Supporting Information for

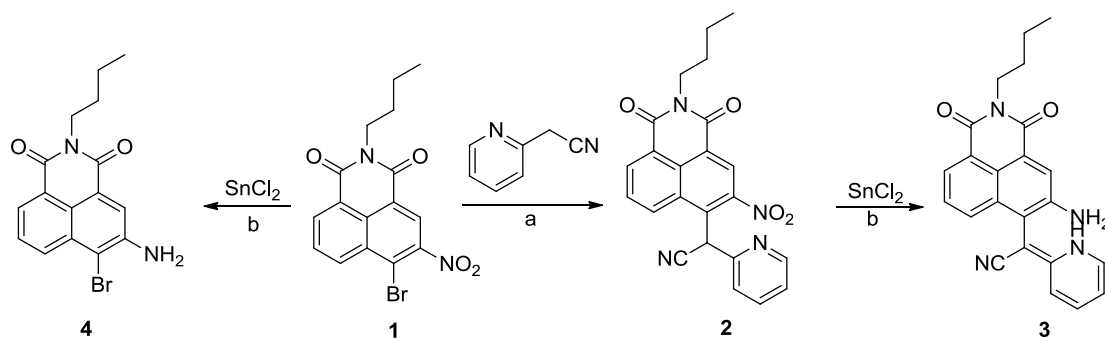**Reversible and selective chemochemosensor based on intramolecular NH⋯NH$_2$ hydrogen bonding for cyanide and pH detection**

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Scheme S1. Synthesis of chemosensor **3** and its cartoon-type representation; Reagents and conditions: (a) NaH, N_2, THF, 2-(cyanomethyl)pyridine, r.t., 70% yield; (b) $SnCl_2$, r.t., 79% yield.

Materials and instruments

Unless otherwise noted, solvents and reagents were analytical grade and used without further purification. THF were distilled from Na prior to use. UV-visible absorption spectra were obtained on a SHIMADZU UV-1800 spectrophotometer. Fluorescence emission spectra were obtained on a Hitach F-4600 Fluorescence spectrophotometer. IR were recorded on NICOLET 6700 FT-IR. NMR spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for ^{1}H) or Bruker AM-400 spectrometer (100 MHz for ^{13}C NMR), and chemical shifts were reported in parts per million (ppm, δ) downfield from internal standard Me_4Si (TMS). Multiplicities of signals are described as follows: s --- singlet, br. s --- broad singlet, d --- doublet, t --- triplet, m --- multiplet. Coupling constants were reported in hertz (Hz). HRMS were recorded on solanX 70 FT-MS spectrometer with methanol and water (v/v = 1:1) as solvent.

***N*-butyl-4-bromo-3-nitro-1,8-naphthalimide (1)** was synthesized according to the literature reported procedure[1].

Synthesis of 2-(*N*-butyl-3-nitro-1,8-naphthalimide)-2-(pyridin-2-yl)acetonitrile (2): To a solution of NaH (60% in oil) (1.60 g, 40 mmol) in 30 mL anhydrous THF was added 2-cyanomethylpyridine (0.70 g, 5.60 mmol) under N_2 at room temperature, after 30 min the mixture was then added **1** (1.50 g, 4 mmol). The reaction mixture was stirred at room temperature for another 2 h. After the reaction was completed, the reaction mixture was quenched with a mixture of saturated ammonium chloride solution and hydrochloric acid (2N). The anhydrous solution was extracted with EA (25 mL × 3). The organic layer was dried with anhydrous sodium sulfate, concentrated and purified by column chromatography eluting with PE/EA (5:1) to give **2** (1.12 g, 70%) as a black solid with a mp of 137−138 ℃. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.94 (s, 1H), 8.65 (d, *J* = 7.5 Hz, 1H), 8.58 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 4.0 Hz, 1H), 7.78 (dd, J_1 = 7.0, J_2 = 9.0 Hz 1H), 7.70 (dd, *J* = 8.0, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.23-7.20 (m, 1H), 6.60 (s, 1H), 4.12 (t, *J* = 7.5 Hz, 2H), 1.67-1.61 (m, 2H), 1.38-1.34 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.7, 19.9, 29.8, 94.8, 98.9, 109.6, 112.7, 116.0, 120.5, 122.0, 123.5, 127.1, 128.7, 136.6, 136.8, 147.2, 149.2, 150.3, 154.2, 154.7, 163.6, 163.9; IR (KBr) 3080, 2959, 2873, 2157, 1712, 1680, 1597, 1586, 1466, 1435, 1435, 1355, 1277, 1233, 1112, 995, 803, 790, 761 cm^{-1}; HRMS-ESI (m/z): [M+H]$^+$ (calcd for $C_{23}H_{19}N_4O_4$) 415.14063; Found 415.14214.

Synthesis of (*E*)-2-(5-amino-2-butyl-1, 3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-6-yl)-2-(pyridin-2(1H)-ylidene)acetonitrile (3):

2 (0.15 g, 0.36 mmol) and $SnCl_2$ (0.60 g, 3.20 mmol) were dissolved in (20 mL) EA, the reaction mixture was stirred under N_2 at room temperature for 1 h. After the reaction was completed, the solution was filtered and saturated Na_2CO_3 (aq) (150 mL) was then added. The resulting suspension was then extracted with ethyl acetate, washed with brine, and dried over anhydrous

sodium sulfate, concentrated and purified by column chromatography eluting with PE/EA (2:1) to give **3** (0.11 g, 79%) as a red solid with a mp of 218−220 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.17 (s, 1H), 8.70 (d, J = 4.5 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.31 (s, 1H), 8.31 (d, J = 6.5 Hz, 1H), 7.87 (dd, J_1 =8.0, J_2 = 7.5 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.52 (dd, J_1 =J_2 = 8.0 Hz, 1H), 7.29 (dd, J_1 =5.5, J_2 = 6.5 Hz, 1H), 6.87 (s, 2H), 4.06 (t, J = 7.5 Hz, 2H), 1.66-1.60 (m, 2H), 1.40-1.35 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.6, 19.7, 29.5, 109.5, 113.6, 118.7, 121.7, 122.9, 125.6, 128.8, 129.3, 131.1, 132.7, 133.2, 136.6, 138.2, 147.4, 149.3, 153.1, 153.2, 162.0, 162.7; IR (KBr) 3445, 2957, 2926, 2856, 2375, 1681, 1652, 1500, 1463, 1427, 1384, 1233, 1166, 1092, 810, 776, 607 cm^{-1}; HRMS-ESI (m/z): [M+H]$^+$ (calcd for $C_{23}H_{21}N_4O_2$) 385.16645; Found 385.16645.

Synthesis of N-butyl-4-bromo-3-amino-1,8-naphthalimide (4): **2** (0.15 g, 0.40 mmol) were dissolved in a mixture of ethyl acetate (20 mL) and THF (10 mL), warmed to 70 ℃ and under N_2. $SnCl_2$ (0.60 g, 3.20 mmol) was then added and the reaction mixture was stirred for 2 hours at 70 ℃. After cooling, the solution was filtered and saturated Na_2CO_3 (aq) (150 mL) was then added. The resulting suspension was then extracted with ethyl acetate, washed with brine, and dried over anhydrous sodium sulfate, concentrated and purified by column chromatography eluting with PE/EA (15:1) to give **4** (0.10 g, 72%) as a yellow solid with a mp of 192−193 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 7.0 Hz, 1H), 8.13 (s, 1H), 8.79 (dd, J_1 = 8.0, J_2 = 7.5 Hz, 1H), 6.34 (s, 2H), 4.01 (t, J = 7.5 Hz, 2H), 1.63-1.57 (m, 2H), 1.39-1.31 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.7, 19.8, 29.6, 106.6, 121.1, 121.7, 121.8, 122.1, 125.7, 128.2, 129.7, 131.4, 145.2, 162.9, 163.2; IR (KBr) 3323, 2961, 1694, 1650, 1618, 1420, 1339, 1285, 1231, 1078, 778, 749; HRMS-ESI (m/z): [M+H]$^+$ (calcd for $C_{16}H_{16}BrN_2O_2$) 347.03952; Found 347.03742.

Typical procedure of NMR titration of 3 with cyanide ions: ^{1}H NMR titrations (500 MHz) were performed with a DMSO-d_6 solution of **3** (0.04 mol L^{-1}, 0.5mL) and a DMSO-d_6 solution of TBACN (1.5 mol L^{-1}). The TBACN solution was introduced in portions (7, 14, 28, 42, 70 and 126 μL; 14 μL corresponds to 1.0 equiv) and, after every addition, the solution was maintained for 1 min at 298K.

References

[1] a) J. Yeow, A. Kaur, M. D. Anscomb, E. J. New, *Chem. Commun*. **2014**, *50*, 8181−8184; b) X. Zeng, X. Zhang, B. Zhu, H. Jia, Y. Li, *Dyes and Pigments* **2012,** *94,* 10−15.

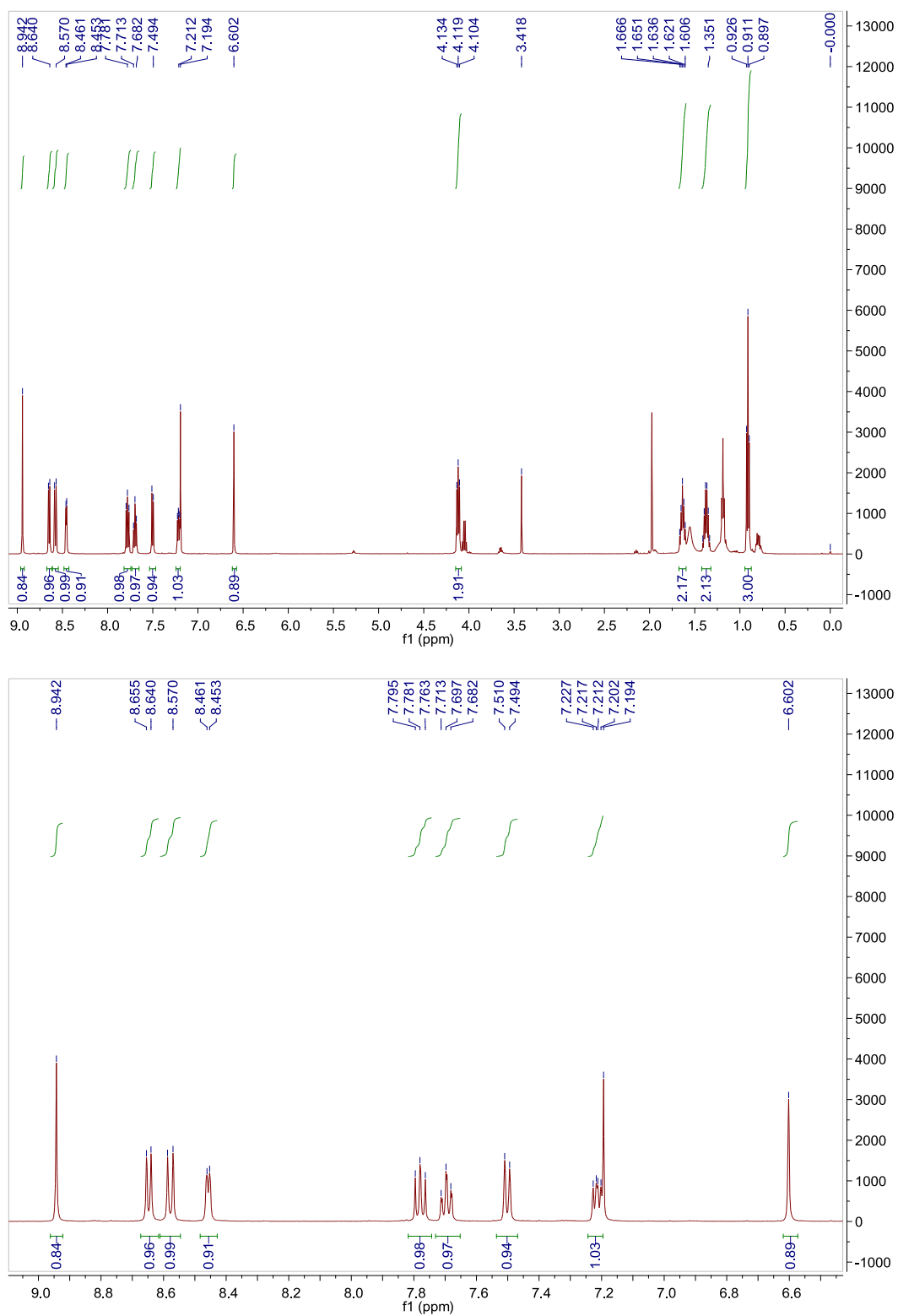## 1. ^{1}H, ^{13}C NMR, IR and HRMS-ESI copies of the compound 2.

