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Article

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A 2D-Covalent Organic Framework with Interlayer Hydrogen Bonding Oriented Through Designed Non-Planarity

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ABSTRACT: We report the synthesis and characterization of a new class of 2D-covalent organic frameworks, called COFamides, whose layers are held together by amide hydrogen bonds. To accomplish this, we have designed monomers with a non-planar structure that arises from steric crowding, forcing the amide side groups out of plane with the COF sheets orienting the hydrogen bonds between the layers. The presence of these hydrogen bonds provides significant structural stabilization as demonstrated by comparison to control structures that lack hydrogen bonding capability, resulting in lower surface area and crystallinity. We have characterized both azine and imine-linked versions of these COFs, named COFamide-1 and -2, respectively, for their surface areas, pore sizes and crystallinity. In addition to these more conventional characterization methods, we also used variable temperature infrared spectroscopy (VT-IR) methods and van der Waals density functional calculations to directly observe the presence of hydrogen bonding.

Introduction – 2D-covalent organic frameworks (COFs)[1] are a class of crystalline porous polymers comprised of covalently linked two-dimensional sheets which assemble through non-covalent interactions[2-4] – typically aromatic stacking or dipolar interactions, generating a crystalline structure. The degree of relative crystallinity or pore fidelity can be changed by specifically tuning the non-covalent interactions between monomers through a variety of methods including modifying the electronic structure of the aromatic rings,[5-7] introducing donor-acceptor complexes,[7] dipole cancellation between layers,[8] and monomer planarity.[9,10] However, despite the ubiquity of hydrogen bonding in self-assembled architectures in both Nature and synthetic supramolecular chemistry, there have been few reports of COFs that make use of hydrogen bonding between layers,[11-14] though there have been many reports of COFs containing *intra*layer hydrogen bonds which serve to stabilize the dynamic imine bonds to hydrolysis.[15-17]

There are only a few examples of hydrazone[18,19] or urea[12] containing COFs where interlayer hydrogen bonding is observed or predicted, reported in literature. Several COFs have been reported that have interlayer C-H···O, and C-H···N hydrogen bonding through sidechain interactions,[13,14,20] however, more canonical N-H···O hydrogen bonding interactions similar to those found between amide groups found in Nature, or in synthetic polymers such as Kevlar or Nylon, are much rarer.

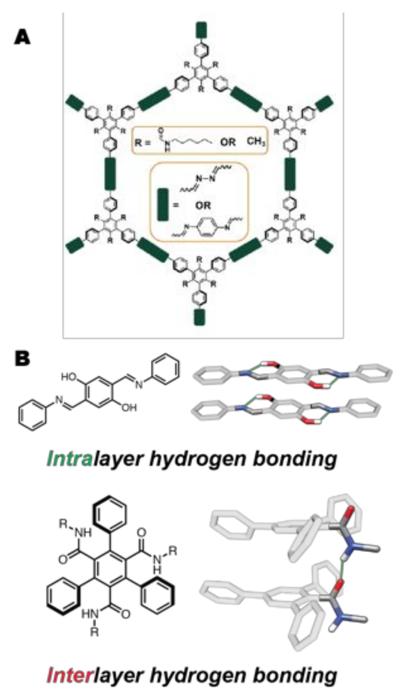

Figure 1. (A) Structure of the amide and control COFs linked through azine and imine bonds. (B) Co-planar hydrogen bonding functional groups will promote *intra*layer hydrogen

bonding (O-H···N), whereas out of plane amides can form hydrogen bonding interactions between layers (N-H···O).

Despite the difficulty in their preparation, there is a lot of potential for 2D-polymers with correlated hydrogen bonding between layers. Some reports have shown that hydrogen bonding can affect the photophysical[18] or electrochemical[13,14] properties of COFs. A recent theoretical study[21] reported that 2D-materials, known as "graphamid" demonstrate mechanical properties exceeding those of *para*-aramid polymers such as Kevlar, owing to the amide hydrogen bonding between the layers. One of the most important structural features of graphamid is that the amide groups are forced out of plane with the aromatic rings by steric hindrance thereby orienting the hydrogen bonding interactions between layers. In practice, the synthesis of materials like graphamid is difficult due to the lack of dynamic reversibility in the formation of amide bonds as well as the preparation of monomers with the correct orientation of hydrogen bonding groups. As hydrogen bonding interactions are directional, the relative orientation between donor and acceptor is critical to their formation. Functional groups capable of acting as hydrogen bond donors or acceptors, such as amides or imines, tend to adopt a co-planar orientation with aromatic rings in order to remain in conjugation with the π-system. In 2D-COFs, this will typically result in hydrogen bonding interactions being oriented within the layers, rather than between them.

