Rapid, Ambient Temperature Synthesis of Imine Covalent Organic Frameworks Catalyzed by Transition Metal Nitrates

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Supporting Information Placeholder

ABSTRACT Covalent Organic Frameworks (COFs) are crystalline, porous organic materials with promise for applications including catalysis, energy storage, electronics, gas storage, water treatment, and drug delivery. Conventional solvothermal synthesis approaches to COFs require elevated temperatures, inert reaction environments, and long reaction times. Here, we report that transition metal nitrates can catalyze the rapid synthesis of imine COFs. We tested a series of transition metal nitrates as catalysts for the synthesis of a model COF and found that all transition metal nitrates produced crystalline COF products for reactions conducted at ambient temperatures. The reactions were insensitive to the presence of oxygen. $Fe(NO_3)_3{\cdot}9H_2O$ was found to produce the most crystalline product, and by optimizing the catalyst loading we found that crystalline COF could be produced within 10 minutes. We further tested $Fe(NO_3)_3{\cdot}9H_2O$ as a catalyst for 6 different COF targets varying in linker lengths, substituents, and stabilities, and found that $Fe(NO_3)_3{\cdot}9H_2O$ effectively catalyzed the synthesis of all imine COFs tested. This work demonstrates a simple, low-cost approach for the synthesis of imine COFs and will significantly lower the barrier for the development of imine COFs for various applications.

Covalent organic frameworks (COFs) are crystalline and porous organic networks that have shown promise for applications including catalysis, energy storage, electronics, gas storage, water treatment, membrane separations, and drug delivery.[1–5] Imine COFs are of particular interest for applications because they exhibit excellent stability in water and various organic solvents.[5] However, imine COFs are typically synthesized in batch, high temperature (120 °C) solvothermal or hydrothermal reactions that require 3 days or longer to achieve significant yields and good crystallinity.[3,5–7] Hence, simpler, lower-cost, and more rapid approaches to the synthesis of imine COFs are needed.

A number of studies have explored alternative, faster, and less energy-intensive approaches to the synthesis of imine COFs. Marder and coworkers developed an approach to produce imine COFs under solvothermal conditions within four hours using mild activation procedures to avoid pore collapse.[8] Wang and coworkers developed a general method to synthesize imine COFs in 160 seconds under electron bean radiation.[9] Exposure to light,[10] reaction in a microwave,[11,12] and sonication[13] can also promote reversible reactions and tremendously decrease the required reaction time. In all of these examples, acetic acid was employed as the catalyst for imine COF synthesis.

Developing new catalysts for COF synthesis can further reduce the cost and time required to synthesize COFs, but very few catalysts for imine COF synthesis have been studied. A number of studies have utilized *p*-toluenesulfonic acid (PTSA) as a catalyst for COF synthesis,[14–16] with the advantage that it can be used to catalyze solid state reactions. However, large amounts of PTSA are required, which may make it difficult or expensive to recycle the catalyst, and solid-state reactions come with additional challenges in terms of blending and processing the starting materials and final products. Metal triflates can catalyze the rapid synthesis of imine

COFs,[17,18] but the best metal trfilate catalyst for COFs relies on the expensive, rare-earth element scandium.[19,20]

