A lanthanide MOF with nanostructured node disorder

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ABSTRACT: The synthesis and structural characterization of a new metal organic framework, UoB-100(Dy), is reported. Average structure refinements indicate that the node is disordered between two orientations of the nonanuculear secondary building unit (SBU). By performing 3D diffuse scattering (DS) analysis and Monte Carlo (MC) simulations, we confirm the presence of strong correlations between the metal clusters of UoB-100(Dy). These nodes assemble into a complex and novel nanodomain structure. Quantum mechanical calculations identify linker strain as the driving force behind the nanodomain structure. The implications of such a nanodomain structure for the magnetic, gas storage, and mechanical properties of lanthanide MOFs are discussed.

Over the past century, structural disorder has been established as a useful tool for the tuning of physical properties of functional materials. Disorder in La_{1-x}Ca_xMnO₃ and Cu_xMn, for example, is known to result in colossal magnetoresistance (CMR)¹⁻³ and spin-glass behavior,^{4,5} respectively. Although such structural disorder can be random, it is more often correlated.^{6,7} Depending on the interactions which drive these correlations, 'nanodomains' i.e. regions of local order, may emerge.^{8–17} In the relaxor ferroelectric PbMg_{1/3}Nb_{2/3}O₃ (PMN), local polar regions of a few nanometers wide are responsible for its remarkable ferro- and piezo-electricity.^{8–14} The transport properties of perovskite solar-cell materials are similarly linked to such structural nanodomains.¹⁷ Explaining the origin of these behaviors is challenging, as the structures of these disordered materials span multiple length-scales.¹⁸ To study nanostructures crystallographically, one must look at the weak, diffuse scattering (DS) signal running between, through, and on top of the Bragg-peaks, as it reports on the correlations between disordered degrees of freedom.

The presence and significance of disorder in metal-organic frameworks (MOFs) has only recently gained widespread awareness.¹⁹ Disorder in MOFs is not uncommon, however, as many MOF will exhibit linker- or cluster-defects to some extent. This vacancy disorder tends to be correlated, as one defect likely affects the probability of neighboring defects. A canonical example is UiO-66, in which cluster vacancy defects assemble into synthetically-tunable nanodomains,^{10,16,20} with the nanostructure affecting its mechanical properties.²¹ Similarly, the disordered distribution of components in mixed-metal and/or mixed-linker MOFs, also known as multivariate (MTV) MOFs, may be correlated, which in turn determines their corresponding chemistry.^{22–25} Incorporating low-symmetry components in MOF structures may also lead to orientational disorder. Examples are the linker 2,6-ndc in DUT-8(Ni),²⁶ the node in Zr MOF c-(4,12)MTBC-M₆,²⁷ and both the node and linker in TRUMOF-1—where orientational disorder of the bent linker 1,3-bdc is crucial to its unique aperiodic connectivity.²⁸

Similar to Zr-MOFs,²⁷ lanthanide-MOFs (Ln-MOFs) are known to be structurally diverse, as a result of the highly versatile coordination numbers of the SBU.³³ Together with the unique physical properties of rare-earth metals, this variety in SBU geometry makes Ln-MOFs attractive as magnetocaloric materials,³⁴ luminescent probes,^{30–32} and heterogeneous catalysts.^{35–38} Given this structural diversity and range of potential applications, it is surprising that, to our knowledge, correlated disorder has not been investigated in Ln-MOFs.

In this context, we developed an interest in designing a Ln-MOF with nanostructured disorder. In our approach, we selected dysprosium (Dy) as the node component and a customized linker L designed for its flexibility and lower symmetry; two linker properties known to introduce complexity in MOF design.^{27,41,42} As anticipated, the

structure of the obtained MOF, to which we refer to as UoB-100(Dy), is governed by node disorder, which we discover to be nanostructured. In this communication, we report its synthesis, average structure and nanostructure, as derived from both Bragg scattering and 3D diffuse scattering analysis.

