Electronic Supplementary Material (ESI) for Analyst.

Electronic Supplementary Materials

A Novel Water-Soluble Sulfonated Porphyrin Fluorescence Sensor for Sensitive Assays of H_2O_2 and Glucose

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1. Synthesis of H_2TEHPPS

1.1 Synthesis of *meso*-Tetrakis-(3-ethoxy-4-hydroxy) phenyl Porphyrin (H_2TEHPPy)

A mixture of 3-ethoxy-4-hydroxy-benzaldehyde (6 g, 36.1 mmol) and propionic acid (100 mL) was heated to 110 ℃ with stirring. Pyrrole (2.5 mL, 36.1 mmol) was successively and slowly added in the mixture and the resulting mixture was refluxed for 1.5 h. After the mixture was cooled to 50 ℃, methanol (100 mL) was added to it and the mixture stood overnight at 0 ℃. The mixture was filtered and washed with methanol until the methanol washing was colorless. The resulting purple solid was dried to give crude H_2TEHPPy and the residue was purified by LC eluted with methanol to obtain pure H_2TEHPPy (1.7 g). Yield 22 %. IR (KBr), ῡ/cm^{-1}: 3500, 3440, 3321, 3069, 3042, 2977, 2933, 2896, 1604, 1558, 1505, 1470, 1343, 1253, 1228, 1037, 977, 891, 864, 795, 715, 616. MS, *m/z* 855.15 $[M+H]^+$. ^{1}H NMR($CDCl_3$), δ:-2.78 (2H, NH), 1.49-1.59 (12H, CH_3), 4.2-4.26 (8H, OCH_2), 6.0-6.05 (4H, OH), 7.28-7.33 (4H, Ar2H), 7.68-7.70, (4H, Ar5H), 7.72-7.74 (4H, Ar6H), 8.89-8.91 (8H, Pyrrol).

1.2 Synthesis of *meso*-Tetrakis-(3-ethoxy-4- methoxymethoxy)phenyl Porphyrin (H_2TEMOMPPy)

Anhydrous K_2CO_3 (0.48 g, 3.47 mmol) was added in a solution of H_2TEHPPy (0.3 g, 0.35 mmol) containing DMF(30 mL) and chloromethyl methyl ether (0.1 mL, 1.4 mmol) was added in dropwise. The mixture was heated to 40 ℃ and allowed to react overnight. Water was poured and the mixture was extracted by acetidine. Then acetidine was evaporated under reduced pressure and the residue was dried at 100 ℃ for 3 h. The crude product was further purified by column chromatography [silica gel, V(CH_2Cl_2)/V(Methanol) = 200:1]. Yield 89 %. IR (KBr), ῡ/cm^{-1}: 3316, 3123, 3046, 2976, 2924, 2895, 2850, 2823, 1600, 1579, 1505, 1470, 1257, 1226, 1153, 1130, 1077, 1040, 979, 891, 865, 801, 740, 615. MS: *m/z* 1031 $[M+H]^+$. ^{1}H NMR(DMSO), δ:-2.90 (2H, NH), 1.39-1.42 (12H, CH_3), 3.62 (12H, OCH_3), 4.18-4.18 (8H, OCH_2), 5.47 (8H, O-CH_2-O), 7.87-7.50, (12H, ArH), 8.91 (8H, Pyrrol).

1.3 Synthesis of *meso*-Tetra (3-ethoxy-4-hydroxy -5-sulfonate)phenyl Porphyrin (H_2TEHPPS)

Chlorosulfonic acid (80.4 mmol, 0.55 mL) was added dropwise $CHCl_3$ (7 mL) containing H_2TEMOMPPy (0.3 g, 0.29 mmol). Then the mixture reacted at room temperature for 30 min. The resulting solution was poured into an ice-water mixture, then filtered through a sintered frit and the green precipitate was collected, washed several times with water and dried to give H_2TEHPPS (0.27 g). Yield 80 %. IR (KBr), ῡ/cm^{-1}: 3600-3300, 3125, 2957, 2925, 2875, 2850, 1606, 1585, 1508, 1470, 1347, 1251, 1231, 1171, 1101, 1068, 1017, 967, 844, 799, 732, 597, 530. ^{1}H NMR(DMSO), δ:-0.580 (2H, N-H), 1.055-1.577 (12H, CH_3), 4.160-4.488 (8H, OCH_2), 5.288 (4H, ArOH), 7.733-8.310 (8H, ArH), 8.613-8.722 (8H, Pyrrol), 11.361 (4H, SO_3H).

