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Structure and electronic properties of rare earth DOBDC metal-organic-frameworks

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Here, we apply density functional theory (DFT) to investigate rare-earth metal organic frameworks (RE-MOFs), $\text{RE}_{12}(\mu_3\text{-OH})_{16}(\text{C}_8\text{O}_6\text{H}_4)_8(\text{C}_8\text{O}_6\text{H}_5)_4$ (RE=Y, Eu, Tb, Yb), and characterize the level of theory needed to accurately predict structural and electronic properties in MOF materials with 4f-electrons. A two-step calculation approach of geometry optimization with spin-restricted DFT and large core potential (LCPs), and detailed electronic structures with spin-unrestricted DFT with a full valence potential + Hubbard U correction is investigated. Spin-restricted DFT with LCPs resulted in good agreement between experimental lattice parameters and optimized geometries, while a full valence potential is necessary for accurate representation of the electronic structure. The electronic structure of Eu-DOBDC MOF indicated a strong dependence on the treatment of highly localized 4f-electrons and spin polarization, as well as variation within a range of Hubbard corrections ($U = 1\text{--}9\text{ eV}$). For Hubbard corrected spin-unrestricted calculations, a U value of 1–4 eV maintains the non-metallic character of the band gap with slight deviations in f-orbital energetics. When compared with experimentally reported results, the importance of the full valence calculation and the Hubbard correction in correctly predicting the electronic structure is highlighted.

Introduction

Understanding the impact of density functional theory (DFT) method selection on systems with f-electron containing elements is essential for the design, prediction, and development of advanced materials. It is necessary to identify a reliable and efficient approach for calculating the optimized geometries and resulting electronic structures of rare-earth containing organic-based systems. This allows for the investigation of novel properties unique to this class of materials, such as adsorption properties of recently developed metal-organic-frameworks (MOFs).¹ The treatment of lanthanide 4f-electrons is not straightforward in DFT as optical properties, including luminescence, are ideally described by multiple configurations of the open shell 4f-electrons in the ground state electronic structure. High accuracy and multi-reference methods such as complete active space self-consistent field (CASSCF) and configuration interaction singles (CIS) are commonly implemented to describe excited states of 4f-electrons.^{2,3} These methods are computationally expensive resulting in the bulk of the literature focusing on molecular lanthanide complexes, rather than periodic solid-state systems.^{4,5,6,7} The structural and electronic properties of lanthanides are highly

dependent on local coordination environments,⁸ therefore the treatment of lanthanide elements in molecular complexes offer insight, but are not directly applicable to three dimensional (3D) solid state materials. On the other hand, work investigating the properties of 3D lanthanide oxide^{9,10,11,12} and lanthanide hydride¹³ solid state materials has also be performed. Within this previous work, f-electrons are treated by including them both in the core¹³ and in the valence^{10, 12}, with and without the Hubbard correction, and using a series of exchange-correlation functions. The variation in previously reported methodologies for simulation of rare earth oxides complicates the selection of appropriate computational methods in future studies. Furthermore, this previous work does not replicate the binding environment in organic lanthanide complexes. Herein, this work seeks to fill the gap in our understanding of the ideal DFT based approach for simulating materials that exhibit both organic lanthanide complexes and solid-state lanthanide oxide properties, such as rare-earth metal-organic frameworks (RE-MOFs).

The MOF structure is composed of metal ions coordinated by organic linkers. MOFs have proven effective for catalysis¹⁴, gas storage,^{15,16} gas adsorption,¹⁷ and gas separations^{18,19} based on their ability to selectively interact with gaseous species. Novel adsorption materials are being designed and tested to eliminate acid gases from streams without additional energy intensive processing steps. As an example, common flue gas streams contain small yet caustic concentrations of acid gases, including NO_x , SO_x , CO_2 and water vapor.^{20,21} The zeolitic imidazolate framework (ZIF) class of MOFs have demonstrated durability to acid gas

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constituents.^{22,23} These phases have been effective in homogeneous gas conditions, but have shown more complex behavior in the presence of humidity and multiple gas species, complicating deployment of ZIFs for gas separation applications.^{23,24,25}

Ongoing research is focused on developing MOF materials with tunable gas separation properties and high durability targeted to specific gas streams, including a new class of MOFs with rare earth (RE) metal centers.^{1,26} This materials family of RE-MOFs is constructed from a hexanuclear metal cluster, akin to the well-known Zr-based building block encountered in the UiO-66 framework and related materials.²⁷ Recent studies have identified multiple adsorption sites in the hexanuclear clusters in Zr-MOFs that may play a role in tuning gas interactions.^{28,29,30} The previously synthesized RE-MOFs are composed of RE = Y, Yb, Eu, Nb and Tb (replacing Zr in the hexanuclear metal cluster) and the 2,5-dihydroxyterephthalic acid (DOBDC) linker. These RE-DOBDC MOFs have been recently investigated for the feasibility to bind and degrade chemical warfare agents,^{22, 31} indicating promising use for selective separation of chemical species.

RE-based frameworks, and specifically trivalent species across the lanthanide series, offer benefits of related coordination geometry and high coordination stability. The isostructural characteristics of trivalent RE-DOBDC MOFs implies tunability for structure-property relationships with only minor changes in reactant stoichiometry. By changing the RE metal of the MOF, localized structural changes are induced that may result in chemical specificity in adsorption applications.

