[Supporting Information]:

One-Pot Cascade Syntheses of Microporous and Mesoporous Pyrazine-Linked Covalent Organic Frameworks as Lewis-Acid Catalysts

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Section 1. General Information

1.1 Materials and Methods

All starting materials and solvents, unless otherwise noted, were obtained from J&K Scientific Ltd. and used without purification. All products were isolated and handled under nitrogen using either glovebox or Schlenk line techniques.

¹H NMR spectra were recorded on an AV400 NMR spectrometer. ¹³C NMR spectra were recorded on an AVIII 500 MHz solid-state NMR spectrometer. The FTIR spectra (KBr) were obtained using a SHIMADZU IRAffinity-1 Fourier transform infrared spectrophotometer. TGA was carried out under nitrogen on a SHIMADZU DTG-60 thermal analyzer at a heating rate of 10°C min⁻¹ to 800°C with N₂ flow rate was 30 mL min⁻¹. PXRD data were collected on a PANalytical B.V. Empyrean powder diffractometer using a Cu K α source (λ = 1.5418 Å) over the range of 2 θ = 2.0–40.0 with a step size of 0.02° and 2 s per step. The sorption isotherm for N₂ was measured by using a Quantachrome Autosorb-IQ analyzer with ultra-high-purity N₂ (99.999% purity). To estimate pore size distributions for PZ-COFs, nonlocal density functional theory (NLDFT) was applied to analyze the N₂ isotherm on the basis of the model of N₂@77K on carbon with slit pores and the method of non-negative regularization. The SEM images were obtained on JEOL JSM6700 scanning electron microscope. The TEM images were accomplished with JEOL JEM-2100F transmission electron microscope operated at an accelerating voltage of 200 kV.

1.2 Synthesis of model molecule



1,2-diaminobenzene (110.0 mg, 1.0 mmol) with 1,2-dihydroxybenzene (108.0 mg, 1.0 mmol) were dissolved in 5.0 mL acetic acid (AcOH), followed by adding $K_2Cr_2O_7$ (100.0 mg, 0.3 mmol). After refluxing for 24 h, the model molecule was obtained. ¹H NMR (400 MHz, DMSO-d₆) δ 7.99 (m, 4 H), 8.26 (m, 4 H).

1.3 Synthesis of PZ-COF-1



A Pyrex tube measuring o.d. × i.d. = $10 \times 8 \text{ mm}^2$ was charged with hexahydroxy triphenylene (HHTP, 32.4 mg, 0.1 mmol), 1,2,4,5-tetraminobenzene (TAB·4HCl, 42.6 mg, 0.15 mmol) and K₂Cr₂O₇ (100.0 mg, 0.34 mmol) in a mixed solution of NMP (0.1 mL), mesitylene (1.0 mL) and acetic acid (AcOH, 6.0 mol/L, 0.1 mL). The tube was flash frozen at 77 K (LN₂ bath), evacuated to an internal pressure of 0.15 mmHg and flame sealed. Upon sealing the length of the tube was reduced to *ca*. 13 cm. The reaction mixture was heated at 120 °C for 3 days to afford a black precipitate which was isolated by filtration over a medium glass frit and washed with H₂O (20.0 mL X 3), *N*,*N*-dimethylformamide (DMF, 20.0 mL X 3), and acetone (20.0 mL X 3), respectively. The product was immersed in anhydrous THF (20.0 mL) for 24 h, during which the activation solvent was decanted and freshly replenished three times. The solvent was removed under vacuum at 80 °C to afford PZ-COF-1 as a black powder (35.4 mg, 85%). Anal Calcd for C₂₇H₉N₆: C, 77.69; H, 2.17; N, 20.13. Found: C, 77.99; H, 2.15; N, 19.86.

