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The synthesis and characterization of CCOFs

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ABSTRACT

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The comparison of the properties of CCOFs

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Covalent organic frameworks (COFs) are a class of crystalline, porous organic polymers with highly ordered structures. They are composed mainly of light elements (H, B, C, N and O) connected by dynamic covalent bonds. The specificity of their physical and chemical properties: high crystallinity, customizable pore size and shape, large specific surface area, and high stability in a wide range of solvents make COFs unique among all types of porous organics. The synthesis of covalent organic frameworks is mainly classified into: solvothermal synthesis, microwave synthesis, ionothermal synthesis, and room temperature synthesis. Chiral covalent organic frameworks (CCOFs), which are materials constructed from organic structural units with enantiomeric purity and linker substituents and assembled by condensation reactions, are a subtype of COFs with well-defined crystal structures. During this experiment, Tp-based CCOFs materials were synthesized and characterized.

Key words: Covalent organic frameworks; synthesis; CCOFs

CONTENTS

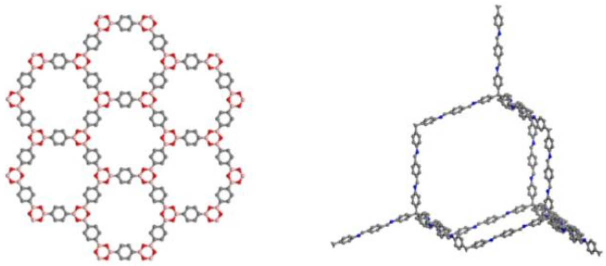
1 INTRODUCTION

1.1 Background of COFs and chiral COFs

With the advancement of science and technology, porous materials have garnered increasing attention and development. Among them, the most noteworthy organic porous materials - covalent organic frameworks (COFs) - have experienced unprecedented progress over the past century, owing to their favorable physical and chemical properties. COFs are primarily composed of lightweight elements such as C, H, B, O, and N, among others, which contribute to their characteristic of being low-density lightweight materials [1]. Covalent organic frameworks (COFs) are a class of polymers that can be entirely predicted and designed through guided polymerization of building blocks and geometric coordination between monomers. The unique structure of COFs, characterized by a closed molecular space and interfaces, facilitates their interactions with electrons, ions, molecules, photons, and more. This distinct feature greatly expands the potential for designing and developing COF materials[2]. COFs and CCOFs are both types of covalent organic frameworks, but they differ in terms of their composition and properties.

1.1.1 Theory of COFs and chiral COFs

From a molecular level analysis, COFs are composed of organic molecules with strong covalent bonds (B-O, C-N, C=N), which contribute to the excellent stability of COFs under chemical reagents and high temperatures. COFs can be classified into two main categories: two-dimensional structures COFs and three-dimensional structures COFs, as illustrated in FIGURE 1. From a topological perspective, 2D COFs consist of a honeycomb-like planar structure, while 3D COFs exhibit a spatial network structure. Whether it is the planar network structure of 2D COFs or the spatial network structure of 3D COFs, both demonstrate excellent crystallinity.



二维COF (COF-1)

三维COF（COF-300）

FIGURE 1. Schematic Diagram of COFs

In chemical reactions, the stereochemistry of chiral molecules has a significant impact on the process and outcome of the reaction. Due to the different symmetries, chiral molecules can exist as two or more enantiomers, each possessing distinct physical and chemical properties. These enantiomers may exhibit markedly different chemical reactivity, such as their impact on optical rotation, interaction with other chiral compounds, reaction rates, and product selectivity, among others. Chirality aids in understanding and designing the properties and reaction behavior of molecules, and it facilitates the development of new drugs and materials.

Both COFs and chiral COFs are types of crystalline materials, but they differ in terms of their composition and properties. COFs are porous materials composed of organic molecules connected by covalent bonds. They are typically synthesized by forming covalent bonds between organic building units, resulting in highly ordered crystalline structures. COFs exhibit features such as high surface area, tunable pore size, and chemical stability, making them suitable for a wide range of applications such as gas storage, separation, and catalysis.

Chiral COFs are similar to COFs, but they contain both organic and inorganic components. In chiral COFs, organic building units are connected to inorganic metal nodes via covalent bonds, forming organic-inorganic hybrid materials. Compared to COFs, chiral COFs exhibit enhanced stability, mechanical strength, and their properties can be tuned by modifying the nature and quantity of the inorganic components. They also hold potential applications in catalysis, sensing, energy storage, and other fields.

