A spin-crossover framework endowed with pore-adjustable behavior by slow structural dynamics

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Host-guest interactions play critical roles in achieving switchable structures and functionalities in porous materials, but design and control remain challenging. Here, we report a two-dimensional porous magnetic compound, [FeII(prentrz)₂PdII(CN)₄] (prentrz = (1Ε,2Ε)−3-phenyl-N-(4H-1,2,4-triazol-4-yl)prop-2-en-1-imine), which exhibits an atypical pore transformation that directly entangles with a spin state transition in response to water adsorption. In this material, the adsorption-induced, non-uniform pedal motion of the axial prentrz ligands and the crumpling/unfolding of the layer structure actuate a reversible narrow quasi-discrete pore (nqp) to large channel-type pore (lcp) change that leads to a pore rearrangement associated with simultaneous pore opening and closing. The unusual pore transformation results in programmable adsorption in which the lcp structure type must be achieved first by the long-time exposure of the nqp structure type in a steam-saturated atmosphere to accomplish the gate-opening adsorption. The structural transformation is accompanied by a variation in the spin-crossover (SCO) property of FeII, i.e., two-step SCO with a large plateau for the lcp phase and two-step SCO with no plateau for the nqp phase. The unusual adsorption-induced pore rearrangement and the related SCO property offer a way to design and control the pore structure and physical properties of dynamic frameworks.

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The development of flexible metal-organic frameworks (MOFs) or soft porous crystals (SPCs) whose porous structures can be reversibly altered in response to the sorption of guest molecules has attracted burgeoning attentions\(^3\). Such adaptive structural transformability, usually ascribed to the interplay between the guest molecules and flexible host frameworks, is associated with advanced properties in the field of gas separation, sensing, and magnetic switching\(^6\)-\(^10\). In the past decades, many porous crystals that demonstrate guest-controllable porous expansion/contraction have been reported\(^11\)-\(^26\). Two remarkable compounds are \([Cu(aip)\{(H_2O)\}_{n}(solvent)\] and \([Al(OH)_3(solvent)\]{(TzDB)\}\], \(aip = 5\)-azidoisophthalate, \(TzDB = 4,4'-(1,2,4,5\)-tetrazine-3,6-diyl)dibenzoate), where the porous structure can be transformed by chemical reactions between host framework and guests, therefore exhibit intriguing self-accelerating absorption and domino-type porous transformation, respectively\(^27\)-\(^29\). These results encourage the further exploration of superior flexible MOFs whose porous structure can be reformed by unusual host-guest interactions. In general, MOFs composed of conformation-variable ligands are susceptible to the chemical environmental variations induced by guest adsorption\(^8\),\(^17\),\(^27\),\(^29\) particularly when the local rotation or reorientation of ligands can be propagated in the global structure through cooperative motions of the framework. Such flexible features can be enhanced in two-dimensional (2D) framework materials as layer architectures that are assembled further via weak inter-layer intermolecular interactions possess inherent structural ductility\(^30\),\(^33\).

Structural transformations may affect the electronic configuration of magnetic centers, leading to switchable magnetic properties. The adsorption-responsive magnetic functions of SPCs broaden the prospect of applications and provide a new way to explore the mechanism of host-guest interactions through coupling effects\(^34\)-\(^36\). A CO\(_2\)-induced paramagnetic–to–ferrimagnetic variation was recently demonstrated in a porous compound, \([Ru_6(F_2PhCO_2)_{14}](TCNQ(OEt))_2\)·3DMC (TCNQ(OEt) = 2,5-die-thoxy-7,8,8-tetracyanoquinodimethane; F\(_2\)PhCO\(_2\) = 2,4,6-trifluorobenzoate; DCM = dichloromethane), as a result of electron transfer and a structural transition involved in the adsorption of CO\(_2\) molecules\(^37\). In addition to radical molecules, the spin-crossover (SCO) compounds of 3\(d^1\)–3\(d^2\) metal ions, whose spin states can be interconverted between high-spin (HS) and low-spin (LS) states in response to external stimuli, are also susceptible to the structural changes in the coordination geometry of metal centers\(^38\)-\(^41\). Therefore, the intercorrelation between the guests and SCO frameworks potentially leads to intriguing magnetic switching that directly entangles the structural transformations involved in guest adsorption.

