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A Large Molecular Cluster with High Proton Release Capacity

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We present a single molecular polyoxometalate cluster ($K_{41}[(P_2W_{12}Nb_6O_{62})_6\{Mn_3(OH)_3(H_2O)_6\}_4\{Mn_3Na(H_2O)_{16}\}] \cdot 26H_2O$) with controllable releasing large amounts of protons (~40 per molecule) in its aqueous solution upon addition of a base. The deprotonation/protonation process is reversible with the clusters remaining intact. This molecule can also absorb up to 11 protons per cluster when acid HCl was added into its original aqueous solution. To best of our knowledge, such large proton absorption/release capacity along with excellent stability is unprecedented.

Polyoxometalates (POMs) are a large family of metal-oxo clusters with well-defined structures, diverse properties, and wide applications.^{1–21} As the solutions of metal aquo complexes can protonate their coordinated water ligands,^{22, 23} some POMs can act as weak Brønsted acids.^{24–31} For example, four protons on the lacunary sites of Keggin-type POMs are acidic and can be neutralized by TBAOH in DMSO;^{28, 29} Mizuno et al. illustrated the reversible protonation/deprotonation behavior of silicodcatungstates;³¹ we also reported that Keplerate-type $\{Mo_{72}Fe_{30}\}$, $\{Mo_{72}Cr_{30}\}$ and $\{Mo_{72}V_{30}\}$ behaved like weak acids by deprotonating several protons from their water ligands coordinated to the metal centers, depending on the environmental pH.^{27, 30} Such POM aqueous solutions are usually acidic.

However, these clusters can only release a few protons and/or become unstable at higher pH when lots of base is introduced, and this limits their applications. Here we show a single POM

molecule with formula $K_{41}[(P_2W_{12}Nb_6O_{62})_6\{Mn_3(OH)_3(H_2O)_6\}_4\{Mn_3Na(H_2O)_{16}\}] \cdot 26H_2O$ ($K_{41}\text{-1} \cdot 26H_2O$, **K-1**, Figure 1),³² which is an extremely weak acid but can release a large number of protons upon addition of base from its coordinated water ligands. The polyanion consists of six Well-Dawson phosphoniobotungstate $\{P_2W_{12}Nb_6\}$ units, being alternately connected by four trinuclear $\{Mn_3(OH)_3(H_2O)_6\}$ clusters and four $\{Mn(H_2O)_4\}$ moieties in an egg fashion, as reported earlier (Figure S1 and Table S1).³² It

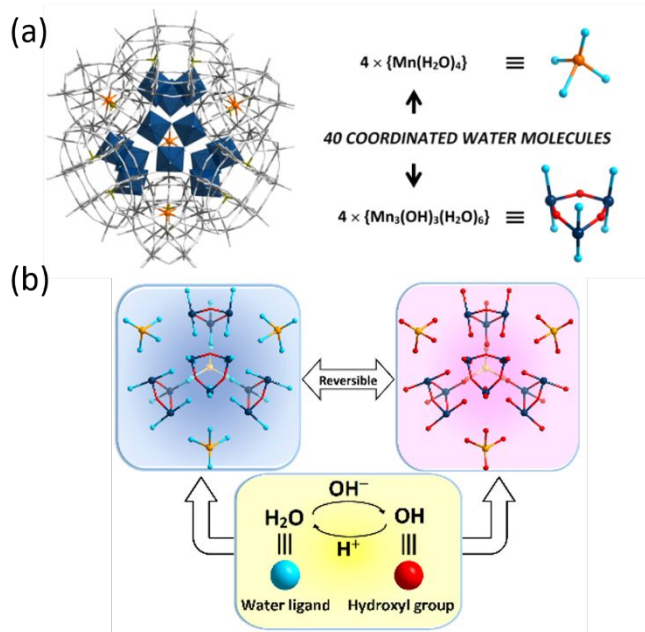


Figure 1. Combined polyhedral/ball-and-stick representation of polyanion **1** and illustration of the reversible protonation/deprotonation process of the cluster. (a) Color code: MnO_6 octahedra (dark teal), Mn/Na spheres (light orange), W/Nb/O (gray), P (dark yellow). (b) The reversible transformation between the water ligands from the protonated form **1a** (blue) and the hydroxyl groups from the deprotonated

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form **1b** (red) of the cluster upon base/acid titration. Water ligand is used as an example here.

carries 41 negative charges with 41 K^+ cations as counterions (Table S2). To our understanding, in aqueous solution, all 26 crystal water molecules will be likely released because they are not covalently bonded with the cluster; however, the 40 water ligands, coordinated to Mn(II) and Mn(III), are capable to release protons in mild basic environment, along with the 12 bridge oxygen atoms.