Fig. S1. ^{1}H NMR (CDCl$_3$, 500 MHz) spectra of compound **2.**

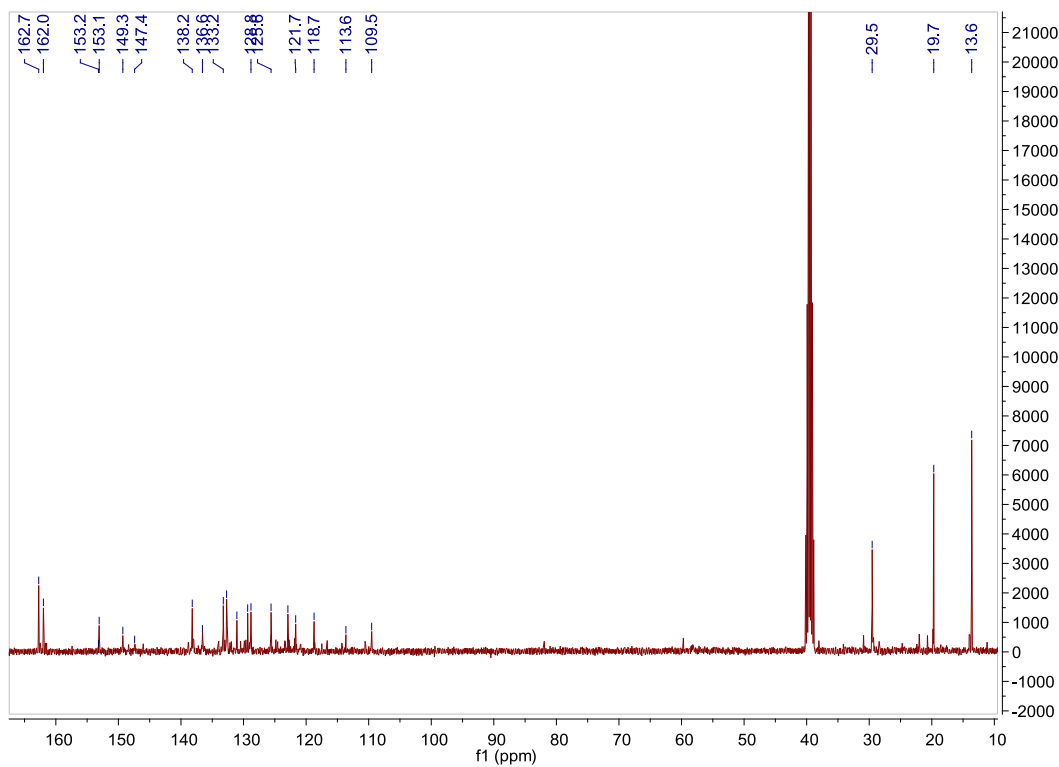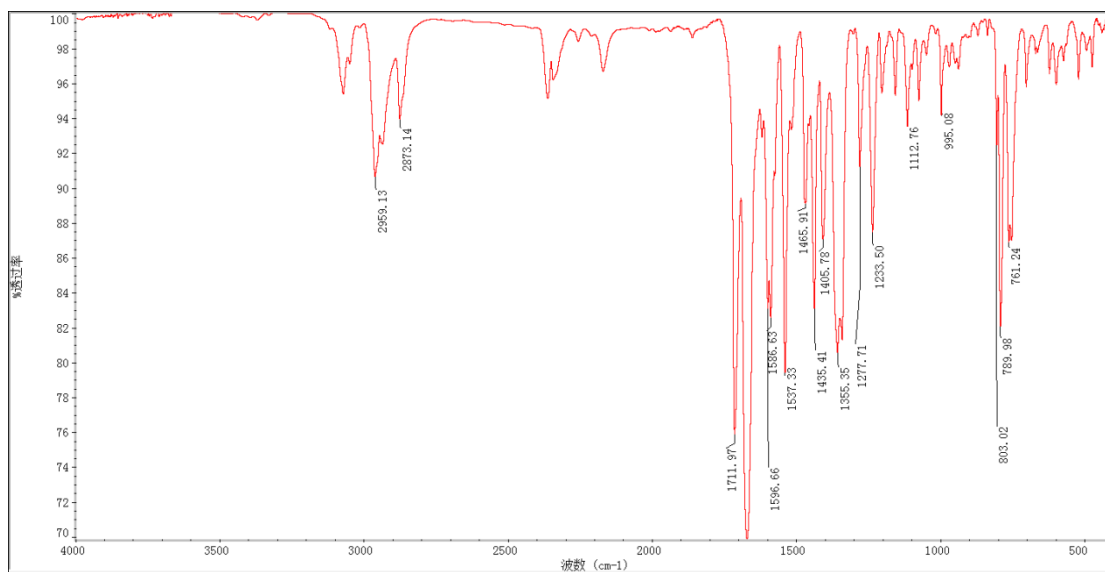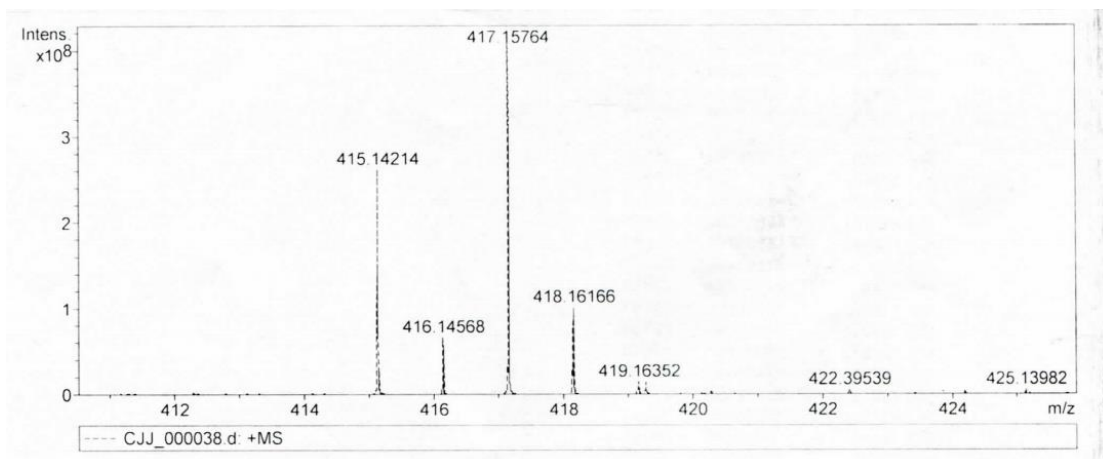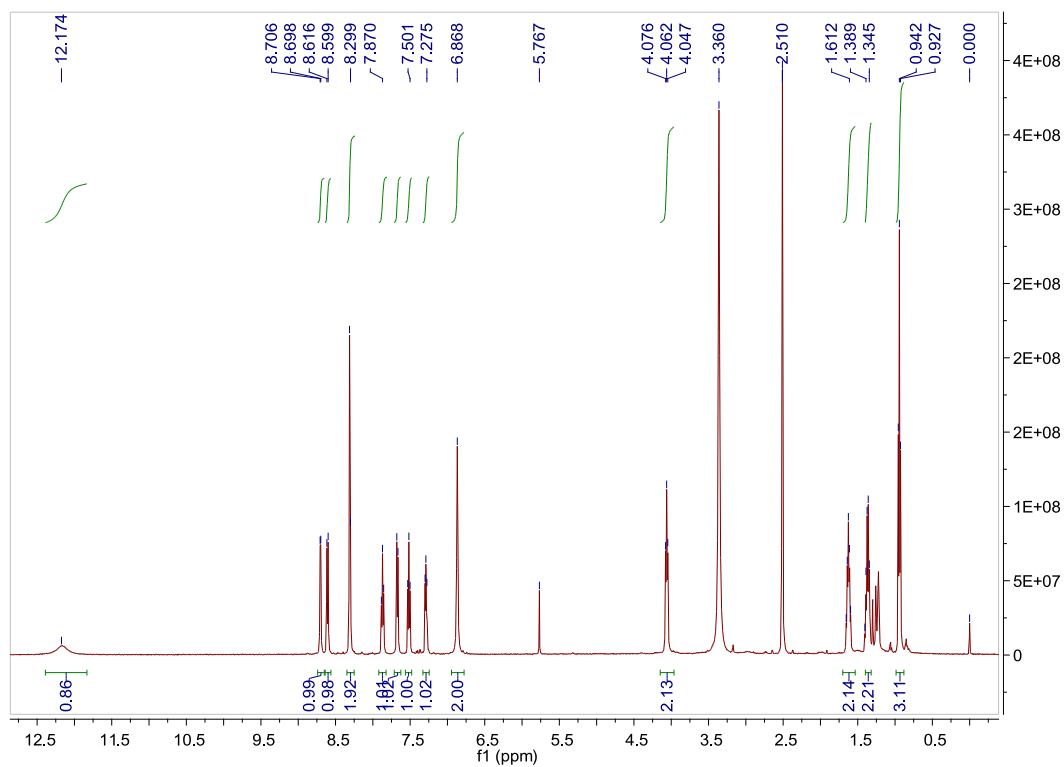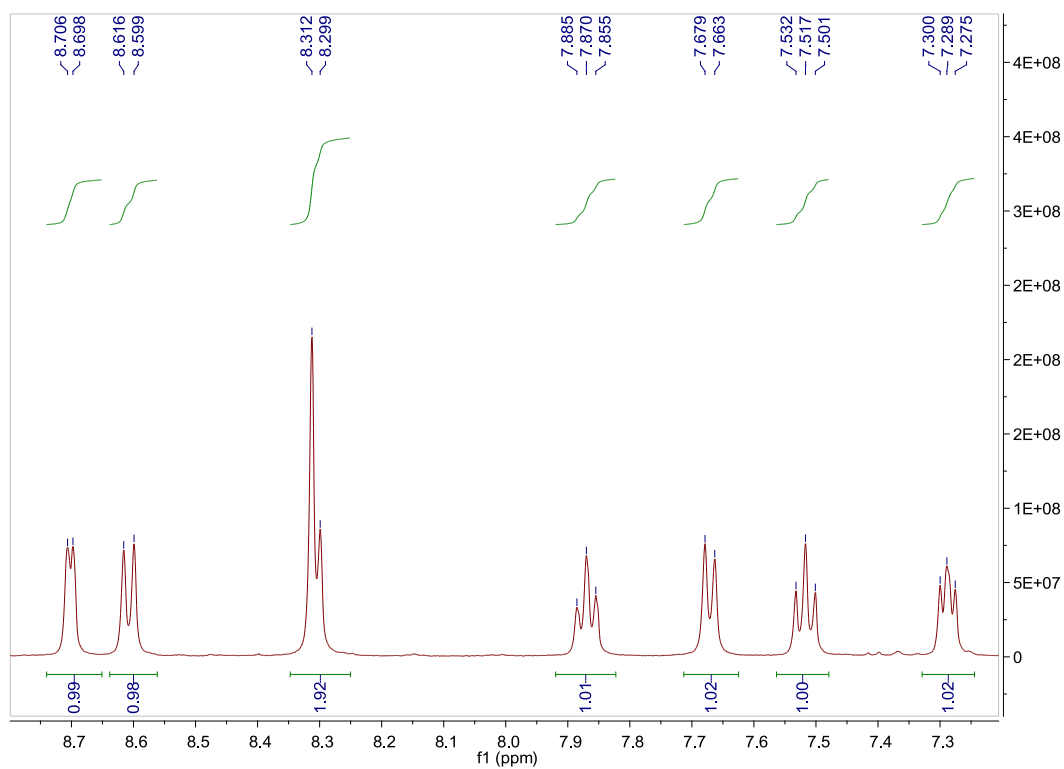**Fig. S2.** ^{13}C NMR (DMSO-d_6, 100 MHz) spectra of compound **2.**
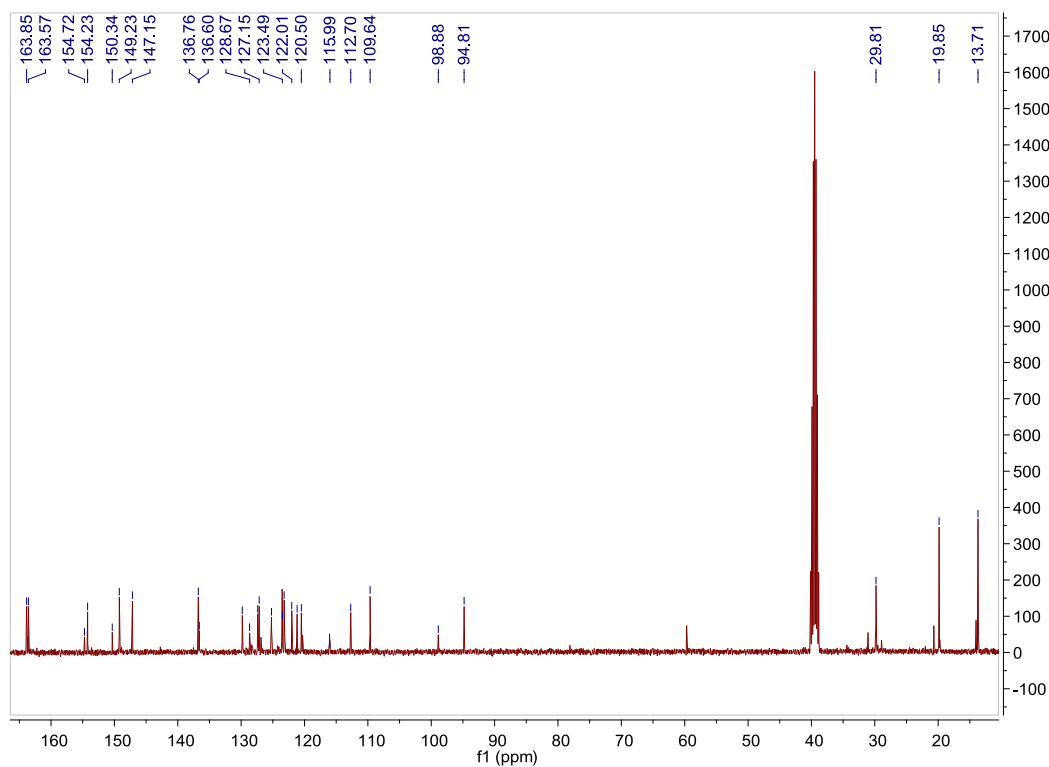

