Supplementary Information for

Cationic Polycarbonate-Grafted Superparamagnetic Nanoparticles with Synergistic Dual-Modality Antimicrobial Activity

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Materials. Dimethyl 2-hydroxyethyl phosphonate were purchased from Tokyo Chemical Industry Co., Ltd. N-(3,5-trifluoromethyl)phenyl-N'-cyclohexylthiourea (TU) was synthesized according to the previous reference.[1] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was dried with CaH_2, distilled, then stored over molecular sieves. Phosphate-buffered saline (PBS) was purchased from BASE and diluted to the desired concentration before usage. Luria Bertani (LB) broth and Bacto Agar were purchased from Becton and Dickinson Company. *E. coli* (ATCC8739) and *S. aureus* (ATCC 6538) were obtained from ATCC and used according to the protocols. All other chemicals were commercially available from Aldrich and used as received.

Synthesis of MTC-$OCH_2CH_2CH_2Br$. 2, 2-Bis(hydroxymethyl)propionic acid (bis-MPA) (9.00 g) and KOH (4.45 g) were dissolved in DMF (50 ml) under 100 °C (1 h) until a homogeneous solution was formed and benzyl bromide (13.80 g) was then added. DMF was then evaporated under vacuum when the solution was cooled to room temperature after 16 h stirring at 100 °C. The residues were dissolved in ethyl acetate/hexane, washed with water twice, dried over $MgSO_4$, filtered and dried under vacuum. The resulting solid was

recrystallized from toluene (1.2 ml/g crude) to give a pure benzyl-2,2-bis(methylol)propionate white solid. Yield: 9.59 g (64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (s, -CH_3), 3.73 (d, -CH_2OH), 3.92 (d, -CH_2OH), 5.19 (s, -CH_2Ar), 7.36 (m, *Ar*H).

Triethylamine (26.85 g, 266.00 mmol) was added dropwise to a mixture of benzyl-2,2-bis(methylol)propionate (9.59 g, 42.77 mmol), ethyl chloroformate (27.33 g, 251.56 mmol) and tetrahydrofuran (670 ml) at 0 °C in 30 min and the solution was stirred at room temperature for additional 2 h. Then, triethylamine hydrochlorides were filtered off and the resulting filtrates were concentrated under reduced pressure. White crystals were obtained after recrystallizing form ethyl acetate. **(1)** Yield: 4.50 g (42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, -CH_3), 4.22 (d, -CH_2OH), 4.70 (d, -CH_2OH), 5.22 (s, -CH_2Ar), 7.35 (m, *Ar*H).

Monomer **(1)** (4.50 g), ethyl acetate (45 ml) and P_d/C (296 mg) were stirred under H_2 for 24 h. THF (250 ml) was added after the evacuation of the H_2 and the mixtures were filtered through THF-wetted Celite. MTC-OH was obtained as a white solid after the evaporation of filtrates. Yield: 2.20 g (79%). ^{1}H NMR (300 MHz, D_2O): δ 1.18 (s, -CH_3), 4.61 (d, -OCH_2OO-), 4.70 (d, -OCH_2OO-).

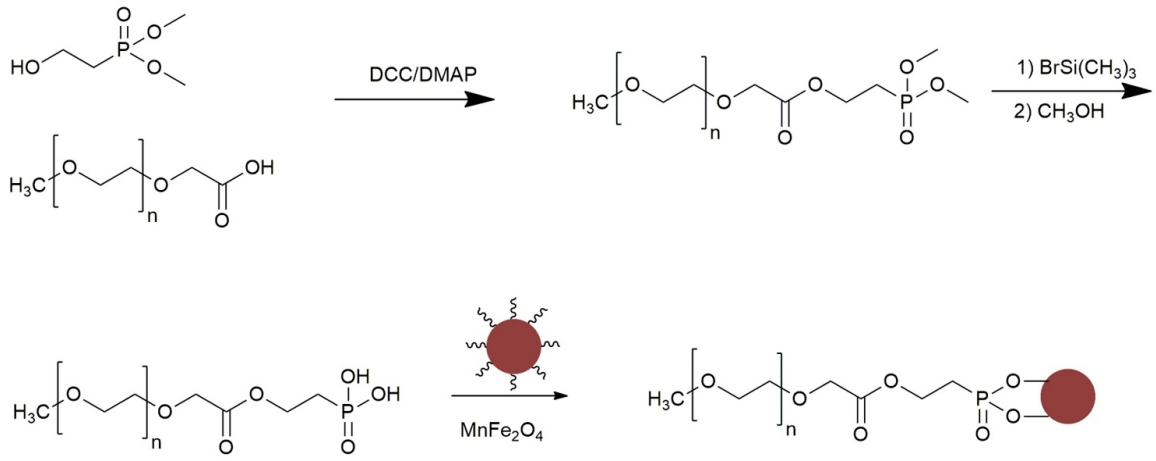
MTC-OH (2.20 g, 13.75 mmol) was dissolved in a co-solvent of THF (50 ml)/DMF (1 ml) and a solution of oxalyl chloride (3.25 g, 25.00 mmol) in THF (20 ml) was added dropwise to the mixture at 0 °C in 30 min. The reaction was then kept at 50 °C under nitrogen for another 4 h. Then, the volatiles were removed under reduced pressure and the residues were re-dissolved in THF (25 ml). An additional 3-bromopropanol (1.34 g, 9.63 mmol), pyridine (1.2 g, 15.2 mmol) and THF (50 ml) were added at 0 °C in 30 min. The reaction mixture was stirred at 0 °C for another 30 min before it was warmed to room temperature and stirred for 16 h. The precipitate that formed was filtered and volatiles were removed under reduced

