Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Covalent-Reaction-Induced Interfacial Assembly to Transform Doxorubicin into Nanophotomedicine with Highly Enhanced Anticancer Efficiency

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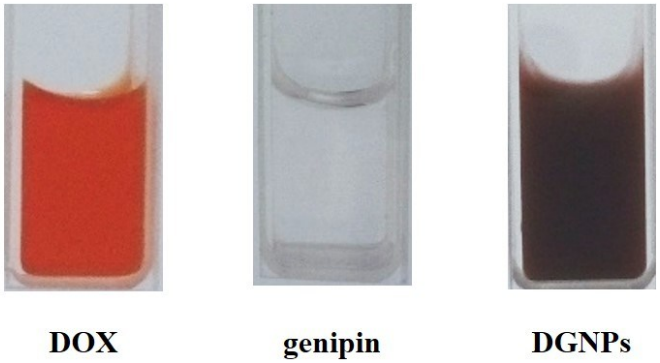


Fig. S1 Photo images of DOX aqueous solution, genipin aqueous solution and DGNP dispersion.

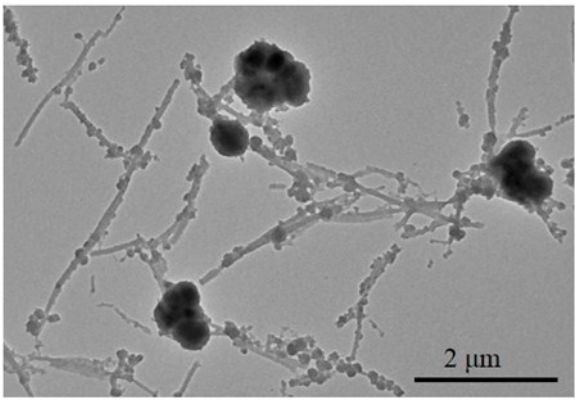


Fig. S2 TEM image of DOX assemblies.

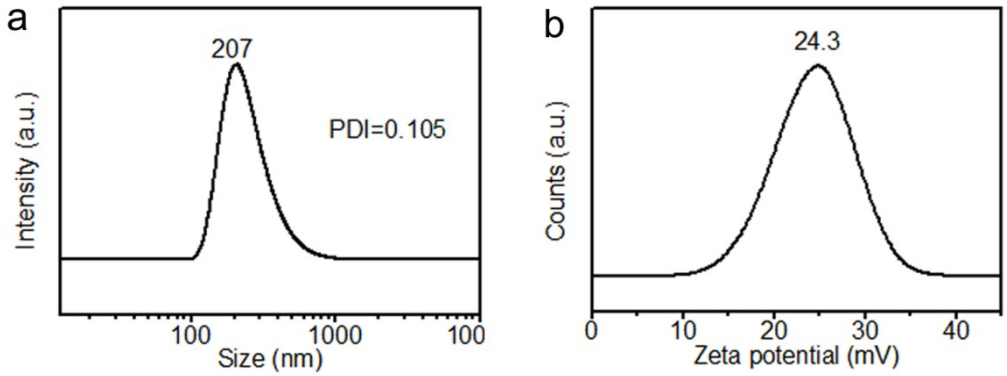


Fig. S3 a) Size distribution of DGNPs measured by DLS (PDI = 0.105). b) Zeta potential of DGNPs.

