

Scandium/Alkaline Metal–Organic Frameworks: Adsorptive Properties and Ionic Conductivity

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(5) Supporting Information

ABSTRACT: Several synthetic approaches have been employed to obtain novel $\{[ScM(\mu_4\text{-}pmdc)_2(H_2O)_2]\cdot solv\}_n$ [EHU1(Sc,M)] (where M = Li, Na; pmdc = pyrimidine-4,6-dicarboxylate; solv = corresponding solvent) compounds. The synthesis method is crucial to determine the type of alkaline that could be hosted in the structure as well as the crystallinity, adsorption performance, and ionic conductivity of the resulting materials. Compared with other synthetic methods, a heat-assisted solvent-free procedure has proven to be the most effective route, giving materials with adsorption capacities close to those expected from GCMC (Grand Canonical Monte Carlo) calculations. Despite the presence of alkaline ions in the framework, the pristine materials exhibit rather low con-



ductivity values of ca. 10^{-7} S cm⁻¹. The concentration of charge carriers has been increased by means of a doping approach that incorporates divalent transition metal ions to the structure and forces an increase of the alkaline ions, thus raising the ionic conductivity by 1 order of magnitude. Additionally, soaking the samples in solutions containing alkaline salts led to materials possessing an even higher number of carriers achieving conductivity values among the best results reported for MOFs at room temperature, i.e., 4.2×10^{-4} and 9.2×10^{-5} S cm⁻¹ for EHU1(Sc,Li) and EHU1(Sc,Na) obtained by the solvent-free procedure, respectively.

INTRODUCTION

Metal–organic frameworks (MOFs) constitute a rapidly growing class of materials due to their permanent porosity, high surface area, large pore volume, adjustable pore size, uniform distribution, and shape.^{1–6} This is the reason why they have emerged as promising candidates for adsorptive separations and purification purposes, particularly those concerning the CO₂ capture and sequestration technologies.^{7–10} Moreover, these materials have been extensively investigated for possible applications in sensing,^{11,12} drug delivery,^{13,14} catalytic activity,^{15,16} optoelectronics,^{17,18} and magnetism,¹⁹ since they benefit from their hybrid metal– organic nature. However, although lithium-ion conductivity of these materials has been observed, only few reports concerning the use of MOFs as Li-ion battery electrolytes have been published to date.^{20,21} Characterized by a high specific energy and efficiency, Li-ion batteries have become the energy storage systems of choice for consumer electronics.^{22,23} Electrolyte

research plays a key role in this technology expansion, where the development of new solid electrolytes possessing high conductivity values at temperatures up to 60 °C would be of great importance.²⁴ Currently, macroporous membranes swelled in organic electrolyte are mainly employed as Li-ion battery separators.²⁵ They lack rigidity and may be pierced by lithium dendrites causing cell failure.²⁶ In this regard, the use of MOFs as solid separators could afford the required coexistence of rigidity and dynamics to avoid the latter problems.²⁷ Additionally, the actual concerns on the global lithium resources availability are stimulating the battery research toward the use of other naturally abundant elements, for instance, Na, which could also lead to inexpensive batteries for portable electronics and stationary applications.^{28,29}

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In terms of construction, MOFs are set under equilibrium conditions between metal and ligands, so the variation of the kinetics by means of the synthetic factors could give profound changes on the sample crystallinity and, consequently, on the physical properties of the material. For instance, it has been stated that the space charge of solid interfaces, besides the adsorption behavior, exerts a crucial influence on the conductivity.³⁰ In our research group we extensively employed pyrimidine-4,6-dicarboxylic acid (H₂pmdc) according to its ability to coordinate to different metal centers by displaying several coordination modes owing to its large number of donor atoms.^{31–35} In fact, architectures from 1D to 3D polymers can be achieved depending on the ion size and charge of the metal atoms.³⁶ In particular, this system has us allowed to successfully give rise to a series of porous MOFs of formula {[CdM(μ_4 $pmdc)_2(H_2O)_2$ solv $_n$ ($M^{II} = Cd, Mn, Zn$) that behave as good CO₂ adsorbents under certain preparation conditions.³⁷ This framework features two markedly different coordination environments, which allows selective replacement of the metals and in turn enables the properties of the material to be tailored. Taking this fact into consideration, we selected scandium(III) to partially replace cadmium(II) in the parent MOF due to its similar ion size and coordination indices (see Supporting Information).^{38–40} This trivalent metal also imposes a charge imbalance that requires monovalent ions to be present in the crystal structure ($M^{3+} + M^+$: 2 × pmdc²⁻). Sc³⁺ ion is, as well, a very good candidate to bypass the poorly reversible reactions observed for most of the MOFs employed as cathode materials given its null occupation of 3d orbitals. It also features higher M-O bond stability in the resulting material regarding charge variations, and it brings about long-range electron delocalization by means of the stabilization of mixed-valence states.

Therefore, two new heterometallic MOFs have been designed employing scandium(III) and alkaline metals as monovalent ions. These materials provide, in addition to a high specific surface area, an ordered distribution of alkaline ions among the crystal structure. Taking advantage of that structural characteristic, two different procedures have been designed to endow the insulating material with additional alkaline ions in an attempt to obtain ionic conductor MOFs.

EXPERIMENTAL SECTION

Chemicals. All chemicals were of reagent grade and used as commercially obtained. The starting material pyrimidine-4,6-dicarboxylic acid was prepared following the previously reported procedure.⁴¹ The stock solution of ScCl₃ (1.45 M) was prepared dissolving 0.4999 g of Sc₂O₃ in 1.8 mL of HCl (37%) and adding water up to 5 mL in a calibrated flask.

