Electronic Supplementary Information (ESI) for:

Discrimination and detection of NO_2, NH_3 and H_2S using sensor array based on three ambipolar sandwich tetradiazepinoporphyrazinato/phthalocyaninato europium double-deckers

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§ This manuscript is dedicated to the memory of our friend Prof. Larisa G. Tomilova.

Experimental section

Materials and chemicals

Bis(2,3,9,10,16,17,23,24-octabutylphthalocyaninato) europium (**1**), {tetrakis(5,7-bis(4-*tert*-butylphenyl)-6*H*-1,4-diazepino)[2,3-*b,g,l,q*]porphyrazinato}{2,3,9,10,16,17,23,24-octabutylphthalocyaninato} europium (**2**) and bis{tetrakis(5,7-bis(4-*tert*-butylphenyl)-6*H*-1,4-diazepino)[2,3-*b,g,l,q*]porphyrazinato} europium (**3**) were synthesized according to the previously described procedures.[1-3] All other reagents and solvents were of reagent grade and used as received.

Thin film deposition

The nanostructures of compounds **1**, **2** and **3** were fabricated by using the solution-based method named quasi-Langmuir-Shäfer (QLS) according to the following procedure.[4] And there is no further treatment after preparation. In the present case, 10-layer QLS films of **1-3** were obtained for I-V and sensing experiments, respectively.

Characterization

Electronic absorption spectra were recorded on a Hitachi U-3900 UV-visible spectrophotometer. X-ray diffraction (XRD) experiments were carried out on BrukerAXSD8 ADVANCE X-ray diffractometer with copper (Kα) radiation. SEM images were obtained using a JEOL JSM-6700F field-mission scanning electron microscope.

Electrical measurements

The fundamental electrical and sensor measurements were performed using a Keysight B2910A precision source/measure unit with an incorporated DC voltage supply, always at room temperature. Current–voltage (I–V) curves were registered from – 10 to 10 V with 1 V increments. Conductivity obtained from I–V curve can be calculated as reported previously.[5] Before gas sensing measurement, the stability of current of the devices has been tested by I-V measurement in the range (−10 and +10 V) for the continuous 20 cycles. The current of the devices showed a relative stable behaviour vs. time. So, the effect of the value of relative humidity on the surrounding atmosphere on the response properties was neglected in the present case. On the other hand, the gas-sensing properties of samples have been examined by exposing the corresponding films to different concentrations of gas and measuring the current changes of the films at a constantly polarized voltage of 5 V. All experiments have been conducted at least twice to ensure reproducibility.

Gas sources for sensing experiments

Sensing experiments were carried out in a cuboid Teflon sensor chamber (*ca.* 30 cm^3 as internal volume). The desired NO_2, NH_3 or H_2S concentrations were produced by diluting a mixture NO_2/N_2 (20 ppm NO_2, from Qingdao Ludong Gas., Ltd, China), NH_3/N_2 (500 ppm NH_3, from Qingdao Ludong Gas., Ltd, China) or H_2S/N_2 (50 ppm H_2S, from Qingdao Ludong Gas., Ltd, China) with

dry N_2 using two CS200 Mass Flow Controllers (total mass flow: 0.1 $L \cdot min^{-1}$ for NO_2, NH_3 or H_2S and 2 $L \cdot min^{-1}$ for diluent gas N_2), respectively. All tests consisted of the exposure of the sensor to "a static atmosphere" followed by exposure to a known concentration of NO_2, NH_3 or H_2S. Some slight deviations in the control of recovery time is inevitably, which will result in a slightly higher current than the starting current.