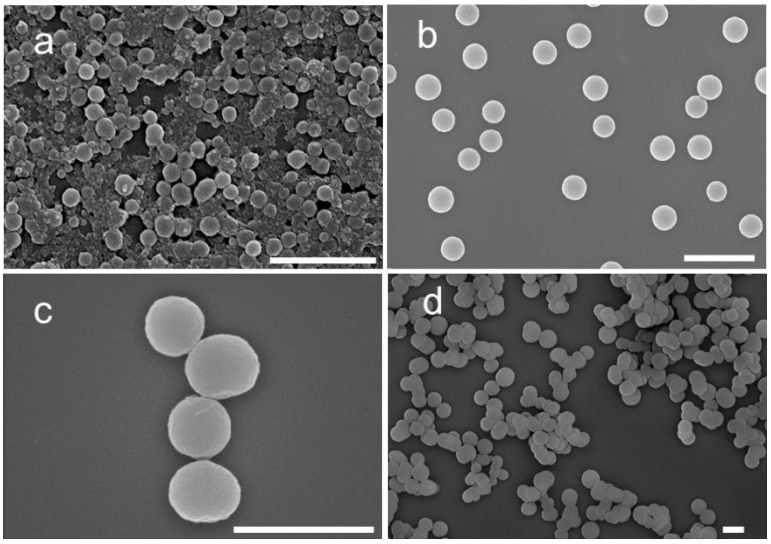


Fig. S4 SEM images of DGNPs when the assembly molar ratio ($M_{Genipin}$: M_{DOX}) was changed. The reaction temperature was set at 30 °C. a) 5:2; b)5:3; c) 5:4; d) 5:5. The scale bars are 1 μm.

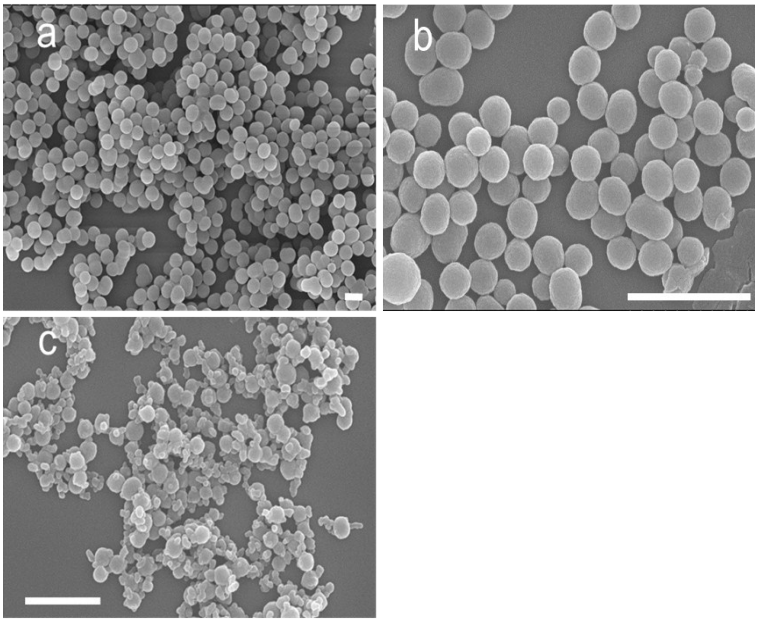


Fig. S5 SEM images of DGNPs when the reaction temperature was changed. The assembly ratio ($M_{Genipin}$: M_{DOX}) was set at 5:3. a) 30 °C; b) 40 °C; c) 50 °C. The scale bars are 1 μm.

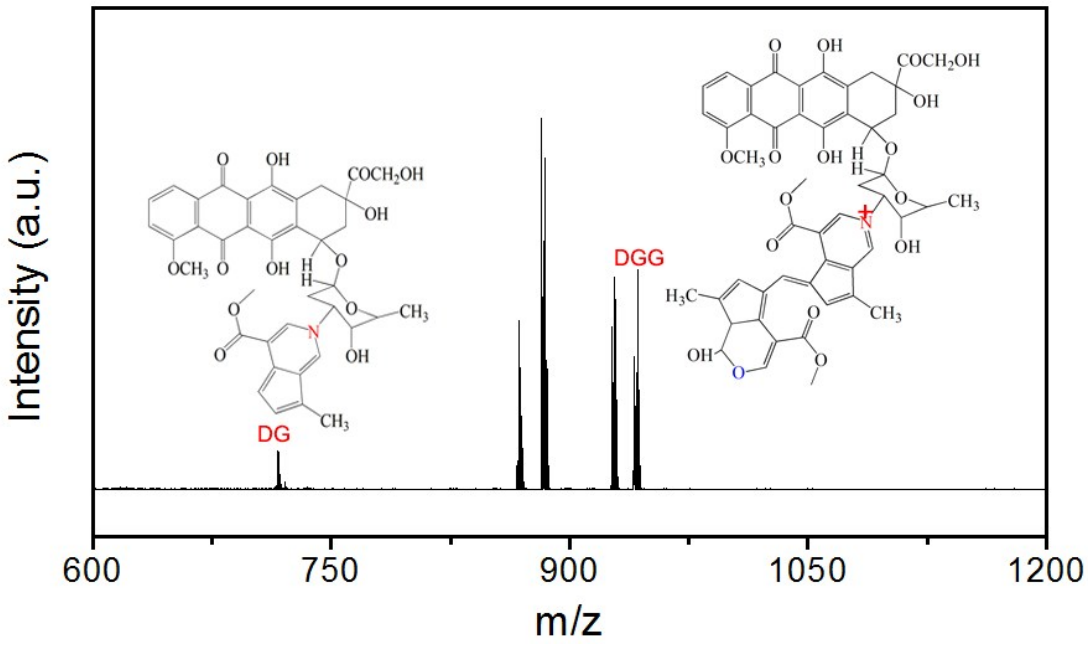
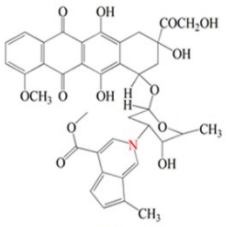


