Supporting information

Achieving of Two-Photon Fluorescence Bioimaging and Photodynamic Therapy for D-A Conjugated Polymers through Manipulating Twisted Intramolecular Charge Transfer

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Materials

3,7-dibromo-2,8-dioctyldibenzothiophene-*S,S*-dioxide ($RSO-Br_2$), 3,7-dibromo-9,9-dioctylfluorene[2,3-*b*]benzo[*d*]thiophene-*S,S*-dioxide ($BTOF-Br_2$), 2,10-dibromo-9,9-dioctylfluorenebis[2,3-*b*;6,7-*b*]-benzo[*d*]thiophene-*S,S*-dioxide ($FBTO-Br_2$) were purchased from Volt-Amp Optoelectronics Tech. Co., Ltd, Dongguan, China., and used without further purification.

N^1,N^4-bis(4-octylphenyl)-N^1,N^4-diphenylbenzene-1,4-diamine(M1), N^1,N^4-bis(4-bromophenyl)-N^1,N^4-bis(4-octylphenyl)benzene-1,4-diamine(M2), N^1,N^4-bis(4- octyl-phenyl)-N^1,N^4-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl) benzene-1,4-diamine(M3) were synthesized according to the literatures.[1,2] Unless specified elsewhere, all reagents and starting materials were of commercial grade and used as received. Toluene for Suzuki coupling polycondensation was dealt with concentrated sulfuric acid (H_2SO_4) several times, dried by anhydrous $MgSO_4$, and further purified by atmospheric distillation under an atmosphere of dry argon.

Synthesis of M3: A mixture of M2 (2.38 g, 3.0 mmol), bis(pinacolato)diboron (1.90 g, 7.5 mmol), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$, 109.7 mg, 0.15 mmol), potassium acetate (1.47 g, 15 mmol) were stirred in dioxane (50 mL). The reaction mixture was kept at 90 °C for 12 h under an argon atmosphere. When cooled down to room temperature, it was sequentially diluted with dichloromethane, washed with water and dried over $MgSO_4$. After solvent removal, the residue was purified by silica gel column chromatography (petroleum ether/dichloromethane = 5/1, v/v) to afford M3 as a white solid (1.97 g, yield: 74%). ^{1}H NMR (500 MHz, D6-Benzene, ppm) δ: 7.26-7.19 (m, 8H), 7.12 (t, 4H), 7.09 (s, 4H), 7.05 (d, 4H), 6.88 (d, 2H), 2.55 (t, 4H), 1.62 (m, 4H), 1.40-1.25 (m, 20H), 0.95 (t, 6H). MS (MALDI-TOF): m/z: 889.32; elemental analysis calcd (%) for $C_{58}H_{78}N_8B_2N_2O_4$:

78.37, H 8.85, N 3.15; found: C 78.13, H 8.56, N 2.97.

