<Supporting Information>

Symmetry-guided syntheses of mixed-linker Zr metal-organic frameworks with precise linker locations

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I. Experimental section

General procedures

All reagents were purchased from commercial sources and used without further purification. Elemental analyses were conducted using the Thermo Scientific Flash 2000 elemental analyzer at the Ulsan National Institute of Science and Technology, Korea. The Fourier-transform infrared (FT-IR) spectra of KBr samples were recorded on the Nicolet iS10 FT-IR spectrophotometer (4000–400 cm^{-1}). ^{1}H nuclear magnetic resonance (NMR) spectra (400 MHz) were recorded on the Agilent 400-MR DD2 NMR spectrometer. Powder X-ray diffraction (PXRD) data were recorded on the Bruker D2 Phaser automated diffractometer at room temperature using a step size of $2\theta = 0.02°$. Simulated PXRD patterns based on single-crystal data were calculated using the Materials Studio software[S1].

Preparation of MOFs

Synthesis of $[Zr_6O_4(OH)_4(NDC)_4(H_2O)_8](TFA)_4$ (ZRN-bcu). $ZrOCl_2·8H_2O$ (96.7 mg, 0.300 mmol) was added to 5 mL of *N,N*-dimethylformamide (DMF) containing 32.4 mg (0.150 mmol) of H_2NDC while stirring the solution. After addition of 1.1 mL (14 mmol) of HTFA, the solution was kept in an oven at 120 °C for 7 d to produce transparent colorless single crystals of **ZRN-bcu** suitable for single-crystal X-ray diffraction.

Preparation of ZRN-w and ZRN-a from ZRN-bcu. Single crystals of **ZRN-bcu** were soaked in 10 mL of DMF, which was refreshed 5 times during soaking for 1 d to remove the reactants remaining in the solvent pore. Soaking was repeated using acetone to remove DMF. The harvested crystals were exposed to ambient conditions to produce **ZRN-w** single crystals suitable for single-crystal X-ray diffraction. Activated **ZRN-a** was obtained by heating **ZRN-w** at 120 °C under vacuum for 1 d. However, **ZRN-a** reverted to **ZRN-w** under ambient conditions within 1 h. Yield of **ZRN-w** = 66.0 mg (85.3% based on amount of H_2NDC used in **ZRN-bcu** synthesis). FT-IR (KBr, 4000–400 cm^{-1}): 3384 (br, w), 3070 (w), 2972 (w), 1938 (w), 1791 (w), 1664 (s), 1606 (s), 1556 (s), 1495 (m), 1481 (m), 1420 (vs), 1364 (s), 1205 (s), 1158 (s), 1039 (w), 969 (w), 923 (w), 851 (w), 828 (w), 790 (s), 727 (m), 665 (s), 609 (w), 525 (w), 478 (s).

Preparation of [$Zr_6O_4(OH)_4(NDC)_6$] (ZRN-fcu). ZRN-fcu was prepared via the same procedure as **ZRN-bcu** using $ZrOCl_2·8H_2O$ and H_2NDC at a 1:1 mole ratio in the presence of HTFA. $ZrOCl_2·8H_2O$ (96.7 mg, 0.300 mmol) was added to 5 mL of DMF containing H_2NDC (62.8 mg, 0.300 mmol) while stirring the solution. After addition of HTFA (0.1 mL), the solution was kept in an oven at 120 °C for 7 d to produce crystalline **ZRN-fcu**.

Preparation of hybrid 12-c fcu Zr MOFs containing both NDC and BDC via one-pot solvothermal reaction.

[$Zr_6O_4(OH)_4(NDC)_{6-x}(BDC)_x$] (ZRNB-H9:1) was synthesized using H_2NDC and H_2BDC as the dicarboxylate linkers at a 9:1 mole ratio. $ZrCl_4$ (0.0583 g, 0.25 mmol) was dissolved in 8 mL of DMF, and 2 mL of HAc was added to the solution. H_2NDC (0.121g, 0.54 mmol) and H_2BDC (0.01g, 0.06 mmol) were dissolved in 10 mL of DMF. The two solutions were mixed slowly in a 30-mL vial, which was then heated to 120 °C for 7 h. The white crystalline powder obtained was washed with DMF and acetone. The other hybrid Zr MOFs, **ZRNB-H8:2**, **ZRNB-H7:3**, **ZRNB-H6:4**, **ZRNB-H5:5**, **ZRNB-H4:6**, and **ZRNB-H3:7**, were synthesized similarly employing H_2NDC:H_2BDC mole ratios of 8:2, 7:3, 6:4, 5:5, 4:6, and 3:7, respectively.

Preparation of Zr MOFs containing both NDC and BDC via post-synthetic linker insertion.

Synthesis of [$Zr_6O_4(OH)_4(NDC)_4(DOBDC)(H_2O)_7$](DOBDC) (ZRN-DOB). Approximately 70 mg of **ZRN-bcu** single crystals was soaked in 10 mL of DMF, which was refreshed 5 times during soaking for 1 d. After repeating the same soaking procedure using MeOH, the crystals were added to a 5 mL 0.06 M MeOH solution of H_2DOBDC, and the solution was kept under ambient conditions for 2 d. Subsequently, the crystals were further soaked in 10 mL of fresh MeOH, which was refreshed 5 times in 1 d to remove the H_2DOBDC ligand remaining in the solvent pore. **ZRN-DOB** crystals suitable for single-crystal X-ray diffraction were collected. **ZRN-DOB-amb** was obtained by exposing **ZRN-DOB**

to ambient conditions. Activated **ZRN-DOB-a** was obtained by heating **ZRN-DOB-amb** at 120 °C under vacuum for 1 d. FT-IR (KBr, 4000–400 cm^{-1}): 3362 (br, w), 2961 (w), 2921 (w), 1605 (s), 1563 (s), 1496 (m), 1421 (vs), 1363 (s), 1239 (m), 1202 (w), 1141 (w), 1114 (w), 922 (w), 786 (s), 664 (s), 559 (w), 476 (s).

Synthesis of $[Zr_6O_4(OH)_4(NDC)_4(NBDC)_2(H_2O)_4]$ (ZRN-NB). **ZRN-NB** was prepared similarly to **ZRN-DOB** using a 0.06 M MeOH solution of H_2NBDC. **ZRN-NB-amb** was obtained by exposing **ZRN-NB** to ambient conditions. Activated **ZRN-NB-a** was obtained by heating **ZRN-NB-amb** at 120 °C under vacuum for 1 d. FT-IR (KBr, 4000–400 cm^{-1}): 3385 (br, w), 3065 (w), 2967 (w), 2925 (w), 1651 (m), 1606 (s), 1580 (s), 1559 (s), 1538 (s), 1493 (m), 1420 (vs), 1360 (s), 1253 (w), 1200 (w), 1138 (w), 1105 (w), 1065 (w), 923 (w), 783 (m), 747 (w), 719 (w), 665 (m), 585 (w), 569 (w), 478 (s).

Synthesis of $[Zr_6O_4(OH)_4(NDC)_4(ABDC)_2]$ (ZRN-AB). **ZRN-AB** was prepared similarly to **ZRN-DOB** using a 0.06 M MeOH solution of H_2ABDC. Activated **ZRN-AB-a** was obtained by heating **ZRN-AB** at 120 °C under vacuum for 1 d. FT-IR (KBr, 4000–400 cm^{-1}): 3358 (br, w), 3058 (w), 2962 (w), 1606 (s), 1556 (s), 1496 (m), 1421 (vs), 1363 (s), 1254 (w), 1202 (w), 1140 (w), 1105 (w), 964 (w), 922 (w), 786 (m), 665 (s), 585 (w), 476 (s).

II. Crystallographic data collection and structural refinement

Single crystals of ZRN-bcu, ZRN-w, ZRN-DOB, ZRN-NB, ZRN-NB-amb, and ZRN-AB were coated with paratone-N oil, and diffraction data were measured at either 250 or 298 K with synchrotron radiation using the ADSC Quantum 210 CCD detector with a silicon (111) double-crystal monochromator at the 2D SMC beamline of the Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX software[S2] was used for data collection and HKL3000sm (version 703r)[S3] for cell refinement, reduction, and absorption correction. All crystal structures were solved by direct method and refined by full-matrix least-squares calculation using the SHELXS and SHELXL programs, respectively, of the SHELXTL software package (version 2008).[S4]

$[Zr_6O_4(OH)_4(NDC)_4(H_2O)_8](TFA)_4$ (ZRN-bcu). Colorless block-shaped crystal, 0.060 × 0.060 × 0.060 mm^3, $C_{56}H_{44}O_{40}F_{12}Zr_6$, FW = 2132.23 g/mol, tetragonal, space group $I4/mmm$, $a = b = 17.445(3)$ Å, $c = 22.934(5)$ Å, $V = 6979(2)$ Å^3, $Z = 2$, μ ($\lambda = 0.650$ Å) = 2.194 mm^{-1}, 51,191 reflections collected of which 4,582 are unique ($R_{\mathrm{int}} = 0.1437$). Two zirconium atoms (site occupancies of 0.25 at Wyckoff 4*e* site of 4*mm* symmetry and 0.125 at Wyckoff 8*h* site of *m*.2*m* symmetry), a μ^3-O (or OH) ligand (site occupancy of 0.5 at Wyckoff 16*n* site of .*m*. symmetry), an NDC ligand (site occupancy of 0.25 at Wyckoff 8*f* site of ..2/*m* symmetry), a ligated water molecule (site occupancy of 0.5 at Wyckoff 16*l* site of *m*.. symmetry), and a statistically disordered trifluoroacetate (TFA) anion (total site occupancy of 0.25 at Wyckoff 16*n* site of .*m*. symmetry) were observed as an asymmetric unit. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of NDC were assigned an isotropic displacement coefficient of U(H) = 1.2U (C), and their coordinates were allowed to ride on their respective atoms. Least-squares refinement of the structural model was performed under geometry and displacement parameter restraints, such as DFIX, DANG, FLAT, ISOR, SIMU, and DELU, with the hydrogen atoms of the μ^3-OH site and water molecules excluded. Final refinement was performed with modification of the structural factors for the electron densities of the disordered solvents [2942 Å^3 per unit cell (42.7% of the total unit cell volume), 560 electrons corresponding to 14 DMF molecules per unit cell] using the

SQUEEZE option of the PLATON program.[S5] Refinement of the structure converged at final $R1$ = 0.1050 and $wR2$ = 0.2841 for 1,915 reflections with $I > 2\sigma(I)$, $R1$ = 0.1817, and $wR2$ = 0.3324 for all 4,582 reflections. The largest difference peak and hole were 1.594 and -2.104 e/Å^3, respectively.

