Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Connecting Defects and Amorphization in UiO-66 and MIL-140 Metal-organic Frameworks: A Combined Experimental and Computational Study

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SI-1: Elemental Analysis

Crystalline: $[Zr_6O_4(OH)_4(O_2C\text{-}C_6H_4\text{-}CO_2)_6]$

Calculated: C 34.63 % H 1.68 %
Found: C 29.63 % H 2.26 %

Amorphous: $[Zr_6O_4(OH)_4(O_2C\text{-}C_6H_4\text{-}CO_2)_6]$

Calculated: C 34.63 % H 1.68 %
Found: C 32.14 % H 2.45 %

Crystalline: $[ZrO(O_2C\text{-}C_{10}H_6\text{-}CO_2)]$

Calculated: C 44.83 % H 1.87 %
Found: C 42.35 % H 1.65 %

Amorphous: $[ZrO(O_2C\text{-}C_{10}H_6\text{-}CO_2)]$

Calculated: C 44.83 % H 1.87 %
Found: C 40.10 % H 2.13 %

Crystalline: $[ZrO(O_2C\text{-}C_{12}H_8\text{-}CO_2)]$

Calculated: C 48.38 % H 1.30 %
Found: C 42.67% H 2.13 %

Amorphous: $[ZrO(O_2C\text{-}C_{12}H_8\text{-}CO_2)]$

Calculated: C 48.38 % H 1.30 %
Found: C 41.25% H 2.01 %

SI-2: NMR Calculations

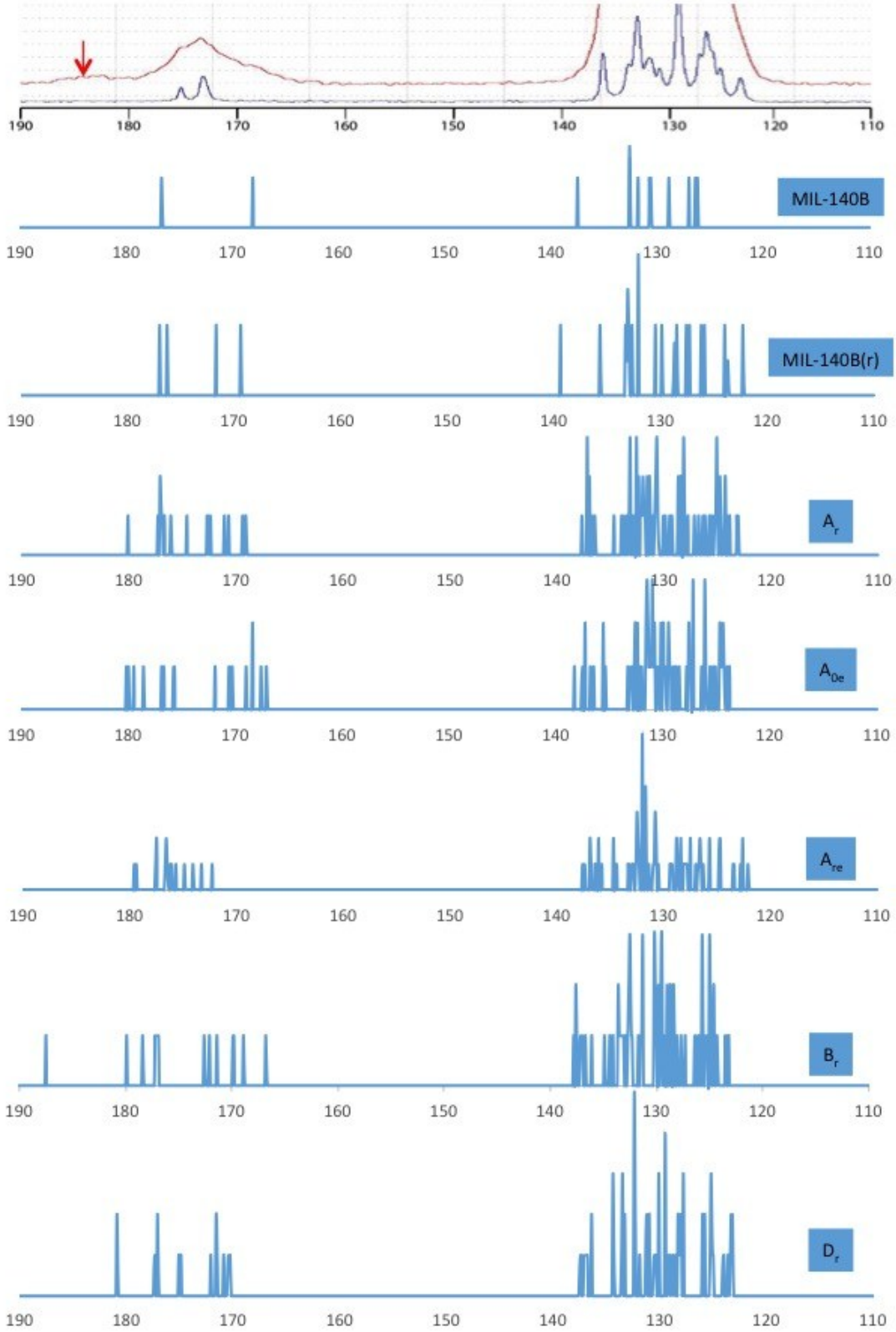

Figure S1. Top) Experimental ^{13}C MAS NMR spectra of **MIL-140B** crystallized (blue) and amorphous (red). Bottom) simulated ^{13}C spectra computed from the parent **MIL-140B** model, the newly derived **MIL-140B(r)** and selected defective models, obtained at the PBE-D3 level.

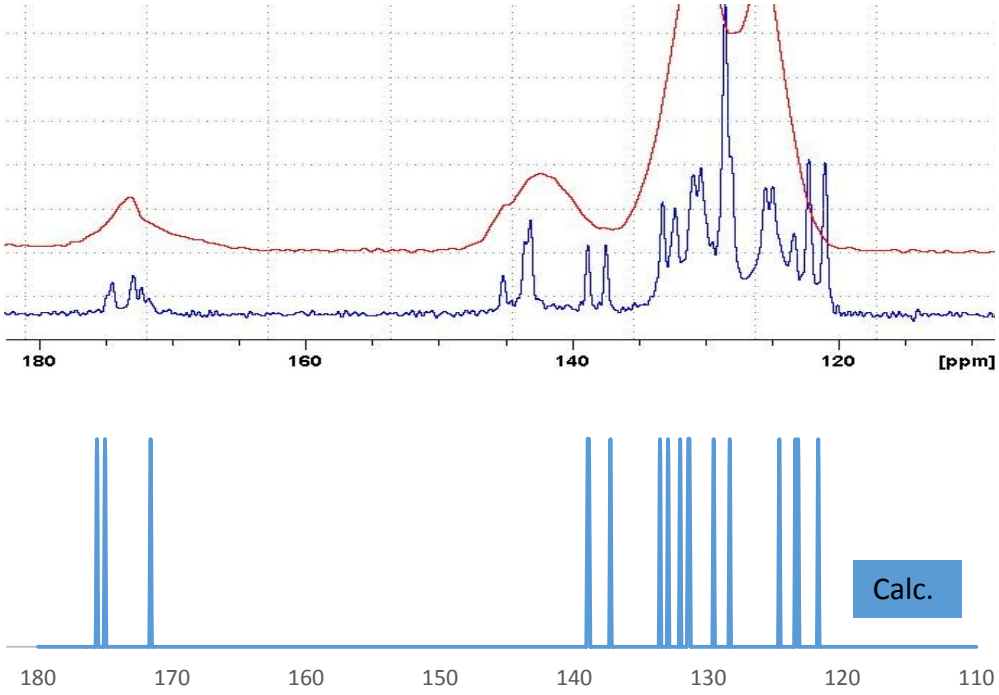

Figure S2. Top) Experimental NMR ^{13}C spectra of **MIL-140C** crystallized (blue) and amorphous (red). Bottom) simulated ^{13}C spectra computed from the fully relaxed geometry of **MIL-140C** crystal structure (optB88-vdW entry).

