

A Water Stable Magnesium MOF That Conducts Protons over 10^{-2} S cm^{-1}

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S Supporting Information

ABSTRACT: From the outset of the study of MOFs as proton conductors, both conductivity and hydrolytic robustness of the materials have needed to be improved. Here, we report a layered magnesium carboxyphosphonate framework, PCMOF10, that shows an extremely high proton conductivity value of 3.55×10^{-2} S·cm⁻¹ at 70 °C and 95% RH. Moreover, PCMOF10 is water stable owing to strong Mg phosphonate bonding. The 2,5-dicarboxy-1,4-benzenediphosphonic acid (H₆L) linker anchors a robust backbone and has hydrogen phosphonate groups that interact with the lattice water to form an efficient proton transfer pathway.

Growing global energy demands require research efforts aimed at the discovery and development of alternative energy technologies.¹ Fuel cell technology is a key part of present and future opportunities.² Better electrolyte materials are critical to enhancing cost efficiency of fuel cells. With regard to research on potential electrolyte materials, a wide variety of compounds such as ceramic oxides and hydroxides,³ oxoacids,⁴ polymers,⁵ carbon nanotubes,⁶ and their blends and/or adducts have been investigated as proton conductors.

Metal–organic frameworks (MOFs) have emerged as novel proton conducting materials.^{7,8} The crystallinity and tunability of MOFs offer a convenient platform to design materials for targeted applications. While gas permeability is a detriment to a fuel cell membrane, the micropores in MOFs can be used to advantage by loading them with proton carriers such as water or a less volatile species. Furthermore, the precise pore structure and even location of guest carriers in a MOF can be visualized creating a useful handhold for modeling proton conduction in solids. MOFs can be fabricated into thin films,⁹ and incorporated into mixed-matrix membranes¹⁰ thus increasing their viability in industrial applications.

Proton-conducting MOFs (PCMOFs) broadly fall under two categories: those of interest for operation under low-temperature (<100 °C) hydrated conditions, and those that conduct protons under anhydrous conditions above 100 °C.⁸ As in any proton electrolyte, an efficient hydrogen bonded pathway between proton carriers is key with the operating temperature range often being dictated by the volatility of the carrier, typically water.^{11,12} Complementarity of the pK_a's of the functional groups in the proton transfer pathway plays a key role in determining conductivity.

While the crystallinity of PCMOFs enables their use as model for developing structure activity relationships in proton

conductors, the promise of genuine applicability has typically required both higher values of proton conductivity and also more robust networks than reported for PCMOFs to date. A decade ago, the robustness issue could be generalized to MOF materials, but significant advances in this regard have been made since then¹³ including for PCMOFs.^{14,15b} There have also been steadily increasing values of proton conduction in MOFs reported, and there are now a handful of materials that give proton conduction values in excess of the 10^{-2} S·cm⁻¹ benchmark, albeit typically in a less robust framework.^{15a} Here, we report a proton-conducting MOF, Mg₂(H₂O)₄(H₂L)·H₂O (H₆L = 2,5-dicarboxy-1,4-benzene-diphosphonic acid), PCMOF10, that merges water stability and high proton conduction. PCMOF10 is a new material with a robust layered structure that conducts protons at 3.55×10^{-2} S·cm⁻¹ at 70 °C and 95% RH. X-ray crystallography confirms the presence of hydrogen phosphonate groups and positionally ordered water molecules to form an efficient proton transfer pathway in the MOF pores. Beyond the reproducible high humidity conductivity measurements, water stability is confirmed by immersion in water and retention of both the structure and properties of PCMOF10.

