Supporting Information

Gold Nanorods Enhanced Two-photon Excitation Fluorescence of Conjugated Oligomers for Two-photon Imaging Guided Photodynamic Therapy

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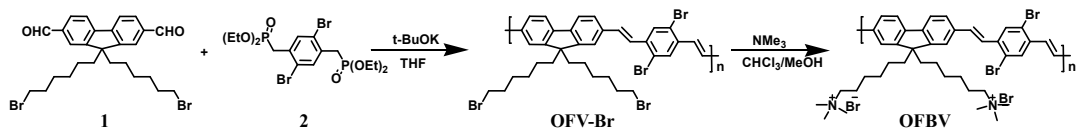
Synthesis of OFBV

Scheme S1 displays the synthesis routes of the water conjugated polymer used in our experiment.Oligo-[9,9-bis(6"-bromohexyl)fluorene-2,7-ylenevinylene-co-alt-1.4-(2,5-dibromophenylene)] (OFV-Br) was synthesized by using a previously reported method via the Witting-Horner condensation reaction between dialdehyde and 1,4-bis(diethylphosphinatylmethyl) phenylene in dry THF by slowly adding 1 equiv of t-BuOK.[1,2] Water soluble cationic conjugated oligomer OFBV was obtained by quaternization of the neutral polymers OFV-Br in excess of trimethylammonium in methanol/chloroform at room temperature for 48 h.The molecular weights of theneutral polymers were determined by gel permeation chromatography(GPC) using THF as the eluent. The number-averagedmolecular weights (Mn) for OFV-Br was determined to be 4200 with PDI (Mw/Mn) = 1.26. Thenumbers of repeat unit for OFV-Bris7.



Scheme S1 Sythesis procedures of the water soluble conjugated oligomerOFBV.

Poly(9,9-bis(6''-(bromohexyl)fluorene-2,7-ylenevinylene-co-alt-1,4-(2,5-dibromophenylene))(OFV-Br).

2,7-Diformyl-9,9-di(6'-bromohexy) fluorene (0.5 mmol) and 1,4-bis(diethylphosphinatyl methyl)-2,5-dibromobenzene (0.5 mmol) in dry THF (20 mL) was stirred at room temperature. After potassium tert-butoxide (2 mmol) was slowly added, the solution was stirred for 4h at room temperature before being quenched with

dilute aqueous HCl (20 mL). The solution was then poured into methanol (250 mL) under stirring. The precipitate was collected by filtration. The crude polymer was dissolved in THF, precipitated in methanol three times, and then dried under vacuum to give a yellow solid product. ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.98-7.31 (m, 12H), 3.27 (br, 4H), 2.05 (br, 4H), 1.65-1.58 (br, 4H), 1.22-1.10 (br, 8H), 0.61 (br, 4H); GPC: Mn=4200, Mw=5300, PDI=1.26.

Poly(9,9-bis(6''-(N,N,N-trimethyl-ammonium)hexyl)fluorene-2,7-ylenevinylene-co-alt-1,4-(2,5-dibromophenylene))(OFBV).

OFV-Br were dissolved in THF (20 mL). Trimethylamine (5 mL, 30%) in ethanol was then added. The mixture was stirred for 48 h at room temperature. The solid products PFBV was obtained after evaporation of the solvent at vacuum. ^{1}H NMR (300MHz, DMSO-*d*6, δ): 8.24-7.44 (m, 12H), 3,18 (br, 18H), 2.97 (br, 4H), 2.01 (br, 4H), 1.47 (br, 4H),1.10-1.06 (br, 8H), 0.53 (br, 4H).

