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ORGANIC ESTERS OF {V₆O₁₉}; SYNTHONS THAT DETECT AND CATALYTICALLY DECONTAMINATE USING AIR.

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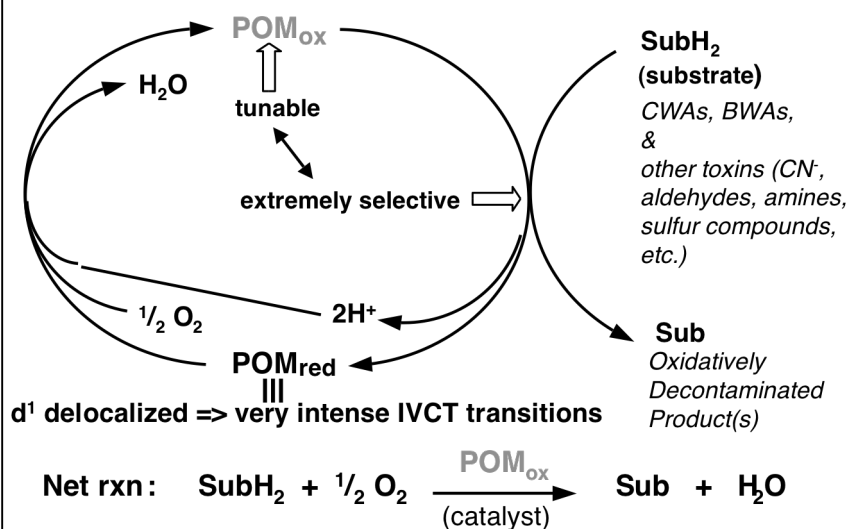
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INTRODUCTION

Materials that would detect chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) by a simple rapid and dramatic color change are sought. Also materials that can decontaminate CWAs and TICs under benign conditions¹⁻⁴ are attractive. Catalytic decontamination that requires only the ambient environment (air and water vapor at atmospheric temperature and pressure) is highly attractive but clearly very hard to realize.⁵⁻⁷ Two general processes that achieve both detection and aerobic decon are shown in Figure 1. We have recently developed some systems that do both. We report a general synthetic approach to many materials with both capabilities that is based on esterified hexavanadate units (formula [V₆O₁₉]⁸⁻).

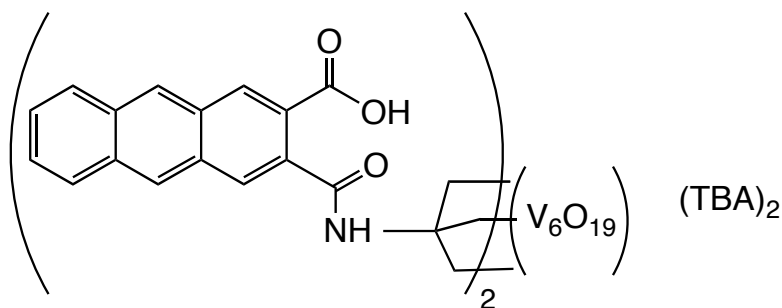
Figure 1 (right). General processes exhibited by POM esters (POM_{ox,red}). Detection involves reduction of lightly colored oxidized POM, top, by several TICs and CWA simulants to form intensely colored, reduced POM, bottom. Catalytic decontamination involves reoxidation of POM_{red} to POM_{ox} by exposure to air/O₂; net reaction at bottom.



RESULTS AND DISCUSSION

Reaction of tris(hydroxymethyl)aminomethane (“Tris”) with decavanadate, $(\text{TBA})_3\text{H}_3[\text{V}_{10}\text{O}_{28}]$, $\text{TBA} = n\text{-Bu}_4\text{N}$, in dry dimethylacetamide (DMA) under Ar results in production of the bis(triester) complex, $\text{TBA}_2[\text{V}_6\text{O}_{13}\{(\text{CH}_2\text{O})_3\text{C}(\text{NH}_2)\}_2]$ in ca. 20% yield. Reaction of functionalized anhydrides, $(\text{RCO})_2\text{O}$, where R = many organic function-bearing groups, with this bis(triester) POM, $\text{TBA}_2[\text{V}_6\text{O}_{13}\{(\text{CH}_2\text{O})_3\text{C}(\text{NH}_2)\}_2]$, produces the corresponding derivatized POMs in nearly quantitative yield. One example we address here is the anthracyl functionalized hexavanadate derivative (**1**) shown in Figure 2.

Figure 2. (right) Structure of complex **1**. This readily prepared complex undergoes a dramatic color change when reduced and catalyzes air-based oxidation of the mustard (HD) simulant, 2-CEES.



