Ionic Conductivity in the Metal–Organic Framework UiO-66 by Dehydration and Insertion of Lithium *tert*-Butoxide

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Metal–organic frameworks (MOFs) are a class of microporous materials consisting of metal ion nodes linked together by multitopic organic ligands. These compounds have been studied extensively in recent years for their record high surface areas and a wide range of related potential applications. Most research in this context has been devoted to gas storage and separations,[1] with the number of reports on liquid-phase separations, catalysis, sensing, and biomedical applications increasing rapidly.[2] A key advantage that MOFs bring to such applications is the possibility of introducing complex chemical surface functionality, thereby imparting intended chemical and physical properties to the materials. Indeed, the presence of organic linkers in MOFs offers an important difference with most other porous crystalline solids, and this has sparked the rapid development of a collection of synthetic strategies aimed at introducing functional groups at these positions.[3]

The metal cations present in the MOF crystal lattice are organized in well-defined inorganic structural motifs, commonly referred to as secondary building units (SBUs), which often occur as one-dimensional chains or zero-dimensional clusters.[4] Although these inorganic substructures can exhibit a high density of functional groups, such as bridging OH groups, and the substructures contribute significantly to the adsorption properties of the material,[5] surprisingly little attention has been devoted to the post-synthetic functionalization of the inorganic units within MOFs. The few reports that exist on functionalization of the OH groups found within a number of important MOF structures exclusively discuss approaches in which reactants are immobilized upon exchange of the OH proton.[6] In this work, we show how a novel two-step procedure involving dehydration of inorganic clusters followed by lithium alkoxide grafting leads to superior solid ionic conductors as compared to materials prepared by direct deprotonation. The resulting solid electrolytes are potentially useful for enhancing the operation of next-generation lithium batteries.

The framework of UiO-66 ($Zr_6O_4(OH)_4(bdc)_6$; bdc^{2-} = 1,4-benzenedicarboxylate) is constructed of $Zr_6O_4(OH)_4$-$(O_2CR)_{12}$ clusters in which the μ_3-O and μ_3-OH ligands originate from water present during the synthesis and the carboxylate groups are part of the bdc^{2-} ligands linking the clusters together (Figure 1).[7] The remarkable thermal and chemical stability of this Zr^{4+}-based MOF material led to significant efforts to synthesize functionalized variants of the UiO-66 framework. Successful strategies that have been
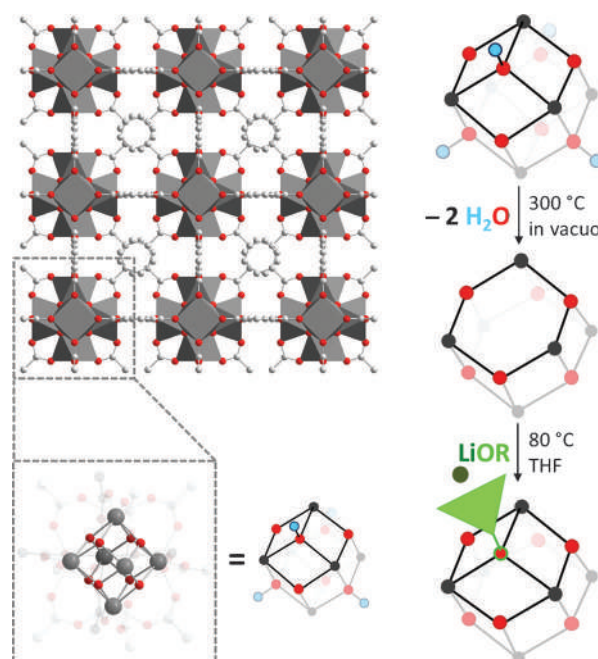

Figure 1. Representation of the grafting process, involving insertion of a lithium alkoxide in dehydrated UiO-66. On the left, the position of the $Zr_6O_4(OH)_4(O_2CR)_{12}$ clusters in the crystal lattice and the structure of the cluster core is shown. On the right, the two-step modification process is depicted, which consists of dehydration of the cluster core and subsequent grafting of lithium *tert*-butoxide. Zr gray, O red, C dark green, H blue. The aliphatic part of the grafted alkoxide is represented by a light green triangle.

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reported include the crystallization using functionalized bdc^{2-} derivatives,[8] post-synthetic organic transformations in the pores,[8a,9] post-synthetic decoration of the aromatic rings with metal carbonyl complexes,[10] and post-synthetic ligand exchange.[11] Notably, all of these approaches are aimed at introducing desired functional groups in the organic portion of the UiO-66 framework.

