Electronic Supplementary Information

Construction of bifunctional 2-fold interpenetrated Zn(II) MOFs exhibiting selective CO₂ adsorption and aqueous-phase sensing of 2,4,6-trinitrophenol

Sandeep Singh Dhankhar, Nayuesh Sharma and C. M. Nagaraja*

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India. Tel: 91- 1881-242229. Email: cmnraja@iitrpr.ac.in

Contents:

1. Synthesis procedure for N, N'-bis(5-isophthalic acid)naphthalenediimide (H₄BINDI) ligand

2. X ray crystallography

3. Figure S1. PXRD patterns for MOF1 (a) pattern simulated from single crystal X-ray diffraction, (b) as-synthesized sample and (c) isolated sample after vigorous stirring in water for 3 days.

4. Figure S2. FT-IR spectrum of MOF1

5. Figure S3. PXRD patterns for MOF2 (a) pattern simulated from single crystal X-ray diffraction, (b) as-synthesized sample and (c) for isolated sample after vigorous stirring in water for 3 days.

6. Figure S4. FT-IR spectrum of MOF2.

7. Scheme S1. Coordination modes of ligand in MOF1 and 2.
8. **Table S1.** Selected Bond lengths (Å) and Angles (°) for MOF1.

9. **Table S2.** Selected hydrogen bonding geometry (Å, °) for MOF1.

10. **Table S3.** Selected bond lengths (Å) and angles (°) for MOF2.

11. **Table S4.** Selected hydrogen bonding geometry (Å, °) for MOF2.

12. **Figure S5.** UV-vis absorption spectra of as-synthesized MOF1 and 2 along with the filtrate obtained after treating with water for 3 days.

13. **Figure S6.** Pore pictures of MOF1 and 2 showing pore size of 1D channels before and after interpenetration.

14. **Figure S7.** PXRD patterns of MOF1 (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample (c) for sample activated at 393 K for 20 hours.

15. **Figure S8.** PXRD patterns of MOF2 (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample (c) for the sample activated at 393 K for 20 hours.

16. **Figure S9.** (a) N₂ adsorption-desorption isotherms of MOF1 (a) and for MOF2 (b) carried out at 77K.

17. Analysis of Gas adsorption Isotherms

18. **Figure S10.** CO₂ adsorption isotherm for MOF1 at 273 K (the solid line shows the best fit to the data using Langmuir-Freundlich equation).

19. **Figure S11.** CO₂ adsorption isotherm for MOF1 at 298 K (the solid line shows the best fit to the data using Langmuir-Freundlich equation).

20. **Figure S12.** Enthalpy of CO₂ adsorption for MOF1 calculated using Clausius-Clapeyron equation.

21. **Figure S13.** Carbon dioxide adsorption isotherms for MOF2 carried out at 273 and 298K.
22. **Figure S14.** Carbon dioxide adsorption isotherms of MOF2 carried out at 273K (a) and 298K (b) (the solid line shows the best fit to the data using Langmuir-Freundlich equation).

23. **Figure S15.** Enthalpy of carbon dioxide adsorption for MOF2 calculated using Clausius-Clapeyron equation.

24. **Figure S16.** Normalized emission spectra of MOF1 and 2 dispersed water (excitation wavelength of 360 nm).

25. **Figure S17.** Quenching of the emission spectra of MOF1 dispersed in water upon addition of varying concentration of TNP.

26. **Figure S18.** Emission spectra of MOF1 dispersed in water with addition of nitro analytes (RDX, TNT, DNT, NT, DNB and NB) and TNP (100 µM).

27. **Figure S19.** Reduction in emission intensity of MOF1 upon addition of 0.6 ppm of TNP in water.

28. **Figure S20.** Stern-Volmer plot for determination of $K_{sv}$ for quenching of emission intensity of MOF1 by TNP in aqueous-phase.

29. **Figure S21.** (a) Quenching in the emission intensity of MOF2 upon addition of various NACs. (b) Reduction in the emission intensity of MOF2 upon incremental addition of TNP in aqueous-phase.

30. **Figure S22.** Changes in the emission spectra of water dispersed MOF2 upon addition of various NACs.

31. **Figure S23.** Emission spectra of water dispersed MOF2 upon addition of various NACs (RDX, TNT, DNT, NT, DNB and NB) and TNP.

32. **Figure S24.** Percentage quenching of the emission intensity of MOF2 upon addition of TNP and various NACs (RDX, TNT, DNT, NT, DNB and NB).
33. **Figure S25.** Reduction in emission intensity of MOF2 upon addition of different concentrations of TNP in water.

