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COMMUNICATION

Microwave synthesis and gas sorption of calcium and strontium metal–organic frameworks with high thermal stability†

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Two new calcium and strontium metal–organic frameworks [Ca(SBA)] (CYCU-1) and [Sr(SBA)] (CYCU-2) were prepared by microwave-assisted reactions. Both rigid frameworks are thermally stable up to about 450 °C. As verified by N₂, CO₂, and H₂ sorption measurements, the thermally activated CYCU-1 and CYCU-2 exhibit significant microporosity.

Porous metal–organic frameworks (MOFs) have attracted much attention because of their various applications in gas storage, separation, catalysis, magnetism, luminescence, and biological drug delivery.^{1–7} Numerous MOFs have been synthesized with various metal ions and organic aromatic carboxylates. The alkaline earth MOFs have been less studied compared with transition or lanthanide metal-based MOFs. Their ionic chemistry in water and their varied coordination numbers make use of these metal ions to generate MOFs with permanently accessible porosity challenging.⁸ Only a few results on calcium and strontium MOFs capable of gas sorption have been reported in the literature.⁹ Nitrogen gas sorption measurements with microporous type-I isotherms on calcium MOFs (non-heterometallic Ca-MOFs) have not been reported. In this communication, we describe our results on the facile synthesis of two microporous materials, [Ca(SBA)]·0.45H₂O (CYCU-1_{as}) and [Sr(SBA)]·0.2H₂O (CYCU-2_{as}), with microwave irradiation¹⁰ with Ca(II) and Sr(II) ions and 4,4'-sulfonyldibenzoate acid (H₂SBA).‡ To our knowledge, this work is the first example of the facile synthesis of permanent accessible and porous Ca(II)-MOFs.

Single-crystal X-ray diffraction shows that the compounds CYCU-1_{as} and CYCU-2_{as} possess similar extended 3D frameworks.§ In CYCU-1_{as}, the asymmetric unit contains one Ca (Sr for CYCU-2_{as}) atom, one SBA ligand, and lattice water molecules (Fig. 1a). The Ca (II) and Sr(II) ions are seven-coordinated and bind six oxygen atoms from the carboxylate groups belonging to five SBA ligands and one oxygen from the SO₂ group in the other SBA ligand. The SBA ligand

overall is hexadentate μ_6 , bridging six metals and bound through each of its five oxygen atoms. All of the Ca–O bond distances range from 2.30(2) to 2.88(2) Å. In CYCU-2_{as}, the Sr–O bond distances range from 2.42(2) to 2.93(2) Å (Table S1†). As shown in Fig. 1b, the inorganic motif displays a zigzag 1D chain formed by a triangular edge-sharing CaO₇ monocapped trigonal prism. These 1D chains are further connected by the μ_6 -SBA ligands in two directions to generate the 3D framework of CYCU-1_{as}. The lattice water molecules are located in the rhomboidal and zigzag channels. The rhomboidal channels were constructed along the *b*-axis having a cross-section of approximately 8.5 × 8.4 Å² (Fig. 2a; between benzene ring centers and considering the van der Waals radii of carbon atoms; 8.8 × 8.8 Å² for CYCU-2_{as}). The diagonal distance inside the zigzag pores (Fig. 2b) is approximately 12 Å. The solvent accessible volumes (SAVs) calculated without including water molecules by PLATON¹¹

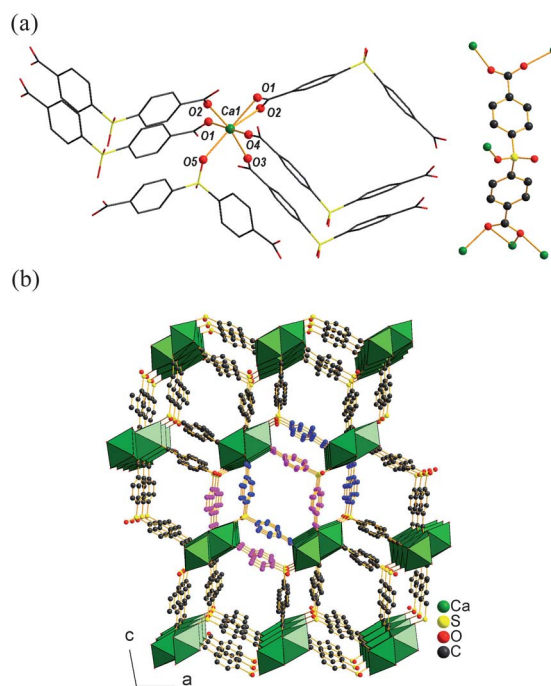


Fig. 1 (a) The coordination spheres of a calcium atom and the coordination environment of the 4,4'-SBA ligand in **1**. (b) The 3D structure view of **1** with the channels along the *b*-axis.

