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## Swift and Efficient Nuclear Spin Conversion of Molecular Hydrogen Confined in Prussian Blue Analogs

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The ortho-isomer of molecular hydrogen (o-H<sub>2</sub>) was converted to the para-isomer (p-H<sub>2</sub>) within 600 s by using Prussian blue analogs,  $\{M^{II}_{3}[Cr^{III}(CN)_{6}]_{2}\}$  (MCr; M = Mn 2 3 4 and Ni), as nuclear-spin conversion catalysts. The swift 5 conversion was confirmed by in-situ Raman microspectroscopy under an H<sub>2</sub> gas atmosphere (100 kPa) in a low 6 temperature range (20-90 K). The o-p ratio observed in MCr deviated from the theoretical value based on the 8 9 Boltzmann distribution of H<sub>2</sub> in a free rotational state to the para-rich proportion, which suggested the promotion of the o-p conversion at higher temperature. 10 11

12 Keywords: Nuclear spin conversion, Prussian blue 13 analogs, *In-situ* Raman microspectroscopy

14 H<sub>2</sub> is a highly promising alternative energy source to 15 conventional fossil fuels because of its high gravimetric energy density and an environmentally friendly combustion 16 product of H<sub>2</sub>O. Among conventional physical methods for 17 18 H<sub>2</sub> storage, liquefaction is commonly used in industrial 19 settings because it facilitates the highest volumetric energy 20 density and transportation efficiency. Long-period storage 21 of liquid H<sub>2</sub>, however, is limited by not only technical 22 problems related to the storage vessel but also a latent "boil-23 off problem" caused by nuclear spin conversion between 24 nuclear spin isomers. H<sub>2</sub> is comprised of two nuclear spin 25 isomers, *i.e.*, ortho-H<sub>2</sub> (o-H<sub>2</sub>; I = 1, J = odd) and para-H<sub>2</sub> (p-26 H<sub>2</sub>; I = 0, J = even), where I and J are total nuclear spin 27 angular momentum and rotational quantum number, 28 respectively (Figure 1a).<sup>1</sup> Their rotational energy levels 29  $(E_{\rm rot})$  are quantized by the J value according to the Pauli 30 exclusion principle. Moreover, the isomer ratio ([o-H<sub>2</sub>]/[p-31  $H_2$ ) is a function of temperature (T) based on the 32 Boltzmann distribution with the rotational constant (B) of H<sub>2</sub> 33 and the Boltzmann constant (k), where B/k = 84.837 K (eq 1, 34 Figure 1b).<sup>1</sup>



**Figure 1.** (a) Rotational energy diagram of nuclear spin isomers for  $H_2$ , where *I*,  $E_{rot}$ , *B*, *J*, and *n* denote total nuclear spin angular momentum, rotational energy, rotational constant, rotational quantum number, and degeneracy number, respectively. (b) Temperature-dependent nuclear spin isomer ratio ([o-H<sub>2</sub>]/[p-H<sub>2</sub>]).

$$[\text{o-H}_2]/[\text{p-H}_2] = \sum_{J=\text{odd}} \left[ 3(2J+1) \exp\left\{\frac{-BJ(J+1)}{kT}\right\} \right] / \sum_{J=\text{even}} \left[ (2J+1) \exp\left\{\frac{-BJ(J+1)}{kT}\right\} \right]$$
(1)

