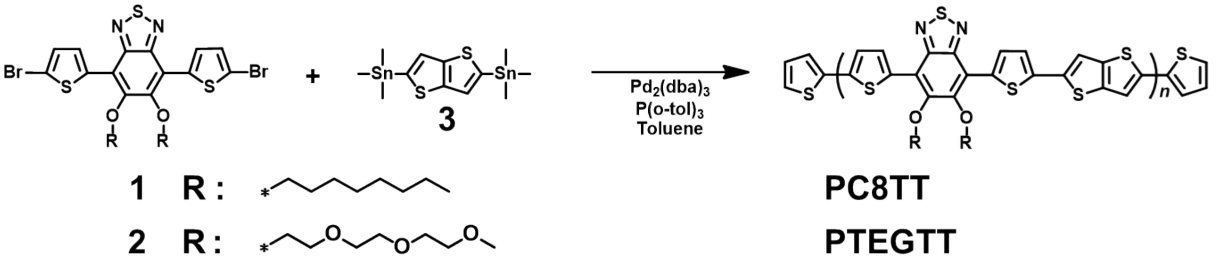
Supporting Information

Enhancing NO_2 Sensing Performance and Stability: Low-Crystallinity Conjugated Polymers with Localized Aggregates via Ethylene Glycol Pendants

Jung-Won An,[a,b] Ho-Won Jang,[b] Ji-Soo Jang *[a,c] and Junwoo Lee*[d]



Scheme S1. Scheme for PC8TT and PTEGTT.

Synthesis of the series of polymers. Specific ratio of monomers (4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole or 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzo[c][1,2,5]thiadiazole) and 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene, $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol), and P(*o*-tol)$_3$ (2.4 mg, 0.008mmol) are used for polymerization at 105 °C for 2 h in toluene. The polymer solution was precipitated in methanol and filtered using filter paper. The resulting polymer was further purified through Soxhlet extraction using acetone and hexane, and collected with chloroform. To purify the residual catalyst in the solution, flash column chromatography was performed using chloroform. The product dissolved in chloroform was then concentrated under reduced pressure and precipitated once again in methanol.

PC8TT. 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (100 mg, 0.140 mmol) and 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (59 mg, 0.126 mmol) were used. (82mg, 86%) GPC (CB, 40 °C): M_n = 8.05 kDa, M_w = 21.25 kDa, $Đ$ = 2.64. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.63-8.27 (br, Ar-*H*), 7.53-6.73 (br, Ar-*H*), 4.51-3.81 (br, -C*H*$_2$), 2.25-1.73 (br, -C*H*$_2$), 1.72-1.11 (br, -C*H*$_2$), 1.10-0.75 (br, -C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 150.72, 137.56, 131.61, 127.89, 124.27, 124.27, 123.51 (Ar-*C*), 74.52, 31.85, 30.46, 29.59, 29.34, 26.09, 22.67, 14.10 (-*C*H$_2$ and -*C*H$_3$).

