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Supporting Information For:

Cerium based azide- and nitro-functionalized UiO-66 frameworks as turn-on fluorescent probes for the sensing of hydrogen sulphide

*Amlan Buragohain and Shyam Biswas**

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039 Assam, India

* To whom correspondence should be addressed. E-mail: sbiswas@iitg.ernet.in; Tel: 91-3612583309.

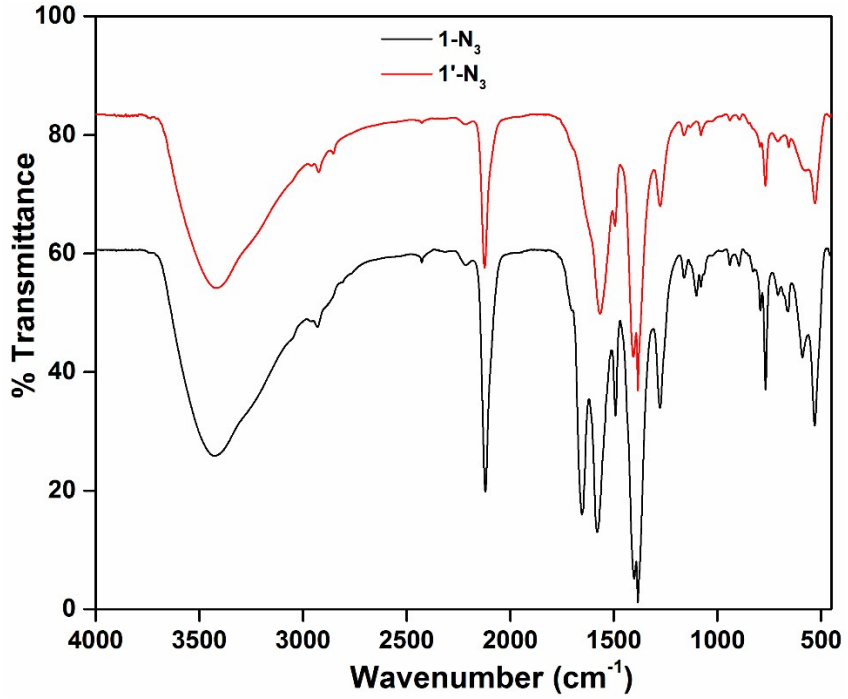

Figure S1. FT-IR spectra of as-synthesized **1-N_3** (black) and activated (red) **1´-N_3** compound.

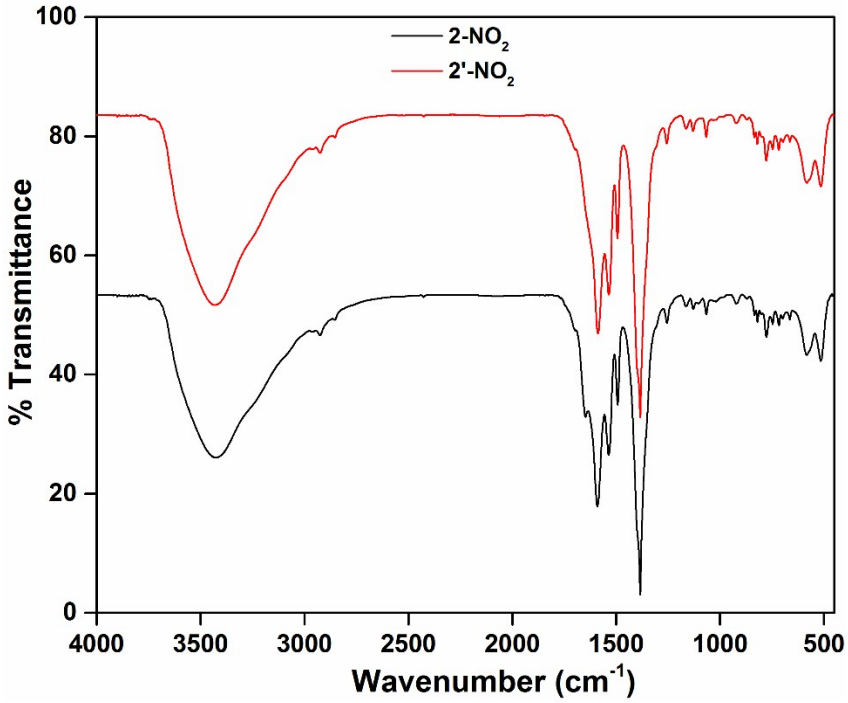

Figure S2. FT-IR spectra of as-synthesized **2-NO_2** (black) and activated **2´-NO_2** (red) compound.

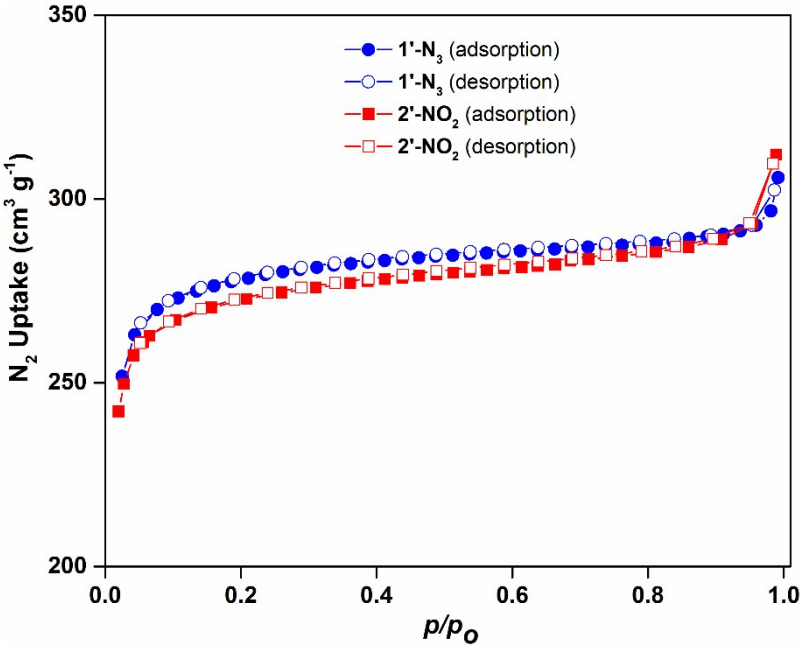

Figure S3. N_2 adsorption (solid symbols) and desorption (empty symbols) isotherms of the thermally activated **1´-N_3** (blue, circles) and **2´-NO_2** (red, squares) recorded at –196 °C.

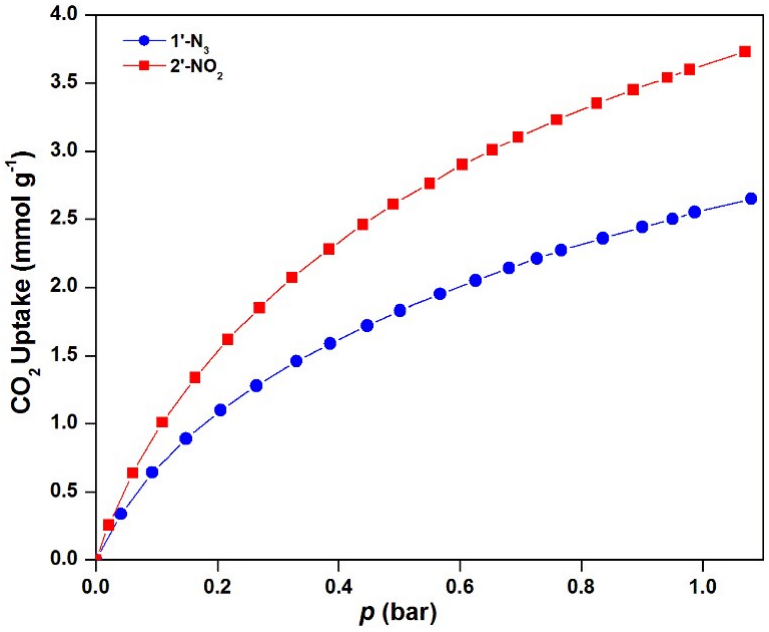

Figure S4. Low-pressure CO_2 adsorption isotherms of the thermally activated **1´-N_3** (blue, circles) and **2´-NO_2** (red, squares) measured at 0 °C.

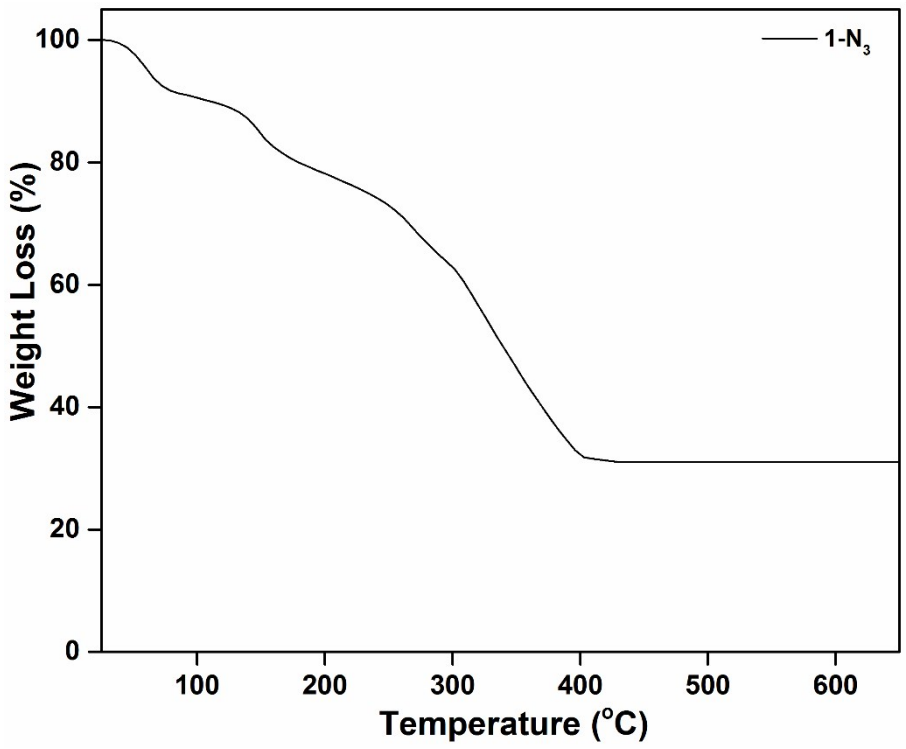

Figure S5. TG curves of as-synthesized **1-N_3** compound recorded in an air atmosphere in the temperature range of 25-650 °C with a heating rate of 5 °C min^{-1}.

