

DESIGN AND APPLICATION OF METAL-ORGANIC FRAMEWORKS (MOFs) IN CATALYSIS ROLE OF STRIGOLACTONES IN RICE

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Abstract

Metal-Organic Frameworks (MOFs) have emerged as a versatile class of materials with significant potential in the field of catalysis. These porous, crystalline structures are composed of metal ions coordinated to organic ligands, creating a highly tunable architecture that can be tailored for specific catalytic applications. This review explores the design principles of MOFs, focusing on the selection of metal nodes and organic linkers to optimize catalytic performance. We discuss the various synthesis strategies, including solvothermal and microwave-assisted methods, that influence the structural properties and catalytic efficiency of MOFs. The application of MOFs in diverse catalytic processes, such as heterogeneous catalysis, photocatalysis, and electrocatalysis, is examined with emphasis on their role in environmental remediation, energy conversion, and organic transformations. Strigolactones (SLs) are a class of plant hormones that play a crucial role in regulating various aspects of rice growth and development. This review delves into the biosynthesis, signaling pathways, and physiological functions of strigolactones in rice. Strigolactones influence several key processes, including tillering, root architecture, and response to environmental stress. By modulating the architecture of rice plants, SLs contribute to optimal resource allocation and enhance crop productivity. Recent advancements in molecular biology and genetic engineering have shed light on the complex regulatory networks governed by SLs, revealing their interaction with other plant hormones such as auxins and cytokinins.

Keywords: MOFs, Strigolactones, Rice, Catalysis

Introduction

Metal-Organic Frameworks, often known as MOFs, are a novel category of materials that have attracted a lot of attention and interest owing to the distinctive structural features they possess and the potential uses they might have in a variety of scientific domains. In the formation of extremely porous, crystalline structures, metal-organic frameworks (MOFs) are composed of metal ions or clusters that are coupled to organic ligands. These structures can be methodically engineered and functionalized for specific applications. A large surface area, configurable porosity, and diversified chemical activity are some of the benefits that MOFs provide over typical catalytic materials. One of the most promising uses of MOFs is in the field of catalysis, where they offer major advantages over traditional materials. For the first time ever, the ability to accurately manipulate the spatial arrangement of catalytic sites inside MOFs presents potential that have never been seen before to improve the efficiency and selectivity of reactions. An overview of the

fundamental elements of metal-organic frameworks (MOFs) includes their synthesis, structural properties, and the principles that guide their design for catalytic applications. This introduction gives an overview of these essential aspects. We also provide an overview of the topics that will be covered in this review, with a particular emphasis on recent developments in the catalytic use of MOFs and a focus on the potential of these materials to revolutionize industrial processes, environmental remediation, and the creation of sustainable energy. Strigolactones (SLs) are a relatively new addition to the pantheon of plant hormones; nonetheless, due to the myriad of roles they play in plant growth and environmental adaptation, they have quickly become a focus topic of research in the field of plant biology. Now recognized as essential regulators of plant design and signaling molecules engaged in both endogenous and external processes, strigolactones were initially found as germination stimulants for parasitic plants. However, they have since been rediscovered for their other roles. In rice, which is a staple crop for more than half of the world's population, SLs serve critical roles in regulating tillering, root development, and responses to a variety of abiotic stimuli. The delicate equilibrium between strigolactone production and signaling is what supports optimal plant development, which is something that is very necessary for obtaining high yields and being resistant to stress in rice farming. The purpose of this introduction is to lay the groundwork for a more in-depth investigation of the production of strigolactones, signaling pathways, and the many physiological activities that they perform in rice. Additionally, we examine the possible implications of strigolactone research in agricultural biotechnology, with the objective of increasing rice production and sustainability in response to difficulties posed by global food security.

