

2-CEESO

Building a shp: A Rare-Earth Metal–Organic Framework and Its Application in a Catalytic Photooxidation Reaction

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Cite This: *Chem. Mater.* 2021, 33, 4163–4169





simulant, 2-chloroethyl ethyl sulfide (2-CEES), with Tb-CU-10 showing a half-life for conversion to the less toxic 2-chloroethyl ethyl sulfoxide (2-CEESO) of 3.5 min under O_2 and 22 min under air.

INTRODUCTION

Metal-organic frameworks (MOFs) are hybrid materials composed of metal ions or clusters interconnected by organic linkers, giving rise to open structures with accessible pores.¹⁻⁴ MOFs have been studied for many potential applications including, but not limited to, gas adsorption,^{5,6} catalysis,^{7,8} photocatalysis, ^{9,10} chemical sensing, ^{11,12} and wastewater remediation. ^{13–16} Rare-earth (RE) metals, which include scandium, yttrium, and the 15 lanthanoids, have been used to synthesize a diverse library of MOFs, including many with unique structures and properties driven by the high coordination numbers and geometries of RE-metals.¹⁷ Like other classes of MOFs, RE-MOFs have been reported with several different secondary building units (SBUs),²⁰ including inorganic nodes that are metal ions,^{21,22} chains,^{23–25} or clusters.^{5,26-29} In 2013, Eddaoudi et al. showed that the use of fluorinated modulators, such as 2-fluorobenzoic acid, favors the formation of RE-cluster nodes instead of the ion or chain nodes that tend to preferentially form in the presence of carboxylic acid linkers.¹⁸ This includes RE-cluster nodes with high nuclearity and connectivity, giving rise to MOFs with complex and intricate topologies, some of which are likely to be inaccessible with other metals. $^{29-32}$ In one example, a MOF with an shp topology, named RE-shp-MOF-1 (RE = Y(III)) and Tb(III)), was reported,33 representing one of the four edge transitive (4,12)-c nets where a double six-membered ring (d6R) building block acts as a 12-connected (12-c) node. RE-shp-MOF-1 is composed of square, tetratopic porphyrinbased linkers (5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin; H₄TCPP) and 12-connected nonanuclear Y(III)-cluster nodes, giving a structure with 1D triangular channels. In another example, RE-shp-MOF-5 was reported, composed of 12-c nonanuclear RE(III)-cluster nodes and rectangular 1,2,4,5-

time that the 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H_4TBAPy) linker is

integrated in the **shp** topology. RE-CU-10 is explored as a heterogeneous photocatalyst for the selective oxidation and detoxification of a sulfur mustard

tetrakis(4-carboxyphenyl)benzene (BTEB) linkers.³⁵ The same 12-connected nonanuclear RE(III)-cluster was used as a building block in the synthesis of RE-**pek**-MOF-1 (RE = Y(III) and Tb(III)), RE-**aea**-MOF-1 (RE = Y(III)),³⁶ Eu(III)-based PCN-905-SO₂ and PCN-906-O,³⁷ and in the recently reported RE-**htp**-MOF-1 (RE = Y(III), Ho(III), and Er-(III)).³⁸

D_{6h} SBU

shp (12-c,4-c)

In this work, we report the synthesis of a new RE-MOF, RE-CU-10 (RE = Y(III) and Tb(III); CU, Concordia University), with shp topology, composed of nonanuclear RE(III)-cluster nodes and a rectangular tetratopic pyrene-based linker, 1,3,6,8tetrakis(p-benzoic acid)pyrene (H₄TBAPy) (Figure 1). The shp topology has not yet been reported for a MOF composed of tetratopic H₄TBAPy linkers since the use of this linker tends to favor the formation of scu and csq topologies driven by the formation of eight-connected hexanuclear cluster nodes (NU-901 (scu, Zr_6 -cluster),^{39,40} Ce-CAU-24 (scu, Ce₆-cluster),⁴¹ or NU-1000 (csq, Zr₆-cluster or Ce₆-cluster)).^{41,42} Finally, RE-CU-10, with a high density of pyrene chromophores, ~11 Å channels, and high porosity, is applied for the photocatalytic oxidation and detoxification of a sulfur mustard simulant, 2chloroethyl ethyl sulfide (2-CEES), demonstrating performance under O2 and air that is comparable to the best MOF catalysts reported for this application.

