

Supplementary Information

Synthesis of thermo-sensitive polymer with super narrow molecular weight distribution: PET-RAFT polymerization of N-isopropyl acrylamide mediated by cross-linked zinc porphyrins with high active site loadings

*Fanfan Li, Yi Yu, Hanyu Lv, Guiting Cai and Yanwu Zhang**

School of Chemical Engineering, Zhengzhou University, 100# Science Road,

Zhengzhou, 450001, P.R. China

*Corresponding author.

*E-mail address: zhangyanwu@zzu.edu.cn

Experimental section

Materials

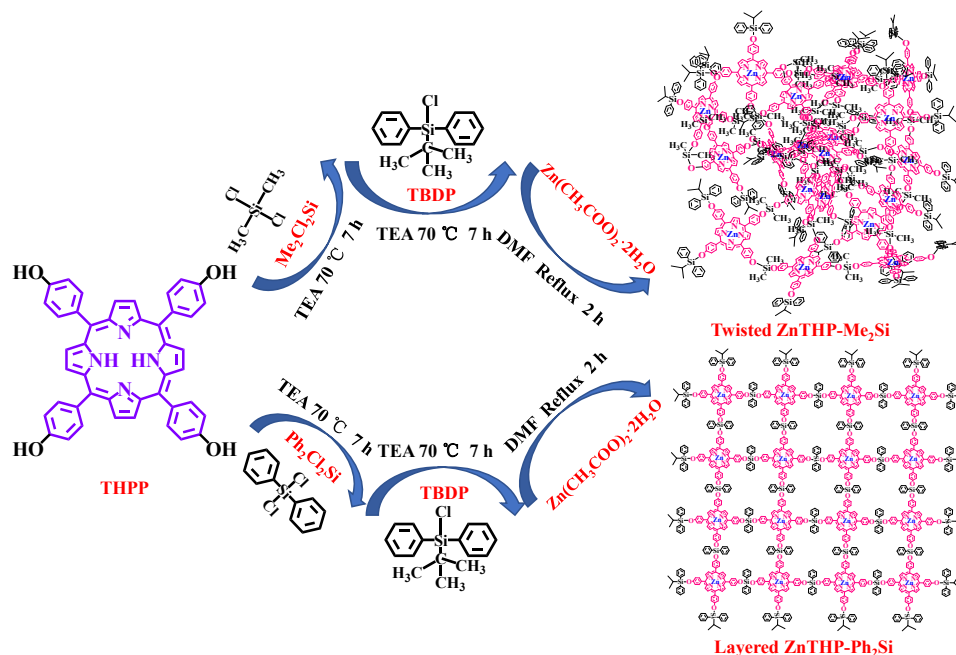
5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin (THPP, 98%, J&K), N,N-dimethylformamide (DMF, 99.9%, Sigma-Aldrich), Triethylamine (TEA, 99%, Sigma-Aldrich), dichlorodimethylsilane (Me_2SiCl_2 , 99%, J&K), dichlorodiphenylsilane (Ph_2SiCl_2 , 98%, J&K), tert-butyldiphenylchlorosilane (TBDP, 98%, J&K), zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99%, Sigma-Aldrich), methanol (99.5%, Sigma-Aldrich), N-isopropyl acrylamide (NIPAm, 99%, J&K), dimethyl sulfoxide (DMSO, 99%, Sigma-Aldrich), 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, made in laboratory), tetrahydrofuran (THF, 99%, Sigma-Aldrich), ether

(99%, Sigma-Aldrich), dichloromethane (99%, Sigma-Aldrich).

