Supporting Information

EXPERIMENTAL DETAILS

General information

PTCDA was purchased from Alfa Aesar. All reagents and solvents were purchased from Beijing Chemical Reagent Corporation, China, and were used as received, unless indicated otherwise. The prepared sample was studied by SEM (Hitachi S4800 field emission scanning electron microscope), TEM (JEOL 2010 transmission electron microscopes), UV–vis spectra (Hitachi U-3010 spectrometer) and fluorescence spectra (Hitachi F-4500 spectrofluorometer), and Fourier Transform Infrared Spectrometer (TENSOR-27), X-ray diffraction (XRD; Rigaku D/max-2500), atomic force microscope (AFM, NT-MDT). The current-voltage (I-V) characteristics were measured using a Keithley Semiconductor Characterization System (SCS-4200).

Synthesis of PZn NPs: PZn (perylene tetracarboxylic zinc) NPs were synthesized by the method we reported previously.[35] Briefly, 0.9 mg of zinc acetate dehydrate was dissolved in 10 ml of methanol and heated to 60℃, and then 0.45 mg of potassium hydroxide was added to form zinc oxide nanoparticles in several minutes. Then 100 mg of 3,4,9,10-perylenetetracarboxylic potassium (PK), which was prepared by reacting PTCDA with potassium hydroxide in room temperature (r.t.), was dispersed in 5 ml of methanol and added into the ZnO NP solution and refluxed at 60℃ for three days. After cooling down to room temperature, the yellow precipitate of PZn Nps was collected by centrifugation and washed wish methanol several times and dispersed in ethanol.

Synthesis of ZnS/PTCDA core-shell nanoparticles: The ZnS/PTCDA core-shell nanoparticles (ZPNPs) were prepared by reacting PZn NPs with hydrogen sulfide. First, 25 mg PZn NPs was dispersed in 60 mL deionized water and heated to 70 ℃, then a flow of hydrogen sulfide produced by dropping dilute sulphuric acid (35%, 100 ml) to solid sodium hydrosulfide (40 g) was supplied. After 5 minutes, the solution turned from yellow to red, and was kept at this temperature for two hours. After cooling down to r.t., the red precipitates were centrifuged and washed with water and ethanol several times.

Detection of aniline (VOCs): 10 ml (1 mg/ml) ZPNPs colloid in water were spin-coated on the SiO_2 substrate (1.5 x 1.5 cm^2) to form a thin film. Atomic force microscope (AFM) analysis indicated the thickness of the film was about 100 nm, as shown in Figure S1. Two Pt electrode (0.5 x 0.5 cm^2), the distance between which was 0.2 cm, was deposited on the surface of the film. The delection of VOCs was measured in a homemade vacuum steel chamber (2.85 L) with two electodes, an inlet and outlet. The current-voltage of the film was monitored using Keithley Semiconductor Characterization System (SCS-4200). In a typical measurement, the ZPNPs film was placed in the steel chamber, the steady-state current-voltage curve of the film was recorded in the N_2 atmosphere first, and then the VOC gas was injected into the chamber and the corresponding stable current-voltage curve of the film was recorded. In the recovery process, the VOC gas was pumped away by vacuum pump and the film sensor restored in the N_2 atmosphere at room temperature. The VOC gases were obtained by volatilization of the liquid of the compounds in a steel box and diluted to the needed concentrations. The current-voltages of the ZPNPs film to benzene, toluene, aniline, phenylenediamine, chlorobenzene, o-xylene, m-xylene, o-dichlorobenzene, benzaldehyde, acetophenone, benzonitrile, ethanol, acetonitrile, dichloromethane, n-butylamine, trimethylamine, triethylamine and water were recorded.

