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metal-organic frameworks

Ligand preferences in ytterbium ions complexation with carboxylate-based

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Two coordination polymers of ytterbium were synthesized by employing 4,4',4"-s-triazine-2,4,6triyl-tribenzoic acid (H₃TATB), 4,4',4-benzene-1,3,5-triyl-tribenzoic acid (H₃BTB), and 3,5pyridinedicarboxylic acid (3,5-PDC) ligands and were characterized by single-crystal X-ray diffraction analysis. Reaction of ytterbium(III) chloride in the presence of H₃BTB and 3,5-PDC ligands gives preferred complexation with the 3,5-PDC ligand, producing [Yb₂(3,5-PDC)(ClO₄)₃][NH(Me)₃] (1). However, under exactly the same reaction conditions, reaction of ytterbium(III) chloride in the presence of 3,5-PDC and H₃TATB resulted in complexation with H₃TATB to form [(CH₃)₂NH₂][Yb₄(TATB)₄(HCO₂)(H₂O)₂]-3H₂O (**2**). The crystal structure results showed a layered structure for **1** and a metal-organic framework structure for **2**. This indicates that the complexation preference of the ytterbium ion is H₃TATB \geq 3,5-PDC \geq H₃BTB. Conversely, the uncomplexed ligand in the metal-organic framework (**2**) is an auxiliary agent during the synthesis, which shows polytopic linker controls crystal properties, to form suitable crystals for single-crystal structure determination. The prepared coordination compounds were used as heterogeneous catalysts in an oxidation amidation reaction with different aldehydes and benzylamine hydrochloride.

Keywords: Inorganic polymer; MOF; Ytterbium; Single-crystal; Amidation

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1. Introduction

Metal-organic frameworks (MOFs) are crystalline materials constructed from organic struts and metal-containing nodes as secondary building units (SBUs) [1, 2]. These compounds are of considerable interest owing to their remarkable framework topologies and design flexibility, which has led to their widespread use in gas storage [3-8], gas separation [9-13], catalysis [14-16], sensor [17-19], and drug delivery applications [20-23].

Many techniques have been used to synthesize MOFs and grow high-quality single crystals [24], including the diffusion method, hydrothermal and solvothermal process, microwave-assisted synthesis, sonochemical and mechanochemical techniques, and the modulating ligands approach. In the modulator ligand approach, modulators can control crystal properties, such as the shape, size, stability, and growth rate of the crystal. Typically, monocarboxylate molecules, such as acetic acid, benzoic or formic acid, and other monocarboxylic acids, are used as modulators [25, 26]. In research on the various methods of preparing MOFs, the effect of polytopic linkers as auxiliary modifying ligands has not been investigated; further work on this issue will help in understanding the formation of MOFs in the presence of at least two types of polytopic linkers.

In this work, we report the synthesis of two new ytterbium complexes with polycarboxylates. The crystal structures and catalytic performances were also investigated. We used three types of carboxylate-based ligands (scheme 1) under certain conditions. To study the role of the auxiliary modifying ligand in the formation of the two synthesized ytterbium coordination polymers, we applied polycarboxylate framework-forming linkers, which competed with the other ligand in the framework formation. Reaction of YbCl₃ with 4,4',4"-s-triazine-2,4,6-triyl-tribenzoic acid (H₃TATB) in the presence of 3,5-pyridinedicarboxylic acid (3,5-PDC) resulted in the formation of a three-dimensional MOF with rod-shaped SBUs. Conversely, when 4,4',4-benzene-1,3,5-triyl-tribenzoic acid (H₃BTB) was used instead of H₃TATB under exactly the same reaction conditions, an unexpected layered structure coordination polymer with 3,5-PDC, perchlorate, trimethylammonium ion, and Yb(II) and Yb(I) ions was formed. The single-crystal structure of the latter compound, along with the infrared spectroscopy and elemental analysis, demonstrate that perchlorate was formed *in situ* through an oxidation and reduction reaction. There is a preference between the two carboxylic-based ligands toward

complexing with Yb(III), in which one of the ligands acts as a modifier. Furthermore, in extension of our work, we used the prepared coordination polymers as heterogeneous catalysts in an oxidation amidation reaction from different aldehydes and benzylamine hydrochloride.