34. **Figure S26.** Stern-Volmer plot for determination of quenching constant ($K_{sv}$) for TNP with MOF2 dispersed in aqueous-phase.

35. **Figure S27.** Relative energies of HOMO and LUMO orbitals of various NACs.

**Synthesis of N, N'-bis(5-isophthalic acid)naphthalenediimide (H$_4$BINDI) ligand**

N,N'-bis(5-isophthalic acid)naphthalenediimide (H$_4$BINDI) was synthesized according to a previously reported procedure.\textsuperscript{1} 1,4,5,8-tetracarboxyldianhydride (0.67 g, 2.5 mmol) was taken into a 100 mL round bottomed flask and suspended in 12.5 mL acetic acid. The mixture was stirred for 10 min. To this solution, 5-aminoisophthalic acid (0.905 g, 5.0 mmol) was added and the solution allowed reflux for 12 h. The reaction was allowed to cool to room temperature and water (10 ml) was added to precipitate the product. The product was collected by filtration washed with ethanol and dried in vacuum to yield 1.2 g of off-white solid (isolated yield = 1.2 g, 77%). The compound was re-crystallized from DMF as an off-yellow material and characterized by both $^1$H and $^{13}$C NMR spectra. $^1$H NMR data (DMSO-$d_6$): $\delta$ = 13.53(s, 4H); 8.74(s, 4H); 8.59(s, 2H); 8.34(s, 4H). $^{13}$C NMR data (DMSO-$d_6$): $\delta$ = 166.6 (-COOH); 163.6(-C=O); 137.0 (Aromatic -CH); 134.8 (Aromatic -CH); 130.8 (Aromatic -CH); 130.5(Aromatic –CH); 127.7 (Aromatic -CH); 127.3 (Aromatic -CH).
X-ray Crystallography

As synthesized crystals of MOF1 and 2 were coated with paratone-N and then placed on top of glass fiber pip and then the goniometer is placed on diffractometer. The data collections were done at 298K for both the compounds. Single crystal X-ray structural data of MOF1 and MOF2 were collected on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromated Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)) operating at 50 kV and 30 mA. The SAINT² program was used for integration of diffraction profiles and absorption correction was made with SADABS program.³ The structures were solved by SIR 92⁴ and refined by full matrix least square method using SHELXL-2013⁵ and WinGX system, Ver 2013.3.⁶ The non-hydrogen atoms in all the structures were located from the difference Fourier map and refined anisotropically. All the hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using riding model with isotropic thermal parameters. The uncoordinated solvent water hydrogen atoms have been not added. The formula of MOF1-2 was determined based on the elemental analyses and TGA. The potential solvent accessible area or void space was calculated using the PLATON⁷ software. All the crystallographic and structure refinement data of the MOF1 is summarized in Table S1. Selected bond lengths and angles are given in Table S2 and S4 and selected hydrogen bond details of the MOF1 and MOF2 are summarized in Table S3 and S5 respectively. The crystallographic information file is deposited with the CCDC number 1868716 and 1868717 for MOF1 and MOF2 respectively.
Figure S1. PXRD patterns for MOF1 (a) pattern simulated from single crystal X-ray diffraction, (b) as-synthesized sample and (c) isolated sample after vigorous stirring in water for 3 days.

Figure S2. FT-IR spectrum of MOF1
Figure S3. PXRD patterns for MOF2 (a) pattern simulated from single crystal X-ray diffraction, (b) as-synthesized sample and (c) for isolated sample after vigorous stirring in water for 3 days.

Figure S4. FT-IR spectrum of MOF2.
Figure S5. UV-vis absorption spectra of as-synthesized MOF1 and 2 along with the filtrate obtained after treating with water for 3 days.

Scheme S1. Coordination modes of ligand in MOF1 and 2
Table S1. Selected bond lengths (Å) and angles (°) for MOF1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn1-O1</td>
<td>1.934(3)</td>
<td></td>
</tr>
<tr>
<td>Zn1-O2</td>
<td>1.915(3)</td>
<td></td>
</tr>
<tr>
<td>Zn1-O7</td>
<td>1.982(3)</td>
<td></td>
</tr>
<tr>
<td>Zn1-N1</td>
<td>2.008(3)</td>
<td></td>
</tr>
<tr>
<td>O1-Zn1-O2</td>
<td>114.03(8)</td>
<td></td>
</tr>
<tr>
<td>O1-Zn1-O7</td>
<td>111.87(9)</td>
<td></td>
</tr>
<tr>
<td>O1-Zn1-N1</td>
<td>101.27(8)</td>
<td></td>
</tr>
<tr>
<td>O2-Zn1-O7</td>
<td>97.36(9)</td>
<td></td>
</tr>
<tr>
<td>O2-Zn1-N1</td>
<td>126.17(8)</td>
<td></td>
</tr>
<tr>
<td>O7-Zn1-N1</td>
<td>105.85(8)</td>
<td></td>
</tr>
</tbody>
</table>

Table S2. Selected hydrogen bonding geometry (Å, °) for MOF1.

