Electronic Supplementary Information

# Multiwalled carbon nanotubes/tetra-*β*-isoheptyloxyphthalocyanine cobalt(II) composite with high dispersibility for electrochemical detection of ascorbic acid

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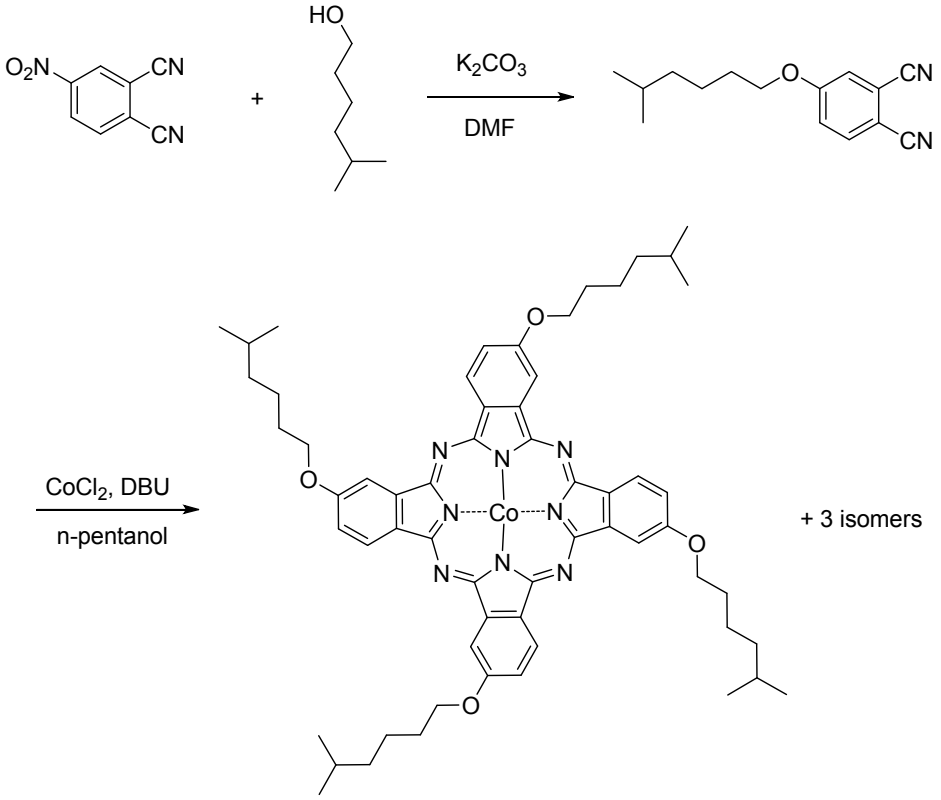
**Experiment details**

***1.1. Materials***

All chemicals and solvents in this work were of analytical grade and were used as-received. 5-Methyl-1-hexanol and 4-nitrophthalonitrile were purchased from Sigma-Aldrich Co. LLC. and Acros Chemical Co., respectively, and were used without further purification. The synthetic scheme of tetra-*β*-isoheptyloxyphthalocyanine cobalt(II) (PcCo) is shown in scheme S1.




Scheme S1. Synthetical scheme of tetra-*β*-isoheptyloxyphthalocyanine cobalt(II)

***1.2. Instrument and methods***

Elemental analyses of C, H and N were carried out on a Vario EL elemental analyzer. $^{1}H$ NMR spectra ($CDCl_3$ solutions) were recorded at 500 MHz on a Bruker Advance AV-500 instrument. EI and MALDI-TOF mass spectra were performed using an Agilent spectrometer (HP 5973N) and a Bruker microflex LT (Bruker Daltonics, Bremen, Germany) mass spectrometer, respectively. UV/Vis absorption spectra were recorded with a Lambda 35 UV/VIS spectrometer (Perkin-Elmer, USA). FT-IR spectra were recorded on a Nicolet FT-IR NEXUS spectrometer (Thermo

Scientific).

