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A Family of Porous Lonsdaleite-e Networks Obtained through Pillaring of Decorated Kagomé Lattice Sheets

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Ⓢ *Supporting Information*

ABSTRACT: A new and versatile class of metal−organic materials (MOMs) with augmented lonsdaleite-e (**lon-e**-a) topology is presented herein. This family of **lon-e** nets are built by pillaring of hexagonal two-dimensional kagomé (**kag**) lattices constructed from well-known $[Zn_2(CO_2R)_4]$ paddlewheel molecular building blocks (MBBs) connected by 1,3-benzenedicarboxylate (bdc^{2-}) linkers. The pillars are $[Cr_3(\mu_3\text{-}O)(RCO_2)]_6$ trigonal prismatic primary MBBs decorated by six pyridyl moieties (tp-PMBB-1). The three-fold symmetry (D_{3h}) of tp-PMBB-1 is complementary with the alternating orientation of the axial sites of the paddlewheel MBBs and enables triple cross-linking of the **kag** layers by each pillar. These MOMs represent the first examples of axial-to-axial pillared undulating **kag** layers, and they are readily fine-tuned because the bdc^{2-} moieties can be varied at their 5-position without changing the overall structure. This **lon-e** platform possesses functionalized hexagonal channels since the **kag** lattices are necessarily eclipsed. The effects of the substituent at the 5-positions of the bdc^{2-} linkers upon gas adsorption, particularly the heats of adsorption of carbon dioxide and methane, were studied.

Metal−organic materials (MOMs) assembled from metal ions or clusters (nodes) and organic multifunctional ligands have attracted considerable scientific interest over the past two decades. In particular, the modular nature of their structure and the resulting ability to fine-tune properties (especially extra-large surface area) have rendered them as promising candidates for a variety of potential applications.[1] In comparison to other classes of porous materials (e.g., zeolites), the pore dimension and functionality of MOMs are both amenable to fine-tuning by applying well-established crystal engineering strategies. This ability to control structure has thus far been particularly fruitful in development of materials for gas purification and storage, catalysis, small-molecule separations, and chemical sensing.

Whereas the design of the structure of MOMs gained momentum following Robson's seminal contributions over 20 years ago,[2] exponential growth over the past decade can be attributed to the discovery of permanent porosity in MOMs by Kitagawa[3] and Yaghi.[4] These reports were quickly followed by the discovery that metal−carboxylate clusters could serve as nodes for the generation of frameworks with extra-large surface area.[5] In this context, the following metal carboxylate clusters are particularly versatile at sustaining families of MOMs: 4-c "square paddlewheels" $[M_2(RCO_2)_4]$;[6] 6-c "basic zinc acetate" octahedra $[Zn_4(\mu_4\text{-}O)(RCO_2)_6]$;[5a,b] 6-c trigonal prisms $[M_3(\mu_3\text{-}O)(RCO_2)]_6$ (M = Cr, Fe);[5g,7] and 12-c $[Zr_6O_4(OH)_4(RCO_2)_{12}]$[8] clusters. Several of the families of networks sustained by these clusters might be described as platforms since their network topology is robust enough to allow systematic structure/property studies. Examples of such MOM platforms include **pcu**,[5b] **tbo**,[6,9] **nbo**,[10]and **rht**[5f,11] topology nets. In this context, pillared MOMs are of special interest since they potentially allow the variation of more than one component and thus further increase the possibilities for systematic fine-tuning. Axial-to-axial pillared square grids with **pcu** topology are exemplified by hexafluorosilicate ("SIFSIX") nets[12] and pillared paddlewheel nets ("DMOFs").[13] In these platforms, the axial-to-axial pillaring strategy usually results in saturated metal centers (SMCs). In contrast, ligand-to-ligand pillaring can be accomplished with cross-linked 1,3-benzenedicarboxylate (bdc^{2-}) linkers which typically afford **lvt** or **nbo** topology nets with unsaturated metal centers (UMCs) when square grid (**sql**)[14] or hexagonal 2-periodic kagomé lattices (**kag**)[15] are pillared, respectively.[10]