<table>
<thead>
<tr>
<th>D–H⋯A</th>
<th>H⋯A</th>
<th>D⋯A</th>
<th>D–H⋯A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12-H12…O2W i</td>
<td>2.46(3)</td>
<td>3.308(6)</td>
<td>156(3)</td>
</tr>
<tr>
<td>C15-H15…O6 ii</td>
<td>2.4200</td>
<td>3.150(4)</td>
<td>135.00</td>
</tr>
<tr>
<td>C16-H16…O3</td>
<td>2.4400</td>
<td>3.240(5)</td>
<td>144.00</td>
</tr>
<tr>
<td>C12-H12…O6</td>
<td>2.48(3)</td>
<td>2.810(4)</td>
<td>102(2)</td>
</tr>
</tbody>
</table>

Symmetry operations: i = 2+x, y, z; ii = -1+x, y, z
**Table S3.** Selected bond lengths (Å) and angles (°) for MOF2.

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn1-O1</td>
<td>2.344(4)</td>
<td>O1-Zn1-N2</td>
</tr>
<tr>
<td>Zn1-O2</td>
<td>2.176(3)</td>
<td>O2-Zn1-O3</td>
</tr>
<tr>
<td>Zn1-O3</td>
<td>2.059(3)</td>
<td>O2-Zn1-O4</td>
</tr>
<tr>
<td>Zn1-O4</td>
<td>2.062(3)</td>
<td>O2-Zn1-N1</td>
</tr>
<tr>
<td>Zn1-N1</td>
<td>2.148(4)</td>
<td>O2-Zn1-N2</td>
</tr>
<tr>
<td>Zn1-N2</td>
<td>2.125(4)</td>
<td>O3-Zn1-O4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O3-Zn1-N1</td>
</tr>
<tr>
<td>O1-Zn1-O2</td>
<td>57.50(12)</td>
<td></td>
</tr>
<tr>
<td>O1-Zn1-O3</td>
<td>87.25(12)</td>
<td></td>
</tr>
<tr>
<td>O1-Zn1-O4</td>
<td>149.80(12)</td>
<td></td>
</tr>
<tr>
<td>O1-Zn1-N1</td>
<td>91.75(15)</td>
<td></td>
</tr>
</tbody>
</table>

**Table S4.** Selected hydrogen bonding geometry (Å, °) for MOF2.

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>H···A</th>
<th>D···A</th>
<th>D-H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14-H14…O6</td>
<td>2.47(6)</td>
<td>2.833(5)</td>
<td>101(4)</td>
</tr>
<tr>
<td>C15-H15…O4</td>
<td>2.5100</td>
<td>3.050(6)</td>
<td>117.00</td>
</tr>
<tr>
<td>C21-H21…O3</td>
<td>2.5900</td>
<td>3.053(7)</td>
<td>111.00</td>
</tr>
<tr>
<td>C20-H20…O4</td>
<td>2.4800</td>
<td>3.019(6)</td>
<td>117.00</td>
</tr>
<tr>
<td>C23-H23…O3W¹</td>
<td>2.4700</td>
<td>3.389(10)</td>
<td>171.00</td>
</tr>
</tbody>
</table>

Symmetry operations: i = x, 2-y, ½+z
Figure S6. Pore pictures of MOF1 and 2 showing pore size of 1D channels before and after interpenetration.
Figure S7. PXRD patterns of MOF1 (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample (c) for sample activated at 393 K for 20 hours.

Figure S8. PXRD patterns of MOF2 (a) pattern calculated from the single crystal X-ray data (b) for as-synthesized sample (c) for the sample activated at 393 K for 20 hours.
Analysis of Gas adsorption Isotherms

Clausius-Clapeyron Equation\(^8,9\) was used to calculate the enthalpies of hydrogen adsorption. By using Langmuir Freundlich equation\(^10\) an accurate fit was retrieved which gives a precise prediction of hydrogen adsorbed at saturation. A modification of Clausius-Clapeyron equation is used for calculations.

\[
\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{\text{ads}} \times \frac{T_2 - T_1}{R \times T_2 T_1}
\]

\[\text{------(i)}\]

where, \(P_1\) and \(P_2\) = pressures for isotherm at 77K and 87K respectively.

