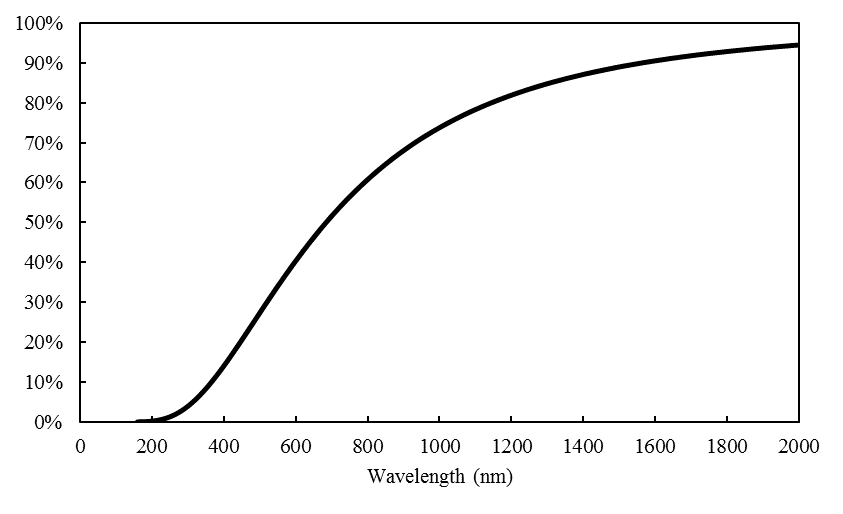
**The Search for Efficient and Stable Metal-Organic Frameworks for Photocatalysis: Atmospheric Fixation of Nitrogen**

Amro M. O. Mohamed†\*, Yusuf Bicer†

†Division of Sustainable Development, College of Science and Engineering, Hamad Bin Khalifa University, Qatar Foundation, Doha, Qatar

\*Corresponding author at [ammohamed@hbku.edu.qa](mailto:ammohamed@hbku.edu.qa)

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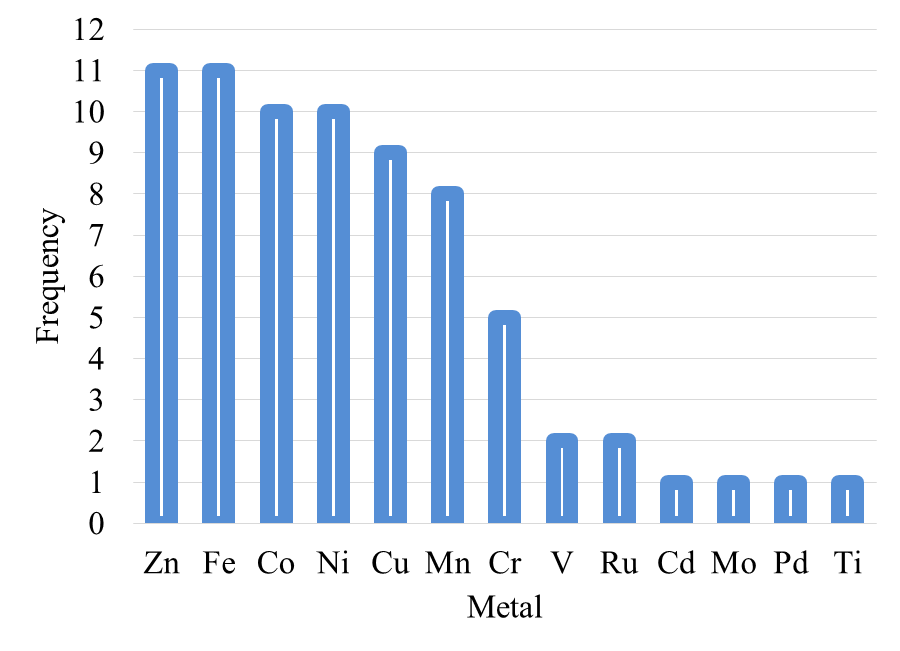
**Figure S1.** Wavelength (nm) vs. the amount of captured sunlight

Table S1. Potential (V) vs. SHE for the three steps 2e- reduction of nitrogen at atmospheric conditions