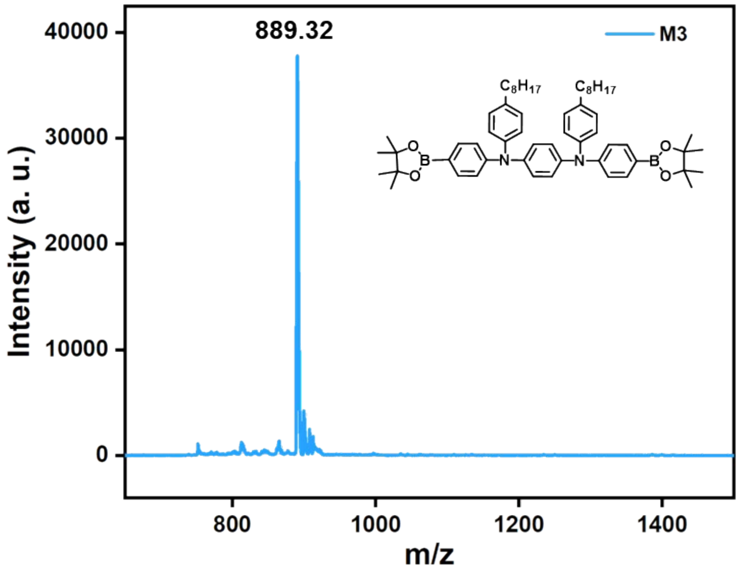
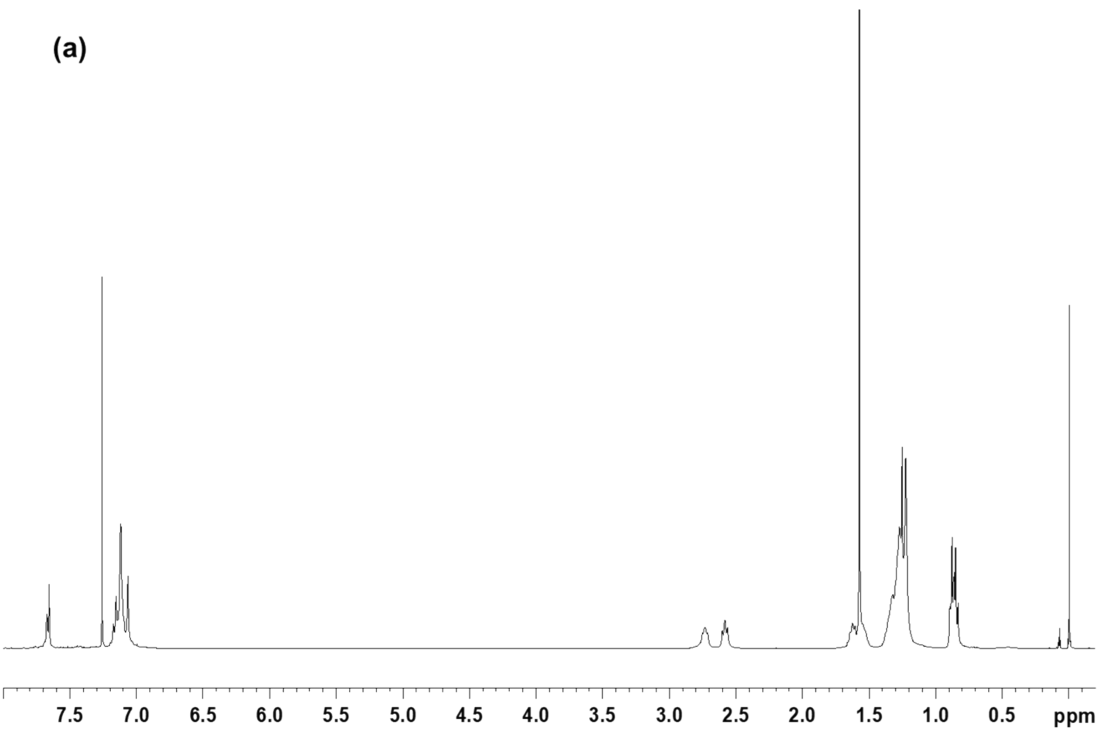


Figure S1 Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrum of compound M3. The inset is its chemical structure.



