Synthesis of –C=N– Linked Covalent Organic Frameworks via the Direct Condensation of Acetals and Amines

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B. Materials and Instrumentation

Materials

All reagents, unless otherwise stated, were purchased from commercial sources and used without further purification. Tetrahydrofuran (THF) was dried using the standard procedures. 2,5-Diethoxyterephthalohydrazide[1] and 1,3,5-tris(4-amino-phenyl)benzene[2] were synthesized according to the reported procedures.

Instrumentation

Liquid $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. High resolution mass spectra (HRMS) data were obtained with a Bruker maxis 4G (Data Analysis 4.0) instrument. Elemental analysis was carried out on a VarioEL V3.00 elemental analyzer (Elementar Analysensysteme GmbH). Powder X-ray diffraction (PXRD) data were collected with a PANalytical X'Pert Pro Diffractometer operated at 40 kV and 40 mA with Cu Kα radiation (step size of 0.017° and step time of 8.40 s). Fourier transform Infrared (FT-IR) spectra were recorded on a Nicolet NEXUS 670 instrument. Solid-state NMR measurements were performed on a Bruker WB Avance II 400 MHz spectrometer. The $^{13}$C CP MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe and with a sample spinning rate of 10.0 kHz; a contact time of 2 ms (ramp 100) and a pulse delay of 3 s were applied. Scanning Electron Micrograph (SEM) images were obtained with a Hitachi S-4800 microscope operated at an accelerating voltage of 5.0 kV. The samples were prepared by dropping the suspension of COF materials in ethanol on a silicon pellet, then dried and coated with gold. Thermogravimetric analysis (TGA) was performed on a STA PT1600 Linseis instrument over the temperature range of 25 to 800 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. The samples were outgassed at 120 °C for 8 h before the measurement. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) and Langmuir methods, respectively. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional
theory (NLDFT) method. Gas chromatography (GC) analysis was performed on an Agilent 7890A instrument with a flame ionization detector equipped with an HP-5 capillary column.
C. Synthetic Procedures

Synthesis of 6,6'-bis(dimethoxymethyl)-3,3'-bipyridine (I)

S1\textsuperscript{[3]}, S2\textsuperscript{[4]}, and S3\textsuperscript{[4]} were synthesized according to the reported procedures.

A degassed solution of S2 (464 mg, 2 mmol), S3 (837 mg, 3 mmol), Na\textsubscript{2}CO\textsubscript{3} (636 mg, 6 mmol), and Pd(PPh\textsubscript{3})\textsubscript{4} (231 mg, 0.2 mmol) in a mixed solvent (DMF/H\textsubscript{2}O = 10/1, 12 mL) was stirred at 70 °C for 15 hours under Ar atmosphere. After cooling to room temperature, the mixture was diluted with water and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with water (3 × 20 mL) and dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/acetone = 5/1) to obtain I as a white solid, 477 mg, yield: 78%.

\textsuperscript{1}H NMR data for I (400 MHz, CDCl\textsubscript{3}): \( \delta \) (ppm) 8.83 (t, \( J = 0.8 \) Hz, 2H), 7.93 (dd, \( J = 8.0, 2.0 \) Hz, 2H), 7.66 (d, \( J = 8.0 \) Hz, 2H), 5.43 (s, 2H), 3.44 (s, 12H).

\textsuperscript{13}C NMR data for I (100 MHz, CDCl\textsubscript{3}): \( \delta \) (ppm) 157.1, 147.5, 135.1, 133.0, 121.4, 103.7, 53.7.

HRMS m/z calcd. for C\textsubscript{16}H\textsubscript{20}N\textsubscript{2}O\textsubscript{4} [M + H]\textsuperscript{+}: 305.1496; found: 305.1503.

Synthesis of 1,3,5-tris(6-(dimethoxymethyl)pyridin-3-yl)benzene (7)

A degassed solution of S2 (928 mg, 4 mmol), K\textsubscript{2}CO\textsubscript{3} (2.07 g, 15 mmol), 1,3,5-
tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene[5] (456 mg, 1 mmol), and Pd(PPh\textsubscript{3})\textsubscript{4} (347 mg, 0.3 mmol) in DMF (60 mL) was stirred for 24 hours at 90 °C under Ar atmosphere. After cooling to room temperature, the solution was diluted with water and extracted with dichloromethane (3 × 50 mL). The combined organic phase was washed with water (3 × 50 mL) and dried over with anhydrous Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel (CH\textsubscript{2}Cl\textsubscript{2}/MeOH = 40/1) to give 7 as light yellow oil, 447 mg, yield: 84%. \textsuperscript{1}H NMR data for 7 (400 MHz, CDCl\textsubscript{3}): δ (ppm) 8.93 (d, J = 2.0 Hz, 3H), 8.02 (dd, J = 8.0, 2.0 Hz, 3H), 7.79 (s, 3H), 7.70 (d, J = 8.0 Hz, 3H), 5.47 (s, 3H), 3.47 (s, 18H). \textsuperscript{13}C NMR data for 7 (100 MHz, CDCl\textsubscript{3}): δ (ppm) 156.8, 147.7, 139.6, 135.7, 135.3, 125.9, 121.4, 103.8, 53.8. HRMS m/z calcd. for C\textsubscript{30}H\textsubscript{33}N\textsubscript{3}O\textsubscript{6}[M + H]\textsuperscript{+}: 532.2442; found: 532.2458.

