

ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Solution-Processed Nanoporous Organic Semiconductor
Thin Films: Toward Health and Environmental Monitoring of
Volatile Markers

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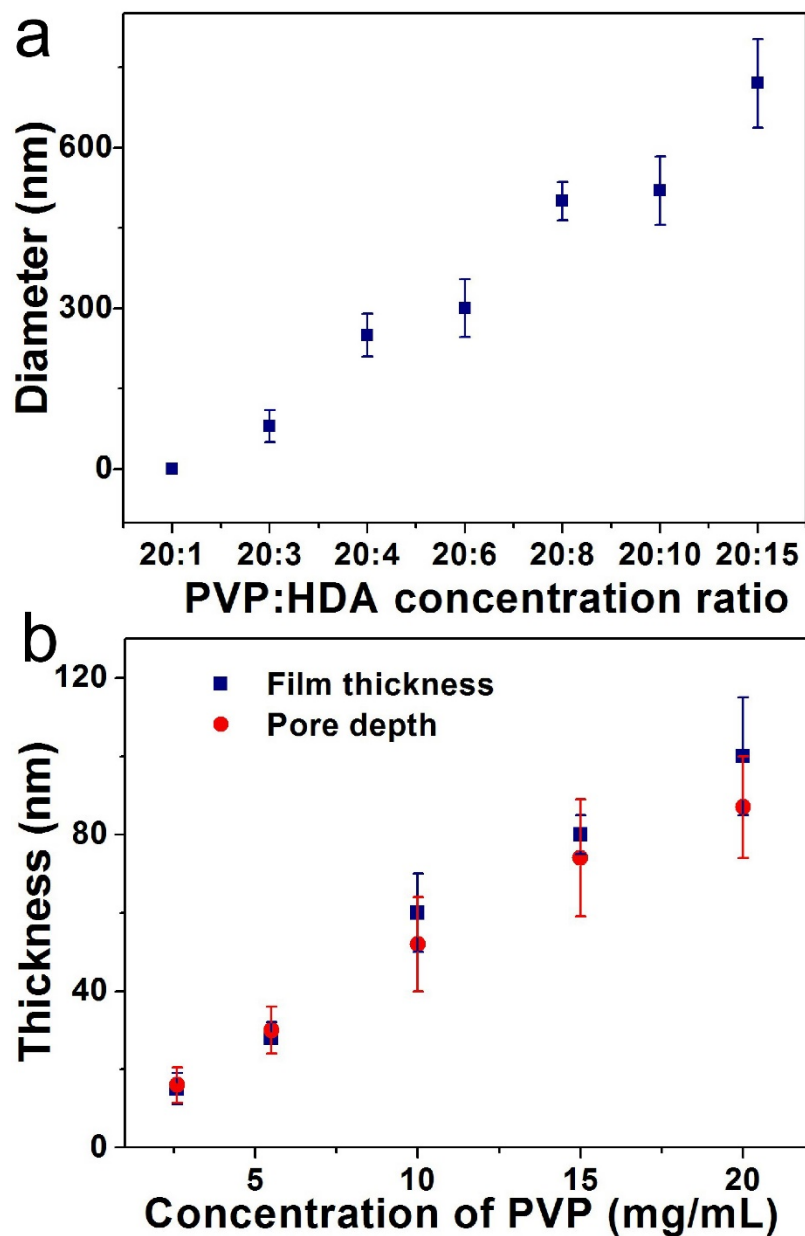
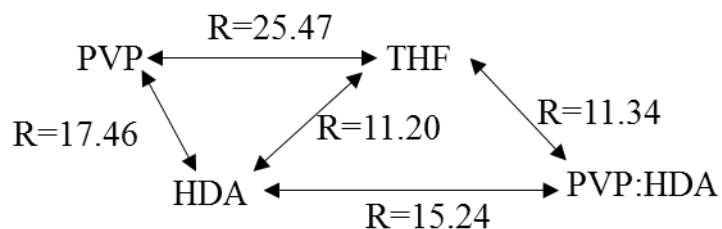


Figure S2. Structure characteristics of the nanoporous PVP:HDA modified template. (a) PVP:HDA weight ratio dependent pore diameter, with the PVP concentration of 5.5 mg/mL. These data were obtained from AFM height images, some of which shown in Figure 1. (b) Thickness and pore depth as a function of PVP concentration. The PVP:HDA weight ratio is 20:4. The error bars represent the standard deviation from at least five independent measurements.

Table S1. Hansen solubility parameters for various materials and calculated molecular distance. The distance between different molecules is calculated by the equation

$$R^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad \text{Equation (S1)}$$

Materials	Hansen solubility parameter		
	Dispersion (δ_D)	Polarity (δ_P)	H-bond (δ_H)
PVP	20.33	29.26	14.47
HDA	20.52	13.82	6.32
PVP-HDA (stoichiometry ratio=2.6:1)	20.77	0.92	14.41
THF	16.75	5.69	7.98



We infer that addition of HDA decreases the miscibility of PVP with THF. This inference is made on the following basis: 1) HDA interacts with THF more favorably as compared to PVP with THF, as evidenced by the much smaller HDA-THF distance as compared to the PVP-THF distance. 2) HDA interacts with THF more favorably as compared to with PVP:HDA, as evidenced by smaller HDA-THF distance compared to the HDA – PVP:HAD distance. These conditions suggest THF/HDA solution to be phase separated from the crosslinked PVP:HDA phase with increasing HDA concentration.

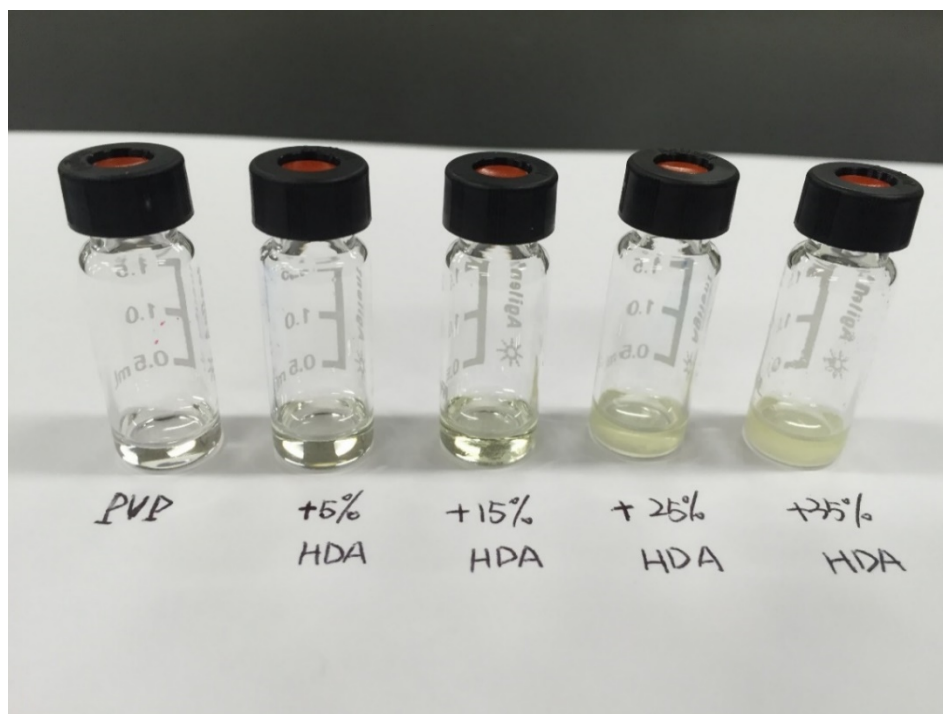


Figure S3. Photograph of PVP-THF solution with increasing levels of HDA concentration for studying the effects of HDA on miscibility. The prepared clear PVP-THF solution is at a high PVP concentration of 300 mg/ml close to but below the solubility limit. The other prepared solutions are at the same PVP concentration, but with HDA crystalline powders added from 5 to 35 wt% with respect to PVP. After shaking for 24 hours, fluffy white precipitates can be observed in solutions with HDA concentration of 15-35 wt%. The amount of precipitates increases with increasing HDA concentration.

Supplementary Note 1. Proposed mechanism of nanopore formation in PVP:HDA

Combining the miscibility test with nanopore morphology characterizations, we propose the following mechanism to explain the HDA-controlled pore formation during spin coating (Figure S4): (1-2) first solvent evaporation occurs which increases the solution concentration to surpass the miscibility limit, at which point THF-rich domains nucleate as discrete islands embedded in the continuous PVP-rich domains. (2-3) Subsequently the phase-separated domains continue to grow while THF continues to evaporate until the entire film solidifies. Due to THF evaporation, the THF-rich domains are converted into pores in the polymer film. When a very small amount of HDA is added, the miscibility between the solvent and the solute is high and the driving force for microphase separation is low. In this case, the microphase separation is inhibited, or in other words, its induction time is too long relative to the spin coating time scale. With increasing amount of HDA, the miscibility decreases, thus increasing the driving force for microphase separation. When the induction time for microphase separation is lower than the processing time scale, microphase separation can occur during spin coating. Further increases the amount of HDA causes the microphase separation to occur earlier. This allows more time for the domains to grow, leading to formation of larger pores.

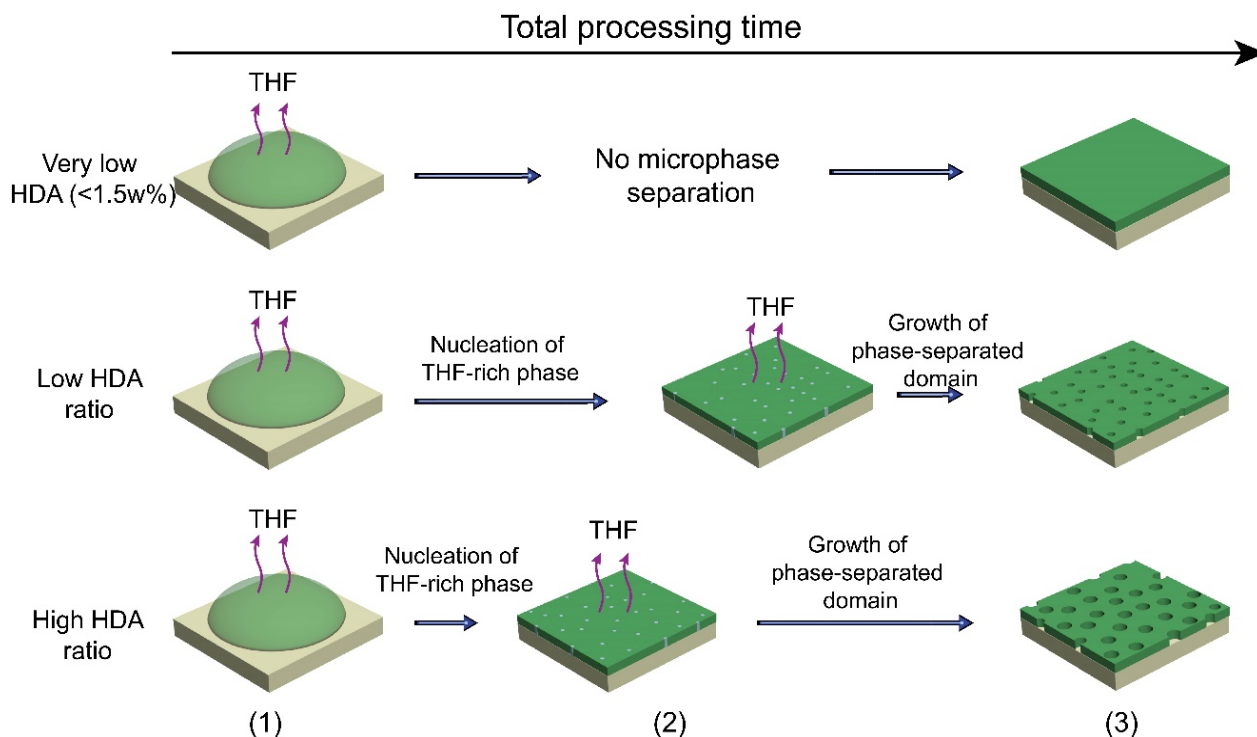


Figure S4. Schematic illustration of HDA-controlled pore formation process. (1) Solvent THF evaporation concentrates the solution to the miscibility limit; (2) Initiation of microphase separation triggered by the nucleation of THF-rich domains; (3) Growth of the phase-separated domains, and complete solvent removal to leave pores in the solidified films. Increasing HDA concentration causes the phase separation to occur earlier, prolonging the growth period and inducing larger pores.