Characterization

Fourier transform-infrared (FT-IR) spectra were recorded on an FT-IR Nicole spectrometer over the range of 4000-500 cm^{-1} . UV-Vis absorption spectra were acquired on Shimadzu UV-2450 spectrometer. Fluorescence spectra were recorded on F-4500 Fluorescence spectrophotometer. ^1H NMR spectroscopy was conducted on a Bruker AV 400 spectrometer with $\text{Si}(\text{CH}_3)_4$ as an internal standard. Atomic absorption spectrophotometer (AAS) measurements were carried out with TAS-990 F. Thermogravimetric analysis (TGA) from 30-900 $^\circ\text{C}$ was carried out on a SDT Q600 in nitrogen atmosphere using a 10 $^\circ\text{C}/\text{min}$ ramp without equilibration delay. The transmission electron microscopy (TEM) was observed by using Tecnai G20 instrument operated at an acceleration voltage of 100 kV. To prepare the TEM samples, a small drop of the sample solution with an appropriate concentration was carefully deposited onto a carbon-coated copper electron microscopy (EM) grid and dried overnight at 40 $^\circ\text{C}$ and under vacuum condition. Scanning electron microscope (SEM) images were recorded on a JEOL JSM-7500F instrument operating at 15 kV. The X-ray diffraction (XRD) patterns were carried out on D8 diffractometer (Bruker) with $\text{Cu K}\alpha$ radiation. N_2 adsorption-desorption tests were proceeded at 77 K by Quantachrome iQ2. Vacuum degassing was operated at 100 $^\circ\text{C}$ for 24 h, equilibrium time is 3 min. The materials were measured in liquid nitrogen environment. Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano equipped with a 4 mW He-Ne laser (7) operating at $\lambda = 633 \text{ nm}$. Gel permeation chromatography (GPC) measurement was carried out by an Agilent 1100 series equipped with an RI-G1362A RI detector and a PL gel Mixed-C column using DMF as the mobile phase at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$ at 25 $^\circ\text{C}$. MALDI-TOF analyses were performed on an Applied Biosystems 4700 proteomics analyzer 72020. Photo-polymerization was carried out in the reaction vessel where the reaction mixtures were irradiated by LED lights (6 W). The samples were irradiated at 577 nm for green light. The multicolored LED light bulb

with remote control was purchased from NVC.



Scheme S1 The synthesis of ZnTHP- Me_2Si and ZnTHP- Ph_2Si

Cross-linking of THPP by Me_2SiCl_2 (The preparation of THPP- Me_2Si). First, a 25.00 mL three-port flask was degassed using nitrogen. THPP (33.75 mg, 0.05 mmol) and DMF (10.00 mL) were added into flask to form the homogeneous solution. Then TEA (12.65 mg, 0.13 mmol, 0.02 mL) and Me_2SiCl_2 (12.80 mg, 0.10 mmol, 12.00 μL) were added into reaction solution drop by drop. The mixture was degassed again with nitrogen. After, the mixture was preheated to 70 °C and reaction for 7 h. Then TEA (12.65 mg, 0.13 mmol, and 0.02 mL) and TBDP (55.00 mg, 0.20 mmol, 0.05 mL) were added to reaction solution drop by drop. Continue to reaction for 7 h at 70 °C. After the reaction, the methanol (8.50 μL) was added into reaction solution, and the mixture keeps reacting for 0.5 h, and then cooling to room temperature. Later, the product was concentrated under reduced pressure and washed by deionized water (100 mL \times 3). The green product (THPP- Me_2Si) was collected via centrifugation and vacuum drying. Yield: 69%. The $-\text{CH}_3$ of Me_2SiCl_2 has low spatial resistance so that the cross-linked THPP can be twisted at will in space. Therefore, THPP- Me_2Si could own a twisted and folded three-dimensional space structure.

The preparation of ZnTHP-Me₂Si. THPP-Me₂Si (27.00 mg) was dissolved in DMF (10.00 mL) and stirred at 140 °C under nitrogen atmosphere in 25.00 mL three-port flask, and then the saturated methanol solution with Zn(CH₃COO)₂·2H₂O (0.20 g, 0.92 mmol, 10.00 mL) was dropped into reaction solution. Next, the reaction liquid was stirred for 2 h without light. After, the product was concentrated under reduced pressure and washed by deionized water (100 mL × 3). The purple product (ZnTHP-Me₂Si) was centrifuged and collected by vacuum drying. Yield: 85%.

