

Supporting Information

D-A-D organic fluorescent probes for NIR-II fluorescence

imaging and efficient photothermal therapy of breast cancer

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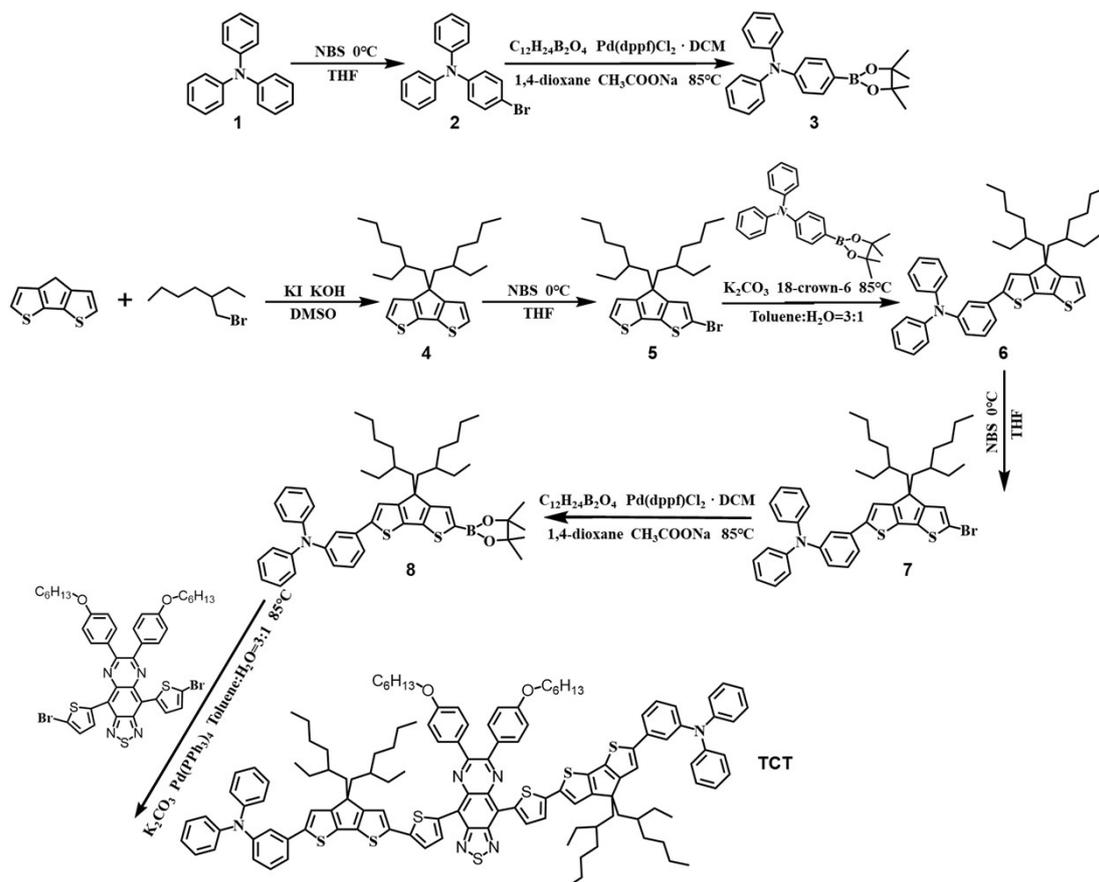


Figure S1 TCT synthesis scheme.

1. Synthesis of 4-bromo-N, N-diphenylaniline

Triphenylamine (TPA) (3 mmol, 0.733 g, 1 eq) and 20 ml tetrahydrofuran (THF) were added to a 100 ml round-bottom flask, vacuumed, filled with nitrogen, and then wrapped with tin foil. Subsequently, N-bromosuccinimide (NBS) (3 mmol, 0.534 g, 1 eq) was slowly added to the round-bottom flask. The reaction was carried out at 0°C for 12 h in the dark. After the reaction was completed, it was allowed to stand at room temperature. Then the organic layer was extracted with ethyl acetate (EA), washed with saturated salt water, and dried with anhydrous MgSO₄, and then the colorless oily product was obtained by filtration and vacuum distillation. Finally, 4-bromo-N, N-

diphenylaniline (intermediate **2**) (2.66 mmol, 0.8634 g) was obtained by silica gel column chromatography with n-hexane as eluent, and the yield was 88.7 %.

2. Synthesis of N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline

Add intermediate **2** (2.5 mmol, 0.81 g, 1 eq), bis(pinacolato)diboron ($C_{12}H_{24}B_2O_4$) (3.75 mmol, 0.952g, 1.5 eq), and 1,1'-bis(diphenylphosphine)ferrocene-palladium dichloride dichloromethane adduct ($Pd(dppf)Cl_2 \cdot DCM$) (0.125 mmol, 0.102 g, 0.05 eq) into anhydrous 1,4-dioxane (25ml), then also add CH_3COONa (10 mmol, 0.8 g, 4 eq) in 100ml round bottom flask. Then it was vacuumed filled with nitrogen, and placed in a condensation reflux device at 85 °C for 12 h. The product was cooled to room temperature and extracted 3-4 times with dichloromethane (DCM) and salt water to separate the yellow liquid at the bottom. Subsequently, anhydrous $MgSO_4$ sulfate was added to stand for 30 min to remove water, followed by suction filtration and rotary evaporation. Finally, a pale-yellow oily product N, N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (intermediate **3**) (2.05 mmol, 0.7626 g) was obtained with a yield of 82%. The TOF characterization is shown in the following **Figure S2**.

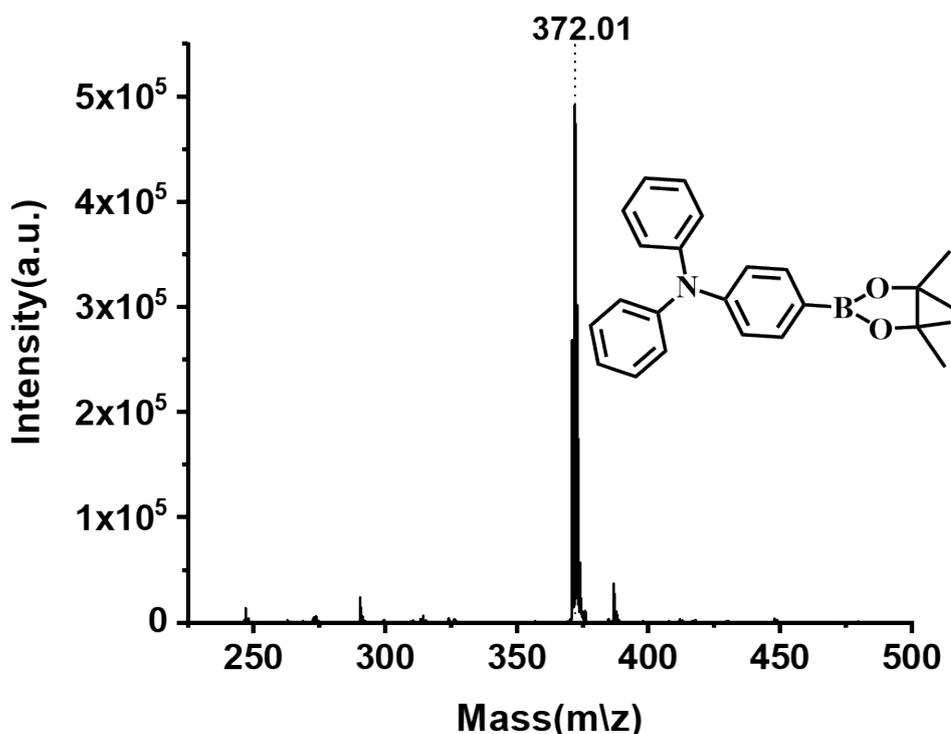


Figure S2 Time of Flight Mass Spectrometry (TOF) characterization of intermediate **3**.

3. Synthesis of 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene

4H-Cyclopenta[2,1-b:3,4-b'] dithiophene (CPDT) (3 mmol, 0.5337 g, 1 eq), 2-ethyl-hexyl bromide (6 mmol, 1.1589 g, 2 eq), KI (0.6 mmol, 0.9960 g, 0.2 eq) and 30 mL anhydrous DMSO were added to a 100 mL round-bottom flask. Then the round-bottomed flask was vacuumed, filled with N₂, and repeated multiple times. Next, add KOH (12 mmol, 0.6732 g, 4 eq) and react at room temperature for 15 h. After the completion of the reaction, saturated salt water and n-hexane were used to extract 3-4 times. Then, anhydrous magnesium sulfate was added and allowed to stand for 30 min to remove all water. After filtration and vacuum distillation, the crude product was obtained. After the completion of the reaction, saturated salt water and n-hexane were used to extract 3-4 times. Then anhydrous magnesium sulfate was added to stand for 30 min to remove water, and the crude product was obtained by filtration and vacuum distillation. The 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (intermediate 4) (2.394 mmol, 0.9623 g) was purified by silica gel column chromatography with n-hexane as eluent, and the yield is 79.7%.

