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ARTICLE

Dual-fixations of europium cation and TEMPO species on metal-organic frameworks for aerobic oxidation of alcohols†

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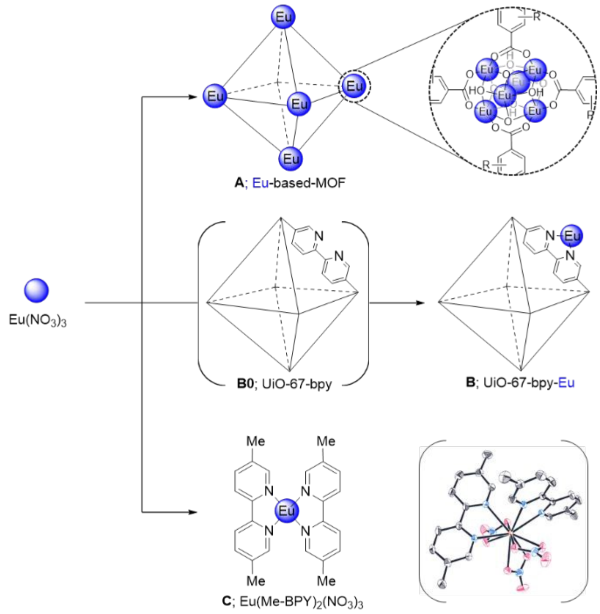
The efficient and selective aerobic oxidation of alcohols has been investigated with judicious combinations of europium-incorporated and/or TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl)-functionalized zirconium-based porous metal-organic frameworks (MOFs). Although MOFs are well-known catalytic platform for the aerobic oxidation with radical-functionalities and metal nanoparticles, these systematic approaches for metal cation and/or radical species allows many interesting aspects for cooperation between metal and TEMPO for the aerobic oxidation of alcohols. The role of TEMPO as the oxidant in the heterogeneous catalytic aerobic oxidation of alcohols was revealed through a series of comparisons between metal-anchored, TEMPO-anchored, and metal and TEMPO-anchored MOF catalysis. The fine tunability of MOF allowed the homogeneously and doubly functionalized catalysts for organic reaction in the heterogeneous media. In addition, the well-defined and carefully designed heterogeneous molecular catalysts displayed reusability along with better catalytic performance than the homogeneous systems within identical coordinating ligands. The role of metal-cation fixation should be carefully revised to control their coordination and maximize the catalytic activity. Lastly, metal cation-fixed MOF displayed better substrate tolerances and reaction efficiency than TEMPO-anchored MOF or mixture MOF systems.

Introduction

The selective oxidation of alcohols to aldehydes and ketones is one of the most important transformations in organic chemistry that is also widely used in pharmaceuticals, agrochemicals, and fine chemicals.[1] Typically, while traditional oxidations (*e.g.*, Jones oxidation, Dess-Martin oxidation, and Swern oxidation) require strong oxidants and generates more than an equivalent of byproducts under the harsh conditions. Compared with traditional oxidants, aerobic oxidation is a clean, low cost, atom economic, and sustainable methods because it uses molecular oxygen as a final oxidant.[2] Therefore, various metal-catalyzed aerobic oxidations have been developed, and typically transition metal-catalyzed aerobic oxidations of alcohols also require organic oxidants such as TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) to efficiently turn over the catalytic cycle.[3]



Scheme 1 Preparation of Eu-based MOFs in nodes and Eu-anchored MOFs in ligands.

Metal-organic frameworks (MOFs), porous inorganic/organic hybrid materials, have attracted increasing interest in catalytic applications over the last two decades.[4] First, the construction of metal clusters or the incorporation of metal cations into the secondary building units (SBUs) could be considered for catalysts such as Lewis acid catalysis.[5] In addition, one of the major advantages of MOFs, the tunability of the ligands (*i.e.*, the functionalization of the ligands), could allow the introduction of coordinating functionalities and external metal catalysts onto the frameworks. Pore engineering and metal derivatization of MOFs allow to be used in various heterogeneous catalysis applications.[6] Cu- and Pd-anchored or palladium nanoparticle-embedded MOFs were reported as efficient catalysts for

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aerobic oxidation.[7] Moreover, materials functionalized with the radical oxidant TEMPO have widely been reported and utilized for the selective aerobic oxidation of alcohols to aldehydes.[8]

