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Chemical Conversion of Linkages in Covalent Organic Frameworks

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ABSTRACT: The imine linkages of two layered, porous covalent organic frameworks (COFs), TPB-TP-COF $[C_6H_3(C_6H_4N)_3]_2[C_6H_4(CH)_2]_3$, **1**, and 4PE-1P-COF $[(C_6H_4N)_4][C_6H_4(CH)_2]_2$, **2**, have been transformed into amide linkages to make the respective isostructural amide COFs, **1'** and **2'** by direct oxidation with retention of crystallinity and permanent porosity. Remarkably, the oxidation of both imine COFs is complete, as assessed by FT-IR and ^{13}C CP-MAS NMR spectroscopy and demonstrates (a) the first chemical conversion of a COF linkage, and (b) how the usual 'crystallization problem' encountered in COF chemistry can be bypassed to access COFs, such as these amides, typically thought to be difficult to obtain by the usual *de novo* methods. The amide COFs show improved chemical stability relative to their imine progenitors.

Covalent organic frameworks (COFs) are formed from molecular organic building units linked by covalent bonds to form crystalline, porous, extended solids.[1,2] On a fundamental level, their structure can be divided into two components: linkers (building units) and linkages (bonds formed between those units upon reticulation). The great promise of COFs is rooted in the idea that the entire structure is organic and thus may be modified through the extensive tools of molecular synthesis. Accordingly, a large number of COFs have been modified post-synthetically to introduce functionalities onto the linkers and tailor the pores.[3-7] While this has expanded the applications of COFs, it is, however, the linkage and its chemistry that dictate the fundamental chemical and physical properties, as well as the inherent limitations of the material. To date, direct modification of the linkage has not been achieved. Instead, the manner in which new linkages are accessed is through *de novo* synthesis. The intrinsic constraint this places on COF chemistry is that one is required to overcome the crystallization problem: for each new linkage, conditions must be found such that the reaction is sufficiently reversible to allow for dynamic error correction.[8,9] Thus, chemistries based on linkages with limited microscopic reversibility are left unexplored.

Here, we introduce an approach that bypasses the crystallization problem in making new COF linkages. Specifically, two layered imine COFs, TPB-TP-COF (**1**)[5,9] and 4PE-1P-COF (**2**)[10,11], were used as starting materials and subjected to mild, oxidative conditions to convert the imine linkages quantitatively and give the amide-linked COFs, $\{[C_6H_3(C_6H_4NH)_3]_2[C_6H_4(CO)_2]_3$, **1'** and $[(C_6H_4NH)_4][C_6H_4(CO)_2]_2$, **2'**$\}$, without losing their underlying topology, crystallinity and permanent porosity (Figure 1). In essence, each imine framework was treated as a discrete molecule and subjected to a reaction normally carried out in molecular organic chemistry, leading to a completely new material. This method constitutes a new direction in COF chemistry where making new linkages is no longer subject to the trial-and-error and inherent uncertainties of *de novo* synthesis. The new COFs, **1'** and **2'**, extend the amide functionality, already prevalent and important in biological macromolecules and synthetic polymers, into the realm of porous, crystalline materials. In this context, we show that these amides exhibit chemical stability superior to that of their imine progenitors.

Efforts to generate amide-linked materials using this new methodology commenced with the eclipsed honeycomb material **1** (Figure 1a). This COF was obtained from tris(4-aminophenyl)benzene and terephthalaldehyde by solvothermal synthesis in butanol and *o*-dichlorobenzene at 120 ˚C for three days (see Supporting Information, Section S2). Likewise, the eclipsed kagome material **2** was synthesized solvothermally from 1,1,2,2-tetrakis(4-aminophenyl)-ethene and terephthalaldehyde in dioxane at 120 ˚C for four days (Figure 1b). These two materials were then subjected to oxidation.