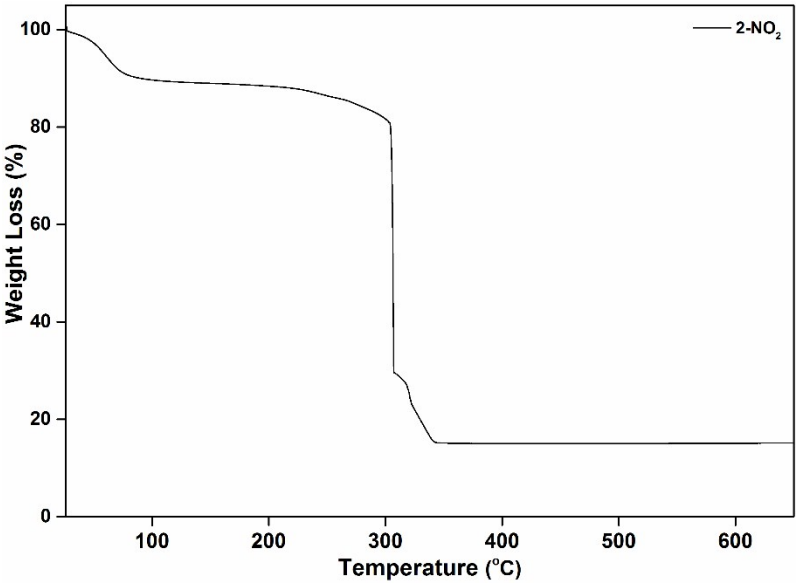

Figure S6. TG curves of as-synthesized **2-NO_2** compound recorded in an air atmosphere in the temperature range of 25-650 °C with a heating rate of 5 °C min^{-1}.

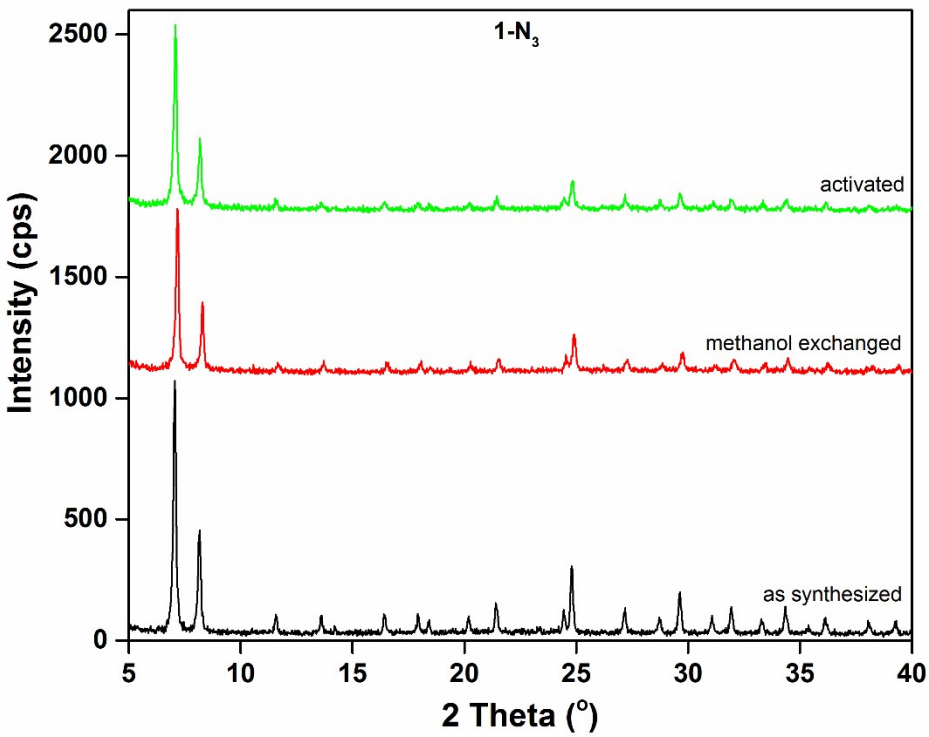

Figure S7. XRPD patterns of **1-N_3** compound in different forms: (i) as-synthesized (black), (ii) methanol-exchanged (red) and (iii) activated at 90 °C (green).

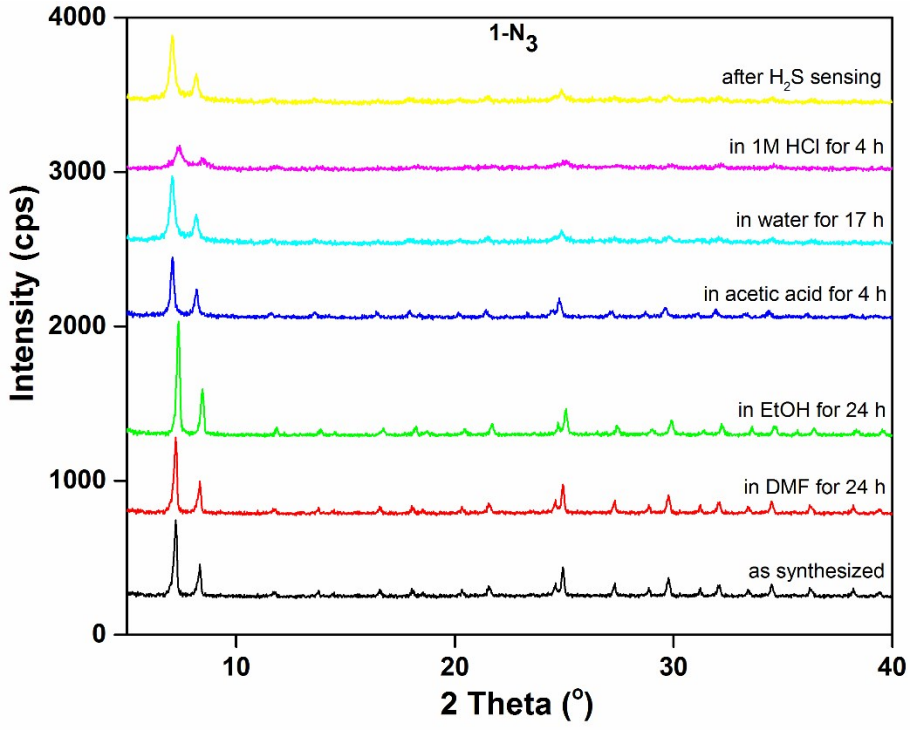

Figure S8. XRPD patterns of **1-N_3** compound in different solvents: as-synthesized (black), DMF (red), EtOH (green), acetic acid (blue), water (cyan), 1M HCl (pink) and after H_2S sensing experiment (yellow).

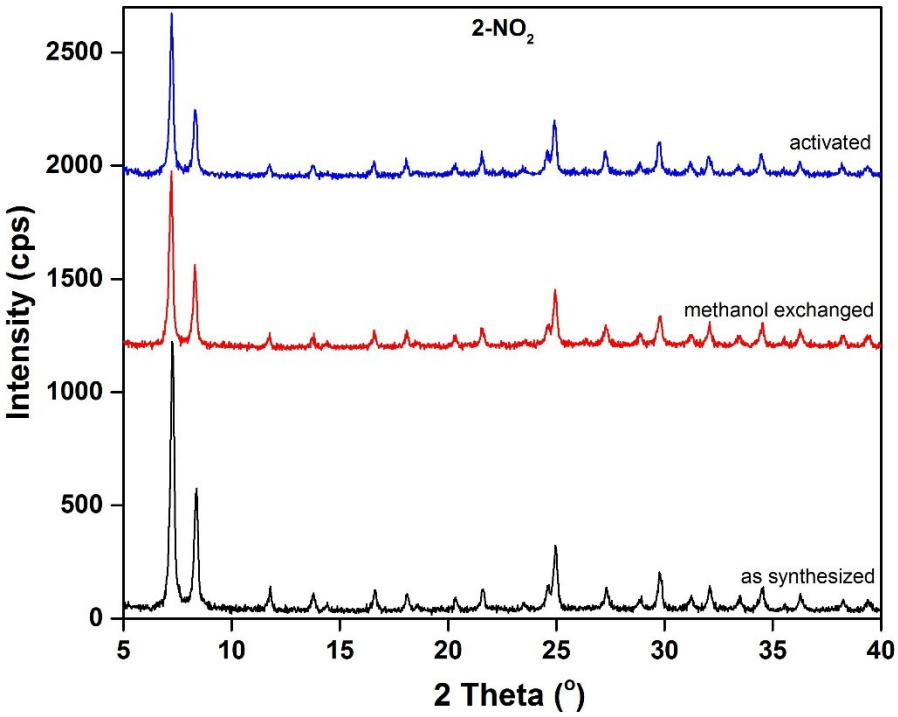

Figure S9. XRPD patterns of **2-NO_2** compound in different forms: (i) as-synthesized (black), (ii) methanol-exchanged (red) and (iii) activated at 90 °C (blue).

