A redox-activated theranostic nanoplatform: toward glutathione-response imaging guided enhanced-photodynamic therapy

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Figure S1. Synthetic route for RA. The details for iv: RC (0.38 mmol) and K$_2$CO$_3$ (0.38 mmol) were suspended in DMF (3 mL). Propargyl bromide (1.14 mmol) was added and the reaction mixture was stirred at room temperature for 48 h under argon. Upon addition of 10 mL water, the precipitated complex was washed with water (4×30 mL), and purified by chromatography over alumina by using MeCN as eluent.
Figure S2. $^1$H NMR spectrum of RA. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.09 (d, $J = 7.5$ Hz, 2H), 8.90 (d, $J = 8.4$ Hz, 2H), 8.86 (d, $J = 8.2$ Hz, 2H), 8.50 (d, $J = 8.6$ Hz, 2H), 8.23 (ddd, $J = 8.0, 4.4, 1.4$ Hz, 4H), 8.12 (td, $J = 8.0, 1.4$ Hz, 2H), 8.03 (d, $J = 4.7$ Hz, 2H), 7.91 (dd, $J = 8.2, 5.3$ Hz, 2H), 7.86 (d, $J = 4.9$ Hz, 2H), 7.60 (ddd, $J = 7.2, 5.8, 3.1$ Hz, 4H), 7.39 – 7.34 (m, 2H), 5.03 (d, $J = 2.4$ Hz, 2H), 3.69 (t, $J = 2.4$ Hz, 1H).
Figure S3. $^{13}$C NMR spectrum of RA. $^{13}$C NMR (151 MHz, DMSO) δ 171.89, 165.13, 157.26, 157.05, 151.87, 151.85, 145.45, 138.38, 138.23, 130.86, 130.62, 128.34, 128.21, 127.13, 126.61, 124.91, 124.83, 78.88, 78.61, 53.16.

Figure S4. TOF-MS for [C$_{43}$H$_{30}$N$_8$O$_2$Ru]$^{2+}$: Calc. 792.15, found m/z 396.0713 (M$^{2+}$/2).
Figure S5. 1,3-diphenylisobenzofuran (DPBF) was used as trap to monitor the rate of system to generate $^{1}\text{O}_2$, and the absorption spectra DPBF was recorded at 30 s intervals. The rate of singlet oxygen generation was determined from the decrease absorption intensity at 414 nm over time. (A) Time-dependent absorption spectra of DPBF (in DMF, 10 μM) interval 30 s upon irradiation at 450 nm. Time dependent absorption spectra of DPBF (in DMF, 10 μM) upon irradiation at 450 nm in the presence of 2 μM (B) [Ru(bpy)$_3$]$^{2+}$, (C) RC and (D) RA.
Figure S6. In the absence or presence of RA (10 μM), changes in the absorption spectra of \( p \)-nitrosodimethylaniline (RNO) (25 μM) at 440 nm upon 450 nm irradiation in aerated PBS were measured. \([\text{Ru(bpy)}_3]^{2+}\) was used as the standard, the \( ^1\text{O}_2 \) quantum yield of \([\text{Ru(bpy)}_3]^{2+}\) is 0.18 in H\(_2\)O.\(^1\)

Figure S7. (A) The geometric structure of RA. (B) HOMO–LUMO distribution of RA and the energy of first excited triplet state (T1) of RA (B3LYP/SDD/6-311G** by Gaussian 09).\(^2\,^3\)
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Figure S13. Relationship between (A) longitudinal or (B) transverse rates of DCMn-RA and the different GSH concentrations.

Figure S14. Emission spectra of DCFH incubated with two photosensitizers in presence or absence of 10 mM GSH after 1 min irradiation (450 nm, 15 mW/cm²).
Figure S15. (A) Mean fluorescence intensity of cells for Figure 5(A) and Figure 5(B), respectively. (B) Intracellular GSH detections of MDA-MB-231 cells after various treatments, including blank group as a control, free RA, DCMn and DCMn-RA.

Figure S16. Confocal images of MDA-MB-231 cells incubated with DCMn-RA. Red channel image was obtained from DCMn-RA. The blue channel image was obtained from Hoechst (nucleus). Scale bars =20 μm.

Figure S17. Cytotoxicity of free RA for MDA-MB-231 cells treated with LPA (a GSH synthesis enhancer, 0.5 mM) or NEM (a GSH scavenger, 0.5 mM) before irradiation.