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■ Polyoxometalates

Controlled Reactivity Tuning of Metal-Functionalized Vanadium Oxide Clusters

Katharina Kastner,[a] Johannes Forster,[a] Hiromichi Ida,[b] Graham N. Newton,[b] Hiroki Oshio,[b] and Carsten Streb*[a]

Dedicated to Prof. Dr. Rolf W. Saalfrank on occasion of his 75th birthday

Abstract: Controlling the assembly and functionalization of molecular metal oxides $[M_xO_y]^{n-}$ (M = Mo, W, V) allows the targeted design of functional molecular materials. While general methods exist that enable the predetermined functionalization of tungstates and molybdates, no such routes are available for molecular vanadium oxides. Controlled design of polyoxovanadates, however, would provide highly active materials for energy conversion, (photo-) catalysis, molecular magnetism, and materials science. To this end, a new approach has been developed that allows the reactivity tuning of vanadium oxide clusters by selective metal functionalization. Organic, hydrogen-bonding cations, for example, dimethylammonium are used as molecular placeholders to block metal binding sites within vanadate cluster shells. Stepwise replacement of the placeholder cations with reactive metal cations gives mono- and difunctionalized clusters. Initial reactivity studies illustrate the tunability of the magnetic, redox, and catalytic activity.

In supramolecular chemistry, the predictable synthesis of a target compound is difficult to achieve because complex self-assembly mechanisms often do not allow a high degree of reaction control.[1] In inorganic supramolecular chemistry, this is particularly obvious for molecular metal oxides, or polyoxometalates (POMs). POMs are anionic transition metal oxo clusters formed by the spontaneous self-assembly of oxometalate precursors[2] and a variation of the reaction conditions gives access to a vast number of different cluster architectures.[2,3] However, this synthetic approach inherently lacks the precise control required for predetermined cluster assembly, and often the resulting architectures cannot be predicted. This level of control, however, is required for the targeted synthesis of materials with specific structure and chemical reactivity.[4]

One notable exception in POM chemistry where controlled functionalization is possible are lacunary clusters: these species are obtained by controlled hydrolysis of the parent anion, for example, the Keggin anion $[SiW_{12}O_{40}]^{4-}$ or the Dawson anion $[P_2W_{18}O_{62}]^{6-}$. In the case of the Keggin anion, lacunary clusters such as the monovacant $[SiW_{11}O_{39}]^{8-}$ or the divacant $[SiW_{10}O_{34}]^{8-}$ are formed,[2c] which feature one or several vacant coordination sites. These binding sites can be functionalized with metal cations, giving species such as $[M(H_2O)SiW_{11}O_{39}]^{n-}$ and $[\{M(H_2O)\}_2SiW_{10}O_{38}]^{n-}$ (M: metal cation).[2c,5] Using this approach, functional molecular materials for energy conversion,[6] (photo-)catalysis,[7] molecular magnetism,[8] supramolecular chemistry[9] and materials science[10] have been developed. However, to-date, this approach is limited to tungstate-[2c,3b] and molybdate-based[11] lacunary clusters, and no analogous strategy exists in vanadium oxide chemistry.[12] Controlled and predictable access to metal-functionalized vanadates, however, would allow researchers to exploit their potential as tunable, highly reactive molecular materials in solar energy conversion,[12d,f,g] redox catalysis,[13a] molecular electronics,[13b] and magnetism[13c] as well as metal oxide nanostructures.[13d]

We have recently taken the first steps towards controlled metal functionalization in vanadium oxide cluster chemistry: a chloride-templated dodecavanadate cluster, $(DMA)_2[V_{12}O_{32}Cl]^{3-}$ (= **{V$_{12}$}**; DMA = dimethylammonium) was developed that is capable of selective metal-ion binding. **{V$_{12}$}** features two hexagonal metal binding sites that are blocked by hydrogen-bonded DMA placeholder cations (Figure 1).[14] Reaction of **{V$_{12}$}** with transition metals allows the selective replacement of one DMA cation, giving the mono-functionalized cluster anions $[M(L)V_{12}O_{32}Cl]^{n-}$ (= **{MV$_{12}$}**, M = Fe^{III}, Co^{II}, Cu^{II}, and Zn^{II}; L = ligand, for example, MeCN, Cl$^-$), see Figure 1. Density-functional theory calculations suggested that the second DMA cation can in principle be replaced also.[14]