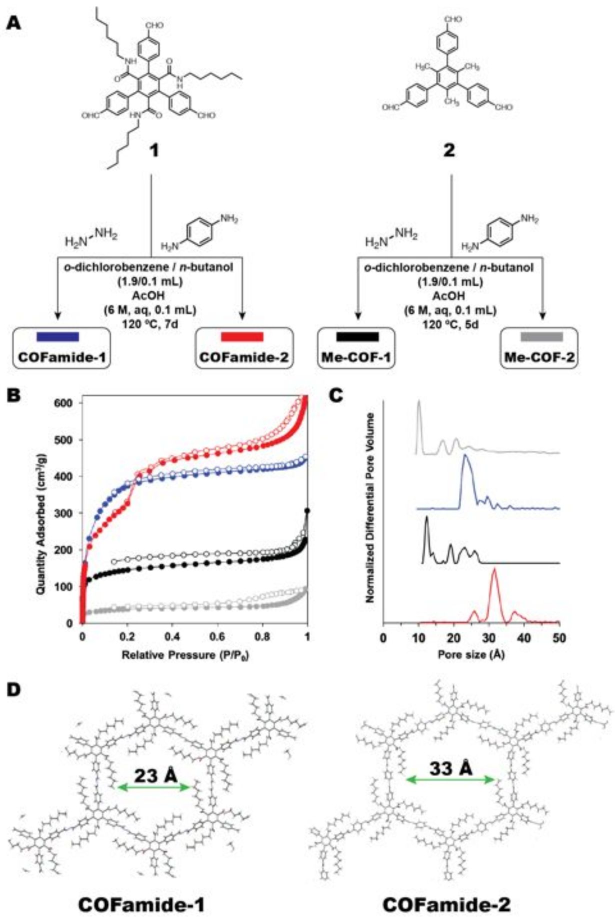

Figure 2. (A) Synthesis of azine and imine COFs used in this study. (B) Nitrogen adsorption isotherms of all COFs, COFamide-1 (blue), COFamide-2 (red), Me-COF-1 (black), Me-COF-2 (grey). The filled circles are the adsorption isotherms and the open circles are desorption isotherms. (C) Non-local density functional theory (NLDFT) pore size distributions of all COFs. (D) Crystal structure models of COFamide-1 and -2, built in Materials Studio, with their predicted pore sizes. These values match closely with the measured NLDFT pore size distributions.

In order to create COFs capable of *inter*layer hydrogen bonding, we have designed a monomer containing secondary amides at the 1,3,5-positions of the central phenyl ring (Figure 1A). Since the 2,4,6-positions are substituted with phenyl groups, the amides adopt an out of plane conformation due to the steric bulk of the phenyl rings to facilitate *inter*layer hydrogen bonding during the polymer synthesis. Here the amide carbonyl oxygen of one layer will act as the hydrogen bond-acceptor while the amide hydrogen (N-H) in the adjacent layer will act as the hydrogen bond-donor during the COF assembly (Figure 1B). This design was inspired by a previous report on self-assembled columnar liquid crystals derived from benzene-1,3,5-triamides.[22] Out-of-plane sidechains have been used previously in other COFs systems to impart additional functionality.[23] The amide containing COF monomer (**1**) was synthesized as described in Scheme S1. Hexylamides were used as they significantly improve the solubility of **1**, which is beneficial not only for its purification, but also for the COF polymerization reaction as well.

Results and Discussion – Monomer **1** was polymerized with both hydrazine and *p*-phenylenediamine to form the azine[24-27] and imine-linked COFs, respectively (see also Scheme S2). These reactions were carried out in a solvent mixture of *o*-dichlorobenzene (1.9 mL) and *n*-butanol (0.1 mL) with acetic acid used as a catalyst (6 M_{aq}, 0.1 mL) for 5d to yield the azine-linked COFamide-1 and imine-linked COFamide-2, respectively (Figure 2A). As a control, we have synthesized monomer **2** which is symmetrically analogous to **1** except the amide groups have been replaced with methyl groups that are incapable of hydrogen bonding. **2** was polymerized using the same conditions as monomer **1**.

The Brunauer-Emmett-Telller (BET) surface areas of each COF were measured by nitrogen adsorption (Figure 2B). COFamide-1 and -2 had significantly higher surface areas (1390 and 1202 m^2/g, respectively) than MeCOF-1 and -2 (623 and 138 m^2/g, respectively). The pore size distributions, determined using the NLDFT model (Figure 2C), showed that COFamide-1 and -2 have narrow pore distributions, which center around the predicted pore sizes calculated from computational models of each COF (Figure 2D). In contrast, the pore sizes of MeCOF-1 and -2 are much smaller than expected based on the models of an eclipsed COF structure, with multiple pore sizes present. Additionally, the isotherms of COFamide-1 and -2 have shapes more closely resembling type IV isotherms, indicative of pore sizes >20 Å, whereas MeCOF-1 and -2 have type I isotherms (*i.e.,* sharp uptake at low pressures) which is consistent with their microporous character.

The formation of the azine and imine-linkages in COFamide-1 and -2 were confirmed by Fourier transform infrared spectroscopy (FT-IR) through the attenuation of the aldehyde carbonyl stretching vibration (1693 cm^{-1}) and the appearance of the azine (1633 cm^{-1}) or imine (1631 cm^{-1}) vibrations (Figure S1). For the control COFs, Me-COF-1 and Me-COF-2, the FT-IR spectra are shown in Figure S2. Solid state NMR experiments on the synthesized COFs (Figure S21-S24) also supports this conclusion.

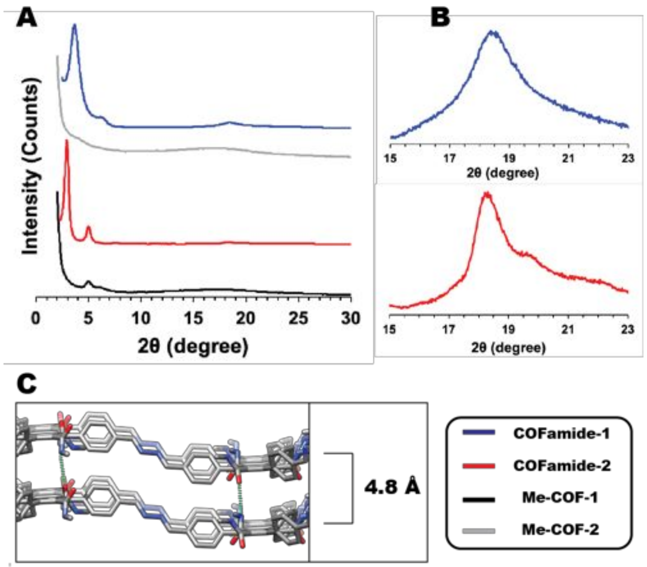

Figure 3. (A) PXRDs of all COFs. (B) Expanded region containing the 001 reflection of COFamide-1 and -2. (C) Side view of the COFamide-1 layers. The out of plane ring conformations forces the layers apart so that they have an *inter*layer distance of 4.8 Å as calculated from the 2θ of the 001 hkl reflection, larger than that of a typical COF held together by van der Waals, or π-stacking interactions (3.0-3.5 Å). The locations of the expected hydrogen bonds are highlighted with green, dashed bonds. COFamide-1 (blue), COFamide-2 (red), Me-COF-1 (black), Me-COF-2 (grey).

