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Electronic Supplementary Information

Polymer-based flexible NO_x sensors with ppb-level detection at room temperature using Breath-figure molding

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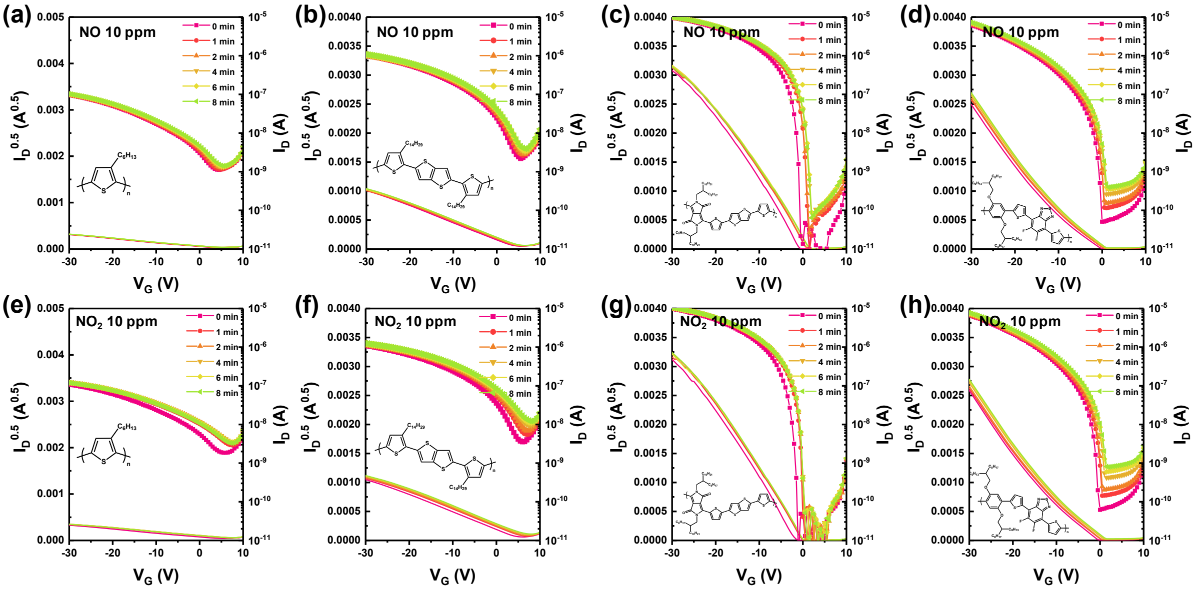

Fig. S1 Time-dependent transfer curve behaviours of (a) P3HT, (b) PBTTT, (c) DPP-DTT and (d) PP2DTFBT-DTT after exposure to 10 ppm NO. Time-dependent transfer curve behaviours of (e) P3HT, (f) PBTTT, (g) DPP-DTT and (h) PP2DTFBT-DTT after exposure to 10 ppm NO_2.

Supplementary Note. The calculation of paracrystalline disorder and GIXD analysis details

In order to perform the crystallinity analysis between polymer thin films by GIXD, there are several methods to know, such as orientation peak analysis, pole figure analysis, degree of crystallinity, and paracrystalline disorder analysis. In the case of there is a clear difference in orientation peaks (q_{xy} or q_z direction), we can easily compare the disorder parameters (or crystallinity) between polymer films. For example, Figure S2 showed highly oriented edge-on structures, with well-developed Bragg diffraction peaks of up to (004) in the q_z direction in DPP-DTT and up to (003) in the q_z direction in PPDT2FBT-DTT. Therefore, we can qualitatively confirm DPP-DTT has higher crystallinity than PPDT2FBT-DTT. In addition, there paracrystalline disorders ($g_{(010)}$) are 12.62% and 13.84% for DPP-DTT and PPDT2FBT-DTT, respectively. The most obvious method for crystallinity analysis is to obtain the degree of crystallinity, but it is difficult to comparatively analyze thin films of other casting conditions in this way, since the thickness and incident beam conditions must be exactly matched between the films to be compared. Therefore, we performed crystallinity analysis using pole figure analysis or paracrystalline disorder. There are two directions in q_z and q_{xy}, and then we can obtain paracrystalline disorder parameters of $g_{(l00)}$ and $g_{(010)}$ for each. However, as shown in GIXD image, DPP-DTT and PPDT2FBT-DTT polymers (also same in P3HT and PBTTT case) have long-range lamellar order but less order in π-stacks, which directly related in charge transport direction. Therefore, it is reasonable to make a comparison between $g_{(010)}$ values with higher paracrystalline disorder values (means more amorphous). Unfortunately, there polymers have only single peak in q_{xy} direction, so we estimate paracrystalline disorder by single peak-width estimation. In the case of comparison between DPP-DTT films (pristine, BF-S, BF-M and BF-L), all films showed well-developed Bragg diffraction peaks of up to (004) in the q_z direction. Therefore, it is hard to compare qualitatively analysis, so that we calculated paracrystalline disorder parameters of films along π-stacks direction.

