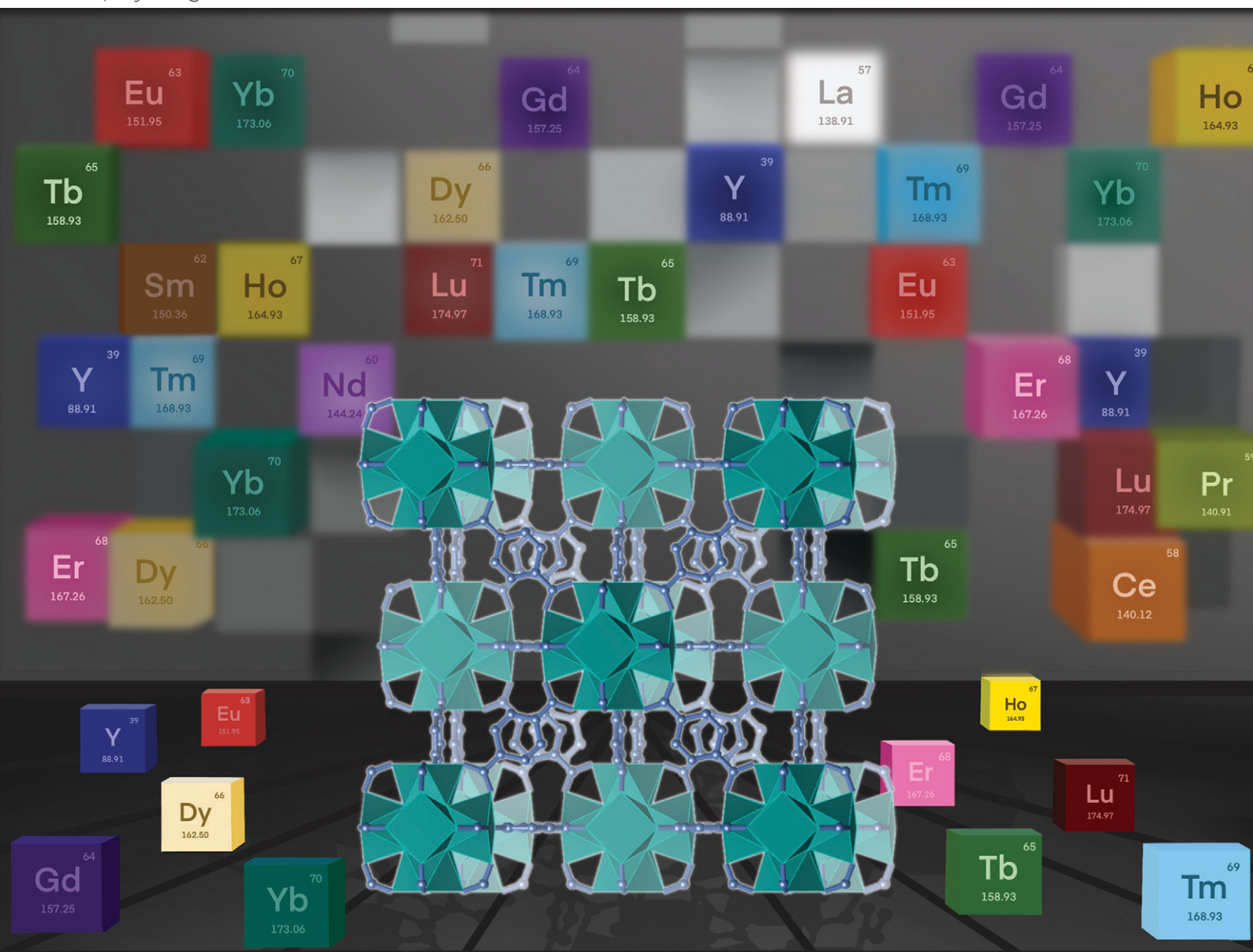


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HIGHLIGHT

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Developments in the discovery, synthesis, and characterization of RE(III)-UiO-66 and its structural analogues

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New metal–organic frameworks (MOFs) are continuously being designed and discovered. As new MOFs emerge in the literature, they are catalogued according to different features, such as the nature of their metal nodes or linkers, structural arrangement, or physical properties, to name a few. In this highlight, developments in the history, synthesis, and characterization of a rare-earth cluster-based MOF with **fcu** net, specifically RE-UiO-66, are discussed including analogues with substituted terephthalic acid linkers. Examples demonstrating the photophysical properties of these MOFs are included to highlight their potential applications related to photoluminescence such as white light emission and temperature sensing.