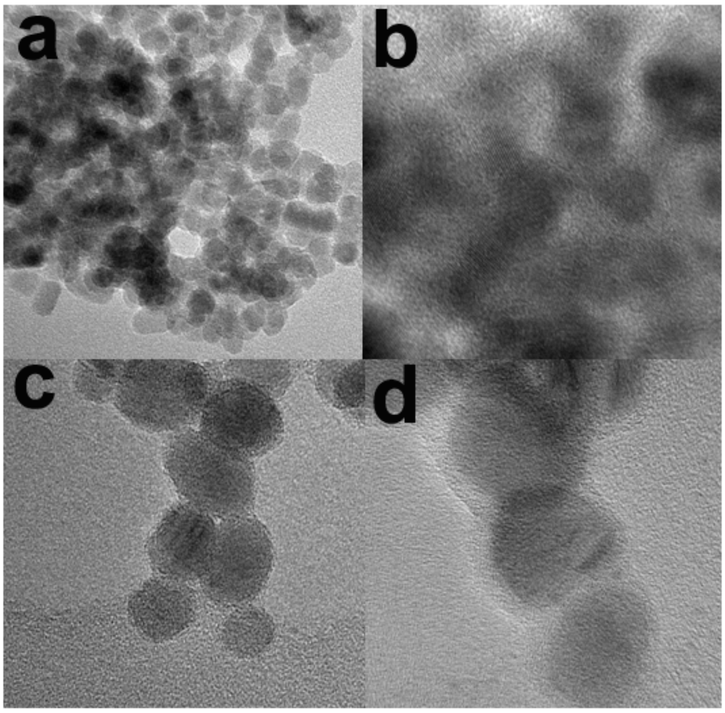

Figure S1 (a) TEM and (b) HRTEM images of PZn nanoparticles, (c) and (d) high-magnification TEM images of ZPNPs.

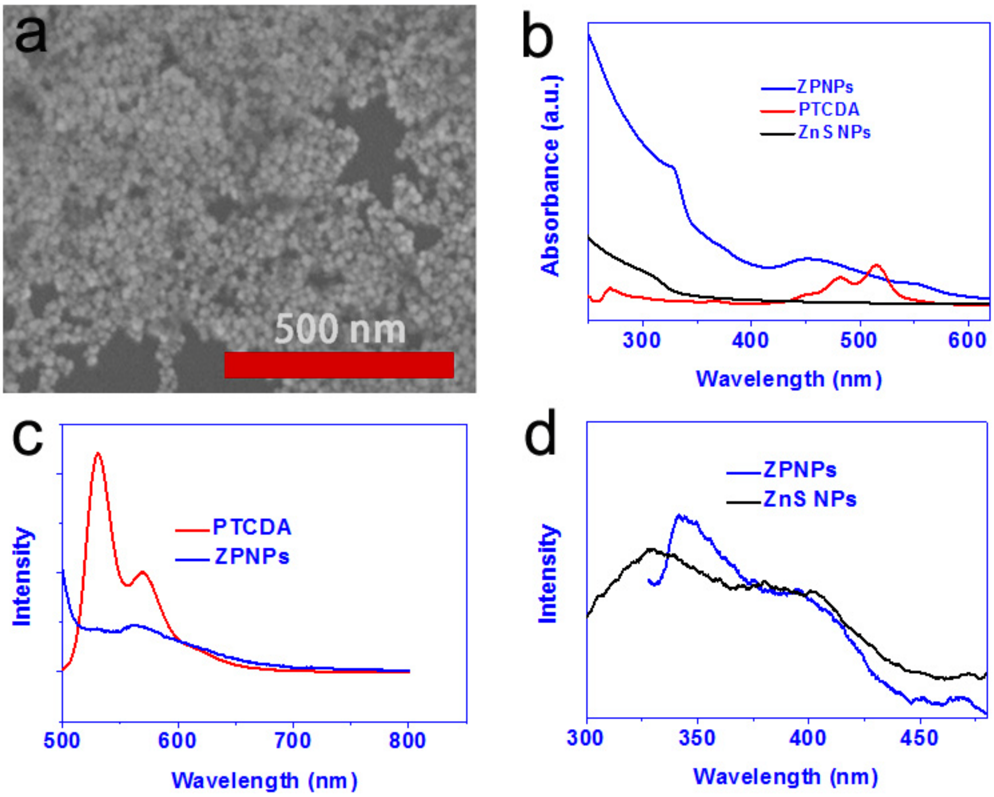

Figure S2.(a) SEM image of the ZPNPs. b）UV-vis absorption spectrum of ZPNPs and ZnS NPs in ethanol, PTCDA in DMF solution; (c) fluorescence emission spectrum of ZPNPs in ethanol and PTCDA in DMF solution, using a 480 nm excitation; (d) fluorescence emission spectrum of ZPNPs and ZnS NPs in ethanol, using a 300 nm excitation.