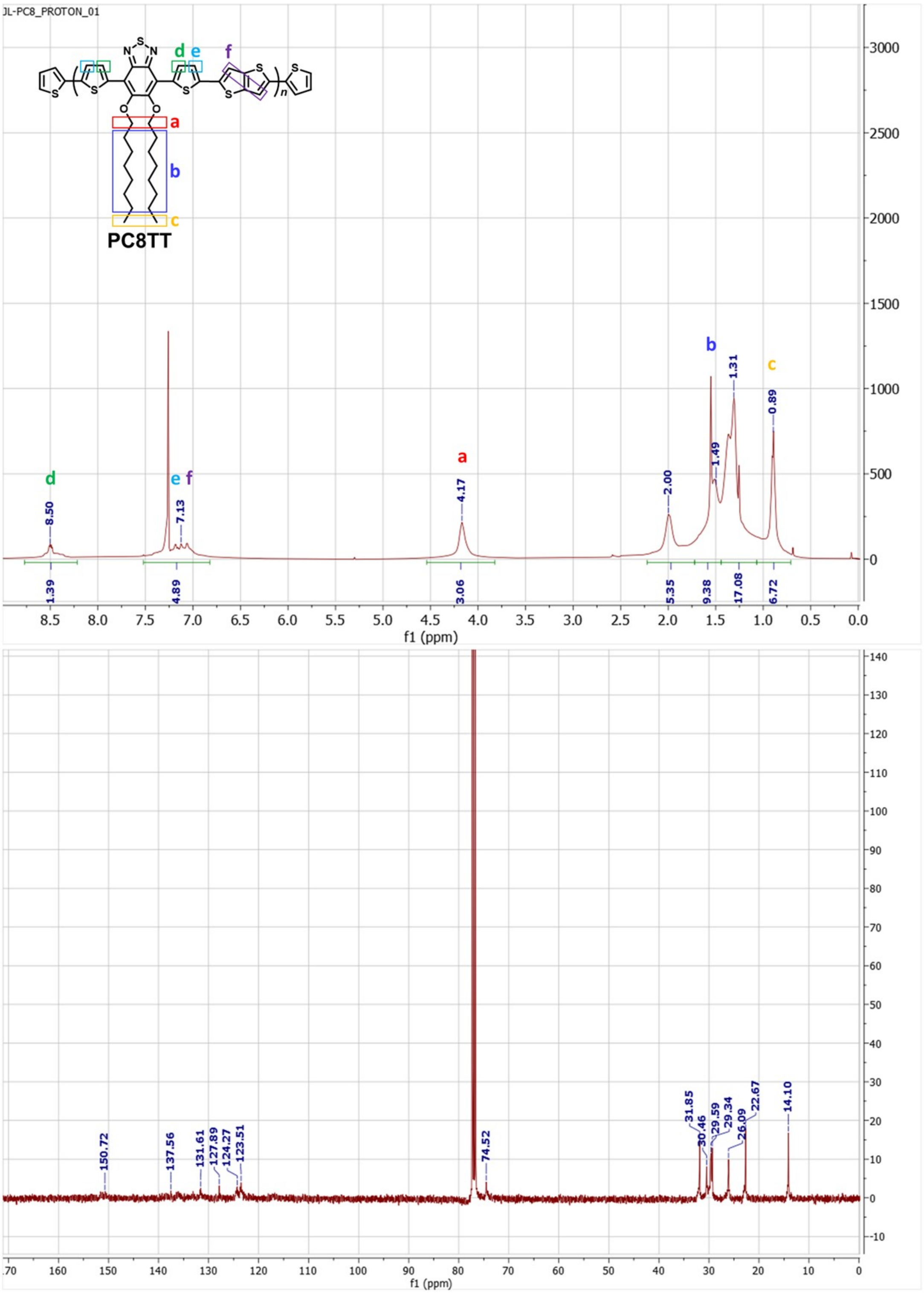
PTEGTT. 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzo[c][1,2,5]thiadiazole (200 mg, 0.256 mmol) and 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (109 mg, 0.233 mmol) were used. (73mg, 38%) GPC (CB, 40 °C): M_n = 7.97 kDa, M_w = 19.21 kDa, $Đ$ = 2.41. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.75-8.25 (br, Ar-*H*), 7.52-6.55 (br, Ar-*H*), 4.53-4.31 (br, -C*H*$_2$), 4.30-4.11 (br, -C*H*$_2$), 4.10-3.78 (br, -C*H*$_2$), 3.77-3.43 (br, -C*H*$_2$), 3.42-3.12 (br, -C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 150.45, 136.33, 131.17, 129.69, 124.38, 123.67 (Ar-*C*), 73.66, 72.90, 71.91, 70.65, 70.50, 59.02, 29.68 (-*C*H$_2$ and -*C*H$_3$).

