Supplementary Information of the Manuscript

Bowl- and porous sphere-shaped supramolecular assemblies and their application as templates for confined assembly of gold nanoparticles

Fang-Ming Xu, Jian-Ping Xu*, Li-Ping Lv, Jian Ji*.

Department of Polymer Science, Key Laboratory of Macromolecule Synthesis and Functionalization of Minster of Education, Zhejiang University, Hangzhou, 310027, China. E-mail: jianping_xu@zju.edu.cn; jijian@zju.edu.cn,Tel/Fax. (+)86-571-87953729

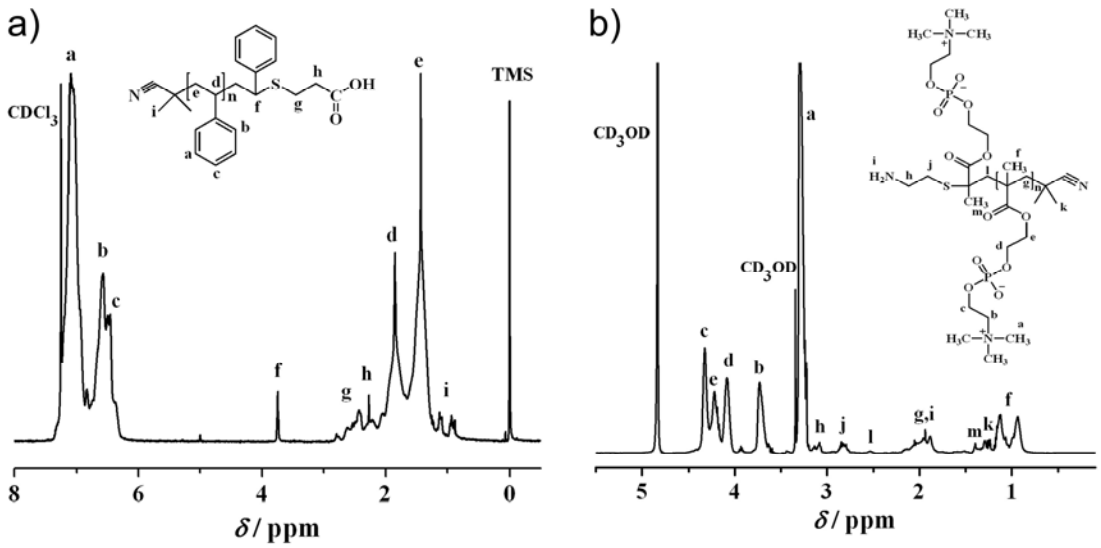

Figure S1. ^{1}H-NMR spectra of polymers: a) PSt-COOH, b) PMPC-NH_2

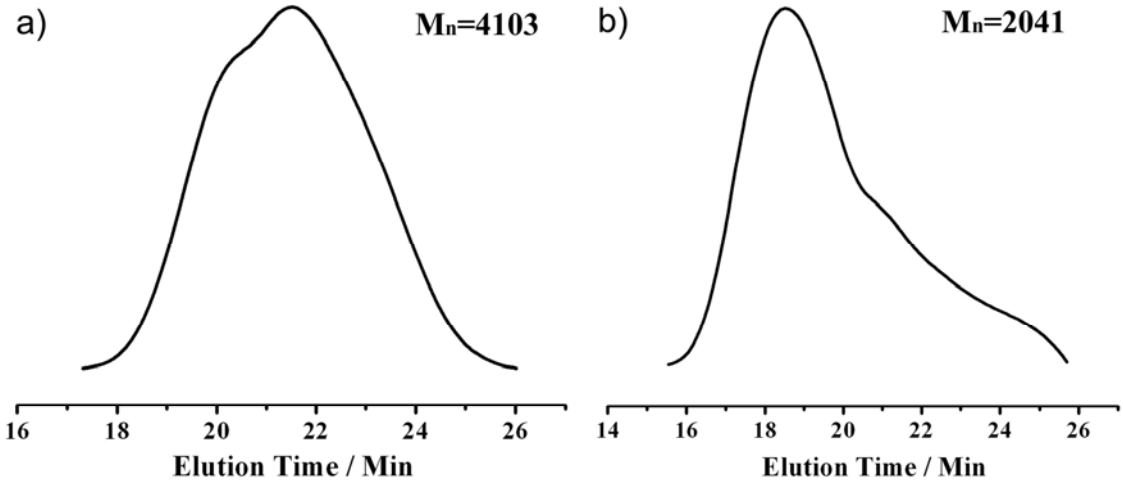

Figure S2. GPC characterization of polymers: a) PSt-COOH, b) PMPC-NH_2

The number averaged molecule of PMPC-NH_2 and PSt-COOH were 2041 and 4103, the polydispersity indices are 3.06 and 1.73，respectively.

