

Supporting Information

A tailored and red-emissive type I photosensitizer to potentiate photodynamic immunotherapy

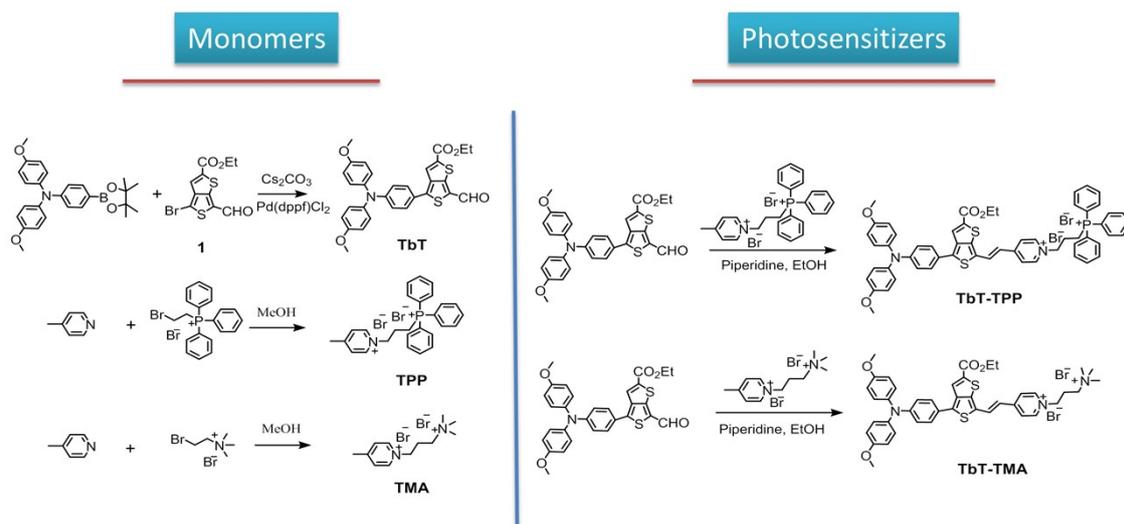
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Scheme S1. The synthesis routes for photosensitizers TbT-TPP and TbT-TMA.

a)

$V_{\text{(Toluene)}}/V_{\text{(DMSO)}}$	0 %	50 %	70 %	90 %	95 %	97 %	98 %	99 %
Size (nm)	5.6 ± 0.9	6.8 ± 1.4	8.7 ± 1.5	9.6 ± 0.7	11.6 ± 2.1	14.8 ± 0.8	19.3 ± 0.9	23.4 ± 1.3

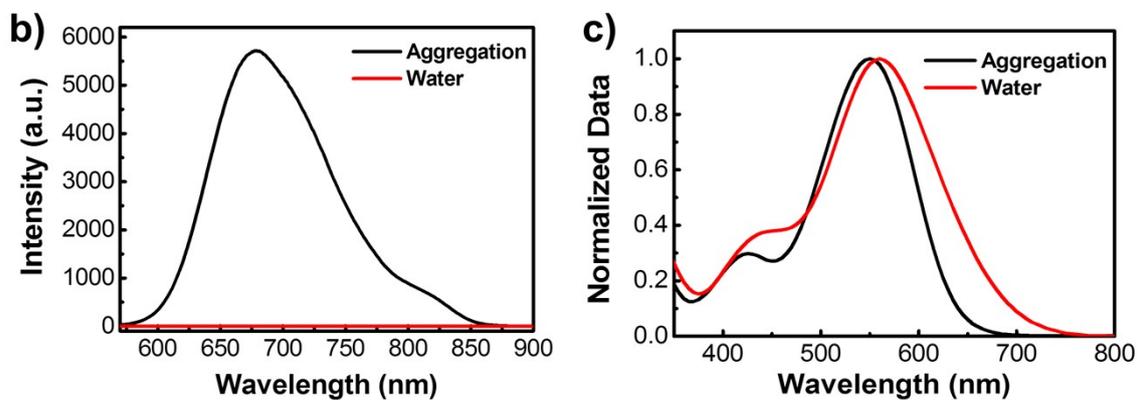


Fig. S1 a) Hydrodynamic diameters of TbT-TPP (10 μM , 2 mL) in Toluene/DMSO mixtures with different toluene fractions. Normalized b) fluorescence intensity and c) absorbance of TbT-TPP (10 μM , 2 mL) in aggregation and water.

