Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION to:

Targeting biomarkers in the gas phase through a chemoresistive electronic nose based on graphene functionalized with metal phthalocyanines

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CONTENT:

1. Gas exposures set up

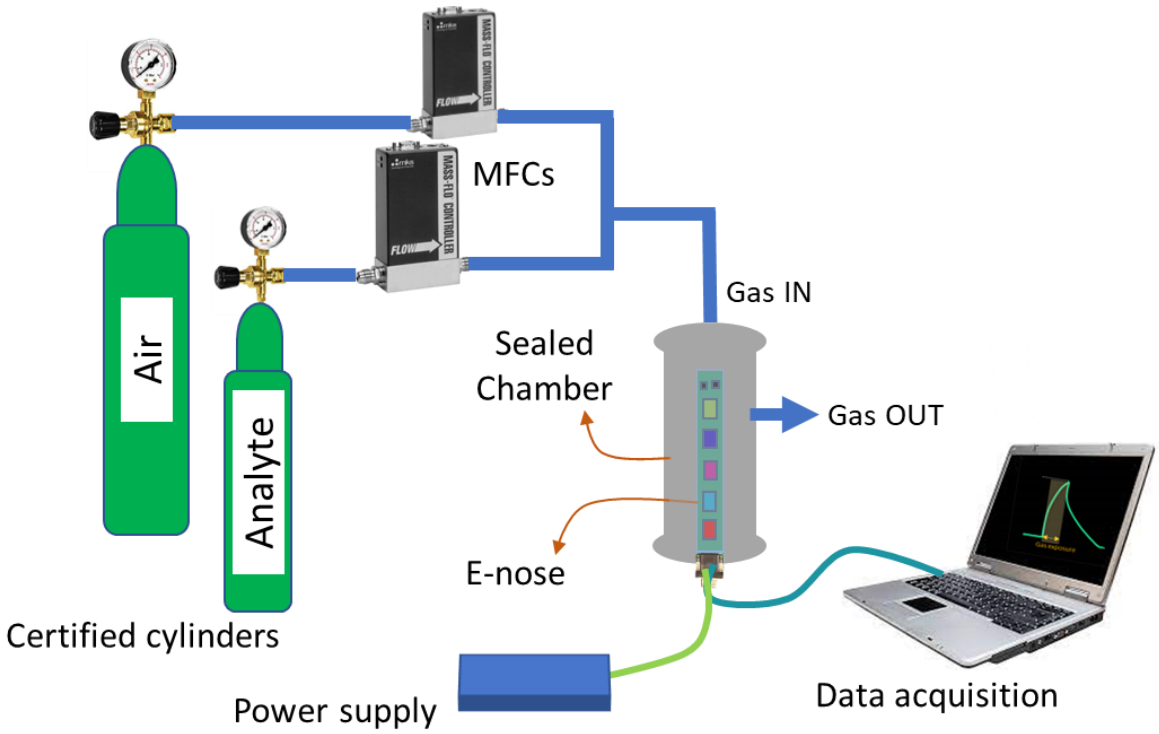

Figure S1: schematic set up for the gas exposures. The system comprises a homemade steal sealed chamber, connected to 2 mass flow controllers (MFCs), a PC for data acquisition, a certified cylinder filled with air and certified cylinders containing the target gas molecules (S.I.A.D Spa). The MCF connected to the air cylinder has a maximum flow of 500 sccm, while the max flow of the MFC connected to the analyte cylinders is 200 sccm. A power supply is connected to the platform hosting the developed samples and mounted inside the chamber.