$[Zr_6O_4(OH)_4(NDC)_4(H_2O)_8](TFA)_4\cdot 12(H_2O)$ (ZRN-w). Colorless block-shaped crystal, 0.040 × 0.040 × 0.040 mm^3, $C_{56}H_{68}O_{52}F_{12}Zr_6$, FW = 2348.42 g/mol, orthorhombic, space group *Immm*, a = 11.677(2) Å, b = 17.804(4) Å, c = 25.696(5) Å, V = 5342.3(18) Å^3, Z = 2, μ (λ = 0.700 Å) = 0.667 mm^{-1}, 28,057 reflections collected of which 4,293 are unique (R_{int} = 0.0640). Two zirconium atoms (site occupancies of 0.5 at Wyckoff 8*n* site of *..m* symmetry and 0.25 at Wyckoff 4*j* site of *mm*2 symmetry), two μ^3-O (or OH) ligands (site occupancies of 0.5 at Wyckoff 8*m* site of *.m.* symmetry and 0.5 at Wyckoff 8*l* site of *m..* symmetry), an NDC ligand (site occupancy of 0.5 at Wyckoff 8*k* site of -1 symmetry), two ligated water molecules (total site occupancy of 1.0 at two different Wyckoff 8*n* sites of *..m* symmetry), a statistically disordered TFA anion (total site occupancy of 0.5 at Wyckoff 8*l* site of *m..* symmetry), and six water sites (total site occupancy of 1.5 at four different Wyckoff 8*l* sites of *m..* symmetry, Wyckoff 8*m* site of *.m.* symmetry, and a general position) were observed as an asymmetric unit. All non-hydrogen atoms were refined anisotropically. The hydrogen atom of one hydrogen-bonded ligated water molecule was found in the difference Fourier map, and its position was refined using an assigned isotropic displacement coefficient of U(H) = 1.5U (O). The hydrogen atoms of NDC were assigned an isotropic displacement coefficient of U(H) = 1.2U (C), and their coordinates were allowed to ride on their respective atoms. Least-squares refinement of the structural model was performed under geometry and displacement parameter restraints, such as DFIX, DANG, FLAT, ISOR, SIMU, and DELU, with the hydrogen atoms of the μ^3-OH site and the other water molecule excluded. Refinement of the structure converged at final $R1$ = 0.0593 and $wR2$ = 0.1848 for 3,337 reflections with $I > 2\sigma(I)$, $R1$ = 0.0737, and $wR2$ = 0.1955 for all 4,293 reflections. The largest difference peak and hole were 1.514 and -1.196 e/Å^3, respectively.

$[Zr_6O_4(OH)_4(NDC)_4(DOBDC)(H_2O)_7](DOBDC)$ (ZRN-DOB). Colorless block-shaped crystal, 0.062 × 0.060 × 0.058 mm^3, $C_{64}H_{50}O_{43}Zr_6$, FW = 2054.36 g/mol, tetragonal, space group *P*4/*mnc*, a = b =

17.439(3) Å, $c = 22.592(5)$ Å, $V = 6871(2)$ Å^3, $Z = 2$, μ ($\lambda = 0.700$ Å) = 0.469 mm^{-1}, 60,100 reflections collected of which 4,460 are unique ($R_{\mathrm{int}} = 0.0645$). Two zirconium atoms (site occupancies of 0.25 at Wyckoff 4*e* site of 4.. symmetry and 0.5 at Wyckoff 8*h* site of *m*.. symmetry), a μ^3-O (or OH) ligand, an NDC ligand (site occupancy of 0.25 at Wyckoff 8*f* site of ..2/*m* symmetry), one forth DOBDC ligand (site occupancies of 0.125 at two Wyckoff 8*g* sites of ..2 symmetry and 0.125 at a statistically disordered general position), and one and three forth ligated water molecules (site occupancies of 0.5 and 0.375 at two different Wyckoff 8*h* sites of *m*.. symmetry) were observed as an asymmetric unit. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of NDC and some of the hydrogen atoms of DOBDC were assigned an isotropic displacement coefficient of U(H) = 1.2U (C), and their coordinates were allowed to ride on their respective atoms. Least-squares refinement of the structural model was performed under geometry and displacement parameter restraints, such as DFIX, DANG, FLAT, ISOR, SIMU, and DELU, with the hydrogen atoms of the μ^3-OH site, one ligated water molecule, and dihydroxyl substituents of DOBDC excluded. Final refinement was performed with modification of the structural factors for the electron densities of the disordered solvents [1976 Å^3 per unit cell (28.8% of the total unit cell volume), 88 electrons corresponding to ~4.9 methanol (MeOH) molecules per unit cell] using the SQUEEZE option of the PLATON program.[S5] Refinement of the structure converged at final $R1 = 0.0710$ and $wR2 = 0.2047$ for 3,501 reflections with $I > 2\sigma(I)$, $R1 = 0.0842$, and $wR2 = 0.2150$ for all 4,460 reflections. The largest difference peak and hole were 5.562 and -1.486 e/Å^{-3}, respectively.

[$Zr_6O_4(OH)_4(NDC)_4(NBDC)_2(H_2O)_4$] (ZRN-NB). Colorless block-shaped crystal, 0.047 × 0.045 × 0.040 mm^3, $C_{64}H_{42}N_2O_{40}Zr_6$, FW = 2026.31 g/mol, tetragonal, space group *I*4/*mmm*, $a = b = 14.955(2)$ Å, $c = 26.077(5)$ Å, $V = 5832(2)$ Å^3, $Z = 2$, μ ($\lambda = 0.700$ Å) = 0.550 mm^{-1}, 34,972 reflections collected of which 3,181 are unique ($R_{\mathrm{int}} = 0.0399$). Two zirconium atoms (site occupancies of 0.25 at Wyckoff 4*e* site of 4*mm* symmetry and 0.125 at Wyckoff 8*h* site of *m*.2*m* symmetry), a μ^3-O (or OH) ligand (site occupancy of 0.5 at Wyckoff 16*n* site of .*m*. symmetry), an NDC ligand (site occupancy of 0.25 at Wyckoff 8*f* site of ..2/*m* symmetry), an NBDC ligand (site occupancy of 0.25 at Wyckoff 8*i* site of *m2m* symmetry), and a ligated water molecule (site occupancy of 0.25 at Wyckoff 16*l* site of *m*.. symmetry) were observed as an asymmetric unit. The nitro oxygen atoms of NBDC could not be identified in the difference Fourier map and were not included in the structural model. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of NDC were assigned an isotropic displacement coefficient of U(H) = 1.2U (C), and their coordinates were allowed to ride on their respective atoms. Least-squares refinement of the structural model was performed under geometry and displacement parameter restraints, such as DFIX, DANG, ISOR, SIMU, and DELU, with the hydrogen atoms of the μ^3-OH site, NBDC, and ligated water molecule excluded. Final refinement was performed with modification of the structural factors for the electron densities of the disordered solvents [3055 Å^3 per unit cell (52.9% of the total unit cell volume), 657 electrons corresponding to ~36.5 MeOH molecules per unit cell] using the SQUEEZE option of the PLATON program.[S5] Refinement of the structure converged at final $R1 = 0.0677$ and $wR2 = 0.1923$ for 2,723 reflections with $I > 2\sigma(I)$, $R1 = 0.0758$, and $wR2 = 0.1995$ for all 3,181 reflections. The largest difference peak and hole were 2.513 and -2.154 e/Å^3, respectively.

[$Zr_6O_4(OH)_4(NDC)_4(NBDC)_2$] (ZRN-NB-amb). Colorless block-shaped crystal, 0.045 × 0.045 × 0.040 mm^3, $C_{64}H_{34}N_2O_{36}Zr_6$, FW = 1954.25 g/mol, tetragonal, space group $I4/mmm$, $a = b = 14.839(2)$ Å, $c = 26.030(5)$ Å, $V = 5732(2)$ Å^3, $Z = 2$, μ ($\lambda = 0.700$ Å) = 0.555 mm^{-1}, 31,877 reflections collected of which 3,064 are unique ($R_{\text{int}} = 0.0670$). Two zirconium atoms (site occupancies of 0.25 at Wyckoff 4*e* site of 4*mm* symmetry and 0.125 at Wyckoff 8*h* site of *m*.2*m* symmetry), statistically disordered μ^3-O and μ^3-OH ligands (site occupancy of 0.25 at Wyckoff 16*n* sites of .*m*. symmetry), an NDC ligand (site occupancy of 0.25 at Wyckoff 8*f* site of ..2/*m* symmetry), and an NBDC ligand (site occupancy of 0.25 at Wyckoff 4*c* site of *mmm* symmetry) were observed as an asymmetric unit. The statistically disordered nitro group of NBDC was identified in the difference Fourier map and included in the structural model. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of NDC were assigned an isotropic displacement coefficient of U(H) = 1.2U (C), and their coordinates were allowed to ride on their respective atoms. Least-squares refinement of the structural model was performed under geometry and displacement parameter restraints, such as DFIX, DANG, ISOR, SIMU, and DELU, with the hydrogen atoms of the μ^3-OH site and NBDC excluded. Final refinement was performed with modification of the structural factors for the electron densities of the disordered solvents [2688 Å^3 per unit cell (46.9% of the total unit cell volume), 641 electrons corresponding to ~35.6 MeOH molecules per unit cell] using the SQUEEZE option of the PLATON program.[S5] Refinement of the structure converged at final $R1 = 0.0868$ and $wR2 = 0.2613$ for 1,722 reflections with $I > 2\sigma(I)$, $R1 = 0.1242$, and $wR2 = 0.3003$ for all 3,064 reflections. The largest difference peak and hole were 1.222 and -1.972 e/Å^3, respectively.