Polymer properties

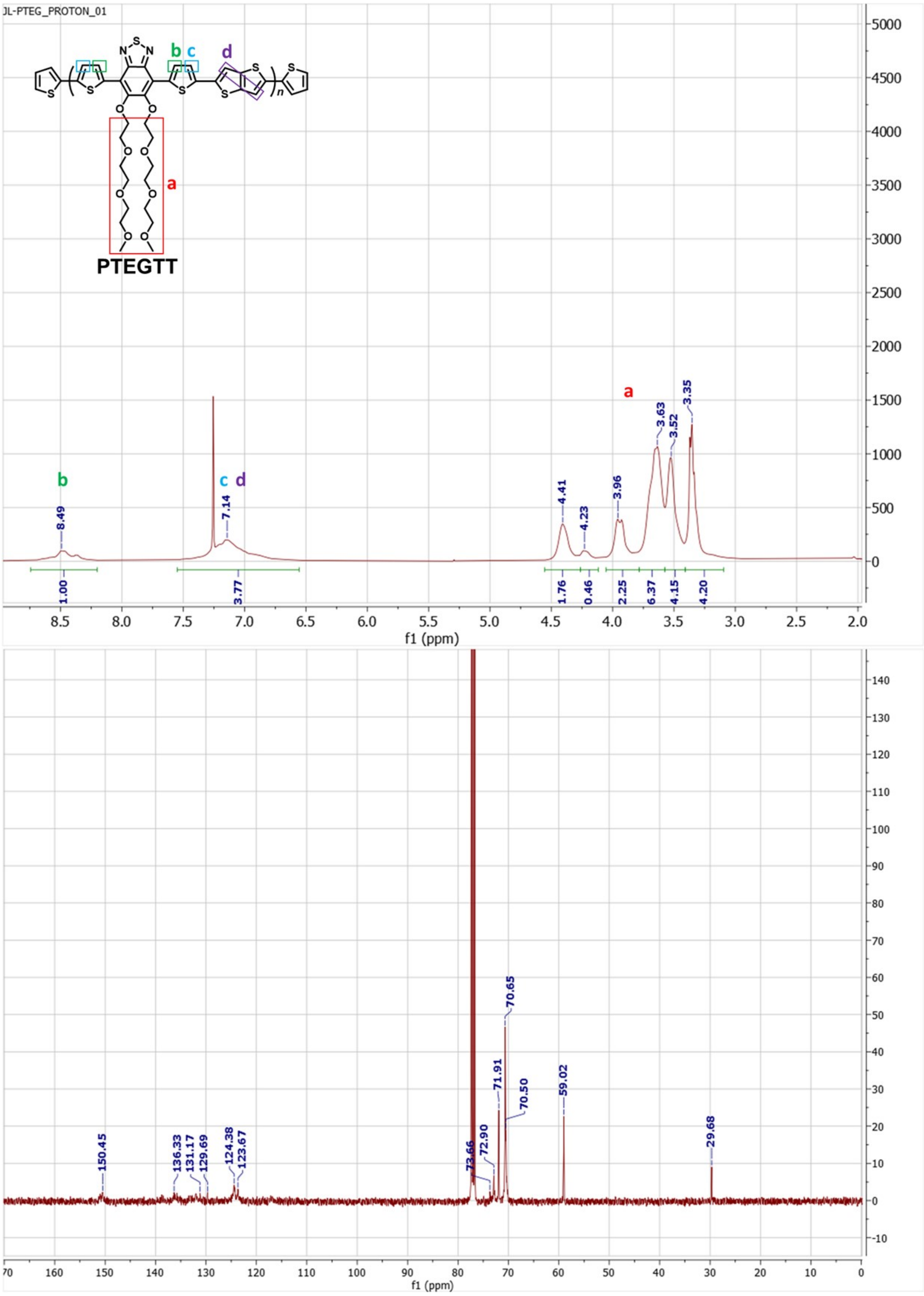
Number-average molecular weight (M_n) and dispersity ($Đ$) were determined using a size exclusion chromatography (SEC) with a TOSOH HLC solution with chlorobenzene eluent by comparison with a calibration curve of polystyrene standards. The UV-Vis absorption spectra were measured with a Cary UV/Vis spectrophotometer. Thermogravimetric analysis (TGA) and Differential scanning calorimetric (DSC) measurements were performed using TGAQ50 and a Perkin-Elmer Pyris 1 DSC instrument under nitrogen atmosphere at heating rates of 10 °C/min. Electrochemical cyclic voltammetry (BioLogic/VMP3 instrument model system) were recorded in a computer-controlled potentiostat conventional three-electrode system using a glassy carbon disk, platinum wire, and silver wire as a working electrode, counter electrode, and a quasi-reference electrode, respectively, in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NBF_4) at a scan rate of 20 mV/s. Ferrocene is used as internal standard to calculate frontier orbital energy levels of copolymers. Films were coated on the carbon electrode. The surface morphology was scanned using an atomic force microscope (AFM) of Bruker FastScan equipped with Nanoscope Analysis (ver. 1.9). 2D-grazing incidence wide-angle X-ray scattering (2D-GIWAXS) was performed using a synchrotron radiation on the NSLS-II CMS beam line at the Brookhaven National Laboratory (BNL). Powder X-ray diffraction (PXRD) was conducted using Xeuss 3.0.

