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Duncan Johnstone, Francesca Firth, Clare Grey, Paul A. Midgley, Matthew Cliffe, Sean M. Collins

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Direct imaging of correlated defect nanodomains in a metal-organic framework

Duncan N. Johnstone,† Francesca C. N. Firth, Clare P. Grey, Paul A. Midgley, Matthew J. Cliffe, and Sean M. Collins†,*

1Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, UK
2Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
3School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK
4School of Chemical and Process Engineering and School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Email: *S.M.Collins@leeds.ac.uk, †dnj23@cam.ac.uk

Abstract

Defect engineering can enhance key properties of metal-organic frameworks (MOFs). Tailoring the distribution of defects, for example in correlated nanodomains, requires characterization across length scales. However, a critical nanoscale characterization gap has emerged between the bulk diffraction techniques used to detect defect nanodomains and the sub-nanometre imaging used to observe individual defects. Here, we demonstrate that the emerging technique of scanning electron diffraction (SED) can bridge this gap. We directly image defect nanodomains in the MOF UiO-66(Hf) over an area of ca. 1 000 nm and with a spatial resolution ca. 5 nm to reveal domain morphology and distribution. Based on these observations, we suggest possible crystal growth processes underpinning synthetic control of defect nanodomains. We also identify likely dislocations and small angle grain boundaries, illustrating that SED could be a key technique in developing the potential for engineering the distribution of defects, or “microstructure”, in functional MOF design.
Synthetic control of property-determining defects and the distribution of these defects in crystalline materials (i.e. microstructure) enables “defect engineering” of specific functionality in metal organic frameworks (MOFs).1,2 MOFs comprise metal ions or clusters connected in a network by organic ligands or linkers. Missing linker or missing metal cluster defects augment MOF porosity and introduce open metal sites, improving gas storage, separation, and catalytic performance.3–5 Correlated defect nanodomains are typified by the MOF UiO-66, which contains nanoscale domains of missing metal clusters under appropriate synthesis conditions.2,6 These nanodomains significantly enhance high-pressure gravimetric gas sorption7 and enable tuning of negative thermal expansion.6 Analogous correlated defect structures are exploited technologically in, for example, relaxor ferroelectrics9, thermoelectrics10 and nickel-based superalloys.11 However, the morphology and distribution of defect nanodomains in MOF microstructure has not been observed directly. For correlated defects and the distribution of defects more broadly to play a similarly significant role in functional MOF design, as in other solid-state applications, detailed structural characterization is required on length scales from the atomic to the bulk.

Measurement of the bulk defect concentration in MOFs is possible via compositional analysis using, for example, thermogravimetric analysis and NMR spectroscopy of digested solutions.4,12 These methods yield the ensemble average defect concentration13,14 but offer no information regarding the local defect arrangement.5 The relative distribution of defects and their local chemical environment has been obtained in a variety of defective MOFs through bulk spectroscopic techniques such as FTIR15, NMR16 and EXAFS13, as well as total scattering X-ray diffraction methods probing correlated disorder.6 While these spectroscopic and diffraction techniques provide information regarding local defect arrangement in the ensemble average, they do not offer direct spatially resolved measurement of how the defect distribution may change throughout the sample. Spatially resolved techniques such as confocal fluorescence microscopy,17 fluorescence lifetime imaging,18 and atomic force microscopy19 have revealed defect structures in microscopic detail but have been limited to ca. 200 nm diffraction limited spatial resolution or have been constrained to the use of fluorescent tags or to the surfaces of particles. These important techniques therefore provide limited direct evidence for defect distribution on the atomic- and nano-scale.
Transmission electron microscopy (TEM) offers the spatial resolution for atomic- and nanoscale defect characterization but MOFs typically undergo significant damage under a low cumulative electron dose ca. $10^{-20}$ e$^{-}$ Å$^{-2}$. Such damage may be avoided by using low-dose electron microscopy techniques, which have recently been pushed forwards by the development of direct electron detectors. These developments have allowed MOFs and other beam sensitive materials to be studied in various new ways. For example, 3D electron diffraction (3D-ED) has been used to achieve direct structure solution, similar to single crystal X-ray diffraction, from individual microcrystals of MOFs, microporous zeolites and covalent organic frameworks. However, while analysis of diffuse scattering in 3D-ED data has revealed stacking disorder and twinning, this technique does not offer spatially resolved characterization below the scale of a particle. High-resolution (HR) TEM imaging can provide sub-particle defect characterization and direct electron detection has enabled HRTEM imaging of individual defects as well as the atomic structure at grain boundaries and surfaces. However, HRTEM requires thin (< ca. 100 nm) samples, restricting the technique to the study of nanoscale MOF particles or thin edges of larger MOF particles, and the field of view at high magnification is limited to ca. 20 nm in most cases. Direct observation of the defect and crystal phase distribution at lengths ca. 20-500 nm has therefore not yet been possible, limiting insights into the morphology, orientation, and distribution of defect nanodomains. We address this characterization gap using the emerging TEM-based technique of scanning electron diffraction (SED) performed with an electron-counting type direct electron detector to obtain crystallographically rich data using an electron dose ca. $5 \text{ e}^{-} \text{Å}^{-2}$ (see Methods).