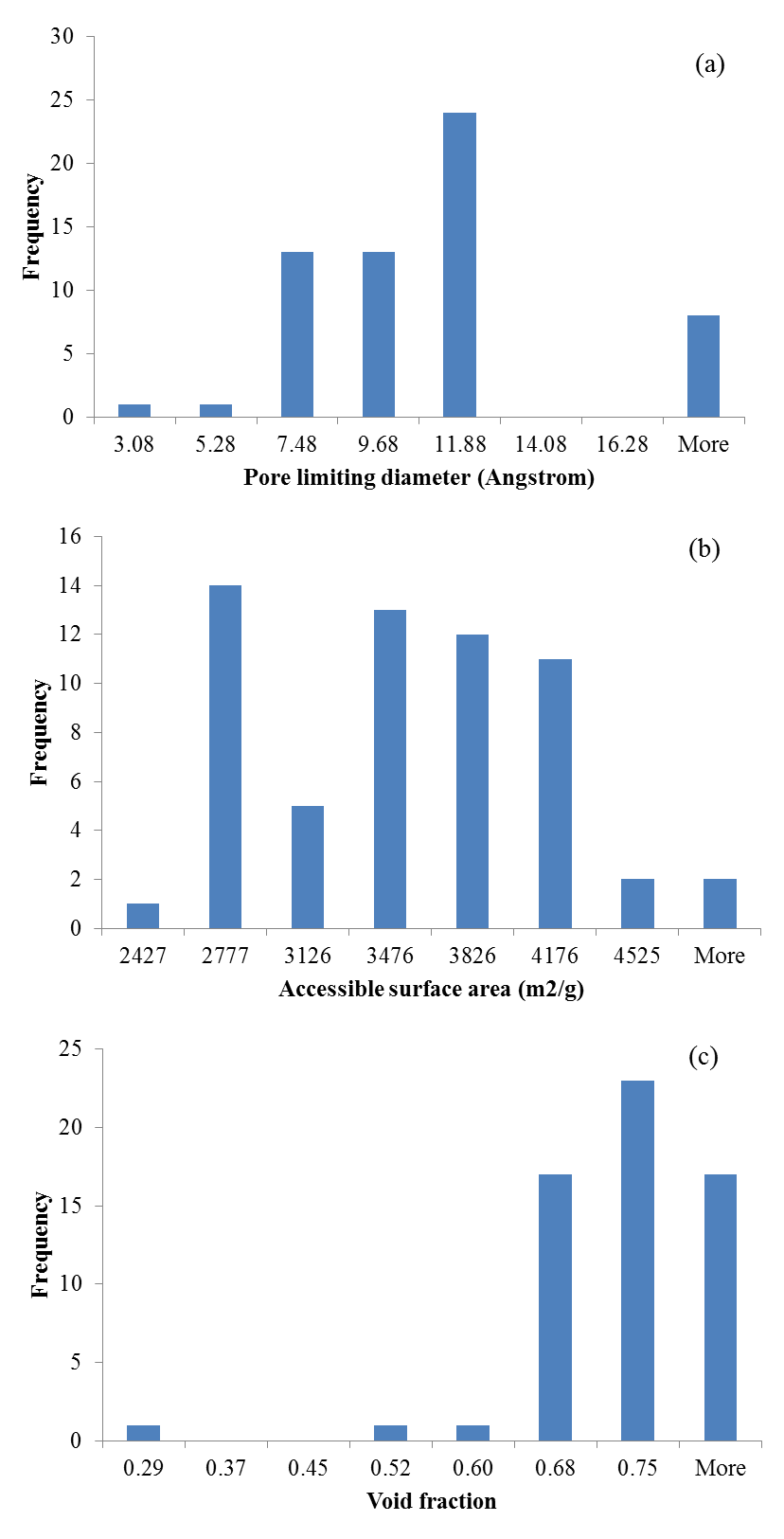
|  |  |
| --- | --- |
| **Reaction** | **Potential (V) vs. SHE** |
|  | -1.260 |
|  | +0.434 |
|  | +0.995 |
|  | 0.000 |
|  | +1.230 |

Table S2. MOFs types and associated metal and organic linker in the 60 MOF dataset

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **MOF type** | **Metals** | **Organic linker** | | | |
| **M2Cl2(BTDD)**  **M2Cl2(BBTA)** | **Mn2+, Fe2+, Co2+, Ni2+** | **(BBTA)** | | **(BTDD)** | |
| **M2(DOBDC)**  **M2(mDOBDC)**  **M2(DOBPDC)** | **Mn2+, Fe2+, Co2+, Ni2+** | **(DOBDC)** | **(mDOBDC)** | | **(DOBPDC)** |
| **M-BTC** | **Cr2+, Co2+, Ni2+, Cu2+, Zn2+, Mo2+, Rh2+/3+, Pd2+** |  | | | |
| **M-MIL-88B** | **Sc3+, Ti3+, V3+, Cr2+/3+, Fe2+/3+** |  | | | |
| **M-BTT**  **M-BTP** | **M-BTT (Cr2+, Mn2+, Fe2+, Co2+, Ni2+, Cu2+, Cd2+)**  **M-BTP (Ni2+, Cu2+)** | **(BTP)** | | **(BTT)** | |
| **M-MOF-5** | **V2+, Cr2+**  **Mn2+, Fe2+**  **Co2+, Ni2+** |  | | | |
| **M2(DSBDC)** | **Mn2+**  **Fe2+** |  | | | |
| **Cu-CFA-8** | **Cu** |  | | | |
| **Co(L-RR)** | **Co** |  | | | |
| **Cu8I4(DMTRZ)4**  **Cu3(DMTRZ)4(ox)2** | **Cu** |  | | | |



