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A novel Ca(II) coordination polymer with 3-(3-carboxyphenyl)-isonicotinic acid: design, DFT analysis, and catalytic efficiency

Tai Xi-Shi[1*], Wang Li-Hua[2], Saud I. Al-Resayes[3] and Mohammad Azam[3*]

Abstract

The traditional strategies to improve the catalytic performance of metal complexes mainly focus on the selection of ligands and central metal ions. Herein, a novel calcium(II) coordination polymer, abbreviated as $[Ca(L)(H_2O)_3]_n \cdot H_2O$, was synthesized by assembling 3-(3-carboxyphenyl)-isonicotinic acid (H_2L), NaOH, and calcium perchlorate tetrahydrate. Its structure was thoroughly investigated using elemental analysis, infrared spectroscopy, UV/vis spectroscopy, and thermogravimetric analysis. The structure of the calcium(II) coordination polymer was further ascertained by single-crystal X-ray diffraction, revealing that each Ca(II) ion is eight-coordinated with five oxygen atoms from three different L ligands and three oxygen atoms from three coordinated water molecules, forming a distorted square antiprism geometry. To gain further insight into the structure, DFT studies were also conducted. The frontier molecular orbitals of the Ca(II) coordination polymer show that the DFT energy gap is 0.12279 Ha (3.34 eV). The electrostatic potential results reveal that regions with higher electrostatic potential are primarily concentrated in the six-member carbon ring structures of the Ca(II) coordination polymer. Conversely, areas with lower potential are mainly located near oxygen and nitrogen atoms. Additionally, the catalytic efficiency of the studied polymer showed that it can achieve a 68.7% conversion of benzyl alcohol and a 40.1% yield of benzaldehyde under 5 bar of O_2 for 2 h in THF.

Keywords Calcium(II) coordination polymer, Crystal structure, DFT studies, Catalytic studies

Introduction

Calcium, the fifth most abundant element in the Earth's crust, is found in rocks such as limestone and gypsum. Its biocompatibility, structural function in bone, and low toxicity facilitate a diverse array of environmental, biological, and industrial applications [1–3]. With the rising demand for sustainable and eco-friendly chemical processes, calcium in catalysis has gained significant interest as a promising candidate for sustainability due to its unique abundance, affordability, non-toxicity, and moisture tolerance, thereby positioning it as a promising substitute to precious metals in catalytic applications, particularly in multicomponent reactions [4]. Moreover, Calcium's intrinsic physicochemical properties further

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enhance its catalytic potential. Its low electronegativity (1.0) and stable + 2 oxidation state allow it to form bonds with anions, while its relatively large ionic radius supports diverse coordination chemistry. These characteristics have led to the development of novel calcium(II) complexes with promising applications in multicomponent reactions, biodegradable materials, and pharmaceuticals [5]. However, despite these advancements, calcium complex catalysis remains relatively underexplored compared to transition metals, leaving significant opportunities for future research and development. Furthermore, calcium's Lewis acidity can be finely tuned through tailored ligand systems, allowing for precise control of catalytic activity [6, 7]. From the above literatures, it can be seen that calcium complexes have been reported in many catalytic processes in the past decade, including styrene polymerization, intramolecular hydrogenation and asymmetric 1,4-addition. Moreover, these complexes have demonstrated multifunctional properties, serving as photosensitizers [8], potential COX-2 inhibitors [9], and inhibitors of human nasopharyngeal cancer cell proliferation [10]. Furthermore, they exhibit luminescence properties [11], the ability to adsorb and retain small molecules [12], the detection and selective elimination of copper ions [13], and the formation of porous bio-MOFs with significant molecular adsorption capacity [14]. Additionally, calcium complexes have been used in the thermodynamic separation of hexane isomers and in the effective separation of xylene isomers [15, 16], as well as in removing endocrine-disrupting compounds from water [17].

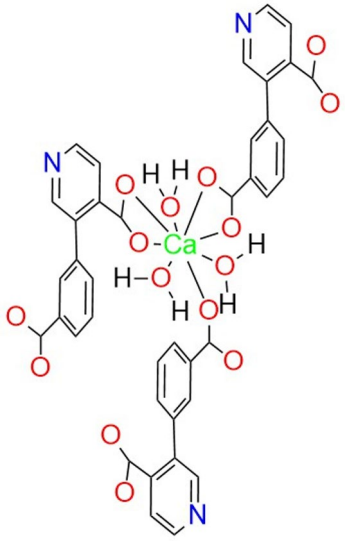

Fig. 1 The coordination mode of Ca(II) in the studied coordination polymer

Over the past years, carboxylate ligands, one of the excellent podands, have been widely studied in coordination chemistry for constructing coordination polymers (CPs) and supramolecular architectures due to their flexible coordination modes [18–21]. CPs, also exhibit a wide range of applications in gas storage, separation, luminescence, magnetism, sensing, and catalysis [22–24].

Considering the broad coordination behavior and chemical significance of carboxylic acids, our research group has previously developed and studied several metal complexes derived from carboxylic acid–based ligands [25–31]. To further enrich the catalytic activity of calcium carboxylate complexes, we chose a ligand, 3-(3-carboxyphenyl)isonicotinic acid (H_2L), containing carboxylic acid-pyridine groups to investigate the structure and catalytic activity of its calcium complexes. Herein, we describe the synthesis and structural characterization of a novel calcium(II) coordination polymer, $[Ca(L)(H_2O)_3]_n \cdot H_2O$, obtained from the reaction of 3-(3-carboxyphenyl)isonicotinic acid (H_2L), NaOH, and calcium perchlorate tetrahydrate (Fig. 1). The studied calcium(II) coordination polymer was thoroughly characterized by elemental analysis, IR and UV–vis spectroscopy, thermogravimetric analysis, and single-crystal X-ray diffraction. Density functional theory (DFT) calculations were performed to gain a deeper insight into its electronic and structural properties. Furthermore, the catalytic performance of the calcium(II) coordination polymer was evaluated in the oxidation of benzyl alcohol.

Experimental

Materials and measurements

3-(3-Carboxy-phenyl)-isonicotinic acid (H_2L), NaOH, and calcium perchlorate tetrahydrate were all of analytical grade and used without further purification. C, H, and N were analyzed using an Elementar Vario III EL elemental analyzer (Elementar, Germany). UV-Vis spectra were recorded using a PERSEE T9 spectrophotometer (Beijing, China) with 1 cm path length quartz cuvettes. IR spectra were obtained with a FTIR-850 spectrophotometer (Tianjin Gangdong). TG-DTA analysis was performed on a HENVEN HCT-2 thermal analyzer (Beijing, China). The single crystal data of the Ca(II) coordination polymer were collected using a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA). The liquid-phase oxidation products were analyzed with a GC-6890 gas chromatograph (Purkinje General Instrument Co., Ltd., China) equipped with an SE-54 capillary column.

