Inorganic Chemistry

An Isoreticular Series of Zinc(II) Metal–Organic Frameworks Derived from Terpyridylcarboxylate Ligands

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S Supporting Information

ABSTRACT: An isoreticular family of seven microporous metal– organic frameworks of the general form [ZnL] have been synthesized, where L is a 4'-substituted 2,2':6',2"-terpyridine-4,4"dicarboxylate ligand. Each framework adopts an interpenetrated zeolitic gismondine (**gis-c**) topology and possesses one-dimensional square channels with ca. 9.0 Å apertures running down the crystallographic *c* axis. Gas adsorption measurements with N₂, H₂, CH₄, and CO₂ confirm their permanent porosity. The ligand functional groups, which include phenyl, 2-tolyl, 4-chlorophenyl, 4nitrophenyl, 2-thienyl, 3-thienyl, and 4-pyridyl, line the channel walls and tune the gas adsorption properties of these materials.



INTRODUCTION

Metal-organic frameworks (MOFs) are a class of porous materials constructed using metal ions and organic ligands.¹ These materials have attracted much attention because of the potential applications related to their porous nature, in particular, in gas capture and storage,² separation,³ and catalysis⁴ and as precursors for the formation of functional materials.⁵ A distinct advantage that MOFs possess over other porous materials such as zeolites and porous carbons is their modular nature, which allows their properties to be tuned through the judicious choice of ligand components and the variation of metal ions or cluster types. For example, the systematic variation of the spatial disposition of the donor atoms of a ligand, appending functional groups to the ligand backbone, and the degree of interpenetration will modulate the pore size and environment and can be used to enhance the interaction between the frameworks and specific sorbates.⁶

To isolate the role that functional groups play in the gas sorption behavior of MOFs independent of the pore size, topology, and degree of interpenetration, investigations on the isoreticular series of MOFs containing different functional groups are invaluable. Several well-known families of isoreticular MOFs have been shown to have their properties tuned through the inclusion of ligands containing differing functional groups with retention of the overall framework topology. Several well-known series of isoreticular MOFs include the IRMOF,⁷ MOF-74,⁸ UiO-66,⁹ and MUF-7¹⁰ series.

2,2':6',2"-Terpyridine and its derivatives are common ligands in coordination chemistry because of their strong tridentate binding mode and relative ease of synthesis and functionalization.¹¹ Carboxylate groups are ubiquitous in coordination polymer chemistry because of their anionic nature and the plethora of potential coordination modes that they can adopt and cluster types that they can form.¹² Ligands based on 2,2':6',2"-terpyridine-4,4"-dicarboxylic acid derivatives combine these features and, through the divergent arrangement of the carboxylate groups, are expected to form polymeric materials when bound to metal ions.¹³ Surprisingly, to date, they have seldom been studied in the development of MOFs.

In the current contribution, we report a systematic examination of a new family of isostructural Zn^{II} -MOFs based on 2,2':6',2"-terpyridine-4,4"-dicarboxylate linking ligands (Scheme 1). The Kröhnke terpyridine synthesis necessitates the incorporation of an aromatic substituent at the 4' position

Scheme 1. Synthesis of Ligands H_2L1-H_2L7 Used in the Current Study



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Figure 1. (a) Reaction of H_2L1 with zinc nitrate in acidic, aqueous DMF that produced crystals of 1. The asymmetric unit of 1 is shown. (b) 2–7, produced under reaction conditions similar to those with the appropriate ligand.

of the ligands. Through systematic and facile modification of the functional group at this position, seven novel ligands based on the 2,2':6',2"-terpyridine-4,4"-dicarboxylic acid core were realized. The functional groups were chosen to alter the steric and electronic nature of a potential framework. A particular focus was given to groups containing strongly electronwithdrawing substituents and Lewis acidic sites because these have been shown to alter the gas sorption behavior. The functional groups include 4'-phenyl (H₂L1), 4'-(2-tolyl) (H_2L2) , 4'-(4-chlorophenyl) (H_2L3) , 4'-(4-nitrophenyl) (H_2L4) , 4'-(2-thienyl) (H_2L5) , 4'-(3-thienyl) (H_2L6) , and 4'-(4-pyridyl) (H_2L7). The solvothermal reaction of H_2L1-H_2L7 with zinc nitrate resulted in the formation of crystalline materials that were structurally identified as an isoreticular MOF family, 1–7, and shown to adopt a zeolitic gis-c topology. The impact of the identity of the ligand substituent on the gas adsorption properties of these materials has been studied.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise specified, all reagents and starting materials were of reagent grade, purchased from standard suppliers and used as received. NMR spectra were recorded on an Agilent 400-MR instrument operating at 400 MHz for ¹H and 101 MHz for ¹³C. All samples were dissolved in dimethyl sulfoxide (DMSO)- d_{6} , and spectra were referenced to the residual solvent peak. IR spectra were measured on a Bruker Alpha Platinum ATR Fourier transform infrared (FT-IR) spectrometer in the range 4000–550 cm⁻¹.

