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Converting Unstable Imine-Linked Network into Stable Aromatic Benzoxazole-Linked One via Post-Oxidative Cyclization

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Supporting Information

ABSTRACT: Efficiently converting unstable linkages into stable linkages is an important objective in the chemistry of covalent organic frameworks (COFs), because it enhances stability and preserves crystallinity. Here, unstable imine-linked COF was converted into stable aromatic benzoxazole-linked COF (BO-COF) *via* post-oxidative cyclization, based on chemistry used to form fused-aromatic ladder-like rigid-rod polymers. The structure of the porous BO-COF was confirmed by transmission electron microscopy, and infrared and solid-state nuclear magnetic resonance spectroscopies, powder X-ray diffraction patterns and nitrogen adsorption-desorption isotherms. The efficient post-treatment of unstable reversible COF converted it into stable irreversible COF, which had significantly improved thermal and chemical stabilities as well as high crystallinity. This strategy can be universally applied for the synthesis of stable fused-aromatic COFs, expanding their practical applications.

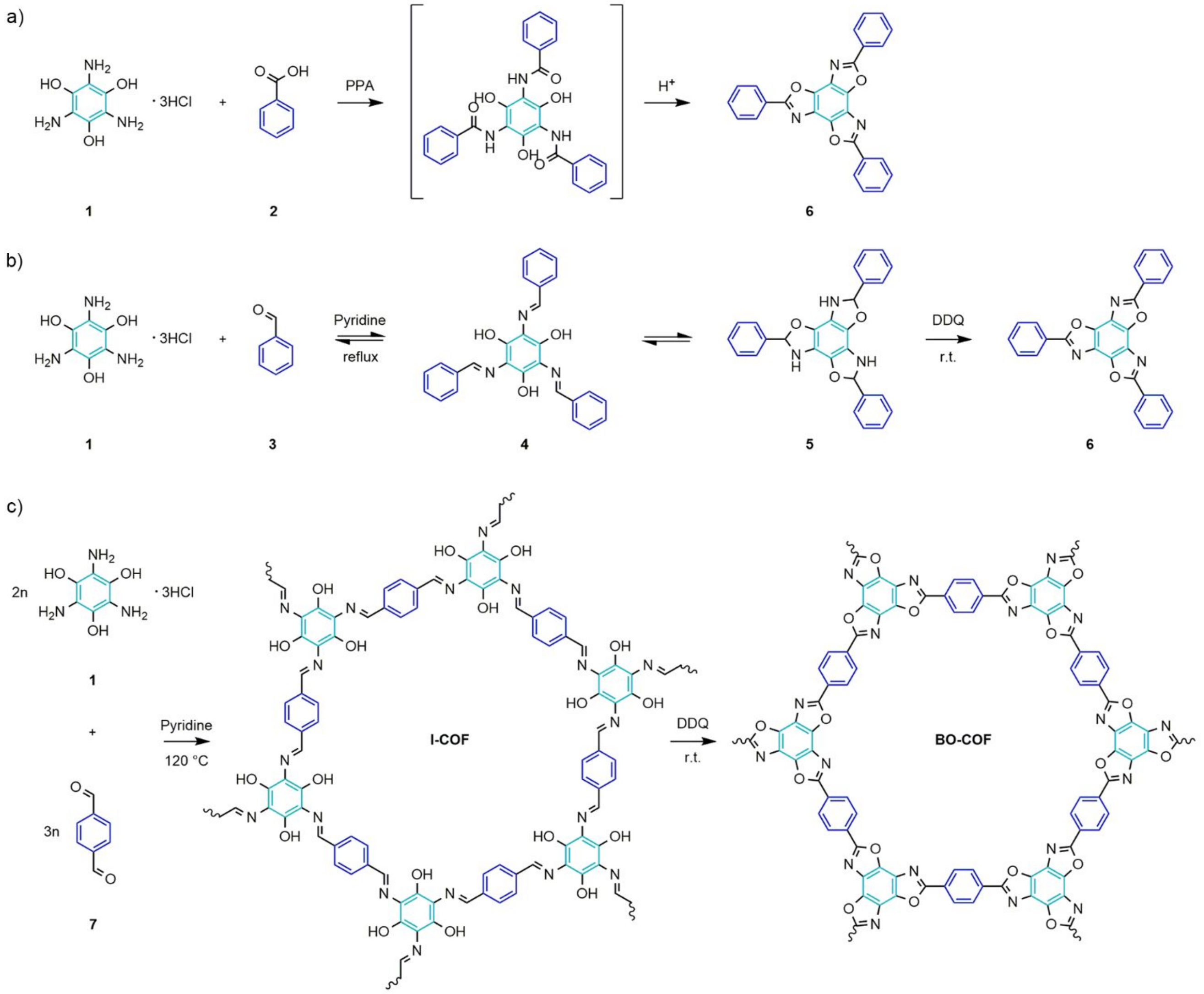
Linking organic molecules by covalent bond into extended structures leads to linear one- (1D), two- (2D) and three-dimensional (3D) polymer structures. Typically, the formation of porous 2D and 3D network polymers is governed by kinetically controlled reactions, which lead to amorphous materials. This makes it difficult to ascertain their physical properties, which are related to precisely controlled crystalline structures, and this limits their specific applications[1,2]. Crystalline materials can be achieved with thermodynamically controlled reactions by forming reversible bonds, a process which is known as dynamic covalent chemistry (DCC)[3]. Most current chemistry employs this approach, which leads to COF materials with high crystallinity and permanent porosity[4]. For instance, if the linkages in COFs are not ideally connected, they can be thermally dissociated and reconnected into correct conformations, resulting in long-range ordered materials[5]. On the other hand, the reversibility of chemical bonds simultaneously implies the resulting COFs will be unstable. It is a significant challenge to convert unstable reversible bonds *via* post-treatment of unstable bonds in COFs into stable irreversible bonds while preserving high crystallinity.