In this work, a 2D SCO compound, \([Fe^{II}(prentrz)_2Pd^{II}(CN)_4]_x\) (1), which possesses a Hofmann-type structure that usually has a porous structure\(^42\)-\(^47\), is designed and synthesized using a conformationally flexible organic molecule, prentrz, as an axial ligand. The difference from typical SPCs, whose pores expand with pressure increases (Fig. 1)\(^1\),\(^2\), is the unusual pore rearrangement accompanied by simultaneous pore opening and closing caused by the non-uniform pedal motion of the prentz ligand around its N–N single bond and global crumpling/ unfolding of the layer structure in response to the adsorption of guest water molecules. The atypical pore transformation is accompanied by a distinct adsorption process in which to be activated first by long-time exposure in saturated steam to accomplish the slow dynamics between nqp and lcp structures. The direct variant multistep spin transition of the nqp and lcp phases is a result of the flexible framework and the host-guest interactions.

Results

Crystal structures of the lcp and nqp phases. The pristine single crystals were synthesized by the slow diffusion of a CH\(_3\)OH solution of prentz and K\(_2\)[Pd(CN)\(_4\)] into a H\(_2\)O solution of FeSO\(_4\)·7H\(_2\)O. Crystals of the lcp phase I·9/2H\(_2\)O were obtained by stabilizing the as-grown crystals that contained H\(_2\)O and MeOH mixture guests in air for 3 h (Supplementary Fig. 1). Single-crystal X-ray diffraction (SC-XRD) analysis showed that the compound crystallizes in the triclinic \(P\)1 space group (Supplementary Table 1). In the crystal, Fe\(^{II}\) ions are equatorially coordinated by four N atoms from four [Pd(CN)\(_4\)]\(^{2-}\) ligands that bridge the metal centers in a 2D network with two axial positions occupied by two prentrz ligands (Fig. 2 and Supplementary Fig. 2). The asymmetric unit of the framework in lcp phase contains two crystallographically independent Fe\(^{II}\) ions lying in the inversion centers, two prentz ligands with different conformations (conformer 1 for Fe1 and conformer 2 for Fe2), and one [Pd(CN)\(_4\)]\(^{2-}\) bridging ligand (Supplementary Fig. 3a). The 2D coordination networks were assembled further via intermolecular interactions into a 3D porous structure with channel pores (13.2 × 4.4 Å\(^2\)) extending along the crystallographic c-axis (Fig. 2c and Supplementary Fig. 4, regardless of the vander Waals radii\(^48\),\(^49\)). According to SC-XRD, elemental and thermogravimetric analyses, the pores accommodate 9/2 H\(_2\)O molecules per Fe\(^{II}\) atom (Supplementary Fig. 5a). The porous nature of framework was supported by a CO\(_2\)-adsorption measurement (Supplementary Fig. 6).

