Full length article

MOF-based multi-stimuli-responsive supramolecular nanoplatform equipped with macrocycle nanovalves for plant growth regulation

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A B S T R A C T
Controllable and on-demand delivery of agrochemicals such as plant hormones is conducive to improving agrochemicals utilization, tackling water and environmental pollution, reducing soil acidification, and realizing the goals of precision agriculture. Herein, a smart plant hormone delivery system based on metal-organic frameworks (MOFs) and supramolecular nanovalves, namely gibberellin (GA)-loaded CLT6@PCN-Q, is constructed through supramolecular host-guest interaction to regulate the growth of dicotyledonous Chinese cabbage and monocotyledonous wheat. The porous nanoscale MOF (NMOM) with a uniform diameter of ~97 nm modified by quaternary ammonium (Q) stalks is served as a cargo reservoir, followed by the decoration of carboxylated leaning tower[6]arene (CLT6) based nanovalves on NMOM surfaces through host-guest interactions to fabricate CLT6@PCN-Q with a diameter of ~101 nm and a zeta potential value of ~13.2 mV. Interestingly, the as-fabricated supramolecular nanoplatform exhibits efficient cargo loading and multi-stimuli-responsive release under various external stimuli including pH, temperature, and competitive agent spermine (SPM), which can realize the on-demand release of cargo. In addition, GA-loaded CLT6@PCN-Q is capable of effectively promoting the seeds germination of wheat and stem growth of dicotyledonous Chinese cabbage and monocotyledonous wheat (1.86 and 1.30 times of control groups, respectively). The smart supramolecular nanoplatform based on MOFs and supramolecular nanovalves paves a way for the controlled delivery of plant hormones and other agrochemicals for promoting plant growth, offering new insights and methods to realize precision agriculture.

Statement of significance
To achieve controllable and sustainable release of cargos such as agrochemicals, a smart MOF-based multi-stimuli-responsive supramolecular nanoplatform equipped with supramolecular nanovalves was fabricated via the host-guest interaction between quaternary ammonium stalks-functionalized nanoMOFs and water-soluble leaning tower[6]arene. The as-prepared supramolecular nanoplatform with uniform diameter distribution demonstrated good cargo release in response to various external stimuli. The initiation of synthetic macrocycles could effectively reduce cargo loss in the pre-treatment process. This type of supramolecular nanoplatform exhibited good promoting effect on seed germination and plant growth of dicotyledonous Chinese cabbage and monocotyledonous wheat. As an eco-friendly, controlled, and efficient cargo delivery system, this supramolecular nanoplatform will be a promising candidate in precision agriculture and controlled drug release to attract the broad readership.

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1. Introduction
Agrochemicals including fertilizers, pesticides, and growth regulators play a crucial role in increasing crop yields, improving food safety, and ensuring the sustainable development of modern agriculture [1,2]. Among them, plant growth regulators, a class of natural or synthetic organic compounds with similar biological effects as plant hormones, can effectively regulate the growth and development of plants, mainly including auxins, cytokinins, abscisic acid, salicylic acid, nitric oxide, gibberellins (GAs), jasmonates, ethylene, and brassinosteroids. These substances can en-

