Supplementary information

Exploring the interaction of decavanadate with methylene blue, toluidine blue and rhodamine B

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Table S1. Bond lengths (Å) and angles (°) for the V_{10} anion in **2,3-ampV$_{10}$** and **MBV$_{10}$**

	2,3-ampV$_{10}$	**MBV$_{10}$**
	Bonds (Å)	
V1-O1	1.609(3)	1.595(6)
V1-O2	1.901(2)	2.048(5)
V1-O3	2.064(2)	1.846(6)
V1-O4	1.864(2)	1.827(6)
V1-O5	1.799(2)	1.910(6)
V1-O14	2.345(2)	2.330(5)
V2-O2	1.784(2)	1.684(5)
V2-O6	1.616(2)	1.676(5)
V2-O7	1.972(2)	2.009(6)
V2-O13	1.860(2)	1.894(6)
V2-O14	2.236(2)	2.106(5)
V3-O3	1.683(2)	1.845(6)
V3-O7	1.926(2)	2.057(5)
V3-O8	1.687(2)	1.597(6)
V3-O9	1.942(2)	1.789(6)
V3-O14	2.098(2)	2.273(6)
V4-O4	1.807(2)	1.833(6)
V4-O9	1.979(2)	1.879(6)
V4-O10	1.615(2)	1.604(5)
V4-O11	1.843(2)	1.892(6)
V4-O14	2.239(2)	2.322(5)
V5-O5	1.846(2)	1.763(5)
V5-O11	1.870(2)	1.882(5)
V5-O12	1.616(2)	1.595(7)
V5-O13	1.859(2)	1.966(5)
V5-O14	2.294(2)	2.274(6)
	Angles (°)	

O1-V1-O2	101.7(2)	100.0(3)
O1-V1-O3	100.2(1)	102.3(3)
O1-V1-O4	102.5(1)	104.5(3)
O1-V1-O5	105.3(1)	101.5(3)
O1-V1-O14	173.2(1)	173.2(2)
O2-V1-O3	81.75(9)	84.2(2)
O2-V1-O4	153.2(1)	155.4(2)
O2-V1-O5	91.8(1)	82.3(2)
O2-V1-O14	76.95(9)	73.4(2)
O3-V1-O4	82.72(9)	93.1(2)
O3-V1-O5	154.5(1)	154.4(3)
O3-V1-O14	73.01(8)	78.6(2)
O4-V1-O5	92.9(1)	90.2(3)
O4-V1-O14	77.67(9)	82.1(2)
O5-V1-O14	81.47(9)	76.8(2)
O2-V2-O6	102.7(1)	106.6(3)
O2-V2-O7	92.8(1)	94.2(3)
O2-V2-O13	95.4(1)	99.4(3)
O2-V2-O14	82.20(9)	86.9(2)
O6-V2-O7	100.8(1)	95.2(3)
O6-V2-O13	101.7(1)	99.0(3)
O6-V2-O14	174.8(1)	165.9(2)
O7-V2-O13	153.7(1)	156.6(2)
O7-V2-O14	76.95(8)	79.8(2)
O13-V2-O14	79.49(9)	82.0(2)
O3-V3-O7	97.2(1)	87.9(2)
O3-V3-O8	106.7(1)	102.2(3)
O3-V3-O9	97.7(1)	95.7(2)
O3-V3-O14	87.55(9)	80.1(2)
O7-V3-O8	97.0(1)	99.3(3)
O7-V3-O9	156.48(9)	154.7(2)

O7-V3-O14	81.34(9)	75.0(2)
O8-V3-O9	96.0(1)	104.3(3)
O8-V3-O14	165.71(9)	173.8(3)
O9-V3-O14	81.24(9)	81.0(2)
O4-V4-O9	91.31(9)	91.6(3)
O4-V4-O10	101.9(1)	104.1(3)
O4-V4-O11	95.5(1)	91.5(3)
O4-V4-O14	81.66(9)	82.2(2)
O9-V4-O10	100.1(1)	102.3(3)
O9-V4-O11	154.6(1)	154.9(3)
O9-V4-O14	76.98(8)	77.9(2)
O10-V4-O11	102.4(1)	101.1(3)
O10-V4-O14	175.5(1)	173.6(3)
O11-V4-O14	79.80(9)	77.9(2)
O5-V5-O11	90.4(1)	95.5(3)
O5-V5-O12	103.4(1)	105.0(3)
O5-V5-O13	91.7(1)	93.3(2)
O5-V5-O14	81.96(9)	81.1(2)
O11-V5-O12	101.9(1)	102.5(3)
O11-V5-O13	155.2(1)	152.4(2)
O11-V5-O14	77.81(9)	79.3(2)
O12-V5-O13	101.7(1)	100.4(3)
O12-V5-O14	174.6(1)	173.3(3)
O13-V5-O14	77.97(9)	76.3(2)

Table S2. Decavanadate salts containing aminopyridines as counterions found in the CCDC database