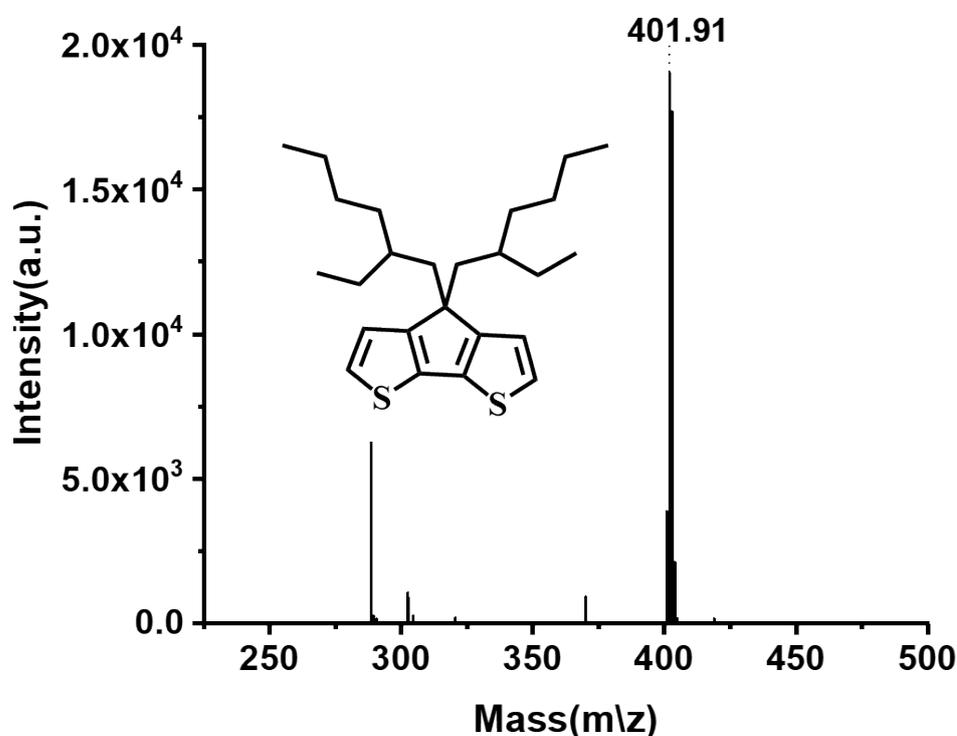


Figure S3 Time of Flight Mass Spectrometry (TOF) characterization of intermediate 4.

4. Synthesis of 2-bromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene

The intermediate product **4** (2 mmol, 0.8038 g, 1 eq) and 25 mL THF have been added to a 100 mL round bottom flask. The round-bottomed flask was completely wrapped with tin foil paper and vacuumed, and then N₂ was introduced (15 min). Slowly add NBS (2.2 mmol, 0.3916 g, 1.1 eq) dropwise under N₂ environment and ice water bath conditions, and react in the dark for 12 h. After the reaction was completed, it was reduced to room temperature and extracted 3-4 times with DCM and saturated salt water. Then an excess of anhydrous MgSO₄ was added and allowed to stand for 30 minutes to remove moisture. Next, the crude product is obtained by filtration and vacuum distillation. The crude product was purified by silica gel column chromatography using DCM as eluent. Finally, the yellow oily product 2-bromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (intermediate **5**) (1.545 mmol, 0.7403 g) was obtained in 77.2% yield.

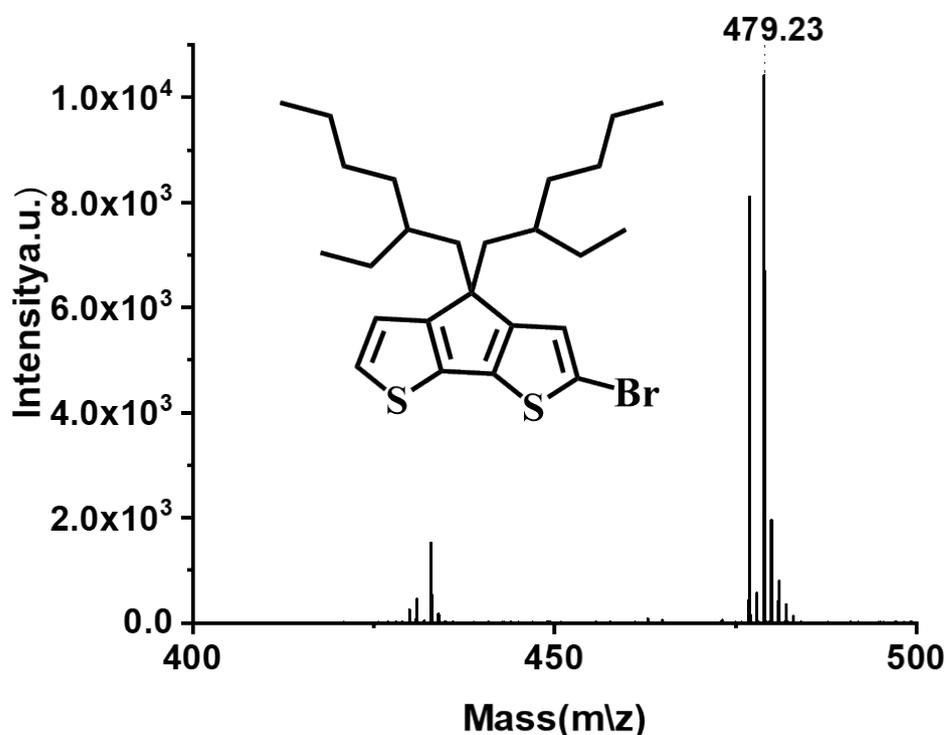


Figure S4 Time of Flight Mass Spectrometry (TOF) characterization of intermediate **5**.

5. Synthesis of 3-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-N,N-diphenylaniline

Intermediate **3** (1.5 mmol, 0.558 g, 1 eq), intermediate **5** (1.5 mmol, 0.7188 g, 1 eq), K_2CO_3 (6 mmol, 0.8292 g, 4 eq), 18-crown-6 (0.015 mmol, 0.0040 g, 0.003 eq) were placed in a 100 mL round-bottom flask. After adding 30 mL toluene and 10 mL deionized water, the mixture was vacuumed and filled with N_2 , repeated 2-3 times, and the reaction was carried out at 85°C for 24 h. When the reaction was completed, it was reduced to room temperature and extracted with DCM and saturated salt water 3 times. Then anhydrous $MgSO_4$ was added and allowed to stand for 30 min to remove water. After filtration and vacuum distillation, the crude product was obtained. Finally, the crude product was purified by silica gel column chromatography with DCM/n-hexane (1:3) as eluent, and then subjected to vacuum distillation to obtain a yellowish-brown oily product 3-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-N,N-diphenylaniline (intermediate **6**) (1.065 mmol, 0.687 g), with a yield was 72%.

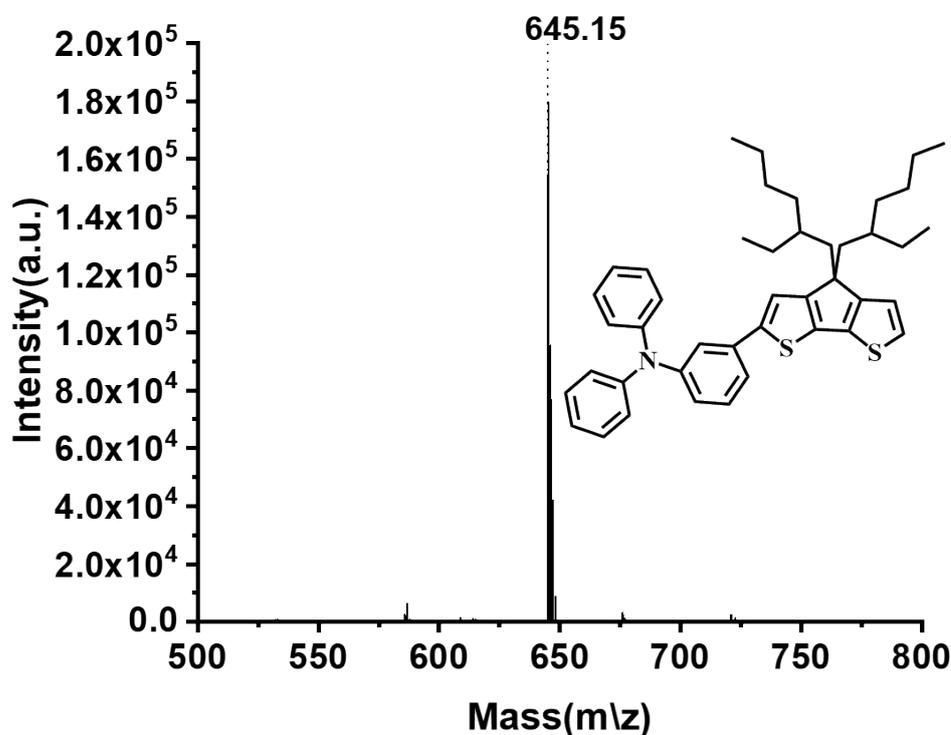


Figure S5 Time of Flight Mass Spectrometry (TOF) characterization of intermediate **6**.