42 The ortho-para (o-p) conversion is a spin-forbidden process with conversion rates of  $\sim 10^{10}$  s in the gas state,<sup>1</sup> 43 1.14%  $h^{-1}$  in the liquid state,<sup>2a</sup> and approximately 1.9%  $h^{-1}$ 44 in the solid state.<sup>2b-d</sup> Moreover, this conversion is an 45 46 exothermic reaction with a heat of conversion of ~1.4 kJ 47 mol<sup>-1</sup> for o-H<sub>2</sub>, which is higher than the heat of vaporization 48 of  $H_2$  (0.9 kJ mol<sup>-1</sup>). Thus, liquid  $H_2$ , prepared by an 49 immediate cooling process without any catalytic treatment. 50 still contains ~75% of o-H<sub>2</sub>, which generates heat through 51 the o-p conversion.<sup>3</sup> This is termed as the boil-off problem. 52 Although solid catalysts to promote o-p conversion have 53 been actively developed to solve this problem, such as 54 magnetic materials<sup>4</sup> and diamagnetic metals,<sup>5</sup> several challenges remain regarding the conversion rate and 55 56 efficiency. These challenges arise because of the low 57 contact probability between the catalyst surface and o-H<sub>2</sub>. 58 Even when amorphous solid water systems are used as the 59 o-p conversion catalysts, sophisticated techniques for 60 sample preparation and extremely low handling temperature 61 are required.<sup>6</sup> Several mechanisms for the activated o-p 62 conversions by giant inhomogeneous surface electric fields 63 of non-magnetic materials have also been theoretically proposed.<sup>5g,7</sup> From the abovementioned viewpoint, porous 64 65 materials with a high surface area and readily accessible 66 space can be considered excellent o-p conversion catalysts. 67 Hence, porous coordination polymers (PCPs), also known as 68 metal-organic frameworks (MOFs), have the potential to be used as o-p conversion catalysts.8 MOF-5 and MOF-74 have 69 70 catalyzed o-p conversion; however, the detailed mechanism 71 of the observed conversion has not been elucidated.<sup>9a-c</sup> On 72 the other hand, we have reported a high catalytic ability of a 73 Hofmann-type PCP,  $\{Fe^{II}(pyrazine)[Pd^{II}(CN)_4]\}$ , for o-p 74 conversion, which was accelerated by the perturbation of the 75 electric field gradient through site-exchange of H<sub>2</sub> confined 76 in the nano-sized pores around the boiling point of H<sub>2</sub> 77 (20.27 K).9d In order to improve the conversion temperature, 78 we focused on energy level splitting of the triply 79 degenerated ground state of  $o-H_2$  (J = 1) because the 80 splitting may increase the p-H<sub>2</sub> proportion based on the 81 Boltzmann distribution.<sup>4h,5g</sup> This phenomenon also has been 82 reported in a Prussian blue analog (PBA) having a defective structure (Figure 2)<sup>10c</sup> PBAs are cyanide-bridged PCPs with 83 84 diverse properties, such as high H<sub>2</sub> adsorption ability<sup>10</sup> and a magnetic property<sup>11</sup> derived from the 3-D porous structure.<sup>12</sup> 85 86 Therefore, in this research, we selected PBA-based porous 1 magnets,  $\{M^{II}_{3}[Cr^{III}(CN)_{6}]_{2}\cdot nH_{2}O\}$  (MCr·nH<sub>2</sub>O; M = Mn 2 and Ni), as new o-p conversion catalysts and verified the 3 effect of magnetic perturbation induced in PCPs on o-p 4 conversion as an additional factor to improve conversion 5 temperature.



7 **Figure 2.** Schematic crystal structure of defective Prussian blue 8 analogs (PBAs),  $\{M_A^{II}_3[M_B^{III}(CN)_6]_2 \cdot nH_2O\}$  ( $M_AM_B \cdot nH_2O$ ), where C, 9 N, O, divalent M<sub>A</sub>, and trivalent M<sub>B</sub> are colored in gray, cyan, red, 10 purple, and yellow, respectively, and lattice H<sub>2</sub>O molecules and H 11 atoms of coordinated H<sub>2</sub>O molecules are omitted for clarity.

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12 MCr·nH<sub>2</sub>O were prepared by mixing aqueous 13 solutions of M<sup>II</sup>Cl<sub>2</sub>·xH<sub>2</sub>O and K<sub>3</sub>[Cr<sup>III</sup>(CN)<sub>6</sub>] (see Supporting 14 Information). Energy dispersive X-ray fluorescence 15 (EDXRF) and scanning electron microscopy with energy 16 dispersive X-ray (SEM-EDX) analysis of MCr·nH<sub>2</sub>O 17 indicated that the componential ratio ([M]/[Cr]) is consistent 18 with the calculated value of 1.5 and the contamination of K<sup>+</sup> 19 is below 0.1% in each batch (Figure S1 and Tables S1, S2). The number of total lattice and coordinated H<sub>2</sub>O molecules 20 21 (*n*) was determined to be 14 for **MnCr** and 15 for **NiCr** by 22 elemental analysis and thermogravimetry analysis (TGA) of 23 MCr $\cdot$ *n*H<sub>2</sub>O (Figure S2). The trace amount of K<sup>+</sup> was 24 ignored at this stage. In the Fourier transform infrared (FT-25 IR) spectra of  $MCr \cdot nH_2O$ , the O-H stretching mode 26 (v(OH)) and H-O-H bending mode  $(\delta(H_2O))$  were observed in 3800-2900 cm<sup>-1</sup> and around 1610 cm<sup>-1</sup>, respectively 27 28 (Figure S3). The powder X-ray diffraction (PXRD) patterns 29 of  $MCr \cdot nH_2O$  were in good agreement with the typical diffraction pattern of PBAs (Figure S4).<sup>12</sup> 30

