Electronic Supplementary Material (ESI) for Polymer Chemistry.

One-pot approach to synthesize hyperbranched poly(*thiol* ether amine) (hPtEA) through sequential “thiol‐ene” and “epoxy‐amine” click reaction

Jing Yu, Zhilong Su, Hongjie Xu, Xiaodong Ma, Jie Yin, Xuesong Jiang*

School of Chemistry& Chemical Engineering, State Key Laboratory for Metal
Matrix Composite Materials, Shanghai Jiao Tong University,

Shanghai 200240, People’s Republic of China.

Tel.: +86-21-54743268; Fax: +86-21-54747445. E-mail: ponygle@sjtu. edu. cn

1. Kinetics of thiol-ene photo-click reaction.

The plot of the conversion ratio of the thiol-ene click reaction *vs.* reaction time was obtained according to the intensity of hydrogen which belongs to the ene recorded by ^{1}H-NMR spectra. Strong decrease of the intensity was founded when the solution was exposed to the UV light for 10 min (conversion ratio of the thiol-ene click reaction is about 46%), indicating that the photo-click reaction could occur at room temperature after removing oxygen. After 2 hours, the peaks almost disappeared completely with the conversion ratio up to 100%, revealing that the ene was reacted entirely.

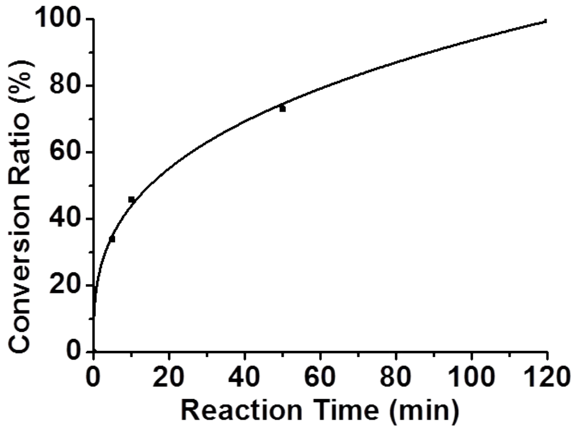

Figure S1. Plot of the conversion ratio of the thiol-ene click reaction *vs.* reaction time according to the intensity of hydrogen which belongs to the ene.

As shown in **Figure S2a**, a new peak ascribed to split product of I2959 would appear at 4.07 ppm (tri) after UV-irradiation for 120 min. Meanwhile, according to **Figure S2b**, the signal at 4.05 ppm (multi) which was ascribed to peak 3 was decreasing along UV-irradiation and disappeared finally after UV-irradiation for 120 min.

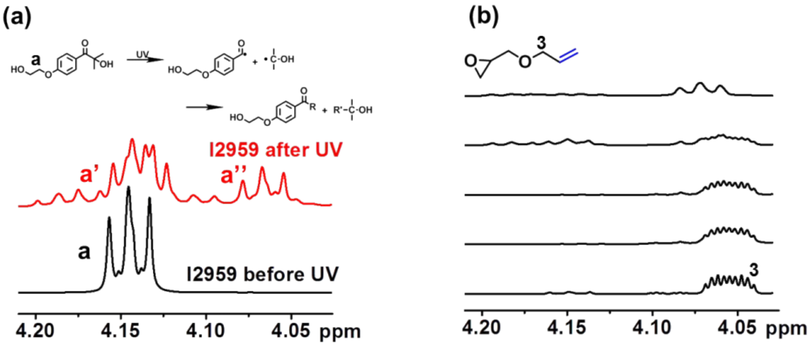

Figure S2. (a) ^{1}H-NMR spectra of I2959 before and after irradiation. (b) Enlarged view of ^{1}H-NMR spectra from 4.03 to 4.21 ppm.

2. Kinetics of epoxy-amine click reaction.

The plot of the conversion ratio of the epoxy-amine click reaction *vs.* reaction time was obtained according to the intensity of hydrogen which was beside the epoxy recorded by ^{1}H-NMR spectra. Strong decrease of the intensity was founded when the solution was heated for 40 min (conversion ratio of the thiol-ene click reaction is about 53%), indicating that the click reaction has occured under nitrogen atmosphere. After 4 hours, the peaks almost broaden completely with the conversion ratio up to 95%, resulting to the formation of ^{1}H-NMR spectra which belongs to typical macromolecules, revealing that hPtEA has been prepared successfully.

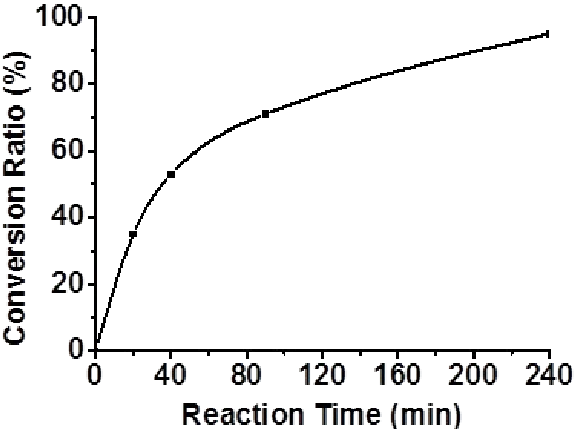

Figure S3. Plot of the conversion ratio of the epoxy-amine click reaction *vs.*reaction time according to the intensity of hydrogen beside the epoxy.