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hance crop resistance, increase crop yields, and improve crop quality. As a kind of plant growth regulation, GA can break seed dormancy via improving enzyme activity, promote plant growth by accelerating cell division and elongation, stimulate fruit growth, prevent organ shedding, and boost crop yields [3]. However, in recent years, the abuse of agrochemicals and the defects of traditional drug delivery methods have generated serious problems, such as soil acidification, environmental pollution, and grain crisis [4,5]. Therefore, it is of great significance to develop a convenient and eco-friendly agrochemical delivery system for improving the efficiency of agrochemicals, enhancing the stability of agrochemicals and controlling the release kinetics of agrochemicals during delivery [6,7]. The emergence of multifunctional nanovehicles provides an important cornerstone for the controllable delivery of agrochemicals [8–10]. Recently, some inorganic/organic nanovehicles including silica-based nanomaterials, metal/metal oxide nanomaterials and carbon-based nanomaterials, polymer micelles, and dendrimers [11–16], have been fabricated to deliver agrochemicals, however, they suffer from severe drawbacks of low cargo loading capacity, poor biodegradability, and uncontrollable drug release, severely restricting their applications in agriculture [14,17]. As a class of fantastic and emerging organic-inorganic hybrids, metal-organic frameworks (MOFs) have been widely used in catalysis [18,19], adsorption/separation [20–22], nonlinear optics [23], sensing and detection [24,25], and drug delivery [26–31], due to their remarkable physicochemical features including facile synthesis and functionalization, diverse composition, tunable pore size, flexible structure, high surface area, large cargo load capacity, good bio-compatibility, and fine biodegradability [32–38]. Particularly, compared to the traditional MOF-based nanovehicles, nanoscale MOFs (NMOFs) possessing smaller sizes, higher bioactivities, stronger chemical/colloid stabilities, and larger surface areas are able to achieve the controlled cargo release and improve the safety of nanovehicles [39,40]. Therefore, the construction of eco-friendly NMOFs with the prominent superiorities is of great significance for improving the effective utilization of agrochemicals and reducing environmental pollution.

Supramolecular macrocycles—a unique host that can form supramolecular inclusion complexes with guests through dynamic and reversible host-guest interactions—have been applied to construct smart supramolecular composites with stimuli-responsive features in the past few decades [41–52]. Particularly, pillar[n]arenes (n = 5–15), especially water-soluble pillar[5,6]arenes, have been applied to construct intelligent nanocomposites for cargo delivery due to their suitable cavity sizes, unique host-guest properties, and good biocompatibilities [53–57]. However, pillar[6]arene with large cavity suffers from low synthesis yield and difficulty in purification, severely limiting its further application. In view of this, we designed and synthesized a leaning tower[6]arene (LT6) conveniently with high synthetic yield, good cavity adaptability, outstanding guest binding ability, and less substituents, which opens a door for exploring the important function of supramolecular macrocycles in the drug delivery field [58–63]. Thus, we envision that water-soluble macrocycles can be utilized as nanovales modified on the surface of porous NMOFs through host-guest interactions, to endow smart supramolecular nanoplatforms with stimuli-responsive features and controllable drug release behavior for delivering agrochemicals, which greatly improve the loading ability and successfully achieve controlled release effect of agrochemicals.

Herein, by bridging the advantages of NMOFs and supramolecular macrocycles, we prepare a smart supramolecular plant hormone delivery system, namely GA-loaded CLT6@PCN-Q, for achieving the controlled release of GA and the regulated growth of dicotyledenous Chinese cabbage and monocotyledenous wheat (Fig. 1). The surface of PCN NMOF is modified with quaternary ammonium (Q) stalks through coordination, followed by the encapsulation of rhodamine B (RhB)/GA to fabricate RhB-/GA-loaded PCN-Q. Subsequently, through the host-guest interaction between the CLT6 nanovalves and Q stalks, CLT6 is decorated on the surface of RhB-/GA-loaded PCN-Q to construct the supramolecular hormone delivery system of RhB-/GA-loaded CLT6@PCN-Q for efficient cargo loading and controlled drug release. Experimental results indicate that the supramolecular nanoplatform exhibited controllable cargo release behavior under various stimuli of pH, temperature, and competitive agent spermine (SPM). Furthermore, plant growth regulation experiments demonstrate that GA-loaded CLT6@PCN-Q could effectively promote seed germination, plant growth, and organic matter accumulation of dicotyledenous Chinese cabbage and monocotyledenous wheat. This intelligent supramolecular delivery system based on NMOFs and supramolecular macrocycles provides an effective method for the controllable delivery of plant hormones and other agrochemicals to regulate plant growth and increase crop yields, which is of great importance for ensuring the sustainable development of modern agriculture.