Cross-linking of THPP by Ph₂SiCl₂ (The preparation of THPP-Ph₂Si). A 25 mL three-port flask was degassed with nitrogen, THPP (33.75 mg, 0.05 mmol) and DMF (10.00 mL) were added into flask, then added TEA (12.65 mg, 0.13 mmol, 0.02 mL) and Ph₂SiCl₂ (25.32 mg, 0.10 mmol, 0.03 mL) to reaction solution drop by drop. The mixture was degassed again with nitrogen. After, the mixture was placed in an oil bath preheated to 70 °C and allowed to stir for 7 h. Then TEA (12.65 mg, 0.13 mmol, and 0.02 mL) and TBDP (55 mg, 0.20 mmol, 0.05 mL) were added to reaction solution drop by drop. Continue to reaction for 7 h at 70 °C. After the reaction, the methanol (8.50 μL) was added into reaction solution, and the mixture keeps reacting for 0.5 h, and then cooling to room temperature. Afterwards, the product was concentrated under reduced pressure and washed by deionized water (100 mL × 3). The green product (THPP-Ph₂Si) was collected via centrifugation and vacuum drying. Yield: 76%. The -Ph of Ph₂SiCl₂ has greater spatial resistance so that the cross-linked porphyrins could not be twisted at will in space. Therefore, THPP-Ph₂Si owns a lamellar three-dimensional space structure.

The preparation of ZnTHP-Ph₂Si. THPP-Ph₂Si (27.00 mg) was dissolved in DMF (10.00 mL) and stirred at 140 °C under nitrogen atmosphere in 25 mL three-port flask, and then the saturated methanol solution with Zn(CH₃COO)₂·2H₂O (0.20 g, 0.92 mmol, 10.00 mL) was dropped into reaction solution. Next, reaction liquid was stirred for 2 h. After, the product was concentrated under reduced pressure and washed by deionized water (100 mL × 3). The purple product (ZnTHP-Ph₂Si) was centrifuged and

collected by vacuum drying. Yield: 83%

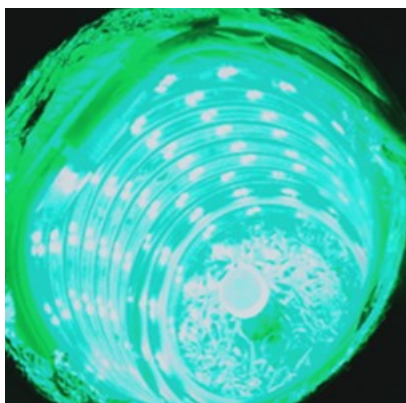


Fig. S1 LED green strip light setup used in this study.

PET-RAFT polymerization of monomer NIPAm mediated by photo-catalysts in the presence of DDMAT. For photo-catalyst-mediated RAFT polymerization, a reaction solution consisting of DMSO (0.50 mL), NIPAm (0.47 g, 4.19 mmol), DDMAT (7.60 mg, 0.02 mmol) and photo-catalyst was added into a 4 mL glass vial. The glass vial was sealed with a rubber septum and the solution was degassed with nitrogen for 30 min. The reaction mixture was then irradiated under green LED light ($\lambda_{\text{max}} = 577 \text{ nm}$, 6 W, intensity = 0.134 mW/cm^2) at 25 °C. After 11 h irradiation, aliquots of the reaction mixtures were withdrawn to measure monomer conversion and number-average molecular weights (M_n , $^1\text{H NMR}$) by $^1\text{H NMR}$. The final solution was purified via precipitation in ether/THF (1/1, v/v). The precipitated product was collected. Yield: 91%. The experimental device is shown in Figure S1.

