

Supporting information

Tuning Sensing Efficacy of Anthraimidazolidione-Based Charge Transfer Dyes: Nitro Group Positioning Impact

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EXPERIMENTAL SECTION:

General. All chemicals (reagents and chemicals) were bought from the best-known local chemical suppliers, such as Alfa Aldrich, TCI, Spectrochem, Alfa Acer, etc, and used without further purification. Solvents were distilled and dried before use. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX system and were reported in wave numbers (cm^{-1}). On the other hand, ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Advance DRX 400 spectrometer operating at 400 and 100 MHz for ^1H and ^{13}C NMR spectroscopy ($\text{DMSO}-d_6$), respectively. Chemical shifts were reported in ppm downfield from the internal standard, tetramethyl silane (TMS). Mass spectra were recorded on a Micromass Q-TOF Micro TM spectrometer.

Spectroscopic studies. The UV-vis spectroscopic studies were recorded on a Shimadzu model 2100 spectrometer. The slit-width for the experiment was kept at 5 nm. Sensing was carried out by adding required amounts of metal ions (tetrabutylammonium salts) to acetonitrile-water (8:2) mixture solution of **1**, **2**, **3** (1×10^{-5} M). For the CH_3CN -water mixture medium, the pH of the aqueous fraction was neutral.

Detection and Quantitation limits (LOD and LOQ) determination:

The detection limit was calculated based on the UV-VIS and fluorescence titration.

To determine the standard deviation the values from the titration curves were used. we calculated the value for the limit of detection by the following equation.

$$\text{Limit of Detection} = 3\sigma/k$$

$$\text{Limit of Quantitation} = 10\sigma/k$$

Where, σ is the standard deviation of blank measurements [also defined as signal-to-noise (S/N) ratio], k is the slope of intensity versus sample concentration.

Stoichiometry determination by Job plot.

The Job's plot is a method of continuous variation for determining the stoichiometry of interaction between the two species. The total molar concentration of the two binding species (here, **1** and CN^- ions) was kept constant (1×10^{-4} M) and the mole fraction was varied. Further, the change in absorbance was plotted against the mole fraction. The maxima or minima thus obtained gave the stoichiometry of interaction. In all cases, we have plotted $\Delta A * [\text{CN}^-]$ vs $[\text{1}] / \{[\text{CN}^-] + [\text{1}]\}$. Where, $\Delta A = A - A_0$, A = absorbance of probe molecule after addition of metal ions at specific wavelengths, and A_0 = absorbance of probe molecule without metal ions. $[\text{1}] / \{[\text{CN}^-] + [\text{1}]\}$ is the mole fraction of the probe molecule in the mixture.

Binding constant calculation.

For compound **1**, we followed the Benesi-Hildebrand equation for 1:1 stoichiometry. The changes in absorbance were recorded at λ_{max} (nm).

$$\frac{1}{A - A_0} = \frac{1}{K_a(A_{max} - A_0)[CN^-]} + \frac{1}{A_{max} - A_0}$$

where A and A_0 represent the absorbance of **1** in the presence and absence of CN^- , respectively, A_{max} is the maximum absorbance of **1** in the presence of an excess amount of CN^- and $[CN^-]$ is the concentration of CN^- ion added, and K_a is the binding constant. A plot of $x = 1/[CN^-]$ against $y = 1/A_{max} - A_0$ yielded a slope of $1/K (A_{max} - A_0)$ from where the binding constant was calculated.

Scanning Electron Microscopy:

A solution of **1** (concentration 10 μ M) in water was drop cast over double-sided tapes attached to the brass stubs and air-dried for 48 h. The samples were then coated with gold vapor and analysed on a Quanta 200 SEM operated at 15 kV.

¹H NMR Titration Studies. ¹H NMR titration studies of compound **1** (5 mM) were performed with perchlorate salts of Cu^{2+} (1.0 eq.) in DMSO- d_6 medium. The spectra were recorded using identical parameters.

Synthetic Scheme 1:

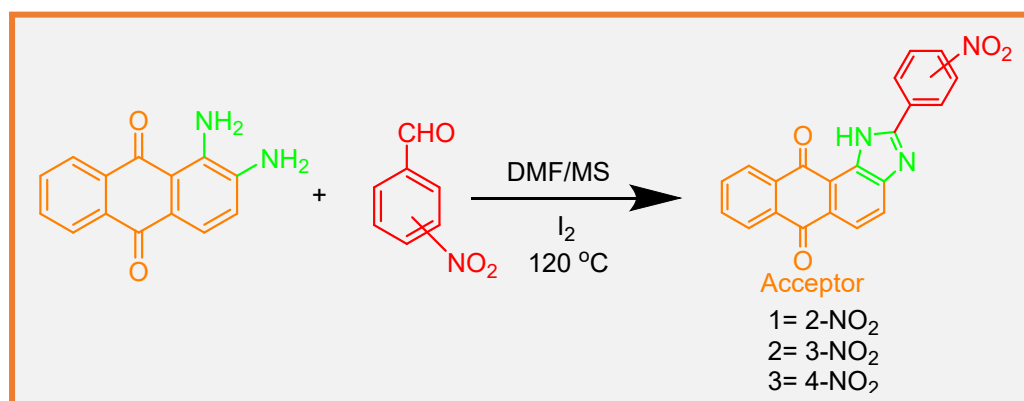


Figure S1: Schematic scheme of synthesis of compounds **1**, **2** and **3**

To a solution of 1,2 diamino anthraquinone (238 mg, 1.0 mmol) in DMF (4 mL) molecular beads (4Å) and substituted benzaldehyde (1.0 mmol) was added under stirring (Scheme 1). After adding I_2 (0.234g, 1 mmol), the mixture was heated at 120 °C for 10 hrs. The completion of the reaction was monitored by TLC. The reaction mixture was then cooled to room temperature and ice-cold water (30 mL) was added to it. The precipitate obtained after filtration was washed with water and further purified by column chromatography using eluent a mixture of $CHCl_3/MeOH$ (99.5:0.5) to get the desired product.

