Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supplementary Information

Regioisomer-Manipulating Thio-Perylenediimide Nanoagents for Photothermal/Photodynamic Theranostics

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Table S1. Photophysical properties of reported perylene agents.

PTT agents	PCE (%)	Laser irradiation	Concentration
PLAC−PDI NPs [1]	42%	730 nm, 0.5 W cm^{-2}	0.60 mg mL^{-1}
TNMs [2]	41 %	660 nm, 1 W cm^{-2}	50 μM
PDS-PDI [3]	40 %	660 nm, 0.5 W cm^{-2}	0.5 mg mL^{-1}
PDI-PEG [4]	43%	660 nm, 1W cm^{-2}	100 μg mL^{-1}

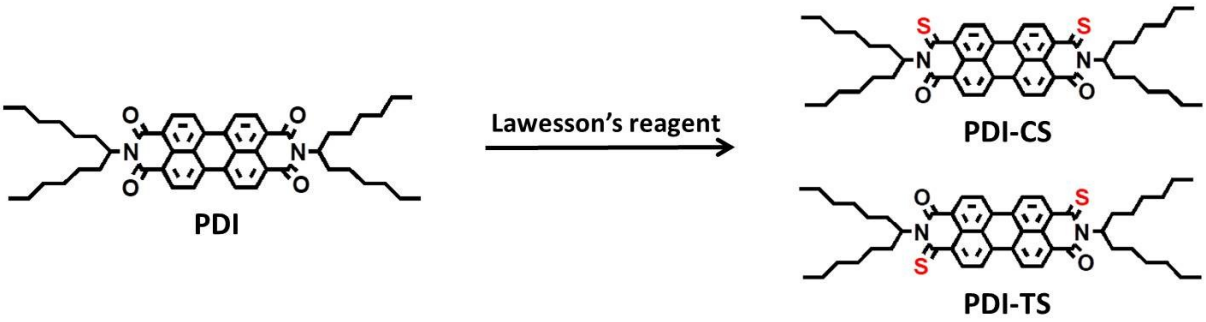

Fig. S1. Synthesis and structures of PDI-CS and PDI-TS.

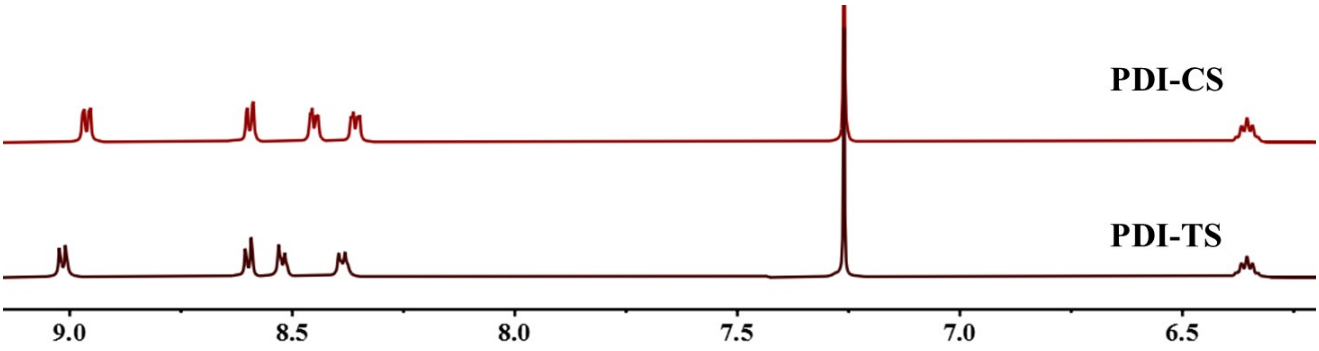

Fig. S2. Partial ^{1}H NMR spectra of PDI-CS, PDI-TS.