Upon heating UiO-66 under dynamic vacuum, water is eliminated from the cluster core to generate Zr_6O_6 units, without affecting the integrity of the crystal lattice.[12] The coordinatively unsaturated Zr^{4+} sites exposed upon dehydration of the cluster core have previously been shown to behave as strong Lewis acid sites with catalytic activity.[13] Based on this observation, we attempted the functionalization of UiO-66 by first dehydrating the material and subsequently contacting it with an alkoxide base, in this case lithium *tert*-butoxide (LiO*t*Bu). Figure 1 illustrates how an alkoxide anion is expected to interact in a μ_3 capping fashion with three hard, oxophilic open Zr^{4+} sites in the Zr_6O_6-$(O_2CR)_{12}$ cluster core.[14] We will hereafter refer to this insertion process as grafting.

The UiO-66 framework remains intact upon grafting, as confirmed by powder x-ray diffraction (Supporting Information, Figure S1). As would be expected, and in line with materials with functionalized organic ligands, the incorporation of bulky species decreases the specific Langmuir surface area from $1020 \pm 3\ m^2 g^{-1}$ to $510 \pm 9\ m^2 g^{-1}$ (Supporting Information, Figure S2). To determine the degree of grafting, the ratio of aliphatic to aromatic protons from the *t*BuO$^-$ anion and the framework bdc^{2-} linker, respectively, was determined by ^{1}H NMR spectroscopy upon dissolution of the compound in [D$_6$]DMSO and HF (Supporting Information, Figure S3).[8a] Assuming two possible grafting sites per cluster, approximately 25% of the available sites were found to be occupied by *t*BuO$^-$ anions. Interestingly, metals analysis consistently yielded a Li:Zr ratio too high for the observed *t*BuO$^-$ content, indicating that Li$^+$ and *t*BuO$^-$ are not introduced in a stoichiometric ratio. Depending on the UiO-66 synthesis batch and preparation method, an excess of up to one Li per cluster was observed. As reported previously, the UiO-66 framework most likely contains defects in the form of missing bdc^{2-} linkers.[12,15] Detailed FTIR studies have shown that a small fraction of OH groups persists at elevated temperature and under vacuum, which suggests that these are isolated OH groups compensating the negative charge of missing linkers.[12a] In our case, direct deprotonation of these OH groups during the LiO*t*Bu treatment most likely accounts for the extra Li. To exclude observations that are due to batch-to-batch variations in defect density,[12a] all experiments reported herein were performed on a single batch of UiO-66, synthesized as described in the Supporting Information.

The FTIR spectra in Figure 2 provide insight into the changes that occur upon cluster dehydration and subsequent grafting. Dehydration causes the asymmetric component of the carboxylate modes to blue-shift.[12] After grafting, this shift is partially reversed, as would be expected for the
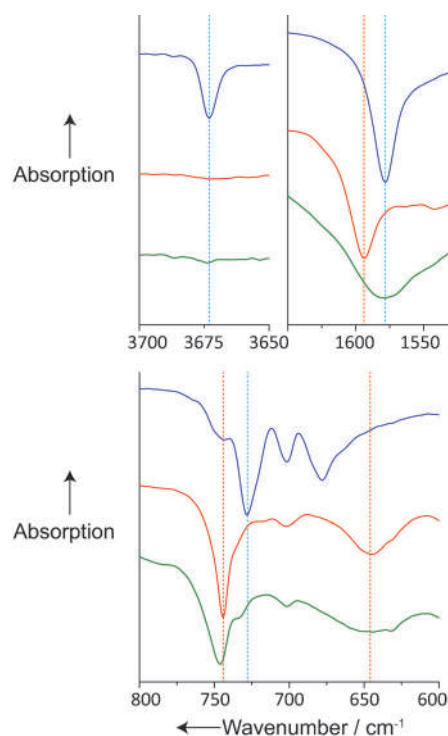

Figure 2. Comparison of FTIR spectra upon grafting of LiO*t*Bu in dehydrated UiO-66. Blue hydrated, red dehydrated, green grafted samples. Top left, top right, and bottom panels show the μ_3-OH stretch region, the asymmetric carboxylate stretch region, and the skeletal modes region of the spectra, respectively. The most important peaks in the hydrated (blue) and dehydrated materials (red) are indicated by vertical lines. Note that spectra in different panels are shown with various scaling factors to highlight differences.