The experimental determination of crystallinity of the COFs was carried out using powder X-ray diffraction (PXRD) measurements. The COFamide-1 and 2 displayed sharp diffraction peaks which can be attributed to their long-range order while Me-COF-1 and -2 were largely amorphous with only small low angle reflections (Figure 3A). We attribute the difference in bulk crystallinity of the amide and reference COFs to the improved layer stacking interactions that arise from the properly oriented amide hydrogen bonding between layers. Previous work has established that disruption of critical *inter*layer interactions can result in poor COF surface area, pore fidelity and overall crystallinity.[28,29] X-ray crystallographic analysis of 1,3,5-trimethyl, 2,4,6-triphenylbenzene[30] indicates that the torsion angles of the phenyl rings are quite severe, being nearly perpendicular to the central benzene ring (~103°). Previous work[9] has shown that even smaller torsions angles in triphenylbenzene-based COF monomers than those reported here, result in significant reductions in crystallinity and accessible surface area.

Out of plane phenyl ring torsions, or non-planar aromatic systems have been attributed to both improved,[31-33] and reduced[9,10,27] crystallinity in COFs. Unless the non-planar monomer units can effectively "slip-stack" with one another, these torsions tend to act mostly as steric hindrance between the layers which reduces crystallinity and surface area.[10,27] In the case of the amide functionalized COFs here, the out of plane torsions orient the N-H···O hydrogen bonds between layers, which overcomes the steric hindrance seen in the Me-COFs, resulting in ordered COF materials when the amide functional groups are present. Analysis of the powder X-ray diffraction patterns of these COFs further supports this hypothesis. Normally, the 001 reflection in a 2D-COF appears around 25º and corresponds to the *inter*layer stacking distance (3.0-3.5 Å) where van der Waals and π-stacking interactions are expected. Interestingly, this peak in COFamide-1 and 2 appeared at around 18.5º (Figure 3B). This reflection can be attributed to the increased interlayer distance which is 4.8 Å as calculated using Bragg's Law. Models for both COFs were built in Materials Studio in the P6*m* space group (Figure S4, S10) and minimized in P1 using the universal force field (UFF). The simulated PXRDs of the eclipsed structure of both COFs match well with our experimental data indicating that COFamide-1 and 2 are arranged in an eclipsed fashion rather than staggered (Figure S3, S9). These crystal structure models predict layer to layer stacking distances of ~5.2 Å, similar to the experimental value (~4.8 Å) by PXRD (Figure 3C). These expanded layer stacking distances also provide more room for the amide hydrogen bonds to become properly oriented. We measured the N-H···O distance (acceptor amide carbonyl oxygen of one layer to the donor amide hydrogen (N-H) of the adjacent layer) in the refined model and found them to be ~2.6 Å, which is within the range of conventional hydrogen bonding (Figures S5, S11). In contrast, though the monomer geometry and interplane distances of MeCOF-1 and -2 should be similar to COFamide-1 and -2, we did not observe strong crystallinity in either of these COFs. We hypothesize that this could be explained by either the presence of disordered sheets with pore sizes reminiscent of a staggered A-B type stacking pattern, or pore collapse during activation due to weak interlayer interactions.[34]

To further explore the effects of the interlayer amide hydrogen bonding on these COFs, we carried out solvent stability studies on COFamide-1 and -2. COFamide samples were suspended in several solvent systems such as 1,4-dioxane, dimethylformamide (DMF), trifluoroacetic acid (TFA), sulfuric acid (18 M and 1 M_{aq}) and NaOH (1M_{aq}). Both COFs dissolved completely in the strongly acidic conditions (TFA and 18 M sulfuric acid), but retained their crystallinity in the other solvents (Figure S25). We hypothesize that under strongly acidic conditions the relatively labile imine linkages are hydrolyzed resulting in the destruction of the COF backbone. Since the hydrogen bonding interactions are directed out of plane in this case, they do not assist in stabilizing the dynamic linkages as some in plane hydrogen bonding interactions have been reported to do in other systems, where these interactions result in increased hydrolytic stability.[15-17] However, solvents that can disrupt hydrogen bonding, such as DMF, 1,4-dioxane, and mild acid or base conditions ($1M_{aq}$ H_2SO_4 and NaOH), do not damage the crystalline structure of COFamide-1. However, the aqueous conditions do reduce the crystallinity of COFamide-2, likely due to the lower relative stability of the imine linkages relative to the azine linkages of COFamide-1. In comparison, COF-43 for example, can be exfoliated and lose its bulk crystallinity when immersed in polar organic solvents that can participate in hydrogen bonding, despite it having much more hydrolytically stable hydrazone linkages.[35]

