Electronic Supplementary Material (ESI) for Dalton Transactions
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Supplementary Information For:

A Dual Functional MOF-Based Fluorescent Sensor for Intracellular Phosphate and Extracellular 4-Nitrobenzaldehyde

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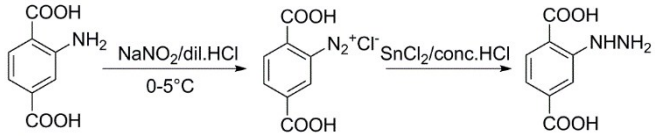
Synthesis of $H_2BDC\text{-}N_2H_3$ ligand:

The synthesis of the $H_2BDC\text{-}N_2H_3$ ligand involves two steps (Scheme S1). It was synthesized by using 2-amino-1,4-benzenedicaroxylic acid ($H_2BDC\text{-}NH_2$) as the starting material.

First step: $H_2BDC\text{-}NH_2$ ligand (1.81 g, 10 mmol) was dissolved in 20 mL of conc. HCl and stirred at 0 °C until complete dissolution is achieved. After that an aqueous solution of $NaNO_2$ (0.70 g, 10.14 mmol in 5 mL water) was added slowly to the mixture and kept under stirring conditions at 0 °C for 2 h.

Second step: After completion of 2 h, a mixture of $SnCl_2{\cdot}2H_2O$ (4.50 g, 19.94 mmol) in 15 mL conc. HCl was added slowly to the solution obtained in the first step. The resulting mixture was stirred for 3 h at room temperature. The precipitate was filtered and repeatedly washed with water until neutral pH is obtained. The pale yellow colored product was finally washed with ethanol (2 × 3 mL) and diethyl ether (2 × 3 mL), and dried in a conventional oven at 60 °C for 4 h. Yield: 1.18 g (6.0 mmol, 60%). ^{1}H-NMR (600 MHz, DMSO-d_6): δ = 8.04 (s, 1H), 7.90 (s, 1H), 7.80 (d, 1H), 7.06 (d, 1H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 168.36, 166.58, 147.26, 135.79, 131.91, 120.42, 117.07, 114.63 ppm. ESI-MS (m/z): 195.0331 for $(M\text{-}H)^-$ ion (M = mass of $H_2BDC\text{-}N_2H_3$ ligand). In Figures S1-S3 (Supporting Information), the NMR and mass spectra for the $H_2BDC\text{-}N_2H_3$ ligand are shown.



Scheme S1. Reaction scheme for the preparation of $H_2BDC\text{-}N_2H_3$ ligand.

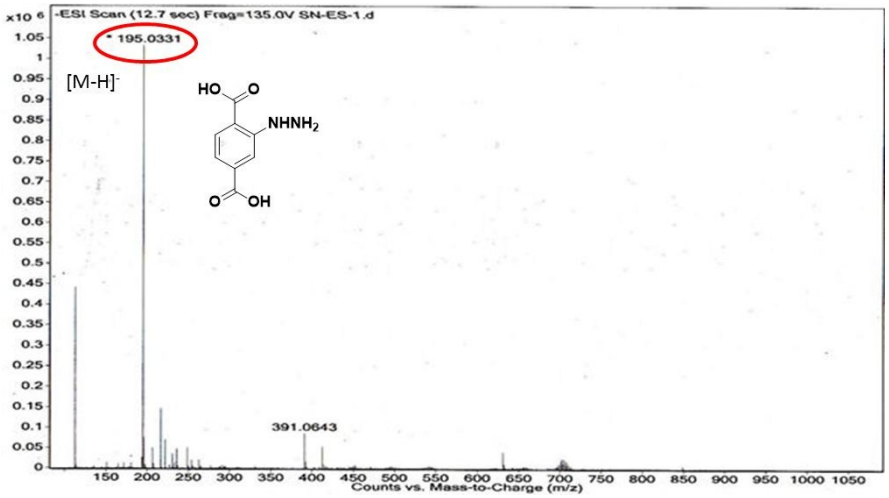


Figure S1. ESI-MS spectrum of the $H_2BDC\text{-}N_2H_3$ ligand in methanol. The spectrum shows m/z (negative ion mode) peak at 195.0331, which corresponds to $(M\text{-}H)^-$ ion (M = mass of $H_2BDC\text{-}N_2H_3$ ligand).

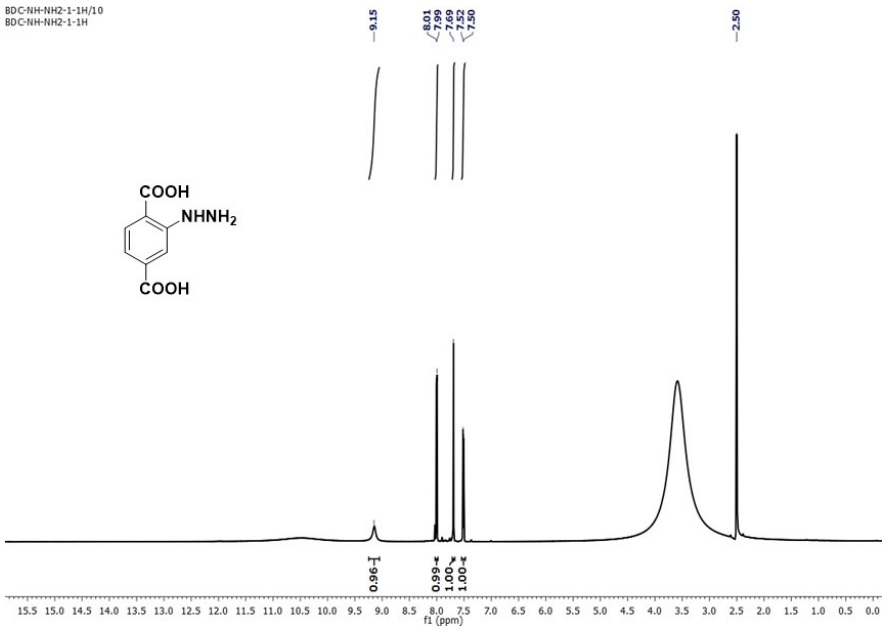


Figure S2. ^1H NMR spectrum of the $H_2BDC\text{-}N_2H_3$ ligand in DMSO-d_6.

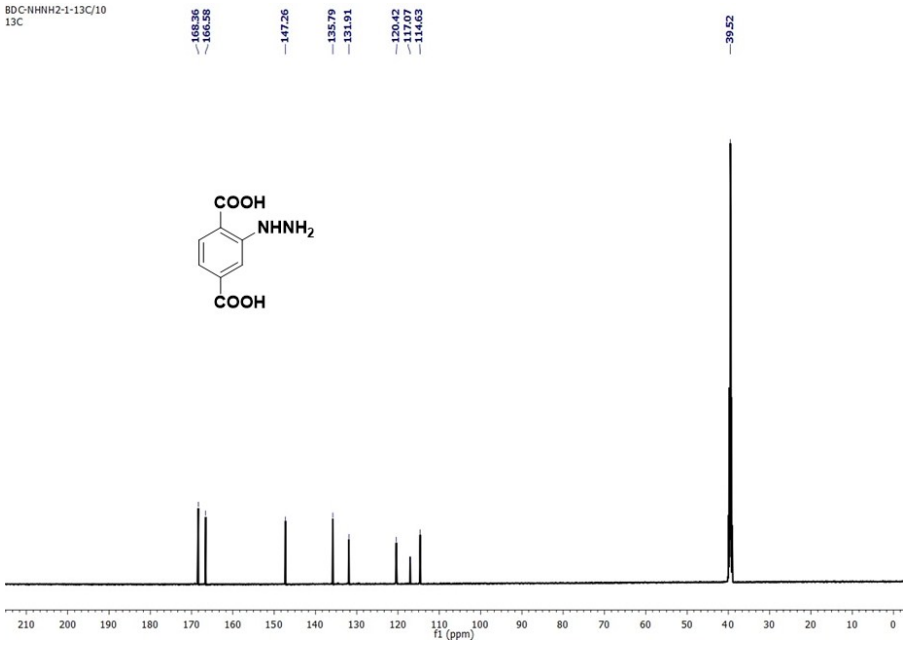


Figure S3. ^{13}C NMR spectrum of the $H_2BDC\text{-}N_2H_3$ ligand in DMSO-d_6.