To test our hypothesis, we titrated concentrated KOH aqueous solutions into the solution of **K-1** and monitored its pH change. **K-1** can be easily dissolved in water. The number of protons released per cluster upon titration can be calculated from the solution pH when compared with theoretical pH values. For all the experiments, deionized water was used after boiling for sample preparation and all the sample preparation and titration experiments were performed in a glovebox (supplied with N_2), which was free of carbon dioxide (CO_2). In addition, titration of the same KOH solution into deionized water was conducted as a control group to eliminate the effect of CO_2 residue in either solvent or glove box (Table S4).

The pH of a 0.30 mg/mL **K-1** aqueous solution and deionized water are 8.14 and 6.69 (Table S3), respectively, which suggests that no free protons were released from the cluster in its solution. Interestingly, when extra base was added into the aqueous solution of **K-1**, the pH of the resulting solution did not increase greatly compared to the calculated value. For example, when 13.1 equivalents of KOH ($pH = 11.86$, $n_{KOH}/n_{POM} = 13.1:1$) was added into 1.0 mL of 0.30 mg/mL **K-1** solution at room temperature, the pH of the mixed solution quickly increased to 8.80. This value did not change in the following several days and is remarkably lower than the pH value of 10.03, when the same amount of KOH is added to 1.0 mL deionized water. This suggests that substantial protons are released from **1** to neutralize the added OH^- . Calculation shows that at this point, each **1** cluster can release 9.4 protons, and neutralized 72% of the added base.

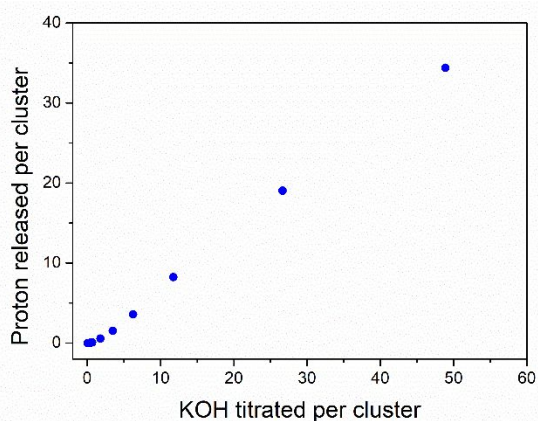


Figure 2. The number of released protons per cluster vs. the amount of added KOH per cluster.

Further KOH titration induces more proton release from **K-1** (Table S5): when 48.9 equivalents of KOH was added into the **K-1** aqueous solution ($n_{KOH}/n_{POM} = 48.9:1$), the solution pH

increased to 9.35, indicating that 34.4 protons were released from each of **1** based on calculation. That is, ~70% of added base was neutralized. These protons can come from the 40 coordinated water molecules, where each coordinated water is expected to provide one proton and theoretically, 40 protons could be released by each cluster (Figure 1). Overall, a nearly linear relationship between the number of released protons versus the amount of KOH added (Figure 2) was found, which indicates an acid-base reaction. During the titration, **K-1** solution kept clear and the clusters are stable, as confirmed by IR, ESI-MS, UV-Vis, SAXS and dialysis studies (Figures S2-10 and Table S6). This cluster can release more protons if the titration continued. However, the solution would turn turbid and precipitation would be observed. It is possible that the 40 coordinated waters and twelve bridge oxygens render up to 92 potential protons, but we are concerned about the stability of **1** if too much base is added and considered that each **1** can release up to 40 protons. In another experiment, KOH were also titrated into the solution of **1** at higher concentration (1.0 mg/mL). The result suggests that each cluster can neutralize up to 12.8 OH^- if 16 equivalents of KOH was added (release of protons, Figures S11, S12). More KOH will lead to precipitation.

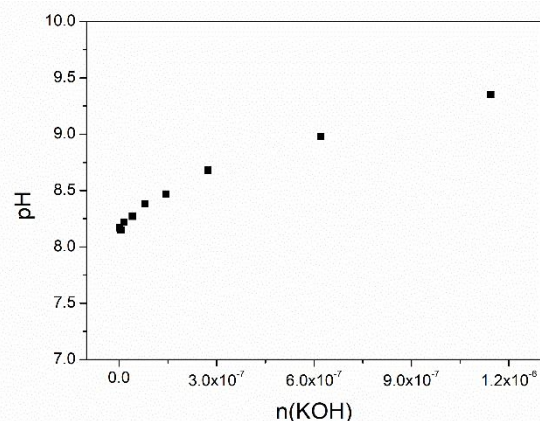


Figure 3. Titration curve of titrating concentrated KOH solution into 1.0 mL of 0.30 mg/mL **K-1** aqueous solution.