Mass spectra were recorded on either a Dionex Ultimate 3000 or a Bruker MaXis 4G spectrometer, operated in high-resolution positiveion electrospray mode. Elemental analysis was carried out by Campbell Microanalytical Laboratory, University of Otago, Otago, New Zealand. Thermogravimetric analysis (TGA) was carried out on an TA Instruments SDT Q600 TGA/DSC apparatus. All samples were heated on alumina crucibles under a nitrogen flow of 100 mL/min. Heating cycles consisted of heating at 1 °C/min to 800 °C. Powder Xray diffraction (XRD) data were collected using an Oxford Agilent SuperNova instrument using Cu K α (λ = 1.5418 Å) radiation and an Atlas CCD area detector. Samples were prepared by grinding of the applicable compound and packing inside an open glass tube. A baseline correction was manually applied using the baseline feature within the Origin data analysis software. Gas sorption isotherms were carried out on a Quantachrome Autosorb iQ2 instrument. Freshly prepared MOF samples were activated by washing with N,Ndimethylformamide (DMF) and then soaking in acetone for 48 h. The acetone was regularly refreshed during this time. The samples were then transferred to a preweighed analysis tube. The acetone was then removed by holding the sample at high vacuum for 18 h at 25 °C. Accurate sample masses were calculated by using degassed samples after the activated samples were backfilled with nitrogen. All sorption measurements used ultrahigh-purity gases.

Synthesis of 4'-Phenyl-2,2'.6',2"-terpyridine-4,4"-dicarboxylic Acid (H₂L1). The synthesis of H₂L1 is typical for the ligand family and was adapted from work by Husson et al.¹⁴ To a solution of methyl-2-acetylisonicotinate (3.55 g, 20 mmol) in ethanol (45 mL), was added freshly distilled benzaldehyde (1.1 g, 10 mmol), followed by potassium hydroxide (1.53 g, 27 mmol). The resulting solution darkened and was allowed to stir until the formation of a visible



Figure 2. (a) Connectivity of 1 through ligand L1. Each zinc(II) ion is defined as a four-coordinate node. (b) Topological representation of the **gis-c** network of 1 along the crystallographic *a* (left) and *c* (right) axes. Different colors represent independent interpenetrated frameworks. (c) Square one-dimensional channels directed along the crystallographic *c* axis. Black arrows represent C–C distances in the narrowest (inner) and widest (outer) parts of the pore. The yellow arrow represents a Zn–Zn distance. Because of tetragonal symmetry, all distances perpendicular to those shown are identical. (d) Structure of 1 with an overlaid solvent-accessible surface (rendered in cream) created using a 1.2 Å probe. Undulating one-dimensional channels can be seen running along the crystallographic *c* axis. Compounds 2–7 are isostructural to 1 and adopt analogous connections and channel shape.

precipitate (around 30 min). To this was added a 35% aqueous ammonia solution (21 mL), which led to the disappearance of the aforementioned precipitate. Stirring was continued at room temperature for a further 20 h, after which the K⁺/NH₄⁺ salt of the final product was precipitated as a brown solid. This was filtered off, washed with ethanol, then redissolved in the minimum amount of water, and acidified with HCl to a pH of 4. This resulting solid was filtered and washed with water until the washings were neutral. It was then successively washed with ethanol and then diethyl ether and the lightbrown powder air-dried. Yield: 0.65 g (1.6 mmol, 17%). Mp: >330 °C. ¹H NMR (400 MHz, DMSO- d_6): δ 7.45–7.59 (m, 3H), 7.86 (d, J = 6.5 Hz, 2H), 7.90 (d, J = 5.1 Hz, 2H), 8.68 (s, 2H), 8.89 (d, J = 5.1 Hz, 2H), 8.93 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆): δ 117.3, 118.3, 122.0, 125.5, 128.0, 128.2, 135.8, 138.2, 148.4, 149.0, 153.7, 154.4, 164.6. HR-ESMS. Calcd for $C_{23}H_{16}N_3O_4$ [M + H⁺]: m/z 398.1133. Found: *m/z* 398.1140. Selected IR (cm⁻¹): 3028 br, 2781 br, 1714 s, 1593 s, 1550 m, 1361 m, 1276 s, 1221 s, 759 s, 691 s, 665 s.

