Supporting Information for

*m*-Benziporphodimethene—an New Porphyrin Analogue Fluorescence

Zinc(II) Sensor

Chen-Hsiung Hung*, Gao-Fong Chang*, Anil Kumar*, Geng-Fong Lin, Li-Yang Luo*, , Wei-Min Ching*, and Eric Wei-Guang Diau*

*a* Institute of Chemistry, Academia Sinica, Nankang, Taipei 105 Taiwan. Fax: 886-2-27831237. E-mail: chhung@chem.sinica.edu.tw

*b* Department of Chemistry, Tamkang University, Tamsui, Taipei 251 Taiwan

*c* The Department of Applied Chemistry, National Chiao Tung University, Hsinchu, 300 Taiwan
**Synthesis of 1:** A solution of α, α'-dihydroxy-1, 3-diisopropylbenzene (98 mg, 0.50 mmol), benzaldehyde (102 μL, 1.01 mmol) and pyrrole (104 μL, 1.51 mmol) in CH₂Cl₂ (150 mL) was treated with BF₃·OEt₂ (13 μL, 0.10 mmol) and stirred at 27 °C. Two hours later, DDQ (374 mg, 1.65 mmol) was added into the reaction mixture, and stirring was continued for two hours under 27 °C. The reaction was quenched with triethylamine (10 drops) and then the solvent was removed in vacuum. The crude mixture was dissolved in minimum amount of CH₂Cl₂ and was purified by chromatography [SiO₂ (400 mL), eluted by CH₂Cl₂] to give 1 (72 mg, 0.136 mmole) [Rf = 0.11, CH₂Cl₂] in 27 % yield as a red powder.

**1H NMR (400MHz, CDCl₃, 298K):** δ = 1.75 (s, 12H; meso-CH₃), 6.19 (s, 2H; 13,14-H), 6.83 (ab quartet, 3J(H,H) = 4.54, 4H; 8,9,18,19-H), 7.29-7.48 (m, 13H; 2,3,4-H and meso-phenyl), 8.00 (s, 1H; 22-H), 12.46 (s, 1H; NH);

**13C NMR (400 MHz, CDCl₃, 298K):** δ = 29.17, 42.33, 121.50, 123.32, 125.12, 127.45, 127.78, 128.54, 129.06, 131.94, 136.83, 138.27, 138.46, 139.05, 147.38, 152.15, 182.20;

**UV-Vis (CH₃CN) [λmax/nm (log ε)]:** 349 (4.56), 514 (4.28), 542 (4.31); Anal. Found (calc for C₃₈H₃₃N₃·0.5C₆H₁₄): C 84.08 (85.67); H 7.32 (7.01); N 7.31 (7.31); HR-FAB-MS (m/z): calcd. [MH]+ = 532.2752 obs. [MH]+ =532.2745

**Synthesis of Zn•1:** Anhydrous zinc chloride (51.3 mg, 0.376 mmol) was dissolved in CH₃CN, added into a solution of 1 (10 mg, 0.0188 mmol) in 30 mL CH₂Cl₂/CH₃CN (1:2), and added 1 drop of 2,6-lutidine into the solution. After two minutes of stirring, the solvent was removed under reduced pressure. Dried residue was dissolved in CH₂Cl₂ and excess zinc salt was extracted using distilled water. The organic layer was collected and solvent was removed in vacuo, and the dried product was dissolved in hexane. Slow evaporation of hexane yielded crystalline form of Zn•1 (9.1 mg, 77 %). 

**1H NMR (400 MHz, Acetone-d₆, 298 K):** δ = 1.97 (s, 6H; meso-CH₃), 2.14 (s, 6H; meso-CH₃), 6.05 (s, 2H; 13,14-H), 6.76 (d, 3J(H,H) = 4.70, 2H; 9,18-H), 6.98 (d, 3J(H,H) = 4.70, 2H; 8,19-H), 7.31-7.53 (m, 13H; 2, 3, 4-H, meso-phenyl), 8.69 (s, 1H; 22-H); UV-Vis (CH₃CN) [λmax/nm (log ε)]: 350 (4.58), 593 (4.29), 639 (4.56); Anal. Found (calc for C₃₈H₃₃N₃ZnCl): C 71.38 (72.48); H 5.57 (5.13); N 5.85 (6.68); HR-FAB-MS (m/z): calcd. [M-Cl]+ = 594.1888; obs. 594.1880.
Supporting Figure 1. The ORTEP diagram of 1 in 30% probabilities of ellipsoids.
Supporting Figure 2. Job plot for the reaction of 1 with Zn$^{2+}$ ion. Equimolar solutions ($3.75 \times 10^{-5}$ M) of 1 and Zn$^{2+}$ (from ZnCl$_2$) in CH$_3$CN were prepared. To obtain the plot, 1 and Zn$^{2+}$ solutions were mixed in various volume ratios (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1). Neat 2,6-lutidine was added to each volume ratio to give a 0.014 M final concentration of 2,6-lutidine.
Supporting Figure 3. The fluorescence intensity changes when 1 (2 x 10^-5 M) was treated with 0.1 equiv. of Zn^{2+} and then 0.1 equiv. of HCl.
Supporting Figure 4. The fluorescence intensity changes when 1 (1 x 10⁻⁵ M) was treated with 5 equiv. of Zn²⁺ and increasing amount of HCl.