To characterize those changes for a wide range of RE elements, optimized structures are calculated via DFT. Previous DFT methods have shown success in analysis of the electronic and optical properties of semiconducting materials.^{32,33,34,35} Higher level DFT can then be applied to describe the nontrivial ground state electronic structures of lanthanides containing 4f-electrons. Due to the combined lanthanide-organic structure and range of possible compositions, these RE-MOFs provide an excellent platform upon which to study the effects of different DFT methods in determining best practices for modeling the geometries and electronic structures of f-electron containing systems.

The RE-MOFs with RE=Y, Eu, Tb, and Yb are chosen for investigation because they have all been experimentally synthesized, and they enable a comparative investigation into the structural geometry and ground state electronic structure between non-f-electron containing RE-MOFs (e.g. Y) and f-electron containing analogs (e.g. Eu). By choosing a set of previously synthesized RE-MOFs for initial DFT investigations, experimentally determined structures are available for direct validation of the calculated optimized geometries, allowing for the assessment of the accuracy of the proposed DFT approach. The optimum DFT method can then be applied to the remainder of the lanthanide series in future work, providing the opportunity for directed

computational design of currently non-synthesized RE-DOBDC MOFs.

As discussed above, DFT calculations of materials containing 4f-electrons are not guaranteed to produce reasonable results. They require forethought to correctly account for the effects of the all electron potential on geometry and electronic structure calculations. As the RE 4f-electrons are highly localized to the nucleus, they can be treated with a large core potential (LCP), which places the f-electrons within the core of the potential. The implementation of LCPs is a viable option for structure optimizations. However, it removes the optically active 4f-electrons from the valence electronic structure, possibly introducing error into the calculated electronic structure. One caveat of selecting a LCP for structural optimization is the choice of oxidation state of the RE element. Lanthanide RE elements are generally most stable in a +3 oxidation state, but there are outliers: Ce, Eu, and Yb. These RE elements are known to adopt an oxidation state other than +3 due to the loss of a lone f-electron (Ce⁴⁺) or gaining an additional electron to complete a half 4f (Eu²⁺) and total 4f (Yb²⁺) orbital shell.³⁶ This is discussed further in the manuscript.

Herein, bulk three-dimensional (3D) periodic systems of RE-DOBDC MOFs are studied with two goals in mind: i) to investigate the level of theory necessary to achieve agreement between calculated geometries and experimental structures of RE-DOBDC MOFs (RE=Y, Eu, Tb, Yb) and ii) to investigate the f-electrons in the electronic structure of Eu-DOBDC MOFs for varying values of a Hubbard U correction. The magnitude of an all electron 4f potential are parameterized by detailed investigation of two analogs of differing RE elements: Y- and Eu-DOBDC MOFs. These two structures are chosen to allow for direct comparison between a RE-MOF that has no f-electrons, Y, and a RE-MOF that has a complex f-electron containing electronic structure, Eu (4f⁶). The results from a range of DFT methodologies can indicate the required modeling approach to correctly calculate optimized geometries, ground state electronic structure, choose potentials, and identify Hubbard correction values.

Computational methods

The following computational procedure is a reproducible process for optimizing RE-DOBDC MOF structural geometries and maintaining consistency when interchanging RE elements into the framework. The experimental structure for Eu-DOBDC MOF has been determined;¹ it consists of a Eu₁₂(μ₃-OH)₁₆(C₈O₆H₄)₈(C₈O₆H₅)₄ unit cell with a tetragonal structure, P 4/mnc, shown in **Figure 1**. This structure is used as a starting point for all DFT structure optimizations of RE-DOBDC MOFs, where Eu is replaced by other RE elements (RE=Y, Tb, Yb).

Ground state electronic structures and geometries are optimized using DFT as implemented in the Vienna Ab initio Simulation Package (VASP)^{37,38} code in a plane wave basis

set,^{39,40} with projector-augmented wave (PAW) potentials.^{41,42} All LCP used a 1000 eV cutoff energy, converged to a force accuracy of 0.01 eV/atom. Structural optimizations were carried out at the gamma point and checked with a 2x2x2 k-point sampling, showing negligible differences in the structure or energy. A gaussian smearing of 0.01eV is used for smearing of the electron occupation. Additionally, no thermally excited electron occupation occurs due to the large band gap in RE-DOBDC MOFs. Optimizations utilizing the full 4f-electron Eu potential are carried out using a 400eV cutoff energy, while all other convergence criteria are kept consistent.

The generalized gradient approximation (GGA) exchange correlation functional of Perdew, Burke, and Ernzerhof designed for solids and surfaces (PBEsol)⁴³ is chosen for consistency with recent successes in RE-MOFs³¹ and lanthanide oxide materials.¹⁰ Other previous transition metal MOF calculations have been successfully investigated using PBE.^{44,45} However, the structural results calculated for RE-DOBDC MOFs with PBE and PBEsol are minimally different when compared to experimental values. Therefore, PBEsol-D3 is selected for this work. Given a known application of RE-DOBDC MOF materials is gas molecule adsorption, the DFT-D3 method of Grimme⁴⁶ with Becke-Jonson damping⁴⁷ is added as a van der Waals correction.

Optimization of the RE-DOBDC MOF structures followed previous DFT procedures^{31,45,44} for structural optimization of MOFs. The structural relaxation consists of three steps: optimization of atomic positions, optimization of atomic position, cell shape, and cell volume, and re-optimization of atomic positions.

