Gas-responsive porous magnet distinguishes the electron spin of molecular oxygen

Wataru Kosaka,1,2 Zhaoyuan Liu2, Jun Zhang2, Yohei Sato3, Akihiro Hori4, Ryotaro Matsuda4, Susumu Kitagawa3 & Hitoshi Miyasaka1,2

Gas-sensing materials are becoming increasingly important in our society, requiring high sensitivity to differentiate similar gases like N₂ and O₂. For the design of such materials, the driving force of electronic host-guest interaction or host-framework changes during the sorption process has commonly been considered necessary; however, this work demonstrates the use of the magnetic characteristics intrinsic to the guest molecules for distinguishing between diamagnetic N₂ and CO₂ gases from paramagnetic O₂ gas. While the uptake of N₂ and CO₂ leads to an increase in Tc through ferrimagnetic behavior, the uptake of O₂ results in an O₂ pressure-dependent continuous phase change from a ferrimagnet to an antiferromagnet, eventually leading to a novel ferrimagnet with aligned O₂ spins following application of a magnetic field. This chameleonic material, the first with switchable magnetism that can discriminate between similarly sized N₂ and O₂ gases, provides wide scope for new gas-responsive porous magnets.
In this Internet of Things age, it is essential to control how information is processed when only slight differences within the data exist, leading to the notion of sensing. The development of highly sensitive devices for ubiquitous gas and innocuous small molecule sensing is one of the major challenges in the field of materials science. A magnetic change can be beneficial for providing a responsive signal in such a sensing device, and would be advantageous for gas detection owing to contactless operation and detection independent of the sample shape of the host framework. Further, devices that respond quickly with easy operability and readability for ON/OFF updates are desirable; the availability of spin freedom in host-guest interactions for gas sensing is an innovative technique that could make this possible. For instance, distinguishing between nitrogen ($N_2$) and oxygen ($O_2$) gases is exceedingly difficult because of their similar size and boiling points. Detecting a magnetic change induced by the intrinsic magnetic nature of these gases (i.e., diamagnetic $N_2$ and paramagnetic $O_2$) would represent a major breakthrough in gas-sensing technologies. For this purpose, however, a drastic phase change in magnetism, not just small modifications of magnetic properties, is necessary. The gas-induced magnetic response has also been investigated using Fe$^{II}$ spin-crossover systems; however, magnetic discrimination between $O_2$ and $N_2$ has never been observed. Meanwhile, drastic magnetic changes induced by solvation/desolvation have prompted lively discussions on magnetic sponges and spin-crossover systems. This has also been investigated using Fe$^{II}$ spin-crossover systems; however, magnetic discrimination between $O_2$ and $N_2$ has never been observed. Altough, magnetic discrimination between $O_2$ and $N_2$ has never been observed. This occurs independent of the applied field, indicating the onset of ferrimagnetic ordering (details of the comparison between the magnetic transition temperature $T_C$ (or $T_N$ for antiferromagnetic ordering) for this type of layered magnetic material should be strongly affected by intra-layer exchange interactions between the $[Ru_2]^{2+}$ units and TCNQ(MeO)$_2$ units in 1 remains unchanged (Supplementary Table 2, 3, Supplementary Note 1). Compound 1 becomes 1-solv when exposed to DCM/DCE vapor for 12 h at 300 K (Supplementary Fig. 2b), indicating a common magnetic sponge behavior (vide infra).

### Results

#### Crystal structure of the pristine framework.

To develop gas-responsive porous magnets, we chose a layered ferrimagnet, $[[Ru_2(3,5-F_2PhCO_2)_4]_2(TCNQ(MeO)_2)]_3(DCM)-1.5(DCE)$ (1-solv; $3,5-F_2PhCO_2 = 3,5$-difluorobenzoxa; TCNQ(MeO)$_2$ = 2,5-dimethoxy-7,8,8-tetracyanoquinodimethane; DCM = dichloromethane; DCE = 1,2-dichloroethane), obtained from an electron-donor (D)/acceptor (A) 2:1 assembly that involves an electron transfer, where the paddle-wheel-type $[Ru_2(3,5-F_2PhCO_2)_4]$ subunit (abbreviated as $[Ru_2]$) is D and TCNQ(MeO)$_2$ is A. Compound 1-solv crystallized in the triclinic space group $P-1$, where two different $[Ru_2]$ units and one TCNQ(MeO)$_2$ molecule, with respective inversion centers, were structurally isolated ($Z = 1$) with a charge assignment of $[-[Ru(II)_{II}^{II}]_{II}^{II}]^{-} + S_{A}$ (Fig. 1a,b, Supplementary Fig. 1a, Supplementary Table 1–3, Supplementary Note 1 and 2). The set of two $[Ru_2]$ units and TCNQ(MeO)$_2$ constructs a fishnet-like two-dimensional network lying on the (100) plane that stacks along the $a$-axis (Fig. 1a,b). The inter-layer distances defined by the vertical ($l_1$) and inter-unit translational ($l_2 = a -$ axis; Fig. 1b) distances between the planes are 9.78 Å and 10.65 Å, respectively (Supplementary Table 8), and the crystallization solvents (3(DCM)-1.5(DCE)) are located between the layers with a solvent accessible volume of 713 Å$^3$ (32% of total volume).

