

## Electronic Supporting Information (ESI)

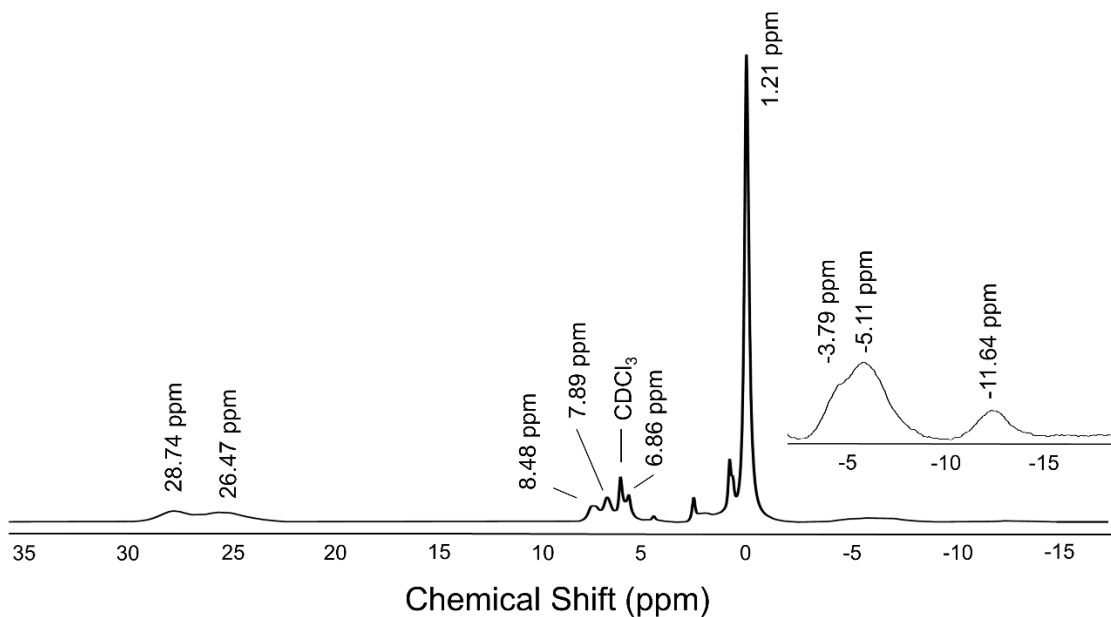
### Coordination-induced Bond Weakening of Water at the Surface of an Oxygen-deficient Polyoxovanadate Cluster