This nearly linear relationship between number of released protons versus the amount of added KOH, as well as ~70% neutralized base during titration, also suggests that the protons released by coordinated water ligands show continuous increments in successive acid dissociation constants (pK_a). For a weak polyprotic acid with large difference between successive pK_a , when being titrated with a strong base, it would show multiple distinguishable titration stages, with visible equivalent points (Figure S13, for example, titrating KOH into phosphorous acid solution); however, if the differences between successive pK_a values are small, the titration curve will not show any steep pH change, instead, a small but continuous pH change will be observed (Figure 3).³³ Because the deprotonated cluster will carry more negative charges, the deprotonation will become more and more difficult, as a result, leading to larger pK_a values. In other words, during the titration process, **1a** with different degrees in deprotonation co-existed with others, which causes

the pH changes small and continuous. Based on the results above, this is a neutralization process of the very weak acid **1** and OH⁻, with the transformation of the protonated form (**1a**) into its deprotonated form (**1b**, conjugated base of **1a**). It is unusual to see a single molecule releases such a large number of protons from its coordination waters, especially **1a** is an extremely weak acid (pH = 8.14 for its aqueous solution). This unique phenomenon differs from most of the known clusters. It is also expected that the deprotonated form **1b** can return to the protonated form **1a** with the addition of acid, i.e. the protonation/deprotonation process is reversible. When 1.0 mL 0.3 mg/mL **K-1** solution was titrated with 13 equivalents of KOH at room temperature, the pH value immediately goes up to ~8.8 as described. Followed by adding 13 equivalents of HCl, the solution returns to pH~8.3, which was stable for over one week. During the acidification process, each **1b** takes ~9.4 protons, same amounts of protons released from each **1a** when reacting with KOH, suggesting that the protonation/deprotonation process is reversible. In addition, this reversible protonation/deprotonation process is reproducible for at least three cycles, without showing any significant difference (Figure 4).

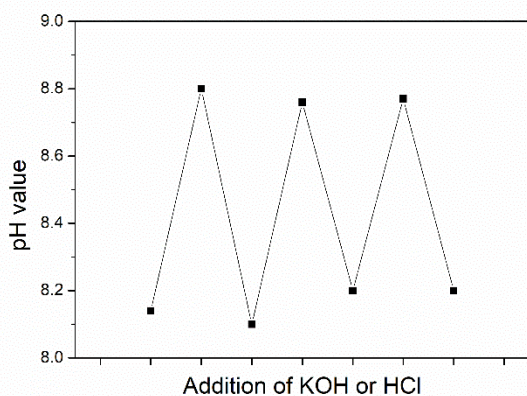


Figure 4. pH change of 0.30 mg/mL solution of **K-1** with the addition of 13 equivalents of KOH followed by the addition of same amounts of HCl in the three cycles.

For most simple transition metal ions, such as Mn²⁺, Cu²⁺, their solutions cannot tolerate such large amounts of extra base, where precipitation would be formed (low K_{sp} value).³⁴ Forming clusters is a good approach to protect transition metal ions in aqueous solution from precipitation in the presence of base. It should be noted that in our experiments, removal of carbon dioxide (CO₂) in water and air is necessary because CO₂ can neutralize the base in solution and therefore greatly affect the titration result (Figure S14 and Table S4). With CO₂, where the experiments were performed in air without special protection, the apparent pH values of titrated solutions (both titrated deionized water and solution of **K-1**) are much lower than those obtained in glovebox. For example, the pH value of freshly prepared **K-1** aqueous solution (0.3 mg/mL) in and out of a glovebox are 8.14 and 7.20, showing that the lower pH of the latter solution came from the deprotonation of dissolved CO₂

(H₂CO₃); accordingly, when the same amount of KOH (~7 equivalents) was titrated into the **K-1** aqueous solution, the measured pH values are 8.47 and 7.82. After titration, the pH values of the basic solutions in air would gradually increase in following several days and finally reach ~7 (Figure S15), which is completely different from the case in glovebox, where the pH of the titrated solution did not show any obvious change within one week.

