

## Electronic Supplementary Information

### Thermochromic VO<sub>2</sub> Films from Ammonium Citrato-oxovanadate (IV) with Excellent Optical and Phase Transition Properties

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**Table S1** Bond lengths [Å] and angles [deg] for CA-V(IV)

V(1)-O(6)	1.6106(14)	O(6)-V(1)-O(5)	105.31(7)	O(14)-C(10)-C(9)	107.15(14)
V(1)-O(5)	1.9659(12)	O(6)-V(1)-O(7)#1	101.01(7)	O(14)-C(10)-C(11)	111.84(14)
V(1)-O(7)#1	2.0189(14)	O(5)-V(1)-O(7)#1	153.54(6)	C(9)-C(10)-C(11)	112.39(15)
V(1)-O(2)	2.0286(14)	O(6)-V(1)-O(2)	94.99(7)	O(14)-C(10)-C(12)	109.40(14)
V(1)-O(3)#1	2.0449(14)	O(5)-V(1)-O(2)	87.77(5)	C(9)-C(10)-C(12)	109.36(15)
V(1)-O(5)#1	2.1937(12)	O(7)#1-V(1)-O(2)	87.28(6)	C(11)-C(10)-C(12)	106.67(14)
O(5)-C(3)	1.424(2)	O(6)-V(1)-O(3)#1	87.62(7)	C(7)#2-C(11)-C(10)	110.62(15)
O(5)-V(1)#1	2.1937(12)	O(5)-V(1)-O(3)#1	93.25(6)	C(7)#2-C(11)-H(11A)	109.5
O(7)-C(6)	1.297(2)	O(7)#1-V(1)-O(3)#1	90.49(6)	C(10)-C(11)-H(11A)	109.5
O(7)-V(1)#1	2.0189(14)	O(2)-V(1)-O(3)#1	176.85(6)	C(7)#2-C(11)-H(11B)	109.5
O(8)-C(6)	1.231(2)	O(6)-V(1)-O(5)#1	163.61(7)	C(10)-C(11)-H(11B)	109.5
O(1)-C(1)	1.234(2)	O(5)-V(1)-O(5)#1	75.90(5)	H(11A)-C(11)-H(11B)	108.1
O(4)-C(4)	1.239(2)	O(7)#1-V(1)-O(5)#1	79.65(5)	O(9)-C(7)-O(10)	121.56(18)
O(2)-C(1)	1.299(2)	O(2)-V(1)-O(5)#1	101.40(5)	O(9)-C(7)-C(11)#2	120.58(17)
O(3)-C(4)	1.272(2)	O(3)#1-V(1)-O(5)#1	75.99(5)	O(10)-C(7)-C(11)#2	117.82(16)
O(3)-V(1)#1	2.0449(14)	C(3)-O(5)-V(1)	120.89(10)	C(10)-C(9)-C(8)	113.22(15)
C(3)-C(2)	1.533(2)	C(3)-O(5)-V(1)#1	107.43(10)	C(10)-C(9)-H(9A)	108.9
C(3)-C(5)	1.535(2)	V(1)-O(5)-V(1)#1	104.10(5)	C(8)-C(9)-H(9A)	108.9
C(3)-C(4)	1.544(2)	C(6)-O(7)-V(1)#1	134.53(12)	C(10)-C(9)-H(9B)	108.9
C(5)-C(6)	1.515(3)	C(1)-O(2)-V(1)	118.60(12)	C(8)-C(9)-H(9B)	108.9
C(5)-H(5A)	0.97	C(4)-O(3)-V(1)#1	117.50(12)	H(9A)-C(9)-H(9B)	107.7
C(5)-H(5B)	0.97	O(5)-C(3)-C(2)	111.16(14)	O(13)-C(8)-O(12)	122.31(19)
C(2)-C(1)	1.513(3)	O(5)-C(3)-C(5)	107.98(14)	O(13)-C(8)-C(9)	116.74(18)
C(2)-H(2A)	0.97	C(2)-C(3)-C(5)	111.01(14)	O(12)-C(8)-C(9)	120.95(16)
C(2)-H(2B)	0.97	O(5)-C(3)-C(4)	109.36(13)	O(16)-C(12)-O(15)	123.65(17)
V(2)-O(11)	1.6054(15)	C(2)-C(3)-C(4)	107.78(14)	O(16)-C(12)-C(10)	120.07(17)
V(2)-O(14)#2	1.9539(13)	C(5)-C(3)-C(4)	109.53(15)	O(15)-C(12)-C(10)	116.28(15)
V(2)-O(10)	2.0163(14)	C(6)-C(5)-C(3)	115.85(15)	H(4C)-N(4)-H(4D)	108.4
V(2)-O(12)	2.0512(14)	C(6)-C(5)-H(5A)	108.3	H(4C)-N(4)-H(4A)	110
V(2)-O(15)	2.0560(14)	C(3)-C(5)-H(5A)	108.3	H(4D)-N(4)-H(4A)	110
V(2)-O(14)	2.1938(13)	C(6)-C(5)-H(5B)	108.3	H(4C)-N(4)-H(4B)	110
O(15)-C(12)	1.275(2)	C(3)-C(5)-H(5B)	108.3	H(4D)-N(4)-H(4B)	110
O(14)-C(10)	1.416(2)	H(5A)-C(5)-H(5B)	107.4	H(4A)-N(4)-H(4B)	108.5
O(14)-V(2)#2	1.9539(13)	O(8)-C(6)-O(7)	120.48(18)	H(3C)-N(3)-H(3D)	108.1
O(9)-C(7)	1.233(2)	O(8)-C(6)-C(5)	118.48(17)	H(3C)-N(3)-H(3A)	109.6
O(10)-C(7)	1.297(2)	O(7)-C(6)-C(5)	121.04(16)	H(3D)-N(3)-H(3A)	109.6
O(13)-C(8)	1.235(2)	O(4)-C(4)-O(3)	123.99(18)	H(3C)-N(3)-H(3B)	109.6
O(12)-C(8)	1.278(2)	O(4)-C(4)-C(3)	119.77(17)	H(3D)-N(3)-H(3B)	109.6
O(16)-C(12)	1.238(2)	O(3)-C(4)-C(3)	116.23(15)	H(3A)-N(3)-H(3B)	110.3
C(10)-C(9)	1.522(2)	C(1)-C(2)-C(3)	110.85(15)	H(2E)-N(2)-H(2F)	108.9
C(10)-C(11)	1.539(2)	C(1)-C(2)-H(2A)	109.5	H(2E)-N(2)-H(2C)	110.9
C(10)-C(12)	1.539(2)	C(3)-C(2)-H(2A)	109.5	H(2F)-N(2)-H(2C)	110.9

