Building a Shp: A New Rare-Earth Metal-Organic Framework and Its Application in a Catalytic Photo-Oxidation Reaction

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The design and synthesis of new metal-organic frameworks (MOFs) is important from both a fundamental and application standpoint. In this work, a novel, highly-connected rare-earth (RE) MOF with shp topology is reported, named RE-CU-10 (RE = rare-earth, CU = Concordia University), comprised of nonanuclear RE(III)-cluster nodes and tetratopic pyrene-based linkers. This represents the first time that the 1,3,6,8-tetrakis(p-benzoic acid)pyrene (H4TBAPy) linker is integrated in the shp topology. Y-CU-10 was explored as a heterogeneous photocatalyst for the selective oxidation and detoxification of a sulfur mustard simulant, 2-chloroethyl ethyl sulfide (2-CEES), showing a halflife for conversion to the less toxic 2-chloroethyl ethyl sulfoxide (2-CEESO) of 6.0 min.

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Building a shp: A New Rare-Earth Metal–Organic Framework and its Application in a Catalytic Photo-oxidation Reaction

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Abstract: The design and synthesis of new metal–organic frameworks (MOFs) is important from both a fundamental and application standpoint. In this work, a novel, highly-connected rare-earth (RE) MOF with **shp** topology is reported, named RE-CU-10 (RE = rare-earth, CU = Concordia University), comprised of nonanuclear RE(III)-cluster nodes and tetratopic pyrene-based linkers. This represents the first time that the 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H₄TBAPy) linker is integrated in the **shp** topology. Y-CU-10 was explored as a heterogeneous photocatalyst for the selective oxidation and detoxification of a sulfur mustard simulant, 2-chloroethyl ethyl sulfide (2-CEES), showing a half-life for conversion to the less toxic 2-chloroethyl ethyl sulfoxide (2-CEESO) of 6.0 min.

Introduction

Metal–organic frameworks (MOFs) are hybrid materials comprised 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 fifteen lanthanides, 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.^{17–20} Like other classes of MOFs, RE-MOFs have been reported with several different secondary building units (SBUs), 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 **shp** topology, named RE-**shp**-MOF-1 (RE = Y(III), and Tb(III)) was reported,³³ representing one of two edge transitive (4,12)-c nets where a double six-membered ring (d6R) building block acts as a 12-connected (12-c) node.³⁴ RE-**shp**-MOF-1 is comprised of square, tetratopic porphyrin-based 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, comprised of 12-c nonanuclear RE(III)-cluster nodes and rectangular 1,2,4,5-tetrakis(4-

carboxyphenyl)benzene (BTB) linkers. 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)), and RE-**aea**-MOF-1 (RE = Y(III)), when combined with tritopic linkers.³⁵

In this work, we report the synthesis of a new RE-MOF, RE-CU-10 (RE = Y(III), Tb(III), CU = Concordia University), with **shp** topology, comprised of nonanuclear RE(III)-cluster nodes and rectangular tetratopic pyrene-based linkers, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H₄TBAPy) (Figure 1). The **shp** topology has not yet been reported for a MOF comprised of tetratopic H₄TBAPy linkers, since the use of this linker tends to favor the formation of **scu**, and **csq** topologies driving the formation of 8-connected hexanuclear cluster nodes (NU-901 (**scu**, Zr₆-cluster),^{36,37} Ce-CAU-24 (**scu**, Ce₆-cluster)³⁸, or NU-1000 (**csq**, Zr₆-cluster or Ce₆-cluster)).^{38,39} Finally, RE-CU-10, with a high density of pyrene chromophores, ~13 Å channels, and high porosity is applied for the photocatalytic oxidation and detoxification of a sulfur mustard simulant, 2-chloroethyl ethyl sulfide (2-CEES).

Results and Discussion

The combination of the tetratopic linker H₄TBAPy with Y(III), or Tb(III) in the presence of 2-fluorobenzoic acid (2-FBA) 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* $\bar{3}$ m1, comprised of a nonanuclear cluster, which appears as a RE₁₈ cluster due to disorder (Figure S1 and S2). A similar phenomenon was observed in the metal cluster of PCN-223, a

Figure 1. Structure of RE-CU-10, showing the RE₉-cluster node and 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene linker.