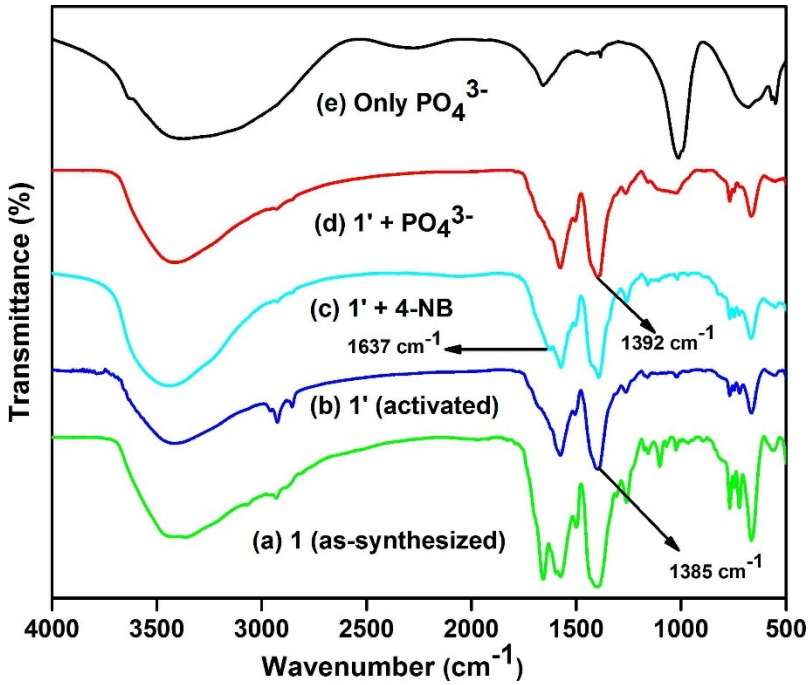


Figure S4. FT-IR spectra of (a) as-synthesized **1**, (b) activated **1′**, (c) **1′** after treatment with 4-NB, (d) **1′** after treatment with Na_3PO_4 (Zr/P = 0.6), and (e) only Na_3PO_4.

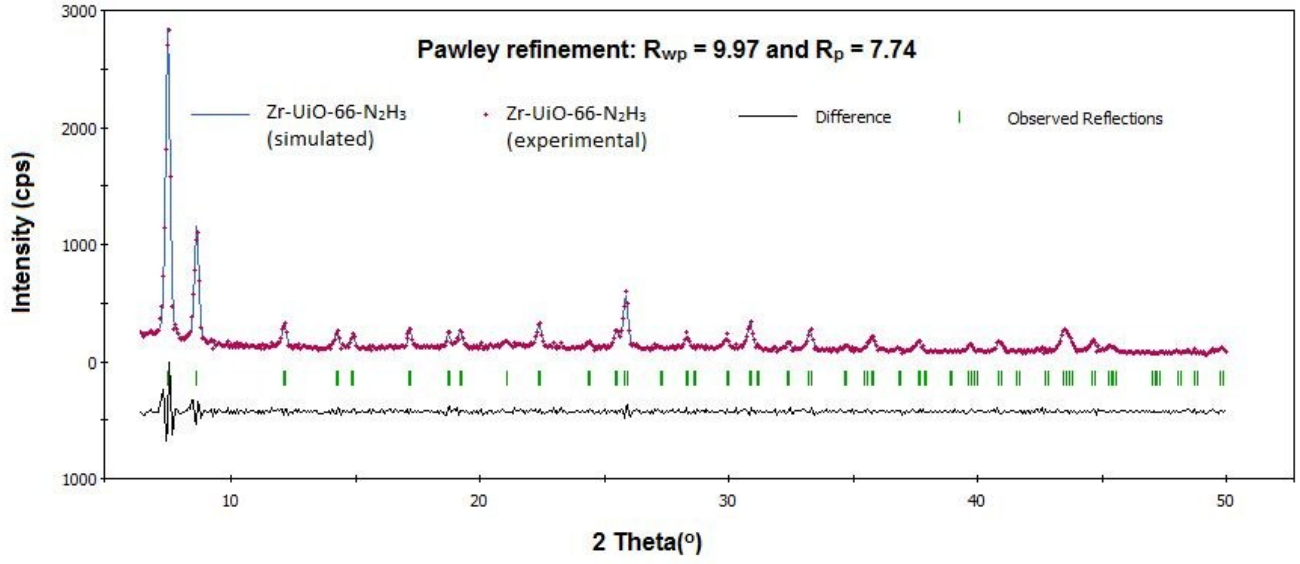


Figure S5. Pawley fit for the XRPD pattern of as-synthesized **1**. Blue lines and red dots denote calculated and observed patterns, respectively. The peak positions and difference plot are displayed at the bottom (R_{wp} = 9.97, R_p = 7.74).

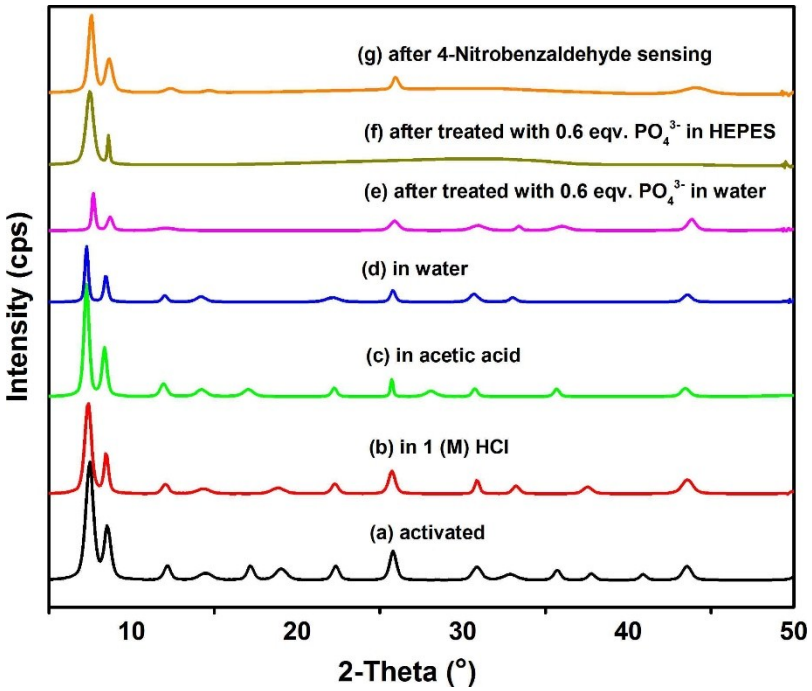


Figure S6. XRRD patterns of compound **1** in different forms: (a) activated, (b) **1′** after treatment with 1(M) HCl, (c) **1′** after treatment with acetic acid, (d) **1′** after treatment with water, (e) **1′** after phosphate sensing experiment in water, (f) **1′** after phosphate sensing experiment in HEPES (10 mM, pH = 7.4) and (g) **1′** after 4-NB sensing experiment.

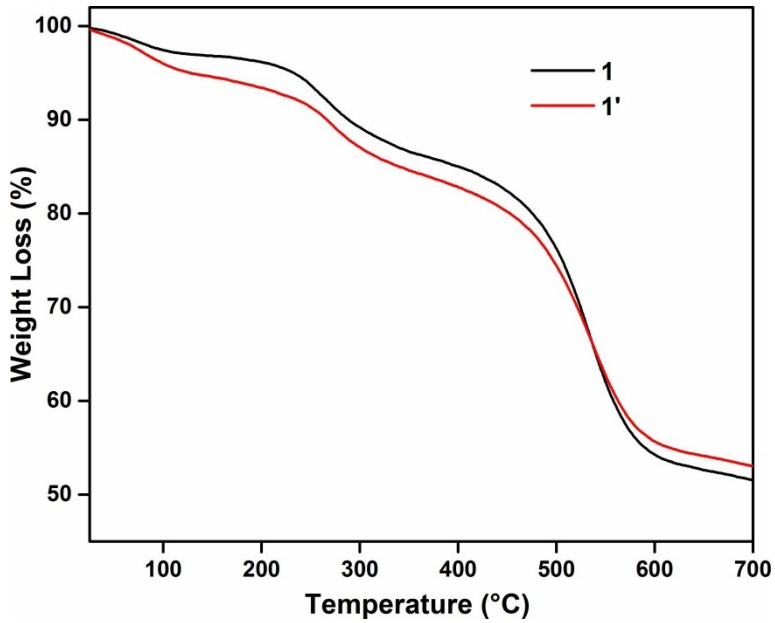


Figure S7. TG curves of as-synthesized **1** (black) and thermally activated **1′** (red) recorded in an air atmosphere in the temperature range of 25-700 °C with a heating rate of 10 °C min^{-1}.

