Catechol boronate formation and its electrochemical oxidation

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Supporting Information

MATERIALS AND GENERAL METHODS

Reagents and solvents were purchased from various commercial sources and used without further purification unless otherwise stated. Spectroscopic grade MeOH was used in titration experiments. All reactions were carried out in oven- or flame-dried glassware in an inert atmosphere of argon. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates with silica gel 60 F254 or with aluminum oxide 60 F254 neutral. Flash column chromatography was performed using 40-63 μm (230-400 mesh) silica gel or alumina (80-200 mesh, pH 9-10) as the stationary phases. ^{1}H NMR spectra were recorded at 300 MHz. All chemical shifts were reported in δ units relative to tetramethylsilane. $CDCl_3$ was treated with alumina gel prior to use.

Spectrophotometric and fluorimetric tritration experiments were conducted on a Varian Cary 100 Bio UV-Visible Spectrophotometer and a Varian Cary Eclipse Fluorescence Spectrophotometer, respectively, following published procedures (refs. 6 and 9)

The cyclic voltammograms were acquired in MeOH containing $NaNO_3$ (0.15 M) or Bu_4NPF_6 (0.1 M) as supporting electrolyte using a CHI600C Electrochemical Analyzer. The data were collected in a single compartment cell with a glassy carbon working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode at scan rate of 100 mV/s. In controlled-potential bulk electrolysis experiment a Pt gauze electrode instead was used as the working electrode. Approximately 15 mL sample was used with magnetic stirring.

(A) SYNTHESIS

Compound 1. 2-formylphenylboronic acid (FW = 149.94, 150 mg, 1 mmol) and 9-(methylaminomethyl)anthracene (FW = 221.30, 221mg, 1 mmol) were added in dry 1,2-dichloroethane (4 mL) and stirred for 19 h, after which sodium triacetoxyborohydride (FW = 211.94, 424 mg, 2 mmol) was added and allowed to react for 6 h. Brine (4 mL) was added and the reaction mixture was partitioned between DCM and water. Aqueous layer was washed with DCM three times. Organic fractions were combined and dried over Na_2SO_4. After solvent removal the crude product was purified through a short alumina gel plug using 5% MeOH in DCM to afford a pale yellow powder (FW = 355.24, 354 mg, 100%). ^{1}H NMR (300 MHz, CD_3OD, Figure S1) δ 2.47 (s, 3H, CH_3), 4.46 (s, 2H, CH_2), 5.13 (s, 2H, CH_2), 7.28-7.58 (m, 7H, ArH), 7.70-7.73 (d, J = 7.2 Hz, 1H, ArH), 8.10-8.23 (m, 4H, ArH), 8.67 (s, 1H, ArH).

Compound 6. To a solution of 2-hydroxy-4-methoxybenzaldehyde (FW = 152.15, 524 mg, 3.4 mmol), 30% H_2O_2 (0.469 mL, 4.1 mmol), and THF/H_2O (5:1, 15 mL total) NaOH (FW = 40, 165 mg, 4.1 mmol) in H_2O (20 mL) was added at rt. The reaction mixture was placed in an ice bath. After 1 h, HCl (0.01 M) was added until a pH of 3 was reached. The reaction mixture was partitioned between water and Et_2O. The organic layer was collected and washed with aqueous $Na_2S_2O_3$ solution (0.1 M) before filtered through a silica gel/Na_2SO_4 plug. Upon solvent removal a red oil was obtained (FW = 140.14, 33 mg, 66%). ^{1}H NMR (300 MHz, CD_3OD, Figure S2) data was consistent with literature report (Bernet, A.; Seifert, K. *Helv. Chim. Acta* **2006**, *89*, 784-796).

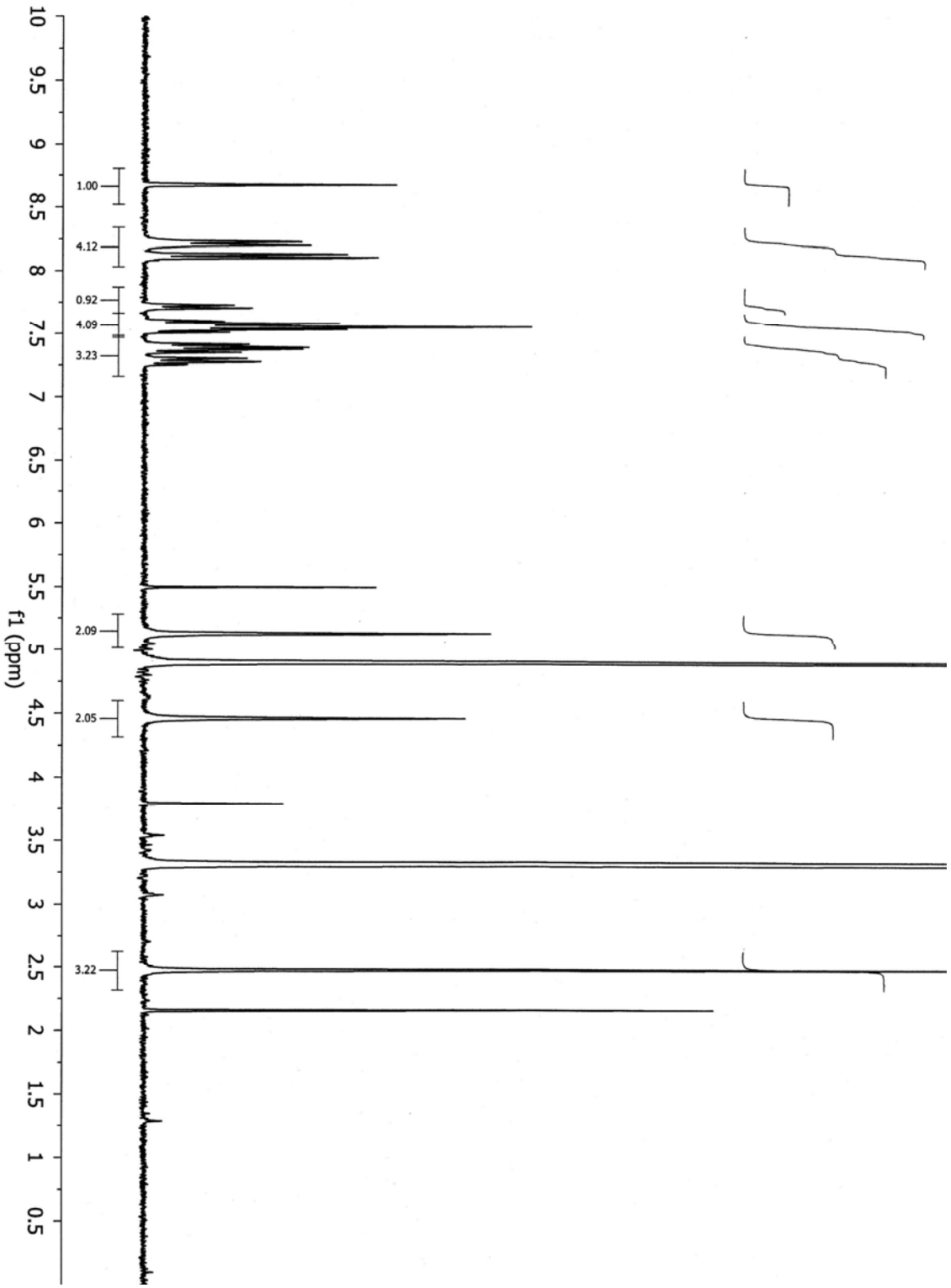

Figure S1. ^{1}H NMR (300 MHz, CD_3CD) of compound **1**.