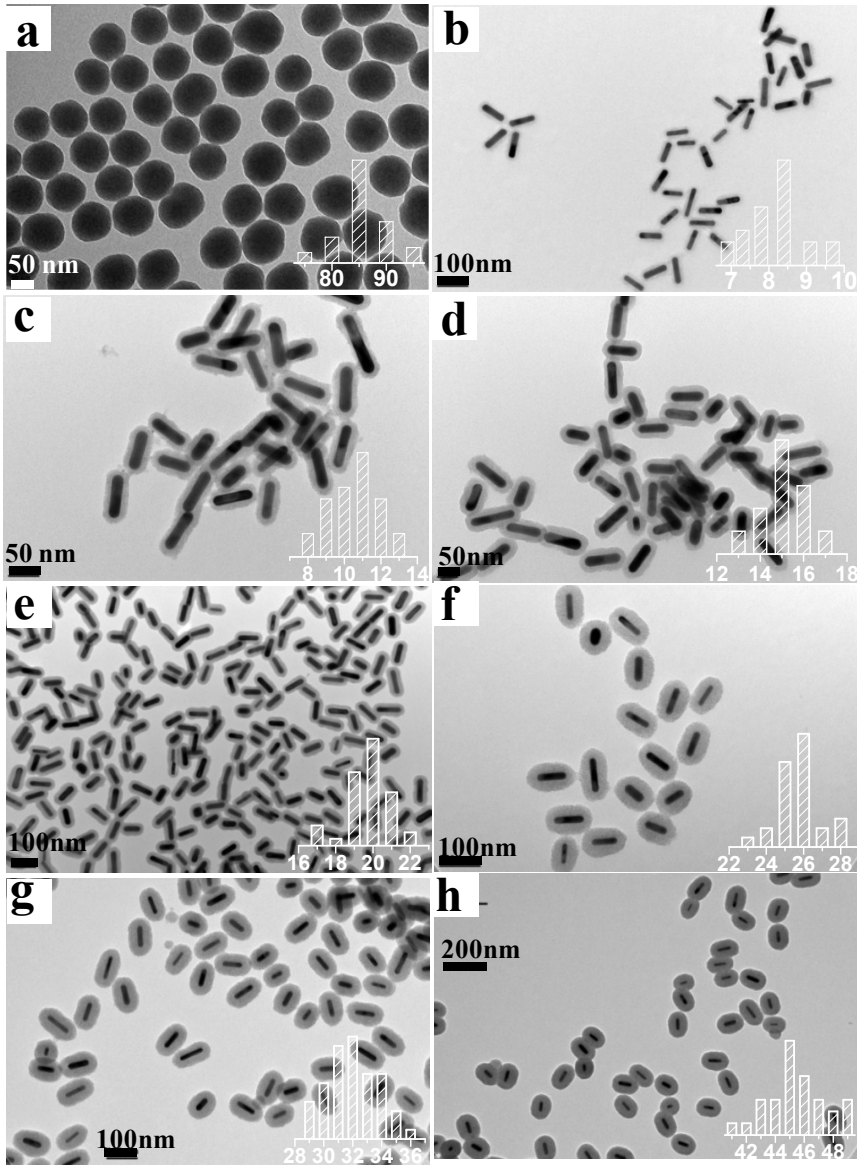


Figure S1(a) TEM images of SiO_2 (85±3 nm), and Au NR/SiO_2 with different silica shell thickness:(b) 8.5±0.7 nm, (c) 11±1.4 nm, (d)15±1.2 nm, (e) 20±1.2 nm, (f) 26w nm, (g) 32±1.8 nm and (h) 45±1.5 nm (Insets are particle size distribution histograms).

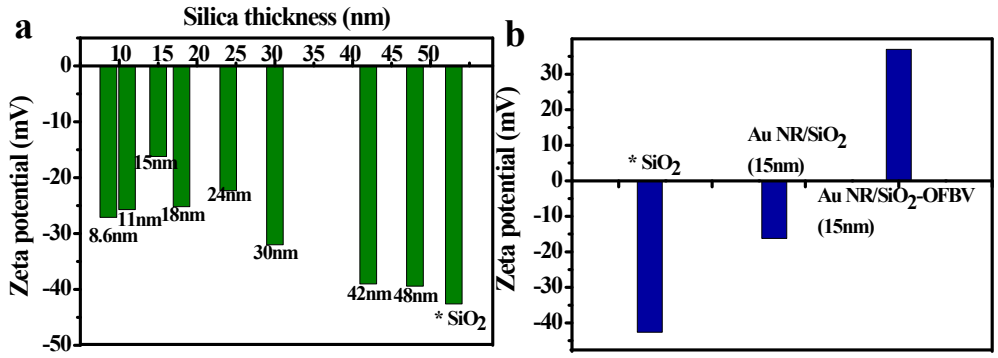


Figure S2 Zeta potentials of AuNR/SiO_2 with different silica thickness (a)and AuNR/SiO_2(15 nm) before and after OFBV adsorption (b).