The crystals of the nqp phase I·4/3H\(_2\)O were obtained by heating I·9/2H\(_2\)O to 433 K for 48 h under vacuum and cooling in air to rehydration. Upon water desorption and re-adsorption, the structural transformation can be fully characterized at the atomic level by SC-XRD owing to the single-crystal-to-single-crystal nature. In this hydrous crystal, the basic structural features are retained, and the \(P\)1 space group is the same as that of the I·9/2H\(_2\)O, while the cell parameters and direction undergo significant changes (Fig. 2d and Supplementary Table 2). Accordingly, one and a half Fe\(^{II}\) ions (Fe1 lies in the inversion center), three prentz ligands (conformer 1 for Fe1 and conformers 2 and 2’ for Fe2), and one and a half [Pd(CN)\(_4\)]\(^{2-}\) ligands are found in the asymmetric unit of the framework (Supplementary Fig. 3b). The most significant structural changes occur in the prentz ligands, which perform pedal rotation and reorientation upon water desorption (Fig. 2d)\(^30\). The directional shift of the axial ligands induces a large contraction in the pore size that converts the large channel pores in I·9/2H\(_2\)O to the narrow quasi-discrete pores in I·4/3H\(_2\)O, with a decrease in interlayer distance from 14.618(3) Å
to 13.296(5) Å (Supplementary Fig. 7). The narrow pores of this hydrous crystal accommodate 4/3 $\text{H}_2\text{O}$ molecules per Fe$^{II}$ atom according to the SC-XRD, elemental and thermogravimetric analyses (referred to 1·4/3$\text{H}_2\text{O}$, Supplementary Fig. 5b). Although Powder X-ray diffraction (PXRD) experiments revealed that in situ generated 1 by heating 1·9/2$\text{H}_2\text{O}$ at 433 K for 48 h under vacuum possessed the similar contracted structure as that of nqp phase 1·4/3$\text{H}_2\text{O}$, 1 and 1·4/3$\text{H}_2\text{O}$ were not exactly the same phases (Supplementary Fig. 8). However, an attempt to obtain the crystal structure of completely dehydrated crystal of 1 failed because of the poor diffraction. The phase purity of lcp phase 1·9/2$\text{H}_2\text{O}$ and nqp phase 1·4/3$\text{H}_2\text{O}$ was confirmed by Rietveld refinement pattern (Supplementary Fig. 9).

During the dehydration process, the axial prentrz ligands undergo different molecular motions and the concomitant molecular reorientations lead to a rearrangement in the pore configuration, i.e., the channel state of the ABABAB mode in the lcp phase is converted to the A’A’B’A’A’B’ mode in the nqp phase (A: open channel; B: closed channel). Although numerous flexible MOFs manifesting structural transformations in response to guest adsorption/desorption have been reported, such a guest adsorption-actuated statistical rearrangement of the pore configuration accompanied by simultaneous opening and closing of pores is very uncommon in porous materials.

**Water adsorption isotherms.** The adsorption properties of this material were examined by performing vapor adsorption/desorption isotherms measurements under different activating conditions. The 1·9/2$\text{H}_2\text{O}$ was activated in situ under vacuum at 433 K for 48 h to ensure that the water molecules were completely removed. After that, the water adsorption isotherm started with a flat plateau in $P/P_0 = 0.08$ range. The adsorption behavior may indicate structural transformation from closed framework to nqp framework, corresponding to the transition from 1 to 1·4/3$\text{H}_2\text{O}$ (Fig. 3a, up). The uptake saturated at $P/P_0 = 0.89$, corresponding to the adsorption of ~1.4 $\text{H}_2\text{O}$ per Fe$^{II}$. This result is consistent with the 4/3 $\text{H}_2\text{O}$ molecules identified by SC-XRD of 1·4/3$\text{H}_2\text{O}$, suggesting no nqp-to-lcp gate-opening transition occurred in this sample. However, water adsorption was enhanced significantly when the above anhydrous 1 or 1·4/3$\text{H}_2\text{O}$ was left in the steam atmosphere ($P/P_0 = 0.9$) for 4 days and was then activated under vacuum at 303 K for 6 h (or directly activated 1·9/2$\text{H}_2\text{O}$ at 298 K for 6 h). As shown in Fig. 3a (middle), the uptake instantly reached ~1.1 $\text{H}_2\text{O}$ per Fe$^{II}$ at $P/P_0 = 0.02$ and then increased slightly to 1.78 $\text{H}_2\text{O}$ per Fe$^{II}$ at $P/P_0 = 0.64$, after which the adsorption suddenly reached 4.5 $\text{H}_2\text{O}$ per Fe$^{II}$ at $P/P_0 = 0.86$. The absorption of 4.5 $\text{H}_2\text{O}$ per Fe$^{II}$ at $P/P_0 = 0.86$ is consistent with the single-crystal structural analyses of 1·9/2$\text{H}_2\text{O}$, indicating the gate-opening transition of this sample.

