CO_2-actuated Control of Fe(II) Spin Crossover in a Hofmann-type Metal-Organic Framework

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The increased anthropogenic emission level of CO_2 urges the development of CO_2-responsive materials, but is it possible to regulate the inherent electronic properties through weak physisorption of a ubiquitous gas such as CO_2? Herein, we intended to answer this imperative question by the first case of CO_2-actuated variable spin-state stabilization in an interdigitated Hofmann-type metal-organic framework $[Fe^{II}Pd(CN)_4L_2]$ (**1**, L = methyl isonicotinate) [1].

Compound **1** did not adsorb N_2 (77 K) and O_2 (90 K). In contrast, a sharp transition appeared in the CO_2 adsorption isotherm and isobar, indicating the occurrence of gated adsorption. Magnetic measurements were conducted using a home-built gas cell under an external magnetic field of 1 kOe and varied CO_2 pressure (Fig. 1a), showing a wide shift in transition temperature ($T_{1/2}$) from 178 K at P_{CO2} = 0 kPa to 229 K at P_{CO2} = 100 kPa (defined by the average of cooling and heating). Interestingly, the emergence of a stepped behavior in the heating process below P_{CO2} = 10 kPa and overlapping magnetic susceptibility values above P_{CO2} = 10 kPa elucidate the selective low-spin state stabilization correlated with the extent of CO_2 accommodation. Based on the magnetic response and phase transition diagrams obtained under respective P_{CO2} (Fig. 1b), a plausible scenario of the spin-state switching can be interpreted as [**1**(ls) + **1**'(ls)] → [**1**(hs) + **1**'(ls)] → **1**(hs) at $P_{CO2} \leq$ 10 kPa, **1**'(ls) → **1**(hs) at 10 kPa < $P_{CO2} \leq$ 32 kPa, and **1**'(ls) → **1**'(hs) → **1**(hs) at P_{CO2} = 100 kPa, where **1** and **1**' represent CO_2-free and CO_2-accommodated states, respectively. The cooperative CO_2 adsorption with spin transition based on the varied CO_2 pressure corroborates a novel case for developing CO_2-responsive magnetic materials.

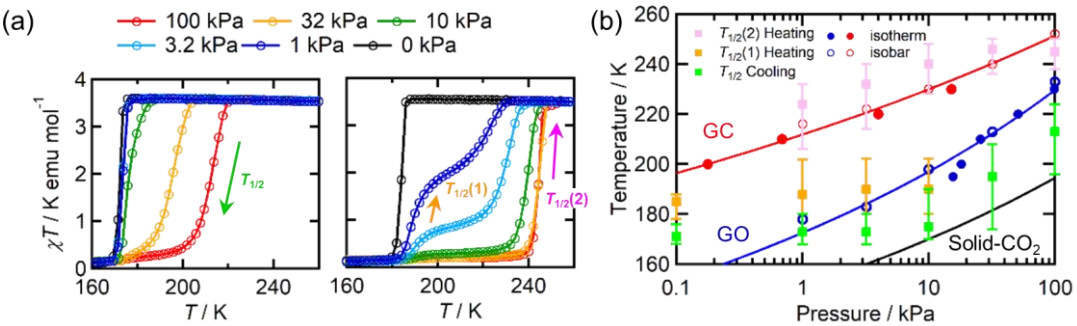

Fig. 1 (a) χT-T plots under CO_2 on cooling (right) and heating (right). (b) T-P phase diagram

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