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Nano-Biohybrids: In Vivo Synthesis of Metal–Organic Frameworks inside Living Plants

Metal–organic frameworks (MOFs) are shown to be biomimetalized inside of living plants for the first time. The plant roots can actively take up both metal ions and organic ligands, leading to the formation of MOFs in the plant xylem without harming the plants. The in situ generation of materials inside complex living organisms can allow for unique hybrid organisms to be engineered, potentially as an alternative to genetic engineering.

Nano-Biohybrids: In Vivo Synthesis of Metal–Organic Frameworks inside Living Plants

Joseph J. Richardson* and Kang Liang*

Plants have a complex passive fluid transport system capable of internalizing small molecules from the environment, and this system offers an ideal route for augmenting plants with functional nanomaterials. Current plant augmentation techniques either utilize permeabilizing agents or plant cuttings to allow for the preformed nanomaterials to be integrated into the plant. A so far unexplored concept is the formation of the functional material, in situ, from precursors small enough to be passively internalized through the roots without harming the plants. Metal–organic frameworks are ideal for in situ synthesis as they are composed of metal ions coordinated with organic ligands, and the precursors are small enough to be transported into and through plants. Moreover, it is recently found that metal–organic frameworks can mineralize around single-celled organisms in mild aqueous conditions without significant detrimental effects to the coated organism. Herein, the synthesis of two types of metal–organic frameworks, $\text{Zn}(\text{Melm})_2$ and $\text{Ln}_2(\text{BDC})_3$, is reported inside a variety of plants using mild reaction conditions. Small-angle X-ray scattering and in situ synchrotron experiments help elucidate the formation kinetics and crystal phases of the nano-biohybrid plants. Plants augmented with luminescent metal–organic frameworks are utilized for small molecule sensing, although other applications, such as pathogen sensing, proton conductive plants, improved CO_2 capture, bacteria-free nitrogen fixation, drought and fungi-resistance, and enhanced photosynthesis and photocatalysis, are foreseeable. Overall, the in situ generation of functional materials inside of fully intact plants can lead to more complex nano-biohybrid sensors and organisms augmented with superior performance characteristics.

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The integration of functional materials into and around living systems represents an emerging branch of augmentation engineering with potential applications in sensing, electronics, catalysis, and robotics.^[1–4] This is generally accomplished by growing or attaching the functional material onto cells or organisms,^[5,6] modifying or altering the cell or organism to take up the functional materials, or by synthesizing the material inside of the living system.^[4,7–11] Plants are ideal candidates for bioaugmentation and nanobionics, due to their vascular network and use of passive forces for transporting fluids and molecules or particles dispersed in fluids.^[12] For example, the ability for plants to sequester metals from the environment is remarkable, and is currently being harnessed for bioremediation.^[13–15] Foreign organic molecules can also naturally accumulate in plants,^[15–17] however human intervention, such as trimming the plant at the stem, can allow for larger molecules to be accumulated through cohesive and adhesive forces.^[4] Historically, this method has been used for dying plants,^[18] although more recently conductive polymers containing poly(3,4-ethylenedioxythiophene) have been incorporated into living plant clippings to engineer functional conductive biohybrid materials.^[4] Particulate matter such as nanoparticles and nanotubes can sometimes be too large to be passively taken up by plants and plant clippings,^[19] but have been incorporated into plants either through infiltration into the roots or leaves using specific permeabilizing solutions^[20] or surface modification,^[2,3] or by techniques such as vacuum filtration.^[21] However, a so far unexplored option for incorporating functional materials into plants is the in situ synthesis of the material in vivo, which could open the door for advanced sensors among other applications.

A recent promising innovation in bioaugmentation is the growth of metal–organic frameworks (MOFs) around bioentities, including biomolecules,^[22–25] viruses,^[26] and even living prokaryotic and eukaryotic cells.^[5,27] MOFs are a class of synthetic and natural^[28] nanoporous materials with potential for a wide variety of applications, including gas capture, catalysis, separation, proton conductivity, and biomedicine.^[29–33] MOFs are composed of metal ions or clusters bridged by organic

