



Pyridinium Linkers and Mixing Anions In Cationic Metal-Organic Frameworks

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Complete List of Authors:	Lin, Jian-Bin; University of Calgary, Department of Chemistry Shimizu, George; University of Calgary, Department of Chemistry

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Pyridinium Linkers and Mixed Anions in Cationic Metal-Organic Frameworks†

Jian-Bin Lin and George K. H. Shimizu*

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Pyridinium linkers direct the formation of a cationic metal organic framework [Cu(ipq)]A (where $H_2ipq^+ = 1-(3,5-dicarboxyphenyl)-4-(pyridin-4-yl)pyridinium$, $A^- = NO_3^-, BF_4^-, BF_4^-/PF_6^-$), CALF-32(A), where intra-pore anions can be varied and mixed to control porosity and gas uptake.

Metal organic frameworks (MOFs) are porous coordination polymers touted for their modular synthetic routes and options for systematic variation.¹ MOFs as new solid sorbents could exhibit selective capture of CO₂ and a low energy penalty for release of the gas giving more efficient overall capture.² Low partial pressure CO₂ capture is enhanced by higher heats of adsorption. Metal ions with open sites³ or having active organic nitrogen sites⁴ elevate CO₂-MOF interactions yielding higher heats of adsorption. Studies of charge-separated MOFs, where charged units other than the framework metals and ligating functional groups are incorporated into the linkers/pores are much less common. Most of these efforts are focused on impregnation of secondary metal cations in the pores of anionic MOFs.⁵ While there are reports of anion exchange in MOFs,⁶ to our knowledge, there is no report on the doping of anions in a cationic framework for improving CO₂ capture.

Pyridinium linkers are cationic with a highly electropositive quaternized nitrogen. When incorporated into a MOF, this charge could yield a framework with high affinity for the quadrupole of CO₂ molecules.⁷ Moreover, the anions included in the pores could augment CO₂ affinity by supplying additional polarizing sites or through stronger confinement effects. Here we report the design and synthesis a MOF with cationic struts. The pyridinium-containing linker, 1-(3,5-dicarboxyphenyl)-4-(pyridin-4-yl)pyridinium hexafluorophosphate, (H₂ipq)(PF₆), was synthesized (Zincke reaction)⁸ and incorporated into the structurally characterized [Cu(ipq)]NO₃·2DMF₂·2H₂O, CALF-32(NO₃) (CALF = Calgary Framework) and analogues with different included anions in the same parent framework. CALF-32(NO₃) collapses upon activation but analogues with A⁻ = BF₄⁻ and BF₄⁻/PF₆⁻ combinations retain more open structures and demonstrate higher CO₂ uptake and CO₂ selectivity. Notably, CALF-32(BF₄)_{0.6}(PF₆)_{0.4} has a surface area of almost 1000 m² g⁻¹.

The CALF-32 family, ([Cu(ipq)]A·guest, A⁻ = NO₃⁻, BF₄⁻, BF₄⁻/PF₆⁻) could be obtained solvothermally by reacting Cu(NO₃)₂ or Cu(BF₄)₂ with H₂ipq⁺ in *N,N*-dimethylformamide (DMF) and ethanol at 80 °C for 12 hrs (See Supporting Information). CALF-32(NO₃) crystallizes in the monoclinic space group *P2₁/c*, with one copper atom, one ipq⁺ ligand, one nitrate anion, two DMF and two water molecules in the