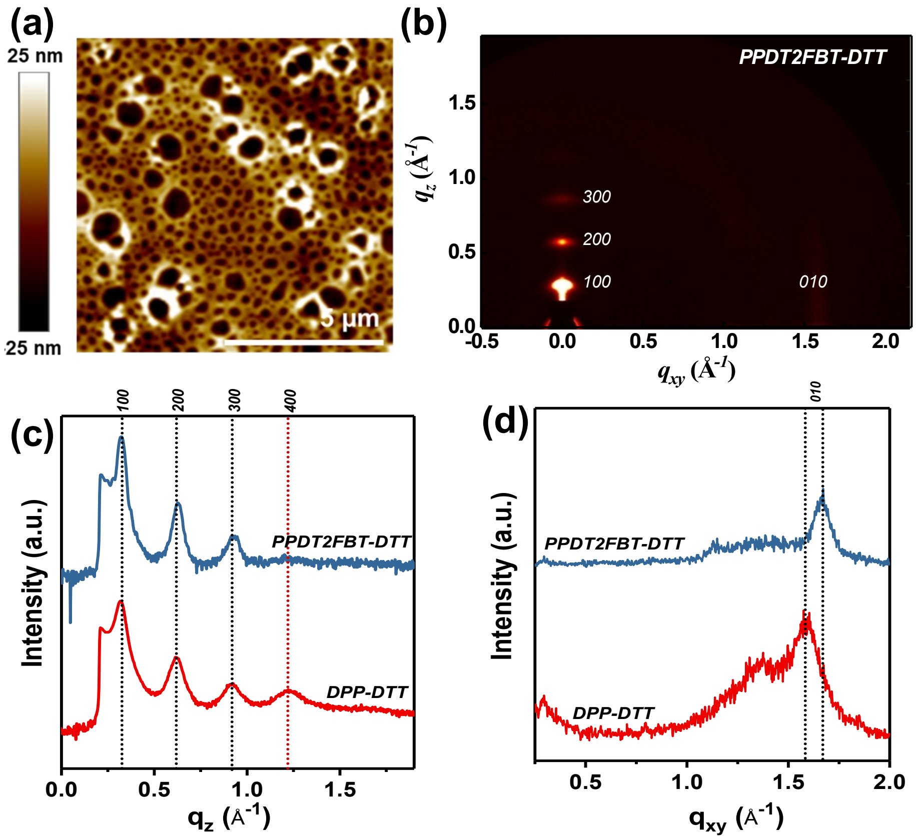

Fig. S2 (a) AFM topographical image of BF-molding in PPDT2FBT-DTT film (formation condition is same in BF-M of DPP-DTT film). (b) GIXD pattern of PPDT2FBT-DTT pristine film. The DPP-DTT and PPDT2FBT pristine film profiles extracted from their GIXD image along (c) with q_z direction and (d) q_{xy} direction.

