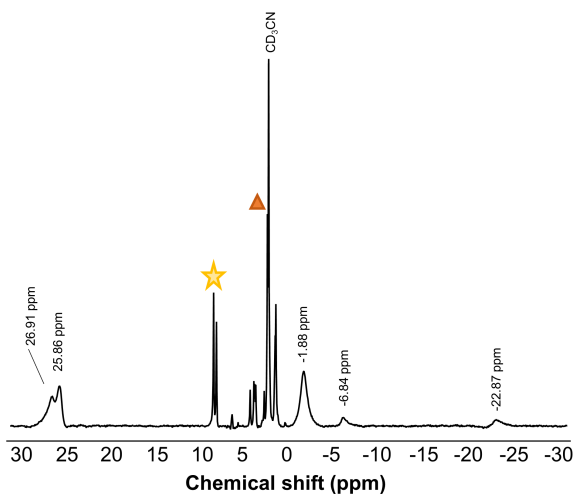


Electronic Supporting Information  
Accelerated Rates of Proton Coupled Electron Transfer to Oxygen Deficient  
Polyoxovanadate-alkoxide Clusters

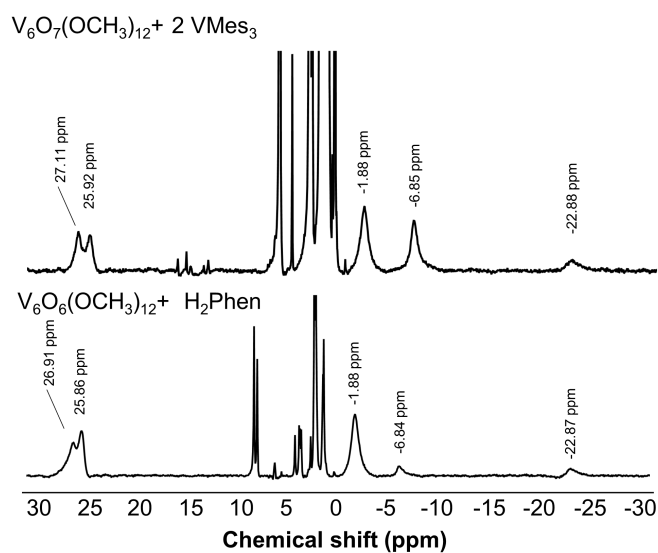
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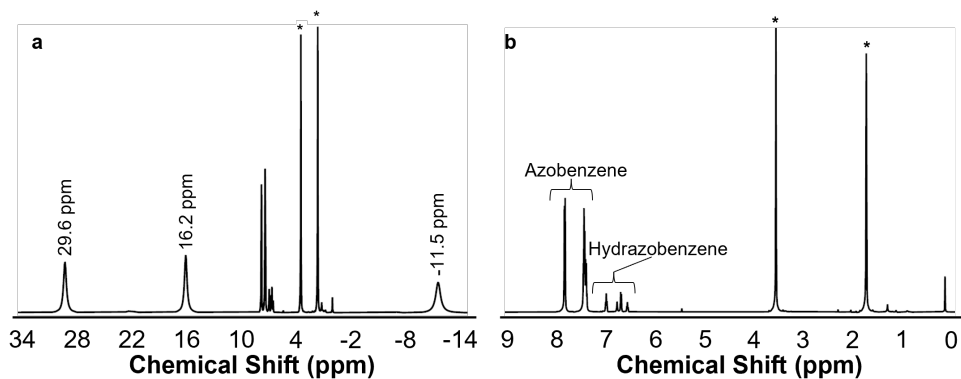
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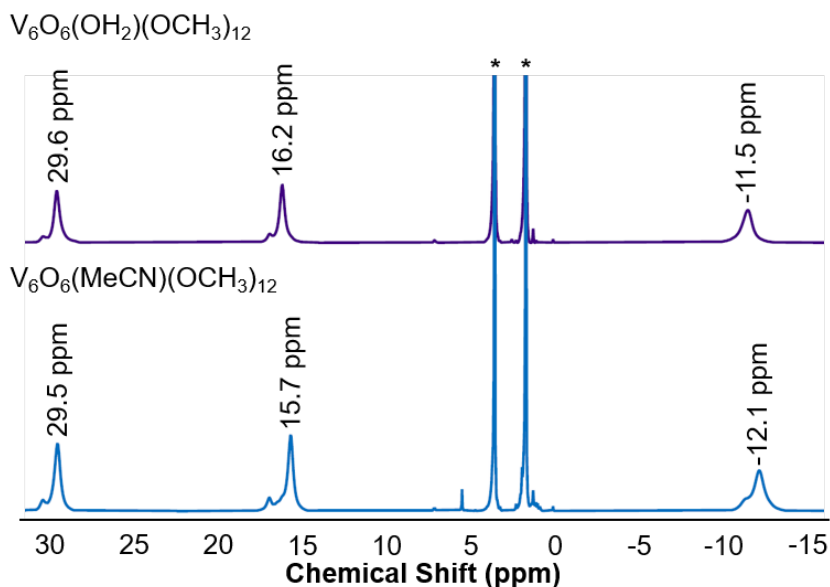
**Figure S1.**  $^1\text{H}$  NMR spectrum of the reaction of  $[\text{V}_6\text{O}_7]^0$  with two equivalents of 5,10-dihydrophenazine ( $\text{H}_2\text{Phen}$ ) at 294 K in  $\text{CD}_3\text{CN}$  after 3 minutes. Orange triangle represent  $\text{H}_2\text{O}$  (2.13 in  $\text{CD}_3\text{CN}$ ) product and yellow star denotes phenazine.



**Figure S2.**  $^1\text{H}$  NMR spectrum of  $[\text{V}_6\text{O}_7]^0 + 2$  equivalents of  $\text{VMes}_3(\text{THF})$  (2019, top)<sup>1</sup> and the synthesis of  $[\text{V}_6\text{O}_5(\text{MeCN})_2]^0$  using 2 equivalents of HAT reagent ( $\text{H}_2\text{Phen}$ ) (2023, bottom) at 294 K in  $\text{CD}_3\text{CN}$ .



**Figure S3.**  $^1\text{H}$  NMR spectrum of the reaction of  $[\text{V}_6\text{O}_7]^0$  with one equivalent of hydrazobenzene (Hydz) at 294 K in  $\text{THF-d}_8$ , a- paramagnetic region showing the three peaks associated with  $[\text{V}_6\text{O}_6(\text{OH}_2)]^0$ , b- diamagnetic region showing the formation of azobenzene and residual hydrazobenzene. Notable in this crude reaction mixture is the lack of formation of  $\text{H}_2\text{O}$ , indicating it remains bound to the cluster.



**Figure S4.**  $^1\text{H}$  NMR spectra of  $[\text{V}_6\text{O}_6(\text{MeCN})]^0$  (blue, bottom) and  $[\text{V}_6\text{O}_6(\text{OH}_2)]^0$  (purple, top) at 294 K in  $\text{THF-d}_8$ .

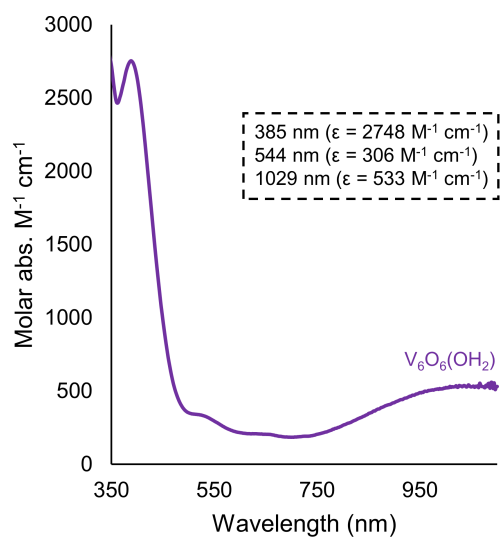
**Table S1.** Crystallographic parameters of the molecular structure obtained for complex  $[\text{V}_6\text{O}_6(\text{OH}_2)] \cdot \text{THF}_2$ .

