

**SYNTHESIS, CHARACTERIZATION, AND PROTON CONDUCTION
BEHAVIOUR OF COORDINATION POLYMERS DERIVED FROM OXY
PHOSPHORUS LIGANDS**

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ABSTRACT

The work presented in this thesis is a systematic study to develop a rational synthesis of organo-amine mediated zinc phosphite/phosphonate-based coordination assemblies. The use of phosphite/ phosphonate diesters instead of conventional oxy-phosphorus acids in hydro-/solvothetical reactions provides an insight into the genesis of higher dimensional structural motifs *via* the isolation of intermediate phases. Several new organic-inorganic hybrids have been isolated and further, their proton conduction behaviour has been studied. The inclusion of imidazole/imidazolium cations in the structural frameworks, such as $[\text{H}_2\text{Im}]_2[\text{Zn}_3(\text{HPO}_3)_4]$ and $[\text{Zn}(\text{HPO}_3)(\text{HIm})]$ offers an intrinsic proton source to enable high proton conductivity on the order of 10^{-3} - 10^{-4} S cm^{-1} at 35 and 77% RH in the temperature range of 25-100 °C. The synthetic approach has been extended to the zinc phosphonate family. The results are described in chapter III. In chapter IV, new cadmium phosphites, $[\text{Cd}\{\text{OP}(\text{O})(\text{OH})\text{H}\}_2(4,4'\text{-bipy})]$, $[\text{H}_2\text{pip}][\text{Cd}(\text{O}_3\text{PH})_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ and a mixed ligand coordination polymer, $[\text{Cd}(\text{OAc})(\text{ox})_{0.5}(\text{bix})]$ formed by *in situ* formation of oxalate (ox) ligand are reported. Impedance measurement studies between 25-75 °C under 77 % RH reveal ultrahigh proton conductivity on the order of 10^{-1} - 10^{-2} S cm^{-1} . These can be regarded as important additions to the known family of high proton conducting materials. The synthesis and structural aspects of related cadmium phosphate esters, $[\text{Cd}\{\text{OP}(\text{O})(\text{OMe})_2\}_2(4,4'\text{-bipy})]$ and $[\text{Cd}\{\text{OP}(\text{O})(\text{OMe})_2\}_2(\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2)]$ are summarized in chapter V; the latter being formed by *in situ* N-formylation of piperazine under solvothetical conditions in presence of DMF as solvent. The study has been extended to explore the reaction of phosphate triesters with elemental tin

at elevated temperatures (180 °C). The method offers a viable route to $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OR})_2\}_2$, (R = Me, Et). The reactions invariably proceed *via* the concomitant formation of Sn-C and Sn-O-P bonds. A facile metal ion metathesis is observed upon the reaction of $\text{Me}_2\text{Sn}\{\text{OP}(\text{O})(\text{OMe})_2\}_2$ with $\text{Zn}(\text{OAc})_2$ under ambient conditions and resulted in the isolation of $\text{Zn}\{\text{OP}(\text{O})(\text{OMe})_2\}_2$ as a crystalline solid.