ChemComm



COMMUNICATION

View Article Online

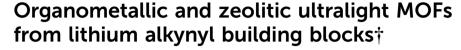


Cite this: Chem. Commun., 2025. **61**. 11637

Received 28th February 2025, Accepted 23rd June 2025

DOI: 10.1039/d5cc01112d

rsc.li/chemcomm



Ruichen Zhang, Tom O'Brien, Fauzi Abdilah, Dab Andrew J. P. White, a Paul D. Lickiss Da and Robert P. Davies **

Organometallic lithium-carbon(alkynyl) secondary building units have been used to construct a range of novel one-, two-, and threedimensional lithium metal organic framework (MOF) materials. The 3D Li-MOF exhibits a zeolitic Ita topology, and is notable for its low density and high theoretical porosity.

Over the past two decades, the field of metal-organic frameworks (MOFs) and related reticular structures has experienced significant growth with the MOF subset in the CSDS database now comprising of over 120 000 structures (Database CSD version 5.44 Jun 2023).¹ The majority of these MOFs are constructed from transition metal centers or nodes combined with organic linkers based on carboxylic acids or nitrogen-containing heterocycles. However, a smaller subset of lithium-based MOFs has been explored as 'ultralight' materials for portable applications, such as hydrogen or methane storage, where weight is often a critical factor.^{2,3} These lithium MOFs have often employed carboxylic acid or nitrogen-based heterocycle linkers repurposed from transition metal MOF studies, and as a result commonly contain extended (1D, 2D or even 3D) rather than discrete (0D) metal-based nodes.^{4,5} This can lead to minimal or no porosity in the resultant materials. By leveraging alternative functionalities and adapting well-known lithium stacking and laddering principles, we aim to generate discrete lithium secondary building units (Li SBUs) that can be assembled into innovative ultralight porous MOF materials.

In the work reported herein the use of organometallic lithium acetylide based clusters for MOF construction is explored. In addition to offering a potential new pathway to ultralight MOF materials, this research aims to enhance our

understanding of aggregation modes for lithium acetylides which are less studied compared to those for lithium amides, imides, and aryl/alk-oxides.6 Moreover, the use of metal carbon bonds for MOF construction remains largely unexplored, with the first examples of metal acetylide MOFs only recently reported for copper(I)⁷ and silver(I)⁸ materials.

Initial efforts focussed upon building lithium acetylide secondary building units (SBUs) and then connecting these together to form coordination networks using 1,4-dioxane as a bridging ligand. Using this approach, the oxygen atoms in the dioxane can act as Lewis base donors to diametrically opposed lithium cations, thus acting as linkers for adjacent SBUs. A similar approach has previously been shown to be successful by Henderson and colleagues for the assembly of Li₄(OAr)₄ cubane clusters into networks.9,10

Three acetylenes - phenylacetylene, trimethylsilylacetylene, and cyclopropylacetylene - were initially examined. Metallation of the acetylene with nBuLi in a mixed hexane-dioxane solvent followed by recrystallisation led to the formation of three corresponding coordination network/MOF structures (IMP-35, IMP-36 and IMP-37) which have been characterised using single crystal X-ray diffraction (see ESI† for full details). Each new Li-MOF contains a unique lithium acetylide SBU determined in part by the steric and electronic requirements of the original acetylene.

 $[\text{Li}_2(C \equiv \text{CPh})_2(\text{dioxane})_2]$ (IMP-35) contains dimeric SBUs based upon four-membered Li₂C₂ rings (Fig. 1a). The carbanion centres on the acetylide asymmetrically bridge two lithium cations. A similar dimeric motif has been previously reported for $[LiC \equiv CPh(tmpda)]_2$ where tmpda is the bidentate ligand *N,N,N',N'*-tetramethyl-1,3-propanediamine. ¹¹ Each lithium in IMP-35 coordinates to two oxygen atoms from two different dioxane molecules. These dioxanes sit almost perpendicular to the Li₂C₂ rings and form double bridges to adjacent SBUs to give a 1D polymeric motif (Fig. 1b). These 1D chains are aligned along the crystallographic 100 direction with voids between the chains containing additional non-coordinated dioxane molecules (one per SBU, see ESI†).

