

## Supporting Information

### Electrochemical Discrimination of Phthalic Acid among Three Phthalic Acid Isomers Based on an *N*-Butylaminomethyl-Ferrocene Derivative

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## Experimental Section

**Chemicals and materials.** 1,1'-Diformylferrocene, 1-butylamine, NaBH<sub>4</sub>, and Boc<sub>2</sub>O were purchased from Aldrich Co. (USA) and used as received. Ferrocene, anhydrous dimethyl sulfoxide (DMSO), acetonitrile, phthalic acid, isophthalic acid, terephthalic acid, 2-hydroxybenzoic acid, 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU), tetrabutylammonium perchlorate (TBAP), and silver nitrate were purchased from Sigma-Aldrich, Inc. (USA).

**Synthesis of compound 1.** A solution of 1,1'-diformylferrocene (100 mg) and 1-butylamine (138 mg, 2.2 equiv.) in dry CH<sub>3</sub>OH (20 mL) was stirred at room temperature for 12 h. NaBH<sub>4</sub> (52 mg, 0.65 equiv.) was added to this solution at 0 °C and then stirred for 1 h. After the solvent was removed under vacuum, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified using column chromatography on silica gel (elution with CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH-NH<sub>4</sub>OH 10:0.5:0.2) to give 97 mg of **1** as a gummy solid. Yield: 63%. TLC R<sub>f</sub> 0.15 (CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH-NH<sub>4</sub>OH 10:1:0.2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) □ 0.84 (t, *J* = 7.3 Hz, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 1.26 (m, 4H, -CH<sub>2</sub>), 1.42 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.56 (t, *J* = 7.3 Hz, 4H, -CH<sub>2</sub>NH), 3.45 (s, 2H, -NH), 4.00 (t, *J* = 6.8 Hz, 4H, NHCH<sub>2</sub>Fc), 4.00 (d, *J* = 1.8 Hz, 4H, FcH), 4.08 (d, *J* = 1.8 Hz, 4H, FcH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 14.4 (2C), 20.9 (2C), 32.3 (2C), 49.2 (1C), 49.6 (1C), 68.7 (4C), 69.4 (4C), 86.9 (2C); HR-FAB mass Calcd for (C<sub>20</sub>H<sub>33</sub>N<sub>2</sub>Fe)<sup>+</sup>: *m/z* 357.1993, Found: *m/z* 357.1996 (M+H)<sup>+</sup>.

**Synthesis of compound 2.** A mixture of **1** (52 mg, 0.22 mmol) and Boc<sub>2</sub>O (157 mg 0.72 mmol) in MeOH (10 mL) was stirred at room temperature for 12 h. After the reaction was

completed, the solvent was removed. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated until dry. The residue was purified using silica gel (elution with 20% EtOAc in hexane) to give **2** in 65% yield. TLC R<sub>f</sub> 0.87 (CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH-NH<sub>4</sub>OH 10:1:0.2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.84 (bt, 6H), 1.24 (m, 4H), 1.37 (m, 4H), 1.43 (s, 18H), 3.05 (bt, 4H), 3.99 (bd, 4H, FcH), 4.15 (bd, 4H, FcH), 4.82 (bs, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.4, 20.6, 27.9, 46.3, 46.8, 69.4, 70.6, 71.3, 79.7, 155.5; HR-FAB mass Calcd for (C<sub>30</sub>H<sub>48</sub>O<sub>4</sub>N<sub>2</sub>Fe)<sup>+</sup>: *m/z* 556.2963, Found: *m/z* 556.2968 (M)<sup>+</sup>.