Zr₆-based MOF comprised of H₄TCPP linkers with **shp** topology, where the hexanuclear Zr(IV)-cluster was disordered over three positions, appearing as a Zr₁₈-cluster.⁴⁰ 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 six-fold symmetry and the appearance of an **shp** net.⁴¹ It should be noted that the scanning electron microscopy (SEM) images taken of 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 **shp** topology.⁴² Based on SEM images (Figure 2), ¹H-NMR spectroscopy (Figure S3 and S4) and thermogravimetric analysis (TGA) (Figure S5) of RE-CU-10, we conclude that the experimental chemical formula for Y-CU-10 is DMA₃[Y₉(μ₃-OH)₁₂(μ₃-O)₂(TBAPy)₃(2-FBA)₂].2DMF and for Tb-CU-10 is DMA₃[Tb₉(μ₃-OH)₁₂(μ₃-O)₂(TBAPy)₃(2-FBA)₂].(DMF)(2-FBA), confirming the presence of a nonanuclear RE(III)-cluster node, and **shp** topology. Although not all of the bridging hydroxy and/or oxo ligands could be assigned by SCXRD due to the level of disorder in the structure, the cluster possesses similar connectivity and spatial arrangement of RE-metals as the nonanuclear cluster reported in Y-**shp**-MOF-1³³ and pek-MOF-1.³⁵ Each individual nonanuclear RE(III)-cluster is coordinated by twelve crystallographically independent TBAPy linkers, 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 shows the formation of a (4,12)-c MOF, building a net with **shp** topology (Figure 1, Figures S6-S10). The carboxylphenyl groups in RE-CU-10 are rotated from

the plane of the pyrene core, showing a dihedral angle of ~58°. This angle is similar or inferior in magnitude compared to other **shp** MOFs made with different tetratopic linkers and nonanuclear RE(III)-clusters (~59° Y-**shp**-MOF-5,⁴³ ~68° for RE-**shp**-MOF-1),³³ and also similar to the dihedral angle of ~60° found for the same linker in NU-1000 (**csq** topology).⁴⁴ 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 structure features one-dimensional triangular channels along the “c” axis of 13 Å in diameter, and 12 Å hexagonal-prismatic cages enclosed by six linkers and two metal clusters (Figure S7 and S8.).

Figure 2. Scanning electron microscopy (SEM) (a, c) and optical microscopy (b, d) images of bulk microcrystalline samples of Y-CU-10 (a, b) and Tb-CU-10 (c, d).

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 showed a reversible type-1 isotherm with a calculated BET surface area (pore diameter) of 1750 m²g⁻¹ (11 Å), and 1780 m²g⁻¹ (11 Å) for Y-, and Tb-CU-10, respectively (Figure 3b, Figure S11), after activation under vacuum at 120 °C. Scanning electron microscopy shows the characteristic hexagonal-prismatic microcrystals derived from the trigonal space group, and as expected for a MOF with **shp** topology. 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 μ₃-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 RE-CU-10 is stable up to 450 °C, comparable to other RE-cluster-based MOFs.^{33,43} ¹H-NMR spectroscopy of digested

samples of RE-CU-10 shows the presence of the TBAPy linker, DMF and 2-FBA modulator (Figure S3 and S4).

Figure 3. (a) Simulated and experimental PXRD patterns of RE-CU-10, and (b) nitrogen adsorption-desorption isotherms of RE-CU-10 (inset: pore size distribution plots)

Given that RE-CU-10 has a moderate density of pyrene chromophores (3 pyrene linkers per RE₉-node) coupled with 13 Å channels that can aid in diffusion of reactants and products, we expected the MOF to perform well in the selective oxidation of the sulfur mustard simulant 2-CEES to 2-CEESO. Sulfur mustard is a chemical warfare agent that was used for the first time during WWI. Unfortunately it is still a potential threat for public health today, due to its stockpiling and potential production from nations that have not signed or followed ratification of the Chemical Weapons Convention treaty (CWC).⁴⁵ Sulfur mustard is a very reactive alkylating agent which causes the failure of cellular functions,⁴⁶ presenting as a strong blistering agent that causes acute and chronic injuries to the skin, eyes and respiratory system.^{47,48} Sulfur mustard accumulated in facilities or present in 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 nontoxic sulfoxide derivative.