Organic part	Formulation	CCDC# refcode	Ref.
2-aminopyridine	$[2\text{-ampH}]_6[V_{10}O_{28}]\cdot 2H_2O$	DEFPIO, DEFPIO01, DEFPIO02,	1-3
	$[\{Cu(2\text{-amp})_2(H_2O)\}_2H_2V_{10}O_{28}]\cdot 4H_2O$	FASBEI	4
3- aminopyridine	$[\{Co(3\text{-amp})(H_2O)_5\}]_2[3\text{-ampH}]_2[V_{10}O_{28}]\cdot 6H_2O$	SUDGEG	5
	$[3\text{-ampH}]_6[V_{10}O_{28}]\cdot 2H_2O$	AROYOW	6
4- aminopyridine	$[4\text{-dmampH}]_4[H_2V_{10}O_{28}]\cdot 5H_2O$*	ROSYEG	7
	$[4\text{-ampH}]_{10}[\{Na(H_2O)_6\}\{HV_{10}O_{28}\}][V_{10}O_{28}]\cdot 15H_2O$	SUDGIK	5
	$[\{4\text{-ampH}\}_6\{Co(H_2O)_6\}_3][V_{10}O_{28}]_2\cdot 14H_2O$	SUDGOQ	5
	$[\{4\text{-ampH}\}_{10}\{Zn(H_2O)_6\}][V_{10}O_{28}]_2\cdot 10H_2O$	SUDGUW	5
	$[4\text{-dmampH}]_6[V_{10}O_{28}]\cdot 16H_2O$	ZADHUK, ZADHUK01	8, 9
	$[4\text{-dmampH}]_6[V_{10}O_{28}]\cdot H_2O$	XEHZIW	9
	$[4\text{-dmampH}]_4(NH_4)_2[V_{10}O_{28}]\cdot 8H_2O$	WULQIF	10
4- dimethylaminopyridinium	$[(C_7H_{11}N_2)_4][Mg(H_2O)_6][O_{28}V_{10}].4H_2O$	LOPGOQ	11

*dmampH = dimethylaminopyridinium cation

CCDC = Cambridge Crystallographic Data Centre

Table S3. Tentative assignments for the infrared absorption spectrum (cm^{-1}) of $(2,3\text{-ampH})_6[V_{10}O_{28}]\cdot 4H_2O$ (**2,3-ampV$_{10}$**)[12, 13]

Tentative assignments	**2,3-ampV$_{10}$**
ν(O–H) and ν(N–H)	3551, 3356 and 3176
$\nu(C–C)_{ring}$, δ(N–H) or $\delta(O–H)_{water}$	1653
$\nu(C–C)_{ring}$ and δ(N–H)	1566
$\delta(CH_3)$	1470, 1387, 1362 and 1304
ν(C=N)	1252
ν(V=O)	947
ν_{as}(V–O) ν_{sym}(V–O) and δ(C–H)	839 and 737
δ(V–O–V)	594 and 453
δ(C–N–C)	538

ν = stretching, ν_{as} = asymmetric stretching, ν_{sym} = symmetric stretching, and δ = in- or out-of-plane bending

Table S4. Tentative assignments for the IR (cm^{-1}) spectra registered for **MBV_{10}** and **TBV_{10}** [14-17]

Assignement	MBV_{10}	TBV_{10}
ν(O–H) and ν(N–H)	3450 and 3348	3314 and 3188
δ(N-H)	-	1599
ν(C=N), ν(C–C)	1599, 1221	1649
ν(C=S^+)	1489	1486
δ(C–H)	1441, 1392, 1252 and 1178	1323, 1487
δ(C–N)	1153	1385
ν(C–S–C)	1040	1025
ν(V=O)	964	959
ν_{as}(V–O) and ν_{sim}(V–O)	831 and 760	827 and 744
δ(V–O–V)	607	663

ν = stretching, ν_{as} = asymmetric stretching, ν_{sim} = symetric stretching e δ = in-plane angular deformation

Table S5. Final discoloration values of MB solution at 10.0 mg L^{-1} and TB at 10.0 mg L^{-1} bleached by **2,3–ampV$_{10}$** represented by aritmetic mean (%) ± standard deviation (SD) in the different reaction conditions

Reaction condition	Reaction time (min)	MB* bleaching (%) ± SD	TB * bleaching (%) ± SD
General investigation (pH 6)			
10.0 mg of **2,3–AmpV$_{10}$** + $AM_{(aq)}$ a 10.0 mg L^{-1}	15	89.88±0.57	70.27±0.79
Effect of **2,3–AmpV$_{10}$** *amount (pH 6)*			
16 mg of **2,3–AmpV$_{10}$** + dye solution	15	NA	77.28±1.17
4.0 mg of **2,3–AmpV$_{10}$** + dye solution	15	86.54±1.48	49.50±4.46
2.0 mg of **2,3–AmpV$_{10}$** + dye solution	15	82.67±0.24	NA
1.0 mg of **2,3–AmpV$_{10}$** + dye solution	15	32.10±2.05	NA
Presence of peroxide			
10.0 mg of **2,3–AmpV$_{10}$** + dye solution + 1.0 mL de H_2O_2 35%	10	90.50±0.64	NA
pH 3			
10.0 mg of **2,3–AmpV$_{10}$** + dye solution, pH 3	15	93.18±0.73	83.57±1.10