31 The dehydrated samples, MCr, were prepared by 32 heating MCr·nH<sub>2</sub>O at 120°C for 24 h under vacuum. In the 33 FT-IR spectra, the broad bands of v(OH) and  $\delta(H_2O)$  modes 34 disappeared and the  $v(C \equiv N)$  band slightly broadened 35 without a large wavenumber shift, indicating the removal of 36 H<sub>2</sub>O molecules and the retainment of the cyanide-bridged 37 framework after the dehydration treatment, respectively 38 (Figure S3, Table S3). The PXRD patterns exhibited 39 essentially the same results before and after the dehydration 40 treatment, except for a broadening and a higher angle shift 41 in almost all the peaks, which suggested shrinkage and distortion of the lattice by a change in the coordination 42 43 geometry of the MII sites, with the elimination of coordinated H<sub>2</sub>O (Figure S4). The Brunauer-Emmett-Teller 44 45 specific surface areas (SABET) of the dehydrated samples, 46 MnCr and NiCr, were estimated from the results of N<sub>2</sub> adsorption at 77 K to be 683 and 620 m<sup>2</sup> g<sup>-1</sup>, respectively, 47 48 which were in the same range of the SABET values of other reported PBAs (Figure S5, Table S4).<sup>10</sup> In the H<sub>2</sub> adsorption 49 50 measurement at 77 K, both of MnCr and NiCr exhibited 51 type-I behavior of typical microporous materials in the

52 IUPAC classification,<sup>13</sup> with an adsorption amount of ~0.7 53 H<sub>2</sub> molecules per pore at 100 kPa (Figures 2, 3).



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55 Figure 3. H<sub>2</sub> adsorption ( $\bullet$ ) and desorption ( $\circ$ ) isotherms of MnCr 56 (red) and NiCr (green) at 77 K.



**Figure 4.** Temperature-dependent *in-situ* Raman spectra of (a) **MnCr** and (b) **NiCr** under reduced pressure (black line) and  $H_2$  gas tamosphere at 100 kPa (colored lines) using an excitation laser with a wavelength of 532 nm. Neutral density (ND) filters with a total optical density (OD) of 1.6 were used to weaken the intensity of the excitation laser.

64 The nuclear spin state of H<sub>2</sub> confined in MCr was 65 confirmed by in-situ Raman microspectroscopy under 100 66 kPa of H<sub>2</sub> atmosphere (Figure 4). The spectra indicated by 67 bottom black lines in Figures 4(a) and 4(b) were obtained 68 under reduced pressure at 90 K, where the observed broad 69 Raman bands around 394 cm<sup>-1</sup> for MnCr and 525 cm<sup>-1</sup> for 70 NiCr were assigned to the vibration modes of the host 71 framework. After the injection of H2 gas, two Raman-active 72 bands newly appeared around 354.5 and 587.8 cm<sup>-1</sup> at 90 K 73 (Figure 4, red line). These bands were assigned to the 74 rotational transition of  $S_0(0)$  ( $J = 2 \leftarrow 0$ ) for confined p-H<sub>2</sub> 75 and  $S_0(1)$  ( $J = 3 \leftarrow 1$ ) for confined o-H<sub>2</sub> on comparison with 76 the spectra of the desorption state and considering the 77 Boltzmann distribution of H<sub>2</sub> (eq 1). Moreover, Raman