The activation-method dependent water adsorption was verified by a continuous adsorption/desorption-cycles measurement. As shown in Fig. 3b, when the sample prepared from a long-time heating (14 h) at 433 K under vacuum condition was placed in a steam atmosphere with $P/P_0 = 0.9$, it underwent two-step water adsorption: a rapid partially water adsorption of ~1.7 $\text{H}_2\text{O}$ per Fe$^{II}$, and later a very slow water adsorption (97 h) of ~4.5 $\text{H}_2\text{O}$ per Fe$^{II}$ that reflected the 1·4/3$\text{H}_2\text{O}$-to-1·9/2$\text{H}_2\text{O}$ gate-
opening structural change. When the regained sample of 1.9/2H₂O was not dehydrated thoroughly under a mild condition (303 K under vacuum for 10 h) with ~0.2–0.5 H₂O per FeII retained, the sample manifested an abrupt one-step water adsorption (10 min) to ~4.5 H₂O per FeII in a steam atmosphere with P/P₀ = 0.9. The distinct adsorption properties suggest that the samples prepared from different activating methods undergo different adsorption processes and imply that a small amount of lattice water molecules in structure have a very large impact on the flexibility of the whole framework. The two-step water adsorption was confirmed by another sample activated at 400 K under vacuum for 22 h (Supplementary Fig. 10). Notably, the PXRD pattern after two isothermal vapor ad/de-sorption or the adsorption-desorption-cycles measurement revealed that the
Fig. 3 Water adsorption isotherms and corresponding structural transformations probed by PXRD. a Isothermal vapor adsorption (solid red) and desorption (open red) of the sample activated at 433 K under vacuum for 48 h (up), isothermal vapor adsorption (solid blue) and desorption (open blue) of the sample activated at 298 K under vacuum (middle) and isothermal vapor adsorption (solid green) and desorption (open green) of the physical mixture (nqp and lcp phases) at 298 K under vacuum (down). b The continuous water adsorption-desorption cycles in different activated conditions. The abnormal drop of “Uptake” line marked by star at 1200 min is ascribed to the change of heating source (Furnace and water bath). c PXRD patterns upon water adsorption and desorption. 19/2H2O loses water rapidly upon heating (323 K), which leads to a partially dehydrated sample that can return to the lcp phase immediately by spraying with a water mist. Such rapid water adsorption of the partially dehydrated sample was performed two times to confirm the phenomenon. However, the completely dehydrated sample 1 prepared from long-time heating (433 K) under vacuum can rehydrate to nqp phase 1·4/3H2O within 60 min, while cannot recover to lcp phase smoothly upon water adsorption. In the measured sample, it took 4 days after leaving the 1 or 1·4/3H2O in saturated steam. The PXRD patterns of the physical mixture of two phases did not show any significant change after spraying the water mist for 60 min. The gray, blue and red peaks denote the character peaks of structures of partially dehydrated, lcp and nqp framework, respectively.

![Graph](image)

Fig. 4 Temperature dependence of the $\chi_T$ curves of lcp phase 1·9/2H2O and nqp phase 1·4/3H2O upon heating and cooling. The two-step SCO with a large plateau of lcp phase 1·9/2H2O (a) and a two-step SCO without plateau of nqp phase 1·4/3H2O (b).

crystallinity and framework of nqp and lcp structure type samples can both be revived by rehydration, and further reflected the different structural flexibilities between anhydrous 1, nqp phase 1·4/3H2O and lcp phase 1·9/2H2O (Supplementary Fig. 11).