In summary, the main difference between COFs and chiral COFs lies in their composition, with chiral COFs incorporating both organic and inorganic components, thereby imparting improved stability and tunability of properties.

1.1.2 Applications of COFs and CCOFs

In the aspect of gas storage and adsorption, COFs possess unique characteristics such as low density, high specific surface area, controllable pore size distribution, and excellent stability, making them highly capable in gas storage and adsorption. COFs materials are primarily used for the storage of methane, hydrogen, and ammonia. According to the congratulatory message published by Nature to commemorate the 15th anniversary of COFs, COFs materials are regarded as one of the most promising gas adsorption materials available today.

CCOFs (Chiral Covalent Organic Frameworks), with their highly tunable pore size and surface area, are excellent materials for gas storage and adsorption. Firstly, the covalent bonds connecting the units in CCOFs can form highly ordered pore structures. The size of these pores can be adjusted by controlling the structure and arrangement of the organic units to accommodate the adsorption and storage requirements of different gases. Secondly, due to the high specific surface area and porous structure of CCOFs, they can accommodate a large number of gas molecules. Additionally, CCOFs exhibit highly selective gas adsorption capabilities, meaning they can selectively adsorb certain gas molecules while repelling others. Finally, the adsorption and storage performance of CCOFs can be optimized by adjusting their pore structures and surface chemistry. This allows them to meet the requirements of various gas storage and adsorption applications. Therefore, as a novel material for gas storage and adsorption, CCOFs have broad prospects for application.

In the field of catalysis, COFs, with their high porosity, chemical stability, and design versatility, have emerged as candidates for efficient heterogeneous catalytic solutions[3]. COFs are typically post-synthetically modified with chiral functional groups for asymmetric catalysis applications [4]. Due to their specific and spatially defined orientations, these functional groups induce specific interactions with reagents and substrates in the pore interface region, thereby facilitating the selective formation of enantiomers. Therefore, chiral COFs have been synthesized for asymmetric catalysis applications [5].

In the field of biomedical applications, the tunable porosity and multifunctional pore walls of COFs, achieved through pre- or post-synthetic modifications, allow for the preparation of customized COFs capable of efficient drug delivery with highly controlled diffusion and release rates. Additionally, the high covalent reversibility found in many COF structures can be advantageous for biomedical applications, as strategically designed COFs using appropriate monomers and linkers can undergo controlled biodegradation after fulfilling their intended tasks within the organism[6]. CCOFs can be utilized as drug delivery carriers due to their ability to encapsulate drugs within their porous structures, protecting them from degradation and facilitating controlled release over time. The high surface area of CCOFs also enables high drug loading capacity.

Furthermore, the tunable pore size of CCOFs allows for selective drug release based on the size and chemical properties of the drugs. This is particularly useful in targeted drug delivery, where drugs are released only at specific sites in the body, minimizing side effects and increasing the effectiveness of treatment. Overall, CCOFs have the potential to enhance the efficacy and safety of drug delivery, making them an exciting research area in the pharmaceutical field.

1.2 The synthesis methods of chiral COFs

Chiral organic covalent frameworks (COFs) refer to three-dimensional framework structures with special structures and properties that are constructed from chiral organic molecules. The synthesis of chiral organic COFs is of great significance for the development of new functional materials, drugs, and catalysts.

Compared to achiral covalent organic frameworks, chiral organic frameworks have received less attention. Currently, the synthesis methods of chiral organic COFs mainly include enantioselective chemical methods, dynamic covalent chemistry methods, and multiple bond construction methods. Among them, enantioselective chemical methods involve the use of chiral inducers, chiral ligands, or chiral catalysts to promote the asymmetric reactions of chiral organic molecules and achieve the construction of chiral organic molecules. Dynamic covalent chemistry methods utilize principles of molecular recognition and self-assembly to connect chiral organic molecules through reversible covalent bonds. Multiple bond construction methods utilize the construction of conjugated systems and control the connection modes and positions of bonds to achieve the construction of chiral organic covalent frameworks[20].

The construction mechanism of chiral organic covalent frameworks involves processes such as chiral recognition, chiral transfer, and chiral amplification. Chiral recognition refers to the selective interaction between chiral organic molecules and other molecules or ions, including intermolecular hydrogen bonding, van der Waals forces, charge transfer, and other interactions. Chiral transfer refers to the process of transferring chiral information from chiral inducers or chiral ligands to chiral organic molecules. Chiral amplification refers to the process where chiral information continuously expands during the reaction, leading to highly chiral compounds by amplifying the differences in chirality.