Complex **1** on exposure to the mustard (HD) simulant, 2-chloroethyl ethyl sulfide, $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_3$ (CEES) turns very dark blue. This color results from the reduced hexavanadate core, and specifically from transitions between states in this POM unit that involve delocalized electrons. This color change is dramatic and rapid even in the presence of small concentrations of CEES and constitutes a simple color-change basis of detection. Simultaneously CEES is oxidized to the corresponding sulfoxide, the HD analogue of which is nearly nontoxic (and far less toxic than mustard sulfone). Similar rapid reductions of the hexavanadate unit are seen with other toxic compounds, that are consequently oxidized.

When the dark blue reduced **1**, produced by reaction of CEES, is exposed to the air, the hexavanadate core is reoxidized to the light orange oxidized starting form of the bis(triester) hexavanadate complex. This reoxidation completes a catalytic cycle for decontamination based solely on ambient air (cycle in Figure 1).

In addition to the color change detection and catalytic air-based decontamination capabilities of **1** and many other accessible structurally analogous bis(triester) V_6 polyanions, these units self assemble into structures that have other attractive properties including porosity. We illustrate this here using just one new example, namely **1**. Figure 3 shows the X-ray structure of **1** but also the 3-dimensional porous structure that forms via π -stacking between the anthracene moieties and $\text{C-H}\cdots(\text{O})\text{POM}$ hydrogen bonding when **1** crystallizes.

CONCLUSIONS

A new family of functionalized hexavanadate complexes have been prepared that self assemble into a range of porous and other structures that exhibit the properties of the

hexavanadate precursor: color-change detection and catalytic air-based decontamination of reducing CWAs and TICs.

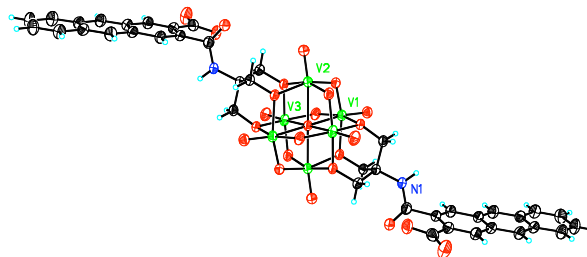
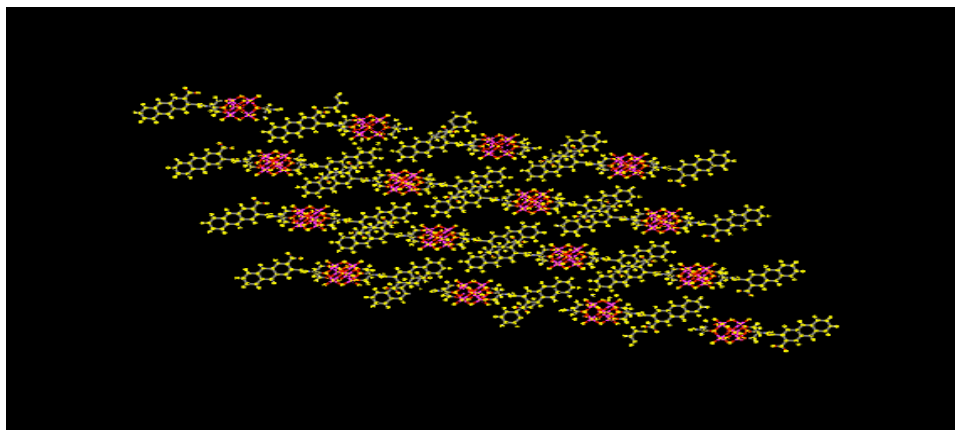


Figure 3. X-ray structure of **1** monomer (right) and the 3D porous structure it forms on crystallization (below).



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REFERENCES

1. Yang, Y. C.; Baker, J. A.; Ward, J. R., *Chem. Rev.* **1992**, 92, (8), 1729-1743.
2. Wagner, G. W.; Procell, L. R.; Yang, Y.; Bunton, C. A., *Langmuir* **2001**, 17, (16), 4809-4811.
3. Cronce, D. T. patent 6,376,436, 2002.
4. Hill, C. L.; Okun, N. M.; Hillesheim, D. A.; Geletii, Y. V., In *Anti-Terrorism and Homeland Defense: Polymers and Materials*, ACS Symposium Series 980, Chapter 12, Reynolds, J. G.; Lawson, G. E.; Koester, C. J., Eds. American Chemical Society: Washington, D.C., 2007; pp 198-209.
5. Okun, N. M.; Anderson, T. M.; Hill, C. L., *J. Am. Chem. Soc.* **2003**, 125, (11), 3194-3195.
6. Okun, N. M.; Tarr, J. C.; Hilleshiem D. A.; Zhang, L; Hardcastle, K. I.; Hill, C. L, *J. Mol. Catal. A: Chem.* **2006**, 246, 11-17.
7. Hill, C. L.; Anderson, T. M.; Han, J.-W.; Hillesheim, D. A.; Geletii, Y. V.; Okun, N. M.; Cao, R.; Botar, B.; Musaev, D. G.; Morokuma, K., *J. Mol. Catal. A: Chem.* **2006**, 251, 234-238.