Supplementary Information

Cationic conjugated polymer with high 808 nm NIR-triggered photothermal conversion for antibacterial treatment

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Experimental Section

Synthesis of Compound 1. Compound 1 was synthesized through a Buchwald-Hartwig reaction of BINAP with 3,3'-dibromo-2,2'-bi-thiophene. 3,3'-dibromo-2,2'-bithiophene (1.296 g, 4 mmol), NaOtBu (1.538 g, 16 mmol), $Pd_2(dba)_3$ (0.256 g, 0.28 mmol) and BINAP (0.697 g, 1.12 mmol) were added into toluene (40 mL) that had been dried by molecular sieve, and the mixed solution was stirred at room temperature for 15 min. Then, 5-(dimethylamino) amylamine (0.83 mL, 5.2 mmol) was added in the mixed solution drop by drop. The mixture was heated to 110 ℃ and stirred overnight under nitrogen protection. The reaction solution was extracted by dichloromethane and dried with magnesium sulfate. The brown oily liquid was obtained by silica gel column chromatography (0.78 g, 67 %). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.04 (s, 2 H), 4.11 (t, J = 6.6 Hz, 2 H), 2.38 (t, J = 7.5 Hz, 2 H), 2.35 (s, 6 H), 1.85 (m, 2 H), 1.56 (m, 2 H), 1.31 (m, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.72, 122.68, 114.47, 110.81, 58.86, 47.03, 44.65, 29.88, 26.38, 24.45. HRMS (ESI): m/z: 293.1140 ($[M+H]^+$).

Synthesis of Monomer 1. NBS (1.100g, 6.3mmol) was dissolved in DMF in the ice bath. Chloroform (35 mL) and compound 1 (0.783 g, 2.6mmol) were added into the reaction flask and kept in the ice bath. The mixed solution was stirred until compound 1 was completely dissolved. NBS was added into the reaction flask and reacted in the dark for 4 h. The reaction solution was extracted by chloroform and dried with magnesium sulfate. The dark yellow solid was obtained by silica gel column chromatography (0.60 g, 51 %). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.0 (s, 2 H), 4.10 (t, J = 6.0 Hz, 2 H), 2.56 (t, J = 6.0 Hz, 2 H), 2.47 (s, 6 H), 1.83 (m, 2 H), 1.61 (m,

2 H), 1.29 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.35, 114.85, 114.21, 109.97, 57.81, 47.01, 43.23, 29.45, 24.35, 23.90. HRMS (ESI): m/z: 450.9331 ($[M+H]^+$).

Synthesis of PDTPBT-pre. Monomer 1 (0.068 g, 0.15 mmol) and monomer 2 (0.059 g, 0.15 mmol) were dissolved in THF (10 mL) under nitrogen atmosphere. Then $Pd(PPh_3)_4$ (0.009 g, 0.0075 mmol) and K_2CO_3 (1 mL, 2 M) solution were added into the reaction vessel sequentially, followed by stirring the mixture solution for 12 h under 80 ^oC. After the reaction, THF was removed by rotary evaporation. The mixture was dissolved in DMF and dialyzed by a dialysis membrane (MWCO: 3.5 kDa) for 3 days. Then the black solid was obtained after freeze drying (35 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.34 - 7.00 (m), 4.21 (br), 2.19 (br), 1.94 (br), 1.48-1.26 (m). GPC: *Mn* = 18965, *Mw* = 24359, PDI = 1.28.

Synthesis of PDTPBT. Furthermore, the quaternary ammonium group was introduced to the side chain for better solubility. The PDTPBT-pre (0.036 g, 0.08 mmol) was completely dissolved into $CHCl_3$ (3 mL), and then CH_3I (0.15 mL, 2.4 mmol) was added into the solution. The reaction mixture was stirred until the precipitate appeared. Eventually, the black product was collected after the removal of the solvent (46 mg, 98%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.64 - 7.55 (m), 3.41 (m), 3.00 (m), 2.55 (b), 1.97-1.72 (b), 1.22 (m).