Table 1 Crystal data for Ca(II) coordination polymer

Empirical formula	$C_{13}H_{15}NO_8Ca$
Formula weight	353.34
Temperature/K	305.42(10)
Crystal size/mm^3	0.16×0.14×0.11
Crystal system	triclinic
Space group	*P*-1
a/Å	7.0268(3)
b/Å	10.0119(4)
c/Å	11.1217(3)
α/°	86.202(3)
β/°	78.661(3)
γ/°	81.564(3)
Volume/Å^3	758.29(5)
Z	2
ρ_{calc}, mg/mm^3	1.548
S	1.078
F(000)	368
Index ranges	$-9 \le h \le 9$, $-9 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	9354
Independent reflections	2800[*R*(int) = 0.0251]
Data/restraints/parameters	3335/4/218
Goodness-of-fit on F^2	1.029
Refinement method	Full-matrix least-squares on F^2
Final *R* indexes [I >= 2σ (*I*)]	$R_1 = 0.0348$, $wR_2 = 0.0854$
Final *R* indexes [all data]	$R_1 = 0.0436$, $wR_2 = 0.0895$

Synthesis of Ca(II) coordination Polymer, $[Ca(L)(H_2O)_3]_n \cdot H_2O$

The Ca(II) coordination polymer was synthesized using the following method: 3-(3-carboxy-phenyl)-isonicotinic acid (0.1215 g, 0.5 mmol), NaOH (0.040 g, 1.0 mmol), and calcium perchlorate tetrahydrate (0.1555 g, 0.5 mmol) were added to a 100 mL flask containing 25 mL of water-ethanol mixture (1:2, v/v). The reaction mixture was stirred and heated to 80 °C for 4 h; thereafter, it was cooled to room temperature while continuing to stir for an additional 3 h. The resultant solution was filtered, yielding colorless crystals of $[Ca(L)(H_2O)_3]_n \cdot H_2O$ after 30 days. Anal. Calcd: C, 44.15; H, 4.25; N, 3.96%. Found: C, 43.82; H, 4.52; N, 4.00%.

Crystal structure determination

A colorless single crystal of the Ca(II) coordination polymer, with dimensions of 0.16 × 0.14 × 0.11 mm³, was selected for X-ray diffraction analysis on a Rigaku XtaLAB Synergy R, DW system, HyPix diffractometer utilizing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 305.42(10) K. The structure was determined by direct methods using SHELXT-2014/5 [32] and refined by full-matrix least-squares on F² with SHELXL-2018/3 [33]. The important crystallographic data for the Ca(II) coordination polymer are summarized in Table 1. The cif of the Ca(II) coordination polymer is shown in Supplementary material.

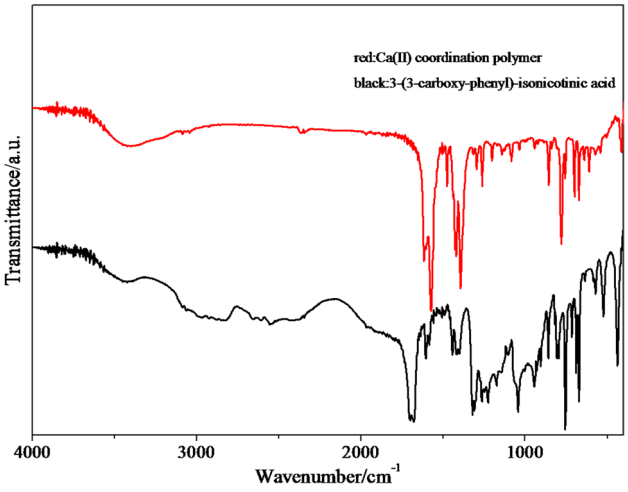

Fig. 2 IR spectra of 3-(3-carboxy-phenyl)-isonicotinic acid and calcium(II) coordination polymer

General procedure for the oxidation of benzyl alcohol

Typically, 0.02 g of Ca(II) coordination polymer catalyst, 1.0 mmol of benzyl alcohol, and 7 mL of tetrahydrofuran (THF) were added to a 10 mL stainless-steel high-pressure reactor. The reactor was purged with pure O_2 three times to ensure an oxygen-rich atmosphere, and the O_2 pressure was maintained at 5 bar. The reaction was carried out at 80 °C for 2 h under vigorous stirring at 2000 rpm using a heated magnetic stirrer. After the reaction, the catalysts were collected by centrifugation (RCF:13,000 × g, 10 min), washed three times with ethanol, and subsequently dried at 80 ℃ for reuse. The clear solution was injected into a chromatographic vial for gas chromatography (GC-6890, Purkinje General Instrument Co., Ltd., Beijing, China) using a SE-54 capillary column (30 m × 0.25 mm × 0.25 mm).

Results and discussion

Infrared spectroscopy

The infrared spectra of 3-(3-carboxy-phenyl)-isonicotinic acid and Ca(II) coordination polymer are shown in Fig. 2. The free ligand exhibits a strong absorption band at approximately 1707 cm^{-1}, attributed to the C = O stretching vibration of the carboxylic acid moiety [34]. The spectrum of the Ca(II) coordination polymer displays two characteristic bands at 1612 and 1424 cm^{-1}, which correspond to the asymmetric