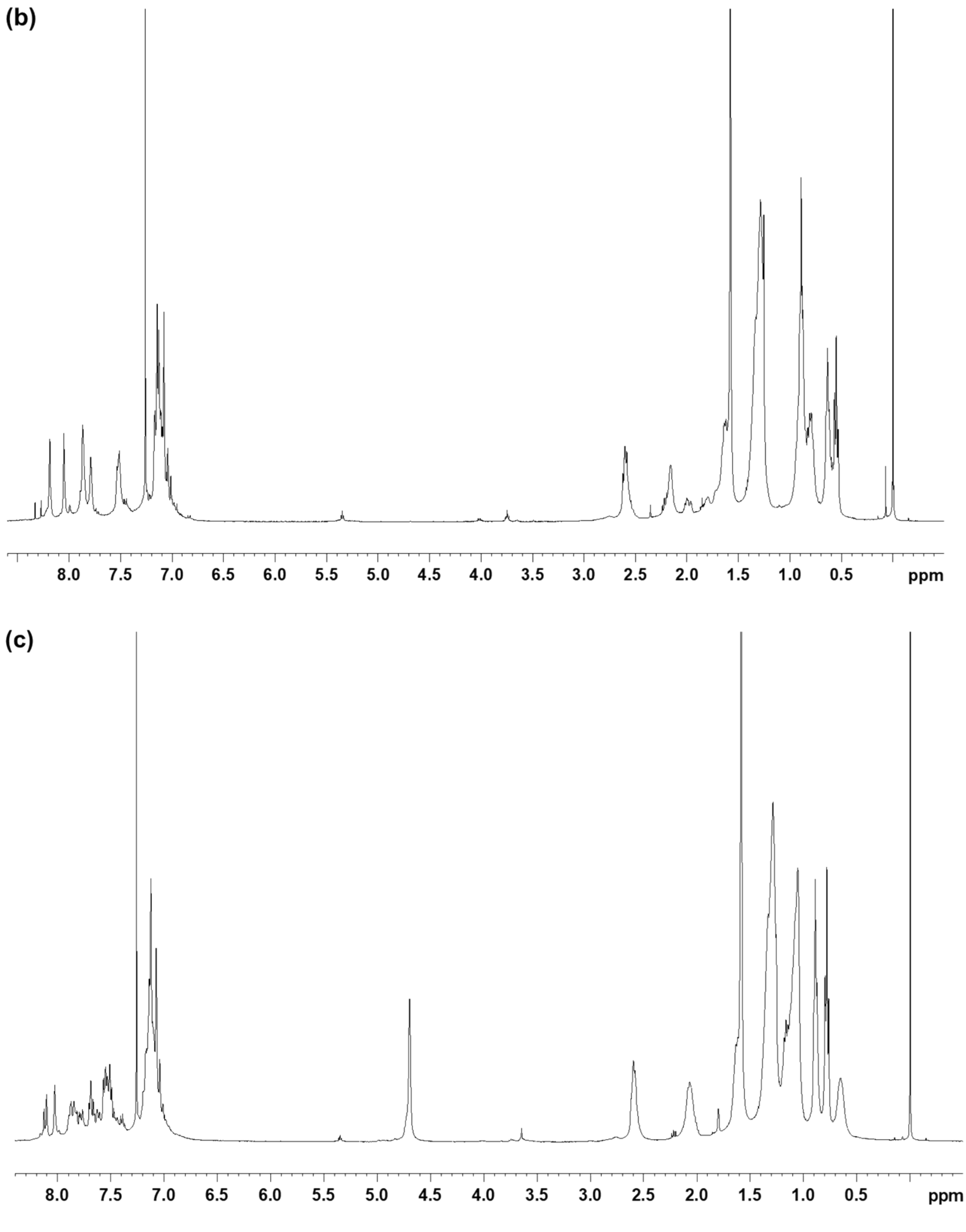


Figure S2. ^{1}H NMR spectra of PDA3 (a), PDA5 (b) and PDA7 (c).

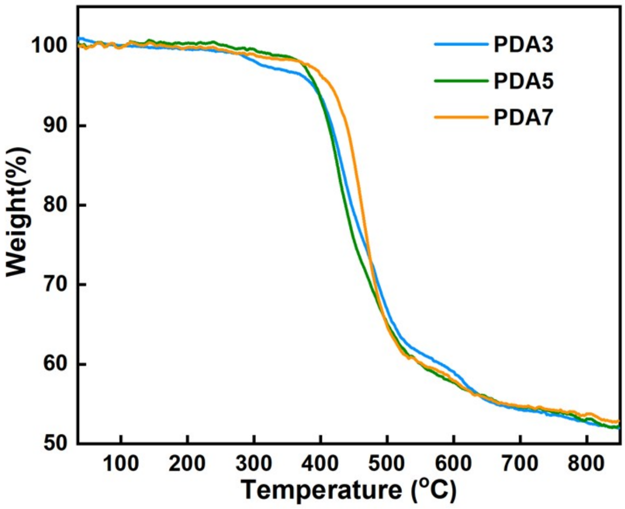


Figure S3. Thermogravimetric analysis (TGA) spectra of polymers PDAs.

