

Supporting Information

Electrically Conductive Coordination Polymer for Highly Selective Chemiresistive Sensing of Volatile Amines

Siping Wang,[†] Jie Liu,[‡] Hongmei Zhao,[†] Zhifen Guo,[†] Hongzhu Xing,^{,†} Yuan Gao^{*,‡}*

[†]Provincial Key Laboratory of Advanced Energy Materials, College of Chemistry, Northeast Normal University, Renmin Street 5268, Changchun 130024 (China)

[‡]State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Qianjin Street 2699, Changchun 130012 (China)

Email: xinghz223@nenu.edu.cn; gaoyuan@jlu.edu.cn

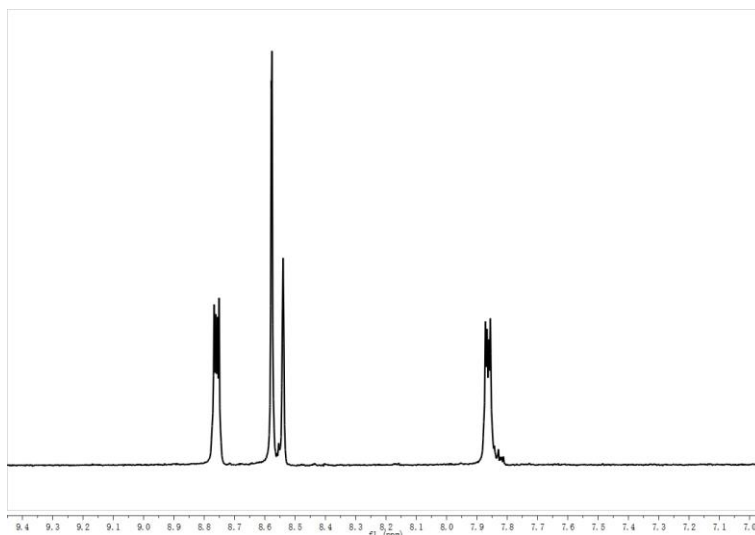
1. Characterizations and experimental details

1.1 Physical Characterizations

Powder X-ray diffraction patterns (PXRD) were recorded with Rigaku D-MAX 2550 diffractometer using Cu-K α radiation (λ = 0.15417 nm) at room temperature with 2θ ranging from 3 to 40 degree. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heat rate of 10 °C/min from room temperature to 800 °C under air atmosphere. Scanning Electron Microscopy (SEM) measurement was taken on a HITACHI SU-8010 with an acceleration voltage of 3 kV. The Fourier transform infrared (FTIR) spectrum was recorded with KBr pellet in the range of 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Elemental analysis was carried out on a Perkin-Elmer 2400 elemental analyzer. ¹H NMR spectrum was recorded at 25 °C on a Bruker Avance III HD 600 MHz.

1.2 Synthesis of ligand

All chemicals in analytical grade were purchased and used without further purification. The ligand is synthesized through Sonogashira coupling reaction. Diethyl 5-ethynylisophthalate (271mg, 1.1mmol), 9,10-dibromoanthracene (168mg, 0.5 mmol), Pd(PPh₃)₂Cl₂ and CuI were added into the solution of triethylamine and DMF (1:1, v/v). The mixture was refluxed under N₂ atmosphere. The reaction was quenched with water, extracted with CHCl₃, washed with brine and dries over MgSO₄. Recrystallization from CHCl₃ gave the product as a red solid. The product (200mg, 0.3mmol) was suspended in 50mL of ethanol and 50mL of H₂O. To which KOH (160.5mg, 3mmol) was added and the mixture was stirred under reflux for overnight. Organic solvent was removed using a rotary evaporator and diluted hydrochloric acid was added to the remaining aqueous solution until it became acidic (pH = ~ 2 to 3). The precipitate was collected by filtration, washed several times with water and dried under vacuum to give ligand as a dark red solid in 80% yield. ¹H NMR (600 MHz, DMSO-d₆) δ : 8.762 (*d*, 4H), 8.579 (*s*, 4H), 8.541 (*s*, 2H), 7.867 (*d*, 4H). IR (KBr): ν = 2922, 1694, 1593, 1437, 1202 cm⁻¹. Both NMR and IR data are in good accordance with those reported in the literature.¹ Elemental analysis: Anal: C 73.56% H 2.73%. Calc: C 73.65% H 3.25%.