In this contribution, we report a new approach to pillaring of **kag** nets that involves self-assembly of **kag** lattices and $[Cr_3(\mu_3\text{-}O)(RCO_2)]_6$ trigonal prismatic primary molecular building blocks (MBBs) decorated by six pyridyl moieties (tp-PMBB-1).[16] **kag** nets based upon paddlewheel MBBs[15] are an attractive target for study since they can be readily fine-tuned through the 5-position of bdc^{2-}[17] or through the use of related angular linkers.[18] The 5-position of bdc^{2-} linkers can also be used for ligand-to-ligand pillaring of **kag** layers, which usually affords **nbo** (or **fof**) nets,[10] but can also result in **ssa** (or **sty**)[19] nets, among others. The relationship between **nbo**/**fof**[20] and **ssa**/**sty**[19a] nets is addressed in the Supporting Information (SI). A recently reported method using angular or partially flexible trigonal heterofunctional ligands resulted in **rtl**-type networks[21] sustained by ligand-to-axial pillared **kag** nets. An axial-to-axial pillaring strategy by connection of UMCs similar to that which sustains SIFSIX nets and DMOFs has been reported in the case of linear 1,4-bdc^{2-} and dabco/bipy,[22] but not for undulating **kag** lattices formed from angular linkers such as 1,3-bdc^{2-}.We herein present a new strategy that renders 2-periodic **kag** lattices into a 3-

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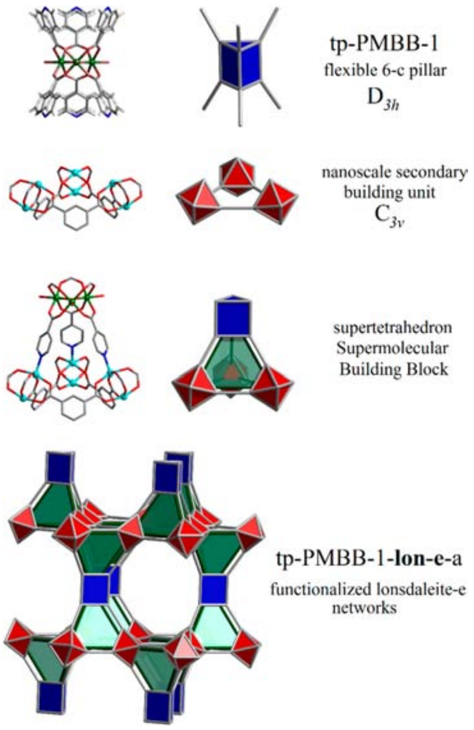
periodic MOM platform: pillaring by a preformed decorated MBB that complements the triangular motif that forms **kag** lattices. Specifically, our previously reported tp-PMBB-1,[16b,c] a water-stable and easily synthesized hexapyridyl cluster, fulfills the requirements in terms of dimensions and symmetry to serve as a 6-connected pillar for the generation of pillared **kag** networks (Scheme 1 and Figure 2b−d, below).

Scheme 1. Hierarchal Construction of tp-PMBB-1-lon-e Networks Involving kag Nets That Are Triply Connected through Three-Fold-Symmetric Pillars (tp-PMBB-1) That Connect Triangular Units



This family of compounds is comprised of tp-PMBB-1 clusters that generate a supertetrahedron when they bond to the axial sites of the three tilted paddlewheel moieties of a 2-D **kag** net (Scheme 1). The partial flexibility of trigonal prismatic MBBs[7,23] in general, and of tp-PMBB-1 moieties[16b,c] in particular, enables a good fit with the triangular unit of the **kag** nets. Connection of the vertices of each supertetrahedron then affords an augmented lonsdaleite-e net with **lon-e**-a topology, tp-PMBB-1-**lon-e**. The nomenclature we use represents both the preformed building block (tp-PMBB-1) and the topology of the resulting net as classified by TOPOS[24] in conjunction with the terminology rules of the RCSR[25] database. Suffixes identify the functional group at the 5-position of 1,3-bdc. The formation of a diamondoid (**dia**) net is precluded because the supertetrahedra are forced by the trigonal prismatic nature of tp-PMBB-1 into an eclipsed arrangement (for further details see SI). We herein report the synthesis, structure, and gas sorption properties of nine variants of this platform based upon changing the 5-substituent of bdc^{2-} or the use of 2,5-furandicarboxylate (fdc^{2-}).

