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Self-assembled one dimensional functionalized metal–organic nanotubes (MONTs) for proton conduction†

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Two self-assembled isostructural functionalized metal–organic nanotubes have been synthesized using 5-triazole isophthalic acid (5-TIA) with In(III) and Cd(II). In- and Cd-5TIA possess one-dimensional (1D) nanotubular architecture and show proton conductivity along regular 1D channels, measured as 5.35×10^{-5} and 3.61×10^{-3} S cm^{-1} respectively.

Metal–Organic Frameworks (MOFs) are a new class of materials that offer the advantage of precise control over architectural as well as framework topologies with specific applications such as gas storage, catalysis and drug delivery.[1] Although there have been several reports of MOFs with diverse architectures, still discrete metal–organic nanotubular structures are extremely rare.[2] Only a handful of literature reports are available where self-assembled Metal–Organic Nanotubes (MONTs) have been constructed using capping agents (like ethylene diamine, phenanthroline) or secondary linkers (like 4,4′ bipyridine, iodine).[3] However most of these reports reveal only the structural details of the MONTs without showcasing any fundamental application. Moreover, most of the MONTs reported in the literature are interconnected by metal ions[4] leaving only one or two examples of self-assembled hydrogen bonded MONTs.[5]

Herein, we report the design and synthesis of two isostructural self-assembled functionalized MONTs, In-5TIA [In($C_{10}O_4N_3H_5$)$_2$-(C_2H_8N)(H_2O)] and Cd-5TIA [Cd($C_{10}O_4N_3H_5$)$_2$(C_2H_8N)$_2$(H_2O)], using In(III) and Cd(II) ions as metal centers with 5-triazole isophthalic acid (5-TIA) as an organic building block. Both In-5TIA and Cd-5TIA consist of one dimensional single walled self-assembled nanotubes with 7.85 and 8.23 Å inner dimensions respectively. These MONTs are held together by weak C–H···O hydrogen bonding[6] to form the self-assembled architecture. It is also noteworthy that Cd-5TIA and In-5TIA MONTs show high proton conductivity of 3.61×10^{-3} S cm^{-1} and 5.35×10^{-5} S cm^{-1} at ambient temperature (301 K) and 98% relative humidity (RH). We have also collected the proton conductivity data of the literature reported self-assembled indium isophthalic acid based MONT (In-IA)[7] to systematically study the proton conduction pathways in these MONTs (Fig. 1). To the best of our knowledge, In-5TIA and Cd-5TIA are the first examples of self-assembled functionalized metal–organic nanotubes (MONTs) which show properties like proton conductivity.

Isophthalate building blocks are well-known for the synthesis of Metal–Organic Polyhedras (MOPs).[8] Self-assembled MONT architecture has already been reported[7] with isophthalic acid as the organic building unit and In(III) as a metal center with a small inner dimension (4.8 Å) (Fig. 1a). One would assume that the angle between two carboxylate groups of the isophthalate scaffold (115°) favors the formation of the nanotubular architecture. This motivated us to choose 5-TIA as the organic ligand, which possesses the specific geometry as well as functionalization of the outer core to achieve these large functionalized nanotubular architectures (Fig. 1b). 5-TIA offers a triazole moiety on the five positions of the isophthalate scaffold, which could hold these nanotubes in close proximity *via* hydrogen bonding and