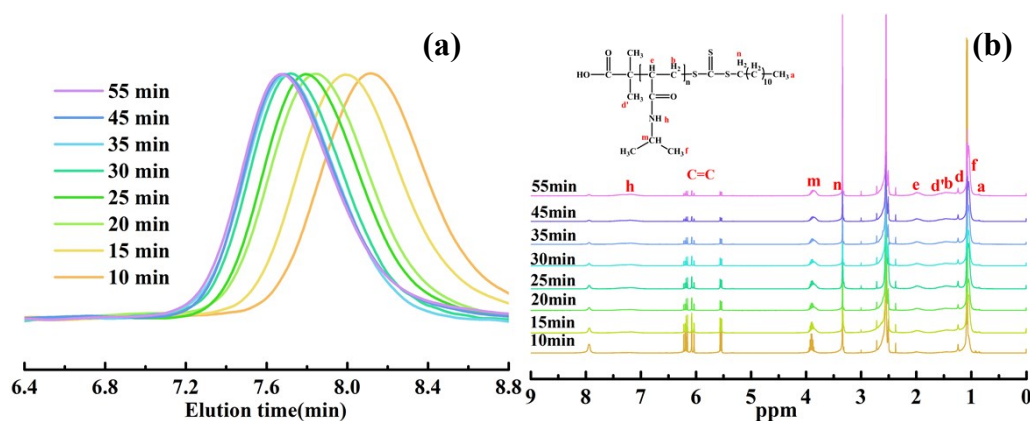


Fig. S2 The GPC curves (a) and $^1\text{H NMR}$ spectra (b) of PNIPAm mediated by the

ZnTHP with a mole ratio of NIPAm : DDMAT = 200:1 under green light.

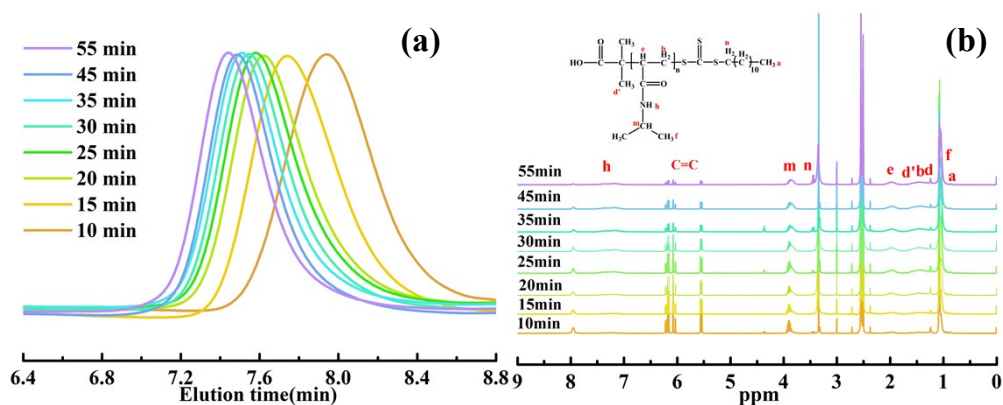


Fig. S3 The GPC curves (a) and ¹H NMR spectra (b) of PNIPAm mediated by the ZnTHP-Me₂Si with a mole ratio of NIPAm : DDMAT = 200:1 under green light.