bands of free H<sub>2</sub>, which correspond to the energy gap 1 2 between the initial and final states of each  $S_0(0)$  and  $S_0(1)$ transitions, were observed at 354 and 587 cm<sup>-1</sup>, respectively 3 (Figure 1a).<sup>14</sup> In both types of MCr (MnCr and NiCr), the 4 increase of total peak intensities of  $S_0(0)$  and  $S_0(1)$ 5 6 transitions as the temperature decreased suggests an increase 7 in the amount that is adsorbed, because the Raman bands of 8 free-H<sub>2</sub> were not detected in the measurement condition. 9 The peak intensity of p-H<sub>2</sub> gradually increased with cooling, 10 whereas that of o-H<sub>2</sub> gradually decreased with cooling and almost vanished around 30 K (Figure 4). In addition, time-11 12 profiles of the intensity of both  $S_0(0)$  and  $S_0(1)$  transitions 13 showed rapid saturation and constancy during the 14 integration processing (600 s), which suggested that the 15 system reached an equilibrium state at initial process. 16 Consequently, the o-p conversion for H<sub>2</sub> confined in MCr was completed with a time constant of 600 s at its longest. 17 This was based on the laser exposure time (30 s) and the 18 19 cumulative number (20 times).



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Figure 5. Temperature-dependent abundance ratio of the nuclear spin isomer ( $[0-H_2]/[p-H_2]$ ) for  $H_2$  confined in **MnCr** (red) and **NiCr** (green), estimated ratio obtained in cooling process from room temperature without catalytic treatment (pink), and theoretical ratio in thermal equilibrium based on the Boltzmann distribution of  $H_2$  in a free rotational state (black). The inset is an enlarged view of the low temperature region.

29 The [o-H<sub>2</sub>]/[p-H<sub>2</sub>] values observed in MCr were 30 calculated from the integrated values of the peak areas of 31  $S_0(0)$  and  $S_0(1)$  transitions obtained from the spectrum of the 32 desorption state (Figure 4, black line) as the baseline, where 33  $f_{T,P}(v)$  and v are the function of spectra at a certain 34 temperature (T) and pressure (P), and the Raman shift, 35 respectively (eq. 2, Figure 5). In the controlled experiments, 36 wherein only a nickel-plated Raman sample cell without 37 MCr was used, the  $[0-H_2]/[p-H_2]$  value was constant in the 38 temperature range from 90 to 20 K and the time range of 39 600 s, indicating that there is no effect of the instrument on

the o-p conversion (Figures S6, S7). Figure 5 shows 40 41 observed  $[0-H_2]/[p-H_2]$  values in MCr. In both cases, the 42 observed [0-H<sub>2</sub>]/[p-H<sub>2</sub>] values decreased with lowering 43 temperature, and the observed values were lower than the 44 theoretical values of free H<sub>2</sub> above 40 K, which indicated 45 successful increase in the conversion temperature. In 46 addition, over the entire measurement temperature range, 47 the observed full width at half maximum (FWHM) of both 48 the  $S_0(0)$  and  $S_0(1)$  transitions in **MCr** (~6 cm<sup>-1</sup>) was larger 49 than those obtained by the abovementioned controlled 50 experiments (~3 cm<sup>-1</sup>), which suggests a rotational restraint of  $H_2$  confined in MCr (Figures 5, S6). Because the 51 52 Boltzmann distribution relating to the [o-H<sub>2</sub>]/[p-H<sub>2</sub>] value 53 depends on only the rotational constant (B) of  $H_2$  (eq 1), the 54 resultant deviation of the o-p ratio suggests the rotational 55 restraint of the confined o-H2. Such rotational restraint 56 would be caused by the locally anisotropic potential fields 57 derived from the structural defects of MCr, which is 58 supported by rotational-vibrational density of states for H<sub>2</sub> confined in a PBA, Cu<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub>.<sup>10c</sup> Because the [o-59 60 H<sub>2</sub>]/[p-H<sub>2</sub>] values observed for {Fe(pyrazine)[Pd(CN)<sub>4</sub>]} having a non-defective porous structure followed the 61 Boltzmann distribution,<sup>9d</sup> the resultant deviation for MCr 62 63 suggested the contribution of a defective porous structure to provide a para-enriched isomer ratio. The similar results of 64 65 both types of MCr suggest the importance of the defective 66 porous structure instead of the framework components for 67 achieving effective o-p conversion and ratio.