GPC measurement. The molecular weight of polymer was measured by laser light scattering gel chromatography system (VISCOTEK TM, Malvern). The chromatographic column was cleaned with THF before the measurement of molecular weight. The input concentration of PDTPBT was 0.5 mg/mL and the injection volume

was 100 μL. The weight-average molecular weight (Mw) and number-average molecular weight (Mn) were 24,359 Da and 18,965 Da, respectively, with the polydispersity index (PDI) of 1.28.

Bacteria culture. In order to explore the antibacterial activity of conjugated polymers against gram-positive bacteria and negative bacteria, MRSA and *E.coli* were employed as the model bacteria, respectively. A single colony of MRSA coated on solid brain heart infusion (BHI) agar plate was selected and added into liquid BHI medium (20 - 25 mL). The bacteria solution was shaken overnight at 37 °C. *E. coli* was cultured in LB (lysogeny broth), and other culture process were same as that of MRSA.

Photothermal conversion efficiency. The Photothermal conversion efficiency was calculated by following equation:

$$\eta = \frac{hS\Delta T_{max} - Q_{dis}}{I\left(1 - 10^{-A_{808}}\right)} \quad (1)$$

$$hS = \frac{m_s C_s}{\tau} \quad (2)$$

$$t = -\tau \ln(\theta) \quad (3)$$

$$\theta = \frac{\Delta T}{\Delta T_{max}} \quad (4)$$

η denotes the photothermal conversion efficiency, h represents the heat transfer coefficient, S means the surface area of the container. ΔT_{max} is the maximum temperature change of the samples under laser irradiation, Q_{dis} is the heat dissipated from the solution and container, I is the laser power, A_{808} is the absorbance of PDTPBT solution at 808 nm. In equation (2), m_s is the mass of the irradiated solution and C_s is the heat capacity of the solution. Time constant τ can be obtained from the linear fitting

of time versus -ln(θ) by equation (3). As shown in Fig 4(b), τ was calculated as 221.6 s. In equation 2, m_s was 1 g and C_s was 4.2 J g^{-1} $℃^{-1}$. The hS was calculated as 0.01895 W/℃. Q_{dis} and A_{808} were 0.0454 W and 0.726, respectively. ΔT_{max} was 32.4 ℃ according to experimental results. Thus, the photothermal conversion efficiency was calculated as 71.1% by equation (1).

Supporting figures

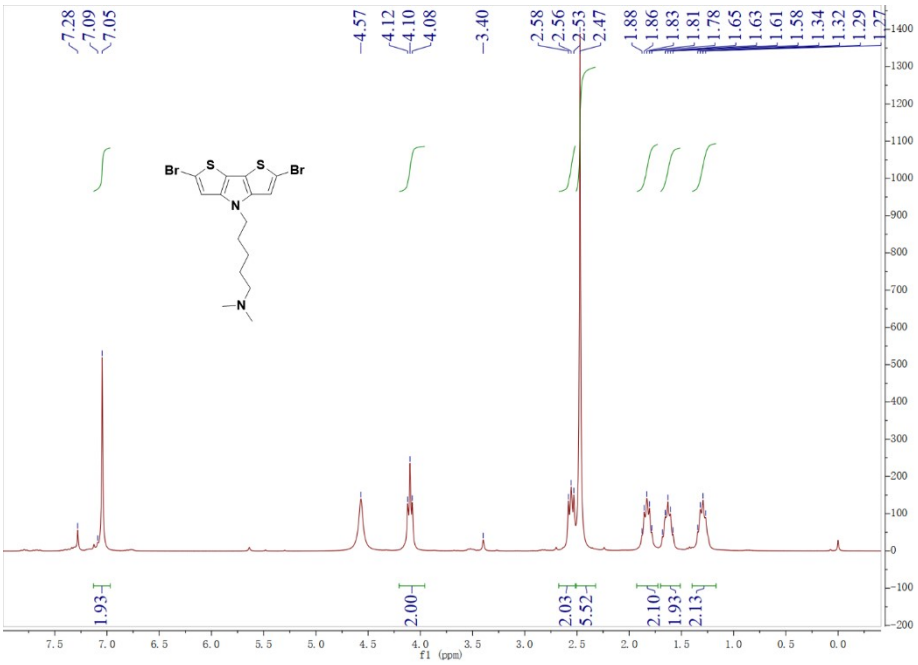

Fig. S1 ^{1}H NMR spectrum of Monomer 1.