Structural transformation investigated by powder X-ray diffraction (PXRD) and micro-Raman spectroscopy. To understand the different water adsorption properties, in situ PXRD was performed to probe the structural differences in the samples prepared from different activating methods. When the crystal sample of 1·9/2H2O in lcp phase was subjected to mild activation, i.e., thermal treatment (323 K) or exposed to vacuum, new peaks appeared in the higher-angle region within 1 min and increased gradually with time, indicating the contraction of partially dehydrated framework (Fig. 3c) and Supplementary Figs. 5, 12–14. The lcp phase could be recovered immediately by spraying water mist on the partially dehydrated samples. The desorption-adsorption process had been repeated two times to confirm the rapid water adsorption of the sample (Fig. 3c and Supplementary Fig. 15). The complete lcp-to-nqp structural transition of all samples was unexpectedly difficult, since the characteristic peaks of partially dehydrated framework remained even after the same was heated at 433 K under vacuum for 18 h (Supplementary Fig. 16). Therefore, the sample was heated to 433 K under vacuum for 48 h in the third cycle to obtain completely dehydrated sample of 1. However, the resulting anhydrous 1 could rehydrate to nqp phase 1·4/3H2O within 60 min, while cannot recover to lcp phase smoothly upon water desorption after being sprayed with water mist as in the former two cycles. Similar to the water-adsorption measurements, the backward nqp-to-lcp structural transition could only be achieved by leaving the nqp sample in saturated steam for a long time (~four days in the measured sample, see Fig. 3c and Supplementary Figs. 17 and 18). These results suggest that the lcp structural characteristics of partially dehydrated framework can persist in the sample prepared under mild activating conditions, and such flexible framework plays a vital role in the doubled water adsorption24,51–54.

Further experiments confirmed that the partially dehydrated samples rather than a physical mixture of two pure phases because the PXRD patterns of a physical mixture of the lcp phase 1·9/2H2O and nqp phase 1·4/3H2O did not show any significant change after spraying the water mist (Fig. 3c).

In order to further verify that the activation-method dependent adsorption properties are related to structural difference between nqp and partially dehydrated frameworks, micro-Raman spectra experiments (spot diameter ~2 μm) were performed on single crystals35,36. As shown in Supplementary Fig. 19, the Raman spectra of lcp and nqp phases present delicate difference in two regions: the bands around 1170 cm$^{-1}$ (C–C stretch modes of prentz ligands) and 1140 cm$^{-1}$ (CH-bending of prentz ligands)57. In the nqp single crystal, the bands at around 1170 and 1140 cm$^{-1}$ persisted up to 3 days in saturated steam, and then converted to the characteristic bands of lcp structure type. For comparison, the bands at around 1140 cm$^{-1}$ remained unchanged as the lcp single crystal 1·9/2H2O under mild activation (a constant N2 gas), suggesting the lcp structural characteristics of partially dehydrated framework. The Raman spectrum of partially dehydrated single crystal can change to that of lcp struture type within 10 min in a humidity of 80%. The distinct responses of nqp and partially dehydrated single crystals in the micro-Raman spectra verify the structural dependent water adsorption property in this material.