In RE-MOFs, the RE metal is found in clusters that are coordinated to the DOBDC organic linker in both bidentate and monodentate binding. When the DOBDC linker has a monodentate binding coordination, there is a higher degree of atomic freedom and an increased possibility of linker rotation. By starting optimization calculations with a structure slightly different from the symmetry positions, the model relaxes to a lowest energy configuration without an initial position or symmetry bias.

To resolve the first goal of achieving accurate structures, geometry optimizations are calculated with spin-restricted DFT for RE-DOBDC MOFs (RE=Y, Eu, Tb, Yb) using trivalent LCPs. Two types of Eu PAW potentials are provided within VASP: a full valence potential of Eu [Kr]5s²6s²5p⁶5d⁰4f⁷ which has a [Kr] core and 5s²6s²5p⁶5d⁰4f⁷ treated as valence; a Eu LCP, representing Eu(III), which is a PAW potential that treats the Eu 6s²5p⁶5d¹ electrons as valence and places [Kr]5s²4f⁶ in the core. Accurate geometries are dependent on applying LCPs with the correct oxidation state. Lanthanides are assumed trivalent, and a +3 oxidation state is used for Eu and Yb based on previously published experimental photoluminescence (PL) spectra of Eu- and Yb-DOBDC MOFs.^{1,26}

The second goal of this paper, how to characterize 4f-electrons in Eu-DOBDC MOF through DFT, requires a more extensive set of calculations. To correctly account for the Eu

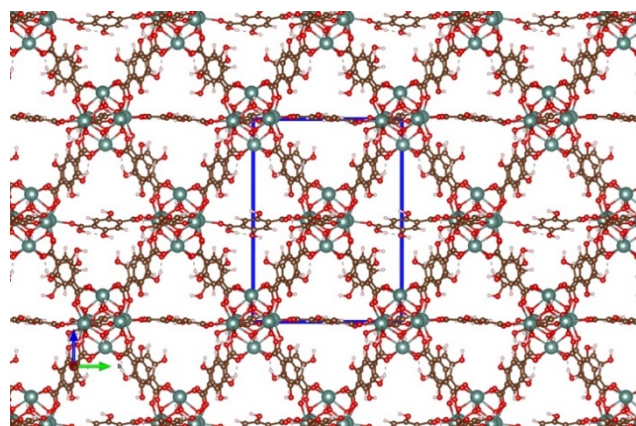


Figure 1. Periodic 3D structure of activated Eu-DOBDC with a single unit cell centrally located and highlighted by a blue box. Colors: Eu(green), O(red), C(brown), and H(white)

4f-electrons in the electronic structure, spin-unrestricted DFT with a full 4f valence potential is used. This investigation of 4f characterization in lanthanides is focused on the Eu-DOBDC structure due to reports of unique luminescence properties^{48, 49} from their sharp ⁵D₁→⁷F_J emission peak⁵⁰, that requires accurate simulations of the 4f-electrons from the Eu metal centers. From previous characterization of Eu being in a +3 oxidation state for Eu-DOBDC MOF,¹ the expected f valence structure is 4f⁶. Due to the open shell nature of the 4f-electrons, the magnetic nature of lanthanide materials must be accounted for. Previous literature has shown measured and calculated magnetic susceptibility of Eu³⁺ in the range of $\mu_{eff} = 3.26$.^{51,52} For the spin-unrestricted DFT calculations, an initial magnetic moment of 3.5 μ_B is applied to all Eu atoms and the total spin value is undefined. The initial magnetic moment is set to direct the calculation close to a potential local minimum corresponding to the experimentally known value.

To correctly describe the highly-localized 4f-electrons in lanthanide elements, a Hubbard correction based on the method of Dudarev *et al.*,⁵³ Eq. 1, is used. This method bridges the orbital dependent method of Anisimov *et al.*,⁵⁴ with a rotationally invariant functional from Liechtenstein *et al.*,⁵⁵ and has been applied as:

$$E_{GGA+U} = E_{GGA} + \frac{(\bar{U}-\bar{J})}{2} \sum_{\sigma} [Tr(\rho^{\sigma}) - Tr(\rho^{\sigma} \rho^{\sigma})] \quad (1)$$

where $\bar{U}$ and $\bar{J}$ are the spherically averaged matrix elements of the screened Coulomb electron-electron interaction and exchange, respectively, and ρ^{σ} is the density matrix of the 4f-electrons with spin projection σ . Furthermore, Dudarev's approach adds that the values of U and J are treated as one value, $U_{eff} = U - J$, which will be referred to only as U going forward.^{10,56,57}

The investigation of a Hubbard U correction, applied to the Eu 4f-electrons in Eu-DOBDC MOF, allows for comparison of calculated electronic structures with experimentally determined PL spectra. Through analysis of density of states (DOS) and projected density of states (PDOS), it is possible to compare relative orbital energy

alignments with characteristic PL peak energies. The analysis of a range of U values provides parameterization for achieving reasonable ground state electronic structures that will be applied in future calculations.

Results and discussion

DFT is used to investigate RE-DOBDC MOFs, $\text{RE}_{12}(\mu_3\text{-OH})_{16}(\text{C}_8\text{O}_6\text{H}_4)_8(\text{C}_8\text{O}_6\text{H}_5)_4$ (RE=Y, Eu, Tb, Yb), and characterize the level of theory needed to accurately predict structural and electronic properties in materials with 4f-electrons.