Fig. S6 MS spectrum of assembled DGNPs, using DHB as the matrix.

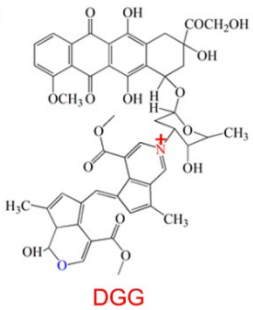
a



GEOM	S_1		S_2		S_3	
	Energy (eV/nm)	f	Energy (eV/nm)	f	Energy (eV/nm)	f
S_0	2.14/578	0.0002	2.61/476	0.0165	2.73/454	0.0100

GEOM	S_0 (eV)	T_1 (eV)	T_1-S_0 (eV)
T_1	0.51	1.71	1.20

b



GEOM	S_1		S_2		S_3		S_4	
	Energy (eV/nm)	f	Energy (eV/nm)	f	Energy (eV/nm)	f	Energy (eV/nm)	f
S_0	1.84/673	0.0001	2.02/614	0.0000	2.19/566	0.0001	2.30/540	0.4223

GEOM	S_0 (eV)	T_1 (eV)	T_1-S_0 (eV)
T_1	0.24	1.12	0.88

Fig. S7 The calculation data of a: DG; b: DGG in DGNPs in H_2O solution.

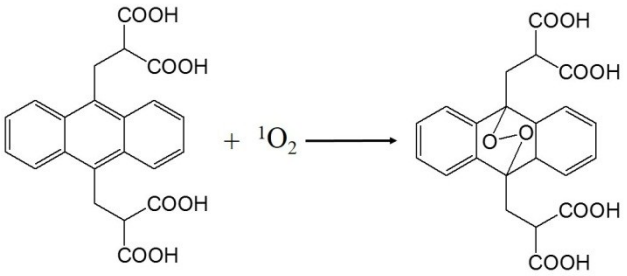


Fig. S8 The reaction between chemical trapping agent ABDA reacted with $^1O_2$.

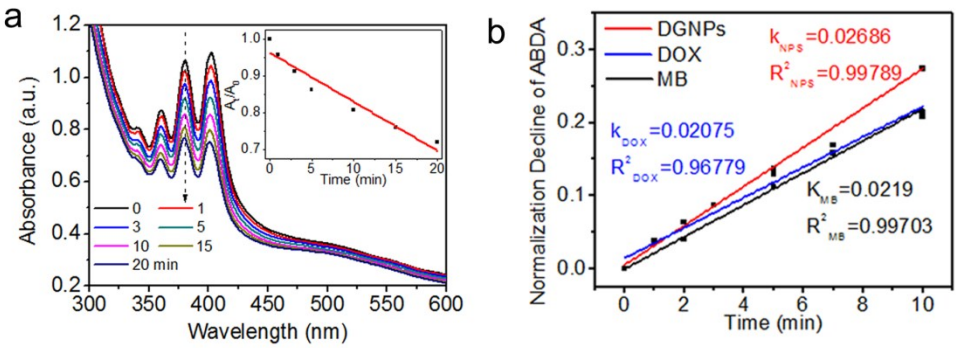


Fig. S9 a) Time-dependent UV-Vis spectra of ABDA in the presence of DGNPs (Inset: corresponding normalized absorbance of ABDA at 378 nm as a function of irradiation time). b) Normalization decline of ABDA caused by $^1O_2$ oxidation plotted against irradiation time at 378 nm in the presence of different drugs and the percentage at the end point (irradiation at 635 nm).