NA = Data not available,

* monitored absorption wavelength for MB = 664 nm and for TB = 630 nm

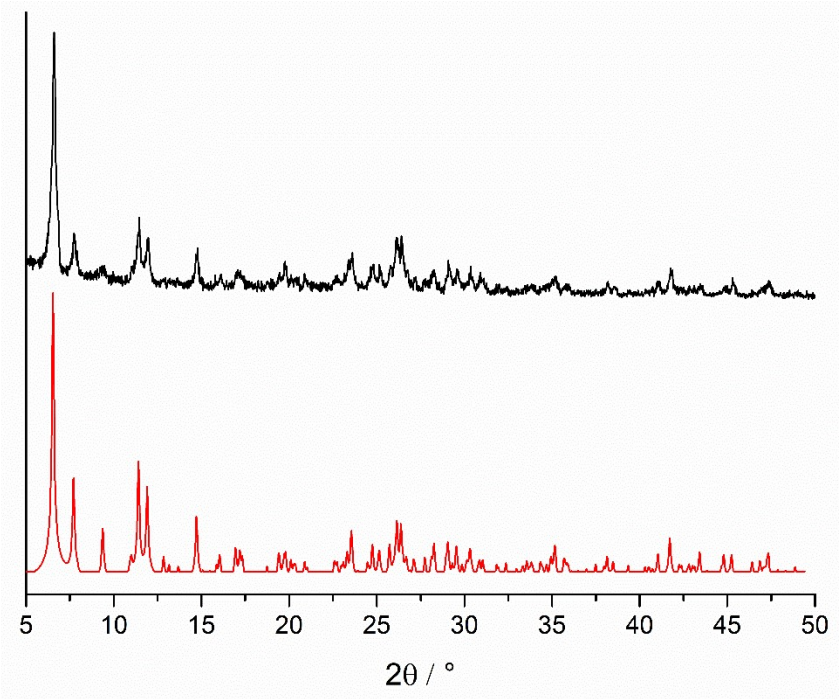


Figure S1. Calculated (red line) and experimental (black line) PXRD patterns of **2,3-ampV$_{10}$**. Main peaks in the experimental diffractogram are located at 6.6, 7.7, 11.5, 12.0, 14.8, 17.2, 19.7, 23.6, 24.8, 26.1, 28.2, 29.1 and 30.3° 2θ.

