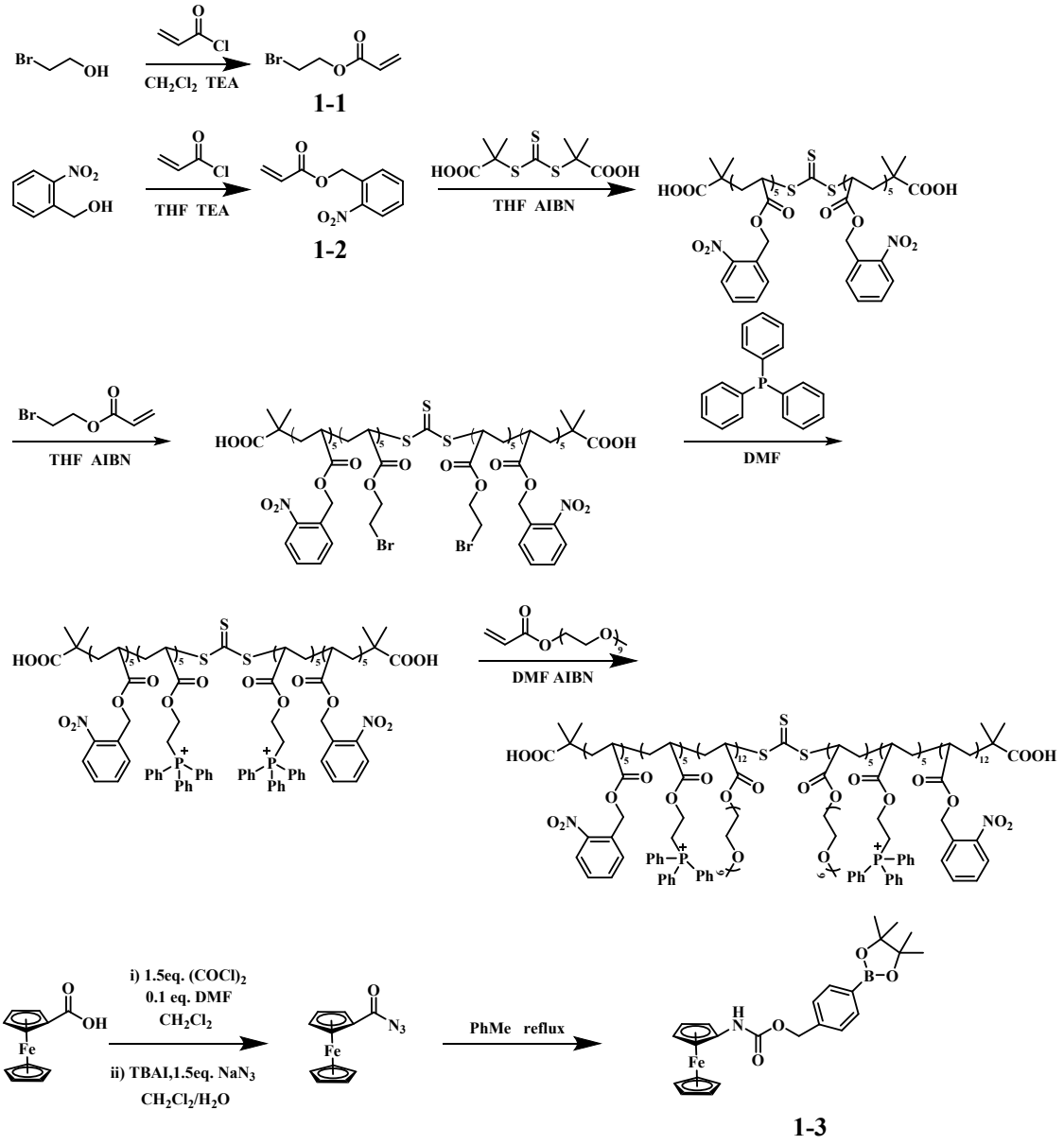
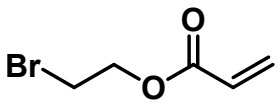
Supporting Information

Experimental Section

Synthesis procedures



1. Synthesis and characterization of PNBE-TPP



1-1

Synthesis of 2-bromethyl acrylate (BEA, 1-1). 4 g of 2-bromethyl acrylate (0.032 mol) and triethylamine (0.038 mol) were added to a three-necked flask containing 40 mL of anhydrous dichloromethane at 0 ^{o}C for 15 min. A solution of 3.5 g of acryloyl chloride (0.038 mol) in 20 mL anhydrous dichloromethane was slowly added dropwise to the flask using a pressure equalizing dropping funnel at 0 ^{o}C, N_2 atmosphere. The solution was continuously stirred for 30 min under an ice bath and then the ice bath was removed. The solution was stirred at room temperature overnight and then filtered. The filtrate was washed thoroughly with 150 mL of deionized water (2 times). The organic phase was collected and washed twice with saturated sodium chloride, and then dried with $MgSO_4$. The solvent was removed using a rotary evaporator at room temperature. The dried solution was filtered, and the filtered was passed through a column of neutral alumina, to obtain a light yellow liquid (yield: 70%).

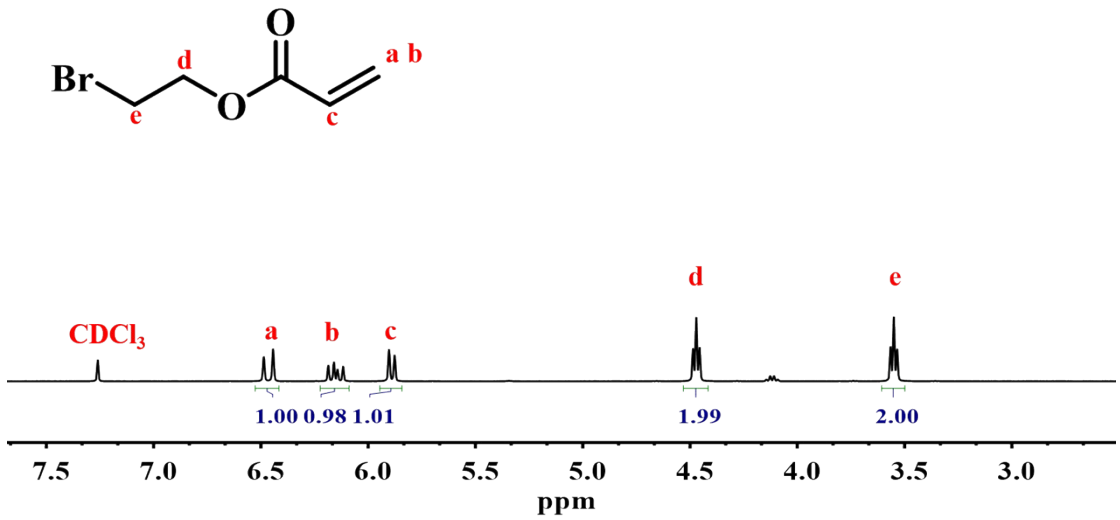
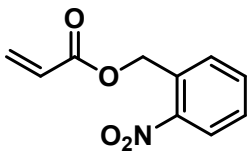