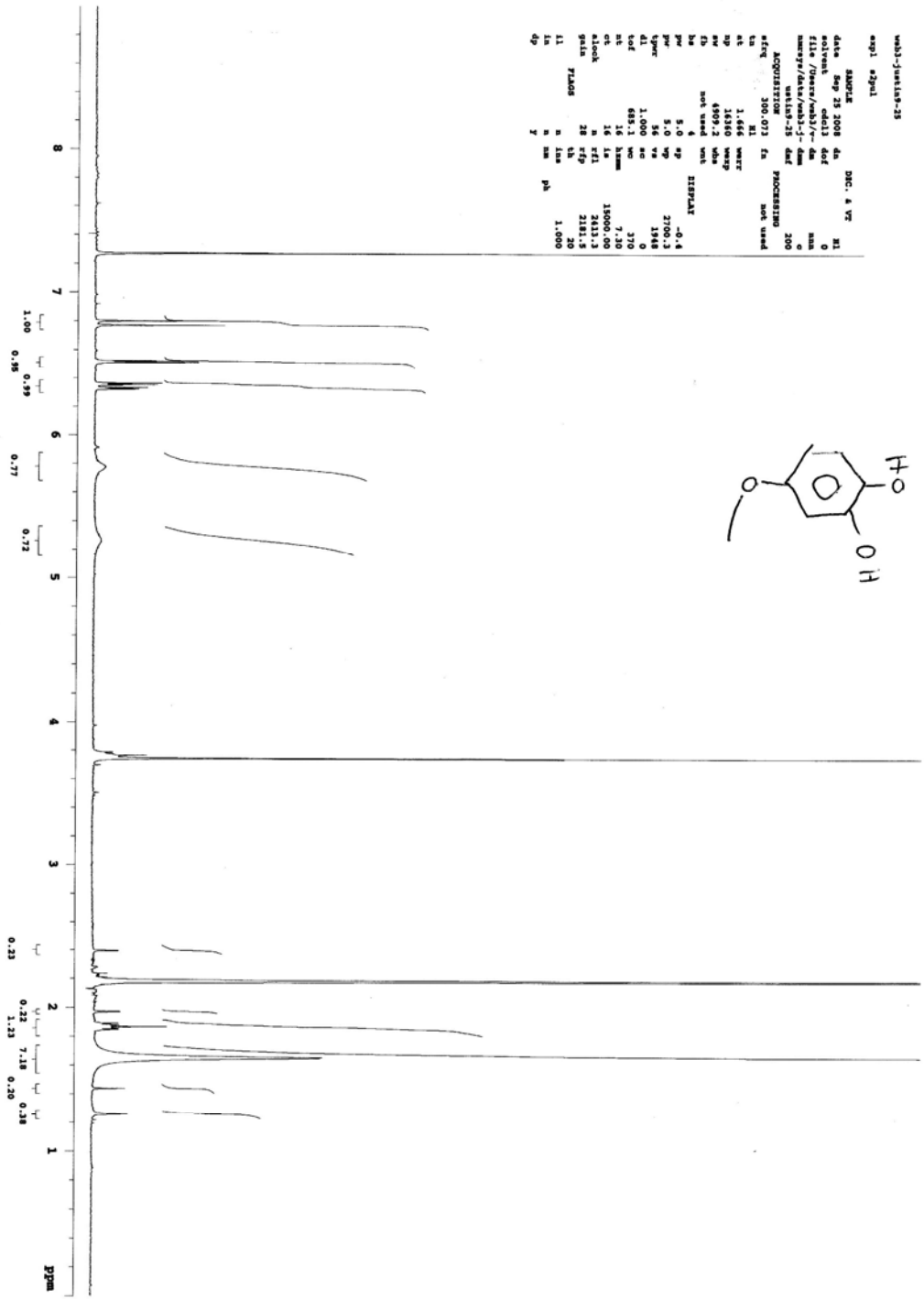

Figure S2. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **6**.

(B) X-RAY CRYSTAL STRUCTURES

(1) Compound **1** crystallized from DCM.

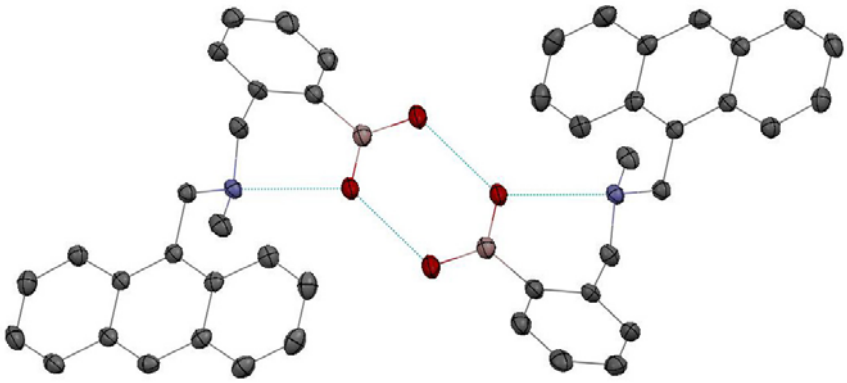

Figure S3. Dimer of compound **1** in the solid state.

(2) Compound **1** crystallized from MeOH.

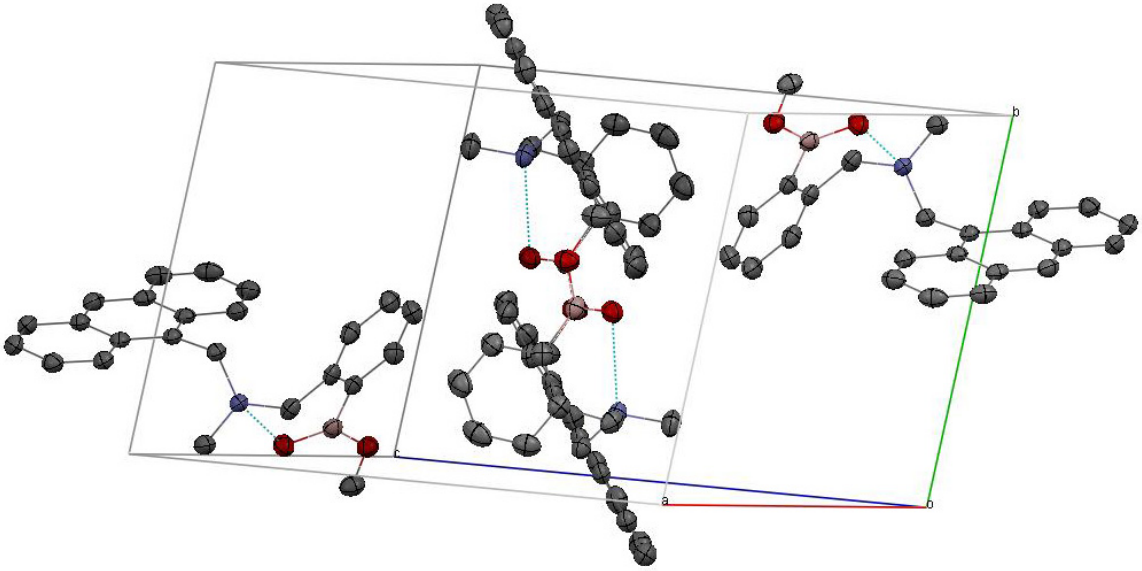

Figure S4. The unit cell view of **1** crystallized from methanol.

