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# Supporting Information

# Conjugated/nonconjugated Alternating Copolymers for Enhanced NIR-II Fluorescence Imaging and NIR-II Photothermal-Ferrotherapy

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## 1. Experimental Section

### 1.1 Materials

4,8-bis (5-bromo-4 - (2-octyldodecyl) thiophene-2-yl) - benzo [1,2-c: 4,5-c '] bis [1,2,5] thiadiazole (BBTD),6,7-Bis(4-(hexyloxy)phenyl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (TTQ), 1,6-bis (5-trimethylbenzoyl) thiophene-2-yl) hexane (C6), 1,10-bis (5-trimethylbenzoyl) thiophene-2-yl) decane (C10) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (2T), Trimethyl thiophene (T) were purchased from Suzhou Nakai Technology Co., tetrakis(triphenylphosphine)palladium and tris (o-methylphenyl) phosphorus were obtained from J&K Scientific Ltd., , amino methoxy polyethylene glycol ($NH_2$-mPEG, Mw = 2K, Da), dopamine (DA) and Pluronic F-127 were purchased from Shanghai Macklin Biochemical Co., Other chemical catalysts are purchased from commercial sources (such as Aladdin chemical reagent company and Shanghai Macklin Biochemical Co., Ltd, etc.). Among them, toluene was dried and distilled with $N_2$ before use. Unless otherwise indicated, all the synthetic procedures of compounds

were performed in an anhydrous and oxygen-free condition, and all original regents except toluene were directly used. Dulbecco's modified eagle medium (DMEM), fetal bovine serum (FBS), and mouse breast cancer cells (4T1 cells) were achieved from KeyGEN BioTECH.

### 1.2 Instrumentations Characterization

The $^1$H NMR spectra were performed on a Bruker Ultra Shield Plus 400 MHz spectrometer at 298 K by choosing $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Gel permeation chromatography (GPC), determining the number-average molecular weight (Mn) and polydispersity (PDI) of the polymers, was performed with THF as the eluent using Shim-pack GPC-80 X columns. The morphology of nanoparticles was observed by a transmission electron microscope (TEM, Hitachi HT7700), whose acceleration voltage is 100 KV. Dynamic light scattering (DLS) analysis was conducted on a commercial laser light scattering spectrometer (ALV-7004; ALV-GmbH, Langen, Germany) equipped with a multi-τ digital time correlator and a He-Ne laser (λ = 632.8 nm). The hydrodynamic diameters (Dh) data were extracted through a CONTIN analysis. All samples we used for the test were optically cleared by filtration via 0.45 μm Millipore filter. The scattering angle was set up to 90° and all tests were conducted under room temperature. A Shimadzu UV-3600 spectrophotometer was utilized to record the absorption spectra of our samples at room temperature. NIR-II fluorescence spectra were measured using an NIR-II spectrophotometer (Fluorolog 3, Horiba), with an excitation wavelength of 808 nm obtained from a diode laser operating at 25.0 ± 0.5 °C. The 808 nm and 1064 nm laser were purchased from Changchun New Industries Optoelectronics Technology Co., Ltd. The *in vitro* and *in vivo* NIR-II FI imaging experiments were conducted on an NIR-II fluorescence imaging system (Wuhan Grand-imaging Technology Co., Ltd) under the 808 nm laser irradiation. A 640 × 512 pixel two-dimensional InGaAs array from Princeton Instruments in NIR-II fluorescence windows

was equipped in this NIR-II FI system. All photothermal tests were detected using a Fotric 225 instrument (IR thermal camera, ± 2 °C) purchased from Fotric Co., Ltd (Shanghai, China). The methyl thiazolyl tetrazolium (MTT) analysis was conducted using a PowerWave XS/XS2 microplate spectrophotometer (BioTek, Winooski, VT). The flow cytometry experiments were performed using a Flow Sight Imaging Flow Cytometer (Novocyte2040R, Aglient, U.S.A). The flow cytometry experiments were performed using a Flow Sight Imaging Flow Cytometer (Merck Millipore, Darmstadt, Germany). The NIR-II fluorescence imaging experiments were performed by an in vitro and in vivo NIR-II imaging system (Wuhan Grand-imaging Technology Co., Ltd) with 1064 nm LP filters and two types of lenses (50 or 100 mm) under an 808 laser. A 640 × 512 pixel two-dimensional InGaAs array from Princeton Instruments in NIR-II fluorescence windows was equipped in this NIR-II fluorescence imaging system.

### 1.3 Synthesis of six polymers and two small molecules

#### 1.3.1 Preparation of BBTD-2T, BBTD-C6, BBTD-C10

4,8-bis (5-bromo-4 - (2-octyldodecyl) thiophene-2-yl) - benzo [1,2-c: 4,5-c '] bis [1,2,5] thiadiazole (BBTD) (70.9 mg, 0.055 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (2T) (27.2 mg, 0.055 mmol), $Pd_2$ (dba) $_3$ (0.5 mg, 0.0016 mmol), $P(o\text{-}tol)_3$ (2.0 mg, 0.00218 mmol) and anhydrous toluene (2.5 ml) were added into a 10 mL polymerization tube to keep the whole system in an anhydrous and oxygen free environment. Then, it was placed in an oil bath and the temperature was maintained at 100 °C for reaction. When the color of the reaction solution changed from dark green to red brown, the reaction ended. Cool it to room temperature, extract the reaction solution, settle with methanol, then filter, and finally obtain black solid as the final BBTD-2T product. Yield: 41 mg.

BBTD (70.9 mg, 0.055 mmol), 1,6-bis (5-trimethylbenzoyl) thiophene-2-yl) hexane (C6 ) (31.8 mg, 0.055 mmol), $Pd_2$ (dba) $_3$ (0.5 mg, 0.0016 mmol), P (o-tol) $_3$ (2.0 mg, 0.00218 mmol) and anhydrous toluene (2.5 mL) were added into a 10 ml polymerization tube to maintain an anhydrous and oxygen free environment for the whole system. Then, they were placed in an oil bath and the temperature was maintained at 100 °C for reaction. When the color of the reaction solution changed from dark green to light green, the reaction was ended. Cool it to room temperature, extract the reaction solution, settle with methanol, then filter, and finally obtain dark green solid as the final BBTD-C6 product. Yield: 43 mg.

BBTD (70.9 mg, 0.055 mmol), 1,10-bis (5-trimethylbenzoyl) thiophene-2-yl) decane (C10) (35.1mg, 0.055 mmol), $Pd_2$ (dba) $_3$ (0.5 mg, 0.0016 mmol), P(o-Tol) $_3$ (2.0 mg, 0.00218 mmol) and anhydrous toluene (2.5 mL) to maintain the whole system in an anaerobic environment and then placed in an oil bath at 100 °C to end the reaction when the color changes from dark green to light green. Make it cool to room temperature, extract the reaction liquid with methanol settlement, then extract the filter, and finally get the green solid is the final BBTD-C10 product. Yield: 44 mg.

### 1.3.2 Preparation of TTQ-2T, TTQ-C6, TTQ-C10

Adding 6,7-Bis(4-(hexyloxy)phenyl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (TTQ) (47.45 mg, 0.055 mmol), 2T (13.58 mg, 0.0275 mmol), P(o-Tol) $_3$ (2.0 mg, 0.00218 mmol), $Pd_2$ (dba) $_3$ (0.5 mg, 0.0016 mmol) and anhydrous toluene (2.5 mL) to 10 mL tubes maintained the whole system in an anaerobic environment and then placed in an oil bath at 100 °C for the reaction when the color changed from dark green to red brown. Make it cool to room temperature, extract the reaction liquid with methanol settlement, then extract the filter, and finally get the black solid is the final product TTQ-2T. Yield: 39 mg.

TTQ (47.75mg, 0.055 mmol), C6 (21.73 mg, 0.0376 mmol), $Pd_2$ (dba) $_3$ (0.5 mg, 0.0016 mmol), P (o-Tol) $_3$ (2 mg, 0.00218 mmol) and anhydrous toluene (2.5 mL) to support the whole system in an oil bath for 100℃ when the color changes from dark green to brown. Make it cool to room temperature, extract the reaction liquid with methanol settlement, then extract the filter, and finally get the black solid is the final product TTQ-C6. Yield: 41 mg.

TTQ (47.75 mg, 0.055 mmol), C10 (21.73 mg, 0.0183 mmol), $Pd_2$ (dba) $_3$ (0.5 mg, 0.0016 mmol), P (o-Tol) $_3$ (2 mg, 0.00218 mmol) and anhydrous toluene (2.5 ml) were added into a 10 ml polymerization tube to maintain an anhydrous and oxygen free environment for the whole system. Then, it was placed in an oil bath and the temperature was maintained at 100 ℃ for reaction. When the mixture of reaction became viscous, the reaction ended. Cool it to room temperature, extract the reaction solution, settle with methanol, then filter, and finally obtain black solid as the final product TTQ-C10. Yield: 40 mg.

