

Gated CO₂ Adsorption Behavior in One-Dimensional Porous Coordination Polymers Based on Paddlewheel-Type Dimetal Complexes: What Determines Gate-Opening Temperatures?

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Gated CO₂ adsorption behavior was investigated in a series of one-dimensional chains based on paddlewheel diruthenium(II, II) complexes. A newly synthesized compound demonstrated gated behavior at a significantly higher temperature of 385 K under 100 kPa of CO₂ than that reported in previous research for this type of chain compounds, which usually occurred at a temperature range of 200–270 K. This specificity is ascribed to the higher topological dimensionality of pores for CO₂ accommodation that was observed in this chain.

Low-dimensional coordination polymers such as one-dimensional chains often exhibit gated guest sorption accompanying structural transition at a temperature (T_G) [1], which is associated with an external pressure induced by the guest (P_G), which is characteristic to the material and guest used. This phenomenon can be evaluated in the Clausius–Clapeyron (CC) relationship with the 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, the gated CO₂ adsorption behavior was investigated in a one-dimensional chain based on a benzoate-bridged paddlewheel diruthenium(II,II) complex with a phenazine (phz) linker, $[\text{Ru}_2(p\text{-MeOPhCO}_2)_4(\text{phz})]$ (**1**), where $p\text{-MeOPhCO}_2^-$ represents p -anisate [2].

The gas-adsorption isotherm and isobar of **1** for CO₂ were measured using an automatic volumetric adsorption apparatus connected to a cryostat system (Fig. 1a). Surprisingly, compound **1** underwent gate-opening/closing at a significantly higher T_{GC} of 385 K under $P_{\text{CO}_2} = 100$ kPa than those previously reported for such chain compounds, which usually appeared in the temperature range of 200–270 K [3]. CC analysis resulted in 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 ; compound **1** results in a much smaller $|\Delta S_G|$ in the series. In situ powder/single-crystal x-ray diffraction measurement under CO₂ revealed the crystal structure of the CO₂-accommodated phase (**1**⊃CO₂, Fig. 1b). Only compound **1** produced a CO₂-accessible two-dimensional topological pore in its CO₂-adsorbed phase of **1**⊃CO₂ (Fig. 1c). In contrast, the others reported previously produced one-dimensional or discrete topological pores for CO₂ accommodation.

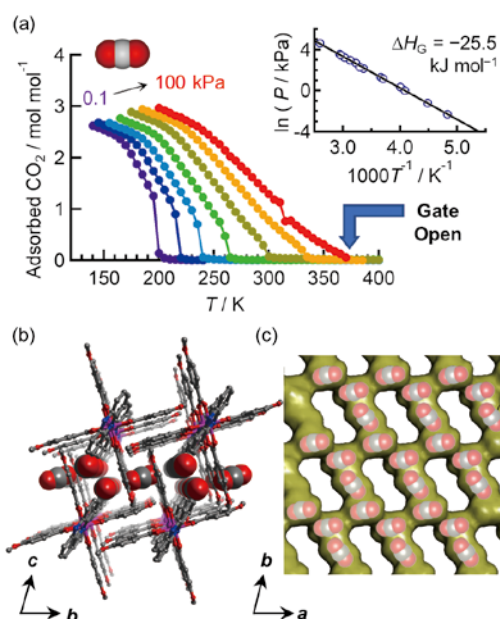


Fig. 1(a) CO₂ adsorption isobars for **1** at several CO₂ pressures measured upon cooling. (inset) Log-scale plots of CO₂ pressure versus the inverse of the gate-opening temperature (Clausius–Clapeyron analyses). (b) Views of the crystal structure of **1**⊃CO₂ along a -axis. (c) Connolly surface representation of micropores (probe radius: 1.4 Å) with CO₂ adsorption sites for **1**⊃CO₂.

These findings strongly reflect the degree of freedom of CO₂ molecules in pores, which is related to ΔS_G .

References

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