(3) Complex of **1**/**2**

The solutions of **1** (0.1 M in MeOH, 1 mL) and **2** (0.1 M in DCM, 1 mL) were mixed. The solvent was removed to afford an off-white powder. The powder was rinsed with MeOH for 3 times before dried on a vacuum manifold. The resulting powder was redissolved in MeOH. The solution was filtrated through glass fiber and transferred to a sample vial. The vial was loosely capped so that the solvent (MeOH) was allowed to

slowly evaporate. Transparent crystals formed at the bottom of the vial over a course of 3-4 days. X-ray diffraction data were collected.

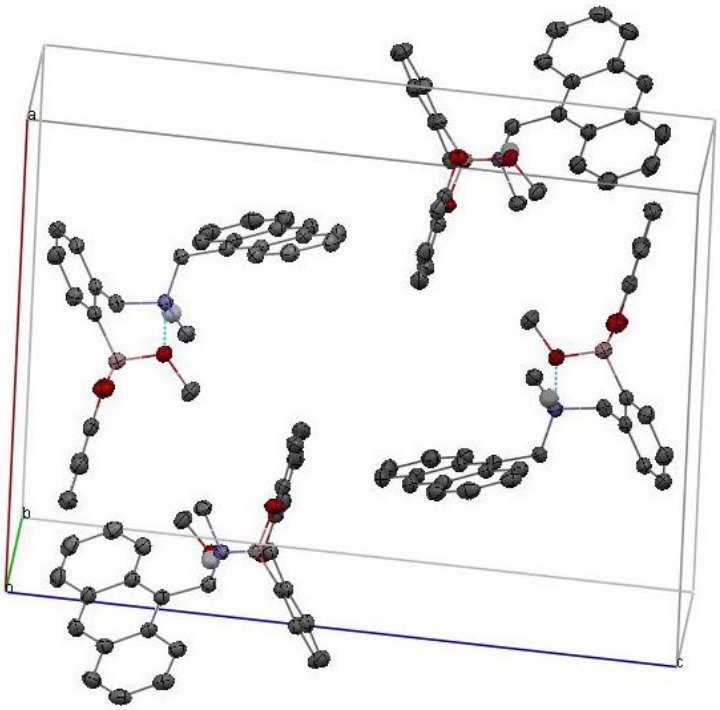

Figure S5. The unit cell view of complex **1/2**.

(4) Complex of **1**/**8**

The crystals for X-ray diffraction were prepared using the same method for complex **1**/**2**. The π-π stacks between aromatic moieties can be seen in Figure S4.

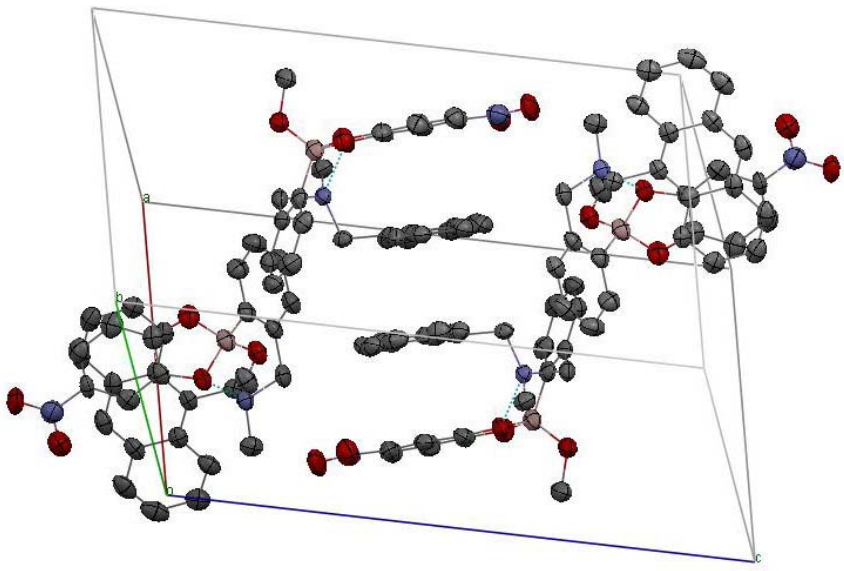

Figure S6. The unit cell view of complex **1/8**.

(C) CYCLIC VOLTAMMOGRAMS

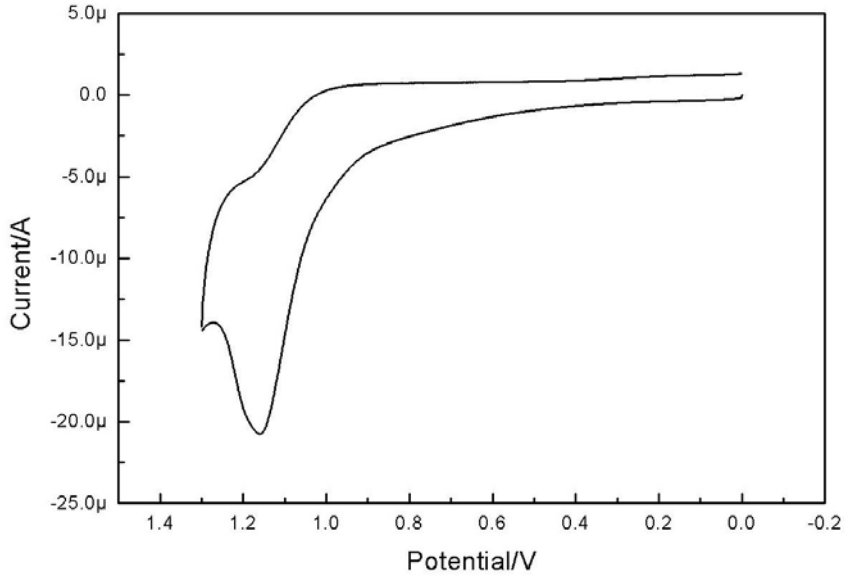

Figure S7. Cyclic voltammogram of **1** (0.3 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 1.16 V.

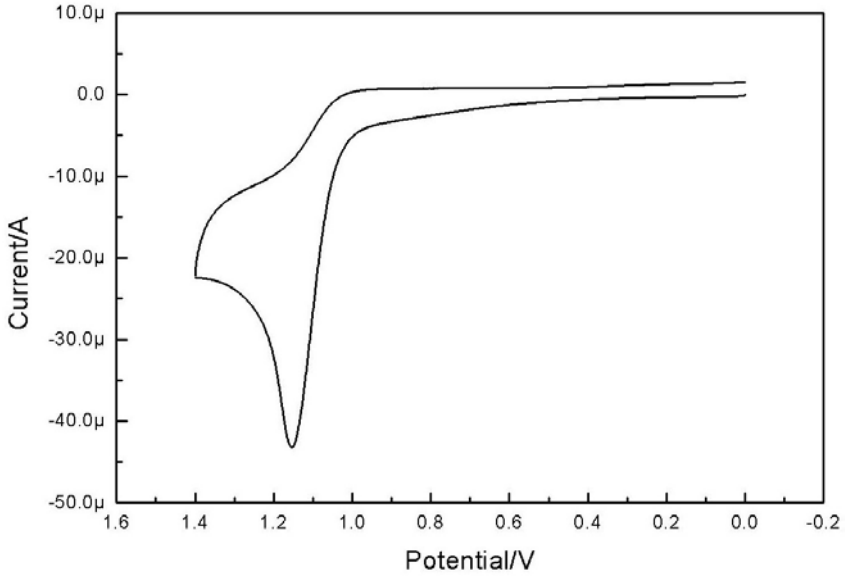

Figure S8. Cyclic voltammogram of anthracene (2 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 1.15 V.