### 1.3.3 Preparation of T-BBTD-T and T-TTQ-T

BBTD (141.8 mg, 0.11 mmol), Trimethyl thiophene (T) (123.15mg, 0.33mmol), PD2 (dba) $_3$ (2mg, 0.0064mmol), P (o-tol) $_3$ (7mg, 0.00763 mmol) and anhydrous toluene (5.0 mL) were added into two 10ml bottles, wrapped with tinfoil and protected from light. The mixture of BBTD, T, PD2 (DBA) $_3$ and P (o-tol) $_3$ in toluene was subjected to three freeze-thaw cycles, and then heated to 120 ℃ under anhydrous and oxygen free conditions and stirred overnight. After cooling, the crude product obtained by evaporation is purified by column chromatography to obtain green solid powder T-BBTD-T. Yield: 37 mg.

TTQ (94.9mg, 0.11 mmol), T (123.15mg, 0.33mmol), PD2 (dba) $_3$ (2mg, 0.0064mmol), P (o-tol) $_3$ (7mg, 0.00763 mmol) and anhydrous toluene (5mL) were added into two 10ml bottles,

wrapped with tinfoil and protected from light. The mixture of TTQ, T, $Pd_2$ (DBA) $_3$ and P (o-tol) $_3$ in toluene was subjected to three freeze-thaw cycles, and then heated to 120 ℃ under anhydrous and oxygen free conditions and stirred overnight. After cooling, the crude product obtained by evaporation is purified by column chromatography to obtain green solid powder T-TTQ-T. Yield: 29 mg.

### 1.3.4 Preparation of PMA-AD-PEG

Poly (IB-alt-MAnh) (2250.0 mg, molecular weight (Mw) 6 kDa), dopamine (DA) (28.72 mg 0.18 mmoL), $NH_2$-PEG-2K (750 mg) and TEA (0.5 mL) were dissolved in 300 mL of dry N, N-Dimethylformamide (DMF) under the vacuum conditions and stirred at room temperature. After 6 days, DMF was removed by reduced pressure distillation, and the residual solid was dissolved in appropriate amount of deionized water. To remove unreacted $NH_2$-PEG and other impurities, the obtained solution was further purified by dialysis against water for 7 days with a dialysis bag ($M_W$ 14000 Da).

## 1.4 Fabrication of nanoparticles based on conjugated polymers and conjugated polymers

BBTD6@PMA: BBTD-C6 were prepared by a conventional nanoprecipitation method with poly PMA-AD-PEG and amphiphilic copolymer F-127 at molar ratio of 1:2. First, BBTD-C6 (1mg) was dissolved in anhydrous tetrahydrofuran (THF) (3 mL). The THF solution was then rapidly injected into deionized water(10mL) containing poly PMA-AD-PEG (10mg) and amphiphilic copolymer F-127(20mg). Finally, THF was evaporated, and BBTD6@PMA were obtained.

BBTD6/$Fe^{2+}$@PMA: CNAPs copolymer BBTD-C6 and $Fe^{2+}$ ions were incorporated into poly PMA-AD-PEG and amphiphilic copolymer F-127 at molar ratio of 1:2 to form

BBTD6/$Fe^{2+}$/PMA-AD-PEG nanoparticles. First, CANPs BBTD-C6 was dissolved in anhydrous tetrahydrofuran (THF). The THF solution was then rapidly injected into deionized water containing poly PMA-AD-PEG and amphiphilic copolymer F-127. Under agitated conditions, 1 mL $FeSO_4$ solution (0.1mmol $mL^{-1}$) is injected into the nanoparticle solution by drops and stirred overnight. Finally, THF was evaporated, and BBTD6@PMA were obtained.

**1.5 Photostability**

The photostability of nanoparticles aqueous solutions in water were determined by Shimadzu UV-3600 spectrophotometer. Firstly, 1.0 mL nanoparticles solution (0.1 mg $mL^{-1}$) was mixed with 1 mL water, respectively, and then the corresponding photostability was determined by continuous irradiation with 1064 nm laser for 30 min. Finally, the fluorescence intensity of 1064 nm was plotted as a function of time.

**1.6 *In vitro* photothermal effect and photothermal conversion efficiency**

To evaluate the photothermal effect of the BBTD6@PMA and BBTD/Fe@PMA, 100 μL of three nanoparticle solutions with concentrations of 0.1, 0.08, 0.06 and 0.02 mg $mL^{-1}$ were successively irradiated with 1064 nm laser (1.0 W $cm^{-2}$, 7 min). The temperature changes of the three nanoparticle solutions were performed with an IR thermal camera, and these data were recorded every 30 s.

As we all known, the nature of photothermal therapy is that photothermal agents having the inherent ability to absorb NIR light convert NIR laser energy into heat. Hence, it is important to first explore the photothermal conversion efficiency (ŋ) of the NPs. To study the photothermal conversion behavior of BBTD6@PMA and BBTD/Fe@PMA, a thermal imaging camera (Fotric 225, Fotric Precision Instruments, USA, ± 2 °C) was used to perform the thermal imaging of NPs

in an aqueous solution. First, an aqueous solution of nanoparticles (0.1 mg $mL^{-1}$) was configured, 100 μL of which was added into a 200 μL centrifuge tube. The temperature changes of a fixed concentration of NPs (0.1 mg $mL^{-1}$) were irradiated with a 1064 nm laser (1.0 W $cm^{-2}$, 8 min), and then the laser was shut off. Finally, we can obtain a temperature increase and drop curve.

The photothermal conversion efficiency (ŋ) was calculated using equations (1) and (2) expressed below. The photothermal conversion efficiency of the BBTD6/Fe@PMA was determined to be through the collected data and equation.

$$\eta = [hS(T_{max}-T_{suur})-Q_{dis}]/[I(1-10^{-A1064})] \quad (1)$$

$$\tau_s = m_D C_D/hS \quad (2)$$

The parameters S, h, $T_{max}$, $T_{surr}$, $Q_{dis}$, I and $A_{1064}$ are the container's surface area, heat-transfer coefficient, maximum laser-trigger temperature, indoor temperature, heat dissipation caused by the light absorbing of quartz cuvette, intensity of laser (1.0 W $cm^{-2}$) and absorbance of BBTD6/Fe@PMA at 1064 nm, respectively.

Parameter $\tau_s$ is the time constant of the sample system. The parameters $m_D$ and $C_D$ are the mass and heat capacity of the solvent, respectively.

### 1.7 *In vitro* Cellular Uptake

4T1 cells were cultured in DMEM with 10% fetal bovine serum. And cells were maintained at 37 °C and 5% $CO_2$ conditions. The 4T1 cells were also used for the assessment of cellular uptake. First, 4T1 cells were cultured with DMEM in CLSM culture dishes (Costar) until the cell density increased to $1 \times 10^2$ cells $mL^{-1}$ per well. Subsequently, the medium was replaced by one of the two groups, including 1 mL fresh DMEM medium alone and the 1mL mixture of fresh DMEM medium and BBTD6@PMA-FITC (0.01 mg $mL^{-1}$), respectively. The treated cells were further incubated at 37 °C and 5% CO2 condition for 12 h. After 12 h, the cells were washed twice

to remove the cell debris and were then incubated with 4,6-Diamidino-2-phenylindole (DAPI) dye solution for 10 min. Finally, the cells were imaged using CLSM (Olympus Fluoview FV1000, Olympus Corp., Japan).

### 1.8 *In vitro* Photocytotoxity Assay

The 4T1 cells were used for the *in vitro* cytotoxicity assessment of BBTD6/Fe@PMA by MTT assays. First, cells, seeded at $2 \times 10^4$ cells/well, were cultured in DMEM in 96-well plates at 37 °C and 5% $CO_2$ condition for 24 h. Then, the medium was replaced by a mixture of fresh DMEM medium and different concentrations of BBTD6@PMA and BBTD6/Fe @PMA (0,6.25, 12.5 25, 50 and 100μg $mL^{-1}$), following which the selected wells (BBTD6@PMA + laser group and BBTD6/Fe@PMA + laser) were irradiated under 1064 nm laser illumination (1.0 W $cm^{-2}$) for 5 min and further incubated at 37 °C and 5% CO2 for 24 h. The BBTD6@PMA and BBTD6/Fe @PMA treated wells (BBTD6@PMAgroup and BBTD6/Fe @PMA group) were not irradiated with 1064 nm laser illumination. Afterwards, the medium was replaced with 100 μL of fresh DMEM medium, and 20 μL of MTT (5 mg $mL^{-1}$) was added to each well. Finally, after 4 h of incubation, the upper supernatant was removed, and 100 μL of DMSO was added. Cell viability was calculated by measuring the absorbance at 490 nm using a PowerWave XS/XS2 microplate spectrophotometer.

### 1.9 Assessment of NIR-II Photothermal/ferrotherapy Effect *in vitro* by Confocal Imaging and Flow Cytometry

The 4T1 cells were used for the assessment of the photothermal effect by confocal imaging. Firstly, the 4T1cells were cultured with DMEM in CLSM culture dishes (Costar) until the cell density increased to $1 \times 10^5$ cells $mL^{-1}$ per well. Subsequently, the medium was replaced with a

mixture medium (100 μg $mL^{-1}$) of the fresh DMEM medium and BBTD6@PMA or BBTD6/Fe @PMA for 12h in the dark, the media were removed, the cells were washed by PBS and replaced with fresh DMEM. The selected wells were then irradiated with or without the 1064 nm laser illumination (1.0 W $cm^{-2}$, 5 min), respectively. After 24 h of apoptosis, the cells were washed twice to remove the cell debris and were then incubated with calcein- AM/propidium iodide (PI) dye solution for 10 min. Finally, the cells were imaged using CLSM (Olympus Fluoview FV1000, Olympus Corp., Japan).

