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Supporting Information

Fluorescence-Enhanced Covalent Organic Framework Nanosystem for Tumor Imaging and Photothermal Therapy

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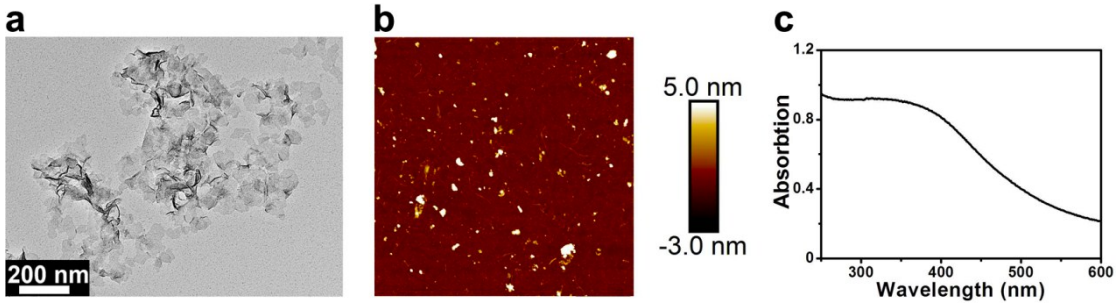

Figure S1. Characterization of MnO_2 NSs. a) TEM, b) AFM image and c) UV-Vis spectrum of MnO_2 NSs.

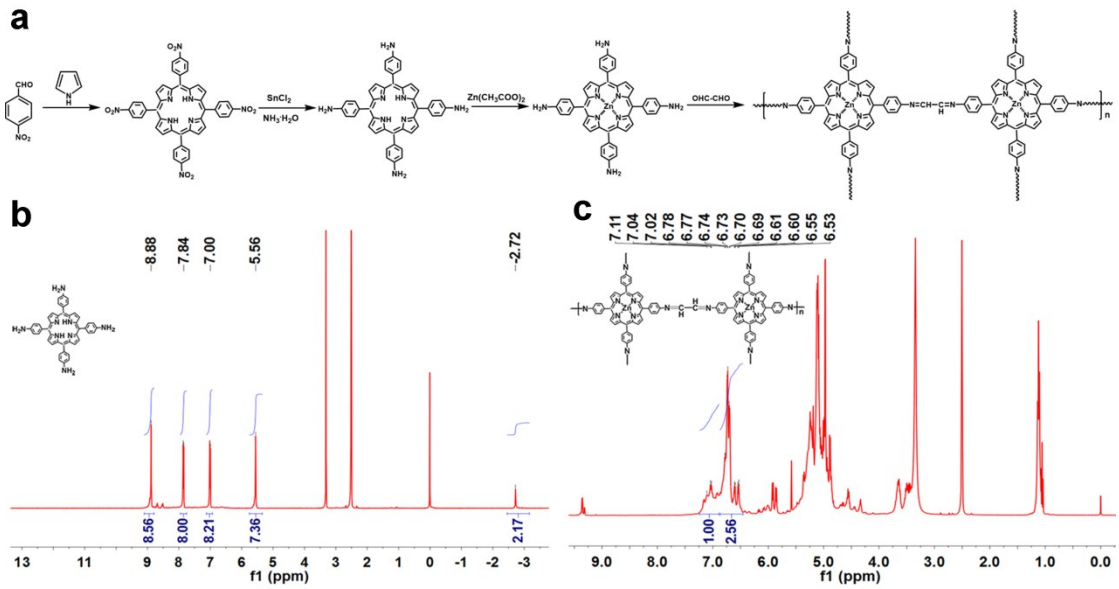

Figure S2. The scheme and characterization. a) Illustration of the synthesis of the ZnCOF. The H[1]NMR spectrum of b) TAPP and c) ZnCOF.

^{1}H NMR (DMSO) δ: −2.72 (2H, inner NH), 5.56 (8H, Ph-NH_2), 7.00, 7.84 (8H, Ar-H), 8.88, 8.92 (8H, pyrrole-βCH) (**Figure. S2b**)

^{1}H NMR (DMSO) δ: 6.53-6.78 (2H, Ar-H), 7.02-7.11 (2H, -CH=N-) (**Figure. S2c**).