asymmetric unit. As shown in Fig. 1a, a pair of copper ions form a paddlewheel unit with four carboxylate groups in the equatorial plane and two pyridyl nitrogen atoms from ipq⁺ ligands in the axial sites. The overall structure exhibits a (3,6)-connected *rtl* topology considering the ligand and paddlewheel cluster as three and six connecting nodes, respectively. The Cu complex of 5-(pyridin-4-yl)isophthalic acid (H₂pip), the same linker as in the present study but with the pyridinium unit removed, has been reported and forms the same topology structure but with a neutral framework.⁹ In CALF-32(NO₃), the NO₃⁻ anions are located in the large channel along the *a* axis with O···H-C hydrogen bonding (O···C 3.3-3.6 Å) and electrostatic attractions between O and pyridinium N atoms (O···N 3.15(1) Å) (Fig. 1b). The NO₃⁻ anions partially separate the large channels into cages with a diameter of ca. 4.7 Å excluding vdW radii. These channels are further connected through 3.6 Å windows to give 3D pores (Fig. 1c and 1d). The solvent accessible volume of CALF-32(NO₃) is 47% calculated by PLATON.¹⁰ Interestingly, although the synthesis had a 2:1 ratio of NO₃⁻ and PF₆⁻, the crystal structure shows exclusively nitrate anions in the pores, an observation further confirmed by ¹⁹F NMR of dissolved samples (Fig. S1a and b). The guest solvent molecules were refined as DMF and water, and this was corroborated by the elemental analysis and thermogravimetric analysis (TGA) data. The TGA data shows stability of CALF-32(NO₃) to 210 °C after ca. 30% weight loss (Fig. S2).

Upon activation under a range of conditions (multiple solvent combinations and heating cycles but excluding supercritical CO₂), CALF-32(NO₃) was observed to lose crystallinity as verified by the powder X-ray diffraction (PXRD) (Fig. S3) in all cases. N₂ sorption at 77 K exhibited no uptake but CO₂ sorption at 195 K showed a type-I behaviour with only a Langmuir surface area of 118 m² g⁻¹ (Table S2 and Fig. S4). This is attributed to the contraction of the framework after activation compared to the single-crystal structure.

To investigate the effect of the impregnated anions on the framework stability and gas sorption properties, the BF₄⁻ anion was introduced into the CALF-32 framework by using Cu(BF₄)₂ and H₂ipqBF₄ as reactants. PXRD showed the BF₄⁻ salt gave the isomorphous phase CALF-32(BF₄) (Fig. S3). TGA showed that CALF-32(BF₄) was stable to 240 °C, 30 °C higher than CALF-32(NO₃) (Fig. S2). While CALF-32(NO₃) showed no N₂ uptake, for CALF-32(BF₄), the N₂ sorption at 77 K showed a type-I isotherm with a Langmuir surface area of 248 m² g⁻¹ (Table S2 and Fig. S4). PXRD showed the shift of the [100] peak to higher angle attributed to shrinkage of the *a* axis (Fig. S3). The loss of other peaks may be due to

distortion of the framework and displacement of anions. The CO₂ sorption isotherm measured at 195 K showed a two-step adsorption behavior with a 2nd step gate opening pressure at $P/P_0 = 0.028$. This may be ascribed to the expansion of framework at higher temperature compared with the N₂ sorption.¹¹ The Langmuir surface area calculated from the first step is 206 m² g⁻¹ and the total surface area is 408 m² g⁻¹ (Table S2 and Fig. S4).

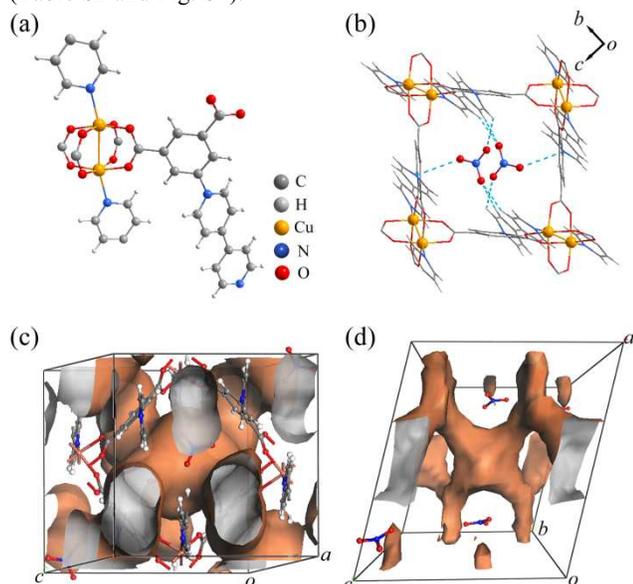


Fig. 1 (a) Coordination environment, (b) embedding of NO₃⁻ anions in the channel view along *a* axis, 3D (c) porous channels and (d) accessible guest surface in CALF-32(NO₃).