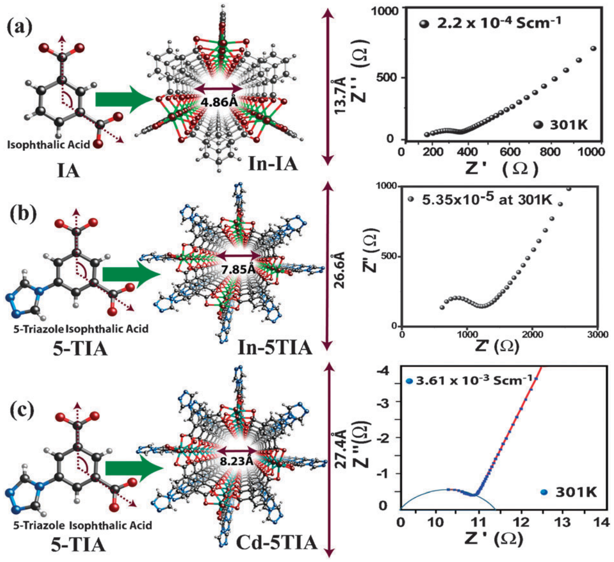

Fig. 1 Structures of In-IA, In-5TIA and Cd-5TIA MONTs: (a) schematic representation of IA ligand forming a three centered MONT with In(III) and its proton conductivity at 301 K and 98% humidity. (b) Schematic view of functionalized 5-TIA ligand forming a four centered MONT with In(III) and its proton conductivity at 301 K and 98% humidity. (c) Schematic view of functionalized 5-TIA ligand forming a four centered MONT with Cd(II) and its proton conductivity at 301 K and 98% humidity.

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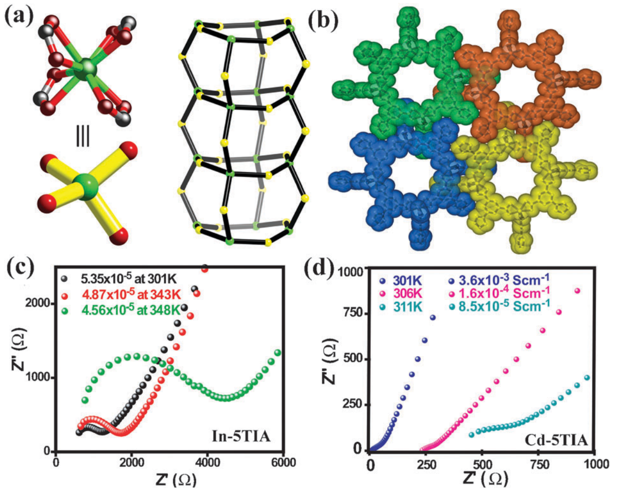

Fig. 2 (a) Simplified view of an eight-connected indium center, yellow sticks indicate each μ_1-CO_2^- carboxyl group connected with an octahedral In(III) node and self-assembled MONTs are arranged in a three-dimensional manner. (b) Packing view of simplified self-assembled MONTs. (c) Proton conductivity plots of In-5TIA at higher temperature showing decrease in proton conductivity. (d) Proton conductivity plots of Cd-5TIA at higher temperature showing decrease in proton conductivity.

create functionalization on the outer wall of these nanotubes. The asymmetric unit of In-5TIA (space group *P*4/*n*; isostructural to Cd-5TIA) consists of one octahedral In(III) ion and two 5-TIA molecules. Each In(III) SBU is coordinated to eight oxygens from four μ_1-CO_2^- functionalities and each carboxylate group of 5-TIA chelates to one In(III) site (Fig. 2a). Each 5-TIA ligand is coordinated to two different In(III) ions with an In–5TIA–In angle of 126° (for Cd-5TIA, the Cd–5TIA–Cd angle is 124.7°). This $M(CO_2)_4$ type of SBU could be found in some In(III) based MOFs[9] but it is very rare among Cd(II) based MOFs. In the crystal structure of In-5TIA each In(III) SBU extends through *a* and *b* axes where four In(III) ions are linked by four 5TIA *via* μ_1-CO_2^- carboxyl groups to generate an $[In_4(5TIA)_4]$ square grid (Fig. 2a). These $[In_4(5TIA)_4]$ squares are infinitely connected to μ_1-CO_2^- functionalities of 5TIA ligands along the *c* axis to produce a 1D nanochannel containing $[In_8(5TIA)_{12}]$ boxes (Fig. 2a) where all the triazole moieties of 5TIA molecules point to the periphery of the MONT (Fig. 2b). The interior and exterior wall cross-sectional diameter of these nanotubes of In-5TIA is 7.85 and 26.6 Å whereas for Cd-5TIA, it is 8.23 and 27.4 Å respectively. These independent MONTs are further self-assembled *via* C–H···O hydrogen bonding [D = 3.645(7) Å, d = 2.811(5) Å, θ = 150.0(3)°] to produce an interesting 3D supramolecular aggregate along the *bc* plane where the triazole functionality of one MONT is interdigitated with another MONT and *vice versa* (Fig. 2b). The whole framework of In-5TIA and Cd-5TIA bears negative charge due to the coordination of each metal [In(III) or Cd(II)] atom to the four carboxylate ligands. However, after careful investigation of these two isostructural MOFs, we propose that the single negative charge of In-5TIA SBU was balanced by one dimethyl ammonium cation. Whereas in Cd-5TIA, two negative charges at SBU were neutralized by two dimethyl ammonium cations. These cations were heavily disordered, which was confirmed by the elemental analysis of In-5TIA and Cd-5TIA (see Section S2 in ESI†).

