

Electronic Supplementary Information for

Two-Dimensional Semiconducting Covalent Organic Nanosheets for Highly Sensitive and Stable NO₂ Sensing under Humid Condition

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Materials and instruments: 2,4,6-Tris(5-bromothiophene-2-yl)-1,3,5-triazine and 2,5-bis(trimethylstannyl)thieno-(3,2-b)thiophene were purchased from Luminescence Technology (Lum-Tec). Tetrakis(triphenylphosphine)palladium(0) was purchased from Alfa-Aesar. Mesitylene was obtained from Sigma-Aldrich. All the reagents were stored in a glovebox charged with N₂. Fourier transform infrared (FT-IR) spectra were obtained on a Jasco FT/IR-4100 spectrometer with a range of 650–4000 cm⁻¹. UV–Vis spectra were obtained on a Shimadzu UV-2600 spectrophotometer (Shimadzu, Japan) using a WI (halogen) lamp and a D2 (deuterium) lamp operating from 220 to 850 nm. Powder X-ray diffraction (XRD) patterns were obtained on an Empyrean Series 2 (PANalytical B.V., Netherlands) diffractometer with Ni-filtered Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) equipped with a 5-mm fixed incident beam mask and a 1.60 mm anti-scatter slit. The measurement angle ranged from 3 to 70° with time step increments of 0.0525° and 0.75 s per step. N₂ adsorption-desorption isotherm curves were obtained using a Belsorp-minilli (Bel Japan Inc.) instrument using N₂ gas at 77 K. Scanning electron microscopy (SEM) images were obtained utilizing a Quanta 250 FEG (FEI Company, Hillsboro, OR) instrument. The sample surfaces were coated with Au/Pd plasma for 60 s, and the SEM images were obtained using a 15 kV electron beam. Transmission electron microscopy (TEM) images were recorded using a JEM-2100F (JEOL) high-resolution electron microscope at a voltage of 200 kV. The TEM samples were prepared by drop-casting it from an N-methyl-2-pyrrolidone suspension on carbon films with 200 mesh copper grids (Electron Microscopy Sciences) after the samples were dispersed in EtOH. The suspensions were prepared using a Sonics VCX 130 ultrasonic processor (130 W power output, 20 kHz frequency) with a 3 mm homogenizer probe (Standard 630-0422, Vibra-Cell™). The sonicator was run at 20% power and frequency of one pulse per second with a 2.5 s pulse length for 30 min.

Synthesis of CON-10: 2,4,6-Tris(5-bromothiophene-2-yl)-1,3,5-triazine (50 mg, 0.09 mmol), 2,5-bis(trimethylstannyl)thieno-(3,2-b)thiophene (62 mg, 0.1 mmol), and Tetrakis(triphenylphosphine)palladium(0) (4.1 mg, 4 mol%) in mesitylene solvent was refluxed at 170 °C for 72

h under N₂ atmosphere. After cooling, the mixture was vigorously stirred in methanol. A red precipitation was obtained which was filtered and purified by continuous Soxhlet extraction using methanol, ethanol, dichloromethane, tetrahydrofuran (THF), and acetone (4 h per step) to obtain a dark red powder.

Preparation of solution: CON-10 suspensions were prepared by dissolving 4 mg of CON in 1 mL of ethanol, chlorobenzene with 1-chloronaphthalene (CB/1-CN), THF, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) with ultrasonication for 30 min, followed by preparing the sample for TEM analysis as described in the instruments section.

Fabrication of CONs FET: CON-10 materials were deposited between two or more interdigitated Au electrodes on a SiO₂/Si substrate via a drop-casting method from their ethanol suspension, and back-gated through an insulating SiO₂ layer to fabricate field-effect transistor (FET) configurations. The device had an electrode spacing of 3 μm and a dielectric thickness of 500 nm.