Herein, we report that transition metal nitrates catalyze the rapid synthesis of imine COFs at ambient temperatures with excellent yields. Transition metal nitrates have been previously employed as catalysts for the synthesis of Schiff bases. Mobinikhaledi et al. used copper nitrate to synthesize Schiff bases rapidly and efficiently under ambient conditions.[21] In another report, Mobinikhaledi et al. utilized a series of metal nitrates ranging from 5 mol% to 20 mol% in the synthesis of Schiff bases containing benzimidazole moiety at room temperature.[22] Through optimization of different reaction conditions, they found that 5 mol% of $Ni(NO_3)_2{\cdot}6H_2O$ in methanol successfully generated Schiff bases with high yield and within just 20 to 30 min. Motivated by these findings, we explored the application of transition metal nitrates in synthesis of imine COFs. We tested six different transition metal nitrates for use as catalysts in the synthesis of imine COFs under systematically varying reaction conditions and characterized the products through a combination of Fourier transform infrared (FT-IR) spectroscopy, powder X-ray diffractions (PXRD) and nitrogen sorption analysis. We found that catalytic amounts of transitional metal nitrates, in particular $Fe(NO_3)_3{\cdot}9H_2O$, effectively catalyzed Schiff-base reactions and produced highly crystalline COFs at room temperature and for reaction times as short as 10 minutes. Furthermore, the reaction was not sensitive to oxygen or water. Transition metal nitrates are low-cost, abundantly catalysts, and this work demonstrates a simple and rapid approach to imine COFs. We expect this will significantly lower the barriers for synthesis and further development of COFs for various applications.

We evaluated six different transition metal nitrates for the synthesis of imine COFs: $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_3{\cdot}6H_2O$, $Mn(NO_3)_3{\cdot}6H_2O$, $Cu(NO_3)_3{\cdot}6H_2O$, and $Co(NO_3)_3{\cdot}6H_2O$. For simplicity, these catalysts will be referred to as M-NO, where M is the transition metal (e.g., $Fe(NO_3)_3{\cdot}9H_2O$ will be referred to as Fe-NO). We initially evaluated these transition metal catalysts for the synthesis of TAPB-OMePDA COF through the Schiff-base polycondensation between 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 2,5-dimethoxyterephthalaldehyde (OMePDA), as shown in Figure 1. We used this COF as a model system because it exhibits excellent crystallinity and porosity under a variety of synthesis and activation conditions, as demonstrated by us[23] and others.[8,24] To test each transition metal catalyst, we dissolved a stoichiometric ratio of TAPB and OMePDA in 1,2-dichlorobenzene (DCB) and *n*-butanol (1:1, v/v) and added 5 mol % catalyst, relative to NH_2 functional groups. The reaction mixture was sonicated to ensure the full dissolution of catalyst and then reacted at ambient temperature, without any purging or heating of the reaction mixture. Upon sonication, insoluble powders rapidly formed, and the mixture immediately turned cloudy and reddish. The reaction was allowed to proceed for two hours before recovering the powders by filtration and washing with solvent and supercritical CO_2 ($ScCO_2$) prior to analysis.

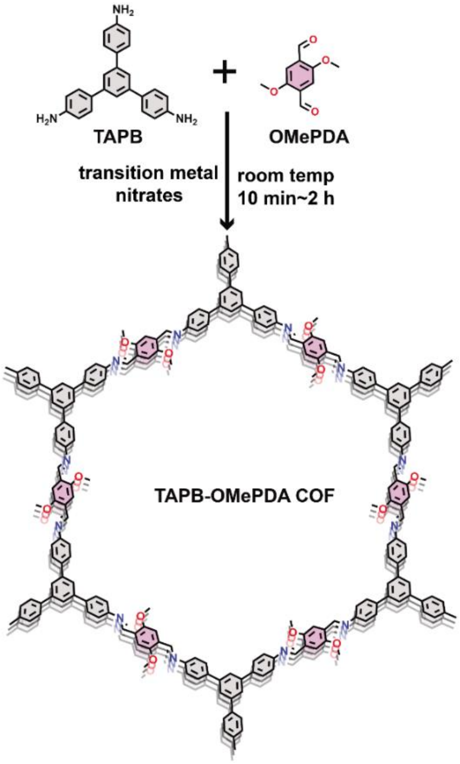

Figure 1. Rapid synthesis of TAPB-OMePDA COF catalyzed by transition metal nitrates.