Synthesis of H_2L2-H_2L7 . The same procedure as that for the synthesis of H_2L1 was followed for the synthesis of H_2L2-H_2L7 by substituting benzaldehyde for the relevant aldehyde. Synthetic and analytical details are given in section S1 in the Supporting Information.

Synthesis of [Zn(L1)] (1). The synthesis of 1 is typical for the family of MOFs reported here. H_2L1 (0.10 g, 0.25 mmol) was dissolved in a DMF (25 mL), water (5 mL), and concentrated nitric acid (2.3 mL) solution. To this was added zinc nitrate hexahydrate (0.075 g, 0.25 mmol), and the orange solution was mixed thoroughly and then dispersed evenly into 4 mL screw-cap vials, which were heated at 90 °C for 24 h. Orange single crystals suitable for XRD deposited directly from the hot solution and were collected by

filtration. Yield: 0.066 g (0.11 mmol, 46%). Anal. Calcd for $C_{23}H_{13}N_3O_4Zn \cdot CH_2O_2 \cdot C_3H_7NO$: C, 55.92; H, 3.83; N, 9.66. Found: C, 56.32; H, 3.83; N, 9.31. Selected IR (cm⁻¹): 3414 br, 3068 br, 1634 s, 1557 s, 1356 s, 1241 m, 1093 w, 1016 w, 821 w, 786 m, 705 s, 630 w. *Postactivation* Anal. Calcd for $C_{23}H_{13}N_3O_4Zn \cdot H_2O$: C, 57.70; H, 3.16; N, 8.78. Found: C, 57.72; H, 3.53; N, 8.40. Selected IR (cm⁻¹): 1607 s, 1553 s, 1478 w, 1359 s, 1240 m, 1015 w, 875 w, 821 w.

Synthesis of 2–7. A procedure similar to that for the synthesis of 1 was followed for the synthesis of 2–7 by substituting H_2L1 with the relevant ligands H_2L2-H_2L7 . Synthetic and analytical details are given in section S2 in the Supporting Information.

X-ray Crystallography. X-ray crystallographic data collection and refinement was carried out on an Oxford Agilent SuperNova instrument with focused microsource Cu K α (λ 1.5418 Å) or Mo K α (λ 0.71073 Å) radiation and an Atlas CCD area detector. All structures were solved using SHELXT and refined by full-matrix leastsquares procedures using SHELXL-2015 within OLEX-2.¹⁵ Hydrogen atoms were included in calculated positions or manually assigned from residual electron density where appropriate, with isotropic displacement parameters 1.2 times the isotropic equivalent of their respective carrier atoms. The functions minimized were $\sum w(F_o^2 - F_c^2)$, with w = $[\sigma^{2}(F_{o}^{2}) + aP^{2} + bP]^{-1}$, where $P = [\max(F_{o})^{2} + 2F_{c}^{2}]/3$. As discussed in the text, where voids containing highly disordered solvent molecules were present, the SQUEEZE routine was carried out.¹⁶ This technique was employed only when sensible explicit modeling of the electron density due to solvent molecules was not possible and where a considerable benefit to the refinement was gained. The detailed



Figure 3. Adsorption isotherms of 1-7 for N_2 (a) and H_2 (b) at 77 K. Filled symbols: adsorption. Open symbols: desorption.

crystallographic data and selected bond lengths and angles for 1-7 are listed in section S3 in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. The ligands H_2L1-H_2L7 were synthesized from methyl 2-acetylisonicotinate, following an adapted procedure for the synthesis of 4'-(2-furanyl)-2,2':6',2"-terpyridine-4,4"-dicarboxylic acid, using a range of substituted phenyl and heterocyclic aldehydes to install various functional groups on the ligand scaffold (Scheme 1).¹⁴ The reported modest yields are typical of the Kröhnke terpyridine synthesis.^{11a}

