

Supporting information

for

**Polylysine derivative coated black phosphorus as a nanoplatform for
photothermal-chemotherapy to enhance anti-tumor efficiency**

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$^1\text{H-NMR}$ data of PLL-SS- NH_2 and its intermediate:

PLL. $^1\text{H-NMR}$ (600MHz, $\text{DMSO-}d_6$): δ 8.84 (s, 1H, NH), 8.36 (s, 2H, NH_2), 3.79 (t, 1H, CH), 3.10 (s, 2H, CH_2), 1.76 (s, 2H, CH_2), 1.46 (s, 2H, CH_2), 1.36 (d, 2H, CH_2).

PLL-SA. $^1\text{H-NMR}$ (600MHz, $\text{DMSO-}d_6$): δ 8.02 (d, 1H, NH), 7.82 (s, 1H, NH), 4.12 (dd, 1H, CH), 2.99 (d, 2H, CH_2), 2.40 (s, 2H, CH_2), 2.37 (d, 2H, CH_2), 1.63 (t, 2H, CH_2), 1.35 (m, 2H, CH_2), 1.24 (m, 2H, CH_2).

PLL-SS- NH_2 . $^1\text{H-NMR}$ (600MHz, D_2O): 8.49 (d, 1H, NH), 7.02 (d, 1H, NH), 4.14 (s, 1H, CH), 3.50 (t, 1H, CH), 3.17 (s, 2H, CH_2), 2.98 (t, 2H, CH_2), 2.88 (s, 2H, CH_2), 2.85 (q, 2H, CH_2), 2.56 (s, 2H, CH_2), 2.49 (m, 2H, CH_2), 1.67 (d, 2H, CH_2), 1.50 (s, 2H, CH_2), 1.35 (s, 2H, CH_2).

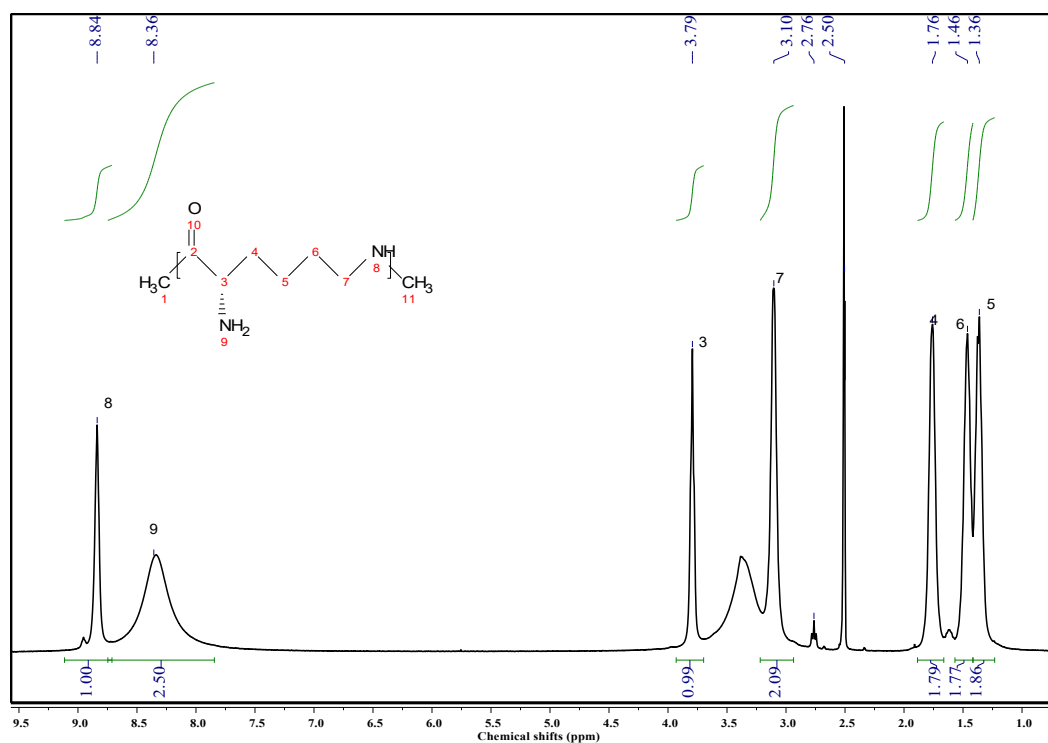


Fig. S1. $^1\text{H-NMR}$ spectrum of PLL.