2. Life time of H_2TEHPPS

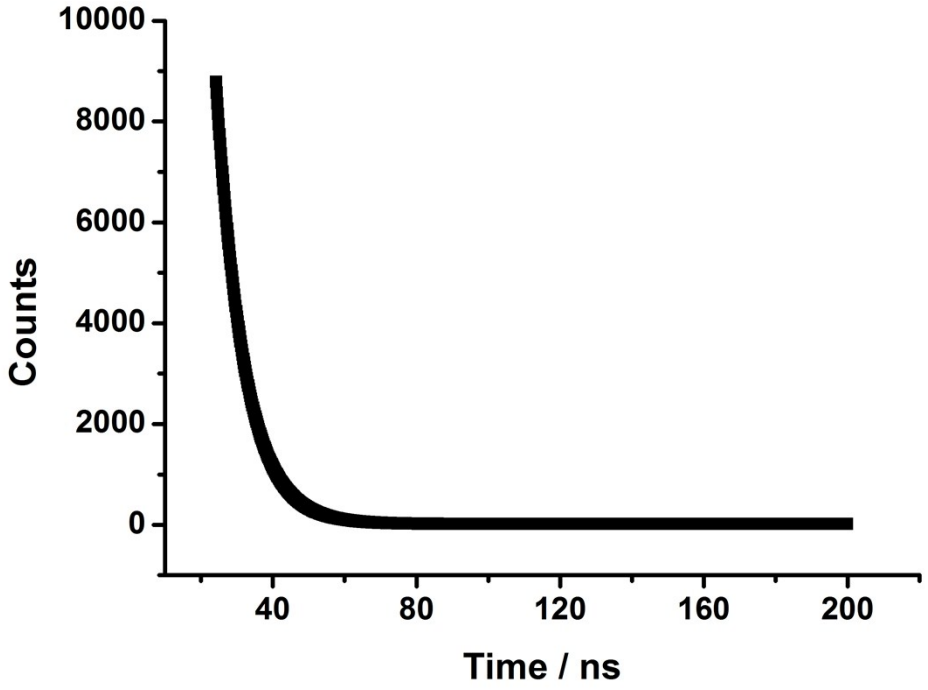

Figure S1. Fluorescence decay curves for H2TEHPPS

(excitation at 419 nm, emission at 646 nm)

3. Fluorescence quenching of H_2TEHPPS upon Fe^{3+}

From the quenching fluorescence emission spectra, a good linear relationship of F_0/F versus [Fe^{3+}] was obtained with a correlation coefficient of 0.9980 (R^2 = 0.9960) in a range of 0 – 20 μM.