Synthesis of {[ScNa(μ_4 -pmdc)₂(H₂O)₂]·5H₂O}_n [EHU1(Sc,Na)-S1]. A 0.300 mmol amount of ScCl₃ (207 μ L of 1.45 M solution) was added to 25 mL of a water solution containing 0.600 mmol of H₂pmdc (0.1224 g). A 1 M NaOH solution was added dropwise until a white precipitate appeared (pH 2.8–4.6). The mixture was sealed into a Teflon-lined stainless steel autoclave under autogenous pressure and heated at 170–180 °C for 3 days. Then it was slowly cooled down to room temperature (2 °C/h), and a polycrystalline sample of EHU1(Sc,Na)-S1 was achieved. Anal. Calcd for C₁₂H₁₈N₄NaO₁₅Sc (526.24 g mol⁻¹): C, 27.39; H, 3.45; N, 10.65; Na, 4.37; Sc, 8.54. Found: C, 27.57; H, 3.37; N, 10.42; Na, 4.54; Sc, 8.73. FT-IR (KBr, cm⁻¹): 3435 (s), 3230 (m), 3115 (m), 1670 (vs), 1645 (sh), 1625 (s), 1595 (sh), 1545 (m), 1475 (w), 1435 (m), 1380 (vs), 1305 (sh), 1285 (w), 1205 (sh), 1185 (w), 1015 (w), 945 (w), 920 (w), 845 (w), 815 (w), 725 (sh), 720 (s), 700 (m), 655 (w), 620 (m), 590 (m), 545 (m), 450 (m). Synthesis of {[$ScNa(\mu_4-pmdc)_2(H_2O)_2$]·DMF·2H₂O}_n [EHU1-(Sc,Na)-S2]. A 25 mL amount of a dimethylformamide (DMF)/ methanol (MeOH) (1:1) solution containing 0.300 mmol of ScCl₃ (207 μ L of 1.45 M solution), 0.600 mmol of H₂pmdc (0.1224 g), and 0.300 mmol of NaCl (0.0175 g) was heated by following the abovementioned solvothermal procedure at 120–160 °C. A mixture of polycrystalline sample with few, small, and bad quality single crystals was achieved. Anal. Calcd for C₁₅H₁₉N₅NaO₁₃Sc (545.28 g mol⁻¹): C, 33.04; H, 3.51; N, 12.84; Na, 4.22; Sc, 8.24. Found: C, 32.88; H, 3.65; N, 13.13; Na, 4.58; Sc, 8.14. FT-IR (KBr, cm⁻¹): 3455 (s), 3225 (sh), 3115 (sh), 3030 (w), 2925 (w), 1650 (vs), 1620 (sh), 1595 (s), 1545 (s), 1465 (w), 1450 (w), 1426 (m), 1380 (vs), 1315 (m), 1285 (w), 1205 (sh), 1190 (m), 1100 (w), 1030 (w), 930 (w), 890 (w), 845 (w), 810 (w), 745 (s), 720 (sh), 700 (s), 585 (w), 535 (w), 460 (w).

Synthesis of {[ScNa(μ_4 -pmdc)₂(H₂O)₂]·5H₂O}_n [EHU1(Sc,Na)-SF1]. This compound is achieved by means of an oven-heating solvent-free procedure. To that end, 0.310 mmol of H₂pmdc (0.0633 g) was thoroughly hand ground with 0.155 mmol of sodium chloride (0.0091 g) by means of a mortar until a fine homogeneous powder was obtained. Then 0.075 mmol of Sc_2O_3 (0.0103 g) was ground with the previous mixture, and the resulting powder was sealed into a long-stem glass vacuole (1 cm \times 10.8 cm, 1 mL capacity) and placed in an oven. There it was heated up to 110 °C, maintained at this temperature for 72 h, and cooled down to room temperature (1.5 °C/h). Anal. Calcd for C₁₂H₁₈N₄NaO₁₅Sc (526.24 g mol⁻¹): C, 27.39; H, 3.45; N, 10.65; Na, 4.37; Sc, 8.54. Found: C, 27.26; H, 3.33; N, 10.80; Na, 4.28; Sc, 8.39. FT-IR (KBr, cm⁻¹): 3425 (s), 3230 (sh), 3115 (sh), 1655 (vs), 1630 (sh), 1600 (s), 1560 (s), 1470 (w), 1426 (sh), 1385 (s), 1355 (vs), 1305 (sh), 1285 (w), 1205 (m), 1100 (w), 1040 (w), 915 (w), 855 (w), 810 (w), 745 (s), 730 (sh), 695 (s), 535 (w), 495 (w), 460 (w).

Synthesis of { $[ScNa(\mu_4-pmdc)_2(H_2O)_2] \cdot 6H_2O_{]n}$ [EHU1(Sc,Na)-SF2]. This compound is obtained following the previously described solvent-free procedure but using 0.155 mol of sodium nitrate (0.0132 g) instead of sodium chloride. Anal. Calcd for $C_{12}H_{20}N_4NaO_{16}Sc$ (544.25 g mol⁻¹): C, 26.48; H, 3.70; N, 10.29; Na, 4.22; Sc, 8.26. Found: C, 26.42; H, 3.54; N, 10.46; Na, 4.17; Sc, 8.31. FT-IR (KBr, cm⁻¹): 3430 (s), 3235 (sh), 3115 (sh), 1665 (vs), 1635 (s), 1610 (s), 1560 (s), 1470 (w), 1430 (m), 1380 (sh), 1355 (vs), 1310 (sh), 1210 (m), 1100 (w), 1035 (w), 1015(sh), 915 (w), 855 (w), 815 (w), 745 (s), 730 (sh), 690 (w), 635 (w), 595 (w), 530 (w), 480 (w).