Figure 1. Illustration of metal–organic framework (MOF) formation inside of plants. a) Plants are augmented with two different classes of MOFs: b) $\text{Zn}(\text{Melm})_2$ is formed in a one-step process due to the slow formation kinetics in water, while c) $\text{Ln}_2(\text{BDC})_3$ is formed in a two-step process by sequential incubation with the precursors. d,e,h–k) $\text{Zn}(\text{Melm})_2$ formed inside of reed clippings using a one-step process. Elemental maps of the augmented plant in (d) using EDX mapping. h) Carbon (red), i) oxygen (green), j) nitrogen (purple), and k) zinc (blue). SEM images of d,e) augmented and f,g) naked plants. Note that (e) is a magnified image of the region in the white box of (d), and (g) is magnified image of the region in the dashed white box in (f). 1 cm of the reed was removed from the base before imaging the cross-sections. d–g) False coloring highlights the MOFs (yellow) and plant material (green).

linkers,^[31] and were traditionally synthesized under harsh solvothermal conditions,^[34] however the presence of biomolecules and bioentities allows for greatly expedited MOF growth in aqueous ambient conditions.^[24] MOFs have thus far been used as a protective coating, allowing for enzymes to retain their activity after harsh treatment,^[24,35,36] protecting virus capsids from denaturation by solvents,^[26] and allowing yeast to remain viable after treatment with lytic enzymes and antifungal agents.^[5] However, the in situ growth of MOFs inside living organisms has not yet been accomplished, nor has

the integration of MOFs with multicellular organisms been achieved. Success in this endeavor could open the door for complex biosensors, or long lasting plants. Therefore, the integration of MOFs with plants represents a unique step for both the bioaugmentation and MOFs fields.

Herein, we demonstrate that different MOFs can be synthesized inside of living plants, utilizing both plant clippings and fully intact plants. The metal salts and organic linkers are small enough to be taken up by plants through cohesive and adhesive forces, and the precursors accumulate around the biomolecules

in the plants, allowing the MOFs to grow. For slower forming MOFs, such as the model MOF composed of 2-methylimidazole (MeIm) and zinc ions ($\text{Zn}(\text{MeIm})_2$)^[32] the plant clipping can be added directly into a solution of both MOF precursors mixed in water. For MOFs that form more rapidly, such as lanthanide terephthalates (BDC), namely $\text{Eu}_2(\text{BDC})_3$ or $\text{Tb}_2(\text{BDC})_3$,^[37] the plant cutting can be added to a single precursor in water, followed by washing and subsequent addition into an aqueous solution of the other precursor (**Figure 1**). The organic ligand should be incorporated before the metal ion for lanthanide MOFs, or in other words the plant should be incubated with the larger precursor followed by incubation with the smaller precursor. Small and wide angle X-ray scattering (SAXS and WAXS), scanning electron microscopy (SEM) combined with elemental mapping and fluorescence microscopy were used to confirm MOF formation. This method was also utilized in an intact plant, rather than a plant clipping, which demonstrates that MOFs can be grown inside of a living organism, and more generally that functional materials can be synthesized inside of a plant. Finally, the fluorescent signal from the lanthanide MOFs inside the plants was used to detect the presence of acetone.^[38] Overall, this process is unique conceptually, and a variety of other applications can be envisioned through harnessing the specific properties of both living plants and MOFs,^[39] such as biosensors,^[40] conductive biomaterials,^[41] or greenhouse gas capture.^[30]

Composed of 2-methylimidazole (MeIm) and zinc ions, $\text{Zn}(\text{MeIm})_2$ can form in aqueous media depending on the conditions,^[42–44] however using our conditions it does not readily form in water without the presence of biomolecules or bioentities.^[24] For our experiments, both precursors were mixed in water at a final concentration of $40 \times 10^{-3} \text{ M Zn}^{2+}$ and $160 \times 10^{-3} \text{ M MeIm}$, after which the plant clippings were added to the mixed solution. Initial tests were conducted with a reed due to the large xylem size and therefore rapid liquid transport. In situ SAXS/WAXS studies were conducted to determine the relative speed of formation $\approx 1 \text{ cm}$ and $\approx 7 \text{ cm}$ above the base of the clipping (**Figure S1**, Supporting Information). A predominantly ZIF-8 phase formed within the first 8 h and the crystalline peaks continued to grow in intensity throughout the experiment. Therefore, overnight incubation was used for all subsequent $\text{Zn}(\text{MeIm})_2$ experiments. After MOF formation, SEM images demonstrated the presence of particles primarily inside the xylem, with few MOFs in the phloem (**Figure 1**; **Figures S1 and S2**, Supporting Information). Fluorescence imaging at the cellular level^[45] revealed that the MOFs were primarily in the xylem and located on the cell walls, similar to our previous experiments on growing MOFs on unicellular organisms (**Figure S3**, Supporting Information).^[5,27] Additionally, MOFs were found on the outside of the plant below the precursor waterline, which is also expected as the precursors can easily grow around the polysaccharides on the plant surface.^[46] Elemental mapping utilizing energy dispersive X-ray spectroscopy (EDX), confirmed the presence of zinc and elevated nitrogen content in comparison to what was observed in an untreated reed where no zinc was present (**Figure S4**, Supporting Information), suggesting the presence of $\text{Zn}(\text{MeIm})_2$. The background nitrogen and zinc levels for the naked reed matched literature values ($\approx 5\%$ and $<1\%$,