In the construction of chiral COF materials, it is necessary to balance and resolve the conflict between material asymmetry and high crystallinity. Therefore, precise control over the chiral characteristics, functional group types, and crystallinity of chiral COF materials is an important task in this process[17].

2 EXPERIMENT

2.1 Chemcials and apparatus

2.1.1 Chemicals

TABLE 1.Chemicals

Chemicals	Formula	Concentration（%）
MOP	$C_9H_6O_6$	98
Mesitylene	C_9H_{12}	98
1,4-Dioxane	$C_4H_8O_2$	99.5
(R)-1-PEA	$C_8H_{11}N$	99.65
(S)-1-PEA	$C_8H_{11}N$	99.71
Methanol	CH_2OH	99.5

2.1.2 Experimental apparatus

TABLE 2. Experimental apparatus

Apparatus	Standard
Analytical balance	SQP
Oil bath	GG-17
Vacuum filter	D16C
Ultrasonic Cleaner	KQ-300DE
Magnetic stirrer	ZNCL-BS140*140

2.2 Sample Preparation

1,3,5-triformylphloroglucinol (32mg, 0.15mmol) and p-phenylenediamine (24.3mg, 0.45mol) were mixed in a Pyrex tube. 3ml of a mixed solution of trimethylbenzene/diethyl ether (1:1 V/V) was added into the Pyrex tube. Either (S)-alpha-methylbenzylamine or (R)-alpha-methylbenzylamine (19.34 μl, 0.15mol) separately was added into the mixture. The mixture was then subjected to ultrasonication to achieve a homogeneous dispersion, followed by three cycles of degassing. The test tube was sealed and heated at 120℃ under closed conditions for three days. After heating, it was cooled to room temperature and collected.

2.3 Characterization Methods

Characterization analysis of chemical substances aims to determine the chemical and physical properties, as well as structural features of substances to gain a deeper understanding of their nature and behavior. This analysis typically involves the use of various instruments and techniques. Characterization analysis of chemical substances has significant importance in many fields such as materials science, pharmaceuticals, biology, environmental science, and chemical engineering.

In materials science, characterization analysis can be used to determine the purity, crystal structure, and lattice parameters of materials, thus optimizing their preparation and performance. In pharmaceuticals, characterization analysis can be employed to ascertain the purity, composition, and structure of drugs to ensure their quality and safety. In environmental science, characterization analysis can be used to detect the types and concentrations of pollutants and determine their sources and migration pathways. In chemical engineering, characterization analysis can aid in the design and optimization of chemical reactions and manufacturing processes.

Therefore, characterization analysis of chemical substances is crucial for achieving better product and process designs, ensuring product quality and safety, and safeguarding the environment and human health.

2.3.1 X-ray Diffraction（XRD）

X-ray diffraction (XRD) is a commonly used material characterization technique that can be employed to analyze crystal structure and properties. In XRD testing of chiral COFs (Covalent Organic Frameworks) materials, valuable crystal structure information such as lattice constants and crystal symmetry can be obtained. Additionally, XRD testing enables the determination of the crystallinity of chiral COFs materials, which refers to the quantity and size of crystal phases present in the material. This information allows for the analysis and investigation of the physical and chemical properties of chiral COFs materials[18].

In addition, X-ray diffraction (XRD) can also be used to determine the structure of molecules, especially biological molecules such as proteins and nucleic acids, and it is widely applied in the fields of biochemistry, structural biology, and materials science. The working principle of X-ray diffraction is based on the diffraction effect of crystals on X-rays. When X-rays are irradiated onto a crystal, the regularly arranged atoms within the crystal lattice will diffract (deviate) the X-rays. The diffracted X-rays form a characteristic pattern of spots on a detector, which can be used to determine the arrangement of atoms in the crystal.

2.3.2 Fourier Transform Infrared Sepectroscopy（FTIR）

FTIR stands for Fourier Transform Infrared Spectroscopy. It is used to obtain the infrared spectrum of a substance, which represents its absorption or emission of infrared radiation. The measured spectrum can be used to identify the chemical composition of a substance, specifically the types of functional groups present, by comparing it with spectral libraries.