Synthesis of { $[ScLi(\mu_4-pmdc)_2(H_2O)_2] \cdot 5H_2O$ }_n [EHU1(Sc,Li)-SF2]. The compound is obtained following the previously described solventfree procedure but using 0.155 mol of lithium nitrate (0.0107 g). Anal. Calcd for C₁₂H₁₈LiN₄O₁₅Sc (510.19 g mol⁻¹): C, 28.25; H, 3.56; Li, 1.36; N, 10.98; Sc, 8.82. Found: C, 28.51; H, 3.45; Li, 1.53; N, 10.77; Sc, 8.71. FT-IR (KBr, cm⁻¹): 3430 (s), 3235 (sh), 3115 (sh), 1660 (vs), 1630 (s), 1605 (s), 1560 (s), 1480 (w), 1425 (sh), 1385 (s), 1360 (vs), 1305 (sh), 1205 (m), 1100 (w), 1035 (w), 920 (w), 855 (w), 815 (w), 745 (s), 730 (sh), 690 (s), 600 (w), 535 (w), 490 (w). Synthesis of {[Sc_{0.95}Na_{1.05}Cd_{0.05}(µ₄-pmdc)₂(H₂O)₂]·6H₂O}_n [**Cd**@ EHÚ1(Sc,Na)-SF2]. This compound is obtained by the previously described solvent-free procedure in which 0.071 mmol of Sc₂O₃ (0.0098 g), 0.162 mmol of NaNO3 (0.0138 g), and 0.008 mmol of $Cd(OH)_2 \cdot 2H_2O$ (0.0015 g) were mixed with previously hand ground 0.310 mmol of H₂pmdc (0.0633 g). Anal. Calcd for $C_{12}H_{20}Cd_{0.05}N_4Na_{1.05}O_{16}Sc_{0.95}$ (548.77 g mol⁻¹): C, 26.26; H, 3.67; N, 10.21; Cd, 1.02; Na, 4.40; Sc, 7.78. Found: C, 26.02; H, 3.64; N, 10.11; Cd, 1.01; Na, 4.36; Sc, 8.32. FT-IR (KBr, cm⁻¹): 3430 (s), 3235 (sh), 3115 (sh), 1670 (vs), 1640 (s), 1610 (s), 1560 (s), 1475 (w), 1430 (m), 1360 (vs), 1300 (sh), 1280 (sh), 1235 (sh), 1215 (m), 1100 (w), 1035 (w), 925 (w), 855 (m), 815 (w), 745 (s), 730 (sh), 695 (s), 635 (w), 595 (w), 530 (m), 480 (w).

Synthesis of { $[Sc_{0.95}Ll_{1.05}Cd_{0.05}(\mu_4-pmdc)_2(H_2O)_2] \cdot 5H_2O\}_n$ [Cd@ EHU1(Sc,Li)-SF2]. This compound is obtained following the synthesis of Cd@EHU1(Sc,Na)-SF2 but using 0.162 mmol of LiNO₃ (0.0112 g) instead of NaNO₃. Anal. Calcd for C₁₂H₁₈Cd_{0.05}Li_{1.05}N₄O₁₅Sc_{0.95} (513.91 g mol⁻¹): C, 28.05; H, 3.53; Cd, 1.09; Li, 1.42; N, 10.90; Sc, 8.31. Found: C, 27.64; H, 3.48; Cd, 1.08; Li, 1.40; N, 10.74; Sc, 9.14. FT-IR (KBr, cm⁻¹): 3430 (s), 3235 (sh), 3115 (sh), 1660 (vs), 1630 (s), 1610 (s), 1560 (s), 1470 (w), 1430 (m), 1385 (sh), 1355 (vs), 1305 (sh), 1235 (sh), 1205 (m), 1105 (w), 1035 (w), 920 (w), 855 (w), 815 (w), 745 (s), 730 (sh), 695 (s), 630 (w), 600 (w), 530 (w), 450 (w).

Synthesis of {[$Sc_{0.95}Na_{1.05}Mn_{0.05}(\mu_4-pmdc)_2(H_2O)_2$]· GH_2O }_n [Mn@EHU1(Sc,Na)-SF2]. The same solvent-free procedure was employed grinding 0.071 mmol of Sc_2O_3 (0.0098 g), 0.162 mmol of NaNO₃ (0.0138 g), and 0.008 mmol of Mn(acetate)_2·4H_2O (0.0020 g) over previously ground 0.310 mmol of H₂pmdc (0.0633 g) to give rise to **M n @ E H U 1 (S c , N a)** - **S F 2**. A n a 1. C a l c d f o r $C_{12}H_{20}N_4Mn_{0.05}Na_{1.05}O_{16}Sc_{0.95}$ (545.90 g mol⁻¹): C, 26.40; H, 3.69; Mn, 0.50; N, 10.26; Na, 4.42; Sc, 7.82. Found: C, 25.98; H, 3.63; Mn, 0.50; N, 10.10; Na, 4.35; Sc, 8.75. FT-IR (KBr, cm⁻¹): 3430 (s), 3235 (sh), 3115 (sh), 1670 (vs), 1635 (s), 1615 (s), 1560 (s), 1465 (w), 1435 (m), 1360 (vs), 1310 (m), 1280 (sh), 1240 (w), 1210 (m), 1110 (w), 1040 (w), 925 (w), 855 (m), 815 (w), 745 (s), 730 (sh), 695 (s), 620 (w), 585 (w), 530 (m), 470 (w), 435 (w).

Synthesis of {[$Sc_{0.95}Li_{1.05}Mn_{0.05}(\mu_4-pmdc)_2(H_2O)_2$]·5H₂O}_n [**Mn@ EHU1(Sc,Li)-SF2**]. This compound is obtained following the synthesis of **Mn@EHU1(Sc,Na)-SF2** but using 0.162 mmol of LiNO₃ (0.0112 g). Anal. Calcd for C₁₂H₁₈Li_{1.05}Mn_{0.05}N₄O₁₅Sc_{0.95} (511.03 g mol⁻¹): C, 28.20; H, 3.55; Li, 1.43; Mn, 0.54; N, 10.96; Sc, 8.36. Found: C, 27.69; H, 3.49; Li, 1.43; Mn, 0.53; N, 10.76; Sc, 9.39. FT-IR (KBr, cm⁻¹): 3430 (s), 3235 (sh), 3115 (sh), 1670 (vs), 1640 (sh), 1605 (s), 1565 (s), 1470 (w), 1430 (m), 1385 (s), 1360 (vs), 1305 (sh), 1235 (sh), 1205 (m), 1105 (w), 1040 (w), 1015 (sh), 915 (w), 855 (w), 815 (w), 745 (s), 730 (sh), 695 (s), 635 (w), 530 (w), 445 (m).

Excess amounts of ligand and alkaline salts have been employed in all solvent-free syntheses to ensure a complete reaction of Sc_2O_3 , such that there is no more nonreacted reagent in the resulting samples. Moreover, samples were washed with a water/ethanol mixture to ensure that starting H₂pmdc and alkaline salts are removed and dried in open atmosphere (X-ray powder patterns confirm the purity of the samples).

