Spatiotemporal studies of the one-dimensional coordination polymer $[Fe(ebtz)_2(C_2H_5CN)_2](BF_4)_2$: tug of war between the nitrile reorientation versus crystal lattice as a tool for tuning the spin crossover properties.

Autorzy

Maria Książek

Marek Weselski

Marcin Kaźmierczak

Aleksandra Tołoczko

Miłosz Siczek

Piotr Durlak

Juliusz A. Wolny

Volker Schünemann

Joachim Kusz

Robert Bronisz

Rok wydania

2020

Czasopismo

Chemistry-A European Journal

Numer woluminu

26

Strony

14419-14434

DOI

10.1002/chem.202002460

Kolekcja

Naukowa

Streszczenie

Reaction of 1,2-di(tetrazol-2-yl)ethane (ebtz) with $Fe(BF_4)_2 \cdot 6H_2O$ in different nitriles yields one-dimensional coordination polymers $[Fe(ebtz)_2(RCN)_2](BF_4)_2 \cdot n$RCN ($n$=2 for R=$CH_3$ (**1**) and n=0 for R=C_2H_5 (**2**) C_3H_7 (**3**), C_3H_5 (**4**), CH_2Cl (**5**)) exhibiting spin crossover (SCO). SCO in **1** and **3**–**5** is complete and occurs above 160 K. In **2**, it is shifted to lower temperatures and is accompanied by wide hysteresis ($T_{1/2}^{\downarrow}$=78 K, $T_{1/2}^{\uparrow}$=123 K) and proceeds extremely slowly. Isothermal (80 K) time-resolved single-crystal X-ray diffraction studies revealed a complex nature for the HS→LS transition in **2**. An initial, slow stage is associated with shrinkage of polymeric chains and with reduction of volume at 77 % (in relation to the difference between cell volumes $V_{HS}-V_{LS}$) whereas only 16 % of iron(II) ions change spin state. In the second stage, an abrupt SCO occurs, associated with breathing of the crystal lattice along the direction of the Fe–nitrile bonds, while the nitriles reorient. HS→LS switching triggered by light (808 nm) reveals the coupling of spin state and nitrile orientation. The importance of this coupling was confirmed by studies of $[Fe(ebtz)_2(C_2H_5CN/C_3H_7CN)_2](BF_4)_2$ mixed crystals (**2 a**, **2 b**), showing a shift of $T_{1/2}$ to higher values and narrowing of the hysteresis loop concomitant with an increase of the fraction of butyronitrile. This increase reduces the capability of nitrile molecules to reorient. Density functional theory (DFT) studies of models of **1**–**5** suggest a particular possibility of **2** to adopt a low (140–145°) value of its Fe-N-C(propionitrile) angle.

Słowa kluczowe

coordination polymers, iron, spatiotemporal effects, spin crossover

Adres publiczny

http://dx.doi.org/10.1002/chem.202002460

Język

Angielski

Strona internetowa wydawcy

onlinelibrary.wiley.com

Typ publikacji

Artykuł