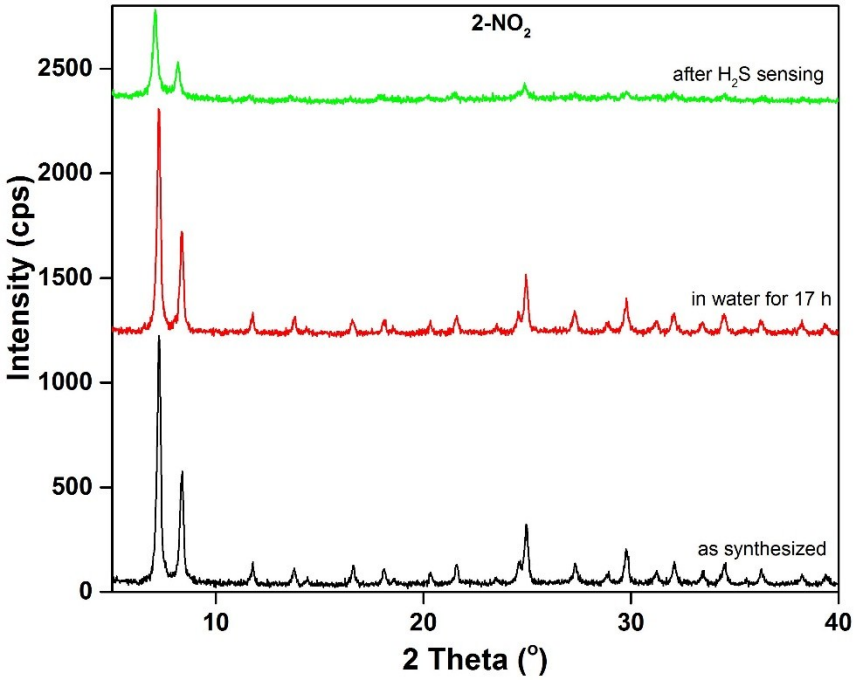

Figure S10. XRPD patterns of **2-NO_2** compound in water (red) and after H_2S sensing experiment (green).

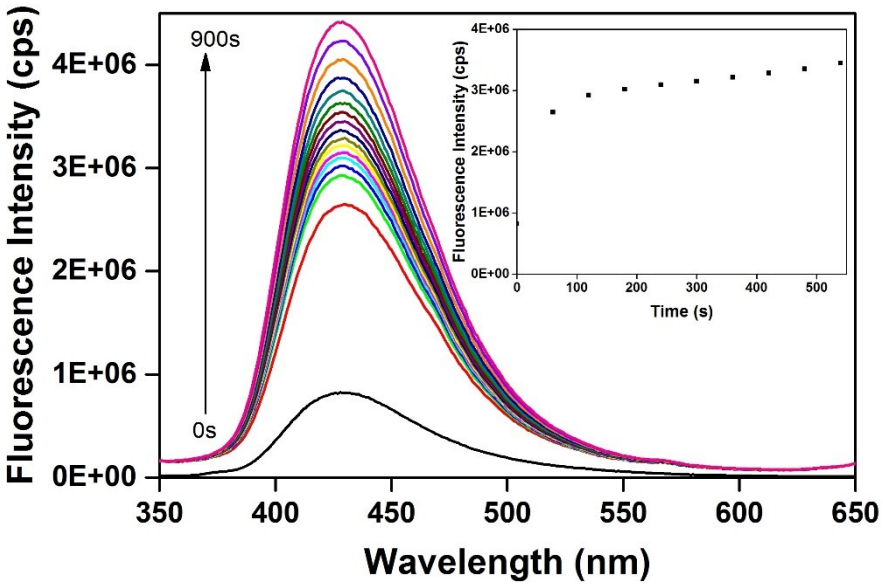

Figure S11. Fluorescence turn-on response of Zr-UiO-66-N_3 towards addition of NaHS at a regular time interval (60 s) up to 900 s. Inset: Time-dependence of the emission intensity at 429 nm.

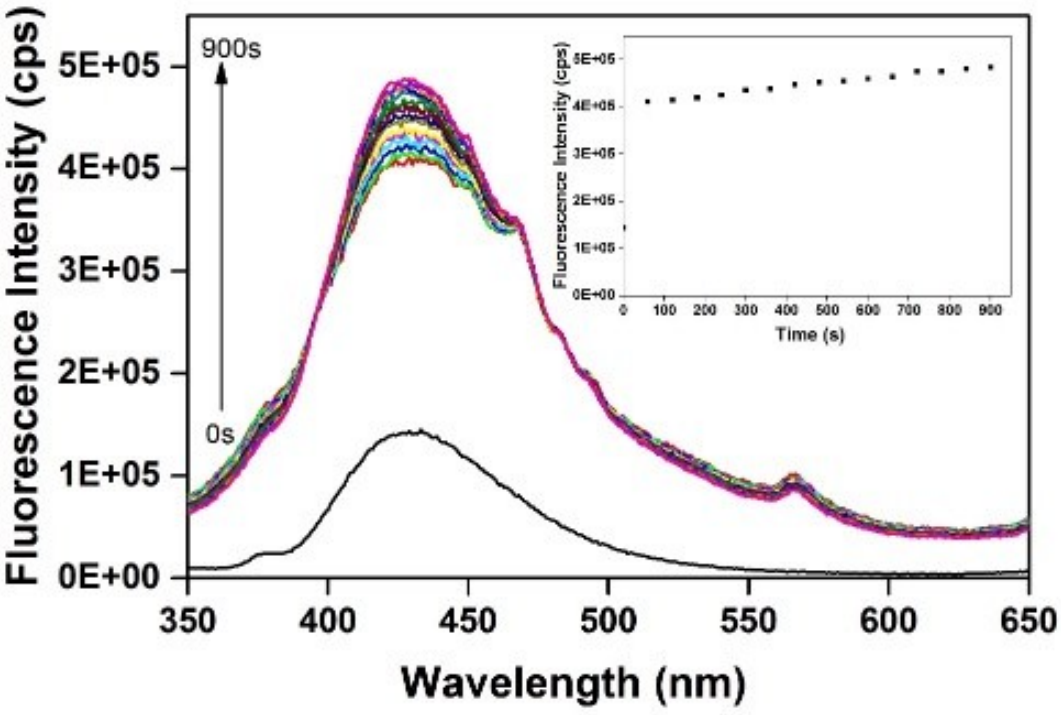

Figure S12. Fluorescence turn-on response of Zr-UiO-66-NO_2 towards addition of NaHS at a regular time interval (60 s) up to 900 s. Inset: Time-dependence of the emission intensity at 429 nm.

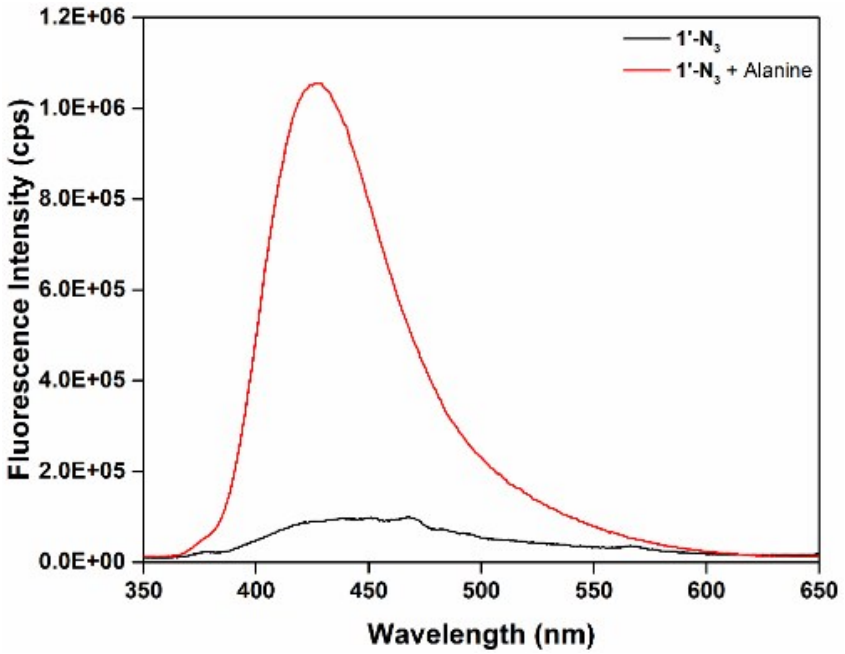

Figure S13. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of alanine at 900 s.

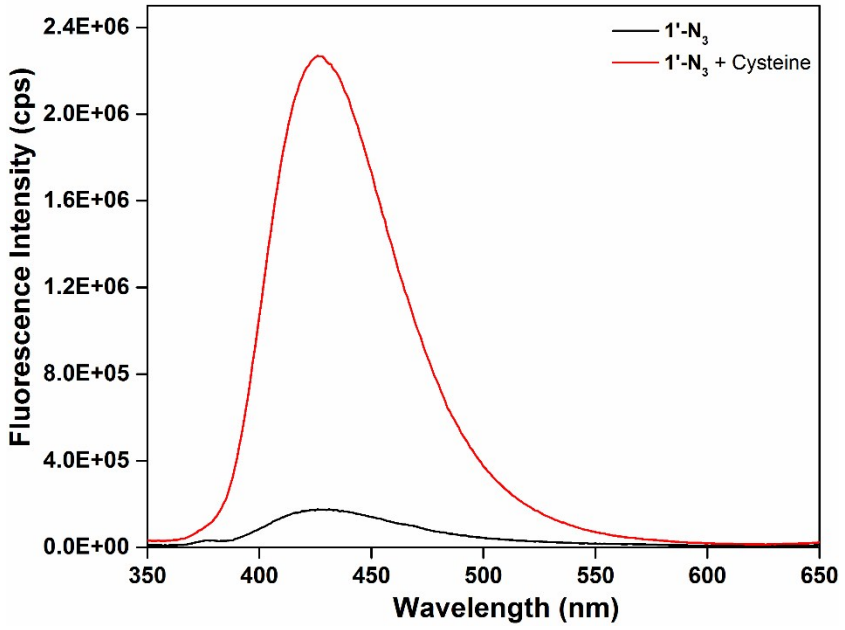

Figure S14. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of cysteine at 900 s.

