Electronic Supplementary Information for:

A fivefold linker length reduction in an interpenetrated metal-

organic framework via sequential solvent-assisted linker exchange

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Section S1. Experimental details.

Materials. All of the materials for syntheses were obtained commercially and used without further purification. All the solvents used were of analytical grade.

Instrumentation. ¹H NMR spectra were collected on a Bruker AVANCE III HD 400 MHz spectrometer. Powder X-ray diffraction patterns for capillary-encapsulated samples were obtained at room temperature with a Bruker MX IµS microsource (Cu-K α radiation) and ApexII CCD detector. TG analyses of the compounds were performed on a SDT 2960 thermal analyzer from room temperature to 800 °C at a heating rate of 10 °C/min under air atmosphere. Elemental analyses (EA) were conducted using a Perkin-Elmer 240 elemental analyzer. Infrared spectra (IR) were recorded on a Bruker TENSOR 27 FT-IR spectrometer in the 4000 ~ 400 cm⁻¹ region with KBr pellets. N₂ and CO₂ sorption isotherms were collected on a Micromeritics ASAP 2020.

Synthesis of parent material {[Zn₃L₂(DPNDI)]·5DMA·15H₂O}*_n* (Zn-DPNDI). H₃L (100 mg, 0.23 mmol), ZnCl₂ (50 mg, 0.37 mmol), and DPNDI (100 mg, 0.34 mmol) were dissolved in a mixture of DMA and methanol (1:1, 15 mL) in a Teflon-lined stainless steel vessel (25 mL). The solution was heated in an oven at 90 °C for 3 days, and then cooled to room temperature. Red block crystals (Zn-DPNDI) which were suitable for single-crystal X-ray analysis were obtained by filtration. The obtained crystals were washed with fresh mixture of DMAc and methanol, dried in air. Yield: 67% (based on zinc). The resulting formula was derived from crystallographic data, elemental analysis, and TGA. Anal. Calcd. for C₉₈H₁₁₇N₉O₃₆Zn₃: C, 53.67; H, 5.38; N,

5.75%. Found: C, 54.49; H, 5.53; N, 5.04%. IR (KBr pellet, v/cm⁻¹): 3455 (w), 3042 (w), 2933 (w), 1725 (w), 1600 (s), 1553 (m), 1506 (w), 1396(s), 1344 (m), 1255 (w), 1186 (w), 1132 (w), 1072 (w), 1020 (m), 972 (w), 864 (w), 817 (w), 779 (m), 706 (w), 669 (w), 598 (w), 553 (w) 486 (w).

Synthesis of {[Zn₃L₂(BPE)]·4DMA·17H₂O}_{*n*} (Zn-BPE) *via* SALE: Zn-DPNDI crystals were dried on a filter paper (110 mg, 0.05 mmol) and placed in a 2-dram screw cap vial, and a DMA solution (2 mL, 0.5 M) of BPE was added. The vial was capped and placed in an isothermal oven at 100 °C for 3 days. The solution was removed, replaced with 2 ml fresh BPE solution and the mixture was again heated at 100 °C for the second 3 days. Following a third 3 days again with a new solution of BPE at the same temperature. The progress of the linker exchange reaction was monitored by ¹H NMR. The synthesis of Zn-BPE required replacement of the solution of BPE every 48 h (three exchange cycles). Anal. Calcd. for $C_{82}H_{110}N_6O_{33}Zn_3$: C, 51.73; H, 5.82; N, 4.41%. Found: C, 51.90; H, 6.08; N, 4.49%. IR (KBr pellet, v/cm⁻¹): 3433 (m), 3047 (w), 2939 (w), 1938 (w), 1610 (vs), 1550 (s), 1506 (m), 1402(vs), 1261 (m), 1182 (w), 1136 (w), 1070 (w), 1018 (m), 974 (w), 858 (m), 818 (w), 783 (s), 713 (m), 675 (w), 597 (w), 559 (w) 490 (w).