2. Materials and methods

2.1. Materials

5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin (H2TCP, GA), and zirconyl chloride octahydrate (ZrOCl2·8H2O) were purchased from Aladdin. Benzoic acid, RhB, 3-bromopropionic acid, and trimethylamine solution (30 wt%) were purchased from Energy Chemical. SPM was purchased from Sigma-Aldrich. Carboxylated leaning tower[6]arene (CLT6) was synthesized according to the reported literature [60]. Chinese cabbage seeds and wheat seeds were purchased from Jiqiu RuiFeng Ecological Agriculture Development Co., Ltd. Ultrapure water with a resistivity of 18.25 MΩ cm at 25 °C was prepared by Milli-Q system. All reagents were not further purified unless specified.

2.2. Characterization

Scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images were recorded on JEOL JSM 6700F and JEM 2100F instruments with an accelerating voltage of 200 kV, respectively. Fourier transform infrared (FT-IR) spectra and UV-vis spectra were measured on a Vertex 80 V spectrometer with a resolution of 4 cm−1 and Shimadzu UV-2550 spectrometer, respectively. Average hydrodynamic diameter and Zeta potential were collected on a Zetasizer Nano ZS 90 instrument at 25 °C in ultrapure water with a 90 °C detection angle. 1H NMR spectra was recorded on a Bruker AVANCEIII 400 MHz instrument at 25 °C. Powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) results were obtained on Rigaku Smart Lab III powder diffractometer and STA 449 thermogravimetric analyzer under ambient conditions with a heating rate of 10 °C/min, respectively. Plant culture experiments were carried out at 25 ±2°C.

2.3. Synthesis of quaternary ammonium stalk

The quaternary ammonium (Q) stalk was synthesized according to the reported literatures with a slight modification [64,65]. Briefly, 3-bromopropionic acid (1 g, 6.53 mmol), trimethylamine solution (20 mL, 30 wt%), and ethanol (2 mL) were added into a flask and stirred at room temperature for 3 days. Then, the product Q was obtained by condensation and washed with ethanol to give a white powder (0.94 g, yield: 67.9%). 1H NMR (400 MHz, 298 K, D2O) δ 3.65 (t, 2H), 3.15 (s, 9H), 2.89 (t, 2H) ppm.
2.4. Stoichiometry determination between CLT6 and Q

The total concentration of CLT6 host and Q were fixed at 1 mM in D$_2$O. Meanwhile, the mole fractions of CLT6 and Q varied from 0 to 1. The chemical shifts were recorded by $^1$H NMR spectra.

2.5. Association constant measurement between CLT6 and Q

According to the nonlinear least-squares curve-fitting method, the association constant of host-guest complex was calculated from the following equation ($\Delta \delta$ is the change of chemical shift of G at $[H]_0$, $[G]_0$ is the fixed initial concentration of G, and $[H]_0$ is the initial concentration of host):

$$\Delta \delta = \frac{0.5(\alpha)^2((C_0/2+H_0)+1/K_a)-(\sqrt{[C_0/2+H_0+1/K_a]-4[C_0/2+H_0])}}{(1/K_a)}$$

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2.6. Preparation of PCN

PCN NMOF was fabricated according to the reported literature [66]. 100 mg of H$_2$TCPP, 300 mg of ZrOCl$_2$·8H$_2$O, and 2.8 g of benzoic acid were added into a flask containing 100 mL of N,N-dimethylformamide, and then the mixture was stirred at 90°C for 5 h. PCN product was collected by centrifugation (10000 rpm, 30 min), washed with N,N-dimethylformamide and acetone, and dried in a vacuum oven.