6. Synthesis of 3-(6-bromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-N,N-diphenylaniline

The above intermediate **6** (1.0 mmol, 0.645 g, 1 eq) was added to a 100 ml round-bottom flask, and then 20 ml tetrahydrofuran (THF) was added, vacuumed, and filled with nitrogen. Then NBS (1.2 mmol, 0.2136 g, 1.2 eq) was dissolved in 5 mL THF and slowly added to a round-bottomed flask. The reaction was carried out at 0°C for 12 h in the dark. After the reaction was completed, the organic layer was extracted with ethyl acetate and washed with saturated salt water 3-4 times. MgSO₄ was used to remove water by standing for 30 min, and then the crude product was obtained by filtration and vacuum distillation. Finally, the crude product was separated by silica gel column chromatography with DCM as eluent to obtain a yellowish-brown oily product 3-(6-bromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-N,N-diphenylaniline (intermediate **7**) (0.8680 mmol, 0.6285 g) was obtained by silica gel column chromatography with DCM as eluent, and the yield was 86.8%.

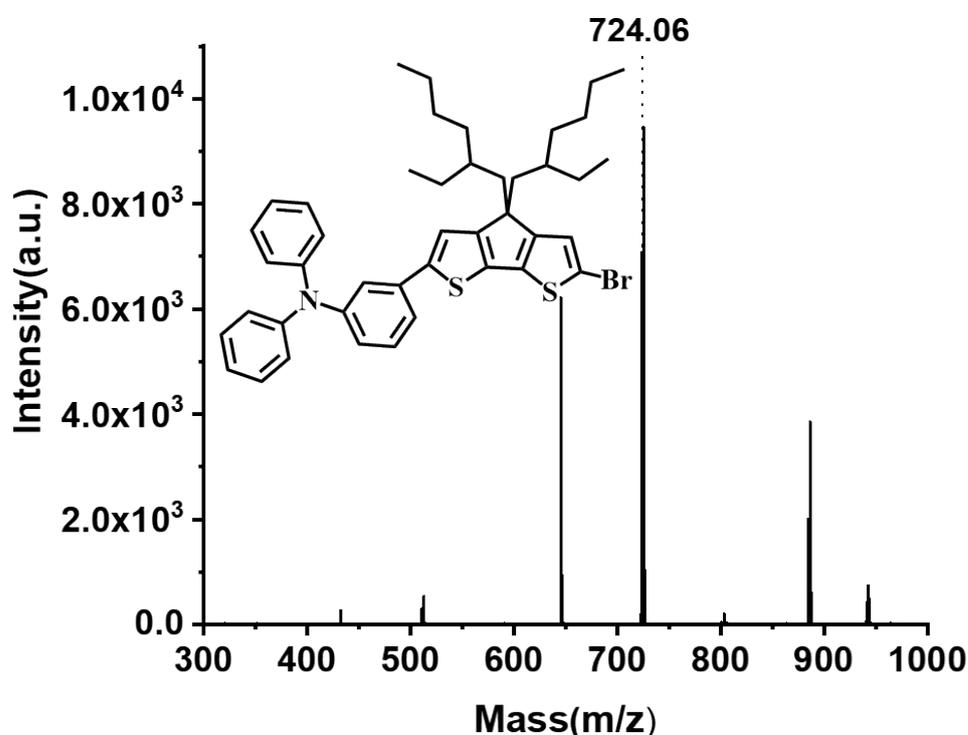


Figure S6 Time of Flight Mass Spectrometry (TOF) characterization of intermediate **7**.

7. Synthesis of 3-(4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-N,N-diphenylaniline

Intermediate 7 (0.87mmol, 0.6299g, 1 eq), $C_{12}H_{24}B_2O_4$ (1.0 mmol, 0.2538 g, 1.2 eq), $Pd(dppf)Cl_2 \cdot DCM$ (0.0435 mmol, 0.0355 g, 0.05 eq), CH_3COONa (3.48 mmol, 0.2780g, 4 eq) and anhydrous 1,4-dioxane (25 mL) were added to a 100 mL round-bottom flask. Then vacuum, through N_2 , placed in a condensation cycle device at 85 °C for 12 h. After the reaction was completed, it was cooled to room temperature, and then DCM and saturated salt water were added to extract 2-3 times to separate the yellow liquid at the bottom. Then anhydrous $MgSO_4$ was added to remove the water, and the crude product was obtained by suction filtration and vacuum rotary evaporation. Finally, the dark yellow oily substances 3-(4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-N,N-diphenylaniline (intermediate 8) (0.70 mmol, 0.539 g) was obtained by silica gel column chromatography with DCM as eluent, the yield was 80.35%.

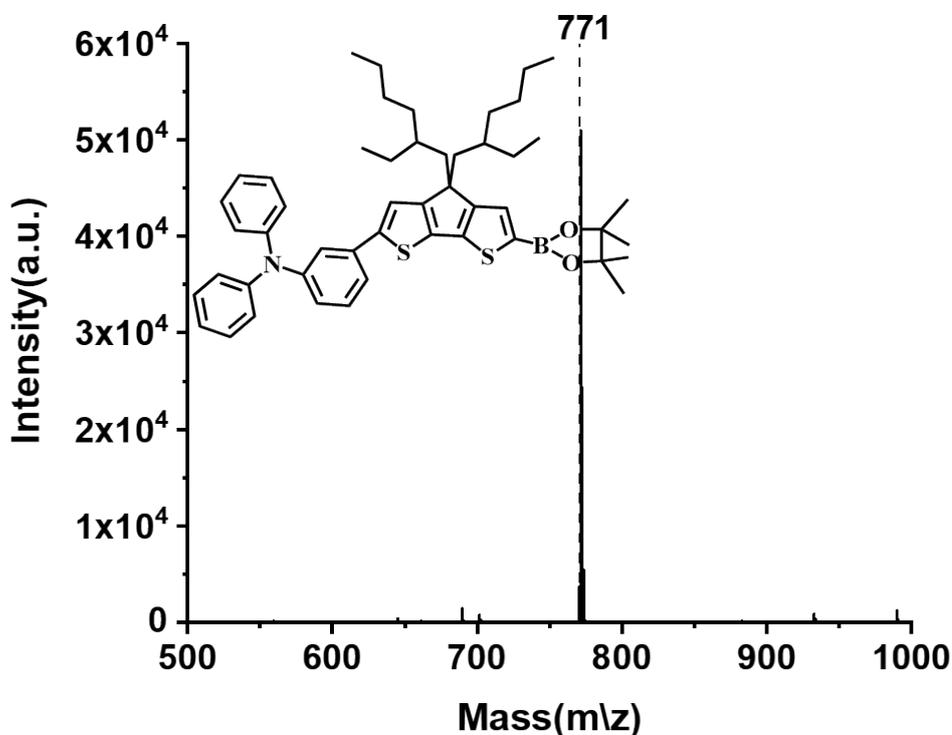


Figure S7 Time of Flight Mass Spectrometry (TOF) characterization of intermediate 8.

8. Synthesis of the final product TCT

The above intermediate **8** (0.70 mmol, 0.539 g, 1 eq), $C_{40}H_{38}Br_2N_4O_2S_3$ (0.35 mmol, 0.3022 g, 0.5 eq), K_2CO_3 (2.8 mmol, 0.3864 g, 4 eq) and $Pd(PPh_3)_4$ (0.021 mmol, 0.0243 g, 0.03 eq) were placed in a 100 mL round-bottom flask. Then, 30 mL toluene and 10 mL deionized water were added. After vacuuming and passing N_2 , this process needs to be repeated 2-3 times, followed by a condensation reflux reaction at $85^\circ C$ for 24 h. After the reaction was completed, it was cooled to room temperature and extracted with EA and saturated salt water 3-4 times. Then anhydrous $MgSO_4$ was added to stand for 30 min, and the crude product was obtained by filtration and vacuum rotary evaporation. Finally, the dark green solid product 3,3'-(((6,7-bis(4-(hexyloxy)phenyl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline-4,9-diyl)bis(thiophene-5,2-diyl))bis(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-6,2-diyl))bis(N,N-diphenylaniline) (TCT) (0.108 mmol, 0.2151 g) was purified by silica gel column chromatography with DCM as eluent, the yield was 15.45 %.