 Received:
 March 15, 2021

 Revised:
 May 11, 2021

 Published:
 May 27, 2021







Figure 1. Structure of RE-CU-10 showing the RE_9 -cluster node and 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene linker.

RESULTS AND DISCUSSION

The combination of the tetratopic linker H₄TBAPy with Y(III), or Tb(III) in the presence of 2-fluorobenzoic acid (2-HFBA), under solvothermal conditions in DMF, yields the MOF RE-CU-10. Single-crystal X-ray diffraction (SCXRD) shows that RE-CU-10 crystallizes in the trigonal space group $P\overline{3}m1$ and is composed of a nonanuclear RE-cluster, which appears as a RE₁₈-cluster due to disorder (Figures S1 and S2). Analogous disorder of the nonanuclear RE-cluster has been observed in other RE-MOFs, including Y-shp-MOF-1,³³ Y-shp-MOF-5,³⁵ Y-kce-MOF-1,⁴³ and Y-ken-MOF-1.³⁸ A similar phenomenon was also observed in the metal cluster of PCN-223, a Zr_6 -based MOF composed of H_4TCPP linkers with shp topology, where the hexanuclear Zr(IV)-cluster is disordered over three positions, appearing as a Zr₁₈-cluster.⁴⁴ In a different interpretation by Farha et al., the disordered Zr₁₈-cluster in NU-904 (scu topology) was found to be caused by merohedral twinning in the structure where three scu nets overlap, giving sixfold symmetry and the appearance of an shp net.⁴⁵ It should be noted that the scanning electron microscopy (SEM) images taken from NU-904 show prolate spheroid-shaped particles, indicative of the scu topology and different from the hexagonal-shaped particles expected to be observed for MOFs with the shp topology.^{46,47} Based on SEM images (Figure 2a,c), ¹H-NMR spectroscopy (Figures S3 and S4), and thermogravimetric analysis (TGA) (Figure S5), we conclude that RE-CU-10 possesses the shp topology with an experimental chemical formula for Y-CU-10 of DMA₃[Y₉(μ_3 - $OH)_{12}(\mu_3-O)_2(TBAPy)_3(2-FBA)_2]$ ·2DMF and for Tb-CU-10 of DMA₃[Tb₉(μ_3 -OH)₁₂(μ_3 -O)₂(TBAPy)₃(2-FBA)₂]·(DMF)-(2-HFBA). Although not all of the bridging hydroxyl and/or oxo ligands could be assigned by SCXRD due to the level of disorder in the structure, the cluster possesses similar



Figure 2. Scanning electron microscopy (SEM) images of microcrystalline samples of Y-CU-10 (mean size, 89 μ m) (a) and Tb-CU-10 (mean size, 90 μ m) (c). Optical microscopy images of single crystals of Y-CU-10 (mean size, 152 μ m) (b) and Tb-CU-10 (mean size, 226 μ m) (d).

connectivity and spatial arrangement of RE-metals as the nonanuclear cluster reported in Y-shp-MOF-1³³ and pek-MOF-1.³⁶ Each individual nonanuclear RE(III)-cluster is coordinated by 12 crystallographically independent TBAPy4linkers, giving a 12-connected (12-c) node. All carboxylates coordinated to the cluster bridge adjacent RE atoms and arrange to form a d6R hexagonal prism (Figure 1). Structural and topological analysis of the resulting structure show the formation of a (4,12)-c MOF, building a net with the shp topology (Figure 1 and Figures S6-S10). The carboxylphenyl groups in RE-CU-10 are rotated from the plane of the pyrene core, showing a dihedral angle of \sim 58°. This angle is similar or inferior in magnitude compared to other shp MOFs made with different tetratopic linkers and nonanuclear RE(III)-clusters $(\sim 59^{\circ} \text{ Y-shp-MOF-5}^{35} \text{ and } \sim 68^{\circ} \text{ for RE-shp-MOF-1})^{33}$ and also similar to a dihedral angle of $\sim 60^{\circ}$ found for the same linker in NU-1000 (csq topology).⁴⁸ This highlights the diversity of topologies that can be made with RE(III)-cluster nodes owing, in part, to the existence and stability of high nuclearity clusters with somewhat flexible coordination geometries. The crystalline structure features one-dimensional triangular channels along the *c* axis of 10 Å in diameter and 9 Å hexagonal-prismatic cages enclosed by six linkers and two metal clusters (Figures S6 and S7).