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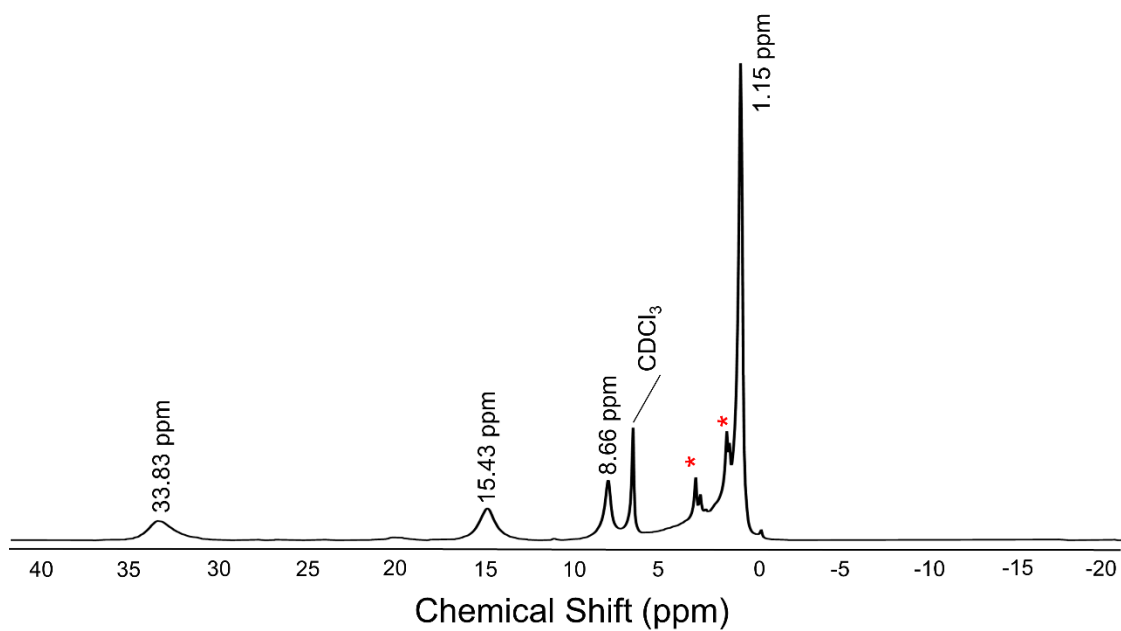
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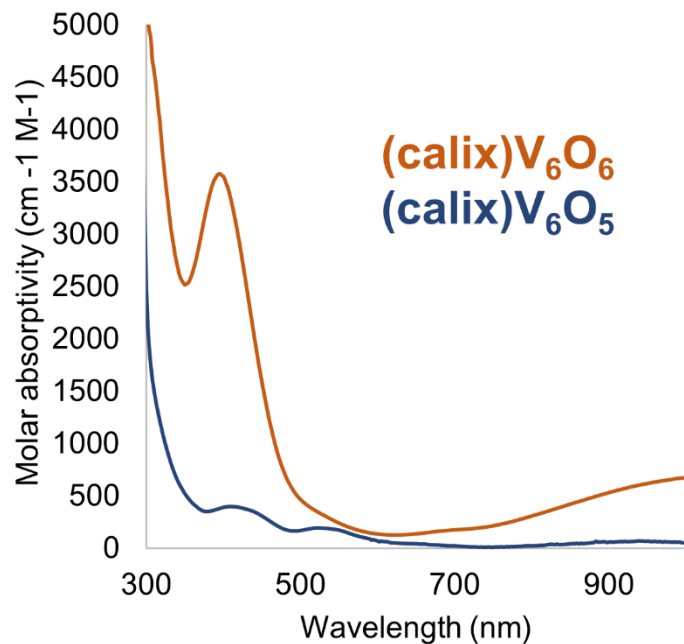
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**Figure S1.**  $^1\text{H}$  NMR spectrum of  $(\text{calix})\text{V}_6\text{O}_5(\text{OH}_2)$ , collected in  $\text{CDCl}_3$  at  $21^\circ\text{C}$ .



**Figure S2.**  $^1\text{H}$  NMR spectrum of  $(\text{calix})\text{V}_6\text{O}_6$ , collected in  $\text{CDCl}_3$  at  $21^\circ\text{C}$ , red asterisk indicates residual THF solvent.