^a Department of Chemistry, Molecular Sciences Research Hub, Imperial College White City Campus, Wood Lane, London W12 0BZ, UK. E-mail: r.davies@imperial.ac.uk

^b Department of Chemical Engineering, Politeknik Negeri Bandung, Bandung 40559, Indonesia

[†] Electronic supplementary information (ESI) available: Full experimental and crystallographic details. CCDC 2383649-2383652. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/

Communication ChemComm

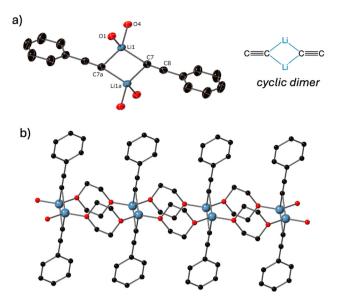


Fig. 1 (a) Molecular structure of the SBU in IMP-35 and a simplified schematic of its core. Thermal ellipsoids shown at 40% probability. (b) View of a section of the extended 1D structure in IMP-35. C: black, O: red, Li: grey blue, H atoms are omitted for clarity.

In contrast $[\text{Li}_4(C \equiv \text{CSiMe}_3)_4(\text{dioxane})_3]$ (IMP-36) is built from tetrametallic SBUs based upon a four-rung ladder structural motif (Fig. 2a). Although aggregation via laddering is well known for lithium amides (LiNR_2) , as far as we are aware this is the first example of laddering in lithium acetylide chemistry. Each lithium is four coordinate, with the outer lithium cations (Li1 and Li4) coordinated by two acetylide and two dioxane molecules and the inner lithium cations (Li2 and Li3) by three acetylides and one dioxane. The six dioxane molecules form

linkages to four adjacent SBUs via two double bridges (similar to those observed in IMP-35) and two single bridges. This results in the formation of a 2D square grid material (Fig. 2b) with $\rm Li_4C_4$ SBU nodes and $\rm sql$ topology. Additional non-coordinated dioxane molecules are sited in the pores (one per SBU, see ESI†).

Use of the less sterically bulky cyclopropylacetylene gave the novel structure $[Li_8(C \equiv CC_3H_4)_8(dioxane)_4]$ (IMP-37). In this material two Li₄C₄ hetero-cubanes are joined together along one edge to form an octametallic Li₈C₈ SBU (Fig. 3a). Cubane formation for lithium acetylides has been previously reported in the literature, for example in the structures of $[(LiC \equiv CPh)_4(tmhda)_2]^{13}$ and $[(LiC \equiv CtBu)_4(thf)_4]^{14}$. In addition, the fusion of several cubanes to form extended aggregates has also been documented for the decamer [(LiC= $CtBu)_{10}(Et_2O)_4^{15}$ and dodecamer $[(LiC \equiv CtBu)_{12}(thf)_4]^{14}$ However, in these previously reported structures the heterocubanes are face sharing (also referred to as stacking of cyclic Li₂C₂ units¹⁶), rather than the novel edge sharing motif seen in IMP-37. Each lithium cation in IMP-37 is four coordinate, with six of the eight lithium cations (those in the non-edge sharing positions - Li1, Li2 and Li3) also coordinating to the oxygen centre of a dioxane molecule. Four of these six dioxanes then bridge to neighbouring Li SBUs, whilst the other two dioxanes are mono-coordinate and hence topologically redundant. This gives an overall 2D layered network structure for IMP-37 (Fig. 3b). Considering each Li SBU as a separate fourconnecting topological point allows assignment as sql topology.12

Encouraged by these initial attempts, we then sought to incorporate the Lewis donor site into the acetylide unit itself, thus negating the need for additional dioxane molecules to

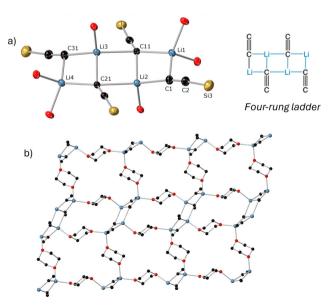


Fig. 2 (a) Molecular structure of the SBU in **IMP-36** and a simplified schematic of its core. Thermal ellipsoids shown at 40% probability. (b) View of a section of the extended 2D sheets in **IMP-36**. C: black, O: red, Li: grey blue, Si: gold, H atoms are omitted for clarity.