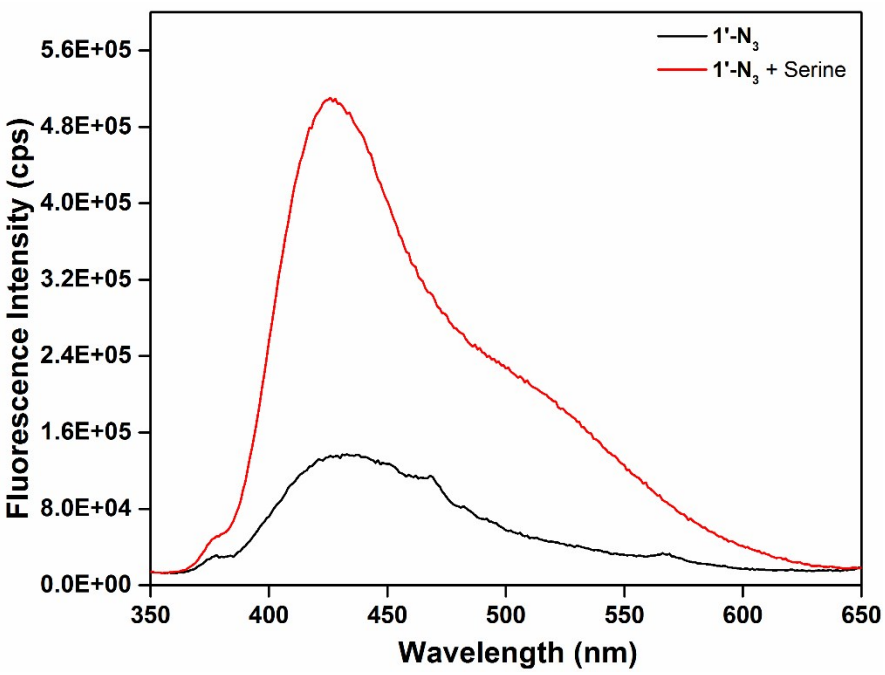

Figure S15. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of serine at 900 s.

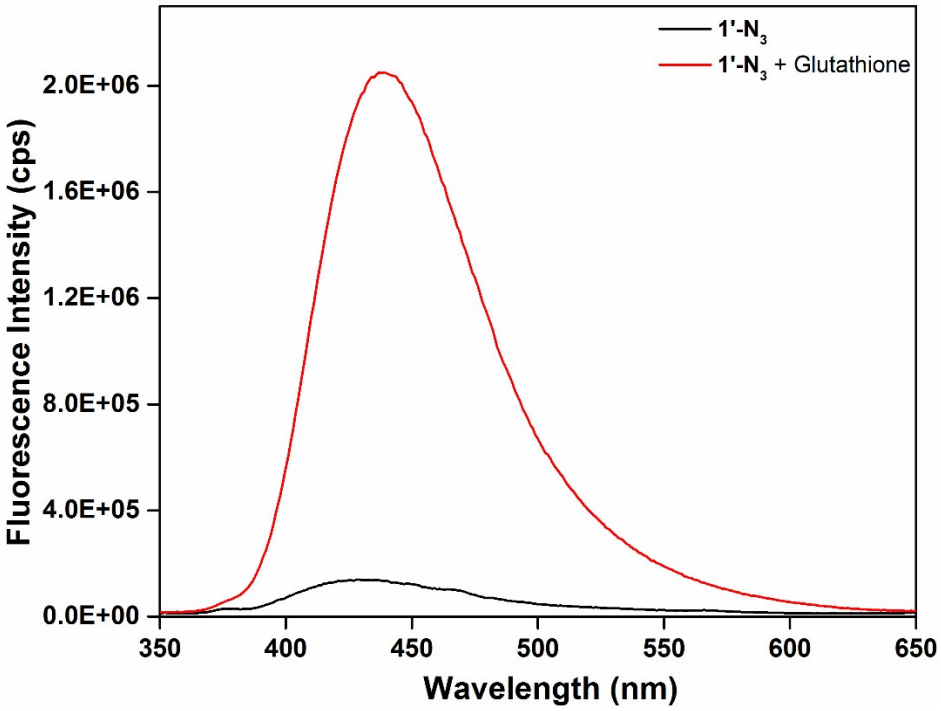

Figure S16. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of glutathione at 900 s.

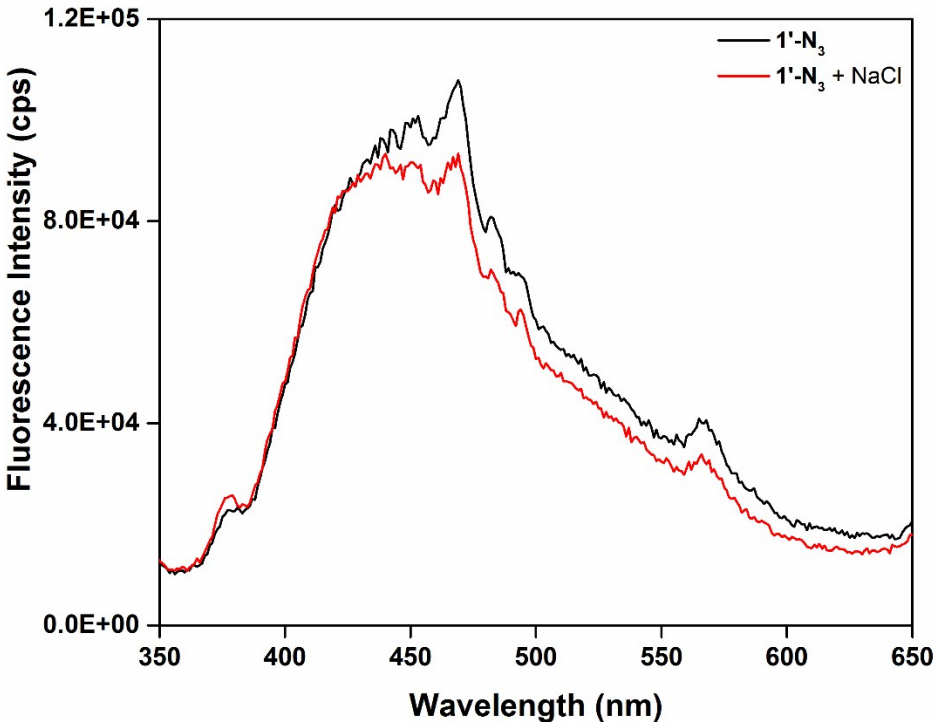

Figure S17. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of NaCl at 900 s.

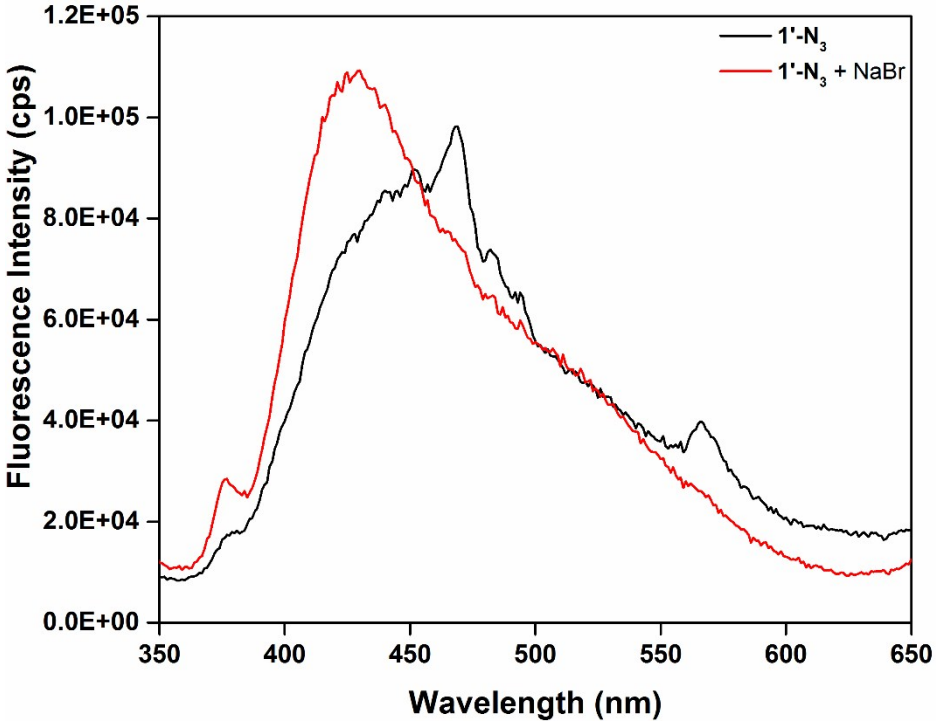

Figure S18. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of NaBr at 900 s.

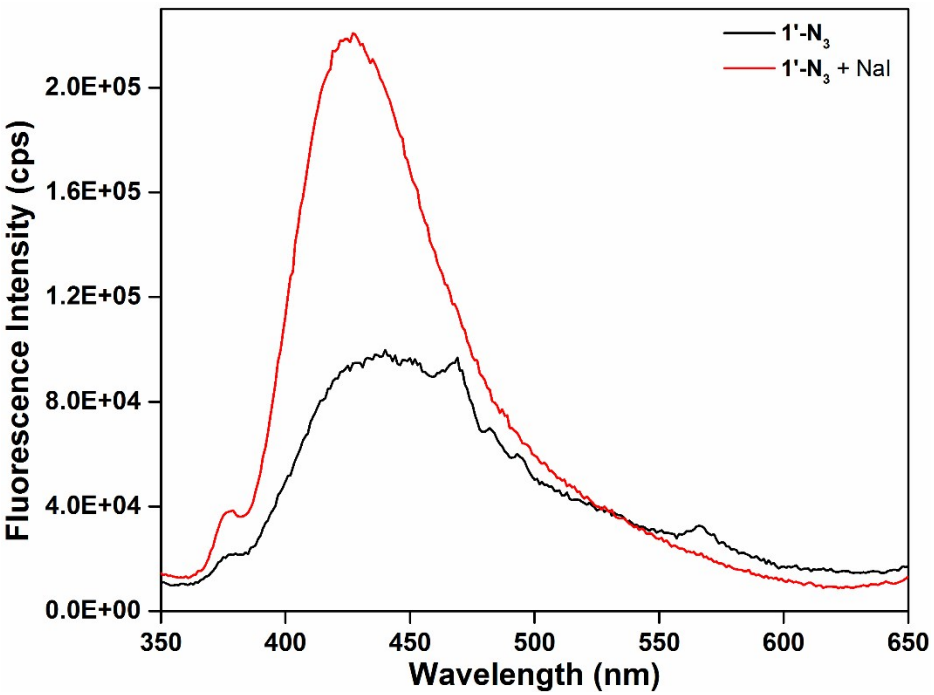

Figure S19. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of NaI at 900 s.