Compound	$[\text{V}_6\text{O}_6(\text{OH}_2)] \cdot \text{THF}_2$
Empirical formula	$\text{C}_{20}\text{H}_{54}\text{O}_{21}\text{V}_6$
Formula weight	936.27
Temperature / K	100.00(10)
Wavelength / Å	1.54184
Crystal group	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	$a = 92190(2) \text{ \AA}$ $b = 10.6059(2) \text{ \AA}$ $c = 18.4535(2) \text{ \AA}$ $\alpha = 96.3890(10)^\circ$ $\beta = 90.1810(10)^\circ$ $\gamma = 91.4940(10)^\circ$
Volume / Å <sup>3</sup>	1792.46(6)
Z	2
Reflections collected	54875
Independent reflections	7646
Completeness (theta)	99.4% (74.504°)
Goodness-of-fit on $F^2$	1.117
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0360$
Largest diff. peak and hole	0.535 and -0.490 e.Å <sup>-3</sup>

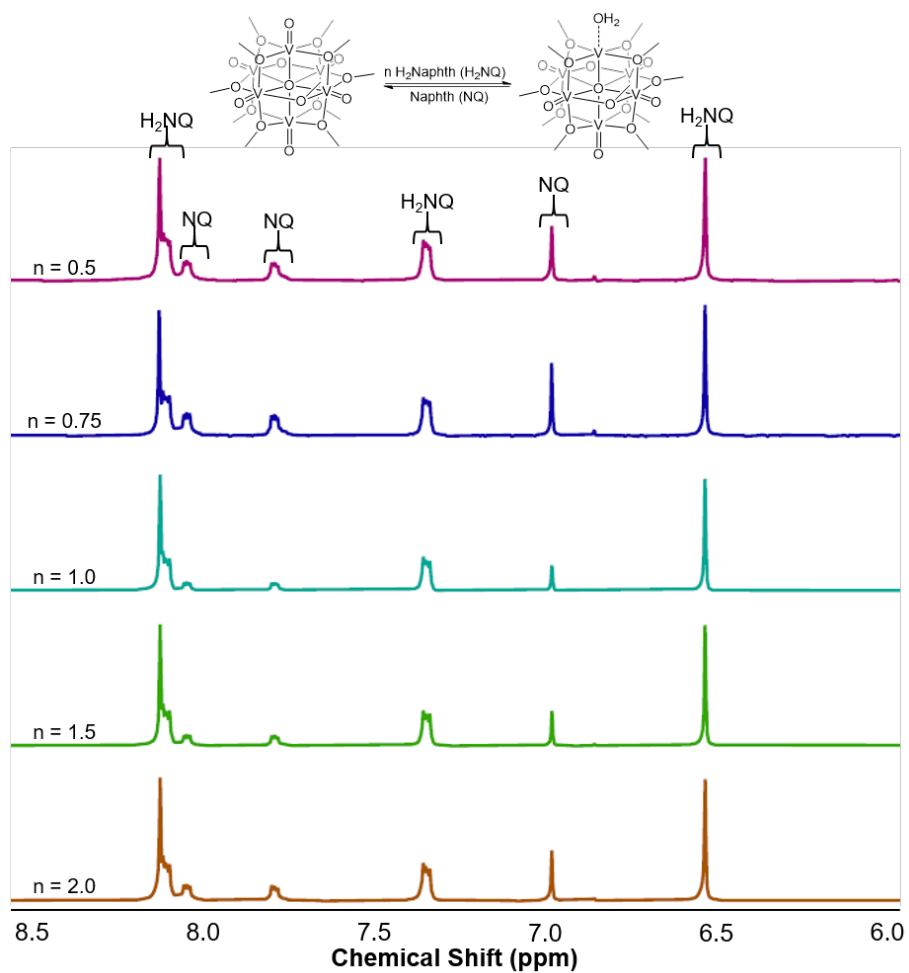
**Table S2.** Bond valence sum calculations on the V ions of  $[\text{V}_6\text{O}_6(\text{OH}_2)]^0$ .

Oxidation State	V1 <sup>a</sup>	V2	V3	V4	V5	V6
V <sup>III</sup>	<b>3.067</b>	3.885	3.936	3.909	3.939	4.421
V <sup>IV</sup>	3.141	<b>3.978</b>	<b>4.030</b>	<b>4.002</b>	<b>4.033</b>	4.526
V <sup>V</sup>	3.376	4.242	4.297	4.267	4.299	<b>4.820</b>

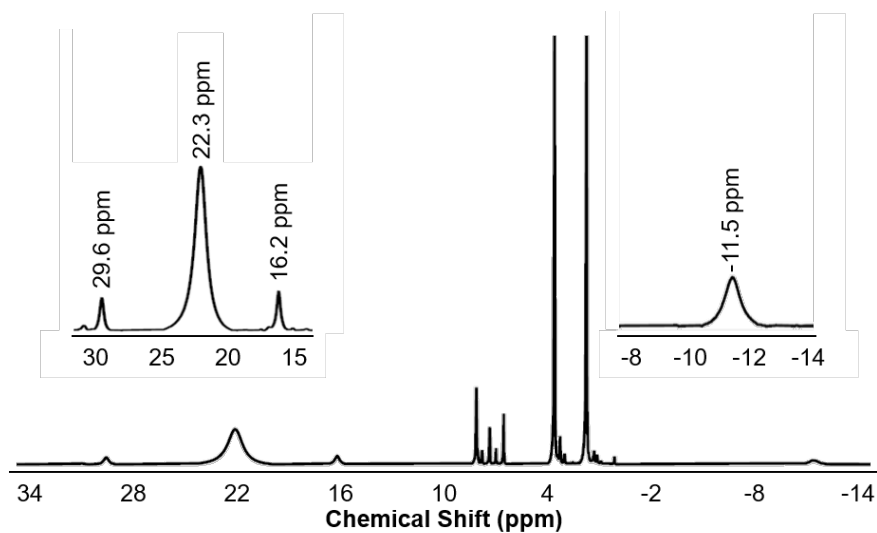
<sup>a</sup>V1 bears a terminal aquo ligand



**Figure S5.** Electronic absorption spectrum of  $[\text{V}_6\text{O}_6(\text{OH}_2)]^0$  recorded at 294 K in THF, bands are labeled in figure inset.



