

Supplementary Document

for

A Novel Copper(II) Phthalocyanine Modified Multiwalled Carbon Nanotube-Based Electrode for Sensitive Electrochemical Detection of Bisphenol A

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Synthesis of (E)-3-(4-(3,4-dicyanophenoxy)-3-methoxyphenyl)acrylic acid (1)

Synthesis of (E)-3-(4-(3,4-dicyanophenoxy)-3-methoxyphenyl)acrylic acid (1) was done chemically as literature [1]. Firstly, *trans*-4-hydroxy-3-methoxycinnamic acid (Ferulic acid) (2.89 mmol, 0.56 g) was dissolved in dry DMF (50 mL) and then 4-nitrophthalonitrile (2.89 mmol, 0.5 g) was added into the solution. The solution was mixed to obtain a homogeneous mixture for 15 mins. After that anhydrous K₂CO₃ (11.56 mmol, 1.59 g) was added separately in the solution for 2 hours. The system was refluxed for 72 hours under a nitrogen atmosphere at 45-50 °C (Fig. S1). The system was cooled to the room temperature at the end of the reaction and diluted HCl was added to arrange of pH as 2. The solid particles were obtained in one hour. They were filtered and then washed with water, hexane and diethyl ether. After drying process, light brown particles were recrystallized in MeOH. The final product was soluble in organic solvents such as MeOH, EtOH, acetone, chloroform and THF. Yield 0.832 g (90.1%), M.p. 225-226 °C, Anal. Calc. for C₁₈H₁₂N₂O₄ (MA: 320.30 g/mol): C, 67.50; H, 3.78; N, 8.75. Found: C, 67.30; H, 3.70; N, 8.65%. FT-IR (KBr), ν_{\max} /(cm⁻¹): 3300-2500 (broad peak, carboxylic acid-COOH), 3073-3047 (Ar-CH), 2981-2944 (aliphatic -CH, -CH₃), 2231 (C≡N), 1688 (C=O), 1589-1487 (C=C), 1246 (Ar-O-Ar), 1077, 952, 862. ¹H-NMR (MeOD₃, 500 MHz, δ :ppm): 7.85-7.83 (d, 1H, Ar-H), 7.69-7.65 (d, 1H, Ar-H), 7.41-7.39 (dd, 1H Ar-H), 7.29 (s, 1H Ar-CH=), 7.27 (d, 1H, Ar-H), 7.21 (d, 1H, Ar-H), 7.19-7.18 (d, 1H, Ar-H), 6.53-6.50 (d, 1H, =CH-COO), 3.78 (s, 3H, O-CH₃). ¹³C-NMR (MeOD₃, 500 MHz, δ :ppm): 170.23, 163.28, 153.05, 145.33, 144.60, 136.96, 135.74, 124.15, 123.14, 122.22, 121.75, 120.47, 118.56, 116.85 (C≡N), 116.39 (C≡N), 113.78, 109.76, 56.24. MS (LC-MS) m/z. Calculated: 320.30 Determined: 359.31 [M + K]⁺.

Synthesis of (E)-3-(2,9,16,23-tetrakis-(4-oxy-3-methoxyphenyl) acrylic acid)phthalociyaninato copper(II) (2)

Chemical synthesis was done for (E)-3-(2,9,16,23-tetrakis-(4-oxy-3-methoxyphenyl) acrylic acid)phthalociyaninato copper(II) compound. (E)-3-(4-(3,4-dicyanophenoxy)-3-methoxyphenyl)acrylic acid (0.623 mmol, 0.20 g) was dissolved in n-pentanol (3 mL). Anhydrous Cu(CH₃COO)₂ (0.156 mmol, 0.028 g) was added in the solution and the system in the closed test tube was heated to 80 °C under nitrogen atmosphere. 5 drops of DBU was added in the solution was kept for 24 hours at 150 °C (Fig. S2). While the temperature was increasing, the color of the solution changed from dark brown to dark green. Then, the solution was cooled to room temperature and poured into diluted HCl solution. Green

precipitates were filtered and washed in n-hexane, acetone, dichloromethane, chloroform, diethyl ether and ethyl acetate. Dried products were soluble in THF, MeOH, water, DMSO and DMF. Yield: 0.064 g (30%). M.p. >300 °C. Anal. Calc. for C₇₂H₄₈CuN₈O₁₆ (MA: 1344.74 g/mol): C, 64.48; H, 3.78; N, 8.24. Found: C, 64.30; H, 3.67; N, 8.15%. FT-IR (KBr), $\nu_{\max}/(\text{cm}^{-1})$: 3070 (Ar-CH), 2930–2870 (aliphatic CH), 1640 (C=O), 1593–1465 (C=C), 1264 (Ar-O-Ar), 1091, 980, 821. MALDI-TOF MS: Calculated: 1344.74, Found: 1347.31 [M+2H]⁺. UV-Vis (THF, 1×10⁻⁵ M): λ_{\max}/nm (log_ε): 678 (4.98), 342 (4.66).

Synthesis and characterization of compounds (1) and (2)

In the first step of synthesis, *trans*-4-hydroxy-3-methoxycinnamic acid and 4-nitrophthalonitrile were dissolved in DMF, and anhydrous potassium carbonate was added in the solution. The solution was refluxed under nitrogen atmosphere for 72 hours at 45 °C. Then, the solution was cooled and diluted HCl was added in the system to obtain precipitates. The formed precipitate was washed with ultra-pure water for neutralization, then the precipitate was washed with hexane and diethyl ether and dried. At the end of the procedure, (E)-3-(4-(3,4-dicyanophenoxy)-3-methoxyphenyl)acrylic acid (**1**) was synthesized. The structure of (**1**) was confirmed by elemental analysis, FT-IR, ¹H-NMR, ¹³C-NMR and LC-MS techniques.