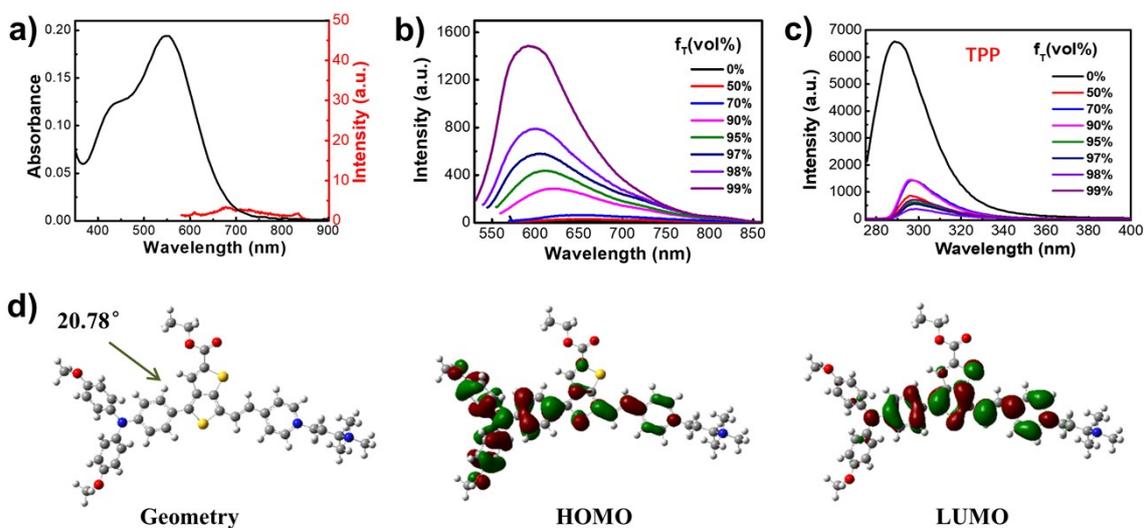


Fig. S2 a) Absorbance and fluorescence intensity of TbT-TMA (10 μ M, 2 mL) in water. Fluorescence spectra of b) TbT-TMA(10 μ M, 1 mL) and c) TPP(10 μ M, 1 mL) in DMSO/Toluene mixtures with different toluene fractions. d) Optimized geometries and HOMO, LUMO of TbT-TMA.