Characterization of Gas Sensing: The sensor was located in a horizontal-type tube furnace and electrically connected to an electrical measuring system (Keithley 2400). The NO₂ concentration was controlled by adjusting the relative flow rates of the target gas. In addition, dry air and NO₂ gas sensing tests were performed by monitoring the changes in electrical resistance at various temperatures. Sensor response (S) is defined as $S = R_a/R_g$, in which R_g and R_a are the resistances measured in air with and without NO₂ gas, respectively. The response and recovery times were defined as the times required to reach 90% of the saturated response during adsorption and desorption, respectively.

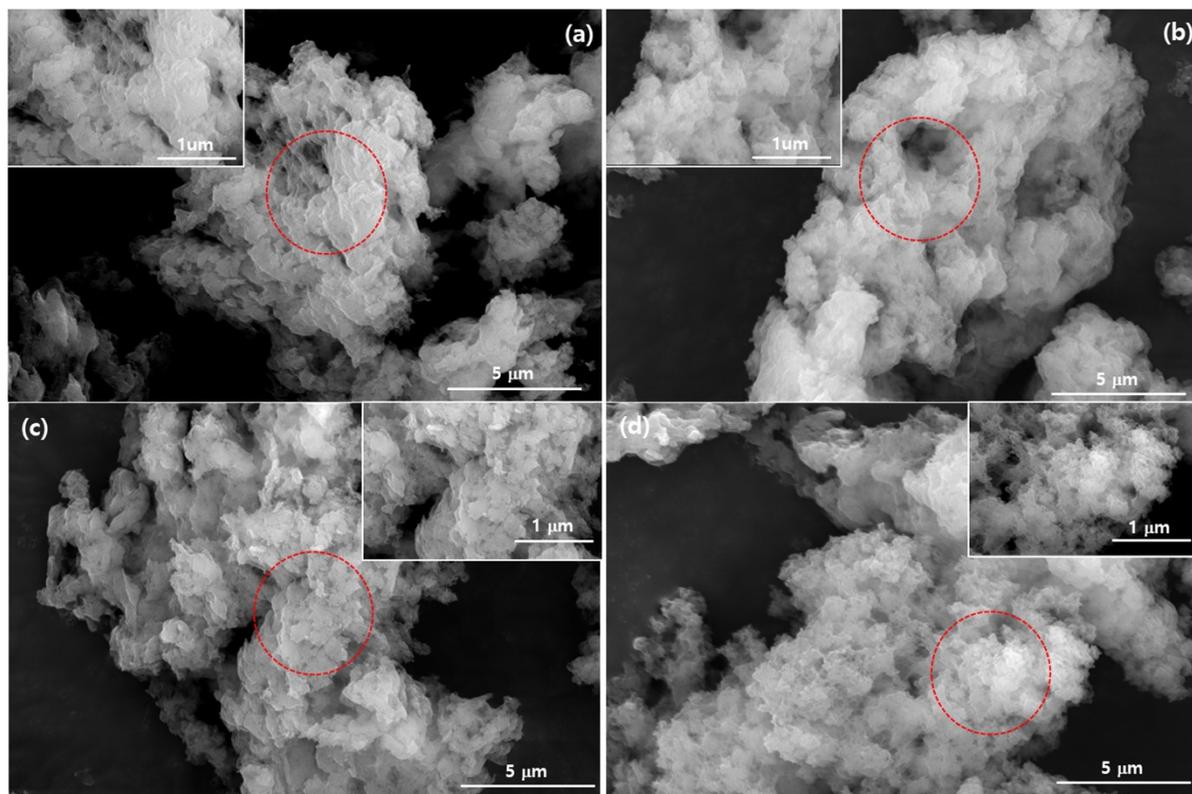


Figure S1. SEM images of CON-10 activated (a) under vacuum only, (b) at 100 °C and vacuum, (c) 200 °C and vacuum, and (d) 300 °C and vacuum