FT-IR spectra of (**1**) and (**2**) were shown in Fig. S3. There was no peak around 1365 cm⁻¹ corresponding –NO₂ groups indicating the full reaction of 4-nitrophthalonitrile. Besides, obtained peaks around of 2231 cm⁻¹, 1688 cm⁻¹ and a splayed peak between 2600-3300 cm⁻¹ supported the (–C≡N), carbonyl (C=O) and hydroxyl of carboxyl groups (COOH), respectively on the structure of (**1**). Indeed, no peaks around of 3380 cm⁻¹ (–OH) supporting the full reaction of *trans*-4-hydroxy-3-methoxycinnamic acid to form of (**1**). Aliphatic C–H peaks at 2900 cm⁻¹ and Ar-O-Ar ether peak at 1246 cm⁻¹ supported the formation of (**1**). ¹H-NMR spectra of (**1**) also supported the formation of the supposed structure of substance (**1**). Chemical shifts around of 7.85-7.83, 7.69-7.65 ve 7.41-7.39 ppm was corresponding of aromatic protons to which the nitrile groups are attached. (Fig. S4a). Other aromatic protons were determined in 7.27, 7.21 and 7.19-7.18 ppm as three total protons. The chemical shifts around of 7.29, 6.53-6.50 and 3.78 ppm were related with Ar-CH= for one proton bonded aromatic ring, =CH-COO for one proton and –CH₃ for three protons, respectively. Any peak was observed for –OH for dimerization [2]. ¹³C-NMR spectra can be seen in Fig. S4b. The carbon peaks bonded with nitrile groups were determined at 116.85 and 116.39 ppm. –OH,

bonded carbon was also seen at around of 56.24 ppm (Fig. S4b). ^{13}C -NMR spectra also supported the formation of a compound with total of 18 peaks for the carbon atom. (1). The supposed peak at 359.31 $[\text{M}+\text{K}]^+$ in the mass spectra also confirms the synthesized of (1) (Fig. S4c).

FT-IR spectra of (2) can be seen in Fig.S3. Any peak observed around of 2231 cm^{-1} supported the formation of phthalocyanine compound by cyclotetramerization reaction. Besides, the peaks around of 1640 cm^{-1} and 2600-3300 cm^{-1} supported the carboxyl group and hydroxyl groups, respectively on the structure of (2). The peaks at 1264 cm^{-1} and 2930-2870 cm^{-1} were related with Ar–O–Ar ether and aliphatic –CH and –CH₃ supporting the formation of (2). UV-Vis spectra of (2) can be seen in Fig. S5a. Two bands Q and B at 600-750 and 300-350 nm, respectively were seen in UV spectra of phthalocyanine [3,4]. The peaks observed at 678 nm and 342 nm in the DMF of (2) supported the formation of compound (2). Obtained $[\text{M}+2\text{H}]^+$ m/z 1347.31 in MALDI-TOF MS supported the formation of (2) (Fig. S5b).

FT-IR characterization of electrodes

FT-IR spectroscopy was used in the characterization of functional groups formed on the electrode surface. Characteristic IR bands of CuPc/MWCNT-COOH/PGE are shown in Fig. S6. The bands belong to the functional groups are given in sequence (ATR, 4.000–600 cm^{-1}): The signals at 3462 cm^{-1} and 1656 cm^{-1} belong to the -OH and C = O vibrations of the carboxyl groups, respectively. These signals, which are caused by -COOH groups in both MWCNT-COOH and CuPc structure, are evidence of the presence of these functional groups on the electrode surface. It is also possible to say that the signals just below 3000 cm^{-1} belong to the aliphatic -CH and -CH₃ groups, while the signals from 1200-1300 cm^{-1} represent ether groups of CuPc [5].

XPS characterization of electrodes

XPS analysis were carried out to determine the chemical structure of modified electrode (Fig. S11). A composite structure was prepared in the electrode preparation step to use of selective determination of BPA. In this concept, Cu2p and C1s XPS spectra were analyzed to determine the composite structure (hybrid) of structure of CuPc/MWCNT-COOH/PGE. Fig. S11a and Fig. S11b showed the Cu2p and C1s XPS spectra of CuPc/MWCNT-COOH/PGE, respectively. Obtained peaks around of 935 eV and 955 eV in Cu2p XPS spectra of CuPc/MWCNT-COOH/PGE, which were related with the covalent bond of central atom and Pc, supported to the formation of hybrid system [6]. Besides, only one peak was determined at

the around of 285.7 eV in the C1s XPS spectra of CuPc/MWCNT-COOH/PGE [7]. This also mainly related with peak of carbon on the structure of the carbon nanotube including hybride material.

References

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Supplementary Figures (Figures S)

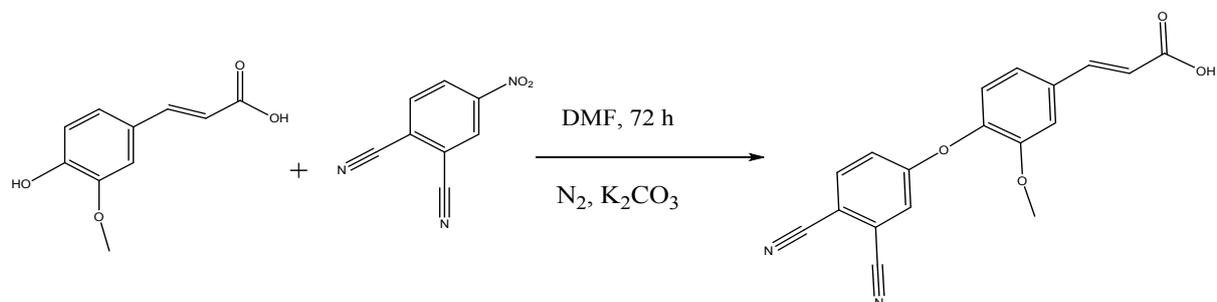


Fig. S1 Synthesis scheme of (E)-3-(4-(3,4-dicyanophenoxy)-3-methoxyphenyl)acrylic acid (1).