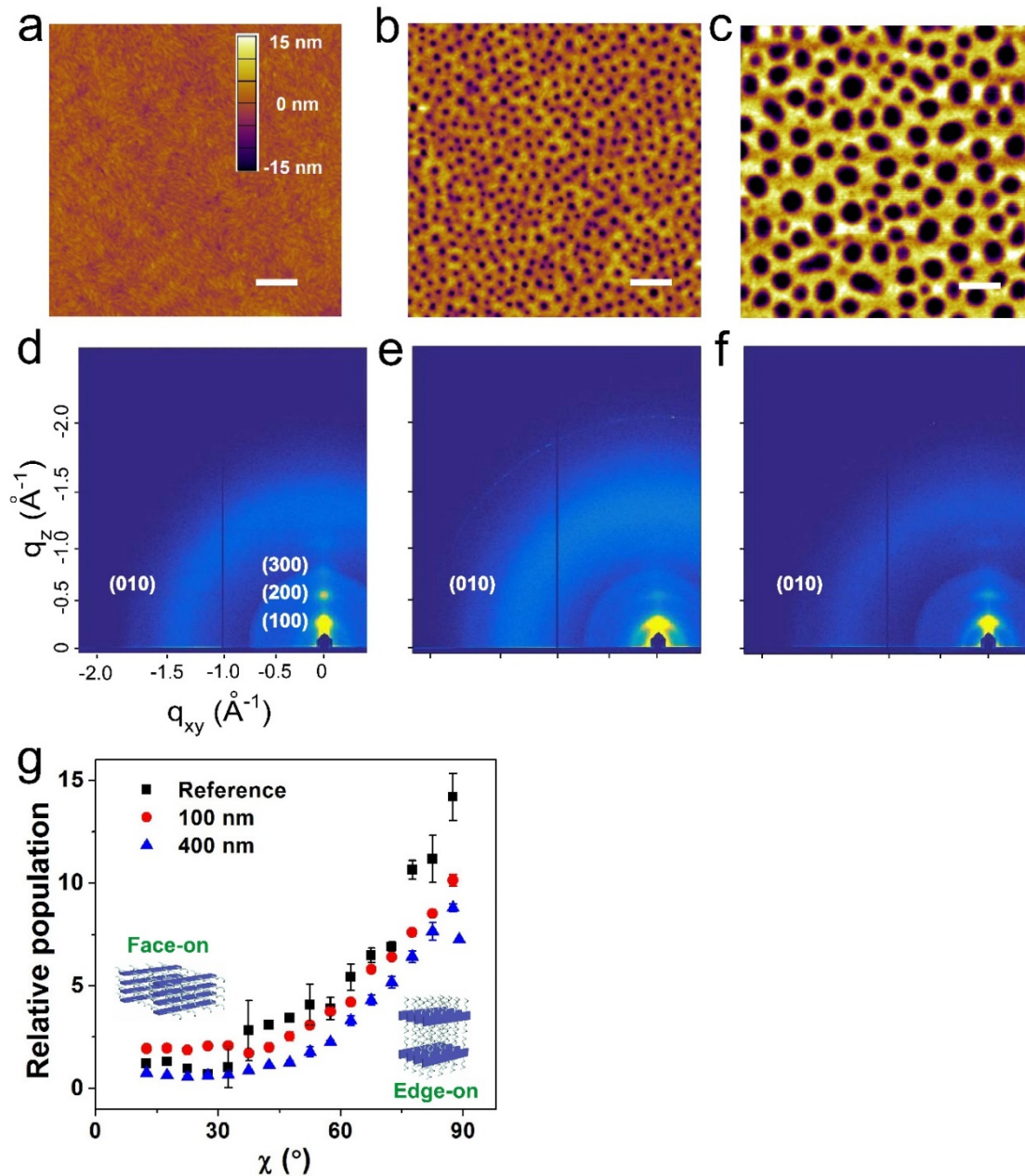


Figure S5. Characterization of spin-coated DPP2T-TT film. (a-c) AFM images and (d-f) GIXD images of spin-coated DPP2T-TT films on PVP:HDA with (a, d) 0 nm, (b, e) 100 nm and (c, f) 400 nm pores. The scale bars are 1 μm in all images. (g) Comparison of geometrically corrected orientation distribution for spin-coated DPP2T-TT film with various pore structure. The error bars were standard errors of calculated (010) peaks areas from multipeak fitting.

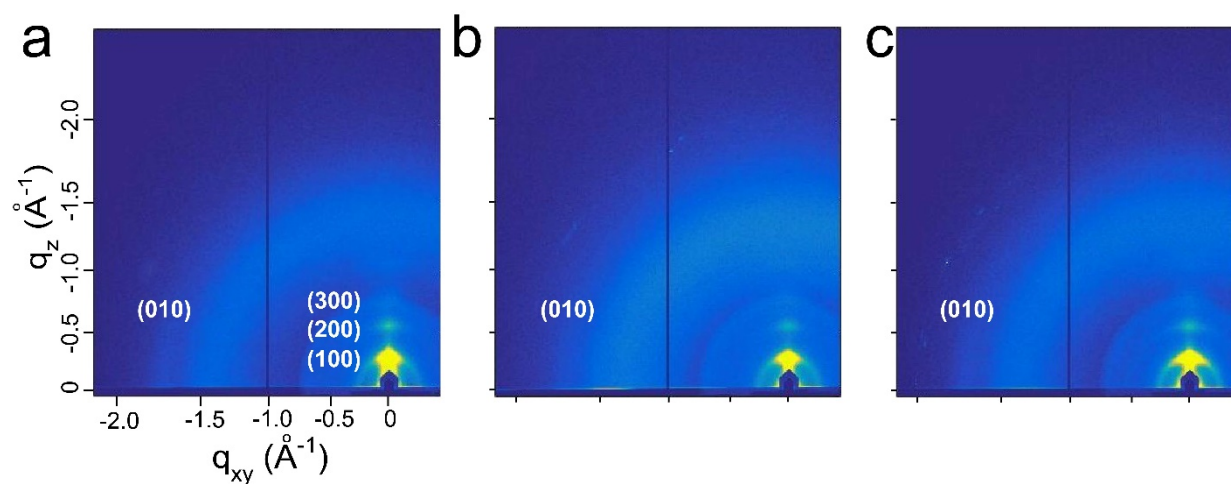
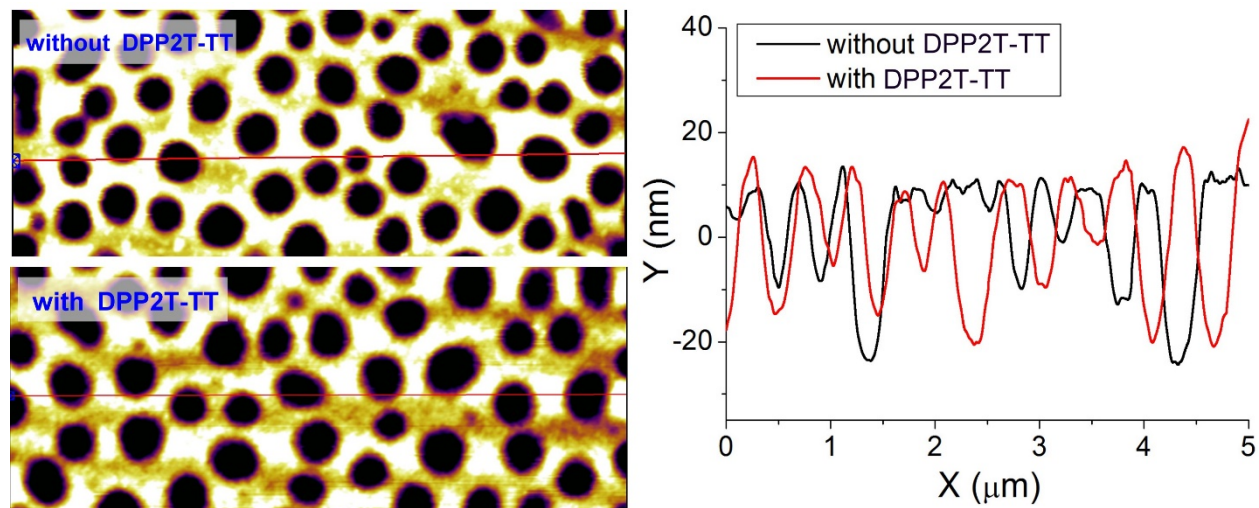


Figure S6. GIXD investigations of printed DPP2T-TT film. DPP2T-TT films on PVP:HDA with (a) 0 nm, (b) 100 nm and (c) 400 nm pores. The diffraction patterns were obtained with the printing direction perpendicular to the incident beam, complementing Fig. 2d-f wherein the diffraction pattern corresponds to parallel scans.

Table S2. Comparison of pore structures before and after the deposition of DPP2T-TT. The concentration of PVP is 5.5 mg/mL for template layer fabrication, while DPP2T-TT was deposited on the template layer from chlorobenzene solution (5 mg/mL) via spin coating. The corresponding thickness of the DPP2T-TT layer was measured to be 23 nm on average. The figures compare the AFM height images before and after DPP2T-TT deposition. Depth profile is shown along the red horizontal line.



Before the deposition of DPP2T-TT		After the deposition of DPP2T-TT	
Diameter (nm)	Depth (nm)	Diameter (nm)	Depth (nm)
89.0±10.3	20.1±3.7	90.5±8.5	18.9±2.5
140.4±15.0	22.1±8.5	130.8±14.2	21.7±3.8
254.5±12.2	31.5±7.6	239.6±9.2	32.0±8.5
300.0±16.6	33.5±9.5	312.0±13.4	31.7±6.2
500.0±6.8	35.0±5.6	482.0±10.8	33.7±11.4
714.0±15.0	38.9±6.8	719.2±13.30	34.1±12.8

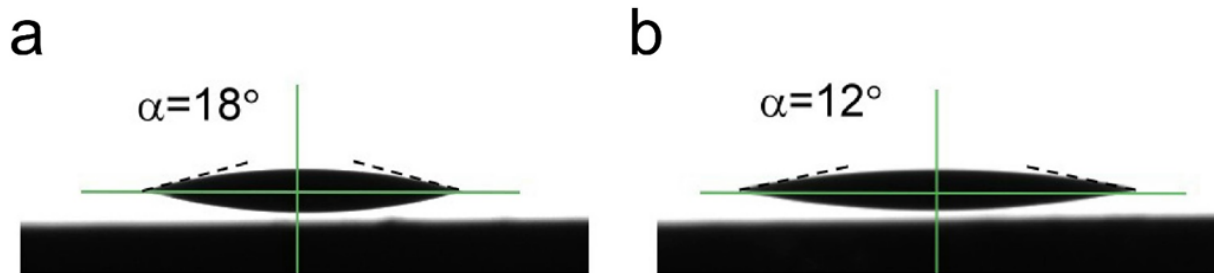


Figure S7. Contact angle of DPP2T-TT/chlorobenzene drop on substrate which is (a) nonporous and (b) with pore diameter of ~ 400 nm and pore depth of ~ 30 nm. For the liquid droplet on a porous surface in the Wenzel state, the apparent contact angle is modified and relates to the intrinsic contact angle by the following equation:

$$(1 + \cos\theta) = \phi(1 + \cos\theta_0) \quad \text{Equation (S2)}$$

where θ and θ_0 are the apparent contact angle and the intrinsic contact angle respectively; ϕ is the dimensionless parameter, denoting the surface area ratio $A_{\text{porous}}/A_{\text{nonporous}}$.^[1] To validate that the DPP2T-TT ink drop is in the Wenzel state when in contact with the porous surface, we calculated the apparent contact to compare with the measured one. The surface area ratio is estimated to be 1.014 and the intrinsic contact angle is 11.9° , which is comparable to the measured contact angle $\sim 12^\circ$. This simple calculation validates that the ink drop wets the entire contour of the porous substrate.

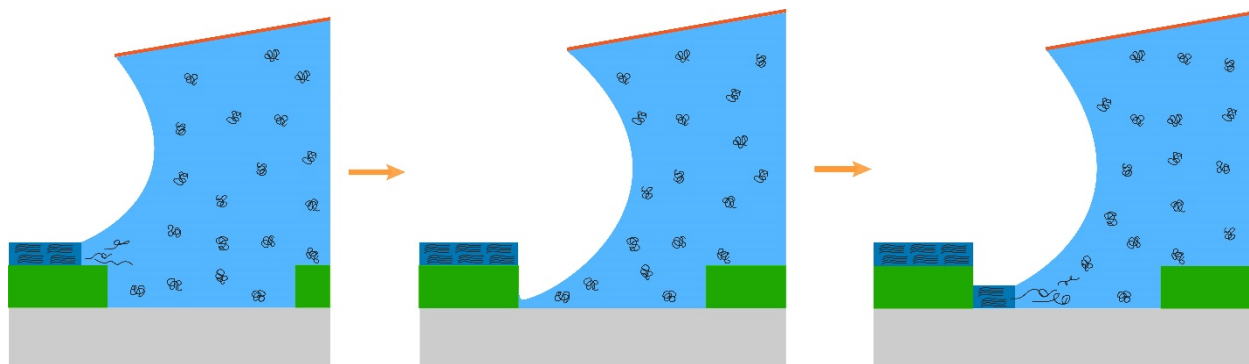


Figure S8. Mechanism of OSC deposition on the porous template. Schematic illustrating the inferred molecule deposition process during the meniscus-guided coating.

