Unveiling the Physical Properties of Non-Planar Copper Hexahydroxytriptycene Metal-Organic Frameworks for High-Capacity Aqueous Zn-Ion Batteries

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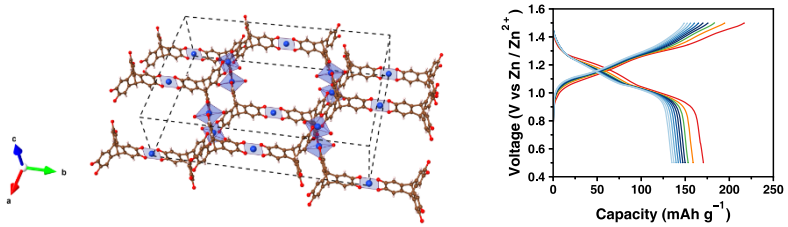
Recently, the emergence of quasi two-dimensional (2D) metal-organic frameworks (MOFs) has ushered in a new platform for electronics, sensing, and electrochemical energy storage devices, owing to their tunable physical properties and high crystallinity. In our previous studies[1,2], we revealed the crucial role played by intralayer π-d conjugation and interlayer π-π interaction in the electrochemical performance of planar 2D MOFs, particularly in terms of specific capacity and cycling stability. In contrast, this work seeks to provide a comprehensive understanding of the charge storage mechanism inherent in non-planar copper hexahydroxytriptycene (Cu-HHTT) MOFs. In this unique architecture, the C_3 symmetric HHTT ligand lacks fully π conjugation, and the aromatic rings stand perpendicular to the 2D plane, resulting in the absence of interlayer π-π interaction.

The synthesis of Cu-HHTT MOFs employed both diffusion and solvothermal methods, yielding single crystals and polycrystalline powders with distinctive stacking models. Solid-state electrochemistry for Cu-HHTT MOFs were conducted in an aqueous Zn-ion battery, utilizing 1M $ZnSO_4/H_2O$ as the electrolyte. Impressively, Cu-HHTT MOF delivered a substantial reversible capacity of ~150 mAh/g, corresponding to a 1.5-electron reaction per Cu, thereby suggesting the dual redox activity of Cu ions and HHTT ligands. To delve deeper into the charge storage mechanism of non-planar Cu-HHTT MOF, electron spin resonance (ESR) and magnetic susceptibility studies of pristine MOFs and electrochemical intermediates are planned, promising further insights into the function of π conjugation and interlayer π-π interaction.



Crystal structure of Cu-HHTT MOF and charge-discharge profiles Zn/Cu-HHTT battery.

1) Q. Chen *et. al.*, *J. Am. Chem. Soc.* **2023**, *145*, *2*, 1062-1071. 2) Q. Chen *et. al.*, *J. Vis. Exp.* **2023**, *196*, e65335.