Fig. S1 ^{1}H NMR spectrum of 2-bromethyl acrylate.



1-2

Synthesis of 2-nitrobenzyl acrylate (NBA, 1-2). Typically, 2-notrobenzyl alcohol (7.6 g, 50mmol) was dissolved in 40 mL of dry THF in a three-necked flask under N_2 atmosphere. Triethylamine (7 mL, 50 mmol) was then added to the mixture and stirred at 0 °C for 15 min. Afterward, 4.52 g of acryloyl chloride (50 mmol) was added dropwise via a funnel with stirring at 0 °C over a period of 1 h. The reaction solution was then allowed to stirred at room temperature for overnight. THF was evaporated by a rotary evaporator, and the crude production was dissolved in 80 mL of ethyl acetate. The solution was washed thoroughly with 80 mL of deionized water (3 times).

The organic phase was collected and washed twice with saturated sodium chloride, and then dried with Na_2SO_4. The solvent was removed using a rotary evaporator at room temperature. The dried solution was filtered, and the filtered was passed through a silica gel column chromatography with 6:1 hexane/ethyl acetate affording a yellow viscous liquid (yield: 95%).

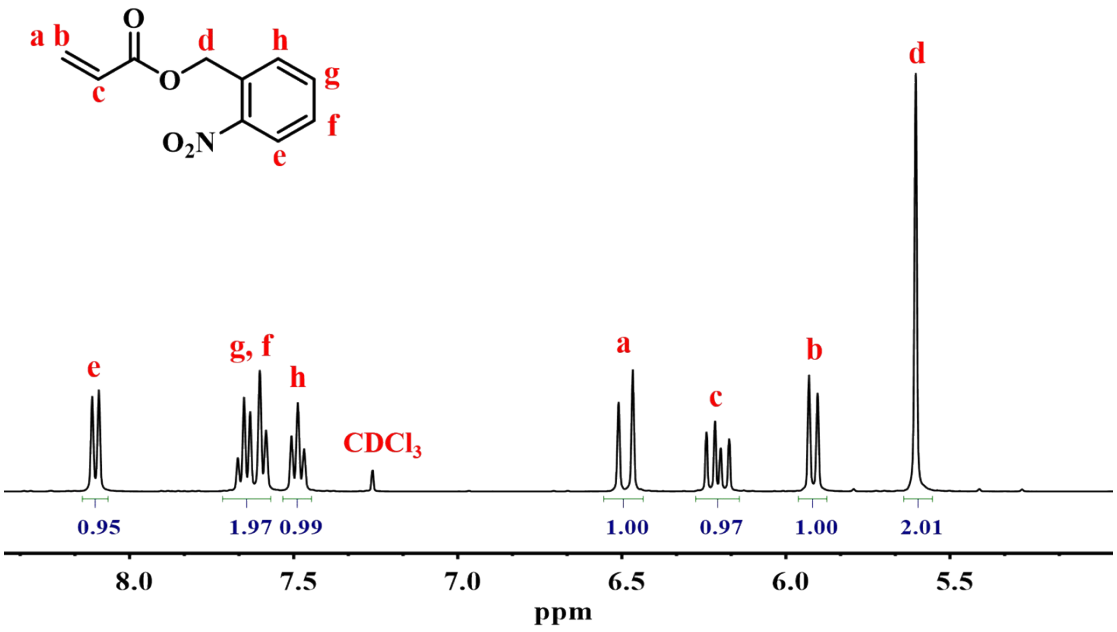


Fig. S2 ^{1}H NMR spectrum of 2-nitrobenzyl acrylate.