The dicarboxy, diphosphonate ligand, H₆L, was synthesized by a previously published protocol.¹⁶ PCMOF10 was synthesized solvothermally in a Teflon-lined autoclave, by adding Mg(NO₃)₂·6H₂O (0.41 mmol) and H₆L (0.48 mmol) to a mixture of 3 mL methanol and 3 mL H₂O and heating to 150 °C. Colorless plate-like single crystals were obtained after 72 h. The powder X-ray diffraction (PXRD) pattern of a bulk sample matched that simulated from the single crystal X-ray data (Figure 2). PCMOF10 crystallizes with the formula Mg₂(H₂O)₄(H₂L)·H₂O, and possesses a two-dimensional layered architecture. The structure can be envisaged to be composed of edge-shared zigzag ladders (along the *c*-direction) made up of MgO₆ octahedra and CPO₃ tetrahedra, forming four- and eight-membered rings. These ladders are pillared by H₂L molecules to form a two-dimensional grid-like structure (Figure 1a). These layers stack along the *a*-axis and are separated by a distance of 8.753(4) Å. Each of the magnesium atoms (Mg(1) and Mg(2)) is octahedrally coordinated to two water molecules, a carboxylate oxygen, and three phosphonate oxygens (Mg–O = 1.951(3)–2.164(4) Å). Each phosphonate group is monoprotonated (O(5), O(12)), and these, along with coordinated water molecules (O(6), O(9)–O(11)) and carboxylate oxygen atoms (O(13), (O14)) line the interlayer

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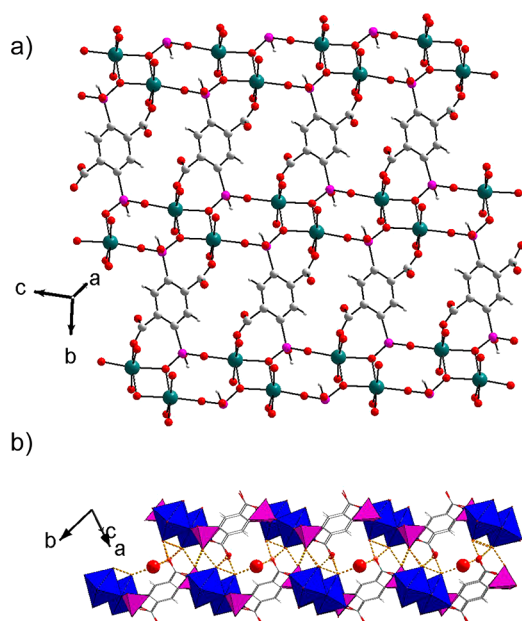


Figure 1. Single crystal structure of PCMOF10. (a) Zigzag ladders pillared by ligand molecules to give a two-dimensional grid. (b) Hydrogen bonding array formed via O–H...O type hydrogen bonds between the lattice water molecule and intralayer oxygen atoms. Lattice water molecules are shown in brown.

spaces. These groups interact together with lattice water molecules ($O(w)$) to form an extensive O–H...O hydrogen-bond network (Figure 1b, Figure S7, Table S2, Supporting Information). The donor–acceptor ($D\cdots A$) distances of these hydrogen bonds range from 2.200 (3) to 3.030(3) Å. The shortest hydrogen bond distance is observed between the lattice water molecule (O_w) and one of the coordinated water molecules ($O10$), while the longest is observed between the lattice water molecule and a carboxylate oxygen atom ($O14$). The presence of this hydrogen-bonded pathway in a hydrated and acidic interlayer region suggested that this material could be a good proton conductor; this also necessitated studying water stability.

To assess the hydrolytic stability of PCMOF10, an as-synthesized sample was soaked in water for a week. PCMOF10 shows excellent water stability as the PXRD patterns of the as-synthesized and water-soaked samples were in good agreement with each other (Figure 2). PXRD was also run on a sample while actually immersed in water to confirm that the structure was not swelling upon hydration, a possibility with a layered material. This resilience toward swelling is possibly due to the fact that aromatic rings within a layer are not pi-stacked (separated by 5.59(5) Å) meaning that water can pass between the rings and hence layers. Additionally, mass balance confirmed the water-immersed sample was not dissolving. Regarding thermal stability, thermogravimetric analysis (TGA) (Figure S1) showed a weight loss of 19.03% below 210 °C, attributable to the loss of lattice and coordinated water molecules (calcd: 19.54%). The loss of water up to the temperature of 210 °C indicates the strong interaction of the solvents with the framework. Beyond this temperature, there is a gradual weight loss, likely involving the decomposition of the organic moiety. Of note here is that whereas phosphonate coordination chemistry can promote more stable materials, this is typically accompanied by an increasingly amorphous nature.