pressure. The crude product was then re-dissolved with CH_2Cl_2 (160 ml) and washed with water (3 × 120 ml). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated to give a yellow solid. The crude product was further purified by column chromatography silica (1:1 = ethyl acetate/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, -CC*H*$_3$), 2.15 (quin, -CH_2C*H*$_2$$CH_2$-), 3.62 (t, -C*H*$_2$Br), 4.23 (d, -C*H*$_aH_b$-), 4.38 (t, -OC*H*$_2$$CH_2$-), 4.70 (d, -$CH_a$*H*$_b$-).

Calculation graft density of PrBrT on the nanoparticle from TGA data. Firstly, the weight of polymer was divided by the molecular weight of the polymer and multiplied by Avogadro's number to calculate the number of polymer molecules lost. Then, the weight of total nanoparticles was divided by weight of one nanoparticle to obtain the number of $MnFe_2O_4$ nanoparticles. The weight of one nanoparticle can be calculated from the volume and density (5.368 g/cm³). As one nanoparticle diameter is around 10 nm. The calculated nanoparticle (NP) weight is around 2.809×10^{-18} g/NP. The average number of polymer grafts can be calculated by Equation S1, where weight fraction of the polymer is 42% and the rest is nanoparticle core weight fraction. The result is 213 grafts per nanoparticle with the graft density about 0.68 chain/nm^2.

$$N_{\text{grafts per nanoparticle}} = \frac{W_{\text{polymer}} / M_{\text{polymer}}}{W_{\text{MnFe2O4 nanoparticle}} / M_{\text{MnFe2O4 nanoparticle}}}$$

Equation S1



Scheme S1. Schematic representation of $MnFe_2O_4$@PEG synthesis.

