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### Enhanced Structural Organization in Covalent Organic Frameworks Through Fluorination

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**Abstract:** Herein we report a structure-function study of imine COFs comparing a series of novel fluorine containing monomers to their non-fluorinated analogue. We found that the fluorine containing monomers produced 2D-COFs with not only greatly improved surface areas (over 2000  $m^2$ /g compared to 760  $m^2$ /g for the non-fluorinated analogue), but also with improved crystallinity and larger, better defined pore diameters. We then studied the formation of these COFs under varying reaction times and temperatures to obtain a greater insight into their mechanism of formation.

Covalent organic frameworks (COFs)<sup>[1]</sup> are a class of crystalline porous polymers synthesized utilizing dynamic covalent bonds<sup>[2]</sup> such as boronate esters, [1a,1b] imines, [3] hydrazones, [1c,4] triazines,<sup>[5]</sup> and azines.<sup>[6]</sup> These materials have attracted remarkable attention due to their well-defined structures, high porosity, and potential applications in gas storage,<sup>[1a,7]</sup> catalysis,<sup>[4, 8]</sup> and as materials for electrical energy storage.<sup>[3b, 9]</sup> In 2D-COFs, the structure and properties are dictated by both covalent bond formation under thermodynamic control, and by non-covalent interactions between aromatic rings that enables the formation of periodically aligned molecular columns.<sup>[6e]</sup> There have been a number of excellent studies<sup>[10]</sup> that attribute the efficiency of non-covalent packing in COF formation to forces as wide ranging as monomer planarity,<sup>[6d]</sup> and molecular recognition through templated docking.<sup>[9a,11]</sup> Given that each of these hypotheses have proven to be successful in making specific types of COFs, it is clear that more studies into the role of noncovalent packing are imperative for the development of general design rules.

The purpose of the work reported here is to further elucidate the importance of aromatic interactions between individual sheets during COF formation. Interactions between aromatic rings are controlled by a variety of factors including substituent effects that change the electron density or polarization of the  $\pi$ -cloud. Many explanations<sup>[12]</sup> have been posited to explain the nature of aromatic stacking interactions, but empirically, electron deficient rings are known to preferentially adopt face-to-face arrangements. Since this co-facial orientation is representative of the structure of most 2D-COFs, we hypothesized that we could bias toward the formation of stacked COF sheets by incorporating electron withdrawing substituents onto the periphery of our COF monomers. We chose to use fluorine substitution for this study as it is not only electron withdrawing, but similar in steric bulk to hydrogen, thereby allowing a closer

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comparison between fluorinated and non-fluorinated monomers without introducing significant steric effects. We have synthesized two fluorine containing 1,3,5-triphenylbenzene derivatives to take advantage of this co-facial stacking preference, and were gratified to see that the addition a few fluorine atoms results in a drastic change not only in the crystallinity, but also the pore size and surface area of the resulting COFs.

Monomers NF, TF-1, and TF-2 were synthesized through a Suzuki cross-coupling reaction (see Supporting Information for details). All three COFs were prepared solvothermally in glass ampoules by polymerizing monomers NF, TF-1 or TF-2 with hydrazine (Figure 1).



Figure 1. Schematic representation of the synthesis of the azine-linked COFs.

Though several solvent systems were tested, a mixture of odichlorobenzene(DCB)/n-butanol/6M aqueous acetic acid (1.9/0.1/0.1 by vol.) was found to be optimal.

To help determine the 2-D structure of each COF, powder X-ray diffraction (PXRD) measurements were performed. TF-COF 1 exhibited diffraction peaks at 3.67, 6.09, 9.28, 12.80 and 24.83°. TF-COF 2 exhibited diffraction peaks at 3.71, 6.19, 9.43, 12.41 and 23.70°. The peaks of both the COFs were assigned to the (100), (110), (120), (130), and (001) reflections, respectively. The only peaks clearly observed for NF-COF appeared at 3.67 and 6.09, indicating a lower level of crystalline order (Figure 2a). Computational models of each COF were created using Materials Studio in both staggered and eclipsed arrangements. The calculated PXRD patterns of the eclipsed TF-COFs (Figure 2b,c) match well with the experimental pattern. Significant enhancement in the resolution of the diffraction peaks was observed with both TF-COFs compared to NF-COF. Interestingly, the (001) reflection, attributed to the interlayer spacing between COF sheets, is much more prominent for both the TF-COFs than for NF-COF, indicating a higher degree of long range order. SEM images of each COF are shown in Figure 2d-f. Notably, the fluorinated COFs display crystallite morphology as opposed to the smooth, spherical agglomerates of NF-COF. Previous studies have attributed this to improved COF crystallinity owing to more organized interlayer stacking.<sup>[13]</sup> The surface area and pore size distributions of each COF were determined through nitrogen sorption measurements at 77 K (Figure 3). The NF-COF exhibits a type-I adsorption isotherm. However, both the fluorinated COFs exhibit type-IV isotherms, indicating the presence of mesopores (Figure 3e). The Brunauer-Emmett-Teller (BET) surface areas of TF-COF 1 and TF-COF 2 are 1820 and 2044 m<sup>2</sup>/g, respectively, compared to only 760 m<sup>2</sup>/g for NF-COF. To the best of our knowledge 2044 m<sup>2</sup>/g is among the highest reported for 2D-COFs to date and COF surface areas over 2000 m<sup>2</sup>/g are rare.<sup>[8b]</sup> The pore size distributions for each COF (Figure 3f) were obtained from the nitrogen isotherms using the density functional theory method (DFT). The pore size distribution of NF-COF displays not only the expected pore size of 25 Å, but also has many other smaller pores. In combination with its type-I isotherm and poorly resolved diffraction pattern, it seems likely that the 2-D structure of NF-COF is poorly ordered and is not well represented by the hexagonal crystalline model often used to describe these COFs. TF-COFs 1-2, however, display much more well defined pore structures. Both of these COFs have properties that are reminiscent of an eclipsed layer arrangement that demonstrate excellent agreement with the simulated pore diameters.



Figure 2. Experimental PXRDs of (A) NF-COF (black), (B) TF-COF 1 (red), (C) and TF-COF 2 (blue) with Pawley refined spectra, simulated eclipsed models and difference spectra (purple, green and orange, respectively). Insets: Modeled eclipsed structures of COFs (C, grey; O, red; N, blue; F, light green. (H atoms are omitted for clarity). (D), (E) and (F) are SEM images of NF-COF, TF-COF 1 and TF-COF 2, respectively.



Figure 3. (A), (C) and (E) N<sub>2</sub> adsorption (solid circles) and desorption (open circles) isotherms (77 K) of 1 d RT, 1 d 120 °C and 3 d 120 °C COFs, respectively. (B), (D) and (F) PSD plots of 1 d R, 1 d 120 °C and 3 d 120 °C COFs, respectively. (G) BET surface areas and (H) and mass recovery (%) of COFs.

A previous report<sup>[10c]</sup> on the synthesis of imine COFs found that the COF polymers initially formed porous materials that would equilibrate to more crystalline materials over time. We performed several polymerizations of our COFs at different temperatures and reaction times to observe their formation behavior. Each COF was prepared with reaction times of 1d at either room temperature or 120 °C and 3d at 120 °C. After each experiment, the BET surface area, pore size distribution, and PXRD measurements (Figure S1) were carried out. These experiments revealed several interesting properties. Surprisingly, TF-COFs 1-2 display type-IV isotherms after only 1d at RT (Figure 3a) with a narrow pore size distribution (Figure 3b). As the temperature and reaction times increased, the surface areas for both fluorinated COFs increased significantly with the largest increase coming after heating to 120 °C for one day. However, NF-COF did not display the same improvement in crystallinity or display pore size distribution narrowing over time. The surface area for NF-COF does increase with increasing reaction time and temperature, but nowhere near as significantly as the TF-COFs 1-2, particularly after heating for only one day. Fourier transform infrared (FTIR) spectra of the COFs confirmed the formation of the azine linkage through disappearance of the

carbonyl (1690 cm<sup>-1</sup>) and the appearance of the azine (1622 cm<sup>-1</sup> <sup>1</sup>) stretches (Figure S2). These spectra reflect that the formation of the azine linkages form rapidly and are the major product (compared to the starting aldehydes) within 1d at 120 °C for all three COFs. In addition to this, the mass balances of each polymerization were recorded (Figure 3h) and it was found that more than 70% of the expected yield was recovered for each reaction regardless of the time or temperature. Longer reaction times at high temperatures resulted in somewhat higher yields (TF-COF 2 was ~90% for example), but overall the indication is that, consistent with previous work, [10c] a kinetic product appears to form first, followed by slow reorganization into a crystalline product with well-defined 2-D structure in the cases of TF-COFs 1-2. This work is novel in that, rather than modifying the reaction conditions, we have changed the chemical structure of the monomers. In other words, the electronic structure of the monomers can also favorably drive the conversion of the polymeric material from the non-crystalline kinetic product, to the thermodynamically favorable crystalline COF product. The presence of electron withdrawing fluorine substituents could serve to make the azine linkages more reactive and avoid the formation of kinetic traps. The fluorine atoms also could cause

polarization in the aromatic rings which would lead to stronger cofacial interactions.<sup>[12b]</sup> This effect should be especially pronounced in the case of TF-COF 2 as all three of the fluorine atoms are on the same ring, and indeed, TF-COF 2 has highest surface area observed in this study. A previous report<sup>[6d]</sup> on a related series of azine-linked COFs showed that crystallinity and surface area were improved by planarizing the monomers. In this case, we do not observe a correlation between torsion angle and surface area, and in fact, the highest surface area materials (TF-COF 2) has the largest torsion angle (Figure S20). We believe that these observations show that COF polymerization and crystallization can be controlled effectively through the careful design of both the steric and electronic structure of the monomers.

In conclusion, we have synthesized two novel fluorinated COFs that have significantly improved physical properties compared with an isostructural non-fluorinated variant. This work demonstrates that modifications to the electronic structure of COF monomers can result in an immense improvement in the structural properties of the COFs. We believe that these design principles can be applied to other types of COFs and future work will be directed towards further elucidating these principles.

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**Keywords:** fluorinated covalent organic frameworks • azine covalent organic frameworks • structural organization of covalent organic frameworks • 2D-COFs • COF forming mechanism

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#### COMMUNICATION

**Improved layer stacking:** A strategy to improve the crystallinity and the surface area of 2D-COFs significantly by simple variation in the electronic structure of non-planar precursors by fluorination.



Sampath B. Alahakoon, Gregory T. McCandless, Arosha A. K. Karunathilake, Christina M. Thompson and Ronald A. Smaldone\*

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