Electronic Supplementary Information

Enhanced efficacy of photothermal therapy by combining semiconducting polymer with an inhibitor of heat shock protein

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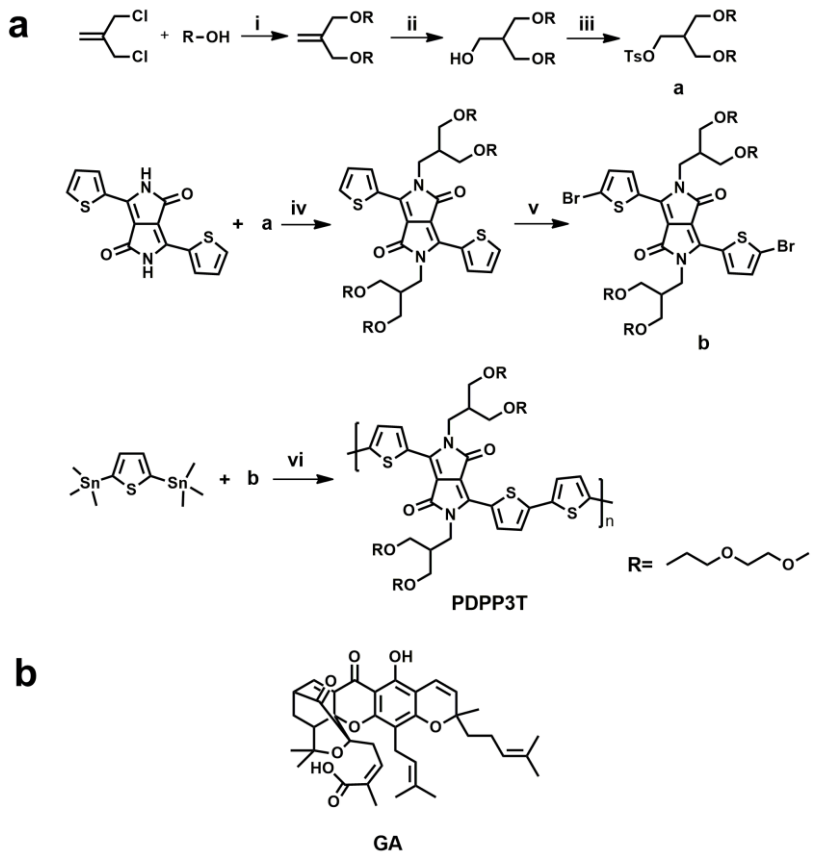
Characterization. ^{1}H NMR spectra were measured with Bruker Avance NMR spectrometer (400 MHz). Molecular weight of PDPP3T was measured by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as the standard and chloroform as the eluent. Elemental analysis was performed on a Bio-Rad elemental analyzer. The absorption and PL spectra were obtained from a UV-3600 UV-vis-NIR spectrophotometer (Shimadzu) and PerkinElmer LS-55 Spectrofluorophotometer respectively. DLS and TEM results of the nanoparticles were determined by Malvern Zeta-sizer Nano and JEOL JEM-1011 electron microscope (acceleration voltage of 100 kV). CLSM images were taken by using a Zeiss LSM 700 (Zurich, Switzerland). PA imaging was measured on MSOT inVision 128 small animal imaging system (iThera Medical GmbH).

Synthesis of polymer PDPP3T. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13-8.60 (br), 7.18-6.83 (br), 4.33-3.13 (br), 2.63-2.29 (br). Anal. Calcd. for $C_{46}H_{66}N_2O_{14}S_3$: C, 57.12; H, 6.88; N, 2.90; S, 9.95. Found: C, 56.27; H, 6.35; N, 2.77; S, 10.19.



Scheme S1 a) The synthetic routes of PDPP3T. Reaction conditions: i) NaH in THF at 0 ^{o}C and then 65 ^{o}C; ii) BH_3/THF at 0 ^{o}C then NaOH (aq), H_2O_2 (aq) at r.t.; iii) $(CH_3)_3N$·HCl, TsCl (4-Toluene sulfonyl chloride), Et_3N in DCM, r.t.; iv) K_2CO_3, Bu_4NBr, DMF, 120 ^{o}C; v) NBS, DCM, r.t.; vi) $Pd_2(dba)_3$, P(o-tolyl)$_3$, chlorobenzene/DMF (10:1, v/v), 135 ^{o}C. b) The chemical structure of GA.

