[Electronic Supplementary Information]

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

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A.	Summary of Figures and Tables	S02
B.	Materials and Instrumentation	S03
C.	Synthetic Procedures	S05
D.	Model Reaction	S08
E.	FT-IR Spectra	S10
F.	<sup>13</sup> C CP MAS NMR Spectra	S12
G.	Structure Modeling and Powder X-Ray Diffraction Analysis	S15
H.	N <sub>2</sub> Adsorption-Desorption Analysis	S26
I.	Thermogravimetric Analysis	S31
J.	Scanning Electron Micrographs	S33
K.	Solubility Test of Dimethyl Acetal	S34
L.	Liquid NMR Spectra	S35
M.	References	S37

## A. Summary of Figures and Tables

Fig. S1	Gas chromatogram of 2-pyridinaldehyde	S08
Fig. S2	Possible mechanism for the formation of Schiff base	S08
Fig. S3	ESI-MS spectra of the mother liquor in the preparation of LZU-20	S09
Fig. S4	FT-IR spectra of LZU-20 and the starting materials	S10
Fig. S5	FT-IR spectra of LZU-21 and the starting materials	S10
Fig. S6	FT-IR spectra of LZU-22 and the starting materials	<b>S</b> 11
Fig. S7	<sup>13</sup> C CP MAS NMR spectrum of LZU-20	S12
Fig. S8	<sup>13</sup> C CP MAS NMR spectrum of LZU-21	S13
Fig. S9	<sup>13</sup> C CP MAS NMR spectrum of LZU-22	S14
Tab. S1	Pawley refined cell parameters	S15
Fig. S10	PXRD of LZU-20, observed and simulated (staggered)	S16
Tab. S2	Fractional atomic coordinates for the unit cell of LZU-20	S17
Fig. S11	PXRD of LZU-20 synthesized with different solvent combinations	S18
Fig. S12	PXRD of LZU-20 synthesized with different reaction time	S18
Fig. S13	PXRD of LZU-20 after treatment in aqueous solution with different pHs	S19
Fig. S14	PXRD of LZU-21, observed and simulated (eclipsed)	S20
Fig. S15	PXRD of LZU-21, observed and simulated (staggered)	S20
Tab. S3	Fractional atomic coordinates for the unit cell of LZU-21	S21
Fig. S16	PXRD of LZU-21 after treatment in aqueous solution with different pHs	S22
Fig. S17	PXRD of LZU-22, observed and simulated (eclipsed)	S23
Fig. S18	PXRD of LZU-22, observed and simulated (staggered)	S23
Tab. S4	Fractional atomic coordinates for the unit cell of LZU-22	S24
Fig. S19	PXRD of LZU-22 after treatment in aqueous solution with different pHs	S25
Fig. S20	Langmuir surface area plot of LZU-20	S26
Fig. S21	BET surface area plot of LZU-20	S26
Fig. S22	Langmuir surface area plot of LZU-21	S27
Fig. S23	BET surface area plot of LZU-21	S27
Fig. S24	Pore-size-distribution of LZU-21	S28
Fig. S25	Langmuir surface area plot of LZU-22	S28
Fig. S26	BET surface area plot of LZU-22	S29
Fig. S27	Pore-size-distribution of LZU-22	S29
Tab. S5	Experimental and calculated surface areas	S30
Fig. S28	TGA curves of as-synthesized and activated LZU-20	S31
Fig. S29	TGA curve of activated LZU-21	<b>S</b> 31
Fig. S30	TGA curves of as-synthesized and activated LZU-22	S32
Fig. S31	SEM images of LZU-20	S33
Fig. S32	SEM images of LZU-21	S33
Fig. S33	SEM images of LZU-22	S33
Fig. S34	Solubility test of dimethyl acetal 1	S34

#### **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<sup>[1]</sup> and 1,3,5-tris(4-amino-phenyl)benzene<sup>[2]</sup> were synthesized according to the reported procedures.

#### Instrumentation

Liquid <sup>1</sup>H and <sup>13</sup>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 Ka 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 <sup>13</sup>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 (1)



S1<sup>[3]</sup>, S2<sup>[4]</sup>, and S3<sup>[4]</sup> were synthesized according to the reported procedures.