Instead of base, when acid HCl, was titrated into **K-1** solution, the measured pH values are higher than the calculated values. This suggests that cluster **1** can also behave like a Brønsted base in the presence of an acid (Figure 5). Each **1** cluster can absorb up to ~11 protons if 26.6 equivalents of HCl was added, likely due to the proton attachment to the terminal oxygens (12 in total) of the cluster, and the addition of more acid cannot trigger further proton absorption.

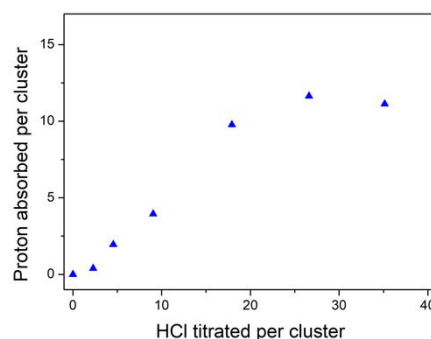


Figure 5. The number of absorbed protons per cluster vs. the amount of added HCl per cluster into 1.0 mL of 0.3 mg/mL solution of **K-1** at room temperature.

In summary, we report a completely reversible deprotonation/protonation process of the coordinated water molecules from a single molecular cluster in aqueous solution. Because of the large amount of protonated water ligands and terminal oxygens, this giant cluster can neutralize a large amount of extra base (up to 40) or acid (up to 12) with maintaining the pH of the solution within a relatively narrow range, showing a very high capacity of reversible releasing/absorbing protons. At the same time, the cluster exhibits impressive high stability when be exposed to large amount of base, distinguishing itself from simple salts of the same transition metal ions. Therefore, this cluster shows the potential as a high-capacity proton donor system with buffering features.

Conflicts of interest

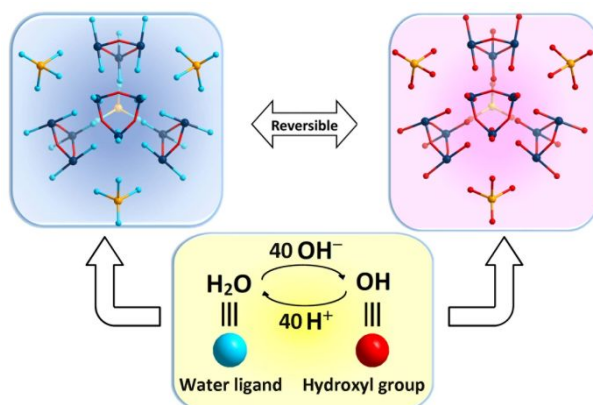
There are no conflicts to declare.

