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Electron Transitions in a Ce(III)-Catecholate Metal-Organic Framework

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A rare three-dimensional catecholate-based Ce(III) metal-organic framework (MOF), denoted as NU-1701, has been synthesized and crystallographically characterized. Density functional theory calculations highlight various possible electronic transitions that may present in NU-1701. These transitions are competitive and indicate increased lanthanide character of Ce(III).

The most commonly known metal-organic frameworks (MOFs) are generally assembled from first and second row transition-metal cluster nodes and carboxylic acid-containing linkers, given each component's ease of tunability and thermal stability.¹⁻² Different linker motifs are comparatively underexplored, but may introduce new properties to a MOF that are unachievable with carboxylic acids. Hexahydroxytriphenylene (HHTP), for instance, is a tritopic catecholate linker that endows MOFs with excellent proton conductivity³⁻⁴ and electroconductivity.⁵⁻⁶ Another significant characteristic of HHTP is its seven possible oxidation states,⁷ which are advantageous for tuning redox activity.⁸ There are only a handful of three-dimensional MOFs with this style of linker,^{4,9} but the vast majority are two-dimensional,³ with single crystal growth being difficult due to preferred growth along the axis of pi-pi stacking, as well as fast kinetic formation of five-member chelate rings.¹⁰ Thus, more MOFs containing HHTP must be synthesized to determine design rules, and their electronics should be studied to understand and best apply each framework's inherent redox-activity.

One metal species that could particularly benefit from HHTP's nature is Ce(III). In its tetravalent state, cerium is primarily known as an oxidation catalyst in the form of ceria¹¹ or cerium-

oxo clusters.¹² While it serves as an important intermediate following ligand-metal charge transfer (LMCT) in Ce(IV) species, Ce(III) is a powerful photo-reductant in its own right. This has been attributed to electron transitions upon photoexcitation that induce metal-to-ligand charge transfer (MLCT).¹³ Recent work has demonstrated its capabilities in C-C bond activation,¹³ halogen abstraction,¹⁴ and ring expansion,¹⁵ among other reactions,¹⁶ within the homogeneous regime. Photocatalytic activity in these reactions often improves with introduction of a sensitizer,¹⁷ demonstrating a need to couple Ce(III) to photoactive species for efficient catalysis. In the heterogeneous catalysis regime, Ce(III) materials with atomic-level characterization are sparse; while the role of Ce(III) as part of CeO₂¹¹ and as a supported heterogeneous catalyst is known,¹⁸ few MOF materials are built from Ce(III) nodes,¹⁹⁻²² and only one has shown significant catalytic activity at the Ce nodes.²³ As with HHTP, more work is necessary to determine appropriate synthetic conditions and structure-property relationships to take full advantage of the redox ability of Ce(III).

Herein, we report the synthesis of **NU-1701**, a three-dimensional Ce(III)-based framework with HHTP linkers. We also examine its metal-centred charge transfer ability through density of state (DoS) calculations and catalytic dehydroxymethylation experiments. The work presented here applies DoS calculations to the **NU-1701** framework that contains both photoactive nodes and linkers. **NU-1701** is the first Ce-based MOF that does not have carboxylic acid linkers and is one of few three-dimensional catecholate frameworks. This study is also among the first instances wherein a Ce(III) hybrid material is modelled using DoS calculations.

The Ce-catecholate based MOF **NU-1701** (Fig. 1) was synthesized solvothermally *via* a combination of cerium acetate trihydrate and HHTP. Powder X-ray diffraction confirms that **NU-1701** is synthesized phase-pure (Fig. S1) as octahedral crystals (Fig. S2). The crystal structure, determined from X-ray diffraction, demonstrates a cubic *Fd-3m* framework with hexagonal cage pores (Figs. 2C and 2D). **NU-1701** shares its structure with other three-dimensional Ln-HHTP (Ln = La, Y, Nd)