Fig. S3. IR spectra of compound **2.**

Fig. S4. ESI mass spectra of compound **2**.

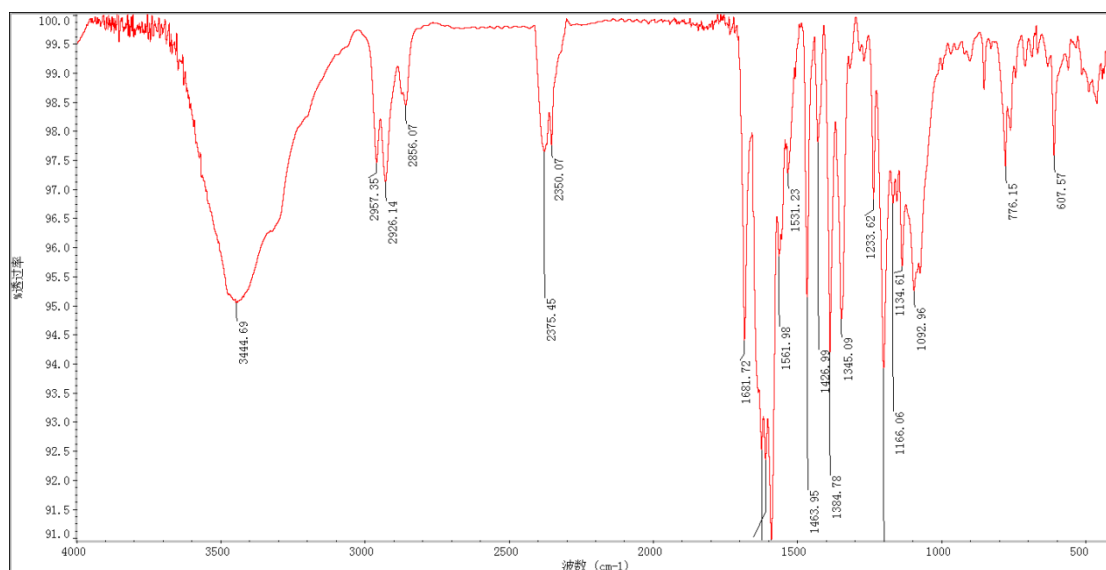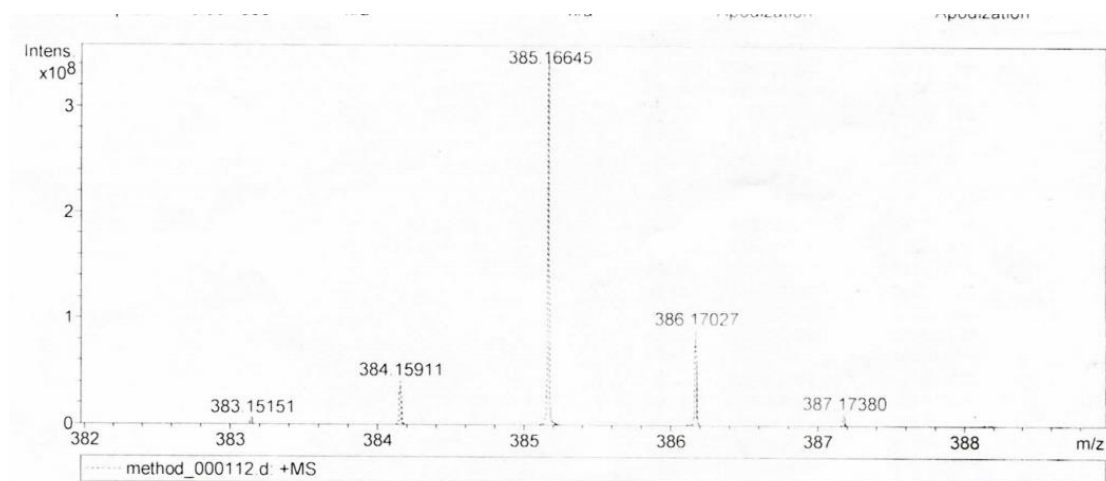## 2. ^{1}H, ^{13}C NMR, IR and HRMS-ESI copies of the compound 3.

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Fig. S5. ^{1}H NMR (DMSO-d_6, 500 MHz) spectra of compound **3.**

Fig. S6. ^{13}C NMR (DMSO-d_6, 100 MHz) spectra of compound **3.**

Fig. S7. IR spectra of compound **3.**

Fig. S8. ESI mass spectra of compound **3**.

3. ^{1}H, ^{13}C NMR, IR and HRMS-ESI copies of the compound 4.

