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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-11-2018-008957.R1
Article Type:	Communication

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Improved Synthesis of β -Ketoenamine-Linked Covalent Organic Frameworks via Monomer Exchange Reactions

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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β -ketoenamine-linked covalent organic frameworks (COFs) offer excellent structural versatility and outstanding aqueous stability, but their stability complicates obtaining samples with high crystallinity and surface areas. In contrast, imine-linked COFs are often isolated with superior materials quality. Here we synthesize several β -ketoenamine-linked COFs, including two unreported structures, with unmatched crystallinity and high surface areas by preparing the corresponding imine-linked COF and exchanging its triformylbenzene monomers with triformylphloroglucinol.

Covalent organic frameworks (COFs) are an emerging class of permanently porous, crystalline polymers formed by linking monomers into two- and three-dimensional networks.¹ The first COFs featured boronate ester and boroxine linkages that are susceptible to hydrolysis.² Nitrogen-based linkages offer

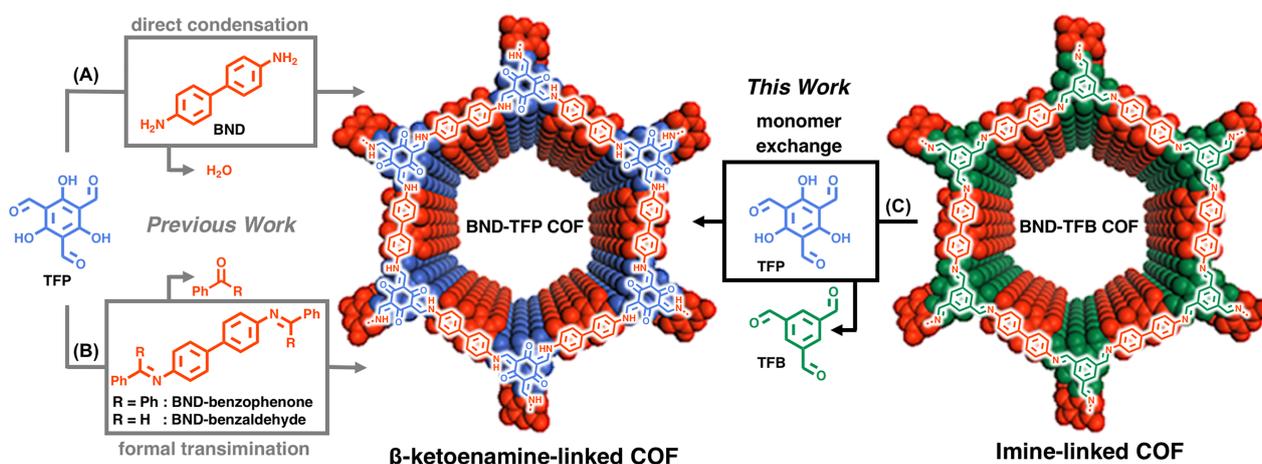
enhanced chemical stability,³⁻⁴ and the exceptional stability of β -ketoenamine-linked COFs has been exploited in studies of pseudocapacitive energy storage,⁵⁻⁶ aqueous separations,⁷ and proton conduction.⁸⁻⁹ These COFs are formed by the direct condensation of multifunctional amines (Scheme 1A) with triformylphloroglucinol (TFP) in which imine formation is accompanied by a tautomerization that imparts increased stability.¹⁰ Although this stability is desirable in the isolated material, it reduces the possibility of exchange processes that correct defects during the polymerization. Consequently, β -ketoenamine-linked COFs typically exhibit smaller average crystalline domain sizes and lower surface areas and pore volumes than imine-linked networks.

Here we introduce a new approach to prepare β -ketoenamine-linked COFs with improved materials quality by first preparing imine-linked COFs using 1,3,5-triformylbenzene (TFB) as the trigonal node, which is subsequently exchanged with triformylphloroglucinol (Scheme 1). This approach builds on our previously developed transimination strategy (Scheme 1B) that provides both imine- and β -ketoenamine-linked COFs with improved quality as compared to using the free amine

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*Electronic Supplementary Information (ESI) available: Experimental procedures and additional characterization of all COFs. See DOI: 10.1039/x0xx00000x



Scheme 1. Preparation of β -ketoenamine-linked 2D COFs from direct condensation, formal transimination, and monomer exchange approaches.

monomers.¹¹ Here, an imine-linked 2D COF that is isostructural to the desired framework is formed and isolated, after which exchange is performed to give the less dynamic and more stable β -ketoenamine-linked material. Thus, even the limited error-correction available to the β -ketoenamine linkage is sufficient to obtain a high-quality COF, and the favourable thermodynamics of the formation of this linkage promotes complete exchange.

Five previously reported imine-linked COFs with TFB as the node were synthesized using conditions that provide the greatest crystallinity and porosity.^{11–14} Monomer exchange was conducted by exposing these imine-linked COFs to one equivalent of TFP (with respect to TFB) in a deoxygenated mixture of 1,4-dioxane, mesitylene, and 6 M $\text{CH}_3\text{CO}_2\text{H}$ (3:3:1 volume ratio) at 120 °C for 3 days. The collected material was washed with hot DMF, acetone, and ethanol before activation under dynamic vacuum at 120 °C overnight. Characterization of the activated materials by Fourier transform infrared spectroscopy (FT-IR), ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy, and elemental analysis (see Supplementary Information – sections IX–XI) is consistent with full conversion to the β -ketoenamine linkage. Additionally, following the completion of each reaction, soluble organics were extracted, isolated, and characterized by ^1H NMR spectroscopy (Figure S80). These studies reveal that only the displaced TFB (80% mass recovery in the case of BND-TFB COF, Table S7), and no TFP, was present. Stoichiometric studies (see SI section XIV) reveal that when a substoichiometric amount of TFP (0.5 equiv) was used, a COF with both imine- and β -ketoenamine-containing bonds was formed, demonstrating partial exchange. On the other hand, when either one equivalent or an excess amount of TFP (1.5 equiv) was used, complete exchange was observed. Yet, BND-TFP COF exhibited the highest surface area (Figure S84) when exactly one equivalent of TFP was used, which is sufficient to facilitate complete exchange due to the favourable thermodynamics of the enamine-forming tautomerization step.

Following monomer exchange on imine-linked BND-TFB COF containing benzidine as the multifunctional amine, β -ketoenamine-linked BND-TFP COF was obtained with crystallinity (Figure 1A) exceeding previous reports as determined by powder X-ray diffraction (PXRD).^{11,14–22} The measured Brunauer–Emmett–Teller surface area (S_{BET}) of 1536 m^2/g also surpasses the highest previously reported value of 1102 m^2/g for this COF synthesized via acid-catalysed solvothermal conditions (Figure 1B).¹¹ The BND-TFP COF's S_{BET} is lower than that of the BND-TFB COF (1948 m^2/g), in part because the β -ketoenamine-linked structure has a 10% reduction in Connolly surface area (SI section XV). The average domain size of BND-TFB (140 nm) and BND-TFP COF (120 nm), as determined by Scherrer analysis, are similar following monomer exchange, suggesting that the exchange process preserves the long-range order of the original imine-linked COF (Table S7). FT-IR spectroscopy (Figure 1C) indicated the disappearance of the aldimine C=N stretch (1693 cm^{-1}) and the emergence of the enamine C–N stretch (1286 cm^{-1}). CP-MAS NMR spectroscopy (Figure 1D) showed the emergence of peaks

at 106 and 184 ppm, characteristic of the β -ketoenamine linkage, and the attenuation of the peak at 159 ppm, which corresponds to the imine linkage. These observations indicated complete exchange to the β -ketoenamine-linked structure within the sensitivity limits of each technique.