SED is a four-dimensional scanning transmission electron microscopy (4D-STEM) technique in which a two-dimensional diffraction pattern is acquired at each position as a focused electron probe is scanned across the sample, as depicted in Figure 1a. The use of a highly parallel probe (ca. 1 mrad convergence angle) enables crystallographic analysis of separated Bragg disks but limits the electron probe size, and consequently the spatial resolution, to ca. 2-5 nm. Scanning yields spatially resolved diffraction data over a field of view of ca. 1 000 nm, ideal for characterizing nanoscale defect domains. SED has recently been applied to characterize correlated defects, for example, using the symmetry within individual convergent beam diffraction disks to map domains in relaxor ferroelectrics and superlattice reflections as signatures of correlated disorder in
meteorites. Further, SED has been applied to beam sensitive materials revealing crystallinity in organic molecular crystals, polymers and MOFs. Here, we apply SED to directly visualize nanoscale defect domains in Uio-66(Hf).

Uio-66(Hf) is the prototypical system forming correlated defect domains in MOFs. The Uio-66 structure consists of metal oxyhydroxide clusters that are coordinated by terephthalate (1,4-benzenedicarboxylate) ligands, giving rise to a net with 12 connected nodes with the fcu topology and the nominal formula $[M_6O_4(OH)_4]_x[CoH_4(COO_2)]_6$, where $M = Zr$, Hf, or other tetravalent metals. The Uio-66 family exhibits high chemical, thermal, and mechanical stability among MOFs and the presence of defects in Uio-66 can be controlled by introducing competing ligands (modulators) such as monocarboxylic acids or water and varying the reaction temperatures and time, resulting either in ‘linker vacancies’, where the bidentate ligand is replaced by a monodentate species, or in cluster vacancies. The defect-free fcu crystal structure of Uio-66 has a cubic-F lattice and so Bragg diffraction only occurs for “parent reflections” ($hkl$) where $h$, $k$, and $l$ are either all odd or all even integers. At high defect concentrations, metal cluster vacancies order into correlated defect nanodomains, which consist of an 8-coordinate cubic-P defect phase with reo topology. The breaking of the face-centring symmetry means that the reo phase diffracts introducing additional primitive “superlattice reflections” ($hkl$) where $h$, $k$, and $l$ are a mixture of both odd and even integers. The observation of these superlattice reflections, both in selected area electron diffraction (SAED) and powder X-ray diffraction (XRD) experiments, has previously demonstrated the existence of defect nanodomains in Uio-66(Hf). However, the size, morphology, and local orientation of these nanodomains have remained ambiguous due the length scales probed by the characterization techniques applied to date.

In this work, we use superlattice reflections observed in SED experiments to directly image reo defect nanodomains in Uio-66(Hf) particles, as illustrated in Figure 1b. Our SED analysis directly reveals key details of the correlated defect microstructure including domain size, morphology, local orientation and spatial distribution. Further, our analysis reveals inherent defects in otherwise single crystal Uio-66(Hf) octahedral particles. These insights are complementary to bulk XRD and sub-nanometre resolution STEM measurements that we perform on a series of Uio-66(Hf) samples with controlled defect densities. Together, our multi-modal measurements convey previously hidden
aspects of defect clustering and establish crucial experimental evidence for understanding crystal growth in defect engineered MOFs.

Results and discussion

We prepared a series of defective UiO-66(Hf) powders with synthetically controlled missing metal cluster defects by using formic acid as a modulator during synthesis and altering the molar ratio of HfCl₄ to terephthalic acid (H₂BDC) to obtain different defect densities.⁴,⁶ Four samples were produced with HfCl₄:H₂BDC molar ratios of 6:5, 1:1, 3:4 and 3:5 in order of decreasing defect density. Hereafter, we refer to samples in this series as n(Hf):m(BDC) UiO-66, where n and m define the molar ratio of precursors in the reaction mixture without necessarily implying the metal:linker ratio in the product. This synthesis primarily produced octahedral particles for all defect densities as observed in scanning electron microscopy (SEM) images (Supplementary Figure 1).