In this study, we have additionally installed recently developed europium-based aerobic oxidation catalysts into TEMPO-functionalized MOFs to maximize the tunability and control of single catalytic sites deep in the MOF pores. Although europium is an underexplored, lanthanide metal species relative to transition metals for redox catalysis and oxidative organic transformations, both europium-based MOFs (Eu in the SBU) and europium-anchored MOFs (Eu in the ligand) are well-known systems due to their unique coordination environments and photophysical properties.[9] Since Eu-SBU-based MOFs show superior stabilities and Eu^{3+} can be installed in various common chelating groups, such as bipyridyl, europium catalysis is a good target for MOF-based heterogeneous catalysis toward aerobic oxidation of alcohols based on molecular level design and modifications. Therefore, in the present work, four classes of MOF-based catalysts for aerobic oxidation could be prepared along with their mixtures: Eu-based MOFs, Eu-anchored MOFs, TEMPO-functionalized MOFs (known system), Eu and TEMPO-anchored MOFs (dual functionalization of a single MOF), and applied to the aerobic oxidation of alcohols. In addition, the catalytic efficiencies of europium cations in MOFs have been extensively studied by comparing with homogeneous system, for the first time. Lastly, useful mechanistic information could be acquired by comparing these four unique, finely tuned heterogeneous catalyst systems.

Results and discussion

Heterogenization of Eu cation for the aerobic oxidation of alcohols

The recently developed, Eu-catalyzed aerobic oxidation of alcohols to the corresponding aldehydes was selected as a model reaction since Eu catalysis has two factors that make it well suited for heterogenization with MOFs.[10] First, both Eu-based MOFs (*i.e.*, the SBU of the MOF consists of Eu(III)) and Eu-anchored MOFs are well established in the literature.[11] To achieve Eu loading in the ligand, Zr-based UiO-67-bpy (UiO = University of Oslo, bpy = 2,2'-bipyridyl) was prepared due to its superior chemical and physical stabilities. MOFs in the UiO series are based on the $Zr_6O_4(OH_4)$ cluster as the SBU, and these clusters are connected to 12 carboxylate ligands.[12] In addition, Eu-based fcu MOFs reported by the Eddaoudi group generally have very similar frameworks to the Zr-based UiO MOFs. Eu-based fcu MOFs also have 12 BDC ligands derivatives (BDC = benzene-1,4-dicarboxylic acid; NDC = naphthalene-1,4-dicarboxylic acid was used for MOF preparation) connecting the with Eu_6 SBUs.[9a] The second advantage of Eu catalysis is the photoluminescence (PL) properties of Eu. Interestingly, Eu^{2+} and Eu^{3+} are easily distinguished by their PL spectra. While Eu^{3+} has strong PL signals at approximately 550 – 700 nm, Eu^{2+} does not have intense peaks in the same range of wavelength.[10,13] Therefore, the oxidation state of Eu (*e.g.*, Eu^{2+} or Eu^{3+}) after incorporation into the MOFs can be easily confirmed.

Table 1 Eu-catalyzed aerobic oxidation with various catalytic species[a]

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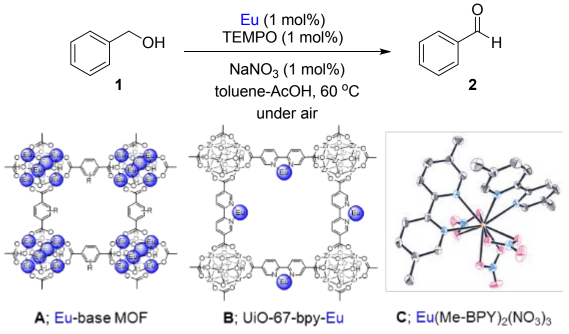

Entry	Europium catalyst	Conv. (%)[b]
1	—	<1
2	**A1**; Eu-MOF-1 with NDC	<1
3	**A2**; Eu-MOF-2 with DOBDC	<1
4	**B0**; UiO-67-bpy	<1
5	**B**; UiO-67-bpy-Eu	98[c]
6	**C**; $Eu(Me\text{-}BPY)_2(NO_3)_3$	56
7	**B**; UiO-67-bpy-Eu^{2nd}	99[c]
8	**B**; UiO-67-bpy-Eu^{3rd}	99[c]

[a] All reactions were performed on a 0.25-mmol scale: benzyl alcohol (**1a**, 0.25 mmol), Eu catalyst (1 mol%), TEMPO (0.5 mg), $NaNO_3$ (0.2 mg), toluene (1 mL), and acetic acid (0.1 mL). [b] GC conversion with >99% selectivity. [c] Isolated yield.