Scheme 1. Schematic representation of ligands.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Aldrich and Merck and used without purification. The syntheses of 1,3,5-tris(4-acetylphenyl)benzene, 4,4',4"-benzene-1,3,5-triyl-tribenzoic acid (H₃BTB) and 4,4',4"-s-triazine-2,4,6-triyl-tribenzoic acid (H₃TATB) were adapted from published methods [27, 28]. FT-IR spectra were recorded on a Bomem MB-Series FT-IR spectrometer. Thermal analysis (TGA-DTA) was carried out using a Bahr STA-503 instrument at a heating rate of 10 °C min⁻¹ in air. The N₂ adsorption-desorption analysis was performed at 77 K using a BELSORP-mini instrument (BEL Japan, Inc.). CHN analyses were performed on a Thermo Finnigan Flash EA112 elemental analyzer. X-ray powder diffraction (XRD) pattern was recorded on a STOE diffractometer with Cu-K_a radiation ($\lambda = 1.5418$ Å). Single-crystal structure data were collected on a STOE IPDS diffractometer equipped with graphite monochromated Mo-Ka radiation at 298 K. The structures were solved by direct methods and refinement was achieved by full matrix least squares of F² using the SHELXL97 crystallographic software package. Crystallographic data along with the refinement parameters for **1** and **2** are listed in

table S1.

2.2. Synthesis of [Yb₂(C₇H₃NO₄)(ClO₄)₃][NH(Me)₃]₂ (1)

For the synthesis of **1**, 3,5-PDC (0.01 g, 0.06 mmol) and H₃BTB (0.01 g, 0.23 mmol) were dissolved in a solution containing DMF (4.0 mL, 52 mmol), H₂O (1.0 mL, 55 mmol) and 5 drops HNO₃. To this solution, YbCl₃·6H₂O (0.03 g, 0.08 mmol) was added, and the mixture was stirred at room temperature until complete dissolution. The final solution was transferred to a small glass container and sealed. The sample was heated to 110 °C with a rate of 0.5 °C min⁻¹ and kept at this temperature for 72 h, and then cooled to room temperature over 48 h. Colorless needle-like crystals were obtained in 29.4% yield (based on Yb). FTIR (KBr, cm⁻¹): 2974, 2938, 2739, 2677, 2495, 1610, 1547, 1473, 1433, 1397, 1144, 1089, 1034, 845, 805, 772, 719, 627. Anal. Calcd. (Found) for $C_{13}H_{23}Cl_3N_3O_{16}Yb_2$: C 16.79 (17.28); H 2.49 (2.67); N 4.52 (5.16).

2.3. Synthesis of $[(CH_3)_2NH_2][Yb_4(C_{24}H_{12}N_3O_6)_4(HCO_2)(H_2O_2)]\cdot 3H_2O(2)$

Compound **2** was synthesized exactly like **1** except using H₃TATB instead of H₃BTB. In detail, 3,5-PDC (0.01 g, 0.06 mmol) and H₃TATB (0.01 g, 0.23 mmol) were dissolved in a solution containing DMF (4.0 mL, 52 mmol), H₂O (1.0 mL, 0.055 mol) and 5 drops HNO₃. Then YbCl₃·6H₂O (0.03 g, 0.08 mmol) was added into the primary solution and dissolved while stirring at room temperature. The final solution was transferred to a glass container and sealed. The sample was heated to 110 °C with a rate of 0.5 °C min⁻¹ and kept at this temperature for 72 h and then cooled to room temperature over 48 h. White cubic crystals were obtained. FTIR (KBr, cm⁻¹): 3048, 2923, 2852, 1677, 1548, 1503, 1420, 1400, 1193, 1100, 883, 1089, 819, 777, 700, 565, 500, 399. Anal. Calcd. (Found) for C₉₉H₆₇N₁₃O₃₁Yb₄: C 45.27 (44.32), H 2.57 (2.76), N 6.93 (7.32).