1.3 Synthesis of **1**

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (92 mg, 0.3 mmol), H_4L (55 mg, 0.1 mmol) and 2M HNO_3 (2 ml, aq.) in a mixed solvent of DMF/ CH_3CN (5 ml, v/v = 2/1) was sealed in a 25 mL Teflonlined stainless steel autoclave. The autoclave was heated at 100 °C for 5 days and then cooled to room temperature. Orange crystals were obtained. Yield: 70% based on the ligand. Elemental analysis: $\text{C}_{74}\text{H}_{40}\text{O}_{21}\text{N}_2\text{Cd}_2$ (**1**) Anal: C 58.60% H 3.02% N 2.42%. Calc: C 58.52% H 2.88% N 2.21%.

1.4 Electrical conductivity measurements

High-quality single crystals without cracks were selected under microscope for electrical conductivity measurement by a two-probe method, where the crystal was immobilized between two blocks of conducting silver resins to support ohmic contact. The electrical conductivity measurement for crystal sample was recorded with a Keithley 4200 SCS and a Cascade M150 probe station in a clean and shielded box at room temperature in air by sweeping the voltage from −5 V to 5 V. As shown in Table S1, crystals with different sizes of conduction channels were tested. Owing to that the obtained I - V curve do not reveal the influence of the length and cross-sectional area of the conduction channel for each crystal, the I - V curve was transformed into relationship between current density versus electric field strength (J - E curve in Figure 2c) to compare the electrical conductivity in different crystal samples.

Table S1. The conductivities and sizes of conduction channels for different crystals

Samples	Length (um)	Width (um)	Thickness (um)	Conductivity (S/cm)
1	360	70	20	1.23×10^{-6}
2	350	45	15	1.55×10^{-6}
3	330	50	15	1.04×10^{-6}

1.5 Chemiresistive sensing measurement

The chemiresistor was fabricated as follows: after **1** was carefully grinded for about one hour in a mortar, deionized water was added to make a paste. Then the paste was coated on an alumina tube (4 mm in length, 1.2 mm in external diameter, 0.8 mm in internal diameter), followed by attachment of a pair of gold electrodes. The gas-sensing properties for the fabricated sensor were investigated using a RQ-2 series Intelligent Test Meter (China). After the sensor was placed in the device, the sensing performance was tested by recording the changing of resistance of the coating layer when it was exposed in air atmosphere and in VOCs atmosphere (mixed with air) under laboratory condition (30%RH, 22°C). Humidity is an important issue considering the gas sensor application, the resistance of the sensor under air atmosphere at different relative humidity (RH from 30% to 80%) was measured. Results suggest the sensor is not sensitive to water molecule by showing nearly constant resistance.

A typical testing procedure is as follows: Fresh air (atmospheric air) was first introduced into the chamber, and then calculated amount of target gas or liquid was injected into the chamber. The fans were used to mix target gas with air uniformly. When the response reached a constant value, the target gas was removed by a pump and fresh air was introduced into the testing chamber to let the sensor recover. For the target gas obtained from liquid, the concentration of target gas was calculated by the following formula,

$$C = (22.4 \times \rho \times \varphi \times V_1 \times 1000) / (M / V_2)$$

where C (ppm) is the target gas concentration, ρ (g mL^{-1}) is the density of the liquid, φ is the required gas volume fraction, V_1 (μL) is the volume of liquid, V_2 is the volume of the chamber, and M (g mol^{-1}) is the molecular weight of the liquid. The

response of the sensor was defined as $(R_a - R_g) / R_a \times 100\%$, where R_a and R_g stand for resistances of the sensor in air and in target gas, respectively.²

