Electronic Supplementary Material

A colorimetric and "turn-on" fluorimetric chemosensor for selective detection of cyanide and its application in food sample

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CONTENTS

1. General Methods

Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 at 600 MHz spectra. ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. UV–visible spectra were recorded on a Shimadzu UV–2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF–5301 fluorescence spectrophotometer. Melting points were measured on an X–4 digital melting-point apparatus. The infrared spectra were performed on a Digilab FTS–3000 FT–IR spectrophotometer.

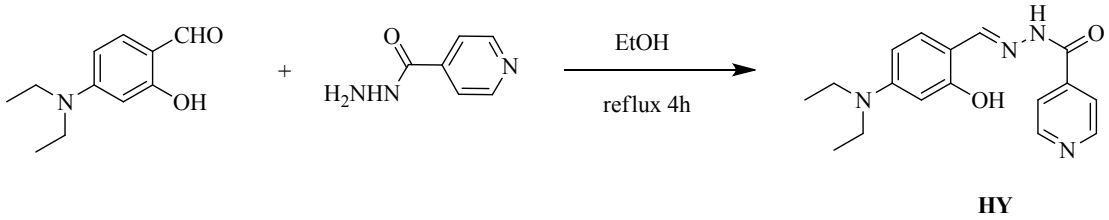
All the UV–vis experiments were carried out in DMSO on a Shimadzu UV–2550 spectrometer. Any changes in the UV–vis spectra of the synthesized compound kept the ligand concentration constant (2.0×10^{-5} M) in all experiments. Tetrabutylammonium salt (1.0×10^{-3} M) of anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and ClO_4^-) and sodium salt (1.0×10^{-3} M) of anions (CN^- and SCN^-) were used for the UV–vis experiments.

All the fluorescence spectroscopy was carried out in DMSO on a Shimadzu RF–5301 spectrometer. Any changes in the fluorescence spectra of the synthesized compound kept the ligand concentration constant (2.0×10^{-5} M) in all experiments. Tetrabutylammonium salt (1.0×10^{-3} M) of anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and ClO_4^-) and sodium salt (1.0×10^{-3} M) of anions (CN^- and SCN^-) were used for the fluorescence experiments

For ^{1}H–NMR titrations, the solution of **HY** was prepared in DMSO–d_6 and the appropriate concentrated solution of guest was prepared in DMSO–d_6. Aliquots of the two solutions were mixed directly in NMR tubes.

2. Synthesis of sensor molecule HY

The synthesis route of sensor **HY** is demonstrated in Scheme 1. An ethanol solution (25 mL) of 4-(Diethylamino)salicylaldehyde (0.966 g, 5 mmol), isonicotinyl hydrazide (0.685 g, 5 mmol) were stirred under reflux 4h. After cooling to room temperature, the yellow precipitate was filtered, washed with hot absolute ethanol three times, then recrystallized with ethanol to get yellow product **HY** in 88% yield. m. p 193℃-196℃. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 11.98 (s, 1H), 11.25 (s, 1H), 8.76 (dd, 2H), 8.43 (s, 1H), 7.80(dd, 2H), 7.22 (d, 1H), 6.26 (dd, 1H), 6.11 (d, 1H), 3.35 (q, 4H), 1.09 (t, 6H); ESI-MS m/z: Calcd for $[C_{17}H_{20}N_4O_2 + H]^+$ 313.16; Found $[C_{17}H_{20}N_4O_2 + H]^+$ 313.20.



HY

Scheme S1 Synthesis of the sensor compound **HY**.

