

## Post-synthesis functionalized Covalent Organic Frameworks as proton conduction materials

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### EXPERIMENTAL RESULTS

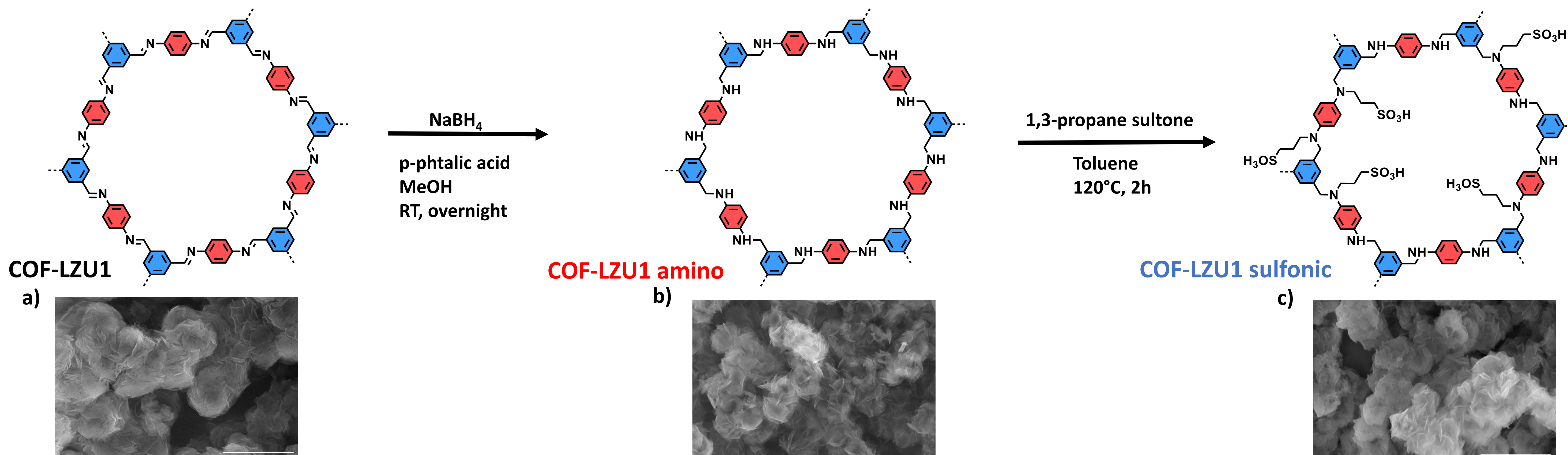


Figure 1. Synthetic procedure for the post-synthesis functionalization of COF-LZU1. SEM micrographs of a) COF-LZU1, b) COF-LZU1 amino and c) COF-LZU1 sulfonic. All the scale bars are 2  $\mu\text{m}$ .