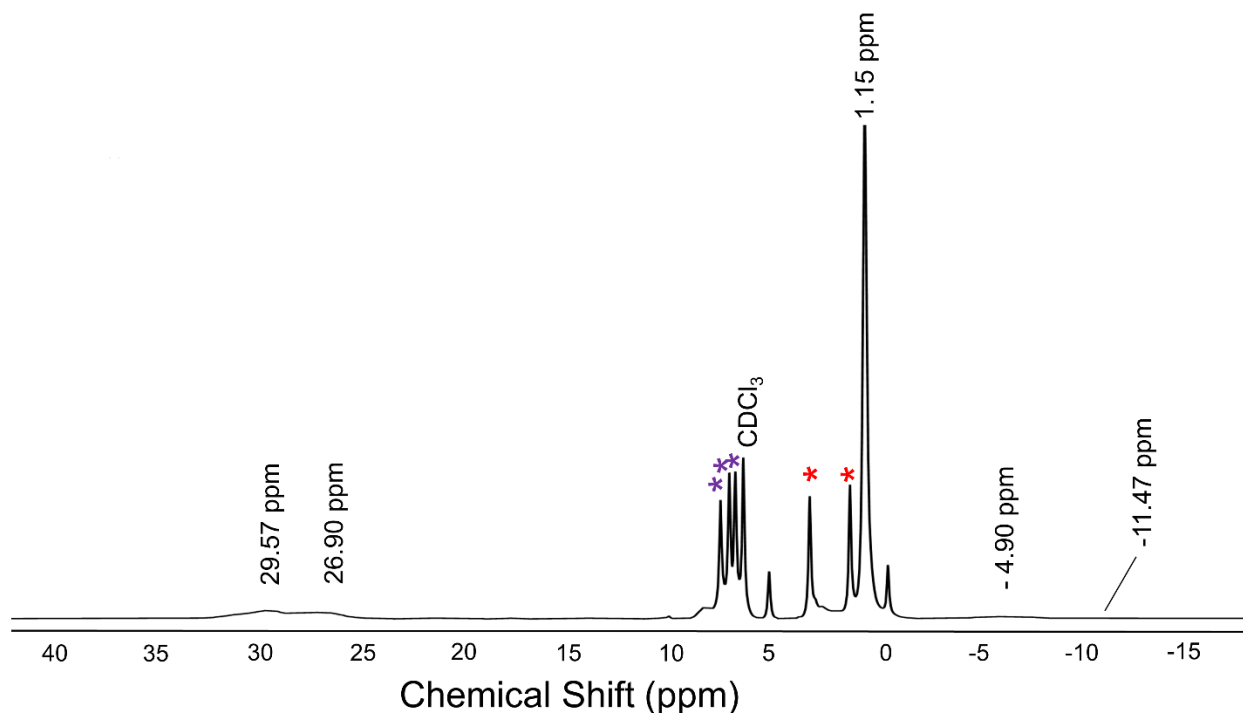
**Figure S3.** Electronic absorption spectra of **(calix)V<sub>6</sub>O<sub>5</sub>(OH<sub>2</sub>)** (blue), and **(calix)V<sub>6</sub>O<sub>6</sub>** (orange) in tetrahydrofuran.

**Table S1:** Crystallographic parameters for molecular structure of **(calix)V<sub>6</sub>O<sub>5</sub>(OH<sub>2</sub>)**.

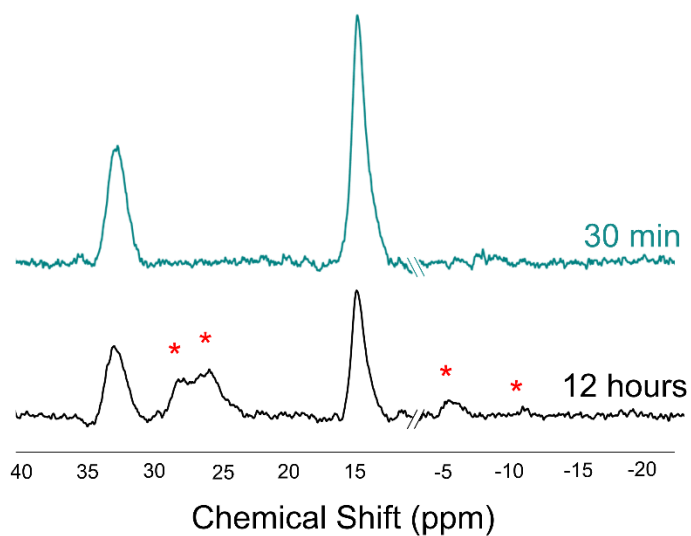
Empirical formula	C <sub>52</sub> H <sub>76</sub> O <sub>19</sub> V <sub>6</sub>
Formula weight	1577.57
Temperature / K	173.00(10) K
Wavelength / Å	1.54184 Å
Crystal system	orthorhombic
Space group	<i>Pbcm</i>
Unit cell dimensions	<i>a</i> = 14.4807(2) Å <i>b</i> = 27.8595(5) Å <i>c</i> = 18.7836(2) Å $\alpha$ = 90° $\beta$ = 90° $\gamma$ = 90°
Volume / Å <sup>3</sup>	7577.78(19) Å <sup>3</sup>
Z	4
Reflections collected	48002
Independent reflections	8377 [ <i>R</i> (int) = 0.0397]
Completeness to theta = 67.684°	99.9%
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.038
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0644, <i>wR</i> 2 = 0.1861
Largest diff. peak and hole	0.665 and -0.479 e.Å <sup>-3</sup>