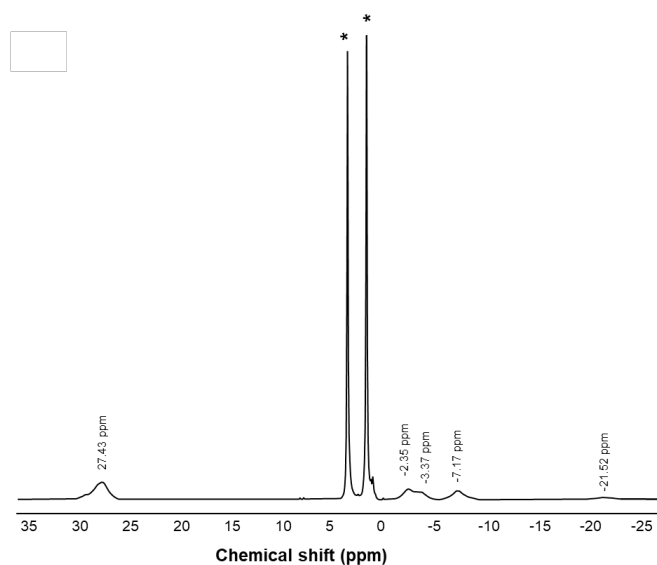
**Figure S6.**  $^1\text{H}$  NMR spectra of reactions of 1,4-dihydroxynaphthalene ( $\text{H}_2\text{Naphth}$ ) with  $[\text{V}_6\text{O}_7]^0$  at various reductant:cluster ratios at 21 °C for 7 days recorded in  $\text{THF-d}_8$  at 294 K.



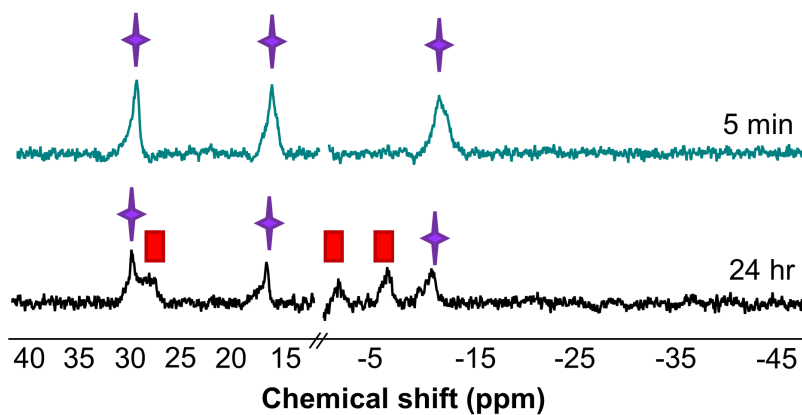
**Figure S7.** <sup>1</sup>H NMR spectrum of the reaction of  $[\text{V}_6\text{O}_7]^0$  with one equivalent of  $\text{H}_2\text{Naphth}$  at 294 K after 7 days in  $\text{THF-d}_8$ .

**Table S3.** BDFE<sub>adj</sub> calculated for  $[\text{V}_6\text{O}_6(\text{OH})_2]^{0-}$  from equilibrium reactions described in Figure S6, using the equation outlined in the Experimental section in the main text.

n	1,4-Dihydroxynaphthalene						Naphthoquinone						BDFE <sub>adj</sub> (kcal/mol)		
	8.1 ppm (4 H)		7.3 ppm (2 H)		6.5 ppm (2 H)		Avg. Conc.	8.0 ppm (2 H)		7.8 ppm (2 H)		7.0 ppm (2 H)		Avg. Conc.	
	Integral	Conc. <sup>a</sup>	Integral	Conc. <sup>a</sup>	Integral	Conc. <sup>a</sup>		Integral	Conc. <sup>a</sup>	Integral	Conc. <sup>a</sup>	Integral			Conc. <sup>a</sup>
0.5	3.47	0.87	1.76	0.88	1.70	0.85	<b>0.87</b>	1.07	0.54	0.91	0.46	0.84	0.42	<b>0.47</b>	
0.75	4.40	1.10	2.17	1.09	2.15	1.08	<b>1.09</b>	1.12	0.56	1.00	0.5	0.86	0.43	<b>0.50</b>	
1.0	4.92	1.23	2.46	1.23	2.48	1.24	<b>1.23</b>	1.16	0.58	1.00	0.5	0.91	0.46	<b>0.51</b>	
1.5	7.03	1.76	3.48	1.74	3.47	1.74	<b>1.74</b>	1.05	0.53	1.00	0.5	0.87	0.44	<b>0.49</b>	
2.0	8.61	2.15	4.30	2.15	4.29	2.15	<b>2.15</b>	1.05	.525	1.00	0.5	0.88	0.44	<b>0.49</b>	
<sup>a</sup> Relative concentration of either 1,4-dihydroxynaphthalene or naphthoquinone was determined by dividing the integral by the number of protons a given signal(s) corresponds with.															
Avg.															
Std. Dev.															
<b>62.3</b>															
<b>0.1</b>															

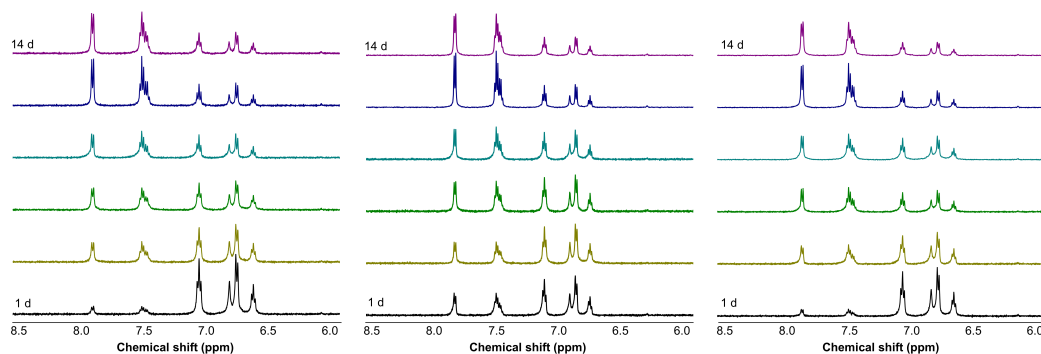


**Figure S8.**  $^1\text{H}$  NMR spectrum of  $[\text{V}_6\text{O}_5(\text{OH}_2)(\text{MeCN})]^{0}$  at 294 K in  $\text{THF-d}_8$  (indicated by asterisks).



**Figure S9.**  $^1\text{H}$  NMR spectra in the paramagnetic region of reaction of Hydrazine with one equivalent of  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  at  $21^\circ\text{C}$  for after 5 min (top, teal) and 1 day (bottom, black) recorded in  $\text{THF-d}_8$  at 294 K. Purple stars indicate starting material  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  and red squares indicate the formation of  $[\text{V}_6\text{O}_5(\text{MeCN})(\text{OH}_2)]^{0}$ .



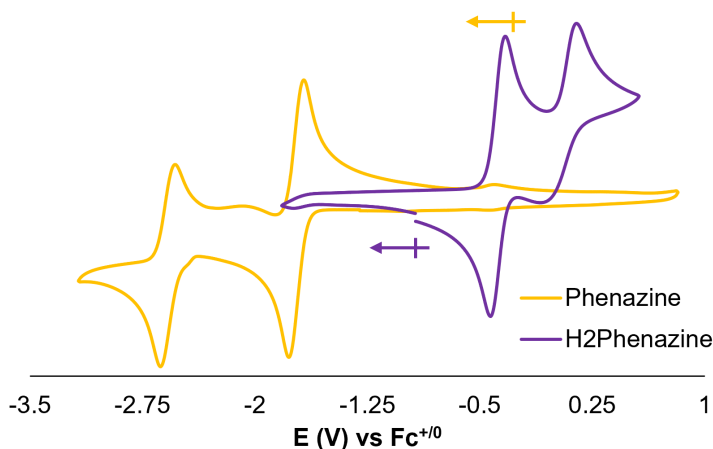


**Figure S10.**  $^1\text{H}$  NMR spectra in the diamagnetic region of reaction of Hydrazobenzene with one equivalent of  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  at 294 K, over 14 days in  $\text{THF-d}_8$ , trial A-C (left to right). Growth of oxidized organic reagent (Azo) is seen at 7.5 and 7.9 ppm.