2. Comparison between Raman spectra collected on phthalocyanine powder and on the developed samples

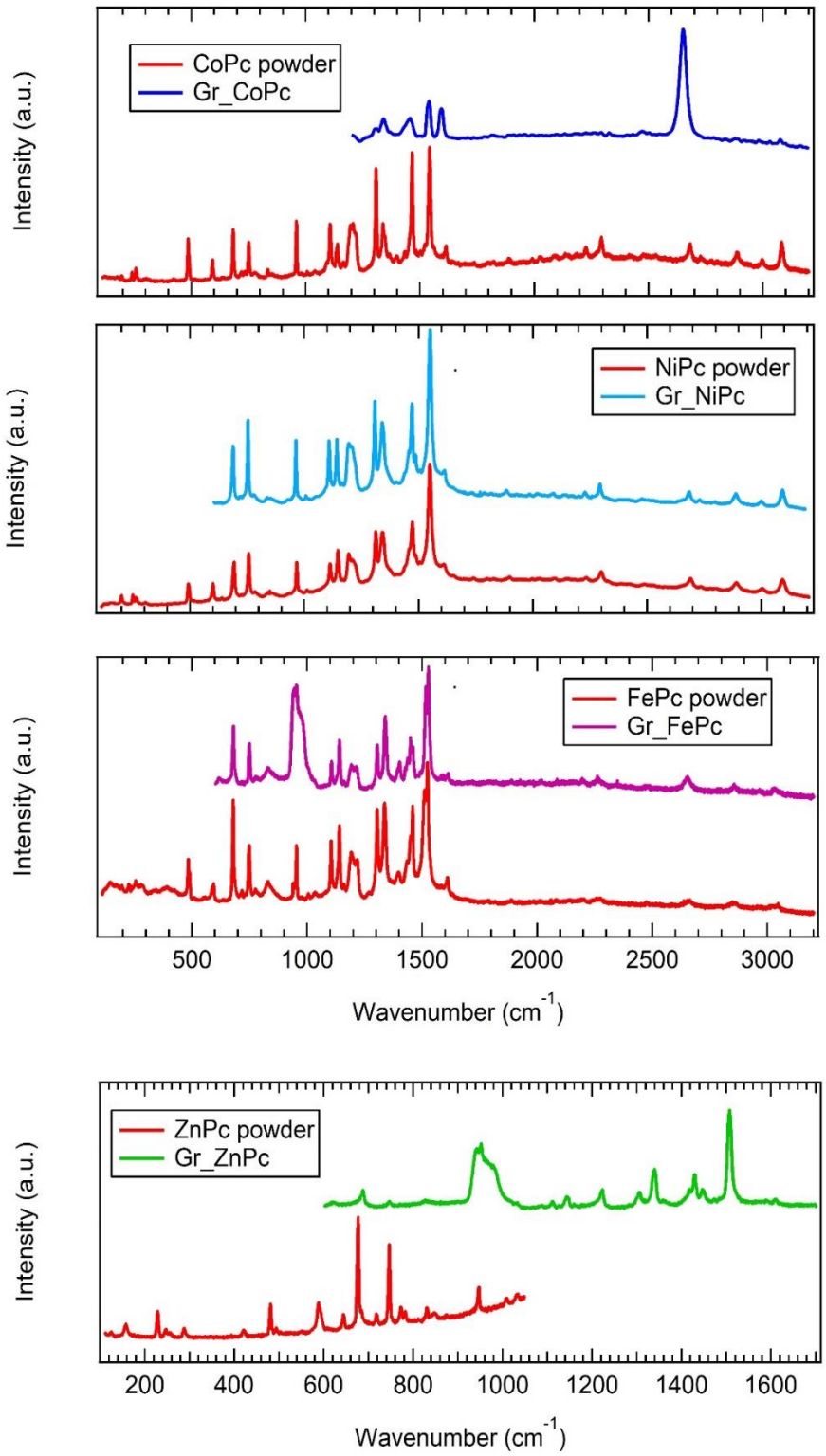

Figure S2: Comparison between the Raman spectra of the phthalocyanine powder (red spectra) and the Raman spectra of graphene on Si/Si_3N_4 functionalized with the phthalocyanine. Of note, regarding ZnPc both spectra span a different range than the other samples: indeed, the ZnPc powder spectrum range is cut at 1050 cm^{-1} while the Gr_ZnPc one is cut at 1660 cm^{-1}, due to luminescence.