Based on the outcomes of the CALF-32(BF₄) study, it was hypothesized that a larger anion could help prevent structural collapse and enhance porosity. Numerous attempts were made to prepare the isomorphous CALF-32(PF₆) using Cu(PF₆) and H₂ipqPF₆ but these invariably gave mixtures of different structures. However, by varying the reactant ratio of Cu(BF₄)₂ and H₂ipqPF₆ to 1:1 and 2:3, two CALF-32 analogues were obtained with mixed BF₄⁻/PF₆⁻ anions. Solution ¹⁹F NMR on dissolved complexes reproducibly gave BF₄⁻/PF₆⁻ ratios of 4:1 and 3:2 by integrating the BF₄⁻ and PF₆⁻ peaks (Fig. S1d/e) for the 1:1 and 2:3 metal/ligand ratios, respectively.

Although the stabilities of CALF-32(BF₄)_{0.8}(PF₆)_{0.2} and CALF-32(BF₄)_{0.6}(PF₆)_{0.4} from TGA were similar with CALF-32(BF₄) (Fig. S2), they both showed improved gas sorption abilities. For CALF-32(BF₄)_{0.8}(PF₆)_{0.2}, the PXRD pattern was similar to the pure BF₄⁻ compound after activation (partial collapse) but N₂ sorption at 77 K gave a type-I isotherm with a Langmuir surface area of 317 m² g⁻¹, 20% higher than the pure BF₄⁻ MOF (Table S2 and Fig. S4). CO₂ sorption at 195 K showed the same two-step pattern observed for the BF₄⁻ system with Langmuir surface areas 314 m² g⁻¹ and 600 m² g⁻¹ calculated from the first step and total sorption, respectively (Table S2 and Fig. S4). The gate opening pressure of the 2nd step is $P/P_0 = 0.039$.

For CALF-32(BF₄)_{0.6}(PF₆)_{0.4}, after activation, the PXRD pattern showed partial structural collapse but did retain some degree of crystallinity (Fig. S3). Notably, the Langmuir surface area is much higher than those of the other three

CALF-32 derivatives and reaches 955 m² g⁻¹ from N₂ sorption at 77 K and 1186 m² g⁻¹ from CO₂ sorption at 195 K. The pore volume calculated from N₂ sorption at $P/P_0 = 0.95$ is 0.35 cm³ g⁻¹. This is the same value for the pore volume obtained from an *in silico* constructed model based on the single-crystal structure of CALF-32(NO₃) and altering the NO₃⁻ anions to (BF₄)_{0.6}(PF₆)_{0.4}.

Comparing CO₂ sorption at 273 K and 1 bar, the capacity of CALF-32(NO₃) is only 3.4 wt% (0.8 mmol g⁻¹). CALF-32(BF₄), with the slightly higher Langmuir surface area, adsorbs almost double the CO₂ of CALF-32(NO₃) and reaches 6.6 wt% (1.5 mmol g⁻¹) at 273 K and 1 bar. More interesting, the doping of PF₆⁻ anion significantly increases the CO₂ uptake, which ranges from 8.8 wt% (2.0 mmol g⁻¹) for CALF-32(BF₄)_{0.8}(PF₆)_{0.2} to 21 wt% (4.8 mmol g⁻¹) for CALF-32(BF₄)_{0.6}(PF₆)_{0.4} at 273 K and 1 bar (Table S2 and Fig. S5).

