Electronic Supplementary Information

Conjugated Polyelectrolyte Blend as Perturbable Energy Donor-Acceptor Assembly with Multicolor Fluorescence Response to Proteins

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Experimental

Instrument

UV-vis absorption spectra were recorded on a Shimadzu UV-1700 spectrometer. PL measurements were carried out on a Perkin Elmer LS-55 equipped with a xenon lamp excitation source and a Hamamatsu (Japan) 928 PMT, using 90 degree angle detection for solution samples. Photographs of the polymer solutions and thin films were taken using a Canon EOS 500D Digital camera under a hand-held UV-lamp with λ_{max} = 365 nm. All PL and UV measurements were carried out at 24 ± 1 ºC.

Materials

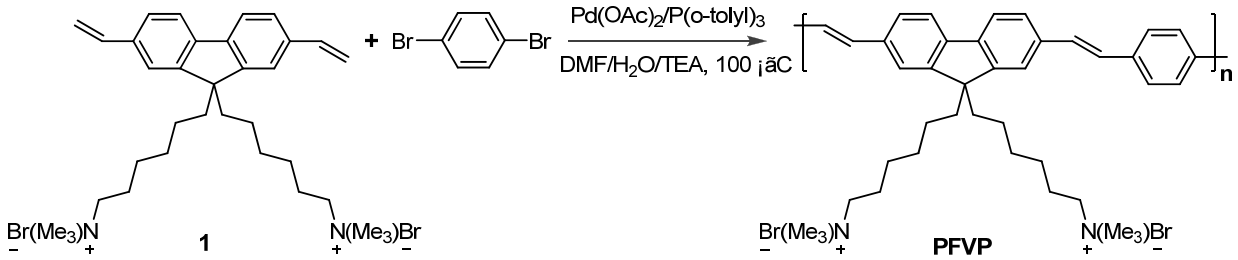
All proteins were purchased from Sigma-Aldrich Chemical Company and were used as received. Fetal Bovine Serum was purchased from HyClone. 10×PBS buffer with pH = 7.4 (ultrapure grade) is a commercial product of 1st BASE Singapore. MilliQ water (18.2 MΩ) was used to prepare the buffer solutions from the 10×PBS stock buffer. 1×PBS contains NaCl (137 mM), KCl (2.7 mM),

Na_2HPO_4 (10 mM), and KH_2PO_4 (1.8 mM). Fresh stock solutions for PFVP (1 mM), PFVBT (1 mM), and proteins (1 mM) were prepared before use.

Synthesis

9,9-Bis(6'-(*N,N,N,*-trimethylammonium)-hexyl)-2,7-divinylfluorene dibromide (**1**) and PFVBT are synthesized according to our previous report.[1]

Synthesis of poly[9,9-bis(6'-(N,N,N,-trimethylammonium)-hexyl)fluorenyldivinylene-alt-1,4-phenylene] (PFVP). A Schlenk tube was charged with **1** (140 mg, 0.212 mmol), 1,4-dibromobenzene (50 mg, 0.212 mmol), $Pd(OAc)_2$ (2 mg, 9 μmmol), and P(*o*-tolyl)$_3$ (15 mg, 49 μmol) before it was sealed with a rubber septum. The Schlenk tube was degassed with three vacuum-argon cycles to remove air. Then, DMF (1 mL), H_2O (0.5 mL), and triethylamine (1 mL) was added to the Schlenk tube and the mixture was frozen, evacuated, and thawed three times to further remove air. The polymerization was carried out at 100 °C under vigorous stir for 12 h. It was then filtered through 0.22 μm syringe driven filter and the filtrate was poured into acetone. The precipitate was collected and redissolved in methanol. Finally, the polymer was purified by dialysis against Mill-Q water using a 6.5 kDa molecular weight cutoff dialysis membrane for 5 days. After freeze-drying, PFVP (116 mg, 81%) was obtained as green fibers. ^{1}H NMR (500 MHz, CD_3OD, δ ppm): 8.45-7.07 (m, 14 H), 3.62 (br, 4 H), 3.29 (br, 18 H), 2.45 (br, 4 H), 1.86 (br, 4 H), 1.48 (br, 8 H), 0.90 (br, 4 H).