**Table S2.** Bond valence sum (BVS) calculations for crystallographically independent vanadium ions in **(calix)V<sub>6</sub>O<sub>5</sub>(OH<sub>2</sub>)** based on X-ray crystallographic data collected at 100 K. Table reflects the results of BVS calculations using V-O bond valence parameters (*r*<sub>0</sub>) for different oxidation states of vanadium.

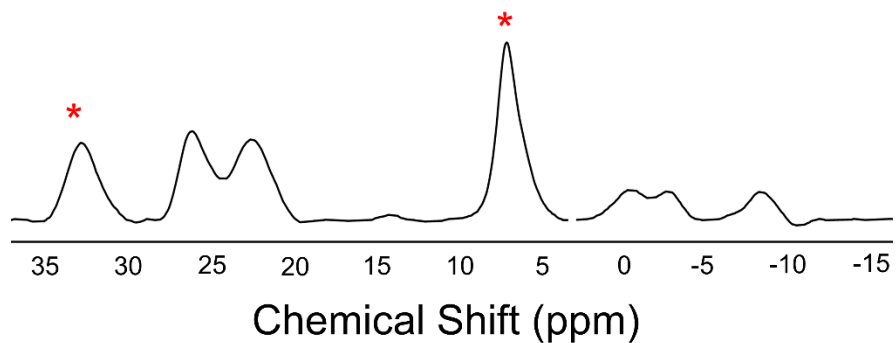
<b>(calix)V<sub>6</sub>O<sub>5</sub>(OH<sub>2</sub>)</b>	V1	V2	V3	V4	V5
V(III)	<b>3.194</b>	3.826	3.921	<b>3.051</b>	3.814
V(IV)	3.270	<b>3.917</b>	<b>4.015</b>	3.124	<b>3.905</b>
V(V)	3.513	4.178	4.278	3.359	4.167



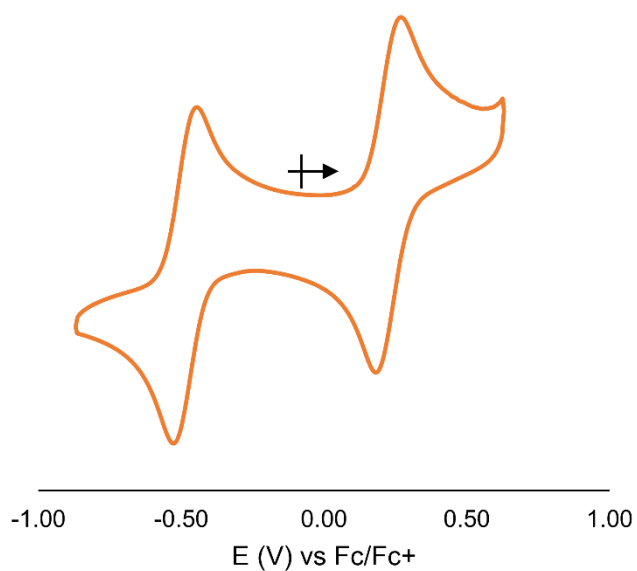
**Figure S4.**  $^1\text{H}$  NMR spectrum of crude reaction of **(calix) $\text{V}_6\text{O}_6$**  with hydrazobenzene after 5 hours at 25 °C. Red asterisks are residual solvent (THF) and purple asterisk indicate azobenzene.