Introduction

It has been more than 30 years since the important early contributions of Robson,¹ Yaghi,^{2–4} Kitagawa,⁵ and Férey⁶ to the field of metal–organic frameworks (MOFs). MOFs are porous materials with tunable surface area, density, stability, and chemical properties.^{7,8} This tunability is a consequence of the high number of synthetic building block combinations that can be used to produce MOFs.⁹ Being a subset of coordination polymers and networks, MOFs are mainly crystalline, 2 or 3-dimensional materials with the potential for porosity.¹⁰ Structurally speaking, MOFs are scaffolding-like materials containing inorganic building units (single metal ions, chains, or clusters) connected with each other *via* organic building units (multitopic ligands) called linkers. As a result of their chemical versatility, and in turn their structural tunability, MOFs have been studied for a wide range of applications including, but not limited to, gas adsorption,^{11–13} catalysis,^{14–16} chemical sensing,^{17,18} and water treatment.^{19–21}

Reticular chemistry is an approach described by Yaghi and O’Keeffe to design, synthesize, and catalogue MOFs based on their net structures.^{22,23} In principle, understanding the geometry and connectivity of the building blocks that compose a MOF with a particular net can be used to create a template to build new MOFs with building blocks that present similar (or the same) geometry and connectivity as

the first ones.²⁴ In the MOF field, these building blocks are represented by the inorganic nodes, and organic linkers, with the former being the main component of the secondary building unit (SBU) of the MOF.²⁵

As the number of reported MOFs increased in the 1990s and early 2000s, a procedure became necessary to describe their structures and distinguish them from other closely related systems.²⁴ For example, in organic chemistry when an alkene is described it is important to denote whether it is the *E*, or the *Z* stereoisomer. The same is true with structures of such complexity as MOFs, wherein a 4-connected net can be represented by multiple descriptors and can take many forms. These representative nets, in the field of MOF chemistry, are given a bolded three-letter code and collected in the Reticular Chemistry Structure Resource (RCSR).²⁴

One of these nets is the one described by a single 12-connected vertex (or node), called **fcu** (Fig. 1a).²⁶ The **fcu** net receives its name from the face-centred cubic unit cell. In the MOF field, the foremost **fcu** net structure is exemplified by Zr-UiO-66 (UiO = University of Oslo, Fig. 1b).²⁷ Since its original report, in 2008 by Cavka, Lillerud *et al.*,²⁸ Zr-UiO-66 has attracted the attention of many researchers due to its structural robustness,^{29,30} reproducible synthesis,³¹ scalability,³² and application potential.^{33–35}

Zr-UiO-66 is most often synthesised solvothermally in *N,N*-dimethylformamide (DMF) using terephthalic acid (H₂BDC) and a Zr(IV) salt, from which a hexanuclear cluster forms (Fig. 1b and c).^{28,31,36} Other additives, called modulators,^{37,38} are often added to the reaction mixture to slow down the Zr(IV)–O(linker) bond formation, allowing for 3-dimensional structure propagation and for some control over defects,³⁹ crystallinity,⁴⁰ or crystal size.^{40,41} Zr-UiO-66 has a face centred-cubic unit cell and crystallizes in the *Fm* $\bar{3}$ *m* space

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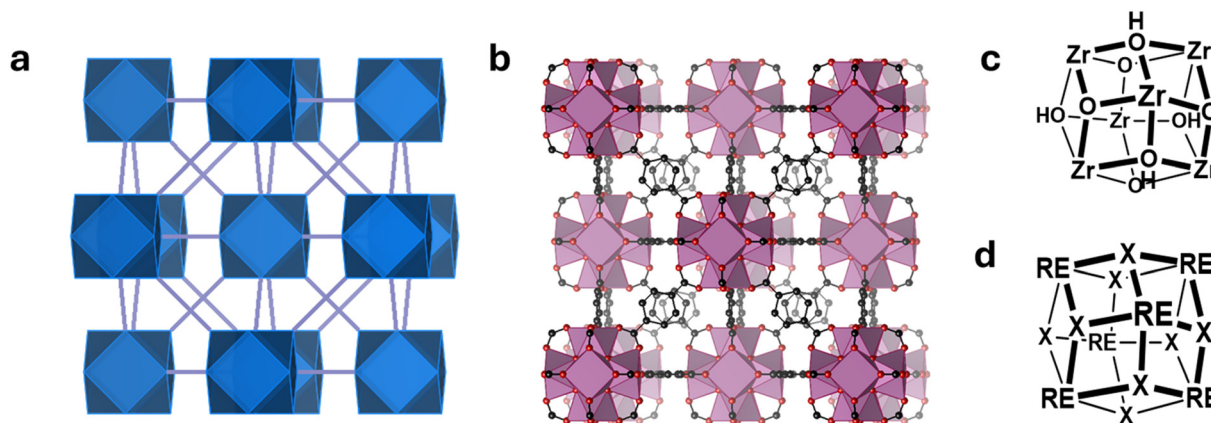


