

Supporting Information

Functionalized nanohybrids with rod shape for improved chemo-phototherapeutic effect against cancer by sequentially generating singlet oxygen and carbon dioxide bubbles

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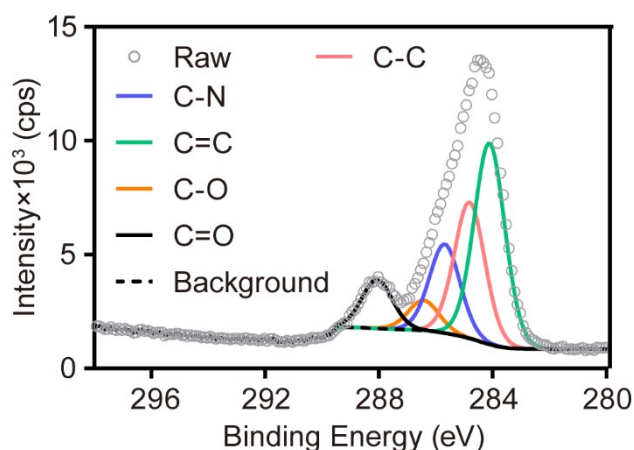


Fig. S1. High-resolution C 1s XPS spectra of PRMSs@ZF.

Table S1. DLC data of DOX or ICG-loaded samples.

Drug-loaded samples	DLC ($\mu\text{g}/\text{mg}$)
Da-RMSs	696.5
Da-PRMSs	981.4
IDa-PRMSs@ZF (DOX)	810.9
IDa-PRMSs@ZF (ICG)	489.9
I-PRMSs@ZF	540.6

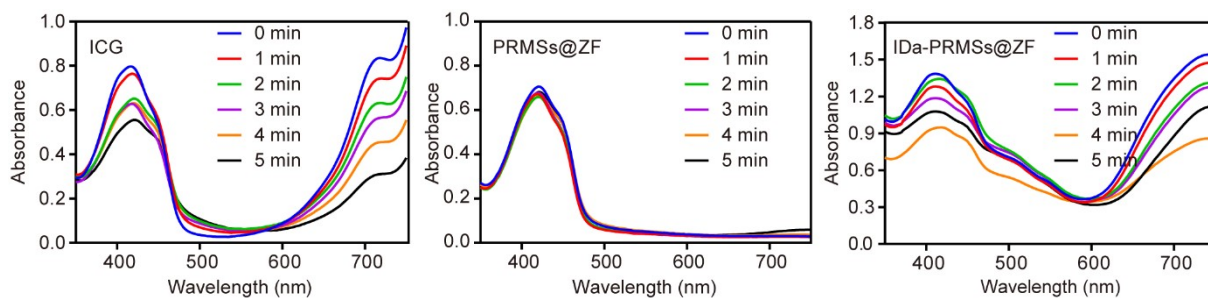


Fig. S2. UV-vis-NIR scanning spectra of ICG, PRMSs@ZF and I-PRMSs@ZF premixing with DPBF under irradiation.

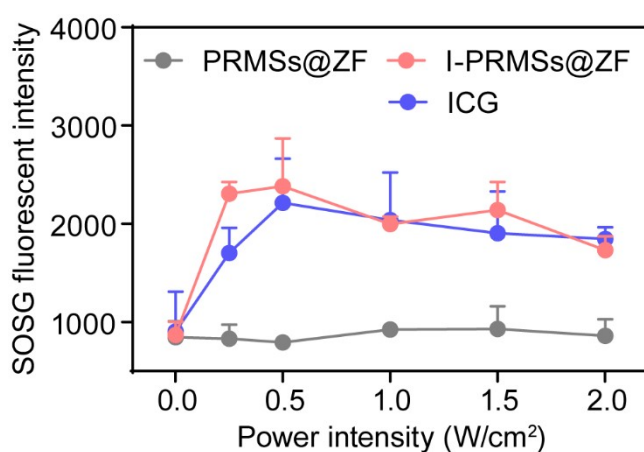


Fig. S3. Fluorescence intensity of SOSG as a function of laser irradiation time.