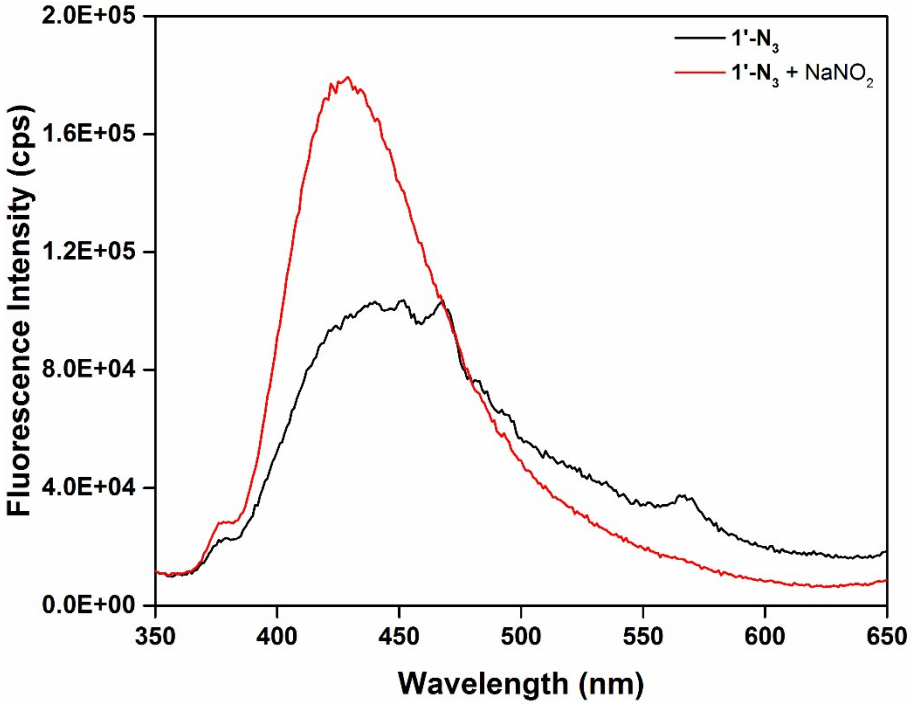

Figure S20. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of $NaNO_2$ at 900 s.

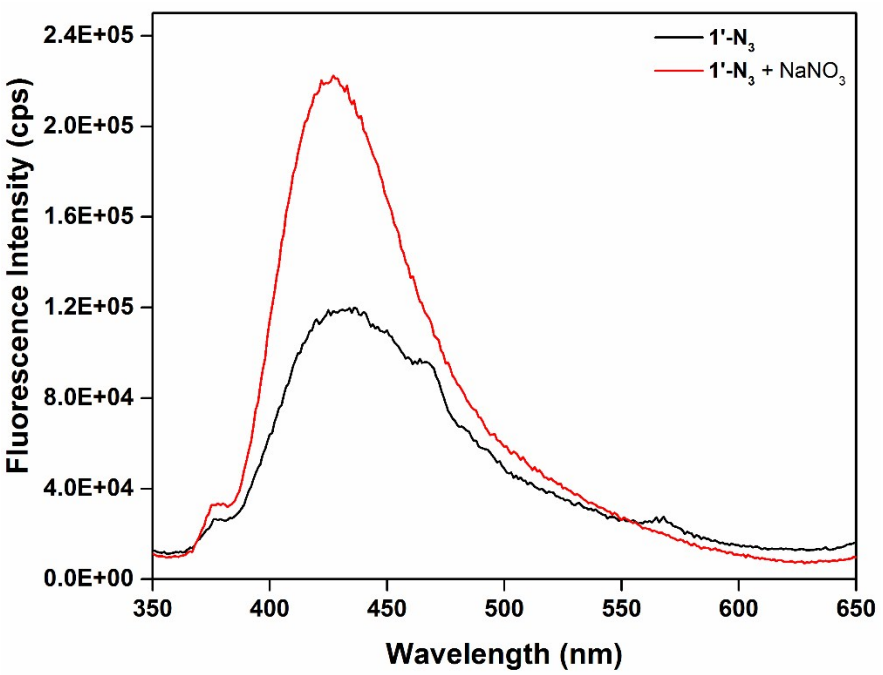

Figure S21. Fluorescence response of **1´-N_3** compound before (black) and after (red) addition of $NaNO_3$ at 900 s.

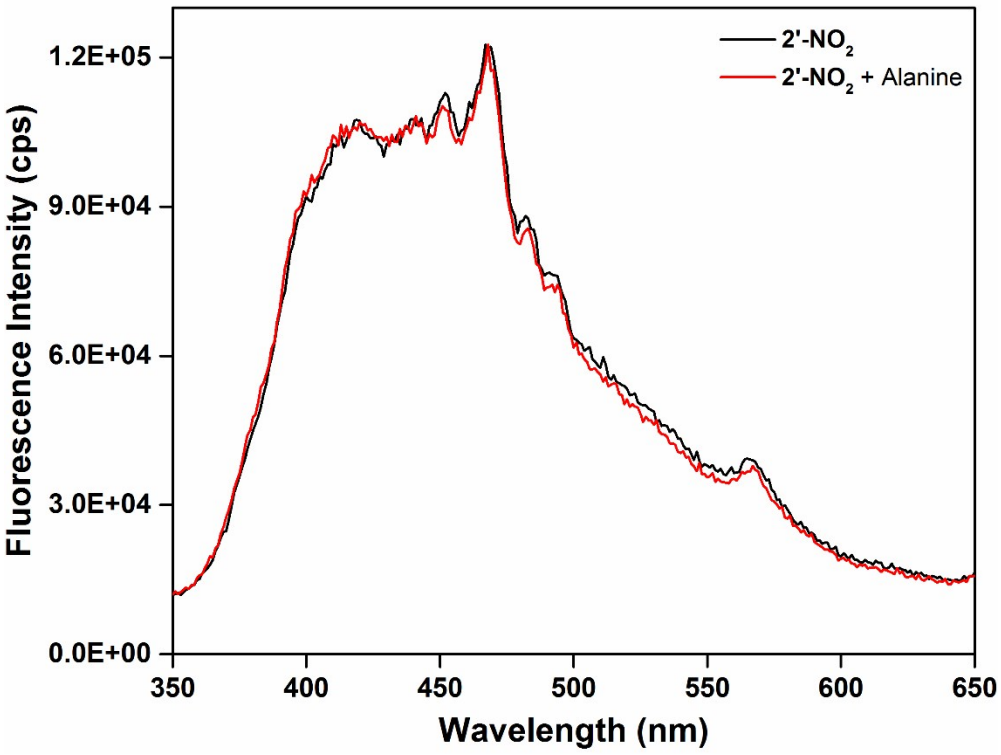

Figure S22. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of alanine at 900 s.

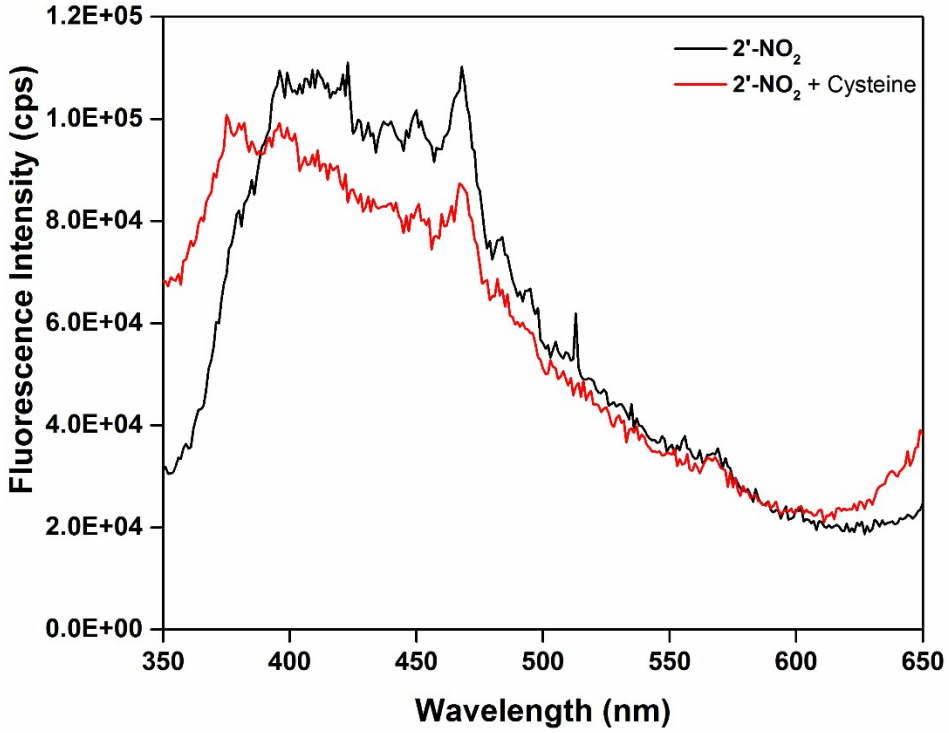

Figure S23. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of cysteine at 900 s.