Thermal gravimetric analysis (TGA) revealed that both In-5TIA and Cd-5TIA retain their stability at temperature as high as 150 °C (see Fig. S13–S15 in ESI†), which was further confirmed by *in situ* Variable Temperature Single Crystal X-Ray Data (see Section S7 in ESI†). In order to confirm the phase purity of the bulk materials, powder X-ray diffraction (PXRD) experiments were carried out on In-5TIA and Cd-5TIA. All major peaks of experimental PXRDs of In-5TIA and Cd-5TIA match well with those of simulated PXRDs, indicating their reasonable crystalline phase purity (Fig. S4 and S7, ESI†). Variable Temperature Powder X-Ray Diffraction (VTPXRD) performed on as-synthesized In-5TIA and Cd-5TIA (from 25 °C to 150 °C) further confirms their stability and crystallinity at elevated temperatures (see Fig. S16–S17 in ESI†).

Ion conduction can occur intrinsically through the solid[10] material by some carrier-mediated pathway (*e.g.*, water/hydronium for H^+ ions) in pores of the material. The proton conductivity values were measured for In-5TIA and Cd-5TIA as 5.35×10^{-5} S cm^{-1} and 3.61×10^{-3} S cm^{-1}, respectively, at ambient temperature (301 K) with 98% RH (Fig. 1b and c). The conductivities were determined from the semicircle in the Nyquist plots, as shown in Fig. 1. These values are highly humidity-dependent and dropped from 5.35×10^{-5} S cm^{-1} and 3.61×10^{-3} S cm^{-1} at 98% RH to 1.25×10^{-5} S cm^{-1} and 3.14×10^{-5} S cm^{-1} at 20% RH, respectively, for In-5TIA and Cd-5TIA at 301 K (Fig. S33 and S35, ESI†), which indicates gradual decrease in proton conductivity upon decreasing humidification and establishes the role of water in proton conduction. At 298 K and 1 bar pressure, the water vapor uptake of In-5TIA and Cd-5TIA is 15 wt% and 14 wt% respectively. Interestingly, proton conductivity of Cd-5TIA is far more humidity sensitive than that of In-5TIA, evident from a sharp drop in proton conductivity upon lesser humidification (Fig. S33–S36, ESI†). This humidity sensitive proton conductivity behavior of Cd-5TIA is similar to that of $(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$ (8×10^{-3} S cm^{-1} at 98% RH while 6×10^{-6} S cm^{-1} at 298 K 70% RH).[11e] Ramping the sample results in dislocation of the adsorbed water molecules, leading to lower proton conductivity at elevated temperature (Fig. 2c and d). In-5TIA outperforms MIL-53 based MOFs (10^{-6}–10^{-7} S cm^{-1})[11a] and PCMOF-3 (3.5×10^{-5} S cm^{-1}),[11b] whereas Cd-5TIA outperforms ferrous oxalate dehydrate (1.3×10^{-3} S cm^{-1})[11c] and cucurbituril (1.3×10^{-3} S cm^{-1}),[11d] although it possesses a lower proton conductivity value than $(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$ (8×10^{-3} S cm^{-1})[11e] at 298 K (Table S5, ESI†). Contrary to other proton conducting MOFs,[11h] In-5TIA and Cd-5TIA show proton conductivity in a wide range of temperatures, from 277 K (2.8×10^{-5} S cm^{-1} for In-5TIA and 3×10^{-5} S cm^{-1} for Cd-5TIA) to 368 K (2.7×10^{-5} S cm^{-1} for In-5TIA and 1.2×10^{-5} S cm^{-1} for Cd-5TIA) [Tables S3–S4 and Fig. S27–S32, ESI†],[12] proving their potential in various applications. For In-5TIA, the proton conductivity value increases with increase in temperature from 277 K to 312 K, and then decreases steadily up to 368 K whereas for Cd-5TIA proton conductivity increases with increase in temperature from 277 K to 301 K and then decreases up to 368 K (Fig. 2 and Fig. S27–S32, ESI†). However, we acknowledge that both In-5TIA and Cd-5TIA

