

Electronic Supplementary Information

***p*-Aminophenol sensor based on tetra- β -[3-(dimethylamine)phenoxy] phthalocyanine cobalt(II)/multiwalled carbon nanotube hybrid**

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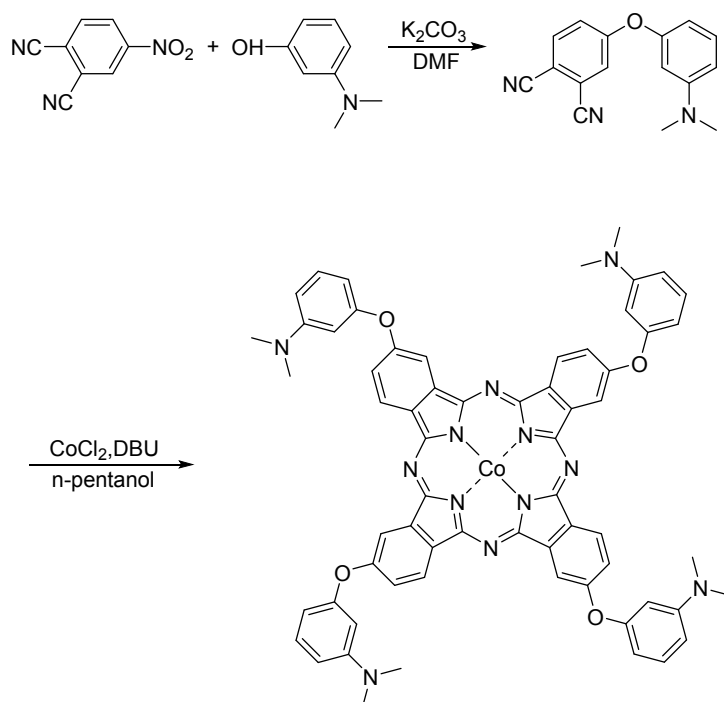
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Experiment details

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 used without further purification. The synthetic scheme of tetra- β -[3-(dimethylamino)phenoxy] phthalocyanine cobalt(II) (aPcCo) is shown in scheme S1.



Scheme S1. Synthetical scheme of tetra- β -[3-(dimethylamino)phenoxy] phthalocyanine cobalt(II)

1.2. Instrument and methods

Elemental analyses of C, H and N were carried out on a Vario EL elemental analyzer. 1H 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-[3-(dimethylamino)phenoxy] phthalonitrile

4-Nitrophthalonitrile (6.92 g, 0.04 mol) was dissolved in 150 mL of dry DMF at room temperature, and 3-dimethylaminophenol (6.6 g, 0.048 mol) was added. After stirring for 15 min, 13.07 g of finely ground anhydrous K_2CO_3 (0.094 mol) was added and stirred under nitrogen at room temperature for 96 h. Then, the mixture was poured into 200 mL of ice-water, filtered and the filter residue to dryness. After the crude product was purified by silica gel chromatography with an eluent CH_2Cl_2 , and 4-[3-(dimethylamino)phenoxy]phthalonitrile was obtained. Yield: 8.53g (81%). 1H NMR ($CDCl_3$, TMS, δ ppm): 2.97 (s, 6H, CH_3), 6.34 (t, 1H), 6.61 (d, 1H), 6.63 (t, 1H), 7.23 (t, 1H), 7.26 (t, 1H), 7.29 (t, 1H), 7.70(s, 1H).