$[Zn_6(5\text{-R-bdc})_6[Cr_3O(isonic)_6(H_2O)_2(OH)]]\cdot y$solv (R = H, CH_3, $C(CH_3)_3$, NO_2, NH_2, OH, OCH_3, Br; solv = DMF, MeOH) and $[Zn_6(2,5\text{-fdc})_6[Cr_3O(isonic)_6(DMF)_3]X]\cdot y$solv (X = NO_3^-, OH^-) crystallize in the hexagonal space group $P6_3/mmc$ with two formula units per unit cell. Each variant is based upon a 2-periodic undulating **kag** net generated by $[Zn_2(CO_2)_4]$ paddlewheel MBBs connected by bdc^{2-} or fdc^{2-}linkers (Figure 1b). The axial positions of the paddlewheel moieties are capped by symmetry and size-congruent tp-PMBB-1 moieties (D_{3h} vs C_{3v}). This leads to eclipsed AAA packing of the **kag** lattices (Figure 1b) with hexagonal channels of diameter from 6.9 to 12.2 Å along [001], depending on the steric bulk of R (Figure 1c).

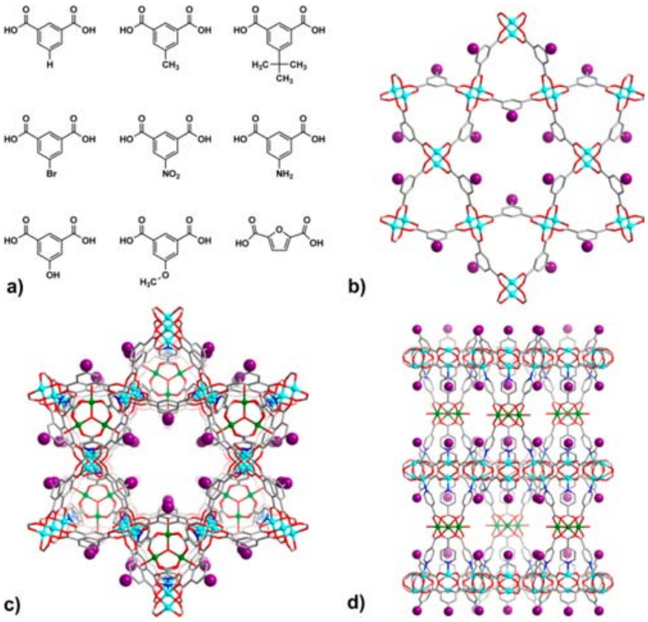


Figure 1. (a) The nine angular linkers used to generate tp-PMBB-1-**lon-e** networks. (b) Single **kag** lattice shown along [001]; purple spheres represent the position of the R groups attached to each bdc^{2-} linker. (c) AAA **kag** lattices pillared by tp-PMBB-1 viewed along [001]. (d) tp-PMBB-1-**lon-e** viewed along [110] (hydrogen atoms have been omitted for clarity).

This self-assembled structure exhibits three distinct cages: the aforementioned supertetrahedral cage (Figure 2a); a truncated trigonal bipyramidal cage (Figure 2b) between the eclipsed triangular faces of the **kag** net; and face-shared octahedral cages formed by the hexagonal channels (Figure 2c) along [001] (see SI for additional details).