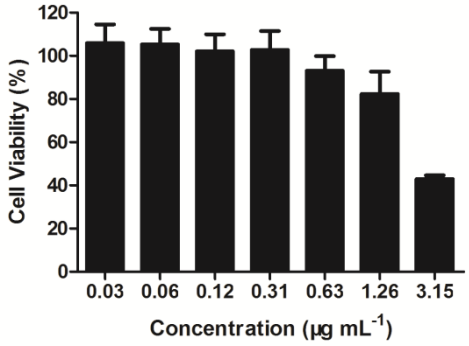


Fig. S1 Viabilities of HepG2 cells treated with GA after incubation for 24 h at 37 ℃. All the results were repeated three times, and presented as mean ± SD.

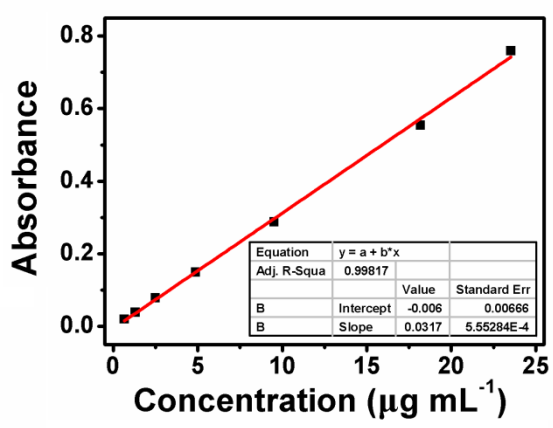


Fig. S2 The standard curve of PDPP3T in THF.

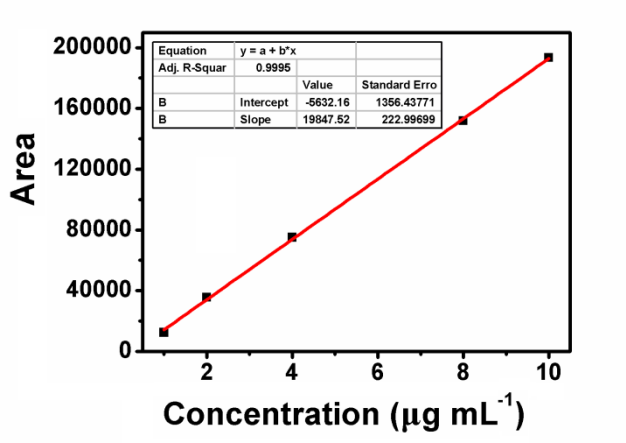


Fig. S3 The standard curve of GA determined by HPLC.

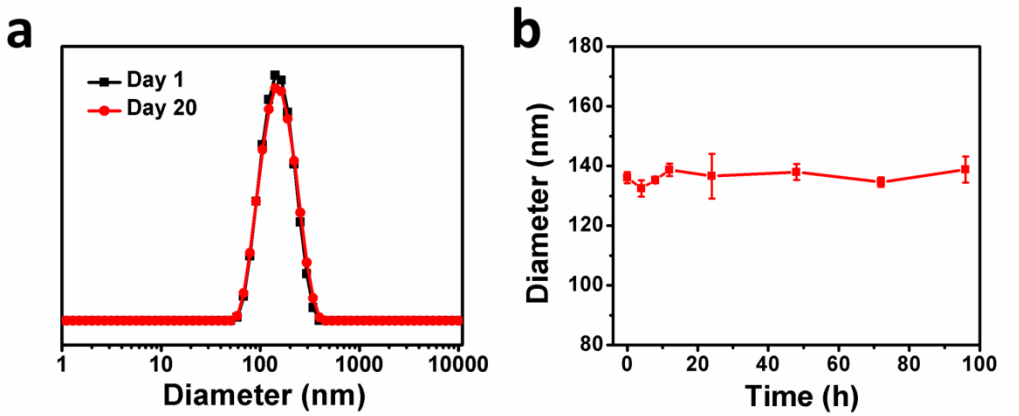


Fig. S4 a) Size and size distribution of PGNPs at the 1st and the 20th day determined by DLS. b) Changes of the diameter of PGNPs in PBS (pH 7.4) containing 10% FBS as a function of time measured by DLS.