The solvothermal reaction of H_2L1-H_2L7 with zinc nitrate in DMF/aqueous HNO₃ at 90 °C yielded a series of crystalline materials, 1–7, suitable for single-crystal XRD studies (Figure 1). Compounds 1–7 crystallize in the tetragonal space group $I4_1/acd$, are isostructural, and contain one [ZnL] component in the asymmetric unit. The zinc(II) ions adopt five-coordinate geometry, with the ligands coordinated in a tridentate chelating fashion typical of 2,2':6',2"-terpyridine ligands. The remaining two sites of the zinc(II) coordination sphere are occupied by monodentate carboxylate groups from adjacent [ZnL] units. In each case, the metal ions adopt a distorted square-pyrimidal geometry, as shown by the low τ_5 parameters, which range from 0.04 to 0.20 ($\tau_5 = 0$ corresponds to square-pyramidal; $\tau_5 = 1$ corresponds to trigonal-ipyramidal; Table S3).¹⁷

The carboxylate groups connect [ZnL] units together and result in the formation of a 3D framework with the zeolitic gis $(4^3 \cdot 6^2 \cdot 8)$ topology in which the single crystallographically unique [ZnL] unit acts as a 4-connected node (Figure 2a). Within this topology, large eight-membered rings create channels that are directed down the crystallographic a and baxes. Smaller four-membered rings create channels directed along the crystallographic c axis. The aryl and heterocyclic functional groups on the 4' position of the terpyridine ligands, H_2L1-H_2L7 , partially block the former channels but line the latter. The functional groups are twisted with regard to the central pyridine ring of the ligand, with torsion angles ranging from $3.4(5)^{\circ}$ to $36.3(4)^{\circ}$ (Table S3). The structure is 2-foldinterpenetrated, with independent networks interacting through $\pi - \pi$ interactions (Figure S10). The interpenetration serves to block the channels running parallel with the a and baxes but does not hinder the size or shape of the channels running parallel with the c axis (Figure 2b). Despite interpenetration, significant void volume exists within the structures and is mainly located within square-shaped onedimensional channels that run along the crystallographic *c* axis

(Figure 2c,d). The undulating nature of the channel is caused by the tight four-membered rings of the gis topology at the narrow points and the wide, flared out substituents at the 4' position of the ligand. Owing to the high void volume and disorder of the solvent molecules, these channels were subjected to the SQUEEZE routine within PLATON.¹⁶ These calculations showed that the potential solvent-accessible void volume represents 32-41% of the unit cell, indicating that the compounds could display porosity upon removal of the occluded solvent (Table S3). The percentage void space scales with the increased steric bulk of the functional group. Despite the metal ions being five-coordinate, no solvent-accessible open metal sites exist within the framework. In each of the structures 1-7, the functional groups at the 4' position of the ligand line the interior of the one-dimensional channels in the respective MOF and are expected to affect the gas sorption properties of each framework.

Gas Adsorption. To activate the MOFs, 1–7 were soaked in acetone for 48 h and then placed under high vacuum for 18 h at 25 °C to remove the residual solvent from the pores of the frameworks. Powder XRD, TGA, and elemental analysis revealed that crystallinity was retained postactivation (section S2 in the Supporting Information) and that no residual solvent remained in the pores. In order to assess the ability of 1–7 to adsorb N₂, H₂, methane (CH₄), and carbon dioxide (CO₂), low-pressure adsorption isotherms were measured at a range of temperatures.

The N₂ gas adsorption isotherms of the activated MOFs were measured at 77 K to determine the surface areas of 1-7 (Figure 3a). The MOFs 1-3 and 5-7 showed type 1 isotherms. Among these, those containing aryl and pyridyl functional groups showed similar maximum gravimetric uptake while those containing the thienyl functional groups displayed slightly reduced uptake. The MOFs showing type 1 isotherms containing aryl and pyridyl functional groups have Brunauer-Emmett–Teller (BET) surface areas of $810-900 \text{ m}^2/\text{g}$. The MOFs containing the five-membered thienyl rings have lower surface areas of $690-730 \text{ m}^2/\text{g}$ (Table S4), and this is probably responsible for the lower maximum sorption capacity. Compound 4, containing the 4-nitrophenyl substituent, displays very low N2 uptake at 77 K. Similarly low values at 195 and 298 K indicate that this is not just due to diffusion limitations within the one-dimensional channels at 77 K but rather that compound 4 appears to be nonporous with respect to N₂ in this pressure range.