As Eu-based fcu MOFs, two isostructural fcu MOFs were successfully prepared following reported procedures by simply employing two ligands from derivatizations (**A1**: Eu-MOF-1, known fcu MOF with NDC ligand; and **A2**: Eu-MOF-2 with DOBDC, DOBDC = 2,5-dihydroxybenzene-1,4-dicarboxylic acid). In addition, to anchor Eu cations, bpy-functionalized UiO-67 (**B0**: UiO-67-bpy) was synthesized with BPYDC (2,2'-bipyridyl-5,5'-dicarboxylic acid) as described in Scheme 1.[14] Subsequent metalation with $Eu(NO_3)_3$ afforded UiO-67-bpy-Eu (**B**). The bulk crystallinities of **A1**, **A2**, **B0**, and **B** after metalation were confirmed by powder X-ray diffraction (PXRD), and Eu-metalation did not impact the frameworks of UiO-67 (Fig. S1 in the ESI†). The PL spectra confirmed the 3+ oxidation state of the Eu in **A1**, **A2** and **B** (Fig. S2†).[10]

The homogeneous system was modified to allow a direct comparison between heterogeneous and homogeneous Eu catalysis. Since the previous homogeneous Eu-catalyzed aerobic oxidation was performed within simple $Eu(NO_3)_3$,[10] which lacks external chelating ligands, we synthesized $Eu(Me\text{-}BPY)_2(NO_3)_3$ (**C**, Me-BPY = 5,5'-dimethyl-2,2'-bipyridyl) by the coordination of Me-BPY ligands to $Eu(NO_3)_3$, allowing confirmation of effect of the bipyridyl on the catalysis. The structure of the Eu-Me-BPY complex was determined by single-crystal X-ray diffraction (Table S1 and Fig. S3,† and Cambridge Crystallographic Data Centre Deposit # 1962612), and it was utilized for the direct comparison of the aerobic oxidation.

Next, conditions for the catalytic reaction were screened using several Eu-MOFs and Eu species. In the absence of catalyst, the aerobic oxidation did not proceed under mild heating (60 °C, entry 1 in Table 1). Both Eu-based MOFs, **A1**: Eu-MOF-1 with NDC and **A2**: Eu-MOF-2 with DOBDC, were ineffective in the aerobic oxidation (entries 2 and 3) even though both had Eu(III)

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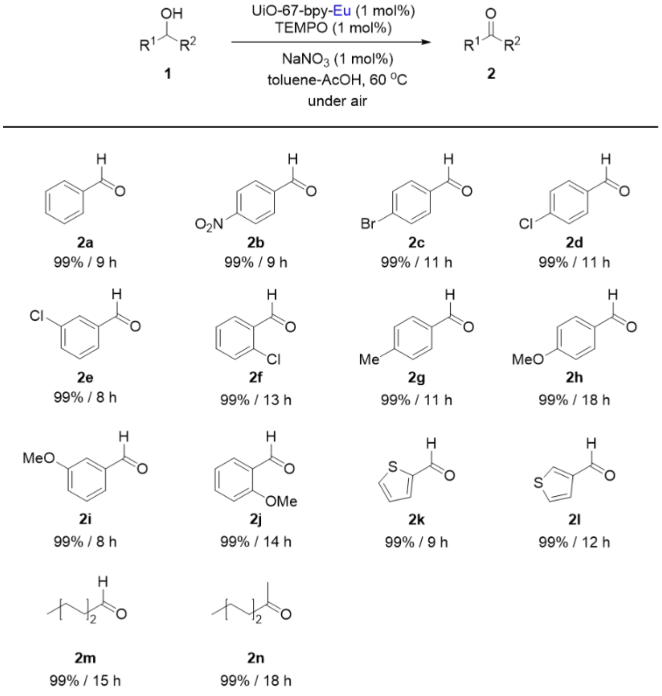
cations in their SBU, which are confirmed by the strong signals for Eu(III) in their solid-state PL spectra (Fig. S2†). While pristine UiO-67-bpy (**B0**) also showed no catalytic activity in this aerobic oxidation (entry 4), the benzyl alcohol substrate (**1a**) was fully converted to benzaldehyde (**2a**) with Eu-anchored UiO-67-bpy-Eu (**B**, >98% conversion, entry 5). In the direct comparison between the homogeneous and heterogeneous systems with external bipyridyl ligands, the MOF-based catalysts were much more efficient than homogenous catalysis with Eu(Me-BPY)$_2$(NO$_3$)$_3$ (**C**, entry 6). We attributed this difference to the nature of the framework. Since in the MOFs, the bipyridyl functionality is fixed on the ligand (*i.e.*, in the strut of the framework), each Eu^{3+} cation could only coordinate with one bipyridyl group (*i.e.*, two coordination sites), in which accessible sites to substances remained. However, in the homogeneous system, an additional bipyridyl ligand could bind with the Eu^{3+} cation since the coordination number of Eu^{3+} is greater than 6.[15] Therefore, the nature of the framework system (*i.e.*, the MOF) prevents the formation of the coordinatively saturated metal species and produces a single active catalytic site with labile chelating groups such as NO$_3^-$.