#### Crystal structure of the dried phase.

Compound 1-solv gradually releases the crystallization solvents upon increasing temperature, producing the solvent-free porous compound $[[Ru_2(3,5-F_2PhCO_2)_4]_2(TCNQ(MeO)_2)]_3$ (1), which is stable at temperatures up to 450 K with its crystallinity intact (Supplementary Fig. 2a). Similar to 1-solv, 1 crystallized in the triclinic $P-1$ space group ($Z = 1$, Fig. 1c,d, Supplementary Fig. 1b, Supplementary Table 1 –3, Supplementary Note 1 and 2). Although the fishnet-like network was preserved with a slightly shortened (relative to 1-solv) $l_1$ of 9.46 Å, with a lengthened $l_2$ of 10.84 Å ($\neq a$-axis; Fig. 1d), the structural features of the network are drastically altered from an almost flat form in 1-solv to a wavy form in 1 (Fig. 1c,d,e), resulting in a reduction of the void volume to 147 Å$^3$ (7.5% against total volume). Of note, the electronic state of [Ru$_2$] and TCNQ(MeO)$_2$ units in 1 remains unchanged (Supplementary Table 2, Supplementary Fig. 2a, Supplementary Note 3), indicating a common magnetic sponge behavior (vide infra).

#### Magnetic sponge behavior.

The spins of the $[Ru_2]^{II,II}(S = 1)$ and $[Ru_2]^{II,II}(S = 3/2)$ moieties interact antiferromagnetically with the radical spin of TCNQ(MeO)$_2$; over the layered network forming a ferrimagnetically ordered layer, which is followed by three-dimensional ferrimagnetic ordering with inter-layer ferromagnetic interactions. The magnetic transition temperature $T_C$ (or $T_N$ for antiferromagnetic ordering) for this type of layered magnetic material should be strongly affected by intra-layer exchange interactions between the $[Ru_2]^{II,II}+$ units and TCNQ(MeO)$_2$$^{\pm}$, as well as inter-layer dipole interactions, Figure 1f shows the temperature dependence of field-cooled dc magnetization (FCM) of 1-solv and 1 in a 1 kOe dc field ($H_d$). In both compounds, an abrupt increase in the FCM is observed near 80 K without a subsequent decrease at lower temperatures. This occurs independent of the applied fields, indicating the onset of ferrimagnetic ordering (details of the comparison between 1-solv and 1 are described in Supplementary Fig. 3 and Supplementary Note 3 and 4); however, their $T_C$ values differ (i.e., 83 K and 76 K for 1-solv and 1, respectively), as evaluated from remnant magnetization (RM) (inset of Fig. 1f) and ac susceptibility data (Supplementary Fig. 3b, e, Supplementary Note 3).

#### Gas sorption capability.

In addition to the magnetic sponge capabilities for crystallization solvents, 1 has the ability to adsorb gases such as $CO_2$, $N_2$, and $O_2$: the gas-adsorbed phase is defined as 1 $\supset$ Gas. Figure 2a shows their sorption isotherms (a log-scale plot is shown in Supplementary Fig. 4). For $N_2$, 1 has a non-porous nature at 77 K because of the slow diffusion of gaseous molecules into the void space; however, 1 acts as an adsorbent at 120 K, where the 1st gate-opening is observed at a pressure of 3.2 kPa, as found in other low-dimensional porous systems, and reaches an adsorption amount of 27 mL (stp) g$^{-1}$ (2.3 mol per formula unit) at 99 KPa. The CO$_2$ adsorption isotherm at 195 K shows a steep rise at relatively low pressures, where the adsorption amount is 102 mL (stp) g$^{-1}$ (8.7 mol per formula unit) at 99 kPa, even though a gate-opening modification should be involved. The $O_2$ adsorption isotherm at 90 K shows a stepwise feature; 1st and 2nd gate-opening transitions at ca. 0.1 kPa and 3.5 kPa, respectively, reaching an adsorbed amount of 110 mL (stp) g$^{-1}$ (9.5 mol per formula unit) at 99 kPa; however, only the...
1st gate-opening at ca. 3.1 kPa is observed when measured at 120 K, eventually reaching an adsorbed O₂ amount of 64 mL (stp) g⁻¹ (5.5 mol per formula unit) at 99 kPa.

