2nd generation Hofmann-type networks – Introducing multifunctionality into spin-switchable frameworks

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Spin-switchable Hofmann-type Fe(II)-networks based on M(CN)₄ (M=Ni, Pd, Pt) as square planar building block and a ditopic N-heterocycle as *e.g.* pyrazine, 4,4'-bipyridine,... combine magnetism with host-guest chemistry.¹ A second generation of extended Hofmann-type networks was obtained by introduction of an acetylene-unit in the M-CN bond (figure 1), resulting in metallated tetrakis(cyanoacetylides) as expanded building blocks.² Thereby, not only was a notable increase in pore volume of about 120 % achieved, but the polarity of the PCP's inner surface could also be modified. For the growth of single-crystals a novel electrolytic crystallization approach was developed, providing the necessary Fe(II)-ions by anodic oxidation of Fe in a non-aqueous medium (figure 2). In the present contribution the second generation of bimetallic Fe-M, (M=Ni, Pd, Pt) Hofmann-type networks is presented and discussed with regard to its structural, magnetic and spectroscopic properties. A special emphasis is placed on the host-guest chemistry of the networks, as governed by the extended pores bearing alkyne-moieties.





Figure 1 Extended Hofmann-type network ([Fe(pz)(Pd(C₃N)₄)] with pyrazine (pz) as ditopic ligand

Figure 2 Electrolytic crystallization of the networks

1 M. Ohba, K. Yoneda, G. Agusti, M. C. Munoz, A. B. Gaspar, J. A. Real, M. Yamasaki, H. Ando, Y. Nakao, S. Sakaki, S. Kitagawa, *Angew. Chem. Int. Ed.*, **2009**, *48*, 4767. 2 D. Müller, C. Knoll, M. Seifried, J.M. Welch, G. Giester, M. Reissner, P. Weinberger, *Adv. Mat.*, **2018**, *submitted*