Supplementary material

Self-assembly of Flavin Mononucleotide and Cationic Polythiophene in Aqueous Media: Spectroscopic Studies and Sensing Applications

Li Zhang [a], Shuanghong Li [a], Yanan Sun [a], Keren Xiao [a], Gang Song [b], Pingan Lu [c], Shutao Yin [a], Kunlun Huang [a], and Zhiyi Yao [a] *

[a] College of Food Science and Nutritional Engineering, China Agricultural University and Key Laboratory of Safety Assessment of Genetically Modified Organism (Food Safety), Ministry of Agriculture, Beijing 100083, China

[b] Guangdong Provincial Key Laboratory of Radionuclides Pollution Control and Resources, Guangzhou University, Guangzhou 510006, P. R. China

[c] College of Health and Environment, Beijing Union University

***Corresponding author:** E-mail: yaozy@cau.edu.cn. Tel: +86-10-62737055; Fax: +86-10-62737055

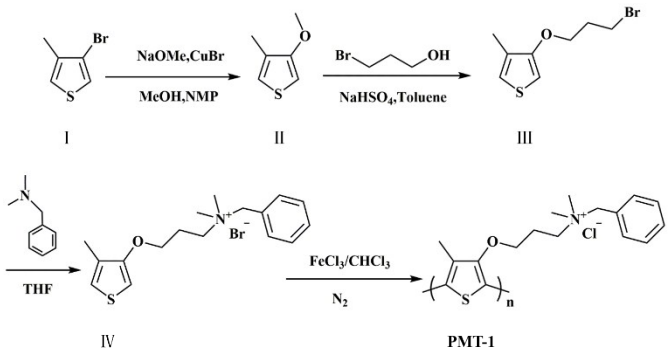

Fig. S1. Synthesis route of PMT-1

Compound Ⅱ and Ⅲ were synthesized and purified as reported previously [1]

3-(4-Methyl-3'-thienyloxy) propyl dimethyl benzylamine bromide (Ⅳ). Mixing 3-(3-Bromo) propoxy-4-methylthiophene (200mg, 0.852mmol) and N, N-Dimethyl benzylamine (12mL) in a sealed tube and the mixture were heated at 50 °C for 48 hours. After the reaction is completed, the mixture is transferred to a rotary flask for rotary treatment to remove unreacted reactants. The obtained mixture was dissolved in a small amount of methanol, followed by addition of a large amount of diethyl ether and centrifugation to obtain a white precipitate, which was collected 112 mg (36%) as product. ^{1}H NMR (D_2O, 300 MHz) δ7.47(5H, m), 6.93(1H, d, J = 3.0 Hz), 6.40(1H, d, J = 3.0 Hz), 4.42(2H, s), 4.07(2H, t, J = 5.7 Hz), 3.31(2H, m,), 2.99(6H, s), 2.26(2H, m), 1.93(3H, s). ^{13}C NMR (D_2O, 300MHz) δ154.31(s), 132.49(s), 128.95(s), 128.84(s), 126.74(s), 120.54(s), 98.10(s), 67.57(s), 66.38(s), 60.72(s), 49.85(s), 49.80(s), 49.75(s), 48.63(s), 21.94(s), 11.55(s). Exact mass calcd for $[M\text{-}Br]^+$: 290.1573. Found: 290.1582.

Polymer PMT-1. 100 mg (0.27 mmol) of Ⅳ and 175 mg (1.08 mmol) of anhydrous $FeCl_3$ were added in 25 mL dry $CHCl_3$, and the mixture was stirred for 24h at 30 °C

under N_2 atmosphere in a Shrek tube. After the reaction is completed, the mixture was washed three times with methanol. Then, a large amount of methanol and a small amount of hydrazine were added to the obtained mixture to be overnight. The mixture after overnight is centrifuged, and obtain a methanol solution of the product, which is subjected to rotary distillation to obtain pure product PMT-1 (28.4mg, 28.4%).