[$Zr_6O_4(OH)_4(NDC)_4(ABDC)_2$] (ZRN-AB). Colorless block-shaped crystal, 0.044 × 0.040 × 0.038 mm^3, $C_{64}H_{38}N_2O_{32}Zr_6$, FW = 1894.28 g/mol, tetragonal, space group $I4/mmm$, $a = b = 14.872(2)$ Å, $c = 26.123(5)$ Å, $V = 5778(2)$ Å^3, $Z = 2$, μ ($\lambda = 0.700$ Å) = 0.547 mm^{-1}, 34,633 reflections collected of which 2,908 are unique ($R_{\text{int}} = 0.0447$). Two zirconium atoms (site occupancies of 0.25 at Wyckoff 4*e* site of 4*mm* symmetry and 0.125 at Wyckoff 8*h* site of *m*.2*m* symmetry), a μ^3-O (or OH) ligand (site occupancy of 0.5 at Wyckoff 16*n* site of .*m*. symmetry), an NDC ligand (site occupancy of 0.25 at Wyckoff 8*f* site of ..2/*m* symmetry), and an ABDC ligand (site occupancy of 0.25 at Wyckoff 4*c* site of *mmm* symmetry) were observed as an asymmetric unit. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of NDC and ABDC were assigned an isotropic displacement coefficient of U(H) = 1.2U (C), and their coordinates were allowed to ride on their respective atoms. Least-squares refinement of the structural model was performed under geometry and displacement parameter restraints, such as DFIX, DANG, ISOR, SIMU, and DELU, with the hydrogen atom of the μ^3-OH site excluded. Final refinement was performed with modification of the structural factors for the electron densities of the disordered solvents [3055 Å^3 per unit cell (52.9% of the total unit cell volume), 657 electrons corresponding to ~36.5 MeOH molecules per unit cell] using the SQUEEZE option of the PLATON program.[S5] Refinement of the structure converged at final $R1 = 0.0644$ and $wR2 = 0.1924$ for 2,344 reflections with $I > 2\sigma(I)$, $R1 = 0.0758$, and $wR2 = 0.2032$ for all 2,908 reflections. The largest difference peak and hole were 2.066 and -2.100 e/Å^3, respectively.

Powder X-ray diffraction of ZRN-a

The activated **ZRN-a** for the PXRD measurement was also obtained via the following procedure. As-synthesized **ZRN-bcu** crystals wetted by DMF were ground on a mortar and washed with fresh acetone thrice. The ground crystalline powder sample wetted by acetone was transferred to a glass capillary with an inner diameter of 0.5 mm and activated under vacuum at room temperature. The temperature was then slowly raised to 393 K and kept for 1 h. After cooling down to 298 K, the sample was kept for an additional hour under vacuum. The activated sample in the capillary was kept under N_2 at 1 bar during diffraction data collection.

The PXRD data of **ZRN-a** were collected with synchrotron radiation (λ = 0.90008 Å) using the ADSC Quantum 210 CCD detector at a 100-mm distance with a silicon (111) double-crystal monochromator at the 2D SMC beamline of the Pohang Accelerator Laboratory. The sample was rotated for 360° during the 3-s exposure time. The two-dimensional diffraction image was converted to the corresponding one-dimensional diffraction pattern using the *Fit2D* program.[S6] The first 19 diffraction peaks were indexed to an orthorhombic unit cell with cell parameters of a = 10.1103 Å, b = 18.9714 Å, and c = 25.1857 Å using the DICVOL program in the DASH software package (M_{19} = 5.8, F_{19} = 22.7 (0.0133, 63)). Profile fitting based on the diffraction data at 2θ = 3.88–38.44° was carried out using the Le Bail algorithm in the JANA2006 software.[S7] The systematic extinction conditions of the Bragg reflections suggested three possible space groups, *I*222 (#23), *Imm*2 (#44), and *Immm* (#71). Crystal structure solution and subsequent Rietveld refinement were successfully carried out in the *Immm* space group, which is the same as that of the **ZRN-w** single crystal, using the JANA2006 software. The structure solution was obtained using the charge flip method. The two Zr sites and several associated oxygen atom sites of the hexanuclear cluster $[Zr_6O_4(OH)_4(COO)_{12}]$ centered at a Wyckoff 2*c* site of *mmm* symmetry were located. Rounds of Rietveld refinements of the positional parameters, under the appropriate geometry restraints for bond distances and angles around the Zr atoms and a single fixed atomic displacement parameter for all atoms, and subsequent difference Fourier syntheses revealed the electron densities corresponding to the remaining carbon atoms of the NDC ligand and TFA anions. The geometries of the latter two were also restrained using the appropriate bond distances and angles while constraining the carbon atoms of NDC to be flat during the refinement of the structural model using the diffraction data up to $2\theta = 54.97°$. The statistically disordered fluorine sites of the two TFA anions could be identified in the difference Fourier map. Final refinement of the structural model with the riding hydrogen atoms of NDC successfully converged to final $R_p = 0.0531$ and $R_{wp} = 0.0695$.

Summary of the crystallographic data of all the crystals is given in Tables S1-S7. CCDC 1896107-1896112 contain the supplementary crystallographic data for the single crystals. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

III. Structural flexibility, stability, and porosity of ZRN-bcu

Under ambient conditions, as-synthesized **ZRN-bcu** crystals undergo reversible single-crystal-to-single-crystal transformation to a new crystalline phase with smaller pore dimension, **ZRN-w** (Figures S5). The **ZRN-w** crystals are very stable in water. The PXRD pattern of **ZRN-w** soaked in water for one month does not show any indication of loss in crystallinity (Figure S6).

Single-crystal structure analysis shows that **ZRN-w** is isoreticular to **ZRN-bcu** (Figures S2 and S7. However, the tetragonal crystal system of **ZRN-bcu** is distorted to the orthorhombic one of **ZRN-w** with reduced solvent pore volume. This distortion is mediated by lattice water molecules that are strongly hydrogen bonded to Zr clusters along the *a*-axis (Figure S8). The intercluster distance along this direction decreases significantly from 17.445(3) to 11.677(2) Å. During the transformation from **ZRN-bcu** to **ZRN-w**, NDC^{2-} rotates by ~180° to relieve steric repulsion from neighboring ligands caused by the contraction along *a*-axis (Figure S9).

To investigate the thermal stability of **ZRN-w**, a variable temperature PXRD experiment was performed under N_2 atmosphere. While there are no significant changes in the PXRD pattern of **ZRN-w** below 60 °C, a new set of diffraction peaks appears at 70 °C. Above 80 °C, the **ZRN-w** PXRD pattern completely disappears and only the new set is present. The new state corresponds to activated **ZRN-w** (**ZRN-a**), which is stable up to 250 °C and starts to lose its crystallinity at 300 °C (Figure S10). Interestingly, once **ZRN-a** is formed at high temperatures, it remains stable in dry air even at 300 °C. However, it is immediately converted back to **ZRN-w** upon exposure to ambient conditions (Figure S11).

Ab initio PXRD structure determination of **ZRN-a** and Rietveld refinement of the structural model (Figure S12) show the complete removal of all water molecules, that is, those ligated to the Zr sites and the water molecules hydrogen bonded to them. The TFA counter anions are ligated to the Zr sites via both intra- and intercluster bridging modes to form a network with 10-c **bct** topology (Figure S13). The permanent porosity of **ZRN-a** is confirmed by N_2 adsorption at 77 K (Figure S14). Its specific pore volume, estimated from an N_2 uptake amount of 218 cm^3/g at 0.99 P/P_0, is 0.34 cm^3/g, which agrees well with the one calculated from the single-crystal structure, 0.33 cm^3/g. Its Brunauer-Emmett-Teller (BET) surface area is 861 m^2/g.

IV. Supplementary Tables

Table S1. Crystal data and structure refinement for **ZRN-bcu**.

Empirical formula	$C_{56}H_{44}O_{40}F_{12}Zr_6$	
Formula weight	2132.23	
Temperature	243(2) K	
Wavelength	0.650 Å	
Crystal system	Tetragonal	
Space group	*I*4/*mmm*	
Unit cell dimensions	a = 17.445(3) Å	α = 90°
	b = 17.445(3) Å	β = 90°
	c = 22.934(5) Å	γ = 90°
Volume	6979(2) $Å^3$	
Z	2	
Density (calculated)	1.015 Mg/m^3	
Absorption coefficient	2.194 mm^{-1}	
F(000)	2096	
Crystal size	0.060 x 0.060 x 0.060 mm^3	
Theta range for data collection	1.624 to 33.319°.	
Index ranges	−27<=h<=27, −28<=k<=28, −38<=l<=38	
Reflections collected	51191	
Independent reflections	4582 [R(int) = 0.1437]	
Completeness to theta = 22.955°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.880 and 0.880	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4582 / 147 / 141	
Goodness-of-fit on F^2	0.977	
Final R indices [I>2sigma(I)]	R1 = 0.1050, wR2 = 0.2841	
R indices (all data)	R1 = 0.1817, wR2 = 0.3324	
Extinction coefficient	0.0129(16)	
Largest diff. peak and hole	1.594 and −2.104 $e·Å^{-3}$	

Table S2. Crystal data and structure refinement for **ZRN-w**.

Empirical formula	$C_{56}H_{68}F_{12}O_{52}Zr_6$	
Formula weight	2348.42	
Temperature	298(2) K	
Wavelength	0.700 Å	
Crystal system	Orthorhombic	
Space group	Immm	
Unit cell dimensions	a = 11.677(2) Å	α = 90°.
	b = 17.804(4) Å	β = 90°.
	c = 25.696(5) Å	γ = 90°.
Volume	5342.3(18) $Å^3$	
Z	2	
Density (calculated)	1.460 Mg/m^3	
Absorption coefficient	0.667 mm^{-1}	
F(000)	2336	
Crystal size	0.040 x 0.040 x 0.040 mm^3	
Theta range for data collection	1.561 to 29.549°.	
Index ranges	-16<=h<=16, -25<=k<=25, -36<=l<=36	
Reflections collected	28057	
Independent reflections	4293 [R(int) = 0.0640]	
Completeness to theta = 24.835°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.974 and 0.974	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4293 / 144 / 210	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1848	
R indices (all data)	R1 = 0.0737, wR2 = 0.1955	
Extinction coefficient	0.0074(7)	
Largest diff. peak and hole	1.514 and –1.196 e.$Å^{-3}$	

Table S3. Crystal data and structure refinement for the PXRD data of **ZRN-a**.