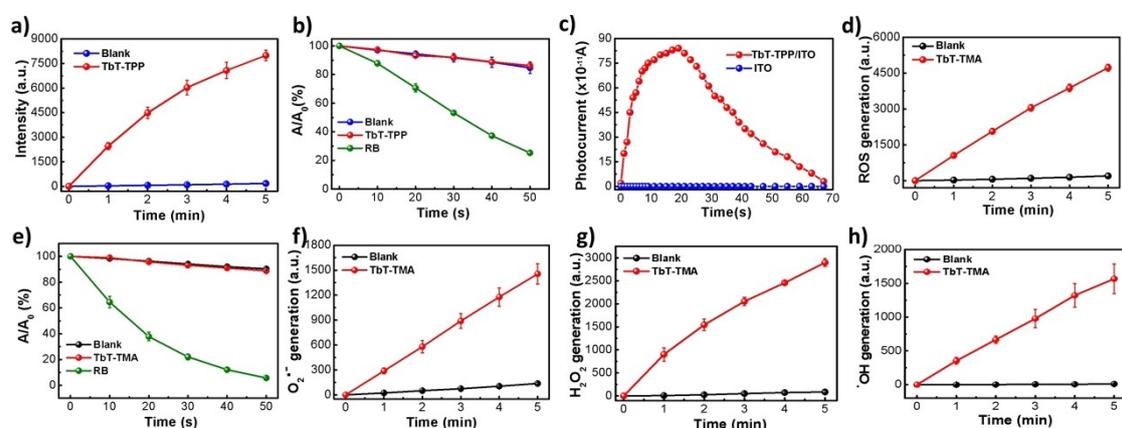


Fig. S3 a) Fluorescence intensity of DCFH for total ROS detection of TbT-TPP (1 μM , 1 mL) under white light irradiation (1 mW/cm^2 , 5 min). b) Decomposition rates of DPBF for $^1\text{O}_2$ of TbT-TPP (5 μM , 2 mL) and RB (5 μM , 2 mL) under white light irradiation (5 mW/cm^2 , 50 s), A and A_0 are the absorbance of DPBF at 410 nm. c) Photocurrent response of the TbT-TPP (10 mM) modified ITO or bare ITO electrode to white laser (500-700 nm). A voltage of 0.5 V was used. d) Fluorescence intensity of DCFH for total ROS detection of TbT-TMA (1 μM , 1 mL) under white light irradiation (1 mW/cm^2 , 5 min). e) Decomposition rates of DPBF for $^1\text{O}_2$ of TbT-TMA (5 μM , 2 mL) and RB (5 μM , 2 mL) under white light irradiation (5 mW/cm^2 , 50 s), A and A_0 are the absorbance of DPBF at 410 nm. f) Fluorescence intensity of DHE for O_2^- , g) Hydrogen Peroxide Assay Kit for H_2O_2 , and h) APF for $\cdot\text{OH}$ of TbT-TMA under white light irradiation (5 mW/cm^2 , 5 min).

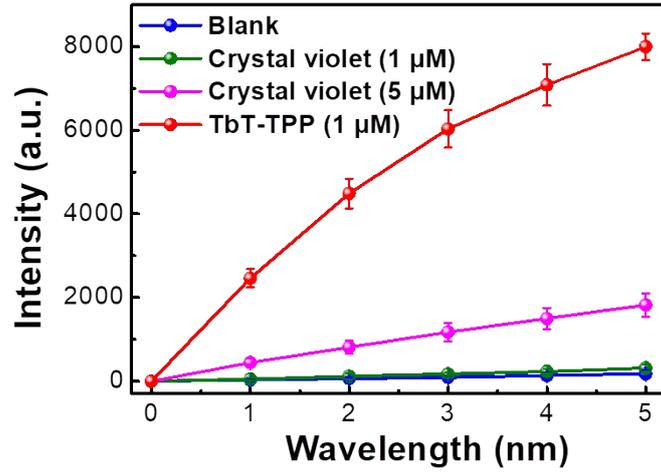


Fig. S4 Fluorescence intensity of DCFH for total ROS detection of TbT-TPP (1 μM) and crystal violet (1 μM , 5 μM) under white light irradiation (1 mW/cm^2 , 5 min).