Crystal structures under gases. To elucidate the gas-inserted structure, in situ powder X-ray diffraction (PXRD) of 1 were measured under 100 kPa of N₂ at 130 K, O₂ at 94 and 130 K, and CO₂ at 204 K (Fig. 2b), which illustrate the occurrence of structural transformations upon gas adsorption. Two types of gas-adsorbed temperature-dependent phases exist at 130 and 94 K under O₂, which can be associated with the 2nd gate-opening step in the adsorption isotherm for O₂. Additionally, the PXRD pattern of 1 ⊃ O₂ at 130 K is very similar to that of 1 ⊃ N₂ at 130 K in that it does not undergo the 2nd gate-opening transition.

Hereafter, O₂-adsorbed phases observed at 130 K and 94 K are denoted as 1 ⊃ O₂-I and 1 ⊃ O₂-II, respectively. Notably, the gas-induced structural changes are reversible (Supplementary Fig. 5); after evacuating the CO₂ gas from 1 ⊃ CO₂, the PXRD pattern reverts to the original pattern of 1. In the case of 1 ⊃ N₂, slight heating to 150 K in addition to evacuation is required to promote desorption of N₂. Of note, the PXRD pattern for 1 ⊃ O₂-II becomes that for 1 ⊃ O₂-I by evacuating at 94 K, but it does not return to the pattern of 1, indicating that the 1 ⊃ O₂-I phase corresponds to an intermediate phase stabilized at low pressures of O₂ even at 94 K (vide infra), which eventually turns into 1 after evacuate at 300 K.

Finally, the crystal structures of 1 ⊃ N₂, 1 ⊃ O₂-I, and 1 ⊃ CO₂ were determined by in situ single crystal X-ray diffraction (SCXRD) under gas-pressure controlled atmospheres...
Supplementary Fig. 6, 7, 9, and 10, Supplementary Table 4–6, Supplementary Note 5–7), and it of 1 ⊃ O₂-II was evaluated from the in situ PXRD data using the Rietveld refinement technique (Supplementary Fig. 8, Supplementary Table 7, Supplementary Note 6). For 1 ⊃ N₂, 1 ⊃ O₂-I, and 1 ⊃ CO₂, the accommodated gases were reasonably determined with occupancy numbers of 4N₂, 5.2O₂, and 5CO₂, respectively, which were displayed in Fig. 2c and Supplementary Fig. 9 and 10 (the O₂ molecules for 1 ⊃ O₂-II have less accuracy, so only the framework structure is discussed). The inter-layer distances, which are
defined by $l_1$ and $l_2$ (= $a’$-axis) between planes, have decreased (but $l_2 > 10.3\text{ Å}$; Supplementary Table 8, where inter-layer ferromagnetic interaction is expected even for $1 \supseteq \text{O}_2$ and $1 \supseteq \text{N}_2$\textsuperscript{[19,48]} in all $1 \supseteq \text{Gas}$ structures compared to 1, which manifests structurally as a change from the wavy layer form in 1 to a quasi-flat layer form in $1 \supseteq \text{Gas}$, resulting from a reduction in the Ru–N–C bending angle (av. 159–161° for $1 \supseteq \text{Gas}$ vs. 140.3° for 1, Supplementary Table 8). Hence, the guest-molecule accessible volume between the layers in $1 \supseteq \text{Gas}$ increase relative to 1 (147 Å\textsuperscript{3}), as expected from the gas adsorption capability (335–546 Å\textsuperscript{3} for $1 \supseteq \text{Gas}$, Supplementary Table 8). Importantly, the structural frameworks of $1 \supseteq \text{N}_2$ and $1 \supseteq \text{O}_2$ at 130 K are almost identical; three distinguishable gas-accommodation sites (Site-A–C; Supplementary Fig. 10) were commonly realized even for $1 \supseteq \text{CO}_2$, where a close-up view of gas-sandwiched mode at Site-A, which was most likely associated with the difference of magnetism between $1 \supseteq \text{N}_2$ and $1 \supseteq \text{O}_2$ (vide infra), was depicted in Fig. 2d. The Site-A included two molecules of N\textsubscript{2} or O\textsubscript{2} with a similar arrangement; two gas molecules at Site-A were relatively close to the TCNQ(MeO\textsubscript{2}) moieties, where the barycenter-to-barycenter distance between N\textsubscript{2}/O\textsubscript{2} and the quinonoid ring (C6) of the TCNQ(MeO\textsubscript{2}) moiety was 3.79(5) and 3.86(5) Å, respectively, and the inter-guest barycenter distance of N\textsubscript{2}–N\textsubscript{2}/O\textsubscript{2}–O\textsubscript{2} was 4.82(6) and 4.85(6) Å, respectively (Fig. 2d). The torsion angle of C6–N\textsubscript{2}/O\textsubscript{2}–N\textsubscript{2}/O\textsubscript{2} was 114.8(3)° and 114.6(3)° for $1 \supseteq \text{N}_2$ and $1 \supseteq \text{O}_2$, respectively (Fig. 2d). To accommodate an additional 4 mol per formula unit of gas, a subsequent enlargement in the inter-layer distance is required, as observed in $1 \supseteq \text{O}_2$–II and $1 \supseteq \text{CO}_2$ (Fig. 2c).