Scheme 2 Substrate scope for various alcohols using UiO-67-bpy-Eu (Condition I).

Then, Eu-anchored UiO-67-bpy-Eu, **B** was employed for the aerobic oxidation of alcohols under the optimized reaction conditions and generally showed good reactivity for various primary and secondary alcohols (Scheme 2). The oxidation reactions were finished for full conversion (>99% by GC) and >99% selectivity to aldehyde (toward carboxylic acid, by ^{1}H NMR) within 8-18 h. A series of alcohol substrates with electron-withdrawing groups (**2b**-**2f** in Scheme 2) and electron-donating groups (**2g**-**2j** in Scheme 2) were successfully converted to corresponding aldehydes. Indeed, all *ortho*-, *meta*-, and *para*-substituted primary alcohols with chloro and methoxy groups were successfully converted to the corresponding aldehydes (**2d**-**2f** for chloro group and **2h**-**2j** for methoxy group) with good conversions (>99% conversions for 6 examples). For the heteroaromatic alcohols, both 2-thiophene and 3-thiophene showed excellent conversions (**2k**, and **2l**). Lastly, aliphatic alcohols were subjected to the optimized conditions, both hexanal (**2m**) and 2-heptanone (**2n**) were successfully synthesized in good conversion from primary alcohol and secondary alcohol.

The best catalyst, Eu-anchored **B** was characterized in detail for physical properties. The full N$_2$ isotherms (at 77 K) were acquired to determine the porosity and surface area of Eu-anchored MOFs. The Brunauer-Emmett-Teller (BET) surface areas of **B0** and **B** were generally decreased from 1828 m^2/g to 671 m^2/g and pore volume was also decreased from 0.96 cm^3/g to 0.36 cm^3/g upon europium metalation (Fig. S4 and Table S2†). The existence of NO$_3^-$ in **B** was confirmed by FT-IR (Fig. S5†), and thermogravimetric analysis (TGA) also indicated the multispecies in the frameworks (Fig. S6†).

Last, the recyclability, the major advantage of heterogeneous catalysis of **B** was studied. The Eu-anchored **B** could be recycled by simple centrifugation without structural changes or changes in the catalytic activity (entries 7, 8 in Table 1 and Fig. S7†). Indeed, the hot filtration test was performed during the reaction (at 3 h), and the conversion of benzyl alcohol (**1a**) to benzaldehyde (**2a**) was halted at around 30%, which displayed the heterogeneous characteristic of Eu-catalysis in this condition (Fig. S8†).

Strategical Combination with TEMPO-functionalized MOFs for the aerobic oxidation of alcohols.

