Supplementary information for:

Colorimetric and Fluorescent Detection of Protamine with an Anionic Polythiophene Derivative

Materials. All chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Aladdin, and Beijing chem. Reagents Co. (Beijing, China) and were used as received. Water-soluble polythiophene derivative, PMTEMA, was synthesized and purified with reference to the previously report.[S1]

Sample preparation. As a typical procedure, the stock solution of PMTEMA, proteins and enzyme were prepared in pure water and mixed directly to give a mixture with the desired concentration of each component in 20 mM phosphate buffer (pH = 8.5). The sample was measured by UV-visible/fluorescence spectrometer immediately. Control experiments for addressing the selectivity of the sensor toward protaimne were carried out under the identical conditions. For serum samples preparation, fetal bovine serum (FBS) was diluted 10-fold with PBS and the following procedures were similar to those conducted in buffer solution stated above.

Measurements. Absorption and emission spectra were collected by using a HITACHI U-3900 UV-VIS spectrophotometer and a HORIBA Scientific Fluorolog®-3 spectrofluorometer, respectively. ^{1}H-NMR spectra were carried out on a Bruker DPX300 spectrometer. The photographs of the sensing solution color change were taken using a camera (Nikon).

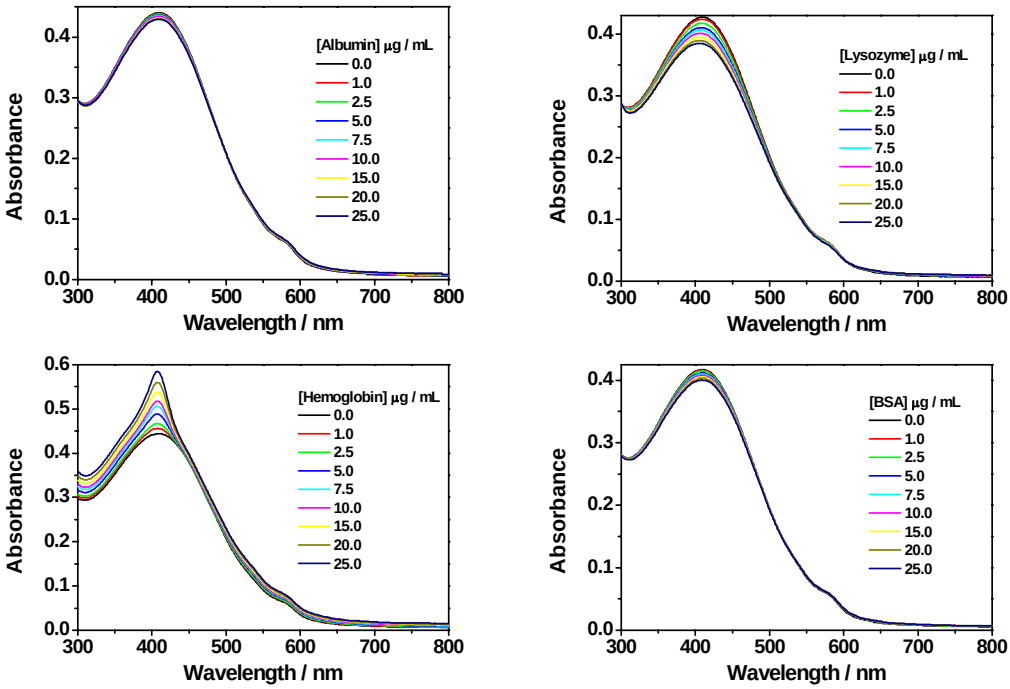

Fig. S1 Absorption spectra of PMTEMA (1.0×10^{-4} M) responding to different concentrations of proteins in 20 mM phosphate buffer (pH 8.5) as indicated.

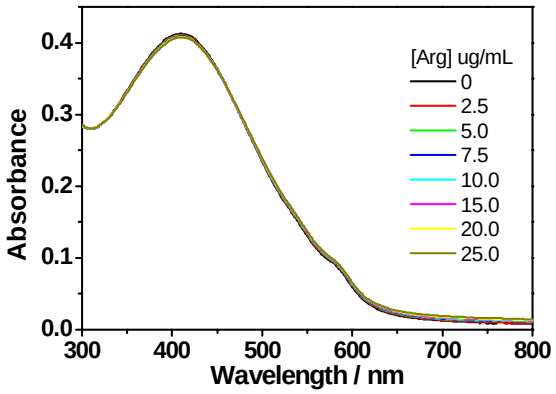

Fig. S2 Absorption spectra of the PMTEMA (1.0×10^{-4} M) in the presence of increasing amounts of arginine in 20 mM phosphate buffer (pH 8.5).

