Supporting Information

Aqueous Phase Sensing of Cyanide Ion Using a Hydrolytically Stable Metal-organic Framework

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Experimental Section:

Synthesis of bio-MOF-1: The synthesis method of bio-MOF-1 was carried out according to previous literature reports ¹. To a solution of adenine (0.25 mmol) and 4,4'-biphenyl dicarboxylic acid (H₂BPDC) (0.39 mmol) in DMF (30 ml), was added dropwise a solution of Zinc acetate dihydrate (0.15 mmol) in water (5 ml). A white precipitate formed was dissolved after the addition of nitric acid (0.3 ml), and the resultant solution was heated at 130°C for 24 h to afford transparent rod-like crystals. Crystals of regular morphology were collected by filtration, washed with DMF and dried in air. *Elemental analysis:* C₁₃₂H₁₅₈N₃₀O₄₄Zn₈ = Zn₈(Ad)₄(BPDC)₆O- $_2(NH_2(CH3)_2)^+$, 8DMF, 11H₂O Calcd. C, 46.74; H, 4.70; N, 12.39. Found C, 47.55; H, 4.74; N, 12.4.

Synthesis of bio-MOF-1⊃**DAAC:** Crystals of bio-MOF-1 were immersed in a aqueous solution of solution of DAAC.HCI (1mmol) for 7 days to yield **bio-MOF-**1⊃**DAAC** MOF/ dye composites. The products were washed thoroughly with MeOH, DMF, H₂O four times each to remove residual DMASMI on the surface of bio-MOF-1 and dried at 100°C for 4 h. The resulting deep yellow compound was obtained as crystalline powder form. **Elemental Analysis**: Found C, 52.55; H, 5.34; N, 13.7.

Recyclability Experiment: To check the Recyclability about 30mg of desolvated **bio-MOF-1 DAAC** in H₂O was taken and 0.75 mmol of tetrabutylammonium cyanide was added and kept for about 10 days. After the completion of the reaction the solid compound owas further dipped in aqueous solution of DAAC.HCI (1mmol) for about 7-10 days. Elemental Analysis: Found (for recycled **bio-MOF-1 DAAC**): C, 54.43; H, 4.11; N, 11.7.

Cell viability assay

5 x 10^3 MCF-7(human breast cancer) cell lines were seeded per well in 96-well µL plate and incubated at 37 °C in a 5% CO₂ incubator overnight for attachment. Cells were then treated with bio-MOF-1⊃DAAC and DACC-CN in different concentrations (0, 3, 6.25, 12.5, 25, 50 µg/ml). After 24 h, 20 µl of MTT reagent (5 mg/ml) was added to each well and incubated for another 4 h at 37 °C. Formazan crystals were then solubilized in 100 µL of the solubilization buffer (10 gm SDS in 0.1 N HCl) and incubated overnight. Absorbance was measured by spectrophotometer at 550 nm. The percent cell viability was calculated considering the untreated cells as 100 percent viability and thus cytotoxicity of the bio-MOF-1⊃DAAC and DACC-CN was determined.

Cellular internalization

1.5 x 10^4 MCF-7 cells were seeded in a lab tek chamber slide 8 well (per well) and incubated at 37° C in a 5% CO₂ incubator overnight for attachment. Cells were then treated with 20 µl MOF-1⊃DAAC (1mg/2ml autoclaved water with constant

sonication) for 6h. Cells were then washed thrice with PBS (pH = 7.4) and treated with CN⁻ (0.01mmol) and incubated in dark at 37 °C for 30 min. Staining solution was aspirated and cells are washed thrice with PBS. The lab-tek chamber slide 8 wells were subjected to fluorescence imaging using a CLSM (Zeiss LSM 710).

Materials: Zinc acetate dihydrate, 4,4'-biphenyl dicarboxylic acid, Adenine, 3,6-Diaminiacridine Hydrchloride (DAAC.HCI) were purchased from Sigma-Aldrich, dry solvents and other chemicals were obtained locally. These chemicals were used without further purification. (Caution: Tetrabutyl ammonium cyanide is hazardous and should be used with precaution)

Physical measurements: All fluorescence measurements were done on Jobin Yvon Fluoroax-4 spectro fluorometer. Powder X-ray diffraction patterns were recorded on Bruker D8 Advanced X-Ray diffractometer using Cu K α radiation (λ = 1.5406 Å) in 5° to 40° 2 θ range. Gas adsorption measurements were studied using BelSorp-max instrument from Bel Japan. The UV-Vis measurements were performed using Chemito SPECTRASCAN UV-2600. The fluorescence images of cells were taken using Olympus Inverted IX81 equipped with Hamamatsu Orca R2 microscope.

Fluorescence study: 1 mg of desolvated **bio-MOF-1**⊃**DAAC** is weighed and added to a fluorescence cuvette (path length of 1cm) containing 2 mL of HEPES buffer under stirring. The fluorescence response in 360-650 nm range upon excitation at 455 nm was measured *in-situ* after incremental addition of freshly prepared aqueous analyte solutions (0.1 mM or Saturated) and corresponding fluorescence intensity was monitored at 506 nm. The solution was stirred at constant rate during fluorescence measurement and maintains homogeneity of solution.



Figure S1: Porous view of bio-MOF-1 along *c* axis.



Figure S2: Perspective view of bio-MOF-1 along *c* axis.