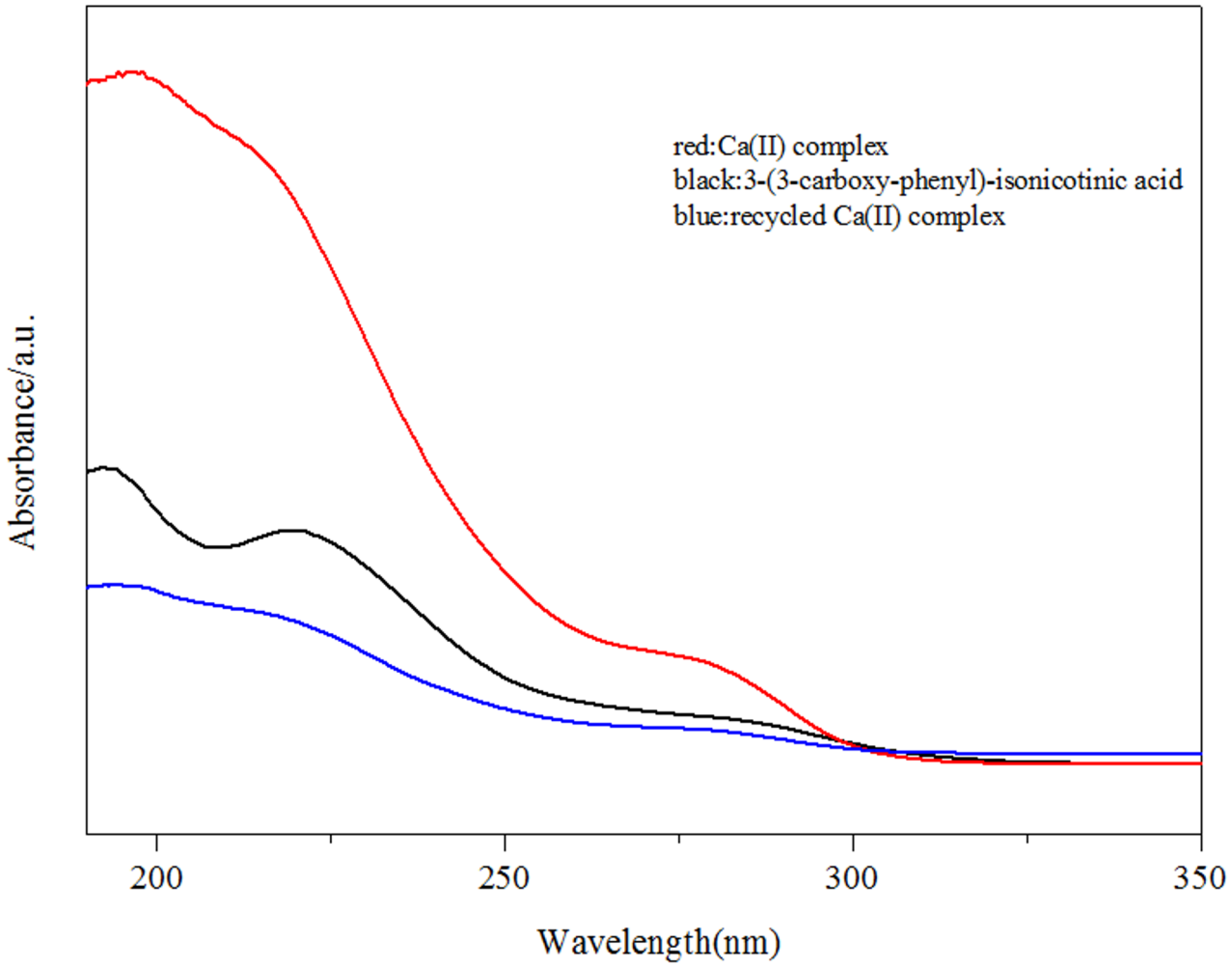

Fig. 3 UV-Vis spectra of the 3-(3-carboxy-phenyl)-isonicotinic acid, Ca(II) coordination polymer, and the recycled Ca(II) coordination polymer

($\nu_{as}(COO^-)$) and symmetric ($\nu_s(COO^-)$) stretching vibrations, respectively. This shift indicates that the carboxylate oxygen atoms are coordinated to the Ca(II) centers. The free ligand also exhibits C = N absorption band at approximately 1606 cm^{-1}, in Ca(II) coordination polymer, it shows at 1608 cm^{-1}, showing that the N atom does not coordinate with Ca(II) ion. Furthermore, the broad absorption band observed at ca. 3415 cm^{-1} (stretching C-H and O-H bonds) corroborates the presence of water molecules within the coordination polymer [35].

UV-Vis spectra

The UV-vis spectra of the 3-(3-carboxy-phenyl)-isonicotinic acid, Ca(II) coordination polymer, and the recycled Ca(II) coordination polymer are shown in Fig. 3. The free ligand displays two distinct absorption bands at 192 and 220 nm, attributable to the π–π* of benzene ring or the *n*–π* transition of the C = O and pyridine ring in the free 3-(3-carboxy-phenyl)-isonicotinic acid ligand [36]. Upon coordination with Ca(II) ion, the coordination polymer exhibits a single absorption band at 198 nm, indicating a change in the electronic environment of the ligand due to the formation of calcium(II) coordination polymer. However, the disappearance of the second band indicates that coordination to the Ca(II) ion alters the conjugation and electron distribution within the ligand framework. Notably, the recycled Ca(II) coordination polymer displays a similar absorption band at 197 nm (π–π*), indicating that the electronic structure of the complex remains essentially unchanged after catalysis. This observation confirms that the Ca(II) coordination polymer catalyst exhibits excellent structural integrity and stability under the specified reaction conditions.