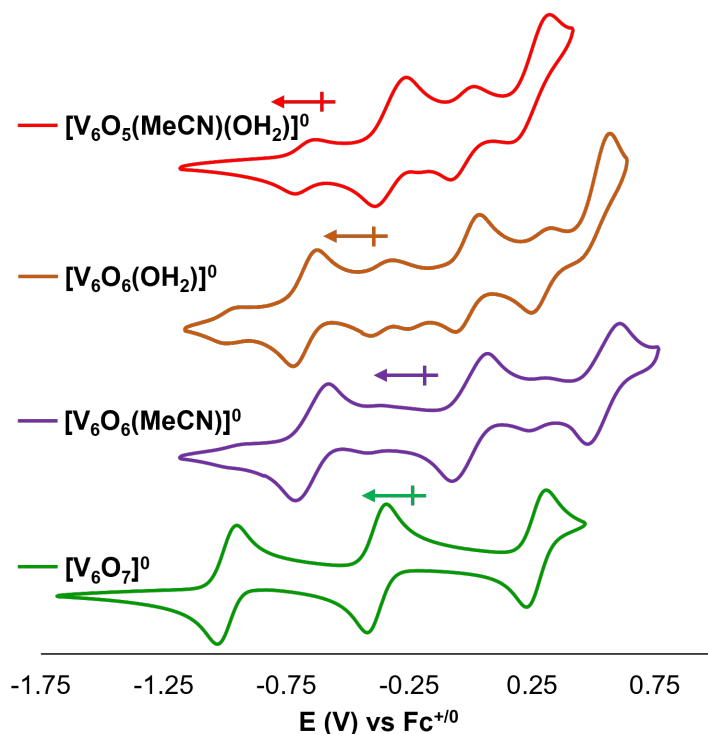
**Table S4.**  $\text{BDFE}_{\text{adj}}$  calculated for  $[\text{V}_6\text{O}_5(\text{MeCN})(\text{OH}_2)]^{0}$  from equilibrium reactions described in Figure S9, using the equation outlined in the Experimental section in the main text.

Trial	Hydrazobenzene					Azobenzene <sup>b</sup>					$\text{BDFE}_{\text{adj}}$ (kcal/mol)	
	7.06 ppm (4 H)		6.77 ppm (6 H)		Avg. Conc.	7.92 ppm (4 H)		7.52 ppm (6 H)		Avg. Conc.		
	Integral	Relative Conc. <sup>a</sup>	Integral	Relative Conc. <sup>a</sup>		Integral	Relative Conc. <sup>a</sup>	Integral	Relative Conc. <sup>a</sup>			
A	0.52	0.13	0.70	0.116	0.125	1	0.25	1.55	0.258	0.254	60.6	
B	0.50	0.125	0.63	0.105	0.115	1	0.25	1.55	0.258	0.254	60.7	
C	0.45	0.113	0.54	0.09	0.102	1	0.25	1.58	0.263	0.256	60.7	
											Avg.	60.7
											Std. Dev.	0.1

<sup>a</sup> Relative concentration of either hydrazobenzene or azobenzene was determined by dividing the integral by the number of protons a given signal(s) corresponds with.



**Figure S11.** CV of 2 mM  $\text{H}_2\text{Phen}$  (purple) and  $\text{Phen}$  (orange) collected at  $100 \text{ mVs}^{-1}$  in  $\text{THF}$  with 200 mM  $[\text{nBu}_4\text{N}][\text{PF}_6]$  supporting electrolyte.



**Figure S12.** CV of 1 mM  $[\text{V}_6\text{O}_7]^0$  (green),  $[\text{V}_6\text{O}_6(\text{MeCN})]^0$  (purple),  $[\text{V}_6\text{O}_6(\text{OH}_2)]^0$  (orange), and  $[\text{V}_6\text{O}_5(\text{MeCN})(\text{OH}_2)]^0$  (red) collected at  $100 \text{ mVs}^{-1}$  in THF with 200 mM  $[\text{nBu}_4\text{N}][\text{PF}_6]$  supporting electrolyte versus  $\text{Fc}^{+/0}$ . Due to electrochemical instability of the O-atom deficient species, some features of the corresponding oxidized complex are observed on the CV timescale.

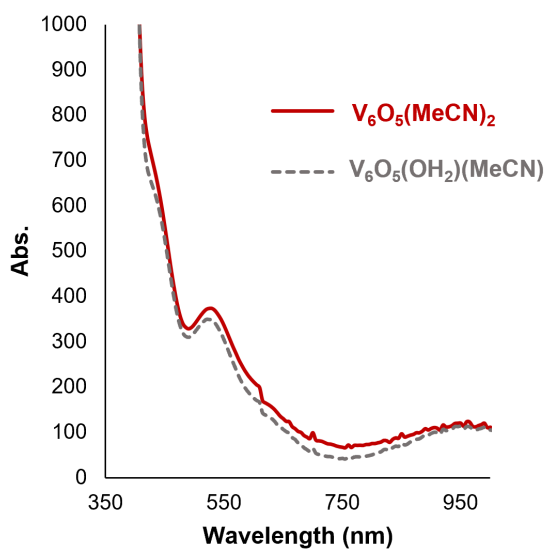
**Table S5.** Redox potentials of  $[\text{V}_6\text{O}_7]^0$ ,  $[\text{V}_6\text{O}_6(\text{MeCN})]^0$ ,  $[\text{V}_6\text{O}_6(\text{OH}_2)]^0$ ,  $[\text{V}_6\text{O}_5(\text{MeCN})(\text{OH}_2)]^0$ , Phen, and  $\text{H}_2\text{Phen}$  from CVs in Figure S12 (vs  $\text{Fc}^{+/0}$ ). The position of the open circuit voltage is denoted by the red border lines

$[\text{V}_6\text{O}_7]^0$	$[\text{V}_6\text{O}_6(\text{MeCN})]^0$	$[\text{V}_6\text{O}_6(\text{OH}_2)]^0$	$[\text{V}_6\text{O}_5(\text{MeCN})(\text{OH}_2)]^0$	Phen	$\text{H}_2\text{Phen}$
-0.994	-0.646	-0.674	-0.325	-2.57	-0.387
-0.385	-0.0197	-0.0231	0.222	-1.72	0.0240
0.267	0.523	0.467	-	-	-

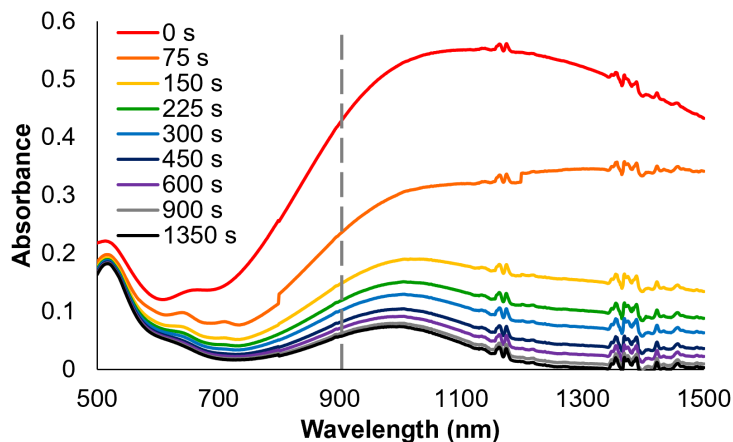
**Table S6.** Determination of the average  $pK_a$ 's of  $H_2Phen$ , “[ $V_6O_6(OH_2)$ ] $^{2+}$ ”, and “[ $V_6O_5(MeCN)(OH_2)$ ] $^{2+}$ ” in THF using the Bordwell Equation.