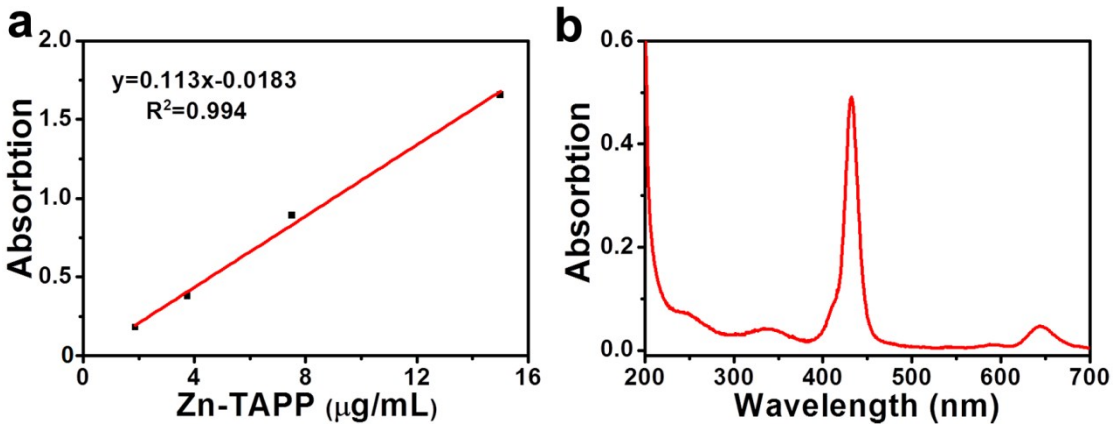

Figure S3. Quantitative Characterization of Zn-TAPP in COF by UV-Vis spectrum. a) The stander curve between concentration and absorbtion of Zn-TAPP. b) The supernatant UV-Vis spectrum of MnO_2/ZnCOF@Au&BSA NSs degradation products.

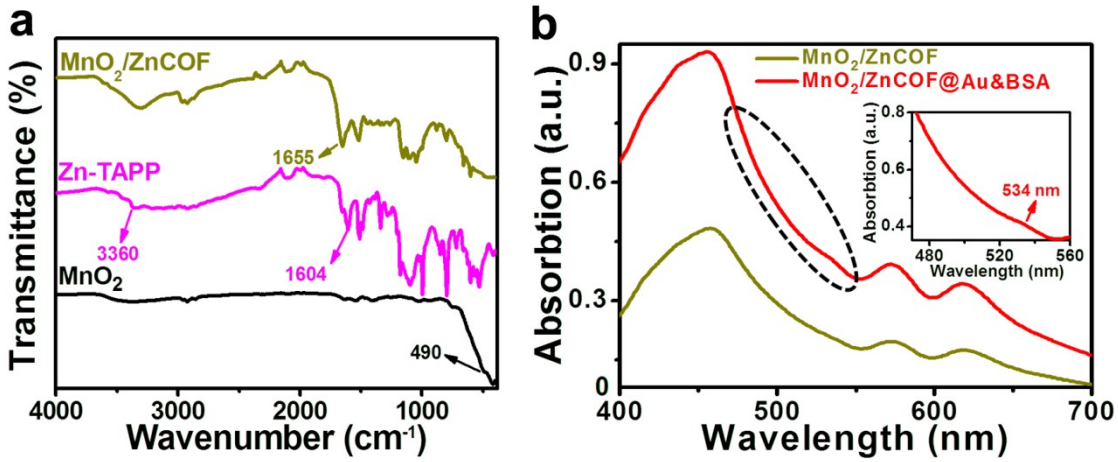

Figure S4. The FT-IR and UV-Vis characterization. a) The FT-IR spectral of MnO_2, Zn-TAPP and MnO_2/ZnCOF NSs. b) The UV-Vis spectral of MnO_2/ZnCOF NSs and MnO_2/ZnCOF@Au&BSA NSs. The insert image is an enlargement of the black oval framed areas.

