

## **Supporting Information**

### **Synthesis of New Mixed-Metal Ammonium Vanadates: Cation Order versus Disorder, and Optical and Photocatalytic Properties**

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**Table S1.** Selected bond Distances (Å), Angles (°) and Bond Valence Sums for **I**.<sup>a</sup>

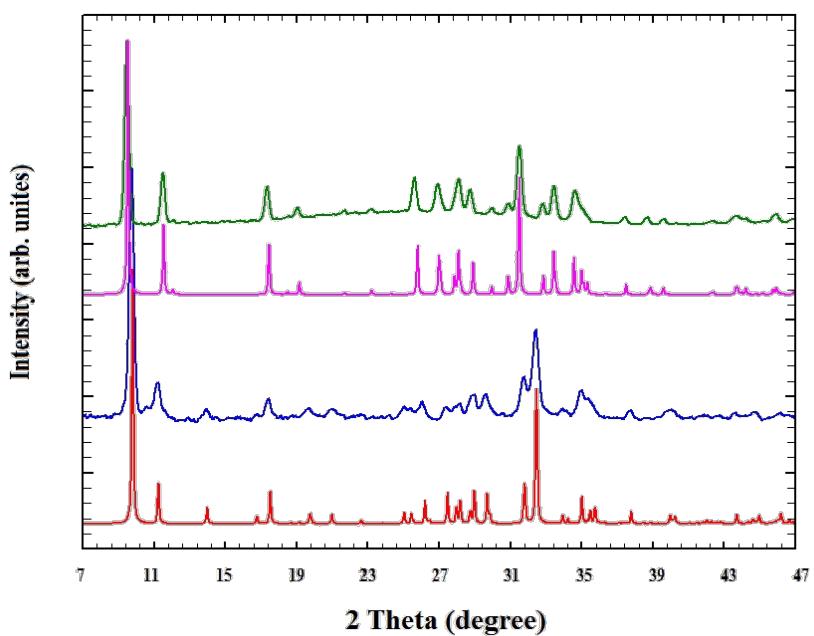
<b>Atom1</b>	<b>Atom2</b>	<b>Distance</b>	<b>Intra-Polyhedral Angles</b>	
Mn1	O6	2.2813(17)	O6 – Mn1 – O7	95.54(9)
	O7	2.127(3)	O6 – Mn1 – O7'	84.46(9)
	$\Sigma S_{ij}$	1.864	O7 – Mn1 – O7	180
Mn2	O2	2.2358(14)	O5 – Mn2 – O2	88.84(8)
	O5	2.053(2)	O2 – Mn2 – O2'	103.88(9)
	$\Sigma S_{ij}$	2.184		
V1	O3	2.131(2)	O3 – V1 – O4	73.03(7)
	O4	1.8642(8)	O3 – V1 – O5	151.24(12)
	O5	1.663(2)	O4 – V1 – O6	102.91(9)
	O6	1.652(3)	O4 – V1 – O5	100.52(8)
	$\Sigma S_{ij}$	5.069	O5 – V1 – O6	103.56(14)
V2	O1	1.613(3)	O1 – V2 – O2	104.63(13)
	O2	1.709(2)	O1 – V2 – O3	105.02(8)
	O3	1.8784(8)	O2 – V2 – O3	99.25(8)
	O4	1.8642(8)	O2 – V2 – O4	152.49(12)
	$\Sigma S_{ij}$	5.035	O3 – V2 – O4	73.40(7)

<sup>a</sup>  $S_{ij} = \exp[(R_0 - R_{ij})/B]$ , B = 0.37,  $R_0 = 1.790 \text{ \AA}$  for  $\text{Mn}^{\text{II}} - \text{O}$ ,  $R_0 = 1.803 \text{ \AA}$  for  $\text{V}^{\text{V}} - \text{O}$ .