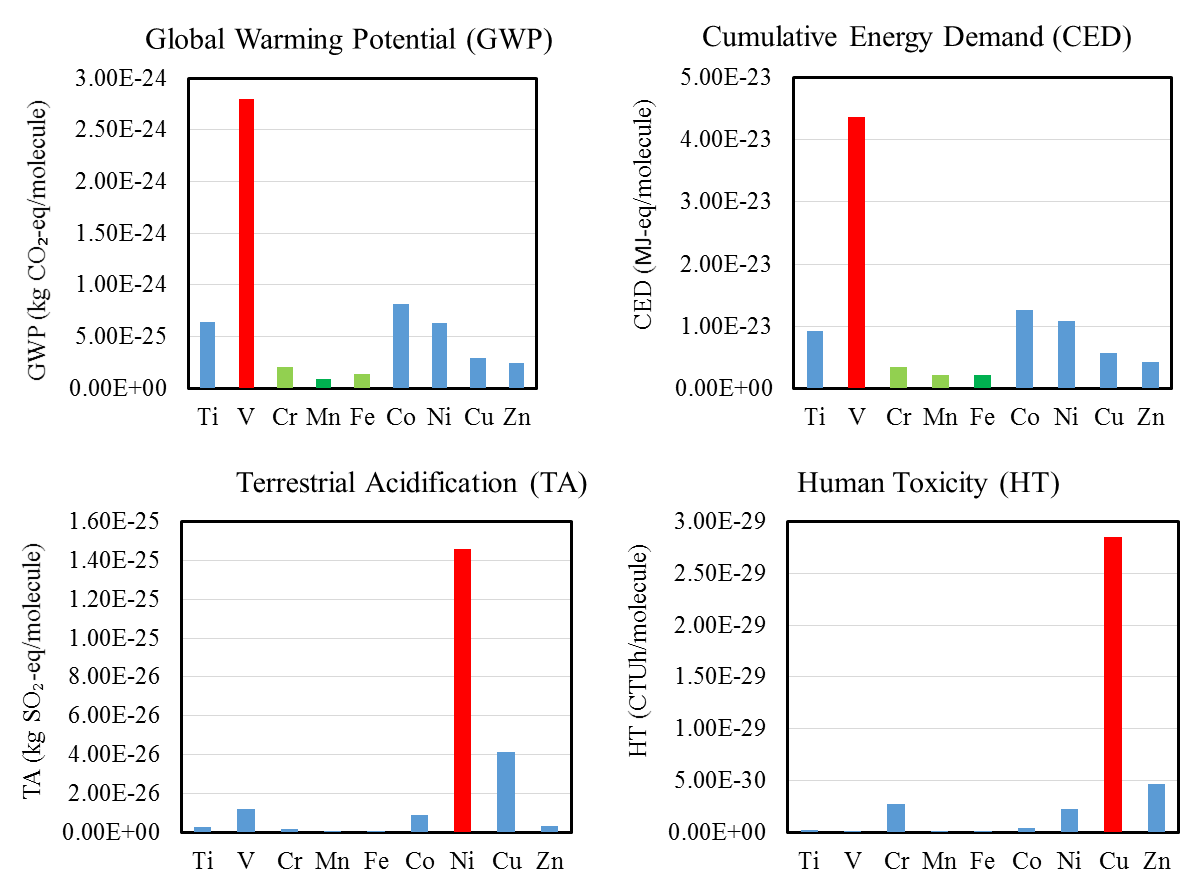
**Figure S2.** Frequency of appearance of different metal elements in the dataset



**Figure S3.** Histogram plots for (a) pore limiting (b) average available surface area and (c) void fraction



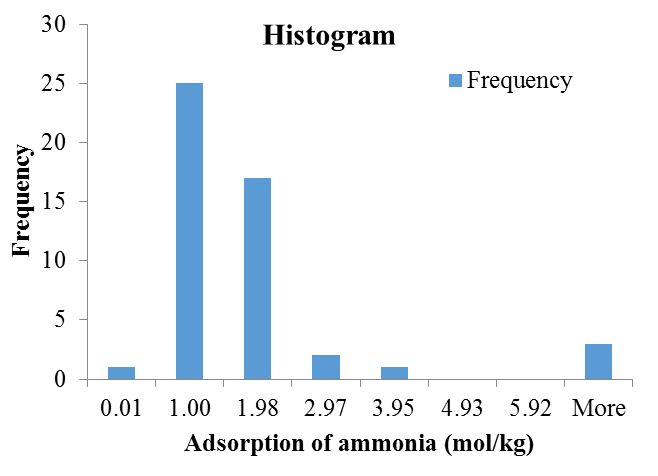
**Figure S4.** Process of screening CoRE MOFs for photocatalytic activity

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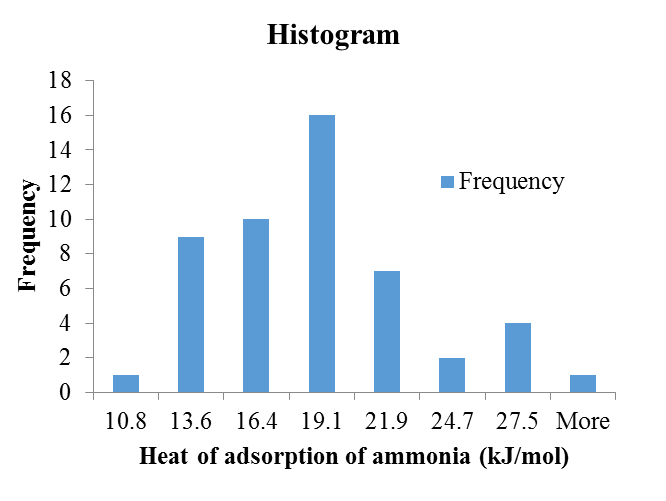
**Figure S5.** Summary of the main categories for first-raw transition metals comparison

