Supporting information

Hydroporphyrin-Doped Near Infrared Emitting Polymer Dots for Cellular Fluorescence Imaging

Connor Riahin[a], Adam Meares[a], Nopondo N. Esemoto[a], Marcin Ptaszek[a] Michael LaScola[b], Narendra Pandala[b], Erin Lavik[b], Mengran Yang[c], Gary Stacey[c], Dehong Hu[d], Jeremiah C. Traeger[d], Galya Orr[d] and Zeev Rosenzweig,*[,a]

[a]Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, Maryland, 21250, USA. E-Mail: zrosenzw@umbc.edu.

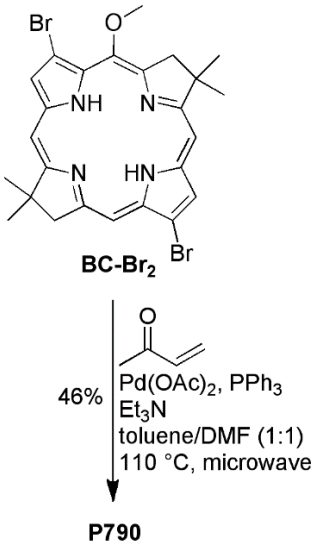
[b]Department of Chemical Biological and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland, 21250, USA.

[c] Division of Plant Sciences and Biochemistry, University of Missouri, Columbia, MO 65211

[d] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, 99354

1.1 Synthesis and Characterization of Bacteriochlorin P790

The synthesis of the bacteriochlorin P790 is described in scheme S1 and below:



Scheme S1 - Synthesis of **P790**.

A Schlenk flask was charged with 3-buten-2-one (298 μl, 3.60 mmol), TEA (50 μl, 0.36 mmol) and a mixture of anhydrous toluene/DMF (5 ml, 1:1) and the resulting mixture was degasses twice by freeze-thaw cycle. Separately, in a septum-capped microwave tube, samples of **BC-Br$_2$** (20.0 mg, 0.036 mmol), PPh_3 (47.2 mg, 0.18 mmol) and $Pd(OAc)_2$ (0.8 mg, 0.002 mmol) were placed and purged with N_2 for 20 min. The solution from the Schlenk flask was transferred to a microwave tube and irradiated in a CEM microwave. A complete cycle involved irradiation at 250W for a ~5 min to reach a target temperature of 110 °C. This was followed by a hold time of 45 min at 110 °C. After that reaction mixture was allowed to cool to ~50 °C After each cycles, UV-Vis and TLC were used to monitor reaction progress. After three cycles, essentially all starting bacteriochlorin was consumed. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate, washed (water and brine), dried (Na_2SO_4), and concentrated. Column chromatography (silica, dichloromethane/ethyl acetate, 5:1) afforded a red product; 8.9 mg, 46 % ^{1}H NMR ($CDCl_3$) δ -1.37 (s, 1H), -1.14 (s, 1H), 1.94 (s, 6H), 1.95 (s, 6H), 2.67 (s, 3H), 2.68 (s, 3H), 4.28 (s, 3H), 4.37 (s, 2H), 4.38 (s, 2H), 7.32 (d, *J* = 16.3 Hz, 1H), 7.41 (d, *J* = 16.3 Hz, 1H), 8.54 (s, 1H), 8.57 (s, 1H), 8.78 (s, 1H), 8.83-8.84 (m, 2H), 8.90-8.91 (m, 1H), 9.38 (d, *J* = 16.3 Hz, 1H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.0, 28.4, 31.0, 31.1, 45.7, 45.7, 47.8, 51.9, 64.2, 95.3, 98.0, 98.4, 118.7, 120.1, 127.8, 128.7, 129.0, 129.7, 129.8, 134.7, 135.3, 136.3, 136.7, 136.9, 139.8, 156.6, 161.9, 171.0, 171.1, 198.4, 199.2. HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{33}H_{36}N_4O_3$, 537.2860; Found 537.2840. λ_{abs} = 775 nm, λ_{em} = 780 nm, Φ_f = 0.17 (toluene), 0.15 (DMF).