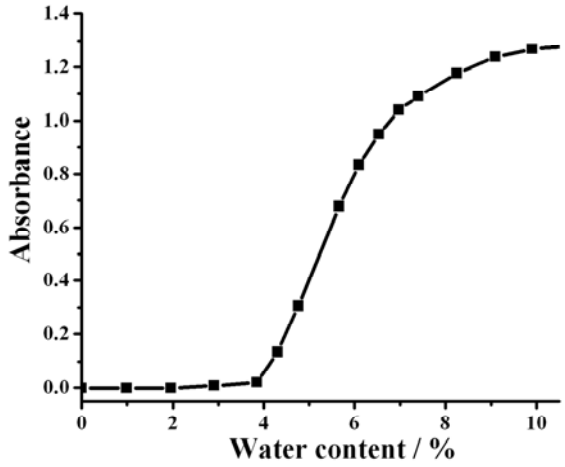

Figure S3. Light absorbance at 500 nm as a function of added water content in the supramolecuar assembling system. The initial polymer concentration was 7 C_0, molar ratio of the two blocks was 1/1, THF content in solvent mixture was 50 %.

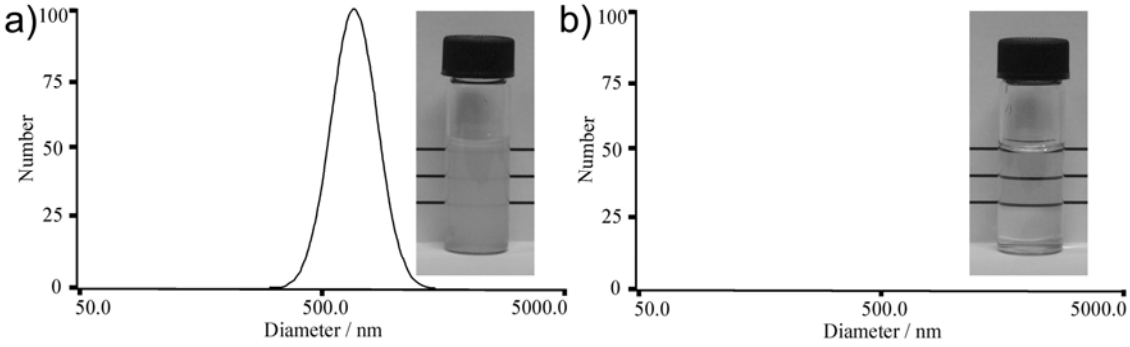

Figure S4. a) Number average diameter of the solution in which the pure water was used to induce the assembly of polymers. b) Number average diameter of the solution in which 0.5 M NaCl solution was used. The insert shows digital photos of the two solutions. The left one is induced by pure water; the right one is induced by 0.5 M NaCl. (the initial polymer concentration was 30 C_0, molar ratio of the two blocks was 1/1, THF content in solvent mixture was 50% for the two samples)

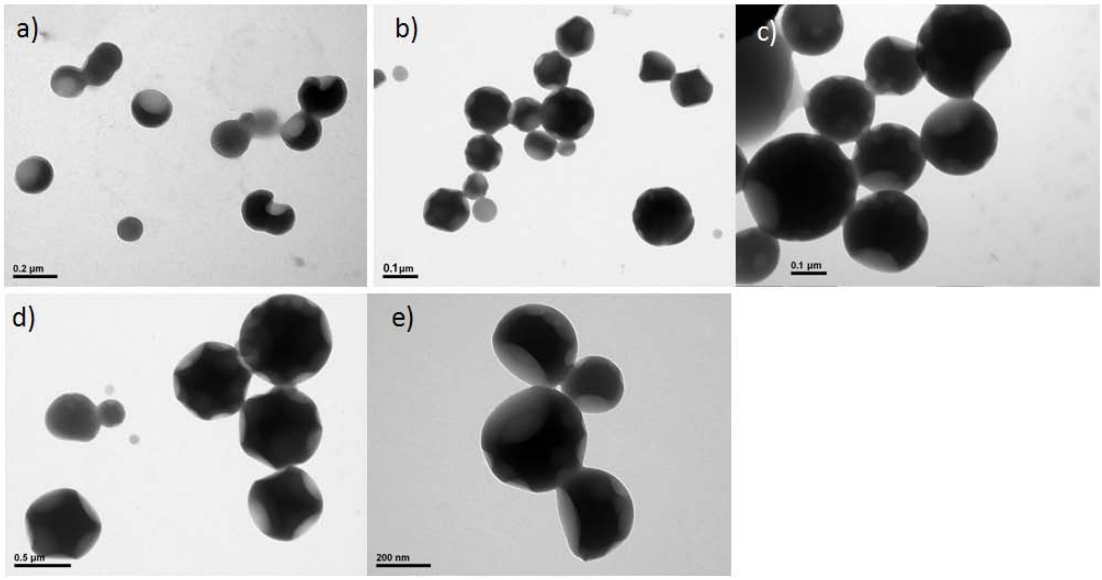

Figure S5. TEM images of intermediate stages of assemblies formed before the molar ratio of PMPC-NH_2 to PSt-COOH reaches 1/1 (PMPC-NH_2/PSt-COOH): (a) 1/6, (b) 1/5, (c) 1/4, (d) 1/3, (e) 1/1.5 (the initial concentration of PSt-COOH was kept constant at 0.014 mg/ml for all samples).