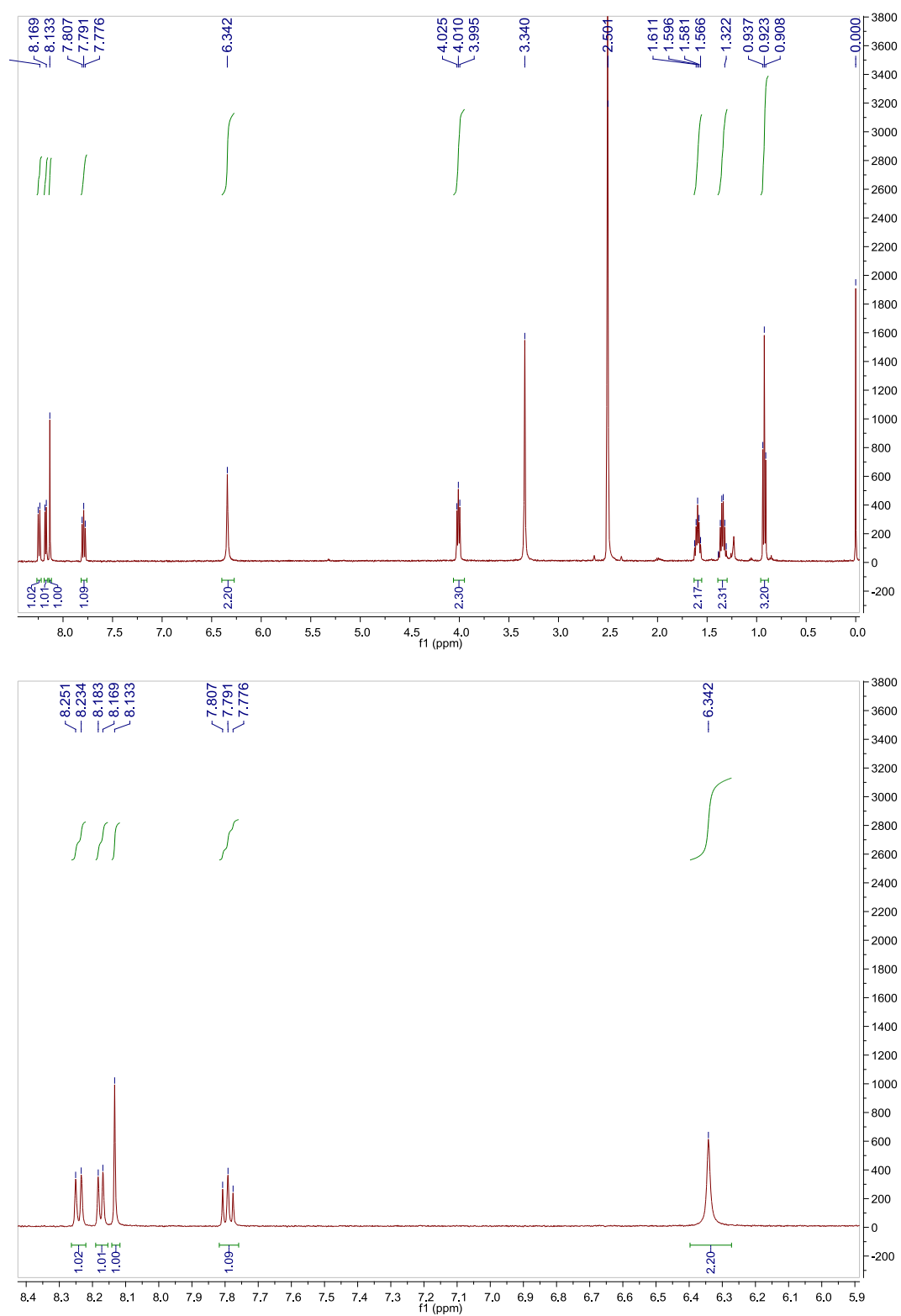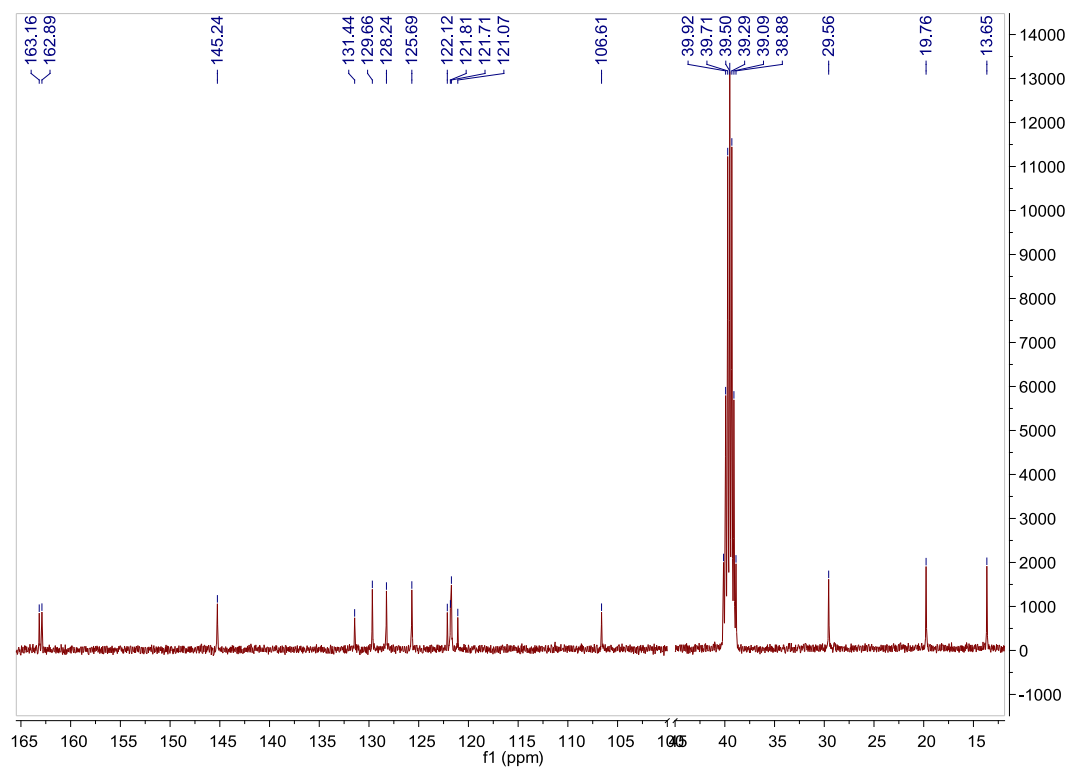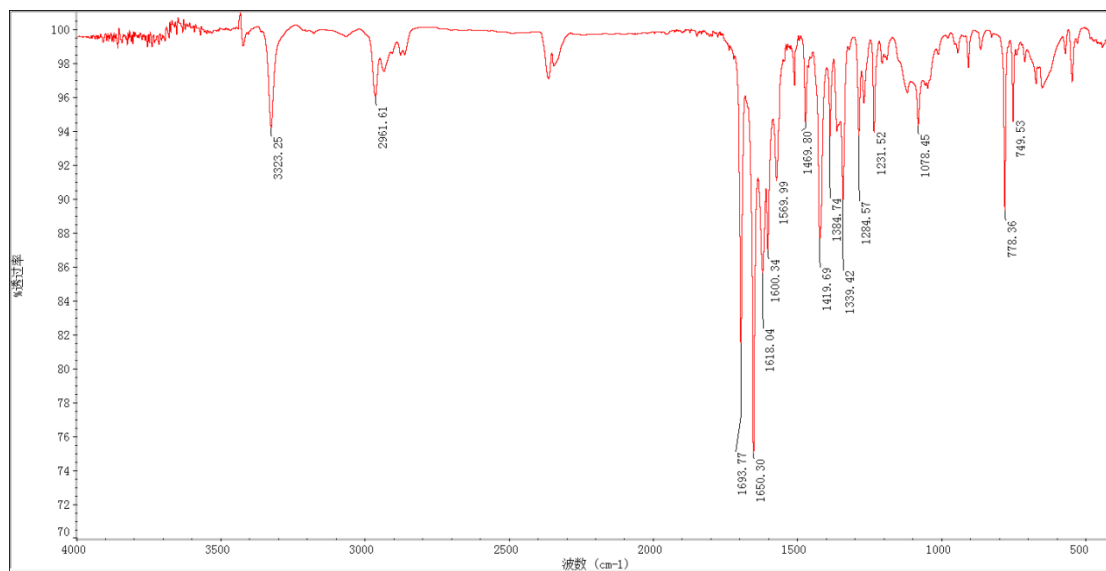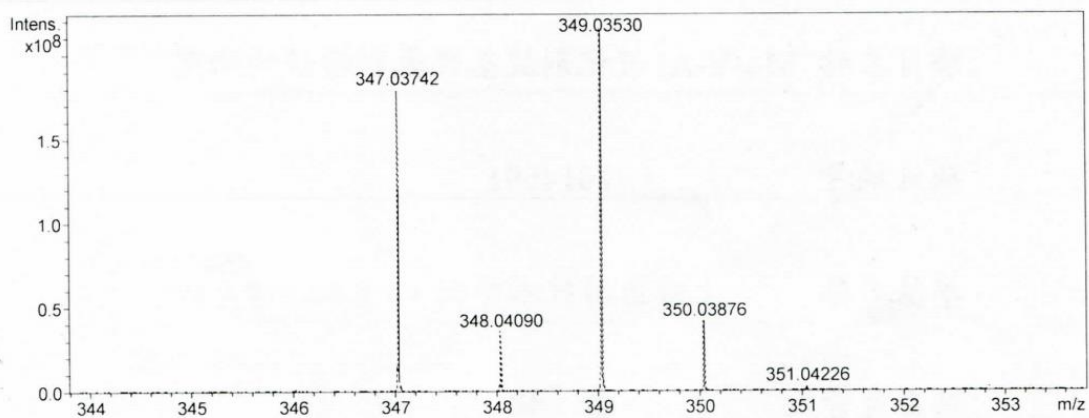**Fig. S9.** ^{1}H NMR (DMSO-d_6, 500 MHz) spectra of compound **4.**

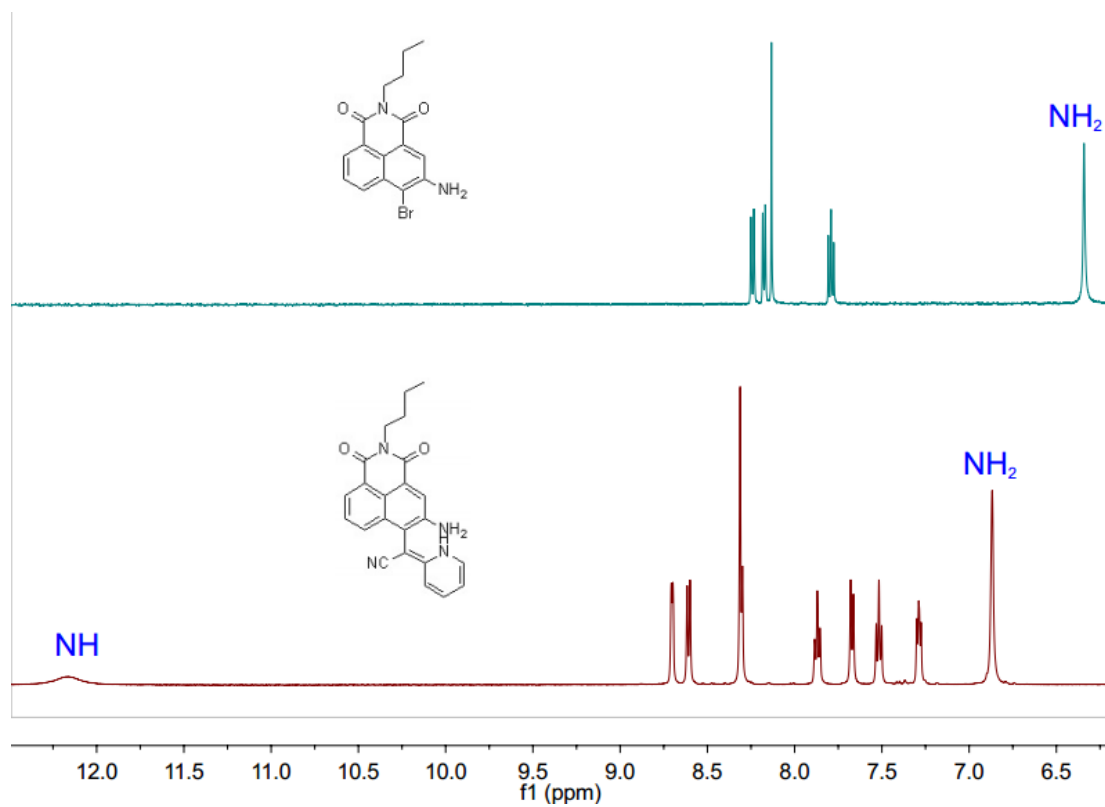**Fig. S10.** ^{13}C NMR (DMSO-d_6, 100 MHz) spectra of compound **4.**

Fig. S11. IR spectra of compound **4.**

Fig. S12. ESI mass spectra of compound **4**.

