Spin crossover and second harmonic generation of cyanido-bridged metal assemblies

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Keywords: *Magnetic complexes, Spin crossover, Second harmonic generation*

Cyanido-bridged metal assemblies are attractive magnetic compounds for which magnetic properties and functionalities can be designed by elaborate selection of building blocks.[1] In the cyanido-bridged assemblies, spin crossover is a fundamental magnetic property as well as long-range magnetic ordering. Various functional spin crossover systems have been reported since spin crossover was observed at a Prussian blue analogue.[2] Herein, we present spin crossover compounds based on cyanido-bridged Fe-Nb assemblies and their optical properties like second harmonic generation. The chiral and achiral Fe-Nb complexes, $Fe^{II}_2[Nb^{IV}(CN)_8](L)_8 \cdot 6H_2O$ (L = *R*-1-(3-pyridyl)ethanol: ***R*-FeNb**; *S*-1-(3-pyridyl)ethanol: ***S*-FeNb**; *rac*-1-(3-pyridyl)ethanol: ***rac*-FeNb**), were synthesized.[3] All complexes have an identical 3D cyanido-bridged coordination network in which the Fe^{II} site are coordinated to two cyanides and four pyridylethanol molecules (Figure 1a), and show a gradual incomplete spin crossover. For the chiral compounds of ***R*-FeNb** and ***S*-FeNb**, second harmonic generation was observed, and the intensity of the second harmonic (SH) light was modulated by the spin crossover (Figure 1b).

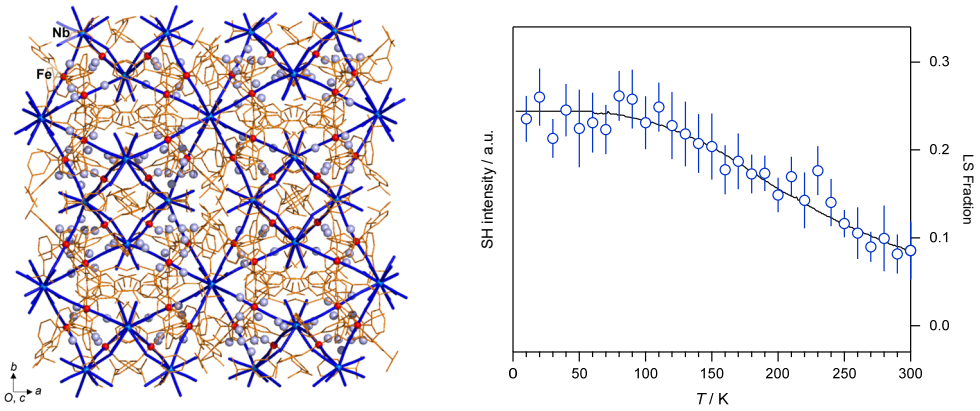

Figure 1. (a) Crystal structure of ***R*-FeNb**, (b) Temperature dependency of the SH light intensity (blue circles) for ***R*-FeNb** with the fraction change of the low spin (LS) state estimated from the magnetic susceptibilities.

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