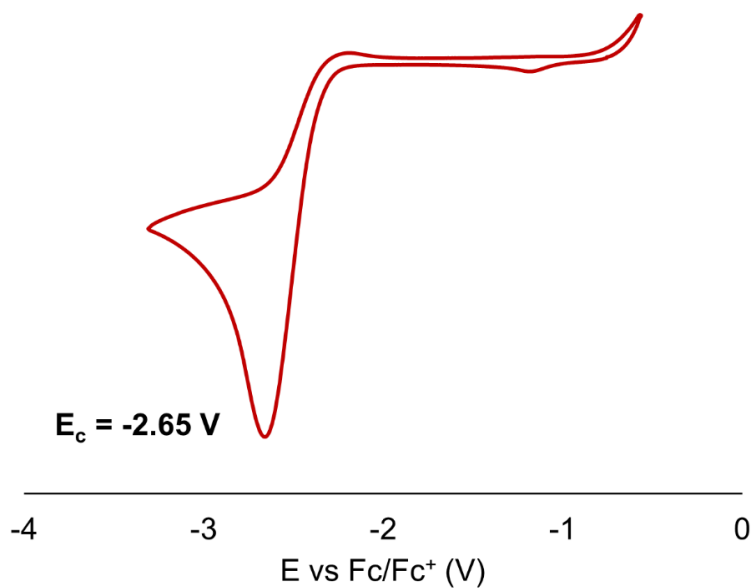
**Figure S5.**  $^1\text{H}$  NMR spectrum **(calix) $\text{V}_6\text{O}_6$**  + 1 eq  $\text{H}_2\text{NQ}$  after 30 minutes (top, teal) in  $\text{THF-d}_8$ . Reaction reached equilibrium at 25 °C after 12 hours (bottom, black). Red asterisks indicate the formation of **(calix) $\text{V}_6\text{O}_5(\text{OH}_2)$** .



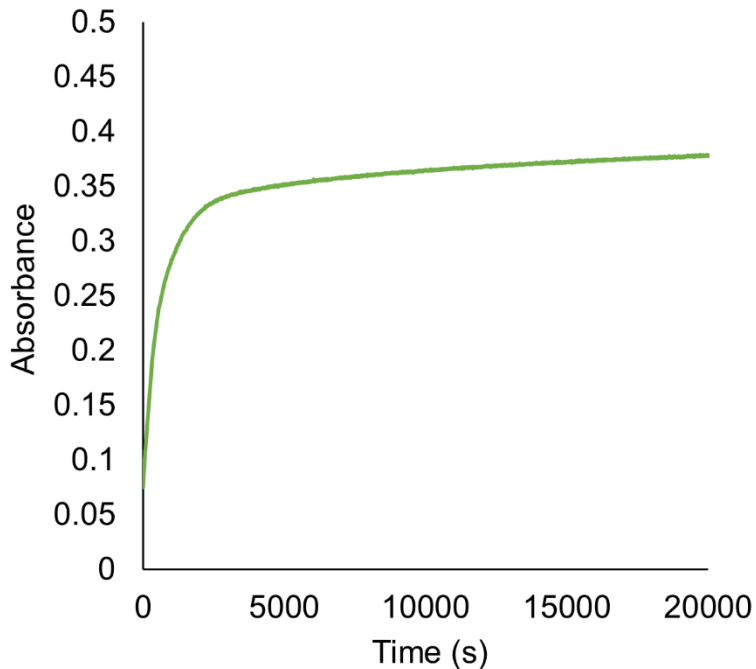
**Figure S6.**  $^1\text{H}$  NMR spectrum of  $(\text{calix})\text{V}_6\text{O}_5(\text{OH}_2) + 1 \text{ eq NQ}$  in  $\text{THF-d}_8$ . Red asterisks indicate the formation of  $(\text{calix})\text{V}_6\text{O}_6$  after 12 at  $25^\circ\text{C}$ .