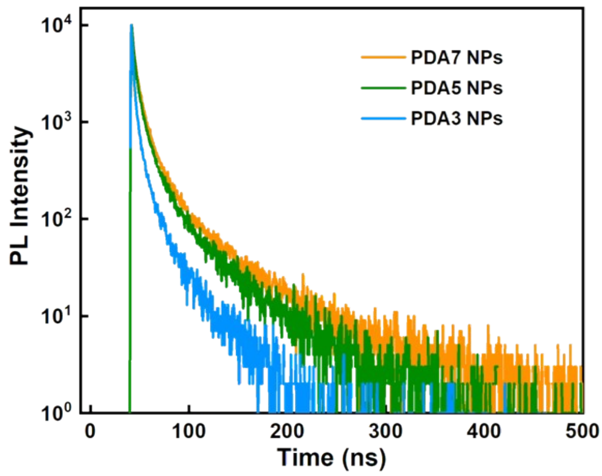


Figure S4. Time-resolved fluorescence decay curve of polymers PDAs in pure film state at room temperature.

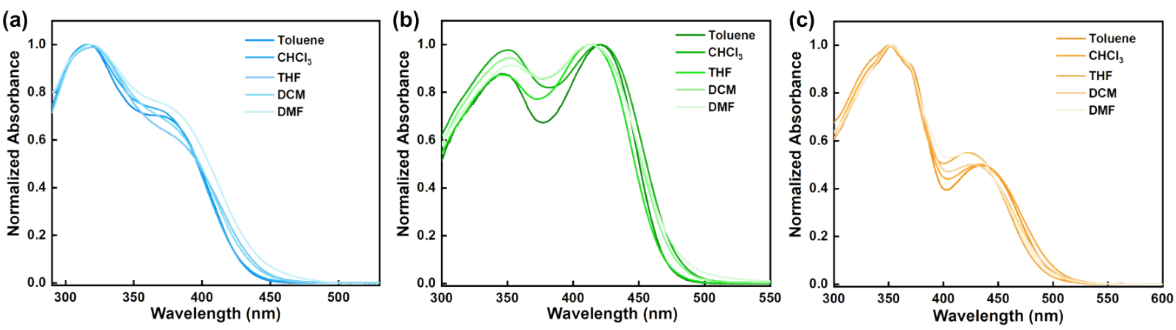


Figure S5. UV-vis absorption spectra of PDA3 (a), PDA5 (b) and PDA7 (c) in various solvents.

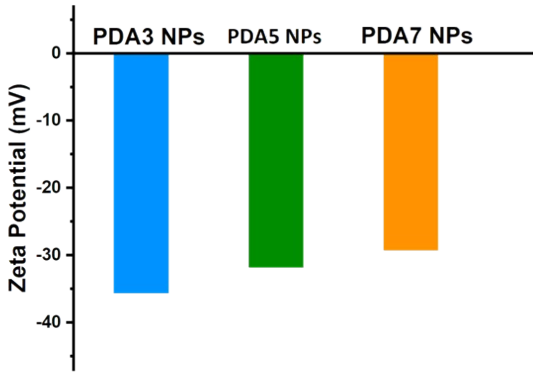


Figure S6. The zeta potentials of PDAs NPs in ultra-pure water.

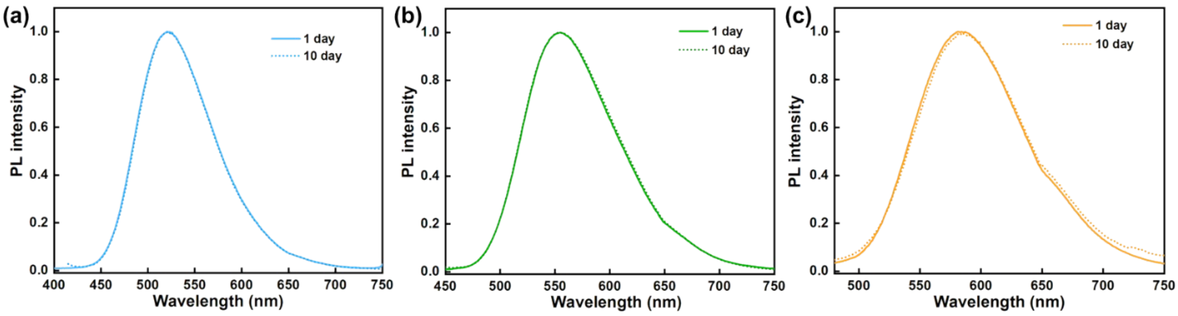


Figure S7. PL spectra of PDA3 NPs (a), PDA5 NPs (b) and PDA7 NPs(c).

