

**Phthalocyanine sensor array based on sensitivity and current changes
for highly sensitive identification of three toxic gases in ppb levels**

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Experimental section

1.1 Materials

All of reagents were purchased from Aldrich and were not further processed during use unless otherwise noted. Solvent removal of water follows the general method. Column chromatography was carried out on silica gel (300–400 mesh) with the indicated eluents. Target compounds **1-4** were prepared according to the similar method in the literature¹.

1.2 Measurements and characterizations

UV-vis absorption spectra were recorded on a Hitachi U-3900 spectrophotometer. MALDI-TOF mass spectrum was collected by a Bruker BIFLEX III ultra-high-resolution. Electrochemical measurement was tested with a BAS CV-50W voltammetric analyzer. The electrolysis cell is a three-electrode system including three inlets for the glassy carbon disk (working electrode, 3.0 mm in diameter), the Pt (counter electrode), and the reference electrode was Ag/Ag⁺ (0.01 M AgNO₃ in chromatographically pure acetonitrile solution), which was combined to the solution by a Luggin capillary, whose tip was set close up to the glassy carbon electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fc⁺/Fc) couple. Typically, a 0.1 mol L⁻¹ solution of [Bu₄N][ClO₄] in DMF containing 0.5 mmol L⁻¹ of sample was purged with nitrogen for 10 min, then the voltammogram was recorded at room temperature. X-ray diffraction (XRD) experiments were carried out on a Bruker D8 FOCUS X-ray diffractometer with copper (K α) radiation ($\lambda = 1.5406$ Å). Scanning electron microscope (SEM) images were collected under ambient conditions using the tapping mode with a NanoscopeIII/Bioscope scanning probe microscope from digital instruments. The fundamental electrical and sensor measurements were performed by using a Keysight B2910A precision source/measure unit with an incorporated direct current voltage

supply. The electrometer was controlled by Quick IV Measurement Software. Current–voltage (I–V) curves were registered in the voltage range of $-10 \sim +10$ V. For gas sensing experiments, the samples were constantly polarized at $+10$ V. Repeating all experiments to ensure repeatable results. Conductivity, σ , can be calculated by following equation based on Current–voltage (I–V) curves, $\sigma = dI / ((2n-1)LhV)$, where d is the interelectrode spacing, I the current, n the number of electrode digits, L the overlapping length of the electrodes, and h the electrode thickness as the film thickness exceeds that of the ITO electrodes in present case, V is the voltage. Sensing experiments were carried out in a cuboid Teflon sensor chamber of 11.5 (length) x 2.5 (width) x 1.5 (height) cm^3 . The desired NO_2 , NH_3 or H_2S concentration was produced by diluting a mixture of NO_2/N_2 (20 ppm NO_2 , from Qingdao Ludong Gas Co., Ltd, China), NH_3/N_2 (500 ppm NH_3 , from Qingdao Ludong Gas Co., Ltd, China) or $\text{H}_2\text{S}/\text{N}_2$ (50 ppm H_2S , from Qingdao Ludong Gas Co., Ltd, China) with dry N_2 using two CS200 Mass Flow Controllers (total mass flow: $0.1 \text{ L} \cdot \text{min}^{-1}$ for NO_2 , NH_3 or H_2S and $2 \text{ L} \cdot \text{min}^{-1}$ for diluent gas N_2 , unless otherwise stated, nitrogen is dry gas), respectively. In the present case, dry N_2 (purity: 99.99%) gas was selected as the carrier gas during all the sensing measurements.

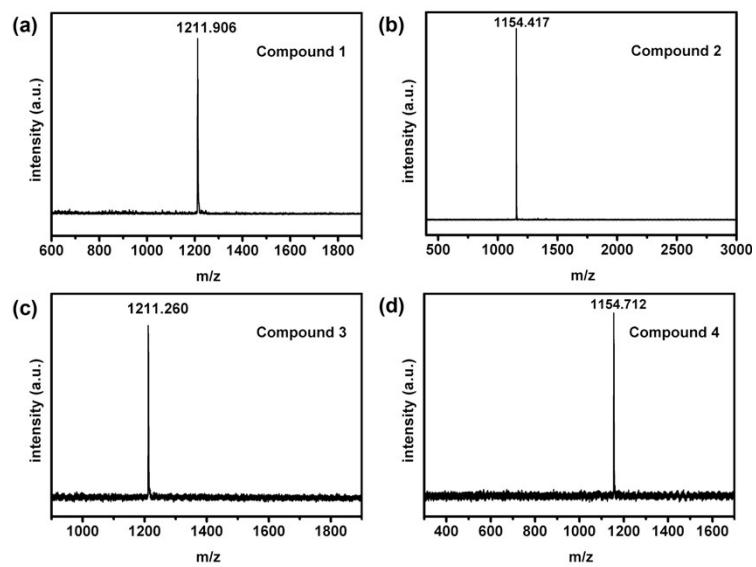
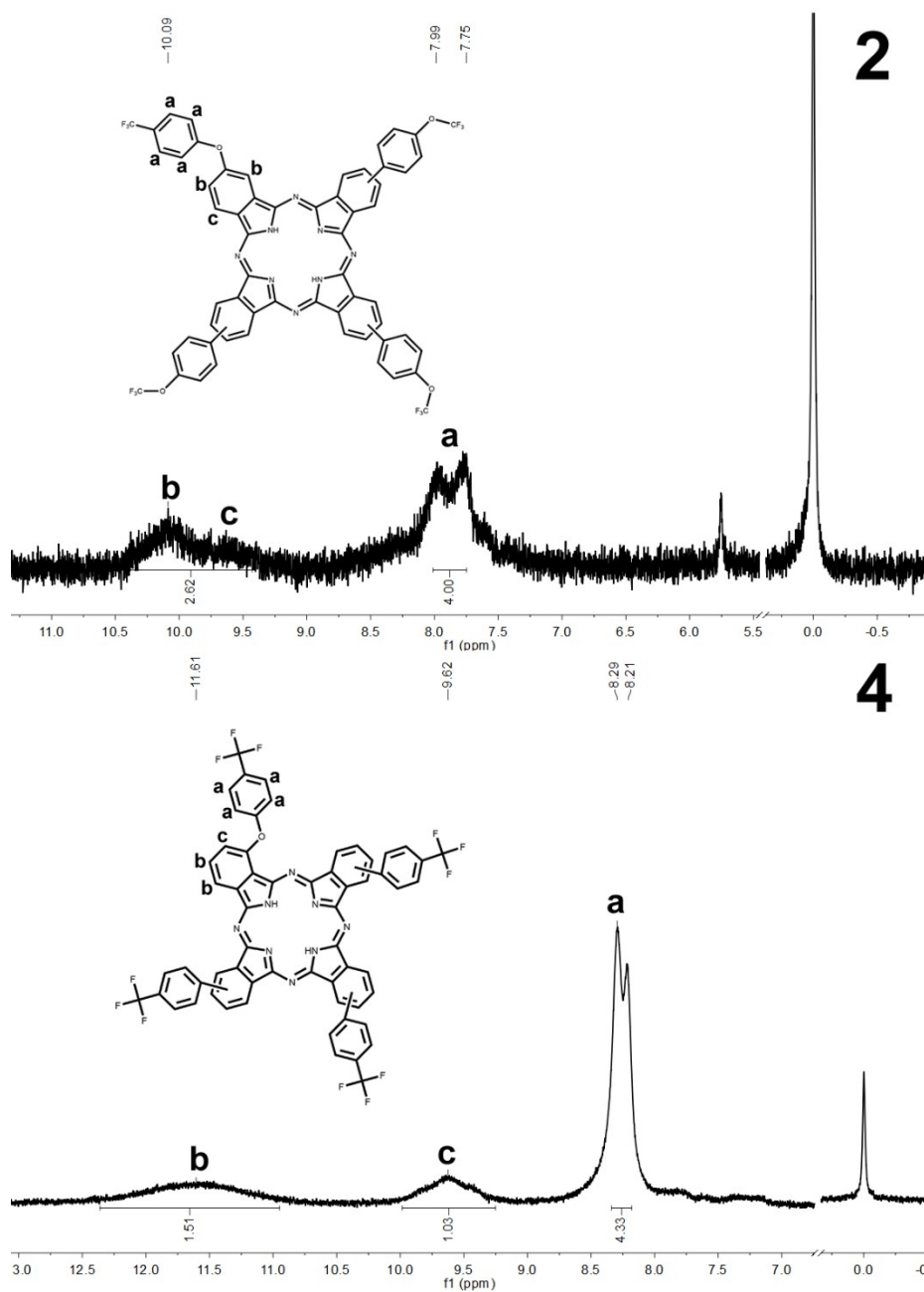


Fig.S1. MALDI-TOF mass spectrum of CoPc[β -O(4-CF₃-Ph)₄] (a), H₂Pc[β -O(4-CF₃-Ph)₄] (b), CoPc[α -O(4-CF₃-Ph)₄] (c) and H₂Pc[α -O(4-CF₃-Ph)₄] (d).



2: ¹H NMR (400 MHz, (CD₃)₂SO): δ 7.99, 7.75 (d, 16H, a), 9.65, 10.09 (br, 12H, b, c)

4: ¹H NMR (400 MHz, (CD₃)₂SO): δ 8.29, 8.21 (d, 16H, a), 9.62 (br, 4H, c), 11.61 (br, 8H, b)

Fig.S2. ¹HNMR of H₂Pc[β-O(4-CF₃-Ph)₄] (**2**) and H₂Pc[α-O(4-CF₃-Ph)₄] (**4**)

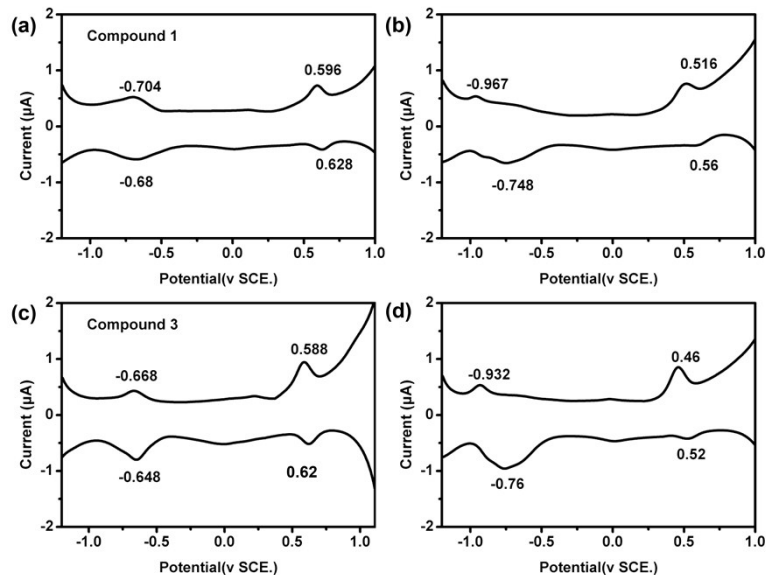


Fig.S3. Differential pulse voltammetry (DPV) of CoPc[β -O(4-CF₃-Ph)₄] (a), H₂Pc[β -O(4-CF₃-Ph)₄] (b), CoPc[α -O(4-CF₃-Ph)₄] (c) and H₂Pc[α -O(4-CF₃-Ph)₄] (d) in DMF containing 0.1 mol L⁻¹ [Bu₄N][ClO₄] vs SCE.