3. Results and discussion 3.1. *Synthesis*

In an attempt to prepare ytterbium(III) MOF from ytterbium(III) chloride, 4,4',4"-benzene-1,3,5triyl-tribenzoic acid, and 3,5-pyridinedicarboxylic acid by solvothermal method in DMF, an unprecedented coordination polymer with a layer structure was formed,

[Yb₂(3,5-PDC)(ClO₄)₃][NHMe₃] (1). When 4,4',4"-benzene-1,3,5-triyl-tribenzoic acid was

replaced by 4,4',4"-s-triazine-2,4,6-triyl-tribenzoic acid and the reaction was carried out under exactly the same conditions, the formation of a new MOF was observed,

[(CH₃)₂NH₂][Yb₄(C₂₄H₁₂N₃O₆)₄(HCO₂)(H₂O)₂]·3H₂O (**2**). Evidence and characterization data showed that during the formation of **1**, a perchlorate ion was produced and integrated into the structure. The FT-IR spectrum clearly showed the formation of the perchlorate ion in the *in situ* reaction. The perchlorate ion must have originated from an oxidation-reduction process during the hydrothermal reaction. Moreover, single-crystal X-ray diffraction showed that a trimethylammonium cation formed and combined into the structure of **1**, which is probably due to the reduction of DMF [29]. Since YbCl₃·6H₂O was the only chlorine source to be oxidized, Yb(III) and DMF were reduced in a parallel process. A redox electron exchange resulted in chloride and DMF transformation. The formation of perchlorate in an *in situ* catalytic reaction during the solvothermal processes is unusual. For example, a catalytic reaction in the solvothermal synthesis of coordination polymers and a chemical transformation of perchlorate to chloride have previously been reported [30], but the reverse of this, *i.e.*, a transformation of chloride to perchlorate, has not been observed.

Addition of modulating ligands during MOF synthesis can control crystal quality [31, 32]. The modulating agents are usually monocarboxylic acids, such as trifluoroacetic acid, acetic acid, and benzoic or formic acids, which slow the nucleation of MOF crystals and lead to the growth of larger and better-shaped crystals. Herein, H₃BTB acted as a modifying agent and competed with 3,5-PDC in the formation of 1, whereas in the formation of 2, 3,5-PDC acted as a modifying agent, and polytopic H₃TATB integrated into the MOF and suitable crystals formed. Other lanthanide complexes with similar structures have been synthesized in the absence of a "modifying agent" [33]. We also utilized the same procedure, but the resulting patterns are different from the reported structures. Therefore, it can be postulated that the presence of both ligands is necessary to successfully generate the reported MOFs. The tendency of coordination of H_3BTB to Yb in 1 indicated that H_3BTB is an auxiliary agent over 3.5-PDC, and in 2, it is evident that the coordination power of the ligands is in order of $H_3TATB \ge 3,5$ -PDC. Herein, in both cases, the polytopic linkers, H₃BTB and 3,5-PDC, act as modifier agents, and the modifiers form complexes during the synthesis of the coordination polymers. Concomitantly, modifiers slow down the synthetic process of more thermodynamically favorable compounds and finally facilitate the formation of high-quality crystals. It seems that the coordination motif of TATB is

almost the same as that of BTB, but they show different preferences under the same reaction conditions and compositions. The difference in the structural preferences of TATB⁻³ and BTB⁻³ ligands can be attributed to the middle ring of the BTB⁻³ ligand, which is spatially more hindered than the TATB⁻³ ligand because of the hydrogens on the middle benzene ring that directly influence properties and behavior of the ligand. This could be a reason for the different coordination preference of the ligands under the same conditions.