Device fabrication and measurement

Interdigitated electrodes (IDEs) were produced on a 4-inch SiO_2/Si substrate (1 µm/550 µm) using a lift off method based on photolithography. The IDEs were made up of Pt/Ti (80 nm/30 nm) and arranged in a 1 × 1 mm^2 area with 20 electrodes, with 5 µm gaps between each electrode. Two types of conductive inks, PC8TT and PTEGTT, were prepared by uniformly dispersing the 5mg of each polymer in 400 mL of 2-methylanisole. After enough time for mixing in the sonication bath, these inks were separately loaded with 2 uL each on the IDEs of the SiO_2/Si substrates and completely dried at 65°C for 2 hours and 24 hours of room temperature storage in a desiccator to evaluate their response to NO_2 under various conditions. To investigate the sensing characteristics of the conducting polymers, a tube furnace was used at temperatures of 25°C and 100°C, with relative humidity levels from 10% to 80%. The chemical flow was calibrated by mixing the dry air with water vapor (produced by a bubbler) and target analytes, including NO_2, Toluene, NH_3, CH_3COCH_3, C_2H_5OH, o-C_8H_{10}, HCHO, SO_2, $C_4H_8O_2$, p-C_8H_{10}, and C_6H_6, respectively, utilizing a mass-flow controller to maintain a constant flow rate of 1000 sccm. Sensor resistance was measured using a Keithley 2401 source meter, and all data were recorded using Lab VIEW software.



H^1/C^{13} NMR spectrum of **PC8TT**



H^1/C^{13} NMR spectrum of **PTEGTT**

Fig. S1 H^1/C^{13} NMR spectroscopy of all the polymers.

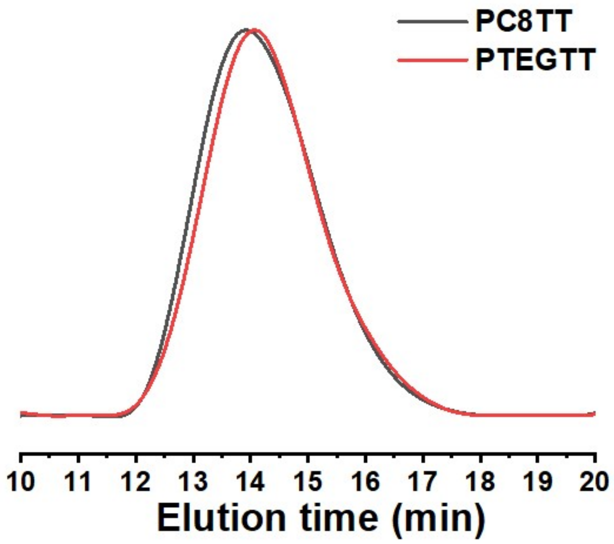


Fig. S2 GPC profiles.

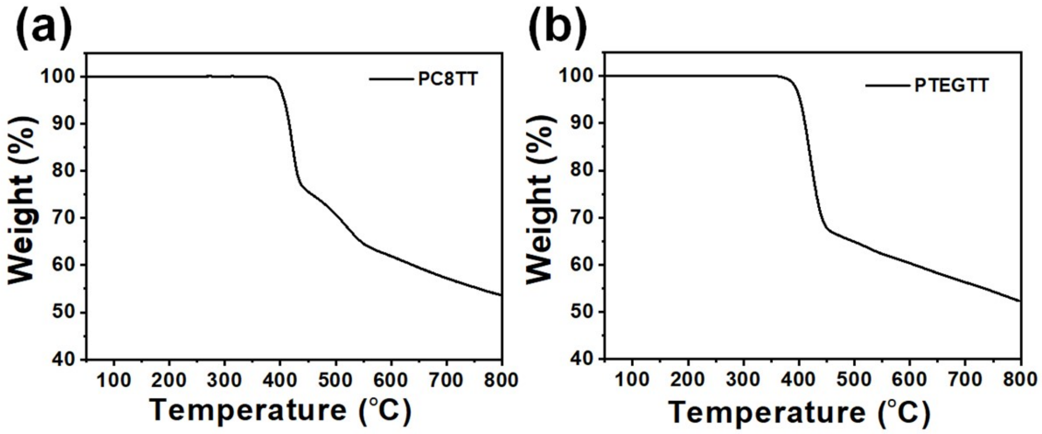


Fig. S3 Thermal properties of (a) PC8TT and (b) PTEGTT.