3. ^{1}H NMR spectrum of HY

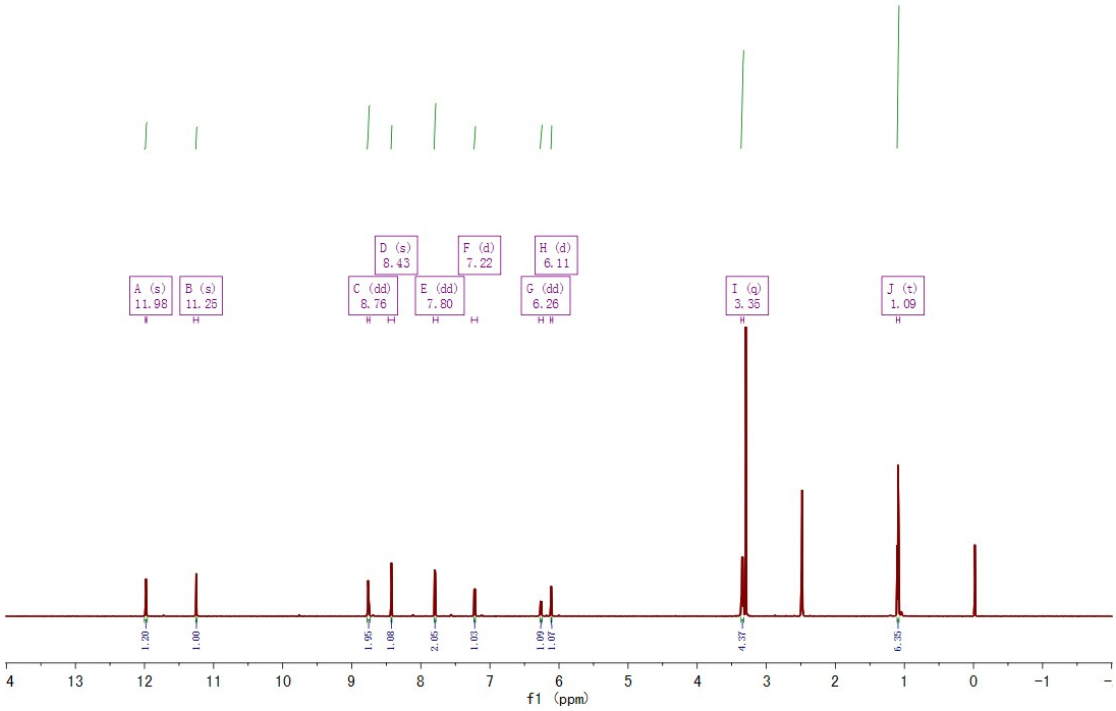


Fig. S1 ^{1}H–NMR spectrum of **HY** in DMSO–d_6.

4. ^{13}C NMR spectrum of HY

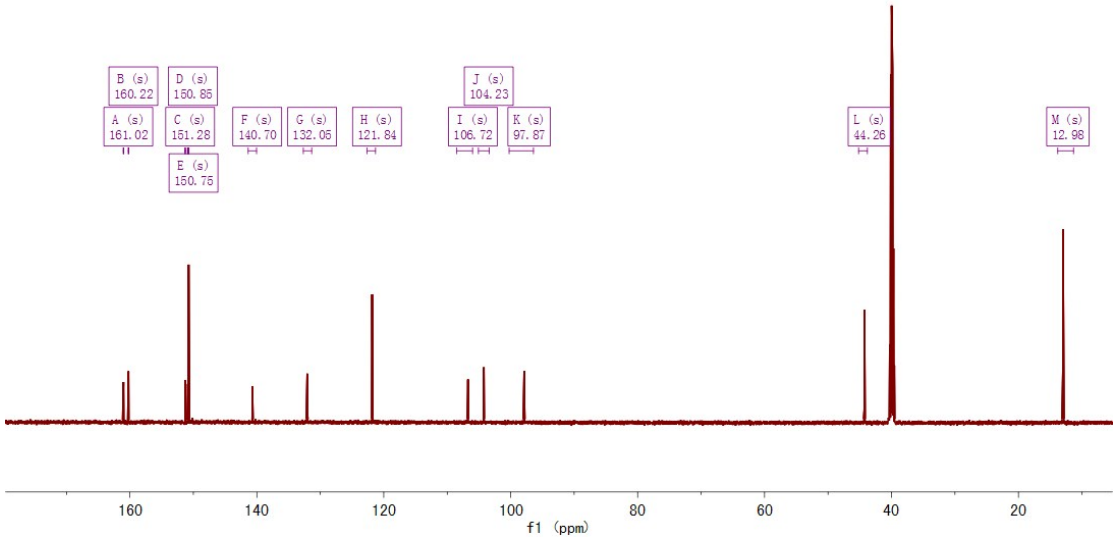


Fig. S2 ^{13}C–NMR spectrum of **HY** in DMSO–d_6.