The Synthesis and characterization of **P640** were reported in ref. 35. Absorption and emission data: λ_{abs} = 635 nm, λ_{em} = 640 nm, Φ_f = 0.22 (toluene).

The synthesis and characterization of **P660** were reported in ref. 33. Absorption and emission data: λ_{abs} = 649 nm, λ_{em} = 660 nm, Φ_f = 0.28 (toluene).

The synthesis and characterization of **P690** were reported in ref. 9. Absorption and emission data: λ_{abs} = 681 nm, λ_{em} = 687 nm, Φ_f = 0.48 (toluene), 0.36 (DMF).

The synthesis and characterization of **P710** were reported in refs. 36 and 5. Absorption and emission data: λ_{abs} = 709 nm, λ_{em} = 711 nm, Φ_f = 0.25 (toluene).

The synthesis and characterization of **P640** were reported in ref. 9. Absorption and emission data: λ_{abs} = 799 nm, λ_{em} = 802 nm, Φ_f = 0.17 (toluene), ~0.01 (DMF).

1.2 Absorption and Fluorescence Spectra of Chlorins and Bacteriochlorins in Tetrahydrofuran (THF)

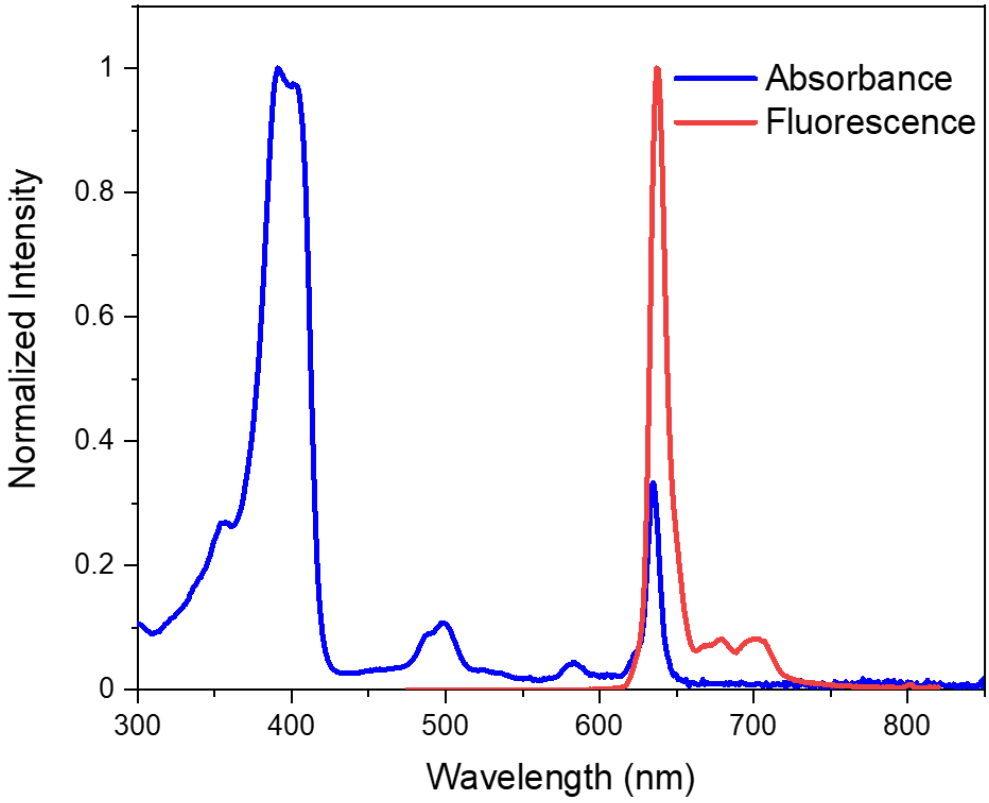


Figure S1: Absorption and fluorescence spectra of P640 in THF