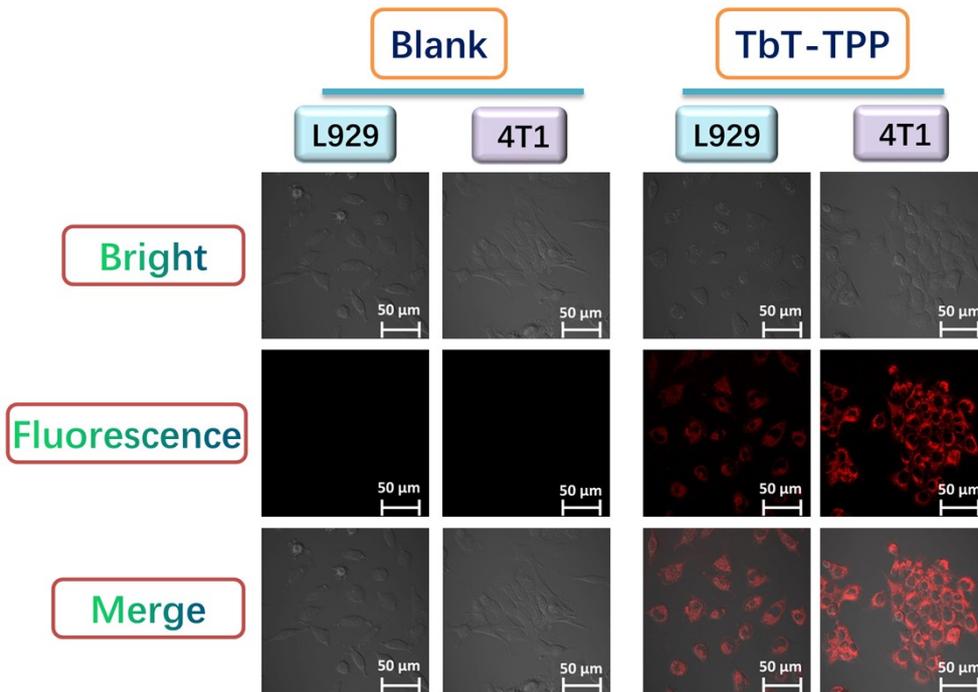


Fig. S5 CLSM images of 4T1 cells and L929 cells after incubated with TbT-TPP (10 μM) under normoxic condition.

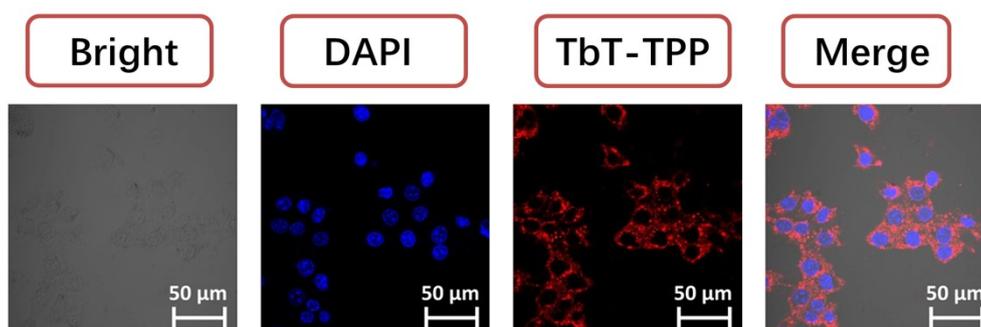


Fig. S6 CLSM images of 4T1 cells after incubation with TbT-TPP (10 μM) and DAPI.

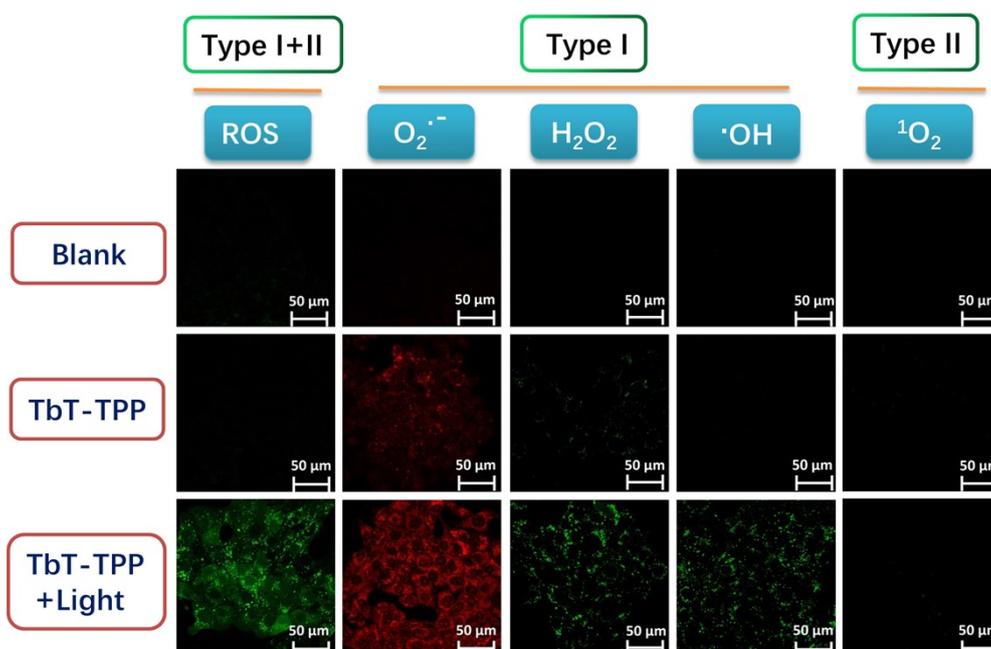


Fig. S7 CLSM images of intracellular ROS generation in 4T1 cells stained with DCFH-DA, DHE, Hydrogen Peroxide Assay Kit, APF and SOSG as indicators (10 μM) after incubation with TbT-TPP (10 μM) without or with white light irradiation (20 mW/cm², 20 min) under hypoxic conditions.