Empirical formula	$C_{56}H_{28}O_{32}F_{12}Zr_6$	
Formula weight	1988.2	
Temperature	298 (2) K	
Wavelength	0.90008 Å	
Crystal system	Orthorhombic	
Space group	*Immm*	
Unit cell dimensions	a = 10.120(3) Å	$\alpha = 90°$
	b = 18.979(7) Å	$\beta = 90°$
	c = 25.280(8) Å	$\gamma = 90°$
Volume	4856(3) Å^3	
Z	2	
Density (calculated)	1.357 Mg/m^3	
Absorption coefficient	1.33 mm^{-1}	
F(000)	1928	
Data collection mode	Transmission	
Specimen mounting	0.5 mm glass capillary	
Data collection range, 2θ	2.018 ° to 54.967°	
Data exclusion collection, 2θ	2.018 ° to 3.869°	
Step size, 2θ	0.014°	
Profile function	Pseudo-Voigt	
Background function	Manual background combined with 14 Legendre polynoms	
Refinement method	Rietveld profile fitting	
Data points / restraints / parameters	3871 / 41 / 67	
Final R_p	0.0531	
Final R_{wp}	0.0695	
Goodness-of-fit on F^2	2.27	
Max change/s.u	0.0480	
Largest diff. peak and hole	1.10 and −0.94 e.Å^{-3}	

Table S4. Crystal data and structure refinement for **ZRN-DOB**.

Empirical formula	C64 H50 O43 Zr6	
Formula weight	2054.36	
Temperature	250(2) K	
Wavelength	0.700 Å	
Crystal system	Tetragonal	
Space group	*P*4/*mnc*	
Unit cell dimensions	a = 17.439(3) Å	α = 90°.
	b = 17.439(3) Å	β = 90°.
	c = 22.592(5) Å	γ = 90°.
Volume	6871(2) Å^3	
Z	2	
Density (calculated)	0.993 Mg/m^3	
Absorption coefficient	0.469 mm^{-1}	
F(000)	2036	
Crystal size	0.062 x 0.060 x 0.058 mm^3	
Theta range for data collection	1.776 to 27.999°.	
Index ranges	-23<=h<=23, -23<=k<=23, -30<=l<=30	
Reflections collected	60100	
Independent reflections	4460 [R(int) = 0.0645]	
Completeness to theta = 24.835°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.973 and 0.971	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4460 / 266 / 292	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0710, wR2 = 0.2047	
R indices (all data)	R1 = 0.0842, wR2 = 0.2150	
Extinction coefficient	0.0051(9)	
Largest diff. peak and hole	5.562 and −1.486 e.Å^{-3}	

Table S5. Crystal data and structure refinement for **ZRN-NB**.

Empirical formula	$C_{64}H_{42}N_2O_{40}Zr_6$	
Formula weight	2026.31	
Temperature	250(2) K	
Wavelength	0.700 Å	
Crystal system	Tetragonal	
Space group	*I*4/*mmm*	
Unit cell dimensions	a = 14.955(2) Å	α = 90°.
	b = 14.955(2) Å	β = 90°.
	c = 26.077(5) Å	γ = 90°.
Volume	5832(2) Å^3	
Z	2	
Density (calculated)	1.154 Mg/m^3	
Absorption coefficient	0.550 mm^{-1}	
F(000)	2000	
Crystal size	0.047 x 0.045 x 0.040 mm^3	
Theta range for data collection	1.897 to 33.456°.	
Index ranges	-21<=h<=21, -22<=k<=22, -38<=l<=38	
Reflections collected	34972	
Independent reflections	3181 [R(int) = 0.0399]	
Completeness to theta = 24.835°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.978 and 0.975	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3181 / 190 / 109	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1923	
R indices (all data)	R1 = 0.0758, wR2 = 0.1995	
Extinction coefficient	0.0069(7)	
Largest diff. peak and hole	2.513 and −2.154 e.Å^{-3}	

Table S6. Crystal data and structure refinement for **ZRN-NB-amb**.

Empirical formula	$C_{64}H_{34}N_2O_{36}Zr_6$	
Formula weight	1954.25	
Temperature	293(2) K	
Wavelength	0.700 Å	
Crystal system	Tetragonal	
Space group	*I*4/*mmm*	
Unit cell dimensions	a = 14.839(2) Å	α = 90°.
	b = 14.839(2) Å	β = 90°.
	c = 26.030(5) Å	γ = 90°.
Volume	5732(2) Å^3	
Z	2	
Density (calculated)	1.132 Mg/m^3	
Absorption coefficient	0.555 mm^{-1}	
F(000)	1920	
Crystal size	0.045 x 0.045 x 0.040 mm^3	
Theta range for data collection	1.911 to 33.303°.	
Index ranges	-21<=h<=21, -22<=k<=22, -37<=l<=37	
Reflections collected	31877	
Independent reflections	3064 [R(int) = 0.0670]	
Completeness to theta = 24.835°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.978 and 0.975	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3064 / 40 / 104	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0868, wR2 = 0.2613	
R indices (all data)	R1 = 0.1242, wR2 = 0.3003	
Extinction coefficient	0.019(2)	
Largest diff. peak and hole	1.222 and −1.972 e.Å^{-3}	

Table S7. Crystal data and structure refinement for **ZRN-AB**.

Empirical formula	$C_{64}H_{38}N_2O_{32}Zr_6$	
Formula weight	1894.28	
Temperature	250(2) K	
Wavelength	0.700 Å	
Crystal system	Tetragonal	
Space group	*I*4/*mmm*	
Unit cell dimensions	a = 14.872(2) Å	α = 90°
	b = 14.872(2) Å	β = 90°
	c = 26.123(5) Å	γ = 90°
Volume	5778(2) Å^3	
Z	2	
Density (calculated)	1.089 Mg/m^3	
Absorption coefficient	0.547 mm^{-1}	
F(000)	1864	
Crystal size	0.044 x 0.040 x 0.038 mm^3	
Theta range for data collection	1.907 to 33.459°.	
Index ranges	−20<=h<=20, −18<=k<=18, −36<=l<=36	
Reflections collected	34633	
Independent reflections	2908 [R(int) = 0.0447]	
Completeness to theta = 24.835°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.980 and 0.976	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2908 / 97 / 89	
Goodness-of-fit on F^2	1.110	
Final R indices [I>2sigma(I)]	R1 = 0.0644, wR2 = 0.1924	
R indices (all data)	R1 = 0.0758, wR2 = 0.2032	
Extinction coefficient	0.0082(9)	
Largest diff. peak and hole	2.066 and −2.100 e·Å^{-3}	

V. Supplementary Figures

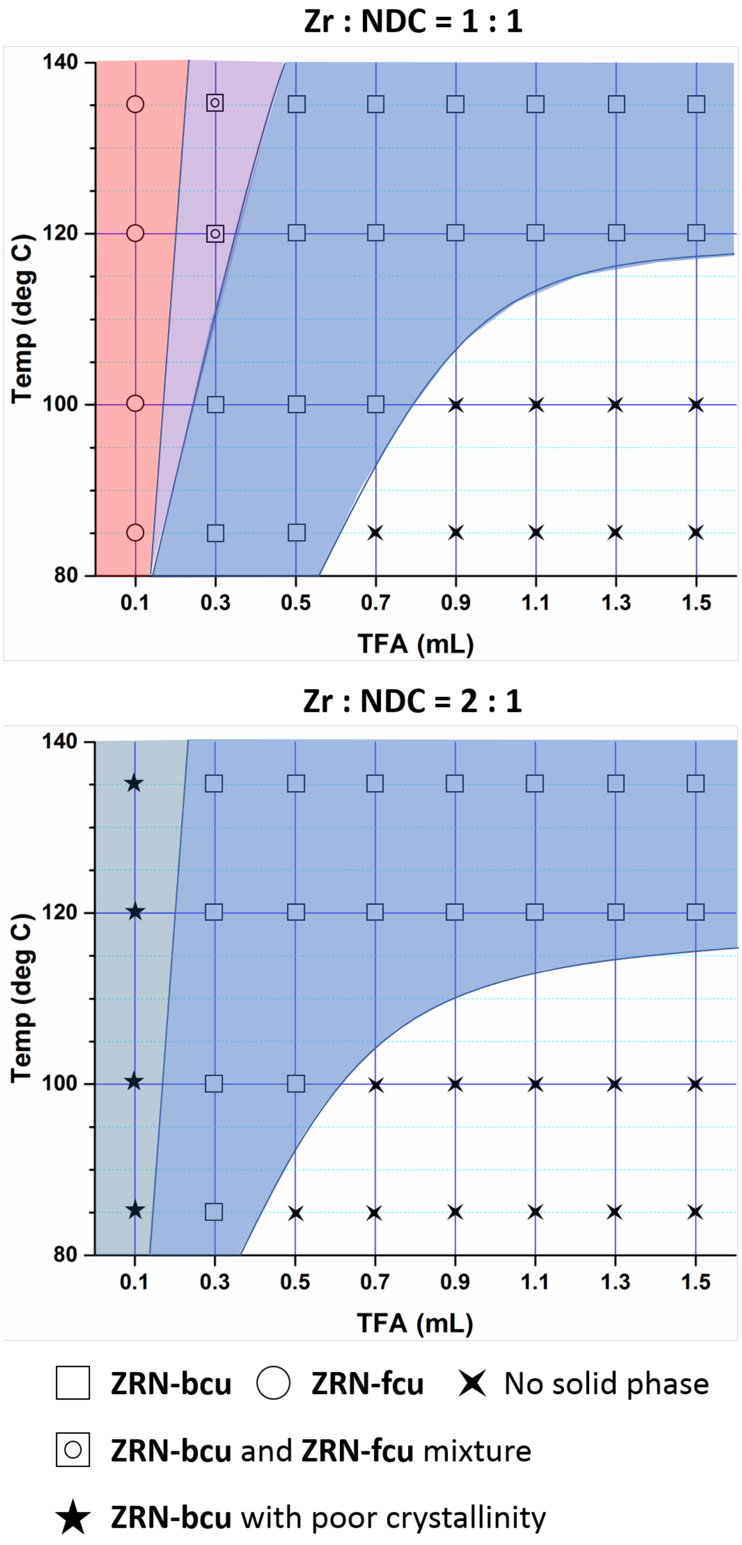

Fig. S1 Synthetic conditions for **ZRN-bcu** and **ZRN-fcu**.