The linker, L, was designed to contain four carboxylate donors so as to encourage high connectivity but with a low-symmetry backbone capable of adopting multiple orientations. The outer benzoate groups additionally impart a degree of flexibility, via rotation about the benzoic acid-triazine bond. The synthesis of L was conducted via 'telescoped' condensation of pyridine-2,6-dicarbohydrazide with the appropriate 1,2-dicarbonyl (Scheme S1). The formation of related pyridinyl-1,2,4-triazine ligands has been previously reported.^{43,44} The initial benzoin addition reaction between aldehydes was performed using thiamine hydrochloride⁴⁵ replacing the more toxic route that employs KCN as catalyst.⁴⁶ For the conversion of the benzoin to a benzil, a Kornblum oxidation was chosen via an acid catalysed alcohol-halide substitution reaction. As before, other routes for this conversion are available, including routes using chlorine, nitric acid, and ammonium nitrate, but as with the first step the Kornblum oxidation was chosen under safety considerations.⁴⁷⁻⁵² Acid hydrolysis was used to convert the ester groups to carboxylic acid groups, avoiding the use of alkaline bases typically used in saponification reactions due to the propensity of benzil groups undergoing 1,2-rearrangments to form α -hydroxy-carboxylic acids.⁴⁸ The reactive bis(carboximidhydrazide)pyridine was obtained by reacting pyridine-2,6-dicarbonitrile with hydrazine monohydrate which was performed via a method adapted from Sagot et al.⁴⁹ The final step in the synthesis of L proceeded via a method adapted from Tai et al,⁴⁴ and simply involved dissolving both reagents in a minimum of DMF followed by heating at 80 °C overnight. All steps of the linker synthesis are relatively simple with minimal work up, using accessible and low hazard materials. The conformation of unbound L was determined by single crystal X-ray diffraction (SCXRD) (see S.I. for details).

UoB-100(Dy) was prepared as yellow hexagonal crystals from the reaction of $Dy(NO_3)_3.6H_2O$ with L in N,N'dimethylformamide using 2-fluorobenzoic acid as a modulator (see S.I. for details). SCXRD date was collected at a range of temperatures (100-300K) and with either Cu-K α or Mo-K α radiation to ensure the best quality data for either diffuse reflectance or Bragg diffraction. As a result data collected at 100K (Cu-K α radiation) was used for diffuse scattering studies and data collected at 250K (Mo-K α radiation) for average structure refinement (see S.I. for details).



Figure 1 (a) Average crystal structure shown from above (i.e. along the c-axis) and the side. Color scheme: Dy = gray polyhedra, C = black, O = red, N = blue. Linker in the top image is shown with ellipsoids at 50% probability. (b) The average structure of the Dy node (top left) can be understood as a superposition of two nonanuclear clusters at a different orientation (top right). Each cluster has a corresponding hexapole charge distribution (middle). For simplicity, we represent these hexapole orientations as black and white hexagonal tiles (bottom). (c) Antiferrohexapolar arrangements are electrostatically favorable, both between clusters stacked along the columns (i.e. along c) and within the same layer (i.e. in the ab plane.)

The structure of UoB-100(Dy) comprises Dy-based secondary building units (SBUs) bridged by twelve tetracarboxylate linkers, L. The framework formed by UoB-100(Dy) contains Dy9 SBUs that have been observed for other rare-earth (RE) MOFs with both tetracarboxylate⁵³⁻⁵⁹ and tricarboxylate linkers.^{60,61} Previous examples of MOFs containing the RE9 SBU have all been prepared using rigid linkers with little opportunity for alternative conformations. Even so, disorder of the SBU has been observed⁵³⁻⁵⁶ but no previous understanding of the correlation of the disorder has been proposed.

The crystal structure of UoB-100(Dy) is highly disordered, as can be derived from the many partially occupied atom sites in the average structure refinement [Fig. 1(a)]. We interpret the crystal structure by first considering the metal-containing secondary building unit (SBU), which is centered around the 1b Wyckoff site (D_{6h} point symmetry). There are two symmetry-distinct Dy sites: 12o and 6m. Thus, there are 18 Dy atoms per SBU in total, although each of which has an occupancy of 0.5. This probability indicates that each SBU in the real structure contains 9 Dy atoms. In principle, there are C(18, 9) = 48620 possible nodes with this correct number of Dy atoms. However, on closer inspection, only two of these configurations are chemically feasible: the closest contact between the nearest 12o Dy sites is 2.21 Å and the closest contact between 12o and 6m Dy sites is 2.66 Å. We reason that it is unlikely that pairs of Dy atoms are separated by such short distances and therefore exclude node geometries that include these small separations. Only two configurations satisfy these local rules, as shown in Figure 1(b). We will go on to show experimentally that these nonanuclear clusters indeed exist in the local structure.

Besides the node disorder, it is clear from the average structure that the linker is disordered between two orientations: one where the linker points "up" along the c-axis, and one where it points "down". Since the scattering from the linker disorder is expected to be much weaker than the significantly heavier Dy atoms in the nodes, it is difficult to resolve correlations in linker orientation experimentally. For this reason, we solely focus on the dominant node disorder in our initial model.

The presence of the disordered nodes raises the question: how are these nodes distributed in space? To answer this question, we need to understand the interactions between the nodes. In our approach, we represent the local configurations with hexapole charge distributions, maintaining their D_{3h} point symmetry [Fig. 1(b)]. Based on electrostatic arguments, it is expected that 'antiferro-hexapolar' interactions are favoured between such neighbouring nodes, both along the c-axis and in the ab-plane, as shown in Figure 1(c). Because of the smaller separations as well as the better overlap between the nodes along the c-axis, we expect correlations to be greater along this direction.