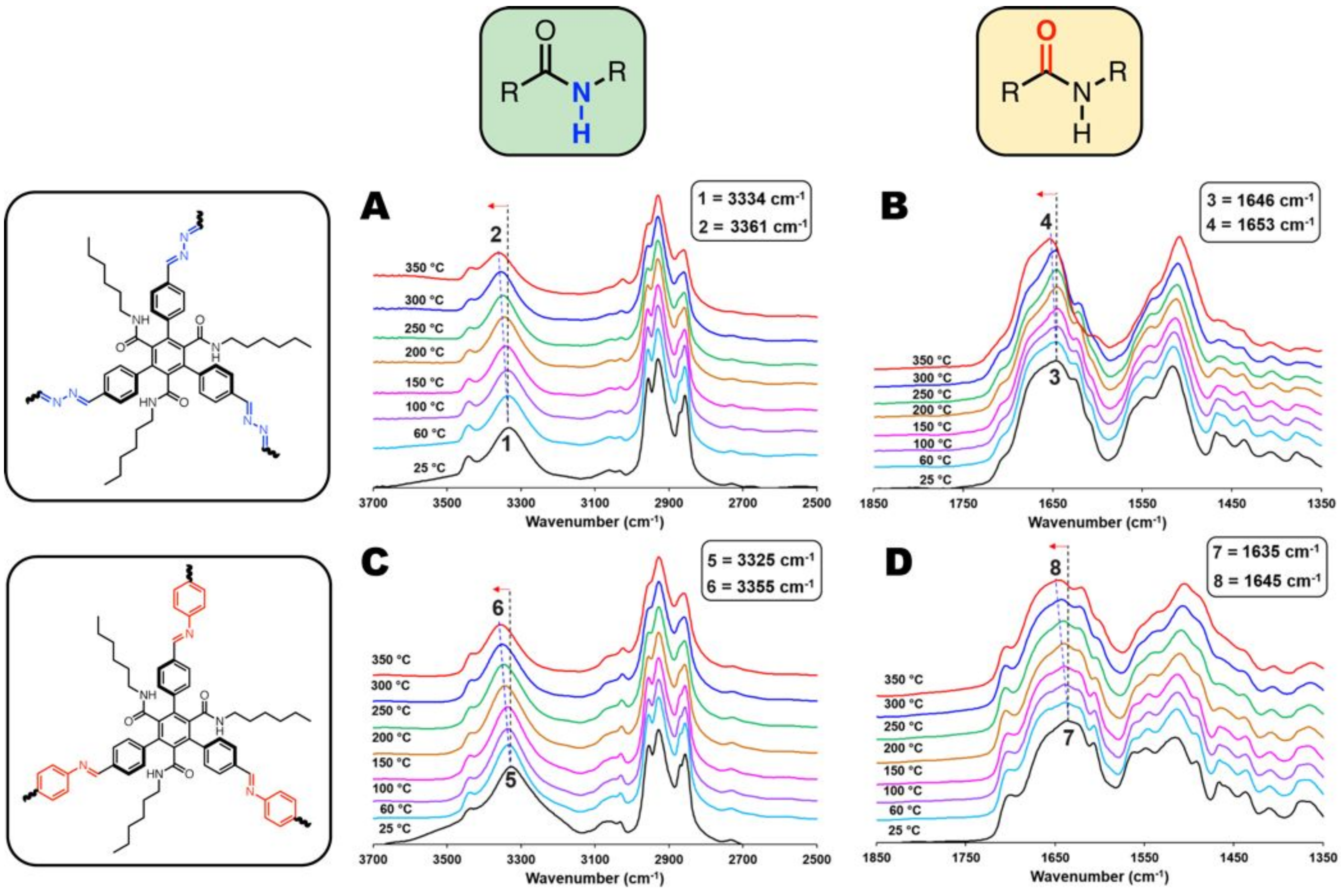

Figure 4. Variable temperature IR spectra of COFamide-1 and -2. COFamide-1: (A) Expanded amide N-H stretching region and (B) Zoomed in amide carbonyl stretching region. COFamide-2: (C) Expanded amide N-H stretching region and (D) Zoomed in amide carbonyl stretching region.

The synthesis of each COF was tested using a variety of different solvent systems. The optimized solvent system described in Figure 2A gives the highest overall surface areas for the COFamides, though others were tested (Table S1-S2). The use of pure *o*-dichlorobenzene, a solvent which should favor hydrogen bonding between the amide containing monomers, results in a COF with a slightly lower surface area compared the optimized conditions. In contrast, using pure 1,4-dioxane does not result in any precipitate or polymeric material of any kind, despite the fact that it does not result in exfoliation or loss of crystallinity when the COFamides are soaked in it *after* they have been synthesized under optimized conditions. Along with the poor crystallinity of the MeCOFs in our hands, we believe this supports the fact that hydrogen bonding interactions are critical for the formation of the COFamides. Furthermore, it provides some indication of the weak nature of the van der Waals and aromatic stacking interactions in these contorted triphenylbenzene systems. Previous mechanistic studies[36,37] of COFs have indicated that 2D sheets formed in solution can act as a template for continued COF polymerization and long-range order. If these interactions are disrupted, it can result in either poor crystallinity, or the aforementioned pore collapse during activation.

Spectroscopic Studies of COFs – Even though multiple experimental techniques including room temperature FT-IR analysis and solvent stability tests under harsh conditions have been previously reported to characterize *inter*layer hydrogen bonding in COFs,[12,18-20] direct observation can still be challenging. We expected that the presence of strong hydrogen bonding interactions would lead to significant frequency shifts in IR spectrum of the functional groups directly involved in the hydrogen-bonded bridges. In order to directly observe these hydrogen bonding interactions, we performed variable temperature FT-IR experiments (VT-IR, Figure 4). In previous spectroscopic studies of amide containing polymers[38-40] the hydrogen bonding is disrupted at elevated temperatures resulting in the amide carbonyl and amide N-H bond stretching frequencies blue shifting due to the increase in bond orders of the carbonyl and N-H bonds.