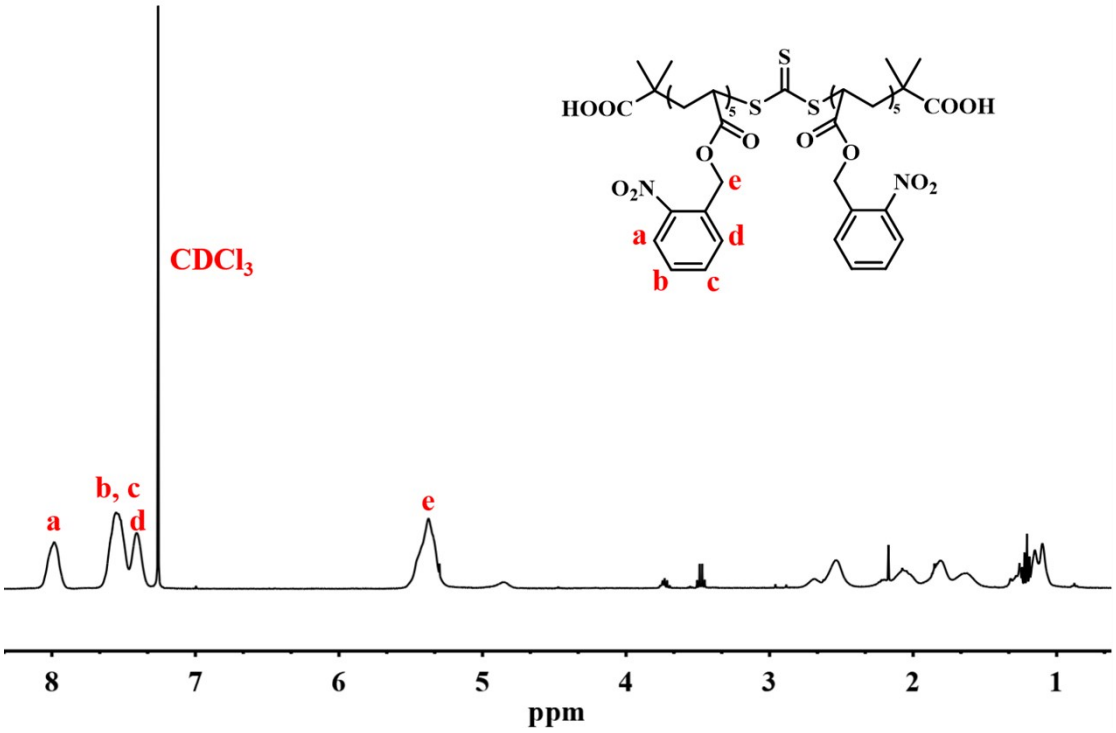


Fig. S3 ^{1}H NMR spectrum of PNBA.

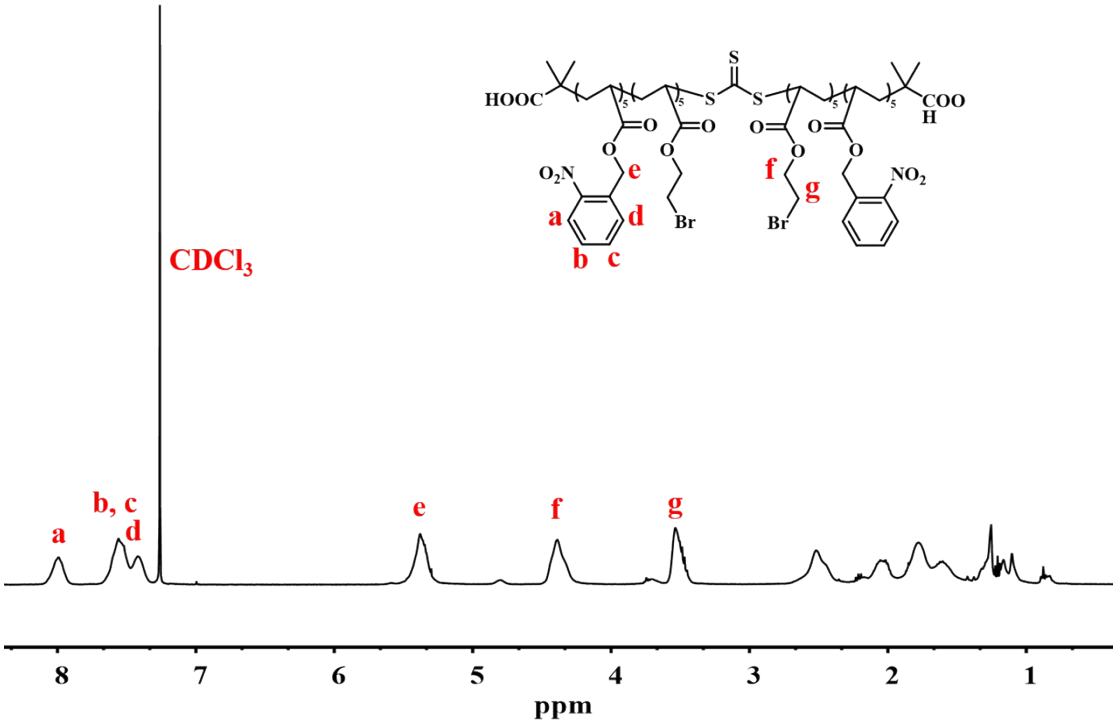


Fig. S4 ^{1}H NMR spectrum of $PNBA_{10}$-*b*-$PBEA_{10}$.

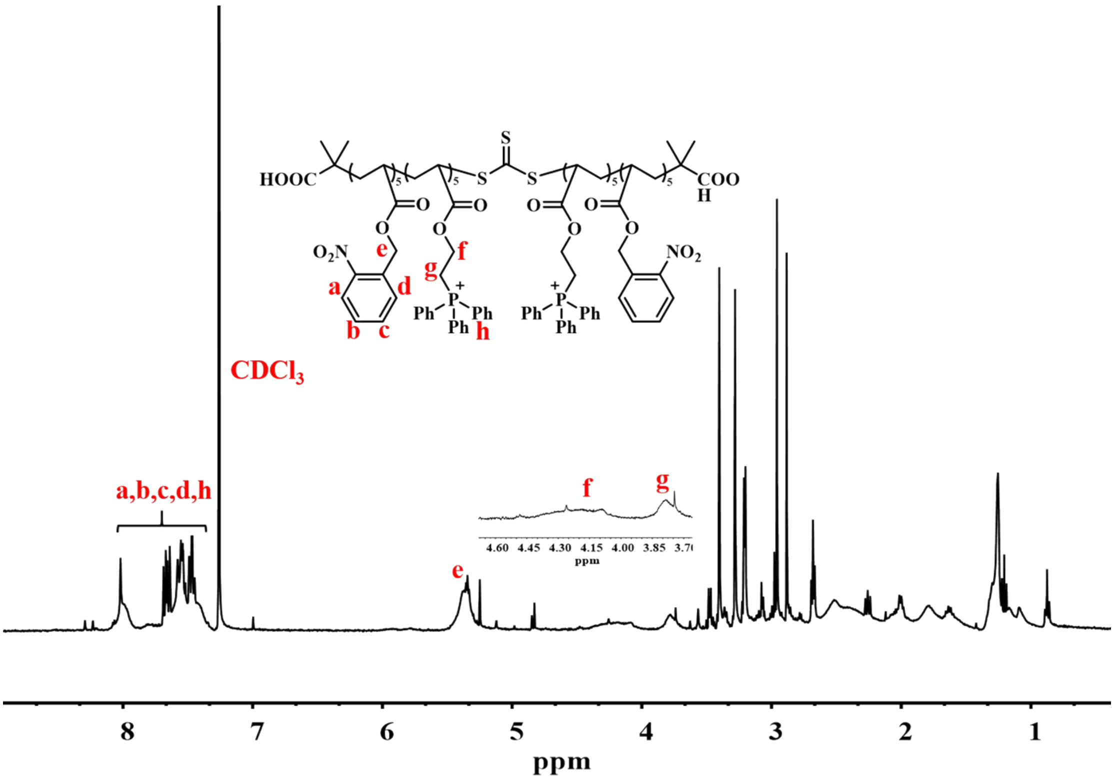


Fig. S5 ^{1}H NMR spectrum of TPP-linked PNBA$_{10}$-*b*-PBEA$_{10}$.

