

Expanding the dimensionality of bis(tetrazolyl)alkane-based Fe(II) coordination polymers by the application of dinitrile coligands

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Reactions between 1,2-di(tetrazol-2-yl)ethane (ebtz), 1,6-di(tetrazol-2-yl)hexane (hbtz) or 1,1'-di(tetrazol-1-yl)methane (1ditz) and $\text{Fe}(\text{BF}_4)_2$ in the presence of adiponitrile (ADN), glutaronitrile (GLN) or suberonitrile (SUN) resulted in the formation of coordination polymers $[\text{Fe}(\mu\text{-ebtz})_2(\mu\text{-ADN})](\text{BF}_4)_2$ (**1**), $[\text{Fe}(\mu\text{-hbtz})_2(\mu\text{-ADN})](\text{BF}_4)_2$ (**2**), $[\text{Fe}(\mu\text{-1ditz})_2(\text{GLN})_2](\text{BF}_4)_2 \cdot \text{GLN}$ (**3**) and $[\text{Fe}(\mu\text{-1ditz})_2(\mu\text{-SUN})](\text{BF}_4)_2 \cdot \text{SUN}$ (**4**). It was established that the application of dinitriles allows an increase in the dimensionality of the ebtz and hbtz based systems while maintaining the structure of the polymeric units characteristic of previously studied mononitrile based analogues. In **3** and **4**, regardless of the type of dinitrile coligand, the motif of 2D polymeric layers constituted by 1ditz molecules remains preserved. However, the dimensionality of 1ditz based networks is governed by the coordination modes of dinitriles. **3**, based on a shorter molecule of glutaronitrile, crystallizes as a two-dimensional (2D) coordination polymer. In this compound, dinitriles coordinate monodentately or play the role of guest molecules. The substitution of glutaronitrile with suberonitrile enables the bridging of neighboring polymeric layers, resulting in a 3D network. The intentional selection of bis(tetrazoles) and dinitriles as building blocks has led, as expected, to obtaining systems with the structure of the first coordination sphere consisting of four tetrazole rings and two axially coordinated nitrile molecules. It created the conditions required for the occurrence of thermally induced spin crossover. Magnetic measurements and single crystal X-ray diffraction studies were used for the characterization of the spin crossover properties of **1–4**.

Adres publiczny

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