Supporting information

Formation of Hybrid Gold Nanoparticle Network Aggregates by Specific Host-Guest Interactions in a Turbulent Flow reactor

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Reagents

Reagents and solvents were purchased from Sigma-Aldrich and used as received without further purification otherwise noted. First-generation poly(propylene imine) dendrimer (PPI) with amino terminal groups was purchased from Symo-Chem.

Synthesis of Ad-PPI

This compound was prepared as reported before.[1] To a solution of DAB-dend-$(NH_2)_4$ (0.2526 g) in dry chloroform (5 mL) was added 1-adamantyl isocyanate (0.6138g). After stirring for 2 h, the homogeneous solution *wa*s precipitated in diethyl ether to remove the excess of isocyanate. Then, the precipitated *wa*s filtered off and dried in vacuo. Ad-PPI was analyzed by ^{1}H-NMR on a Bruker 400 MHz system. ^{1}H-NMR (CDCl$_3$): δ = 1.41 (s, 4H, NCH$_2$CH$_2$CH$_2$CH$_2$N), 1.62-1.65 (m, 32H, NCH$_2$CH$_2$CH$_2$NHCONH and *H*-2), 1.93-2.03 (m, 39H, *H*-4 and *H*-3), 2.35-2.40 (m, 12H, NCH$_2$CH$_2$CH$_2$CH$_2$N and NCH$_2$CH$_2$CH$_2$NHCONH), 3.17 (q, 8H, NCH$_2$CH$_2$CH$_2$NHCONH), 5.07 (s, 4H, CH$_2$NHCONH), 5.76 (t, 4H, CH$_2$NHCONH). The mass analysis was performed using the electrospray ionization with a Voyager DE-RP and a micromass LCT from Waters. Mass: Calcd. For C$_{60}$H$_{100}$N$_{10}$O$_4$: 1025.5. Found 1025.3.
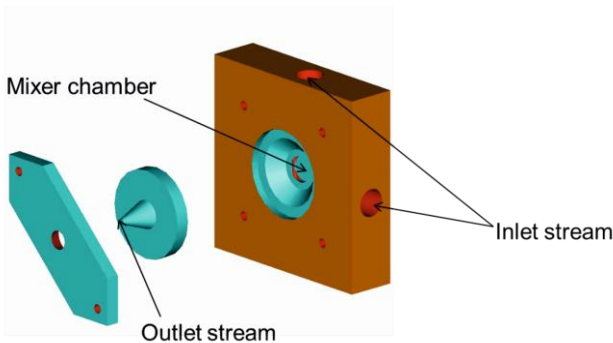
Fig. S1 Schematic of the MIVM.

Table S1 Dimensions of the MIVM.

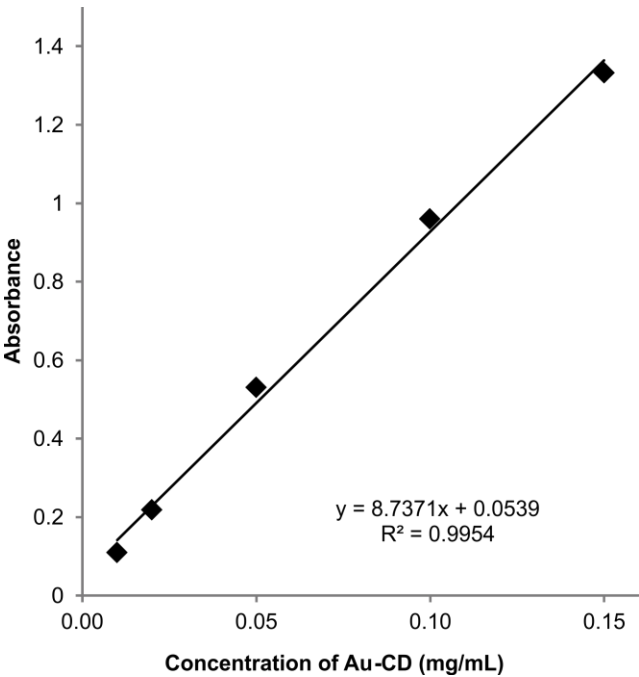|	
Diameter$_{mixer}$ (m)	0.0059
diameter$_{inlet\ stream}$ (m)	0.0011
diameter$_{outlet\ stream}$ (m)	0.0013

$y = 8.7371x + 0.0539$
$R^2 = 0.9954$

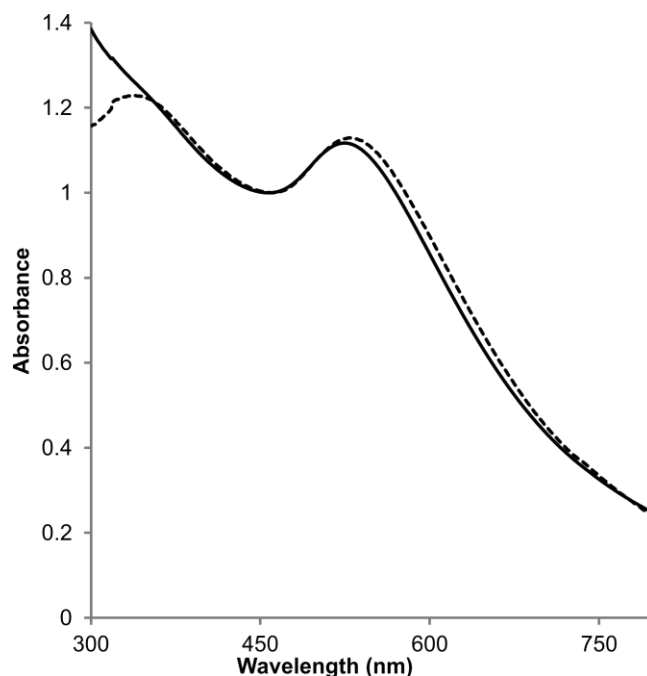**Fig. S2.** UV/vis calibration curve of Au-CD for different concentrations in DI water.

Fig. S3 UV/vis spectra of hybrid gold nanoparticle network aggregates using [CD]:[AdPPI]:[AdPEG]= 1:4:8 and compared with Au-CD nanoparticles (solid line) and aggregates (dashed line).
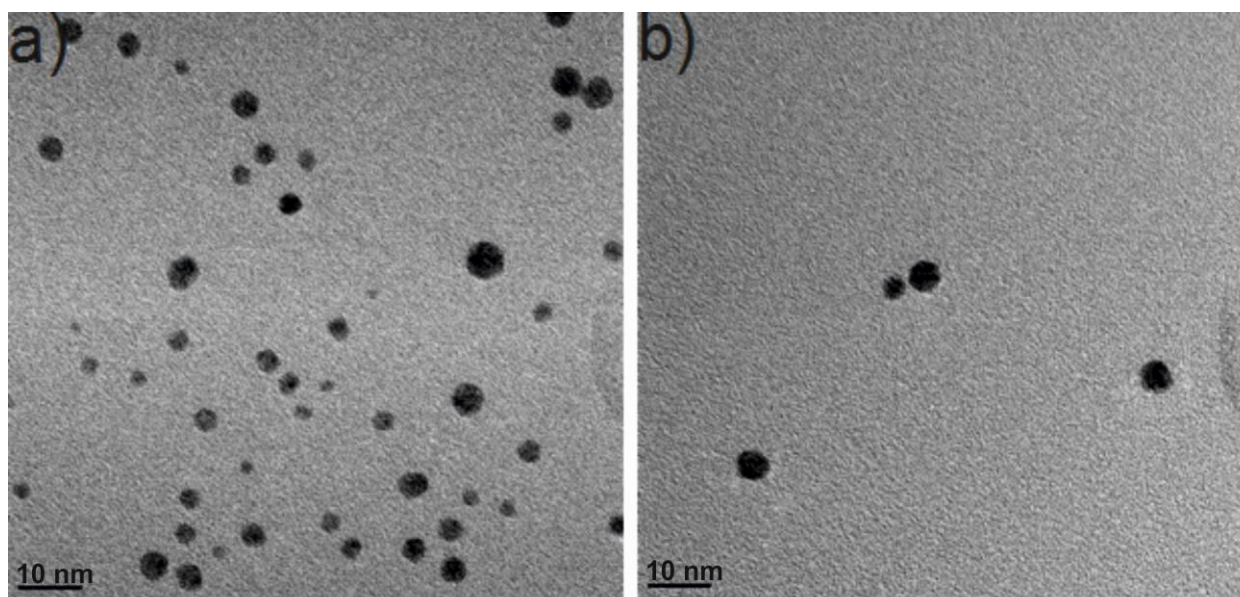