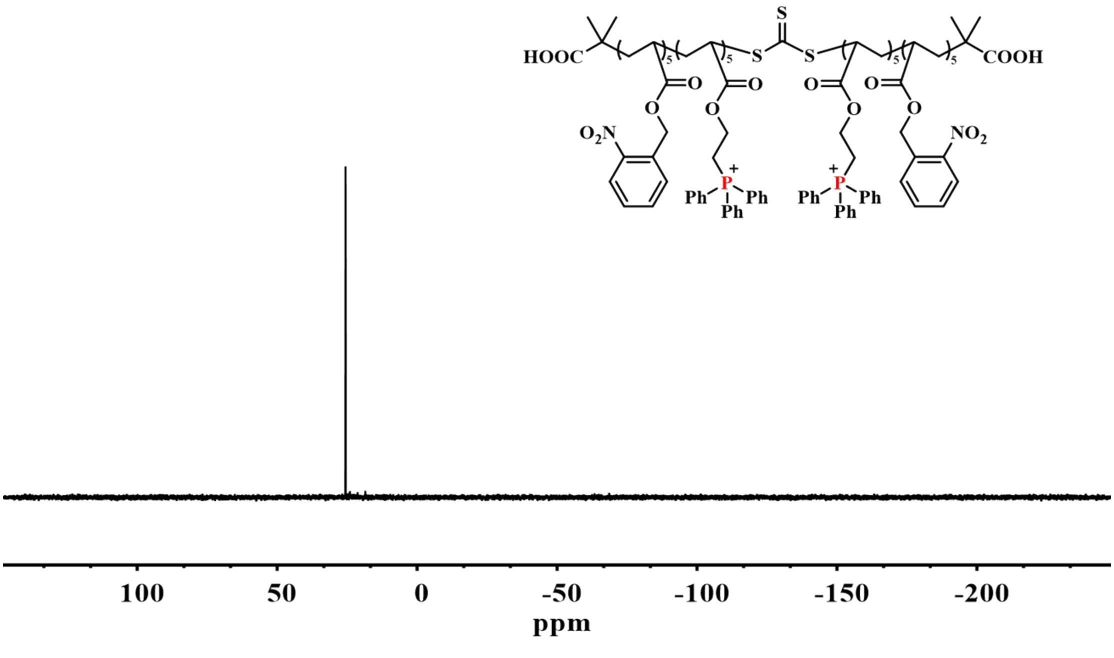


Fig. S6 ^{31}P NMR spectrum of TPP-linked PNBA$_{10}$-*b*-PBEA$_{10}$.

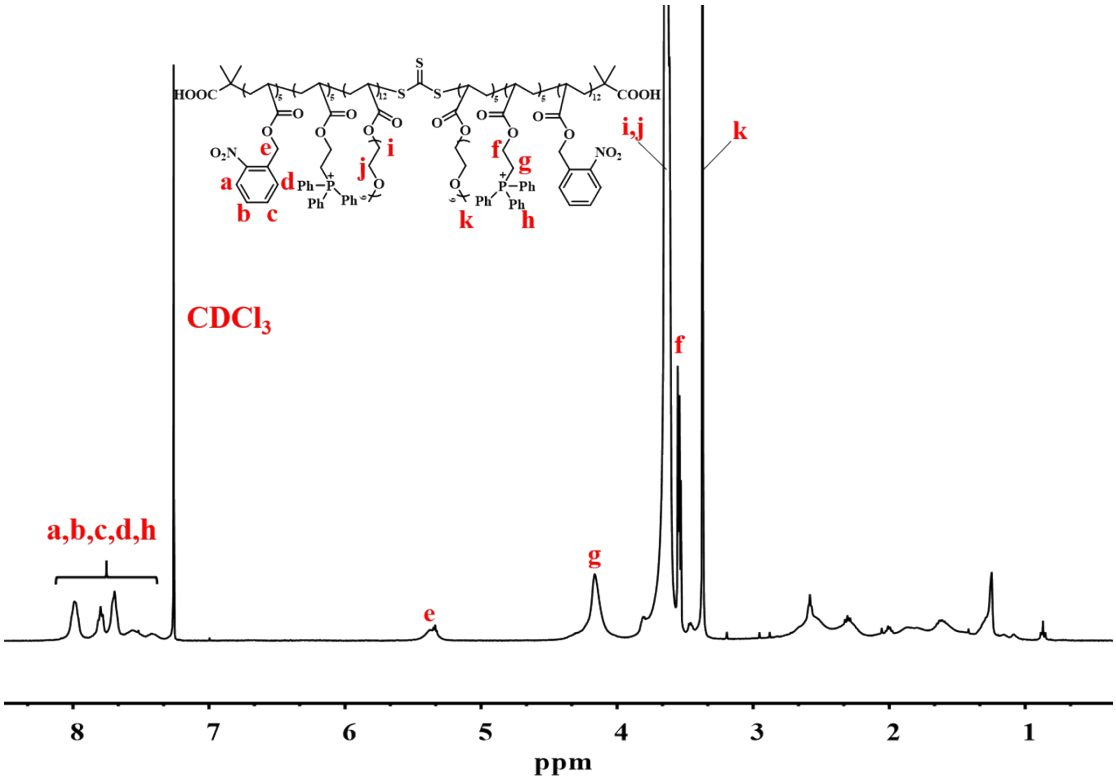
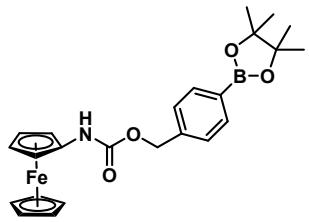


Fig. S7 ^{1}H NMR spectrum of TPP-linked PNBA$_{10}$-*b*-PBEA$_{10}$-*b*-PEG$_{24}$.