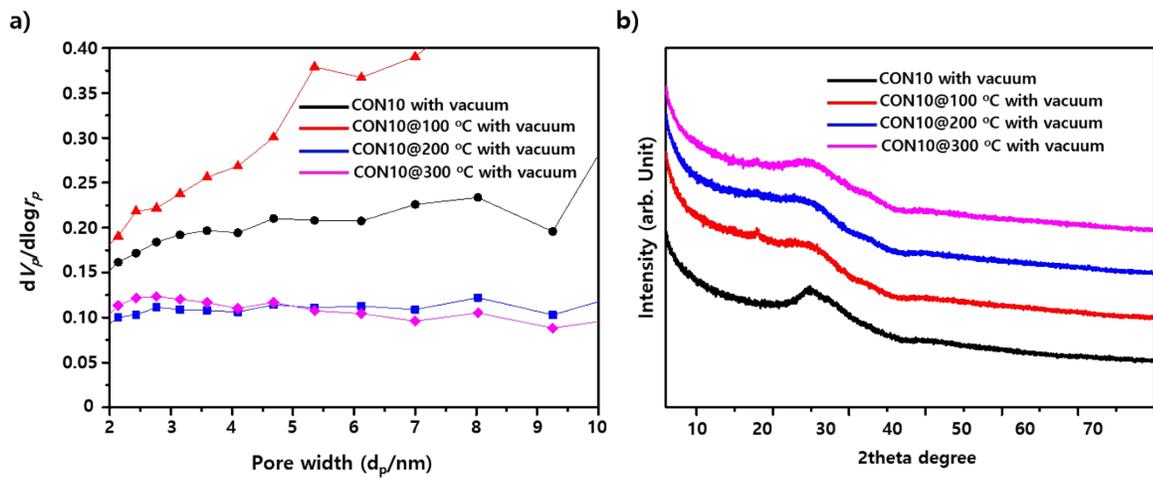


Figure S2. (a) BJH pore-size distribution profiles of CON-10 and (b) PXRD patterns of CON-10 after activation at various conditions.

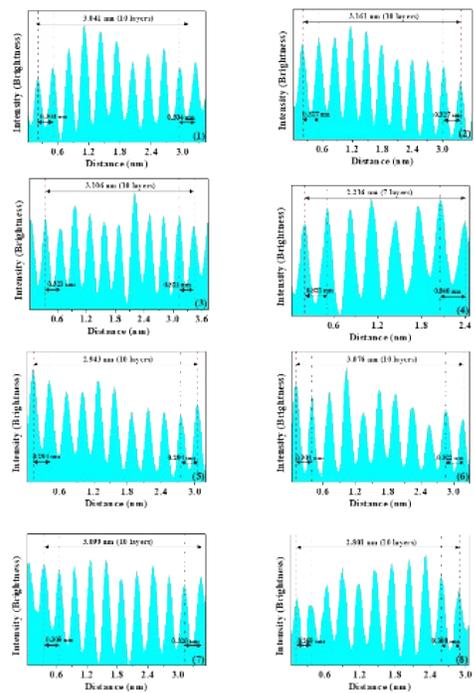
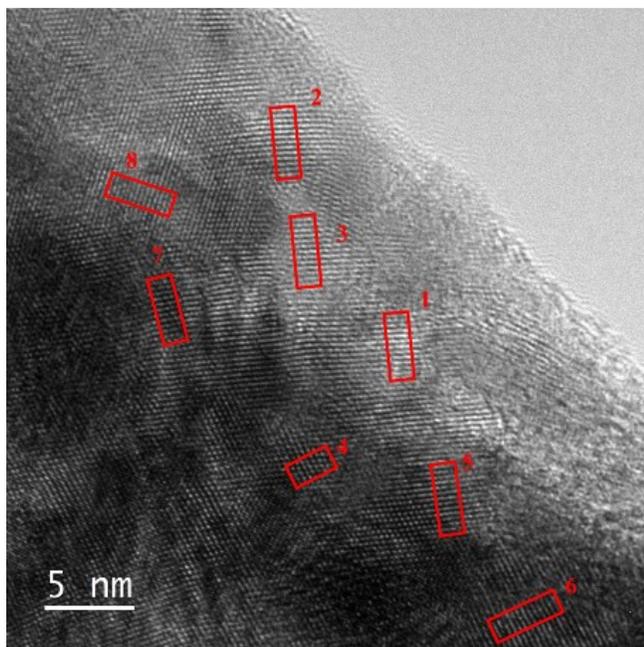


Figure S3. Magnified TEM image of CON-10 showing the stacked morphology (left side) and the lattice distance profiles (right side) in the red-lined regions.