Fig. S4 TEM images a) as-prepared Au-TEG NPs and b) after attempted assembly of Ad dendrimers and Au-TEG NPs in the MIVM. For the MIVM, the initial concentration of Au-TEG in streams 1 and 3 is 0.1 mg/mL, respectively, and for AdPPI in streams 2 and 4 is 18 µM, respectively, using Re=15,000.
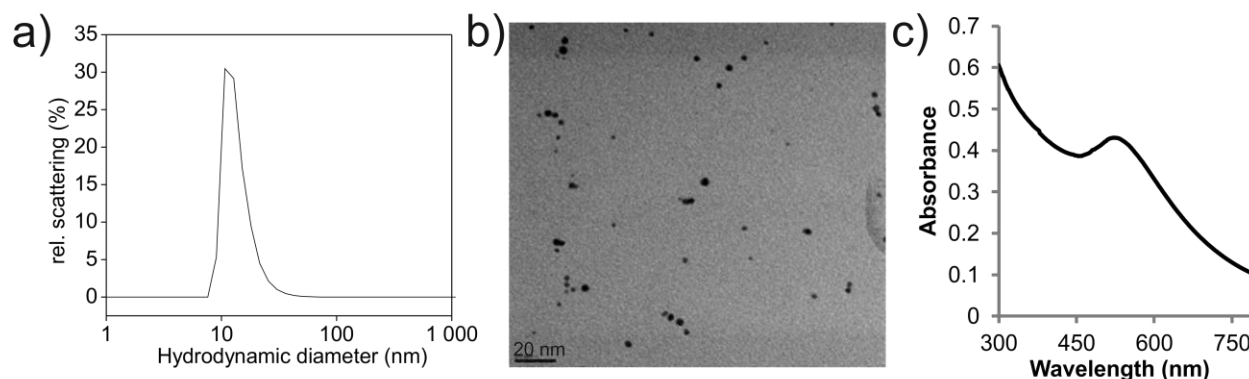
Fig. S5 a) DLS, b) TEM image and c) UV absorbance of Au-CD NPs and free CD upon mixing in the MIVM. For the MIVM, the initial concentration of Au-CD in streams 1 and 3 is 0.1 mg/mL, respectively, and for CD in streams 2 and 4 is 19.8 mM, respectively, using Re=15,000.

The number average diameter and the error bar calculations

For the aggregate size analysis of Figs. 6 and 7, the log values of the number average diameter (d_n) were calculated using the arithmetic mean from all the measurements, and the min and max errors bars were calculated using the 0.159 and 0.841 percentiles (corresponding to +/-1 standard deviation for a Gaussian distribution), respectively, from all the measurements.

Statistical analysis for Fig. 7

First, the $\log_{10}$ of each d_n for each measurement was calculated. Then, the histograms of all these values were plotted as shown in Fig. S6-8. This histograms were assumed to follow a log-normal distribution. Then, the arithmetic mean of the $\log_{10}$ number diameter was calculated for each run. Finally, the t-test was performed using the previous values for all the cases in Fig. 7 as shown in Table S2-4. We used the two-tailed, two-sample t-test with unequal variance (heteroscedastic).
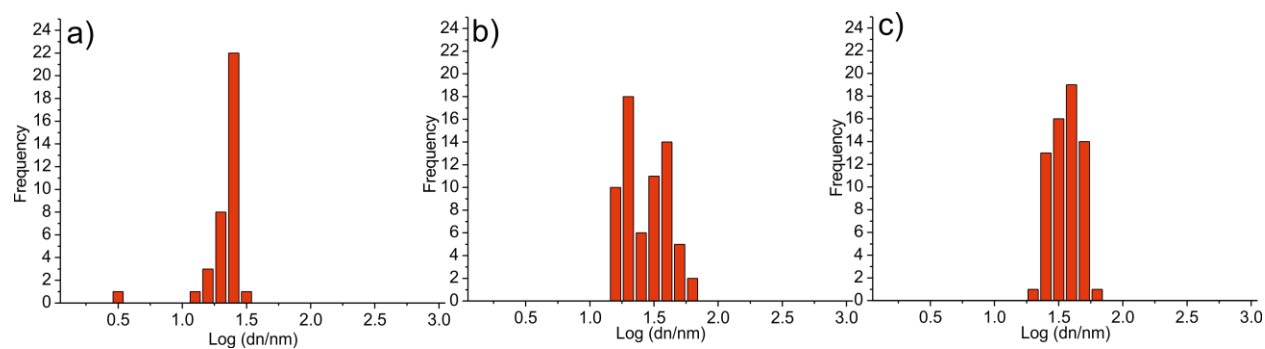
Fig. S6 Histograms of network aggregates obtained at a [CD]:[AdPPI]:[AdPEG] ratio of 1:4:8 from DLS a) by hand, b) under laminar flow and c) under turbulent flow

