

## Electronic Supporting Information

### Platform of Near-infrared Light-induced Reversible Deactivation Radical Polymerization: Upconversion Nanoparticle as Internal Light Sources

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#### Experimental section

##### Materials

*n*-Butyl acrylate, vinyl acetate and methyl methacrylate were used as monomers after passing through a neutral alumina column. 2-(Ethoxycarbonothioyl)sulfanyl propanoate (EXEP), 2-((phenoxy-carbonothioyl)thio) ethyl propanoate (PXEP) and 3-azidopropyl 3-(((2-methoxy-2-oxo-1-phenylethyl)thio)carbonothioyl)thio) propanoate (AMP) were synthesized according to literature procedures used as RAFT agent. Upconverting nanoparticles (UCNP) were used as internal lamp which were purchased from Nanjing hengna biological technology Co. Ltd. and used as received. UCNPs were characterized by TEM and the result was given in Figure S1.

##### Analyses

**Nuclear Magnetic Resonance (NMR)** spectra were recorded on a Bruker Avance III HD operating at 300 MHz for <sup>1</sup>H and <sup>13</sup>C using CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard.

**Gel Permeation Chromatography (GPC)** was used to characterize the number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) of synthesized polymers. The TOSOH HLC-8320 (GPC) system equips with a TSK gel Multi pore HZ-N (3) 4.6 × 150 mm column. Tetrahydrofuran (THF) served as the eluent with a flow rate of 0.35 mL min<sup>-1</sup>. GPC samples were injected using a TOSOH HLC-8320 GPC plus autosampler. The molecular weights were calibrated with PS standards.

**Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry** measurement was performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. The compound trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, > 98 %) served as matrix. The matrix and cationizing sodium trifluoroacetate salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in CHCl<sub>3</sub> at a concentration of 10 mg/mL.

**UV-vis** spectra of RAFT agents were recorded using a Hitachi U-3900 spectrophotometer at room temperature.

**Photopolymerization** was carried out in the NMR tube where the reaction mixture were irradiated by a continuous-wave (CW) 980 nm laser (Xi'an Saipulin Laser Technology Institute,

China) with tunable power of 0-2W.

### **Procedure for the polymerization of *n*-butyl acrylate (*n*-BA) in the presence of PXEP using UCNP**

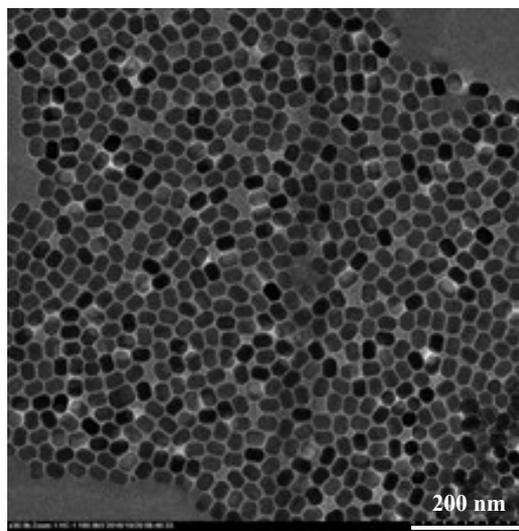
Polymerization of BA was carried out in a NMR tube with *n*-BA (0.446 g, 3.47 mmol), PXEP (11.7 mg, 43.4  $\mu\text{mol}$ ), UCNP (200  $\mu\text{L}$  of UCNP stock solution, 5  $\text{mg mL}^{-1}$  in cyclohexane). Then the solution was deoxygenated by three standard freeze-pump-thaw cycles. And the tube was flame-sealed. Subsequently, the tube was irradiated in FIR Laser (2W,  $\lambda = 980 \text{ nm}$ ) at ambient temperature. After the required time, the reaction mixture was removed from the laser source. The tube was carved, and the contents contacted with air. Next moment, the mixture contents were poured in disposable plastic cup whose weight had been known. The tube was washed with THF. And liquid after washing was also poured in the cup. The polymers were dried at room temperature under vacuum to constant weight. The conversion of BA was gravimetrically determined.