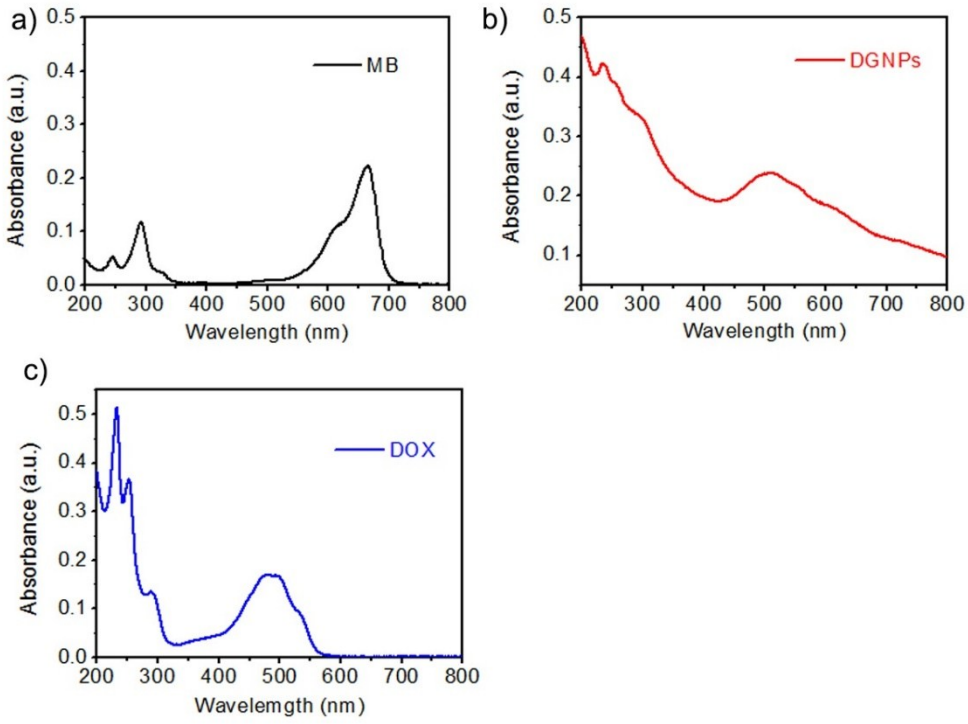


Fig. S10 UV-Vis spectra of a) MB, b) DGNPs, and c) DOX.

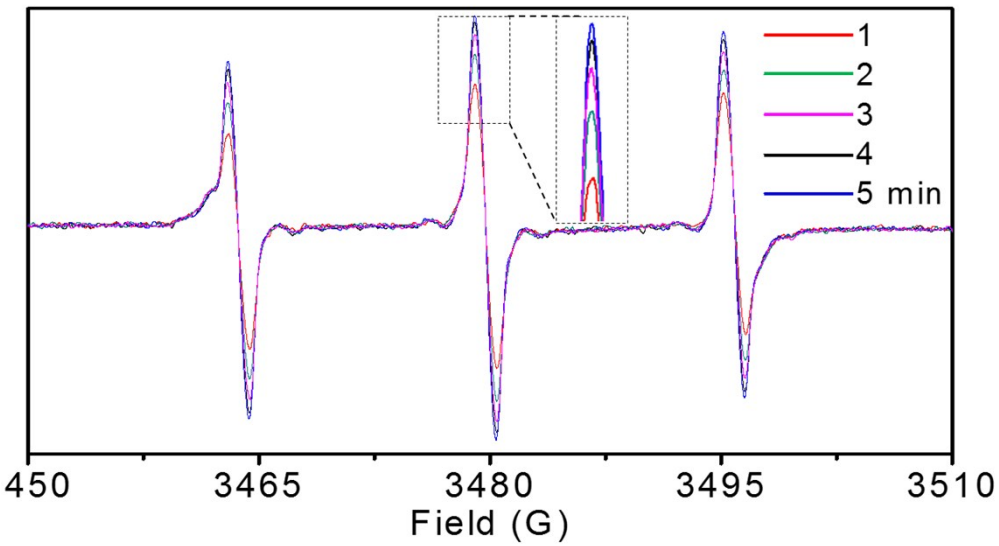


Fig. S11 Time-dependent EPR spectra of DGNPs, using TEMP as an agent trapping $^1O_2$.