The 4T1 cells were used for the assessment of the photothermal effect by flow cytometry. First, the 4T1 cells were cultured with DMEM in 6-well plates until the cell density increased to 1 × $10^5$ cells $mL^{-1}$ per well. The medium was then replaced with a mixture medium of fresh DMEM medium and BBTD6@PMA or BBTD6/Fe @PMA (100 μg $mL^{-1}$) for 12h in the dark, the media were removed, the cells were washed by PBS and replaced with fresh DMEM.. Subsequently, the selected wells were irradiated with or without the 1064 nm laser illumination (1.0 W $cm^{-2}$, 5 min), respectively. After 24 h of apoptosis, the wells underwent two iterations of supernatant removal and the 500 μL PBS addition to remove dead cells. The PBS was then removed and EDTA was added, and the cells were dissolved in an incubator at 37 °C and 5% $CO_2$ condition for 7 min. Later, 1 mL of DMEM was added, and the cells were transferred into a 15 mL centrifuge tube. After the cells were centrifuged for 3 min, the supernatant was removed, Annexin V-FITC/PI dye solution was added to the collected cells for staining, and the cells were tested by Novocyte2040R.

**1.12 Animal model**

All experiments using animals were performed according to the specifications of The National Regulation of China for Care and Use of Laboratory Animals, and the protocol was

approved by the Jiangsu Administration of Experimental Animals. 4T1 tumor-bearing mice (age 5-6 weeks) were obtained from the Jiangsu KeyGEN BioTECH. 4T1 tumors were planted by hypodermic injection of suspension of 4T1 cells into the right armpit of mice. The tumor volume was calculated as the following equation:

$$V=0.5\ LW^2 \quad (1)$$

The parameter L and W are the longitudinal and transverse diameters of the tumor, respectively.

### 1.13 *In vivo* NIR-II Fluorescence Imaging of Vascular system and Tumor

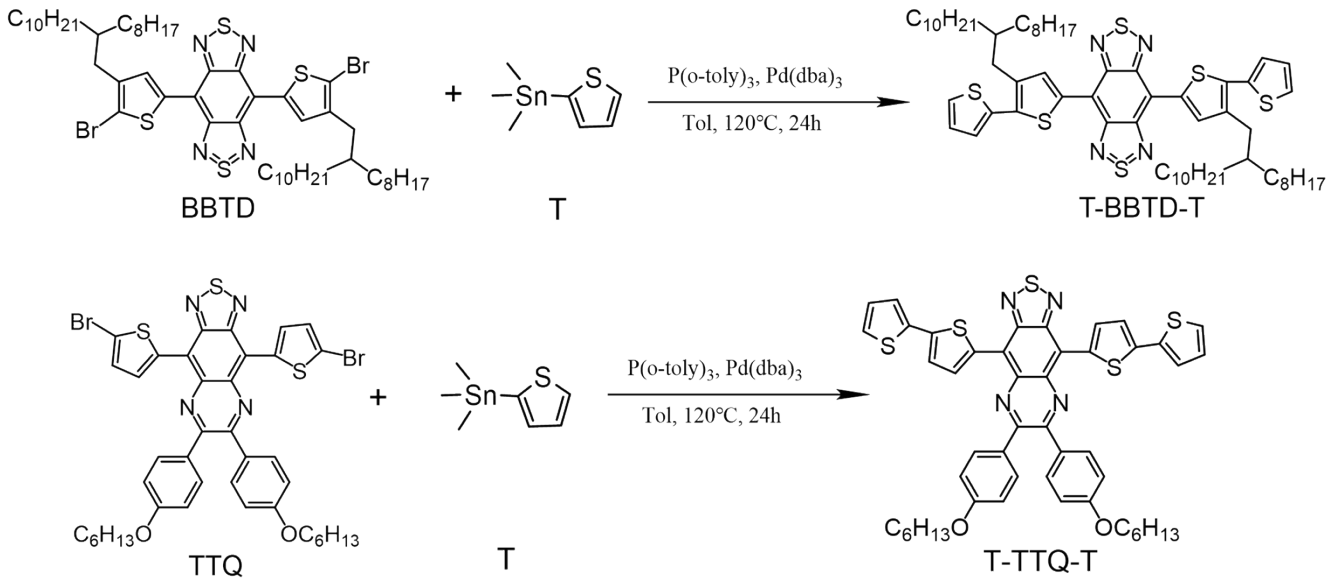
For further biological applications, NIR-II fluorescence images of the vascular system (including the body vessel) and tumor were captured using the NIR-II fluorescence imaging system. When the average tumor volume of 4T1 tumor-bearing mice reached approximately 100 $mm^3$, the mice were intravenously injected with BBTD6/Fe@PMA solution (100 μL, 2 mg $mL^{-1}$). The mice were then anesthetized, following which the comatose mice were fixed upside down in the NIR-II fluorescence imaging system. The NIR-II fluorescence imaging of the entire body and the vasculatures of the hind limb and belly vessel were performed under the 808 nm laser excitation with 1064 nm LP filter. Subsequently, these images of the vasculatures of the hind limb and belly vessel were processed using Image J software to obtain their corresponding full width at half maximum (FWHM) and signal background ratio (SBR). Meanwhile, real-time *in vivo* NIR-II fluorescence imaging was performed at different post-injection times under the 808 nm laser excitation with 1064 nm LP filter. Finally, the NIR-II fluorescence signal intensity of NIR-II images was measured using the NIR-II *in vivo* imaging system software.

In addition, to examine the biodistribution of BBTD6/Fe@PMA, 4T1 tumor-bearing mice were sacrificed on 20 h post injection of BBTD6/Fe @PMA. The tumor and the main organs (heart, liver, spleen, lung, and kidney) were excised and subsequently placed in the NIR-II fluorescence system. Their images were captured with 1064 LP filter under the 808 nm laser excitation. It was found that the strong NIR-II fluorescence signal was mainly observed in the tumor, liver and spleen.

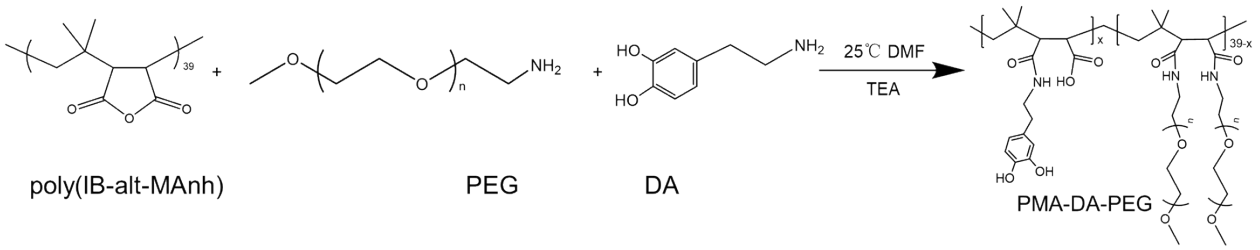
### 1.14 *In vivo* Photothermal therapy (PTT)/ ferrotherapy

When the average tumor volume of 4T1 tumor-bearing mice reached approximately 100 $mm^3$, the mice were randomly divided into four groups (five mice per group). Two groups of mice were administered with PBS intravenously, while the other groups of mice were intravenously injected with BBTD6/Fe@PMA (100 μL, 2 mg $mL^{-1}$). Two groups of mice injected with PBS were treated with or without 1064 nm laser illumination, so do the other groups of mice injected with BBTD6/Fe@PMA. When the mice of the two groups irradiated by the 1064 nm laser excitation were intravenously injected for 24 h, they were anesthetized and subsequently exposed to the 1064 nm laser on the tumor site for 5 min with a power density of 1.0 W $cm^{-2}$. In addition, the temperature changes of the tumor sites were recorded, and *in vivo* photothermal images were captured. Afterwards, these mice were housed under SPF conditions. Tumor size, tumor weight, and body weight were monitored and measured every two days. At 15 days, these mice were sacrificed, and the tumors were collected. The collected tumors were fixed in 4% neutral-buffered paraformaldehyde and embedded in paraffin for hematoxylin-eosin (H&E) staining, and the images of the histological tumor sections were obtained.