1.6 Single crystal X-ray diffraction

Single-crystal X-ray diffraction data of **1** was collected on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) under room temperature. Raw data of the structure was processed using SAINT software and absorption corrections data were carried out using SADABS program. The crystal structure was solved by direct method and refined by full-matrix least-squares on F^2 with anisotropic displacement using SHELXTL (Table S2). CCDC 1517717 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

REFERENCES

- (1) Gole, B.; Shanmugaraju, S.; Bar, A. K.; Mukherjee, P. S. Supramolecular polymer for explosives sensing: role of H-bonding in enhancement of sensitivity in the solid state. *Chem. Commun.* **2011**, 47, 10046–10048.
- (2) Xiao, Y.; Yang, Q.; Wang, Z.; Zhang, R.; Gao, Y.; Sun, P.; Sun, Y.; Lu, G. Improvement of NO₂ gas sensing performance based on discoid tin oxide modified by reduced graphene oxide. *Sens. Actuat. B: Chem.* **2016**, 227, 419–426.

Table S2. Crystal data and structure refinement parameters for **1**.

empirical formula	C ₇₄ H ₅₁ Cd ₂ N ₂ O ₂₁
formula weight	1528.99
crystal system	Triclinic
space group	<i>P</i> -1
<i>a</i> / Å	12.921(3)
<i>b</i> / Å	14.363(4)
<i>c</i> / Å	18.846(5)
α / °	102.390(10)
β / °	96.159(11)
γ / °	108.064(9)
<i>V</i> / Å ³	3190.3(15)
<i>Z</i>	2
Density (g cm ⁻³)	1.592
<i>F</i> (000)	1546
θ range collected	2.550 to 25.160
limiting indices	-15 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 17, -22 ≤ <i>l</i> ≤ 22
Reflections collected / unique	70640 / 11449
data / restraints / parameters	11449 / 930 / 42
<i>R</i> _{int}	0.0572
goodness-of-fit on <i>F</i> ²	1.078
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0459, <i>wR</i> ₂ = 0.1164
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0671, <i>wR</i> ₂ = 0.1376

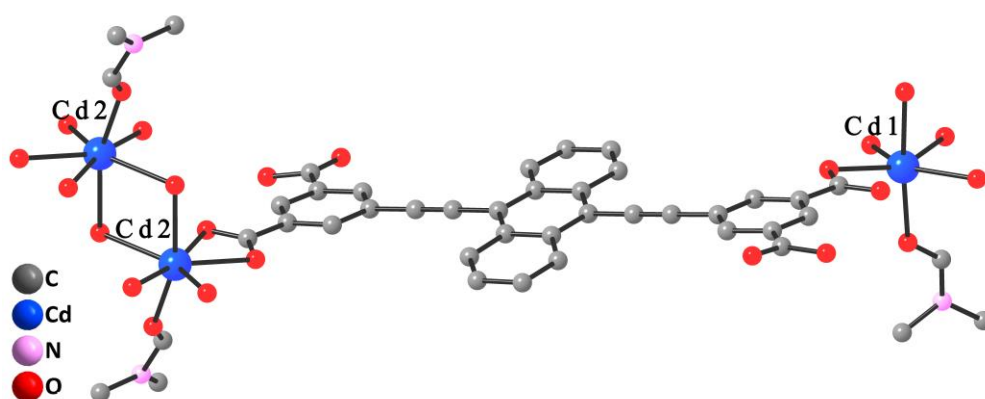


Fig. S1 Coordination mode between cadmium ions, ligand and DMF molecules.