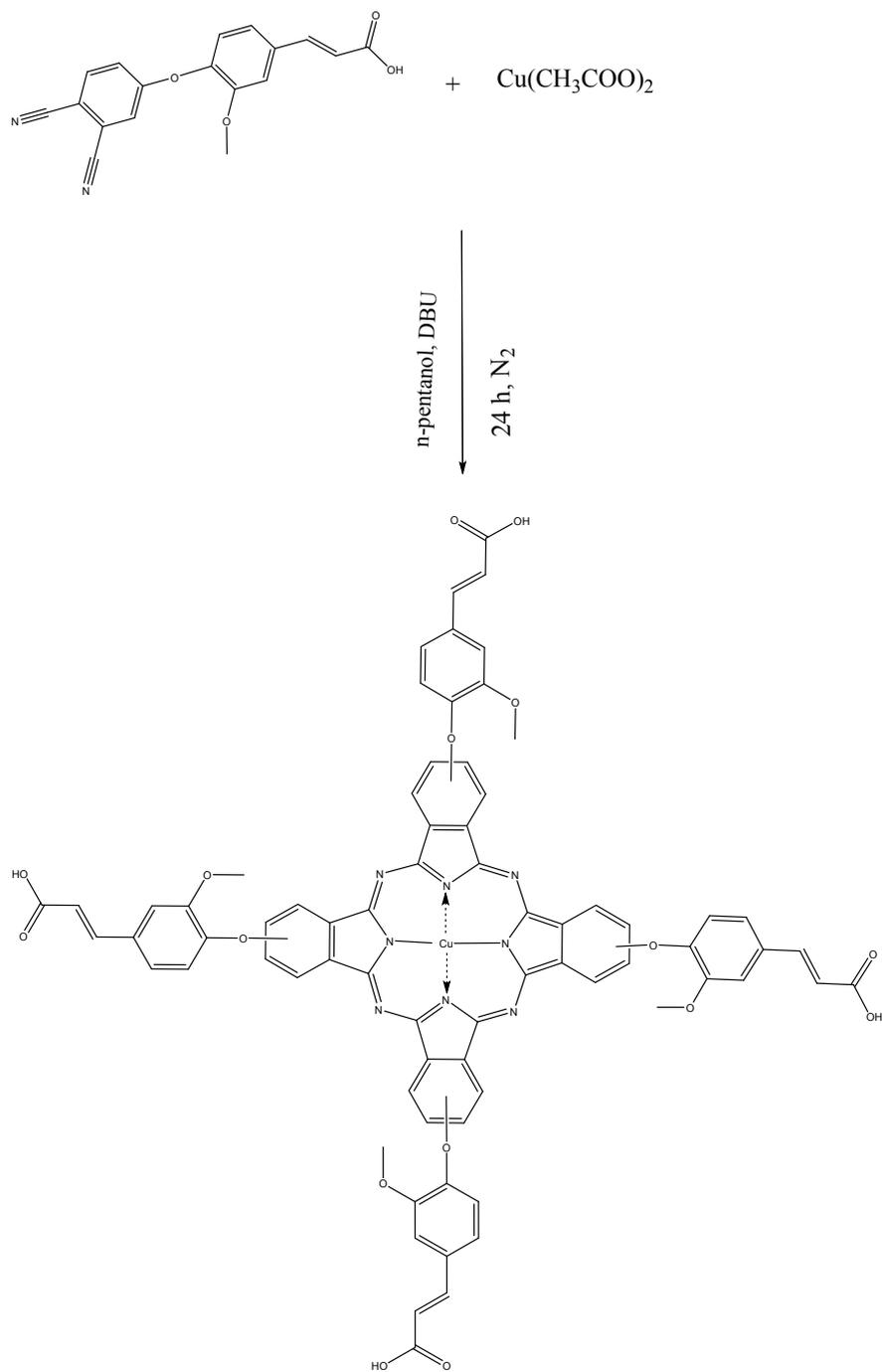


Fig. S2 Synthesis schema of (E)-3-(2,9,16,23-tetrakis-(4-oxy-3-methoxyphenyl) acrylic acid)phthalocyaninato copper(II) (**2**).

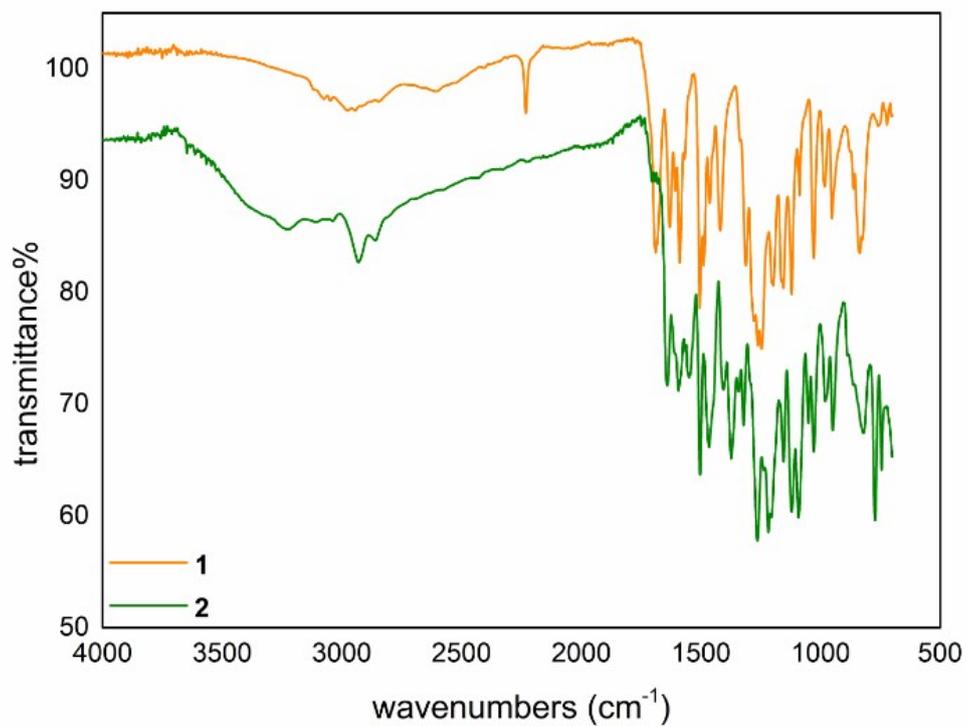


Fig. S3 FT-IR spectra of (1) and (2).