Fig. 1 (a) fcu net, (b) structure of UiO-66, (c) [Zr₆O₄OH₄]¹²⁺ cluster of Zr-UiO-66, and (d) [RE₆X₈]¹⁰⁺ cluster of RE-UiO-66, where X = OH or F.

group, with a lattice parameter, a , of 20.7 Å. The MOF is comprised of two distinct types of cages, an octahedral one of 12 Å diameter and a tetrahedral cage of 7.5 Å, both with 6 Å apertures (Fig. 1b).⁴² As a result of this structure, the calculated theoretical pore volume of Zr-UiO-66 is 0.77 cm³ g⁻¹, and its surface area is 1160 m² g⁻¹.⁴³

The fcu net of Zr-UiO-66 is defined by a 12-connected node that comes from the inorganic building block – a Zr(IV)-hexanuclear cluster, which is bridged to 12 other clusters through BDC²⁻ linkers.³¹ In this hexanuclear cluster, Zr(IV) ions are bridged through hydroxo, or oxo ligands (Fig. 1c). It is the high connectivity of this building block (12), and the strength of the Zr(IV)–O bond that contributes significantly to the high thermal, mechanical, and chemical stability of Zr-UiO-66.²⁷

In addition to being an attractive MOF for various applications,⁴⁴ Zr-UiO-66 has acted as a structural model for the discovery of a myriad of isorecticular MOFs that have since been described in literature. Structures isorecticular to Zr-UiO-66 with fcu net have been reported using different tetravalent metals (Zr(IV),²⁸ Hf(IV),⁴⁵ Ce(IV),⁴⁶ Th(IV),⁴⁷ U(IV),⁴⁸ Pu(IV)⁴⁹) with H₂BDC and many other linear ditopic linkers.^{27,46,48,50–52}

An interesting group of metals with versatile coordination chemistry for constructing SBUs for MOFs are the rare-earths (REs) – which include yttrium, scandium, and the series of fifteen lanthanoids.⁵³ What is interesting about the RE ions, from a structural perspective, is their diverse coordination chemistry with small energetic differences between different coordination numbers and geometries, with the latter being primarily dictated by ligand steric effects.⁵⁴ The variability in coordination number and geometry of RE ions adds complexity to structure prediction and synthesis of RE-MOFs, but it also opens the door for the discovery of new structures, comprised of diverse metal nodes,^{55–57} sometimes with highly connected nets.^{58,59} Moreover, the lanthanoid ions have unique electronic properties dictated by their 4f electron configurations,⁶⁰ which contributes to their potential in applications such as sensing,⁶¹ near-infrared emission,^{62,63} single molecule magnets,⁶⁴ and white-light emission,⁶⁵ amongst many others. While these applications are not

exclusive to RE-MOFs, they can certainly take advantage of the unique properties of lanthanoids to perform the intended purpose.

In addition to the various tetravalent metal analogues of UiO-66, RE(III) ions can also be used to form the 12-connected hexanuclear cluster required to make UiO-66 isostructures. The first example of RE(III)-hexanuclear clusters being used to synthesize an fcu MOF was reported by Xue, Eddaoudi *et al.*⁶⁶ They reported seven structures, obtained with Y(III) and Tb(III) using asymmetric heterofunctional ditopic linkers (Fig. 2). Most importantly, Xue, Eddaoudi and coworkers demonstrated that in order to synthesise the RE(III) hexanuclear clusters *in situ*, a fluorinated linker, or modulator, had to be used.^{66–68} Since this initial report, the library of RE(III)-based fcu MOFs has been in constant expansion.