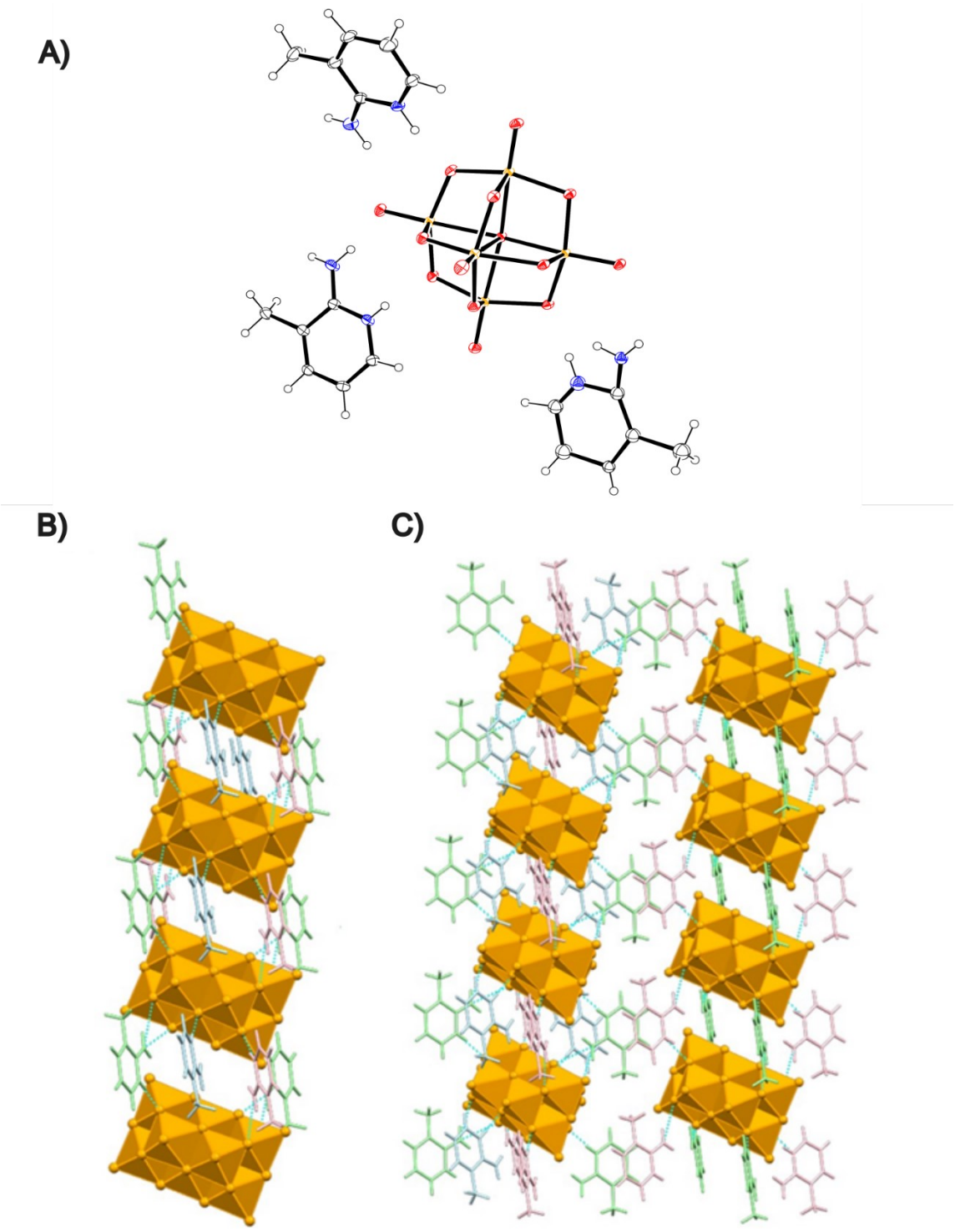


Figure S2. A) ORTEP view of the asymmetric unit of **2,3-ampV$_{10}$**. Ellipsoid probability 35%, for the disordered 2-amino-3-methylpyridinium cation just the model with the bigger occupancy factor is reported. B) Chain formed by the 2,3-ampH$^+$ cation and V_{10} anions interactions in **2,3-ampV$_{10}$** (view along the *b* axis). C) 2,3-ampH$^+$ cation and V_{10} anions network (view along the *b* axis). Color scheme: V = yellow, O = red, N = blue.

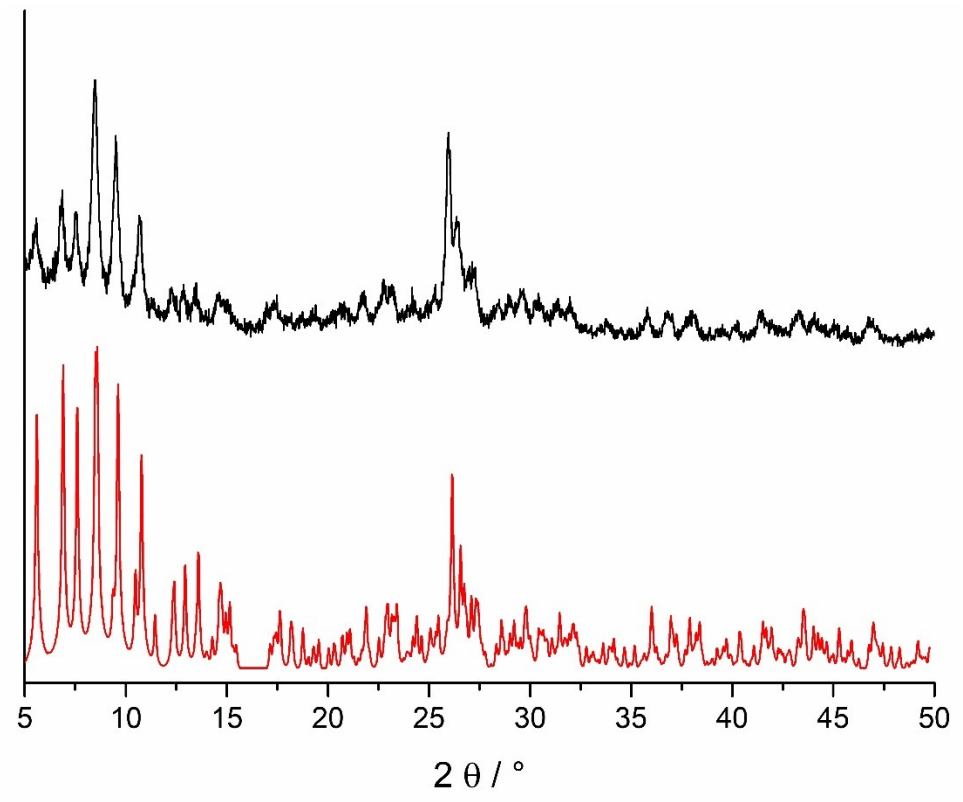


Figure S3. Calculated (red line) and experimental (black line) PXRD patterns of **MBV_{10}**. Main peaks in the experimental diffractogram are located at 5.6, 6.9, 7.5, 8.5, 9.5, 10.6, 26, 26.4, and 27.1° in 2θ.

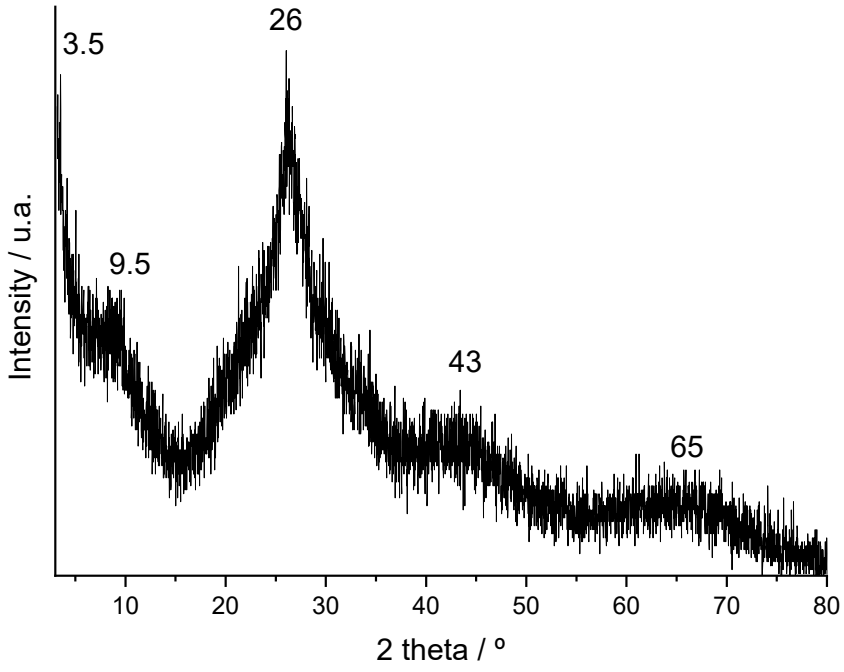


Figure S4. PXRD pattern of **ATV_{10}**.