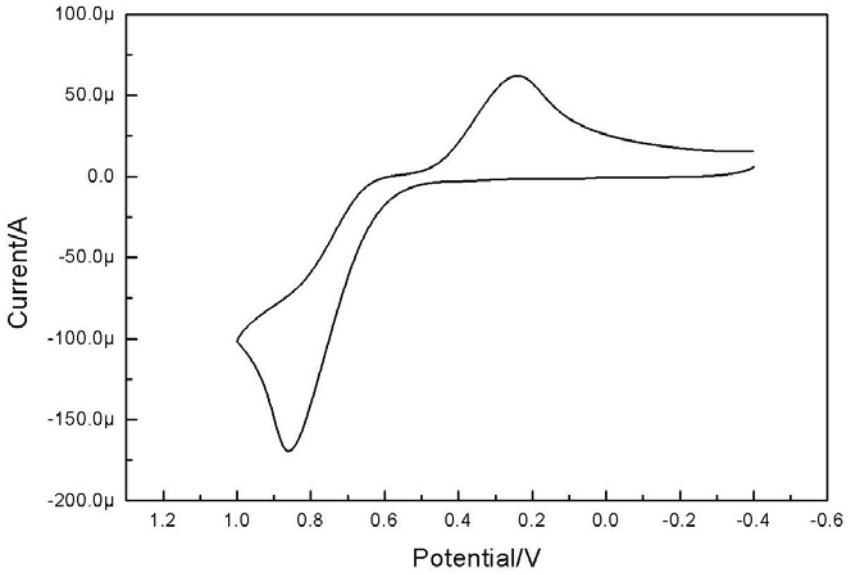

Figure S9. Cyclic voltammogram of **2** (catechol, 5 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.84 V; E_{pc} = 0.24 V.

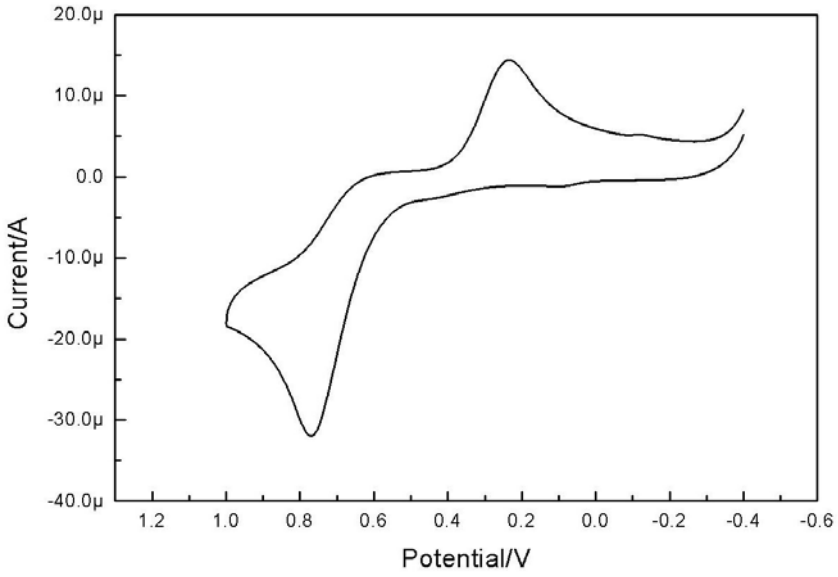

Figure S10. Cyclic voltammogram of **3** (4-fluorocatechol, 0.6 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.77 V; E_{pc} = 0.23 V.

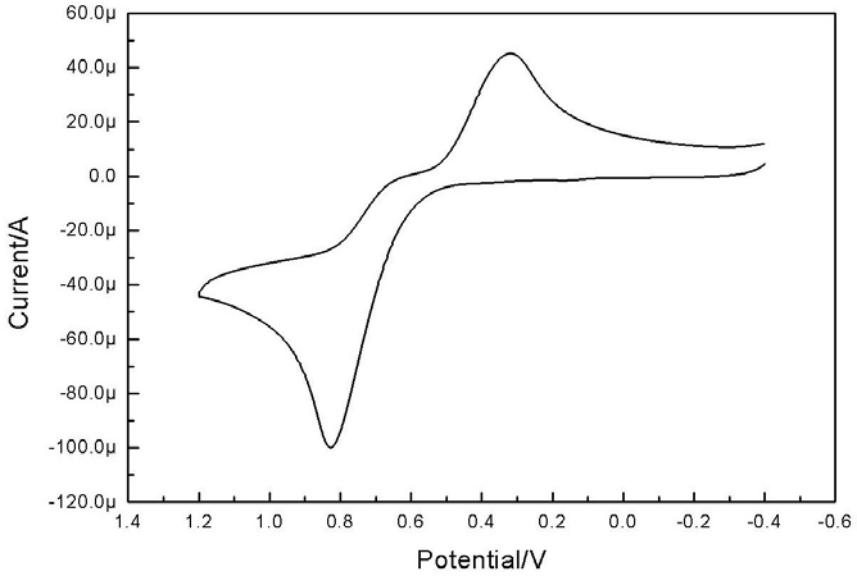

Figure S11. Cyclic voltammogram of **4** (4-chlorocatechol, 3 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.83 V; E_{pc} = 0.32 V.

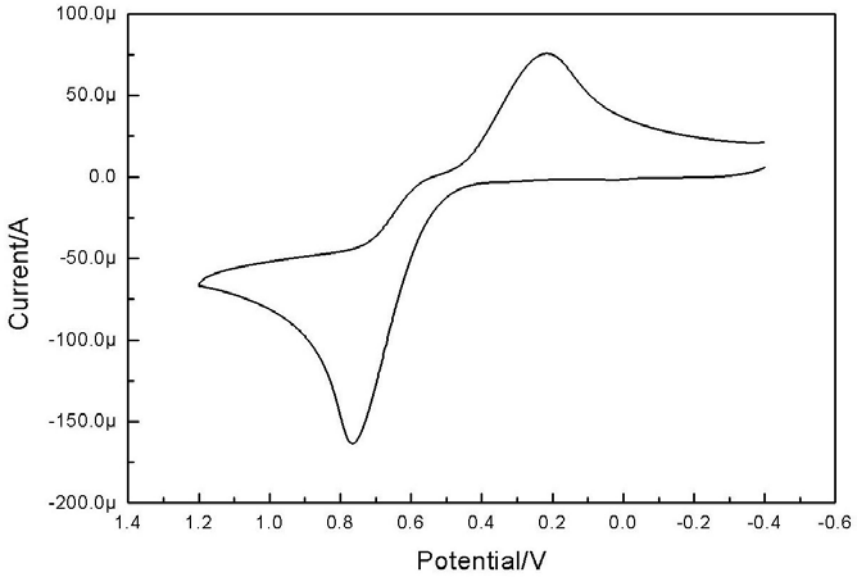

Figure S12. Cyclic voltammogram of **5** (4-methylcatechol, 5 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.77 V; E_{pc} = 0.22 V.