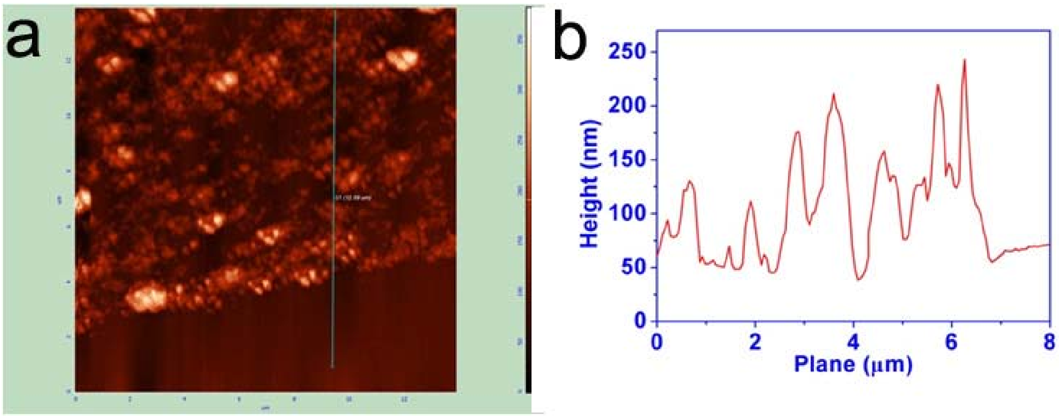

Figure S3. (a) AFM image of the ZPNPs film; (b) height map the film along the marked line in (a).

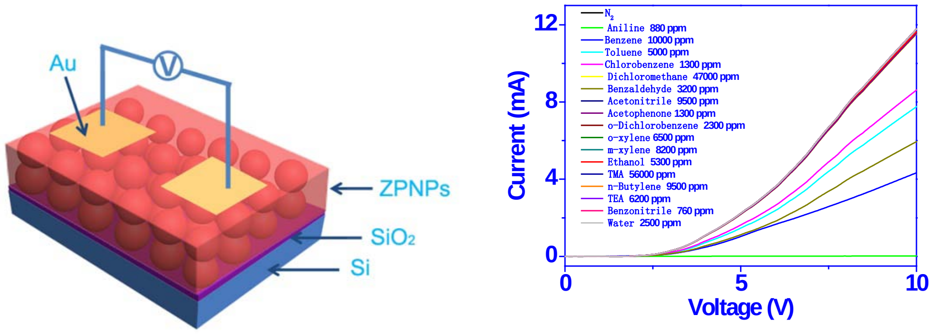

Figure S4. (a) schematic model of the ZPNPs film sensor; (b) Current-voltage curves of the sensor in nitrogen and when exposed to a series of VOCs and water vapor.

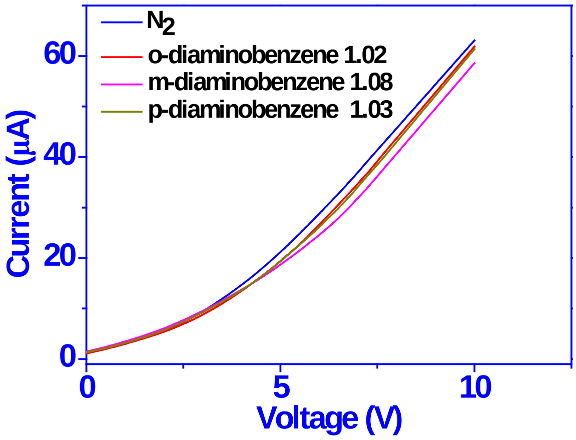

Figure S5. The current-voltage curve of the ZPNPs sensor before and after exposed to phenylenediamines.

