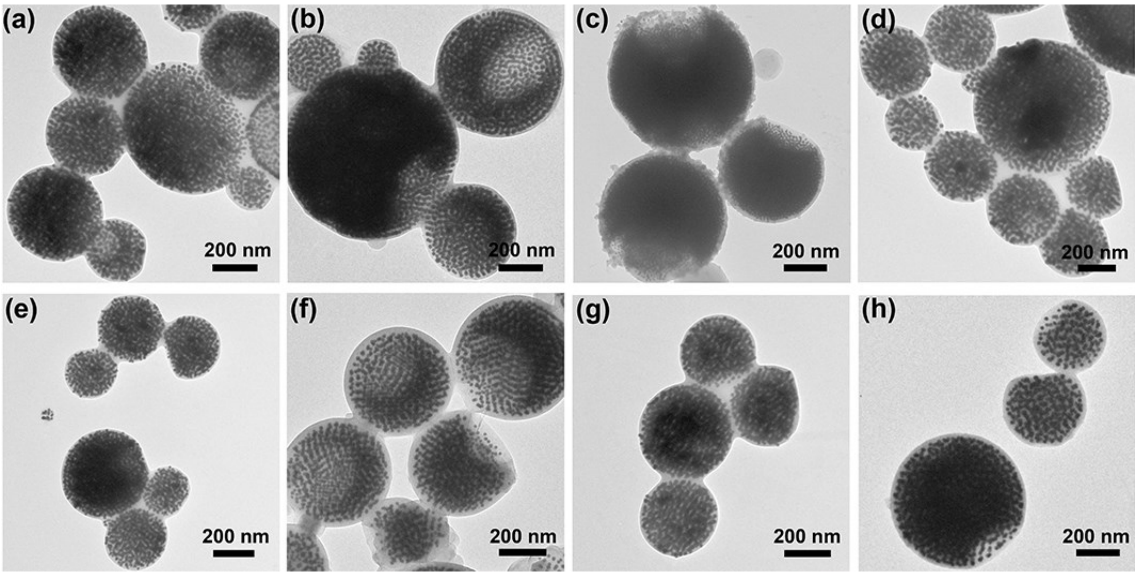

Figure S9. (a-d) TEM images of 15-AuNP@PS_{12k} assemblies and (e-h) 15-AuNP@PS_{20k} assemblies obtained in bulky solution at different volumetric ratios of Au@PS THF to water: (a, e) 0.25; (b, f) 0.5; (c, g) 1.0; (d, h) 2.0.

Supplementary References:

1 T. M. Squires, S. R. Quake, Microfluidics: fluid physics at the nanoliter scale, *Rev. Mod. Phys.*, 2005, **77**, 977-1024.

2 J. M. Lim, A. Swami, L. M. Gilson, S. Chopra, S. Choi, J. Wu, R. Langer, R. Karnik, O. C. Farokhzad, Ultra-high throughput synthesis of nanoparticles with homogeneous size distribution using a coaxial turbulent jet mixer, *ACS Nano*, 2014, **8**, 6056-6065.

3 B. Das, M. N. Roy, D. K. Hazra, Densities and viscosities of the binary aqueous mixtures of tetrahydrofuran and 1,2-dimethoxyethane at 298, 308 and 318 K, *Indian J. Chem. Technol.*, 1994, **1**, 93-97.