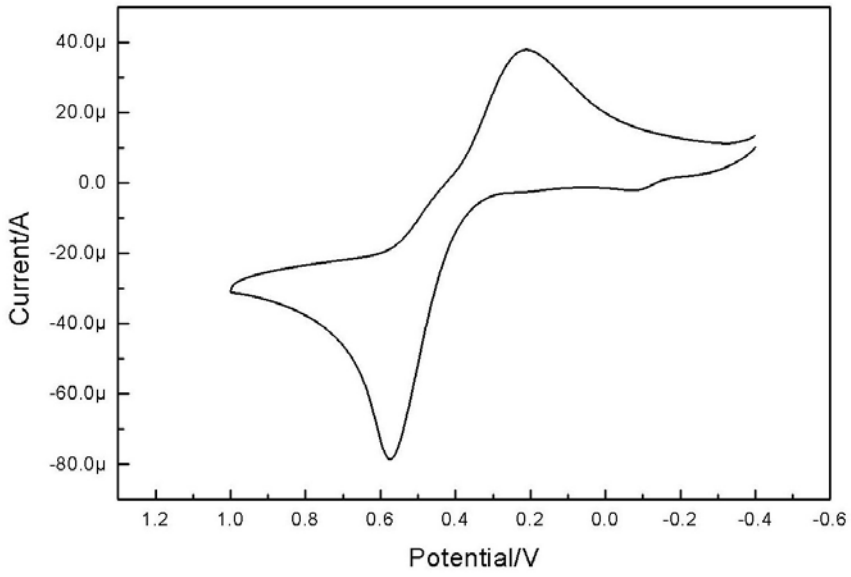

Figure S13. Cyclic voltammogram of **6** (4-methoxycatechol) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.57 V; E_{pc} = 0.21 V.

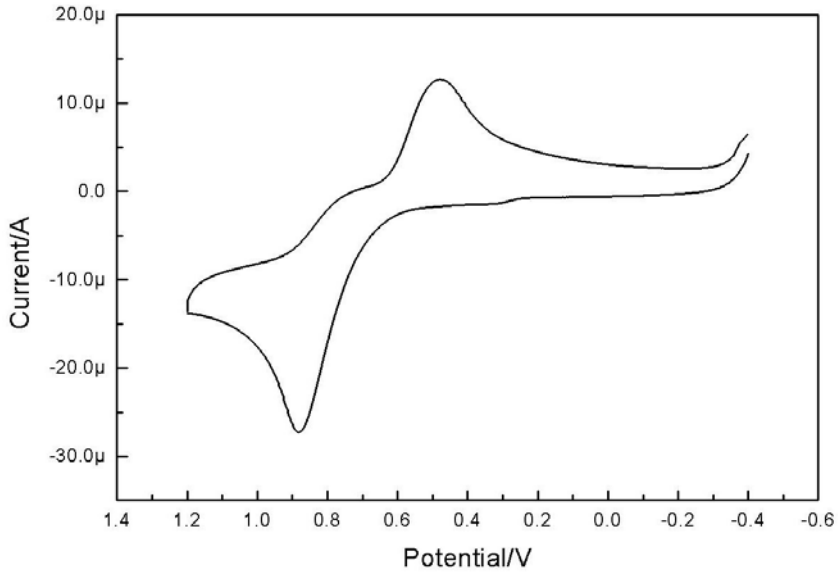

Figure S14. Cyclic voltammogram of **7** (4-cyanocatechol, 0.9 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.88 V; E_{pc} = 0.48 V.

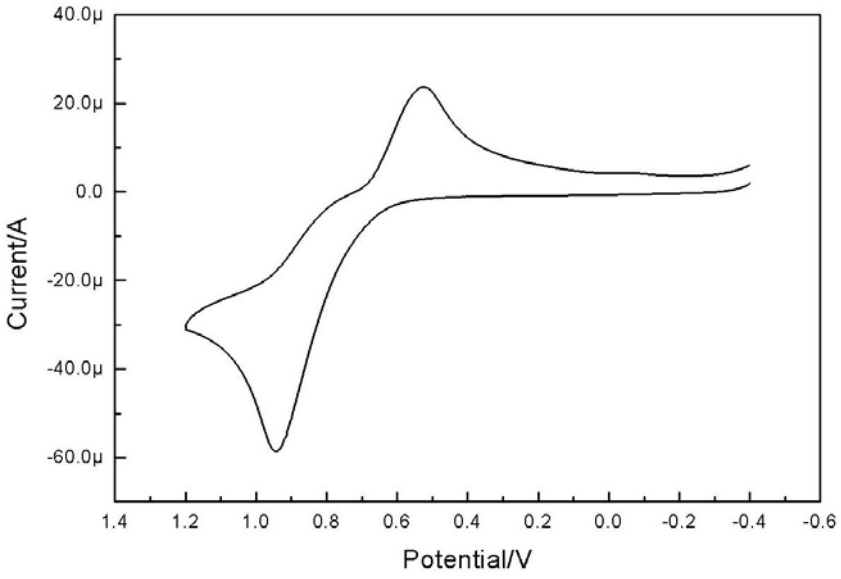

Figure S15. Cyclic voltammogram of **8** (4-nitrocatechol, 2 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.91 V; E_{pc} = 0.54 V.

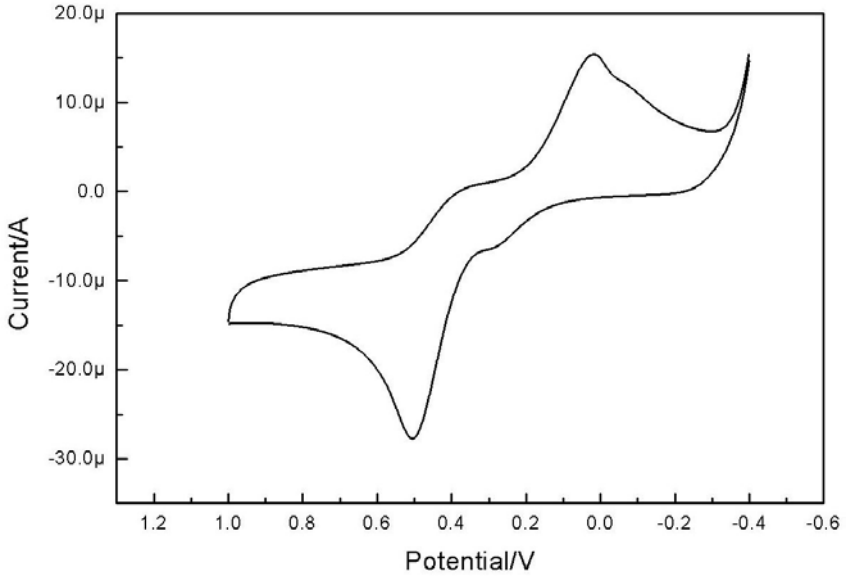

Figure S16. Cyclic voltammogram of **9** (1,2,4-benzenetriol, 0.3 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.50 V; E_{pc} = 0.03 V.

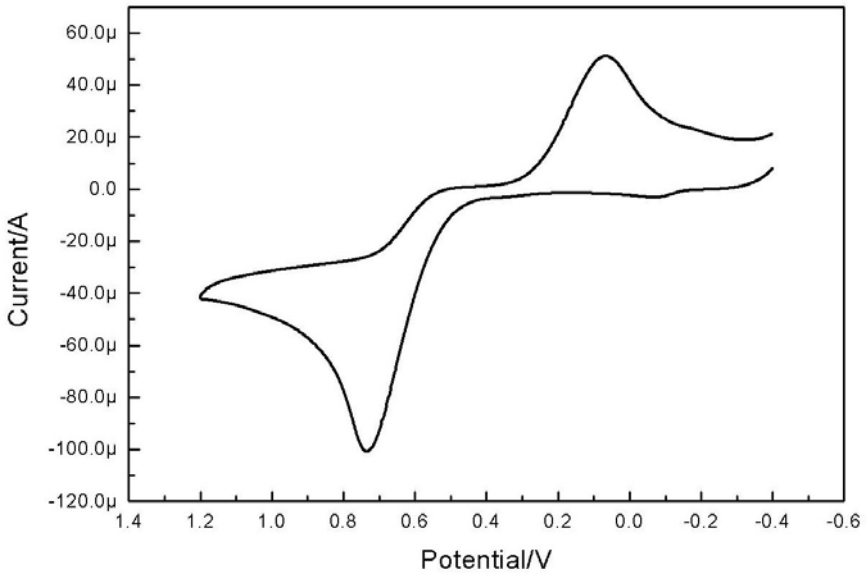

Figure S17. Cyclic voltammogram of hydroquinone (3 mM) in MeOH. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl. E_{pa} = 0.74 V; E_{pc} = 0.07 V.