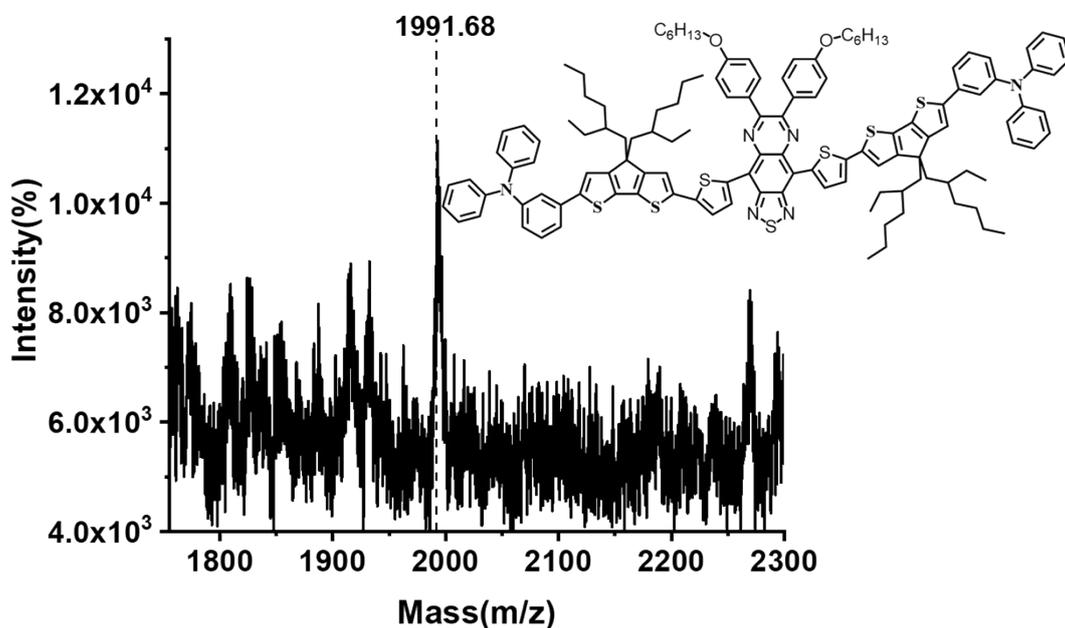


Figure S8 Time of Flight Mass Spectrometry (TOF) characterization of TCT molecules.

9. Preparation of TCT-NPs and calculation of encapsulation efficiency

TCT-NPs were prepared by nanoprecipitation method: Firstly, 36 mL water was placed in a 100 mL round bottom flask for later use, and then 1 mg TCT and 5 mg DSPE-mPEG2000 were dissolved in 4 mL THF to form a mixed solution. The mixed solution was quickly poured into water under ultrasound for 3 min. After the ultrasound was completed, 2mL ($500 \mu\text{g}\cdot\text{mL}^{-1}$) TCT-NPs were obtained by vacuum rotary evaporation or freeze-drying.

The above 1 mL TCT-NPs aqueous solution ($500 \mu\text{g}\cdot\text{mL}^{-1}$) was placed in a dialysis bag with a molecular weight cut-off of 3500 Dalton, sonicated for 10 min, dialyzed for 48 h, and lyophilized after ultrasonication. Then the sample was accurately weighed (3.2 mg) and dissolved with ethyl acetate, and its absorbance was measured at 635 nm ($A_{635} = 0.145$) (**Figure S9 b**).

The absorbance-concentration standard curve was established. Firstly, 1 mg TCT molecules were dissolved in ethyl acetate to prepare solutions with concentrations of 2.5, 5.0, 10, 20, 30, 50, 75, 100, 120, 150, and 200 $\mu\text{g}\cdot\text{mL}^{-1}$, and then Uv-Vis-NIR was used to test their absorbance at 635 nm (**Figure S9 a**). Linear regression of absorbance (A_y) to concentration (C_y) was performed, and the linear regression equation was $A_y = 0.0005C_x - 0.0003, r = 0.991$ (**Figure S9 c**). $A_{635}=0.145$ was substituted into the regression equation, and the concentration of TCT was $290.6 \mu\text{g}\cdot\text{mL}^{-1}$. In other words, 1 mL TCT-NPs solution contained 0.29 mg TCT and 2.91 mg DSPE-mPEG2000. Finally, the encapsulation efficiency of TCT in the TCT-NPs solution was 58.12 %.

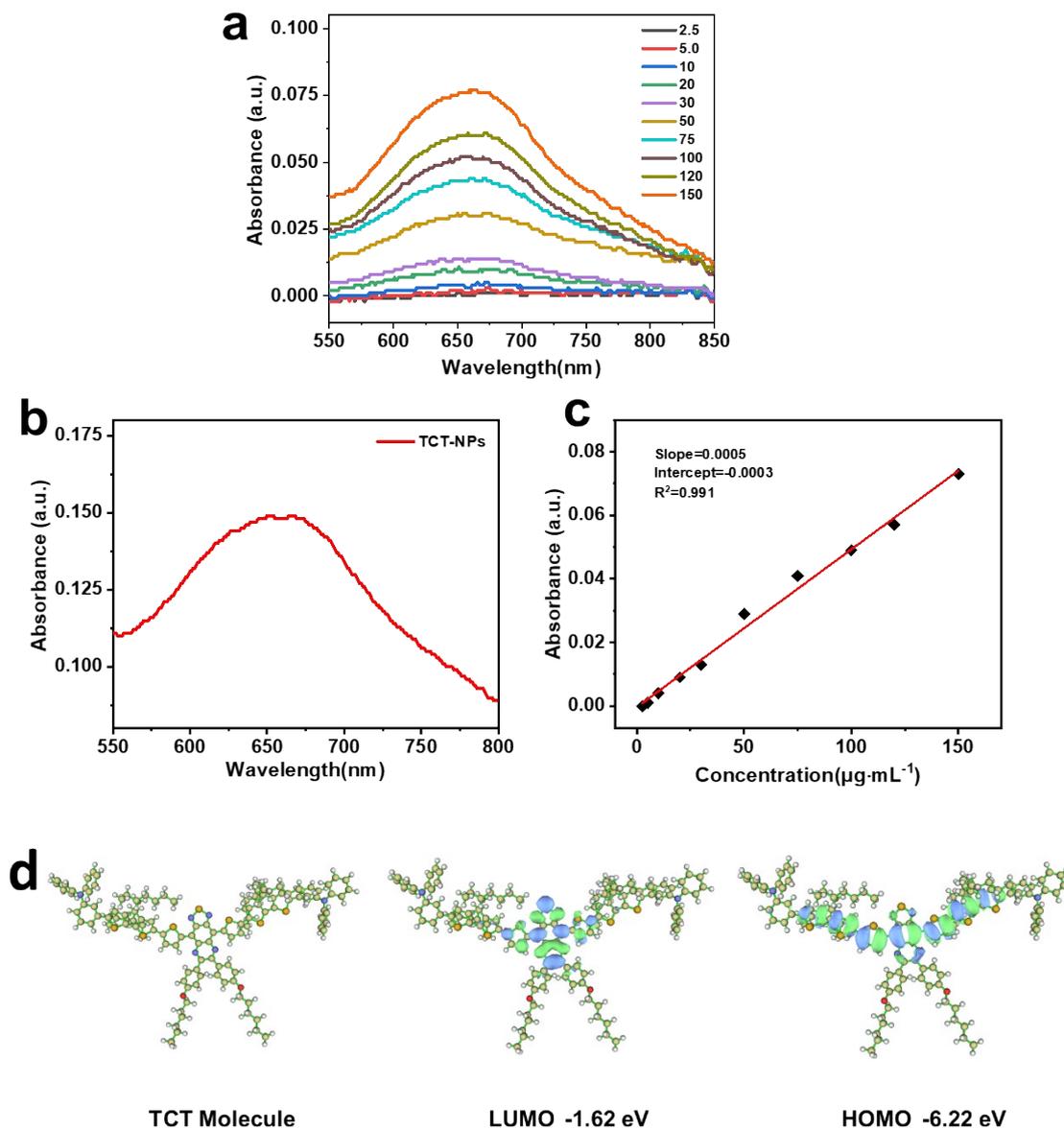


Figure S9 Encapsulation efficiency test of TCT-NPs: **(a)** UV absorption spectra of different concentrations of TCT; **(b)** UV absorption spectra of TCT-NPs after dialysis; **(c)** The regression equation was obtained by linear regression of the absorbance A_y of TCT molecule to the concentration C_x . **(d)** The HOMO and LUMO of TCT molecule were calculated by $\omega\text{B97X-D}/6\text{-}31\text{G}$ (d) method.

