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Supporting Information For:

Post-Synthetic Modification of a Metal–Organic Framework with Chemodosimeter for Rapid Detection of Lethal Cyanide via Dual Emission

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Materials and Methods:
The preparation of thieno[2,3-b]thiophene-2,5-dicarboxylic acid (H₂TDC) and 2-cyano-3-(pyren-1-yl)acrylic acid (CPAA) chemodosimeter was carried out by following literature protocols. The ¹H NMR spectra of these ligands are shown in Figures S1-S2. All other reagent grade starting materials were used as received from the commercial suppliers. Perkin Elmer Spectrum Two FT-IR spectrometer was used to record fourier transform infrared (FT-IR) spectra in the region of 400-4000 cm⁻¹. The following indications are used to characterize absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh) and broad (br). Thermogravimetric analyses (TGA) were carried out with a Mettler-Toledo TGA/SDTA 851e thermogravimetric analyzer in a temperature range of 30-700 °C under air atmosphere at a heating rate of 5 °C min⁻¹. Ambient temperature X-Ray powder diffraction (XRPD) patterns were measured on a Bruker D2 Phaser X-ray diffractometer operated at 30 kV, 10 mA using Cu-Kα (λ = 1.5406 Å). The nitrogen sorption isotherms up to 1 bar were recorded using a Quantachrome Autosorb iQ-MP gas sorption analyzer at -196 °C. Before the sorption measurements, the compounds were degassed for 12 h under dynamic vacuum at 120 °C. Steady state fluorescence studies were performed with a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. DFT calculations were carried out with Gaussian 09 package using 6-31+G (d,p) basis set with B3LYP method.

Figure S1. ¹H NMR spectrum of H₂TDC ligand.
Figure S2. $^1$H NMR spectrum of CPAA ligand.

Figure S3. XRPD patterns of as-synthesized (a), methanol exchanged (b) and thermally activated (c) forms of 1.
Figure S4. XRPD patterns of 1' before (a) and after post-synthetic ligand exchange (b).

Figure S5. FT-IR spectra of as-synthesized 1 (red) and thermally activated 1' (black).
Figure S6. FT-IR spectra of P-1' before (black) and after (red) treatment with cyanide.

Figure S7. ¹H NMR spectra of 1' (a) and P-1' (b) after framework digestion in K₃PO₄/D₂O. In ¹H NMR spectrum of digested P-1', presence of the new peaks were observed for the pyrene protons (blue shaded area) along with the proton peaks of H₂TDC ligand (red shaded area).

Digestion protocol: 10 mg of MOF sample was added to 0.5 mL of DMSO-ireccional. To this solution was added 0.3 mL of saturated K₃PO₄ in D₂O. After shaking for 10 min, the MOF sample was dissolved and the organic phase was collected and analyzed by ¹H NMR spectroscopy.
Figure S8. $^1$H NMR spectrum of P-1' after digestion in K$_3$PO$_4$/D$_2$O. To calculate the percent of conversion, the peaks corresponding to H$_2$TDC ligand was set to an integration of 1 and all new peaks were integrated accordingly. For P-1', these new peaks are all approx. $\sim$0.30 with respect to protons of H$_2$TDC ligand, corresponding to $\sim$23% incorporation of CPAA ligand in the framework.

Figure S9. TG curves of as-synthesized 1 (black) and activated 1' (red) recorded in an air atmosphere in the temperature range of 25-700 °C with a heating rate of 5 °C min$^{-1}$. 
Figure S10. TG curves of P-1 recorded in an air atmosphere in the temperature range of 25-700 °C with a heating rate of 5 °C min⁻¹.

Figure S11. FE-SEM images of 1' (a, b) and P-1'(c, d) in different magnifications.
Figure S12. $N_2$ adsorption (solid symbols) and desorption (empty symbols) isotherms of $1'$ (weed green squares) and $P-1'$ (black circles) measured at $-196 \, ^\circ C$.

Figure S13. Hydrolytic stability of $P-1'$ in different pH media.
Figure S14. Structure of CPAA probe and its different potential sites.

Figure S15. Change in the fluorescence intensity of \( P-1' \) upon addition of 2 mM aqueous solution (150 µL) of various anions.
Figure S16. Time-dependent fluorescence enhancement of P-1' at 433 nm upon addition of different concentrations of CN\(^-\) ion.

Figure S17. Change in the fluorescence intensity of P-1' upon addition of 2 mM CN\(^-\) solution (150 \(\mu\)L) in presence of other competitive anions (150 \(\mu\)L).
Figure S18. Change in the fluorescence intensity of P-1' as a function of CN⁻ concentration.

Table S1. Comparison of the various existing fluorescent materials for the sensing of CN⁻.

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<th>Sl No.</th>
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<th>Sensing Medium</th>
<th>LOD</th>
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<td>P-1'</td>
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**Figure S19.** XRPD patterns of P-1' before (a) and after (b) cyanide sensing.
**Figure S20.** Suppression of ICT (intramolecular charge transfer) due to addition of cyanide ion to the CPAA probe.

**Figure S21.** $^1$H NMR spectrum of (a) P-1' and (b) cyanide treated P-1' digested in K$_3$PO$_4$/D$_2$O. The appearance of the new peak at 5.79 ppm in the $^1$H NMR spectrum of cyanide treated P-1' supports the proposed nucleophilic addition of cyanide to the vinyl group of the pyrene moiety.
Figure S22. $^1$H NMR spectrum of cyanide treated P-1' after digestion. The peaks corresponding to H$_2$TDC ligand were set to an integration of 1 and all new peaks were integrated accordingly. For cyanide treated P-1', the new peak (H$_b$) at 5.79 ppm is approx. 0.16 with respect to protons of H$_2$TDC ligand. Due to nucleophilic attack of cyanide, the integration value of vinylic proton (H$_a$) decreases from ~0.30 to ~0.14. Hence, percentage conversion of incorporated CPAA ligand to its cyanide adduct is ~53% under sensing conditions.

References: