Influence of conformational changes on spin crossover properties and superstructure formation in 2D coordination polymers $[Fe(hbtz)_2(RCN)_2](ClO_4)_2$.

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Streszczenie

2D structurally related iron(ii) coordination networks {[Fe(hbtz)2(RCN)2](ClO4)2}∞ featuring, besides tetrazol-2-yl rings in the first coordination sphere, also axially coordinated propionitrile or allyl cyanide molecules (R = C3H5-, ; R = C2H5- ,) were synthesized. Thermally induced spin crossover (SCO) in takes place in two poorly resolved stages (T(1)1/2(↓) = T(1)1/2(↑) = 198 K, T(2)1/2(↓) = 170 K, T(2)1/2(↑) = 171 K) whereas in complete and relatively gradual one step SCO (T1/2(↓) = T1/2(↑) = 160 K) occurs. Diversification of the SCO properties of the complexes originates from the ability of coordinated allyl cyanide in to undergo conformational alterations, which is not observed for propionitrile molecules in . SCO in is accompanied by a non-monotonic change of the contribution of allyl cyanide conformers which is related to reconstruction of the network of intermolecular contacts established between polymeric layers. The coordination network exhibits extraordinary elasticity and in the second stage SCO, accompanied by conformational changes of allyl cyanide, triggers a crystallographic phase transition which leads to the formation of a superstructure. What is important, the formation of the superstructure is not caused by long range ordering of HS and LS iron(ii) ions. The structural alteration is associated with corrugation of the polymeric skeleton and disappearance of nitrile disorder. Irradiation of a single crystal of at 15 K with laser light (520 nm) allowed producing a novel low temperature HS phase of in which, contrary to the high temperature HS phase, disordering of anion and allyl cyanide molecules is not observed and the corrugated nature of the polymeric layer, characteristic of the LS phase, is preserved.