Temperature and Light-dependent Low-frequency Absorbance in Spin-crossover Systems

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Fe(II) spin-crossover (*SCO*) complexes are promising candidates for designing switchable molecular materials in a wide range of the electromagnetic spectrum, especially in the low-frequency (LF) terahertz (THz) region.[1,2] In this context, a novel one-dimensional spin-crossover network (Fig. 1a) based on Fe(II) complexes with 4-cyanopyridine (4-CNPy) and the $[Hg^{II}(SCN)_4]^{2-}$ building block has been designed with the formula of $[Fe^{II}(4\text{-CNPy})_2][Hg^{II}(\mu\text{-SCN})_2(SCN)(4\text{-CNPy})]_2$ (**1**). The magnetic measurement of compound **1** reveals a complete *SCO* effect with $T_{1/2}$ = 86 K due to the transformation of a low-spin state (LS, S = 0, $t_{2g}{}^6e_g{}^0$) from a high-spin state (HS, S = 2, $t_{2g}{}^4e_g{}^2$) in the Fe^{II} centers. **1** shows an intense sub-terahertz (sub-THz) absorbance of around 0.85 THz at room temperature (Fig. 1b). Upon cooling, the THz spectra show a significant blueshift and intensity increase owing to the reduced anharmonic thermal vibrations. A new peak at 0.98 THz appears around $T_{1/2}$ associated with *SCO* behavior. The switching of this peak can be achieved by photoirradiation with 658 nm and 785 nm laser lights at 10 K because of the Light-induced spin-state trapping (LIESST) and reverse-LIESST effects, respectively (Fig. 1c). The phonon-mode analysis is also well supported by quantum chemical calculations. This work indicates the importance of *SCO* materials for exploring the potential temperature- and photo-responsive switching effects in the rarely investigated THz region.

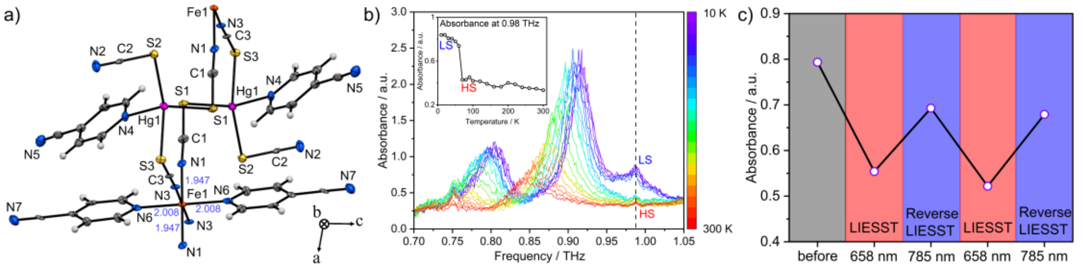

Figure 1. (a) Structural unit of **1** at 80 K. (b) Temperature dependencies of the THz-TDS spectra of **1**. Inset: the absorbance at 0.98 THz with temperature. (c) The absorbance at 0.98 THz before and after photoirradiation with 658 nm and 785 nm lasers at 10 K.

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