C(11)-C(7)#2	1.514(3)	C(1)-C(2)-H(2B)	109.5	H(2E)-N(2)-H(2D)	110.9
C(11)-H(11A)	0.97	C(3)-C(2)-H(2B)	109.5	H(2F)-N(2)-H(2D)	110.9
C(11)-H(11B)	0.97	H(2A)-C(2)-H(2B)	108.1	H(2C)-N(2)-H(2D)	104.3
C(7)-C(11)#2	1.514(3)	O(1)-C(1)-O(2)	122.08(18)	H(17A)-O(17)-H(17B)	108.5
C(9)-C(8)	1.524(3)	O(1)-C(1)-C(2)	120.16(17)	H(18A)-O(18)-H(18B)	108.3
C(9)-H(9A)	0.97	O(2)-C(1)-C(2)	117.73(16)	H(1C)-N(1)-H(1D)	108.2
C(9)-H(9B)	0.97	O(11)-V(2)-O(14)#2	107.41(7)	H(1C)-N(1)-H(1A)	109.8
N(4)-H(4C)	0.8999	O(11)-V(2)-O(10)	96.99(8)	H(1D)-N(1)-H(1A)	109.8
N(4)-H(4D)	0.9	O(14)#2-V(2)-O(10)	87.63(6)	H(1C)-N(1)-H(1B)	109.8
N(4)-H(4A)	0.9	O(11)-V(2)-O(12)	100.98(7)	H(1D)-N(1)-H(1B)	109.8
N(4)-H(4B)	0.9001	O(14)#2-V(2)-O(12)	151.50(6)	H(1A)-N(1)-H(1B)	109.5
N(3)-H(3C)	0.8998	O(10)-V(2)-O(12)	86.50(6)		
N(3)-H(3D)	0.8999	O(11)-V(2)-O(15)	89.64(7)		
N(3)-H(3A)	0.8999	O(14)#2-V(2)-O(15)	92.61(6)		
N(3)-H(3B)	0.9	O(10)-V(2)-O(15)	172.98(6)		
N(2)-H(2E)	0.9	O(12)-V(2)-O(15)	89.98(6)		
N(2)-H(2F)	0.8999	O(11)-V(2)-O(14)	164.35(7)		
N(2)-H(2C)	0.9002	O(14)#2-V(2)-O(14)	74.63(5)		
N(2)-H(2D)	0.9	O(10)-V(2)-O(14)	98.61(5)		
O(17)-H(17A)	0.8499	O(12)-V(2)-O(14)	78.73(5)		
O(17)-H(17B)	0.8501	O(15)-V(2)-O(14)	74.72(5)		
O(18)-H(18A)	0.85	C(12)-O(15)-V(2)	113.09(12)		
O(18)-H(18B)	0.85	C(10)-O(14)-V(2)#2	123.06(10)		
N(1)-H(1C)	0.9	C(10)-O(14)-V(2)	107.56(10)		
N(1)-H(1D)	0.8999	V(2)#2-O(14)-V(2)	105.37(5)		
N(1)-H(1A)	0.9	C(7)-O(10)-V(2)	121.53(12)		
N(1)-H(1B)	0.9	C(8)-O(12)-V(2)	134.42(13)		