1.4 Synthesis of PZ-COF-2



Similar to PZ-COF-1, HHTP (32.4 mg, 0.1 mmol) was treated with 3,3'-diaminobenzidine (DABZ, 27.6 mg, 0.15 mmol) and $K_2Cr_2O_7$ (100.0 mg, 0.34 mmol) in a mixed solution of NMP (0.1 mL), mesitylene (1.0 mL) and AcOH (6.0 mol/L, 0.1 mL). The tube was flash frozen at 77 K (LN₂ bath), evacuated to an internal pressure of 0.15 mmHg, and flame sealed. Upon sealing the length of the tube was reduced to ca. 13 cm. The reaction mixture was heated at 120 °C for 3 days to afford a black precipitate which was isolated by filtration over a medium glass frit and washed with H₂O (20.0 mL X 3), DMF (20.0 mL X 3), and acetone (20.0 mL X 3), respectively. The product was immersed in anhydrous THF (20.0 mL) for 24 h, during which the activation solvent was decanted and freshly replenished three times. The solvent was removed under vacuum at 80°C to afford PZ-COF-2 as a black powder (44.1 mg, 83%). Anal Calcd for $C_{36}H_{15}N_6$: C, 81.35; H, 2.84; N, 15.81. Found: C, 81.50; H, 2.88; N, 15.62.

1.5 Synthesis of Mn/PZ-COFs



Manganese(II) acetate (173.0 mg, 1.0 mmol) was dissolved in 10.0 mL of methanol, and then PZ-COF-1 (83.5 mg, 0.2 mmol) or PZ-COF-2 (106.3 mg, 0.2 mmol) was added. The mixture was kept stirring for 24 h at room temperature. The resulting solid was isolated by centrifugation and washed with methanol (20.0 mL X 3), then dried at 85 °C under vacuum for 8 h to yield Mn/PZ-COFs as a black powder, 89.1 mg for PZ-COF-1 or 112.6 mg for PZ-COF-2. The manganese content in Mn/PZ-COFs was 6.3 wt% for PZ-COF-1 or 6.6 wt% for PZ-COF-2 as determined by ICP. Anal Calcd for Mn/PZ-COFs as [Mn(OAc)₂]_{0.163n}@(C₂₇H₉N₆)_n: C, 74.53; H, 2.26; N, 18.86; Mn, 2.01. Found: C, 74.66; H, 2.19; N, 18.93; Mn, 2.33. Anal Calcd for Mn/PZ-COF-2 as [Mn(OAc)₂]_{0.217n}@(C₃₆H₁₅N₆)_n: C, 77.81; H, 2.89; N, 14.77; Mn, 2.09. Found: C, 77.52; H, 2.81; N, 14.36; Mn, 2.11.

1.6 Catalytic reactions



A typical cyanosilylation procedure was performed as follows: a quantity of 44.6 mg (0.1 mmol) of Mn/PZ-COF-1 or 56.3 mg (0.1 mmol) of Mn/PZ-COF-2 was suspended in dry dichloromethane (CH₂Cl₂, 6.0 mL) followed by the addition of the aldehyde (1.0 mmol) and trimethylsilylcyanide (1.0 mmol). The reaction mixtures were stirred at room temperature under Ar. The yields of the reactions were determined by ¹H-NMR spectroscopy and were calculated based on the starting materials. Catalytic recyclability was checked for four times with the same batch of catalyst, and no obvious decrease in activity was observed. ¹H NMR (400 MHz, CDCl₃) for α -(trimethylsilyloxy)phenylacetonitrile (Ar = phenyl): δ 0.23 (s, 9H), 5.52 (s, 1H), 7.40 (m, 2H), 7.42 (m, 1H), 7.46 (d, 2H); α -(trimethylsilyloxy)biphenylacetonitrile (Ar = biphenyl): δ 0.26 (s, 9H), 5.52 (s, 1H), 7.46 (m, 2H), 7.55 (d, 2H), 7.58 (d, 2H), 7.63 (d, 2H); α -(trimethylsilyloxy)naphthylacetonitrile (Ar = 1-naphthyl): δ 0.20 (s, 9H), 5.52 (s, 1H), 7.49 (m, 1H), 7.56 (m, 1H), 7.62 (m, 1H), 7.70 (d, 1H), 7.90 (d, 2H), 8.16 (d, 1H); α -(trimethylsilyloxy)methoxyphenylacetonitrile (Ar = methoxyphenyl): δ 0.20 (s, 9H), 3.89 (s, 3H), 5.50 (s, 1H), 7.01 (d, 2H), 7.82 (d, 2H); α -(trimethylsilyloxy)nitrophenylacetonitrile (Ar = nitrophenyl): δ 0.29 (s, 9H), 5.59 (s, 1H), 7.69 (d, 2H).