At 298 K and 1 bar, CALF-32(BF₄)_{0.6}(PF₆)_{0.4} can store up to 15 wt% (3.4 mmol g⁻¹) of CO₂. This is lower than MOFs with open metal sites, such as MOF-74-M/CPO-27-M (24 – 36 wt% or 5.5 – 8.2 mmol g⁻¹),^{3a} but it is comparable to other high performing MOFs even functionalized with organic amine, such as CuBTri-mmen (15.4 wt% or 3.5 mmol g⁻¹),¹² Bio-MOF-11 (15.2 wt% or 3.5 mmol g⁻¹)^{4a} and Zn₂(ox)(atz)₂ (14.3 wt% or 3.3 mmol g⁻¹) at 298 K and 1 bar.^{4c,13} CALF-32(BF₄)_{0.6}(PF₆)_{0.4} performs better than the neutral isostructural framework [Cu(pip)] (H₂pip = 5-(pyridin-4-yl)isophthalic acid), which adsorbs 13.5 wt% (3.1 mmol g⁻¹) of CO₂ at 298 K and 1 bar with no anions in the pores.¹⁴

Regarding the partial collapse of the structures, the excellent CO₂ adsorption in CALF-32(BF₄)_{0.6}(PF₆)_{0.4} could be repeated more than once on the same sample indicating that, while partial collapse is occurring, the extent of the collapse is attenuated. Although none of the CALF-32 family could retain the exact framework without some degree of collapse, the PXRD and gas sorption experiments confirm that the doping of PF₆⁻ anions limits the contraction of the framework and significantly enhances porosity. Recently, outstanding CO₂ capture ability has been demonstrated by Zaworotko, Eddaoudi et al, in a system in which SiF₆²⁻ dianions play a key role in defining the pore character.¹⁵

The effect of incorporating pyridinium and anions to augment guest affinity is further confirmed by the CO₂ adsorption enthalpies. The zero-coverage adsorption enthalpies were estimated from the CO₂ sorption isotherms at 273 K and 298 K by using the virial equation. Obtained values ranged from 31 – 35 kJ mol⁻¹ for the CALF-32 derivatives with the highest value for CALF-32(BF₄)_{0.6}(PF₆)_{0.4} (Table S2 and Fig. S6/7). For comparison, the CO₂ adsorption enthalpy of neutral [Cu(pip)] is 28 kJ mol⁻¹.¹⁴ The enhanced CO₂ heat of adsorption and total uptake would benefit from the pyridinium in the framework and BF₄⁻/PF₆⁻ anions in the pores.¹⁵ While many factors contribute to the isosteric heat of adsorption, and with the partial structural collapse precise assignment of these factors is not possible, the higher value is as expected based on the uptakes.

The amounts of N₂ and CH₄ adsorbed by the CALF-32 series are much lower than those of CO₂. At 273 K and 1 bar, the N₂ adsorption ranged from 0.1 wt% for CALF-32(NO₃) to

0.8 wt% for CALF-32(BF₄)_{0.6}(PF₆)_{0.4}. For CH₄ adsorption, CALF-32(BF₄)_{0.6}(PF₆)_{0.4} adsorbs 2.1 wt% at 273 K and 1 bar, while the other three adsorb less than 0.5 wt% (Table S2 and Fig. S5). The selectivities of CO₂ over N₂ and CH₄ were estimated from ideal adsorbed solution theory (IAST)¹⁶ by fitting the isotherms with Langmuir–Freundlich method (Fig. S8). The N₂ and CH₄ mole fractions were chosen to be 0.87 and 0.5, respectively. As shown in Fig. 2 and Table S2, the separation ratios of CO₂/N₂ and CO₂/CH₄ for CALF-32(NO₃) are 63 and 19 at 273 K and 1 bar, are significantly higher than those for [Cu(pip)] (26 and 5 for CO₂/N₂ and CO₂/CH₄, respectively).¹⁴ The selectivity of CO₂ for CALF-32(BF₄) is similar to the NO₃ complex but dramatically increases to 157 for CO₂/N₂ and 47 for CO₂/CH₄ in CALF-32(BF₄)_{0.8}(PF₆)_{0.2}. These CO₂ selectivities exhibited by CALF-32(BF₄)_{0.8}(PF₆)_{0.2} are among highest yet reported for a MOF even functionalized with open metal sites or amino groups.^{2a,15,17} Interestingly, the selectivities of CO₂/N₂ and CO₂/CH₄ for CALF-32(BF₄)_{0.6}(PF₆)_{0.4} decrease to be 98 and 14 at 273 K and 1 bar although this MOF has higher capacity for CO₂.