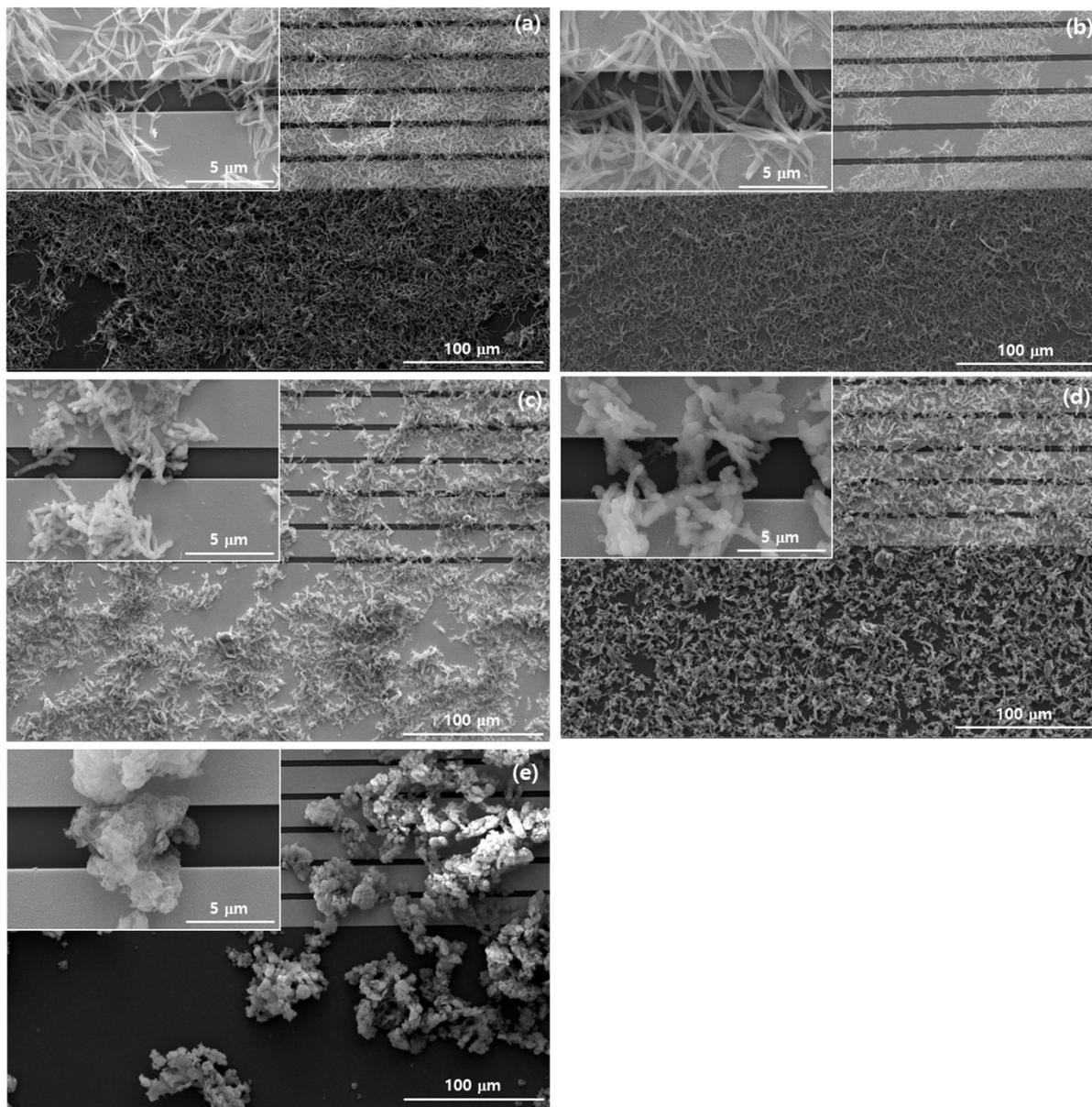


Figure S4. SEM images of CON-10 drop-casted on IDE substrates from (a) CB/1-CN, (b) THF, (c) DMF, (d) DMSO and (e) ethanol suspensions after 1 h of ultrasonication with a homogenizer.

