SUPRAMOLECULAR CONTROL OF ELECTRON-TRANSFER-COUPLED SPIN TRANSITIONS IN MOLECULAR PRUSSIAN BLUE ANALOGUES

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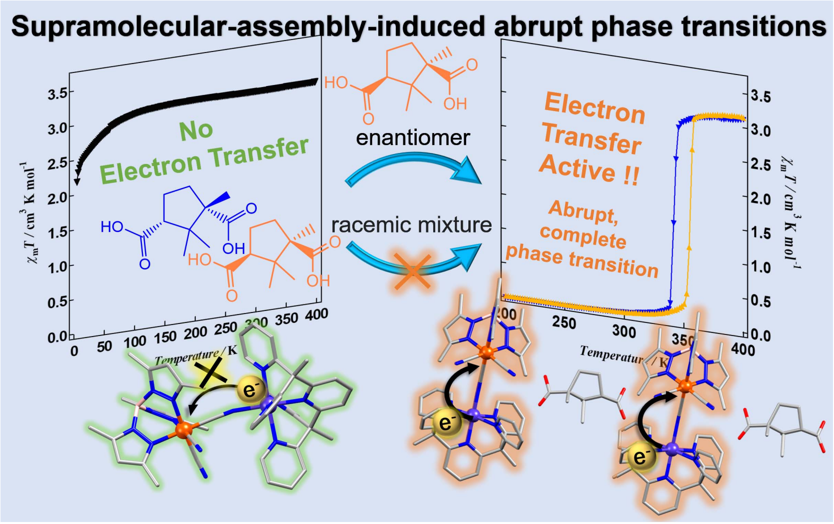
The design of cooperative electronic phase transitions in molecular materials remains a fundamental challenge in coordination chemistry. In particular, discrete cyanide-bridged Co–Fe units—molecular analogues of Prussian blue—often fail to exhibit abrupt switching behavior due to insufficient intermolecular cooperativity.

Here we demonstrate that hydrogen-bond-directed supramolecular assembly provides a powerful strategy to induce abrupt and complete electron-transfer-coupled spin transitions (ETCST) in such minimal building blocks [1]. While the parent dinuclear $[CoFe(CN)_3(L1)(L2)]^+$ units remain electronically inert across a wide temperature range, cocrystallization with an enantiopure chiral hydrogen-bond donor generates one-dimensional hydrogen-bonded chain architectures that undergo sharp, thermally driven phase transitions with clear hysteresis. Structural analysis reveals that hydrogen bonding to terminal cyanide ligands stabilizes the low-temperature electronic state and enables cooperative lattice reorganization.

Furthermore, comparison between enantiopure and racemic hydrogen-bond donors demonstrates that microscopic structural ordering critically determines the completeness of the phase transition, highlighting the intimate correlation between supramolecular organization and electronic-state switching.

This work establishes hydrogen-bond engineering as a versatile approach for activating and controlling cooperative electron-transfer phenomena in molecular Prussian blue analogues.



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[1] Y. Sekine, S. Hayami et al., *J. Am. Chem. Soc.* 2024, 146, 24238–24243