In each VT-IR experiment, spectra were collected at temperatures ranging from room temperature up to 350 °C. Upon heating the sample, the vibrational frequencies that correspond to amide N-H and amide carbonyl started shifting towards the higher wavenumber region (Figure 4A and B, respectively) with no effect on the other vibrational peaks in the spectrum. In COFamide-1, the amide N-H vibrational peak appears at 3334 cm^{-1} at room temperature. When the sample is heated to 350 °C the peak moved gradually to 3361 cm^{-1} with an overall shift of 27 cm^{-1} (Figure 4A). This shift upon heating can be attributed to the disruption of the hydrogen bonding and an increase in the N-H bond order because of the formation of free N-H sites. The amide carbonyl vibration peak at room temperature appears at 1646 cm^{-1}, and it gradually shifts to 1653 cm^{-1} with an overall shift of 7 cm^{-1} when heated to 350 °C (Figure 4B). This also can be attributed to the increasing bond order due to the formation of free amide carbonyls with increasing temperature. In COFamide-2 similar vibrational shifts were observed as of COFamide-1 (Figure 4C and D). These observations are consistent with the previous variable temperature IR studies on polyamides.[38-40]

Computational Studies – Though the simulated crystal structure models and PXRD data support the presence of hydrogen bonding, we sought to obtain atomic scale information about the hydrogen bonding through theoretical calculations. To accomplish this, we employed density functional theory (DFT) calculations using the van der Waals density functional (vdW-DF) that is capable of accurately representing intermolecular interactions such as hydrogen bonding.

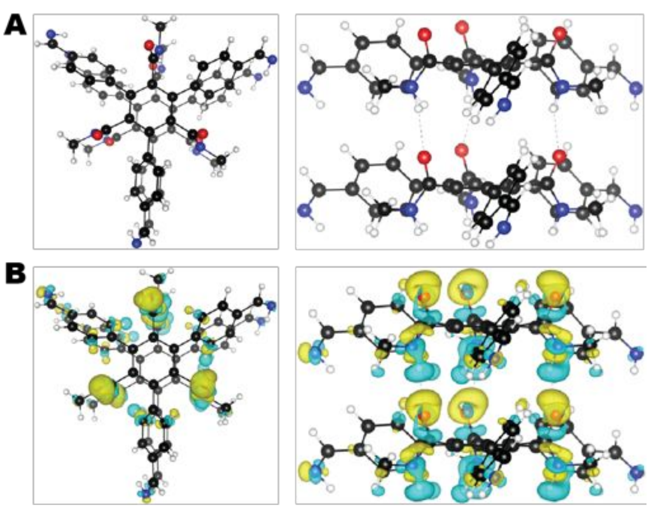

Figure 5. (A) Computational model of stacked molecules of monomer **1** with hydrogen bonding depicted by dotted lines. (B) Induced charge densities at an iso-level of 0.0015 electrons/Å^3. Yellow areas represent a charge accumulation and blue areas a depletion upon bringing the layers together. Three "chains" of induced charge per fragment become visible, showing the hydrogen bonds that link the layers together.

The COF structure was reduced to a repeating fragment that consisted of two 2-dimensional layers with hydrogen termination where necessary (Figure 5A). The structure was properly periodic in the direction perpendicular to the layers and contained a total of 144 atoms in the repeat unit cell. *Ab initio* calculations were performed at the DFT level, using VASP[41,42] in conjunction with the vdW-DF method.[43-46] The plane-wave energy cut-off was set at 600 eV and the SCF convergence condition was set to be 10^{-3} meV. To get an optimal separation between the layers of the COF, the lattice parameter was allowed to change in the direction perpendicular to the plane of the 2D-layers. The structure was optimized until all forces between atoms were smaller than 1 meV/Å. The total energy of the optimized 2-layer structure and single-layer structures were used to calculate the binding energy between the layers. Induced charge densities were calculated as the difference between the fully self-consistent density of the 2-layer system minus the corresponding single-layer densities. Induced charge densities thus show the rearrangement of charge density upon bringing the layers together and help identifying the formation of bonds and/or interactions.

The optimized COF structure had an interplanar distance of 5.03 Å, when measured from the benzene molecule in one layer to the benzene in another. This is similar to the 4.8 Å measured experimentally, and the 5.2 Å distance from the molecular mechanics based crystal structure calculations performed in Materials Studio using the universal force field (UFF). The binding energy between the two layers of the fragments depicted in Figure 5A was calculated to be 152.97 kJ/mol (1.58 eV), resulting in a binding energy per unit area of 0.47 kJ/mol/Å^2 (4.49 meV/Å^2) for the entire COF structure. We calculated the N-H···O hydrogen bonding distance to be 2.09 Å. While this is smaller than the value from our simulated crystal structure, it is still well within the range of a canonical hydrogen bonding interaction.

Induced charge densities are shown in Figure 5B. The plot shows an increase in electron density at the oxygen atoms and a decrease around hydrogen atoms—a clear indication of a hydrogen bonding interaction. We find most of the density change concentrated along the functional groups containing the hydrogen binding atoms. The induced charge densities along with the bond distance and binding energy show that the layers of the COF are more strongly held together by the N-H···O hydrogen bonds.

Conclusions – In summary, we were able to design and synthesize a COF with an extended network of hydrogen bonding through amide functional groups. Due to steric crowding, the amide units adopt an out of plane conformation which promotes *inter*layer (rather than *intra*layer) hydrogen bonding between pendant amide groups when assembled into a crystalline framework. When compared to a control COF without amide groups, COFamide-1 and -2 display significantly improved material properties such as bulk crystallinity and surface area. These improved material properties were attributed to the 2D assembly directed through strong *inter*layer hydrogen bonding. We have also demonstrated the value of VT-IR as a tool to experimentally observe the existence of hydrogen bonding between layers in a COF. From a practical perspective, amide hydrogen bonding is important for mechanical strength in polymeric materials, therefore, reliable and designable methods to incorporate these interactions in COFs could help expand them into new applications. We also see this design strategy as a general method that will allow for the synthesis of new COF materials. Furthermore, this will enable monomers that are too sterically bulky to interface with one another to be effectively incorporated into 2D-COFs by independently stabilizing the eclipsed stacking mode.