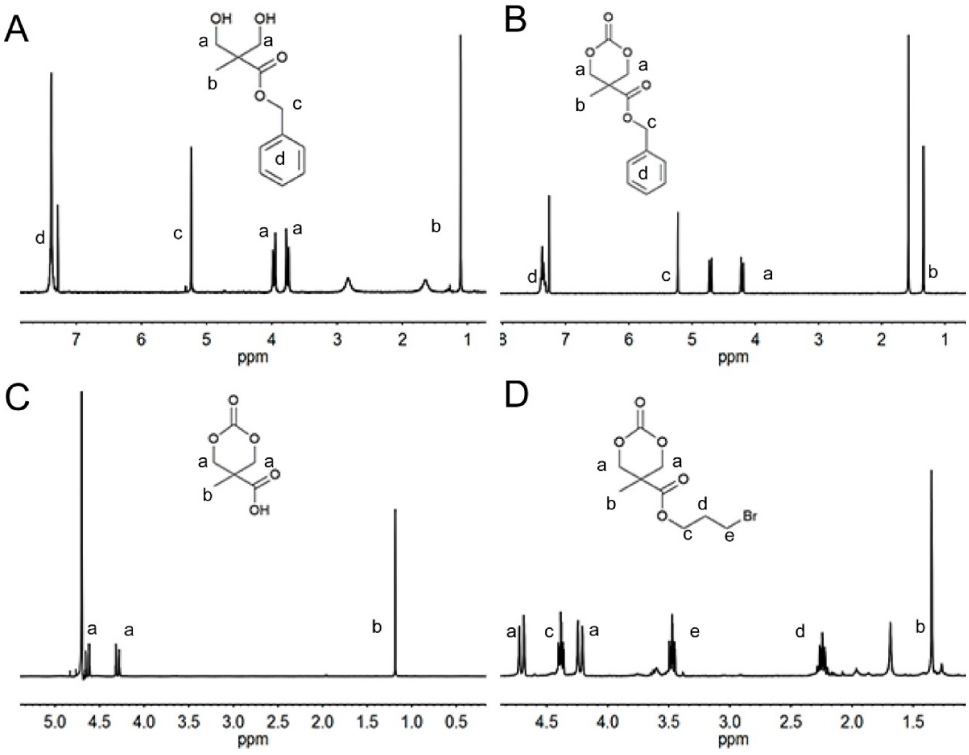


Figure S1. ^{1}H NMR spectra for MTC-$OCH_2CH_2CH_2Br$ synthesis.

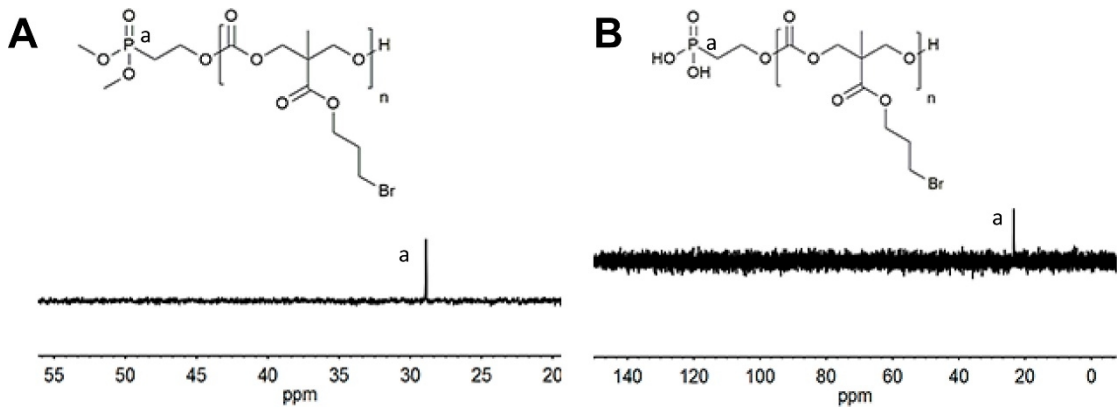


Figure S2. ^{31}P NMR spectra for poly(MTC-$OCH_2CH_2CH_2Br$)-methylphosphonate (A) and poly(MTC-$OCH_2CH_2CH_2Br$)-phosphonic acid (B) in $CDCl_3$.

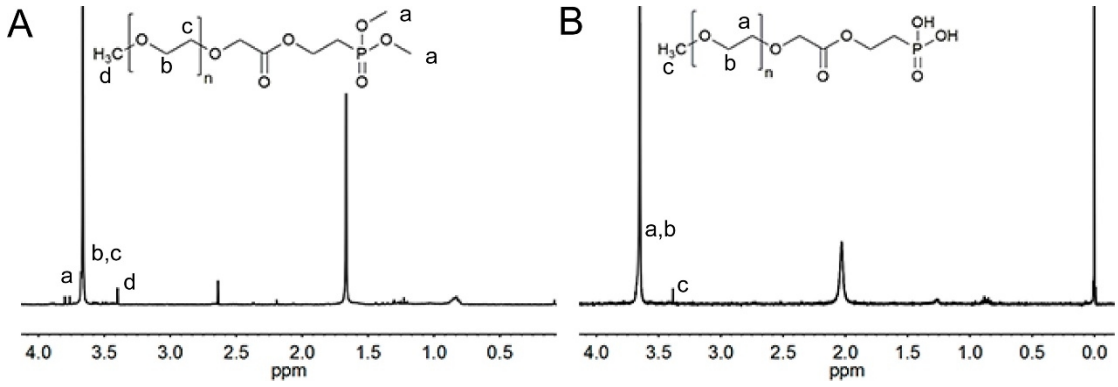


Figure S3. ^{1}H NMR spectra for mPEG-methylphosphonate (A) and mPEG-phosphonic acid (B) in $CDCl_3$.