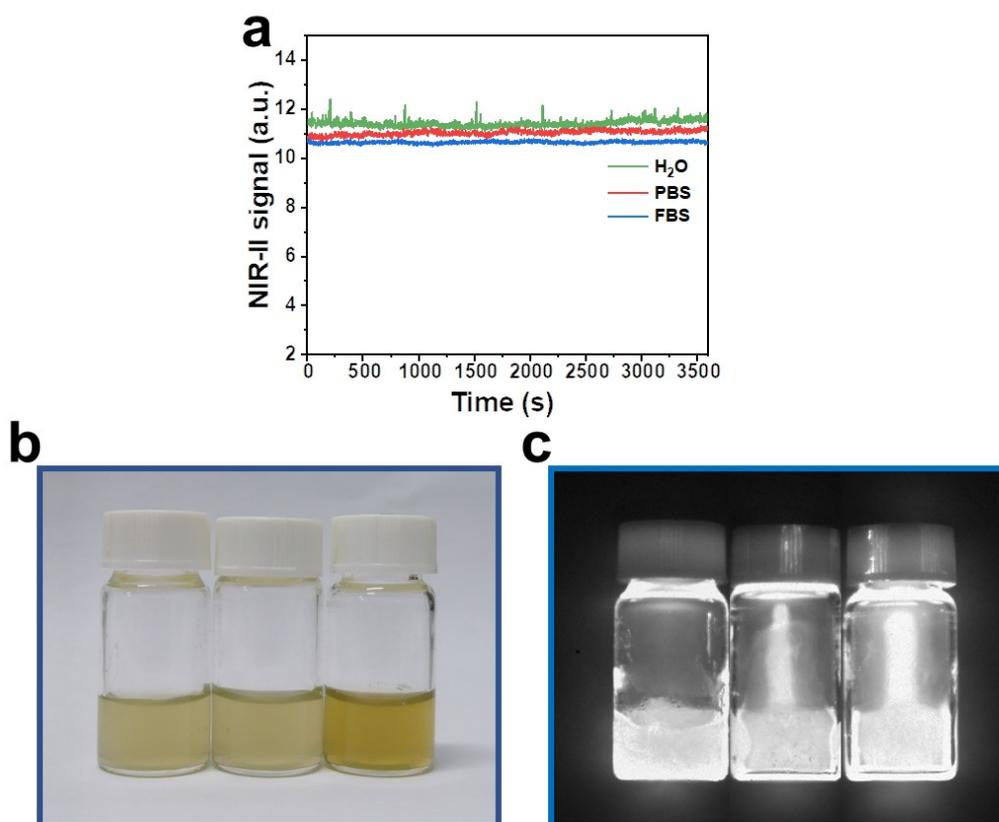


Figure S10 (a) Fluorescence stability of the TCT-NPs dissolved in H₂O, PBS, and FBS (150 $\mu\text{g}\cdot\text{mL}^{-1}$), respectively. (b) The optical images and (c) the corresponding NIR-II fluorescence image (808 nm excitation, 1 $\text{W}\cdot\text{cm}^{-2}$, 100 ms exposure time) of 150 $\mu\text{g}\cdot\text{mL}^{-1}$ solution prepared by dissolving TCT-NPs in different solvents (from left to right, H₂O, PBS, and FBS) were obtained.

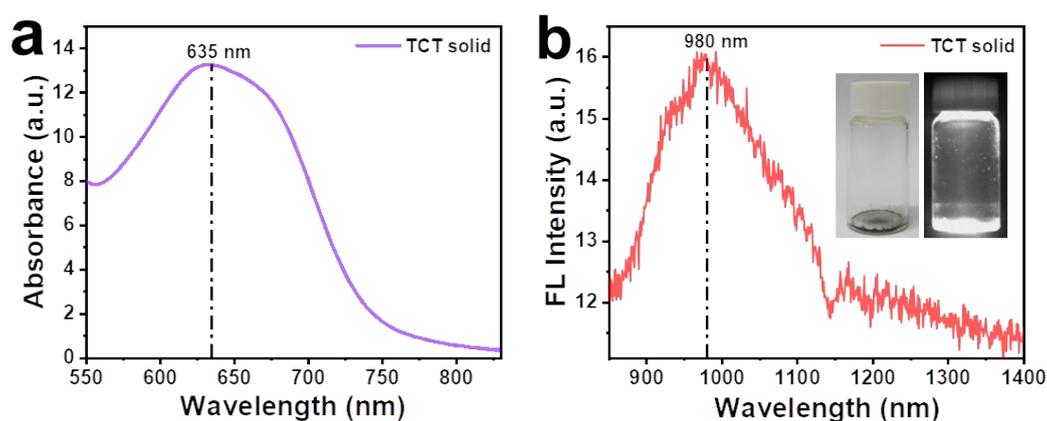


Figure S11 (a) UV-Vis absorption spectra of TCT in solid state and (b) its PL spectra under 808 nm excitation (1 $\text{W}\cdot\text{cm}^{-2}$). The insets show the optical image of the TCT solid (left) and its NIR-II fluorescence image (right) under 808 nm laser irradiation (1 $\text{W}\cdot\text{cm}^{-2}$).

10. Determination of Photoluminescence Quantum Yield (QY)

The test of the quantum yield of TCT-NPs is the same as that reported in the previous literature [1-2]. We used NIR-II fluorescent dye IR-26 as the standard sample and dissolved it in DCM solvent with five concentrations of solution (**Figure S12**). Their absorbances at 808 nm were 0.017, 0.042, 0.062, 0.081, and 0.095, respectively, detected by the UV-Vis-NIR spectrometer. Then the fluorescence intensity was measured by fluorescence spectrometer, and the fluorescence intensity was expressed by the integral area in the range of 900 nm-1500 nm. Then the fitting plot of the absorbance and fluorescence intensity of IR-26 was plotted to obtain its slope_{IR-26}. Similarly, the slope of TCT-NPs (slope_{sample}) in an aqueous solution can be obtained.

It is known that at 20°C, the refractive index of water is 1.333, and the refractive index of DCM is 1.424, QY(IR-26)=0.5%. Finally, taking into the following QY calculation formula equation (1), the QY of TCT-NPs can be obtained to be 0.364 %.

$$QY_{\text{sample}} = QY_{\text{IR26}} \times \frac{\text{slope}_{\text{sample}}}{\text{slope}_{\text{IR26}}} \times \frac{n_{\text{sample}}^2}{n_{\text{IR26}}^2} \quad \backslash * \text{MERGEFORMAT (1)}$$

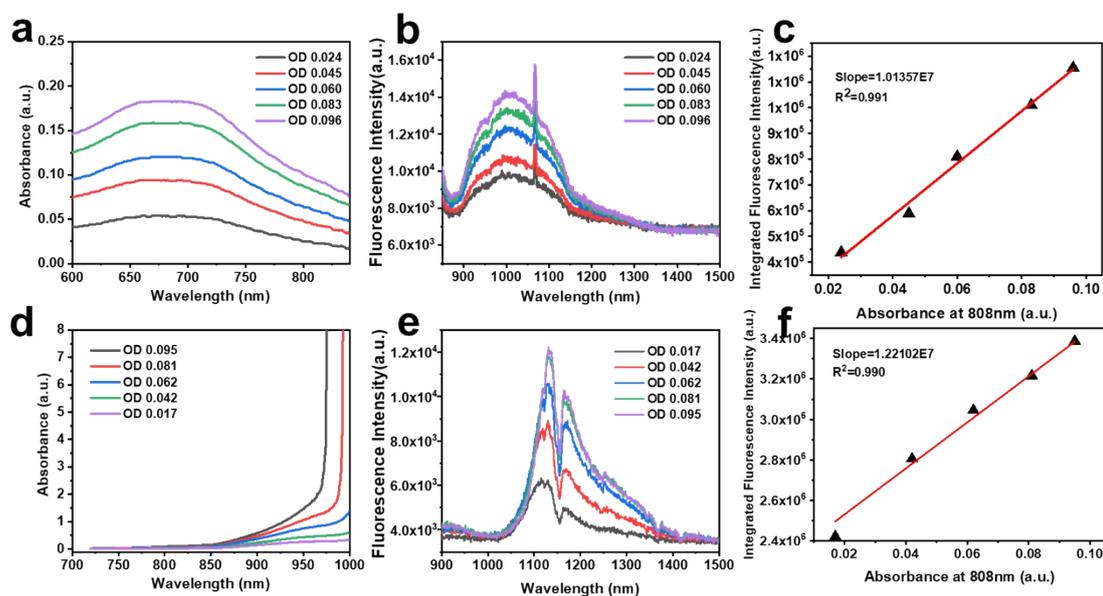


Figure S12 Quantum yield characterization of TCT-NPs: **(a)** Absorption spectra of TCT-NPs with different concentrations; **(b)** Emission spectra of TCT-NPs with different concentrations (Ex=808 nm); **(c)** Fitting graph of absorbance and fluorescence intensity of TCT-NPs; **(d)** Absorption spectra of different concentrations of IR-26 (dissolved in DCM); **(e)** The emission spectra of IR-26 at

different concentrations (Ex=808 nm); (f) IR-26 absorbance and fluorescence intensity fitting diagram.