Conventional method of MOFs synthesis:

In the traditional approach, the term "MOF synthesis" often refers to the method that involves the use of electric heating during the synthesis process. Methods that are considered conventional include both solvothermal and non-solvothermal procedures. The reaction is carried out in a container that is sealed, and the temperature of the reaction mixture is increased to a level that is higher than the boiling point of the solvent. This is an example of a solvothermal process. When this procedure is carried out, a high pressure is produced within the closed container, which is primarily responsible for regulating the reaction. Following the interaction of the linkers with the metal ions that take place in the closed reaction chamber, nucleation takes place, which is then followed by growth, which ultimately results in the production of highly crystalline MOF structures. This methodology has resulted in the synthesis of a great number of metal organic frameworks. Solvothermal synthesis was used to produce highly crystalline metal-organic frameworks based on zinc. Through the use of solvothermal synthesis, two-dimensional fluorinated metal organic frameworks such as F-MOF-4, Cu-F-MOF-4B, and Zn-F-MOF4B were produced. To produce highly crystalline MIL101(Cr), a hydrothermal method was utilized in the synthesis process. Unlike the non-solvothermal process, which may be carried out at room temperature or at a temperature that can be fixed at the boiling point of the solvent, the reaction in the non-solvothermal process takes place at room temperature. It was decided to use a nonsolvothermal technique at room temperature in order to synthesize a variety of metal-organic frameworks (MOFs), including Cu-BTC MOF, UiO-66, Zn-based metal organic frameworks, and others. The rate of nucleation and development of metal organic frameworks may be precisely controlled in a non-solvothermal way by adjusting the temperature of the reaction or by evaporating the solvent at a temperature that is slightly higher than the initial temperature.

Microwave assisted MOFs synthesis:

Microwave (MW) aided molecularly fabricated (MOF) synthesis involves the interaction of electromagnetic waves with solid or liquid materials. This interaction leads to a high molecular orientation in the materials that are either the solvent or the reactant. An increase in temperature occurs as a consequence of these factors in the reaction media. When using MW aided synthesis, it is possible to keep the temperature of the reaction medium at a high and consistent level during the whole process. In order to ensure that electromagnetic waves are able to interact strongly with the reaction medium, the solvents that are utilized in MW aided synthesis have the ability to be selective. Through the use of this method, the first Cr-based MIL-100 metal organic framework was successfully synthesized. After some time had passed, this method was utilized to produce IRMOF-1, 2, and 3.

Mechanochemical synthesis of MOFs:

Through the process of mechanochemical synthesis, the intermolecular bonds are broken by the mechanical force, and at the same time, the molecules of the reactant undergo a chemical change, which results in the production of the product. As a result of the fact that the entire process takes place in a solvent-free environment, the method is extremely environmentally friendly. Through the use of this method, the first metal-organic framework (MOF) to be synthesized was a three-dimensional Cu-based MOF [Cu(INA)₂], with isonicotinic acid serving as the linker. HKUST-1, MOF-14, and [Zn(EIm)₂] MOFs were artificially produced by a mechanochemical technique after the first research was published.

Applications of metal organic frameworks

Metal organic frameworks have attained remarkable research interest due to their wide-spread applications in the field of catalysis, sensing, adsorption and separation, biological applications etc., as shown in Figure 1

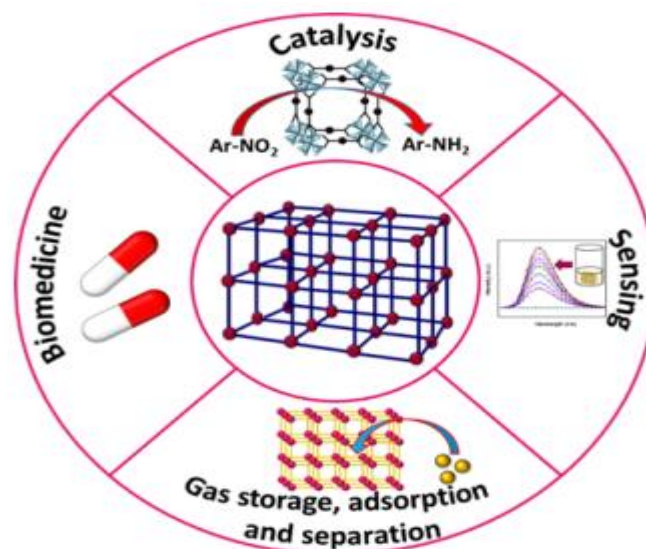


Figure 1: Various applications of metal organic frameworks.