Compound **1**: yellow solid (yield 85%); mp: 300-302 °C ($R_f = 0.4$ at $CHCl_3:MeOH$ (99.5:0.5)), FT-IR (ATR): $\tilde{\nu} = 3405, 1667, 1583, 1533, 1489, 1422, 1322, 1295, 1200, 1150, 1110, 849$; ¹H-NMR (400MHz, DMSO- d_6 , 25 °C): δ (ppm)= 13.76 (s, 1H), 8.24 (m, 3H), 8.20 (m, 1H), 8.10 (m, 1H), 8.00 (m, 1H), 7.90 (m, 3H), 7.84 (m, 1H); ¹³C-NMR ($CDCl_3$): 119.370, 121.192, 124.909, 125.497, 125.928,

126.745, 127.309, 128.933, 132.073, 132.652, 133.302, 133.484, 133.605, 133.733, 134.787, 134.977, 149.040, 149.322, 155.510, 182.953, 183.648; (m/z): Calcd. for (C₂₁H₁₁N₃O₄): 369, found: 368

Compound **2**: yellow solid (yield 86%); mp: 295-297 °C (R_f = 0.4) FT-IR (ATR): $\tilde{\nu}$ = 3243, 2822, 2749, 1622, 1651, 1483, 1410, 1033, 972; ¹H-NMR (400MHz, DMSO-*d*₆, 25 °C): δ (ppm)= 13.7(s, 1H) 9.30 (s, 1H), 8.80 (m, 3H), 8.30 (s, 1H), 8.12 (m, 3H), 7.83 (m, 2H); ¹³C-NMR (CDCl₃): 114.74, 121.10, 122.02, 126.50, 127.61, 128.75, 133.75; (m/z): Calcd. for (C₂₁H₁₁N₃O₄): 369, found:368

Compound **3**: yellow solid (yield 88%); mp: 290-292 °C (R_f = 0.4), FT-IR (ATR): $\tilde{\nu}$ = 3388, 3067, 1655, 1583, 1511, 1344, 1285, 844; ¹H-NMR (400MHz, DMSO-*d*₆, 25 °C): δ (ppm)= 13.7 (s, 1H), 8.20 (m, 3H), 8.10 (m, 1H), 8.00 (m, 1H), 7.90 (m, 3H), 7.80 (m, 2H); ¹³C NMR (DMSO-*d*₆): 183.53, 182.71, 149.77, 146.61, 146.58, 134.89, 134.71, 133.58, 133.48, 128.55, 127.24, 126.67, 121.63, 114.94, 113.03; (m/z): Calcd. for (C₂₁H₁₁N₃O₄): 369, found:370 (M+H)⁺