Table S3. Relative charge carriers ratio of the four studied MOFs

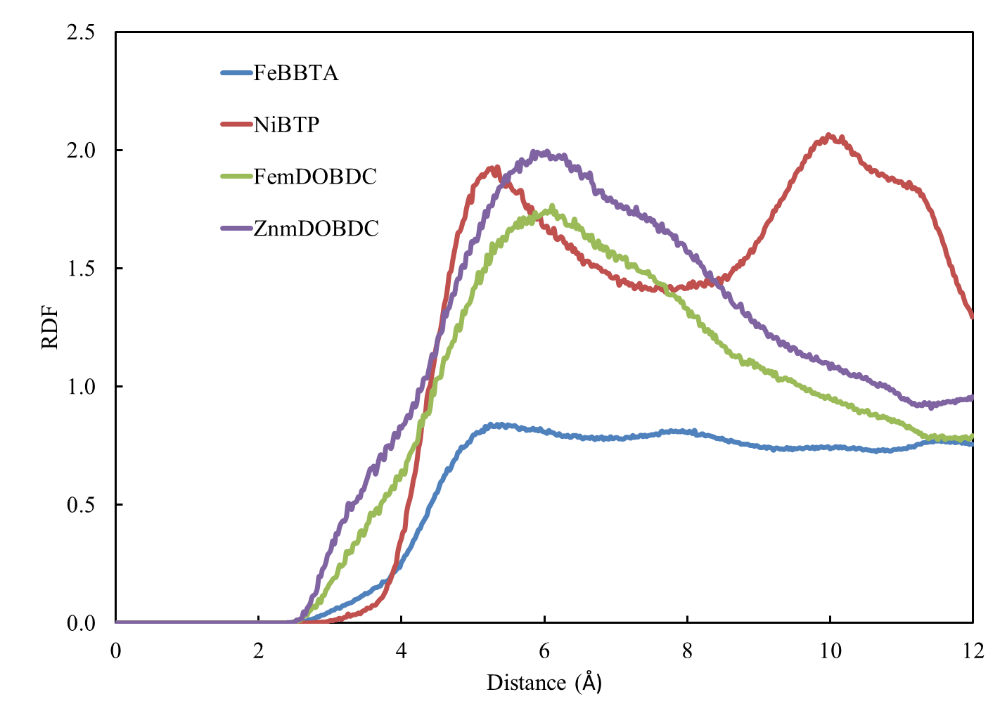
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Fe2Cl2BBTA | | Fe2(mDOBDC) | | Zn2(mDOBDC) | |
| Path | D | Path | D | Path | D |
|  | 0.10 |  | 0.97 |  | 0.41 |
|  | 0.24 |  | 1.05 |  | 36.54 |
|  | 0.04 |  | 1.46 |  | 11.44 |
|  | 0.35 |  | 0.15 |  | 0.51 |
|  | 0.22 |  | 1.71 |  | 33.70 |
|  | 0.14 |  | 5.89 |  | 0.52 |
|  | 0.07 |  | 2.67 |  | 0.47 |
|  | 1.72 |  | 0.76 |  | 0.42 |
|  | 0.25 |  | 0.93 |  | 14.61 |
|  | 0.04 |  | 1.48 |  | 13.36 |
|  | 0.49 |  | 0.15 |  | 0.43 |
|  | 1.00 |  | 3.44 |  | 3.93 |
|  | 0.05 |  | 2.13 |  | 0.45 |
|  | 0.19 |  | 5.41 |  | 0.40 |



**Figure S6.** Adsorption of ammonia histogram in the dataset



**Figure S7.** Histogram of the heat of adsorption of ammonia variability in the dataset

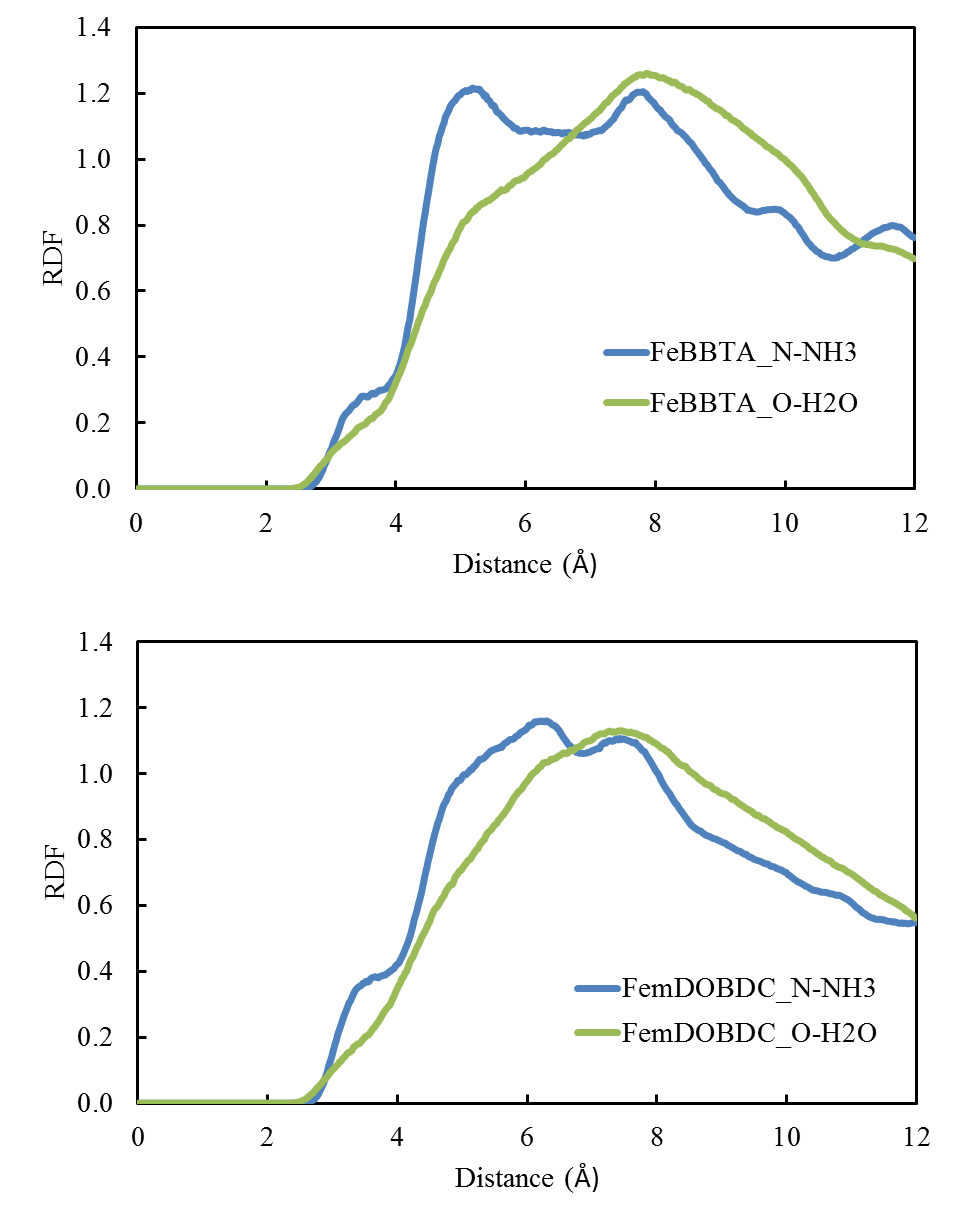
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**Figure S8.** Radial distribution function plots for N-N2 – Metal in the metal-organic frameworks (Fe2Cl2(BBTA), Ni-BTP, Fe2(mDOBDC) and Zn2(mDOBDC))