To date, post-treatment methods used to convert reversible into irreversible bonds have mainly focused on the tautomerization of the enol-to-keto linkage[6]. However, this keto linkage is unstable in alkaline conditions, because of the backward formation of keto-to-enol[7]. As an alternative, a method of converting an imine linkage (Schiff base) to another stable linkage *via* post-treatment has been recently introduced[8-10]. However, to increase practicality it is still necessary to develop more solid approaches.

The key to any new approach is the selection of a stable linkage. Therefore, we focused on the classic linear fused-aromatic rigid-rod polymers to find stable linkages. These aromatic heterocyclic polymers, including polybenzoxazoles (PBOs), had been intensively studied from the 1960s through the 1980s, since the dramatic advances of the aerospace industries that demanded high-temperature and high-performance structural polymers[11]. Due to the formation of irreversible aromatic rings as polymer forming reaction, all fused-aromatic rings structures of PBOs have enable to demonstrate high thermal and chemical stability along with ultrahigh mechanical properties[12,13]. Classically, benzoxazole linkages are formed by an irreversible process, *e.g.*, the formation of aromatic rings between ortho-aminophenol (Ph-(NH_2)-OH) and benzoic acid (Ph-COOH) in the presence of acid catalyst at elevated temperature[14,15]. The thermodynamic energy gain after forming aromatic oxazole rings by double condensation ($-2H_2O$ per reaction) prevents the reverse reaction (Scheme 1a). The other for synthesis of benzoxazole linkage is oxidative cyclization of phenolic Schiff bases derived from the condensation of 2-aminophenols and aldehydes[16]. However, reversibility is required for the formation of highly crystalline COFs[17]. Therefore, reversable reaction should be included during the formation of benzoxazole linkage. The synthesis of benzoxazole-linked COF by one-pot protocol has been recently reported[18-20]. These one-pot protocol kinetically leads to the rapid formation of oxazole rings by irreversible oxidation before "defect-correcting" for positional ordering, hence minimize the reverse reaction. Also, the post-modification of imine to benzoxazole linkage by heterogeneous linker exchange has recently been reported[21]. However, this approach is fundamentally different the direct conversion in this work.