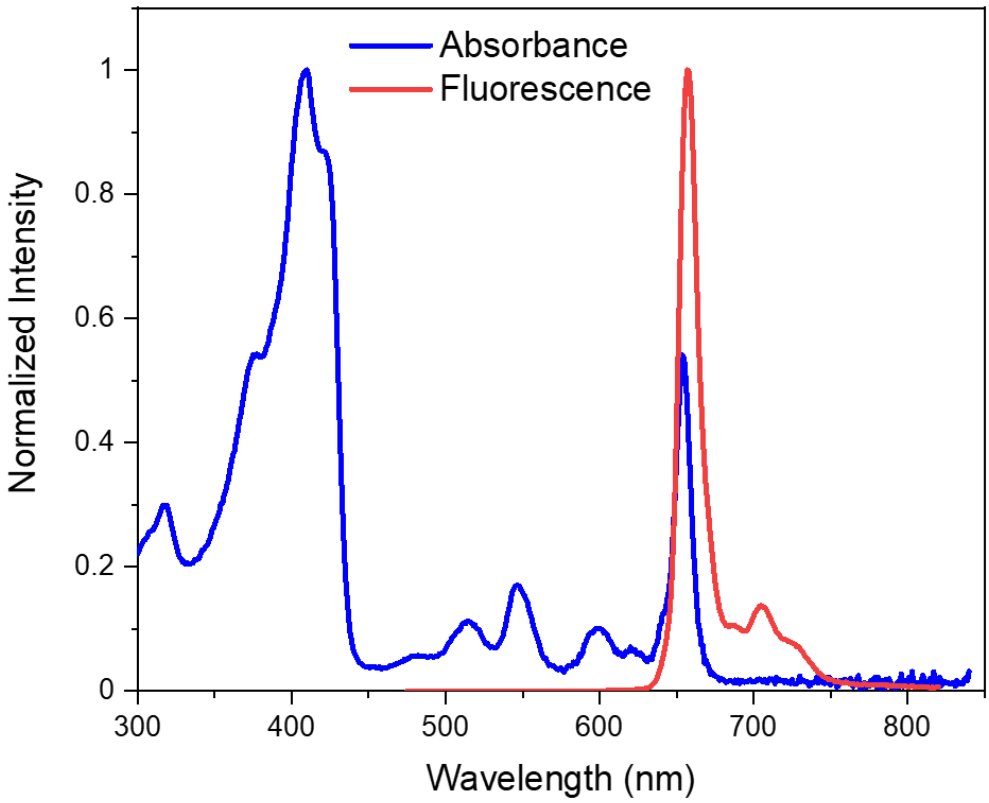


Figure S2: Absorption and fluorescence spectra of P660 in THF

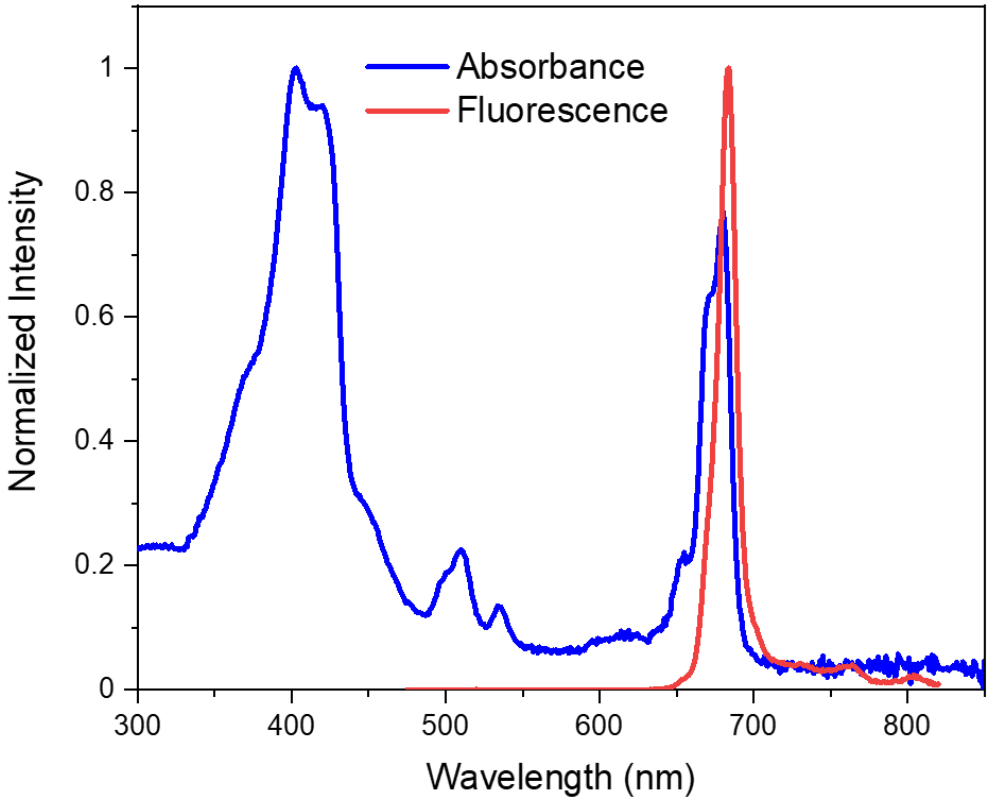


Figure S3: Absorption and fluorescence spectra of P690 in THF

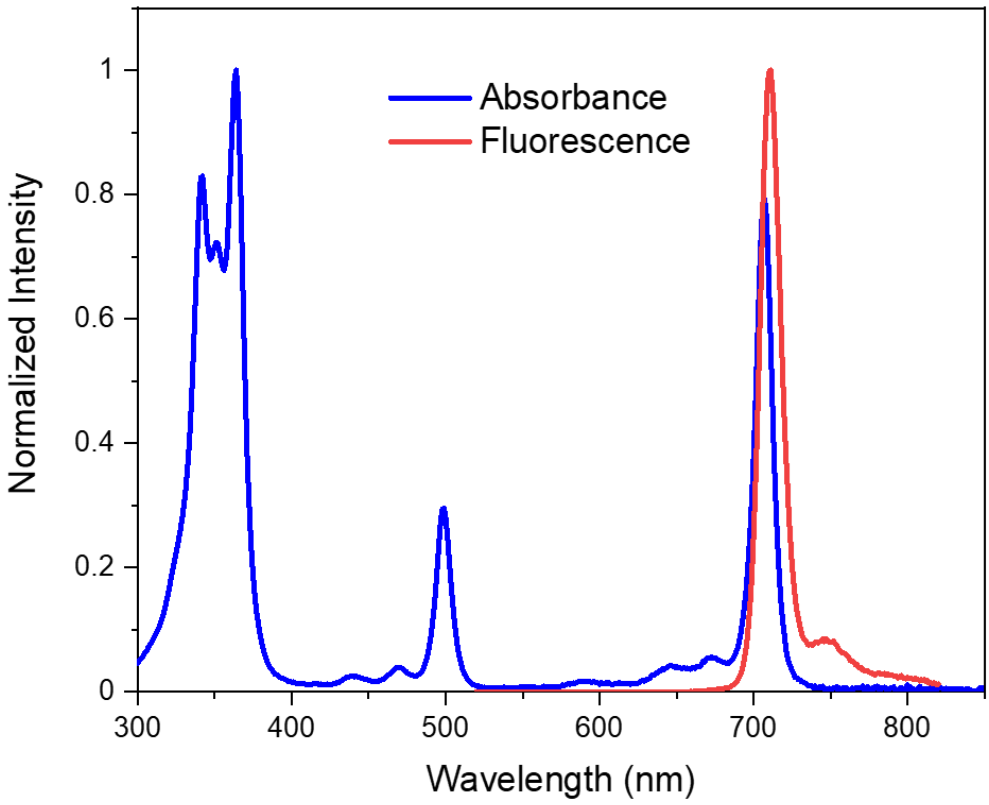


Figure S4: Absorption and fluorescence spectra of P720 in THF

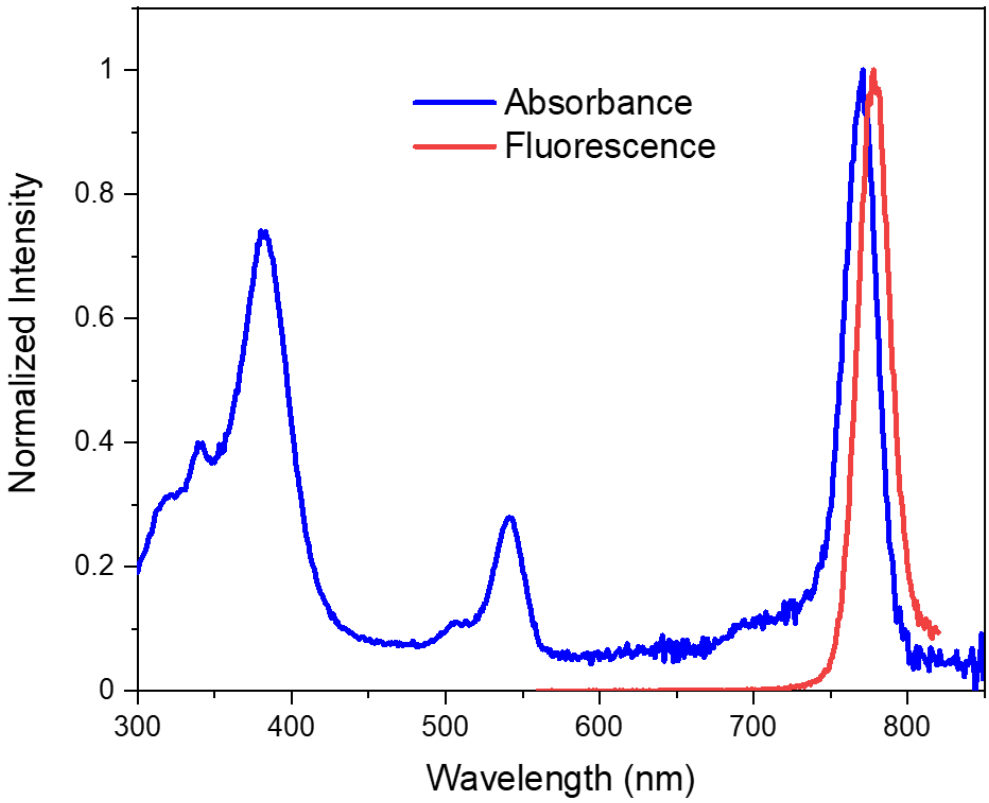