TEMPO, the organic oxidant is a key molecule for the aerobic oxidation. TEMPO can catalyze the aerobic oxidation with radical reagents or cooperate redox cycle of metal (Scheme S1†).[16] The heterogeneous, MOF-based catalysis for aerobic oxidation was initiated with TEMPO moiety. Due to the tunability of MOFs, the organic oxidant can be covalently bound into the MOF pores to perform the aerobic oxidation, for example, Cu-catalyzed click chemistry.[8c,8d] TEMPO-functionalized MOFs have recently been achieved with Zr-based MOFs, UiO-67-TEMPO (**D**), and successfully applied to aerobic oxidation. In addition, the combination of homogeneous Eu(NO$_3$)$_3$ salt and TEMPO-functionalized MOF **D** displayed good catalytic performance for the aerobic oxidation of alcohols under mild condition.[8c] Since the same MOF platform, UiO-67, was employed to prepare the analogous system with Eu-anchored MOFs (Scheme 3), the pores of Zr-based MOFs were further tuned by the fixation of metals and oxidants, together. MOFs are good heterogeneous platform for multi-functionizations and the tandem catalytic reactions.[17] More than two different, sequential catalytic sites could be installed together in a single MOF's pore by ligand-mixing strategy.[18] Therefore, both BPYDC and TEMPO-functionalized ligands were mixed and incorporated in to the UiO-67 frameworks, and Eu-metalation followed for combining two catalytic cycles (the redox cycle of Eu and the redox cycle of TEMPO) in a single MOF pore (Scheme 3).

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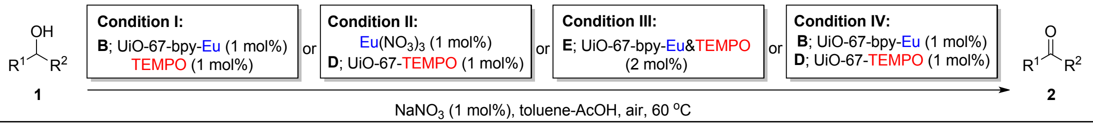
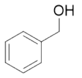
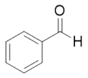
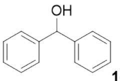
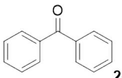
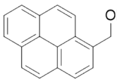
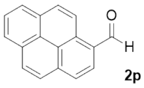
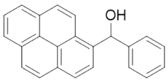
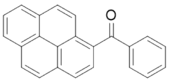
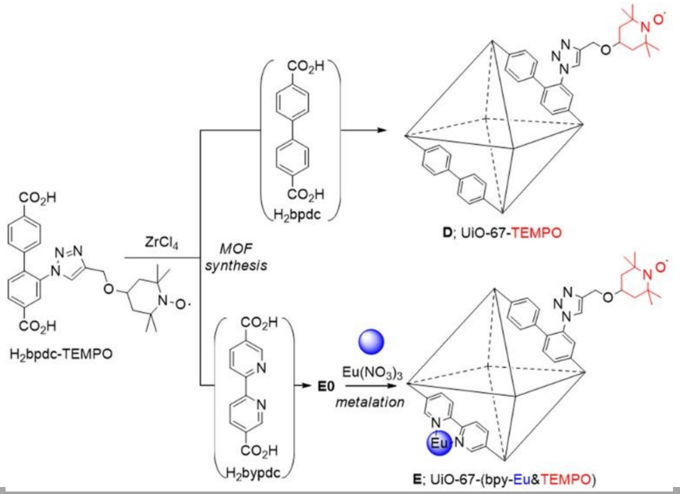
Table 2 Eu-loaded, TEMPO-functionalized UiO-67s versus ligand mixture in the framework versus crystal mixtures in solution for the aerobic oxidation of alcohols[a]



Entry	Substrate	Product	Condition I Yield[b] / Time	Condition II Yield[b] / Time	Condition III Yield[b] / Time	Condition IV Yield[b] / Time
1	 **1a**	 **2a**	99 / 9	99 / 9	68 / 18	70 /18
2	 **1o**	 **2o**	99 / 9	99 / 9	49 / 18	48 / 18
3	 **1p**	 **2p**	99 / 18	68 / 18	42 / 18	45 / 18
4	 **1q**	 **2q**	85[c] / 18	60[c] / 18	30[c] / 18	28[c] / 18

[a] All reactions were performed on a 0.25-mmol scale: **1** (0.25 mmol), UiO-67-bpy-Eu (2 mg), TEMPO (0.4 mg), and $NaNO_3$ (0.2 mg) for Conditions I; 1 (0.25 mmol), UiO-67-TEMPO (3 mg), Eu(NO_3)$_3$ (1 mg), and $NaNO_3$ (0.2 mg) for Conditions II; UiO-67-(bpy-Eu&TEMPO) (6 mg), and $NaNO_3$ (0.2 mg) for Conditions III; **1** (0.25 mmol), UiO-67-bpy-Eu (2 mg), UiO-67-TEMPO (3 mg), and $NaNO_3$ (0.2 mg) for Conditions IV in the solvent mixture (toluene 1 mL + AcOH 0.1 mL) at 60 °C. [b] Based on the GC conversion with >99% selectivity. [c] Isolation yield.