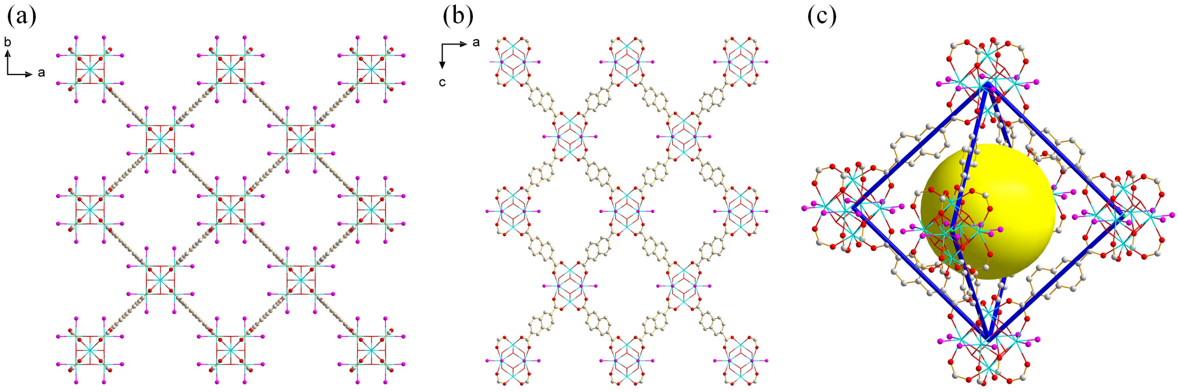

Fig. S2 Ball-and-stick diagrams of **ZRN-bcu** viewed along the (a) *c* and (b) *b* axes. (c) [4^4] Tile of **ZRN-bcu** with 8-c node. The space inside the tile is highlighted by a yellow dummy sphere. The TFA anions in the framework are omitted for clarity.

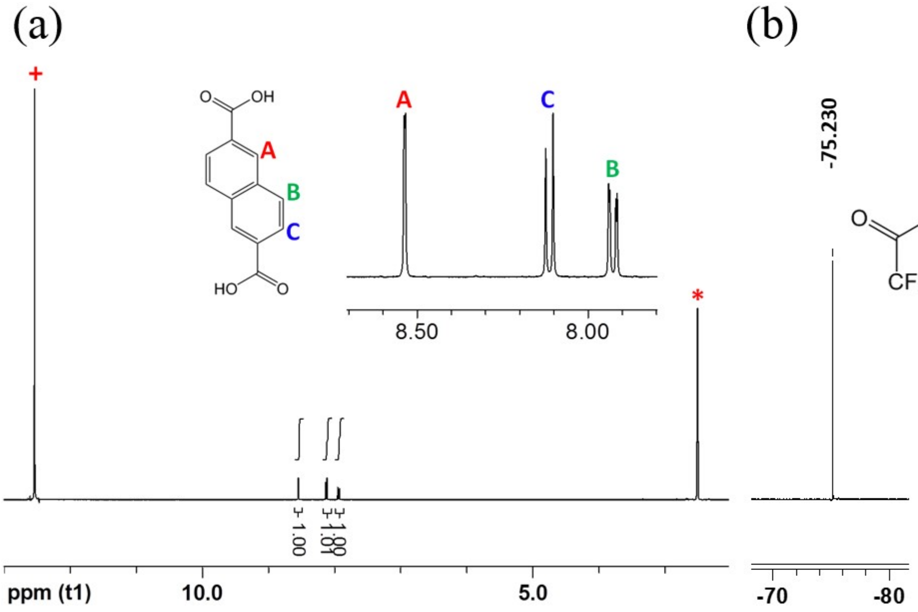

Fig. S3 (a) ^{1}H and ^{19}F NMR spectra of **ZRN-a** in DMSO-d_6/D_2SO_4. The red asterisk indicates the DMSO proton peak, while the red cross indicates the H_2SO_4 proton peak.

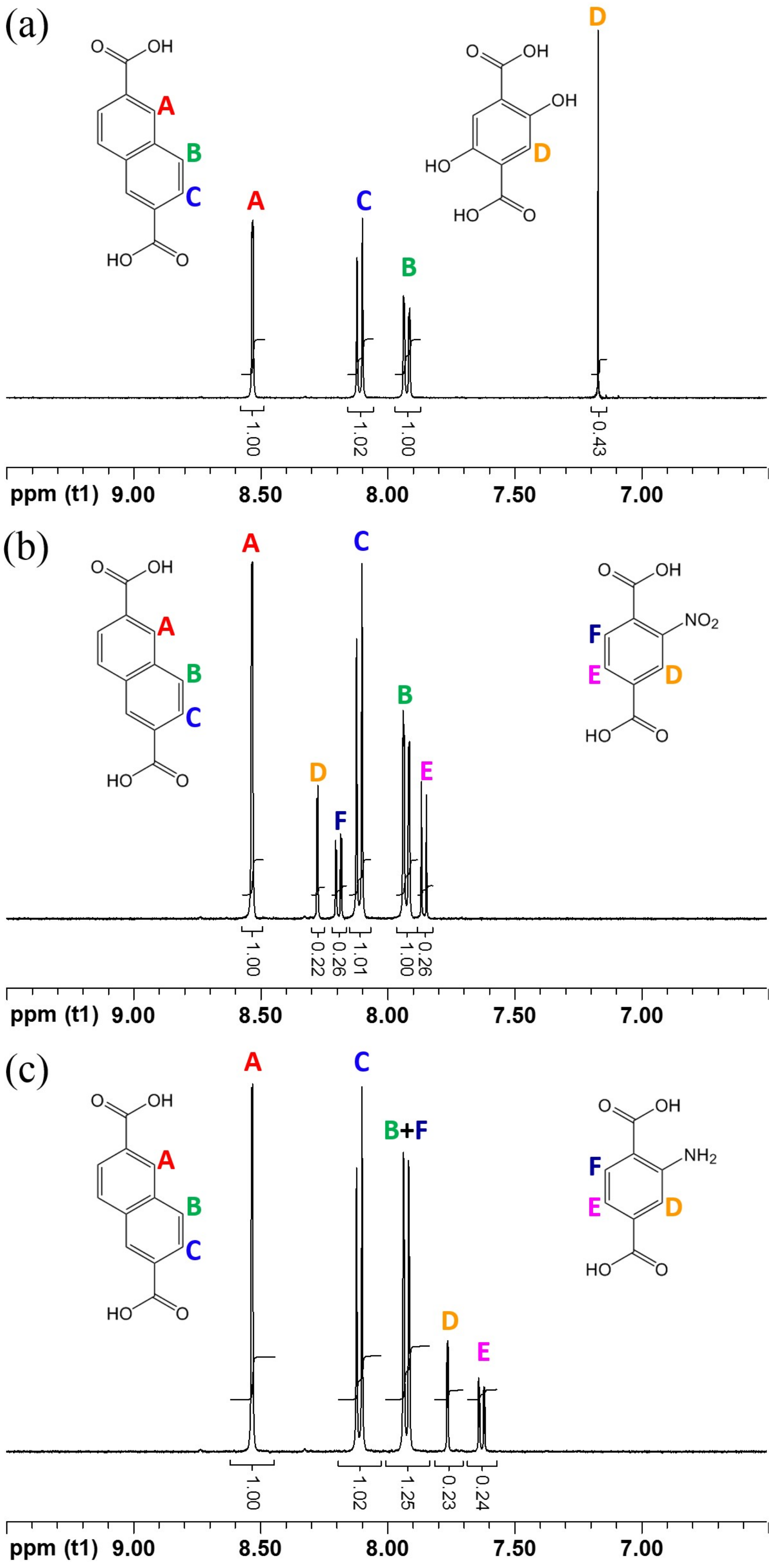

Fig. S4 ^{1}H NMR spectra of (a) **ZRN-DOB-a**, (b) **ZRN-NB-a**, and (c) **ZRN-AB-a** in DMSO-d_6/D_2SO_4.

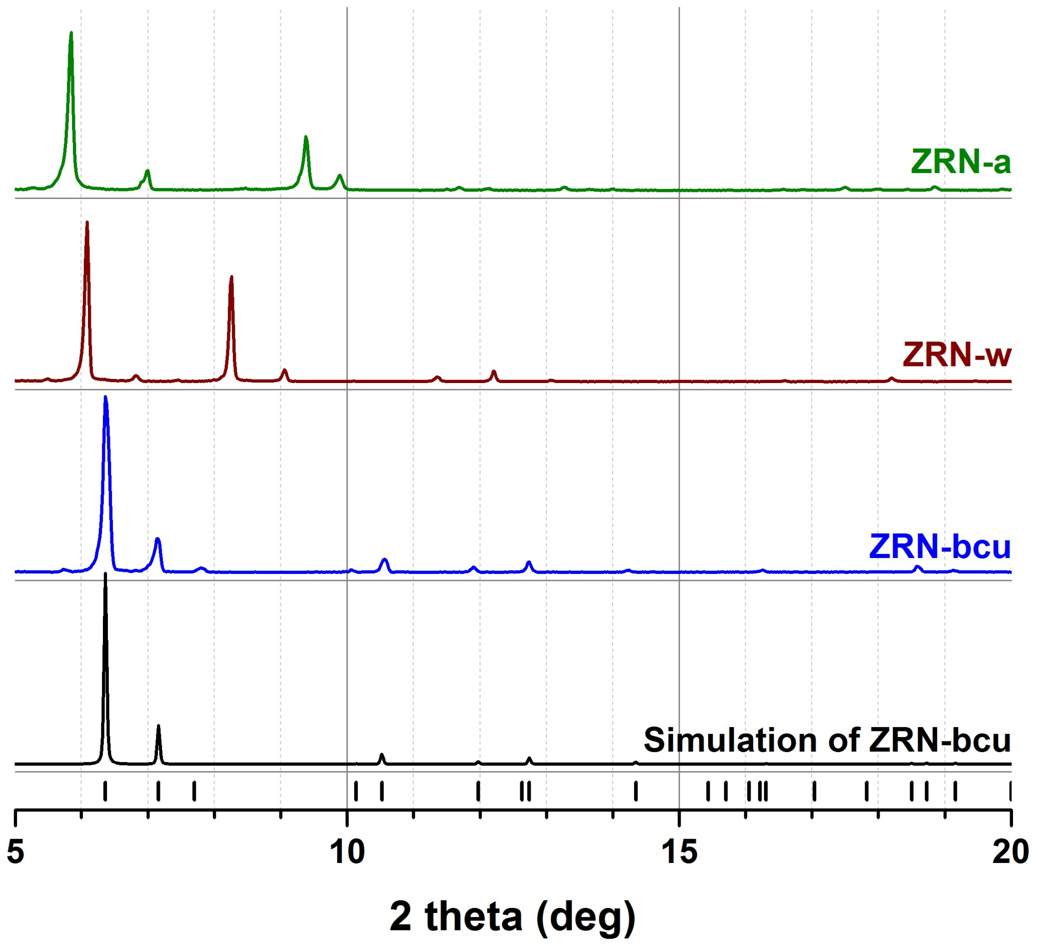

Fig. S5 PXRD patterns of **ZRN-bcu**, **ZRN-w**, and **ZRN-a**.