3.2. Single-crystal structures

3.2.1. Molecular structure of [Yb₂(C₇H₃NO₄)(ClO₄)₃][NH(Me)₃]₂ (1). Single-crystal X-ray analysis revealed that 1 crystallized in the monoclinic system in the space group of C2/m. Selected bond lengths and angles are listed in table S2. The asymmetric unit contains half Yb(I) and half Yb(II) ions, half 3,5-PDC ligand, one and half μ_3 -bridging perchlorates, and one trimethylammonium cation. Carboxylate oxygens of 3,5-PDC are coordinated bidentate through bridging of O1 and O2 to two crystallographically independent pairs of Yb ions. These two crystallographically independent ytterbium ions, Yb1 and Yb2, exhibit two different coordination geometries in the complex. As illustrated in figure 1, the Yb1 has a seven-coordinate pentagonal bipyramidal geometry, with two oxygens from two different 3,5-PDC ligands occupying the axial sites with an O1-Yb1-O1ⁱⁱ angle of 167(3)°, and five further oxygens, O3, O6, O9, O9ⁱ and O11, from perchlorate ions were positioned in the equatorial sites of the pentagonal plane. The O1—Yb1 and O1ⁱⁱ—Yb1 bond lengths, 2.187(6) Å, are in the range of those observed in other carboxylate-bridged ytterbium coordination polymers, such as [Yb₂(bdc)₃(e-urea)₄] [34], Yb-PVDC-2 [35] and [Yb₂(TP)₃(H₂O)₂]₂ [36]. The other Yb1—O bonds are formed by coordination of oxygens from three crystallographically independent perchlorates. These oxygens that formed the pentagonal plane can be differentiated into two types. In the first type, two crystallographically independent perchlorates adopt a μ_3 -bridging mode to link three ytterbium ions while in the second type, the third perchlorate forms a μ -O9 bridge between Yb1 and Yb1ⁱ while also forming a chelate with Yb1 through O9ⁱ and O11. The bond lengths of O3— Yb1 and O6-Yb1 are shorter than those of O9-Yb1, O9i-Yb1 and O11-Yb1. The angles of O1-Yb1-O_{eq} (eq: O3, O6, O9, O9ⁱ and O11) and O1ⁱⁱ-Yb1-O_{eq} are ca. 84° to 95°. The sum of the angles in the pentagonal plane, O3-Yb1-O6, O3-Yb1-O9, O6-Yb1-O11, O9-Yb1-O9ⁱ, and O11-Yb1-O9ⁱ, is very close to 360°. The extrusions above 72° are to

compensate for the smaller value of O9-Yb1-O9ⁱ and the chelate angles. In contrast to the coordination geometry of Yb1, the coordination geometry of Yb2 is best described as distorted octahedral with four oxygens of four different μ_3 -bridged perchlorate anions, O4, O4ⁱⁱⁱ, O7 and O7ⁱⁱⁱ, and two carboxylate oxygens, O2 and O2ⁱⁱⁱ, from two 3,5-PDC ligands. The span of the O2—Yb2 and O2ⁱⁱⁱ—Yb2 bond lengths is in the range of that reported in previous studies for CUmof-9 [37] and [NH₃(CH₂)₂NH₃]_{0.5}[Yb(OBA)₂(H₂O)] [38]. Apparently, for each octahedral center, the μ_3 -bridged perchlorates are a monodentate ligand. The perchlorates that bonded to Yb2 trans with bond lengths of 2.218(5) and 2.215(5) Å are almost identical. Although the bond angles O2-Yb2-O7ⁱⁱⁱ, O4ⁱⁱⁱ-Yb2-O4 and O7-Yb2-O7ⁱⁱⁱ are nearly in accord with octahedral geometry, the other bond angles around Yb2 with values of 85(1(2)° and 94.9(2)° are somewhat different. Moreover, the bond lengths show that the octahedral coordination sphere around Yb2 is distorted from an ideal octahedral environment. Finally, 1 possesses a 2-D polymeric layer structure and is connected to a 3-D network by supramolecular interactions (figure 2). 2D layers are separated by 3.21 Å, in which trimethylammonium cations stabilize the molecular structure by inter-layer NH...O hydrogen bonding and weak CH...O interactions, forming a 3-D supramolecular network in the *ab* plane.

3.2.2. Molecular structure of [(CH₃)₂NH₂][Yb₄(C₂₄H₁₂N₃O₆)₄(HCO₂)(H₂O)₂]·3H₂O (2).

Complex **2** crystallized in the orthorhombic system with the Fddd space group. Selected bond lengths and angles are listed in table S3. The asymmetric unit contains one crystallographically distinct Yb(III), one TATB³⁻, half a water molecule, one-quarter of a formate, one-quarter of a dimethylammonium, and 0.75 of the uncoordinated water molecule in the chemical formula. The chemical formula of **2** can be expressed by

 $[(CH_3)_2NH_2)]_{0.25}$ [Yb(C₂₄H₁₂N₃O₆)(HCO₂)_{0.25}(H₂O)_{0.5}]·0.75(H₂O). The chemical formula moiety is multiplied by four in order to make the formula moiety a whole number, and this may give an impression that there is more than one type of ytterbium ion.

