



X-Ray Powder Diffraction Peak Predictor for Characterization of Isoreticular Metal-Organic Frameworks: An Online Resource

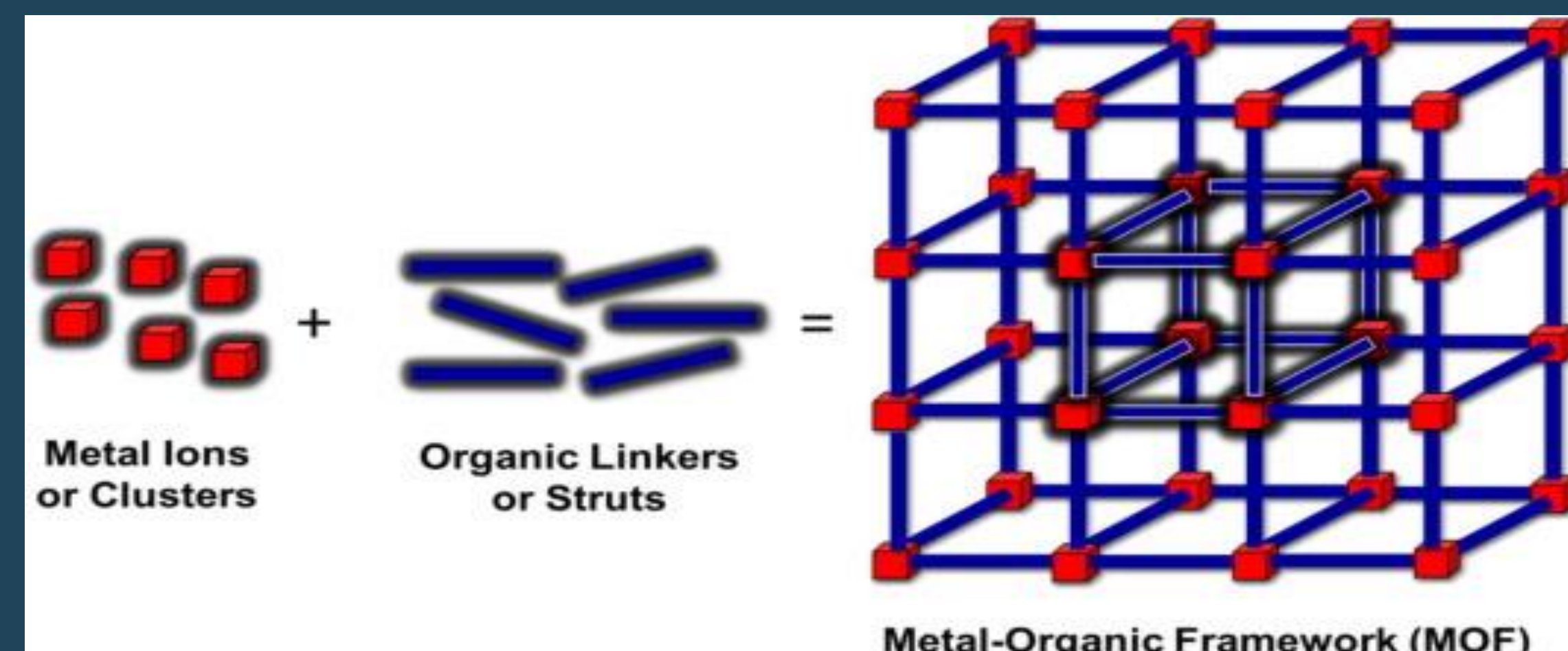
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Introduction

- Metal-Organic Frameworks (MOFs) are hybrid materials made up of metal ions/clusters nodes that are linked by organic ligands to form cage-like coordination networks.



- The organic-inorganic hybrid nature of MOFs allow for extensive tunability and have potential applications in catalysis, sensing of pollutants, water harvesting, gas storage, carbon dioxide sequestration and molecular filters, among others.