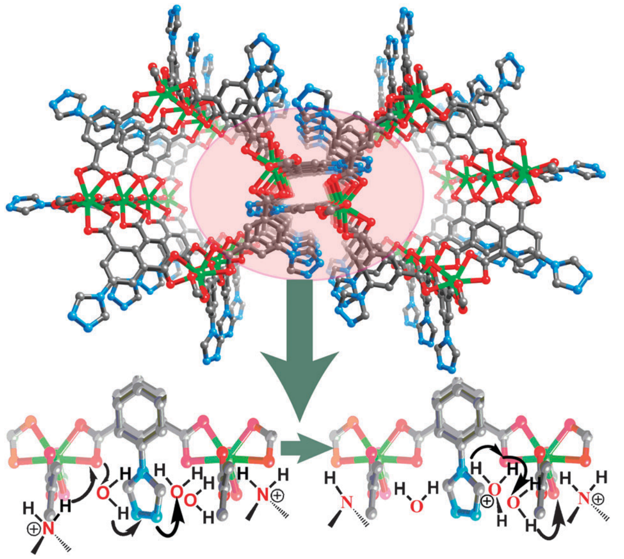

Fig. 3 Schematic representation of the Grotthuss proton hopping mechanism along 1D nanochannels for In-5TIA and Cd-5TIA MONTs. The arrows indicate the possible movement of the H^+.

show proton conductivity till 368 K. To further compare the proton conducting efficiency of In-5TIA and Cd-5TIA, we have collected the proton conductivity data of the literature reported MONT architecture (In-IA) (Fig. 1a), which reveal that In-IA and In-5TIA have comparable proton conductivity (5.35×10^{-5} S cm^{-1} for In-5TIA and 2.20×10^{-4} S cm^{-1} for In-IA, respectively, at 301 K and 98% RH) as both materials contain one dimethyl ammonium cation per SBU within the framework. Accordingly, Cd-5TIA shows higher proton conduction (3.61×10^{-3} S cm^{-1} at 301 K and 98% RH) than In-5TIA and In-IA as Cd-5TIA possesses two dimethyl ammonium cations per SBU inside the framework (Fig. 3, Fig. S43 and S44 and page S51, ESI†). In-5TIA and Cd-5TIA show considerably lower activation energy values than In-IA (0.137 eV for In-5TIA and 0.163 eV for Cd-5TIA whereas 0.47 eV for In-IA). Thus, proton conductivity in In-5TIA and Cd-5TIA follows mainly the Grotthuss proton hopping mechanism[13] whereas proton conductivity of In-IA follows chiefly a vehicular mechanism, which hints at the role of the triazole moiety in providing proton conducting pathways in In-5TIA and Cd-5TIA and hence the advantages of functionalization of the framework. The activation energy value of In-5TIA (0.137 eV) is comparable to that of nafion based membrane electrolytes (0.22 eV),[14] and is the lowest activation value reported till date for MOF based proton conducting materials (Table S5, ESI†). Cd-5TIA also possesses a low activation energy value of 0.163 eV.

In conclusion, we could design and synthesize two isostructural single-walled functionalized metal–organic nanotubes (MONTs) by using 5-TIA as a single organic building block and In(III) or Cd(II) as a metal node. These large MONTs are held together by hydrogen bonding interactions, leading to unique supramolecular nanotubular arrays. In this work, 5-TIA serves a dual purpose, constructing nanotubular architecture using a single organic precursor linked with an In(III) or Cd(II) node, as well as functionalizing the pore wall with triazole moieties. The triazole decorated pores along with dimethyl ammonium cations and the Cd(II) or In(III) bound carboxylate moiety provide a unique pathway for proton conduction under humid conditions, showing noticeably high proton conductivity values across a wide range of temperatures and 98% relative humidity. Moreover, proton conductivity shown by Cd-5TIA (3.61×10^{-3} S cm^{-1} at 301 K) is at a high position among the proton conducting MOFs reported till date. We have also studied and compared the proton conductivity of the literature reported MONT architecture (In-IA). We expect that this finding will lead to many new applications previously unrealized in nanotube based porous materials.

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