5. Mass spectrum of HY

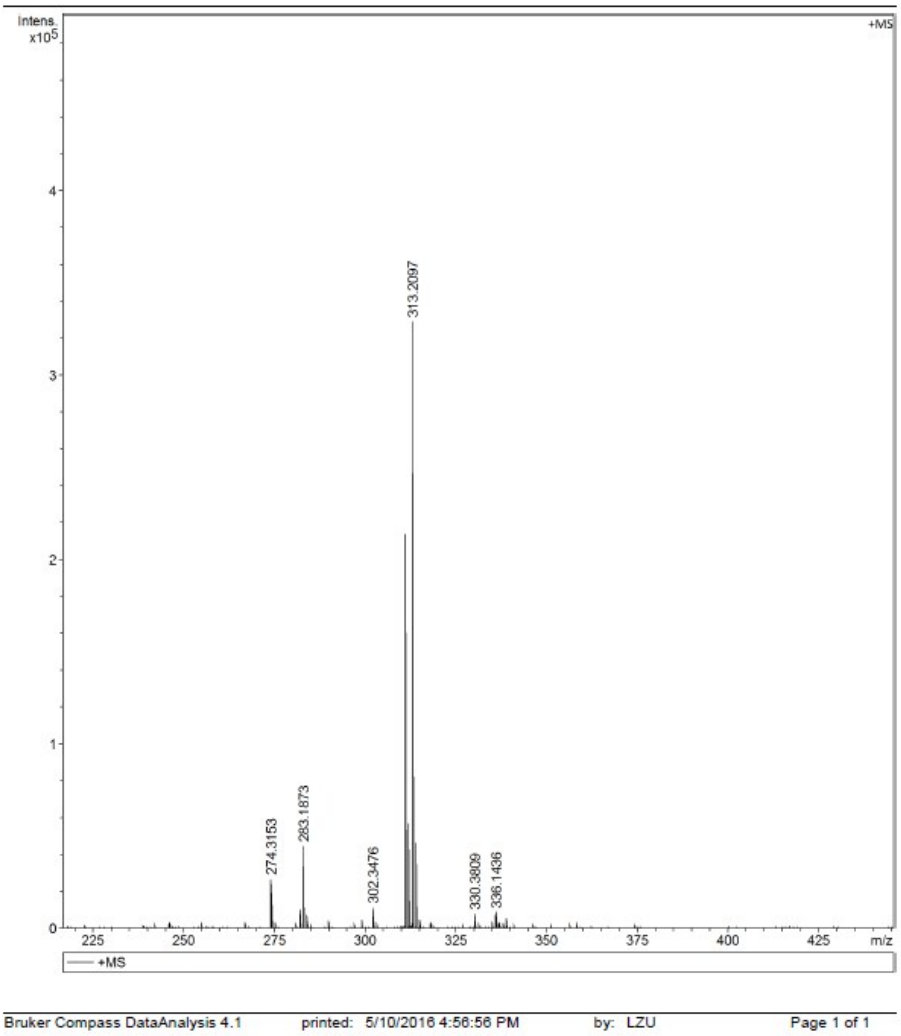


Fig. S3 Mass spectrum of **HY**.

6. Determination of Detection Limit

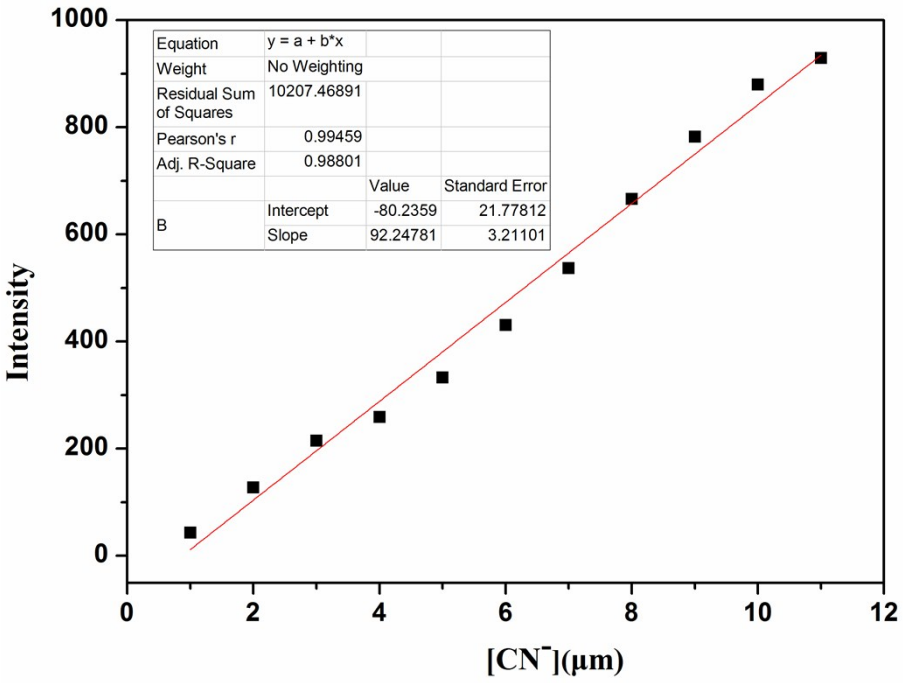


Fig. S4 The photograph of the fluorescent spectrum linear range.