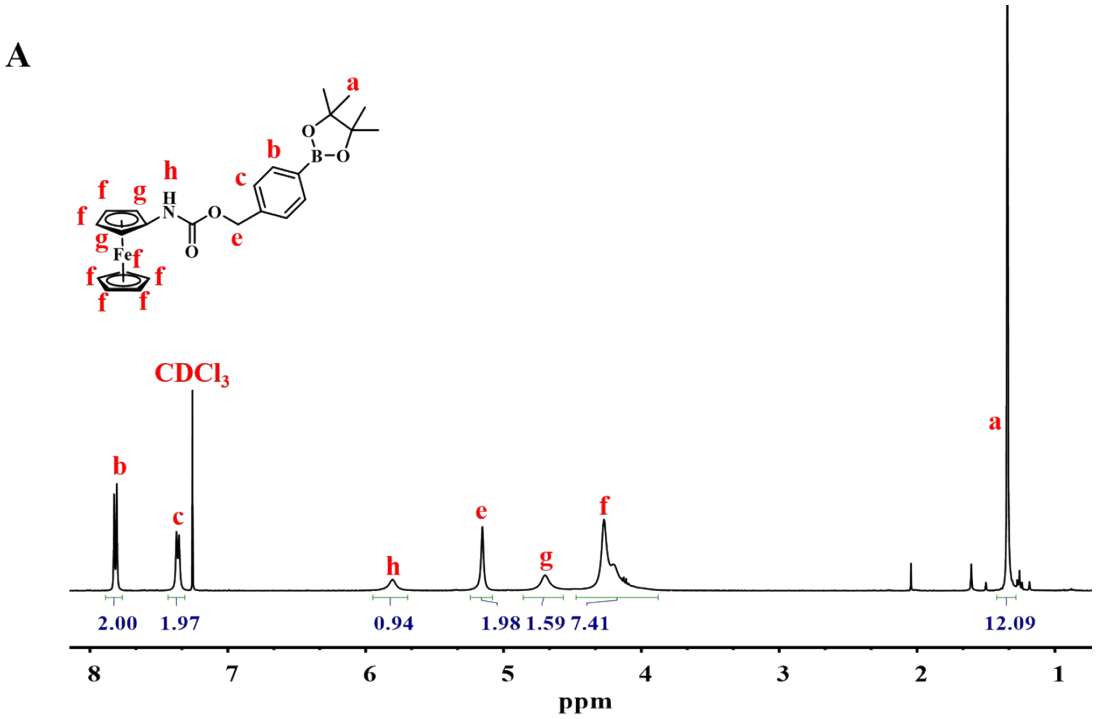


1-3

Synthesis of prodrug Fe (1-3). Typically, ferrocenoyl azide was needed to synthesisze. 4 g of ferrocenecarboxylic acid (17.4 mmol) in anhydrous dichloromethane (40 mL) was added oxalyl chloride (3 ml, 34.8mmol) followed by a drop of DMF under an ice bath. Then, the ice bath was removed and the reaction was still stirred for 3 hours at room temperature before being concentrated using a rotary evaporator. The residue was added in anhydrous dichloromethane (40 mL) and cooled to 0 ^{o}C. 0.06 g of tetrabutylammonium bromide (0.18 mmol) was added followed by a solution of sodium azide (1.7 g, 26.2 mmol) in water (8 mL). The reaction mixture

was then stirred at room temperature for 16 hours. The reaction was quenched with water (40 mL) and the organics separated. The aqueous layer was extracted with dichloromethane (2 times). The organics was obtained and dried over $MgSO_4$, then the solvent was removed by a rotary evaporator. The crude production was purified by silica gel column chromatography (1:1 hexane/CH_2Cl_2) affording orange solid (80%).

510 mg of ferrocenoyl azide (1 mmol) and 936 mg of 4-(hydroxymethyl)phenylboronic acid pinacol ester (2 mmol) were reaction together according to general procedure.[1] The crude production was purified by silica gel column chromatography (9:1 hexane/EtOAc) affording orange solid (70%).