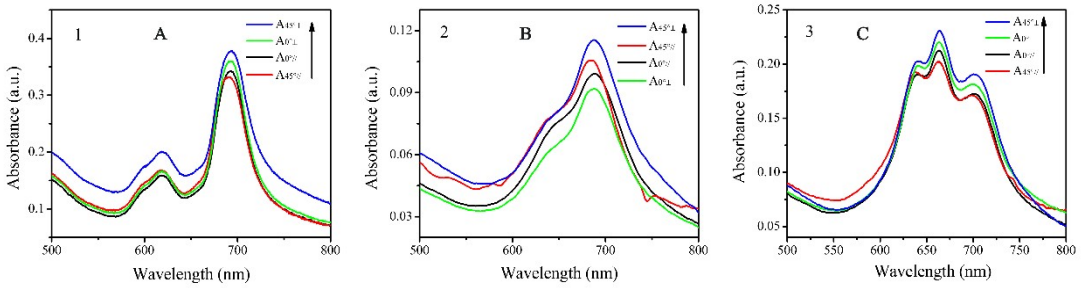

Fig. S1 The polarized electronic absorption of the QLS films **1**-**3** (A-C).

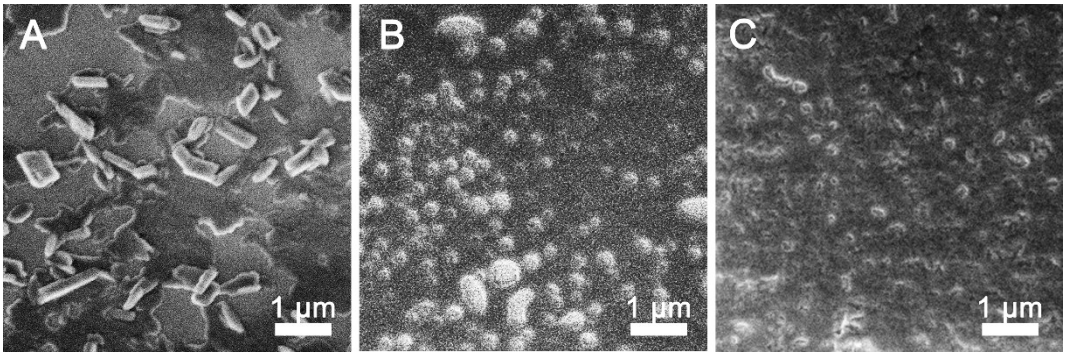

Fig. S2 SEM images of the QLS films **1**-**3** (A-C).