Initially, the RE-DOBDC MOF systems are assessed with spin restricted DFT and LCPs, placing the Eu 4f-electrons in the core. This approach reduces the computational cost and may indicate a time efficient method for accurately representing experimentally determined structures.

To appropriately treat spin polarized Eu systems, accurate parameterization must be included to correct for tightly bound interaction energies of the f-electrons. Therefore, a series of calculations are performed to understand the magnitude of applied Hubbard corrections, and their impact on resulting geometric and electronic structures of RE-MOFs. Results enabled the best fit to experimental values. The selected parameters are applied to the initial structure to compare optimized structures from spin restricted localized potential and spin unrestricted valence potentials to identify the optimum methodology to model geometric and structural features of RE-DOBDC MOFs.

Structural Validation

In RE-DOBDC MOFs, the central metals clusters have structures similar to rigid lanthanide oxide materials¹³ as

well as framework flexibly due to rotation and contraction of the DOBDC organic linkers, a unique feature of MOF materials⁵⁸. A comparison of lattice parameters and pair distribution functions (PDFs) from experimental and computational results provides structural validation for the atomistic models.

Here, a direct comparison is made between the computational model of Eu-DOBDC MOF and the published single crystal X-ray diffraction file.¹ The initial structural characterization of calculated lattice parameters, density, and band gap for the optimized RE-DOBDC MOFs are presented in **Table 1**. The resulting optimized structure for Eu-DOBDC MOF is in excellent agreement, with a difference of less than 1% in lattice parameters and volume when compared to experiment.

During the geometry optimization process, the resulting lattice parameters show a minimal distortion of the unit cell, indicating a loss of the initial tetragonal geometry. This distortion stems from the non-uniformity in linker coordination throughout the material. Two binding coordination are exhibited in the unit cell (**Figure 1**), $(\text{C}_8\text{O}_6\text{H}_4)_8$ and $(\text{C}_8\text{O}_6\text{H}_5)_4$. The $\text{C}_8\text{O}_6\text{H}_4$ linker is coordinated in a bidentate fashion, having all four carboxylic group O bound to a RE atom. The linker coordination of $\text{C}_8\text{O}_6\text{H}_5$ is bidentate for one carboxylic group but monodentate at the opposite end of the DOBDC. The change from a bidentate to a monodentate coordination increases the degree of freedom of four DOBDC linkers in the unit cell. This variation in material flexibility provides an opportunity for slight shifting of the relative hexanuclear metal clusters away from their tetragonal geometric positions, causing the distortion of the unit cell.

Table 1. Lattice parameters, band gap energy, material density, and specified interatomic distances for activated RE-DOBDC (RE=Y, Eu, Tb, Yb) MOFs calculated with spin-restricted DFT and LCPs are compared with experimental values.

	Element	Lattice Parameters (Å)			Volume (Å³)	E _g (eV)	ρ (g/cm³)	Average Distance (Å) (std. dev.)		
		a	b	c				RE-RE	RE-O DOBDC	RE-O μ ₃ -OH
PBEsol-D3	Yb	15.16	15.20	20.87	4804	1.74	1.68	3.74 (0.043)	2.32 (0.064)	2.28 (0.072)
	Y	15.40	15.51	21.10	5040	1.63	1.22	3.83 (0.044)	2.36 (0.061)	2.33 (0.058)
	Tb	15.47	15.57	21.17	5100	1.47	1.48	3.86 (0.039)	2.39 (0.063)	2.35 (0.056)
	Eu	15.53	15.61	21.31	5167	1.53	1.43	3.91 (0.036)	2.41 (0.067)	2.38 (0.053)
Expt. ¹	Eu	15.56	15.56	21.33	5163		1.43	3.98 (0.040)	2.40 (0.019)	2.38 (0.025)

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A known feature of trivalent lanthanides is the contraction of ionic radius as the series progresses due to the increased shielding by the 4f-electrons.^{13,59,60} In comparing the lattice parameters and total volumes of the calculated framework metal clusters, the trend in lanthanide elements in the RE-MOF of $\text{Eu} > \text{Tb} > \text{Yb}$ follows the expected lanthanide contraction. The calculated Eu-DOBDC MOF structure has the largest cell volume of $5167 \text{ \AA}^3$ ($\rho = 1.43 \text{ g/cm}^3$) while the Yb-DOBDC MOF structure has the smallest cell volume of $4804 \text{ \AA}^3$ ($\rho = 1.68 \text{ g/cm}^3$). The Y-DOBDC MOF structure has a cell volume of $5040 \text{ \AA}^3$ ($\rho = 1.22 \text{ g/cm}^3$) and falls, as expected, between Tb and Yb due to atomic radii

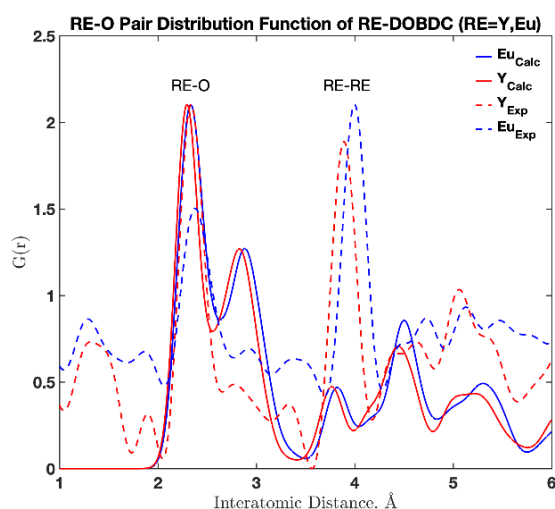


Figure 2. Comparison of PBEsol-D3 calculated (solid) and experimental (dashed) pair distribution functions of activated RE-DOBDC where RE= Y(blue) and Eu(red).

ordering. Therefore, arranging by calculated results, the cell volume order of calculated materials is $\text{Eu} > \text{Tb} > \text{Y} > \text{Yb}$. This provides good qualitative agreement with known ordering of size and its indirect effect on material parameters.