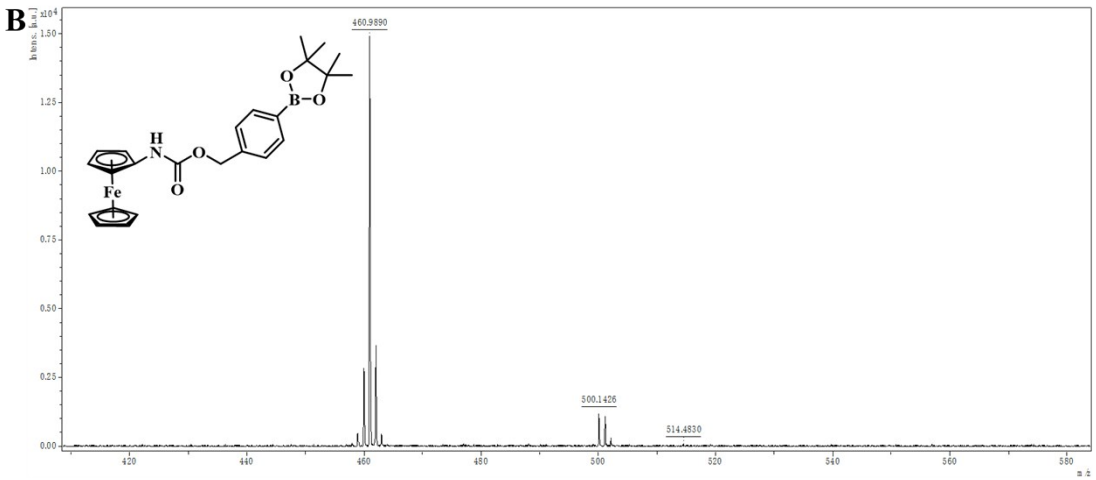
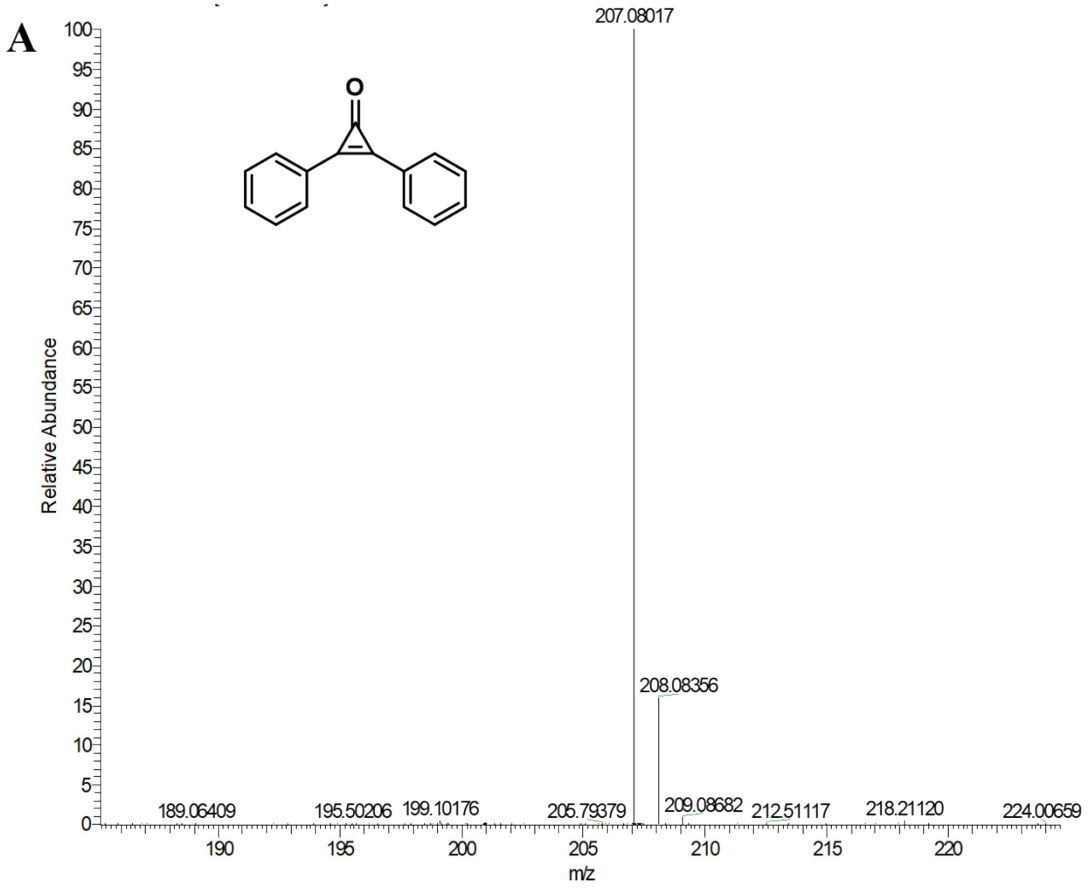


Fig. S8 (A) ^{1}H NMR spectrum of aminoferrocene-based prodrug; (B) Mass spectrum of aminoferrocene-based prodrug.



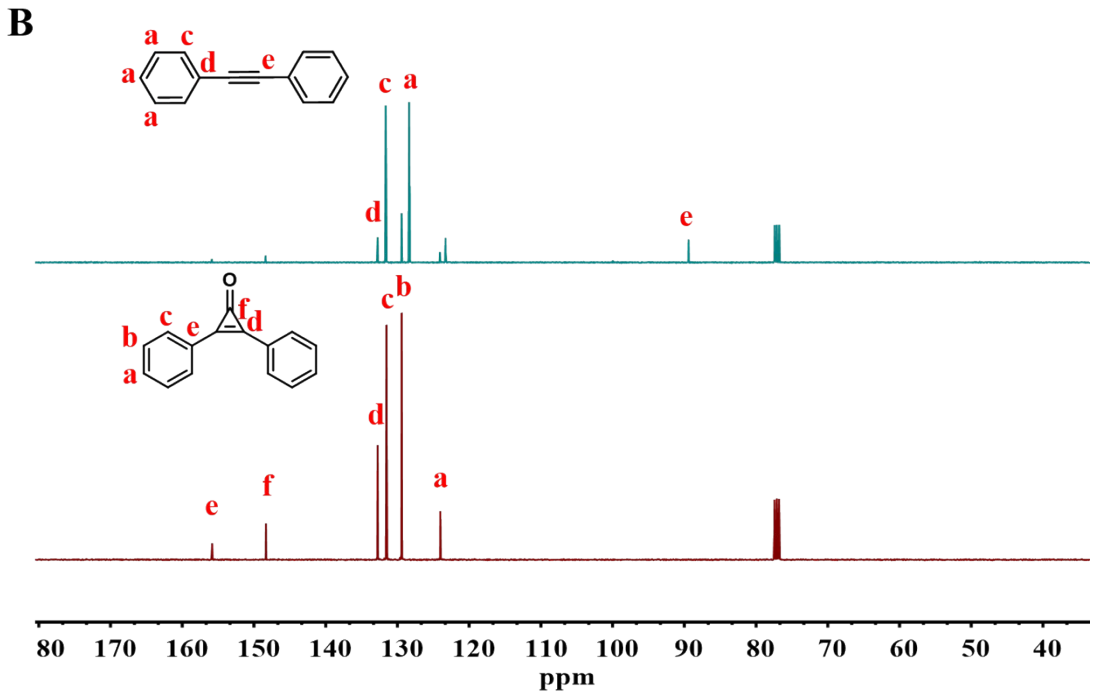


Fig. S9 (A) Mass spectrum of diphenylcyclopropenone; (B) ^{13}C NMR spectrum of diphenylcyclopropenone and diphenylcyclopropenone after UV irradiation. 10 mg of diphenylcyclopropenone was dissolved in 0.6 mL $CDCl_3$ and then irradiated under a handheld UV lamp (365 nm) for 8 min.