SED data obtained from all four defective UiO-66(Hf) samples were used to perform crystallographic analysis and to form numerous images post facto. Annular dark field (ADF) images were produced by plotting the integrated diffraction signal in an annular range as a function of probe position (see Methods). Such an ADF image of a typical octahedral particle of the most defective 6(Hf):5(BDC) UiO-66 material is shown in Figure 2a. Diffraction patterns from selected regions of this particle, isolated computationally from the SED dataset, are shown in Figure 2b-c. Bragg reflections are observed beyond 1 Å⁻¹ resolution indicating that significant electron beam induced damage was avoided. Both diffraction patterns shown in Figure 2b-c contain a 011 systematic row of reflections and have been recorded near, but not exactly at, the [011] zone axis. These patterns therefore contain many of the same reflections as illustrated in Figure 1b. By comparing particle morphology observed in the ADF image with the diffraction data from the same area, the facets were indexed as the {100} and {111} facets of a truncated octahedron, as predicted by a Wulff construction⁴³ (Figure 2a and Supplementary Figures 2-3).

Diffraction contrast images were formed by plotting the integrated diffracted intensity of selected Bragg disks as a function of probe position to form “virtual dark field” (VDF) images.⁴⁴ VDF images were formed by summing several reflections to enhance the signal-to-noise ratio and, to some extent, to integrate over small mis-orientations across the field of view. Superlattice reflections
(unique to the \textit{reo} defect phase) were observed only in some regions of the most defective 6(Hf):5(BDC) UiO-66(Hf) particle (Figure 2b-c), whereas parent reflections (measured from both fcu and reo phases) were observed across the whole particle, as expected. We note that, in contrast to our XRD measurements where superlattice peaks are broadened, the superlattice reflections measured in SED are comparably sharp relative to the parent reflections because the defect domains are larger than the electron probe size. A VDF image formed using the parent reflections (marked in Figure 2b) is shown in Figure 2d and reveals a continuous region, indicating a slightly deformed crystal, on the right side of the particle. A VDF image for the reo-specific superlattice reflections is shown in Figure 2e, revealing rectangular domains in a lamellar structure of reo and fcu material. The largest rectangular domains have a short dimension of <50 nm and a long dimension of >100 nm. The domains appear to be preferentially orientated with the long axis of the domain perpendicular to a particle facet. We note that domains are imaged in projection in SED and are only observed if they are in a suitable orientation for Bragg diffraction. As such, VDF images outline two dimensions of the three-dimensional defect domains, and domains that are not aligned with the orientation of the parent particle will not be detected in this near zone axis configuration. Our observations are therefore consistent with prior studies showing that the reo defect domains are epitaxial with the fcu structure.\textsuperscript{3,6} Studying multiple particles likely captures the characteristic features of the domains given the high symmetry of the octahedral particles. Overlap of multiple domains in projection cannot be ruled out and some domain sizes may appear larger as a result. We therefore complement our VDF imaging with domain size estimates from XRD measurements of the ensemble, as below. Additional examples of defect nanodomains observed by SED are presented in Supplementary Figures 6-9.

The left side of the particle appears dark in Figure 2d-e, indicating a change in crystal orientation. Indexing diffraction patterns from each side of the particle (marked in Figure 2f) shows that both sides are near to the \([0\bar{1}1]\) zone axis, suggesting only a small (<3°) change in the orientation. VDF images formed using the parent fcu reflections recorded on each side of the particle (Figure 2i) allow us to map the distribution of the two orientations and reveal the presence of a small angle grain boundary. Such a small angle grain boundary could be formed by an arrangement of inherent dislocations, which have been observed in other MOFs\textsuperscript{17,19} but not previously detected in
UiO-66. Using superlattice reo reflections \{1\overline{2}2\} on either side of the grain boundary to produce VDF images, we were able to observe how defect domains extend across this boundary (Figure 2). We find that many defect domains are continuous across the grain boundary despite the small change in crystal orientation. However, the observation that some domains are not continuous across the boundary suggests that this interface emerged during synthesis. The presence of these microstructural features highlights deviations from pristine single crystal growth.