Fourier transform infrared (FT-IR) spectroscopy, powder X-ray radiation diffraction (PXRD) and nitrogen sorption measurements revealed that the Schiff-base reaction was successful and produced a crystalline and highly porous product. FT-IR (Figures S1–S2) spectra revealed the formation of imine linkages with the appearance of an absorption band at1619 cm^{-1} and attenuation of the peak at 1685 cm^{-1}, corresponding to imine (C=N stretching) and aldehyde (C=O stretching) functional groups, respectively.[25,26] PXRD (Figure 2a) measurements showed that all solids possessed crystalline structures consistent with previous reports and in agreement with simulated structures with AA stacking (Figure S3). The samples produced using Fe-NO catalyst had the most prominent crystalline peaks, with a peak at $2\theta = 2.7^{o}$ several orders of magnitude higher in intensity compared with other products. The product from the Fe-NO catalyzed reaction also had the smallest full width at half-maximum (FWHM) values (Table S2). Nitrogen sorption isotherms of these samples (Figure 2b) and corresponding Brunauer–Emmett–Teller (BET) surface areas (Figures S4–S5) demonstrated that the products were highly porous and that Fe-NO produced samples with the highest porosities among all M-NO catalysts tested. Samples synthesized using Fe-NO and Ni-NO had surface areas of 1345 and 1214 m^2 g^{-1}, respectively, which were higher than those synthesized using other metal nitrates. All samples had BET surface areas larger than 650 m^2 g^{-1}, indicating that all transition metal nitrate catalysts successfully produced highly porous COFs. Pore size distributions of these samples were calculated using nonlocal density function theory (NLDFT) and are shown in Figure 2c. Samples catalyzed by Fe-NO had the narrowest pore size distributions centered around 2.7 nm, which matches that for prior reports of highly crystalline TAPB-OMePDA COF.[27] Samples synthesized using Ni-NO and Mn-NO catalysts also had relatively narrow pore size distributions, while samples prepared using Zn-NO, Cu-NO, and Co-NO exhibited broader pore size distributions.

We also studied the effect of reaction time for different catalysts by analyzing samples produced after 2 hours and 3 days of total reaction time. Samples produced by Fe-NO and Ni-NO exhibited similar surface areas and crystallinities after 2 hours and 3 days of reaction time, indicating that 2 hours of reaction at ambient conditions was sufficient to produce highly crystalline product. After 3 days, crystallinity increased slightly, and Fe-NO and Ni-NO produced more crystalline samples compared to other metal nitrate catalysts as evidenced by more prominent PXRD peaks (Figure S6), narrower pore size distributions (Figures S7 – S8), and higher surface areas (Figure S9 – S10). These results demonstrate that transition metal nitrates, especially Fe-NO, are excellent catalysts for imine COF synthesis.

We next focused on the Fe-NO catalyst and optimized the catalyst loading. We chose six different catalyst loadings ranging from 1 mol% to 10 mol% relative to NH_2 groups, which corresponded to less than 3.5 mol% relative to TAPB monomers. All other reaction conditions were kept the same, and reactions were conducted at ambient temperatures and for 2 h reaction times. The samples produced with 10 mol%, 7 mol% and 5 mol% Fe-NO showed highest crystallinities and specific surface areas as evidenced by PXRD and nitrogen sorption measurements, respectively (see Figures 3a-b and Figures S11 – S12). These samples had surface areas of 1674, 1326, and 1345 m^2 g^{-1}, respectively. They also exhibited narrower pore size distributions than other samples (Figure S13).

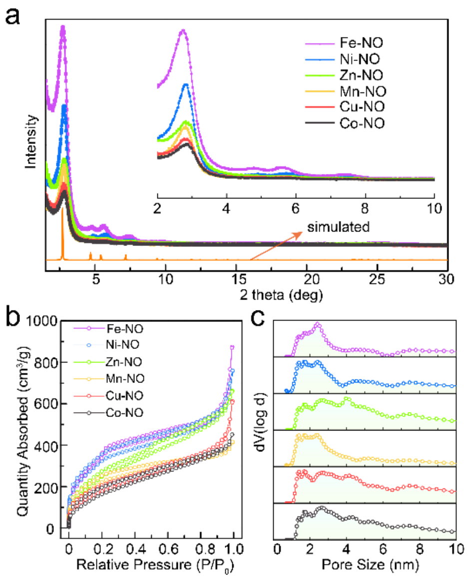

Figure 2. (a) PXRD spectra, (b) nitrogen sorption isotherms, and (c) corresponding pore size distributions for TAPB-OMePDA COFs synthesized with different transition metal nitrates.