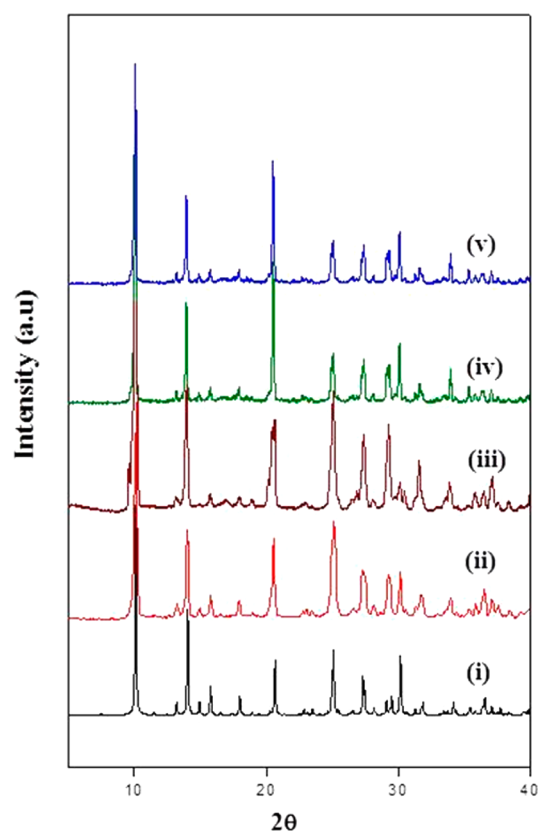


Figure 2. PXRD patterns of PCMOF10: (i) simulated, (ii) as-synthesized, (iii) wet sample, (iv) treated with water for 1 week, (v) postimpedance.

In PCMOF10, the water stability is merged with order in single crystal and bulk phases.

To assess proton conductivity, AC impedance analysis was carried out on an as-synthesized, powdered sample of PCMOF10. Figure 3 shows Nyquist plots as a function of temperature at 95% RH. The semicircle in the high-frequency region represents the bulk and grain boundary resistances, while the low frequency tail represents the blocking of the mobile charge at the electrode interface, indicating ionic conduction. The conductivities at each temperature were measured after equilibration for a period of 24 h. At 95% RH, PCMOF10 exhibits a proton conductivity of $3.55 \times 10^{-2} \text{ S cm}^{-1}$ at 70 °C. This is among the very highest values for any proton-conducting MOF and was reproducible after consecutive heating and cooling cycles (Figure 3b). Above this temperature, a drop in conductivity is observed as is typical for many water-mediated proton conductors that undergo dehydration at elevated temperatures.^{7,8,17} This is supported by impedance measurements performed under varying humidity conditions (Figure S4). At 70 °C, the conductivity value of $3.55 \times 10^{-2} \text{ S cm}^{-1}$ drops to $4.17 \times 10^{-4} \text{ S cm}^{-1}$ at 70% RH, after which it decreases rapidly to $0.72 \times 10^{-7} \text{ S cm}^{-1}$ at 40% RH (Figure S2). The high humidity dependence of proton conductivity observed here is typical in MOFs as individual conducting pathways involving water can be confined to narrow and rigid pores.

The activation energy for proton transfer in PCMOF10 is 0.4 eV, which is on the higher end of values for a Grotthuss mechanism (Figure S3). The proton transfer pathway (Figure 1b, Figure S7) in PCMOF10 involves lattice and coordinated

