

Fig S1. $^1\text{H-NMR}$ spectrogram of (A) BR6 and (B) BR647. For BR6: ($\text{d}_6\text{-CDCl}_3$, 400Hz) δ ppm 6.52 (ddd,1H), 6.21-6.08 (m,1H), 5.88 (dd,1H), 4.45 (t,2H), 3.26-2.85 (m,2H); for BR647: ($\text{d}_6\text{-DMSO}$, 400Hz) δ ppm 4.28-4.00 (m,4H), 2.91 (dt,4H), 2.77-2.53 (m,4H), 2.43-2.18 (m,6H), 1.65-1.14 (m,4H). (C) GPC curves of BR647. M_n 3983 Da, M_w 6649 Da, PDI 1.67.

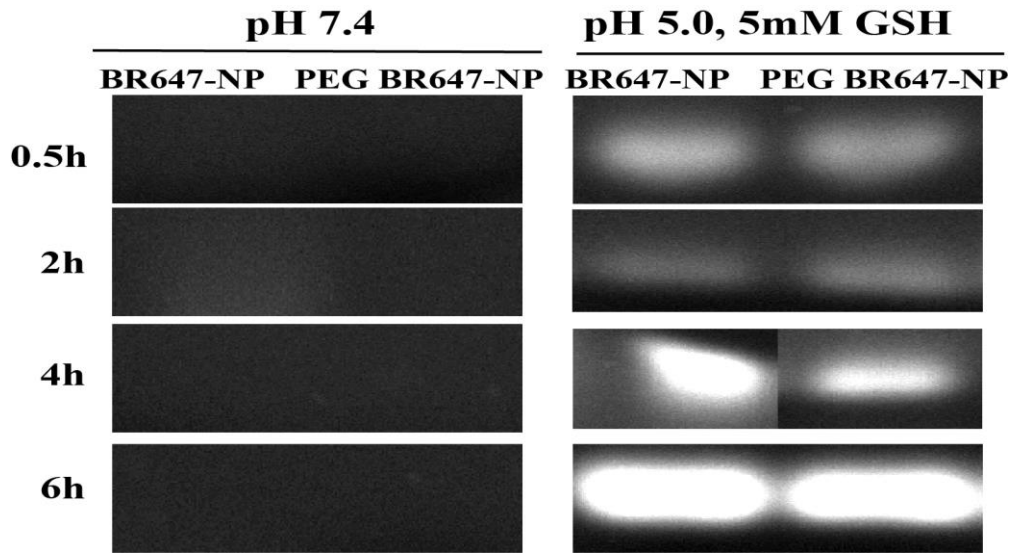
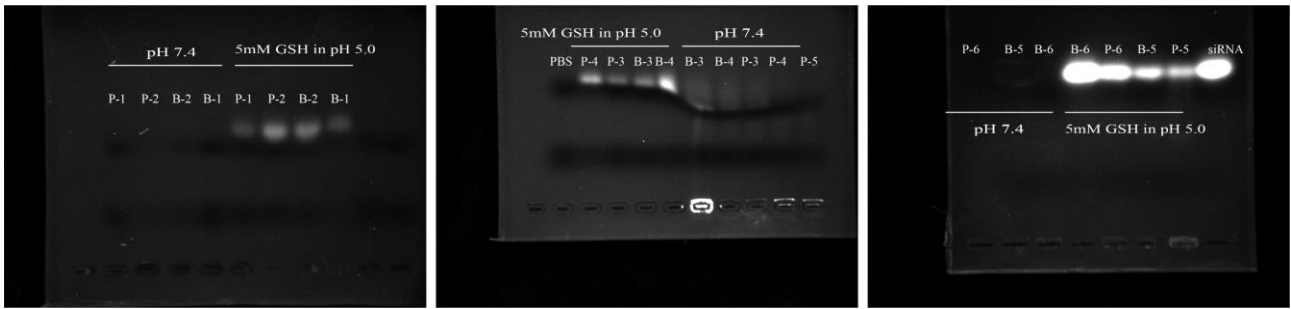


Fig S2. The release of BR647-NPs in PBS (pH 7.4) and 5 mM GSH PBS (pH 5.0) was evaluated by agarose gel. B: BR647-NP, P: PEG BR647-NP. 1: 15 min, 2: 0.5 h, 3: 2 h; 4: 4 h, 5: 5h, 6: 6 h.