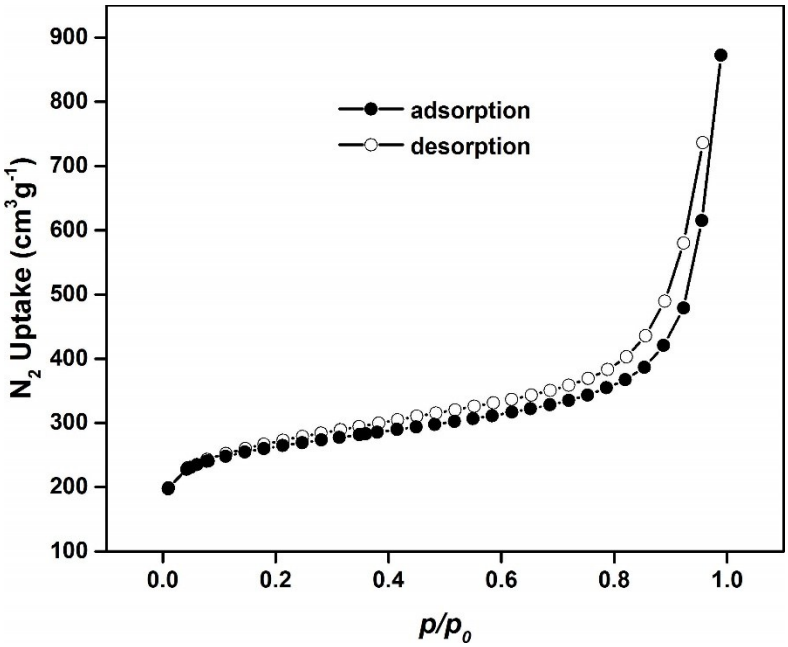


Figure S8. N_2 adsorption (black circles) and desorption (red circles) isotherms of **1′** measured at –196 °C.

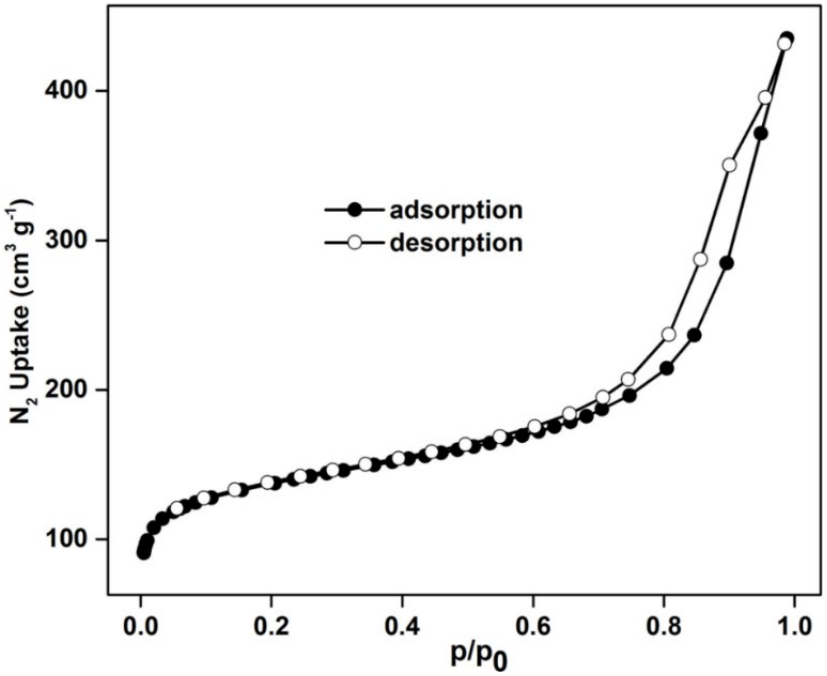


Figure S9. N_2 adsorption (solid circles) and desorption (empty circles) isotherms of **1′** recovered after the phosphate sensing experiment. The isotherms were measured at -196 °C.

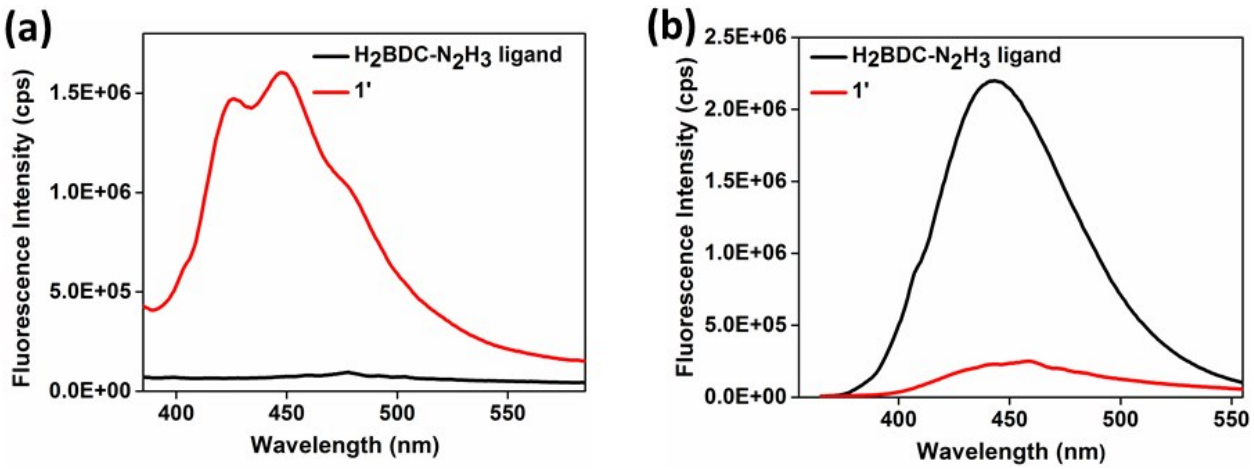


Figure S10. (a) Solid-state luminescence spectra of free $H_2BDC\text{-}N_2H_3$ ligand and **1′**. (b) Luminescence spectra of free $H_2BDC\text{-}N_2H_3$ ligand and **1′** in the aqueous medium.

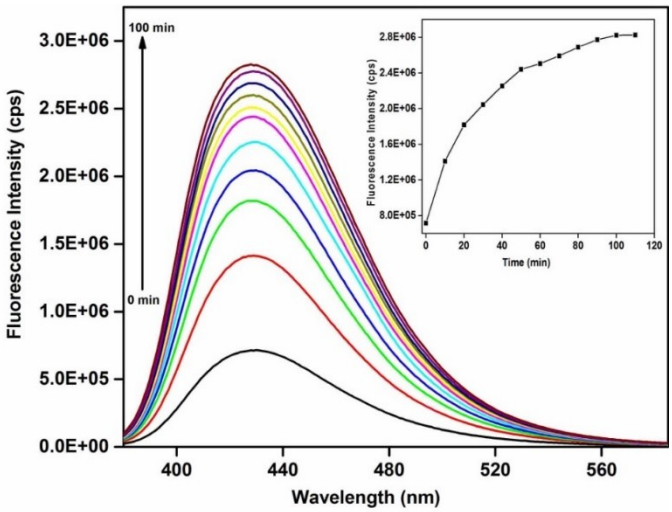


Figure S11. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer, pH = 7.4) with time upon the addition of 400 μL of 2 mM Na_3PO_4 solution (in 10 mM HEPES buffer, pH = 7.4).

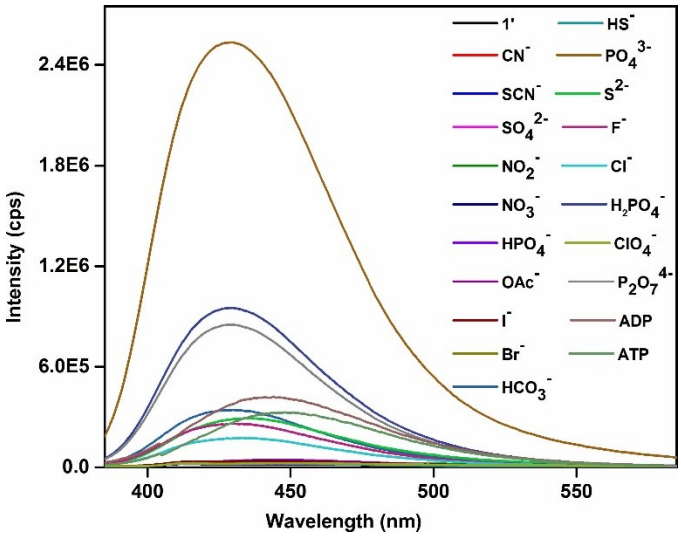


Figure S12. Enhancement of the fluorescence intensity of **1′** (suspended in water) with time upon the addition of 400 µL of 2 mM Na_3PO_4 solution (in water).