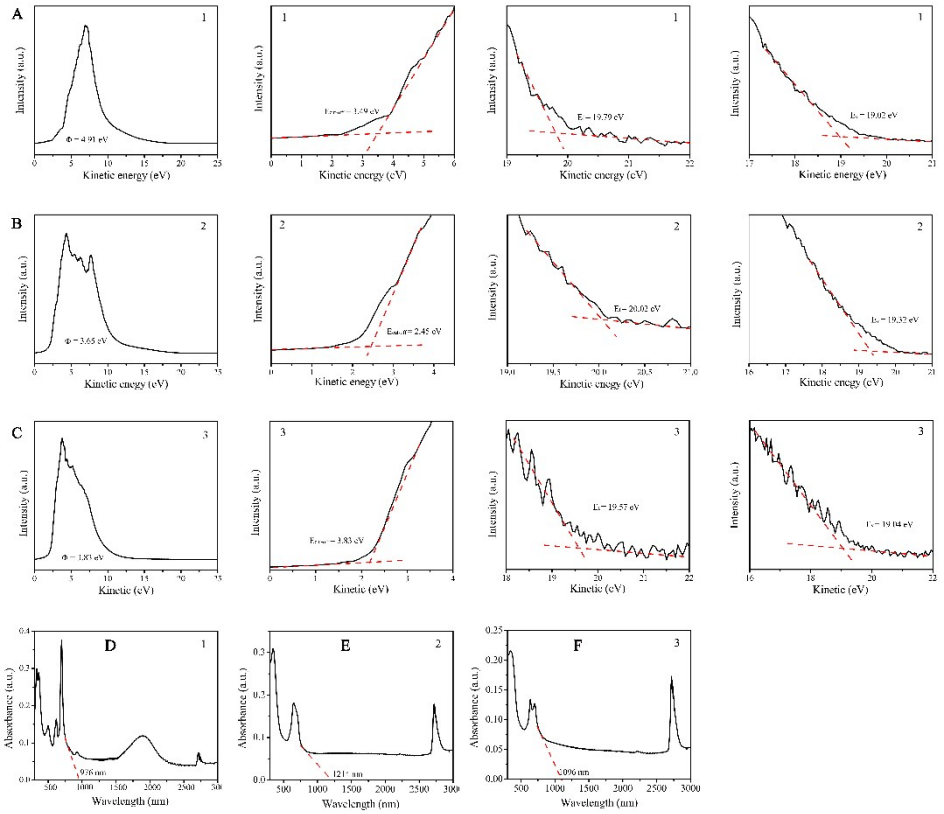

Fig. S3 UPS spectra (UV excitation by He I=21.2 eV) (A-C) and the VIS-NIR spectra (D-F) of the QLS films **1**-**3**. $\Phi(\text{work function}) = h\nu - \left|E_{\text{cut - off}} - E_f\right|$ [6]

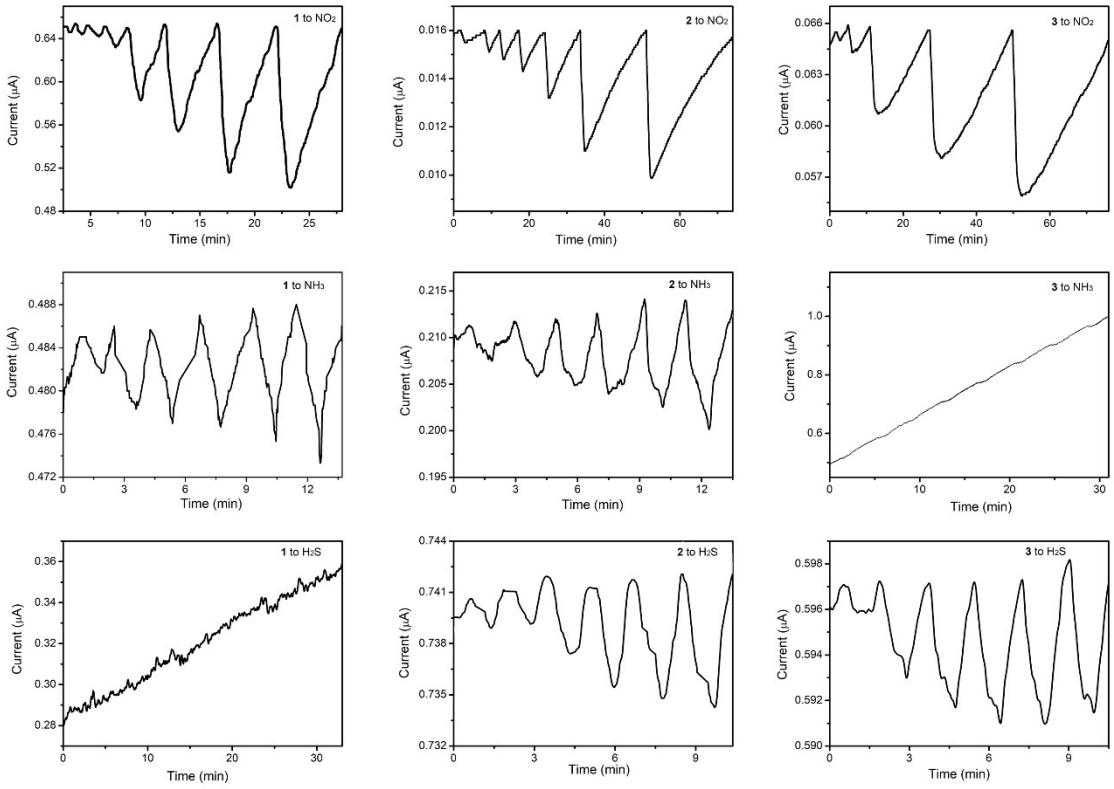

Fig. S4 The original experimental curves for the QLS films of compounds **1-3** exposed to toxic gases.