ASSOCIATED CONTENT

Supporting Information

Additional information and experimental results, including solvent stability tests, solid-state NMR spectra, and additional synthesis information are included in the Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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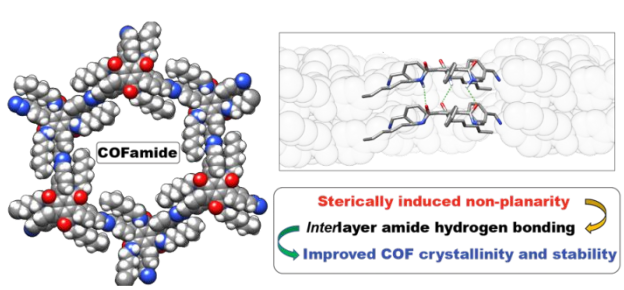
TOC



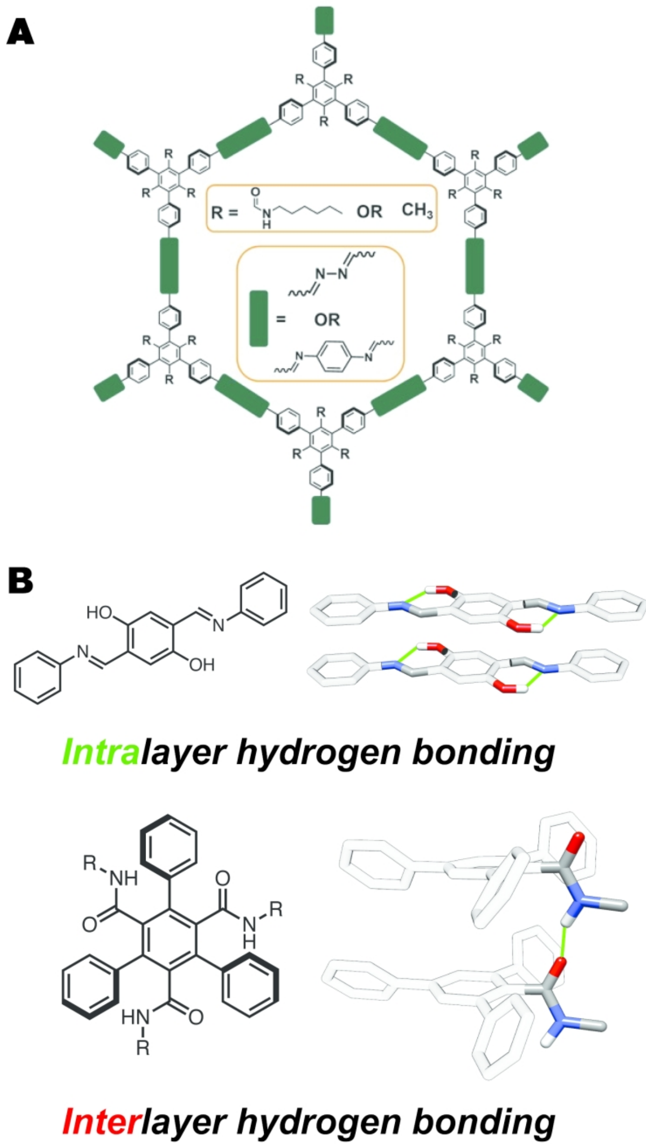


Figure 1. (A) Structure of the amide and control COFs linked through azine and imine bonds. (B) Co-planar hydrogen bonding functional groups will promote intralayer hydrogen bonding (O-H···N), whereas out of plane amides can form hydrogen bonding interactions between layers (N-H···O).