### **Procedure for kinetic studies of polymerization of BA in the presence of PXEP using UCNP**

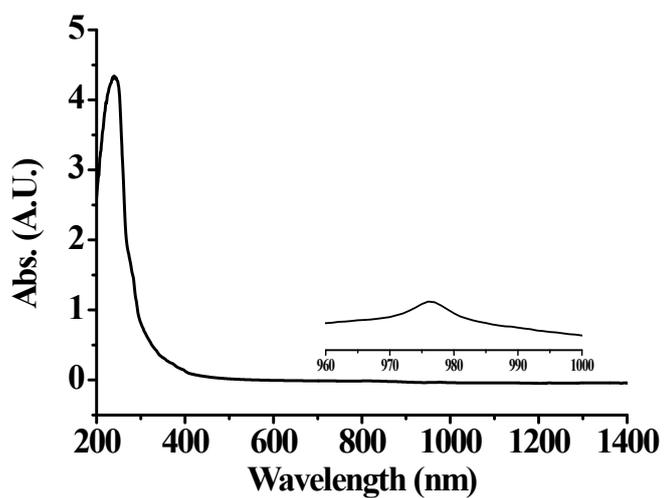
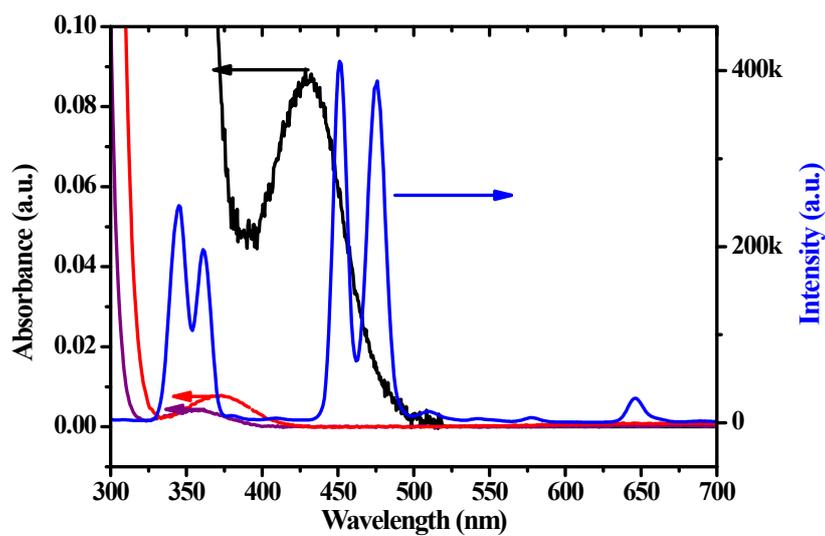
A reaction stock solution consisting of BA (0.892 g, 6.94 mmol) and PXEP (23.4  $\text{mg}$ , 86.7  $\mu\text{mol}$ ) was prepared in a glass vial. About 200  $\mu\text{L}$  of stock solution was transferred into a NMR tube covered with aluminum foil. Then approximately 40  $\mu\text{L}$  UCNP stock solution was added to the tube. Subsequently, the solution was degassed by three standard freeze-pump-thaw cycles. The tube was sealed and placed under a 980 nm Laser lamp at ambient temperature. At timed intervals, the NMR tube was taken away from Laser lamp. The monomer conversions were analyzed by  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ). And the number average molecular weights ( $M_n$ ) and molecular weight distributions ( $\text{Đ}$ ) were determined by GPC (THF).

### **Chain extension experiment**

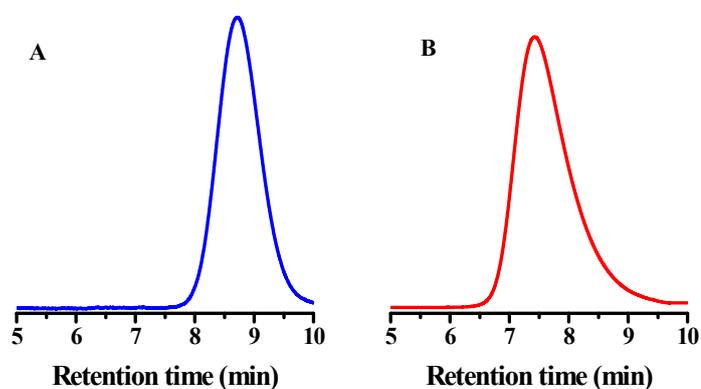
The procedure of the chain extension experiment was similar to the polymerization above except that PXEP was substituted by the polymer.