mechanism proposed in Figure 1, and the spectrum resembles more closely that of the hydrated UiO-66 sample. The broadness of the peak after grafting indicates heterogeneity in the carboxylate environments, consistent with only a quarter of the available μ_3 capping sites being occupied by *t*BuO$^-$ anions.[16] Upon dehydration, the skeletal modes of the MOF undergo substantial changes, owing to removal of the bridging μ_3-OH groups, which leads to a lowering of the local symmetry.[12] As anticipated for the grafted sample, no symmetry restoration takes place and the spectrum overlaps with that of the dehydrated sample. These observations suggest that, after grafting, the O atom of *t*BuO$^-$ can be considered part of the cluster core, which underlines the difference between the type of functionalization presented here and so-called dative post-synthetic modifications.[3,17] The latter refers to the coordination of species to open metal sites that appear in some MOFs after removal of relatively weakly binding solvent molecules. Importantly, the FTIR spectrum for the grafted sample remains unchanged upon heating to 300°C, and grafting does not seem to affect the thermal stability of the material (Supporting Information, Figure S4).

The ionic conductivity of the LiO*t*Bu-grafted samples was assessed by ac impedance spectroscopy using stainless steel electrodes. To this end, propylene carbonate was added to solvate the Li$^+$ ions within the pores, similar to the inclusion
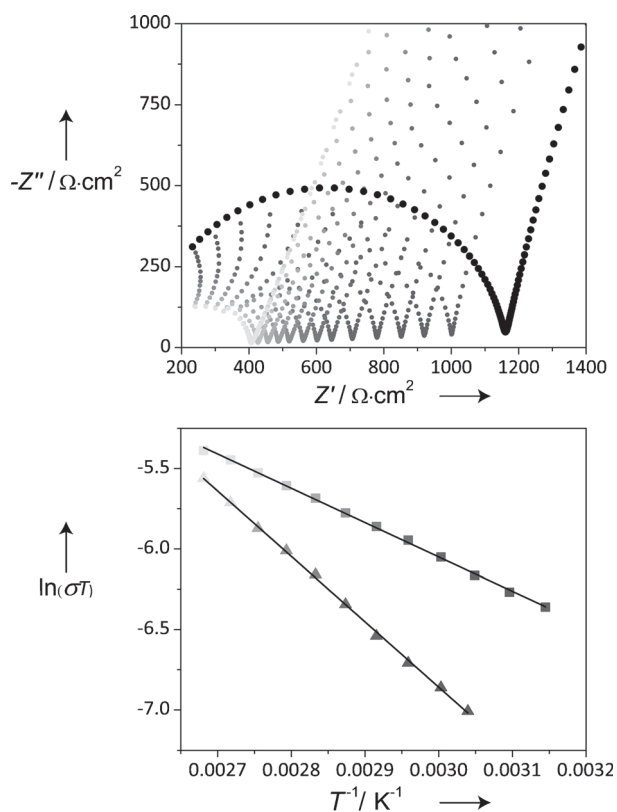
Figure 3. Ionic conductivity data. Upper panel: Nyquist plots of the ac impedance data obtained for the LiO*t*Bu-grafted UiO-66 material at different temperatures. Data collected at 293 K are shown in black, while grayscale data points illustrate the increase in ionic conductivity upon raising the temperature from 313 K (dark grey) to 383 K (light grey) at 5 K intervals. Lower panel: Arrhenius plot of ionic conductivity data for a sample of LiO*t*Bu-grafted UiO-66 (■) and the UiO-66 material that was deprotonated with LiO*t*Bu after rehydration (▲). The difference in activation energies for ionic conduction in both materials is evident from the slope of the linear fit of both datasets (black lines).

of water[18] or organic guest molecules[19] in proton conducting MOFs. The resulting free-flowing powder was pressed into pellets using insulating plastic dies. As shown in Figure 3, the resulting Nyquist plot reveals one semicircle with a characteristic capacitive tail at low frequencies. The tail illustrates the blocking nature of the stainless steel electrodes towards Li$^+$ ions. From these data, the room temperature ionic conductivity of the LiO*t*Bu-grafted UiO-66 sample was determined to be 1.8×10^{-5} S cm^{-1}. Notably, these results are on par with current solid polymer electrolytes[20] and, to the best of our knowledge, are only the second example of metal ion conduction in a MOF.[17b] Preliminary results indicate that adding a free Li$^+$ salt together with the introduction of propylene carbonate increases the conductivity of this material by up to two orders of magnitude (Supporting Information, Figure S5), most likely by improving interparticle contacts, as observed previously.[17b]