## 2. Figures




**Scheme S1.** The synthetic route of the small molecule T-BBTD-T and T-TTQ-T.




**Scheme S2.** The synthetic route of the small molecule PMA-DA-PEG.

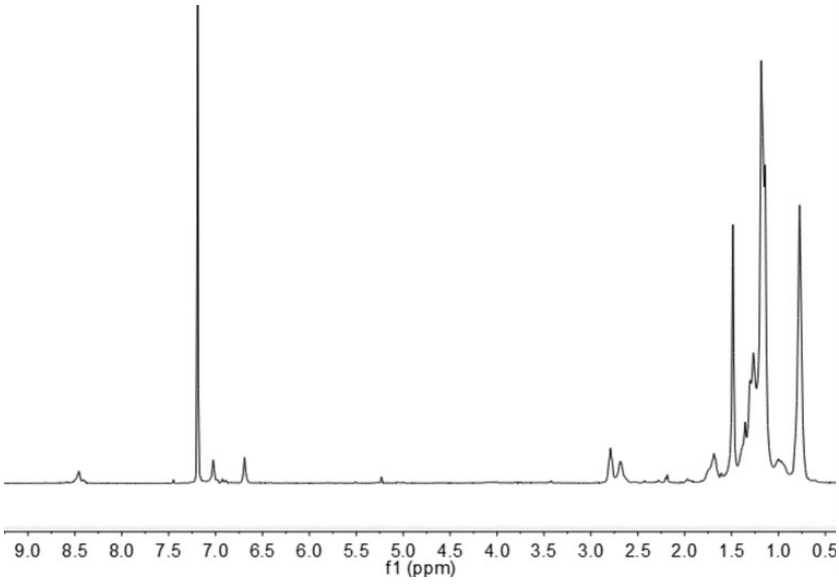



**Fig. S1** $^{1}$H NMR spectrum of BBTD-C10 in $CDCl_3$.

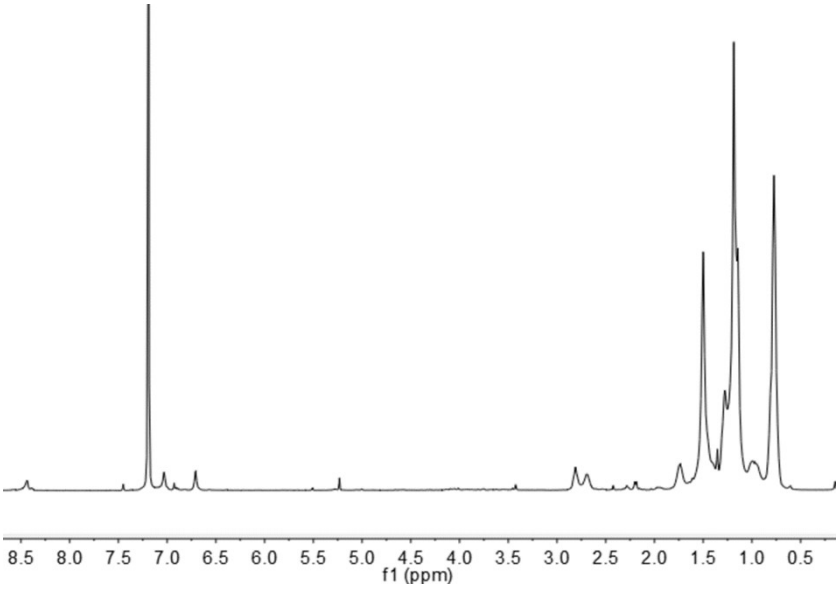



**Fig. S2** $^{1}$H NMR spectrum of BBTD-C6 in $CDCl_3$.

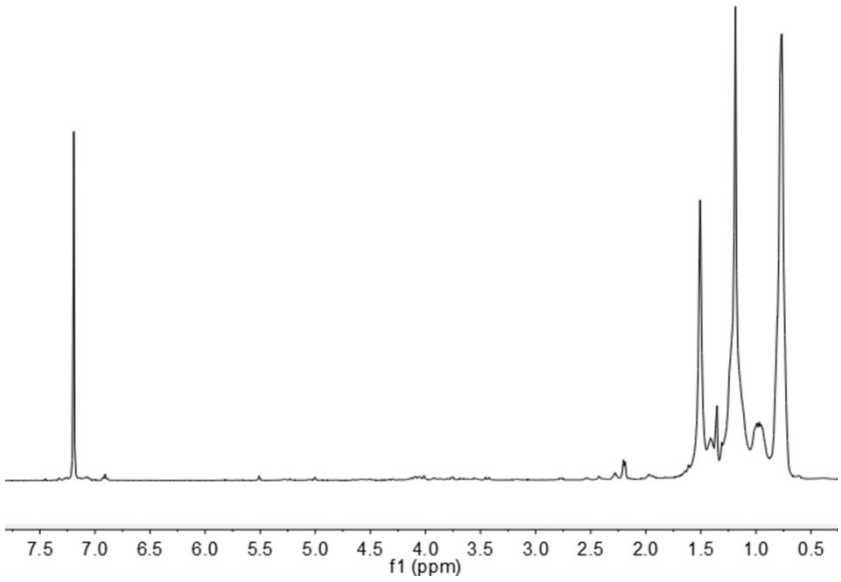



**Fig. S3** $^{1}$H NMR spectrum of BBTD-2T in $CDCl_3$.

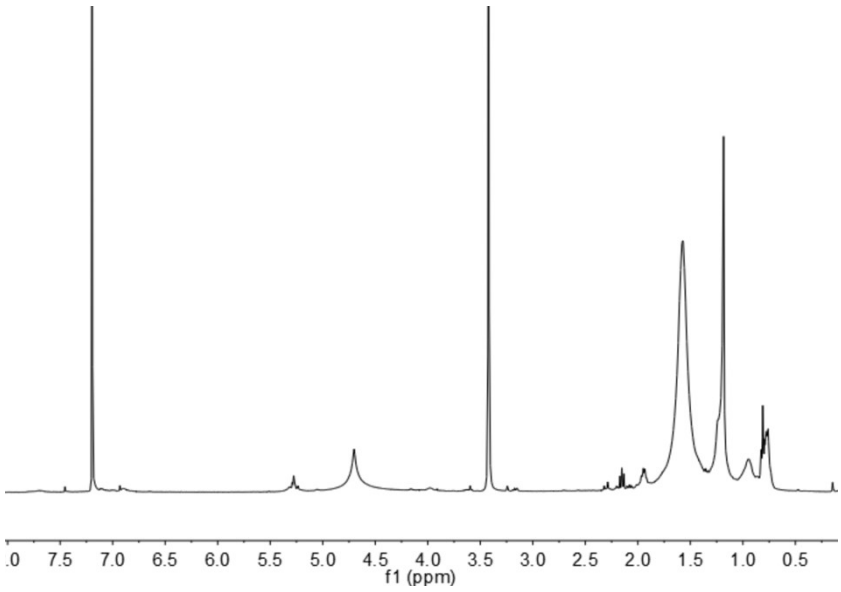



**Fig. S4** $^{1}$H NMR spectrum of TTQ-C10 in $CDCl_3$.

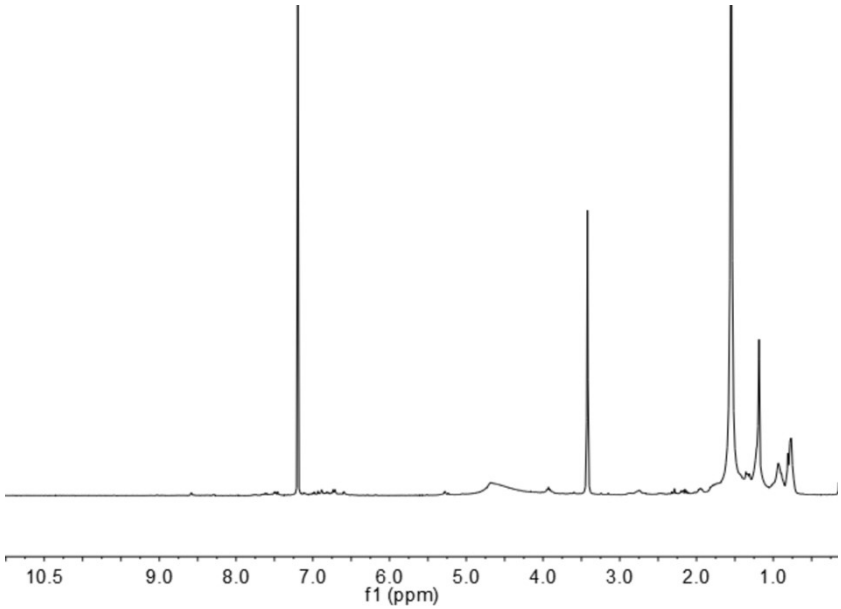



**Fig. S5** $^{1}$H NMR spectrum of TTQ-C6 in $CDCl_3$.

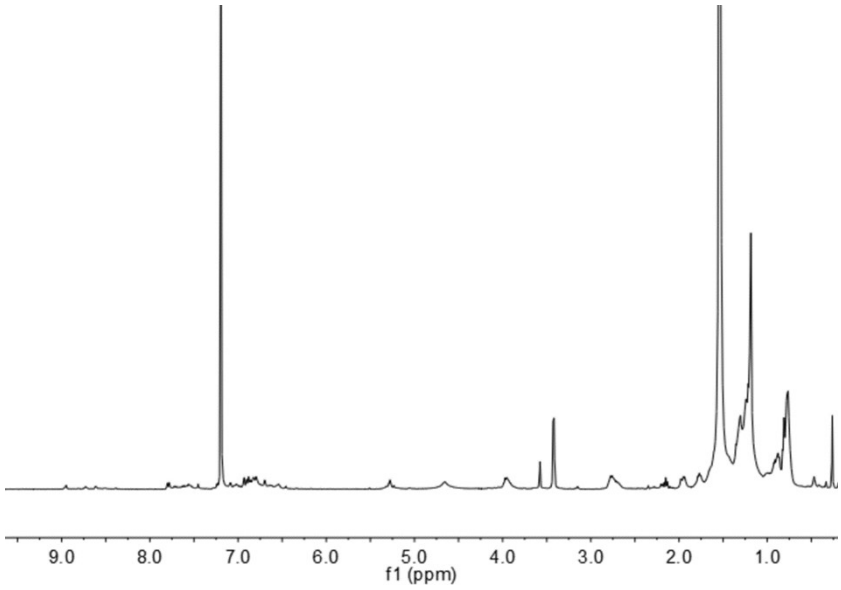