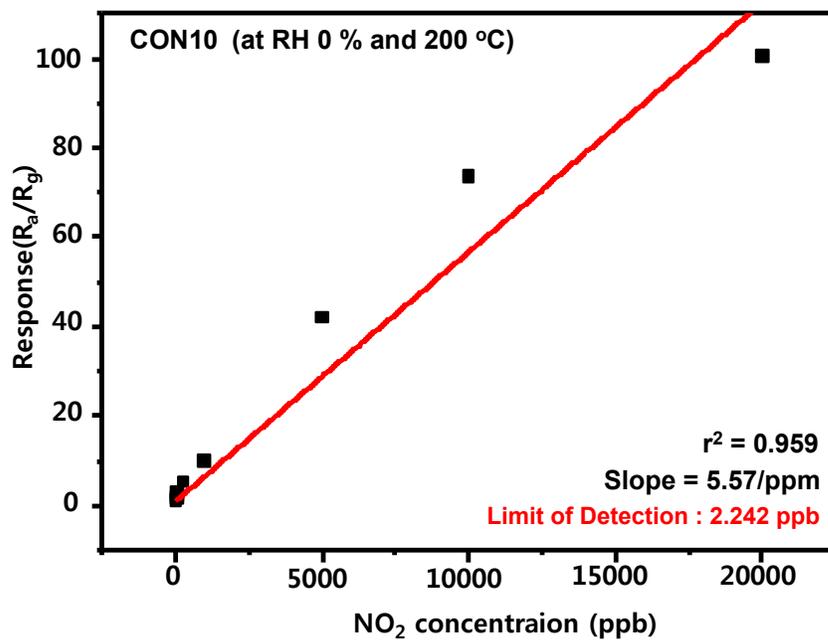


Figure S5. Measured response values of the CON10 sensor as a function of NO₂ concentration at the working temperature of 200 °C under arid condition (RH = 0). The curves exhibit good linear correlation and the linear sections were used to estimate the LOD, which was found to be 2.242 ppb.