Gas storage, adsorption and separation:

MOFs are crystalline solids that have a persistent porosity and a huge surface area. Because of these characteristics, they are able to store a wide variety of gas molecules, solids, and liquids inside their

frameworks. Excellent porosity is exhibited by MOFs containing divalent metal ions, such as HKUST-1. As a result, these MOFs are able to absorb methane (CH₄) gas molecules. PCN-250(Fe₂ M) MOFs, where M=Fe, Co, Ni, Mn, and Zn, are utilized in CH₄ storage applications. There are advantages to using flexible MOFs rather than rigid MOFs when it comes to gas storage performance. As an instance, MIL-53(Al) has the capability of absorbing a substantial quantity of CH₄ gas at room temperature MOF-177, and it has been reported for use in CO₂ storage applications. Additionally, MOFs are exceptionally effective in removing hazardous compounds from water. As an illustration, UiO-66 and PCN-222 were utilized as dye adsorbents that were poisonous.

Catalysis:

In a wide variety of heterogeneous chemical processes, MOFs perform exceptionally well as catalysts. There is a clear correlation between the catalytic activity of metal-organic frameworks (MOFs) and metal centers. This is due to the fact that the secondary building blocks of MOFs acting as Lewis acids for a variety of chemical processes. In Friedel-Crafts processes, for instance, MIL-100(Fe) was utilized as a Lewis acid catalyst. Interactions between epoxides that include regioselective ring-opening Condensation processes such as Claisen-Schmidt, Knoevenagel, and cyanosilylation, among others, are examples of condensation reactions. A process involving aldol condensation may be carried out with UiO-66. In addition to these, MOFs have the potential to function as light harvesting materials in the field of photocatalysis. PCN-22, for instance, was utilized as a photocatalyst in the light-driven alcohol oxidation reaction. MIL101(Fe), on the other hand, is an effective photocatalyst in the photocatalytic water oxidation reaction.

Synthesis of MOF

Because of their structural diversity, the rarity of their features, and their ability to be customized for certain activities, metal-organic frameworks (MOFs) constructed from inorganic nodes and organic linkers have garnered a lot of interest. Both the organic linkers and the metal centers contribute to the right design of the structure of MOFs. The organic linkers actively engage in shear connections, while the metal centers perform the function of joints. To manufacture metal-organic frameworks (MOFs), there are numerous ways, which will be briefly mentioned here.

Hydrothermal/Solvothermal Synthesis

The most comprehensive dynamical products are often produced by the use of hydrothermal synthesis, which is typically employed for the purpose of producing sustainable metal-ligand linkages across the framework. The production of MOF using hydrothermal synthesis is made possible by heating the reaction mixture for an extended period of time at high pressure and temperature. According to the pace at which the material dissolves in hot water while being subjected to strong vapor tension and maintained at a temperature fluctuation that is allying, the opposing nodes of the reactor produce single crystals. As an additional point of interest, the 'solvothermal' technique makes use of appropriate solvents in addition to water throughout the material synthesis. The procedure is a consequence of the formation of crystals of a high quality; nevertheless, in general, hydrothermal and solvothermal processes are slow and require higher temperatures for optimal performance. A diagrammatic representation of the steps involved in the synthetic method that makes use of hydrothermal and solvothermal processes is presented in Figure 2. Crystals of copper (4, 4'-bpy)NO₃ (H₂O) with a rectangular parallelepiped form are produced by the hydrothermal process. This approach makes use of 4, 4'-bipyridine as a nitrogen donor aromatic ligand.

The $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$ complex, also known as HKUST-1, is synthesized by the hydrothermal process in a manner that is analogous. The carboxylic group is utilized as a functional group. The MOFs with the desired properties may be synthesized using the hydrothermal technique by means of simple metal ions self-assembling at the adaptive bis-(imidazole) binding sites. This method makes use of transition metals such as cobalt, nickel, and zinc.