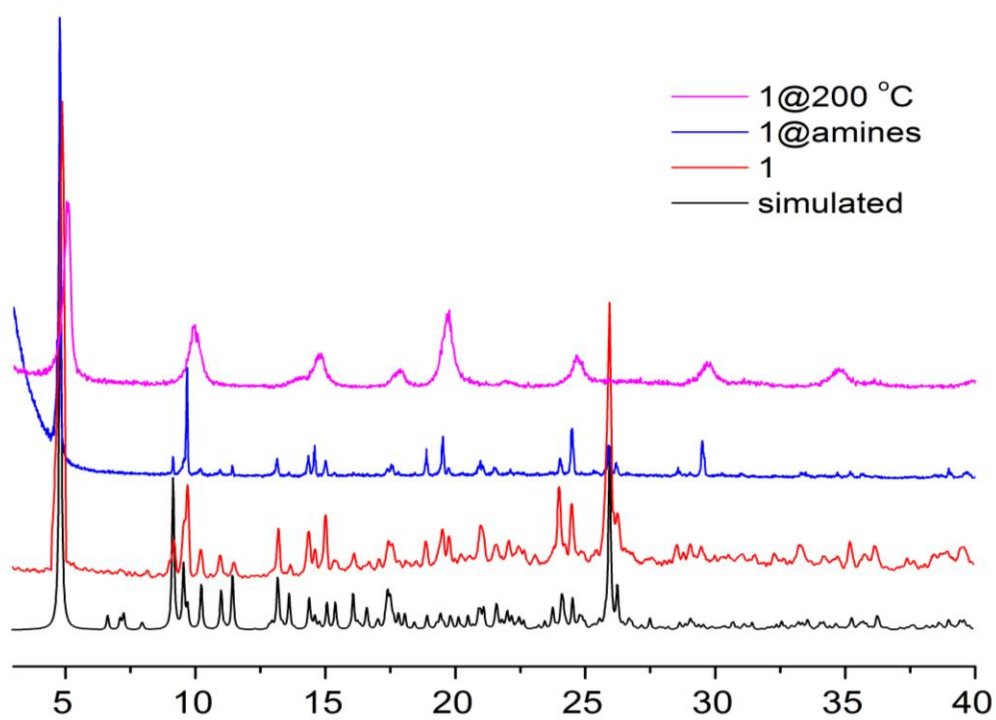


Fig. S2 PXRD patterns of simulated (black), **1** (red), and **1** after amines sensing (blue) and **1** calcinated at 200 °C for one hour (purple).

