SUPPLEMENTARY INFORMATION

A sensitive colorimetric detection of CN\(^{-}\) and AcO\(^{-}\) anions in semi-aqueous environment through a coumarin–naphthalene conjugate azo dye

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Scheme S1: (i) Ethylacetoacetate/piperidine/EtOH/Δ, (ii) Br₂/CHCl₃/EtOH/r.t., (iii) thiourea/EtOH/r.t., (iv) a. H₂SO₄/AcOH, b. NaNO₂/H₂O/0°C, c. alk. β-naphthol.

Figure S1: ¹H NMR spectrum of 2 in CDCl₃.

Figure S2: ¹H NMR spectrum of 3 in CDCl₃.

Figure S3: ¹H NMR spectrum of 4 in CDCl₃.

Figure S4: ¹H NMR spectrum of 5 in CDCl₃.

Figure S5: ¹H-NMR spectrum of probe 5 in DMSO-d₆.

Figure S6: ¹³C NMR spectrum of 5 in CDCl₃.

Figure S7: FT-IR spectrum of probe 5.

Figure S8: ESI-MS spectrum of probe 5.

Figure S9: Stacked ¹H NMR spectra of probe 5 (2.0 x 10⁻² M) upon addition of AcO⁻ (0 - 2.0 equiv) in CDCl₃.

Figure S10: ¹H NMR spectra of probe 5 upon addition 0.5 equiv. of CN⁻ in CDCl₃.

Figure S11: ¹H NMR spectra of probe 5 upon addition 1.0 equiv. of CN⁻ in CDCl₃.

Figure S12: ¹H NMR spectra of probe 5 upon addition 2.0 equiv. of CN⁻ in CDCl₃.

Figure S13: Stacked ¹³C NMR spectra of probe 5 and 5+CN⁻ in CDCl₃.

Figure S14: FT-IR spectrum of 5+CN⁻.

Figure S15: ESI-MS spectrum of 5+CN⁻.

Figure S16: ESI-MS spectrum of 5+AcO⁻.

Figure S17: Absorption spectra of probe 5 in solvent of different polarity.

Table-S1: Photophysical property of probe 5 in solvent of different polarity.

Figure S18: Absorption spectra of probe 5 (10 µM) after interaction with F⁻, CN⁻, AcO⁻ in (a) acetonitrile, (b) acetonitrile:H₂O (1:1, v/v), (c) DMSO and (d) DMSO:H₂O (1:1, v/v).

Figure S19: Interaction of probe 5 with different metal ions in aqueous ethanol (1:1; v/v).

Figure S20: Interaction of probe 5 (10 µM) with different anions in pure ethanol.
**Figure S21:** Bar Diagram of probe 5 (10 µM) after interaction with different anions.

**Figure S22:** Benesi-Hildebrand plot of probe 5 (10 µM) with (a) CN$^-$ and (b) AcO$^-$ ions.

**Figure S23:** Change in absorption spectra of probe 5 (10 µM) upon addition of different concentration of (a) AcO$^-$ (b) CN$^-$. 

**Figure S24:** Change in absorption spectra of probe 5 (10 µM) at different pH in HEPES buffer (DMSO:H$_2$O; 9:1 v/v).

**Figure S25:** DFT method optimized minimum energy structure for azo and hydrazone form and HOMO-LUMO energy level for probe 5.
Materials and Chemicals: All the reagent and solvents were purchased from Sigma-Aldrich Chemical Pvt. Ltd. Stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Solvent were purified prior to use. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda-35 UV-vis spectrophotometer using a quartz cuvette (path length = 1cm). Infrared (IR) spectra were recorded in potassium bromide (KBr) on Varian-3100 FT-IR spectrometer. 1H NMR spectra were recorded (chemical shift in δ ppm) on a JEOL AL 300 and 500 FT-NMR (300 and 500MHz) spectrometer, using tetramethylsilane (TMS) as internal standard. All the spectroscopy experiments were carried out at room temperature. The stock solution of probe 5 (1 x 10⁻³) were prepared in EtOH and diluted to obtained 10 μM in mixture of EtOH and H₂O (1:1, v/v) for absorption measurement. The stock solution of different anions (1 x 10⁻¹ M) was prepared by dissolving their inorganic salt in water. The anion interaction studies were performed by addition of 1 x 10⁻¹ M of different anions.