Scheme S1 Synthesis of PFVP

Results

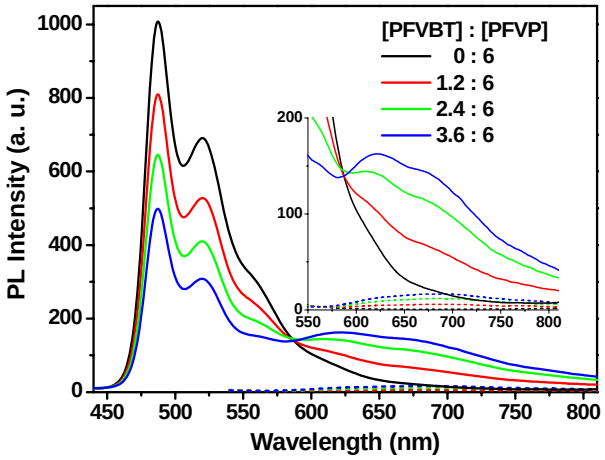


Fig. S1 PL spectra of PFVP/PFVBT mixtures in 25 mM PBS with the ratio ranging from 0 to 0.6. [PFVP] = 6 μM, excitation at 430 nm (solid line) or 515 nm (dashed line).

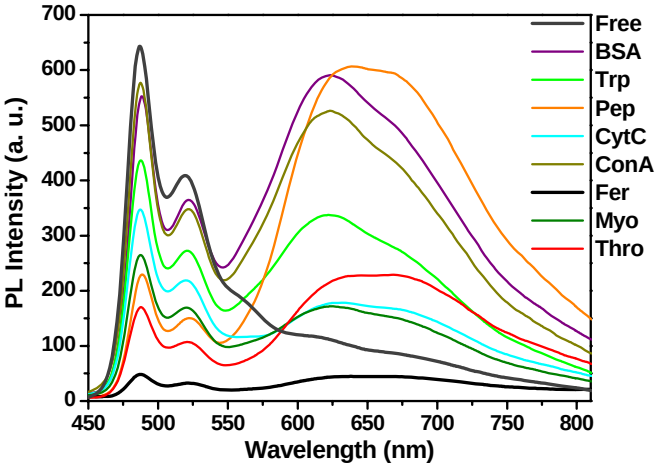


Fig. S2 PL spectra of PFVP/PFVBT blend in 25 mM PBS at pH = 7.4 in the absence and presence of proteins. [PFVP] = 6 μM and [PFVBT] = 2.4 μM. [Con A] = 1 μM, [BSA] = 0.7 μM, [Typ] = 0.9

μM, [CytC] = 0.8 μM, [Myo] = 0.9 μM, [Pep] = 0.6 μM, [Thro] = 0.6 μM, [Fer] = 0.6 μM. Excitation at 430 nm.

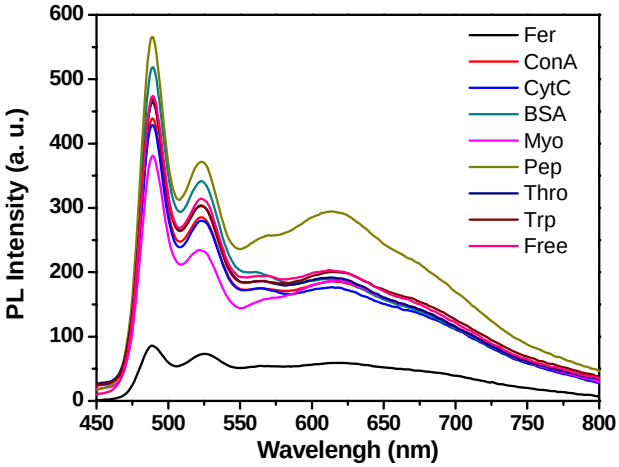


Fig. S3 PL spectra of PFVP/PFVBT blend in 25 mM PBS containing 10 vol% serum in the absence and presence of proteins. [PFVP] = 6 μM and [PFVBT] = 2.4 μM. [Con A] = 4.0 μM, [BSA] = 3.5 μM, [Typ] = 4.2 μM, [CytC] = 4.0 μM, [Myo] = 4.5 μM, [Pep] = 3.6 μM, [Thro] = 3.6 μM, [Fer] = 3.2 μM. Excitation at 430 nm.

Reference:

1 K. Y. Pu, L. Cai and B. Liu, *Macromolecules* 2009, 42, 5933-5940.