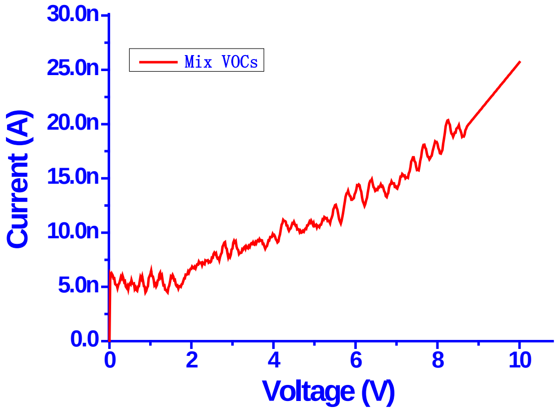

Figure 6 The current-voltage curve of competition experiment using mix VOCs (mixed the saturated vapor of aniline, benzene, toluene, chlorobenzene, and benzaldehyde). The ZPNPs sensor exposed to mix VOCs.

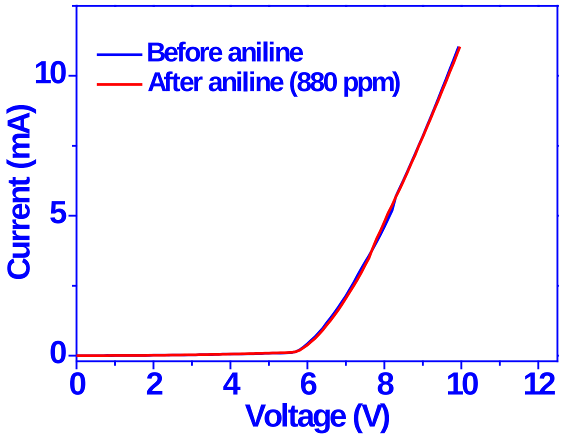

Figure S7. Current-voltage curve of the ZnS NP film sensor before and after exposed to aniline (880 ppm).

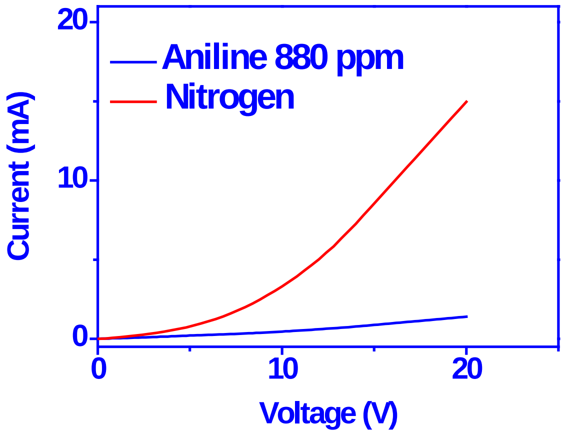

Figure S8. Current-voltage curve of the PTCDA film sensor before and after exposed to aniline at the concentration of 880 ppm.

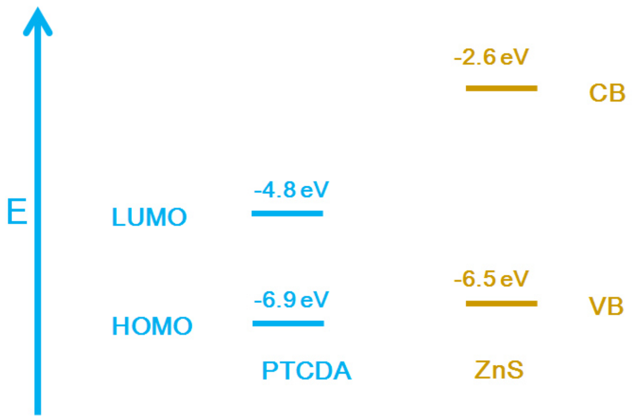

Figure S9 Energy level alignments of PTCDA and ZnS relative to vacuum level.[39, 40]