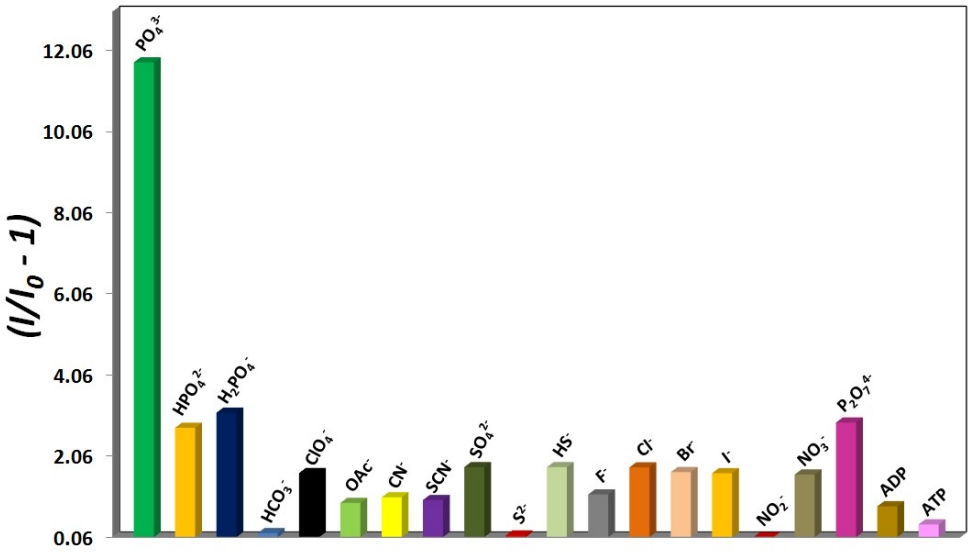


Figure S13. Change in the fluoresecnce intensity of the suspension of **1′** (in 10 mM HEPES buffer, pH = 7.4) upon the addition of the solutions of different anions. All the anions were added as HEPES buffer solutions.

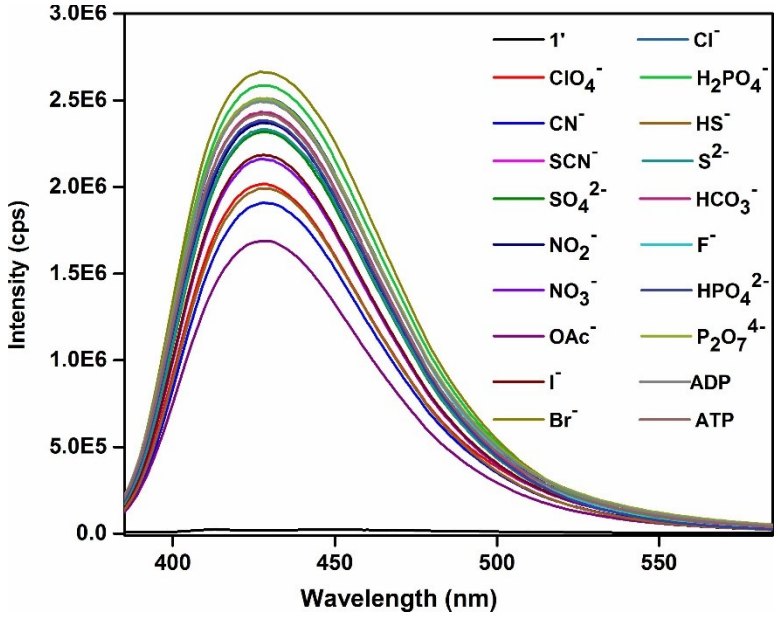


Figure S14. Enhancement of the fluorescence intensity of **1′** (suspended in water) with time upon the addition of 400 µL of 2 mM PO_4^{3-} solution (in water).

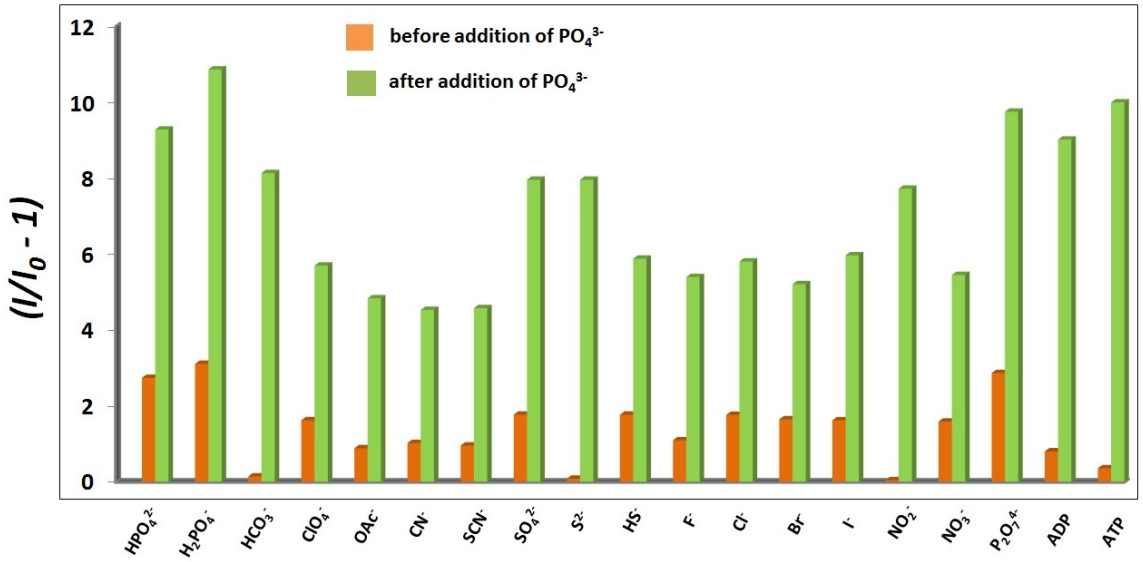


Figure 15. Change in the fluoresecnce intensity of the suspension of **1′** (in 10 mM HEPES buffer, pH = 7.4) upon the addition of PO_4^{3-} solution in the presence of other potentially competing anions. All the anions were added as HEPES buffer solutions.

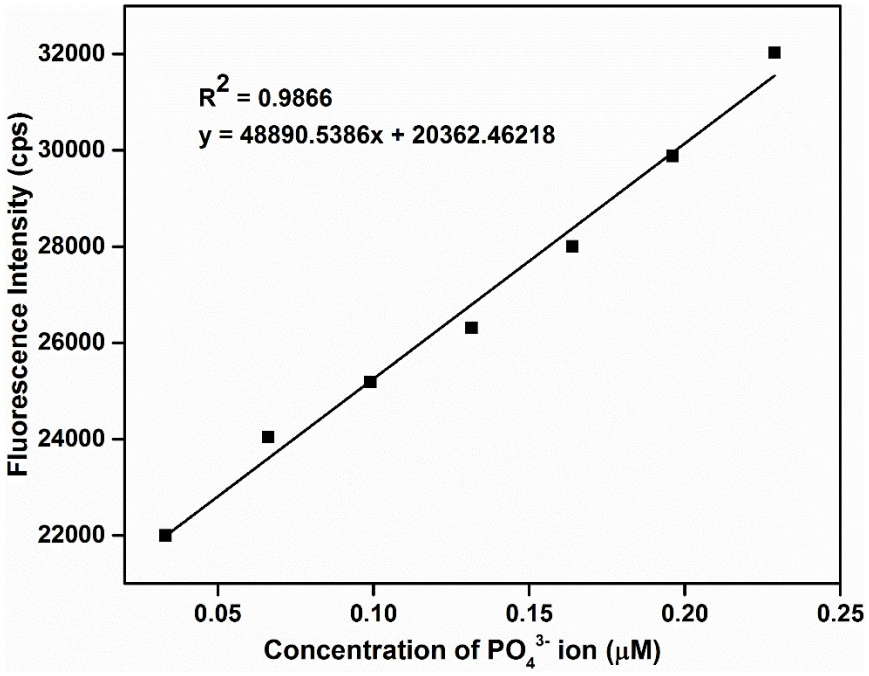


Figure S16. Change in the fluorescence intensity of **1′** as a function of concentration of PO_4^{3-} ion in water.

