

HOST-GUEST CHEMISTRY IN SECOND GENERATION SPIN-SWITCHABLE HOFMANN TYPE NETWORKS: LARGER PORES FOR LARGER GUESTS

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A main goal of nowadays spin crossover (SCO) research is the development of materials suitable for technological applications. Multifunctional materials, combining the SCO effect with an additional property (*e.g.* luminescence, NLO, etc.) would notably broaden the scope of applicability.^[1]

Currently we focus on the development of spin-switchable metal organic frameworks with extended pore-size. Such porous spin-switchable hosts could act as multifunctional materials by the mere incorporation of a functional guest. The most famous class of spin-switchable porous networks is the one of Hofmann-type networks, based on $\{\text{Fe}[\text{M}^{\text{II}}(\text{CN})_4]_{\infty}\}$ ($\text{M}=\text{Ni}, \text{Pd}, \text{Pt}$) layers stacked by symmetrical bifunctional N-ligands. The limited pore-size determined by the CN unit limits the scope of possible guests to small molecules (*e.g.* SO_2 , CO_2). Therefore, an extension of the $[\text{M}^{\text{II}}(\text{CN})_4]^{2-}$ fragment of the well-known Hofmann-type networks^[2] was performed, elongating the CN fragment by addition of an acetylene unit in the M-CN bond, resulting in metallated tetrakis(cyanoacetylides) $[\text{M}^{\text{II}}(\text{C}_3\text{N})_4]^{2-}$ as expanded building blocks. This led to second generation Hofmann-type networks with hysteretic SCO behavior beyond room-temperature (Figure 1) and extended pore size (Figure 2) thus broadening the spectrum of possible guest molecules.

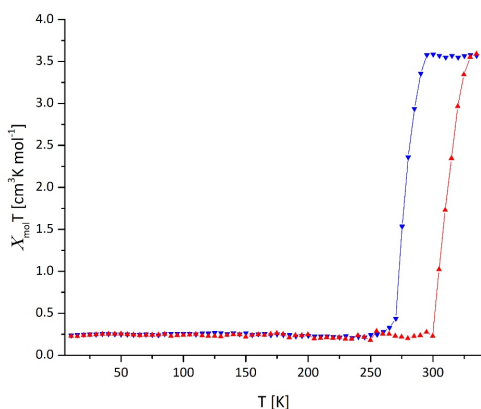


Figure 1: Magnetic behavior of $[\text{Fe}(\text{pz})][\text{Pd}(\text{C}_3\text{N})_4]$

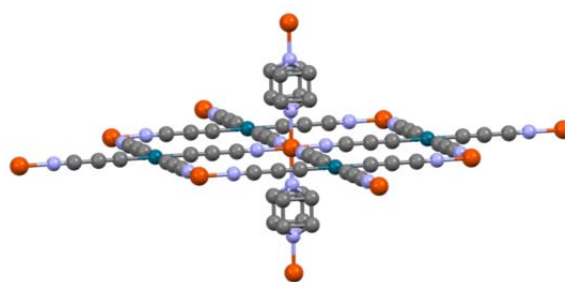


Figure 2 : Second generation Hofmann-type network $[\text{Fe}(\text{pz})][\text{Pd}(\text{C}_3\text{N})_4]$, view along a-axis

[1] A. B. Gaspar, V. Ksenofontov, M. Seredyuk, P. Gülich, *Coord. Chem. Rev.*, 2005, 249, 2661.

[2] V. Niel, J. Mari, M.-Agudo, M. C. Munoz, A. B. Gaspar, J. A. Real, *Inorg. Chem.*, 2001, 40, 3838.