To test our hypothesis and analyse the correlations of the node disorder experimentally, we turn to diffuse scattering (DS). A full description of the data collection, treatment, and 3D- Δ PDF extraction can be found in the S.I. We observe significant DS in the *Okl* and *hOl* layers, structured into sharp planes perpendicular to I [Fig. 2(a-b)]. The linewidth of these planes is resolution limited (FWHM < 0.03 r.l.u.), implying a correlation length along the c direction of $\zeta x > 14$ nm. In addition, there are maxima around $[h, k, l + \frac{1}{2}] : h, k, l \in Z$ within these planes of DS, corresponding to a shorter-range correlation of $\zeta x = 3.9$ nm. Accordingly, we observe strong features in the *Oyz* and *xOz* layers of the 3D- Δ PDF, with alternating signs along the z direction and the same sign along the x- and y directions [Fig. 2(c)]. We first note that the features of alternating signs along z correspond to the observed planes of DS, using the condition $\ell = n + \frac{1}{2}$: $n \in Z$. Therefore, antiferrohexapolar correlations apply along the z direction. Second, we derive the shorter-range correlations in the xy plane to be ferrohexapolar, based on the same sign of the features within these planes [Fig. 2(c-d)]. Thus, while our electrostatic arguments correctly predicted antiferrohexapolar correlations along z, they cannot explain the ferrohexapolar interactions correlations present in the xy plane.



Figure 2 Comparison of DS and 3D- Δ PDF obtained from experiment (left of each pane) and the best fit of the Monte Carlo model described in the text (right). (a) hOl and (b) $hk\frac{1}{2}$ planes of diffuse scattering. The purple rhombuses show the region bounded by $[70\frac{1}{2}] \pm [\frac{1}{2}\frac{1}{2}0]$ used for fitting, and the inset shows this region enlarged. The (c) xOz plane and (d) xyO planes of the 3D- Δ PDF Insets highlight the regions around r = [100] and [005] cell-vectors for panes (c) and (d), respectively.

To better understand the correlated disorder governing the system, we turn to a microscopic model of the SBU orientations using a Monte Carlo (MC) approach. This method involves generating a representative sample of the statistical distribution of disordered super-cells. It is evident from the $3D-\Delta PDF$ that the node orientations are not random, hence a method of including these correlations in our simulation is necessary. Given that the correlation length along *c* is long, we make the approximation that the disorder is present only in the *ab* plane, with long-range antiferrohexapolar correlations persisting in the *c* direction. Within the plane, the tendency for ferrohexapolar interactions can be encoded in the Hamiltonian,

$$E_{MC} = J_{\perp} \sum_{\langle ij \rangle} \mathbf{S}_i \, \mathbf{S}_j$$

where Sj = ±1 represents which of the two states in Fig. 1(b) is present at site j in the lattice; $J\perp$ is the coupling constant of nearest neighbors (denoted $\langle ij \rangle$). Since the coupling in the ab plane is ferrohexapolar ($J\perp > 0$), neighbors favour the same spin state. We parameterise the value of $J\perp$ by fitting simulated data to experimental scattering using a small, representative area of intense DS (shown in purple in Figure 2(b)). The procedure for calculating DS from our model and fitting to data is detailed in the S.I.. In this way, correlations present in the 2048 atoms of our supercells can be encoded with a single parameter: $J\perp /T_{eff} = 0.1361$.

The DS and 3D-ΔPDF cuts calculated from our final MC model are shown in Figure 2, demonstrating exceptional agreement with experimental data. Notably, the agreement of the features corresponding to the node-node correlation functions (shown in the insets of [Fig. 2(c-d)]) confirms that we have correctly identified the two SBU

orientations [Fig. 1(b)]. Furthermore, the agreement of the extent of these correlations in real-space shows that we have correctly reproduced the nanoscale correlations of these SBU orientations.

A simplified representation of the local structure of UoB-100(Dy) is given in Figure 3(a). We clearly observe two features that exist on the nanoscale: the extremely long-range correlations along c, and the shorter-range ($\zeta x \sim 5$ nm) correlations in the ac plane, of antiferrohexapolar and ferrohexapolar nature, respectively.

In our analysis, we have deliberately neglected the disorder of the linker, because its effect on the DS signal is weak. However, in the 3D- Δ PDF [Fig. 2(d)], there is some weak evidence for correlations between the internode distances, which emerges due to correlations between the node orientation and the linker. Understanding these correlations is complex, as they depend on the orientation of both the node and the linker. Instead of modelling this disorder and comparing to data, we take a theoretical approach to understanding this linker relaxation in response to the orientations of the SBUs it is bound to. More specifically, we use the experimentally derived oxygen positions for the ferro- and antiferrohexapolar node orientations to constrain a density functional theory (DFT) optimisation of the linker geometry. The details of this simulation are given in the S.I.