Estimation of Binding Constant: The absorption experimental data were utilized to calculate association constants by Benesi-Hildebrand method (B-H method) employing equations (1) for 1:1 stoichiometry.

\[
\frac{1}{(I - I_o)} = \frac{1}{(I - I_f)} + \frac{1}{K(I - I_f)}[M]
\]  \hspace{1cm} (1)

Where K is the association constant, I is the absorbance of the free probe 5, I_o is the observed absorbance of the 5+CN⁻ and 5+AcO⁻ in equation (1) complex, and I_f is the absorbance at saturation level.
Scheme S1: (i) Ethylacetoacetate/piperidine/EtOH/Δ, (ii) Br$_2$/CHCl$_3$/EtOH/r.t., (iii) thiourea/EtOH/r.t., (iv) a. H$_2$SO$_4$/AcOH, b. NaNO$_2$/H$_2$O/0°C, c. alk. β-naphthol.
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Figure S5: $^1$H-NMR spectrum of probe 5 in DMSO-$d_6$. 
Figure S6: $^{13}$C NMR spectrum of 5 in CDCl$_3$. 
Figure S7: FT-IR spectrum of probe 5.
Figure S8: ESI-MS spectrum of probe 5.
**Figure S9:** Stacked $^1$H NMR spectra of probe 5 (2.0 x $10^{-2}$ M) upon addition of AcO$^-$ (0 - 2.0 equiv) in CDCl$_3$. 
Figure S10: $^1$H NMR spectra of probe 5 upon addition 0.5 equiv. of CN$^-$ in CDCl$_3$. 
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Figure S12: $^1$H NMR spectra of probe 5 upon addition 2.0 equiv. of CN$^-$ in CDCl$_3$. 
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<table>
<thead>
<tr>
<th>Properties</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\varepsilon$ (cm$^{-1}$M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>283, 299, 346, 496</td>
<td>2.0148 x 10$^4$, 1.6219 x 10$^4$, 1.6983 x 10$^4$, 1.4167 x 10$^4$</td>
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<td>DMSO</td>
<td>284, 329, 390, 502</td>
<td>2.8858 x 10$^4$, 1.9112 x 10$^4$, 1.5106 x 10$^4$, 1.0403 x 10$^4$</td>
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<td>DCM</td>
<td>286, 302, 344, 498</td>
<td>1.9461 x 10$^4$, 1.7070 x 10$^4$, 1.5609 x 10$^4$, 1.3732 x 10$^4$</td>
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<tr>
<td>H$_2$O</td>
<td>280, 309, 365, 481</td>
<td>1.6209 x 10$^4$, 1.3306 x 10$^4$, 1.1003 x 10$^4$, 0.7277 x 10$^4$</td>
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<tr>
<td>Dioxane</td>
<td>286, 303, 348, 499</td>
<td>1.9479 x 10$^4$, 1.6896 x 10$^4$, 1.6722 x 10$^4$, 1.4419 x 10$^4$</td>
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<td>MeCN</td>
<td>287, 333, 389, 499</td>
<td>3.0822 x 10$^4$, 2.1164 x 10$^4$, 1.5870 x 10$^4$, 1.1193 x 10$^4$</td>
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<tr>
<td>EtOH</td>
<td>284, 303, 348, 499</td>
<td>1.8554 x 10$^4$, 1.5935 x 10$^4$, 1.6983 x 10$^4$, 1.4322 x 10$^4$</td>
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<tr>
<td>EtOH-H$_2$O</td>
<td>285, 304, 350, 498</td>
<td>1.5435 x 10$^4$, 1.5870 x 10$^4$, 1.5183 x 10$^4$, 1.3393 x 10$^4$</td>
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<tr>
<td>DMSO-H$_2$O</td>
<td>287, 331, 386, 498</td>
<td>2.8006 x 10$^4$, 1.9287 x 10$^4$, 1.44193 x 10$^4$, 1.0229 x 10$^4$</td>
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<tr>
<td>ACN-H$_2$O</td>
<td>287, 321, 387, 499</td>
<td>2.5693 x 10$^4$, 1.7661 x 10$^4$, 1.3393 x 10$^4$, 0.9464 x 10$^4$</td>
</tr>
</tbody>
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