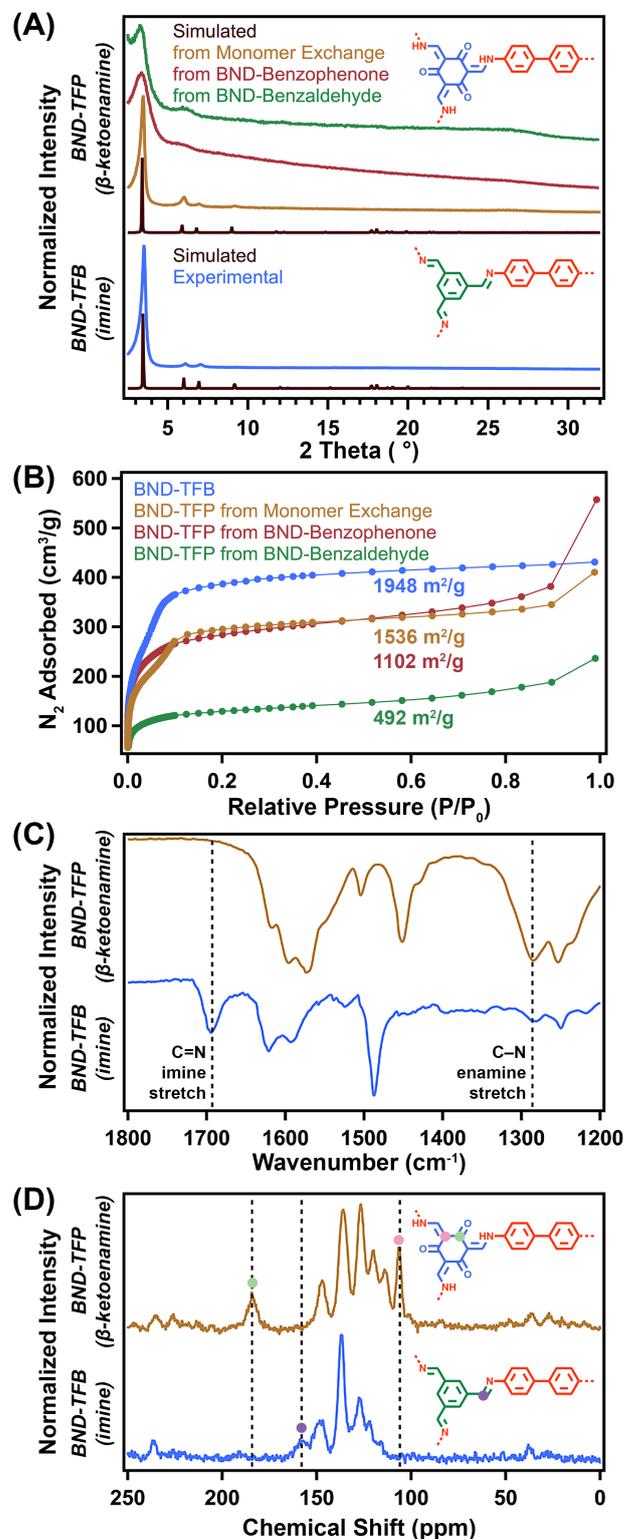


Figure 1. (A) PXRD patterns, (B) nitrogen adsorption isotherms, (C) CP-MAS NMR, and (D) FT-IR for BND-TFB and BND-TFP COFs.