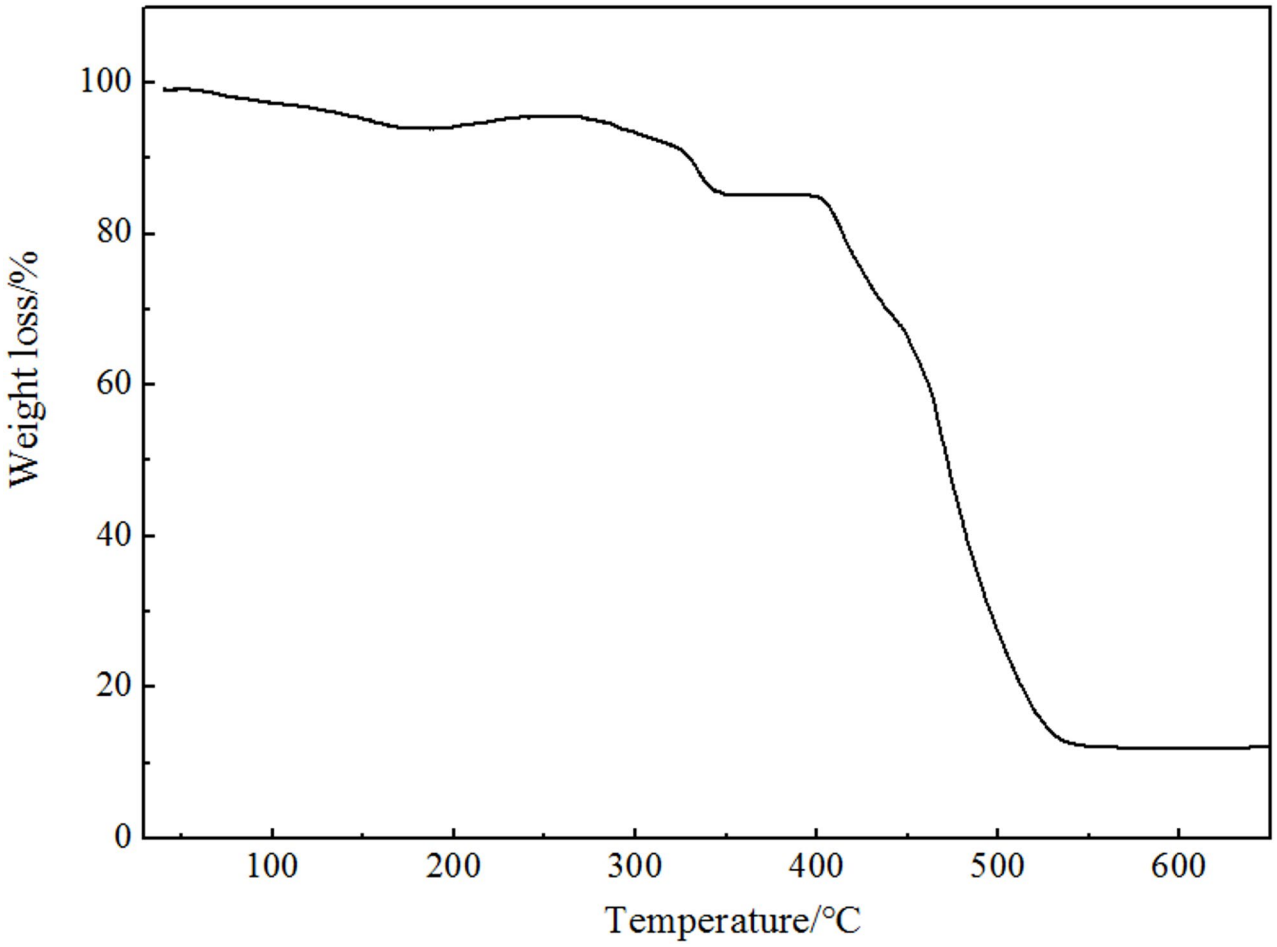

Fig. 4 Thermogravimetric (TG) curve indicating the thermal stability of the calcium(II) coordination polymer

Thermogravimetric analysis

The thermal stability curve of the Ca(II) coordination polymer is shown in Fig. 4. As shown in the Fig. 4, the Ca(II) coordination polymer undergoes three distinct phases of weight loss when subjected to heating. The first phase occurs at approximately 25–170 °C, with an observed weight loss of 5.85% (calculated: 5.09%), resulting from the removal of one lattice water molecule and absorbed water. The second stage, at around 170–347 °C, exhibits 14.91% weight loss (calculated: 15.28%), corresponding to the loss of three coordinated water molecules. The third, and most significant, weight loss occurs between 400 °C and 550 °C, resulting from the decomposition of the deprotonated 3-(3-carboxy-phenyl)-isonicotinic acid ligand. This process finally produces calcium oxide (CaO) as the final residue, with an overall weight loss of 87.26% (calculated: 84.15%). The thermal properties closely match the findings from elemental analysis and single-crystal X-ray diffraction, confirming the proposed composition and structural stability of the studied coordination polymer.

Structural description of Ca(II) coordination polymer

The asymmetric unit of the Ca(II) coordination polymer is shown in Fig. 5, while the selected bond lengths and angles are listed in Table 2. The one-dimensional (1D) chain structure, formed by the bridging effect of oxygen atoms from the carboxylate (COO^-) groups, is shown in Fig. 6. Furthermore, these 1D chains are connected through O–H···N hydrogen-bonding interactions, resulting in the formation of a two-dimensional (2D) layered framework, as depicted in Fig. 7. The three-dimensional (3D) supramolecular network, stabilized by π–π stacking interactions and O–H···O hydrogen bonds, is illustrated in Fig. 8. The asymmetric unit of the Ca(II) coordination polymer comprises one Ca(II) ion, one deprotonated 3-(3-carboxyphenyl)-isonicotinic acid ligand, three coordinated water molecules, and one lattice water molecule. Each Ca(II)

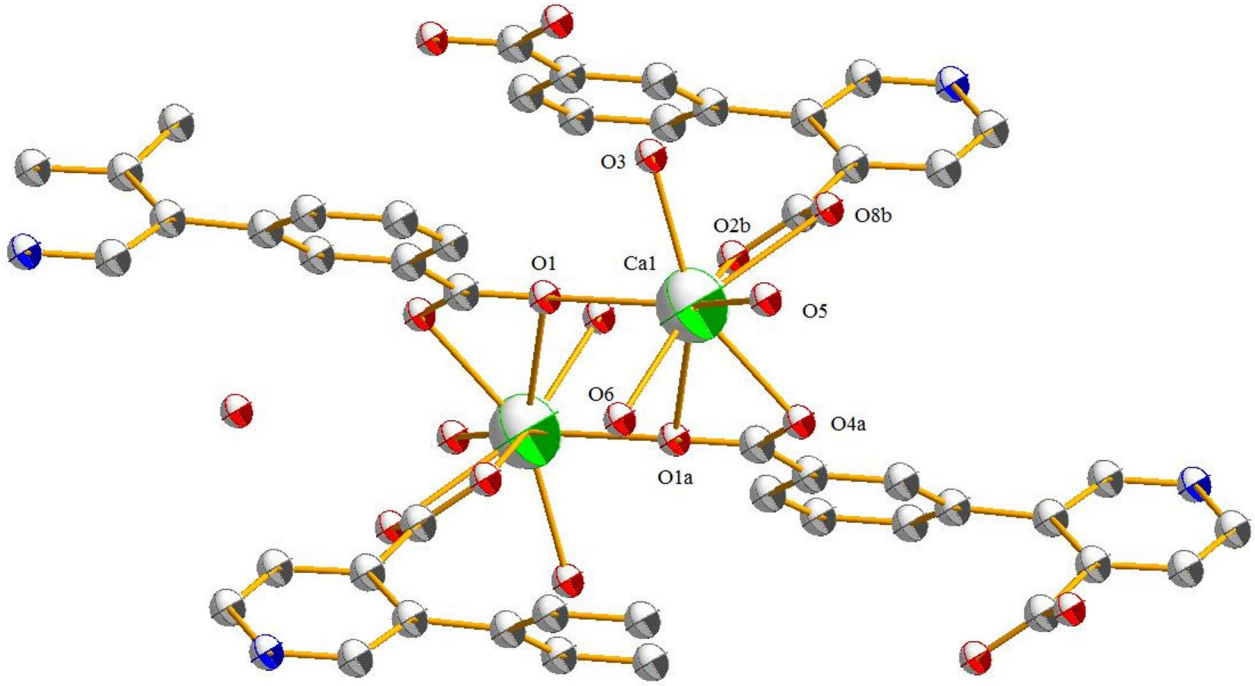

Fig. 5 The asymmetric unit of the Ca(II) coordination polymer (symmetry operation: a:-*x*, 1-*y*, 2-*z*; b:1-*x*, 1-*y*, 2-*z*)