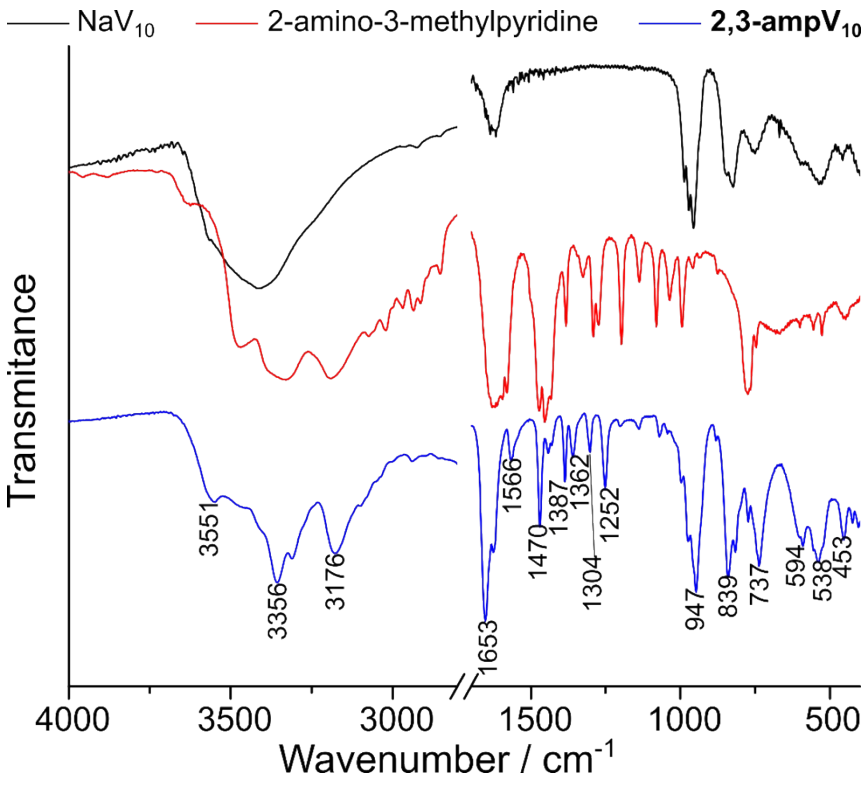


Figure S5. Infrared absorption spectrum of $(2,3\text{-ampH})_6[V_{10}O_{28}]\cdot 4H_2O$ (**2,3-ampV$_{10}$**) as compared to its starting materials.

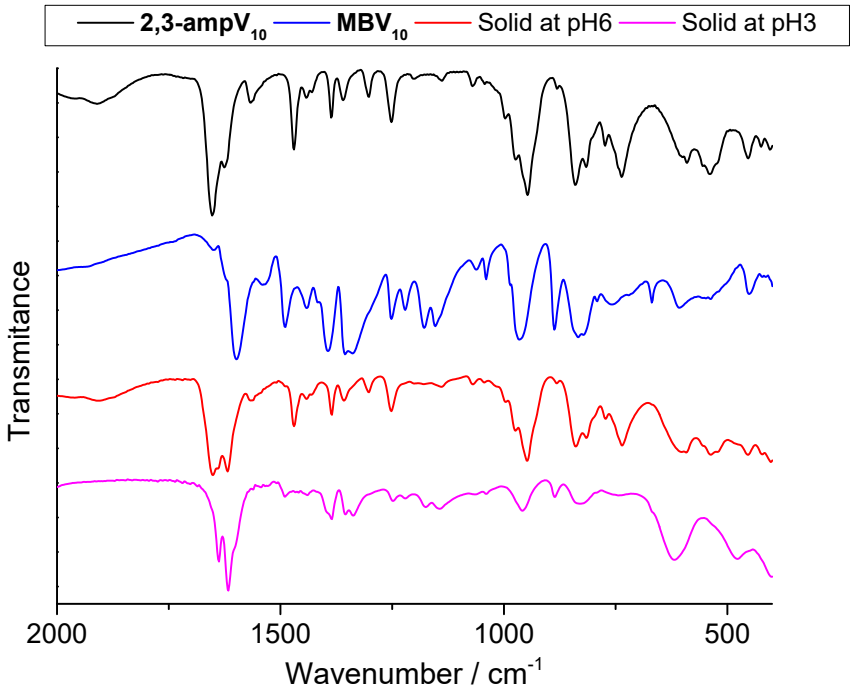


Figure S6. IR spectrum recorded for the remain solids isolated from MB bleaching reactions with **2,3-ampV$_{10}$**.