In **2**, the ytterbium is connected to a chelating-bridging $-CO_2$ group as well as to oxygens of five other bridging $-CO_2$ groups. Disorder resulted from occupation of a coordination site by a water molecule for half of the time and a unidentate formate for half of the time. This disorder site along with seven ligating oxygens of the TATB³⁻ ligand brought the coordination number of ytterbium to eight. However, multiplication of the formula moiety by four can change the

interpretation. In the new formula, $[(CH_3)_2NH_2][Yb_4(C_{24}H_{12}N_3O_6)_4(HCO_2)(H_2O)_2]\cdot 3H_2O$, three species, Yb1-formate-Yb1, Yb1(water) and Yb1ⁱ(water), overlapped. Similarly, the eighth coordination site was occupied by a bridging formate ion for half of the time (figure 3a). Partial occupancy feature can also explain the in situ catalysis of DMF to formate. In this configuration, the O1ⁱ-O3ⁱⁱ-O5^{iv} and O2-O4ⁱⁱⁱ-O6^v planes form the two triangular bases of the prism with dihedral angle 9.03°. The distances between Yb1 and the centroid of these two bases are 1.476 and 1.457 Å, respectively. This geometry is not regular among the three other possible choices for eight-coordinate complexes. A half of O1_w and half of O7 caps the lateral face of O2-O3ⁱⁱ-O5^{iv}-O6^v, and O1 caps the lateral face of O1ⁱ-O3ⁱⁱ-O2-O4ⁱⁱⁱ. The criteria for assignment of geometry are based on a comparison of the observed polyhedra with the most favorable one following a set defined by Porai–Koshits and Aslanov, as $\delta 1 = 8.06^\circ$, $\delta 2 = 11.58^\circ$, $\delta 3 = 37.81$, 49.77° , $\delta 4 = 26.45^{\circ}$, $\phi 1 = 16.60$, 9.75° , $\phi 2 = 30.64^{\circ}$ and $\omega = 89.97$ and 87.84° . The theoretical values for a bicapped trigonal prism are $\delta 1 = 0^\circ$, $\delta 2 = 21.7^\circ$, $\delta 3 = \delta 4 = 48.2^\circ$, $\phi 1 = 16.1^\circ$ and $\omega =$ 83.7° [39, 40]. The coordination geometry can be best described as a distorted bicapped trigonal prism or square-face bicapped; however, it should be noted that the Yb1 coordination geometry can be described as an intermediate between two ideal forms, *i.e.*, square antiprism ($\delta 1 = 0^\circ$, $\delta 2 =$ 0° , $\delta 3 = \delta 4 = 52.5^{\circ}$, $\phi 1 = 24.5^{\circ}$, $\omega = 77.4^{\circ}$) and bicapped trigonal prism. The Yb–O bond lengths vary from 2.219(6) to 2.878(8) Å, and a mean value for Yb-O distances, as statistically analyzed in version 1.18 of ConQuest, is 2.326 Å with a maximum of 3.187 and minimum of 1.708 Å. This is in the normal range of values observed for other compounds. The O-Yb-O bond angles are 49.0(2)–154.3(3)°. Each carboxylate connects two identical Yb^{III} ions and the YbO₈ polyhedron constructed a 1D inorganic chain with Yb...Yb distances of 4.086 and 5.343 Å and extended in two directions that are almost mutually perpendicular. This compound represents another example of MOFs constructed with rod-shaped SBUs. Three SBUs are connected by rigid TATB³ to form a 3D coordination framework (figure 3b). The formate ions also connect two SBUs in different orientations, but merely consolidate the network. The dihedral angles between the central triazine and the three benzene rings are 3.00°, 4.77° and 18.89° and the dihedral angles among the three benzene rings are 7.59°, 19.84° and 20.33°. The dihedral data indicate that the TATB³⁻ is rather unsymmetrical and not as flat as reported [41, 44]. Herein, the solvent-accessible volume (SAV) was calculated by PLATON analysis as 1491.6 Å³, which is 8.2% of the unit-cell volume. There are eight voids with approximately 170 Å³ in the unit cell.

The low porosity can be associated with the higher coordination number (eight) of the Yb1 ions. S-triazine rings of each TATB³⁻ were rotated and oriented to stack on top of one another to form a parallel-displaced π - π stacking, which can help improve thermal stability.