Section 2. Figures S1-37

Figure S1. (a) ¹H NMR spectra of DAA, 1,2-dihydroxybenzene and 1,2-diaminobenzene, and (b) ¹³C NMR spectra of DAA.



Figure S2. TEM image of PZ-COF-1.



Figure S3. TEM image of PZ-COF-2.



Figure S4. FT-IR spectrum of HHTP.



Figure S5. FT-IR spectrum of TAB.



Figure S6. FT-IR spectrum of DAB.



Peak (cm ⁻¹)	Assignment and Notes for PZ-COF-1
3553.03 (w)	O—H stretch from OH groups at the surface of crystallites
1542.15 (m)	Aromatic ring C=C stretching from phenyl rings
1483.32 (w)	Aromatic ring C=C vibrational mode
1447.63 (s)	Aromatic ring C=C stretching from pyrazine linkages
1255.71 (s)	C=N stretching from pyrazine linkages
1179.96 (w)	C—H in plane bending modes
1045.85 (w)	C—H in plane bending modes
998.21 (w)	Aromatic ring stretching
868.02 (w)	Aromatic C—H out-of-plane bending
815.92 (m)	Aromatic C—H out-of-plane bending
537.19 (w)	Aromatic ring bending

Figure S7. FT-IR spectrum of PZ-COF-1.



Peak (cm ⁻¹)	Assignment and Notes for PZ-COF-2
3453.69 (w)	O—H stretch from OH groups at the surface of crystallites
1683.98 (w)	C-C stretching from aromatic rings
1653.13 (w)	Aromatic ring vibration mode
1553.73 (s)	Aromatic ring C=C stretching from phenyl rings
1447.64 (s)	Aromatic ring C=C stretching from pyrazine linkages
1265.35 (s)	C=N stretching from pyrazine linkages
1024.05 (w)	C—H in plane bending modes
914.38 (w)	Aromatic C—H out-of-plane bending
812.01 (m)	Aromatic C—H out-of-plane bending
668.40 (w)	Out of plane phenyl ring deformation
528.52 (w)	Aromatic ring bending

Figure S8. FT-IR spectrum of PZ-COF-2.



Figure S9. Solid-state ¹³C NMR spectra of PZ-COF-1 (* sidebands).



Figure S10. Solid-state ¹³C NMR spectra of PZ-COF-2 (* sidebands).



Figure S11. TG analysis of PZ-COF-1 (a) and PZ-COF-2 (b).



Figure S12. PXRD patterns of PZ-COF-1 before (a) and after 24 h treatment with HCl (1 M) (b) and NaOH (1 M) (c).



Figure S13. PXRD patterns of PZ-COF-2 before (a) and after 24 h treatment with HCl (1 M) (b) and NaOH (1 M) (c).



Figure S14. Calculated PXRD pattern of PZ-COF-1 based on an eclipsed structure in the space group of *P*6/mmm.



Figure S15. Calculated PXRD pattern of PZ-COF-1 based on a staggered structure in the space group of $P6_3$ /mmc.



Figure S16. The comparison of PXRD patterns for PZ-COF-1: experimental (a, black) as well as calculated based on an eclipsed structure (b, blue) and a staggered structure (c, red). Inset: enlarged experimental PXRD pattern.



Figure S17. Calculated PXRD pattern of PZ-COF-2 based on an eclipsed structure in the space group of *P*6/m.



Figure S18. Calculated PXRD pattern of PZ-COF-2 based on a staggered structure in the space group of $P6_3/m$.



Figure S19. The comparison of PXRD patterns for PZ-COF-2: experimental (a, black) as well as calculated based on an eclipsed structure (b, blue) and a staggered structure (c, red). Inset: enlarged experimental PXRD pattern.



Figure S20. BET plot of PZ-COF-1 calculated from N₂ adsorption isotherm at 77 K.