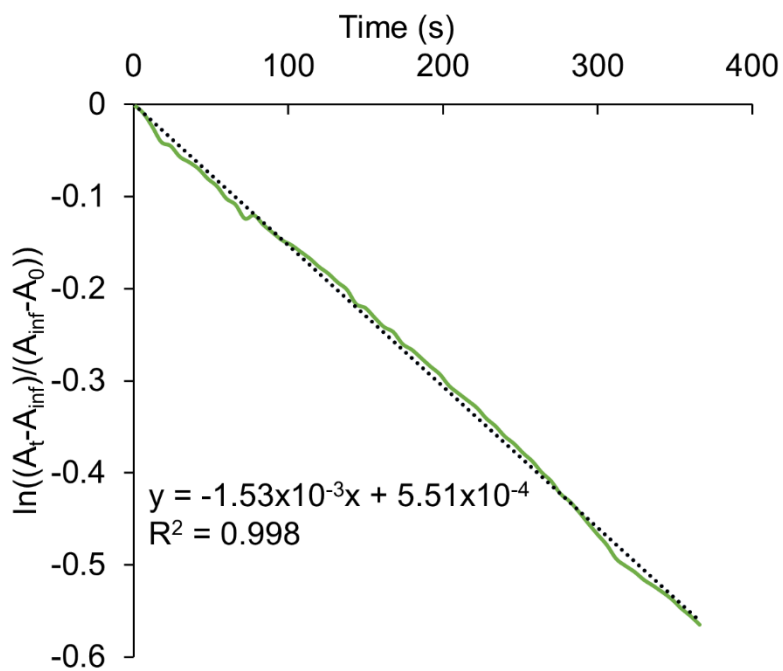
**Figure S7.** Cyclic voltammogram  $1 \text{ mM } (\text{calix})\text{V}_6\text{O}_6$  with  $100 \text{ mM } [\text{NBu}_4][\text{PF}_6]$  electrolyte at a scan rate of  $20 \text{ mV s}^{-1}$  in THF.



**Figure S8.** Cyclic Voltammogram of the irreversible reduction of TEMPO in THF vs Fc/Fc<sup>+</sup> with 0.1 M TBAPF<sub>6</sub> as a counter electrolyte.