**Table S4.** Self-diffusivity and single gas permeability of nitrogen, water, and ammonia in Fe2Cl2(BBTA), Ni-BTP, Fe2(mDOBDC), and Zn2(mDOBDC)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| MOF | Diffusion coefficients (cm2/s) | | | Permeability (Ko Dself) | | | Selectivity (Pi/Pj) | |
| H2O | N2 | NH3 | H2O | N2 | NH3 | N2/ H2O | NH3/ H2O |
| Fe2Cl2 (BBTA) | 1.12E-04 | 1.71E-04 | 1.73E-04 | 3.94E-10 | 7.14E-09 | 5.13E-09 | 0.055 | 0.719 |
| Ni  BTP | 8.67E-06 | 3.11E-04 | 3.68E-04 | 1.75E-09 | 1.08E-10 | 1.44E-08 | 16.10 | 133.153 |
| Fe2  (mDOBDC) | 5.03E-05 | 1.33E-04 | 1.17E-04 | 2.84E-10 | 5.88E-09 | 6.62E-09 | 0.048 | 1.126 |
| Zn2  (mDOBDC) | 8.59E-05 | 9.46E-05 | 1.23E-04 | 2.07E-10 | 1.91E-10 | 1.34E-09 | 1.083 | 7.003 |

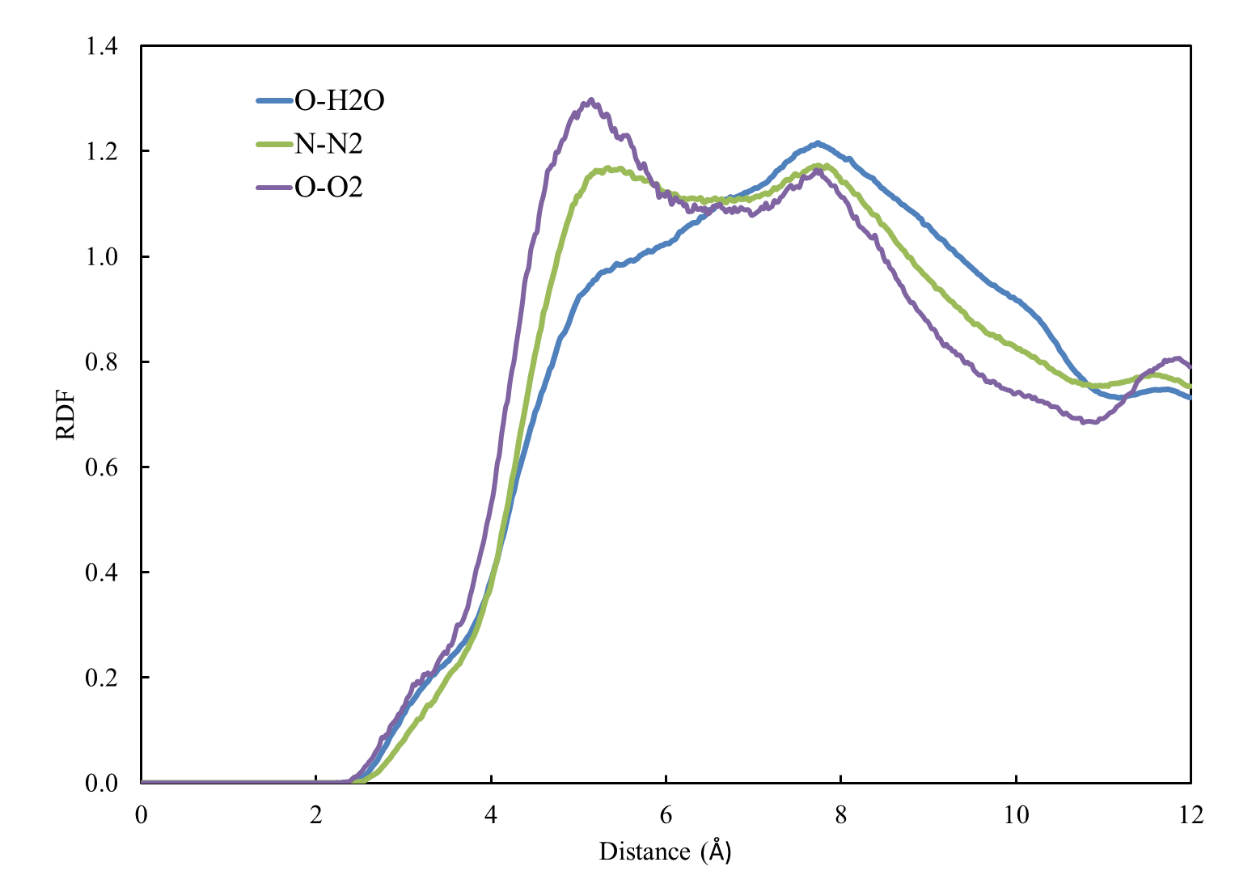
|  |
| --- |
|  |



**Figure S9.** Radial distribution function plots for water and ammonia – Metal in the metal-organic frameworks (Fe2Cl2(BBTA), Ni-BTP, Fe2(mDOBDC) and Zn2(mDOBDC)) (equimolar mixture)

**Table S5.** Self-diffusivity of water and ammonia in Fe2Cl2(BBTA), Ni-BTP, Fe2(mDOBDC) and Zn2(mDOBDC) in equimolar mixture

