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## Polyoxometalate-based gelating networks for entrapment and catalytic decontamination†

Kevin P. Sullivan,<sup>a</sup> Wade A. Neiwert,<sup>‡,§</sup> Huadong Zeng,<sup>§,a</sup> Anil K. Mehta,<sup>a</sup> Qiushi Yin,<sup>a</sup> Daniel A. Hillesheim,<sup>¶</sup> Skanda Vivek,<sup>||</sup> Panchao Yin,<sup>||</sup> Daniel L. Collins-Wildman,<sup>a</sup> Eric R. Weeks,<sup>||</sup> Tianbo Liu<sup>c</sup> and Craig L. Hill<sup>||</sup> \*<sup>a</sup>

**We report the synthesis and characterization of a new class of organic/inorganic hybrid polymers composed of covalently-bound 1,3,5-benzenetricarboxamide linkers and anionic polyoxovanadate clusters with varying counter-cations. These materials form gels within seconds upon contact with polar aprotic organic liquids and catalyze the degradation of odorants and toxic molecules under mild conditions including aerobic oxidation of thiols, hydrogen peroxide-catalyzed oxidation of sulfides, and hydrolysis of organophosphate chemical warfare agent analogues.**

Inorganic/organic polymers are important in multiple disciplines as they allow for synergy between the physical properties of traditional polymers and versatility in function of inorganic compounds.<sup>1–3</sup> Polyoxometalates (POMs), oligomeric aggregates of metal cations bridged by oxide anions, have received significant attention for their applications in many fields, including catalysis, energy conversion, memory storage, and medicine, among others.<sup>4,5</sup> Combining POMs with organic components to create organic/inorganic hybrid molecules or polymers allows for the rational design of multifunctional compounds with unique properties.<sup>6–10</sup>

Materials that respond to external stimuli play an increasing role in a diverse range of applications, including protection against chemical or biological threats.<sup>11–13</sup> Three-dimensional polymer systems can swell through adsorption of solvent molecules,

producing a significant change in volume between the swollen and unswollen states, making them attractive for materials designed to protect against toxic compounds.<sup>11,14,15</sup> Development of materials for the sequestration and decontamination of chemical warfare agents (CWAs), including organophosphorus (OP) nerve agents such as Sarin and VX, and blister agents such as sulfur mustard (HD), has been a priority for decades due to their high toxicity and potential for large-scale release.<sup>16</sup> Several types of materials have been shown to catalyze hydrolysis of OP agents or oxidation of HD into nontoxic products,<sup>17,18</sup> and entrapment of CWAs through gelation has been reported,<sup>19</sup> but a material that could both sequester and catalytic decontaminate toxic molecules would represent a significant advance in the field of protective materials.

We report here a polymer composed of  $C_3$ -symmetric 1,3,5-benzenetricarboxamide units covalently connected with POM clusters. The material forms gels upon simple addition of a liquid, including the chemical warfare agent analogue dimethyl methylphosphonate (DMMP). This polymer and its derivatives are additionally capable of catalyzing both hydrolysis of nerve agent simulants and aerobic oxidation reactions under mild conditions. The physical and chemical properties of the polymer can be readily altered through exchange of the POM counter cations, allowing for the creation of a wide variety of new responsive and reactive materials.

Reaction of  $C_6H_3(CONHC(CH_2OH)_3)_3$  (trisBTA) and  $(TBA)_3-[H_3V_{10}O_{28}]$  in *N,N*-dimethylacetamide (DMA) affords a gel material that is isolated as a red insoluble powder with the formula  $[(n-C_4H_9)_4N]_{2n}[(V_6O_{13})_n\{((OCH_2)_3CNHCO)_3C_6H_3\}_x\{((OCH_2)_3CNHCO)_2((HOCH_2)_3CNHCO)C_6H_3\}_y\{((OCH_2)_3CNHCO)((HOCH_2)_3CNHCO)_2C_6H_3\}_z]$  (TBA-polyV<sub>6</sub>, x = triply bound trisBTA, y = doubly-bound trisBTA, z = singly-bound trisBTA) (Fig. 1a).