Synthesis and structure of RE-UiO-66

The first reported RE analogue of UiO-66 was obtained with Ce(IV) and H₂BDC linkers.⁴⁶ Like Zr-UiO-66, it is formed by

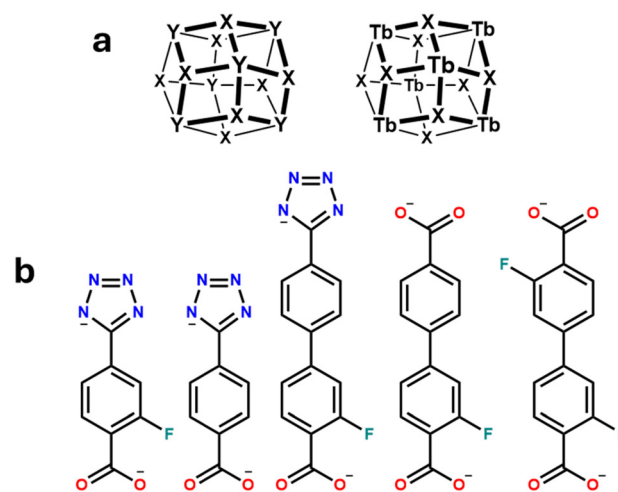


Fig. 2 (a) Clusters and (b) linkers used by Eddaoudi *et al.* to obtain RE(III) fcu MOFs.

hexanuclear clusters where the Ce(IV) ions are bridged by $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ groups, $[\text{Ce}_6\text{O}_4(\text{OH})_4]^{12+}$. The synthesis of this MOF does not require fluorinated modulators and can be achieved in short times (15 min) using DMF as a solvent.

While Ce is commonly found in the +4 oxidation state, the other RE ions have a preference for the +3 oxidation state.⁶⁹ Although some RE(III)-UiO-66 analogues with substituted BDC²⁻ linkers were reported in 2015,⁶⁷ 2017,⁷⁰ 2018,⁷¹ 2019 (ref. 72) and 2020,⁷³ the first synthesis of RE(III)-UiO-66 using non-functionalized BDC²⁻ linkers was reported by our group in 2021.⁷⁴ The solvothermal procedure developed to obtain RE-UiO-66 led to eight RE(III) analogues (RE = Y, Eu, Gd, Tb, Ho, Er, Tm, Yb), using the corresponding RE(III) nitrates as precursors and 2,6-difluorobenzoic acid (2,6-dFBA) as the fluorinated modulator. Moreover, we showed that the addition of nitric acid, and the utilisation of dimethylacetamide (DMAc), instead of the more commonly used DMF, led to a more reproducible synthetic procedure for obtaining phase pure RE-UiO-66. In a more recent article, we showed that RE(III) acetates can be used as precursors for the synthesis of RE-UiO-66, in place of RE(III) nitrates.⁷⁵ Furthermore, the MOFs synthesized using RE(III) acetates do not present significant differences from those synthesized with RE(III) nitrates in terms of crystallinity, porosity, or overall quality. While RE(III) nitrate precursors are more commonly used for the synthesis of RE(III) cluster-based MOFs, the utilisation of acetates presents advantages such as lower toxicity and hygroscopicity. Avoiding the latter can address issues with synthetic reproducibility attributed to varying humidity conditions in laboratory environments.

In the original article on the synthesis of RE-UiO-66, we solved the structure of the Tm(III) analogue by single-crystal X-ray diffraction (SCXRD), while the other seven analogues were confirmed by powder X-ray diffraction (PXRD).⁷⁴ Scanning electron microscopy (SEM) images of RE-UiO-66 show octahedral particles, usually in the range of 1–20 μm . N₂ adsorption-desorption measurements were performed on samples activated at 80 °C under vacuum for 20 h, giving rise to type Ia isotherms, with Brunauer-Emmett-Teller (BET) surface areas in the range 1000–1300 m² g⁻¹. It should be noted that we did not observe any evidence of dimethylammonium (DMA) counterions, or capping ligands in our original report on RE-UiO-66, suggesting that the MOFs may have contained defects. However, more recently we have synthesized samples of RE-UiO-66 with DMA counterions and acetate capping ligands (from the decomposition of the DMAc solvent, or from RE(III) acetate precursors), which leads to a decrease in the BET surface areas obtained (650–1230 m² g⁻¹).⁷⁵