3. FT-IR spectra of hPtEA, hPtEA-AN and SA-hPtEA-AN

In comparison to hPtEA, the new peaks at 725 cm^{-1} and 1342 cm^{-1} that appear in the spectrum of hPtEA-AN should be attributed to anthracene moieties and the decrease of peak at 3383 cm^{-1} could be explained by the fact that reaction of amino groups with epoxy made the content of NH reduced , indicating the introduction of anthracene moieties. Besides, the further decrease of peak at 3383 cm^{-1} should be attributed to the reaction of amino groups with anhydride while generation of new peak at 1732 cm^{-1} belongs to the stretching vibration of C=O bond in the FT-IR spectrum of SA-hPtEA-AN, which both can indicate SA-hPtEA-AN has been successfully prepared.

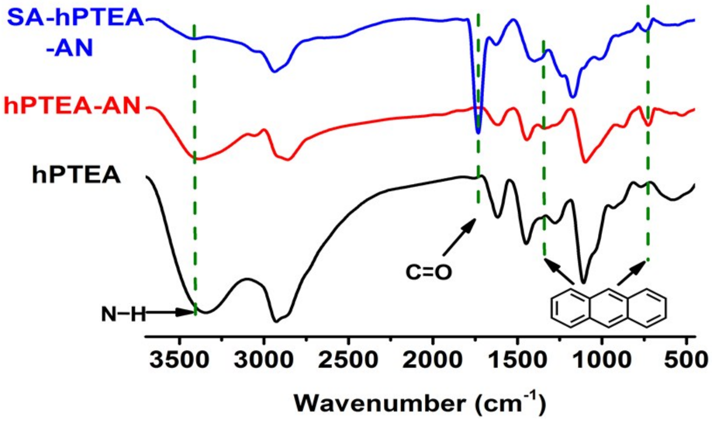

Figure S4. FT-IR spectra of hPtEA, hPtEA-AN and SA-hPtEA-AN.

4. Kinetics of photodimerization of anthracene for SA-hPtEA–AN microspheres

The kinetics of photodimerization of SA-hPtEA–AN was investigated by UV-vis spectra. The UV-vis spectra of SA-hPtEA–AN aqueous solution (0.6 mg/mL, 10 mL) which was exposed to the UV light for different irradiation time were recorded under the condition that the solution was diluted 10 times with DMF, a good solvent for SA-hPtEA–AN, to make the un-crosslinking moieties dissolved well. Strong scattering was founded when the solution was irradiated for 1min (degree of photodimerization of anthracene is about 50%), indicating that the tightly crosslinking system could not be destroyed by organic solvents. To make the microspheres even more stable, we choose 5min as irradiation time (degree of photodimerization of anthracene >75%).

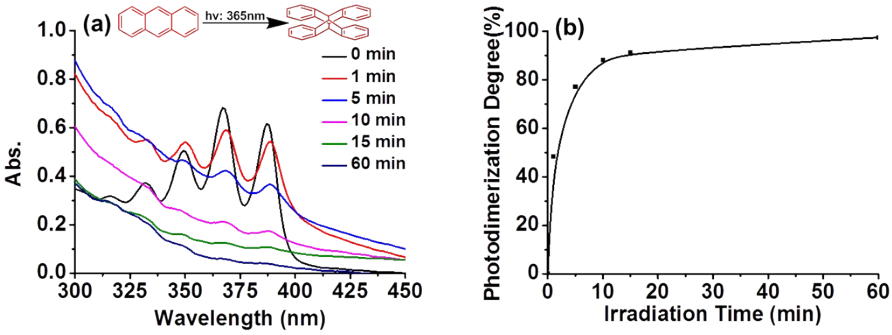

Figure S5. (a) UV-vis spectra of kinetics of photodimerization of anthracene for SA-hPtEA–AN microspheres. (b) plot of degree of photodimerization of anthracene moieties *vs.* irradiation time.

5. Proposed mechanism of the encapsulation and controlled released of MO

The strong fluorescence of SA-hPtEA–AN microgel was significantly weakened even to quenched after encapsulation of MO molecules, but was enhanced after release of MO. This phenomenon can be ascribed to the emission at 416 nm not being entirely absorbed by MO molecules after release of MO. As a result, the fluorescence of SA-hPtEA–AN microgel was recovered.

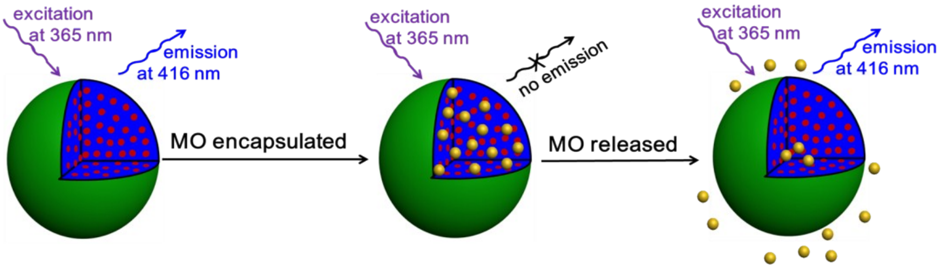

Figure S6. Proposed mechanism of the encapsulation and controlled released of MO.