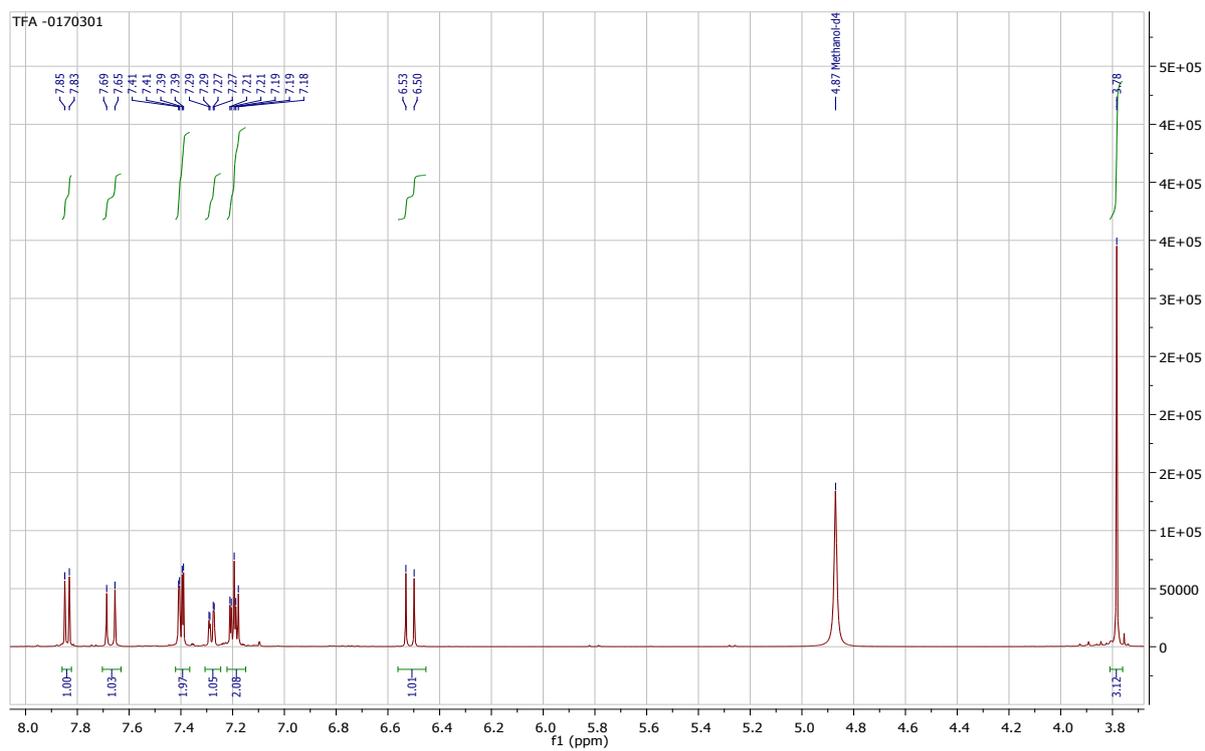


Fig. S4a ¹H-NMR spectra of (1).

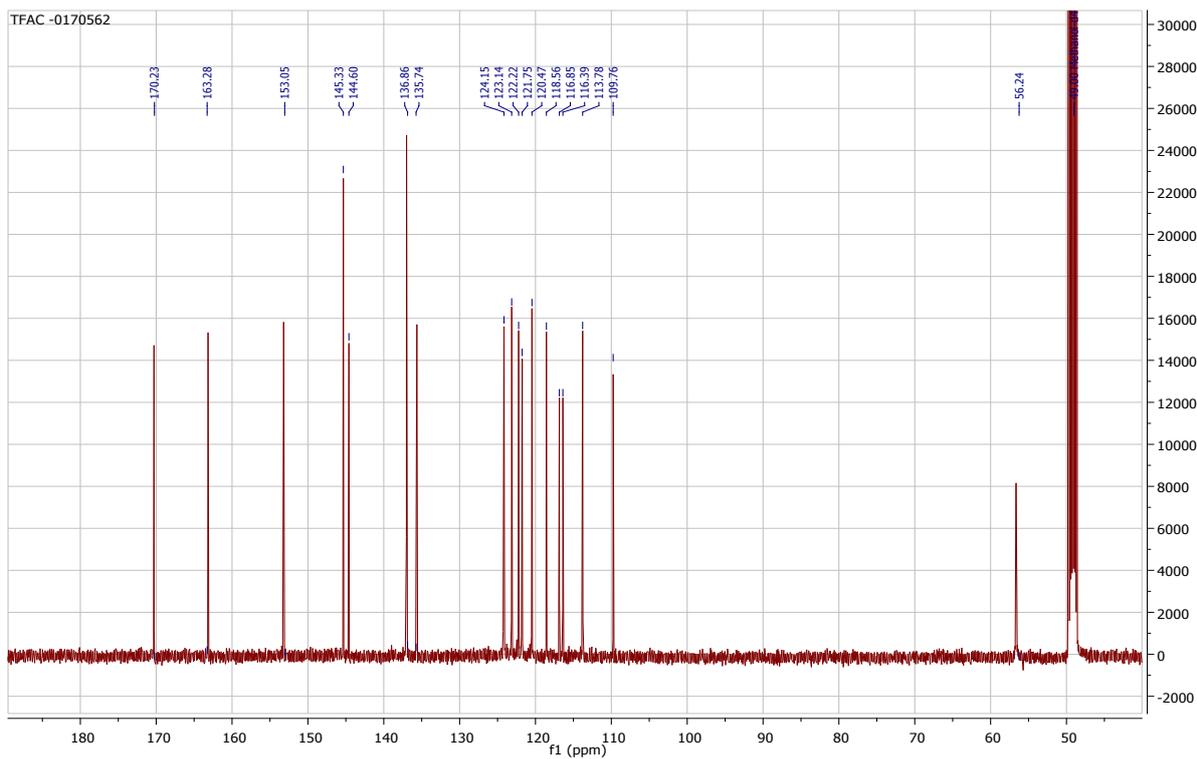


Fig. S4b ^{13}C -NMR spectra of (1).