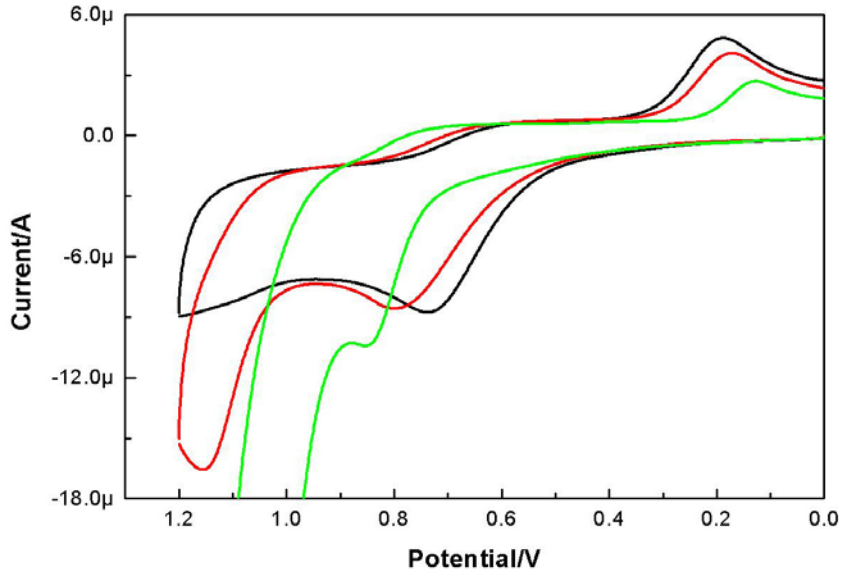

Figure S18. Cyclic voltammogram of **3** (0.2 mM) in MeOH in the presence of 0 (black), 0.1 mM (red), and 4.9 mM (green) of **1**. $NaNO_3$ (0.15 M) was used as the supporting electrolyte. Working electrode: glassy carbon electrode; scan rate: 100 mV/s; reference electrode: Ag/AgCl.

(D) FLUORESCENCE TITRATION SPECTRA

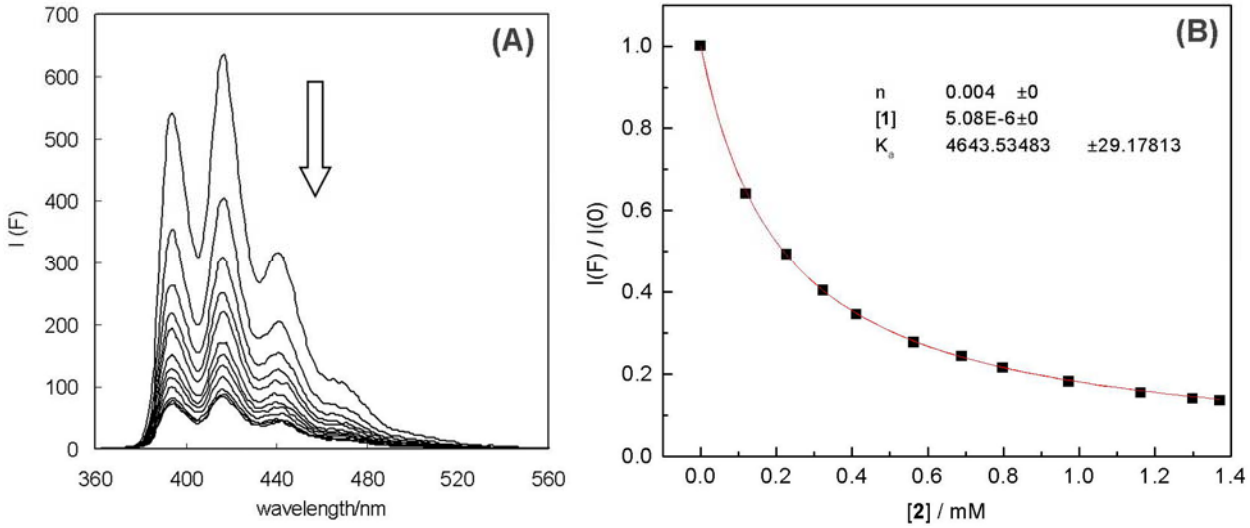

Figure S19. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of **2** (0 – 1.4 mM). (B) Relative fluorescence intensity at 415 nm vs. [**2**]. The solid line is a theoretical fitting curve using a 1:1 binding isotherm.

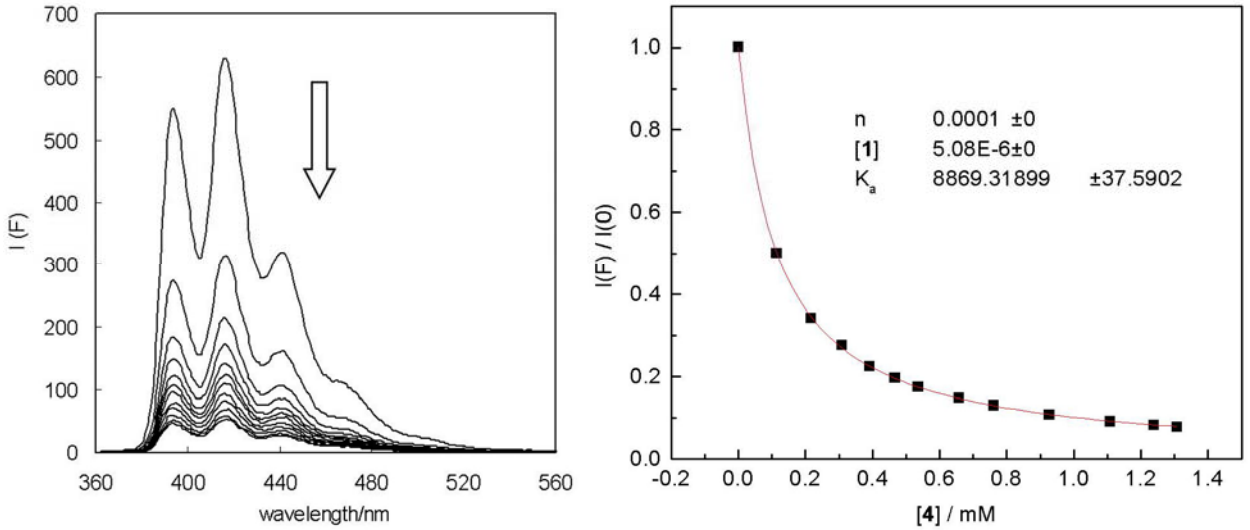

Figure S20. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of **4** (0 – 1.3 mM). (B) Relative fluorescence intensity at 416 nm vs. [**4**]. The solid line is a theoretical fitting curve using a 1:1 binding isotherm.