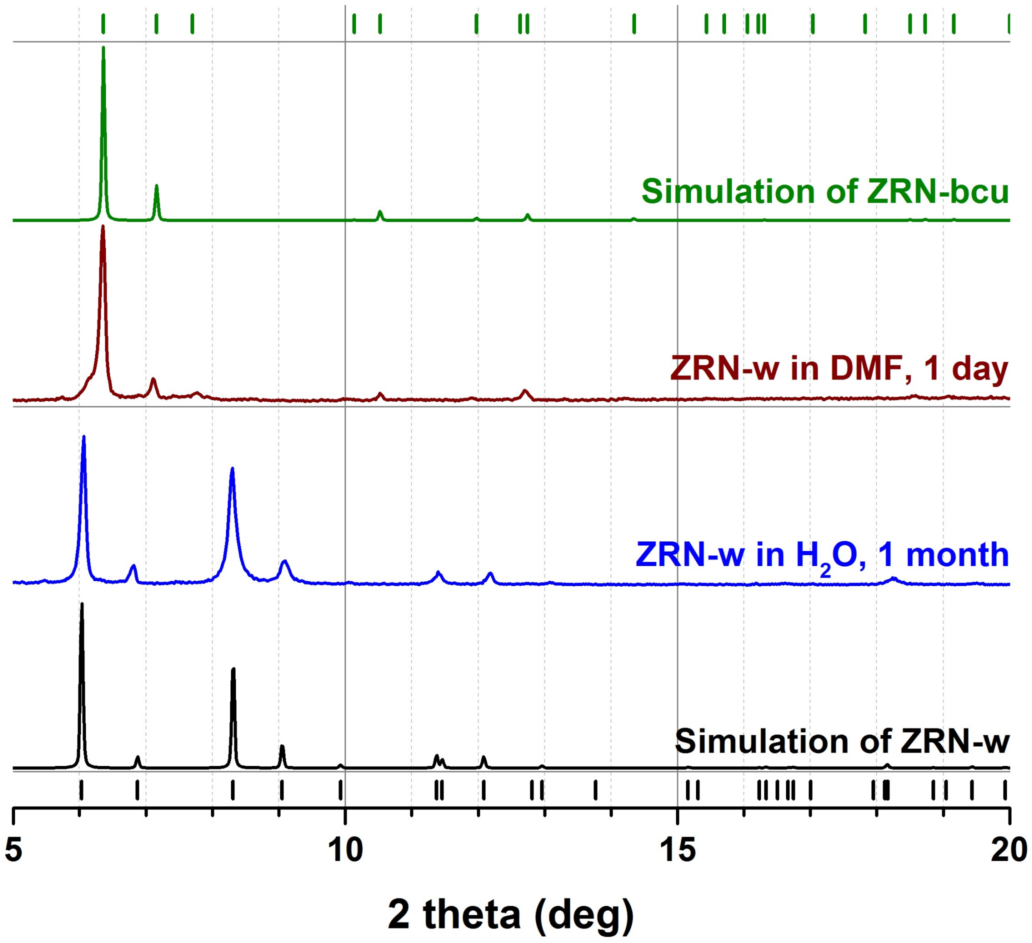

Fig. S6 Stability of **ZRN-w** in water and its reversible transformation to **ZRN-bcu** in DMF. PXRD patterns of **ZRN-w** soaked in water for 1 month and in DMF for 1 d.

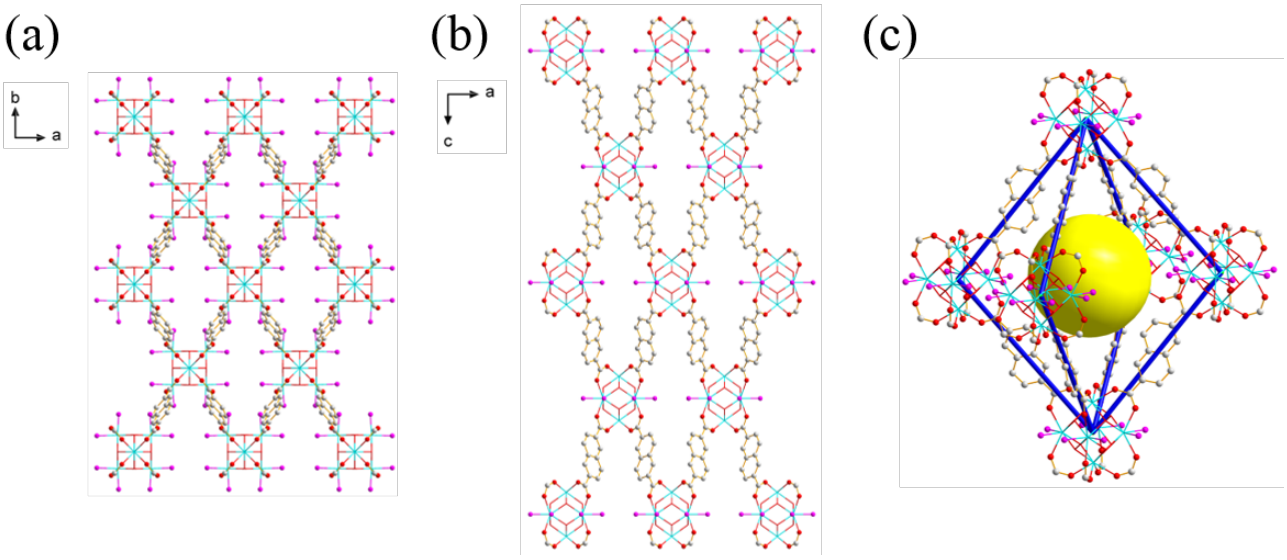

Fig. S7 Ball-and-stick diagrams of **ZRN-w** viewed along the (a) *c* and (b) *b* axes. (c) [4^4] Tile of **ZRN-bcu** with 8-c node. The space inside the tile is highlighted by a yellow dummy sphere. The TFA anions in the framework are omitted for clarity.

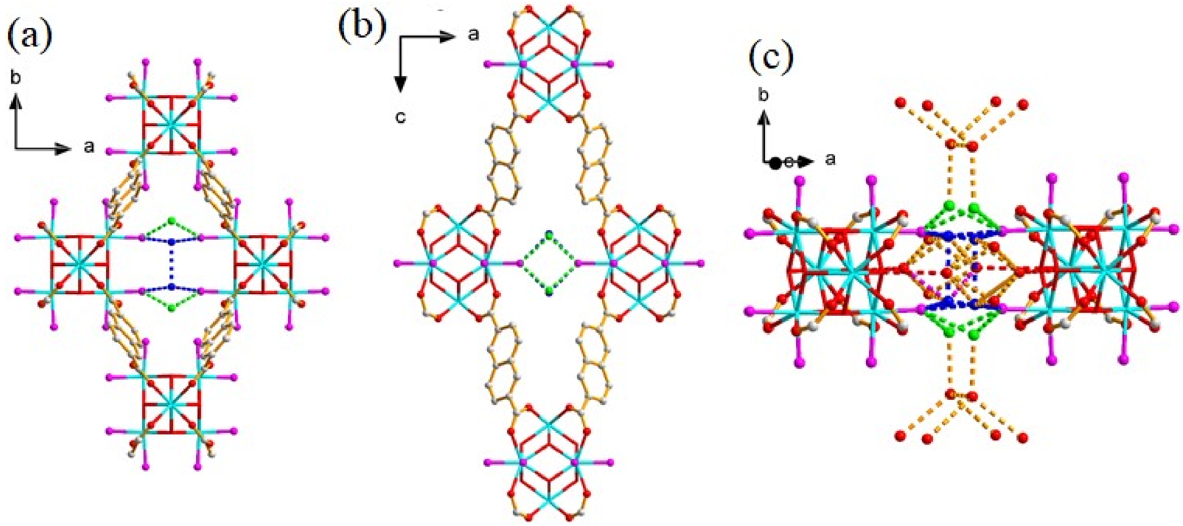

Fig. S8 Ball-and-stick diagrams of the hydrogen-bonded water molecules in **ZRN-w** viewed along the (a) *c* and (b) *b* axes. Statistically disordered water molecules (green and blue) are hydrogen bonded to the ligated water molecules (pink). (c) Additional water molecules with partial occupancies (red) are hydrogen bonded to the statistically disordered water molecules shown in green.

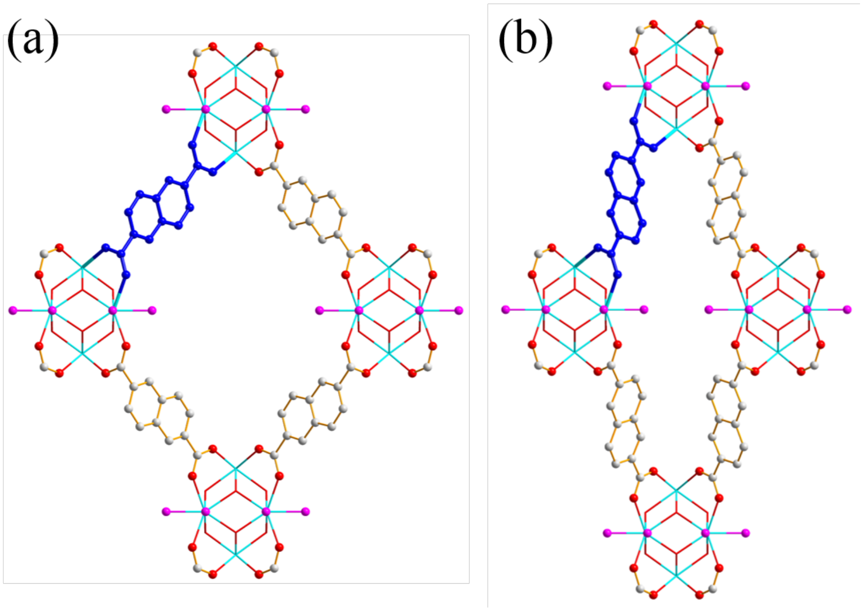

Fig. S9 Conformations of NDC linkers in (a) **ZRN-bcu** and (b) **ZRN-w**.