X-ray Diffraction Data Collection. The X-ray powder diffraction (PXRD) patterns were collected on a Phillips X'PERT powder diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) over the range 5° < 2θ < 50° with a step size of 0.02°, a variable automatic divergence slit, and an acquisition time of 2.5 s per step at 25 °C. Indexation of the diffraction profiles was made by means of the FULLPROF program (pattern-matching analysis).⁴² Variable-temperature X-ray powder diffraction measurements were run under ambient atmosphere with heating rates of 5 °C min⁻¹; a complete diffraction pattern was measured every 20 °C.

Physical Measurements. Elemental analyses (C, H, N) were performed on an Euro EA Elemental Analyzer, whereas the metal content was determined by inductively coupled plasma (ICP-AES) and absorption spectrometry performed on a Horiba Yobin Yvon Activa spectrometer and a PerkinElmer Analyst 100, respectively. The IR spectra (KBr pellets) were recorded on a FTIR 8400S Shimadzu spectrometer in the 4000-400 cm⁻¹ spectral region. Thermal analyses (TG/DTA) were performed on a TA Instruments SDT 2960 thermal analyzer in a synthetic air atmosphere (79% $N_2/21\%$ O_2) with a heating rate of 5 °C min⁻¹. All samples were activated in vacuo for 6 h at temperatures ranging from 100 to 200 °C depending on the sample. Nitrogen physisorption data were recorded with a Micromeritics Tristar II 3020. The specific surface area was calculated from the adsorption branch in the relative pressure interval using the Brunauer-Emmett-Teller (BET) method⁴³ and the consistency criteria proposed by Walton and Snurr that is commonly applied for MOFs,^{44,45} while the micropore volume was estimated by fitting the measured N₂ isotherms with the *t*-plot method.⁴⁶ The volumetric carbon dioxide physisorption data were recorded in a Micromeritics ASAP 2020 porosity analyzer at 298 and 273 K and in a Hiden IGA automatic gravimetric porosimeter at 196 K (ethanol/dry ice mixture). Solid state NMR measurements were performed in a Bruker Avance 400 spectrometer equipped with a 89 mm wide bore, 9.4 T superconducting magnet (Larmor frequencies of 400.14 (¹H), 376.51 (¹⁹F), 155.51 (⁷Li), 100.61 (¹³C), 97.20 (⁴⁵Sc), and 88.80 (¹¹³Cd) MHz). Powdered samples were placed in 4 mm zirconia

rotors. All reported data were acquired at room temperature. A standard Bruker double-resonance 4 mm cross-polarization (CP)/ magic angle spinning (MAS) NMR probe head was used. The 45 Sc measurements were performed at MAS spinning rates of 11 kHz and the rest at 7 kHz. All spectra were acquired using a single-pulse sequence with the exception of the 13 C spectra that were acquired with a CP/MAS pulse sequence, 3 ms CP contact time, and sideband suppression (seltics), and the 113 Cd spectra were acquired with a CP/MAS sequence, both with proton decoupling (see Supporting Information for further details). Scanning electron microscopy (SEM) measurements were performed on a Jeol JSM 6400.

Computational Details: GCMC Calculations. Force-field based Grand Canonical Monte Carlo (GCMC) simulations of singlecomponent (N₂ and CO₂) adsorption were carried out using the SORPTION module included in the Accelrys "Materials Studio" package.⁴⁷ The theoretical background of GCMC simulations is described in detail elsewhere.⁴⁸ For comparison with experimental data, simulations of single-component isotherms were carried out under the same conditions for each adsorbate (P < 1 bar; N₂ at 77 K, CO₂ at 196, 273, and 298 K). The simulations of adsorption isotherms involved 4 million equilibration steps and 6 million production steps.

Models of Fluid Molecules. In all simulations, dispersive and electrostatic interactions were taken into account. Dispersive interactions were modeled using a Lennard–Jones (LJ) 12-6 potential. Parameters to represent the interaction between different atom types were calculated using Lorentz-Berthelot mixing rules. A cutoff radius of 12.5 Å was employed for dispersive interactions. Electrostatic interactions were modeled by assigning point charges to the atomic sites, and an Ewald summation was used to account for the periodicity of the simulation box. The representation of the models and parameters used for the fluid molecules can be found elsewhere.³⁷ The selection of the models and parameters used to define the fluid molecules has been done based on previous studies. For the N2 molecule, the LJ parameters were taken from the TraPPE model.⁴ This model simulates the quadrupolar moment of the N₂, placing two negative charges (-0.482) in the positions of the nitrogen atoms and a positive one in the center of mass (+0.964). The LJ parameters used to represent the CO₂ interactions were taken from the work of García-Sánchez and co-workers⁵⁰ and consist of a modified version of the TraPPE potential model. The combination of these parameters with the distribution of the charges calculated in a previous work has proved to be suitably adjusted to experimental data of different MOFs.⁵¹

Models of Adsorbents. In all cases $2 \times 2 \times 2$ supercells were employed. The LJ parameters for all atoms of the adsorbents were taken from the universal force field (UFF).⁵² The partial charges to represent the electrostatic potential inside the pores were derived from DFT calculations using the ESP method as described by Singh and Kollman,⁵³ which is implemented in the DMOL3 code.⁵⁴ For this calculation the DNP basis set and the PBE exchange-correlation functional were selected.⁵⁵

Conductivity Measurements. Electrochemical impedance spectroscopy (EIS) was performed using a Solartron 1260 gain phase analyzer from 1 MHz down to 1 Hz. The collected materials were pressed into 5 mm diameter pellets by uniaxial pressing at 3 T for 1 min. The pellets were placed in a Swagelok cell firmly closed to ensure the good contact between the electrolyte and the stainless steel plungers. The cell assembly was performed in air, exposing the pellet to atmospheric moisture. Once sealed the system was isolated from the atmosphere. Z-view software was used to fit the EIS data using a parallel RC compound in series with an open Warburg function. EHU1(Sc,Li)·(LiBF₄) and EHU1(Sc,Na)·(NaPF₆) samples were soaked in 1 M solutions of LiBF4 and NaPF6 salts, respectively, in dimethyl carbonate (DMC) and stirred overnight. The resulting mixtures were then filtered, rinsed with an excess of DMC, and dried at 60 °C under vacuum. Arrhenius plots were obtained from the measurements at different temperatures from 20 to 100 °C.