Here, we report the conversion of reversible imine-linked COF (I-COF) to irreversible benzoxazole-linked COF (BO-COF) *via* post-oxidative cyclization. Compared to one-pot irreversible synthesis, this strategy is able to preserve the original topology, crystallinity and porosity of the resultant COF, while enhancing thermal and chemical stability. The aim of this work is to improve the crystallinity of stable COF by stepwise reaction, which fixes the ordered structure of framework before transforming stable benzoxazole linkage and to visualize crystalline COF by transmission electron microscopy. We selected 2,3-dichloro-5,6-

Scheme 1. Schematic presentation of the oxidative cyclization of I-COF into BO-COF[a]



[a](a) Classic formation of benzoxazole ring between TABT (1) and benzoic acid (2) to form benzoxazole compound (6) by one-step irreversible condensation in a PPA medium. (b) Model reaction between TABT (1) and benzaldehyde (3) to form a reversible imine compound (4), its tautomeric intermediate benzoxazoline structure (5), and final conversion into a benzoxazole compound (6) by oxidative cyclization with DDQ. (c) Synthesis of I-COF from the reaction between TABT (1) and TPA (7), then, the oxidative cyclization of I-COF into BO-COF by DDQ.

dicyano-1,4-benzoquinone (DDQ) as the oxidant, because it not only promotes the reaction in a straightforward way, but can also be easily removed after the reaction. Based on the formation of a model compound (Scheme 1b), our strategy for post-oxidative cyclization resulted in a BO-COF with high crystallinity and porosity. As a result of stable rigid benzoxazole linkages, the resulting BO-COF exhibited excellent thermal and chemical stability compared to I-COF.

The synthesis of BO-COF was carried out using a two-step reaction sequence (Scheme 1c): (1) the formation of I-COF and (2) the oxidative cyclization of I-COF into BO-COF. First, I-COF was obtained from the reaction between 1,3,5-triamino-2,4,5-benzenetriol (TABT, **1**) and terephthaldehyde (TPA, **7**) by solvothermal synthesis in methanol and mesitylene at 120 °C for 3 days. To achieve the highest crystallinity and porosity, the reaction condition was optimized (Supporting Information (SI) section S3). As-synthesized I-COF has very poor stability, even in ambient moisture[22] (Figure S2), because of the residual pyridinium chloride in I-COF (see SI section S3). Accordingly, we subsequently explored the post-modification of I-COF into BO-COF by oxidative cyclization. As seen in scheme 1b and scheme S1, the imine (-C=N-) linkages on the ortho-position of the phenolic hydroxyl moieties (**4**) were easily cyclized into aromatic benzoxazoline rings (**5**). As a result, the selection of the appropriate oxidant is important to efficiently oxidize benzoxazoline (**5**) into a benzoxazole (**6**) linkage[23,24]. While optimizing the reaction condition, DDQ was found to be the best oxidant, and resulted in the highest degree of crystallinity for the conversion of I-COF to BO-COF (SI section S4). Hence, BO-COF was synthesized by treating I-COF with DDQ in dichloromethane at room temperature for 3 days (see SI section S2).

The conversion of the imine-linkage before and after oxidative cyclization was monitored by Fourier-transform infrared (FT-IR) and carbon thirteen (^{13}C) cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopies. The FT-IR spectra of the BO-COF exhibited the O-C=N stretching band of the benzoxazole linkage at 1630 cm^{-1}. The disappearance of the C=N stretching band of the imine-linkage at 1610 cm^{-1} indicates