Calculation of PDFs offers a more rigorous assessment of specific atomic configuration. The calculated RE-O PDFs for optimized Y- and Eu- DOBDC MOFs are compared with experimentally collected PDFs¹, see **Figure 2**. From the experimental PDFs, the prominent peaks near $2.5 \text{ \AA}$ and $4 \text{ \AA}$ are identified as the primary RE-O and RE-RE interatomic distances, respectively¹. The total RE-O PDF is comprised of all possible interatomic distances between RE-O, O-O, and RE-RE elements. The contribution of each set of interatomic distances to the total is shown in the supporting information (SI), **Figure S1** and **Figure S2** for Y and Eu, respectively.

There are two distinct types of O atoms in the structure. The first are O atoms found in the hexanuclear clusters characterized as $\mu_3\text{-OH}$ bridging hydroxides, which are

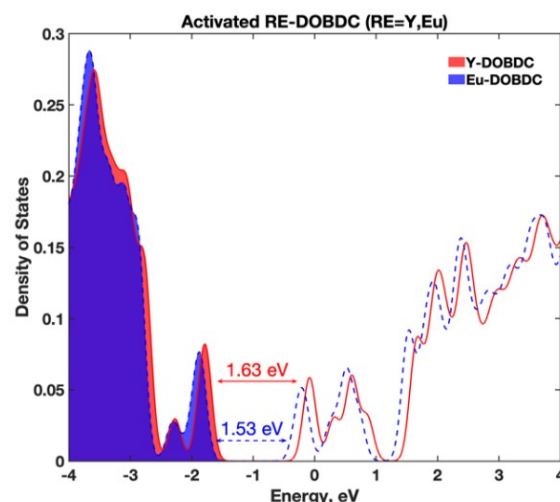


Figure 3. Density of states for RE-DOBDC, with RE=Y(red/solid line), Eu(blue/dashed line), optimized with PBEsol-D3. The shaded and unshaded regions represent electronically occupied and unoccupied states, respectively.

bound to three RE elements. The second type are the O atoms in the carboxylic groups on the DOBDC linkers that are coordinated to RE atoms of the hexanuclear clusters. Each of these RE-O bond distances, RE-O($\mu_3\text{-OH}$) and RE-O(DOBDC), comprise the primary RE-O peak near $2.5 \text{ \AA}$ (**Table 1**).

The best comparison of calculated values with experimental measurements is for the Eu-DOBDC MOF, which has single crystal X-ray diffraction data to validate against the calculated results. A comparison of the lattice parameters, total volume, Eu-O($\mu_3\text{-OH}$), Eu-O(DOBDC), and Eu-Eu values highlight the accuracy of the optimized geometry. The largest difference in the calculated interatomic distances is the Eu-Eu distance, with a computational Eu-Eu bond distance of $3.91 \text{ \AA}$ compared with a value of $3.98 \text{ \AA}$ from experiment,¹ a decrease of $0.08 \text{ \AA}$, or 2% in the simulated results. Both calculated Eu-O distances are within $0.01 \text{ \AA}$ of the experimental values, further confirming the accuracy of the RE-DOBDC MOF structures.

The overall trends between the other RE elements, the lattice parameters, total volume, and specific bond distances of the RE-RE and RE-O are analysed. The overall trend follows that of lanthanide contraction due to the increased shielding of the 4f-electrons^{13,59,60} and comparison of the calculated Eu-DOBDC MOF structure with experiment demonstrated excellent agreement of both interatomic distances and cell volume and density. Based on the results above, the use of spin-restricted DFT with LCPs has provided accurate geometric structures of RE-DOBDC MOFs.

