Electronic Supplementary Information

Constructing New Metal-Organic Frameworks with Complicated Ligands Generated from “One-Pot” In Situ Reactions

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S1. Materials and instruments

All reagents and solvents (AR grade) were commercially purchased and used as received. $^1$H NMR data were collected on a BRUKER AVANCE III HD 400M NMR spectrometer. FT-IR spectra were recorded on an IRAffinity-1 instrument. TGA data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 10 °C min$^{-1}$ under air atmosphere. The powder X-ray diffraction (PXRD) patterns were recorded on a BRUKER D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178$) at room temperature. Simulation of the PXRD patterns was carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via internet at https://www.ccdc.cam.ac.uk/. Gas adsorption-desorption isotherms were obtained using a Micrometrics ASAP 2020.

S2. Ligand scope and synthesis

![Chemical structures of ligands](image)

Fig. S1 The ligand scope in present work.
Synthesis of $\text{H}_2\text{L}6'$

![Scheme S1 Synthesis of $\text{H}_2\text{L}6'$.](image)

To a solution of 1-bromo-4-nitrobenzene (5.0 g, 24.8 mmol), dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (9.5 g, 29.7 mmol) and $\text{K}_2\text{CO}_3$ (5.1 g, 37.1 mmol) in 1,2-dimethoxyethane (DME, 120 mL) and $\text{H}_2\text{O}$ (30 mL) $\text{Pd(PPh}_3\text{)}_4$ (1.4 g, 1.2 mmol) was added under nitrogen atmosphere. The resulting mixture was stirred at refluxing temperature. After 24 h the resulting yellow suspension was cooled to room temperature and a precipitate was filtered off. The solid was washed with water (50 mL × 3), and then with EtOH (50 mL × 3). Drying on the air resulted dimethyl 4'-nitro-[1,1'-biphenyl]-3,5-dicarboxylate (5.3 g, 67.9%) as a yellow powder.

To a solution of dimethyl 4'-nitro-[1,1'-biphenyl]-3,5-dicarboxylate (5.3 g, 16.8 mmol) in THF (50 mL), MeOH (50 mL) and $\text{H}_2\text{O}$ (50 mL) was added NaOH (2.7 g, 67.2 mmol). The resulting mixture was stirred at 70 °C for 24 h. After evaporation of THF and MeOH, the aqueous residue was acidified with 2 M HCl to pH = 3. The resulting precipitate was filtered and washed with $\text{H}_2\text{O}$ (40 mL × 3) and then MeOH (40 mL × 3). The solid was dried at 60 °C in vacuum to give 4'-nitro-[1,1'-biphenyl]-3,5-dicarboxylic acid as a yellow solid (4.3 g, 89.1%).

Synthesis of $\text{H}_2\text{L}7'$

![Scheme S2 Synthesis of $\text{H}_2\text{L}7'$.](image)

To a solution of 1,3-dibromo-5-nitrobenzene (5.0 g, 17.8 mmol), (4-
(methoxycarbonyl)phenyl)boronic acid (9.6 g, 53.4 mmol) and K₂CO₃ (9.8 g, 71.2 mmol) in 1,2-dimethoxyethane (DME, 120 mL) and H₂O (30 mL) Pd(PPh₃)₄ (1.0 g, 0.9 mmol) was added under nitrogen atmosphere. The resulting mixture was stirred at refluxing temperature. After 36 h resulting yellow suspension was cooled to room temperature and a precipitate was filtered off. The solid was washed with water (50 mL × 3), and then with EtOH (50 mL × 3). Drying on the air resulted dimethyl 5'-nitro-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (5.1 g, 73.2%) as a yellow powder.

To a solution of dimethyl 4'-nitro-[1,1'-biphenyl]-3,5-dicarboxylate (5.1 g, 13.0 mmol) in THF (50 mL), MeOH (50 mL) and H₂O (50 mL) was added NaOH (2.1 g, 52.1 mmol). The resulting mixture was stirred at 70 °C for 24 h. After evaporation of THF and MeOH, the aqueous residue was acidified with 2 M HCl to pH = 3. The resulting precipitate was filtered and washed with H₂O (50 mL × 3) and then MeOH (50 mL × 3). The solid was dried at 60 °C in vacuum to give 5'-nitro-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid H₂L₇' as a yellow solid (3.5 g, 73.9%).

S3. MOF synthesis

Synthesis of BUT-101

Cu(NO₃)₂·3H₂O (0.02 mmol, 5 mg) and H₂L₆' (0.01 mmol, 3 mg) were ultrasonically dissolved in 1 mL of DMA. To the solution in a 4 mL glass vial were added 0.2 mL of deionized water. The vial was sealed and then heated at 80 °C for 24 h in an oven. After cooling to room temperature, the blue rod-like crystals of BUT-101(Cu) [(Cu(L₆)(H₂O)₂)] were collected by filtration, and washed with DMA and acetone. Yield 2.9 mg (78% based on H₂L₆' ligand).

Zn(NO₃)₂·6H₂O (0.02 mmol, 6 mg) and H₂L₆' (0.01 mmol, 3 mg) were ultrasonically dissolved in 1 mL of DMF. To the solution in a 4 mL glass vial were added 0.5 mL of methanol. The vial was sealed and then heated at 80 °C for 48 h in an oven. After cooling to room temperature, the yellow block crystals of BUT-101(Zn) [Zn(L₆)(H₂O)₂] were collected by filtration, and washed with DMF and acetone.
Yield 2.6 mg (70% based on H₂L₆' ligand).

**Synthesis of BUT-102**

Cd(NO₃)₂·4H₂O (0.02 mmol, 6 mg) and H₂L₆' (0.01 mmol, 3 mg) were ultrasonically dissolved in 1 mL of DMF. To the solution in a 4 mL glass vial were added 0.3 mL of methanol and 1 mL of deionized water. The vial was sealed and then heated at 70 °C for 24 h in an oven. After cooling to room temperature, the lamellar crystals of BUT-102 [Cd(L₆)(H₂O)] were collected by filtration, and washed with DMF and acetone. Yield 2.5 mg (62% based on H₂L₆' ligand).