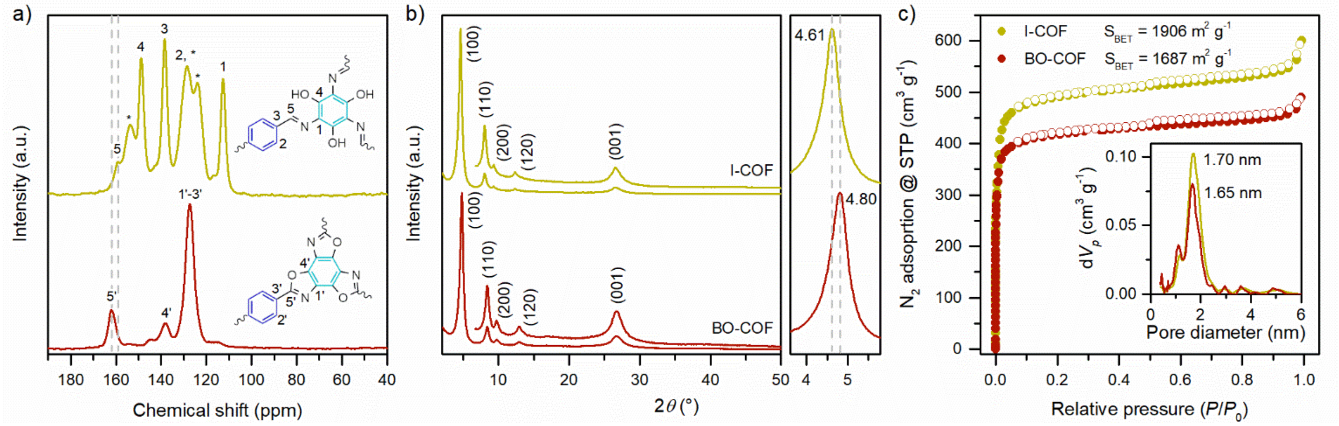


Figure 1. Structural characterizations of I-COF and BO-COF. (a) ^{13}C CP-MAS NMR spectra. Asterisks in I-COF denote the unremoved pyridinium chloride. Inset, assignment of the ^{13}C CP-MAS NMR signals in the chemical structure. (b) PXRD patterns, indicating retention of crystallinity after oxidative cyclization (left). Enlargement of (100) reflection, showing the reduction of unit cell dimensions (right). (c) The permanent microporosities were measured by nitrogen adsorption-desorption isotherms. Filled circles: adsorption; open circles: desorption. Inset is the corresponding pore size distribution profile calculated from adsorption data using the cylindrical pore NLDFT model.

the conversion of imine into benzoxazole linkages. Furthermore, new bands at 1490 cm^{-1} and 1080 cm^{-1} appeared in the spectrum of the BO-COF. The peaks are assignable to the symmetric and asymmetric C-O-C stretching bands in the benzoxazole linkage (Figure S4)[19,25].

Clear indication of the structural characterization was also observed by CP-MAS NMR analysis. In the ^{13}C CP-MAS NMR spectrum of BO-COF, the 5 signal at 159 ppm indicating the imine carbon in I-COF was attenuated after oxidative cyclization. Indeed, a new 5' signal was observed at 162 ppm, attributed to the formation of a benzoxazole linkage (Figure 1a). The assignment of these signals was confirmed by comparing with the model compound (Figure S5).

The crystallinity of I-COF and BO-COF was measured by powder X-ray diffraction (PXRD). Small shifts in the (100) reflection of the powder patterns of I-COF and BO-COF support the reduction in pore size caused by the oxidative cyclization of imine linkages into benzoxazole linkages (Figure 1b). Extended structures based on a hexagonal layered hcb topology were modeled for the I-COF (space group *P*6, No. 168) and BO-COF (space group *P*6/M, No. 175). The experimental patterns for I-COF and BO-COF were in good agreement with the energetically most favorable eclipsed models. On the other hand, the staggered model gave a PXRD pattern that deviated widely from the experimental one. Pawley refinement[26,27] of the experimental patterns provided unit cell parameters of I-COF ($a = b = 22.37$ Å, $c = 3.55$ Å) and BO-COF ($a = b = 21.12$ Å, $c = 3.38$ Å), led to low residuals values in the I-COF ($wR_p = 3.73\%$, $R_p = 2.85\%$) and BO-COF ($wR_p = 3.31\%$, $R_p = 2.46\%$), respectively (Figure S6).