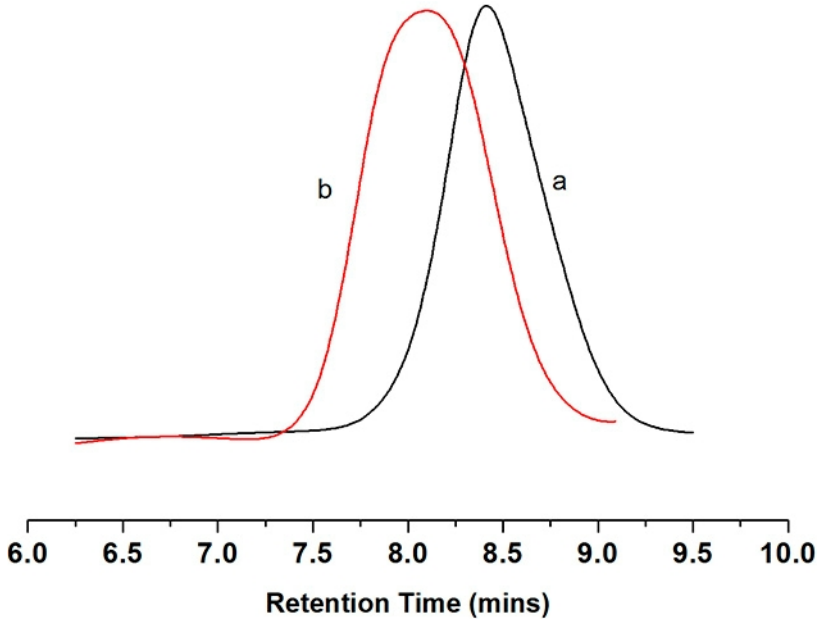


Figure S4. GPC curves of poly(MTCOCH$_2$CH$_2$CH$_2$Br): (a) M_n= 4000 Da, PDI = 1.47; (b) M_n = 6600 Da, PDI = 2.20.

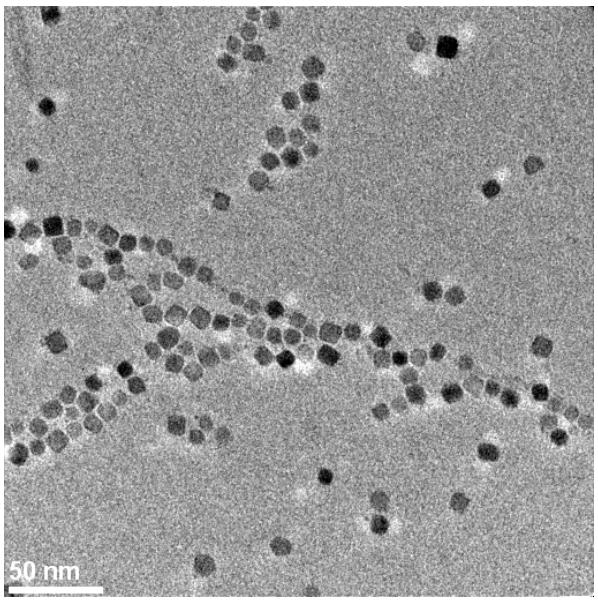


Figure S5. TEM image of $MnFe_2O_4$ nanoparticles capped with oleic acid.

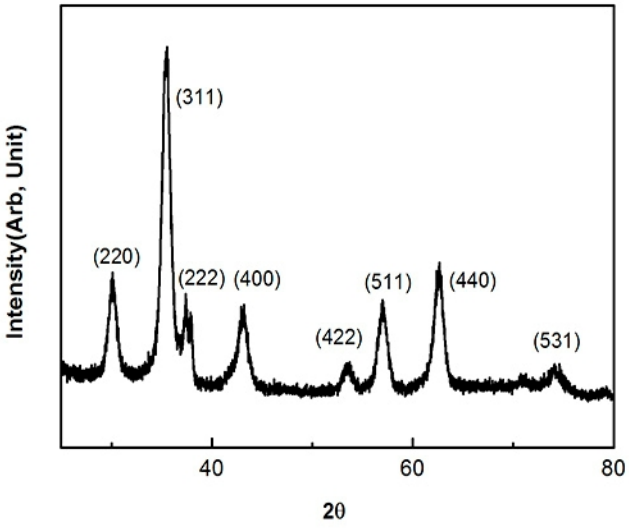


Figure S6. XRD pattern of $MnFe_2O_4$ nanoparticles.