### 1.3. Synthesis of 4-isoheptyloxyphthalonitrile

5-Methyl-1-hexanol (5.3 g, 0.045 mol) was dissolved in DMF (60 mL) under a nitrogen atmosphere and 4-nitrophthalonitrile (5.3 g, 0.06 mol) was added to the solution. After stirring for 10min, finely ground anhydrous potassium carbonate ($K_2CO_3$) (10.0 g, 0.072 mol) was added portion-wise over 3 d with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 5 days. Then the solution was poured into ice-water (100 mL) and then was extracted with $CHCl_3$. The organic extracts were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to give yellow oil. After the crude product was purified by silica gel chromatography with an eluent $CHCl_3/CH_3OH$ (20:1), and 4-isoheptyloxyphthalonitrile was obtained. Yield: 4.03 g (55%). Anal. Calcd (found) for $C_{15}H_{18}N_2O$: C, 74.35 (74.28); H, 7.49 (7.57); N, 11.56 (11.61). $^1H$ NMR ($CDCl_3$, TMS, δ ppm): 0.93 (s, 6H, $CH_3$), 1.27 (m, 2H, $CH_2$), 1.30 (m, 2H, $CH_2$), 1.64 (m, 1H, CH), 1.68 (m, 2H, $CH_2$), 4.31 (t, 2H, $CH_2$), 7.19 (d, 1H), 7.23 (d, 1H), 7.67 (t, 1H). FT-IR spectra (KBr pellets) ν: 3082, 2961, 2937, 2874, 2230, 1597, 1560, 1491, 1320, 1253, 1092, 980, 836, 523 $cm^{-1}$. EI-MS Calcd (Found): m/z= 242(242)[$M^+$].

### 1.4. Synthesis of tetra-*β*-isoheptyloxyphthalocyanine cobalt(II) (PcCo)

4-isoheptyloxyphthalonitrile (0.54 g, 2.25 mmol), anhydrous $CoCl_2$ ( 0.2 g, 1.5 mmol) and *n*-pentanol (12 mL) were placed in a round-bottom flask in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.8 mL) under a nitrogen atmosphere and held at reflux temperature for 12 h. After cooling to room temperature, the solvent was eliminated by vacuum distillation. The crude product was purified by silica gel column chromatography using toluene as eluent to give blue crystals of tetra-β-isoheptyloxyphthalocyanine cobalt(II) (PcCo). Yield: 0.18 g (32%). Anal. Calcd (found) for $C_{60}H_{72}N_8O_4Co$: C, 70.09 (70.02); H, 7.06 (6.99); N, 10.90 (10.84). Electronic absorption spectrum (UV-Vis) in $CH_2Cl_2$: $\lambda_{max}$ (nm) = 669, 605. FT-IR spectra (KBr pellets) ν: 2962, 2934, 2874, 1611, 1526, 1468, 1416, 1345, 1268, 1236,

1123, 1098, 1061, 974, 819, 751 $cm^{-1}$. MALDI-MS Calcd (Found): *m/z*= 1027.50(1027.42) [$M^+$]. 2055.00(2054.87)[$2M^+$], 3082.50(3082.97)[$3M^+$].