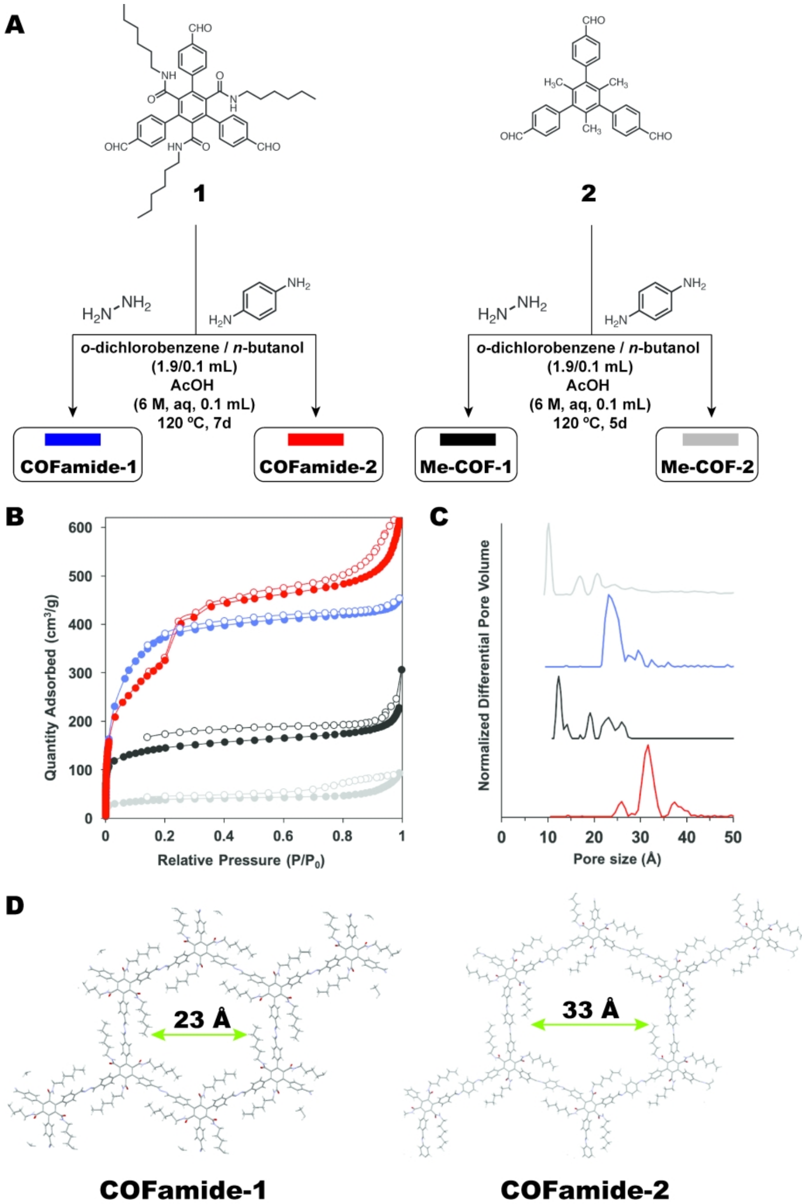


Figure 2. (A) Synthesis of azine and imine COFs used in this study. (B) Nitrogen adsorption isotherms of all COFs, COFamide-1 (blue), COFamide-2 (red), Me-COF-1 (black), Me-COF-2 (grey). The filled circles are the adsorption isotherms and the open circles are desorption isotherms. (C) Non-local density functional theory (NLDFT) pore size distributions of all COFs. (D) Crystal structure models of COFamide-1 and -2, built in Materials Studio, with their predicted pore sizes. These values match closely with the measured NLDFT pore size distributions.

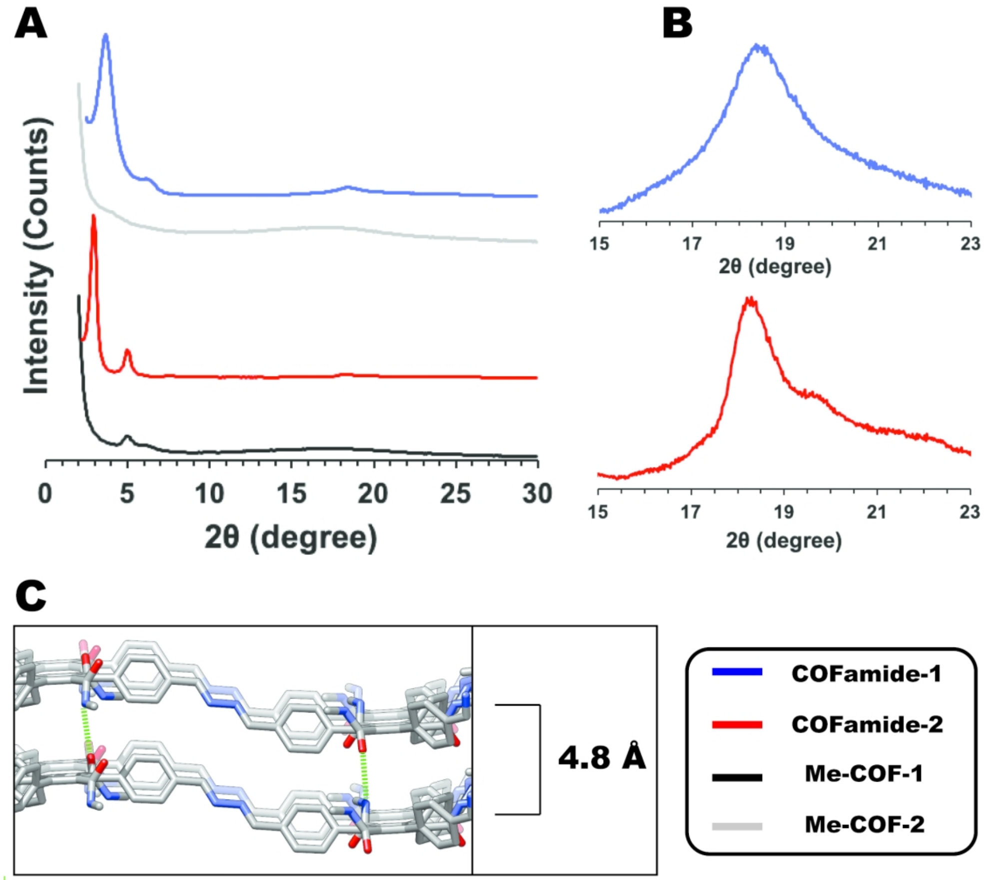


Figure 3. (A) PXRDs of all COFs. (B) Expanded region containing the 001 reflection of COFamide-1 and -2. (C) Side view of the COFamide-1 layers. The out of plane ring conformations forces the layers apart so that they have an interlayer distance of 4.8 Å as calculated from the 2□ of the 001 hkl reflection, larger than that of a typical COF held together by van der Waals, or π-stacking interactions (3.0-3.5 Å). The locations of the expected hydrogen bonds are highlighted with green, dashed bonds. COFamide-1 (blue), COFamide-2 (red), Me-COF-1 (black), Me-COF-2 (grey).