Table S3. Molecular packing in printed DPP2T-TT films analyzed from GIXD images. Two-dimensional diffraction patterns were integrated along the polar angle χ to obtain a one-dimensional plot of intensity vs q . The one-dimensional diffraction pattern was subsequently deconvoluted with background subtraction to accurately determine the peak positions and the corresponding peak widths represented by the full width at half maximum (FWHM).

Organic thin films	Printing direction	Without pores	100 nm pores	400 nm pores
Lamella spacing (Å)	par	23.35±0.01	23.22±0.02	23.07±0.02
	perp	23.18±0.02	23.38±0.02	23.28±0.02
π - π Stacking distance (Å)	par	3.57±0.05	3.55±0.05	3.56±0.03
	perp	3.56±0.04	3.58±0.07	3.57±0.04
FWHM of π - π stacking peak (Å ⁻¹)	par	0.16±0.01	0.14±0.03	0.16±0.02
	perp	0.15±0.02	0.15±0.01	0.15±0.01

Table S4. Molecular packing in spin-coated DPP2T-TT films analyzed from GIXD images.

Organic thin films	Without pores	100 nm pores	400 nm pores
Lamella spacing (Å)	23.20±0.05	23.35±0.09	23.21±0.06
π - π stacking distance (Å)	3.69±0.07	3.68±0.02	3.68±0.02
FWHM of π - π stacking peak (Å ⁻¹)	0.22±0.06	0.27±0.03	0.26±0.02

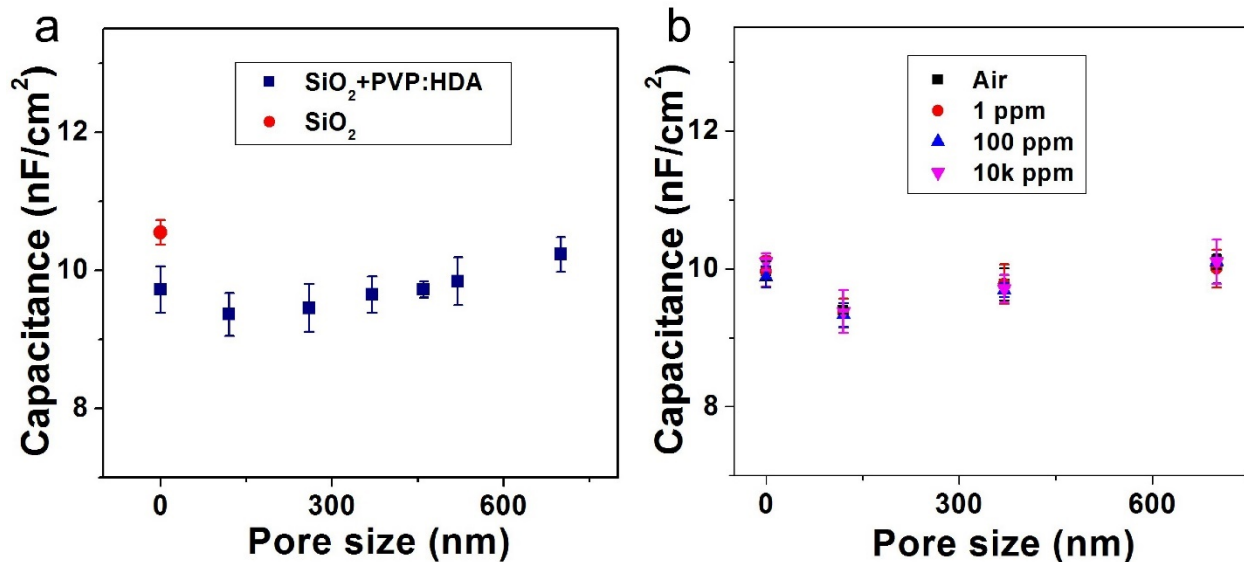


Figure S9. Capacitance of template modified dielectric. (a) The plots represent the capacitance of the 300 nm SiO₂ dielectric layer combined with the PVP:HDA template layer as a function of pore sizes. (b) Capacitance of template modified dielectric layer under various ammonia concentrations. The thickness of the modified layer is kept at 30±8 nm.

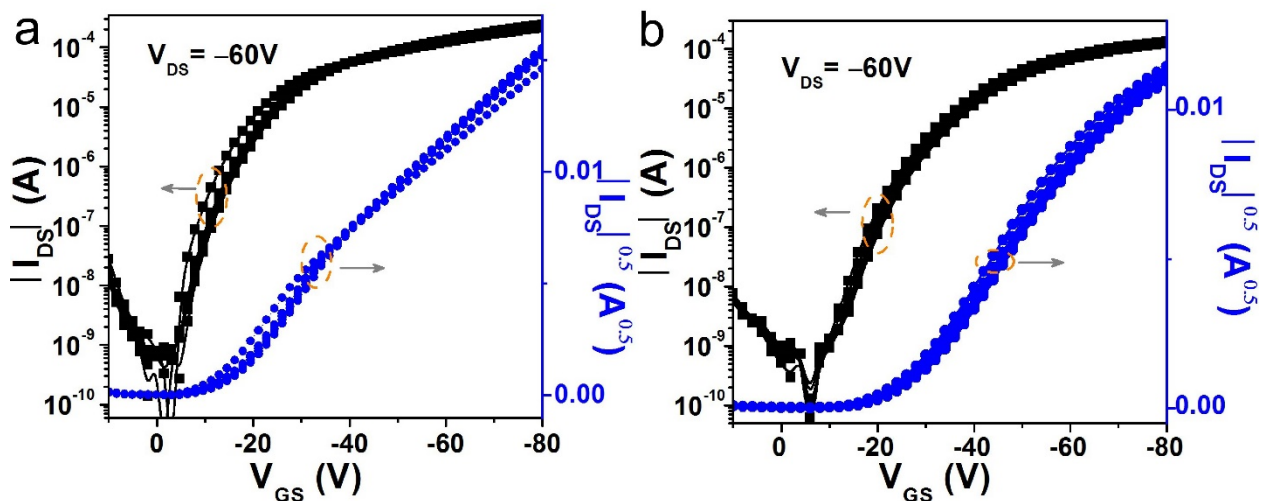


Figure S10. Stability measurements (5 sweeps) under ambient conditions for DPP2T-TT OFETs (a) without and (b) with pores.

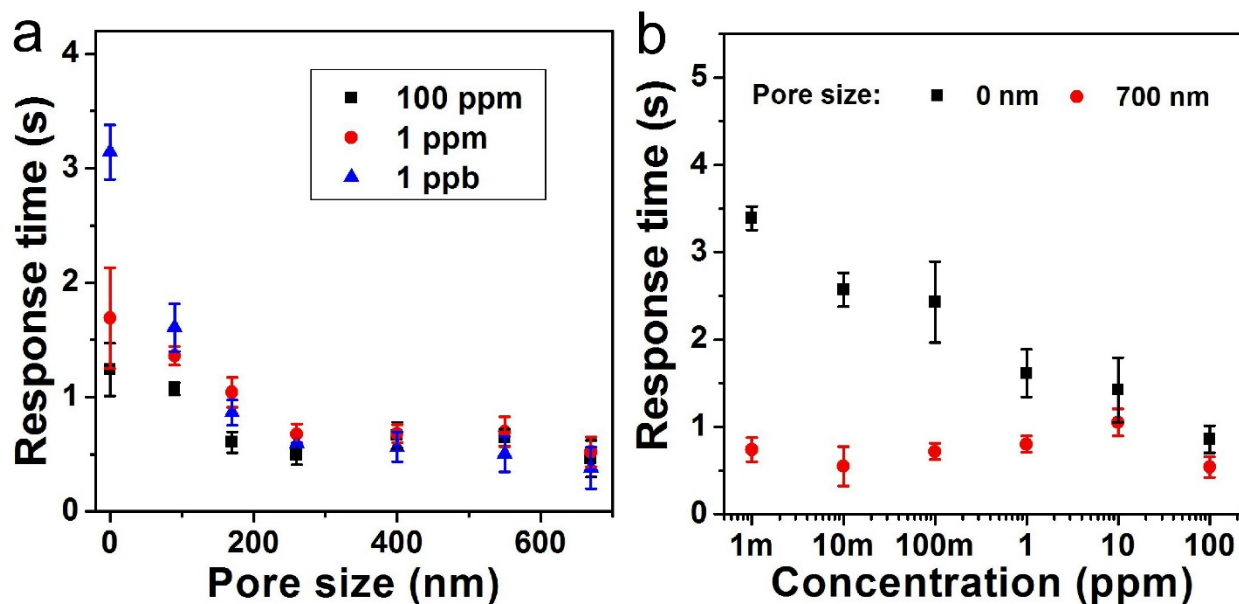


Figure S11. Response time of DPP2T-TT sensors to NH₃ gas. (a) Response time as a function of pore size in DPP2T-TT sensors. (b) Response time of DPP2T-TT as a function of NH₃ concentration, comparing devices without pores and with 700 nm pores. Error bars were calculated from 6-8 measurements on 3-4 independent samples at each condition.

Table S5. Recently reported sensing performance of OFET based NH₃ sensors.

Organic thin films	Limit of detection	Sensitivity ($\Delta I/I_0$)	Response time	Fabrication of the active layer	Ref.
Nanoporous DPP2T-TT	<1 ppb	27.8% (1 ppb) 51% (100 ppb)	0.4 s-1s	Spin-coating/printing	This work
pDPPCOOH-BT	10 ppb	12.5% (1 ppm)	>5 s	Spin-coating	[2]
HTEB ultrathin film	100 ppb	41% (100 ppb) 57% (500 ppb)	5-32 s	Solution shearing	[3]
CuPc-TPFB CoPc-TPFB ultrathin film	450 ppb	CuPc-TPFB 26% (450 ppb) CoPC-TPFB 28% (450 ppb)	9-120 s/>300s	Thermal evaporation	[4]
Pentacene	500 ppb	23% (3 ppm)	~100 s	Thermal evaporation	[5]
Graphene	500 ppb	10% (10 ppm)	>3600 s	Chemical vapor deposition	[6]
DPPT-TT	-	50% (10 ppm)	~5 s	Bar-coating	[7]

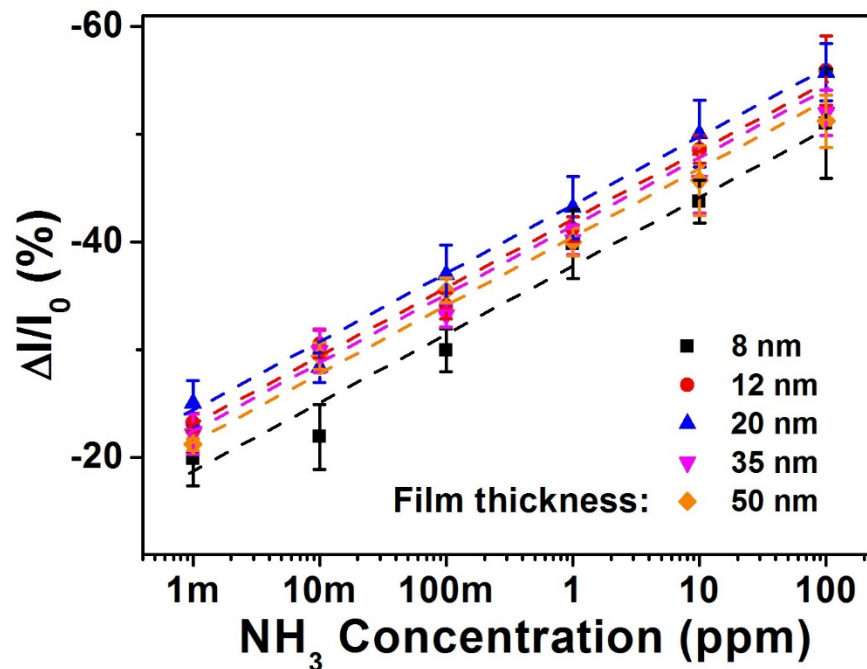
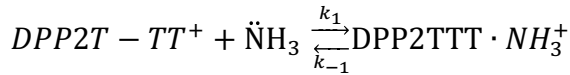


Figure S12. Film thickness dependent sensing performance of DPP2T-TT sensors to NH₃ gas. Sensitivity of DPP2T-TT devices with various film thicknesses as a function of ammonia concentration. The devices were constructed with a pores diameter of 400 nm. The error bars were calculated from more than five devices.