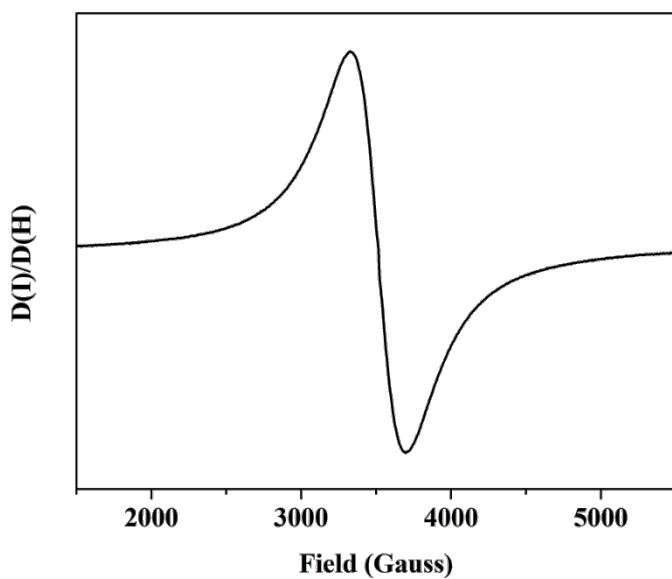
**Table S2.** Selected bond Distances (Å), Angles (°) and Bond Valence Sums for **II**.<sup>a</sup>

<b>Atom1</b>	<b>Atom2</b>	<b>Distance</b>	<b>Intra-Polyhedral Angles</b>	
Co1	O7	2.0722(12)	O7 – Co1 – O10	85.74(5)
	O10	2.055(2)	O7 – Co1 – O10'	94.26(5)
	$\Sigma S_{ij}$	2.18	O7 – Co1 – O7'	180
Co2	O6	1.9788(12)	O6 – Co2 – O8	90.80(6)
	O8	2.1657(10)	O6 – Co2 – O9	89.42(6)
	O9	2.1787(10)	O8 – Co2 – O9	103.24(5)
	$\Sigma S_{ij}$	2.014		
V1	O1	1.6124(18)	O1 – V1 – O3	108.07(5)
	O3	1.7979(12)	O1 – V1 – O9	107.00(9)
	O9	1.7147(17)	O3 – V1 – O9	107.92(5)
	$\Sigma S_{ij}$	4.971		
V2	O2	1.6204(18)	O2 – V2 – O3	101.54(4)
	O3	1.9288(11)	O2 – V2 – O4	98.19(8)
	O4	2.0753(17)	O2 – V2 – O8	102.19(9)
	O8	1.7089(17)	O3 – V2 – O4	70.64(5)
	$\Sigma S_{ij}$	4.831	O4 – V2 – O8	159.62(8)
V3	O4	1.8510(7)	O4 – V3 – O5	139.73(7)
	O5	1.8198(7)	O4 – V3 – O6	100.70(6)
	O6	1.6680(12)	O4 – V3 – O7	103.71(7)
	O7	1.6545(13)	O5 – V3 – O7	104.04(7)
	O3	2.3461(13)	O5 – V3 – O6	100.48(7)
	$\Sigma S_{ij}$	4.998	O7 – V3 – O3	98.09(5)