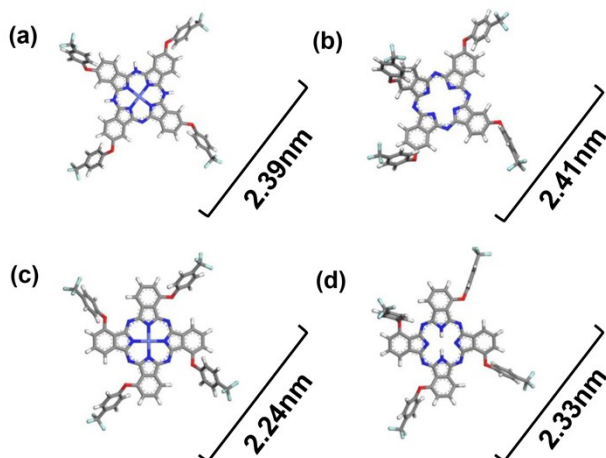


Fig.S4. The molecular dimension with a typical D_{4h} symmetry of CoPc[β -O(4-CF₃-Ph)₄] (a) : 2.39 nm; H₂Pc[β -O(4-CF₃-Ph)₄] (b) : 2.41 nm; CoPc[α -O(4-CF₃-Ph)₄] (c):2.24 nm; H₂Pc[α -O(4-CF₃-Ph)₄] (d) : 2.33 nm. (In fact, each of four compounds should contain four isomers with D_{4h} , D_{2h} , C_{2v} and C_s symmetry).

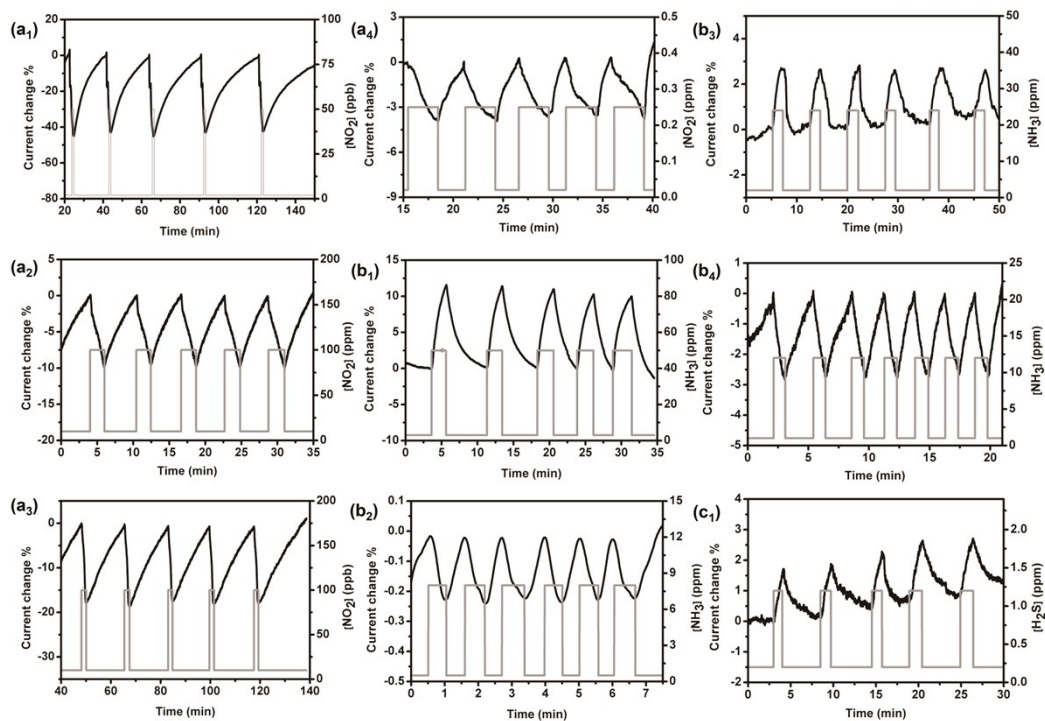


Fig.S5. Reproducibility test to NO₂, NH₃, H₂S for the devices of 1-4. a₁-a₄) Response of 1-4 to 0.04 ppm, 1.1 ppm, 1.0 ppm, 0.5ppm NO₂, respectively; b₁-b₄) Response of 1-4 to 96 ppm, 1.6 ppm, 48 ppm, 18 ppm NH₃, respectively; c₁) Response of 1 to 1.6 ppm H₂S.

Table S1. Half-wave redox potentials of **1-4** (V vs SCE) in DMF containing 0.1 mol L⁻¹ [Bu₄N][ClO₄] together with the HOMO and LUMO.

