Proton-Conduction Behavior in Flexible Free-Standing Membranes of Coordination Polymers

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Membranes assembled from coordination polymer (CP) nanosheets have attracted much interest as a new strategy for constructing flexible free-standing membranes, which can contribute to CP-based flexible electronics and intelligent wearable devices. Our recent work demonstrated that the H^+–OH^--type rectifier shows a prominent proton rectification behavior, including a highly flexible Cu_2(CuTCPP) CP membrane (H_4CuTCPP: copper(II) tetrakis(4-carboxyphenyl)porphyrin) composed of paddlewheel-type Cu(II) dimers and tetradentate $CuTCPP^{4-}$ ligands.[1] In this study, we fabricated a series of Cu_2(MTCPP) (M = Ni(II), Cu(II), and Zn(II))[2] membranes to investigate the effect of proton concentration and mobility on the rectification behavior.

Three kinds of Cu_2(MTCPP) nanosheets were obtained by a solvothermal method. After the exfoliation procedure, the free-standing membranes with good flexibility were obtained separately by a vacuum filtration method (Figures 1a-c). Cross-sectional SEM images revealed that the membranes are formed by stacking the nanosheets and have a thickness of approximately 8 μm (Figures 1d-f). Out-of-plane XRD patterns also proved that the membranes have good orientation along the stacking direction (// *c* axis). The in-plane proton-conduction behavior of the membranes with different bending conditions is also discussed.

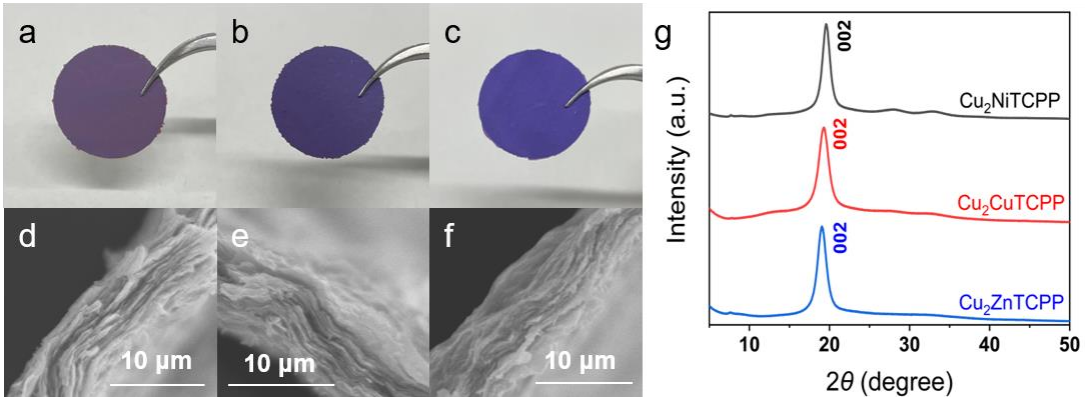

Figure 1. (a-c) Photographs and (d-f) cross-sectional SEM images of Cu_2MTCPP free-standing membranes (a,d: M = Ni(II), b,e: M = Cu(II), c,f: M = Zn(II)). (g) Out-of-plane XRD patterns of Cu_2MTCPP free-standing membranes.

1) J. Lu *et al.*, *Angew. Chem. Int. Ed.* **2022**, *61*, e202213077; 2) H. M. Shen *et al.*, *Chem. Eng. J.* **2022**, *443*, 136126.