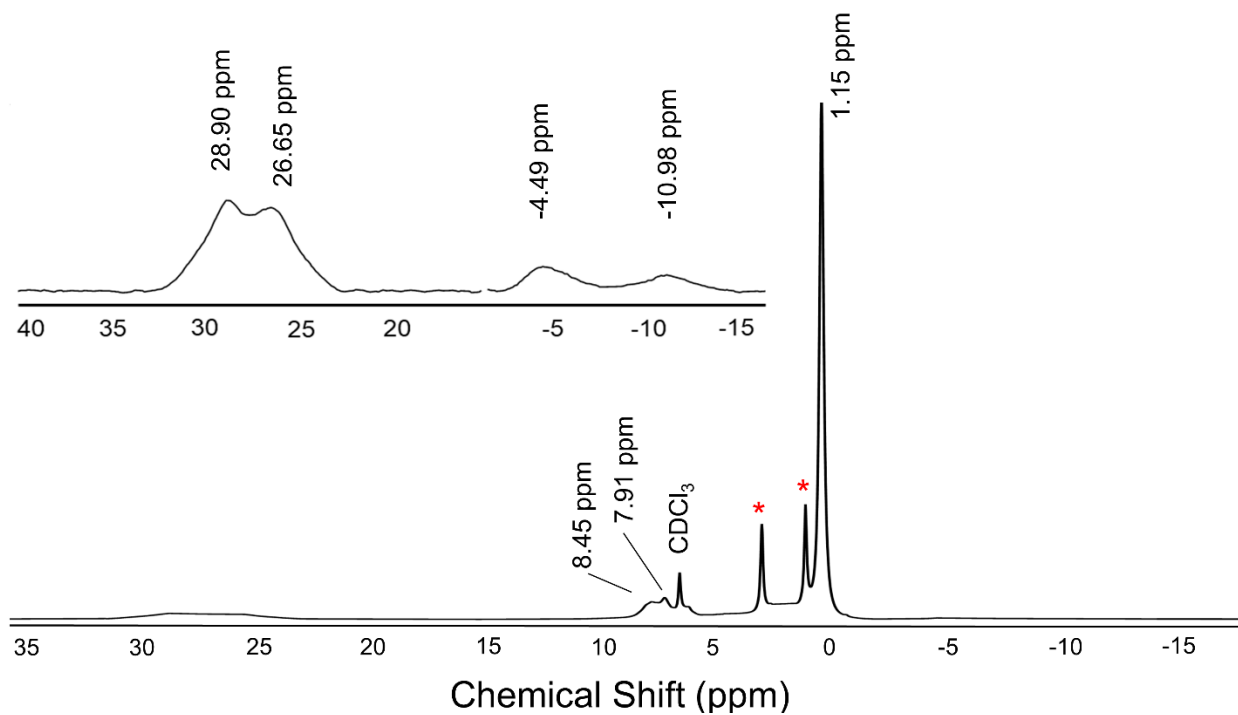


**Figure S9.** Absorbance trace for the reaction between 0.5 mM (**calix**)V<sub>6</sub>O<sub>5</sub>(OH<sub>2</sub>), and 43 mM TEMPO in THF. The extent of the reaction was monitored at 900 nm. Experiment was performed at 25 °C.

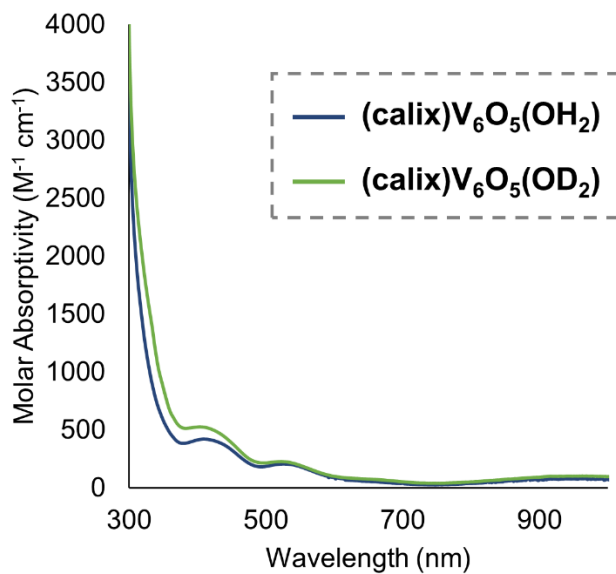


**Figure S10.** Plot used to obtain the pseudo first-order rate constant for kinetic experiments performed in this work. Plotting  $\ln(A_t - A_{inf}/A_{inf} - A_0)$  against time results in a linear trend, from which the  $k_{obs}$  value can be determined from the absolute value of the slope.  $A_t$  = absorbance at time =  $t$ ,  $A_{inf}$  = absorbance at equilibrium, and  $A_0$  = initial absorbance.