The permanent porosities of the I-COF and BO-COF were confirmed by low-pressure nitrogen adsorption-desorption isotherms at 77 K. Both COFs exhibited a high nitrogen uptake at relatively low pressures, which is indicative of microporous materials (Figure 1c). The Brunauer-Emmett-Teller surface areas (S_{BET}) were estimated to be 1906 m^2 g^{-1} for I-COF (theoretical surface area: 2319 m^2 g^{-1}) and 1687 m^2 g^{-1} for BO-COF (theoretical surface area: 1995 m^2 g^{-1}) (Figure S7). The loss in surface area of BO-COF can be attributed to a decrease in pore size and crystallinity after oxidative cyclization. The pore size distributions were calculated from the nitrogen isotherms using a non-local density functional theory (NLDFT) model. The results showed a reduction in pore size from I-COF (1.70 nm) to BO-COF (1.65 nm). The reduction in pore size, which corresponds to the observed reduction in lattice parameter in the PXRD results (inset of figure 1c), is due to oxidative cyclization from the imine-linkage to the benzoxazole linkage.

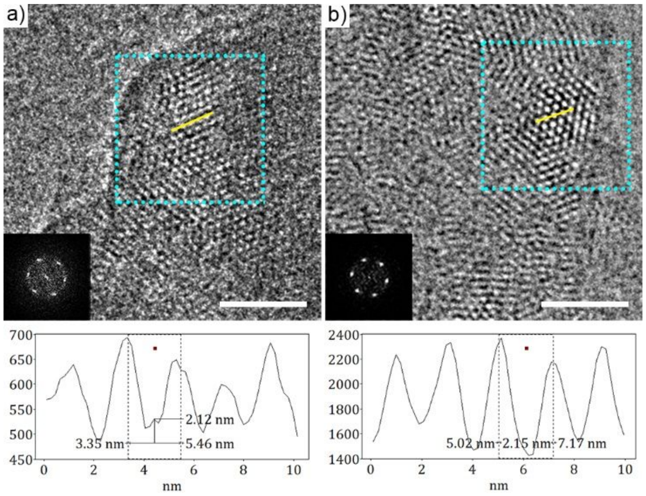


Figure 2. Morphologies of BO-COF. (a,b) TEM images of BO-COF. Inset: corresponding fast Fourier transform of the marked area (cyan dash line). Bottom: corresponding height profiles of the marked line (yellow line). Scale bars: 20 nm.

The morphologies of I-COF and BO-COF were visualized by electron microscopy. Scanning electron microscopy (SEM) revealed elongated rod shapes composed of small flakes (Figure S8). Further investigations were conducted using high-resolution transmission electron microscopy (HR-TEM) but only for BO-COF, because I-COF had low-electron beam stability[28]. HR-TEM images of BO-COF show an ordered, hexagonal porous structure oriented along the <001> direction with a periodicity of 2.1 ± 0.05 nm, in precise agreement with the pore-to-pore distance of 2.1 nm in the refined eclipsed model (Figure 2). Both HR-TEM images and corresponding fast-Fourier transformation (FFT) of the BO-COF confirmed its crystallinity, and the calculated lattice distance of 1.8 ± 0.05 nm corresponds to the (100) plane of the eclipsed model, and matched the refined PXRD pattern well (Figure S9).