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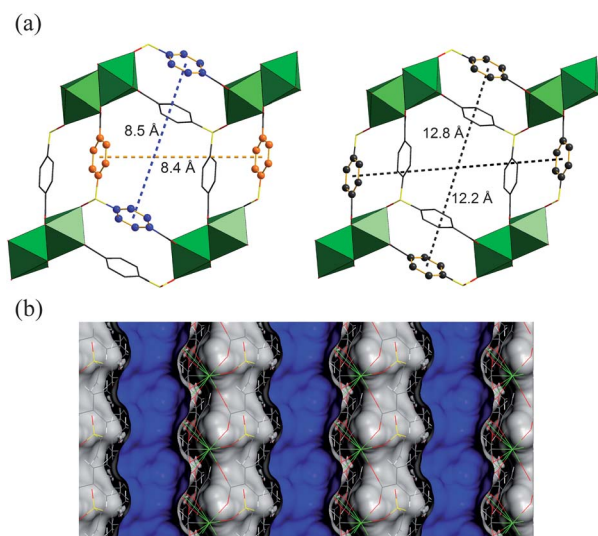


Fig. 2 (a) The pore dimensions of **CYCU-1_{as}** with the cross-section (left) and the diagonal distances (right). (b) Schematic presentation of the zigzag open channels.

analysis are 259.7/303.9 Å³, which are 17.6%/19.3% of the unit cell volume for compounds **CYCU-1_{as}**/**CYCU-2_{as}**. The higher SAVs for **CYCU-2** might correspond to the larger unit cell volume than **CYCU-1** when the crystal radius of Sr(II) is larger than Ca(II). A topological analysis revealed that compounds **CYCU-1_{as}** and **CYCU-2_{as}** can both be described as a *pcu* α -Po primitive cubic, as defined by the Reticular Chemistry Structure Resource,¹² or as a uninodal 6-connected net with a Schläfli symbol of {4¹².6³}, as determined using TOPOS.¹³

The dehydrated frameworks of **CYCU-1/CYCU-2** were also characterized by single-crystal X-ray diffraction by heating **CYCU-1_{as}**/**CYCU-2_{as}** at 200 °C for 5 h.[§] The compounds **CYCU-1**/**CYCU-2** still have their original neutral framework and contain no lattice water inside the pores. The channels of **CYCU-1/CYCU-2** running along the *b*-axis have a cross-section of approximately 8.4 × 8.3/8.8 × 8.7 Å². The SAVs are 250.7/303.8 Å³, which are 17.2%/19.2% of the unit cell volume. These values indicate that the pore sizes and volumes are almost the same as the hydrated phases. The higher solvent accessible volume for **CYCU-2** might correspond to the larger unit cell volume than **CYCU-1** while the crystal radius of Sr(II) is larger than Ca(II).

Thermogravimetry analyses (Fig. 3) show that the first weight loss between 50–200 and 50–240 °C corresponds to the loss of water

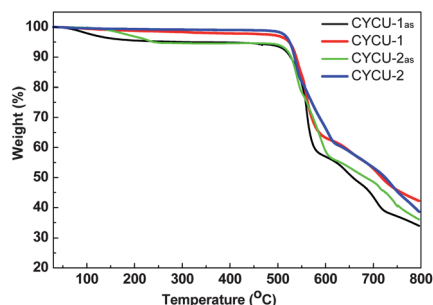


Fig. 3 Thermogravimetric analysis results.

molecules inside the pores of Ca/Sr MOFs. The dehydrated **CYCU-1** and **CYCU-2** phases remained stable up to 450 °C, until the organic ligands started to decompose and the framework appeared to collapse. In the reported MOFs containing SBA ligands, mostly compounds have displayed their highly thermal stabilities which might be due to the incorporation of SBA ligands.^{5b,14} These are general behaviors that are consistent with powder X-ray diffraction patterns at various temperatures. Few extra peaks are raised under increasing temperatures and vacuum in **CYCU-2**, indicating the framework might fractionally twist.

The gas sorption isotherms of **CYCU-1** and **CYCU-2** were measured for N₂, H₂, and CO₂ gases. The low-pressure N₂ adsorption measurements performed on **CYCU-1** and **CYCU-2** at 77 K showed type I isotherms, which are characteristic of microporous materials (Fig. 4a). The surface areas and pore volumes, which were fitted from the data, gave a Brunauer–Emmett–Teller (BET) surface area of 224/79 m² g^{−1} and a Langmuir surface area of 274/96 m² g^{−1}. The pore size distribution derived from the N₂ adsorption isotherms using the Horvath–Kawazoe (HK) method¹⁵ suggests pore sizes of approximately 8.4/12.3 Å and 8.1 Å for **CYCU-1** and **CYCU-2** (Fig. S11†). These data clearly indicate that both structures have a very similar pore size distribution and they are in agreement with the values calculated from the single-crystal structure. The pore volume was calculated by the HK method in the micropore range with the values of 0.65 and 0.52 cm³ g^{−1} for **CYCU-1** and **CYCU-2**, respectively. The H₂ adsorption isotherms of **CYCU-1/CYCU-2** (Fig. 4b) were acquired at 77 K and 1 atm; the samples were able to take up 0.7/0.2 wt% H₂. To our knowledge, both values are the first reported hydrogen uptake measurements for calcium- and strontium-based MOFs.