Figure S21. BET plot of PZ-COF-2 calculated from N₂ adsorption isotherm at 77 K.



Figure S22. H₂ adsorption-desorption isotherms for PZ-COF-1 (a) and PZ-COF-2 (b) at 77 K.



Figure S23. CO₂ adsorption-desorption isotherms for PZ-COF-1 (a) and PZ-COF-2 (b) at 273 K.



Figure S24. CH₄ adsorption-desorption isotherms for PZ-COF-1 (a) and PZ-COF-2 (b) at 273 K.



Figure S25. PXRD patterns of PZ-COF-1 (a) and Mn/PZ-COF-1 (b).



Figure S26. PXRD patterns of PZ-COF-2 (a) and Mn/PZ-COF-2 (b).



Figure S27. SEM image of Mn/PZ-COF-1.



Figure S28. SEM image of Mn/PZ-COF-2.



Figure S29. EDX mapping analysis of Mn/PZ-COF-1.



Figure S30. EDX mapping analysis of Mn/PZ-COF-2.



Figure S31. N₂ adsorption-desorption isotherms of PZ-COF-1 (a) and Mn/PZ-COF-1 (b).



Figure S32. N₂ adsorption-desorption isotherms of PZ-COF-2 (a) and Mn/PZ-COF-2 (b).



Figure S33. XPS spectra of (a) Mn(Ac)₂, (b) Mn/Phen, (c) Mn/PZ-COF-1 and (d) Mn/PZ-COF-2.



Figure S34. Concentration (%) versus time (h) for the cyanosilylation of 4-methoxybenzaldehyde on Mn/PZ-COF-1 (black curve) and Mn/PZ-COF-2 (red curve).



Figure S35. Concentration (%) versus time (h) for the cyanosilylation of 4-nitrobenzaldehyde on Mn/PZ-COF-1 (black curve) and Mn/PZ-COF-2 (red curve).



Figure S36. Concentration (%) versus time (h) for the entry 1 based on Mn/PZ-COF-1 (a) and the catalyst removed from the reaction mixture after 1 h (b).



Figure S37. PXRD patterns of Mn/PZ-COF-1 before (a) and after (b) the catalytic reaction.



Figure S38. PXRD patterns of Mn/PZ-COF-2 before (a) and after (b) the catalytic reaction.



Figure S39. The recyclability study of PZ-COF-1 for entry 1. The TOF of four different catalytic cycles is $9.01 \times 10^3 h^{-1}$, $8.97 \times 10^3 h^{-1}$, $8.96 \times 10^3 h^{-1}$ and $8.92 \times 10^3 h^{-1}$, respectively.



Figure S40. The recyclability study of PZ-COF-2 for entry 2. The TOF of four different catalytic cycles is $8.95 \times 10^3 \text{ h}^{-1}$, $8.94 \times 10^3 \text{ h}^{-1}$, $8.89 \times 10^3 \text{ h}^{-1}$ and $8.87 \times 10^3 \text{ h}^{-1}$, respectively.

Section 3. Tables S1-4

Table S1. Unit cell parameters and fractional atomic coordinates for PZ-COF-1 on the basis of an eclipsed structure.

Space group		P6/mmm	
Calculated unit cell		$a = b = 25.184$ Å, $c = 3.439$ Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$	
Measured unit cell		$a = b = 25.761$ Å, $c = 3.555$ Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$	
Pawley refinement		$R_{\rm p} = 0.69\%; wR_{\rm p} = 1.72\%$	
atoms	Х	У	Z
C1	0.00000	0.55593	0.50000
C2	0.49970	0.05543	0.50000
С3	0.60971	0.16401	0.50000
C4	0.66483	0.21917	0.50000
C5	0.66669	0.27661	0.50000
01	0.60927	0.10977	0.50000
H1	0.70506	0.49035	0.50000
H2	0.00000	0.40105	0.50000