In 2015, Hupp, Farha *et al.* demonstrated that the sulfur mustard simulant, 2-CEES could be selectively oxidized and detoxified to the less toxic 2-CEESO, by using the MOF PCN-

222/MOF-545 as a photosensitizer to generate singlet oxidation under LED irradiation.⁴⁹ The group has since studied several different pyrene-containing MOFs for the degradation of 2-CEES and sulfur mustard, including NU-1000 (**csq**)^{50,51}, postsynthetically modified NU-1000 (**csq**)^{52,53} and NU-400 (**fcu**).⁵⁴ These materials are comprised 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-CU-10 were suspended in methanol in a microwave vial and purged with oxygen for 30 minutes. 2-CEES and the internal standard, mesitylene, were added and the mixture was excited using a UV LED photoreactor ($\lambda_{\text{max}} = 390\text{--}400$, see details in SI). Under optimized conditions, using 0.9 mol% of Y-CU-10 as a catalyst (1.728 μmol), CEES can be completely selectively oxidized to CEESO within 15 min (half-life 6.0 min) (Figure 4b). GC-FID analysis indicates that no sulfone product was formed during the process. The half-life for the selective oxidation of 2-CEES by Y-CU-10 is comparable to that reported for NU-1000 (6.2 min half-life), a MOF with fewer pyrene chromophores per node (2 pyrene linkers per Zr₆-node) but larger 30 Å channels. This result demonstrates the trade-off between higher pyrene chromophore density vs. pore aperture size.

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

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 **shp** topology comprised of TBAPy linkers – a linker that has not yet been observed in the **shp** topology. RE-CU-10 demonstrates permanent porosity, with surface areas of 1750–1780 m²/g, and thermal stability in air up to 450 °C. In addition, the moderate density of pyrene chromophores per mole along with the microporosity of Y-CU-10, allows for the moderately fast, and selective photocatalytic oxidation and detoxification of a sulfur mustard simulant, 2-CEES, at low catalytic loadings (0.9 mol%), with a conversion half-life of only 6 min.

Conflicts of interest

There are no conflicts to declare.

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Supplementary information

S.1 Materials

All solvents and reagents were purchased from commercial sources. *N,N'*-dimethylformamide (DMF), acetone, tetrahydrofuran, methanol, and glacial acetic acid were purchased from Fisher Scientific (Fisher Chemical). 1,4-dioxane, 2-fluorobenzoic acid, $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, and $\text{Tb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ were purchased from Alfa Aesar. 2-chloroethyl ethyl sulfide was purchased from Sigma Aldrich. 1,3,6,8-tetrabromopyrene was purchased from TCI America. 4-methoxycarbonylphenylboronic acid, potassium phosphate tribasic, mesitylene and tetrakis(triphenylphosphine)palladium (0) were purchased from Acros Organics. NMR solvents D_2SO_4 and DMSO-d_6 were purchased from Sigma Aldrich. All solvents and chemicals were used without further treatment.

S.2 Instrumentation

Single crystal X-ray diffraction (SCXRD) data were measured on a Bruker D8 Venture diffractometer equipped with a Photon 200 area detector, and $I\mu\text{S}$ microfocus X-ray source (Bruker AXS, $\text{CuK}\alpha$ source). All measurements were carried out at room temperature for Tb-CU-10, while Y-CU-10 was measured at 150(2) K on crystals coated with a thin layer of amorphous oil to decrease crystal deterioration, structural disorder, or any related thermal motion effects and to improve the accuracy of the structural results. Structure solution was carried out using the SHELXTL package from Bruker.¹ The parameters were refined for all data by full-matrix-least-squares or F^2 using SHELXL.² It should be noted that portions of the nonanuclear clusters could not be modeled due to the severe disorder, and the disordered molecules in the MOF pores, which could not be reliably modeled using discrete atoms, were subtracted by SQUEEZE, using the PLATON software.³ Due to the unknown nature of the solvent in the channels, it was omitted from the reported formula. All of the nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and allowed to ride on the carrier atoms. All hydrogen atom thermal parameters were constrained to ride on the carrier atom. All materials showed strong diffuse scattering in the form of diffuse Bragg peaks and scattering between them. The major disorder in these structures were observed for phenyl rings and carboxylates in which they were split and successfully modeled.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer (measurement made over a range of $2^\circ < 2\theta < 40^\circ$ in 0.02° step with a 0.200 s scanning speed) equipped with a LYNXEYE linear position sensitive detector (Bruker AXS, Madison, WI). Neat samples were smeared directly onto the silicon wafer of a proprietary low-zero-background sample holder. Data was collected using a continuous coupled $\theta/2\theta$ scan with Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation operating at 40 kV and 40 mA.