2.7. Preparation of PCN-Q

PCN (100 mg) was dispersed into ultrapure water and sonicated for 30 min to give a PCN dispersion. Then, excess quaternary ammonium was added into the above-mentioned PCN dispersion and stirred for 10 h. Subsequently, PCN-Q was obtained by centrifugation (10000 rpm, 30 min) and washed with ultrapure water 3 times for the subsequent experiments.

2.8. Preparation of RhB-/GA-loaded CLT6@PCN-Q

PCN-Q (10 mg) was dispersed into ultrapure water. Then, GA (10.4 mg) or RhB (14.4 mg) was added into the above dispersion and stirred for 12 h. Subsequently, CLT6 (10 mg/mL, 5 mL) was added into the mixture and stirred for another 12 h. RhB-/GA-loaded CLT6@PCN-Q was obtained by centrifugation (10000 rpm, 30 min), washed with high-purity water three times, and dried in a vacuum drying oven. Meanwhile, CLT6@PCN-Q and RhB-/GA-loaded PCN-Q was prepared according to the above-mentioned method just by replacing RhB/GA or CLT6 with water. Besides, the supernatant and washed solution after centrifugation were collected and measured by UV-vis spectroscopy to calculate the drug loading capacity and encapsulation efficiency.

Loading capacity = mass of loaded cargo / mass of loaded nanoparticles
Encapsulation efficiency = (mass of loaded cargo / mass of total cargo) × 100%

2.9. Controlled release experiments

RhB, a classic dye molecule with a similar size to GA, has a UV-vis characteristic absorption peak at 553.5 nm, and the pattern and intensity of the absorption peak are easy to observe. Therefore, RhB was selected as a model cargo to evaluate the cargo release behavior of RhB-loaded CLT6@PCN-Q under different stimuli by UV-vis spectra at a regular interval. In brief, RhB-loaded CLT6@PCN-Q (0.4 mg) was encapsulated in a dialysis bag, which was placed in a quartz cuvette containing 3 mL phosphate buffer solution (PBS, pH 7.0, 6.0, and 5.0) under mild stirring. The amount of the released RhB at different times was determined by a standard curve made from RhB concentration and absorbance using UV-vis spectra. Meanwhile, the amount of the released RhB at different temperature (20°C and 35°C) and in the presence of competitive binding agent SPM were performed. The release behavior of RhB from RhB-loaded PCN-Q was also recorded to study the effect of CLT6 nanovales on cargo release. Besides, the loading capacities of GA in GA-loaded PCN-Q and GA-loaded CLT6@PCN-Q were calculated using the method in the reported literature [67]. In addition, the release mechanism of RhB from the RhB-loaded CLT6@PCN-Q was evaluated by the Higuchi model. The equation is as follows (Q is the cumulative release of cargo at time t, and K is the kinetic constant)

\[ Q = Kt^{1/2} \]

2.10. Chinese cabbage and wheat culture

Chinese cabbage seeds and wheat seeds were shaken vigorously in a 10% potassium permanganate aqueous solution for 5 min, and washed with ultrapure water for three times. Subsequently, the cleaned seeds were immersed in warm water at 45°C for 30 min. After that, the pretreated seeds were sown in dishes (16 seeds per dish, three parallel per treatment) covered with double filter paper. Then, the ultrapure water, CLT6@PCN-Q dispersion, free GA solution (20 mg L⁻¹), and GA-loaded CLT6@PCN-Q dispersion (equivalent to 20 mg L⁻¹ free GA) were added into the dishes on day 0 and day 2, respectively. All the dishes were cultured at 25°C for 14 h in light and 10 h in dark. The germinations of Chinese cabbage seeds and wheat seeds were recorded at regular intervals. The stem lengths, plant heights, fresh weights, and dry weights were also measured with a ruler after culture (5 days for Chinese cabbage and 4 days for wheat).

2.11. Statistical analysis

All experiments were performed at least in triplicate, and the results were represented as mean±SD. One-sample t test in origin was chosen to analyze the difference of data and a value of *p < 0.05 was considered significant.

