

Supporting Information

**Thiol-ene Photocrosslinked Hybrid Vesicles Based on the co-assembly of
POSS and Poly(ether amine) (PEA)**

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Experimental Section

Materials

Poly(propylene glycol) diglycidyl ether (PPO-DE, Sigma-Aldrich, $M_n=640$ g/mol), Jeff amine L100 (Hunstman, $M_n=1000$ g/mol), Acryloyl chloride (AC, Bangcheng Chemical Reagent, Shanghai, China), Photoinitiator I-907 (Tronly, Changzhou, China), Nile Red (NR, TCI Chemical Reagent), Rose Bengal (RB, Sinopharm Chemical Reagent) were all used without further purification. Octamercaptopropyl polyhedral oligomeric silsesquioxane (POSS-SH) and grafted poly(ether amine) (gPEA: $M_n=1.9 \times 10^4$ g/mol, $M_w/M_n=2.3$) was synthesized in our lab according to previous report^{1,2}. Other chemicals are of analytical grade except as noted.

Synthesis of acrylated poly(ether amine) (A-PEA)

Acryloyl chloride (AC, 75 mmol, 6.1 mL) was added dropwise to a solution of gPEA (15 mmol, in terms of its structural units), and triethylamine (TEA, 75 mmol, 10.4 mL) in chloroform (50 mL) and stirred in an ice bath to keep the reaction temperature at 0-5 °C for 3 h, then at room temperature for another 12 h. The mixture

obtained was washed by deionized water for several times and the organic layer was evaporated by rotary to remove solvent to get A-PEA and the yield is about 83 %.

Preparation of POSS@PEA Vesicles

The mixture of 10 mg POSS-SH and 100 mg A-PEA was dissolved in 1 mL tetrahydrofuran (THF), and then trace amount of photoinitiator I-907 was added. The solution was left to equilibrate at 30 °C while ultrapure water was added very slowly to the solution (10 mL of water per hour to 1 mL of polymer solution). The polymer solution was gently stirred during the water addition until 1 h, and then equilibrated at 30 °C for 24 h. The solution obtained was exposed under an ultraviolet LED lamp (Uvata) at 365 nm with intensity about 8.4 mW/cm² for 1h to make the vesicles crosslinked, and then the solution with crosslinked POSS@PEA-1/10 vesicles was dialyzed against ultrapure water for 24 h to remove THF using cellulose membrane with a molecular weight cutoff of 3500, and crosslinked POSS@PEA-1/10 vesicles aqueous solution was obtained. Crosslinked POSS@PEA-1/30 and POSS@PEA-1/50 assemblies were prepared similarly, while A-PEA and POSS-SH in feed was 30:1 and 50:1 (w/w), respectively.

Measurement

¹H NMR spectra was acquired with Mercury Plus spectrometer (Varian, Inc., USA) operating at 400 MHz by using CDCl₃ as solvent and TMS as an internal standard at room temperature.

Infrared absorption spectra (IR) measurements were carried out with Spectrum 100 Fourier transformation infrared absorption spectrometer (Perkin Elmer, Inc., USA). The samples were prepared by dropping the polymer solution onto a KBr film and dried below an infrared lamp.

The DLS measurements were performed in the crosslinked POSS@PEA vesicles solution using a ZS90 Zetasizer Nano ZS instrument (Malvern Instruments Ltd., U.K.) equipped with a multi- τ digital time correlation and a 4 mW He-Ne laser ($\lambda=633$ nm)