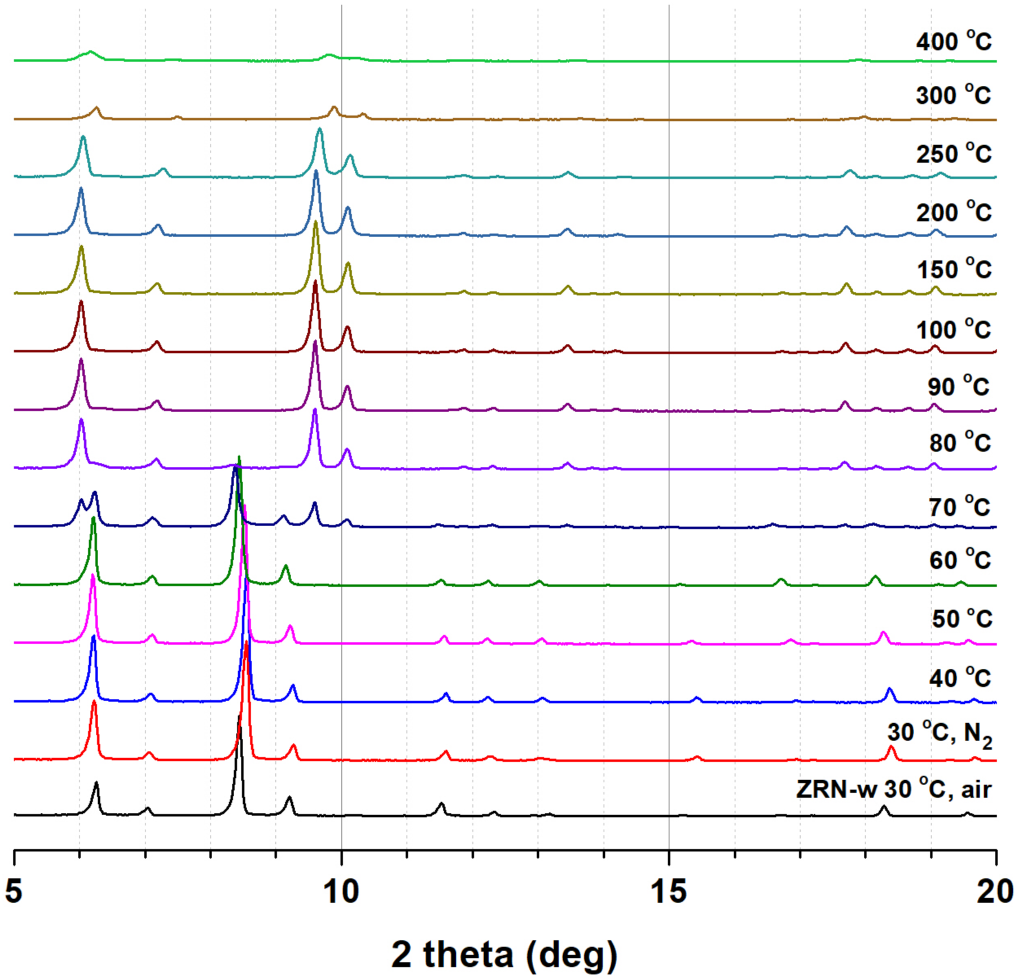

Fig. S10 Variable temperature PXRD patterns of **ZRN-w** under N_2.

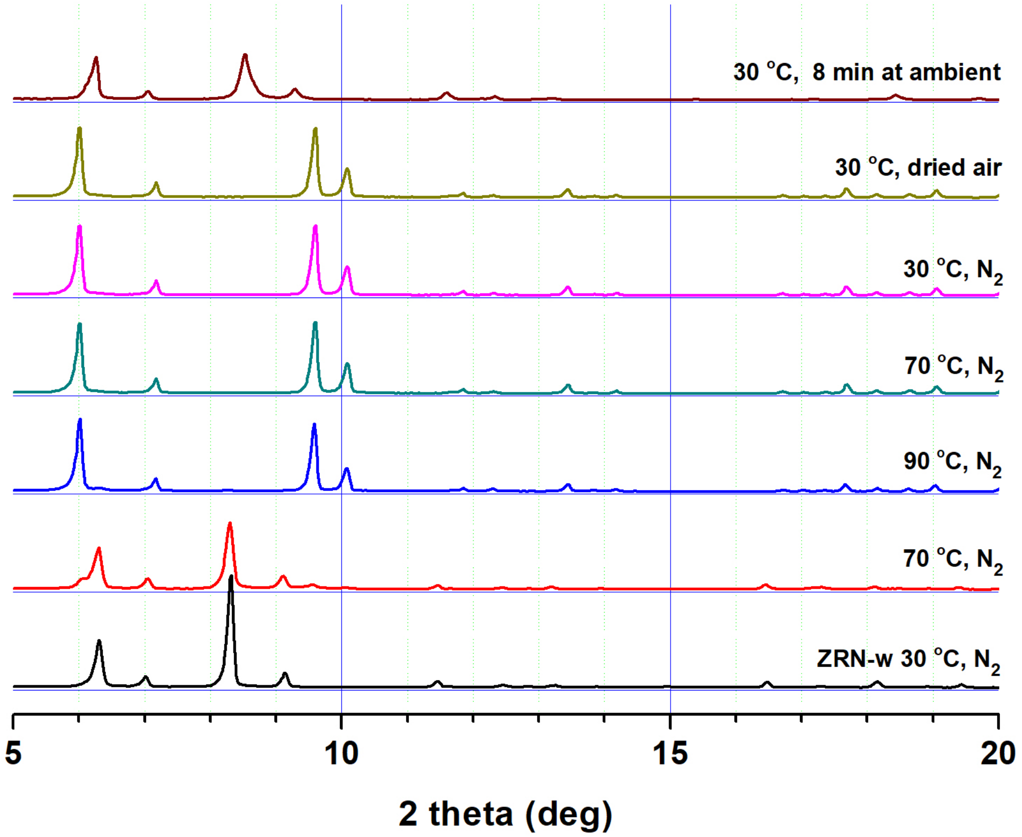

Fig. S11 Variable temperature PXRD patterns of **ZRN-w** under N_2, dry air, and ambient conditions.

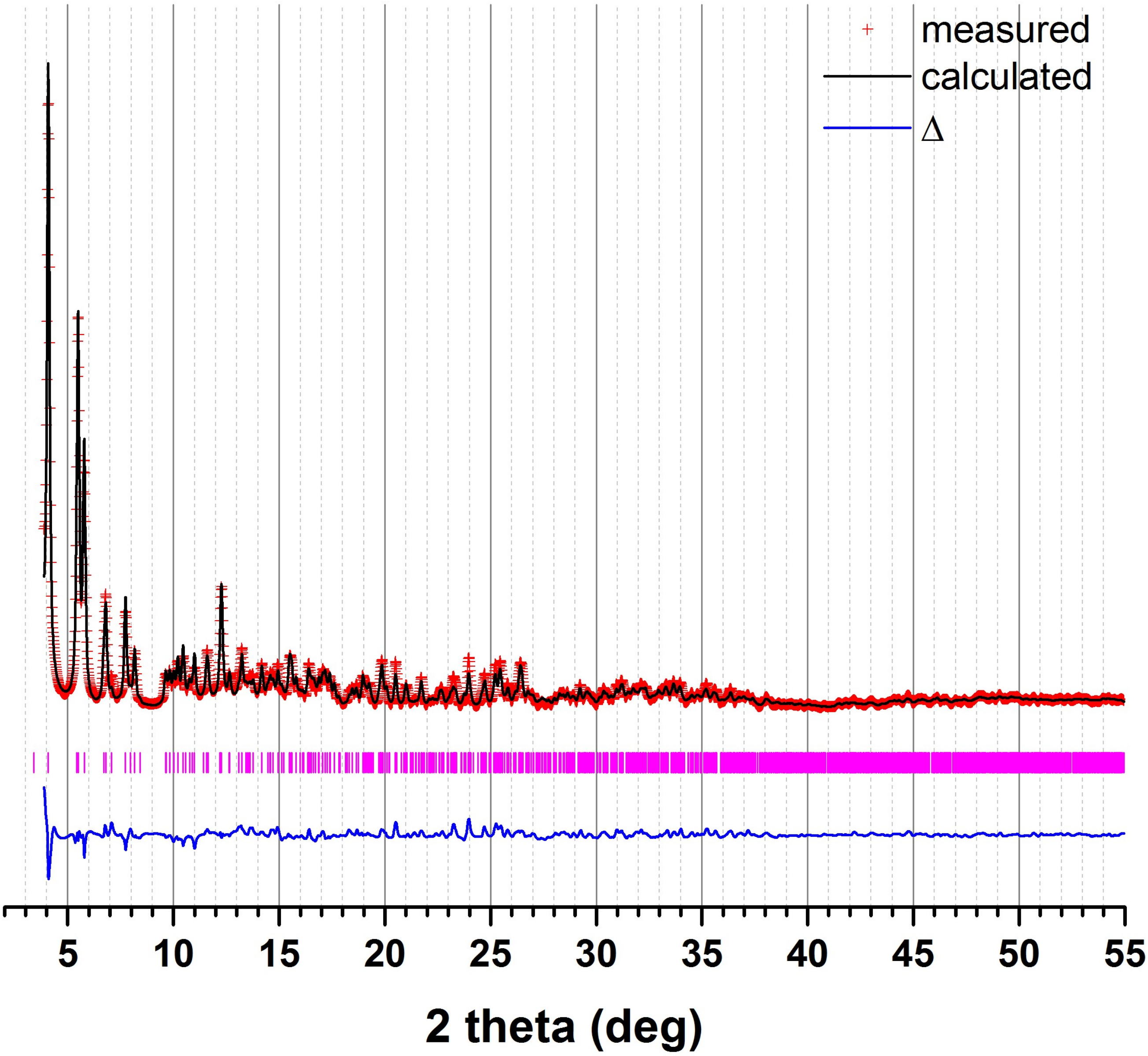

Fig. S12 Final Rietveld refinement profiles for **ZRN-a**. The red crosses represent the experimental diffraction intensity profile, while the solid black line is the calculated profile. The Bragg reflection positions (purple vertical bar) and difference intensity curve (solid blue line) are plotted at the bottom.