Compound	Oxd ₁ /V	Red ₁ /V	E _{HOMO} ^a /eV	E _{LUMO} ^a /eV	ΔE _{1/2} ^b /V
1	0.61	-0.69	-5.48	-4.17	1.31
2	0.54	-0.86	-5.40	-4.01	1.39
3	0.60	-0.66	-5.47	-4.21	1.26
4	0.49	-0.85	-5.36	-4.02	1.34

^a Calculated from empirical formula of HOMO = -(Oxd₁ + 4.44 eV); LUMO = -(Red₁ + 4.44eV).

^b ΔE_{1/2} = Oxd₁-Red₁, i.e. the HOMO LUMO gap of corresponding molecule.

Table S2. NO₂ detection properties for films of some representative phthalocyanine-based compounds at the room temperature.

Compounds	p/n-type (NO ₂)	LOD (ppm)	Method	Sensitivity (%ppm ⁻¹)	Range (ppm)	Ref.
CoPc[β-O(4-CF ₃ -Ph) ₄] (1)	n	0.003	SA ^[a]	616	0.02-0.1	-
H ₂ Pc [β-O(4-CF ₃ -Ph) ₄] (2)	n	0.03	SA	10.8	0.5-0.9	-
CoPc[α-(4-CF ₃ -Ph) ₄] (3)	n	0.198	SA	19.9	0.2-1	-
H ₂ Pc[α-(4-CF ₃ -Ph) ₄] (4)	n	0.25	SA	4.4	0.5-1.25	-
(Pc)Eu{Pc[(OC ₂ H ₄) ₃ OCH ₃] ₈ }Eu{Pc[(OC ₂ H ₄) ₃ OCH ₃] ₈ }	n	0.05	QLS ^[b]	60	0.05-0.5	2
EuPc [Pc(OH) ₈]	n	0.05	QLS	-	0.05-0.25	3
Eu[Pc(OH) ₈] ₂	n	0.5	QLS	-	0.5-1.5	3
Eu ₂ (Pc) ₂ (TPyP)	n	0.4	QLS	32	0.4-0.9	4
H ₂ Pc(OCH ₂ CF ₃) ₄	n	0.1	QLS	7.5	0.1-0.5	5
Eu ₂ [Pc(OCH ₂ CF ₃) ₄] ₃ (× phase)	n	0.02	QLS	412	0.02-0.06	6
H ₂ [Pc(OCH ₂ C ₃ F ₇) ₈]	n	0.05	DC	30.4	0.05-0.9	7
Zn[Pc(OCH ₂ C ₃ F ₇) ₈]	n	0.1	DC	24.4	0.1-0.75	7
H ₂ [Pc(OCH ₂ (CF ₂) ₆ CF ₃) ₄]	n	0.1	DC	7.54	0.1-1	8
H ₂ [Pc(OCH ₂ (CF ₂) ₆ CF ₃) ₄]	n	0.1	VD ^[c]	12.1	0.1-1	8
[{Pc(OC ₄ H ₉) ₈ } ₈ Y{BiPc(OC ₄ H ₉) ₁₂ } ₈ Y{Pc(OC ₄ H ₉) ₈ } ₈]	n	0.5	QLS	-	0.5-3	9
H ₂ {Pc(15C5) ₃ [(OC ₈ H ₁₇) ₂]} ₈ /CdS	n	0.05	QLS	20	0.5-2.5	10
H ₂ {Pc(15C5) ₃ [(OC ₈ H ₁₇) ₆]} ₈ /CdS	n	0.05	QLS	19.6	0.5-2.5	10
H ₂ [Pc(OC ₈ H ₁₇) ₈]/CdS	n	0.05	QLS	5.6	0.5-2.5	10
(TPyP)Eu ₂ [Pc(OC ₄ H ₉) ₈] ₂	n	0.4	QLS	-	0.4-0.9	11
Eu ₂ [PcS(C ₆ H ₁₃) ₈] ₃	n	0.1	QLS	23.4	0.1-0.5	12
[Pc(SC ₆ H ₁₃) ₈] ₂ Eu ₂ [BiPc(SC ₆ H ₁₃) ₁₂] ₂ Eu ₂ [Pc(SC ₆ H ₁₃) ₈] ₂	n	0.1	QLS	46.7	0.1-0.5	12
[Pc(SC ₆ H ₁₃) ₈] ₈ Eu[Pc(SC ₆ H ₁₃) ₈] ₈ Cd[Pc(SC ₆ H ₁₃) ₈] ₈ Eu[Pc(SC ₆ H ₁₃) ₈] ₈	n	0.25	QLS	11.6	1.25-2.5	13
Gd ₂ [Pc(OPhF) ₈] ₃	n	0.05	QLS	6.4	0.05-0.25	14
Tb ₂ [Pc(OPhF) ₈] ₃	n	0.05	QLS	11	0.05-0.25	14