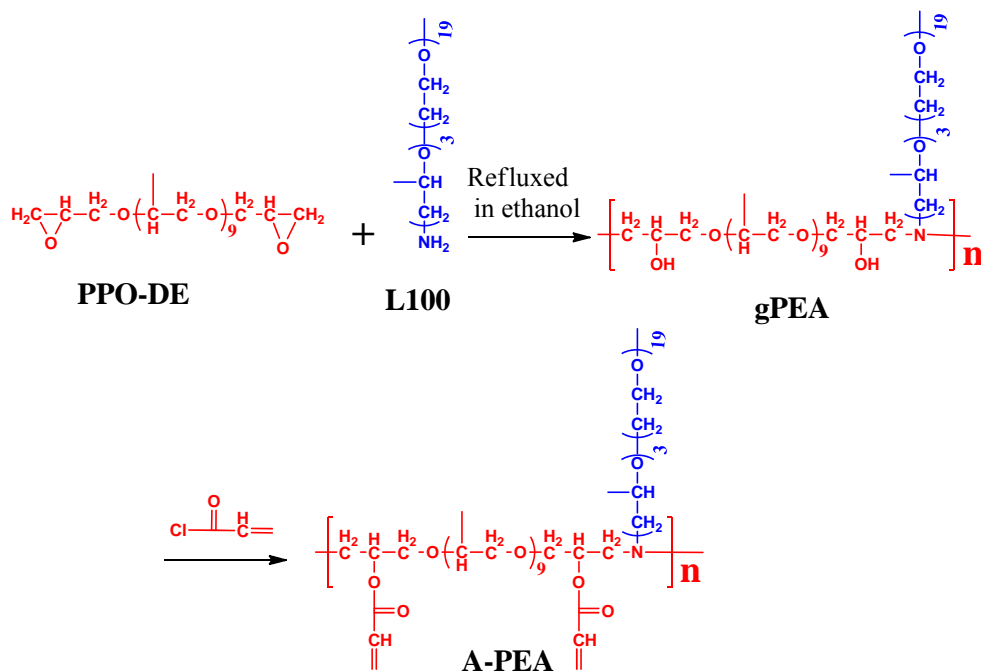
at an angle of 90° . Regularized Laplace inversion (CONTIN algorithm) was applied to analyze the obtained autocorrelation functions. The crosslinked POSS@PEA vesicles solution was diluted by 10 times before measurement.

The TEM images were obtained using a JEM-2100 (JEOL Ltd., Japan) transmission electron microscope operated at an acceleration voltage of 200 kV. The sample was prepared by dropping the crosslinked POSS@PEA vesicles solution onto copper grids coated with a thin polymer film while the excess solution was removed by filter paper, and then dried at 30°C for 24h. No staining treatment was performed for the measurement.

The SEM images were obtained using a JSM-7401F (JEOL Ltd., Japan) field emission scanning electron microscope operated at an acceleration voltage of 1 kV or 5 kV. The samples were prepared by dropping the crosslinked POSS@PEA vesicles solution onto silica wafers, and dried at 30°C for 24h. Then the samples were sputter coated with gold to minimize charging.

The UV-visible spectra of the dyes before and after addition of POSS@PEA-1/10 vesicles were carried out with a UV-2550 spectrophotometer (Shimadzu, Japan). The solutions were equilibrated for 15 min before measurement, and the concentration of the dyes and POSS@PEA-1/10 vesicles is 0.1 mg/mL and 1 mg/mL, respectively.

Results



Scheme S1. The total synthesis process of A-PEA.

As there is hydroxyl group in the backbone of gPEA, which can be further functionalized by some other chemicals easily, here we attempt to modify gPEA with acryloyl chloride to obtain acrylated poly(ether amine) (A-PEA), and the synthesis process is also shown in Scheme S1. The successful functionalization of gPEA with acryloyl chloride was confirmed by ^1H NMR and FT-IR (Figure S1). In comparison with gPEA, the existence of acryl groups in A-PEA is proved by signals at ~ 6.43 , ~ 6.12 , and ~ 5.96 ppm in ^1H NMR spectrum of A-PEA, and the structure of A-PEA can be also supported by new peak at 1720cm^{-1} assigned to C=O stretching vibration absorption in FT-IR spectrum of A-PEA.

