

Three-Way Switching in a Multifaceted [CoFe] Chain

The drive to develop new materials that show *bistability*, that is, the ability to exist in more than one stable physical state under identical environmental conditions, is stimulated by the potential applications that such materials may have in future switching or data storage technologies. A heterometallic cobalt-iron ([CoFe]) chain complex was synthesized and found to be thermally-convertible between paramagnetic semiconducting and diamagnetic insulating phases and to display photo-switchable single chain magnetism at low temperatures. The *multibistability* of electronic and magnetic properties shown by the [CoFe] complex opens up exciting possibilities for the future of nano-scale switchable components.

Cyanide ions can act as linear bridges between metal ions, mediating significant electronic and magnetic coupling between nearest neighbors. Some multinuclear cyanide-bridged transition metal clusters can have more than one stable state (electronic, magnetic, chromic, etc.) under identical physical conditions. Such materials can be described as displaying *bistability*, and have the potential to operate as nano-scale switches: their states are interconverted upon application of appropriate external stimuli (heat, light, pressure, etc.). In particular, heterometallic iron/cobalt cyanide-bridged compounds can display a phenomenon termed electron-transfer-coupled spin transition (ETCST), in which a paramagnetic $\text{Co}^{\text{II}}(\text{HS})\text{-Fe}^{\text{III}}(\text{LS})$ (HS = high spin state, LS = low spin state) high-temperature (HT) phase can be reversibly converted to a diamagnetic $\text{Co}^{\text{III}}(\text{LS})\text{-Fe}^{\text{II}}(\text{LS})$ state at low temperature (LT) as a result of $\text{Co}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$ electron transfer and subsequent Co^{III} spin state transition (HS \rightarrow LS). The transition can be reversed at very low temperatures if the sample is irradiated by light of sufficient energy, allowing a meta-stable (HT*) magnetic

phase to be trapped [1]. This research aimed to investigate the interplay between electronic conductivity (and/or permittivity) and ETCST, an area as yet unexplored for molecular ETCST-active systems but with great potential importance in future switching technologies.

A chiral heterometallic chain coordination polymer was synthesized, in which cobalt and iron building blocks were combined in a square-wave type structure (Fig. 1) [2]. The [CoFe] chain showed thermal ETCST with wide hysteresis between a paramagnetic HT phase and a diamagnetic LT phase at close to room temperature. Single-crystal X-ray diffraction data collected at BL-8B at the Photon Factory meant that the structural changes associated with the HT \rightarrow LT transition could be followed in a single crystal, thus elucidating the effects of the ETCST phenomenon. The [CoFe] chain also showed light-induced ETCST to a meta-stable HT* phase at low temperature, in which it displayed single chain magnet (SCM) properties. Thus the complex could be converted to two distinct states, HT and HT*, from the LT state.

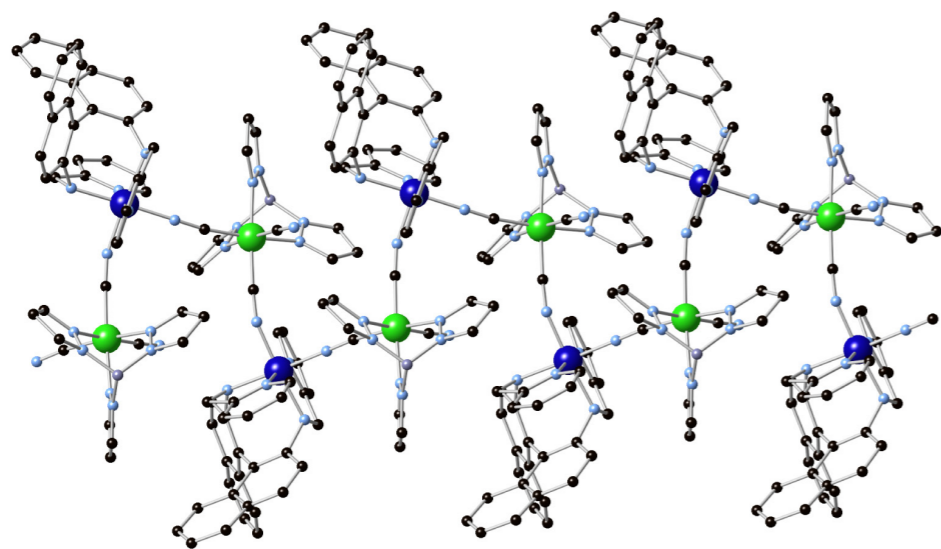


Figure 1: X-ray determined crystal structure of the [CoFe] chain (collected on BL-8B). Iron ions in green and cobalt in blue.