**Magnetic properties under diamagnetic gases, CO$_2$ and N$_2$.** Upon gas adsorption, a significant structural change is induced without alteration in the oxidation state of each unit in the D$_2$A layer; in situ infrared (IR) spectroscopy proves the preservation of TCNQ(MeO$_2$)$^{2-}$, even under a 100 kPa gas atmosphere (Supplementary Fig. 11). Therefore, in situ magnetic measurements were conducted in Quantum Design MPMS-7S by accurately handling the gas pressure; the pressure in a homemade cell (Supplementary Fig. 11) were commonly realized even for $1 \supseteq \text{CO}_2$, where a close-up view of gas-sandwiched mode at Site-A, which was most likely associated with the difference of magnetism between $1 \supseteq \text{N}_2$ and $1 \supseteq \text{O}_2$ (vide infra), was depicted in Fig. 2d. The Site-A included two molecules of N\textsubscript{2} or O\textsubscript{2} with a similar arrangement; two gas molecules at Site-A were relatively close to the TCNQ(MeO\textsubscript{2}) moieties, where the barycenter-to-barycenter distance between N\textsubscript{2}/O\textsubscript{2} and the quinonoid ring (C6) of the TCNQ(MeO\textsubscript{2}) moiety was 3.79(5) and 3.86(5) Å, respectively, and the inter-guest barycenter distance of N\textsubscript{2}–N\textsubscript{2}/O\textsubscript{2}–O\textsubscript{2} was 4.82(6) and 4.85(6) Å, respectively (Fig. 2d). The torsion angle of C6–N\textsubscript{2}/O\textsubscript{2}–N\textsubscript{2}/O\textsubscript{2} was 114.8(3)° and 114.6(3)° for $1 \supseteq \text{N}_2$ and $1 \supseteq \text{O}_2$, respectively (Fig. 2d). To accommodate an additional 4 mol per formula unit of gas, a subsequent enlargement in the inter-layer distance is required, as observed in $1 \supseteq \text{O}_2$–II and $1 \supseteq \text{CO}_2$ (Fig. 2c).

**Magnetic properties under a paramagnetic O$_2$ gas.** The magnetic behavior of the material under an O$\textsubscript{2}$ atmosphere is completely different from that under N\textsubscript{2} and CO$_2$ and varies with the O$\textsubscript{2}$ pressure ($P$$_{\text{O}_2}$) (Fig. 4). Similar to $1 \supseteq \text{N}_2$ and $1 \supseteq \text{CO}_2$, the sample was evacuated down to 0.1 Pa with a turbo-molecular pump at 353 K and the gas was introduced at 200 K up to an inner gas pressure of ~116 kPa. The gassealed cell was then cooled at a sweep rate of 0.5 K min$^{-1}$ to 120 K for N\textsubscript{2}, 195 K for CO$_2$, and 100 K for O\textsubscript{2}. Each cell was maintained at its respective temperature for 10 h to reach adsorption equilibrium. Once the inner pressure of each cell was obtained, the gas-sealed cell was held at 100 K or 120 K for the FCM measurements.

Figure 3a shows the temperature dependence of FCM at 100 Oe for $1 \supseteq \text{N}_2$ and $1 \supseteq \text{CO}_2$ prepared in situ, together with that for 1. Upon insertion of N\textsubscript{2} and CO$_2$, $T_C$ drastically increases to 88 K for $1 \supseteq \text{N}_2$ and 92 K for $1 \supseteq \text{CO}_2$ from 76 K for 1 (under vacuum) even under a weaker magnetic field of 5 Oe (Supplementary Fig. 13), establishing the existence of a ferrimagnetic ground state under N\textsubscript{2} and CO$_2$ atmospheres, where $T_C$ was determined from a disappeared point of RM (Supplementary Fig. 14). Since N\textsubscript{2} exists in the gas phase at 88 K in bulk, the change in $T_C$ is not caused by external N\textsubscript{2}. In addition, N\textsubscript{2} and CO$_2$ are diamagnetic species. Therefore, the variation in $T_C$ results from the adsorbed gases. Given that the decrease in $T_C$ from 1-solv to 1 was induced by considerable structural changes, inversely, the increase in $T_C$ for $1 \supseteq \text{N}_2$ and $1 \supseteq \text{CO}_2$ relative to 1 likely results from a reduction in structural deformation; the wavy layer in 1 is modified into a quasi-flat layer in $1 \supseteq \text{N}_2$ and $1 \supseteq \text{CO}_2$ and/or a modification in the inter-layer environment occurs, resulting from closely packed gases (Fig. 3c). Even with such a drastic change in $T_C$, the magnetic-field dependence of the magnetization (M–H) is essentially preserved from 1 (Fig. 3b), although the coercive field ($H_c$) of $1 \supseteq \text{CO}_2$ is somewhat larger than that of 1 and $1 \supseteq \text{N}_2$. Note that the anomalous steps around zero field for 1, $1 \supseteq \text{N}_2$, and $1 \supseteq \text{CO}_2$ (1 $\supseteq$ O\textsubscript{2} as well; vide infra) could be caused by a small number of free crystals that follow the magnetic field.