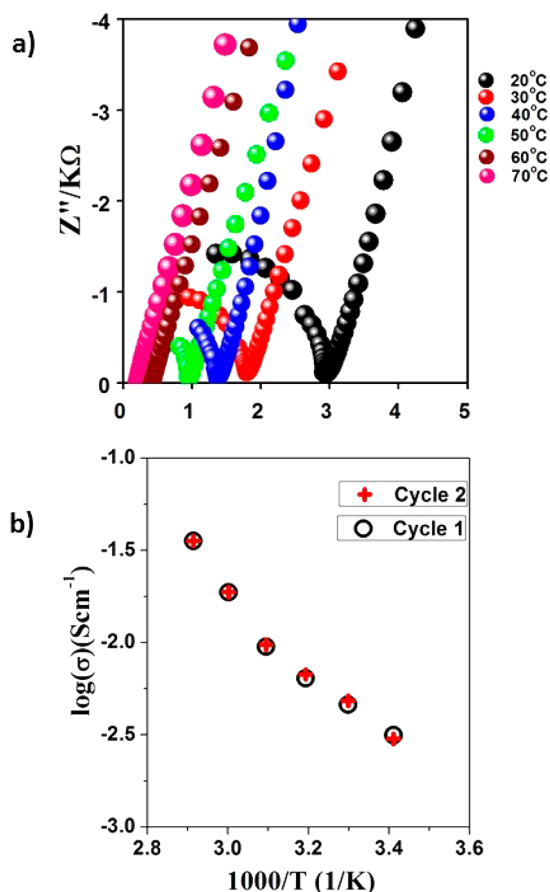


Figure 3. (a) Nyquist plots from AC impedance data of PCMOF10 at 95% RH and varying temperatures between 20 and 70 °C. (b) Log of conductivity as a function of inverse temperature for repeat cycles of PCMOF10.

water molecules, along with oxygen atoms from both the hydrogen phosphonate and carboxylate groups. It is likely that the activation energy value could be a consequence of the heterogeneity of the functional groups possessing varying pK_a 's lining the interlayer spaces. Similar behavior has been reported earlier by Kitagawa et al. in a series of substituted MIL-53 frameworks.¹⁸ Proton conductivity studies on $M(OH)(bdc-R)$ ($M = Fe, Al$; $H_2bdc = 1,4$ -benzenedicarboxylic acid) frameworks revealed that, for frameworks with heterogeneous groups ($R = -H, -NH_2$), the E_a values were in the range of 0.45–0.47 eV, while for frameworks with homogeneous groups ($R = -COOH$), E_a values of 0.21 eV were observed. The integrity of the sample in the present study is maintained, as conformed first by the reproducible conduction data, and this is corroborated by the pre- and postimpedance PXRD patterns (Figure 2). Monoprotonated phosphonic acid groups, like those observed in PCMOF10, have been reported in other MOFs.¹⁹ Cabeza et al. recently reported an alkaline earth metal phosphonocarboxylate MOF, CaPiPhtA, which possesses a pillared layered structure in which monoprotonated phosphonic acid groups protrude into interlayer spaces.¹⁷ This MOF and its derivatives exhibited conductivity values of the order of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C and 98% RH.

PCMOF10 is among the highest proton conducting MOFs under hydrated conditions; there are only a few other MOFs that exhibit conductivities of this order. These include: $\{[(Me_2NH_2)_3(SO_4)]_2[Zn_2(ox)_3]\}_n$ ^{11d} that consists of anionic

zinc oxalate layers, $[Zn_2(ox)_3]^{2-}_n$ interpenetrated by a cationic supramolecular net of $[(Me_2NH_2)_3SO_4]^+_n$. It conducts protons at $4.2 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ under ambient temperatures and 98% RH; PCMOF-2^{1/2}, reported earlier by our group,^{15a} is a mixed sulfonate-phosphonate MOF containing 1D channels which conducts protons at $2.1 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 85 °C and 90% RH; UiO-66(SO_3H)₂,¹⁴ a UiO-66 framework functionalized with sulfonic acid groups that shows a high conductivity of $8.4 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 80 °C and 90% RH; and $H_2SO_4@MIL-101$,²⁰ a MIL-101 framework whose pores were loaded with H_2SO_4 , which exhibits a conductivity of $6.0 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 80 °C and 20% RH.