Here, we show how stepwise metal incorporation into **{V$_{12}$}** can be used to control cluster reactivity; examples in redox, magnetic, and catalytic activity are given. To this end, the DMA-placeholder-blocked **{V$_{12}$}** was allowed to react with $MnCl_2\cdot4H_2O$ in acetonitrile solution at room temperature. Crystallization of the mother liquor gave green block crystals, and single-crystal X-ray diffraction (SC-XRD, see the Supporting Information) confirmed the formation of the mono-manganese-functionalized species $(nBu_4N)_3(DMA)[(MnCl)V_{12}O_{32}Cl]\cdot EtOAc$

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[a] K. Kastner, J. Forster, Prof. Dr. C. Streb
Institute of Inorganic Chemistry, Ulm University
Albert-Einstein-Allee 11, 89081 Ulm (Germany)
E-mail: carsten.streb@uni-ulm.de
Homepage: http://www.strebgroup.net

[b] H. Ida, Dr. G. N. Newton, Prof. Dr. H. Oshio
Graduate School of Pure and Applied Sciences, University of Tsukuba
Tennodai 1-1-1, Tsukuba 305-8571 (Japan)

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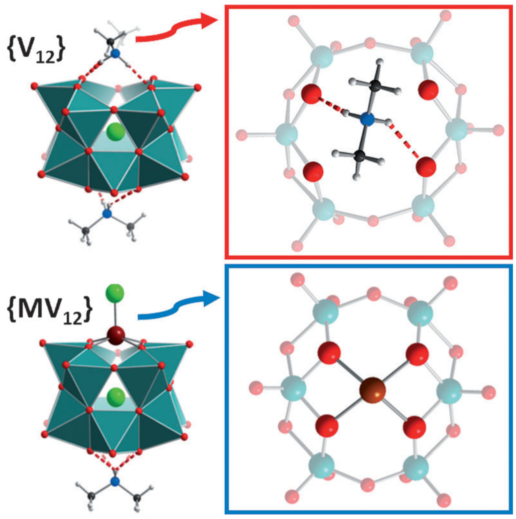

Figure 1. Top: **{V$_{12}$}** featuring two DMA cations (left) and detailed illustration of the DMA-blocked binding site (right). Bottom: the mono-functionalized **{MV$_{12}$}** (left, here: $M=Zn^{2+}$)[14] and detailed illustration of the metal coordination mode (right). Color scheme: V: teal; Cl: light green; Zn: brown; O: red, N: blue; C: gray; H: white.

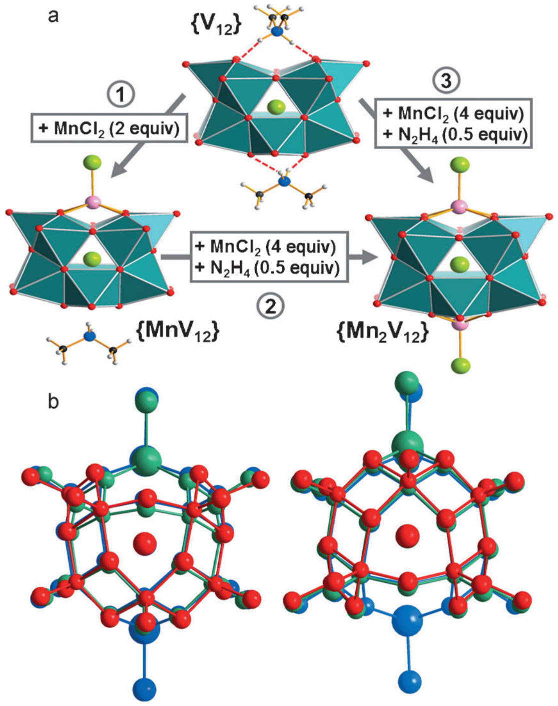

Figure 2. a) (1) Mono-functionalization of **{V$_{12}$}** with Mn^{II} giving **{MnV$_{12}$}**; (2) di-functionalization by reacting **{MnV$_{12}$}** with Mn^{II}, giving **{Mn$_2$V$_{12}$}**; (3) one-pot di-functionalization of **{V$_{12}$}** giving **{Mn$_2$V$_{12}$}**. Color scheme: see Figure 1. b) Overlay of the metal oxide frameworks of **{V$_{12}$}** (red), **{MnV$_{12}$}** (green) and **{Mn$_2$V$_{12}$}** (blue).