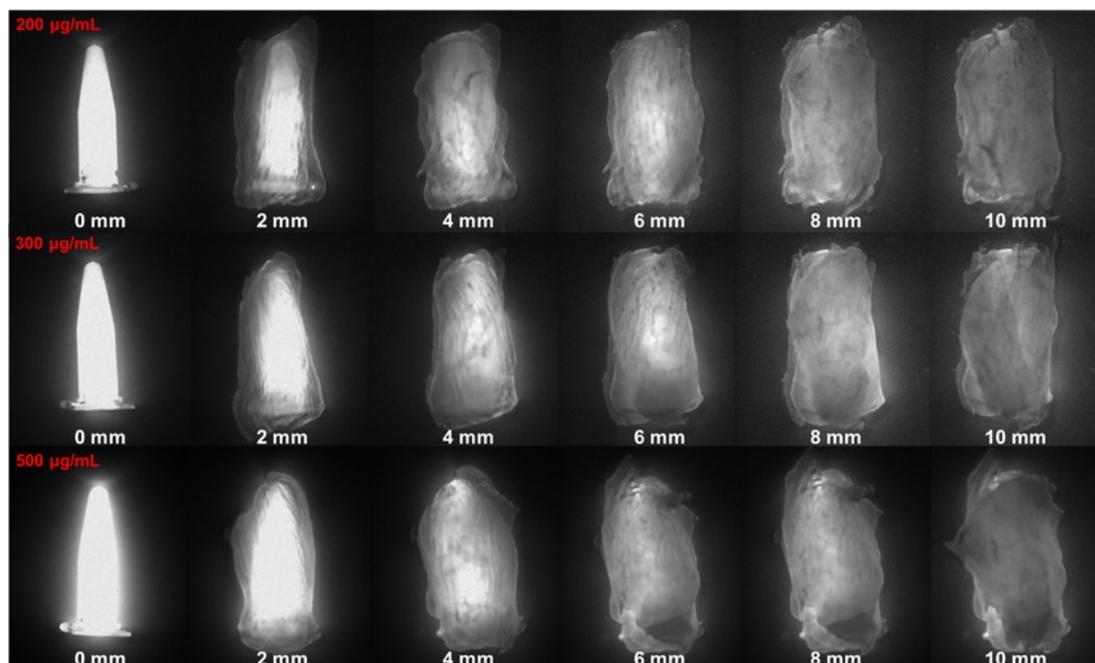


Figure S13 TCT-NPs fluorescence penetration depth test (808 nm excitation, 200 $\mu\text{g}\cdot\text{mL}^{-1}$, 300 $\mu\text{g}\cdot\text{mL}^{-1}$, 500 $\mu\text{g}\cdot\text{mL}^{-1}$, 850 nm long-pass filter, 100 ms exposure time).

11. Calculation of TCT-NPs photothermal conversion efficiency.

The 500 $\mu\text{g}\cdot\text{mL}^{-1}$ TCT-NPs aqueous solution was continuously irradiated with a 660 nm laser ($0.6 \text{ W}\cdot\text{cm}^{-2}$) for 870 s until the solution reached the steady-state temperature. The temperature-time curve of the solution was recorded, and then the photothermal conversion efficiency was calculated according to Equation (2):

$$\eta = \frac{hS(T_{\text{max}} - T_{\text{surr}}) - Q_{\text{dis}}}{I(1 - 10^{-A_{660}})} \quad \text{MERGEFORMAT (2)}$$

Where, h is the heat transfer coefficient, S represents the surface area of the container. T_{max} and T_{surr} represent the steady-state temperature ($64.2 \text{ }^\circ\text{C}$) and temperature of the surrounding environment ($33.8 \text{ }^\circ\text{C}$), respectively. Q_{dis} represents the heat loss of light absorbed by the solvent and the container. I is the laser power of the incident light source ($0.6 \text{ W}\cdot\text{cm}^{-2}$), and A_{660} represents the absorbance intensity of the sample at 660

nm (0.748) from **Figure S14**. The value of hS can be obtained by Equation (3):

$$hS = \frac{m_D c_D}{\tau_S} \quad \backslash * \text{MERGEFORMAT (3)}$$

$$t = -\tau_S \ln \theta = -\tau_S \ln \left(\frac{T - T_{\text{surr}}}{T_{\text{max}} - T_{\text{surr}}} \right) \quad \backslash * \text{MERGEFORMAT (4)}$$

Equation (3), m_D and c_D represent the mass of deionized water (0.5 g) used to dissolve TCT-NPs and the heat capacity of solvent ($c_D = 4.2 \text{ J/g}$), respectively. τ_S was the time constant of the heat transfer of the system which was determined to be $\tau_S = 155.42$ from **Figure S15** and Equation (4). Therefore, hS was calculated to be 0.01756W. Q_{dis} represents the heat dissipation of light absorbed by water and quartz sample cell, so Q_{dis} is calculated according to Equation (5):

$$Q_{\text{dis}} = \frac{m_D c_D (T_{\text{max (water)}} - T_{\text{surr}})}{\tau_{\text{(water)}}} \quad \backslash * \text{MERGEFORMAT (5)}$$

Where $T_{\text{max (water)}}$ is 26.8°C , $\tau_{\text{(water)}}$ is 357. Therefore, Q_{dis} was calculated to be 0.0211W. According to the obtained data and Equation (2), the photothermal conversion efficiency of TCT-NPs was determined to be 40.1 %.

Similarly, the photothermal conversion coefficients of the other concentrations ($150 \mu\text{g}\cdot\text{mL}^{-1}$, $200 \mu\text{g}\cdot\text{mL}^{-1}$, and $300 \mu\text{g}\cdot\text{mL}^{-1}$) of TCT-NPs aqueous solution were 14、16.3、30.5, respectively, as shown in **Table S1**.

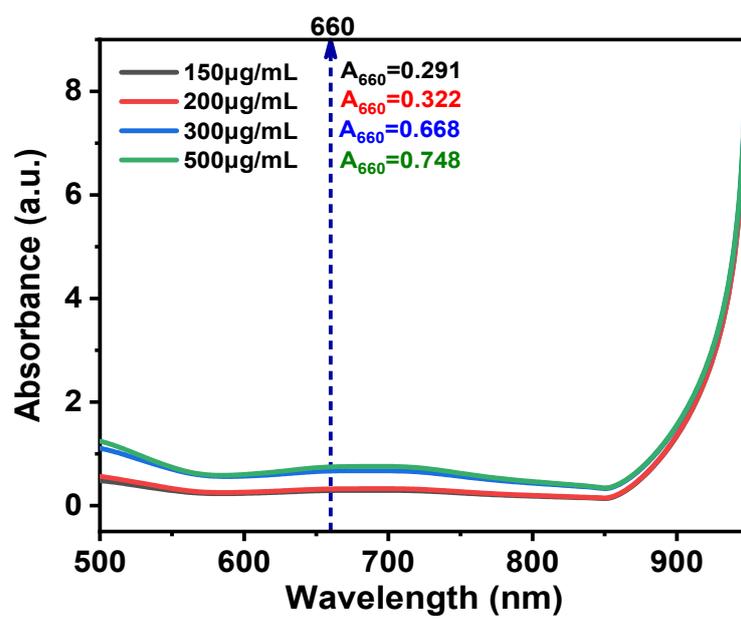


Figure S14 The absorbance intensity of TCT-NPs aqueous solution with different concentrations at 660 nm.