3. Results and discussion

3.1. Binding mode of CLT6 macrocycle and Q stalk

First of all, ¹H NMR spectra were recorded to confirm that the CLT6 nanovales could coordinate with Q stalks through the host-guest interaction. After the addition of 1.0 equiv. CLT6, all the proton signals in Q (H₃, H₄, and H₅) showed obvious upfield shifts (Δδ = -0.31, -0.32 and -0.36 ppm) in comparison with the proton signals of free Q, which was due to the shielding effect of the CLT6 on Q. At the same time, the proton signals assigned to CLT6 (H₁, H₂, H₃, H₄, and H₅) demonstrated that the downfield shifts were caused by the deshielding effect, indicating that CLT6 and Q could form supramolecular host-guest complex (Fig. S1-S3). Subsequently, the binding mode between CLT6 and Q was determined to be 1:1 using Job’s plot method (Fig. S4). Furthermore, ¹H NMR titration results indicated that the association constant (Kₐ) between CLT6 and Q was (3.38±0.83) × 10² M⁻¹ calculated by the nonlinear least-squares curve-fitting method (Fig. S5). All the experimental results verified that CLT6 could accommodate Q with a binding stoichiometry of 1:1 through host-guest interactions.

3.2. Characterization

In this fabrication, PCN as GA reservoir was fabricated via a traditional hydrothermal method, followed by the synthetic post-modification of Q on its surface through the coordination between Zr clusters on the surface of PCN and the carboxylic groups of Q to obtain PCN-Q [66]. Moreover, according to the host-guest interaction of CLT6 and Q, the CLT6-based nanovales were decorated on the surface of PAN-Q to give the supramolecular nanoplatform CLT6@PCN-Q. As shown in Fig. S6, SEM image demonstrated that PCN MOF possessed an average diameter of 97 nm with spherical morphology. Meanwhile, the average hydrodynamic diameter of PCN measured by dynamic light scatting (DLS) method was 105.7 nm, which was consistent with the SEM results. After modification with Q and capping with CLT6 nanovales on MOF surfaces, the obtained CLT6@PCN-Q showed a diameter of 101 nm according to the SEM and TEM images (Fig. 2a, b, and S7), and the average hydrodynamic diameter of CLT6@PCN-Q was 141.8 nm measured by DLS experiment (Fig. 2c). Besides, the PXRD patterns showed that PCN-Q and CLT6@PCN-Q had the same characteristic diffraction peaks as PCN (Fig. 2d), indicating that the crystallization of PCN still existed after the various modifications. FT-IR spectra further confirmed the successful preparation of CLT6@PCN-Q. The characteristic peak at 1070 cm⁻¹ was assigned to the stretching vibration of Q, and the peak at 1047 cm⁻¹ was corresponded to the vibration of =C–O–C– in CLT6, indicating the successful modification of Q stalks capped with CLT6 (Fig. S8a). In addition, TGA results of PCN and PCN-Q showed that the amount of Q modified on the surface of PCN was 4% of weight loss in the range of 200°C to 400°C, and 6.5% of weight loss between PCN-Q and CLT6@PCN-Q, which was attributed to CLT6-based nanovales on the surface of CLT6@PCN-Q (Fig. 2e). In addition, the Brunauer–Emmett–Teller (BET) surface area of PCN was decreased from 1294 m² g⁻¹ to 450.4 m² g⁻¹ after the modification of Q stalks, yet decreased to 270.8 m² g⁻¹ after the capping of CLT6 on the surface (Figure S8b). Furthermore, the zeta potential values changed from +18.9 mV to +29.8 mV after the modification of positive Q stalks on the PCN surface, and then turned to -13.2 mV owing to the capping of CLT6 macrocycles (Fig. 2f), which indicated the successful fabrication of the supramolecular nanoplatform.