3. AFM characterization

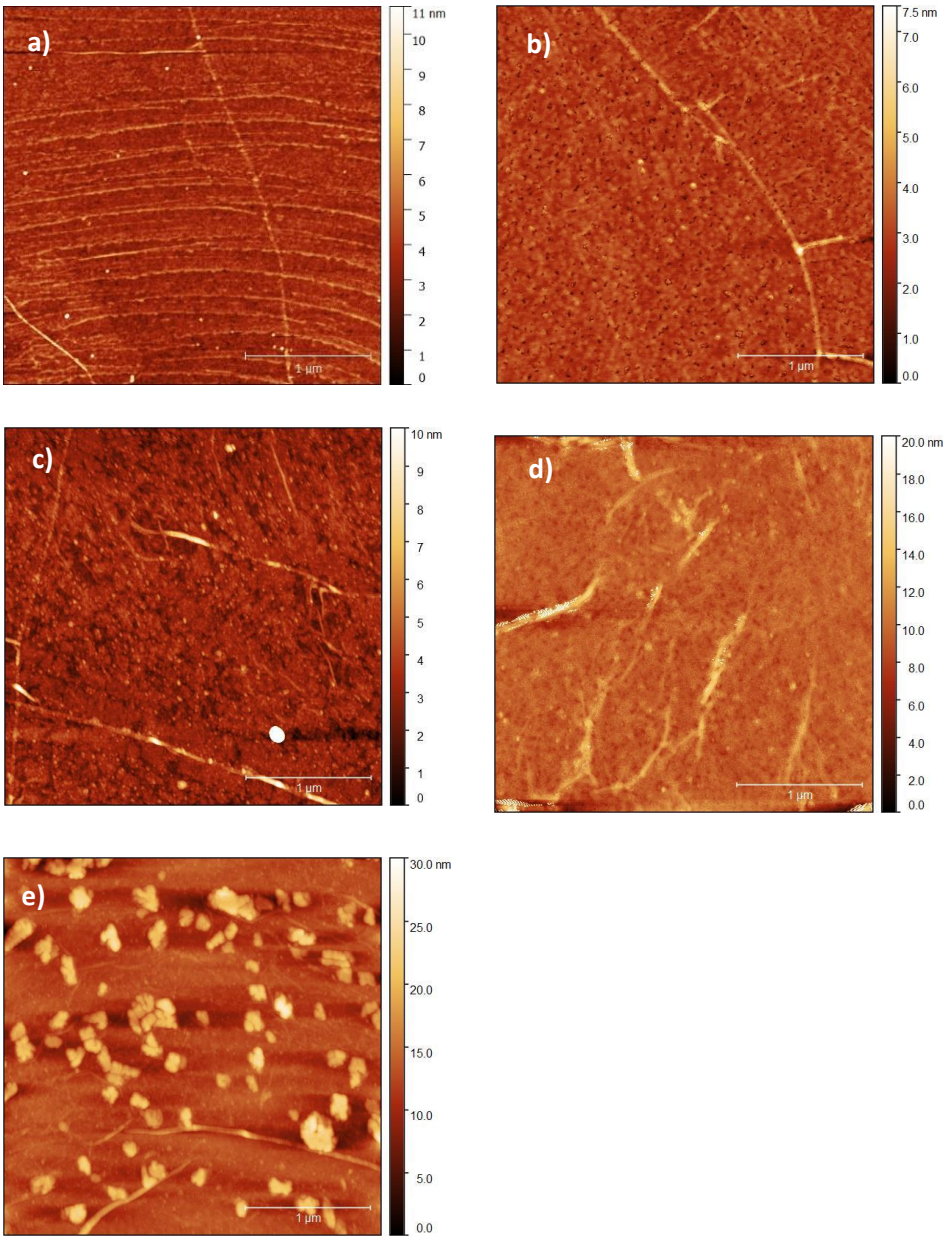

Figure S3: AFM images of: pristine graphene (a), and graphene functionalized with CoPc (b), FePc (c), NiPc (d), ZnPc (e) layers.

4. Batch-to-batch reproducibility

Table S.I: Baseline resistance of the graphene layers selected to develop the sensors, measured before the functionalization. The values are comparable, indicating a sample-to-sample baseline resistance reproducibility.

Sensor	Baseline resistance (kΩ)
Gr_CoPc	2.11 ± 0.01
Gr_FePc	2.05 ± 0.01
Gr_NiPc	2.12 ± 0.01
Gr_ZnPc	2.15 ± 0.01
Gr_pristine	2.06 ± 0.01

Table S.II: Baseline resistance of the graphene layers measured before the functionalization (R_0_before) and after the functionalization (R_0_after) and value of the roughness, evaluated on several AFM images, for the Gr_CoPc_A, B and C samples prepared for the reproducibility tests. The values are always comparable to the ones registered for the sample used in the e-nose (Gr_CoPc), proving a batch-to-batch reproducibility.

	Gr_CoPc	Gr_CoPc_A	Gr_CoPc_B	Gr_CoPc_C
R_0_before (kΩ)	2.11 ± 0.01	2.12 ± 0.01	2.05 ± 0.01	2.15 ± 0.01
R_0_after (kΩ)	0.738 ± 0.001	0.742 ± 0.001	0.739 ± 0.001	0.742 ± 0.001
Roughness (pm)	0.31 ± 0.12	0.28 ± 0.08	0.27 ± 0.09	0.30 ± 0.10

Table S.III: Baseline resistance of the graphene layers measured before the functionalization (R_0_before) and after the functionalization (R_0_after) and value of the roughness, evaluated on several AFM images, for the Gr_NiPc_A, B and C samples prepared for the reproducibility tests. The values are always comparable to the ones registered for the sample used in the e-nose (Gr_NiPc), proving a batch-to-batch reproducibility.