Here, we have presented a water stable MOF, PCMOF10, which conducts protons above $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 70 °C and 95% RH. Of the five MOF materials that obtain the benchmark of $10^{-2} \text{ S}\cdot\text{cm}^{-1}$, only the UiO-66 example and PCMOF10 are stable in water. In the case of PCMOF10, water stability does not mean simply compositional stability but also resistance to swelling. These aspects are critical for the continued development and future implementation of PCMOFs in actual devices such as fuel cell membrane electrode assemblies. Finally, while there are now some very robust MOF platforms amenable to a wide range of functionalization,^{7,8,21,22} PCMOF10 represents a new MOF structure showing there is still opportunity for discovery of new frameworks.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthesis procedures, impedance analysis, crystallographic details. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04399.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) U.S. Department of Energy, U.S. Energy Information Administration. International Energy Outlook 2013 (Report: DOE/EIA-0484(2013)), 2013.
- (2) U.S. Department of Energy, Fuel Cell Technologies Office. Multi-Year Research, Development, Demonstration Plan. 3.4. Technical Plan—Fuel Cells, 2012.
- (3) (a) Iwahara, H. *Solid State Ionics* **1996**, 86–88, 9. (b) Wang, S.; Zhao, F.; Zhang, L.; Chen, F. *Solid State Ionics* **2012**, 213, 29.
- (c) Kreuer, K.-D. *Annu. Rev. Mater. Res.* **2003**, 33, 333.
- (4) (a) Vilčiauskas, L.; de Araujo, C. C.; Kreuer, K.-D. *Solid State Ionics* **2012**, 212, 6. (b) Boysen, D. A.; Uda, T.; Chisholm, C. R. I.; Haile, S. M. *Science* **2004**, 303, 68.
- (5) (a) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, 104, 4535. (b) Brum, F. J. B.; Zanatta, F. G.; Marczyński, E. S.; Forte, M. M. C.; Pollet, B. *Solid State Ionics* **2014**, 263, 62. (c) Portale, G.; Carbone, A.; Martinelli, A.; Passalacqua, E. *Solid State Ionics* **2013**, 252, 62.
- (6) (a) Jheng, L.-C.; Huang, C.-Y.; Hsu, S. L. *Int. J. Hydrogen Energy* **2013**, 38, 1524. (b) Asgari, M. S.; Nikazar, M.; Molla-abbasi, P.; Hasani-Sadrabadi, M. M. *Int. J. Hydrogen Energy* **2013**, 38, 5894.

(7) Yoon, M.; Suh, K.; Natarajan, S.; Kim, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 2.

(8) (a) Ramaswamy, P.; Wong, N. E.; Shimizu, G. K. H. *Chem. Soc. Rev.* **2014**, *43*, 5913. (b) Horike, S.; Chen, W.; Itakura, T.; Inukai, M.; Umeyama, D.; Asakura, H.; Kitagawa, S. *Chem. Commun.* **2014**, *50*, 10241. (c) Tang, Q.; Liu, Y.; Liu, S.; He, D.; Miao, J.; Wang, X.; Yang, G.; Shi, Z.; Zheng, Z. *J. Am. Chem. Soc.* **2015**, *137*, 913.

(9) (a) Liu, J.; Sun, F.; Zhang, F.; Wang, Z.; Zhang, R.; Wang, C.; Qiu, S. *J. Mater. Chem.* **2011**, *21*, 3775. (b) Bradshaw, D.; Garai, A.; Huo, J. *Chem. Soc. Rev.* **2012**, *41*, 2344. (c) Xu, G.; Otsubo, K.; Yamada, T.; Sakaida, S.; Kitagawa, H. *J. Am. Chem. Soc.* **2013**, *135*, 7438.

(10) (a) Liang, X.; Zhang, F.; Feng, W.; Zou, X.; Zhao, C.; Na, H.; Liu, C.; Sun, F.; Zhu, G. *Chem. Sci.* **2013**, *4*, 983. (b) Wu, B.; Lin, X.; Ge, L.; Wu, L.; Xu, T. *Chem. Commun.* **2013**, *49*, 143.