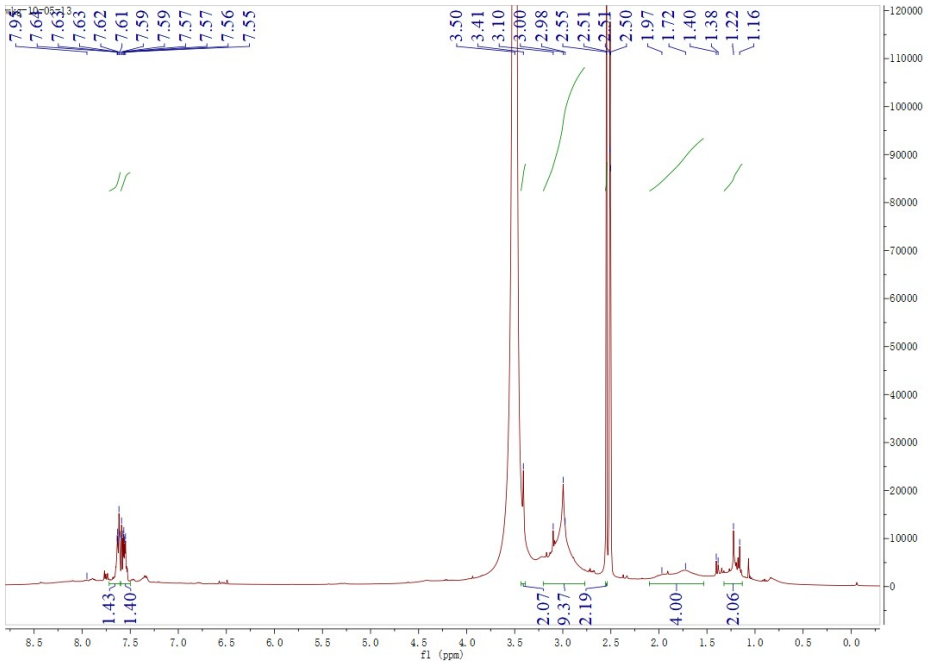

Fig. S2 ^{1}H NMR spectrum of PDTPBT.

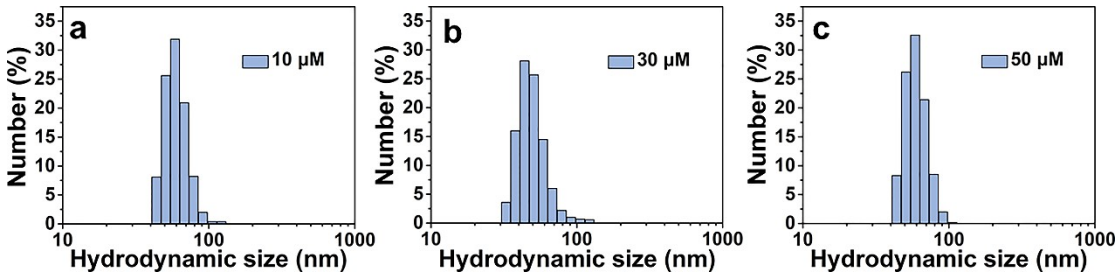

Fig. S3 Size distribution of PDTPBT at different concentrations.