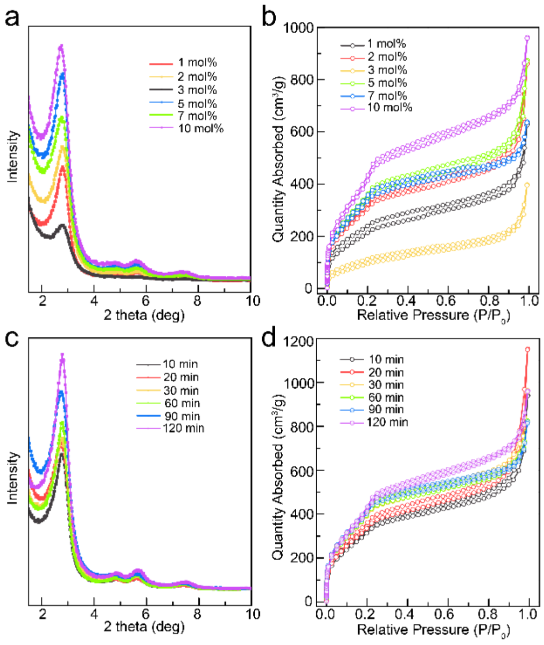

Figure 3. (a) PXRD patterns and (b) nitrogen sorption isotherms for TAPB-OMePDA COFs synthesized using different amounts of Fe-NO for 2 hours; (c) PXRD patterns and (d) nitrogen sorption isotherms for TAPB-OMePDA COFs synthesized using 10 mol% Fe-NO for different times ranging from 10 minutes to 2 hours.

Next, we explored the effect of reaction time by varying the total reaction time from 10 minutes to 2 hours for 10 mol% Fe-NO as catalyst and keeping all other reaction conditions unchanged. The crystallinity and porosity increased with time as evidenced by PXRD (Figure 3c) and nitrogen sorption analysis (Figure 3d, Figures S14 – S16). However, after 10 minutes of reaction time, all samples had very high surface areas of 1233 m^2 g^{-1} or greater, ranging from 1233 m^2 g^{-1} for 10 min reaction time to 1674 m^2 g^{-1} for 120 min (Figure S14). These results indicate that highly crystalline COF formed within 10 minutes of reaction time. The surface area values were comparable to other studies reporting the synthesis of TAPB-OMePDA COF using acetic acid catalyst at 120 °C for 3 days[28–30] and only slightly lower than that reported by Marder and coworkers using solvothermal conditions along with nitrogen flow activation[8]. All samples showed narrow pore size distributions (Figure S16), further demonstrating that 10 mol% Fe-NO successfully catalyzed the synthesis of highly crystalline TAPB-OMePDA COF with regular porosity.