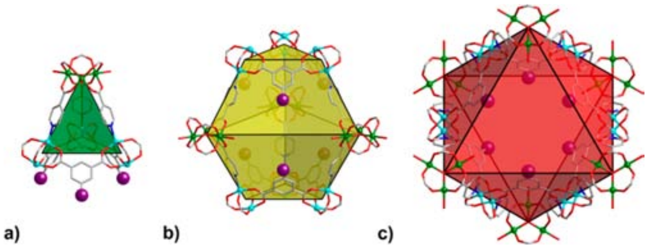


Figure 2. (a) Supertetrahedral, (b) truncated trigonal bipyramidal, and (c) octahedral cages sustained by tp-PMBB-1-**lon-e**; purple spheres represent potential functional groups (hydrogen atoms have been omitted for clarity).

The synthesis of nine functionalized isostructural **lon-e** networks facilitated a systematic study of this platform in the context of gas sorption, in particular the effects of specific functional groups upon gas uptake and heat of adsorption (Q_{st}). As-synthesized crystalline samples were activated as follows: soaking in fresh DMF at room temperature (rt) for 2 days;

immersion in MeCN at rt for 5 days (solvent was exchanged twice daily); degassing at rt (until outgas rate <20 μmHg/min). The porosity of five variants was confirmed by surface area measurements with N_2 at 77 K. tp-PMBB-1-**lon**-**e**-NH_2 and -OH were not found to exhibit porosity, which we attribute to blocking of the pores by residual ligands and/or lower stability, perhaps caused by electronic effects. Thermogravimetric analysis (see SI) revealed a gradual weight loss instead of a plateau for the nonporous variants. Such behavior has been observed previously through comparison of MIL-88(Fe)[26] and its amino-functionalized derivative NH_2_MIL-88(Fe).[27] The porous tp-PMBB-1-**lon**-**e** variants exhibit apparent surface areas (Brunauer−Emmett−Teller model) as follows: -fdc, 2071 m^2/g; -H, 1649 m^2/g; -NO_2, 768 m^2/g; -Br, 732 m^2/g; -*t*-Bu, 546 m^2/g. The measured surface areas are consistent with the steric bulk of the R group reducing pore size and blocking cages. CO_2 and CH_4 adsorption isotherms were subsequently collected at 273 and 298 K (Figure 3, top, presents CO_2 isotherms; CH_4 isotherms are given in SI). The isosteric heats of adsorption for CO_2 are plotted in Figure 3, bottom.

The effect of functional groups on CO_2 uptake is as follows based on 273 K data: *t*-Bu > H ≈ fdc ≈ NO_2 > Br. We report herein the uptake per mole of material to mitigate the effect of density (for gravimetric uptake values, see SI). Polar groups have been shown to enhance CO_2 sorption,[28] although Walton et al.[13d] studied DMOFs and found little effect from polar groups but considerable effect from methyl groups. Their findings are in good agreement with ours, especially for CO_2 uptake when alkyl groups are present vs Br substituents. In the case of tp-PMBB-1-**lon**-**e** variants, the uptake values correlate with pore size and functionality rather than surface area. This is exemplified by tp-PMBB-1-**lon**-**e**-*t*-Bu, which exhibits a higher uptake for CO_2 than all of the higher surface area variants. Isosteric heats of adsorption were calculated from the 273 and 298 K data (Figure 3a,b) using the virial equation (see SI)[29] and range from around 19 to 26 kJ/mol. In addition, tp-PMBB-1-**lon**-**e**-*t*-Bu exhibits the highest Q_{st} at both zero coverage and higher loadings together with the highest Henry constant (K_H) (see SI). We attribute its better performance to the confined pore space generated by the bulky *tert*-butyl groups. tp-PMBB-1-**lon**-**e**-fdc exhibits the highest surface area, which we attribute to the smaller size of fdc^{2-} with respect to bdc^{2-}. The introduction of 5-substituents considerably reduces surface area, which might hinder accessibility to the tetrahedral and the trigonal bipyramidal cages. Other structural features, e.g., the angle subtended at the flexible tp-PMBB-1 moiety (differences in C-μ_3O−C angles are <1°), are invariant. Further studies to address how ligand flexibility might impact porosity and carbon dioxide sorption are currently underway in our laboratory.