SCO properties of the samples in different phases. SCO properties of the magnetic centers in the 2D Hofmann structure are usually sensitive to the geometric variations of the coordination sphere and guest variation38. Therefore, we measured the temperature-dependent magnetic susceptibilities of 1·9/2H2O, 1·4/3H2O, and partially dehydrated samples with different heating time to investigate magnetic switchings corresponding to water adsorption and desorption (Fig. 4 and Supplementary Fig. 22). Figure 4a shows the $\chi_M$ versus $T$ plot of I·9/2H2O, in
which the $\chi_M T$ values are 3.48–3.57 cm$^3$ K mol$^{-1}$ at 210 – 250 K and 0.16 – 0.17 cm$^3$ K mol$^{-1}$ at 50 – 65 K, corresponding to the full HS state ($\gamma_{HS} = 1$) and full LS state ($\gamma_{HS} = 0$), respectively. During the SCO process, a stepwise spin transition with a wide intermediate plateau (74 K) is observed over a temperature range of 118 – 192 K. The $\chi_M T$ values of 1.72 – 1.89 cm$^3$ K mol$^{-1}$ at this intermediate temperature range indicate that the sample is in the HS$_0$L$_{0.5}$S$_{0.5}$ state. The two-step spin transition is accompanied by substantial thermal hysteresis loops of ca. 9 K ($T_{C41} = 196$ K, $T_{C51} = 205$ K) and 15 K ($T_{C21} = 166$ K, $T_{C22} = 181$ K). Such a hysteretic spin transition is usually caused by strong cooperative interactions among the magnetic centers. The shifts in the Fe–N bond lengths confirm the spin transition of Fe$^{II}$ ions in 1/9/2H$_2$O. The average Fe–N bond lengths are 2.167(5) Å at 250 K and 1.964(5) Å at 150 K, respectively, indicating that a complete HS-LS transition of Fe1 occurs in the first step spin transition upon cooling (Supplementary Figs. 23–25 and Table 3). The average Fe2–N bond length shortens from 2.160(4) Å at 150 K to 1.970(4) Å at 85 K, showing that Fe2 undergoes a complete spin transition at the lower temperature range. Therefore, the two-step spin transition of 1/9/2H$_2$O is accounted for by the two metal centers in the asymmetric unit, respectively. The $\chi_M T$ values of 1/4/3H$_2$O are the same as those of 1/9/2H$_2$O over the temperature range of 200 – 250 K, suggesting a full HS state ($\gamma_{HS} = 1$) of 1/4/3H$_2$O at high-temperature range (Fig. 4b). Upon cooling, the $\chi_M T$ value shows a slight decrease until 160 K. It then decreases abruptly and finally reaches 1.28 cm$^3$ K mol$^{-1}$ at 50 K. An obscure inflection point at 147 K indicates that the 1/4/3H$_2$O sample undergoes a two-step but incomplete spin transition (Supplementary Fig. 26). The average Fe1–N bond lengths of 2.134(9) Å at 250 K and 1.949(6) Å at 100 K (Supplementary Table 4), respectively, suggest that Fe1 ion in 1/4/3H$_2$O undergoes a complete SCO. While for Fe2 ion, an incomplete SCO is concluded as the average Fe2–N bond lengths shorten from 2.144(10) Å at 250 K to 2.062(7) Å at 100 K. The $\chi_M T$ value shows unchange at 50 K with different scan rates (10, 5, 2, and 1 K min$^{-1}$), suggesting the incomplete spin transition of Fe2 was not kinetically trapped (Supplementary Fig. 27). The water adsorption-induced SCO variations can be attributed to the geometric changes in the coordination spheres of Fe$^{II}$ ions and the shifts in the intermolecular interactions, which in turn affect the electron states of the coordinated ligands. For the SCO properties of partially dehydrated samples, a hysteretic spin transition at 133 – 147 K emerged when 1/9/2H$_2$O was partially desolvated. Upon further water molecules losing, a series of variations in the total SCO properties were accompanied by the intermediate hysteresis loop increasing, resulting in the three- and four-step SCO. Though the SCO variation of partially dehydrated samples cannot be ruled out as the linear combination of dehydrated and non-dehydrated particles, the partially dehydrated samples with relatively minimal water molecules showed the incomplete SCO with the same $T_{C1/2}$ as that of nqp phase 1/4/3H$_2$O, suggesting that the host-guest interaction affecting SCO behavior is determined by the amount of water molecules and dynamic framework. Bonds. Moreover, the Fe–N coordination bonds of prentrz in II, III, IV, and V undergo distinct shifts in their bond direction during water adsorption (Supplementary Fig. 28). As a comprehensive result, ligands II and IV exhibit the most remarkable reorientations in their principal molecular directions, while those of ligands I, III, V, and VI show minor changes. The non-uniform direction shifts of the axial linear ligands repartition the lattice structure (Fig. 5b). Remarkably, the large reorientation of ligand II during water adsorption enlarges channel A’ and closes channel A2. The