- Thus, MOFs are a very promising new class of functional materials and can contribute to meeting the Sustainable Development Goals (SDGs) such as Clean Water and Sanitation (SDG6), Life Below Water (SDG14) and Life On Land (SDG15).

- Reticular synthesis is a popular design approach used to make families of structures with identical network topologies, but varying physical and chemical properties, known as Isoreticular MOFs (IRMOFs).

- However, the growth of single crystals can be challenging when synthesizing MOFs, often leading to micro-crystalline products, and structural characterization can prove to be difficult.

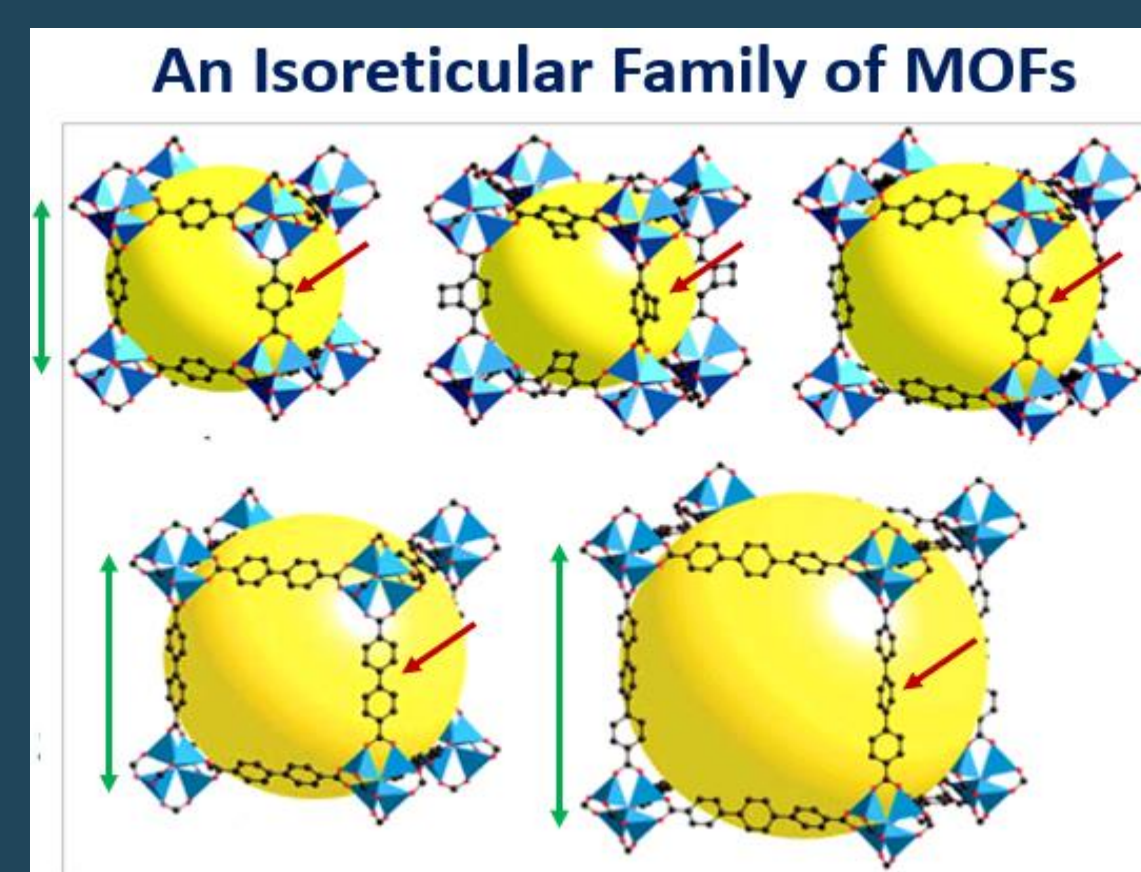
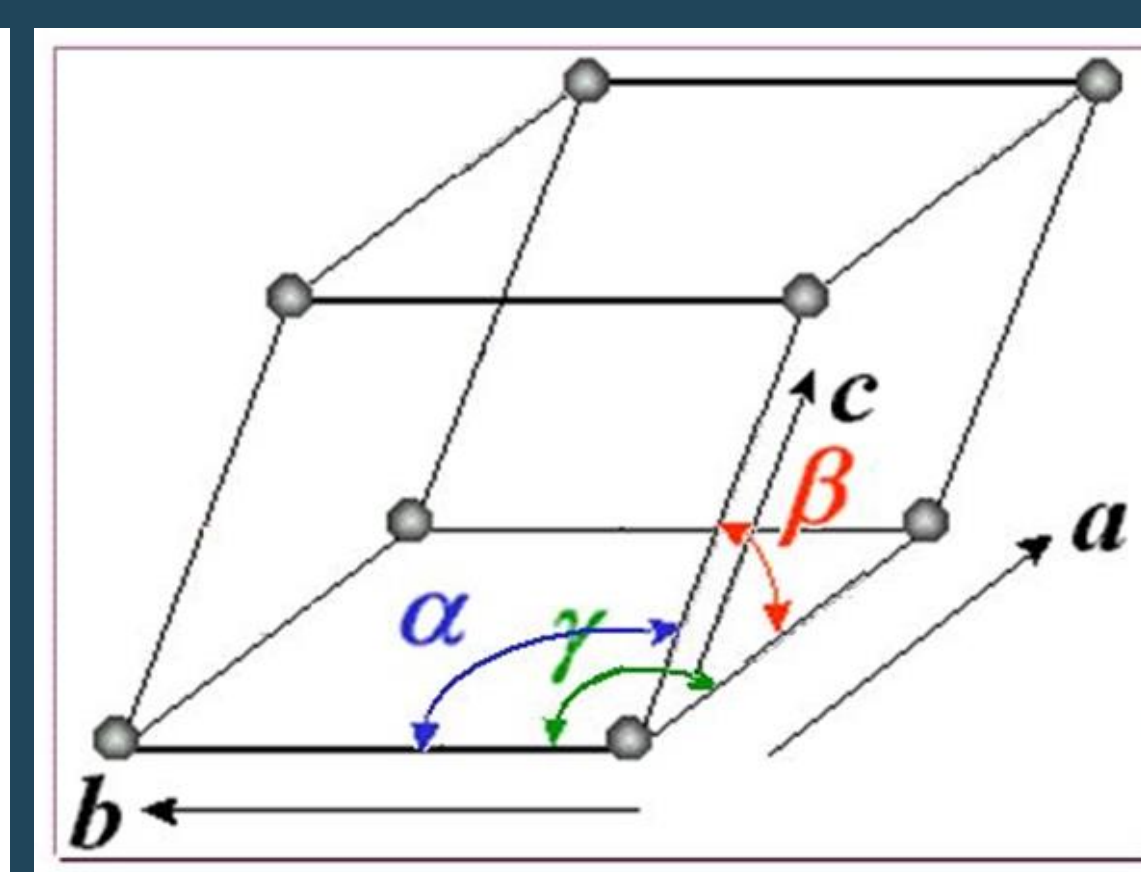
- We present a resource that predicts the peak positions of an iso-reticular MOF, which is used for structural confirmation by comparison with the sample X-ray Powder Diffraction (XPD).