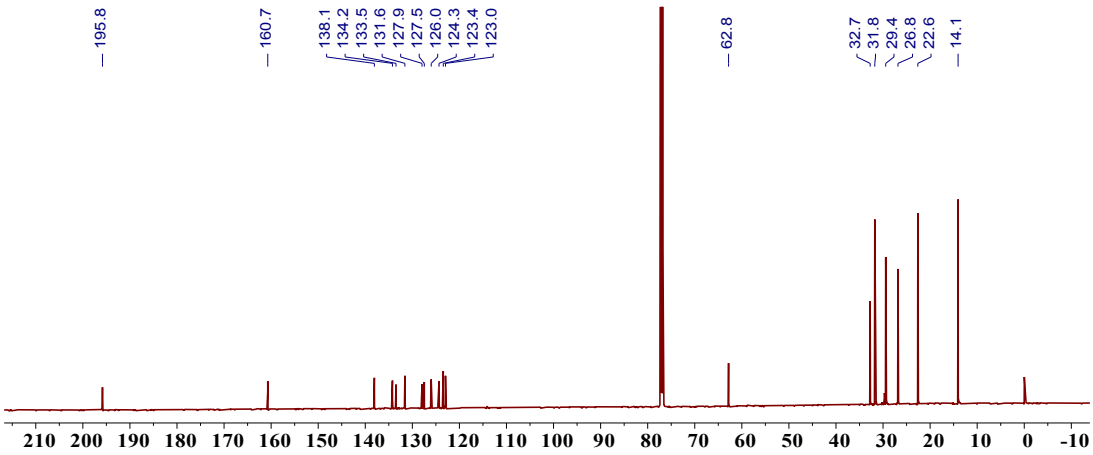

Fig. S3. ^{13}C NMR spectrum of PDI-CS.

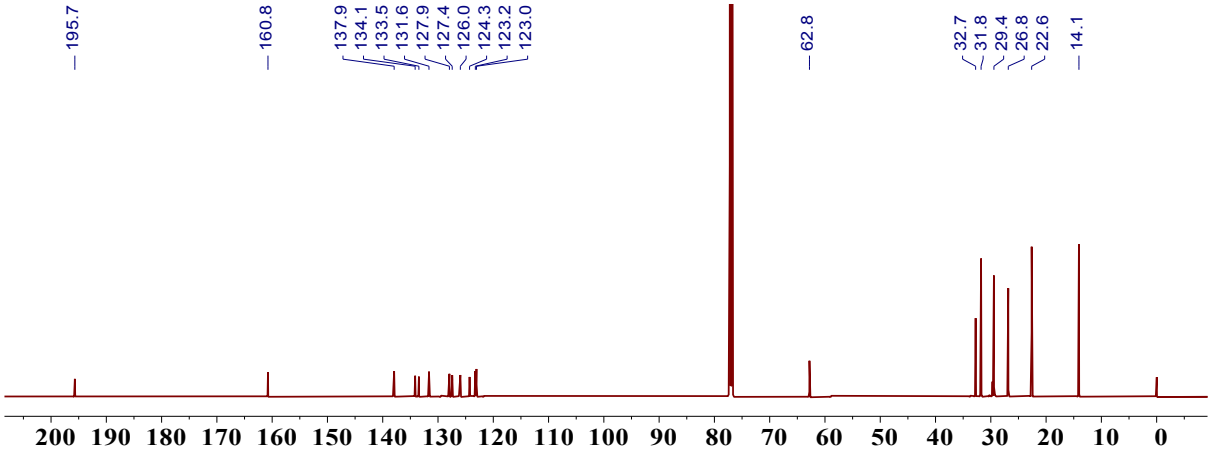

Fig. S4. ^{13}C NMR spectrum of PDI-TS.

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : D20200628

Sample Serial Number: PDI-CS

Operator : DONG Date: 2020/04/03

Operation Mode: DART POSITIVE

Elemental composition search on mass 787.43

m/z= 782.43-792.43

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
787.4323	787.4325	-0.34	20.5	$C_{50}H_{63}O_2N_2S_2$
	787.4332	-1.17	29.5	$C_{58}H_{59}S$
	787.4312	1.37	21.0	$C_{48}H_{61}ON_5S_2$
	787.4344	-2.64	26.0	$C_{52}H_{57}O_4N_3$
	787.4299	3.06	16.0	$C_{47}H_{65}O_5NS_2$
	787.4292	3.94	25.5	$C_{53}H_{59}O_2N_2S$
	787.4357	-4.34	25.5	$C_{54}H_{59}O_5$
	787.4285	4.77	16.5	$C_{45}H_{63}O_4N_4S_2$

Fig.S5. HRMS of PDI-CS. calcd for $C_{50}H_{62}N_2O_2S_2$, 786.4253 m/z, found $[M+H]^+$ 787.4323.