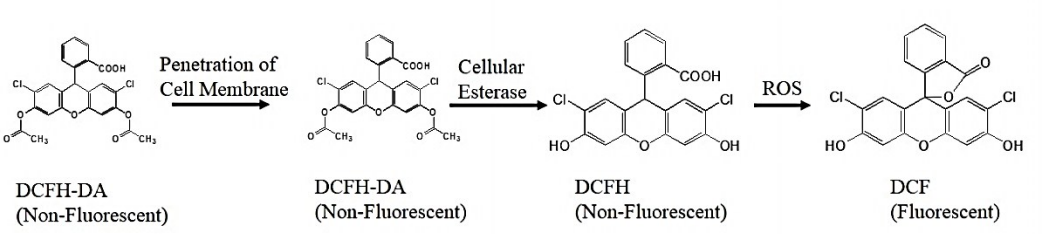


Fig. S12 Principle of DCFH-DA as a probe to detect intracellular ROS.

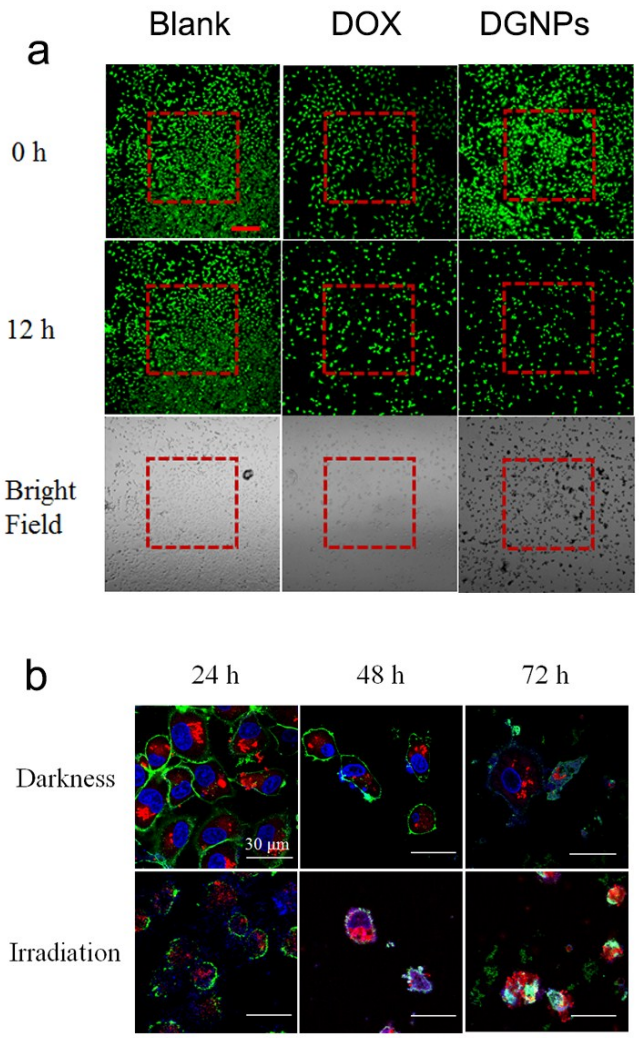


Fig. S13 *In situ* observation of A549 cells before and after different treatments (without any drugs, DOX and DGNPs, respectively). All the three groups were stained with Calcein, AM. The region bounded by the red dashed line was irradiated with the 635 nm laser for 20 min and cultured for another 12 h. The other part was kept in the dark. Scale bars: 200 μm. a) CLSM images of different groups. The red regions were irradiated. b) CLSM images of A549 treated with DGNPs under darkness or irradiation. The tumor cells were stained by Hoechst 33342 (blue) and Alexa 488 (green) without irradiation. Red dots are DGNPs with autofluorescence excited by 559 nm laser.