In 2024, we developed a new procedure to grow larger (~100 μm) single crystals of RE-UiO-66, while also adding Sm-, and Lu-UiO-66 to the library.^{74,76} The procedure involves using a solvent mixture DMAc:HCOOH (3:1) and using higher temperatures and longer reaction times (140 °C and 4 days). Although it should be noted that the procedure to

obtain single crystals does not yield phase pure samples, so should only be used when single crystals are required over bulk microcrystalline powders. RE-UiO-66 crystallizes in the cubic space group *Fm* $\bar{3}$ *m*. There is one eight-coordinated crystallographically independent RE(III), with a square antiprismatic coordination geometry. The presence of an additional oxygen atom was also observed in a ninth coordination site. While the exact identity of that terminal ligand could not be determined, it is believed to correspond to a coordinated solvent molecule (likely water). The MOF presents the expected octahedral and tetrahedral cages, of 12 and 7 Å, respectively. Using the single crystal X-ray structures obtained for RE-UiO-66 (RE = Lu(III) to Sm(III)), the effect of the ionic radii of the lanthanoids on structural parameters was also studied. We observed an increase in the unit cell parameter when moving from Lu(III) to Sm(III), which is expected due to the increasing ionic radii of the RE(III).⁷⁶ Furthermore, a weak linear correlation was found between the thermal stability of the framework and the ionic radii, with Lu-UiO-66 presenting the highest thermal stability, collapsing at 460 °C. On the other hand, Sm-UiO-66 presented a low thermal stability, collapsing at 423 °C. Eu-UiO-66 behaved as an outlier, exhibiting a decomposition temperature lower than expected (400 °C). This latter observation was hypothesized to be due to a transition through a less stable Eu(II) intermediate.⁷⁷

Given that the hexanuclear cluster in the Zr(IV) analogue is bridged by $\mu_3\text{-O}$ and $\mu_3\text{-OH}$,⁷⁸ at the time of our first publication on RE-UiO-66 we⁷⁴ (and others)^{66,67} believed that the RE(III) hexanuclear cluster was bridged by $\mu_3\text{-OH}$ groups. However, Vizuet, Balkus *et al.*⁷⁹ showed that assigning these ligands as $\mu_3\text{-F}$ groups led to a better crystallographic fit, leading to thermal/displacement ellipsoids and atomic displacement parameters that were larger than the RE sites, as expected. They further confirmed that the RE(III) clusters of Ho-UiO-66 contained fluoro groups by X-ray photoelectron spectroscopy (XPS). Shortly after, Christian, Rimsza *et al.*⁸⁰ used DFT calculations to determine that replacing $\mu_3\text{-OH}$ groups by $\mu_3\text{-F}$ groups in RE-UiO-66 increases the formation enthalpy of the MOF, resulting in increased stability. Zwanziger, Murugesu *et al.*⁸¹ later evaluated the fluorine content of Y-UiO-66 using solid state ¹⁹F nuclear magnetic resonance (NMR) spectroscopy and detected multiple resonances, suggesting a mixture of fluoro and hydroxo groups bridging the cluster.

Unlike the neutral Zr(IV) and Ce(IV)-UiO-66 analogues, the RE(III) analogues are anionic, and a counterion is needed to balance the charge. While DMA, formed by the decomposition of the solvent, was expected to be the counterion, it was not detected in these MOFs until 2024.⁷⁵ The counterion can be detected by infrared (IR) spectroscopy and ¹H NMR spectroscopy, with peaks around 3600 cm⁻¹ and 2.7 ppm, respectively. In a defect-free MOF, two DMA cations are needed to balance the charge. However, the presence of acetate in the ¹H NMR spectra of many RE-UiO-66 analogues suggests that the MOF is defective. By considering that the



Highlight

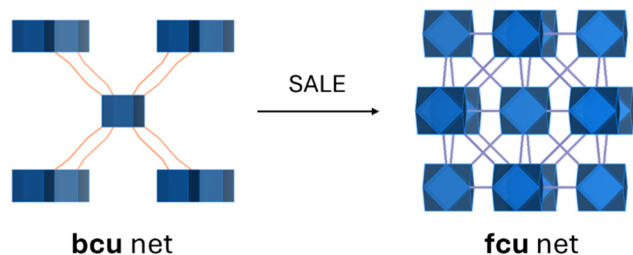


Fig. 5 fcu net obtained from SALE and linker installation on a bcu net.