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number : D20200630

Sample Serial Number: PDI-TS

Operator : DONG Date: 2020/04/03

Operation Mode: DART POSITIVE

Elemental composition search on mass 787.43

m/z= 782.43-792.43

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
787.4323	787.4325	-0.35	20.5	$C_{50}H_{63}O_2N_2S_2$
	787.4332	-1.18	29.5	$C_{58}H_{59}S$
	787.4312	1.35	21.0	$C_{48}H_{61}ON_5S_2$
	787.4344	-2.65	26.0	$C_{52}H_{57}O_4N_3$
	787.4299	3.05	16.0	$C_{47}H_{65}O_5NS_2$
	787.4292	3.93	25.5	$C_{53}H_{59}O_2N_2S$
	787.4357	-4.36	25.5	$C_{54}H_{59}O_5$
	787.4285	4.76	16.5	$C_{45}H_{63}O_4N_4S_2$

Fig. S6. HRMS of PDI-TS. calcd for $C_{50}H_{62}N_2O_2S_2$, 786.4253 m/z, found $[M+H]^+$ 787.4323.

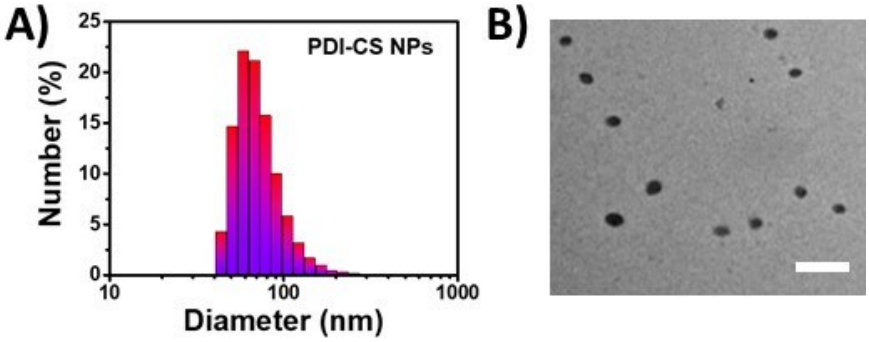

Fig. S7. (A) DLS measurement and (B) TEM image PDI-CS NPs (scale bar: 200 nm).

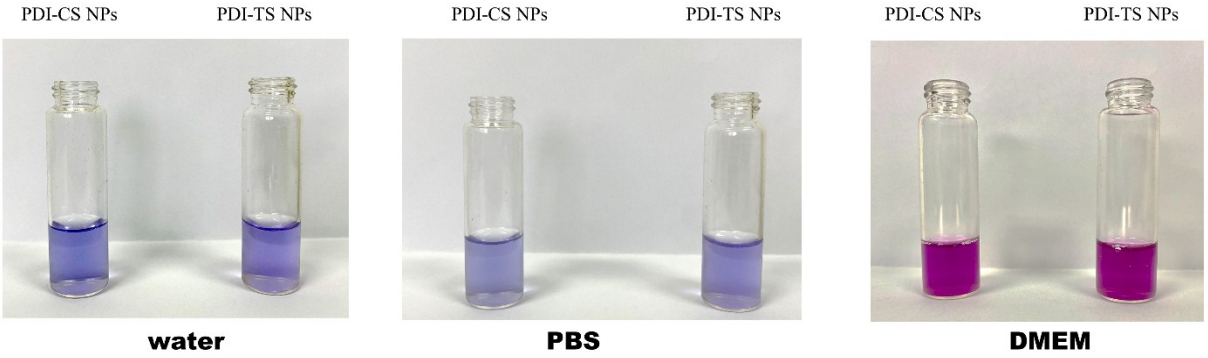

Fig. S8. The stability of PDI-CS and PDI-TS NPs in different solution after being stored in 4 ℃ refrigerator for four weeks.

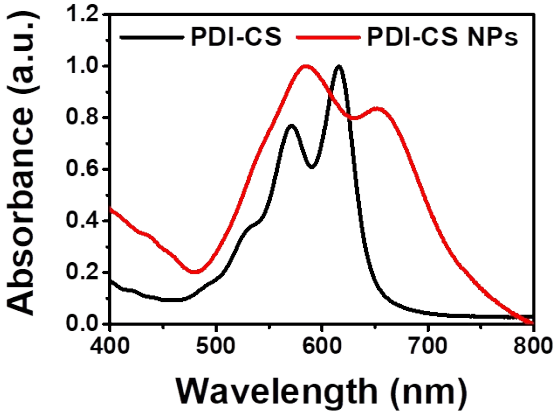

Fig. S9. UV-vis absorption spectra of PDI-CS in THF and NPs in deionized water.