Since the detail characterizations of UiO-67-TEMPO were previously reported,[8c] the additional characterizations for mixed UiO-67-(bpy&TEMPO), **E0** were followed. The porosity of UiO-67-(bpy-Eu&TEMPO), **E** was confirmed by N_2 full isotherm at 77K (609 m^2/g, Fig. S4†), and thermal stability was analyzed (Fig. S9†). The ^{1}H NMR spectrum after acid digestion confirmed the ratio of the BPYDC and BPDC-TEMPO ligands (3:2 molar ratio, Fig. S10†). In addition, the metalation ratio of UiO-67-bpy-Eu (**B**) and UiO-67-(bpy-Eu&TEMPO) (**E**) was determined by inductively coupled plasma optical emission spectrometry (ICP-OES), and generally, more than 70% of the bipyridyl sites on UiO-67-bpy MOFs were decorated with Eu^{3+} cations (Table S3†). Finally, the chemical stability of newly synthesized UiO-67 analogues were investigated. It was widely reported that Zr(IV)-based UiO MOFs generally good chemical and physical stabilities than other MOFs due to the highly oxophilic character of Zr(IV).[12,19] Not surprisingly, UiO-67-bpy-Eu, UiO-67-TEMPO, UiO-67-(bpy&TEMPO), and UiO-67-(bpy-Eu&TEMPO) were maintained their frameworks in various organic solvents such as acetone, dichloromethane, pyridine, and water. The main frameworks were decomposed under 1M HCl aqueous condition, which is evidenced by PXRD (Fig. S11†).



Scheme 3 Preparation of TEMPO-functionalized and Eu&TEMPO-functoinalized MOFs.

As summarized in Table 2, UiO-67-bpy-Eu (**B**, Eu-fixed, Condition I in Scheme 2), UiO-67-TEMPO (**D**, TEMPO-fixed, Condition II) and UiO-67-(bpy-Eu&TEMPO) (**E**, Eu and TEMPO-fixed together, Condition III) were employed for the aerobic oxidation of alcohols and compared to the oxidation of alcohols under the optimized reaction conditions. At the same time, the mixtures of crystalline UiO-67-bpy-Eu and UiO-67-TEMPO were also investigated to compare their reactivities for the aerobic oxidation of alcohols (Conditions IV in Table 2). UiO-67-bpy-Eu and UiO-67-TEMPO (1 mol%) were both employed for the aerobic oxidation of alcohols and compared to the oxidation of alcohols with external TEMPO (1 mol%) or Eu(NO_3)$_3$ (1 mol%). Both Eu-anchored and TEMPO-functionalized UiO-67s (Conditions I & Conditions II in Table 2) generally showed good reactivities for benzylalcohol (**1a**) and diphenyl methanol (**1o**).

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In the case of bulky substrates such as pyrenyl methanol and phenyl pyrenyl methanol (**1p** and **1q**), relatively higher conversions were observed with UiO-67-bpy-Eu / TEMPO (Conditions I, 99% and 85%) than UiO-67-TEMPO / Eu (Conditions II, 68% and 60%), respectively. Neither fixed system (*e.g.*, ligand mixture in the framework, Conditions III) nor physical mixture of crystals in solution (Conditions IV) efficiently catalyzed the aerobic oxidation since the three redox cycles should be incorporated together and placed nearby.

A comparison of Conditions I-IV for the conversion of benzyl alcohol (**1a**) to benzaldehyde (**2a**) demonstrated that Eu cation in Eu-BPY should be quite labile and the mobility of Eu could be critical for alcohol oxidation since TEMPO was fully fixed in Conditions II, III and IV (entry 1 in Table 2). If the coordination of Eu^{3+} in Eu-BPY complex is not in equilibrium, the catalytic conversion using Conditions IV should be restricted to only surface-to-surface collisions for cooperative redox cycles. Otherwise, the mobilities of NO_3^- or O_2 species in the solutions should be carefully considered, and the sequence of redox cycles in the proposed general mechanism of aerobic oxidation (Scheme S1†) needs to be revisited since Eu-anchored **B** displayed good reusability in Table 1 (Fig. S7†). In addition, the similar conversions achieved with Conditions III and IV for all substrates indicate the presence of mobile oxidants in reaction mixtures.