SI-3: Defective Models

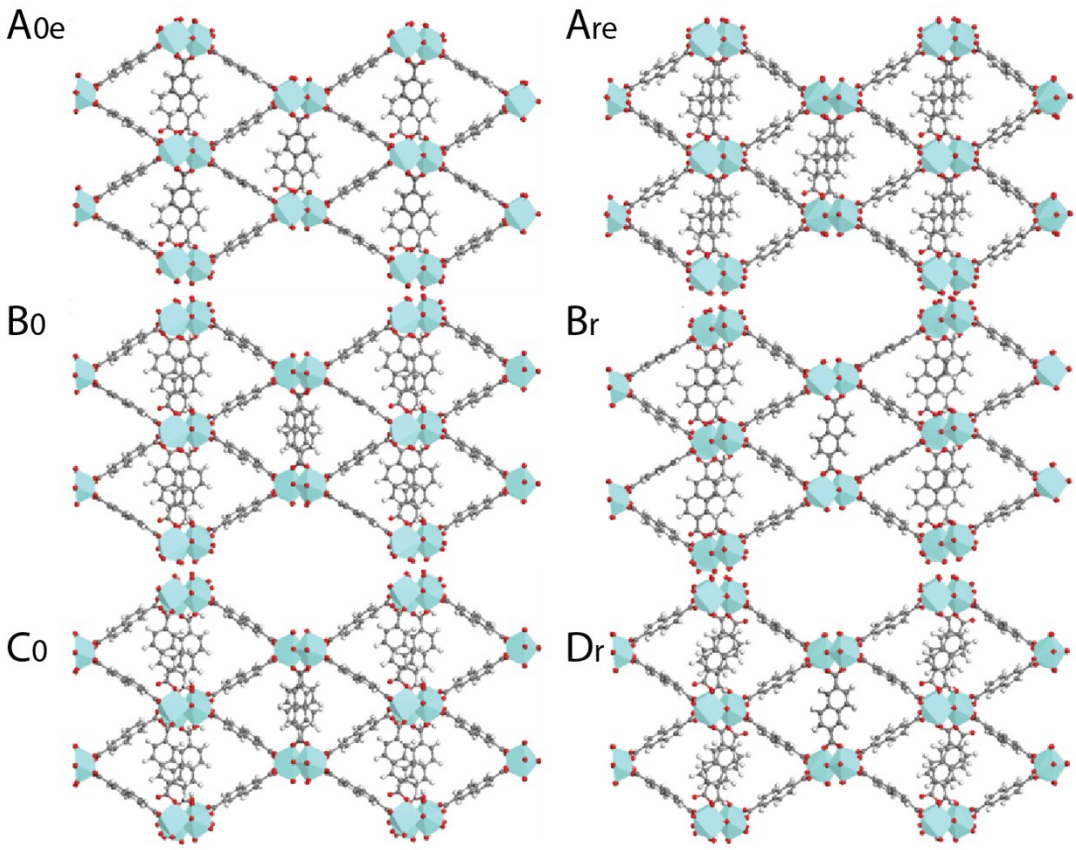

Figure S3: The most relevant defective structures of **MIL-140B** viewed along the *c*-axis containing two H_2O molecules per unit cell. All models have chemisorbed H_2O molecules on Zr-centers inducing different orientation and binding of the linkers.