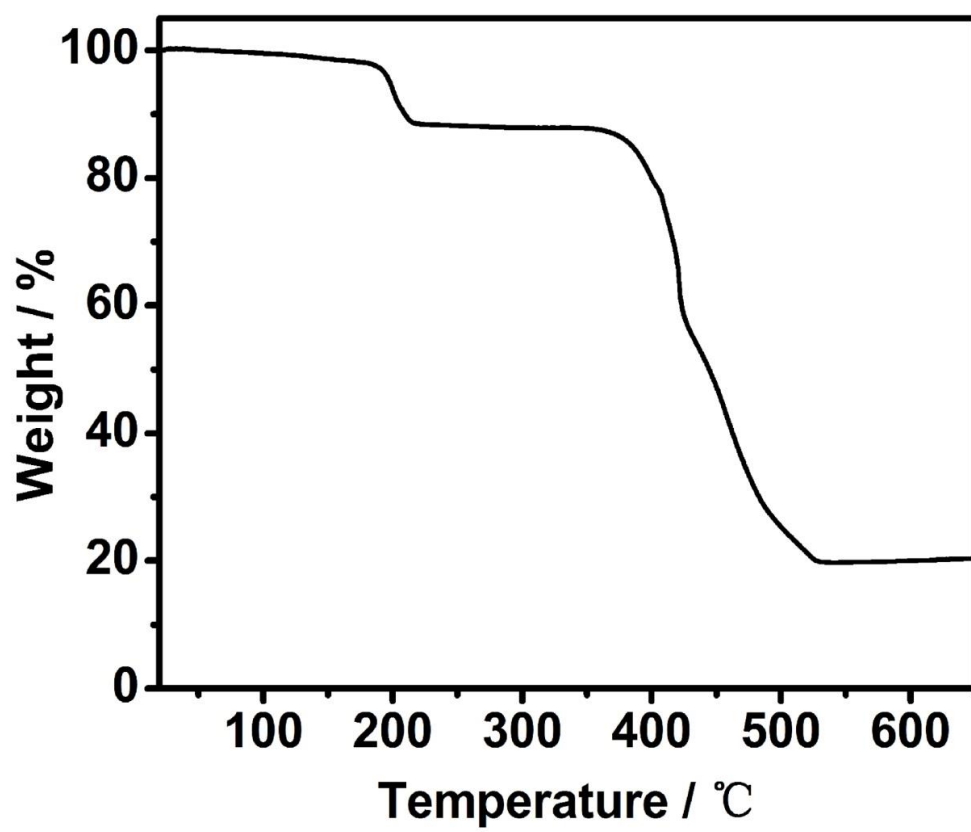


Fig. S3 TG curve.

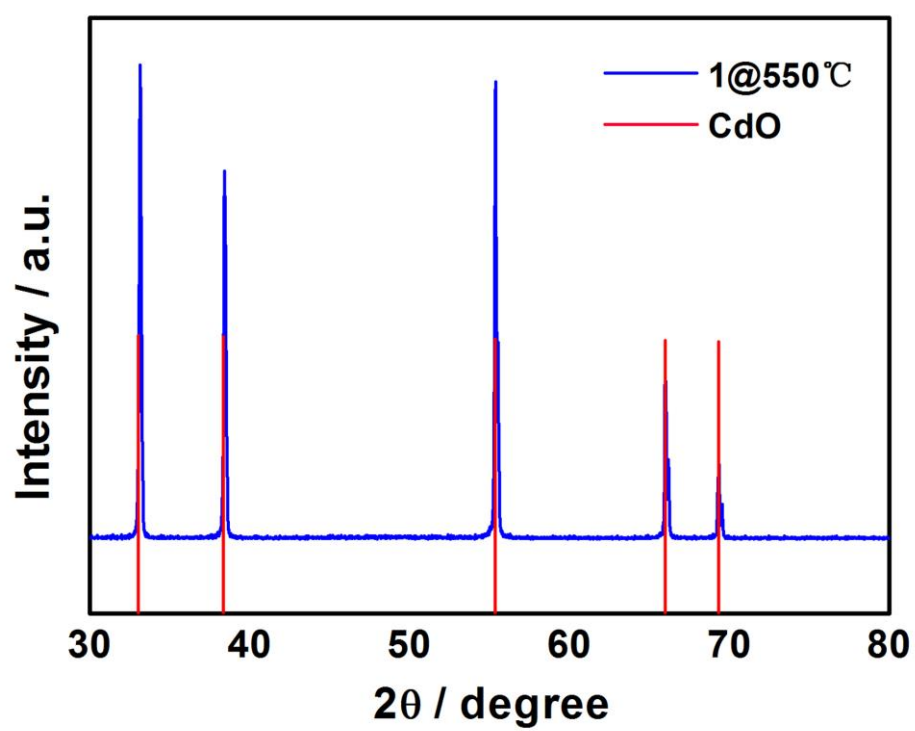


Fig. S4 PXRD pattern of **1** pyrolyzed at 550 °C.