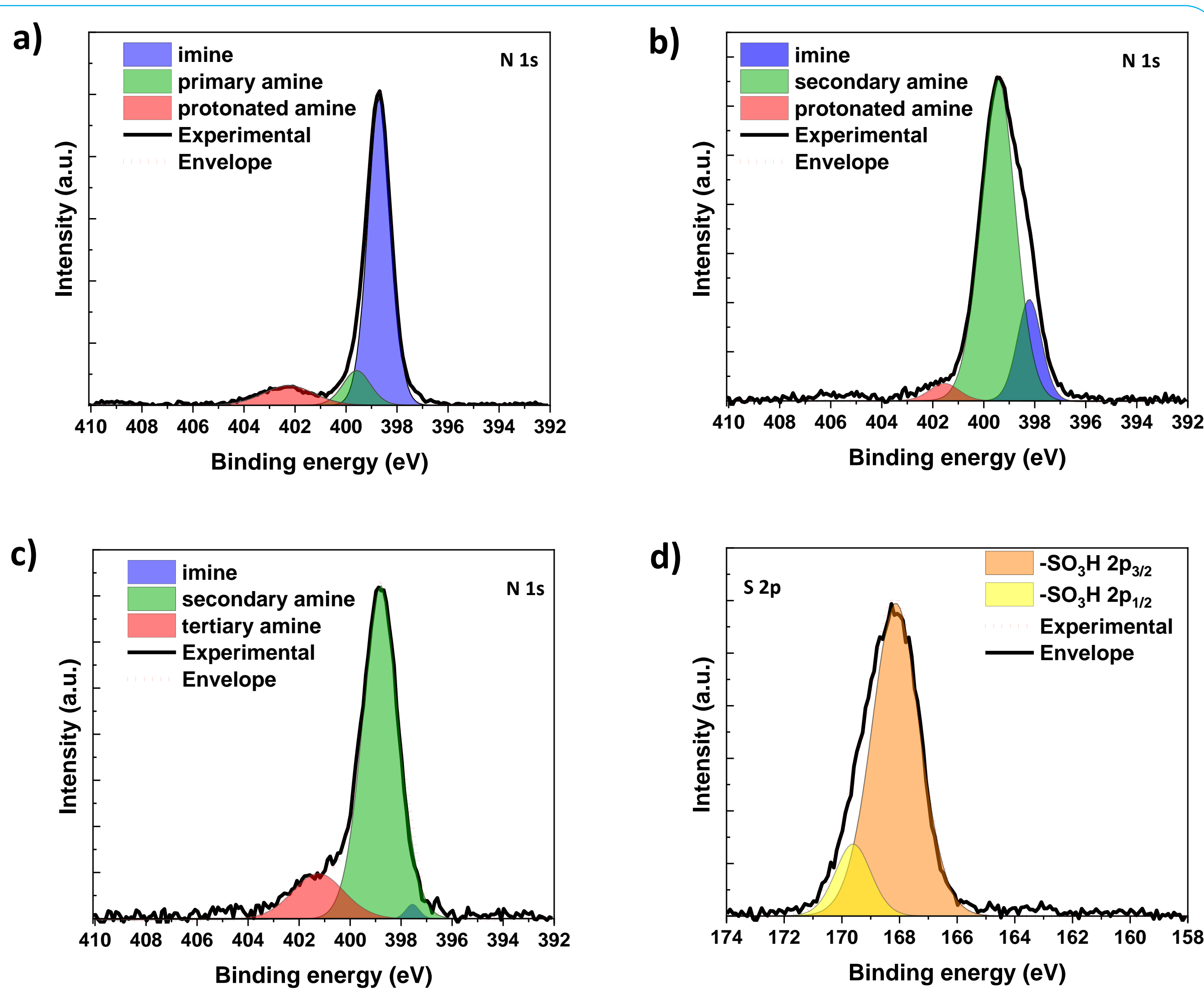


Figure 2. a-c) High resolution XPS spectra of N 1s for a) COF-LZU1, b) COF-LZU1 amino and c) COF-LZU1 sulfonic. d) High resolution XPS spectra of S 2p for COF-LZU1 sulfonic.