Bulk microcrystalline samples of RE-CU-10 (Figure 2) were synthesized, and the phase purity of the product was confirmed by powder X-ray diffraction (PXRD) (Figure 3a). N₂ adsorption analysis shows a reversible type I isotherm with calculated BET surface areas (pore diameter) of 1800 m² g⁻¹ (11 Å) and 1780 m² g⁻¹ (11 Å) for Y- and Tb-CU-10, respectively (Figure 3b and Figure S11), after activation under vacuum at 120 °C. Although we would expect Tb-CU-10 to have a lower gravimetric surface area than Y-CU-10, factors such as activation and the presence of structural defects (i.e., missing linkers or missing nodes) can contribute to the gravimetric surface areas being more similar. SEM shows the



Figure 3. (a) Calculated PXRD pattern of RE-CU-10 obtained from the Y-CU-10 SCXRD data and experimental PXRD patterns of bulk Y- and Tb-CU-10. (b) Nitrogen adsorption-desorption isotherms of RE-CU-10 (inset: pore size distribution plots).

characteristic hexagonal-prismatic microcrystals derived from the trigonal space group and as expected for a MOF with the shp topology (Figure 2a,c). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) shows the expected absorption bands from the symmetric and asymmetric carboxylate stretching (Figure S12) as well as O-H stretching bands corresponding to μ_3 -OH ligands in the nonanuclear RE(III)-cluster node. Thermogravimetric analysis (TGA) of activated samples of RE-CU-10 under air (Figure S5) shows that decomposition occurs at 450 °C, comparable to other RE-cluster-based MOFs.^{33,35} Variable temperature PXRD (VT-PXRD) analysis performed up to 305°C (the limit of the instrumentation used) shows that RE-CU-10 remains stable to 305 °C (Figure S13) without any indication of amorphization or phase transformations occurring in this temperature range. ¹H-NMR spectroscopy of digested samples of RE-CU-10 shows the presence of the TBAPy⁴⁻ linker, DMF, and 2-FBA modulator (Figures S3 and S4).

Given that RE-CU-10 has a high density of pyrene chromophores (three pyrene linkers per RE_9 -node, see Table S1 for more details) coupled with 11 Å channels that can aid in diffusion of reactants and products, we expected the MOF to perform well in the selective photooxidation of the sulfur mustard simulant 2-CEES to 2-CEESO (Figure 4a). Sulfur mustard is a chemical warfare agent that was used for the first time during WWI. Unfortunately, it is still a potential threat to public health today due to its stockpiling and potential production from nations that have not signed or followed



Time (min)

Figure 4. (a) Conversion of 2-CEES to 2-CEESO using RE-CU-10 as a catalyst under UV-LED irradiation and (b) conversion vs time for the selective oxidation of 2-CEES by Tb-CU-10 under O_2 saturation, as determined by GC-FID analysis.

ratifications of the Chemical Weapons Convention treaty (CWC).⁴⁹ Sulfur mustard is a very reactive alkylating agent that causes failure of cellular functions,⁵⁰ presenting as a strong blistering agent that causes acute and chronic injuries to the skin, eyes, and respiratory system.^{51,52} Sulfur mustard accumulated in facilities or present at inadequate disposal sites must be destroyed in an efficient and controlled manner, and one method to safely detoxify the compound involves selective oxidation to its less toxic sulfoxide derivative.