Our direct observations of the orientation, size, and morphology of defect domains in 6(Hf):5(BDC) UiO-66 were contextualised using XRD analysis of our series of defective UiO-66(Hf) samples (Figure 3, Supplementary Figures 4 & 5, and Supplementary Table 1). Pawley refinement with a \textit{hkl}-dependent isotropic size-broadening produced a refined domain size of 51.6 ± 1.6 nm for the 6(Hf):5(BDC) UiO-66(Hf) sample, as shown in Figure 3a. This domain size estimate is remarkably consistent with the sizes observed in Figure 2. XRD analysis of the less defective 3(Hf):4(BDC) UiO-66(Hf) sample yielded a Pawley-refined domain size 31 ± 5 nm, as shown in Figure 3b. SED analysis of this less defective sample is presented in Figure 4 and a VDF image formed using superlattice reflections (Figure 4e) reveals that the reo domains are similar but smaller and less coherent, with sizes consistent with those estimated from XRD. The VDF image formed using parent reflections (Figure 4d) shows both sharp changes in the diffraction contrast, producing a V-shape structure resembling diffraction contrast from dislocations, and an intensity modulation with a pitch ca. 50 nm that we attribute to intensity variation with thickness. Further analysis of other samples in our series of defective UiO-66(Hf) samples (see Supplementary Figure 6-9) confirmed the trend that defect domain size increases and becomes more block-like in morphology as defect concentration increases. As the fraction of the bulk powder analysed by SED is inevitably small, multi-modal diffraction studies are crucial to produce a validated model. In this case, SED directly visualizes the reo domain and extended defect characteristics while the XRD analysis provides complementary information on the ensemble powder.

The block-like lamellar structure of rectangular domains observed by SED microscopy in several more defective 6(Hf):5(BDC) UiO-66(Hf) particles (Figure 2 and Supplementary Figures 6-7) and the more fragmented but similar morphology domain structure in less defective 3(Hf):4(BDC) UiO-66(Hf) particles (Figure 4 and Supplementary Figures 8-9) are reminiscent of phase separated
microstructures produced in diffusion-limited transformations such as eutectic growth and spinodal decomposition. Previous work has demonstrated that the concentration of modulating ligands, such as formate or water, in the reaction mixture dictates the competitive formation of reo and fcu. Our observations are consistent with local fluctuations in concentration during crystal growth controlling the local phase competition. While formate is in substantial excess, terephthalate binds more strongly. When the local concentration of terephthalate becomes sufficient to outcompete formate binding, fcu nucleation and growth can occur. The growth of the fcu phase will use up the locally available terephthalate until the local formate concentration reaches sufficient excess to outcompete the terephthalate interactions leading to reo growth. Further, the formation of numerous nearby reo and fcu domains of similar size and shape, and the absence of any single phase reo particles, points to reo growth co-located and in tandem with fcu growth. This co-localization may also be consistent with the tendency for block-like domains to be observed with the long axis of the domain perpendicular to a particle facet, which is the growth front as the particle expands. This means that the larger block-like domains could potentially be supplied with formate by short range lateral diffusion at the growth front, similar to eutectic growth. Our SED measurements therefore provide direct evidence for potential diffusion limited MOF crystal growth processes.

To examine the defect domain structure on the sub-nanometre scale we performed aberration-corrected bright-field (BF) STEM imaging of the 6(Hf):5(BDC) UiO-66(Hf) sample, as shown in Figure 5. The BF-STEM image (Figure 5a) was obtained near to the [011̅] orientation and spatial frequencies characteristic of {100} and {011} planes of the reo structure are observed in the fast Fourier transform (FFT) of the BF-STEM image (Figure 5b). The BF-STEM image shows amplitude modulation along the [100] direction (Supplementary Figure 10) consistent with alternating rows of metal clusters in the reo structure containing half the metal clusters in the column as compared with the fcu structure in this [011] orientation. These image features are highlighted in the structural model presented in Figure 5c alongside a simplified schematic model of the lattice in the [0̅11] zone axis orientation (Figure 5d). The orientation of the defect region is consistent with our SED observations and points to cluster terminations at the particle surface, consistent with prior HRTEM studies. The lattice model (Figure 5) identifies {211} planes as the likely interface on
the longer sides of the rectangular reo domains, while there appears to be some preference for termination at \{111\} planes on the short dimension within UiO-66(Hf). The {211} type planes pass through metal clusters and the cluster-ligand attachment sites, which may be linked to the mechanism by which formate modulators compete with terephthalate linkers. 4–6