Compound	BDFE (kcal mol $^{-1}$ )	$E^0$ <sup>a</sup> (V, vs $Fc^{+/0}$ )	$E^0$ (avg) (V, vs $Fc^{+/0}$ )	$C_G$ (kcal mol $^{-1}$ )	$pK_a$
$H_2Phen$	59.2	-1.72, -2.57	-2.15	59.9	35.6
“[ $V_6O_5(MeCN)(OH_2)$ ] $^{2+}$ ”	60.7	-0.646, -0.0197	-0.0514	59.9	1.45
“[ $V_6O_6(OH_2)$ ] $^{2+}$ ”	62.3	-0.0231, 0.467	0.222	59.9	-1.98

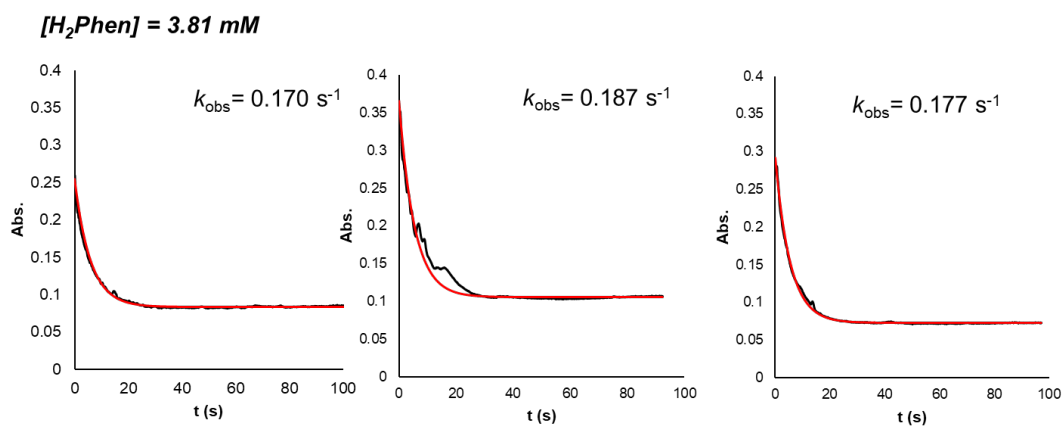
<sup>a</sup>  $1e^-$  redox potentials of respective species. For  $H_2Phen$ , the reduction events of  $Phen$  were used. For cluster species, the oxidation potentials of the [ $V_6O_5(MeCN)(OH_2)$ ] $^0$  and [ $V_6O_6(OH_2)$ ] $^0$  were used.



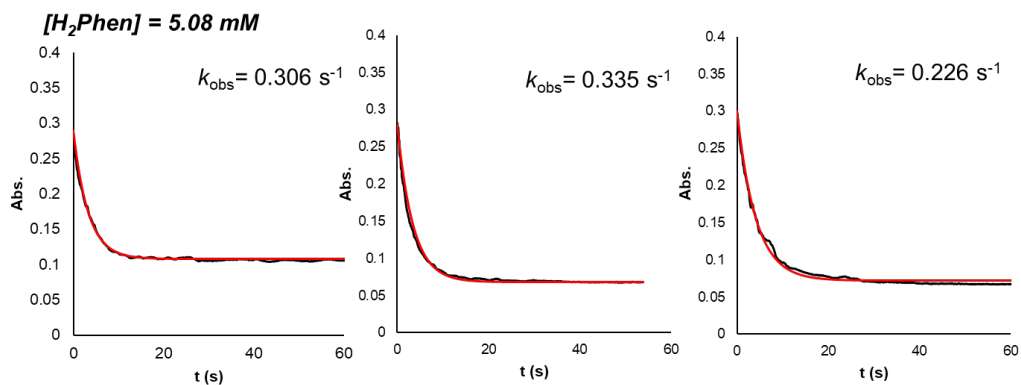
**Figure S13.** Electronic absorption spectrum of [ $V_6O_5(OH_2)(MeCN)$ ] $^0$ , grey dotted trace and [ $V_6O_5(MeCN)_2$ ] $^0$ , red trace, recorded at 21 °C in THF.



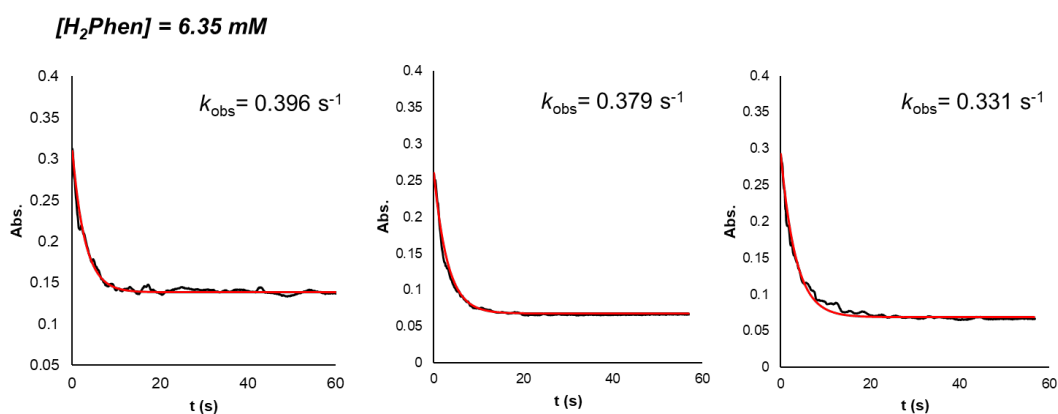
**Figure S14.** UV-Vis NIR of  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.83 mM)+ 1 eq  $\text{H}_2\text{Phen}$  (0.83 mM) over time at 238 K in MeCN.



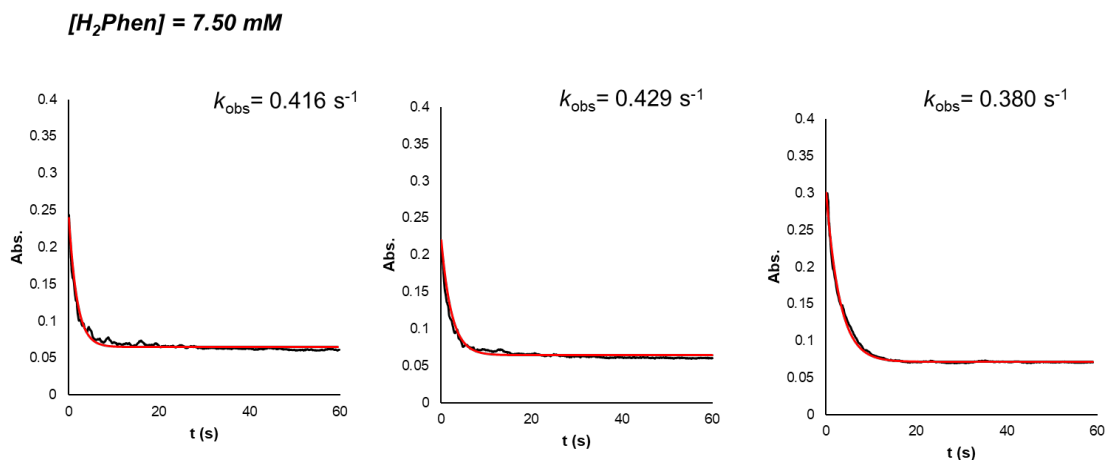
**Figure S15.** Plot of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{H}_2\text{Phen}$  (3.81 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 258 K, with raw data (black) and a fit curve (red). Concentration of  $\text{H}_2\text{Phen}$  for each reaction is noted, alongside the fit-derived  $k_{\text{obs}}$ . Triplicate data sets are reported.



