Poster Presentation

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Influence of ligand modulation on proton conductivity in self-assembled architectures

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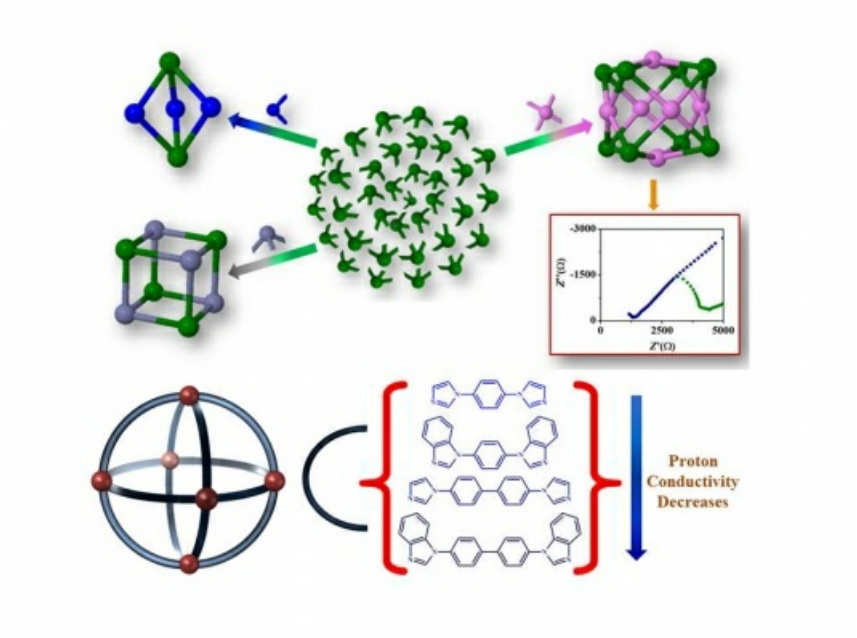
Development of advanced proton-conducting materials by mimicking the conduction mechanism of nafion sparked immense interest due to their potential applications in fuel cells and electronic devices.1 In this context, organic polymers and perovskite-type oxides are most widely studied due to their significantly high proton conductivity while modular porous crystalline metal-organic frameworks (MOFs) have proved to be possible candidates for proton-conducting applications.2 Recently, our group has shown that self-assembled discrete architectures can be promising alternatives with very high conductivity even at low humidity.3 Herein, we report the synthesis of six new discrete heterometallic cages (Pd-Co, Pd-Fe, Zn-Co, Zn-Fe, Mn-Co, Mn-Fe) via metal-ligand coordination bonding approach and they have been characterized by mass spectrometry and single crystal X-ray diffraction methods. Of the six heterometallic cages, two have coordinated water molecules attached to the metal ions, therefore giving us the opportunity to explore the proton conductivity of these materials. As both heterometallic systems are similar in nature, the resulted proton conductance values did not differ much. We hypothesize that simple chemical changes incorporated into the ligand moieties can result in significant changes in the proton conductance values; so we synthesize four new homometallic molecular spheroids via metal-ligand coordination of two pseudo linear bisimidazole and bisbenzimidazole ligands and Pd(NO3)2 independently. The molecular spheroids were characterized by NMR, mass spectroscopy and single crystal X-ray diffraction techniques. The impedance measurements clearly showed a trend in the proton conductance values of the spheroids. As the hydrophobicity (increase in number of carbon atoms) of the systems increased by changing the length and substituent or both, the resulting proton conductance value decreased. Thus, the proton conductivity is inversely related to the hydrophobicity of the molecular spheroids. Therefore, simple chemical modulation of ligand moieties can incorporate excellent proton conducting behavior in discrete self-assembled architectures making them prospective materials in fuel cell technology.

[1] Heinzel, A. et al. (2001) Nature, 414, 345-352.
[2] George K. H. Shimizu et al. (2009) Nat. Chem., 1, 705-710.
[3] Mukherjee, P. S. et al. (2014) Chem. Eur. J., 20, 5649-5656.



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