Electronic Supplementary Materials

A Novel Water-Soluble Sulfonated Porphyrin Fluorescence Sensor for Sensitive Assays of H$_2$O$_2$ and Glucose

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1. Synthesis of H$_2$TEHPPS

1.1 Synthesis of *meso*-Tetrakis-(3-ethoxy-4-hydroxy) phenyl Porphyrin (H$_2$TEHPPy)

A mixture of 3-ethoxy-4-hydroxy-benzaldehyde (6 g, 36.1 mmol) and propionic acid (100 mL) was heated to 110 °C 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 °C, methanol (100 mL) was added to it and the mixture stood overnight at 0 °C. The mixture was filtered and washed with methanol until the methanol washing was colorless. The resulting purple solid was dried to give crude H$_2$TEHPPy and the residue was purified by LC eluted with methanol to obtain pure H$_2$TEHPPy (1.7 g). Yield 22 %. IR (KBr), $\tilde{\nu}$/cm$^{-1}$: 3500, 3440, 3321, 3069, 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$_3$), $\delta$: -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, Ar$_2$H), 7.68-7.70, (4H, Ar$_5$H), 7.72-7.74 (4H, Ar$_6$H), 8.89-8.91 (8H, Pyrrol).

1.2 Synthesis of *meso*-Tetrakis-(3-ethoxy-4-methoxymethoxy)phenyl Porphyrin (H$_2$TEMOMPPy)

Anhydrous K$_2$CO$_3$ (0.48 g, 3.47 mmol) was added in a solution of H$_2$TEHPPy (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 °C 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 °C for 3 h. The crude product was further purified by column chromatography [silica gel, $V$(CH$_2$Cl$_2$)/$V$(Methanol) = 200:1]. Yield 89 %. IR (KBr), $\tilde{\nu}$/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), $\delta$: -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$_2$TEHPPPS)

A mixture of 3-ethoxy-4-hydroxy-benzaldehyde (6 g, 36.1 mmol) and propionic acid (100 mL) was heated to 110 °C 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 °C, methanol (100 mL) was added to it and the mixture stood overnight at 0 °C. The mixture was filtered and washed with methanol until the methanol washing was colorless. The resulting purple solid was dried to give crude H$_2$TEHPPy and the residue was purified by LC eluted with methanol to obtain pure H$_2$TEHPPy (1.7 g). Yield 22 %. IR (KBr), $\tilde{\nu}$/cm$^{-1}$: 3500, 3440, 3321, 3069, 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$_3$), $\delta$: -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, Ar$_2$H), 7.68-7.70, (4H, Ar$_5$H), 7.72-7.74 (4H, Ar$_6$H), 8.89-8.91 (8H, Pyrrol).

1.2 Synthesis of *meso*-Tetrakis-(3-ethoxy-4-methoxymethoxy)phenyl Porphyrin (H$_2$TEMOMPPy)

Anhydrous K$_2$CO$_3$ (0.48 g, 3.47 mmol) was added in a solution of H$_2$TEHPPy (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 °C 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 °C for 3 h. The crude product was further purified by column chromatography [silica gel, $V$(CH$_2$Cl$_2$)/$V$(Methanol) = 200:1]. Yield 89 %. IR (KBr), $\tilde{\nu}$/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), $\delta$: -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$_2$TEHPPPS)

1. Synthesis of H$_2$TEHPPS

1.1 Synthesis of *meso*-Tetrakis-(3-ethoxy-4-hydroxy) phenyl Porphyrin (H$_2$TEHPPy)
Chlorosulfonic acid (80.4 mmol, 0.55 mL) was added dropwise CHCl₃ (7 mL) containing H₂TEMOMPPy (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 H₂TEHPPS (0.27 g). Yield 80 %. IR (KBr), δ/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. ¹H NMR(DMSO), δ: -0.580 (2H, N-H), 1.055-1.577 (12H, CH₃), 4.160-4.488 (8H, OCH₂), 5.288 (4H, ArOH), 7.733-8.310 (8H, ArH), 8.613-8.722 (8H, Pyrrol), 11.361 (4H, SO₃H).
2. Life time of H$_2$TEHPPS

Figure S1. Fluorescence decay curves for H$_2$TEHPPS
(excitation at 419 nm, emission at 646 nm)

3. Fluorescence quenching of H$_2$TEHPPS 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$_2$TEHPPS (10 μM); 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$_2$TEHPPS.

**Figure S3.** Influence of common anions to the fluorescence of H$_2$TEHPPS. Excitation wavelength 419 nm; emission wavelength 646 nm
Figure S4. Influence of common cations to the fluorescence of $\text{H}_2\text{TEHPPS}$. 

Excitation wavelength 419 nm; emission wavelength 646 nm