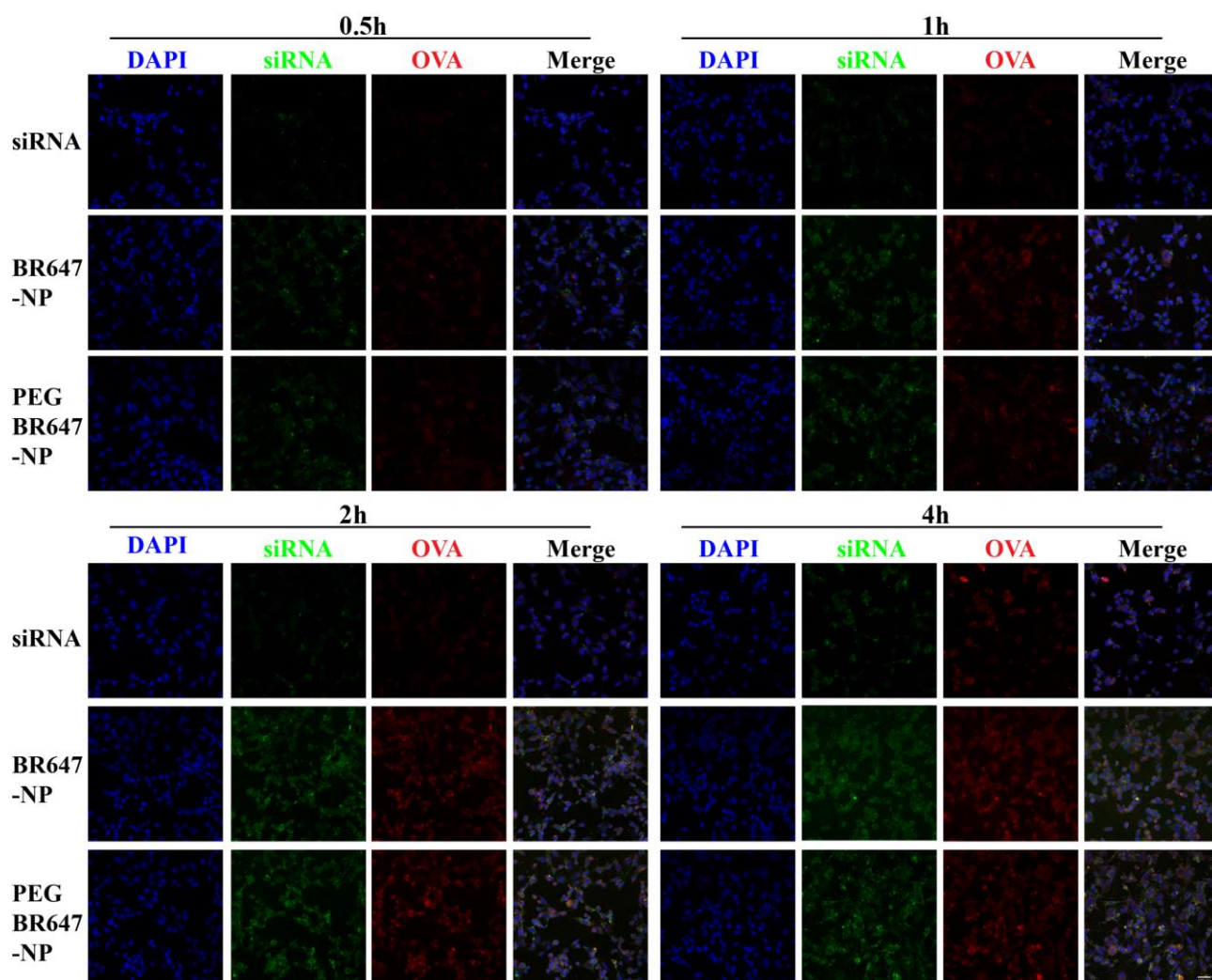


Fig S3. Fluorescence imaging of DC_{2.4} cells after 0.5, 1, 2 and 4 h incubation with BR647-NPs@FAM-STAT3 siRNA/CY3-OVA and FAM-STAT3 siRNA/CY3-OVA solution (50 nM FAM-STAT3 siRNA, 2 μ g/mL CY3-OVA). Nuclei are stained with DAPI (blue), FAM labeled STAT3 siRNA is green, CY3 labeled OVA is red ($\times 200$, scale bar: 100 μ m).