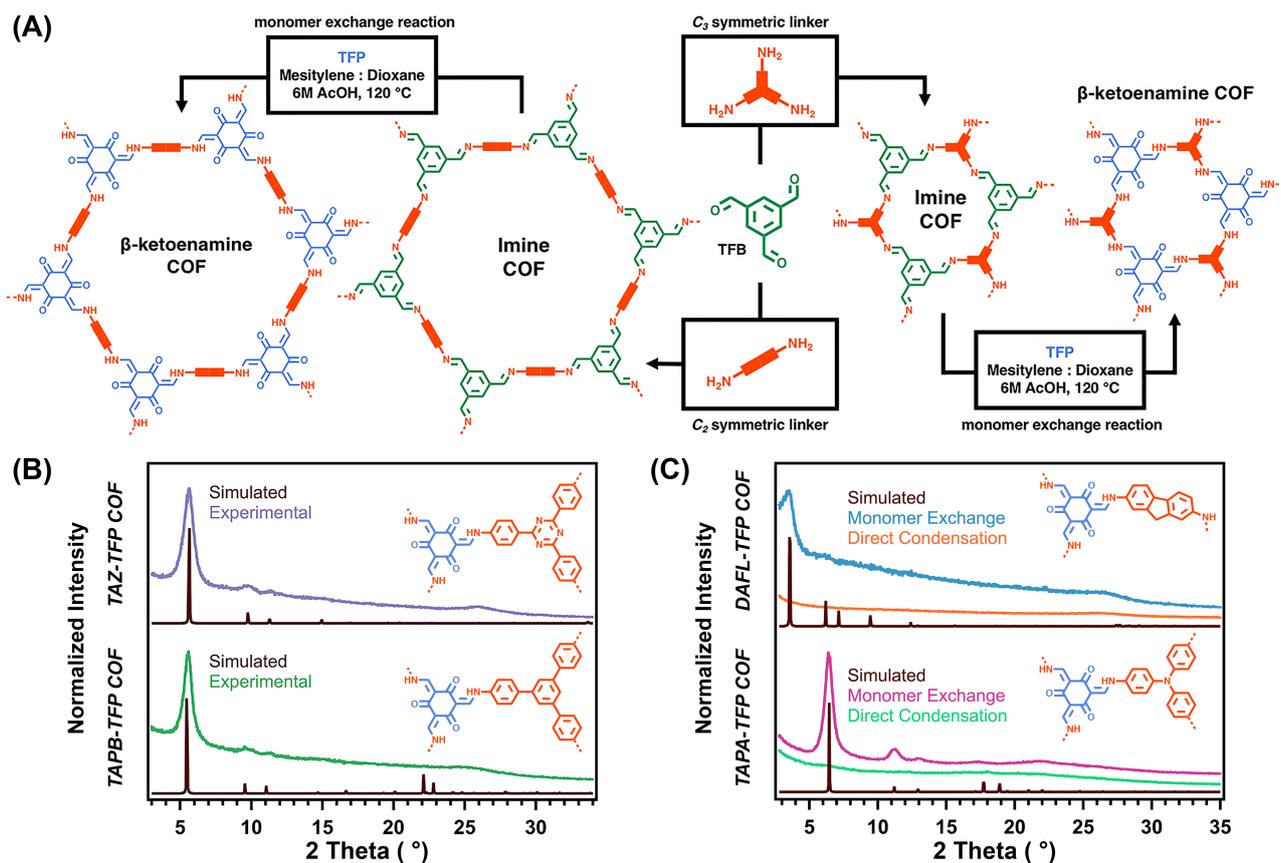


Figure 2. (A) Reaction Scheme and (B,C) PXRD patterns for TAZ-TFP, TAPB-TFP, TAPA-TFP, and DAFL-TFP COFs.

To investigate the role of transimination in improving materials quality, BND-TFP COF was synthesized using benzaldehyde-protected benzidine (BND-benzaldehyde) under the same synthetic conditions for monomer exchange. The secondary aldimine bonds in the monomer mimic the transimination that occurs during monomer exchange of the imine-linked COF wherein the hydrolysed benzaldehyde can act as a modulator. BND-TFP COF synthesized using benzophenone-capped benzidine (BND-benzophenone) is also used for comparison.¹¹ The crystallinity and S_{BET} of BND-TFP synthesized by monomer exchange is greater than that synthesized using either BND-benzaldehyde or BND-benzophenone (Figure 1). Therefore, the enhanced materials quality attained by monomer exchange is not solely because the COF is formed via a transimination rather than a direct condensation process. This control experiment further suggests that TFP directly replaces TFB in the network without disrupting the existing long-range order.

To evaluate the generality of the monomer exchange approach, we targeted two additional frameworks for which both β -ketoenamine- and the corresponding imine-linked COFs were reported (Figure 2). Tris(aminophenyl) benzene- (TAPB-TFP) and tris(aminophenyl) triazine-containing (TAZ-TFP) COFs were isolated with crystallinities surpassing previous reports as determined by PXRD (Figure 2B).^{20-21,23-25} S_{BET} values of 1148 m^2/g and 815 m^2/g for TAZ-TFP and TAPB-TFP COFs, respectively (Figure S23 and S24), exceed previously highest reported values

of 825 m^2/g and 527 m^2/g , respectively.^{20,24} The domain size of the β -ketoenamine-linked COFs are similar to their corresponding starting imine-linked COFs supporting that crystallite size, within error, is preserved subsequent to monomer exchange (see Table S7). CP-MAS NMR and FT-IR spectra verify complete conversion to the β -ketoenamine linkage (Figures S61, S62, S66, and S67).