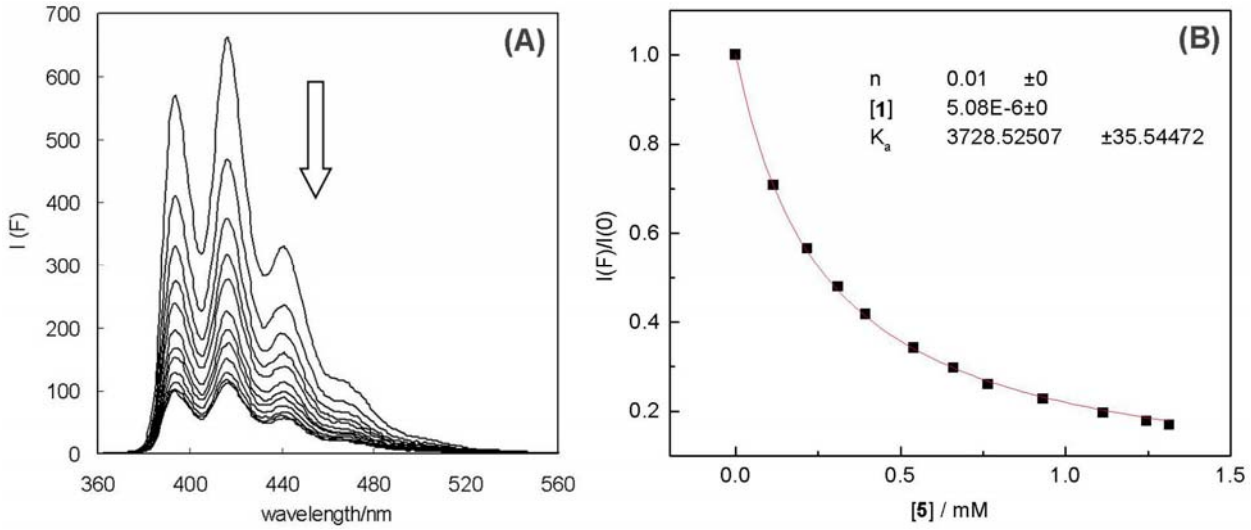

Figure S21. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of **5** (0 – 1.3 mM). (B) Relative fluorescence intensity at 416 nm vs. [**5**]. The solid line is a theoretical fitting curve using a 1:1 binding isotherm.

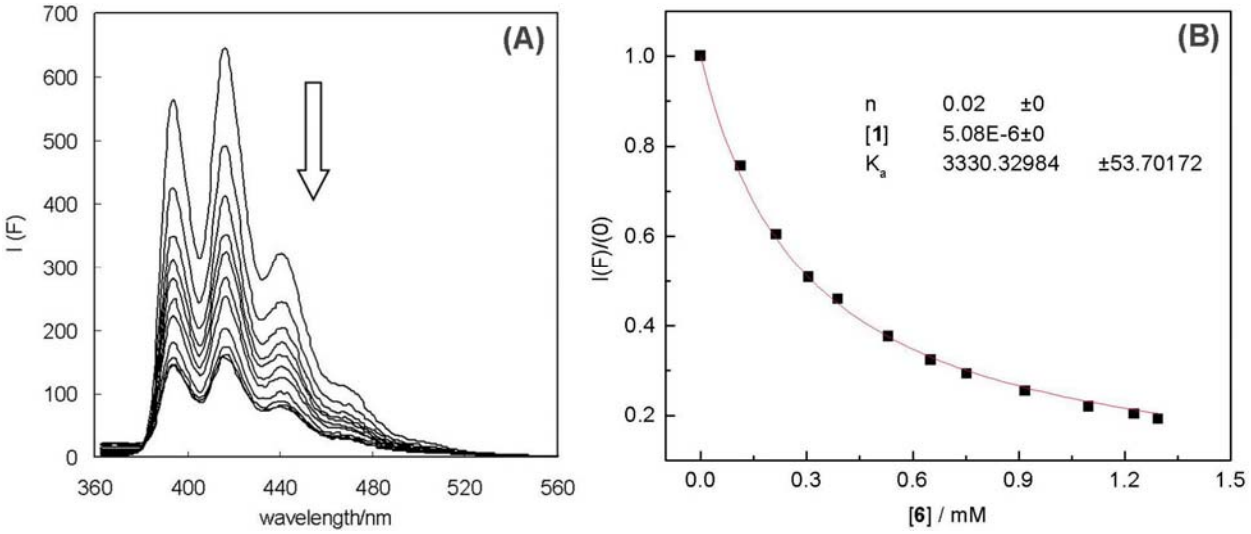

Figure S22. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of **6** (0 – 1.3 mM). (B) Relative fluorescence intensity at 416 nm vs. [**6**]. The solid line is a theoretical fitting curve using a 1:1 binding isotherm.

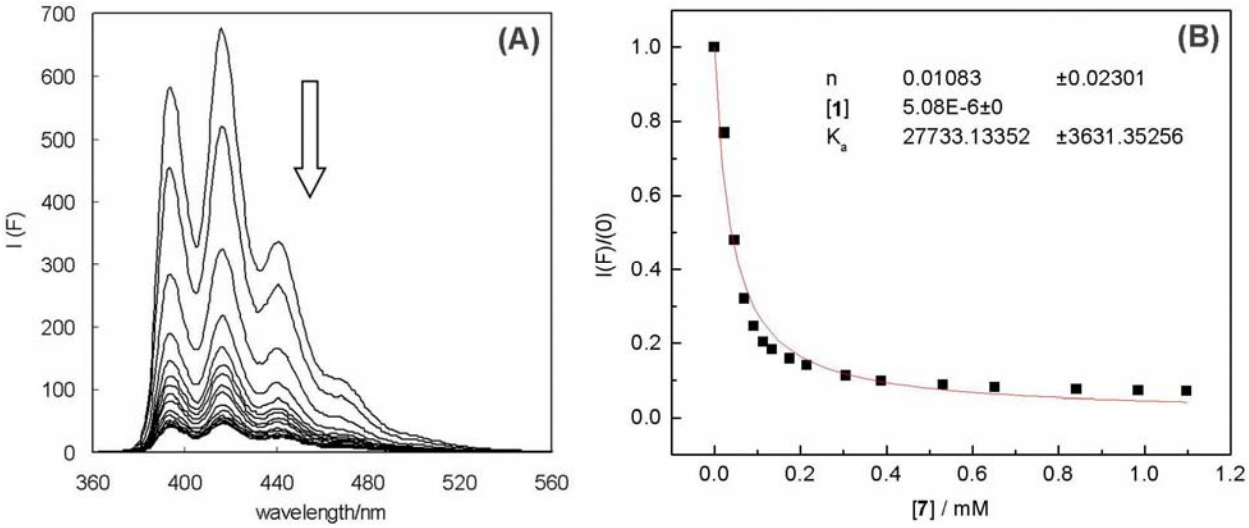

Figure S23. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of **7** (0 – 1.1 mM). (B) Relative fluorescence intensity at 416 nm vs. [**7**]. The solid line is a theoretical fitting curve using a 1:1 binding isotherm.