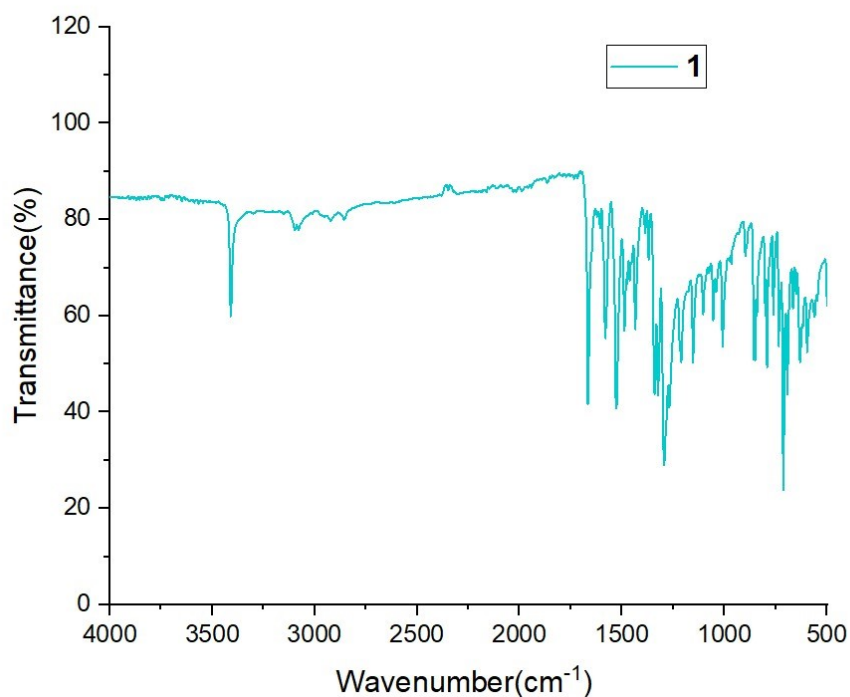


Figure S1: FT-IR spectra of compound **1**

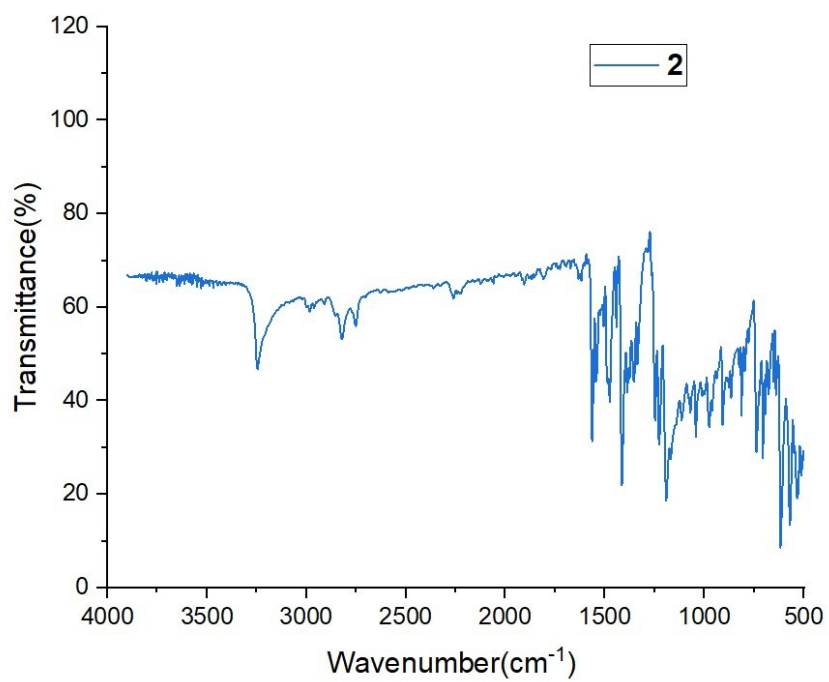


Figure S2: FT-IR spectra of compound 2

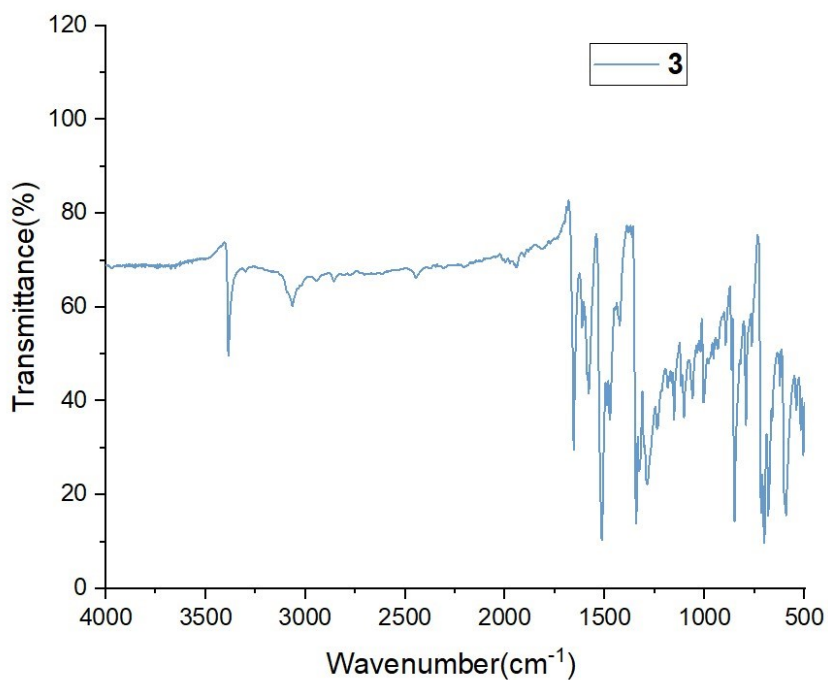


Figure S3: FT-IR spectra of compound 3

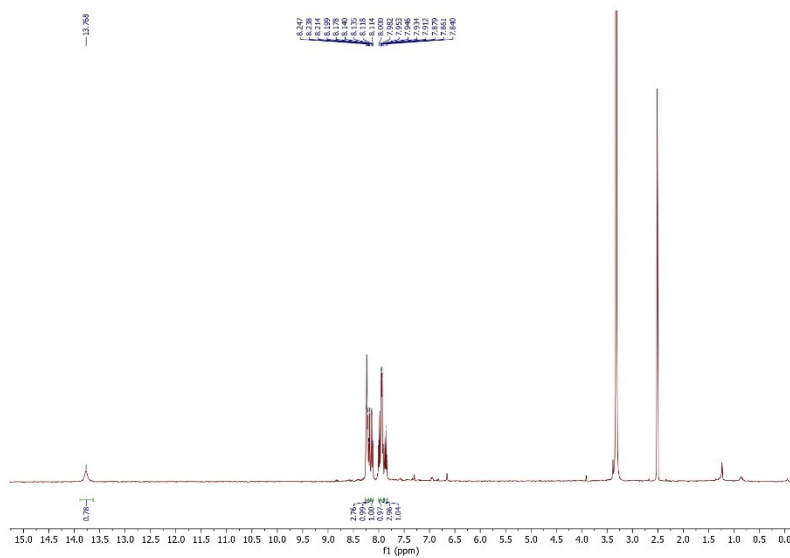


Figure S4: ^1H -NMR spectra of compound **1**

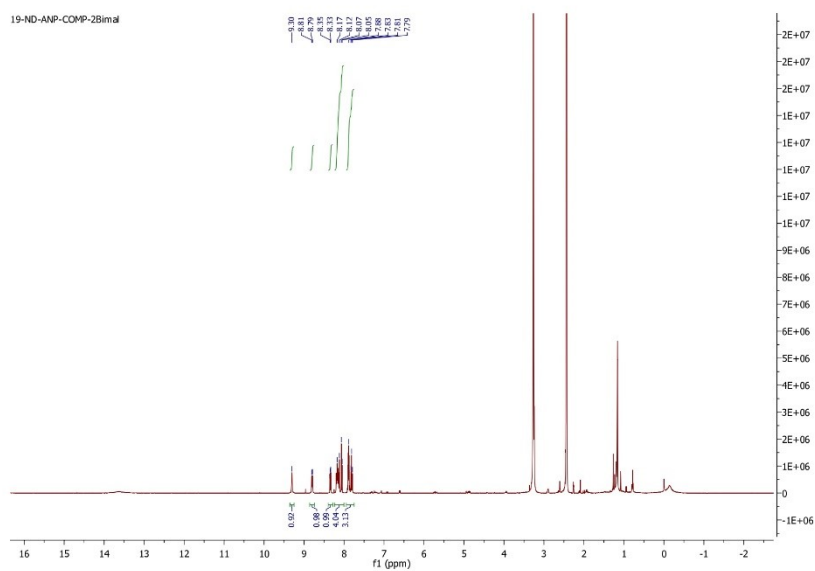


