

## A Nanoporous Piezoelectric Material: Metal-organic Framework ZIF-8

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Metal-organic frameworks (MOFs) are highly tuneable 3D-nanoporous structures composed by organic linkers and metal nodes. Due to their crystalline nanoporous nature traditional applications like gas storage and molecular separation have been explored since the beginning of the MOF field in the early nineties of the last century. However, due to their nanoporosity they are also prime candidates for piezoelectric energy harvesting. Indeed porosity decreases the dielectric constant, which enhances the Figure of Merit for piezoelectric energy harvesting. Combine this with the tuneability of the topology and building blocks of the materials, and you have a materials class that is very interesting to explore for piezoelectricity. Yet, only two papers briefly mention piezoelectricity of MOFs: in one the  $d_{22}$  value of a homochiral framework is measured to be about 7 pC/N;<sup>1</sup> in the other piezoresponse force microscopy was performed on a polar  $Ba^{2+}$  based MOF, however only results with regard to its ferroelectric properties were discussed.<sup>2</sup>

We focused our attention to ZIF-8, a material build up from  $Zn^{2+}$  and imidazolate that shows high chemical and thermal stability. Importantly, for this MOF a low dielectric constant of 2.3-2.45 with a low loss factor is already reported.<sup>3</sup> We found through a combination of X-ray diffraction and second-harmonic generation microscopy (SHGM), that the material belongs to a piezoelectric point group, namely Td. We compared a series of different synthesis conditions (temperatures, microwave versus conventional oven etc.) and found that slower syntheses conditions lead to higher SHG-activity. This means that the internal structure of these crystals is organized to a greater extent in a non-centrosymmetric manner. In fact, for our slowest synthesis, the nonlinear optical coefficient related to the SHG-activity ( $\langle d_{\text{eff}} \rangle = 0.25 \pm 0.04$  pm/V) closely matched the theoretically determined value of 0.29 pm/V. Polarization dependent analysis of the SHG-images showed that the decreasing non-centrosymmetric order in faster syntheses is caused by randomization of the orientation of the organic linkers in otherwise single crystals.<sup>4</sup> With piezoresponse force microscopy we confirmed the piezoelectric nature of these crystals, and compared the lateral and vertical piezoelectric response for different crystal facets.

To conclude, we found a crystalline, nanoporous solid, namely ZIF-8 that combines a clear piezoelectric response with a low dielectric constant. It is a promising material for mechanical energy harvesting.

### References:

[1] P. Yang et al. J. Chem. Mater. 2012, 22, 2398-2400. [2] K.A. Asha et al. CrystEngComm, 2016,18, 1046-1053. [3] S. Eslava et al. Chem. Mater. 2013, 25, 27-33. [4] S. Van Cleuvenbergen et al. Chem. Mater. 2016, 28, 3203-3209.