^a SA: Self-assembly; ^b QLS: quasi-Langmuir-Shäfer; ^c VD: vacuum deposited

Table S3. NH₃ detection properties for films of some representative phthalocyanine-based compounds at the room temperature.

Compounds	p/n-type (NH ₃)	LOD (ppm)	Method	Sensitivity (%ppm ⁻¹)	Range (ppm)	Ref.
CoPc[β-O(4-CF ₃ -Ph) ₄] (1)	n	0.42	SA	0.17	4-24	-
H ₂ Pc [β-O(4-CF ₃ -Ph) ₄] (2)	p	4	SA	0.015	4-24	-
CoPc[α-(4-CF ₃ -Ph) ₄] (3)	n	2.4	SA	0.052	4-28	-
H ₂ Pc[α-(4-CF ₃ -Ph) ₄] (4)	p	5.1	SA	0.11	6-30	-
(Pc)Eu{Pc[(OC ₂ H ₄) ₃ OCH ₃] ₈ }Eu{Pc[(OC ₂ H ₄) ₃ OCH ₃] ₈ }	p	5	QLS	0.17	5-25	2
EuPc[Pc(OH) ₈]	p	2.5	QLS	-	2.5-12.5	3
Eu ₂ (Pc) ₂ (TPyP)	p	5	QLS	0.04	5-30	4
Ho(Pc)[Pc(OPh) ₈]	p	15	QLS	0.0018	200-800	15
Ho[Pc(OPh) ₈] ₂	n	15	QLS	0.0089	200-800	15
Eu ₂ (Pc) ₂ [T(OH)PP]	P	15	QLS	0.0046	200-800	16
Eu ₂ (Pc) ₂ [cis-T(OH) ₂ PP]	p	15	QLS	0.0082	200-800	16
Eu ₂ (Pc) ₂ [trans-T(OH) ₂ PP]	p	15	QLS	0.0026	200-800	16
CoPc	p	25	VD	0.15	25-300	17
s-CoPc	p	25	VD	0.071	25-300	17
[{Pc(OC ₄ H ₉) ₈ }Y{BiPc(OC ₄ H ₉) ₁₂ }Y{Pc(OC ₄ H ₉) ₈ }]	p	7.5	QLS	-	7.5-200	9
(TPyP)Eu ₂ [Pc(OC ₄ H ₉) ₈] ₂	p	1	QLS	-	1-20	11
Gd ₂ [Pc(OPhF) ₈] ₃	p	5	QLS	0.043	5-20	14
Tb ₂ [Pc(OPhF) ₈] ₃	p	0.15	QLS	0.14	1-5	14

^a SA: Self-assembly; ^b QLS: quasi-Langmuir-Shäfer; ^c VD: vacuum deposited

Table S4. H₂S detection properties for films of some representative phthalocyanine-based compounds at the room temperature.

Compounds		p/n-type (H ₂ S)	LOD (ppm)	Method	Sensitivity (%ppm ⁻¹)	Range (ppm)	Ref.
CoPc[β-O(4-CF ₃ -Ph) ₄]	(1)	n	0.1	SA	1.04	0.4-2.4	-
cPcCo-HQ-aCNT		p	0.005	SA	-	0.02-5.12	18
Au-CoPc		p-n	0.1	VD	-	0.1-50	19
CuPc-OTFT		p-n	100	VD	-	100-500	20
ZnO-CoPc		p-n	10	VD	-	10-50	21
ZnPc-FET		n	0.05	VD	-	0.02-20	22

^a SA: Self-assembly; ^b QLS: quasi-Langmuir-Shäfer; ^c VD: vacuum deposited

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