	Gr_NiPc	Gr_NiPc_A	Gr_NiPc_B	Gr_NiPc_C
R_0_before (kΩ)	2.12 ± 0.01	2.14 ± 0.01	2.08 ± 0.01	2.13 ± 0.01
R_0_after (kΩ)	1.50 ± 0.01	1.51 ± 0.01	1.48 ± 0.01	1.52 ± 0.01
Roughness (pm)	0.48 ± 0.17	0.39 ± 0.12	0.34 ± 0.11	0.44 ± 0.16

5. Exposures to low ammonia concentration and recovery time analysis

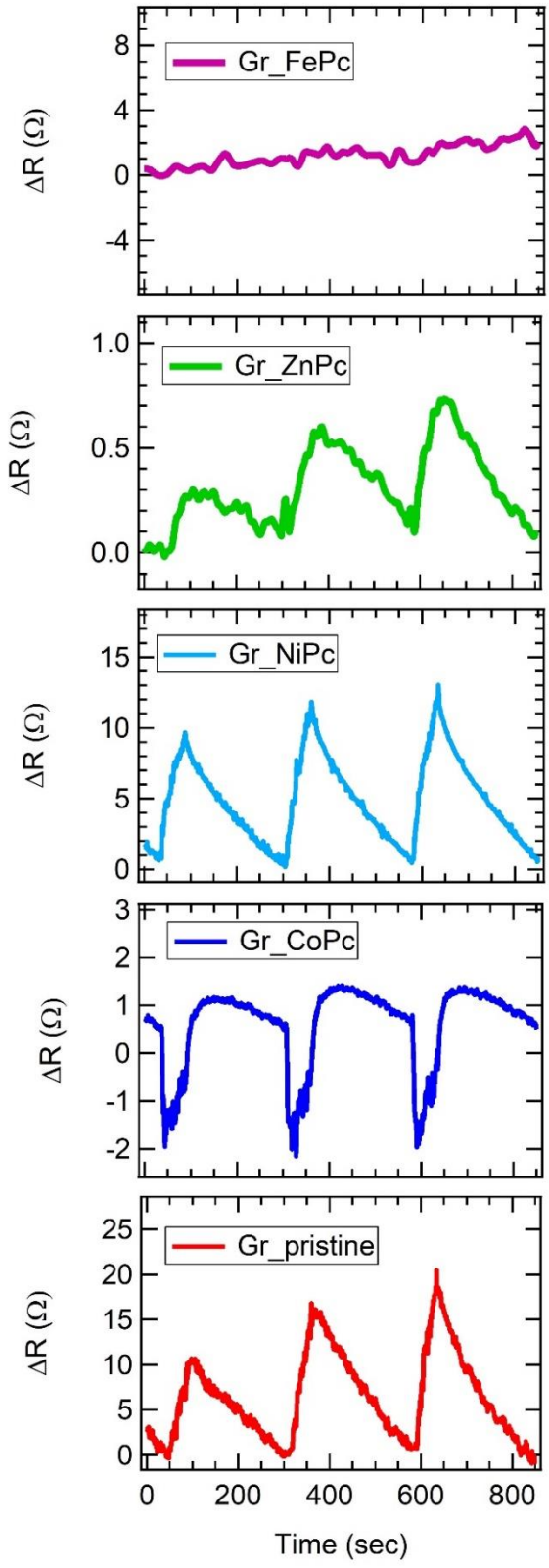

Figure S4: Variation of the resistance value of the sensor array to 1.4 ppm, 2.5 ppm and 3.7 ppm ammonia exposures. Gr_FePc does not show a response, in agreement with the evaluated detection limit of 8 ppm. All the other sensors respond and then completely recover after each expsure.

Table S.IV: Recovery time as function of ammonia concentration for all the prepared sensors. Recovery time is here defined as the time required by the resistance value to fall by 80% with respect to the value achieved during the exposure. Data evaluated from the exposures presented in Figure S4.

