Supporting Information

A Novel Inorganic–Organic Hybrid for Detection of Nitrite anion with Extremely High Sensitivity and Selectivity

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Experimental section:

1. Materials

Sodium nitrite was purchased from Aladdin Chemistry Co. Ltd.; PbI_2, benzidine, HI, ethanol, *N*, *N'*-dimethyl formamide (DMF) were received from Sinopharm Chemical Reagent Co. Ltd.. They were directly used without further purification. Water was deionized and distilled before use.

2. Measurements.

The FT-IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer in 4000–400 cm^{-1} region using KBr pellets. The analyses of carbon, nitrogen and hydrogen contents were performed on an Elementar Vario MICRO microanalyser. PXRD pattern was collected on a MiniFlex II diffractometer using Cu-K_α radiation (λ = 1.540598 Å) at 30 kV and 15 mA. The simulated pattern of **1** was derived from the Mercury Version 1.4 software (http://www.ccdc.cam.ac.uk/products/mercury/). The pH was measured by a pHB-5 portable pH meter. Optical absorption spectra were measured on a PerkinElmer Lambda-900 UV/Vis/NIR spectrophotometer. The ESI-MS spectrum was measured by ThermoFinnigan DECAX-30000 LCQ Deca XP ion trap mass spectrometry.

3. X-ray crystallographic study

The X-ray diffraction measurement was performed on a Rigaku Ultrax-Saturn 70 diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data

set was collected using an ω scan technique and corrected for Lp effects. The primitive structure was solved by the direct method using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software. The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The final structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon and nitrogen atoms were generated geometrically, while those of water molecules were not included. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC 849193. This datum can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

4. Synthesis of crystalline (H₂DAB)(Pb₂I₆)·2H₂O (DAB = benzidine) (1)

A mixture of PbI_2 (0.231 g, 0.25 mmol), DAB (0.046 g, 0.25 mmol), ethanol (1 mL), and concentrated HI (5.0 mL, 45%) was heated at 150 °C for 1.5 days in a sealed 25-mL Teflon-lined stainless steel vessel. Upon cooling at 3 °C·h^{-1} to room temperature, light yellow acicular crystals of **1** were obtained in 95% yield (based on PbI_2). Elem. Anal. (%) Calcd.: C, 10.30; H, 1.29; N, 2.00. Found: C, 10.53; H, 1.34; N, 1.95. IR(KBr, cm^{-1}): 3492 (m), 2931 (m), 2595 (w), 1605 (m), 1573 (m), 1493 (s), 1397 (w), 1321 (w), 1203 (w), 1110 (m), 1012 (w), 800 (m), 506 (m).

5. Experimental procedure of sodium nitrite detection using 1

1 mL DMF solution of **1** (100 μM) was dropped into 4 mL aqueous solution of sodium nitrite with different concentration. The UV-Vis absorption spectra, color and pH values of the obtained solutions were measured (Figures 2,4, 5b).

6. Synthesis of (H₂DAB)I₂

2 mL HI (45%) was added dropwise into a solution of DAB (0.092 g) in 25 mL ethanol at room temperature under stirring for 2 h. The pale yellow solid was collected by filtration, washed with water and ethanol, and dried under vacuum at 30 °C in 86% yield (based on DAB). Other correlative compounds $H_2DAB(NO_3)_2$, $H_2DAB(BA)_2$ (BA = benzoic acid), and H_2DABCl_2 were synthesized using the same method.

7. Experimental procedure of sodium nitrite detection using (H$_2$DAB)I$_2$

1 mL DMF solution of (H$_2$DAB)I$_2$ (100 μM) was dropped into 4 mL aqueous solution of sodium nitrite with different concentrations. The UV-Vis absorption spectra of obtained solutions were measured. Other correlative compounds H$_2$DAB(NO$_3$)$_2$, H$_2$DAB(BA)$_2$ (BA = benzoic acid), and H$_2$DABCl$_2$ were texted using the same method (Figure S6).