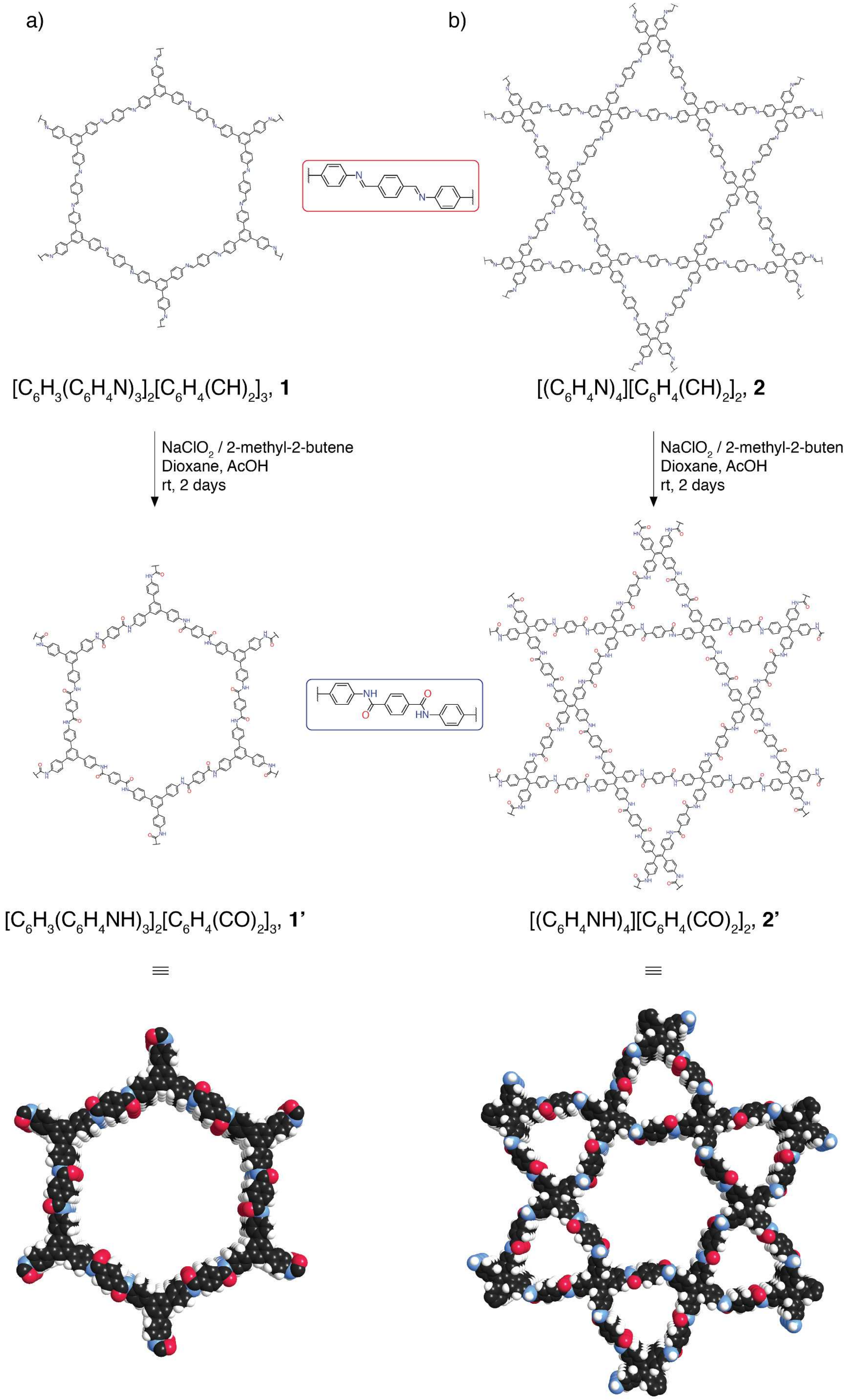

Figure 1. a) Conversion of imine TPB-TP-COF (**1**) to Amide TPB-TP-COF (**1'**) under oxidative reaction conditions. b) Oxidation of imine 4PE-1P-COF (**2**) to amide 4PE-1P-COF (**2'**). In the space-filling diagram, carbon, nitrogen, oxygen, and hydrogen atoms are represented as black, blue, red, and white spheres, respectively.

The exploration of the COF oxidation conditions began with those previously reported for the conversion of imines to amides.[12] These conditions involve sodium chlorite as an oxidant, a phosphate buffer, and 2-methyl-2-butene, which is proposed to scavenge hypochlorous acid generated as a byproduct of the reduction of chlorite. However, the crystallinity of the resulting material was poor. Through reaction optimization, it was discovered that replacement of the phosphate buffer with acetic acid afforded a greater degree of crystallinity as well as increased surface area. By adding more olefin scavenger, the crystallinity was further improved. Ultimately, **1’** and **2’** were obtained from **1** and **2** by treatment with sodium chlorite (11 eq. per one imine functionality), acetic acid (10 eq.), and 2-methyl-2-butene (100 eq.) in dioxane for 48 h, with the sodium chlorite being added in two equal portions 24 h apart (SI, Section S2).