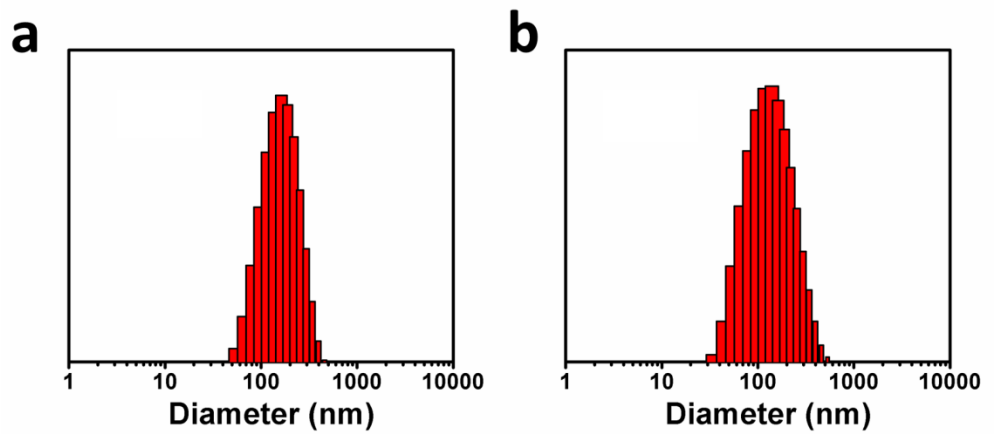


Fig. S5 Size and size distribution of PNPs and GNPs determined by DLS.

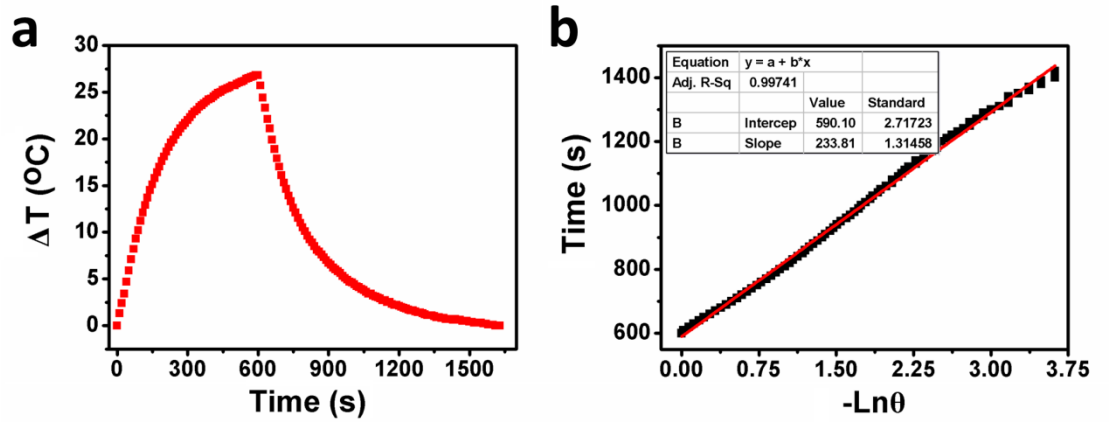


Fig. S6 a) The photothermal response of PGNPs in water (5 μg mL^{-1}) with laser irradiation (808 nm, 1.0 W cm^{-2}, 10 min) and then the laser was shut off. b) Linear time data versus -Ln θ obtained from the cooling period of a).

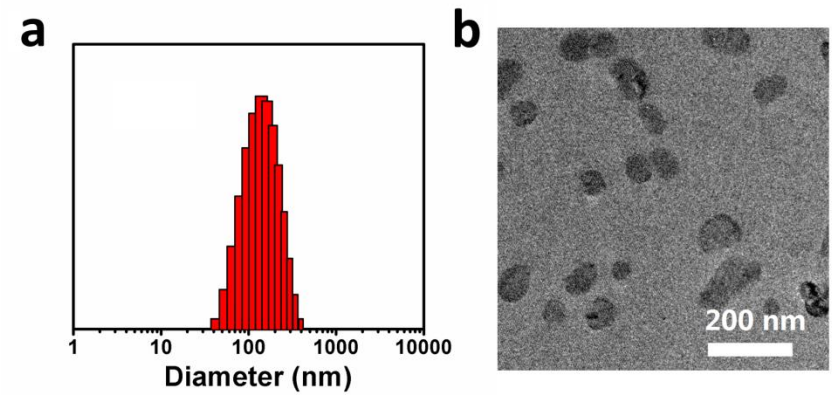


Fig. S7 a) DLS result and b) TEM image of PGNPs after 6 cycles of heating-cooling.