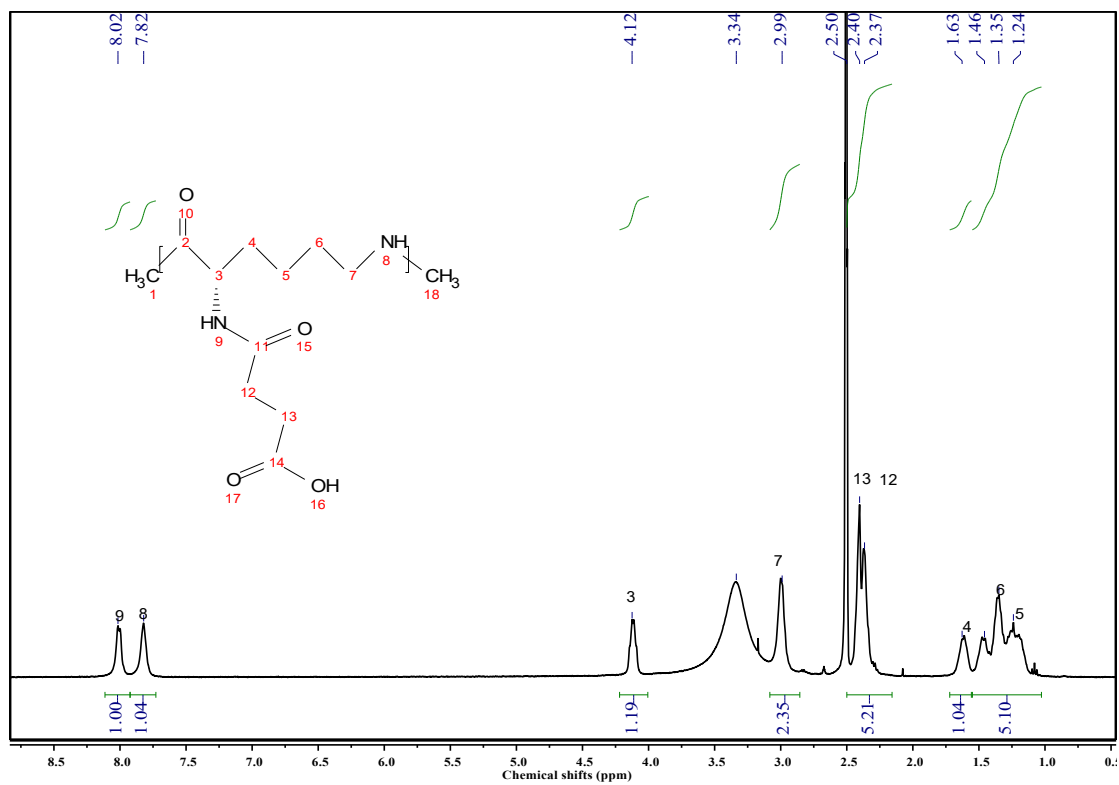


Fig. S2. ¹H-NMR spectrum of PLL-SA.

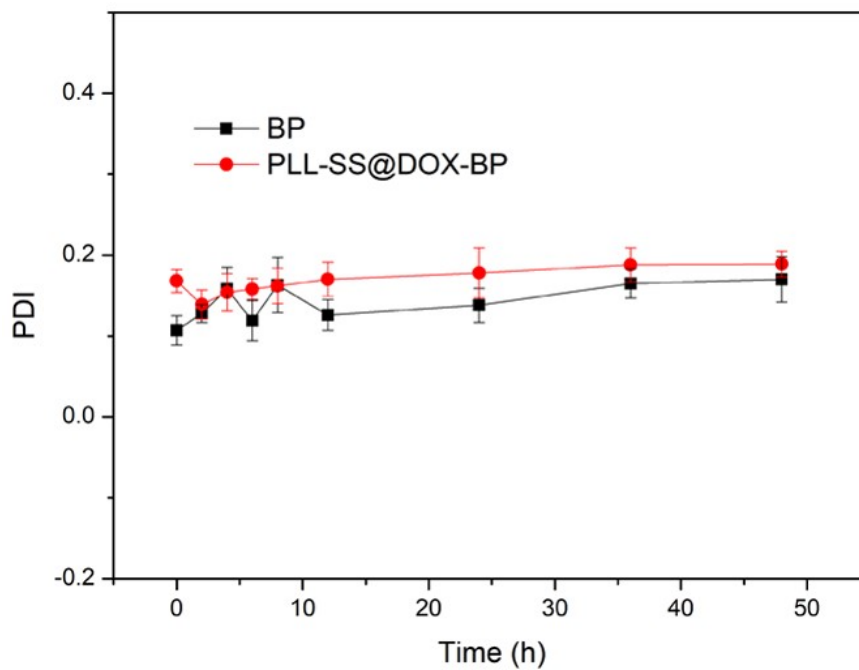


Fig. S3. The PDI changes of BP nanosheets and PLL-SS@DOX-BP nanocomposites at ambient temperature in darkness during 48 h.