Progression of the amidation reaction was monitored by Fourier transform infrared (FT-IR) spectroscopy (Figure 2a). The oxidized product **1’** exhibited the emergence of a C=O amide stretch (1651 cm^{-1}), and the disappearance of the C=N imine stretch (1622 cm^{-1}) found in **1**. These characteristic imine and amide stretches are corroborated by the spectra obtained for a molecular model (SI, Section S3). FT-IR spectra of **2** and **2’** showed similar appearance and disappearance of these characteristic vibrations (Figure 2b).

Conversion of the materials from imine to amide was also observed by ^{13}C cross polarization magic-angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR). In the ^{13}C CP-MAS NMR spectra of **1’** at natural abundance, the imine carbon peak at 157 ppm was no longer present after oxidation. Indeed, a new peak, attributed to the amide carbonyl, was observed at 166 ppm (SI, Section S4). In addition, small shifts in the frequency of the aromatic carbon resonances between **1** and **1’** supports the oxidation of the imine functionality to the amide. Analogous results were obtained for CP-MAS NMR spectra of **2** and **2’**.

To unambiguously determine the degree of conversion from imine to amide, further ^{13}C CP-MAS NMR experiments were performed with ^{13}C-labeled terephthalaldehyde (50% enriched at the aldehydic carbon) to improve the signal to noise ratio (Figure 2c,d). This enabled monitoring the transformation of the nitrogen-bound carbon from imine to amide for **1’** and **2’** and provided evidence for the excellent conversion of both substrates. The imine peak was absent in the ^{13}C CP-MAS NMR spectra of the amide materials across various cross-polarization contact times between 100 μs and 7 ms.

The crystallinity of the amide material was measured by powder X-ray diffraction (PXRD). The obtained powder pattern for **1’** is in good agreement with the expected amidated structure (SI, Section S5). This analysis indicates that the symmetry of **1** (space group *P*6, No. 168) is conserved, implying that the eclipsed stacking configuration is retained (Figure 2e). Slight changes in unit cell parameters were found between the amide ($a = b = 36.54$, $c = 4.05$ Å) and the imine ($a = b = 35.93$, $c = 4.42$ Å). The PXRD pattern of **2’** demonstrates similarly high crystallinity (Figure 2f) and agrees well with that of the predicted model structure. While the amide material provided evidence of slight unit cell changes ($a = b = 38.93$, $c = 5.45$ Å, compared to $a = b = 38.61$, $c = 5.82$ Å for the imine), no significant structural rearrangement of the material was observed during the transformation.

After structural elucidation of **1’** and **2’**, all materials were solvent exchanged and activated (SI, Section S2). Permanent porosity of all materials was then confirmed by N_2 sorption (Figure 2g and h). Resulting Brunauer-Emmett-Teller (BET) surface areas of 1250 and 655 m^2 g^{-1} were estimated for **1** and **1’**, respectively. N_2 iso-

