

Supporting Information

A simple chemosensor for the dual-channel detection of cyanide in water with high selectivity and sensitivity

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Materials and apparatus

All reagents for synthesis were of analytical grade, commercially and were used without further purification. All the anions were added in the form of tetrabutylammonium (TBA) salts. Which were purchased from Sigma–Aldrich Chemical, stored in a vacuum desiccators. Melting points were measured on an X–4 digital melting point apparatus and were uncorrected. UV–vis spectra were recorded on a Shimadzu UV–2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF–5310. ¹H NMR spectra were recorded on a Mercury–600BB spectrometer at 600 MHz and ¹³C NMR spectra were recorded on a Mercury–600BB spectrometer at 150 MHz with DMSO–*d*₆ as solvent. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker–FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer.

Fluorescence quantum yield of **HY** and **HY–CN[–]** adduct was determined by the following equation.¹

$$\Phi = \Phi_R \frac{I A R n^2}{I_R A n R^2}$$

where Φ is fluorescence quantum yield, I is the integrated fluorescence intensity, n is the refractive index of solvent, and A is the optical density (absorption). The subscript R refers to the reference of quinine sulfate.

Synthesis of the chemosensors **HY**

Compound **HY** can be readily prepared by a simple reaction of 3-hydroxy-2-naphthoic acid and 2-hydroxy-1-naphthaldehyde (Scheme 1). 3-hydroxy-2-naphthoic acid (0.94 g, 5 mmol) and 98% H₂SO₄ (30 μL, 10 mol%) was reflux in 40 mL methanol for 8 hours at 65 °C to give 2-hydroxy-3-naphthoate. Soon afterwards, 2-hydroxy-3-naphthoate (2.02g, 10 mmol) and hydrazine monohydrate (0.5 g, 10 mmol) were mixed in 30 mL ethanol stirred under reflux for 24 hours at 80 °C. After cooling to room temperature, poured into 200 mL distilled water, the yellow precipitate was filtered, washed three times with hot absolute ethanol, then got the compound 3-hydroxy-2-naphthohydrazide. Then 3-hydroxy-2-naphthohydrazide (1.01 g, 5 mmol), 2-hydroxy-1-naphthaldehyde (0.86 g, 5 mmol) and catalytic amount of acetic acid (AcOH) were combined in absolute ethanol (30 mL). The solution was stirred under reflux at 80 °C for 24 hours. After cooling to room temperature, the yellowish precipitate was filtered, then recrystallized with EtOH to give a yellowish powder product **HY** (1.56 g) in 83.6 % yield (m. p. >300 °C). ¹H NMR (600 MHz, DMSO-*d*₆) δ 12.75 (s, 1H), 12.23 (s, 1H), 11.29 (s, 1H), 9.56 (s, 1H), 8.52 (s, 1H), 8.34 (d, *J* = 8.6 Hz, 1H), 7.98–7.86 (m, 3H), 7.78 (t, *J* = 9.3 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.46–7.32 (m, 3H), 7.25 (d, *J* = 8.9 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 163.09 (s), 158.11 (s), 153.93 (s), 147.58 (s), 135.95 (s), 132.85 (s), 131.67 (s), 130.57 (s), 128.86 (s), 128.65 (s), 128.29 (s), 127.77 (s), 127.66 (s), 126.79 (s), 125.82 (s), 123.82 (s), 123.49 (s), 120.92 (s), 119.70 (s), 118.84 (s), 110.64 (s), 108.59 (s). IR (KBr, cm⁻¹) ν: 3409 (–