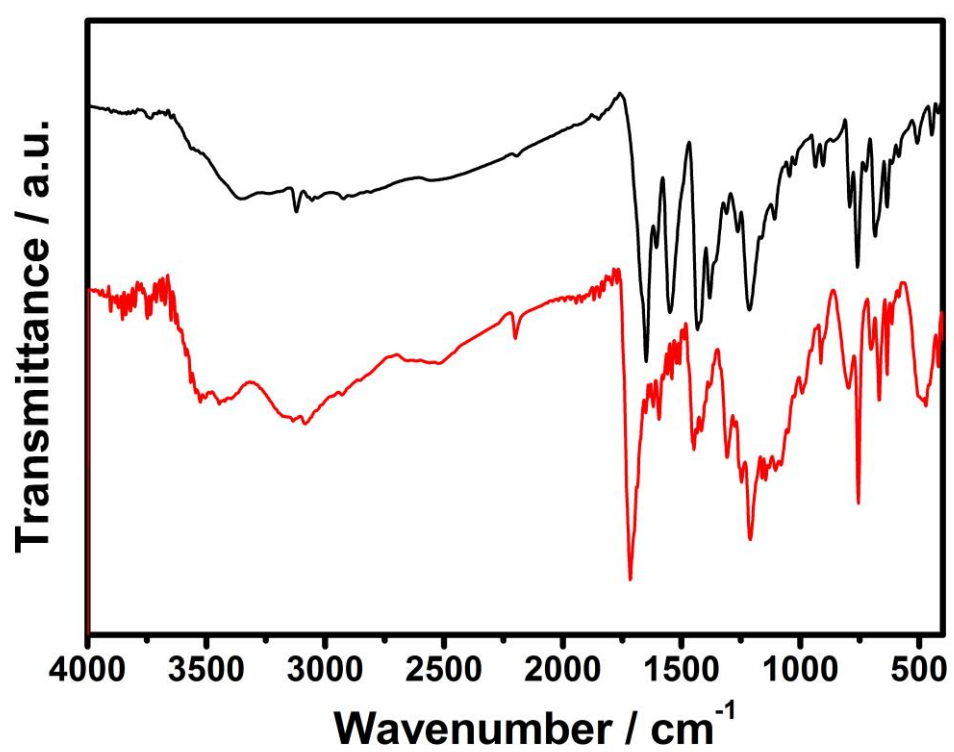


Fig. S5 FTIR spectrum of **1** (black) and H₄L (red).

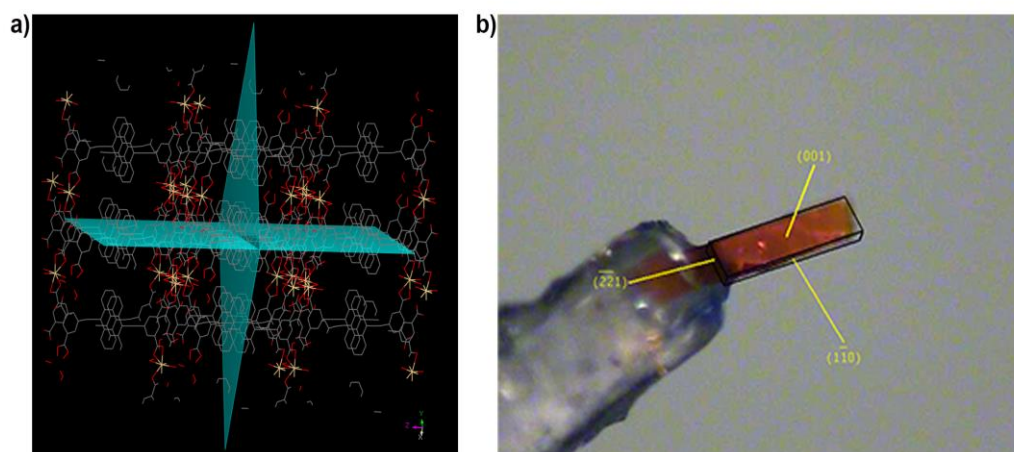


Figure S6 The crystal structure a) and crystal indexing b) figures. The vertical and horizontal planes (light blue) in figure a) corresponds to the indexed faces of (001) and (1-10) in figure b), respectively. The π - π stacking of ligand in the structure is along [110] direction, which is parallel to the long axis of the crystal.