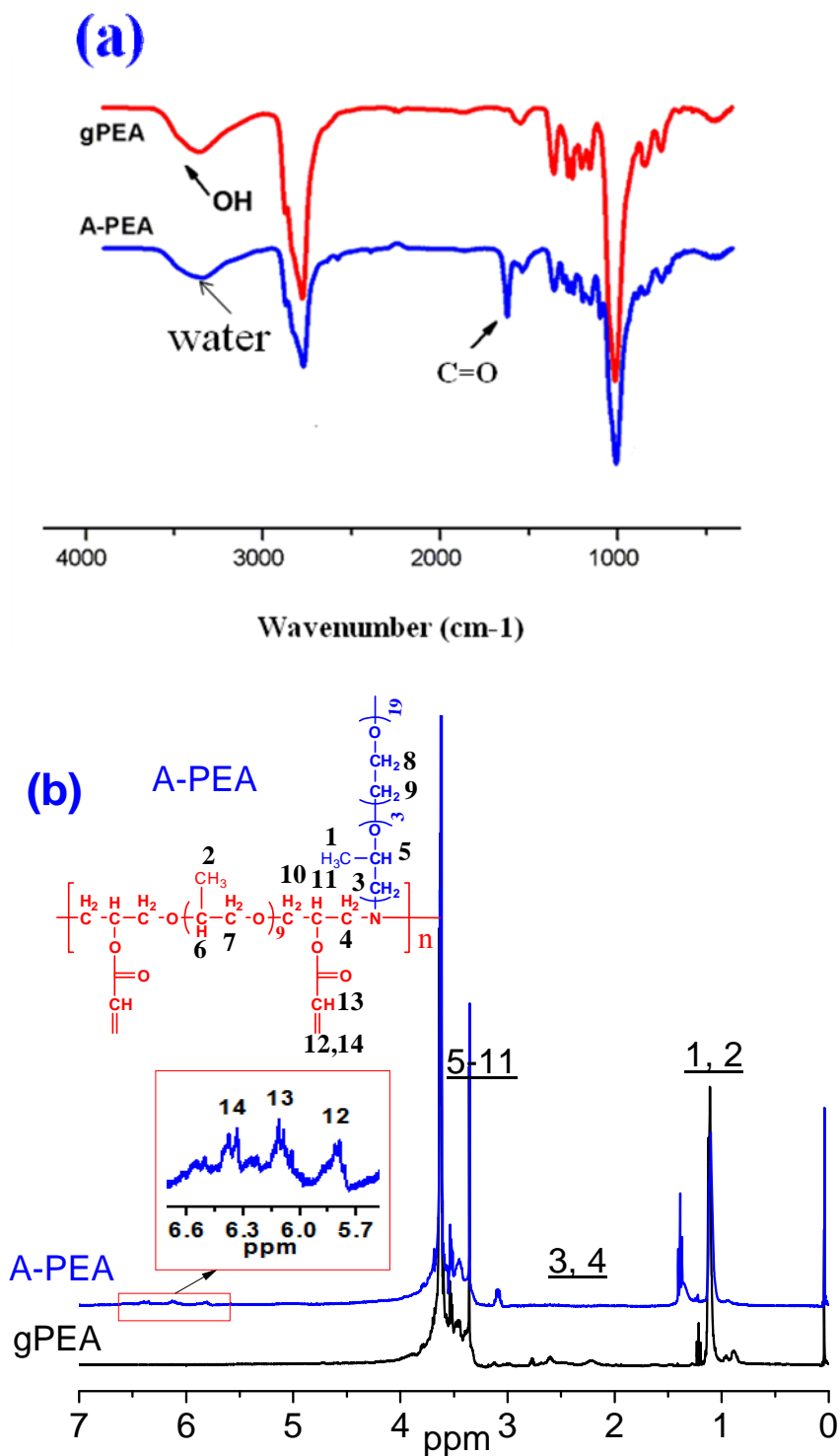


Figure S1. (a) FT-IR spectra of gPEA and A-PEA, (b) ^1H NMR of gPEA and A-PEA using CDCl_3 as solvent

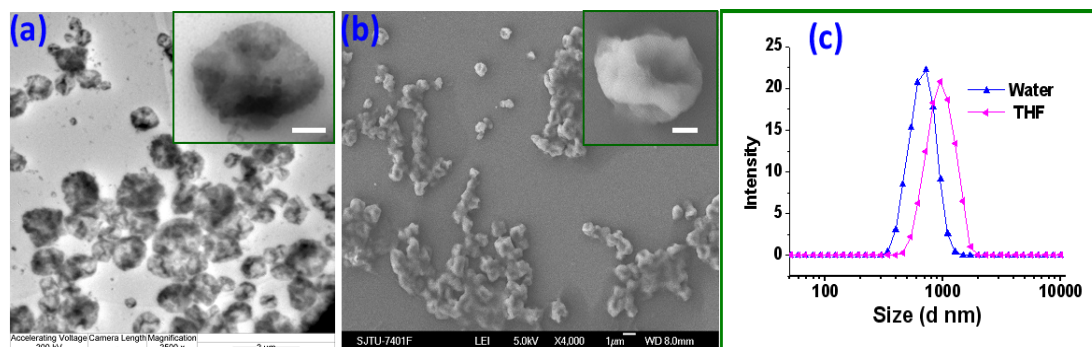


Figure S2. (a) TEM image of the vesicles formed by POSS@PEA-1/10 in water. The scale bar of the inset image indicates 200 nm. (b) SEM image of the vesicles formed by POSS@PEA-1/10 in THF. The scale bar of the inset image indicates 200 nm. (c) The size distribution of the vesicles formed by POSS@PEA-1/10 in water and THF, respectively.