Solid-state cross-polarization magic angle spinning (CP-MAS) <sup>13</sup>C NMR on TBA-polyV<sub>6</sub> reveals POM-bound trisBTA linkers in the product and confirms the covalent attachment between the linkers and POM units, indicated by a shift in the alcohol methylene peak upon binding to the hexavanadate units (Fig. 1b). A single peak in both solid-state and solution <sup>51</sup>V NMR spectra confirms the presence of hexavanadate (V<sub>6</sub>) units within the

<sup>a</sup> Department of Chemistry, Emory University, Atlanta, GA 30322, USA.

E-mail: chill@emory.edu

<sup>b</sup> Department of Physics, Emory University, Atlanta, GA 30322, USA

<sup>c</sup> Department of Polymer Science, University of Akron, Akron, OH 44325, USA

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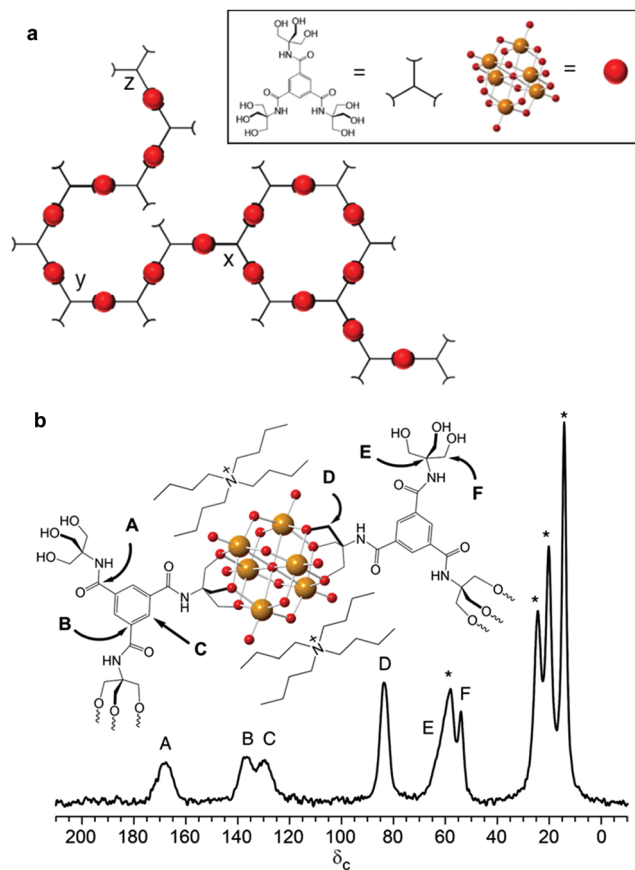
‡ Present address: Department of Chemistry, Bethel University, St. Paul, MN 55112, USA.

§ Present address: McKnight Brain Institute, University of Florida, Gainesville, FL 32611, USA.

¶ Present address: ABT Molecular Imaging, Inc., Louisville, TN 37777, USA.

|| Present address: School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332, USA.

\*\* Present address: Chemical Engineering and Materials Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