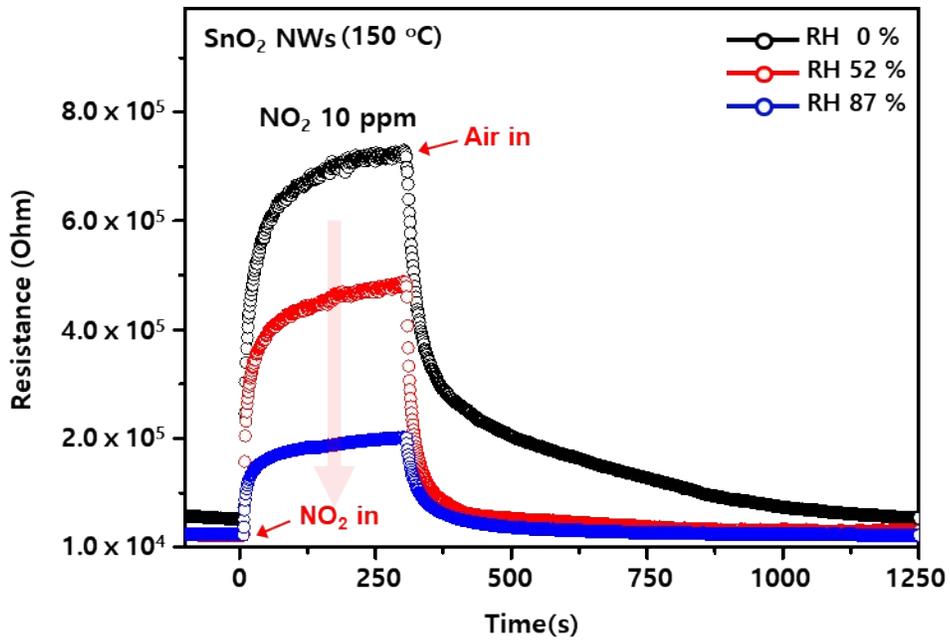


Figure S6. Sensing behaviors of typical SnO₂ nanowire, grown using the VLS method, toward NO₂ at RH levels of 0, 52, and 87 %. The introduction of humid air significantly decreases the sensor resistance.

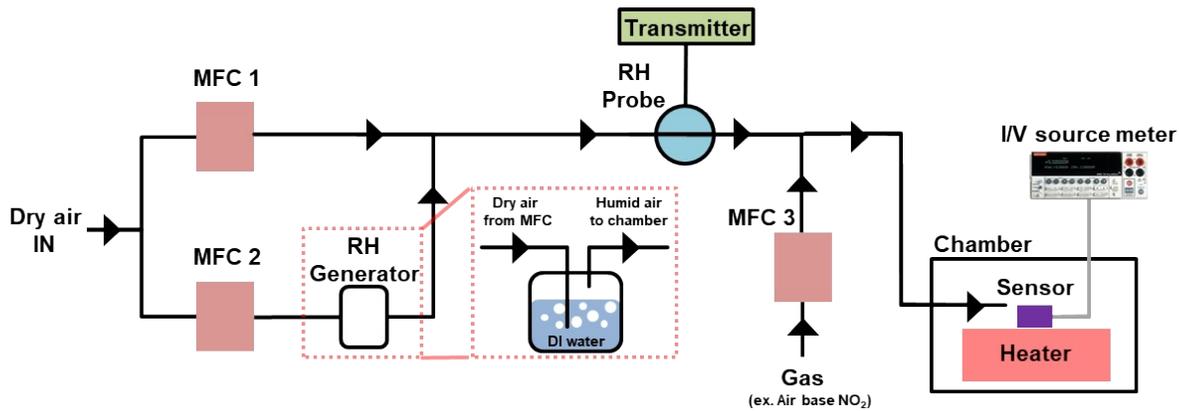
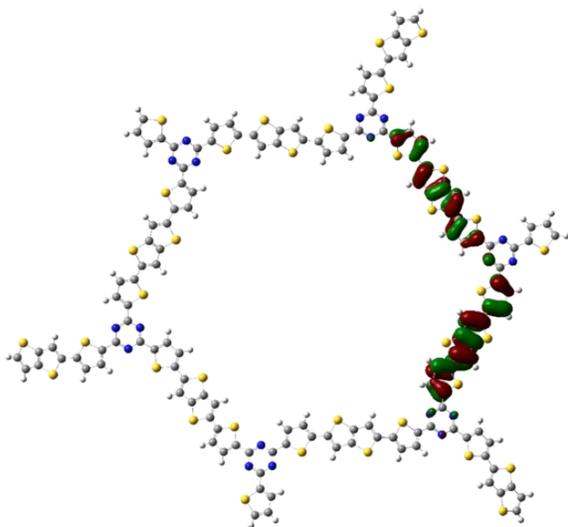


Figure S7. A Schematic of gas sensor measurement system

The relative humidity of the base air can be controlled by the MFC1 and MFC2, as shown in Figure S6. Initially, the base air flows in two directions (to the MFC1 and MFC2 lines). The air flowing through the MFC 2 passes through the bubbler-type R. H. generator reaching up to ~ 90% relative humidity. Because the air passing through the MFC 1 is still dry (Synthetic Dry Air), the relative humidity of the air can be adjusted from 0 to ~90% by appropriately adjusting the flow ratio between the MFC 1 and MFC 2. In order to control the ppb level of NO₂, the MFC3 for controlling the flow rate of standard 5 ppm-NO₂ gas (minimum production concentration, Air base) was installed behind of the humidity adjustment module. To adjust the NO₂ concentration down to 20 ppb in various humidity levels, we set the flow rate of controllable humid air to 498 sccm (MFC 1 + MFC 2) and the 5 ppm-NO₂ gas passing through the MFC 3 to 2 sccm. Please note that the reliable minimum flow of our MFC was 2 sccm, which made us unable to further dilute the NO₂ gas below 20 ppb.