Supporting graphics:
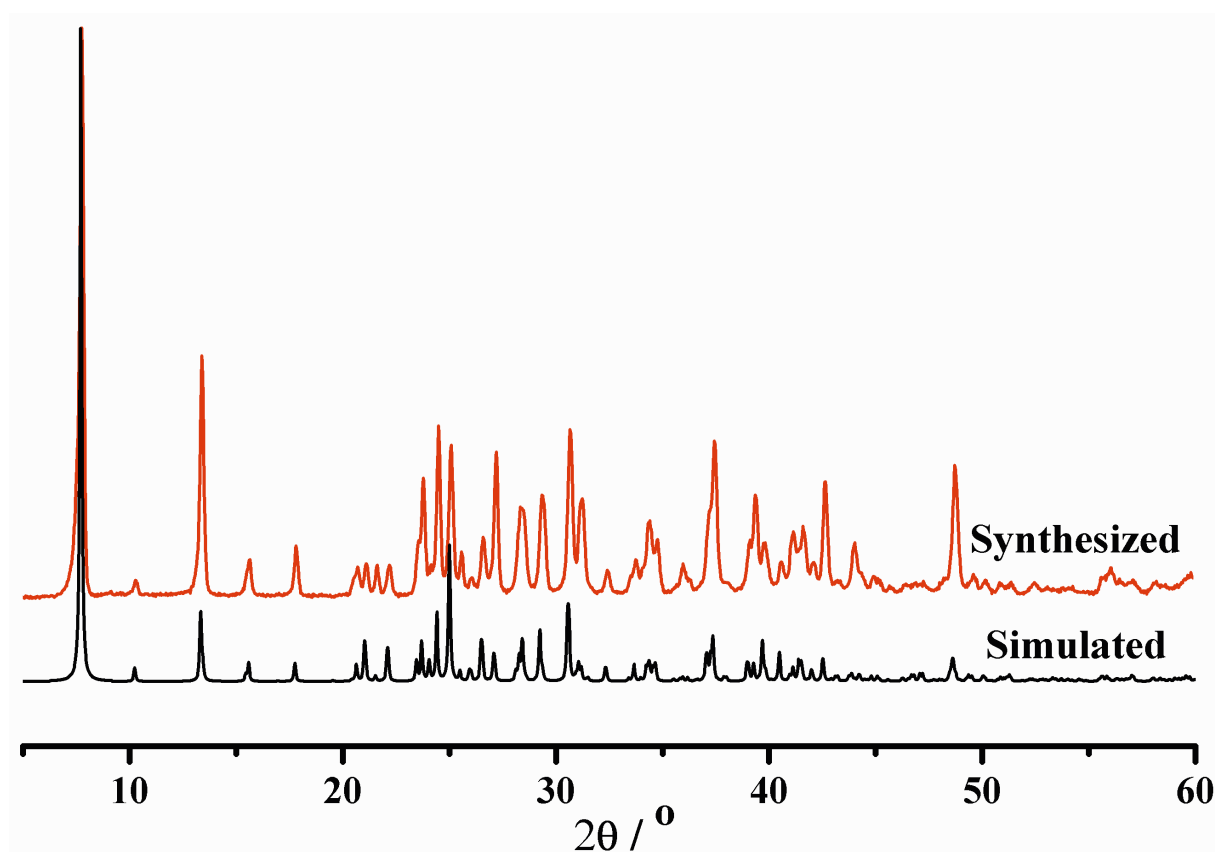
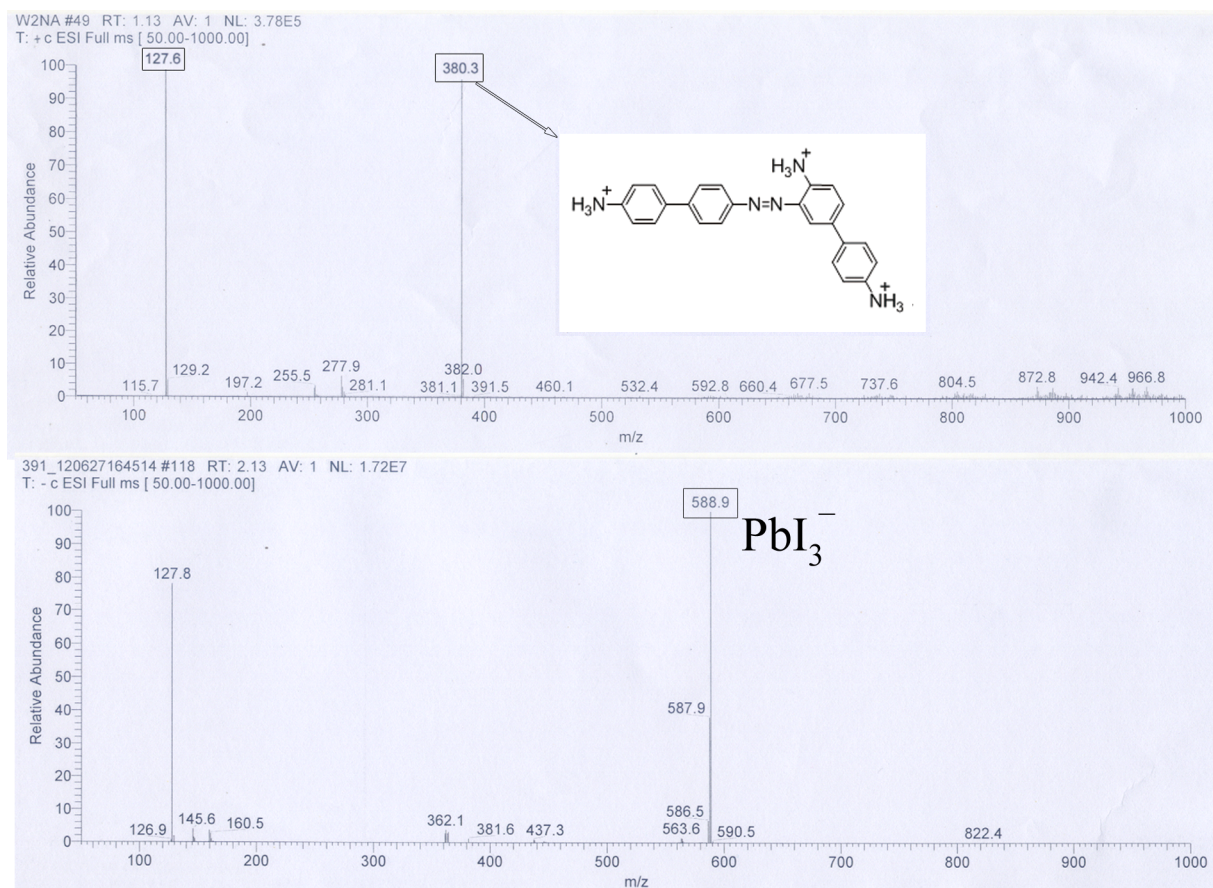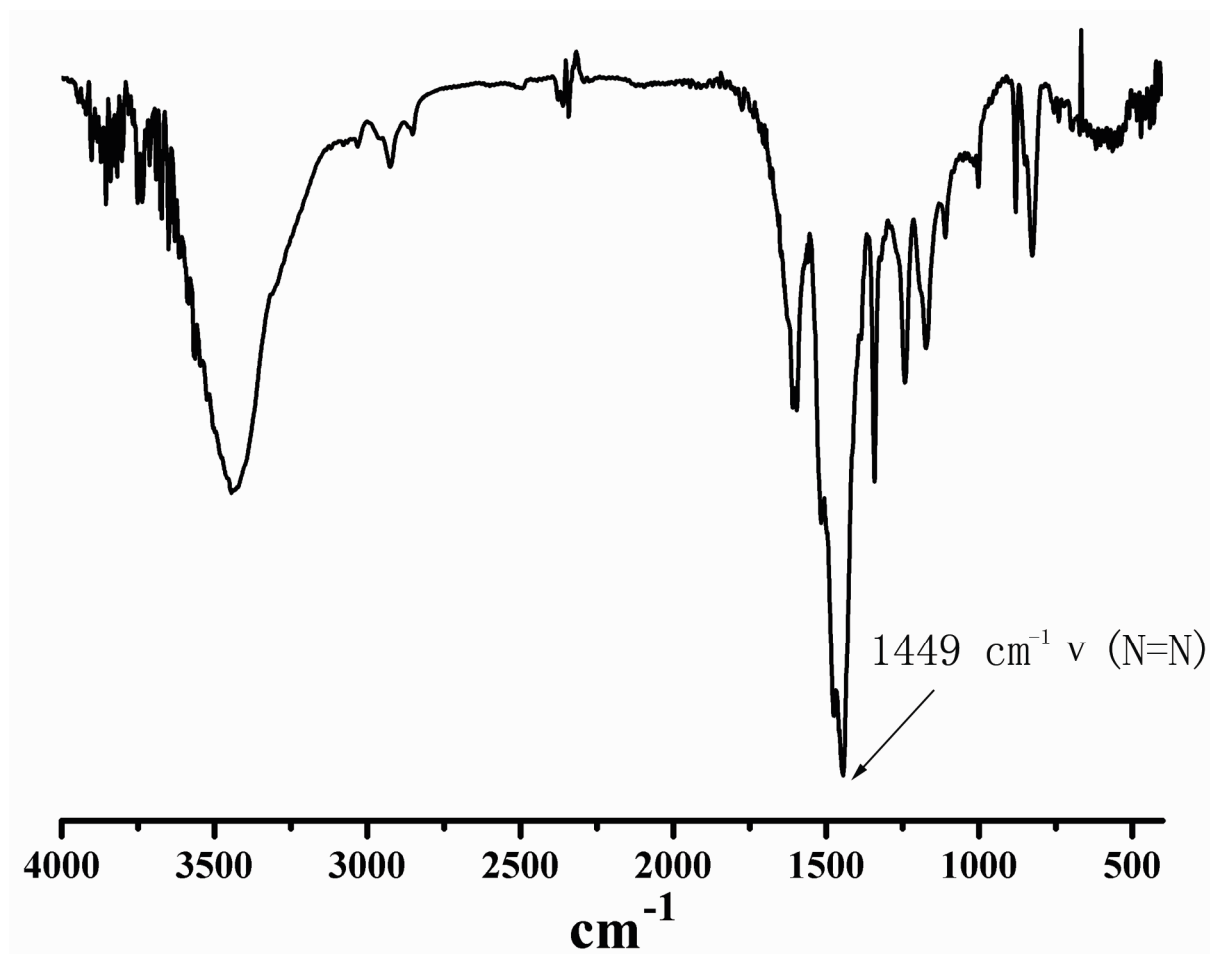**Fig. S1.** PXRD patterns of **1**.