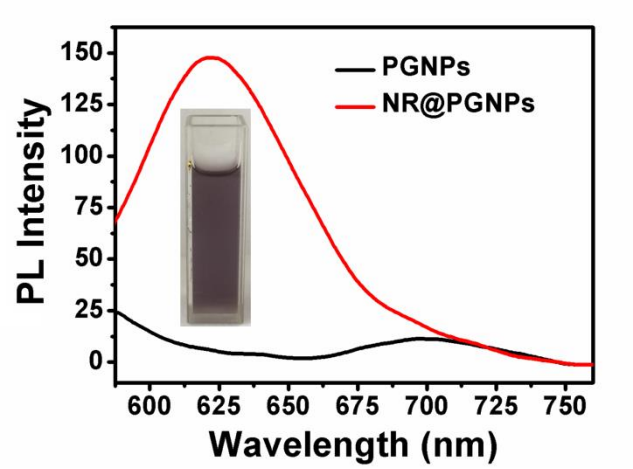


Fig. S8 PL spectra of PGNPs and NR@PGNPs in water. Inset: the picture of NR@PGNPs in water.

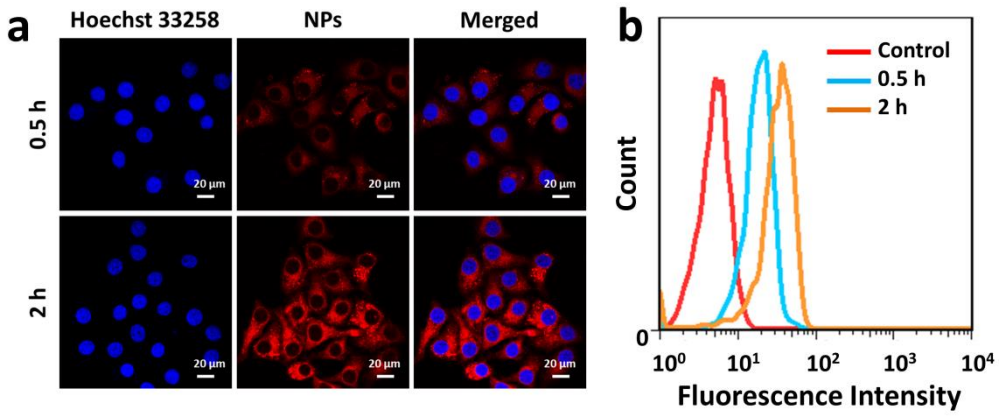


Fig. S9 a) CLSM images of HepG2 cells incubated with NR@PGNPs at 37 °C for 0.5 and 2 h. Pictures correspond to the fluorescence of Hoechst 33258 (blue), NR@PGNPs (red) and merged images from left to right. b) FCM analysis of HepG2 cells incubated with NR@PGNPs at 37 ℃ for 0.5 and 2 h.

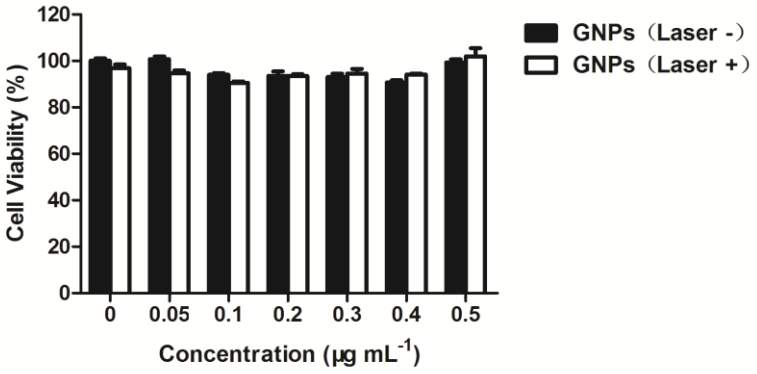


Fig. S10 Cell viabilities of HepG2 cells treated with GNPs with or without 808 nm laser irradiation (1.0 W cm^{-2}, 10 min).

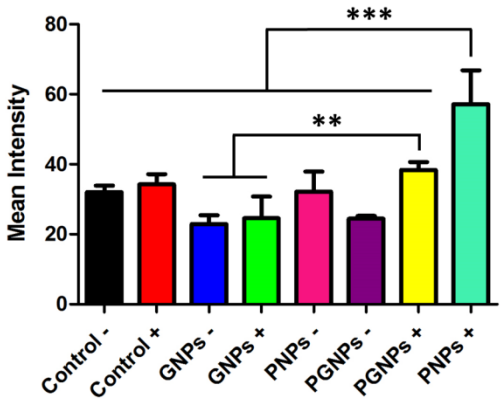


Fig. S11 Mean intensity of immunofluorescence images for HSP90 1 h post treatment in HepG2 cells. The HepG2 cells were treated with PBS, GNPs, PNPs and PGNPs under 808 nm laser irradiation (1.0 W cm^{-2}, 10 min) or not.