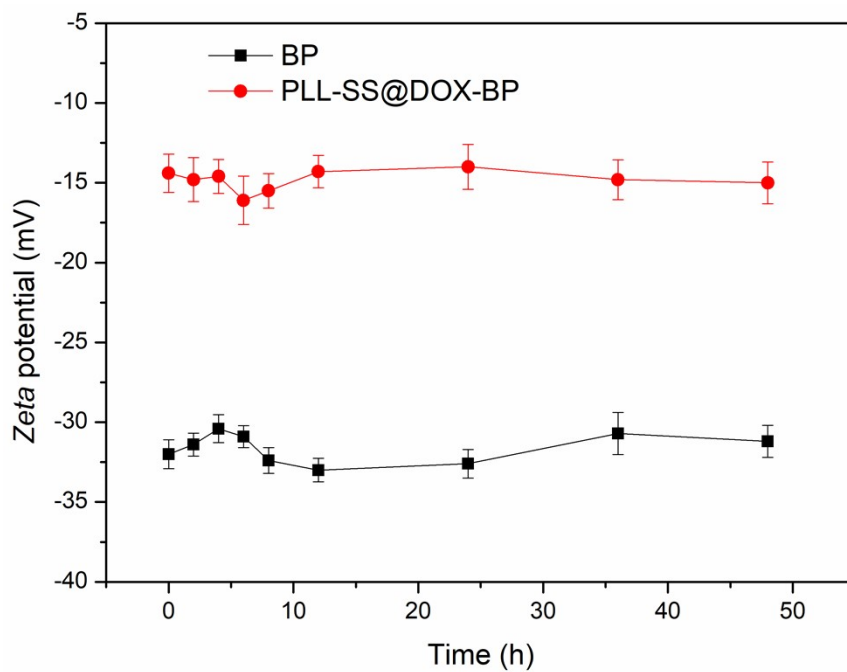


Fig. S4. The *zeta*-potential changes of BP nanosheets and PLL-SS@DOX-BP nanocomposites at ambient temperature in darkness during 48 h.

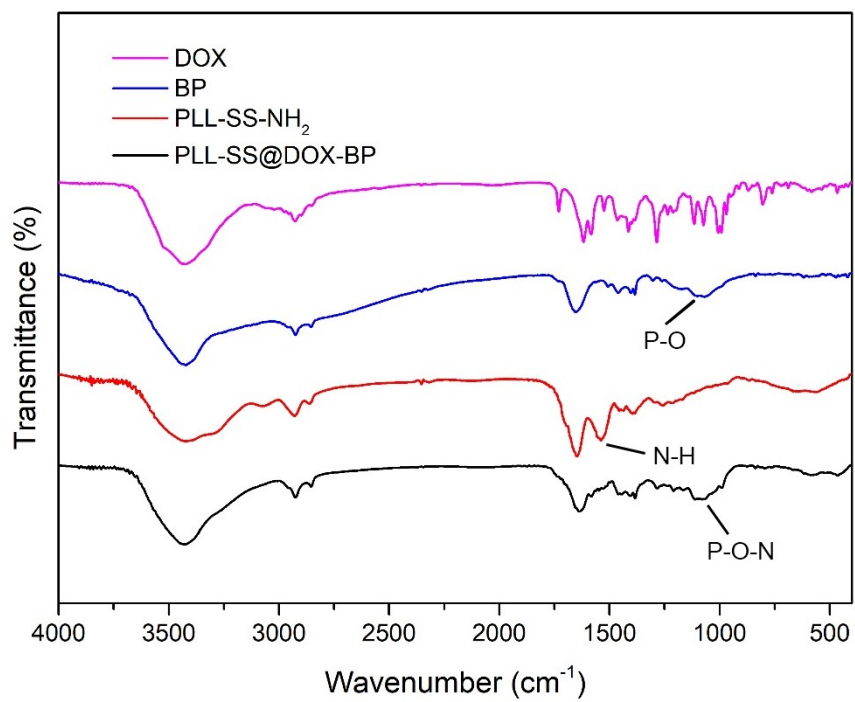


Fig. S5. FT-IR spectra of different preparations.