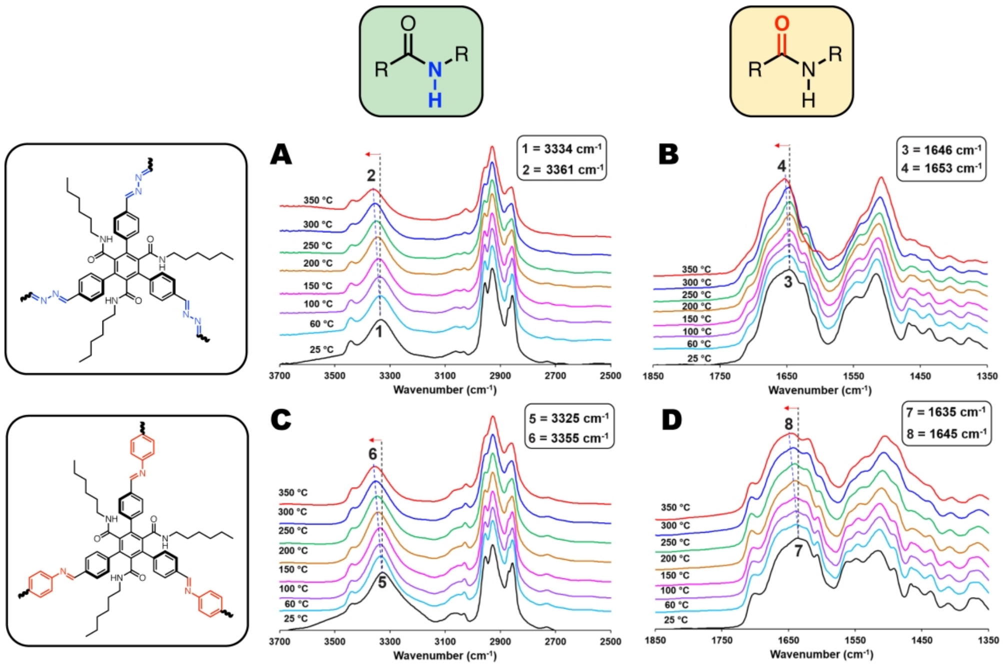


Figure 4. Variable temperature IR spectra of COFamide-1 and -2. COFAmide-1: (A) Expanded amide N-H stretching region and (B) Zoomed in amide carbonyl stretching region. COFAmide-2: (C) Expanded amide N-H stretching region and (D) Zoomed in amide carbonyl stretching region.

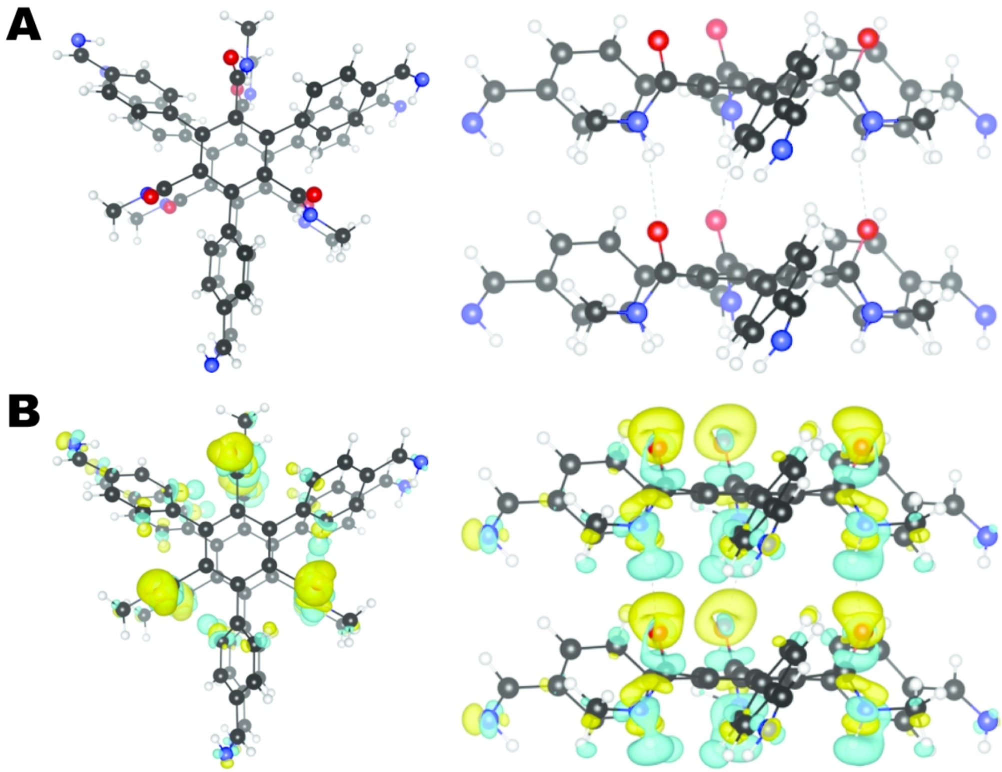
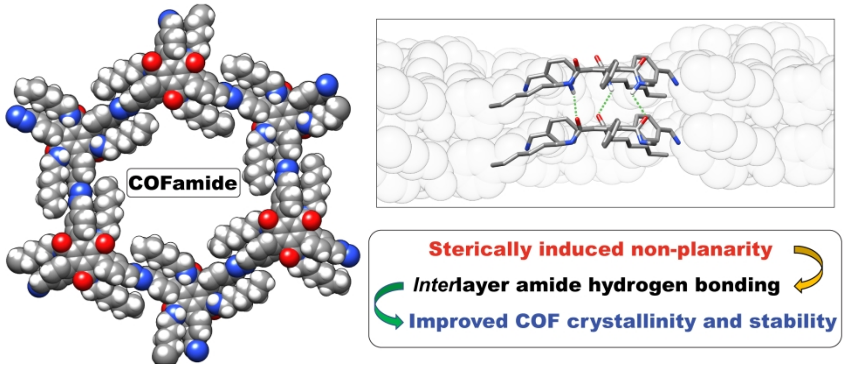


Figure 5. (A) Computational model of stacked molecules of monomer 1 with hydrogen bonding depicted by dotted lines. (B) Induced charge densities at an iso-level of 0.0015 electrons/Å3. Yellow areas represent a charge accumulation and blue areas a depletion upon bringing the layers together. Three "chains" of induced charge per fragment become visible, showing the hydrogen bonds that link the layers together.


COFamide
Sterically induced non-planarity
*Inter*layer amide hydrogen bonding
Improved COF crystallinity and stability

TOC Graphic