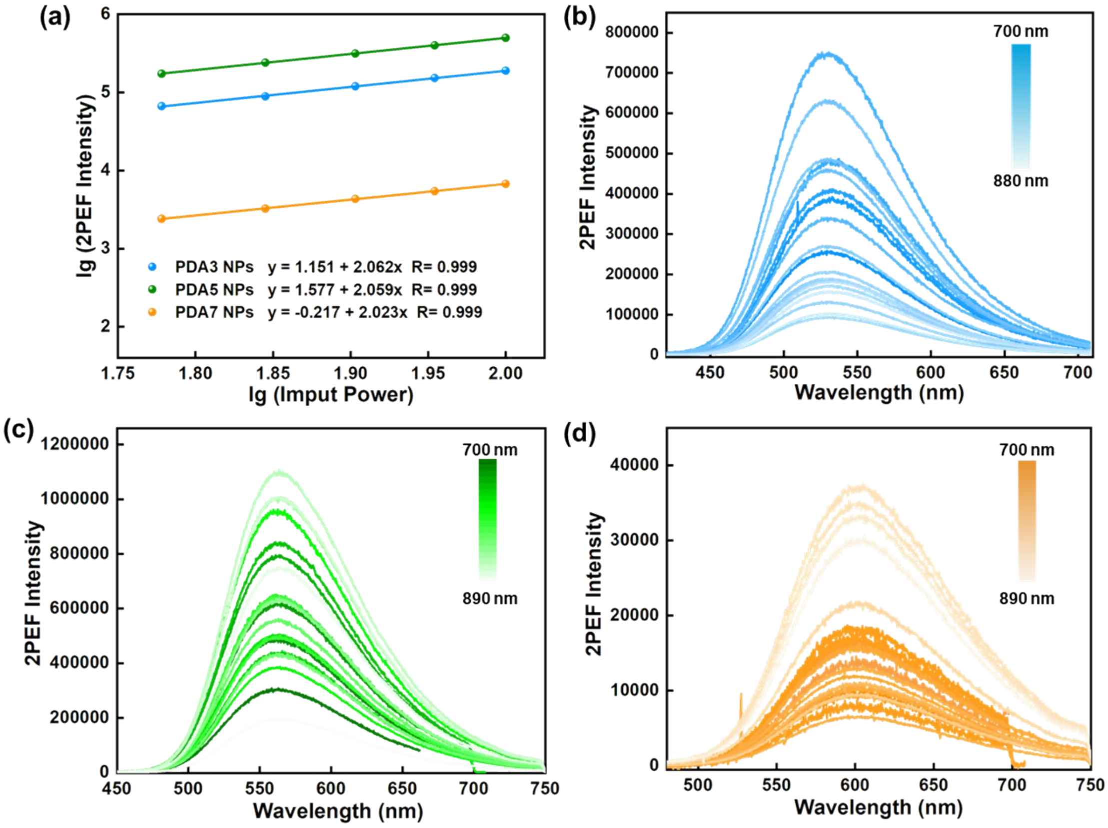


Figure S8. (a) The log-log plot of laser excitation power against TPEF emission intensities at 800 nm, and PL spectra of PDA3 NPs (b), PDA5 NPs (c) and PDA7 NPs (d).