(=$(n\mathrm{Bu}_4\mathrm{N})_3$**{MnV$_{12}$}**·EtOAc) in yields of about 39 % (see Figure 2 and the Supporting Information). **{MnV$_{12}$}** is virtually isostructural to the **{MV$_{12}$}** species described above[14] and also features one hydrogen-bonded DMA placeholder cation. The Mn^{II} ion is coordinated to the metal binding site by four V-O-Mn coordination bonds, and long-range electrostatic interactions between the manganese and the chloride template (d(Mn···Cl) ca. 3.2–3.4 Å) are observed; the Mn coordination environment is completed by a terminal chloro ligand. Bond valence sum (BVS) calculations gave the expected oxidation states (V^{V}, Mn^{II}); no protonation of the cluster shell was found.

In the next step, we investigated whether **{MnV$_{12}$}** can be functionalized further by a second Mn^{II} center. Initial studies had suggested that the dimanganese-functionalized cluster is formed as a minor product in solution (based on ESI mass spectrometry); however, no crystalline product was obtained. It was hypothesized that the product yield might be increased by reduction of the vanadate shell, as this should improve the electrostatic interactions between the cluster anion and the Mn^{II} cation. Therefore, **{MnV$_{12}$}** was allowed to react with $MnCl_2·4H_2O$ (4 equiv) in acetonitrile solution in the presence of the reducing agent $N_2H_4·H_2O$ (0.5 equiv). Diffusion of ethyl acetate into the reaction solution gave one crystalline product and SC-XRD (see Supporting Information) showed that the difunctionalized species $(n\mathrm{Bu}_4\mathrm{N})_4[(\mathrm{MnCl})_2\mathrm{V}_{12}\mathrm{O}_{32}\mathrm{Cl}]$ (=**{Mn$_2$V$_{12}$}**) was obtained (yield ca. 40 %). Structural analysis shows two Mn^{II} centers coordinated to the metal binding sites; their mode of coordination is virtually identical to the binding mode described above for the monofunctionalized **{MnV$_{12}$}**. Structural overlay of the metal oxide framework of **{V$_{12}$}**, **{MnV$_{12}$}**, and **{Mn$_2$V$_{12}$}** showed that significant changes in the vanadium oxide framework geometry are observed upon Mn^{II} coordination (Figure 2 and Supporting Information); the structural flexibility of the vanadate shell suggests that incorporation of larger cations (e.g. f-block metal cations) should also be possible. ESI mass spectrometry showed that both **{MnV$_{12}$}** and **{Mn$_2$V$_{12}$}** are stable in solution and can be transferred into the gas phase without de-metalation of the manganese ions from the cluster shell (see the Supporting Information).

Charge balance considerations and BVS calculations indicate the presence of one delocalized V^{IV} center in **{Mn$_2$V$_{12}$}**; charge delocalization is not unexpected as all V centers are in identical square-pyramidal [VO$_5$] coordination environments.[15] This was further substantiated by the observation of inter-valence charge-transfer (IVCT) transitions between $\lambda \approx$ 800–1600 nm (see the Supporting Information). SQUID magnetometry ($T=$ 1.8–300 K, see the Supporting Information) confirmed the presence of one reduced V^{IV} center in **{Mn$_2$V$_{12}$}** and gave $\chi_m T$ values (at 300 K) of 9.16 emu mol^{-1} K for **{Mn$_2$V$_{12}$}** and 4.4 emu mol^{-1} K for **{MnV$_{12}$}**; the results are in line with the expected spin-only values.[16] Further, antiferromagnetic exchange was observed for **{Mn$_2$V$_{12}$}**, highlighting that magnetic interactions within the cluster shell are tunable by incorporation of the desired paramagnetic metal ions.[16] Electrochemical analyses show that manganese incorporation allows tuning of the electronic and redox properties: **{MnV$_{12}$}** shows three quasi-reversible redox-processes while **{Mn$_2$V$_{12}$}** features six quasi-reversible redox couples (see the Supporting Information), making the materials interesting for multi-electron transfer and storage.[6c]