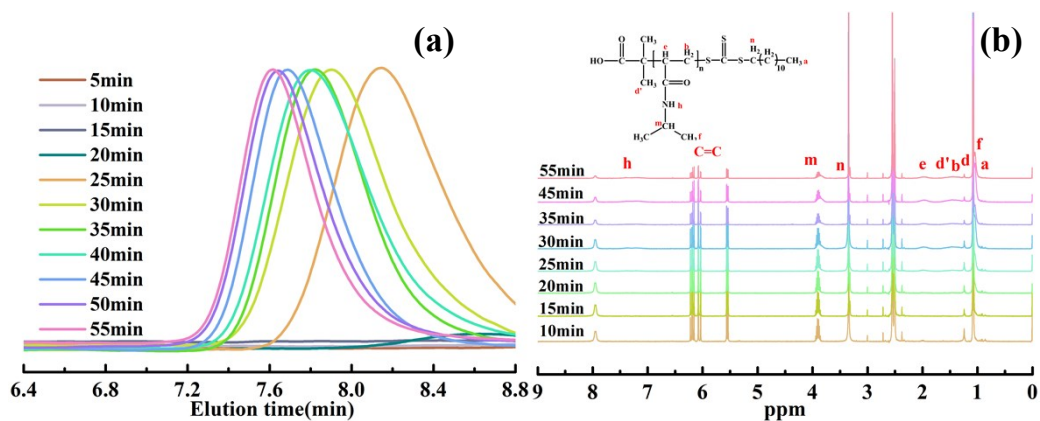


Fig. S4 The GPC curves (a) and ¹H NMR spectra (b) of PNIPAm mediated by the ZnTHP-Ph₂Si with a mole ratio of NIPAm : DDMAT = 200:1 under green light.

The proposed mechanism for PET-RAFT polymerization described in Scheme 1 is based on the photo-redox reaction between the photo-catalyst and thiocarbonylthio compound. So, the interaction mechanism between ZnTHP-Me₂Si or ZnTHP-Ph₂Si and DDMAT was investigated via the combination of fluorescence spectroscopy and UV-Vis absorption (Fig. S5). The quenching experiment is employed to demonstrate a PET or energy transfer process between two molecules.^{S1-4} As shown in Fig. S5a and S5c, the fluorescences of ZnTHP-Me₂Si and ZnTHP-Ph₂Si, upon excitation at $\lambda_{\max} = 577$ nm, are quenched in the presence of DDMAT, which confirm there are the electron or energy transfer process between ZnTHP-Me₂Si or ZnTHP-Ph₂Si and DDMAT. The

corresponding UV-Vis spectra also marginally split into two peaks at 605 nm as the reaction goes on (Fig. S5b and S5d). However, the fluorescence intensity of ZnTHP-Me₂Si is slightly significantly declined with the reaction time in comparison with that of ZnTHP-Ph₂Si. Combining the studies from UV-Vis absorption and fluorescence spectroscopy, we conclude that ZnTHP-Me₂Si has stronger photosensitivity and can catalyze reaction rapidly after irradiation. To clarify that ZnTHP-Me₂Si and ZnTHP-Ph₂Si present strong affinity to trithiocarbonate, we have performed UV-Vis spectra of ZnTHP-Me₂Si/DDMAT and ZnTHP-Ph₂Si/DDMAT in DMSO before and after light irradiation. Boyer and co-workers reported that trithiocarbonate compounds can coordinate to zinc porphyrins in DMSO, which is supported by the appearances of a new absorption peak at 620 nm.^{S5} For the polymerization mediated by ZnTHP-Me₂Si when DDMAT as chain transfer agent, the similar new absorption peak is observed at 618 nm after light irradiation for 11 h (Fig. S6a). In the case of ZnTHP-Ph₂Si, the UV-Vis spectrum displays a new signal at 620 nm as same condition (Fig. S6b). It has been reported that radicals can add to the β,β' -position of porphyrins, forming chlorin and bacteriochlorin-like derivatives and therefore causing changes in the observed electronic spectra during polymerization.^{S5,S6} Moreover, ZnTHP-Me₂Si-mediated-polymerization mixture exhibits a marginal red shift (2 nm) from 563 nm to 565 nm in the presence of DDMAT absorption before and after 11 h of green light irradiation. This interaction is resulted from the formation of hydrogen bonding between the pyrrole of ZnTHP-Me₂Si and acid groups of DDMAT.