4. The ^{1}H NMR spectra of compound 3 and 4

Fig. S13. ^{1}H NMR (DMSO-d_6, 500 MHz) spectra of compound **3** and **4.**

5. The I_{max} of chemosensor **3** in various polar solvents
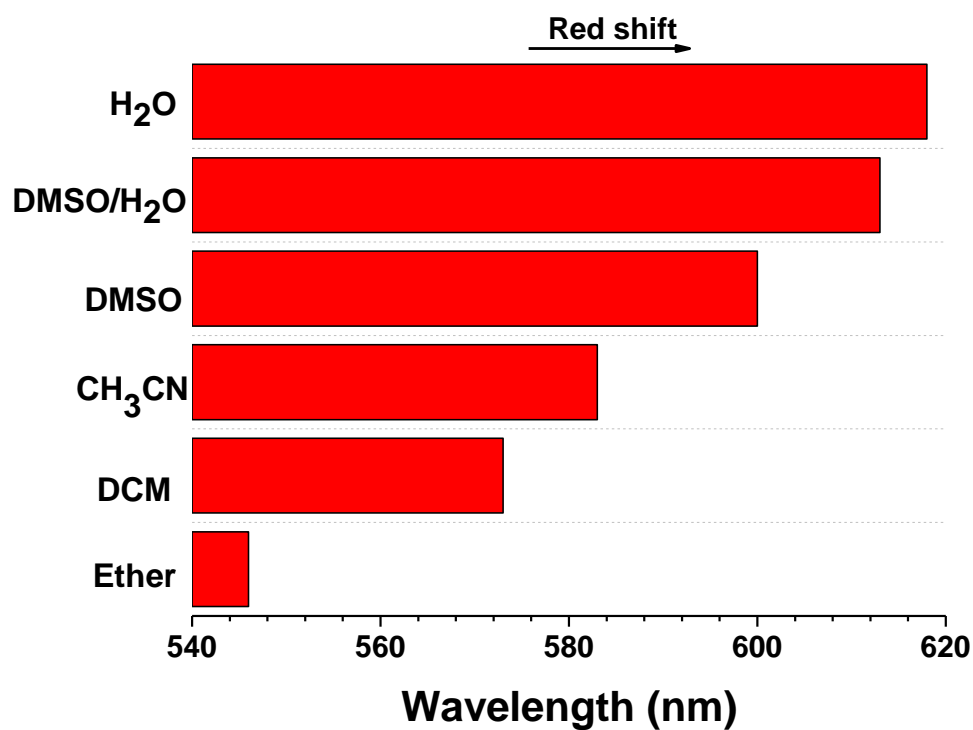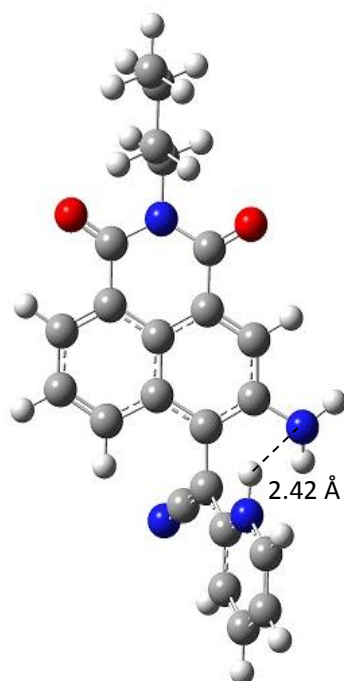

Fig. S14. The fluorescent maximum emission wavelength of chemosensor **3** in diethyl ether, dichloromethane, acetonitrile, dimethyl sulfoxide, dimethyl sulfoxide/water (1:1, v/v), and water. Excitation at 480 nm.

6. DFT calculation for chemosensor **3**

Fig. S15. The optimized structure of chemosensor **3** at the level of M06-2X functional with 6-31+G (d, p) basis set.

7. UV-visible spectra of chemosensor **3**
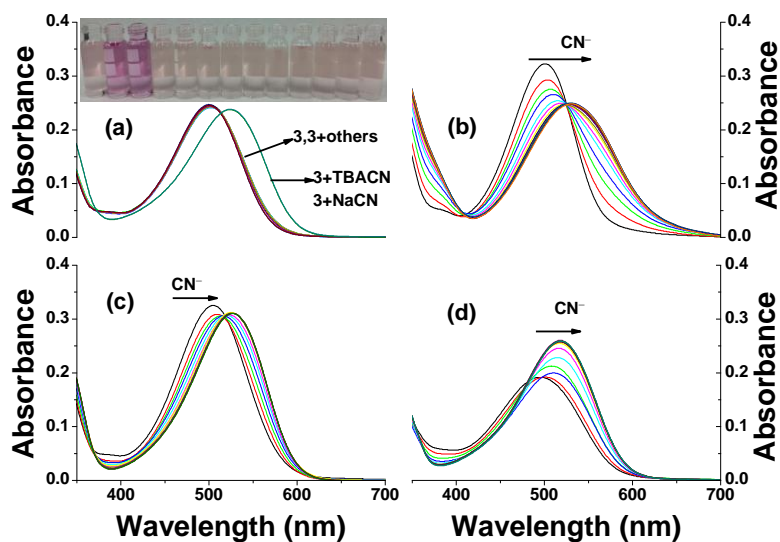
Fig. S16. UV−visible spectral changes of 20 μmol L^{-1} solution of **3** (a) in DMSO/H$_2$O (1:1) with various anions (4.0 equiv) (Inset: from left to right: **3** only, NaCN, TBACN, F$^-$, AcO$^-$, H$_2$PO$_4^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, BF$_4^-$, ClO$_4^-$); (b) in DMSO (1.5 equiv); (c) in DMSO/H$_2$O (1:1) (4.0 equiv); and (d) in H$_2$O (10.0 equiv) upon titration with TBACN.

8. The UV detection limit of the chemosensor **3** with CN⁻ in DMSO
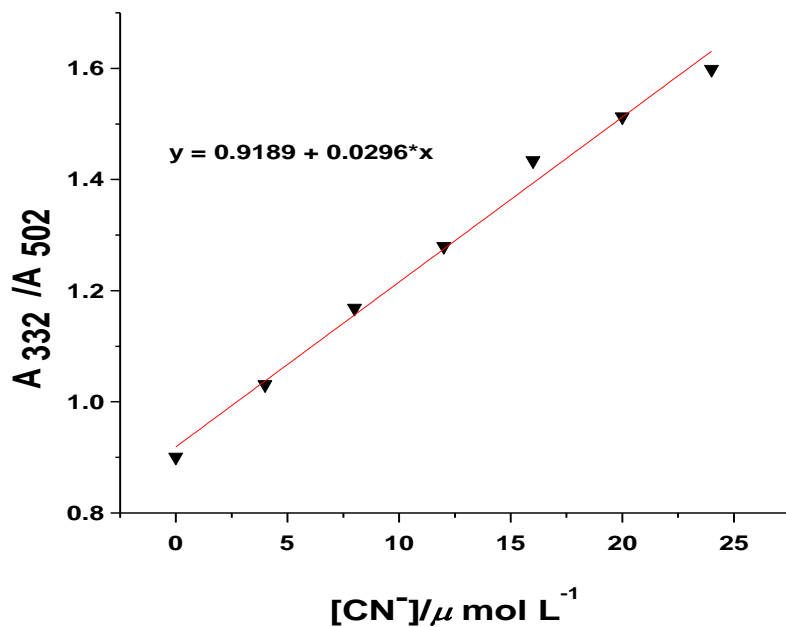
Fig. S17. Absorbance intensity ratio (A_{332}/A_{502}) of chemosensor **3** (20 μmol L^{-1}) as a function of CN⁻ concentration from 0-24 μmol L^{-1} (0–1.2 equiv) in DMSO.
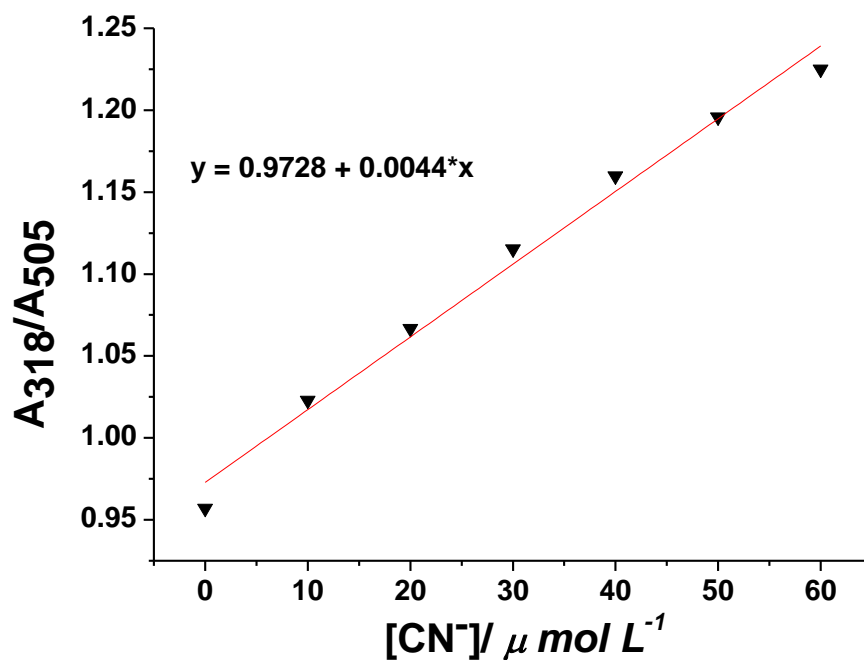
SD	N
0.02548	7

The result of the analysis as follows:

Linear Equation: y = 0.9189 + 0.0296 * x, R^2 = 0.9902

S = 2.96 * 10^4, K = 3, δ = 0.02548

LOD = K * δ/S = 2.58 μmol L^{-1}

9. The UV detection limit of the chemosensor **3** with CN^- in $DMSO/H_2O$

Fig. S18. Absorbance intensity ratio (A_{318}/A_{505}) of chemosensor **3** (20 μmol L^{-1}) as a function of CN^- concentration from 0-60 μmol L^{-1} (0-3.0 equiv) in $DMSO/H_2O$ (1:1, v/v).