**Table S2** Atomic coordinates (  $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ )

for CA-V(IV)

	x	y	z	U(eq)
V(1)	5176(1)	9373(1)	3991(1)	15(1)
O(5)	6487(1)	9506(1)	4942(1)	15(1)
O(7)	6789(2)	10677(2)	6427(1)	24(1)
O(8)	9175(2)	10560(2)	6366(1)	36(1)
O(1)	7732(2)	4974(2)	4737(1)	35(1)
O(4)	7585(2)	6224(2)	6848(1)	33(1)
O(6)	6270(2)	9035(2)	3038(1)	28(1)
O(2)	5788(2)	7189(2)	4666(1)	24(1)
O(3)	5560(2)	8403(2)	6657(1)	24(1)

C(3)	7645(2)	8193(2)	5484(1)	16(1)
C(5)	8874(2)	8640(2)	5803(2)	21(1)
C(6)	8254(2)	10042(2)	6219(1)	21(1)
C(4)	6892(2)	7533(2)	6405(1)	19(1)
C(2)	8381(2)	6994(2)	4867(2)	21(1)
C(1)	7255(2)	6319(2)	4739(1)	21(1)
V(2)	-364(1)	3579(1)	10677(1)	17(1)
O(11)	-178(2)	2498(2)	11748(1)	32(1)
O(15)	1958(2)	2449(2)	10402(1)	24(1)
O(14)	53(1)	4661(1)	9180(1)	16(1)
O(9)	-4661(2)	5883(2)	11687(1)	39(1)
O(10)	-2669(2)	4778(2)	10768(1)	25(1)
O(13)	-1805(2)	2106(2)	8560(1)	44(1)
O(12)	-918(2)	2415(2)	9853(1)	28(1)
O(16)	3310(2)	1189(2)	9275(1)	28(1)
C(10)	1160(2)	3535(2)	8726(1)	16(1)
C(11)	2206(2)	4137(2)	7991(1)	21(1)
C(7)	-3266(2)	5484(2)	11474(1)	21(1)
C(9)	263(2)	2907(2)	8240(1)	22(1)
C(8)	-898(2)	2444(2)	8933(2)	23(1)
C(12)	2238(2)	2280(2)	9516(1)	19(1)
N(4)	3625(2)	9508(2)	1458(1)	25(1)
N(3)	3974(2)	4033(2)	1238(1)	34(1)
N(2)	12247(2)	8721(2)	7010(2)	40(1)
O(17)	6789(2)	1520(2)	1001(2)	47(1)
O(18)	3826(2)	6283(2)	6066(2)	49(1)
N(1)	6819(3)	3546(2)	6673(2)	37(1)