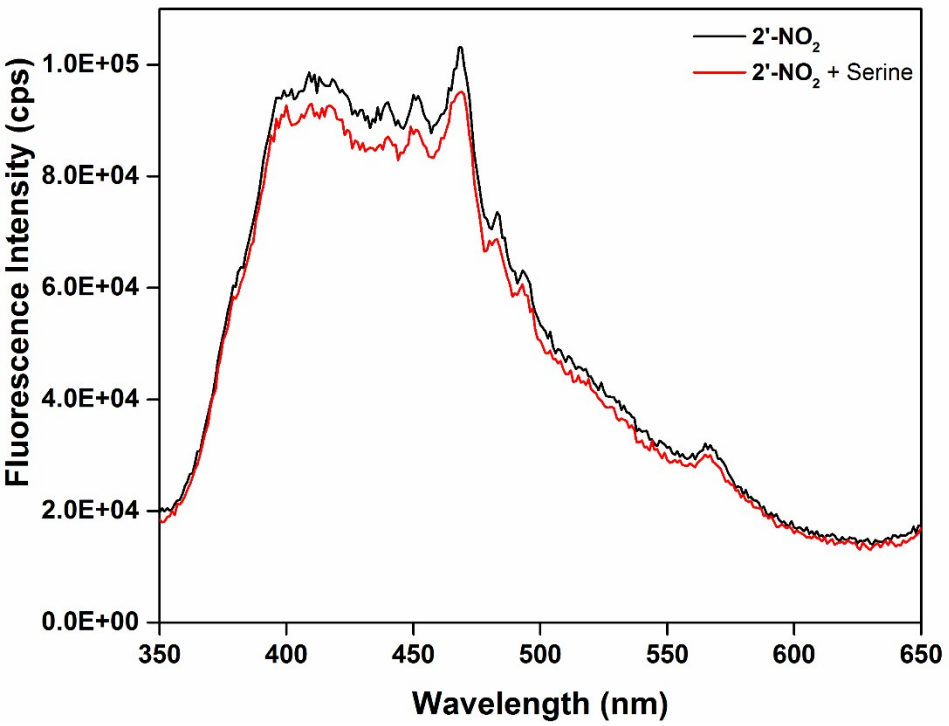

Figure S24. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of serine at 900 s.

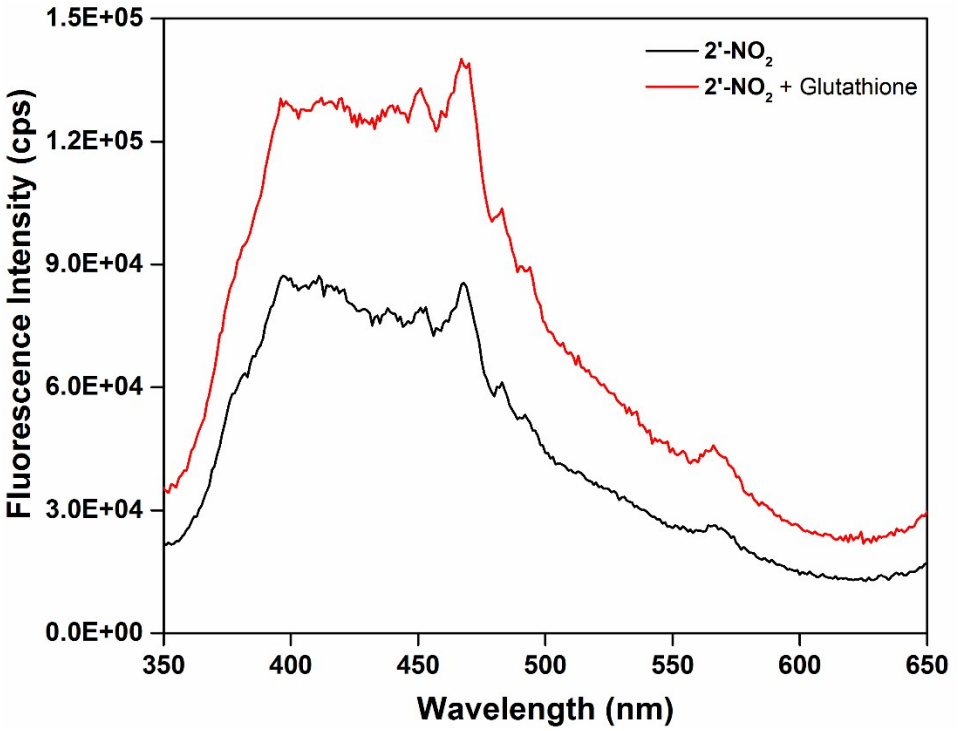

Figure S25. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of glutathione at 900 s.

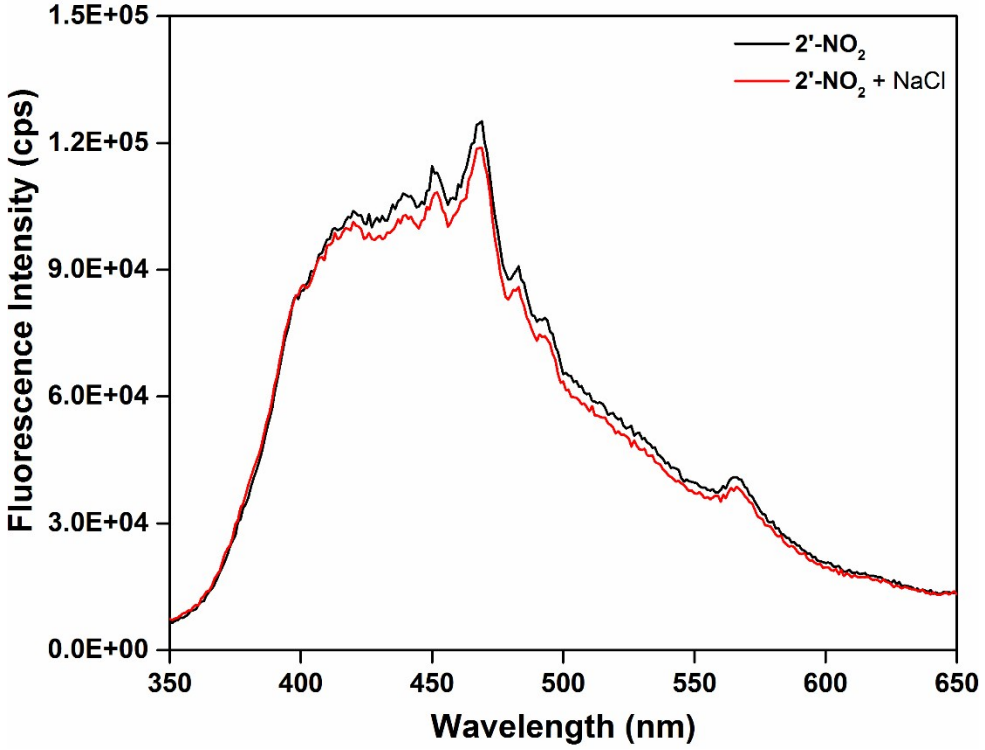

Figure S26. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of NaCl at 900 s.

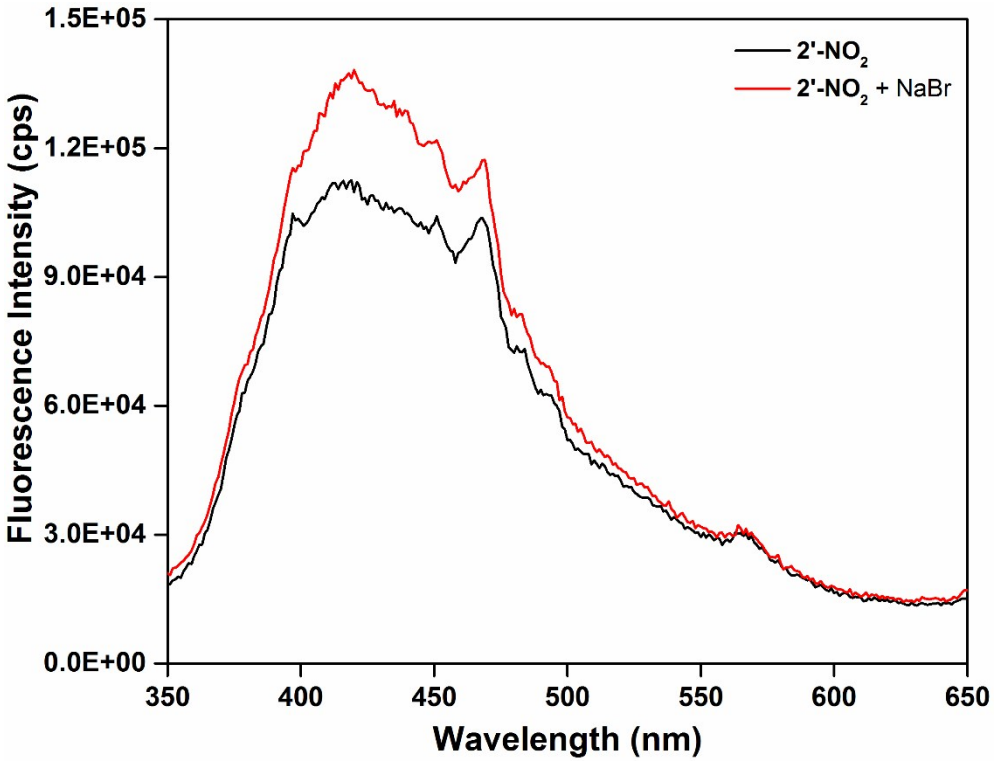

Figure S27. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of NaBr at 900 s.

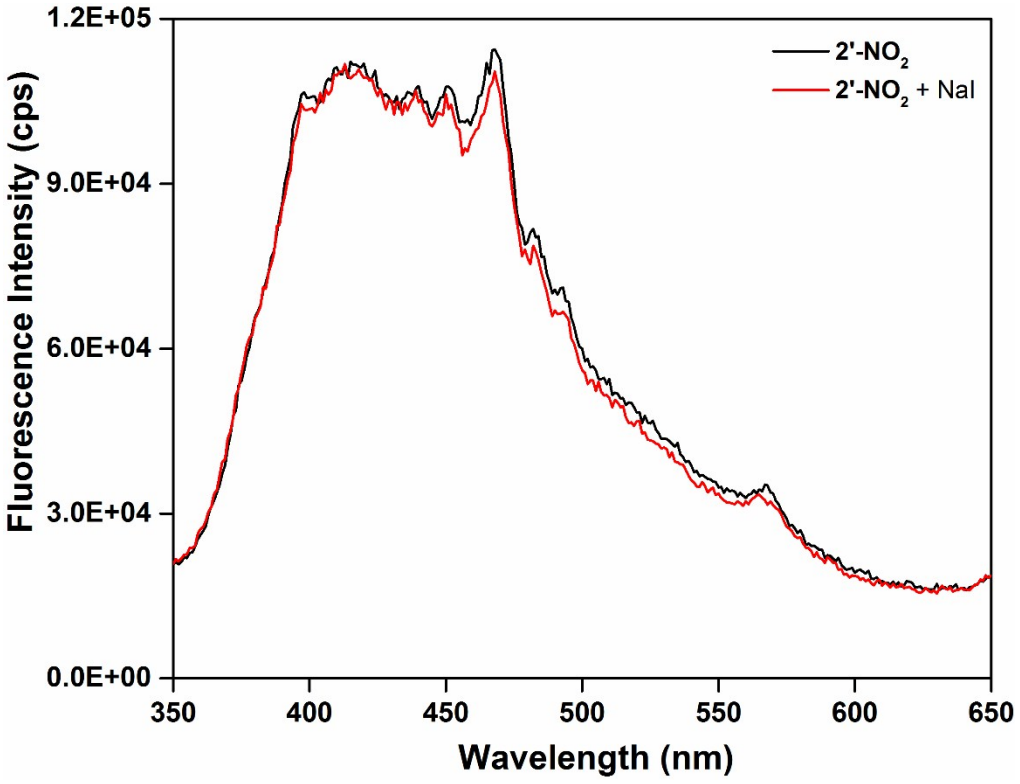

Figure S28. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of NaI at 900 s.