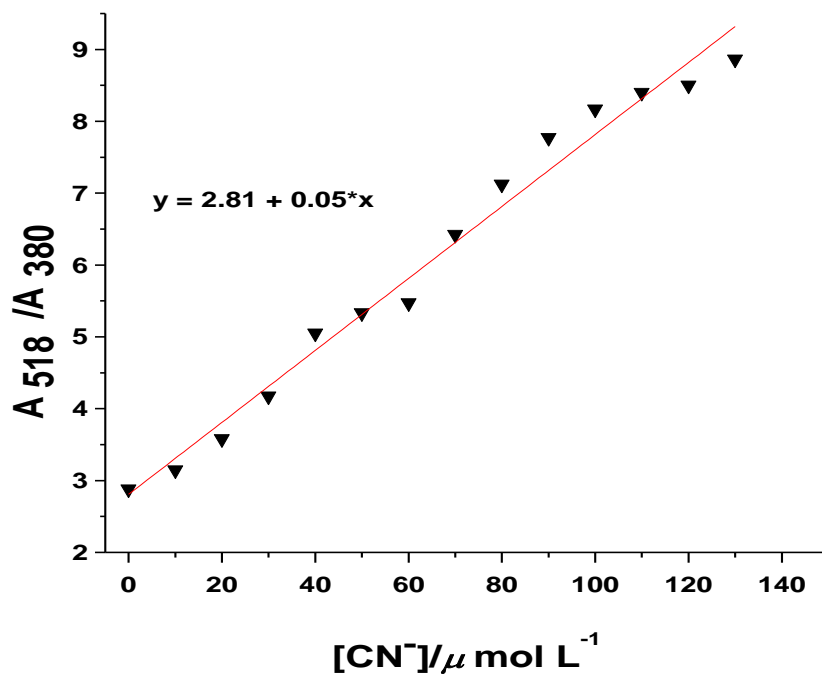| SD	N
0.0117	7

The result of the analysis as follows:

Linear Equation: $y = 0.9728 + 0.0044 * x$, $R^2 = 0.98531$

$S = 4.4 * 10^3$, $K = 3$, $\delta = 0.0117$

$LOD = K * \delta/S = 7.98$ μmol L^{-1}

10. The UV detection limit of the chemosensor **3** with CN$^-$ in H$_2$O

Fig. S19. Absorbance intensity ratio (A$_{518}$/A$_{380}$) of chemosensor **3** (20 μmol L^{-1}) as a function of CN$^-$ concentration from 0-130 μmol L^{-1} (0–6.5 equiv).

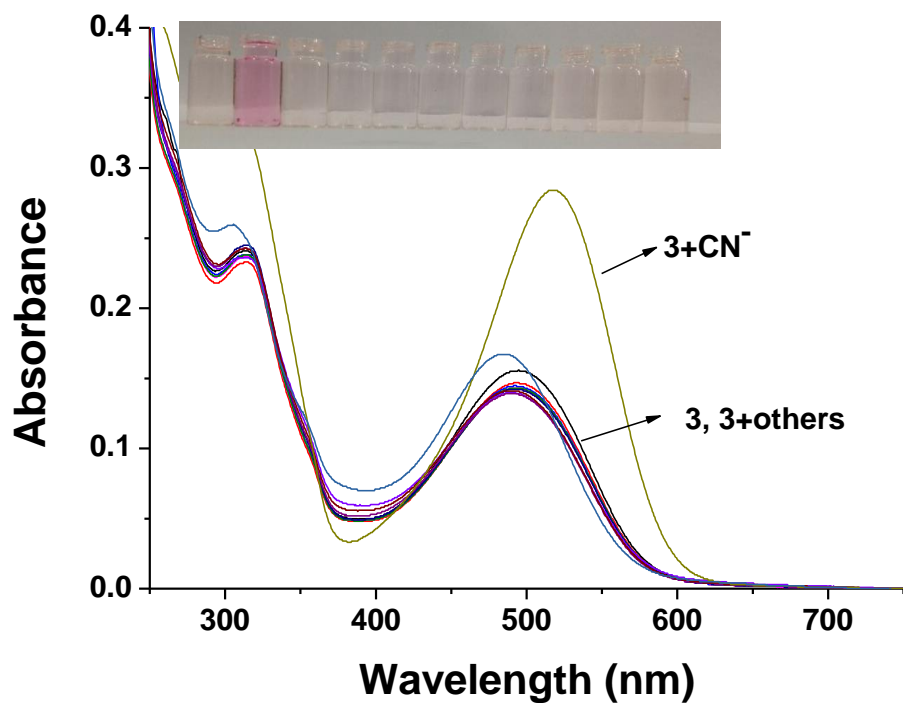| SD	N
0.29351	14

The result of the analysis as follows:

Linear Equation: y = 2.81 + 0.05 * x, R^2 = 0.98073

S = 5 * 10^4, K = 3, δ = 0.29351

LOD = K * δ/S = 17.61 μmol L^{-1}

11. UV-visible spectra of chemosensor **3** in the presence of different anions in H$_2$O.


Fig. S20. UV-visible spectra of chemosensor **3** (20 μmol L^{-1}) in the presence of different anions (ca. 10.0 equiv) in H$_2$O; Color change of chemosensor **3** with different anions (from left to right: **3** only, CN$^-$, F$^-$, AcO$^-$, H$_2$PO$_4^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, BF$_4^-$, ClO$_4^-$).

12. Interference experiments of chemosensor **3** toward cyanide in H$_2$O.
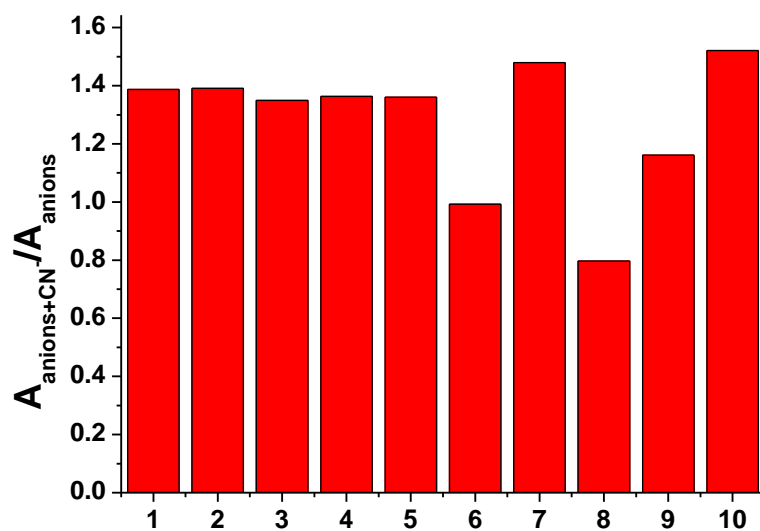
Fig. S21. Absorbance intensity ratio of chemosensor **3** toward cyanide and other anions (10.0 equiv, from left to right: H$_2$PO$_4^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, HSO$_4^-$, BF$_4^-$, AcO$^-$, ClO$_4^-$, F$^-$) in H$_2$O.

13. The response time of chemosensor **3** to CN$^-$ in aqueous media
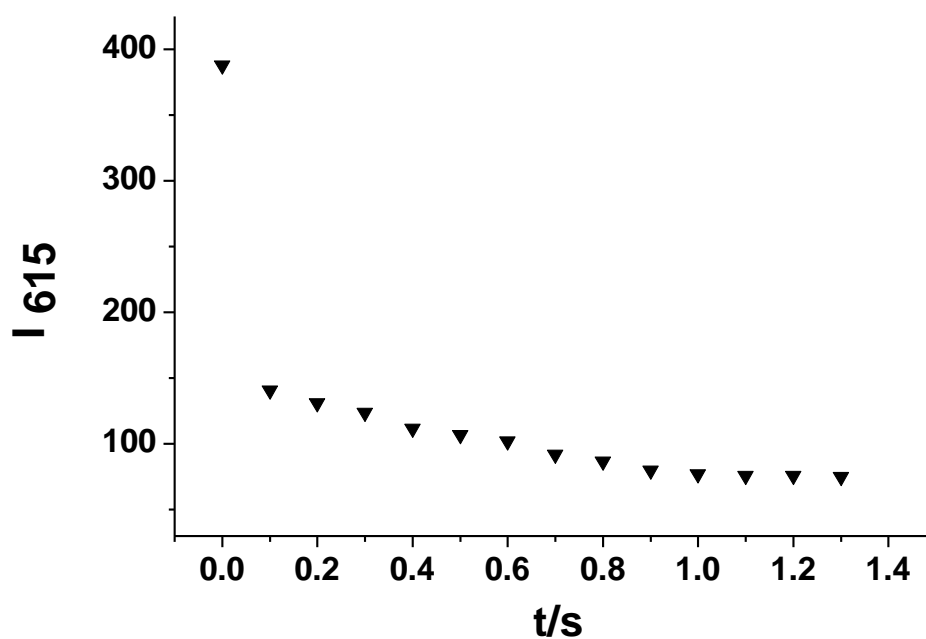
Fig. S22. The time-dependent behavior of chemosensor **3** in aqueous media upon addition of 6.0 equivalent cyanide ions.

14. Fluorescence spectra of chemosensor **3** in the presence of different cations in H_2O
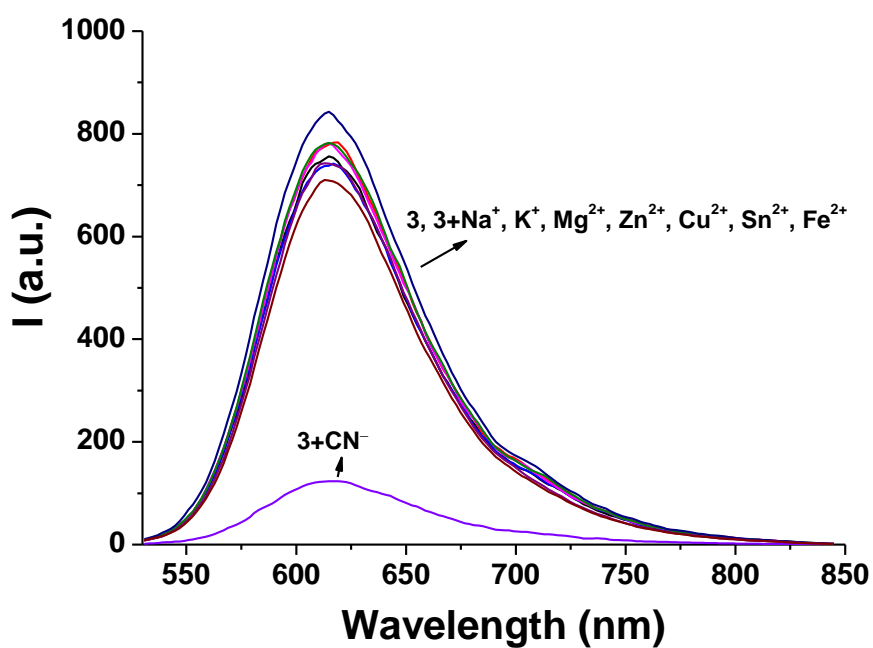
Fig. S23. Fluorescence intensity changes of **3** with other heavy metal ions. Fluorescence spectra (excitation at 515 nm) of **3** (20 μmol L^{-1}) with 6.0 equivalents of various metal ions (NaCl, KCl, KI, $CuSO_4\cdot5H_2O$, $ZnCl_2$, $MgSO_4\cdot7H_2O$, $FeSO_4\cdot7H_2O$, $SnCl_2$, TBACN) were recorded in $DMSO/H_2O$ (1:1 *v/v*).