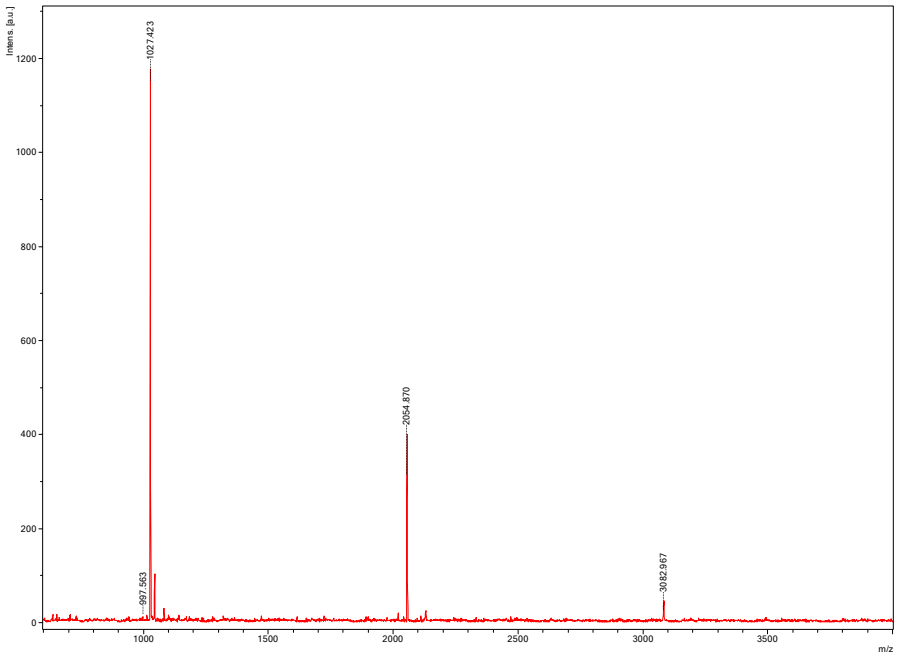



**Fig. S1** MALDI mass spectra of tetra-*β*-isoheptyloxyphthalocyanine cobalt(II)

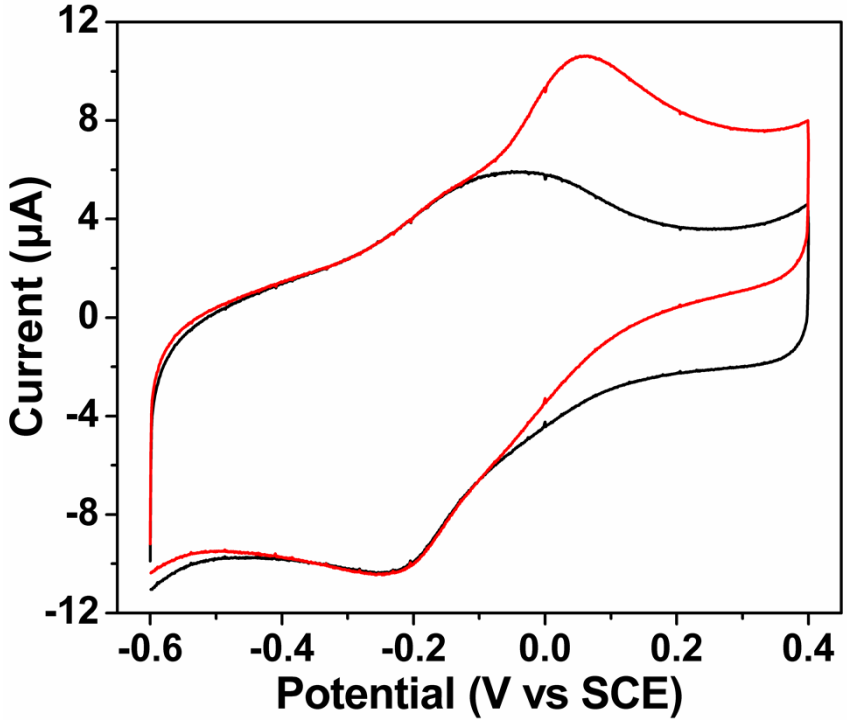



**Fig. S2** CVs of aMWCNT/PcCo/GCE in 0.1 M PBS (pH = 7.0) containing 0 mM (black line) and 1.0 mM AA (red line), respectively, scan rate: 10 $mV \cdot s^{-1}$.