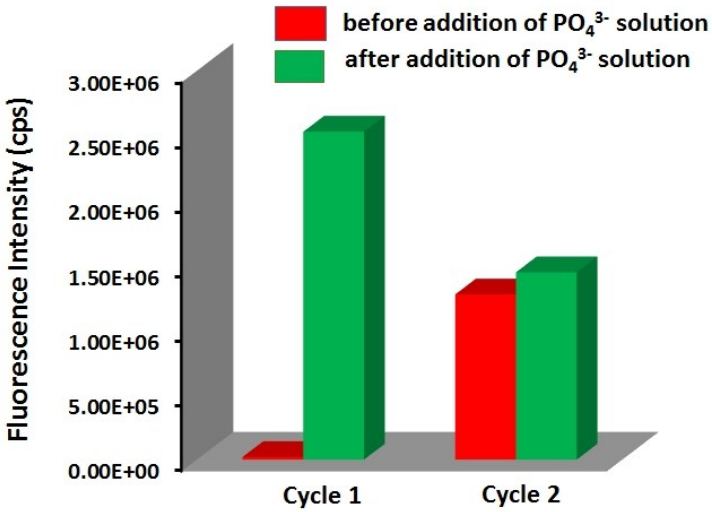


Figure S17. Recyclability test for the fluorescence *turn-on* response of the aqueous suspension of **1′** towards 2 mM PO_4^{3-} solution.

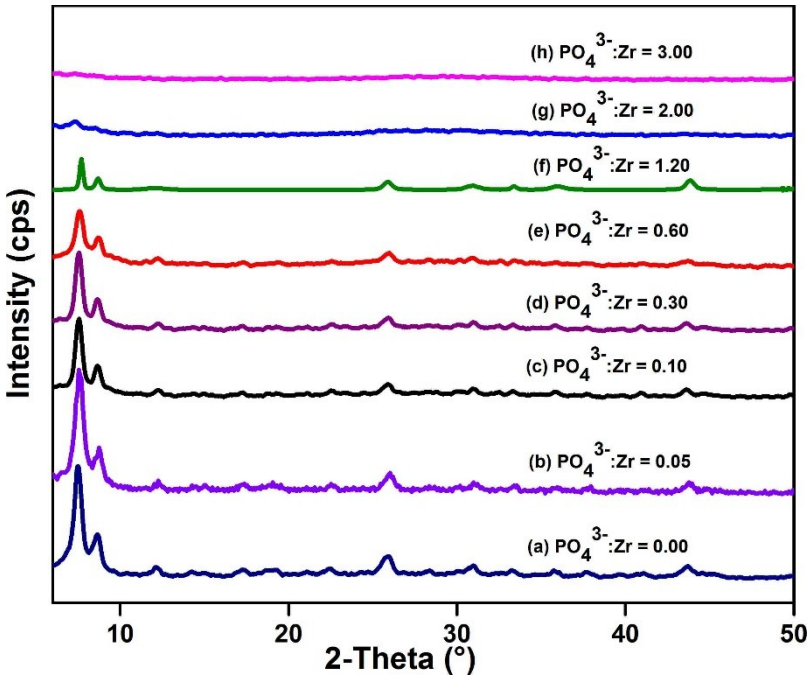


Figure S18. XRRD patterns of compound **1′** after treatment with different molar ratio of phosphate with respect to zirconium: **1′** after treatment with (a) PO_4^{3-}:Zr = 0.00, (b) PO_4^{3-}:Zr = 0.05, (c) PO_4^{3-}:Zr = 0.10, (d) PO_4^{3-}:Zr = 0.30, (e) PO_4^{3-}:Zr = 0.60, (f) PO_4^{3-}:Zr = 1.20, (g) PO_4^{3-}:Zr = 2.00 and (h) PO_4^{3-}:Zr = 3.00.

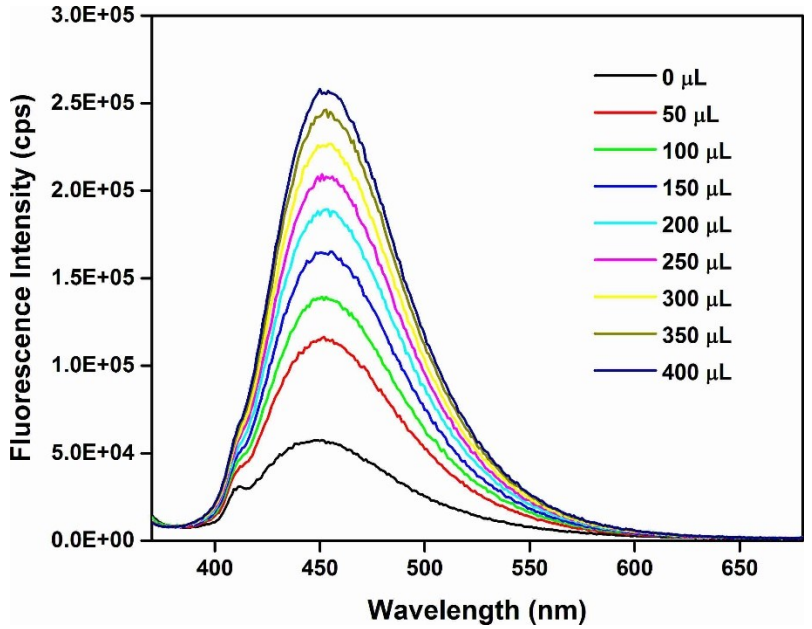


Figure S19. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer at pH = 3.4) upon gradual addition of 400 µL of 2 mM aqueous solution of PO_4^{3-} ion (λ_{ex} = 360 nm, λ_{em} = 430 nm).

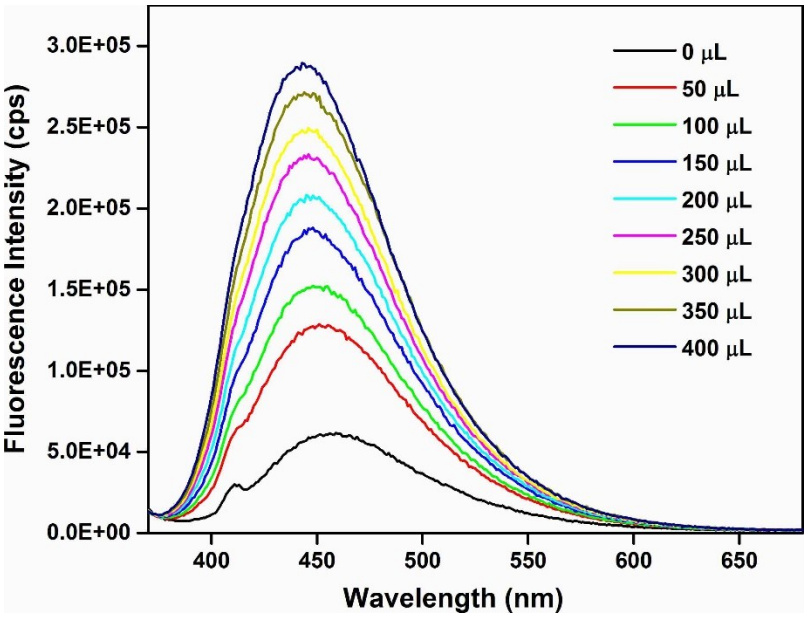


Figure S20. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer at pH = 5.4) upon gradual addition of 400 μL of 2 mM aqueous solution of PO_4^{3-} ion (λ_{ex} = 360 nm, λ_{em} = 430 nm).

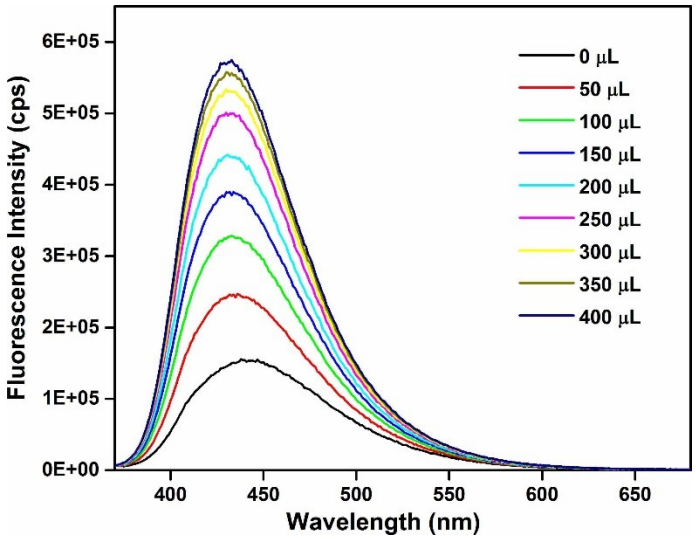


Figure S21. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer at pH = 7.4) upon gradual addition of 400 μL of 2 mM aqueous solution of PO_4^{3-} ion (λ_{ex} = 360 nm, λ_{em} = 430 nm).