Figure S5: Absorption and fluorescence spectra of P790 in THF

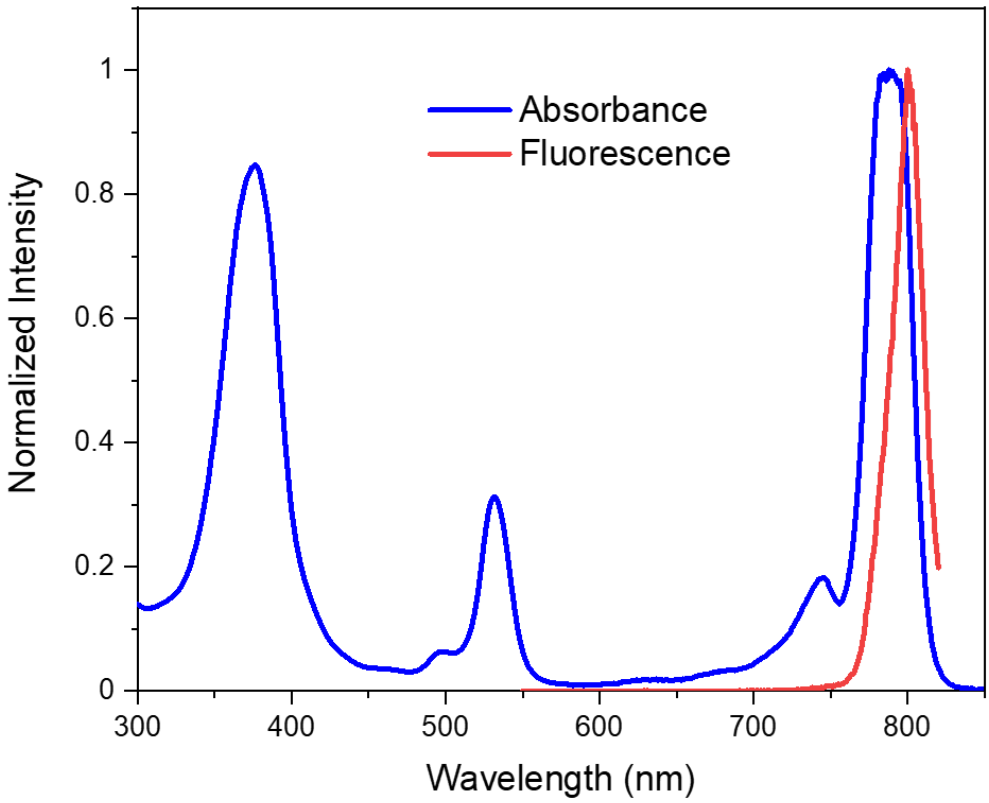


Figure S6: Absorption and fluorescence spectra of P820in THF

1.3 zeta potential measurements of porphyrin doped polymer dots

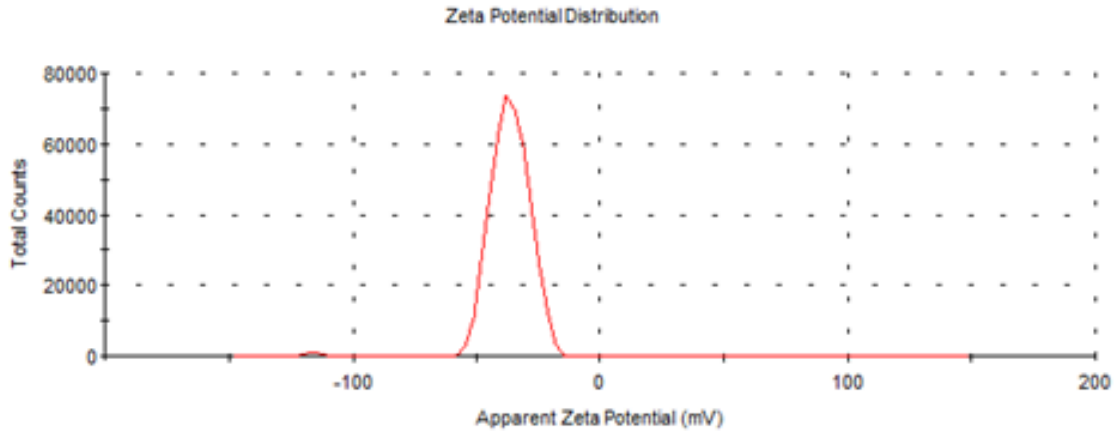


Figure S7: Zeta potential distribution of PFBT polymer dots.