Synthesis of {[Zn₃L₂(PYZ)]·2DMA·4H₂O}_n (Zn-PYZ) via SALE. Zn-BPE (95 mg, 0.05 mmol) obtained from the previous step was soaked in pyrazine/DMA solution (2 ml, 0.5 M) and heated at 100 °C for 9 days. The synthesis required replacement of the solution of PYZ every 3 days (three exchange cycles). The product (Zn-PYZ) was thoroughly washed with fresh DMA. Anal. Calcd. for $C_{66}H_{60}N_4O_{18}Zn_3$: C, 56.89; H,

4.34; N, 4.02. Found: C, 56.22; H, 5.00; N, 4.68%. IR (KBr pellet, v/cm⁻¹): 3417 (m), 2931 (w), 1938 (w), 1606 (vs), 1544 (m), 1392(vs), 1265 (w), 1111 (w), 1014 (w), 860 (m), 785 (s), 708 (w), 675 (w), 588 (w).

Section S2: Single crystal X-ray diffraction analyses.

Single-crystal X-ray diffraction data for Zn-DPNDI and Zn-BPE were collected on a Bruker SMART APEX CCD diffractometer^[S1] equipped with a graphitemonochromated Mo-K α radiation ($\lambda = 0.71076$ Å) or Cu-K α radiation ($\lambda = 1.54178$ Å) at 101 K or 200 K using the ω -scan technique, respectively. Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. Adsorption corrections were applied using the SADABS routine.^[S2] All the structures were solved with direct methods (*SHELXS*)^[S3] and refined by full-matrix least squares on F^2 using OLEX2.^[S4] which utilizes the SHELXL-2015 module.^[S5] All non-hydrogen atoms were refined anisotropically. Displacement parameter restraints were used in modeling the ligands. Hydrogen atoms were placed geometrically on their riding atom where possible. The lattice water and DMA molecules are highly disordered in Zn-MOFs and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these solvent molecules were removed using the SQUEEZE^[S6] routine of PLATON; structures were then refined again using the data generated. The contents of the solvent region are not represented in the unit cell contents in the crystal data. Crystal data containing space group, lattice parameters and other relevant information for the title complexes are summarized in Table S1. Relevant bond lengths and bond angles are displayed in Table S2. More details on the crystallographic data are given in the X-ray rystallographic files in CIF format. Full details of the structure determinations have been deposited with Cambridge Crystallographic Data Center under reference numbers CCDC 1912351 for Zn-DPNDI and 1912352 for Zn-BPE, and are available free of charge from CCDC.

Complexes	Zn-DPNDI	Zn-BPE
Empirical formula	C ₇₈ H ₄₂ N ₄ O ₁₆ Zn ₃	$C_{66}H_{40}N_2O_{12}Zn_3$
Formula weight	1487.26	1249.11
Temperature / K	101.15	200.00
Wavelength / Å	0.71076	1.54178
Crystal system	orthorhombic	orthorhombic
Space group	Pban	Pban
a/Å	27.9512(8)	31.8382(4)
b/Å	32.0897(8)	28.3102(3)
c/Å	25.2538(6)	19.3354(3)
<i>α</i> /°	90	90
$\beta^{\prime \circ}$	90	90
γ/°	90	90
Volume/Å ³	22651.3(10)	17427.9(4)
Ζ	8	8
Density (calculated) / $g \cdot cm^{-3}$	0.872	0.952
Absorption coefficient / mm^{-1}	0.675	1.323
F(000)	6048	5088
Reflections collected	107224	79050
Independent reflections	19943 ($R_{\rm int} = 0.2014$)	13924 ($R_{\rm int} = 0.0477$)
Data / restraints / parameters	19943 / 62 / 910	13924 / 130 / 748
Goodness-of-fit on F^2	1.011	1.037
${}^{a}R_{1}, {}^{b}wR_{2} \left[I > 2\sigma \left(I\right)\right]$	0.0567, 0.1376	0.1247, 0.4500
${}^{a}R_{1}, {}^{b}wR_{2}$ (all data)	0.1192, 0.1500	0.1390, 0.4700
Largest diff. peak and hole	0.45 and -0.58 e.Å ⁻³	2.86 and -1.73 e.Å ⁻³

Table S1: Crystal structure and refinement details of complexes.