The adsorption and desorption of CO₂ for **CYCU-1** and **CYCU-2** have hysteresis loops at the temperature of 298 K. The maximum CO₂ adsorptions of **CYCU-1/CYCU-2** (Fig. 4c) at 1 atm are 1.37/1.17 mmol g^{−1}, respectively. These values are comparable to

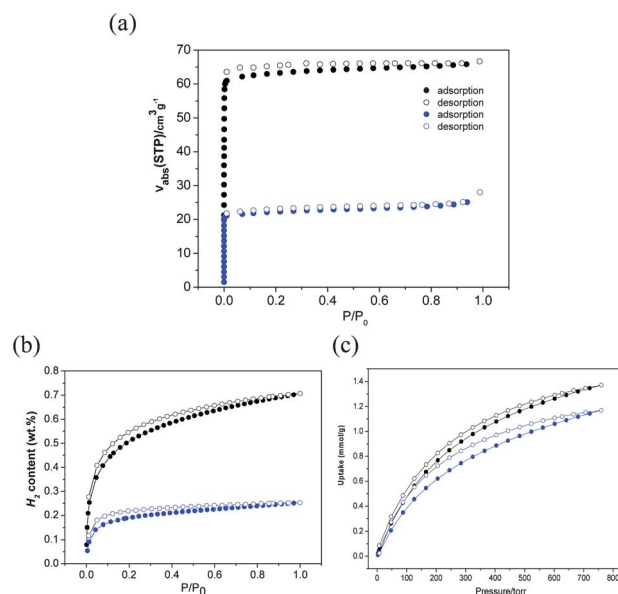


Fig. 4 (a) N₂ adsorption isotherms of **CYCU-1** (black) and **CYCU-2** (blue) at 77 K. (b) H₂ adsorption isotherms at 77 K. (c) CO₂ adsorption isotherms at 298 K.

some results on USO-3-In-A (1.59 mmol g⁻¹), SNU-9 (1.25 mmol g⁻¹), MOF-5 (microwave synthesis, 1.12 mmol g⁻¹), ZIF-8/ZIF-100 (1.02/0.96 mmol g⁻¹), and UMCM-1 (0.91 mmol g⁻¹).¹⁶ The maximum CO₂ adsorption of **CYCU-1** is 1.97 mmol g⁻¹ at 1 atm and 195 K (Fig. S12†). Clearly, the unique structural factors of zigzag pores in **CYCU-1** and **CYCU-2** described above contribute significantly to the CO₂ uptake. The interaction of CO₂ molecules with the polar sulfone groups might increase the CO₂ uptake capability which has been reported in the previous sulfone-functionalized zinc metal-organic framework.¹⁷ The isosteric heat of adsorption at zero coverage for CO₂ calculated using the Clausius–Clapeyron equation is about 28 kJ mol⁻¹ (Fig. S13†). As displayed in Fig. S3 and S6†, the electron density (from X-ray powder diffraction patterns) of **CYCU-2** resides more in the zigzag pores than that of **CYCU-1**. This may explain why the values of gas sorption for **CYCU-2** are lower than for **CYCU-1**.

In conclusion, we have successfully synthesized two new Ca and Sr metal-organic frameworks using microwave-assisted solvothermal reactions. Both compounds contain 3D microporous frameworks that are constructed from 1D inorganic chains linked by organic SBA ligands. Both frameworks display high thermal stability up to approximately 450 °C and demonstrate gas adsorption of N₂ and H₂ at 77 K and of CO₂ at room temperature, making them good candidates for CO₂ storage and other potential applications because of their facile preparation and abundance on Earth.

