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Ultrabright Organic Fluorescent Microparticles for *in-vivo* Tracing Applications

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All the reagents and materials were purchased from J&K Chemical Co. (China), and are of analytical grade. The solvents were purified by the standard procedures. NMR(^{1}H, ^{13}C) spectra were recorded on a Bruker ADVANCE III 400MHz spectrometer at room temperature. The ^{1}H and ^{13}C chemical shifts (δ) are reported in parts per million and the TMS was used as an internal standard.

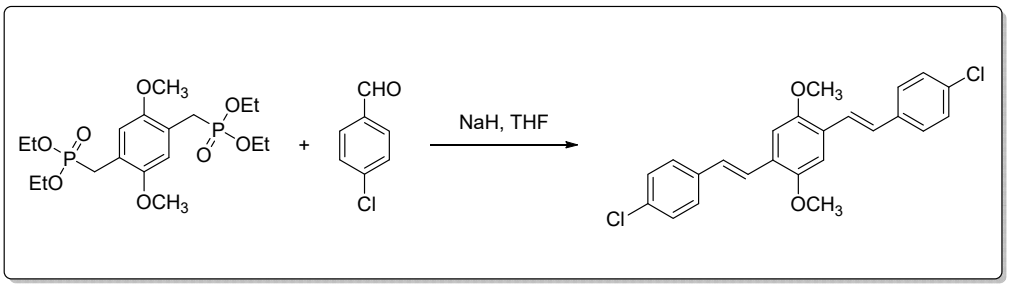

Fig. S1. The synthesis for the OPV-Cl.[1]

OPV molecular was synthesized via the Horner–Wadsworth–Emmons coupling reaction.[2] To the 2,5-bismethoxy-1,4-xylene-bis(diethyl phosphonate) and 4-chlorobenzaldehyde mixture in THF cooled in an ice bath was added 2 eq. NaH in small portions during a 30 min period. The reaction mixture was stirred at RT for 3 h and poured into water. The phase was extracted with CH_2Cl_2. The pooled organic phases were washed with water, dried over anhydrous $MgSO_4$, filtered, and evaporated. The product was separated by flash chromatography on silica gel by means of CH_2Cl_2/petroleum ether (1:5). A purified sample was obtained by crystallization from the toluene/hexanes.

OPV-Cl: ^{1}H NMR (400M, CDCl3) 7.48 (d, J = 8.0 Hz, 4H), 7.45 (d, J = 16.0 Hz, 2H), 7.32 (d, J = 8.4 Hz, 4H), 7.11 (s, 2H), 7.07 (d, J = 16.4 Hz, 2H), 3.93 (s, 6H);

^{13}C NMR (100M, CDCl3) 151.56, 136.33, 133.05, 128.80, 127.78, 127.73, 126.47, 123.81, 109.15, 56.31;