In this method, the sample is irradiated with infrared radiation. Some of the infrared radiation is absorbed by the sample, while the rest passes through. In this process, the molecular absorption and transmission are displayed in the spectrum, forming the molecular fingerprint of the sample. The fingerprint of the sample is characterized by absorption peaks, which correspond to the changing frequencies between atomic bonds in the material. Since different materials have different atomic compositions, the infrared spectra of different substances are unique.

The diagram below (FIGURE 2) illustrates how an FTIR spectrometer works. During the measurement process, an infrared beam enters the interferometer and is directed to the beam splitter. The beam is then split and directed towards a fixed mirror and a moving mirror. Subsequently, the beams are recombined and directed onto the sample.

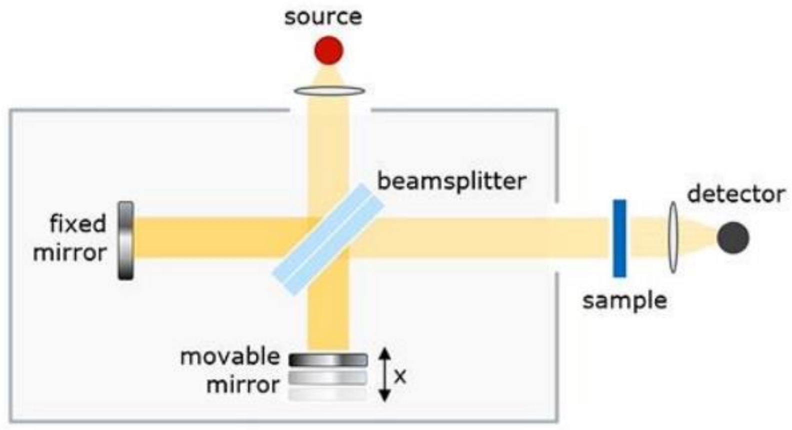


FIGURE 2. FTIR working principle

2.3.3 Scanning electron microscope (SEM)

Scanning Electron Microscopy (SEM) is a microscope that uses a focused electron beam to image the surface of a sample. When the electron beam scans the sample's surface, it interacts with the sample, and the resulting signals can be used to generate an image. SEM is particularly useful for examining the surface morphology of various materials, including metals, ceramics, and biological samples. It can provide high-resolution images and has a very large depth of field, allowing researchers to examine the surface features and topography of the sample in detail. SEM is also used in various analysis techniques, including Energy-Dispersive X-ray Spectroscopy (EDS) and Electron Backscatter Diffraction (EBSD). EDS allows for the determination of the sample's chemical composition, while EBSD is used to study the sample's crystal structure and orientation. SEM has a wide range of applications, including materials science, nanotechnology, biomedical research, and forensic science. It is a powerful tool for academic research and industrial quality control.

2.3.4 Circular dichroism（CD）

Circular Dichroism (CD) is a reliable method for determining the chirality of compounds and is a spectroscopic technique used to analyze molecular chirality. This technique measures the difference in absorption of left-handed circularly polarized light and right-handed circularly polarized light by a sample to obtain its CD spectrum. Circular dichroism can be used to analyze the chirality, conformation, and stability of molecules, especially in the fields of biochemistry, biophysics, and medicinal chemistry. The principle of circular dichroism is based on the differential absorption of circularly polarized light by chiral molecules. When left-handed circularly polarized light and right-handed circularly polarized light pass through a chiral molecule, both types of light are absorbed, but to different extents. By measuring the difference in absorption of left-handed and right-handed circularly polarized light in the sample, the CD spectrum can be obtained. In a CD spectrum, positive values indicate greater absorption of left-handed circularly polarized light, while negative values indicate greater absorption of right-handed circularly polarized light by the sample. Circular dichroism has broad applications. In biochemistry, it can be used to study the conformation, folding, and stability of proteins and nucleic acids, as well as the interaction of small molecules with them. In medicinal chemistry, circular dichroism can be used to analyze the structure and stability of chiral compounds and evaluate the interaction between drug molecules and proteins. Additionally, circular dichroism can be used to study changes and interactions in macromolecular structures and analyze the conformation and properties of optically active molecules.

3 RESULTS

3.1 Characterization and analysis of sample

The characterization methods of covalent organic frameworks (COFs) used in this study include circular dichroism (CD), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR).