**Table S3** Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for CA-V(IV)

	U11	U22	U33	U23	U13	U12
V(1)	14(1)	17(1)	15(1)	-6(1)	1(1)	-4(1)
O(5)	12(1)	13(1)	17(1)	-4(1)	-1(1)	-3(1)
O(7)	17(1)	31(1)	28(1)	-14(1)	-2(1)	-7(1)
O(8)	24(1)	38(1)	55(1)	-20(1)	-2(1)	-16(1)
O(1)	30(1)	19(1)	56(1)	-13(1)	-5(1)	-5(1)
O(4)	33(1)	21(1)	32(1)	5(1)	0(1)	-3(1)
O(6)	27(1)	32(1)	23(1)	-12(1)	7(1)	-8(1)
O(2)	19(1)	18(1)	34(1)	-6(1)	0(1)	-7(1)
O(3)	20(1)	22(1)	24(1)	0(1)	5(1)	-6(1)
C(3)	11(1)	15(1)	20(1)	-4(1)	-1(1)	-3(1)
C(5)	14(1)	23(1)	28(1)	-8(1)	-2(1)	-6(1)
C(6)	19(1)	23(1)	20(1)	-3(1)	-3(1)	-8(1)

C(4)	19(1)	18(1)	20(1)	-2(1)	-2(1)	-7(1)
C(2)	14(1)	18(1)	28(1)	-8(1)	2(1)	-3(1)
C(1)	20(1)	17(1)	24(1)	-5(1)	0(1)	-5(1)
V(2)	19(1)	15(1)	16(1)	-4(1)	2(1)	-7(1)
O(11)	44(1)	27(1)	23(1)	1(1)	2(1)	-16(1)
O(15)	23(1)	23(1)	19(1)	-4(1)	-3(1)	0(1)
O(14)	16(1)	15(1)	16(1)	-7(1)	1(1)	-5(1)
O(9)	24(1)	52(1)	50(1)	-29(1)	14(1)	-19(1)
O(10)	19(1)	34(1)	26(1)	-14(1)	3(1)	-11(1)
O(13)	45(1)	67(1)	41(1)	-14(1)	-4(1)	-41(1)
O(12)	37(1)	31(1)	27(1)	-13(1)	7(1)	-23(1)
O(16)	23(1)	22(1)	32(1)	-9(1)	4(1)	-1(1)
C(10)	16(1)	17(1)	16(1)	-7(1)	2(1)	-6(1)
C(11)	24(1)	25(1)	18(1)	-8(1)	6(1)	-12(1)
C(7)	21(1)	22(1)	21(1)	-5(1)	5(1)	-10(1)
C(9)	22(1)	26(1)	22(1)	-13(1)	1(1)	-10(1)
C(8)	20(1)	21(1)	30(1)	-10(1)	-1(1)	-8(1)
C(12)	16(1)	18(1)	23(1)	-6(1)	1(1)	-7(1)
N(4)	26(1)	27(1)	22(1)	-2(1)	-1(1)	-12(1)
N(3)	36(1)	35(1)	30(1)	-5(1)	-5(1)	-13(1)
N(2)	28(1)	43(1)	52(1)	-3(1)	-3(1)	-19(1)
O(17)	49(1)	40(1)	61(1)	-21(1)	18(1)	-26(1)
O(18)	54(1)	63(1)	46(1)	-14(1)	4(1)	-39(1)
N(1)	46(1)	29(1)	33(1)	-6(1)	7(1)	-13(1)

**Table S4** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for CA-V(IV)

	x	y	z	U(eq)
H(5A)	9527	7815	6295	26
H(5B)	9530	8781	5238	26
H(2A)	8680	7439	4226	25
H(2B)	9312	6213	5189	25
H(11A)	2828	3390	7616	26
H(11B)	1565	5026	7533	26
H(9A)	995	2044	7999	26
H(9B)	-291	3657	7678	26
H(4C)	3101	10447	1122	30
H(4D)	3058	8968	1461	30
H(4A)	4554	9099	1168	30
H(4B)	3786	9520	2079	30
H(3C)	4452	4624	1303	41