Figure S5: ^1H -NMR spectra of compound **2**

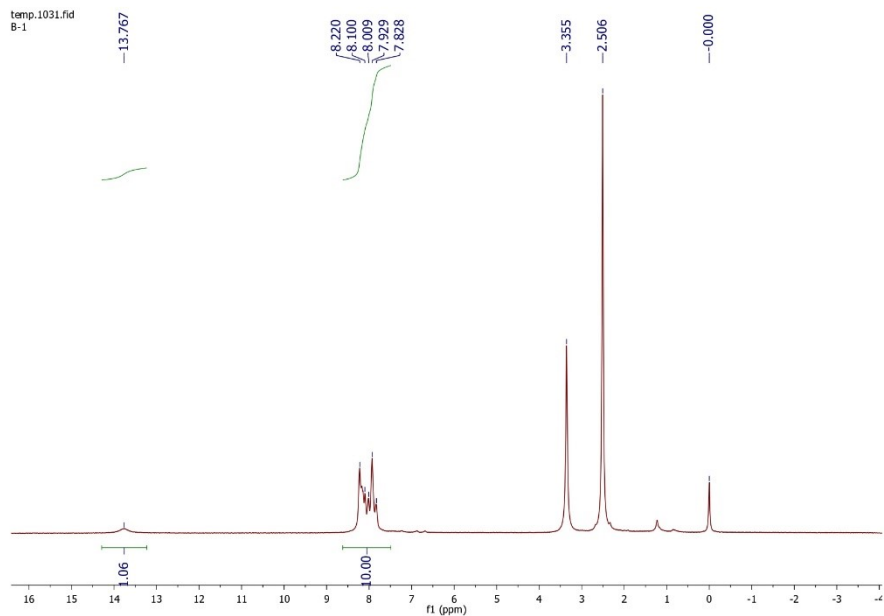


Figure S6: ^1H -NMR spectra of compound **3**

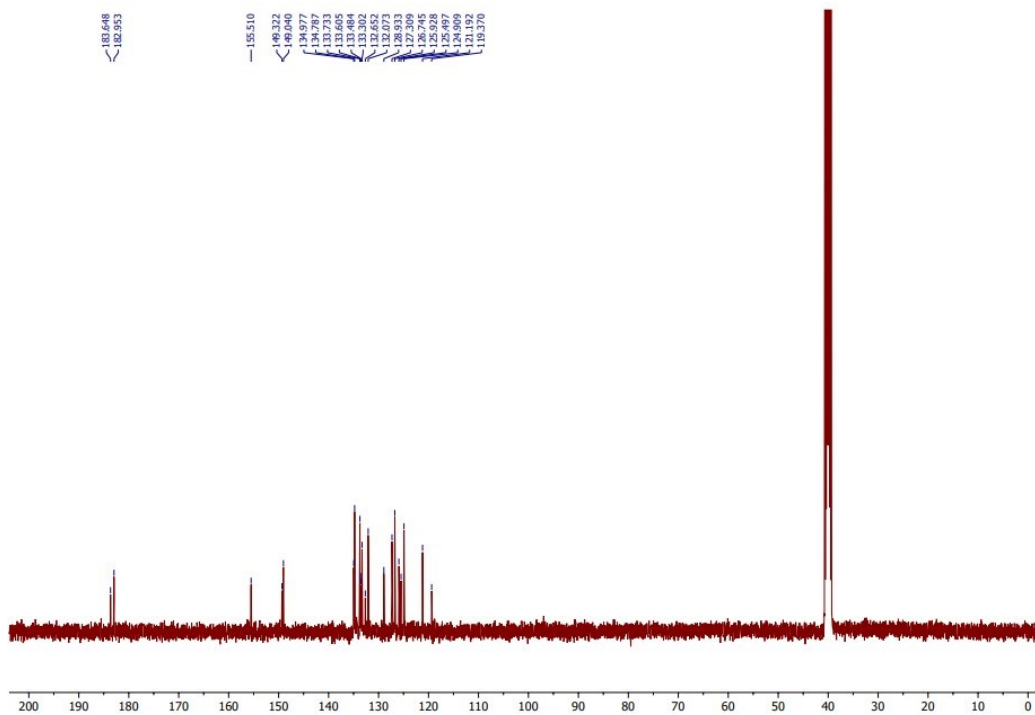


Figure S7: ^{13}C -NMR spectra of compound **1**

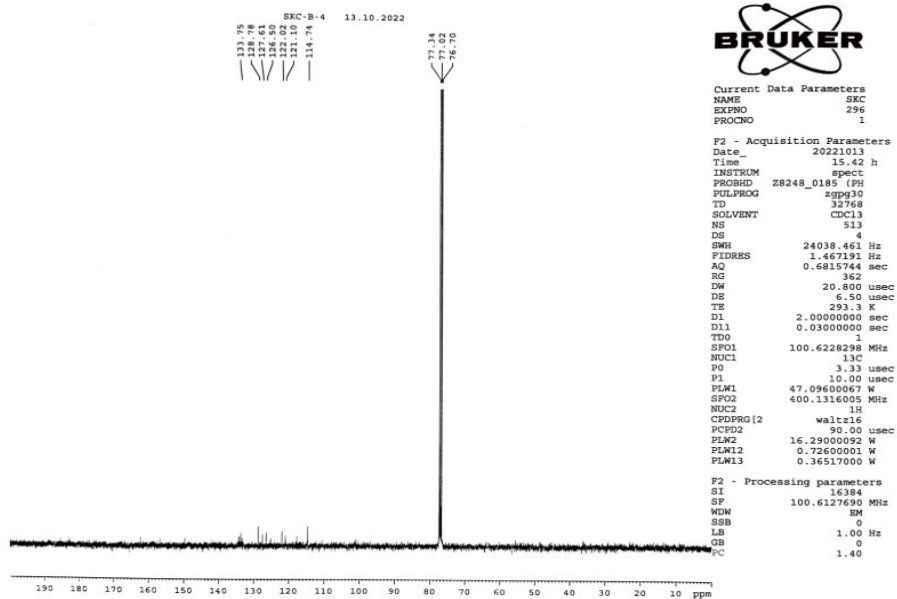


Figure S8: ¹³C-NMR spectra of compound 2

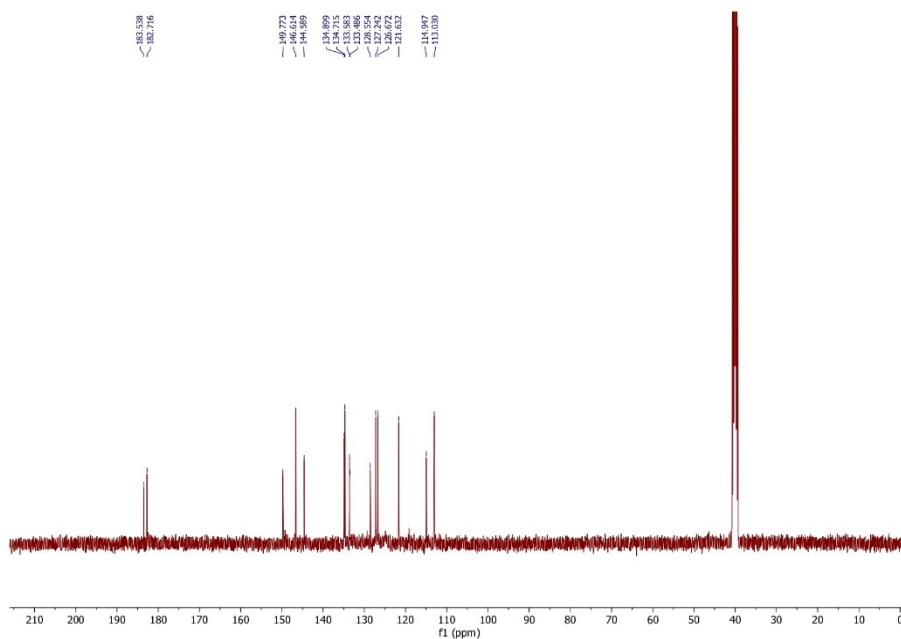


Figure S9: ¹³C-NMR spectra of compound 3