Supplementary Note 2. Sensing mechanism and reaction model

In OFET, the charge carriers accumulate and transport in the conducting channel at the semiconductor-dielectric interface. When the device is exposed to ammonia, a change in the charge carrier density takes place due to charge transfer reaction between ammonia and polymer resulting in a current change. Specifically, ammonia molecules act as electron donors to the p-channel, leading to a decrease of the source-drain current. Previous studies on the transduction mechanism of resistive gas sensors show that the sensing performance is determined by two processes: gas diffusion and surface reaction.^[8,9]

In thin film devices employed in this work, we estimated that the diffusion time scale is much smaller than the device response time scale. Considering ammonia diffusion in a solid film of 20-30 nm thick (h) and a diffusion coefficient (D) of 10^{-9} cm²/s, the time scale for diffusion is on the order of 10^{-4} s estimated from equation $t=h^2/D$, which is at least three orders of magnitude shorter than the measured response time. Therefore, we infer that the sensing process is in the reaction-limited regime with the Damköhler number (D_a) much less than 1 (D_a = reaction rate/ diffusion rate). This simplifies the reaction-diffusion problem into a simple reaction problem. We assume the reaction is a first-order homogenous reaction as the following:



with the gate induced hole carriers $DPP2T-TT^+$ ($C_{DPP2TTT^+}$) homogenously distributed in the conductive channel, and analyte NH_3 (C_{NH_3}) uniformly distributed through the film and inside the pores. The evolution of the $DPP2TTT \cdot NH_3^+$ (C) can be formulated as^[8,10]

$$\frac{\partial C}{\partial t} = R \quad \text{Equation (S3)}$$

$$R = k_1 C_{NH_3} C_{DPP2TTT^+} - k_{-1} C \quad \text{Equation (S4)}$$

where t is the time, R is the charge-transfer reaction rate, k_1 and k_{-1} represent the forward and backward reaction rate coefficients respectively. Combining equation S3 and S4 gives

$$\frac{\partial C}{\partial t} = k_1 C_{NH_3} C_{DPP2TTT^+} - k_{-1} C = k_1 (C_0 - C) C_{NH_3} - k_{-1} C \quad \text{Equation (S5)}$$

where C_0 is the gate voltage induced hole concentration, C_{NH_3} is the ammonia concentration. Solving equation S5 yields

$$C = \frac{C_0}{1 + \frac{k_{-1}}{k_1 C_{NH_3}}} (1 - e^{-(k_1 C_{NH_3} + k_{-1})t}) \quad \text{Equation (S6)}$$

In this case, C corresponds to the reduced hole concentration directly. The source-drain current (I) is proportional to the charge carrier concentration (n) in the conductive channel following $I \propto nq\mu$, wherein, q is the elementary charge and the mobility μ is constant. Therefore, the sensitivity relates to C as the following

$$\Delta I/I_0 = \frac{n' - n_0}{n_0} = \frac{-C}{C_0} = -\frac{1}{1 + \frac{k_{-1}}{k_1 C_{NH_3}}} (1 - e^{-(k_1 C_{NH_3} + k_{-1})t}) \quad \text{Equation (S7)}$$

where n_0 and n' are hole concentrations in the conductive channel before and after reaction with NH_3 . Equation S7 informs that the response time and sensitivity are controlled by the reaction rate constants (k_1 and k_{-1}) and ammonia concentration (C_{NH_3}). Specifically, a higher forward reaction rate constant and higher ammonia concentration lead to faster response and better sensitivity. This relationship is illustrated in Figure S13.

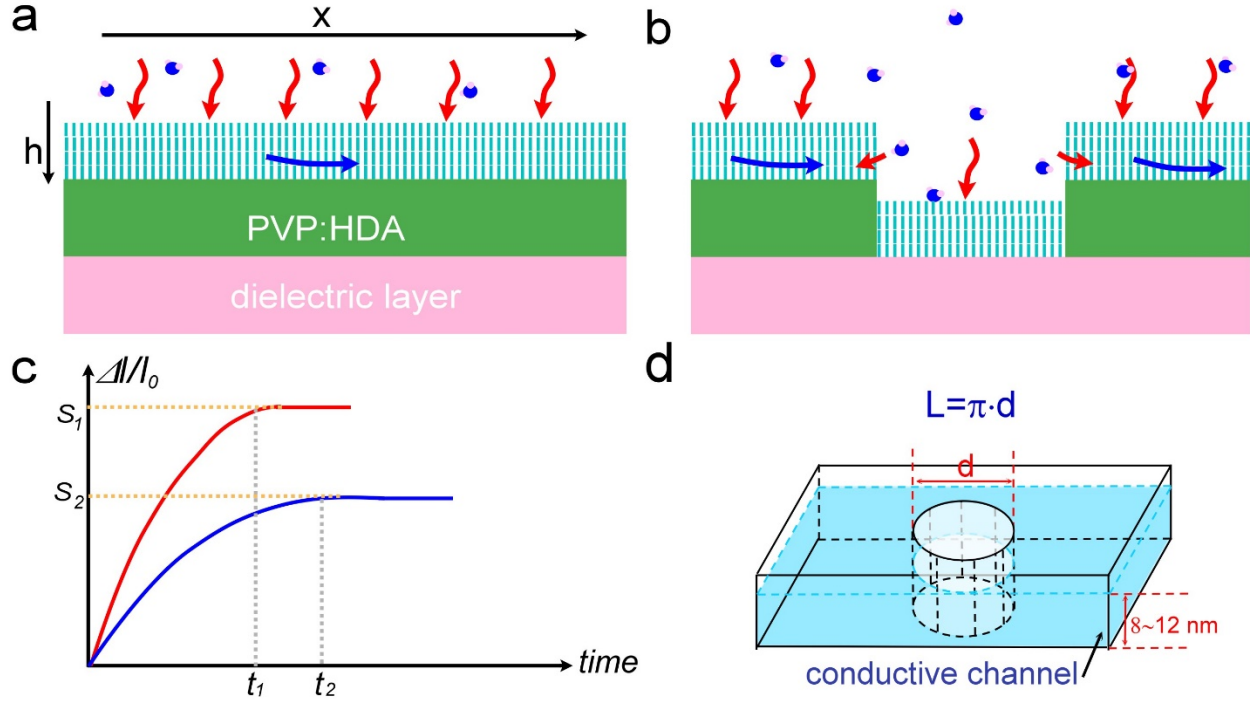


Figure S13. Sensing mechanism of nanoporous DPP2T-TT OFET devices. Cross-section view comparing OFET devices (a) without and (b) with pores. (c) Dynamics responses comparing nonporous (blue) and nanoporous (red) cases respectively. S_1 and S_2 are the sensitivities of nanoporous and nonporous OFET sensors, t_1 and t_2 represent the corresponding response time. (d) Schematic illustrating the reaction sites in the semiconductor layer.

Table S6. Calculated reaction constants as a function of pore sizes obtained from fitting the dynamic monitoring curves with Equation S7.

Pore diameter	0 nm	170 nm	260 nm	410 nm	550 nm	670 nm	720 nm
$A_s/A_t (\times 10^{-2})$	0	0.34 ± 0.1	0.52 ± 0.2	0.83 ± 0.1	1.09 ± 0.2	1.27 ± 0.1	1.19 ± 0.1
$k_1 (\times 10^8 \text{ s}^{-1})$	0.798	1.81	3.04	3.30	4.32	6.27	6.10
$k_{-1} (\text{s}^{-1})$	0.64	1.18	1.53	1.27	1.37	1.74	1.42

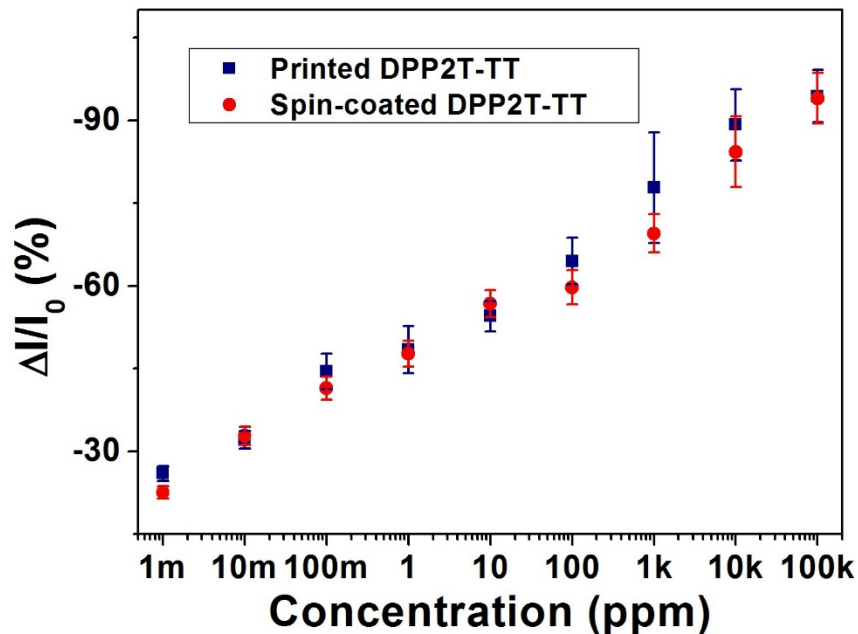


Figure S14. Comparison of sensing performance of solution-processed DPP2T-TT sensors. The current response shown are DPP2T-TT based OFET devices in the presence of NH_3 . The DPP2T-TT films were fabricated via the printing method (navy squares) and the spin-coating method (red points), respectively.

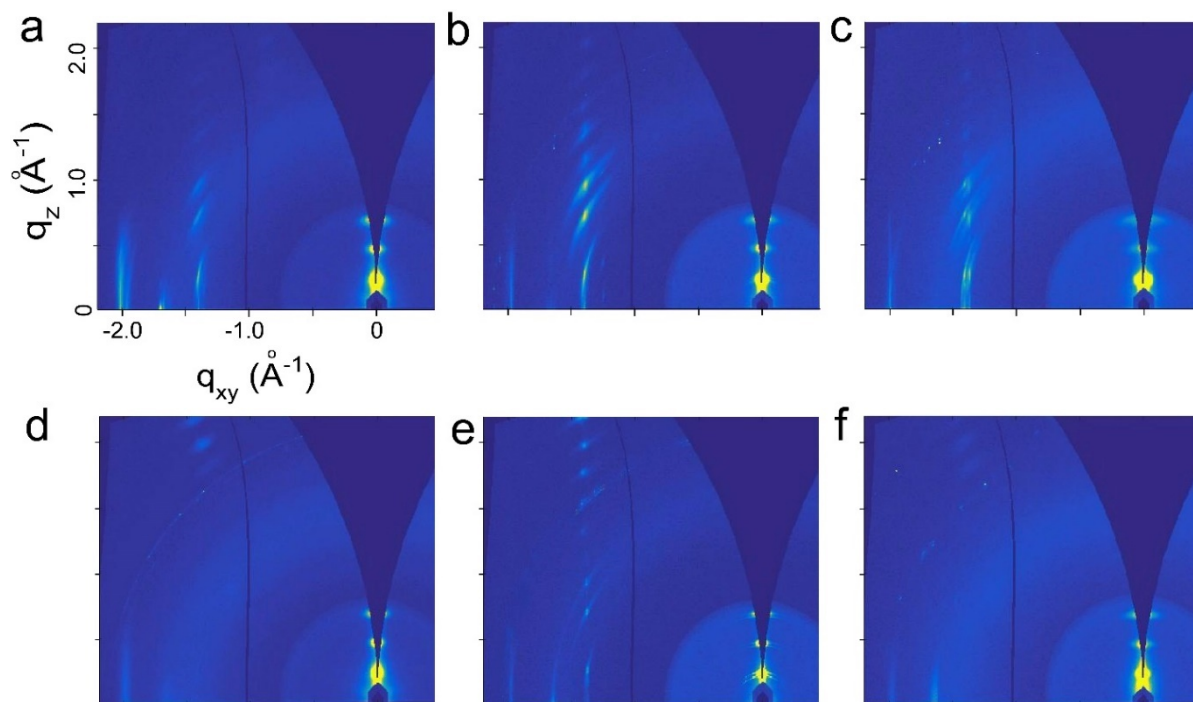


Figure S15. GIXD images of C_8 -BTBT thin films. GIXD images of (a-c) spin-coat and (d-f) printed C_8 -BTBT films on PVP:HDA with (a, d) 0 nm, (b, e) 100 nm and (c, f) 400 nm pores. The printing direction is parallel to the incident beam, which is also the charge transport direction in the transistor devices.

