

Design and Development of Functionalized Pillar-Layered MOFs

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Metal-Organic Frameworks (MOFs) represent a diverse class of porous materials that can be truly designed in terms of their inorganic and organic components, offering a wide spectrum of tuneable properties. Despite being solids, such materials have shown unique structural flexibility phenomena under external stimuli (e.g. temperature, host-guest interactions, pressure and light), paving the way to state-of-the-art responsive materials for applications such as selective gas separation [1]. In particular, pillar-layered (PL) MOFs have attracted great interest in terms of their framework flexibility [2]. More specifically, DUT-8(M) (M: Ni, Co, Cu, Zn) is a representative PL-MOF family with a typical “gate-opening” behaviour that has shown to hold great promise for separation applications [3]. This mixed-ligand framework consists of 2D grids (layers) formed by paddle-wheel metal clusters which are connected by naphthalene dicarboxylate (NDC) ligands. These grids are pillared by a tertiary diamine, DABCO, leading to an open 3D structure with **pcu** topology (Figure 1). The flexible behaviour arises from the ability of the inorganic node to act as a “hinge”, and thus the alteration of the metal centres has enabled the fine tuning of the framework’s flexibility [4]. Despite the study of the metals’ nature effect, to the best of our knowledge, the effect on the flexibility of the nature of the organic ligand, in terms of their functional groups, which has been shown to have an impact on the flexibility phenomenon in similar systems [5], hasn’t been investigated for DUT-8.

Herein, we explore for the first time the layer-forming ligand functionalization of the DUT-8 framework. Three novel structures were successfully synthesized and characterized by introducing different functionalities on the organic linker. One of them lead to a topologically identical framework as the DUT-8(M) system (Figure 1), while the other two resulted to completely different topologies with intriguing properties. Synthetic conditions, crystal structures, stability investigations and sorption properties will be presented and discussed.

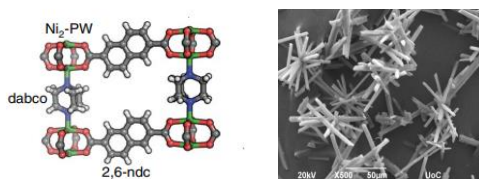


Figure 1: (Left) DUT-8(Ni) Pillar-Layered structure (Right) Representative SEM image of the isostructural DUT-8 single crystals.

References

- [1] Giasemi K. Angeli, Edward Loukopoulos, Konstantinos Kouvidis, Artemis Bosveli, Constantinos Tsangarakis, Emmanuel Tylianakis, George Froudakis, and Pantelis N. Trikalitis, *J. Am. Chem. Soc.*, **143**, 10250-10260 (2021).
- [2] S. Ehrling, E. M. Reynolds, V. Bon, I. Senkovska, T. E. Gorelik, J. D. Evans I, M. Rauche, M. Mendt, M. S. Weiss, A., E. Brunner, U. Kaiser, A. L. Goodwin and S. Kaskel, *Nature Chemistry*, **13**, 568–574 (2021).
- [3] Linda Bondorf, Jhonatan Luiz Fiorio, Volodymyr Bon, Linda Zhang, Mariia Maliuta, Sebastian Ehrling, Irena Senkovska, Jack D. Evans, Jan-Ole Joswig, Stefan Kaskel, Thomas Heine, Michael Hirscher, *Science Advances*, **8**, eabn7035, (2022).
- [4] Nicole Klein, Herbert C. Hoffmann, Amandine Cadiou, Juergen Getzschmann, Martin R. Lohe, Silvia Paasch, Thomas Heydenreich, Karim Adil, Irena Senkovska, Eike Brunner and Stefan Kaskel, *J. Mater. Chem.*, **22**, 10303, (2012).
- [5] Sebastian Henke, Andreas Schneemann, Annika Wütscher, and Roland A. Fischer, *J. Am. Chem. Soc.*, **134**, 9464–9474 (2012).

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