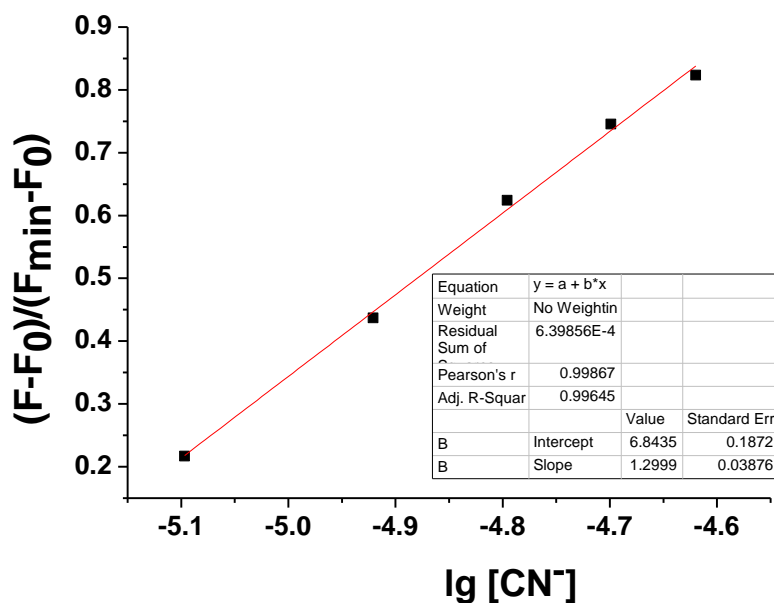15. Linear fluorescence response of chemosensor **3** to CN$^-$ in DMSO/H$_2$O
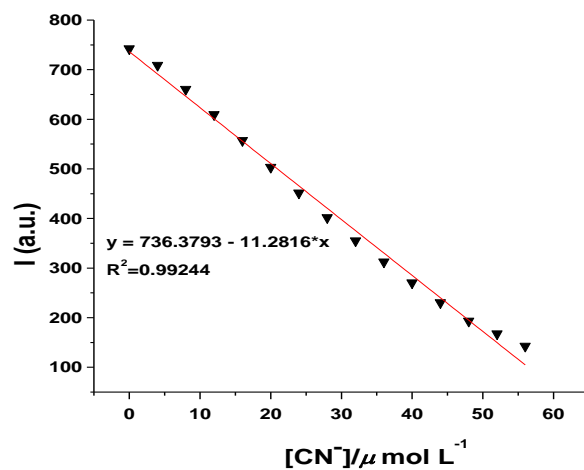
Fig. S24. Linear fluorescence response of chemosensor **3** to CN$^-$ concentration ranging from 0 to 56 μmol L^{-1} (0-2.8 equiv) in DMSO/H$_2$O (1:1, *v/v*).

16. The fluorescence detection limit of the chemosensor **3** with CN$^-$ in DMSO.

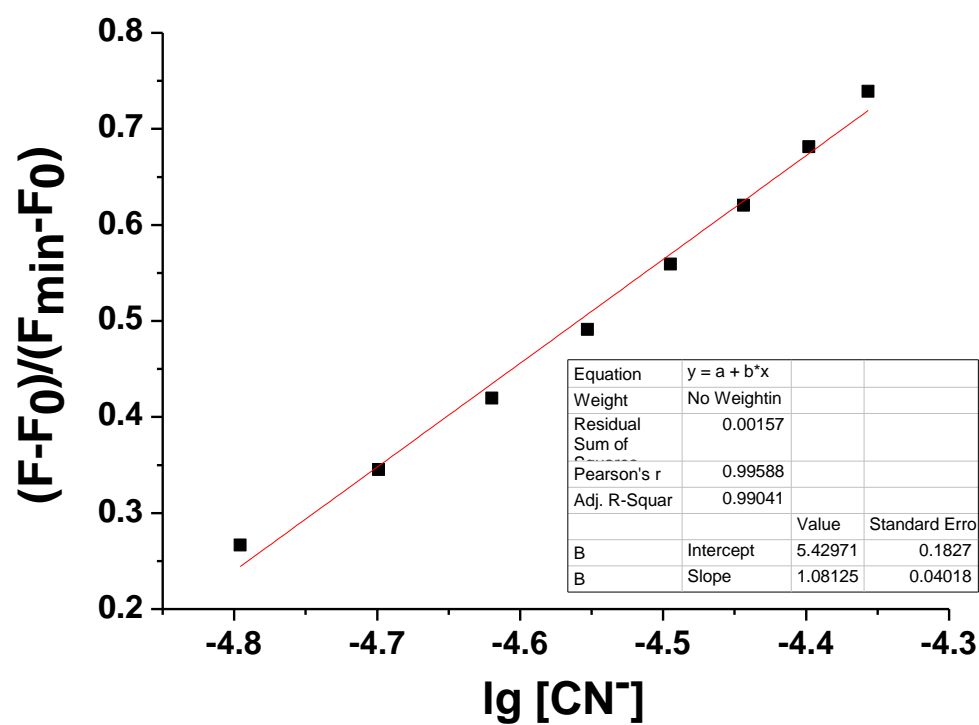| Equation	y = a + b*x		
Weight	No Weightin		
Residual Sum of	6.39856E-4		
Pearson's r	0.99867		
Adj. R-Squar	0.99645		
		Value	Standard Err
B	Intercept	6.8435	0.1872
B	Slope	1.2999	0.03876

Fig. S25. Response of fluorescence intensity to changing CN$^-$ concentrations in DMSO. ([**3**] = 20 μmol L^{-1}, [CN$^-$] = 5000 μmol L^{-1}, λ_{ex} = 515 nm, λ_{em} = 520 nm).

The result of the analysis as follows:

Linear Equation: y = 6.8435 + 1.2999 * x, R^2 = 0.99645

LOD = K * δ/S = 0.034 μmol L^{-1}

17. The fluorescence detection limit of the chemosensor **3** with CN^- in DMSO/H_2O.

Fig. S26. Response of fluorescence intensity to changing CN^- concentrations in DMSO/H_2O (1:1, *v/v*). ([**3**] = 20 μmol L^{-1}, [CN^-] = 5000 μmol L^{-1}, λ_{ex} = 515 nm, λ_{em} = 525 nm).
The result of the analysis as follows:
Linear Equation: y = 5.42971 + 1.08125 * x, R^2 = 0.99041
LOD = K * δ/S = 0.045 μmol L^{-1}

18. The fluorescence detection limit of the chemosensor **3** with CN^- in H_2O.

y = 5.75 + 1.162*x

Equation	y = a + b*x		
Weight	No Weightin		
Residual Sum of Squares	0.03235		
Pearson's r	0.985		
Adj. R-Squar	0.96596		
		Value	Standard Erro
B	Intercept	5.7545	0.33792
B	Slope	1.1618	0.07694
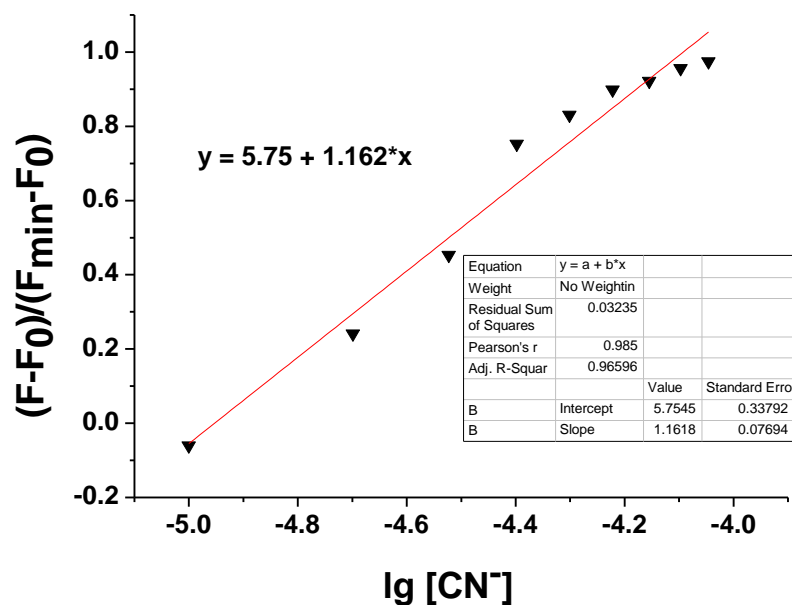
Fig. S27. Response of fluorescence intensity to changing CN^- concentrations in H_2O. ([**3**] = 20 μmol L^{-1}, [CN^-] = 5000 μmol L^{-1}, λ_{ex} = 480 nm, λ_{em} = 500 nm).
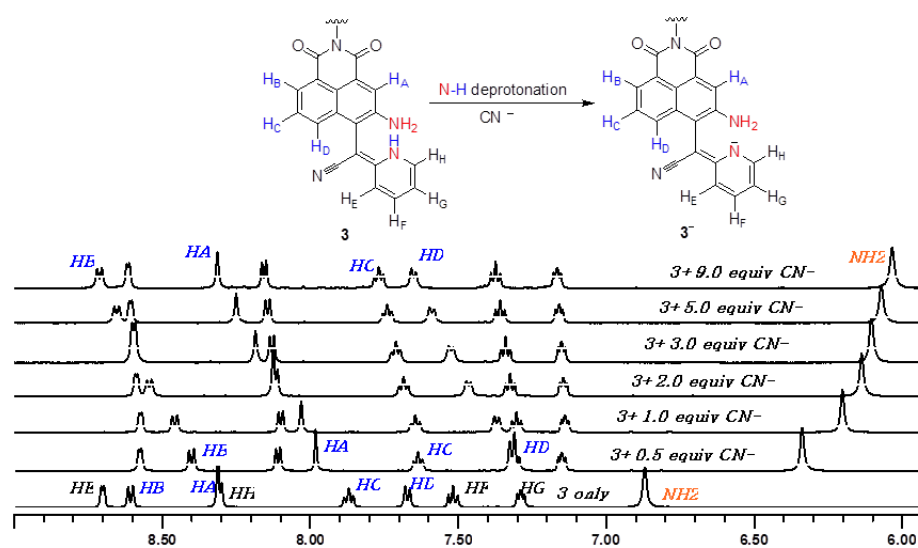
SD	N
0.06798	9