H(3D)	3442	3884	1798	41
H(3A)	3312	4486	729	41
H(3B)	4689	3148	1139	41
H(2E)	11893	8143	7480	48
H(2F)	13285	8383	7064	48
H(2C)	11988	8721	6407	48
H(2D)	11784	9686	7058	48
H(17A)	7486	1738	645	56
H(17B)	6805	712	894	56
H(18A)	3335	5926	5792	59
H(18B)	4060	5759	6646	59
H(1C)	6160	3782	7179	44
H(1D)	6856	2681	6563	44
H(1A)	6478	4276	6131	44
H(1B)	7773	3435	6824	44

**Table S5** Torsion angles [deg] for CA-V(IV)

O(6)-V(1)-O(5)-C(3)	-76.23(13)
O(7)#1-V(1)-O(5)-C(3)	97.69(16)
O(2)-V(1)-O(5)-C(3)	18.34(12)
O(3)#1-V(1)-O(5)-C(3)	-164.65(12)
O(5)#1-V(1)-O(5)-C(3)	120.68(13)
O(6)-V(1)-O(5)-V(1)#1	163.10(7)
O(7)#1-V(1)-O(5)-V(1)#1	-22.99(14)
O(2)-V(1)-O(5)-V(1)#1	-102.34(6)
O(3)#1-V(1)-O(5)-V(1)#1	74.68(6)
O(5)#1-V(1)-O(5)-V(1)#1	0
O(6)-V(1)-O(2)-C(1)	49.10(15)
O(5)-V(1)-O(2)-C(1)	-56.08(14)
O(7)#1-V(1)-O(2)-C(1)	149.92(14)
O(5)#1-V(1)-O(2)-C(1)	-131.21(14)
V(1)-O(5)-C(3)-C(2)	34.43(18)
V(1)#1-O(5)-C(3)-C(2)	153.46(11)
V(1)-O(5)-C(3)-C(5)	156.42(11)
V(1)#1-O(5)-C(3)-C(5)	-84.55(13)
V(1)-O(5)-C(3)-C(4)	-84.46(15)
V(1)#1-O(5)-C(3)-C(4)	34.57(15)
O(5)-C(3)-C(5)-C(6)	45.0(2)
C(2)-C(3)-C(5)-C(6)	167.06(16)
C(4)-C(3)-C(5)-C(6)	-74.0(2)
V(1)#1-O(7)-C(6)-O(8)	160.29(16)
V(1)#1-O(7)-C(6)-C(5)	-20.3(3)
C(3)-C(5)-C(6)-O(8)	-170.62(18)