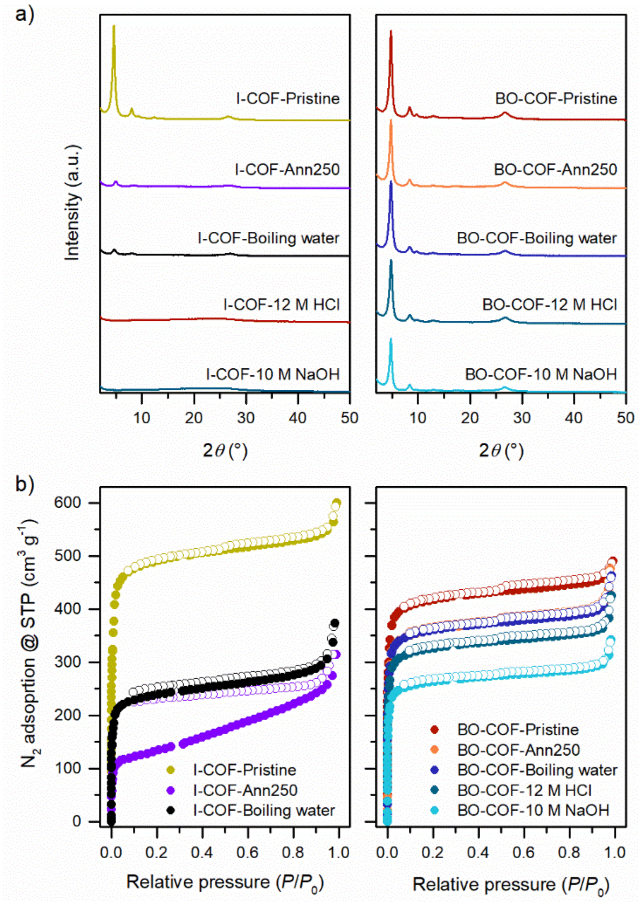


Figure 3. Thermal and chemical stability of I-COF and BO-COF after treatment in various conditions for 3 days. (a) PXRD patterns. (b) Nitrogen adsorption-desorption isotherms at 77 K. Filled circles: adsorption, open circles: desorption.

As demonstrated in a linear polybenzoxazole (PBO) analogue[29,30], the benzoxazole linkage has high thermal and chemical stabilities. Therefore, we performed stability tests on both I-COF and BO-COF in order to prove the irreversibility of the benzoxazole linkage. First, to confirm that crystallinity was retained at high temperature, both I-COF and BO-COF were heat treated at 250 °C in air atmosphere for 1 h. Thermogravimetric analysis (TGA) thermograms indicated that both COFs exhibited no weight loss at 250 °C in air and nitrogen atmosphere (Figure S10). In addition, both COFs were exposed to boiling water, 12 M hydrochloric acid (HCl) and 10 M sodium hydroxide (NaOH) solutions for 3 days (see SI section S1), respectively, and were subsequently analyzed by FT-IR, PXRD and N_2 sorption. As expected, the I-COF showed the near or complete loss of crystallinity and porosity after the treatments. Furthermore, the decomposition of I-COF in the acid and base solutions could be easily confirmed with the naked eye (Figure S11). In contrast, BO-COF retained its physical properties after treatments (Figure 3; Figure S12-S14).

Further treatments of the BO-COF were conducted, including with methanesulfonic acid (MSA), 1 M sulfuric acid (H_2SO_4) and 1 M sodium borohydride ($NaBH_4$) solutions. The results indicated full retention of crystallinity and porosity (Figure S13). However, after treatments in acid and base media, a small decrease in crystallinity and surface area of BO-COF was observed. This effect was associated with minor structural deformation and adsorbed small molecules. Overall, the results demonstrated that BO-COF had high thermal and chemical stability, suitable for practical applications.

In summary, we were able to synthesize stable fused-aromatic benzoxazole-linked COF with high crystallinity and porosity. The key strategy was to form irreversible aromatic benzoxazole rings from reversible imine linkages using oxidative cyclization. This approach allows the resulting COF to not only retain its topology, crystallinity and porosity, but also results in significantly improved thermal and chemical stability, suitable for practical applications. This simple reaction protocol is a synthesis of other fused-aromatic frameworks with crystallinity and porosity, and thus widens their applications from wet chemistry to device applications.