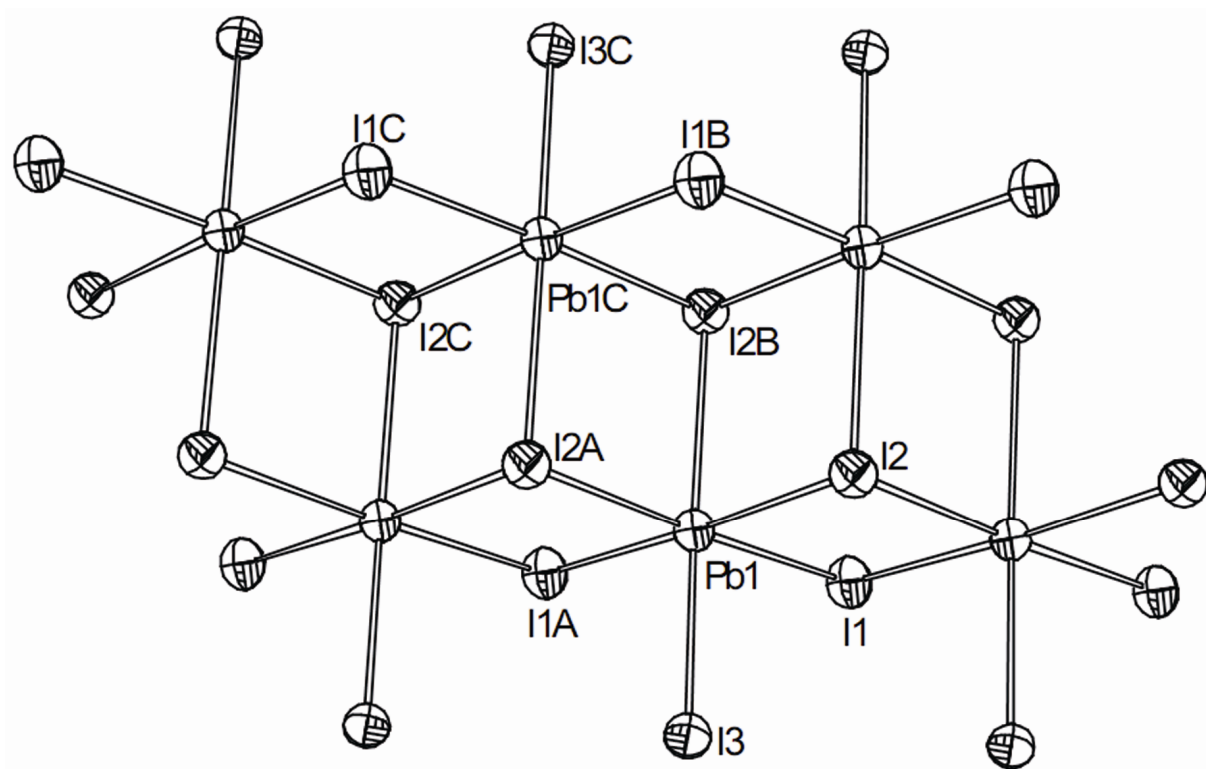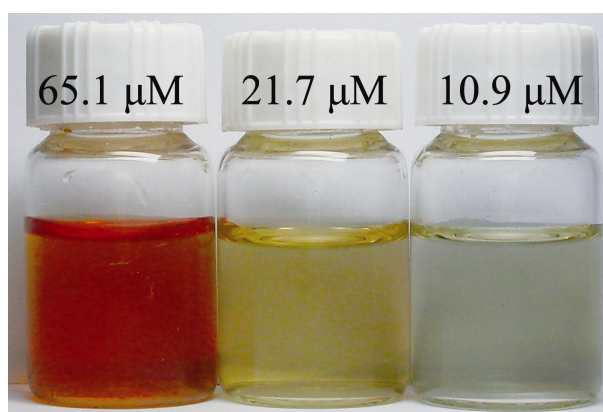
Fig. S2. The 1-D chain structure of $[Pb_2I_6]^{2-}$ ion in **1** extending along the $[1\ 0\ 0]$ direction. Symmetry codes: A = –x, –y, –z; B = 1+x, y, z; C = –1–x, –y, –z.