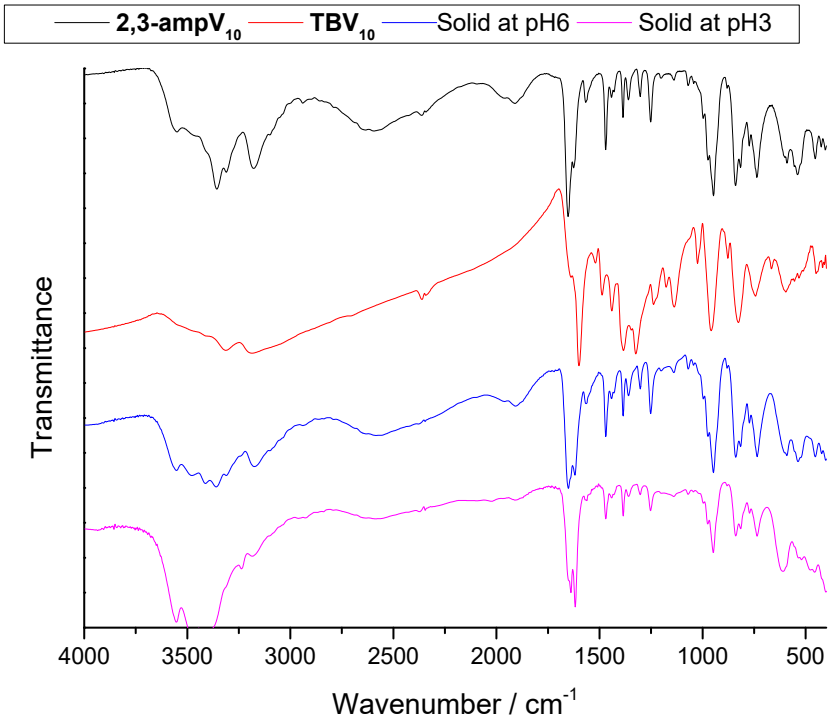


Figure S7. IR spectrum recorded for the solids isolated from TB bleaching reactions with **2,3-ampV$_{10}$**.

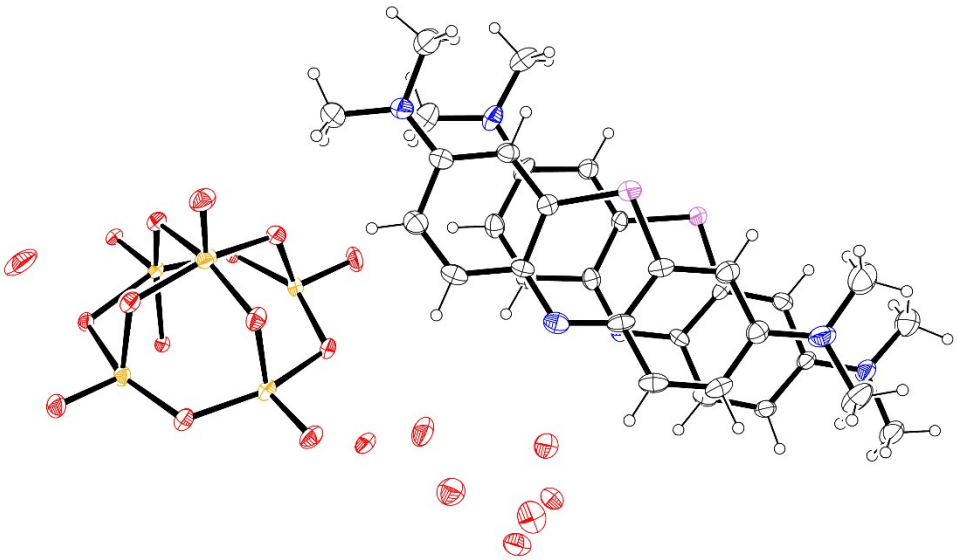


Figure S8. ORTEP view of the asymmetric unit of **MBV$_{10}$**. Ellipsoid probability 30%. Color scheme: V = yellow, O = red, N = blue and S = purple.