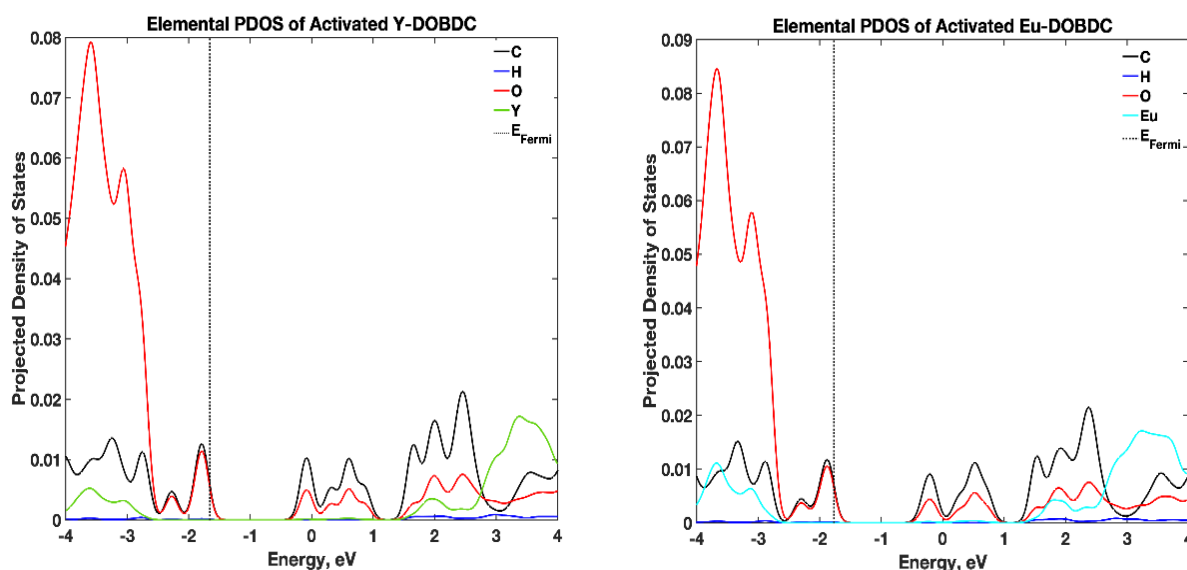


Figure 4. Projected density of states (PDOS) for activated Y-DOBDC (a, left) and Eu-DOBDC (b, right) calculated with PBEsol-D3 using LCPs. The PDOS is analysed by element type C (black), H (blue), O (red), Y (green), and Eu (teal). The Fermi energies are indicated with vertical dashed lines.

Electronic Structure

Starting from the optimized geometries (see above), the calculated electronic structure is first visualized through density of states (DOS). Ground state DOS provides fundamental insight into the distribution of energies and localizations of the electron density. The goal of this section is to identify the importance of including a full 4f valence potential in lanthanide containing materials, focusing on two RE-DOBDC MOFs: Y-DOBDC and Eu-DOBDC. The Y and Eu systems represent two analogues of the RE-DOBDC materials that either contain (Eu) or do not contain (Y) 4f-electrons. Comparison of isostructural materials with and without f-electrons provides insight to the fundamental electronic structure of the materials and the direct effect of the 4f-electron addition. Additionally, the activated Y-DOBDC MOF contains an even number of electrons within VASP, providing minimal difference in electronic structures calculated with and without spin. This allows the initial investigation of electronic structure beginning with spin-restricted DFT. The spin-restricted DOS for Y- and Eu-DOBDC MOFs is presented in **Figure 3**, with individual spectra presented in the SI, **Figure S3-S4**. For the Eu-DOBDC MOF the LCP is investigated as it is employed during the geometry optimization scheme. The LCP is not expected to provide the correct electronic structure but generates a baseline Eu-DOBDC MOF electronic structure to compare against future calculations.

Initial analysis of the spin-restricted DOS, **Figure 3**, show the Y and Eu both display a similar electronic structure when f-electrons are not considered. The calculated band structure of Y and Eu, **Figure 3**, is used to highlight the consistency between Y and Eu with using a trivalent LCP for Eu. The quantitative band gap value is expected to be underestimated due to inflated electron-electron repulsion energies inherent to DFT.⁶¹

Similarities are seen in the shape and electronic energy state distribution in the energy region near the valence and conduction band edge (VBE/CBE). Due to the lack of f-electrons in Y-DOBDC MOF, it is expected that photoemission is from a ligand-to-ligand charge transfer⁶². This mechanism results in electronic states near the band edges, which partake in radiative processes, are localized on atomic species other than Y. The LCP Eu-DOBDC MOF electronic structure is expected to also show localization of the band edge states away from Eu, due to similarities in Eu and Y.

The calculated PDOS for both the Y and Eu systems (**Figure 4**) indicate the electronic states near the VBE and CBE are comprised of states localized on C and O. As there are multiple O environments within the material, the localization on the DOBDC O atoms is visualized by plotting the partial charge densities and is included in **Figure S5**. Furthermore, the C and O states are calculated to be 2p states, as indicated by the calculated orbital decomposed DOS, shown in **Figure S6** for Y- and **Figure S7** Eu-DOBDC MOF. The calculated localization of charge density on the DOBDC linkers confirms our expectation for the Y system. However, the characteristic emission peaks of Eu^{3+} are expected to occur from 4f-electron states localized near the VBE. The absence of Eu states at the VBE in **Figure 4** is due to the lack of 4f-electrons in the Eu^{3+} LCP, indicating that additional corrections are needed to accurately describe the 4f-electron states. To note, the VB for both Y- and Eu-DOBDC are completely occupied, and the states just above the Fermi energy result from the broadening used in plotting the DOS.

Ultimately, based on the previous discussion of the RE-DOBDC MOF geometries, the LCP methodology appears sufficient for carrying out calculations in which 4f-electrons do not play a strong role, resulting in qualitatively accurate large-scale calculations of RE-DOBDC MOFs.