3.3. Controlled cargo release

In general, the UV-vis characteristic absorption peak of GA suffers from low peak strength and high susceptibility to other substances, causing the difficulty to quantify the cargo loading capacity in the supramolecular nanoplatform. Meanwhile, we tried to study the release behavior of GA by high performance liquid chromatography method, however, in the actual sample determination, the complex absorption peaks of the sample and the low absorption intensity of GA made the determination of GA inaccurate. Therefore, the classic dye molecule RhB with a similar size to GA and a UV-vis characteristic absorption peak at 553.5 nm, was selected as a model cargo via analogy method to evaluate
the controlled release behavior under different stimuli by recording the UV-vis spectrum at a regular interval. According to the FT-IR spectra, the peaks at 1078 cm\(^{-1}\) and 923 cm\(^{-1}\) correspond to the stretching vibration of C–O–C, and the peak at 1346 cm\(^{-1}\) is attributed to the stretching vibration of C–N bond in RhB (Fig. S8), suggesting that RhB has been successfully encapsulated into the CLT6@PCN-Q reservoir. Meanwhile, to evaluate the loading capacity of RhB/GA in RhB-/GA-loaded CLT6@PCN-Q, the standard curve of RhB was plotted based on the UV-vis spectra of RhB at 553.5 nm under various concentrations (Fig. S9). Subsequently, according to the Lambert–Beer law and the reported calculation method [67], the loading capacities of GA in GA-loaded PCN-Q and GA-loaded CLT6@PCN-Q were calculated to be 0.18 g g\(^{-1}\) and 0.27 g g\(^{-1}\), and the encapsulation efficiencies were 17.31% and 25.96%, respectively, demonstrating that the installation of CLT6-based nanovalves in supramolecular nanoplatform could effectively reduce the drug loss during pretreatment.

Subsequently, the release kinetics of RhB in supramolecular nanoplatform with or without CLT6 nanovalves under various stimuli including pH, temperature, and competitive agent SPM were investigated. As shown in Fig. S10a, RhB release from RhB-loaded PCN-Q reached 20.3% at 240 min, but the release from RhB-loaded CLT6@PCN-Q was negligible under the same condition, further illustrating the importance of CLT6-based nanovalves. Under pH 7 condition, only negligible RhB was released from RhB-loaded CLT6@PCN-Q, however, with an enhanced solution acidity,
release of RhB increased successively at lower pH (pH 6.0 and 5.0) (Fig. 3a), which was due to the weakened host-guest interaction between the negatively charged CLT6 macrocycles and the positively charged Q stalks on the surface of RhB-loaded CLT6@PCN-Q resulting from the protonation of carboxylate groups of CLT6 under acidic conditions. Moreover, the release behavior of RhB from RhB-loaded CLT6@PCN-Q was also studied at different temperatures. The elevated temperature could accelerate the RhB release by reducing the stability of the inclusion complex of CLT6 and Q stalks through host-guest interaction (Fig. 3b). Furthermore, polyamines, commonly exist in plant tissues, were used as another stimulus to investigate the controlled release of cargo from the supramolecular nanoplatform, and SPM was selected as a model stimulant to study the release behavior of RhB [68–70]. The system showed a negligible RhB release without the addition of SPM. In sharp contrast, the release amount of RhB was significantly increased upon the addition of SPM with a concentration of 10 mM (Fig. 3c), which could be attributed to the strong competitive binding effect of SPM and CLT6. The association constant between CLT6 and SPM was determined to be \((4.59 \pm 0.82) \times 10^4 \text{ M}^{-1}\), which was much higher than that between CLT6 and Q stalks determined to be \((3.38 \pm 0.83) \times 10^3 \text{ M}^{-1}\) [62]. In addition, the release mechanism of RhB in the RhB-loaded CLT6@PCN-Q was evaluated by the Higuchi model [71]. The results showed that the cumulative release (Q6) of RhB was in a good relationship with the square root of time during the slow-release process of RhB from RhB-loaded CLT6@PCN-Q with /without the stimuli of pH, temperature, and SPM, indicating that the release behavior followed the Fick diffusion mechanism (Figure S10b-d). Overall, the as-prepared supramolecular nanoplatform could achieve the controlled release and on-demand delivery of RhB under various stimuli including pH, temperature, and competitive agent through the adjustable host-guest interaction between Q stalks and CLT6 macrocycles in the nanoplatforms (Fig. 3d).