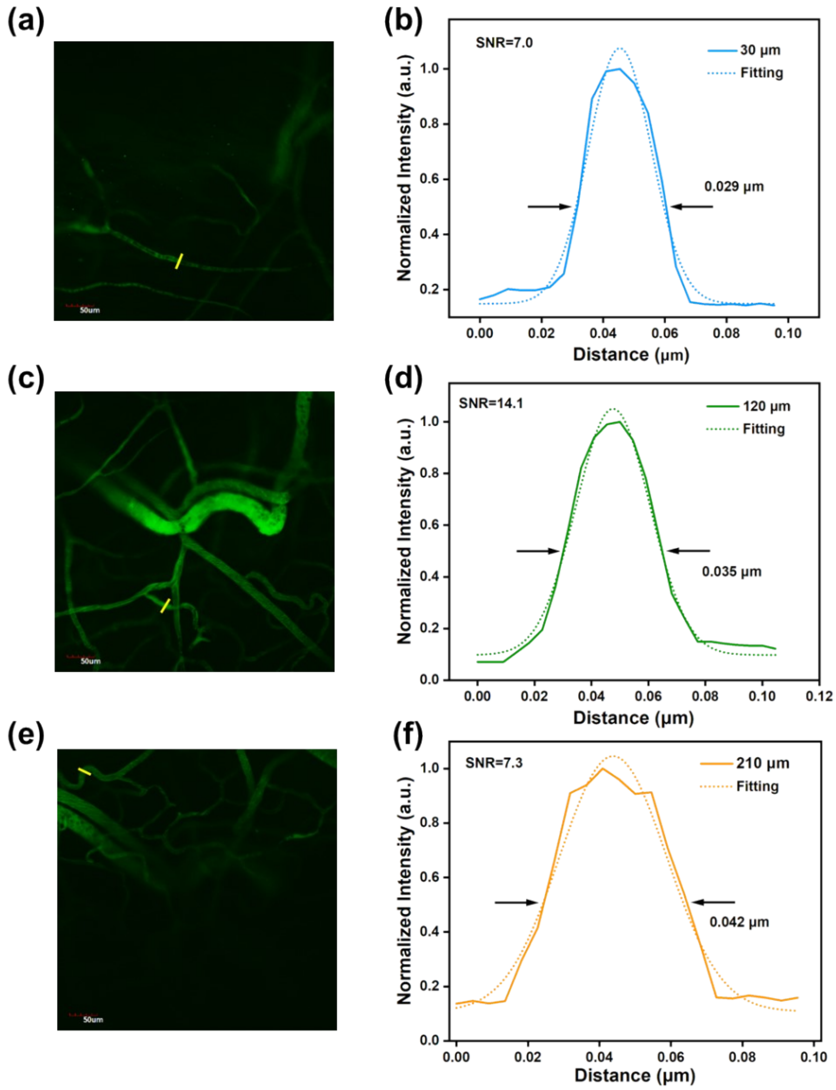


Figure S9. Signal-to-noise ratio (SNR) of two-photon bladder vasculature images along the solid yellow line at the depth of 30 μm (a, b), 120 μm (c, d) and 210 μm (e, f) measured from the two-photon fluorescence intensity line profiles across the blood vessels.

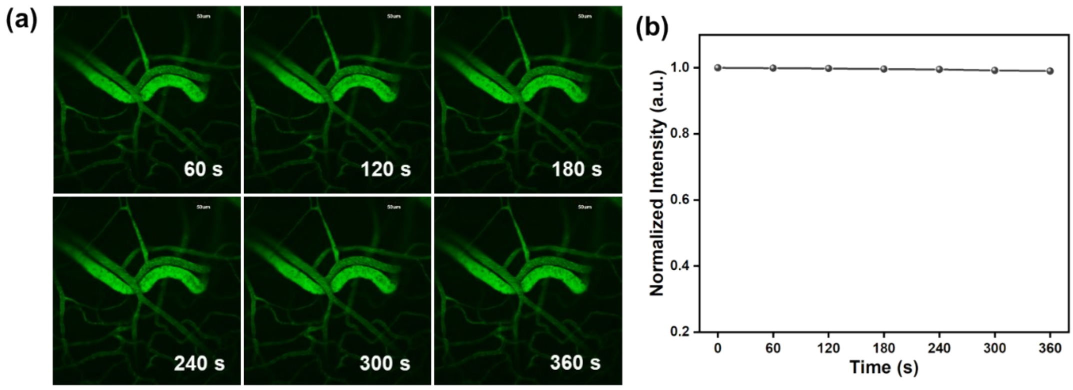


Figure S10. (a) Real-time tracing the blood flow in mice bladder in presence of PDA5 NPs (2 mg/kg, 250 μL solutions per mouse) upon two-photon excitation (λ_{ex}=840 nm; λ_{em}=500–550 nm). Scale bar: 50 μm. (b) The fluorescence intensity changes of two-photon fluorescence imaging at different times.