In 2015, Farh *et al.* demonstrated that the sulfur mustard simulant, 2-CEES, could be selectively oxidized and detoxified to the less toxic 2-chloroethyl ethyl sulfoxide (2-CEESO) by using the MOF PCN-222/MOF-545 as a photosensitizer to generate singlet oxygen under LED irradiation.⁵³ The group has since studied several different pyrene-containing MOFs for the degradation of 2-CEES and sulfur mustard, including NU-1000 (**csq**),^{54,55} postsynthetically modified NU-1000 (**csq**),^{56,57} and NU-400 (**fcu**).⁵⁸ These materials are composed of hexanuclear Zr(IV)-cluster nodes and tetratopic or ditopic pyrene-based linkers in NU-1000 and NU-400, respectively. In all cases, the linker behaves as a photosensitizer for the generation of singlet oxygen, under LED irradiation, which subsequently selectively oxidizes 2-CEES.

Activated samples of Y- and Tb-CU-10 were suspended in methanol and purged with oxygen for 20 min. 2-CEES and the internal standard, mesitylene, were added, and the mixture was excited using a UV LED photoreactor ($\lambda_{max} = 400-410$ nm; Figure S14, see details in the Supporting Information). Under

optimized conditions, using 3.6 mg (0.99 μ mol, 0.5 mol %) or 4.1 mg (0.95 µmol, 0.5 mol %) of Y- and Tb-CU-10 as a catalyst, respectively, 2-CEES can be completely and selectively oxidized to 2-CEESO within 15.0 min (half-life 5.0 min) and 12.5 min (half-life 3.5 min) for Y- and Tb-CU-10, respectively (Figure 4b). Gas chromatography-flame ionization detector (GC-FID) analysis, ¹H-NMR spectroscopy, ¹³C-NMR spectroscopy, and high-resolution-mass spectrometry (HR-MS) of the supernatant indicate that no sulfone product was formed during the process (Figures S15–S22 and Tables S2–S6). The half-life for the selective oxidation of 2-CEES by Y- and Tb-CU-10 is shorter than those reported for NU-1000 (6.2 min half-life, 0.5 mol %)⁵⁴ and NU-400 (10.2 min half-life, 1 mol %)⁵⁸ under O₂ saturation. The outstanding photocatalytic performance of RE-CU-10 is attributed to the balance between the porosity, high pyrene density, and pore aperture size (Table S1), a balance offered by the **shp** topology. It should be noted that the heavier atomic mass of Tb (158.93 u) compared to Y (88.91 u) and Zr (91.22 u) may also play a role in the efficiency of singlet oxygen production via stabilization of the spin-forbidden pyrene triplet state through the heavy atom effect.⁵⁹ Alternatively, there is the potential for energy transfer in Tb-CU-10 since Tb(III) has sharp emission bands (491, 547, 588, and 624 nm),⁶⁰ some of which overlap with the absorption bands of pyrene and could thus enhance light harvesting and singlet oxygen production (Figure S14).

The recyclability of Y-CU-10 (Figure S23a) and Tb-CU-10 (Figure 5a) was demonstrated by completing three successive reactions, where in between each run, the MOF was isolated



Figure 5. (a) Reusability of the catalyst Tb-CU-10 over three successive photocatalytic oxidations of 2-CEES under $O_{2(g)}$ saturation. (b) PXRD analysis of Tb-CU-10 after three photocatalytic reactions.

and washed with fresh methanol before being reused (see the Supporting Information for details). The increase in time from 12.5 to 30 min that is required to achieve 100% conversion in subsequent cycles can be attributed to the unavoidable loss of the catalyst after isolation and washing since negligible degradation of the MOFs is observed, as confirmed by PXRD (Figure 5b and Figure S23b), N₂ sorption isotherms (Figure S24), and inductively coupled plasma–mass spectrometry (ICP-MS) (Figure S25 and Table S7).