respectively),^[47] and these values increased to $\approx 15\%$ and 23% , respectively (**Figure S5**, Supporting Information). With these positive results, MOFs were then grown in a more complex plant clipping, namely a rose. The stem clearly showed the presence of $\text{Zn}(\text{MeIm})_2$ particles under SEM (**Figure S6**, Supporting Information). Synchrotron SAXS and WAXS were necessary for determining the presence and crystal phase of the MOFs, as standard laboratory X-ray techniques, such as powder X-ray diffraction, are too weak to detect the trace amount of MOF formed in the plants. Moreover, SAXS plots with high levels

Figure 2. Luminescent lanthanide MOFs formed inside of plant clippings using the two-step method. Camera and microscope images using a UV light: Fluorescence microscopy image of $\text{Tb}_2(\text{BDC})_3$ MOFs formed by a) incubating the water lily stem first in the organic ligand followed by subsequent incubation in the metal ion, and b) incubating the water lily stem first in the metal ion followed by subsequent incubation in the organic ligand. Camera image using a UV light for excitation: c) The stem in (a); d) the stem in (a) and (c) after cross-sectioning. e) $\text{Eu}_2(\text{BDC})_3$ MOFs formed in a water lily leaf and stem. The leaf was bisected for imaging. f) SEM image of a cross-section of the stem imaged in (a), (c), and (d) with false coloring to highlight the MOFs (yellow) and plant material (green).

of noise are expected because of the low quantities of MOFs inside the plants, similar to what we found in our previous reports.^[5] SAXS/WAXS studies confirmed the presence of crystalline materials in the rose stem, petals, and leaves (Figure S7, Supporting Information). Interestingly, the standard crystal phase of $\text{Zn}(\text{MeIm})_2$, namely ZIF-8, was only partially observed in the rose stem. The diamondoid (*dia*) phase *dia*- $\text{Zn}(\text{MeIm})_2$ was also observed in the rose stem and for the other portions of the rose, and reed. Previously, the *dia* phase was discovered to occur for $\text{Zn}(\text{MeIm})_2$ formed in the presence of water,^[48,49] and more recently was demonstrated to form when $\text{Zn}(\text{MeIm})_2$ is synthesized in water around cotton fibers, i.e., cellulose.^[46] The presence of the *dia* phase is therefore expected in some tissue, as cellulose is found in high-quantities in the cell walls of plant cells. Lignin on the other hand leads to pure the ZIF-8 phase (Figure S8, Supporting Information), which helps explain why ligneous tissue, such as the rose stem where the xylem cell walls are coated in lignin, shows a predominantly ZIF-8 phase. The reed showed penetration of the $\text{Zn}(\text{MeIm})_2$ roughly 10 cm up from the base of the plant as determined by SAXS/WAXS, likely due to the rapid fluid transport in reeds. Finally, the concentration of MeIm was tripled while keeping the Zn^{2+} concentration fixed, and fluorescence microscopy images showed similar structures on the outside of the plant cell walls, suggesting that the synthesis conditions are amenable to a wide range of precursor ratios (Figure S9, Supporting Information), as seen for $\text{Zn}(\text{MeIm})_2$ studies in the literature.^[42] Collectively, the SAXS/WAXS, SEM, and EDX results confirmed that MOF was grown inside of the plant cuttings.