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}$

bond lengths (Å)					
Zn1-O1#1	1.959(3)	Zn1-N4	2.018(3)		
Zn1-O3	1.992(3)	Zn1-O13#2	1.943(3)		
Zn2-O9#3	1.930(3)	Zn2-O11	1.967(2)		
Zn2-O16#4	1.953(3)	Zn2-N1#5	2.011(3)		
Zn3-O3	2.207(3)	Zn3-O7#3	2.088(3)		
Zn3-O8#1	2.059(3)	Zn3-O11	2.129(2)		
Zn3-O14#4	2.026(3)	Zn3-O15#2	2.053(3)		
bond angle (°)					
O1#1-Zn1-O3	102.63(11)	O1#1-Zn1-N4	99.81(13)		
O3-Zn1-N4	118.19(13)	O13#2-Zn1-O1#1	108.36(12)		
O13#2-Zn1-O3	120.34(11)	O13#2-Zn1-N4	105.15(13)		
O9#3-Zn2-O11	118.89(11)	O9#3-Zn2-O16#4	107.01(12)		
O9#3-Zn2-N1#5	113.13(12)	O11-Zn2-N1#5	111.35(12)		
O16#4-Zn2-O11	103.01(11)	O16#4-Zn2-N1#5	101.20(12)		
O7#3-Zn3-O3	87.06(10)	O7#3-Zn3-O11	90.69(10)		
O8#1-Zn3-O3	88.76(10)	O8#1-Zn3-O7#3	174.94(10)		
O8#1-Zn3-O11	93.29(10)	O8#1-Zn3-O15#2	95.21(11)		
O11-Zn3-O3	175.77(10)	O14#4-Zn3-O3	94.32(10)		
O14#4-Zn3-O7#3	96.10(11)	O14#4-Zn3-O8#1	87.06(11)		
O14#4-Zn3-O11	89.49(10)	O14#4-Zn3-O15#2	176.93(11)		
O15#2-Zn3-O3	87.80(10)	O15#2-Zn3-O7#3	81.77(11)		
O15#2-Zn3-O11	88.32(10)				

Table S2. Selected Bond Lengths (Å) and Angle (°) for Zn-DPNDI.

Symmetry codes: #1: 1/2 + x, 1 - y, + z; #2: 3/2 - x, 3/2 - y, +z; #3: 1/2 - x, 3/2 - y, +z; #4: -1/2 + x, 1 - y, +z; #5: +x, +y, -1 + z.

bond lengths (Å)					
Zn1-O1	1.987(5)	Zn1-O10#1	1.934(5)		
Zn1-O11#2	1.973(5)	Zn1-N1	2.003(7)		
Zn2-O1	2.131(6)	Zn2-O2	2.040(5)		
Zn2-O5#1	2.057(5)	Zn2-O6#2	2.242(6)		
Zn2-O7#2	2.036(5)	Zn2-O8#3	2.065(5)		
Zn3-O3	1.962(5)	Zn3-O6#2	1.981(5)		
Zn3-O9#3	1.933(5)	Zn3-N2#4	1.996(9)		
bond angle ()					
O1-Zn1-N1	111.9(2)	O10#1-Zn1-O1	118.9(2)		
O10#1-Zn1-O11#2	105.7(2)	O10#1-Zn1-N1	112.7(2)		
O11#2-Zn1-O1	103.0(2)	O11#2-Zn1-N1	102.6(2)		
O1-Zn2-O6#2	177.1(2)	O2-Zn2-Zn1	120.16(16)		
O2-Zn2-O1	93.0(2)	O2-Zn2-O5#1	175.9(2)		
O2-Zn2-O6#2	87.9(2)	O2-Zn2-O8#3	96.2(2)		
O5#1-Zn2-O1	90.86(19)	O5#1-Zn2-O6#2	88.2(2)		
O5#1-Zn2-O8#3	82.2(2)	O7#2-Zn2-O1	89.46(19)		
O7#2-Zn2-O2	86.0(2)	O7#2-Zn2-O5#1	95.7(2)		
O7#2-Zn2-O6#2	93.35(19)	O7#2-Zn2-O8#3	177.8(2)		
O8#3-Zn2-O1	89.8(2)	O8#3-Zn2-O6#2	87.3(2)		
O3-Zn3-O6#2	103.3(2)	O3-Zn3-N2#4	101.2(3)		
O6#2-Zn3-N2#4	117.2(3)	O9#3-Zn3-O3	105.0(3)		
O9#3-Zn3-O6#2	119.9(2)	O9#3-Zn3-N2#4	107.6(3)		

Table S3. Selected Bond Lengths (Å) and Angle (°) for Zn-BPE.