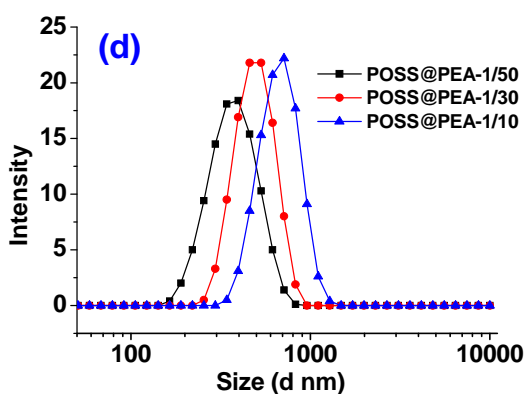
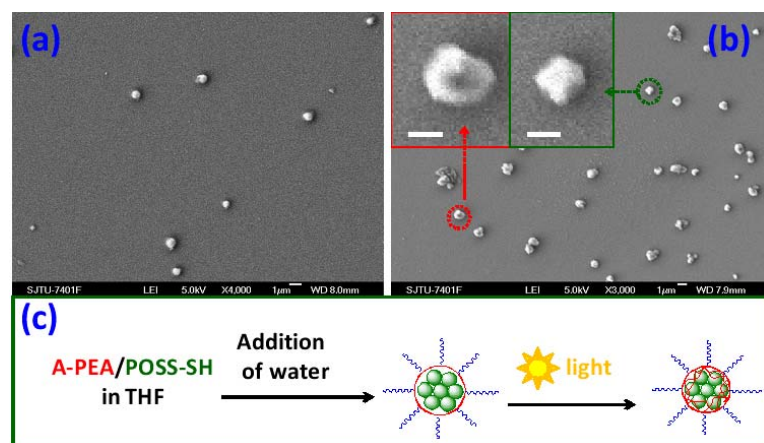


Figure S3. (a) SEM image of the particles formed by POSS@PEA-1/50 in water. (b) SEM image of the vesicles and particles formed by POSS@PEA-1/30 in water. The scale bars indicate 500 nm. (c) The proposed mechanism of formation of POSS@PEA particles in aqueous solution. (d) The size distribution of the vesicles and particles formed by POSS@PEA.

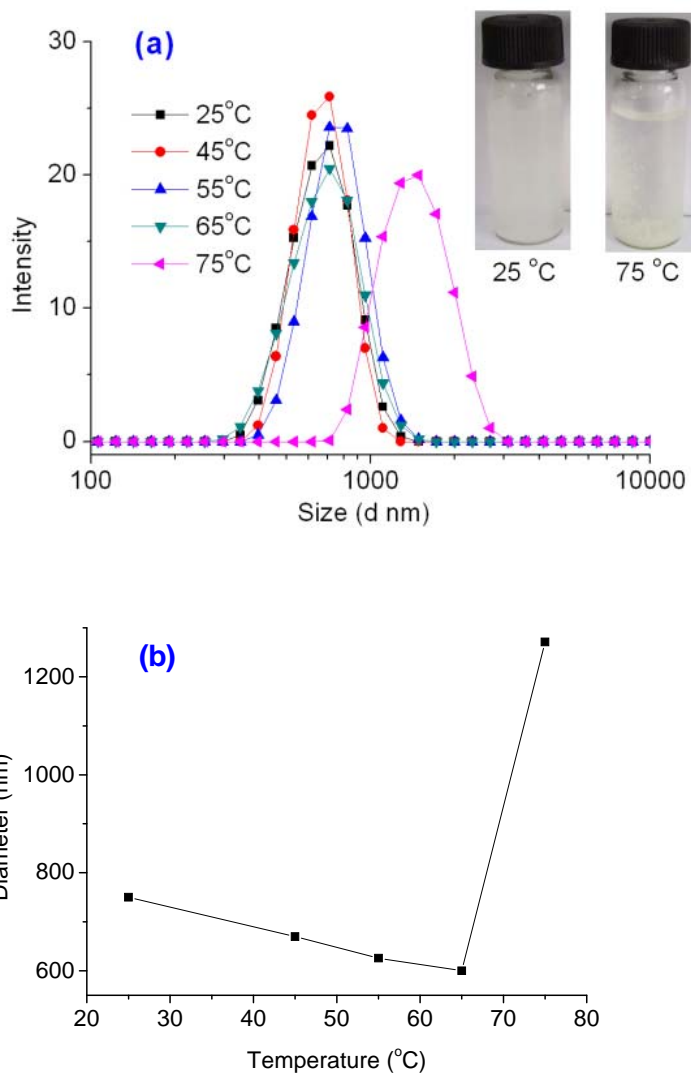


Figure S4. (a) The size distribution of the vesicles formed by POSS@PEA-1/10 at different temperatures in citrate buffer solution (pH= 7.4). (b) Z-average diameters of POSS@PEA-1/10 vesicles at different temperatures obtained by DLS.