a)



b)

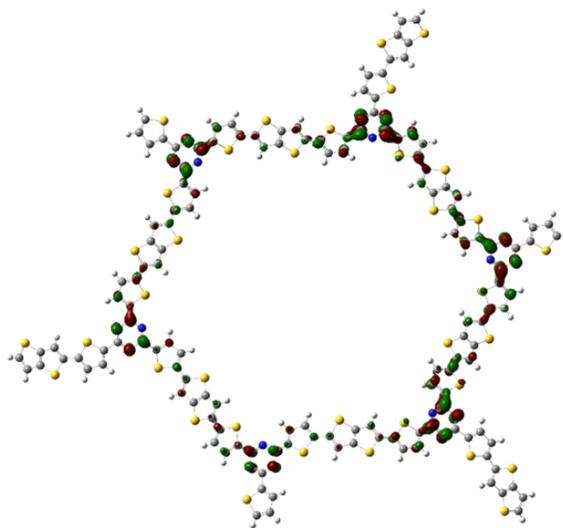


Figure S8. Frontier orbital density maps of the CON-10 unit structure calculated using DFT at the B3LYP/6-31G level; (a) the HOMO state and (b) the LUMO state.

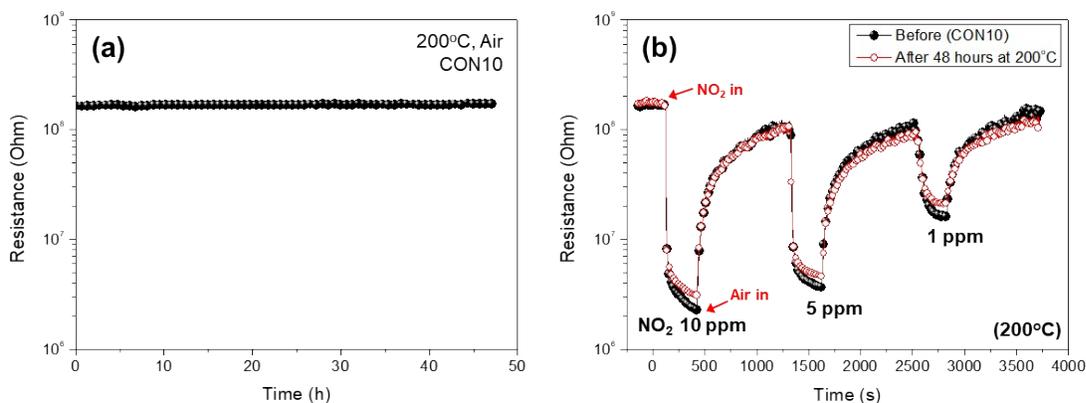


Figure S9. (a) time-dependent resistance variation of CON-10 sensor at 200 °C for 48 hours (2 days), (b) dynamic response curves of CON-10 to 1, 5 and 10 ppm of NO₂ gas at 200 °C before and after the thermal stability test

For investigating the long-term stability of CON-10 sensor, we tried to further measure the time-dependent variation of sensor resistance for 48 hours at 200 °C. As shown in Figure S9, the sensor resistance was found to be well maintained without thermal fluctuation, keeping its initial resistance value constant. This implies the CON-10 sensor is not affected by the long-term thermal treatment. Figure (b) exhibits the dynamic response curves of CON-10 sensor toward various NO₂ concentrations before and after the long-term thermal test. In this experiment, negligible change (< 5 %) in NO₂ response was observed even after the thermal test done for 48 hours, conforming good reproducibility of the sensor