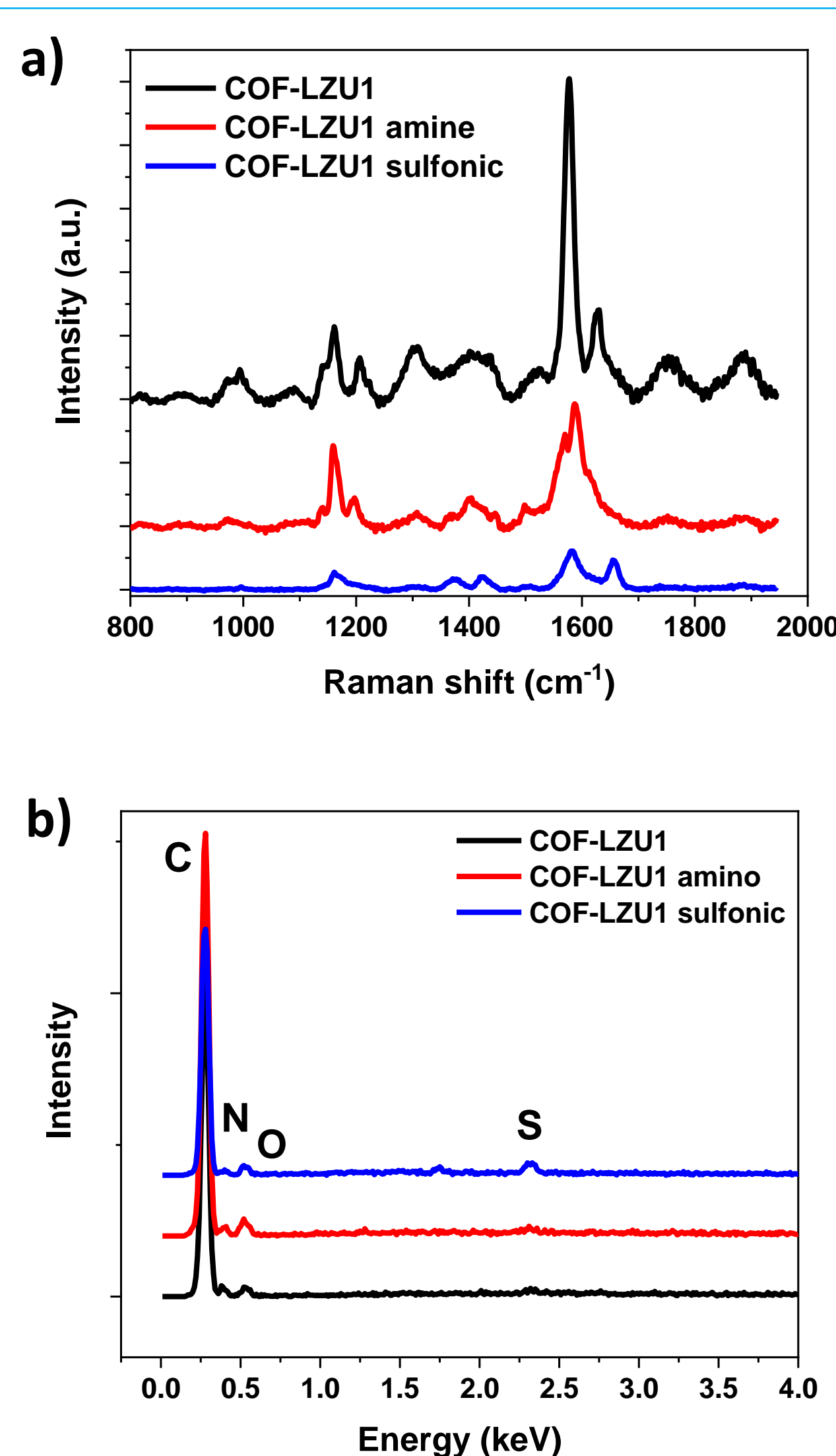


Figure 3. a) Raman spectra of the synthesized COFs recorded with a 20  $\times$  objective (maximum power of 0.02 mW) and the 532 nm laser line. Five accumulations were acquired with an acquisition time of 1 s. b) EDX spectra of the synthesized COFs.

