Supporting information

A Mixed Ligand Route for Construction of Tetrahedrally Coordinated Lithium Frameworks

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Experimental details:

Synthesis of bis(imidazolyl)methane: In a 250 ml flask, 17.984 g NaOH, 4.752 g imidazole and 441 mg tetraethylammonium bromide (TEAB) were dissolved in a mixed solution of 25 g H_2O and 100 ml methylene chloride. The solution was stirred and heated under reflux condition for about 24 hours and white precipitate forms. Extraction was performed thereafter by adding extra methylene chloride and water. The product was obtained by rotating evaporation of the extract.

Synthesis of bis(2-methylimidazolyl)methane: The synthesis of bis(2-methylimidazolyl)methane is very similar to its imidazolyl analogue. However, the imidazole was replaced by 5.743 g 2-methylimidazole and the reaction time became approximate 72 hours.

Synthesis of Li(bim)[CH$_2$(im)$_2$] (MVLIF-1): 88 mg Li_2S, 91 mg CH$_2$(im)$_2$ and 73 mg benzimidazole was loaded in a 20 ml Teflon-lined vial and 5.158 g of anhydrous acetonitrile solvent was added. After stirring for 4 hours, the resulted turbid solution was placed in a 90 °C oven. In about 72 hours, the vial was allowed to cool at room temperature and large amount of colorless crystals were obtained.

Synthesis of Li(im)[CH$_2$(mim)$_2$] (MVLIF-2): 48.5 mg Li_2S, 55.3 mg CH$_2$(mim)$_2$ and 22.3 mg imidazole was loaded in a 20 ml Teflon-lined vial and 5.121 g of anhydrous acetonitrile solvent was added. After stirring for 4 hours, the resulted turbid solution was placed in a 120 °C oven. In about 48 hours, the vial was allowed to cool at room temperature and large amount of colorless crystals were obtained.

Powder X-ray diffraction: Powder X-ray diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 30kV and 30mA (Cu Kα radiation, λ = 1.5418Å). The data collection was performed with a step size of 0.03° and counting time of 3s per step. The 2-theta angular range is from 5 to 40°.

Single crystal X-ray diffraction: Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated MoKλ radiation (λ = 0.71073 A), operating in the λ and λ scan mode. The SADABS program was used for absorption correction. The structure was solved by direct methods followed by successive difference Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SHELXTL and final full-matrix refinements were against F^2.[1]

Gas sorption measurements: H_2 gas sorption experiments were carried out on a Micromeritics ASAP 2010 surface area and pore size analyzer. Prior to the measurement, powder samples of MVLIF-1 and MVLIF-2 were dried by using the “degas” function of the surface area analyzer for 20 hours at 160 °C and 140 °C, respectively. The H_2 sorption measurements were performed at 77K.

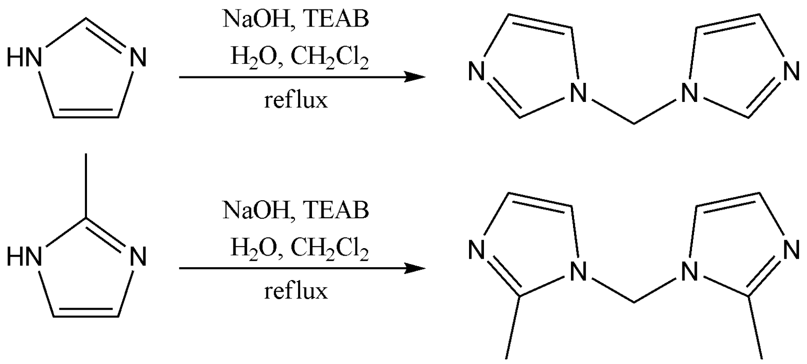
References:

[1] G. M. Sheldrick, *SHELX97—Programs for Crystal Structure Analysis*, release 97–2; Institüt für Anorganische Chemie der Universität Göttingen, Göttingen, Germany, **1998**.

Table S1. Summary of Crystal Data and Structural Refinement Results of MVLIF-*n*

	MVLIF-1	MVLIF-2
formula [a]	Li(bim)[CH_2(im)$_2$]	Li(im)[CH_2(mim)$_2$]
FW	272.24	250.24
crystal system	Trigonal	orthorhombic
space group	$P3_2$	$P2_12_12_1$
a, Å	8.9721(8)	9.23(4)
b, Å	8.9721(8)	9.46(4)
c, Å	15.304(3)	14.73(6)
α, deg	90	90
β, deg	90	90
γ, deg	120	90
V, Å^3	1066.9(2)	1287(10)
Z	3	4
d_{calcd}, g cm^{-3}	0.766	0.778
R_1, wR_2 [b]	0.0300, 0.0680	0.0540, 0.1312
net [c]	qzd	dia

[a] bim = benzimidazolyl; im = imidazolyl; mim = 2-methylimidazolyl. [b] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$ and $wR_2 = \{\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [c] For definitions of three-letter abbreviation, see Reticular Chemistry Structure Resource (http://rcsr.anu.edu.au/).



Scheme S1. Synthesis of the bis(imidazolyl)methane and bis(2-methyl-imidazolyl)methane.

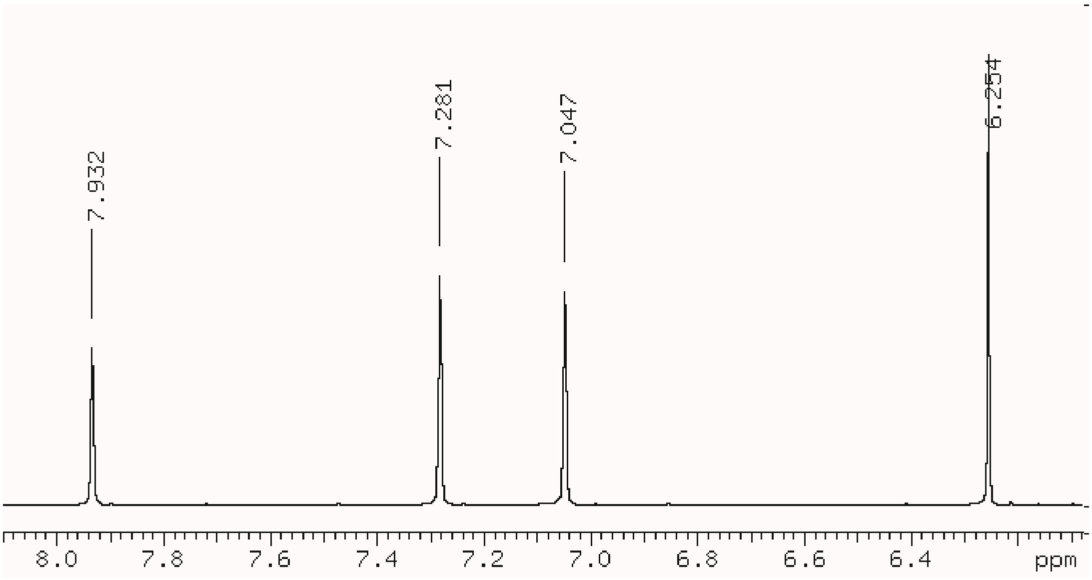


Figure S1. ^{1}H NMR spectra of ligand bis(imidazolyl)methane (100mM in D_2O, pH=9.90).

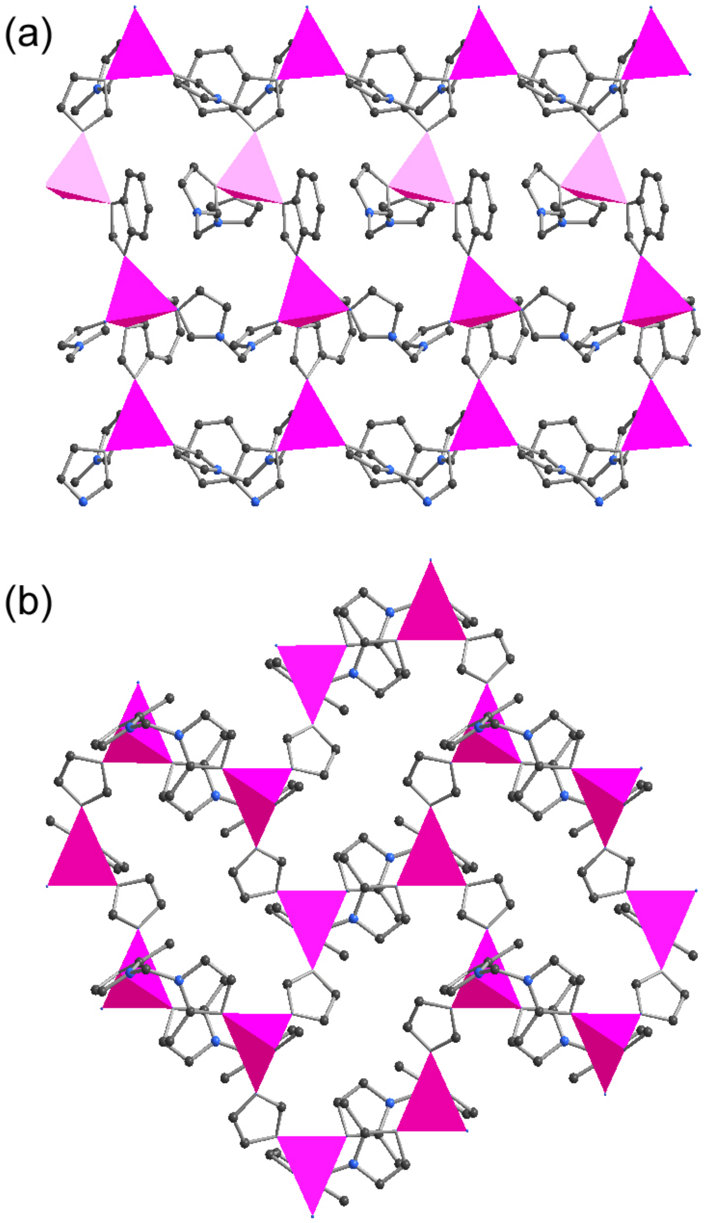
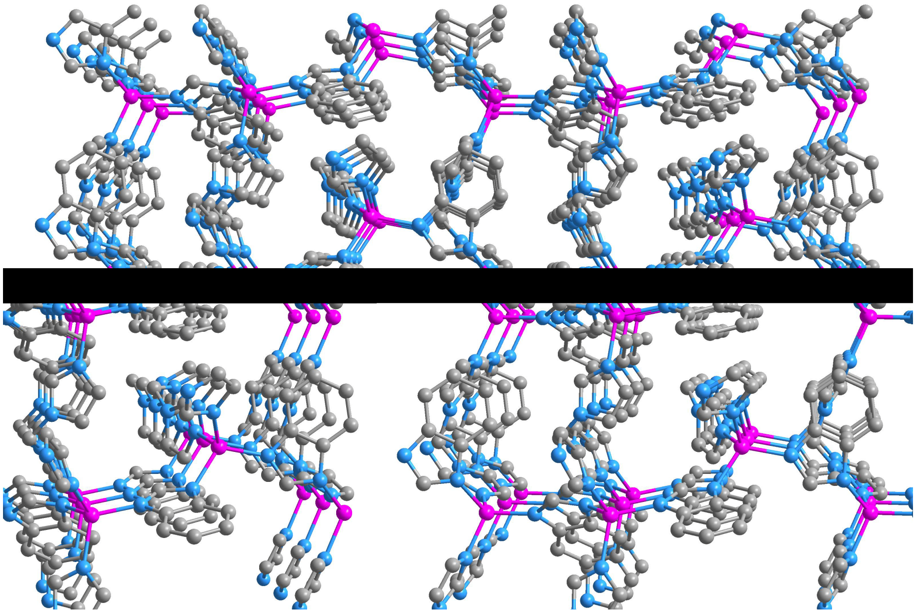


Figure S2. Framework structures of (a) MVLIF-1 and (b) MVLIF-2. (purple tetrahedron: LiN$_4$; blue: N; black: C)



[redacted]

Figure S3. Perspective view of 3D structure of MVLIF-1 along a axis direction.

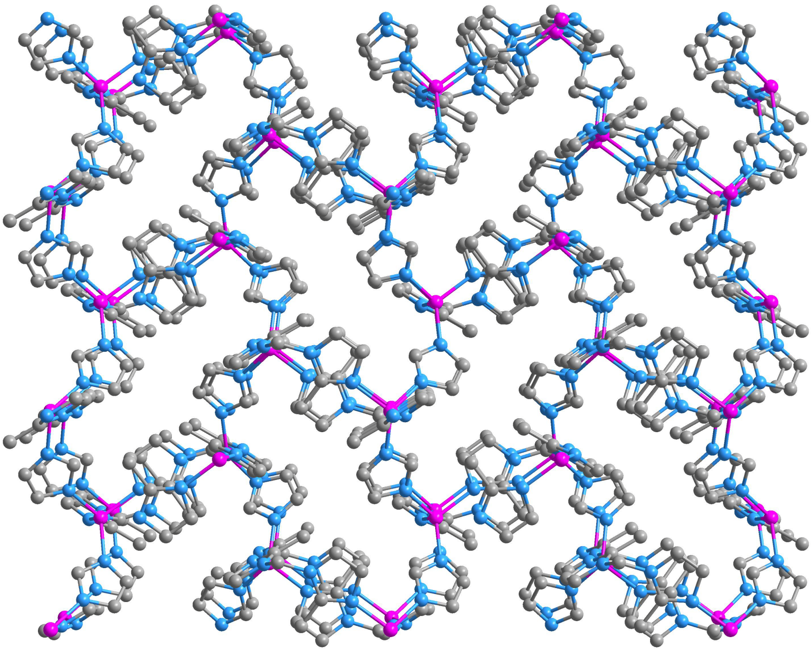


Figure S4. Perspective view of 3D structure of MVLIF-2 along a axis direction.

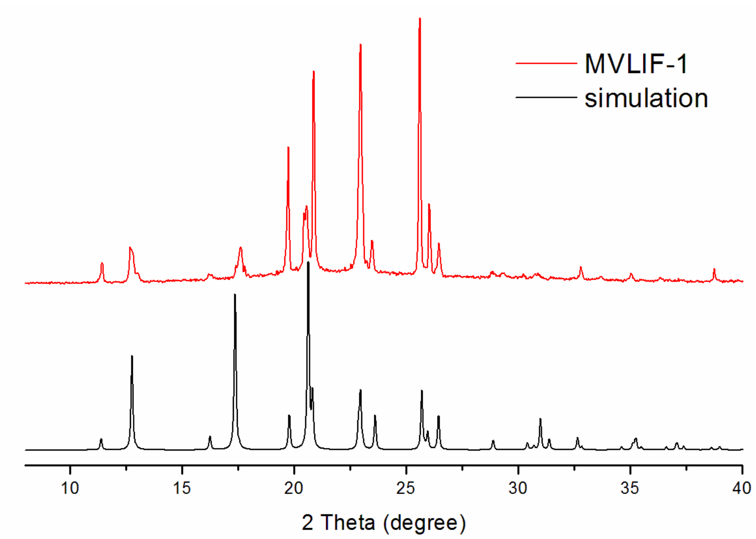


Figure S5. Powder XRD pattern of MVLIF-1. (red: as-synthesized sample; black: simulation)

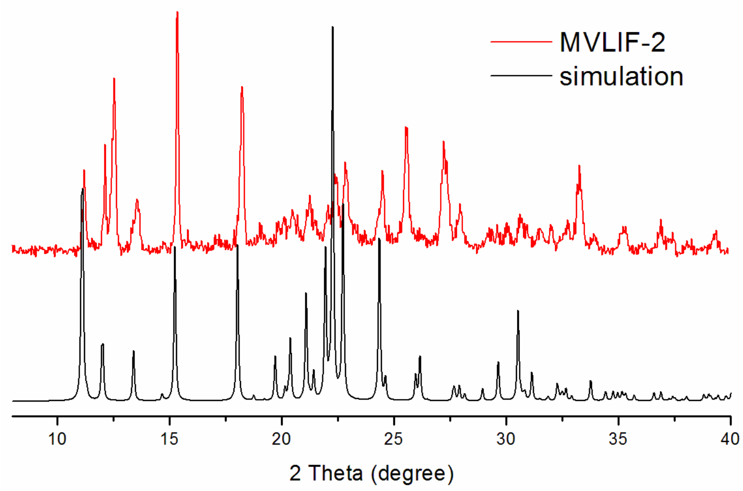


Figure S6. Powder XRD pattern of MVLIF-2. (red: as-synthesized sample; black: simulation). A minor unidentified phase is present as shown by an extra peak at about 12 degree.

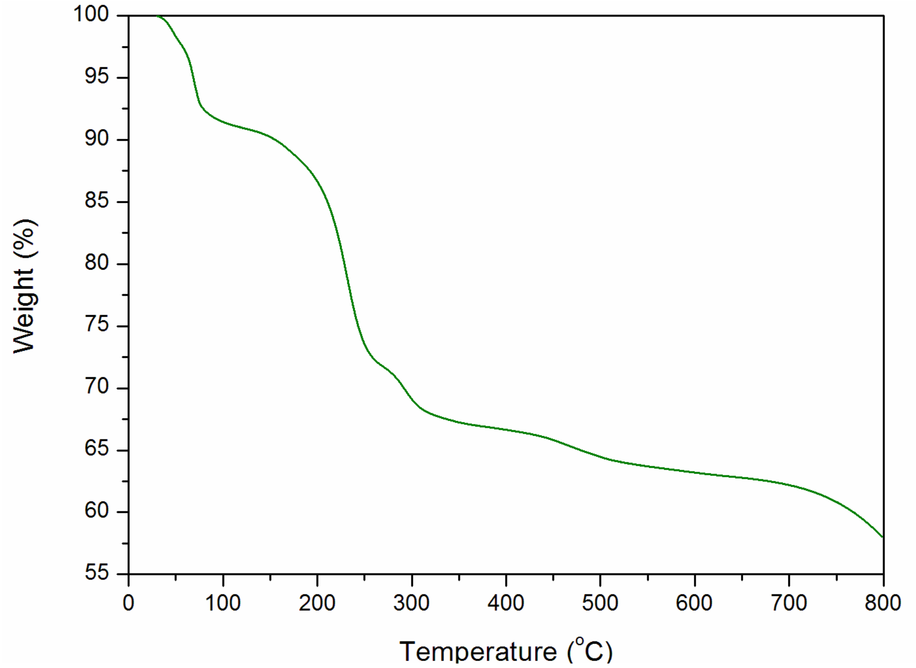


Figure S7. Thermogravimetric analysis for MVLIF-2.