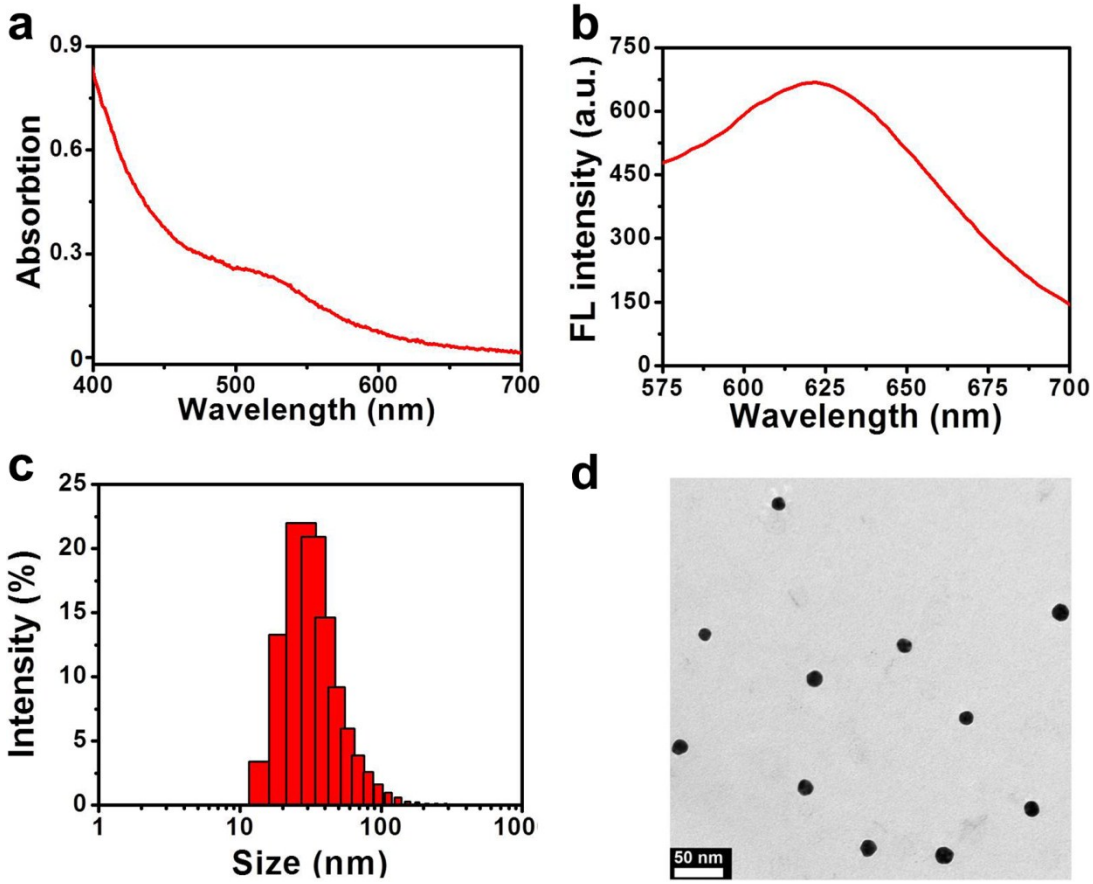

Figure S5. Characterization of Au NPs. a) UV−Vis absorption spectrum, b) FL spectrum (Ex: 432 nm), c) the size distribution and d) TEM characterization of Au NPs.

The light yellow of Au NPs showed an obvious UV absorption and significant fluorescent emission at 520 and 627 nm, respectively. The size distribution and TEM results demonstrated the dimension of Au NPs is estimated to be 20 to 30 nm (**Figure S5**).

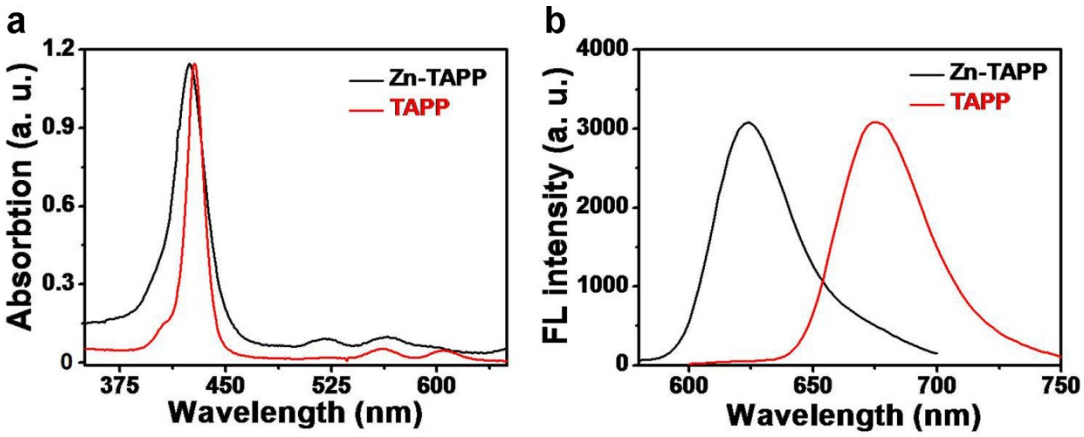

Figure S6. Characterization of TAPP and Zn-TAPP. a) The UV-Vis spectrum and b) FL spectrum of Zn-TAPP and TAPP.