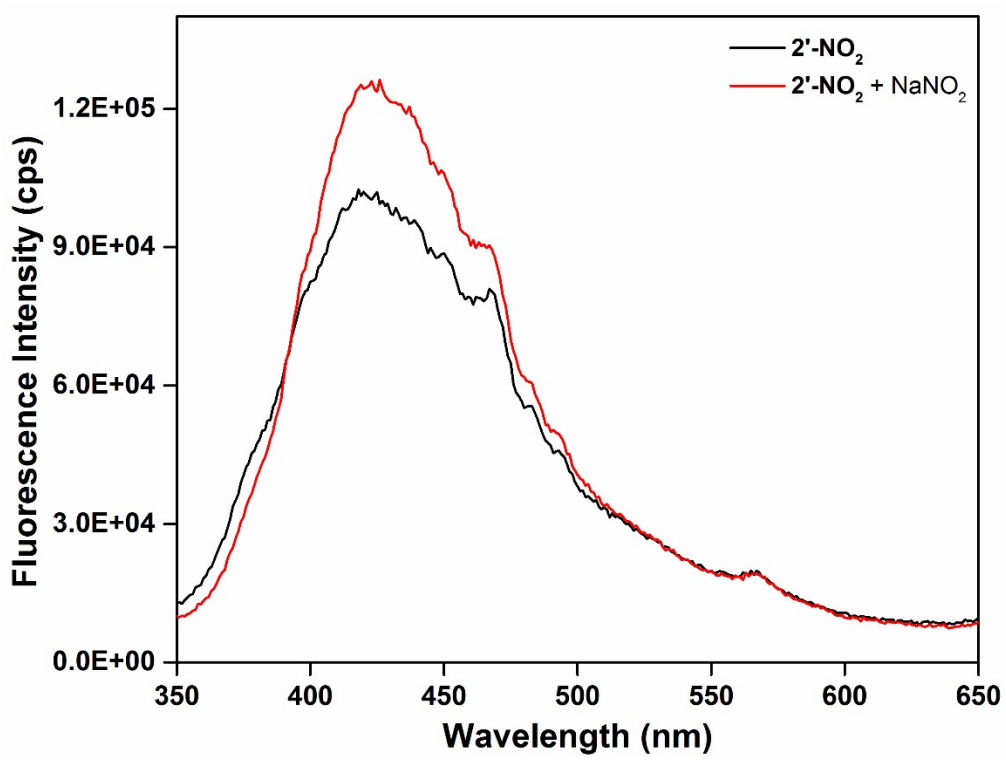

Figure S29. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of $NaNO_2$ at 900 s.

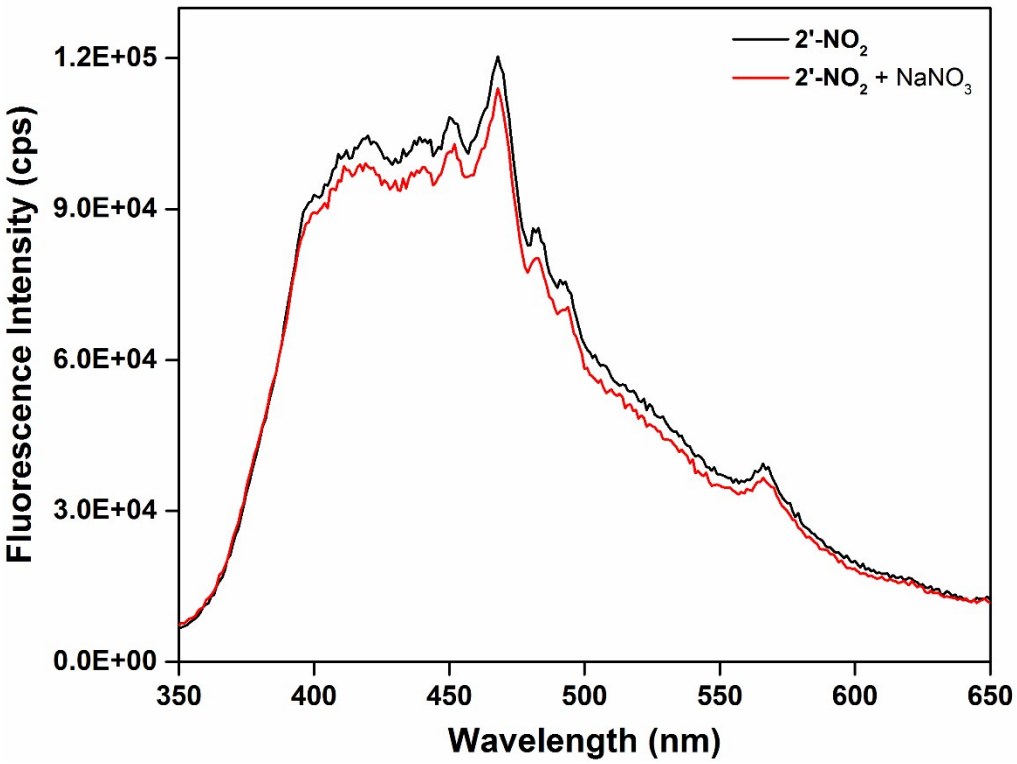

Figure S30. Fluorescence response of **2´-NO_2** compound before (black) and after (red) addition of $NaNO_2$ at 900 s.

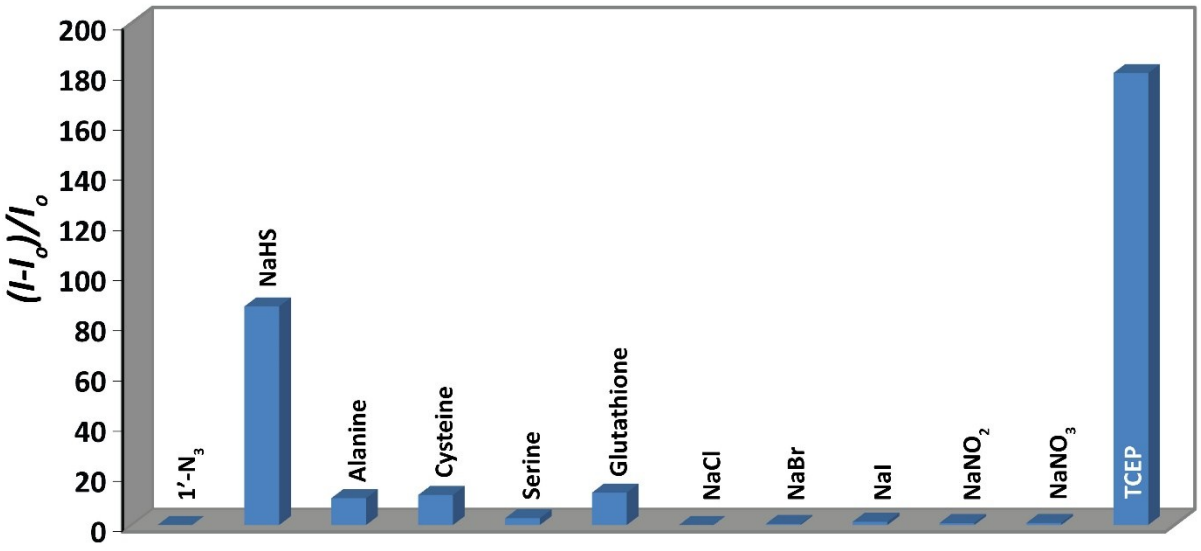

Figure S31. Relative fluorescence response of **1′-N_3** towards TCEP (10 equivalents per azide group) after 900 s of analyte addition.

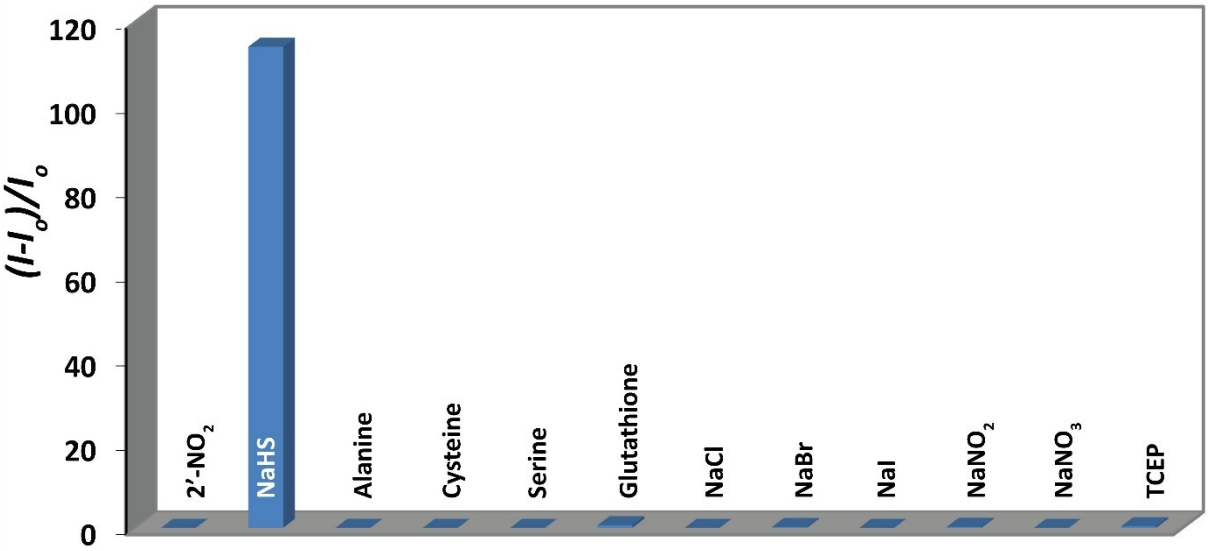

Figure S32. Relative fluorescence response of **2′-NO_2** towards TCEP (10 equivalents per azide group) after 900 s of analyte addition.

