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High Hydroxide Conductivity in a Chemically Stable Crystalline

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A chemically stable cationic MOF encapsulating *in-situ* formed water-hydroxide supramolecular anionic chain is realized for high hydroxide (OH⁻) ion conductivity in solid-state (Type A). High OH⁻ ion conductivity and low activation energy of MOF demonstrates the advantage of *in-situ* incorporation of OH⁻ ion to achieve efficient OH⁻ ion conduction in solid-state.

Metal-organic frameworks (MOFs) are porous crystalline solid, which combine the properties arising from both inorganic and organic building units in a single material.¹ The designable architecture, high-surface area, host-guest chemistry, and responsiveness make crvstalline nature MOFs indispensable material for future smart technology.² MOFs have already been employed in diverse areas including gas storage/separations. catalvsis. sensing. biomedical applications. magnetism, crystallography, electrical conductivity, and clean energy applications.³ In recent past, MOFs have developed as new class of solid-state ion conducting material.⁴ The design flexibility of MOFs along with cheap starting materials, good thermal stability, and feasibility in hybridization offers several advantages for development of solid-state ion conductor. Also, owing to crystalline nature in combination with design flexibility, MOFs can serve as promising model compound for better understanding of ion transport mechanism and optimizing the conduction path on nano-scale.⁵ The MOFs have shown great potential as proton conducting material working in humid and/or anhydrous conditions.⁶ Unlike, proton conducting MOFs, the anion conducting MOFs are still rare. The in-situ incorporation of

conducting species in MOF matrix is known to provide enhanced ionic conductivity.^{6g} However, till now only postsynthetic modification approach has been utilized to achieve hydroxide (OH⁻) and chloride (Cl⁻) ion conduction in MOFs (Type B).^{6a,7} Especially, the OH⁻ ion conductors are getting increased attention for the development of low cost and efficient alkaline fuel cells.⁸

In organic polymers, the high OH⁻ conductivity is achieved by covalently bound onium-class cations and free OH⁻ anions under humid conditions.^{8,9} Thus we hypothesize that, the high OH⁻ conductivity in MOFs might be achieved if one can synthesize cationic MOF framework with *in-situ* incorporated free OH⁻ as counter ions hydrogen bonded with water molecules inside the MOF matrix and will provide optimum concentration and path for efficient OH⁻ ion transport through matrix (Scheme 1). Despite the advantages, to the best of our knowledge *in-situ* incorporation of OH⁻ ion (Type A OH⁻ ion conductor)^{7a} for synthesis of efficient OH⁻ conducting MOF is yet to be realized.⁷



Scheme 1 Schematic representation of cationic MOF with anionic supramolecular chain of hydroxide anions and water molecules inside the MOF pore for efficient hydroxide ion conduction.

Regardless of designable nature of MOF framework, the tailored arrangement of ions and/or guest molecules in MOF matrix is difficult. Also owing to the large number of possible MOF structures, the synthesis and characterization of every possible MOF is not feasible. In this regard, identification of potential MOF structures reported in literature using screening

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Fig. 1 (a) Fitting of raw PXRD data of compound 1by Rietveld analysis. The black and redlines represent experimental and fitted data respectively. The residual discrepancy is shown in blue. (b) Tris-chelated cationic [Ni2(μ -pymca)3]1+ subunit with propeller like structure. (c) 2D cationic honeycomb sheets of MOF 1 arranged in AA fashion forming 1D hexagonal channel filled with OH- and water molecules. (d) Electron density distribution for MOF 1 derived from MEM analysis in ab plane (002). Contour lines are drawn from 0 to 0.5 e/Å3 at interval of 0.05 e/Å3.

based approach is extremely useful to get compounds with desired structure and/or property.¹⁰ Further the knowledge gained from these compounds can be used for design and development of efficient solid-state ion conducting materials. The $[M_2(\mu-pymca)_3]OH\cdot nH_2O$ MOF composed of 2 dimentioanal (2D) honeycomb cationic framework $[M_2(\mu-pymca)_3]^{1+}$ forming 1D channel filled with *in-situ* formed free OH⁻ ions and water molecules creating 1D anionic supramolecular chain, which can provide an efficient path for OH⁻ transport (Type A).¹¹ However the MOFs were never realized for ionic conductivity previously.