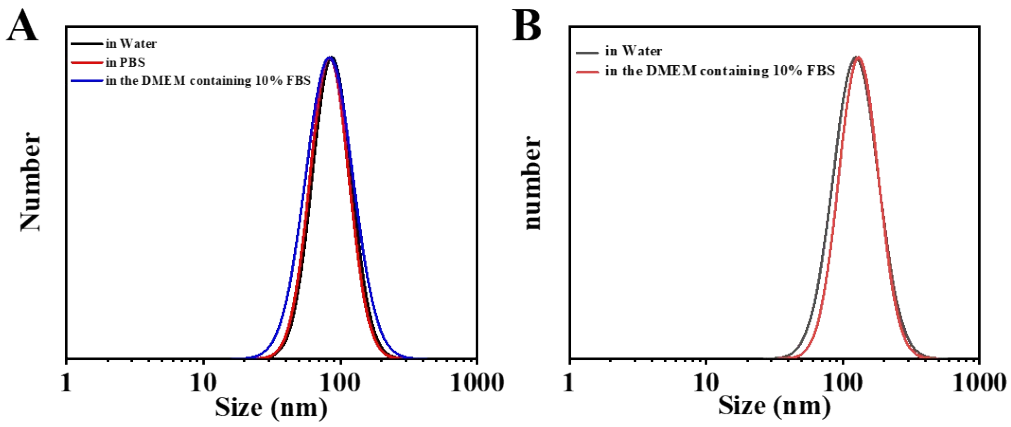


Fig. S10 (A) DLS diameters of Mito-PNBE micelles in different solvents. (B) DLS diameters of Fe-CO@Mito-PNBE micelles in different solvents.

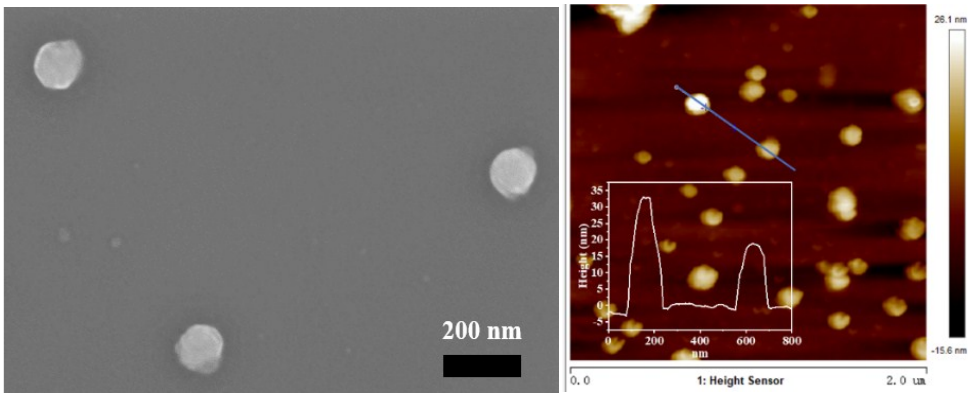


Fig. S11 TEM and AFM images of Mito-PNBE micelles.

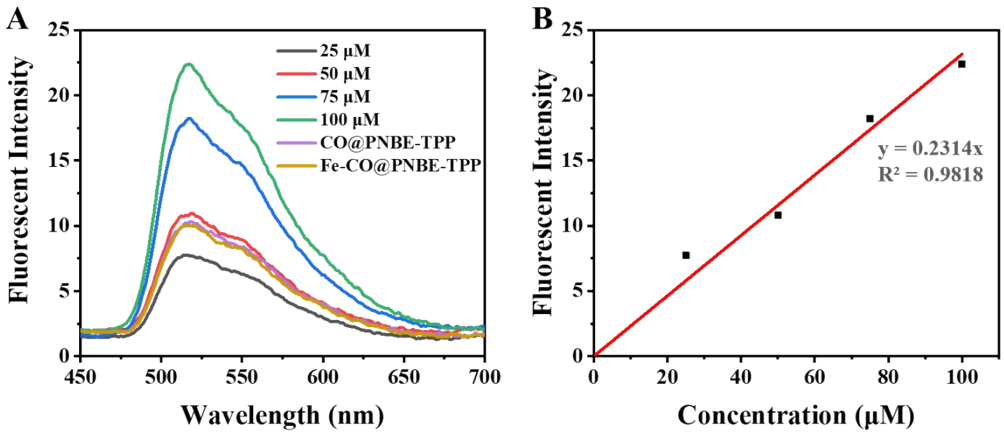


Fig. S12 (A) Fluorescent spectra changes of the probe system (FL-CO-1, 5 μM and $PdCl_2$, 5 μM) upon addition of different concentration of prodrug CO in water (with 10% DMSO, v/v) at 25 °C. λ_{ex}= 490 nm. (B) A linear relationship of fluorescence intensity changes of the probe system at 517 nm against the concentration of prodrug CO from 0 to 100 μM. The data were fitted (red line) by the equation: y=0.2314×[CO] with R^2=0.9818. CO@PNBE-TPP: DLE (%) = 9.13, DLC (%) = 1.50; Fe-CO@PNBE-TPP: DLE (%) = 9.06; DLC (%) = 1.29.

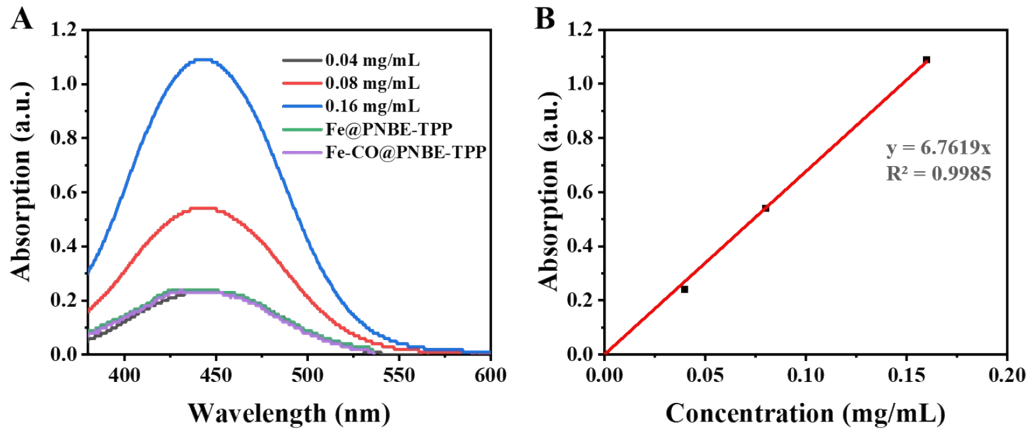


Fig. S13 (A) UV absorption spectra changes of different concentration of aminoferrocene-based prodrug in DMSO at 25 °C. (B) A linear relationship of absorption value changes of aminoferrocene-based prodrug at 442 nm against the concentration from 0 to 0.16 mg/mL. The data were fitted (red line) by the equation: y=6.7619×[Fe] with R^2=0.9985. Fe@PNBE-TPP: DLE (%) = 14.79, DLC (%) = 5.59; Fe-CO@PNBE-TPP: DLE (%) = 14.17, DLC (%) =5.29.