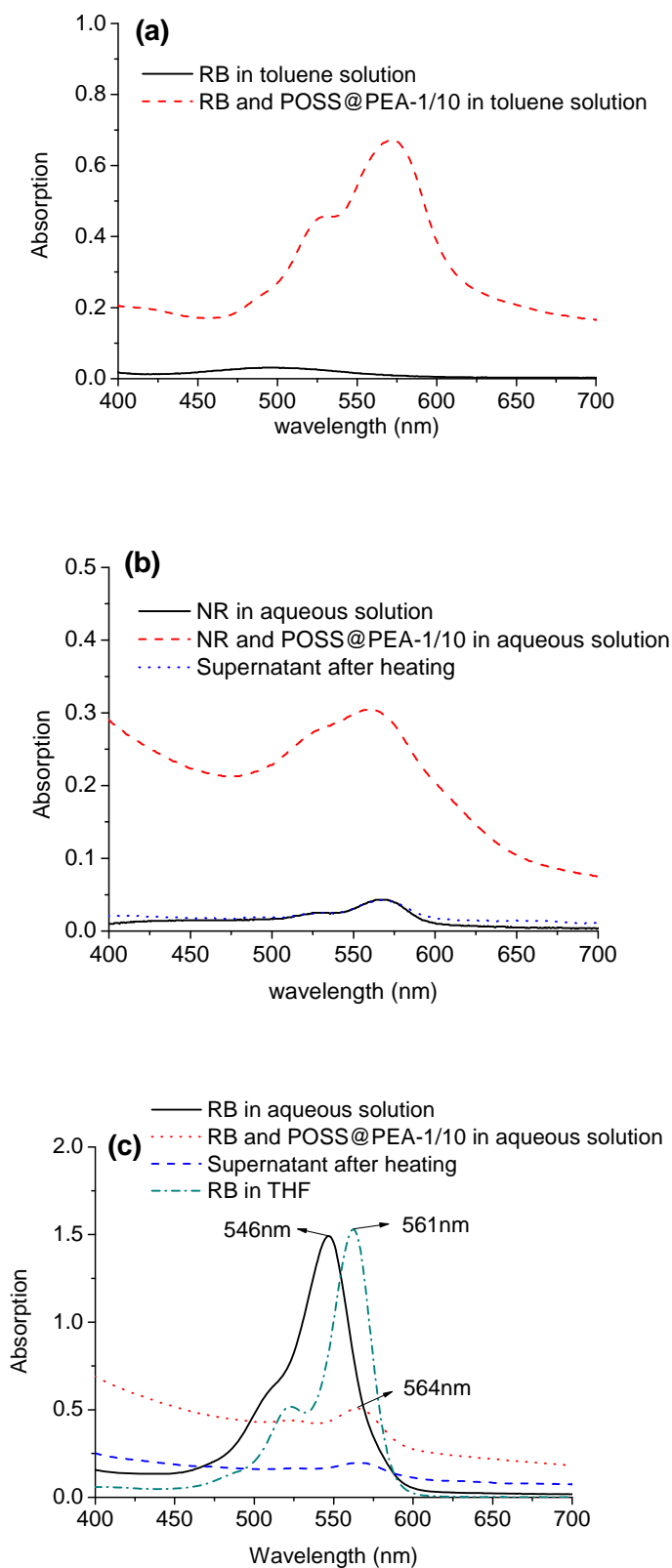


Figure S5. (a) UV-vis spectra of Rose Bengal in toluene before and after

addition of POSS@PEA-1/10 vesicles at room temperature. (b) UV-vis spectra of Nile Red in water before and after addition of POSS@PEA-1/10 vesicles at room temperature as well as in supernatant after heating to high temperature (75 °C). (c) UV-vis spectra of Rose Bengal in water before and after addition of POSS@PEA-1/10 vesicles at room temperature as well as in supernatant after heating to high temperature (75 °C). The concentration of dyes and POSS@PEA-1/10 vesicles is 0.1 mg/mL and 1 mg/mL, respectively.

Reference

1. H. Lin, X. Wan, X. Jiang, Q. Wang and J. Yin, *Adv Funct Mater*, 2011, **21**, 2960–2967
2. Y. R. Ren, X. S. Jiang, R. Liu and J. Yin, *J Polym Sci Pol Chem*, 2009, **47**, 6353-6361.