SI-4: Total Scattering Experiments

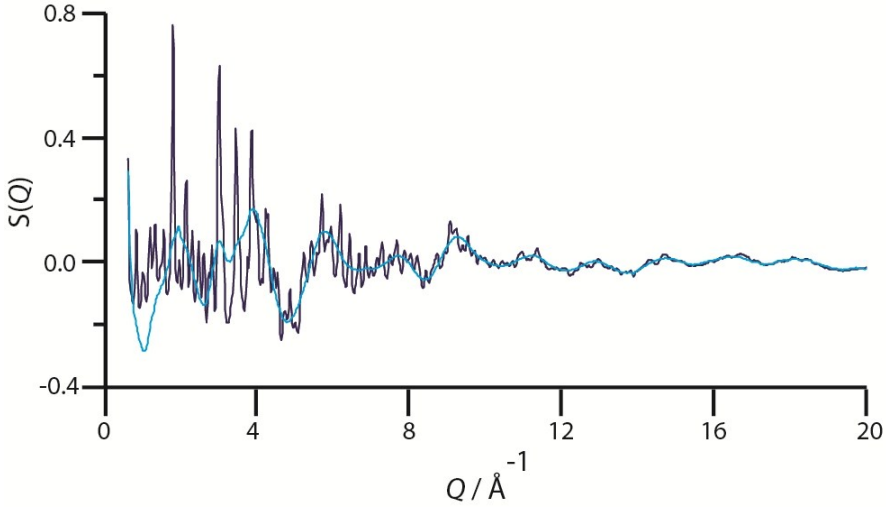

Figure S4. X-ray total scattering function *S*(*Q*) for crystalline (dark blue) and amorphous (light blue) **UiO-66.**

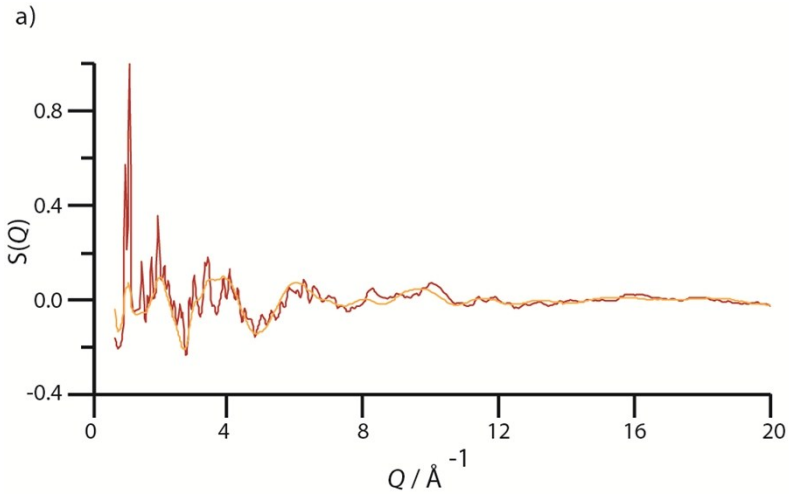

Figure S5. X-ray total scattering function *S*(*Q*) for crystalline (red) and amorphous (orange) **MIL-140B.**

