Supplementary Information:

# Ion-in-Conjugation Polymer Enables Detection of NO<sub>2</sub> with Parts-Per-Trillion Sensitivity and Ultrahigh Selectivity

Chuang Yu, <sup>a</sup> Hong-Zhen Lin, <sup>b</sup> Jin Zhou, <sup>a</sup> Xue-Feng Cheng, <sup>a</sup> Jing-Hui He, <sup>\*a</sup> Hua Li, <sup>a</sup> Qing-Feng Xu, <sup>a</sup> Na-Jun Li, <sup>a</sup> Dong-Yun Chen <sup>a</sup> and Jian-Mei Lu<sup>\*a</sup>

a. College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou Nano Science and Technology, National United Engineering Laboratory of Functionalized Environmental Adsorption Materials, Soochow University, Suzhou 215123, P. R. China.

b. i-LAB, Suzhou Institute of Nano-Tech and Nano-Bionics (SINANO), Chinese Academy of Sciences, Suzhou 215123, P. R. China

Fax: +86 512 65880367; Tel: +86 512 65880368;

E-mail: jinghhe@suda.edu.cn; lujm@suda.edu.cn

## **Experimental Section**

## Materials

Squaric acid, p-phenylenediamine, n-butanol and tetrahydrofuran are purchased from Alfa Aesar, TCI and Sinopharm Chemical Co., Ltd. All chemical reagents are analytical grade and used without further purification.

## Theoretical calculation.

The density functional theory calculations were implemented in the Dmol<sup>3</sup> code with generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) exchange–correction functional. The total energy and electron transfer were calculated using Polarized double numerical basis set. In geometric optimizations, an energy convergence tolerance of 10<sup>-6</sup> Ha (1 Ha=27.2114 eV), maximum atomic forces of 0.002 Ha/Å and maximum displacement 0.005 Å were employed. A TS (Tkatchenko-Scheffler) scheme was performed to consider the weak interaction in our

simulations.<sup>1, 2</sup>.

#### Synthetic method of p-PPS and o-PPS and preparation of the sensor device

First, 570 mg of squaraine (5 mmol) and 540 mg of p-phenylenediamine (5 mmol) are dissolved in 100 ml n-butanol, and the suspension is added to a two-necked flask. Then, the suspension is refluxed and stirred magnetically at 125 °C for 12 h. When the reaction is completed and cooled to room temperature, the solvent is removed from the filtrate to give a residue, and the obtained crude is washed several times with tetrahydrofuran (THF) and deionized water. Finally, the red powder that is obtained is dried under vacuum at 75 °C for 12 h. In addition, the synthesis of o-PPS is carried out as follows. A two-necked flask consisting of 108.18 mg p-phenylenediamine (1 mmol) and 170.16 mg 3,4-diethoxycyclobut-3-ene-1,2-dione (1 mmol) dissolved in 40 ml ethyl alcohol, which are refluxed at 78 °C for 12 h. After removing the solvent, the solid that is obtained is washed several times with alcohol and water. Finally, the dark-green powder is obtained by vacuum-drying.

50 mg of PPS (p-PPS or o-PPS) is mixed with 1 mL of ethyl ethanol, and the mixture is dispersed by sonication to obtain a well-dispersed suspension. Subsequently, brush-coating the mixture onto an interdigital electrode (IDES, electrode distance and channel width both 200  $\mu$ m) fabricated by jetting Ag-Pd paste on ceramic plates through a metal-jetting system (MJ-10, Beijing Elite Tech Co., Ltd., China) as a good measure. Finally, the coated device is dried at 70 °C for 2 h for further testing.

#### Test Device and gas distribution

The p-PPS-based sensing performance test is performed with the Keithley 4200 semiconductor test system. During the testing process, the prepared sensor device is placed in a 1.2-L chamber, and we use nitrogen as the carrier gas (figure S5) to ensure the accuracy of the experimental data. Before the test, the sensor device is blown with nitrogen until the current is not changed to eliminate the interference of other gases, and then the target gas is purged into the chamber. Furthermore, the time interval between each single I-V test is fixed at 4 min/10 min (target gas/nitrogen). To exclude the influence of airflow on test results, we controlled the flow rate of the inlet airflow to 200 mL/min.

### **Measurement equipment**

Ultraviolet-visible absorption spectroscopy is tested using a Shimadzu UV-3600 spectrophotometer. X-ray diffraction measurements are carried out using a Multiple Crystal X-ray Diffractometer (X'Pert PRO, PANalytical). The rate of different gas flows is controlled by a PERMEATER (PD-1B-2). The performance of electrochemistry is measured by a semiconductor characterization system (Keithley 4200-SCS) under a fixed total flow (200 sccm) of different concentrations of target gases. Solid-state NMR (SSNMR) experiments are performed on a Bruker Advance III HD 400 spectrometer. 1D 13C cross-polarization (CP)/MAS spectra are recorded using a CP contact time of 1.5 ms, a recycle delay of 5 s and 1024 scans with a SPINAL-64 high power 1H decoupling sequence during acquisition. The sum frequency generation (SFG) spectrometer laser system is set up by EKSPLA. The incident angle of the visible beam is 60°, and the incident angle of the infrared beam is 55°. The IR pulses at approximately 2750-3000 cm-1 and the visible signal at 532 nm are approximately 25 ps at 50 Hz. The energy of the visible and IR beams is generally less than 20 mJ, and the photodamage of the studied sample can be ignored during the examination process.



**Fig. S1** (a) synthetic routes of o-PPS (b) The SEM image of o-PPS (c) the powder of p-PPS and o-PPS



Fig. S2 Elements mapping image of sensor device based on p-PPS



**Fig. S3** X-ray photoelectron energy spectra of O 1s (a) and N 1s (b) (c) XRD patterns of p-PPS (d) Solid-state NMR 13C cross polarization spectrum of p-PPS. Peaks are assigned using the alphabet labels with respect to the structural scheme



**Fig. S4** a) The IR spectra of p-PPS compared with theoretical calculation b) The IR spectra of o-PPS compared with theoretical calculation



Fig. S5 The schematic diagram of the gaseous diluting method.



**Fig. S6** (a) Temporal responses with increasing NO<sub>2</sub> concentrations from1 ppb to 10 pm based on p-PPS (b) Response/recovery time at 80 ppb NO<sub>2</sub>



Fig. S7 (a) Transient responses of o-PPS with increasing NO2 concentrations from 5 ppb to 10 ppm (b) SFG spectra of o-PPS film before and after  $NO_2$  adsorption.



Fig. S8 Repeat response based on p-PPS at 80 ppt



Figure S9 Other proposed binding models of NO<sub>2</sub> on a p-PPS chain



Fig. S10 The planer conjugated structure of PDBS



**Fig. S11** (a) Normalized current of different flow rate of carrier gases at 80 ppb of NO<sub>2</sub> (b) Normalized current of different temperature at 80 ppb of NO<sub>2</sub>

- 1. X. Li, T. Guo, L. Zhu, C. Ling, Q. Xue and W. Xing, *Chem. Eng. J.*, 2018, **338**, 92-98.
- 2. X. Li, L. Zhu, X. Chang, D. He, Q. Xue and W. Xing, J. Mater. Chem. A, 2018, 6, 12404-12410.