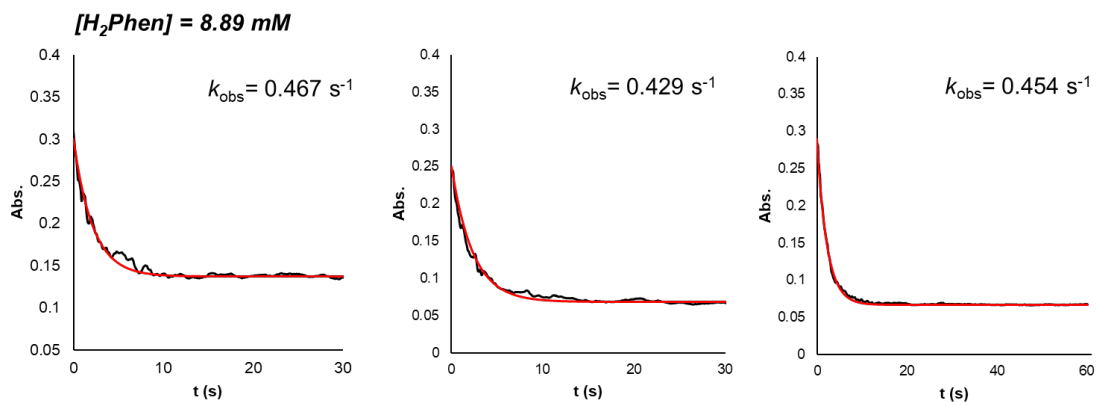
**Figure S16.** Plot of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{H}_2\text{Phen}$  (5.08 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 258 K, with raw data (black) and a fit curve (red). Concentration of  $\text{H}_2\text{Phen}$  for each reaction is noted, alongside the fit-derived  $k_{\text{obs}}$ . Triplicate data sets are reported.



**Figure S17.** Plot of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{H}_2\text{Phen}$  (6.35 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 258 K, with raw data (black) and a fit curve (red). Concentration of  $\text{H}_2\text{Phen}$  for each reaction is noted, alongside the fit-derived  $k_{\text{obs}}$ . Triplicate data sets are reported.

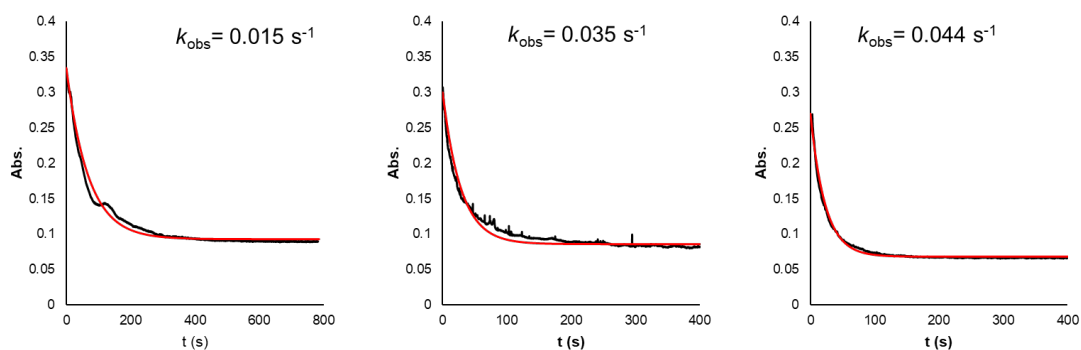


**Figure S18.** Plot of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{H}_2\text{Phen}$  (7.50 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 258 K, with raw data (black) and a fit curve (red). Concentration of  $\text{H}_2\text{Phen}$  for each reaction is noted, alongside the fit-derived  $k_{\text{obs}}$ . Triplicate data sets reported.

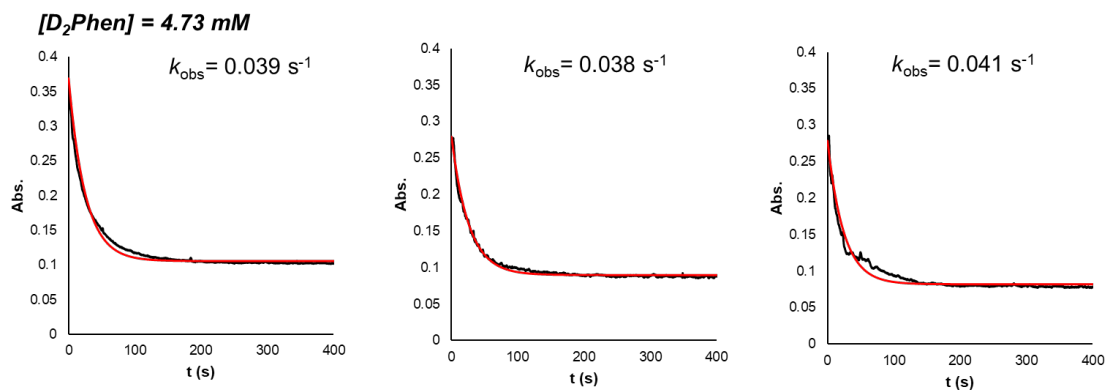


**Figure S19.** Plot of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{H}_2\text{Phen}$  (8.89 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 258 K, with raw data (black) and a fit curve (red). The fit-derived  $k_{\text{obs}}$  is noted. Triplicate data sets are reported.

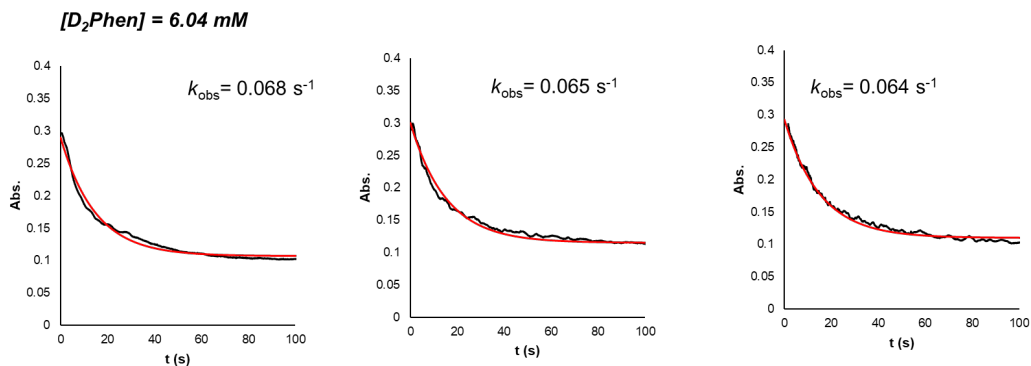
**[D<sub>2</sub>Phen] = 3.75 mM**



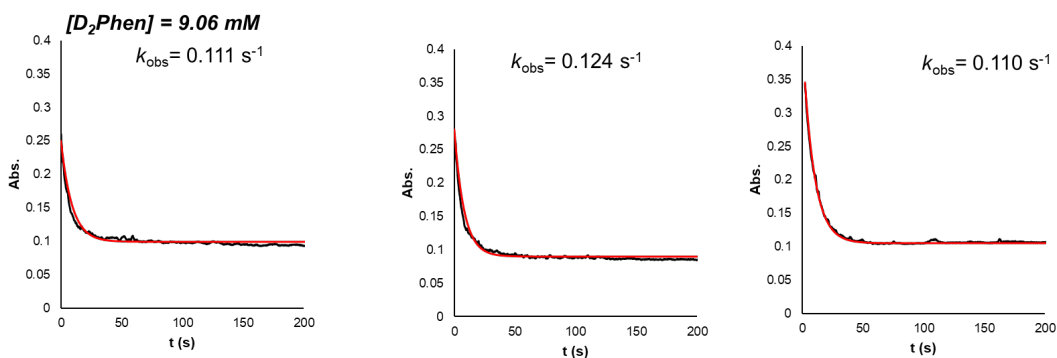
**Figure S20.** Plots of absorbance at 900 nm over time for reactions between  $[V_6O_6(MeCN)]^0$  (0.75 mM) and excess  $D_2Phen$  (3.75 mM) under pseudo-first order conditions recorded in  $CH_3CN$  at 258 K, with raw data (black) and a fit curve (red). The fit-derived  $k_{obs}$  is noted. Triplicate data sets are reported.