---

**Fig. 3** Variation of magnetic properties under diamagnetic gases, CO\textsubscript{2} and N\textsubscript{2}. a FCM curves at a 100 Oe magnetic field for 1 measured under vacuum (black) and $1 \supseteq \text{CO}_2$ (green) and $1 \supseteq \text{N}_2$ (red) under a 100 kPa gas atmosphere. b Magnetic hysteresis loops at 1.8 K for 1 measured under vacuum (black), $1 \supseteq \text{CO}_2$ (green), and $1 \supseteq \text{N}_2$ (red) under a 100 kPa gas atmosphere. c Schematic representation for the alternation between 1 and $1 \supseteq \text{CO}_2$ and $1 \supseteq \text{N}_2$ upon CO\textsubscript{2} and N\textsubscript{2} adsorptions, respectively.
$T_C$ of $1 \supset O_2$ increases once at low pressures of $P_{O_2} < 1$ kPa (e.g., $T_C = 90$ K at $P_{O_2} \leq 0.1$ kPa; vacuum pressure level at 100 K). However, under higher pressures, the FCM curve shows an anomaly with a cusp, indicating the onset of antiferromagnetic ordering; for example, $T_N = 71$ K at 1 kPa, which gradually increases to $T_N = 98$ K at 100 kPa with increasing $O_2$ pressure (Fig. 4a). The variation in $T_N$ with $O_2$ pressure was also confirmed by the magnetization measurements by varying the $O_2$ pressure at each temperature (Supplementary Fig. 15). The initial increase in $T_C$ at low $O_2$ pressures ($P_{O_2} < 1$ kPa) is likely caused by the same mechanism found in $1 \supset N_2$ and $1 \supset CO_2$ (Fig. 3c), which could be attributed to the redress of the layered structure, i.e., the modification from a wavy form of $1$ to a quasi-flat form in $1 \supset O_2$-I (the first step in Fig. 4b). Meanwhile, the drastic change of the magnetic phase from ferrimagnetism to antiferromagnetism could be obtained whether for: (1) a structural change associated with the transformation from $1 \supset O_2$-I to $1 \supset O_2$-II, or (2) the magnetic contribution of the adsorbed $O_2$ molecules. To examine these possibilities, PXRD patterns (from both of common lab level and high resolution synchrotron level) were measured by varying the $O_2$ pressure at a fixed temperature in the range of 70–100 K (Supplementary Fig. 16 and 17), and the structural transition pressure ($P_c$) from $1 \supset O_2$-I to $1 \supset O_2$-II at each temperature was plotted in a $T$–$P_{O_2}$ phase diagram together with $T_N$, where the $T_N$ line separates the magnetic phases between the paramagnetic/ferrimagnetic phase and the antiferromagnetic phase, and the $P_c$ line distinguishes between the $1 \supset O_2$-I and $1 \supset O_2$-II phases (Fig. 5). Importantly, the $T_N$ line is independent of the $P_c$ line, and antiferromagnetism in the $1 \supset O_2$-I phase is present (the pale blue area in Fig. 5). Since the $1 \supset O_2$-I and $1 \supset N_2$ structures are identical with $l_2 > 10.3$ Å expected as a regime for inter-layer ferromagnetic interactions$^{39,40}$, and indeed, $1 \supset N_2$ is ferrimagnetic, the antiferromagnetism in $1 \supset O_2$-I results from the magnetic contribution of the adsorbed $O_2$ molecules, which is caused by long-range antiferromagnetic correlations via intercalated $O_2$ spins; the most likely packing mode associated with the $O_2$-mediated magnetic pathway was shown in Fig. 2d. Further, the continuous shift in $T_N$ is likely dependent on the number of $O_2$ spins between layers, which act as magnetic mediators couple layer’s ordered spins together.