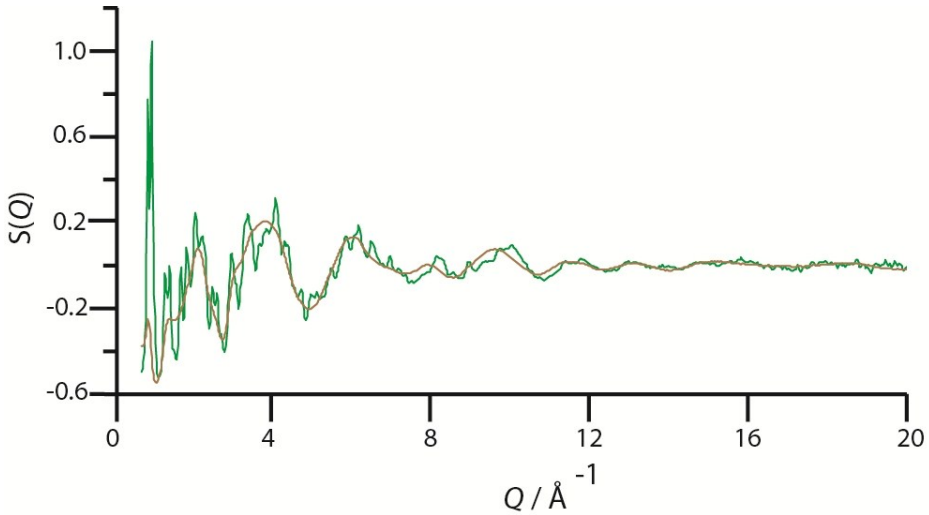

Figure S6. X-ray total scattering function *S*(*Q*) for crystalline (green) and amorphous (brown) **MIL-140C**.

SI-5: Predicted partial pair distribution functions

It is noticeable that there are more features in the calculated PDFs below than in the experimental PDFs in the main text, which may arise because of the high atomic displacement parameters from atoms belonging to the flexible organic ligands, which cause longer correlation contributions from the organic ligand to be more damped with respect to Zr….Zr contributions. Partial PDFs involving H have also been omitted in the PDFs below, as they contribute little to the overall PDF.

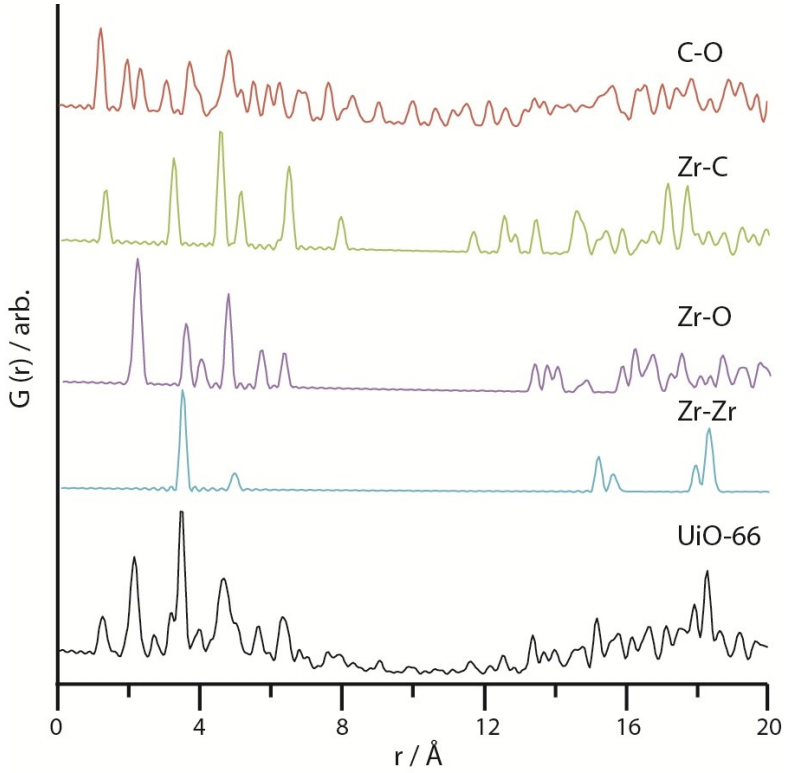

Figure S7. Partial pair distribution functions (upper plots) and total X-ray pair distribution function (lowermost plot – black line) for **UiO-66** calculated from the published crystalline structure using PDFgui.[1, 2]