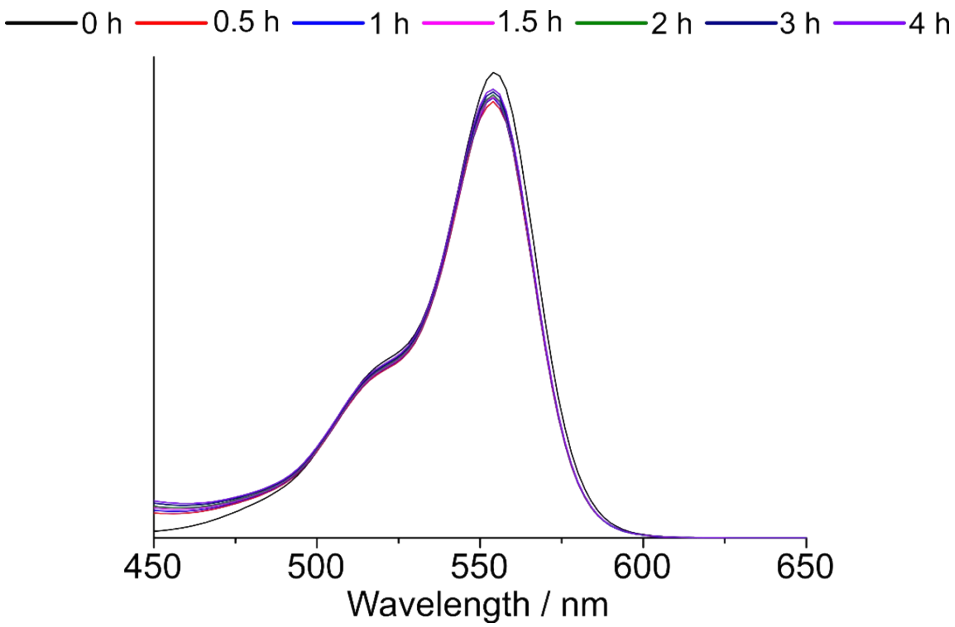
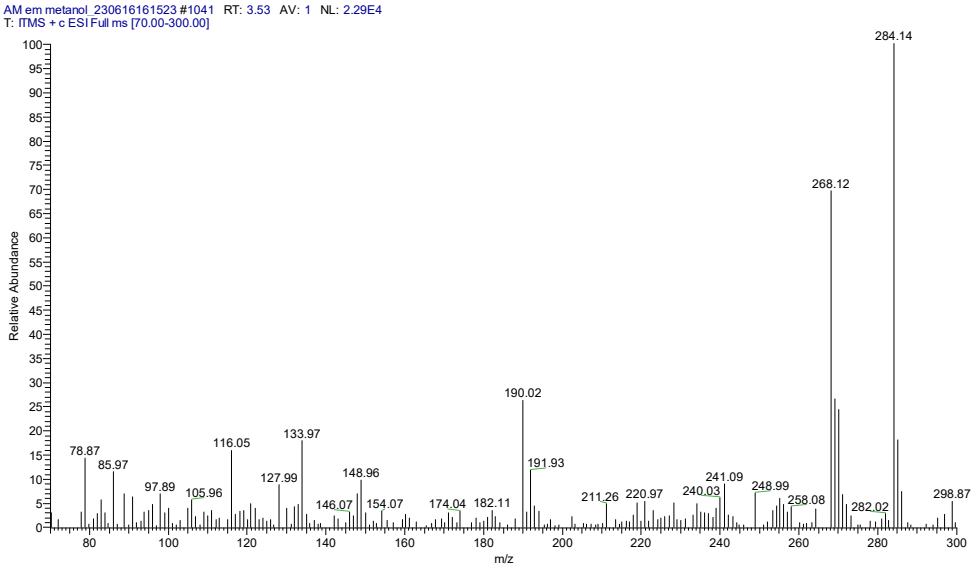


Figure S9. Electronic spectra registered for the supernatants of the bleaching reactions using 10 mg of **2,3-ampV$_{10}$** in 10 mg L^{-1} aqueous solution of RB in time.

A)



B)

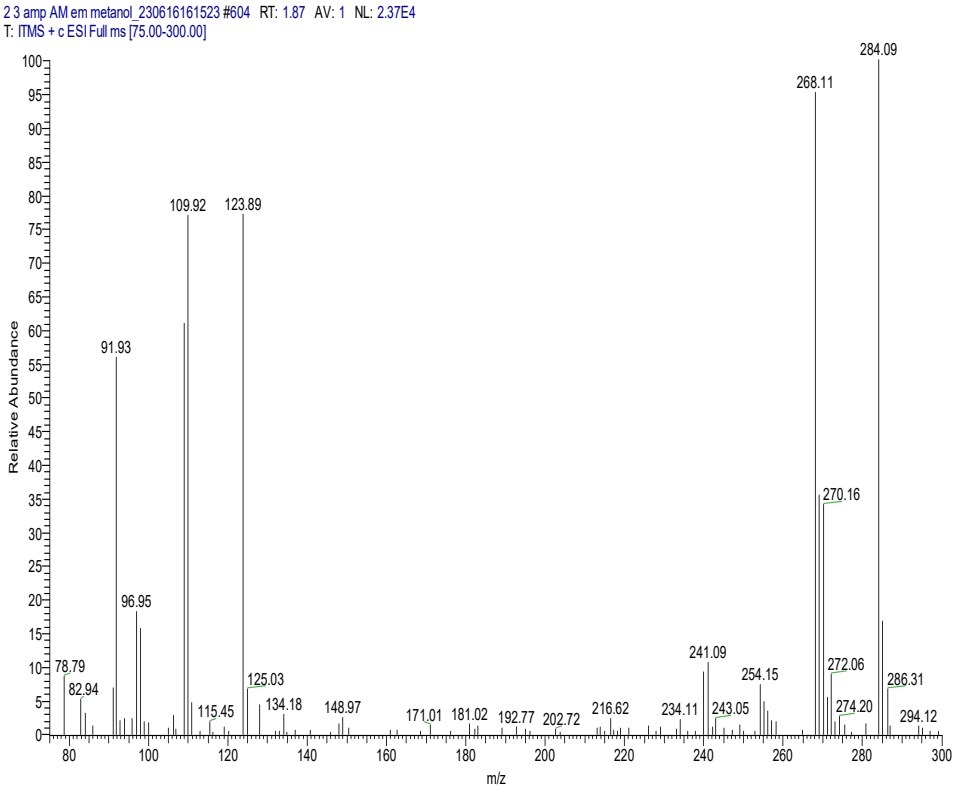
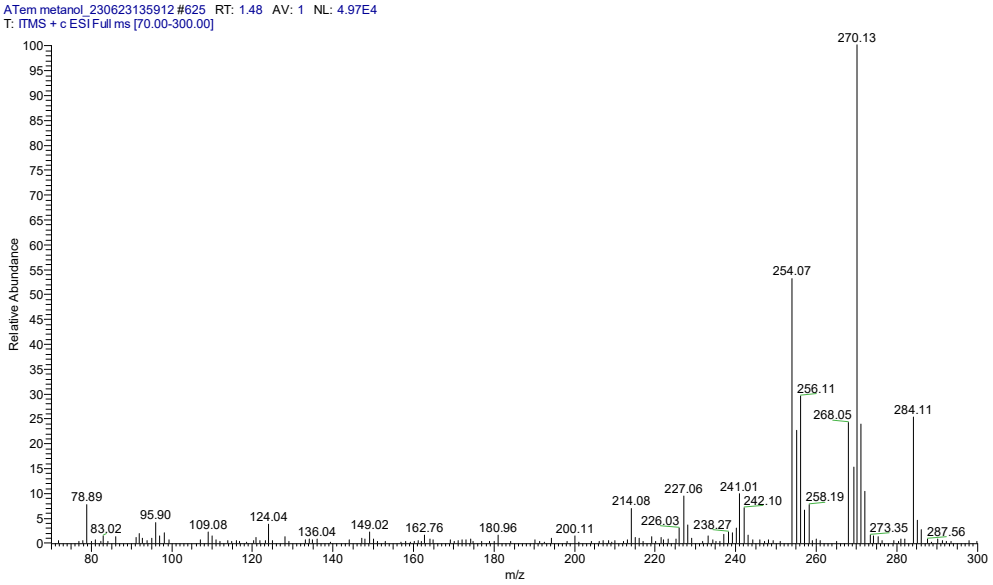