Symmetry codes: #1: 1/2 + x, 1 - y, +z; #2: -x, 1/2 + y, +z; #3: 1/2 - x, 1/2 - y, +z; #4: +x, +y, -1 + z.



Fig. S1. Perspective view of the coordination environments in **Zn-DPNDI**. Symmetry codes: A: 1/2 + x, 1 - y, +z; B: 3/2 - x, 3/2 - y, +z; C: 1/2 - x, 3/2 - y, +z; D: -1/2 + x, 1 - y, +z; E: +x, +y, -1 + z.



Fig. S2. The 2D structure composed of Zn^{2+} ions and L^{3-} ligands in complex **Zn-DPNDI**.



Fig. S3. The adjacent layers are pillared by DPNDI ligands to form a 3D pillared-layered network in complex **Zn-DPNDI**.



Fig. S4. The 2-fold interpenetration of 3D pillared-layered network in complex Zn-DPNDI.



Fig. S5. The Schematic view of the 2-fold interpenetration structure of Zn-DPNDI.



Fig. S6. Perspective view of the coordination environments in **Zn-BPE**. Symmetry codes: A: #1: 1/2 + x, 1 - y, +z; B: -x, 1/2 + y, +z; C: 1/2 - x, 1/2 - y, +z; D: +x, +y, -1 + z.



Fig. S7. The 3D pillared-layered network in complex **Zn-BPE**.



Fig. S8. The 2-fold interpenetration of 3D pillared-layered network in complex Zn-BPE.



Fig. S9. The 3D pillared-layered network in complex Zn-PYZ.



Fig. S10. The 2-fold interpenetration of 3D pillared-layered network in complex Zn-PYZ.

Section S3. ¹H NMR measurements.

NMR of MOFs. Approximately 5 mg of MOF crystals (filtered and washed with DMA) were placed in a 1.5-dram vial containing deuterated dimethyl sulfoxide (DMSO). 2 drops of D_2SO_4 were added and the crystals were sonicated to achieve complete dissolution. The sample was then transferred to an NMR tube. The ¹H NMR spectra were obtained by locking to DMSO.



Fig. S11. The ¹H NMR spectrum of **Zn-DPNDI**.



Fig. S12. The ¹H NMR spectrum of the linker-exchange process in **Zn-DPNDI** with BPE after 1 day (20% exchange).



Fig. S13. The ¹H NMR spectrum of the linker-exchange process in **Zn-DPNDI** with BPE after 2 days (50% exchange).



Fig. S14. The ¹H NMR spectrum of the linker-exchange process in **Zn-DPNDI** with BPE after 4 days (79% exchange).



Fig. S15. The ¹H NMR spectrum of the linker-exchange process in **Zn-DPNDI** with BPE after 6 days (88% exchange).



Fig. S16. The ¹H NMR spectrum of the linker-exchange process in **Zn-DPNDI** with BPE after 9 days (100% exchange).



Fig. S17. The ¹H NMR spectrum of the linker-exchange process in **Zn-BPE** with PYZ after 1 days (15% exchange).



Fig. S18. The ¹H NMR spectrum of the linker-exchange process in **Zn-BPE** with PYZ after 2 days (51% exchange).



Fig. S19. The ¹H NMR spectrum of the linker-exchange process in **Zn-BPE** with PYZ after 4 days (85% exchange).



Fig. S20. The ¹H NMR spectrum of the linker-exchange process in **Zn-BPE** with PYZ after 6 days (93% exchange).



Fig. S21. The ¹H NMR spectrum of the linker-exchange process in **Zn-BPE** with PYZ after 9 days (100% exchange).

Section S4. SALE Processes.



Scheme S1. Scheme of the transformation from Zn-DPNDI to Zn-BPE, and from Zn-BPE to Zn-PYZ.



Fig. S22. Microscopic images of SALE progress in **Zn-DPNDI** crystals with BPE linker: (a) parent crystals; (b) SALE for 1 day; (c) SALE for 2 days; (d) SALE for 4 days; (e) SALE for 6 days; (f) SALE for 9 days.