Fig. 4 Variation of magnetic properties under a paramagnetic $O_2$ gas. a $O_2$-pressure dependence of FCM curves at a 100 Oe magnetic field for $1$. b Schematic representations for the alternations of $1 \supset O_2$ dependent on the applied $O_2$ pressure and external magnetic fields. c Field-dependence of the magnetization at 1.8 K for $1$ measured at several $O_2$ pressures, where the inset represents the differential plots on the basis of the $M$–$H$ curve for $1$. 
Thus, the present porous layered magnet 1 magnetically discriminates O₂ from N₂ and CO₂, at least at P₉₅ ≥ 1 kPa.

The magnetic switching between the ferrimagnetic phase under vacuum with the 1 ⊃ O₂-I structure and the antiferromagnetic phase of 1 ⊃ O₂ is quite fast and reversible (Fig. 6); the change from the ferrimagnetic phase to the antiferromagnetic phase is completed in <1 min at 85 K.

Generally, the solid states of bulk O₂ exist in the α-dimer form with a spin singlet at T < 24 K. Compound 1 ⊃ O₂-II eventually has ~9 O₂ molecules per D₂A layer unit, like a buried oxygen layer between ferrimagnetic D₂A layers; at least, some of them certainly act as a paramagnetic mediator in the pores. Interestingly, the antiferromagnetic phase of 1 ⊃ O₂-II transforms to a ferrimagnetic phase in the presence of an applied magnetic field (Supplementary Fig. 18), giving the much higher saturated magnetization (Mₛ) value of 9.29 nmT compared to 2.22 nmT for 1 at 7 T (1.8 K), including a fully opened hysteresis curve (Hₑ = 0.70 T) (Fig. 4c). On the basis of the M–H curve for 1, the differential plots clarify the contribution of the O₂ spins in the bulk magnetism of 1 ⊃ O₂-II (Fig. 4d), giving rise to a new magnetic field-induced ferrimagnet. These magnetic alternations by gases are completely reversible upon adsorption/desorption under vacuum with heating (Supplementary Fig. 19).

**Discussion**

The magnetic change caused by the introduction of guest gas molecules into a porous magnet can be attributed to three triggers: (i) an electronic trigger that causes spin emergence in the framework as a result of host-guest electron transfers (i.e., formation of new magnetic pathways in the framework); (ii) a structural trigger resulting from magnetostructural modifications associated with gate-opening/closing transitions induced by gas adsorption/desorption, respectively (i.e., modification of the magnetic pathways); and (iii) a paramagnetic guest trigger resulting from the formation of new magnetic pathways or dipole–dipole interactions where paramagnetic gas molecules themselves magnetically mediate the transition to another magnetic ground state. The present gas-responsive porous magnet results from triggers (ii) and (iii); in particular, the insertion of free oxygen molecules achieves a magnetic phase change from a ferrimagnet to an antiferromagnet based on trigger (iii). The fact of magnetic ordering via paramagnetic O₂ molecules gives an opportunity to investigate the intrinsic nature of oxygen molecules in closed nano-sized porous spheres and provides a new application methodology based on paramagnetic molecules as switchable magnetic mediators. As a rapidly emerging field, this class of gas-responsive porous magnets is the most important target in the development of functional molecular porous materials.

**Methods**

**Physical measurements.** IR spectra were measured with KBr pellets using a Jasco FT/IR-4200 spectrometer. Thermogravimetric analyses (TGA) were performed using a Shimadzu DTG-60H apparatus under a N₂ atmosphere in the temperature range from 298 K to 673 K at a heating rate of 5 K min⁻¹. Unless otherwise noted, PXRD were collected on a Rigaku Ultima IV diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at room temperature for the sample sealed in a silica glass capillary with an inner diameter of 0.5 mm with θ scan. PXRD patterns for 1 ⊃ O₂ and 1 ⊃ N₂ with the synchrotron radiation (λ = 0.799999(6) Å) were collected at SPring-8 (BL44B2)³⁷. Magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL on a polycrystalline sample in the temperature range of 1.8–300 K at a dc field of 1 kOe. Diamagnetic contributions were collected for the sample holder, Nujol, and for the sample using Pascal’s constants.⁴⁸ Fresh samples taken immediately from the stock liquids were used for the magnetic measurements of 1-solv, and the formula determined by single-crystal X-ray crystallography was used for data analyses. Details for in situ IR spectra and gas adsorption-magnetic measurements are described in Supplementary Methods.
Received: 13 June 2018 Accepted: 27 November 2018
Published online: 21 December 2018

