PRF# 58377-DNI10
Project Title: Hydrogen Bond Directed Synthesis of Covalent Organic Framework Materials
Principal Investigator: Chenfeng Ke
Affiliation: Department of Chemistry, Dartmouth College

Year 1 Progress Report

Part 1. Synthesis and 3D-printing of Covalent Organic Frameworks (COFs). COFs are usually synthesized as insoluble micrometer-sized crystalline powders, which limits their application for gas storage and catalysis due to the processing challenges and limited form factors. During the funding period (year 1), we developed a general method to build self-standing 3D-printed COFs monolith with controlled macroscopic architecture, good structural integrity, high mechanical strength, high crystallinity, and hierarchical pores.

In our design (**Fig. 1**), the polycondensation of the amino- and aldehyde starting materials are inhibited, which formed amorphous oligo-imine and polymer imine materials in the aqueous environment. Pluronic F127 was introduced to the reaction and co-assembles with these imine mixtures, affording a viscoelastic hydrogel that is suitable for direct ink write (DIW)-based 3D printing. The hydrogel ink was subsequently 3D-printed into a designed structure, e.g. pyramid lattice as shown in **Fig. 1**. The solvent of the 3D-printed monolith was evaporated first, and the monolith was heated for extensive imine condensation. After being heated, Pluronic F127 and unreacted species in the 3D printed monolith were removed by solvent extraction, affording hierarchical porous structures in the monolith. The monolith was further annealed in a solvent mixture to allow an amorphous-to-crystalline transformation, affording crystalline COF monolith with a high measured surface area.

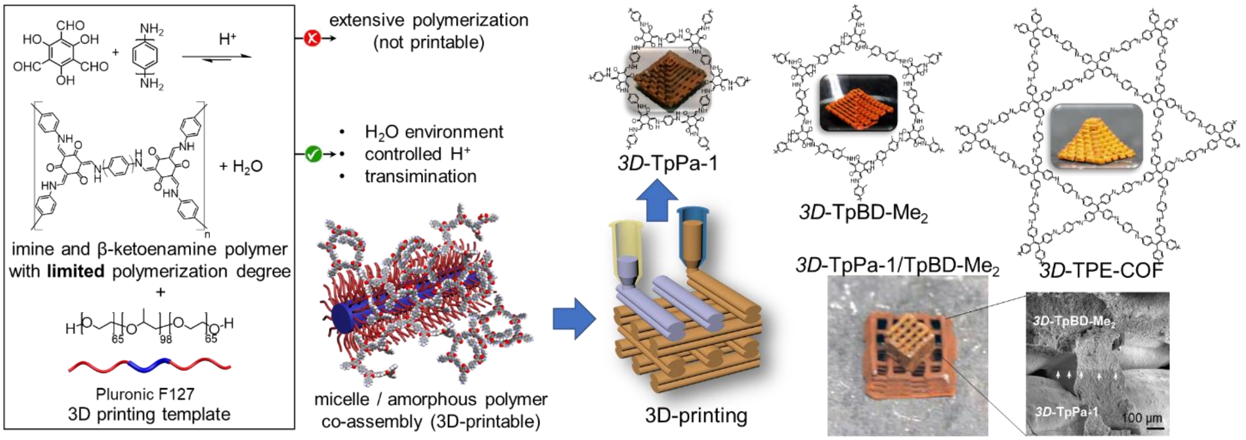

Fig. 1. Schematic illustration of the synthesis and fabrication of 3D-printed COF monoliths through an amorphous-to-crystalline transformation. Images of three COF monoliths including *3D*-TpPa-1, *3D*-TpBD-Me_2, *3D*-TPE-COF, and a dual-COF monolith *3D*-TpPa-1/TpBD-Me_2 are shown on the right.

Two β-ketoenamine COFs (TpPa-1 and TpBD-Me_2) were fabricated using this method and an imine-based COF (TPE-COF) was fabricated in a similar manner. To inhibit the fast polycondensation of tetrakis-(4-aminophenyl)-ethene and terephthalaldehyde, an imine starting material instead of the dialdehyde was employed during the COF synthesis and fabrication. *3D*-TpPa-1, *3D*-TpBD-Me_2, and *3D*-TPE-COF monoliths possess high crystallinity confirmed by powder X-ray diffraction analysis, high surface areas measured by nitrogen sorption experiments, and hierarchical porous features demonstrated in the scanning electron microscopy (SEM) investigations. FT-IR, solid-state ^{13}C NMR and elemental analysis confirmed the chemical structure of these COF monoliths and indicated complete removal of F127 template. Through multi-material 3D-printing, two COFs were integrated into one heterogenous monolith. SEM experiments revealed that a seamless interface was formed between two COFs due to the imine exchange taking place at the interface, which demonstrates a new method to integrate two COF materials together. The research progress was published in the *Journal of American Chemical Society* as a communication earlier this year (*J. Am. Chem. Soc.*, **2019**, *141*, 5154–5158. 10.1021/jacs.9b01561).

Part 2. Synthesis and crystallization of hydrogen-bonded monomers for framework development. The main challenge associated with the COF materials is the difficulty in balancing their crystallinity and chemical stability. To address this challenge, we have proposed to develop crosslinked organic framework materials through single-crystal to single-crystal transformation. In year 1, we have synthesized two monomers and obtained their single crystal structures in the solid-state (**Fig. 2**). The piperazine-based monomer **1** is a linear molecule, which forms edge-to-edge hydrogen bonds with the nearby monomers resulting in a 1D H-bonded network. Single crystal X-ray diffraction (SCXRD) analysis reveals that monomer **1** crystallizes in monoclinic space group $P2_1/c$ (a = 4.73, b = 13.34, c = 18.74, β = 96.13) and neighboring monomers are connected by H-bonding between the melamine moieties. These monomers are tightly packed along the *a*-axis.