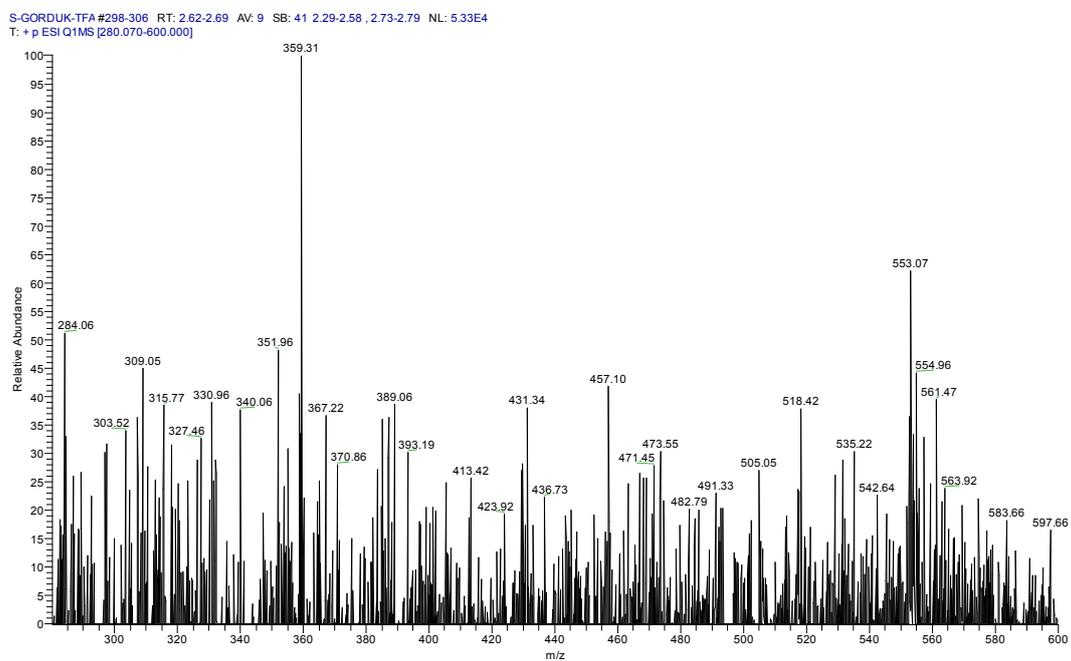


Fig. S4c LC-MS/MS spectra of (1).

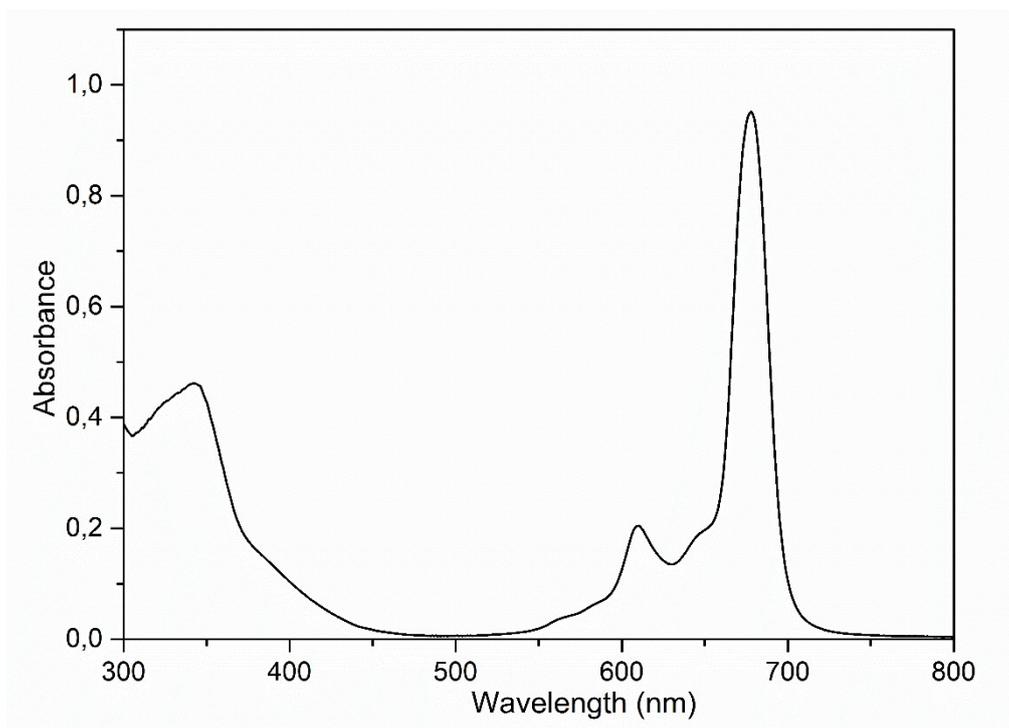


Fig. S5a UV-vis spectrum of (2).

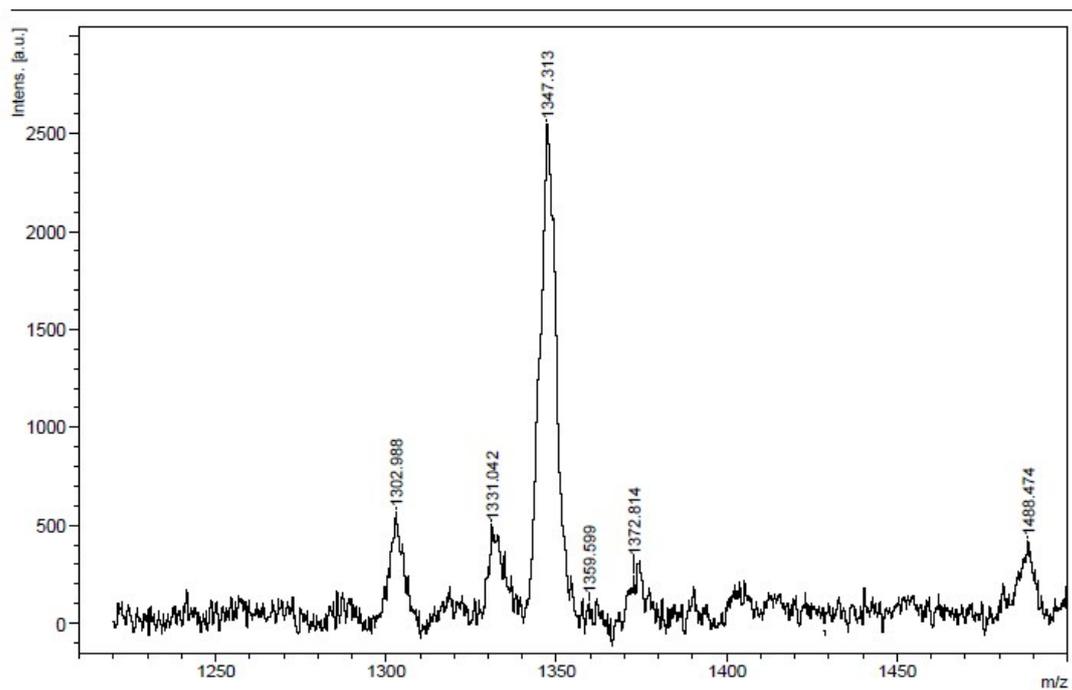


Fig. S5b MALDI-TOF MS spectrum of (2).