Linear Equation: Y = 92.24781× X －80.2359 R = 0.98801

$S = 9.225 \times 10^7$ $\delta = \sqrt{\frac{\Sigma(F - \bar{F})2}{(N-1)}} =$ 1.603 (N = 10) K = 3

$LOD = K \times \delta / S = 5.21 \times 10^{-8}$ M

7. The UV-vis and fluorescence spectra of HY adding F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- ClO_4^-, CN^- and SCN^-dissolved in pure water (50 equiv.) in the DMSO/H_2O (v/v = 7:3) solution (λ_{ex}=375 nm)

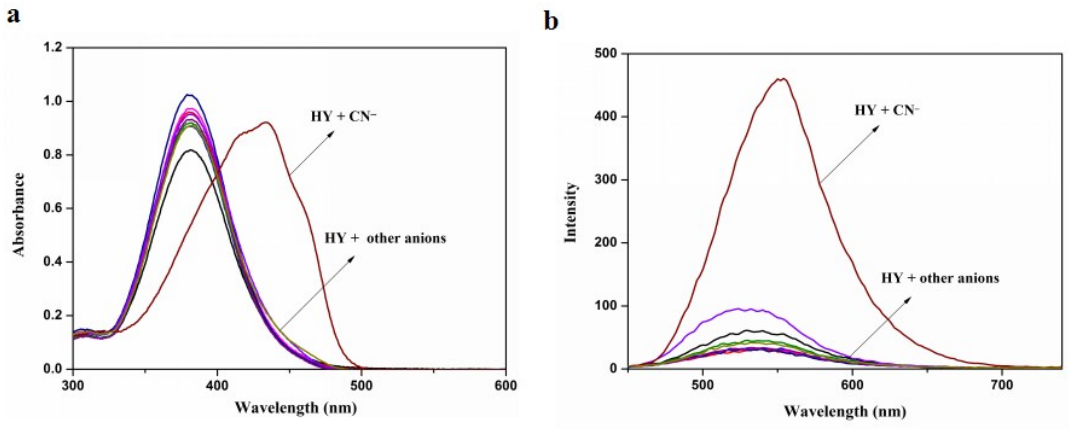


Fig. S5 a) Absorbance spectra data b) Fluorescence emission data of **HY** adding F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- ClO_4^-, CN^- and SCN^-dissolved in pure water (50 equiv.) in the DMSO/H_2O (v/v = 7:3) solution (λ_{ex}=375 nm).

8. Mass spectrum change of HY + CN^-.

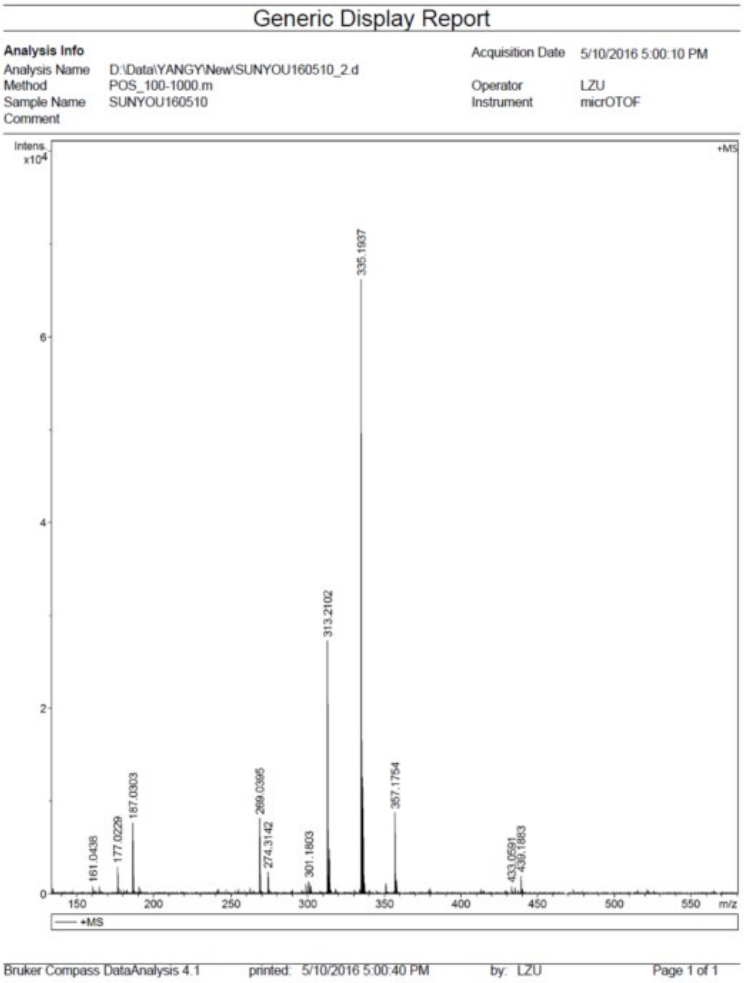


Fig. S6 Mass spectrum change of **HY + CN^-**.