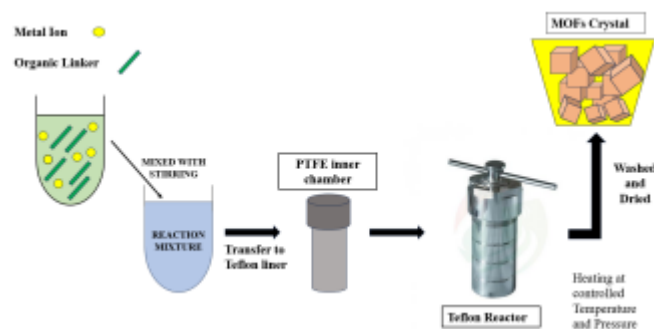


Fig. 2. Schematic of the hydrothermal/solvothermal synthesis of metal organic frameworks.

varied applications and uses An exciting Friedel-Crafts reaction with catalytic activity that makes use of the redox characteristics of Fe(III) was demonstrated by the hydrothermal reaction, which resulted in the production of a polycrystalline Fe-MIL-100 powder with a very large achievable and long-lasting porosity. Because of its low cost, large abundance, excellent catalytic activity, and electrochemical properties, nickel (II) is a typical transition metal ion that has garnered a substantial amount of interest. Utilizing Ni(II) and the-benzene tricarboxylate as a ligand, the hydrothermal technique is utilized in order to facilitate the synthesis of Ni-MOFs. There is a significant amount of potential for the utilization of nickel-based compounds in the electrochemical sector as electrode surface modifications and electrocatalysts, provided that the appropriate design is implemented. The synthesis of the Mg-MOF-nNH₂ with double ligands is accomplished by the solvothermal technique. In this particular structure, magnesium serves as the metal center, and 2,5-dihydroxyterephthalic acid and 2-amino terephthalic acid are the ligands. For these MOF samples, the micropore volume of Mg-MOF-1/8NH₂ is measured to be 0.46 cm³ g⁻¹. The materials that were synthesized also had a high specific surface area, which is measured at 924.19 square meters per gram. Similarly, the Mn/Fe-MOF@Pd1.0 may be obtained by a solvothermal technique that only requires one step. Metal-organic frameworks (MOF) are derived from Mn²⁺ and Fe³⁺, whereas Pd is doped inside the MOF itself. The activity of Fe-MOF with regard to catalysis is comparable to that of an enzyme. The introduction of Pd further synergizes the acid tolerance and stability of the Mn/Fe-MOF solid, while the presence of bimetallic active sites increases the catalytic activity of the material being prepared.

Ultrasonic Methods

In an enclosing reaction setting (that is, enclosing temperature and atmospheric pressure), ultrasonic-assisted synthesis provides a technology that is reasonably benign to the environment for the synthesis of metal-organic frameworks (MOFs) by reducing the amount of time required for the reaction. Additionally, the ultrasonication synthesis methodologies eliminate the need for safety considerations, which presents a chance to improve upon the twelve principles of green chemistry. A approach that is both inexpensive and safe for the environment is the ultrasonication technique, which is one of the many different procedures for the synthesis of MOF. It is possible for it to provide a high yield while working in a solvent-free reaction at

the temperature and pressure of the surrounding environment. In contrast to previous approaches, the ultrasonic-assisted MOF synthesis is not only feasible and containable, but it also manufactures the product in a short amount of time while yielding a large amount. Ultrasonic cavitation is a relatively novel method for the production of metal-organic frameworks (MOFs), and it has lately garnered more attention. An investigation into the effects of ultrasonic irradiation on the $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$, also referred to as Cu-BTC MOF, was carried out for the first time by Khan and colleagues in the year 2009. When compared to the techniques of microwave irradiation and electronically controlled synthesis, the reaction time for the ultrasonically aided synthesis of metal-organic frameworks (MOFs) becomes much shorter. Additionally, a restricted sonication allowed for the reduction in size of the MOF particles; nevertheless, an increase in the sonication period from six to forty-five minutes caused the MOFs to aggregate. The urea-containing metal-organic frameworks, also known as TMU-31 and TMU-32, were synthesized by the applications of the sonochemical irradiation approach. In addition, the morphology of MOF is determined by a number of characteristics, including the starting concentrations of the reagent and the length of time that it is exposed to radiation. In light of the findings, it has been determined that these MOFs are capable of achieving a homogenous plate form at a concentration of 0.005 M and a maximum power supply of 360 W. These MOFs were also used to evaluate and compare the phenol sensing capabilities of the materials. According to the findings, hydrogen-bonding and packing interactions play a significant part in the process of phenol detection. The incorporation of urea into the structure of the MOF is very necessary in order for the framework to be able to detect phenol. There is further work to be done in order to complete the synthesis of MOFs that include embedded porphyrin units. Despite the fact that it takes a significant amount of time to synthesize when the reaction conditions are well-regulated, it is frequently noticed that a mixed phase with a variety of crystal forms is produced. The tetrakis (4-carboxyphenyl) porphyrin and zirconyl chloride octahydrate are utilized in the sonochemical synthesis process, which results in the production of high-purity uniform-sized Zr-based porphyrinic MOF-525 and MOF-545. Further, benzoic acid was found to influence the synthesis of MOF-525, whereas trifluoroacetic acid was found to modify the creation of MOF-545. Synthesis of the zinc-based MOF is accomplished by the use of adipic acid as an aliphatic ditopic linker through the use of solvothermal and sonochemical processes. The creation of MOFs can be made more efficient by the use of ultrasonic irradiation, which also results in the reduction of particle sizes. The electrochemical reduction of carbon dioxide was used to evaluate the catalytic efficiency of the samples, with carbon monoxide and hydrogen being the sole byproducts of the process. When employing the ultrasonic approach, on the other hand, it was noted that the potential function of solvent in the yield of MOF formation was not taken into account. Within the scope of this work, the textural characteristics of Cu-BTC are investigated in relation to the impacts of solvents, including binary and ternary combinations. In addition, the production of MOF is determined by a number of ultrasonic factors, including the duration of the sonication process and the power supply (referred to in Figure 2). Through the use of a mixture of three solvents, specifically water (H_2O), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and dimethylformamide (DMF), the sonication process was carried out for a duration of two hours at a power level of 750 watts. Using this method, the amount of copper metal-organic framework (Cu-MOF) that is produced is increased.