MS (APCI+) 411.4 [M+1]+

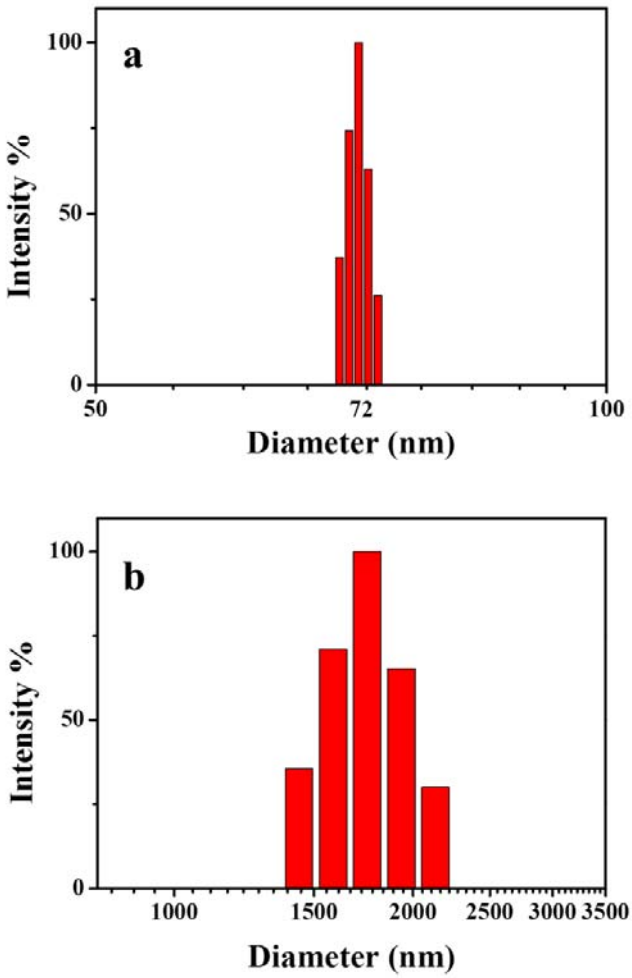

Fig. S2. Particle size distribution of OPV-Cl nanoparticles (a) and microparticles (b) measured by dynamic light scattering.

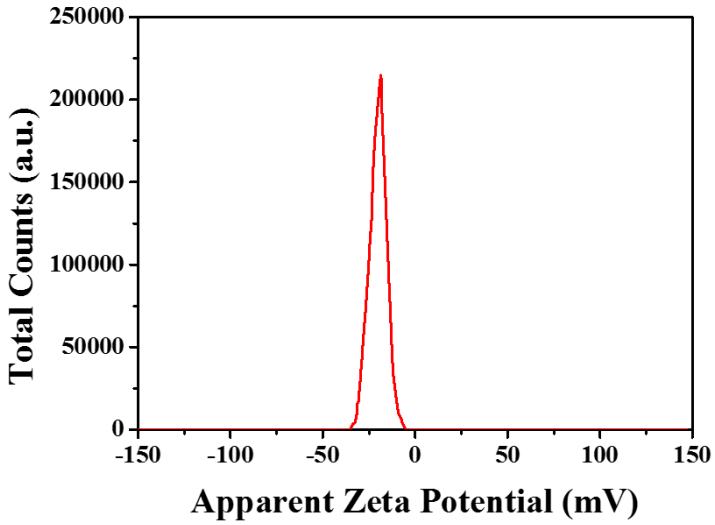

Fig. S3. The zeta potential for the OPV-Cl microparticles (-20.1±0.68 mV)