As $\text{Zn}(\text{MeIm})_2$ does not rapidly and readily form in water without a seeding agent,^[24] lanthanide MOFs ($\text{Eu}_2(\text{BDC})_3$ or $\text{Tb}_2(\text{BDC})_3$) capable of rapidly forming in water were also tested.^[50,51] These MOFs have a strong fluorescence and have been used for biomimetic mineralization around proteins patterns.^[23] In this instance, a two-step synthesis process was used, where the plant clipping was added to one of the

MOF precursors, after which the plant clipping was rinsed and added to the other MOF precursor. We hypothesized that the organic ligand (disodium terephthalate, Na_2BDC) would be better for the first incubation stage, as the metal ion (Eu^{3+} or Tb^{3+}) is small enough to move through the pores of the MOF and so would not be hindered by MOF growth. This should allow the metal ions to permeate further into the plant in comparison to the larger BDC ligand, which cannot fit through the MOF pores and would therefore be more likely to just form at the stem base.^[52,53] In this instance, a water lily leaf was used for MOF growth as it allowed for easy cross-sectioning and manipulation. The plant clipping was incubated with the first precursor overnight, and then only incubated with the second precursor for 3 h to observe how deep in the stem the MOF could grow (Figure S9, Supporting Information). There was a deep penetration of the Tb^{3+} (3 cm penetration) for the clipping incubated with BDC first (Figure 2; Figure S10, Supporting Information), and shorter incubation times did not allow for significant metal progression up the stem (Figure S11, Supporting Information). On the other hand, there was significantly less penetration when the Tb^{3+} was used first (<0.5 cm penetration). This trend was confirmed by analyzing cross-sections and stem slices under a fluorescence microscope and UV light. Cross-sections up the stem showed that the fluorescence, and therefore MOFs, were largely relegated to the base of the stem when the plant was first incubated with the organic ligand (BDC). After growth in flowers, the vasculature of the flower petals could be visualized under a UV light (Figure S12, Supporting Information). This confirmed our hypothesis that the smaller precursor should be incubated last. SEM images of the stem of the sample where the metal was incubated second showed the presence of lanthanide MOF platelets at different stages of formation (Figure 2; Figure S13, Supporting Information). These experiments demonstrated that the in situ growth of MOFs is not relegated to ZIF-8.

Figure 3. Luminescent lanthanide MOFs formed inside of a fully intact plant using the two-step method. Fluorescence microscopy images of $\text{Tb}_2(\text{BDC})_3$ (green) as visualized in the cross-section of a) the stem and b) leaf. Camera images of c) leaf, d) stem and leaf, and e) root as visualized under a UV light. f–i) 2D SAXS plots of (c)–(e) with the approximate measurement spots shown in white arrows (see Figure S12 in the Supporting Information for plots). Note (a) and (b) show some plant autofluorescence (red) in the microscopy images.

The small size of the MOF precursors inspired us to try synthesizing MOFs in fully intact plants (i.e., not clippings) through mass flow of the MOF precursors into the roots followed by transport through the xylem. The two-step process was utilized by incubating the plant roots in the BDC solution first, followed by washing and subsequent incubation in Tb^{3+} solution. The uptake of the precursors and in situ growth was hampered in the intact plant when compared to the plant clippings as analyzed under a UV light. This is not surprising as the uptake of an organic molecule through the roots is markedly slower than the transport through the xylem of the stem,^[54–56] the MOFs could be synthesized inside of the living plant although the MOF grew in specific segments of the plant. Specifically, not all of the leaves showed the fluorescent signature of the MOFs. Similarly, the MOFs only grew in specific xylem tubes associated with one region of the plant as visualized under a UV light (Figure 3). These asymmetries in synthesis could be from asymmetries in uptake and transport due to the differences in xylem maturity in the various stems.^[57] SAXS measurements at different locations in the plant demonstrated crystalline MOFs in the roots, stem, and leaves and scattering from single crystals could be seen, confirming asymmetries in MOF growth (Figure 3; Figure S14, Supporting Information). Moreover, synthesizing the MOFs through the roots did not appear to negatively impact the plant (Figure S15, Supporting Information). This experiment represents both the first incorporation of functional materials into fully intact living plants and the first synthesis of MOFs inside of an intact living organism.