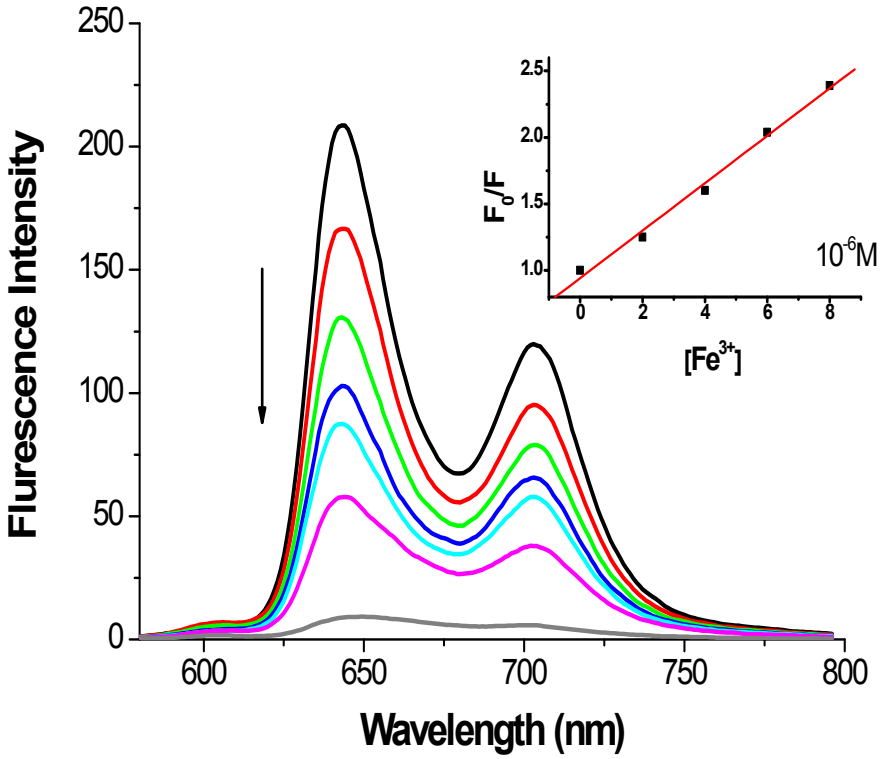

Figure S2. Fluorescence quenching upon adding Fe^{3+} to a solution of H_2TEHPPS (10 □M); From top to bottom, the concentrations of Fe^{3+} are 0, 2, 4, 6, 8, 10 and 20 μM, respectively.

4. Influence of common ions to the fluorescence of H_2TEHPPS.

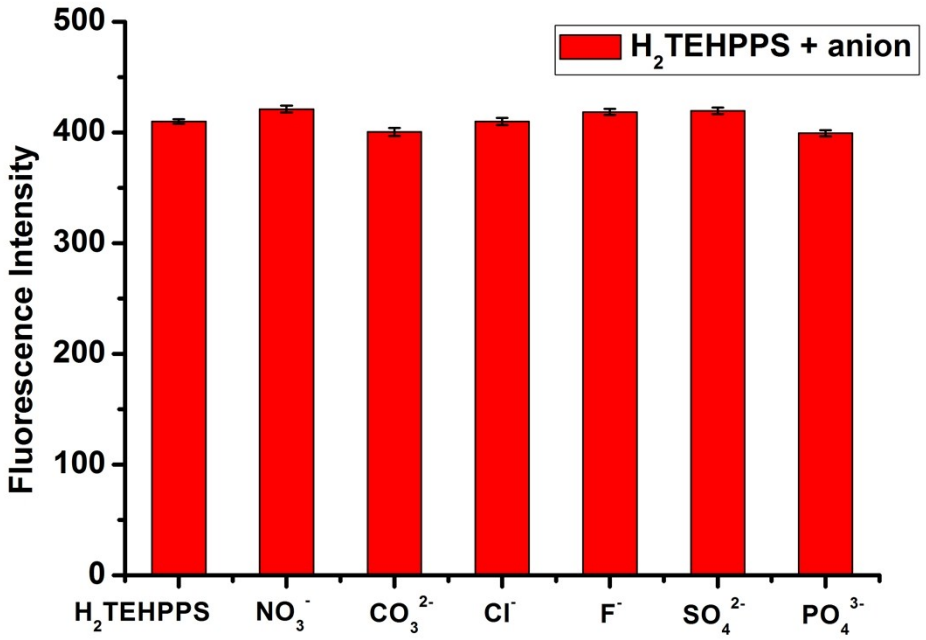

Figure S3. Influence of common anions to the fluorescence of H_2TEHPPS. Excitation wavelength 419 nm; emission wavelength 646 nm