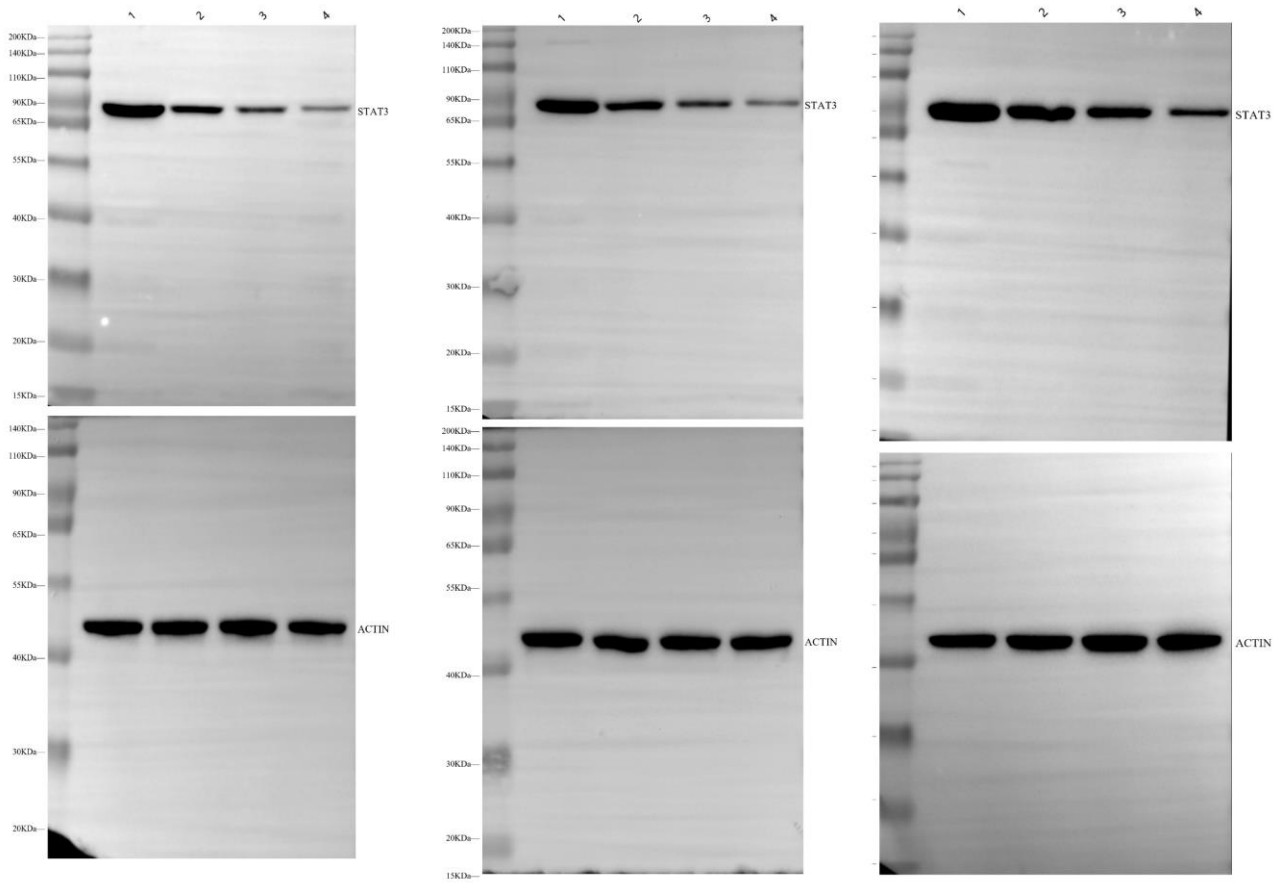


Fig S4. The expression of STAT3 in B16F10 cells. B16F10 cells were pretreated with PBS (1), STAT3 siRNA/OVA (2), BR647-NP (3), PEG BR647-NP (4) (50 nM STAT3 siRNA and 2 μ g/mL OVA) for 72 h (n=3).

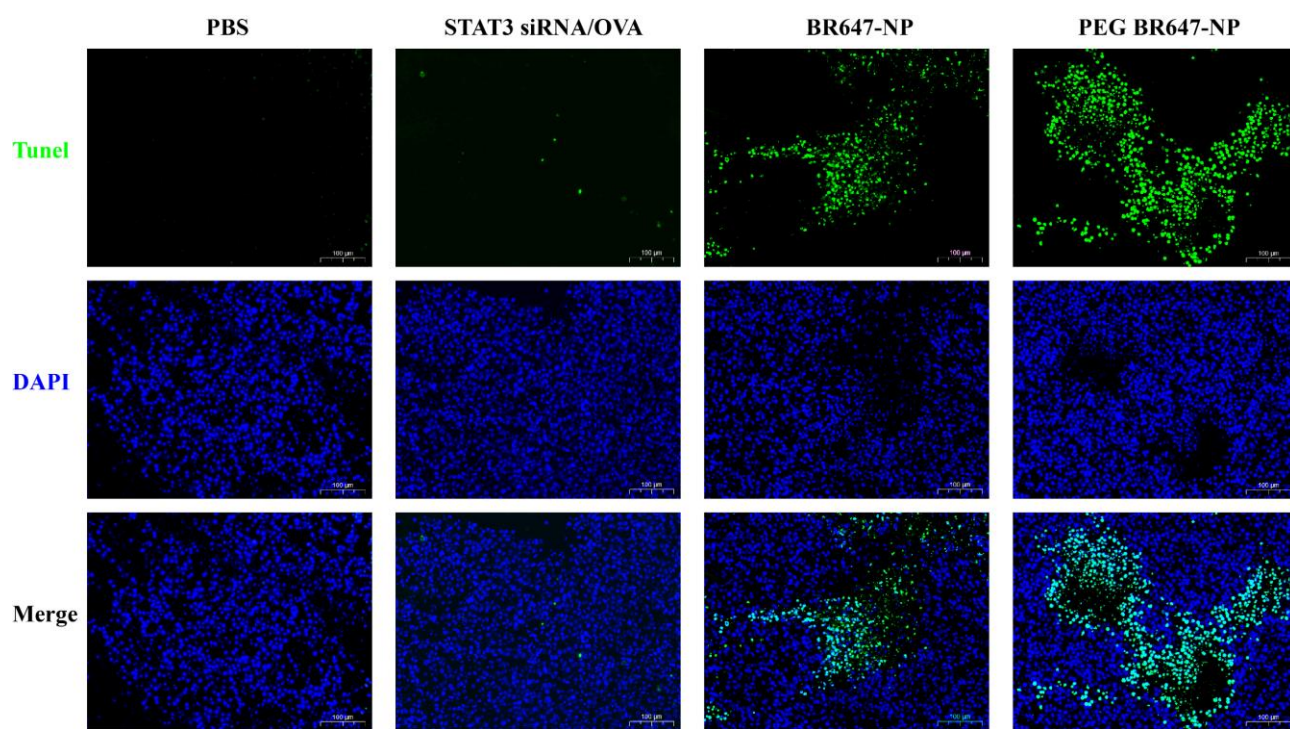


Fig S5. Cell apoptosis in tumors was detected using TUNEL assay ($\times 200$, scale bar: 100 μm). B16-OVA tumor-bearing C57BL/6 mice were s.c. injected every 5 days for a total of 3 immunizations (1 nmol/mouse STAT3 siRNA and 40 μg /mouse OVA).