The UV−Vis absorption spectrum and FL spectrum of the Zn-TAPP and TAPP samples were measured (**Figure S6**). The intense absorption and emission peaks were observed at 428 nm and 675 nm for TAPP molecular. After the insertion of Zn^{2+} to the free base porphyrin, the new peaks were observed (Ab: 424 nm, Em: 624 nm). The hipsochromic shifts were attributed to the interaction between the central zinc ion and the π-conjugate system, which caused the structure changes of π-conjugate system.[1]

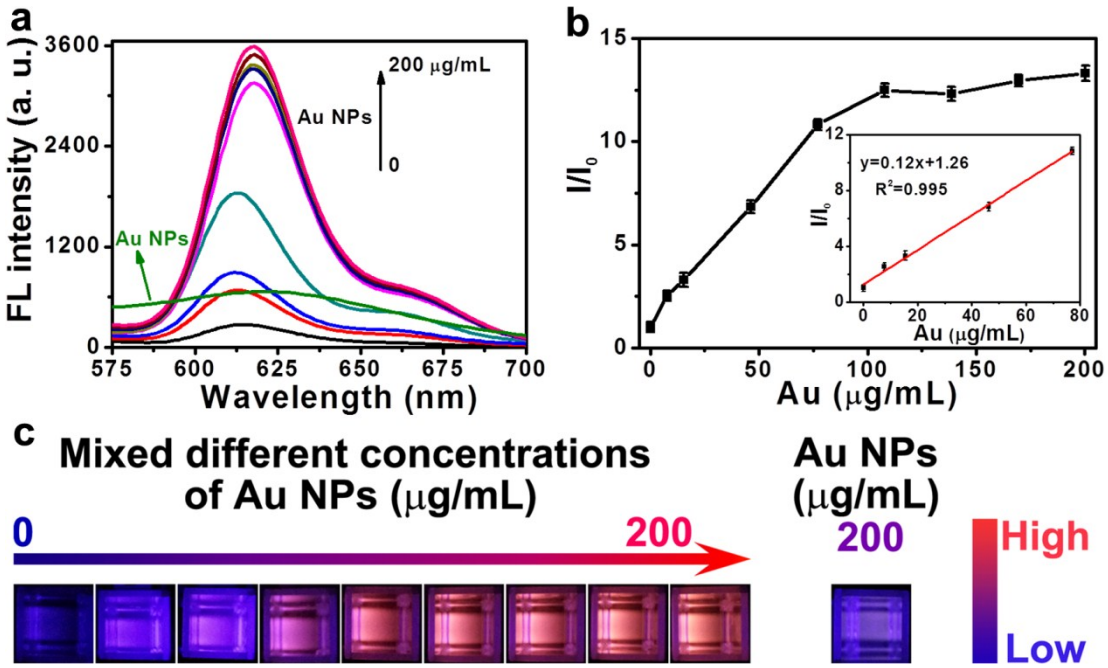

Figure S7. ***In vitro*** **FL spectrum characterization of Zn-TAPP with Au NPs.** a) FL spectrum of the Zn-TAPP (110 μg/mL) upon addition of different concentrations of Au NPs at 0, 7.7, 15.4, 46.2, 77, 107.8, 138.6, 169.4 and 200 μg/mL, respectively. b) The relative FL intensity (I_0: the FL intensity of pure Zn-TAPP; I: the FL intensity of Zn-TAPP&Au NPs). Inset: the fitted calibration line in the linear region of 0-77 μg/mL Au NPs. c) The FL photographs corresponding to the (a) FL spectra.

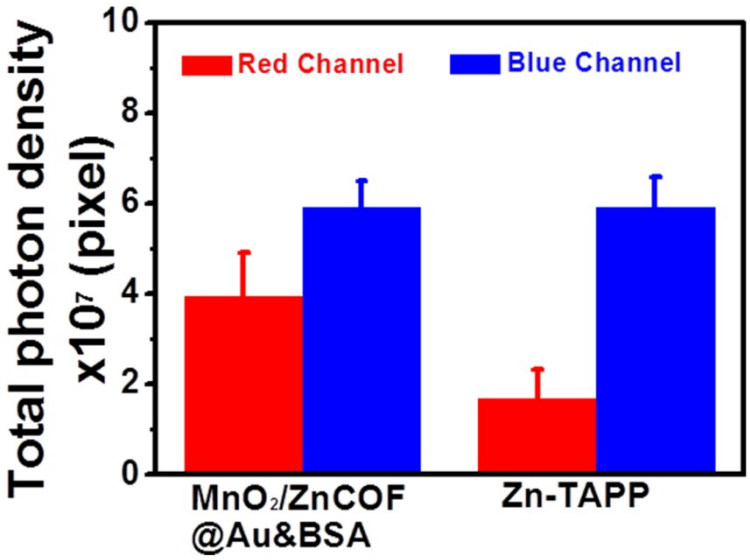

Figure S8. The FL intensity quantitation analysis of MnO_2/ZnCOF@Au&BSA NSs and Zn-TAPP group with the same number of cells (about 60). The red channel and blue channel represents the PSs of Zn-TAPP and DAPI, respectively