To test the broader effectiveness of transition metal nitrates as catalysts for imine-COF synthesis, we used the Fe-NO catalyst and targeted a series of COFs varying in structure and stability (Figure 4). All the COFs selected as targets have been previously synthesized using acetic acid as a catalyst,[23,30–34] with the exception of TAPB-BPDA COF which has only been previously synthesized using $Sc(OTf)_3$ catalyst.[17] We altered the linker length (i.e. BPDA) and the substituents of aldehyde monomers (i.e. vinyl-PDA, C8PDA) in order to test the functional group tolerance of the Fe-NO catalyst. We also targeted COFs of different structural stability. Prior work has shown that some COFs are more robust under different activation processes and maintain excellent crystallinity and surface area, while other COFs are fragile and lose crystallinity when activated using polar solvents.[8,23,24] We selected both fragile (TAPB-PDA, TAPB-BPDA, TAPT-PDA) and robust COFs (COF-V, TAPB-C8PDA, TAPT-OMePDA) for synthesis using Fe-NO catalyst. All reactions were conducted using 10 mol% Fe-NO for 2 hours, and samples were thoroughly washed and dried using $ScCO_2$ prior to analysis. FT-IR spectra of the final solid products (Figures S17–S22) confirmed the successful imine polycondensation for all samples tested and were consistent with previous reports.[17,23,30,31,35–37] All samples exhibited excellent crystallinity as evidenced by prominent peaks in the PXRD spectra (Figure 4a-f), which were consistent with both previous studies and simulated eclipsed, layered structures (Figure 4a-f and Figures S23–S28). We further calculated their pore size distributions using NLDFT method and found all samples possessed narrow pore size distributions (Figure S29). BET surface areas for TAPB-PDA COF, TAPB-BPDA COF, COF-V, TAPB-C8PDA COF, TAPT-PDA COF and TAPT-OMePDA COF were 1397, 981, 1392, 1202, 937, and 2058 m^2 g^{-1}, respectively (Figure 4h). Notably, Fe-NO was successful in catalyzing the synthesis of highly crystalline TAPB-BPDA COF, which has not previously been synthesized using acetic acid catalyst. We also could not produce crystalline TAPT-PDA COF using solvothermal methods with acetic acid catalyst and various solution conditions (see Supporting Information). This is consistent with two previous reports that reported TAPT-PDA COFs with limited crystallinity and low porosity.[35,36] However, highly crystalline powders could be synthesized within 2 hours utilizing Fe-NO catalyst. To compare the quality of COFs we synthesized with those from other reports, in Table S3 we compared the BET surface areas produced using Fe-NO with the highest values from prior reports. COF-V, TAPB-C8PDA COF, TAPT-PDA COF and TAPT-OMePDA COF synthesized through our approach showed higher BET surface areas than the highest records from previous reports.[30–34] These experiments demonstrated the general effectiveness of Fe-NO catalyst for imine COF synthesis, and it is likely that COFs with even higher quality can be produced with additional optimization.

Our results demonstrate that transition metal nitrates are effective catalysts for the synthesis of imine COFs. Unlike conventional solvothermal methods and a recent report using electron irradiation to rapidly synthesize COFs,[9] reactions catalyzed by metal nitrates were effective at ambient temperatures and without the need for purging the reaction to eliminate oxygen. Compared to $Sc(OTf)_3$ catalyst,[17,18] metal nitrates are lower-cost and more abundant. Additionally, the excellent solubility of metal nitrates in various alcohols and acetonitrile make them promising for the interfacial synthesis of COF films. We are actively pursuing the use of transition metal nitrates to synthesize imine COF films and membranes.

In conclusion, we demonstrated that transition metal nitrates, particularly $Fe(NO_3)_3 \cdot 9H_2O$, are excellent catalysts for imine-COF synthesis. We were able to synthesize TAPB-OMePDA COF with high crystallinity and surface areas within 10 minutes, and produced a series of crystalline imine-COFs rapidly at ambient temperatures. We expect this will significantly lower the barriers for synthesis and further development of COFs for various applications.