Table S7. Molecular packing in C₈-BTBT films characterized by GIXD.

Organic thin films	Spin-coated film			Printed film		
	Without pores	100 nm pores	400 nm pores	Without pores	100 nm pores	400 nm pores
Lamella spacing (Å)	26.54±0.02	26.50±0.02	26.50±0.02	26.65±0.02	27.84±0.01 26.47±0.02	26.95±0.02
FWHM of (002) peak (Å ⁻¹)	0.057±0.002	0.047±0.001	0.049±0.001	0.046±0.001	0.006±0.000 0.028±0.001	0.047±0.001
Stacking distance of peak at Q _{xy} = 2 (Å ⁻¹)	3.20±0.001 3.11±0.000	3.17±0.001	3.14±0.001	3.16±0.001	3.81±0.000 3.16±0.001	3.17±0.002
FWHM of peak at Q _{xy} = 2 (Å ⁻¹)	0.045±0.002 0.031±0.000	0.024±0.001	0.024±0.002	0.074±0.001	0.025±0.002 0.011±0.001	0.053±0.003

Table S8. Charge transport characteristics of C₈-BTBT based OFET devices.

Pore size	Treated conditions ^a	Mobility ^b (cm ² V ⁻¹ s ⁻¹) Avg(Max)	V _{th} (V) Avg(Min)	Log (I _{on} /I _{off}) Avg(Max)
0 nm	Without PEI	1.49 (1.83)	-22.4 (-20.2)	6.3(6.8)
	With PEI	1.22 (1.26)	-26.2 (-24.3)	5.9 (6.2)
300 nm	Without PEI	2.53 (2.8)	-13.2 (-3.0)	4.6 (5.5)
	With PEI	2.20 (2.7)	-33.0 (-30.0)	5.3 (6.0)

^a The devices were fabricated with Ag as source-drain electrodes and measured in the air.

^b Porosity in the device is not accounted for when calculating the mobility, which may lead to an underestimation of mobility in nanoporous devices.

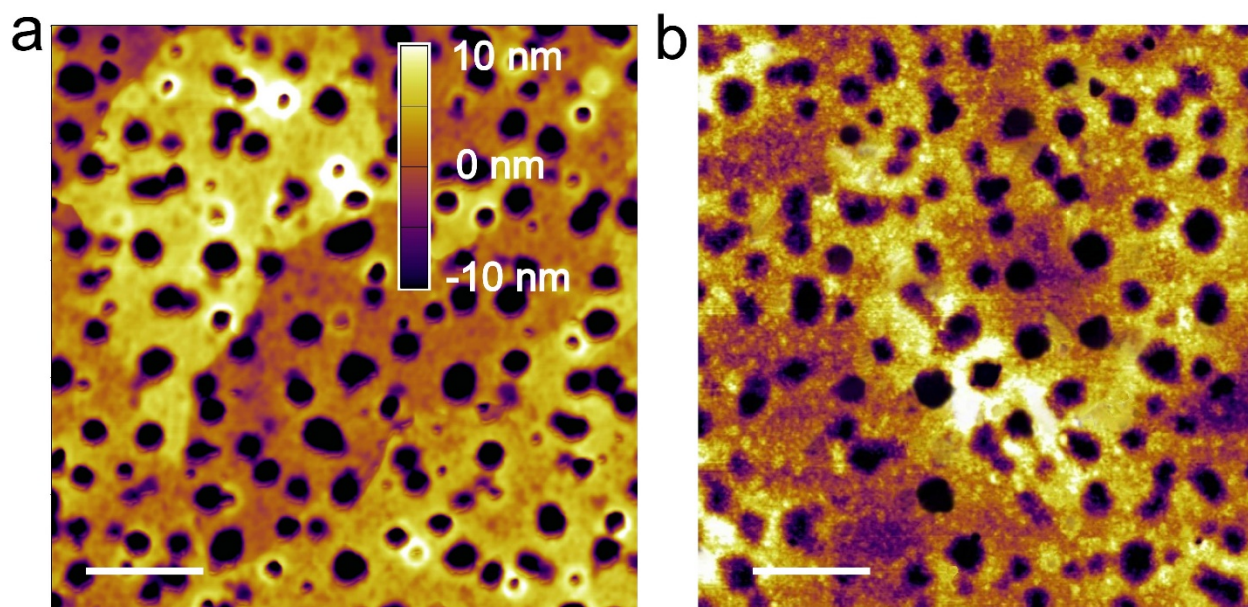


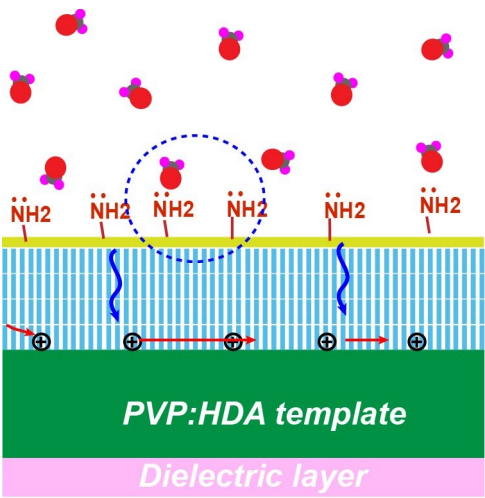
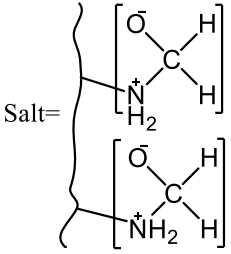
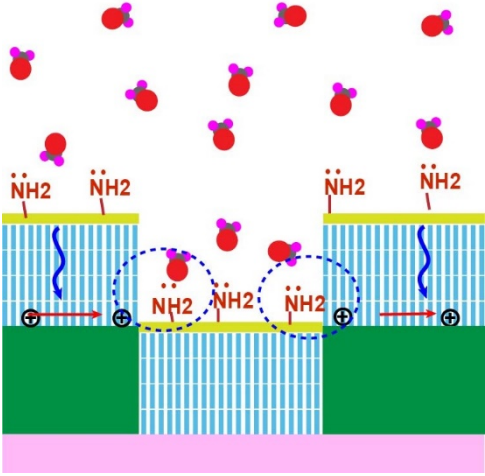
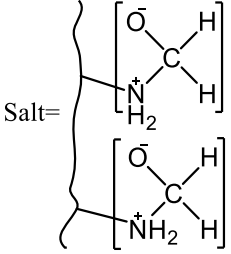
Figure S16. AFM image for C₈-BTBT film (a) before and (b) after PEI coated. The device was deposited with pores. Scale bar: 1 μ m.

Supplementary Note 3. Sensing mechanism for C₈-BTBT/PEI based formaldehyde sensor.

After spin-coated on the top of C₈-BTBT devices, PEI reduces the organic semiconductor through a redox reaction (instead of a charge-transfer reaction)^[11, 12], which leads to formation of electron-carriers in the semiconducting layer while leaving positively charged amine groups (e.g. $-\text{NR}_2^+$) in the PEI layer, as listed in Table S9. These electron-carriers diffuse from the top surface into the bottom conductive channel to neutralize the holes and reduce the on-current. When the device is exposed to CH₂O, CH₂O reacts with PEI to form salt, releasing the positive charge into the semiconducting layer. The hole carriers then diffuse from the top surface into the buried conductive channel to increase the on-current.

Comparing with and without nanopores, the initial reaction rate (differential) is significantly enhanced in nanopore devices, corresponding to a shortened total response time (integrated) (Figure S17). How does the presence of nanopores enhance the reaction rate between CH₂O and PEI-coated devices? We hypothesize that, in the nanopores, the fastest reaction occurs at the bottom of the pore wall in direct contact with the conductive channel (Table S9). In contrast, without nanopores, the reaction takes place at the top surface. There are two key differences between the reactions at the nanopore wall and that at the top surface. At the bottom of the nanopore wall, 1) positively charged C₈-BTBT in the conductive channel is engaged in the reaction, instead of neutral C₈-BTBT at the top surface; 2) the π electrons of C₈-BTBT is exposed at the pore wall to the reactants, whereas at the top surface, the reactants ‘see’ the alkyl chains instead due to edge-on stacking (GIXD images in Figure S15). Both factors are key to enhanced reaction rates with the presence of nanopores.

Table S9. Proposed formaldehyde sensing mechanism of C8-BTBT/PEI OFET sensors

Device structure	Reaction mechanism
 <p style="text-align: center;">Devices without pores</p>	<p>Step 1:</p> $C_8BTBT + PEI \cdot NH_2 \leftrightarrow C_8BTBT^- + PEI \cdot NH_2^+$ $C_8BTBT^+ + C_8BTBT^- \rightarrow C_8BTBT$ <p>Step 2:</p> $C_8BTBT + PEI \cdot NH_2^+ + CH_2O \leftrightarrow C_8BTBT^+ + [Salt]$ <div style="text-align: center;"> <p>Salt=</p>  </div>
 <p style="text-align: center;">Device with pores</p>	<p>Step 1:</p> $C_8BTBT^+ + PEI \cdot NH_2 \leftrightarrow C_8BTBT + PEI \cdot NH_2^+$ <p>Step 2:</p> $C_8BTBT + PEI \cdot NH_2^+ + CH_2O \leftrightarrow C_8BTBT^+ + [Salt]$ <div style="text-align: center;"> <p>Salt=</p>  </div>

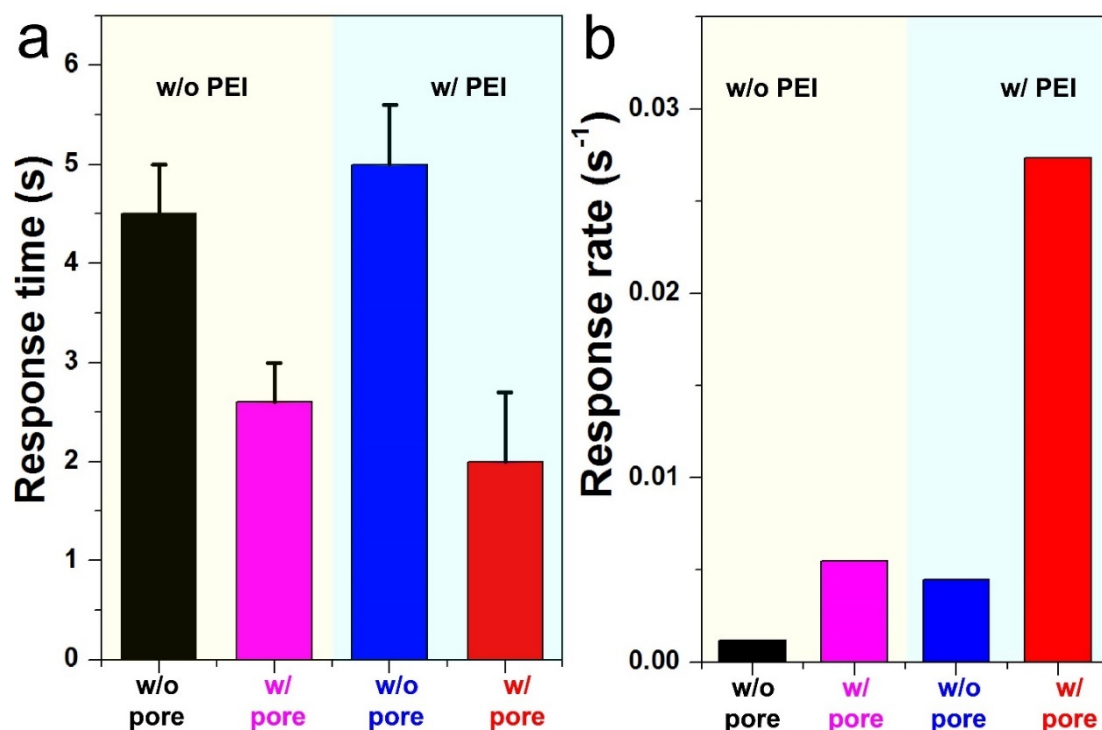


Figure S17. Sensitivity and response time for formaldehyde sensing. (a) Integrated response times of corresponding devices to 1 ppm formaldehyde of C₈-BTBT/PEI transistor devices with (red) and without (blue) pores as compared to C₈-BTBT transistor device with (magenta) and without (black) pores over a wide range of formaldehyde gas concentration. (b) Initial response rate of C₈-BTBT devices upon exposure to 1 ppm formaldehyde. These data were calculated from the slopes of the dynamic monitoring curves.