9. Effect of pH the UV-vis and fluorescence spectra of HY + CN^-.

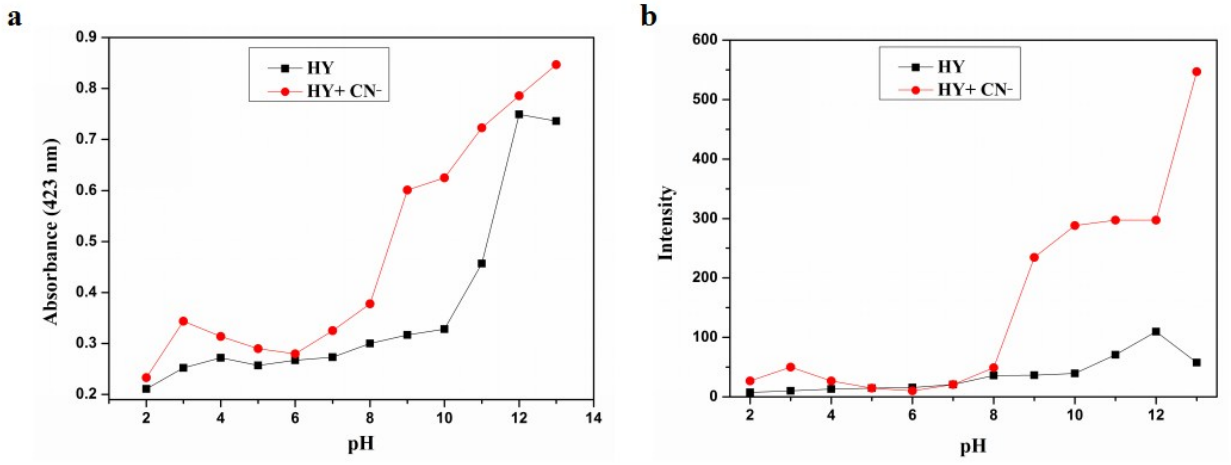


Fig. S7 Effect of pH on the a) UV-vis and b) Fluorescence spectra of **HY** (2.0×10^{-5} M) in response to CN^- (50 equiv.) from 2 to 13 in DMSO/H_2O (v/v=7:3) solution.

10. A part of the literatures were provided in the followed table:

Table **S1**:

Journal Year. Volume. Page	Response channel	Water content	Detection limits	Application	single crystal data
This work	Colorimetric and fluorometric (Off-On)	DMSO/H_2O (v/v = 7:3).	Fluorometric: 5.21×10^{-8} M	a) INHIBIT molecular logic gates; b) test trips; c) detection in food sample	Yes
Organic Letters 15 (2013) 2386–2389	Fluorometric (Off-On)	DMSO/H_2O (v/v = 99:1)	—	—	—
Talanta 152 (2016) 39–44	Colorimetric and fluorometric (Off-On)	DMSO/buffer (v/v = 9:1)	—	—	Yes
New J. Chem.39 (2015) 4041–4046	Colorimetric and fluorometric (Off-On)	DMSO/H_2O (v/v = 3:2)	1.2×10^{-9} M	test trips	—
Tetrahedron 72 (2016) 1244–1248	Colorimetric and fluorometric (Off-On)	THF/H_2O (v: v = 99:1)	—	—	—
Tetrahedron 70 (2014) 1889–1894	Colorimetric and fluorometric (Off-On)	DMSO/H_2O (v/v = 9:1)	4.0×10^{-7} M	—	Yes

[1] T. F. Robbins, H. Qian, X. Su, R. P. Hughes, and I. Aprahamian, Organic Lett. 15 (2013) 2386–2389.

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[3] J. H. Hu, J. B. Li, J. Qi and You Sun, New J. Chem.39 (2015) 4041–4046.

[4] Q. Zhang, J. Zhang, H. Zuo, C. Wang, and Y. Shen, Tetrahedron 72 (2016) 1244–1248.

[5] P. Zhang, B. B. Shi, X. M. You, Y. M. Zhang, Q. Lin, H. Yao, T. B. Wei, Tetrahedron 70 (2014) 1889–1894.