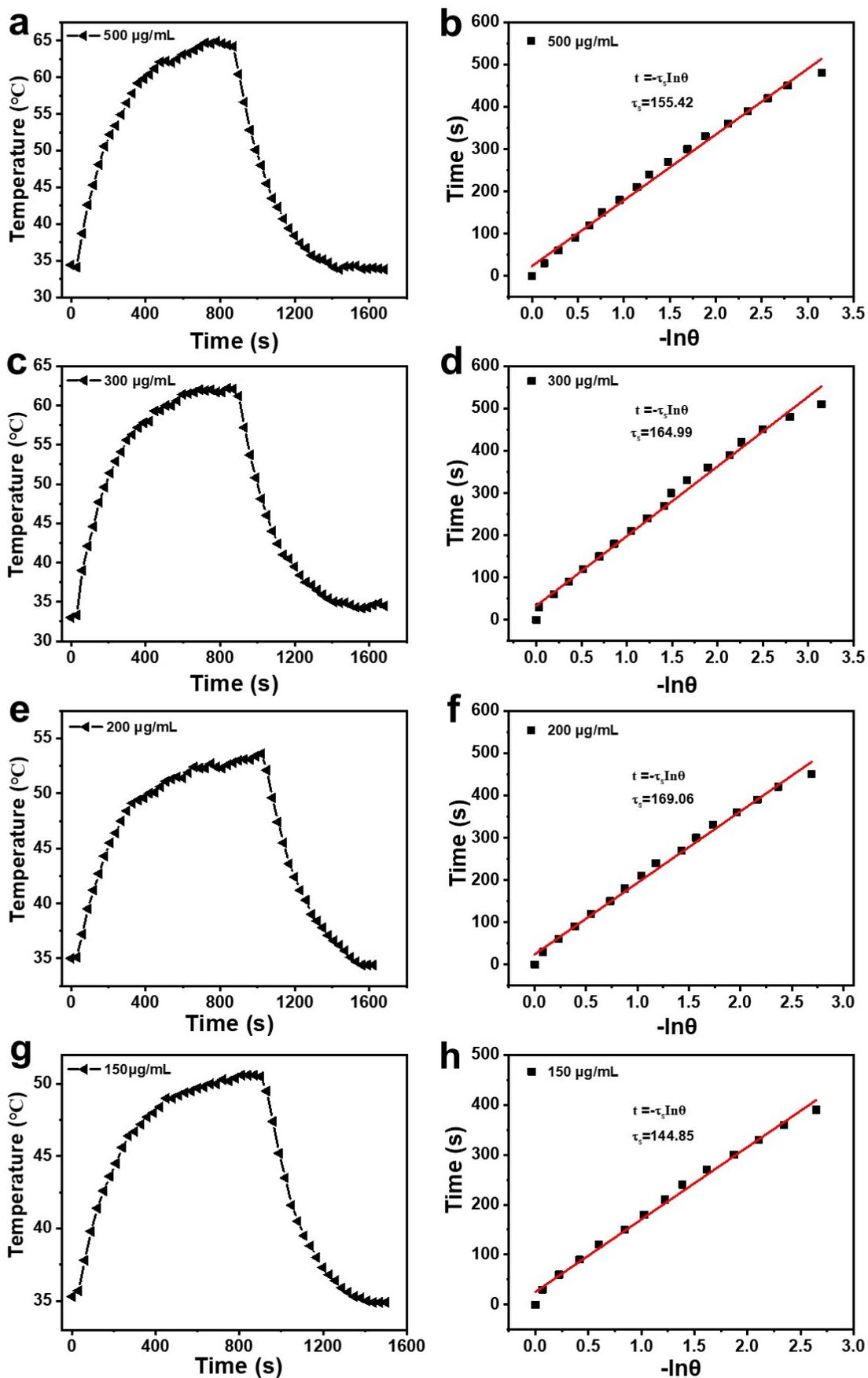


Figure S15 The photothermal conversion efficiency of TCT-NPs aqueous solution with different

concentrations ($500 \mu\text{g}\cdot\text{mL}^{-1}$, $300 \mu\text{g}\cdot\text{mL}^{-1}$, $200 \mu\text{g}\cdot\text{mL}^{-1}$, and $150 \mu\text{g}\cdot\text{mL}^{-1}$) irradiated by 660 nm laser ($0.6 \text{ W}\cdot\text{cm}^{-2}$) to a stable temperature and then cooled to room temperature was evaluated (corresponding to **Figure S15 a, c, e, g**). The photothermal efficiency can be obtained by linear fitting of the negative natural logarithm of cooling time and temperature (**Figure. S15 b, d, f, h**).

Table S1. Photothermal conversion coefficient of TCT-NPs with different concentrations.

	$150 \mu\text{g}\cdot\text{mL}^{-1}$	$200 \mu\text{g}\cdot\text{mL}^{-1}$	$300 \mu\text{g}\cdot\text{mL}^{-1}$	$500 \mu\text{g}\cdot\text{mL}^{-1}$
η	14	16.3	30.5	40.1

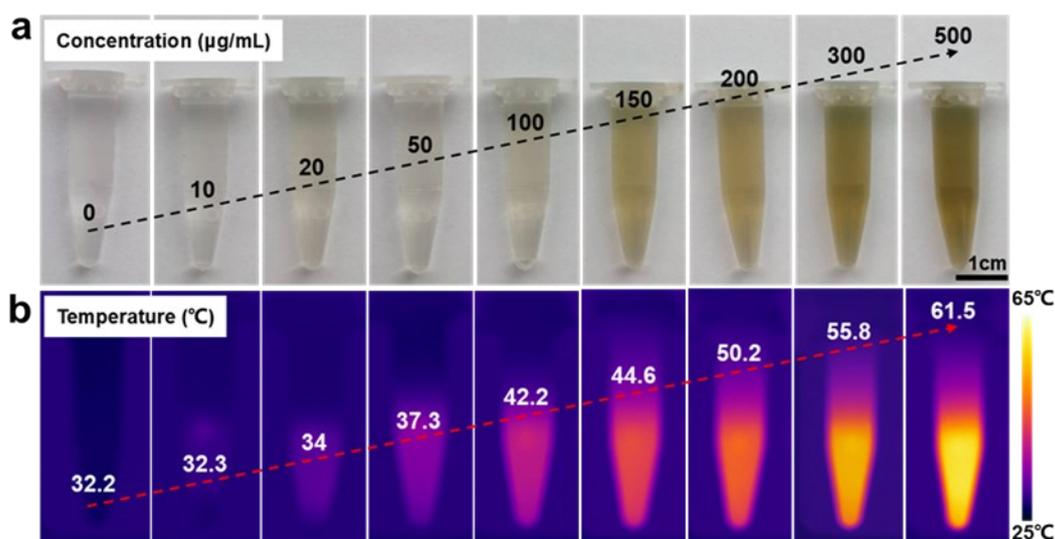


Figure S16 In vitro photothermal properties of TCT-NPs: **(a)** Optical images of different concentrations of TCT-NPs aqueous solution in plastic test tubes (0.5 mL). **(b)** The thermal images of TCT-NPs aqueous solutions with different concentrations after continuous laser irradiation (660 nm, $0.6 \text{ W}\cdot\text{cm}^{-2}$) for 10 min. Read the temperature from the center of the plastic tube surface.

12. Cytotoxicity evaluation of TCT-NPs

The cytotoxicity of TCT-NPs on HepG2, NIH-3T3, and 4T1 cells was quantitatively characterized by the MTT method. The cytotoxicity test of TCT-NPs on 4T1 cells was taken as an example to explain the operation process in detail.

Firstly, the frozen 4T1 cells were thawed and centrifuged with DMEM (2 mL). After centrifugation, the medium was discarded and 5mL of fresh DMEM was added again to form a cell suspension. Then it was transferred to a T25 cell culture bottle and cultured in a cell incubator (37 °C, carbon dioxide concentration of 5 %) for 24 h. When the cell adhesion rate was more than 80 %, the dead cells were washed with PBS and digested with trypsin (1 mL) for 3 min. Then, DMEM medium (2 mL) was added to terminate the digestion, the medium was discarded after centrifugation, and fresh DMEM (5.5 mL) was added again to dilute evenly. Cell suspension (100 μ L) with approximately 1×10^4 cells was added to each well in a 96-well plate and cultured in an incubator for 24 h.