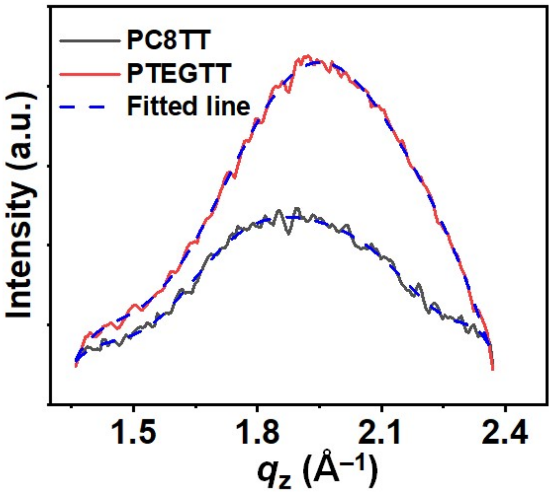


Fig. S4 X-ray diffraction spectra on out-of-plane of the polymers with fitted line.

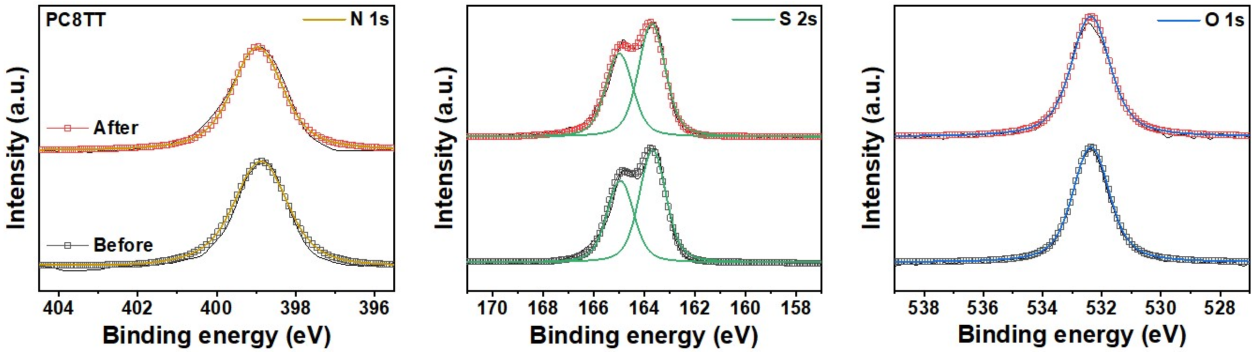


Fig. S5 XPS profiles of PC8TT on N 1s, S 2s, and O 1s.

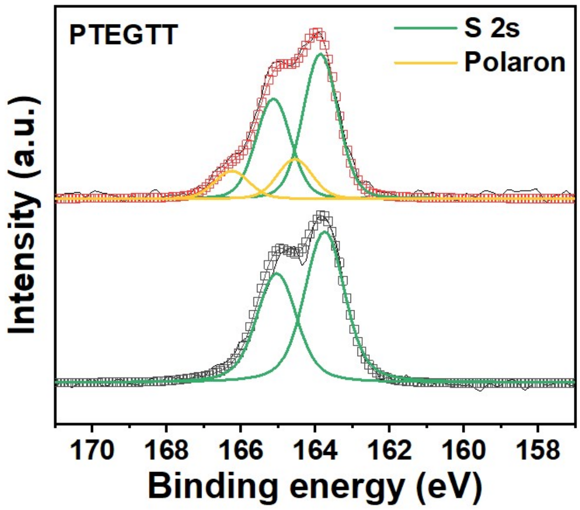


Fig. S6 XPS profiles of PTEGTT on S 2s.