ion is eight-coordinated, involving five oxygen atoms (O1, O1a, O4a, O2b, and O8b) from three separate deprotonated 3-(3-carboxyphenyl)-isonicotinic acid ligands and three oxygen atoms (O3, O5, and O6) from three coordinated water molecules. The coordination environment around the Ca(II) center has a distorted square antiprismatic geometry, with O1, O3, O2b, and O8b forming the lower base, and O5, O6, O1a, and O4a forming the upper base of the square antiprism. In the Ca(II) coordination polymer, the carboxylate O atoms of the deprotonated 3-(3-carboxy-phenyl)-isonicotinic acid ligands show two different coordination modes. The carboxyl oxygen atoms attached to the pyridine ring coordinate to a single Ca(II) ion in a bidentate mode, while those connected to the benzene ring bridge two Ca(II) ions in a tridentate manner. The bond angles around the Ca(II) center range from 50.25(4)° for O1a–Ca1–O4a to 154.85(5)° for O6–Ca1–O8b. The Ca–O bond lengths are as follows: Ca1–O1a = 2.7069(14) Å, Ca1–O1 = 2.3547(12) Å, Ca1–O4a = 2.4613(13) Å, Ca1–O6 = 2.4021(13) Å, Ca1–O8b = 2.5912(13) Å, Ca1–O2b = 2.4406(12) Å, Ca1–O5 = 2.3993(13) Å, and Ca1–O3 = 2.4174(15) Å. These bond lengths are consistent with those reported for similar Ca(II) coordination polymers in the literature [37, 38]. The Ca(II) coordination polymer forms a one-dimensional (1D) chain through the bridging effect of oxygen atoms from the carboxylate (COO^-) groups (Fig. 6). These 1D chains are further connected through O–H···N and O–H···O hydrogen bonds, along with π–π stacking interactions, to form a two-dimensional (2D) layered structure (Fig. 7) and extend into a three-dimensional (3D) supramolecular network (Fig. 8).

DFT calculations of the Ca(II) coordination polymer

The molecular electrostatic potential and orbital simulations of the Ca(II) coordination polymer were performed using the DMol3 module in Materials Studio 2020, with the generalized gradient approximation (GGA) from the Perdew-Burke-Emzerhof (PBE) functional employed for calculating the exchange-correlation functions. The ionic-electron interactions were simulated by optimizing the ultra-soft pseudomotif for each element in the Ca(II) coordination polymer. The geometry optimization parameters included an energy convergence tolerance of 1×10^{-5} Ha, a force convergence of 0.002 Ha A^{-1}, a maximum displacement of 0.005 A, and a self-consistent field tolerance of 1×10^{-6}. All Electron calculations were conducted using the DNP basis set. Density functional theory (DFT) calculations at the B3LYP/6-31G(d) level were used to determine the frontier molecular orbitals (Fig. 9) and electrostatic potential (Fig. 10). The frontier molecular orbitals of the Ca(II) coordination polymer show that the HOMO orbital (-0.25635

Table 2 Selected bond lengths and angles of Ca(II) coordination polymer symmetry operation: a:-*x*, 1-*y*, 2-*z*; b: 1-*x*, 1-*y*, 2-*z*.

Bond	d	Angle	(°)
Ca1-O1	2.3547(12)	O1-Ca1-O1a	74.10(4)
Ca1-O4a	2.4613(13)	O1-Ca1-O4a	124.21(5)
Ca1-O6	2.4021(13)	O1-Ca1-O6	76.92(5)
Ca1-O8b	2.5912(13)	O1-Ca1-O8b	128.23(4)
Ca1-O2b	2.4406(12)	O2b-Ca1-O1	85.57(4)
Ca1-O5	2.3993(13)	O5-Ca1-O1	135.64(5)
Ca1-O3	2.4174(15)	O1-Ca1-O3	78.18(5)
Ca1-O1a	2.7069(14)	O4a-Ca1-O1a	50.25(4)
		O4a-Ca1-O8b	79.28(5)
		O6-Ca1-O1a	76.76(4)
		O6-Ca1-O4a	85.96(5)
		O6-Ca1-O8b	154.85(5)
		O6-Ca1-O2b	144.25(5)
		O3-Ca1-O6	113.62(6)
		O8b-Ca1-O1a	107.89(4)
		O2b-Ca1-O1a	68.49(4)
		O2b-Ca1-O4a	78.45(4)
		O8b-Ca1-O2b	51.74(4)
		O5-Ca1-O1a	131.43(5)
		O5-Ca1-O4a	88.22(5)
		O5-Ca1-O6	76.27(4)
		O8b-Ca1-O5	82.98(4)
		O5-Ca1-O2b	134.28(4)
		O5-Ca1-O3	81.07(5)
		O3-Ca1-O1a	147.21(5)
		O3-Ca1-O4a	154.34(5)
		O5-Ca1-O8b	76.32(5)
		O3-Ca1-O2b	92.44(5)

Ha (-6.976 eV)) is mainly distributed on the six member ring, while the LUMO orbital (-0.13356 Ha (-3.634 eV)) is primarily distributed on the pyridine ring. The DFT energy gap is 0.12279 Ha (3.34 eV). The electrostatic potential (using the reverse rainbow scale with isosurface = 0.8) of the Ca(II) coordination polymer shows that red areas indicate higher potential values, while blue areas represent lower potentials. Blue signifies the highest electron contribution, whereas red denotes the least. Computational results reveal that regions with higher electrostatic potential are primarily concentrated in the six-membered carbon ring of the crystal framework, whereas areas with lower potential are mainly located near oxygen and nitrogen atoms.

Catalytic performance

The oxidation of benzyl alcohol with O_2 as the sole oxidant was selected as a model reaction to investigate the catalytic activity of the Ca(II) coordination polymer. The oxidation process was highly dependent on reaction temperature (Fig. 11). The catalytic activity of the blank (without catalyst) was very low, with a benzyl alcohol conversion of 5.5% for the oxidation of benzyl alcohol at 80°C within 2 h under 0.5 MPa of O_2 using THF as the solvent. The Ca(II) coordination polymer exhibited good activity and selectivity for benzaldehyde in the selective oxidation of benzyl alcohol, with benzoic acid as the primary by-product and small amounts of benzyl benzoate. At a lower temperature of 70 ℃, the reaction proceeded slowly, resulting in only 40.4% conversion of benzyl alcohol with a benzaldehyde yield of 30.3% under 5 bar of O_2 for 2 h in THF. As the reaction temperature increased to 80 ℃, the conversion improved significantly, reaching a 68.7% conversion and a 40.1% yield of benzaldehyde. When the temperature was elevated to 90 °C, the