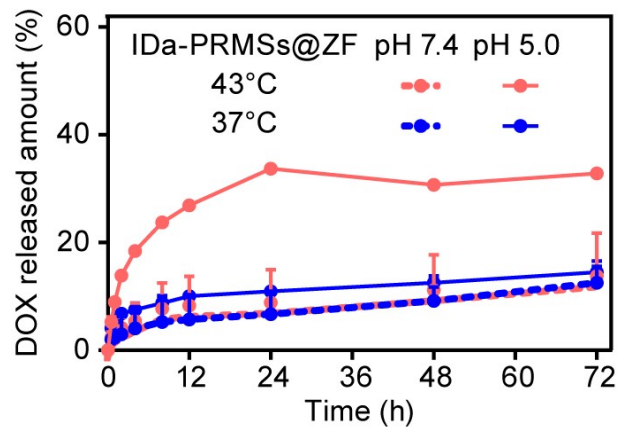


Fig. S4. Release curves for DOX in different release medium at 37 °C and 43 °C.

Table S2. Parameters describing release characteristics of DOX in different pH solutions at 43 °C.

Kinetic model	Parameter	Formulation: IDa-PRMSs@ZF	
		pH 7.4	pH 5.0
Zero-order	R^2_{adj}	0.1753±0.0148	-0.3306±0.0951
	k_0	0.2332±0.1397	0.6356±0.0098
First-order	R^2_{adj}	0.2215±0.0458	-0.1216±0.0891
	k_1	0.0026±0.0017	0.0089±0.0002
Higuchi	R^2_{adj}	0.8388±0.0166	0.6090±0.0388
	k_H	1.8056±1.0903	5.1650±0.0578
Korsmeyer-Peppas	R^2_{adj}	0.9729±0.0056	0.8993±0.0025
	k_{KP}	3.5141±2.0405	12.3129±0.3015
	n	0.3102±0.0085	0.2553±0.0104
Peppas-Sahlin	R^2_{adj}	0.9729±0.0085	0.9782±0.0032
	k_1	3.3163±2.2641	10.6732±0.3867
	k_2	0.0541±0.4805	-0.8353±0.0752
	m	0.3197±0.1183	0.4937±0.012
Hixson-Crowell	R^2_{adj}	0.2061±0.0355	-0.1930±0.0913
	k_{HC}	0.0008±0.0005	0.0026±0.0000
Hopfenberg	R^2_{adj}	0.1238±0.0515	-0.2620±0.1003
	k_{HB}	0.0000±0.0000	0.0000±0.0000
	n	125.4184±68.3715	1125.6711±90.8598
Baker-Lonsdale	R^2_{adj}	0.8500±0.0240	0.6741±0.0347
	k_{BL}	0.0001±0.0001	0.0006±0.0000
Makoid-Banakar	R^2_{adj}	0.9760±0.0010	0.9799±0.0030
	k_{MB}	3.4783±1.7365	9.7226±0.3613
	n	0.2954±0.0907	0.4672±0.0180
	k	-0.0008±0.0043	0.0117±0.0003
Quadratic	R^2_{adj}	0.5195±0.0831	0.4679±0.0461
	k_1	-0.0001±0.0000	-0.0002±0.0000
	k_2	0.0055±0.0036	0.0194±0.0001

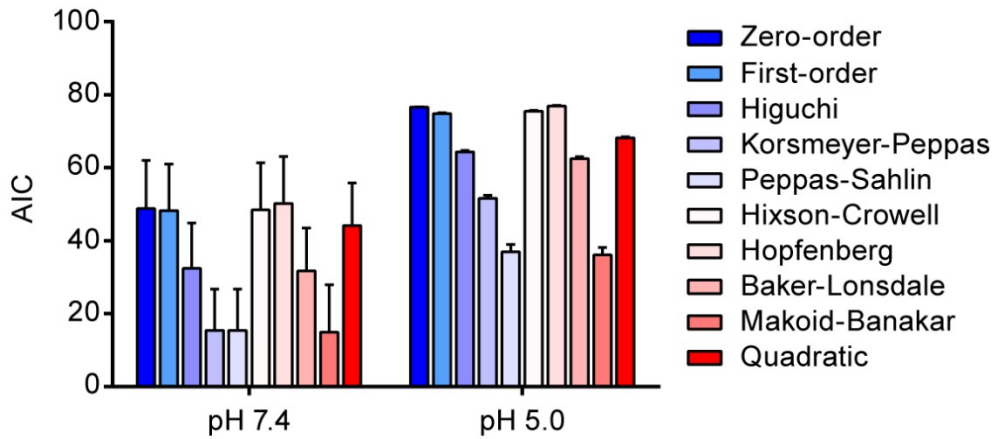


Fig. S5. The AIC value to evaluate goodness of fit after fitting the data in Fig. S1 at 43 °C.