We were further able to show that the one-pot difunctionalization of **{V$_{12}$}** is also possible (Figure 2): to this end, **{V$_{12}$}** was allowed to react with $MnCl_2·4H_2O$ (4 equiv) and $N_2H_4·H_2O$ (0.5 equiv) in acetonitrile at room temperature. Diffusion crystallization of the reaction mixture gave single crystals of **{Mn_2V_{12}}** in yields of about 49%; product purity was confirmed by SC-XRD, EA, ICP-MS, ESI-MS, FT-IR, and UV-Vis methods.

Based on their (electro-) chemical properties, the clusters were considered promising candidates for oxidative C–H-activation catalysis.[17] Initial catalytic tests used acetonitrile solutions of the respective cluster anion (1 mol%), the substrate 9,10-dihydroanthracene, and the oxidant *t*BuOOH (12 equiv). Both manganese-functionalized vanadates showed C–H activation reactivity, and the formation of the product anthracene was observed. Moderately higher zeroth order rate constants were observed for **{Mn_2V_{12}}** (k_{obs}(**{Mn_2V_{12}}**) = 1.2 μM h^{-1}) compared with **{MnV_{12}}** (k_{obs}(**{MnV_{12}}**) = 1.0 μM h^{-1}). The non-functionalized **{V_{12}}** showed no catalytic activity and simple manganese salts (e.g. $MnBr_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot H_2O$) showed significantly lower oxidative activity, even when employed at 15 mol% (see Figure 3 and the Supporting Information).

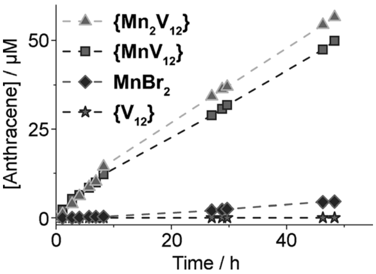

Figure 3. C–H-activation catalysis by **{MnV_{12}}** and **{Mn_2V_{12}}** illustrating the oxidation of 9,10-dihydroanthracene to anthracene in the presence of the catalyst **{MnV_{12}}** or **{Mn_2V_{12}}** (1 mol%) and the oxidant *t*BuOOH (12 equiv) in acetonitrile. The observed zeroth order rate constants are k_{obs},(**{MnV_{12}}**) = 1.0 μM h^{-1} and k_{obs},(**{Mn_2V_{12}}**) = 1.2 μM h^{-1}. The references **{V_{12}}** (1 mol%) and $MnBr_2 \cdot 4H_2O$ (15 mol%) showed only marginal catalytic activity.

In summary, we present a novel synthetic strategy that allows the stepwise functionalization of vanadium oxide clusters by incorporation of reactive metal centers. The concept gives access to a family of redox, magnetically, and catalytically active, stable functionalized vanadates. Stepwise as well as one-pot mono- and difunctionalization are possible, making this route extremely versatile. Structural and theoretical analyses as well as preliminary experimental studies show that the binding sites should also be able to accommodate larger s-, p-, d-, and f-block metal cations. In future work, new binding site geometries will be targeted by combining the concepts of templated bottom-up self-assembly and supramolecular binding site blockage.

Experimental Section

Crystallographic details

Crystallographic data and structure refinement for {MnV_{12}}: Triclinic space group, $P\bar{1}$, $a = 19.826(4)$, $b = 20.867(4)$, $c = 23.792(5)$ Å, $\alpha = 73.94(3)$, $\beta = 73.59(3)$, $\gamma = 88.77(3)^\circ$, $V = 9056$ (4) Å^3, $Z = 4$, $\rho = 1.436$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.438$ mm^{-1}, $T = 150(2)$ K, 177676 reflections measured, 36924 unique ($R_{int} = 0.0502$), 2076 refined parameters, $R_1 = 0.0581$, $wR_2 = 0.1984$, GooF = 1.151.

