Supporting information

Chemodosimetric sensing of hydrazine via an irreversible reaction-based sensor and its multifunctional applications

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Figure S1: LC-MS Spectra of the probe showing $[M+1]^+$ peak.



Figure S2: ¹H-NMR Spectra of the probe in CDCl₃.



Figure S3: ¹³C-NMR Spectra of the probe in CDCl₃

Sl. No	Probe	LOD	Method	Ref.
1		3.67 µM	Fluorometric	1
2		143 ppb	Colorimetric	2
3	NC_CN NC_CN COOH	0.12 μM	Fluorometric	3
4	O OEt	75.09 ppb	Fluorometric	4
5		7 ppb	Fluorometric	5
6		5.4 ppb	Fluorometric	6
7	N CN CN	8.87 nM	Fluorometric	7

Table S1: List of malononitrile based senosrs for hydrazine

8	CN	1.77 ppb	Colorimetric	This	
	NC			work	
<u>\$3</u>					

Table S2: List of malononitrile based senosrs for CN-ion

S1	Probe	LOD	Method	Ref.
<u>no.</u> 1		0.427 μM	Colorimetric and fluorometric	8
2	CN CN	0.23 μΜ	Colorimetric and fluorometric	9
3		6.8 µM	Colorimetric and fluorometric	10
4		8.11 μM	Colorimetric and fluorometric	11
5	R= n-C ₈ H ₁₇	0.5 μΜ	Colorimetric and fluorometric	12
6		1.1 μM	Colorimetric	13
7		1.47 μΜ	Colorimetric and fluorometric	14





Figure S4: (a) Detection limit and (b) binding constant plot of the probe with hydrazine.



Figure S5: Absorption spectra of the probe with different amines.



Figure S6: (a) Overlaid absorption spectra of probe 1 (10^{-5} M) with TBACN (10^{-4} M) in THF, (b) Absorbance at 386 nm and 428 nm with increasing concentration of CN⁻. (c) Time dependent absorption spectra of the probe (10^{-6} M) with TBACN (10^{-5} M), (d) Absorbance *vs* time plot of probe 1 at 386 nm. Inset: colour changes of the probe with CN⁻.



Figure S7: (a) Detection limit and (b) binding constant plot of the probe with CN⁻.



Figure S8: Overlaid absorption spectra of probe 1 (10^{-4} M) with Na₂S (10^{-3} M) in THF:H₂O.



Figure S9: Absorption spectra of the probe with different anions.



Figure S10: Absorption spectra of the probe with cyanide after removal of S^{2-} (solvent: THF:H₂O).



S1: Preparation of Starch/PVA based composite film:

Starch/PVA/Probe film was prepared by solution casting method. Starch solution was prepared by adding 4 g of Potato starch in 100 ml of water. Then 3 g of polyvinyl alcohol was added to the starch solution. The mixed solution was stirred continuously for 30 min at 90°C to get a homogeneous gel solution. Then 0.05 g of the probe was added to the above mixed solution with continuous stirring for 6 hours at room temperature. Glycerol (5 ml) was used as a plasticizer. The suspension so formed was poured onto glass petri dish. The blend films were dried at 60°C for 12 hours.



Figure S11: (a) Test strips of probe 1 with different anions, (b) colour changes with increasing concentration of cyanide, (c) Colour changes of probe 1 in the solid state upon addition of cyanide solution in THF.



Figure S12: Colour changes of the probe in the vapor phase upon exposure to 10⁻⁴ M hydrazine solution.

Table S3: Determination of hydrazine concentration in water samples

Sample	Hydrazine	Hydrazine	Recovery
	spiked (M)	detected (M)	%
Тар	0	0	NA
water 1	1.2×10^{-5}	1.17×10^{-5}	97.5%
Тар	0	0	NA
water 2	2.5×10^{-6}	2.53 × 10 ⁻⁵	101.2%



Figure S13: Absorption spectra of the probe with water samples for detection of hydrazine. (a) Tap water 1, (b) Tap water 2.



Figure S13: Calibration curve of the probe with CN^{-} in THF:H₂O.