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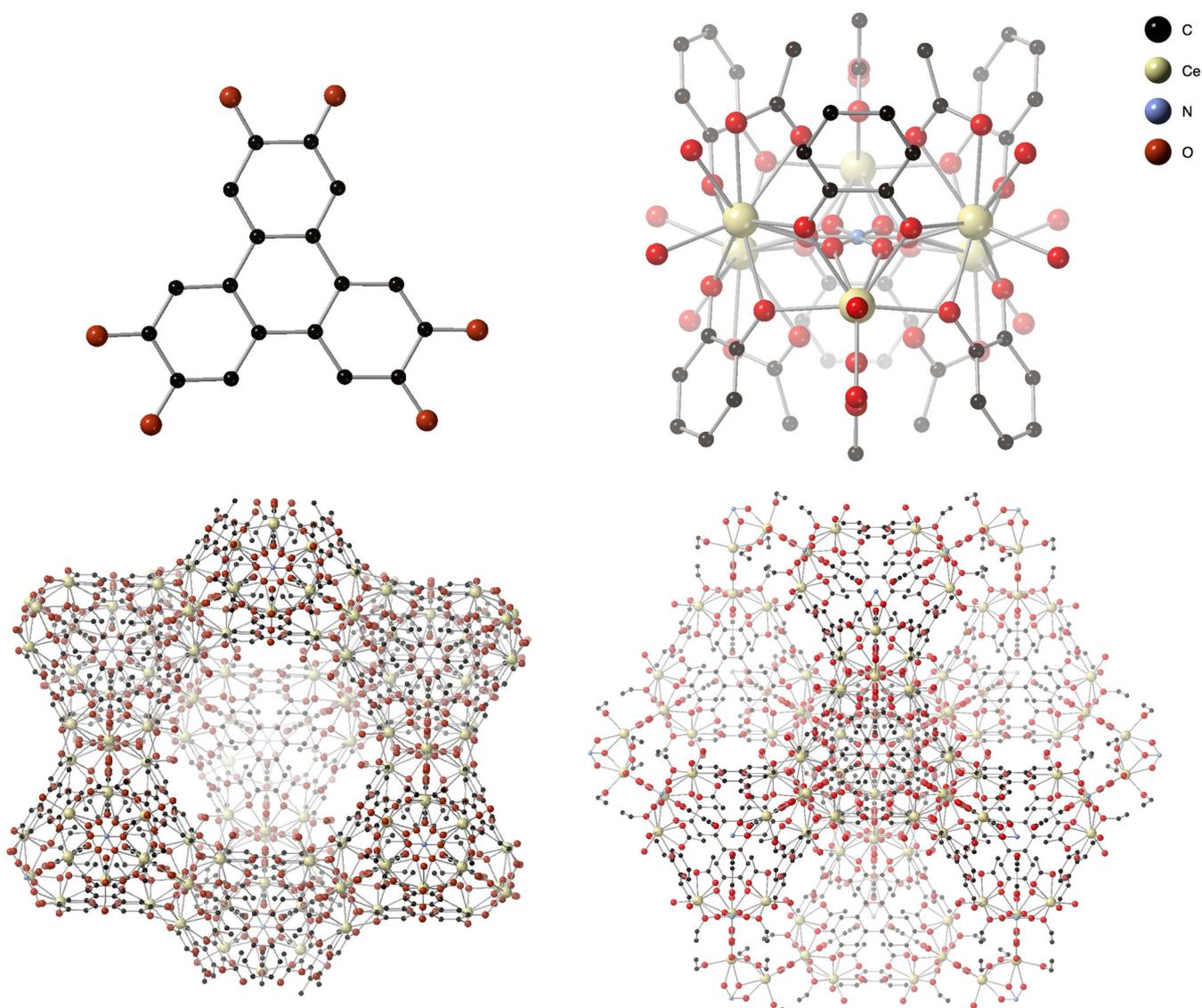


Figure 1. HHTP linker (top left), Node structure of **NU-1701** with alternating acetates and HHTP linkers (top right), A single cage of **NU-1701** (bottom left), **NU-1701**, showing multiple cages (bottom right). Carbon atoms are black, Ce atoms are yellow, N atoms are blue, and O atoms are red. H atoms omitted for clarity.

frameworks previously reported by Dinca *et al.*⁹ The nodes of **NU-1701** consist of a six-member ring of staggered cerium atoms (**Fig. 2B**), akin in shape to the chair conformation of cyclohexane. The HHTP linkers alternate between bridging two Ce atoms and chelating to a single Ce atom. A μ_6 -NO₃ moiety bridges the inside of the node, while disordered acetates, hydroxyls, and water molecules cap each cerium and provide charge balance. The nitrate anion is likely a product of dimethylimidazolidinone oxidation during synthesis. By ¹H nuclear magnetic resonance of base-digested **NU-1701** (**Fig. S3**), the acetate content was determined to be 1.2 acetates per node, suggesting that hydroxyls are the primary charge balancing molecules. This is further confirmed with thermogravimetric analysis, which shows a decrease in weight between 80 °C and 150 °C (**Fig. S4**) corresponding to lost water. The Type I/IV hybrid N₂ isotherm and pore size distributions we