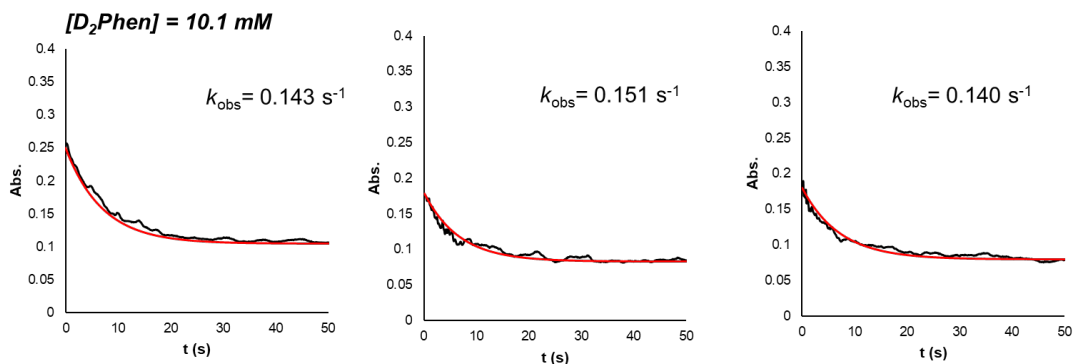
**Figure S21.** Plots of absorbance at 900 nm over time for reactions between  $[V_6O_6(MeCN)]^0$  (0.75 mM) and excess  $D_2Phen$  (4.73 mM) under pseudo-first order conditions recorded in  $CH_3CN$  at 258 K, with raw data (black) and a fit curve (red). The fit-derived  $k_{obs}$ . Triplicate data sets are reported.



**Figure S22.** Plots of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{D}_2\text{Phen}$  (6.04 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 258 K, with raw data (black) and a fit curve (red). Concentration of  $\text{D}_2\text{Phen}$  for each reaction is noted, alongside the fit-derived  $k_{\text{obs}}$ .



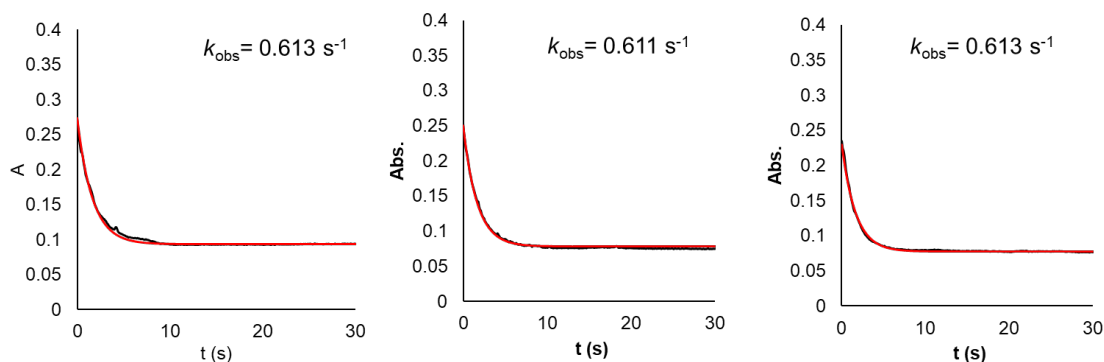
**Figure S23.** Plots of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{D}_2\text{Phen}$  (9.06 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 15 °C, with raw data (black) and a fit curve (red). The fit-derived  $k_{\text{obs}}$  is noted. Triplicate data sets are reported.



**Figure S24.** Plots of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^{0}$  (0.75 mM) and excess  $\text{D}_2\text{Phen}$  (10.1 mM) under pseudo-first order conditions recorded in  $\text{CH}_3\text{CN}$  at 258 K, with raw data (red) and a fit curve (black). The fit-derived  $k_{\text{obs}}$  is noted. Triplicate data sets are reported.

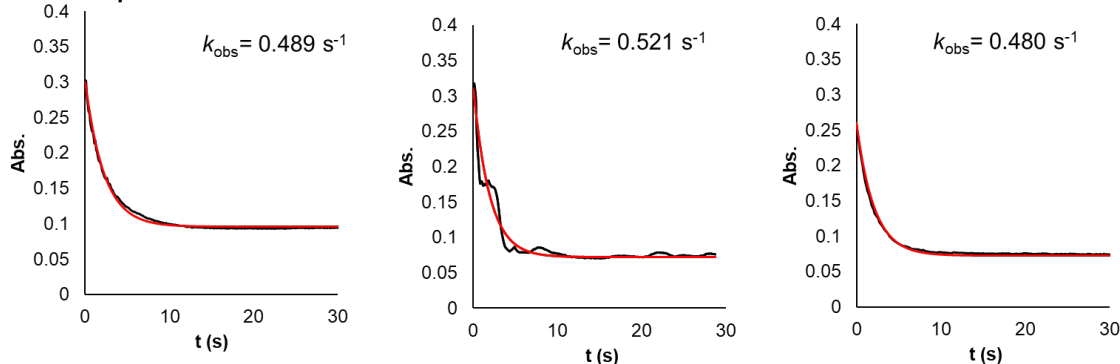


**Temperature: 278 K**



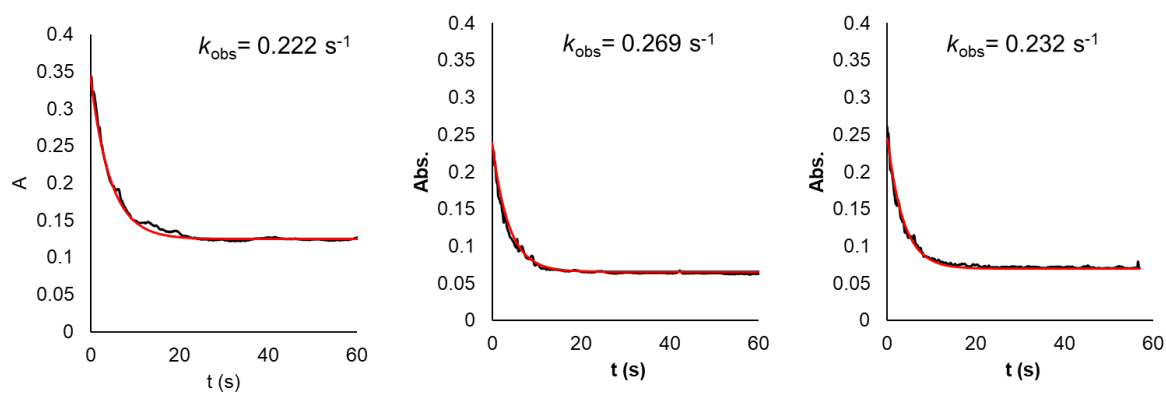
**Figure S25.** Plots of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^0$  (0.75 mM) and  $\text{H}_2\text{Phen}$  (7.26 mM) recorded in  $\text{CH}_3\text{CN}$  at 278 K, with raw data (black) and a fit curve (red), providing  $k_{\text{obs}}$ . Triplicate data sets are reported.