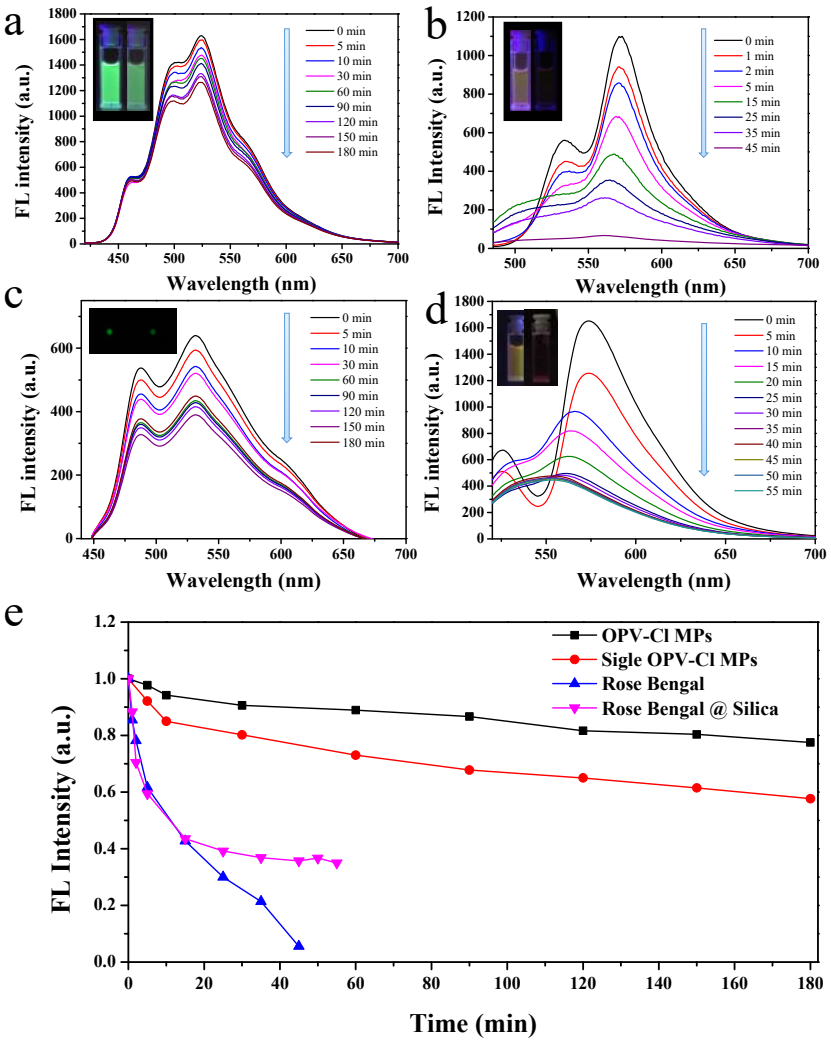

Fig. S4. The fluorescence emission spectra of a) OPV-Cl microparticle suspension (1.0×10^{-5} M, DMSO/H_2O=1:9) under continuous irradiation of 265 nm (8w) UV light; b) Rose Bengal solution (1.0×10^{-5} M, H_2O) under continuous irradiation of 265 nm (8w) UV light; c) The single OPV-Cl microparticle on the glass under continuous irradiation of 265 nm (8w) by micro-spectroscopy; d) suspension of Rose Bengal loaded at silica (1.0×10^{-5} M, H_2O) under continuous irradiation of 265 nm (8w); e) The photo-bleaching kinetic traces of OPV-Cl microparticles suspension, Rose Bengal solution, single OPV-Cl microparticle and suspension of Rose Bengal loaded at silica.

The inset show the fluorescent emission change before and after 3h irradiation. After the 3h irradiation, the OPV-Cl microparticle suspension and the single particle still showed strong fluorescence, but the Rose Bengal solution was completely bleached after 1h irradiation. The emission of Rose Bengal loaded at the silica gel is more stable than in solution, however, the emission is peak is changed. We have reason to believe that Rose Bengal has completely changed. Therefore, the OPV-Cl microparticle suspension has much better photon-stability

compared with Rose Bengal.

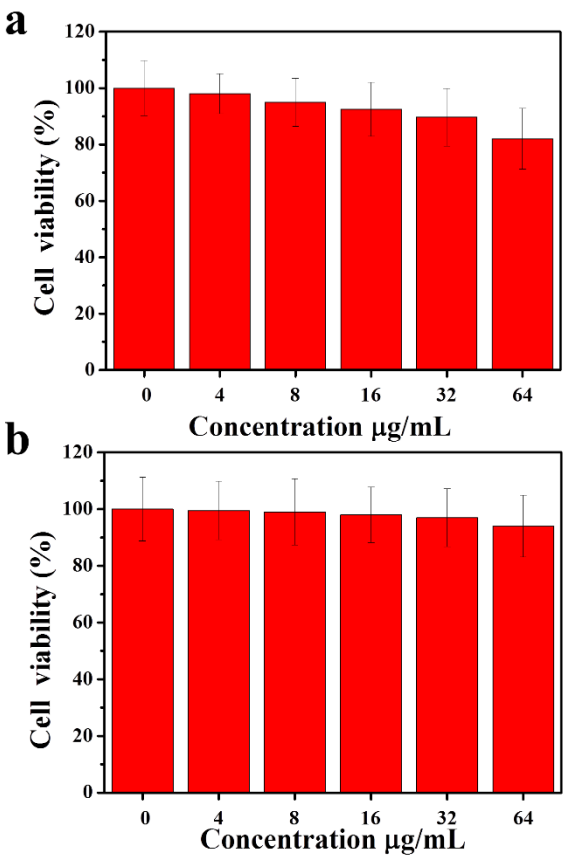

Fig. S5. Viability of MCF-7 cells at various concentrations of OPV-Cl (a) nanoparticles and (b) mciropariticle.