To assess the activity of RE-CU-10 under conditions that may be more amenable to real-world applications, the photooxidation of 2-CEES was also evaluated under air. Using the same catalyst loading of 0.5 mol %, 2-CEES was converted to 2-CEESO under air with half-lives of 21 and 22 min for Y- and Tb-CU-10, respectively (Figure S26a,b and Tables S8 and S9), with full conversions occurring at 70 and 120 min, respectively. PXRD patterns of the recovered catalyst (Figure S26c.d) show that the overall structure of RE-CU-10 is maintained, but Tb-CU-10 undergoes an observable loss of crystallinity. ICP-MS was used to confirm that 12 mol % Y-CU-10 and Tb-CU-10 was degraded over the 120 min reaction, compared to only 2-3 mol % degradation observed under O_2 (Table S7). It is important to note that this loss of crystallinity and degradation is not observed for either MOF over three subsequent reaction cycles under O_2 (75 min total) and is also not observed when the MOF is suspended in MeOH and purged with air for 120 min (Figure S27), suggesting that the washing steps in between catalytic cycles and availability of O₂ may contribute to mitigating degradation of RE-CU-10.

CONCLUSIONS

The ability of rare-earth metals to form high nuclearity clusters, coupled with their versatile coordination numbers and geometries, allows for the synthesis of structures that are not as easily accessible with *d*-block metals. In this report, the nonanuclear RE(III)-cluster, which acts as a d6R node, enables the synthesis of RE-CU-10, a MOF with the shp topology composed of TBAPy⁴⁻ linkers, a linker that has not yet been observed in the **shp** topology.^{61,62} RE-CU-10 demonstrates permanent porosity, with surface areas of 1780-1800 m² g⁻¹ and thermal stability in air up to 450 °C. In addition, the high density of pyrene chromophores along with the microporosity of RE-CU-10 allows for the fast and selective photocatalytic oxidation and detoxification of a sulfur mustard simulant, 2-CEES, at low catalytic loadings (0.5 mol %), with a conversion half-life of only 3.5 min under O2 (Tb-CU-10) and 21 min under air (Y-CU-10). These promising reaction kinetics, coupled with the wide range of topologies that can be accessed using RE-metals, demonstrate the potential of RE-MOFs as photocatalysts for the selective oxidation and detoxification of 2-CEES.

EXPERIMENTAL SECTION

Synthesis of Y-CU-10. Single crystals of Y-CU-10 were obtained solvothermally in a 4 dram vial containing H₄TBAPy (13.8 mg, 0.02 mmol), $Y(NO_3)_3$ ·xH₂O (31.6 mg, 0.08 mmol of assuming hexahydrate), and 2-fluorobenzoic acid (1261.0 mg, 9.0 mmol), suspended in 7.0 mL of DMF, 0.576 mL (0.032 mol) of distilled water, and 1.6 mL (0.028 mol) of glacial acetic acid. The vial was sealed, and the suspension was sonicated for 10 min and placed into a preheated oven at 120 °C for 72 h. Yellow single crystals were separated by centrifugation, washed three times with fresh DMF over

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Crystal structures of Y-CU-10 and Tb-CU-10 were deposited at the Cambridge Crystallographic Data Centre (CCDC) (deposition numbers 1998090-1998091).

ACKNOWLEDGMENTS

V.Q.-N. thanks Concordia University for the Anne Harper Pallen Entrance Scholarship, the Concordia International Tuition Award of Excellence, and the Howarth and Majewski research group members for offering a friendly and supportive research environment. V.Q.-N. also thanks Prof. Majewski for helpful discussion regarding organic synthesis, and photochemical characterization techniques. V.Q.-N. and A.J.H. thank Prof. Tomislav Friščić for access to PXRD and SCXRD facilities, Petr Fiurasek (Centre Québécois sur les Matériaux Fonctionnels) for help with TGA, Prof. Yves Gélinas for access to and help with GC-FID measurements, and Dr. David Polcari (Systems for Research) for access to the Phenom benchtop SEM instrument. We thank Dr. Heng Jiang from Concordia's Centre for Biological Applications of Mass Spectrometry for ICP-MS and HR-MS analysis. We acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC) [funding reference number: DGECR-2018-00344] and Cette recherche a été financée par le Conseil de recherches en sciences naturelles et en génie du Canada (CRSNG) [numéro de reference: DGECR-2018-00344]. All structural figures were made using VESTA 3.63