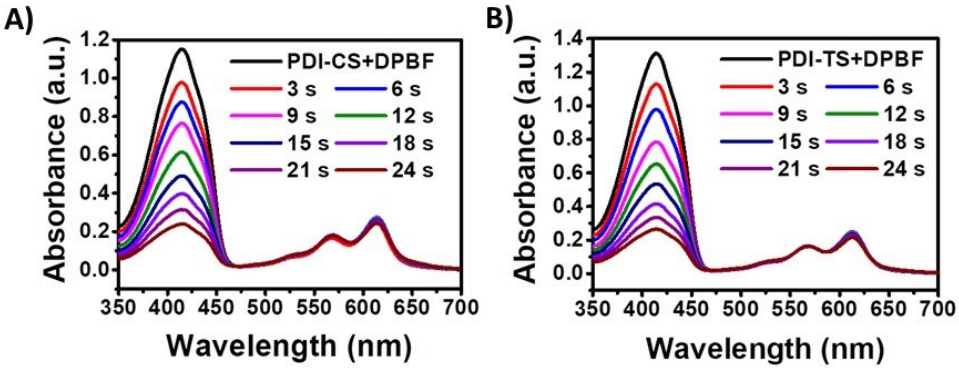

Fig. S10. Absorbance of (A) PDI-CS and (B) PDI-TS with DPBF after photodecomposition by ROS generation upon light irradiation at 20 mW cm^{-2}.

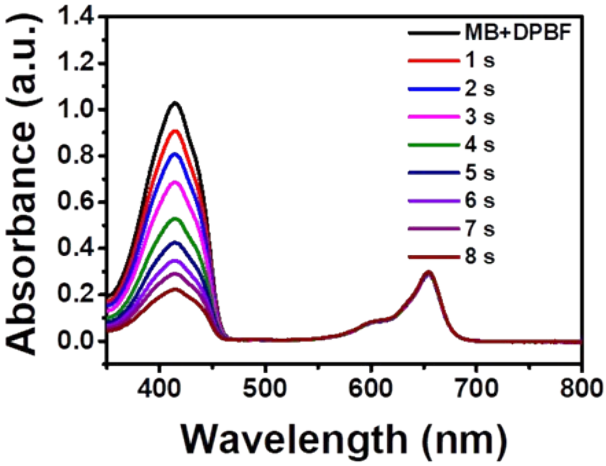

Fig. S11. Absorbance of DPBF after methylene blue (MB) by ROS generation upon light irradiation at 20 mW cm^{-2}.