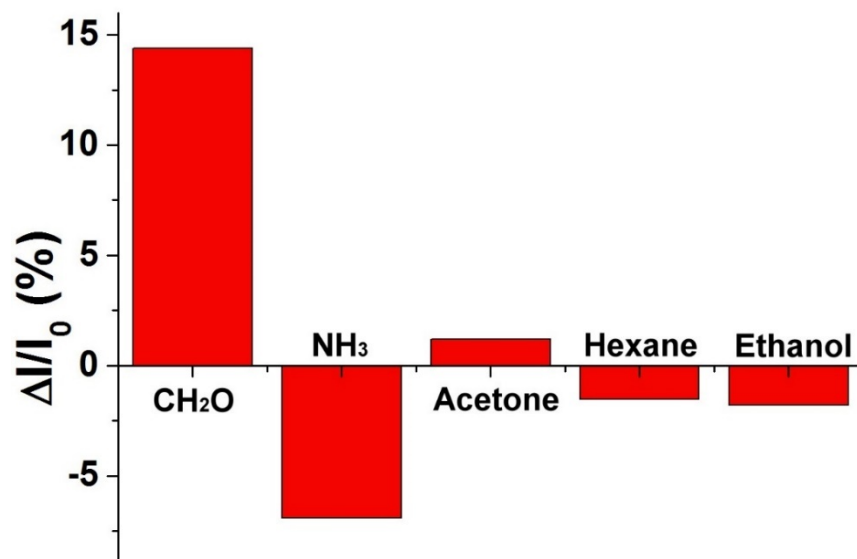


Figure S18. Selectivity of PEI coated nanoporous C₈-BTBT sensors. Figure shows current response of nanoporous C₈-BTBT OFETs to various gases with a concentration of 10 ppb. The sensing measurements were carried out with a gate voltage of -40 V and drain voltage of -40 V.

Table S10. Reported concentrations of ammonia in breath of healthy and diseased subjects

Volunteers	Controls (ppb _v)		Diseased (ppb _v)		Reference
	Mean	range	Mean	range	
Subjects of various age and gender		422-2389 ^a			13
Subjects of various age and gender	833	248-2935 ^a			14
End-stage renal disease	960	425-1800 ^b	4800	820-14700	15
Renal failure	250			2800-5700	16
End-stage renal disease	280±120		914.5±301.4 ^c or 964.4±402.4 ^d		17
End-stage renal disease		120-300 ^b (10% error)		920-1700 (10% error)	18

^aThe data was calculated with samples from different age/gender;

^bThe data was measured with dialyzed sample

^c by cavity ring-down spectroscopy

^d by ion mobility spectrometry

We note that the wide distribution of breath ammonia concentrations in each state is largely due to subject-to-subject variation. Specifically, the studies referenced below show that subjects of different age groups and gender exhibit very different level of breath ammonia concentration. However, for each subject at a particular health state, the standard deviation of the breath ammonia concentration is significantly less, ranging from 10-50% of the mean within the period of the study (months). This necessitates the development of low-cost sensing technologies for personalized health monitoring, in which case the baseline of sensor response can be established for each individual for long term health monitoring. Our study shows the first step towards achieving this goal using low-cost, solution-processed flexible electronic chips.

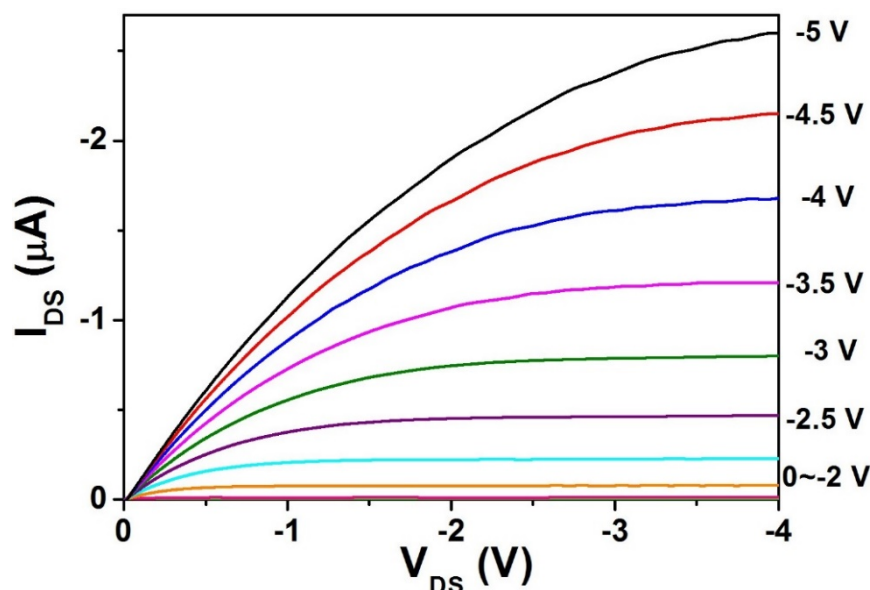


Figure S19. Output characteristics of flexible OFET with DPP2T-TT as the semiconductor layer.

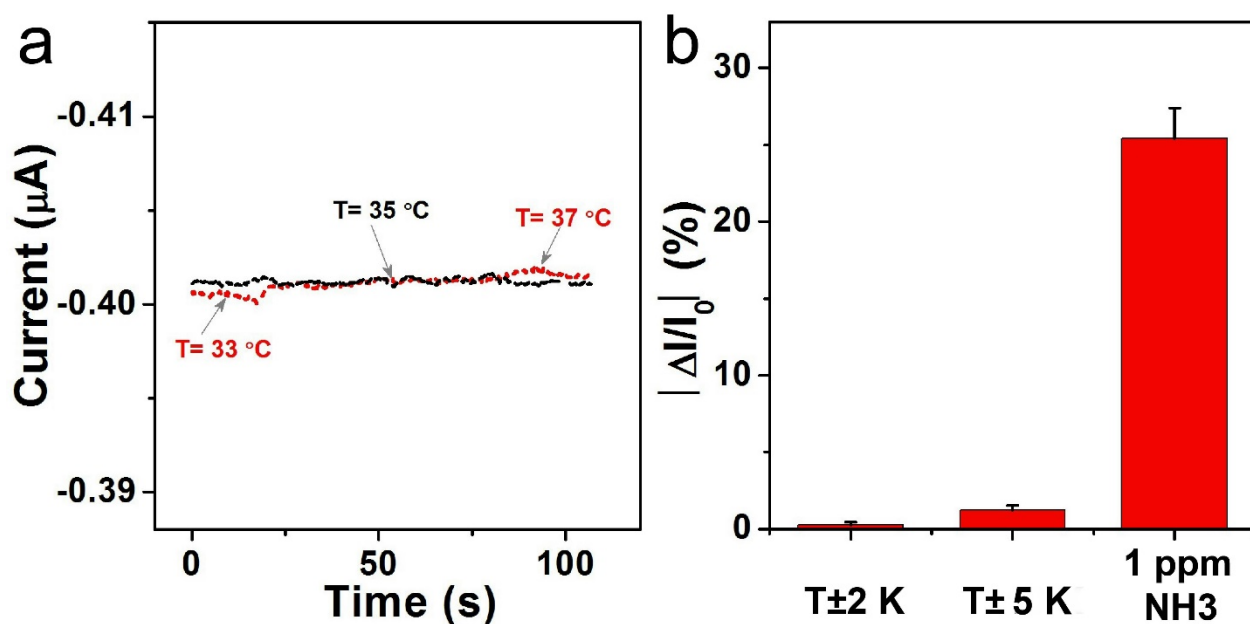


Figure S20. Effect of temperature fluctuations on sensing performance. (a) Dynamic current response of nanoporous DPP2T-TT sensors at constant 35°C and with varying temperatures between 33-37°C. (b) Sensitivity of nanoporous DPP2T-TT devices to temperature fluctuations vs. to 1 ppm NH_3 . The temperature of end-expired breath varies by $\sim 2^\circ\text{C}$, ranging from 33.3-35.5°C, with a mean of 34.5°C both men and women considered¹⁹. When the temperature varies between 33-37°C. Only very slight current fluctuation of $\sim 0.2\%$ were observed as a result of the 4°C temperature fluctuations around a mean of 35°C. Furthermore, the small changes caused by 2°C and 5°C temperature fluctuations are insignificant compared to the response to 1 ppm ammonia.

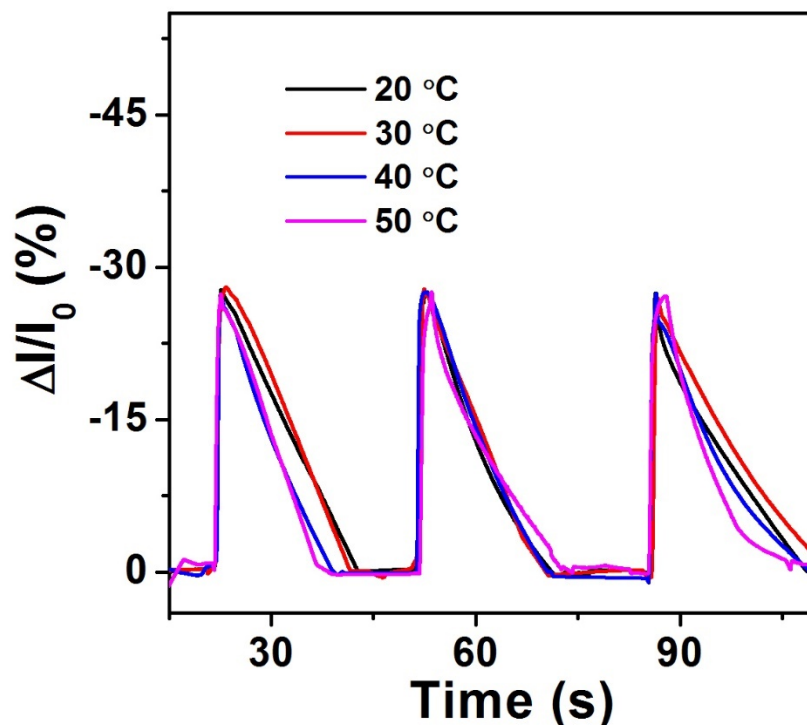


Figure S21. Effect of environment temperature to sensitivity. Dynamic-sensing response curve of nanoporous DPP2T-TT FET devices to 1 ppb ammonia under various environment temperatures. The pore size is ~ 600 nm. The sensitivity $\Delta I/I_0\%$ to ammonia was found independent of environment temperature. This result is not surprising, because both the current change ΔI and the baseline I_0 vary with respect to environment temperature and the effects cancel out.

Supplementary Note 4. Effect of humidity on sensitivity and selectivity.

Here, we will discuss the humidity calibration curve, the effect of humidity on sensitivity and selectivity, and the impact of breath humidity fluctuations on sensing performance. We will further demonstrate two separate methods to eliminate the humidity effect: humidity compensation and sample de-humidification. We note that these methods have been successfully developed and demonstrated in previous works using nanomaterial sensing platforms.^[20-22] Here we show that these methods can also apply to the flexible electronics sensing platform.

Human breath usually exhibits $>80\%$ relative humidity^{20,21}. Correspondingly, we prepared samples with relative humidity (RH) ranging from 60% to 100% using air as the carrier gas and measured current responses using nanoporous DPP2T-TT field-effect transistors. We chose to perform these measurements in ambient air to mimic practical applications. In contrast, previous studies frequently used vacuum or inert environment (e.g. N_2) for measuring sensing performance or studying sample humidity effect. In these studies, the impact of ambient humidity and oxygen was neglected. In our study, the sensors were first equilibrated in ambient air prior to measurements, and then subjected to sample gas to measure the current response. We measured both control samples with only moisture in air to obtain the humidity calibration curve (Figure S22a), and the samples with various ammonia concentrations in the presence of high sample humidity (Figure S22b and S22c). We can see that sample relative humidity alone does significantly alter the current response, and follows a linear trend to yield a humidity calibration

curve. The current response to ammonia systematically shifts positive with increasing RH, a trend consistent with the humidity calibration curve (Figure S22). The humidity effect can be fully compensated following an established procedure²⁰. In other words, the sensitivity to humidity and VOC is additive. The compensated data falls on the same curve regardless of the sample RH% levels prior to compensation (open circles in Figure S22c). The compensated data corresponds to the current response of samples prepared without water moisture added (Figure S22b), measured at the lab ambient conditions (Both of the sample and ambient are at a RH=56%, at 25°C). We note that the ambient humidity alone (sensing of carrier gas in ambient air) also impacts the sensing response. This can be addressed by simply measuring calibration curves (for sample humidity) at the corresponding ambient humidity to perform humidity compensation. Alternatively, the ambient humidity can be tightly controlled, as most laboratories do.