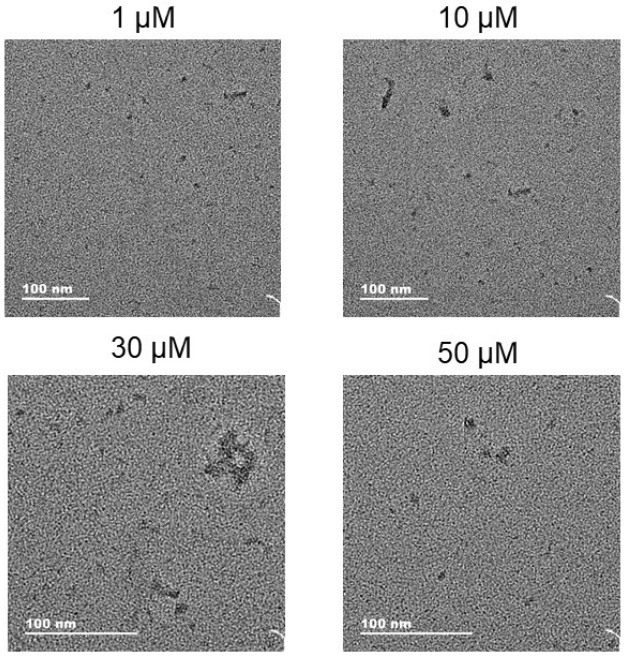

Fig. S4 TEM images of PDTPBT in aqueous solution at different concentrations.