A degassed solution of **S2** (464 mg, 2 mmol), **S3** (837 mg, 3 mmol), Na<sub>2</sub>CO<sub>3</sub> (636 mg, 6 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (231 mg, 0.2 mmol) in a mixed solvent (DMF/H<sub>2</sub>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<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/acetone = 5/1) to obtain **1** as a white solid, 477 mg, yield: 78%. <sup>1</sup>H **NMR** data for **1** (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C **NMR** data for **1** (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 157.1, 147.5, 135.1, 133.0, 121.4, 103.7, 53.7. HRMS m/z calcd. for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup>: 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<sub>2</sub>CO<sub>3</sub> (2.07 g, 15 mmol), 1,3,5-

tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene<sup>[5]</sup> (456 mg, 1 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (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<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 40/1) to give 7 as light yellow oil, 447 mg, yield: 84%. <sup>1</sup>H NMR data for 7 (400 MHz, CDCl<sub>3</sub>):  $\delta$  (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). <sup>13</sup>C NMR data for 7 (100 MHz, CDCl<sub>3</sub>):  $\delta$  (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<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>6</sub> [M + H]<sup>+</sup>: 532.2442; found: 532.2458.

#### Synthesis of LZU-20

6,6'-Bis(dimethoxymethyl)-3,3'-bipyridine **1** (0.09 mmol, 27.4 mg) and 1,3,5tris(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  $[C_{30}H_{20}N_4]_n$ : 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  $[C_{30}H_{25}N_6O_4]_n$ : 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  $[C_{18}H_{12}N_4]_n$ : 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).



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



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**.





**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 -C=N- stretch at 1622 cm<sup>-1</sup>, 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 -C=N- stretch at 1618 cm<sup>-1</sup>, indicating the formation of hydrazone bonds.



**Fig. S6** FT-IR spectra of **LZU-22** (a) and 1,3,5-tris(6-(dimethoxymethyl)pyridine-3yl)benzene (b). The FT-IR spectrum of **LZU-22** showed a -C=N- stretch at 1622 cm<sup>-1</sup>, indicating the formation of azine bonds.

## F. <sup>13</sup>C CP MAS NMR Spectra



**Fig. S7** Solid state <sup>13</sup>C CP MAS NMR spectrum of **LZU-20**. The assignments of <sup>13</sup>C chemical shifts of **LZU-20** were indicated in the chemical structure. The asterisks denote the spinning sidebands.



**Fig. S8** Solid state <sup>13</sup>C CP MAS NMR spectrum of **LZU-21**. The assignments of <sup>13</sup>C chemical shifts of **LZU-21** were indicated in the chemical structure. The asterisks denote the spinning sidebands.



**Fig. S9** Solid state <sup>13</sup>C CP MAS NMR spectrum of **LZU-22**. The assignments of <sup>13</sup>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)<sup>[9]</sup> 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-LZU1**<sup>[10]</sup>, while each edge was replaced by (*N*,*N'E*,*N*,*N'E*)-*N*,*N'*-([3,3'-bipyridine]-6,6'-diylbis(methan-ylylidene))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  $a = b = 44.879 (\pm 0.380)$  Å and  $c = 3.552 (\pm 0.029)$  Å (with *Rwp* of 7.14% and *Rp* 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.

	Space group	$R_{wp}$ and $R_p$ values	Unit cell parameters
I 711_20	P6/m	$R_{wp} = 7.14 \%$	$a = b = 44.879 (\pm 0.380) \text{ Å}$
LL0-20		$R_p = 5.29\%$	$c = 3.552 (\pm 0.029) \text{ Å}$
1 711 21	Р6	$R_{wp} = 5.83 \%$	$a = b = 44.820 (\pm 0.360) \text{ Å}$
LZU-21		$R_p = 3.70 \%$	$c = 3.875 (\pm 0.031) \text{ Å}$
	P6/m	$R_{wp} = 6.33 \%$	$a = b = 29.842 (\pm 1.924) \text{ Å}$
LZU-22		$R_p = 4.54 \%$	$c = 3.421 (\pm 0.200) \text{ Å}$

Tab. S1 Pawley refined cell parameters.



Fig. S10 The experimental (black) and simulated (red) PXRD patterns of LZU-20 based on the staggered structure.

LZU-20: Space group: <i>P6/m</i> (No. 175)							
$a = b = 44.879 (\pm 0.380) \text{ Å}; c = 3.552 (\pm 0.029) \text{ Å}$ $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$							
Atom	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)	Atom	x (Å)	y (Å)	<i>z</i> (Å)
C1	0.08968	-0.43616	0.00000	C14	0.20349	-0.36721	0.00000
N2	0.07847	-0.47034	0.00000	C15	0.23966	-0.35045	0.00000
C3	0.04485	-0.49501	0.00000	N16	0.14895	-0.42186	0.00000
C4	0.01788	-0.48704	0.00000	H17	0.04041	-0.51951	0.00000
C5	0.02955	-0.45111	0.00000	H18	0.01295	-0.44192	0.00000
C6	0.06467	-0.42600	0.00000	H19	0.07173	-0.40052	0.00000
C7	0.12502	-0.41196	0.00000	H20	0.13258	-0.38640	0.00000
C8	0.29577	-0.35089	0.00000	H21	0.30480	-0.30083	0.00000
C9	0.31681	-0.31451	0.00000	H22	0.24726	-0.42086	0.00000
C10	0.25858	-0.36829	0.00000	H23	0.18738	-0.44818	0.00000
C11	0.23737	-0.40489	0.00000	H24	0.19179	-0.35272	0.00000
C12	0.20119	-0.42188	0.00000	H25	0.25137	-0.32440	0.00000
C13	0.18373	-0.40332	0.00000				

Tab. S2 Fractional atomic coordinates for the unit cell of LZU-20.