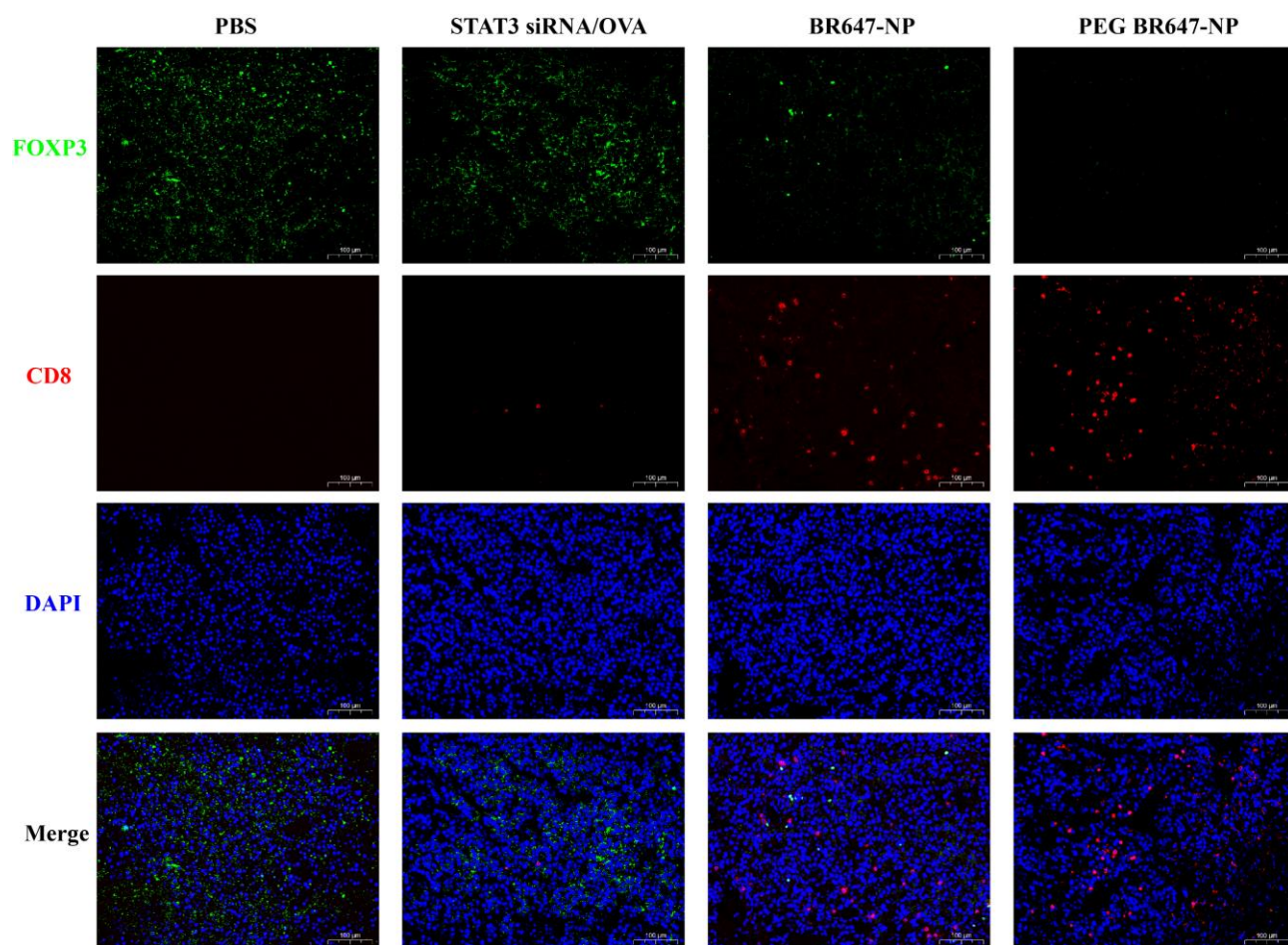


Fig S6. CD8 and FOXP3 immunofluorescent staining test results in tumors of different groups ($\times 400$, scale bar: 100 μm).