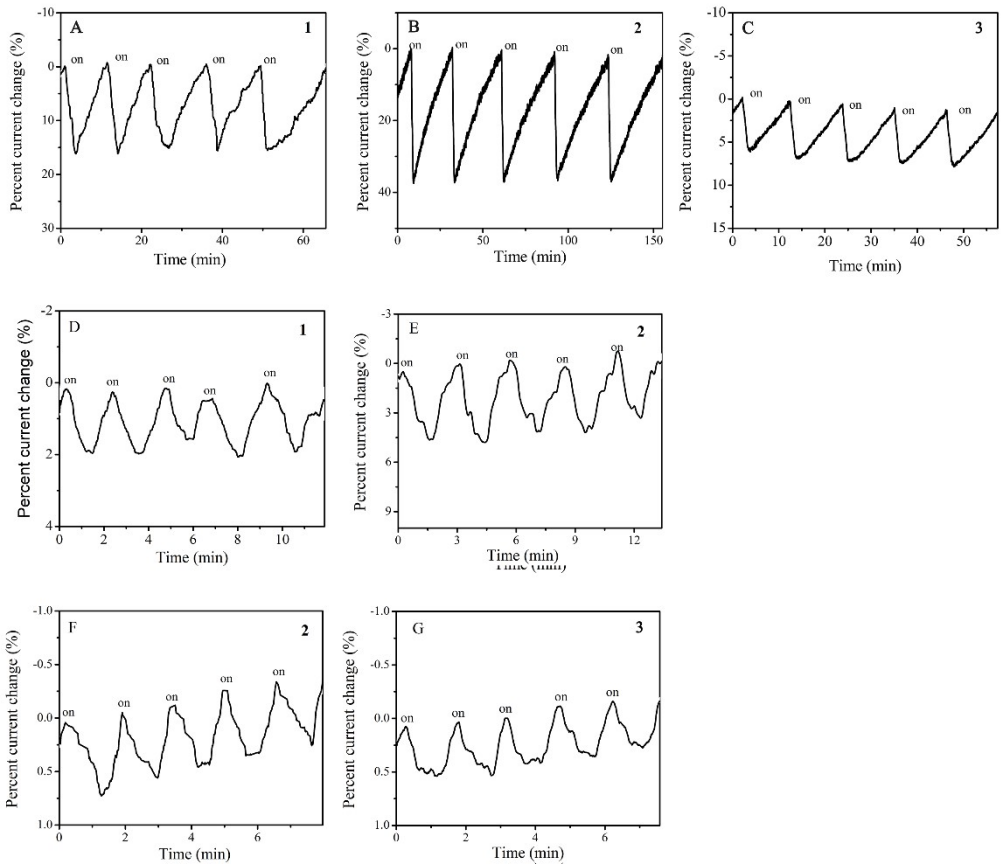

Fig. S5 The stability of the QLS films **1**-**3** (A-G). A-C is exposed to the NO_2 at the concentration of 500 ppb (exposure: 1 min) of **1**-**3**; D-E is to the NH_3 at the concentration of 12.5 ppm (exposure: 1 min) of **1**-**2**; G-H is to the H_2S at the concentration of 400 ppb (exposure: 400 ppb) of **2**-**3**.

Table S1 Electronic absorption data for compounds **1-3** in CH_2Cl_2 and their QLS films.

Compound	in CH_2Cl_2	QLS films
$[^{nBu}Pc]_2Eu$ (**1**)	330,356,492,616,685	329,356,492,618,692
$[^{tBuPh}DzPz][^{nBu}Pc]Eu$ (**2**)	354,640,698	345,684
$[^{tBuPh}DzPz]_2Eu$ (**3**)	367,631,696	367,638,662,702

Table S2 The polarized electronic absorption data for QLS films **1**-**3**.

Compound	$A_{//0}$	$A_{\perp 0}$	D_0（$A_{//}/A_{\perp}$）	$A_{45//}$	$A_{45\perp}$	D_{45}（$A_{//}/A_{\perp}$）	*Theta*
1	0.343	0.360	0.953	0.332	0.378	0.878	48.4°
2	0.099	0.092	1.076	0.104	0.115	0.904	44.3°
3	0.229	0.225	1.018	0.224	0.275	0.815	38.4°

Table S3 The summary of sensing response data for NO_2, NH_3 and H_2S of the QLS films **1**-**3**.