ASSOCIATED CONTENT

Supporting Information

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

Synthesis and characterizations (PDF)

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) Das, S.; Heasman, P.; Ben, T.; Qiu, S. L., Porous Organic Materials: Strategic Design and Structure-Function Correlation. *Chem. Rev.* **2017,** *117*, 1515-1563.

(2) Stewart, D.; Antypov, D.; Dyer, M. S.; Pitcher, M. J.; Katsoulidis, A. P.; Chater, P. A.; Blanc, F.; Rosseinsky, M. J., Stable and ordered amide frameworks synthesised under reversible conditions which facilitate error checking. *Nat. Commun.* **2017,** *8*, 1102.

(3) Feng, X.; Ding, X. S.; Jiang, D. L., Covalent organic frameworks. *Chem. Soc. Rev.* **2012,** *41*, 6010-6022.

(4) Huang, N.; Wang, P.; Jiang, D. L., Covalent organic frameworks: a materials platform for structural and functional designs. *Nat. Rev. Mater.* **2016,** *1*, 16068.

(5) Colson, J. W.; Dichtel, W. R., Rationally synthesized two-dimensional polymers. *Nat. Chem.* **2013,** *5*, 453-465.

(6) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R., Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. *J. Am. Chem. Soc.* **2012,** *134*, 19524-19527.

(7) Segura, J. L.; Mancheno, M. J.; Zamora, F., Covalent organic frameworks based on Schiff-base chemistry: synthesis, properties and potential applications. *Chem. Soc. Rev.* **2016,** *45*, 5635-5671.

(8) Waller, P. J.; Lyle, S. J.; Popp, T. M. O.; Diercks, C. S.; Reimer, J. A.; Yaghi, O. M., Chemical Conversion of Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2016,** *138*, 15519-15522.

(9) Haase, F.; Troschke, E.; Savasci, G.; Banerjee, T.; Duppel, V.; Dorfler, S.; Grundei, M. M. J.; Burow, A. M.; Ochsenfeld, C.; Kaskel, S.; Lotsch, B. V., Topochemical conversion of an imine-into a thiazole-linked covalent organic framework enabling real structure analysis. *Nat. Commun.* **2018,** *9*, 2600.

(10) Li, X. L.; Zhang, C. L.; Cai, S. L.; Lei, X. H.; Altoe, V.; Hong, F.; Urban, J. J.; Ciston, J.; Chan, E. M.; Liu, Y., Facile transformation of imine covalent organic frameworks into ultrastable crystalline porous aromatic frameworks. *Nat. Commun.* **2018,** *9*, 2998.

(11) Stevens, M. P., *Polymer Chemistry: An Introduction*. Oxford Univ. Press: Oxford, 1999.

(12) Yang, H. H., *Aromatic High-Strength Fibers*. John Wiley & Sons, Inc.: New York, 1989.

(13) So, Y. H.; Heeschen, J. P.; Bell, B.; Bonk, P.; Briggs, M.; DeCaire, R., Study of the mechanism for poly(p-phenylene)benzoxazole polymerization - A remarkable reaction pathway to make rigid-rod polymers. *Macromolecules* **1998,** *31*, 5229-5239.

(14) Hein, D. W.; Alheim, R. J.; Leavitt, J. J., The use of polyphosphoric acid in the synthesis of 2-aryl- and 2-alkyl-substituted benzimidazoles, benzoxazoles and benzothiazoles. *J. Am. Chem. Soc.* **1957,** *79*, 427-429.

(15) So, Y. H.; Heeschen, J. P.; Murlick, C. L., A MECHANISTIC STUDY OF POLYBENZOXAZOLE FORMATION WITH MODEL COMPOUNDS. *Macromolecules* **1995,** *28*, 7289-7290.

(16) Chen, Y.; Zeng, D. X., Study on photochromic diarylethene with phenolic Schiff base: Preparation and photochromism of diarylethene with benzoxazole. *J. Org. Chem.* **2004,** *69*, 5037-5040.

