

**Supporting Information for**  
**Near-infrared Light induced Cationic Polymerization based on**  
**Upconversion and Ferrocenium Photochemistry**

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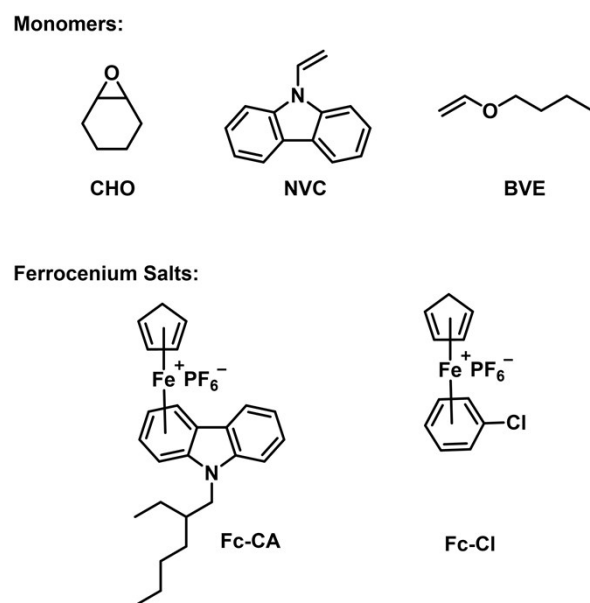
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## Materials:

$\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$  were purchased from Shandong Yutai chemical reagent company. 1-Octadecene (ODE, 90%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. All the other reagents were purchased from Adamas (China) Co., Ltd and used without any further purification. The chemical structures of the monomers and the photoinitiators were shown in Figure S1.

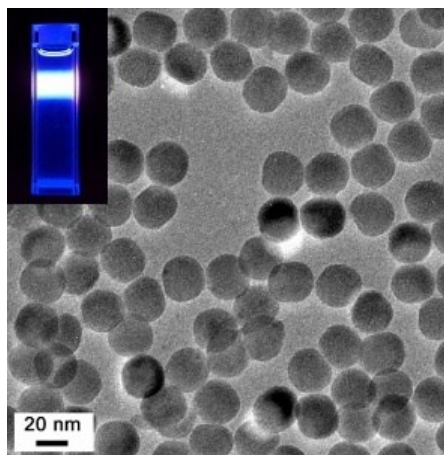


**Fig S1** Chemical structures of the monomers and the photoinitiators

## Preparation of $\text{NaYF}_4:\text{Yb},\text{Tm}$ nanocrystals:

Upconverting nanoparticles (UCNPs)  $\text{NaYF}_4:18\%\text{Yb}, 0.5\%\text{Tm}$  nanocrystals were synthesized according to the literature<sup>[1]</sup> with a typical procedure: 1 mmol of  $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$  (RE = 81.5 mol% Y, 18 mol% Yb, 0.5 mol% Tm) was dissolved in a mixture containing 15 mL of ODE (15 mL) and 6 mL of OA. Under argon protection, the solution was heated to 160 °C for 30 min to form the lanthanide oleate complexes. A gentle flow of argon gas was employed to cool the solution to room temperature. During this time, a solution of  $\text{NH}_4\text{F}$  (4 mmol) and  $\text{NaOH}$  (2.5 mmol) dissolved in 10 mL of methanol was added to the flask and the mixture was stirred for 30 min. The temperature was then increased to 50 °C for evaporating methanol from the reaction mixture; in succession, the solution was heated to 300 °C under an argon atmosphere for 60 min and then cooled to room temperature naturally. The resulting solid

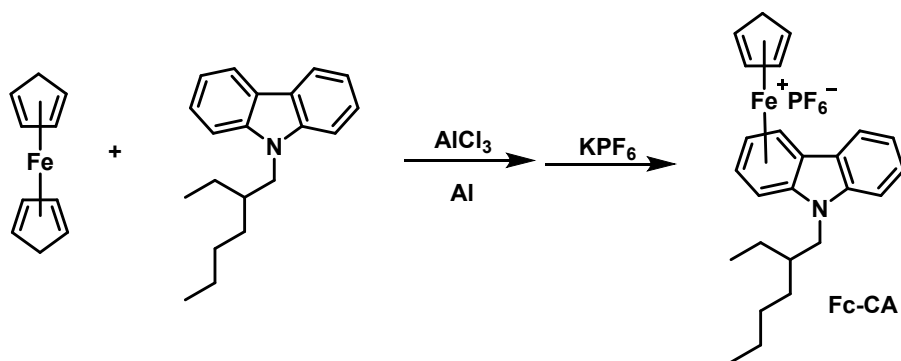
products were precipitated by addition of ethanol, collected by centrifugation at 8500 rpm for 8 min and washed with ethanol three times. The transmission electron microscopy (TEM) image as shown in Figure S2 indicated that the average diameters of the obtained nanoparticles are approximately 20 nm.