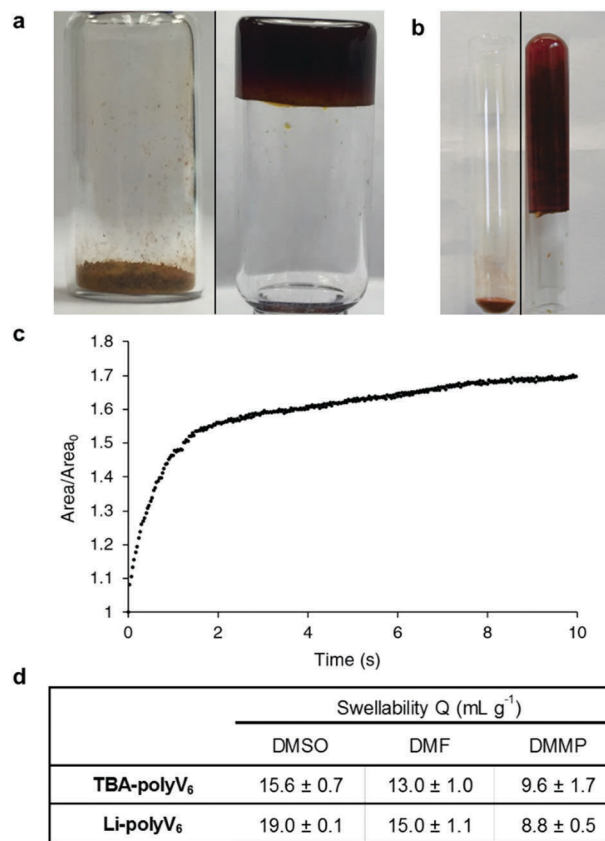


**Fig. 1** (a) Representation of TBA-polyV<sub>6</sub>, indicating triply-bound (x) doubly-bound (y) and singly-bound (z) linkers. (b) Solid-state <sup>13</sup>C NMR of TBA-polyV<sub>6</sub>. TBA<sup>+</sup> (\*) peaks are indicated. Orange and red spheres represent V(V) and O<sup>2-</sup>, respectively.

polymer (Fig. S1, ESI<sup>†</sup>).<sup>20</sup> Comparisons between the V–O stretching frequencies in the infrared spectrum of the polymer to a known monomeric hexavanadate further supports the presence of V<sub>6</sub> units (Fig. S2, ESI<sup>†</sup>).<sup>21</sup>

Deconvolution of the solid-state <sup>13</sup>C NMR spectrum as well as XPS data indicate that the polymer is composed of highly branched strands (Fig. S3 and S4, ESI<sup>†</sup>). These extensively cross-linked fiber structures can be seen in electron microscopy images of the material (Fig. S5, ESI<sup>†</sup>). The extensively cross-linked structure of the polymer results in the material possessing a relatively high BET surface area of 430 m<sup>2</sup> g<sup>-1</sup>.

TBA-polyV<sub>6</sub> exhibits remarkable physical properties in the presence of polar aprotic liquids, entrapping them upon contact and forming gels within seconds (Video S1, ESI<sup>†</sup>). This rapid gelation behavior was visualized under a microscope, and image analysis was used to obtain a qualitative measure of the swelling kinetics (Fig. 2c and Video S2, ESI<sup>†</sup>). These gels remain stable to inversion indefinitely after swelling, and can be returned to the contracted solid form through addition of a nonpolar solvent such as toluene or diethyl ether, demonstrating both rapid and reversible organogel-forming activity. The swelling parameters for several organic solvents are shown in Fig. 2d. This gelation behavior is attributed to both pore-filling



**Fig. 2** (a) Swelling of TBA-polyV<sub>6</sub> (left) in the presence of dimethyl methyl phosphonate (DMMP) (right). (b) Swelling of TBA-polyV<sub>6</sub> (left) in the presence of DMF (right). (c) Analysis of swelling rate using particle tracking after exposure to DMF. (d) Swelling behavior measured in mL of liquid per gram of material after 24-hour exposure.

of the crosslinked polymer and hydrogen-bonding interactions, as is observed in other 1,3,5-tricarboxamide-based polymers (Fig. S6, ESI<sup>†</sup>).<sup>22</sup> Comparing the swelling capability of TBA-polyV<sub>6</sub> to other absorbent materials reveals its high capacity for organic liquid entrapment (Fig. S7, ESI<sup>†</sup>).

Significantly, we observed that TBA-polyV<sub>6</sub> can form gels when exposed to OP agent analogues. Addition of the G-series nerve agent analogue DMMP results in a substantial index of swellability (*Q*) value of 10 mL g<sup>-1</sup> (Fig. 2a and d), also with rapid swelling kinetics. Studies using highly-crosslinked polymers have demonstrated correlations between swelling capability in polar organic liquids such as DMF and CWAs such as HD and OPs.<sup>19</sup>