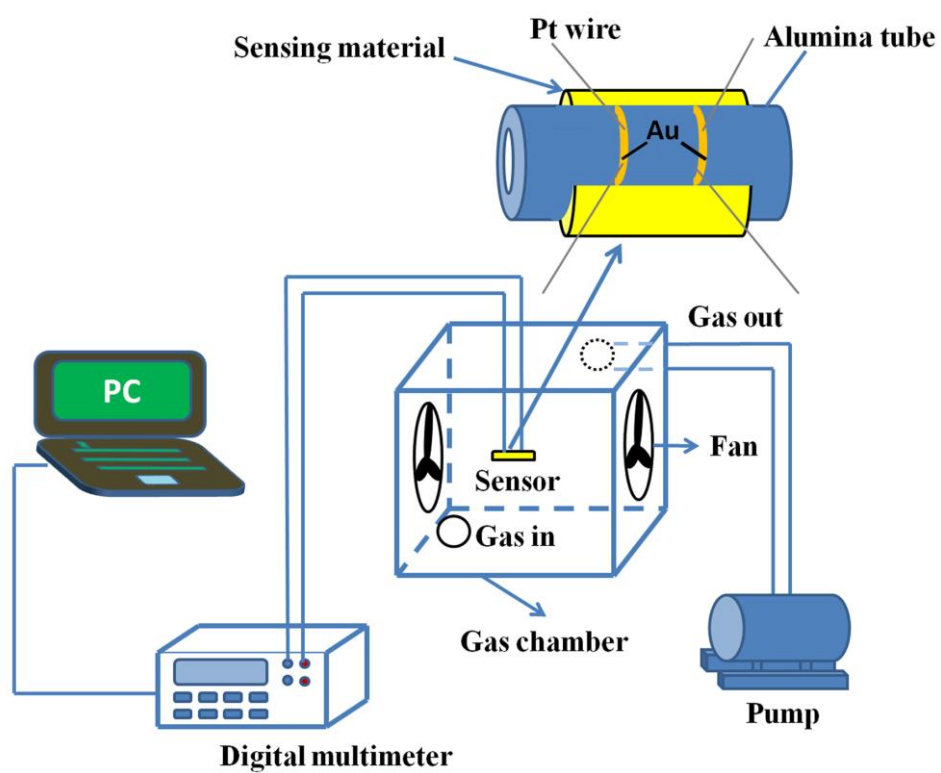


Fig. S7 A scheme of the chemiresistive sensing device.