The result of the analysis as follows:

Linear Equation: y = 5.75 + 1.162 * x, R^2 = 0.96596
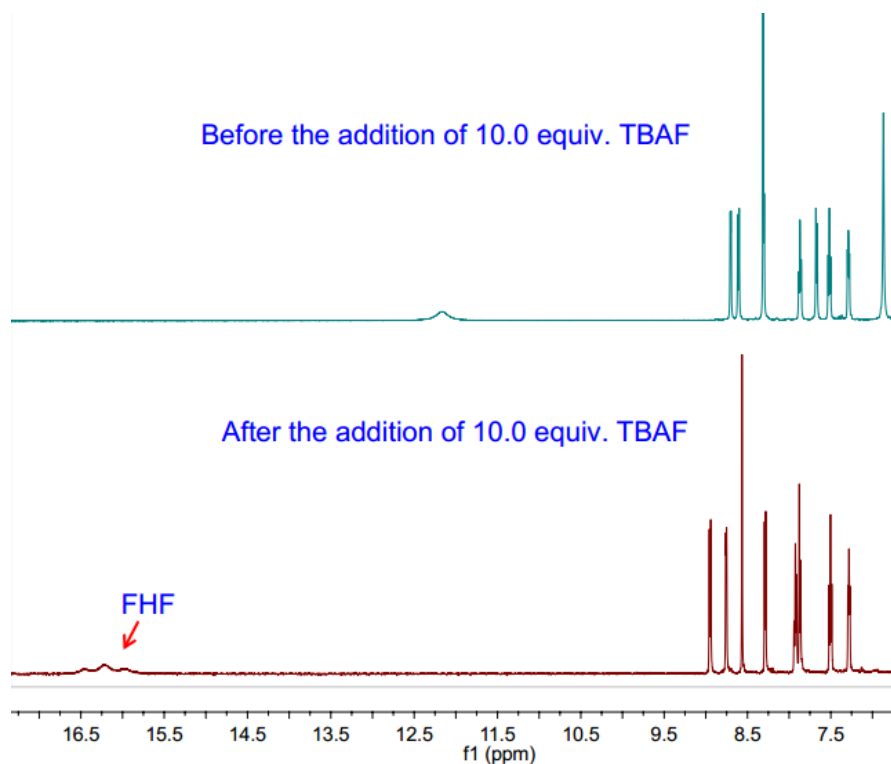
S = 1.16 * 10^6, K = 3, δ = 0.06798

LOD = K * δ/S = 0.18 μmol L^{-1}

19. The ^{1}H NMR spectra of the chemosensor **3** with CN$^-$ in DMSO-d_6.

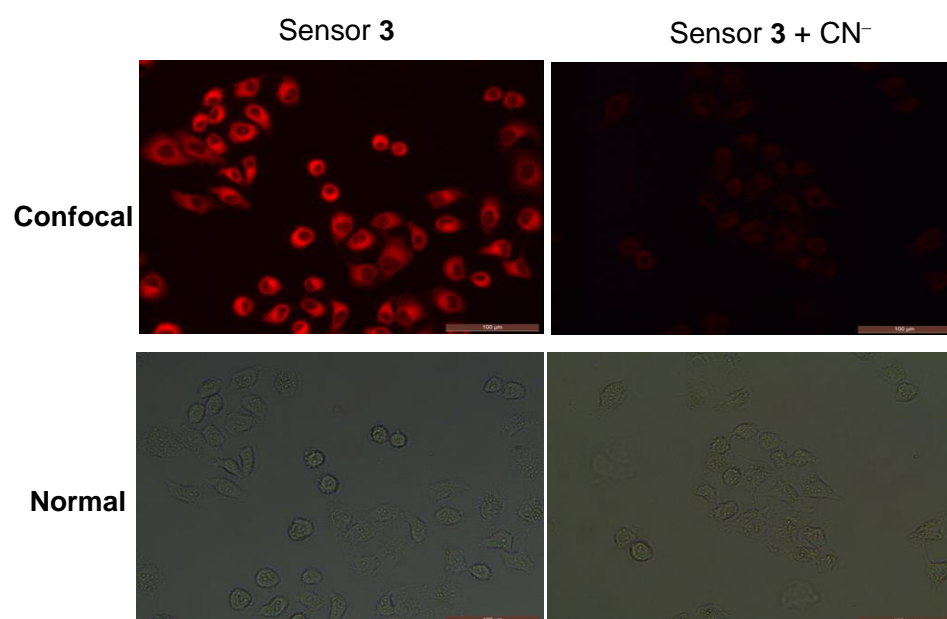**Fig. S28.** ^{1}H-NMR titration spectra of chemosensor **3** (4.0×10^{-2} mol L-1) in DMSO-d_6 upon addition of CN ions (as TBA salts in DMSO-d_6) at 298 K.

20. The ^{1}H NMR spectra of the chemosensor **3** with F$^-$ in DMSO-d_6.

Fig. S29. The ^{1}H NMR spectra of the chemosensor **3** (0.04 mol L^{-1}) followed by the addition of 10.0 equiv. TBAF in DMSO-d_6.

21. Confocal microscopic images of Hela cells.

Sensor **3**   Sensor **3** + CN⁻

Fig. S30. Confocal fluorescence microscope images of Hela cells in the presence of chemosensor **3** (10 μmol L^{-1}). The fluorescence images were recorded after 10 min of treatment of CN⁻ (10 μmol L^{-1}) at 37 ℃.

22. Fluorescence spectra of chemosensor **3** at different pH values in DMSO/H$_2$O.
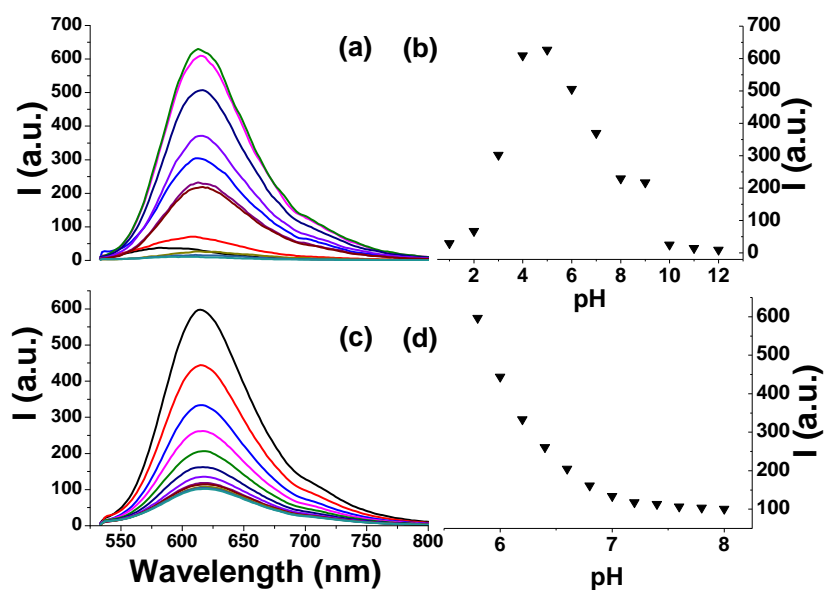

Fig. S31. Fluorescence spectra of chemosensor **3** at different pH values (515 nm excitation) in DMSO/H$_2$O (1:1) ranging from (a) 1−14, (c) 5.8−8.0. (b) Relationship between the pH and the fluorescence intensity at 615nm ranging from (b) 1−14, (d) 5.8−8.0.

23. Fluorescence spectra of chemosensor **3** at different pH values in H_2O.
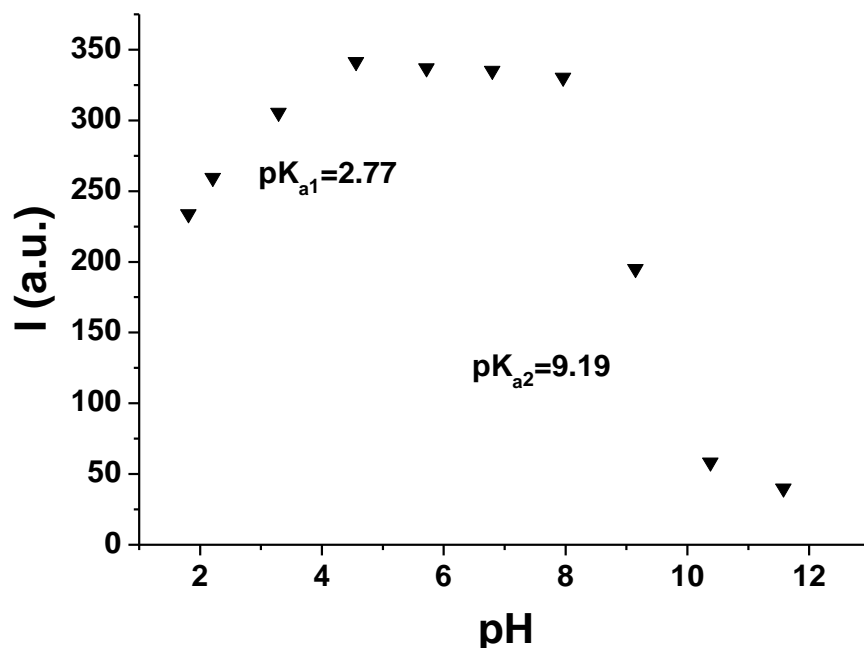
Typical procedure of the pK_a value obtained: $\log[(F_{max}-F)/(F-F_{min})]=pK_a-pH$, where F is the fluorescence emission intensity at 618 nm.
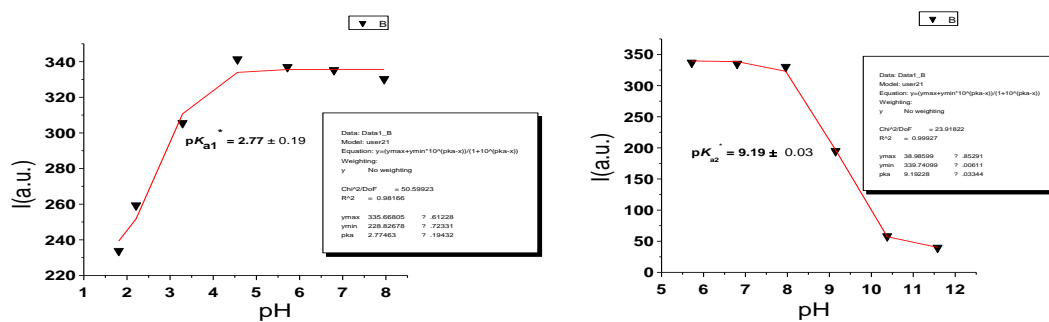
Fig. S32. Relative intensity of **3** at 618 nm in Britton-Robinson buffer solution as a function of pH, pK_{a1} and pK_{a2} values are calculated.