Tab	le	1.	Summary	of	the	Explored	Synt	hesis	Conditions	for	EHU1	(Sc,Na)	Compounds
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code	formula	synthetic route	solvent/metal source	T (°C)	pН
EHU1(Sc,Na)-S1	$\{[ScNa(\mu_4-pmdc)_2(H_2O)_2]\cdot 5H_2O\}_n$	hydrothermal	H ₂ O/ScCl ₃ /NaOH	170-180	2.8-4.6
EHU1(Sc,Na)-S2	$\{[ScNa(\mu_4-pmdc)_2(H_2O)_2]\cdot DMF\cdot 2H_2O\}_n$	solvothermal	(DMF:MeOH)/ScCl ₃ /NaCl	120-160	1.5
EHU1(Sc,Na)-SF1	{[ScNa(μ_4 -pmdc) ₂ (H ₂ O) ₂]·5H ₂ O} _n	solvent-free	-/Sc ₂ O ₃ /NaCl	110	
EHU1(Sc,Na)-SF2	$\{[ScNa(\mu_4-pmdc)_2(H_2O)_2]\cdot 6H_2O\}_n$	solvent-free	$-/Sc_2O_3/NaNO_3$	110	

RESULTS AND DISCUSSION

Comments on the Synthesis of EHU1(Sc,M) Compounds. The synthesis method plays a key role in determining not only the type of alkaline ion that can be hosted at the structure of EHU1(Sc,M) but also the crystallinity of the resulting material, a fact that affects the adsorption performance and ionic conductivity. Thus, prior to any analysis of the physical properties of these compounds, several synthetic routes and conditions were examined for EHU1(Sc,Na) (Table 1). The synthetic study is divided into two major routes, such as solvothermal (S) and solvent free (SF), each of which have been explored through two alternative procedures (S1/S2 and SF1/SF2, respectively). Overall, an almost proportional improvement of the samples crystallinity is observed along the S1 \rightarrow S2 \rightarrow SF1 \rightarrow SF2 sequence, which is inferred from PXRD (see Supporting Information).

The good performance of the solvent-free synthesis^{56–60} can be attributed to the slow diffusion of the reactants within the melt formed by the hydrated nitrate/chloride salts (given their hygroscopic nature). Consequently, this method allowed us to obtain EHU1(Sc,Li)-SF2, although the pure potassium counterpart could not be isolated in spite of all synthetic efforts. SEM micrographs on EHU1(Sc,M)-SF2 (M = Li, Na) samples show the presence of small twinned cubes with a somewhat regular size distribution of ca. 10 μ m (Supporting Information). Notwithstanding the latter assertions, the great dissolving capacity of the DMF/MeOH mixture^{61–63} leads to low-quality single crystals along with the polycrystalline powder of EHU1(Sc,Na)-S2, which afford reliable unit cell parameters and identification of metal positions in the structure.

Structural Description of EHU1(Sc,M) Compounds. Details of the PXRD refinement of EHU1(Sc,M) (M = Li, Na) compounds are summarized in Table 2. These compounds are

Table 2. Crystallographic Data and Structure Refinement Details of EHU1(Sc,M)-SF2 Compounds

EHU1(Sc,Li)-SF2	EHU1(Sc,Na)-SF2
$C_{12}H_{18}N_4LiO_{15}Sc$	$\mathrm{C_{12}H_{20}N_4NaO_{16}Sc}$
510.05	544.03
Im-3m	Im-3m
18.742(2)	18.878(2)
6584(1)	6728(1)
1.26/1.06	1.34/1.46
4.75/1.49	4.88/1.23
	EHU1(Sc,Li)-SF2 C ₁₂ H ₁₈ N ₄ LiO ₁₅ Sc 510.05 <i>Im-3m</i> 18.742(2) 6584(1) 1.26/1.06 4.75/1.49

isostructural to a family of porous compounds with {[CdM(μ_4 pmdc)_2(H_2O)_2]·solv}_n (M^{II} = Cd, Mn, Zn) formula.³⁷ Their crystal structure consists of a 3D neutral metal–organic framework that is the result of the junction of two different molecular building blocks (MBB, Figure 1) established by Sc³⁺ and alkaline (M⁺) ions coordinated to the pmdc ligands. The MBB in Figure 2a consists of four chelating N/O moieties of pmdc that are coordinated to the scandium atom (Sc), rendering a N₄O₄ donor set that resembles a triangular



Figure 1. Representation of MBBs of EHU1(Sc,Na) obtained from the DFT structure optimization. Color coding: blue (oxygen), green (nitrogen), pink (hydrogen), red (metal).

dodecahedron. Therefore, this building block can be regarded as a tetrahedral node from the topological point of view. The MBB in Figure 2b is built up by the coordination of four nonchelating atoms and two coordination water molecules, displaying a distorted octahedral geometry. The connectors are arranged around alkaline ions (M) describing a pseudosquareplanar building unit. Hence, the pmdc ligand exhibits the μ_4 - $\kappa^2 N, O: \kappa^2 N', O': \kappa O'''$ coordination mode. Geometry optimizations by means of periodic dispersion-corrected DFT (density functional theory) support the metal distribution over the two crystallographically independent centers present in the crystal structure (energy difference of around 18–19 kcal mol⁻¹ between the two alternative distributions). Moreover, ⁴⁵Sc solid state NMR measurements show the presence of a unique and quite symmetrical environment ($\eta_{\rm O}$ of 0.15 and 0.06 for lithium and sodium counterparts) in concordance with the octacoordinated site. The comparison between the experimental and the DFT-simulated diffractograms shows an acceptable agreement for both compounds (Figure 2).