Acknowledgment

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Notes and references

- M. T. Pope and A. Müller, *Angew. Chem., Int. Ed.*, 1991, **30**, 34-48.
- L. Cronin and A. Müller, *Chem. Soc. Rev.*, 2012, **41**, 7333-7334.
- N. V. Izarova, M. T. Pope and U. Kortz, *Angew. Chem., Int. Ed.*, 2012, **51**, 9492-9510.
- B. Rausch, M. D. Symes, G. Chisholm and L. Cronin, *Science*, 2014, **345**, 1326-1330.
- K. Y. Monakhov, W. Bensch and P. Kögerler, *Chem. Soc. Rev.*, 2015, **44**, 8443-8483.
- J.-S. Qin, D.-Y. Du, W. Guan, X.-J. Bo, Y.-F. Li, L.-P. Guo, Z.-M. Su, Y.-Y. Wang, Y.-Q. Lan and H.-C. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 7169-7177.
- X.-B. Han, Y.-G. Li, Z.-M. Zhang, H.-Q. Tan, Y. Lu and E.-B. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 5486-5493.
- Z.-M. Zhang, T. Zhang, C. Wang, Z. Lin, L.-S. Long and W. Lin, *J. Am. Chem. Soc.*, 2015, **137**, 3197-3200.
- Y. Wu, R. Shi, Y.-L. Wu, J. M. Holcroft, Z. Liu, M. Frascioni, M. R. Wasielewski, H. Li and J. F. Stoddart, *J. Am. Chem. Soc.*, 2015, **137**, 4111-4118.
- Z. Xiao, K. Chen, B. Wu, W. Li, P. Wu and Y. Wei, *Eur. J. Inorg. Chem.*, 2016, **2016**, 808-811.
- W.-H. Fang, L. Zhang and J. Zhang, *J. Am. Chem. Soc.*, 2016, **138**, 7480-7483.
- P. Yin, B. Wu, E. Mamontov, L. L. Daemen, Y. Cheng, T. Li, S. Seifert, K. Hong, P. V. Bonnesen and J. K. Keum, *J. Am. Chem. Soc.*, 2016, **138**, 2638-2643.
- C. Zhang, W. Bu, D. Ni, C. Zuo, C. Cheng, Q. Li, L. Zhang, Z. Wang and J. Shi, *J. Am. Chem. Soc.*, 2016, **138**, 8156-8164.
- M. A. Moussawi, N. Leclerc-Laronze, S. Floquet, P. A. Abramov, M. N. Sokolov, S. Cordier, A. Ponchel, E. Monflier, H. Bricout and D. Landy, *J. Am. Chem. Soc.*, 2017, **139**, 12793-12803.
- S. Özkar and R. G. Finke, *J. Am. Chem. Soc.*, 2017, **139**, 5444-5457.
- S. Saha, D. H. Park, D. C. Hutchison, M. R. Olsen, L. N. Zakharov, D. Marsh, S. Goberna - Ferrón, R. T. Frederick, J. T. Diulus and N. Kenane, *Angew. Chem.*, 2017, **129**, 10274-10278.
- J. Dong, J. Hu, Y. Chi, Z. Lin, B. Zou, S. Yang, C. L. Hill and C. Hu, *Angew. Chem., Int. Ed.*, 2017, **56**, 4473-4477.
- B. Li, W. Li, H. Li and L. Wu, *Acc. Chem. Res.*, 2017, **50**, 1391-1399.
- Y. L. Wu, X. X. Li, Y. J. Qi, H. Yu, L. Jin and S. T. Zheng, *Angew. Chem.*, 2018, **130**, 8708-8712.
- J. C. Ye, J. J. Chen, R. M. Yuan, D. R. Deng, M. S. Zheng, L. Cronin and Q. F. Dong, *J. Am. Chem. Soc.*, 2018, **140**, 3134-3138.
- G. Paille, M. Gomez-Mingot, C. Roch-Marchal, B. Lassalle-Kaiser, P. Mialane, M. Fontecave, C. Mellot-Draznieks and A. Dolbecq, *J. Am. Chem. Soc.*, 2018, **140**, 3613-3618.
- E. Constable, *Comprehensive coordination chemistry II: from biology to nanotechnology*, Newnes, 2003.
- B. C. Bunker and W. H. Casey, *The aqueous chemistry of oxides*, Oxford University Press, 2016.
- L. Ruhlmann, L. Nadjó, J. Canny, R. Contant and R. Thouvenot, *Eur. J. Inorg. Chem.*, 2002, **2002**, 975-986.
- D. G. Musaev, K. Morokuma, Y. V. Geletii and C. L. Hill, *Inorg. Chem.*, 2004, **43**, 7702-7708.
- R. Prabhakar, K. Morokuma, C. L. Hill and D. G. Musaev, *Inorg. Chem.*, 2006, **45**, 5703-5709.
- T. Liu, B. Imber, E. Diemann, G. Liu, K. Cokleski, H. Li, Z. Chen and A. Mueller, *J. Am. Chem. Soc.*, 2006, **128**, 15914-15920.
- A. Sartorel, M. Carraro, A. Bagno, G. Scorrano and M. Bonchio, *Angew. Chem., Int. Ed.*, 2007, **46**, 3255-3258.
- A. Sartorel, M. Carraro, A. Bagno, G. Scorrano and M. Bonchio, *J. Phys. Org. Chem.*, 2008, **21**, 596-602.
- M. L. Kistler, T. Liu, P. Gouzerh, A. M. Todea and A. Müller, *Dalton Trans.*, 2009, 5094-5100.
- K. Sugahara, S. Kuzuya, T. Hirano, K. Kamata and N. Mizuno, *Inorg. Chem.*, 2012, **51**, 7932-7939.
- D. Zhang, F. Cao, P. Ma, C. Zhang, Y. Song, Z. Liang, X. Hu, J. Wang and J. Niu, *Chem. Eur. J.*, 2015, **21**, 17683-17690.
- D. C. Harris, *Quantitative chemical analysis*, Macmillan, 2010.
- D. R. Lide, *CRC handbook of chemistry and physics*, CRC press, 2004.

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A single polyoxometalate cluster with controllable and reversible protons release/absorption capability (~ 40 per molecule) in its aqueous solution.