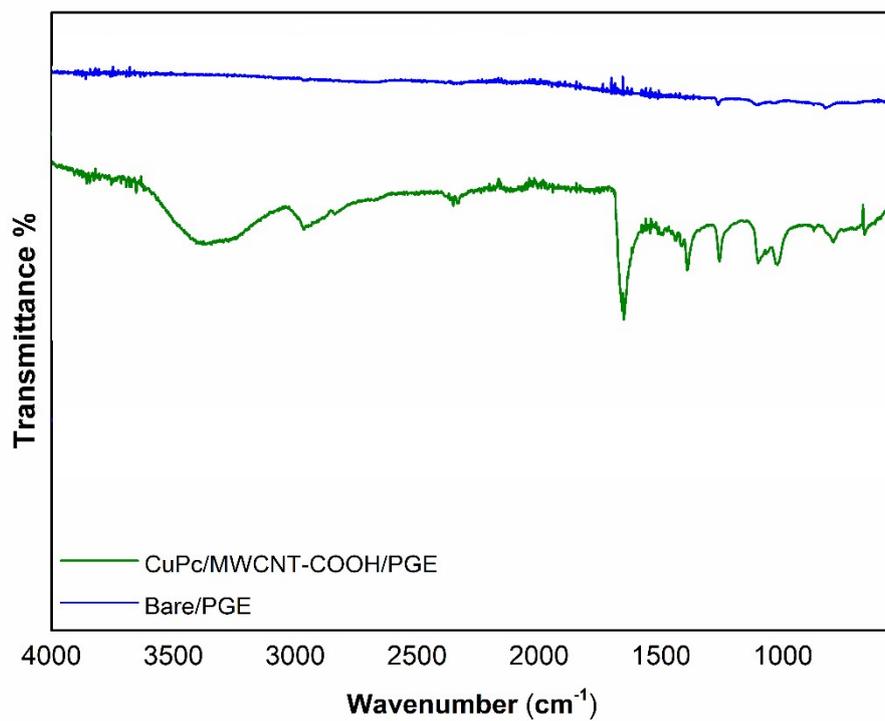


Fig. S6 FT-IR spectra of PGE and CuPc/MWCNT-COOH/PGE.

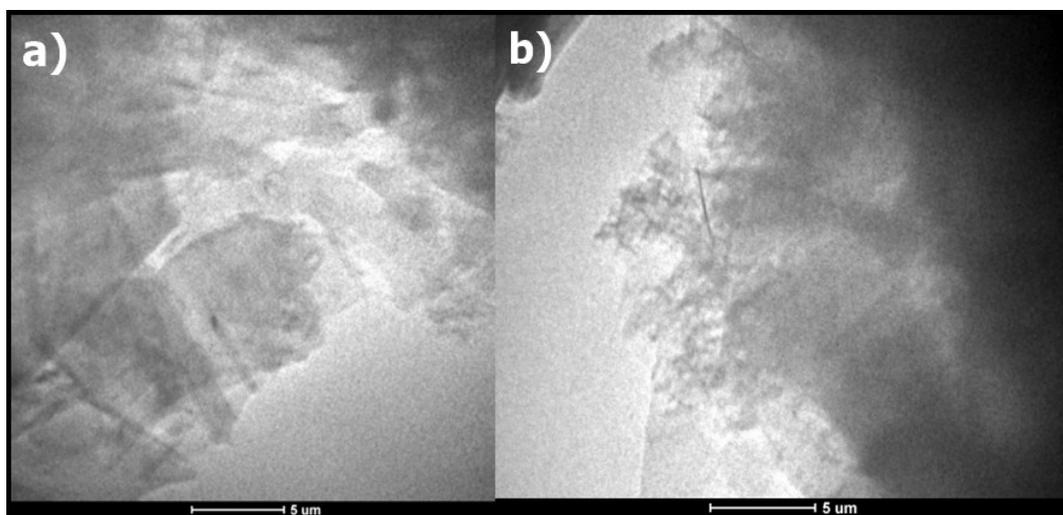


Fig. S7 TEM images **a)** PGE and **b)** CuPc/MWCNT-COOH/PGE

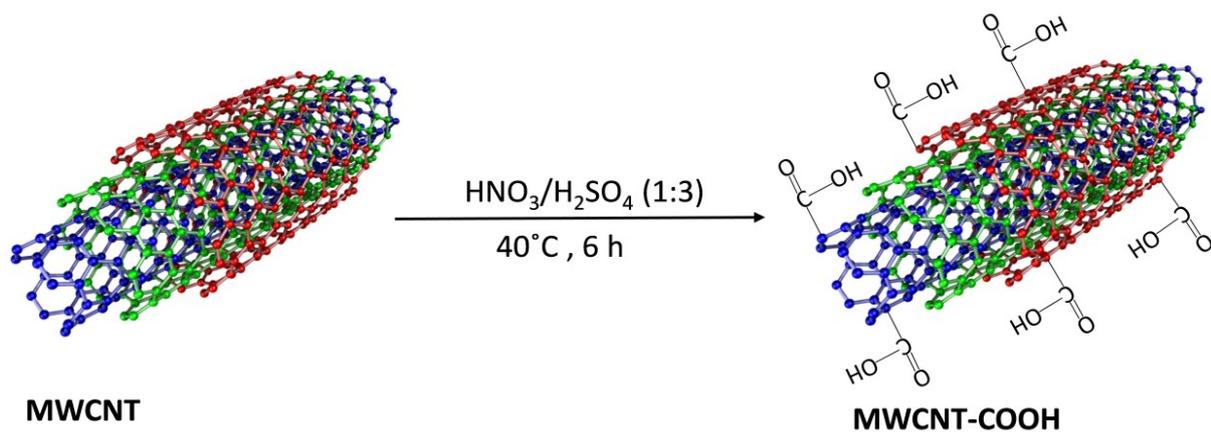


Fig. S8 Chemical preparation of -COOH modified MWCNT.