The junction of four tetrahedral and two square-planar MBBs gives rise to a bigger building unit (β -cage, in which the metal centers are arranged into truncated octahedra) that is further connected through the whole crystal structure by sharing solely the M1 vertices (Figure 3). The resulting packing generates an **nbo** topological network with the $(6^4.8^2)$ point symbol, $^{64-66}$ which leaves an intersecting 3D channel system of voids filled with solvent molecules. The accessible volume varies slightly according to the alkaline atom and represents 42-47% of the unit cell volume.⁶⁷ Additionally, the pore system of these compounds is modulated according to the solvent and synthetic route employed. A deep analysis of the porous structure by a Monte Carlo procedure described elsewhere⁶⁸ concluded that there are three main contributions to the unit cell voids: a large cubic cavity surrounded by six β -cages (diameter of 9.38 Å), eight smaller cubes delimited by six pyrimidine rings, and bottleneck tunnels interconnecting the previous cavities with diameters ranging from 5.85 to 6.15 Å. It is worth noting that atoms occupying the M site lie on the faces of the largest cubic pore, so they could behave as open-metal sites once the





Figure 2. Experimental diffractograms and those simulated from DFToptimized models together with pattern-matching analyses.

coordination water molecules are released (see TG analyses in the Supporting Information). However, the examination of the coordinatively unsaturated (*cus*) metal environments on the DFT-optimized anhydrous structures reveals that they are recessed into the surface in an attempt to maximize their coordination to both carboxylate oxygen atoms (Figure S6).

Gas Adsorption Properties on EHU1(Sc,M) Compounds. Gas adsorption and ionic mobility on these porous materials are closely related because of the need of a highly accessible network of channels so that ionic charge carriers can better diffuse through it. Therefore, routine gas adsorption measurements become a good test to evaluate the viability of a porous material in terms of ionic conductivity, since a wellordered channel system (characteristic of highly crystalline materials) is required. Permanent porosity of EHU1(Sc,M) compounds was studied by means of N₂ adsorption isotherms at 77 K. All adsorption curves show a sharp knee at relatively low pressures ($P/P_0 < 0.01$) followed by a plateau, indicative of a rapid filling of the micropores (see Supporting Information). Table 3 gathers the results of BET analysis, which shows a clear trend for the experimental surface area values that fit rather well



Figure 3. Structural analysis of **EHU1(Sc,M)**: (a) arrangement of the β -cage fraction, (b) junction of β -cages, and (c) pore-size distribution.

 Table 3. Comparison between Experimental and Simulated

 Accessible Surface Areas of EHU1(Sc,M)

 Compounds

compound		$S_{\rm BET}^{a}$	mol/unit cell ^b	V^{c}
EHU1(Sc,Li)_Simulation		1090	52	6713
EHU1(Sc,Li)-SF2		762	39	6384
EHU1(Sc,Na)_Simulation		1046	52	7349
EHU1(Sc,Na)	SF2	848	43	6755
	SF1	703	36	
	S2	631	32	
	S1	207	10	
-		1.		

^{*a*}BET specific surface area (m² g⁻¹). ^{*b*}N₂ molecules adsorbed per unit cell. ^{*c*}Unit cell volume (Å³).

the crystallinity envisaged from the PXRD patterns of the samples.

The surface areas obtained from the optimized crystal structures for each system can be used as a reference value to get insight into the accessibility of the pore channel system. Experimental surface areas for solvent-free samples, although slightly below, are close to the simulated values, which clearly indicates that solvent-free route (i.e., EHU1(Sc,M)-SF2 samples) provides the best results.

 CO_2 adsorption isotherms were conducted at 298, 273, and 196 K, covering the low-pressure range (0–1 bar) (Figure 4), since it is a molecular probe that provides complementary information on the pore network due to its different features. In fact, at 196 K the simulations yield a different CO_2 uptake for lithium and sodium compounds (37.0 vs 47.1 molecules/cell), with these values being somewhat below those corresponding to N₂ adsorption (52 molecules/cell), which can be explained by the different size of the probes together with the presence of narrow adsorption cavities (Table 4). Close to saturation, the deviations between the experimental and the GCMC-simulated isotherms (21.1% and 16.1% at ca. P = 0.9 bar for EHU1(Sc,Li) and EHU1(Sc,Na)) are similar to that found for N₂ (25.0% and 17.3%), which stands not only for the



Figure 4. Experimental and simulated CO₂ adsorption isotherms at (a) 298, (b) 273, and (c) 196 K for EHU1(Sc,M) compounds.

Table 4. Experimental and Simulated CO_2 Uptakes (mmol g^{-1}) of EHU1(Sc,M) Compounds at Different Temperatures

		expe	rimental	DFT			
compound	T(K)	uptake ^a	molecules ^b	uptake ^a	molecules ^b		
EHU1(Sc,Li)	298	2.65	12.2	2.83	13.0		
	273	3.87	17.8	4.46	20.5		
	196	6.08	29.2	8.02	37.0		
EHU1(Sc,Na)	298	2.54	12.2	2.54	12.2		
	273	3.51	16.9	4.13	19.8		
	196	8.23	39.5	9.8	47.1		
^a CO ₂ uptake at ~0.9 bar. ^b CO ₂ molecules per unit cell.							

suitability of the selected computational method but also indicates that both adsorbates probe a similar fraction of the accessible pore. At higher adsorption temperatures (273 and 298 K) a better fitting is observed between the experimental and the simulated uptakes. As far as we are aware, the reported capacities at 273 K (17.0% and 15.4% for EHU1(Sc,Li) and EHU1(Sc,Na), respectively) can be considered as moderately high since they outperform those obtained for many wellknown MOFs, such as MIL-53(Al, Cr), MOF-5, MOF-177, or even most of ZIF materials,⁶⁹ which makes these compounds of relevance to postcombustion flue gases purification. $^{70-72}$ It is worth noting that at low loadings (see isotherms at 273 and 298 K) the experimental curve for EHU1(Sc,Na) exceeds the simulated one, which can be related with the presence of structural defects that diminish the total porosity but increase the adsorbate-adsorbent interactions. In this context, CO₂ adsorption enthalpies (Q_{st}) of lithium and sodium counterparts were also calculated using the modified Clausius-Clapeyron equation by fitting adsorption isotherms at 273 and 298 K (see Supporting Information).^{73,74}

The Q_{st} values at zero coverage approach 28 and 36 kJ mol⁻¹, respectively, to subtly decay to an almost constant value of ca. 25 kJ mol⁻¹ during the whole loading range, in good agreement with those estimated from the simulated isotherms (ca. 24 kJ mol⁻¹). These values, although being rather high, lie far below those attributed to open-metal sites,^{4,75–78} in good agreement with the hindering experimented by the metal atom in the *cus* M position. In concordance to the latter, the CO₂ average occupation maps provided by GCMC calculations on the DFT-optimized EHU1(Sc,Na) reveal that the smaller cubes and bottleneck tunnels are, in fact, the preferred adsorption sites along the accessible surface (Figure S18).