**Fig. S6** $^{1}$H NMR spectrum of TTQ-2T in $CDCl_3$.

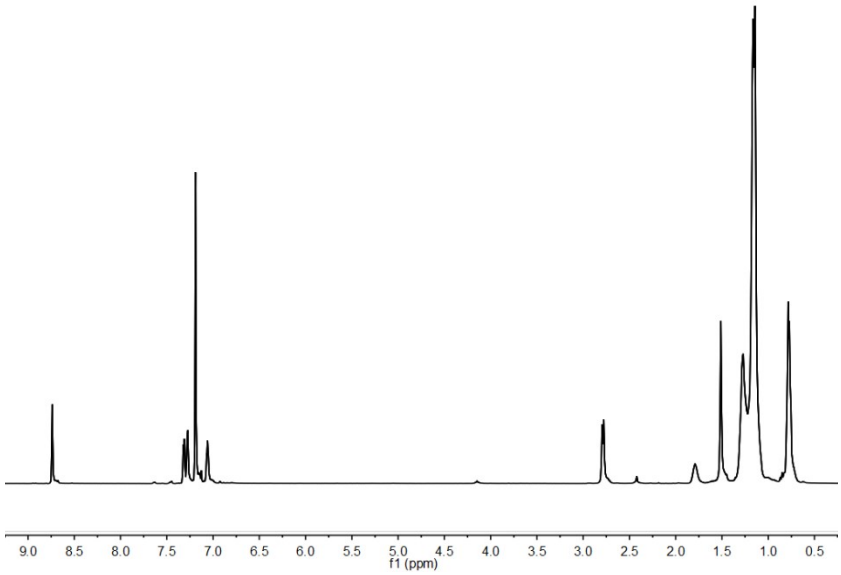



**Fig. S7** $^{1}$H NMR spectrum of T-TTQ -T in $CDCl_3$.

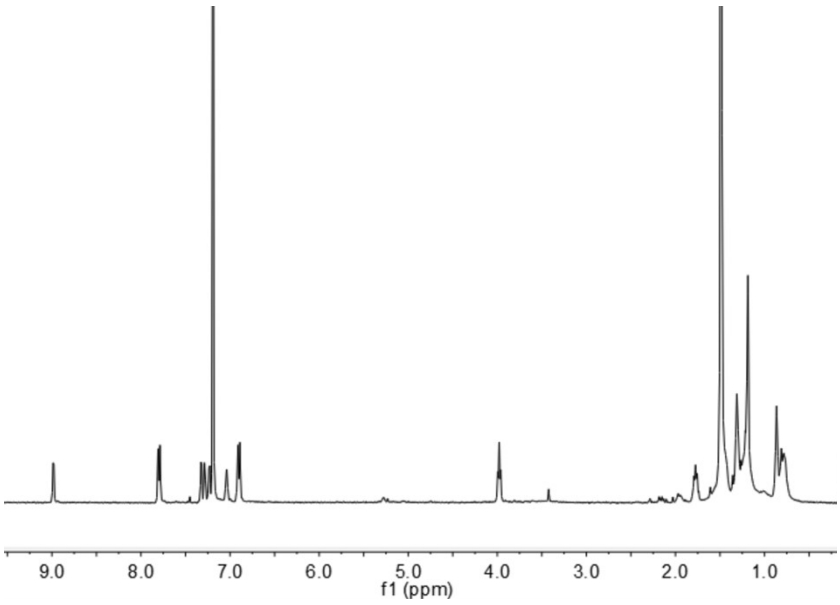



**Fig. S8** $^{1}$H NMR spectrum of T-BBTD-T in $CDCl_3$.

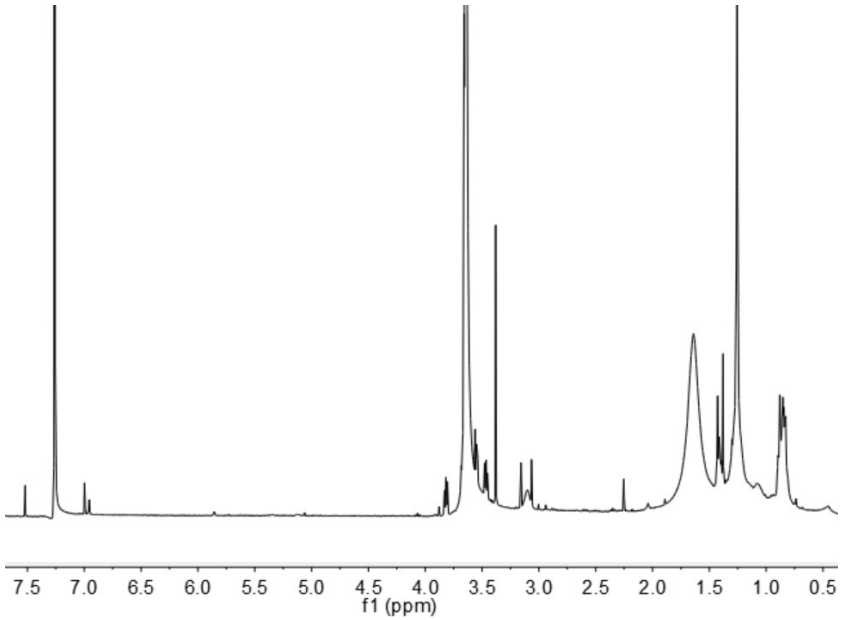



**Fig. S9** $^{1}$H NMR spectrum of PMA-DA-PEG in $CDCl_3$

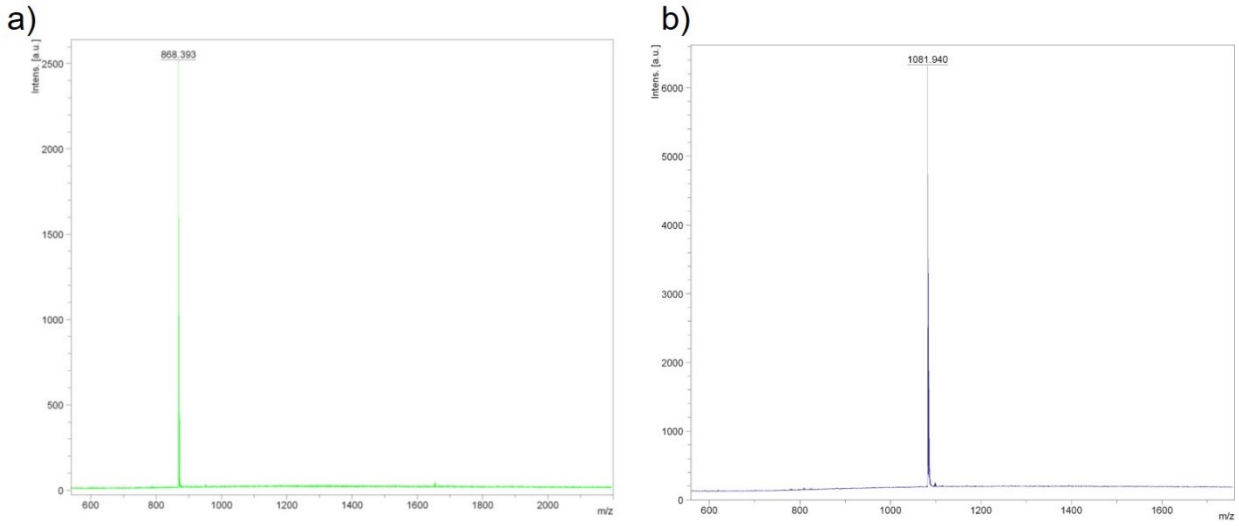



**Fig. S10** MALDI-TOF mass spectrometry of a) T-TTQ-T, b) T-BBTD-T

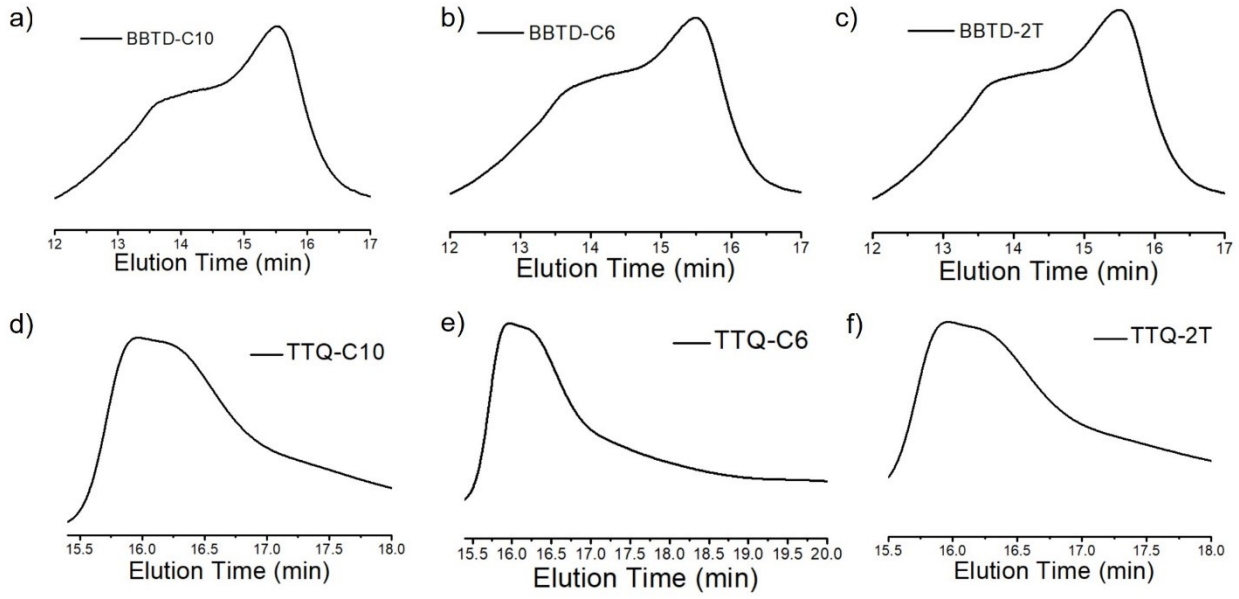



