Complex Aggregation of TPPS and PEG-*b***-P4VP in Confined Space**

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Figure S1. Hydrodynamic diameter distribution of blank emulsion: a) and polymer-containing emulsions with different polymer concentrations in the water pool: b) 4.7 mg/mL; c) 14 mg/mL; d) 23.3 mg/mL. Measurements were performed at the scattering angle of 90° at ambient temperature.



Figure S2. Full UV-vis spectra of TPPS-containing emulsions with different porphyrin concentrations in the water pool. Measurements were performed 12 h after the samples were prepared at ambient temperature.



Figure S3. Hydrodynamic diameter distribution of TPPS-containing emulsions with different porphyrin concentrations. Measurements were performed at the scattering angle of 90° at ambient temperature.

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Figure S4. AFM images of dry blank emulsion a) and TPPS-containing emulsion droplets with different porphyrin concentrations in the water pool: b) $C_{TPPS}=0.204$ mmol/L; c) $C_{TPPS}=3.06$ mmol/L.



Figure S5. Full UV-vis spectra of different complex emulsions. Measurements were performed 12 h after the samples were prepared at ambient temperature.



Figure S6. Hydrodynamic diameter distribution of the complex aggregates of the broken complex emulsions at different time: a) E_{s204} ; b) E_{h3060} . Measurements were performed at the scattering angle of 90° at ambient temperature.



Figure S7. AFM images of TPPS-containing emulsion samples after emulsion breakage a) E_{204} ; b) E_{3060} ;

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Figure S8. Hydrodynamic diameter distribution of complex aggregates of the broken complex emulsions at different time intervals after the water pool was adjusted to basic: a) E_{s204} ; b) E_{h3060} . Measurements were performed at the scattering angle of 90° at ambient temperature.



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Figure S9. AFM images of neat polymer aggregates obtained at different time intervals after breaking the polymer-containing emulsion a) immediately; b) after 10mins; c) after 30mins; d) after 1h. The polymer concentration in the water pool is 4.7 mg/mL.