Frameworks 1-3 and 5-7 showed significant H₂ gas uptake at 77 K with adsorption capacities that ranged from 1.17 to



Figure 4. (a) CH₄ adsorption isotherms for 1-7 at 273 K. (b) CH₄ adsorption isotherms for 1-7 at 298 K. (c) Isosteric enthalpy of adsorption (Q_{st}) of 1-7 toward CH₄ calculated from isotherms measured at 273 and 298 K.

1.47% by weight at 1 atm, which corresponds to approximately 3 gas molecules per formula unit (Figure 3b and Table S5). The uptake values are similar to that observed for IRMOF-1 (1.32%).¹⁸ On the other hand, compound 4 showed minimal adsorption of H₂ at 77 K. Calculation and experimental data have shown that a linear relationship exists between the H₂ storage capacities and specific surface areas.^{2d} This holds true for this series of MOFs (Figure S13), indicating that the electronic properties of the functional groups do not play a significant role in the adsorption of H₂ at this temperature.

CH4 isotherms were measured at both 273 and 298 K. All compounds display near-linear adsorption behavior with no appreciable hysteresis (Figure 4a,b). The isotherm of compound 4 showed that this framework has the lowest capacity for CH₄ adsorption. The gradients of this set of isotherms, which in the linear region corresponds to the Henry coefficient and is a measure of the density of adsorption sites with high affinity for the adsorbent for the adsorbate, indicate that the pyridyl functional group in 7 has a beneficial impact on CH_4 adsorption. To quantify this more clearly, heats of adsorption were calculated and found to lie in the range 17.9-25.5 kJ/mol (Figure 4c), which is at the high end for MOFs especially considering that no open metal sites are present.¹⁹ The MOFs with the highest heats of adsorption were shown to be 7 (4-pyridyl), 5 (2-thienyl), 6 (3-thienyl), and 4 (4nitrophenyl), all containing polar functional groups. This metric underscores the utility of including these groups to boost the affinity of a framework for CH₄. The invariability of Q_{st} as a function of gas uptake indicates that the binding sites are relatively homogeneous and that surface-CH4 interactions are much more important than CH₄-CH₄ interactions in this pressure range.

 CO_2 isotherms were measured at 195, 273, and 298 K (Figure 5). All compounds absorbed CO_2 at 195 K, with 1–3 and 5–7 exhibiting similar uptake values that reach saturation at around P = 0.1 atm. Compound 4 exhibited a slightly lower maximum gravimetric uptake than the other materials, which indicates a lower accessible pore volume. It also showed a stepped sorption curve, more easily visualized when a logarithmic pressure scale is used (Figure S14).

At 273 K, compounds 1-3, 6, and 7 display conventional CO_2 adsorption isotherms (Figure 5c). The maximum uptake values at 1 atm, which range from 13.66 to 16.42 wt % (cf. 6.61 wt % for IRMOF-1),¹² are high with regard to those of previously reported MOFs in the literature.^{2c} For both 4 and 5, a distinct step in the adsorption branch is evident at intermediate pressures. The gradient of the step is much sharper for 4 than for 5. Hysteresis is observed in this pressure region for the desorption branch (Figure 5d). These isotherms are indicative of an underlying structural change during the adsorption process.²⁰ The total gravimetric uptake of 4 and 5 at 1 atm is approximately equal to that seen in the other samples (Table S7). The first step in the adsorption isotherm of 4 corresponds to the adsorption of ca. 0.8 molecules of CO₂ per formula unit (0.46 atm) and rises to ca. 1.9 molecules adsorbed per formula unit at 1 atm. For 5, the steps in the adsorption correspond to 1.0 molecule of CO₂ at 0.51 atm and 2.0 molecules at 1 atm. At 298 K, each of 1-7 showed a gradual uptake of CO_2 (Figure 5b). At 1 atm, there are a range of maximum uptake values: 3 showed the highest adsorption (61.1 cm^3/g), while 4 showed the lowest adsorption (31.8 cm^3/g). Compounds 4 and 5, which showed hysteretic behavior at 273 K, display the lowest maximum uptake at 1 atm. Although at 298 K 4 and 5 show uptake similar to the rest of the series



Figure 5. (a and b) CO₂ adsorption isotherms for 1–7 at 195 and 298 K, respectively. (c) CO₂ adsorption isotherms for 1–3, 6, and 7 at 273 K. (d) CO₂ adsorption isotherms for 4 and 5 at 273 K. (e) Isosteric enthalpy of adsorption (Q_{st}) of 1–3, 6, and 7 toward CO₂ calculated from isotherms measured at 273 and 298 K.

below 0.2 atm, they start to plateau at a much lower pressure and display lower maximum uptake than the other frameworks.