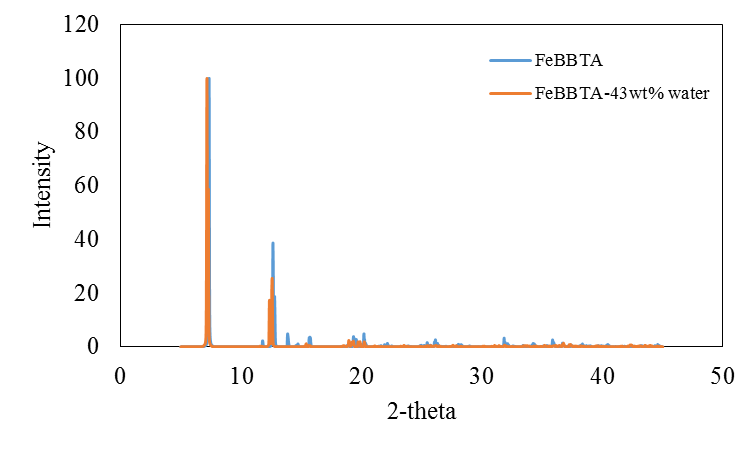
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| MOF | Diffusion coefficients (cm2/s) | | Diffusivity ratio (NH3/H2O) | |
| H2O | NH3 | Equimolar | From single gas |
| Fe2Cl2  (BBTA) | 8.21E-05 | 6.42E-05 | 1.28 | 1.54 |
| Fe2  (mDOBDC) | 1.19E-04 | 8.97E-05 | 1.33 | 2.33 |
| Zn2  (mDOBDC) | 1.38E-04 | 9.08E-05 | 1.52 | 1.43 |



**Figure S10.** Radial distribution function plots for water and nitrogen – Metal in the metal-organic frameworks (Fe2Cl2(BBTA) in the presence of oxygen

**Table S6.** Thermodynamic water stability figure of the four MOFs (DFT calculations using PBE functional)

|  |  |  |
| --- | --- | --- |
| MOF | Weight fraction |  |
| **%** | **eV/molecule (H2O)** |
| Fe2Cl2 (BBTA) | **43** | **-0.487** |
| 10 | -0.373 |
| Fe2(mDOBDC) | **39** | **-0.579** |
| 10 | -0.914 |
| Zn2(mDOBDC) | **35** | **-0.238** |
| 10 | -0.334 |
| Ni-BTP | **53** | **-0.238** |
| 10 | -1.204 |



**Figure S11.** PXRD comparison between pristine Fe2Cl2(BBTA) and water-saturated Fe2Cl2(BBTA)

**Synthesis steps in producing the studied MOFs**

The following steps produce the BBTA linker: (1) nitration process of nitrobenzene to produce m-1,3-Dinitrobenzene [1] (2) hydrogenation of m-1,3-Dinitrobenzene in the presence of methanol to produce m-phenylenediamine [2](3) nitration process in the presence of Sulphuric and Acetic Acid of m-phenylenediamine to produce 4,6-Dinitrobenzene-1,3-diamine [3] (4) acetylation process to produce 1,5-bis(acetylamino)-2,4-dinitrobenzene [4](5) hydrogenation process in the presence of ethanol and hydrochloric acid followed by NaNO2 treatment to produce 1,7-Diacetyl-1,7-dihydrobenzo[1,2-d:4,5-d’]bistriazole [5] (6) treatment with methanol solution and sulphuric acid to produce 1,5-Dihydrobenzo[1,2-d:4,5-d’]bistriazole (BBTA linker) [5]. In the final step (7), BBTA is reacted with Iron(II) Sulphate using DMF and methanol as solvents and in the activation, processes to produce Fe2Cl2(BBTA) [6]. It is important to note that substitution of Iron Chloride with Iron Sulphate was done because of data availability. DMF is approximated with dimethylamine.

The mDOBDC linker was produced via the resorcinol pathway, where resorcinol is reacted with KHCO3 and CO2 to deliver the product. The following steps are followed to make resorcinol [7] and then the desired organic ligand: (1) production of m-DIPB using the reaction between cumene and propene, followed by hydroperoxidation of m-DIPB to m-DHP using oxygen (2) oxidation of byproduct m-HHP to m-DHP with hydrogen peroxide, sulphuric acid, toluene, and ether, followed by the decomposition of m-DHP to resorcinol and acetone (3) reaction of resorcinol, carbon dioxide and KHCO3 [8] (substitution to sodium bicarbonate was done for data availability reason). Synthesis of Zn2(mDOBDC) and Fe2(mDOBDC) [9] was carried out using the synthesized linker with metal source (Zinc+hydrogen chloride) for Zn2(mDOBDC) and Iron (II) Sulphate for Fe2(mDOBDC) case.

BTP linker was synthesized following four steps: (1) benzene is reacted with dry sodium methylate, acetone, and methyl formate followed by addition of phosphoric acid and water (2) the product 1,3,5-triacetyl benzene is reacted morpholine, elemental sulfur, and solution of acetic and sulphuric acids to produce 1,3,5-benzentriacetic acid (3) where it is reacted with POCl3 and treated with NaClO4 (4) the product is then added to methanol and ethanol steps to produce 1,3,5-tris(1H-pyrazol-4-yl)benzene (BTP) [8]. BTP is then reacted with Nickel using solvents including DMF and methanol to produce Ni-BTP [10]. It has to be noted that several approximations and substitutions were included in the study. DMF is replaced by dimethylamine, methyl acetate in the place of methyl formate, caprolactam instead of morpholine, sodium hypochlorite to replace NaClO4.