3.3. X-ray powder diffractions

The powder X-ray diffraction (PXRD) patterns of compounds were recorded and compared to those generated from corresponding single-crystal data (figure 4). The good correlation between the simulated patterns and the ones obtained from PXRD indicates the high phase purity of the solids. The slight differences between some of the reflection intensities of the simulated and experimental patterns can be attributed to the variation in the orientation of the powder samples during collection of the experimental PXRD data.

3.4. Infrared spectroscopy

The symmetric and asymmetric stretching vibrations of carboxylate in the FT-IR spectrum of **1** (figure 5a) were observed at 1470 and 1610 cm⁻¹, respectively. The Δv (v_{as} - v_s) value is below 200 cm⁻¹, which indicates that carboxylate coordinated bidentate to ytterbium [45]. Meanwhile, the stretching vibrations of perchlorate were observed at 1096 and 629 cm⁻¹, confirming the formation of perchlorate during synthesis [46].

In contrast to the FT-IR spectrum of **1**, the FT-IR spectrum of **2** is attributed to formation of HCO₂⁻, and various coordination modes of the carboxylate are present. The FT-IR spectrum of **2** (figure 5b) showed three intense bands at 1622, 1544 and 1401 cm⁻¹ in addition to three shoulders at 1561, 1508 and 1359 cm⁻¹ in the carbonyl region. These imply two coordination modes for the carboxylate ligand, as confirmed by single-crystal X-ray analysis. Furthermore, the FT-IR spectrum showed bands at 2921 and 2847 cm⁻¹ which correspond to the C-H stretching of formate ions [47]. The formation of formate is associated with the hydrolysis or decarboxylation of DMF, which is very common in high-temperature solvothermal synthesis [48]. For further clarification of the formate ion decomposition and its conversion to CO₂ during heat treatment, as noticed in TGA-DTA analyses (*in situ*), the FT-IR spectrum of the compound after heat treatment at 350 °C was recorded. As figure 5c shows, the C-H stretch of the formate ion after heat treatment collapsed, which indicates decomposition of the formate ion. Notably, identical X-ray powder diffraction patterns of **2** before and after heat treatment prove that the structure remains intact after heat treatment.

3.5. Thermal analysis

To investigate the thermal stability of the prepared compounds for possible use as catalysts and precursors for fabrication of ytterbium oxide, thermal analyses (TGA-DTA) were carried out in air from 30-750 °C. As the TGA curve of **1** in figure 6a shows, there is a slight weight loss from 150-200 °C. The weight loss is accompanied with an endothermic peak in the same temperature range, which is attributed to loss of solvent. Furthermore, the TGA curve shows about 53 wt.% loss of **1** from 350-500 °C. This weight loss, along with an exothermic peak in the DTA curve in the same temperature, implies collapse of the structure due to combustion of the 3,5-PDC and reflects the stability of the complex up to 300 °C.

The thermal behaviors of **1** and **2** are similar to some extent. However, the latter does not exhibit significant weight loss to 400 °C, which illustrates the higher stability of **2** with respect to **1**. This higher stability of **2** could be attributed to its 3-D network. As figure 6b shows, there are two distinct weight losses for **2** with a total weight loss of approximately 64%. The first weight loss of 11% up to 440 °C, along with an endothermic peak in the DTA curve centered at 380 °C, can be attributed to the decomposition of dimethyl ammonium formate and its transformation to CO₂ and the release of trapped and coordinated water without collapse of the structure up to 440 °C. The second weight loss at 460-670 °C is associated with the combustion of the TATB⁻³ as indicated by the exothermic peak in its DTA curve.

3.6. Surface area analysis

The N₂ adsorption-desorption behavior of **2** after activation was examined at 77 K. Analysis of isotherm (figure S1) led to the BET surface area of 5.6 m²/g (Langmuir 50.8 m²/g), a pore volume of 0.0097 cm³/g and a pore size of 1.2 nm. The low surface reveals that nitrogen molecules with a kinetic diameter of 3.64 Å scarcely adsorb on the activated compound owing to its narrow windows [49, 50]. As shown by the isolated yellow spheres in figure 7, there are no open channels to connect pores and this reflects in the low surface area of **2**. Such a low N₂ adsorption isotherm was previously reported for isostructures of a series of multifunctional lanthanide-organic frameworks [33].