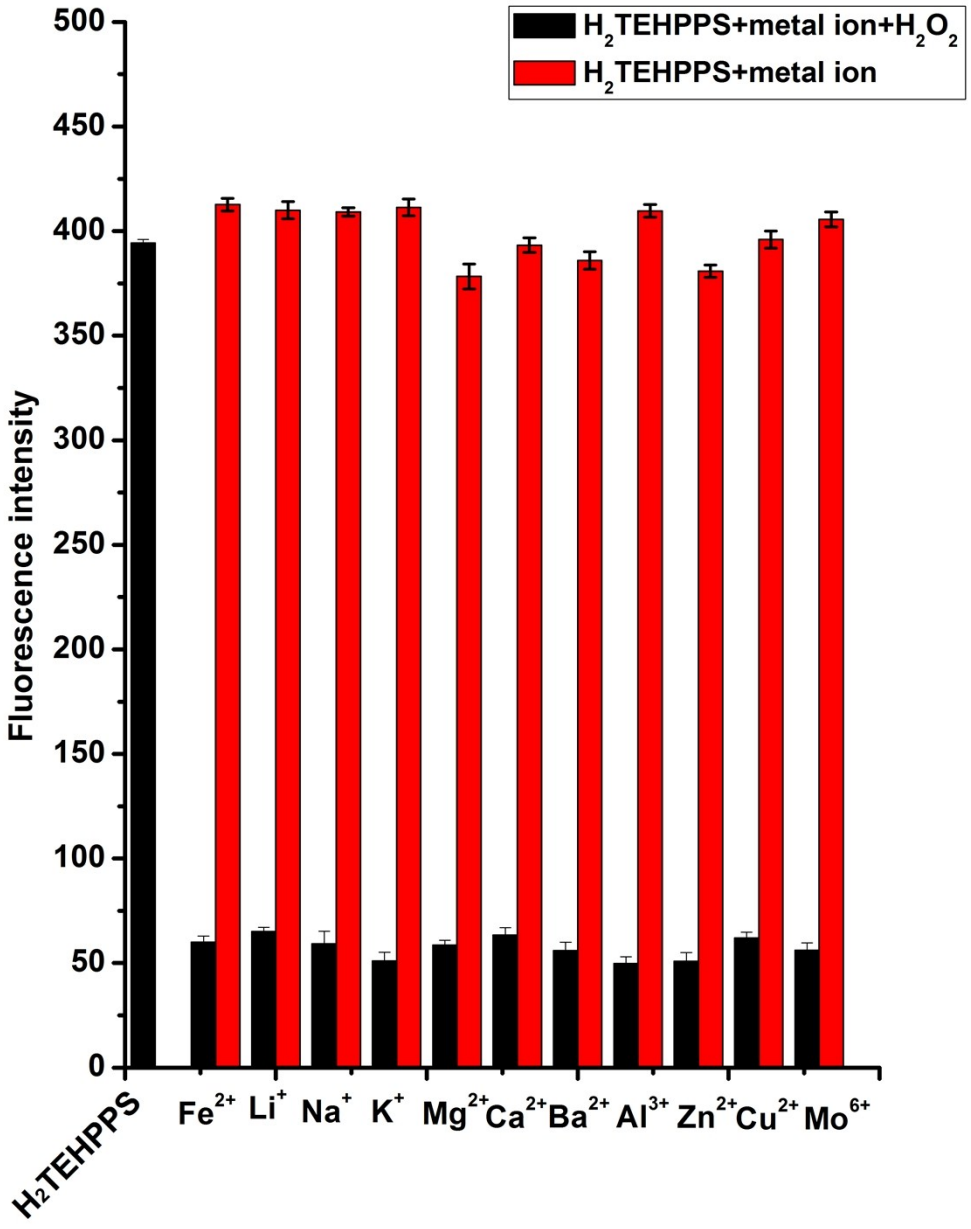

Figure S4. Influence of common cations to the fluorescence of H_2TEHPPS. Excitation wavelength 419 nm; emission wavelength 646 nm