Approach / Methodology

- All iso-reticular members have the same network topology and thus adopt the same crystal system even if the unit cell dimensions are expected to vary presenting an opportunity for structural confirmation.

- That is, if the unit cell dimension of any member is known, then the 2θ peak positions of an iso-reticular structure can be calculated by estimating the respective changes in cell dimensions based on variations of the organic linker.



- The peak positions, which are 2θ values, can be calculated from d-spacings using Bragg's Law:

$$n\lambda = 2d \sin \theta$$

- The d-spacings and subsequently the expected 2θ values can be calculated using simplified reciprocal-space metric tensors, as the crystal system and the unit cell dimensions are known.

- Cubic $1/d^2 = (h^2 + k^2 + l^2) / a^2$
- Tetragonal $1/d^2 = (h^2 + k^2) / a^2 + l^2 / c^2$
- Orthorhombic $1/d^2 = h^2 / a^2 + k^2 / b^2 + l^2 / c^2$
- Monoclinic $1/d^2 = h^2 / (a^2 \sin^2 \beta) + k^2 / b^2 + l^2 / (c^2 \sin^2 \beta) - 2 h l \cos \beta / (a c \sin^2 \beta)$
- Hexagonal $1/d^2 = 4 (h^2 + h k + k^2) / 3 a^2 + (l^2 / c^2)$