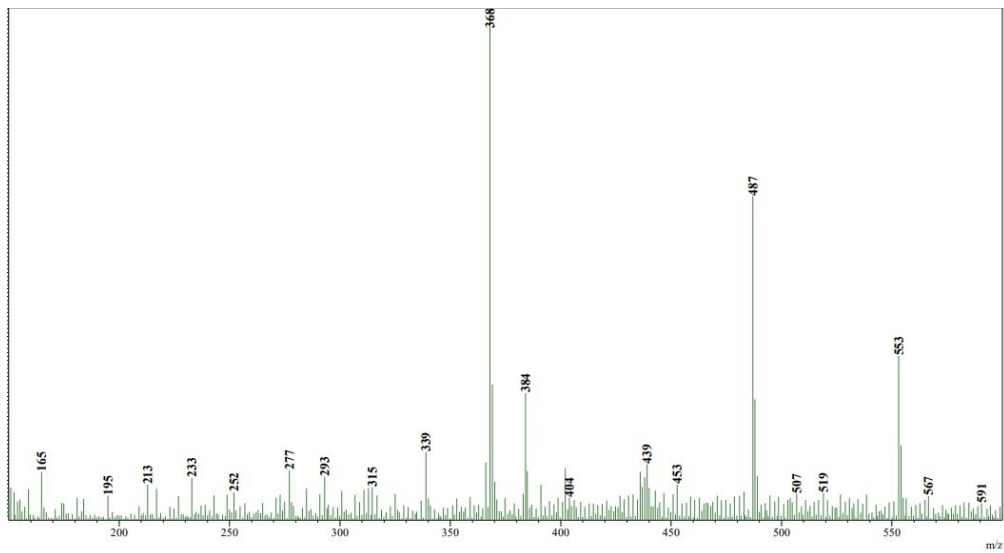


Figure S10: Mass spectra of compound 1

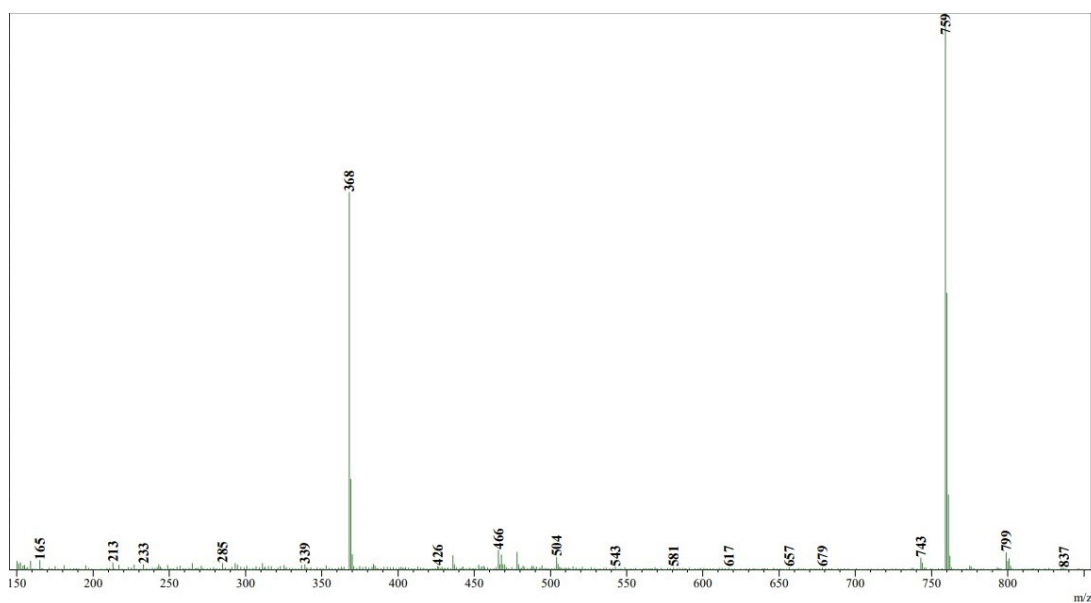


Figure S11: Mass spectra of compound 2

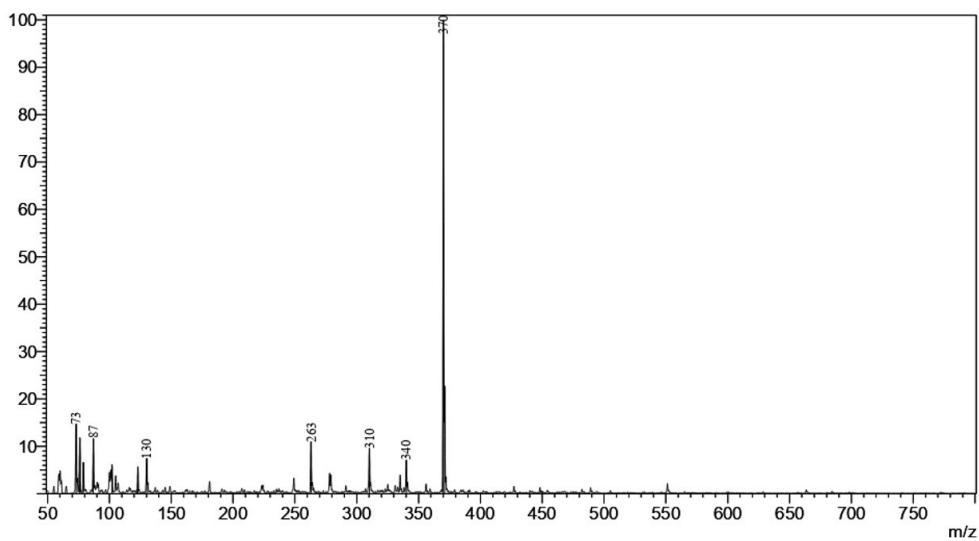


Figure S12: Mass spectra of compound 3

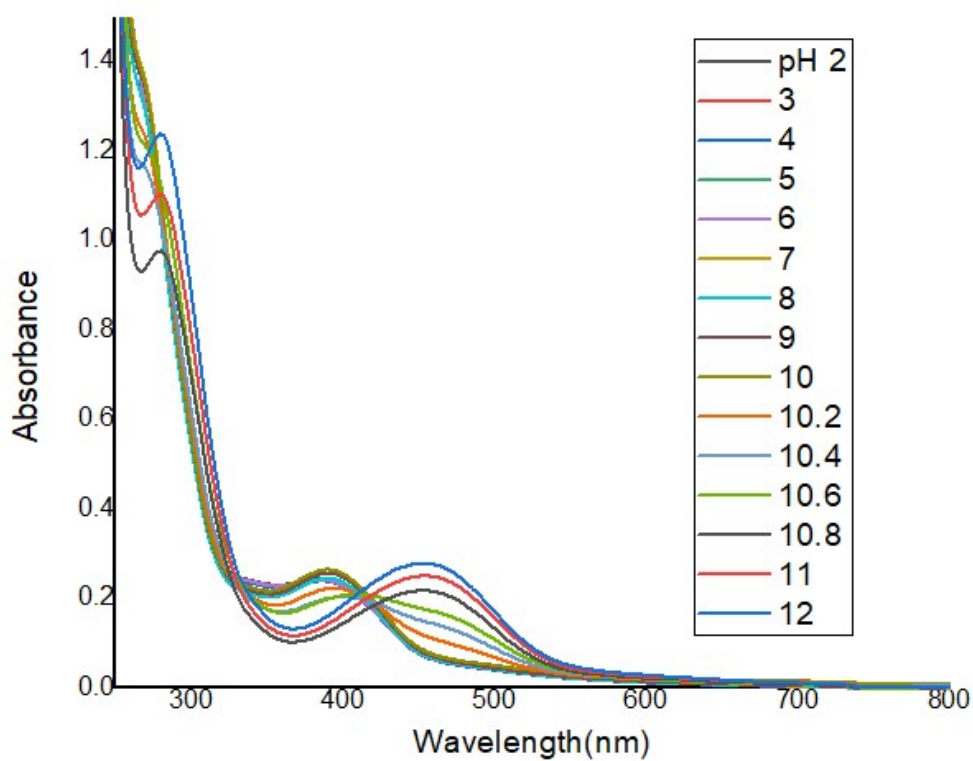


Figure S13: UV-visible spectra of compound 1 at different pH conditions in buffer medium