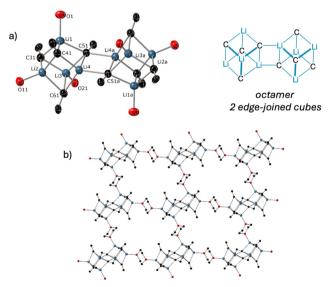


Fig. 3 (a) Molecular structure of the SBU in IMP-37 and a simplified schematic of its core. Thermal ellipsoids shown at 30% probability. (b) View of a section of the extended 2D sheets in IMP-37 with cyclopropyl groups and non-bridging dioxanes omitted for clarity. C: black, O: red, Li: grey blue, H atoms are omitted for clarity.

a)

ChemComm

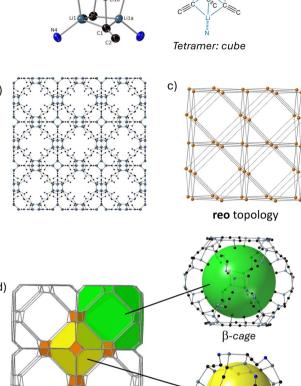


Fig. 4 (a) Molecular structure of the SBU in IMP-38 and a simplified schematic of its core. Thermal ellipsoids shown at 30% probability; (b) view of a section of the extended 3D structure in IMP-38 with cyclopropyl groups and non-bridging dioxanes omitted for clarity. (c) Topological map assuming unimodal 8-c nodes based on Li₄C₄ cubanes; (d) topological map for IMP-28 in which individual metal and carbonanion centres act as 4-c nodes. C: black, N: blue, Li: grey blue, H atoms are omitted for clarity.

Ita topology

connect the SBUs. Hence, metalation of 3-dimethylamino-1propyne containing a Lewis Basic amine functionality led to the new 3D-periodic structure [Li₄(C \equiv CCH₂NMe₂)₄] **IMP-38.** Interestingly this MOF material could be obtained from a range of different solvent systems, including in the presence of coordinating solvents such as dioxane without any dioxane incorporation into the 3D network.

Initial inspection of IMP-38 reveals the presence of Li₄C₄ cubane SBUs (Fig. 4a). As well as bridging three acetylide carbanions, each lithium cation in the SBU is also coordinated by the nitrogen atom of an adjacent dimethylaminopropynide unit. This results in the assembly of the cubic 8-connected SBUs into a 3D-periodic structure (Fig. 4b) with reo topology and point symbol (38.48.58.64) (Fig. 4c). However, a more holistic view of IMP-38 in which the individual lithium and carbanion centres are considered as individual topological nodes, reveals

a lta topology (Fig. 4d), which although well known in zeolite chemistry is currently rare for MOF materials. This topology is based upon Linde Type A zeolite where Li cations in IMP-38 are surrogate for the Al cations in the zeolite, acetylide carbanions for Si, and the bent CCH₂NMe₂ unit (C-C-N bond angle 114.6°) a direct replacement for the di-coordinate oxygen. The α and β (sodalite) zeolite cages can be clearly identified within the MOF (Fig. 4d) with approximate diameters of 13.0 and 11.6 Å respectively (shortest atom to atom distance).