reorientation of ligand IV opens channel B2 and closes the narrow channel A3 in the nqp phase. Therefore, the A’A’A’A’A’ array of the pore configuration in the nqp phase transforms to the ABABAB mode in the lcp phases (Fig. 5c and Supplementary Fig. 29). During water adsorption, the 2D networks connected by Fe–N coordination bonds also demonstrate remarkable structural flexibility that manifest as a crumpling/unfolding of the layer structure (Fig. 5d and Supplementary Fig. 30). The fluctuations of the layer structure assist in the reorientation of the coordination bonds of the axial ligands. The 3D framework of this compound is secured by the π–π interactions between the prentrz ligands in the adjacent layers (Supplementary Fig. 31). The substantial interlayer interactions prevent the large relative displacement of the layer structures. Consequently, the adsorption-induced structural transformation manifests a reorientation of axial ligands accompanied by a minor sliding motion of the coordination layers (Supplementary Fig. 32). The lattice structure repartitioned by the inconstant reorientation of axial ligands in this soft porous compound is different from the typical adsorption-induced structural transformations, such as the lattice displacement or hinging motion of organic ligands around the metal nodes (Fig. 1), therefore, leading to an unusual pore rearrangement in this compound, rather than only the framework breathing in typical flexible MOF$_{4,1,2,3,7,21,37}$. During the pore rearrangement from the nqp phase to the lcp phase upon adsorption, the water molecules residing in channels A1 and A3 of 1/4/3H$_2$O need to be evacuated to close the pores (Fig. 5c and Supplementary Movie 1). Such simultaneous pore opening and closing increases the energy barrier from the nqp phase to the lcp phase. This is particular in the present case because the excluded water molecules exhibit strong hydrogen bonds with the N atoms of the framework with O–N distances of 2.754(2) Å and 2.908(3) Å (250 K, Fig. 5c and Supplementary Fig. 31 and Table 5). Hence, the onset of nqp–to–lcp structural transformation is extremely time consuming. However, once the lcp domains are generated, the high energy barrier should be reduced significantly by the interfacial effect between the expanded lcp and contracted nqp phases. The interfacial interactions are effectively transmitted by the fluctuations of the Fe–N (≡C–Pd) coordination bonds, slippage of the layer structures, and π–π interactions between the prentrz ligands in different layers (Supplementary Fig. 33 and Supplementary Movie 1). Therefore, smooth gate opening-related water adsorption can be realized in self-accelerating structural transformation. Density functional theory calculations were performed to investigate the energy variations upon water adsorption and support the experimental results (Fig. 6 and Supplementary Fig. 34). The adsorption structures were optimized on the unit cells of the nqp and lcp phases. Owing to the different asymmetric units of the nqp and lcp phases, the number of atoms (2nqp = 3lcp) was balanced to make direct energetic comparisons (Supplementary Fig. 35). For a completely desolvated sample, the nqp phase is energetically preferred compared to the lcp phase, and it can be stabilized further by 173 kcal mol$^{-1}$ when four water molecules are loaded in the unit cell. This calculation is
Fig. 5 Detailed structural transformation upon water adsorption. a Conformations of flexible prentz ligands in the lcp (1·9/2H₂O) and nqp (1·4/3H₂O) phases. b Local pedal rotations of prentz molecules and the directional shifts of axial Fe−N coordination bonds. The ligands III, IV, and V perform in-plane pedal rotations around their N−N single bonds, and ligands II, III, IV, and V undergo distinct directional shifts with angles of 12.9°, 22.1°, 37.8°, and 18.0°, respectively. The pedal rotations and the reorientations of Fe−N bonds have opposite influences on the principal directions of axial ligands. Consequently, ligands II and IV show the most significant shifts in their molecular orientations (as dashed lines indicated). c The directional shift of ligand II upon adsorption expands channel A₁' and closes channel A₂', while the directional shift of ligand IV opens channel B₁' and closes channel A₃'. Accordingly, the four water molecules accommodated in pore A₂' and A₃' of nqp phase must be evacuated to facilitate the nqp-to-lcp lattice transformation. d The coordination layer demonstrated a remarkable crumpling/unfolding motion to assist the reorientation of the Fe−N coordination bonds. The structures of lcp (1·9/2H₂O) and nqp (1·4/3H₂O) phases are drawn in blue and red, respectively.