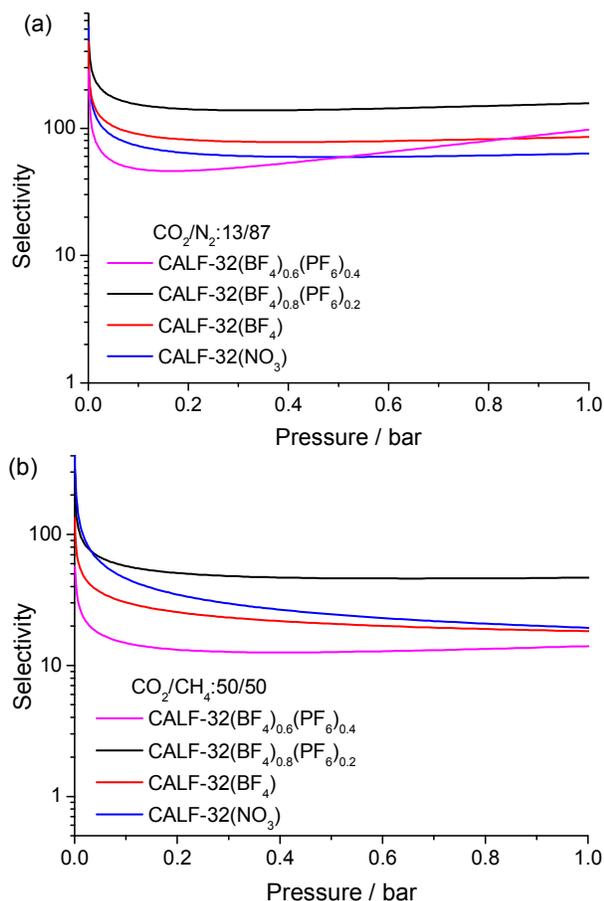


Fig. 2 Selectivity for (a) CO₂/N₂:13/87 and (b) CO₂/CH₄:50/50 gas mixture in CALF-32(A) predicted by IAST at 273 K.

We have reported a new MOF structure, CALF-32(A), incorporating cationic pyridinium units in the struts and different anions in the pores including mixtures of anions. Incorporation of larger anions in the pores is shown to augment the structural stability and the porosity. Most significantly, it was shown that mixed anion (BF₄⁻/PF₆⁻)

species had by far the best performance for CO₂ capture both in regards to capacity and selectivity. The isosteric heats of CO₂ sorption in CALF-32(A) are increased to 31 – 35 kJ mol⁻¹. Selectivities for gas capture are reported and CALF-32(BF₄)_{0.8}(PF₆)_{0.2} seems to be the best for increasing selectivity of CO₂, while CALF-32(BF₄)_{0.6}(PF₆)_{0.4} would be the best for uptake capacity at room temperature.

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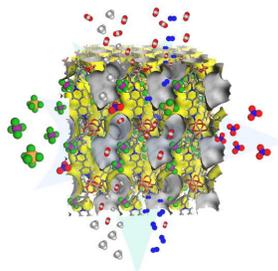
Notes and references

Department of Chemistry, University of Calgary, 2500 University Dr NW, Calgary AB, T2N 1N4, Canada. Fax: +1 403 2899488; Tel: +1 403 2205347 Email: gshimizu@ucalgary.ca

† Electronic Supplementary Information (ESI) available: The additional experiment, crystallographic data, gas sorption and selective data, ¹⁹F NMR, TGA curves, PXRD, and sorption isotherms. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

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Short text and illustration for table of contents:



Mixing anions in a cationic metal-organic framework with pyridinium linkers significantly enhances CO₂ selectivity and uptake capacity.