**Synthesis of LZU-20**

6,6'-Bis(dimethoxymethyl)-3,3'-bipyridine 1 (0.09 mmol, 27.4 mg) and 1,3,5-tris(4-aminophenyl)benzene 2 (0.06 mmol, 21.1 mg) were weighed into a glass ampoule (volume ca. 10 mL, body length 18 cm, neck length 9 cm). To the ampoule were added anhydrous THF (0.4 mL), mesitylene (0.6 mL), and 3 M aqueous acetic acid (0.2 mL). The ampoule was flash frozen in a liquid nitrogen bath, and evacuated to an internal pressure of 0 mbar using a Schlenk line, and flame sealed, reducing the total length by ca. 10 cm. Upon warming to room temperature, the ampoule was placed in an oven, heated to 120 °C, and left undisturbed for 7 days. The obtained solid was transferred into a vial and wash with acetone (3 × 5 mL) and THF (3 × 5 mL). The solid was stirred in THF for 12 hours, then decanted the solvent, and dried at 90 °C for 12 hours to yield LZU-20 as brown powder, 32.6 mg, yield: 88%. Elemental analysis (%): Calcd. for [C\textsubscript{30}H\textsubscript{20}N\textsubscript{4}]\textsubscript{n}: C 82.55; H 4.62; N 12.84. Found: C 77.62; H 4.52; N 12.22.
**Synthesis of LZU-21**

**LZU-21** was synthesized via a similar procedure as for **LZU-20**. Condensation of 1,3,5-tris(6-(dimethoxymethyl)pyridin-3-yl)benzene *7* (0.04 mmol, 21.3 mg) and 2,5-diethoxyterephthalohydrazide *8* (0.06 mmol, 16.9 mg) in a mixture of THF/mesitylene/3 M HOAc (5/5/2 by volume, 1.1 mL) at 120 °C for 7 days resulted in **LZU-21** as white powder, 27.0 mg, yield: 88%. Elemental analysis (%): Calcd. for \([\text{C}_{30}\text{H}_{25}\text{N}_{6}\text{O}_{4}]_n\) : C, 67.53; H, 4.72; N, 15.75. Found: C, 59.90; H, 4.40; N, 14.72.

**Synthesis of LZU-22**

**LZU-22** was synthesized via a similar procedure as for **LZU-20**. Condensation of 1,3,5-tris(6-(dimethoxymethyl)pyridin-3-yl)benzene *7* (0.06 mmol, 31.9 mg) and hydrazine hydrate *9* (0.09 mmol, 5.6 mg, 80%) in a mixture of THF/mesitylene/3 M HOAc (2/3/1 by volume, 1.1 mL) at 120 °C for 7 days afforded **LZU-22** as a yellowish-brown powder, 22.1 mg, yield: 96%. Elemental analysis (%): Calcd. for \([\text{C}_{18}\text{H}_{12}\text{N}_{4}]_n\) : C 76.04; H 4.25; N 19.71. Found: C 66.16; H 4.26; N 15.18.
D. Model Reaction

General procedure for the model reaction:

2-(Dimethoxymethyl)pyridine 3 (30.6 mg, 0.2 mmol) and aniline 4 (22.4 mg, 0.24 mmol) were weighed into a glass ampoule. To the ampoule were added THF (0.4 mL), mesitylene (0.6 mL), and 0.2 mL of HOAc (3.0 M). The ampoule was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of 0 mbar using a Schlenk line, then flame sealed. Upon warming to room temperature, the ampoule was heated to 120 °C for a certain time. The reaction mixture was analyzed via gas chromatography (Agilent 7890A equipped with a 30 m HP-5 column).

![Gas chromatogram](image)

**Fig. S1** The gas chromatogram of 2-pyridinaldehyde. The signal of 2-pyridinaldehyde is located at 8.459 min under the test conditions.