68 In order to verify the perturbation effect of the 69 magnetic field in the pore on o-p conversion, the in-situ 70 Raman spectroscopy was conducted again by using 71 magnetized PBAs. MnCr showed a ferrimagnetic ordering 72 at 108 K (Figure S8). NiCr showed a ferromagnetic 73 ordering at 18 K (Figure S9). The different magnetic 74 behavior from that of NiCr·nH<sub>2</sub>O reflects a change in the 75 magnetic interaction and a decrease in the magnetic domain size resulting from changes in the geometry and d electron 76 configuration of the M<sup>II</sup> sites due to dehydration.<sup>11d,11j</sup> 77 78 Because the magnetic ordering temperature of NiCr is 79 lower than the measurement temperature, only MnCr was 80 used for the evaluation of the magnetic perturbation. For magnetization of MnCr, a commercial neodymium magnet 81 82 of 2000 Oe was embedded into the backside of the Raman 83 sample cell, in which the magnetic field is sufficiently 84 strong to magnetize MnCr. The magnetized MnCr 85 exhibited a quick conversion within 600 s (Figure S10); however, there was no notable difference in the isomer ratio 86 87 between the magnetized and the non-magnetized MnCr 88 (Figure S11). From the viewpoint of the proposed 89 mechanism of o-p conversion through excitation by external 90 stimuli,<sup>5g,7</sup> the inner magnetic field and paramagnetic metal 91 ions might play a part in the promotion of the o-p conversion. Here diamagnetic  $Zn^{II_3}[Co^{III}(CN)_6]_2$  (ZnCo) is 92 93 expected to give significant information about effects of 94 paramagnetic centers on the o-p conversion, but the o-p 95 ratio could not be evaluated by this measurement due to a 96 broad fluorescent band of ZnCo overlapping with the 97 Raman bands of  $S_0(0)$  for p-H<sub>2</sub> and  $S_0(1)$  for o-H<sub>2</sub>.

In conclusion, two magnetic PBAs, MnCr ( $SA_{BET}$  = 1 2 683 m<sup>2</sup> g<sup>-1</sup>) and NiCr ( $SA_{BET} = 620 \text{ m}^2 \text{ g}^{-1}$ ), showed type-I H<sub>2</sub> adsorption behavior and exhibited a swift o-p conversion 3 4 within the time constant of 600 s, which was confirmed by 5 in-situ Raman microspectroscopy under an H<sub>2</sub> gas 6 atmosphere and applied magnetic field (0 and 2000 Oe). 7 Furthermore, the deviation of the o-p ratio  $([o-H_2]/[p-H_2])$ 8 below the theoretical abundance ratio based on the 9 Boltzmann distribution of free H<sub>2</sub> suggested the promotion 10 of the o-p conversion at higher temperatures. These results indicated the feasibility of PBAs having a defective porous 11 framework as swift and efficient o-p conversion catalysts. 12 13

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## 20 **References and Notes**