References
1. Vermesan, O. et al. Internet of things strategic research roadmap. in internet of things: global technological and societal trends. In: Vermesan, O., Friesi, P., (eds). pp. 9–52 (River Publishers: Delft, The Netherlands, 2011).
2. Potrykal, R. A. Multivariable sensors for ubiquitous monitoring of gases in the era of internet of things and industrial internet. Chem. Rev. 116, 11877–11923 (2016).
3. Poling, B. E., Prausnitz, J. M. & O'Connell, J. P. The Properties of Gases and Liquids. 5th edn, (McGraw-Hill, New York, 2000).
4. Smith, A. R. & Klosek, J. A review of air separation technologies and their role in the era of internet of things and industrial internet. Chem. Rev. 116, 257–202 (2013).
5. Arroyo, J. A. R. et al. Guest-induced modification of a magnetically active ultramicroporous, gismondine-like, copper(II) coordination network. J. Am. Chem. Soc. 130, 3978–3984 (2008).
6. Kaye, S. S., Choi, H. J. & Long, J. R. Generation and O2 adsorption studies of the microporous magnets Cr3O4(C2N3)(2)(Tc = 75 K) and Cr3O4(C2N3)(2)H2O (Tc = 219 K). J. Am. Chem. Soc. 130, 16921–16925 (2008).
7. Southon, P. D. et al. Dynamic interplay between spin crossover and host-guest function in a nanoporous metal-organic framework material. J. Am. Chem. Soc. 131, 10998–11009 (2009).
8. Arcis-Castillo, Z. et al. Reversible chemisorption of sulf dioxide in a spin crossover porous coordination polymer. Inorg. Chem. 52, 12777–12783 (2013).
9. Coronado, E., Giménez-Marqués, M., Espallargas, G. M., Rey, F. & Vitórca-Yrezábal, I. J. Spin-crossover modification through selective CO2 sorption. J. Am. Chem. Soc. 135, 15986–15989 (2013).
10. Coronado, E. & Espallargas, G. M. Dynamic magnetic MOFs. Chem. Soc. Rev. 42, 1525–1539 (2013).
11. Maspoç, D., Ruiz-Molina, D. & Veciana, J. Old materials with new tricks: multifunctional open-framework materials. Chem. Soc. Rev. 36, 770–818 (2007).
12. Dechambois, P. & Long, J. R. Microporous magnets. Chem. Soc. Rev. 40, 3249–3265 (2011).
13. Maspoç, D. et al. A nanoporous molecular magnet with reversible solvent-induced mechanical and magnetic properties. Nat. Mater. 2, 190–195 (2003).
14. Dzhioe, S., Arau, K., Sato, T. & Hashimoto, K. Humidity-induced magnetization and magnetic pole inversion in a cyanobridged metal assembly. Nat. Mater. 3, 857–861 (2004).
15. Moriyama, N. et al. Reversible magnetic phase transition between a ferromagnet and a paramagnet in a single-crystal MOF with a sandwich structure. J. Am. Chem. Soc. 132, 11943–11951 (2010).
16. Lekarova, J. et al. Dynamic interplay between spin-crossover and host-guest function in a nanoporous metal-organic framework material. Angew. Chem. Int. Ed. 42, 3760–3763 (2003).
17. Halder, G. J. et al. Elucidating the mechanism of a two-step spin transition in a nanoporous metal–organic framework. J. Am. Chem. Soc. 130, 17552–17562 (2008).
18. Hola, M. et al. Bidirectional chem-switching of spin state in a microporous framework. Angew. Chem. Int. Ed. 48, 4767–4771 (2009).
19. Itoh, M. et al. Magnetic properties of oxygen physisorbed in Cu-tans-1,4-cyclohexanedicarboxylic acid. Mol. Cryst. Liq. Cryst. 306, 1–7 (1997).
20. Kitaura, R. et al. Formation of a one-dimensional array of oxygen in a microporous metal-organic solid. Science 298, 2358–2361 (2002).
21. Takamizawa, S., Nakata, E. & Akatsu, K. T. Dynamic behavior of a 1D molecular-oxygen system included within a transformable single-crystal adsorbent. Angew. Chem. Int. Ed. 45, 2216–2221 (2006).
22. Hori, A. et al. Spin-dependent molecular orientation of O2–O2 dimer formed in the nanoporous coordination polymer. J. Phys. Soc. Jpn. 82, 084703 (2013).
23. Hori, A. et al. Host-field magnetization process of O2 adsorbed in a microporous coordination polymer (1+1 at various temperatures. J. Phys. Conf. Ser. 200, 022018 (2010).
24. Kobayashi, T. et al. Magnetic properties of molecular oxygen adsorbed in micro-porous metal-organic solids. Prog. Theor. Phys. Suppl. 159, 271–279 (2005).
25. Murakami, Y. et al. Neutron diffraction study of oxygen monolayers. Phys. B 213–214, 233–235 (1995).
26. Mori, W. et al. Magnetic properties of oxygen physisorbed in Cu-tans-1,4-cyclohexanedicarboxylic acid. Mol. Cryst. Liq. Cryst. 306, 1–7 (1997).
27. Kanda, E., Haseda, T. & Otsuka, A. Temperature-sensitive magnetic property of solid oxygen. Physica 20, 131–132 (1954).
28. DeFotis, G. D. Magnitism of solid oxygen. Phys. Rev. B 23, 4714–4740 (1981).
29. Nomura, T. et al. Novel phase of solid oxygen induced by ultrahigh magnetic field. Phys. Rev. Lett. 112, 247201 (2014).
30. Kobayashi, T. et al. Emergence of novel phase of solid oxygen in ultrahigh magnetic field. J. Phys. Conf. Ser. 568, 042018 (2014).
31. Miyasaka, H. Control of charge transfer in donor/acceptor metal–organic frameworks. Acc. Chem. Res. 46, 248–257 (2013).
32. Miyasaka, H., Campos-Fernández, C. S., Clérac, R. & Dunbar, K. R. Hexagonal layered materials composed of [M2O3(C2N3)]n (M = Ru and Rh) donors and TCNQ acceptors. Angew. Chem. Int. Ed. 39, 3831–3835 (2000).
33. Miyasaka, H., Izawa, T., Takahashi, N., Yamashita, M. & Dunbar, K. R. Long-range ordered magnet of a charge-transfer Ru41+ TQC2 two-dimensional network compound. J. Am. Chem. Soc. 128, 11358–11369 (2006).
34. Fujukura, H. et al. Charge-disproportionate ordered state with δ = 0.75 in a chemically sensitive donor/acceptor D19+ A19+ layered framework. Chem. Commun. 51, 7795–7798 (2015).
35. Kosaka, W., Fujukura, H. & Miyasaka, H. Electron-transferred donor/acceptor ferrimagnet with Tc = 91 K in a layered assembly of paddlewheel [Ru3]n units and TQC2. Inorg. Chem. 40, 10001–10006 (2001).
36. Kosaka, W., Itoh, M. & Miyasaka, H. Metamagnetism with Tc = 97 K in a layered assembly of paddlewheel [Ru3]n units and TQC2: an empirical rule for interlayer distances determining the magnetic ground state. Mater. Chem. Front. 2, 497–504 (2018).