Electrochemical Properties: Ionic Conductivity. As previously stated, the presence of lithium and sodium cations in a porous Sc^{III}-organic framework makes EHU1(Sc,Li) and EHU1(Sc,Na) compounds potential candidates for battery electrolyte applications. The mechanism of ion conduction in solids depends, among others, on factors such as concentration, mobility, and charge of the conductive ions. Given the porous nature of MOFs, charge carriers mobility may involve not only an intrinsic (ion diffusion through the channels) but also an extrinsic (migration through interparticle phases) mechanism. In fact, a recent work by Tominaka and Cheetham⁷⁹ points out that proton conduction in many MOFs seems to be dominated by hydrated interparticle phases when pressed into pellets. Nevertheless, the low conductive values achieved by electrochemical impedance spectroscopy (EIS) for the pristine EHU1(Sc,M) compounds (in the order of 10^{-7} S cm⁻¹) dismisses such a proton conduction mechanism (Table 5). In

Table 5. Room Temperature Results of ac Impedance Spectroscopy for as-Synthesized and Doped EHU1(Sc,M)-SF2 Compounds

compound	$R(\Omega)$	$R (\Omega \text{ cm})$	thckness ^a	$\sigma (\mathrm{S \ cm^{-1}})^{b}$			
EHU1(Sc,Li)	5.0×10^{-5}	2.6×10^{-6}	0.74	3.8×10^{-7}			
Cd@EHU1(Sc,Li)	4.0×10^{-4}	5.7×10^{-5}	0.27	1.7×10^{-6}			
Mn@EHU1(Sc,Li)	2.3×10^{-5}	8.8×10^{-5}	1.01	9.5×10^{-7}			
EHU1(Sc,Na)	1.7×10^{-6}	9.1×10^{-6}	0.72	1.1×10^{-7}			
Cd@ EHU1(Sc,Na)	5.3×10^{-5}	2.9×10^{-6}	0.71	3.4×10^{-7}			
Mn@ EHU1(Sc,Na)	1.3×10^{-5}	5.2×10^{-5}	0.93	2.0×10^{-6}			
Thickness (mm). ^b Ionic conductivity.							

the intrinsic conduction, the occurrence of an ordered and noncollapsed porous structure is a key factor to allow ion diffusion, a fact that is governed by the crystallinity of the sample. Taking into account the targeted conductivity value for a battery electrolyte (above 10^{-3} S cm⁻¹),⁸⁰ different strategies have been envisaged to enhance the mobility of charge carriers in MOFs.^{81–84} All these approaches are based on postsynthetic modifications of the compounds in order to attain structures with a significantly higher number of free charge carriers.

However, we focused on this issue through a one-pot synthetic approach through the doping of EHU1(Sc,M) with divalent metal ions. To that end, we took advantage of the flexibility demonstrated by this MOF to replace metal atoms, i.e., isostructural EHU1(Cd) and EHU1(Mn) compounds.³⁷ Hence, four new materials were successfully prepared by doping EHU1(Sc,Li)-SF2 and EHU1(Sc,Na)-SF2 samples with a 5% of Cd^{II} and Mn^{II} salts (see Experimental Section) to render Cd@EHU1(Sc,M) or Mn@EHU1(Sc,M) samples. PXRD, elemental, and thermogravimetric analyses confirmed that doped samples preserve the initial MOF structure. Interestingly, an increase by 1 order of magnitude on the conductivity by EIS spectroscopy was observed for the doped samples. Taking Cd@EHU1(Sc,Li) as a reference ¹¹³Cd CP/ MAS NMR spectra indicate that these doping atoms occupy a unique site in the structure, in good agreement with the assumption of a partial replacement of Sc(III) by Cd/Mn(II) atoms in the crystal structure, and consequently the presence of an excess of lithium ions to neutralize the charge imbalance. These hypotheses are confirmed by the broadening of the main peaks in all NMR spectra in addition to the occurrence of a minor component in the ⁷Li spectrum at a chemical shift of -1.6 ppm that could be assigned to the somewhat unbound aquo lithium complexes (Supporting Information), which points out that conductivity improvement could come from the mobility of these ions. Moreover, minor components are also detected in the ⁴⁵Sc and ¹³C spectra owing to local structural distorsions taking place in the surroundings of the exchanged metal sites. However, the decrease of the mean particle size observed in the SEM images of the doped samples does not allow discarding an extrinsic contribution to the overall enhancement of the conductivity (Supporting Information).

In light of these results, we opted for a soaking procedure previously reported by Wiers et al.,⁸ which has proven to be an adequate way to boost the conductivity of gel polymer electrolytes. According to it EHU1(Sc,Li)-SF2 and EHU1-(Sc,Na)-SF2 materials were soaked overnight in solutions containing LiBF₄ or NaPF₆ salts in DMC, giving rise to the ionic conductivities shown in Table 6.

Table 6. Results of ac Impedance Spectroscopy for Soaked EHU1(Sc,M) Compounds and Best Results Found for Alkaline-Based MOF Conductors

compound ^a	ion ^b	σ^{c}	T^d	T.S. ^e	ref
EHU1(Sc,Li)·(LiBF ₄) ^{f}	Li ⁺	4.2×10^{-4}	25	270	
EHU1(Sc,Na)·(NaPF ₆) ^f	Na^+	9.2×10^{-5}	25	310	
$[\mathrm{Zr}_6\mathrm{O}_4(\mathrm{OH})_2(\mathrm{bdc})_6]$ -UiO-66 ^g	Li^+	1.8×10^{-5}	r.t.	540	85
Mg ₂ (dobdc)-MOF-74 ^h	Li^+	3.1×10^{-4}	27	380	20