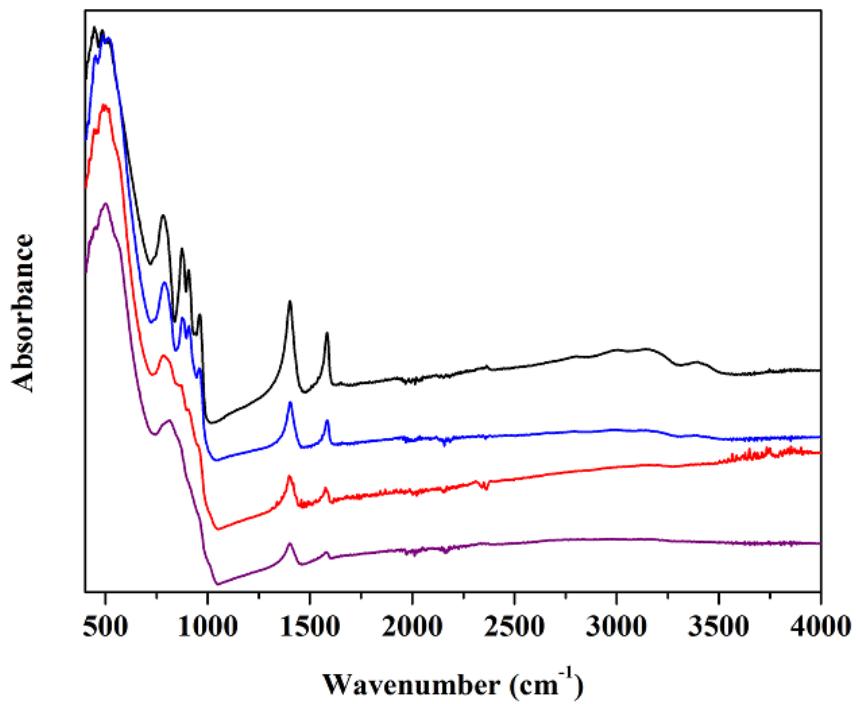
<sup>a</sup>  $S_{ij} = \exp[(R_0 - R_{ij})/B]$ , B = 0.37,  $R_0 = 1.692 \text{ \AA}$  for  $\text{Co}^{II} - \text{O}$ ,  $R_0 = 1.803 \text{ \AA}$  for  $\text{V}^V - \text{O}$ .



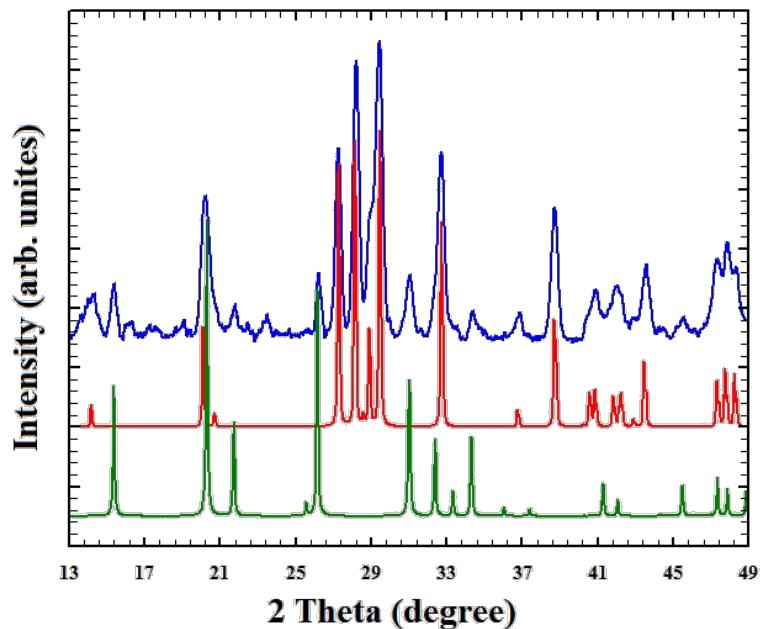
**Figure S1.** Powder XRD patterns of compound I: as synthesized (green) and calculated (pink); and II: as synthesized (blue) and calculated (red).