Our multiscale structural analysis shows that defect nanodomains in defect-engineered UiO-66(Hf) exhibit a block-like lamellar morphology and occur in a preferred orientation, extending perpendicular to \{111\} planes and sometimes perpendicular to other low index facets, with interfaces between reo and fcu domains on {211} planes. These characteristics remain similar across systematically varied defect densities but become more evident at high defect density. The domain size can be both controlled by synthesis and adequately inferred from XRD analysis, which are complemented by insights into the anisotropic domain morphology and distribution observed using SED. These experimental observations place previously unreported constraints on models seeking to explain defect clustering and crystal growth in MOFs, motivating further modelling of the growth kinetics to enhance understanding of synthetic control of defect structures. Together with our observations of inherent defects, i.e. grain boundaries and likely dislocations confined to the interior of the UiO-66 crystal, our observations highlight the utility of SED to reveal the distribution of defects, i.e. microstructure, within MOFs. The ability to characterize this microstructure in MOFs opens the possibility of extending the concept of defect engineering to “microstructure engineering” as a route to enhanced performance in MOFs, driven by continued development of tools for correlated defect imaging to relate defect distribution to key properties.
Methods

Synthesis

UiO-66(Hf) samples were produced using a procedure adapted from Ref. 8 HfCl₄ (Acros Organics, 99 %, 0.3 mmol, 96.1 mg) and terephthalic acid (H₂BDC) (Alfa Aesar, 98 %, 0.25-0.5 mmol, 41.5-83.0 mg) were added to a 23 mL PTFE-lined steel autoclave, followed by N,N-dimethylformamide (DMF, Alfa Aesar, 99 %, 4 mL), and formic acid (Fisher, 98/100 %) (2.0 mL). The autoclave was sealed and heated at 150°C for 24 hours. The resulting white microcrystalline powder was filtered under vacuum, washed on the filter (DMF, 5 mL) and the solid product dried. Unreacted ligand was removed by washing each sample with DMF (12 mL) at 60°C for 24 hours, followed by two further 2-hour washing cycles. After each wash, residual DMF was removed after centrifugation of the mixture at 8000 rpm for 15 minutes. Finally, any residual DMF was removed by heating at 200°C for 24 hours. Four samples were produced using 0.25 mmol, 0.3 mmol, 0.4 mmol, and 0.5 mmol H₂BDC corresponding to HfCl₄:H₂BDC molar ratios of 6:5, 1:1, 3:4 and 3:5.

Scanning electron diffraction

SED data were acquired using a JEOL ARM300CF fitted with an ultrahigh-resolution pole piece, a cold field emission gun, and aberration correctors in both the probe-forming and image-forming optics (Diamond Light Source, UK). The instrument was operated at 200 kV. A nanobeam configuration was obtained by switching off the aberration corrector in the probe-forming optics and using a 10 μm condenser aperture to obtain a convergence semi-angle <1 mrad and a diffraction-limited probe diameter of ca. 5 nm. The probe current was measured using a Faraday cup as ca. 2 pA and the exposure time was 1 ms per probe position. The estimated electron fluence, assuming a disk-like probe, was ca. 5 e/Å². A diffraction pattern was acquired at every probe position using a Merlin-Medipix hybrid counting-type direct electron detector (Quantum Detectors, UK).

SED data were processed using pyxem-0.10.0. The diffraction patterns were aligned, re-binned and calibrated prior to analysis (see Supplementary Information). ADF images were formed by integrating between an inner angle (θ_inner = 12.6 mrad) and an outer angle (θ_outer = 25.6 mrad) as a function of probe position. VDF images were obtained by manual selection of Bragg disks, which were assigned as reo or fcu/reo reflections based on pattern symmetry and validated against
the measured diffraction vector magnitude. The VDFs associated with all Bragg disks in each category were then summed to produce VDFs less sensitive to minor variations of intensity at particular scattering vectors, as is typical due to small variations in thickness or sample orientation. All diffraction patterns shown are presented as the square-root of the recorded intensity to rebalance intensity variation between low and high angle reflections for improved visualization. This intensity scaling was applied only for visualization and not prior to the formation of VDF images. All VDF images were normalized to their respective maximum intensities when forming colour overlays.

X-ray diffraction & Pawley refinement

Powder X-ray diffraction (PXRD) patterns were measured using a PANalytical Empyrean diffractometer (Cu Kα radiation, λ = 1.541 Å) over the 2θ range 2-60°, using a step size of 0.017° and a scan speed of 0.020°s⁻¹. All analysis of powder diffraction data, including Pawley refinement, was carried out using the TOPAS Academic 4.1 software.