Figure S10. ESI-MS scan of MB (10 mg L^{-1}) in positive mode: **A)** before and **B)** after the reaction with 10 mg of **2,3-ampV_{10}**.

A)



B)

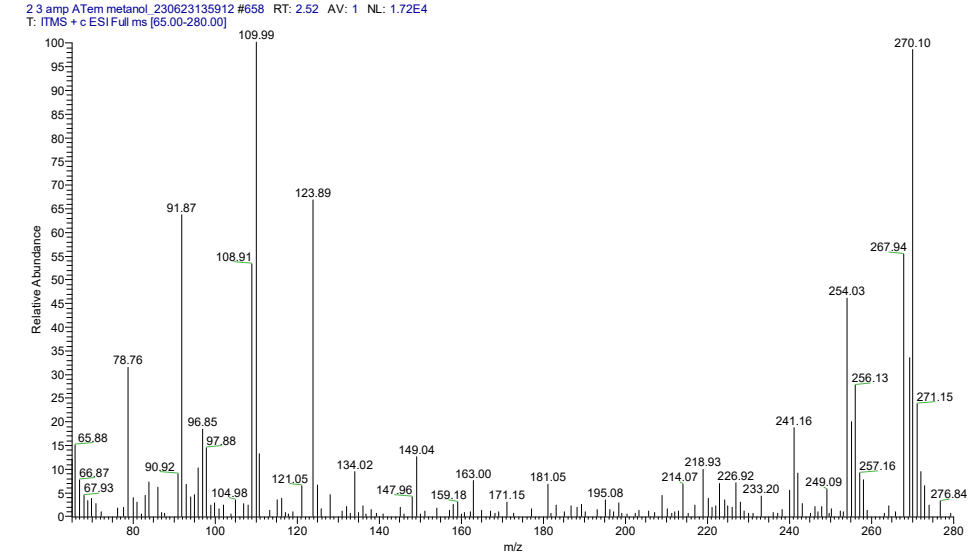


Figure S11. ESI-MS scan of TB (10 mg L^{-1}) in positive mode: **A)** before and **B)** after the reaction with 10 mg **2,3-ampV_{10}**.

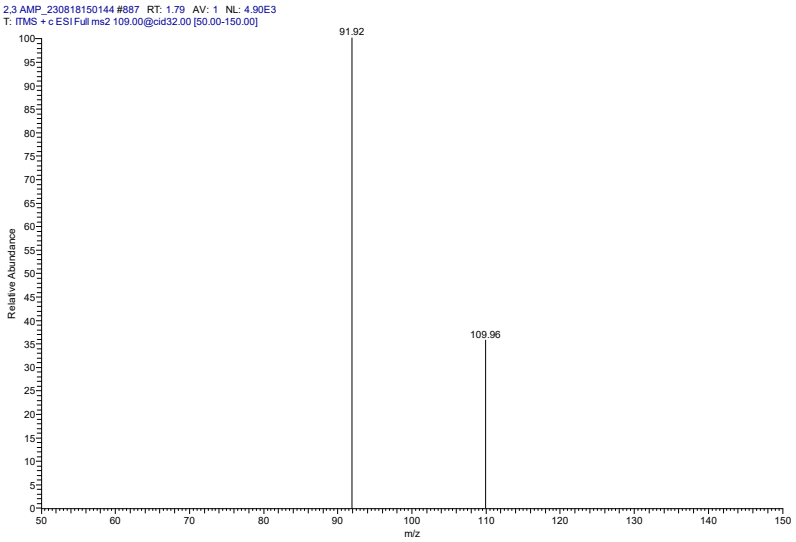


Figure S12. ESI-MS scan of 2-amino-3-methylpyridine in methanol in positive mode. The mass spectra showed peaks at *m/z* 109.9 that corresponded to the protonated form of 2,3-ampH$^+$. The peak at *m/z* 91.9 may correspond to $C_6NH_6^+$.

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