3.2 Analysis of XRD

The X-ray diffraction patterns of (R)-TpPa-1 and (S)-TpPa-1 obtained in the experiment are shown in Figure 3.1. Figure (a) presents a comparison of the powder diffraction patterns of (R)/(S)-TpPa-1 with the simulated TpPa-1. Figure (b) displays the simulated crystal lattice of TpPa-1. Figures (c) and (d) illustrate the schematic representation of the calculated molecular pore size and interlayer spacing using mathematical algorithms.

Based on the crystal plane indices of TpPa-1 and the data from the XRD pattern, we can calculate the molecular pore size using the Bragg equation:

$$d = \frac{n\lambda}{2sin\theta} \qquad （1）$$

$\lambda = 1.5406Å$

$\theta =$ Glancing angle

$n =$ Diffraction order

$d =$ Layer spacing（Å）

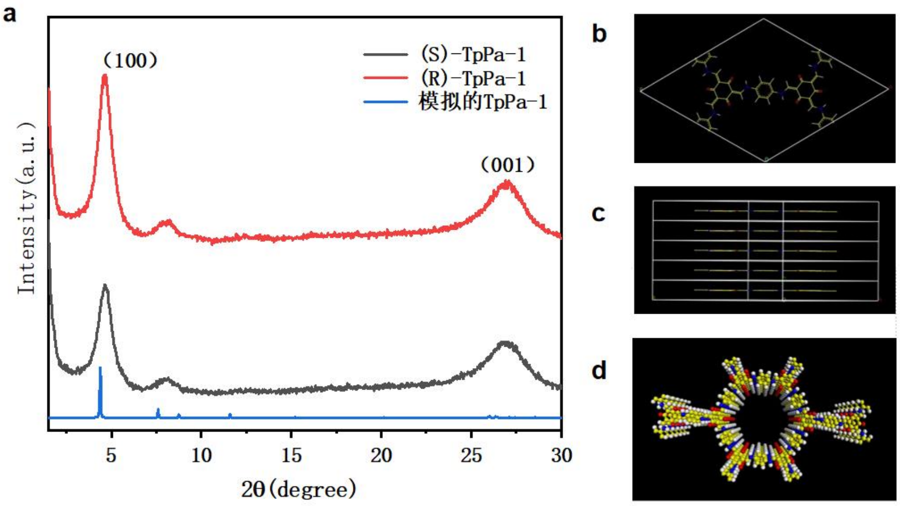


FIGURE 3. (a) XRD spectrum and its theoretical simulated spectrum for TpPa-1 AA stacking; (b) Computer-simulated top view of the unit cell; (c) Side view of the unit cell; (d) Computer-simulated TpPa-1 AA stacking unit cell structure.

TABLE 3.(R)-TpPa-1Lattice coefficient

No.	Theta (°)	Interplaner spacing d(Å)	Miller indices(hkl)
1	4.65	18.988	100
2	26.7	3.336	001

TABLE 4.Lattice coefficient of (S)-TpPa-1

No.	2 Theta (°)	Interplaner spacing d(Å)	Miller indices (hkl)
1	4.378	18.866	100
2	25.986	3.336	001

The powder X-ray diffraction (PXRD) pattern of (R)/(S)-TpPa-1 (Figure 3 (a)) shows distinct diffraction signals at 4.5°, 8.31°, and 27.06°, which are in good agreement with the powder XRD pattern of TpPa (Figure 3 (a)) at 4.4°, 8.75°, and 26°.

By performing multi-peak fitting and calculations using the Bragg equation, the pore size of (R)-TpPa-1 is determined to be 18.988 Å, and the interlayer spacing (as shown in Figure 3 (c)) is 3.336 Å. Similarly, the pore size of (S)-TpPa-1 is determined to be 18.866 Å, and the interlayer spacing (as shown in Figure 3 (c)) is 3.336 Å.

In order to observe the crystallinity of the synthesized chiral COFs, XRD analysis was conducted on the products and TpPa. From the graph, the peak intensity at (100) is observed in both (R)-TpPa-1 and (S)-TpPa-1. At the peak position (001).

3.2.1 Analysis of FTIR

FTIR stands for Fourier Transform Infrared Spectroscopy. It is a technique used for analysis using an infrared spectrometer. In FTIR analysis, the sample is exposed to a series of infrared light of different wavelengths. These lights are absorbed by the chemical bonds present in the sample, resulting in a unique infrared spectrum. This spectrum displays the types and quantities of chemical bonds present in the sample, enabling the determination of its composition and structure.