The physical and chemical properties of TBA-polyV<sub>6</sub> can be readily altered by exchange of the TBA<sup>+</sup> counter cations. We employed this strategy to exchange the TBA<sup>+</sup> cations for a variety of cations, but focus here on the lithium (Li-polyV<sub>6</sub>) and zirconium (Zr-polyV<sub>6</sub>) substituted analogues. Exchange occurs without changing the structure of the polymer (Fig. S8 and S9, ESI<sup>†</sup>), but alters the gelation capability of the material as demonstrated by the increased Li-polyV<sub>6</sub> index of swellability in DMF and DMSO relative to TBA-polyV<sub>6</sub> (Fig. 2d). Thus, we establish the ability to tailor this new class of materials to

exhibit desired swelling based on judicious counter cation choice.

Hexavanadate POMs are known to be active towards the oxidation of sulfides.<sup>23,24</sup> To demonstrate the applicability of TBA-polyV<sub>6</sub> for air-based oxidative removal reactions, we conducted studies on the catalytic oxidation of propane thiol (PrSH) to dipropyl disulfide (PrSSPr). This representative odorant is fully oxidized to the non-odorous disulfide, using oxygen to reoxidize the reduced POM units (130 turnovers in ~6 days) (Fig. S10 and S11, ESI†). TBA-polyV<sub>6</sub> is red in its powder state and yellow when dispersed in solvent. Upon reduction of the POM, the material becomes dark green, providing a colorimetric detection capability (Fig. S10 and S12, ESI†).

More significantly, TBA-polyV<sub>6</sub> catalyzes oxidation of the HD simulant 2-chloroethyl ethyl sulfide (CEES) by the mild and environmentally-friendly oxidant hydrogen peroxide. CEES is completely and rapidly oxidized in the presence of TBA-polyV<sub>6</sub> and H<sub>2</sub>O<sub>2</sub> (Fig. 3), showing its promise as an effective catalyst for the removal of HD under mild conditions. Additionally, this reaction selectively forms the less toxic 2-chloroethyl ethyl sulfoxide (CEESO) without overoxidation to the harmful 2-chloroethyl ethyl sulfone (CEESO<sub>2</sub>) product (Fig. S13, ESI†). Both Zr-polyV<sub>6</sub> and Li-polyV<sub>6</sub> also exhibit catalytic sulfoxidation activity (Fig. S14, ESI†) compared to related heterogeneous sulfoxidation catalysts.<sup>25,26</sup> Through these two exemplary oxidation reactions, we demonstrate the applicability of the TBA-polyV<sub>6</sub> polymer for catalytic oxidation of toxic or odorant molecules under mild conditions.

Both polyoxometalate-catalyzed hydrolysis of phosphoester bonds and hydrogen-bond-donor-catalyzed hydrolysis of OP agents have been demonstrated in recent studies.<sup>27–29</sup> We were therefore encouraged to examine the effectiveness of these

polymers towards hydrolysis of OP analogues. TBA-polyV<sub>6</sub> catalyzes the hydrolytic breakdown of the OP nerve agent analogue diethyl cyanophosphonate (DECP) to the nontoxic diethyl phosphate (Fig. S15, ESI†), likely through the formation of multiple hydrogen-bonding interactions between the polymer and DECP.<sup>28</sup> However, it is less effective against more realistic and challenging OP agent analogues. Zr-Based materials have received a great deal of attention for their high activities towards hydrolysis of OP nerve agents, particularly in recent work using Zr-based metal-organic frameworks (MOFs).<sup>17,30</sup> Accordingly, the Zr-substituted Zr-polyV<sub>6</sub> shows significant activity for catalyzing the hydrolysis of dimethyl *p*-nitrophenylphosphate (DMNP) and achieves full conversion to the hydrolysis products with a *t*<sub>1/2</sub> of 25 min (Fig. 4), which is comparable to the activity of several zirconium-based MOF catalysts.<sup>30</sup> We show, therefore, that this polymer material can easily be tuned to significantly enhance its catalytic hydrolysis activity.