(11) (a) Yamada, T.; Sadakiyo, M.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 3144. (b) Sadakiyo, M.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 9906. (c) Pardo, E.; Train, C.; Gontard, G.; Boubekeur, K.; Fabelo, O.; Liu, H.; Dkhil, B.; Lloret, F.; Nakagawa, K.; Tokoro, H.; Ohkoshi, S.; Verdaguer, M. *J. Am. Chem. Soc.* **2011**, *133*, 15328. (d) Nagarkar, S. S.; Unni, S. M.; Sharma, A.; Kurungot, S.; Ghosh, S. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 2638.

(12) Horike, S.; Umeyama, D.; Kitagawa, S. *Acc. Chem. Res.* **2013**, *46*, 2376.

(13) Burtch, N. C.; Jasuja, H.; Walton, K. S. *Chem. Rev.* **2014**, *114*, 10575 and references within.

(14) Phang, W. J.; Jo, H.; Lee, W. R.; Song, J. H.; Yoo, K.; Kim, B.; Hong, C. S. *Angew. Chem., Int. Ed.* **2015**, *54*, 5142.

(15) (a) Kim, S. R.; Dawson, K. W.; Gelfand, B. S.; Taylor, J. M.; Shimizu, G. K. H. *J. Am. Chem. Soc.* **2013**, *135*, 963. (b) Taylor, J. M.; Dawson, K. W.; Shimizu, G. K. H. *J. Am. Chem. Soc.* **2013**, *135*, 1193.

(16) Ivan, N.; Benin, V.; Morgan, A. B. *Synth. Commun.* **2013**, *43*, 1831.

(17) Bazaga-García, M.; Colodrero, R. M. P.; Papadaki, M.; Garczarek, P.; Zoń, J.; Olivera-Pastor, P.; Losilla, E. R.; León-Reina, L.; Aranda, M. A. G.; Choquesillo-Lazarte, D.; Demadis, K. D.; Cabeza, A. *J. Am. Chem. Soc.* **2014**, *136*, 5731.

(18) Shigematsu, A.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2011**, *133*, 2034.

(19) (a) Bazaga-García, M.; Papadaki, M.; Colodrero, R. M. P.; Olivera-Pastor, P.; Losilla, E. R.; Nieto-Ortega, B.; Aranda, M. A. G.; Choquesillo-Lazarte, D.; Cabeza, A.; Demadis, K. D. *Chem. Mater.* **2015**, *27*, 424. (b) Colodrero, R. M. P.; Angeli, G. K.; Bazaga-García, M.; Olivera-Pastor, P.; Villemain, D.; Losilla, E. R.; Martos, E. Q.; Hix, G. B.; Aranda, M. A. G.; Demadis, K. D.; Cabeza, A. *Inorg. Chem.* **2013**, *52*, 8770.

(20) Ponomareva, V. G.; Kovalenko, K. A.; Chupakhin, A. P.; Dybtsev, D. N.; Shutova, E. S.; Fedin, V. P. *J. Am. Chem. Soc.* **2012**, *134*, 15640.

(21) (a) Bao, S.-S.; Otsubo, K.; Taylor, J. M.; Jiang, Z.; Zheng, L.-M.; Kitagawa, H. *J. Am. Chem. Soc.* **2014**, *136* (26), 9292–9295. (b) Kundu, T.; Sahoo, S. C.; Banerjee, R. *Chem. Commun.* **2012**, *48*, 4998.

(22) (a) Bureekaew, S.; Horike, S.; Higuchi, M.; Mizuno, M.; Kawamura, T.; Tanaka, D.; Yanai, N.; Kitagawa, S. *Nat. Mater.* **2009**, *8*, 831. (b) Mallick, A.; Kundu, T.; Banerjee, R. *Chem. Commun.* **2012**, *48*, 8829. Shigematsu, A.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2011**, *133*, 2034. (c) Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, I. L.; Shimizu, G. K. H. *Nat. Chem.* **2009**, *1*, 705. (d) Dong, X.-Y.; Wang, R.; Wang, J.-Z.; Zang, S.-Q.; Mak, T. C. W. *J. Mater. Chem. A* **2015**, *3*, 641.