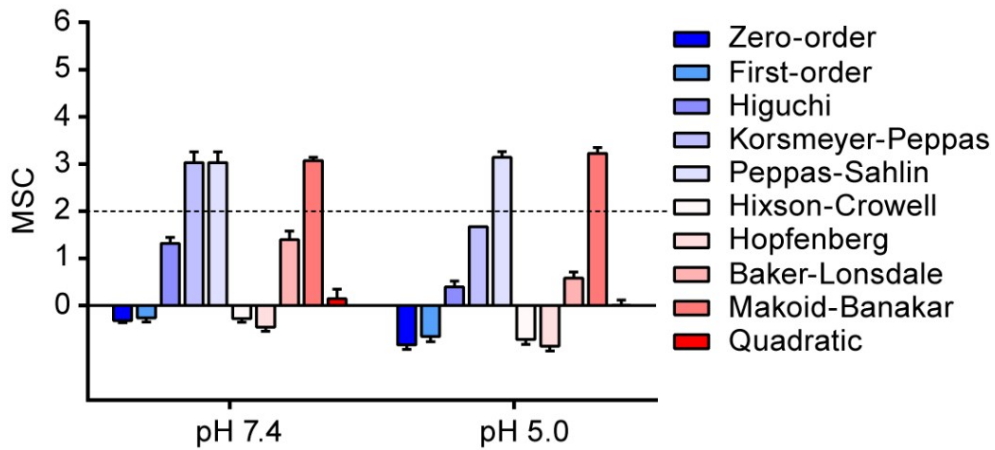


Fig. S6. The MSC value to evaluate goodness of fit after fitting the data in Fig. S1 at 43 °C.

Table S3. Parameters describing release characteristics of DOX from IDa-PRMSs@ZF at different pH values with/without NIR irradiation.

Kinetic model	Parameter	Formulation: IDa-PRMSs@ZF			
		pH 7.4	pH 5.0	pH 7.4+N	pH 5.0+N
Zero-order	R^2_{adj}	-0.0532±1.4502	-0.5893±0.0166	-0.8815±0.6929	-0.2447±0.3534
	k_0	0.1980±0.0156	0.2590±0.0315	0.4383±0.0669	1.1194±0.0411
First-order	R^2_{adj}	-0.0180±1.3937	-0.5125±0.008	-0.7219±0.6334	0.3014±0.2004
	k_1	0.0021±0.0002	0.0029±0.0004	0.0054±0.0011	0.0295±0.0059
Higuchi	R^2_{adj}	0.5508±0.3740	0.5300±0.0097	0.4901±0.3131	0.7403±0.1148
	k_H	1.4771±0.3508	2.0753±0.2466	3.5585±0.6583	8.8752±0.5035
Korsmeyer-Peppas	R^2_{adj}	0.9646±0.0143	0.9882±0.0054	0.9432±0.0322	0.9348±0.0049
	k_{KP}	2.5960±3.5406	5.5155±0.7078	8.1630±2.8014	16.6875±3.1605
	n	0.6825±0.6947	0.2216±0.0031	0.2572±0.0512	0.3150±0.0410
Peppas-Sahlin	R^2_{adj}	0.9870±0.0088	0.4925±0.6965	0.9676±0.0180	0.9950±0.0012
	k_1	2.6748±3.5377	5.0846±0.3472	8.1331±3.0199	13.9245±3.6773
	k_2	-0.3102±0.4457	-0.4311±0.0480	-0.7719±0.4724	-0.8598±0.4295
	m	0.6102±0.3465	0.3689±0.1147	0.4032±0.0332	0.5497±0.0658
Hixson-Crowell	R^2_{adj}	-0.0298±1.4127	-0.5382±0.0109	-0.7767±0.6546	0.1138±0.2572
	k_{HC}	0.0007±0.0001	0.0009±0.0001	0.0017±0.0003	0.0071±0.0011
Hopfenberg	R^2_{adj}	-0.1340±1.5843	-0.7019±0.0089	-0.8656±0.6863	0.2430±0.2172
	k_{HB}	0.0047±0.0066	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000
Baker-Lonsdale	n	128.7732±181.9149	247.3225±106.6744	647.7313±164.0333	3894.3580±1421.2128
	R^2_{adj}	0.5628±0.3490	0.5565±0.0064	0.5490±0.2794	0.8526±0.0669
	k_{BL}	0.0000±0.0000	0.0001±0.0000	0.0002±0.0001	0.0020±0.0003
Makoid-Banakar	R^2_{adj}	0.9947±0.0028	0.9878±0.0052	0.9630±0.02110	0.9948±0.0021
	k_{MB}	2.5880±2.8600	5.4947±0.8393	7.4372±2.5604	13.1073±3.4290
	n	0.3658±0.0948	0.2207±0.0286	0.3508±0.0407	0.5234±0.0866
	k	-0.0065±0.0183	0.0003±0.0015	0.0055±0.0010	0.0109±0.0018
Quadratic	R^2_{adj}	0.4829±0.7056	0.0608±0.0747	0.0135±0.4433	0.5896±0.1920
	k_1	0.0000±0.0001	-0.0001±0.0000	-0.0001±0.0000	-0.0004±0.0000
	k_2	0.0039±0.0037	0.0069±0.0006	0.0129±0.0029	0.0336±0.0024