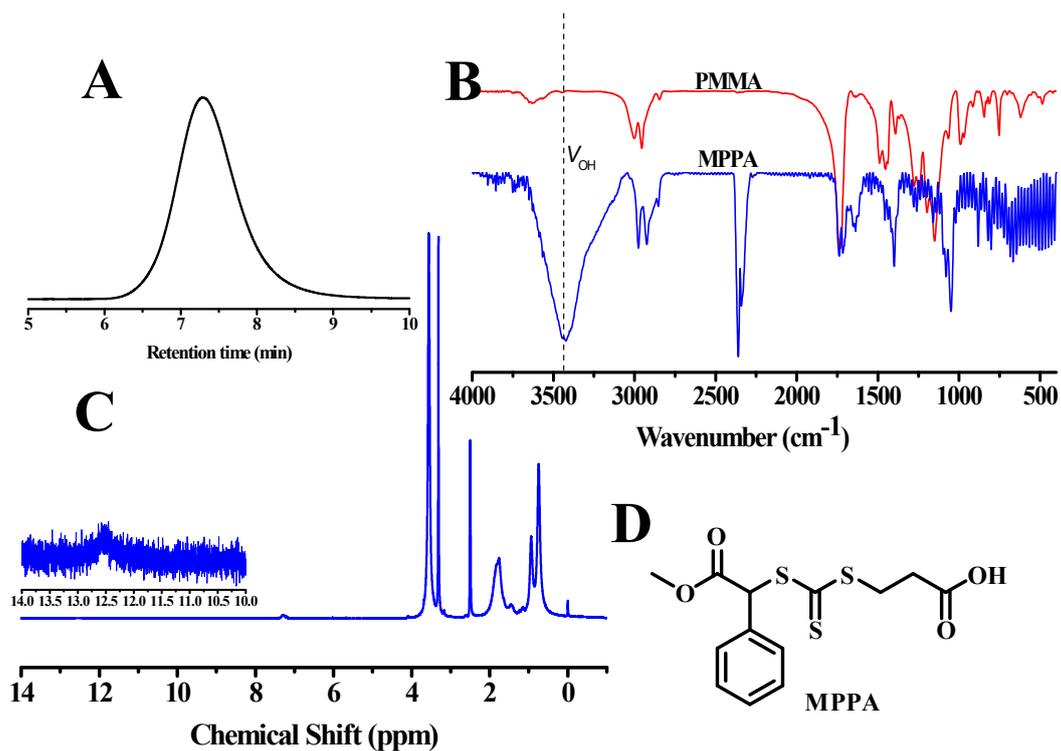
**Figure S1** Typical TEM images of  $\text{NaYF}_4:\text{Yb/Tm}$  (UCNP).



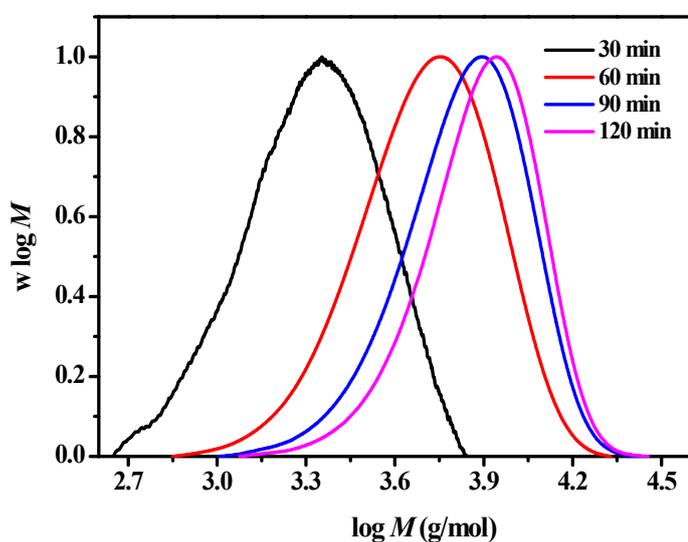
**Figure S2.** UV-vis absorption spectra of PXEP (red), EXEP (purple), AMP (black), UCNPs and UCNPs emission characterization.



**Figure S3.** The GPC curves of PVAc (A) and PMMA (B).



**Figure S4** (A) GPC curve of PMMA; (B) FT-IR spectra of the polymer and RAFT agent; (C)  $^1H$  NMR spectrum of PMMA obtained in  $DMSO-d_6$ . (D) The structure of RAFT agent.



**Figure S5.** Molecular weight distributions of PBA at different times points.