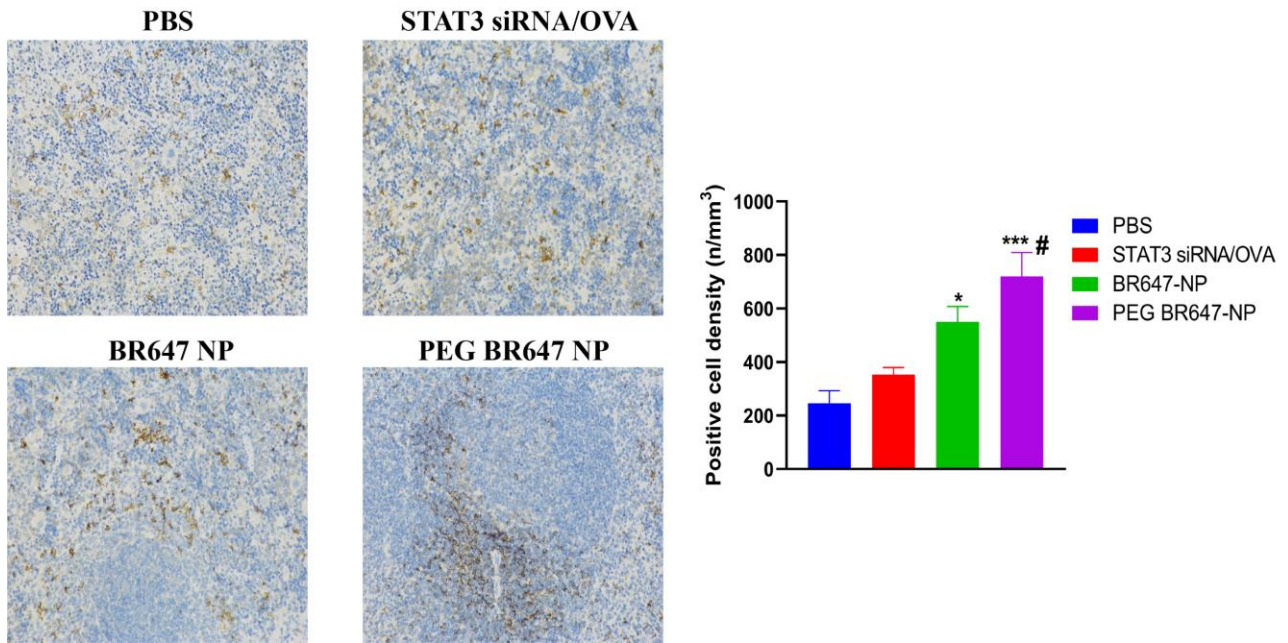


Fig S7. CD8 immunohistochemical test results in spleen of different groups, and the CD8⁺T cells density of all groups (n = 3). **P* < 0.05 and ****P* < 0.001 vs STAT3 siRNA/OVA, #*P* < 0.05 vs BR647-NP (×200).