Table S4. Parameters describing release characteristics of DOX from ID-PRMSs@ZF at different pH values with/without NIR irradiation.

Kinetic model	Parameter	Formulation: ID-PRMSs@ZF			
		pH 7.4	pH 5.0	pH 7.4+N	pH 5.0+N
Zero-order	R^2_{adj}	-1.3164±0.8169	-0.5865±0.0897	-0.9511±0.4974	-0.3824±0.3566
	k_0	0.3027±0.0473	0.6263±0.0754	0.4157±0.024	0.8850±0.0772
First-order	R^2_{adj}	-1.2017±0.7709	-0.3449±0.0380	-0.7833±0.4598	0.0119±0.3497
	k_1	0.0035±0.0006	0.0087±0.0016	0.0051±0.0004	0.0159±0.0025
Higuchi	R^2_{adj}	0.1557±0.3527	0.5934±0.0403	0.5232±0.2042	0.7521±0.1073
	k_H	2.5042±0.4434	5.0357±0.6423	3.3535±0.2853	6.9060±0.4622
Korsmeyer-Peppas	R^2_{adj}	0.8700±0.0799	0.9745±0.0092	0.9042±0.0288	0.9430±0.0013
	k_{KP}	7.3204±2.3920	12.0848±1.8040	7.0469±1.3811	12.2725±0.6110
	n	0.1930±0.0473	0.2474±0.0063	0.2730±0.0359	0.3237±0.0369
Peppas-Sahlin	R^2_{adj}	-	0.9954±0.0034	0.9591±0.0033	0.9938±0.0016
	k_1	-	11.7642±1.3444	6.2681±1.1969	10.0981±1.2004
	k_2	-	-1.0579±0.1450	-0.4853±0.1591	-0.5858±0.2005
	m	-	0.3945±0.0275	0.4801±0.0111	0.5508±0.0595
Hixson-Crowell	R^2_{adj}	-1.2406±0.7867	-0.4274±0.0562	-0.8411±0.4734	-0.1267±0.3547
	k_{HC}	0.0011±0.0002	0.0026±0.0004	0.0016±0.0001	0.0043±0.0006
Hopfenberg	R^2_{adj}	-1.4467±0.8568	-0.4951±0.0422	-0.9113±0.4923	-0.0589±0.3748
	k_{HB}	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000
	n	324.5137±12.2957	381.0174±77.8103	388.5797±303.3902	3226.1003±2246.1147
Baker-Lonsdale	R^2_{adj}	0.2037±0.3267	0.6674±0.0239	0.5779±0.1836	0.8339±0.0865
	k_{BL}	0.0001±0.0000	0.0005±0.0002	0.0002±0.0000	0.0010±0.0002
	R^2_{adj}	0.8776±0.0854	0.9941±0.0041	0.9583±0.0019	0.9940±0.0023
Makoid-Banakar	k_{MB}	6.7615±2.4953	10.8508±1.2299	5.7837±1.0123	9.5127±1.0697
	n	0.2789±0.0787	0.3402±0.0250	0.4441±0.0099	0.5260±0.0738
	k	0.0050±0.0014	0.0051±0.0017	0.0095±0.0018	0.0103±0.0014
Quadratic	R^2_{adj}	-0.3171±0.5629	0.2794±0.0138	0.2094±0.2158	0.5601±0.1926
	k_1	-0.0001±0.0000	-0.0002±0.0000	-0.0001±0.0000	-0.0003±0.0000
	k_2	0.0093±0.0017	0.0182±0.0029	0.0130±0.0017	0.0263±0.0015