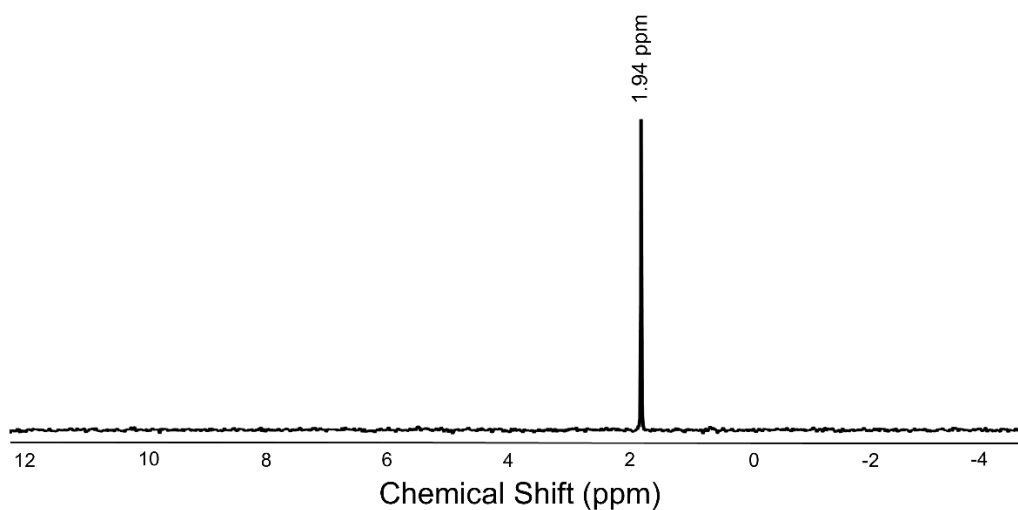




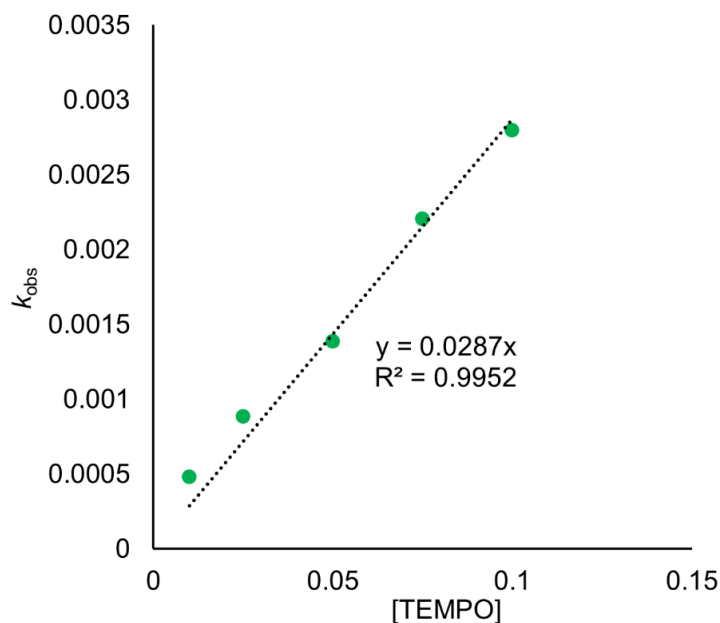
**Figure S11.**  $^1\text{H}$  NMR spectrum of  $(\text{calix})\text{V}_6\text{O}_5(\text{OD}_2)$  in  $\text{CDCl}_3$ , red asterisks indicate residual THF.



**Figure S12.** Comparison of the electronic absorption spectra for  $(\text{calix})\text{V}_6\text{O}_5(\text{OH}_2)$  and  $(\text{calix})\text{V}_6\text{O}_5(\text{OD}_2)$ . Both samples were collected in THF at 21 °C. The similarity of both spectra suggests the successful isolation of the deuterated cluster.



**Figure S13.**  $^2\text{H}$  NMR spectrum of TEMPO-D in tetrahydrofuran after a reaction of  $(\text{calix})\text{V}_6\text{O}_5(\text{OD}_2)$  with 2 eq. TEMPO.



**Figure S14.** Plot of the observed rate constant,  $k_{\text{obs}}$ , collected for the reaction between  $(\text{calix})\text{V}_6\text{O}_5(\text{OD}_2)$  and TEMPO against the concentration of TEMPO originally in solution. Each experiment was run with 0.5 mM of  $(\text{calix})\text{V}_6\text{O}_5(\text{OD}_2)$  initially in the solution. The linear trend of the plotted results indicates first order with respect to TEMPO, where the second order rate constant for the reaction,  $k_{\text{PCET-D}}$ , is determined from the slope of the best fit line with a Y-intercept of 0. Of note,  $k_{\text{PCET-D}}$  is equal to  $\frac{1}{2}$  the slope of the line in order to account for the two chemically identical D atoms at the reduced cluster.