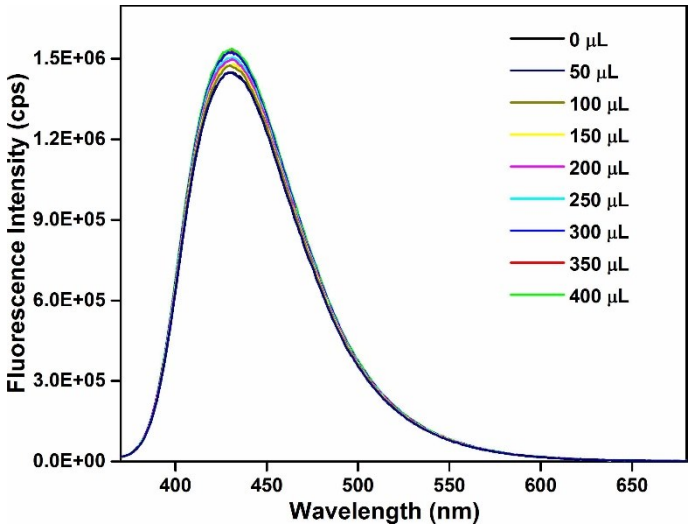


Figure S22. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer at pH = 9.4) upon gradual addition of 400 µL of 2 mM aqueous solution of PO_4^{3-} ion (λ_{ex} = 360 nm, λ_{em} = 430 nm).

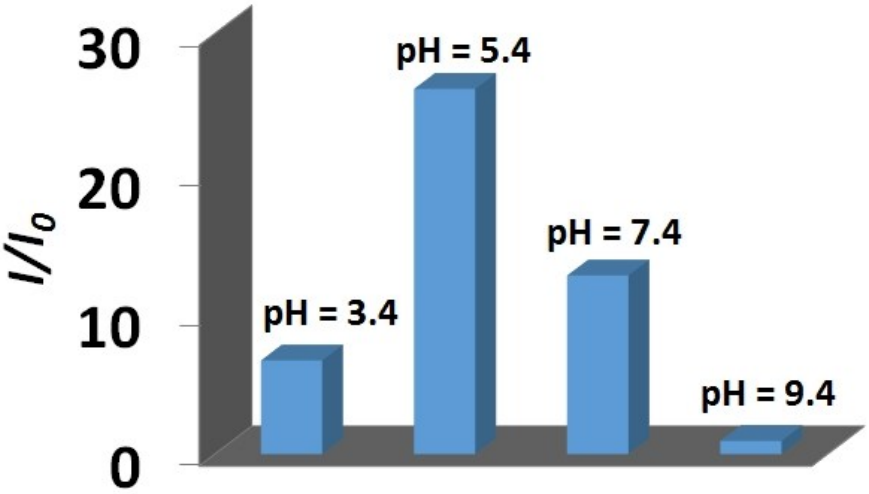


Figure S23. Change in the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer) at different pH values upon the addition of 400 µL of 2 mM Na_3PO_4 solution (in 10 mM HEPES buffer).

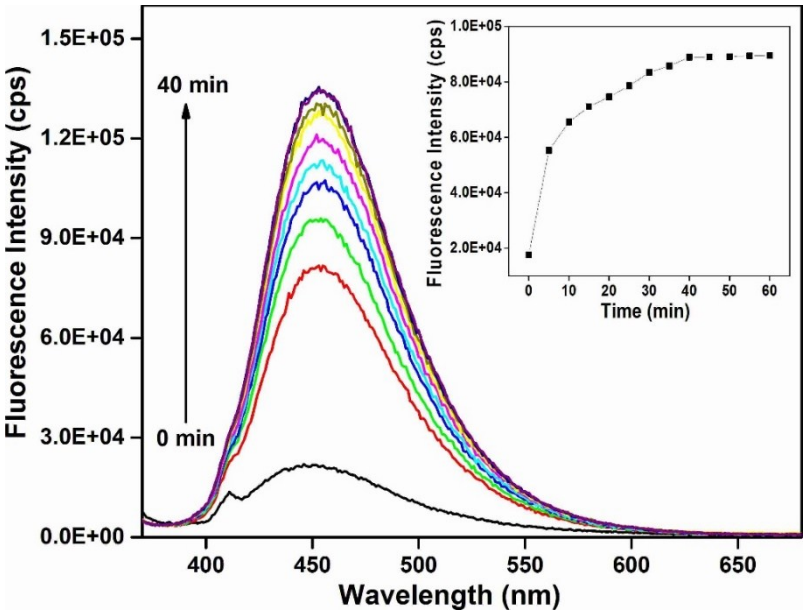


Figure S24. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer at pH = 3.4) with time upon the addition of 400 μL of 2 mM Na_3PO_4 solution (in 10 mM HEPES buffer pH = 3.4).

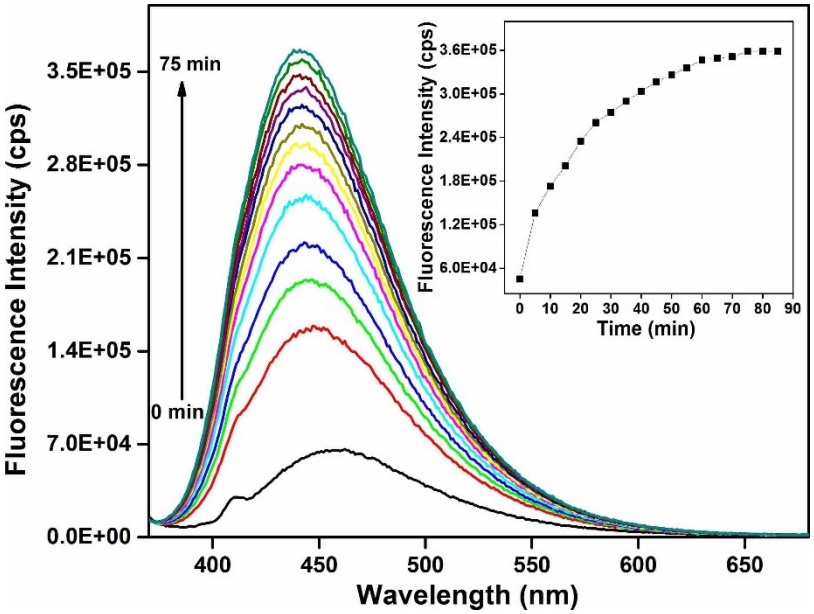


Figure S25. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer at pH = 5.4) with time upon the addition of 400 μL of 2 mM Na_3PO_4 solution (in 10 mM HEPES buffer pH = 5.4).

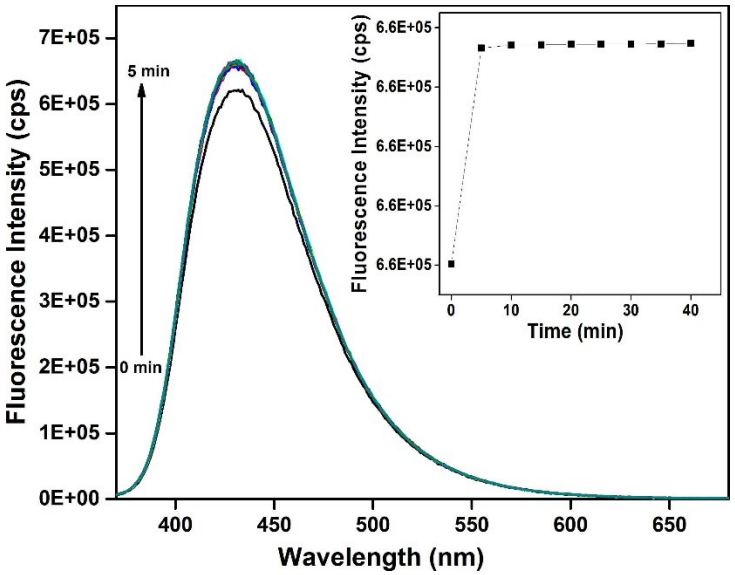


Figure S26. Enhancement of the fluorescence intensity of **1′** (suspended in 10 mM HEPES buffer at pH = 9.4) with time upon the addition of 400 μL of 2 mM Na_3PO_4 solution (in 10 mM HEPES buffer pH = 9.4).