Fig. S23. SEM images of **Zn-DPNDI** (a), **Zn-BPE** (b) and **Zn-PYZ** (c) during the sequential solvent-assisted linker exchange process. Insert pictures are the corresponding microscopic images of Zn-MOF crystals. Note that after two step post-synthetic treatments, the crystal sizes became too small to perform single crystal X-ray diffraction studies because of the fragile nature of MOF crystals.

Section S5. Powder X-ray diffraction data.



Fig. S24. Powder XRD pattern of **Zn-DPNDI** as synthesized and simulated PXRD pattern from the corresponding single crystal data.



Fig. S25. Powder XRD pattern of **Zn-BPE** as-synthesized obtained *via* SALE of **Zn-DPNDI** for 9 days and simulated PXRD pattern from the corresponding single crystal data.



Fig. S26. Powder XRD pattern of **Zn-PYZ** as-synthesized obtained *via* SALE of **Zn-BPE** for 9 days and simulated PXRD pattern from the structural model.



Fig. S27. The simulated PXRD patterns of Zn-MOFs from the corresponding single crystal data or the structural model.



Fig. S28. Time-dependent PXRD patterns of SSALE progress for **Zn-BPE** material with PYZ linker.



Fig. S29. Powder XRD patterns of the activated Zn-DPNDI-a and the sample after adsorption experiment. For comparison, the experimental PXRD pattern of the parent Zn-DPNDI is included as well.



Fig. S30. Powder XRD patterns of the activated **Zn-BPE-a** and the sample after adsorption experiment. For comparison, the experimental PXRD pattern of the **Zn-BPE** is included as well.



Fig. S31. Powder XRD patterns of the activated Zn-PYZ-a and the sample after adsorption experiment. For comparison, the experimental PXRD pattern of the Zn-PYZ is included as well.

Section S6. Thermogravimetric analysis data.



Fig. S32. TGA curve for as-synthesized Zn-DPNDI and activated Zn-DPNDI-a.



Fig. S33. TGA curve for the SALE material Zn-BPE and activated Zn-BPE-a.



Fig. S34. TGA curve for the SSALE material Zn-PYZ and activated Zn-PYZ-a.

Section S7. Simulation details.

The material of **Zn-PYZ** synthesized in this study was not able to give high quality single crystal data. In order to confirm the structure of the pillared MOF, PXRD data together with quantum mechanics calculation were used. The linker pyrazine of **Zn-PYZ** was first optimized at the Density Functional Theory (DFT) level of theory using the Becke's three-parameter hybrid exchange function (B3)^[S7] and the correlation function of Lee, Yang, and Parr (LYP)^[S8] along with the 6-311+G(d,p) basis set in all structures. All quantum calculations were done with Gaussian 09.^[S9] The optimized structures of the ligands were then used together with inorganic trinuclear zinc paddlewheel clusters to build the MOF structures in silico using the Materials Studio platform.^[S10] The cell dimensions of **Zn-PYZ** was predicted by indexing the peaks of the corresponding PXRD patterns and by assuming an orthorhombic cell. The structures were then further optimized by using the forcite module of Materials Studio software and the Universal Force Field. After the optimization the simulated PXRD patterns did not change. These patterns were in good agreement with the experimental ones.

Section S8. Gas adsorption of MOFs.

The as-synthesized **Zn-DPNDI** crystals were immersed in DMA for 3 days, during which the solvent exchange was performed for nine times using fresh DMA. This was followed by solvent exchange with acetone for 3 days, 3 times per day. The solvent exchanged **Zn-DPNDI** samples were dried in vacuum at room temperature for 5 hours and then at 130 °C for 5 hours to achieve activated **Zn-DPNDI-a**. To obtain the activated **Zn-BPE-a** and **Zn-PYZ-a**, the same activation procedures as **Zn-DPNDI** for the ligand-exchange materials **Zn-BPE** and **Zn-PYZ** were performed.



Fig. S35. C_2H_6 and C_2H_4 at 298 K absorption (solid) and desorption (hollow) isotherms of Zn-DPNDI–a.



Fig. S36. C₂H₆ and C₂H₄ at 298 K absorption (solid) and desorption (hollow) isotherms of Zn-

BPE-a.



Fig. S37. C₂H₆ and C₂H₄ at 298 K absorption (solid) and desorption (hollow) isotherms of **Zn-PYZ-a**.

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