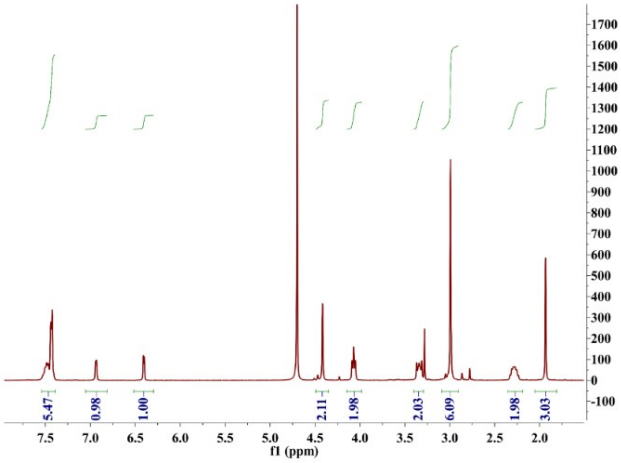

Fig. S2. ^{1}H NMR spectrum of Ⅳ

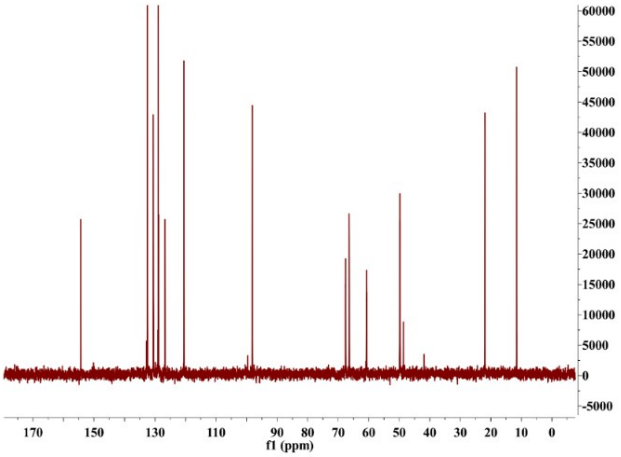

Fig. S3. ^{13}C NMR spectrum of Ⅳ

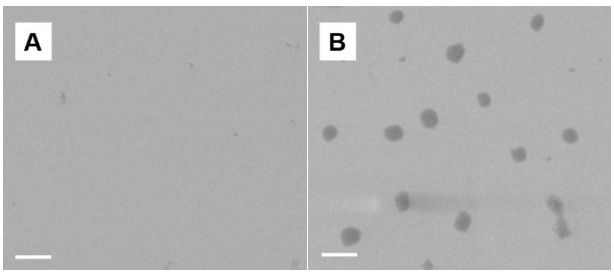

Fig. S4. SEM images of the PMT-1 (A) and PMT-1/FMN (B) complex. Scale bar: 2μm

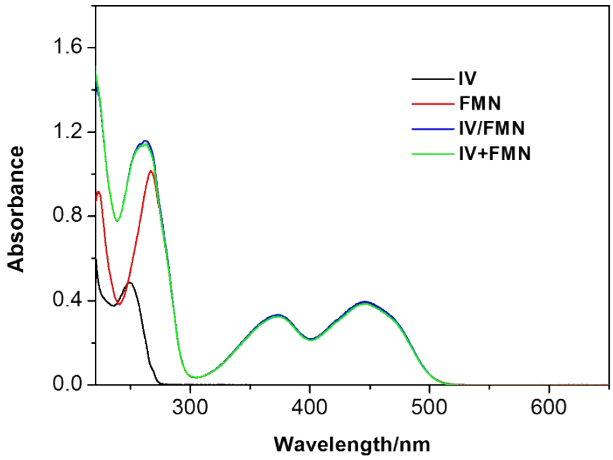

Fig. S5. Absorption spectra of comound IV, FMN, IV/FMN and superposition of IV and FMN (IV+FMN) in HEPES buffer (1mM, pH = 7.4) [IV] = 0.1 mM, [FMN] = 30μM

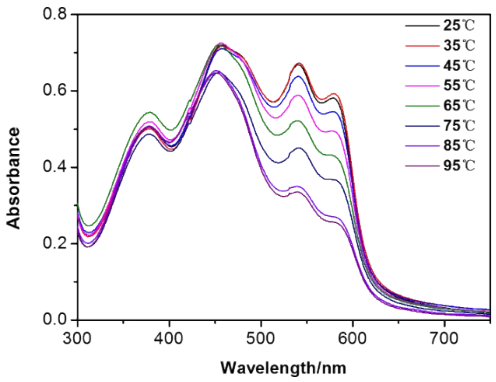

Fig. S6. Absorption spectra of PMT-1 (0.1mM) in the presence of FMN (30 μM) in HEPES buffer (1mM, pH = 7.4) with different temperatures

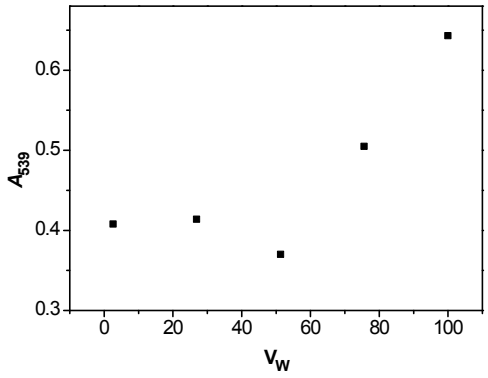

Fig. S7. Solvent composition dependence of the absorbance at 539 nm of PMT-1/FMN in the water/methanol mixed solvents. [PMT-1] = 0.1 mM; [FMN] = 30 μM