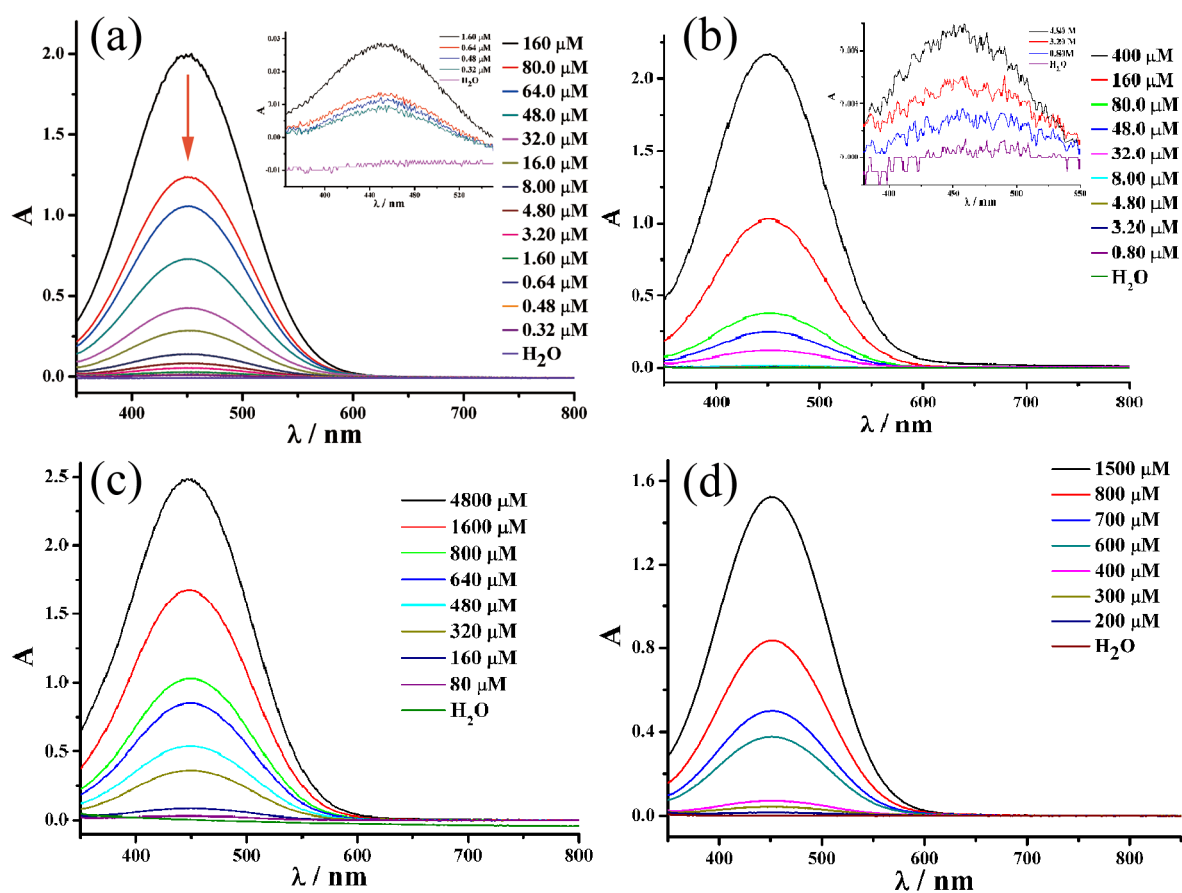
Fig. S3. The MS spectrum of diazotization reaction product of protonated benzidine.

$1449 \ cm^{-1} \ v \ (N=N)$

Fig. S4. FT-IR spectrum of the azo production.

65.1 μM   21.7 μM   10.9 μM

Fig. S5. The photographs of reaction solutions, the concentrations of nitrite are 65.1 μM (3 mg/L), 21.7 μM (1 mg/L), and 10.9 μM (0.5 mg/L).

Fig. S6. UV spectroscopic studies for nitrite sensing upon the same concentration (100 μM) of $(H_2DAB)I_2$ (a), $H_2DAB(NO_3)_2$ (b), $H_2DAB(BA)_2$ (BA = benzoic acid) (c), and H_2DABCl_2 (d) and different concentration of nitrite.