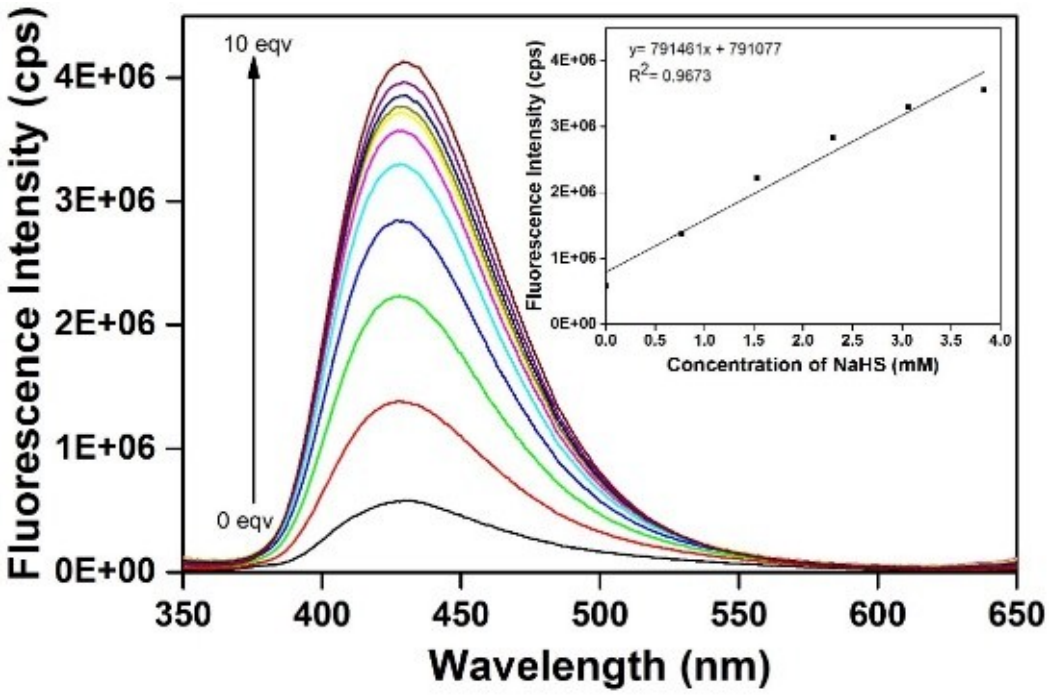

Figure S33. Fluorescence response of Zr-UiO-66-N_3 with increasing concentrations of NaHS. All the experiments were carried out in HEPES buffer (10 mM, pH 7.4).

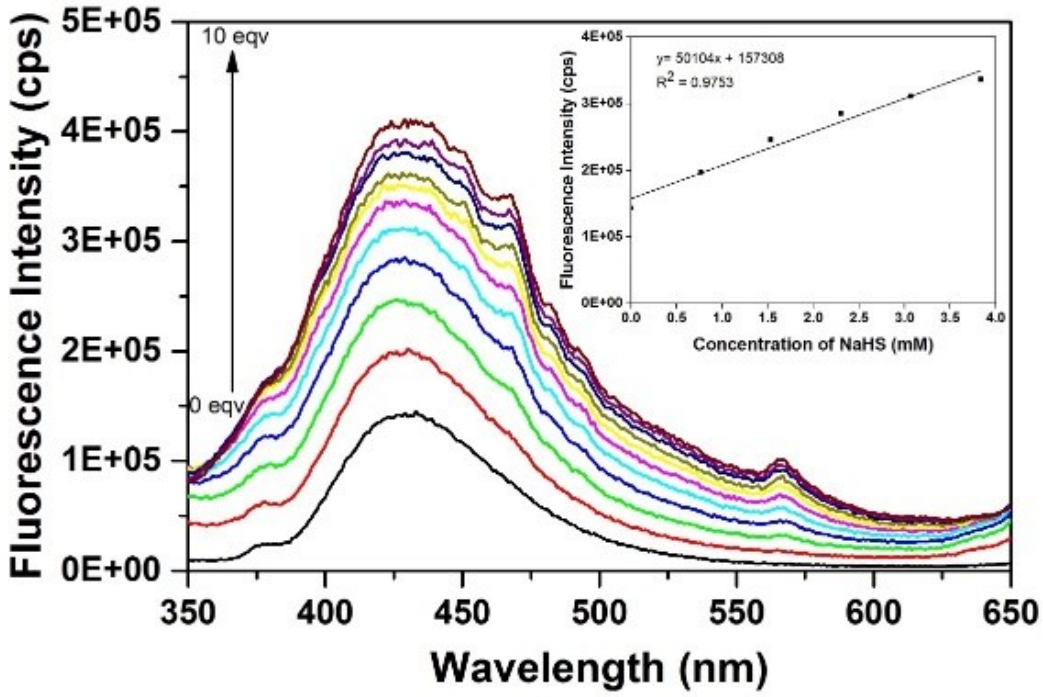

Figure S34. Fluorescence response of Zr-UiO-66-NO_2 with increasing concentrations of NaHS. All the experiments were carried out in HEPES buffer (10 mM, pH 7.4).

Recyclability test for 1′-N_3:

In order to investigate the recyclability of **1′-N_3**, the material was recovered by centrifugation after every fluorescence titration experiment with 10 equivalents of NaHS and washed with water. The material recovered after the first cycle of use displayed a strong fluorescence emission before the addition of NaHS (λ_{ex} = 334 nm) and almost negligible response towards NaHS was observed after the addition of NaHS (Figure S35). After the treatment with NaHS (during first cycle of use), the azide functional group of the material is permanently reduced to amine, which resulted in strong fluorescence emission before the addition of NaHS (during the second cycle of use). The same trend was also observed during the third cycle of fluorescence titration experiment. Thus, the material exhibited poor recyclability.

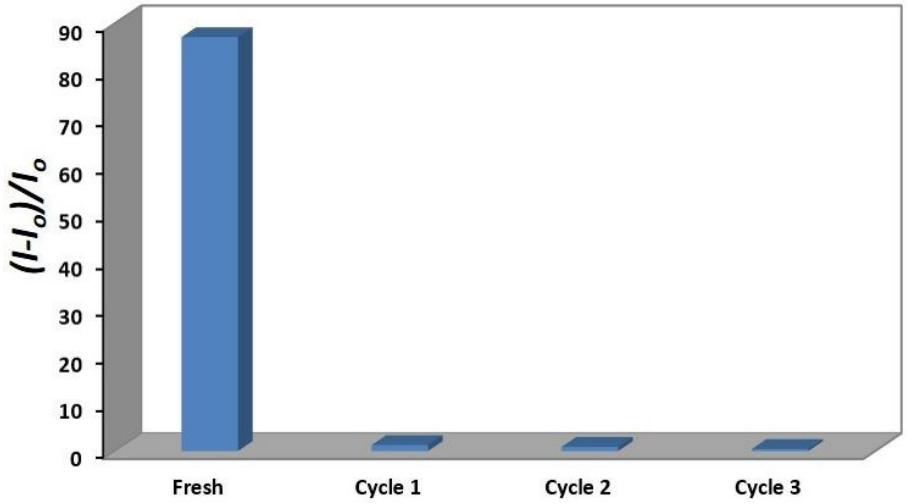

Figure S35. Recyclability test for turn-on response of probe **1′-N_3** towards NaHS.

Table S1. Unit cell parameters of as-synthesized **1-N_3** and **2-NO_2** compounds having cubic unit cells. The values are compared with those of the previously reported Ce-UiO-66 and Ce-UiO-66-NO_2 compounds.[1]

Compound	*a* (Å)	*V* (Å^3)
1-N_3	21.492(12)	9927.5(6)
1-NO_2	21.464(7)	9889.4(13)
Ce-UiO-66	21.4727(3)	9900.6(4)
Ce-UiO-66-NO_2	21.5194(2)	-

Table S2. Specific BET surface areas and micropore volumes of thermally activated **1′-N_3** and **2′-NO_2** compounds. The values are compared with those of the previously reported Ce-UiO-66 and Ce-UiO-66-X compounds.[1]

Compound	BET Surface Area (m^2 g^{-1})	Micropore Volume (cm^3 g^{-1})
1-N_3	835	0.44
1-NO_2	819	0.43
Ce-UiO-66	1282	0.50
Ce-UiO-66-F	1075	0.42
Ce-UiO-66-CH_3	985	0.39
Ce-UiO-66-Cl	770	0.31
Ce-UiO-66-NO_2	727	0.29

Table S3. Comparison of the repose time, detection limit and analyte used for H_2S detection for MOFs reported till date.

Sl. No.	MOF	Response time (s)	Detection Limit (μM)	Analyte	Ref.
1	Ce-UiO-66-N_3	760	12.2	NaSH	Our Work
2	Ce-UiO-66-NO_2	760	34.84	NaSH	Our Work
3	Zr-UiO-66-N_3	180	176.7	NaSH	
4	Zr-UiO-66-NO_2	480	95.4	NaSH	
5	IRMOF-3-N_3	< 120	28.3	NaSH	2
6	Zr-UiO-66-NO_2	≈ 460	188	Na_2S	3
7	Zr-UiO-66-N_3	180	118	Na_2S	4
8	MN-ZIF-90	-	-	-	5
9	Al-TCPP-Cu	-	-	-	6

References:

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