Sample	1.4 ppm	2.5 ppm	3.7 ppm
Gr_pristine	150s	155s	140s
Gr_NiPc	135s	140s	140s
Gr_CoPc	95s	100s	100s
Gr_ZnPc	140s	155s	140s

6. Freundlich fitting parameters and detection limit evaluation

Table S.V: fitting parameter of the calibration curves plotted in Figure 3 of the main text.

Sensor	A	pow	y_0 (Ω)
Gr_FePc	-	-	-
Gr_NiPc	0.004 ± 0.001	0.44 ± 0.01	-0.00018 ± 0.00002
Gr_ZnPc	0.0004 ± 0.0001	0.54 ± 0.02	-0.00005 ± 0.00002
Gr_pristine	0.006 ± 0.002	0.42 ± 0.06	-0.0005± 0.0001

Table S.VI: detection limit for ammonia exposure evaluated according to the formula reported in ref. [71] of the main text: $3[NH_3]/((R-R_0)/\sigma)$.

Sensor	σ (Ω)	dl (ppm)
Gr_FePc	-	8,00
Gr_NiPc	0.096 ± 0.002	0,05
Gr_ZnPc	0.04 ± 0.01	0,05
Gr_pristine	0.354± 0.008	0,17
Gr_CoPc	0.0050 ± 0.0003	0,03

7. Benchmarking for sensitivity and detection limit

Table S.VII: Benchmarking for sensitivity (defined as: $(\Delta R/R_0*100)/[NH_3]$) and detection limit. For literature works [Ref 28, 29, 73-84 in the main text] sensitivity is reported for the lowest concentration tested in each paper and for the best performing sensor. Of note: only articles clearly reporting gas concentration and sensor response/sensitivity have been taken into account for this benchmarking.

Sensor type	**Concentration (ppm)**	**Sensitivity (%ppm^{-1})**	**Detection limit (ppm)**	**Reference (main text)**
Gr_pristine	0.5	0.80	0.17	Present work
Gr_NiPc	0.5	0.64	0.05	Present work
Gr_ZnPc	0.5	0.03	0.05	Present work
Gr_CoPc	0.5	-0.24	0.03	Present work
Gr_FePc	12	0.03	8.0	Present work
Gr/AuNPs	15	0.17	-	73
Gr	2	2.05	0.5	74
Gr/PANI	20	0.18	1	75
TiO2@PPy–GN	50	2.04	1	76
B-doped Gr	1	0.04	$0.6x10^{-2}$	77
Gr	75	0.04	-	78
Gr	100	0.05	-	79
B-doped Gr	32	0.28	-	80
Gr_NBD	0.05	11.78	-	28
Gr-TCN	0.86	6.33	$4.2x10^{-3}$	29
CuPc/rGO	0.4	4.5	-	81
NiPc/rGO	100	0.09	0.4	82
ZnPc:rGO	10	0.003	-	83
cpoPcCo/rGO	100	0.42	$3.7x10^{-3}$	84

8. Ammonia exposures for CoPc layer

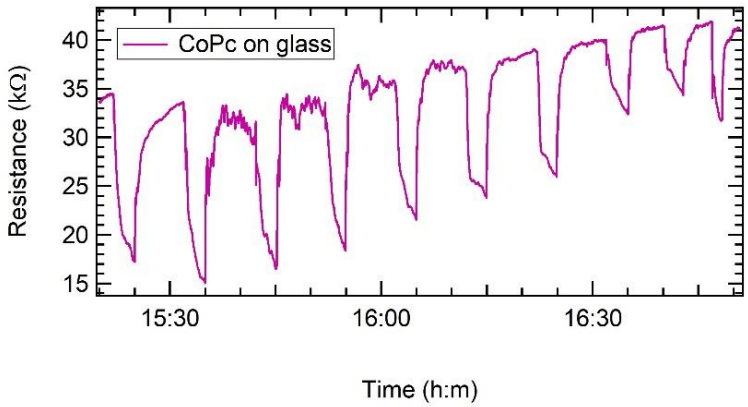

Figure S5: Response of a thick CoPc film on glass substrate upon exposures to several differet ammonia concentration. An n-type doping of the GrPc layer itself is assessed.