![Mechanism](image)

**Fig. S2** The possible mechanism for the formation of 5 by the direct condensation of 3 and 4[6-8].
Fig. S3 The ESI-MS spectra of the mother liquors left upon the preparation of LZU-20 at different reaction time: 30 min (a), 60 min (b), and 150 min (c). No signal of the corresponding aldehyde product (m/z: 212) was observed in the spectra. These results indicate that LZU-20 was directly constructed from dimethyl acetal 1 and amine 2.
**E. FT-IR Spectra**

**Fig. S4** FT-IR spectra of LZU-20 (a), 6,6'-bis(dimethoxymethyl)-3,3'-bipyridine (b), and 1,3,5-tris(4-aminophenyl)benzene (c). The FT-IR spectrum of LZU-20 showed a strong $\text{C}=\text{N}\text{-}$ stretch at 1622 cm$^{-1}$, indicating the formation of imine bonds.

**Fig. S5** FT-IR spectra of LZU-21 (a), 1,3,5-tris(6-(dimethoxymethyl)pyridine-3-yl) benzene (b), and 2,5-diethoxyterephthalohydrazide (c). The FT-IR spectrum of LZU-21 showed a $\text{C}=\text{N}\text{-}$ stretch at 1618 cm$^{-1}$, indicating the formation of hydrazone bonds.
**Fig. S6** FT-IR spectra of **LZU-22** (a) and 1,3,5-tris(6-(dimethoxymethyl)pyridine-3-yl)benzene (b). The FT-IR spectrum of **LZU-22** showed a $\text{-C=N-}$ stretch at 1622 cm$^{-1}$, indicating the formation of azine bonds.
F. $^{13}$C CP MAS NMR Spectra

**Fig. S7** Solid state $^{13}$C CP MAS NMR spectrum of **LZU-20**. The assignments of $^{13}$C chemical shifts of **LZU-20** were indicated in the chemical structure. The asterisks denote the spinning sidebands.
**Fig. S8** Solid state $^{13}$C CP MAS NMR spectrum of **LZU-21**. The assignments of $^{13}$C chemical shifts of **LZU-21** were indicated in the chemical structure. The asterisks denote the spinning sidebands.
Chemical shift | Assignment
--- | ---
193 | Terminal aldehyde groups
163 | 1
152 | 2
148 | 6
136 | 5, 7
122 | 3, 4, 8
44, 26, 22 | Solvents

**Fig. S9** Solid state $^{13}$C CP MAS NMR spectrum of **LZU-22**. The assignments of $^{13}$C chemical shifts of **LZU-22** were indicated in the chemical structure. The chemical shift at 193 ppm was assigned to the signal of terminal aldehyde groups, while the chemical shifts at 44, 26, and 22 ppm originated from the solvents. The asterisks denote the spinning sidebands.
G. Structure Modeling and Powder X-Ray Diffraction Analysis

The structure modeling and Pawley refinement for LZU-20 were conducted with Materials Studio (ver. 6.0) software package. The AA and AB stacking models were constructed from the monomers. The initial lattice of LZU-20 was constructed by using the space group of P6/m with the unit cell parameters of \(a = b = 44.548\) Å and \(c = 3.600\) Å. The supposed hexagonal structure was similar to COF-LZU\(^{10}\), while each edge was replaced by \((N,N'E,N,N'E)-N,N'-([3,3'-bipyridine]-6,6'-diylbis(methylene)bis([1,1'-biphenyl]-4-amine))\) unit. The models were optimized with the MS Forcite module. Compared with the AB model, the AA model produced a PXRD pattern which agrees well with the experimental PXRD pattern. The Pawley method was applied to refine the unit cell and the refined lattice parameters was \(a = b = 44.879\) (± 0.380) Å and \(c = 3.552\) (± 0.029) Å (with \(R_{wp}\) of 7.14% and \(R_p\) of 5.29%).

The structure modeling for LZU-21 and LZU-22 were similar to LZU-20. The Pawley refined cell parameters are listed in Table S1.

Tab. S1 Pawley refined cell parameters.

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<tr>
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<th>Space group</th>
<th>(R_{wp}) and (R_p) values</th>
<th>Unit cell parameters</th>
</tr>
</thead>
</table>
| LZU-20 | P6/m        | \(R_{wp} = 7.14\%\)  
\(R_p = 5.29\%\) | \(a = b = 44.879\) (± 0.380) Å  
\(c = 3.552\) (± 0.029) Å    |
| LZU-21 | P6          | \(R_{wp} = 5.83\%\)  
\(R_p = 3.70\%\) | \(a = b = 44.820\) (± 0.360) Å  
\(c = 3.875\) (± 0.031) Å    |
| LZU-22 | P6/m        | \(R_{wp} = 6.33\%\)  
\(R_p = 4.54\%\) | \(a = b = 29.842\) (± 1.924) Å  
\(c = 3.421\) (± 0.200) Å    |
**Fig. S10** The experimental (black) and simulated (red) PXRD patterns of **LZU-20** based on the staggered structure.
**Tab. S2** Fractional atomic coordinates for the unit cell of LZU-20.