Upon a selective protonation of the N-3 nitrogen atom of the melamine moiety of **1**, we have successfully introduced a strong ion pair interaction along with H-bonding interaction to direct the self-assembled superstructure in the solid-state (**Fig. 2b-c**). Accordingly, we have crystallized monomer **1** in the presence of sulfuric acid and nitric acid. SCXRD reveals that the monomer **1** crystallizes with methyl sulfate in the monoclinic space group $P2_1/c$ (a = 21.28, b = 8.61 c = 17.78, β = 92.70) and with HNO_3 in triclinic *P*-1 space group (a= 8.94, b= 8.95, c= 18.60, α= 86.19, β= 87.36, γ= 74.04). In the solid-state, the N-3 nitrogen atoms in triazine moiety form H-bond with the NO_3^- ion ($d_{\text{N-H}\cdots\text{O}}$ = 2.1 Å) or $MeSO_4^-$ ion ($d_{\text{N-H}\cdots\text{O}}$ = 1.94 Å). In the presence of HNO_3, melamine moieties from two neighboring monomers form a 2D supramolecular chain in an edge-to-edge fashion. The methylated sulfate anions cap the monomers via hydrogen bonding, rather than serving as connecting nodes in the crystal packing. Interestingly in both cases, the melamine moieties are prone to form π-π stacking (d = 4.1 Å), along the *b*-axis, in a slipped parallel fashion.

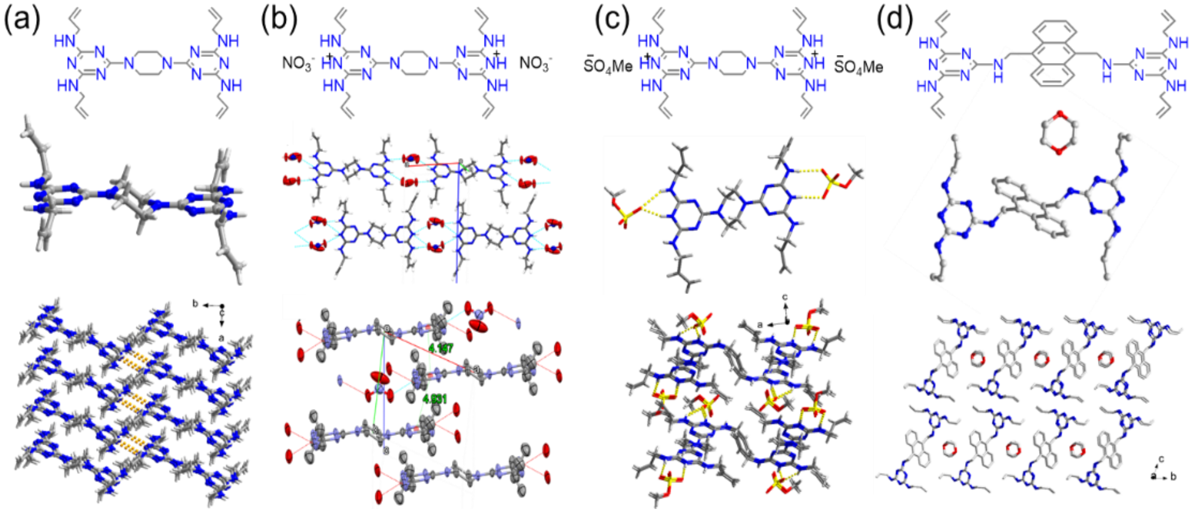

Fig. 2: Solid-state structures of (a) monomer **1**, (b) **1**•2[HNO_3], (c) **1**•2[HSO_3OMe], and (d) monomer **2**.

Anthracene-based monomer **2** is a non-linear molecule and can exist in chair form as well as in boat form and may result in an H-bonded stair-like structure or a macrocyclic structure. SCXRD indicates the monomer **2** crystallizes in the triclinic space group *P*-1 (a = 4.59, b = 12.15, c = 16.83, α = 71.84, β = 86.34, γ = 80.31). In one asymmetric unit, it exists one monomer **2** and a dioxane (**Fig. 2d**). Monomer **2** crystallized in a chair conformation, where the anthracene and the melamine moieties are twisted with a torsion angle of 123.95° on the sides. Neighboring monomers are connected by hydrogen bonding interactions between the melamine moieties in the crystal, forming a supramolecular chain along the *c*-axis. They are also connected by hydrogen bonding interactions between the oxygen atoms in dioxane and the bridging -NH- between the anthracene and melamine moieties in the crystal along the *b*-axis. The 2D plane is tightly packed along the *a*-axis with dioxane molecules filling the voids in monomer **2** crystal.

Impact of the research. We have published one journal paper funded by the ACS PRF program and trained one graduate student, one undergraduate student during the year 1 period. In year 2, we will keep developing crosslinked organic framework materials as described in part 2 of the research report. The PI has been invited to present the research outcome on the 3D-printed COFs (part 1) in the 2019 Porous organic polymer satellite meeting in Germany, CINT annual meeting 2019, as well as the upcoming 2020 Gordon Research Conference on crystal engineering. Part 1 of the research will also form the preliminary results for future grant applications to the National Science Foundation, and the Department of Energy. Part 2 of the research also helped the training of graduate students that produced preliminary results for the NSF CAREER award to this PI.