Pawley refinement of the PXRD data obtained from the 6(Hf):5(BDC), 1(Hf):1(BDC), and 3(Hf):4(BDC) UiO-66(Hf) samples was carried out in space group $Pm\overline{3}m$ with a pseudo-Voigt peak shape and the background modelled using a freely refining Chebyshev polynomial with ten parameters. The reo domain size was determined by modelling the differential peak broadening between fcu/reo-shared Bragg peaks and reo-only scattering, using a crystallite-size-dependent Gaussian size-broadening term with a Scherrer-type $\cos(\theta)$ dependence. Pawley refinement of the 3(Hf):5(BDC) UiO-66(Hf) sample, which contained the lowest defect concentration, required a modified approach as the low intensity of the reo scattering precluded a full Pawley refinement. This refinement was carried out only on data over the 2θ range 3.5-11.0° and the background restricted to a three parameter Chebyshev polynomial and a broad Gaussian peak, centered at $2\theta = 8.21(2)^°$ with FWHM = 1.94(11)°. The Pawley refined lattice parameters, reo domain sizes and $I_{\{100\}}/I_{\{110\}}$ intensity ratios are summarized in Supplementary Table 1.
Scanning transmission electron microscopy
Aberration corrected STEM imaging was performed using the same JEOL ARM300CF microscope as used for SED. The instrument was operated at 300 kV and a high condenser lens excitation and low extraction voltage was used to produce a probe current of ca. 1.8 pA with a 16 mrad convergence semi-angle. BF STEM imaging was performed using a BF detector with an aperture inserted to limit the scattering angles collected to within the direct beam disk and a per pixel dwell times <20 μs.

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Author contributions
D.N.J. and S.M.C. acquired and processed the electron microscopy data and wrote the manuscript. F.C.N.F. synthesized samples and acquired the SEM and XRD data. F.C.N.F. and M.J.C. analysed the XRD data. All authors contributed to design of the study and revision of the manuscript.

Additional information
Supplementary information is available including additional data referenced in the text.
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Figure 1. Illustration of scanning electron diffraction (SED) applied to a defect-engineered UiO-66(Hf) particle. a. A 2D \((k_x, k_y)\) diffraction pattern is recorded in transmission at every probe position in a 2D \((x, y)\) scan. b. Calculated 4D-SED for a defective UiO-66(Hf) octahedral particle (blue) containing defect nanodomains and imaged along the \([0\bar{1}1]\) zone axis. At positions where the defect-free \textbf{fcu} structure occurs (magenta), only “parent reflections” \((hkl)\) where \(h, k,\) and \(l\) are either all even or all odd integers are measured in the \([0\bar{1}1]\) zone axis diffraction pattern. Within defect nanodomains where the defective \textbf{reo} structure (green) occurs, “superlattice reflections” \((hkl)\) where \(h, k,\) and \(l\) are a mixture of odd and even integers, are also measured \([0\bar{1}1]\) zone axis diffraction pattern. These superlattice reflections are used to identify the \textbf{reo} defect nanodomains and are observed because missing metal cluster vacancies in the defective \textbf{reo} phase change the lattice type from cubic-F (\textbf{fcu}) to cubic-P (\textbf{reo}). These vacancies are visualized clearly in the \([001]\) projection of the structure and are visible in the \([0\bar{1}1]\) projections associated with the diffraction patterns shown.
Figure 2. SED reveals defect domains by diffraction analysis and enables direct domain imaging in a defect-engineered UiO-66(Hf) particle with high defect density. 