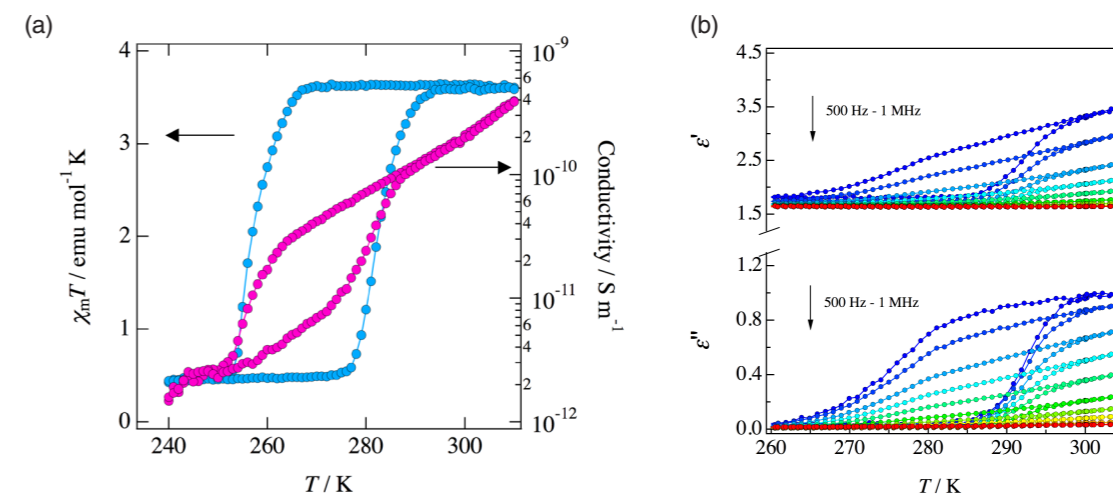


Figure 2: (a) Temperature dependences of the dc conductivity (pink) and magnetic susceptibility (blue) of the [CoFe] chain; (b) frequency dependence of the dielectric constant (ϵ') and dielectric loss (ϵ'') versus temperature.

The one-dimensional nature of the chain, coupled with the observation of thermal ETCST, made it an interesting candidate to investigate the effects of the intermetallic electron transfer and associated dipolar switching on its conductivity and permittivity. The temperature dependence of the dc conductivity (σ_{dc}) and magnetic susceptibility were measured simultaneously (Fig. 2), and the data indicated a strong correlation between magnetic HT \rightarrow LT transition and semiconductor to insulator phase transition. The conductivity measurements exhibited a wide hysteresis loop with an activation energy of 0.38 eV.

The dielectric response was also measured in the thermal ETCST temperature range, and exhibited a similar hysteretic response, likely brought about by the flipping of the dipolar orientations from $\text{Co}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$ to $\text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$ as the electron-transfer processes occurred. By fitting the frequency dependence of the permittivity to a modulus model, the group determined the activation energy (of the relaxation of the dipolar orientations) to be 0.42 eV. The similarity of the two activation energies obtained from the measured data suggests that the charge carrier overcomes the same energy barrier in both conduction and relaxation modes, and that the conduction and permittivity responses rely upon the thermal ETCST.

This is the first example of a link between ETCST and electric conductivity and permittivity in a molecular species, and illustrates the complementary manner in which different physical properties can be combined in switchable coordination compounds, and how different stimuli can be used to access contrasting electronic states. This result may pave the way for the rational design of low-dimensional materials with novel functionalities and applications as multiresponsive components in future technologies.

REFERENCES

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N. Hoshino¹, F. Iijima¹, G.N. Newton¹, N. Yoshida¹, T. Shiga¹, H. Nojiri², A. Nakao³, R. Kumai³, Y. Murakami³ and H. Oshio¹ (¹Univ. of Tsukuba, ²Tohoku Univ., ³KEK-PF)