Table S2. t-test for network aggregates obtained at a [CD]:[AdPPI]:[AdPEG] ratio of 1:4:8

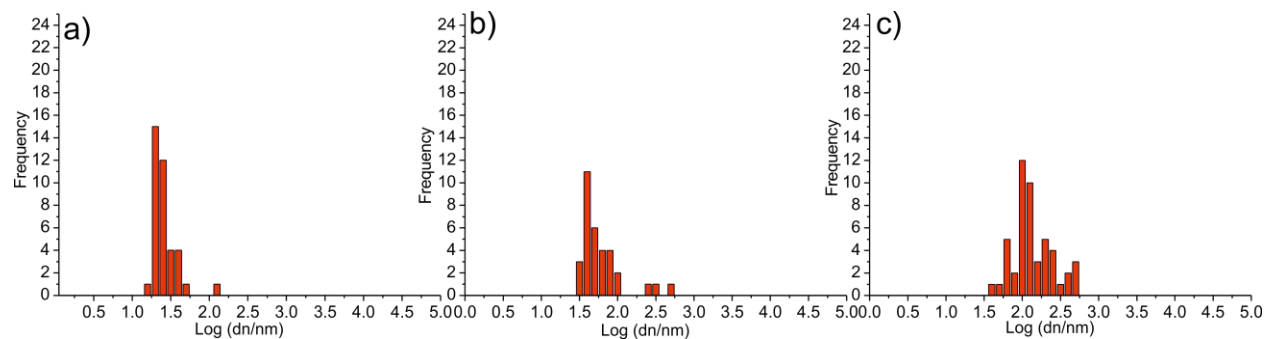| Cases	p
Turbulent vs Laminar	0.11
Turbulent vs By hand	2.97×10^{-6}
Laminar vs By hand	0.07

Fig. S7 Histograms of network aggregates obtained at a [CD]:[AdPPI]:[AdPEG] ratio of 1:5:10 from DLS a) by hand, b) under laminar flow and c) under turbulent flow

Table S3. t-test for network aggregates obtained at a [CD]:[AdPPI]:[AdPEG] ratio of 1:5:10

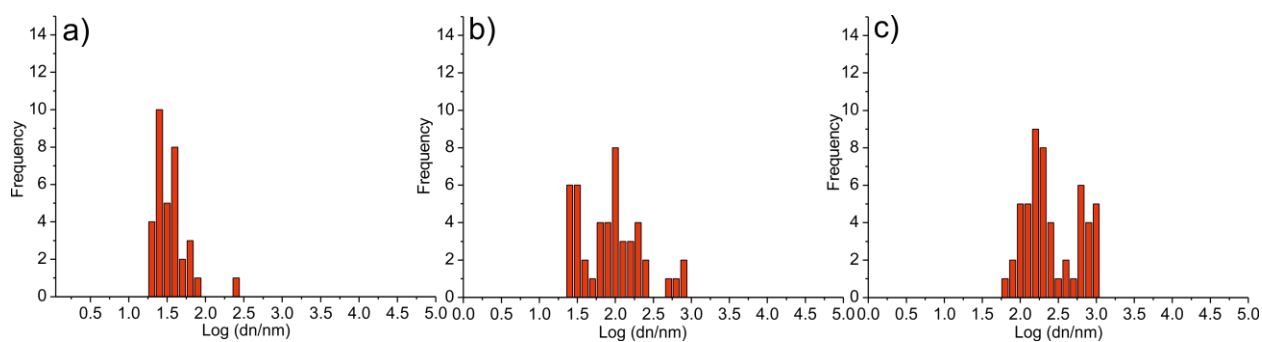| Cases	p
Turbulent vs Laminar	0.012
Turbulent vs By hand	2.21×10^{-7}
Laminar vs By hand	5.83×10^{-3}

Fig. S8 Histograms of network aggregates obtained at a [CD]:[AdPPI]:[AdPEG] ratio of 1:6:12 from DLS a) by hand, b) under laminar flow and c) under turbulent flow

Table S4. t-test for network aggregates obtained at a [CD]:[AdPPI]:[AdPEG] ratio of 1:6:12

Cases	p
Turbulent vs Laminar	9.95×10^{-4}
Turbulent vs By hand	2.63×10^{-7}
Laminar vs By hand	2.37×10^{-2}

References

1.   M. Baars, A. J. Karlsson, V. Sorokin, B. F. W. de Waal and E. W. Meijer, *Angew. Chem. Int. Ed.* 2000, **39**, 4262.