FTIR spectra can exhibit the vibrational modes of various chemical bonds in compounds, including C-H, O-H, N-H, and C=O, among others. FTIR spectra can also reveal interactions between functional groups and compounds, such as hydrogen bonding and van der Waals forces. Therefore, FTIR spectra can be used for compound identification, analysis of their structures, detection of pollutants, and determination of reaction mechanisms, among other applications. Analysis of the FTIR spectra of (R)-TpPa-1 and (S)-TpPa-1 reveals absorption at 1600 cm-1, indicating the presence of carbon-carbon double bonds (1642 cm-1 corresponds to the stretching vibration of carbon-carbon double bonds). At 1500 cm-1, different forms of ring stretching vibrations are observed, indicating that both (R)-TpPa-1 and (S)-TpPa-1 have a cyclic structure. The stretching vibration of the C-N bond is observed at 1250 cm-1, indicating that both (R)-TpPa-1 and (S)-TpPa-1 retain the cyclic structure of TpPa-1 and the carbon-nitrogen single bond. The FTIR spectra are shown in FIGURE 3.

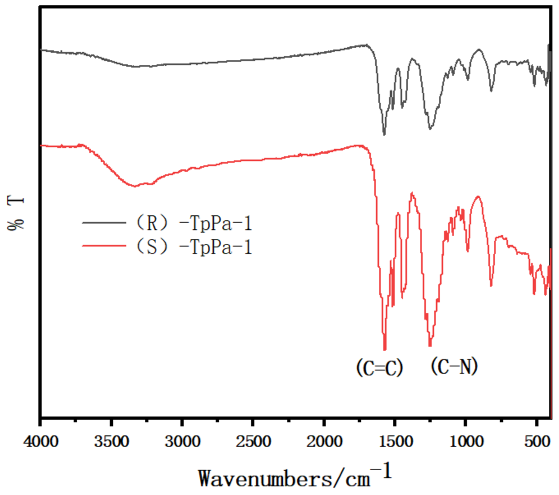
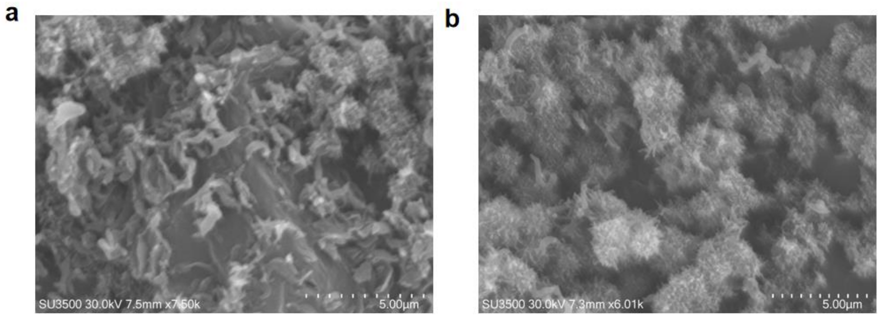


FIGURE 4. FTIR spectra of (R)-TpPa-1 and (S)-TpPa-1

3.2.2 Analysis of SEM

The SEM scan images reveal that the SEM scan image of (R)-TpPa-1 shows a flower-shaped flake-like structure, as shown in Figure 3.3a. On the other hand, the SEM scan image of (S)-TpPa-1 exhibits a spherical and porous structure, as shown in Figure 3.3b. Both images correspond to the characteristic porous and aggregated structure of CCOFs observed in SEM scans. The SEM scan images of (R)/(S)-TpPa-1 obtained from the experiment are shown in Figure 3.3.



PICTURE 5. (a) SEM of (R)-TpPa-1; (b) SEM of (S)-TpPa-1

3.2.3 Analysis of CD

Circular dichroism (CD) spectroscopy can be used to analyze the structure and stability of chiral compounds, as well as evaluate the interactions between drug molecules and proteins. Additionally, CD spectroscopy can be employed to study changes and interactions in macromolecular structures and analyze the conformation and properties of optically active molecules.

From the CD spectroscopy analysis, it can be observed that (R)-TpPa-1 and (S)-TpPa-1 exhibit absorption at a wavelength of 225 nm in the ultraviolet-visible region, indicating absorption in the UV-visible range. This confirms that they possess a single chiral structure, providing evidence that COFs with chiral structures were successfully obtained in the experiment.