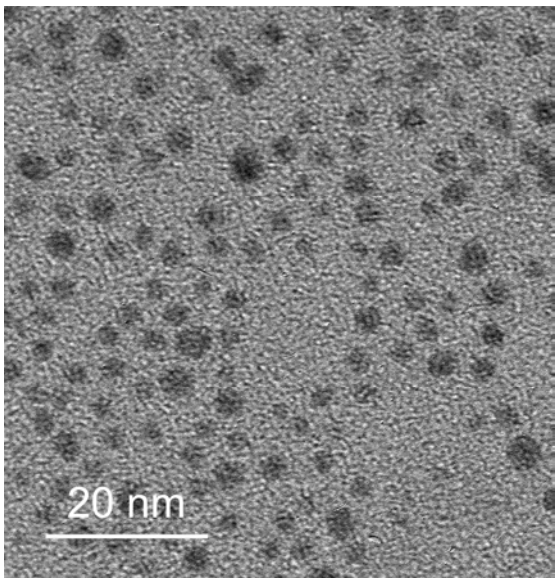

Figure S6. TEM image of the gold nanoparticles.

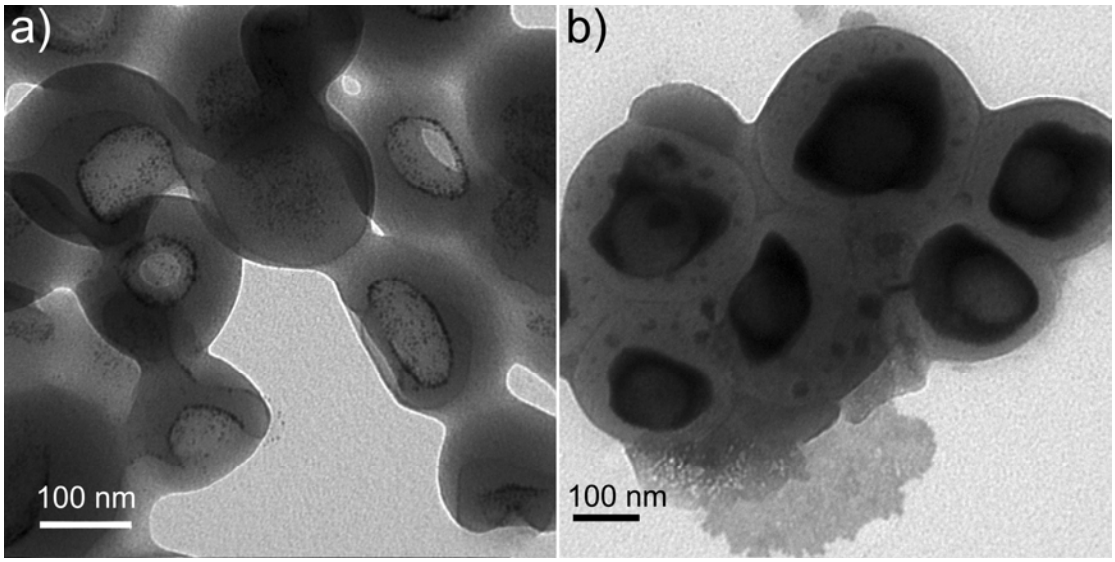

Figure S7. TEM images of gold nanopartocle-polymer composite particles. a) the molar ratio of PSt-COOH to PMPC-NH_2 was 1/1, the mass ratio of gold nanoparticles to polystyrene was 1/20, the overall mass ratio of gold nanoparticles to polymer was 1/30, b) molar ratio of the two blocks PSt-COOH to PMPC-NH_2 was 1/2, the mass ratio of gold nanoparticles to polystyrene was 1/2, the overall mass ratio of gold nanoparticles to polymer was 1/4 (the initial concentration of PSt-COOH was 0.014 mg/ml and THF content in mixed solvent was 50 % for the two samples).

Table S1. The yield for the preparation of nanoparticles and molar ratio of the polymers found in nanoparticles

	calculated value	20 C_0	30 C_0	40 C_0	60 C_0
Yield[a]	……	95 %	98%,	98%	95 %
C[b]	76.47 %,	75.72 %,	75.28 %,	76.70 %,	75.53 %,
N	1.57 %,	1.56 %,	1.54 %,	1.58 %,	1.56 %,
H	7.66 %	7.62%	7.64%	7.68%	7.65%

a) The yield for the preparation of nanoparticles is determined by the mass ratio of freeze dried nanoparticles to the mass of initially added polymer.

b) The molar ratio of the polymers found in nanoparticles was determined by elemental analysis of freeze dried samples.

The initial molar ratio of the two blocks was 1/1, THF content in mixed solvent was 50 % for all samples. C_0 denotes a concentration unit, which is composed of 0.005 mg/mL PSt-COOH and 0.0025 mg/ml PMPC-NH_2. The aqueous solution of all samples was dialysised against pure water to remove organic solvent, the cut-off molecular weight of our dialysis bag is 3500, and this value is higher than Mn of PMPC. The unbounded PMPC should have been removed from the solution.