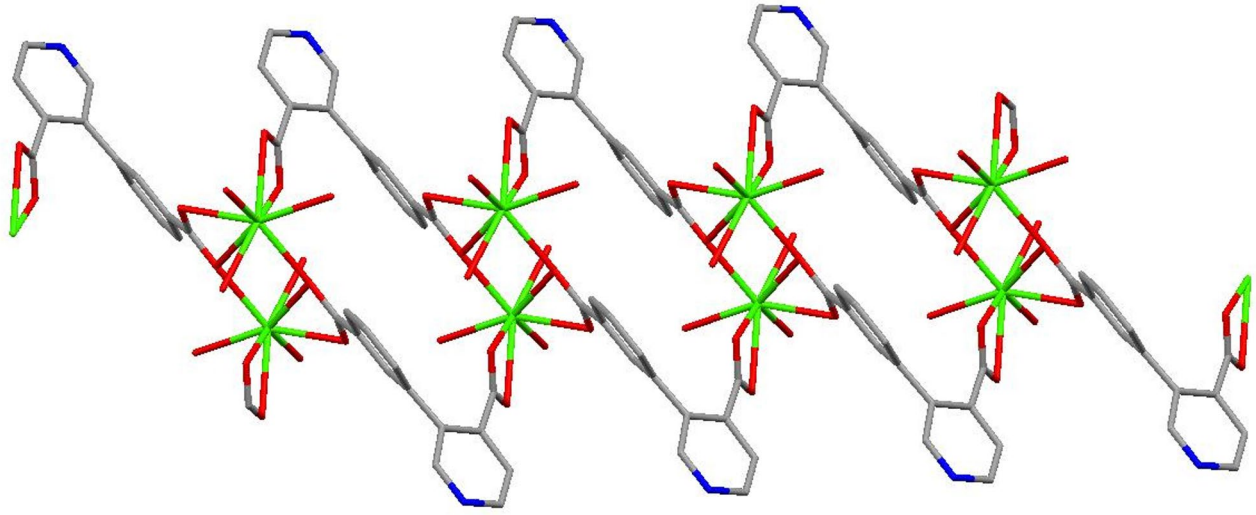

Fig. 6 1D chain structure of the Ca(II) coordination polymer

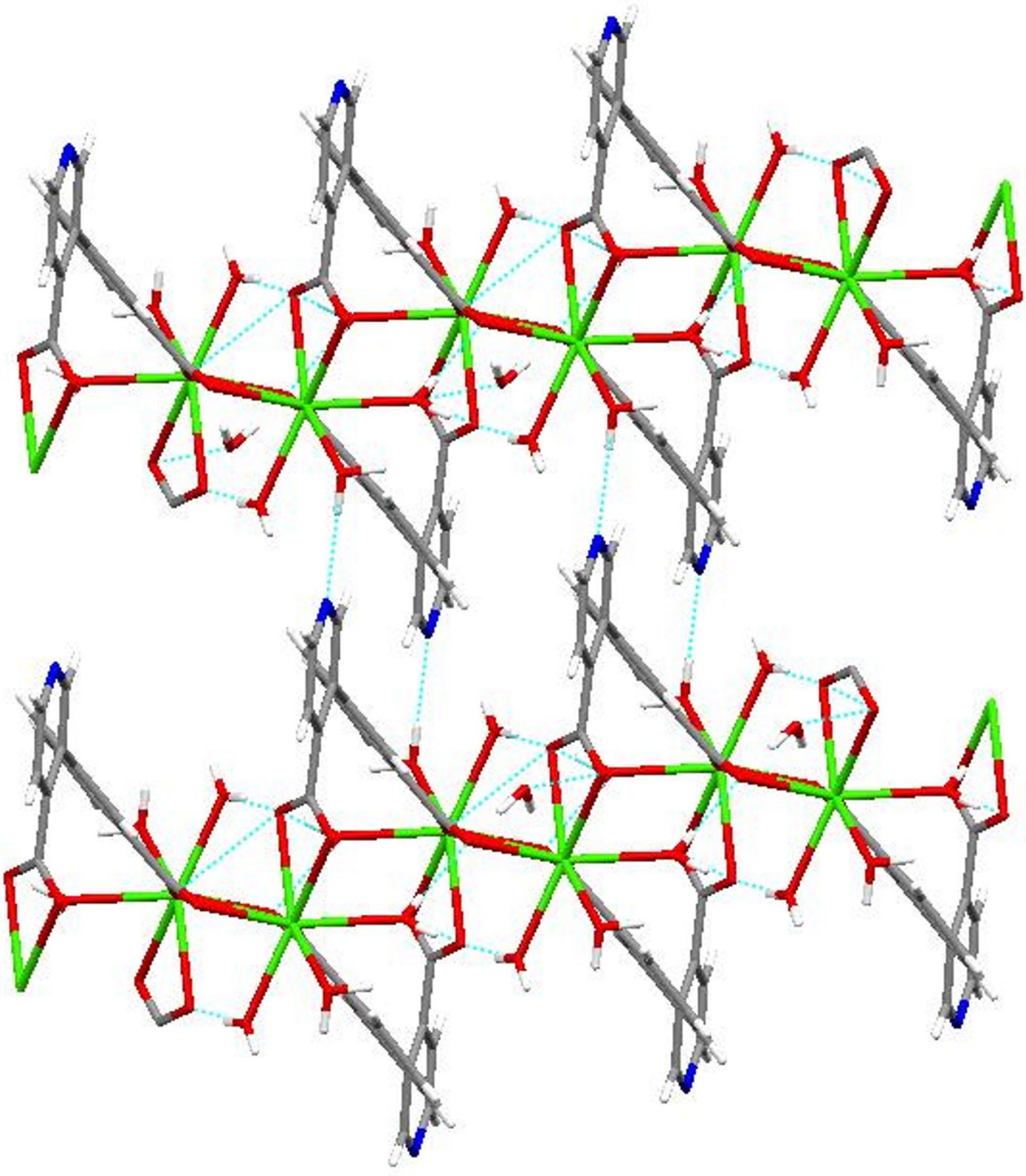

Fig. 7 2D layered structure of the Ca(II) coordination polymer

conversion of benzyl alcohol increased to 78.2%. However, the benzaldehyde yield declined to 37.5% due to the formation of benzoic acid through over-oxidation. These results indicate that 80 °C provides the optimal balance between high benzyl alcohol conversion and benzaldehyde yield. For comparison, Table