Now we discuss the impact of humidity fluctuations. The humidity calibration curve (Figure S22) yields 0.54% current change ($\Delta I/I_0\%$) per 1% variation in sample relative humidity (RH). This is equivalent to $1.7 \times 10^{-3}\%$ change in $\Delta I/I_0\%$ per 1 ppm change of water concentration in the sample. Therefore, 2% fluctuations in breath humidity from person to person will only cause $\sim 1\%$ variation in the current response. In comparison, we measured 7.1% change in $\Delta I/I_0\%$ per decade change in ammonia concentration, or $\Delta I/I_0\% / \log(\text{ppm}_v) = 7.1\%$ independent of the sample relative humidity (Figure S22). We can see that when ammonia concentration changes by close to an order of magnitude as in the case of renal failure, the impact of small humidity fluctuations will be insignificant. In addition, we note that humidity sensors can be used simultaneously with the breath sensors to analyze breath humidity of a particular subject at the time of breath measurement. Humidity compensation can be performed subsequently to eliminate the humidity effect.

We also tested an alternative method – sample de-humidification to eliminate the humidity effect prior to sensing. Desiccation has been demonstrated as an effective method for breath sample de-humidification, without interfering with certain VOCs of interest.^[23] Previous studies identified sodium hydroxide (NaOH) as a very effective dehumidifying agent without removing ammonia.^[24-26] We applied NaOH as desiccants to dry ammonia samples spanning a wide concentration range prior to sensing. The sensing measurements were carried out in dry N₂ environment. Figure S23 shows that the current response to dried ammonia overlaps with those of humid samples after humidity compensation. This result verifies that in both cases, the current responses are only attributed to ammonia, and not to other compounding factors such as sample humidity and test environment. We further tested the sensitivity to ammonia in the presence of dried healthy breath gas. For samples with and without ammonia, both current response curves shifted, but by the same extent. In summary, we show that both humidity compensation and sample de-humidification are effective strategies to eliminate sample humidity effect in the case of ammonia sensing. Under the background of complex VOC mixtures, humidity compensation is likely to be a more suitable approach, so long as the humidity effect is additive.^[20-22,27,28]

Above, we discussed the effect of sample humidity on sensitivity. With regards to selectivity, Table S11 and Figure S24 demonstrates that the sample humidity does not negatively impact selectivity to ammonia in a VOC mixture background. In addition, the humidity effect can also be compensated using the humidity calibration curve in this case.

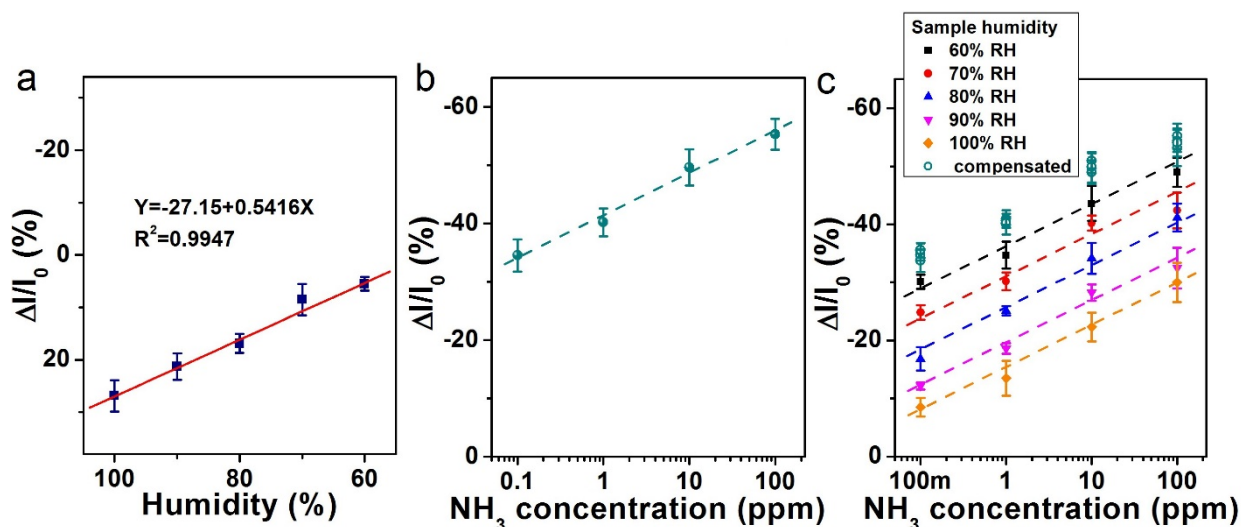


Figure S22. Effect of sample humidity on sensitivity to NH_3 gas. (a) Current response of the porous DPP2T-TT devices to air samples of various RH only. To mimic the conditions during practical applications, we employed air as the carrier gas and performed the measurements in the ambient condition, at RH=56%. The humidity calibration curve yields 0.54% current change ($\Delta I/I_0$ %) per 1% variation in sample RH. This is equivalent to 1.7×10^{-3} % change in $\Delta I/I_0$ % per 1 ppm change of water concentration in the sample. (b) Current response of the porous DPP2T-TT devices to air samples with various concentrations of ammonia only. (c) Uncompensated (closed symbols) and compensated (open circles) current response of the porous DPP2T-TT devices to mixture of ammonia and moisture with air carrier gas. The error bars were calculated from more than 5 devices. The average pore diameter is ~ 600 nm.

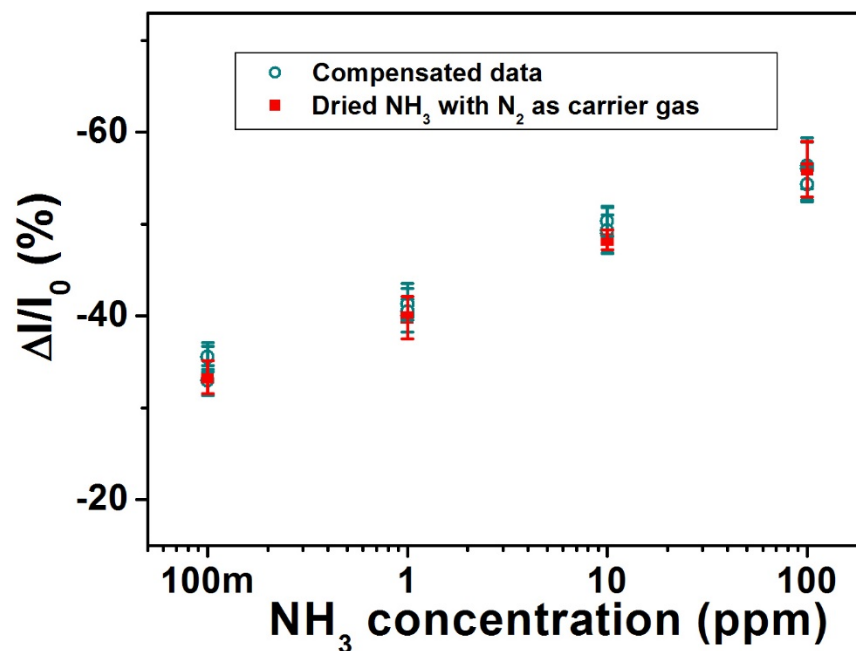


Figure S23. Effectiveness of sample de-humidification using sodium hydroxide desiccants. Current responses of dried ammonia (red dots) is compared with those of compensated humid samples (dark cyan) from Figure S22. The NH₃ was pre-treated with desiccant for 3h and measured in the glovebox (RH~0).

Table S11. Vapor pressure and concentration of analytes in the control sample (mixture A)

VOCs	P₀ in atm (at 25 °C)	P_a/P₀ in mixture A	10⁹ P_a/1atm (ppb)
Ammonia	9.76	0	0
Acetone	0.303	10 ⁻⁶	303
Acetonitrile	0.117	10 ⁻⁶	117
Ethanol	0.065	10 ⁻⁶	65
Formaldehyde	5.12	10 ⁻⁶	5120
Hexane	0.178	10 ⁻⁶	178
Isopropanol	0.058	10 ⁻⁶	58
Toluene	0.037	10 ⁻⁶	37

The VOCs in the control mixture A are among the prominent VOCs found in human breath. We also diversified the VOCs chosen, spanning from highly polar to non-polar molecules, carrying different functional groups. We use this control sample as the background for studying sensor selectivity with respect to ammonia. In the table, we list for each component the saturated vapor pressure at 1 atm and 25°C, its composition expressed in P_a/P₀, and the corresponding concentration in ppb (10⁹ P_a/1atm which is equivalent to ppb_v typically reported in the literature).

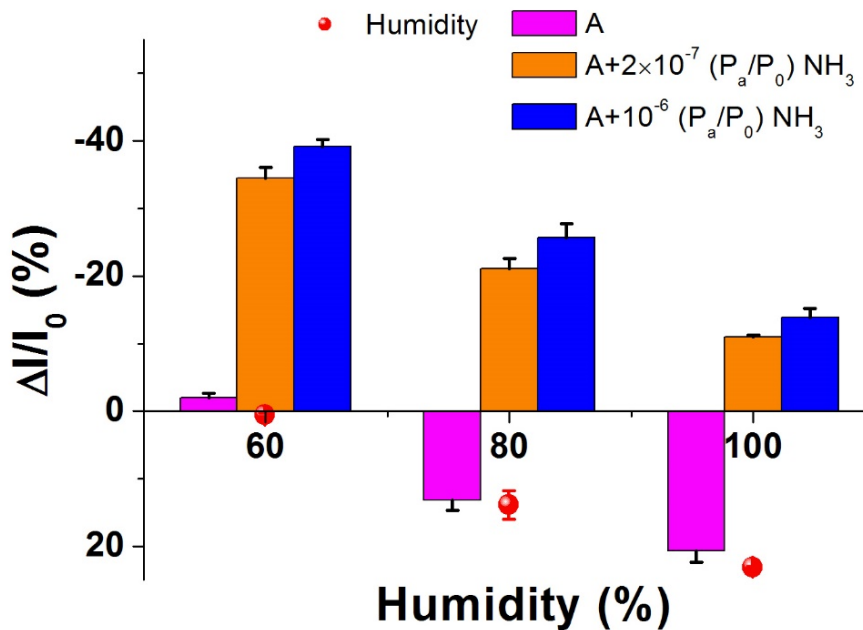


Figure S24. Selectivity to ammonia in VOC mixture of high sample humidity. Mixture A is the control sample (Table S11) - a gas mixture containing acetone, formaldehyde, acetonitrile, hexanes, ethanol, isopropanol and toluene with $P_a/P_0=1 \times 10^{-6}$. Sample humidity calibration was performed using only humid carrier gas (red dots). All measurements were performed in ambient conditions, with ambient temperature of 25 °C and ambient RH=60%. Compared with the control sample (mixture A), the samples with $2 \times 10^{-7} P_a/P_0$ ammonia led to a significantly increased the response of the nanoporous sensors. In addition, increasing the ammonia concentration by five times further increases the current response that is clearly distinguishable and consistent throughout the trials. These results show that the selectivity is not undermined by the VOC background studied. When ammonia level rises by several times as reported in the case of renal failure, we observed clearly discernable changes in the current response in the VOC mixture background. Furthermore, the sample humidity is varied between 60% to 100%, containing the range of breath humidity (>80%). The current responses systematically vary with sample humidity, without influencing the selectivity (as selectivity is relative to the background).