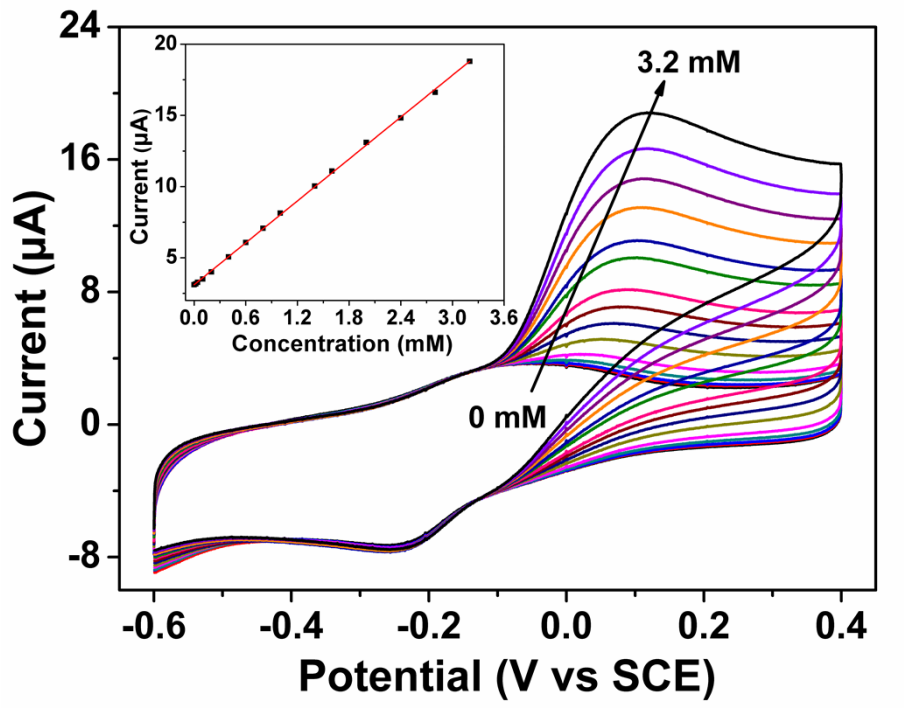



**Fig. S3** CVs of aMWCNT/PcCo/GCE in 0.1 M PBS (pH = 7.0) with different AA concentrations (0, 0.02, 0.04, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 1.6, 2.0, 2.4, 2.8 and 3.2 mM), scan rate: 10 $mV \cdot s^{-1}$. Inset image shows the calibration linear relationship of currents *versus* the AA concentration.

**Table S1** Comparison of the analytical performance of different AA biosensors

| electrode | linear range (μM) | limit detection (μM) | overpotential (mV) | ref |
|---|---|---|---|---|
| GDSP/CPE[a,1] | 150-8000 | 3.775 | 400 | 1 |
| PANI/SPCE[b,2] | 30-270 | 30 | 400 | 2 |
| PEDOT/Ni-Si MCP[c,1] | 20-1400 | 10 | 10 | 3 |
| PANI-ABSA/GCE[d,2] | 35-175 | 7.5 | 150 | 4 |
| PANI-GO/GCE[e,2] | 25-200 | 20 | 514 | 5 |
| TMP/FCs/GCE[f,1] | 110-5000 | 44 | 350 | 6 |
| Pt/MWCNT/GCE | 24.5-765 | 20 | 160 | 7 |
| MWCNT/PNB-3/GCE[h,2] | 50-1000 | 10.8 | 0.0 | 8 |
| CoTNPPc-MWNTs/GCE[f,2] | 10-1600 | 5 | 215 | 9 |
| $[Ni(phen)_2]^{2+}$/MWCNT/GCE[g,2] | 10-630 | 4 | 310 | 10 |
| aMWCNT/PcCo/GCE[1] | 10-1200 | 4.0 | 50.0 | this work |

Remark: a) gold decorated $SiO_2$@polyaniline core–shell modified carbon paste electrode; b) polyaniline modified screen-printed carbon electrode; c) Poly(3,4-ethylenedioxythiophene)-modified Ni/silicon microchannel plate electrode; d) polyaniline nano-networks/p-aminobenzene sulfonic acid modified GCE; e) polyaniline-graphene oxide fibrous nanocomposites; f) trimethylpropylammonium groups/sublimed ferrocene modified GCE; h) multi-walled carbon nanotubes/poly (Nile blue A) modified GCE; f) cobalt(II) tetra-neopentyloxy

phthalocyanine/MWCNT; g) nickel (II)-bis(1,10-phenanthroline) modified MWCNT; 1) pH = 7.0; 2) acid condition.

## References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