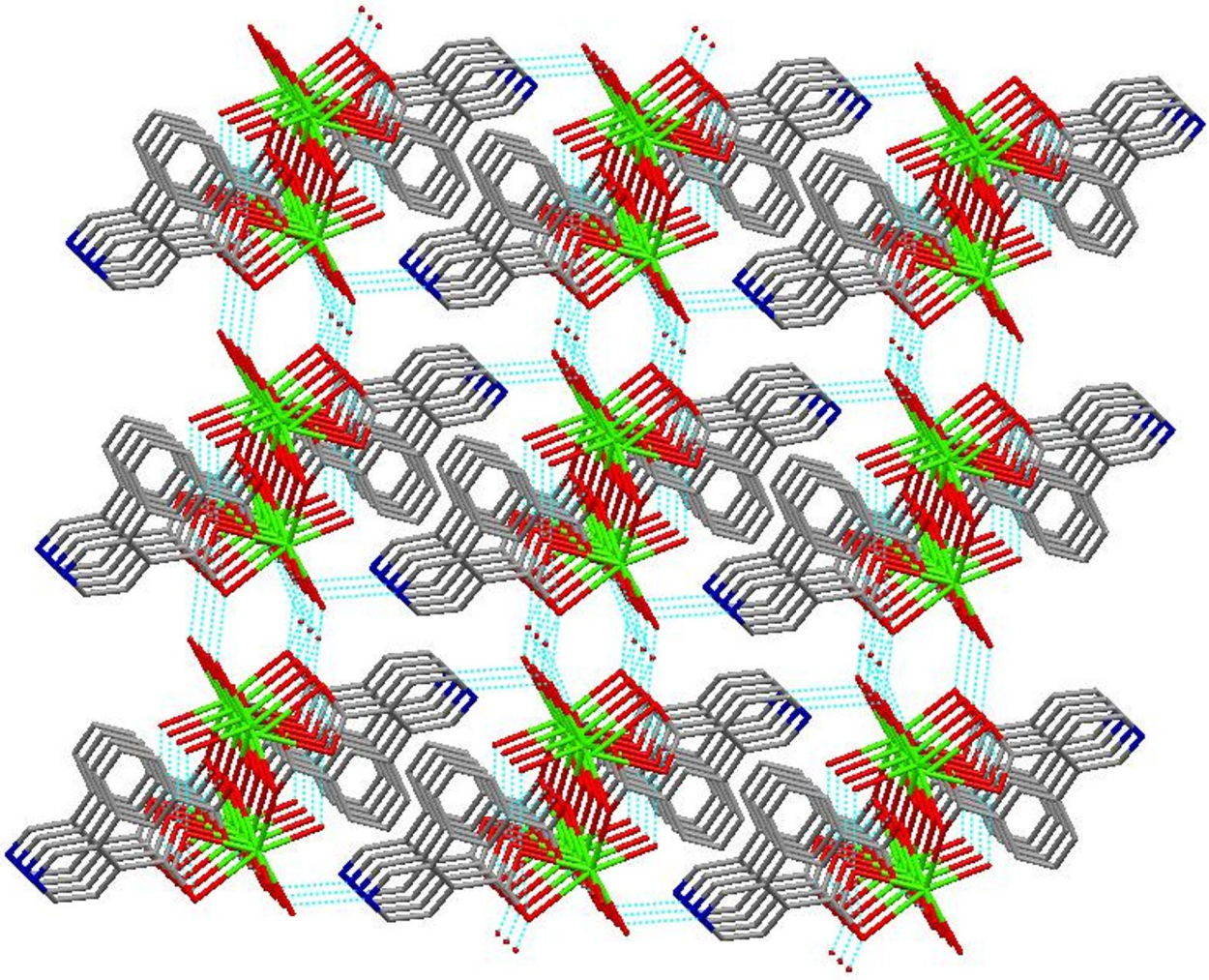

Fig. 8 3D network structure of the Ca(II) coordination polymer

3 shows that the Ca(II) complex synthesized by one-pot synthesis method from disodium 4-formylbenzene-1,3-disulfonate, isonicotinic acid hydrazide, and $Ca(ClO_4)_2.2H_2O$ achieved a benzyl alcohol conversion of 57.0% and a benzaldehyde yield of 34.8% at 130 ℃ under 10 bar O_2 within 6 h in THF [39]. The conversion of benzyl alcohol and the yield of benzaldehyde were 53.8% and 44.8%, respectively, over Ca(II) coordination polymer $[Ca(L)_2(H_2O)_2]_n$ (L = 2-carboxybenzaldehyde) at 130 °C for 3 h under 10 bar of O_2 [40]. The synthesized Ca(II) coordination polymer exhibited remarkable catalytic performance in the conversion of benzyl alcohol, achieving high activity under mild conditions and demonstrating excellent efficiency and potential for practical use.

Catalyst recyclability is a critical parameter for evaluating the practical applicability of heterogeneous catalysts. To assess the stability of the Ca(II) coordination polymer, recycling tests were conducted using the oxidation of benzyl alcohol to benzaldehyde as a model reaction. The reaction was carried out at 80 °C under 5 bar O_2 for 2 h in THF, with the catalyst recovered after each cycle by centrifugation, washed with ethanol, and dried at 80 °C before reuse. As shown in Fig. 12, the freshly prepared Ca(II) coordination polymer exhibited 68.7% benzyl alcohol conversion with a 40.1% benzaldehyde yield at 80 °C under 5 bar O_2 in THF for 2 h. The recycled Ca(II) coordination polymer exhibited excellent catalytic stability, maintaining benzyl alcohol conversions of 67.9%, 67.3%, and 67.5%