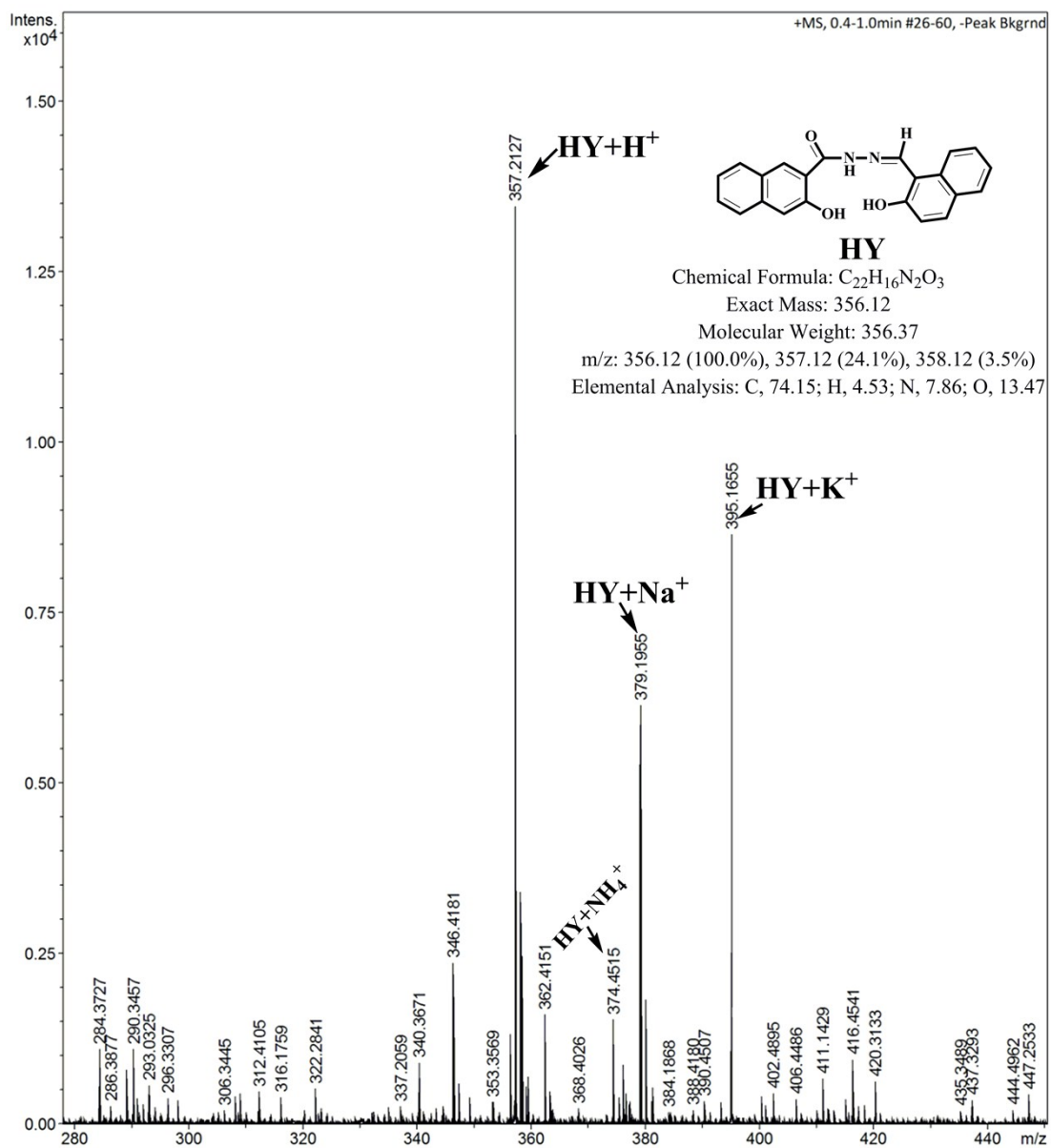


Figure S3 The mass data of HY.