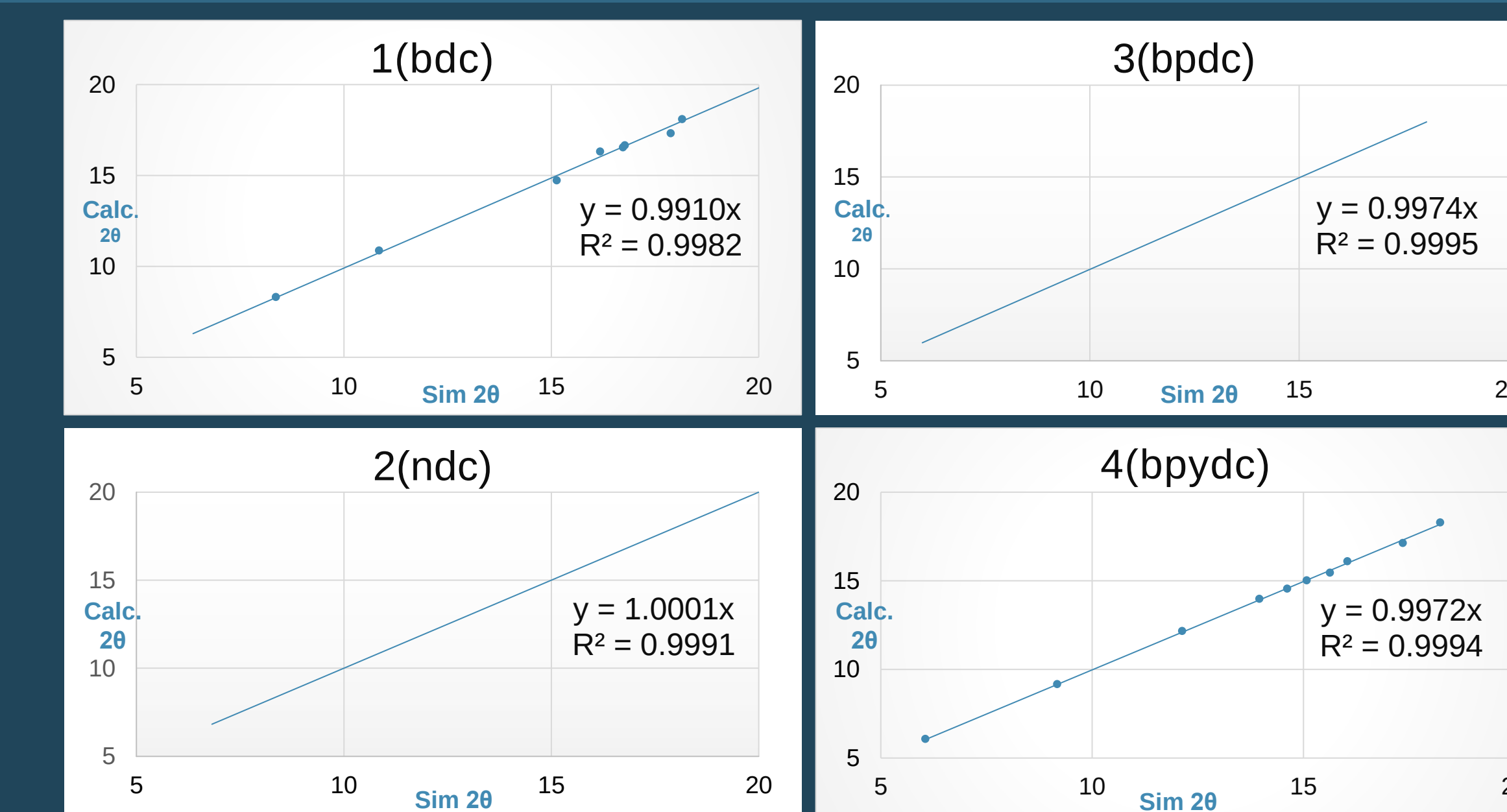
Proof of Concept / Results

- To predict the peak positions of the iso-reticular compounds of IRUWI-01; ****1** (*bdc*), **2** (*ndc*), **3** (*bpdc*) and **4** (*bpydc*), **Deng's** (*bpedc*) analogue is used as a reference to estimate the respective changes in the varying 'a' dimension of the unit cell.

IRUWI-01			
Compound # (Ligand)	True 'a' (Å)	Predicted 'a' (Å)	
1 (<i>bdc</i>)	10.65	10.60	
2 (<i>ndc</i>)	12.88	12.98	
3 (<i>bpdc</i>)	14.56	14.59	
4 (<i>bpydc</i>)	14.76	14.74	

- The corresponding 'a' dimension of the IRUWI-01 structures were approximated by subtracting the difference in ligand length, between *bpedc* and the respective ligands in **1-4**, from the 'a' dimension of Deng's *Sm(bpedc)(HCOO)*^a.

- The results of the **t-tests** for all four compounds proved that there was no significant difference between the means for the True value and the Predicted value (compounds **1** [**P>0.98**] and compounds **2,3 & 4** [**P>0.99**]).



- After calculation of the predicted 2θ values, **ANOVA** and **Pearson** correlation analyses show that the **predicted model** is a good fit with the True value, with all four compounds giving a fit greater than **99.9 %** with **R² > 0.998**.

- This approach was also tested on other iso-reticular families including the SUMOF7^b family which gave a good fit with ANOVA and Pearson values greater than **99.8 %** and **R² > 0.999**.