Crystallographic data and structure refinement for {Mn_2V_{12}}: Monoclinic space group, $P2_1/c$, $a = 24.324(5)$, $b = 16.727(3)$, $c = 24.438(5)$ Å, $\beta = 94.71(3)^\circ$, $V = 9909(3)$ Å^3, $Z = 4$, $\rho = 1.535$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.470$ mm^{-1}, $T = 150(2)$ K, 161699 reflections measured, 20263 unique ($R_{int} = 0.0796$), 1134 refined parameters, $R_1 = 0.0571$, $wR_2 = 0.1408$, GooF = 1.088.

CCDC-1038467 (**{MnV_{12}}**) and CCDC-1038466 (**{Mn_2V_{12}}**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: mass spectrometry · metal oxides · metal-functionalization · polyoxometalates · self-assembly

[1] a) J. M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304–1319; *Angew. Chem.* **1990**, *102*, 1347–1362; b) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319.

[2] a) D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196; *Angew. Chem.* **1996**, *108*, 1242–1286; b) G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418–2421; c) R. W. Saalfrank, H. Maid, A. Scheurer, *Angew. Chem. Int. Ed.* **2008**, *47*, 8794–8824; *Angew. Chem.* **2008**, *120*, 8924–8956; d) B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043; *Angew. Chem.* **2001**, *113*, 2076–2097; e) A. Müller, S. Roy, *Coord. Chem. Rev.* **2003**, *245*, 153–166.

[3] a) Special POM issue: C. L. Hill (Guest ed.), *Chem. Rev.* **1998**, *98*, *1–300*. b) POM-themed issue: L. Cronin, A. Müller (Guest eds.), *Chem. Soc. Rev.* **2012**, *41*, 7333. c) M. T. Pope, *Heteropoly and isopoly oxometalates*, Springer, Berlin, **1983**.

[4] a) D. L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.* **2010**, *49*, 1736–1758; *Angew. Chem.* **2010**, *122*, 1780–1803; b) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; *Angew. Chem.* **1991**, *103*, 56–70. c) POM-themed issue: U. Kortz, T. Liu (Guest eds.), *Eur. J. Inorg. Chem.* **2013**, 1556–1959.

[5] L. Cronin, A. Müller, *Chem. Soc. Rev.* **2012**, *41*, 7333–7334.

[6] D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105–121.

[7] a) Q. S. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle, C. L. Hill, *Science* **2010**, *328*, 342–345; b) A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard, M. Bonchio, *J. Am. Chem. Soc.* **2008**, *130*, 5006.

[8] a) R. Ben-Daniel, L. Weiner, R. Neumann, *J. Am. Chem. Soc.* **2002**, *124*, 8788–8789; b) A. M. Khenkin, I. Efremenko, J. M. L. Martin, R. Neumann, *J. Am. Chem. Soc.* **2013**, *135*, 19304–19310; c) K. Suzuki, F. Tang, Y. Kikukawa, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2014**, *53*, 5356–5360; *Angew. Chem.* **2014**, *126*, 5460–5464; d) W. Guo, Z. Luo, H. Lv, C. L. Hill, *ACS Catal.* **2014**, *4*, 1154–1161.

[9] a) C. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y.-F. Song, D.-L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. K. Brechin, L. Cronin, *Angew. Chem. Int. Ed.* **2008**, *47*, 5609–5612; *Angew. Chem.* **2008**, *120*, 5691–5694; b) S. G. Mitchell, P. I. Molina, S. Khanra, H. N. Miras, A. Prescimone, G. J. T. Cooper, R. S. Winter, E. K. Brechin, D.-L. Long, R. J. Cogdell, L. Cronin, *Angew. Chem. Int. Ed.* **2011**, *50*, 9154–9157; *Angew. Chem.* **2011**, *123*,

9320–9323; c) X. Fang, P. Kögerler, M. Speldrich, H. Schilder, M. Luban, *Chem. Commun.* **2012**, *48*, 1218–1220.

