

Communication

Aminal-Linked Covalent Organic Frameworks through Condensation of Secondary Amine with Aldehyde

Shu-Yan Jiang, Shi-Xian Gan, Xi Zhang, Hui Li, Qiao-Yan Qi, Fu-Zhi Cui, Jian Lu, and Xin Zhao J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b08017 • Publication Date (Web): 06 Sep 2019 Downloaded from pubs.acs.org on September 6, 2019

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Aminal-Linked Covalent Organic Frameworks through Condensation of Secondary Amine with Aldehyde

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Supporting Information Placeholder

ABSTRACT: New linkage chemistry will endow covalent organic frameworks (COFs) with not only structural diversity but also fascinating properties. However, to develop a new type of linkages has been a great challenge. We herein report the first two COFs using aminal as the linkages. These two COFs have been synthesized by condensation of secondary amine and aldehyde. They crystallize in **cpi** net, which is a new topology for COFs. The aminal linkage is found to favor reservation of photophysical property of the monomers due to its tetrahedral geometry and non-conjugated feature. These aminal-COFs exhibit good thermal stability and high chemical stability under neutral and basic conditions.

Covalent organic frameworks (COFs) are a class of crystalline porous organic polymers constructed by linking organic building blocks via covalent bonds.¹ In this context, linkages not only play a crucial role in connecting vertexes and linkers together into well-ordered 2D or 3D network structures, but also have a great influence on the properties of the materials. Benefiting from their tailored structures with permanent porosity, COFs have versatile applications ranging from gas storage,² separation,³ catalysis,⁴ sensing,⁵ drug delivery,⁶ energy storage,⁷ to photo/electronic devices.⁸ Since the pioneering work of Yaghi in 2005,⁹ this field has experienced a rapid growth over the past decade, to which two aspects, developing new structures and exploring new proper-ties/applications, are mainly focused.¹⁰ With the development of COFs, their linkages have evolved from B-O¹¹ and C=N¹² in the early stage to C=C,¹³ C-N,¹⁴ C-O,¹⁵ C-C¹⁶ and even mechanical entanglement¹⁷ in recent years and distinct properties associated with the different linkages have been demonstrated, undoubtedly indicating that new linkage chemistry becomes one of the strong driving forces to push this exciting field forward.

Aminal, also termed N, N-acetal which can be regarded as the product of subsequently attacking a pre-formed imine bond by another amine, exhibits good reversibility similar to imine

bonds.¹⁸ However, while imine has been widely used as linkages in the synthesis of COFs,¹⁹ aminal was never observed in COFs. Although a few examples in literature suggest that aminal linkages are strong enough to produce amorphous microporous polymers,²⁰ to fabricate crystalline materials through aminal chemistry is a great challenge due to the drastic change of the stereo structure during the condensation process, as a result of the transformation from the planar sp^2 hybridization of carbonyl carbon to the tetrahedral sp³ hybridization of aminal carbon. Such a change undoubtedly increases difficulty of COF synthesis in the monomer design and structure prediction. In this communication, we report the construction of two aminal-linked 2D COFs based on an elaborate design. Firstly, non-planar D_{2h}-symmetric tetraaldehydes were chosen to accommodate the space change in the process of the sp²-to-sp³ transformation. Secondly, since condensation of primary amine with aldehyde usually produces imine,¹⁸ secondary amine was used to impede the formation of imine linkages. Based on this design, two aminal-linked 2D COFs with cpi net have been successfully synthesized, through which we have developed not only a new type of linkages but also a new topology for COFs. Moreover, unique property associated with the saturated bond and tetrahedral geometry of aminal has also been demonstrated.

The synthesis of the target COFs was implemented through the condensations of piperazine with D_{2h} -symmetric tetraaldehydes A1 and A2, respectively, inspired by the reaction between benzaldehyde and piperidine (Scheme 1).²¹ Experimentally, the condensation reactions were carried out under solvothermal condensations at 120 °C for 72 h in sealed tubes. The molar ratio between the aldehydes and piperazine is 1:4 and toluene was found to be the optimized solvent after screening a series of solvent systems (Table S1). The COFs were obtained as a pale yellow microcrystalline powder with high crystallinity (termed **Aminal-COF-1**) in 77% yield from tetraaldehyde A1, or white crystallites (termed **Aminal-COF-2**) in 62.5% yield from tetraaldehyde A2, respectively.

Scheme 1. Model Reaction and Synthesis of Aminal-linked COFs.