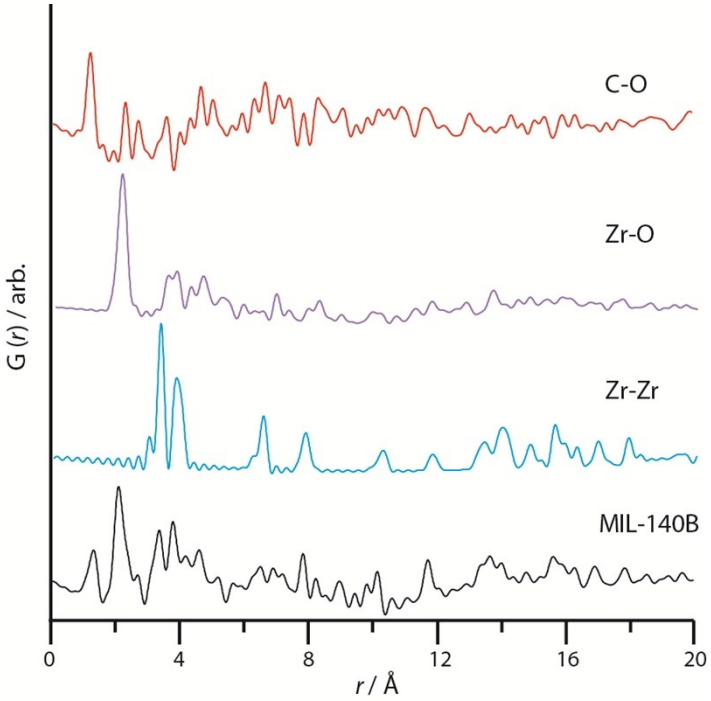

Figure S8. Partial pair distribution functions (upper plots) and total X-ray pair distribution function (lowermost plot – black line) for **MIL-140B** calculated from the published crystalline structure using PDFgui.[1, 3]

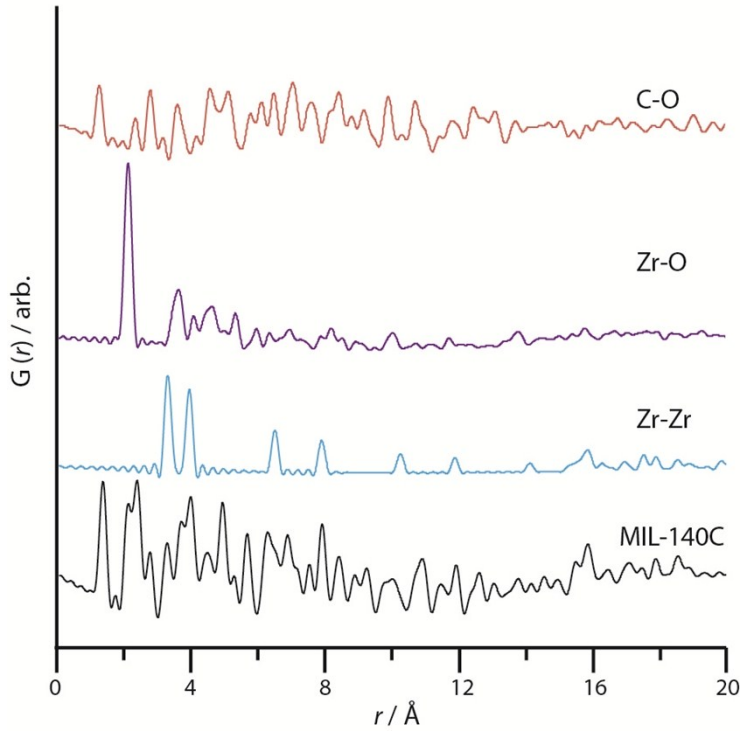

Figure S9. Partial pair distribution functions (upper plots) and total X-ray pair distribution function (lowermost plot – black line) for **MIL-140C** calculated from the published crystalline structure using PDFgui.[1, 3]

References

1. C. L. Farrow, P. Juhas, J. W. Liu, D. Bryndin, E. S. Bozin, J. Bloch, T. Proffen and S. J. L. Billinge, *J. Phys.-Condens. Mat.*, 2007, **19**, 335219.
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