applications in sensing,⁸⁶ bioimaging,⁸⁷ and light emitting diodes.⁸⁸ While inorganic phosphors containing lanthanoid ions exhibit high quantum yields and exceptional thermal and chemical stability, using these ions in MOF metal nodes combines their unique photophysical properties with the characteristic properties of MOFs. MOFs have some advantages over inorganic phosphors including their tunability, controlled spatial distribution of metal ions that prevents agglomeration, and the much lower temperatures required for their synthesis.⁸⁹ However, the lanthanoid ions present the limitation of low molar absorptivity, which leads to weak absorption of photons and subsequent weak luminescence intensity when exciting into the metal.⁹⁰ The “antenna effect” arises from using high molar absorptivity chromophores, which, after excitation, transfer energy to the lanthanoid ions 4f excited states.^{91–95}

In 2022, we studied the photo- and radioluminescent properties of Tb-UiO-66.⁹⁶ When excited at 355 nm into the BDC²⁻ linker, the solid state photoluminescence emission spectrum of Tb-UiO-66 demonstrated the expected green emission bands of Tb(III), corresponding to the transitions $^5D_4 \rightarrow ^7F_{3,4,5,6}$. The decay time of the $^5D_4 \rightarrow ^7F_5$ transition in Tb-UiO-66 was found to be $1048.6 \pm 6.93 \mu s$, which is typical for Tb(III) f-f transitions. The solid state radioluminescence emission spectrum of Tb-UiO-66 was obtained under 50 kVp and 80 μA unfiltered X-ray excitation, and it also exhibited emissions characteristic of Tb(III). These results suggest that linker-to-metal energy transfer is efficient in Tb-UiO-66, since no linker luminescence was observed in either the photo- or radioluminescence emission spectrum.

The photoluminescent properties of Tb(III) and Eu(III)-UiO-66 analogues with functional groups on the terephthalic acid linker have been reported.^{84,97} In the case of Tb-UiO-66 analogues, we carried out calculations to determine the T_1 state energies for various organic linkers (Fig. 6), which included H_2BDC , H_2BDC-F , $H_2BDC-Br$, $H_2BDC-NH_2$ and H_2DOBDC .⁸⁴ According to Latva's rule, ligand(linker)-to-metal energy transfer is more efficient when the energy difference between the organic linker T_1 excited state to the 5D_4 state of Tb(III) is between 2000 and 6000 cm^{-1} .⁹⁸ The T_1 state energies of DOBDC and BDC-NH₂ are lower than that of the 5D_4 state of Tb(III) (20 500 cm^{-1}), indicating that no Tb(III) emission is expected when exciting into these linkers – a result that was confirmed experimentally. On the other hand, BDC, BDC-F and BDC-

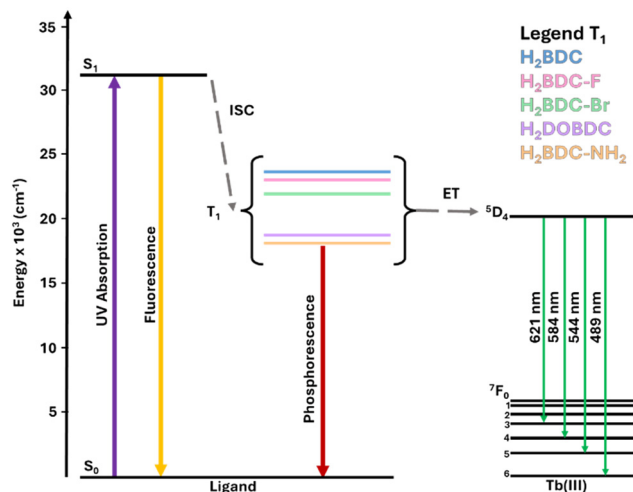


Fig. 6 Energy level diagram depicting the T_1 excited state for the linkers used to synthesize the various analogues of Tb-UiO-66, highlighting the energy transfer from each linker to Tb(III), and the excited state energies of Tb(III).