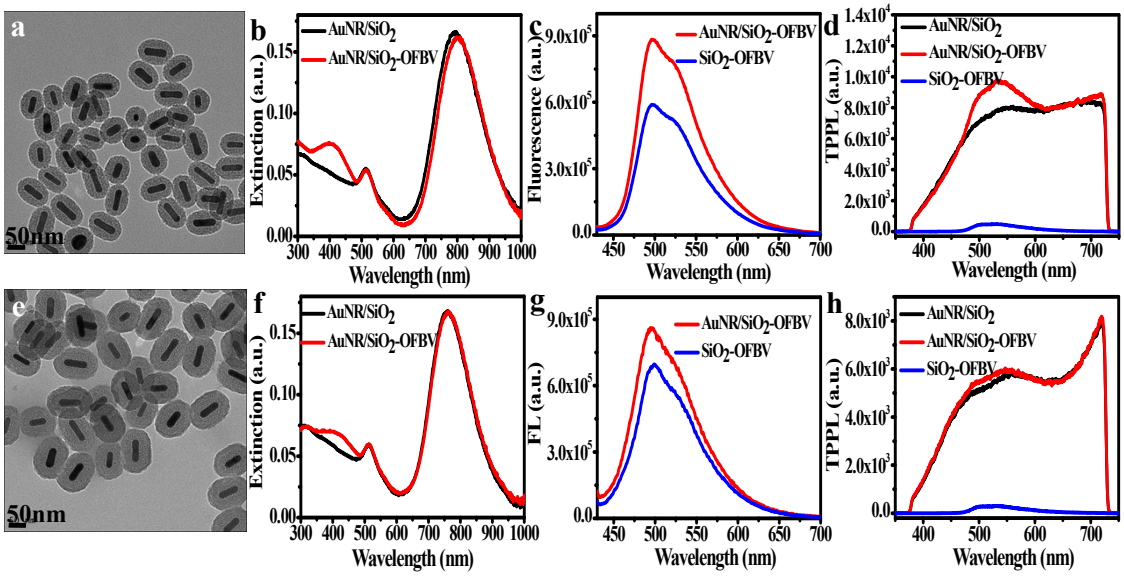


Figure S3 TEM (a, e), extinction spectra (b, f), one-(c, g) and two-photon (d, h) fluorescence spectra of Au NR/SiO_2(26nm)-OFBV and Au NR/SiO_2(45nm)-OFBV in comparison with Au NR/SiO_2 and SiO_2-OFBV.

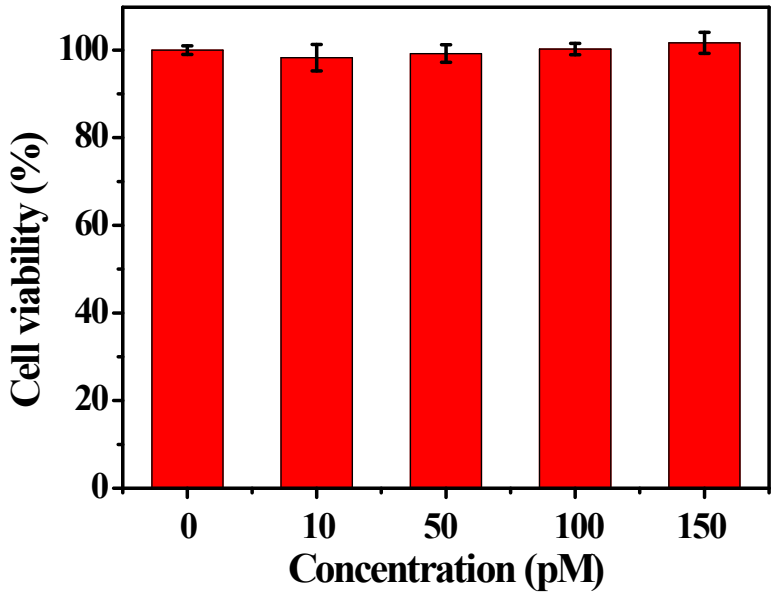


Figure S4 Metabolic viability of HepG2 cells after incubation with AuNR/SiO_2(15nm)-OFBV of different concentrations (in concentration of AuNRs) for 24 h.