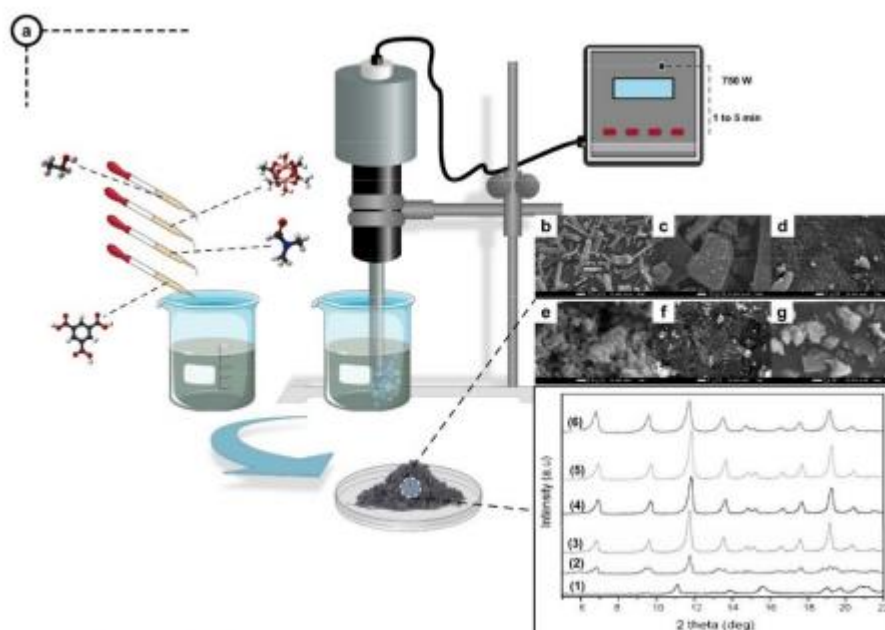


Fig. 3 Microstructure of metal-organic frameworks (MOFs) exposed to different concentrations of dimethyl ether (DMF) for one minute during sonication; XRD patterns of Cu-BTC samples created by ultrasonic irradiation for one minute using varied concentrations of DMF in a water solvent (4 mL) 2) milliliters of ethanol There are six different volumes of DMF, with the following volumes: (1) 0.0 mL, (2) 0.2 mL, (3) 0.5 mL, (4) 1.0 mL, (5) 3.0 mL, and (6) 6.0 mL.