obtained after activation *via* solvent exchange with supercritical-CO₂ show a modest internal surface area (BET = 90 m²/g), as well as pore sizes of approximately 13 Å (**Figs. S5 and S6**) with a pore volume of 0.11 cm³/g; **NU-1701** retains crystallinity after this gentle activation procedure (**Fig. S7**). While we attempted to determine the Ce-OH and Ce-OH₂ stretching frequencies via diffuse reflectance Fourier transform infrared spectroscopy, we observed broad signals in the characteristic -OH stretching vibration region (**Fig. S8**), limiting structural information regarding these functional groups. X-Ray photoelectron spectroscopy of Ce 3d demonstrates that all Ce atoms within **NU-1701** are Ce(III) (**Fig. S9**). The solid-state UV-Vis absorption spectrum of **NU-1701** is dominated by the HHTP linkers: absorbing light strongly in the entire visible light region but absorbing most strongly in the UV region (**Fig. S10**).

Encouraged by the three-dimensionality and strongly light-absorbing nature of **NU-1701**, we examined its electronic transition (MLCT/LMCT) ability by performing density of state (DoS) calculations and approximating the HOMO and LUMO of the Ce(III) node and catecholate linker. These calculations would thus serve as predictors of **NU-1701**'s catalytic performance. Similar calculations have previously been reported by Wu *et al.* to determine the favorability of LMCT within the M-UiO-66 series, of which Ce(IV)-UiO-66 is by far the most capable.²⁴ It should be noted that in Ce(IV)-UiO-66, LMCT is the predominant mode of electronic excitation, and MLCT is absent due to the lack of valence 4f electrons (Fig. S11).

According to the DoS plots (Figure 3), the valence band maxima (VBM) of **NU-1701** (shown in dark red) are composed of catecholate linker 2p orbitals. Conversely, the conduction band minima (CBM), (1.3 eV, orange box) are predominantly the 2p orbitals of the nitrogen atoms within the bridging nitrate (Figure 3). From this, we hypothesize that in **NU-1701**, energetically favorable electronic transitions can occur from linker 2p orbitals to nitrate 2p orbitals. However, in order to move electrons from HHTP to nitrate, the electrons must interact with the cerium atoms in the node, as these moieties are the only connection between HHTP and nitrate. It should also be noted that around 3 eV above the VBM and beyond, there are empty Ce(f) orbitals that significantly overlap with the empty 2p orbitals of the HHTP linker (shown in dark blue). From these

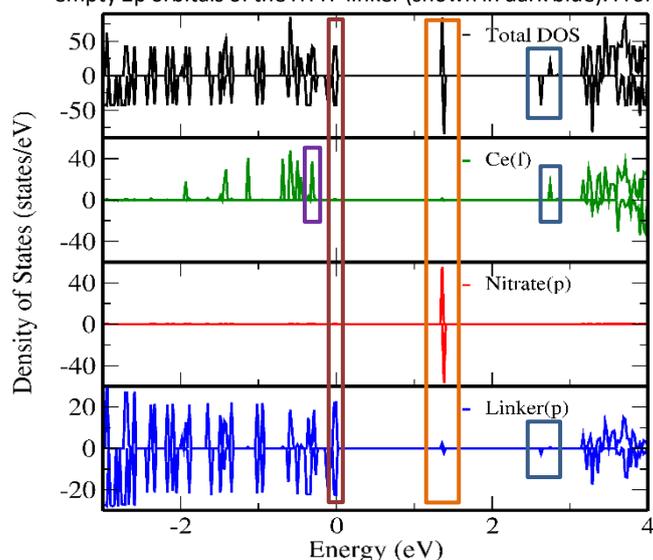


Figure 2. Density of state calculations for **NU-1701** (black), Ce within **NU-1701** (green), nitrate within **NU-1701** (red), and HHTP within **NU-1701** (blue). The purple box denotes occupied Ce(4f) orbitals (-0.2 eV). The dark red box denotes the VBM (approximately 0 eV). The orange rectangle denotes the CBM (1.3 eV). The dark blue rectangles signify empty conduction bands which has significant overlap between Ce(f) and empty HHTP orbitals, and the orange rectangles signify CBM states arising from nitrate 2p orbitals.

observations, we hypothesize a complex cycle of processes for electron transfer within **NU-1701**; these transitions are illustrated in Figure 4. Should the electron be excited in the linker (shown in blue box), it may travel to the Ce atoms of the node (as the empty Ce(4f)