**Temperature: 268 K**

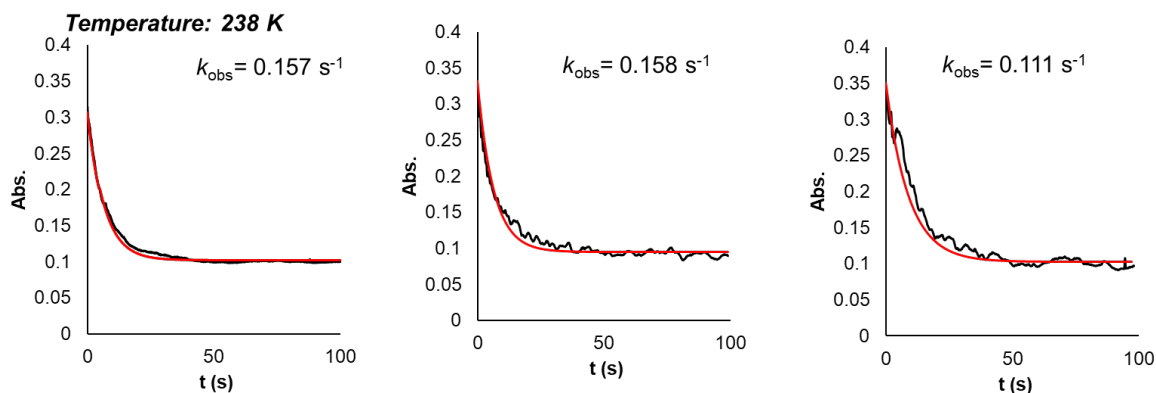


**Figure S26.** Plots of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^0$  (0.75 mM) and  $\text{H}_2\text{Phen}$  (7.26 mM) recorded in  $\text{CH}_3\text{CN}$  at 268 K, with raw data (black) and a fit curve (red), providing  $k_{\text{obs}}$ . Triplicate data sets are reported.

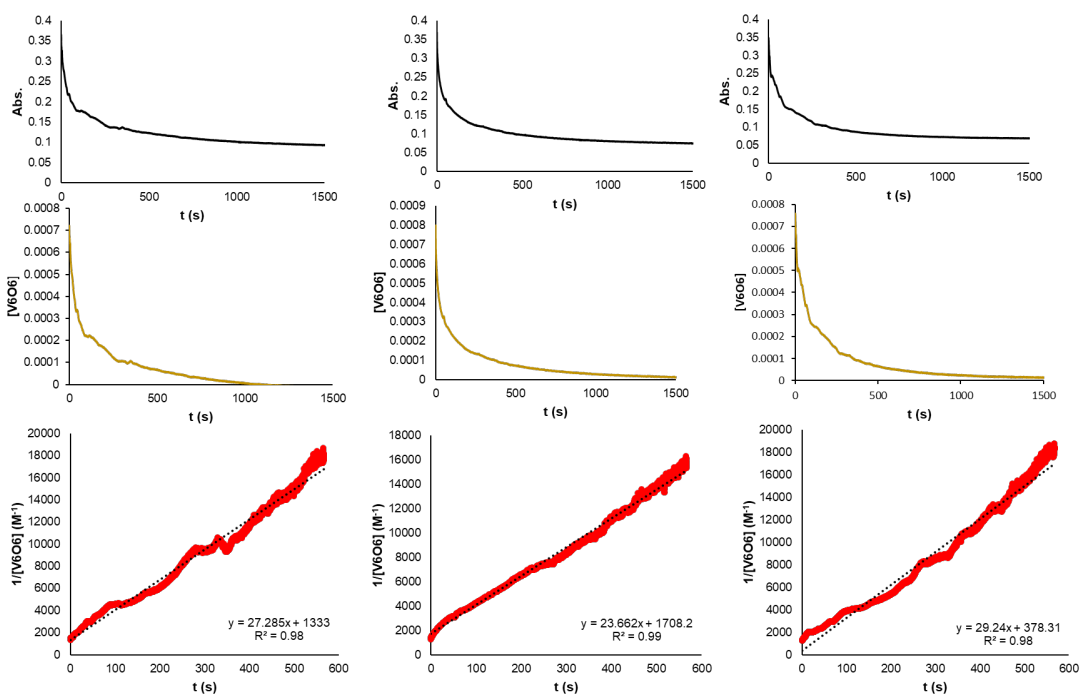
**Temperature: 248 K**



**Figure S27.** Plots of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^0$  (0.75 mM) and  $\text{H}_2\text{Phen}$  (7.26 mM) recorded in  $\text{CH}_3\text{CN}$  at 248 K, with raw data (black) and a fit curve (red), providing  $k_{\text{obs}}$ . Triplicate data sets are reported.



**Figure S28.** Plots of absorbance at 900 nm over time for reactions between  $[\text{V}_6\text{O}_6(\text{MeCN})]^0$  (0.75 mM) and  $\text{H}_2\text{Phen}$  (7.26 mM) recorded in  $\text{CH}_3\text{CN}$  at 238 K, with raw data (black) and a fit curve (red), providing  $k_{\text{obs}}$  and  $k_{\text{exp}}$ .



**Figure S29.**  $\text{V}_6\text{O}_6(\text{MeCN})$  (0.75 mM) + 1 eq  $\text{H}_2\text{Phen}$  (0.75 mM) in MeCN, over 30 minutes at 258 K. Exponential decay of  $\text{V}_6\text{O}_6(\text{MeCN})$  is monitored at 900 nm to least 3 half-lives, (top, black trace). Concentration of  $\text{V}_6\text{O}_6(\text{MeCN})$  converted from absorbance using the following equations:  $[\text{V}_6\text{O}_6]_t = [\text{V}_6\text{O}_6]_0 - [\text{V}_6\text{O}_5]_t$  and  $[\text{V}_6\text{O}_5]_t = (A_0 - A_t) / (\epsilon_{\text{V}_6\text{O}_6} - \epsilon_{\text{V}_6\text{O}_5})^2$ , where @ 900 nm  $\epsilon_{\text{V}_6\text{O}_6} = 415 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_{\text{V}_6\text{O}_5} = 98 \text{ M}^{-1} \text{ cm}^{-1}$ , (middle, yellow trace). Plot of  $1/[\text{V}_6\text{O}_6(\text{MeCN})]$  vs  $t$  (bottom, red trace. Black dotted line indicates linear fit). Dividing the slope by the # of V=O and H-atoms transferred gets a second order  $k_{\text{PCET}} = 3.5 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ . Data sets reported in triplicate.

## References

1. B. E. Petel, A. A. Fertig, M. L. Maiola, W. W. Brennessel and E. M. Matson, *Inorganic Chemistry*, 2019, **58**, 10462-10471.
2. X. Lu, X. Li, Y. Lee, Y. Jang, M. S. Seo, S. Hong, K. Cho, S. Fukuzumi and W. Nam, *Journal of the American Chemical Society* 2020 **142**, 3891-3904.