To understand the catalytic performance depending on the size of substances, the molecular sizes of starting alcohols were simply calculated through B3LYP/6-311G (Fig. S12†) and compared with NLDFT pore size distribution of MOF catalysts (Table S2†).[8c] It reveals the diffusion difficulty of pyrenyl methanol (**1p**) and phenyl pyrenyl methanol (**1q**) to MOF pores (Fig. S4†). While Condition III requires the substrate to enter the pores to interact with both the metal cation and organic oxidant (TEMPO); in the case of Condition IV, two species must enter the pores (*i.e.*, the substrate and oxidant) to perform aerobic oxidation. However, similar conversions were observed with substrates of various sizes, and size discrimination of the substrate was not achieved in the present system due to the mobility of Eu(III) (Table 2).

Conclusions

The europium-catalyzed aerobic oxidation of alcohols with the molecular oxidant TEMPO has been successfully achieved with MOF-based catalysts. Since the catalytic applicability of the redox cycle of europium (Eu^{2+}/Eu^{3+}) was recently revealed, both Eu-based MOFs (Eu-MOF-**1** with NDC and Eu-MOF-**2** with DOBDC) and Eu-anchored Zr-based MOFs have been utilized for the heterogeneous aerobic oxidation of alcohols in the presence of TEMPO as an oxidant. While Eu-based MOF-**1** and Eu-MOF-**2** were completely inert in the aerobic oxidation since all the europium(III) was fixed in the SBUs and fully coordinated, Eu anchored into bipyridyl functionalities on UiO-67-bpy showed good catalytic activity, even higher than the homogeneous $Eu(Me\text{-}BPY_2(NO_3)_3$ species. We attributed the different reactivities to the different coordination environments and numbers of ligands. In the homogeneous system, the coordination sites of Eu(III) are occupied by two bipyridyl ligands and three nitrates, and coordination of the starting material can only occur in the MOF system.

Not only Eu-anchored MOF-based catalysts but also TEMPO-functionalized MOFs have been utilized in aerobic oxidations. Both systems provided good catalytic conversions of alcohols to the corresponding aldehydes or ketones within 8-18 h. The high tunabilities of MOFs allowed the preparation of the dual-functionalized UiO-67-(bpy-Eu&TEMPO) system, and the physical mixtures of UiO-67-bpy-Eu and UiO-67-TEMPO crystals were investigated. A comparison of their catalytic activities revealed the crucial role of TEMPO, and TEMPO is considered as the first oxidant to substrate alcohol for cooperative metal/organic oxidant/O_2 redox cycles. We believe that the mobility of the Eu^{3+} cation is responsible for the reactivities for the TEMPO-fixed heterogeneous systems.

Neither fixed system nor mixture of crystals in solution efficiently catalyzed the aerobic oxidation since the two redox cycles should be incorporated together and placed nearby. In additions, since the first oxidant to substrate is TEMPO species, the TEMPO-fixed system has been found to reduce in the reactivity for bulky sized substrates due to mismatches between pore size of the frameworks and substrate size. Finally, Eu-anchored into bipyridyl functionalities on UiO-67-bpy and molecular TEMPO additive system showed good catalytic activity for various sized alcohols and reusability (Table 1 and Fig. S7†).[8c]

Experimental

Eu-MOF-1 (A1) or Eu-MOF-2 (A2).[9a] 1,4-NDC (10.8 mg, 0.05 mmol for Eu-MOF-1) or 1,4-DOBDC (9.9 mg, 0.05 mmol for Eu-MOF-2) were mixed with $Eu(NO_3)_3{\cdot}5H_2O$ (21.4 mg, 0.05 mmol), 2-fluorobenzoic acid (56 mg, 0.4 mmol), DMF (10 mL), H_2O (2 mL) and 60% HNO_3 (80 μL). The solution was placed in a 20-mL scintillation vial and heated at 115 °C for 60 h. The colorless polyhedral crystals were isolated by centrifugation (3600 rpm) and washed 3 times with DMF (30 mL) and then 3 times with CH3CN (30 mL). Heating at 60 °C under vacuum for 12 h yielded activated-Eu-MOF-1 and 2.