The detection limit of the sensor HY with CN⁻

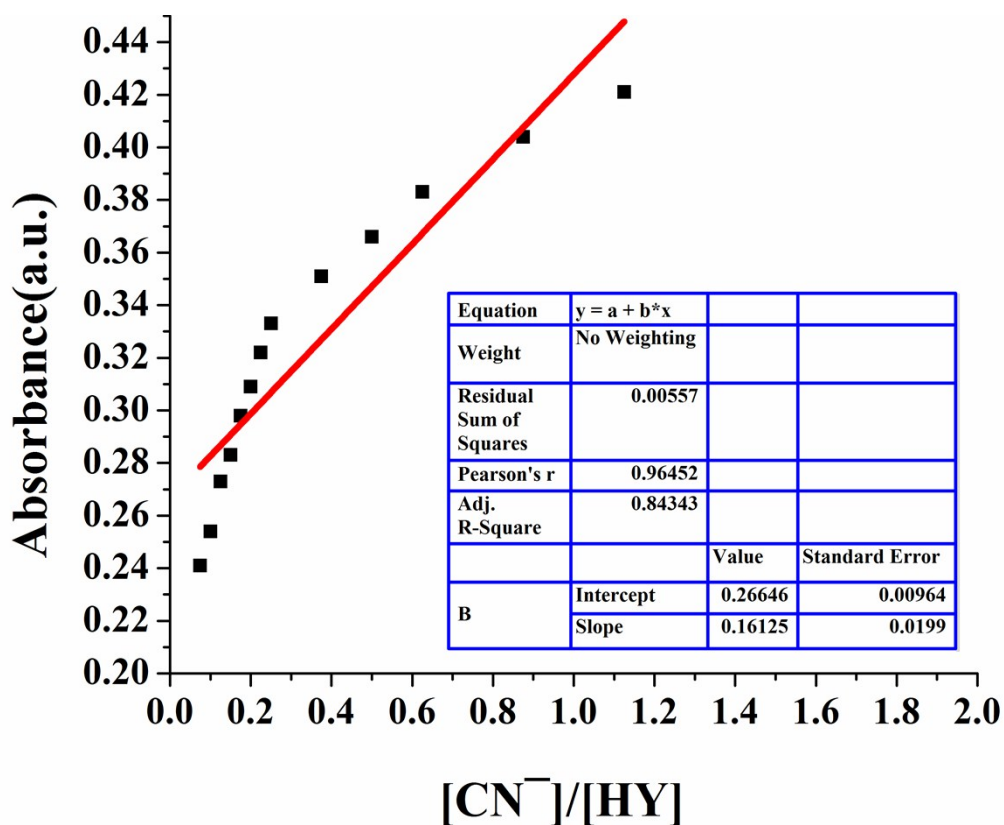


Figure S4. Plot of the absorbance at 420 nm for a mixture of probe **HY** and CN⁻ in DMSO/H₂O (3 : 7, v/v) ($\lambda_{\text{ex}} = 378$ nm).

The detection limit of UV-vis spectra result of the analysis as follows:

Linear Equation: $Y=0.16125X + 0.26646$

$$R^2 = 0.96452$$

$$S = 1.16125 \times 10^7$$

$$\delta = \sqrt{\frac{\sum(F_i - F_0)^2}{N-1}} = 3.23 \quad (N=30)$$

$$K = 3$$

$$\text{LOD} = K \times \delta / S = 8.34 \times 10^{-7} \text{ M}$$

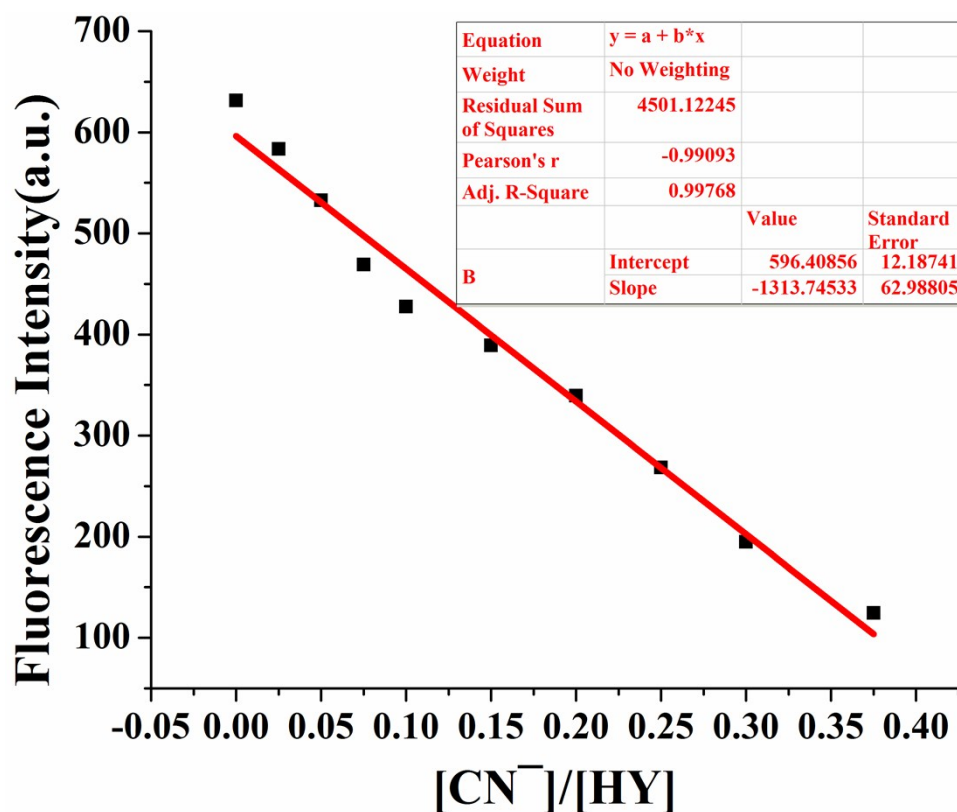


Fig. S5. Plot of the intensity at 502 nm for a mixture of probe **HY** and CN^- in DMSO/ H_2O (3 : 7, v/v).

The detection limit of fluorescence spectra result of the analysis as follows:

$$\text{Linear Equation: } Y = -1313.74533X + 596.40865$$

$$R^2 = 0.99768$$

$$S = 1.31375 \times 10^9$$

$$\delta = \sqrt{\frac{\sum(P_i - P_0)^2}{N-1}} = 12.47 \quad (N=30)$$

$$K = 3$$

$$\text{LOD} = K \times \delta / S = 2.85 \times 10^{-8} \text{ M}$$

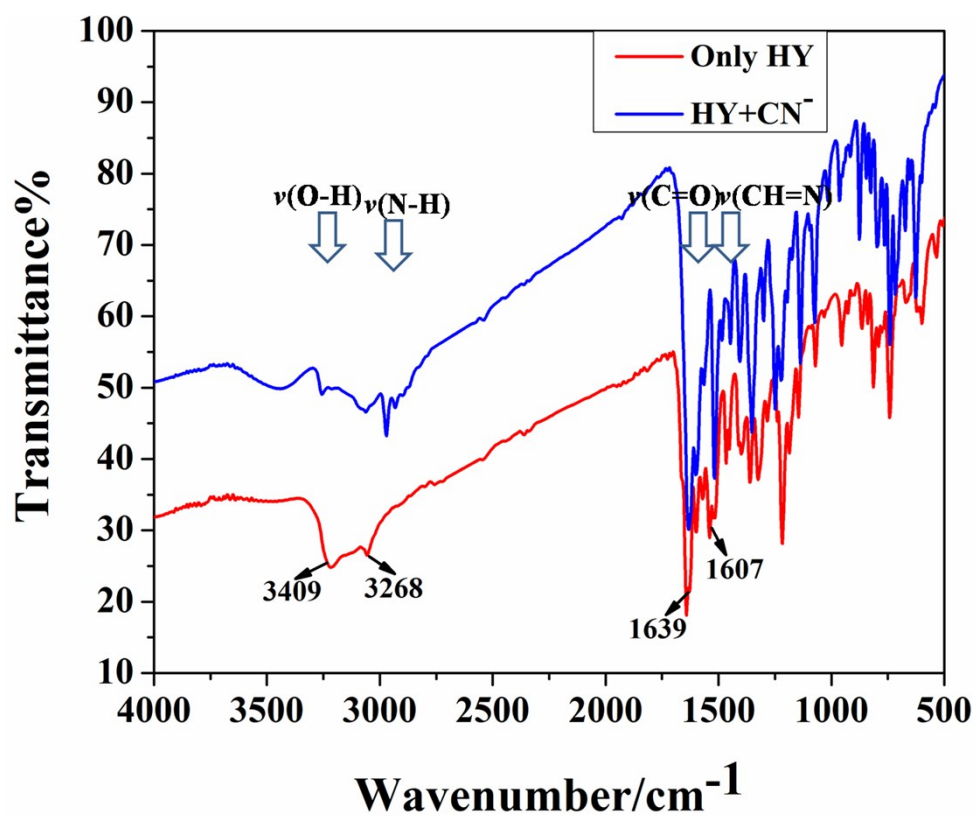


Figure S6 IR spectra of compounds **HY** and **HY+CN⁻**.