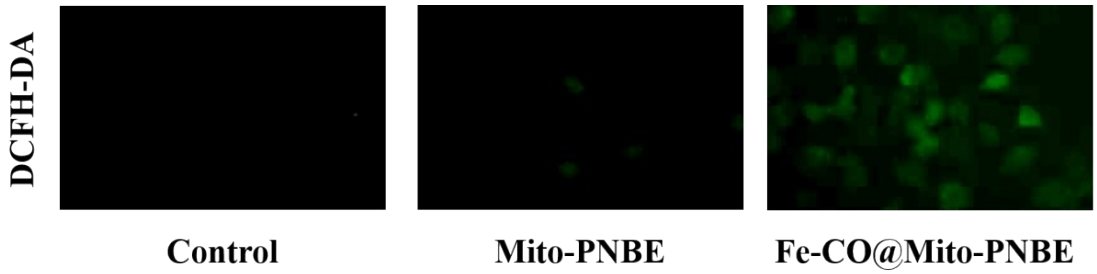


Fig. S14 DCFH-DA (ROS fluorescent label) staining in Hela cells upon being treated with Mito-PNBE and Fe-CO@Mito-PNBE for 4 h and irradiated for 8 min. Control group represents Hela cells in the dark.

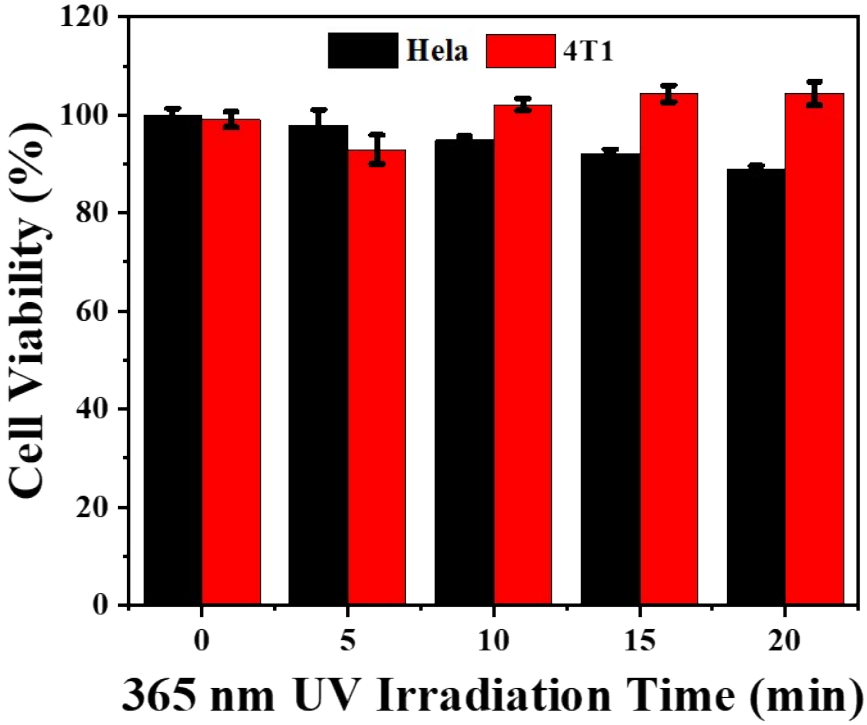


Fig. S15 Hela and 4T1 cells viability after UV irradiation respectively.

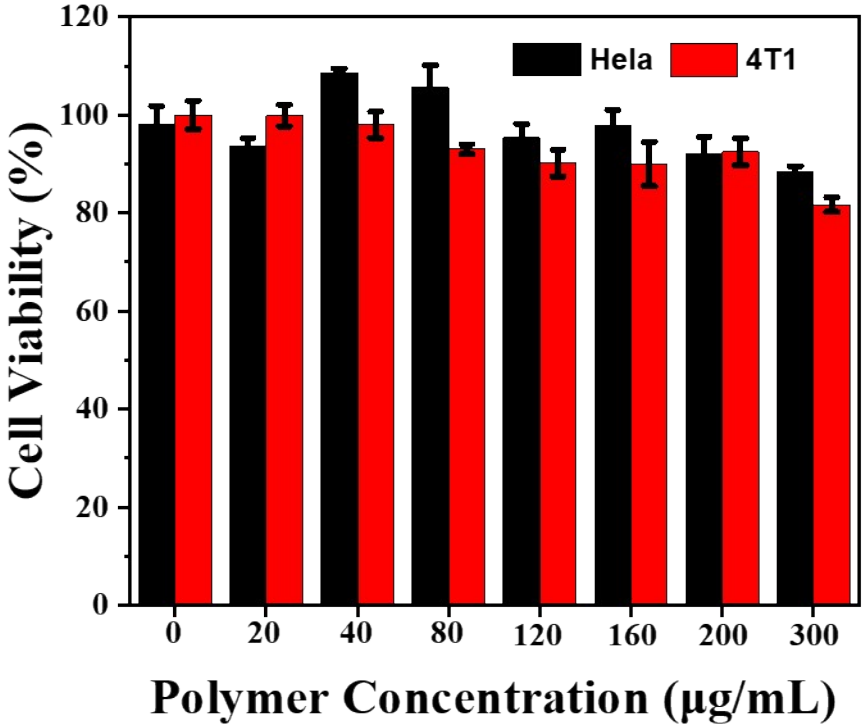


Fig. S16 Hela and 4T1 cells viability after being treated by Mito-PNBE micelles with

various concentrations.

Reference

1. S. Goggins, E. A. Apsey, M. F. Mahon and C. G. Frost, *Org Biomol Chem*, 2017, **15**, 2459-2466.