Consideration on Gated CO_2 Adsorption Behavior in One-Dimensional Porous Coordination Polymers of Phenazine-Linked Paddlewheel Diruthenium Complex

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Low-dimensional coordination polymers such as one-dimensional (1-D) chains often exhibit gated guest sorption accompanying structural transition at a temperature (T_G),[1,2] which is associated with an external pressure of the guest (P_G) characteristic to the material and guest used. This phenomenon can be evaluated in the Clausius–Clapeyron (CC) equation of $d(\ln P_G)/d(1/T_G) = \Delta H_G/R$, where ΔH_G and R are the transition enthalpy and gas constant, respectively. In this study, gated CO_2 adsorption was investigated in a 1-D chain based on a benzoate-bridged paddlewheel diruthenium(II,II) complex with a phenazine (phz) linker, $[Ru_2(p\text{-MeOPhCO}_2)_4(phz)]$ (**1**; p-$MeOPhCO_2^-$ = p-anisate).[3]

Surprisingly, **1** underwent gate-opening (GO)/-closing (GC) at a much higher T_{GC} = 385 K under P_{CO2} = 100 kPa (Fig. 1a) than those previously reported for such chain compounds, which usually appeared in the temperature range of 200–270 K.[1,2] CC analyses gave a similar ΔH_G value for these compounds (inset of Fig. 1a), indicating that the transition entropy ΔS_G in each system plays a key role in shifting T_G; **1** results in a much smaller $|\Delta S_G|$ in the series. The crystal structure of the CO_2-accommodated phase (**1**⊃**CO₂**, Fig. 1b) revealed that Only **1** produced a CO_2-accessible 2-D topological pore in its CO_2-adsorbed phase **1**⊃**CO₂** (Fig. 1c). whereas the others reported previously produced 1-D or discrete (0-D) topological pores for CO_2 accommodation. These findings strongly reflect the degree of freedom of CO_2 molecules in pores, which is related to ΔS_G.

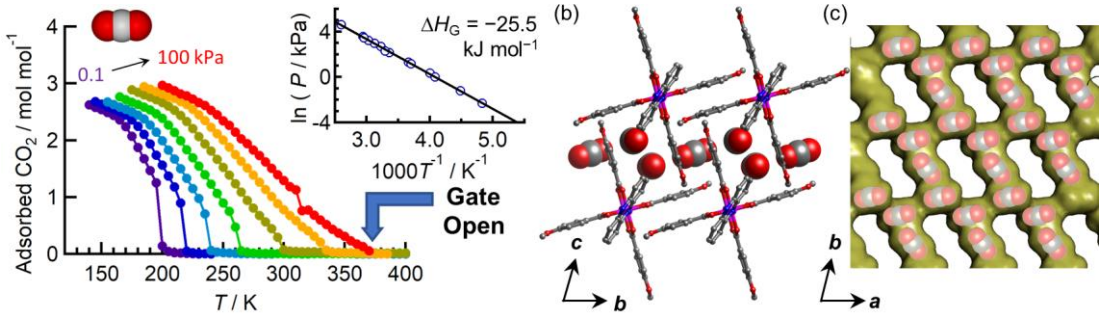

Fig. 1 (a) CO_2 adsorption isobar. (b) Structure of **1**⊃**CO₂**. (c) Connolly surface of micropore for **1**⊃**CO₂**.

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