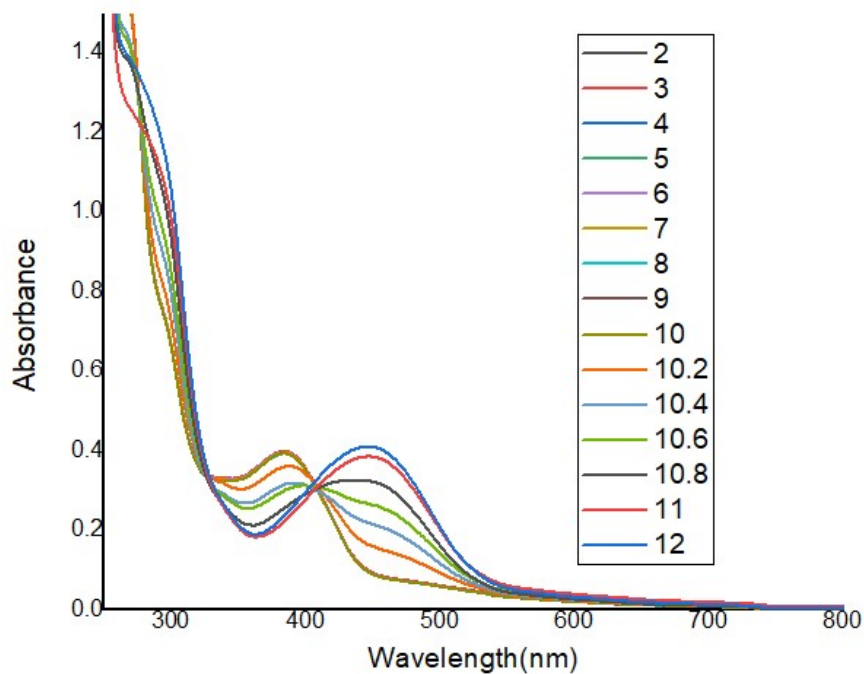


Figure S14: UV-visible spectra of compound 2 at different pH conditions in buffer medium

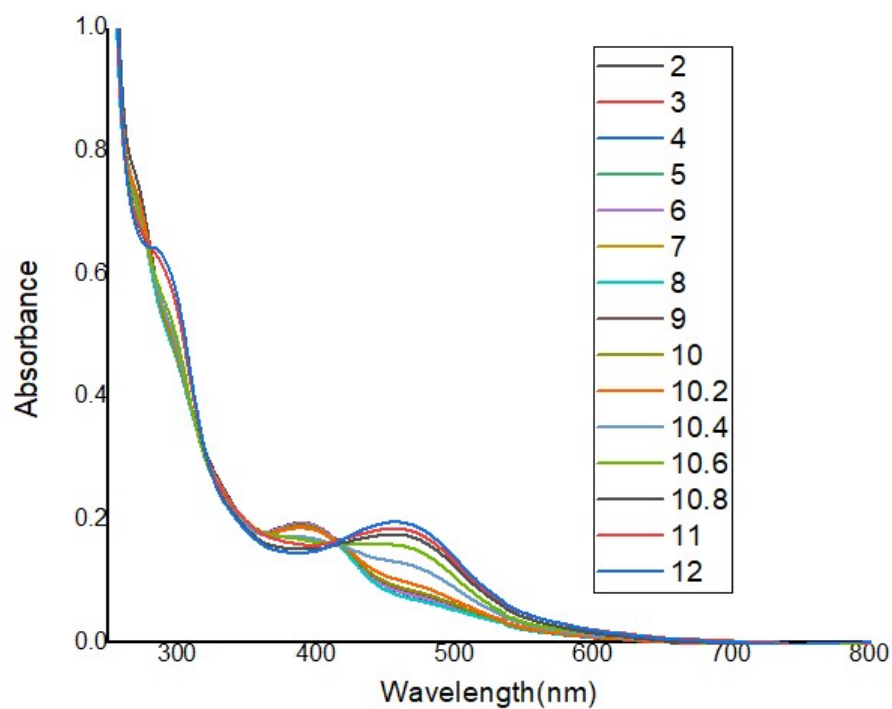


Figure S15: UV-visible spectra of compound **3** at different pH conditions in buffer medium

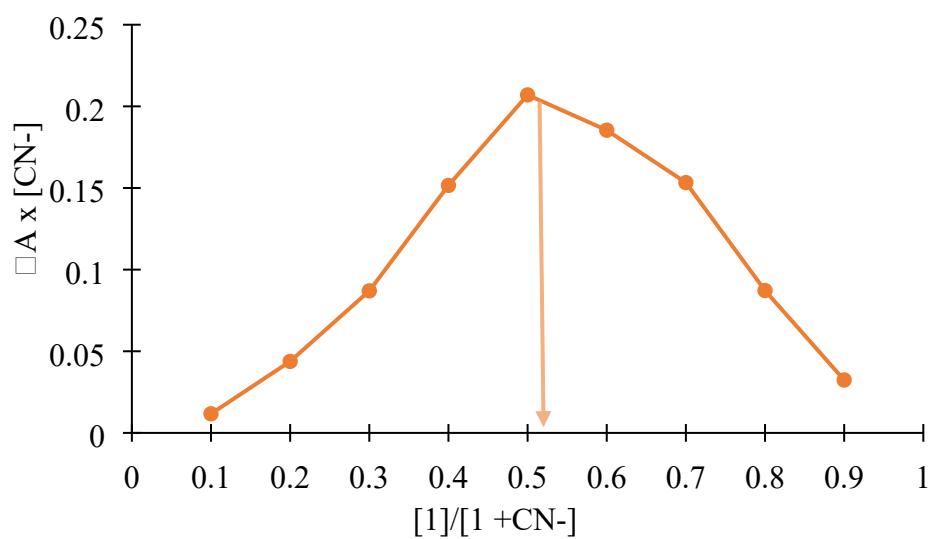


Figure S16: The Job's plot analysis indicating 1:1 stoichiometry of interaction between **1** and CN^- ($1 \times 10^{-4} \text{ M}$) ions.

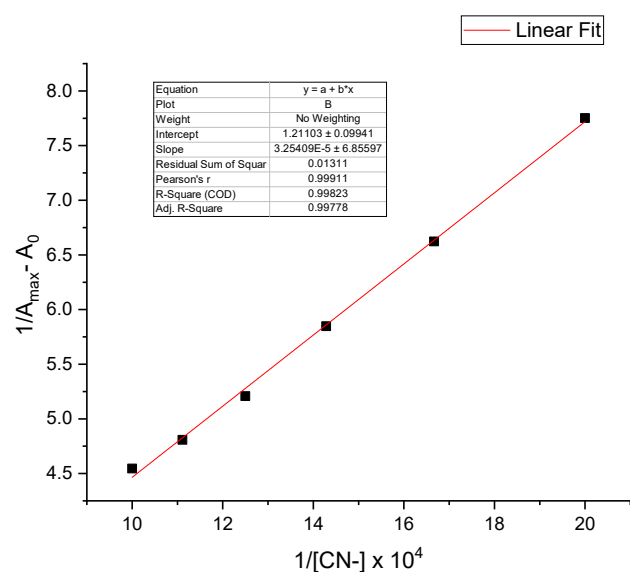


Figure S17: The binding constant (K_a) of the **1-CN⁻** derived from the UV-vis titration data using the Benesi-Hildebrand plot was found to be $2.52 \times 10^5 \text{ M}^{-1}$.