a, ADF-STEM image of a 6(Hf):5(BDC) UiO-66(Hf) particle with regions selected for diffraction analysis marked. b, Integrated electron diffraction pattern the region marked in magenta in a, which yields only parent reflections and is thus obtained from the fcu phase. c, Integrated electron diffraction pattern from the region marked in green in a, which yields both parent reflections and superlattice reflections and is thus obtained from the reo phase. d, VDF image formed by integrating parent reflections, magenta in b, c, as a function of probe position, revealing a region of the particle in a single crystal orientation. e, VDF image formed by integrating superlattice reflections, green in c, as a function of probe position to directly image reo defect domains. f, ADF-STEM image of the same particle with larger regions, i.e. containing both fcu and reo phases, selected for diffraction analysis marked in magenta and yellow. g-h, Integrated electron diffraction patterns from the regions marked in f, which contain both parent and superlattice reflections and reveal a change in orientation between the left- and right-hand side of the particle. i, Composite VDF image formed by integrated parent reflections, magenta in g and yellow in h, revealing a small change in orientation across a boundary. j, Composite VDF image formed by integrated superlattice reflections, green in g and red in h, revealing reo defect domains. Arrows in j indicate a defect domain continuous across the small angle boundary.
Figure 3. Powder X-ray diffraction of defective UiO-66(Hf). Pawley fitting of powder XRD data from two defective UiO-66(Hf) samples. The more defective 6(Hf):5(BDC) UiO-66(Hf) material, as in a, shows stronger superlattice reflections corresponding to the reo phase, e.g. 100, 110, and 210 (marked with arrows) as compared with less defective 3(Hf):4(BDC) UiO-66(Hf) material, as in b.
Figure 4. SED reveals defect domains by diffraction analysis and enables direct domain imaging in a defect-engineered UiO-66(Hf) particle with reduced defect density. a, ADF-STEM image of a 3(Hf):4(BDC) UiO-66(Hf) particle with regions selected for diffraction analysis marked. b, Integrated electron diffraction pattern the region marked in magenta in a, which yields only parent reflections and is thus obtained from the fcu phase. c, Integrated electron diffraction pattern from the region marked in green in a, which yields both parent reflections and superlattice reflections and is thus obtained from the reo phase. d, VDF image formed by integrating parent reflections, marked in b, as a function of probe position, revealing V-shaped defect contrast. e, VDF image formed by integrating superlattice reflections, marked in c, as a function of probe position to directly image reo defect domains.
Figure 5. Lattice resolution imaging of a defect-engineered UiO-66(Hf) particle. a, Bright-field STEM micrograph of a reo domain with the simplified schematic (see c-d for enlarged version) overlaid. Arrows mark dark spots indicating metal clusters at the particle surface. b, Fast Fourier transform (FFT) of the image in a, with spatial frequencies marked with arrows and indexed with respect to crystal planes. c, Representation of the atomic structure of the reo defect structure of UiO-66(Hf) in the [011̅] zone axis orientation. d, Simplified schematic of the lattice. Sites with the full or half the number of metal clusters present in the fcu structure are depicted as solid and transparent red projections of an octahedron, respectively.
Supplementary information:

Direct imaging of correlated defect nanodomains in a metal-organic framework

Duncan N. Johnstone,1, † Francesca C. N. Firth,2 Clare P. Grey,2 Paul A. Midgley,1 Matthew J. Cliffe,3 and Sean M. Collins1,4*

1Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, UK
2Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK
3School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK
4School of Chemical and Process Engineering and School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Email: *S.M.Collins@leeds.ac.uk, †dnj23@cam.ac.uk

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1. Scanning electron microscopy

Samples were sputter coated with Pt to a thickness of 10 nm and secondary electron images were formed using a scanning electron microscope (SEM). The SEM used for this imaging was a TESCAN MIRA3 FEG-SEM operated at 5.0 kV.

Supplementary Figure 1. Scanning electron micrographs of a, 6(Hf):5(BDC) b, 1(Hf):1(BDC) c, 3(Hf):4(BDC) d, and 3(Hf):5(BDC) UiO-66 samples.
2. SED data pre-processing and calibration

SED data were acquired using a Merlin-Medipix hybrid counting-type direct electron detector with 256x256 pixels and, following a system upgrade, with 512×512 pixels. The camera lengths were adjusted to obtain a similar maximum collection angle on both detectors. Data recorded on the 512×512 pixel detector were re-binned to 256×256 pixels as an initial processing step.

Calibration of the scan step size and the diffraction pattern pixel size was performed using a standard 500 nm gold diffraction grating replica with latex spheres (Ted Pella). The cross-grating data was also used to determine residual elliptical distortions of the diffraction patterns due to the post-specimen optics. The rotation between the diffraction pattern and the real space orientation was calibrated using an MoO$_3$ standard (Agar Scientific).

Pre-processing of the SED data included: 1) centring the direct beam in each diffraction pattern within the data array using a cross-correlation routine, 2) applying an affine transformation to correct for elliptical distortion and rotation between the real space scan and the diffraction pattern, as determined by calibration.
3. Particle facet indexation

Particle facets were indexed by comparing the observed particle morphology in annular dark-field images reconstructed from scanning electron diffraction (SED) and the corresponding area averaged electron diffraction pattern from each region, as shown in Supplementary Figure 2.