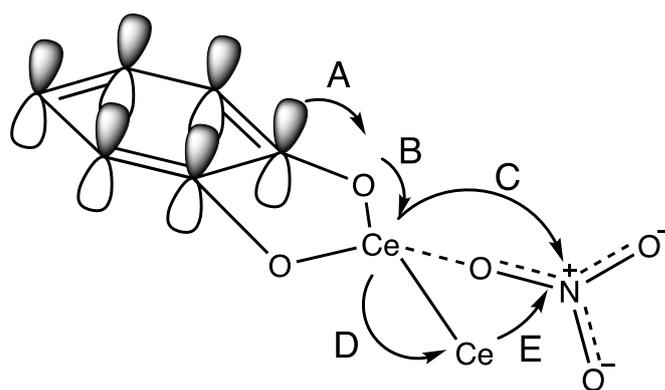


Figure 3. Illustration of electron transfer within a segment of **NU-1701**. **A.** Transfer from a phenyl group of HHTP to the oxygens. **B.** Transfer from HHTP to Ce. **C.** Direct transfer of Ce to the nitrate group. **D/E.** Transfer from a Ce atom to another Ce atom, followed by transfer to nitrate.

orbitals are very close to empty linker orbitals around the 3 eV range). The excited electrons from linker orbitals can further move to nitrate orbitals around 1.3 eV. Thus, electronic excitation from the linker can undergo both LMCT (linker to Ce) and ligand-to-ligand charge transfer (from linker to nitrate). Within ~0.2 eV below the VBM there are also significant contributions from occupied Ce 4f orbitals (shown in purple); electrons present within the Ce 4f orbitals may move to empty Ce 4f orbitals around and above 3 eV above the VBM followed by MLCT (Ce to HHTP) to empty linker 2p orbitals around 3 eV and eventually to nitrate 2p orbitals around 1.3 eV. The DoS plot in **NU-1701** clearly shows various competitive electronic transitions which in turn will slow down the electron transfer to a potential substrate during the photocatalysis reaction. Furthermore, unlike homogeneous Ce(III), which reportedly exhibits 4f → 5d electron transitions,¹³ the Ce(III) atoms of **NU-1701** demonstrate 4f → 4f transitions. This suggests that HHTP may cause Ce(III) to have more lanthanide-like character in a MOF regime.

As experimental verification, we examined **NU-1701** as a catalyst for the coupling of cyclohexanemethanol and diethylmalonate dehydroxylation (Figure 4).²⁵ Comparison of these results to homogeneous CeCl₃ reaction mixtures and other control reactions are in Table 1. We confirmed *via* PXRD that some crystallinity of **NU-1701** remains after reaction (Fig. S12).

Table 1. Catalytic dehydroxylation of cyclohexane and diethylmalonate by a cerium catalyst (reaction scheme below).

Catalyst (mol %)	Reaction Yield (%)
CeCl ₃ 5%	9% ± 2%
5% CeCl ₃ , 5% HHTP	7% ± 0%
5% NU-1701	12% ± 3%

NU-1701 shows a slight increase in conversion over its homogeneous components. HHTP within **NU-1701** may be

slightly photosensitizing Ce without completely blocking coordination (most likely present in the homogeneous mixture of CeCl₃ and HHTP). However, this increase is contingent upon the excited electrons of Ce passing through to HHTP and exclusively going to the substrate. Given the susceptibility of electrons to move through different pathways from the DoS studies, the lack of significant increase in catalytic yield between homogeneous cerium and **NU-1701** is unsurprising.

In this work we have synthesized a new Ce(III)-catecholate MOF **NU-1701**. **NU-1701** is a three-dimensional, porous catecholate MOF assembled from Ce₆ nodes (wherein the Ce atoms are bridged by a single nitrate) and HHTP linkers. HHTP makes significant contributions to the photochemistry of **NU-1701**. However, charge-transfer from Ce to HHTP does not dominate the energy landscape. Several electron-transfer processes compete following excitation of electrons in the framework, with relaxing to the nitrate group p-orbitals as a common endpoint. These observations are supported by dehydroxymethylation experiments, wherein **NU-1701** is slightly more catalytically active over its homogeneous counterparts due to a combination of inefficient charge transfer and the catalytic stability imparted by the framework. This work illustrates that while inclusion of both photoactive nodes and linkers within the same framework greatly complicates the energy landscape, and introduces competitive electron transitions, judicious choice of nodes and linkers can result in MOFs with improved photocatalytic performance. The computational aspects of this study are the first for Ce(III)-MOFs and catecholate-MOFs and future calculations will inform how to pair catecholates with metal species for photocatalysis.

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Conflicts of Interest

Omar K. Farha has a financial interest in NuMat Technologies, a company that seeks to commercialize MOFs.

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