3.4. Plant growth regulation by the supramolecular nanoplatform

To examine the regulation effect of the as-constructed supramolecular nanoplatform (GA-loaded CLT6@PCN-Q) on plant growth, dicotyledonous Chinese cabbage and monocotyledonous wheat were cocultured with GA-loaded CLT6@PCN-Q to study the variance in seed germination rates, stem lengths, seedling height, fresh weights, and dry weights. Firstly, the effect of supramolecular nanoplatform on germination rate of dicotyledonous Chinese cabbage was evaluated. As shown in Fig. 4a, at the beginning of germination, GA-loaded CLT6@PCN-Q group exhibited a higher germination rate of Chinese cabbage seeds compared with the control group and free GA group, indicating that GA could be released from GA-loaded CLT6@PCN-Q nanoplatform with good bioactivity under the stimuli of temperature and endogenous SPM. However, there was no statistical difference in the germination rate from the control group, due to the low concentration of GA at 28 h. Moreove, the germination rate in the CLT6@PCN-Q treatment group was similar to that of the control group, and germination rates of these four groups reached maximum within 28 h. After cultivation for 5 days, the stem lengths and plant heights of Chinese cabbage in each group were recorded and evaluated. As shown in Fig. 4b and
c, the stem lengths and plant heights of CLT6@PCN-Q treatment group corresponded to those of the control group, which indicated that CLT6@PCN-Q had no significant promoting effect on the stem lengths and plant heights of Chinese cabbage. However, the stem lengths in free GA treatment group and GA-loaded CLT6@PCN-Q treatment group were 1.96 times and 1.86 times longer than those of control group, and the plant heights were 1.76 times and 1.8 times higher than those of control group, respectively, which demonstrated that free GA and GA-loaded CLT6@PCN-Q possessed an obvious promotion effect on the stem lengths and plant heights of Chinese cabbage, and GA could be released from GA-loaded CLT6@PCN-Q in a slow-release manner with the stimuli of pH, SPM, and temperature. Moreover, there was no significant difference in the stem lengths and plant heights between free GA group and GA-loaded CLT6@PCN-Q treatment group, revealing that GA could be released from GA-loaded CLT6@PCN-Q with good bioactivity.

Subsequently, the fresh weights and dry weights of Chinese cabbage in each treatment group were evaluated, and there was no significant difference between CLT6@PCN-Q treatment group and control group. However, free GA and GA-loaded CLT6@PCN-Q treatment groups exhibited higher fresh and dry weights compared with the control group, which indicated that Chinese cabbage had enhanced organic matter accumulation after treatment with GA and GA-loaded CLT6@PCN-Q, promoting the growth and increasing the yield of it (Fig. 4d and Fig. S11).

In addition, the promotion effect of the GA-loaded CLT6@PCN-Q on the germination rates and plant heights of the monocotyledon wheat were investigated. CLT6@PCN-Q had no promotion effect on the germination rate of wheat seeds, which was consistent with result of the germination rate on Chinese cabbage. Notably, compared with the control group and the free GA treatment group, GA-loaded CLT6@PCN-Q treated group exhibited an enhanced promotion effect on the germination rate of wheat, indicating that GA could be released from CLT6@PCN-Q under the stimuli of temperature and endogenous SPM to accelerate germination of seeds. Meanwhile, at the beginning of germination, GA-loaded CLT6@PCN-Q showed a low germination promotion effect on wheat seeds than that of free GA due to the slow release of GA. Besides, the germination rate of wheat seeds in the GA-loaded CLT6@PCN-Q treatment group was higher than that of free GA treatment group after cocultured for 16 h, which was attributed to the sustained release of GA from GA-loaded CLT6@PCN-Q (Fig. 5a).