The anomalous gas adsorption behavior of framework 4 can be rationalized by the motion of the two interpenetrating lattices with respect to one another. Upon activation, the lattices move further apart than that observed in the singlecrystal XRD structures. This "closed" form has a smaller pore volume and narrower pore dimensions than the "open" form adopted by the other frameworks. This accounts for the negligible uptake of weakly interacting adsorbates such as N₂ and H₂ and the lower uptake of CH₄ and CO₂ (at lower pressures) around room temperature. Gate opening to the open form occurs during the CO₂ isotherms when the amount of adsorbed gas reaches a critical threshold, as illustrated in Figure S14. This feature has been reported previously for dynamic frameworks in which flexible frameworks switch from narrow or closed-pore to open-pore forms.^{20c,d,21} In the case of 4, the electron-withdrawing nature of the nitro groups may diminish the $\pi - \pi$ interactions between the frameworks, thus making the closed form accessible. Gate opening is not observed for CH₄ or CO₂ at 298 K because of the lower amount of gas adsorbed.

A striking feature seen in this series of MOFs is the effect that the nitrophenyl substituent has on the gas sorption properties. This functional group dramatically reduces the N₂ sorption capacity at all temperatures measured yet retains high CO₂ capacities, making it potentially useful in the separation of these gases. The adsorptive selectivity for CO₂ from a gas mixture can be estimated from the experimental single-component gas adsorption isotherms. The selectivity factor is defined as the molar ratio of the adsorbed quantities at the relevant partial pressures of the gases.^{2c} A hypothetical flue gas comprised of 75% N₂ and 15% CO₂ at 298 K is commonly used to compare MOFs. Although this figure is an approximation and does not take into account the competition of gas molecules for adsorption sites and its accuracy is limited by the low sorption capacity of N₂ at 298 K, it is conveniently and rapidly performed and is useful for evaluating potentially interesting materials, and, indeed, selectivities have been calculated for a range of benchmark materials. Table S8 shows the calculated single-component selectivity factors for 1–7. Compounds 1–3 and 5–7 display modest selectivities, inline with other MOFs. Compound 4, however, is very selective for CO₂ and displays a 35-fold increase in the selectivity compared to the majority of the series. This stems from the very low sorption of N₂ rather than the high sorption of CO₂. Compound 7, incorporating a 4pyridyl functional group, displays the next best selectivity, which is similar to that of HKUST-1.^{2c}

CONCLUSION

In conclusion, we have reported the synthesis of seven new 4'substituted terpyridine-4,4"-dicarboxylic acid based ligands and employed them in the solvothermal synthesis of seven new zinc-organic frameworks that were fully characterized by elemental analysis, IR spectroscopy, TGA, and powder and single-crystal XRD methods. Each ligand differed by the substituent in the 4' position of the terpyridine ligand, with the substituents based on either aryl or heterocyclic moieties. These functional groups line the one-dimensional channels of the resultant MOFs, 1-7, and the structure and gas sorption properties of each were investigated. All frameworks are isostructural and adopt the zeotlitic gis-c topology. Generally, it was observed that the aryl and pyridyl functional groups showed better gas adsorption behavior than the thienyl groups for all gases measured. A notable exception was 4, containing the 4-nitrophenyl substituent, which did not appreciably adsorb N_2 and H_2 gases, indicating that the 4-nitrophenyl substituent dramatically altered the internal pore character. However, this MOF showed a dramatic increase in the sorption and, hence, selectivity for CO₂ over N₂ gas, indicating a potential application of this material in gas separation. Future work will focus on the elucidation of the selectivity of 4 and the use of mixtures of ligands described herein to create multivariate MOFs. Similarly, having established the efficacy of 2,2':6',2"terpyridine-4,4"-dicarboxylic acids as a scaffold for a family of isoreticular zinc MOFs, the number of ligands will be extended to include a range of further substituents to tune the electronic and steric profiles of the ligand and potentially gas sorption behavior of the resulting MOFs. This work will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01632.

Synthesis and characterization of H₂L2–H₂L7 ligands, synthesis and activation of MOFs, IR and TGA data, crystal data and structure refinement, tabulated pore volumes and surface areas, adsorption and desorption isotherms, $Q_{\rm st}$ calculations, and additional references (PDF)

Accession Codes

CCDC 1556307–1556313 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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