^1H -NMR spectra were recorded on a 500 MHz Varian spectrometer and the chemical shifts were referenced to the residual solvent peaks. MOF samples were digested using ~5 drops of D_2SO_4 , followed by sonication and dissolution of the suspension in DMSO-d_6 .

Diffuse reflectance infrared spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR equipped with a MCT detector with a resolution of 1 cm^{-1} .

Thermogravimetric analysis (TGA) was carried out in a TGA/DSC 1 from Mettler Toledo, from room temperature to $800\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$ under air.

Scanning electron microscopy (SEM) images were collected on a Phenom ProX desktop SEM.

MOF samples were activated using a Micromeritics SmartVacPrep instrument equipped with a hybrid turbo vacuum pump. Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics TriStar II Plus instrument.

Gas Chromatography-Flame Ionization Detector (GC-FID) measurements were performed on an Agilent model 6890 with an FID detector and equipped with an HP-5 capillary column. The carrier gas was helium at a flow rate of 1.2 mL per min . The injector was a split/splitless one, used in splitless mode at $300\text{ }^{\circ}\text{C}$. All samples were filtered and diluted with dichloromethane prior to injection. Starting temperature: $70\text{ }^{\circ}\text{C}$, Hold: 0.5 min , Ramp: $30\text{ }^{\circ}\text{C}/\text{min}$, Time: 1 min , Ramp: $75\text{ }^{\circ}\text{C}/\text{min}$, End temperature: $250\text{ }^{\circ}\text{C}$.

LED irradiation was performed using solderless LEDs purchased from RapidLED which were mounted on aluminum to give a homemade irradiation setup. The LEDs were connected in series to a RapidLED 0-10V Dimmable LED driver. The irradiation setup contains four UV LEDs that are mounted in a square, facing each other, $\sim 5\text{ cm}$ apart.

S.3 Synthesis

4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid: synthesis of this organic linker was performed according to a reported procedure.⁴

Y-CU-10: Single crystals of Y-CU-10 were synthesized solvothermally in a 4 dram vial containing H_4TBAPy (13.8 mg , 0.02 mmol), $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (31.6 mg , 0.08 mmol assuming hexahydrate), and 2-fluorobenzoic acid (1261.0 mg , 9.0 mmol), suspended in 7.0 mL of DMF and 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 $120\text{ }^{\circ}\text{C}$ 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 $120\text{ }^{\circ}\text{C}$ for 12 h under ultralow vacuum.

Tb-CU-10: Single crystals were synthesized solvothermally in a 4 dram vial containing H_4TBAPy (6.1 mg , 0.0089 mmol), $\text{Tb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (15.5 mg , 0.036 mmol 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 $120\text{ }^{\circ}\text{C}$ 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 $120\text{ }^{\circ}\text{C}$ for 12 h under ultralow vacuum.

S.4 Disorder in the RE(III)-cluster node

Figure S1. Representation of the disordered RE₉ cluster, highlighting the two different orientations (green and yellow) (a) Observed RE₁₈ cluster, (b) assignment of the two disordered RE₉ clusters, (c) individual arrangement of each RE₉ cluster.

Figure S2. a) Representation of the disordered RE₉ cluster, highlighting the two different orientations (green and yellow) and their corresponding individual arrangement. (a) Observed RE₁₈ cluster, (b) assignment of the two disordered RE₉ clusters, (c) individual representation the RE₉ cluster in the same orientation as in Figure 1, main text, (d) RE₉ cluster in the opposite orientation.

S.5 ¹H-NMR spectroscopy

Figure S3. ¹H-NMR spectrum of a digested sample of Y-CU-10, in D₂SO₄ and DMSO-d₆.

Figure S4. ¹H-NMR spectrum of a digested sample of Tb-CU-10, in D₂SO₄ and DMSO-d₆.

S.6 Thermogravimetric analysis (TGA)

Figure S5. Thermogravimetric analysis plot for RE-CU-10 (RE = Y, and Tb)

S.7 Topological analysis

Figure S6. Representation of **shp** topology of RE-CU-10, highlighting the d6R nonanuclear cluster nodes (pink hexagons) and the cavities between nodes (dark-red spheres). View down “*c*” axis.