**Fig. S11** The GPC curves of BBTD-C10, BBTD-C6, BBTD-2T, TTQ-C10, TTQ-C6 and TTQ-2T using THF as eluent.

**Table S1.** GPC results of the synthesized polymers BBTD-C10, BBTD-C6, BBTD-2T, TTQ-C10, TTQ-C6 and TTQ-2T.

| Sample name | Mn (g $mol^{-1}$) | PDI |
|---|---|---|
| BBTD-C10 | 17800 | 1.436 |
| BBTD-C6 | 15900 | 1.457 |
| BBTD-2T | 16600 | 1.490 |
| TTQ-C10 | 37200 | 1.337 |
| TTQ-C6 | 38900 | 1.512 |
| TTQ-2T | 36800 | 1.501 |

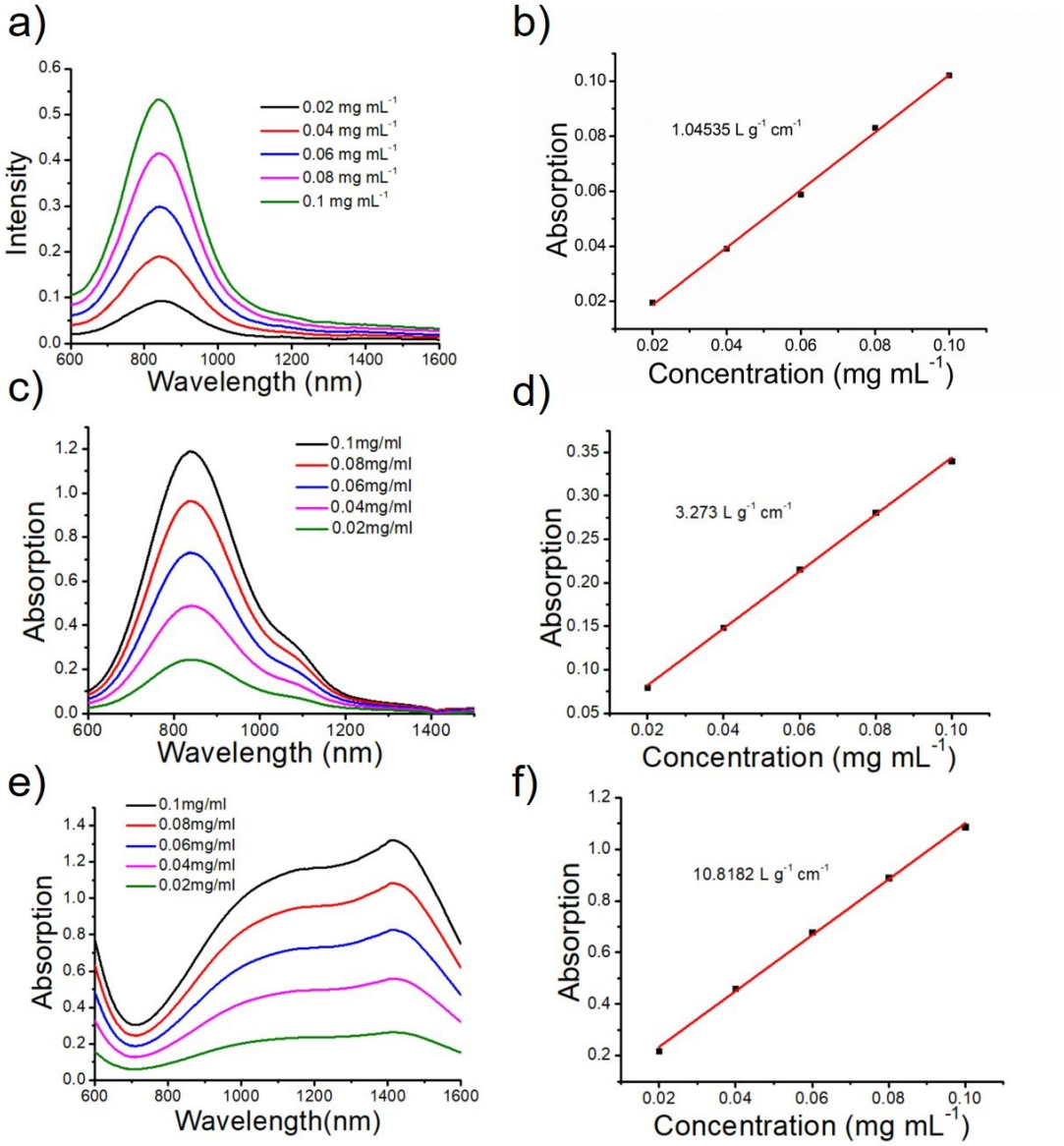



**Fig. S12** Photophysical performances of three conjugated polymers: UV-vis-NIR absorption spectra of (a) BBTD-C10, (c) BBTD-C6 and (e) BBTD-2T in THF at different concentrations. (b), (d) and (f) were their extinction coefficients at their corresponding peaks of 1064 nm, respectively.

