Ultrafast dynamics in optically-charge-transfer-induced phase transitions of cyanido-bridged Co-W assemblies

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Ultrafast photo-responsivity is crucial for advanced photoswitchable materials. Cyanido-bridged metal assemblies have the potential to produce advanced materials with photoswitchable magnetic and optical properties, such as long-range magnetic ordering and THz wave absorption.[1,2] Herein, we report ultrafast dynamics in the cyanido-bridged Co-W assembly, $Cs^{+}_{0.1}(H_5O_2^{+})_{0.9}[Co(4\text{-bromopyridine})_{2.3}\{W(CN)_8\}]$ (**CsCoW**), which shows room temperature bistability and photoinduced ferromagnetism based on the charge-transfer phase transition between low-spin Co^{III}_{LS}-W^{IV} and high-spin Co^{II}_{HS}-W^{V} states.

Time-resolved optical spectroscopy and theoretical studies for the present compound have shown that photoexcitation of the charge-transfer band of Co^{III}_{LS}-W^{IV} state leads to a transient excited state Co^{II}_{LS}-W^{V} state, followed by a spin transition to a Co^{II}_{HS}-W^{V} state within 130 fs. The changes in the electronic state correspond to the decrease and increase of optical density around 600 nm and 700 nm, respectively (Figure 1). The results prove a charge-transfer-induced spin transition (CTIST) process in cyanide-bridged Co-W assemblies. Further experiments in ps time scale revealed that after the fast process a cooperative and thermoelastic process occurs within a few tens of ps near the transition temperature.

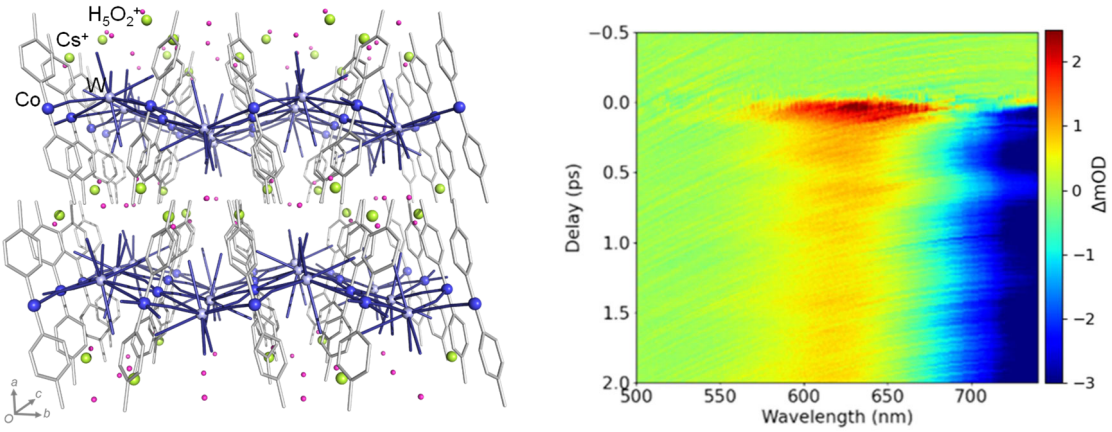

Figure 1. Crystal structure of **CsCoW** with the two-dimensional cyanido-bridged Co-W coordination network (left). Time delay optical density (OD) map of **CsCoW** at room temperature (right).

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