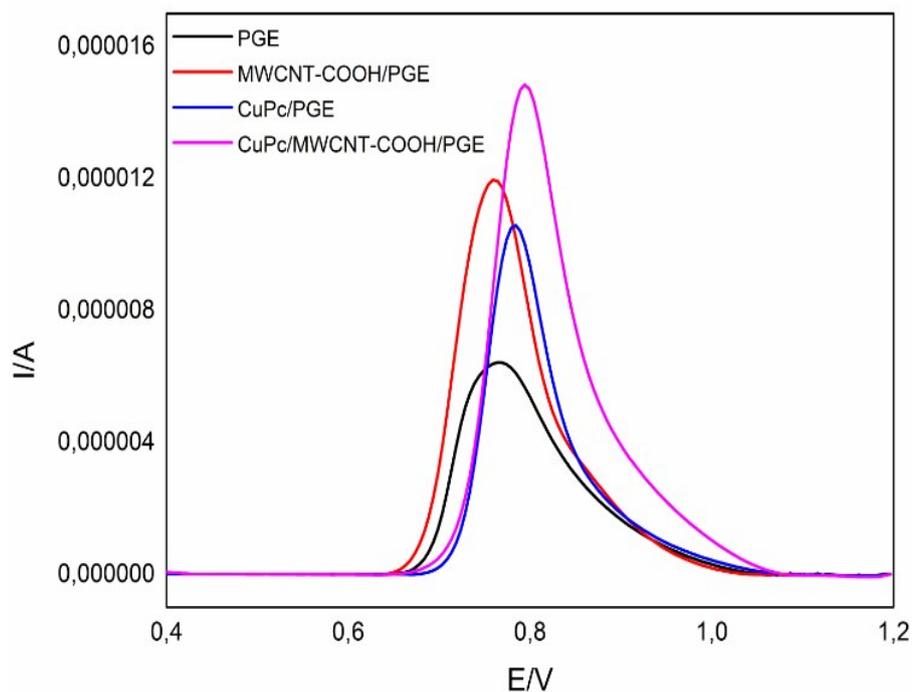


Fig. S9 Differential pulse voltammograms of PGE, CuPc/PGE, MWCNT-COOH/PGE and CuPc/MWCNT-COOH/PGE in 0.1 mM BPA solution (pH 2.0 buffer solution; scan rate 100 mV/s).

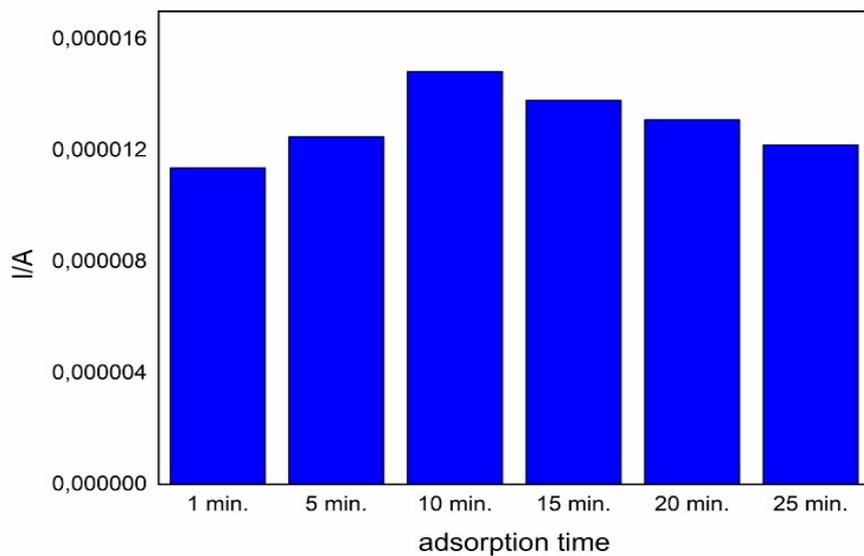
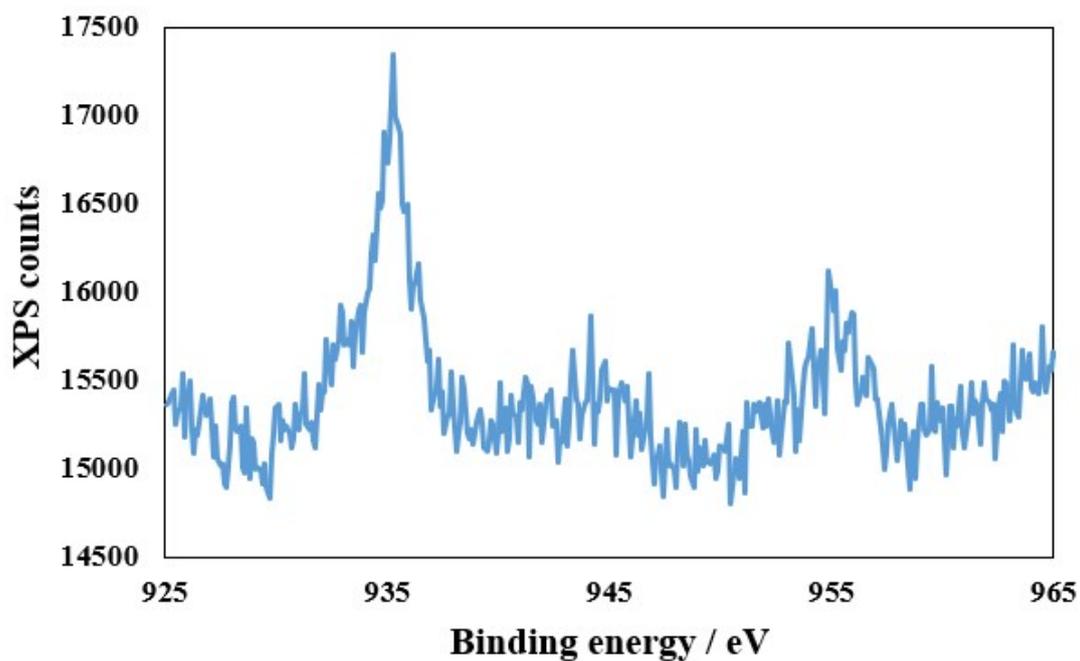


