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Electron Supplementary Information

An Electrochemical Sensor for 3,4-Dihydroxyphenylacetic Acid with Carbon Nanotube as Electronic Transducer and Synthetic Cyclophane as Recognition Element

Jie Yan, Yucheng Zhou, Ping Yu, Lei Su,
Lanqun Mao,* Deqing Zhang, * and Daoben Zhu

Beijing National Laboratory for Molecular Sciences, Center for Molecular Science, Institute of Chemistry, the Chinese Academy of Sciences (CAS), Beijing 100190, China

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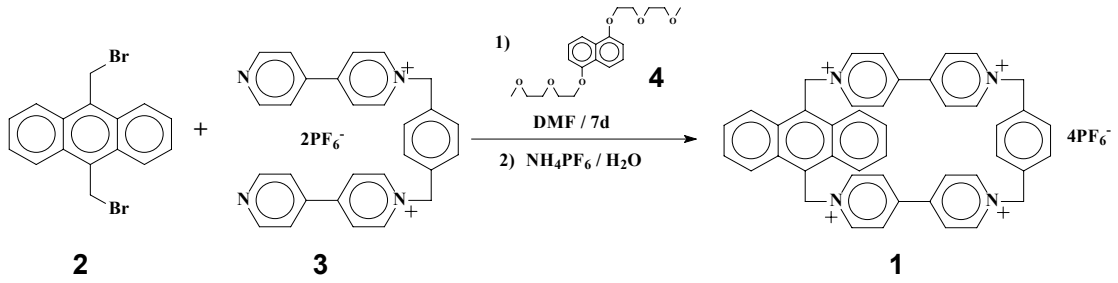
1. Chemicals and Materials. DOPAC, DA and AA were purchased from Sigma. SWNTs were purchased from Nanoport Co. Ltd. (Shenzhen, China). The SWNTs were purified by refluxing the as-received SWNTs in 2.6 M HNO_3 for 10 h. Other reagents were analytical grade or higher and used as received. Aqueous solutions were prepared with doubly distilled water.

2. Synthesis of compound 1.



Compound **1** was synthesized from Compounds **2**[1] and **3**[1], according to literature.[2] Briefly, 0.73 g (2 mmol) **2**, 1.42 g (2 mmol) **3** and 2.19 g (6 mmol) **4** were dissolved in 100 ml dry DMF. The solution was stirred magnetically in dark at room temperature under N_2 atmosphere for 7 days. After that, the solvent was removed in a high vacuum to give red residue, to which an aqueous solution of NH_4Cl (200 mL, 1 M) was added. The mixture was extracted continuously with CH_2Cl_2 for 2 days until the color of the aqueous solution was changed from red to light orange. Then, the aqueous solution was concentrated under a reduced pressure and subjected to column chromatography (silica gel) using CH_3OH/2 M aqueous NH_4Cl solution/CH_3NO_2 (7:2:1, v:v:v) as the eluant. The fractions containing tetracationic cyclophane were collected, and the solvents were removed in vacuum. The residue was re-dissolved in water, and NH_4PF_6 solids were added until no further orange precipitation was observed. After filtration, the orange solid was washed with water (100 mL), dried in vacuum to give complex **1** (0.48 g, 0.4 mmol, 20 %) as an orange power: mp >275 ˚C. ^{1}H NMR (400 MHz, CD_3CN) δ 8.86 (4H, d, J = 6.6 Hz), 8.67 (4H, d, J = 6.6 Hz),

8.57 (4H, dd, J_1 = 6.8 Hz, J_2 = 3.1 Hz), 8.03 (4H, d, J = 6.5 Hz), 7.86 (4H, d, J = 6.1 Hz), 7.83 (4H, d, J = 3.1 Hz), 7.54 (4H, s), 6.99 (4H, s), 5.73 (4H, s); ^{13}C NMR (100 MHz, CDCN) δ 149.2, 148.8, 144.4, 144.1, 135.4, 129.8, 129.4, 128.1, 127.8, 126.7, 126.2, 123.3, 64.0, 56.1; MS (ESI) *m/z* 1055.6 $[M - PF_6^-]^+$, 455.4 $[M - 2PF_6^-]^{2+}$, 255.3 $[M - 3PF_6^-]^{3+}$. HRMS (ESI) calcd for $[C_{48}H_{44}F_{12}N_4P_2]^{2+}$ ($[M - 2PF_6^-]^{2+}$) 455.1107, obsd 455.1105; calcd for $[C_{50}H_{47}F_6N_4O_2P]^{2+}$ ($[M - 2PF_6^- - HPF_6 + CH_3COOH]^{2+}$) 412.1349, obsd 412.1351; calcd for $[C_{48}H_{43}F_6N_4P]^{2+}$ ($[M - 2PF_6^- - HPF_6]^{2+}$) 382.1246, obsd 382.1245.

3. Synthesis and Characterization of 1-SWNT Nanocomposite. The **1**-SWNT adsorptive nanocomposite was prepared by mixing 2 mg of SWNTs and 5 mg of **1** in 10 mL of distilled water under stirring for 24 h at room temperature. The resulting suspension was filtered with a Millipore filter (0.45 μm, Millipore) and the obtained sample was first thoroughly rinsed with distilled water to remove nonadsorbed **1** and then dried at 70 □ for 5 h to obtain the **1**-SWNT adsorptive nanocomposite. The obtained nanocomposite was used for X-ray photoelectron spectroscopy (XPS) and thermal gravimetric (TG) measurements. XPS measurements were performed on an ESCALab220i-XL electron spectrometer from VGScientific using 300 W Al Kα radiation.