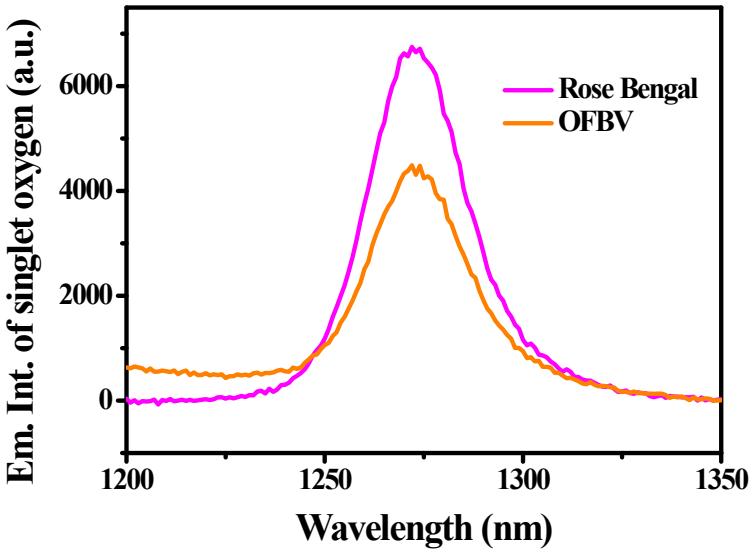


Figure S5 Phosphorescence spectra of singlet oxygen generated by OFBV in CD_3OD under one-photon excitation. Rose Bengal in D_2O was used as the standard.

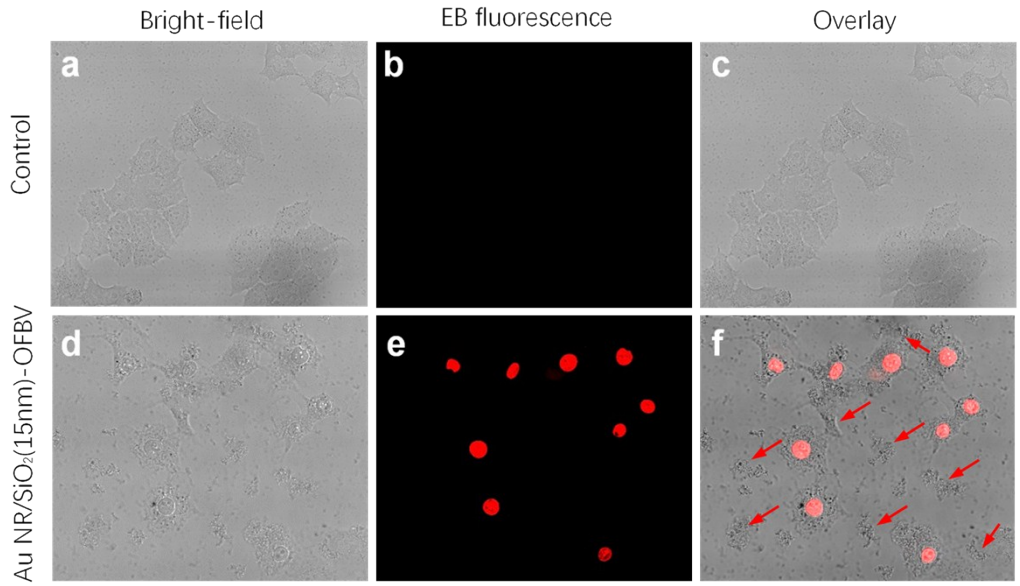


Figure S6 (a, d) Transmission, (b, e) EB fluorescence and (c, f) Overlay images of HepG2 cells with and without AuNR/SiO_2(15nm)-OFBV after irradiations by a 808 nm femtosecond laser for 10 min with power density of 3 W cm^{-2}. Control (a, b, c) and AuNR/SiO_2(15nm)-OFBV (d, e, f).

Table S1 The structure, enhancement factor and single exponential analysis of fluorescence lifetime of SiO_2-OFBV and AuNR/SiO_2-OFBV with different silica shell thickness in aqueous solution.

Samples	Silica shell thickness (nm)	One-photon enhancement factor	Two-photon enhancement factor	Emission lifetime (ps)
AuNR/SiO_2(8.5nm)-OFBV	8.5	0.21	3.7	240
AuNR/SiO_2(15nm)-OFBV	15	0.6	14.2	248
Au NR/SiO_2 (26nm)-OFBV	26	1.4	3.8	270
AuNR/SiO_2(32nm)-OFBV	32	1.2	1.6	292
AuNR/SiO_2(45nm)-OFBV	45	1.15	1.1	322
SiO_2-OFBV	-	1	1	323

Reference:

(1) Mangalum, A.; Gilliard, R. J.; Hanley, J. M.; Parker, A. M.; Smith, R. C. *Org. Biomol. Chem.* **2010**, *8*, 5620.

(2) He, F.; Ren, X. S.; Shen, X. Q.; Xu, Q. H. *Macromolecules* **2011**, *44*, 5373.