Our DFT results show two things. First, in the ferrohexapolar case, the linker is allowed to relax into the pore, bending away from the c-direction by 28.5°. In the antiferrohexapolar case, however, symmetry dictates that the linker must be aligned along c. The large angular relaxation in the ferrohexapolar configuration partially explains the high degree of linker disorder, as reflected by the anisotropic displacement parameters obtained in the average structure refinement [Fig. 1(d)]. Second, with a difference in relaxed energy of $\Delta E = 0.20$ kJ mol-1, the linker is considerably more strained in the antiferrohexapolar configuration than it is in the ferrohexapolar configurations, likely because the latter allows the linker to relax in the pore. While the energy difference itself is not small compared to the thermal energy at the temperature of crystallization, the long correlation length along c indicates that many of these interactions contribute additively to the overall interaction energy between chains. That being said, the relatively small energy difference between confirmations may explain why long-range ferrohexapolar order is suppressed. Overall, these observations explain the preference for ferrohexapolar correlations between the SBUs, as seen experimentally.

There are multiple ways in which the observed nanodomains of UoB-100(Dy) may affect its physical function. First, we note the potential impact of the linker bending, as it occurs within the ferrohexapolar nanodomains, but is absent along their edges. Since the linker bending affects the size of its pore windows, UoB-100(Dy) may exhibit disorder-dependent behaviour concerning gas storage and transport. Or, if the linker bending is a mode of mechanical flexibility, UoB-100(Dy) could show an enhanced elastic stability through combinatorial mechanics, as reported previously for TRUMOF-1.²⁹ Moreover, because the linker possesses a cavity with the ability to coordinate to an added guest component, the possibility of modifying the bending arises. This prospect of nanodomain modification is what sets UoB-100(Dy) apart from other nanostructured disordered systems, such as UiO-66,¹⁶ relaxor ferroelectrics,⁸ high-entropy alloys,⁵⁰ or charge density wave compounds.^{51,52} Finally, as Dy exhibits strong magnetic behavior,⁴⁰ it is likely that the nanostructured disorder affects the magnetic structure and behavior of UoB-100(Dy). It may be interesting probing UoB-100(Dy) for the magnetocaloric effect, which has been reported for Dy-coordination polymers such as DyOHCO₃ and Ln(HCO₂)(C₂O₄).^{62,63}



Figure 3 (a) Representation of one of the nanostructures of UoB-100(Dy), as produced by the MC procedure detailed in the text. The color of the hexagons represents the SBU orientations as shown in Figure 1(b). Note that there is order along *c*, and nanoscale order in the *ab* plane. (b) The structure which represents an antiferrohexapolar arrangement of the SBUs in the plane and DFT-relaxed linker arrangement constrained by these adjacent node geometries. (c) The same arrangement for ferrohexapolar neighbors. The constrained linker geometry optimizes with a lower energy, indicating that this ferrohexapolar node arrangement leads to less strain.

More generally, this study shows the importance of local-structure analysis in MOF chemistry. Often, signs of non-average effects are ignored, leading to the incorrect assignment of components, such as the metal cluster geometry in Zr-MOFs.²⁷ Likewise, structures with similar cluster geometries to UoB-100(Dy) may have been observed before, but difficulty in structure analysis prevented the data from being disclosed. As we demonstrate for UoB-100(Dy), both DS analysis and multimodal modelling are key in deciphering such cases. In parallel with structural disorder analysis, the use of disorder as a tool in framework design becomes increasingly critical. This targeted design is a significant challenge that must not be overlooked, as it involves navigating a large configurational energy landscape and therefore some (synthetic) trial and error. In our case, the approach of combining a flexible linker with a rare-earth metal proved to be efficient. There is no reason to think that the extension to other rare earth elements is not feasible, although it might affect the disordered structure. Ultimately, solving the nanostructured node disorder in UoB-100(Dy) opens a new avenue of exploring the control thereof, be it through the addition of guest components, changing metal type, or other synthetic parameters.

Data availability

The authors declare that all characterisation data generated in this study are provided in the Supplementary Information or within the main manuscript. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers

2368155 and 2370912. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic information files (CIF)

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Author Contributions

SLG, EM and JMB contributed equally to the overall experimental aims of the study. The synthesis of materials and other experimental studies were conducted by SLG and AWL. SC performed analysis of the SCXRD data leading to modelling of the average structure. EM, JMM and ES evaluated the correlated disorder and performed all related modelling. The project was conceived and supervised by NRC. All authors discussed the results, contributed to and have given approval to the final version of the manuscript. ‡These authors contributed equally.

Competing interests

The authors declare no competing financial interest.

Additional information

Supplementary information The online version contains supplementary material available at https://????

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