UiO-67-bpy (B0).[14a] BPYDC (122 mg, 0.5 mmol) and DMF (40 mL) were placed in a 250-mL round-bottom flask equipped with a magnetic stir bar, and the mixture was heated until the solid was fully dissolved. $ZrCl_4$ (117 mg, 0.5 mmol), benzoic acid (1.83 g, 15 mmol), and H_2O (18 μL, 1.0 mmol) were added to the BPYDC solution, and the resulting clear solution was heated with magnetic stirring for 5 days at 130 °C under a nitrogen atmosphere. The colorless microcrystalline powder was isolated by centrifugation (3600 rpm) and washed 5 times with DMF (150 mL) and then 5 times with CH_3CN (150 mL). Heating at 100 °C under vacuum for 12 h yielded activated-UiO-67-bpy.

UiO-67-bpy-Eu (B). The microcrystalline powder of UiO-67-bpy $(Zr_6(O)_4(OH)_4(BPYDC)_6$ (100 mg, 0.28 mmol), $Eu(NO_3)_3{\cdot}5H_2O$ (120 mg, 0.28 mmol) and CH_3CN (10 mL) were placed in a 20-mL scintillation vial and heated at 60 °C for 24 h. The colorless microcrystalline powder was isolated by centrifugation (3600 rpm) and washed 5 times with hot CH_3CN (150 mL). Then, heating at 100 °C under vacuum for 12 h yielded activated-UiO-67-bpy-Eu.

UiO-67-TEMPO (D).[8c,8d] MOF D was synthesized according to the reported literature.

UiO-67-(bpy&TEMPO) (E0): BPYDC (24.4 mg, 0.1 mmol), BPDC-TEMPO (49.4 mg, 0.1 mmol) and DMF (8 mL) were placed in 20 mL scintillation vial and heated until fully dissolved. $ZrCl_4$ (46.6 mg, 0.2 mmol) and conc. HCl (0.25 mL) were added then resulting clear solution was incubated at 85 ^{o}C for 24 h. The colorless microcrystalline powder was isolated by centrifugation (3600 rpm) and washed 5 times with DMF (150 mL) and washed 5 times with CH_3CN (150 mL). Then heating at 50 ^{o}C under vacuum for 12 h yielded the activated **E0**. This procedure was prepared by a reported method with minor modifications.[8c,8d]

UiO-67-(bpy-Eu&TEMPO) (E): This mixed MOF **E** could be obtained by following **B** procedure using **E0** (130 mg, 0.28 mmol) and $Eu(NO_3)_3 \cdot 5H_2O$ (72.8 mg, 0.17 mmol) instead of **B0**. Europium loading was determined by ICP-OES based on the molar ratio of the inserted metal relative to zirconium in the framework.

General procedure for aerobic oxidation

Condition I: the alcohol (**1**, 0.25 mmol), UiO-67-bpy-Eu (2 mg, 0.0025 mmol), TEMPO (0.4 mg, 0.0025 mmol), $NaNO_3$ (0.2 mg, 0.0025 mmol) and toluene (1 mL) were added to a scintillation vial. Acetic acid (0.1 mL) was added to the solution, and then the mixture was stirred at 60 °C for 8 h under air. The resulting mixture was filtered through a syringe filter, and the conversion ratio was determined by GC or the desired product was isolated by silica gel column chromatography.

Conflicts of interest

There are no conflicts to declare.

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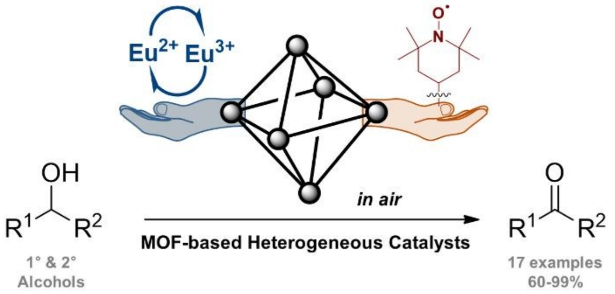

The systematic approaches for Eu and/or TEMPO-functionalized MOFs for aerobic oxidation of alcohols have been performed.