Figure S3: PXRD of bio-MOF-1 (assyn) and to **bio-MOF-1 DAAC** (assyn).



Figure S4: N_2 adsorption isotherm of **bio-MOF-1** \supset **DAAC** at 77K showing considerable decrease in porosity.



Figure S5: UV absorption spectra of **bio-MOF-1** and **bio-MOF-**1 **DAAC**.



Figure S6: Emission profile of bio-MOF-1 and **bio-MOF-1 DAAC** (after 2 days of exchange).



Figure S7: Emission profile of bio-MOF-1 and **bio-MOF-1 DAAC** (after 7 days of exchange).



Figure S8: Visual change in the supernatant solution upon exchange of DMA cations with DACC cations in **bio-MOF-1**.



Figure S9: ¹H-NMR spectra of DAAC, bio-MOF-1 and bio-MOF- $1 \supset DAAC$ digested in HF and dmso-d⁶ showing peaks for DAAC molecules (shown with blue asterisk).



Figure S10: Fluorescence changes of upon addition of F⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**.







Figure S12: Fluorescence changes of upon addition of Br⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1**⊃**DAAC**



Figure S13: Fluorescence changes of upon addition of I⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**



Figure S14: Fluorescence changes of upon addition of NO₂⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**



Figure S15: Fluorescence changes of upon addition of NO₃⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**



Figure S16: Fluorescence changes of upon addition of HCO₃⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1**⊃**DAAC**



Figure S17: Fluorescence changes of upon addition of OAc⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**



Figure S18: Fluorescence changes of upon addition of SCN⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**



Figure S19: Fluorescence changes of upon addition of CN⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**



Figure S20: Turn on response upon gradual addition of of CN⁻ as Tetrabutylammonium salt in aqueous phase to **bio-MOF-1DAAC**



Figure S21: Fluorescence response of **bio-MOF-1 DAAC** as observed under UV light when CN⁻ ions is added to it showing considerable increase in intensity.



Figure S22: Fluorescence response upon addition of CN⁻ ions to bio-MOF-1 DAAC w.r.t. time in seconds



Figure S23: -Linear fit of Fluorescence change vs. conc. upon addition of CN⁻ ions.



Figure S24: Fluorescence response of CN⁻ ions compared to other anions when the anions are added to **bio-MOF-1 DAAC**.



Figure S25: Fluorescence response of CN⁻ ions compared to other anions when the anions w.r.t to different concentration of anions.







Figure S27: Absorption spectra of DAAC and **bio-MOF-1** \supset **DAAC** both in presence and absence of CN⁻ ions.



Figure S28: PXRD pattern of **bio-MOF-1** \supset **DAAC** and **bio-MOF-1** \supset **DAAC** dipped in CN⁻ for about 1 month showing bulk crystallinity and structure retainment.



Figure S29: SEM images of **bio-MOF-1** \supset **DAAC** and (inset) **bio-MOF-1** \supset **DAAC** dipped in CN⁻ for about 1 month showing crystallinity.



Figure S30: Fluorescence response in presence of cyanide ions after recyclability experiments.



Figure S31: MALDI-TOF spectra of the supernatant solution of spectra of **bio-MOF-1 DAAC** treated with CN⁻.



Figure S32: MTT assay of **bio-MOF-1 DAAC** showing good viability even at higher concentration.



Figure S33: Bright field images of MCF-7 cells incubated with a) **bio-** $MOF-1 \supset DAAC$ and b) after the addition of CN^{-} ions.



Figure S34: Electron density map of the HOMO energy state of the ligand of **DAAC** as obtained by using Gaussian Rev D program suite. Structure was optimized by density functional theory by B3LYP method using 6-31+G (d, p) basis set in Gaussian 09 package



Figure S35: Electron density map of the LUMO energy state of the ligand of **DAAC** as obtained by using Gaussian Rev D program suite. Structure was optimized by density functional theory by B3LYP method using 6-31+G (d, p) basis set in Gaussian 09 package

Detection Limit Calculation:

To limit of detection, CN^{-} (20 – 246 µL, 0.1 mM stock solution) was added to probe (desolvated **bio-MOF-1** \supset **DAAC**) (0.5 mg, in 2 mL HEPES buffer) and emission spectra were recorded. By plotting fluorescence intensity with increasing concentration of CN^{-} , at low concentration region slope (*m*) of graph was found to be 1.48x10⁸ mM⁻¹ (R²= 0.97). Standard deviation (σ) was calculated from five blank measurements of probe (**bio-MOF-1** \supset **DAAC**). Detection limit is calculated according to the following formula:

Detection limit: (3σ/m)

Calculation of standard deviation:

 Table S1: Standard deviation for probe

Blank Readings (only probe)	FL Intensity
Reading 1	50430
Reading 2	58595
Reading 3	64514
Reading 4	74235
Standard Deviation (σ)	10024

Calculation of Detection Limit:

 Table S2:
 Detection limit calculation for probe

Slope from Graph (m)	1.48x10 ⁸	mM⁻¹
Detection limit (3 <i>c</i> / <i>m</i>)	2.01 x10 ⁻⁴	mM

Limit of detection is calculated to be $0.2\mu M$, which comes to ~ 5.2ppb.

References:

1. J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen, G. Qian, *Nat. Commun.* **2013**, *4*, 2719.