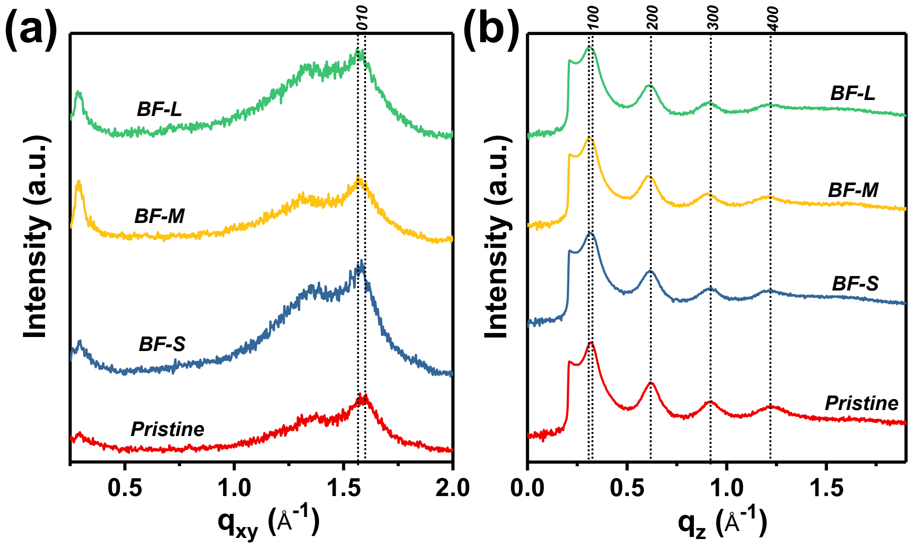

Fig. S3 DPP-DTT (pristine, BF-S, BF-M and BF-L) profiles extracted from their GIXD image (Figure 1) along (a) with q_z direction and (b) q_{xy} direction.

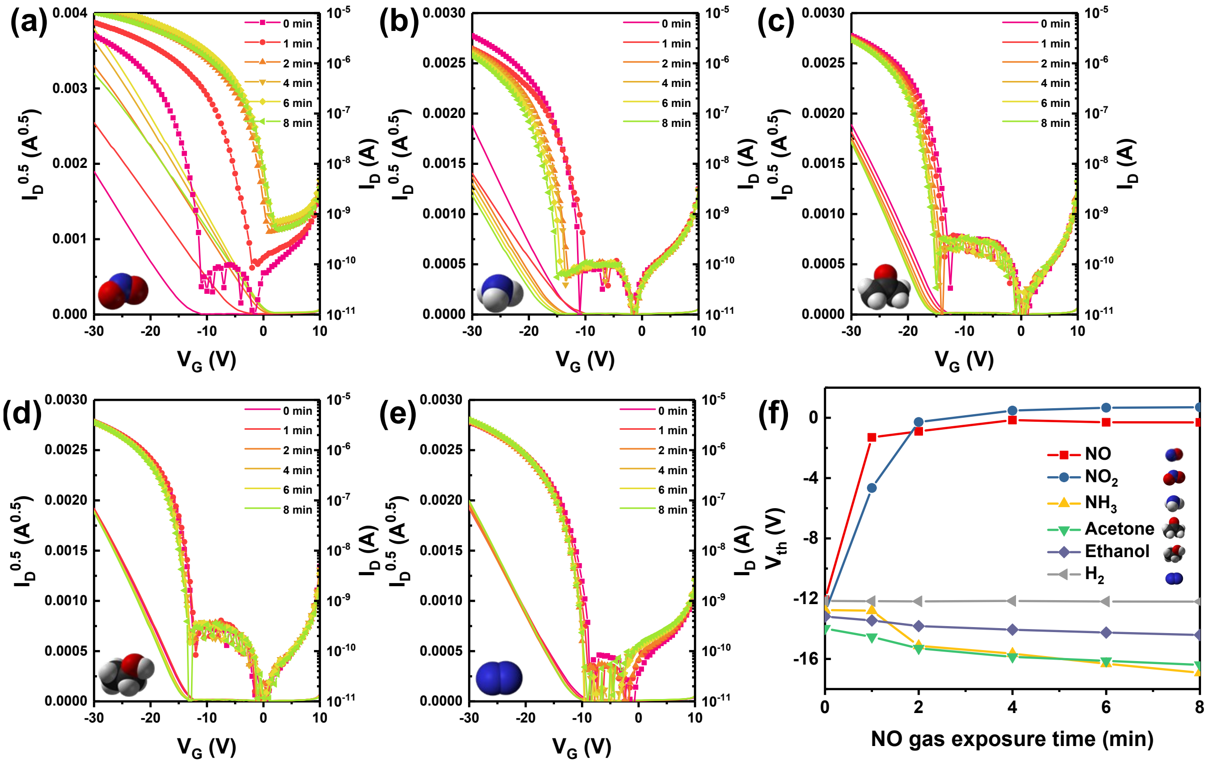

Fig. S4 Time-dependent transfer curve behaviours of BF-M OFETs after exposure to 10 ppm of (a) NO_2, (b) NH_3, (c) acetone, (d) ethanol, and (e) H_2. (f) Corresponding time-dependent threshold voltage shift after exposure to 10 ppm of various gas.