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C(3)-C(5)-C(6)-O(7)	10.0(3)
V(1)#1-O(3)-C(4)-O(4)	167.56(16)
V(1)#1-O(3)-C(4)-C(3)	-12.6(2)
O(5)-C(3)-C(4)-O(4)	162.86(17)
C(2)-C(3)-C(4)-O(4)	41.9(2)
C(5)-C(3)-C(4)-O(4)	-79.0(2)
O(5)-C(3)-C(4)-O(3)	-17.0(2)
C(2)-C(3)-C(4)-O(3)	-137.92(17)
C(5)-C(3)-C(4)-O(3)	101.19(18)
O(5)-C(3)-C(2)-C(1)	-71.94(19)
C(5)-C(3)-C(2)-C(1)	167.84(15)
C(4)-C(3)-C(2)-C(1)	47.88(19)
V(1)-O(2)-C(1)-O(1)	-148.79(17)
V(1)-O(2)-C(1)-C(2)	33.4(2)
C(3)-C(2)-C(1)-O(1)	-143.31(19)
C(3)-C(2)-C(1)-O(2)	34.5(2)
O(11)-V(2)-O(15)-C(12)	141.91(14)
O(14)#2-V(2)-O(15)-C(12)	-110.67(13)
O(12)-V(2)-O(15)-C(12)	40.93(13)
O(14)-V(2)-O(15)-C(12)	-37.39(12)
O(11)-V(2)-O(14)-C(10)	33.1(3)
O(14)#2-V(2)-O(14)-C(10)	132.87(12)
O(10)-V(2)-O(14)-C(10)	-142.01(10)
O(12)-V(2)-O(14)-C(10)	-57.36(11)
O(15)-V(2)-O(14)-C(10)	35.74(10)
O(11)-V(2)-O(14)-V(2)#2	-99.7(3)
O(14)#2-V(2)-O(14)-V(2)#2	0
O(10)-V(2)-O(14)-V(2)#2	85.12(6)
O(12)-V(2)-O(14)-V(2)#2	169.77(7)
O(15)-V(2)-O(14)-V(2)#2	-97.13(6)
O(11)-V(2)-O(10)-C(7)	56.50(16)
O(14)#2-V(2)-O(10)-C(7)	-50.76(15)
O(12)-V(2)-O(10)-C(7)	157.15(15)
O(14)-V(2)-O(10)-C(7)	-124.82(14)
O(11)-V(2)-O(12)-C(8)	-161.97(19)
O(14)#2-V(2)-O(12)-C(8)	23.1(3)
O(10)-V(2)-O(12)-C(8)	101.59(19)
O(15)-V(2)-O(12)-C(8)	-72.33(19)
O(14)-V(2)-O(12)-C(8)	2.08(18)
V(2)#2-O(14)-C(10)-C(9)	-148.69(12)
V(2)-O(14)-C(10)-C(9)	88.79(13)
V(2)#2-O(14)-C(10)-C(11)	-25.11(19)
V(2)-O(14)-C(10)-C(11)	-147.63(12)
V(2)#2-O(14)-C(10)-C(12)	92.85(15)

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V(2)-O(14)-C(10)-C(12)	-29.67(15)
O(14)-C(10)-C(11)-C(7)#2	68.61(19)
C(9)-C(10)-C(11)-C(7)#2	-170.81(15)
C(12)-C(10)-C(11)-C(7)#2	-50.96(19)
V(2)-O(10)-C(7)-O(9)	-160.81(16)
V(2)-O(10)-C(7)-C(11)#2	21.5(2)
O(14)-C(10)-C(9)-C(8)	-51.1(2)
C(11)-C(10)-C(9)-C(8)	-174.39(15)
C(12)-C(10)-C(9)-C(8)	67.34(19)
V(2)-O(12)-C(8)-O(13)	-150.65(18)
V(2)-O(12)-C(8)-C(9)	29.2(3)
C(10)-C(9)-C(8)-O(13)	170.97(19)
C(10)-C(9)-C(8)-O(12)	-8.9(3)
V(2)-O(15)-C(12)-O(16)	-148.27(16)
V(2)-O(15)-C(12)-C(10)	32.09(19)
O(14)-C(10)-C(12)-O(16)	-178.97(16)
C(9)-C(10)-C(12)-O(16)	64.0(2)
C(11)-C(10)-C(12)-O(16)	-57.8(2)
O(14)-C(10)-C(12)-O(15)	0.7(2)
C(9)-C(10)-C(12)-O(15)	-116.39(18)
C(11)-C(10)-C(12)-O(15)	121.83(17)

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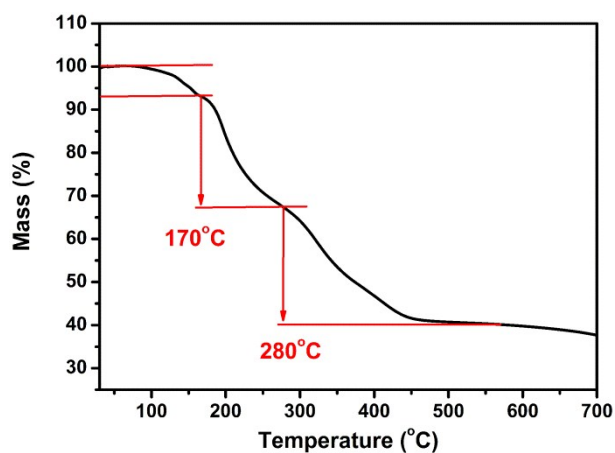


Figure S1. TGA (mass%) spectrum of CA-V(IV) in Ar.