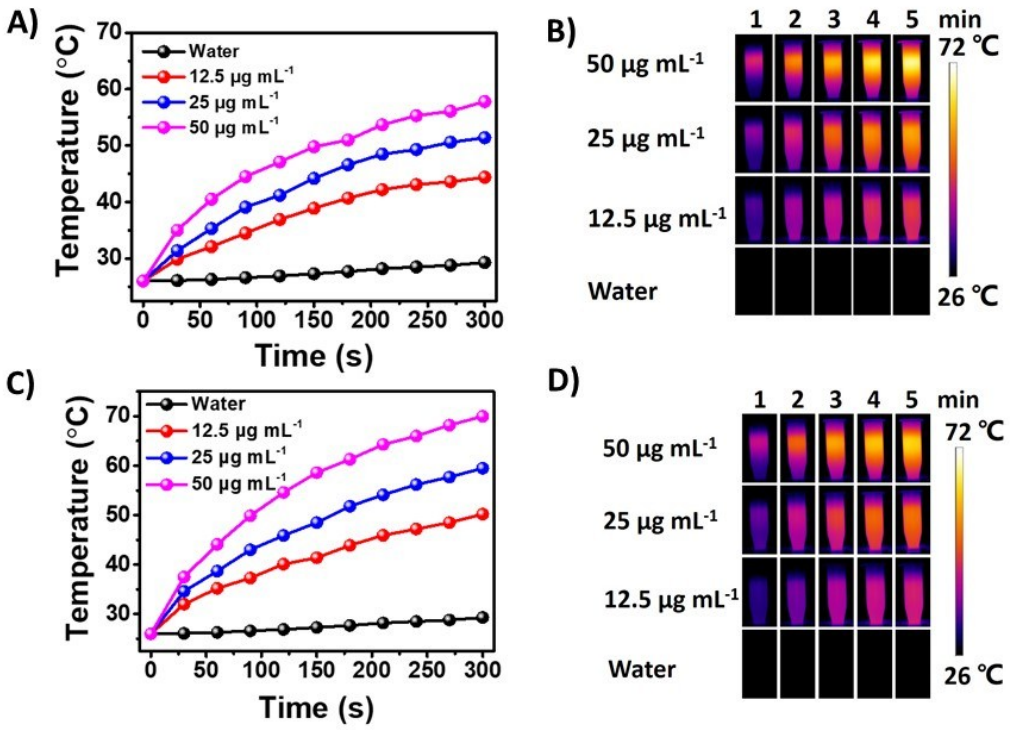

Fig. S12. (A, C) Temperature elevation and (B, D) infrared thermographs of (A, B) PDI-CS and (C, D) PDI-TS NPs aqueous solutions under 660 nm irradiation for 5 min (0.75 W cm^{-2}).

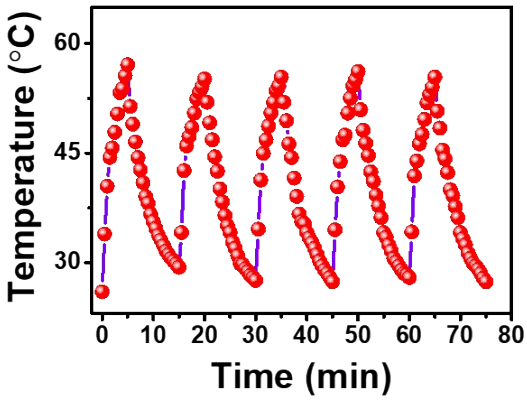

Fig. S13. Temperature profiles of a PDI-CS NPs aqueous dispersion for five laser on/off cycles.

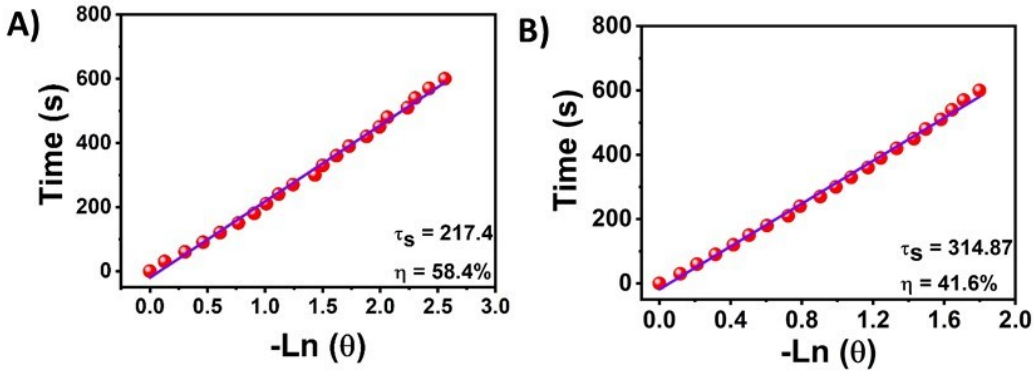

Fig. S14. A plot of time against temperature during the cooling period of (A) PDI-TS NPs and (B) PDI-CS NPs aqueous solution (50 μg mL^{-1}) under irradiation for 10 min with a laser (660 nm, 0.75 W cm^{-2}).

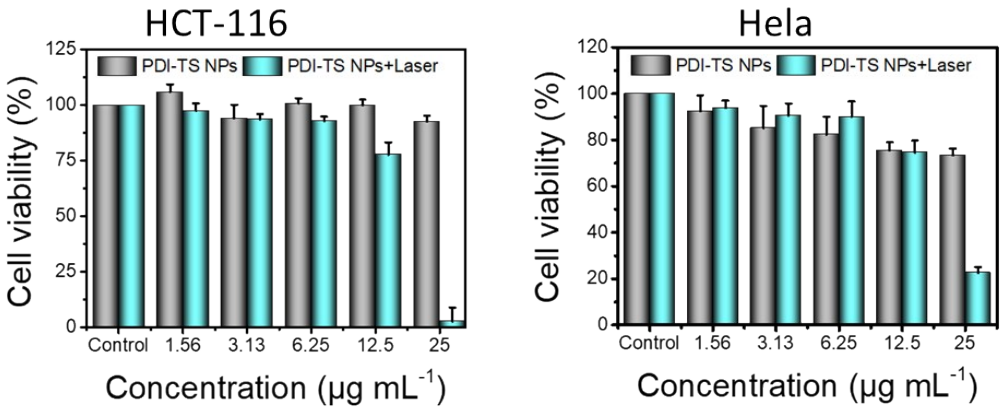

Fig. S15. Cell viability of HCT-116 and Hela cells after treatment with PDI-TS at different concentrations (0, 1.56, 3.13, 6.25, 12.5, 25 μg mL^{-1}) plus with 660 nm laser irradiation at 0.75 W cm^{-2} for 5 min.