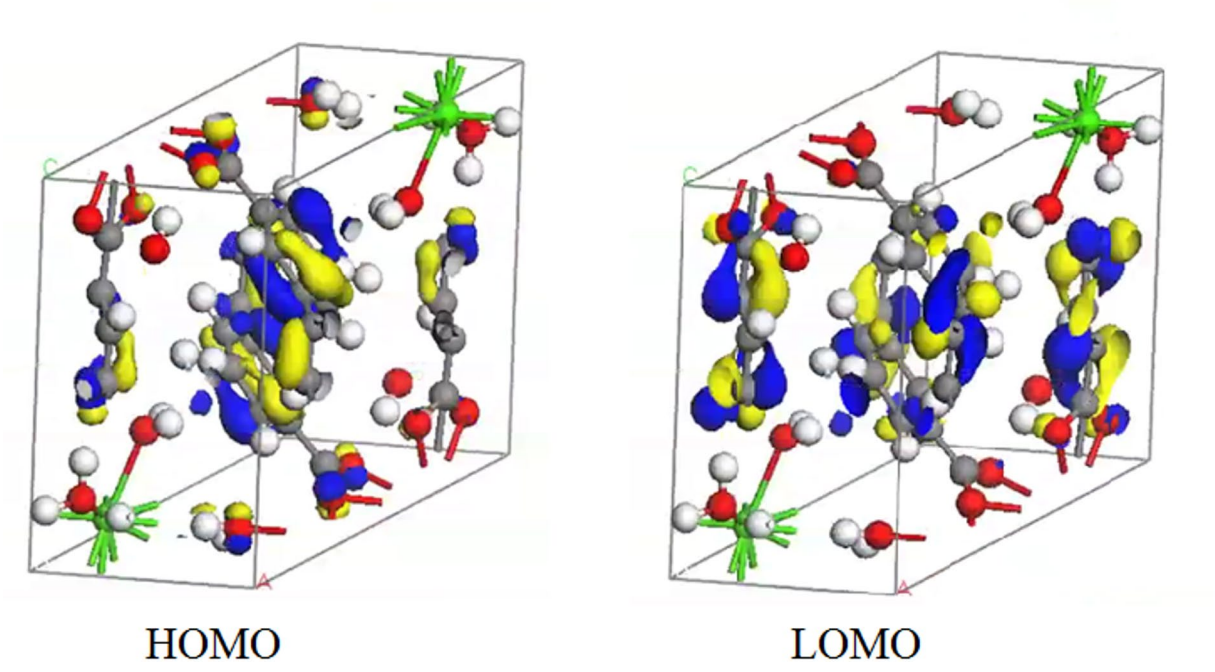

Fig. 9 The frontier molecular orbitals of the Ca(II) coordination polymer

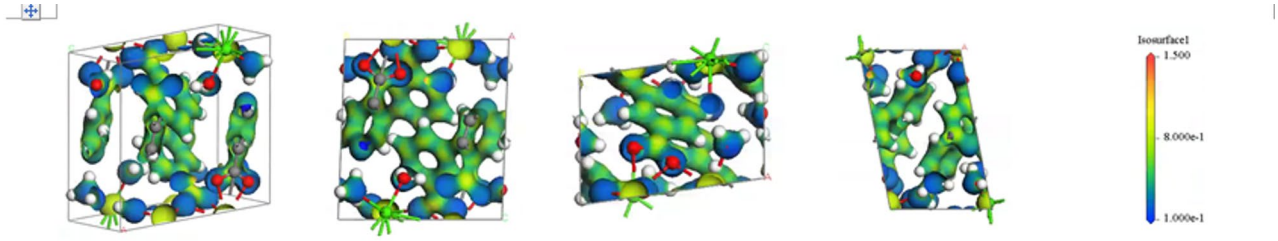

Fig. 10 Electrostatic potential of the Ca(II) coordination polymer

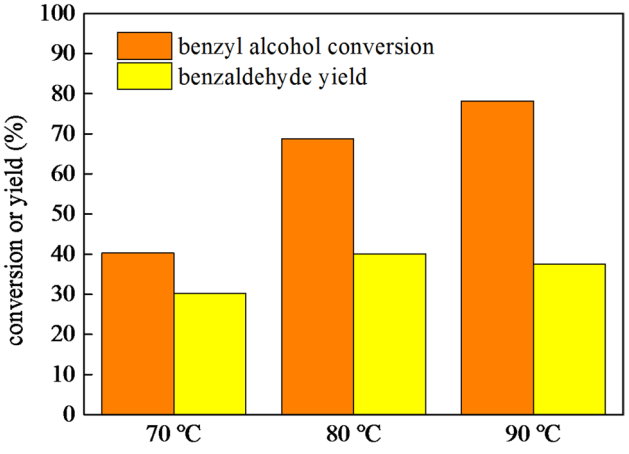

Fig. 11 Catalytic performance of Ca(II) coordination polymer for benzyl alcohol oxidation in THF (reaction conditions: benzyl alcohol (1.0 mmol), catalyst (0.02 g), THF (7 mL), 5 bar of O_2, 2 h)

Table 3 Comparison of catalytic performance of the Ca(II) complex in the oxidation of benzyl alcohol

Ref	Reaction conditions	Conversion of benzyl alcohol	Benzaldehyde yield
this work	80 °C, 5 bar O_2, 2 h	68.7%	40.1%
39	130 ℃, 10 bar O_2, 6 h	57.0%	34.8%
40	130 °C, 10 bar O_2, 3 h	53.8%	44.8%

over three consecutive reaction cycles. Benzaldehyde yields remained highly consistent at 40.0%, 39.5%, and 39.8%, further confirming the catalyst's excellent stability under the given reaction conditions.

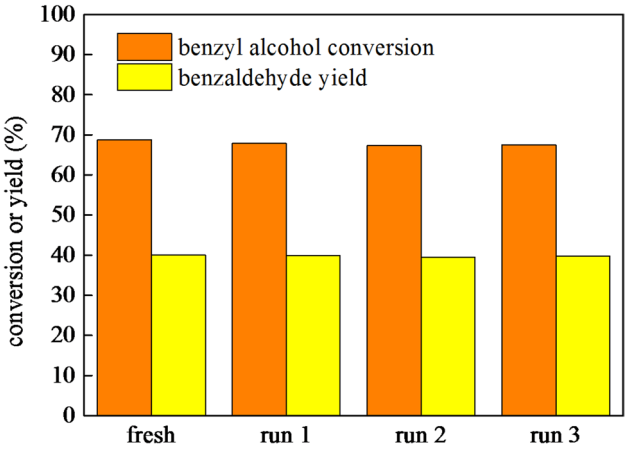

Fig. 12 Recyclability of the Ca(II) coordination polymer for benzyl alcohol oxidation (reaction condition: 1 mmol of benzyl alcohol, 7 mL of THF, 0.02 g of complex, 80 ℃, 5 bar of O_2, 2 h)

Conclusions

A novel Ca(II) coordination polymer, $[Ca(L)(H_2O)_3]_n \cdot H_2O$ was synthesized by assembling 3-(3-carboxy-phenyl)-isonicotinic acid (H_2L), NaOH, and calcium perchlorate tetrahydrate. Its structure was determined using elemental analysis, various spectroscopic studies, thermogravimetric analysis, and single-crystal X-ray diffraction. The crystallographic study revealed that each Ca(II) ion is eight-coordinated, bonding with five oxygen atoms from three different L ligands and three oxygen atoms from three coordinated water molecules, forming a distorted square antiprism geometry. DFT analysis further provided valuable insights into its electronic structure, revealing a HOMO–LUMO energy gap of 0.12279 Ha (3.34 eV). The electrostatic potential results indicate that regions with higher electrostatic potential are mainly concentrated in the six-member carbon ring structures of the Ca(II) coordination polymer, while areas with lower potential are mainly located near oxygen and nitrogen atoms. Catalytic studies revealed that the Ca(II) coordination polymer exhibits remarkable activity, achieving a 68.7% conversion of benzyl alcohol and a 40.1% yield of benzaldehyde under mild oxidative conditions (5 bar O_2, 80 °C, 2 h in THF). These findings highlight its high efficiency, structural stability, and potential as a promising heterogeneous catalyst for selective oxidation reactions.

Supplementary Information

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Supplementary Material 1

Author contributions

All authors contributed to the study. Tai X.S. and Wang L.H. conceived the project and supervised the study, and performed experiments and collected the data. Al-Resayes S.I. and Azam M. analyzed and interpreted the data. Tai X.S. and Azam M. drafted the manuscript. All authors revised the manuscript critically and approved the final version.

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Data availability

CCDC 2478045 contains the supplementary crystallographic data for the Ca(II) coordination polymer. These data can be obtained free of charge viahttps://www.ccdc.cam.ac.uk/structures/search? Ccdc=2478045&Author=Xi-Shi&Access=referee, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

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