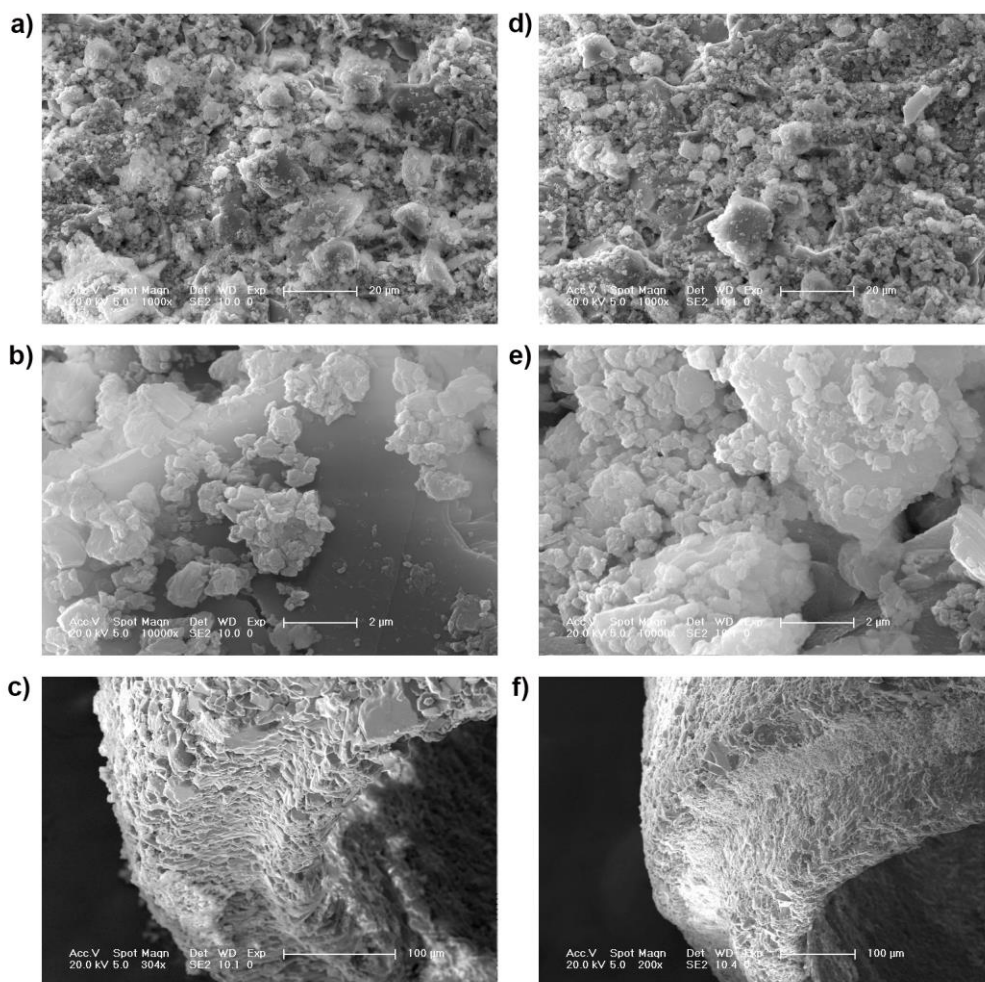


Fig. S8 a-c) SEM pictures of sensor before sensing tests. d-f) SEM pictures of sensor after amine sensing. The thickness of the alumina tube is 200 μm . As shown in Figure c,f), the particle larger than 5 μm are constituents of the alumina tube. In Figure a,b,d,e), the small particle less than 5 μm is coordination polymer.

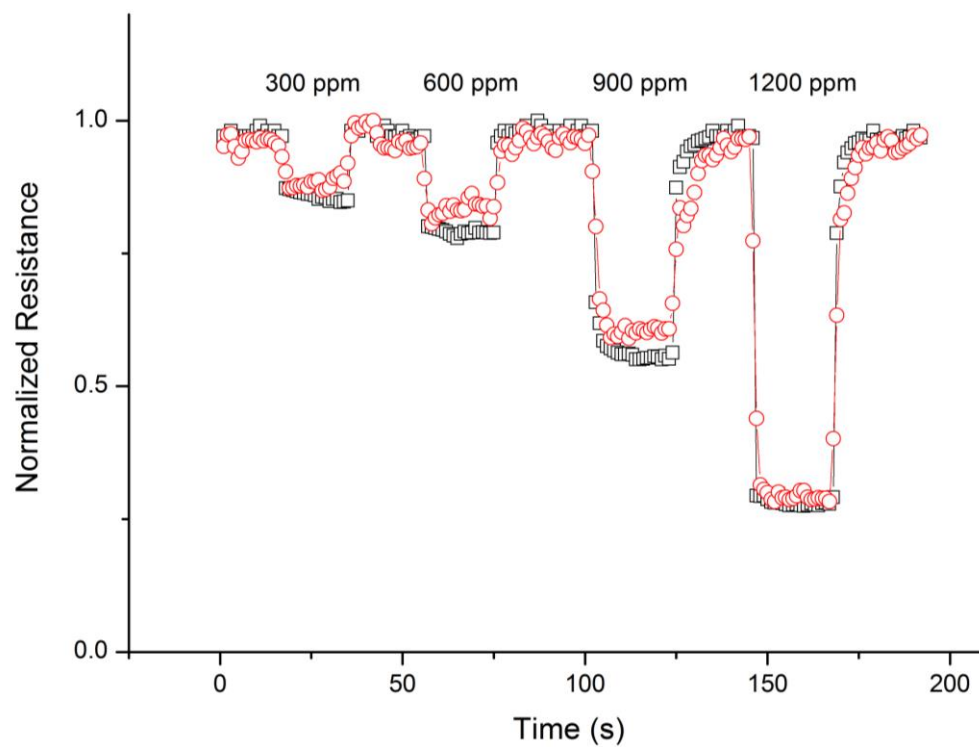


Fig. S9 Resistance of sensor under different ethylenediamine (EDA) concentrations. The red line was tested when the sensor has just been fabricated; the black line was tested when the same sensor was kept under laboratory condition for two months.