**LZU-20**: Space group: *P6/m* (No. 175)

\[ a = b = 44.879 \pm 0.380 \text{ Å}; \quad c = 3.552 \pm 0.029 \text{ Å} \]

\[ \alpha = \beta = 90^\circ, \quad \gamma = 120^\circ \]

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517
Fig. S11 PXRD patterns of LZU-20 synthesized with different solvent combinations (0.2 mL 3 M HOAc, 120 °C, 7 days).

Fig. S12 PXRD patterns of LZU-20 synthesized with different reaction time (THF/mesitylene/3 M HOAc = 2/3/1, 120 °C).
Fig. S13 PXRD patterns of LZU-20 before and after the treatment in aqueous solution with different pHs.
Fig. S14 The experimental (black) and simulated (red) PXRD patterns of LZU-21 based on the eclipsed structure.

Fig. S15 The experimental (black) and simulated (red) PXRD patterns of LZU-21 based on the staggered structure.
**LZU-21**: Space group: $P6_3$ (No. 168)

\[
a = b = 44.820 \pm 0.360 \text{ Å}; c = 3.875 \pm 0.031 \text{ Å} \]

\[
a = \beta = 90^\circ, \gamma = 120^\circ
\]

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Fig. S16 PXRD patterns of **LZU-21** before and after the treatment in aqueous solution with different pHs.
Fig. S17 The experimental (black) and simulated (red) PXRD patterns of LZU-22 based on the eclipsed structure.

Fig. S18 The experimental (black) and simulated (red) PXRD patterns of LZU-22 based on the staggered structure.
Tab. S4 Fractional atomic coordinates for the unit cell of **LZU-22**.

**LZU-22**: Space group: *P6/m* (No. 175)

\[
a = b = 29.842 \pm 1.924 \text{ Å}; \quad c = 3.421 \pm 0.200 \text{ Å}
\]

\[
\alpha = \beta = 90^\circ, \quad \gamma = 120^\circ
\]

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Fig. S19 PXRD patterns of LZU-22 before and after the treatment in aqueous solution with different pHs.
H. N₂ Adsorption-Desorption Analysis

**Fig. S20** Langmuir surface area plot for LZU-20 calculated from the adsorption isotherm.

**Fig. S21** BET surface area plot for LZU-20 calculated from the adsorption isotherm.
**Fig. S22** Langmuir surface area plot for LZU-21 calculated from the adsorption isotherm.

**Fig. S23** BET surface area plot for LZU-21 calculated from the adsorption isotherm.
**Fig. S24** Pore-size-distribution of **LZU-21** calculated from the adsorption isotherm by using the NLDFT method.

**Fig. S25** Langmuir surface area plot for **LZU-22** calculated from the adsorption isotherm.
Fig. S26 BET surface area plot for LZU-22 calculated from the adsorption isotherm.

Fig. S27 Pore-size-distribution of LZU-22 calculated from the adsorption isotherm by using the NLDFT method. The micropores centred at 1.2 nm should be originated from the formation of the staggered structure.
**Tab. S5** Experimental and calculated surface areas.

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<th>LZU-22</th>
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<td>Connolly surface area(^a) (m(^2)/g)</td>
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<td>2594</td>
<td>2600</td>
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<td>Langmuir surface area(^b) (m(^2)/g)</td>
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<td>996</td>
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<td>BET surface area(^c) (m(^2)/g)</td>
<td>200</td>
<td>882</td>
<td>305</td>
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</table>

\(^a\) The Connolly surface areas were calculated with Material Studio (ver. 6.0)[9] software package by using N\(_2\) as probe molecule (radius of 1.84 Å) and with a grid interval of 0.25 Å. \(^b\) The surface areas were calculated from the adsorption data using the Langmuir methods. \(^c\) The surface areas were calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) methods.
I. Thermogravimetric Analysis

Fig. S28 The TGA curves of as-synthesized (black) and activated LZU-20 (red).

Fig. S29 The TGA curve of activated LZU-21.
**Fig. S30** The TGA curves of as-synthesized (black) and activated **LZU-22** (red).
J. Scanning Electron Micrographs

Fig. S31 The SEM images of LZU-20.

Fig. S32 The SEM images of LZU-21.

Fig. S33 The SEM images of LZU-22.
K. Solubility Test of Dimethyl Acetal

Fig. S34 Comparison of the solubility of 6,6'-bis(dimethoxymethyl)-3,3'-bipyridine (1) and the corresponding aldehyde ([3,3'-bipyridine]-6,6'-dicarbaldehyde) in different solvents. From left to right: sample only (a or a’), tetrahydrofuran (b or b’), ethanol (c or c’), acetone (d or d’), dichloromethane (e or e’), 1,4-dioxane (f or f’), and mesitylene (g or g’).
L. Liquid NMR Spectra
M. References