**Table S7.** Inventory data used to model the synthesis of Ni-BTP,

|  |  |
| --- | --- |
| Element | Quantity (kg) |
| STEP 1 |  |
| Benzene | 0.0213 |
| Methyl Acetate | 0.00218 |
| Water (deionized) | 0.00605 |
| Sodium Bicarbonate | 0.00196 |
| Acetone | 0.0021 |
| Ethanol | 9.47E-8 |
| Phosphoric Acid (75%) | 0.00278 |
| STEP 2 |  |
| Sodium Hypochlorite Solution | 0.00378 |
| Phosphorous Oxychloride | 0.00476 |
| Water (deionized) | 0.0141 |
| Dimethylamine | 0.00659 |
| STEP 3 |  |
| Ethanol | 0.0255 |
| Methanol | 0.00676 |
| Water (deionized) | 0.00845 |
| STEP 4 |  |
| Dimethylamine | 0.049 |
| Methanol | 0.0235 |
| Acetic Acid | 0.00032 |
| Water Deionized | 0.000141 |
| Nickel | 0.000159 |

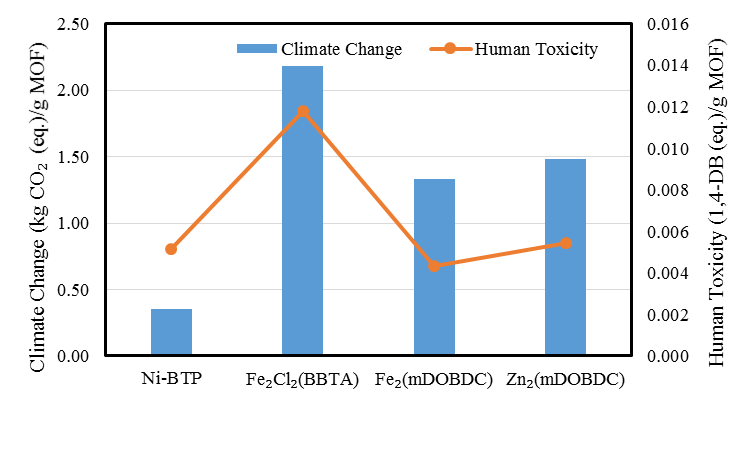
**Table S8.** The inventory data used to model the synthesis of Fe2(mDOBDC) and Zn2(mDOBDC) MOFs

|  |  |  |
| --- | --- | --- |
| Element | Iron Quantity (kg) | Zinc Quantity (kg) |
| STEP 1: DHP |  |  |
| Cumene | 0.00134 | 0.00149 |
| Oxygen | 0.000528 | 0.00059 |
| Propene | 0.000468 | 0.000523 |
| STEP 2: Resorcinol |  |  |
| Hydrogen Peroxide | 0.000108 | 0.000121 |
| Dimethyl Ether | 0.00604 | 0.00674 |
| Sodium Sulphate | 0.000847 | 0.00946 |
| Toluene | 0.022 | 0.0245 |
| Water (deionized) | 0.00932 | 0.0104 |
| Aluminmium Silicate | 0.000847 | 0.000946 |
| Sulphuric Acid | 0.000162 | 0.00018 |
| STEP 3: mDOBDC |  |  |
| Sodium Bicarbonate | 0.00189 | 0.00211 |
| Carbon Dioxide | 0.000832 | 0.00929 |
| Water (deionized) | 0.0189 | 0.0211 |
| STEP 4: Fe2(mDOBDC) and Zn2(mDOBDC) |  |  |
| Dimethylamine | 0.369 | 0.412 |
| Methanol | 0.309 | 0.344 |
| Iron (II) Sulphate | 0.00191 |  |
| Zinc |  | 0.000912 |
| Hydrogen Chloride |  | 0.00101 |

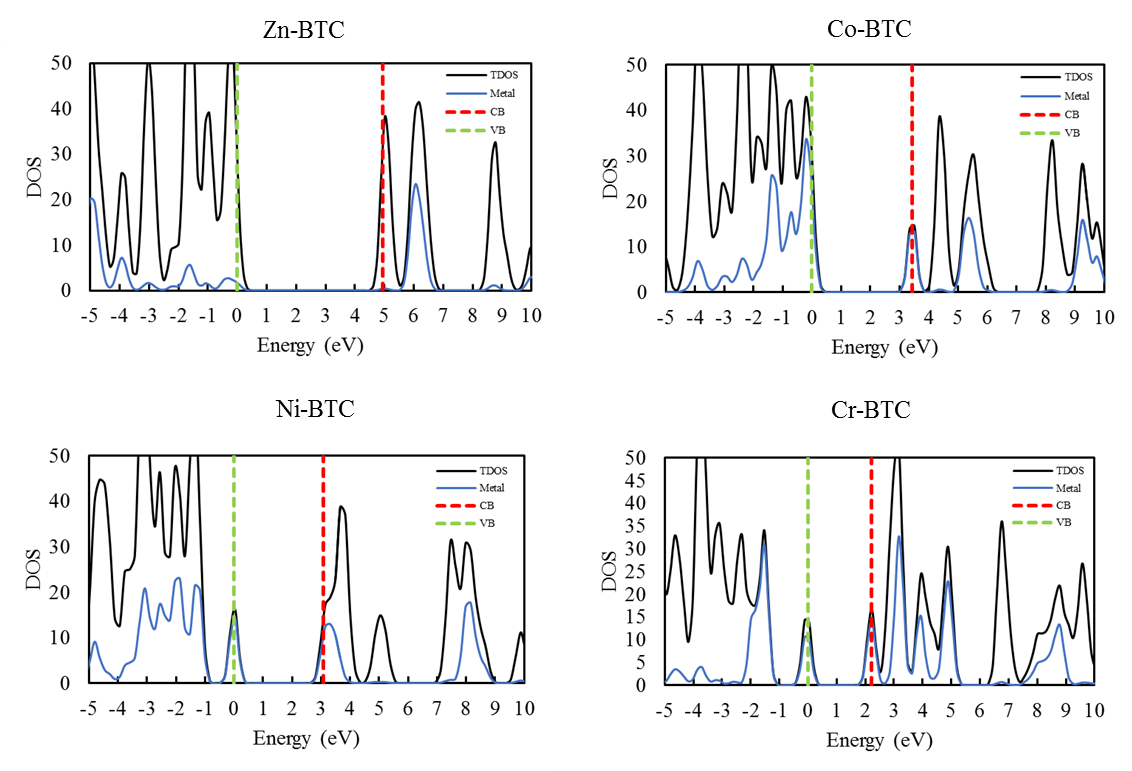
**Table S9.** The inventory data used to model the synthesis of Fe2Cl2(BBTA) MOF