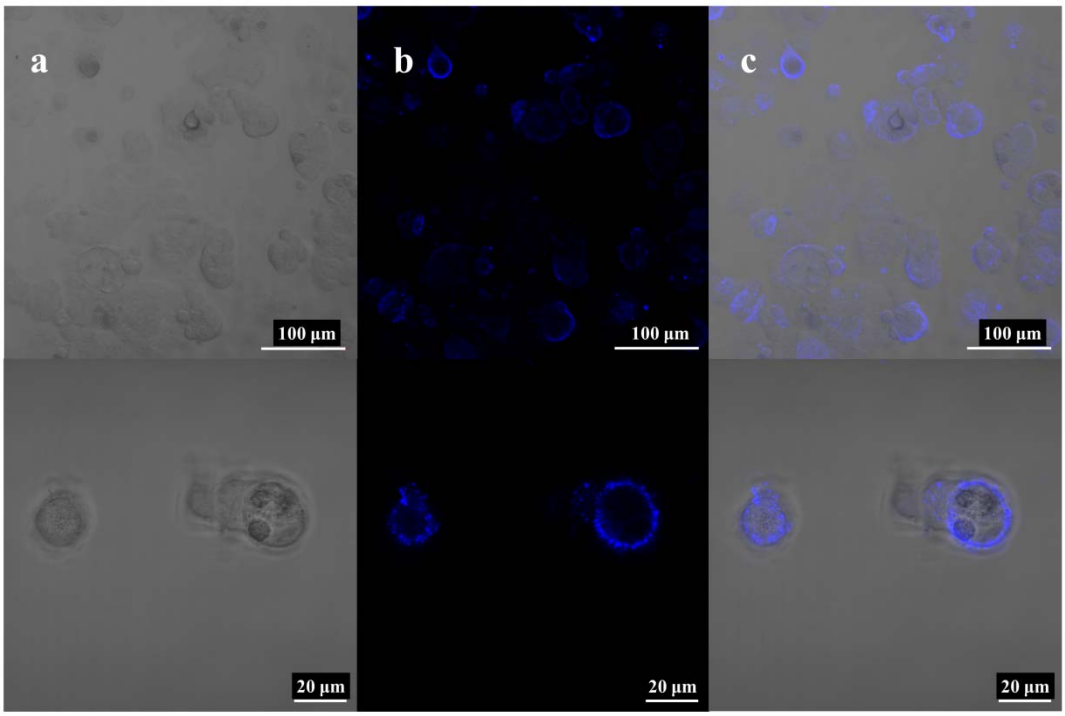

Fig. S6. (a) The bright-field image of MCT-7 cells incubated with OPV-Cl microparticles. (b) The laser scanning confocal microscope (LSCM) image of MCF-7 cells upon excitation at 435 nm. (c) The overlaid picture of LSCM and the corresponding bright-field images.

Note: The microparticles were just around the surface of cell.

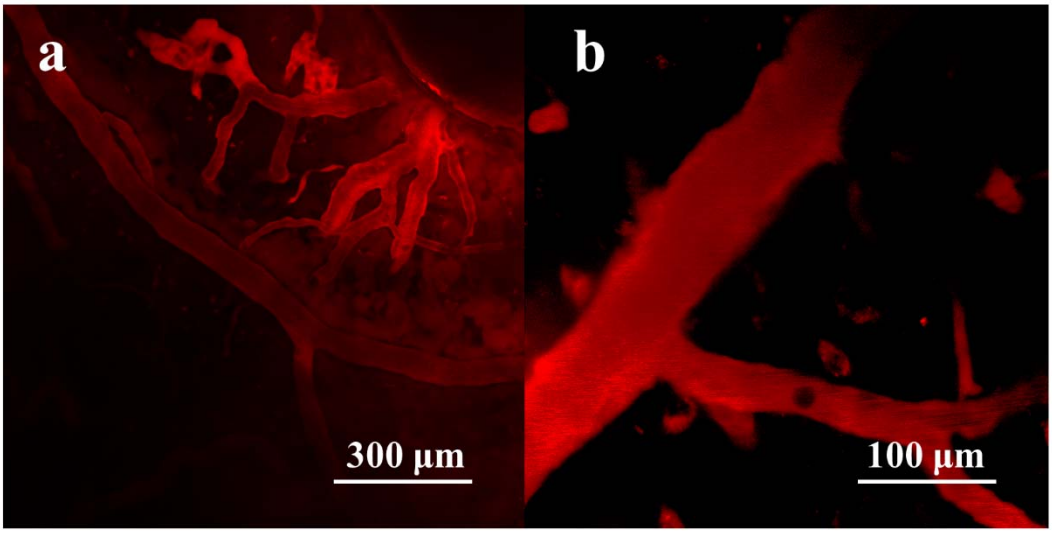

Fig. S7 . The blood plasma labeled with water soluble Texas Red (TR) dextran.

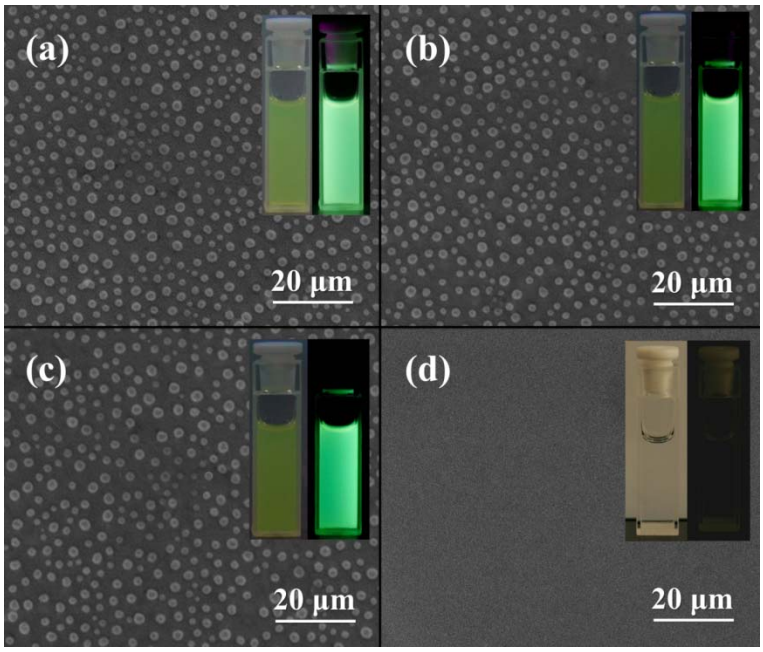

Fig. S8. The FESEM micrographs of the microparticles of the OPV-Cl, the inset show the digital photo of OPV-Cl suspension under room-light (left) and UV irradiation (right): (a) microparticles suspension redispersed in PBS, (b) the suspension standing for five days, (c) the suspension adding mouse serum (1%) standing for five days, (d) the solution throught 0.8 μm filtration membrane after standing five days.

The stability of our OPV-Cl microparticles for the standing time and serum interaction is shown below. There is no significant decomposition and precipitation after five days standing and mouse serum (1%) adding. To further confirm, the dispersion of OPV-Cl microparticles are filtrated by 0.8 μm membrane filtration. The solution is no observed fluorescence. There is no significant decomposition and precipitation for OPV-Cl microparticle.

Video clip: Moving of fluorescent microparticles in the mice brain vessel monitored by fluorescent microscopy (Video).

Reference

[1] C. L. Sun, J. Li, H. W. Geng, H. Li, Y. Ai, Q. Wang, S. L. Pan, H. L. Zhang, Chem. Asian J. 2013, 8, 3091.

[2] a) L. Horner, H. M. R. Hoffmann, H. G. Wippel, Chem. Ber. 1958, 91, 61; b) D. S. Seferos, D. A. Banach, N. A. Alcantar, J. N. Israelachvili, G. C. Bazan, J Org Chem 2004, 69, 1110; c) H.-C. Lin, C.-M. Tsai, G.-H. Huang, J.-M. Lin, J. Polym. Sci., Part B: Polym. Phys. 2006, 44, 783.