Analyte / Cpds	NO_2		H_2S		NH_3	
	Detection limit (ppm)	Sensitivity (% ppm^{-1})	Detection limit (ppm)	Sensitivity (% ppm^{-1})	Detection limit (ppm)	Sensitivity (% ppm^{-1})
1	0.04	26.7	--	--	1	0.2
2	0.02	46.84	0.1	2.34	1	0.39
3	0.1	18.31	0.1	1.62	--	--

Table S4 Sensor array current change map for different gases. The green spot represents the response. The red spot represents no response.

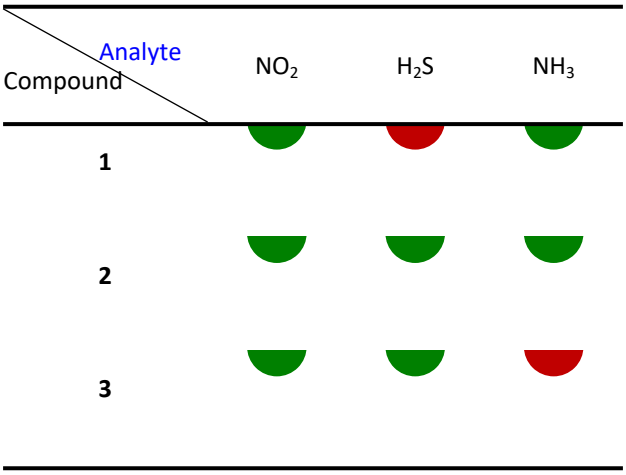

Table S5 Comparison of recently reported sensor arrays.

	Analyte	Sensor array in Ref 44	Sensor array in Ref 45	Sensor array in this work
Detection limit (ppm)	NO_2	0.10	0.02	0.02
	NH_3	3	0.42	0.1
	H_2S	5	0.1	1
Sensitivity (% ppm^{-1})	NO_2	54.6	616	46.84
	NH_3	0.24	0.17	2.34
	H_2S	3.18	1.04	0.39

References

1 V. E. Pushkarev, M. O. Breusova, E. V Shulishov and Y. V Tomilov, Selective synthesis and spectroscopic properties of alkyl-substituted lanthanide(III) mono-, di-, and triphthalocyanines, *Russ. Chem. Bull.*, 2005, **54**, 2087–2093.

2 E. N. Tarakanova, P. A. Tarakanov, A. O. Simakov, T. Furuyama, N. Kobayashi, D. V. Konev, O. A. Goncharov, S. A. Trashin, K. D. Wael, I. V. Sulimenkov, V. V. Filatov, V. I. Kozlovskiy, L. G. Tomilova, P. A. Stuzhin and V. E. Pushkarev, Synthesis and characterization of heteroleptic rare earth double-decker complexes involving tetradiazepinoporphyrazine and phthalocyanine macrocycles, *Dalton Trans.*, 2021, **50**, 6245-6255.

3 E. N. Tarakanova, S. A. Trashin, A. O. Simakov, T. Furuyama, A. V. Dzuban, L. N. Inasaridze, P. A. Tarakanov, P. A. Troshin, V. E. Pushkarev, N. Kobayashi and L. G. Tomilova, Double-decker bis(tetradiazepinoporphyrazinato) rare earth complexes: crucial role of intramolecular hydrogen bonding, *Dalton Trans.*, 2016, **45**, 12041-12052.

4 Y. Chen, M. Bouvet, T. Sizun, Y. Gao, C. Plassard, E. Lesniewska and J. Jiang, Facile approaches to build ordered amphiphilic tris(phthalocyaninato) europium triple-decker complex thin films and their comparative performances in ozone sensing, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12851-12861.

5 H. Ahn, A. Chandekar, B. Kang, C. Sung and J. E. Whitten, Electrical conductivity and vapor-sensing properties of ω-(3-thienyl)alkanethiol-protected gold nanoparticle films, *Chem. Mater.*, 2004, **16**, 3274–3278.

6 W.-T. Koo, S.-J. Choi, S.-J. Kim, J.-S. Jang, H. L. Tuller, I. Kim, Heterogeneous sensitization of metal–organic framework driven metal@ metal oxide complex catalysts on an oxide nanofiber scaffold toward superior gas sensors, *J. Am. Chem. Soc.*, 2016, **138**, 13431-13437.