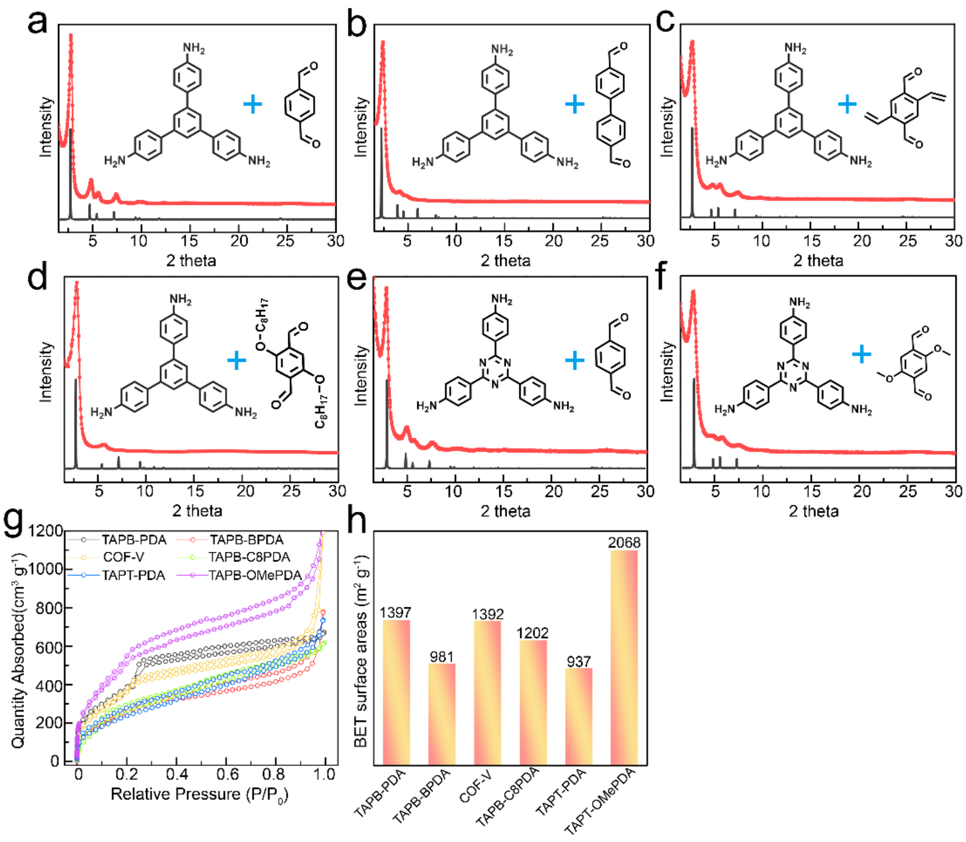

Figure 4. PXRD patterns for (a) TAPB-PDA COF produced by the reaction between TAPB and terephthalaldehyde (PDA), (b) TAPB-BPDA COF produced by the reaction between TAPB and 4,4'-biphenyldicarboxaldehyde (BPDA), (c) COF-V produced by the reaction between TAPB and 2,5-divinylterephthalaldehyde (vinyl-PDA), (d) TAPB-C8PDA COF produced by the reaction between TAPB and 2,5-bis(octyloxy)terephthalaldehyde (C8PDA), (e) TAPT-PDA COF produced by the reaction between 2,4,6-Tris(4-aminophenyl)-1,3,5-triazine (TAPT) and PDA, (f) TAPT-OMePDA COF produced by the reaction between TAPT and OMePDA, (g) nitrogen sorption isotherms and (h) BET surface areas.

ASSOCIATED CONTENT

Supporting Information

Materials, detailed synthesis procedures, summary of BET surface areas for different COFs from previous report, COF AA stacking structures and additional characterization analysis.

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Notes

The authors declare no competing financial interests.

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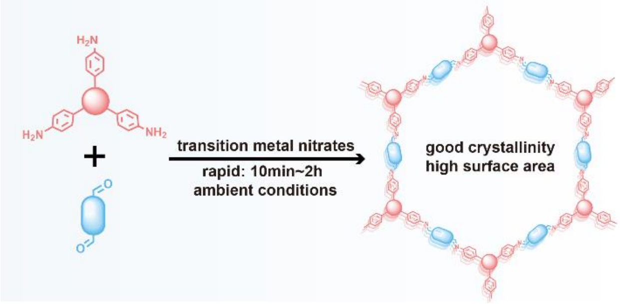

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