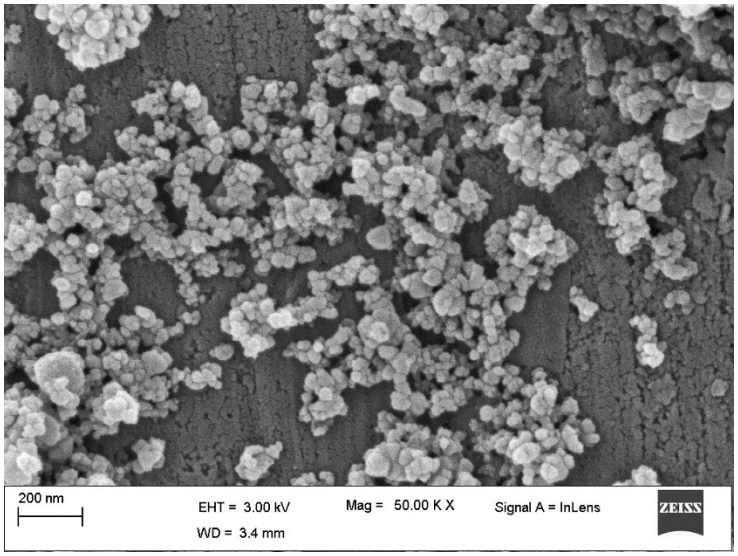


Figure S27. FE-SEM images of **1′**.

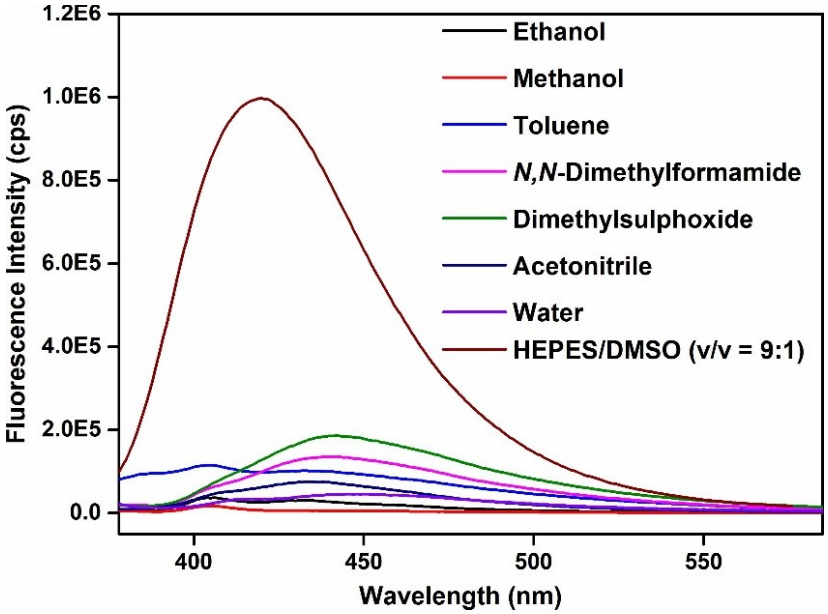


Figure S28. Fluorescence emission spectra of **1′** suspended in different solvents.

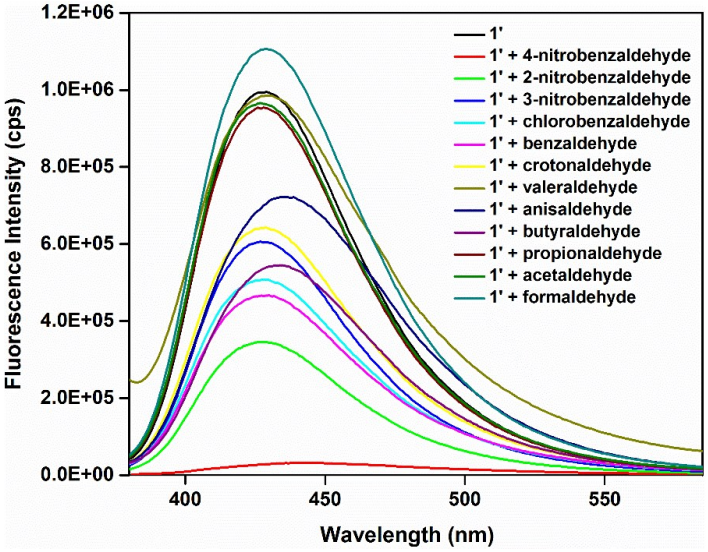


Figure S29. Fluorescence emission spectra representing the selectivity of **1′** towards 4-NB over other competing aldehydes in HEPES/DMSO (v/v = 9:1) mixture. 400 μL of 50 mM aldehyde solutions were added.

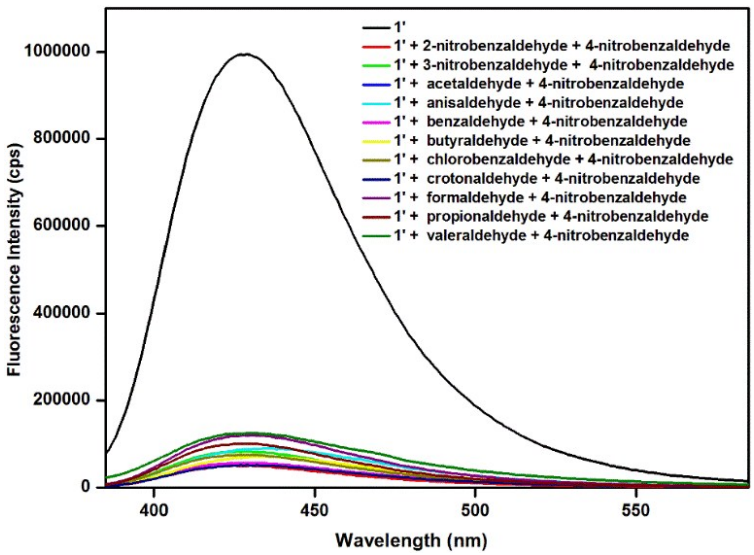


Figure S30. Fluorescence emission spectra representing the selectivity of 4-NB towards **1′** in the presence of other competing aldehydes in HEPES/DMSO (v/v = 9:1) mixture. 400 μL of 50 mM aldehyde solutions were added.

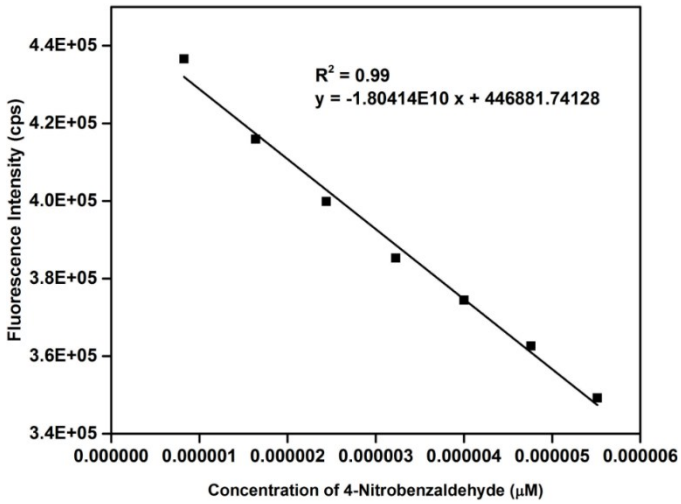


Figure S31. Change in fluorescence intensity of **1′** as a function of concentration of 4-NB solution in HEPES/DMSO (v/v = 9:1) mixture. 4-NB was added as a solution in DMSO.

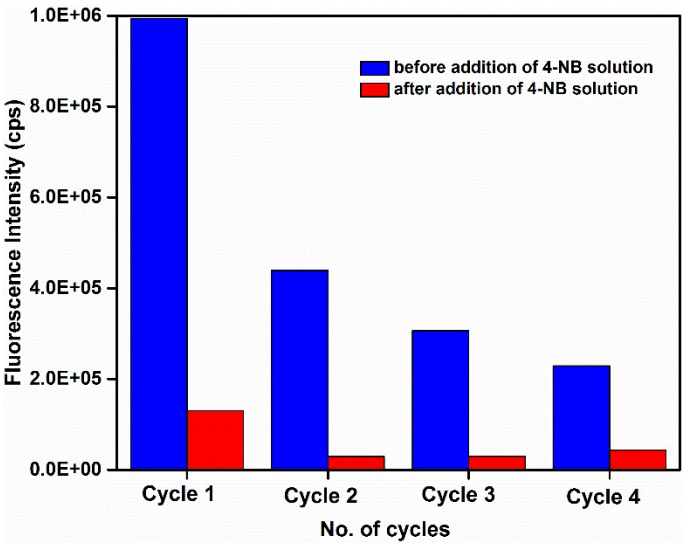


Figure S32. Recyclability of the quenching efficiency of **1′** towards 4-NB in HEPES/DMSO (v/v = 9:1) mixture.