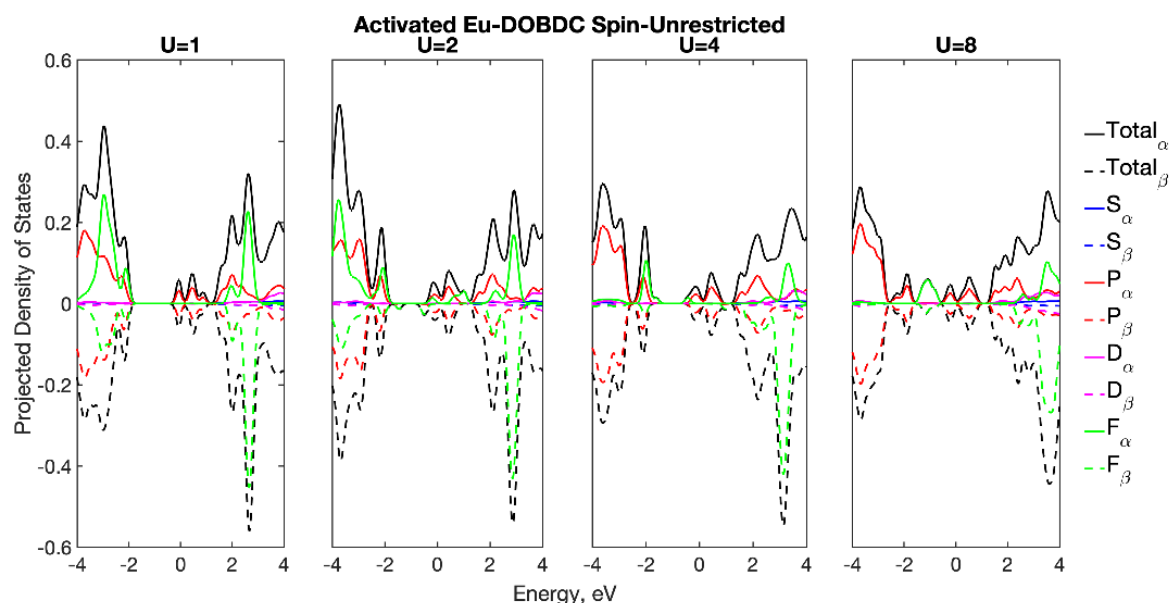


Figure 5. Spin unrestricted PDOS of activated Eu-DOBDC with an applied Hubbard correction of $U(\text{eV})=1, 2, 4$ and 8 plus a magnetic moment of $\mu_{\text{eff}}=3.5$. The spin α (solid) and spin β (dashed) projections show the total (black) DOS and the PDOS contribution.

Spin-unrestricted Hubbard Correction (U)

Results reported earlier in this manuscript have investigated the ability of efficient LCPs to calculate accurate geometric structures and to describe a baseline electronic structure of the Eu-DOBDC MOF in comparison to the Y-DOBDC MOF. However, full 4f valence potentials must be considered to correctly describe the electronic structure of lanthanide materials, due to the open-shell nature of the f-electrons that produce magnetic moments from unpaired electron spins localized around the RE atom.

To maintain consistency and provide the direct effect of 4f-electrons in RE-MOF, the full 4f valence potential plus a Hubbard U correction in spin-unrestricted DFT is used to calculate the ground state electronic structure of the Eu-DOBDC MOF. This type of parameterization in RE-MOFs is needed as each RE element and its surrounding coordination environment has a unique effect on the local electronic structure.

A second objective, following the direct effect of 4f-electrons on electronic structure, is to validate the choice of the +3 oxidation state LCP used for geometry optimization. As mentioned previously, Eu is one of a few lanthanide elements that can exist in an oxidation state other than +3. The lowered ionization potential of $+3 \rightarrow +2$ is the result of Eu^{3+} having a near half-filled 4f shell. A Eu^{3+} is expected to have a $4f^6$ orbital occupation, whereas a Eu^{2+} is expected to have a half filled $4f^7$ occupation.

To sample the effect of the Hubbard correction, U values in the range of 1eV through 9eV are calculated. The U values are applied to the Eu 4f valence electrons and are expected to impact both the energies of 4f-electron states and the total overall DOS electronic state energy distribution. A series of calculations with $U = 1-4$ eV applied to Eu d-electrons indicated minimal change in electronic structure,

Figure S8. The effect on the overall DOS is an induced effect stemming from the shift of the 4f states.

Visualization of the spin-unrestricted PDOS for $U = 1, 2, 4$, and 8 eV are presented in **Figure 5**, while all PDOS for $U = 1-9$ eV are presented in **Figure S9**. The PDOS exhibits a relative population change of 4f-electrons near the VBE and CBE. Additionally, in the spin α (spin up) projection the VBE PDOS intensity is reduced with greater values of U , stemming from the 4f-electrons being driven deeper into the VB. The α projection also indicates with increasing U values an introduction of 4f states at the edge of the CBE, suggesting redistribution of the 4f-electron population from higher energy states in the CB. In the spin β (spin down) projection, similar trends are seen with the 4f-electron density reducing with increasing U values.

Analyzing the PDOS in Eu-DOBDC for $U = 1-9$ eV, **Figure S9**, provides an indication of viable U values for calculating the ground state electronic structure. Eu-DOBDC is characterized by PL and must maintain an open band gap within the material. One effect seen in both the α and β spin projections is the modification of the band gap energy with increasing U values, shown in **Table 2**. This is clear when $U = 6$ eV and 8 eV, both the spin α and spin β projections show a metallic PDOS. The shift in 4f band energies places a large population within the original band gap between the DOBDC linker states.

Table 2. Band gap energies for spin alpha and beta projections and the resulting 4f-electron occupation values for varying Hubbard U values.