We synthesized Ni(II) based new isostructural MOF [Ni2(µpymca)₃]OH·nH₂O (1) via hydrothermal reaction between pymcaH and NiCl₂ at 160 °C for 20 h as greenish crystalline powder. The solid was insoluble in common organic solvents and water. The elements present in bulk sample was determined using energy dispersive X-ray spectroscopy (EDX) analysis of multiple particles of MOF over wide area and multiple synthesis batches (Fig. S1-S4). The EDX analysis of multiple hexagonal particles and multiple batches of 1 displayed the presence of Ni, C, N and O in 1 in bulk sample. FT-IR spectrum of as-synthesized MOF afforded aromatic C-H stretching frequency around 3090 cm⁻¹ and decrease in $v(COO)_{as}$ frequency 1654 cm⁻¹ of pymcaH to 1631 cm⁻¹ in **1** also supported the bond formation (Fig. S5).¹² The Raman spectra of 1 exhibited strong peak at 3083 cm⁻¹ corresponding to aromatic v(C-H) vibrations, which also confirmed the ligand incorporation (Fig. S6). This conclusion was further supported by solid-state ¹H-NMR (ss- ¹H-NMR) of **1**, in which the spectra of 1 displayed the peak ~3.0 ppm assigned to aromatic protons (Fig. S7).^{7b,13} The numerous attempts to obtain **1** as a single crystal suitable for single crystal X-ray diffraction analysis were unsuccessful. However, the as-synthesized powder of 1 was sufficiently crystalline to give intense diffractions identical to $[M_2(\mu-pymca)_3]OH \cdot nH_2O$ diffraction peaks. The structure of 1 was determined via Rietveld refinement analysis of powder pattern (see supporting information). The Rietveld refinement gave good fit with Rwp = 3.2 (Fig. 1a, Table S1).

The compound **1** crystallizes in space group P_{31m} same as reported compound. The central Ni(II) exhibit distorted octahedral geometry with N₃O₃ donor set from three pymca¹⁻ ligands forming tris-chelated cationic $[Ni_2(\mu-pymca)_3]^{1+}$ subunit (Fig. 1b). The cationic $[Ni_2(\mu\text{-pymca})_3]^{1+}$ unit forms propeller like chirality connecting three adjacent subunit forming(6,3) 2D cationic honeycomb structures in ab plane (Fig. 1c, d). The 2D honeycomb sheets are arranged one above the other in AA fashion with inter layer distance of ~6 Å forming 1D channel (Fig. 1d; S8). These channels must be filled with anions and/or solvent molecules to balance the overall charge of cationic framework. The strong peak at 3641 cm⁻¹ in FT-IR spectra of MOF 1 was assigned to stretching vibration v(OH) of hydrated OH⁻ ions (Fig. S5).¹⁴ The temperature-programmed desorption mass spectrometry analysis of multiple batches of MOF 1 showed release of water molecules (H_2O m/z = 18), however no CO_2 (m/z = 44) release was observed from the MOF 1 confirming the existence of free OH⁻ ion in MOF matrix (Fig. S9). Thus the overall molecular formula can be assigned as $[Ni_2(\mu-pymca)_3]OH \cdot nH_2O$. As the coordination number of central metal atom is saturated the hydroxide anion must be present inside the pore. To further confirm the structure of 1 and arrangement of guest molecules by electron density visualization we performed maximum entropy method (MEM) analysis via Rietveld refinement of PXRD data. Fig. 2d shows iso-density contour maps of 1. The MEM analysis of 1 also confirmed the formations of 2D honeycomb sheet structure with alternate arrangements of pyrimidine rings (Fig. S8). The charge localization at the centre of hexagonal ring suggests the arrangements of hydroxide anions along the barycentre of hexagonal rings as expected.

Thermogravimetric analysis (TGA) of 1 under N₂ atmosphere showed thermal stability up to 300 °C with ~10 % weight loss is assigned to removal of water molecules (Fig. S10). Above 300 °C the compound starts decomposing slowly with 70% weight loss. The variable temperature PXRD also confirmed the thermal stability of 1 up to 300 °C in both heating and cooling cycles without alteration of overall structure (Fig. S11). To assess the porosity of 1, N₂ adsorption isotherm at 77 K was measured. The N₂ adsorption showed negligible gas uptake at 77K indicating nonporous nature of 1 (Fig. S12). Further to determine the chemical stability of 1, we treated ~50 mg of as-synthesized compound with 25 mL of boiling water overnight. The compound remained highly stable in boiling water for overnight without any loss in crystallinity or peak shifting as confirmed from PXRD (Fig. S13). The FT-IR spectrum of water treated sample stayed unaltered indicating no change in coordination environment upon boiling water treatment (Fig. S14). The Rietveld refinement of water treated sample also confirmed the stability of MOF (Fig. S15). In addition to water, base stability is very crucial for successful performance of hydroxide ion conducting material. We checked the base stability of 1 in pH range 7 to 14. Compound 1 showed an excellent base stability and remained highly Published on 07 June 2016. Downloaded by UNIVERSITY OF NEBRASKA on 09/06/2016 13:37:36.

stable up to pH 14 as determined form PXRD and FT- IR (Fig. S16-S17). Encouraged from this we further investigated the stability of **1** upon treatment with NaOH (1 Normal). The compound **1** also exhibited high stability towards 1 Normal NaOH and remained highly crystalline (Fig. S13). Similar to water treated MOF sample, the Rietveld refinement of NaOH treated sample also confirmed the base stability of MOF (Fig. S15). The ICP analysis of **1** treated with 1N NaOH showed 0.30% degradation after 8h and 0.31% after 24h (Table S3). The SEM analysis of as-synthesized and NaOH treated sample revealed that compound morphology remained unaffected by base treatment (Fig. S18). The FT-IR spectra of NaOH treated sample established the unaltered coordination environment around central metal atom in compound **1** (Fig. S14).