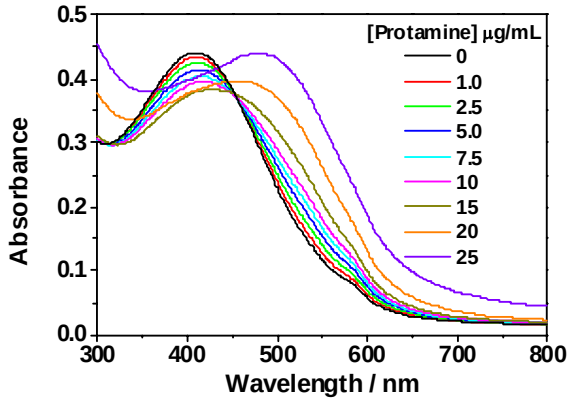

Fig. S3 Absorption spectra of the PMTEMA (1.0×10^{-4} M) in the presence of increasing amounts of protaimne in 10 mM PBS.

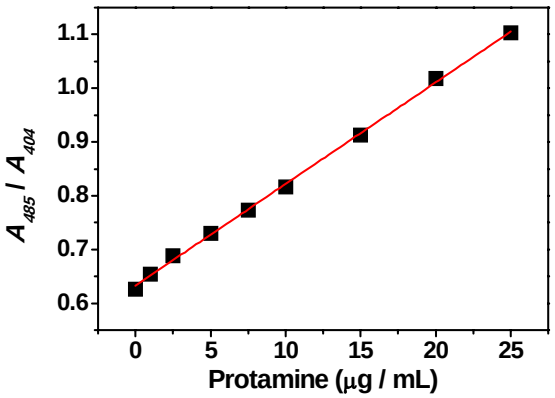

Fig. S4 The relationship between (A_{485}/A_{404}) and the concentration of protamine from 1.0 to 25 μg/mL in PBS. [PMTEMA] = 1.0×10^{-4} M.

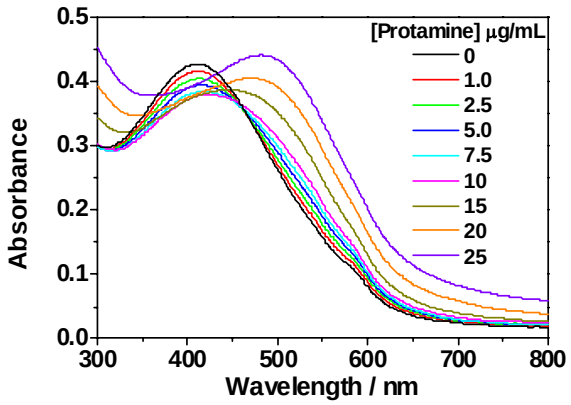

Fig. S5 Absorption spectra of the PMTEMA (1.0×10^{-4} M) in the presence of increasing amounts of protaimne in diluted FBS.

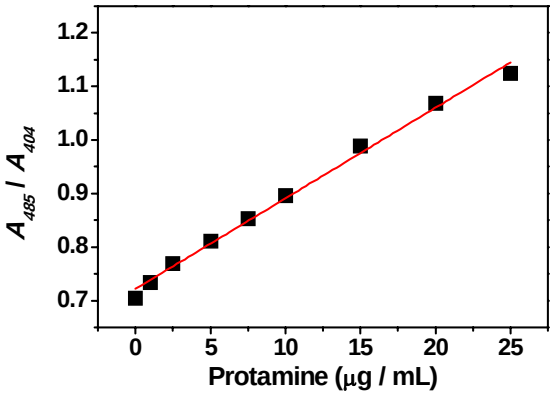

Fig. S6 The relationship between (A_{485}/A_{404}) and the concentration of protamine from 1.0 to 25 μg/mL in diluted FBS. [PMTEMA] = 1.0×10^{-4} M.

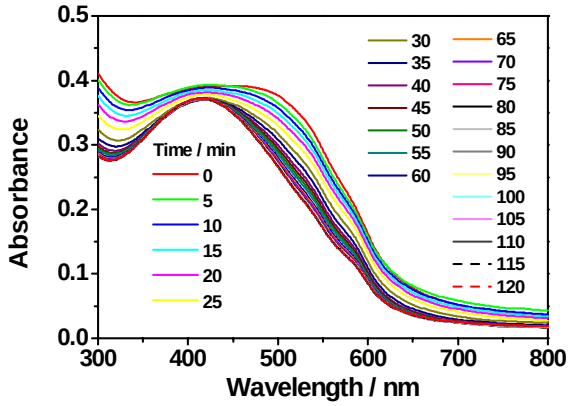

Fig. S7 Time-dependent absorption spectra of the PMTEMA-protamine in the presence of trypsin (8.0 μg/mL) in PBS. [PMTEMA] = 1.0×10^{-4} M, [protamine] = 20 μg/mL.