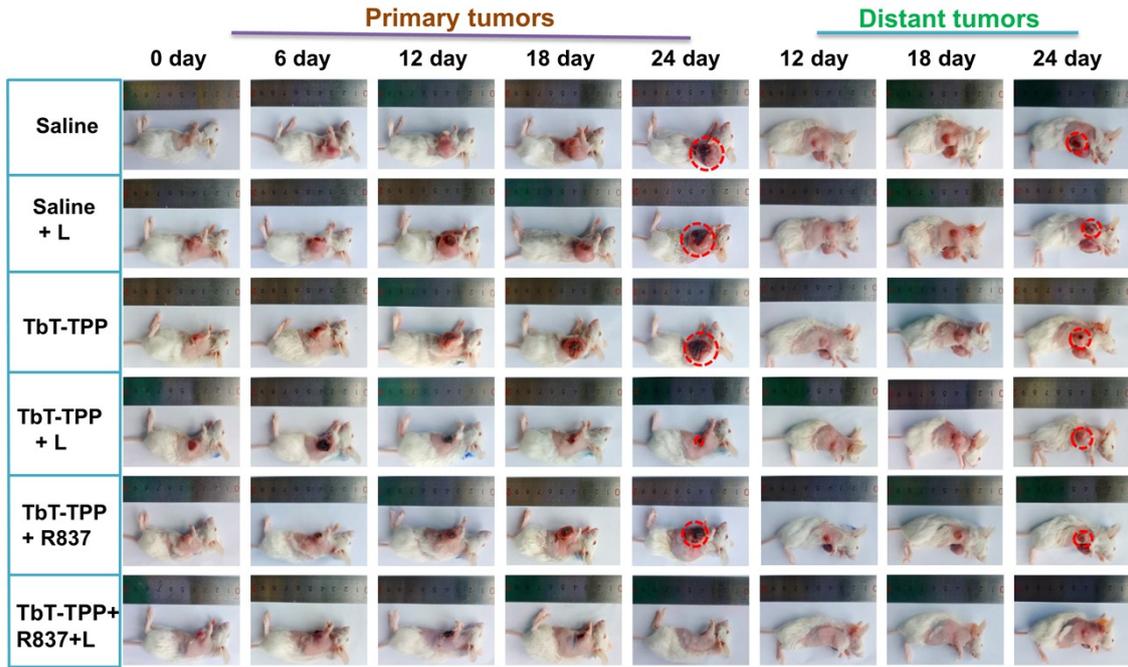


Fig. S8 The representative photographs of 4T1 tumor-bearing mice during different treatments.

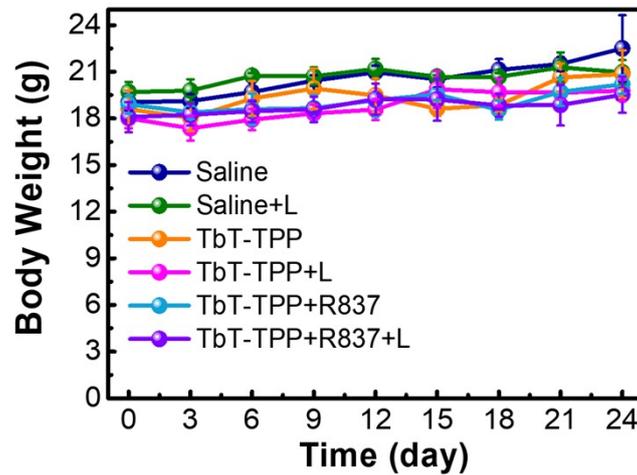


Fig. S9. The body weight changes of the mice treated with different treatments.