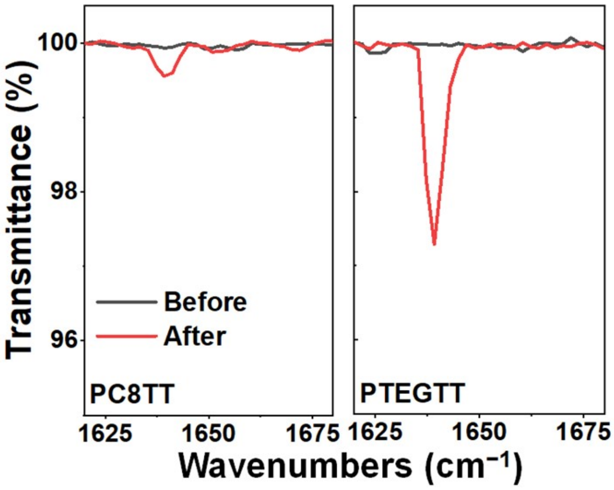


Fig. S7 FTIR spectrum depending on NO_2 exposure.

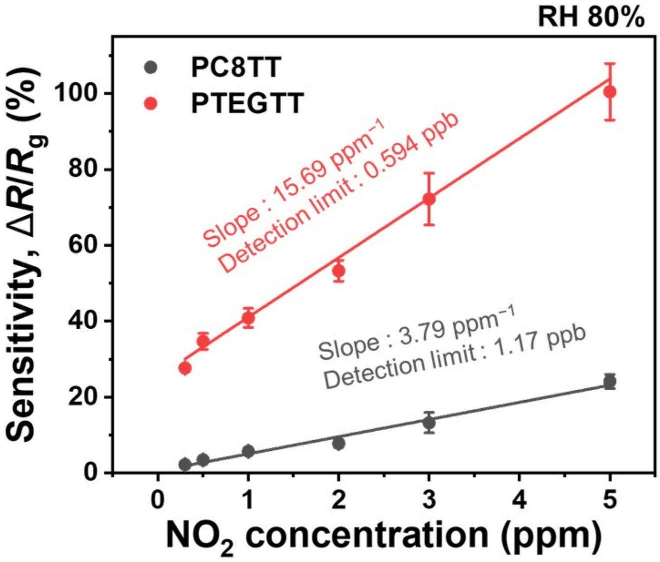


Fig. S8 Sensitivity upon exposure to 0.3-5 ppm NO_2 under high humidity condition (RH 80%).

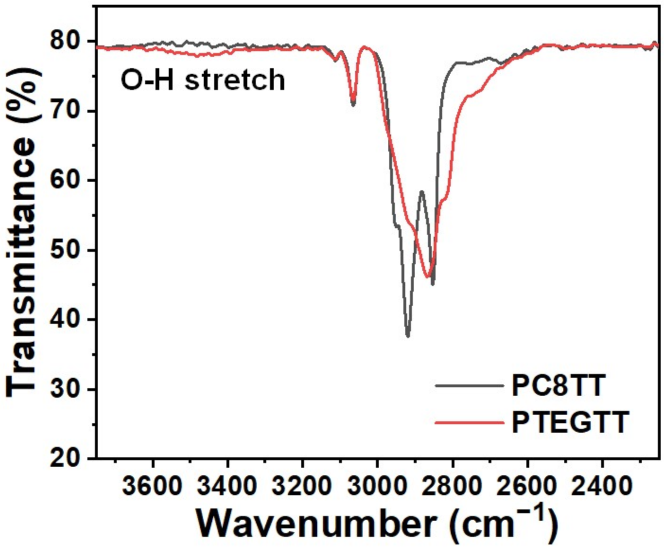


Fig. S9 FTIR spectrum depending on humidity.

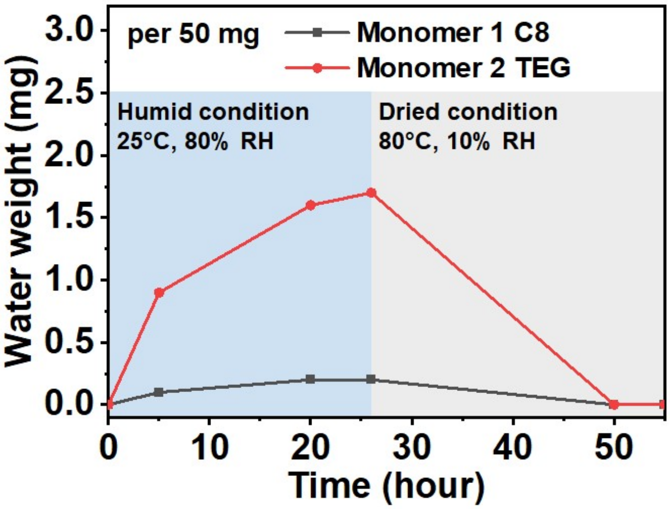


Fig. S10 Weight tracking of core monomers in the polymers.