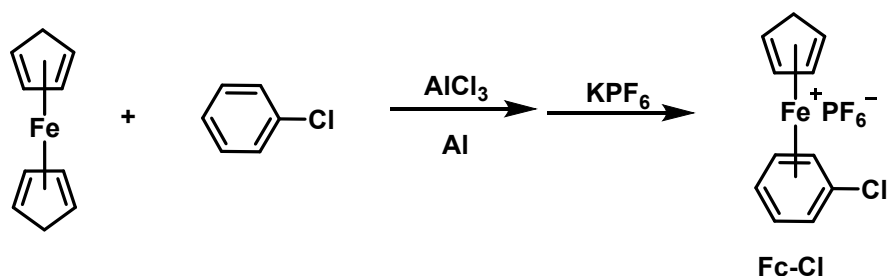
**Figure S2** TEM images of NaYF<sub>4</sub>:18%Yb,0.5%Tm nanocrystals. The inset shows the emitting blue fluorescence of the UCNPs after excitation using a 980 nm laser.

### Synthesis of ferrocenium salts

The ferrocenium salts were prepared according to the literatures<sup>[2]</sup> with a typical procedure: Ferrocene (1.00 g, 5.37 mmol), N-isooctylcarbazole (2.25 g, 8.06 mmol), anhydrous aluminum chloride (2.15 g, 16.1 mmol), and aluminium powder (0.145 g, 5.37 mmol) were stirred in 40 mL of decalin and stirred at 140-150 °C for 8 h. Then the mixture was cooled to room temperature and 10 mL of methanol and 20 mL of deionized water were added to the mixture successively. After filtration and separation of layers, the orange water layer was washed with ether (3 × 30 mL) and then treated with sufficient KPF<sub>6</sub> in water to give complete precipitation. After recrystallization from acetone/and ether, 0.852 g of the product **Fc-CA** was obtained as orange solid with a yield of 28.9%.



The synthesis of **Fc-Cl** was performed using similar preparation procedure to **Fc-CA** instead of direct using chlorobenzene as both aromatic ligand and solvent. The mixture was heat to  $110^\circ\text{C}$  for 8 h and the final light green product was obtained with a yield of 80%.



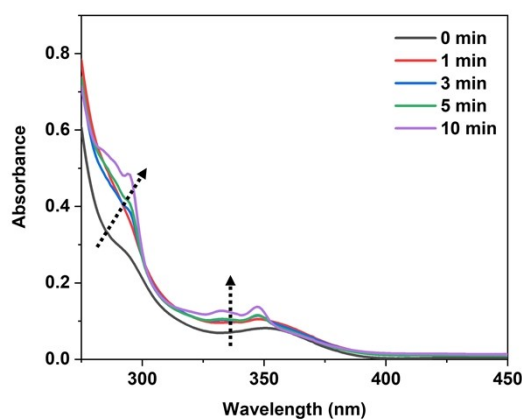
### Photopolymerization:

General procedure: The ferrocenium salts **Fc-CA** (10.9 mg,  $5 \times 10^{-3}$  mmol) and UCNPs (125 mg, 2.5 wt.%) were dissolved in 3 mL of  $\text{CH}_2\text{Cl}_2$  solvent in the Schlenk tube. With stirring, 1 mL 1, 2-epoxycyclohexane (CHO) was added into the mixed solution. Before the irradiation, the solution was degassed by purging dry nitrogen and the whole photopolymerizations were carried out under the nitrogen atmosphere. The polymer was then precipitated in methanol (20 mL) after a certain irradiation time of 980 nm NIR laser with a light intensity of 12 W (the shape of the laser spot is a circle with a 7 mm diameter). After that, the polymer was separated from the mixture after 3 times centrifugation and dried in vacuum for more than 24 hours. All other polymerizations were performed under the same conditions.

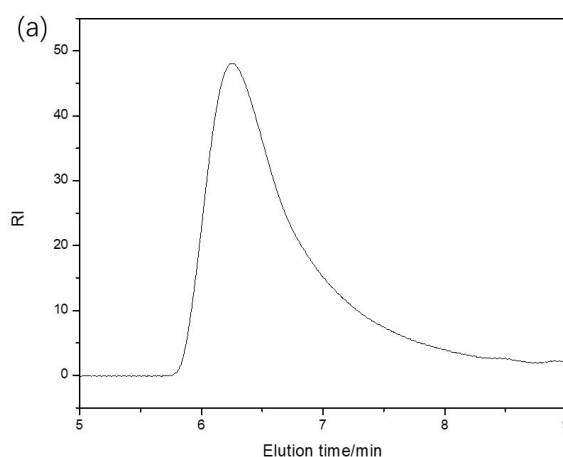
### Characterization:

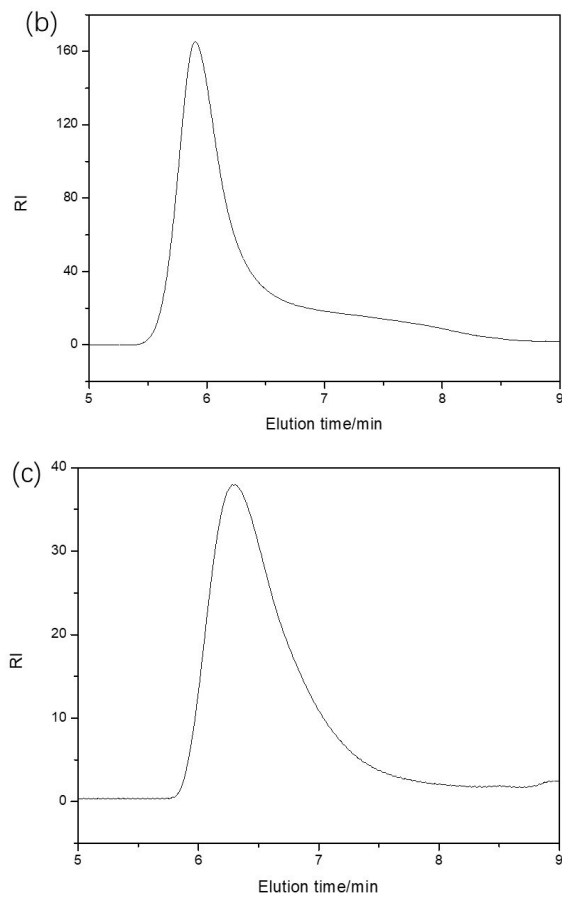
UV-Vis absorption spectra of ferrocenium salts were taken in dichloromethane by a spectrophotometer model as EMCLAB EMC-61PC-UV, while the emission spectrum

of UCNPs was measured in hexane by CARY Eclipse series fluorescence spectrophotometer. The photopolymerization was followed by the measurement of the epoxy group conversion, which was conducted by means of ATR Fourier-transform infrared (ATR-FTIR) spectroscopy during irradiation, employing a Thermal Fisher Nicolet iS10 series. The total epoxy conversion was calculated by integrating the peak between 980 – 945  $\text{cm}^{-1}$  of the two drops of the samples on the ATR platform. Conversions for all samples were determined by the ATR-FTIR. The molecular weights of the polymers were measured by a TOSOH HLC-8320 series GPC using tetrahydrofuran (THF) as the solvent according to PS standard.

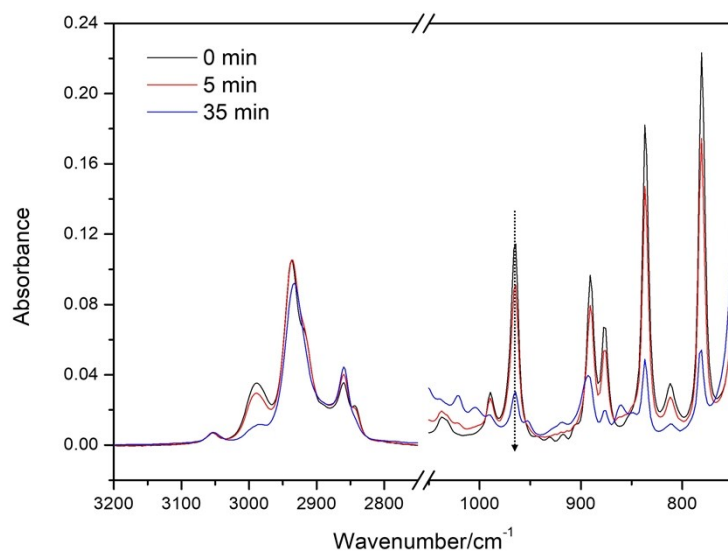


**Figure S3** Photolysis of ferrocenium salt **Fe-CA** in  $\text{CH}_2\text{Cl}_2$  under upconversion illuminance irradiation





**Figure S4** GPC curve of the monomers: (a) CHO; (b) NVC; (c) BVE



**Figure S5** FT-IR spectra of CHO measured with different irradiation time

**Reference:**

- [1] R. Liu, H. Chen, Z. Li, F. Shib, X. Liu, *Polym. Chem.*, **2016**, 7, 2457.
- [2] T. Wang, B. Li, L. Zhang, *Polym. Int.* **2005**, 54, 1251.