Postsynthetic exchange was also successful to access two new β -ketoenamine-linked COFs for which the corresponding imine-linked frameworks were previously reported (Figure 2C).^{12,14} The synthesized tris(aminophenyl)amine-containing TAPA-TFP COF exhibited excellent crystallinity and a S_{BET} value of 823 m^2/g (Figure S26). The diamino fluorene-containing DAFL-TFP COF had a moderate crystallinity and surface area (Figure S25) similar to that of the starting imine-linked COF (Figures S6 and S20), which we attribute to the nonlinear dihedral angle between the two amine functional groups in the DAFL monomer. Both TAPA-TFP and DAFL-TFP COFs maintain their average crystallite size after monomer exchange, and complete exchange is demonstrated by CP-MAS NMR and FT-IR spectroscopies (Figures S63, S64, S68, and S69). To determine whether monomer exchange was advantageous to traditional methods, TAPA-TFP and DAFL-TFP COFs were also prepared through the direct condensation approach. PXRD patterns of the collected materials exhibit no crystallinity (Figure 2C), thus demonstrating that monomer exchange can provide access to

various β -ketoenamine-linked COFs that were otherwise difficult to access directly.

β -ketoenamine linkages are desirable due to their stability in both acidic and basic conditions. To examine this stability relative to that of the starting imine-linked COFs, we exposed samples of BND-TFB and BND-TFP COF to varying concentrations of HCl and NaOH as well as boiling water. After seven days, the solids were collected, washed and activated, and their measured PXRD patterns were compared to the as-synthesized patterns (SI section VIII). Although the imine-linked COF was stable in boiling water, it was degraded in acidic and basic aqueous solutions (Figure S45). After exposure to 9 M HCl, no imine-linked COF was recovered. In contrast, the β -ketoenamine-linked COF was exceedingly stable and exhibited only minor deviations from its original PXRD patterns even upon exposure to 9 M NaOH and 9 M HCl. The stability of β -ketoenamine-linked COFs compares exceptionally well to other known highly stable frameworks, including those with higher degrees of conjugation.²⁶

In summary, a monomer exchange strategy was employed to synthesize β -ketoenamine-linked COFs with crystallinities and surface areas superior to typical condensation approaches. This approach was demonstrated to improve the quality of known COFs and provide novel COF structures that are synthetically inaccessible through previous methods. Exchange does not require excess TFP, and the displaced TFB can be recovered. We expect this general approach to be used to improve the crystallinity and surface area of other β -ketoenamine-linked COFs, particularly for those with interesting redox, optical, and electronic properties that depend on improved long-range order.

Acknowledgements

We acknowledge the Army Research Office for a Multidisciplinary University Research Initiative (MURI) award under grant number W911NF-15-1-0447. A.M.E. is supported by the NSF Graduate Research Fellowship under grant DGE-1324585, the Ryan Fellowship, and the Northwestern University International Institute for Nanotechnology (IIN). This study made use of the IMSERC and EPIC at Northwestern University, both of which have received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF NNCI-1542205 and NSF ECCS1542205, respectively), the State of Illinois, and the IIN.

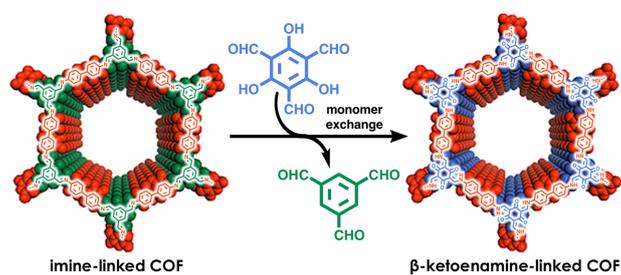
Conflicts of interest

There are no conflicts to declare.

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TOC



β -ketoenamine-linked COFs with improved crystallinity are achieved through monomer exchange of isostructural imine-linked COFs.