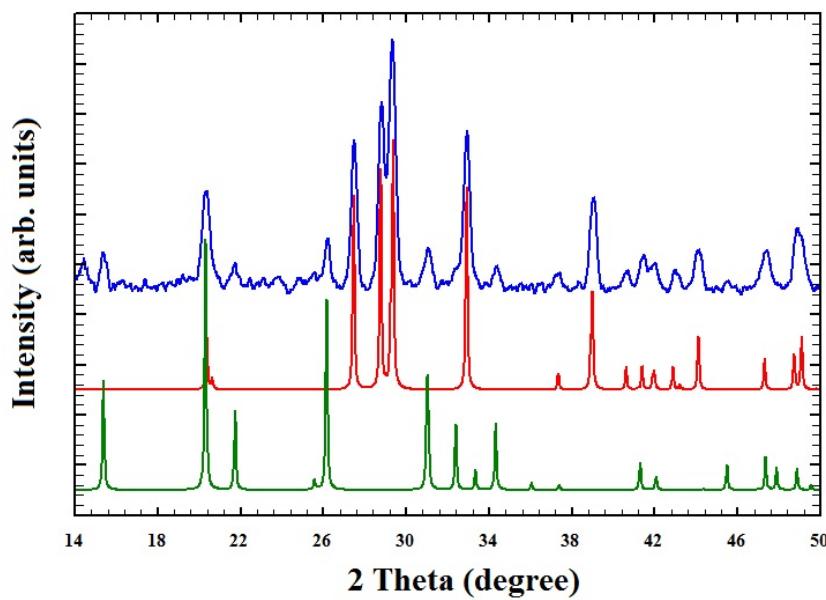
**Figure S2.** EPR spectra of fine powdered sample I.



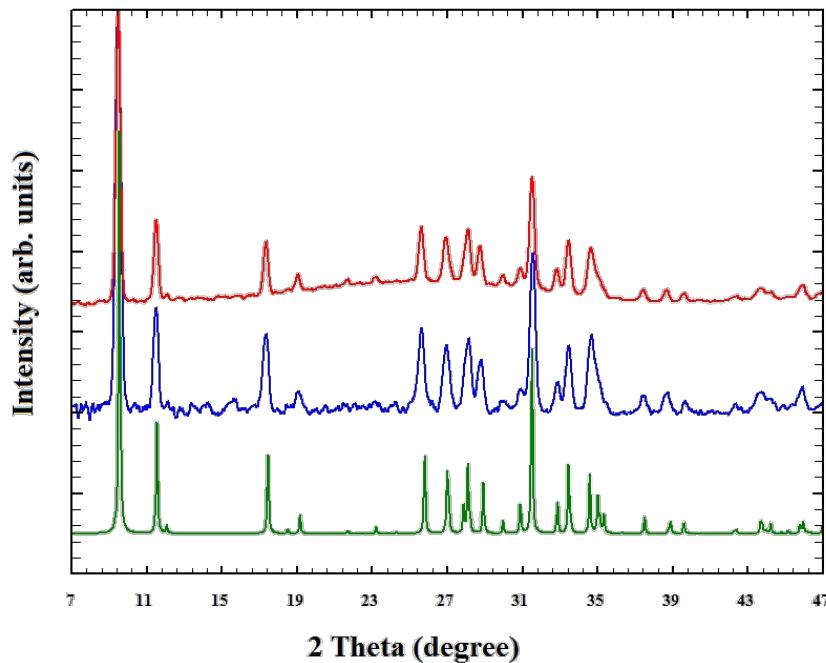
**Figure S3.** IR spectra of **I**: original compound (black), and after 2% (blue), 4% (purple) and 6% (red) weight loss.



**Figure S4.** Powder XRD pattern of the TGA residue of **I** after heating in nitrogen (blue), and the calculated MnV<sub>2</sub>O<sub>6</sub> pattern (red) and the calculated V<sub>2</sub>O<sub>5</sub> pattern (green).



**Figure S5.** Powder XRD pattern of the TGA residue of **II** after heating in nitrogen (blue), and the calculated  $\text{CoV}_2\text{O}_6$  pattern (red) and the calculated  $\text{V}_2\text{O}_5$  pattern (green).



**Figure S6.** Powder XRD patterns of compounds **I**: as synthesized (red), after photocatalytic measurements under UV and visible light for 8 hours (blue) and calculated (green).