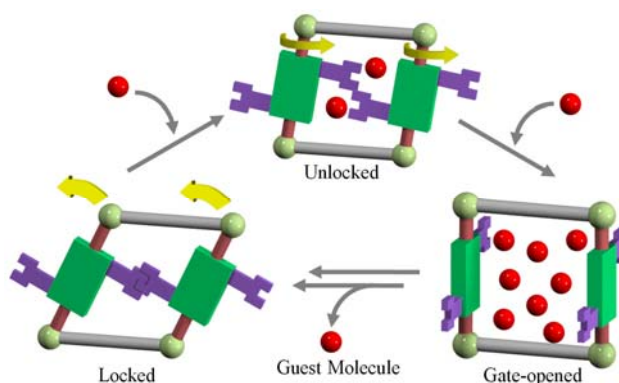


# A Pillared-Layer Coordination Polymer with a Rotatable Pillar acting as a Molecular Gate for Guest Molecules

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The design of pore properties utilizing flexible motifs and functional groups is of importance to obtain porous coordination polymers (PCPs) with desirable functions. We have prepared a 3D pillared-layer coordination polymer,  $\{[\text{Cd}_2(\text{pzdc})_2\text{L}(\text{H}_2\text{O})_2] \cdot 5(\text{H}_2\text{O}) \cdot (\text{CH}_3\text{CH}_2\text{OH})\}_n$  (**1**; pzdc = 2,3-pyrazinedicarboxylic acid; **L** = 2,5-bis(2-hydroxyethoxy)-1,4-bis(4-pyridyl)benzene) showing i) a rotatable pillar bearing ethylene glycol side chains acting as a molecular gate with locking/unlocking interactions triggered by guest inclusion between the side chains, ii) framework flexibility with slippage of the layers and iii) coordinatively unsaturated metal centers (UMCs) as guest accessible sites through the removal of the water coligands. The framework clearly shows reversible single-crystal-to-single-crystal transformations in response to the removal and rebinding of guest molecules, the observation of these processes has provided fundamental clues to the understanding of the sorption profiles. The X-ray structures indicate that the 3D host framework is retained during the transformations, involving mainly rotation of the pillars and slippage of the layers. The structure of dried form **2**,  $[\text{Cd}_2(\text{pzdc})_2\text{L}]_n$ , has no void volume and no water coligands. Interestingly, the adsorption isotherm of water for **2** at 298 K exhibits three distinct steps coinciding with the framework functions. Compound **2** favors the uptake of  $\text{CO}_2$  (195 K) over  $\text{N}_2$  (77 K) and  $\text{O}_2$  (77 K). Above all, we report on a molecular gate with a rotational module exhibiting a locking/unlocking system which accounts for gate-opening type sorption profiles.



Design of pore space via the introduction of a rotational module as a molecular gate with locking/unlocking interactions triggered by guest inclusion.