Fig. S10 Oxidation peak currents of CuPc/MWCNT-COOH/PGE obtained at different immersion time in 1.0 mM BPA solution (pH 2.0 phosphate buffer solution).

a)



b)

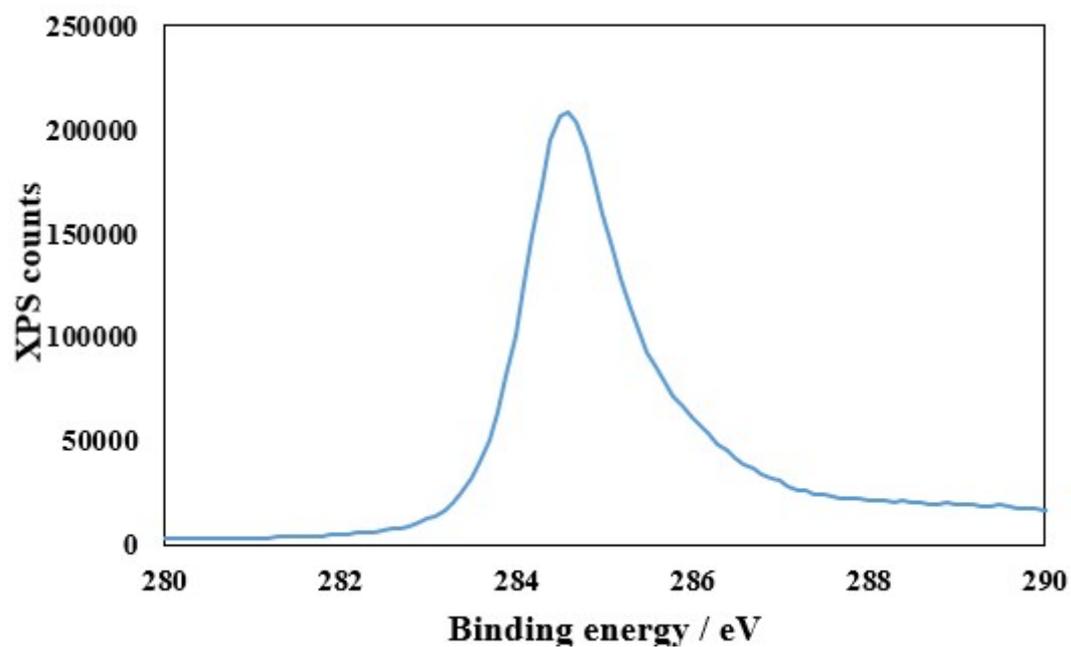
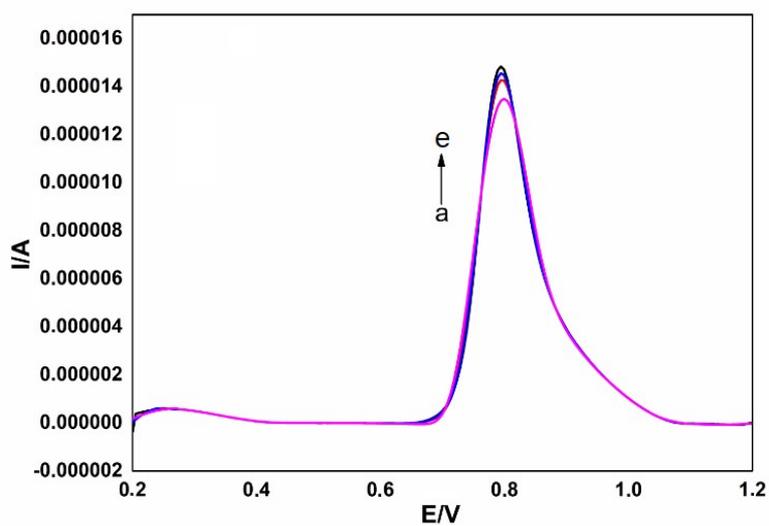


Fig. S11 a) Cu₂p XPS spectra and b) C₁s XPS spectra of CuPc/MWCNT-COOH/PGE

a)



b)

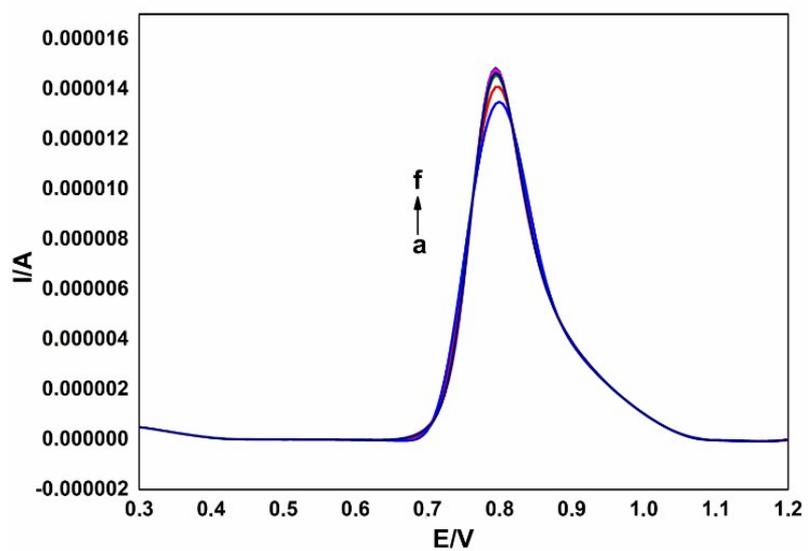


Fig. S12 Differential pulse voltammograms of solutions consisting of interferences **a)** a: methanol, b:Na⁺, c:Cl⁻, d: blank e:SO₄²⁻ ions and **b)** a:Cu²⁺, b:blank, c:Fe³⁺, d:Pb²⁺, e:K⁺, f: Cd²⁺ ions