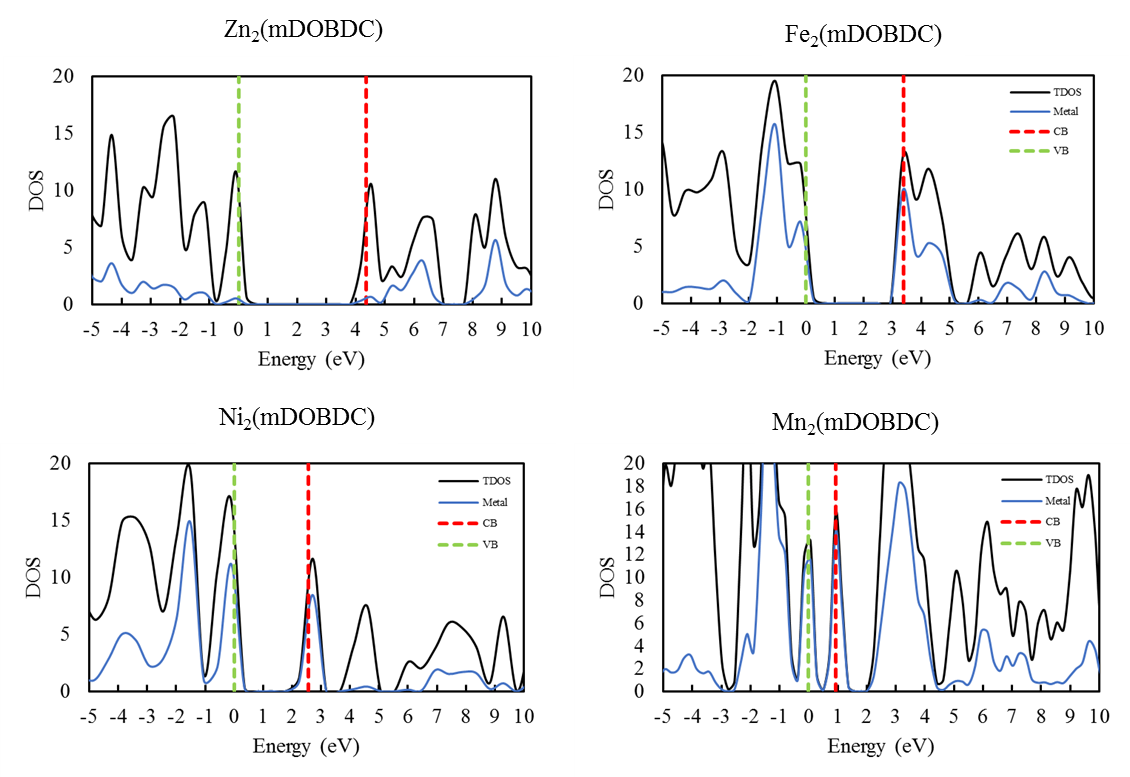
|  |  |
| --- | --- |
| Element | Quantity (kg) |
| STEP 1 |  |
| Nitrobenzene | 0.00813 |
| Nitric Acid (98%) | 0.00208 |
| Sulphuric Acid (96%) | 0.302 |
| STEP 2 |  |
| Hydrogen | 0.000538 |
| Methanol | 0.121 |
| STEP 3 |  |
| Acetic Acid | **0.0559** |
| Sulphuric Acid (96%) | 0.0886 |
| Nitric Acid (98%) | 0.00726 |
| STEP 4 |  |
| Acetic Acid | 0.0102 |
| Water (deionized) | 0.0969 |
| STEP 5 |  |
| Hydrochloric Acid (100%) | 0.00248 |
| Water (deionized) | 0.0455 |
| Hydrogen | 0.000103 |
| Ethanol | 0.0124 |
| Sodium Bicarbonate | 0.000918 |
| STEP 6: BBTA |  |
| Sulphuric Acid (96%) | 0.00249 |
| Methanol | 0.109 |
| STEP 7: Fe2Cl2(BBTA) |  |
| Dimethylamine | 0.472 |
| Methanol | 0.64 |
| Iron (II) Sulphate | 0.001 |

\* Cut-off rules for each unit process: Coverage of at least 95% of mass and energy of the input and output flows, and 98% of their environmental relevance (GaBi Documentation). Percentage supply or production covered: 95% (GaBi Documentation).



**Figure S12.** Comparison between the MOFs in terms of global warming potential and human toxicity impact categories





**Figure S13.** The density of state (states/eV) of M-BTC and M2(mDOBDC) used for the analysis of metal role in the bandgap of MOFs (HSE06 functional)

**Table S10.** Fitting parameters used in modeling the relationship between ligand and structure bandgaps in Fe, Ni, and Mn-based MOFs

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Fitting Parameter | | | | Coefficient of Determination |
| Metal | **a** | **b** | **c** | **d** | **R2** |
| Fe | 1.4231 | 3.9767 | -2.8284 | 2.9554 | 0.8971 |
| Ni | 1.0151 | 8.0554 | -1.2622 | 3.0407 | 0.7918 |
| Mn | 0.2811 | 6.2832 | -2.9143 | 0.6717 | 0.9710 |

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