Microwave-Aided Synthesis

Synthesis achieved with the use of microwaves is the most effective method for carrying out a variety of reactions. Microwave irradiation, in comparison to traditional solvothermal synthesis, shortens the amount of time required for the reaction and accelerates the formation of crystals in porous materials, which would otherwise take several days or weeks to develop using conventional techniques. The major criteria that regulate the yield and crystal formation of the MOFs are the energy of the microwave irradiation, the amount of time the MOFs are exposed to the microwaves, the concentration of the solvents, and the solvent systems. Microwave irradiation demonstrated a favorable influence on the features and qualities of the material. In comparison to hydrothermal synthesis, microwave-assisted synthesis is characterized by its quick heating, rapid kinetics, phase purity, enhanced yield, better dependability, and repeatability. Additionally, it provides an efficient way for regulating the distribution of macroscopic morphology, particle size, and phase selectivity during the synthesis of inorganic solids and nanocomposite materials. This is a significant advantage. Despite the fact that the microwave-assisted methodology is far quicker than the standard solvothermal procedure, the characteristics of the crystals that are formed by this technique are equivalent to those created by the regular method. On the other hand, microwave-assisted techniques have spurred increased interest in researching the effects of irradiation time, power, temperature, solvent concentration, and metal ion/organic linker ratio, for example, on the synthesis of MOF-5 by applying the microwave-assisted methodology. This interest has been prompted by the fact that microwave-assisted approaches have been used. At a temperature of 130 degrees Celsius and a power range of 600 to 1000 watts, the nanocrystal crystallization process is optimized for a number of factors, including time, temperature, and power. According to the findings of this study, the creation of crystals took place under microwave irradiation for

fifteen minutes, and the production of a crystal of superior quality took half an hour to twenty-four hours. In a similar manner, microwave-assisted synthesis results in the production of Zr-based MOF (Zr-fum-fcu-MOF), which has an octahedral structure when the reaction temperature is set at around 100 degrees Celsius. Figure 4 provides a summary of the steps involved in the synthesis process.

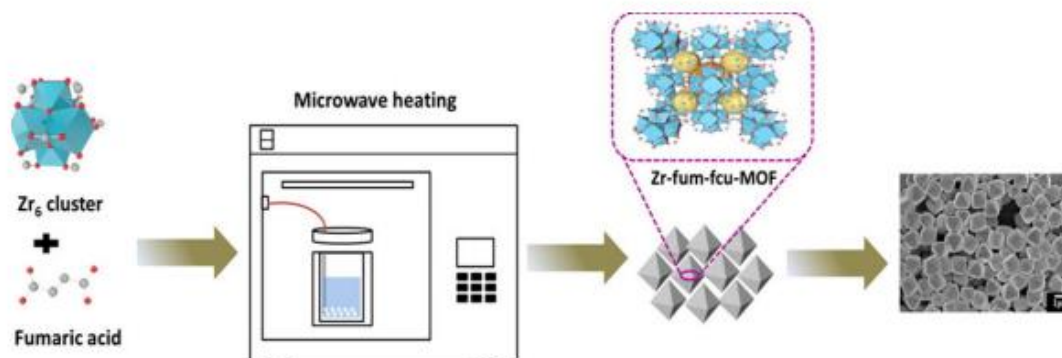


Fig. 4. The Zr (fumarate-face centered cubic) MOF was synthesized with the use of microwaves.

Role of Strigolactones in Rice

Strigolactones (SLs) are a relatively new addition to the pantheon of plant hormones; nonetheless, due to the myriad of roles they play in plant growth and environmental adaptation, they have quickly become a focus topic of research in the field of plant biology. Now recognized as essential regulators of plant design and signaling molecules engaged in both endogenous and external processes, strigolactones were initially found as germination stimulants for parasitic plants. However, they have since been rediscovered for their other roles. In rice, which is a staple crop for more than half of the world's population, SLs serve critical roles in regulating tillering, root development, and responses to a variety of abiotic stimuli. The delicate equilibrium between strigolactone production and signaling is what supports optimal plant development, which is something that is very necessary for obtaining high yields and being resistant to stress in rice farming. The purpose of this introduction is to lay the groundwork for a more in-depth investigation of the production of strigolactones, signaling pathways, and the many physiological activities that they perform in rice. Additionally, we examine the possible implications of strigolactone research in agricultural biotechnology, with the objective of increasing rice production and sustainability in response to difficulties posed by global food security.