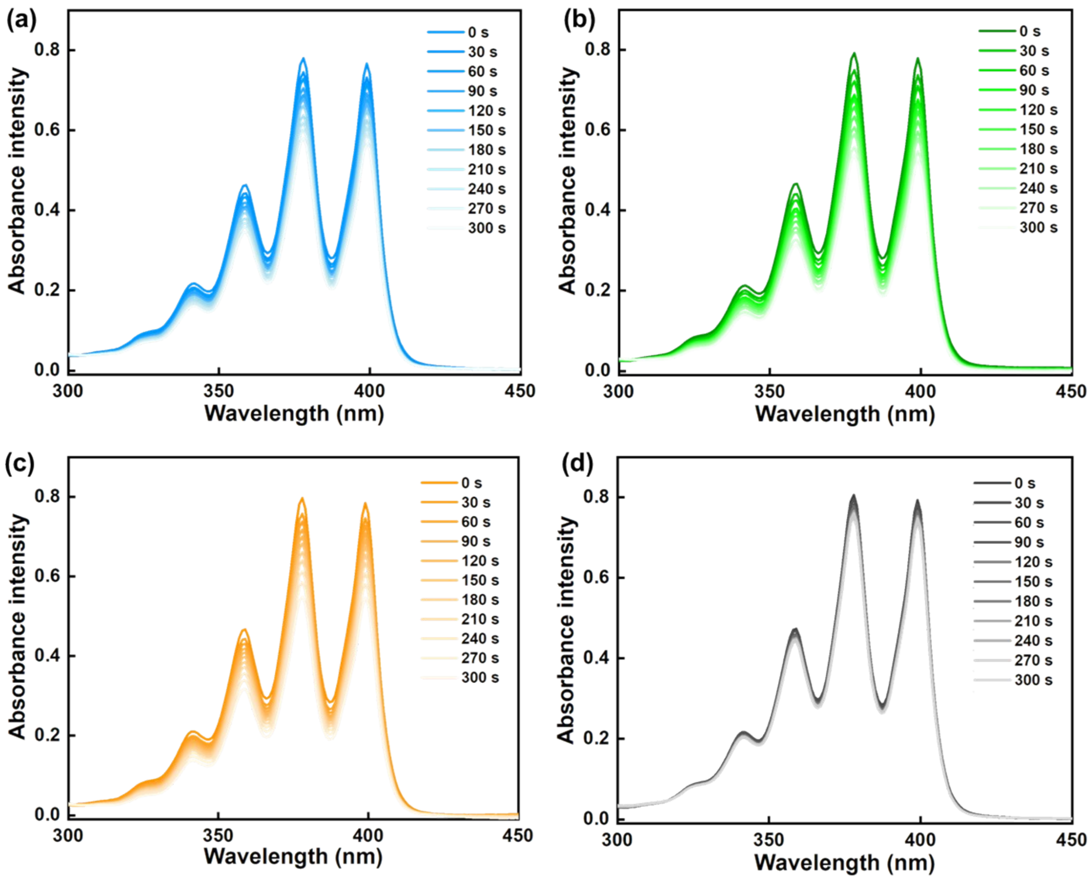


Figure S11. Photo-oxidation of ABDA by singlet oxygen generated upon white light irradiation (400−780 nm, 50 mW cm^{-2}) from PDA3 NPs (a), PDA5 NPs (b), PDA7 NPs (c) in water and pure water (d).

References

1. J. Slota, E. Elmalem, G. Tu, B. Watts, J. Fang, P. Oberhumer, et al. *Macromolecules* 2012, **45**, 1468.

2. G. Tu, S. Massip, P. Oberhumer, X. He, R. Friend, N. Greenham, et al. *J. Mater. Chem.,* 2010, **20**, 9231.