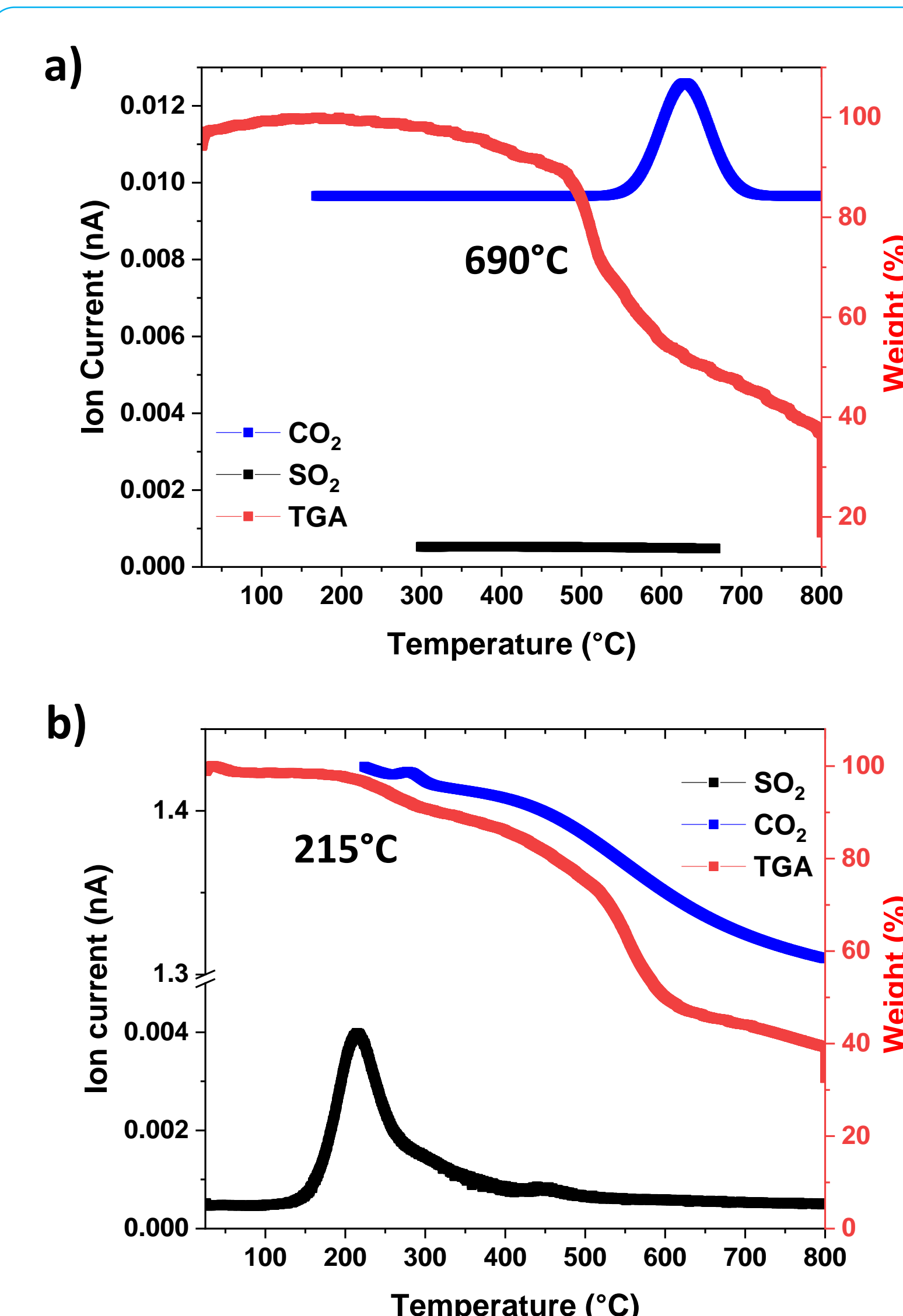


Figure 4. TGA-MS plots of a) COF-LZU1 amino and b) COF-LZU1 sulfonic recorded in  $\text{N}_2$  atmosphere with a 10°C/min rate.

### CONCLUSIONS

Post-synthesis functionalization of COF-LZU1 was carried out by a two-steps process, involving the reduction of the imine bond to obtain a secondary amine [1] and the subsequent reaction with 1,3-propane sultone[2], without any morphological change (Figure 1).

- XPS spectra:** reduction in intensity of the imine peak and appearance of the one for the secondary amine (Figure 2a-b). Appearance of a broad peak related to the tertiary amine (N 1s) and the ones related to the sulfonic acid group (S 2p) (Figure 2c-d)
- Raman spectra:** main peak is the imine stretching for COF-LZU1 and the C-N amine stretching for COF-LZU1 amino; symmetric and asymmetric  $-\text{SO}_3$  and aliphatic C-C stretching bands appear for COF-LZU1 sulfonic. (Figure 3a)
- EDX spectra:** estimation of the degree of functionalization shows a N:S ratio of 5:1 for COF-LZU1 sulfonic (Figure 3b).
- TGA/MS spectra:** COF-LZU1 sulfonic undergoes a weight loss at 215°C, corresponding to the loss of  $\text{SO}_2$  (g) (Figure 4).
- EIS spectra:** dependence of the impedance on the relative humidity (RH). COF-LZU1 sulfonic in dry air conditions behaves as a dielectric or poor electronic conductor, while at high RH, the clear conduction process observed could be associated to ionic (proton) species. (Figure 5)

Further studies will be performed equilibrating the COF pellets at different RH values and temperature, in order to determine the proton conduction mechanism and its activation energy.