ABBREVIATIONS

MOFs, metal-organic frameworks; RE, rare-earth; 2-CEES, 2chloroethyl ethyl sulfide; 2-CEESO, 2-chloroethyl ethyl sulfoxide; H₄TBAPy, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene; SCXRD, single-crystal X-ray diffraction; PXRD, powder X-ray diffraction; VTPXRD, variable temperature powder X-ray diffraction; BET, Brunauer-Emmett-Teller

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the course of 24 h, and later three times with fresh acetone over the course of 24 h. The material was air-dried and then activated at 120 $^{\circ}$ C for 24 h under ultralow vacuum. Yield (activated material): 70%.

Synthesis of Tb-CU-10. Single crystals were obtained solvothermally in a 4 dram vial containing H_4 TBAPy (6.1 mg, 0.0089 mmol), Tb(NO₃)·xH₂O (15.5 mg, 0.036 mmol of assuming pentahydrate), and 2-fluorobenzoic acid (561.1 mg, 4.0 mmol), suspended in 3.1 mL of DMF and 0.713 mL of glacial acetic acid (0.012 mol). The vial was sealed, and the suspension was sonicated for 10 min and placed into a preheated oven at 120 °C for 72 h. Yellow single crystals were separated by centrifugation, washed three times with fresh DMF over the course of 24 h, and later three times with fresh acetone over the course of 24 h. The material was air-dried and then activated at 120 °C for 24 h under ultralow vacuum. Yield (activated material): 35%.

Photooxidation under O₂ Saturation. Activated RE-CU-10 (RE = Y (3.6 mg, 0.99 μ mol, 0.5 mol %) or Tb (4.1 mg, 0.95 μ mol, 0.5 mol %)) was suspended in 1 mL of methanol in a 17 × 83 mm microwave vial and gently ground using a glass rod. The vial was capped and purged with O₂ for 20 min, and then 2-CEES (23 μ L, 0.2 mmol) and mesitylene (internal standard, 10 μ L) were added. The vial was placed in the center of the LED reactor described in the instrumentation section. Conversion of 2-CEES was calculated relative to the internal standard by gas chromatography (GC-FID).

Photooxidation under Air Saturation. Activated RE-CU-10 (RE = Y (3.3 mg, 0.91 μ mol, 0.5 mol %) or Tb (4.3 mg, 0.99 μ mol, 0.5 mol %)) was suspended in 1 mL of methanol in a 17 × 83 mm microwave vial and gently ground using a glass rod. The vial was capped and purged with air for 20 min, and then 2-CEES (23 μ L, 0.2 mmol) and mesitylene (internal standard, 10 μ L) were added. The vial was placed in the center of the LED reactor described in the instrumentation section. Conversion of 2-CEES was calculated relative to the internal standard by gas chromatography (GC-FID).

Photocatalyst (MOF) Recyclability. The ability to recycle and reuse the MOF photocatalysts was studied by suspending activated RE-CU-10 (RE = Y (3.4 mg, 0.94 μ mol, 0.5 mol %) or Tb (4.3 mg, 0.99 μ mol, 0.5 mol %)) in 1 mL of methanol in a 17 \times 83 mm microwave vial, and the catalyst was ground using a glass rod. The vial was capped and purged with O_2 for 20 min, and then 2-CEES (23 μ L, 0.2 mmol) and mesitylene (internal standard, 10 μ L) were added. The vial was placed in the center of the LED reactor described in the instrumentation section. Conversion of 2-CEES was calculated relative to the internal standard by gas chromatography (GC-FID). Once the reaction reached a conversion of 100%, the catalyst was isolated by centrifugation (7500 rpm \times 5 min), washed three times with fresh methanol (2 mL, 7500 rpm \times 5 min), and suspended in 1 mL of methanol. The suspension was purged with O₂ for 20 min, and then 2-CEES (23 µL, 0.2 mmol) and mesitylene (internal standard, 10 μ L) were added to repeat the photocatalytic reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.1c00917.

Instrumentation details, experimental procedures, calculations, gas chromatograms, additional structural figures, and single-crystal X-ray diffraction (PDF)

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