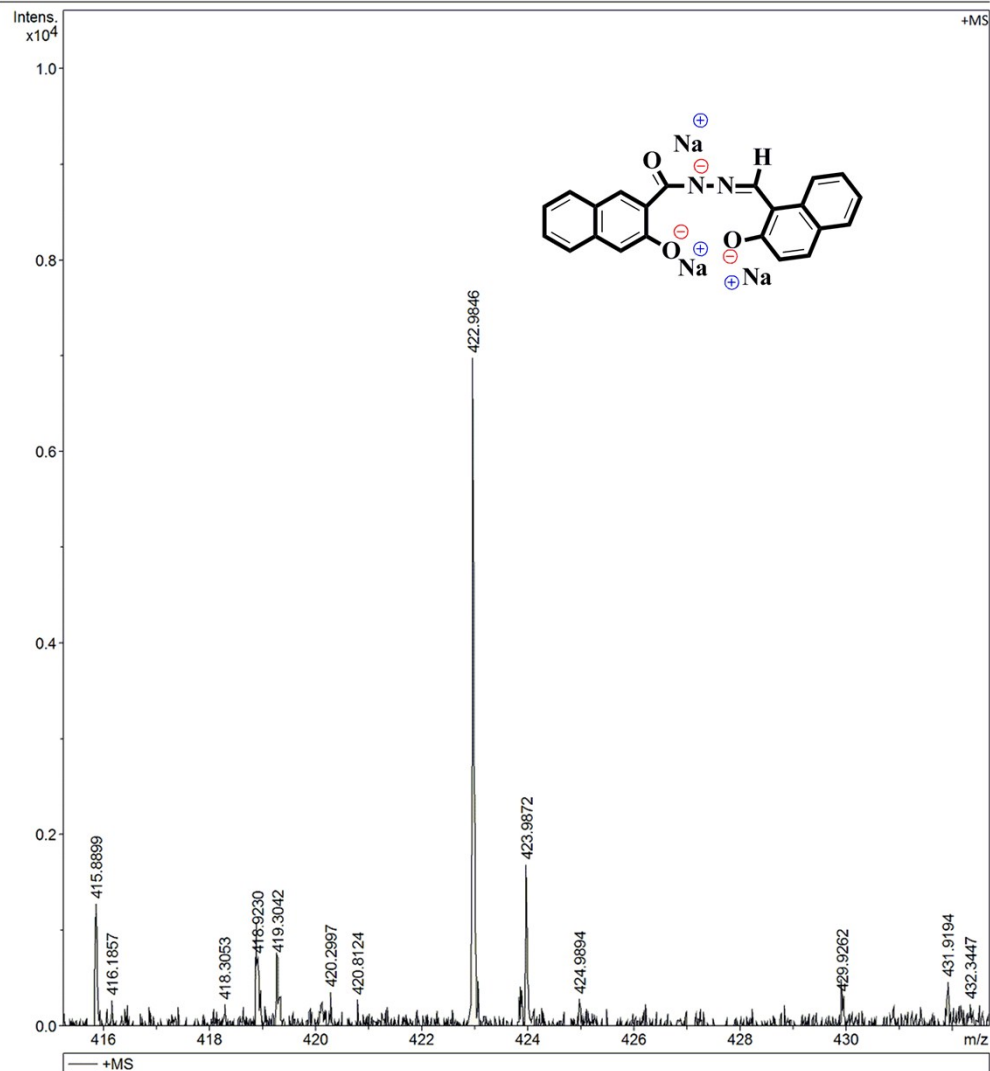
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Operator LZU
Instrument micrOTOF



Bruker Compass DataAnalysis 4.1

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by: LZU

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Figure S7 ESI-MS spectrum of compounds **HY-CN⁻**.

Reference:

- 1 Y. Gabe, Y. Urano, K. Kikuchi, H. Kojima, T. Nagano, *J. Am. Chem. Soc.* 2004, **126**, 3357.

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