3.7. Catalytic activity studies of prepared compounds

The amide functionality is one of the important factors in the preparation of drugs and biopolymers. The amides were traditionally prepared by activation of a carboxylic acid by toxic and corrosive reagents such as thionyl or oxalyl chlorides in high yields and conversions, but this process is not environmentally friendly. Therefore, to avoid these adverse effects, other methodologies, such as oxidative amidation of alcohols and aldehyde, were introduced. Preparation of benzamide derivatives through the oxidative amidation reaction from aldehydes and amine hydrochlorides is quite slow in the absence of catalysts. Recently, to advance the related methodologies, catalytic amidation of aldehydes with amines by homoleptic lanthanide amido complexes has been investigated [51-54]. The promising catalytic activities of lanthanide complexes also encouraged us to explore the catalytic behavior of the new Yb-coordination polymers in the oxidative amidation reaction of aldehydes with benzylamine hydrochloride.

A simple comparison between two newly synthesized coordination polymers showed that 2 has the potential to act as a Lewis acid site; therefore, it was a better candidate for heterogeneous metal-based catalysis in reactions such as an oxidative amidation. In the outset of our work, we utilized a model reaction of benzaldehyde and benzylamine hydrochloride to form N-benzylbenzamide in order to evaluate the catalyst performance of the prepared complexes at room temperature with TBHP, as an oxidant. As can be seen from the entries in table 1, the presence of a catalyst, TBHP, and CaCO₃ is essential to obtain acceptable yields. As entries 2 and 3 show, 2 provided a much higher yield of amide in comparison with 1. The higher activity can be attributed to its pore and framework structure. To study the role of the solvent in the yield. the reaction was carried out using various solvents, and the yields were obtained in the order of acetonitrile > dioxane > water > tert-butanol > tetrahydrofuran > toluene. The role of the solvent in the yield is not well understood at this time; however, the higher stability of 2 with the framework structure in acetonitrile can be speculated. Finally, the efficacy of 2 as the catalyst in the oxidative amidation reaction of benzaldehyde with benzylamine hydrochloride is compared with several previously reported catalysts for the same reaction. As table 2 shows, the efficiency is superior or at least equal, but unfortunately, the base and oxidants are essential for the catalyst. The catalyst recycling test was also performed for the model reaction, and it was found that after four consecutive runs, the isolated yield drops slightly, only 2-3%. With these optimized conditions, this reaction was further explored and generalized with various aldehydes and

benzylamine hydrochloride, and fairly good yields were obtained (table 3). It seems that the conversions of benzamide derivatives were slightly changed by the electron-donating or electron-withdrawing groups.

The plausible reaction mechanism for the oxidation amidation of aldehydes, as shown in scheme 2, begins with deprotonation of the amine hydrochloride salt to produce the corresponding amine. Compound **2** after activation creates open metal coordination sites. Therefore, it can act as a Lewis acid site for the activation of both substrates. The amine is reacted with ytterbium Lewis-acid sites to form a ytterbium amido complex, which consequently reacts with the aldehyde to afford the reactive species B. Further reaction of B with another amine yields C, which may be oxidized by the oxidant to generate the desired product [54, 60].



Scheme 2. The plausible reaction mechanism for oxidation amidation of aldehydes.

4. Conclusion

We have prepared two coordination polymers under hydrothermal conditions. Compound **1** features a two-dimensional layered anionic structure with trimethethylammonium cations between the layers, and **2** exhibits a metal-organic framework with tritopic H₃TATB ligands. Single-crystal diffraction studies showed that ligand preferences through complexation with ytterbium ions are as follows: H₃TATB \geq 3,5-PDC \geq H₃BTB. In the preparation of both compounds, one polytopic ligand acts as an auxiliary modifying agent in the reaction. The results reveal that the carboxylic ligands show a significant role in the formation of high-quality crystals, and it seems that polycarboxylate molecules can also be used as a modifier. Finally, **2** with the framework structure acted as an efficient catalyst in the formation of different benzamides from benzaldehyde derivatives.