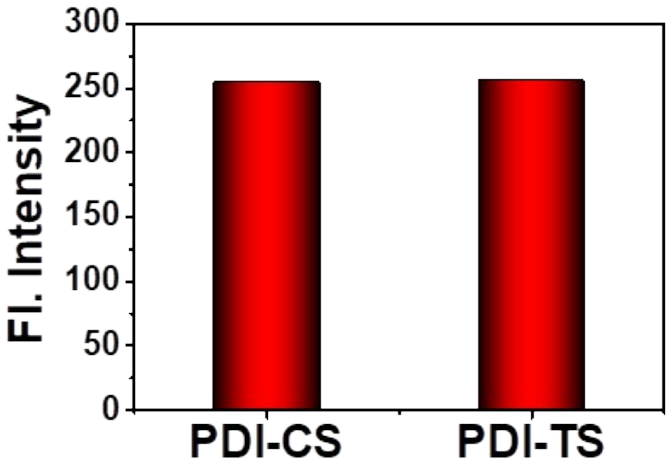

Fig. S16. Fluorescence intensity analysis of ROS production.

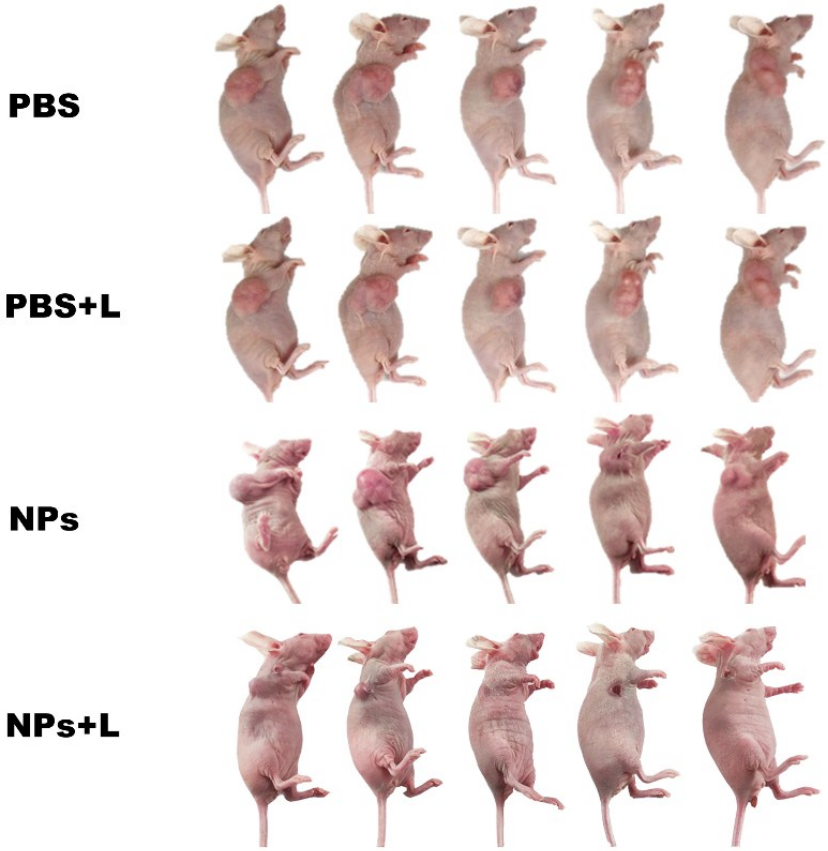

Fig. S17. Representative pictures of tumor-bearing mice after different treatments.

References

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2 S. Zhang, W. Guo, J. Wei, C. Li , X. Liang and M. Yin, *ACS Nano* 2017, **11**, 3797.

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4 S. Zhang, J. Li, J. Wei and M. Yin, *Sci. Bull.* 2018, **63**, 101.