Br were able to sensitize the emission of the Tb(III) ion, exhibiting quantum yields (QYs) of 25, 31 and 6%, respectively (before activation). The QY obtained for Tb(III)-UiO-66 is very similar to that reported for an activated Tb(III)-MOF comprised of metal chain nodes and BDC linkers (26%).⁹⁹

Xing and coworkers,⁹⁷ reported three Eu(III)-UiO-66 analogues using $H_2BDC-OH$, $H_2BDC-NH_2$, and H_2NDC as linkers. The photoluminescence emission spectra of the Eu-UiO-66 analogues, when excited at 360 (Eu-NH₂-BDC) and 394 nm (Eu-BDC-OH, Eu-NDC), display a characteristic red emission at 614 nm corresponding to the $^5D_0 \rightarrow ^7F_2$ transition of Eu(III). Variable-temperature photoluminescence measurements showed that the position of the emission peaks did not change with temperature. However, the three MOFs exhibited stronger emission at lower temperatures, with Eu-BDC-NH₂ presenting a 20.5% enhancement in QY at 140 K, and Eu-BDC-OH and Eu-NDC having their highest enhancements at 170 K (35.9 and 14.9% enhancements, respectively). The photoluminescence QYs at room temperature were found to be 0.35, 1.92 and 5.67% for Eu-BDC-NH₂, Eu-BDC-OH and Eu-NDC, respectively.

Since Gd(III) has higher lying 4f excited states than the other lanthanoids (32 000 cm^{-1} vs. <21 000 cm^{-1}), it is rare to find an organic linker that is capable of

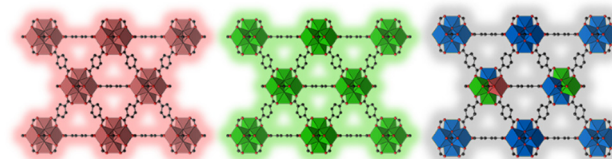


Fig. 7 Structure of Tb-, Eu- and Tb:Gd:Eu-UiO-66 showing the green, red and white emission.



Schott and collaborators¹⁰⁵ reported a theoretical study of the optical properties of a series of analogues of RE-UiO-66, where RE = La(III), Y(III) and Sc(III). The TD-DFT calculations showed that the absorption properties of these RE-UiO-66 analogues can be modulated by using substituted linkers containing electron-withdrawing groups, such as $-\text{CH}_3$, $-\text{OH}$, $-\text{SH}$ and $-\text{NH}_2$. They also observed that using di-substituted linkers containing $-\text{SH}$ and $-\text{NH}_2$ groups results in a shift of the absorption to the visible region, which is an interesting result for the potential application of these MOFs in light harvesting under solar irradiation.

Conclusions

Studies on the photophysical properties of the RE-UiO-66 analogues indicate that carefully tuning the composition of RE(III) ions in the cluster nodes or incorporating substituents on the H₂BDC linker can be useful to modulate their photoluminescence. While RE-UiO-66 analogues have been tested for potential applications, like white light emission and temperature sensing, the applications of these MOFs are still underexplored, particularly in comparison to Zr(IV)-UiO-66. Additionally, the development of thin films of RE-UiO-66 would be advantageous for several applications, but due to limitations in the understanding of growth mechanisms and poor structural control,¹⁰⁶ the synthesis of thin films is a challenge, and only a few examples of thin films of RE-UiO-66 analogues can be found in literature.⁶⁷

It is now widely accepted that the hexanuclear clusters in RE-UiO-66 contain a mixture of μ_3 -OH and μ_3 -F groups, which can be confirmed by SCXRD, XPS, and ^{19}F NMR spectroscopy (solution and solid state) but the exact mechanism leading to the incorporation of μ_3 -F groups in these clusters is still not well understood. Furthermore, the nature of defects (*i.e.*, missing linkers and/or nodes) in RE-UiO-66 analogues has not been studied in depth. Given that defects can play an important role in catalysis and gas adsorption, more research will be needed to have a thorough understanding of how best to prepare RE-UiO-66 analogues for these potential applications. Akin to the rich and ever-growing literature on Zr(IV) -UiO-66, we expect to see a continued increase in the study of RE(III) -UiO-66, a similarly fascinating family of MOFs.

Temperature Increment

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Author contributions

Micaela Richezzi: visualization, writing – original draft, writing – review & editing. P. Rafael Donnarumma: visualization, writing – original draft, writing – review & editing. Ashlee J. Howarth: funding acquisition, supervision, writing – review & editing.

Conflicts of interest

No conflicts to declare.

Data availability

This is a highlight review article that discusses research that was published previously by our group and others. Therefore, no new data were generated as part of this manuscript.

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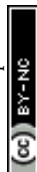
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