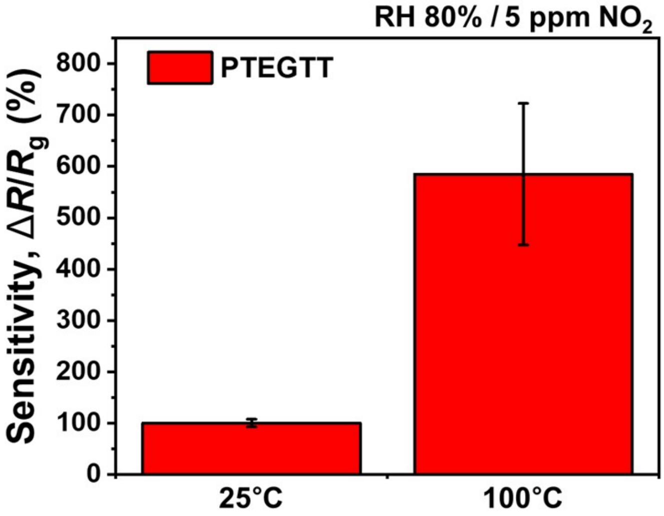


Fig. S11 Sensitivity of PTEGTT upon exposure to 5 ppm NO_2 under high humidity and high temperature condition (RH 80% & 100 °C).

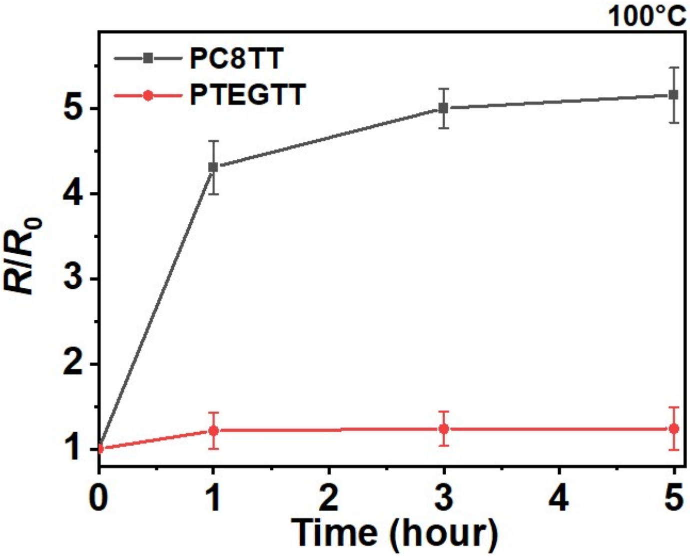


Fig. S12 Resistance tracking of the polymers at 100°C.

Table S1 State-of-the-art CP-based NO_2 sensors operating at room temperature

Polymer	Sensitivity [%]	LOD [ppb]	Temperature [°C]	Relative humidity	Reference
PEDOT:ClO_3 film	54.8 @ 50 ppm	0.726	RT	15%	[1]
Porous multilayer P3HT	22.91 @ 0.5 ppm	30	RT	20%	[2]
PPy thin film	36 @ 100 ppm	10,000	RT	Not recorded	[3]
PorCoPc-CMP	851 @ 30 ppm	2.3	RT	70%	[4]
P3HT-rGO	61.3 @ 10 ppm	500	RT	0%	[5]
PEDOT nanotubes	52 @ 63 ppm	200	RT	Not recorded	[6]
PANI thin film	11 @ 10 ppm	10,000	RT	0%	[7]
15-layers PANI film	65 @ 20 ppm	20,000	RT	Not recorded	[8]
PT thin film	33 @ 100 ppm	10,000	RT	0%	[9]
PTEGTT (40% RH)	9.3 @ 0.1 ppm	0.206	RT	40%	Our work
PTEGTT (80% RH)	27 @ 0.3 ppm	0.594	RT	80%	Our work

References

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