**Supplementary Figure 2.** Facet indexation by comparison of annular dark-field STEM images, reconstructed from SED data, with the average diffraction pattern from the same region for **a**, 3(Hf):5(BDC) and **b**, 6(Hf):5(BDC) UiO-66 samples.
The 2D projected morphologies observed in Supplementary Figure 2 were further related to 3D truncated octahedron models for UiO-66 particles obtained by Wulff construction, as shown in Supplementary Figure 3. The Wulff truncated octahedron has relatively smaller \{100\} facets to differentiate the \{100\} and \{111\} facets clearly. When viewed along a \(<011>\) direction, the truncated octahedron will have square \{100\} faces. Under the assumption of symmetric faceting, the \(~300\) nm \{100\} side length may suggest thicknesses at the edge of the same order as the \{100\} plane lateral dimension when viewed in projection.

Supplementary Figure 3. Comparison of observed particle morphology and a Wulff construction of truncated octahedron. a-b, ADF-STEM images of a, 3(Hf):5(BDC) UiO-66 and b, 6(Hf):5(BDC) UiO-66. c-d, Truncated octahedron determined by a Wulff construction showing square \{100\} and hexagonal \{111\} facets for viewing along c, a low-symmetry orientation and d, a \(<011>\) direction.
4. Powder XRD and Pawley refinement

Supplementary Figure 4. Pawley fitting of PXRD data from 1(Hf):1(BDC) UiO-66 samples.

Supplementary Figure 5. Pawley fitting of PXRD data from 3(Hf):5(BDC) UiO-66 samples.

Supplementary Table 1. Summary of parameters determined by Pawley refinement of powder X-ray diffraction data.

| HfCl₄:H₂BDC ratio | Lattice parameter (Å) | $R_{wp}$ | reo domain size (nm) | peak ratios (110) to (111) |
|-------------------|-----------------------|----------|----------------------|---------------------------|
| 6:5               | 20.6627(3)            | 3.339    | 51.6 (13)            | 0.1325(28)                |
| 1:1               | 20.6655(3)            | 3.588    | 47.4(14)             | 0.10081(22)               |
| 3:4               | 20.686(2)             | 4.303    | 31(5)                | 0.040(5)                  |
| 3:5               | 20.647(10)            | 2.746    | 5.5(4)               | 0.12(3)                   |
5. Defect nanodomain imaging examples

Supplementary Figure 6. Replicate SED analysis for 6(Hf):5(BDC) UiO-66 particles (see also Figure 2). a, ADF-STEM image with regions selected for diffraction analysis marked in magenta and green. b-c, Electron diffraction patterns integrated from the regions marked in a. The arrows mark selected scattering angles used for VDF imaging. d-e, VDF images generated using virtual apertures at the locations marked in b-c.

Supplementary Figure 7. Replicate SED analysis for 6(Hf):5(BDC) UiO-66 particles (see also Figure 2). a, ADF-STEM image with regions selected for diffraction analysis marked in magenta and green. b-c, Electron diffraction patterns integrated from the regions marked in a. The arrows mark selected scattering angles used for VDF imaging. In the absence of a systematic row, for the magenta VDF all high angle detected Bragg spots were used to form the VDF. d-e, VDF images generated using virtual apertures at the locations marked in b-c.
Supplementary Figure 8. Replicate SED analysis for 3(Hf):4(BDC) UiO-66 particles (see also Figure 4). a, ADF-STEM image with regions selected for diffraction analysis marked in magenta and green. b-c, Electron diffraction patterns integrated from the regions marked in a. The arrows mark selected scattering angles used for VDF imaging. In the absence of a systematic row, for the magenta VDF all high angle detected Bragg spots were used to form the VDF. d-e, VDF images generated using virtual apertures at the locations marked in b-c.

Supplementary Figure 9. Replicate SED analysis for 3(Hf):4(BDC) UiO-66 particles (see also Figure 4). a, ADF-STEM image with regions selected for diffraction analysis marked in magenta and green. b-c, Electron diffraction patterns integrated from the regions marked in a. The arrows mark selected scattering angles used for VDF imaging. In the absence of a systematic row, for the magenta VDF all high angle detected Bragg spots were used to form the VDF. d-e, VDF images generated using virtual apertures at the locations marked in b-c.
6. HR-STEM image analysis

**Supplementary Figure 10.** Line profiles showing bright-field STEM image intensity in the 6(Hf):5(BDC) UiO-66 sample across atomic columns **a,** containing two metal clusters per unit cell, **b,** containing one metal cluster per unit cell, and **c,** alternating across columns containing one and two metal clusters per unit cell.