Fig. 6 Energy diagram of water adsorption. The adsorption-induced nqp-to-lcp lattice transformation experiences simultaneous pore opening and closing (nqp-4w to nqp-2w state) with a large energy requirement of 158 kcal mol⁻¹, after which nqp-2w-L/R can be converted to lcp-2w to reduce the lattice energy.
consistent with the experimental observation that 4/3 H$_2$O per Fe$^{II}$ ion can be adsorbed instantly at low pressure. In the nqp–to–lcpc process, upon further water adsorption, the sample experiences simultaneous pore opening and closing, where two water molecules in the channel need to be evacuated to accomplish the pore rearrangement. The nqp-4w–to–nqp-2w process is energy consuming with an entropy gain. The uphill adsorption of this compound plays an important role in the activation-method dependent water adsorption process. The energy barrier in the nqp-4w–to–nqp-2w process should play an important role in the activation-method dependent water adsorption of this compound.

In conclusion, a 2D soft magnetic porous single-crystal compound was prepared utilizing the conformational flexibility of the pretrz ligand and the fluctuation of the 2D coordination network. The water adsorption-induced, non-uniform pedal rotations of the axial ligands accompanied with crumpling/unfolding of the 2D layer structure repartition the lattice structure, which manifests as framework breathing with a rearrangement of the pore configuration. The simultaneous pore opening and closing involved in the pore rearrangement leads to slow nqp–lcpc dynamics, where nqp phase need to long-time exposure in saturated steam to accomplish the nqp–to–lcpc gate-opening adsorption. Moreover, the structural transformation of the magnetic framework shifts the SCO properties of the Fe$^{II}$ magnetic centers. This study presents a adsorption-related pore transformation accompanied by activation-method dependent adsorption. Such an exotic property may be used in materials for gas adsorption, actuation, and sensing.

**Methods**

**Fe$^{II}$(pretrz)$_2$Pd$^{II}$(CN)$_4$·9/2H$_2$O (1·9/2H$_2$O).** An aqueous solution (3 mL) containing Fe$_2$(SO$_4$)$_3$3H$_2$O (0.05 mmol, 13.90 mg) and ascorbic acid (2.0 mg) was prepared by heating the sample of 1·9/2H$_2$O at 323 K for different times (~2 min for 6 h). The adsorption isotherm measurements were then performed under the second measurement, the sample was left in the chamber at P$_0$ = 0.9 mbar, for 6 h. The adsorption isotherm of the setup was described in previous literatures65.

**Sorption experiments.** The vapor adsorption isotherms were recorded on a Rigaku Oxford Diffraction XtaLAB PRO diffractometer equipped with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å). The data of 1/9·2H$_2$O were collected with one sample at 250, 150 and 85 K successively. The data of 1/4·3H$_2$O was collected at 250 K.

**Powder X-ray diffraction (PXRD).** The variable- and room-temperature PXRD data were recorded on a PANalytical diffractometer with Cu Ka radiation equipped with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å). The data of 1/9·2H$_2$O were collected with one sample at 250, 150 and 85 K successively. The data of 1/4·3H$_2$O was collected at 250 K.

**Micro-Raman spectroscopy.** The micro-Raman spectra experiments were performed on a Renishaw InVia confocal Raman spectrometer equipped with a He-Cd laser (442 nm, 5 mW), and nqp phase 1/9·2H$_2$O under a nitrogen flow for 30 min.
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Author contributions
J.-P.X., Z.-S.Y., and J.T. designed the study and wrote the manuscript. J.-P.X. synthesized the materials and performed the experimental measurements. Y.H., B.Z., and J.X. performed the DFT calculations. Z.-K.L. assisted in the magnetic measurements. Z.-S.Y. and J.T. supervised the research. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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