An important consequence of grafting a *t*BuO$^-$ anion is that the negative charge becomes shielded by the bulky aliphatic group. This should result in a weaker interaction with the charge-balancing Li$^+$ ion and consequently a higher

cation mobility compared to the situation where the cation sits directly on a localized and accessible negative charge. To test this hypothesis, a rehydrated sample of UiO-66 was contacted with LiO*t*Bu to deprotonate the Zr$_6$O$_4$(OH)$_4$-(O$_2$CR)$_{12}$ clusters and thus obtain a sample in which the Li$^+$ ions compensate the negative charge of the exposed, deprotonated μ_3-O atoms. Although the Li$^+$ content of this deprotonated UiO-66 sample is four times higher than that of the LiO*t*Bu-grafted sample, the room temperature ionic conductivity is lower at 3.3×10^{-6} S cm^{-1}. In each case, the activation energy for ionic transport was determined by measuring the ionic conductivity at various temperatures in the range 293–383 K (see Figure 3).[21] Even more so than the absolute values of ionic conductivity, the clear difference in the activation energies of 0.18 and 0.35 eV for the grafted and deprotonated materials, respectively, reflects the contrast in local environment of the Li$^+$ ions in two materials. Both the higher activation energy and lower ionic conductivity are indicative of more strongly interacting sites and thus a more localized and accessible negative charge in the directly deprotonated sample.[18e, 22] On the other hand, the activation energy for ionic conduction in the grafted UiO-66 material falls in the range observed for superionic conductors[21, 23] and is even slightly lower than the activation energy of H$^+$ conduction in Nafion.[24] These observations support the grafting mechanism proposed in Figure 1, which leads to screening of the negative charge.

In a battery context, research on solid Li$^+$ electrolytes is mainly driven by potential safety gains through the elimination of volatile or flammable solvents and the suppression of Li dendrite growth by a sufficiently rigid electrolyte material.[20, 25] Dendrite growth is a major concern in rapid charging of current lithium-ion batteries and currently excludes the use of Li metal anodes in secondary batteries, despite the higher energy density of such systems. One important requirement for all prospective electrolytes is that no Li$^+$ blocking passivation layer is formed on the electrode upon electrolyte contact. To evaluate this, a pellet of LiO*t*Bu-grafted UiO-66 was placed in a Swagelok cell with Li metal electrodes on both sides. Impedance spectra obtained from this setup are similar to those observed for Li$^+$ polymer electrolytes and clearly show the non-blocking nature of the electrodes (Supporting Information, Figure S6). Importantly, this symmetrical cell could even be cycled three times before shorting due to Li dendrite formation (Supporting Information, Figure S7). Further, the crystallinity of the grafted UiO-66 material was found to remain intact after contact with Li metal for 3 days at temperatures of up to 363 K, indicating the electrode compatibility of this modified MOF.

Although shorting occurred after a few cycles of the symmetrical cell, this does not necessarily indicate that the mechanical properties of the MOF electrolyte are unsuitable for resisting dendrite growth. Indeed, in the present case the material was evaluated as a fragile pellet of compressed powder without additives, and dendrites are expected to form along grain boundaries. For an actual application, for-

mulation with polymer binders would be appropriate.[26] While measuring the ionic conductivity is standard practice for any prospective Li$^+$ electrolyte, for most electrolytes the measured value is the result of the overall migration of both cations and anions. However, only the portion of the ionic current resulting from Li$^+$ movement is relevant to battery operation and determines the limiting discharge rate. This fraction is estimated to be only 0.2 to 0.4 in typical electrolytes.[20a] A Li$^+$ electrolyte in which the anions are immobilized, as is the case for the LiO*t*Bu-grafted UiO-66 electrolyte reported herein, would not only improve this situation but would also prevent anion migration and subsequent decomposition at the reactive electrodes. The latter mechanism has been identified as an important contributor to capacity fade in batteries.[27]

In summary, the foregoing results demonstrate a new type of post-synthetic modification for the inorganic subunits of UiO-66, one of the most robust and intensely studied MOFs, resulting in a new solid electrolyte potentially suitable for Li-based batteries.

Acknowledgements

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