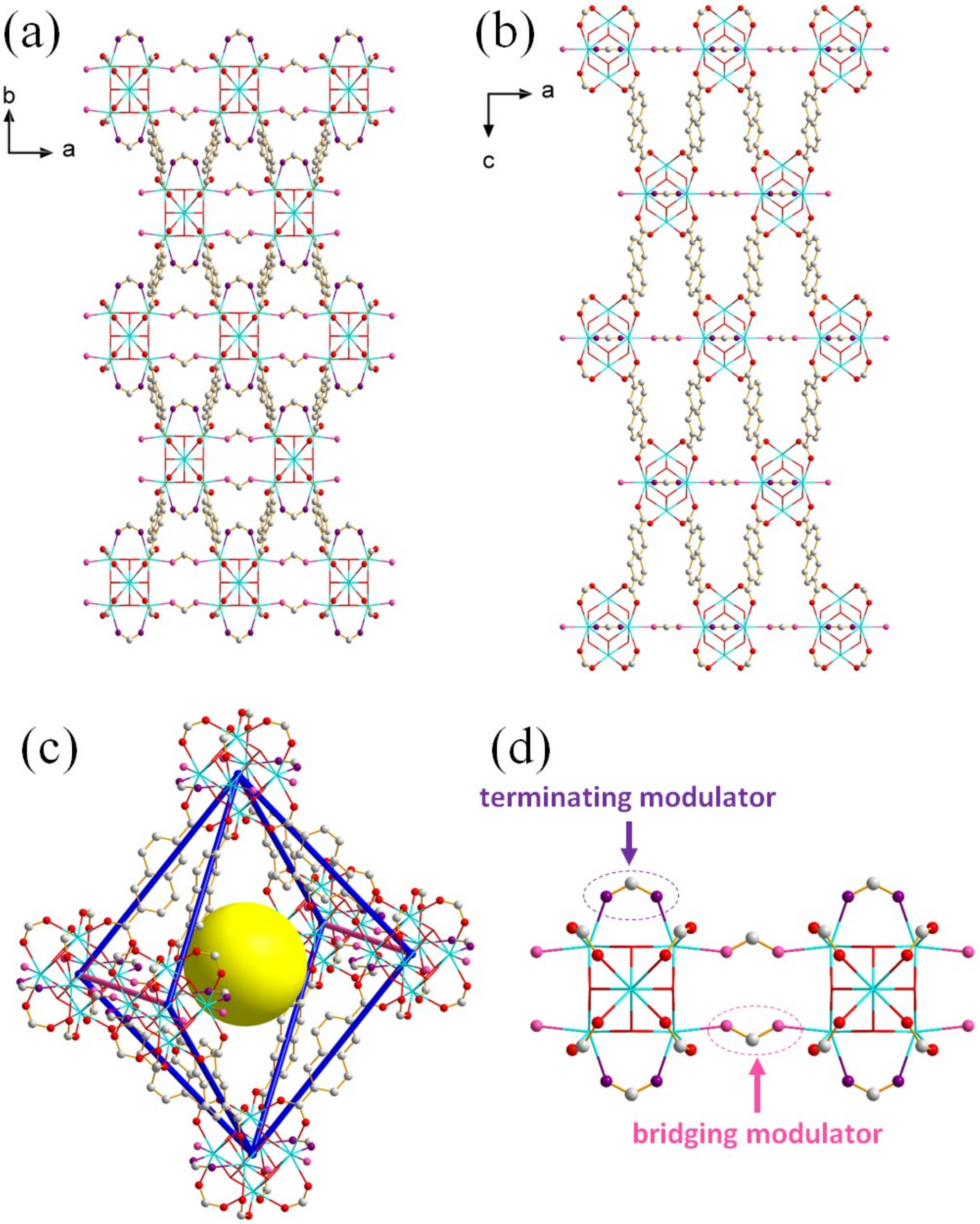

Fig. S13 Ball-and-stick diagrams of **ZRN-a** viewed along the (a) *c* and (b) *b* axes. (c) [$3^4 \cdot 4^2$] Tile of **ZRN-a** with 10-c **bct** topology. The space inside the tile is highlighted by a yellow dummy sphere. (d) Intra- and intercluster bridging modes of TFA anion binding on the Zr sites. The trifluoromethyl groups are omitted for clarity.

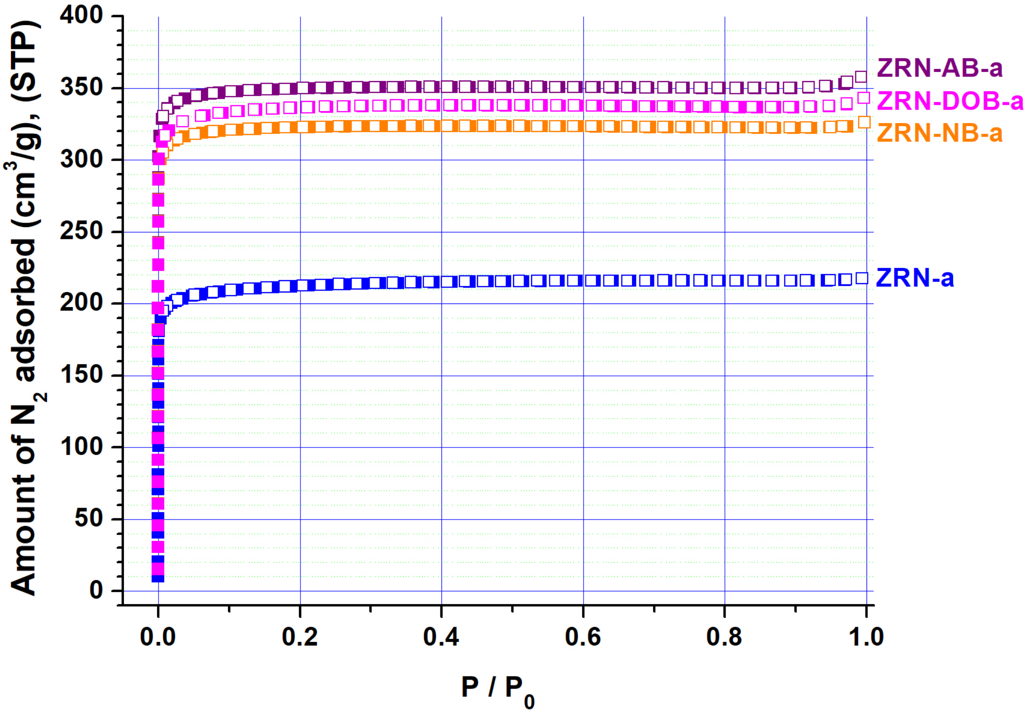

Fig. S14 N_2 adsorption-desorption isotherms of **ZRN-a**, **ZRN-DOB-a**, **ZRN-NB-a**, and **ZRN-AB-a** at 77 K

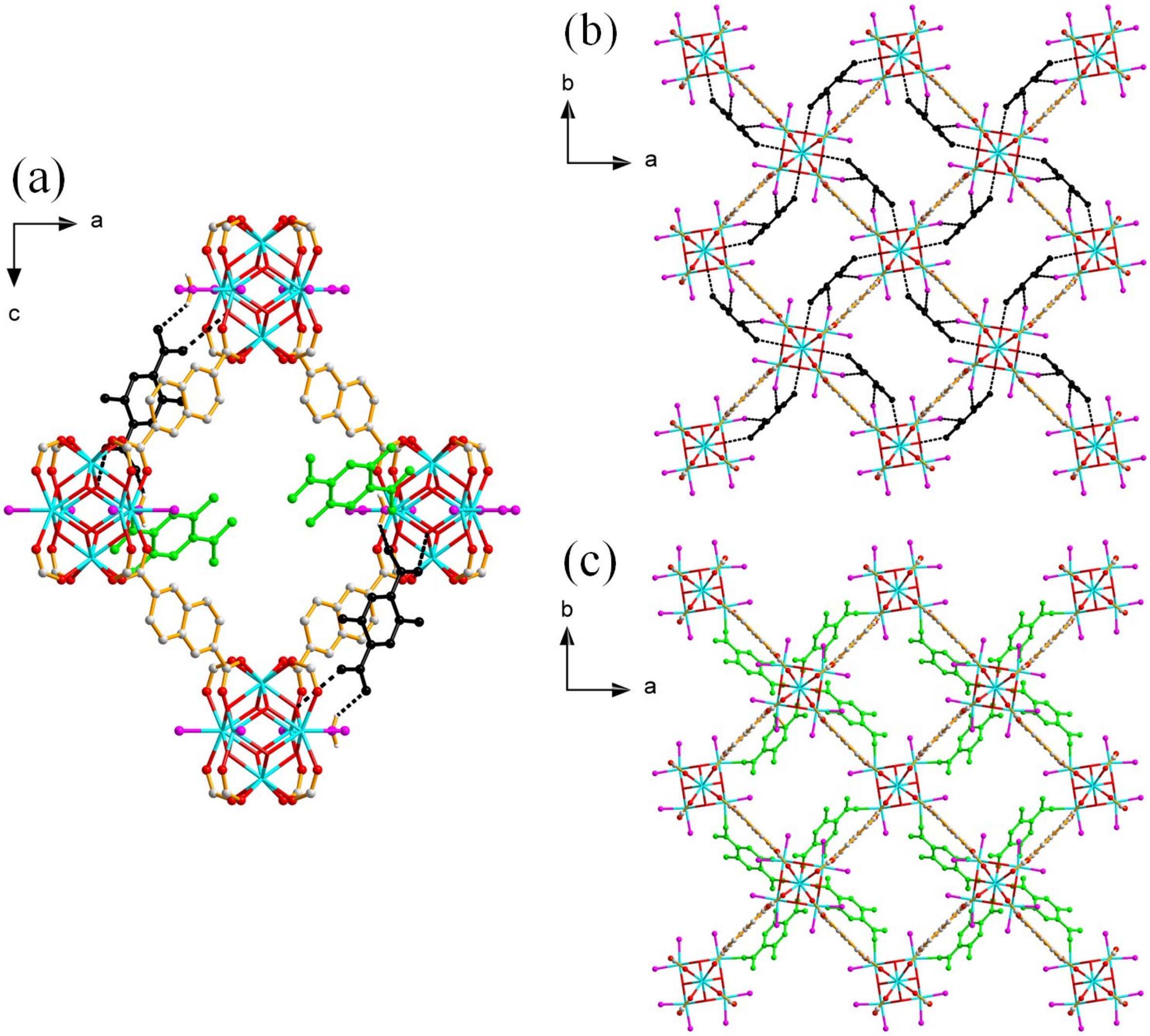

Fig. S15 Ball-and-stick diagrams of **ZRN-DOB**. (a) Statistically disordered DOBDC^{2-} exists in monodentate coordination mode (green) and between Zr clusters (black) in the framework. (b) A statistically disordered DOBDC^{2-} (black) interacts with the framework through both hydrogen bonding and π-π stacking interactions. (c) The other statistically disordered DOBDC^{2-} (green) is ligated to a Zr cluster in monodentate coordination mode. In (a) and (b), the two different DOBDC^{2-} in the framework are drawn separately for clarity.

VI. References

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