1.4. Synthesis of tetra- β -[3-(dimethylamine)phenoxy] phthalocyanine cobalt(II)

A mixture of compound 4-[3-(dimethylamino)phenoxy] phthalonitrile (1.84 g, 6.98 mmol), anhydrous $CoCl_2$ (0.46 g, 3.57 mmol), catalytic amount of (1 mL) DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (1 mL) of 25 mL n-pentanol was held at reflux temperature for 12 h in around-bottom flask under nitrogen. After cooling to room temperature the solvent was eliminated by vacuum distillation. The crude product was purified by silica gel column chromatography using carbon tetrachloride/acetone as (10:1) eluent to give blue crystals of tetra- β -[3-(dimethylamine)phenoxy] phthalocyanine cobalt(II). Yield: 0.72 g (37%). Electronic absorption spectrum (UV-Vis) in DMF: λ_{max} (nm) =666nm. IR, ν_{max} (cm^{-1}): 1266 cm^{-1} , 1471 cm^{-1} , 1500 cm^{-1} , 1572 cm^{-1} , 1605 cm^{-1} , 1724 cm^{-1} , 2871 cm^{-1} , 2927 cm^{-1} . MALDI-MS Calcd (Found): $m/z=1111.36$ (1111.21) [M^+].

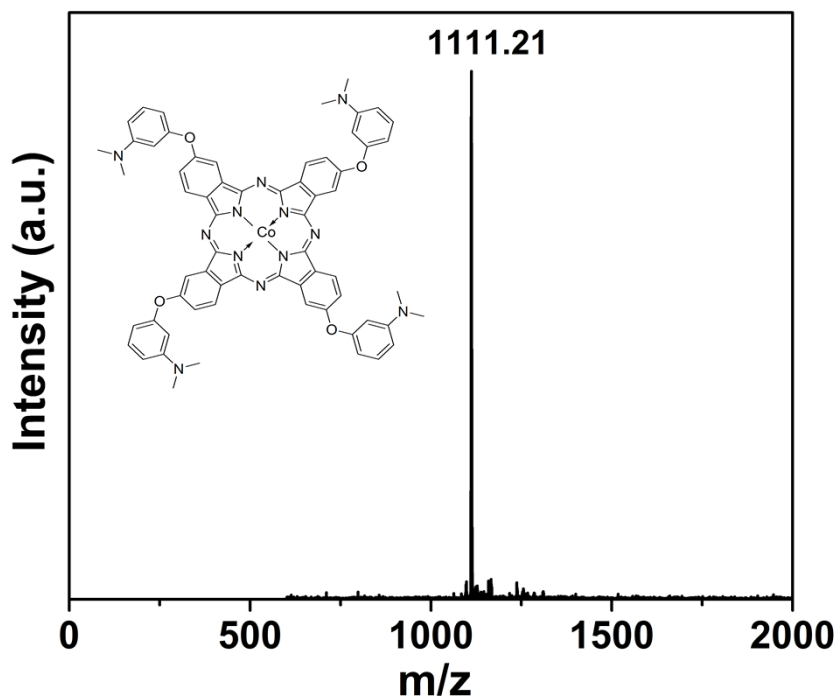


Fig. S1 MALDI mass spectra of tetra- β -[3-(dimethylamino)phenoxy] phthalocyanine cobalt(II)