4. Electrochemical Measurements. Glassy carbon (GC) electrodes (3-mm diameter, BAS) were used as the substrate electrode to construct the electrochemical sensors for selective determination of DOPAC. The electrodes were first polished with the slurry of alumina powders (0.3 and 0.05 μm) on a polishing cloth, then sonicated in acetone and doubly distilled water (each for 5 min) and finally rinsed with distilled water. For confining the **1**-SWNT adsorptive nanocomposite onto GC electrodes to form the electrochemical sensors, the prepared **1**-SWNTs were dispersed into water to form a homogeneous dispersion (2 mg/mL) under sonication and 4 μL of the suspension was coated onto GC electrodes. The electrodes (denoted as **1**-SWNT-modified GC electrodes) were then air-dried. Alternatively,

the **1**-SWNT-modified GC electrodes were also prepared by first casting 5 μL SWNT dispersion in DMF (2 mg/mL) onto the electrodes and then immersing the SWNT-modified electrodes in phosphate buffer (pH 7.0) containing 0.1 mM of **1** for about 7 h. After that, the electrodes were rinsed with doubly distilled water and air-dried.

Electrochemical measurements were carried out on a computer-controlled electrochemical analyzer (CHI660C, CHI, Austin, USA) in a conventional and two-compartment cell. **1**-SWNT-modified GC electrodes were used as working electrode and a platinum spiral wire as counter electrode. All potentials were referred to a KCl-saturated Ag/AgCl electrode. A 0.10 M phosphate buffer (pH 7.0) was used as a supporting electrolyte. Cyclic voltammetric measurements conducted with the **1**-SWNT-modified GC electrodes were subjected to automatic compensation of ohmic potential drop.

References

(1) Asakawa, M.; Dehaen, W.; L'abbé, G.; Menzer, S.; Nouwen, J.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *J. Org. Chem.* **1996**, *61*, 9591-9595).

(2) Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; Gómez-López, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 152-170.

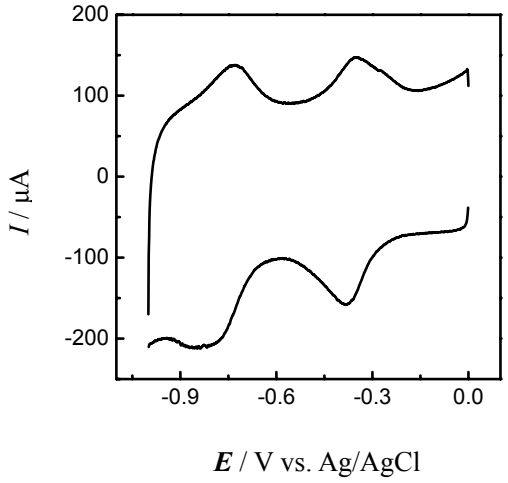


Figure S1. CV obtained at the **1**-SWNT-modified GC electrode in phosphate buffer (pH 7.0) at 100 mV s^{-1}.

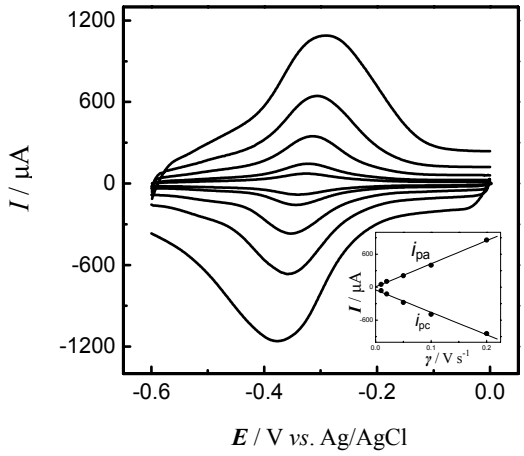


Figure S2. CVs obtained at the **1**-SWNTs confined onto GC electrode in phosphate buffer (pH 7.0) at different scan rates of (from inner to outer) 10, 20, 50, 100 and 200 mV s^{-1}. Inset, plots of peak currents verse potential scan rate.

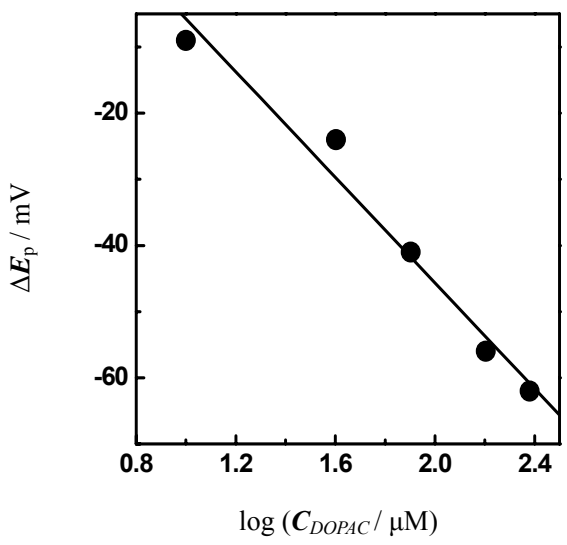


Figure S3. Plot of the shift in the reduction peak potential (ΔE_p) of 1-SWNT-modified GC electrode in 0.10 M phosphate buffer solution versus the logarithm of DOPAC concentration in μM range. The 1-SWNT-modified GC electrode was prepared by confining less amount of 1-SWNTs (2 μL of 1-SWNT dispersion (0.4 mg/mL)) onto electrode. The shift in the peak potential (ΔE_p) was linear with the logarithm of DOPAC concentration within the concentration range from 10 μM to 240 μM with a linear coefficiency of 0.987.