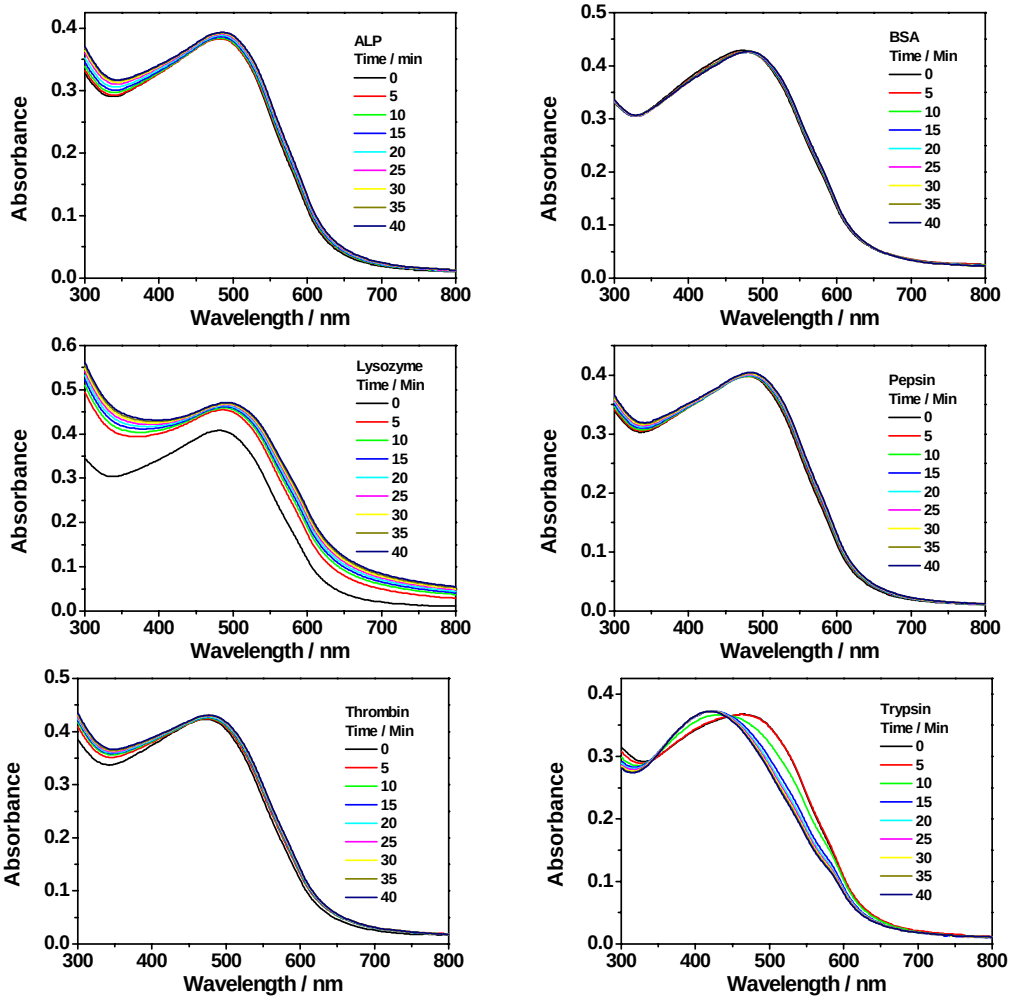

Fig. S8 Time-dependent absorption spectra of PMTEMA-protamine responding to different enzymes in 20mM phosphate buffer (pH = 8.5) as indicated. [PMTEMA] = 1.0×10^{-4} M, [protamine] = 25 μg/mL, [ALP] = 0.1 U/mL, [trypsin] = [BSA] = [lysozmye] = [pepsin] = 6.4 μg/mL, [thrombin] = 1.0 U/mL.

REFERENCE:

S1 Z. Y. Yao, X. P. Hu, B. H. Huang, L. Zhang, L. Liu, Y. L. Zhao and H.-C. Wu, *ACS Appl. Mater. Interfaces* 2013, **5**, 5783.