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- 21 22 23 24 25 26 27 28 29 30 31 32 33 34 a) A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen, Cambridge University Press, London, 1935, b) J. W. Leachman, R. T Jacobsen, S. G. Penoncello, E. W. Lemmon, J. Phys. Chem. 2009, 38, 721.
  - a) R. B. Scott, F. G. Brickwedde, H. C. Urey, M. H. Wahl, J. 2 Chem. Phys. 1934, 2, 454. b) K. Motizuki, T. Nagamiya, J. Phys. Soc. Jpn. 1956, 11, 93. c) F. Schmidt, Phys. Rev. B 1974, 10, 4480. d) I. F. Silvera, Rev. Mod. Phys. 1980, 52, 393.
  - 3 a) A. H. Larsen, F. E. Simon, C. A. Swenson, Rev. Sci. Instrum. 1948, 19, 266. b) G. E. Schmauch, A. H. Singleton, Eng. Chem. 1964, 56, 20. c) S. A. Sherif, N. Zeytinoglu, T. N. Vezirğlu, Int. J. Hydrogen Energy 1997, 22, 683.
- 4 a) K. F. Bonhoeffer, P. Harteck, Z. Phys. Chem. 1929, 4B, 113. b) L. Farkas, L. Sandler, J. Chem. Phys. 1940, 8, 24. c) D. H. 35 36 37 38 Weitzel, O. E. Park, Rev. Sci. Instrum. 1956, 27, 57. d) D. H. Weitzel, W. V. Loebenstein, J. W. Draper, O. E. Park, J. Res. Natl. Bur. Std. 1958, 60, 221. e) K. G. Petzinger, D. J. Scalapino, Phys. Rev. B 1973, 8, 266. f) Y. Ishii, Prog. Surf. Sci. 1986, 21, 39 163. g) E. Ilisca, Prog. Surf. Sci. 1992, 41, 217. h) S. Paris, E. Ilisca, J. Phys. Chem. A 1999, 103, 4964.
- 40 41 5 a) P. Avouris, D. Schmeisser, J. E. Demuth, Phys. Rev. Lett. 42 43 1982, 48, 199. b) S. Andersson, J. Harris, Phys. Rev. Lett. 1982, 48, 545. c) E. Ilisca, Phys. Rev. Lett. 1991, 66, 667. d) K. 44 Fukutani, K. Yoshida, M. Wilde, W. A. Diño, M. Matsumoto, T. 45 Okano, Phys. Rev. Lett. 2003, 90, 096103. e) K. Niki, T. 46 Kawauchi, M. Matsumoto, K. Fukutani, T. Okano, Phys. Rev. B 47 48 2008, 77, 201404. f) K. Fukutani, T. Sugimoto, Prog. Surf. Sci. 2013, 88, 279. g) T. Sugimoto, K. Fukutani, Phys. Rev. Lett. 49 2014, 112, 146101.
- 50 51 52 53 54 55 56 57 58 59 6 a) N. Watanabe, Y. Kimura, A. Kouchi, T. Chigai, T. Hama, V. Pirronello, Astrophys. J. Lett. 2010, 714, L233. b) T. Sugimoto, K. Fukutani, Nat. Phys. 2011, 7, 307. c) M. Chehrouri, J.-H. Fillion, H. Chaabouni, H. Mokrane, E. Congiu, F. Dulieu, E. Matar, X. Michaut, J. L. Lemaire, Phys. Chem. Chem. Phys. 2011, 13, 2172. d) T. Hama, K. Kuwahata, N. Watanabe, A. Kouchi, Y. Kimura, T. Chigai, V. Pirronello, Astrophys. J. 2012, 757, 185. e) H. Ueta, N. Watanabe, T. Hama, A. Kouchi, Phys. Rev. Lett. 2016, 116, 253201.
- 7 a) E. Ilisca, Eur. Phys. Lett. 2013, 104, 18001. b) E. Ilisca, F. 60 Ghiglieno, Eur. Phys. J. B 2014, 87, 235.
- 61 8 a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, Science 2002, 295, 469. b) S. Kitagawa, 62 63 R. Kitaura, S. Noro, Angew. Chem., Int. Ed. 2004, 43, 2334. c) J. 64 L. C. Rowsell, O. M. Yaghi, Micropor. Mesopor. Mater. 2004,

73, 3. d) G. Férey, Chem. Soc. Rev. 2008, 37, 191. e) G. Férey, C. Serre, Chem. Soc. Rev. 2009, 38, 1380.

