Two ways of spin crossover in an iron(II) coordination polymer associated with conformational changes of a bridging ligand.

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Rok wydania

2020

Czasopismo

Dalton Transactions

Numer woluminu

49

Strony

9811-9819

DOI

10.1039/d0dt01696a

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

1,4-Di(1-ethyl-1,2,3-triazol-5-yl)butane (**bbtre**) was prepared by lithiation of 1-ethyl-1,2,3-triazole, followed by alkylation with 1,4-dibromobutane. The ligand **bbtre** forms a three-dimensional network with Fe(II), $[Fe(\mathbf{bbtre})_3](ClO_4)_2{\cdot}2CH_3CN$, that exhibits thermally induced spin crossover (SCO). A change of temperature or change of spin state results in various types of structural transformation, leading to different structures that are stable in strictly defined temperature ranges. As a result, there are three spin crossover transitions arranged *via* two different paths. Thus, cooling below 280 K involves a HT(HS) → LT(HS) (HT, high temperature structure; LT, low temperature structure; HS, high spin) phase transition (PT), which is associated with conformational changes of the **bbtre** molecules and with deformation of the polymeric skeleton. In the LT phase incomplete and reversible LT(HS) ⇄ LT(HS/LS) spin crossover occurs (LS, low spin). In contrast, rapid cooling (of a sample not previously thermally treated) allows the HT(HS) → LT(HS) phase transition to be avoided, and so complete HT(HS) → HT1(LS) SCO occurs. This means that the PT plays the role of a switch, which allows a choice of one of two ways in which the SCO will proceed. After rapid cooling, further heating to 150 K and subsequent cooling results in a reversible HT1(HS) ⇄ HT1(LS) spin crossover ($T^{\downarrow}_{1/2}$ = 130 K, $T^{\uparrow}_{1/2}$ = 131 K). However, raising the temperature to 170–200 K leads to formation of a modulated structure HT2(HS) exhibiting the next reversible HT2(HS) ⇄ HT2(LS) SCO ($T^{\downarrow}_{1/2}$ = 121 K, $T^{\uparrow}_{1/2}$ = 123 K). Finally, heating above 200 K involves the HT2(HS) → LT(HS) PT and results in a LT(HS) structure exhibiting incomplete LT(HS) ⇄ LT(HS/LS) spin crossover.