\(T_1\) and \(T_2\) = temperatures for isotherm at 77K and 87K respectively.

\(\Delta H_{\text{ads}}\) = Enthalpy of adsorption.
\[ R = \text{Universal gas constant} = 8.314 \, \text{J/K/mol}. \]

Pressure is a function of amount of gas adsorbed which was determined by using the Langmuir-Freundlich fit.

\[ \frac{Q}{Q_m} = \frac{B \times P^{(1/t)}}{1 + (B \times P^{(1/t)})} \quad \text{------(ii)} \]

where, \( Q \) = moles of gas adsorbed.

\( Q_m \) = moles of gas adsorbed at saturation.

\( B \) and \( t \) = constants.

\( P \) = Pressure.

By rearranging equation (ii) we get equation (iii)

\[ P = \left[ \frac{Q/Q_m}{B - (B \times Q/Q_m)} \right]^t \quad \text{------(iii)} \]

Substituting equation (iii) into equation (i) we get

\[ \Delta H_{\text{ad}} = R \times T_1 \times T_2 \frac{\left[ \frac{Q/Q_m^{(1)}}{B - (B \times Q/Q_m^{(1)})} \right]^{t1}}{T_2 - T_1} \left[ \frac{Q/Q_m^{(2)}}{B - (B \times Q/Q_m^{(2)})} \right]^{t2} \quad \text{------(iv)} \]

In equation (iv), subscript 1 and 2 are representing data corresponding to 77K and 87K respectively in case of hydrogen gas and 273K and 298K in case of carbon dioxide gas.
**Figure S10.** CO$_2$ adsorption isotherm for MOF1 at 273 K (the solid line shows the best fit to the data using Langmuir-Freundlich equation).

**Figure S11.** CO$_2$ adsorption isotherm for MOF1 at 298 K (the solid line shows the best fit to the data using Langmuir-Freundlich equation).
**Figure S12.** Enthalpy of CO\textsubscript{2} adsorption for MOF1 calculated using Clausius-Clapeyron equation.

**Figure S13.** Carbon dioxide adsorption isotherms for MOF2 carried out at 273 and 298K.
Figure S14. Carbon dioxide adsorption isotherms of MOF2 carried out at 273K (a) and 298K (b) (the solid line shows the best fit to the data using Langmuir-Freundlich equation).
**Figure S15.** Enthalpy of carbon dioxide adsorption for MOF2 calculated using Clausius-Clapeyron equation.

**Figure S16.** Normalized emission spectra of MOF1 and 2 dispersed water (excitation wavelength of 360 nm).
**Figure S17.** Quenching of the emission spectra of MOF1 dispersed in water upon addition of varying concentration of TNP.

**Figure S18.** Emission spectra of MOF1 dispersed in water with addition of nitro analytes (RDX, TNT, DNT, NT, DNB and NB) and TNP (100 µM).
**Figure S19.** Reduction in emission intensity of MOF1 upon addition of 0.6 ppm of TNP in water.

**Figure S20.** Stern-Volmer plot for determination of $K_{sv}$ for quenching of emission intensity of MOF1 by TNP in aqueous-phase.
Figure S21. (a) Quenching in the emission intensity of MOF2 upon addition of various nitroanalytes. (b) Reduction in the emission intensity of MOF2 upon incremental addition of TNP in aqueous-phase.

Figure S22. Changes in the emission spectra of water dispersed MOF2 upon addition of various NACs.
Figure S23. Emission spectra of water dispersed MOF2 upon addition of various NACs (RDX, TNT, DNT, NT, DNB and NB) and TNP.

Figure S24. Percentage quenching of the emission intensity of MOF2 upon addition of TNP and various NACs (RDX, TNT, DNT, NT, DNB and NB).
**Figure S25.** Reduction in emission intensity of MOF2 upon addition of different concentrations of TNP in water.

**Figure S26.** Stern-Volmer plot for determination of quenching constant ($K_{sv}$) for TNP with MOF2 dispersed in aqueous-phase.

$$K_{sv} = 1.29 \times 10^4 \text{ M}^{-1}$$
Figure S27. Relative energies of HOMO and LUMO orbitals of various NACs.

References