IMP-38 is amongst the most porous of all Li-MOFs reported to date with a calculated void volume of 29.1%,17 a calculated gravimetric surface area of 534 m² g⁻¹ (volumetric surface area = $431 \text{ m}^2 \text{ cm}^{-3}$)¹⁸ and a density of 0.806 g cm⁻³ assuming removal of all non-coordinated solvents from within the pores. The maximum pore diameter is 8.62 Å with a pore limiting diameter of 2.53 Å, 18 suggesting it is well suited for potential applications in dihydrogen storage, but less so for larger molecules such as CO2. However, despite these promising theoretical porosity values, it has not been possible to verify them experimentally since IMP-38 undergoes rapid decomposition in air/moisture leading to the formation of LiOH as shown using powder diffraction studies (see Fig. S2.5, ESI†). Despite this we believe this work presents a significant advance in the field of MOF chemistry, being the first example of a new class of zeolitic ultralight Li-MOF material. Studies to extrapolate this work to other metals and linkers using a reticular approach are currently underway, with a goal to improve the stability and porosity of the resultant MOFs to enable practical applications.

We thank Indonesia Endowment Fund For Education (LPDP) for funding (PhD Scholarship to F.A.).

Conflicts of interest

There are no conflicts to declare.

Data availability

Experimental data supporting this article have been included as part of the ESI.† Crystallographic data for IMP-35, IMP-36, IMP-37 and IMP-38 has been deposited at the Cambridge Crystallographic data centre (CCDC) under numbers 2383649 to 2383652, respectively. Additional information on the data refinements is included in the ESI.†

References

- 1 P. Z. Moghadam, A. Li, S. B. Wiggin, A. Tao, A. G. P. Maloney, P. A. Wood, S. C. Ward and D. Fairen-Jimenez, Chem. Mater., 2017, 29, 2618-2625.
- 2 M. A. Alnaqbi, A. Alzamly, S. H. Ahmed, M. Bakiro, J. Kegere and H. L. Nguyen, J. Mater. Chem. A, 2021, 9, 3828-3854.
- 3 D. Banerjee and J. B. Parise, Cryst. Growth Des., 2011, 11, 4704-4720.
- 4 D. Pugh, E. Ashworth, K. Robertson, L. C. Delmas, A. J. P. White, P. N. Horton, G. J. Tizzard, S. J. Coles, P. D. Lickiss and R. P. Davies, Cryst. Growth Des., 2018, 19, 487–497.
- 5 B. F. Abrahams, M. J. Grannas, T. A. Hudson and R. Robson, Angew. Chem., Int. Ed., 2010, 49, 1087-1089.
- 6 R. E. Mulvey, Chem. Soc. Rev., 1991, 20, 167-209.

Communication ChemComm

- 7 L. Jiang, J. Jia, Y. Ma, Y. Tian, X. Zou and G. Zhu, Chem, 2024, 10, 557-566.
- 8 L. Jiang, L. Lin, Z. Wang, H. Ai, J. Jia and G. Zhu, J. Am. Chem. Soc., 2024, 146, 22930-22936.
- 9 D. J. MacDougall, J. J. Morris, B. C. Noll and K. W. Henderson, Chem. Commun., 2005, 456-458.
- J. J. Morris, D. J. Macdougall, B. C. Noll and K. W. Henderson, Dalton Trans., 2008, 3429-3437.
- 11 B. Schubert and E. Weiss, Chem. Ber., 2006, 116, 3212-3215.
- 12 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, Acc. Chem. Res., 2008, 41, 1782-1789.
- 13 B. Schubert and E. Weiss, Angew. Chem., Int. Ed., 2003, 22, 496-497.
- 14 M. Geissler, J. Kopf, B. Schubert, E. Weiss, W. Neugebauer and P. V. R. Schleyer, Angew. Chem., Int. Ed., 2003, 26, 587-588.
- 15 A. M. Borys and E. Hevia, Chem. Commun., 2023, 59, 7032-7035.
- 16 D. R. Armstrong, D. Barr, R. Snaith, W. Clegg, R. E. Mulvey, K. Wade and D. Reed, J. Chem. Soc., Dalton Trans., 1987, 1071-1081.
- 17 A. L. Spek, Acta Crystallogr., 2015, C71, 9-18.
- 18 C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, J. Appl. Crystallogr., 2020, 53, 226-235.