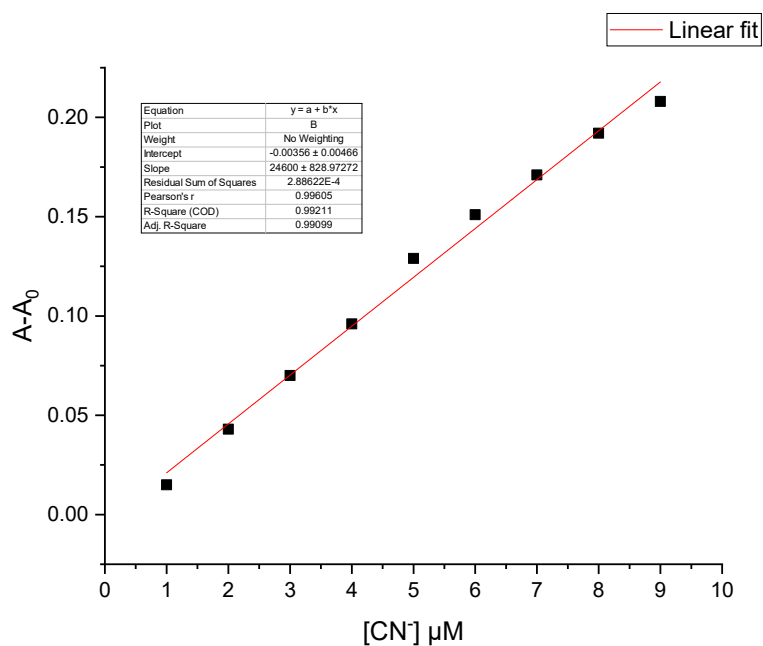


Figure S18: A plot of $A - A_0$ vs $[\text{CN}^-]$, the calculated detection limit (LOD) of **1-CN⁻** was found to be $8.689 \times 10^{-6} \text{ M}$ and the limit of quantitation (LOQ) was found to be $2.896 \times 10^{-5} \text{ M}$.

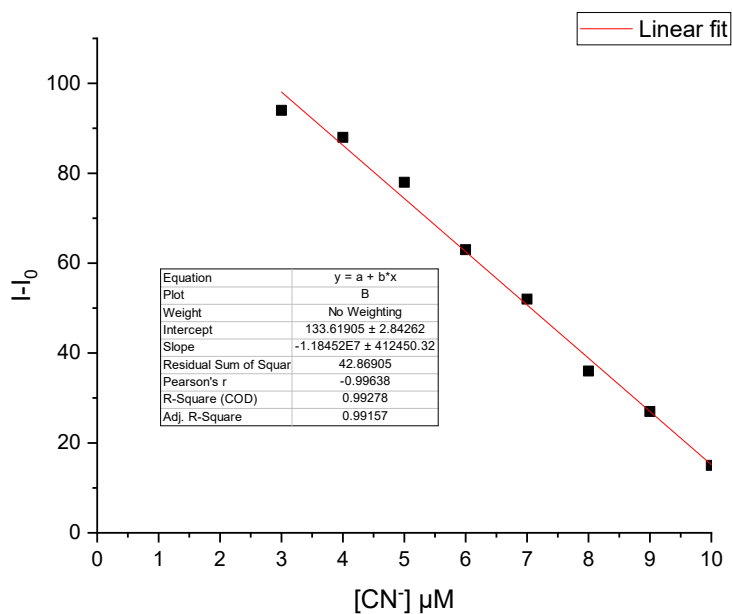


Figure S19: A plot of $I-I_0$ vs $[CN^-]$, the calculated detection limit (LOD) of **1**- CN^- via PL titration was found to be 7.9×10^{-8} M.

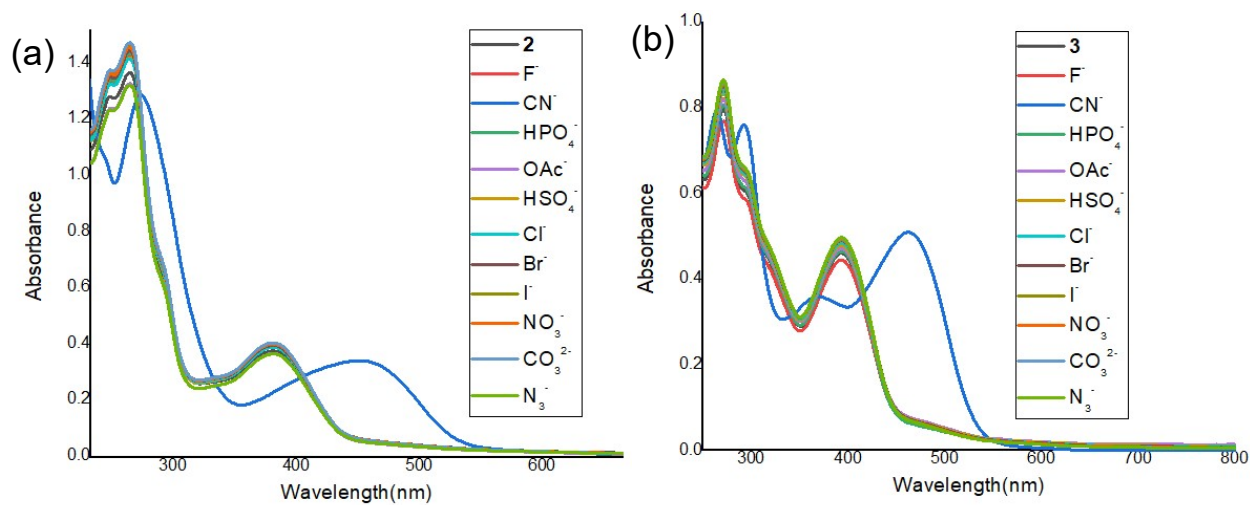


Figure S20: UV-visible spectra of compound (a) **2** and (b) **3** with different anions (10 μ M) in acetonitrile-water (8:2) mixture medium.