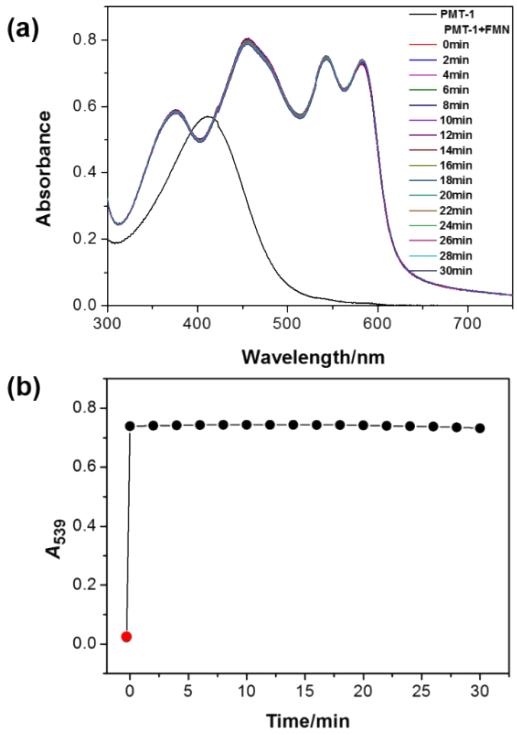

Fig. S8. Absorption spectra (a) and the change of value at 539nm (b) of PMT-1 (0.1mM) and FMN (42μM) over time

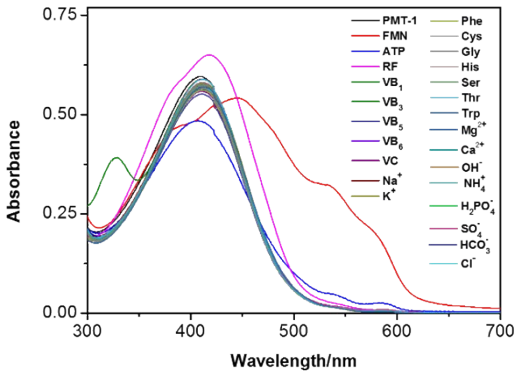

Fig. S9. Absorption spectra of PMT-1 (0.1mM) in the absence and presence of various analytes in HEPES buffer (1mM, pH = 7.4) as indicated. [FMN] = [analytes] = 10μM

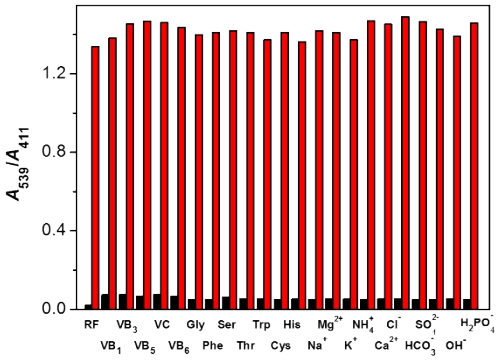

Fig. S10. The relative absorbance of PMT-1/interference in the absence (black bars) and presence (red bars) of FMN in HEPES buffer (1mM pH = 7.4). [PMT-1] =0.1 mM, [FMN] = [interferences] = 30μM

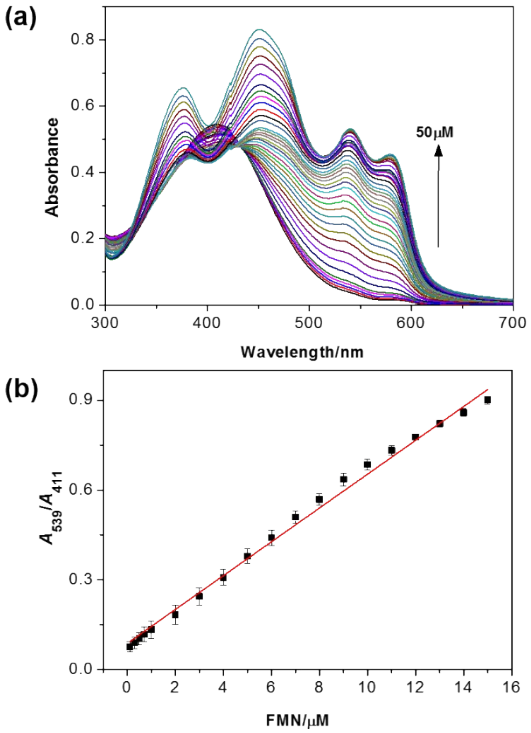

Fig. S11. (a) Absorption spectra of PMT-1 (0.1mM) upon addition of increasing concentration of FMN in HEPES (1mM pH 7.4) containing 10% FBS. (b) Linear relationship of PMT-1 (0.1mM) with different concentrations of FMN in HEPES (1mM pH 7.4) containing 10% FBS

REFERENCES

1 Z. Yao, B. Huang, X. Hu, L. Zhang, D. Li, M. Guo, X. Zhang, H. Yuan, H. Wu, Colorimetric detection of copper ions based on a supramolecular complex of water-soluble polythiophene and ATP. *Analyst* 2013, **138**, 1649-1652.