Next, TCT-NPs and DMEM were prepared into solutions with different concentration gradients (5, 10, 20, 50, and 100 $\mu\text{g} \cdot \text{mL}^{-1}$), and the whole live group (only DMEM) and the whole dead group (only PBS) were set as control groups, which were added to 96-well plates and incubated with cells for 24 h. MTT was weighed in the dark and prepared into MTT solution (5 mg MTT, 1 mL PBS, and 9 mL DMEM) for later use. Then, the solution in the 96-well plate was sucked out, and the cells were washed 3 times with PBS. After that, MTT solution (100 μ L) was added to each well and cultured in an incubator for 4 h. Finally, the MTT solution in the 96-well plate was removed, washed with PBS, and DMSO (100 μ L) was added to each well. Then, the absorbance at 490 nm was detected by a microplate reader in the dark state, and the cytotoxicity of 4T1 cells was calculated by the cell viability formula. The same method was used to test the cytotoxicity of HepG2 and NIH-3T3 cells.

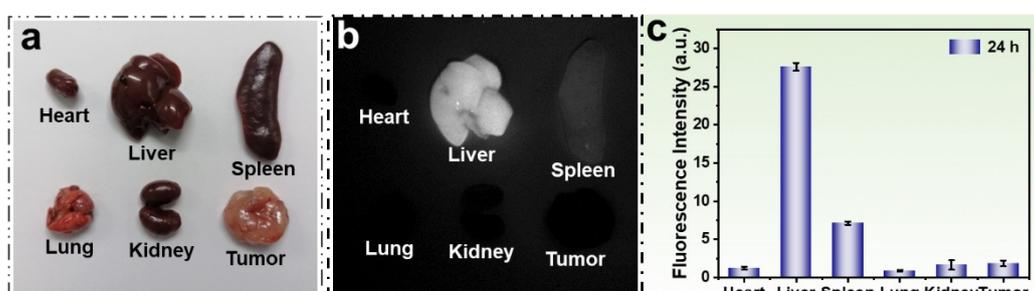


Figure S17 (a) Bright-field images of isolated organs and tumors of tumor-bearing mice 24 h after injection of TCT-NPs; (b) NIR-II fluorescence imaging of isolated organs and tumors of tumor-

bearing mice 24 h after injection of TCT-NPs; (c) Quantitative analysis of the NIR-II fluorescence intensity corresponding to Fig. 4a. Means \pm SD, n = 3.

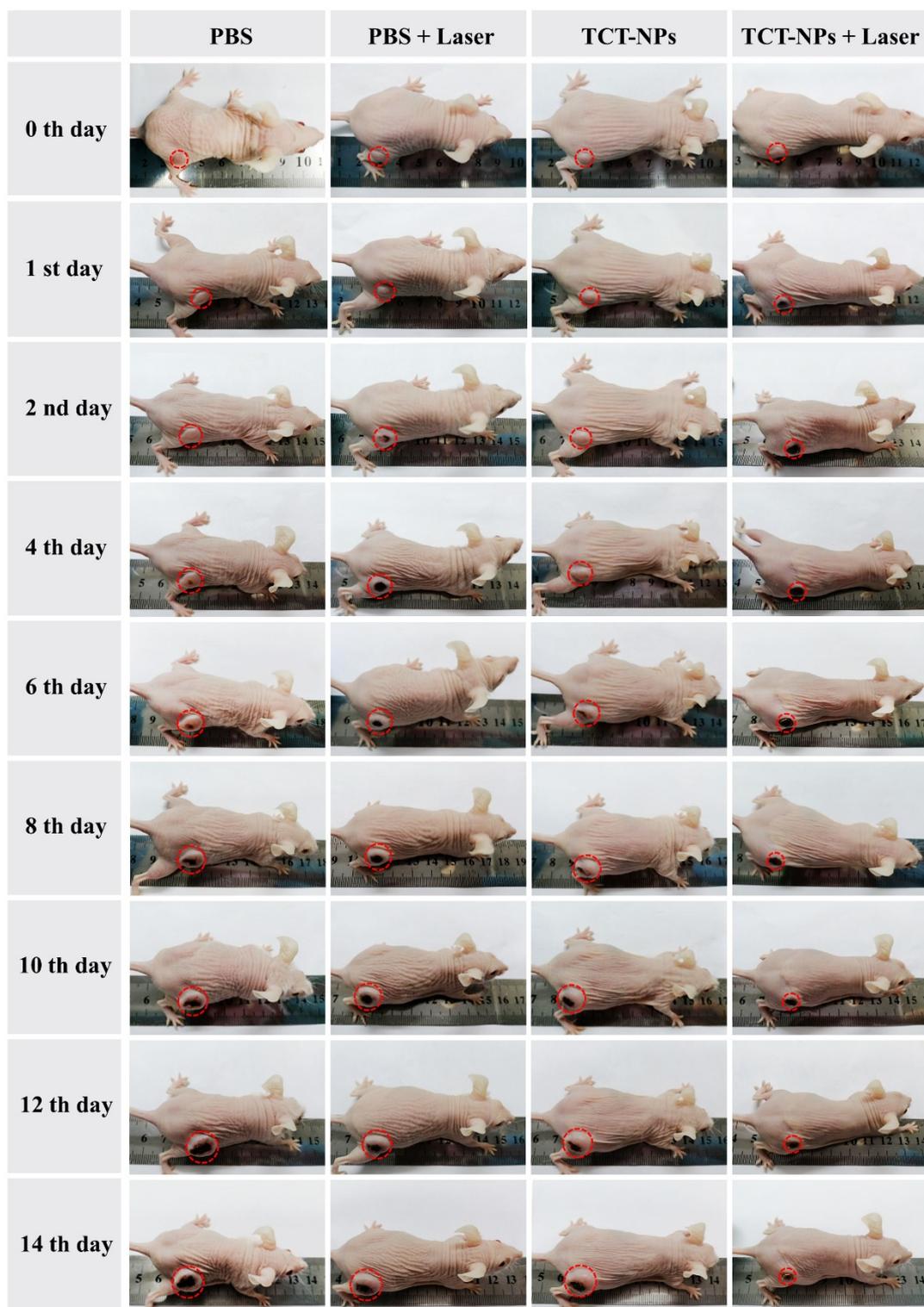


Figure S18 Optical photographs of tumor-bearing mice collected from different groups (PBS, PBS + Laser, TCT-NPs and TCT-NPs + Laser group) during 14 days.

Material :

N-hexane (AR, 97%), DCM (AR, 99.5%), methanol (AR, 99.5%), ethyl acetate (AR, 99.5%), tetrahydrofuran (AR, 99.0%), dimethyl sulfoxide (AR, 99%), 4H-Cyclopenta[2,1-b:3,4-b']dithiophene(CPDT)(98%), tetrabutylammonium iodide (99%), 2-Ethylhexyl bromide (99%), phosphorus oxychloride (99.9%), potassium carbonate (98%), sodium chloride (99.5%), triphenylamine (99%), sodium acetate (99%), 1,4-dioxane (1.6 M in hexane), NBS(99%), C₁₂H₂₄B₂O₄(99%), Pd(dppf)Cl₂·DCM(99%), DSPE-mPEG2000(Mw 2000 Da), thiazole blue (98%), 18-crown-6(99%), tetrakis(triphenylphosphine)palladium(0)(Pd(PPh₃)₄)(99.5%) were purchased from Aladdin. Toluene (AR, 99%), acetone (AR, 99%) and ether (AR, 99%) were purchased from Sinopharm Chemical Reagents Co., Ltd. 4,9-bis (5-bromothiophene-2-yl) -6,7-bis (4-(hexyloxy) phenyl)-[1,2,5]thiadiazolo[3,4-G] quinoxaline(TTQ) was purchased from Nakai Technology Co., Ltd.

Laboratory apparatus:

The molecular weight of the synthesized product was tested by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) (Auto Flex Max) produced by Bruker. The laser particle size and potential analyzer (DLS) (ZeTASizer Nano ZS90) produced by Malvern Instrument Co., Ltd. was used to test the hydrated particle size of the nanoparticles. The TEM images were collected on a transmission electron microscope (JEM-2100 Plus) produced by Japan Electronics Co., Ltd., and the operating voltage was 200 kV. The absorption spectra of the samples were tested by a UV-visible/NIR Spectrophotometer (UH4150) produced by Hitachi High-tech Company. The emission spectrum and fluorescence stability of the samples were tested by the Fluorescence tester (FLS-1000). The photothermal experiment was recorded by the infrared thermal imager (Fotric226) produced by Shanghai Thermal Imaging Mechanical and Electrical Technology Co., Ltd. The samples were evaporated by a rotary evaporator (RV8) produced by IKA company. The Nano-NIR small animal real-time living imaging system (UninanoNIR-II) produced by Huijia Bio-Instrument Company was used for in vivo/vitro fluorescence imaging. The cytotoxicity was

characterized by Spectra Max Series Microplate Reader (Spectra Max M3), and the test wavelength was 490 nm.

References

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