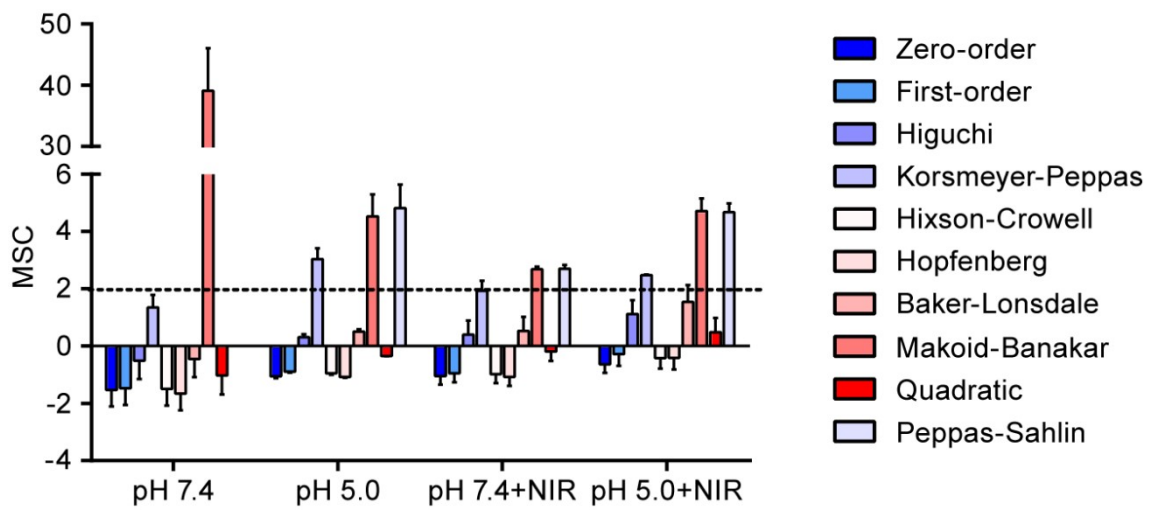


Fig. S7. The MSC value to evaluate goodness of fit after fitting the data in Fig. 4G.

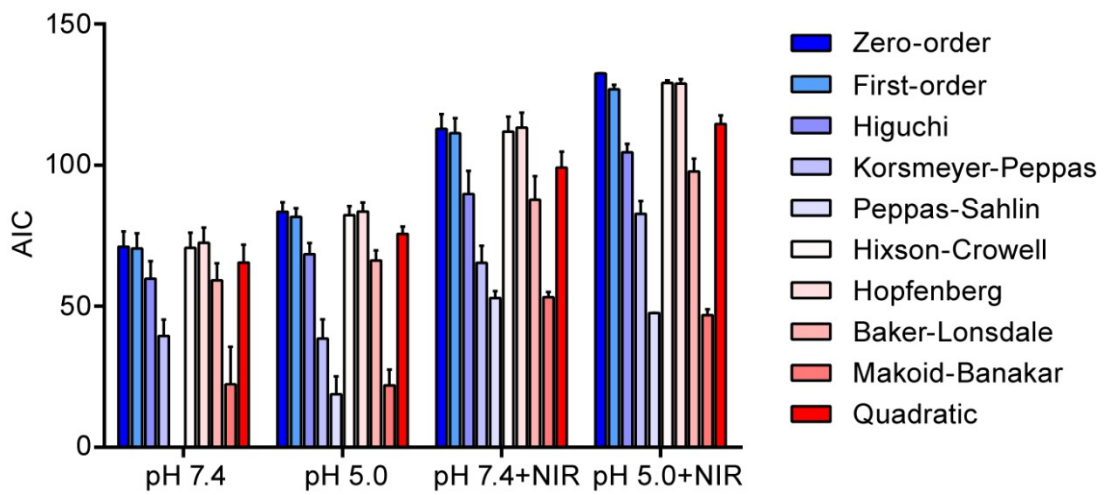


Fig. S8 The AIC value to evaluate goodness of fit after fitting the data in Fig. 4G.