Formation of aminal through the reaction of aldehyde with two eqiv of secondary amine

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Synthesis of aminal-linked COFs and their photographs



The as-obtained crystallites were characterized with Fouriertransform infrared (FT-IR) spectroscopy (Figures S1-S2), solidstate ¹³C and ¹⁵N cross-polarization with magic angle spinning (CP/MAS) NMR (Figures S3-S5), and X-ray photoelectron spectroscopy (XPS) (Figures S6-S7), from which the aminal linkages in the COFs have been identified. Concretely, no vibration band corresponding to N-H group of piperazine (3214 cm⁻¹) is observed and the peak assignable to aldehyde group (1700 cm^{-1}) is dramatically attenuated in the IR spectra of both the two COFs, suggesting high degrees of conversions of the monomers. No vibration peak of C=N shows up, indicating there are no imine linkages in the as-obtained materials. The ¹³C NMR spectra of the two COFs also reveal absence of C=N units in their structures. Instead, signals around 88 ppm are observed. The peaks are assigned to aminal carbon (N-C-N), providing compelling evidence for the formation of aminal linkages. The ¹⁵N spectra of the COFs show two resonances around 50 and 55 ppm, which are different from that of piperazine (37 ppm) and should be assigned to two kinds of aminal nitrogen in different environment. In the XPS spectra, while the XPS survey spectra display strong C1s peaks and N1s peaks with moderate intensity, the peaks corresponding O1s exhibit very low intensities, suggesting the as-formed materials are mainly composed of carbon and nitrogen. The oxygen observed in the XPS spectra, also revealed by the IR data above, is attributed to the residual carbonyl group at the peripheral of the COFs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed phase pure of the COFs, as only one morphology was observed for each COF (Figure S8-S9).

After the COFs were confirmed to be produced through aminal linkages, their crystal structures were elucidated using powder X-ray diffraction (PXRD). The high quality of the PXRD patterns offer direct acquisition of crystal lattice parameters of the COFs based on the abundant peaks after indexing (Figures 1a and 2a). For **Aminal-COF-1**, three high intense diffraction peaks appear at 4.24°, 5.68° and 8.27°, which are attributed to (100), (010) and (110) facets, respectively. Another six weak peaks assignable to (1-20), (210), (120), (4-20), (4-30) and (3-21) facets are observed at 10.49°, 11.87°, 13.53°, 16.40°, 18.95° and 19.98°, respectively. The lattice modeling and Pawley refinement of **Aminal-COF-1** were conducted using Materials Studio, which output the most probable structure of **Aminal-COF-1** with eclipsed (AA) stacking, as the one illustrated in Figure 1e. Pawley refinement produced



Figure 1. (a) Experimental (black) and refined (red) PXRD patterns of **Aminal-COF-1**. (b) Difference plot between the experimental and refined PXRD patterns. Simulated PXRD patterns for (c) eclipsed and (d) staggered structures. Perspective and top views of structural representation of **Aminal-COF-1** in (e) eclipsed and (f) staggered stacking.

the optimized parameters of a = 22.74 Å, b = 16.95 Å, c = 6.06 Å, $\alpha = \beta = 90.00^{\circ}$ and $\gamma = 112.37^{\circ}$. The calculated PXRD diffraction pattern match well with the experimental result (Figure 1c), with $R_{wp} = 4.00\%$ and $R_p = 3.13\%$. Staggered (AB) stacking structure was also simulated (Figure 1f). The comparison of its PXRD profile with the experimental one shows significant deviations (Figure 1d), ruling out the AB stacking model. This type of network structure, consisting of periodic distribution of pentagonal and hexagonal pores in a plane, is identified as **cpi** net.²² To the best of

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our knowledge, this topology has never been observed in COFs before.

In the experimental PXRD pattern of **Aminal-COF-2**, the most intense peak appears at 3.86°, assignable to (100) facet, while other diffraction peaks at 5.28°, 7.61°, 9.78°, 10.85°, 12.52°, 15.85°, 18.43° and 20.54° are attributed to (010), (110)/(2-10), (1-20), (210)/(3-10), (120), (030), (121) and (401) facets, respectively (Figure 2a and Figure S10). The crystal structure of **Aminal-COF-2** was determined to be the one depicted in Figure 2e. **Aminal-COF-2** also adopts eclipsed stacking, as supported by the good agreement between the calculated and experimental PXRD patterns (Figure 2c). Pawley refinement reproduced the experimental PXRD pattern quite well and gave unit cell parameters of a = 24.53 Å, b = 17.88 Å, c = 6.60 Å, $\alpha = \beta = 90.00^{\circ}$ and $\gamma =$ 111.91°, with $R_{wp} = 5.13\%$ and $R_p = 4.13\%$. A staggered stacking structure was also ruled out by the mismatch between the simulated and experimental PXRD patterns (Figure 2d).

Unusually large interlayer distances are observed in the two COFs. A close examination on their crystal structures reveals that the piperazine units in the frameworks adopt a chair conformation, and the aminal units hold a tetrahedral configuration. As a result, the distances between phenyl rings (> 6.0 Å) go beyond that of a typical aromatic stacking and thus the interactions between them are minimized (Figure S11-S14). It is quite different from the COFs with planar linkages, in which aromatic stacking usually is significant.



Figure 2. (a) Experimental (black) and refined (red) PXRD patterns of **Aminal-COF-2**. (b) Difference plot between the experimental and refined PXRD patterns. Simulated PXRD patterns for (c) eclipsed and (d) staggered structures. Perspective and top views of structural representation of **Aminal-COF-2** in (e) eclipsed and (f) staggered stacking.