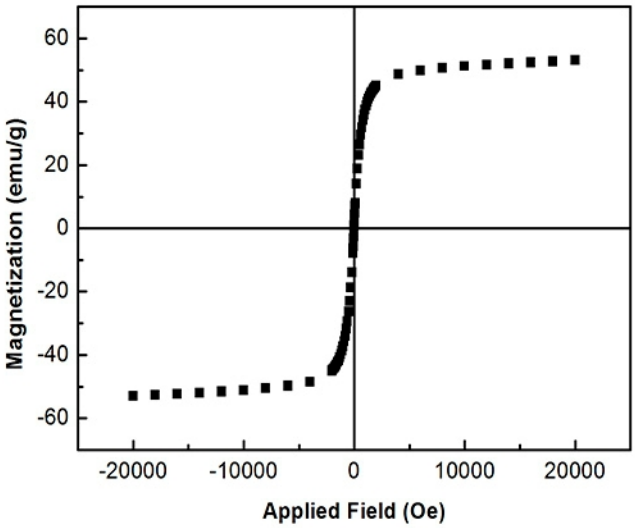


Figure S7. Hysteresis loop of $MnFe_2O_4$ nanoparticles at room temperature.

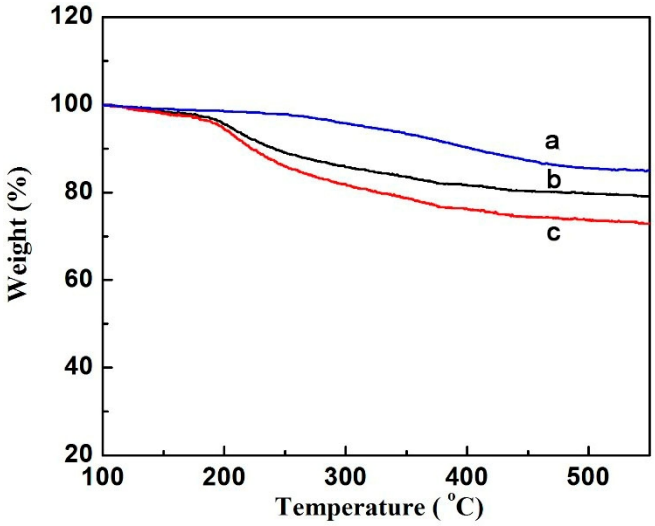


Figure S8. TGA curves of oleic acid capped $MnFe_2O_4$ (a), $MnFe_2O_4$@$PrBrT_{23}$-2 (b), and $MnFe_2O_4$@$PrBrT_{23}$-1 (c) nanoparticles.

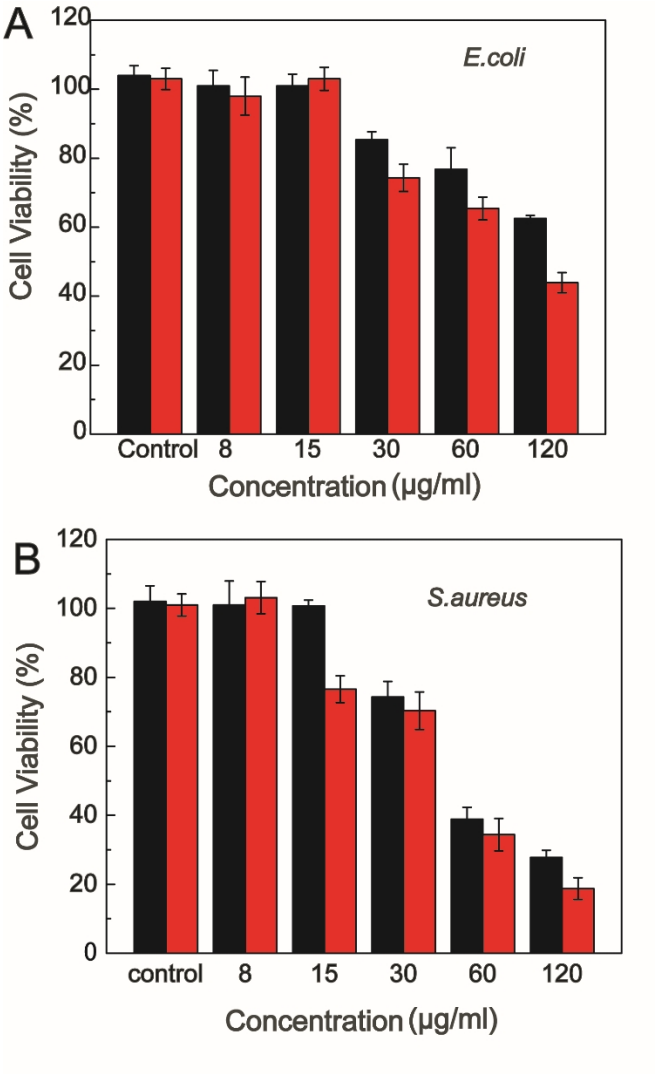


Figure S9. Dependence of bacteria cell viability on the concentration of $MnFe_2O_4$@$PrBrT_{23}$-1 (red) and $MnFe_2O_4$@$PrBrT_{23}$-2 (black) concentrations for *E. coli* (A) and *S. aureus* (B).