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Notes and references

† Microwave synthesis of [Ca(SBA)]·0.4H₂O (**CYCU-1**_{as}). A mixture of 4,4'-sulfonyldibenzoate acid (C₁₄H₁₀O₆S, H₂SBA, 0.1224 g, 0.4 mmol), Ca(NO₃)₂·4H₂O (0.1890 g, 0.8 mmol), ethanol (9.0 ml), and H₂O (1.0 ml) was stirred for 10 min in air. Then the mixture was placed in a 100 ml Teflon autoclave and heated at 150 °C for 20 minutes. The autoclave was cooled to room temperature, washed with fresh EtOH and colorless crystals were collected (0.1077 g, 74.3% yield based on the H₂SBA reagent). Anal. found/calcd: C, 47.77/47.83; H, 2.44/2.52%. IR (KBr, cm⁻¹): 3407(br), 3090(w), 2964(w), 1605(s), 1557(s), 1410(s), 1290(s), 1164(m), 1099(m), 1022(w), 742(s), 614(m), 478(w), 430(w). Microwave synthesis of [Sr(SBA)]·0.1H₂O (**CYCU-2**_{as}). A mixture of 4,4'-sulfonyldibenzoate acid (C₁₄H₁₀O₆S, H₂SBA, 0.1224 g, 0.4 mmol), Sr(NO₃)₂ (0.3384 g, 1.6 mmol), ethanol (7.0 ml), and H₂O (3.0 ml) was stirred for 10 min in air. Then the mixture was placed in a 100 ml Teflon autoclave and heated at 150 °C for 20 minutes. The autoclave was cooled to room temperature, washed with fresh EtOH and colorless crystals were collected (0.1252 g, 78.1% yield based on the H₂SBA reagent). Anal. found/calcd: C, 43.00/42.71; H, 2.46/2.10%. IR (KBr, cm⁻¹): 2983(w), 2876(w), 2665(w), 2541(w), 1695(s), 1419(s), 1288(s), 1159(s), 1105(m), 939(m), 860(m), 719(w), 620(w), 558(w).

§ Crystal data for **CYCU-1**_{as}: C₁₄H_{8.8}CaO_{6.4}S, *M* = 351.56, colourless lamellar, monoclinic, space group *P*₂₁/*n* (no. 14), *a* = 11.8301(5), *b* = 5.5761(2), *c* = 22.7922(9) Å, β = 100.493(2)°, *V* = 1478.36(10) Å³, *Z* = 4, *D*_c = 1.584 g cm⁻³, *F*₀₀₀ = 722, Bruker APEX-II CCD, MoKα radiation, λ = 0.71073 Å, *T* = 295(2) K, 2θ_{max} = 56.7°, 30 296 reflections collected, 3660 unique (*R*_{int} = 0.0347). Final GooF = 1.131, *R*₁ = 0.409, *wR*₂ = 0.1396, *R* indices based on 3104 reflections with *I* > 2σ(*I*). Crystal data for **CYCU-1**: C₁₄H₈CaO₆S, *M* = 344.34, colourless acicular, monoclinic, space group *P*₂₁/*n* (no. 14), *a* = 11.7361(10), *b* = 5.5499(4), *c* = 22.8190(18) Å, β = 100.999(4)°, *V* = 1459.0(2) Å³, *Z* = 4, *D*_c = 1.568 g cm⁻³, *F*₀₀₀ = 704, Bruker APEX-II CCD, MoKα radiation, λ = 0.71073 Å, *T* = 295(2) K, 2θ_{max} = 56.8°, 14 915 reflections collected, 3623 unique (*R*_{int} =

0.0385). Final GooF = 1.037, *R*₁ = 0.0428, *wR*₂ = 0.1072, *R* indices based on 2841 reflections with *I* > 2σ(*I*). Crystal data for **CYCU-2**_{as}: C₁₄H_{8.2}O_{6.1}SSr, *M* = 393.70, colourless columnar, monoclinic, space group *P*₂₁/*n* (no. 14), *a* = 12.1722(5), *b* = 5.7277(2), *c* = 22.9034(9) Å, β = 98.857(2)°, *V* = 1577.75(11) Å³, *Z* = 4, *D*_c = 1.665 g cm⁻³, *F*₀₀₀ = 784, Bruker APEX-II CCD, MoKα radiation, λ = 0.71073 Å, *T* = 295(2) K, 2θ_{max} = 56.6°, 14 143 reflections collected, 3883 unique (*R*_{int} = 0.0297). Final GooF = 1.075, *R*₁ = 0.0324, *wR*₂ = 0.0980, *R* indices based on 3111 reflections with *I* > 2σ(*I*). Crystal data for **CYCU-2**: C₁₄H₈O₆SSr, *M* = 391.88, colourless acicular, monoclinic, space group *P*₂₁/*n* (no. 14), *a* = 12.1704(5), *b* = 5.7317(3), *c* = 22.8977(9) Å, β = 98.851(2)°, *V* = 1578.26(12) Å³, *Z* = 4, *D*_c = 1.649 g cm⁻³, *F*₀₀₀ = 776, Bruker APEX-II CCD, MoKα radiation, λ = 0.71073 Å, *T* = 295(2) K, 2θ_{max} = 56.7°, 14 371 reflections collected, 3894 unique (*R*_{int} = 0.0415). Final GooF = 1.057, *R*₁ = 0.0344, *wR*₂ = 0.0952, *R* indices based on 2908 reflections with *I* > 2σ(*I*).

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