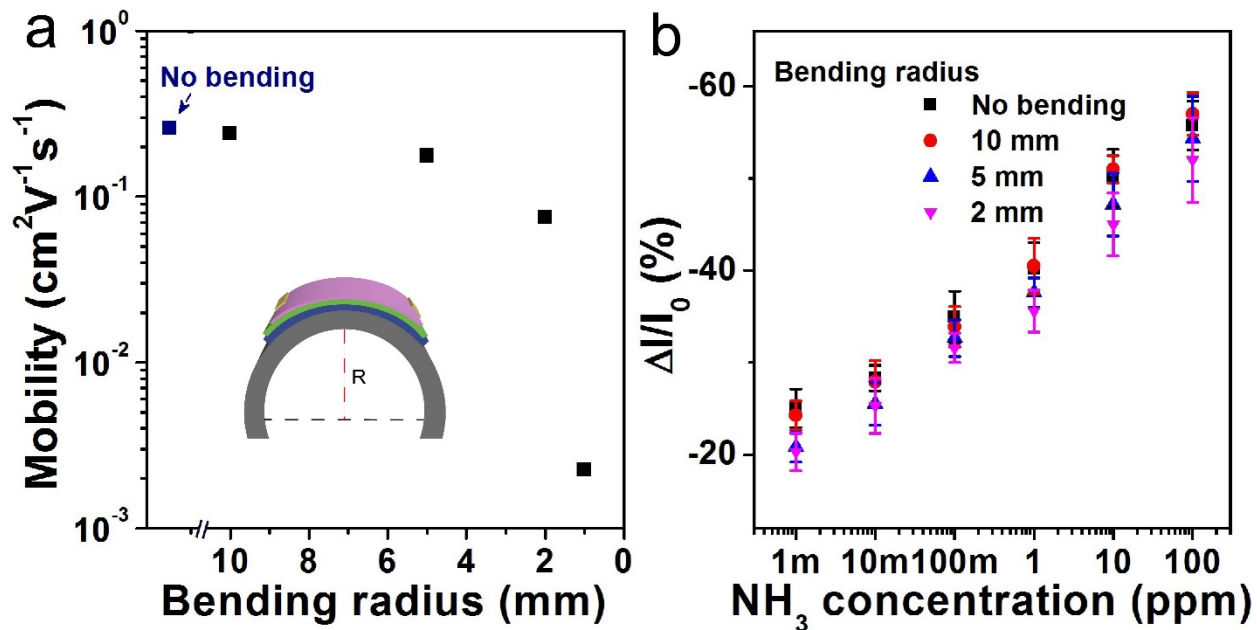


Figure S25. Effect of bending on mobility and sensitivity to ammonia. (a) Impact of bending radius on charge carrier mobility of the flexible DPP2T-TT devices during outward bending. The insert shows the illustration of a bent OFET. (b) Sensitivity of nanoporous DPP2T-TT sensors with various bending radius. In these studies, the substrate used for flexible device fabrication is PET coated with 0.127 mm thick ITO. Gold electrodes were deposited on the semiconducting layer to fabrication top contact bottom gate devices. At a bending radius of 10 mm, charge carrier mobility and ammonia sensitivity hardly changed. For wearable electronics applications, the bending radius is typically on the order of tens of millimeters. Therefore, we expect our sensor chip to be fully compatible with wearable electronics applications. When we continue to decrease the bending radius to down to 2 mm, the charge carrier mobility and the sensitivity start to shift systematically across the entire ammonia concentration range tested. In case if such small bending radius is needed in practical applications, bending calibration curve can be collected to compensate the sensitivity drift, $\Delta I/I_0\%$. When the bending radius is further decreased down to 1mm, the charge carrier mobility drops by $\sim$ two orders of magnitude, indicating that the OFET devices were damaged under high mechanical strain. This is not surprising as high bending strain was shown to be detrimental to electrode-semiconductor and semiconductor-substrate interfaces²⁹. Therefore, below 2mm bending radius, the sensor devices no longer function properly.

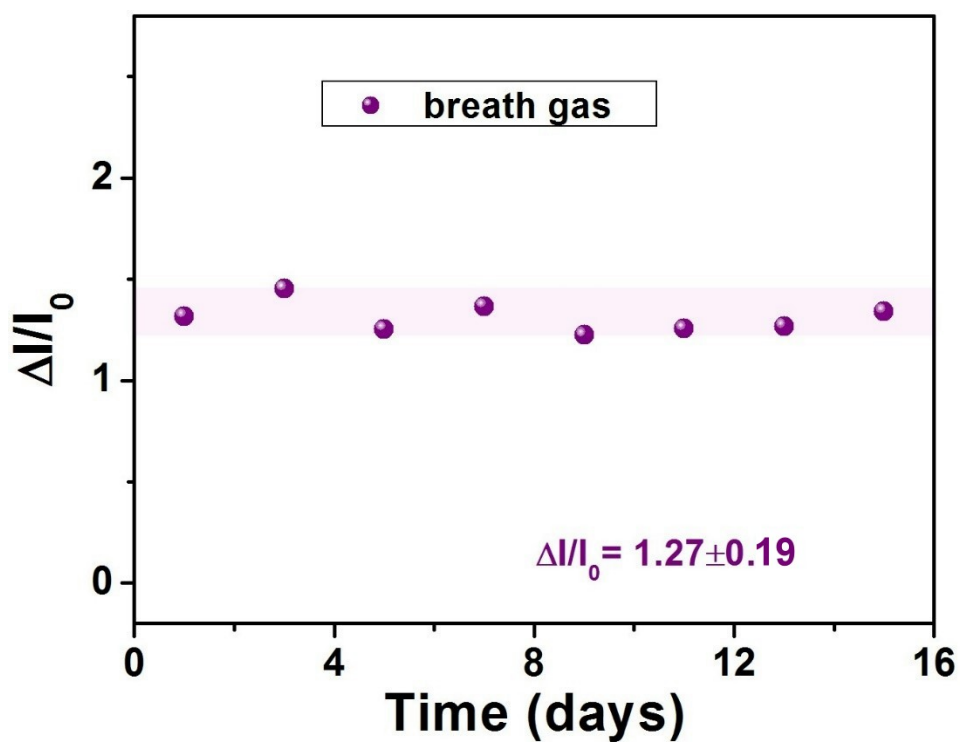


Figure S26. Baseline for the current response of DPP2T-TT based breath sensors to health breath of an individual over a 15-day period. The devices were fabricated on flexible porous substrate and the breath gases were collected from the same volunteer at the same time of the day.

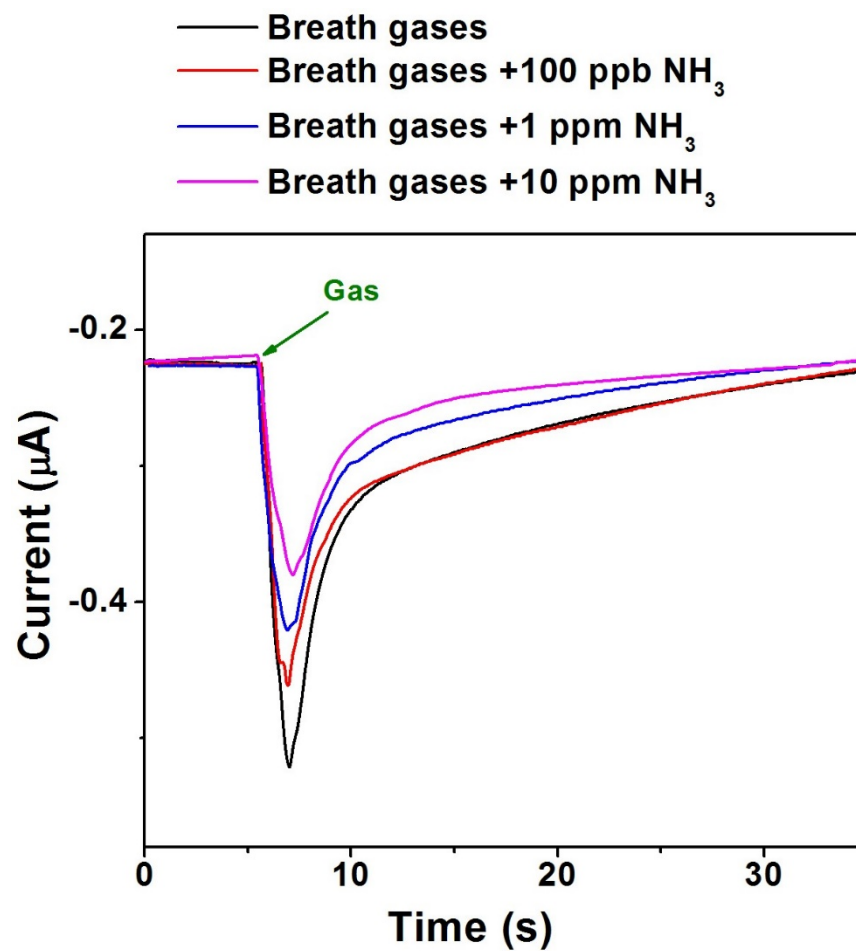


Figure S27. Dynamic monitoring curve of nanoporous flexible breath sensor to healthy breath and simulated breath with higher than unusual ammonia concentrations. For the simulated breath sample, 100 ppb, 1 ppm and 10 ppm NH_3 were added to the health breath gas respectively.

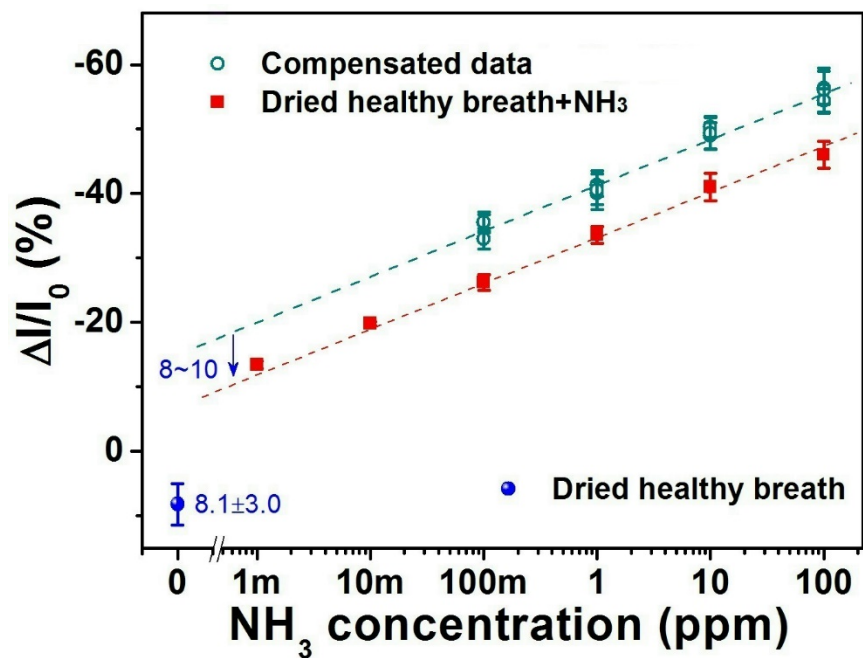


Figure S28. Current response to dried healthy breath samples with various NH_3 . All of the samples were pre-treated with desiccant for 3h and measured in the glovebox ($\text{RH} \sim 0$). The dark cyan circles represent the compensated data with RH calculated in Figure S22.

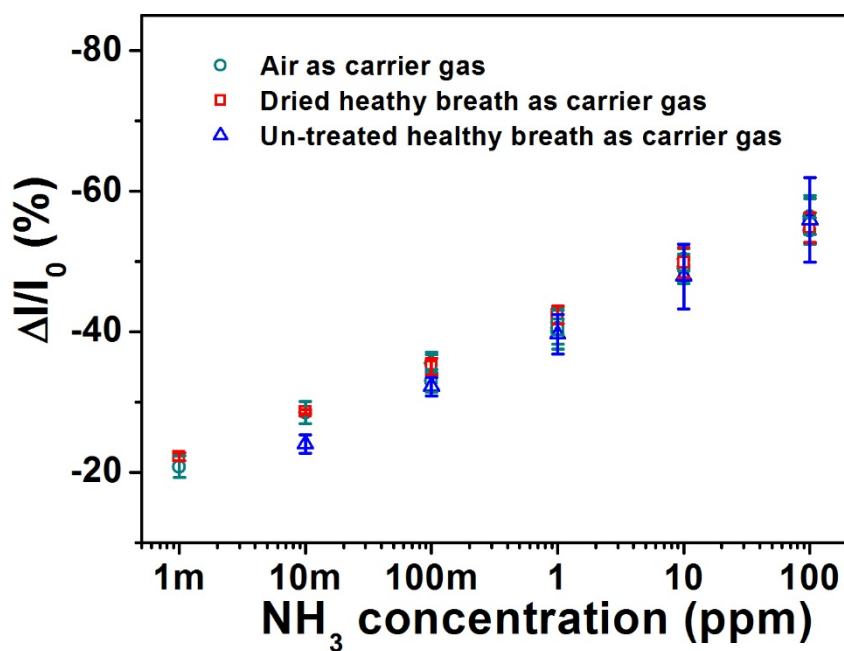


Figure S29. Comparison of current responses to ammonia compensated with air (dark cyan circle), dried healthy breath (red squares) and untreated healthy breath gas (blue triangle) as the carrier gas, over a wide range of ammonia concentration from 10 ppb to 100 ppm. The error bars were calculated with more than 5 devices.

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