^{*a*}bdc = 1,4-benzenedicarboxylate; dobdc = 1,4-dioxido-2,5-benzenedicarboxylate. ^{*b*}Conductive ion. ^{*c*}Ionic conductivity (S cm⁻¹). ^{*d*}Temperature (°C). ^{*b*}Thermal stability (°C). ^{*f*}LiBF₄ and NaBF₄ are the electrolyte salts. ^{*g*}The sample was grafted with LiOtBu; ^{*h*}The sample was grafted with LiOtBu; ^{*h*}The sample was grafted with LiOtBu; ^{*b*}The sample was grafted with LiOtB

The room-temperature conductivities achieved for EHU1-(Sc,Li) and EHU1(Sc,Na) after the soaking are 3 and 2 orders of magnitude greater than those of the pristine materials (Figure 5). Indeed, that of the lithium compound is, as far as we are concerned, the best result reported for Li-containing MOFs materials. Moreover, EHU1(Sc,Na)·(NaPF₆) represents the first MOF to show ionic conductivity in a Na-ion-based MOF. SEM images of the EHU1(Sc,Li)·(LiBF₄) sample show that particles retain their initial morphology and size, although some of them seem to have been etched as a consequence of the soaking procedure (Figure 6). Moreover, deposition of small



Figure 5. Nyquist plots of the ac impedance data for soaked EHU1(Sc,M) compounds.



Figure 6. SEM images of EHU1(Sc,Li) before and after soaking on LiBF₄.

particles over the surface is noticed. ICP-AES analyses of EHU1(Sc,Li)·(LiBF₄) and EHU1(Sc,Na)·(NaPF₆) show a remarkable increase of the Li/Na:Sc ratio (1.8:1 vs 1:1 and 1.7:1 vs 1:1, respectively) compared to the pristine material. Elemental and thermogravimetric analyses give the {[ScLi(μ_4 $pmdc)_2(H_2O)_2]\cdot 2H_2O\cdot 0.8LiBF_4\}_n$ and {[ScNa(μ_4 $pmdc)_{2}(H_{2}O)_{2}]\cdot 2H_{2}O\cdot 0.7NaPF_{6}$, formulae for EHU1- $(Sc,Li)\cdot(LiBF_4)$ and EHU1 $(Sc,Na)\cdot(NaPF_6)$. In fact, PXRD patterns of soaked samples confirm that pristine structures are maintained although the relative intensity of some maxima have been clearly modified, which supports the inclusion of LiBF₄ and NaPF₆ ionic species into the voids of the structure (see 19 F NMR and FTIR spectra in the Supporting Information). This fact is reinforced by the lower content of lattice water molecules per formula in the soaked samples compared to the pristine materials. Paying attention to the NMR spectra it can be concluded that the soaking procedure significantly modulates the crystal structure. Overall, all peaks corresponding to the studied nuclei are broadened, particularly for the ¹H (peak centered at 3.5 ppm of ca. 2.0 $\rm \bar{k}Hz)$ and $\rm ^7Li$ spectra (peak at 0.65 ppm of ca. 1.4 kHz), which is indicative of a major heterogeneity of environments. However, this fact prevents a further study of their mobility through, for instance, the pulse gradient field (PFG-NMR) technique. The 7Li peak can be related with a diverse and disordered minor population of Li atoms in addition to those occupying the M site. Therefore, the increase of the alkaline-ion concentration after soaking appears to be responsible for the enhancement of the conductivity, although it should not be excluded that the alteration of the external surface of the crystallites could also play an important role.

Varying the temperature of the pellets during the measurements revealed Arrhenius-type-activated behavior in both cases (Figure 7). According to the fitting, soaked EHU1(Sc,Li)·(LiBF₄) presents a lower activation barrier than the sodium counterpart (0.25 vs 0.64 eV, respectively). Taking into account the conductivity $(10^{-4} \text{ S cm}^{-1})$ and the activation energy lower



Figure 7. Arrhenius plots of ionic conductivity data obtained for EHU1(Sc,M) compounds soaked in 1 M $LiBF_4$ and $NaPF_6$ DMC solutions.

than 0.4 eV, the EHU1(Sc,Li)·(LiBF₄) material can be referred to as a promising superionic conductor.^{86,87}

CONCLUSIONS

In the present work, two new heterometallic 3D porous scandium(III)/alkaline/pyrimidine-4,6-dicarboxylato frameworks, namely, EHU1(Sc,Li) and EHU1(Sc,Na), have been structurally and chemically characterized, while their permanent porosity has been confirmed by means of adsorption of gases. A thorough synthetic study has allowed achieving materials with the best performance in terms of crystallinity and porosity, both of which are highly correlated given their intricate micropore system. These compounds have proven a high capacity to capture CO_2 at room temperature owing to the strong CO_2 ... host interactions established specifically at two sites of the crystal structure, as inferred from the computed CO_2 average occupation maps. Experimental adsorption performances have been well contrasted with GCMC simulations.

These materials offer a high resistivity (in the order of 10^{-7} S cm⁻¹) in spite of the presence of alkaline ions accessible to the pore network, so two methodologies have been explored to enhance ionic conductivity. On one hand, a slight increase of 1 order of magnitude in the conductivity is generated by doping the material with Cd^{II} and Mn^{II}, which brings a partial replacement of Sc^{III} and admits additional interstitial Li⁺ and Na⁺ aquo complexes. A more promising route to circumvent the inherent insulating nature of these MOFs lies on soaking the samples into solutions containing alkaline salts. In this way, a remarkable increase of the conductivity at ambient temperatures (in the order of 10^{-4} S cm⁻¹) as well as quite low activation energies are achieved. The materials resulting from the soaking procedure retain the pristine crystal structure and host a remarkable content of alkaline electrolyte salt within. This increase of the charge carriers seems to be responsible for the enhancement of the conductivity, although an extrinsic mechanism through interparticle hopping cannot be discarded. EHU1(Sc,Li)·(LiBF₄), with a low activitation energy (0.25 eV), exhibits very promising conductivity in the field of electrolyte materials, and EHU1(Sc,Na)·(NaPF₆) represents, to our

knowledge, the first MOF to show ionic conductivity provided by the Na ion.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.5b03458.

FTIR spectra, chemical analysis, thermal behavior, PXRD data, analysis of porosity based on experimental and simulated adsorption isotherms, SEM images, NMR spectra, and additional Nyquist plots (PDF)

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Notes

The authors declare no competing financial interest.

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