Table S4: Determination of CN⁻ concentration in water samples

Sample	CN-	CN ⁻ detected	Recovery
	spiked (M)	(M)	%
Тар	0	0	NA
water 1	1.2×10^{-4}	1.19×10^{-4}	99.2%
Тар	0	0	NA
water 2	1.4×10^{-4}	1.35×10^{-4}	97%



Figure S15: Absorption spectra of the probe with water samples for detection of CN⁻. (a) Tap water 1, (b) Tap water 2.

S2: Preparation of soil samples for hydrazine sensing

Soil samples were collected from different places like campus, garden and field soil. All the soil samples were weighed in 1g each and added to 5 mL of probe solution (10⁻⁵ M). the solutions are then sonicated for 30 minutes and then centrifuged. The supernatant liquid is again filtered to remove any fine soil particles if present even after centrifugation. The filtrate is then used to record UV-Vis spectra. No spectral changes were observed for all the three samples. Therefore, in the second step a known amount of hydrazine solution in THF is added to the soil samples and the above procedure is repeated for the mixtures and the final solutions were taken for analysis.

Sample	Hydrazine spiked	Hydrazine detected	Recovery %	
	(M)	(M)		
Campus	0	0	NA	
Soli	3 × 10 ⁻⁷	2.85 × 10 ⁻⁷	95%	

 Table S5: Determination of hydrazine concentration in Soil samples

Garden	0	0	NA
soil			
	1.15×10^{-6}	1.13×10^{-6}	98.2%
Field soil	0	0	NA
	1.25×10^{-6}	1.25×10^{-6}	100%

S3: Preparation of food samples for CN⁻ sensing

Food samples were first well crushed in a mortar and then stored in a sealed flask for about 2 hours at room temperature to release CN⁻ out of them. After 2 hours NaOH solution (50 mg in 10 mL water) was added separately to both the samples. The two solutions were then stirred vigorously for about 10 min. The resulting mixture was then centrifuged at 4000 rpm for 20 min. Then the supernatant liquid was used for analysis.



Figure S16: Absorption spectra of the probe (10⁻⁴ M in THF:H₂O) in presence of a) Apple seed extract and b) Sprouted potato extract. (c) Test strips of probe **1** (i) Test strips of probe **1** dipped in apple seed extract and (ii) Test strips of probe half dipped in apple seed extract (iii).



Figure S17: Absorption spectra of the probe with Potato extracts. (a) Day 1, (b) Day 2, (c) Day 7.



Figure S18: RGB component analysis of probe alone, after addition of hydrazine and CN⁻.



Figure S19: 3D surface interactive plot of (a) probe, Probe after addition of (b) hydrazine and (c) CN⁻.



Figure S20: LC-MS spectra of the probe recorded after addition of hydrazine.



Figure S21: ¹H NMR spectral changes of the probe with and without CN⁻ in CDCl₃.



Figure S22: ¹³C NMR spectral changes of the probe with and without CN⁻ in CDCl₃. (Peaks that are not assigned correspond to the carbons of tetrabutyl ammonium ion).



Figure S23: LC-MS spectra of the probe recorded after addition of cyanide.



Figure S24: The ground state optimized geometries of (a) Probe 1 and (b) Probe 1 with Hydrazine.

Molecule	Electronic transition	Calculated transition wavelength	Oscillator strength	Transition electric dipole moment	contribution	Contribution in percent
reactant	S0→S1	436	0.25	3.62	$\begin{array}{c} H-3 \rightarrow L+1 \\ H \rightarrow L \\ H \rightarrow L \end{array}$	1.2 87.2
					H→L+1	6.9
product	S0 \S1	360	0.0001	0.001	H-1→L	46.3
product	30→31	300	0.0001	0.001	$H \rightarrow L+1$	47.6
	50 .52	240	0.210	2.52	$H-1 \rightarrow L+1$	1.8
	50→52	349	0.219	2.32	H→L	95.1

Table S6: Details of electronic spectra of product and reactant calculated from theoretical study



Figure S25: The TD-DFT optimized excited state geometries of (a) Probe 1 and (b) Probe 1 with Hydrazine.

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