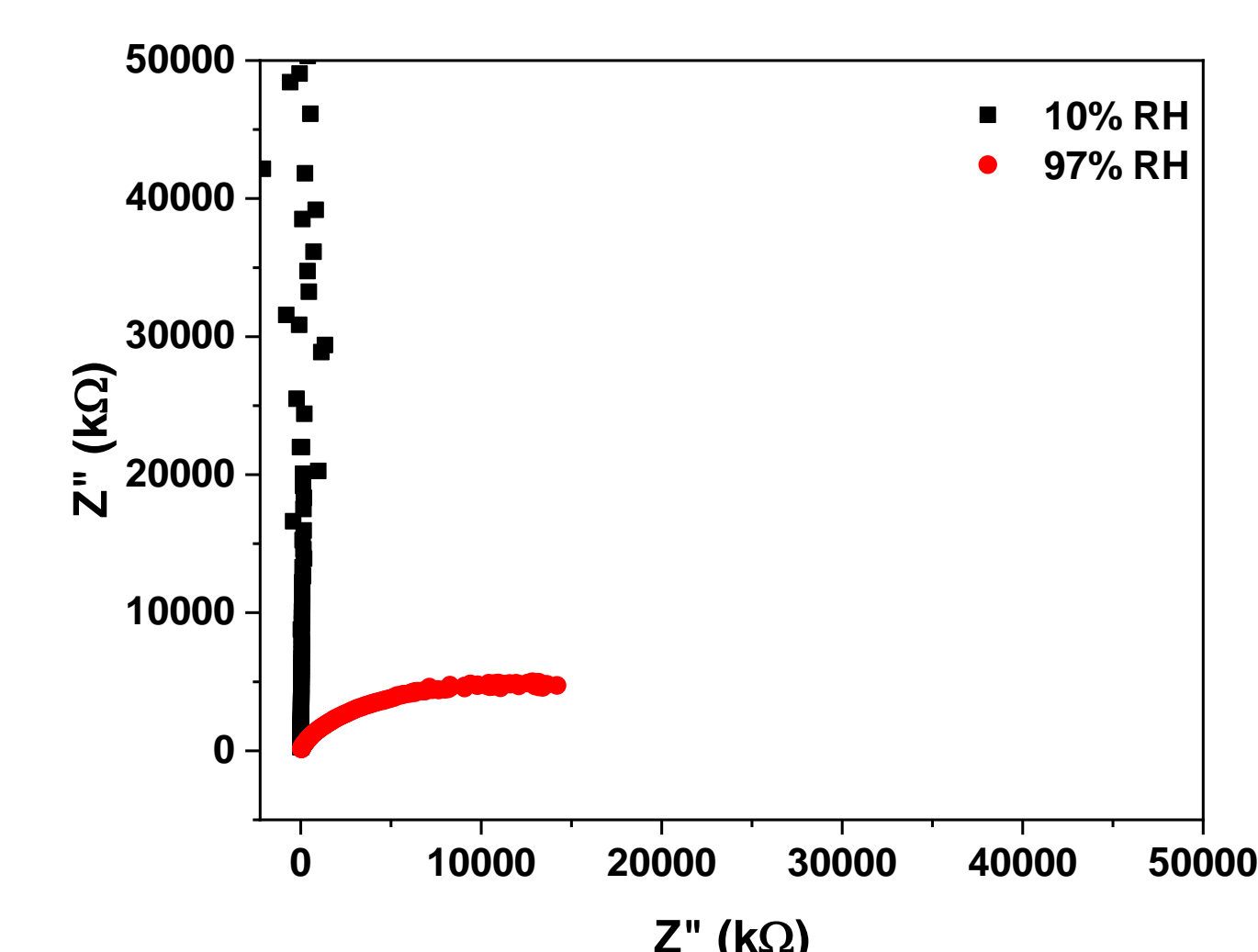


Figure 5. Electrochemical impedance spectra (EIS) of COF-LZU1 sulfonic recorded at 25°C at 10% and 97% relative humidity (RH) on COF-LZU1 sulfonic pellets.

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### REFERENCES

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- Q. Yan, H. Xu, X. Jing, H. Hu, S. Wang, C. Zenga, Y. Gao, *RSC Advances*, (2020), 10, 17396–17403