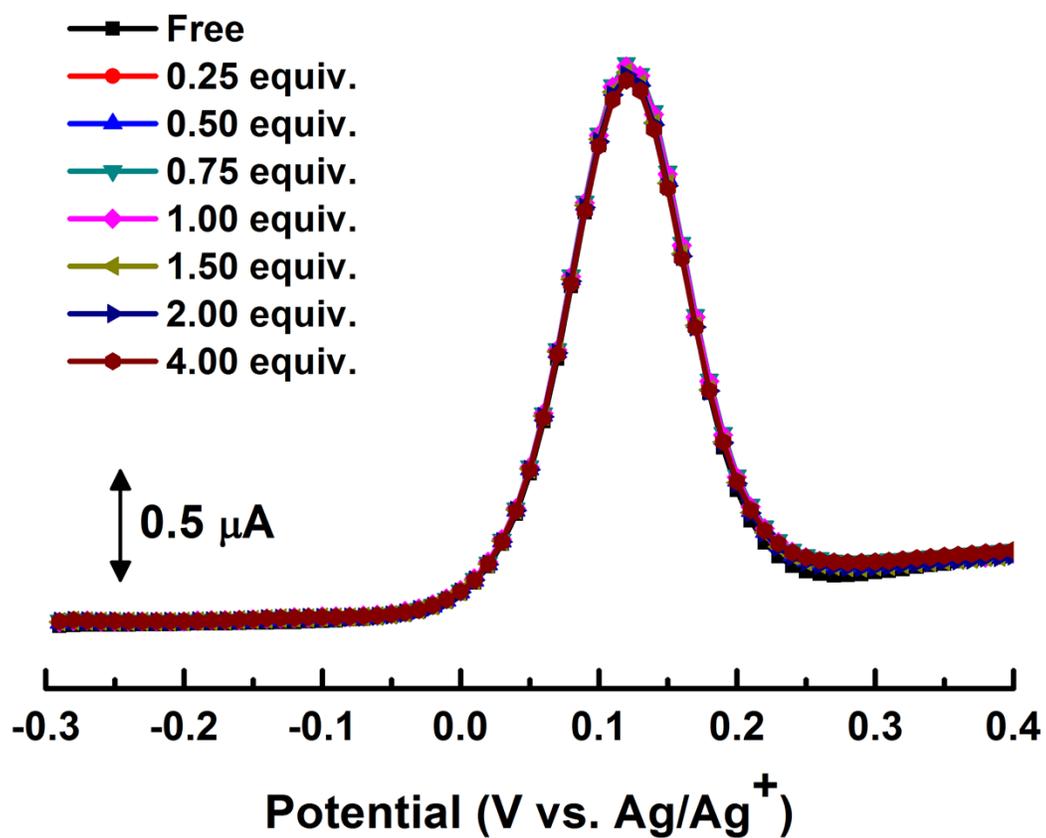
**Electrochemical experiments.** All electrochemical experiments were carried out with an electrochemical analyzer (Model 440, CH Instruments) using a conventional three-electrode cell. The surface of a glassy carbon working electrode was polished with 0.3 μm alumina and then rinsed with deionized water. Residual alumina particles were thoroughly removed by ultrasonication of the working electrode. A Pt wire and an Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub>) electrode were used as a counter and reference electrode, respectively. The experiments were carried out at room temperature in a dry N<sub>2</sub> atmosphere.

**Computational calculations.** The interactions between the compound **1** and phthalic acid isomers were theoretically investigated using Gaussian 09 program.<sup>1</sup> The geometry optimizations and thermodynamic corrections were carried out using the hybrid Becke 3-Lee–Yang–Parr (B3LYP) exchange-correlation functional with the 6-31+G\* basis sets for C, H, N, and O and the LanL2DZ (ECP) basis sets for Fe. For simplicity, the bulk solvent effect was not included in the calculation. In order to obtain the most stable geometries, all possible interaction patterns were optimized. Restrictions on symmetries were not imposed on the initial