The multifunctional polymer TBA-polyV<sub>6</sub>, composed of alternating hexavanadate POM and trisBTA units has been synthesized and characterized and is, to our knowledge, the first example of a material which forms gels upon contact with CWA analogues while simultaneously possessing catalytic oxidation and hydrolysis functions. The catalytic redox processes proceed under mild conditions for the representative odorant propane thiol and the HD analogue CEES. The chemical and physical properties of TBA-polyV<sub>6</sub> can be readily tuned by judicious choice of counter cation, producing the two exemplary compounds Zr-polyV<sub>6</sub> and Li-polyV<sub>6</sub>. Li-polyV<sub>6</sub> exhibits altered gelation properties, while Zr-polyV<sub>6</sub> has increased ability to hydrolyze OP analogues. This class of POM-based polymers represent the first examples of a new type of multifunctional soft material with several potential applications, including responsive catalytic materials for sequestration and decontamination of deleterious compounds.

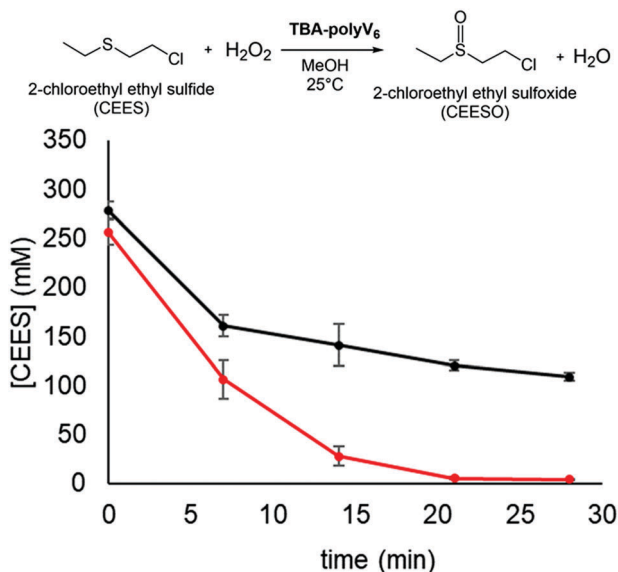


Fig. 3 Oxidation of CEES by H<sub>2</sub>O<sub>2</sub> catalyzed by TBA-polyV<sub>6</sub>. The mole ratio of the catalyzed reaction (●) was 1 V<sub>6</sub>: 120 CEES: 120 H<sub>2</sub>O<sub>2</sub>. The uncatalyzed control reaction (●) was run with the omission of TBA-polyV<sub>6</sub>. Reactions were repeated in triplicate and error bars are reported.

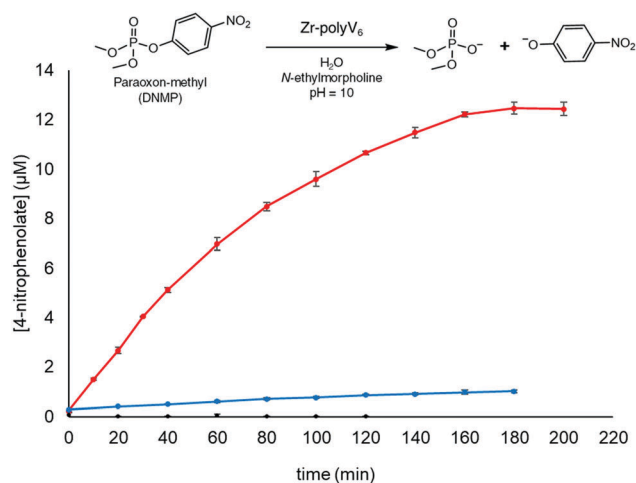


Fig. 4 Hydrolysis of DMNP catalyzed by Zr-polyV<sub>6</sub> (●) in aqueous 0.45 M *N*-ethylmorpholine at pH 10.00, measured through formation of 4-nitrophenolate anion. The DMNP:Zr-polyV<sub>6</sub> ratio was 10:1 based on Zr<sub>4</sub> units. Reactions run without catalyst (●) and TBA-polyV<sub>6</sub> (●) are shown. Reactions were run in triplicate and error bars are reported.

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## Conflicts of interest

There are no conflicts to declare.

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