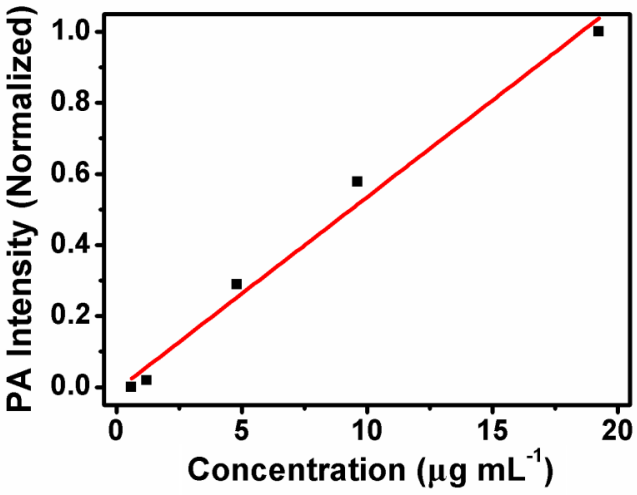


Fig. S12 The intensity of PA signal as a function of concentrations of PGNPs.

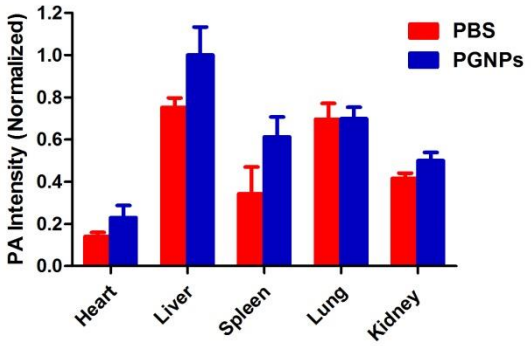


Fig. S13 Ex vivo PA intensities of major organs (heart, liver, spleen, lung and kidney) of mice 24 h post injection.

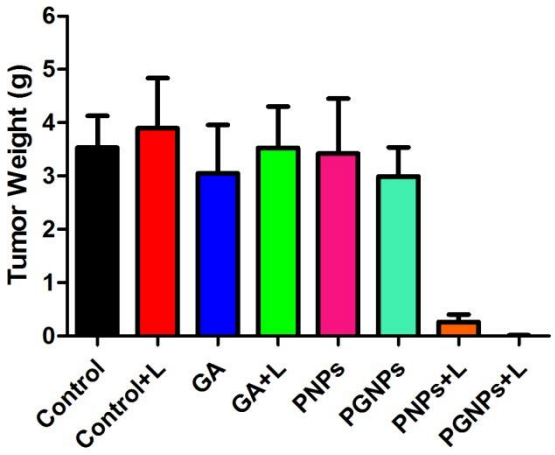


Fig. S14 The tumor weights of mice after different treatments.

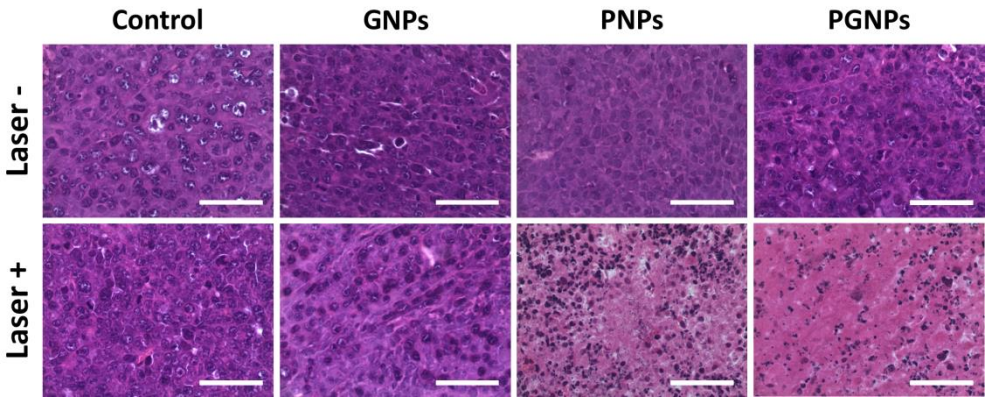


Fig. S15 H&E stained tumor slices collected from mice 2 d post various treatments indicated. Scale bars: 200 μm.