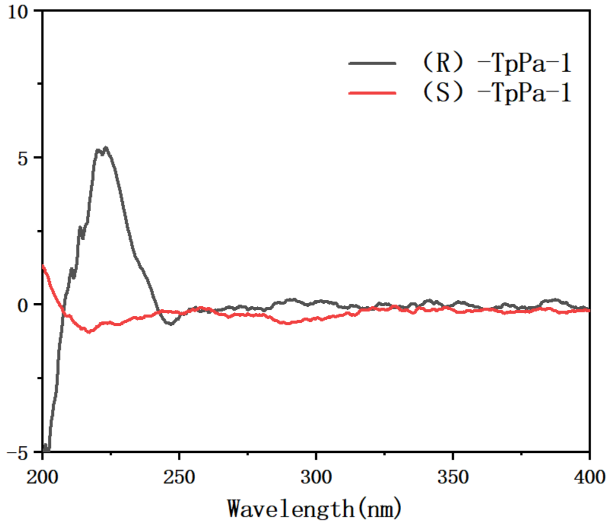


FIGURE 6. CD spectra of (R)-TpPa-1 and (S)-TpPa-1

3.2.4 Chiral Amine 1-PEA Gradient Experiment

To investigate whether aniline competes with chiral amines in the enantioselective reaction, we conducted experiments by controlling the amount of chiral amine (S)-alpha-methylbenzylamine or (R)-alpha-methylbenzylamine in the reaction. The amounts of chiral amine (S)-alpha-methylbenzylamine or (R)-alpha-methylbenzylamine were set at multiples of 0.5, 1, 1.5, and 2, and the yields were measured as shown in table 3.3 and 3.4.

TABLE 5. Yield of (S)-TpPa-1

(S)-TpPa-1	Yield of (S)-TpPa-1（%）
0.5	93
1	95
1.5	83
2	75

TABLE 6. Yield of (R)-TpPa-1

(R)-TpPa-1	Yield of (R)-TpPa-1（%）
0.5	76
1	83
1.5	73
2	65

Based on the yields obtained from Table 3.3 and 3.4, a scatter plot of the yields was generated for analysis. It can be concluded that the competing agents, (S)-alpha-methylbenzylamine or (R)-alpha-methylbenzylamine, may prolong the induction period, inhibit precipitation, and introduce a certain degree of steric hindrance during the accumulation process.

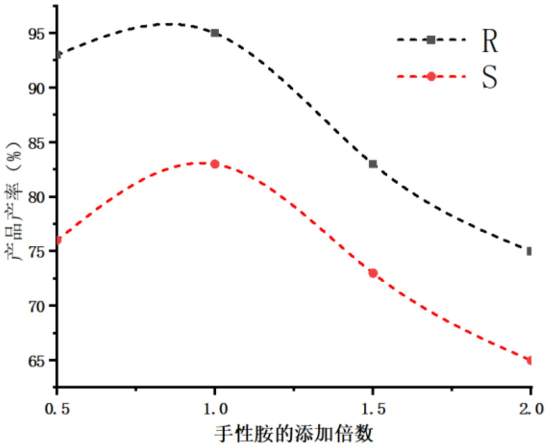


FIGURE 7. Yield of (S)/(R)-TpPa-1

4 DISCUSSION

In this study, we utilized triformyl-based trisphenol and p-phenylenediamine in a mixture of m-xylene and diethyl ether to synthesize the corresponding chiral COFs, (S)-TpPa-1 and (R)-TpPa-1, by adding (S)-alpha-methylbenzylamine or (R)-alpha-methylbenzylamine (19.34 µl, 0.15 mol). X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and circular dichroism (CD) analysis were performed on the synthesized COFs.

Through X-ray diffraction, we gained insights into the crystal structure information, such as lattice constants, crystal symmetry, determination of chiral purity, and crystallinity, which allowed us to simulate the unit cell structure. FTIR analysis revealed that (R)-TpPa-1 and (S)-TpPa-1 both exhibited a cyclic structure while retaining the carbon-nitrogen single bond and carbon-carbon double bond of TpPa-1. SEM observations indicated that both (R)-TpPa-1 and (S)-TpPa-1 exhibited the characteristic porous and aggregated morphology of CCOFs. Circular dichroism analysis provided evidence of the chiral nature of the synthesized COFs.

As research on chiral COFs advances, future studies will explore chiral COFs with novel functionalities, such as multifunctional design and assembly. Chiral COFs hold great potential for various applications and possess significant research value. Further research on the synthesis and application of chiral COFs will continue in the future.

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