Online Resource

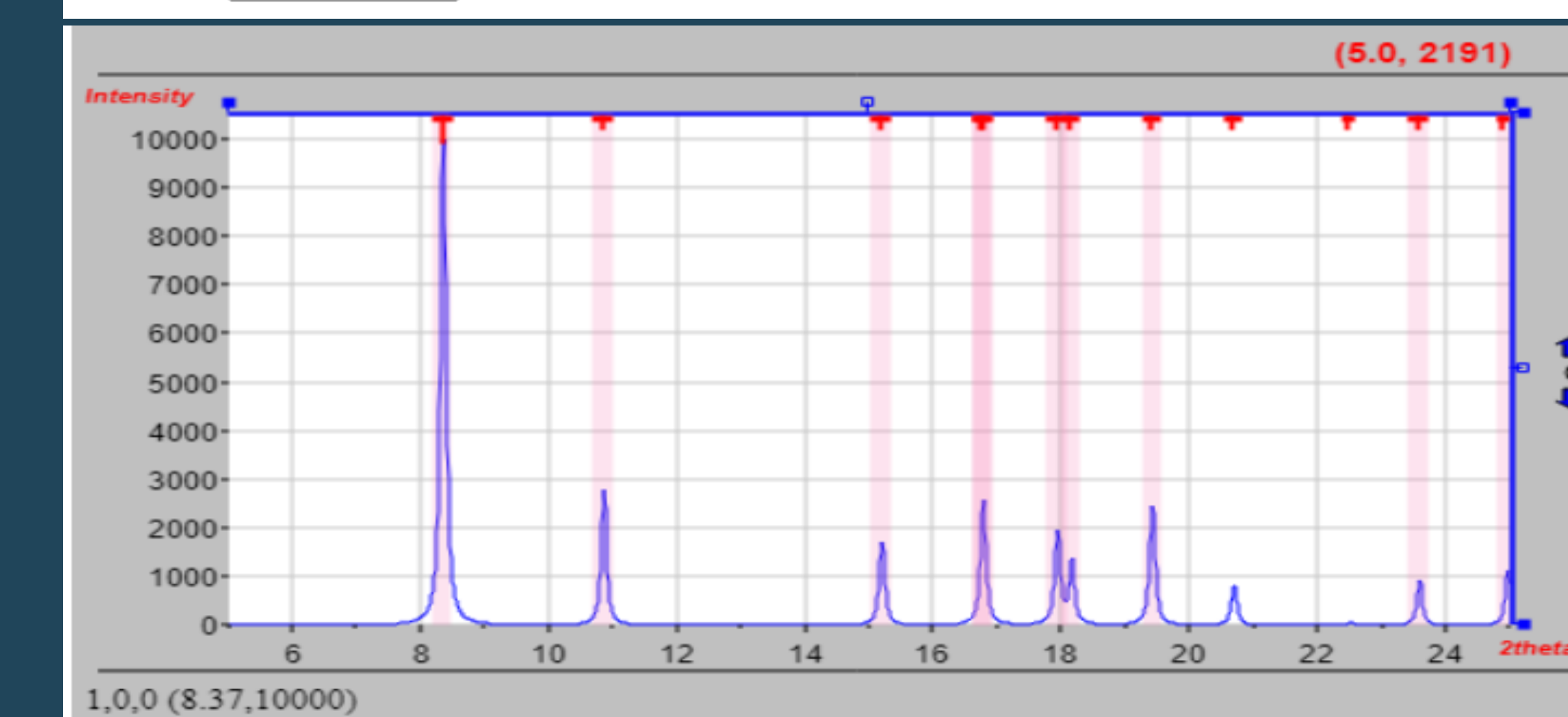
- An online resource in the form of an open-source web application is currently being developed to be made accessible to the wider scientific community.

- The user will simply enter the relevant unit cell information to calculate the predicted 2θ peak positions for comparison.

- This resource also enables the user to see a graphical representation by uploading experimental XPD data for a user-friendly structure confirmation or rejection.

Sample=test1 Crystal system, cs=3 Monoclinic
a=10.6007 b=12.7499 c=6.5671 α=90 β=95.012 γ=90
hkl[0]=1, 0, 0
hkl[1]=1, 1, 0
hkl[2]=0, 1, 1
hkl[3]=2, 0, 0
hkl[4]=1, 1, -1
hkl[5]=1, 1, 1
hkl[6]=2, 1, 0
hkl[7]=0, 2, 1
hkl[8]=2, 1, 1
hkl[9]=2, 2, -1
update and predict

[h, k, l]	d	2theta
1, 0, 0	10.5602	8.3662
1, 1, 0	8.1328	10.8699
0, 1, 1	5.8205	15.2100
2, 0, 0	5.2801	16.7773
1, 1, -1	5.2737	16.7978
1, 1, 1	4.9378	17.9497
2, 1, 0	4.8783	18.1704
0, 2, 1	4.5657	19.4262
2, 1, 1	3.7677	23.5944
2, 2, -1	3.5627	24.9733



Conclusion

- We have shown that a good understanding of this predictive XPD approach, in tandem with other characterization techniques, can be a useful tool in the structural confirmation of iso-reticular MOFs that are difficult to crystallize.

- Utilization of this novel approach can lead to the discovery and characterization of many new iso-reticular MOFs and contribute to our knowledge of crystal engineering in MOFs and create new partnerships in line with SDG17.

^{**1} **1** (*bdc* - benzenedicarboxylate), **2** (*ndc* - naphthalenedicarboxylate), **3** (*bpdc* - biphenyldicarboxylate) and **4** (*bpydc* - bipyridinedicarboxylate), **Deng's** (*bpedc* -biphenylethylenedicarboxylate), ^a – Cryst. Eng. Comm. 2010, 12, 1526; ^b – J. Am. Chem. Soc. 2005, 127, (37), 12788.