**Synthesis of BUT-103**

MnCl₂·4H₂O (0.02 mmol, 4 mg) and H₂L₆' (0.01 mmol, 3 mg) were ultrasonically dissolved in 1 mL of DMF. To the solution in a 4 mL glass vial were added 0.25 mL of ethanol. The vial was sealed and then heated at 90 °C for 40 h in an oven. After cooling to room temperature, the yellow block crystals of BUT-103 [Mn₄(L₆)₄(DMF)₆]·(DMF)₃ were collected by filtration, and washed with DMF and acetone. Yield 11.0 mg (63% based on H₂L₆' ligand).

**Synthesis of BUT-104**

ZrOCl₂·8H₂O (0.02 mmol, 7 mg) and H₂L₇' (0.01 mmol, 4 mg) were ultrasonically dissolved in 2 mL of DMF, and formic acid (0.8 mL) was then added to the solution in a 4 mL glass vial. The vial was then heated at 120 °C for 15 days in an oven. After cooling to room temperature, the yellow block crystals of BUT-104 [Zr₆O₄(OH)₈(L₇-a)₂(H₂O)₄] were harvested by filtration and washed with DMF and acetone. Yield 7.5 mg (68% based on H₂L₇' ligand).

**Synthesis of BUT-105**

Zn(NO₃)₂·6H₂O (0.02 mmol, 6 mg) and H₂L₇' (0.01 mmol, 4 mg) were ultrasonically dissolved in 1 mL of DMF. To the solution in a 4 mL glass vial were added 30 μL of deionized water. The vial was sealed and then heated at 50 °C for 15 days in an oven. After cooling to room temperature, the yellow block crystals of BUT-105
[Zn$_3$(OH)$_2$(L7-b)$_2$(H$_2$O)$_4$] were collected by filtration, and washed with DMF and acetone. Yield 7.9 mg (82% based on H$_2$L7’ ligand).

**Synthesis of BUT-106**

CdCl$_2$·2.5H$_2$O (0.02 mmol, 5 mg) and H$_2$L7’ (0.01 mmol, 4 mg) were ultrasonically dissolved in 1 mL of DMF. To the solution in a 4 mL glass vial were added 0.4 mL of methanol, 0.4 mL of deionized water and 8 μL of 4 M HCl aqueous solution. The vial was sealed and then heated at 80 °C for 72 h in an oven. After cooling to room temperature, the lamellar crystals of BUT-107 [Cd$_7$(L7-c)$_4$(H$_2$O)$_{12}$] were collected by filtration, and washed with DMF and acetone. Yield 4.3 mg (47% based on H$_2$L7’ ligand).

**Synthesis of BUT-107**

In(NO$_3$)$_3$·6H$_2$O (0.02 mmol, 8 mg) and H$_2$L7’ (0.01 mmol, 4 mg) were ultrasonically dissolved in 2 mL of DMF in a 4 mL glass vial, and 16 μL of 4 M HCl aqueous solution was then added to the solution as the modulator. The vial was sealed and then heated at 100 °C for 48 h in an oven. After cooling down to room temperature, the yellow rhombic crystals of BUT-106 [In(L7-d)$_2$] were collected by filtration, and washed with DMF and acetone. Yield 3.3 mg (51% based on H$_2$L7’ ligand).

**Synthesis of BUT-108**

ZrOCl$_2$·8H$_2$O (0.03 mmol, 10 mg) and HL8’ (0.09 mmol, 15 mg) were ultrasonically dissolved in 2 mL of DMF, and formic acid (0.2 mL) was then added to the solution in a 4 mL glass vial. The vial was then heated at 120 °C for 48 h in an oven. After cooling to room temperature, the colorless block crystals of BUT-108(Zr) [Zr$_6$O$_4$(OH)$_4$(L8)$_2$(HCOO)$_6$(H$_2$O)$_2$] were harvested by filtration and washed with DMF and acetone. Yield 16 mg (57% based on HL8’ ligand).

Similar reaction with HfCl$_4$ (0.03 mmol, 10 mg) gave crystals of BUT-108(Hf) [Hf$_6$O$_4$(OH)$_4$(L8)$_2$(HCOO)$_6$(H$_2$O)$_2$]. Yield 17 mg (49% based on HL8’ ligand).

**Synthesis of BUT-109**
ZrOCl$_2$·8H$_2$O (0.03 mmol, 10 mg), HL9' (0.03 mmol, 4 mg) and L9'' (0.02 mmol, 6 mg) were ultrasonically dissolved in 2 mL of DMF, and acetic acid (0.4 mL) was then added to the solution in a 4 mL glass vial. The vial was then heated at 120 °C for 24 h in an oven. After cooling to room temperature, the colorless block crystals of BUT-109(Zr) [Zr$_6$O$_4$(OH)$_{10}$L9$_3$(H$_2$O)$_6$] were harvested by filtration and washed with DMF and acetone. Yield 6.8 mg.

Similar reaction with HfCl$_4$ (0.03 mmol, 10 mg) gave small crystals of BUT-109(Hf) [Hf$_6$O$_4$(OH)$_{10}$L9$_3$(H$_2$O)$_6$]. Yield 7.2 mg.

**S4. Single crystal X-ray crystallography**

The diffraction data of as-synthesized BUT-101--109 were collected in an Agilent Supernova CCD diffractometer equipped with a mirror monochromated enhanced Cu Ka radiation (λ = 1.54184 Å). The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ with anisotropic displacement using the SHELXTL software package. Hydrogen atoms of ligands were calculated in ideal positions with isotropic displacement parameters. Those in amino, coordinated water and hydroxyl groups were not added but were calculated into molecular formula of the crystal data. For these MOFs, the volume fractions of disordered solvents in pores could not be modeled in terms of atomic sites, but were treated by using the MASK routine in the Olex2 software package or the SQUEEZE routine in PLATON. Crystal parameters and structure refinements are summarized in Table S1~S11 (for details, see CCDC 1888829~1888839).

SXRD analyses showed that BUT-101(Cu) and BUT-101(Zn) have isostructural frameworks, consisting of the classical M$_2$(COO)$_4$ paddle wheel SBU (SBU = Secondary Building Units) (Fig. 1a). As expected, the H$_2$L6' ligand in both cases has been successfully reduced to the L6$^{2-}$ ligand in situ without the deliberate addition of
any reductant species. It is noteworthy that the newly created amino group in the \( \text{L6}^{2-} \) ligand has also participated in the coordination with metals by occupying the axis sites of the paddle wheel SBUs with the angle \((\text{M–N–C})\) of 115.40 (BUT-101(Cu)) and 113.66\(^\circ\) (BUT-101(Zn)), respectively. There exists a polyhedral cage in their structure, composing of six \( \text{L6}^{2-} \) ligands covering the faces and six SBUs occupying the vertexes, with window size about 3.6 Å (Fig. S2a). Each cage connects fourteen adjacent cages by sharing the vertexes and faces to form the final 3D framework with 1D channels. The overall structure of BUT-101 is isoreticular with JUC-141 of the eea topology previously reported by G. Zhu et al. Due to the extended backbone of \( \text{L6}^{2-} \) ligand with respect to the 5-aminoisophthlic acid, the 1D channel sizes in BUT-101 are about 6.2 Å and 12.2 Å along (111) (Fig. S2b) and (001) direction (Fig. S2c), respectively, larger than that observed in JUC-141. The solvent-accessible volume of BUT-101(Cu) and BUT-101(Zn) are estimated to be 58.3\% and 56.8\%, by using PLATON.

![Fig. S2](a) The polyhedral cage in BUT-101 and the topological representation of BUT-101 network with 1D channels along the (b) (111) and (c) (001) direction, respectively.

BUT-102 crystallizes in the triclinic crystal system with the \( P\overline{1} \) space group. The asymmetric unit contains one Cd(II) ion, one \( \text{L6}^{2-} \) ligand, and a water molecule. The 6-coordinated Cd(II) center adopts a distorted quadrangular bipyramid coordination geometry, which are generated by four O atoms from three carboxylates, one N atom of the amino on the \( \text{L6}^{2-} \) ligand, and one from the terminal water molecule. Among
the coordinated carboxylates, one is chelated to the Cd(II) ion, and another two carboxylate groups bridge two adjacent Cd(II) ions by the bidentate coordination. Two identical Cd(II) centers are linked into a Cd$_2$ SBU by two bridging carboxylates from two different L6$^{2-}$ ligands (Fig. S3). Each Cd$_2$ SBU connects to four L6$^{2-}$ ligands, and each ligand connects to three Cd$_2$ SBUs to form a 2D layer (Fig. 1b). These layers stack through H-bond and π-π interactions of adjacent parallel benzene rings (distance of benzene centers of about 6.1 Å) to form the final 3D structure of BUT-102.

Fig. S3 The Cd$_2$ cluster in BUT-102.

BUT-103 crystallizes in the monoclinic crystal system (space group $P_2_1$). There are two six-coordinated Mn ions, two L6$^{2-}$ ligands, three DMF coordinated molecules and two free DMF molecules in the asymmetric unit. Mn1 is connected with four carboxylate groups from four different L6$^{2-}$ ligands, among which one is chelated to Mn1 atom, two are bidentate carboxylates, and another adopts the ($\mu^2$-$\eta^2$:$\eta^1$) coordination mode. Mn2 adopts a distorted octahedral coordination geometry through linking to three carboxylate groups from three different L6$^{2-}$ ligands, including two bidentate carboxylate groups shared with Mn1 and the ($\mu^2$-$\eta^2$:$\eta^1$) carboxylate, as well as three DMF molecules occupying another three vertexes of the octahedron. Mn1 and Mn2 are bridged into a Mn$_2$ cluster by three carboxylates (Fig. S4). Each Mn$_2$ SBU connects to four carboxyl groups from four different L6$^{2-}$ ligands, and each ligand connects to two Mn$_2$ SBUs with the free amino groups extending outward, affording a 2D layer (Fig. 1c). These 2D layers stack through H-bond interactions to form the 3D structure of BUT-103.
**Fig. S4** The Mn$_2$ cluster in BUT-103.

BUT-104 crystallizes in the monoclinic crystal system ($\beta = 92.956(7)^{\circ}$, space group C2/m). In BUT-104, the diazo-bond-coupled tetra-topic carboxylate ligand L7-a$^4^-$ can be viewed as a planar rhomboid 4-connected linker and the typical Zr$_6$O$_8$ cluster serves as an 8-connected node, and the entire framework is similar to those of NU-901, NU-902 and NPF-300 with the rare scu topology (Fig. 2a and S5). Large 1D rhombic channels (the diagonal distances of the pores are about 9.6 and 23.8 Å) could be observed in the framework along the c-axis of crystallography. The total solvent-accessible volume in the framework of BUT-104 is estimated to be 75.3%, by using PLATON.

**Fig. S5** (a) The dihedral angles of ligand L7-a$^+$ in BUT-104 network and (b) the topological representation of BUT-104 network with 1D channels along the c-axis.

BUT-105 crystallizes in the trigonal crystal system (space group Rc). There is two and a half crystallographically independent Zn atoms in the asymmetric unit. The six-coordinated Zn1 atom is linked with four oxygen atoms from four different bimonodentate carboxylates of four L7-b$^{4^+}$ ligands and two $\mu$3-O atoms. The four-coordinated Zn2 atom is connected with three carboxylate oxygen atoms from three different carboxylates of three L7-b$^{4^+}$ ligands and one $\mu$3-O atom. The five-coordinated Zn3 atom connects to two oxygen atoms from two different
bimonodentate carboxylates of two L7-b ligands, one \( \mu_3 \)-O atom, and two oxygen atoms from two terminal water molecules. Two Zn1 atoms, two Zn3 atoms and one Zn2 atom are bridged by two \( \mu_3 \)-O atoms to form a Zn\(_5\) cluster (Fig. S6a). Each such Zn\(_5\) building unit connects to eight carboxylates, among which two are monodentate carboxylate, and the others are bimonodentate carboxylates. These carboxylates are from eight different L7-b\(^4\) ligands stretching toward four orientations with two ligands stacking staggered in the same direction through \( \pi-\pi \) interactions of parallel benzene rings. It is worth noting that different with the rhomboid azoic ligand of BUT-104, the L7-b\(^4\) ligand of BUT-105 was generated in an oxidation form of the diazo bond, which could be viewed as an approximate planar rectangular linker. However, the dihedral angles between the central plane and four peripheral benzene rings are different to match the linkage geometry of Zn\(_5\) clusters (Fig. S6b). Each L7-b\(^4\) ligand links to four Zn\(_5\) clusters to give a final 3D framework with nano-sized hexagonal channels in diameter of about 4.0 nm along the \( c \)-axis. Topologically, the Zn\(_5\) SBU can be regarded as an eight-connected node and the L7-b\(^4\) ligand can act as a four-connected linker. Thus the resulting 3D framework can be simplified as a (4,8)-connected network with the point symbol of \( (4^{12}6^{16})(4^6)_2 \), which has not been reported in the literature yet (Fig. S6c). The solvent accessible volume of BUT-105 is up to 76.3\% of the total volume, as estimated by PLATON.

Fig. S6 (a) The Zn\(_5\) cluster and (b) azoxy ligand L7-b\(^4\) with different dihedral angles in BUT-105, and (c) the topological representation of BUT-105 network with 1D channels along the \( c \)-axis.
BUT-106 crystallizes in the monoclinic space group C2/c. The asymmetric unit contains four crystallographically independent Cd(II) ions. The single Cd1 connects four monodentate carboxylates from four different L7-c^4− ligands (Fig. S7a and 2c). Six-coordinated Cd2, seven-coordinated Cd3 and four-coordinated Cd4 are bridged by six carboxylate groups from six different L7-c^4− ligands to form a trimeric Cd3 SBU, and five H2O complete remaining coordination (Fig. S7b). Among the six carboxylates, two monodentate ones are linking to Cd4, and the rest adopt the (μ^2-η^2:η^1) coordination when linking to Cd2 and Cd3. Similar to that in BUT-105, the L7-c^4− ligand in BUT-106 was also generated with an oxidized diazo bond. However, the azoxy L7-c^4− displays two different configurations, which is resulted from varying dihedral angles between the central plane and four peripheral benzene rings in different coordination (Fig. S7c and d). These L7-c^4− ligands connect to single Cd(II) ion and Cd3 SBU alternately, forming the complex (4,4,4,6)-connected 3D framework with the new topology [point symbol of (4^2.8^4)(4^3.6^2.8)_d(4^3.6^6)_z] (Fig. S7e). In the final 3D structure, π-π interactions of adjacent parallel benzene rings could be observed between these stacking L7-c^4− ligands when binding to Cd(II) centers. The solvent accessible volume of BUT-106 is 37.6% of the total volume, as estimated by PLATON.

![Fig. S7](image_url)

*Fig. S7* (a) The single Cd(II) node, (b) Cd3 cluster, (c), (d) two configurations of azoxy ligand L7-c^4− with different dihedral angles in BUT-106, and (e) the topological representation of BUT-106 network along the c-axis.
BUT-107 crystallizes in the orthorhombic crystal system with \textit{Pnna} space group. The asymmetric unit contains one single In(III) ion and one L7-d\textsuperscript{4−} ligand (Fig. S8a and 2d). The In(III) center adopts a distorted square-antiprismatic coordination geometry by bridging four carboxylates from four different L7-d\textsuperscript{4−} ligands. All the carboxylates on the L7-d ligand chelate to the In(III) ion, and each L7-d\textsuperscript{4−} ligand connects to four In(III) ions to form a single 3D anionic network with 1D channels along \textit{b}- and \textit{c}- axis, respectively. Due to the large void in the framework, two such identical and independent single frameworks mutually interpenetrate, reinforcing each other via intermolecular \(\pi-\pi\) interaction between the adjacent parallel benzene rings. Interestingly, for the \textit{trans}-azoic ligand L7-d\textsuperscript{4−} in BUT-107, two terphenyl moieties on two sides of the central diazo bond display a spatial configuration and the dihedral angle between two central benzene rings is 83.281°, close to the right-angle (Fig. S8b). Topologically, the spatial 4-connected L7-d\textsuperscript{4−} linker and 4-connected In(III) node connect alternately to give the single 3D framework with the \textit{ion} topology (Fig. S8c and S8d). The solvent accessible volume of the two-fold interpenetrated BUT-107 is 72.0% of the total volume, as estimated by PLATON.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{s8.png}
\caption{(a) The single In(III) ion and (b) the L7-d\textsuperscript{4−} ligand with two terphenyl moieties nearly perpendicular in BUT-107. (c) The single anionic framework, and (d) the topological representation of BUT-107 viewed along the \textit{c}-axis.}
\end{figure}
BUT-108(Zr) and BUT-108(Hf) are isostructural (Fig. 3). A two-fold interpenetration could be observed in their structure, and the single framework is isostructural with PCN-777 \((\text{spn} \text{ topology})\) stacked by two kinds of cages, causing the face of tetrahedral cage in PCN-777 to extrude. In PCN-777, the TATB organic ligand displays a trigonal-planar geometry, while for BUT-108, the ligand \(L^{83-}\) is in a flat tripod shape (Fig. S9). In BUT-108, six terminal \(\text{HCOO}^-\) (two are in monodentate coordination) and two \(\text{H}_2\text{O}\) entries complete the remaining coordination of the cluster and account for the charge balance. Owning to the interpenetration of frameworks, the solvent accessible volume in BUT-108(Zr) and BUT-108(Hf) are just 64.1% of the total volume, much less than that in PCN-777, as estimated by PLATON.

![Fig. S9 The tripod-shaped ligand \(L^{83-}\) in BUT-108.](image)

BUT-109(Zr) has a 3D framework structure constructed from \(\text{Zr}_6\) clusters and \(L^{92-}\) ligands, seemingly adopting a \(\text{ftw} \) topology with two-fold interpenetration (Fig. 4). Due to the crystallographically imposed symmetry, the \(L^{92-}\) ligand in the structure model is in disorder (Fig. S10). The structural refinement of BUT-109(Zr) indicates that the occupancy of \(L^{92-}\) ligands is close to 0.5. The linear di-carboxylate \(L^{92-}\) ligand was produced from the in situ condensation of \(\text{HL}^{9'}\) and \(L^{9''}\), acting as a 2-connected linker actually. Statistically, the \(\text{Zr}_6\) clusters are linked by six \(L^{92-}\) ligands to form the final 3D framework. Missing linkers thus lead to defects in this \textit{pseudo} 4,12-connected framework and \(\text{OH}/\text{OH}_2\) entities complete the remaining coordination of the \(\text{Zr}_6\text{O}_4(\text{OH})_4\) cluster. Overall, BUT-109(Zr) might have a 6-connected network with full occupancy of \(L^{92-}\) ligand, or other cases, and the formula could be \([\text{Zr}_6\text{O}_4(\text{OH})_{10}(L^{9})_3(\text{H}_2\text{O})_6]\).
Fig. S10 The *pseudo* 4,12-connected single framework of BUT-109(Zr) with L9$^{2-}$ ligand in disorder.
**Table S1.** The crystallographic data and structure refinement for BUT-101(Cu).

| Property                      | Value                        |
|-------------------------------|------------------------------|
| Formula                       | CuC<sub>14</sub>H<sub>15</sub>O<sub>6</sub>N |
| M                             | 354.80                       |
| Crystal system                | Trigonal                     |
| Space group                   | $R_m^3$                      |
| $a$ / Å                       | 18.6355(7)                   |
| $b$ / Å                       | 18.6355(7)                   |
| $c$ / Å                       | 34.4019(12)                  |
| $α$ / °                       | 90                           |
| $β$ / °                       | 90                           |
| $γ$ / °                       | 120                          |
| $V$ / Å$^3$                   | 10346.5(9)                   |
| $Z$                           | 18                           |
| $D_c$ / g cm$^{-3}$           | 0.921                        |
| $μ$ / mm$^{-1}$               | 1.413                        |
| $T$ / K                       | 173.01(10)                   |
| Reflections collected         | 7625                         |
| Independent reflections       | 2276 [$R_{int} = 0.0302$, $R_{sigma} = 0.0257$] |
| Goodness-of-fit on $F^2$      | 1.086                        |
| $R_1$ $^a$, $wR_2$ $^b$ [$I > 2σ(I)$] | $R_1 = 0.0381$, $wR_2 = 0.1216$ |
| $R_1$ $^a$, $wR_2$ $^b$ (all data) | $R_1 = 0.0408$, $wR_2 = 0.1244$ |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.35 / -0.64 |

$^a R_1 = Σ||F_o|-|F_c|| / Σ|F_o|$

$^b wR_2 = {Σ[w(F_o^2-F_c^2)^2]} / {[w(F_o^2)]^{1/2}}$, [$F_o > 4σ(F_o)$]
Table S2. The crystallographic data and structure refinement for BUT-101(Zn).

| Property                        | Value                      |
|---------------------------------|----------------------------|
| Formula                         | ZnC₁₄H₁₃O₆N               |
| \( M \)                         | 356.64                     |
| Crystal system                  | Trigonal                   |
| Space group                     | \( R₃ m \)                 |
| \( a / \text{Å} \)              | 18.4038(8)                 |
| \( b / \text{Å} \)              | 18.4038(8)                 |
| \( c / \text{Å} \)              | 34.5026(19)                |
| \( \alpha / ^\circ \)          | 90                         |
| \( \beta / ^\circ \)           | 90                         |
| \( \gamma / ^\circ \)          | 120                        |
| \( V / \text{Å}^3 \)            | 10120.4(10)                |
| \( Z \)                         | 18                         |
| \( D_c / \text{g cm}^{-3} \)    | 0.947                      |
| \( \mu / \text{mm}^{-1} \)      | 1.591                      |
| \( T / \text{K} \)              | 150.00(10)                 |
| Reflections collected           | 7259                       |
| Independent reflections         | 2221 [\( R_{\text{int}} = 0.0595, R_{\text{sigma}} = 0.0446 \)] |
| Goodness-of-fit on \( F^2 \)    | 1.088                      |
| \( R_1^a, wR_2^b \) [\( I > 2\sigma(I) \)] | \( R_1 = 0.0602, wR_2 = 0.1639 \) |
| \( R_1^a, wR_2^b \) (all data)  | \( R_1 = 0.0645, wR_2 = 0.1673 \) |
| Largest diff. peak and hole (e.Å\(^{-3}\)) | 1.28 / -0.55               |

\(^a\) \( R_1 = \Sigma ||F_o|-|F_c|| / \Sigma |F_o| \)

\(^b\) \( wR_2 = \left\{ \Sigma [w(F_o^2-F_c^2)^2] / [w(F_o^2)]^{1/2}, [F_o^2 > 4\sigma(F_o^2)] \right\}^{1/2} \)
Table S3. The crystallographic data and structure refinement for BUT-102.

| Property                        | Value                  |
|---------------------------------|------------------------|
| Formula                         | CdC_{14}H_{11}O_{3}N   |
| $M$                             | 385.64                 |
| Crystal system                  | Triclinic              |
| Space group                     | $\overline{P}$        |
| $a$ / Å                         | 7.6897(3)              |
| $b$ / Å                         | 8.7992(3)              |
| $c$ / Å                         | 12.7198(4)             |
| $\alpha$ / °                   | 87.203(3)              |
| $\beta$ / °                    | 74.302(3)              |
| $\gamma$ / °                   | 76.159(3)              |
| $V$ / Å³                        | 804.39(5)              |
| $Z$                             | 2                      |
| $D_c$ / g cm$^{-3}$             | 1.592                  |
| $\mu$ / mm$^{-1}$               | 11.054                 |
| $T$ / K                         | 292.50(4)              |
| Reflections collected           | 8628                   |
| Independent reflections         | 2871[$R_{int} = 0.0397$, $R_{sigma} = 0.0387$] |
| Goodness-of-fit on $F^2$        | 1.046                  |
| $R_1$, $wR_2$ [I > 2σ(I)]      | $R_1 = 0.0327$, $wR_2 = 0.0836$ |
| $R_1$, $wR_2$ (all data)       | $R_1 = 0.0356$, $wR_2 = 0.0860$ |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.81 / -0.67 |

$^a R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$^b wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2] / [w(F_o^2)^2]\}^{1/2}$, [$F_o > 4\sigma(F_o)$]
Table S4. The crystallographic data and structure refinement for BUT-103.

| Property            | Value                           |
|---------------------|---------------------------------|
| Formula             | Mn$_4$C$_{74}$H$_{78}$O$_{22}$N$_{10}$ |
| $M$                 | 1679.24                         |
| Crystal system      | Monoclinic                      |
| Space group         | $P2_1$                          |
| $a$ / Å             | 10.0867(10)                     |
| $b$ / Å             | 15.6900(2)                      |
| $c$ / Å             | 15.2941(2)                      |
| $\alpha$ / °       | 90                              |
| $\beta$ / °        | 105.4640(10)                    |
| $\gamma$ / °       | 90                              |
| $V$ / Å$^3$         | 2332.82(5)                      |
| $Z$                 | 1                               |
| $D_c$ / g cm$^{-3}$ | 1.351                           |
| $\mu$ / mm$^{-1}$  | 4.963                           |
| $T$ / K             | 293.00(2)                       |
| Reflections collected | 40263                      |
| Independent reflections | 7367 [R$_{int}$ = 0.0302, R$_{sigma}$ = 0.0214] |
| Goodness-of-fit on $F^2$ | 1.074                    |
| $R_1$,$^a$, w$R_2$,$^b$ [$I > 2\sigma(I)$] | $R_1$ = 0.0463, w$R_2$ = 0.1304 |
| $R_1$,$^a$, w$R_2$,$^b$ (all data) | $R_1$ = 0.0472, w$R_2$ = 0.1312 |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.99 / -0.49 |

$^a$ $R_1=\Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$^b$ w$R_2=\{\Sigma[w(F_o^2-F_c^2)^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$, $[F_o>4\sigma(F_o)]$
Table S5. The crystallographic data and structure refinement for BUT-104.

| Property                  | Value                      |
|---------------------------|----------------------------|
| Formula                   | Zr₃C₄₀H₂₆O₁₈N₂             |
| M                         | 1096.25                    |
| Crystal system            | Monoclinic                 |
| Space group               | C2/m                       |
| a / Å                     | 35.346(2)                  |
| b / Å                     | 18.477(4)                  |
| c / Å                     | 18.0998(12)                |
| α / °                     | 90                         |
| β / °                     | 92.956(7)                  |
| γ / °                     | 90                         |
| V / Å³                    | 11805(3)                   |
| Z                         | 4                          |
| Dc / g cm⁻³               | 0.597                      |
| μ / mm⁻¹                  | 2.362                      |
| T / K                     | 173.00(10)                 |
| Reflections collected     | 22058                      |
| Independent reflections   | 9846 [R_int = 0.1807, R_sigma = 0.2013] |
| Goodness-of-fit on F²     | 0.927                      |
| R₁, wR₂ [I > 2σ(I)]      | R₁ = 0.1305, wR₂ = 0.3114 |
| R₁ (all data)             | R₁ = 0.1846, wR₂ = 0.3681 |
| Largest diff. peak and hole (e.Å⁻³) | 3.51 / -1.58 |

\[ R₁ = \frac{\sum |F_o| - |F_c|}{\Sigma |F_o|} \]
\[ wR₂ = \left( \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right)^{1/2}, [F_o > 4\sigma(F_o)] \]
Table S6. The crystallographic data and structure refinement for BUT-105.

| Formula               | Zn₅C₈₀H₅₄O₂₇N₄          |
|-----------------------|-------------------------|
| M                     | 1830.26                 |
| Crystal system        | Trigonal                |
| Space group           | R̅3c                    |
| a / Å                 | 54.3601(10)             |
| b / Å                 | 54.3601(10)             |
| c / Å                 | 42.0659(13)             |
| α / °                 | 90                      |
| β / °                 | 90                      |
| γ / °                 | 120                     |
| V / Å³                | 107652(5)               |
| Z                     | 18                      |
| Dc / g cm⁻³           | 0.492                   |
| μ / mm⁻¹              | 0.780                   |
| T / K                 | 173.01(10)              |
| Reflections collected | 116821                  |
| Independent reflections | 20392 [R_{int} = 0.1084, R_{sigma} = 0.0651] |
| Goodness-of-fit on F² | 1.001                   |
| R₁ᵃ, wR₂ᵇ [I > 2σ(I)] | R₁ = 0.0938, wR₂ = 0.2655 |
| R₁ᵃ, wR₂ᵇ (all data) | R₁ = 0.1460, wR₂ = 0.3082 |
| Largest diff. peak and hole (e.Å⁻³) | 0.35 / -0.40 |

ᵃ R₁ = Σ|F₀|-|F_c|| / Σ|F₀|

ᵇ wR₂ = [Σ[w(F₀²-F_c²)²] / [w(F₀²)]¹/², [F₀ > 4σ(F₀)]
Table S7. The crystallographic data and structure refinement for BUT-106.

| Property                  | Value                           |
|---------------------------|---------------------------------|
| Formula                   | $\text{Cd}_3\text{C}_{160}\text{H}_{112}\text{O}_{48}\text{N}_8$ |
| $M$                       | 3701.54                         |
| Crystal system            | Monoclinic                      |
| Space group               | $\text{C}2/c$                  |
| $a$ / Å                   | 32.872(2)                      |
| $b$ / Å                   | 19.2171(7)                     |
| $c$ / Å                   | 32.400(3)                      |
| $\alpha$ / °              | 90                              |
| $\beta$ / °               | 105.239(9)                     |
| $\gamma$ / °              | 90                              |
| $V$ / Å³                  | 19748(3)                       |
| $Z$                       | 4                               |
| $D_c$ / g cm$^{-3}$       | 1.240                           |
| $\mu$ / mm$^{-1}$        | 6.500                           |
| $T$ / K                   | 173.00(10)                     |
| Reflections collected    | 36069                           |
| Independent reflections  | 17166 [$R_{\text{int}} = 0.0667$, $R_{\text{sigma}} = 0.0931$] |
| Goodness-of-fit on $F^2$ | 0.909                           |
| $R_1$, $wR_2$ $[^{b}[I > 2\sigma(I)]$ | $R_1 = 0.1068$, $wR_2 = 0.2963$ |
| $R_1$, $wR_2$ (all data) | $R_1 = 0.1747$, $wR_2 = 0.3422$ |
| Largest diff. peak and hole (e.Å$^{-3}$) | 1.91 / -0.80 |

$^{a}R_1 = \sum\left|\frac{|F_o| - |F_c|}{\sum|F_o|}\right|$

$^{b}wR_2 = \left\{\sum\left[w(F_o^2 - F_c^2)^2\right] / [\sum w(F_o^2)^2]\right\}^{1/2}$, $[F_o > 4\sigma(F_o)]$
Table S8. The crystallographic data and structure refinement for BUT-107.

| Formula          | InC_{80}H_{44}O_8N_2 |
|------------------|-----------------------|
| $M$              | 1276.06               |
| Crystal system   | Orthorhombic          |
| Space group      | $Pnna$                |
| $a$ / Å          | 32.0315(3)            |
| $b$ / Å          | 28.2049(3)            |
| $c$ / Å          | 19.8600(2)            |
| $\alpha$ / °     | 90                    |
| $\beta$ / °      | 90                    |
| $\gamma$ / °     | 90                    |
| $V$ / Å$^3$      | 17942.4(3)            |
| $Z$              | 8                     |
| $D_C$ / g cm$^{-3}$ | 0.573                  |
| $\mu$ / mm$^{-1}$ | 2.291                  |
| $T$ / K          | 243.00(2)             |
| Reflections collected | 79338              |
| Independent reflections | 15832 [R$_{int}$ = 0.0422, R$_{sigma}$ = 0.0361] |
| Goodness-of-fit on $F^2$ | 1.031               |
| $R_1$, $wR_2^b$ [I > 2$\sigma$(I)] | $R_1$ = 0.0706, $wR_2 = 0.2197$ |
| $R_1$, $wR_2^b$ (all data) | $R_1$ = 0.0804, $wR_2 = 0.2308$ |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.62 / -0.42 |

$^a R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$^b wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2] / [w(F_o^2)^2]\}^{1/2}, [F_o > 4\sigma(F_o)]$
Table S9. The crystallographic data and structure refinement for BUT-108(Zr).

| Property                        | Value                        |
|---------------------------------|------------------------------|
| Formula                         | Zr$_3$C$_{24}$H$_{19}$O$_{20}$B$_3$ |
| $M$                             | 933.50                       |
| Crystal system                  | Tetragonal                   |
| Space group                     | $I4_1/amd$                   |
| $a$/Å                           | 40.5746(8)                   |
| $b$/Å                           | 40.5746(8)                   |
| $c$/Å                           | 17.0198(4)                   |
| $\alpha$/°                      | 90                           |
| $\beta$/°                       | 90                           |
| $\gamma$/°                      | 90                           |
| $V$ / Å$^3$                     | 28019.7(13)                  |
| $Z$                             | 16                           |
| $D_c$/g cm$^{-3}$               | 0.879                        |
| $\mu$/mm$^{-1}$                 | 3.956                        |
| $T$/K                           | 173.00(10)                   |
| Reflections collected           | 26464                        |
| Independent reflections         | 6381 [$R_{int} = 0.0861$, $R_{sigma} = 0.0625$] |
| Goodness-of-fit on $F^2$        | 1.158                        |
| $R_1$, $wR_2$ [I > 2$\sigma$(I)] | $R_1 = 0.1028$, $wR_2 = 0.2872$ |
| $R_1$, $wR_2$ (all data)       | $R_1 = 0.1378$, $wR_2 = 0.3466$ |
| Largest diff. peak and hole (e.Å$^{-3}$) | 1.15 / -2.40 |

$^a R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$^b wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2}, [F_o>4\sigma(F_o)]\}$
Table S10. The crystallographic data and structure refinement for BUT-108(Hf).

| Formula          | Hf₃C₂₄H₁₉O₂₀B₃                          |
|------------------|----------------------------------------|
| $M$              | 1195.30                                |
| Crystal system   | Tetragonal                             |
| Space group      | $I4_1/amd$                             |
| $a / \text{Å}$   | 40.4997(4)                             |
| $b / \text{Å}$   | 40.4997(4)                             |
| $c / \text{Å}$   | 16.9534(4)                             |
| $\alpha / ^\circ$| 90                                     |
| $\beta / ^\circ$| 90                                     |
| $\gamma / ^\circ$| 90                                     |
| $V / \text{Å}^3$ | 27807.4(9)                             |
| $Z$              | 16                                     |
| $D_C / \text{g cm}^{-3}$ | 1.136              |
| $\mu / \text{mm}^{-1}$ | 8.422          |
| $T / \text{K}$   | 293.00(2)                              |
| Reflections collected | 42600                  |
| Independent reflections | 6304 [R$_{int} = 0.0542$, R$_{sigma} = 0.0344$] |
| Goodness-of-fit on $F^2$ | 1.074          |
| $R_1^a$, $wR_2^b$ [$I > 2\sigma(I)$] | $R_1 = 0.0593$, $wR_2 = 0.1742$ |
| $R_1^a$, $wR_2^b$ (all data) | $R_1 = 0.0673$, $wR_2 = 0.1842$ |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.83 / -1.55 |

$^a R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$

$^b wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / [\Sigma w(F_o^2)^2] \}^{1/2}$, $[F_o > 4\sigma(F_o)]$
Table S11. The crystallographic data and structure refinement for BUT-109(Zr).

| Formula       | Zr₆C₈₄H₅₈O₄₄N₆  |
|---------------|------------------|
| M             | 2402.73          |
| Crystal system| Cubic            |
| Space group   | Im3m             |
| a / Å         | 19.225(2)        |
| b / Å         | 19.225(2)        |
| c / Å         | 19.225(2)        |
| α / °         | 90               |
| β / °         | 90               |
| γ / °         | 90               |
| V / Å³        | 7105(2)          |
| Z             | 2                |
| Dc / g cm⁻³   | 1.107            |
| μ / mm⁻¹      | 4.047            |
| T / K         | 173.01(10)       |
| Reflections collected | 2875          |
| Independent reflections | 601 [Rint = 0.0958, Rsigma = 0.0488] |
| Goodness-of-fit on $F^2$ | 0.968          |
| $R_1$, $wR_2$ [I > 2σ(I)] | $R_1 = 0.1105$, $wR_2 = 0.2898$ |
| $R_1$, $wR_2$ (all data) | $R_1 = 0.1510$, $wR_2 = 0.3488$ |
| Largest diff. peak and hole (e.Å⁻³) | 0.91 / -0.64 |

*a $R_1=\Sigma||F_o|-|F_c|| / \Sigma|F_o|$  

*b $wR_2=\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]^{1/2}$, [F_o>4σ(F_o)]
S5. Powder X-ray diffraction

Fig. S11 PXRD patterns for (a) BUT-101(Cu), (b) BUT-101(Zn), (c) BUT-102, and (d) BUT-103.

Fig. S12 PXRD patterns for (a) BUT-104, (b) BUT-105, (c) BUT-106, and (d) BUT-107.
S6. Activation of the MOF samples

Before NMR, N$_2$ adsorption, FT-IR and TGA measurements, a suspension of as-synthesized sample (about 80 mg for each sample of BUT-101~109) in 10 mL fresh DMF was placed in a centrifuge tube and heated at 80 °C for 24 h in a conventional oven. The sample was soaked in acetone (10 mL) for 2 days at room temperature, when fresh solvents were exchanged every 12 h. The sample was collected by decanting and dried in air. Before tests, the dry sample was loaded in a sample tube and further activated under high vacuum at the temperature of 60 °C for 5 h.

S7. FT-IR

FT-IR spectra of samples for BUT-101~109 were recorded in comparison with the precursors, respectively, to test the coordination between newly formed ligands to metal species in the solvo-thermal reaction, as shown in Fig. S14~S17.
Fig. S14 FT-IR spectra of H$_2$L6' and BUT-101~103.

Fig. S15 FT-IR spectra of H$_2$L7' and BUT-104~107.
**Fig. S16** FT-IR spectra of HL8’ and BUT-108.

**Fig. S17** FT-IR spectra of HL9’, L9” and BUT-109.

**S8. TGA**

To evaluate the thermal stability of BUT-101~109, TGA measurements of their samples were conducted and resulted curves are shown in Fig. S18.
S9. Elemental Analysis

After activation and evacuation of BUT-101–109 samples, their elemental analyses were measured.

BUT-101(Cu): Anal. Calc. for CuC_{14}H_{13}NO_{6} C, 47.39; H, 3.69; N, 3.95; found C, 47.31; H, 3.78; N, 3.89.

BUT-101(Zn): Anal. Calc. for ZnC_{14}H_{13}NO_{6} C, 47.15; H, 3.67; N, 3.93; found C, 47.11; H, 3.76; N, 3.90.

BUT-102: Anal. Calc. for CdC_{14}H_{11}NO_{5} C, 43.60; H, 2.88; N, 3.63; found C, 43.65; H, 2.94; N, 3.57.

BUT-103: Anal. Calc. for Mn_{4}C_{74}H_{76}N_{10}O_{22} C, 52.93; H, 4.68; N, 8.34; found C, 52.88; H, 4.80; N, 8.38.

BUT-104: Anal. Calc. for Zr_{3}C_{40}H_{26}N_{2}O_{18} C, 43.82; H, 2.39; N, 2.56; found C, 43.87; H, 2.51; N, 2.49.
BUT-105: Anal. Calc. for Zn₅C₈₀H₅₄N₄O₂₇ C, 52.50; H, 2.97; N, 3.06; found C, 52.41; H, 3.07; N, 3.02.

BUT-106: Anal. Calc. for Cd₇C₁₆₀H₄₁₂N₈O₄₈ C, 51.92; H, 3.05; N, 3.03; found C, 51.89; H, 3.23; N, 2.95.

BUT-107: Anal. Calc. for InC₈₀H₄₄N₂O₈ C, 75.30; H, 3.48; N, 2.20; found C, 75.43; H, 3.57; N, 2.16.

BUT-108(Zr): Anal. Calc. for Zr₃C₂₄H₁₉B₃O₂₀ C, 30.88; H, 2.05; found C, 30.79; H, 2.27.

BUT-108(Hf): Anal. Calc. for Hf₃C₂₄H₁₉B₃O₂₀ C, 24.12; H, 1.60; found C, 24.03; H, 1.83.

BUT-109(Zr): Anal. Calc. for Zr₆C₈₄H₅₈N₆O₄₄ C, 41.99; H, 2.43; N, 3.50; found C, 42.07; H, 2.84; N, 3.41.

BUT-109(Hf): Anal. Calc. for Hf₆C₈₄H₅₈N₆O₄₄ C, 34.48; H, 2.00; N, 2.87; found C, 34.33; H, 2.35; N, 2.71.

S10. 'H NMR Test

The 'H NMR spectra of H₂L₆', H₂L₇' and HL₈' precursors are shown in Fig. S19, S21 and S24. Before NMR test, the activated samples of BUT-101(Zn) and -108(Zr) (about 20 mg for each) were immersed into a mixture of six drops of DCl (37%) and 0.5 mL of DMSO-d₆, and ultrasonically dissolved, respectively. The samples of BUT-104—107 were similarly treated with D₂SO₄ (98%)/DMSO-d₆. Then the uniform samples were used for 'H NMR test. From the spectra it was found that L7-a and -d (in BUT-104 and -107) as well as L7-b and -c (in BUT-105 and 106) have similar NMR peaks, indicating their same identity. Therefore, spectra of L7-a and -b were taken as the example, respectively. The recorded spectra of L6 (in BUT-101(Zn)), L7-a (in BUT-104), L7-b (in BUT-105), and acidized L8 (in BUT-108(Zr)) are as represented in Fig. S20, S22, S23 and S25. Regrettably, massive efforts on dissolving samples of BUT-109(Zr) and -109(Hf) with various reagents and solvents have failed due to the extremely poor solubility of bulky L9 ligand.
Fig. S19 $^1$H NMR spectrum of H$_2$L6$'$.

Fig. S20 $^1$H NMR spectrum of L6.
Fig. S21 $^1$H NMR spectrum of $\text{H}_2\text{L}^7'$.

Fig. S22 $^1$H NMR spectrum of L7-a.
Fig. S23 $^1$H NMR spectrum of L7-b.

Fig. S24 $^1$H NMR spectrum of HL8'.
Fig. S25 $^1$H NMR spectrum of acidized L8.