The process of Strigolactones' biosynthesis: Important enzymes including D27, CCD7, and CCD8 are responsible for the conversion of carotenoids into strigolactone precursors in the carotenoid pathway, which is the first step in the process of strigolactone biosynthesis in rice. A number of other strigolactone molecules are produced as a result of these precursors undergoing further modifications, which include enzymes such as MAX1. For the purpose of altering SL levels in rice in order to attain desired agronomic features, it is vital to have a solid understanding of the genetic and enzymatic pathways that are responsible for SL production.

Signaling Pathways: The sensing and signal transduction of strigolactones in rice are mediated by receptor proteins such as DWARF14 (D14), which binds SL molecules and sets off a chain reaction of signaling events. This cascade involves interactions with F-box proteins like as D3 and SCF complexes, which

ultimately result in the destruction of transcriptional repressors like D53. This signaling system is responsible for regulating the patterns of gene expression that determine the architecture of rice plants and their responses to stress. In terms of rice physiology, strigolactones are responsible for regulating various important factors, including the following:

Tillering and Shoot Branching: SLs prevent excessive tillering, which ensures that fertilizer is distributed effectively and that the plant architecture is optimized. In many cases, mutants that are weak in SL production or signaling display enhanced tillering, which can have an effect on both yield and the efficiency with which resources are used.

Root Development: SLs have the ability to alter root architecture, which increases the depth and breadth of root systems, which in turn improves the plant's ability to absorb water and nutrients. When there is a lack of water or nutrients, this is especially helpful since it helps to replenish the water supply.

Responses to Stress Strigolactones have a role in abiotic stress tolerance, which enables rice plants to deal with a variety of environmental stresses, including salt, drought, and nutrient deficiencies. SLs contribute to the tolerance of rice to unfavorable environmental circumstances by influencing hormone crosstalk and stress-responsive gene expression. This allows rice to better withstand the effects of stress.

Application in the Field of Agriculture: Putting the understanding of strigolactone biology to use in rice cultivation has the potential to offer various uses, including the following:

Breeding and genetic engineering: Breeders are able to generate rice varieties that have optimum tillering, root architecture, and stress tolerance by modifying SL biosynthesis and signaling pathways. These kinds may be adjusted to specific environmental circumstances.

When it comes to the management of parasitic weeds, having an understanding of the interactions that SL has with parasitic weeds such as *Striga* can help develop tactics that can reduce crop losses caused by these pests. There is a possibility that parasitic weed infestation can be reduced by modifying SL exudation or by using SL analogs.

Enhancing SL-mediated characteristics in rice can help to sustainable agricultural practices by increasing the efficiency with which resources are used, decreasing the amount of chemical inputs that are required, and increasing the crop's resistance to the effects of climate change.

Conclusion

A new category of materials called metal-organic frameworks (MOFs) has great promise as a catalyst. Because of their many desirable characteristics, including as a large surface area, adjustable pore size, and the capacity to integrate various functional groups, they find widespread use in catalysis. The adaptability and effectiveness of MOFs have been proven in a range of chemical processes, including photocatalysis, gas phase catalysis, enzyme mimicry, and heterogeneous catalysis. Enhancing their catalytic performance and broadening their application breadth, new possibilities are being unlocked by the continuous research and development in MOF design. To a large extent, rice's development, growth, and stress responses are controlled by strigolactones (SLs), which are essential plant hormones. In order to maximize resource allocation and adapt to difficult environmental conditions, SLs assist rice plants regulate shoot branching, root growth, symbiotic connections, and stress tolerance. Discovering how SLs work in rice might teach us

a lot about plant biology and maybe even help us develop ways to make our crops more resilient and productive. Innovations in this area have the potential to improve the growth characteristics and tolerance to biotic and abiotic challenges of rice types. Research on strigolactones in rice and metal-organic frameworks (MOFs) for catalysis both show how vital new ways of thinking are to the fields of plant biology and material science. Industrial and agricultural methods are set to be enhanced by these innovations, which will lead to sustainable development and increased food security. Rice plants rely on strigolactones for their development, growth, and ability to respond to stress. Because of their complex functions in controlling plant architecture and reactions to environmental stresses, they are an attractive target for improving rice farming techniques. Innovative uses of SL in rice breeding and biotechnology, as well as the precise molecular mechanisms of its activity, should be the subject of future study. Both the sustainability of rice production systems and the availability of food on a worldwide scale can be improved by the application of strigolactone biology.

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