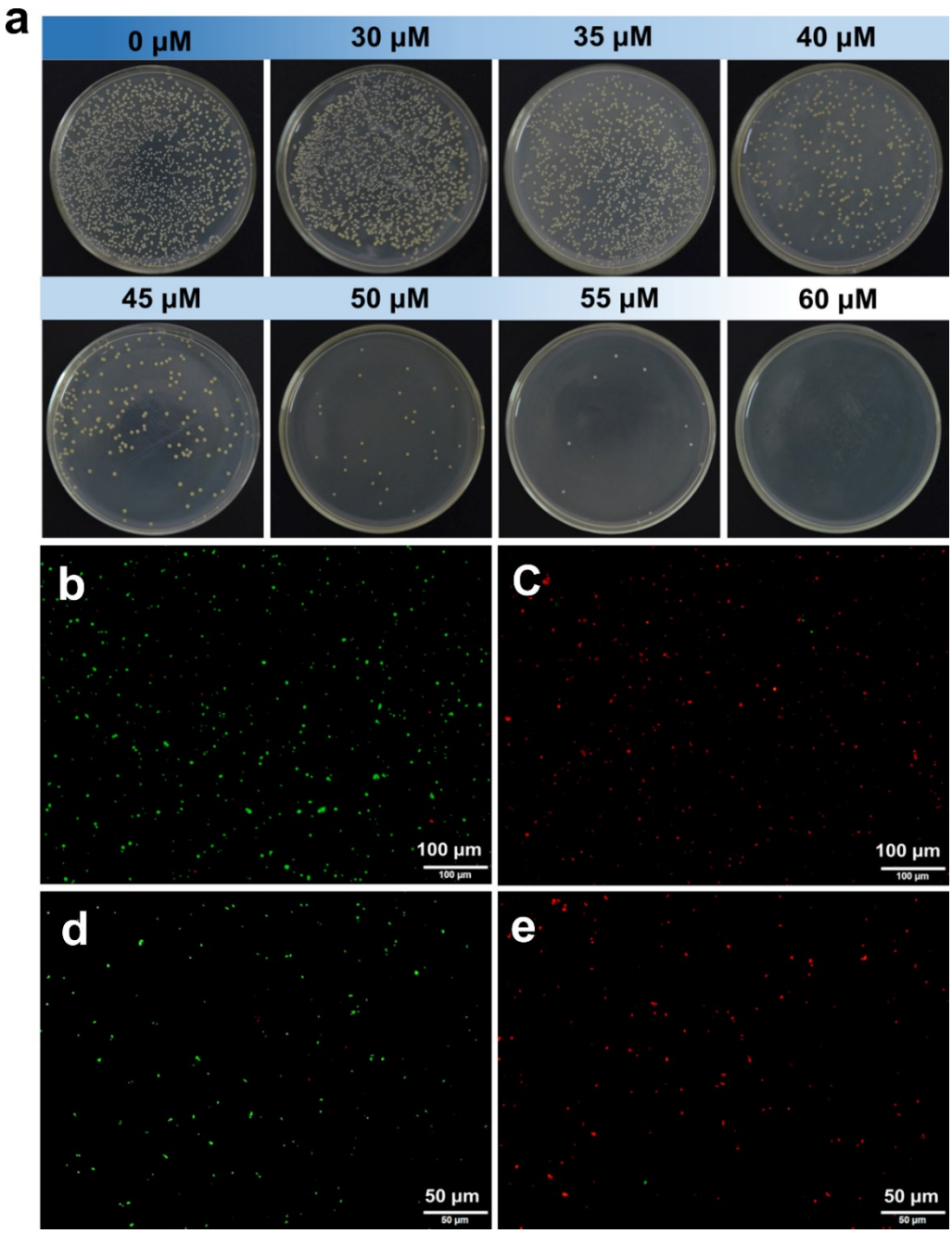

Fig. S5 MRSA growth on Petri dishes at different concentration of PDTPBT (ranging from 0 to 60 μM) after NIR laser (808 nm, 1 W/cm^2) irradiation for 6 min. Fluorescence microscope images of MRSA incubated with PDTPBT under the laser irradiation (1W/cm^2) (b) and (d) or in the dark (c) and (e) for 6 min. [PDTPBT] = 55 μM.

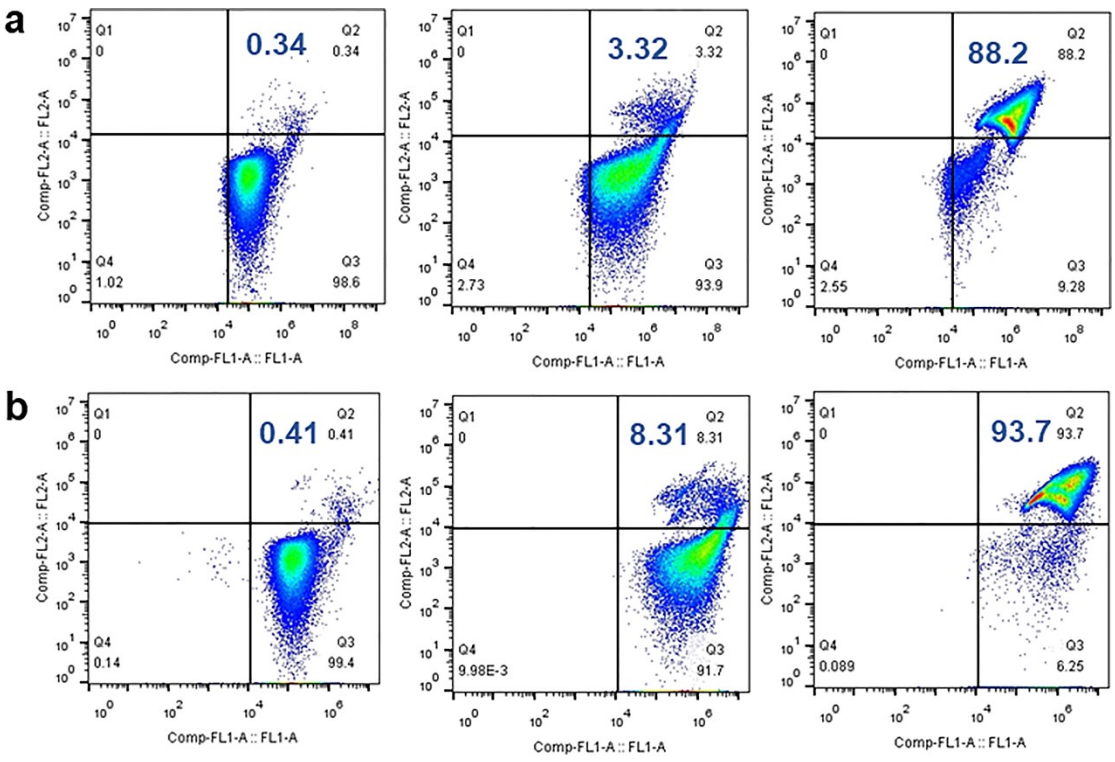

Fig. S6 (a) Cell mortality of *E.coli* by flow cytometry before and after polymer treatment ([PDTPBT] = 0 μM, 15 μM, 35 μM) (b) Cell mortality of MRSA by flow cytometry before and after polymer treatment ([PDTPBT] = 0 μM, 30 μM, 55 μM).