(17) Waller, P. J.; Gandara, F.; Yaghi, O. M., Chemistry of covalent organic frameworks. *Acc. Chem. Res.* **2015,** *48*, 3053-3063.

(18) Pyles, D. A.; Crowe, J. W.; Baldwin, L. A.; McGrier, P. L., Synthesis of benzobisoxazole-linked two-dimensional covalent organic frameworks and their carbon dioxide capture properties. *ACS Macro Lett.* **2016,** *5*, 1055-1058.

(19) Wei, P. F.; Qi, M. Z.; Wang, Z. P.; Ding, S. Y.; Yu, W.; Liu, Q.; Wang, L. K.; Wang, H. Z.; An, W. K.; Wang, W., Benzoxazole-Linked Ultrastable Covalent Organic Frameworks for Photocatalysis. *J. Am. Chem. Soc.* **2018,** *140*, 4623-4631.

(20) Pyles, D. A.; Coldren, W. H.; Eder, Grace M.; Hadad, C. M.; McGrier, P. L., Mechanistic investigations into the cyclization and crystallization of benzobisoxazole-linked two-dimensional covalent organic frameworks. *Chem. Sci.* **2018,** *9*, 6417-6423.

(21) Waller, P. J.; AlFaraj, Y. S.; Diercks, C. S.; Jarenwattananon, N. N.; Yaghi, O. M., Conversion of Imine to Oxazole and Thiazole Linkages in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018,** *140*, 9099-9103.

(22) Ascherl, L.; Evans, E. W.; Hennemann, M.; Di Nuzzo, D.; Hufnagel, A. G.; Beetz, M.; Friend, R. H.; Clark, T.; Bein, T.; Auras, F., Solvatochromic covalent organic frameworks. *Nat. Commun.* **2018,** *9*, 3802.

(23) Cellier, M.; Fabrega, O. J.; Fazackerley, E.; James, A. L.; Orenga, S.; Perry, J. D.; Salwatura, V. L.; Stanforth, S. P., 2-Arylbenzothiazole, benzoxazole and benzimidazole derivatives as fluorogenic substrates for the detection of nitroreductase and aminopeptidase activity in clinically important bacteria. *Bioorg. Med. Chem.* **2011,** *19*, 2903-2910.

(24) Chang, J. B.; Zhao, K.; Pan, S. F., Synthesis of 2-arylbenzoxazoles via DDQ promoted oxidative cyclization of phenolic Schiff bases - a solution-phase strategy for library synthesis. *Tetrahedron Lett.* **2002,** *43*, 951-954.

(25) Wang, Y.; Yu, J. R.; Zhu, J.; Hu, Z. M., Hyperbranched Polybenzoxazoles Incorporated Polybenzoxazoles for High-Performance and Low-K Materials. *J. Polym. Sci., Part A: Polym. Chem.* **2016,** *54*, 1623-1632.

(26) Xu, H.; Gao, J.; Jiang, D., Stable, crystalline, porous, covalent organic frameworks as a platform for chiral organocatalysts. *Nat. Chem.* **2015,** *7*, 905-912.

(27) Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. L., A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework. *Angew. Chem. Int. Ed.* **2008,** *47*, 8826-8830.

(28) Egerton, R. F.; Li, P.; Malac, M., Radiation damage in the TEM and SEM. *Micron* **2004,** *35*, 399-409.

(29) Holmes, G. A.; Rice, K.; Snyder, C. R., Ballistic fibers: A review of the thermal, ultraviolet and hydrolytic stability of the benzoxazole ring structure. *J. Mater. Sci.* **2006,** *41*, 4105-4116.

(30) Agag, T.; Liu, J.; Graf, R.; Spiess, H. W.; Ishida, H., Benzoxazole Resin: A Novel Class of Thermoset Polymer via Smart Benzoxazine Resin. *Macromolecules* **2012,** *45*, 8991-8997.

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