U (eV)	Band gap (eV) α/β	Eu 4f Occupation (e)
1	2.09/2.02	6.37-6.41
2	1.87/0.96	6.28-6.37
3	1.0/1.0	6.22-6.40
4	1.16/1.90	6.22-6.32
5	1.14/1.67	6.21-6.28

6	Closed	6.18-6.23
7	0.82/1.12	6.13-6.21
8	Closed	6.15-6.19
9	1.60/1.63	6.17-6.21

Differences in the f-orbital energy distribution is seen for U values above and below 5 eV. For U values of 1-5 eV, the f-orbitals are primarily localized near the VBE and CBE or create a singular gap state within the material. When U = 6-9 eV, the f-orbitals are distributed either throughout the original band gap of the material or have transitioned primarily into the CB (U=9 eV).

A second distinction is that as Hubbard values increase the band gap for the DOBDC linker ($E_{g,DOBDC}$) drops from 2.2eV with U = 1 eV to 1.75 eV for U = 7 eV, after which $E_{g,DOBDC}$ becomes stable, **Figure S10**. Experimental characterization has indicated that the strongest optical absorption within RE-DOBDC MOFs is contributed by the organic DOBDC linkers, so that $E_{g,DOBDC}$ can be used as a parameter for selecting a correct Hubbard U. From the $E_{g,DOBDC}$ energies increased U values modify the Eu f-electrons and also induce reduction in DOBDC transition energies. The experimental DOBDC emission edge for RE-DOBDC MOFs is measured near ~650 nm (~1.91eV), indicating a Hubbard U range of 1-5 can be appropriately applied. One must use caution in directly applying only singular ground state analysis for Eu emission, as the primary PL is derived from two different spin configurations. However, one can still draw important ground state information from ground state U analysis when investigating the organic DOBDC component.

Spin-restricted v. Spin-unrestricted Simulations

By comparing the spin-restricted and spin-unrestricted calculations it is possible to identify the impact on the geometric and structural properties of Eu-DOBDC MOF containing f-electrons as valence. The inclusion of valence 4f-electrons in Eu compounds requires spin-unrestricted calculations to accurately represent known experimental optical properties. A direct comparison of the spin-restricted and unrestricted DOS for Eu-DOBDC MOF with U = 1 eV can be seen in **Figure S11**. The spin-restricted DOS shows a band gap that is nearly closed, whereas the spin-unrestricted DOS show the spin α and β , respectively, have an open gap to allow for expected emission. Unlike the LCP results, the VBE is composed of Eu 4f-electrons. This is the expected configuration of the electronic structure to match with experimentally measured emission.¹

The resulting DOS, for spin-unrestricted calculations with U values between 1-5 eV, meet the minimum requirement of maintaining an open band gap within the material and indicates that the strong DOBDC optical transition energies are similar to experimental values. The energetic positioning of specific orbital electrons, in relation to the total DOS, can indicate the accuracy of the calculated electronic structure. Eu has characteristic measured PL peaks corresponding to

$^5D_J \rightarrow ^7F_J$ in the range from 700nm to 575nm. The Russel Saunders terms characterizing the emission indicate a spin-flip transition, which can be explored further via constrained DFT or spin-orbit coupling calculations.⁶³

To further help identify a best choice of U value, the PDFs for the spin-unrestricted geometries are calculated, **Figure S12**. The U corrected geometries show a distinction between U = 1 eV and U = 2,4, and 8 eV. The RE-O and RE-RE bond peaks are elongated for U = 1 eV, as compared to the others, and best match with the experimentally measure PDFs.

Investigation of the geometric and electronic structures of RE-DOBDC MOFs identified that the use of spin-restricted DFT with LPCs can provide accurate geometric structures. For investigation of the electronic structure, LPCs do not capture contributions from the RE element. In cases where photoemission is from the ligand, rather than the RE, LPCs may still be adequate, but for a more accurate investigation, a spin-unrestricted calculation with a full valence potential will be necessary. Furthermore, a Hubbard correction in the range of U = 1-5 eV for Eu-DOBDC MOFs is identified to capture the correct band gap and improve the PDF match with experimental values, justifying its use in further simulations.

Conclusions

In conclusion, we have demonstrated a series of DFT studies to characterize the level of theory needed to accurately predict structural and electronic properties in materials with 4f-electrons. This approach accurately calculates geometric structures of $RE_{12}(\mu_3-OH)_{16}(C_8O_6H_4)_8(C_8O_6H_5)_4$ (RE=Y,Eu,Tb,Yb) MOFs with spin-restricted DFT using LPCs. We have also investigated the effect of lanthanide 4f-electrons in Eu-DOBDC MOF by calculating the ground state electronic structure with spin-unrestricted DFT using a full 4f valence potential and Hubbard U corrections. The use of LPCs has proven to be accurate in calculating optimized geometric structures in RE-DOBDC MOF materials. When considering structural geometries, the use of LCP can be substituted for a full valence potential. The approach described provides a time efficient DFT method to achieve accurate geometric structures, which can then be used as a starting point to carry out more sophisticated calculations for investigating the electronic structure. For Hubbard corrected spin-unrestricted calculations, a U value in the range of 1-5 eV maintains a non-metallic (open) band gap with slight deviations in f-orbital energetics. For the Eu-DOBDC MOF structure under investigation, a Hubbard U value of 1 eV maintains a correct energy gap within the material. Comparing calculated results with experimental data, the importance of the full valence calculation and the Hubbard correction in correctly predicting the electronic structure is highlighted. By using this calculation approach and reducing computational cost, it can be readily applied to areas allowing for large scale applications in molecular dynamic and gas adsorption studies. Ongoing work to investigate the

full lanthanide series will help identify chemical trends, allowing for the design of specific chemical environments for future application.

Conflicts of interest

There are no conflicts to declare.

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