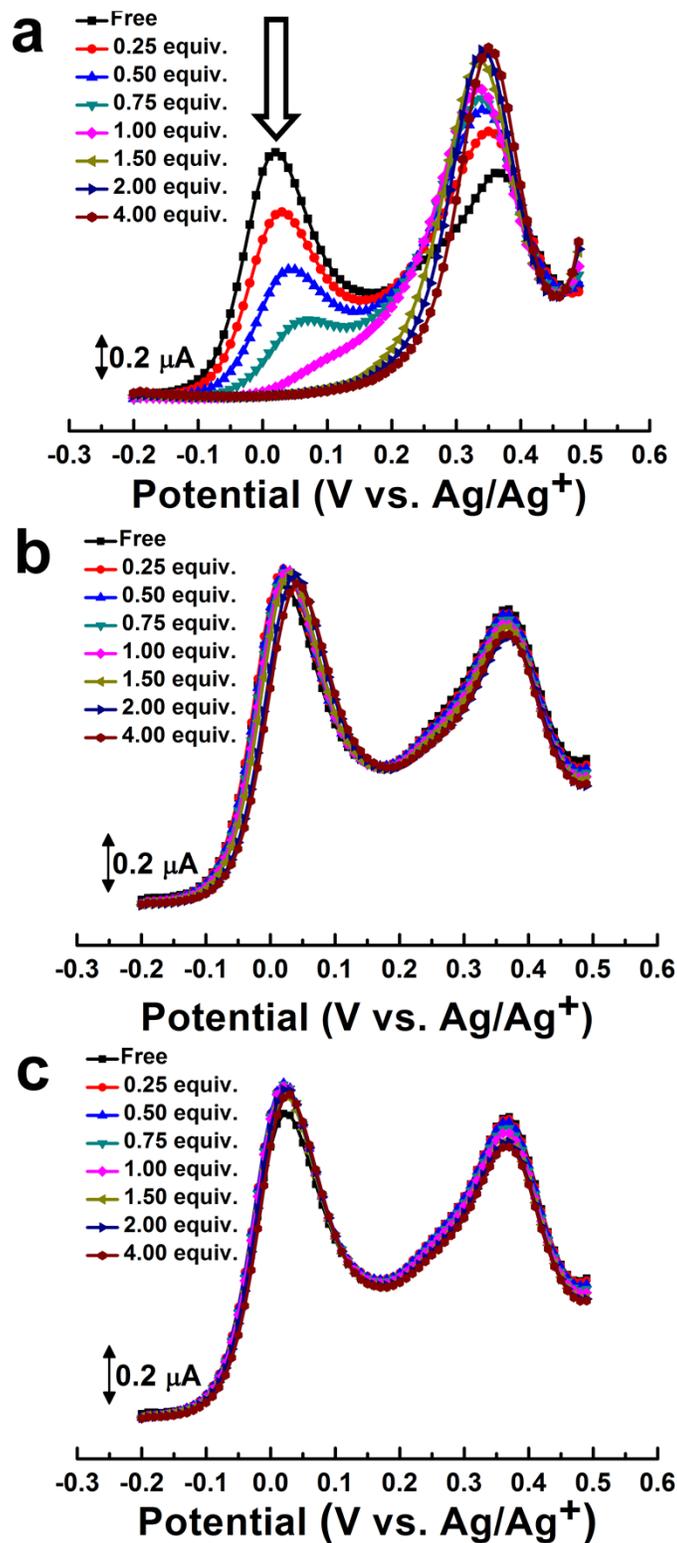
structures. All stationary points were verified as minima through full calculation of the Hessian and a harmonic frequency analysis.

## References

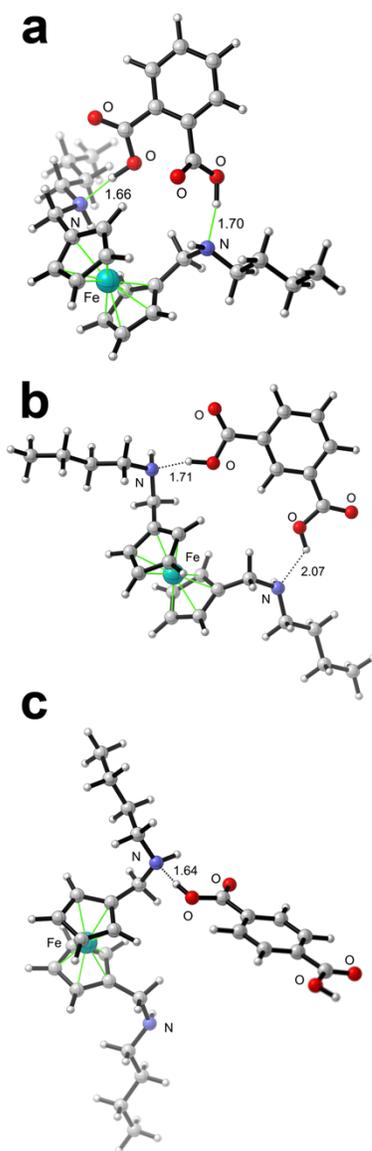
- 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. Gaussian 09, A.1 Revision; Gaussian, Inc., Wallingford, CT, 2009.



**Fig. S1.** DPVs of **2** with 0.00 ~ 4.00 equivalents of phthalic acids in DMSO containing 0.1 M TBAP. Pulse amplitude: 0.05 V.



**Fig. S2.** DPVs of **1** with 0.00 ~ 4.00 equivalents of (a) 2-hydroxybenzoic acids, (b) 3-hydroxybenzoic acids, and (c) 4-hydroxybenzoic acids in DMSO containing 0.1 M TBAP. Pulse amplitude: 0.05 V.



**Fig. S3.** Optimized structures exhibiting the interactions of **1** with (a) phthalic acid, (b) isophthalic acid, and (c) terephthalic acid. The calculated interaction enthalpy ( $\Delta H_{\text{interaction}}$ ) values for **1**-phthalic acid, **1**-isophthalic acid, and **1**-terephthalic acid are -12.1, -3.8, and -2.9 kcal/mol, respectively. Hydrogen bonding distances are given in Å.