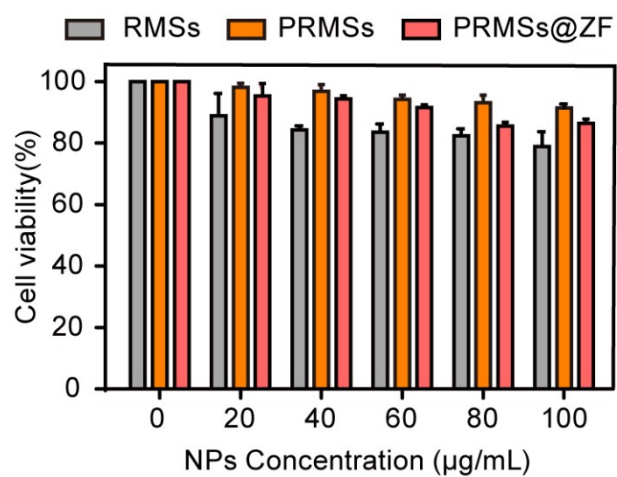


Fig. S9. Cell viability of 4T1 cells after incubation with blank NPs for 24 h.

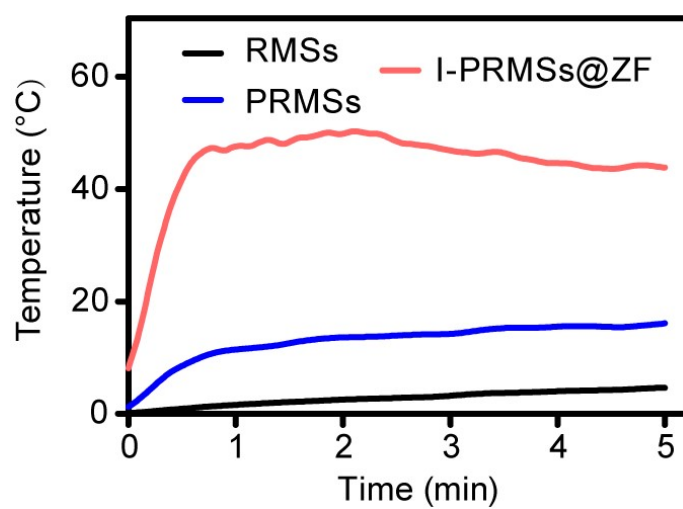


Fig. S10. Temperature variation of cell samples.

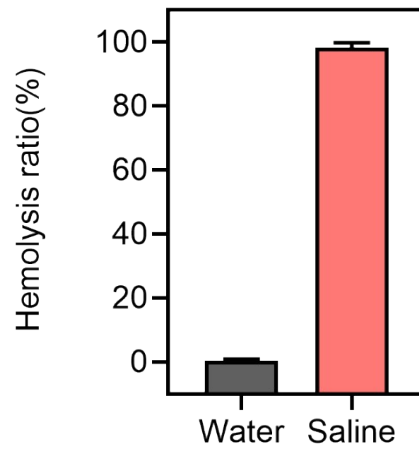


Fig. S11. Hemolytic ratio of water (positive control group) and normal physical saline (negative control group).

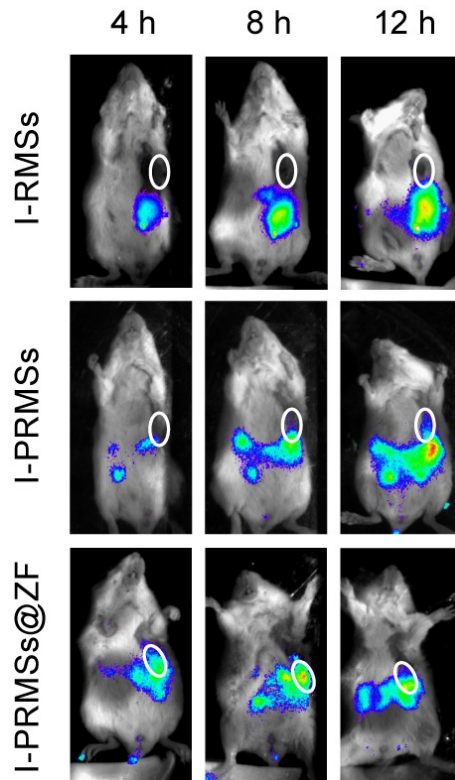


Fig. S12. Biodistribution of ICG-loaded NPs at 4 h, 8 h and 12 h post injection.

Table S5. Inhibition rates of DOX-loaded NPs.

	DOX	Da- RMSs	Da- PRMSs	IDa-PRMSs@ZF	IDa- PRMSs@ZF+NIR
TIR (%)	61.6	58.3	41.3	71.1	83.8