Table S1 The key parameters of recently reported organic gas sensors

Active materials	Gas sensor type	Film structure	Target gas	Detection range	$t_{90,\mathrm{res}}$	$t_{10,\mathrm{rec}}$	Sensitivity[b]	LOD[c]	Detection limit (measured)	Flexibility	Ref.
DPP-DTT (Polymer)	Transistor	Porous active layer (Breath figure molding)	NO	0.01-10 ppm	174-267 s	693 s	774.69 %/ppm	110 ppb	200 ppb	Y	This work
CuPc (Small molecules)	Transistor	Porous PS dielectric (UV-ozone treatment)	NO_2	1-10 ppm	~270 s[a]	~270 s[a]	145.4 %/ppm	415 ppb	1 ppm	N	14
TIPS-Pentacene (Small molecules)	Transistor	Crystalline active layer	NO_2	0.02-20 ppm	100-180 s	360-400 s	1181 %/ppm	20 ppb	300 ppb	N	23
DPPT-TT (Polymer)	Transistor	Ultrathin active layer (Bar coating)	NH_3	10 ppm	~180 s[a]	~180 s[a]	N.A.	N.A.	10 ppm	Y	9
P4TI-CF (Polymer)	Transistor	Plain (Morphology control by molecular engineering)	NH_3	1-100 ppm	60-180 s	~300 s a)	N.A.	N.A.	1 ppm	N	17
C10-DNTT (Small molecules)	Transistor	Monolayer organic crystal (Dual solution shearing)	NH_3	10-100 ppb	~350 s	N.A.	N.A.	N.A.	10 ppb	N	21
DNTT (Small molecules)	Transistor	Porous active layer (PS microsphere removal)	NH_3	0.001-10 ppm	~100 s[a]	~100 s[a]	N.A.	N.A.	10 ppb	N	15
PAni (Conductive polymer)	Resistor	Nanostructure	NH_3	5-200 ppm	112 s	N.A.	N.A.	N.A.	5 ppm	N	6
DPP2T-TT/C8-BTBT (Polymer)	Transistor	Porous PVP-HDA dielectric	NH_3	0.001-100 ppm	0.4-1 s	~25 s[a]	N.A.	N.A.	1 ppb	Y	8
PDPP4T-T (Polymer)	Transistor	Plain (Solution doping with side chain engineering)	CO/ H_2S	0.01-1 ppm/0.001-0.1 ppm	~3 s[a]	N.A.	N.A.	N.A.	10 ppb/1 ppb	N	24
O(Si-Und-BTBT-Hex) (Small molecules)	Transistor	Langmuir-Schaefer monolayer	NH_3/ H_2S	0.2-5 ppm/0.01-10 ppm	~25 s[a]	N.A.	N.A.	50 ppb/10 ppb	200 ppb/10 ppb	N	22
pDPPCOOH-BT (Polymer)	Transistor	Reactive functional groups in active layer	NH_3	0.01-1000 ppm	~5 s[a]	N.A.	N.A.	N.A.	10 ppb	N	26
P3HT (Polymer)	Transistor	Porous P3HT/PS blends film	NH_3	5-50 ppm	~1000 s[a]	~1000 s[a]	N.A.	N.A.	5 ppm	N	19
PBTTT (Polymer)	Transistor	Buffer layer control	NH_3	10-100 ppm	~10 s[a]	~20 s[a]	N.A.	N.A.	10 ppm	N	18
TFB (Small molecules)	Resistor	Porous PVP dielectric	Acetone	0.3-2 ppm	~50 s[a]	N.A.	N.A.	N.A.	300 ppb	N	20
PCDTBT (Polymer)	Resistor	plain	NO	5-100 ppm	60-300 s	60-2100 s	N.A.	N.A.	5 ppm	Y	27

[a] The response/recovery time values are estimated from transient response curves due to they are not reported normalized response of various concentration. [b] Note that some papers using sensitivity parameter as $\Delta I/I_0$, but in this work responsivity (defined as $\Delta I/I_0$ with $\Delta I = I_{gas}-I_0$, where I_{gas} and I_0 is the drain current of the gas-exposed and unexposed OFETs, respectively) and sensitivity (defined as the slope of the linear relationship of responsivity versus gas concentration) are defined for more accurate response parameters, which able to make absolute comparisons between gas sensor reports. [c] Since it is necessary to check whether the calculated LOD value based on the measured responsivity (it can also check the linearity of responsivity in the detection range) and measured detection limit value is valid (measured only detection limit value could be included an error by unexpected noise). From this viewpoint, the LOD value is distinguished from the detection limit (measured) value.