Figure S7. View of RE-CU-10 down the “*a*” axis, highlighting the d6R nonanuclear nodes (pink hexagons) and the cavities between nodes (dark-red spheres).

Figure S8. Simplified representation of **shp** net from the “*c*” axis. RE₉ cluster (pink hexagons), organic linker (black lines).

Figure S9. Simplified view of **shp** net from the “*a*” axis. RE₉ cluster (pink hexagons), organic linker (black lines and red rectangle)

Figure S10. Simplified view of **shp** net with 3D perspective. RE₉ cluster (pink hexagons), organic linker (black lines and red rectangle)

S.8 N₂ Adsorption isotherms

Figure S11. (a) Nitrogen adsorption-desorption isotherm for Y-CU-10 (inset: pore size distribution), and (b) nitrogen adsorption-desorption isotherm for Tb-CU-10 (inset: pore size distribution).

S.9 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

Figure S12. Diffuse reflectance infrared Fourier transform spectrum for RE-CU-10 (RE = Y and Tb)

S.10 Photo-oxidation of 2-chloroethyl ethyl sulfide (2-CEES)

Y-CU-10 (6.28 mg, 1.728 μmol , 0.9 mol %) was suspended in 1 mL of methanol in a 17×83 mm microwave vial. The vial was capped and purged with O_2 for 20 min and then 2-CEES (23 μL , 0.2 mmol) and mesitylene (10 μL) 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).

Table S1. GC-FID data for the conversion of 2-CEES to 2-CEESO using mesitylene as an internal standard

Y-CU-10	CEES		Mesitylene		CEESO	
	Retention time	Area	Retention time	Area	Retention time	Area
T0 min	2.411	92.5198	2.629	84.4		
T5 min	2.0409	48.9612	2.628	78.4299	4.004	32.37
T10 min	2.411	31.5626	2.631	143.32	4.011	115.484
T15 min	2.499	16.9178	2.631	532.321	4.027	511.372
T30 min			2.63	137.397	4.008	131.634
T60 min			2.632	318.363	4.019	324.29

S.11 Crystallographic data

Table S2. Crystallographic data for Tb-CU-10 and Y-CU-10.

Empirical formula	$\text{C}_{68}\text{H}_{36}\text{O}_{22}\text{Tb}_{4.61}$	$\text{C}_{68}\text{H}_{36}\text{O}_{22}\text{Y}_{4.63}$
Formula weight	1938.38	1616.79
Temperature/K	298(2)	150(2)
Crystal system	trigonal	Trigonal
Space group	$P\bar{3}m1$	$P\bar{3}m1$
a/ $\text{\AA}$	22.0962(6)	22.157(3)
b/ $\text{\AA}$	22.0962(6)	22.157(3)
c/ $\text{\AA}$	16.7081(5)	16.370(2)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	90
$\gamma/^\circ$	120	120
Volume/ $\text{\AA}^3$	7064.7(4)	6960(2)
Z	2	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	0.911	0.771
μ/mm^{-1}	11.429	2.804
F(000)	1840.0	1601.0
2θ range for data collection/ $^\circ$	8.002 to 146.058	10.688 to 145.416
Index ranges	$-26 \leq h \leq 27, -27 \leq k \leq 27, -20 \leq l \leq 20$	$-17 \leq h \leq 27, -27 \leq k \leq 22, -20 \leq l \leq 20$
Reflections collected	54310	82327

Independent reflections	5052 [$R_{\text{int}} = 0.0472$, $R_{\text{sigma}} = 0.0234$]	4982 [$R_{\text{int}} = 0.0690$, $R_{\text{sigma}} = 0.0204$]
Data/restraints/parameters	5052/260/212	4982/24/188
Goodness-of-fit on F^2	1.037	1.082
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0327$, $wR_2 = 0.0982$	$R_1 = 0.0567$, $wR_2 = 0.1874$
Final R indexes [all data]	$R_1 = 0.0360$, $wR_2 = 0.1018$	$R_1 = 0.0604$, $wR_2 = 0.1910$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.86/-0.81	1.46/-0.81

S.12 References

1. G. M. Sheldrick, *Acta Cryst. C.*, 2015, **C71**, 3–8.
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4. T. C. Wang, N. A. Vermeulen, I. S. Kim, A. B. F. Martinson, J. F. Stoddart, J. T. Hupp, O. K. Farha, *Nat. Protoc.*, 2016, **11**, 149–162.

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