Supplementary materials

Electronic Supplementary Information (ESI) available: synthesis of 1,3,5-triphenylbenzene, synthesis of 1,3,5-tri(4',4',4''-acetylphenyl)benzene, synthesis of 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (H₃BTB), synthesis of 2,4,6-tri-p-tolyl-1,3,5-triazine, synthesis of 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid (H₃TATB), crystal data for 1 and 2 (table S1), selected bond lengths and angles for 1 (table S2) and selected bond lengths and angles for 2 (table S3). Crystallographic data of 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 151026 (1) and 1517025 (2). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Acknowledgement

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Figure 1. The coordination environment of ytterbium ions in **1** with the ellipsoids drawn at the 30% probability level.



Figure 2. The dotted lines indicate inter-layer NH...O hydrogen bonding and weak CH...O interactions with the ellipsoids drawn at the 30% probability level.



Figure 3. The coordination environment of ytterbium ions in **2** with the ellipsoids drawn at the 30% probability level (a); SBUs are connected by rigid TATB³⁻ ligands to form a 3D framework (b).



Figure 4. Simulated and experimental powder X-ray diffraction patterns of 1 and 2.



Figure 5. FT-IR spectra of 1 (a) and 2 before (b) and after activation (c).



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Figure 7. The yellow spheres illustrate the isolated volume fitted inside the pores without contacting van der Waals surface. Yb green, O red, N blue, C gray and H white.

Entry	Solvent	Time (h)	Yield (%)
1	CH ₃ CN	16	<5
2	CH ₃ CN	16	87
3	CH ₃ CN	16	21°
4	H_2O	16	47
5	t-BuOH	16	39
6	THF	16	16
7	Dioxane	16	73
8	Toluene	16	11
9	CH ₃ CN	12	79
10	CH ₃ CN	8	65
11	CH ₃ CN	4	48

Table 1. Catalytic activity of 2 in oxidative amidation of benzaldehyde with benzylamine hydrochloride salts^a.

(a) Reaction conditions: catalyst (0.03 mmol), benzaldehyde (2 mmol), benzylamine hydrochloride salt (2.4 mmol), base (2.2 mmol), TBHP (70 wt.% in water, 2.2 mmol), solvent (2 mL), at room temperature, base: CaCO₃; (b) isolated yield; (c) compound **1**.

Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield (%)	Ref.
1	Fe(NO ₃) ₃ .9H ₂ O (0.05 mmol), CaCO ₃ (1.1 mmol) and TBHP (1.1 mmol)	CH3CN	60	16	78	[55]
2	MagCNTs@SiO ₂ -linker-CuI (20 mg), Na ₂ CO ₃ (2 mmol.), TBHP (1.5 mmol)	CH ₃ CN	60	6	85	[56]
3	CuSO ₄ ·5H ₂ O (5.0 mol%), CaCO ₃ (1.1 mmol), TBHP (1.1 mmol)	CH ₃ CN	25	24	86	[57]
4	FeSO ₄ ·7H ₂ O (5.0 mol%), CaCO ₃ (1.1 mmol), TBHP (1.1 mmol)	CH ₃ CN	60	16	72	[58]
5	Na ₂ CO ₃ (2 mmol.), TBHP (1.5 mmol), Cu/C (3.68 mol%)	CH ₃ CN	60	6	78	[59]
6	CaCO ₃ (1.1 mmol), TBHP (1.1 mmol), CuI (1.0 mol%), AgIO ₃ (1.0 mol%)	CH ₃ CN	40	6	71	[60]
7	CuBr (20 mol%), CaCO ₃ (2.5 mmol), PhI(OAc) ₂ (50 mol%), TBHP (1.0 mmol)	CH ₃ CN	25	24	75	[61]
10	Compound 2 (1.5 mol%), CaCO ₃ (1.1 mmol), TBHP (1.1 mmol)	CH ₃ CN	25	16	87	This work

Table 2. Comparison of the catalytic efficiency of **2** in oxidative amidation of benzaldehyde with several reported catalysts.

Entry	R ₁	R_2	Yield (%)	Melting point	Ref.
1	Н	Н	87	101-103/102-104	[62]
2	4-Me	Н	69	138-140/137-139	[63]
3	4-OMe	Н	74	127-129/128-131	[64]
4	4-Cl	Н	71	162-164/161-163	[65]
5	4-Br	Н	67	165-167/166-168	[65]
6	4-NO ₂	Н	65	134-137/134-137	[64]

Table 3. Compound **2**-catalyzed synthesis of amides from aldehydes and benzylamine hydrochloride salts.

Graphical Abstarct



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