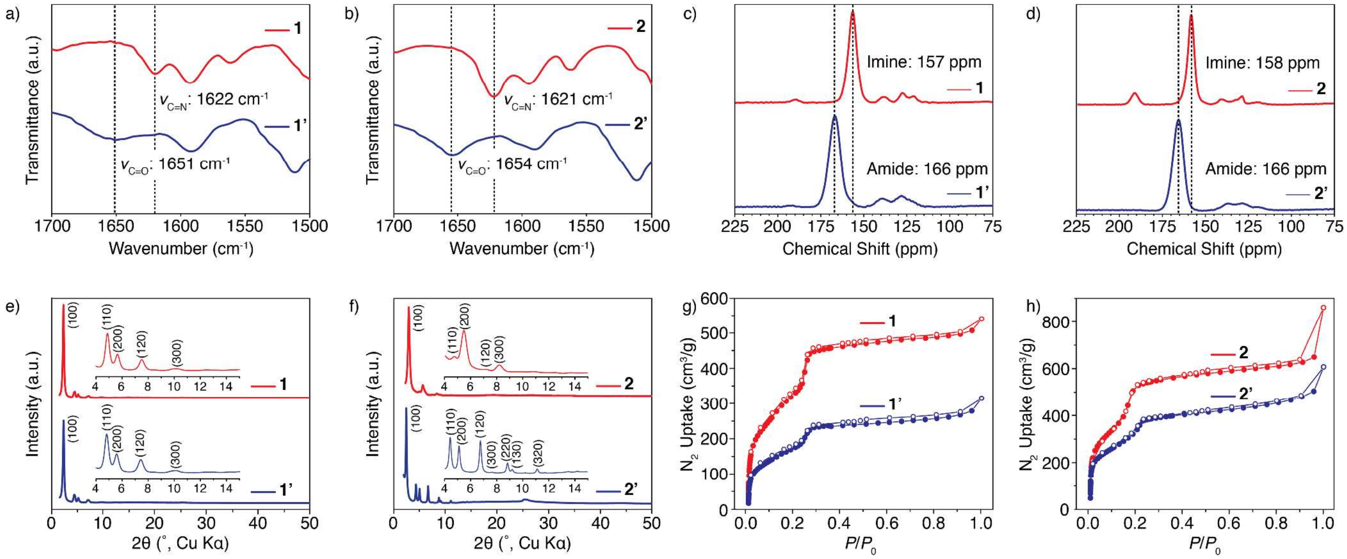

Figure 2. a,b) FT-IR spectra of **1** and **2** before and after oxidation. c,d) Isotopically enriched ^{13}C CP-MAS NMR spectra of COFs **1** and **2** before and after oxidation. e,f) PXRD patterns showing retention of crystallinity for both **1** and **2** after oxidation. g,h) Comparison of N_2 sorption isotherms for materials before and after oxidation. Closed and open circles represent the adsorption and desorption branches, respectively. Uptake is defined as cubic centimeters of N_2 at 1 atm and 0 °C per gram of COF sample.

therms of **2** and **2’** yielded similar results: the amidated material exhibited a lower BET surface area than the imine COF (1520 and 1190 m^2 g^{-1}, measured for the imine and amide respectively). Part of the loss in gravimetric surface area can be attributed to an increase in framework mass and decreased pore volume. Additionally, ^{13}C MAS NMR of **1’** impregnated with d_6-DMSO indicates the presence of included oxidized oligomers within the pores, explaining the additional surface area decrease (SI Section S4). Work is ongoing to determine both, at which point in our synthesis and conversion these oligomers are generated, and how best to remove them from the material.

For both **1’** and **2’**, the measurements show the type IV isotherm seen for their imine counterparts. This further confirms that the amidation procedure does not lead to significant changes in structure.

The chemical stability of the amide materials was examined by PXRD and sorption after 24-hour treatment in 12 M $HCl_{(aq)}$ and 1 M $NaOH_{(aq)}$ (**1** and **1’** in Figure 3, and **2** and **2’** in Figure S15, SI Section S7). The difference between the stabilities of the imine and amide materials is most striking in the case of acidic conditions, where the amides retain crystallinity while the corresponding imines are nearly or completely dissolved and the remaining material rendered entirely amorphous. However, a small decrease in signal to noise and 25-60% decrease in surface area of the amide materials indicate some structural damage upon treatment (SI Section S7). Nonetheless, the differential stability of these materials further corroborates their conversion from imines to amides.

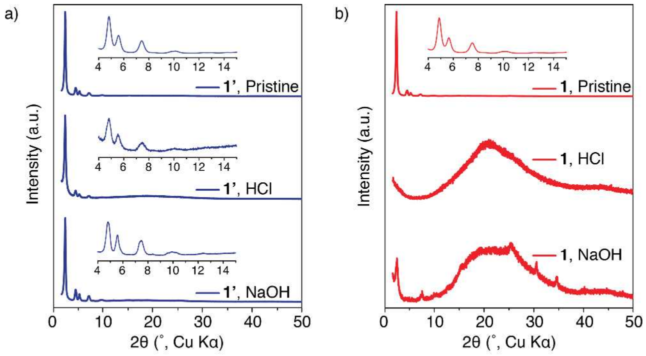

Figure 3. Comparison of diffraction patterns of **1’** (a) and **1** (b) after 24 hour treatment in 12 M HCl and 1 M NaOH.

To conclude, a method of deriving amide-linked COFs from their corresponding imine-linked frameworks has been developed. This reaction is performed under mild conditions and results in amide COFs retaining both crystallinity and permanent porosity. This material also exhibits enhanced stability under aqueous acidic and basic conditions relative to the corresponding imine-linked framework. This method constitutes a new direction in COF chemistry where synthesis of new linkages bypasses the usual crystallization problem encountered in linking organic building blocks into extended structures by covalent bonds.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

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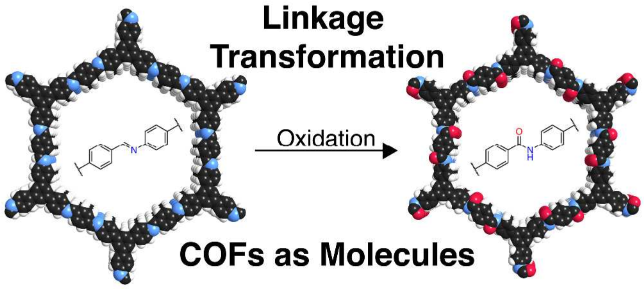
Linkage Transformation
Oxidation
O
N
H
N
COFs as Molecules