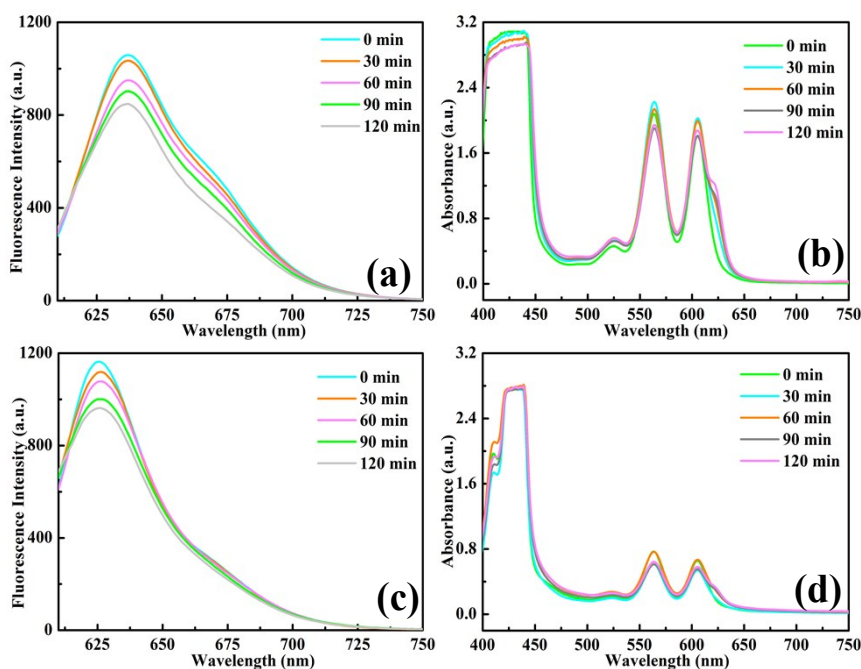


Fig. S5 Fluorescence spectra of ZnTHP-Me₂Si (a) and ZnTHP-Ph₂Si (c) in the presence of a fixed concentration of DDMAT under green light ($\lambda_{\text{max}} = 577 \text{ nm}$, 6 W, intensity = 0.134 mW/cm^2) at different time points with DMSO as solvent; The corresponding UV-Vis spectra of ZnTHP-Me₂Si (b) and ZnTHP-Ph₂Si (d) in DMSO solvent.

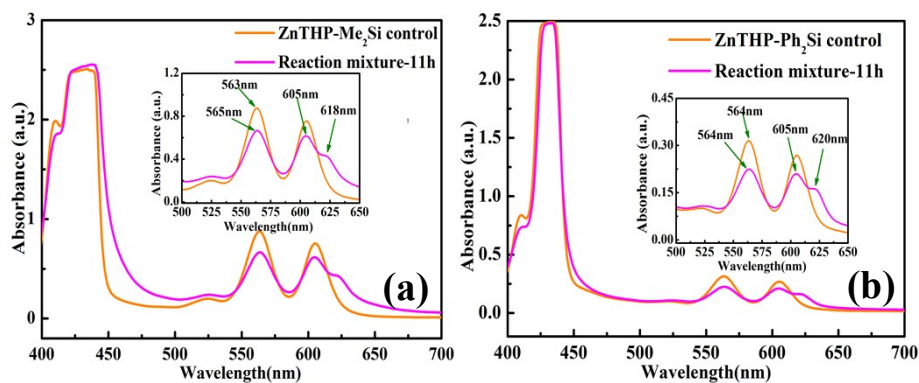


Fig. S6 UV-Vis spectra for ZnTHP-Me₂Si (a) and ZnTHP-Ph₂Si (b) in the presence of DDMAT before and after 11 h polymerization of NIPAm under green light with DMSO as solvent.

Notes and references

S1 N. J. Turro, *Menlo Park*, 1978.

S2 L. Jong, N. Zaveri and L. Toll, *Cheminform*, 2004, **14**, 181-185.

- S3 J. W. Tucker and C. R. J. Stephenson, *J. Org. Chem.*, 2012, **77**, 1617-1622.
- S4 J. N. Demas, E. W. Harris and R. P. M. McBride, *J. Am. Chem. Soc.*, 1977, **99**, 3547-3551.
- S5 J. Yeow, S. Joshi, R. Chapman and C. A. J. M. Boyer, *Angew. Chem. Int. Ed.*, 2018, **57**, 10102-10106.
- S6 A. A. Gridnev and E. M. Nechvolodova, *Theor. Exp. Chem.*, 1989, **25**, 670-675.