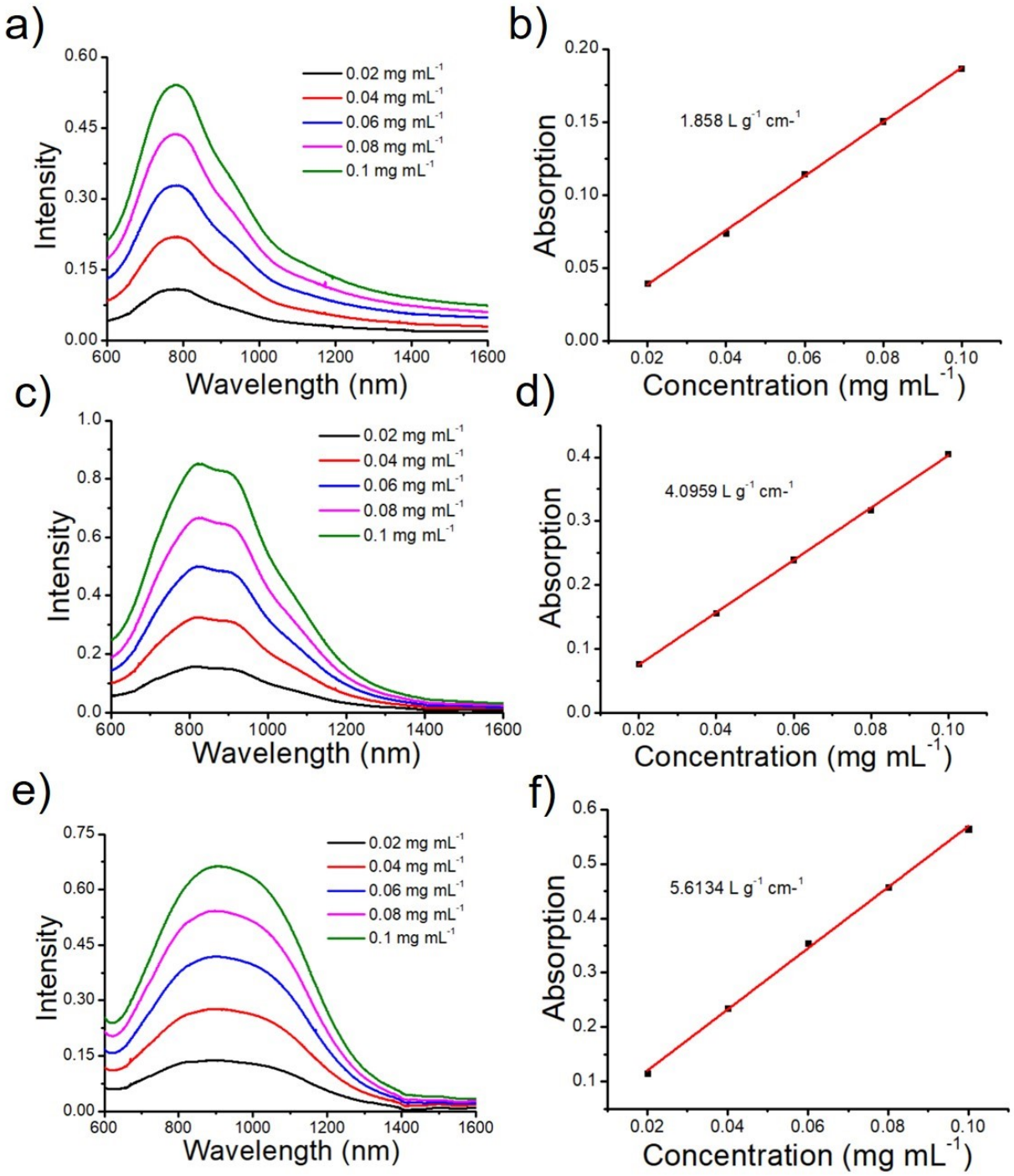



**Fig. S13** Photophysical performances of three conjugated polymers: UV-vis-NIR absorption spectra of (a)TTQ-C10, (c)TTQ-C6 and (e) TTQ-2T in THF at different concentrations. (b), (d) and (f) were their extinction coefficients at their corresponding peaks of 1064 nm, respectively.

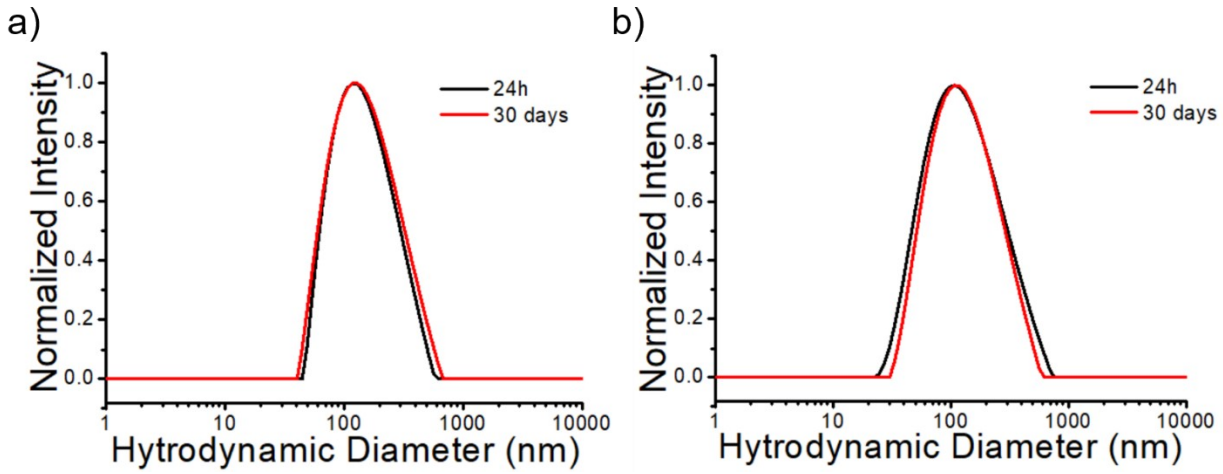



**Fig. S14** Hydrodynamic diameters of (a) BBTD6@PMA and (b) BBTD6/Fe@PMA dispersed in water after storage for 24 h and 30 d, respectively.

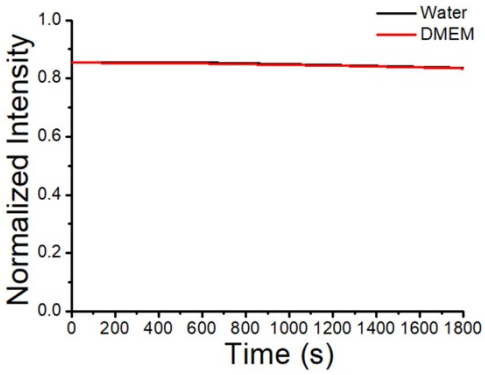



**Fig. S15** Photostability test curves of BBTD/Fe@PMA

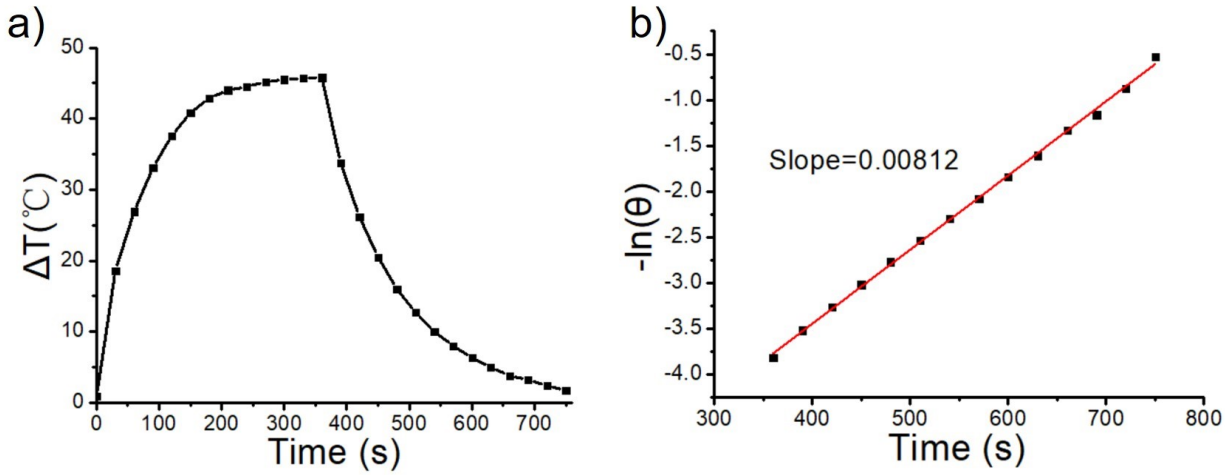


**Fig. S16** Photothermal conversion efficiency of deionized water: (a) The photothermal heating and cooling curves of deionized water under the 1064 nm laser irradiation. (b) Linear time data versus negative natural logarithm was obtained from the cooling period.

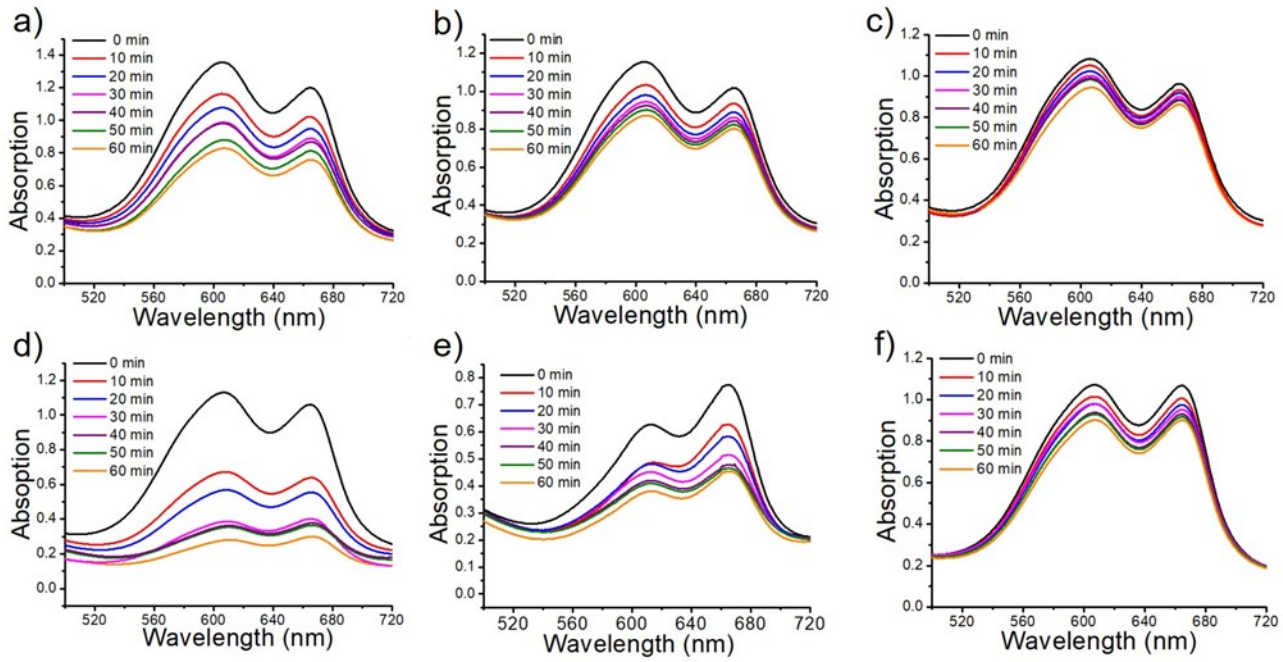



**Fig. S17** The absorption spectrum change curve of MB in different condition (a) pH =5.5; (b) pH =6.8; (c) pH=7.4; (d) pH =5.5+ Laser (e) pH =6.8+ Laser; (f) pH =7.4+ Laser.