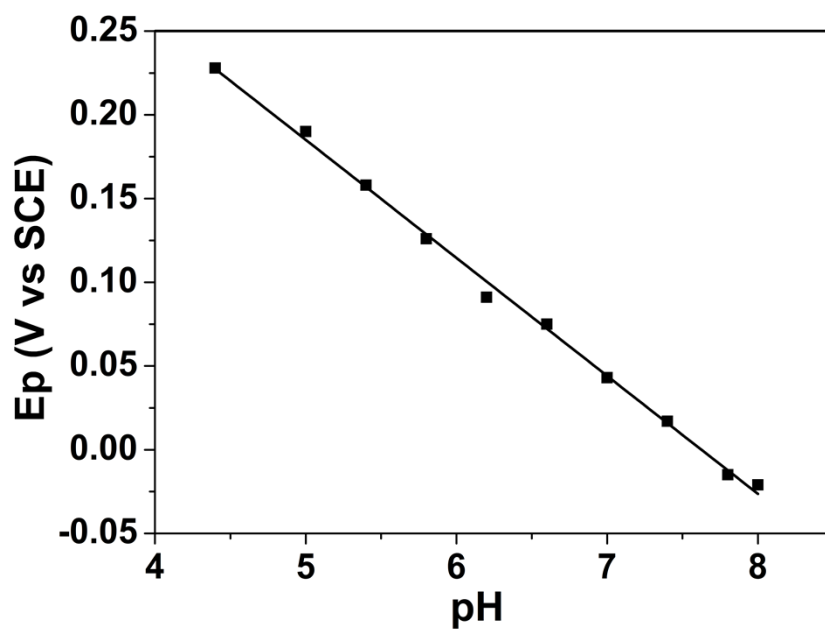


Fig. S2 The relation between the reduction peak potentials and the pH value.

Table S1 Comparison of the analytical performance of different 4-AP sensors

Electrode	Linear range (μM)	Limit detection (μM)	Technique	Ref.
SWNTs/POAPE/GCE ^a	0.2-100	0.06	DPV	1
GR-PANI/GCE ^b	0.2-20 20-100	0.065	DPV	2
PEDOT/GCE ^c	4.0-320	1.2	DPV	3
NH ₂ -SBA-15/CPE ^d	0.1-12	0.02	DPV	4
Graphene-Nafion/GCE ^e	0.5-200	0.051	DPV	5
Hemin-MIP/GCE ^f	10-90	3	Amperometric response	6
Graphene-chitosan/GCE ^g	0.2-550	0.057	DPV	7
AuNPs/SDS-LDH/GCE ^h	0.5-200	NR ¹	DPV	8
aPcCo/CNT/GCE	0.5-300 300-800	0.3	DPV	this work

Remark: a) Single-wall carbon nanotubes/poly(4-aminopyridine) modified GCE; b) Graphene–polyaniline modified GCE; c) Poly(3,4-ethylenedioxythiophene) modified GCE; d) Aminophenol isomers based on functionalized SBA-15 mesoporous silica modified carbon paste electrode; e) Nafion–graphene composite film modified GCE; f) The hemin-based molecularly imprinted polymer grafted onto a glassy carbon electrode; g) Graphene-chitosan composite film modified GCE; h) Gold nanoparticles and an organophilic layered double hydroxide modified GCE. 1) Not reported

Table S2 Electroanalytical application of aPcCo/CNT/GC electrode for 4-AP determination in real samples

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%) (n=3)
1	5	4.7	94	3.22
2	10	9.5	95	2.47
3	15	16.2	108	2.73
4	20	21.5	107.5	2.61

References

- [1] Z. H. Wang, H. F. Zhu, H. Zhang, G. Q. Gao, Z. D. Sun, H. P. Liu and X. L. Zhao, *Electrochim. Acta*, 2009, **54**, 7531-7535.
- [2] Y. Fan, J. H. Liu, C. P. Yang, M. Yua and P. Liu, *Sens. Actuators, B*, 2011, **157**, 669-674.
- [3] S. Mehretie, S. Admassie, T. Hunde, M. Tessema and T. Solomon, *Talanta*, 2011, **85**, 1376-1382.
- [4] S. Duan, X. Zhang, S. Xu and C. L. Zhou, *Electrochim. Acta*, 2013, **88**, 885-891.
- [5] H. Filik, G. Cetintas, S. N. Koc, H. Gulce and I. Boz, *Russ. J. Electrochem.*, 2014, **50(3)**, 243-252.
- [6] J. D. M. Neto, W. D. R. Santos, P. R. Lima, S. M. C. N. Tanaka, A. A. Tanaka, L. T. Kubota, *Sens. Actuators, B*, 2011, **152**, 220-225.
- [7] H. S. Yin, Q. Ma, Y. L. Zhou, S. Y. Ai and L. S. Zhu, *Electrochim. Acta*, 2010, **55**, 7102-7108.
- [8] H. S. Yin, K. Shang, X. M. Meng and S. Y. Ai, *Microchim. Acta*, 2011, **175**, 39-46.