Space group		P6 ₃ /mmc	
Calculated unit cell		$a = b = 25.189$ Å, $c = 6.553$ Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$	
atom	х	У	Z
01	0.22343	0.16610	0.75000
C2	0.27775	0.16690	0.75000
C3	0.33318	0.22254	0.75000
C4	0.33317	0.26555	0.75000
C5	0.38863	0.22234	0.75000
06	0.44298	0.27587	0.75000
C7	0.49724	0.27633	0.75000
C8	0.55244	0.33148	0.75000
C9	0.60992	0.33335	0.75000
C10	0.16922	0.11231	0.75000
C11	0.11410	0.11229	0.75000
C12	0.00003	0.05672	0.75000
H13	0.11858	0.15700	0.75000
H14	0.54800	0.37173	0.75000

Table S2. Unit cell parameters and fractional atomic coordinates for PZ-COF-1 on the basis of staggered structure.

Space group		<i>P</i> 6/m		
Calculated unit cell		$a = b = 32.005$ Å, $c = 3.440$ Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$		
Measured unit cell		$a = b = 32.521$ Å, $c = 3.532$ Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$		
Pawley refinement		$R_{\rm p} = 0.89\%; \ wR_{\rm p} = 1.91\%$		
atom	x	У	Z	
N1	0.60062	0.15279	0.50000	
C2	0.60689	0.19807	0.50000	
С3	0.65295	0.23816	0.50000	
C4	0.66053	0.28595	0.50000	
H5	0.71162	0.46035	0.50000	
C6	0.39016	0.46926	0.50000	
C7	0.39602	0.51532	0.50000	
C8	0.43047	0.4632	0.50000	
N9	0.16456	0.64289	0.50000	
C10	0.20408	0.63745	0.50000	
C11	0.25015	0.67753	0.50000	
C12	0.29211	0.67284	0.50000	
H13	0.45164	0.68170	0.50000	
C14	0.51699	0.45010	0.50000	
C15	0.55742	0.44423	0.50000	
C16	0.52188	0.49668	0.50000	
H17	0.93507	1.51755	0.50000	
H18	0.99640	1.42288	0.50000	
H19	0.91640	1.35430	0.50000	

Table S3. Unit cell parameters and fractional atomic coordinates for PZ-COF-2 on the basis of an eclipsed structure.

Space group		<i>P</i> 6 ₃ /m		
Calculated unit cell		$a = b = 32.018$ Å, $c = 6.512$ Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$		
atom	x	У	Z	
N1	0.16860	0.14502	0.75000	
C2	0.21387	0.15140	0.75000	
C3	0.35839	0.17003	0.75000	
C4	0.44643	0.22247	0.75000	
N5	0.48605	0.26731	0.75000	
C6	0.53134	0.27357	0.75000	
C7	0.57147	0.31964	0.75000	
C8	0.61927	0.32721	0.75000	
C9	0.12913	0.10006	0.75000	
C10	0.08308	0.09405	0.75000	
C11	-0.00617	0.04120	0.75000	
H12	0.08194	0.12701	0.75000	
H13	0.56340	0.34842	0.75000	
C14	-0.05658	-0.25405	0.75000	
C15	-0.09690	-0.30043	0.75000	
C16	0.81649	0.59988	0.75000	
N17	0.11432	0.18043	0.25000	
C18	0.10904	0.21999	0.25000	
C19	0.23603	0.36593	0.25000	
C20	0.27051	0.45252	0.25000	
N21	0.30944	0.49778	0.25000	
C22	0.30403	0.53733	0.25000	
C23	0.34413	0.58341	0.25000	
C24	0.33949	0.62541	0.25000	
C25	0.07534	0.13516	0.25000	
C26	0.08136	0.09514	0.25000	
C27	0.04740	0.00623	0.25000	
H28	0.18400	0.26824	0.25000	
H29	0.37823	0.58453	0.25000	
C30	-0.26629	-0.11683	0.25000	
C31	-0.30799	-0.16341	0.25000	

Table S4. Unit cell parameters and fractional atomic coordinates for PZ-COF-2 on the basis of a staggered structure.

C32	0.58770	0.86406	0.25000
H33	0.24361	1.33679	0.25000
H34	0.31221	1.41678	0.25000
H35	0.14896	1.39815	0.25000
H36	0.08932	1.32957	0.25000
H37	0.02071	1.24953	0.25000
H38	0.11823	1.10328	0.25000