6. Kaye, S. S., Choi, H. J. & Long, J. R. Generation and O2 adsorption studies of the microporous magnets Cr3O4(C2N3)(2)(Tc = 75 K) and Cr3O4(C2N3)(2)H2O (Tc = 219 K). J. Am. Chem. Soc. 130, 16921–16925 (2008).
7. Southon, P. D. et al. Dynamic interplay between spin crossover and host-guest function in a nanoporous metal-organic framework material. J. Am. Chem. Soc. 131, 10998–11009 (2009).
8. Arcis-Castillo, Z. et al. Reversible chemisorption of sulf dioxide in a spin crossover porous coordination polymer. Inorg. Chem. 52, 12777–12783 (2013).
9. Coronado, E., Giménez-Marqués, M., Espallargas, G. M., Rey, F. & Vitórca-Yrezábal, I. J. Spin-crossover modification through selective CO2 sorption. J. Am. Chem. Soc. 135, 15986–15989 (2013).
10. Coronado, E. & Espallargas, G. M. Dynamic magnetic MOFs. Chem. Soc. Rev. 42, 1525–1539 (2013).
Acknowledgements

We thank Dr. Hiroyasu Sato (Rigaku Co.Ltd.) for his help in structural determinations for the gas-accommodated compounds. This work was supported by a Grant-in-Aid for Scientific Research (Grant No. 16H02269, 15K13652, 26810029, and 18K05055), a Grand-in-Aid for Specially Promoted Research (Grant No. 25000007) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (MEXT), the E-IMR project, the Asahi Glass Foundation, Mitsubishi Foundation, and the Support Program for Interdisciplinary Research in Tohoku University. J.Z. is thankful for the JSPS Research Fellowship for Young Scientists (No. 17J02497). iCeMS is supported by the World Premier International Research Institute (WPI) of MEXT.

Author contributions

W.K. and H.M. formulated the project. Z.L. and J.Z. synthesized and characterized the compounds. W.K. performed the gas sorption measurements and the in situ study under gases in the magnetic studies, IR spectroscopy, and PXRD measurements with the refinement of structures. J.Z. performed SCXRD measurements under gases. Y.S. and A.H. conducted in situ PXRD measurements with the synchrotron radiation under gases under the supervision of S.K. and R.M.; W.K. and H.M. wrote the manuscript and all authors discussed the results and revised the paper.

Additional information

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-07889-1.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018