**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: <i>P6</i> (No. 168)							
$a = b = 44.820 (\pm 0.360) \text{ Å}; c = 3.875 (\pm 0.031) \text{ Å}$ $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$							
Atom	<i>x</i> (Å)	y (Å)	z (Å)	Atom	x (Å)	y (Å)	z (Å)
C1	-0.03623	-1.52098	-0.25361	O17	0.04278	-1.52957	-0.27804
C2	-0.01506	-1.53577	-0.26234	C18	0.03037	-1.56296	-0.13045
C3	0.02113	-1.51518	-0.25916	C19	0.06055	-1.56885	-0.07029
C4	-0.07418	-1.54403	-0.23726	H20	-0.02706	-1.56354	-0.26951
05	-0.08738	-1.57134	-0.39362	H21	-0.08309	-1.51369	0.11406
N6	-0.09441	-1.53564	-0.04233	H22	-0.13910	-1.52523	0.27860
N7	-0.13031	-1.55738	-0.03470	H23	0.19851	-1.46161	0.43904
C8	-0.15011	-1.54937	0.13788	H24	0.26074	-1.42190	0.45117
C9	-0.18756	-1.57273	0.14251	H25	0.24556	-1.34958	-0.15627
C10	0.20910	-1.43698	0.30892	H26	-0.31055	-1.60281	0.14599
C11	0.24460	-1.41439	0.31177	H27	0.01164	-1.58326	-0.30648
C12	0.25877	-1.38215	0.14683	H28	0.01770	-1.56486	0.12140
C13	0.23603	-1.37361	-0.01784	H29	0.07255	-1.56912	-0.31987
N14	0.20153	-1.39604	-0.01590	H30	0.05144	-1.59396	0.06132
C15	-0.29662	-1.64230	0.14709	H31	0.08023	-1.54789	0.09344
C16	-0.32002	-1.63022	0.14693				

Tab. S3 Fractional atomic coordinates for the unit cell of LZU-21.



**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.

LZU-22: Space group: <i>P6/m</i> (No. 175)							
$a = b = 29.842 (\pm 1.924) \text{ Å}; c = 3.421 (\pm 0.200) \text{ Å}$ $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$							
Atom	<i>x</i> (Å)	<i>y</i> (Å)	<i>z</i> (Å)				
C1	0.72231	0.36881	0.00000				
C2	0.68790	0.38759	0.00000				
C3	0.78014	0.40476	0.00000				
C4	0.80238	0.45891	0.00000				
C5	0.85547	0.49127	0.00000				
C6	0.88752	0.47028	0.00000				
N7	0.86651	0.41853	0.00000				
C8	0.81496	0.38596	0.00000				
C9	0.94355	0.50373	0.00000				
N10	0.97329	0.48415	0.00000				
H11	0.70281	0.42787	0.00000				
H12	0.78017	0.47791	0.00000				
H13	0.87138	0.53250	0.00000				
H14	0.80272	0.34578	0.00000				
H15	0.96001	0.54507	0.00000				

Tab. S4 Fractional atomic coordinates for the unit cell of LZU-22.



**Fig. S19** PXRD patterns of **LZU-22** before and after the treatment in aqueous solution with different pHs.

### H. N<sub>2</sub> 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.

	LZU-20	LZU-21	LZU-22
Connolly surface area <sup>a</sup> (m <sup>2</sup> /g)	2715	2594	2600
Langmuir surface area <sup>b</sup> (m <sup>2</sup> /g)	257	996	431
BET surface area <sup>c</sup> (m <sup>2</sup> /g)	200	882	305

Tab. S5 Experimental and calculated surface areas.

<sup>a</sup> The Connolly surface areas were calculated with Material Studio (ver. 6.0)<sup>[9]</sup> software package by using N<sub>2</sub> as probe molecule (radius of 1.84 Å) and with a grid interval of 0.25 Å. <sup>b</sup> The surface areas were calculated from the adsorption data using the Langmuir methods. <sup>c</sup> 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





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