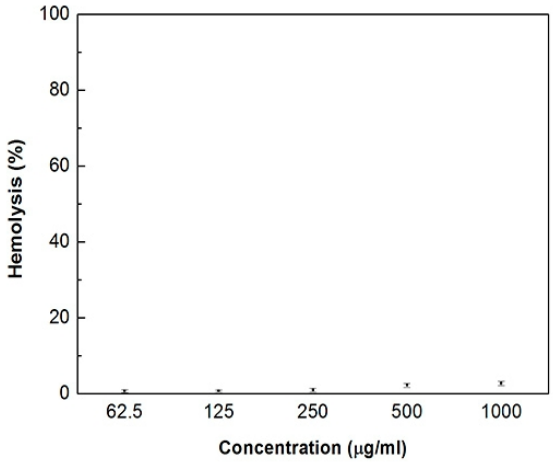


Figure S10. Hemolysis of $MnFe_2O_4$@$PrBrT_{14}$ nanoparticles at different concentrations.

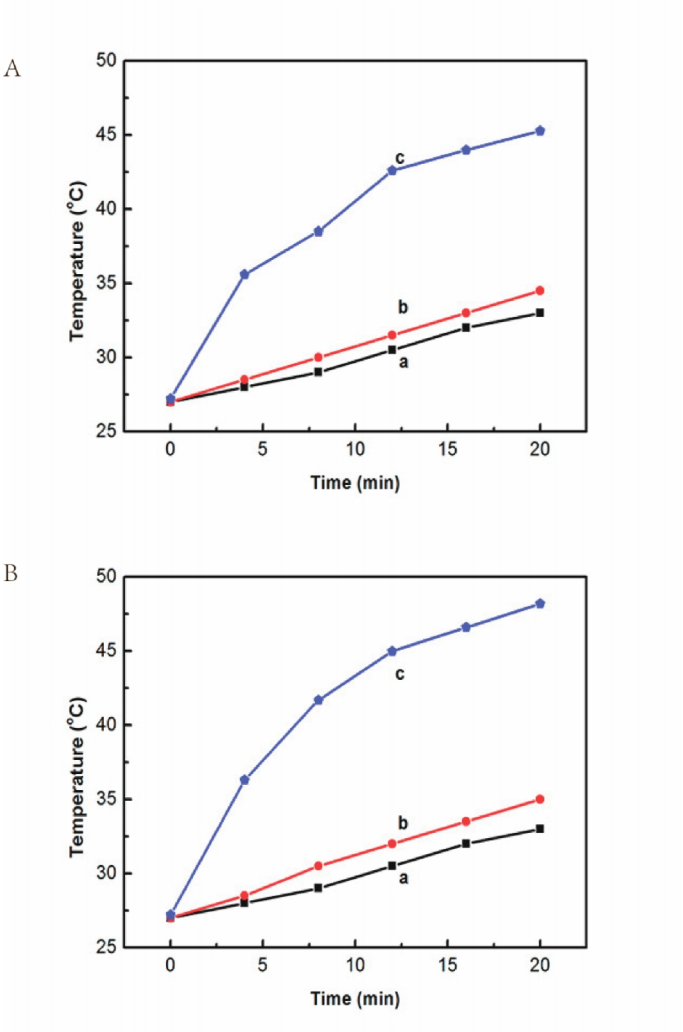


Figure S11. Temperature profiles of pure PBS (a), $MnFe_2O_4$@PrBrT (120 μg/ml) dispersion (b), $MnFe_2O_4$@ $PrBrT_{14}$-bound bacteria (c) by heating at 380 A for *E. coli* (A) and at 410 A for *S. aureus* (B), respectively.

Table S1. Antimicrobial activities of PrBrT and $MnFe_2O_4$@PrBrT

Material	MIC (μg/ml)	
	S.aureus	E.coli
PrBrT	100,000	>100,000
$MnFe_2O_4$@PrBrT	240	480

Reference

(1) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 7863-7871.