A variety of applications arising from plants augmented with MOFs are imaginable, and therefore we set about testing whether our nano-biohybrid plants could be used as chemical sensors. Lanthanide MOFs have been used for sensing a variety of chemicals through changes in fluorescence associated with solvent–metal interactions, for example, fluorescent quenching effect of $\text{Ln}_2(\text{BDC})_3$ upon contact with small molecules can be attributed to the reduced antenna efficiency of the BDC linkers to Ln^{3+} due to the electronic interactions and the competition of absorption for the light source energy between the analytes and the BDC linker.^[58–60] and lanthanide MOFs in solution are able to sense low concentrations of acetone in water (0.5–4.0% acetone).^[38] The $\text{Eu}_2(\text{BDC})_3$ were grown inside of plant clippings, namely flower stem, lotus stem, and lotus leaf. The lotus leaf and flower stem were sliced in two and one half of each was incubated in an aqueous solution of 2% acetone, while the other half was incubated in deionized water. After 2 h, there was a marked difference in fluorescence between the samples incubated with the trace acetone and the specimens incubated in water (Figure 4; Figure S16, Supporting Information). For ease of use, the lotus stem was not sectioned, and only the opening of the stem was incubated in the 2% acetone solution. After 3 h incubation, the stem was removed and rinsed with water before sectioning. A similar decrease in fluorescence was apparent on the inside of the stem (Figure S17, Supporting Information), suggesting that augmented plant stems can be used to detect small molecules in water by capillary transport through the internally coated stem. Moreover, fluorescent MOFs have also been used to sense explosives^[61] and perfluorocarbons, suggesting that they could find use as passive sensors

for vapor or liquid contaminants. For example, plant-MOF hybrid could be used for the in situ detection of contaminants in hydroponics setups.

We demonstrated that different MOFs can be synthesized inside of complex living organisms, namely plants. Different synthesis routes, either one-step or two-step, can be used depending on the speed of synthesis of the MOF. $\text{Zn}(\text{MeIm})_2$ was synthesized in a single step for plant clippings, while lanthanide MOFs ($\text{Eu}_2(\text{BDC})_3$ and $\text{Tb}_2(\text{BDC})_3$) were synthesized in a two-step process for both plant clippings and fully intact plants. In situ synchrotron experiments helped elucidate the time scale and formation of the MOFs at different distances from the opening of the plant clipping. For the two-step process, we found that incubation with the larger precursor should take place before incubation with the smaller precursors to allow for optimal penetration of the MOF precursors and therefore MOF synthesis deeper in the plant. Moreover, by using a functional MOF, in this instance luminescent MOFs,

Figure 4. Small molecule sensing of acetone using a water lily leaf augmented with $\text{Eu}_2(\text{BDC})_3$ MOFs. Camera images of the lotus leaf as visualized under a UV light a,b) before and c,d) after cross-sectioning and incubation with a 2% acetone solution or pure water. Comparison of gray scale values of (c) and (d) as determined by ImageJ for the e) bottom and f) top of the lotus leaf sections exposed to acetone (left) or water (right). The dashed black line in (e) and (f) corresponds to the white lines in (c) and (d).

small molecule sensing can be conducted inside of the plants. Although a small selection of MOFs was synthesized in this study, other MOFs and functional materials could theoretically be synthesized inside of living plants by ensuring the synthesis conditions are within the tolerable conditions of the plant and that the precursor materials are small enough to migrate through the plant. Moreover, the MOFs presented in this study are stable in the presence of salt, fertilizer components (urea), and a major component of soil (humic acid) (Figure S17, Supporting Information), although detailed studies would be required to show the longevity of MOFs in plants for extended periods of time. A limitation is that a diverse range of metal ions can naturally accumulate in plants and could foreseeably interfere with the MOF formation during synthesis. Moreover, as mentioned above the crystallinity of the MOFs is partially dependent on the biomolecules governing mineralization and the process is not yet fully understood. Therefore, rationally engineering the crystal phase of the MOFs could prove challenging. Still, it is foreseeable that the diversity of nano-biohybrid systems will continue to grow in the near future, as it has in the recent past.

Experimental Section

Details of materials, in situ formation of $\text{Zn}(\text{Melm})_2$ and $\text{Ln}_2(\text{BDC})_3$, small molecule sensing, and characterization are documented in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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