Both the COFs exhibited a typical nitrogen sorption isotherm of microporous materials (Figure 3a and 3c).²³ Their BET surface

areas were estimated from the adsorption data in the range of P/P_0 from 0.003 to 0.05, which afforded BET surface areas of 1169 m² $g^{\text{-1}}$ for Aminal-COF-1 and 1168 $m^2 \ g^{\text{-1}}$ for Aminal-COF-2 (Figure S15). The total pore volumes of Aminal-COF-1 and Aminal-COF-2 were calculated to be 0.65 cm³ g⁻¹ and 0.89 cm³ g⁻¹ $(P/P_0=0.99)$, respectively. Their theoretical BET surface areas were calculated to be 1465 $m^2 g^{-1}$ for Aminal-COF-1 and 1934 m² g⁻¹ for Aminal-COF-2 using Zeo⁺⁺ calculation.²⁴ Their pore size distribution (PSD) analysis was generated based on quenched solid-state density functional theory (QSDFT). As shown in Figure 3b and 3d, two narrow peaks are observed in both the PSD profiles (5.2 and 8.2 Å for Aminal-COF-1, 5.4 and 8.2 Å for Aminal-COF-2), indicating existence of two kinds of micropores in the COFs. Based on Zeo⁺⁺ calculations,²⁴ theoretical pore sizes of the pentagonal and hexagonal micropores in Aminal-COF-1 are estimated to be 5.3 and 8.2 Å, while for Aminal-COF-2 are 5.4 and 10.5 Å (Figure S16), which are in good agreement with the experimental results. The PSD results further collaborate the formation of the target aminal-linked 2D dual-pore COFs.



Figure 3. N₂ adsorption-desorption isotherms of (a) **Aminal-COF-1** and (c) **Aminal-COF-2**, and pore size distribution profiles of (b) **Aminal-COF-1** and (d) **Aminal-COF-2**.

Thermogravimetric analysis (TGA) revealed almost no weight loss before 200 °C and 10% weight loss around 320 °C for the aminal-linked COFs, indicating their good thermal stability (Figure S17-S18). Their chemical stability was examined by comparing the PXRD patterns, FT-IR spectra and residues weights of the samples before and after they were soaked in organic solvents, water and aqueous NaOH solutions (1 to 9 M) for a set time, respectively (Figures S19-S26, Tables S2-S3). The experimental results indicate that the COFs display high chemical stability under these conditions (see Supporting Information for details).

The composition of **Aminal-COF-1** was further analyzed with ¹H NMR spectroscopy after it was completely hydrolyzed under acidic condition. The ¹H NMR spectrum shows the molar ratio between tetraaldehyde A1 and piperazine is 1:4 (Figure S27), again confirmed the chemical constitution of the target aminal-linked COF. Elementary analysis of the COFs indicates the contents of carbon, hydrogen and nitrogen are close to their corresponding values, also indicating that as-obtained polymers are in line with the predicted structures of the COFs.

Different from imine-linked COFs in which the frameworks are extendedly conjugated, aminal is saturated and thus aminal-linked COFs do not have extended π -conjugated skeletons. Moreover,

the tetrahedral configuration of aminal makes the interlayer stacking less favorable than that in the 2D COFs assembled via planar linkages (for example, imine, boronate, boroxine). The feature of fewer disturbances is favorable for reservation of properties of functional monomers after they assemble into frameworks. This will benefit customized synthesis of COFs with designed and predicted physical properties. To examine this point, fluorescent properties of the two COFs, monomers A1 and A2 were investigated. The solid-state fluorescence spectra reveal that emission wavelengths of the aminal-COFs are almost same as that of their monomers (Figure 4), clearly indicating that the COFs have retained the photophyscial properties of the monomers. In contrast, for 2D COFs with unsaturated or planar linkages, monomers and frameworks are usually reported to exhibit very different optical features due to the close interlayer packing and/or the dramatic change in the extent of conjugation after the formation of the frameworks,^{5b,25} which makes properties of the COFs hard to precisely design and predict.

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Figure 4. Normalized solid-state fluorescence spectra of the aminal-COFs and monomers.

In summary, for the first time, COFs with aminal linkages have been synthesized. The aminal frameworks crystallize in **cpi** net, a new topology never reported for COFs before. These advances well demonstrate that linkage chemistry of aminal brings new development in the field of COFs and will also broaden the scope of reticular chemistry in terms of new bond connection. The tetrahedral geometry and non-conjugated feature of the aminal linkage distinguishes itself from the unsaturated or planar linkages by reducing disturbance on the properties of monomers, which may bring in more precise design and prediction for the properties of COFs.

ASSOCIATED CONTENT

Supporting Information

Procedures for the preparation of the monomers and COFs, IR spectra, solid-state ¹³C and ¹⁵N CP-MAS NMR spectra, SEM and TEM images, high-resolution PXRD profile, BET plots, TGA traces, additional PXRD profiles, illustration of the crystal structures of the COFs, and fractional atomic coordinates for the unit cells of the COFs. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank the National Science Fund for Distinguished Young Scholars of China (No. 21725404), Shanghai Scientific and Technological Innovation Project (18JC1410600), and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000) for financial support. We also thank Mr. Lubing Bai and Prof. Yuping Wu in Nanjing Tech University for their help in recording the solid-state fluorescence spectra.

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