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- 9 67 a) S. A. FitzGerald, K. Allen, P. Landerman, J. Hopkins, J. 68 Matters, R. Myers, J. L. C. Rowsell, Phys. Rev. B 2008, 77, 69 224301. b) S. A. FitzGerald, J. Hopkins, B. Burkholder, M. 70 71 72 73 74 75 76 77 78 79 80 81 Friedman, J. L. C. Rowsell, Phys. Rev. B 2010, 81, 104305. c) N. Nijem, J.-F. Veyan, L. Kong, H. Wu, Y. Zhao, J. Li, D. C. Langreth, Y. J. Chabal, J. Am. Chem. Soc. 2010, 132, 14834. d) T. Kosone, A. Hori, E. Nishibori, Y. Kubota, A. Mishima, M. Ohba, H. Tanaka, K. Kato, J. Kim, J. A. Real, S. Kitagawa, M. Takata, R. Soc. open sci. 2015, 2, 150006.
  - 10 a) S. S. Kaye, J. R. Long, J. Am. Chem. Soc. 2005, 127, 6506. b) K. W. Chapman, P. D. Southon, C. L. Weeks, C. J. Kepert, Chem. Commun. 2005, 3322. c) M. R. Hartman V. K. Peterson, Y. Liu, S. S. Kaye, J. R. Long, Chem. Mater. 2006, 18, 3221. d) S. S. Kaye, J. R. Long, Catal. Today 2007, 120, 311. e) S. Natesakhawat, J. T. Culp, C. Matranga, B. Bockrath, J. Phys. Chem. C 2007, 111, 1055. f) L. Reguera, C. P. Krap, J. Balmaseda, E. Reguera, J. Phys. Chem. C 2008, 112, 15893. g) J. Jiménez-Gallegos, J. Rodríguez-Hernández, H. Yee-Madeira, E. Reguera, J. Phys. Chem. C 2010, 114, 5043. h) C. P. Krap, J. Balmaseda, L. F. del Castillo, B. Zamora, E. Reguera, Energy Fuels 2010, 24, 581. i) C. P. Krap, J. Balmaseda, B. Zamora, E. Reguera, Int. J. Hydrog. Energy 2010, 35, 10381. j) L. Hu, P. Zhang, Q. Chen, H. Zhong, X. Hu, X. Zheng, Y. Wang, N. Yan, Cryst. Growth Des. 2012, 12, 2257. k) P. Bhatt, S. Banerjee, S. Anwar, M. D. Mukadam, S. S. Meena, S. M. Yusuf, ACS Appl. Mater. Interfaces 2014, 6, 17579.
  - 11 a) T. Mallah, S. Thiébaut, M. Verdaguer, P. Veillet, Science 1993, 262, 1554. b) S. Ferlay, T. Mallah, R. Ouahès, P. Veillet, M. Verdaguer, Nature 1995, 378, 701. c) O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Science 1996, 272, 70. d) M. Verdaguer, A. Bleuzena, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain, Coord. Chem. Rev. 1999, 190-192, 1023. e) S. M. Holmes, G. S. Girolami, J. Am. Chem. Soc. 1999, 121, 5593. f) Ø. Hatlevik, W. E. Buschmann, J. Zhang, J. L. Manson and J. S. Miller, Adv. Mater. 1999, 11, 914. g) N. Usuki, M. Yamada, M. Ohba, H. Ōkawa, J. Solid State Chem. 2001, 159, 328. h) S. Ohkoshi, K. Aria, Y. Sato, K. Hashimoto, Nature Mater. 2004, 3, 857. i) T. Uemura, M. Ohba, S. Kitagawa, Inorg. Chem. 2004, 43, 7339. j) M. Zentkovál, Z. Arnold, J. Kamarád, V. Kavečanský, M. Lukáčová, S. Maťaš1, M. Mihalik, Z. Mitróová, A. Zentko, J. Phys.: Condens. Matter. 2007, 19, 266217. k) S. S. Kaye, H. J. Choi, J. R. Long, J. Am. Chem. Soc. 2008, 130, 16921. 1) H. Ohmagari, R. Ohtani, M. Nakaya, M. Ohba, M. Nakamura, L. F. Lindoy, O. Sato, S. Hayami, Dalton Trans. 2016, 45, 16784.
  - 12 a) H. U. Guedel, H. Stucki, A. Ludi, Inorganica Chim. Acta 1973, 7, 121. b) Z. Lü, X. Wang, Z. Liu, F. Liao, S. Gao, R. Xiong, H. Ma, D. Zhang, D. Zhu, Inorg. Chem. 2006, 45, 999. c) W. Dong, W. Zhang, Y. Ou-Yang, L.-N. Zhu, D.-Z. Liao, K. Yoshimura, Z.-H. Jiang, S.-P. Yana, P. Cheng, J. Magn. Magn. Mater. 2007, 309, 7. d) S. Adak, L. L. Daemen, M. Hartl, D. Williams, J. Summerhill, H. Nakotte, J. Solid State Chem., 2011, 184, 2854.
- 120 13 a) K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 1985, 57, 603. b) M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S.W. Sing, Pure Appl. Chem. 2015, 87, 1051.
  - a) H. P. Gush, W. F. Hare, E. J. Allen, H. L. Welsh, Can. J. Phys. 14 1960, 38, 176. b) W. L. Mao, H. K. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M. Somayazulu, Y. Zhao, Science 2002, 297, 2247. c) T. A. Strobel, E. D. Sloan, C. A. Koh, J. Chem. Phys. 2009, 130, 014506. d) M. J. Matthews, G Petitpas, S. M. Aceves, Appl. Phys. Lett. 2011, 99, 081906. e) L. M. Sutherland, J. N. Knudson, M. Mocko, R. M. Renneke, Nucl. Instrum. Meth. Phys. Res. A 2016, 810, 182.