Fig. 2 (a) Nyquist plot for MOF **1** at 27 °C and 99 % RH. (b) Increase in OH⁻ ion conductivity of MOF **1** upon increasing humidification. (c) Water sorption isotherm of MOF **1** at 298K (filled symbol adsorption, hollow symbol desorption). (d) Nyquist plot for MOF **1** at 27 °C and 99 % RH upon D₂O exposure.

To evaluate the hydroxide ion conducting ability of MOF 1, we performed AC impedance measurements using compacted pellet of powder sample under N₂ atmosphere. The conductivity was determined from Nyquist plot. Fig. 2a shows Nyquist plot for compound 1 at 27 °C 99% relative humidity (RH). Similar to literature reports, the 1 exhibit single semicircle with tail at low frequency in Nyquist plot indicating ionic conductivity through bulk material.^{3q,15} The OH conductivity of **1** was found to be 1.3×10^{-6} Scm⁻¹ at 27 °C and moderate humidity (~50 % RH). The OH conductivity was found to be increasing with increasing humidification and reaches maximum conductivity value of 0.8 $\times 10^{-4}$ Scm⁻¹ at 27 °C and 99 % RH (Fig. 2a,b, S19). The present OH ion conductivity value is highest amongst Type A anion conducting MOFs and ~4 orders higher than previously reported OH conducting MOFs,⁷ with only exception being the post synthetically modified (Type B) Ni based MOF.^{7d} Although the present conductivity is lower than best known inorganic OH conducting materials,¹⁶ the high base stability as against onium class organic polymer is an important advantage for real time application. The overlapping PXRD and FT-IR patterns of MOF 1 before and after impedance analysis confirm the integrity of the MOF 1 during impedance analysis (Fig. S20-S21). We

concluded that, upon increasing humidification the water uptake in hydrophilic 1D hexagonal channels increase and the arrangement of these adsorbed water molecules is strongly related to the observed high OH⁻ conductivity. The water adsorption isotherm of dehydrated sample showed adsorption of water molecules at very low relative pressure (Fig. 2c). This clearly indicates that the dehydrated compound has high affinity for water and regains water of crystallization under humid condition. We also measured conductivity of **1** by exposing it to D₂O vapours (Fig. 2d). The D₂O exposed sample showed conductivity of 4.6×10^{-5} Scm⁻¹ which is less than H₂O exposed sample as expected due to isotope effect. This also confirms the vital role of H₂O in conduction behaviour of MOF **1**.

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Fig. 3 (a) Arrhenius plot for the hydroxide conducting MOF 1. (b) Time dependent conductivity measurements of MOF 1 at 27 °C and 99 % RH. (c) Humidity cycling study of MOF 1 at 27 °C between 50 to 99 % RH.

The OH⁻ conductivity measurements were also performed at different temperatures and constant humidity (95% RH) which showed increase in hydroxide conductivity from 2.5 \times 10^{-5} Scm⁻¹ at 30 °C to 5.6 × 10^{-5} Scm⁻¹ at 90 °C (Fig. 3a, S22). The activation energy E_a was calculated to be 0.19 eV which is quite low. The observed activation energy is comparable to the hydrated OH⁻ ions in liquid¹⁷ and suggests the favourable and efficient transport of OH⁻ ions through 1D channels of MOF 1. The transport mechanism of OH⁻ ions in presence of water has been supported by charge-migration model.¹⁸ Similar to Grotthuss mechanism observed for hydrated H_3O^+ ions it is expected that the charge on OH⁻ ions migrates through protons transferred from adjacent water molecule via hydrogen bonding network resulting in low activation energy. Thus the formation of extended hydrogen bonded supramolecular chain of OH⁻ and water molecules improve the OH⁻ ion conductivity of the material. The detailed investigation of mechanism and structure property relation for further improvements in the OH⁻ conducting ability of the materials are underway. Importantly, the time dependent conductivity measurement did not show any loss in conductivity performance even after 40 h (Fig. 3b). Also, the humidity cycling study between 50 to 99 % RH also revealed that the compound is resistant to the high humidity changes (Fig. 3c).

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The nonporous nature of ${\bf 1}$ towards feed gases like H_2 and O_2 gases at RT is also advantageous to avoid possible fuel mixing, however the detailed investigation is required (Figure S23).

In conclusion, we report here a highly hydroxide conducting MOF [Ni₂(µ-pymca)₃]OH·nH₂O with in-situ incorporated OH⁻ anions (Type A, OH⁻ ion conductor) for the first time. The MOF exhibits excellent chemical stability towards boiling water and highly basic conditions and showed hydroxide conductivity of 0.8×10^{-4} Scm⁻¹ at 27 °C and 99 % RH which is comparable to the best known OH conducting MOF reports. Further the activation energy for hydroxide conduction was found to be 0.19 eV which is comparable to free OH⁻ ions in liquid suggest the interference free transport of OH⁻ ions in MOF. We believe that the present approach for synthesis of highly OH⁻ conductive MOFs will not only stimulate the research in less explored field of solid-state anion conductors but also lessons learned from the present approach will open new avenues for the design and development of different classes of anion conducting materials.

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