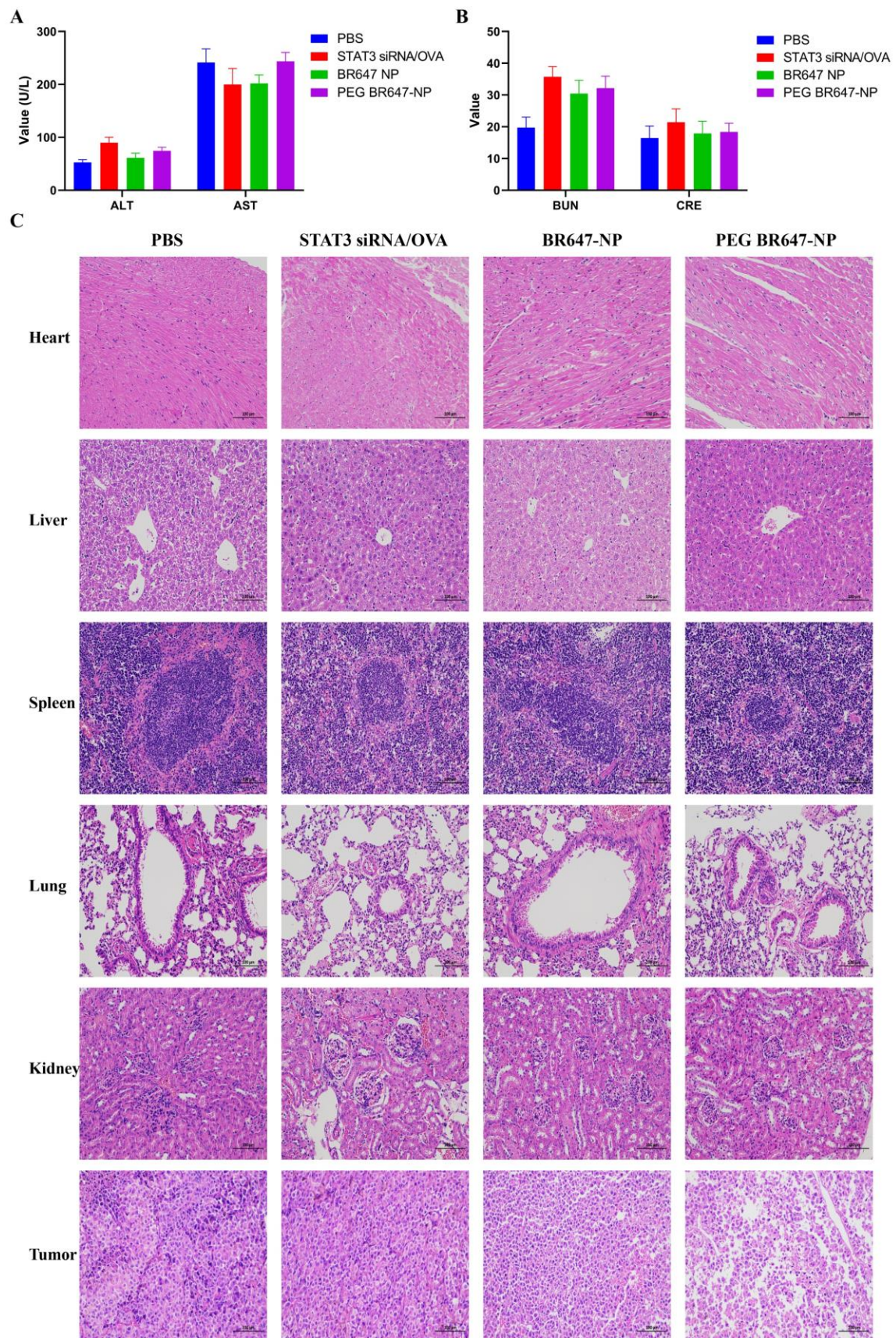


Fig S8. The serum levels of markers for (A) liver function and (B) kidney function (n = 5). (C) H&E staining images of the major organs and tumors (n = 3) ($\times 200$).

Table S1. Optimize the weight ratio of BR647 to siRNA to OVA in BR647-NP.

	50:1:3	150:1:3	500:1:3
Z-average (nm)	231.5 ± 76.95	98.6 ± 12.58	181.2 ± 74.21
PDI	0.474 ± 0.066	0.218 ± 0.014	0.382 ± 0.012
Zeta potential (mV)	10.4 ± 0.72	7.53 ± 0.234	21.3 ± 1.51
Encapsulation Efficiency of siRNA	97.65%	100.99%	65.78%
Encapsulation Efficiency of OVA	51.24%	94.87%	70.48%
Transfection in B16F10 ^a	14.7	25.0	13.1
Transfection in DC2.4 ^a	13.8	22.5	12.3

^a compared to free FAM-STAT3 siRNA solution