Similarly, the stem lengths and plant heights of wheats were also measured after coculturing. CLT6@PCN-Q treated group displayed indistinctive stem lengths and plant heights compared with the control group. Meanwhile, the plant heights in the free GA and GA-loaded CLT6@PCN-Q treatment groups were similar to those in the control group. However, the wheats cocultured with free GA and GA-loaded CLT6@PCN-Q exhibited strong and enhanced stem lengths under the same conditions, that was, stem lengths 1.33 times and 1.30 times as long as those in the control group, respectively. Moreover, there were no significant difference in stem lengths and plant heights between free GA and GA-loaded CLT6@PCN-Q treated group, demonstrating that GA could be released after encapsulated in the CLT6@PCN-Q nanocarrier under the stimuli of pH, SPM, and temperature in monocotyledonous wheat (Fig. 5b and Fig. S12). Overall, in the seed germination stage,
the cultivation temperature was 25±2°C, which could lead to the release of GA from GA-loaded CLT6@PCN-Q. Meanwhile, the increased endogenous SPM during seed germination could trigger the release of GA in GA-loaded CLT6@PCN-Q. In addition, the organic acids secreted by the roots during the plant growth stage could cause the release of GA in the GA-loaded CLT6@PCN-Q. Furthermore, the fresh weights and dry weights in each group were determined. The wheats cocultured with CLT6@PCN-Q showed similar fresh and dry weights compared with the control group, and GA-loaded CLT6@PCN-Q treatment group had higher fresh weights, which indicated that the wheats grew stronger and higher than that of the control group and the free GA treatment group, revealing the good promoting effect of the GA-loaded CLT6@PCN-Q on the growth of wheat plants (Fig. 5c). Besides, there was no significant difference in dry weight among the four groups (Fig. 5d). Importantly, in the GA-loaded CLT6@PCN-Q system, GA was loaded inside the as-prepared smart supramolecular plant hormone delivery system, which could decrease the loss of GA, reduce environmental pollution, and protect GA from degradation and destruction by the external environment, to achieve the purpose of efficiently promoting plant growth and ensuring the sustainable development of modern agriculture [72,73].

4. Conclusions

In summary, a smart supramolecular hormone delivery system, i.e., MOF-based GA-loaded CLT6@PCN-Q equipped with CLT6-based supramolecular nanovalves was prepared to regulate the growth of dicotyledonous Chinese cabbage and monocotyledonous wheat. Through the host-guest interactions between the CLT6 macrocycles and the Q stalks in the supramolecular nanoplatform, CLT6 was successfully installed on the surface of the Q stalks-modified porous NMOFs to achieve efficient cargo loading and controllable cargo release. The experimental results of cargo release showed that the GA-loaded CLT6@PCN-Q possessed controllable RhB release behavior under multiple stimuli of pH, temperature, and competitive agent SPM, which could achieve on-demand cargo delivery under various conditions. The regulation of plant growth experiments revealed that the supramolecular hormone delivery system (GA-loaded CLT6@PCN-Q) had the capabilities for maintaining the GA bioactivity stably, effectively promoting the seeds germination of wheat, stem growth of dicotyledonous Chinese cabbage and monocotyledonous wheat, indicating the versatility of the supramolecular hormone delivery system. The smart nanoplatform combines the merits of MOFs and supramolecular nanovalves based on synthetic macrocycles, stimulating new thinking for the delivery of agrochemicals like plant hormones with controllable release to regulate plant growth and increase crop yields, which possesses great potentials to improve the sustainable development of modern agriculture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Supplementary materials