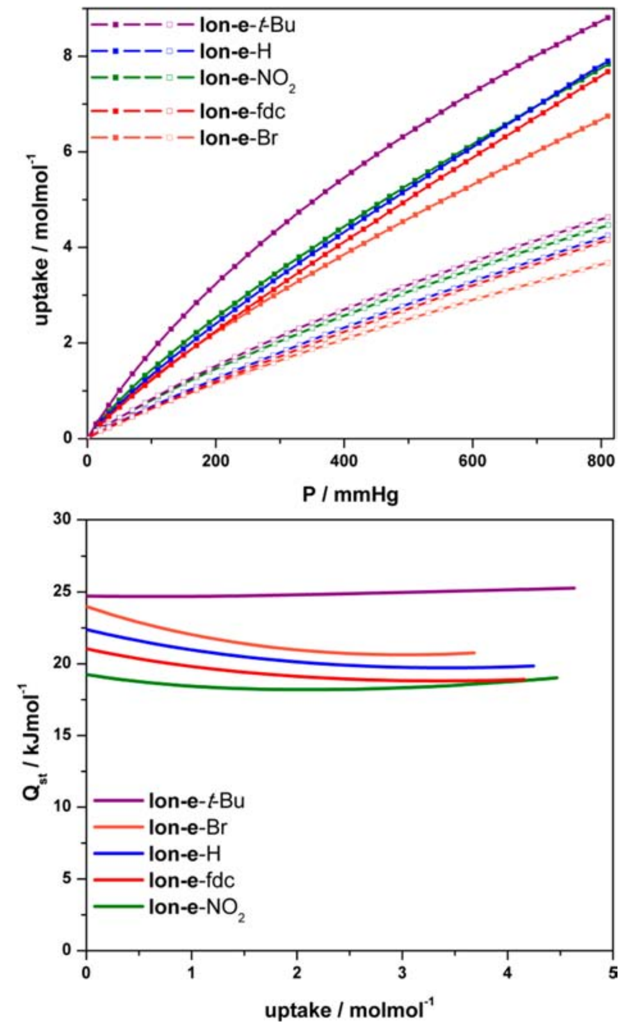


Figure 3. (Top) CO_2 adsorption isotherms collected at 273 and 298 K for five **lon**-**e** networks. (Bottom) Isosteric heat of adsorption of CO_2 as determined from two isotherms.

A similar trend in heat of adsorption was observed for CH_4 sorption at low pressure. As expected, tp-PMBB-1-**lon**-**e**-*t*-Bu exhibits the highest affinity for CH_4, which we attribute to van der Waals interactions with the *tert*-butyl groups and narrower pore size. The Q_{st} value of 20.2 kJ/mol at zero loading is one of the highest reported values and supports the use of alkyl or aryl groups to enhance CH_4−framework interactions.[30,31] tp-PMBB-1-**lon**-**e**-*t*-Bu also surpasses most of the well-known members of the MOF-74 series (Ni, 20.2 kJ/mol; Co, 19.6 kJ/mol; Mn, 19.1 kJ/mol; Mg, 18.5 kJ/mol)[32] as well as MIL-100 and MIL-101 (19 and 18 kJ/mol),[33] which are also based on trigonal prismatic MBBs.

In summary, we herein introduce a new MOM platform that is formed by pillaring the axial sites of a **kag** lattice. Nine examples of this platform were prepared by using substituted bdc^{2-} and fdc^{2-} linkers. Five variants were found to be permanently porous, and CO_2 and CH_4 adsorption measurements reveal that both pore size/confinement and functionality impact uptake and Q_{st}, whereas alkyl groups enhance interactions with CH_4. Conversely, organic Br moieties were found to exhibit weak interactions with both CO_2 and CH_4. We anticipate that tp-PMBB-1-**lon**-**e** will become a versatile platform for facile and systematic study of the fundamental and applied aspects of gas adsorption.

■ ASSOCIATED CONTENT

Supporting Information

Complete single-crystal data (CIF), X-ray powder diffraction, and gas adsorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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