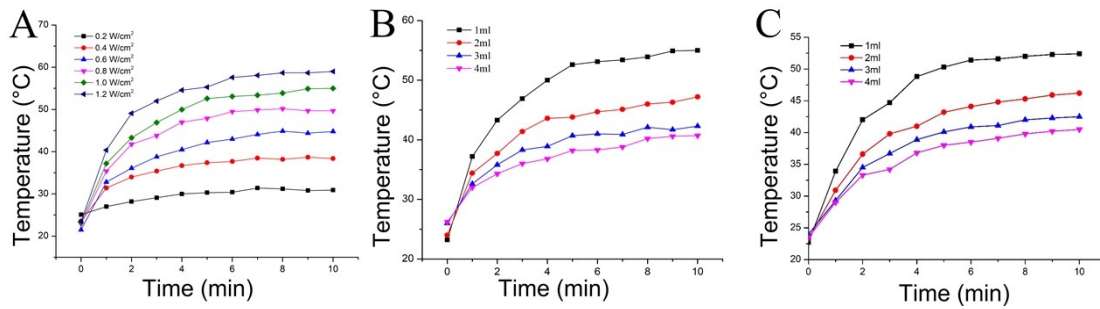


Fig. S6. Photothermal performance of BP nanosheets with different power density of laser irradiation (A); Photothermal performance of BP nanosheets of different concentrations (B); Photothermal performance of PLL-SS@DOX-BP nanocomposites of different concentrations (C).

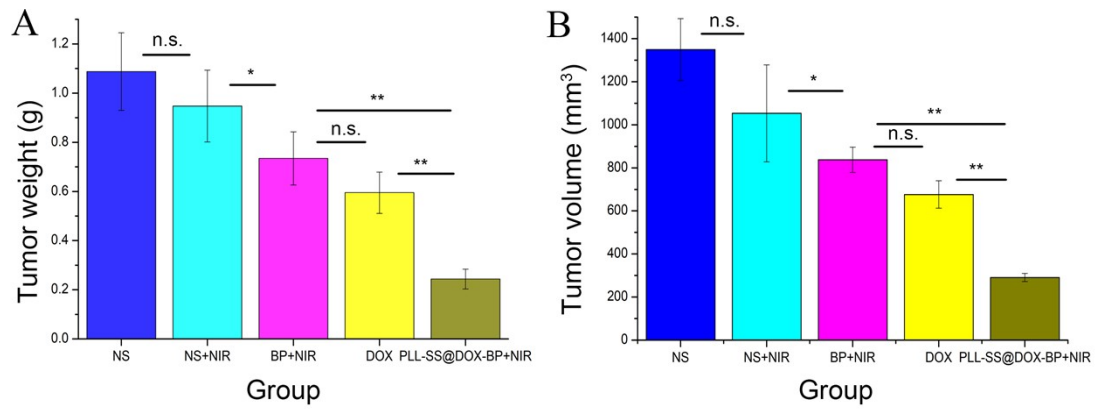


Fig. S7. Tumor weight of different treatment groups (A); Tumor volume of different treatment groups (B).

Table S1. Size distribution, PDI and *zeta*-potential of BP nanosheets and PLL-SS@DOX-BP nanocomposites.

Item	Size (nm)	PDI	<i>Zeta</i> -potential (mV)
BP	83.34 ± 1.25	0.107 ± 0.068	-32.0 ± 0.902
PLL-SS@DOX-BP	187 ± 1.097	0.168 ± 0.014	-14.8 ± 0.153

Table S2. IC₅₀ values of different treatments on 4T1 cells measured *via* CCK-8 assay.

Group	IC ₅₀ (µg·mL ⁻¹)
PLL-SS-NH ₂	-
BP	-
PLL-SS@DOX-BP	1.749 ± 0.079
BP + NIR	-
PLL-SS@DOX-BP + NIR	0.954 ± 0.021
DOX	0.776 ± 0.018

Table S3. *In vivo* pharmacodynamics parameters of each groups.

Group	Tumor weight (g)	Tumor volume (mm ³)	Tumor inhibition rate (%)
NS	1.09 ± 0.16	1349.32 ± 143.88	-
NS + NIR	0.95 ± 0.15	1053.26 ± 225.00	12.91 ± 13.43
BP + NIR	0.73 ± 0.11	838.08 ± 58.71	32.48 ± 9.94
DOX	0.59 ± 0.08	676.58 ± 63.60	45.30 ± 7.73
PLL-SS@DOX-BP	0.24 ± 0.04	290.85 ± 19.01	77.59 ± 3.69