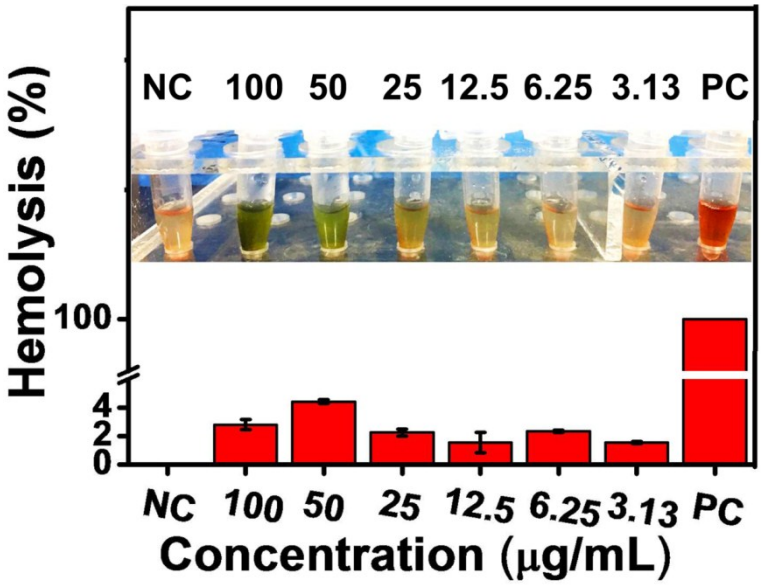

Figure S9. The hemolysis test of MnO_2/ZnCOF@Au&BSA NSs. The analysis of hemolysis and photographs, incubating with increasing concentration of MnO_2/ZnCOF@Au&BSA NSs (3.13-100 μg/mL). Saline and Triton X-100 as negative group (NC) and positive control (PC), respectively.

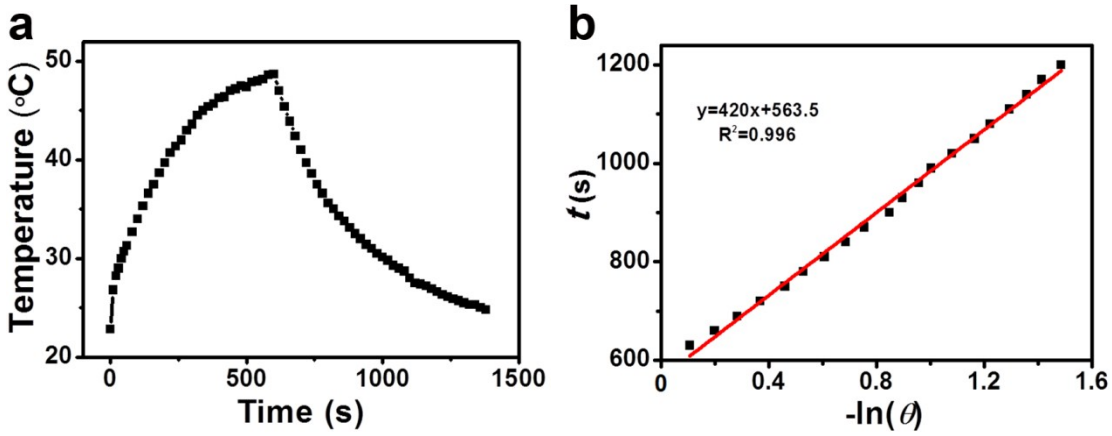

Figure S10. a) Alternate temperature rising and dropping curve of MnO_2/ZnCOF@Au&BSA NSs (c = 50 μg/mL). b) Linear fitting of MnO_2/ZnCOF@Au&BSA NSs to calculate the photothermal conversion efficiency.

Reference

1. Zheng, W., Shan, N., Yu, L., Wang, X. *Dyes and Pigments,* 2008, **77**, 153-157.