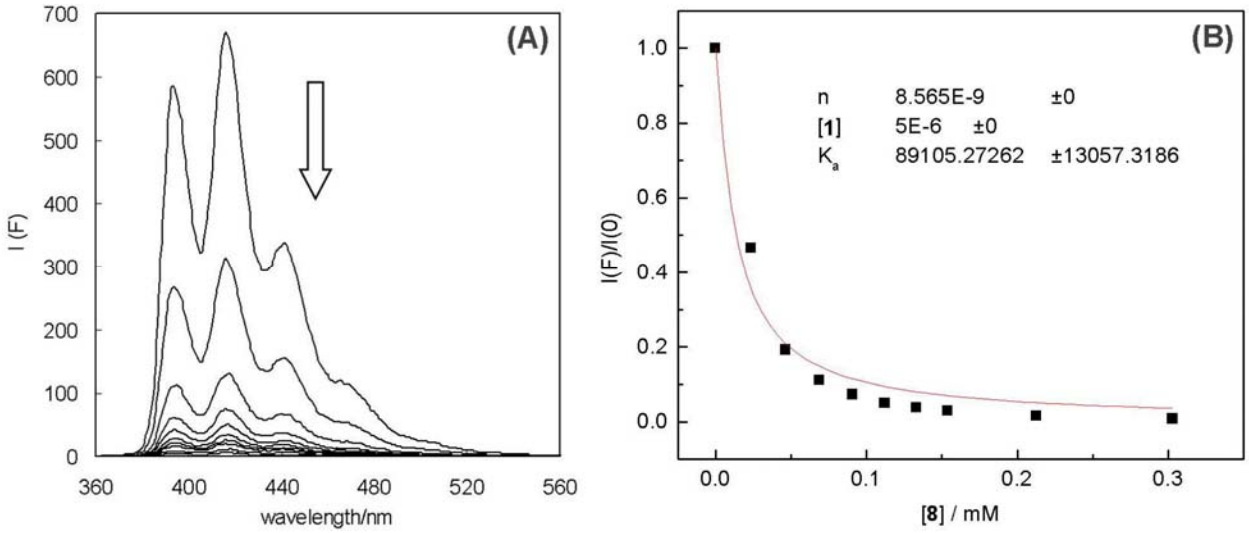

Figure S24. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of **8** (0 – 0.3 mM). (B) Relative fluorescence intensity at 416 nm vs. [**8**]. The solid line is a theoretical fitting curve using a 1:1 binding isotherm.

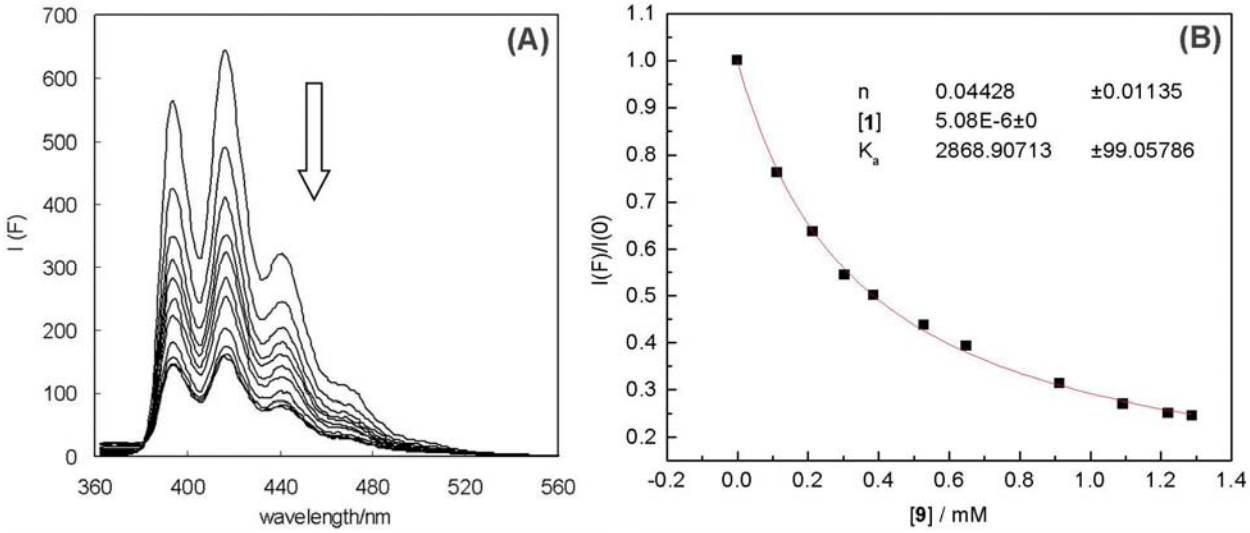

Figure S25. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of **9** (0 – 1.3 mM). (B) Relative fluorescence intensity at 416 nm vs. [**9**]. The solid line is a theoretical fitting curve using a 1:1 binding isotherm.

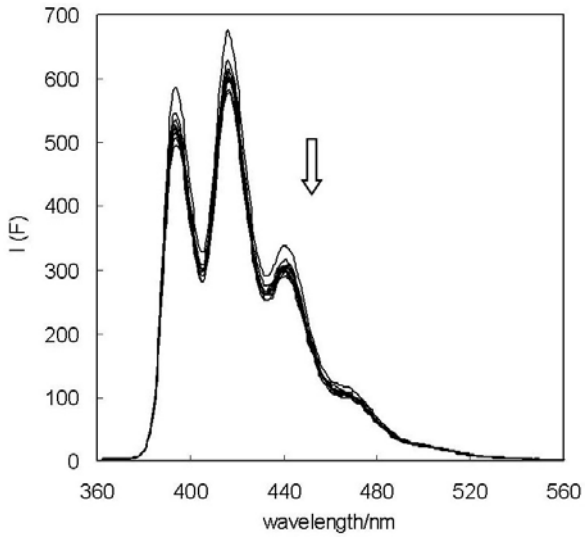

Figure S26. (A) Fluorescence spectral change of **1** (5.1 μM, λ_{ex} = 350 nm) in MeOH with increasing concentration of hydroquinone (0 – 1.3 mM).

(E) ABSORPTION TITRATION SPECTRA

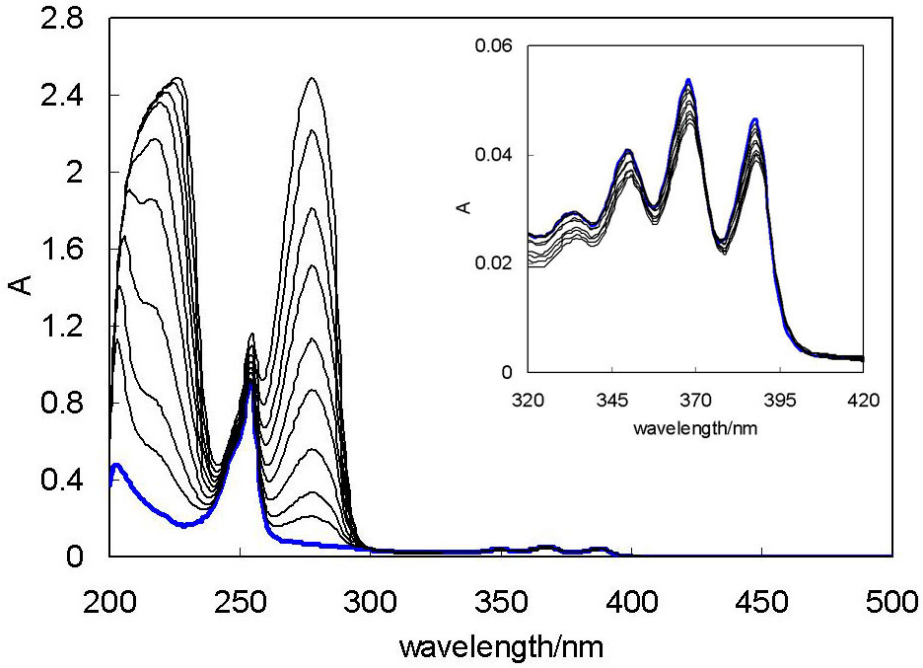

Figure S27. Absorption spectra of **1** (5.1 μM) and **2** (0 – 1.1 mM) in MeOH. The blue spectrum was taken in the absence of **2**. The zoom shot between 320 nm and 420 nm in shown in the inset.