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Post-synthesis functionalized Covalent Organic Frameworks as proton conduction materials

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Covalent Organic Frameworks (COFs) are a class of novel porous materials with tailored functionalities and highly ordered crystalline structures deriving from the reversibility of the crystallization process. Indeed, *de novo* synthesis of COFs with strong covalent connections usually results in amorphous phase rather than crystalline structures.[1] However, the reversibility of the covalent linkages is generally accompanied by poor chemical and thermal stability of these materials, limiting their applications in catalysis, gas storage or separation, etc.[2] Recently, COFs gained growing attention as proton conducting materials, for applications as solid electrolytes in proton exchange membrane fuel cells (PEMFCs).[3] Herein, we report the post-synthesis functionalization of an imine-linked COF (COF-LZU1) towards the enhancement of its proton conductivity. To this end, evolution of the linkage from imine to secondary amine and, finally, to tertiary amine carrying a propylsulfonic moiety was investigated and confirmed by infrared and Raman spectroscopy, thermogravimetric analysis coupled to mass spectrometry, X-ray photoelectron spectroscopy, and energy dispersive X-ray analysis. Scanning electron microscopy images demonstrate the retained morphology (Figure 1). Electrochemical impedance spectroscopy is employed to unravel the proton transport behavior of the synthesized material.

References

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[2] L. Cusin, H. Peng, A. Ciesielski, P. Samorì, *Angew. Chem. Int. Ed.*, 60 (**2021**), 14236–14250
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Figures

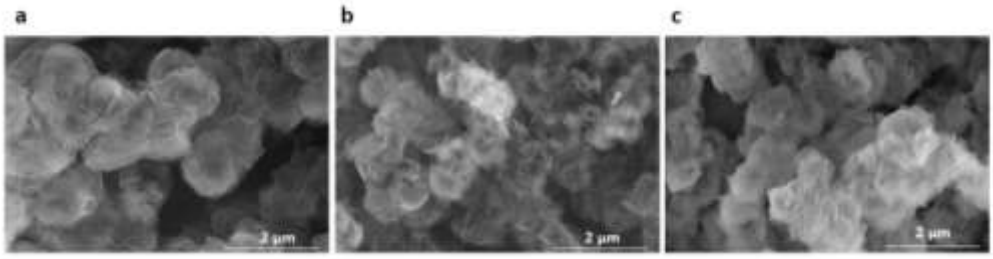

Figure 1: Scanning electron microscopy images of a) imine linked COF LZU1, b) amine-linked and c) propylsulfonic COF.