[10] a) M. Sadakane, M. H. Dickman, M. T. Pope, *Angew. Chem. Int. Ed.* **2000**, *39*, 2914–2916; *Angew. Chem.* **2000**, *112*, 3036–3038; b) B. S. Bassil, M. H. Dickman, I. Römer, B. von der Kammer, U. Kortz, *Angew. Chem. Int. Ed.* **2007**, *46*, 6192–6195; *Angew. Chem.* **2007**, *119*, 6305–6308.

[11] C. Ritchie, C. Streb, J. Thiel, S. G. Mitchell, H. N. Miras, D. L. Long, T. Boyd, R. D. Peacock, T. McGlone, L. Cronin, *Angew. Chem. Int. Ed.* **2008**, *47*, 6881–6884; *Angew. Chem.* **2008**, *120*, 6987–6990.

[12] a) L. A. Combs-Walker, C. L. Hill, *Inorg. Chem.* **1991**, *30*, 4016–4026; b) A. M. Khenkin, L. Weiner, Y. Wang, R. Neumann, *J. Am. Chem. Soc.* **2001**, *123*, 8531–8542.

[13] a) Y. Hayashi, *Coord. Chem. Rev.* **2011**, *255*, 2270–2280; b) S. Inami, M. Nishio, Y. Hayashi, K. Isobe, H. Kameda, T. Shimoda, *Eur. J. Inorg. Chem.* **2009**, 5253–5258; c) C. M. Flynn, M. T. Pope, *Inorg. Chem.* **1970**, *9*, 2009–2014; d) J. Forster, B. Rösner, M. M. Khusniyarov, C. Streb, *Chem. Commun.* **2011**, *47*, 3114–3116; e) K. Kastner, B. Puscher, C. Streb, *Chem. Commun.* **2013**, *49*, 140–142; f) J. Forster, B. Rösner, R. H. Fink, L. C. Nye, I. Ivanovic-Burmazovic, K. Kastner, J. Tucher, C. Streb, *Chem. Sci.* **2013**, *4*, 418–424; g) J. Tucher, L. C. Nye, I. Ivanovic-Burmazovic, A. Notarnicola, C. Streb, *Chem. Eur. J.* **2012**, *18*, 10949–10953; h) K. Kastner, C. Streb, *Crystengcomm* **2013**, *15*, 4948–4955; i) A. Seliverstov, C. Streb, *Chem. Commun.* **2014**, *50*, 1827–1829.

[14] K. Kastner, J. T. Margraf, T. Clark, C. Streb, *Chem. Eur. J.* **2014**, *20*, 12269–12273.

[15] a) K. Monakhov, O. Linnenberg, P. Kozłowski, J. van Leusen, C. Besson, T. Secker, A. Ellern, X. López, J. M. Poblet, P. Kögerler, *Chem. Eur. J.* **2015**, *21*, 2387–2397; b) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239–272; c) P. Kögerler, B. Tsukerblat, A. Müller, *Dalton Trans.* **2010**, *39*, 21–36.

[16] a) Q. Chen, C. L. Hill, *Inorg. Chem.* **1996**, *35*, 2403–2405; b) J. Lehmann, A. Gaita-Arino, E. Coronado, D. Loss, *J. Mater. Chem.* **2009**, *19*, 1672–1677.

[17] a) I. Bar-Nahum, A. M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* **2004**, *126*, 10236–10237; b) M. J. Zdilla, J. L. Dexheimer, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2007**, *129*, 11505–11511.

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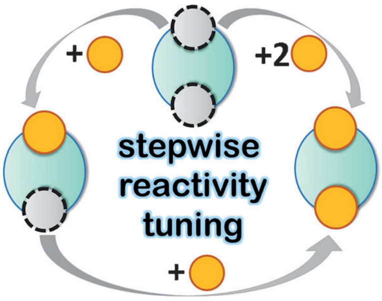
Stepwise functionalization of a vanadium oxide cluster by one or two functional metal centers is achieved by using a molecular placeholder approach. The novel strategy provides access to redox-, catalytically, and magnetically active molecular materials.



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