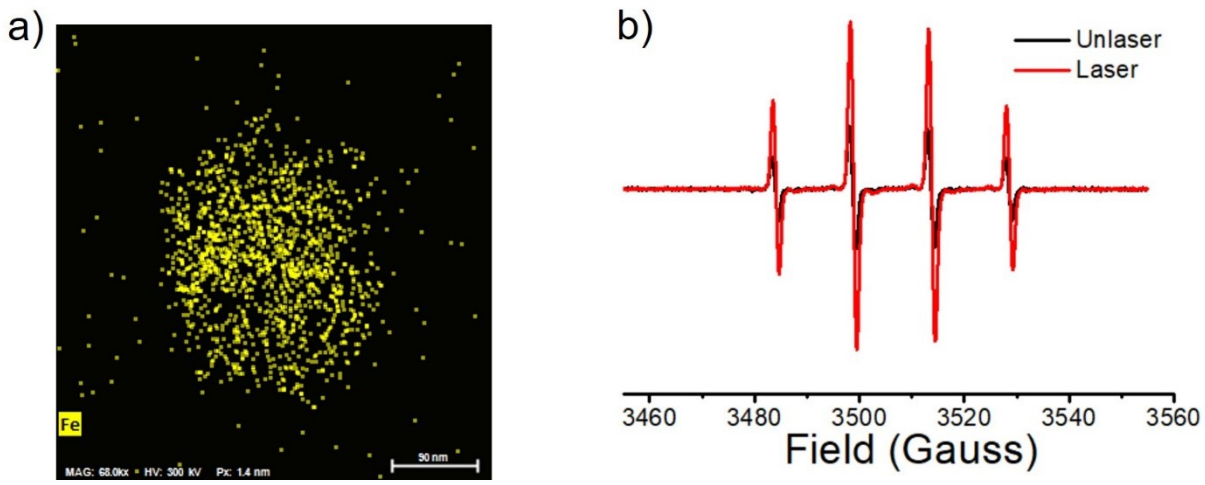



**Fig. S18** (a) TEM-EDS element mapping of BBTD6/Fe@PMA; (b) ESR spectra of aqueous solutions BBTD6/Fe@PMA.

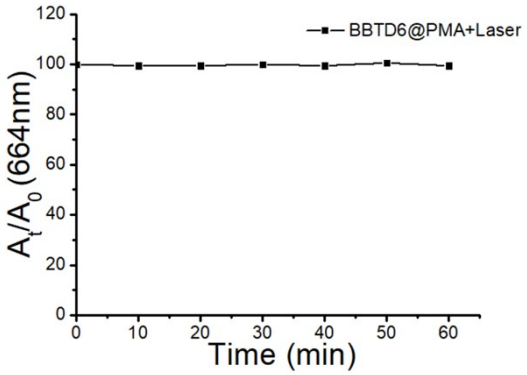



**Fig. S19** ·OH generation profiles of BBTD6@PMA (PH=5.5).

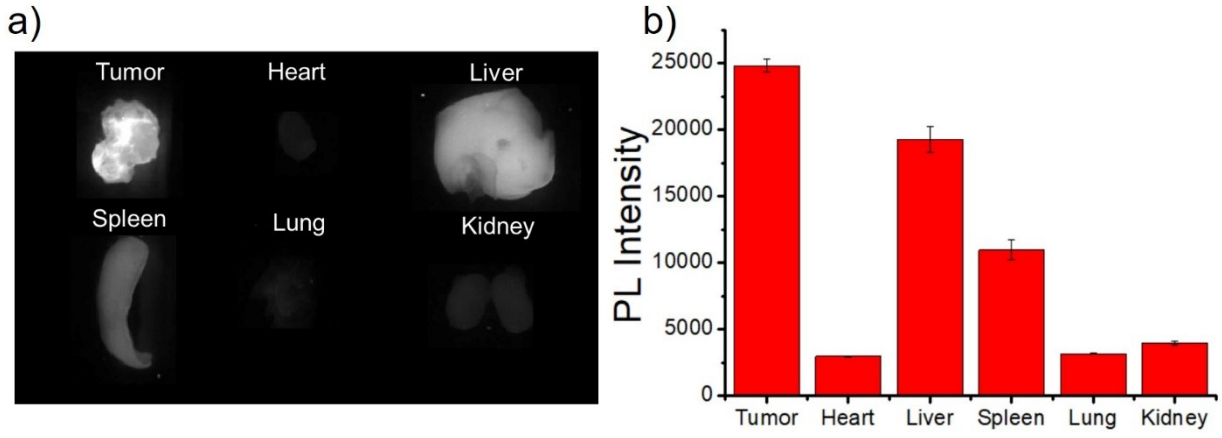


**Fig. S20** (a) *In vitro* NIR-II fluorescence images of tumor and major organs (heart, liver, spleen, lung, and kidney) after 20 h of intravenous injection (808 nm laser, 1064 nm LP filter, 500 ms). (b) Quantitative NIR-II fluorescence intensity of tumor and major organs.

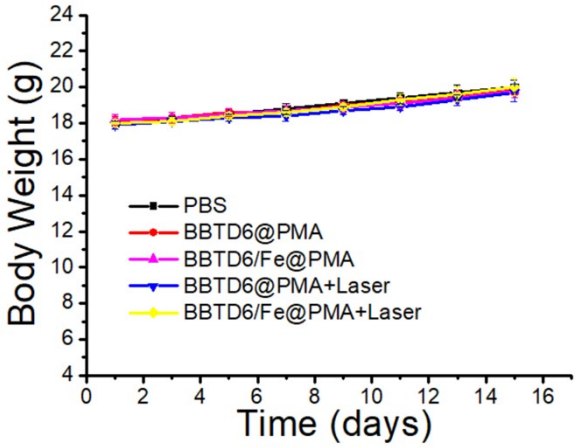



**Fig. S21** Changes of body weight with time for different treatment groups.

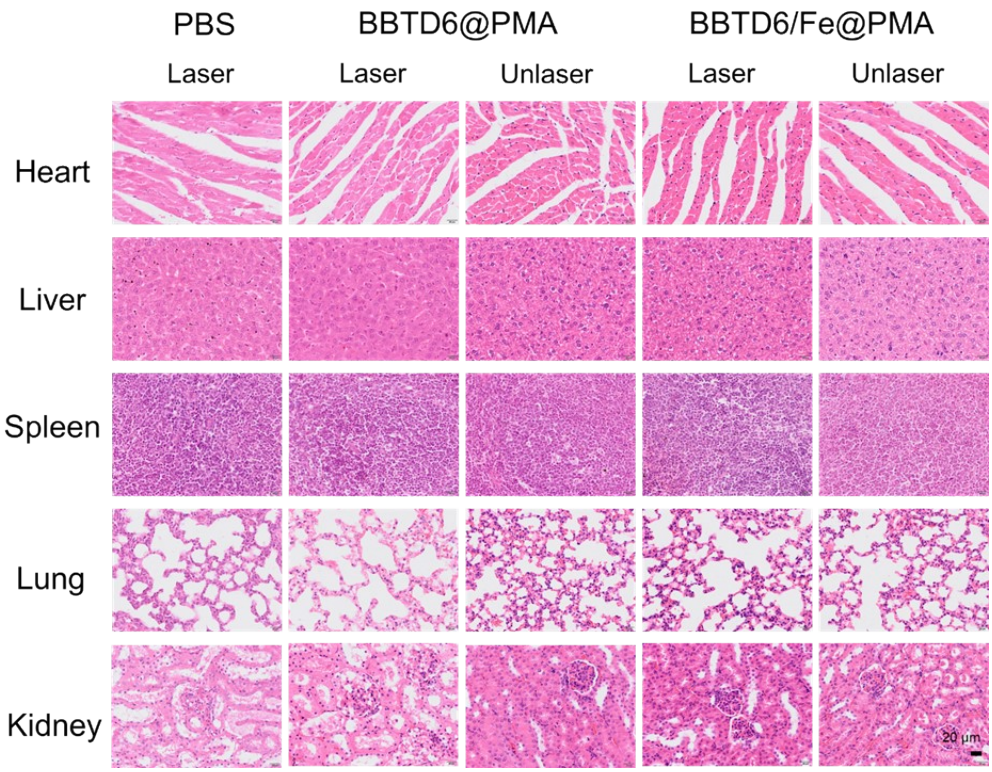



**Fig. S22** H&E staining images of organs (heart, liver, spleen, lung, and kidney) sections obtained from the five treatment group.