9. Raman maps on Gr CoPc

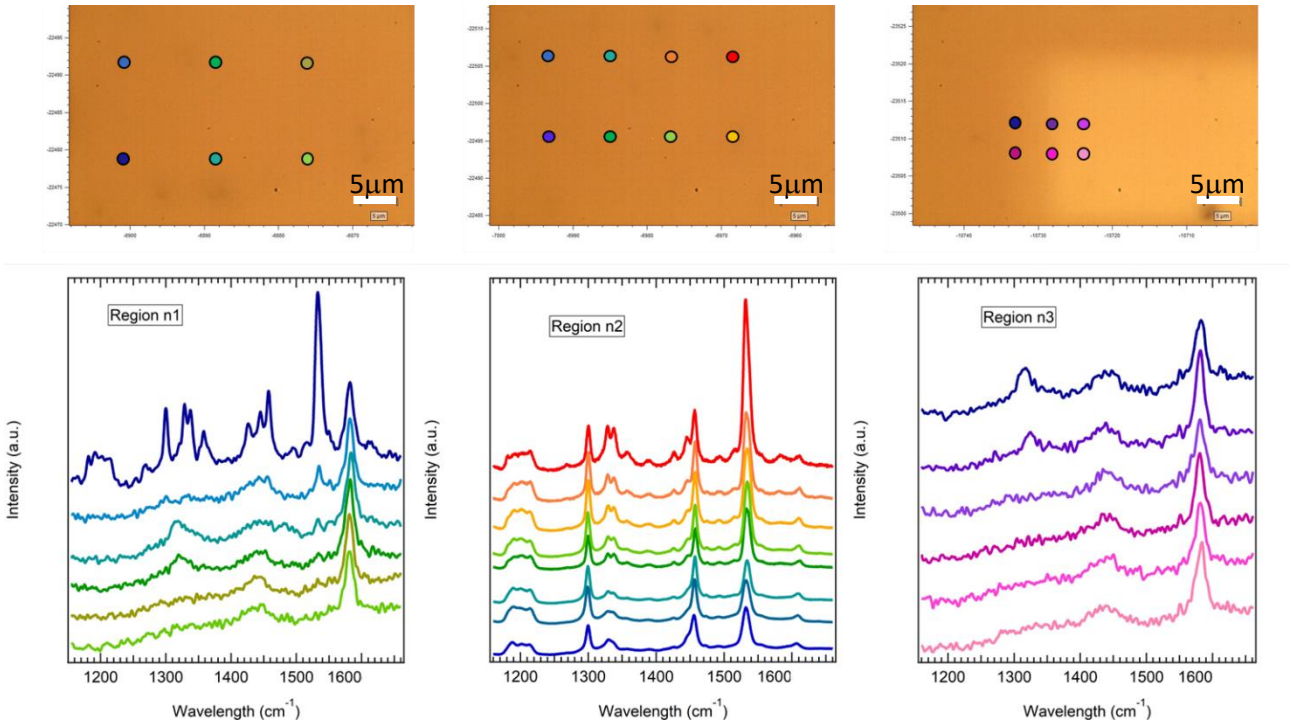

Figure S6: Top side: optical image collected with the sample; the spots where the Raman spectrum has been collected (with a map procedure) are enlighted. Bottom side: corresponding Raman spectra. It is clear that the layer is not completely covered by the phthalocyanine molecules. Indeed, in some spots of region 1 and all spots of region 3 only peaks arcribable to graphene could be found. In region 2 all the spectra report the presence of the phthalocyanine molecules on the graphene layer. Different relative intensity between Gr and Pc peaks implies a different thickness coverage.

10. Details on the $(\Delta R/R_0)_{pos}$ and $(\Delta R/R_0)_{neg}$ evaluation (referred to Figure 5 main text)

In order to estimate the $(\Delta R/R_0)_{pos}$ and $(\Delta R/R_0)_{neg}$ values reported in Figure 5 of the main text, as schematically illustrated in Figure 5-a, we proceed as follow:

- $(\Delta R/R_0)_{neg}$: the R_0 value is the resistance value before the gas exposure, while $\Delta R = R - R_0$ is evaluated considering the difference between the lowest negative value R achieved by the resistance during the exposure and R_0;
- $(\Delta R/R_0)_{pos}$: the R_0 value represents the lowest negative value achieved by the resistance during the exposure, while $\Delta R = R - R_0$ is evaluated considering the difference between the highest positive value R achieved by the resistance during the exposure and R_0.

11. Concentration range of all selected target gas molecules

Table S.VIII: Concentration range of the selected target gas molecules used for the PCA analysis.

Target gas	**Concentration range (ppm)**
Ammonia	0-13.5
Acetone	0-40
Ethanol	0-37
2-propanol	0-40
Benzene	0-1
Sodium hypochlorite	0-0.5
Hydrogen sulfide	0-2.5
Water	0-1000