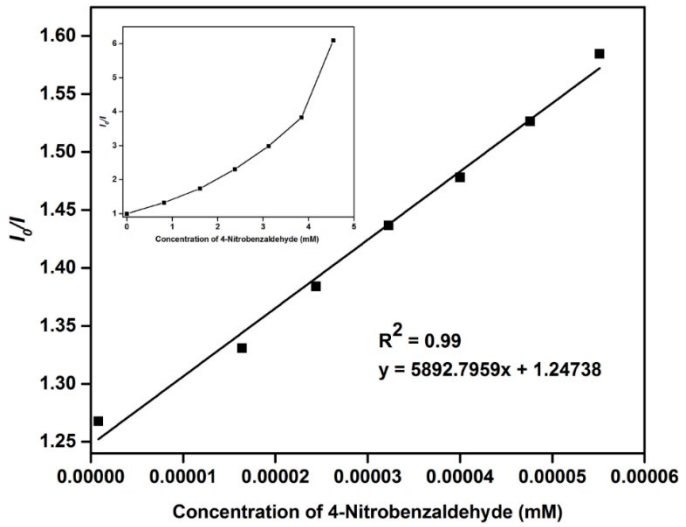


Figure S33. Stern-Volmer plot for the fluorescence quenching of **1′** upon the addition of 4-NB solution. Inset: non-linearity of the plot at higher concetrations of 4-NB solution.

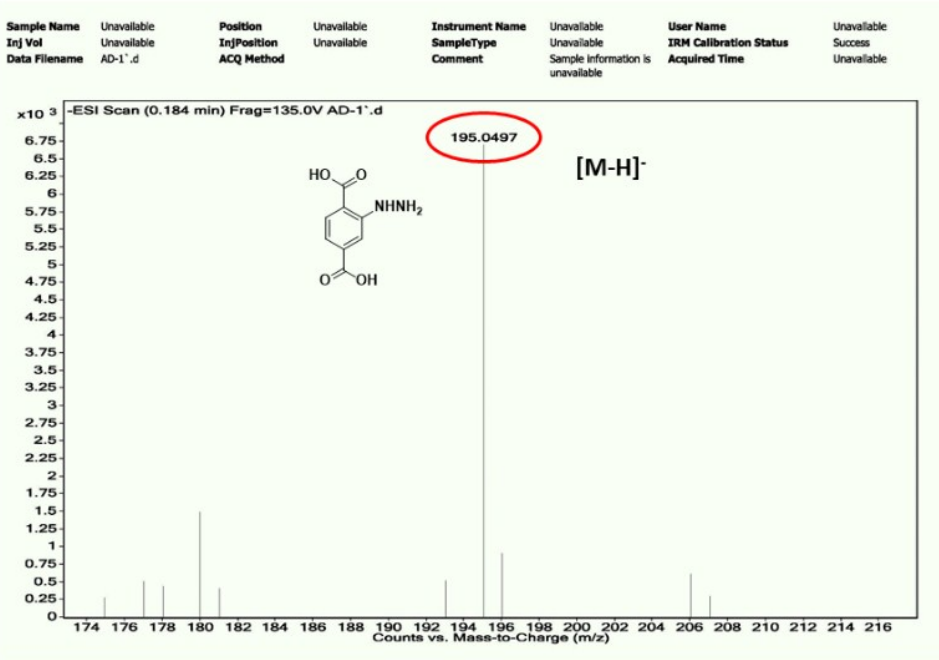


Figure S34. ESI-MS spectrum of the un-treated **1′** (digested in MeOH/HF). The spectrum shows m/z (negative ion mode) peak at 195.0497, which corresponds to $(M\text{-}H)^-$ ion (M = mass of $H_2BDC\text{-}N_2H_3$ ligand).

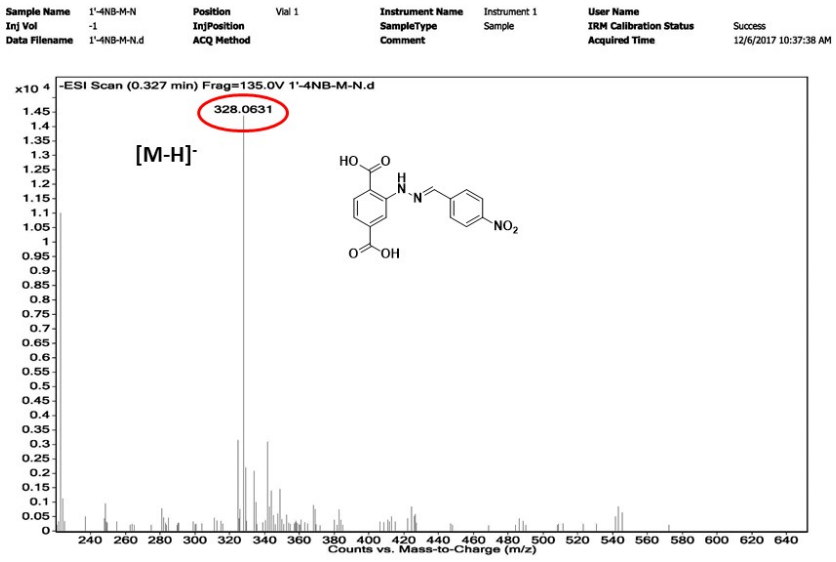


Figure S35. ESI-MS spectrum of the 4-NB treated **1′** (digested in MeOH/HF). The spectrum shows m/z (negative ion mode) peak at 328.0631, which corresponds to $(M\text{-}H)^-$ ion of (*E*)-2-(2-(4-nitrobenzylidene)hydrazinyl)terephthalic acid ligand.

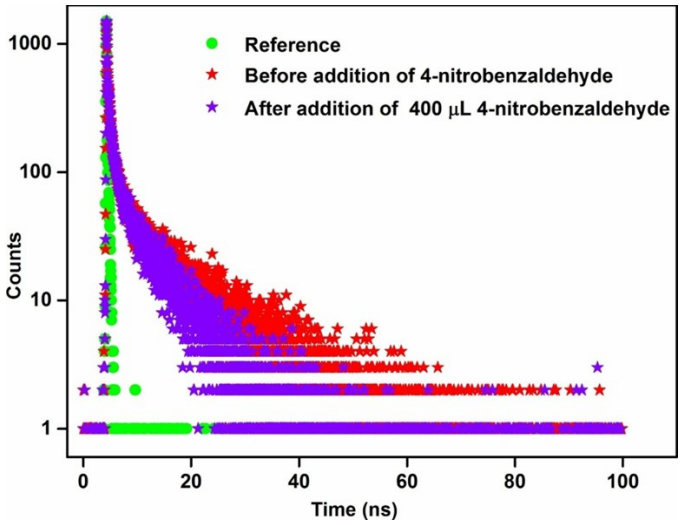


Figure S36. Lifetime decay profile of **1′** before and after the addition of 400 µL of 50 mM 4-NB solution.

Table S1. Unit cell parameters of as-synthesized Zr-UiO-66-N_2H_3 obtained by indexing its XRPD pattern. The obtained values were compared with those of the previously reported un-functionalized Zr-UiO-66 MOF.

Compound Name	Zr-UiO-66-N_2H_3 MOF (This work)	Zr-UiO-66 MOF (Reported)[1]
Crystal System	cubic	cubic
a = b = c (Å)	20.723(4)	20.7004(2)
V (Å^3)	8898.8(26)	8870.3(2)

Table S2. Average excited-state lifetime (<τ>*) values of **1′** before and after the addition of 400 μL of 50 mM 4-NB solution (λ_{ex} = 360 nm, λ_{em} = 430 nm).

Volume of 4-NB Solution Added (μL)	B_1	B_2	a_1	a_2	τ_1 (ns)	τ_2 (ns)	<τ>* (ns)
0	0.3575	0.0070	0.744	0.256	0.516	9.068	2.704
400	0.4874	0.0101	0.787	0.213	0.427	5.557	1.519

* $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$

Table S3. Similarities and dissimilarities observed during the sensing of PO_4^{3-} and 4-NB.

Sl. No.	Factors Considered	Similarity		Dissimilarity	
		PO_4^{3-}	4-NB	PO_4^{3-}	4-NB
1	Selectivity	Highly selective	Highly selective	–	–
2	Sensing Medium	–	–	water and HEPES buffer (10 mM, pH = 7.4)	DMSO/HEPES (9:1, v/v)
3	Nature of Fluorescence Change	–	–	turn-on	turn-off
4	Response Time	–	–	90 min in water and 100 min in HEPES buffer (10 mM, pH = 7.4)	within 1 min
5	Detection Limit	–	–	0.196 μM	4.7 μM
6	Sensing Mechanism	–	–	PO_4^{3-} binds with framework Zr(IV) ions causing partial framework collapse and subsequent release of ligands	$–NHNH_2$ group of ligand forms imine bond with –CHO group of 4-NB

Reference:

1. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851