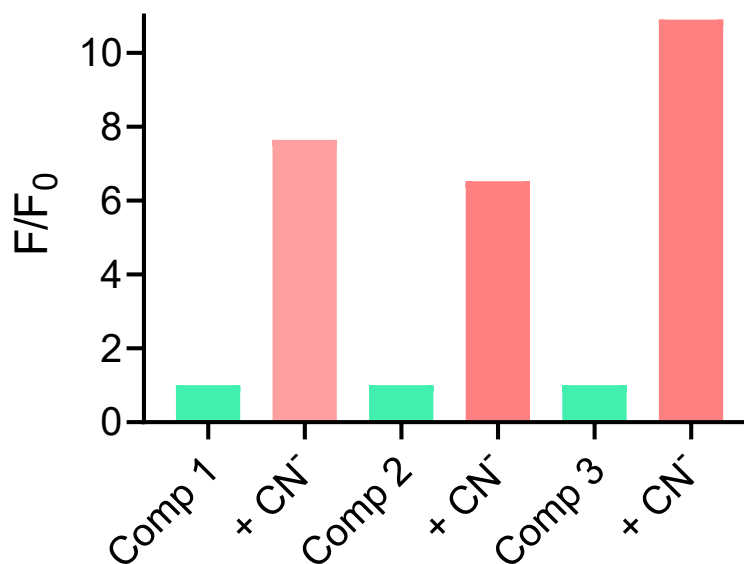


Figure S21: Change in FL intensity of compounds 1-3 with cyanide ions (10 μ M) in acetonitrile-water (8:2) mixture medium.

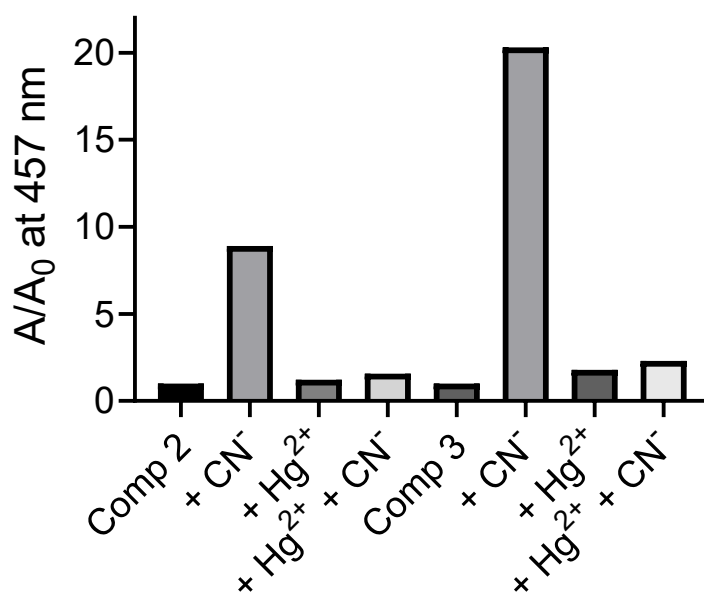


Figure S22: Reversible interactions between compounds 2 and 3 with CN⁻ in acetonitrile-water (8:2) mixture medium.

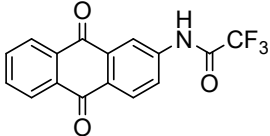
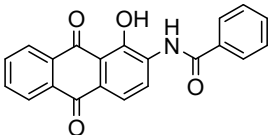

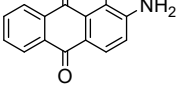
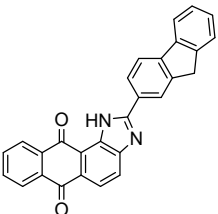
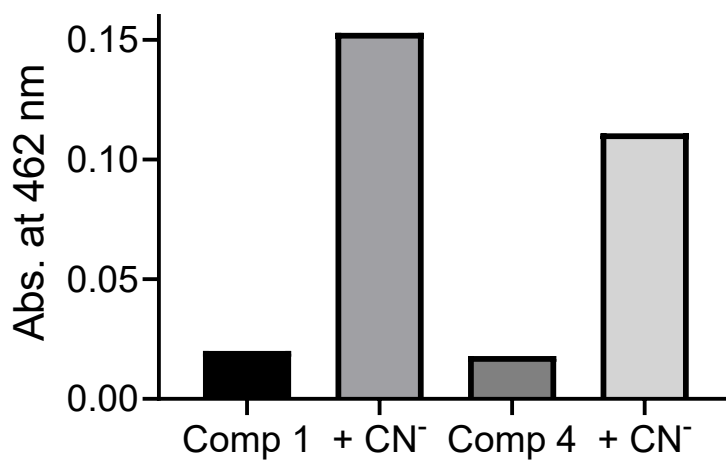
Sensor	Binding Constant	Detection Limit	Solvent	Ref.
	$7.7 \times 10^4 \text{ M}^{-1}$	$0.51 \times 10^{-6} \text{ M}$	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (9:1 v/v)	<i>RSC Adv.</i> , 2014, 4, 8295-8299
	$7.58 \times 10^4 \text{ M}^{-1}$	$0.22 \times 10^{-6} \text{ M}$	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (9.5:0.5 v/v)	<i>Tetrahedron</i> , 2021, 93, 132312
	$2.0 \times 10^4 \text{ M}^{-1}$	$6.61 \times 10^{-6} \text{ M}$	DMF	10.1007/978-95-002-

Figure S23: Changes in absorbance at 462 nm of compounds **1** and **4** with CN^- in acetonitrile-water (8:2) mixture medium.

	$2.11 \times 10^4 \text{ M}^{-1}$	$5.3 \times 10^{-6} \text{ M}$	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (9:1 v/v)	<i>Spectrochim.</i> , 2020, 234,118212
				



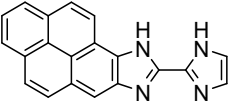
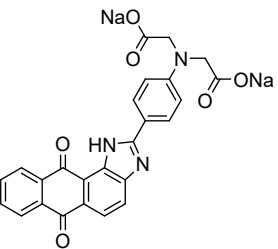
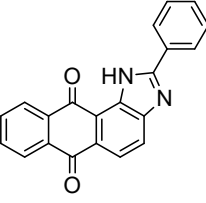
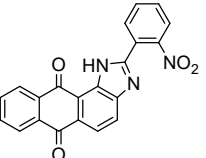
	$1.47 \times 10^3 \text{ M}^{-1}$	$1.1 \times 10^{-6} \text{ M}$	DMSO: H ₂ O (9:1 v/v)	<i>Dalton Trans.</i> , 2015,44, 15994- 16012
	$3.71 \times 10^4 \text{ M}^{-1}$	-	CH ₃ CN (5% DMSO)	<i>J. Org. Chem.</i> 2011, 76, 8215–8222
	$1.16 \times 10^4 \text{ M}^{-1}$	-	CH ₃ CN:HEPES (7:3 v/v)	<i>Org. Lett.</i> 2010, 12, 3406-3409
	$2.52 \times 10^5 \text{ M}^{-1}$	0.08 μM	CH ₃ CN: H ₂ O (8:2 v/v)	Present Work

Table 1: Comparison table for reported CN⁻ sensor with **1**